CRYSTAL ENGINEERING WITH THIOUREAS: A STRUCTURE-BASED INQUIRY

by

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Structural trends applicable to crystal engineering were studied in three classes of thiourea-based compounds. The aim of the study was to identify, predict, and ultimately design reliable single-molecule structural features, which could then be used to engineer crystals with desirable properties. In one class of compounds, this goal was achieved: N-alkyl and N-aryl derivatives of N,N'-bis(3-thioureidopropyl)piperazine adopted an identical conformation in the solid state, which resulted in near-identical crystal packing. A second class of closely related compounds, N-substituted tris(2-thioureidoethyl)amines, showed no such reliability in the solid state, likely because the parent structure lacked hydrogen-bonding functionalities sufficient to control intramolecular structure. In the third class of compounds that we studied, 1-benzoyl-3-(2-pyridyl)thioureas, substitution patterns were often predictive of molecular conformation; however, these intramolecular trends did not lead to recognizable crystal packing motifs. Nevertheless, certain physical properties observed in this last class of compounds—color, solubility, and often crystallinity—were conformer-specific, interestingly without any apparent relevance to crystal lattice structure. Solution-state and solid-state conformational trends in these 1-

benzoyl-3-(2-pyridyl)thioureas have been documented, and speculations as to the source of color in one of the two observed conformations have been noted.

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To my family, without whom none of this work would have been possible.

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CHAPTER I

INTRODUCTION

Due to the often inexorable link between a solid substance's desirable physical or chemical properties and its supramolecular structure, gaining a predictive understanding of the factors that determine solid-state organization is very valuable to materials science research.[1,2] The study of solid-state organization, crystal engineering, has applications in areas as diverse as catalysis,[3-6] thin films,[7,8] liquid crystals,[9,10] drug discovery,[11-14] pigments,[15] metal-organic frameworks,[16-18] non-linear optical and ferroelectronic materials,[19,20] and the development of new technology for information storage.[21-24] Because crystal engineering is a relatively new field, few predictive models for supramolecular organization are currently available;[1,25] consequently, most work still depends heavily on *a posteriori* structure analysis, rather than any theoretical or computational method.[8,26]

Despite nearly 40 years of research directed at the prediction of solid-state behavior, structural similarity—even among highly similar classes of compounds—often appears to be the exception, rather than the rule. The prevalence of structural diveristy periodically evokes lamentations that true predictivity will remain elusive, due to the "mysticism"[27] inherent in crystal structure formation.[28,29] Nevertheless, many examples of

predictable solid-state behavior can be found in the chemical literature,[1] and it can only be surmised that the irregularity observed among other classes of compounds correlates more with observational shortcomings than with some inherent exception to the predictable ordering of the natural world.

Although it is entirely possible that the forces governing crystal formation are sufficiently intricate to surpass human cerebral processing power, it is also quite likely that, given a sufficient quantity of data, an algorithm may someday elucidate the more arcane aspects of solid-state organization, yielding a means of engineering complex solid-state architectures. In the past decade, crystal structure predicition (CSP) software has improved dramatically, and it is now common to find naturally-occurring polymorphs among the 10-100 structures within about 10 kJ/mol of the global minimum.[30] In one recent study, the three lowest-energy DFT(d) optimized crystal structures of a small organic molecule corresponded to the three known polymorphs of that molecule.[31] Nevertheless, the scope of CSP is still quite limited, as its "success depends to a large extent on finding the right combination of model accuracy and computational cost,"[32] and its current incarnation serves only to complement—rather than replace—traditional polymorphic screening.[33]

Despite both its recent progress and its forseeable potential, CSP still has relatively little impact on the intentional design of solid-state materials, the fundamental goal of crystal engineering. The distinction[34] between CSP and crystal engineering can best be characterized as one of different approaches to a similar problem, with different idealized outcomes. CSP aims to successfully model (and predict) molecular mechanics

within a crystal lattice, whereas crystal engineering is very much a materials-based discipline. At best, CSP can predict likely polymorphs of a known (or theoretical) compound, but it cannot determine the molecular structure most apt to form a desirable crystal lattice, and it cannot link structural characteristics with useful physical properties. For this reason, *a posteriori* studies are still the best approach to developing crystal engineering strategies, and the need for crystallographic data is only growing.

While early crystal engineering efforts tended to focus on establishing common crystal packing motifs within certain classes of compounds,[35,36] current research in crystal engineering tends to favor a supramolecular,[29] or network,[8] approach. In this author's humble[§] opinion, the distinction between these methodologies is largely pedantic: both rely on identifying common intermolecular interactions, and thereby developing building blocks by which complex solids may be intentionally designed. For example, in 1989, Desiraju and Gavezzotti described the earlier approach as "statistical in nature, [one which] generalizes from a large amount of crystallographic data and extrapolates from common geometrical motifs therein to derive new structures."[37] Over a decade later, Sharma described the network approach as one which advocates "simplify[ing] complex crystalline structural features into easily identifiable network topologies based on chemical and structural information of the constituent molecular building blocks."[8] These "molecular building blocks" can then be linked into a "network topology" by a series of intermolecular interactions, also known as supramolecular synthons.[17] As far as this author can tell, the primary—and (*vide infra*) most important—difference between

§ Not formally quantified by peer-reviewed methodology

these two methodologies is that the latter approach recognizes the need for a reliable sub-unit, around which complex crystal packing interactions can be designed.

The network approach—and crystal engineering, in general—tends to function most smoothly in inorganic[38,39] and organometallic[17 18] compounds, most likely due to the predictable and relatively rigid coordination geometry around the metal center.[40] In strictly organic compounds, however, crystal engineering—of any variety—is considerably more challenging, as organic compounds tend to exhibit greater conformational flexibility, compared to their metal-centered brethren. (**Figure 1.1**).[43,44]

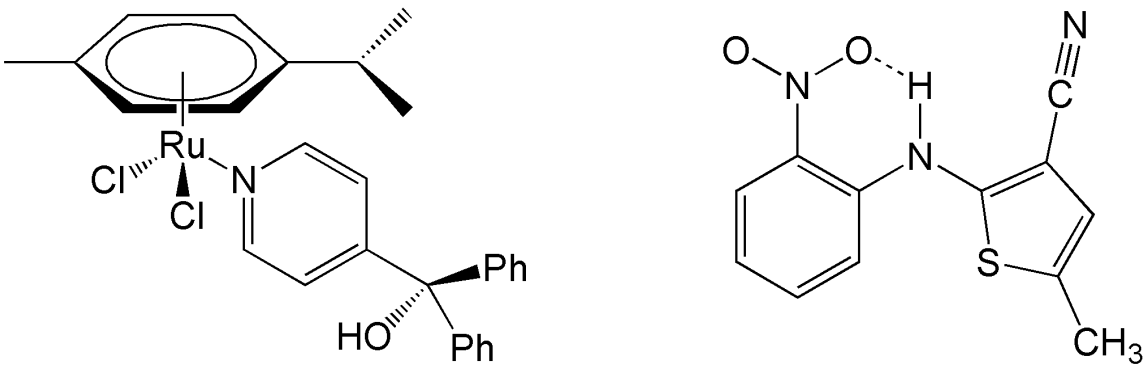


Figure 1.1. Crystal engineering with organometallics vs. "pure" organics. Crystals of the ruthenium complex (left) can grow in five different morphologies, depending on solvent choice—but all crystals share an identical unit cell.[41] Comparatively, the red, orange, and yellow hues of its six polymorphic forms have earned the organic carbonitrile (right) the moniker of "ROY."[42]

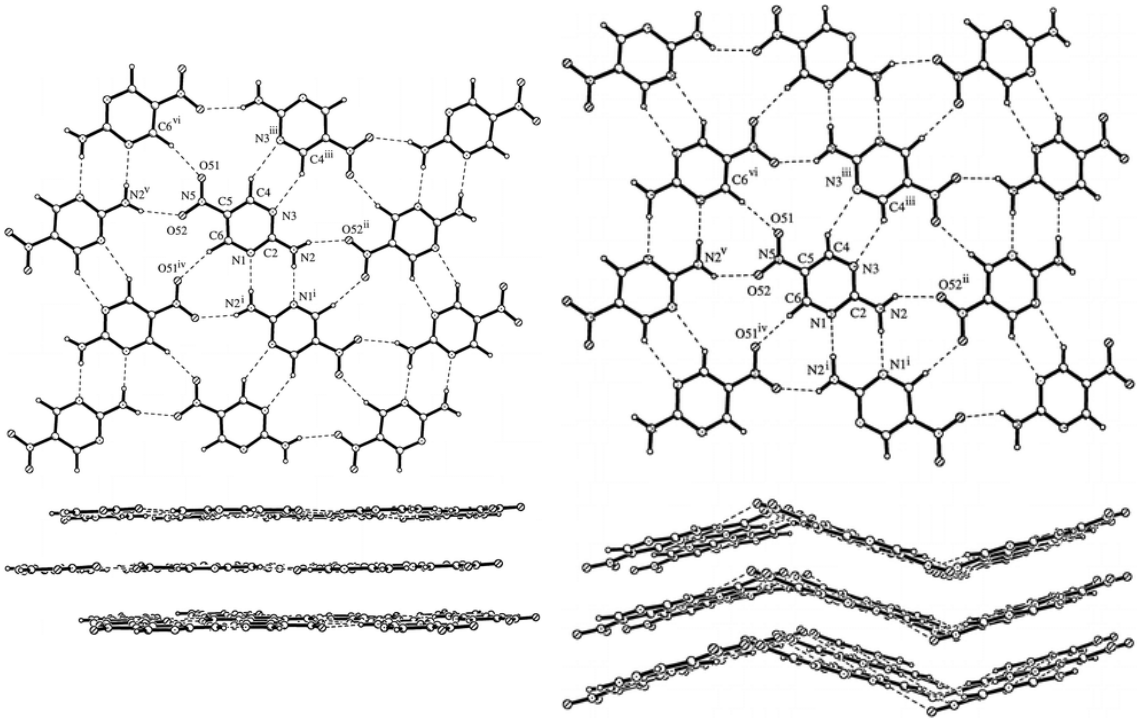
Computational studies performed on various organic molecules have shown that the multiple (local) energetic minima found for a single compound may differ in energy by as little as 10-25 J/mol.[11] Even translated into the crystal lattice, this energy difference tends

to be relatively insignficant: the energies of most polymorphs fall within a range of 1-3 kJ/mol. [11,45,46]

Much of this small variability in crystal lattice energy likely originates in the multitude of weak "hydrogen-bonding" interactions such as CH...X and CH...π,[47] which, in all but the simplest compounds, are liable to overwhelm stronger intermolecular interactions between heteroatomic donor/acceptor pairs. The overall effect of these weak interactions is such that at least one author has referred to a compound's hydrocarbon backbone as a "solid-state functional group," to be considered alongside functional groups more common to crystal engineering studies, such as amides, carboxylic acids, ureas, and alcohols.[48] For example, Forms I and II of 2-amino-5-nitropyrimidine form hydrogen bonds between the same four donor-acceptor pairs, yet have significantly different crystal packing arrangements (**Figure 1.2**).[49] Given the very small difference between many molecules' global and local conformational energetic minima, the energy that can be gained through even very weak, van der Waals-type interactions is likely sufficient to direct crystal lattice formation—in ways that are difficult to predict via "traditional," functional group-based methodologies.

Adding an additional layer of complexity to organic structure prediction, many functional groups are capable of forming more than one supramolecular synthon, thereby reducing the predictability with which "molecular building blocks" may be knit together.[48] Carboxylic acids, for example, commonly form either chains (b) or dimers (a) (**Figure 1.3**) in the solid state;[50] however, in molecules with at least one additional hydrogen-bonding functional group, one of these two homosynthons forms only 34% of

Figure 1.2. Hydrogen bonding patterns and crystal packing in Forms I (left) and II (right) of 2-amino-5-nitropyrimidine.



the time.[51] Comprising the remaining 66% of intermolecular interactions observed among carboxylic acids in the CSD, heterosynthons, or interactions between two different functional groups, were found to be similarly preferential in other classes of compounds, as well. Taken from the same study, the data shown in **Table 1.1** indicate the overall preference for heterosynthon formation when carboxylic acids are present alongside other hydrogen-bonding functional groups. Compounded by the conformational flexibility of organic compounds, this relative lack of predictability in synthon formation clearly incorporates a new degree of difficulty into crystal engineering efforts.

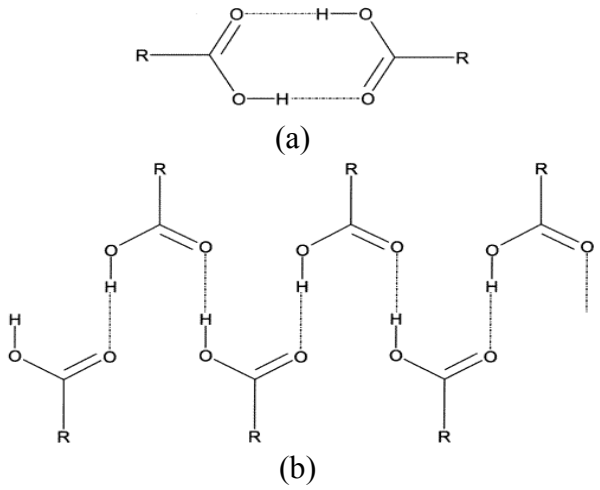


Figure 1.3. Carboxylic acid homosynthons. The two most common intermolecular interactions between COOH groups, (a) dimers and (b) chains, form in 31% and 3%, respectively, of all CSD structures containing at least one COOH unit.

Table 1.1. Supramolecular synthon formation in carboxylic acids containing at least one other hydrogen-bonding functional group.[51] "Refined" structures are those in which the CSD search was limited to molecules containing COOH and the specified functional group, with no additional hydrogen-bonding moieties. The sum of homosynthons and heterosynthons may not be equal to the total number of structures, as both may occur concurrently within one structure, and both may be entirely absent from another.

Functional Group	Cl-	OH	$CONH_2$	Aromatic N	C=O
# CSD Structures	267	1176	177	607	597
# Homosynthons[a]	3 (1%)	235 (20%)	8 (5%)[b]	45 (7%)	167 (28%)
# Heterosynthons	172 (64%)	540 (46%)	101 (57%)	468 (77%)	235 (20%)
# Refined CSD Structures	51	276	19	126	178
# Refined Homosynthons	0 (0%)	82 (30%)	2 (5%)[c]	9 (7%)	111 (62%)
# Refined Heterosynthons	51 (100%)	191 (69%)	16 (84%)	123 (98%)	85 (48%)

[a] COOH...COOH interactions, both cyclic dimers and chains

[b] 52 structures (29% of total) have $CONH_2$...$CONH_2$ homosynthon

[c] 2 structures (11% of total) have $CONH_2$...$CONH_2$ homosynthon

Considering all of these factors, it appears that the best approach to crystal engineering is probably one which avoids the pedantic distinction between earlier and more contemporary methodologies. Functional group interactions are still quite relevant to supramolecular design, as certain synthons—such as the COOH...N_{arom} interaction shown in **Table 1.1**—can be highly dependable in well-defined circumstances. These interactions are particularly relevant when attempting to incorporate flexible organic molecules into network-based synthetic strategies, as reliable *intra*molecular interactions can add a significant degree of predictability to monomeric molecular shape, thereby facilitating complex supramolecular schemes. By discovering functional group interactions that possess the ability to define molecular shape, and incorporating these rigid structural features into new-material design, it will be possible to successfully apply the principles of network-based crystal engineering to flexible organic molecules—and, more than likely, this research will uncover compounds that violate all predetermined principles, but remain quite fascinating, nonetheless.

Incorporating the principles of this "reformatted" approach to crystal engineering, this work deals with the solid-state structural features of a diverse series of thioureas, a class of compounds in which solid-state trends have been repeatedly characterized as difficult to predict.[52] Particularly when compared to the isostructural ureas, which are well-known for the reliability with which they form certain supramolecular synthons,[53-55] thioureas' propensity for structural variability is at times utterly confounding, and must be at least partially responsible for the relative dearth of solid-state studies in the chemical

literature. Otherwise, given both medicinal chemists' burgeoning interest in thiourea-containing compounds[56-60] and the importance of polymorphism in drug discovery,[1,2,11,12,61] it seems unlikely that the crystalline organization of thioureas would have garnered so little apparent interest.

Perfectly in tune with both the promises and the pitfalls of crystal engineering, this work contributes both one of the most reliable crystal packing motifs to be found in the chemical literature (**Chapter III**), and a set of structures (**Chapter II**) that, despite being produced from a series of similar and similarly-related compounds, appear to offer little in the way of predictability. Perhaps also in tune with the highly serendipitous nature of science, on the whole, this work also introduces a series of thioureas (Chapters **IV-VI**) which, although offering very little in terms of crystal lattice prediction, present a fascinating example of the effect that solid-state structure—even on a monomeric level—can have on a compound's physical characteristics. This latter class of thioureas also offers a insight into certain hydrogen-bonding interactions, providing the first experimental backing for a 20-year-old theoretical postulate.

Therefore, despite lacking a unified theory of thiourea crystal structure prediction,[§] this work contributes a great deal to the study of solid-state thioureas—and also to the study of the hydrogen bonding itself. Ultimately, it may be that with thiourea crystal engineering—as with many other facets of existence—the sage advice of this author's father will again prove apt, and comforting:

§ The vicissitudes of crystal lattice formation have thoroughly dashed any delusions of grandeur that this author may once have possessed!

If you get a hit one out of every three times you step up to the plate, you're going to the Hall of Fame. That means that the best of the best still fail two-thirds of the time. Ted Williams, who was at least partially immortal, failed almost 60% of the time in 1941, and he was the last person to crack .400. So don't ever let failure get to you, because failure is part of success. If you got it right every time, there'd be no reason to keep trying...

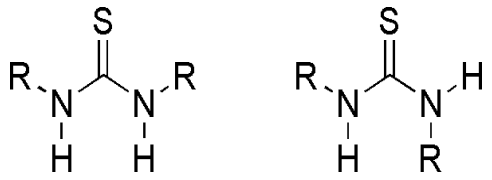
CHAPTER II

TRIS(N-ALKYLTHIOUREIDO)AMINES:

AN EXERCISE IN STRUCTURAL DIVERSITY

Introduction

In contrast to ureas, which, with relatively few exceptions, prefer a *trans-trans* conformation (**Figure 2.1**) in the solid state,[62] thioureas tend to exhibit a significant degree of conformational flexibility: both the *trans-trans* and *trans-cis* conformations are well represented within the chemical literature.[26] While solution-state studies indicate that the *trans-cis* conformer is the predominant solvated species,[63] the approximate ratio of *trans-trans* to *trans-cis* conformers in the solid state appears to coincide with the calculated energy difference between the two species, which, for N,N'-disubstituted thioureas, is approximately 1-2 kcal/mol, in favor of the *trans-cis* conformation. [26] Because the *trans* position is higher in energy for monoalkylated thioureas, by approximately 0.5-1 kcal/mol,[64] it may be that the greater double bond character of the thiourea C=N bonds leads to increased steric repulsion between two



trans-trans *trans-cis*

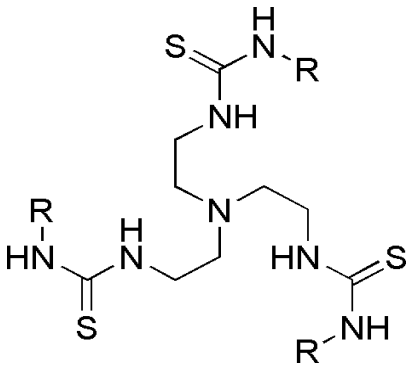
Figure 2.1. Stable conformations of N,N'-disubstituted thioureas.

trans substituents, creating the small observed (and calculated) preference for the *trans-cis* conformation.

Custalcean, *et al*, propose that, at least in the solid state, conformational preferences are closely related to the potential for hydrogen bond formation.[52] Because the energetic difference between the *trans-trans* and *trans-cis* conformations is so small, the energetic benefit of hydrogen bonding may outweigh any destabilization consequent to steric crowding. In relatively simple N,N'-homodisubstituted thioureas[6] and N,N'-disubstituted bis(thioureas),[65] bulky substituents were found to favor the *trans-trans* conformation, likely because steric repulsion in the *cis* position (*i.e.* anti-periplanar to the thiocarbonyl moiety) inhibited hydrogen bond formation. In a related series of bis(thioureas), however, N-substitution appeared to have little impact on the preferred conformation of the thiourea moiety, and hydrogen bonding trends were most closely associated with packing effects originating in other parts of the molecule.[66]

This discrepancy is representative of the difficulties inherent to crystal engineering: patterns of solid state behavior may remain static within a narrowly-defined class of compounds, but do not necessarily translate to similar systems. Rather than representing an inherent limitation of crystal engineering itself, this discrepancy merely reflects our relatively modest understanding of the factors that determine solid-state structure, and emphasizes the need for an increased body of crystallographic data, from which solid-state predictions may be more thoroughly refined. Both the irregularity with which highly similar molecules precipitate from solution, and the potential for solid-state

predictions found in the consistencies that exist even within a diverse body of structures, are exemplified by compounds **1-5** (**Figure 2.2**), the subject of this chapter.



1, R = ethyl
2, R = *n*-propyl
3, R = isopropyl
4, R = *tert*-butyl
5, R = phenyl

Figure 2.2. General structure of compounds **1-5**.

Results

Thioureas **1-5** were prepared from alkyl isothiocyanates and tris(2-aminoethyl)amine, in 60-90% yield. In our initial synthesis, the reaction mixture was stirred at room temperature for 1-3 days, then filtered through a silica plug and washed quickly with ethanol. The resultant product, obtained in somewhat low yield, was sufficiently clean for both spectral analysis and successful crystallization, and we made no attempt to further optimize the reaction.

While resynthesizing thioureas **3** and **5** to obtain full characterization data for these compounds, we used a different synthetic procedure. Instead of stirring the reaction mixture at room temperature for a few days, we refluxed it gently overnight. We also omitted the silica plug, and instead simply removed the reaction solvent (THF) and

recrystallized the solid residue from acetone/hexanes. This procedure increased the product yield from 60-65% to 85-90%, and is certainly the methodology that we would recommend for future synthetic attempts.

Single crystals for X-ray crystallography were grown from either binary or ternary solvent systems, using hexanes as a counter-solvent. We were able to obtain only a single polymorph of each of compounds **2**-**5**, although we observed more than one crystal morphology in both **2** and **4**. We obtained a second polymorph of **1** from ethanol/water—which, interestingly enough, had the same prismatic morphology as the polymorph grown from ethanol/hexanes, albeit a different unit cell—but it was too disordered for further structure elucidation. Consequently, we propose that morphology is not indicative of crystal structure, at least in the case of compounds **1**-**5**. Selected crystallographic data can be found in **Table 2.1**.

Discussion

Highlighting the conformational flexibility of solid-state thioureas, both *trans-trans* and *trans-cis* conformers are present in all crystal structures that we obtained for compounds **1-5**. Two *trans-trans* conformers are present in all compounds except **3**, which has only one *trans-trans* moiety. At first glance, the presence of both thiourea conformations appears to be one of the only common features of these structures—apart from their near-identical atomic composition—as both hydrogen bonding interactions and macroscale crystal packing are otherwise quite disparate. The two *trans-trans* thiourea moieties in compound **1** (R = ethyl) engage in characteristic head-to-tail hydrogen bonding, both intramolecularly and intermolecularly, forming infinite chains of inversely-

Table 2.1. Selected crystallographic data for **1-5**.

Compound	**1**	**2**	**3**	**4**	**5**
Substituent	ethyl	*n*-propyl	isopropyl	*tert*-butyl	phenyl
Formula	$C_{15}H_{33}N_7S_3$	$C_{18}H_{39}N_7S_3$	$C_{18}H_{39}N_7S_3$	$C_{21}H_{45}N_7S_3$	$C_{27}H_{33}N_7S_3$
Crystallization Solvents	ethanol hexanes	ethanol hexanes	dichloroethane hexanes	acetonitrile xylenes hexanes	Dichloroethane hexanes
Crystal Morphology	prisms	prisms	prisms	cubes	needles
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	P1	$P2_1/c$	$P2_1/c$	C2/c
Cell volume ($Å^3$)	2163.4(3)	1207.17(10)	2612.4(3)	2868.8(3)	5445.0(9)
ρ_{calc} (g/cm^3)	1.252	1.237	1.143	1.139	1.346
R-Factor (%)	6.22	5.26	5.05	4.54	4.54
trans-cis : *trans-trans*	2:1	2:1	1:2	2:1	2:1
intramolecular head-to-tail H-bonds[a]	1	1	---	---	2
intermolecular head-to-tail H-bonds[a,b]	2	---	2	4	---
# $R^2_2(8)$ cyclic dimers[b,c]	---	1	2	1	1
# additional intramolecular H-bonds	1	2	1	1	1
# additional intermolecular H-bonds[c]	---	2	4	2	---
Total # of H-bonds[c,d]	7	8	13	13	7

[a] Each head-to-tail bond set (two N-H donors and one C=S acceptor) counted as a single unit
[b] Counted as the number of bond sets *per monomer*, including both donor and acceptor moieties
[c] Each cyclic dimer (two N-H donors and two C=S acceptors) counted as a single unit
[d] Each donor-acceptor interaction counted individually, *e.g.* 1 head-to-tail interaction = 2 H-bonds

oriented monomers, stacked on top of each other via weak van der Waals interactions (**Figure 2.3**). The third thiourea moiety, which adopts the *trans-cis* conformation, forms only a single, intramolecular hydrogen bond—with the central, tertiary nitrogen—and displays no intermolecular hydrogen bonding. apart from very weak S...H(CH_2) contacts ($d_{S...H}$ = 2.912, 2.944 Å) with molecules in neighboring chains. Conversely, compound **5** (R = phenyl), which also contains two *trans-trans* thiourea moieties, forms its crystal lattice from stacked cyclic dimers, comprised of $R^2_2(8)$ interactions between the single *trans-cis* thiourea moiety on two neighboring molecules. While the *trans-trans* thioureas in compound **5** do engage in the expected head-to-tail hydrogen bonding, this occurs only intramolecularly. Other significant crystal packing factors in this compound may include π-stacking ($d_{Ph...Ph}$ = 3.502 Å) and π...H(CH) interactions (2.683 Å). The hydrogen-bonding patterns observed in compound **2** (R = *n*-propyl) are, interestingly enough, much closer to those found in compound **5** than they are to those found in compound **1**. As in compound **5**, the single *trans-cis* moiety in **2** forms an $R^2_2(8)$ cyclic dimer with the *trans-cis* moiety in a neighboring molecule, and the *trans-trans* moieties are involved in intramolecular, head-to-tail hydrogen bonding. Unlike **5**, however, compound **2** does not form two complete intramolecular head-to-tail interactions; instead of interacting with the nearest thiourea sulfur, one *cis* hydrogen interacts with the central amino nitrogen, forming the S(5) intramolecular interaction observed in all thioureas **1**-**5**.

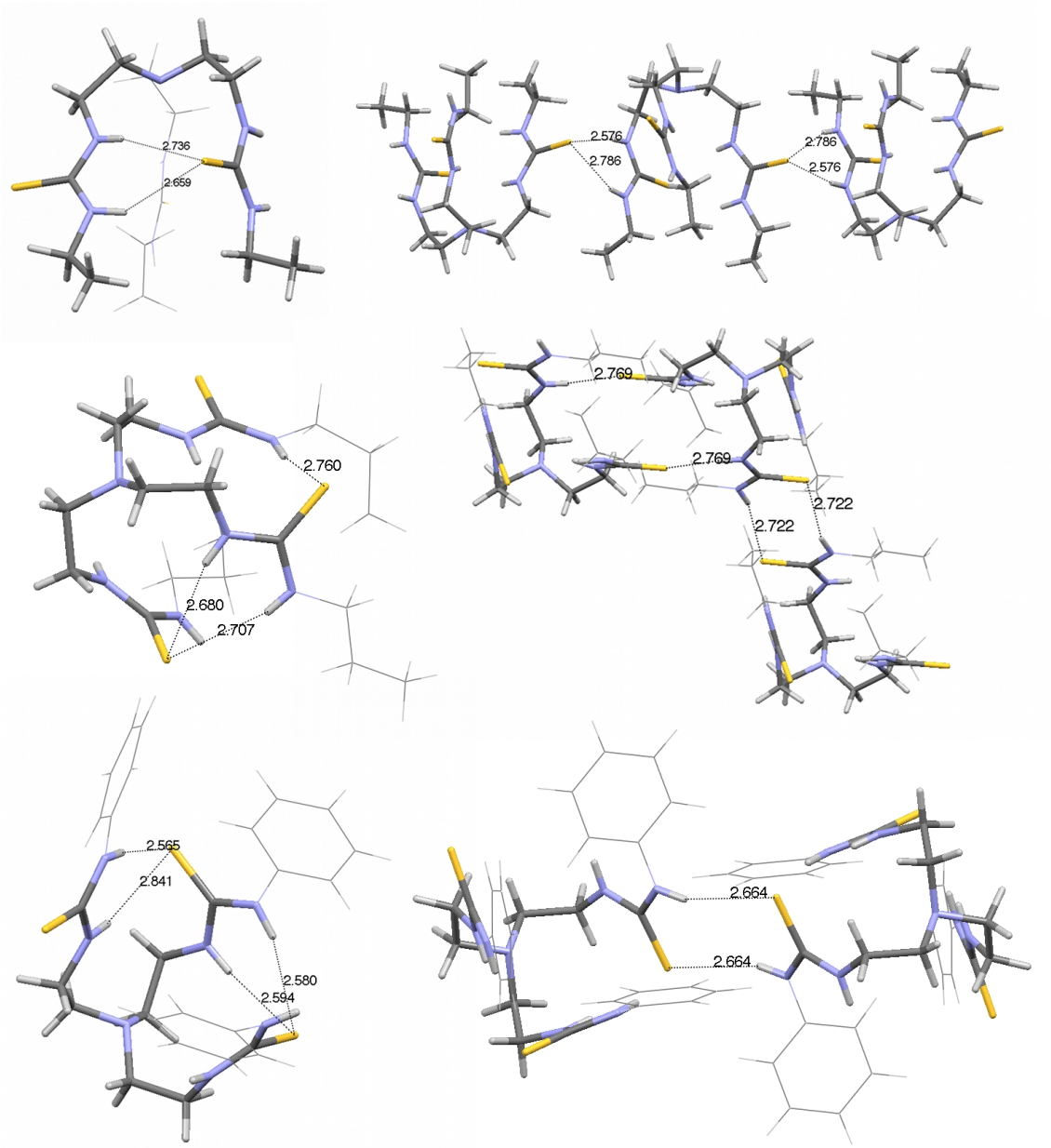


Figure 2.3. Intra- and intermolecular hydrogen bonding patterns in (from top to bottom) compounds **1**, **2**, and **5**. Intramolecular interactions between thiourea moieties are displayed on the left-hand side; for clarity, the N...H(N) interaction between the amino nitrogen and the thiourea hydrogen has been omitted. Intermoleculear hydrogen-bonding interactions for each monomer are shown on the right-hand side.

Also in contrast with **5,** compound **2** forms an additional $R^2_2(20)$ "pseudo-dimer," linking the *cis* hydrogen of the *trans-cis* thiourea moiety on one molecule with the sulfur of the S(5) N...H(N) donor thiourea moiety on another, and *vice versa*.[§] In combination, these dimer-type intermolecular interactions produce zig-zag infinite chains within the crystal lattice; the angle formed through the centroids of the three molecules that form a single, repeating unit of this chain (**Figure 2.3**) is 108.25˚.

Compounds **3** (R = isopropyl) and **4** (R = *tert*-butyl) present a signifcant deviation from the comparable-yet-distinct hydrogen bonding trends observed in **1**, **2**, and **5**. Likely due to the increased steric bulk of their substituents, the thiourea-containing "arms" in **3** and **4** (**Figure 2.4**) are splayed out, rather than concentrated on a single face of the central amino nitrogen, as in **1**, **2**, and **5**. In correlation with this structural change, neither **3** nor **4** form intramolecular hydrogen bonds between thiourea moieties: the sole intramolecular interaction is the S(5) N...H(N) pseudocyle observed in all compounds **1**-**5**.

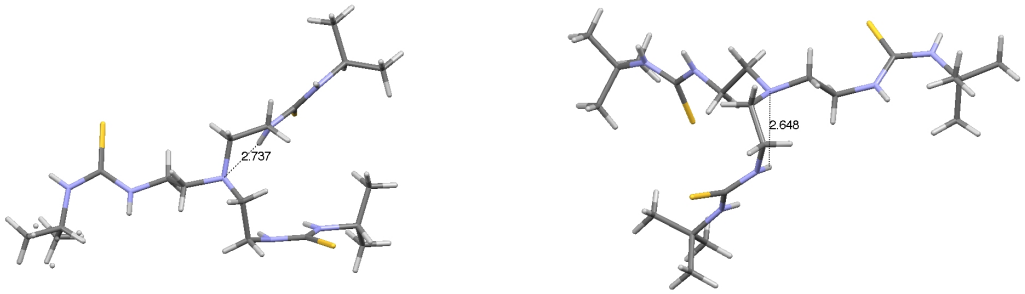


Figure 2.4. Monomeric units of **3** (left) and **4** (right), showing splayed molecular conformation and labeled S(5) N...H(N) intramolecular hydrogen bond.

§ While difficult to describe in words, this interaction is clearly shown in Figure **2.3** (bond length = 2.769 Å vs. 2.722 Å for the $R^2_2(8)$ cyclic dimer.)

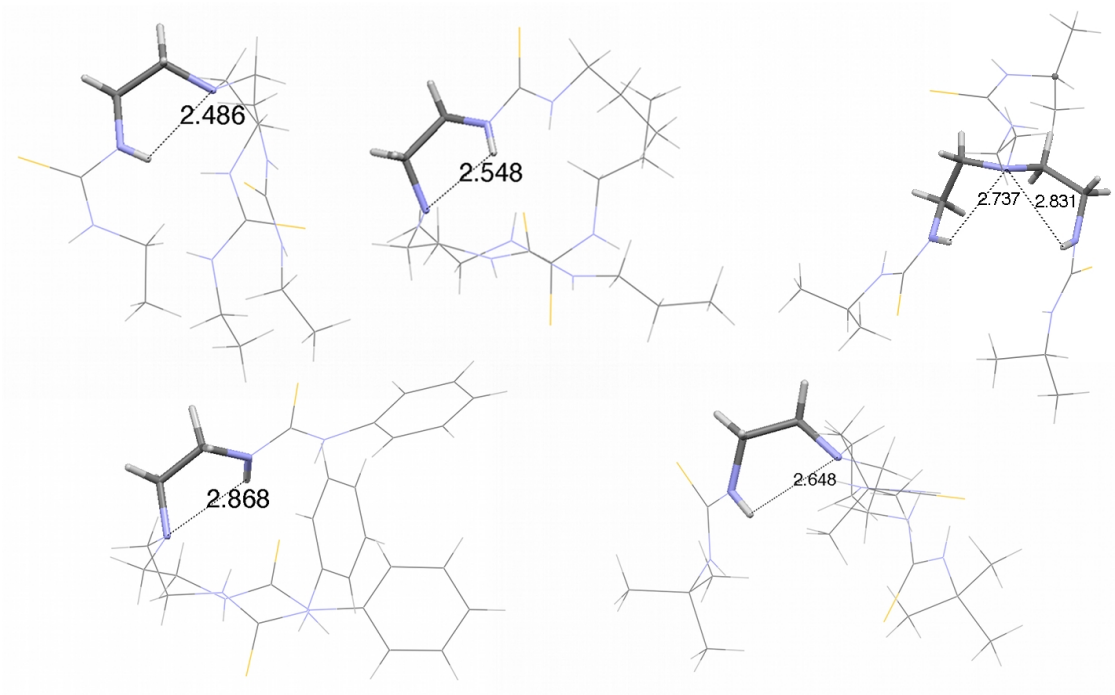


Figure 2.5. Intramolecular S(5) N...H(N) interaction in (clockwise from top left) **1**, **2**, **3**, **4**, and **5**. For clarity, the fragments involved in this interaction are emphasized. In **3**, there are two intramolecular N...H(N) interactions, differing in length by less than 0.1 Å.

As evidenced by the data presented in **Table 2.1**, however, compounds **3** and **4** do not exhibit reduced hydrogen bonding ability as a result of their splayed molecular conformation. Instead, the absence of intramolecular hydrogen bonding appears to correlate with an increase in the total number of hydrogen bonding interactions: 10 in **3** and 13 in **4**, as compared with 7 in **1** and **5**, and 8 in **4**. Additionally, while **1**, **2**, and **5** interact with 2, 3, and 1 molecules/monomer, respectively, each monomer of **3** and **4** forms hydrogen bonds with 5 other molecules, leading to an intricately interwoven

crystal lattice.[§] It is likely that, in compounds **3** and **4**, steric bulk inhibits intramolecular hydrogen bonding, leading to a conformation that better promotes intermolecular interaction.

Regardless of the disparities found among their respective hydrogen-bonding patterns, compounds **1**-**5** do display certain structural similarities. In a foreshadowing of things to come (*vide infra*), each monomer features an S(5) intramolecular hydrogen bond between one thiourea hydrogen and the central, tertiary amino nitrogen (**Figure 2.5**). Bilton, *et al*, calculate the probability of formation (P_s)[‡] for this type of interaction to be 17.5,[67] so its consistent occurrence in **1**-**5** is certainly remarkable. Because the bond lengths (**Table 2.2**) in these interactions are longer than 2.30 Å, the commonly-accepted limit for significant N...H(N) electrostatic interactions,[68,69] it is unlikely that they represent a driving force behind the solid-state organization in **1**-**5**.

Table 2.2. Bond lengths, bond angles, and conformations observed in the S(5) N...H(N) interactions in thioureas **1**-**5**.

Compound	**1**	**2**	**3 (1)**	**3 (2)**	**4**	**5**
$d_{N...H(N)}$ (Å)	2.486	2.548	2.831	2.737	2.648	2.868
$d_{N...N}$ (Å)	2.819	2.870	2.909	3.005	2.874	3.029
donor conformation	*trans-cis*	*trans-trans*	*trans-trans*	*trans-cis*	*trans-trans*	*trans-trans*
> N...H(N) (˚)	108.33	106.84	88.01	100.91	97.44	92.69

§ For this reason, intermolecular interactions in **4** and **5** are not depicted in two-dimensional format; instead, they can be viewed in the attached crystallographic files.

‡ P_s is defined as the percentage of structures in the CSD that form a particular intramolecular contact, relative to the total number of structures that are theoretically capable of forming that contact. In the case of the S(5) N...H(N) interaction, Bilton, *et al*, found 372 structures in the CSD with a NH--$(CH_2)_2$--NR_2 fragment; of these, 65, or 17.5%, exhibited the intramolecular hydrogen bond observed in **1**-**5**.

In addition to the intramolecular N...H(N) interaction, thioureas **1**-**5** exhibit similarities in other structural trends, albeit unrelated to supramolecular architecture or crystal engineering. As was previously observed in unrelated thioureas,[70] elongation of the C=S bond in **1**-**5** correlates well with hydrogen bonding occurrence. When uncoordinated, the average C=S bond length in **1**-**5** is 1.680 Å, close to the mean C=S bond length (1.681 Å) reported by Allen, *et al*, and corresponding to approximately 50% double-bond character.[71] When the S is coordinated to 1, 2, or 3 thiourea hydrogens, the average C=S bond length increases to 1.695, 1.704, and 1.713 Å, respectively, indicating a correlation between hydrogen bonding and decreased double-bond character. A corresponding trend of (S=)C—N bond truncation was also observed, presumably due to resonance support for the elongated C=S bond.

Conclusion

Despite similarity in chemical structure, compounds **1**-**5** exhibit significant diversity in their solid state conformational preferences. Certain consistencies do exist, such as the S(5) N...H(N) intramolecular interaction observed in each structure, but these tris(2-thioureidoethyl)amine derivatives are more exemplary of the unpredictability of solid-state structure than of a set of predictable crystal engineering synthons. Nevertheless, both the S(5) N...H(N) intramolecular interaction and the changes in bond length consequent to hydrogen bonding that we observed in **1**-**5** foreshadow structural features found among more consistent classes of compounds (*vide infra*), and may offer an (albeit shaky) starting point for more reliable solid-state thiourea synthons.

CHAPTER III

THE SPIRAL GALAXY:

A ROBUST THIOUREA SYNTHON FOR CRYSTAL ENGINEERING

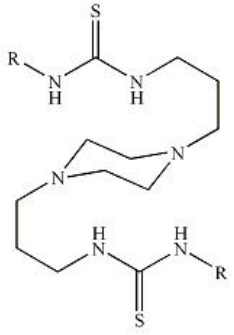
Introduction

While the solid-state behavior of the ureas is well-understood, and often exploited for a variety of chemical applications,[55,72] crystalline organization in the isostructural thioureas remains somewhat more obscure.[26] As a likely consequence of the increased conformational flexibility of thioureas over ureas,[64] observed solid-state trends of the former are more tenuous than those of the latter, and few reliable synthons have been established in the chemical literature.[26] Nevertheless, the strong hydrogen-bonding ability of thioureas has shown utility in areas ranging from anion complexation[73] and organic synthesis[74,75] to non-linear optics,[76] and we believe that improving our understanding of and control over their solid-state behavior will lend greater utility to this very promising functional group.

In order to establish control over the crystalline structure of substituted thioureas, it is necessary to identify reliable, solid-state motifs, which can be both utilized as such, and built upon, in the development of new materials. We noticed, in an unpublished survey of tris(N-substitutedthiourea) derivatives of tris(2-aminoethyl)amine, that,

although these compounds exhibit the structural diversity characteristic of crystalline thioureas, one reliable, solid-state feature can still be found: an intramolecular contact between each central, tertiary nitrogen atom and a hydrogen atom from one of its thiourea "arms," resulting in a five-membered ring. While this motif appeared to contribute little to the organization to these compounds, we found its invariable presence, amid the overwhelming inconsistencies of these compounds, to be of interest.

Focusing on the potential for interaction between attached thiourea moieties and central, tertiary nitrogens, we selected N,N'-bis(3-aminopropyl)piperazine as a candidate for further solid-state investigation. Although we initially believed that the flexibility of the piperazine ring might allow these molecules to form dimeric structures similar to



6: R = n-propyl
7: R = n-pentyl
8: R = isopropyl
9: R = *tert*-butyl
10: R = benzyl
11: R = phenyl

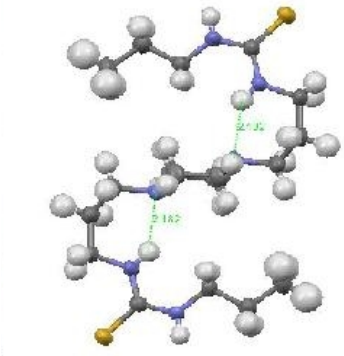


Figure 3.1. The Spiral Galaxy Motif. General structure of thioureas **6-11** (left) and representative crystal structure (right, thiourea **6**)

those reported in a previous work,[10,66] we instead discovered, quite serendipitously, that these compounds presented a heretofore unreported thiourea synthon: the "spiral galaxy," shown in **Figure 3.1**. Named after the appearance of the solid-state structure of thioureas **6-11**, this intramolecular motif forms quite reliably, when a monosubstitued thiourea

moiety is separated from a tertiary nitrogen atom by a 3-carbon, alkyl chain, and may exert signficant control over crystal packing in the compounds that contain it. In this work, we have explored the ubiquitousness of this motif, both in the thiourea derivatives of N,N'-bis(3-aminopropyl)piperazine, and in other molecules with appropriate structural characteristics. Due to the current dearth of reliable thiourea synthons, we believe that this "spiral galaxy" motif will provide significant assistance to the efforts of all those engaged in crystal engineering with these intriguing and useful molecules.

Results and Discussion

Despite the propensity of thioureas to display significant conformational flexibility, five of six N,N'-bis(3-aminopropyl)piperazine derivatives, thioureas **6-11**, form identical intramolecular hydrogen bonds, illustrated by the representative molecular structures of **6** and **7** (**Figure 3.2**). These intramolecular contacts result in the formation of a six-membered ring, with a chair-like conformation, on each face of the molecule. In **10**, this intramolecular contact forms between the piperazine nitrogen and the far thiourea hydrogen, resulting in an 8-membered ring; however, this difference does not appear to result in additional structural changes. The torsion angle found between the carbon-carbon bond in the piperazine ring, and the intramolecular hydrogen bond formed between the adjacent nitrogen atom and the relevant thiourea hydrogen, is approximately 90 degrees, placing the covalently-bound ring and the hydrogen-bound ring in a near-perpendicular arrangement.. With the exception of **11**, which will be discussed in greater detail below, the length of this intramolecular contact increases, from 2.141 A to 2.316 Å,

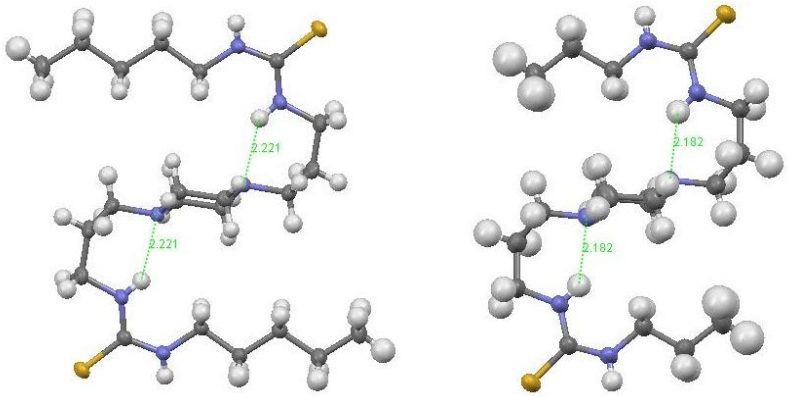


Figure 3.2. Molecular structures of **6** (right) and **7** (left), showing intramolecular hydrogen bonds

in proportion to the relative size of the substituent (**Table 3.1**). Interestingly, even the *tert*-butyl-substituted thiourea **9** forms this intramolecular contact, although its length is significantly extended. This can be contrasted to the observations of Custalcean *et al*,[52] who reported that the solid-state conformation of certain N,N'-dialkylthioureas could be controlled by the bulkiness of the two alkyl substituents. In that work, an N-*tert*-butyl-N'-

Table 3.1. Intramolecular hydrogen bonding in thioureas **6-11**.

Thiourea	Substituent	N…H(N) (Å)	N…N(H) (Å)
6	n-propyl	2.182	2.912
7	n-pentyl	2.221	2.929
8	isopropyl	2.218	2.936
9	*tert*-butyl	2.316	3.009
10	benzyl	2.141	2.946
11	phenyl	2.493	3.011

ethylthiourea adopted the *trans-trans* conformation--as did all other N-*tert*-butyl thioureas, if the N' substituent was bulkier than a simple methyl group--and not the *trans-cis* conformation found in thiourea **9**.

Table 3.2. Intermolecular hydrogen bonding in thioureas **6-10**

Thiourea	Substituent	S...H(N) (Å)	S...N(H) (Å)	Space Group
6	*n*-propyl	2.647	3.452	P-1
7	*n*-pentyl	2.700	3.473	P-1
8	isopropyl	2.631; 2.607	3.460; 3.379	$P2_1/n$
9	*tert*-butyl	2.729	3.519	P-1
10	benzyl	2.651	3.436	P-1

Similarly independent of significant substituent effects, the intermolecular contacts of thioureas **6-10** are also surprisingly identical. Because the formation of the "spiral galaxy" motif forces both thiourea moieties into the *trans-cis* conformation, the sulfur atom and the adjacent thiourea hydrogen atom are ideally located to form an eight-membered cyclic dimer, one of the two most prevalent solid-state thiourea structural motifs, with a neighboring molecule. In thioureas **6-10**, the formation of this cyclic dimer on each face of the molecule results in long chains of identically-configured molecules, which stack in a staggered arrangement (**Figure 3.3**) in the crystal structure. The length of the S...H(N) contact in these structures ranges from 2.607 Å to 2.729 Å, and demonstrates no apparent correlation with substituent size **(Table 3.2**).

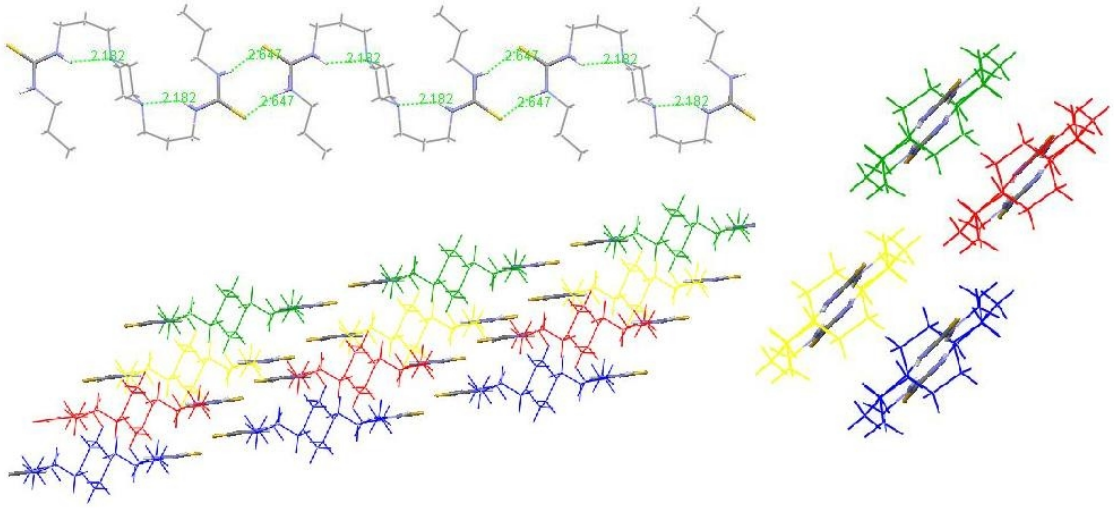


Figure 3.3. Crystal packing in spiral galaxy thioureas **6-10**. Clockwise from upper left: (a) Infinite chain of cyclic dimers; (b) side view of infinite chains (shaded for clarity; thiourea units retain standard coloration); (c) rows of infinite chains

With the exception of **8**, which crystallizes in space group $P2_1/n$, these thioureas also crystallize in the same space group, P-1. The variance seen in **8** is likely due to asymmetry in the three-dimensional environment around the isopropyl substituent, evidenced by non-equivalent S...H(N) bond lengths in the cyclic dimer; the intramolecular contacts and intermolecular contacts remain identical to those of compounds **6**, **7**, **9**, and **10**.

Apart from the definitional differences seen in the space group classification of compound **8**, and the difference in intramolecular ring size seen in **10**, only compound **11**, the bis(N”-phenylthioureido) derivative of N,N'-bis(3-aminopropyl)piperazine, presents a

real deviation from the trends in inter- and intramolecular hydrogen bonding seen in this class of molecules. Crystallizing in space group $P2_1/c$, thiourea **11** forms the predictable, six-membered intramolecular contact, yet its intermolecular contacts, shown in **Figure 3.4**, differ from those present in thioureas **6-10**. Instead of forming a cyclic dimer with a neighboring thiourea molecule, the available hydrogen and sulfur atoms on each "arm" of **11** instead form an eight-membered cyclic dimer with a molecule of DMSO, one of the two crystallization solvents. The bond between the thiourea hydrogen atom and the DMSO oxygen atom is 2.006 Å, and the bond between the thiourea sulfur atom and the α-proton on the DMSO molecule is 2.986 Å; both of these bond lengths fall within range for hydrogen bonding with the specified heteroatom.[77,78] In addition to this cyclic dimer, each DMSO oxygen atom also interacts with the mildly acidic[79] aromatic hydrogen α to the thiourea moiety on a neighboring molecule of **11**, serving as a "bridge" between the two thiourea-containing molecules. This type of hydrogen bonding has been observed in proteins, as well as smaller organic molecules.[80-82] As each molecule of **11** also bonds to two different DMSO molecules, the solvent serves only as a "spacer" between thioureas, an extra linkage in the long chains—albeit with different three-dimensional organization--also seen as a supramolecular motif in compounds **6-10**.

Table 3.3. Crystal morphology, crystallization solvent(s), and space group assignment for thioureas **6-11**

Thiourea	Morphology	Space Group	Crystallization Solvent(s)
6	clear plates	P-1	ethanol/water
7	clear plates	P-1	ethanol/hexanes
8	clear needles	$P2_1/n$	ethanol/hexanes
9	clear prisms	P-1	acetonitrile/water
	clear needles	P-1	DMSO-d_6
10	clear prisms	P-1	ethanol/water
11	clear needles	$P2_1/c$	DMSO/ethyl acetate

Because the presence of DMSO in **11** appears to mostly augment, rather than interrupt, the supramolecular trends seen in **6-10**, we believe that the presence of DMSO in the crystal structure of **11** is probably a consequence of the compound's idiosyncratic solubility, rather than an indictment of the "spiral galaxy" model, itself. Thioureas **6-10** have remarkably similar solubility profiles, and can be reliably crystallized from a variety of different solvents (detailed in **Table 3.3**) but thiourea **11** did not share these solubility trends. Dissolving a non-negligible amount of **11**, even upon sonication-preceded boiling,

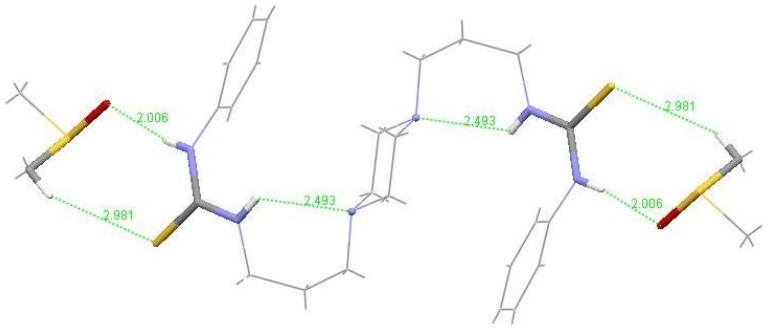


Figure 3.4. Hydrogen bonding in **11**.

was accomplished only in strongly dipolar solvents, such as DMSO, DMF, and N-methylpyrrolidinone, and at high temperatures. It is therefore probable that the same intermolecular contacts seen in **6-10** exist in compound **11**, in its non-solvated form, and that the conditions required to obtain an analytical crystal are responsible for its asynchronous, solvated crystal structure.

Because the "spiral galaxy" motif was so overwhelmingly consistent among the bis(N"-substituted thioureido) derivatives of N,N'-bis(3-aminopropyl) piperazine, we explored the versatility of this synthon in other, structurally appropriate compounds. To form the six-membered, intramolecular contact observed in **6-11**, the target molecule must contain a tertiary amine,[17] separated from the thiourea by a three-carbon alkyl chain.

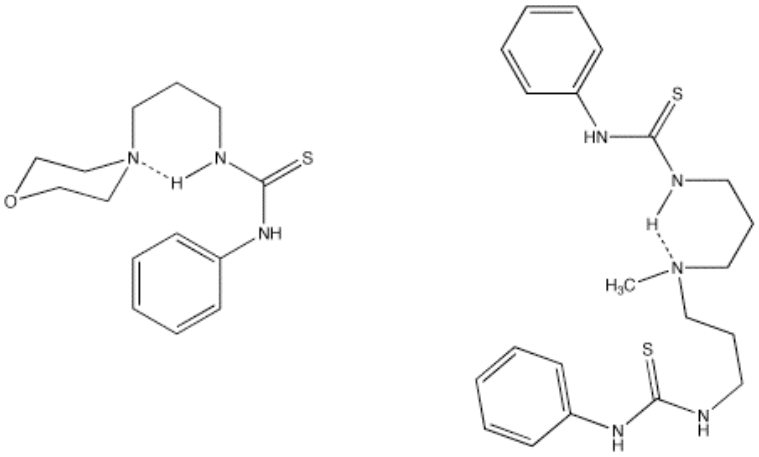


Figure 3.5. Thioureas **12** (left) and **13** (right)

Two compounds, **12** and **13**, shown in **Figure 3.5**, were synthesized, to test the applicability of the "spiral galaxy" motif in other systems: both crystal structures featured the expected intramolecular contact.

Compound **12**, synthesized from N-(3-aminopropyl)morpholine and phenyl isothiocyanate, crystallized in the $P2_1/n$ space group, and, in addition to the six-membered, intramolecular contact, also formed the eight-membered, cyclic dimer seen in compounds **6-10**. The intramolecular hydrogen bond length in **12** was 2.271 Å, which was significantly shorter than that observed in **11**, 2.493 Å, despite the similar structure of these compounds. Interestingly, and possibly suggestive of an explanation for the differing bond lengths, the phenyl substituent in **12** is twisted away from the face of the morpholine ring, whereas, in **11,** the phenyl substituent is almost perfectly parallel to the face of the piperazine ring, with a torsion angle of 0.01 degrees; apparently, sharing the same thiourea substituent as **11** did not cause **12** to deviate dramatically from the trends in solubility and observed intermolecular contacts seen in **6-10**. Because the morpholine ring possessed only one thiourea-containing "arm," these dimers did not form the chains seen in the N,N'-bis(3-aminopropyl)piperazine-derived thioureas; however, weak contacts, with bond lengths of 2.669 Å and 2.544 Å, were observed between the morpholine oxygen atom and two alkyl hydrogen atoms on a neighboring molecule.

In contrast to compound **12**, the intermolecular trends seen in compound **13** were remarkably similar to those observed in compounds **6-10**. Crystallizing in the $P2_{1/c}$ space group, and featuring the "spiral galaxy" -type intramolecular motif, between one of its thiourea "arms," and its central, tertiary nitrogen atom, compound **13** also formed infinite

chains of cyclic dimers, as each thiourea "arm" formed two hydrogen bonds with a single, neighboring molecules. The length of the intramolecular hydrogen bond is 2.083 Å, which correlates well with the trend in bond length vs. substituent size observed in **6-10**; the intermolecular hydrogen bond lengths are 2.514 Å and 2.436 Å, respectively. In addition to these five hydrogen bonds, the crystal structure of **13** also features an intramolecular interaction between one aryl proton and the π-cloud of the other aromatic ring, with the former located 2.763 Å from the mean plane of the latter, which is consistent with known values for this type of interaction.[82,84]

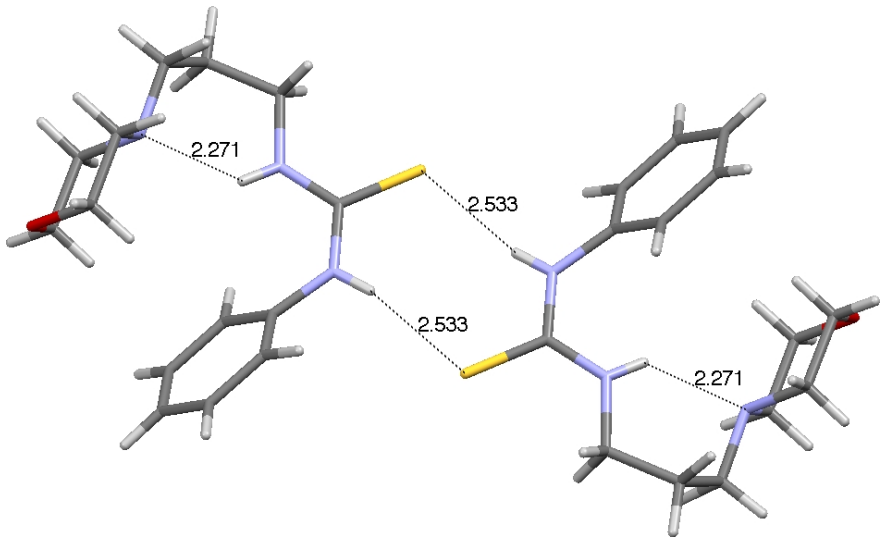


Figure 3.6. Hydrogen bonding in thiourea **12**

Conclusion

We have discovered a new, solid-state structural motif, the "spiral galaxy," common among all reported derivatives of N,N'-bis[3-(N"-substitutedthioureido)-propyl]piperazine. We have also demonstrated that the robustness of this synthon extends to other thioureas, which possess the requisite structural characteristics: a three-carbon chain, separating an N-substituted thiourea moiety and a tertiary amine. The "spiral galaxy" motif also appears to direct intermolecular hydrogen bonding, at least in the N,N'-bis[3-(N"-substitutedthioureido)propyl]piperazine compounds examined in this paper. More work is needed in this area, to determine the consistency of the "spiral galaxy" motif in directing intermolecular hydrogen bonding--and, consequently, crystal packing--in a diverse array of thioureas, to explore its use as a synthetic building block in solid-state design.

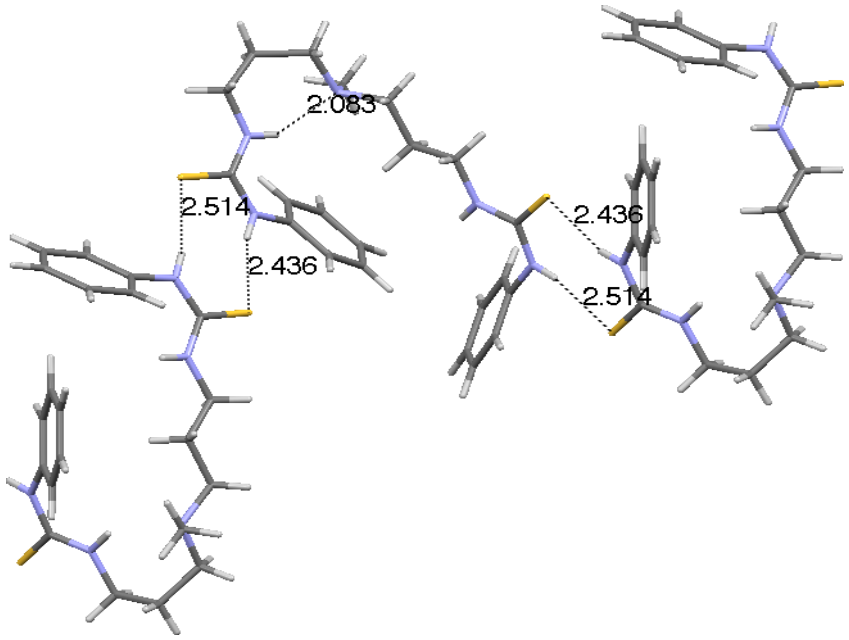


Figure 3.7: Hydrogen bonding in thiourea **13**

CHAPTER IV

A RESONANT COMPETITOR:

INTRAMOLECULAR SUPERNOVA OBLITERATES THE SPIRAL GALAXY

IN N,N'-DISUBSTITUTED THIOUREAS

Introduction

The robustness of the "spiral galaxy" synthon prompted us to subject it to competitive interaction from other functional groups. The structural motif displayed in **Figure 4.1** is well-documented in the chemical literature, among both carbonyl-[83-89] and pyridyl-subsituted[84,90-98] thioureas; this reliability led us to believe that it would pose a significant challenge to the robustness of the "spiral galaxy" interaction. Because, as was mentioned in **Chapter I**, the presence of a competitive functional group tends to decrease the prevalence of a supramolecular homosynthon,[51] we believed it likely that this trend could extend to intramolecular interactions, as well. On the basis of estimated ΔpK_a values, which have been used to predict hydrogen bonding affinity in a wide variety of molecular complexes,[99] we hypothesized that the "spiral galaxy" motif would predominate, in both cases.

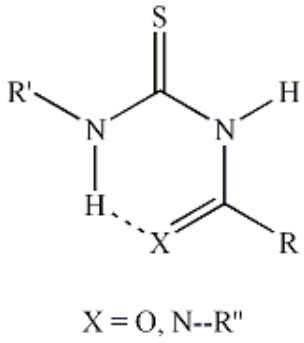


Figure 4.1. Intramolecular interaction(s) selected for competition with the "spiral galaxy" synthon

Results and Discussion

The 2-pyridylthioureido derivative of N,N'-bis(3-aminopropyl)piperazine was initially selected for further investigation, to explore the relative hydrogen-bonding strength of the pyridyl nitrogen and the piperazine nitrogen. As shown in **Figure 4.2**, these two acceptor atoms would be forced to compete for the same thiourea proton, thereby testing the strength of the spiral galaxy motif in compounds with potentially competitive functionalities. The synthesis and isolation of this compound proved difficult; however, a related compound, N-[3-(2-pyridylthioureido)propyl]morpholine, **14** (**Figure 4.3**), was successfully prepared. Because the spiral galaxy motif had been previously observed in **12**, the N-phenyl analog of **14**, we believed that this compound would serve the same purpose as the desired piperazine derivative. On the basis of

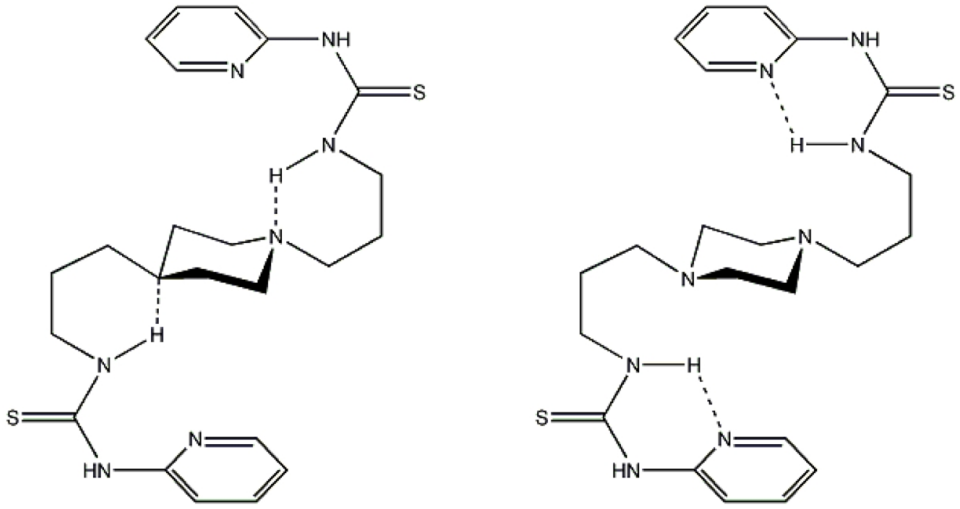


Figure 4.2. Two possible intramolecular hydrogen bonds in N,N'-bis[3-(2-pyridylthioureido)propyl]piperazine

reported pK_a values for the protonated species (7.01-8.69 for N-alkyl morpholines[100,101] and 3.33-6.68 for various related pyridines[102]), we hypothesized that the morpholine nitrogen would form the intramolecular hydrogen bond, due to both its greater basicity and its increased proton affinity.

Both the ^{1}H NMR spectrum (**Figure 4.4**) and the crystal structure of compound **14** clearly indicated that this was not the case. In compounds **6-11**, the thiourea protons were observed as very broad singlets around 6 ppm; however, in the $CDCl_3$ ^{1}H NMR spectrum of compound **14**, the thiourea protons were observed as a triplet at 11.9 ppm, and a singlet 8.8 ppm. While somewhat broadened in comparison with more-upfield aromatic protons, these signals were nevertheless far sharper than a "typical" heteroatomic proton resonance, indicating a low rate of exchange. Far-downfield signals in the ^{1}H NMR have been associated with intramolecular hydrogen bonding in N-(2-pyridyl) thioureas,[103] and the splitting of the signal at 11.9 ppm correlates with the presence of two α-hydrogens on the N-propylmorpholine substituent.

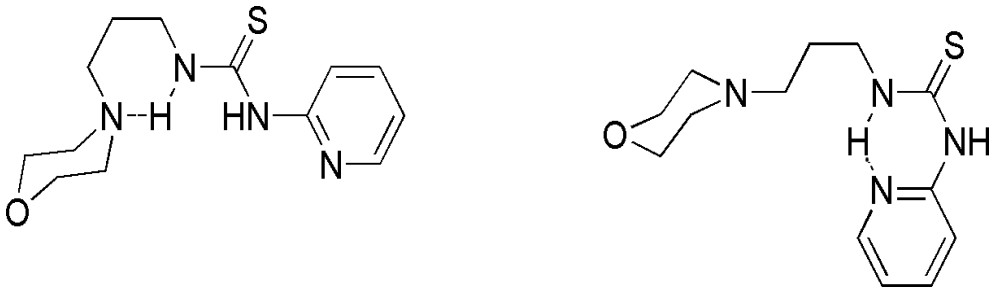


Figure 4.3. Two possible intramolecular hydrogen bonds in N-[3-(2-pyridylthioureido)propyl]morpholine

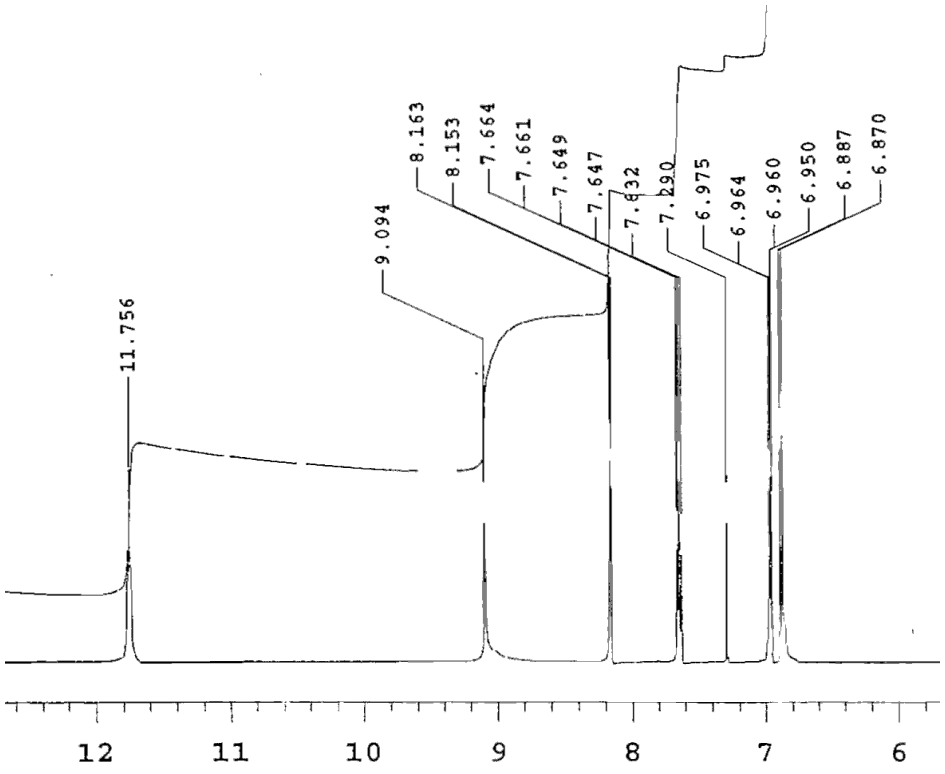


Figure 4.4. Aromatic region of ^{1}H NMR spectrum of **14**. Pyridyl-bound proton can be observed as a broad triplet at 11.756 ppm.

Corroborating the ^{1}H NMR evidence, the crystal structure of **14** shows an intramolecular, six-membered ring, formed between the pyridyl nitrogen and the "contested" thiourea hydrogen. Having adopted the *trans-cis* conformation in order to effect this intramolecular contact, the compound is well-suited to form cyclic thiourea dimers, and a centrosymmetric $R_2^2(8)$ intermolecular interaction ($d_{S\ldots H(N)}$ = 2.587 Å) was indeed observed. Interestingly, despite the non-spiral galaxy-type intramolecular interaction, crystal packing in **14** closely resembled that observed in **6-11**.

Complementing the aforementioned $R_2^2(8)$ interaction, a weak interaction was also observed between the morpholine O and the proton α to the pyridyl nitrogen, forming a centrosymmetric $R_2^2(28)$ dimer. This second dimer served as a proxy for the second $R_2^2(8)$ interaction observed in **6-11**, creating nearly-identical chains of opposite-oriented monomers, which also packed in a staggered arrangement, with no observed π-π interactions (**Figure 4.5**).

Because the intramolecular hydrogen bond observed in **14** did not match our initial prediction—which had been based on literature values for pK_as found for the pyridyl and morpholyl functionalities in related compounds—the pK_as of the diprotic salt of **14** were determined. A sample of **14** was dissolved in acetone, and concentrated HCl (aq) was added dropwise, until the pH of the solution was pink to indicator paper (pH ≃ 1) and a colorless solid precipitated. This solid was washed with water, acetone, and ether; air-dried to constant weight; and confirmed by ^{1}H-NMR to be the diprotic salt of **14**. It was then titrated with 0.05 M NaOH in three separate trials (sample titration curve shown in **Figure 4.6**). In each trial, two equivalence points were observed, corresponding

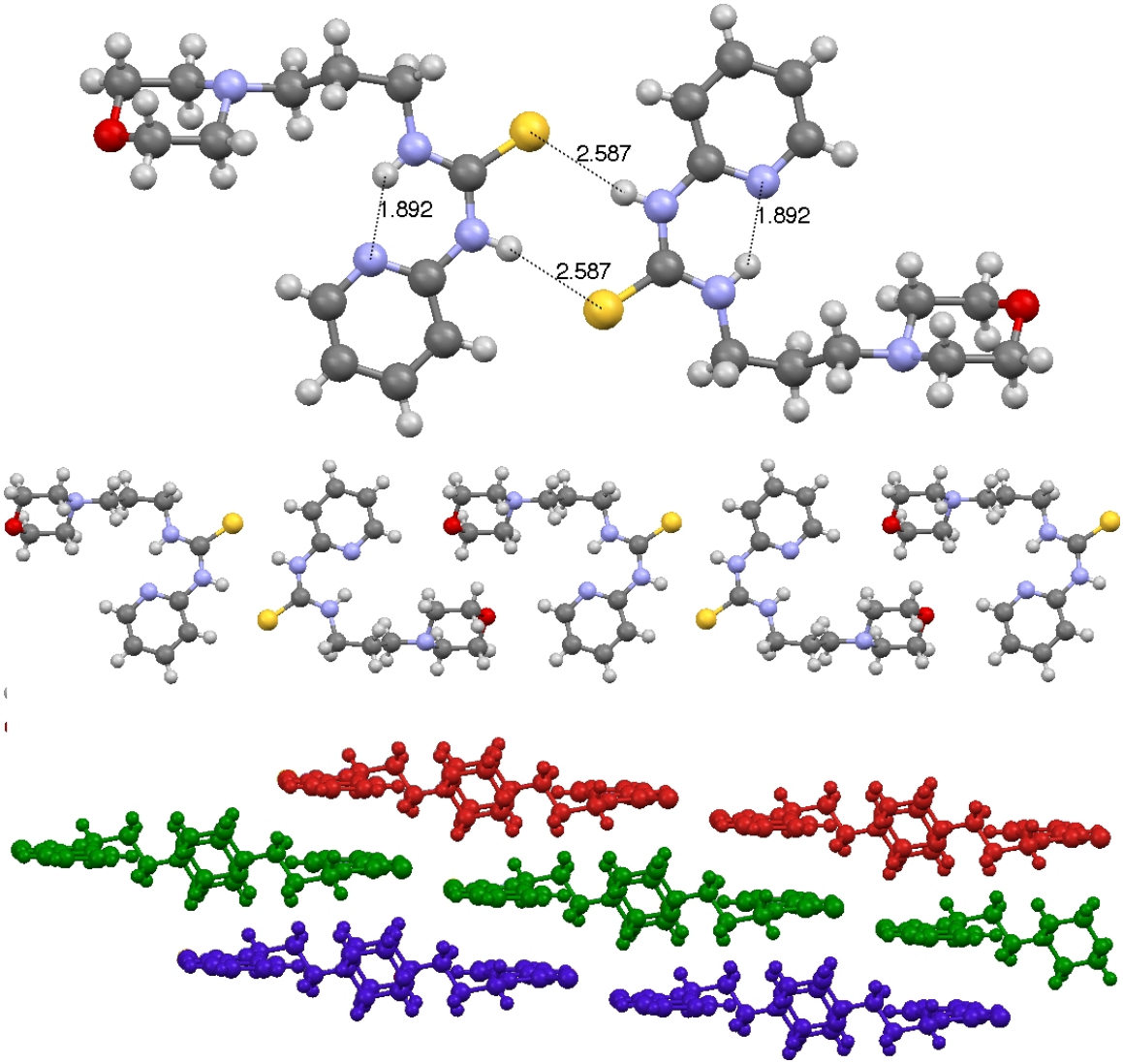


Figure 4.5. Intra- and intermolecular hydrogen bonding and crystal packing in **14**. At top, centrosymmetric $R_2^2(8)$ cyclic thiourea dimer; in the middle, infinite chains formed from $R_2^2(28)$ and $R_2^2(8)$ dimers; at bottom, stacks of infinite chains, colored for clarity.

to pK_as of 3.15 ± 0.05 and 7.3 ± 0.3, which we assigned to the pyridinium and morpholinium ions, respectively. While the latter pK_a value (*i.e.* for the morpholinium proton) falls within the anticipated range, the former is somewhat lower than previous

studies have predicted;[102] this discrepancy can likely be attributed to the solution-state hydrogen bond that forms upon deprotonation.[104]

Because these relative pK_a values did not predict the preferred hydrogen bond acceptor in **14**, we searched the literature for another explanation. Resonance-Assisted Hydrogen Bonding (RAHB) has been described as "the interplay between hydrogen bond and heterodienes (or more generally heteroconjugated systems) [that] can strengthen remarkably the hydrogen bond itself."[105] DFT calculations have shown that, in general, RAHBs (which will be discussed at greater length in **Chapter V**) are approximately twice as strong as ordinary hydrogen bonds,[106] which correlates well with the short $d_{N---H(N)}$ (1.892 Å) observed in **14**.

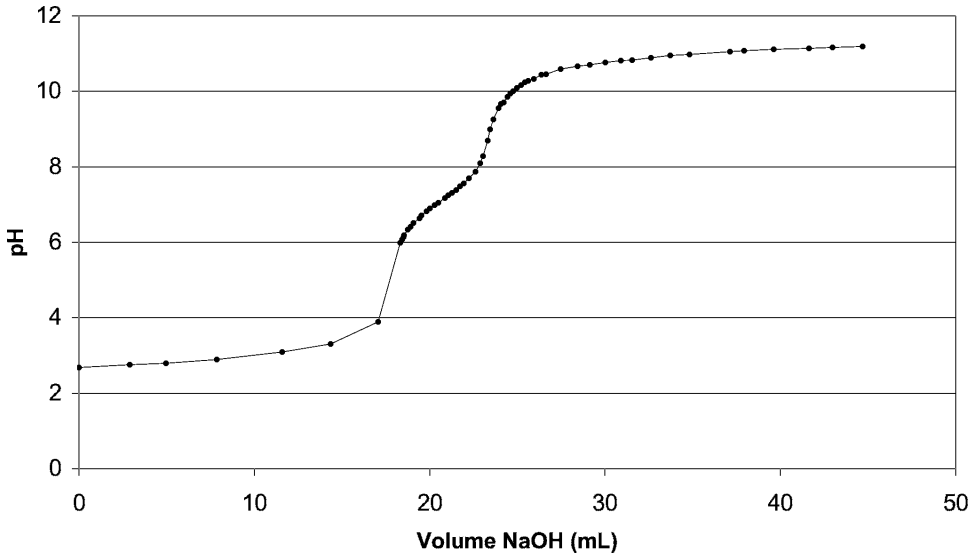


Figure 4.6. Titration of diprotic HCl salt of **14**.

RAHB has also been observed in enolones, enaminones, enaminoimines, enolimines, β-diketones, β-keto-esters, amide-amidine coupling, amide dimers, thymine-adenine coupling, and guanine-cytosine coupling,[105] and we synthesized compound **15**, N,N'-bis[3-(N"-benzoylthioureido)propyl]piperazine to test the plausibilty of RAHB as an explanation for the non-pK_a-based competitive behavior observed in **14**. Because the pK_a of the protonated carbonyl moiety should be less than zero,[107] there is no way that, on the basis pK_a values alone, it could be expected to compete with the piperazinyl nitrogen.

Shown in **Figure 4.7**, the crystal structure of bis(thiourea) **15** suggests that RAHB out-competes the spiral galaxy as an intramolecular hydrogen-bonding motif. As in **14**, the observed intramolecular interaction is between the thiourea proton and the unsaturated substituent attached to the opposing nitrogen (2 per molecule); the tertiary amino nitrogens do not participate in hydrogen bonding. Interestingly, the *trans-cis* thiourea moieties do not form the anticipated $R_2^2(8)$ dimers observed in **6-11**. Instead, monomers are linked by two, single S...H(N) interactions (2.856 Å), one on each "arm" of the piperazine moiety, forming infinite C(4)‡ chains of identically-oriented molecules. These chains are linked by phenyl-RAHB π-π stacking (*vide infra*) between opposite-oriented monomers, resulting in a fully cross-linked supramolecular network structure.

‡ Technically, as each monomer forms two S...H(N) H-bonds with each neighboring molecule (1 as a donor and 1 as an acceptor), this should be categorized as an $R_2^2(30)$ interaction; however, the C(4) interaction is far easier to visualize and understand.

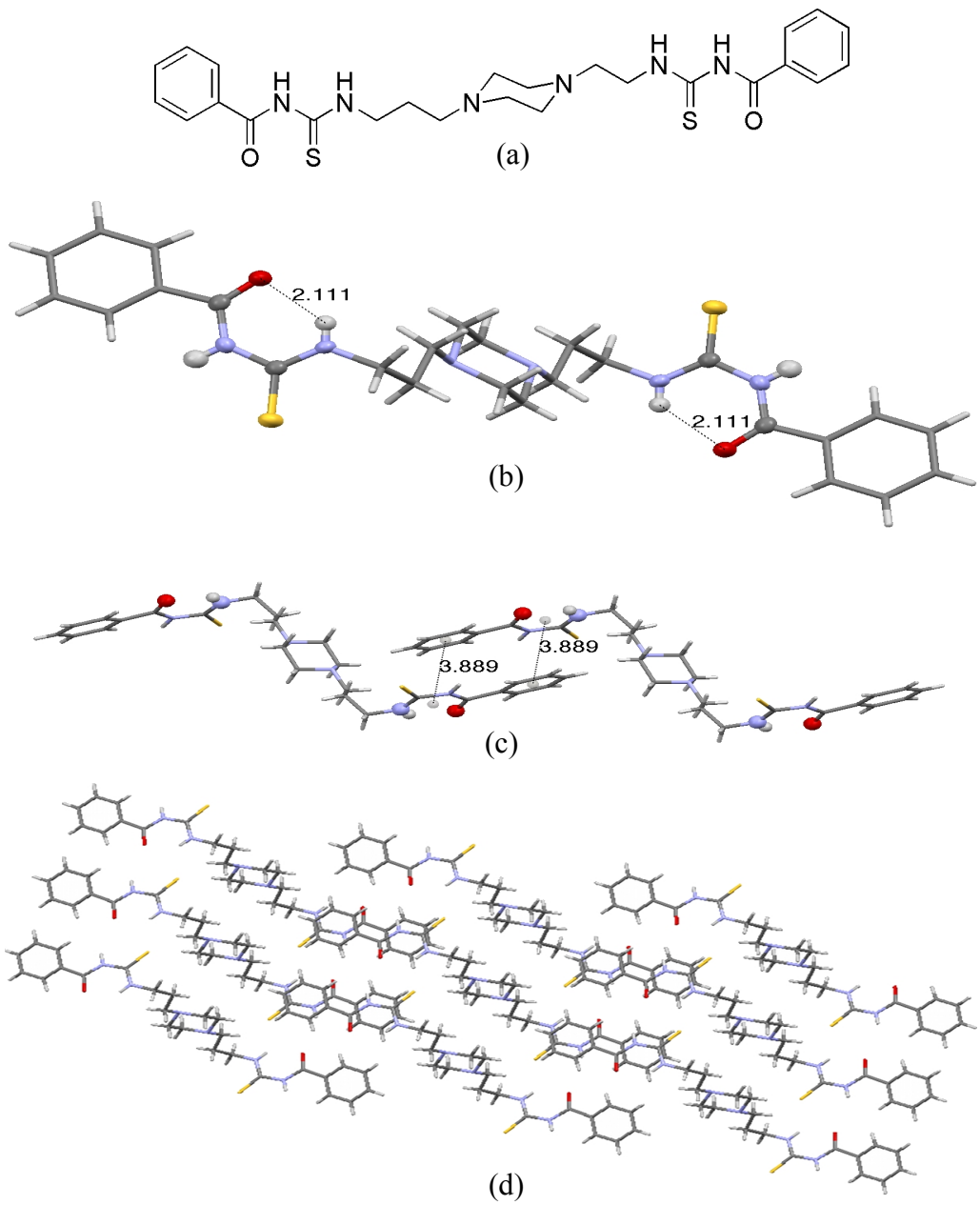


Figure 4.7. Hydrogen bonding and crystal packing in **15**. (a) Chemical diagram of **15**; (b) intramolecular (C=)O...H(N) RAHBs in the single-crystal structure; (c) RAHB-phenyl π-π stacking (centroid-centroid distance = 3.889 Å); (d) crosslinked crystal network. C(4) interactions are apparent on either end of (d); overlapping phenyl rings and RAHB pseudo-rings are also shown.

CHAPTER V

RESONANCE-ASSISTED HYDROGEN BONDING:

A TALE OF TWO CONFORMERS

Introduction

Believed to possess a variety of interesting-yet-underutilized optical and electronic properties,[83] N-aroyl thioureas have shown promise as anion receptors,[108-111] metal chelators,[112-114] antibacterial and antifungal agents,[115,116] building blocks for liquid crystals,[117] plant-growth regulators,[118] and materials useful for molecular recognition[2,75] and non-linear optics.[76,83,119] These compounds reliably assume a well-known conformation, both in solution[83,89] and in the solid state;[84,85] depicted in **Figure 5.1**, this conformation features an S(6) intramolecular hydrogen bond between the carbonyl oxygen and the γ-thiourea proton. Heterocyclic nitrogen acceptors, such as pyridyl,[84,92] pyrimidyl,[10,98] and thiazolyl,[94,120] are known to form a similar S(6) interaction in thioureas; these compounds are well-known NNRTIs,[96,121,122] with high binding affinity and anti-HIV microbicidal IC_{50}'s reported as low as 3.8 nM.[123]

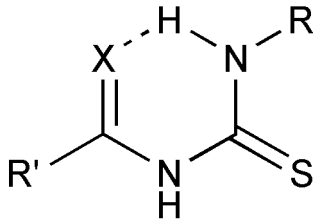


Figure 5.1. S(6) intramolecular RAHB in N-aroyl (X = O; R' = Ph) and N-heterocyclic (X = $NR''(CH)_nR'$); R' = CH, N, S) thioureas

Despite formal cross-conjugation across the thiourea moiety, the type of intramolecular hydrogen bond observed in both N-aroyl and N-heterocyclic thioureas can be classified as a form of Resonance-Assisted Hydrogen Bond[ing] (RAHB), due to the electron delocalization made possible by unsaturated

donor and acceptor groups.[124] Since first proposed in 1989,[105] Resonance-Assisted Hydrogen Bonding (RAHB) has received considerable attention given its crucial role in biological transformations,[125,126] as well as its relevance to the pursuit of a unified theory of hydrogen bonding.[127] Recently, RAHB has been identified as a significant factor in many biological processes, including membrane permeability[128,129] and ligand-receptor binding;[130,131] consequently, RAHB plays an increasingly important role in medicinal chemistry, especially in small-molecule drug design.[132,133] RAHB has also been used as a structural element in the design of new organic syntheses,[134,135] and as a reliable structural motif in crystal engineering.[136]

Despite its importance to these diverse fields, the origin of RAHB has yet to be fully elucidated. Initially ascribed to π-electron delocalization within the pseudo-ring that forms from the donor-acceptor hydrogen bonding interaction, RAHB has also been attributed to charge rearrangement in the electronic σ-framework; recent computational studies have been published on both sides of this debate.[137,138] A notable complication in the study of RAHB is the difficulty of quantifying its effect on molecular structure, as compounds capable of forming such strong hydrogen bonds will, as a rule, form them. While the "open" and "closed" conformations of RAHB systems have been examined by semi-empirical methods,[139,140] there are, to the best of our knowledge, no comparative empirical studies in the chemical literature.

Representing the first structurally characterized example of "open" and "closed" RAHB systems, 1-(3-nitrobenzoyl)-3-(6-methyl-2-pyridyl)-thiourea (**16**) has the capacity to form one of two dramatically different conformations (**16O** and **16N**, **Figure 5.2**), both

in the solid state and in solution. Both conformations are characterized by the presence of a strong, RAHB-type intramolecular hydrogen bond, formed at the expense of the alternative intramolecular hydrogen bond; thus, **16O** represents the "open" conformation of **16N**, and *vice versa*. The experimental data that we have obtained for this compound--x-ray crystal structures of both **16O** and **16N**, as well as solution-state energetic parameters—is corroborated by electronic calculation at the B3LYP/6-311++G(2d,p) level, providing intriguing support for many principles of RAHB theory.

Compound **16** was prepared by treatment of *m*-nitrobenzoylisothiocyanate (prepared from the acid chloride and KSCN) with 2-amino-6-methylpyridine. Crystallization from a mixture of ethyl acetate and hexanes afforded pale-yellow **16O**, while crystallization from acetonitrile afforded bright-yellow **16N**, each of which was characterized by single-crystal x-ray diffraction.

The RAHB-type intramolecular interactions observed in **16O** and **16N** are individually well-documented in the chemical literature, in thioureas which bear either acyl[83-89] or N-heterocyclic substituents, such as pyridine,[84,91-98,120,141] pyrimidine,[92,98] or thiazole.[94,120] When, as in the case of compound **16**, the thiourea bears both types of substituents (and therefore potentially has two low-energy conformations, **16O** and **16N**), RAHB theory predicts[142,143] that the homonuclear N···H(N) interaction should be stronger than the heteronuclear O···H(N) interaction. However, all literature examples of such bifunctional thioureas – with one exception[144]– indicate that the acyl moiety preferentially accepts the intramolecular hydrogen bond, both in the solid state and in solution.[145] While this initially appears to refute RAHB theory, our experimental and computational data for **16N**

16O and **16N** – thus far the only reported example of such a bifunctional thiourea for which *both* conformers have been isolated and crystallographically characterized – provide a satisfying explanation for this apparent inconsistency, as well as a model for the structural changes effected by RAHB.

Results and Discussion

Structural data for **16O** and **16N** provide a quantitative description of the structural effects of both intramolecular RAHBs, as significant changes in bond length are observed as a result of both interactions. Selected bond lengths are reported in **Table 5.1**. Whereas bonds between atoms not involved in either RAHB differ in length between

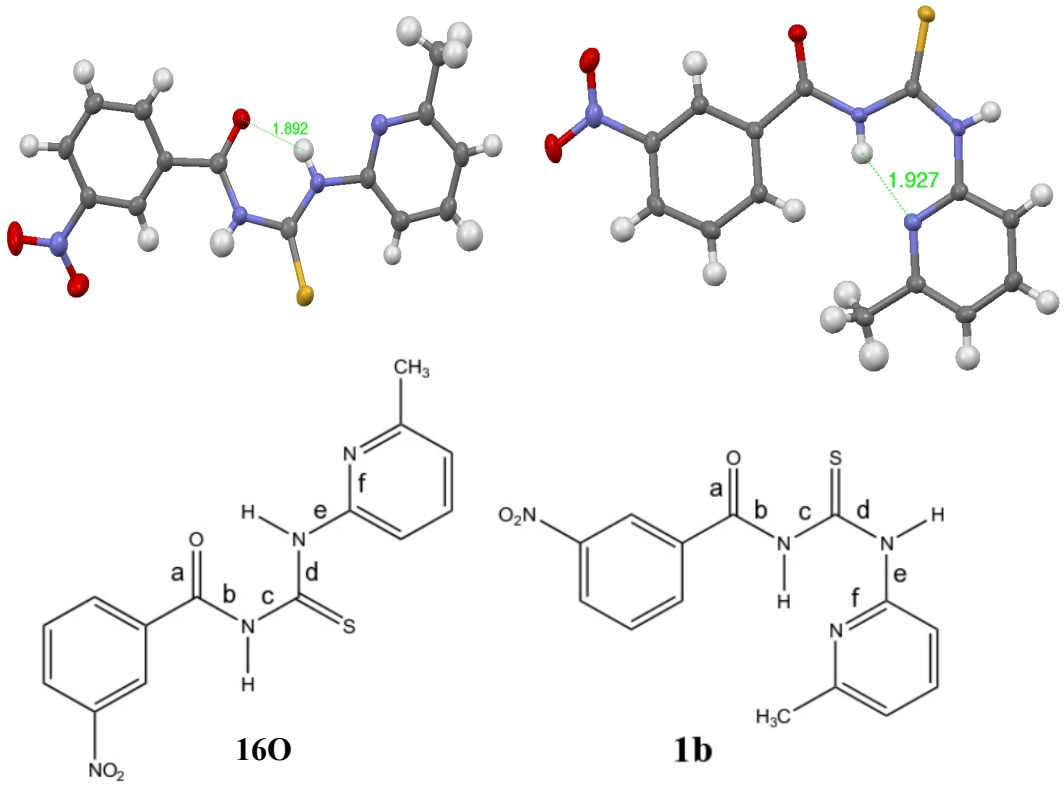


Figure 5.2. Line drawing and single crystal structural drawing of **16O** and **16N**

16O and **16N** by an average of ± 0.008 Å, roughly within experimental error, RAHB-involved bonds vary by as much as ± 0.033 Å. Perhaps most notably, amide-type delocalization[212] is significantly lower in **16N**, as bond *b* (**Figure 5.2**) lengthens from 1.374 Å to 1.394 Å, and bond *a* correspondingly shortens, from 1.222 Å to 1.207 Å. These changes in bond length likely reflect the changes in electron density that correlate with the coordination status of the carbonyl moiety.

Table 5.1. Selected experimentally- and computationally*-derived bond lengths for conformers **16O** and **16N** of 1-(3-nitro-benzoyl)-3-(6-methyl-2-pyridyl)-thiourea. Bond identifiers correspond to those displayed in **Figure 5.2**.

Bond	16O (Å)		16N (Å)		Δ (Å)[a]	
	Exp.[b]	Calc.[c]	Exp.	Calc.	Exp.	Calc.
a	1.222(4)	1.233	1.207(2)	1.217	0.015	0.016
b	1.374(5)	1.383	1.394(2)	1.396	-0.020	-0.013
c	1.405(4)	1.408	1.372(2)	1.377	0.033	0.031
d	1.341(4)	1.345	1.357(2)	1.361	-0.016	-0.016
e	1.418(4)	1.417	1.411(2)	1.413	0.007	0.004
f	1.335(4)	1.345	1.335(2)	1.337	0.000	0.008

*Computational results provided by Prof. Tonglei Li, at the University of Kentucky.
[a] Change in bond length, defined as difference between **16O** and **16N**
[b] From X-ray crystal structure
[c] From gas-phase structures, optimized at the B3LYP/6-311++G(2d,p) level

While of lesser magnitude, the change in the length of bond *e* (1.418 Å in **16O** vs. 1.411 Å in **16N**), corroborated by the change in hybridization calculated via NBO analysis ($sp^{2.70}$ vs. $sp^{2.60}$), also reflects the structural changes resulting from the shifts in electron density produced by RAHB. Recent literature[137] indicates that such changes are

largely produced by electronic rearrangement in the σ-skeleton, a conclusion that is corroborated by our data. Despite formal "cross-conjugation" across the thiourea moiety, the structural effects of RAHB are observed in both of its substituents. Additionally, the fragments of **16O** and **16N** that remain uninvolved in either RAHB do not display significant structural changes resulting from conformational change, as might be expected in conjugated systems undergoing significant π-rearrangement. Computational data also supported this hypothesis, as the interaction between the antibond of the N-H donor and the lone pair(s) of electrons from the hydrogen-bonding acceptor (O in **16O** and N in **16N**) possesses primarily σ-character.

Despite these apparently non-conjugative structural changes, the equalization of bond length predicted by Gilli, *et al.*,[105,146] is unambiguously demonstrated by the structural data for **16O** and **16N**. The Q-value of 0.088 for the heteronuclear RAHB in **16O** is, contrary to prediction, slightly lower than the Q-value for the homonuclear RAHB in **16N**, 0.091. Nevertheless, the standard deviation for the lengths of the four bonds (to non-hydrogen atoms) involved in the RAHB is ± 0.08 in **16O** and ± 0.03 in **16N**, indicating that bond-length equalization is, in accordance with prediction, significantly greater in **16N**. Due to the different types of bonds (as well as the different donor-acceptor pairs) involved in the two RAHB systems, it is likely that the Q-value is not a useful rubric for determining relative RAHB strength in this particular case. NBO donor-acceptor stabilization energy, calculated at the B3LYP/6-311++g(2d,p) level with Gaussian 03 software, proved to be more useful in achieving this goal. Although **16O** was determined to be the low-energy conformer (in the gas phase) by 4.72 kcal/mol

(**Table 5.2**), **16N** possesses greater donor-acceptor stabilization energy for the intramolecular RAHB (-18.46 kcal/mol, vs. -16.84 kcal/mol for **16O**),‡ in accordance with the predictions of RAHB theory.[105,143]

Table 5.2. Selected properties of **16O** and **16N**.

	$E_{optimized}$[a] (Ha)	$E_{lattice}$[b] (kcal/mol)	E_{RAHB}[b] (kcal/mol)	∂ X···**H**(N)[c] (ppm)	m.p.[d] (˚C)	p^a (Debye)
16O	-1382.13556	-127.92	-16.84	12.77	155.6	4.49
16N	-1382.12804	-131.81	-18.46	15.45	160.7	12.44
Δ(**O-N**)	-4.72[e]	3.89	1.62			

[a] Computationally determined at the B3LYP/6-311++G(2d,p) level (single molecule, gas-phase).
[b] Computationally determined for solid-state structure, using Crystal 06[147] and the B3LYP/6-21G(d,p) basis set.
[c] In $CDCl_3$.
[d] Determined by differential scanning calorimetry.
[e] In kcal/mol.

Qualitative methods of determining polymorphic stability[11] led us to conclude that **16N** was the preferred solid-state conformer, given its higher melting point, lower solubility in all tested solvents, slower nucleation, and non-reversible precipitation from a slurry of **16O**. With lattice energy calculations (**Table 5.2**) confirming this qualitative assessment, we suggest that the conformational preference of compound **16** may be determined by factors other than relative RAHB strength. This is corroborated by the

‡ Three intramolecular interactions contribute to the total bond strength of the RAHB in **16O**: lone pair on pyridyl N···H(N): 0.60 kcal/mol; lone pair #1 on O···H(N): 4.21 kcal/mol; lone pair #2 on O···H(N): 12.03 kcal/mol. In **16N**, the lone pair on the pyridyl N...H(N) is the sole contributor to the RAHB.

strong correlation between the results of our NBO analysis and solution-state data collected for compound **16**.

In contrast to prior literature reports of related 1-acyl-3-(2-pyridyl) thioureas, which suggested the presence of only the O···(N) conformer in solution, both **16O** and **16N** are present in all tested solvents.‡ In agreement with gas-phase calculations, **16O** is always the dominant species, albeit to a lesser extent – its relative population ranges from 50:1 in toluene-d_8 to 4:1 in DMSO-d_6, corresponding to energy differences (at 25˚C) of -2.3 kcal/mol and -0.82 kcal/mol, respectively. Variable-temperature NMR studies demonstrate that the predominance of **16O** depends on entropic factors, as **16N** is significantly lower in enthalpy (**Table 5.3**). In $CDCl_3$, ΔH for the conversion of **16O** to **16N** was determined to be -2.01 kcal/mol, while ΔS was -10.1 eu. These data correlate well with the significantly smaller dipole moment (*p*) of **16O** (**Table 5.2**), which would likely lead to decreased solvent ordering about that conformer and a concomitant solution-state conformational preference that is not tied to the relative strength of either intramolecular RAHB. Chemical shift data also lend credence to this hypothesis – at 15.45 ppm, the coordinated proton in **16N** is nearly 3 ppm downfield from that in **16O** (12.77 ppm), consistent with the increased strength of the N···(N) contact predicted by RAHB theory.[105,143]

‡ Discussed at greater length in Chapter **VII**.

Table 5.3. Thermodynamic parameters (kcal/mol) for the **16O → 16N** conformational transformation, in the gas phase (calculated) and in various solvents (experimentally-determined)

$\Delta G_{gas\ phase}$	$\Delta G_{25^\circ C}$ ($CDCl_3$)	$\Delta G_{25^\circ C}$ (DMSO-d_6)	$\Delta G_{25^\circ C}$ (toluene-d_8)	$\Delta G_{25^\circ C}$ (CD_3CN)
4.72	0.97	0.82	2.31	0.96

Conclusion

The equilibrium between **16O** and **16N** represents the first empirical example of "open" and "closed" RAHB, and offers support for many of its principles. Interestingly, computational and experimental data both appear to indicate that conformational stability lacks an inexorable link to relative RAHB strength, as other factors – which may or may not result from the electronic effects of the RAHB – also play a significant role in determining the dominant conformation.

CHAPTER VI

CONFORMATIONAL EXCHANGE IN 1-BENZOYL-3-(2-PYRIDYL) THIOUREAS: THE SOLID STATE

Introduction

The ability to form two different RAHBs imbues 1-aroyl-3-(2-pyridyl) thioureas with a peculiar blend of both structural flexibility and structural rigidity, creating the basis for a fascinating case study of structure-property relationships and crystal structure predictions. Perhaps the most intriguing feature of this class of compounds is that their solid-state physical properties correlate most closely with their respective preferred conformation, rather than their respective substitution pattern. Because it is well-known that altering aromatic substitution patterns often provokes dramatically different physical properties in otherwise identical molecules,[148] especially in relation to color and/or absorption spectra,[149] the conformation-specific physical characteristics of BzPTUs **16-46** suggest the influence of electronic factors unrelated to simple molecular connectivity or chemical composition.

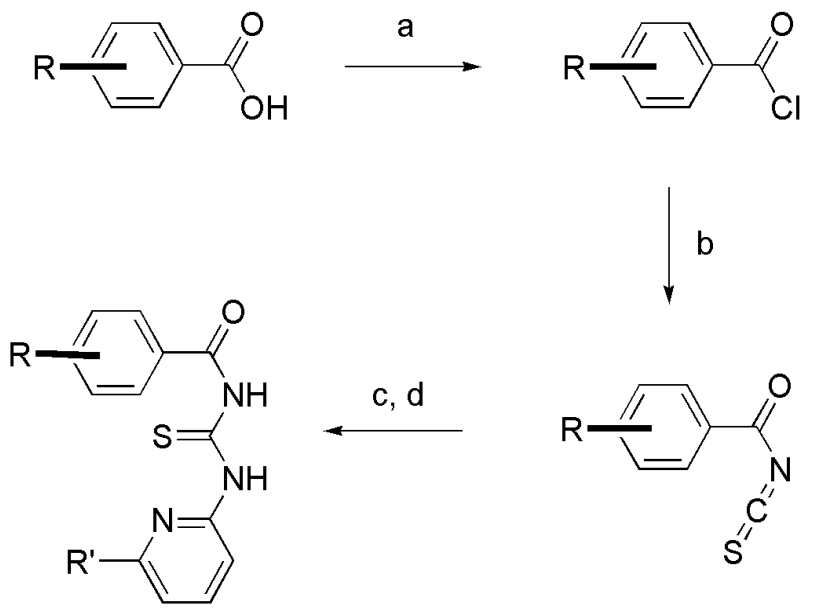
In this chapter, we will explore X-ray crystallographic data from 30 different compounds, describing the general structural characteristics of both conformers, both on

a monomeric level and in terms of crystal packing. We will also describe the influence of substituents on a BzPTU's preferred solid-state conformation, and discuss potential factors contributing to these compounds' conformationally-dependent physical characteristics. Our unusually large sample size of highly similar compounds allows us to explore many structural features from a statistically significant standpoint, and we believe that our work represents not only the solid-state trends in BzPTU structure, but also, in a larger sense, both the pitfalls and the promise of crystal engineering research.

Results

BzPTUs **16-46** were prepared by addition of the corresponding benzoyl isothiocyanate and an aminopyridine, using the procedure outlined in **Scheme 6.1**. Aroyl isothiocyanates were prepared in accordance with the literature procedure for the parent compound, benzoyl isothiocyanate (R = H in **Scheme 6.1**);[150] because these reaction conditions yielded satisfactory results, further optimization was not explored. When the parent benzoyl chloride was not commercially available, it was prepared from the corresponding benzoic acid.[151] We made no attempt to isolate the intermediate isothiocyanates or acid chlorides, as we found that satisfactory yields (65-80%, calculated from the initial amount of either the acid chloride or the isothiocyanate) of BzPTUs could be obtained without additional purification steps. Direct isolation of the BzPTU from the reaction mixture could be achieved by the addition of deionized water, upon completion of the reaction; the precipitated material, after drying, was satisfactorily pure by ^{1}H NMR.‡ Complete synthetic and characterization data can be found in **Appendix A**.

‡ While yield could be increased by removing the reaction solvent and chromatographing the BzPTU



Scheme 6.1. **Synthesis of 16-46**[a]

[a]Reagents and conditions: (**a**) $SOCl_2$, catalytic DMF, reflux, 5-15 min; (**b**) KSCN, MeCN, rt, 1-16 h; (**c**) 2-aminopyridine (R' = H) / 2-amino-6-picoline (R' = 6-CH_3) / 2-amino-5-picoline (R' = 5-CH_3) / 2-amino-3-picoline (R' = 3-CH_3), THF, rt, 2-16 h; (**d**) H_2O, rt, 1 h.

Single crystals suitable for X-ray crystallography were grown at room temperature, from a diverse selection of solvents. Crystals from the same vial as those selected for X-ray crystallography were used for both spectral characterization and elemental analysis. **Table 6.1** contains the experimental conditions under which we obtained single crystals of BzPTUs **16-46**, as well as their relevant physical and spectroscopic properties, and **Table 6.2** contains selected crystallographic data for these

product, we did not believe this improvement sufficient to justify either the time or the significant increase in solvent usage and chromatographic support that it entailed.

same structures. Bonds for which length appears to be conformer-specific, as described previously, are labeled in **Figure 6.1**, and their lengths in BzPTUs **16-22**, **24**, **26-41**, and **43-46**, as determined via X-ray crystallography, are recorded in **Table 6.3**. Full crystallographic data files can be found in **Appendix B**.

Table 6.1: Crystallization solvents, crystal morphologies, and physical and spectroscopic properties related to conformer identification (vide infra) in BzPTUs **16-46**. Melting points reported as a temperature range recorded on MelTemp apparatus; melting points reported as a single integer recorded via DSC.

CMPD	R	R'	Solvent(s)	Morphology	Color	$\nu_{C=O}$ (cm^{-1})	m.p. (˚C)	O / N
16N	3-NO_2	6-CH_3	MeCN	Dodecahedral	Yellow	1716	161	N
16O	3-NO_2	6-CH_3	EtOAc / hexanes	Columnar	Pale yellow	1672	156	O
17N	H	6-CH_3	$CHCl_3$	Cubic	Yellow	1709	140-145 (dec.)	N[a]
17N	H	6-CH_3	MeCN	Cubic	yellow	1709	150	N[b]
17O	H	6-CH_3	THF (wet)	Prisms	colorless	1680	116; 150[c]	O[a]
18	4-NO_2	6-CH_3	Acetone / H_2O	Columnar	Yellow-orange	1715	185-186	N
19	2-OCH_3	6-CH_3	Toluene / EtOH	columnar	colorless	1660	136-138	O
20	4-OCH_3	6-CH_3	DMF (wet)	Hexagonal	Yellow	1707	171-173	N
21	3-Cl	6-CH_3	MeOH	Needles	colorless	1678	161-162	O[a]
22	4-Cl	6-CH_3	Acetone	Prisms	Yellow	1717	166-167	N
23	3-CN	6-CH_3	many	amorphous	Pale yellow	1676, 1717	147-148 (dec.)	O, N[b,d]
24	4-CN	6-CH_3	MeCN	Cubic	Yellow	1720	172-173 (dec.)	N
25	3,4-Cl	6-CH_3	CH_3COOH	Prisms	colorless	1681	167-168	O[b]
26	3,5-Cl	6-CH_3	DCE	prisms	Deep Yellow	1700	175-176 (dec.)	N

Table 6.1. (continued).

CMPD	R	R'	Solvent(s)	Morphology	Color	$\nu_{C=O}$ (cm^{-1})	m.p. (˚C)	O / N
27	4-Br	6-CH_3	DCM	prisms	yellow	1718	166-168 (dec.)	N
28	2-Br	6-CH_3	EtOH / hexanes	columnar	colorless	1667	146-148	O
29	H	H	EtOH	Columnar	Off-white	1674	143-144	O
30O	3-NO_2	H	MeOH	Needles	Pale yellow	1671	176	O
30N	3-NO_2	H	MeCN	powder	Deep yellow-orange	1705	173	N[b]
31	4-NO_2	H	MeOH	Needles	Yellow-orange	1703	178-180	N
32	2-OCH_3	H	DCE / hexanes	Glassy; amorphous	colorless	1660	186-188	O
33	4-OCH_3	H	EtOAc / hexanes	columnar	colorless	1666	155-156	O
34	3-Cl	H	EtOH / hexanes	Columnar	colorless	1673	148-150	O
35	4-Cl	H	THF (wet)	Columnar	colorless	1676	140-142	O[a]
36	3-CN	H	DMF (wet)	Needles	colorless	1675	149-151 (dec.)	O[a]
37a	4-CN	H	DCM	Plates	off-white	1676	177-180 (dec.)	O[a]
37b	4-CN	H	IPA / acetone	Cubic	Pale yellow			O[a]
37c	4-CN	H	$CHCl_3$	Needles	off-white	1677	181-185 (dec.)	O[a]
38	3,4-Cl	H	DCM / acetone	needles	colorless	1674	194-195	O
39	3,5-Cl	H	MeCN; acetone[e]	Columnar; octahedral[e]	Yellow	1704	180-183 (dec.)	N
40	4-Br	H	EtOH	Striated prisms	colorless	1667	160-161	O
41	2-Br	H	EtOH / hexanes	cubic	colorless	1683	104-106	O
42	4-CF_3	H	MeCN	Foliated plates	Yellow-orange	1701	158-160	N
43	3,5-Cl	5-CH_3	DCE	Pentagonal dodecahedron	Yellow	1699	191	N
43	3,5-Cl	5-CH_3	Toluene	Fibrous needles	Colorless	1674	195	O[b]

Table 6.1. (continued).

CMPD	R	R'	Solvent(s)	Morphology	Color	$\nu_{C=O}$ (cm^{-1})	m.p. (˚C)	O / N
44	H	3-CH_3	EtOH / hexanes	Prisms	colorless	1670	131-133	O
45	4-NO_2	3-CH_3	MeCN	Prisms	Pale yellow	1673		O
46	2-Br	3-CH_3	EtOH / hexanes	Needles	colorless	1675		O

[a]Solvate

[b]No X-ray quality crystals were produced, but the conformer present in the amorphous material was confirmed by IR

[c]Endotherm (*vide infra*) observed at 116.2˚C; a second endotherm, presumed to be the melting point, occurs at 150.5˚C

[d]A mixture of both conformers, in approximately equal proportions, precipitated from all tested solvents.

[e]Distinct morphologies obtained from different solvents; both have same unit cell

Table 6.2. Selected crystallographic data for BzPTUs **16-22**, **24**, **26-41**, and **43-46**. Full crystallographic data files can be found in **Appendix B**.

CMPD	Space Group	Formula	*a, b, c* (Å)	α, β, γ (deg)	V (Å^3)	Z	d_{calc} (g/cm^3)	R-Factor (%)	C[a]
16N	$P2_1/n$	$C_{14}H_{12}N_4O_3S$	7.9095(18), 9.972(2), 17.615(4)	90.00, 92.752(4), 90.00	1387.75	4	1.514	3.8	0.76
16O	P1	$C_{14}H_{12}N_4O_3S$	3.888(2), 11.984(7), 15.455(10)	98.299(10), 92.188(11), 98.434(10)	703.563	2	1.493	5.9	0.75
17N	$P2_1/c$	$C_{15}H_{14}N_3OSCl_3$	8.239(2), 19.570(5), 10.609(3)	90.00, 95.5090(4), 90.00	1702.66	4	1.524	3.32	0.66
17O	I2/a	$C_{14}H_{14}N_3O_{1.5}S$	22.125(2), 5.5825(5), 23.134(2)	90.00, 112.6390(10), 90.00	2637.18	8	1.412	3.21	0.77
18	P1	$C_{14}H_{12}N_4O_3S$	8.108(3), 9.351(4), 9.484(4)	90.913(7), 107.255(7), 90.624(7)	686.516	2	1.530	4.02	0.77

Table 6.2. (continued).

CMPD	Space Group	Formula	*a, b, c* (Å)	α, β, γ (deg)	V (Å^3)	Z	d_{calc} (g/cm^3)	R-Factor (%)	C[a]
19	$P2_1/c$	$C_{15}H_{15}N_3O_2S$	7.9072(8), 20.077(2), 9.8693(10)	90.00, 110.242(2), 90.00	1470.01	4	1.362	3.65	0.72
20	P1	$C_{15}H_{15}N_3O_2S$	7.6729(13), 8.8309(15), 11.1319(19)	90.702(3), 94.510(3), 113.241(2)	690.157	2	1.450	3.62	0.77
21	P1	$C_{15}H_{16}N_3O_2SCl$	9.341(2), 9.771(1), 10.285(2)	71.226(3), 75.821(3), 62.355(2)	782.18	2	1.434	3.07	0.74
22	P1	$C_{14}H_{12}N_3OSCl$	8.2738(11), 9.0380(12), 9.9752(13)	80.899(2), 66.546(2), 87.438(2)	675.551	2	1.503	3.16	0.76
24	P1	$C_{15}H_{12}N_4OS$	8.0301(10), 12.3036(15), 14.6822(18)	74.324(2), 81.402(2), 81.197(2)	1371.24	4	1.435	5.52	0.75
26	$P2_1/c$	$C_{14}H_{12}N_3OSCl_2$	9.2966(16), 10.2930(18), 15.738(3)	90.00, 106.729(3), 90.00	1442.23	4	1.567	3.66	0.74
27	P1	$C_{14}H_{12}N_3OSBr$	8.4483(12), 9.0131(13), 9.9963(15)	80.951(2), 66.510(2), 85.899(2)	689.372	2	1.687	2.79	0.75
28	$P2_1/c$	$C_{14}H_{12}N_3OSBr$	11.3779(7), 14.0996(9), 9.3236(6)	90.00, 98.2030, 90.00	1480.42	4	1.571	2.98	0.70
29	$P2_1/n$	$C_{13}H_{11}N_3OS$	5.2724(7), 20.335(3), 11.7435(16)	90.00, 90.372(2), 90.00	1259.04	4	1.357	4.2	0.71
30	$P2_1/n$	$C_{13}H_{10}N_4O_3S$	3.8902(12), 14.372(4), 22.813(7)	90.00, 91.211(5), 90.00	1275.19	4	1.575	4.57	0.77
31	$P2_1/n$	$C_{13}H_{10}N_4O_3S$	4.9793(6), 13.2760(16), 19.753(2)	90.00, 94.136(2), 90.00	1302.38	4	1.542	4.74	0.76
32	$P2_1/c$	$C_{14}H_{13}N_3O_2S$	8.9570(9), 15.7256(16), 10.3383(11)	90.00, 111.8080(10), 90.00	1351.98	4	1.412	3.31	0.74
33	$P2_1/c$	$C_{14}H_{13}N_3O_2S$	12.064(2), 15.599(3), 7.2365(12)	90.00, 90.612(3), 90.00	1361.73	4	1.401	3.47	0.77
34	$P2_1/n$	$C_{13}H_{10}N_3OSCl$	3.9319(6), 14.423(2), 22.706(4)	90.00, 92.806(3), 90.00	1286.11	4	1.507	4.95	0.74

Table 6.2. (continued).

CMPD	Space Group	Formula	*a, b, c* (Å)	α, β, γ (deg)	V (Å^3)	Z	d_{calc} (g/cm^3)	R-Factor (%)	C[a]
35	C2/c	$C_{13}H_{11}N_3O_{1.5}SCl$	28.847(6), 3.8548(7), 24.769(5)	90.00, 105.929(3), 90.00	2648.54	8	1.509	3.59	0.76
36	$P2_1/n$	$C_{17}H_{17}N_5O_2S$	4.0338(3), 15.7779(10), 26.9519(18)	90.00, 90.1090(10), 90.00	1715.35	4	1.376	4.26	0.72
37a	C2/c	$C_{14.5}H_{11}N_4OSCl$	33.415(4), 3.8956(5), 23.215(3)	90.00, 106.891(2), 90.00	2891.56	8	1.492	4.41	0.78
37b	P1	$C_{14.8}H_{11.5}N_4O_{1.2}S$	9.4152(6), 12.2161(8), 12.6685(8)	79.9620(10), 81.9860(10), 79.1500(10)	1400.55	4	1.408	3.87	0.87
37c	P1	$C_{14.2}H_{10.2}Cl_{0.8}N_4OS$	9.476(4), 12.217(5), 12.643(5)	80.248(6), 82.254(6), 78.770(6)	1407.02	4	1.474	5.1	0.8
38	$P2_1/c$	$C_{13}H_9N_3OSCl_2$	12.142(3), 3.8366(10), 28.817(7)	90.00, 98.822(5), 90.00	1326.53	4	1.633	3.91	0.75
39	$P2_1/n$	$C_{13}H_9N_3OSCl_2$	10.9182(17), 8.5112(13), 15.526(2)	90.00, 105.631(2), 90.00	1389.43	4	1.559	3.02	0.72
40	$P2_1/c$	$C_{13}H_{10}N_3OSBr$	4.1131(5), 20.410(3), 15.5094(19)	90.00, 94.927(2), 90.00	1297.18	4	1.722	2.94	0.74
41	Pbca	$C_{13}H_{10}N_3OSBr$	14.2904(10), 9.2601(6), 20.4694(14)	90.00, 90.00, 90.00	2708.73	8	1.649	2.42	0.71
43	$P2_1/n$	$C_{14}H_{12}N_3OSCl_2$	10.7954(12), 8.3644(9), 16.6231(19)	90.00, 101.726(2), 90.000	1467.7	4	1.538	2.85	0.72
44	C2/c	$C_{14}H_{13}N_3OS$	24.295(2), 7.8990(8), 14.0166(14)	90.00, 93.537(2), 90.00	2684.75	8	1.343	4.45	0.71
45	$P2_1/n$	$C_{14}H_{12}N_4O_3S$	11.1286(19), 11.1776(19), 11.963(2)	90.00, 110.005 (2), 90.00	1398.3	4	1.503	3	0.75
46	P1	$C_{14}H_{12}N_3OSBr$	6.4016(13), 10.803(2), 16.578(3)	71.448(3), 82.704(3), 88.942(3)	1077.81	3	1.619	3.33	0.72

[a] Kitaigorodskii packing coefficient[17] = (Molecular Volume[152] x Z) / Unit Cell Volume

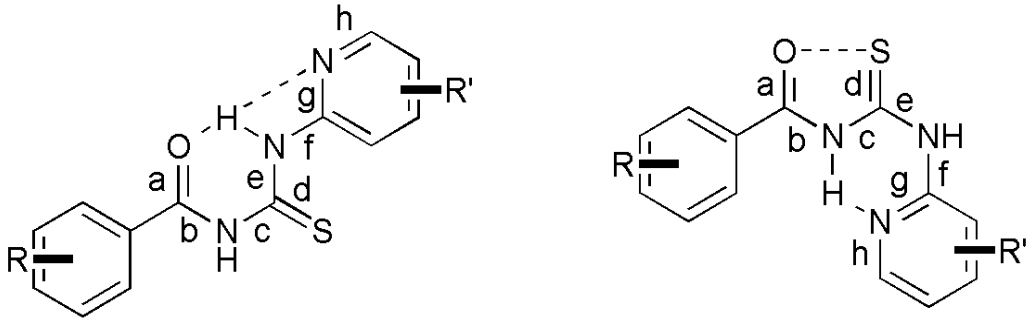


Figure 6.1. Conformers **O** (left) and **N** (right) with labeled bonds. Bond labels are the same for both conformers.

Table 6.3. Lengths of labeled bonds from **Figure 6.1**. For the sake of brevity, uncertainty in bond length has been omitted; however, these values can be found in **Appendix B**.

CMPD	O / N	O...H(N) or N...H(N)[a] (Å)	O...N or N...N[a] (Å)	N...H(N) or S...O[b] (Å)	a (Å)	b (Å)	c (Å)	d (Å)	e (Å)	f (Å)	g (Å)	h (Å)
16N	N	1.927	2.671	2.996	1.207	1.394	1.372	1.671	1.357	1.411	1.335	1.359
16O	O	1.892	2.615	2.263	1.223	1.374	1.405	1.659	1.341	1.417	1.336	1.345
17N	N	1.940	2.667	2.986	1.211	1.397	1.366	1.672	1.357	1.412	1.332	1.354
17O	O	1.978	2.651	2.464	1.224	1.386	1.386	1.681	1.334	1.426	1.329	1.343
18	N	1.918	2.658	2.971	1.205	1.393	1.375	1.668	1.357	1.414	1.335	1.354
19	O	1.899	2.632	2.327	1.228	1.374	1.393	1.660	1.340	1.410	1.334	1.343
20	N	1.945	2.697	2.918	1.207	1.404	1.365	1.674	1.363	1.408	1.337	1.350
21	O	1.916	2.634	2.307	1.226	1.378	1.399	1.658	1.345	1.413	1.343	1.340
22	N	2.004	2.661	3.013	1.209	1.393	1.370	1.671	1.359	1.410	1.335	1.354
24[c]	N	1.840	2.625	3.057	1.202	1.401	1.369	1.667	1.364	1.407	1.337	1.341
24[c]	N	1.940	2.644	3.012	1.200	1.401	1.369	1.667	1.362	1.405	1.334	1.348
26	N	1.958	2.701	2.959	1.217	1.373	1.382	1.656	1.360	1.403	1.335	1.358
27	N	1.981	2.659	3.014	1.208	1.389	1.370	1.674	1.356	1.411	1.338	1.355
28	O	1.934	2.631	2.248	1.229	1.366	1.406	1.661	1.335	1.415	1.340	1.339
29	O	1.852	2.592	2.254	1.225	1.385	1.392	1.665	1.336	1.406	1.330	1.333
30	O	1.925	2.604	2.262	1.224	1.375	1.397	1.660	1.336	1.408	1.330	1.332

Table 6.3. **(continued).**

CMPD	O / N	O...H(N) or N...H(N)[a] (Å)	O...N or N...N[a] (Å)	N...H(N) or S...O[b] (Å)	a (Å)	b (Å)	c (Å)	d (Å)	e (Å)	f (Å)	g (Å)	h (Å)
31	N	1.905	2.664	3.018	1.209	1.386	1.376	1.654	1.367	1.405	1.332	1.349
32	O	1.896	2.644	2.292	1.227	1.374	1.399	1.656	1.344	1.408	1.340	1.339
33	O	1.888	2.632	2.277	1.232	1.388	1.390	1.667	1.339	1.410	1.336	1.339
34	O	1.926	2.620	2.279	1.218	1.389	1.396	1.663	1.339	1.412	1.335	1.331
35	O	1.886	2.594	2.256	1.220	1.388	1.396	1.664	1.338	1.414	1.338	1.335
36	O	1.893	2.608	2.251	1.231	1.371	1.399	1.648	1.347	1.401	1.335	1.332
37a	O	1.886	2.617	2.262	1.226	1.371	1.409	1.661	1.335	1.415	1.336	1.341
37b[c]	O	1.809	2.608	2.290	1.224	1.378	1.402	1.662	1.337	1.419	1.338	1.338
37b[c]	O	1.815	2.603	2.329	1.221	1.382	1.401	1.666	1.335	1.418	1.335	1.342
37c[c]	O	1.869	2.595	2.315	1.224	1.382	1.403	1.667	1.331	1.417	1.328	1.340
37c[c]	O	1,874	2.612	2.249	1.222	1.379	1.398	1.658	1.339	1.412	1.342	1.337
38	O	1.816	2.600	2.270	1.228	1.374	1.407	1.661	1.340	1.411	1.338	1.340
39	N	1.912	2.637	3.051	1.215	1.377	1.377	1.660	1.361	1.402	1.334	1.347
40	O	1.995	2.645	2.260	1.222	1.373	1.401	1.658	1.340	1.409	1.338	1.337
41	O	1.994	2.657	2.590	1.219	1.370	1.391	1.666	1.334	1.425	1.330	1.346
43	N	1.881	2.654	3.055	1.215	1.376	1.382	1.660	1.361	1.402	1.334	1.346
44	O	1.920	2.629	2.564	1.229	1.372	1.391	1.663	1.335	1.438	1.325	1.344
45	O	1.966	2.664	2.515	1.222	1.380	1.398	1.665	1.340	1.434	1.330	1.345
46[c]	O	2.004	2.656	2.614	1.227	1.371	1.393	1.669	1.329	1.439	1.329	1.340
46[c]	O	1.963	2.640	2.584	1.215	1.370	1.398	1.661	1.323	1.424	1.332	1.331
46[c]	O	1.994	2.651	2.442	1.209	1.383	1.394	1.654	1.335	1.432	1.337	1.339

[a] Bond lengths listed are for donor-acceptor separation, both D...H(A) and D...A. In conformer **O**, these values are for O...H(N) and O...N, respectively; in conformer **N**, these values are for N...H(N) and N...N.

[b] Bond lengths refer to the secondary, N...H(N) IMHB in conformer **O**, or the short (*i.e.* less than the sum of their van der Waals radii, 3.2 Å) O...S separation in conformer **N**.

[c] When at least two non-equivalent molecules are present in the unit cell, bond lengths are listed for each molecule.

Because BzPTUs **16-46** invariably form either conformer **O** or conformer **N** in the solid state, very little potential for structural variability—at least on the monomeric level—exists in these compounds. Nevertheless, this conformational rigidity appears to lack an overarching influence on supramolecular architecture, as both intermolecular hydrogen bonding and π-stacking—the two most significant crystal packing forces observed in BzPTUs **16-46—**exhibit dramatic variance across this series of compounds. Although crystal engineering studies of thioureas tend to focus on trends in intermolecular hydrogen bonding,[26] we found it most useful to characterize crystal packing patterns using Desiraju's and Gavezzotti's polynuclear aromatic hydrocarbon structure types,[37] with a few modifications that made them more suited to trends observed in our BzPTUS.

Table 6.4 provides a summary of the dominant intermolecular interactions observed in BzPTUs **16-22**, **24**, and **26-46**, and **Figure 6.2**, which immediately precedes it, provides graphical depictions of these interactions, including both Desiraju's and Gavezzotti's original structure types and our modifications.

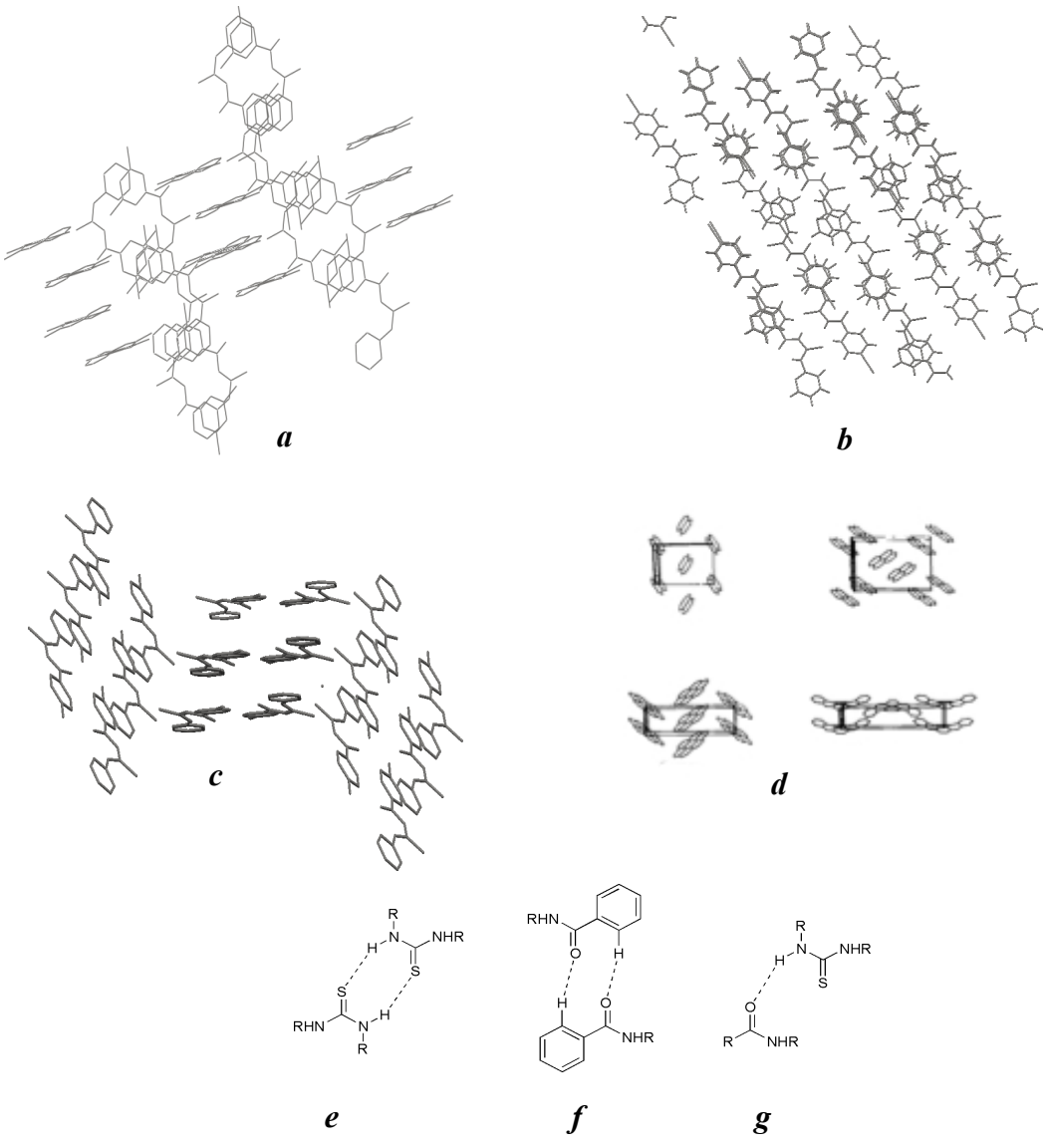


Figure 6.2. Common crystal packing motifs and intermolecular hydrogen bonds observed in BzPTUs **16**-**46**. (*a*) Basketweave, with brick-type π-stacking; (*b*) generalized brick-type π-stacking; (*c*) doubled γ; (*d*) Desiraju's structures (clockwise from top left): herringbone, sandwich herringbone, β, γ; (*e*) $R^2_2(8)$ cyclic thiourea dimer; (*f*) $R^2_2(10)$ aroyl cyclic dimer; (*g*) C(6) or D(6) (C=)O...H(N) interaction.

Table 6.4. Intermolecular hydrogen bonding and crystal packing interactions in BzPTUs **16-22**, **24**, **26-41**, and **43-46**.

CMPD	O / N	Length S...H(N) $R^2_2(8)$ (Å)	Length O...H(Ar) $R^2_2(10)$ (Å)	Length O...H(N) C/D(6) (Å)	π-stacking (Å)					Structure Type
					Ph-Ph	Ph-Pyr	Pyr-Pyr	RAHB-Ph	RAHB-Pyr	
16N	N	2.609	2.372							β
16O	O	2.717	2.453		3.4		3.5			Doubled γ
17N	N	2.645			3.6	3.8				γ
17O	O		2.530							Doubled herringbone
18	N	2.599	2.433			3.5				Sandwich β
19	O		2.523					3.4		Sandwich herringbone
20	N	2.566	2.520		3.4				3.4	Brick γ
21	O				3.4	3.4	3.4			Brick γ
22	N	2.674	2.563			3.6				γ
24	N	2.642, 2.543			3.9				3.3, 3.5	Brick γ
26	N			2.134		3.6			3.3	Basketweave
27	N	2.668	2.565			3.6				γ
28	O			2.003	3.6		3.4			Basketweave
29	O	2.736	2.488					3.9	3.7	Sandwich herringbone
30	O	2.602	2.606		3.4		3.4			γ
31	N			2.337						β
32	O		2.527						3.3	Sandwich herringbone
33	O	2.707	2.571		3.5				3.7	Doubled brick γ
34	O	2.635			3.4		3.5			γ
35	O	2.456			3.4		3.4			Doubled γ
36	O				3.5		3.6			γ
37a	O		2.458		3.5		3.5			Doubled γ
37b[c]	O	2.774, 2.775	2.507, 2.609		3.6	3.5	3.5			Doubled brick γ
37c[c]	O	2.712, 2.822	2.526, 2.494		3.6	3.5	3.5			Doubled brick γ
38	O	2.847	2.368		3.5		3.5			γ

Table 6.4. (continued).

CMPD	O / N	Length S...H(N) $R^2_2(8)$ (Å)	Length O...H(Ar) $R^2_2(10)$ (Å)	Length O...H(N) C/D(6) (Å)	π-stacking (Å)					Structure Type
					Ph-Ph	Ph-Pyr	Pyr-Pyr	RAHB-Ph	RAHB-Pyr	
39	N			2.123	3.4	3.6	3.3			Basketweave
40	O		2.418		3.3		3.3			Doubled γ
41	O									Herringbone
43	N			2.119	3.4	3.2	3.4			Basketweave
44	O	2.755					3.7, 3.5			Basketweave
45	O	2.722		2.600						Herringbone
46	O	2.549	2.110							β

Although we did not observe any predictive correlation between single-molecule conformation and crystal packing interactions, there were nevertheless certain trends that could be observed in preferred packing arrangements. Conformer **N** was more likely to engage in brick-type π-stacking (**Figure 6.2b**), as part of either a γ-type (**Figure 6.2d**) or basketweave-type (**Figure 6.2a**) packing motif. The apparent prevalence of the basketweave motif among conformer **N** structures may actually be related to the packing similarities among 3,5-dichloro BzPTUs **26**, **39**, and **43**, all of which crystallized as conformer **N**, and all of which packed in the basketweave motif. In the absence of aromatic stacking, conformer **N** was also more likely to form "graphite-like" β-sheets (**Figure 6.2d**), in contrast to the herringbone architecture observed exclusively among non-π-stacking, conformer **O** crystal structures. As displayed in **Figure 6.3**, however, these trends could also be related to phenyl substitution patterns, as *para*-substituted BzPTUs showed a distinct preference for the γ-type packing motifs.

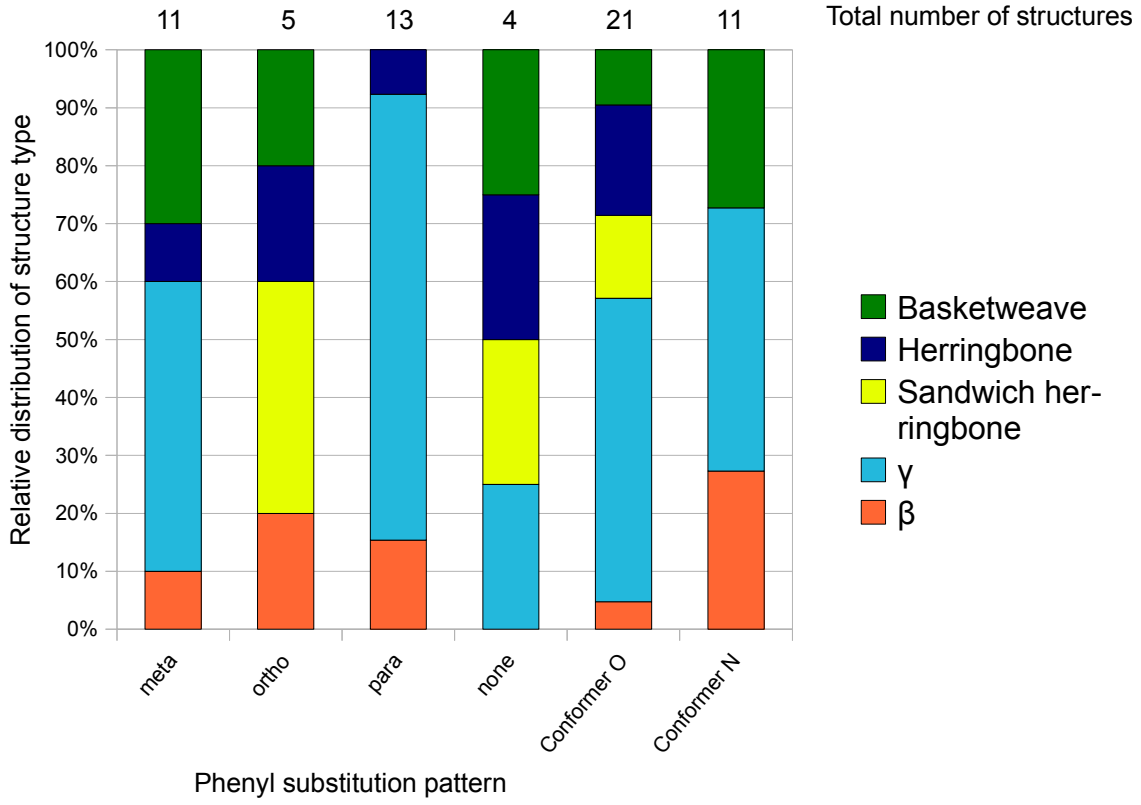
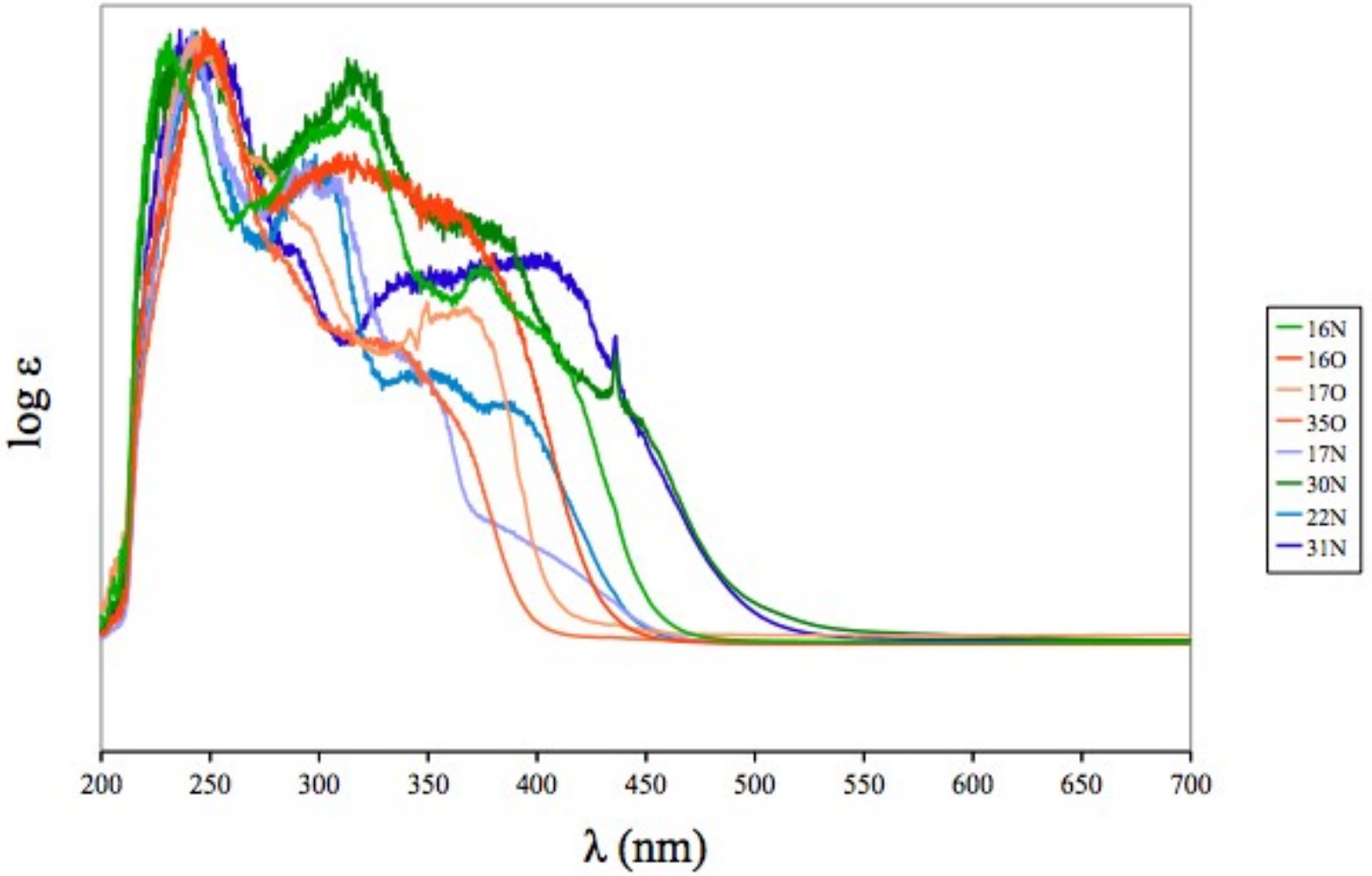


Figure 6.3. Distribution of crystal packing motifs in BzPTUs **16**-**46**, relative to both phenyl substitution (*ortho*, *meta, para,* none [i.e. R = H] and solid-state conformation (conformer **O** / conformer **N**). Variations on a certain packing motif (*e.g.* doubled γ, brick γ, etc.) have been combined into a single structure type (*e.g.* γ). Compound **38** was not included, due to its irregular 3,4-dichlorophenyl substituent (see footnote on page 73 for a more extensive discussion).

In an effort to identify the source of the yellow color in conformer **N**, diffuse reflectance UV-vis spectra were collected for BzPTUs **16O**, **16N**, **17O**, **17N**, **22**, **30**, **31**, and **35**. All conformer **N** compounds displayed absorbance in the visible region ($\lambda > 400$ nm), and, of the conformer **O** compounds, only **16O** displayed significant absorbance above 410 nm (terminating at 440 nm), most likely due to the nitro substituent on its phenyl ring. Visible-light absorbance in **17N** and **35** extended to approximately 450 nm, and, in **16N**, it was detected as high as 475 nm. In **30** and **31**(R = 3-NO_2 / 4--NO_2; R' = H), statistically significant absorbance was detected above 500 nm, extending to nearly 550 nm in **30**, and correlating well with the orange hues observed in both of these compounds. **Figure 6.4** contains a stacked plot of all the UV-vis spectra that we collected, and **Figure 6.5** contains comparative plots of selected UV-vis spectra, which we find far easier to interpret. **Table 6.5** contains absorbance maxima and the corresponding band gaps for each data set. Band gaps were calculated from the slope of the best-fit line through each absorbance maximum.[153]

Figure 6.4. Diffuse reflectance UV-vis spectra for BzPTUs **16O/N, 17O/N**, **22**, **30**, **31**, and **35**. Compounds identified as conformer **O** are shown in warm colors, and compounds identified as conformer **N** are shown in cool colors.



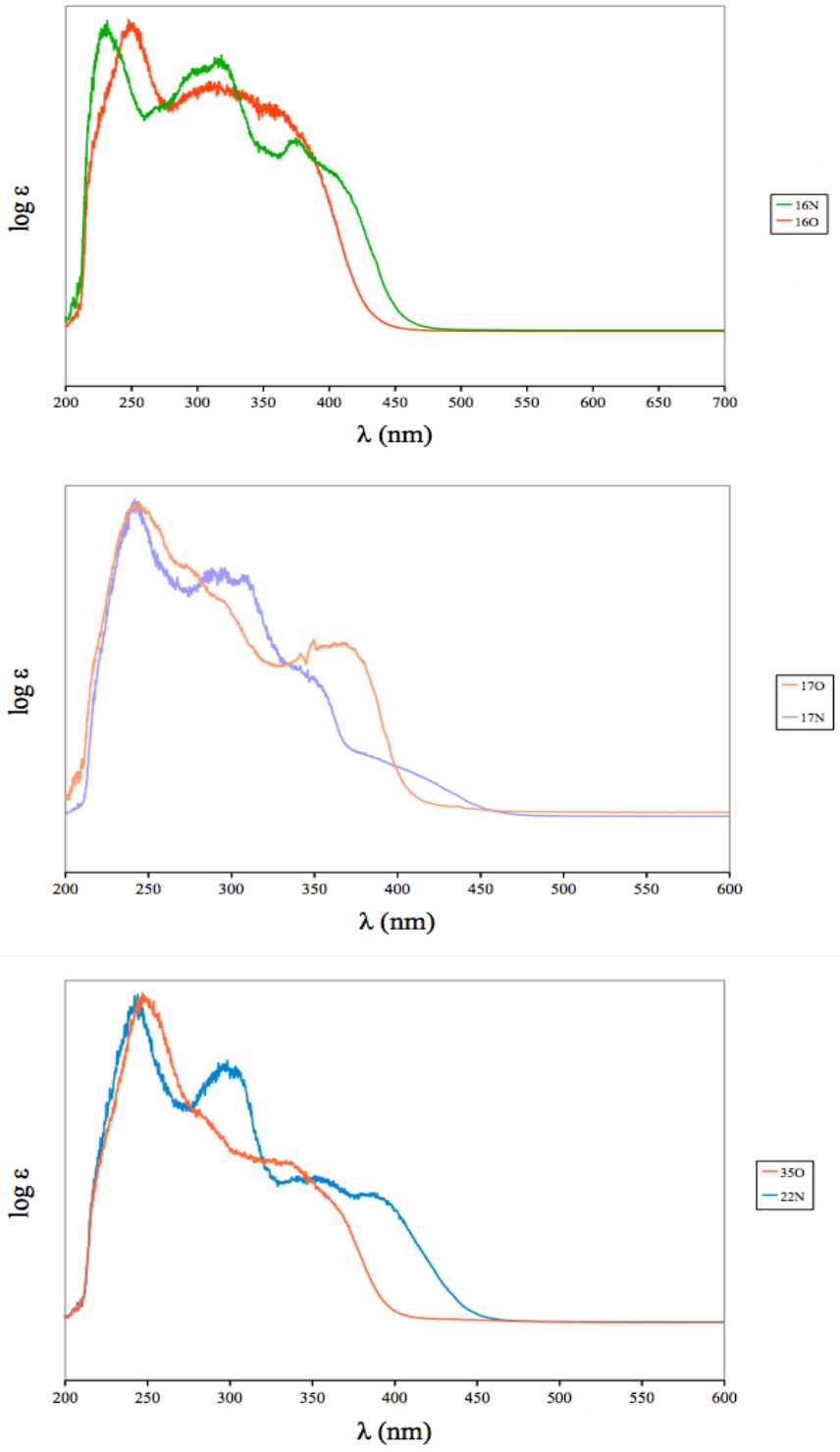


Figure 6.5. Diffuse reflectance UV-vis spectra for **16O/N** (top), **17O/N** (middle), and **22**/**25** (bottom). Dotted line indicates the beginning of the visible region.

Table 6.5. Calculated band gaps and their corresponding wavelengths, as derived from the diffuse reflectance UV-vis spectra of selected BzPTUs.

Compound	Band Gap (eV)	λ (nm)
16N	4.44	279
	3.41	364
	2.78	446
16O	4.22	294
	2.88	430
17N	4.29	289
	3.62	342
	3.15	393
	2.82	440
17O	4.15	299
	3.64	340
	3.1	400
22N	4.45	278
	3.71	334
	2.80	443
30N	4.13	300
	3.25	381
	2.86	433
	2.56	484
31N	4.32	287
	4.16	298
	3.75	331
	2.66	466
35O	4.29	289
	3.67	338
	3.19	388

Differential scanning calorimetry was employed to precisely determine the melting point and the enthalpy of crystallization of conformers **N** and **O**, in the four compounds (**16**, **17**, **30**, and **43**) for which we were able to isolate reasonably pure samples of both conformers. Interestingly, the melting point of conformer **N** was higher than that of conformer **O** only in compound **16**. Melting point is not necessarily an indication of polymorphic stability, however,[46] and in all but **30**, the enthalpy of crystallization is higher in conformer **N** than in conformer **O** (**Table 6.6**).

Table 6.6. Melting point and enthalpy of crystallization in both conformers of BzPTUs **16**, **17**, **30**, and **43**, as determined by differential scanning calorimetry

CMPD	**16N**	**16O**	**17N**	**17O**	**30N**	**30O**	**43N**	**43O**
m.p. (˚C)	161	156	150	150	173	176	191	195
ΔH (kJ/mol)	38.0	33.8	33.0	32.4	41.5	50.9	44.8	42.7

Both the melting point and the enthalpy of crystallization were found to be essentially identical in **17N** and **17O**; however, a broad, endothermic phase transition was observed at 116˚C in **17O**, prior to the melting point transition at 150˚C (**Figure 6.6**). The heat of the transition at 116˚C was found to be 22 kJ/mol, or approximately half the heat of vaporization of water, 41 kJ/mol. Because we observed that **17O** could be readily converted to **17N** by leaving an unsealed vial of **17O** on top of an oven overnight (T ~

80˚C), and our solved crystal structure of **17O** contains 0.5 equivalents of H_2O per unit cell, we believe it highly likely that the first transition corresponds a the loss of water from **17O** (and the concomitant phase transition to **17N**).

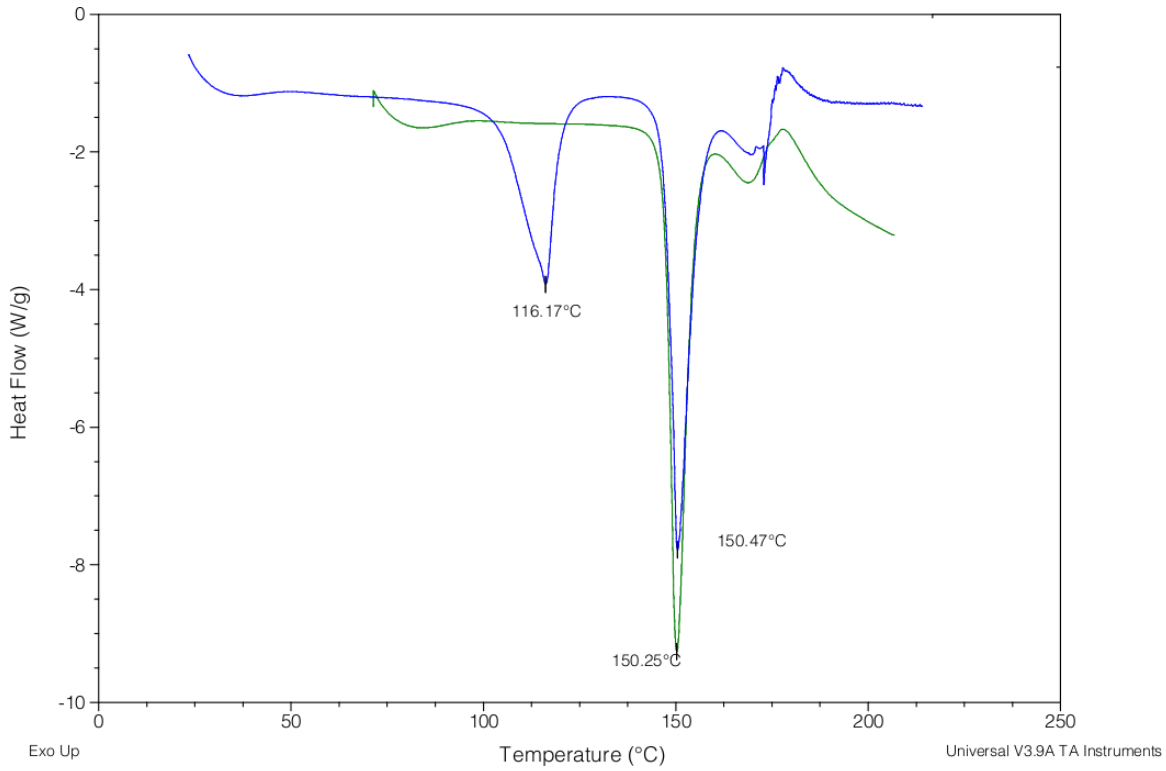


Figure 6.6. Differential scanning calorimetry plot obtained for **17N** (green) and **17O** (blue). The dashed vertical line drawn on the graph illustrates that the beginning of the first endotherm in **17O** approximately corresponds to the vaporization temperature of water. The decomposition that occurs upon melting can be observed in the small peak immediately to the left of the melting endotherm.

Discussion

All BzPTUs **16-46** occupy one of two possible low-energy conformations, conformers **O** and **N**. As was previously discussed, calculations performed for **16** found that conformer **O** was the low-energy conformer in both the gas phase and the solution phase; however, conformer **N** was determined to be the thermodynamically-preferred solid phase conformer, a finding that was in agreement with our empirical observations. In general, the relative solubilities of polymorphs are roughly predictive of their relatively stabilities—especially on a kinetic timeline, as the rate at which a crystal dissolves should be proportionate to the energy it gains (or loses) by forming the intermolecular bonds that allow it to precipitate from solution.[11] Both solubility and rate of dissolution—as far as we have qualitatively observed—are far greater in conformer **O** than in conformer **N**, regardless of solvent choice, and regardless of BzPTU selection; that is, any conformer **N** solid sample has a lower solubility and rate of dissolution than any conformer **O** sample, even if their substitution patterns are completely unrelated to each other.‡

Given the extent to which conformation influences the solubility of BzPTUs **16-46**, it is perhaps unsurprising that the solid-state conformational preferences of these compounds are largely independent of solvent choice. Most BzPTUs crystallize exclusively as either conformer **O** or conformer **N**, regardless of the chosen crystallization solvent; our reasonably exhaustive solvent studies on representative

‡ The one exception to these two trends is **38**, which crystallizes as conformer **O**, yet has both low solubility in most solvents and the highest melting point recorded for any BzPTU that we examined (194-195˚C). Chains of Cl...Cl intermolecular contacts (3.394 Å), which are also observed in 3,5-dichloro BzPTUs **26** and **39**, may account for the enhanced stability of **38**'s crystal lattice.

compounds can be found in **Table 6.7**. Although we were not able to obtain crystals suitable for X-ray analysis from all—or even from most—tested solvents, we found that conformation could be confirmed efficiently via IR spectroscopy, as the carbonyl stretching frequency in conformer **O** (~1670 cm^{-1}) is consistently lower in energy than in it is in conformer **N** (~1710 cm^{-1}), as would be expected from the RAHB that it forms in the former compound. Interestingly, two aspects of intermolecular hydrogen bonding also correlated well with C=O stretch in the IR spectra: the C(6) or D(6) (C=)O...H(N) interaction observed in many conformer **N** species led to a lower-frequency C=O stretch (1700-1705 cm^{-1}, as compared to 1707-1717 cm^{-1} in conformer **N** structures that lacked this interaction), and marginally higher-frequency absorbance (1678-1680 cm^{-1}) was observed in **17O** and **21O**, presumably due to solvent coordination.

Table 6.7. Solvent-structure relationships in BzPTUs **16**, **17**, **21**, **31**, and **33**. For each solvent, the C=O stretching frequencies (cm^{-1}) and corresponding conformations are reported.

CMPD	MeCN	$MeNO_2$	MeOH	CH_3COOH	EtOAc	$(CH_3)_2CO$	THF	$CHCl_3$
16	1716; N[a] 1672; O[a]	1716; N[a] 1672; O[a]	1680; O[b]	1678; O[b]	1672; O[c] 1716; N[c]	1716; N[a] 1672; O[a]	1672; O	1672; O
17	1709; N	1710; N	1709; N	1710; N	1709; N	1709; N	1680; O[d] 1709; N[d]	1709; N
21	1674; O	1674; O	1678; O[b]	1678; O[b]	1673; O	1674; O	1678; O[b]	1674; O
31	1703; N	1703; N	1703; N	1703; N	1703; N	1702; N	1703; N	1703; N
33	1707; N	1707; N	1706; N	1707; N	1707; N	1707; N	1707; N	1707; N 1668; O[e]

[a] Conformer **O** precipitates first; complete conversion to conformer **N** occurs in 3-10 days.

[b] Solvent coordination to O(=C) is likely

[c] Conformer **O** precipitates first; however, conversion to conformer **N** is still incomplete after 48 days.

[d] Both conformers precipitate, in reproducibly attainable quantities (90% **O**; 10% **N**), from the evaporation of a wet THF solution—of any concentration—under ambient conditions.

[e] Allowing a solution of **33** to evaporate rapidly on a salt plate resulted in a mixture of conformers **O** and **N**; however, our many attempts at recrystallization yielded only conformer **N**.

Although our large library of BzPTU crystal structures--and the high consistency in their conformer-specific C=O stretching frequencies—likely contribute a significant amount of accuracy to our IR-based conformational assignments, we nevertheless wanted more experimental evidence to support our assumptions. As in BzPTUs **16-46**, compound **47**, bis(benzoyl)thiourea, has the potential to form one of two competing—albeit chemically indistinguishable—intramolecular (C=)O...H(N) RAHBs, both identical to that found in conformer **O**. Because only one RAHB can form intramolecularly, however, the two C=O moieties in **47** occupy different chemical environments—confirmed by X-

ray data—and therefore show two different stretching frequencies in the IR—one "conformer **O**-like," at 1661 cm^{-1}, and one "conformer **N**-like," at 1716 cm^{-1} (**Figure 6.7**).

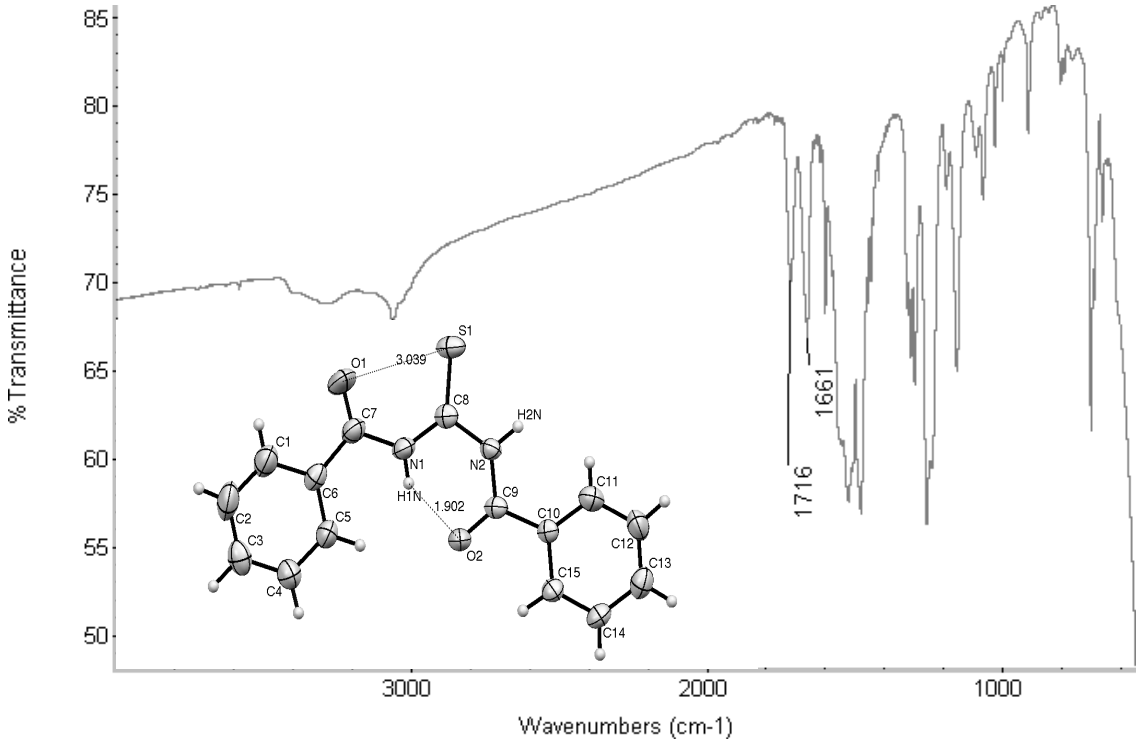


Figure 6.7. IR spectrum and ORTEP diagram (inset) of **47**, showing "conformer **N**-like" and "conformer **O**-like" carbonyl moieties, with their distinct stretching frequencies.

Returning to the data presented in **Table 6.6**, it is evident that solvent effects have only limited influence in determining the conformation of BzPTUs **16**-**46**. Of the five compounds for which we performed formal solvent studies, only **16** displays any significant degree of solvent-specific conformational flexibility—and we believe it likely that this flexibility correlates more with the higher solubility of **16O** in more-polar solvents, rather than any intrinsic solvent properties that stabilize one conformer over

another. As discussed in **Chapter V**, the relative free energies of **16O** and **16N** are essentially identical in acetonitrile and in chloroform, yet only **16O** precipitates from chloroform, while a mixture of both conformers, leading inexorably to **16N**, precipitates from acetonitrile; therefore, it is unlikely that the proportion of conformer **N** in solution has significant relevance to its formation in the solid state. Further exemplifying this disconnect between solution-state conformation, and crystal structure, **20O** and **20N** exist in an approximately 50:1 ratio in chloroform, at 25˚C, yet we have been unable to isolate **20O** in the solid state, under any conditions—and, in the 18 months required to obtain X-ray quality crystals of this compound, we subjected it to over 30 different solvents! **17N** has a similarly small solution-state population (~3%), yet **17O** forms only under a single set of conditions (*i.e.* the slow evaporation of wet THF), and reverts to **17N** upon the slow loss of water at 60˚C; conversely, **26**, which is 12% conformer **N** (in chloroform, at 25˚C) has never—to the best of our knowledge—precipitated from solution as anything other than conformer **O**.

Because conformer **N** is more stable in the solid state than conformer **O** in all of the BzPTUs for which we have observed its formation, we can extrapolate that it is the thermodynamically-preferred polymorph in all BzPTU—even those for which we have only observed the formation of conformer **O**. Regardless of its thermodynamic stability, however, the appearance of a particular polymorph is largely determined by its kinetic accessibility, *i.e.* the barrier to nucleation.[154] If the nucleation of conformer **N** is kinetically disfavored in certain BzPTUs, for whatever reason, we will observe only conformer **O** in the solid state—regardless of the solution-state population of either

conformer, and regardless of the relative thermodynamic stability of either crystalline solid.

Interestingly, despite its negligible impact on solubility, rate of dissolution, and melting point, aromatic substitution appears inexorably—if not always explicably—linked to the kinetic accessibility of conformer **N**, and, therefore, to the observed solid-state conformation. While we have by no means arrived at any method of quantitative prediction, we have observed certain trends in conformational preference that appear to be quite reliable, within this selection of BzPTUs:

1. Highly electron-withdrawing (-NO_2, -CF_3, etc.) R-groups *para* to the carbonyl moiety usually crystallize as conformer **N**, even when R'= H. Compounds **26** and **39**, which also crystallize in this conformation, provide evidence to suggest that electron density *para* to the carbonyl moiety—and not necessarily *para*-substitution—is responsible for this effect.
2. When R'= H, all but the most electronegative R-groups crystallize as conformer **O**.
3. When R'= 6-CH_3, *para*-substituted (4-R) compounds crystallize as conformer **N**, without exception.
4. *Ortho*-substitution on either the phenyl ring (2-R) or the pyridyl ring (3-R') favors conformer **O**.
5. Moderately electron-withdrawing *meta*-substituents (3-R) crystallize as conformer **O** even when R'= 6-CH_3; highly electronegative *meta*-substituents

result in a high degree of conformational flexibility, regardless of pyridyl substitution.

In only four of the 30 BzPTUs that we studied were we able to isolate both conformers in the solid state, although all (except **19** and **32**, *vide infra*) displayed at least some degree of conformational equilibrium in solution, where [conformer **N**] $\propto$ 1/T. Three of these compounds (**16**, **30**, and **43**) have *meta*-substituents on the phenyl ring (3-NO_2, 3-NO_2, and 3,5-Cl, respectively), although, as we noted above, **43**'s symmetrical phenyl-substitution pattern tends to fit trends observed in *para*-substituted BzPTUs (4-R), rather than their *meta*-substituted counterparts. It may be that the 5-methyl substituent on the pyridyl ring does not favor the nucleation of conformer **N** as strongly as the 6-methyl substituent; the published, non-solvate structure of 1-aroyl-3-(4-methyl-2-pyridyl) thiourea[155] (R' = 4-CH_3) is that of conformer **O**; to the best of our knowledge, the corresponding 5-methyl structure has not been reported. By contrast, **17** (R' = 6-CH_3) forms conformer **O** (as an H_2O solvate) only under a single set of conditions (**Table 6.7**), and otherwise crystallizes preferentially as conformer **N**. It is therefore likely that the kinetics of nucleation are affected by both phenyl and pyridyl substitution patterns, and, were we to explore pyridyl substitution patterns in greater depth, we would probably discover that certain substituents evoked the same polymorphic accessibility observed among BzPTUs with electronegative *meta*-substituents.

While we were disappointed that we were unable to obtain more than two sets of polymorphic crystal structures in BzPTUs **16-46**, **16O/N** and **17O/N** nevertheless served to confirm our suspicion that solid-state conformation, rather than a similar substitution

pattern, was responsible for the different structural trends observed in conformers **O** and **N**. Because **Chapter V** covered the structural changes associated with RAHB in conformers **O** and **N**, we will not readdress those topics here: as was previously mentioned, the structural features of these compounds tend to be conformer-specific, and the description of both conformers found in **Chapter V** is generally applicable to all BzPTUs **16-46**. A summary of crystallographically-determined, conformer-specific structural characteristics in BzPTUs **16-46** can be found in **Table 6.8**. For convenience, **Figure 6.1** has been reproduced on the following page, as well.

Unsurprisingly, the lengths of bonds involved in RAHB in either conformer **O** or conformer **N** tend to be highly conformationally-specific, although certain fluctuations relating to pyridyl substitution are also apparent in our data. The partial double-bond character of amide bonds *a* and *b* is lower, on average, in conformer **N**; however, this difference is most pronounced when R' = 6-CH_3, and is actually somewhat negligible when R' = H. The partial double-bond character of thioureido bond **c** is similarly less pronounced in conformer **N** when R = H, although it is still significantly greater than that observed in conformer **O**, regardless of the latter's pyridyl substitution status. It may be that the absence of the 6-CH_3 substituent on the pyridine ring, and the consequent decrease in steric strain, allows a greater contribution of electron density from the pyridyl nitrogen to the pseudo-heterocyclic RAHB, thereby supporting greater conjugation in the otherwise isolated amide bonds. The shorter N...H(N) bond length (Δ = 0.030 Å) when R = H in conformer **N** may be evidence of this stronger interaction.

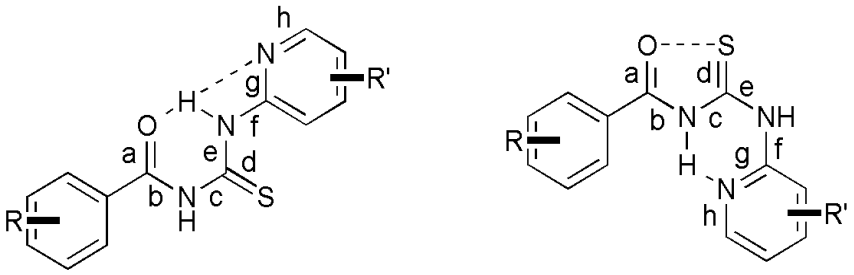


Table 6.8. Average lengths of selected bonds in **16**-**47**, as determined by X-ray crystallography.

Average bond length (Å)	O...H(N) or N...H(N)[a]	O...N or N...N[a]	a	b	c	d	e	f	g	h
Conformer O, all	1.912	2.625	1.224	1.377	1.398	1.662	1.337	1.417	1.335	1.339
Conformer O, R' = 6-CH_3	1.923	2.633	1.226	1.376	1.399	1.663	1.338	1.416	1.338	1.341
Conformer O, R' = H	1.888	2.615	1.224	1.379	1.399	1.662	1.340	1.413	1.335	1.337
Conformer N, all	1.934	2.662	1.208	1.392	1.372	1.667	1.360	1.408	1.335	1.352
Conformer N, R' = 6-CH_3	1.939	2.665	1.208	1.394	1.371	1.669	1.359	1.409	1.335	1.353
Conformer N, R' = H	1.909	2.651	1.212	1.382	1.377	1.657	1.364	1.404	1.333	1.348
47 "O-like"[b]	1.902	2.608	1.233	1.375	1.415	1.629	---	---	---	---
47 " N-like"[b]	---	---	1.203	1.399	1.367	1.629	---	---	---	---

[a]D...H(A) = N...H(N) in conformer **N** and O...H(N) in conformer **O**. D...A = N...N in conformer **N** and O...N in conformer **O**.
[b]"**O-**" and "**N**-like" refer to the coordination status of the carbonyl moiety, where the (C=)O engaged in RAHB is "**O**-like" and the free (C=)O is "**N**-like." Labeled bonds correspond with those in the appropriate conformer.

Interestingly, the lengths of the two sets of amide bonds *a* and *b* in **47** mirror those observed in BzPTUs **16-46**, in the corresponding conformers. In the "**O**-like" (*i.e.* RAHB-involved) carbonyl moiety, the C=O bond is elongated (1.233 Å), and the (O=)C—N bond is shortened (1.375 Å), relative to those in the "**N**-like" carbonyl moiety (1.203 Å and 1.399 Å, respectively). The corresponding bond lengths in conformer **O** (1.224 Å and 1.377 Å) and conformer **N** (1.208 Å and 1.392 Å) are similar enough those in **47** that we believe these structural changes are evoked entirely by intramolecular RAHB, rather than some conformation-dependent peculiarity in the BzPTUs' molecular structure.

Apart from differences in bond length, one of the more striking—and, quite frankly, most fascinating—differences between conformers **O** and **N** is their coloration (or, in the case of conformer **O**, the lack thereof). The distinctive yellow color of conformer **N** is present both in the solid state and in solution, whereas—with the exception of R-NO_2 BzPTUs **16** and **30**—conformer **O** is essentially colorless.‡ Because such a great level of diversity in crystal packing exists in solid-state BzPTUs **16-47**, even among those crystallizing as the same conformer, we concluded that lattice forces likely contribute very little to conformer **N**'s consistently yellow hue. Similarities observed in the single-molecule structures of **16-18**, **20**, **22**, **24**, **26**, **27**, **31**, **39**, **42**, and **43**—all of which crystallize as conformer **N**—led us to propose three potential sources of this low-energy, visible light absorption:

‡ Due to the presence of both conformers in the mother liquor, small amounts of conformer **N** are almost impossible to remove from samples of conformer **O**, as the former's much lower solubility complicates sample washing. Therefore, many conformer **O** crystals appeared "off-white," or very slightly yellow, due to the residual presence of conformer **N** on the crystal surface. This small amount of conformer **N**, identified from its C=O stretch, was detectable in the IR spectra of these compounds, but did not affect either single crystal X-ray data collection or elemental analysis.

1. Charge-transfer behavior across the RAHB, due to facile proton transfer
2. Increased conjugation between the phenyl ring and the carbonyl moiety, due to the greater planarity between these two groups observed in conformer **N**
3. Syn-periplanar orientation (and assumed interaction) of the carbonyl and thiocarbonyl moieties, where $d_{S...O}$ = 2.918 – 3.057 Å (*i.e.* less than the sum of van der Waals radii, 3.32 Å)

The vibrant yellow color observed in **47** quickly eliminated charge-transfer across the RAHB as a viable option for the coloration observed in conformer **N**, as **47**, bis(benzoyl)thiourea, lacks the requisite N...H(N) intramolecular interaction. This compound also lacks obvious visible light chromophores, due to cross-conjugation across the thiocarbonyl moiety, so it is unlikely that the color observed in **47** originates from a different source than that observed in conformer **N**. Increased conjugation between the phenyl and carbonyl moieties in conformer **N** remained a plausible explanation, as the average coplanarity of the phenyl ring and the carbonyl moiety, calculated as the torsion angle between bond **a** and the aromatic C—C bond *cis* to it (∠ O1-C8-C9-C10 in Figure **6.8**), was nearly three times greater in conformer **N** (average torsion = 11.81˚) than in conformer **O** (average torsion = 27.95˚). Even when *ortho*-substituents were not included in the average, the average torsion angle in conformer **O**, 19.1˚, was still significantly smaller than that found in conformer **N**.

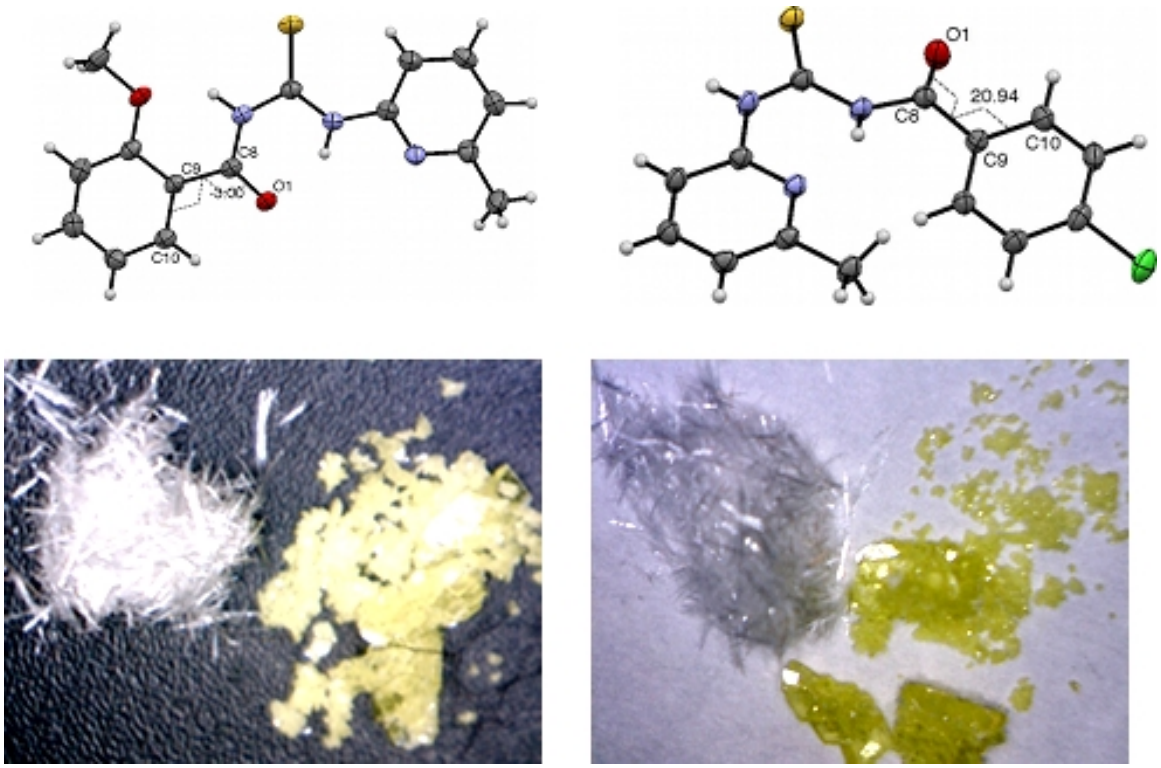


Figure 6.8. ORTEP diagrams (top) and photographs (bottom) of **19** and **22**. Atoms used to calculate torsion angle are labeled at top. Photographs at approximately 10X magnification were captured using a Celestron digital microscope and the Mac OS X image capture program, Photo Booth. To best illustrate the coloration of **19** (fine, colorless, columnar crystals, at left in both images) and **22** (yellow prisms, at right in both images), images were collected on both a black and a white background.

Nevertheless, we were somewhat skeptical of increased phenyl-carbonyl conjugation as the origin of the yellow color in conformer **N**. Despite the lower average torsion angle in conformer **N**, many exceptions exist among BzPTUs **16-46**, with no accompanying change in coloration. BzPTU **19**, for example, shown on the left in **Figure 6.7**, has a phenyl-carbonyl torsion angle of 3.00˚, and is completely colorless; conversely, in BzPTU **22**, shown on the right in **Figure 6.8**, this angle is 20.94˚--yet its

color is quite unequivocally yellow. It is also unlikely that different substitution patterns have any real effect on the extent to which coplanarity is required for electron delocalization—at least in terms of lowering the energy of the BzPTU sufficiently for a visible-wavelength electronic transition—as the phenyl-carbonyl torsion angle in colorless **35**, the R' = H analog of yellow-hued **22**, is only 14.00˚. These inconsistencies observed in phenyl-carbonyl torsion angles appeared incongruous with the uniformity of the yellow color observed in all conformer **N** crystals, and we believed that increased conjugation was likely an oversimplified explanation for the presence of color in conformer **N**.

The final explanation that we considered, an S...O intramolecular interaction related to the syn-periplanar orientation of the carbonyl and thiocarbonyl moieties in all conformer **N** structures, seemed the most likely of the three. This S...O interaction was present both in all conformer **N** structures and in **47**, where it formed between the non-coordinated, "**N**-like" carbonyl oxygen and the thiocarbonyl sulfur, and was absent from all conformer **O** structures, in which the carbonyl and thiocarbonyl moieties were anti-periplanar as a consequence of the intramolecular RAHB. Interestingly, in a survey of published crystal structures of N-benzoyl-N',N'-disubstituted thioureas,[156-160] which lack the capacity to form an S(6) intramolecular RAHB, we found that the carbonyl and thiocarbonyl moieties adopted a more anti-periplanar conformation (torsion angle ~ 100˚), and therefore lacked the S...O close contact observed in conformer **N**. Because the S...O close contact does not appear to be commonplace among benzoyl thioureas, yet is consistent throughout all of our conformer **N** structures, we believed that it was likely to

have some structural significance, quite possibly relating to the yellow color observed, also consistently, in these compounds.

Close contacts (*i.e.* less than the sum of van der Waals radii, 3.32 Å) between oxygen and sulfur have been well-documented in the literature,[161,162] are implicated in a number of biological transformations,[163] and have even been employed as rigidifying structural components of polymeric electrooptic materials[164] and stereochemical directors in asymmetric reactions.[165,166] Despite its relevance to both biochemistry and organic structural and synthetic chemistry, the electronic nature of the S...O interaction has not been definitively characterized. In the literature, this contact has been described, varyingly, as electrostatic,[167] electrostatic-covalent,[162] hypervalent,[168] "prematurely" hypervalent,[162] and, more simply—and perhaps in an effort to circumvent any nomenclatural controversy—non-bonded.[165]

Among reports characterizing the S...O interaction as anything other than purely electrostatic, the general consensus is that this interaction consists of some form of electron donation from oxygen to sulfur, although opinions differ as to the precise nature of this electron donation. Most reports characterize it as an $n_{(O)}$ to $\sigma^*_{(S)}$ interaction,[169] while others believe that, at least in proteins, the donor orbital is actually $\pi_{(HOMO)}$ of the carbonyl bond.[170] Ángyan[162] and Pandya[168] both implicate some measure of d-orbital participation, inferring that the S...O interaction possesses partial covalent character (Ángyan quantifies this covalent character as 10-30% of the total bond composition); however, the relatively low energy estimated for the S...O interaction (3-8 kcal/mol, depending on the computational methodology) indicates that "covalent character" is more

a qualifier of electronic composition than a statement on bond order or atomic connectivity. Nevertheless, even a relatively weak $n_{(O)} \rightarrow \sigma^*_{(S)}$ interaction—especially one with lower energy, d-orbital participation—can result in visible light absorption sufficient to produce empirically observable coloration,[171] and we therefore believe that this is the most plausible explanation for the yellow color in conformer **N** BzPTUs (and **47**).‡

Conclusion

BzPTUs **16-46** crystallize in one of two conformers, both of which feature an S(6) intramolecular RAHB. For most of these BzPTUs, we have found that only one conformer is kinetically accessible in the solid phase; however, we managed to isolate solid samples of both conformers in four of these BzPTUs, and we obtained single crystal X-ray data for two conformer pairs. By observing structure-based conformational preferences in these BzPTUs, we also developed a qualitative sense of the factors that favor conformers **O** and **N**, concluding that methyl substitution at the 6-position on the pyridine ring and electronegative *para*-substitution are the best predictors of conformer **N** in the solid phase. Because crystal packing forces did not correlate well with conformational preference, however, we were unable to use this handle on single-molecule conformational preference to intentionally engineer supramolecular structure.

Nevertheless, we found that single-molecule conformational preference did have a significant impact on the observed physical properties of solid-phase BzPTUs **16-46**, in a

‡ The reality is that we are probably completely off-base, in terms of our suspicions as to where the color originates; however, it is far more entertaining to be wrong about a hypothesis than it is to have no hypothesis at all.

way that was apparently independent of supramolecular architecture. All conformer **N** solids were significantly less soluble—both thermodynamically and kinetically—than their conformer **O** counterparts, and all were also bright, "sulfur yellow," a color which persisted even in solution. Based on similarities between the conformer **N** crystal structures, we concluded that the yellow color most likely originates in the $n_{(O)} \rightarrow \sigma^*_{(S)}$ interaction between the coplanar carbonyl and thiocarbonyl moieties.

Overall, our work with BzPTUs **16-46** exemplifies both the problems and the potential of organic crystal engineering. These compounds exhibit an extraordinary correlation between molecular conformation and certain observed physical properties, yet also display a somewhat mind-boggling incongruousness between these same physical properties and supramolecular structure / crystal packing. While crystal packing must certainly play some role in determining macroscopic properties,[11] its correlation with the physical characterisitics observed in BzPTUs **16-46** remains nebulous, and, in predicting the physical properties of these fascinating compounds, we are better served by considering single-molecule conformation, rather than any trends in supramolecular organization.

CHAPTER VII

CONFORMATIONAL EXCHANGE IN 1-BENZOYL-3-(2-PYRIDYL) THIOUREAS: THE SOLUTION STATE

Introduction

As discussed in Chapters **V and VI**, compound **16**, 1-(3-nitrobenzoyl)-3-(6-methyl-2-pyridyl)thiourea is—to the best of our knowledge—the first experimental example of a "switchable" RAHB-containing system. This compound has the capacity to form two different RAHBs, and the two resultant conformations, **O** and **N** in **Figure 7.1**, are both reproducibly isolable in the solid state, and readily discernable in both ^{1}H- and ^{13}C-NMR. RAHB theory predicts that the homonuclear N...H(N) intramolecular interaction should be lower in energy than the heteronuclear O...H(N) contact, and this preference is reflected in the enhanced crystalline stability of **16N**, the thermodynamically-preferred solid-state conformation. Nevertheless, we

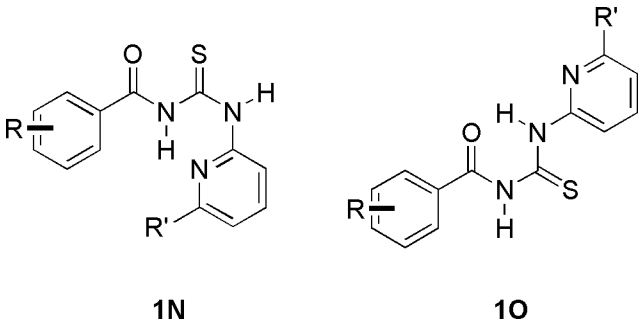


Figure 7.1. General structure of both possible conformers of BzPTUs **16-46**.

found that **16O** is significantly more stable than **16N** both in solution and as determined by our gas-phase calculations, and we concluded it unlikely that the relative strength of the intramolecular RAHB represents the driving force behind phase-specific conformational preference. Because **16N** and **16O** have vastly different electronic characteristics—perhaps best demonstrated by their calculated dipole moments, 12.4 D and 4.5 D, respectively—it is more likely that phase-specific conformational preference is determined by external factors, such as the energetic contributions of substrate-substrate and substrate-solvent interactions.

To further explore the conformational preferences of this intriguing class of compounds, we synthesized a series of 1-benzoyl-3-(2-pyridyl) thioureas (BzPTUs), compounds **16-46**. The enhanced solution-state stability of conformer **O** is ubiquitous among all of these compounds, and all but two display "switchable" behavior in solution, resulting in a dynamic equilibrium between conformers **O** and **N**. To the best of our knowledge, the presence of conformer **N** in solution has never been reported in any such disubstituted BzPTUs, although its appearance in the solid state has been reported in **17**.[144] In many BzPTUs, the proportion of conformer **N** is relatively small, and we believe this omission is likely related to peak overlap (*vide infra*) and the signal-to-noise common in diagnostic ^{1}H NMR scans. As in the solid state, which will be discussed separately, substituent effects play a significant—and relatively predictable—role in determining the extent to which conformer **O** is favored in solution, with conformational free energy differences that are inversely proportional (in terms of absolute magnitude) to Hammett substituent constants. Because few BzPTUs with electron-withdrawing

substituents have been reported, it is entirely possible that the presence of conformer **N** was previously overlooked.

Results and Discussion

Synthesis of Bifunctional Thioureas

BzPTUs **16-46** were prepared from addition of the corresponding benzoyl isothiocyanate and either 2-aminopyridine or 2-amino-6-picoline, using the procedure outlined in **Scheme 6.1**. Aroyl isothiocyanates were prepared in accordance with the literature procedure for the parent compound, benzoyl isothiocyanate (R = H in **Scheme 6.1**);[150] because these reaction conditions yielded satisfactory results, further optimization was not explored. When the parent benzoyl chloride was not commercially available,‡ it was prepared from the corresponding benzoic acid.[151] We made no attempt to isolate the intermediate isothiocyanates or acid chlorides, as we found that satisfactory yields (65-80%, calculated from the initial amount of either the acid chloride or the isothiocyanate) of BzPTUs could be obtained without additional purification steps. Direct isolation of the BzPTU from the reaction mixture could be achieved by the addition of deionized water, upon completion of the reaction; the precipitated material, after drying, was satisfactorily pure by ^{1}H NMR.§

In an effort to reduce solvent waste, we attempted to synthesize the BzPTUs in a quasi-one-pot reaction, adding the aminopyridine directly to the filtrate from Step **b,**

‡ In some cases, the parent benzoyl chloride was commercially available, but we chose to prepare it from the corresponding benzoic acid, which could be obtained, free of charge, from our Reuse Chemical Facility.

§ While yield could be increased by removing the reaction solvent and chromatographing the BzPTU product, we did not believe this improvement sufficient to justify either the time or the significant increase in solvent usage that it entailed.

Scheme 6.1. In BzPTUs that preferred to crystallize as conformer **O** , this process was highly effective; however, BzPTUs that preferred to crystallize as conformer **N** tended to precipitate from the reaction mixture as highly intractable powders, negligibly soluble in all but the most polar solvents (*e.g.* DMSO, DMF, etc.) and effectively useless for both the growth of single crystals and solution-state spectral analysis. Replacing acetonitrile with acetone produced similar results, and THF—by far the best solvent for all BzPTUs **16-46—**could not be used for the synthesis of isothiocyanates, due to its inability to dissolve a sufficient quantity of KSCN. Solvents such as dichlormethane, ethyl acetate, and diethyl ether were similarly ineffective in the synthesis of isothiocyanates, and were also incompatible with the final purification step (*i.e.* the addition of water) of the BzPTU synthesis, so we concluded that the two-pot reaction sequence described in **Scheme 6.1** was the most efficient route to BzPTUs.

Conformer Identification

In RAHBs, strong donor-acceptor interactions tend to result in significant deshielding of the coordinated proton.[127] Because the homonuclear N...H(N) intramolecular interaction (conformer **N**) should be stronger than the heteronuclear O...H(N) interaction (conformer **O**), as a result of better orbital overlap,[142] and in all cases the farthest-downfield signal in the major conformer was > 2 ppm upfield from the farthest-downfield signal in the minor conformer, we hypothesized that the major conformer in all BzPTUs **16-46** was conformer **O**.

Additional 1D spectral evidence corroborated this hypothesis. Amide-type

deshielding of coplanar γ-protons is well-known in thioureas,[89] and should be observed in the pyridyl proton *ortho* to the thiourea moiety (proton F in **Figure 7.2**) only in conformer **O**. A secondary interaction between the RAHB-involved thiourea proton and the pyridyl nitrogen restricts rotation of the pyridyl ring, enforcing the coplanar arrangement of the *ortho*-pyridyl proton and the C=S bond. In accord with these structure-based predictions, this proton displays a downfield shift of ~2 ppm in the major conformer, at a frequency (8.3 ppm) consistent with amide-type deshielding. This large change in chemical shift was observed in all BzPTUs **16-46**, and it was by far the largest chemical shift change observed among C—H protons; only heteroatomic protons A and B displayed such a similarly drastic change in chemical environment, between conformers **O** and **N**. Furthermore, ^{1}H NMR spectra of BzPTUs **19** and **32** show only the F_O frequency, at 8.97 ppm and 8.66 ppm, respectively. Because these compounds do not display dynamic equilibrium between conformers **O** and **N**, likely due to a "locked" conformation produced by a second intramolecular RAHB, which forms between the *ortho*-methoxy substituent and thiourea proton B_O. This conformation appears in the crystal structures that we obtained for both of these compounds (**Figure 7.3**), and, given

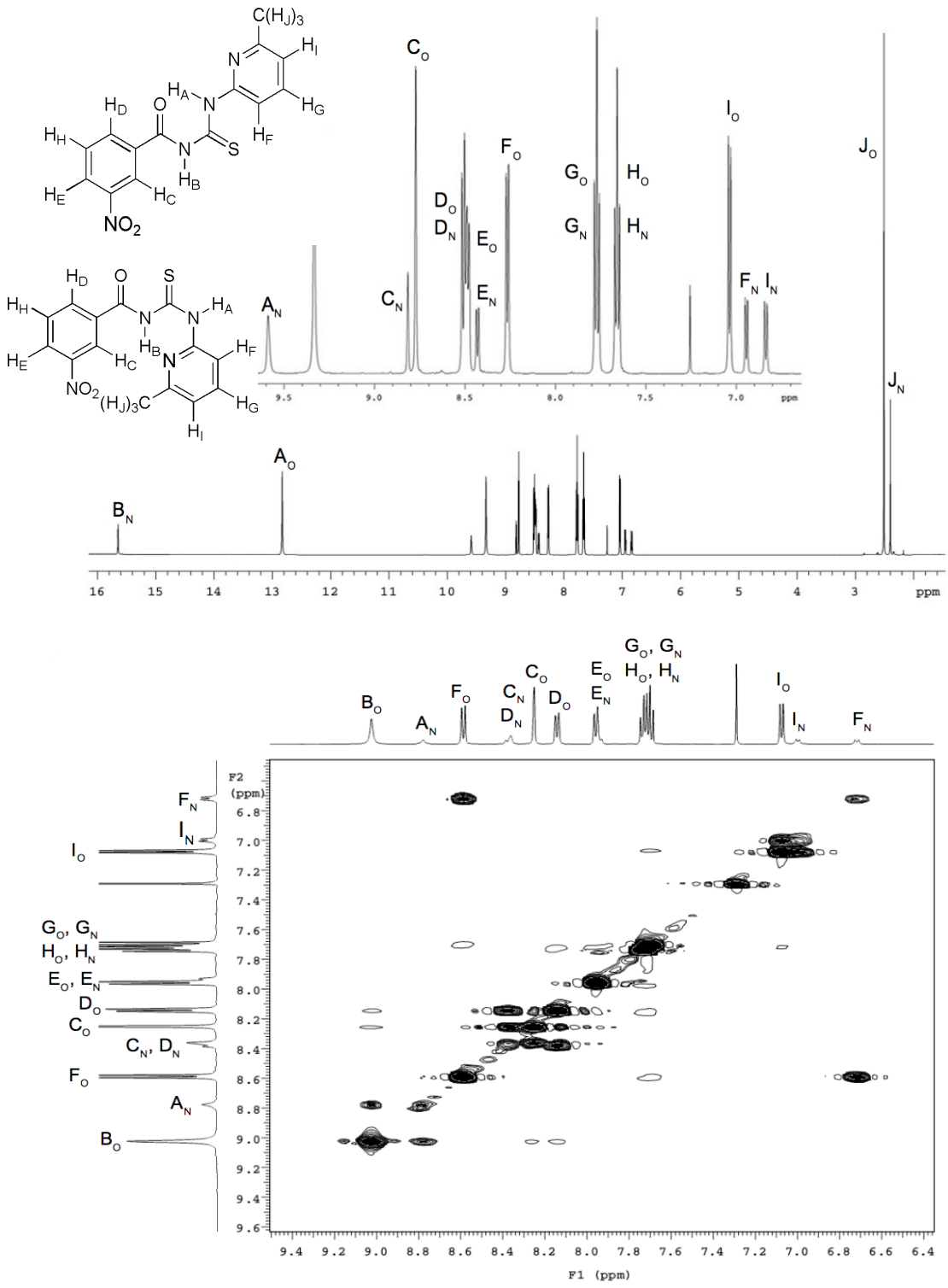


Figure 7.2. Clockwise from top left: **16O** with labeled protons; ^{1}H-NMR spectrum of **16** (inset: zoomed-in view of aromatic region); 2D NOESY spectrum of **23**, where peak assignments are identical to those in **16O/N**; **16N** with labeled protons.

the downfield resonance of proton B_O (11.16 ppm in **32** and 11.11 ppm in **19**), is evidently present in the solution state, as well.

2D NOESY data confirmed proton assignments from the 1D spectra, and provided further confirmation that conformer **O** was indeed the preferred solution-state conformation. Cross-peaks from chemical (e.g. conformational) exchange are of the same phase as the peaks along the diagonal, and are therefore easy to distinguish from NOE-derived cross-peaks, which are inverse-phase. The chemical exchange cross-peak between protons F_O and F_N is clearly evident in **Figure 7.2**, confirming the identity of this proton, as assigned from the 1D spectrum. The predominance of conformer **O** in solution is confirmed by the opposite-phase (i.e. NOE) cross-peaks B_O / C_O and B_O / D_O ; only in conformer **O** are the *ortho*-protons on the phenyl ring sufficiently close to the amide proton to display NOEs, and the far-upfield resonance of B_O (9.01 ppm vs. 12.76 ppm for A_O) indicates that it is not the major conformer's RAHB-involved N—H proton. Additionally, the strong NOE expected between J^4 protons A_N and F_N, which are coplanar in conformer **N** and separated by no more than 2.38 Å in any of our conformer **N** crystal structures, is not observed at this resolution, as would be anticipated if conformer **N** were the predominant solution-state entity.

Variable-Temperature ^{1}H-NMR – Thermodynamic Measurements

Within the range of concentration (0.01 – 0.05 M) that proved optimal for our variable-temperature NMR measurements, we found that conformational equilibrium did

not vary with sample concentration, outside of reasonable estimations of error inherent in NMR peak integration.[172,173] Because both the solubility and rate of dissolution of conformer **N** are significantly lower and slower, respectively, than those of conformer **O**, sample concentration was primarily determined by expediency, *i.e.* one which afforded quick data collection, yet could be achieved in an acceptable period of time, instead of after 8 hours on the sonicator.

Samples were prepared by dissolving 10-20 mg of BzPTUs **16-46** in 0.5 mL $CDCl_3$. For solvent studies performed on **16**, 5-10 mg were dissolved in 0.5 mL of the chosen solvent. Spectra were collected at intervals of 5 – 10˚C, between -15 and 45˚C; specific temperature ranges are reported in **Table 7.1**. In all cases, data were collected at a minimum of five temperatures, over a minimum of 30˚C. For most samples, the low boundary of the temperature range was determined by the lowest temperature that the spectrometer could achieve without external cooling, and the high boundary was determined by the temperature at which peak broadening interfered with integration. In the case of DMSO-d_6, the low boundary of the temperature range was set at 20˚C, 2˚C above the solvent's melting point.

Thermodynamic Measurements – $CDCl_3$

In all BzPTUs **16-46**, conformer **O** was thermodynamically favored in $CDCl_3$. Values of ΔG for the formation of conformer **O** (at 25˚C) ranged from -0.84 kcal/mol (**26**) to -3.3 kcal/mol (**33**); in general, BzPTUS with electron-withdrawing *meta*-substituents on the phenyl ring and/or a 6-CH_3 substituent on the pyridyl ring had the smallest (least

negative) free energy differences between conformers. The magnitude of the stabilization offered by both substitution trends can easily quantified by comparing $\Delta\Delta G_{25^\circ C}$ values from related BzPTUs. When identical R' substituents were present on the pyridyl ring, moving an R group from the *para* position to the *meta* position—for example, as in compounds **16** and **18**—lowered the free energy difference between conformers **O** and **N** by 0.2 ± 0.2 kcal/mol, on average, with a maximum *meta*-stabilization of 0.5 kcal/mol. This trend was not perfectly consistent, however, as conformer **N** in compound **21** (R = *m*-Cl) was actually 0.1 kcal/mol higher in energy, relative to conformer **O**, than in **22** (R = *p*-Cl)

Both improved consistency and greater stabilization of conformer **N** were observed in BzPTUs with a 6-CH_3 pyridyl substituent. Incorporating this methyl group

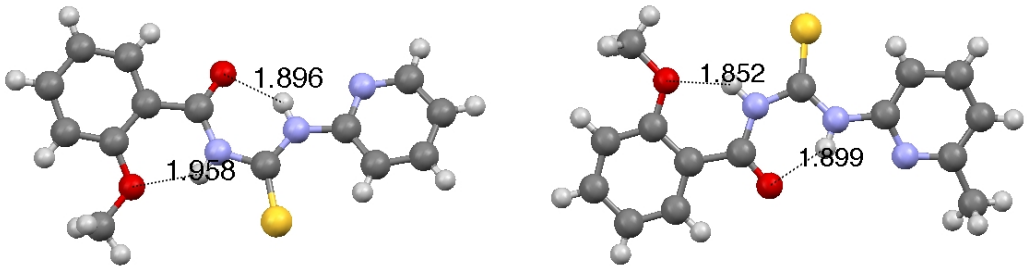


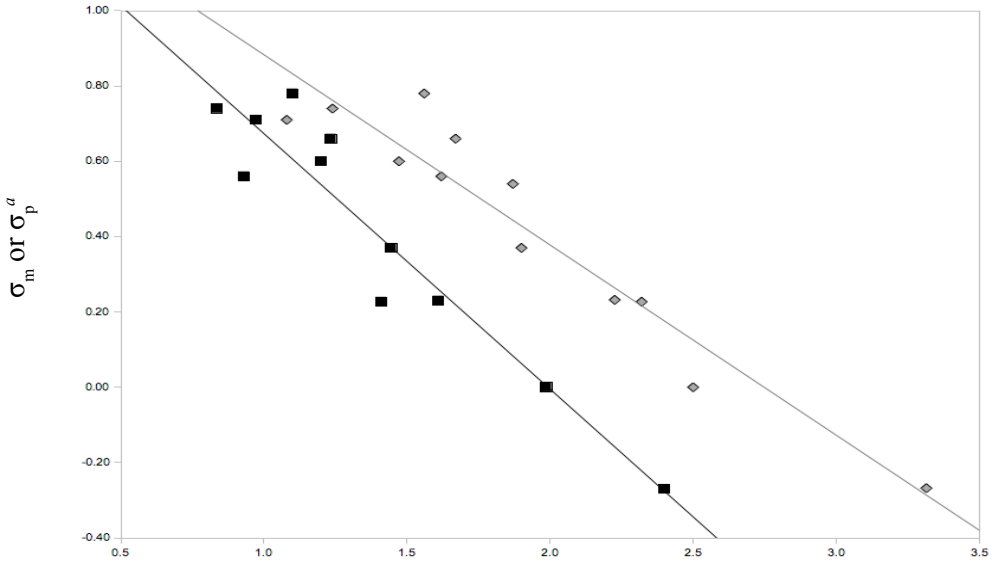
Figure 7.3. X-ray crystal structures of **32** (left) and **19** (right). Dashed lines indicate intramolecular hydrogen bonds; bond lengths are in Å.

stabilized conformer **N** by 0.5 ± 0.3 kcal/mol, relative to 6-H BzPTUs with identical R groups; $\Delta\Delta G_{25^\circ C}$ ranged from 0.9 kcal/mol (BzPTUs **22** and **35**) to 0.1 kcal/mol (BzPTUs **16** and **30**), and in no case was conformer **N** more favored in BzPTUs with a 6-H pyridyl substituent. After accounting for the stabilizing effect of the 6-CH_3 substituent, Hammett

substituent constants[174] were roughly predictive of relative $\Delta G_{25^\circ C}$, where larger values of σ_m and σ_p were associated with the increased stability of conformer **N** (**Figure 7.4**). Because we observed no correlation between Hammett constants and either entropy or enthalpy, we believe that electronegative phenyl substituents serve primarily to weaken the (C=)O...H(N) intramolecular interaction, thereby destabilizing conformer **O** in relation to conformer **N**.

Table 7.1. Thermodynamic parameters for the formation of conformer **O** in chloroform, in BzPTUs **16-46**. Compounds are listed in ascending order, relative to the absolute magnitude of $\Delta G_{25^\circ C}$. Because BzPTUs **19** and **32** do not undergo conformational interconversion, they are not included in this table.

CMPD	R	R'	$\Delta G_{25^\circ C}$ (kcal/mol)	ΔH (kcal/mol)	ΔS (e.u.)	T range (˚C)
26	3,5-Cl	6-CH_3	-0.84	3.0	13.0	-15 – 25
23	3-CN	6-CH_3	-0.93	2.7	12.1	-15 – 30
16	3-NO_2	6-CH_3	-0.97	2.0	10.1	-10 - 45
30	3-NO_2	H	-1.1	1.8	9.7	-10 - 30
18	4-NO_2	6-CH_3	-1.1	1.8	9.7	-15 - 25
25	3,4-Cl	6-CH_3	-1.2	2.8	13.3	-20 - 25
24	4-CN	6-CH_3	-1.2	2.2	11.7	-15 – 35
39	3,5-Cl	H	-1.2	2.4	12.1	5 - 35
22	4-Cl	6-CH_3	-1.4	1.7	10.5	-15 – 25
21	3-Cl	6-CH_3	-1.5	2.7	14.0	-10 - 25
38	3,4-Cl	H	-1.5	2.0	11.2	-10 – 20
31	4-NO_2	H	-1.6	1.9	11.7	-10 - 25
36	3-CN	H	-1.6	1.4	9.9	-20 - 20
37	4-CN	H	-1.7	1.4	10.4	-15 – 25
34	3-Cl	H	-1.9	2.4	14.5	5 - 30
17	H	6-CH_3	-2.0	3.2	17.4	-10 - 25
41	2-Br	H	-2.2	4.1	21.1	- 9 - 30
40	4-Br	H	-2.2	3.8	20.2	-10 - 30
35	4-Cl	H	-2.3	2.4	15.8	-15 – 25
20	4-OCH_3	6-CH_3	-2.4	3.1	17.6	-10 - 30
29	H	H	-2.5	3.1	18.8	-10 - 25
33	4-OCH_3	H	-3.3	5.0	26.5	-10 - 20



[a]Ref. 174

Figure 7.4. Correlation between Hammett substituent constant and conformer **O** / conformer **N** free energy difference in BzPTUs **16-28** (gray) and **29-46** (black)

Despite performing calculations with a variety of basis sets, we were unable to computationally reproduce the solution-state equilibrium between conformers **O** and **N.** The gas-phase energy difference between **16O** and **16N**, -4.72 kcal/mol, calculated at the B3LYP/6-31G++(d,p) level of theory, was four times larger (in terms of absolute magnitude) than the experimentally-determined value of $\Delta G_{25^\circ C}$ for the formation of **O**, -1.0 kcal/mol. This discrepancy is far outside the range of error anticipated for this type of calculation,[175] and is unlikely to result from solvation: additional computational studies, performed at the RB3LYP/6-31G(D) level in Spartan 08, indicated that, in

chloroform, $\Delta G_{N \rightarrow O}$ was 4.89 kcal/mol—even greater than that determined in the gas phase, albeit at a different level of theory. Although we have not observed molecular aggregation in our 2D studies, it may be that dimerization and/or other intermolecular interactions lead to solution-state energy changes that single-molecule computational studies cannot easily reproduce.‡ Lattice energy calculations for **16N/O** indicate that **16N** is the preferred solid-state conformer, by 3.89 kcal/mol, so it may be that some of the intermolecular interactions favoring **16N** are present in solution, thereby lowering the **N/O** free energy difference.

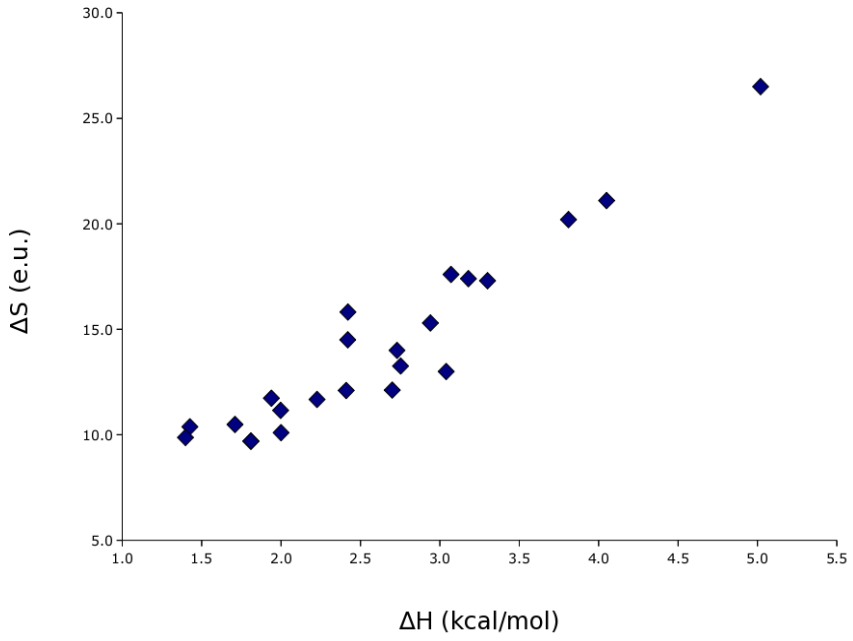


Figure 7.5. Linear correlation between entropy and enthalpy in BzPTUs **16-46**.

‡ It may also simply be that there are no protons within 5-6 Å of the thiourea moiety that would only show NOESY correlations in either the dimerized species *or* the monomer, but not in both.

Entropic and enthalpic values obtained for the **N** → **O** transformation in BzPTUs **16-46** lend some credence to this hypothesis. In all cases, the formation of conformer **O** is associated with an increase in entropy ($\Delta S > 0$), yet enthalpic factors unilaterally favor conformer **N**, by 1.81 to 5.02 kcal/mol. Our computational studies of **16** indicate that the gas-phase dipole moment in **16N** is nearly three times greater than that in **16O**, which is in agreement with both the higher disorder associated with the formation of **16O** and the higher aggregation postulated for **16N**, as an increase in polarity should correlate with stronger intermolecular interactions. Perhaps unsurprisingly, given the consistency in the direction (i.e. mathematical sign) of entropy, enthalpy, and free energy among all BzPTUs **16-46**, we observed a near-linear correlation between entropy and enthalpy (**Figure 7.5**; $R^2 = 0.9$) in these compounds, which may also be consistent with increased intermolecular aggregation in conformer **N**.

These entropic and enthalpic data also appear to provide some rationale behind the quite divergent, phase-specific stabilities of conformers **O** and **N**. If one imagines the solid state to represent the condition wherein $\Delta S \rightarrow 0$, the free energy difference between **O** and **N** will approach ΔH, thereby favoring conformer **N**. Conversely, if one imagines the gas phase as a situation where $\Delta S \rightarrow \infty$, it is clear that enthalpic contributions to ΔG will be quite small, and **O** should be the low-energy conformer. Given that this is exactly what our calculations predict—and, in the case of solid-phase conformers, what our empirical data confirms—we believe that the solution-phase behavior of these BzPTUs can be interpreted (at least qualitatively) as a "transition phase" between each conformer's sphere of dominance.

Thermodynamic Measurements – Solvent Studies

Thermodynamic parameters obtained for **16** in DMSO-d_6, CD_3CN, toluene-d_8, and CD_3OD (**Table 7.2**) indicated that both intermolecular aggregation and solvent polarity play a significant role in stabilizing conformer **N**.

Solvent	$\Delta G_{25^\circ C}$	ΔH	ΔS	**Dielectric Constant**[176]
$CDCl_3$	-0.97	2.0	10.1	4.81
DMSO-d_6	-0.82	6.1	23.3	47.0
CD_3CN	-0.99	1.10	7.2	37.5
toluene-d_8	-2.3	2.6	16.5	2.38

Table 7.2. Thermodynamic parameters for the dynamic equilibrium between **16O** and **16N**, in various solvents. All values are defined for the **16N** → **16O** transition, *i.e.* the formation of **15O**.

As might be expected, conformer **N** is more stable in DMSO-d_6 than in $CDCl_3$, consistent with the greater polarity of DMSO-d_6. In CD_3CN, however, the free energy difference between conformers **N** and **O** is approximately equal to that observed in $CDCl_3$, so polarity alone cannot account for the relative stabilities of **O** and **N** in various solvents. Therefore, molecular aggregation must also play some role in determining the conformational free energy difference, at least in certain solvents. Both $\Delta H_{N\rightarrow O}$ and $\Delta S_{N\rightarrow O}$ are much smaller (*i.e.* less negative) in CD_3CN than in $CDCl_3$, so it may be that molecular aggregation is responsible for the increased stability of conformer **N** in $CDCl_3$, relative to what might be expected purely on the basis of solvent polarity. Because both $\Delta H_{N\rightarrow O}$ and $\Delta S_{N\rightarrow O}$ are even larger in toluene-d_8 than they are in $CDCl_3$, it is unlikely that solvent

ordering and solvent-solute interactions account entirely for these parameters; solute-solute interactions must also play a role in stabilizing conformer **N**.

Variable-Temperature ^{1}H-NMR – Kinetic Measurements

Samples were prepared as for thermodynamic measurements; in the case of kinetic parameters obtained via peak coalescence, the same samples (and spectra) were used for both. From the peak separation in the 1D spectra of BzPTUs **16-46** (**Figure 7.2**), which could be as high as 6 ppm, it was evident that exchange at room temperature, and in $CDCl_3$, was either very fast or very slow on the NMR timescale. Because the solubility of conformer **N** in $CDCl_3$ was significantly lower than that of conformer **O**, yet conformer **O** predominated in solution, we believed that the barrier to interconversion was likely quite high; however, because fast exchange—and a low barrier to interconversion—was theoretically possible, we wanted to determine the free energy of activation for these BzPTUs.

The compounds for which we obtained kinetic data were largely self-selecting: in most cases, 1D ^{1}H-NMR peaks from BzPTUs **16-46** did not coalesce within the sampling range of $CDCl_3$ (i.e. below 55˚C). DMSO-d_6 appeared to accelerate the room-temperature exchange rate—and decrease the coalescence temperature—but its high melting point made it impossible to obtain slow-exchange values for peak separation ($\Delta\nu$), so we were unable to use it for kinetic calculations. Most BzPTUs **16-46** had very low solubility in in CD_3CN, acetone-d_6, and/or toluene-d_8, making it difficult to obtain useful signal-to-noise ratios within reasonable limits for instrument time. Therefore, while we would have

preferred to obtain $\Delta G^{\ddagger}$ for all BzPTUs **16-46**, practical considerations limited our sample pool.

When coalescence was observed, the free energy of activation at that temperature was calculated using Shanan-Atidi's and Bar-Eli's modification of the Erying equation.[177] Because we found that literature reports of these calculations showed significant variance in terms of the actual formula used to calculated $\Delta G^{\ddagger}$, and our own experimentation with these various formulas led us to conclude that only the original (*i.e.* from the Shanan-Atidi and Bar-Eli paper) actually produced values of $\Delta G^{\ddagger}$ that agreed with the thermodynamic energy difference between the two conformers, we have outlined our calculations below.

In kcal/mol, the activation energies for the **N** → **O** and **O** → **N** transitions can be found from the following equations:

$$\Delta G_{O\rightarrow N}^{\ddagger} = 0.00457T_c\{10.62 + \log [X / 2\pi(1 - \Delta n)] + \log(T_c / \Delta \nu)\} \quad (1)^{177}$$

$$\Delta G_{N\rightarrow O}^{\ddagger} = 0.00457T_c\{10.62 + \log [X / 2\pi(1 + \Delta n)] + \log(T_c / \Delta \nu)\} \quad (2)^{177}$$

where T_c is the coalescence temperature, Δn is the difference between the mole fractions of **O** and **N** at coalescence ($n_{\mathbf{O}} - n_{\mathbf{N}}$ at T_c), and $\Delta \nu$ is the low-temperature (*i.e.* slow-exchange, or maximum) peak separation, in Hertz, between the coalescing peaks. The variable X is defined as $2\pi\Delta\nu\tau_{avg}$, where τ_{avg} is the *weighted* average of the lifetimes of the coalescing peaks, during slow exchange. In unequally-populated systems, τ_{avg} can be found by simplifying the following equation:

$$\Delta n = [(X^2 - 2) / 3]^{3/2} \bullet (1 / X) \qquad (3)^{177}$$

After accounting for all constants, and replacing X with $2\pi\Delta\nu\tau_{avg}$, Equation (3) can be reduced to a cubic equation:

$$248.1(\Delta\nu)^3 (\tau_{avg})^3 - 32.65\Delta\nu\tau_{avg} - 2.83 = 0 \qquad (4)$$

which, when solved, will yield τ_{avg} as its positively-signed root.

In some reports,[178] τ_{avg} for unequally-populated sites has been erroneously calculated from the average rate constant, k_{avg}, which may be used to calculate the average lifetime of peaks in equally-populated systems, where the forward and backward rates are equal.

$$k_{avg} = 2.22\Delta\nu = 1/2\tau_{avg} \qquad (5)^{178}$$

This method of finding τ_{avg} cannot, however, be used in unequally-populated systems, as it does not produce a *weighted* average, and therefore does not account for the unequal contributions of the two conformer populations.

Another error that we have noticed in the literature relates to a misprinting of Shanan-Atidi and Bar-Eli's formula, where Equation (3) has been replaced by

$$\Delta n = (X^2 - 2 / 3)^{3/2} \bullet (1 / X) \qquad (5)^{179}$$

Using either Equation (5) or k_{avg} to calculate τ_{avg} for an unequally-populated system will result in a calculated transition state free energy difference that does not correspond to the thermodynamic free energy difference between the two conformers ($\Delta\Delta G^{\ddagger} \neq \Delta G_{TC}^{\ddagger}$). Because the principle of microscopic reversibility prohibits this kind of discrepancy, and only Shanan-Atidi and Bar-Eli's modification of the Eyring equation produces values for $\Delta\Delta G^{\ddagger}$ that correspond with our empirical data for the thermodynamic free energy difference between **O** and **N**, we believe that this is the most reliable method for determining activation energy from coalescence temperature, in unequally-populated systems.

In the BzPTUs for which we observed coalescence in $CDCl_3$, $\Delta G^{\ddagger}$ for the **O** → **N** transition ranged from 16.8 to 18.8 kcal/mol, and from 14.9 and 16.0 kcal/mol in the opposite direction (**Table 7.3**). $\Delta\Delta G^{\ddagger}$ was in all cases comparable (or equivalent) to ΔG at the coalescence temperature; the primary source of error is likely to be found in peak integration.

‡ TC = Coalescence Temperature

Table 7.3. Free energy of activation for selected BzPTUs, at their respective coalescence temperatures

BzPTU	R	X	T_C[a] (°C)	Proton	Δν (Hz)	$\Delta G_{O\rightarrow N}^{\ddagger b}$ (kcal/mol)	$\Delta G_{N\rightarrow O}^{\ddagger b}$ (kcal/mol)	$\Delta\Delta G^{\ddagger}$ (kcal/mol)	ΔG_{TC}[c] (kcal/mol)
40	4-Br	H	25.0	F	30.4	17.3	14.9	2.5	2.2
27	4-Br	CH_3	45.0	F	56.2	17.5	15.5	1.9	1.9
35	4-Cl	H	25.0	F	27.2	17.2	14.9	2.2	2.3
22	4-CN	CH_3	45.0	F	41.1	17.2	15.7	1.5	1.6
23	3-CN	CH_3	35.0	J	12.0	17.1	16.0	1.2	1.2
21	3-Cl	CH_3	55.0	F	55.9	18.6	16.0	2.5	2.5
17	H	CH_3	50.0	F	66.5	18.8	15.7	3.1	3.1
43	4-CF_3	H	40.0	F	34.4	18.4	15.6	2.8	2.8
37	4-CN	H	25.0	F	25.0	16.8	15.0	1.8	1.8
25	3,4-Cl	CH_3	25.0	J	6.0	17.0	15.9	1.2	1.2

[a] Coalescence temperature
[b] Free energy of activation at the coalescence temperature.
[c] Absolute value; calculated from non-coalesced peaks in the 1D spectrum, at the coalescence temperature of the peaks used to calculate $\Delta G^{\ddagger}$.

Because it has been noted that inaccuracies inherent in data collection can lead to grossly inaccurate values of $\Delta G^{\ddagger}$, the free energy of activation for the conformational exchange in **23** was also determined via 2D-EXSY spectroscopy,[180-182] as a means of comparison. 2D-EXSY is identical, in terms of pulse sequence, to 2D-NOESY; dynamic conformational exchange produces cross-peaks of significant intensity, and of the same phase as the peaks found along the diagonal of the spectrum. At very short mixing times (t_m < 100 ms), the intensities of these cross-peaks (I_{ij}) are related to the rate of chemical exchange (k_{ji}) and the initial equilibrium magnetization vector (M_j^0) by the equation[182]

$$I_{ij}(t_m) \approx k_{ji} t_m M_j^0 \qquad (8)$$

The rate constant can then be found as the slope of the best-fit line through a plot of I_{ij} / M_j^0 vs. t_m. M_j^0 is approximated by I_{ij} at $t_m = 0$ ms. To reduce the margin of error inherent in peak integration, the arithmetic mean of all values of I_{ij} / M_j^0 at each t_m was used in creating the rate constant plot. Once the rate constant is known, the Eyring equation can be used to calculate the free energy of activation. A sample plot of I_{ij} / M_j^0 vs. t_m for **23** is shown in **Figure 7.6**.

At 25˚C, we found that the free energy of activation for the conformational exchange between **23N** and **23O** was comparable to that determined for the same compound at 35˚C, the coalescence temperature for protons J_O and J_N. $\Delta G^{\ddagger}$ for the **N** → **O** transformation was found to be 17.6 kcal/mol, 1.6 kcal/mol higher than the value of $\Delta G^{\ddagger}$ found at 35˚C; for the **O** → **N** transition, this parameter was found to be 18.9 kcal/mol, 1.8 kcal/mol higher than at 35˚C. The free energy of activation calculated from 2D EXSY was less precise than that calculated from the coalescence temperature: $\Delta\Delta G_{25^\circ C}^{\ddagger}$ was 0.4 kcal/mol higher than $\Delta G_{25^\circ C}$ (1.3 kcal/mol vs. 0.9 kcal/mol), whereas $\Delta\Delta G_{35^\circ C}^{\ddagger}$ and $\Delta G_{35^\circ C}$ were found to be of the same magnitude (1.2 kcal/mol). Nevertheless, both methods of calculating the free energy of activation produced values which were believable, given the observed peak separation (or lack thereof), and confirmed our suspicion that conformational interconversion was slow on the NMR timescale.

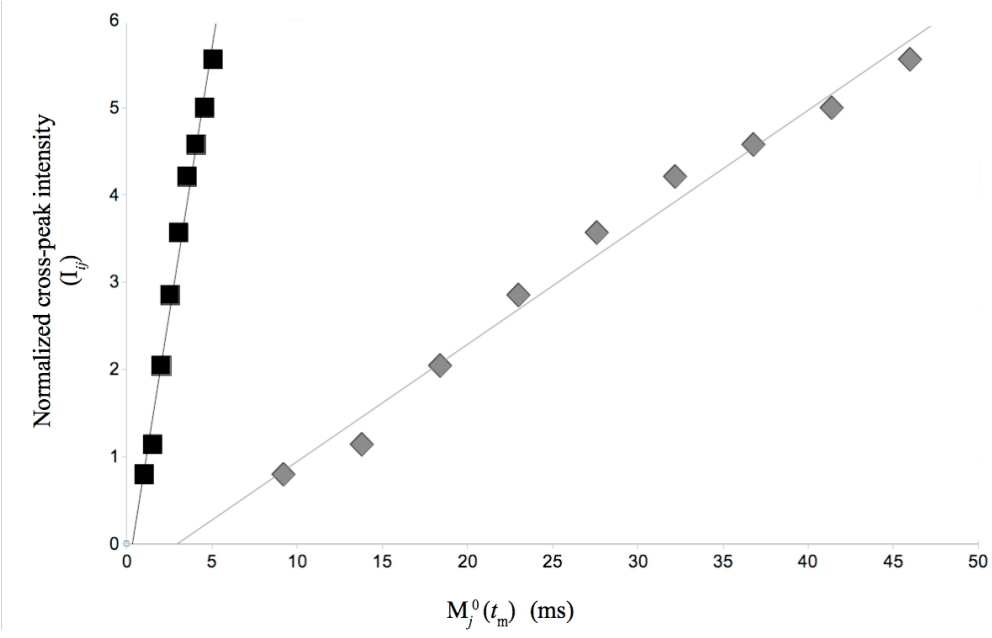


Figure 7.6. 2D EXSY rate constant plot for **23** at 25˚C, for both the formation of **N** (black squares) and the formation of **O** (gray diamonds).

Conclusion

In the absence of a secondary, intramolecular hydrogen bond acceptor, BzPTUs display solution-state conformational equilibrium between conformers **O** and **N**. In all cases, conformer **O** is favored in solution; free energy differences range from 0.9 to 3.3 kcal/mol. After accounting for pyridyl substitution, Hammett substituent constants are roughly predictive of the free energy difference between conformers **O** and **N**, where larger Hammett constants are associated with a greater proportion of conformer **N** in solution. Entropy is likely to be the driving force in determining conformational

equilibrium at room temperature: although enthalpic factors favor conformer **N** by 1.4 to 5.0 kcal/mol, entropy increases (by 9.7 to 27 e.u.) upon the formation of conformer **O**. This solution-state equilibrium can be envisioned as a representative "transition phase" between the gas phase, where entropic considerations would dominate the free-energy equation, and the solid phase, where enthalpic factors would carry greater weight. Unfortunately, as none of these thermodynamic parameters accurately predict the preferred solid-state conformation of BzPTUs **16-46**, it is clear that factors other than solution-state equilibrium play a role in determining solid-state polymorphic preference.

CHAPTER VIII

ALL GOOD THINGS MUST COME TO AN END:

THE DECOMPOSITION OF 1-BENZOYL-3-(2-PYRIDYL)THIOUREAS

Introduction

Alkyl and aryl thioureas are well-known to be stable to both ambient and aqueous conditions. Surprisingly, N-benzoyl thioureas also exhibit low reactivity under similar conditions, most likely as a result of the stabilizing effect of a characteristic, pseudo-heterocyclic resonance-assisted hydrogen bond (**Figure 8.1**). This stability has been recognized to enhance thioureas' catalytic utility in many synthetic procedures, including the asymmetric reduction of carbonyl compounds,[183,184] the asymmetric hydroformylation of styrene[185] and hydrogenation of enamides,[186] and the Heck reaction of aryl halides.[187]

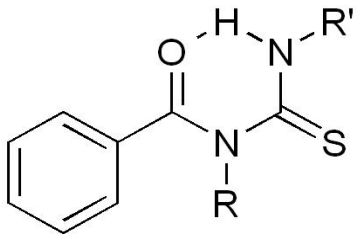
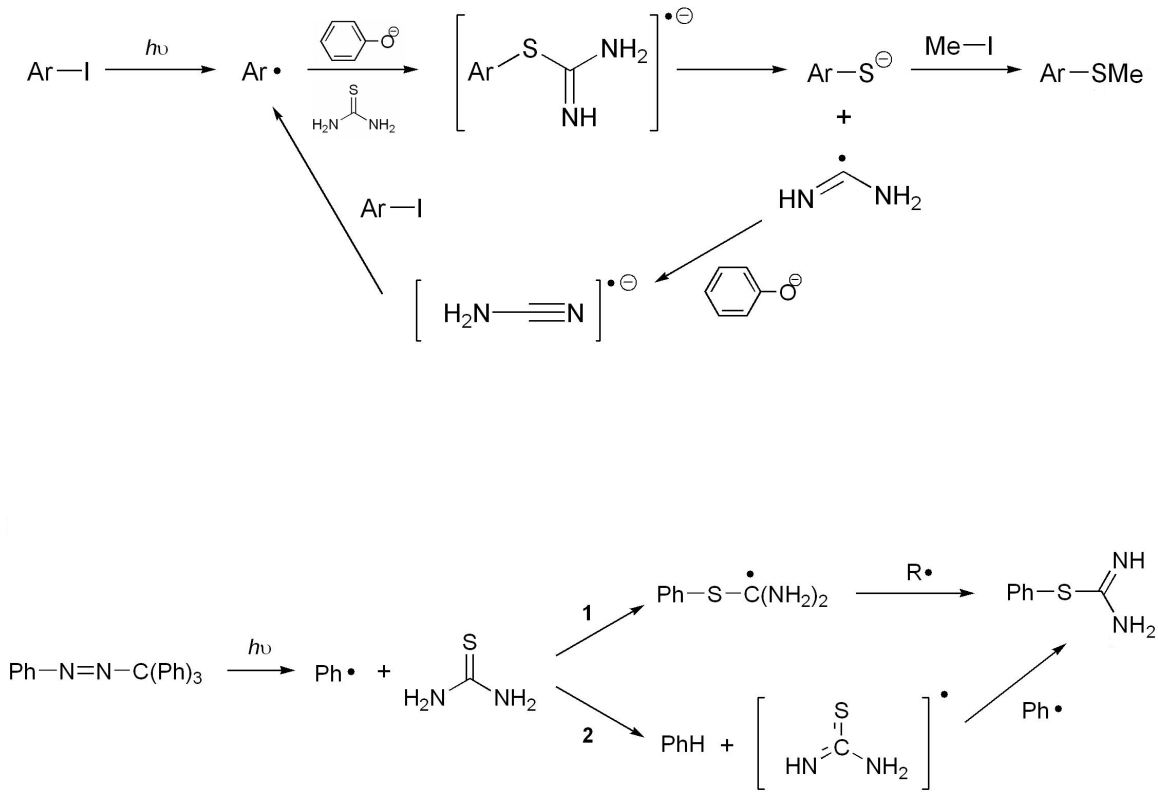


Figure 8.1. Intramolecular hydrogen bonding in N-benzoyl thioureas with at least one N' hydrogen atom

Nevertheless, thioureas do exhibit predictable reactivity under certain conditions; this behavior enhances their utility as a synthetic material. Thioureas are notably used in the production of thiazoles, a heterocycle found in many natural products,[188] as well as in pharmaceuticals,[189] fungicides,[190] and dyes.[191,192] Methods for converting thioureas into

thiazoles include condensation with an α-halo ketone,[193] domino alkylation-cyclization with a propargyl bromide under microwave radiation,[194] and reaction with 1*H*-1-(1′-alkynyl)-5-methyl-1,2,3-benziodoxathiole 3,3-dioxides under basic conditions.[195]

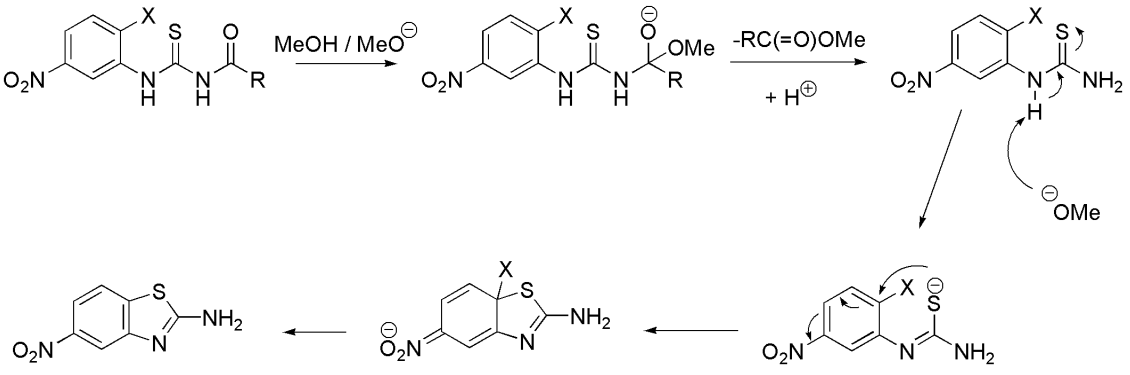
Thiourea anions have also enjoyed recent utility as nucleophilic coupling reagents in the production of aryl sulfides (**Scheme 8.1**). In this reaction, the sulfur nucleophile condenses with a *o*-amide aryl radical species, producing a thiolate anion intermediate, which liberates $[NCN]^{\bullet -}$ and is then quenched with MeI to yield the desired methyl sulfide product.[196] A radical mechanism was also proposed for the formation of S-phenylisothiouronium derivatives from phenylazotriphenylmethane and thiourea;



Scheme 8.1. Proposed mechanisms for aryl sulfide formation via coupling between an aryl radical and anionic/radical thiourea. In the bottom reaction,[15] pathways **1** and **2** indicate the two possible thiourea radical intermediates proposed by the study's authors.

although Ph• clearly plays some role in the radical transformation, the authors of this study speculate that a radical sulfur species, produced by abstraction of the thiourea N—H, may in fact be the active coupling agent.[197]

In the absence of a radical inititator, sulfur arylation is believed to occur via an S_NAr_i transformation. In a methoxide ion-catalyzed process, 1,3-benzothiazoles are produced in high yield from the self-condensation of 1-benzoyl-3-(2-halophenyl) thioureas **(Scheme 8.2**).[198] Upon deprotonation of the thiourea N—H, the resultant anionic sulfur nucleophile displaces the *ortho*-halogen substituent, yielding the cyclized, heterocyclic product. While this reaction bears many similarities to both of the aforementioned radical transformations, the authors report no indication of a radical intermediate, either in the isolated side products or the reaction kinetics. When R = CH_3, methoxide-catalyzed solvolysis at the carbonyl moiety, rather than intramolecular ring formation, was found to be the rate-limiting step; however, when R = C_6H_5, these two



Scheme 8.2. Proposed mechanism of S_NAr_i benzothiazole formation from 1-benzoyl-3-(2-halophenyl) thiourea.

steps are believed to occur in parallel to each other. Interestingly, when R = C_6H_5, cyclization sometimes occurs independently, and the benzodithiazole product retains the N-benzoyl substituent found in the parent thiourea.

Otherwise isostructural with the benzothiazole product formed from the reaction shown in **Scheme 8.2**, the 1-aroylimido-[1,2,4]thiadiazolo-[2,3-a]pyridines (**48**-**53**, **Figure 8.2**) formed from intramolecular cyclization of 1-aroyl-3-(2-pyridyl) thioureas retain the N-aroyl moiety in the final product. A number of heterocyclic thiadiazoles have been reported from the interaction of N,N'-disubstituted thioureas with $CuCl_2$,[116] PCl_5 / $POCl_3$,[199] Ni(II) or Zn(II),[200] and Br_2,[201] but, to the best of our knowledge, no mechanistic studies have been performed.

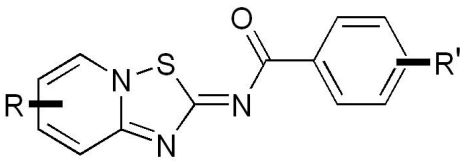


Figure 8.2. Thiadiazoles **48**-**53**. **48**, R, R' = H; **49**, R = H, R' = 3,5-NO_2; **50**, R = 6-CH_3, R' = 4-OCH_3; **51**, R = H, R' = 4-CF_3; **52**, R = 3-CH_3, R' = H; **53**, R = H, R' = 2-Br

Li, *et al*, speculate that cyclization in the presence of $CuCl_2$ likely proceeds through an organometallic intermediate.[116] In their recent work, **48** (R, R' = H) was produced by dropping a dilute solution of BzPTU **29** into a large excess of $CuCl_2$. Although isolated as part of a Cu coordination complex (**Figure 8.3**), an uncoordinated sample of **48** did not appear to coordinate with $CuCl_2$ under the previously optimized conditions, and Li, *et al*, concluded that the coordination complex likely represented the final stage of a Cu-promoted oxidative cyclization. Under the different experimental conditions of their work, Sridevi, *et al*, theorized that S—N bond formation might proceed by nucleophilic attack of the heterocyclic nitrogen on the thiourea sulfur—which presumably had been rendered somewhat electron-deficient by coordination to PCl_5—but presented no evidence to support this idea.[199] Although reaction with Br_2 is the oldest

reported method of [1,2,4]thiadiazolo-[2,3-a]pyridine synthesis, to the best of our knowledge, the literature lacks even the most speculative or mechanistic reports on this topic. Suffice it to say, the mechanism of [1,2,4]thiadiazolo-[2,3-a]pyridine formation is not well-understood, and certainly merits further study.

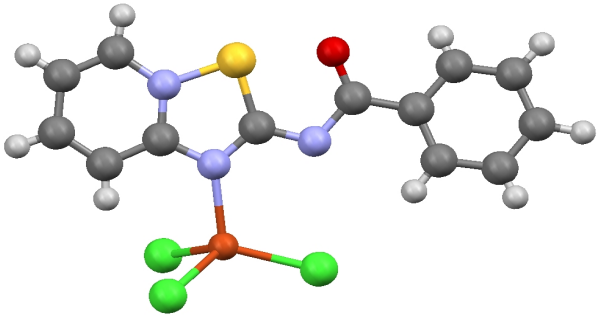


Figure 8.3. X-ray crystal structure of Cu-coordinated **48**.[17]

All studies of the oxidative cyclization of BzPTUs report that at least one equivalent—and usually a large excess—of the reaction-promoting reagent (*e.g.* $CuCl_2$, Br_2, etc.) is required for the transformation. Li, *et al*, reported that, in the absence of a large excess of $CuCl_2$, coordination of BzPTU **29** to the metal center occurred without any evidence of oxidative cyclization, and we have yet to find any reports of this transformation occurring by a catalytic process. [116] We were therefore surprised to isolate five 1-benzoylimido-[1,2,4]dithiazolo-[2,3-a]pyridines (**49-53**) from crystallization vials originally containing their parent BzPTUs—all of which had been set up under normal crystallization conditions, and in the absence of any cyclization-promoting reagent. Close analysis of experimental conditions and molecular structure allow us to conjecture that

the formation of thiadiazoles **49-53** proceeds via the self-catalyzed, heterolytic oxidation of their parent BzPTUs, with a mechanistic pathway similar to that shown for the methoxide-catalyzed process in **Scheme 8.2**.

Additionally, four of these dithiazoles were obtained as single crystals, which are, to the best of our knowledge, the first non-coordinated 1-benzoylimido-[1,2,4]thiadiazolo -[2,3-a]pyridines studied by X-ray diffraction. These polyheterocyclic structures provide a fascinating study of 3-center-4-electron bond formation across three different heteroatoms, and represent some of the scarce known examples of polarized (weak) hypervalent[202] O—S—N bonding.

Results and Discussion

The thiourea precursors (**20**, **40**, **42**, and **44**) for compounds **49-53** were synthesized as previously described; **54** was synthesized using the same methodology (see Experimental Section for details). No evidence of the cyclized product was observed in either the crude ^{1}H-NMR or IR spectra, which were both collected immediately following product isolation.

The conditions under which cyclization occurred varied from compound to compound. Decomposition of **42** and **54** occurred rapidly, most likely as a consequence of heating during the crystallization process, and thiadiazoles **49** and **51** precipitated--as single crystals--from their respective mother liquors in less than 24 hours. Conversely, we found that **20** and **40** were stable, under similar conditions, for well over a year. The thiadiazoles obtained from oxidative cyclization of these thioureas, **50** and **53**, were harvested from the mother liquor found in crystallization vials that had spent 16 and 22 months, respectively, on the shelf. **44** fell in between these two groups, in terms of stability, decomposing to thidiazole **52** in four months.

Solvent effects are unlikely to account for these different decomposition rates. As

shown in **Table 8.1**, most of thiadiazoles **49-53** formed in different solvent systems, and the only real consistency was that each sample was heated to boiling, then cooled to room temperature. Furthermore, extensive solvent studies were performed on **20**, and oxidative cyclization was not observed in any of the resultant samples, although some of them remained on the shelf for over six months. X-ray quality crystals of **20** were obtained from wet DMF—the same solvent system from which **49** precipitated in 24 hours—after approximately three months in a crystallization vial. Similarly, while acetonitrile apparently facilitated cyclization in **42**, it had no such effect in **20**; recrystallization proceeded normally with this latter sample, and we found no evidence of thiadiazole formation in either the precipitate or the mother liquor.

Table 8.1. Details of crystal growth and selected crystallographic data in thiadiazoles **49-53**. Single crystal data was not obtained for **53**; therefore, only crystal growth data is reported for this compound.

Compound		**49**	**50**	**51**	**52**	**53**
Thiourea precursor		**54**	**20**	**42**	**44**	**40**
R		H	6-CH_3	H	3-CH_3	H
R'		3,5-NO_2	4-OCH_3	4-CF_3	H	2-Br
Empirical formula		$C_{13}H_7N_5O_5S$	$C_{13}H_7N_5O_5S$	$C_{13}H_7N_5O_5S$	$C_{14}H_{11}N_3OS$	
Hammett σ value[174]		1.42[a]	-0.268	0.54	0.0	n/a
Solvent(s)		DMF/H_2O	acetone/ hexanes	MeCN	acetone/ hexanes	ethanol/ hexanes
Time[b]		24 h	16 m[c]	24 h	4 m[c]	22 m[c]
Crystal system		orthorhombic	Orthorhombic	triclinic	monoclinic	---
Space group		Pbca	Pbca	P-1	$P2_1/n$	---
Unit cell dimensions	**a (Å)**	12.998(3)	7.1771(11)	7.1910(10)	7.1743(7)	---
	b (Å)	9.6376(19)	14.384(2)	7.5060(10)	17.6933(17)	---
	c (Å)	22.538(4)	26.594(4)	13.2866(18)	9.6301(9)	---
	α (deg.)	90	90	98.390(2)	90	---
	β (deg.)	90	90	97.769(2)	96.128(2)	---
	γ (deg.)	90	90	113.467(2)	90	---
Cell volume (Å^3)		2823.3(10)	2745.4(7)	635.86(15)	1215.4(2)	---
Z		8	8	2	4	---
Density (calc., g/cm^3)		1.625	1.448	1.689	1.472	---
# of independent reflections		3092	2990	2762	2646	---
R (%)		4.24	3.09	5.69	3.09	---

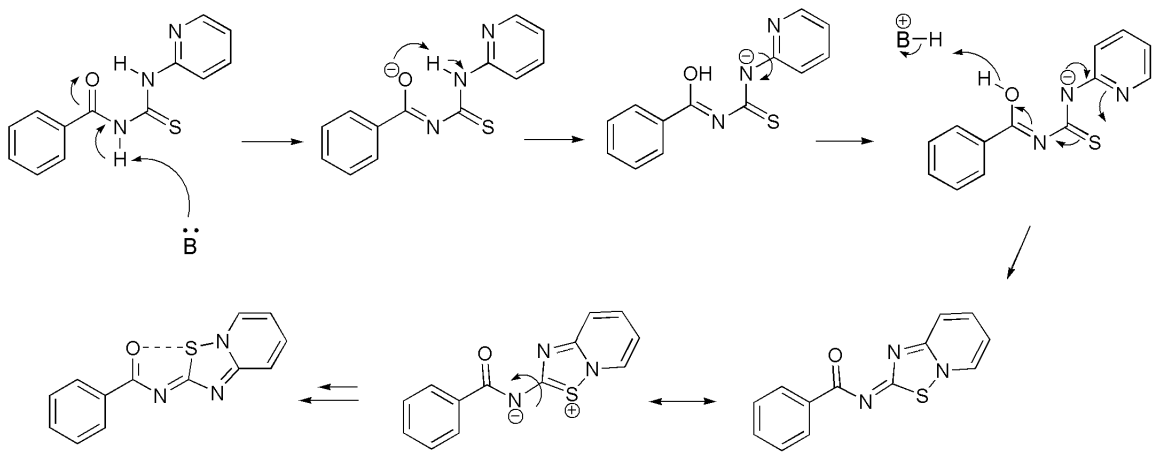
[a]Calculated as the sum of both *m*-NO_2 substituents, each with a σ value of 0.710.

[b]All time designations are approximate, defined as the amount of time that elapsed between the initial crystallization attempt and the realization that decomposition had occurred—and which may, in the case of slowly-decomposing BzPTUs, comprise a significant amount of error.

[c]Months

While we initially hypothesized that oxidative cyclization may have proceeded via a radical pathway, presumably initiated by the oxygen present under ambient conditions, we currently believe it more likely that both hydrogens cleave in a self-catalyzed, heterolytic process, for which a possible mechanism is shown in **Scheme 8.3**. This process is similar to that shown in **Scheme 8.2**; however, the absence of a nucleophile—and the inherent acid/base functionalities of BzPTUs—led us to conclude that oxidative cyclization was more likely to occur in a base-catalyzed process. The parent BzPTUs of thiadiazoles **49-53** possess both a strongly acidic, N-acyl thioureido proton and a non-nucleophilic, moderately basic pyridyl nitrogen. While precise pK_a values for **49-53** have not been determined, the pK_a of an N-benzoyl-N'-aryl thiourea was found to be 13.06 ± 0.04 in a buffered methanolic solution.[198] It is therefore likely that the pK_a of the N-acyl thioureido proton in BzPTUs—especially those with electronegative substituents—is reasonably accessible to even the thioureido-substituted nitrogen, which should have slightly lower proton affinity than unsubstituted pyridine, due to the presence of the electron-withdrawing substituent.[203]

The relative rates of decomposition observed—qualitatively—in BzPTUs **20**, **40**, **42**, **44**, and **55** also support the heterolytic, base-catalyzed mechanistic process schown in **Scheme 8.3**. BzPTUs **42** and **54**, which underwent cyclization—or at least partial cyclization—literally overnight, both have strongly electron-withdrawing phenyl substituents. Conversely, BzPTU 20, with its electron-releasing p-OCH3 phenyl substituent, was stable to many solvent conditions and cyclized only after 16 months in a crystallization vial. While we isolated thiadiazole **53** 22 months after obtaining single crystals of **40** from the same vial, it is entirely possible that cyclization occurred well before that, as the vial had been undisturbed—at the back of a shelf—for over a year



Scheme 8.3. Proposed mechanistic pathway for the self-catalyzed decomposition / oxidative cyclization of BzPTUs **20**, **40**, **42**, **44**, and **54**. The base represented as "B:" is most likely the pyridyl nitrogen of a second BzPTU molecule.

before the tiny brown needles of **53** were first observed. As it has been established that the pK_a values of substituted benzamides correlate linearly with Hammett σ constants,[204] these roughly-established reaction rates appear to support a heterolytic, base-catalyzed cyclization process. Loss of molecular hydrogen in the final step of the cyclization process is supported by the evolution of gas observed upon heating **20** past its melting point, which results in partial conversion to **50**, as determined by ^{1}H-NMR spectroscopy.

All of the thiadiazoles for which we obtained single crystal X-ray data (**49-52**)

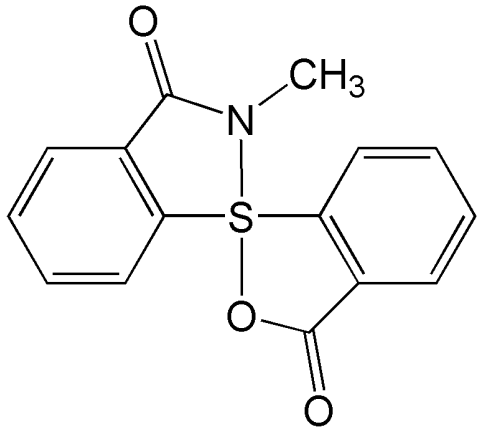


Figure 8.4. Hypervalent O—S—N bond in a spiro-λ^4-sulfane.

featured a 3-center-4-electron bond, formed between the nearly colinear O, S, and N atoms. This type of interaction has previously been described as the sum total of a covalent S—N bond and a highly polarized, hypervalent[202] O—S bond, and the bond lengths that we observed in **49-52** (**Table 8.2**) fit well with this description. The N—S bonds ranged in length from 1.755 Å (**49**) to 1.785 Å (**50**), which is slightly longer than the sum of covalent radii (1.74 Å).[205] These bond lengths were within the range of lengths reported for N—S bonds in spiro-λ^4-sulfanes (1.724 Å[206] to 1.804 Å,[202] **Figure 8.4**), the class of compounds in which this type of N—S—O interaction has been most thoroughly examined; however, they are considerably shorter than the bond lengths (1.889 Å to 1.962 Å) observed in the analogous N—S(R_2)—N hypervalent interaction.[202,207,208] Conversely, the O—S bond lengths observed in **49-52** (2.077 Å to 2.215 Å) are considerably longer than in the symmetrical O—S(R_2)—O interaction (1.84 Å)[202]—although both hypervalent interactions are significantly longer than the sum of the S, O covalent radii, 1.66 Å.[205] Taken together, this variation in the S—O and S—N bonds, relative to the lengths observed in symmetrical, otherwise isostructural compounds, appears consistent with the polarized, hypervalent bond type proposed for this interaction.

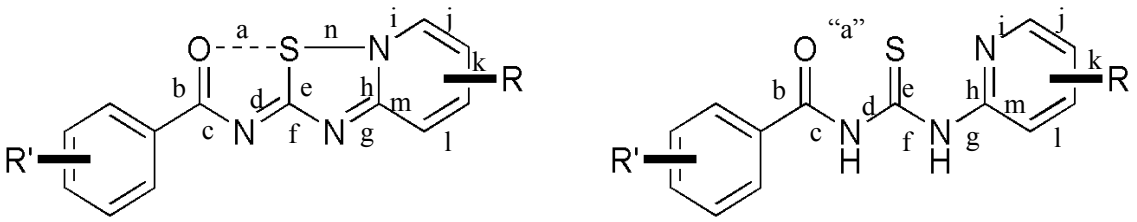


Figure 8.5. Labled bonds in thiadiazoles **49-53** and BzPTUs **16-46**

Table 8.2. Selected bond lengths and angles in **49-52** and BzPTUs **16-46** (italicized). Bonds are identified in **Figure 8.5**. All values are in Å, unless otherwise noted.

Compound	**49**	**50**	**20**	**51**	**52**	**44**	**16-46** (avg.)
a	2.215	2.142	*2.918*	2.077	2.098	---	---
b	1.258	1.268	*1.207*	1.276	1.274	*1.229*	*1.219*
c	1.340	1.346	*1.404*	1.333	1.341	*1.372*	*1.382*
d	1.340	1.334	*1.365*	1.347	1.342	*1.391*	*1.390*
e	1.770	1.774	*1.674*	1.773	1.772	*1.663*	*1.662*
f	1.319	1.322	*1.363*	1.285	1.323	*1.335*	*1.347*
g	1.357	1.351	*1.408*	1.376	1.358	*1.438*	*1.415*
h	1.359	1.362	*1.337*	1.359	1.361	*1.325*	*1.335*
i	1.365	1.373	*1.350*	1.369	1.363	*1.344*	*1.342*
j	1.357	1.372	*1.391*	1.358	1.358	*1.373*	*1.382*
k	1.402	1.402	*1.384*	1.393	1.405	*1.365*	*1.380*
l	1.366	1.369	*1.376*	1.377	1.375	*1.397*	*1.383*
m	1.407	1.408	*1.396*	1.399	1.415	*1.390*	*1.389*
n	1.755	1.785	---	1.770	1.770	---	---
Torsion O=C--C=S (deg.)	2.20	0.89	*1.25*	0.27	0.41	*179.33*	*1.27*[a]*; 172.8*[b]
Torsion O=C--Ph (deg.)	7.86	9.92	*12.59*	4.11	3.62	*36.09*	*12.33*[a]*; 24.24*[b]
∠ N--S--O (deg.)	165.37	165.95	---	166.96	166.85	---	---

[a]Conformer **N**
[b]Conformer **O**

The aromatic character of polyheterocyclic thiadiazoles **49-52** is illustrated both by the planarity observed in the newly formed, 5-membered rings (**Figure 8.6**) and in the delocalization of π-electrons inferred from bond lengths—especially when considered in relation to the corresponding bonds in the parent thioureas. The three amide / thioamide C=N bonds (**c**, **d**, and **f** in **Figure 8.5**) are significantly shorter in **49**-**52** than in BzPTUs **16-46**, decreasing from 1.382 Å, 1.390 Å, and 1.347 Å, respectively, in **16**-**46**, to 1.340 Å, 1.341 Å, and 1.312 Å, also respectively, in the cyclized decomposition products. In **51**, bond **f** very nearly approaches the sum of covalent radii in a formal C=N bond, 1.27 Å,[205] although its length in **49**, **50**, and **52** (~1.32 Å) more closely approximates that of an aromatic C=N bond (1.34 Å in pyridines[209]), which is also observed in bonds **c** and **d**.

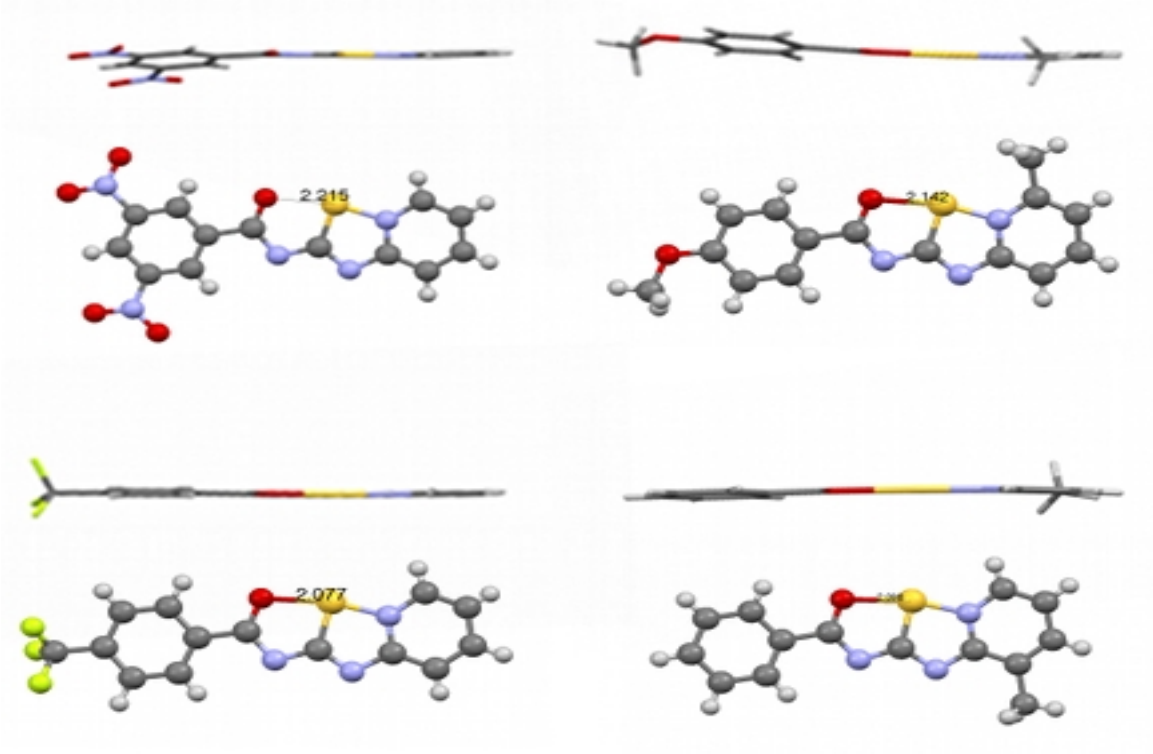


Figure 8.6. Single-molecule structures of (clockwise from upper left) **49**, **50**, **52**, **51**. Planarity of thiadiazole moiety is shown in the side view.

Changes in bond length, presumably related to enhanced electron delocalization, are also evident in both the carbonyl and thiocarbonyl moieties. In BzPTUs **16**-**46**, the average length of the C=S bond is 1.662 Å, which, although demonstrative of the conjugative effects expected from the two C—N bonds in thioureas, is nevertheless comparable to the sum of covalent radii, 1.61 Å.[205] In **49**-**52**, however, the length of bond **e** increases to 1.772 Å, approximating the sum of covalent radii in a C—S [single] bond, 1.76 Å.[205] The C=O bond exhibits similar—albeit less drastic—elongation in the BzPTU decomposition products, increasing from an average of 1.219 Å (1.208 Å in the somewhat more isoelectronic conformer **N** BzPTUs) in **16**-**46** to 1.269 Å in **49**-**53**. For comparison, the sum of covalent radii in C, O single and double bonds have been calculated as 1.33 Å and 1.24 Å, respectively—although it has been noted that polar covalent bonds tend to be shorter than the sum of calculated radii, and crystallographic data from related compounds—such as BzPTUs **16**-**46**—tend to be a more useful means of comparison.[210]

Also reflecting the altered aromatization in the polyheterocyclic decomposition products **49**-**52**, bond **g** and pyridyl bonds **h**-**m** display significant changes in length, relative to their BzPTU precursors. Bond **g**, which at an average of 1.415 Å shows only minor conjugative effects in BzPTUs **16**-**46**, shortens to an average of 1.361 Å in **49-52**. reflecting the aromaticity of the 5-membered dithiazole moiety. While longer than the aforementioned C=N bonds **c**, **d**, and **f**, bond **g** is nevertheless within range of C=N bonds reported in 5-membered nitrogen heterocycles, such as pyrrole or imidazole (~1.37 Å), or indole (~1.36 Å).[209] This elongation may also reflect structural effects relating to the the longer C—S and S—N bonds. Pyridyl bonds **h** and **i** are similar in average length (1.360 Å and 1.368 Å, respectively) to bond **g** in **49**-**52**, although this change represents an elongation—rather than a truncation—from the corresponding bonds in BzPTUs **16**-**46** (1.335 Å and 1.342 Å, respectively). Interestingly, bonds **j**-**m** display a pattern of

alternating lengths in **49**-**52**, corresponding to what may be a significant contribution of traditional diene character, rather than complete aromaticity. At an average of 1.361 Å and 1.372 Å, respectively, bonds **j** and **l** are far closer in length to the sum of covalent radii in C=C bonds (1.34 Å) than in Csp^2—Csp^2 bonds (1.46 Å); while the average lengths of bonds **k** (1.401 Å) and **m** (1.407 Å) clearly indicate at least some degree of conjugation, the difference is nevertheless noticeable. For comparison, the average lengths of bonds **j**-**m** in BzPTUs differ by a maximum 0.009 Å, ranging from 1.380 Å to 1.389 Å—although, as in **49**-**52**, more variation can be found in each individual compound, often relating to substituent effects.

Crystal packing in **49**-**52** is both diverse and reasonably straightforward. All of these thiadiazoles lack hydrogen bond donors, and, as might be expected, aromatic π-stacking appears to be the foremost crystal packing force—at least in **50**-**52**. While there is a π-π interaction (**Figure 8.7a**) between neighboring thiadiazole moieties in **49**, contributing to its sandwich herringbone structure type (**Figure 8.7b**),[37] its nitro substituents also form infinite chains of N...O contacts (**Figure 8.7c**), with one donor group and one acceptor group on each phenyl ring. This type of dipolar, intermolecular interaction has been observed in mononitroarenes,[211] although, by necessity, the donor O and acceptor N are part of the same nitro group, leading to a C(2) chain, instead of the C(6) chain present in **49**. In our structure, $d_{O...N}$ is 2.770 Å, far less than the sum of van der Waals radii (3.07 Å), and appears to be an interaction between the O lone pair and the partially empty p-orbital on the N: the angle between the donor O and the N—C(Ar) (angle O2-N5-C12) bond is 90.03°.

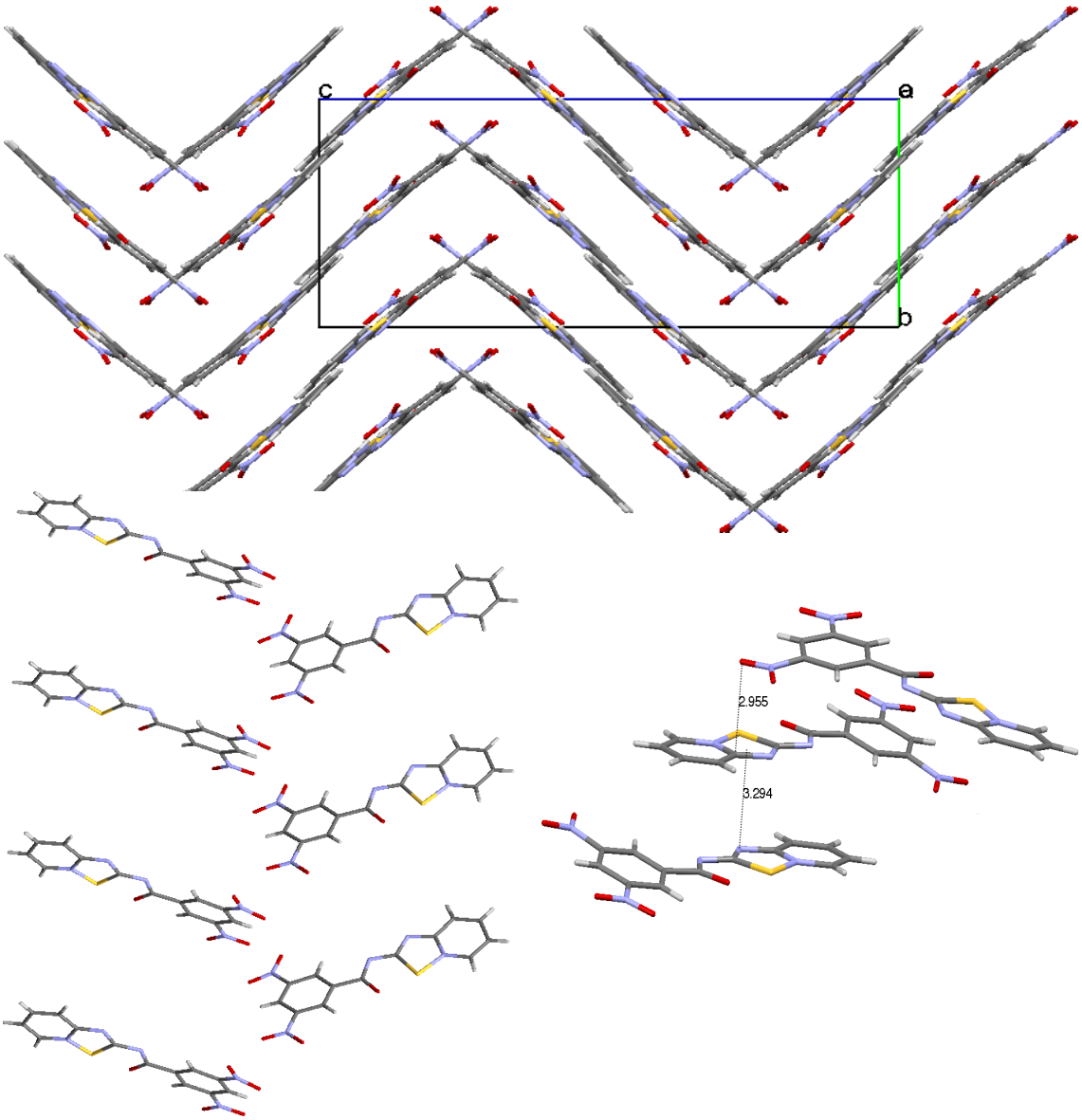


Figure 8.7. Crystal packing interactions in **49**. Clockwise from top: (a) sandwich herringbone structure type (more closely resembles herringbone, but π-π interaction technically classifies it as "sandwich"); (b) π-π interaction between thiadiazole rings (3.924 Å) and π...O(N) contact (2.955 Å); (c) Chain formed by N...O dipolar contact (d*O...N* = 2.770 Å; ∠ *O-N-C(Ar) = 90.03˚)*

Thiadiazoles **50**-**52**, which lack functional groups with strong donor-acceptor capabilities, display crystal packing patterns typical[37] for aromatic systems. Shown as (a) in **Figures 8.8** and **8.9**, alternately-oriented monomers form the backbone of **50**'s γ structure type, where π-π stacking (d = ~3.5 Å) occurs between pyridine rings, and a weak, dimer-like (OCH_2)H...π interaction (2.635 Å) links the π-stacks together. Similar packing behavior is observed in **51** (**Figure 8.8b**), which also crystallizes in the γ structure type. In **51**, however, the alternately-oriented monomers stack more completely on top of each other, leading to phenyl-pyridyl interactions (~3.6 Å) and what appears to be π-π stacking between the planar, hypervalently fused "[1,2,4]-oxathiazole" rings (3.5 Å - 3.6 Å), lending credence to the proposed aromatic character of this 5-membered heterocycle (**Figure 8.9b**). A π-π interaction is also observed between the "oxathiazole" rings in **52** (**Figure 8.9c**). In this compound, two "sandwiched" monomers engage in π-stacking very similar to that observed in **51** ($d_{Ph...Pyr}$ = 3.461 Å); a second π-π interaction between pyridine rings on neighboring "sandwiches" (3.350 Å) leads to a brick-type‡ packing pattern for this compound. Weak H_{Pyr}····· Ph interactions hold the brick-type π-stacks nearly perpendicular to each other (78.10˚), resulting in the basketweave crystal packing structure* assigned to **52**.

‡ **Chapter VI**.

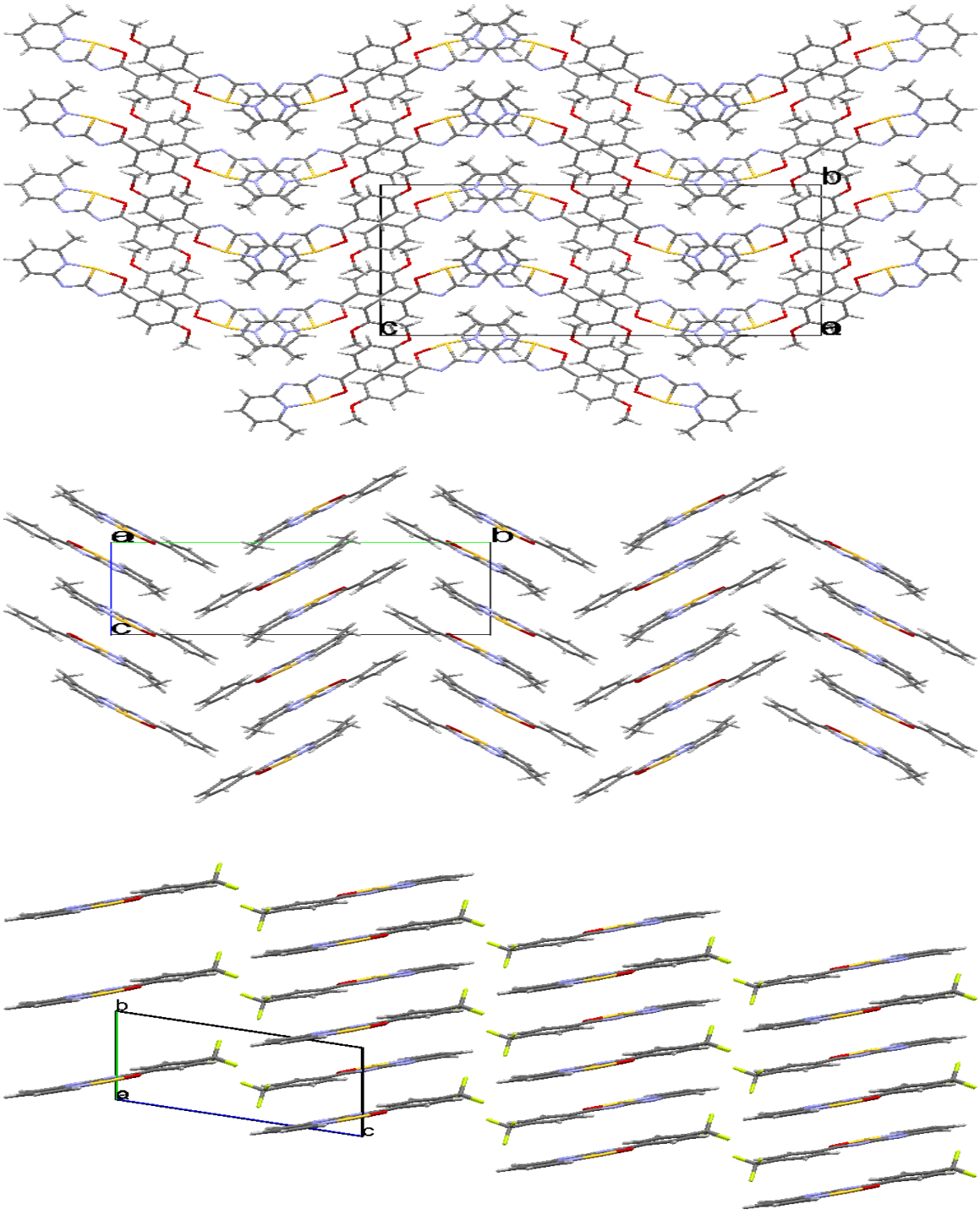


Figure 8.8. Crystal packing interactions in **50**-**52**. All views are along the *a*-axis. From top to bottom: (a) Top-down view of γ-type π-stacking in **50** (dashed line indicates row of stacks); (b) Side-on view of γ-type π-stacking in **51**; (c) basketweave-type crystal packing in **52**.

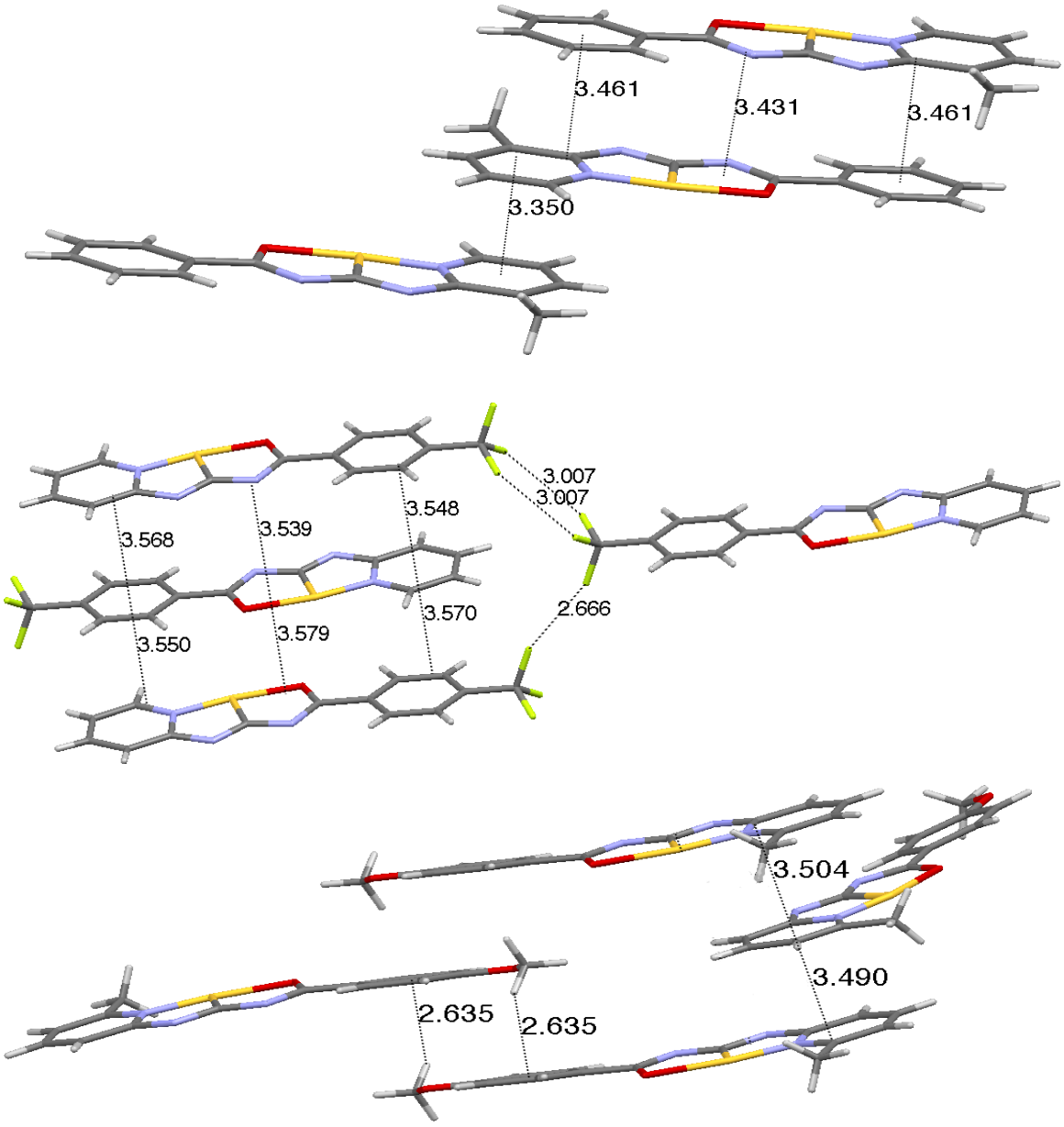


Figure 8.9. Major intermolecular interactions in **50**-**52**. Top to bottom: (a) in **50,** π-π interaction between pyridine rings in (3.504, 3.490 Å) and weak (OCH_2)H...π contact between methoxyphenyl groups (2.635 Å); (b) in **51**, π-π interaction between proposed oxathiazole rings (3.539, 3.579 Å), and also between alternating phenyl and pyridyl rings (3.568, 3.550 Å). An F...F contact (2.666 Å) provides link between γ-stacks; the other F...F interactions (3.007 Å) are outside the sum of van der Waals radii. (c) In **52**, pyridyl-pyridyl interactions (3.350 Å) form the link between alternately-oriented monomers, "sandwiched" together by phenyl-pyridyl interactions (3.461 Å, 2 contacts per "sandwich"), and additional π-stacking between oxathiazoles (3.431 Å).

Conclusion

Although remarkably stable under both ambient and aqueous conditions, BzPTUs will, under certain circumstances, undergo oxidative cyclization, most likely via a self-catalyzed, heterolytic process. The resultant 1-benzoylimido-[1,2,4]thiadiazolo-[2,3-a]pyridine also features a close S—O contact; the very short interatomic distance ($\geq$ 2.2 Å), coupled with the planarity of the interacting groups, electron delocalization inferred from bond lengths in the crystal structures, and apparent π-π interactions in the crystal lattice, may indicate that the five-membered ring formed from this interaction should best be treated as a formally fused [1,2,4]oxathiazole, rather than a weak, intramolecular, van der Waals interaction.

APPENDIX A

EXPERIMENTAL RESULTS

Chapter II

Tris[(N-ethylthioureido)ethyl]amine (1)

2 mL tris(2-aminoethyl)amine (13 mmol) were dissolved in 20 mL THF. Dry nitrogen was bubbled into the flask for 10 minutes, with stirring, and the flask was cooled to 0℃ in an ice-water bath. 3.4 mL (3.4 g, 39 mmol) ethyl isothiocyanate were added by syringe, and the reaction was allowed to return to room temperature, then stirred for two days (40 h). The reaction mixture was then filtered through a 5 cm x 7 cm column of silica gel (100-200 mesh) and washed with 2 x 10 mL EtOH. The solvent was removed on the rotovap, yielding a brittle, orange-yellow solid, which weighed 3.45 g (65%). **IR** (KBr, cm^{-1}) 3237, 3065, 3008, 2968, 2822, **1562**, 1383, 1337, 1299, 1214, 1150, 1090, 1004, 678, 642; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 6.68 (bs, 6H), 3.70 (d, *J* = 4 Hz, 6H), 3.51 (bs, 6H), 2.66 (t, *J* = 5 Hz, 6H), 1.21 (t, *J* = 4 Hz, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) ∂ 181.6, 53.3, 42.8, 39.5, 14.6; **MP** 120-121˚C.

Tris[(N-*n*-propylthioureido)ethyl]amine (2)

2 mL (1.97 g, 19.5 mmol) *n*-propylisothiocyanate were added to 1 mL tris(2-aminoethyl) amine (6.5 mmol) in 10 mL dry THF, at 0℃. The reaction was stirred for 6 hours, the solvent was removed on the rotatory evaporator, and the semisolid reside was recrystallized from ethanol/hexanes (1:4). **^{1}H NMR** (600 MHz, $CDCl_3$) ∂ 6.85 (bs, 3H), 6.71 (bs, 3H), 3.69 (bs, 6H), 3.44 (bs, 6H), 2.65 (t, *J* = 5 Hz, 6H), 1.61 (m, 6H), 0.95 (t, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) ∂ 181.8, 53.3, 46.5, 42.8, 22.6, 11.5; **MP** 111.5-113˚C.

133**Tris[(N-isopropylthioureido)ethyl]amine (3)**

1 mL tris(2-aminoethyl)amine was added, dropwise, to 2.1 mL isopropylisothiocyanate (1.97 g, 19.5 mmol) in 15 mL THF, at 0℃. The reaction was stirred overnight (16 h) and the solvent was then removed on the rotovap. The residue was dissolved in hot ethanol, and hexanes were added until the solution became cloudy. Cubic crystals weighing 1.81 g (61%) were recovered from the flask. **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 6.68 (bs, 6H), 3.44 (bs, 6H), 2.65 (t, 6H), 1.60 (m, 6H), 0.95 (t, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$) ∂ 181.8, 53.3, 46.5, 42.8, 22.6, 11.5; **MP** 151.5-153˚C.

Tris[(N-*tert*-butylthioureido)ethyl]amine (4) 1 mL tris(2-aminoethylamine) was added dropwise to 2.5 mL (2.25 g, 19.5 mmol) in 15 mL dry THF, at 0℃. Heat evolved, and the solution foamed slightly. The reaction was stirred for 16 h, and the solvent was removed on the rotovap. A fluffy, slightly sticky, colorless solid remained on the walls of the flask; this was recrystallized from hot acetone/hexanes, yielding 2.72 g of a white, crystalline solid (85%). Crystals suitable for X-ray analysis were grown from acetonitrile/hexanes, with a quantity of xylenes sufficient to induce mixing between the two layers. **IR** (KBr, cm^{-1}) 3331, 3229, 3068, 3029, 2959, 2804, **1531**, 1354, 1281, 1202, 1055, 690, 671; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 6.41 (bs, 3H), 6.33 (bs, 3H), 3.64 (q, J = 5.5 Hz, 6H), 2.69 (t, J = 5.5 Hz, 6H), 1.46 (s, 27H). **^{13}C NMR** (151 MHz, $CDCl_3$) ∂ 181.0, 53.6, 53.3, 43.1, 29.5; **MP** 160-164˚C (dec.)

Tris[(N-phenylthioureido)ethyl]amine (5)

0.5 mL (0.48 g, 3.3 mmol) tris(2-aminoethyl)amine was dissolved in 20 mL THF, and 1.2 mL (1.35 g, 10 mmol) phenylisothiocyanate was added drop-wise. The reaction mixture was stirred for 4 h, then refluxed gently overnight, and the solvent was removed on the rotatory evaporator. The residue was recrystallized from acetone/hexanes and washed with toluene, yielding 1.64 g (90%) of a colorless, crystalline solid. Colorless needles suitable for X-ray analysis were grown from a dilute solution of isopropanol/hexanes. **IR** (KBr, cm^{-1}) 3358, 3239, 3100, 2922, 2813, 1558, 1508, 1492, 1347, 1313, 1252, 1155,

1093, 758, 696; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.37 (s, 3H), 7.25 (d, 6H), 7.18 (d, 6H), 7.13 (t, 3H), 6.81 (s, 3H), 3.71 (bq, 6H), 2.67 (t, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) ∂ 180.7, 137.1, 129.7, 126.5, 124.8, 53.1, 43.1; **MP** 143-144˚C.

Chapter III

General procedure for the preparation of thioureas 6-13.

In a cool water bath, the appropriate isothiocyanate (2 eq.) was added to N,N'-bis(3-aminopropyl)piperazine (1 eq.), N,N-bis(3-aminopropyl)-N-methylamine (1 eq.), or N-(3-aminopropyl)morpholine (2 eq.), in dry THF (1.5-2 mL / mmol), and stirred overnight (16-20 hours). The solvent was removed, and the white, powdery solid was shown, by ^{1}H NMR, to contain neither starting material nor side product, and was used directly for crystallization.

N,N'-bis[3-(N-propylthioureido)propyl]piperazine (6)

Thiourea **6** was prepared as described above, using n-propyl isothiocyanate and N, N'-bis(3-aminopropyl)pipearzine (100%). Colorless prisms, suitable for X-ray spectroscopy, were grown from ethanol/water, and crystallized in the monoclinic P-1 space group. At a later time, colorless needles precipitated from DMSO- d 6, and were determined to have the same unit cell. An analytical sample was prepared by triturating a small amount of the compound with methylene chloride, in which it has only limited solubility, filtering the precipitated solid, and further drying the thiourea on a vacuum line, for approximately 96 hours, in order to remove the last traces of solvent. **IR** ν_{max} (KBr/cm^{-1}) 1558.10 (C=S); **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 7.18 (bs, 2H, NH), 3.52 (bs, 4H), 3.35 (bs, 4H), 2.50 (m, 12H), 1.76 (m, 4H), 1.65 (m, 4H), 0.98 (t, 6H); **^{13}C NMR** (DMSO-d_6, 75 MHz) ∂ 181.6 (C=S), 55.4 (N-CH_2), 52.8 (N-CH_2), 45.2 (N-CH_2), 42.1 (N-CH_2), 25.9 (CH_2), 22.0 (CH_2), 11.4 (CH_3); **MP** 176-178˚C.

N,N'-bis[3-(N-pentylthioureido)propyl]piperazine (7)

Thiourea **7** was prepared as described above, using n-pentyl isothiocyanate and N, N'-bis(3-aminopropyl)pipearzine (100%). Fine, colorless prisms, suitable for X-ray spectroscopy, were grown from ethanol/hexanes, and crystallized in the monoclinic P-1 space group. An analytical sample was prepared by triturating a small amount of the compound with methylene chloride, in which it has only limited solubility, filtering the

precipitated solid, and further drying the thiourea on a vacuum line, for approximately 96 hours, in order to remove the last traces of solvent. **IR** (cm^{-1}) **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 7.24 (bs, 2H, NH), 6.59 (bs, 2H, NH), 3.46 (bs, 4H), 3.34 (bs, 4H), 2.43 (bt, 11H), 1.71 (m, 4H), 1.57 (m, 4H), 1.30 (m, 9H), 0.86 (t, 6H); **^{13}C-NMR** (DMSO-d_6, 75 MHz) ∂ 181.6 (C=S), 55.4 (N-CH_2), 52.8 (N-CH_2), 43.5 (N-CH_2), 41.9 (N-CH_2), 28.6 (CH_2), 28.5 (CH_2), 25.9 (CH_2), 21.9 (CH_2), 13.9 (CH_3); **EA** Calc. C, 57.60; H, 10.11; N, 18.32; S, 13.98; Found C, 58.35; H, 9.89; N, 17.92; **MP** 127.5-129˚C.

N,N'-bis[3-(N-isopropylthioureido)propyl]piperazine (8)

Thiourea **8** was prepared as described above, using isopropyl isothiocyanate and N, N'-bis(3-aminopropyl)pipearzine (100%). Colorless needles, suitable for X-ray spectroscopy, were grown from ethanol/hexanes, and crystallized in the P2 1/n space group. An analytical sample was prepared by triturating a small amount of the compound with methylene chloride, in which it has only limited solubility, filtering the precipitated solid, and further drying the thiourea on a vacuum line, for approximately 96 hours, in order to remove the last traces of solvent. **IR ν_{max}** (KBr/cm^{-1}) 3223.7 (NH); **^{1}H NMR** (DMSO-d_6, 300 MHz) ∂ 7.38 (bs, 2H, NH), 7.29 (d, 2H, NH), 4.35 (bs, 2H), 3.47 (bs, 4H), 2.46 (m, 12H), 1.75 (m, 4H), 1.24 (d, 12H); **^{13}C NMR** (DMSO-d_6, 75 MHz) ∂ 180.8 (C=S), 55.4 (N-CH_2), 52.7 (N-CH_2), 44.8 (N-CH_2), 41.8 (N-CH_2), 25.9 (CH), 22.3 (CH3); **EA** Calc. C, 53.69; H, 9.51; N, 20.87; S, 15.93; Found: C, 53.79; H, 9.19; N, 20.68; **MP** 151-153˚C.

N,N'-bis[3-(N-tert-butylthioureido)propyl]piperazine (9) Thiourea **9** was prepared as described above, using *tert*-butyl isothiocyanate and N, N'- bis(3-aminopropyl)pipearzine (100%). Fine, colorless plates, suitable for X-ray spectroscopy, were grown from acetonitrile/water, and crystallized in the monoclinic P-1 space group. An analytical sample was prepared by triturating a small amount of the compound with methylene chloride, in which it has only limited solubility, filtering the precipitated solid, and further drying the thiourea on a vacuum line, for approximately 96 hours, in order to remove the last traces of solvent. **IR ν_{max}** (KBr/cm^{-1}) 1525.85 (C=S); **^{1}H NMR** (DMSO-d_6, 300 MHz)

∂ 6.65 (bs, 2H, NH), 5.92 (bs, 2H, NH), 3.64 (bq, 4H), 2.51 (m, 12H), 1.81 (m, 4H), 1.45 (s, 18H); **^{13}C NMR** (DMSO-d_6, 75 MHz) ∂ 181.2 (C=S), 55.5 (N-CH_2), 52.8 (N-CH_2), 52.0 (N-CH_2), 41.4 (N-CH_2), 27.0 (C), 26.0 (CH3); **EA** Calc. C, 55.77; H, 9.83; N, 19.51; S, 14.89; Found C, 55.78; H, 9.58; N, 19.32; S, 14.47; **MP** 169-170˚C (boils).

N,N'-bis[3-(N-benzylthioureido)propyl]piperazine (10)

Thiourea **10** was prepared as described above, using benzyl isothiocyanate and N, N'-bis(3-aminopropyl)pipearzine (100%). Fine, colorless plates, suitable for X-ray spectroscopy, were grown from ethanol/water, and crystallized in the monoclinic P-1 space group. An analytical sample was prepared by triturating a small amount of the compound with methylene chloride, in which it has only limited solubility, filtering the precipitated solid, and further drying the thiourea on a vacuum line, for approximately 96 hours, in order to remove the last traces of solvent. **IR ν_{max}** (KBr/cm^{-1}) 3237.51 (NH); **^{1}H NMR** (DMSO-d_6, 300 MHz) ∂ 7.85 (bs, 2H, NH), 7.48 (bs, 2H, NH), 7.29 (m, 10H), 4.65 (bs, 4H), 3.35 (bs, 4H), 2.25 (m, 12H), 1.61 (m, 4H); **^{13}C NMR** (DMSO-d_6, 75 MHz) ∂ 183.0 (C=S), 140.2 (C), 128.9 (CH), 127.9 (CH), 127.5 (CH), 55.9 (N-CH_2), 53.4 (N-CH_2), 47.7 (N-CH_2), 42.6 (N-CH_2), 26.7 (CH_2); **EA** Calc. C, 62.61; H, 7.68; N, 16.85; S, 12.86; Found C, 62.77; H, 7.65; N, 16.82; **MP** 147-148˚C.

N,N'-bis[3-(N-phenylthioureido)propyl]piperazine (11)

Thiourea **11** was prepared as described above, using phenyl isothiocyanate and N, N'-bis(3-aminopropyl)pipearzine. Due to its poor solubility in most organic solvents, its purity was assured by trituration with boiling DMSO; a white, crystalline solid was collected by vacuum filtration, after cooling to room temperature (65%). Colorless needles, suitable for X-ray spectroscopy, were grown from DMSO/ethyl acetate, and crystallized, as a 1:1 DMSO solvate, in the $P2_1/c$ space group. An analytical sample was prepared by triturating a small amount of the compound with methylene chloride, in which it has only limited solubility, filtering the precipitated solid, and further drying the thiourea on a vacuum line, for approximately 96 hours, in order to remove the last traces of solvent. **IR ν_{max}** (KBr/cm^{-1}) 1523.33 (C=S); **^{1}H NMR** (DMSO-d_6, 300 MHz) ∂ 9.43

(bs, 2H, NH), 7.71 (bs, 2H, NH), 7.30 (m, 8H), 7.06 (t, 2H), 3.44 (bs, 4H), 2.22 (bt, 12H), 1.62 (m, 4H); **^{13}C NMR** (DMSO-d_6, 75 MHz) ∂ 180.1 (C=S), 128.7 (CH), 124.1 (CH), 123.0 (CH), 55.6 (N-CH_2), 52.6 (N-CH_2), 42.8 (N-CH_2), 25.5 (CH_2); **MP** (DMSO solvate) 197-198˚C.

N-[3-(N-phenylthioureido)propyl]morpholine (12)

Thiourea **12** was prepared as described above, using phenyl isothiocyanate and N-(3-aminopropyl)morpholine (100%). Colorless crystals, suitable for X-ray analysis, were grown from acetonitrile/water, and crystallized in the $P2_1/n$ space group. An analytical sample was prepared by crystallization from hot THF, which yielded colorless, octahedral crystals, with an average diameter of 2.5-5 mm, which were washed with acetone and air-dried; a single crystal was submitted for elemental analysis. These crystals were also examined by X-ray spectroscopy, and were found to have the same unit cell as those grown from acetonitrile/water. **IR ν_{max}** (KBr/cm^{-1}) 1529.45 (C=S); **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 7.62 (bs, 1H, NH), 7.44 (t, 2H, CH), 7.30 (t, 1H, CH), 7.23 (d, 2H, CH), 3.81 (bs, 2H), 3.24 (bs, 4H), 2.39 (m, 2H), 2.27 (bs, 4H), 1.75 (m, 2H) **^{13}C NMR** ($CDCl_3$, 300 MHz) ∂ 180.7 (C=S), 137.5 (CH), 130.6 (CH), 127.3 (CH), 125.3 (CH), 66.8 (O-CH_2), 59.8 (N-CH_2), 54.2 (N-CH_2), 46.6 (N-CH_2), 24.9 (CH_2). **EA** Calc. C, 60.18; H, 7.58; N, 15.04; O, 5.73; S, 11.48; Found: C, 60.35; H, 7.46; N, 15.02; S, 11.28; **MP** 126-127˚C.

N,N'-bis[3-(N-phenylthioureido)propyl]-N"-methylamine (13)

Thiourea **13** was prepared as described above, using phenyl isothiocyanate and N, N'-bis(3-aminopropyl)methylamine (100%). Colorless, cubic crystals, suitable for X-ray spectroscopy, were grown from dichloroethane/hexanes, and crystallized in the monoclinic $P2_1/c$ space group. An analytical sample was prepared by recrystallization from acetone; the powdery white solid was washed with acetone over an aspirator, and allowed to air dry overnight. **IR ν_{max}** (KBr/cm^{-1}) 1533.85 (C=S); **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 8.10 (bs, 2H, NH), 7.38 (t, 4H), 7.21 (m, 8H), 3.55 (q, 4H), 2.18 (t, 4H), 1.44 (m, 4H); **^{13}C NMR** ($CDCl_3$, 300 MHz) ∂ 180.2 (C=S), 136.7 (CH), 130.0 (CH), 126.9 (CH), 125.4 (CH), 56.3 (N-CH_2), 45.5 (N-CH_2), 41.9 (N-CH_3), 25.4 (CH_2)**. EA** Calc. 60.69; H,

7.03; N, 16.85; S, 15.43; Found: C, 60.56; H, 6.84; N, 16.67; S, 15.15; **MP** 138-140˚C.

Chapter IV

N-(3-isothiocyanatopropyl)morpholine (14a)

[Not isolated] Isothiocyanate **14a** was prepared in accordance with a modified literature procedure.[213] A stirred solution of 1 mL N-(3-aminopropyl)morpholine (7.1 mmol) and 1.7 g 50% (w/w) NaOH (21.3 mmol) in 10 mL THF was cooled in an ice-water bath, and 1.3 mL carbon disulfide (21.3 mmol) were added drop-wise. A white precipitate formed almost immediately, and a yellow liquid was evident at the bottom of the flask. To facilitate stirring, 10 mL water were added; the mixture turned bright orange, and was stirred for 1 hour, until the starting material had disappeared completely (determined by TLC: silica/acetone/I_2 vapor development). Additional ice was added to the cooling bath, and 1.7 mL "30%" H_2O_2 (21.3 mmol) was added slowly, with care taken to ensure that the temperature of the reaction did not exceed 40℃. [It is important to add the H_2O_2 in small portions, and wait for a few minutes between additons, as temperature spikes generally do not occur immediately upon addition.] Upon the addition of H_2O_2, the color of the reaction mixture faded to a cloudy yellow. The reaction was stirred for 0.5 h, and additional H_2O_2 (0.4-1.0 mL) was added, as necessary, until the reaction reached completion. 10 mL water were added, and the reaction mixture was quickly extracted with 4 x 15 mL Et_2O and dried over Na_2SO_4. The crude yield of **14a** ranged from 65-85%. **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 3.64 (t, J = 4.8 Hz, 4H); 3.56 (t, J = 6.3 Hz, 2H); 2.39 (m, 6H); 1.80 (m, J = 6.3 Hz, 2H); **R_f** 0.55 (acetone/silica).

N-[3-(N'-2-pyridylthioureido)propyl]morpholine (14)

1.1 g (12 mmol) 2-aminopyridine were added to 0.561 g CaH_2 (13 mmol) in 10 mL dry THF (4 Å molecular sieves), under an Ar balloon. The mixture was stirred until bubbling ceased; 2.26 g **14a** (12 mmol) were added, and the reaction was stirred under Ar, overnight and at room temperature. The reaction mixture was filtered over a vacuum, and the solvent was removed on the rotatory evaporator. The residue was then recrystallized from iPrOH, yielding 0.93 g (28%) of an iridescent, colorless, flaky solid. Single crystals suitable for X-ray analysis were grown from layered methanol/hexanes. **^{1}H NMR** (500

MHz, $CDCl_3$) ∂ 11.76 (bt, 1H); 9.09 (bs, 1H); 8.16 (d, *J* = 5 Hz, 1H); 7.65 (m, 1H), 6.96 (dd, 1H, *J* = 5Hz, 7.5Hz); 6.88 (d, *J* = 8.5H, 1H); 3.83 (q, *J* = 6.9Hz, 2H); 3.73 (t, *J* = 4.8Hz, 4H); 2.49 (m, 6H); 1.93 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) ∂ 181.4, 149.0, 137.0, 123.8, 121.8, 66.7, 66.6, 53.6, 53.5, 36.7, 24.6; **MP** 126-127˚C.

N,N'-bis[3-(N"-benzoylthioureido)propyl]piperazine (15)

To a stirred solution of 1.35 mL N,N'-bis(3-aminopropyl)piperazine (6.55 mmol) in 20 mL THF were added 2.17 g benzoyl isothiocyanate, which had been prepared in accordance with a literature procedure.[150] The reaction mixture was stirred overnight, and the solvent was removed on the rotatory evaporator. The crude orange solid weighed 3.8 g, and consisted of approximately a 1:1 mixture of the desired thiourea and what was believed to be a bis(benzamide) side product. The thiourea was liberated as a pale brown, crystalline solid via recrystallization with DMSO/H_2O (1.24 g, 36%), and single crystals suitable for X-ray (and other spectral) analysis were obtained from DMSO/MeOH. **IR** (KBr, cm^{-1}) 3228 (br), 2947, 2813, 1674, **1559**, 1528, 1174, 1141, 1073; **^{1}H NMR** (500 MHz, $CDCl_3$) ∂ 11.28 (bs, 2H); 10.99 (t, J=5.5, 2H); 7.98 (d, J=7.0Hz, 4H); 7.68 (t, J=7.0Hz, 7.5Hz, 2H); 7.58 (t, J=7.0Hz, 7.5 Hz, 4H); 3.71 (q, J=6.0Hz, 7.0Hz, 4H); 2.6-2.3 (m, J=6.0 Hz, 7.0Hz, 12H), 1.84 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) ∂ 181.4, 141, 149.0, 137.0, 123.8, 121.8, 66.7, 66.6, 53.6, 53.5, 36.7, 24.6; **MP** 126-127℃.

Chapter V

3-Nitrobenzoylisothiocyanate (16a)

[Not isolated] 0.972 g (10 mmol) KSCN were dissolved in 20 mL MeCN, at room temperature. 1.86 g 3-nitrobenzoyl chloride (14.9 mmol) were added; the reaction mixture instantly became cloudy. After five minutes of stirring, a yellow color appeared, along with copious quantities of white precipitate (KCl). The reaction was stirred for 2 hours, during which time the color deepened to a chalky, brownish-peach hue, then filtered through a Celite column (7 cm x 7 cm). The solvent was removed on the rotatory evaporator, yielding 2.0 g of a peach-colored solid, which was used without additional purification. **IR** (NaCl, cm^{-1}) 2943, 2839, **1977**, 1675, 1599, 1578, 1486, 1293, 1216, 860, 751; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.90 (t, J = 2.1 Hz, 1H), 8.53 (m, 1H), 8.41 (dt, J = 8.0, 1.0 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H).

1-(3-Nitrobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (16)

The crude isothiocyanate **16a** was added to a stirred solution of 2-amino-6-methylpyridine (1.08 g, 10 mmol) in 15 mL dry THF. The reaction was stirred overnight, at room temperature, and ~10 mL DI water were added, until permanent cloudiness was achieved. The reaction continued to stir for 1 hr, at which point the fluffy, pale yellow precipitate was filtered over a Buchner funnel, washed with water (2 x 10 mL), and allowed to air-dry (2.31 g, 73% yield from the acid chloride). In order to expedite drying, the product could be transferred to a watch glass, and placed on top of a hot oven (ambient temperature ~ 100˚C) with no apparent decrease in either yield or purity. As isolated, the product consisted primarily of **16O**, as determined by IR (KBr).

16O

Pale-yellow needles suitable for x-ray diffraction were grown from ethyl acetate/hexanes. This conformer could also be reproducibly prepared via trituration of the initial product with methanol, ethanol, isopropanol, acetone/water, chloroform, or acetic acid. Trituration with nitromethane, acetonitrile, acetone, or acetone/hexanes also affords **16O**,

but prolonged contact with these solvents leads to the precipitation of **16N** (1-7 days, depending on the solvent/solution concentration). **IR** (KBr, cm^{-1}): 3224 (N-H), 1672 (C=O), 1526 (C=S); **^{1}H NMR** ($CDCl_3$, 300 MHz): ∂ 12.79 (bs, 1H), 9.06 (bs, 1H), 8.78 (t, 1H, J=1.5 Hz), 8.58 (d, 1H, J=8.4 Hz), 8.52 (m, 1H), 8.26 (d, 1H, J=7.8 Hz), 7.80 (t, 1H, J=8.1 Hz), 7.69 (t, 1H, J=7.8 Hz), 7.06 (d, 1H, *J* = 7.2 Hz), 2.55 (s, 3H). **^{13}C NMR** ($CDCl_3$, 500 MHz): ∂ 176.2 (C=S), 164.3 (C=O),158.1 (C-NO_2), 150.4, 140.4, 138.2, 134.7, 133.4, 130.7, 128.2, 123.0, 121.6, 113.1, 24.3; **MP** (DSC) 155.6℃ (dec.).

16N

Bright-yellow crystals suitable for X-ray diffraction were grown from acetonitrile. (**16O** precipitates initially, but disappears as **16N** crystallizes from the resulting slurry.) Trituration of the initial product with nitromethane also provides this conformer. Dissolution of the initial product or of **16O** in acetone or acetone/hexanes yields variable amounts of **16N**; however, the conversion from **16O** is generally incomplete over the the observed period of time (1-30 days). **IR** (KBr, cm^{-1}): 3183 (N-H), 1716 (C=O), 1559 (C=S) cm-1; **^{1}H-NMR** ($CDCl_3$, 300 MHz): ∂ 15.45 (bs, 1H), 8.84 (s, 1H), 8.70 (bs, 1H), 8.53 (d, 1H), 8.45 (d, 1H, *J* = 7.8 Hz), 7.80 (t, 1H), 7.69 (t, 1H), 6.96 (d, 1H, *J* = 7.5 Hz), 6.80 (d, 1H, *J* = 8.7 Hz), 2.44 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz): ∂ 177.7 (C=S), 163.6 (C=O), 155.8 (C-NO_2), 151.6, 140.4, 136.4, 133.4, 130.2, 127.5, 122.6, 119.1, 110.0, 109.7, 23.8; **EA** Calc. C, 53.16; H, 3.82; N, 17.71; O, 15.17; S, 10.14; found C, 53.33; H, 3.60; N, 17.73; S, 9.97; **MP** (DSC) 160.7˚C (dec.)

Chapter VI

General Preparation of Isothiocyanates 17a-13a and 27a.

0.972 g (10 mmol) KSCN were dissolved in 20 mL MeCN. 10 mmol of the appropriate acid chloride were added to the stirred reaction mixture. The reaction mixture instantly grew cloudy, and within a few minutes, copious quantities of white solids were observed to have precipitated. The reaction was monitored by TLC (CH_2Cl_2/silica); the R_f value of the isothiocyanate product was invariably larger than that of the acid chloride. When TLC indicated that the reaction had gone to completion, ~10 mL Et_2O were added to the reaction mixture, precipitating most of the KCl which had remained in solution. The reaction mixture was then filtered through a 7 cm x 7 cm column of Celite. The filter cake was washed once with Et_2O, and the filtrate was liberated of solvent on the rotatory evaporator. The complete disappearance of acid chloride was confirmed by ^{1}H NMR, and the presence of isothiocyanate was confirmed by IR, wherein it displayed a characteristic broad absorption around 1970 cm^{-1}.

General Preparation of BzPTUs 17-46.

The crude isothiocyanate was dissolved in 15 mL THF, and 10 mmol of either 2-aminopyridine or 2-amino-6-picoline were added to the reaction flask. This mixture was stirred at room temperature for 1-16 hours, or overnight, until the isothiocyanate was completely consumed. Water was added until the solution clouded, and then 5 mL more were added to ensure complete precipitation of the product. The reaction was stirred for another hour, and then the precipitate was filtered over a vacuum, washed with 10 mL water, and air dried, yielding a white, yellow, or orange powder that was found, by ^{1}H NMR, to be free of both starting materials and organic side products. Occasionally, a small amount of KCl could be found in the final product; however, this was readily removed by either additional water washes or dissolving the product in chloroform, then filtering off the salt.

1-Benzoyl-3-(2-pyridyl)thiourea (17)

To a stirred solution of 2-aminopyridine (941 mg, 10 mmol) in 15 mL dry THF (4 Å molecular sieves) was added 1.63 g (10 mmol) benzoyl isothiocyanate, which had been prepared according to a literature procedure. The reaction was stirred overnight, at room temperature, and ~10 mL water were added, until permanent cloudiness was achieved. The reaction continued to stir for 1 hr, at which point the pale yellow, cotton candy-like precipitate was filtered over a Buchner funnel, washed with water (2 x 10 mL), and allowed to air-dry (2.64 g, 90%). In order to expedite drying, the product could be transferred to a watch glass, and placed on top of a hot oven (ambient temperature ~ 100˚C) with no apparent decrease in either yield or purity.

17N

Sulfur-yellow, cubic crystals suitable for X-ray analysis were grown from CHCl 3. High-quality crystals could also be reliably produced from acetonitrile, acetone, DCM, and even acetic acid. **IR** (KBr, cm^{-1}) 3200 (br), 3122 (br), 2985, 1714, 1612, 1558, 1528, 1446, 1337, **1247**, 1213, 1197, 1161, 798, 749, 701; **^{1}H NMR** (300 MHz, $CDCl_3$, -9℃) ∂ 15.30 (bs, 1H), 9.23 (bs, 1H), 8.08 (d, 2H), 7.89 (m, 1H), 7.65 (m, 2H), 7.53 (m, 1H), 7.53 (m, 1H), 6.92 (d, 1H), 6.74 (d, 1H), 2.47 (s, 3H); **^{13}C NMR** [not recorded, due to small population of **17N** in solution]; **MP** (DSC) 150.3℃ (dec).

17O

Slender, colorless prisms suitable for X-ray analysis were grown by slow evaporation of a THF solution. Upon prolonged heating above 80-90℃, these crystals lose water and convert into **17N**. **IR** (KBr, cm^{-1}) 3441 (br), 3126 (br), 3069, 1680, 1600, **1525**m 1452m 1320, 1256, 1172, 755, 714, 673; **^{1}H-NMR** ($CDCl_3$, 300 MHz): ∂ 13.00 (bs, 1H), 9.04 (bs, 1H), 8.61 (d, 1H), 7.92 (d, 2H), 7.69 (m, 2H), 7.56 (t, 2H), 7.04 (d, 1H), 2.54 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 125 MHz): ∂ 176.6, 166.1, 157.6, 150.2, 137.7, 133.5, 131.4, 129.0, 127.3, 120.9, 112.9, 23.8; **MP** (DSC) 116℃ [phase transition], 150.5℃ (dec).

4-nitrobenzoylisothiocyanate (18a)

[Not Isolated] To a well-stirred solution of 0.972 g (10 mmol) KSCN in 20 mL MeCN

were added 1.86 g (10 mmol) 4-nitrobenzoyl chloride; large quantities of KCl precipitated immediately. The reaction was monitored by TLC (20% EtOAc in hexanes), which indicated that the acid chloride had been completely consumed in 2 hrs. The orange reaction mixture was filtered through Celite (7 cm x 7 cm), and the filter cake was washed with Et_2O (2 x 10 mL). The solvents were then removed on the rotatory evaporator, yielding 2.0 g of a peach-colored solid, which was used without further purification. **IR** (NaCl, cm^{-1}) 3105, 1958, 1689, 1600, **1529**, 1346, 1244, 1103, 876, 839, 709; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.36 (dt, *J* = 9.3, 1.8 Hz, 2H), 8.26 (dt, *J* = 9.3, 1.8 Hz, 2H).

1-(4-nitrobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (18) To a well-stirred solution of 1.06 g (5.1 mmol) **18a** in 15 mL dry THF were added 0.55 g 6-methyl-2-picoline (5.1 mmol). The reaction was stirred overnight (16h), and ~2 mL water were added to the sulfur-yellow suspension, to ensure full precipitation of the product. The reaction mixture was filtered over a Buchner funnel, washed with water (2 x 10 mL), and dried on top of the oven (T ~ 100℃). 1.28 g of the yellow, powdery product were recovered, and a single crystal suitable for X-ray analysis was grown from methanol/acetone. 79% yield; **IR** (KBr, cm^{-1}) 3184 (br), 3109, 3017, 1715, 1612, 1560, **1520**, 1456, 1441, 1348, 1242, 1156, 867, 796, 712; **^{1}H-NMR** (300 MHz, $CDCl_3$) ∂ 12.77 (bs, 1H), 9.01 (bs, 1H), 8.60 (d, 1H, *J*=8.1 Hz), 8.43 (d, 2H, *J*=9 Hz), 8.12 (d, 2H, *J*=9.3 Hz), 7.70 (t, 1H, *J*=7.5 Hz, 8 Hz), 7.08 (d, 1H, *J*=7.5 Hz); **^{13}C-NMR** (151 MHz, DMSO- d6) ∂ 177.3, 165.7, 154.2, 149.8, 146.9, 144.1, 136.4, 130.6, 123.6, 111.6, 109.9, 23.5; **EA** Calc. C, 53.16; H, 3.82; N, 17.71; Found C, 52.89; H, 3.64; N, 17.49; **MP** 185-186℃.

2-methoxybenzoylisothiocyanate (19a)

[Not Isolated] 1.44 g (14.9 mmol) KSCN were dissolved in 20 mL MeCN, at room temperature. 2.0 mL 2-methoxybenzoyl chloride (14.9 mmol) were added via syringe; the reaction mixture instantly became cloudy. After five minutes of stirring, a yellow color appeared, along with copious quantities of white precipitate (KCl). The reaction was stirred overnight (16h), during which time the color deepened to a chalky orange hue,

then filtered through a Celite column (7cm x 7cm). The solvent was removed on the rotatory evaporator, yielding 2.98 g of a red-orange oil, which contained visible KCl particles. After a second filtration, through a 20 μm membrane, 2.60 g of the oil were collected, and used without additional purification. **IR** (NaCl, cm^{-1}) 2943, 2839, **1977**, 1675 (d), 1599, 1578, 1486, 1293, 1216, 860, 751; **^{1}H-NMR** (300 MHz, $CDCl_3$) ∂ 7.74 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.06 (td, *J* = 8.7, 1.8 Hz, 1H), 6.62 (td, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 8.7 Hz, 1H), 3.26 (s, 3H).

1-(2-methoxybenzoyl)-3-(6-methyl-2-pyridyl)thiourea (19)

To a stirred solution of 2-aminopicoline (564 mg, 5.2 mmol) in 15 mL dry THF (4 Å molecular sieves) was added 1.00 g (5.2 mmol) **19a**. The reaction was stirred overnight, at room temperature, and ~10 mL water were added, until permanent cloudiness was achieved. The reaction continued to stir for 1 hr, at which point the colorless, crystalline precipitate was filtered over a Buchner funnel, washed with water (2 x 5 mL), and allowed to air-dry (1.35 g, 86%, 2 steps). Slender prisms suitable for analysis were grown from ethanol/toluene. **IR** (KBr, cm^{-1}) 3289, 1660, 1595. 1535, 1483, **1456**, 1335, 1185, 1084, 1015, 763; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 13.19 (bs, 1H), 11.11 (bs, 1H), 8.66 (d, 1H), 8.22 (dd, 1H), 7.64 (t, 1H), 7.57 (dt, 1H), 7.13 (t, 1H), 7.04 (d, 1H), 7.00 (d, 1H), 4.00 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) ∂ 177.3, 164.5, 158.0, 157.8, 150.9, 137.9, 135.5, 132.9, 122.0, 120.9, 118.9, 113.1, 111.9, 56.6, 24.3; **MP** 186-188℃.

4-methoxybenzoylisothiocyanate (20a)

[Not Isolated] To a stirred solution of 0.97 g KSCN (10 mmol) in 20 mL MeCN were added 1.72 g *p*-methoxybenzoyl chloride (10 mmol). Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred at room temperature for four hours, and monitored by TLC (R_f = 0.73 / CH_2Cl_2). The reaction mixture was then filtered through a Celite plug (*d* = 7 cm; *h* = 7cm), and the solvent was removed on the rotovap. The resultant yellow solid weighed 1.858 g (crude yield = 96%), and was used without further purification. **IR** (NaCl, cm^{-1}) 1977, 1685, 1603, 1508, **1249**, 1163, 1081, 1025, 862, 843, 786, 750; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.02 (d, *J* = 9 Hz, 2H), 6.96 (d, *J* = 9

Hz, 2H), 3.90 (s, 3H); **R_f** 0.73 (CH_2Cl_2/silica).

1-(4-methoxybenzoyl)-3-(6-methyl-2-pyridyl)thiourea (20)

To a stirred solution of **20a** (0.89 g, 4.6 mmol) in 15 mL THF were added 0.43 g (4.6 mmol) 2-amino-6-methylpyridine; the reaction was stirred for 16 hours (i.e. overnight) at room temperature, and ca. 8 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the sulfur-yellow solids were filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 0.89 g (65%, 2 steps). As prepared, the product was suitable for spectral analysis; sulfur-yellow hexagonal crystals suitable for X-ray diffraction were grown from DMF. **IR** (KBr, cm^{-1}) 3178, 3016, 1707, 1610, 1532, 1509, 1446, 1343, **1235**, 1182, 1077, 1024, 789; **^{1}H NMR** ($CDCl_3$, 300 MHz) # 13.08 (bs, 1H), 8.96 (bs, 1H), 8.60 (d, 1H), 8.89 (dt, 2H), 7.67 (t, 1H), 7.02 (m, 3H), 3.91 (s, 3H), 2.51 (s, 3H); **^{13}C NMR** ($CDCl_3$, 300 MHz) ∂ 177.2 (C=S), 165.9 (C=O),164.2 (C-OCH 3), 158.0, 150.7, 138.0, 129.9, 123.7, 121.1, 114.6, 113.2, 55.8, 24.3; **EA** Calc. C, 59.78; H, 5.02; N, 13.94; Found C, 59.55; H, 4.99; N, 13.95; **MP** 171-173˚C.

3-chlorobenzoylisothiocyanate (21a)

[Not Isolated] To a stirred solution of 0.97 g KSCN (10 mmol) in 20 mL MeCN were added 1.3 mL 3-chlorobenzoyl chloride (1.78 g, 10 mmol). Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred at room temperature for four hours, and monitored by TLC (R_f = 0.84 / CH_2Cl_2). When the reaction was complete, 10 mL Et_2O were added, and the reaction mixture was then filtered through a Celite plug (*d* = 7 cm; *h* = 7cm), washed with 10 mL Et_2O, and stripped of solvent on the rotovap. The resultant brown liquid weighed 2.1 g, and was used without further purification. **IR** (NaCl, cm^{-1}) **1959** (br), 1702, 1593, 1574, 1473, 1425, 1279, 1241, 1117. 1071, 885, 765, 723, 646; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.05 (t, J=1.8Hz, 1H); 7.96 (d, J=8Hz, 1H); 7.64 (m, 1H); 7.46 (t, 8Hz, 1H).

1-(3-chlorobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (21) To a stirred solution of crude

21a in 15 mL THF were added 1.08 g (10 mmol) 2-amino- 6-methylpyridine; the reaction was stirred for 16 hours (i.e. overnight) at room temperature, and ca. 10 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the fluffy white solids were filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 2.35 g (77%, 2 steps). As prepared, the product was suitable for spectral analysis; colorless, cubic crystals were grown from methanol. **IR** (KBr, cm^{-1}) 3229 (br), 3050, 1678, 1558, **1528**, 1458, 1341, 1250, 1151, 785, 733; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.85 (bs, 1H); 8.98 (bs, 1H), 8.58 (d, 1H), 7.91 (t, 1H, J=1.8Hz), 7.78 (d, 1H), 7.66 (m, 2H), 7.49 (t, 1H), 7.04 (d, 1H), 2.54 (s, 3H); **^{13}C NMR** ($CDCl_3$, 300 MHz) ∂ 176.6, 165.1, 158.0, 150.5, 138.1, 135.8, 133.9, 133.7, 130.7, 128.1, 125.6, 121.4, 113.3, 24.3; **MP** 161-162˚C.

4-chlorobenzoylisothiocyanate (22a)

[Not Isolated] To a stirred solution of 0.97 g KSCN (10 mmol) in 20 mL MeCN were added 1.75 g (10 mmol) 4-chlorobenzoyl chloride. Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred at room temperature for four hours, and monitored by TLC. When the reaction was complete, 10 mL Et_2O were added, and the reaction mixture was then filtered through a Celite plug (*d* = 7 cm; *h* = 7cm), washed with 10 mL Et_2O, and stripped of solvent on the rotovap. The resultant yellow oil was used without further purification. **IR** (NaCl, cm^{-1}) 3090, 1989 (br), **1684**, 1593, 1485, 1401, 1255, 1902, 864, 840, 738, 667; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.01 (d, *J*=8.4Hz, 2H), 7.49 (d, *J*=8.4Hz, 2H).

1-(4-chlorobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (22)

To a stirred solution of crude **22a** in 15 mL THF were added 1.08 g (10 mmol) 2-amino-6-methylpyridine; the reaction was stirred for 16 hours (i.e. overnight) at room temperature, and ca. 10 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the chalky yellow solid was filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 2.991 g (98%, 2 steps). As prepared, the product was suitable for spectral

analysis; yellow prisms were grown from the slow evaporation of an acetone solution . **IR** (KBr, cm^{-1}) 3189, 3019, 1716, 1611, 1562, 1533, 1443, 1334, **1244**, 1156, 1093, 792, 749; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.94 (bs, 1H); 9.00 (bs, 1H), 8.60 (d, 1H), 7.88 (d, 2H), 7.69 (t, 1H), 7.56 (d, 2H), 7.06 (d, 1H), 2.55 (s, 3H); **^{13}C NMR** ($CDCl_3$, 300 MHz) ∂ 176.6, 165.3, 157.9, 150.4, 140.3, 137.9, 130.1, 129.6, 129.0, 121.2, 113.1, 24.1; **EA** Calc. C, 54.99; H, 3.96; N, 13.74; Found, C, 54.85; H, 4.02; N, 13.69; **MP** 166-167˚C.

3-cyanobenzoylisothiocyanate (23a)

[Not Isolated] 1.98 g (12 mmol) 3-cyanobenzoyl chloride were prepared from 3-cyanobenzoic acid, using a literature procedure.[214] This amount of the acid chloride was added to a stirred solution of 1.17 g KSCN (12 mmol) in 20 mL MeCN. Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred at room temperature for 2 hours, and monitored by TLC (R_f= 0.71, CH_2Cl_2/silica). When the reaction was complete, 10 mL Et_2O were added, and the reaction mixture was then filtered through a silica plug (*d* = 7 cm; *h* = 7cm), washed with 10 mL Et_2O, and stripped of solvent on the rotovap. The resultant yellow solid weighed 2.258 g (97%), and was used without further purification. **IR** (NaCl, cm^{-1}) 3071, 2230, 1973 (br), **1685**, 1431, 1166, 909, 727; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.34 (s, 1H); 8.29 (d, 7.8 Hz, 1H), 7.93 (d, *J*=7.8 Hz, 1H), 7.66 (t, *J*=7.8Hz, 1H).

1-(3-cyanobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (23)

To a stirred solution of crude **23a** in 15 mL THF were added 1.3 g (12 mmol) 2-amino-6-methylpyridine; the reaction was stirred for 16 hours (i.e. overnight) at room temperature, and ca. 10 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the pale yellow solid was filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 2.25 g (76%, 3 steps). As prepared, the product was suitable for spectral analysis . **IR** (KBr, cm-1) 3254 (br), 2923, 2234, 1676, 1601, **1529**, 1456, 1343, 1262, 1143, 790, 740, 679 (NaCl); **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.76 (bs, 1H), 9.01 (bs, 1H), 8.57 (d, 1H), 8.24 (s, 1H), 8.12 (d, 1H), 7.94 (d, 1H), 7.70 (m, 2H), 7.06 (d, 1H), 2.54 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75

MHz) ∂ 176.1, 164.2, 158.0, 150.2, 148.5, 138.0, 133.5, 133.2, 130.6, 128.0, 122.8, 121.4, 113.1, 24.1; **MP** 147-148 C.

4-cyanobenzoylisothiocyanate (24a)

[Not Isolated] 0.825 g (5 mmol) 3-cyanobenzoyl chloride were prepared from 3-cyanobenzoic acid, using a literature procedure.[214] This amount of the acid chloride was added to a stirred solution of 486 mg KSCN (5 mmol) in 10 mL MeCN. Upon addition, the reaction mixture turned cloudy organge. The reaction was stirred at room temperature for 2 hours, and monitored by TLC (R_f = 0.73, CH_2Cl_2/silica). When the reaction was complete, 10 mL Et2O were added, and the reaction mixture was then filtered through a silica plug (*d* = 7 cm; *h* = 7cm), washed with 10 mL Et_2O, and stripped of solvent on the rotovap. The resultant solid was pale yellow and crystalline, and was used without further purification. **IR** (NaCl, cm^{-1}) 2231, 1967, **1918**, 1695, 1261, 1177, 1095, 860, 750, 674; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.24 (d, *J*=8.4Hz, 2H), 7.84 (d, *J*=8.4Hz, 2H).

1-(4-cyanobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (24)

To a stirred solution of crude **24a** in 10 mL MeCN were added 0.54 g (5 mmol) 2-amino-6-methylpyridine. The deep pink solution turned orange upon addition of the amine; after stirring overnight, the solution was clear and pale yellow. Water was added (10 mL) and the reaction mixture was stirred for an additional hour, at which point 1.04 g of a pale yellow solid (70%, 3 steps) were removed via vacuum filtration. Single crystals suitable for X-ray analysis were grown from acetonitrile. **IR** (KBr, cm^{-1}) 3189 (br), 3040, 2227, 1720, 1677, 1602, 1565, **1533**, 1459, 1350, 1263, 1177, 1152, 854, 793, 749, 532; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.75 (bs, 1H), 9.03 (bs, 1H), 8.58 (d, 1H), 8.41 (d, 2H), 8.11 (d, 2H), 7.69 (t, 1H), 7.07 (d, 1H), 2.55 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.3, 164.8, 150.4, 150.0, 138.2, 135.8, 133.2, 128.4, 121.6, 117.4, 113.2, 24.3; **MP** 172-173℃.

3,4-dichlorobenzoylisothiocyanate (25a)

[Not Isolated] 1.98 g (12 mmol) 3,4-dichlorobenzoyl chloride were prepared from 3-cyanobenzoic acid, using known literature procudures.[214] This amount of the acid chloride

was added to a stirred solution of 1.17 g KSCN (12 mmol) in 20 mL MeCN. Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred at room temperature for 2 hours, and monitored by TLC (R_f = 0.71, CH_2Cl_2/silica). When the reaction was complete, 10 mL Et_2O were added, and the reaction mixture was then filtered through a silica plug (*d* = 7 cm; *h* = 7cm), washed with 10 mL Et_2O, and stripped of solvent on the rotovap. The resultant yellow solid weighed 2.258 g (97%), and was used without further purification. **IR** (NaCl, cm^{-1}) 1949 (br), 1696, 1585, 1546, 1382, 1268, 1227, **1095**, 1032, 893; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 8.34 (s, 1H); 8.29 (d, 7.8 Hz, 1H), 7.93 (d, *J*=7.8 Hz, 1H), 7.66 (t, *J*=7.8Hz, 1H).

1-(3,4-dichlorobenzoy)-3-(6-methyl-2-pyridyl)thiourea (25)

To a stirred solution of 2.32 g (10 mmol) **25a** in 15 mL THF were added 1.08 g (10 mmol) 2-amino-6-methylpyridine; the reaction was stirred for 16 hours (i.e. overnight) at room temperature, and ca. 10 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the white solid was filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 2.7 g (79%, 2 steps). As prepared, the product was suitable for spectral analysis; long, colorless prisms were grown from acetic acid . **IR** (KBr, cm^{-1}) 3163, 2986, 1681, 1542, **1518**, 1437, 1340, 1299, 1284, 1162, 1172, 755, 745; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.80 (bs, 1H), 8.92 (bs, 1H), 8.57 (d, 1H, *J*=8.1Hz), 8.02 (d, 1H, *J*=2.1Hz), 7.68 (m, 3H), 7.05 (d, 1H, *J*=7.5Hz), 2.54 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.3, 164.1, 158.0, 150.3, 138.6, 138.0, 134.1, 131.5, 131.3, 129.8, 126.4, 121.3, 113.1, 24.1; **MP** 167-168℃.

3,5-dichlorobenzoylisothiocyanate (26a)

2.09 g (10 mmol) 3,5-dichlorobenzoyl chloride were added to a stirred solution of 0.97 g KSCN (10 mmol) in 20 mL MeCN. Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred overnight (16 h). The chunky orange suspension was diluted with 10 mL MeCN and filtered through a column of silica gel (200 mesh; *d* = 7 cm; *h* = 1 cm), washed with 5 mL acetone, and stripped of solvent on the rotovap. The resultant orange solid weighed 2.046 g, and was used without further

purification. **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 7.93 (d, *J*=1.8, 2H); 7.64 (t, *J*=1.8, 1H); **R_f** 0.84 (CH_2Cl_2/silica).

1-(3,5-dichlorobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (24)

To a stirred solution of crude **10a** (ca. 10 mmol) in 15 mL THF were added 1.08 g (10 mmol) 2-amino-6-methylpyridine; the reaction was stirred for 16 hours (i.e. overnight) at room temperature, and ca. 15 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the bright yellow solid was filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 2.116 g (62%, 2 steps). As prepared, the product was suitable for spectral analysis; small yellow prisms were grown from dichloroethane . **IR** (KBr, cm^{-1}) 3274, 2917, 1700, 1610, 1558, 1533, 1457, 1340, **1260**, 1237, 1158, 797, 752; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.73 (bs, 1H), 8.94 (bs, 1H), 8.56 (d, 1H), 7.77 (d, 1H), 7.68 (m, 3H), 7.06 (d, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) ∂ 176.3, 163.9, 158.2, 150.4, 138.2, 136.5, 133.7, 126.8, 126.2, 121.5, 113.3, 24.3; **MP** 174-176˚C (dec.)

4-bromobenzoylisothiocyanate (27a)

4.132 g (20 mmol) 4-bromobenzoyl chloride were added to a stirred solution of 1.944 g KSCN (20 mmol) in 30 mL MeCN. Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred overnight (16 h), then filtered through a column of silica gel (100-200 mesh; *d* = 7 cm; *h* = 7 cm), washed with 5 mL Et_2O, and stripped of solvent on the rotovap. The pale brown oil weighed 4.01 g, and was used without further purification. **IR** (NaCl, cm^{-1}) 2045, 1983, **1685**, 1588, 1397, 1254, 1067, 837, 734, 666; **^{1}H-NMR** (300 MHz, $CDCl_3$) ∂ 7.93 (dt, 2H), 6.66 (dt, 2H). **R_f** = 0.78 (CH_2Cl_2/silica).

1-(4-bromobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (27)

To a stirred solution of 2.0 g **27a** (8.6 mmol) in 15 mL THF were added 0.93 g (8.6 mmol) 2-amino-6-methylpyridine; the reaction was stirred for 72 hours (*i.e.* over the weekend) at room temperature. 25 mL water were added to precipitate the product, and

the reaction was stirred for an additional hour, then filtered over a Buchner funnel, washed with water (2 x 15 mL) and ethanol (2 x 5 mL), and air-dried to constant weight, 2.005 g (57%, 2 steps). As prepared, the lemon-yellow product was suitable for spectral analysis; yellow cubic crystals were grown from acetonitrile . **IR** (KBr, cm^{-1}) 3189 (br), 3123, 3083, 3019, 1718, 1611, **1560**, 1534, 1443, 1334, 1246, 1201, 1156, 1069, 1011, 898, 791, 744, 524; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.93 (bs, 1H), 9.04 (bs, 1H), 8.54 (d, 1H), 7.77 (d, 2H), 7.65 (m, 3H), 7.03 (d, 1H), 2.51 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) ∂ 176.5, 165.4, 157.9, 150.4, 137.9, 132.6, 130.6, 129.1, 129.0, 121.2, 113.1, 24.1; **MP** 166-168˚C (dec.)

2-bromobenzoylisothiocyanate (28a)

2.2 g (1.3 mL, 10 mmol) 2-bromobenzoyl chloride were added to a stirred solution of 0.972 g KSCN (10 mmol) in 20 mL MeCN. Upon addition, copious quantities of white precipitate formed (KCl); the reaction was stirred overnight (16 h), then filtered through a column of Celite (*d* = 7 cm; *h* = 7 cm), washed with 5 mL Et_2O, and stripped of solvent on the rotovap. The pale yellow oil weighed 2.25 g, and was used without further purification. **IR** (NaCl, cm^{-1}) **1959**, 1703, 1585, 1565, 1466, 1433, 1273, 1228, 1132, 1092, 1031, 858, 733; **^{1}H NMR** (300 MHz, $CDCl_3$) ∂ 7.95 (m, 1H), 7.72 (m, 1H), 7.42 (m, 2H). $\mathbf{R_f}$ = 0.65 (CH_2Cl_2/silica).

1-(2-bromobenzoyl)-3-(6-methyl-2-pyridyl)thiourea (28)

To a stirred solution of 1.0 g (4.1 mmol) **28a** in 15 mL THF were added 0.379 g (4.1 mmol) 2-amino-6-methylpyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature. The solvent was removed on the rotovap, and the residual solids were recrystallized from isopropanol, yielding 1.0 g (70%) of pale yellow needles. **IR** (KBr, cm^{-1}) 3155 (br), 1667, 1600, **1526**, 1455, 1347, 1168, 1147, 1087, 743; **^{1}H-NMR** ($CDCl_3$, 300 MHz) ∂ 12.69 (bs, 1H), 9.43 (bs, 1H), 8.54 (d, 1H), 7.63 (m, 3H), 7.40 (m, 2H), 7.01 (d, 1H), 2.50 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) ∂ 176.6, 167.1, 158.0, 150.6, 138.2, 135.1, 134.2, 133.3, 130.2, 128.2, 121.4, 113.5, 24.4; **MP** 146-148˚C.

1-(3-nitrobenzoyl)-3-(2-pyridyl)thiourea (30)

2.937 g crude **16a** were added to a stirred solution of 2-aminopyridine (0.941 g, 10 mmol) in 15 mL dry THF. The reaction was stirred overnight, at room temperature, and then ca. 10 mL water were added, until permanent cloudiness was achieved. The reaction continued to stir for 1 hr, at which point the pumpkin-orange precipitate (R_f = 0.41; CH_2Cl_2/silica) was filtered over a Buchner funnel, washed with water (2 x 10 mL), and allowed to air-dry (2.42 g, 81% yield from the acid chloride). After drying, the color of the precipitate was deep ochre-yellow.

30O

Pale yellow needles suitable for X-ray analysis were grown from methanol. **IR** (KBr, cm^{-1}) 3473 (br), 3224, 3093, 1672, 1602, 1558, **1526**, 1457, 1349, 1252, 1150, 1111, 790, 713; **^{1}H NMR** (600 MHz, $CDCl_3$) ∂ 12.84 (bs, 1H), 9.10 (bs, 1H), 8.81 (d, 1H), 8.77 (s, 1H), 8.51 (d, 1H), 8.48 (d, 1H), 8.26 (d, 1H), 7.79 (m, 2H), 7.20 (t, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) ∂ 176.3, 164.1, 151.0, 148.7, 137.9, 133.5, 133.2, 130.6, 128.1, 122.7, 121.8, 116.1, 110.0; **MP** (DSC) 175.8˚C.

30N

Deep yellow crystalline solids could be reproducibly prepared from a variety of solvents, including MeCN, NO2Me, and acetone. **IR** (KBr, cm^{-1}) 3318, 3060, 1701, 1603, 1559 **1525**, 1479, 1426, 1347, 1322, 1266, 1247, 1153, 784, 713; **^{1}H NMR** (300 MHz, $CDCl_3$ / 0.05 M DMSO-d_6) ∂ 15.69 (s, 1H), 11.05 (s, 1H), 8.81 (s, 1H), 8.26 (m, 3H), 7.59 (m, 2H), 7.13 (d, 1H), 6.98 (m, 1H); **MP** (DSC) 173.0˚C.

1-(4-nitrobenzoyl)-3-(2-pyridyl)thiourea (31)

2.0 g crude **18a** was added to a stirred solution of 2-aminopyridine (0.941 g, 10 mmol) in 15 mL dry THF. The reaction was stirred for 1.5 h, at room temperature, and ~5 mL water were added, until permanent cloudiness was achieved. The reaction continued to stir for 1 hr, at which point the pumpkin-orange precipitate was filtered over a Buchner funnel, washed with water (2 x 10 mL), and allowed to air-dry (2.30 g, 76% yield from the acid

chloride). An analytical sample was prepared by recrystallization from acetonitrile. **IR** (KBr, cm^{-1}) 3456 (br), 3318, 1703, **1604**, 1559, 1518, 1481, 1345, 1324, 1247; **^{1}H NMR** (300 MHz, $CDCl_3$, conformer **O**) ∂ 12.90 (bs, 1H), 9.03 (bs, 1H), 8.83 (d, 1H), 8.50 (dd, 1H), 8.42 (dt, 2H), 8.11 (d, 2H), 7.82 (td, 1H), 7.21 (dd, 1H) ; **^{13}C NMR** (75 MHz, DMSO-d_6) ∂ 178.3, 167.8, 151.9, 150.5, 149.2, 138.9, 130.9, 124.1, 122.3, 116.3; **MP** 178-180˚C.

1-(2-methoxybenzoyl)-3-(2-pyridyl)thiourea (32)

To a stirred solution of 2-aminopyridine (490 mg, 5.2 mmol) in 15 mL dry THF (4 Å molecular sieves) was added 1.00 g (5.2 mmol) **19a**. The reaction was stirred overnight, at room temperature, and ~10 mL water were added, until permanent cloudiness was achieved. The reaction continued to stir for 1 hr, at which point the colorless, needle-like precipitate was filtered over a Buchner funnel, washed with water (2 x 10 mL), and allowed to air-dry (1.19 g, 80%). In order to expedite drying, the product could be transferred to a watch glass, and placed on top of a hot oven (ambient temperature ~ 100 ℃) with no apparent decrease in either yield or purity. A glassy, amorphous solid suitable for X-ray analysis was grown via slow evaporation from dichloroethane/hexanes. **IR** (KBr, cm^{-1}) 3294, 3024 (br), 1660, 1578, **1540**, 1480, 1439, 1339, 1148, 1005, 753, 476; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 13.35 (bs, 1H), 11.15 (bs, 1H), 8.89 (d, J = 8.7 Hz, 1H), 8.49 (m, 1H), 8.24 (dd, J = 7.8, 1.8 Hz, 1H), 7.74 (td, J = 7.2, 1.8 Hz, 1H), 7.59 (m, 1H), 7.15 (m, 2H), 7.06 (d, J = 8.7 Hz, 1H), 4.10 (s, 3H); **^{13}C NMR** ($CDCl_3$,75 MHz) ∂ 177.6, 164.7, 158.0, 151.7, 148.8, 137.8, 135.6, 133.1, 122.1, 121.6, 119.0, 116.2, 112.0, 56.7; **MP** 136-138˚C.

1-(4-methoxybenzoyl)-3-(2-pyridyl)thiourea (33)

To a stirred solution of **20a** (0.97 g, 5 mmol) in 20 mL THF was added 0.47 g (5 mmol) 2-aminopyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature, and ca. 15 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the fluffy, white, crystalline needles were filtered over a Buchner funnel, washed with water, and air-dried

to constant weight, 1.198 g (77%, 2 steps). As prepared, the product was suitable for spectral analysis; colorless prisms suitable for X-ray diffraction were grown from ethyl acetate / hexanes. **IR** (KBr, cm^{-1}) 3276 (br), 3010, 2848, 1666, 1603, 1577, **1534**, 1504, 1438, 1336, 1252, 1171, 1164, 1032, 840, 616; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 13.20 (bs,1H), 9.02 (bs, 1H), 8.82 (d, 1H), 8.44 (d, 1H), 7.88 (d, 2H), 7.77 (m, 1H), 7.16 (dd, 1H), 7.01 (dt, 2H), 3.89 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 177.5 (C=S), 166.1 (C=O),164.3 (C-OCH_3), 151.6, 148.9, 137.9, 130.0, 123.7, 121.7, 116.3, 114.7, 55.9; **EA** Calc. C, 58.52; H, 4.56; N, 14.62; Found C, 58.37; H, 4.66; N, 14.67; **MP** 155-156℃; **R_f** = 0.58 (CH_2Cl_2/silica).

1-(3-chlorobenzoyl)-3-(2-pyridyl)thiourea (34)

To 2.1 g crude **21a** in 20 mL THF was added 0.941 g (10 mmol) 2-aminopyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature, and ca. 15 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the fluffy, white needles were filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 2.24 g (77%, 2 steps). As prepared, the product was suitable for spectral analysis; colorless needles were grown from ethanol/hexanes. **IR** (KBr, cm^{-1}) 3224 (br), 3023, 1673, 1552, **1533**, 1440, 1341, 1251, 1167, 771, 784, 738; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 113.02 (bs, 1H), 9.53 (bs, 1H), 8.75 (d, 1H), 8.42 (d, 1H), 7.93 (s, 1H), 7.78 (m, 2H), 7.57 (dq, 1H), 7.44 (t, 1H), 7.16 (dd, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.8, 165.3, 151.2, 148.8, 135.7, 133.9, 133.6, 130.6, 128.1, 125.6, 121.8, 116.2; **MP** 148-150˚C; **R_f** 0.15 (CH_2Cl_2/silica).

1-(4-chlorobenzoyl)-3-(2-pyridyl)thiourea (35)

To 1.432 g crude **22a** in 20 mL THF was added 0.941 g (10 mmol) 2-aminopyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature, and ca. 15 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the fluffy, pale yellow product was filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 1.832 g (63%, 2 steps). As prepared, the product was suitable for spectral analysis; colorless, columnar

crystals were grown from the slow evaporation of a chloroform solution. **IR** (KBr, cm^{-1}) 3355, 3256, 3032, 1676, **1523**, 1438, 1335, 1162, 1120, 1094, 762, 745; **^{1}H NMR** ($CDCl_3$, 600 MHz) ∂ 13.08 (bs, 1H), 9.02 (bs, 1H), 8.81 (d, 1H), 8.45 (d, 1H), 7.86 (d, 2H), 7.80 (t, 1H), 7.52 (d, 2H), 7.19 (dd, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.8, 165.4, 151.2, 148.6, 140.3, 137.7, 130.0, 129.5, 129.0, 121.6, 116.1; **MP** 140-142˚C (dec.)

1-(3-cyanobenzoyl)-3-(2-pyridyl)thiourea (36)

To 1.0 g (5.2 mmol) crude **23a** in 10 mL THF was added 0.49 g (5.2 mmol) 2-aminopyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature, and ca. 15 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the fluffy, pale yellow product was filtered over a Buchner funnel, washed with water, and air-dried to constant weight, 1.1 g (75%, 3 steps). As prepared, the product was suitable for spectral analysis; colorless needles were grown from DMF. **IR** (KBr, cm^{-1}) 3217 (br), 3064, 3032, 2236, 1675, **1534**, 1444, 1349, 1282, 1261, 1191, 1156, 1147, 898, 776, 742, 687; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.92 (bs, 1H), 9.18 (bs, 1H), 8.81 (d, 1H), 8.47 (d, 1H), 8.26 (s, 1H), 8.16 (d, 1H), 7.94 (d, 1H), 7.81 (t, 1H), 7.71 (t, 1H), 7.21 (t, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.5, 164.5, 151.0, 148.7, 137.9, 136.6, 133.1, 131.7, 131.4, 130.2, 127.8, 117.3, 116.2, 113.9; **MP** 149-151˚C (dec.)

1-(4-cyanobenzoyl)-3-(2-pyridyl)thiourea (37)

To a stirred solution of crude **24a** in 10 mL MeCN were added 0.54 g (5 mmol) 2-amino-6-methylpyridine. Upon addition, the reaction mixture turned dark red, and, ca. 10 minutes later, an orange solid suddenly precipitated. Additional MeCN was added to loosen the stir bar (10 mL), and the reaction was stirred for 2 hours at room temperature. The solvent was removed on the rotatory evaporator, yielding 1.493 g of a pale yellow solid (70%, 3 steps), which crystallized in the NMR tube. Single crystals suitable for X-ray analysis were grown from CH_2Cl_2 (**37a**), IPA/acetone (**37b**), and $CDCl_3$ (**37c**). **IR** (KBr, cm-1) 3352, 2231, 1672, 1556, **1532,** 1156, 1123, 755; **^{1}H NMR** ($CDCl_3$, 300

MHz) ∂ 12.91 (bs, 1H), 9.04 (bs, 1H), 8.81 (d, 1H), 8.47 (d, 1H), 8.04 (d, 2H), 7.86 (dd, 2H), 7.81 (td, 1H), 7.21 (dd, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.3, 164.6, 151.1, 148.8, 148.6, 137.8, 135.6, 132.9, 128.2, 121.9, 121.6, 117.3, 116.1, 116.0; **MP** 181-185˚C (**37c**; dec.)

1-(3,4-dichlorobenzoy)-3-(2-pyridyl)thiourea (38)

To 1.3 g (5.6 mmol) **25a** in 10 mL THF was added 0.53 g (5.6 mmol) 2-aminopyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature, and ca. 10 mL water were added to precipitate the product. After the addition of water, the reaction was stirred for an additional hour, and the white solids were collected via vacuum filtration, washed with water, and air-dried to constant weight, 1.62 g (89%, 2 steps). As prepared, the product was suitable for spectral analysis; colorless needles were grown from CH_2Cl_2/acetone. **IR** (KBr, cm^{-1}) 3324, 3011, 1674, 1580, **1526**, 1455, 1440, 1384, 1345, 1253, 1171, 1149, 1140, 1031, 746; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.91 (bs, 1H), 8.90 (bs, 1H), 8.81 (d, 1H), 8.45 (d, 1H), 8.02 (d, 1H); 7.79 (td, 1H), 7.73 (dd, 1H), 7.64 (d, 1H), 7.19 (dd, 1H); **^{13}C NMR** (DMSO-d_6, 151 MHz) ∂ 178.1, 166.7, 151.6, 148.8, 138.6, 136.5, 136.3, 133.1, 131.8, 131.2, 129.3, 122.0, 116.1; **MP** 194-195˚C (dec.)

1-(3,5-dichlorobenzoyl)-3-(2-pyridyl)thiourea (39)

To 2.05 g crude **26a** in 15 mL THF was added 0.94 g (10 mmol) 2-aminopyridine; the reaction was stirred for 18 hours (*i.e.* overnight) at room temperature, and the solvent was removed on the rotovap. The yellow residue was dissolved in 20 mL acetone, then 10 mL water were added, and the chunky yellow precipitate was filtered over a vacuum, and dried to constant weight. 1.957 g (62%, 2 steps) of a bright yellow solid were isolated; as prepared, the product was suitable for spectral analysis. Slender yellow prisims were grown from acetonitrile. **IR** (KBr, cm^{-1}) 3243 (br), 3067, 1702, 1606, 1565, 1530, 1478, 1427, 1324, 1269, 1237, 1204, 872, 774, 748; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.85 (bs,1H); 8.91 (bs, 1H), 8.82 (d, 1H), 8.47 (d, 1H), 7.81 (m, 3H), 7.65 (t, 1H), 7.21 (t, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 177.0, 165.2, 151.2, 148.5, 137.6, 135.4, 132.8, 127.0, 126.5, 121.4, 116.2; **EA** Calc. C, 47.87; H, 2.78; N, 12.88; S, 9.83; Found C, 47.95; H,

2.7; N, 12.8; S, 9.63; **MP** 180-183˚C (dec.); $\mathbf{R_f}$ 0.24 (CH_2Cl_2 / silica).

1-(4-bromobenzoyl)-3-(2-pyridyl)thiourea (40)

To 2.0 g (8.6 mmol) crude **27a** in 15 mL THF was added 0.844 g (8.6 mmol) 2-aminopyridine; the reaction was stirred for 72 hours (*i.e.* over the weekend) at room temperature, then 25 mL water were added, and the mixture was stirred for 0.5 h. The precipitate was collected over a Buchner funnel, washed with water (2 x 15 mL) and ethanol (3 x 5 mL), and dried over a vacuum to yield 1.82 g (54%, 2 steps) of a pale yellow solid; as prepared, the product was suitable for spectral analysis. Slender, colorless columns were grown from acetonitrile. **IR** (KBr, cm^{-1}) 3438, 3049, 1675, 1585, **1551**, 1512, 1483, 1436, 1154, 1121, 1008, 743, 579; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 13.03 (bs, 1H), 8.96 (bs, 1H), 8.83 (d, 1H), 8.50 (d, 1H), 7.81 (m, 3H), 7.71 (d, 2H), 7.19 (dd, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.9, 165.7, 151.3, 148.8, 137.9, 132.7, 130.6, 129.3, 129.2, 121.8, 116.3; **EA** Calc. C, 46.44; H, 3.00; N, 12.50; O, 4.76; S, 9.54; Br, 23.77; Found C, 46.30; H, 2.90; N, 12.47; **MP** 160-161˚C (dec.)

1-(2-bromobenzoyl)-3-(2-pyridyl)thiourea (41) To 1.21 g (5 mmol) **28a** in 15 mL THF was added 0.486 g (5 mmol) 2-aminopyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature, then the solvent was removed on the rotovap, yielding 1.6 g of a pale yellow solid, which likely contained a residual amount of KCl. This solid was triturated with isopropanol, yielding 1.1 g of colorless needles (65%, 2 steps). The addition of water as the final step in the reaction sequence produced a biphasic solution, from which no solids could be precipitated, in both **28** and **41**, and it was therefore necessary to remove the reaction solvent, and recrystallize the crude product, in both cases. **IR** (KBr, cm^{-1}) 3243 (br), 3067, 1702, 1606, 1565, 1530, 1478, 1427, 1324, 1269, 1237, 1204, 872, 774, 748; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.83 (bs, 1H), 9.09 (bs, 1H), 8.82 (d, 1H), 8.50 (d, 1H), 7.80 (dt, 1H), 7.78 (td, 2H), 7.45 (m, 2H), 7.19 (dd, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 176.4, 166.7, 151.1, 148.5, 137.7, 134.7, 133.9, 133.1, 130.1, 127.9, 121.6, 119.4, 116.2; **MP** 104-106˚C.

4-Trifluoromethylbenzoylisothiocyanate (42a)

[Not Isolated] To 1.9 g (9.1 mmol) trifluoromethylbenzoyl chloride in 15 mL MeCN was added 0.89 g KSCN. The reaction mixture was stirred for 1 hr; 10 mL Et_2O were added, and the reaction mixture was filtered through 4 cm x 4 cm Celite. The solvent was removed on the rotatory evaporator, yielding 1.948 g of an orange solid. **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 8.12 (d, J=8.4, 2H), 7.79 (d, J=8.4, 2H).

1-(4-trifluoromethylbenzoyl)-3-(2-pyridyl)thiourea (42)

To crude **42a** in 15 mL THF was added 0.856 g (9.1 mmol) 2-aminopyridine; the reaction was stirred for 16 hours (*i.e.* overnight) at room temperature. 10 mL water were added, and the mixture was left to sit over the weekend (72h). The precipitate was collected over a Buchner funnel, washed with water (2 x 15 mL), and dried over a vacuum to yield 2.358 g (80%, 2 steps) of a bright yellow solid; as prepared, the product was suitable for spectral analysis. Bright orange-yellow plates were grown from acetonitrile; while visually resembling analytical crystals, X-ray spectroscopy determined that these plates were mica-like, and could not be analyzed. **IR** (KBr, cm^{-1}) 3260, 1701, 1607, 1559, 1422, **1333**, 1272, 1248, 1114, 1069, 1017, 770, 766, 717, 693; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.97 (bs, 1H), 9.05 (bs, 1H), 8.82 (d, 1H), 8.47 (d, 1H), 8.04 (d, 1H), 7.81 (m, 3H), 7.20 (dd, 1H)**; ^{13}C NMR** ($CDCl_3$, 151 MHz) ∂ 176.7, 165.3, 151.3, 148.9, 138.0, 135.5, 135.2, 128.3, 126.5, 124.4, 121.9, 116.2 ; **MP** 158-160˚C.

1-(3,5-Dichlorobenzoyl)-3-(5-methyl-2-pyridyl)thiourea (43)

3,5-dichlorobenzoylisothiocyanate was prepared from 2.09 g (10 mmol) of the acid chloride, as described for **26a**. The solvent was not removed from the isothiocyanate; instead, 1.08 g (10 mmol) 2-amino-5-methyl-pyridine were added directly to the MeCN / Et_2O / isothiocyanate filtrate. The mixture was stirred overnight, and then ca. 20 mL water were added to precipitate the product, which was a fluffy, pale-yellow solid, weighing 2.736 g (80%, 2 steps).

43N

A single crystal suitable for X-ray analysis was grown from MeOH. Single crystals were also grown from chloroform; however, these re-dissolved into solution before X-ray data could be collected. **IR** (KBr, cm^{-1}) 3438 (br), 3245, 3066, 2861, 1699, 1598, 1568, 1492, 1380, 1314, **1273**, 1240, 1199, 872, 811, 749; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 15.39 (bs, 1H), 8.66 (bs, 1H), 8.16 (s, 1H), 7.98 (d, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 2.35 (s, 3H); **MP** (DSC) 190.6℃.

43O

Clusters of fiberous needles were prepared from a toluene solution. **IR (**KBr, cm^{-1}) 3425, 3223, 1674, **1536**, 1432, 1389, 1357, 1255, 1164, 1122, 873, 825, 731, 699; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.76 (bs, 1H), 8.92 (bs, 1H), 8.64 (d, J=8.1 Hz, 1H), 8.28 (d, J=2.1 Hz, 1H), 7.76 (d, J=1.8 Hz, 2H), 7.63 (m, 2H), 2.37 (s, 3H); **MP** (DSC) 194.9℃

1-Benzoyl-3-(3-methyl-2-pyridyl)thiourea (44)

To 1.55 g (8.4 mmol) crude benzoyl isothiocyanate in 15 mL THFwere added 0.84 mL (8.4 mmol) 2-amino-3-picoline. Upon addition of the amine, the reaction turned bright orange, and a significant amount of heat is evolved. The reaction was stirred overnight, water was added, and 2.03 g (89%) of a colorless solid were removed by vacuum filtration. Single crystals suitable for X-ray analysis were grown from ethanol / hexanes. **IR** (KBr, cm^{-1}) 3196 (br), 1670, 1599, 1577, **1521**, 1330, 1253, 1155, 777, 715, 672; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.97 (bs, 1H), 9.05 (bs, 1H), 8.82 (d, 1H), 8.47 (d, 1H), 8.04 (d, 1H), 7.81 (m, 3H), 7.20 (dd, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 180.0, 167.3, 149.9, 147.1, 140.1, 134.0, 131.8, 130.7, 129.4, 127.9, 123.8, 17.9; **MP** 131-133˚C.

1-(4-Nitrobenzoyl)-3-(3-methyl-2-pyridyl)thiourea (45)

To 1.05 g (5 mmol) crude **18a** in 15 mL THFwere added 0.5 mL (5 mmol) 2-amino-3-picoline. Upon addition of the amine, the reaction turned bright orange, and a significant amount of heat is evolved. The cloudy orange reaction mixture was stirred overnight, water was added, and 1.392 g (88%) of a colorless solid were removed by vacuum filtration. Pale yellow prisms suitable for X-ray analysis were grown from acetonitrile. **IR**

(KBr, cm^{-1}) 3424 (br), 3223, 3068, 1673, 1605, **1527**, 1451, 1349, 1163, 1027, 1008, 872, 780, 723, 701; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.17 (bs, 1H), 9.74 (bs, 1H), 8.38 (d, 3H), 8.15 (m, 3H), 7.66 (d, 1H), 2.40 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 179.9, 166.6, 150.2, 149.8, 146.3, 139.6, 138.1, 130.3, 123.4, 17.2. **MP** 178-180˚C.

1-(2-Bromobenzoyl)-3-(3-methyl-2-pyridyl)thiourea (46)

To 1.44 g crude **28a** in 10 mL THF was added 0.6 mL (6 mmol) 2-amino-3-picoline. The reaction was stirred overnight, until TLC indicated that the starting material had completely disappeared. The solvent was removed on the rotatory evaporator, yielding 1.95 g of a light yellow powder (93%). Colorless needles suitable for X-ray analysis were grown from ethanol / hexanes. **IR** (KBr, cm^{-1}) 3160 (br), 1675, **1521**, 1452, 1339, 1246, 1160, 1028, 775, 745, 686, 651; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 12.07 (bs, 1H), 9.26 (bs, 1H), 8.42 (d, 1H), 7.66 (m, 3H), 7.42 (m, 2H), 7.25 (t, 1H), 2.41 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 179.9, 166.6, 150.2, 149.8, 146.3, 139.6, 138.1, 130.3, 123.4, 17.2. **MP** 104-106˚C.

N,N'-Bis(benzoyl)thiourea (47)

[Synthesis adapted from a literature procedure.[215]] To a well-stirred solution of 0.76 g (10 mmol) thiourea and 0.28 mL (20 mmol) triethylamine in 20 mL acetonitrile, which had previously been dried over 4 Å molecular sieves, 2.3 mL benzoyl chloride (20 mmol) were added drop-wise. The mixture was heated to a gentle reflux, and after a few hours of stirring, the colorless thiourea-benzoyl chloride suspension became bright yellow. In the morning, the deep red-orange reaction mixture was homogeneous; however, TLC ($CDCl_3$ / silica) showed that the reaction had not gone to completion, and an additional equilvalent of triethylamine was added, in 10 mL MeCN. The reaction was stirred for 10 minutes, at which point TLC indicated that all of the benzoyl chloride had been consumed. The solvent was removed on the rotatory evaporator, and slender orange needles suitable for X-ray analysis were grown from iPrOH/H_2O (52%). **IR** (NaCl, cm^{-1}) 3064, 1716, 1661, 1600, 1521, 1479, 1296, **1257**, 1155, 1066, 914, 700, 663; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 11.78 (bs, 2H), 8.01 (d, 4H), 7.68 (t, 2H), 7.58 (t, 4H); **^{13}C NMR**

($CDCl_3$, 75 MHz) ∂ 177.3, 165.8, 134.1, 132.1, 129.5, 128.0**.** **EA** Calc. C, 63.36; H, 4.25; N, 9.85; O, 11.25; S, 11.28; Found C, 63.38; H, 4.14; N, 9.97; **MP** 167-169℃.

Chapter VIII

General Notes: Because thiadiazoles **49-53** were obtained as decomposition products, and never synthesized directly, synthetic data is not available. Characterization data, however, is detailed below.

1-(3,5-Dinitrobenzoyl)imido-[1,2,4]dithiazolo-[2,3-a]pyridine (49)

Long, slender, brown, columnar crystals suitable for X-ray analysis were obtained from DMF/H_2O. **IR** (NaCl, cm^{-1}) 3101, 1625, 1602, 1538, 1497, 1433, **1321**, 1266, 1155, 1087, 786, 752, 731, 719; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 9.55 (d, *J* = 1.8 Hz, 2H), 9.21 (t, *J* = 1.8 Hz, 1H), 8.58 (d, *J* = 6.3 Hz, 1H), 7.99 (m, 1H), 7.89 (d, 1H), 7.30 (m, 1H); **MP** 298˚C.

1-(4-Methoxybenzoyl)imido-[1,2,4]dithiazolo-5-methyl-[2,3-a]pyridine (50)

Pale brown cubic crystals suitable for X-ray analysis were obtained from ethanol. **IR** (KBr, cm^{-1}) 1604, 1582, 1523, 1491, 1418, 1394, 1375, **1328**, 1258, 1162, 1025, 903, 776; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 8.37 (d, 2H), 8.05 (d, 1H), 7.78 (m, 1H), 6.98 (d, 2H), 6.92 (d, 1H), 3.85 (s, 3H), 2.80 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 177.6, 175.8, 163.2, 156.4, 145.0, 137.5, 131.4, 131.3, 126.0, 116.7, 115.8, 113.7, 55.4, 20.6; **MP** 240-241˚C.

1-(4-Trifluoromethylbenzoyl)imido-[1,2,4]dithiazolo-[2,3-a]pyridine (51)

Pale brown cubic crystals suitable for X-ray analysis were obtained from acetonitrile. Because this compound was obtained as a "lucky crystal," and we were not successful in reproducing it, limited spectral data is available. **IR** (KBr, cm^{-1}) 1607, 1559, **1333**, 1248, 1115.

1-Benzoylimido-[1,2,4]dithiazolo-8-methyl-[2,3-a]pyridine (52)

Yellow columnar crystals suitable for X-ray analysis were obtained from acetone / hexanes. **IR** (KBr, cm^{-1}) 1604, 1582, 1523, 1491, 1418, 1394, 1375, **1328**, 1258, 1162,

1025, 903, 776; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 8.44 (dt, 2H), 8.31 (d, 1H), 7.64 (dt, 1H), 7.50 (m, 3H), 7.05 (t, 1H), 6.92 (d, 1H), 2.69 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 178.4, 171.2, 164.4, 156.3, 137.0, 133.4, 132.7, 130.3, 130.1, 129.8, 129.6, 128.5, 116.1, 17.7; **MP** 193-194˚C.

1-(2-Bromobenzoyl)imido-[1,2,4]dithiazolo-[2,3-a]pyridine (53)

Clusters of fine brown prisms were obtained from ethanol / hexanes. **IR** (KBr, cm^{-1}) 3065, 3028, 1624, 1568, 1529, 1487, 1436, 1379, **1325**, 1264, 1205, 1022, 924, 777, 757; **^{1}H NMR** ($CDCl_3$, 300 MHz) ∂ 8.47 (dt, 1H), 7.88 (ddd, 1H), 7.79 (dt, 1H), 7.71 (d, 1H), 7.43 (td, 1H), 7.33 (td, 1H), 7.18 (td, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz) ∂ 178.4, 171.2, 164.4, 156.3, 137.0, 133.4, 132.7, 130.3, 130.1, 129.8, 129.6, 128.5, 116.1, 17.7.

1-(3,5-dinitrobenzoyl)-3-(2-pyridyl)thiourea (54)

[Not Isolated]. Prepared on 10 mmol scale from the acid chloride, as described in the general procedure for BzPTU preparation in **Chapter VI**. Solvent was removed on the rotovap; crude spectral data is made available, as the product decomposed upon recrystallization. **IR** (KBr, cm-1) 3430, 3268, 3100,1704, 1606, 1540, 1480, 1422, **1344**, 1318, 1280, 1239, 1077, 786, 729, 706; **^{1}H NMR** (DMSO-d_6, 300 MHz) ∂ 12.93 (bs, 1H), 12.47 (bs, 1H), 9.10 (d, 3H), 9.04 (s, 1H), 8.46 (d, 1H), 7.95 (t, 1H), 7.32 (t, 1H).

APPENDIX B

CRYSTALLOGRAPHIC DATA

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N7 C14 1.461(5) . ?
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C1 H1B 0.92(4) . ?
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C2 H2B 0.88(4) . ?
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C4 H4A 1.00(5) . ?
C4 H4B 1.11(8) . ?
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C5 H5B 0.9800 . ?
C5 H5C 0.9800 . ?
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C6 H6B 0.93(3) . ?

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C4 N3 C3 N2 -178.2(4) . . . . ?
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N2 H2N S2  0.76(4) 2.74(4) 3.476(4) 165(3) .
N5 H5N S1  0.78(4) 2.78(4) 3.526(4) 161(4) 4_576
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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S2 S 0.11532(6) -0.07315(6) 0.11998(4) 0.03728(16) Uani 1 1 d . . .
S3 S 0.18362(6) 0.73583(6) 0.48657(5) 0.04087(17) Uani 1 1 d . . .
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N3 N 0.3582(3) 0.1387(3) 0.06363(19) 0.0553(6) Uani 1 1 d . . .
N4 N 0.0362(2) 0.1128(2) 0.31208(14) 0.0310(4) Uani 1 1 d . . .
N5 N 0.0005(2) 0.1672(2) 0.15946(15) 0.0336(4) Uani 1 1 d . . .
N6 N 0.2703(2) 0.4774(2) 0.42550(16) 0.0350(4) Uani 1 1 d . . .
N7 N 0.3072(2) 0.5849(2) 0.30625(17) 0.0377(4) Uani 1 1 d . . .
C1 C 0.4141(2) 0.1379(3) 0.4197(2) 0.0371(5) Uani 1 1 d . . .
C2 C 0.4920(2) 0.1870(3) 0.3407(2) 0.0426(5) Uani 1 1 d . . .
C3 C 0.4340(3) 0.2018(3) 0.1599(2) 0.0436(5) Uani 1 1 d . . .
C4 C 0.3735(7) 0.1691(4) -0.0343(3) 0.115(2) Uani 1 1 d . . .
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H4B H 0.4712 0.1590 -0.0527 0.138 Uiso 1 1 calc R . .
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C18 C 0.2820(5) 0.5537(5) 0.0657(3) 0.0773(11) Uani 1 1 d . . .
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H5N H -0.009(3) 0.139(3) 0.092(3) 0.040(7) Uiso 1 1 d . . .
H6N H 0.290(3) 0.410(3) 0.378(2) 0.040(7) Uiso 1 1 d . . .
H7N H 0.352(3) 0.520(3) 0.271(2) 0.038(7) Uiso 1 1 d . . .
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H1B H 0.384(3) 0.043(3) 0.384(2) 0.041(7) Uiso 1 1 d . . .
H2A H 0.581(3) 0.145(3) 0.325(3) 0.052(8) Uiso 1 1 d . . .
H2B H 0.514(3) 0.292(3) 0.376(2) 0.038(7) Uiso 1 1 d . . .
H7A H 0.214(3) 0.086(3) 0.520(2) 0.040(7) Uiso 1 1 d . . .
H7B H 0.118(3) 0.211(3) 0.526(2) 0.031(6) Uiso 1 1 d . . .
H8A H 0.027(3) -0.007(3) 0.397(2) 0.044(7) Uiso 1 1 d . . .
H8B H 0.153(3) -0.030(3) 0.331(2) 0.038(7) Uiso 1 1 d . . .
H10A H 0.005(3) 0.351(3) 0.290(3) 0.047(8) Uiso 1 1 d . . .
H10B H -0.138(3) 0.296(3) 0.239(2) 0.043(7) Uiso 1 1 d . . .
H11A H 0.049(4) 0.385(4) 0.117(3) 0.086(12) Uiso 1 1 d . . .
H11B H -0.093(4) 0.340(4) 0.079(3) 0.078(11) Uiso 1 1 d . . .
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H12B H -0.186(4) 0.536(4) 0.222(3) 0.068(10) Uiso 1 1 d . . .
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H13B H 0.315(3) 0.351(3) 0.618(2) 0.038(7) Uiso 1 1 d . . .
H14A H 0.261(3) 0.553(3) 0.588(2) 0.035(6) Uiso 1 1 d . . .
H14B H 0.142(3) 0.442(3) 0.528(2) 0.034(6) Uiso 1 1 d . . .
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H17B H 0.466(4) 0.625(4) 0.162(3) 0.076(11) Uiso 1 1 d . . .
H18A H 0.320(4) 0.534(5) -0.009(4) 0.097(14) Uiso 1 1 d . . .
H18B H 0.268(4) 0.461(4) 0.076(3) 0.077(11) Uiso 1 1 d . . .
H18C H 0.188(4) 0.582(4) 0.065(3) 0.081(12) Uiso 1 1 d . . .

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N4 0.0379(10) 0.0304(9) 0.0232(8) 0.0087(7) 0.0001(7) 0.0052(8)
N5 0.0455(11) 0.0324(9) 0.0203(8) 0.0075(7) -0.0012(7) 0.0057(8)
N6 0.0495(11) 0.0266(9) 0.0275(9) 0.0080(8) 0.0060(8) 0.0062(8)
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C5 0.103(3) 0.095(3) 0.0508(18) 0.0359(19) -0.0240(19) -0.033(2)
C6 0.076(2) 0.076(2) 0.0455(16) 0.0280(16) -0.0086(15) 0.0020(17)
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C18 0.090(3) 0.107(3) 0.0499(19) 0.044(2) 0.0123(18) 0.025(2)

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C1 1.462(3) . ?
N1 C13 1.470(3) . ?
N2 C3 1.332(3) . ?
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C16 H16B 1.02(3) . ?
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N4 H4N S3  0.81(3) 2.77(3) 3.410(2) 137(2) 2_566
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
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 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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S2 S -0.01248(5) 0.20786(4) -0.26049(3) 0.04179(15) Uani 1 1 d . . .
S3 S 0.47325(5) -0.33935(4) 0.00274(3) 0.04267(15) Uani 1 1 d . . .
N1 N 0.27683(17) -0.03391(11) -0.13424(8) 0.0390(4) Uani 1 1 d . . .
N2 N 0.2249(2) 0.07948(14) -0.01218(10) 0.0493(5) Uani 1 1 d . . .
N3 N 0.2466(2) 0.22520(16) 0.04973(11) 0.0536(5) Uani 1 1 d . . .
N4 N 0.0084(2) 0.02239(14) -0.21026(10) 0.0471(4) Uani 1 1 d . . .
N5 N -0.1207(2) 0.1272(2) -0.16156(13) 0.0680(7) Uani 1 1 d . . .
N6 N 0.2794(2) -0.31056(13) -0.10711(10) 0.0486(5) Uani 1 1 d . . .
N7 N 0.3656(2) -0.46891(13) -0.09247(10) 0.0495(5) Uani 1 1 d . . .
C1 C 0.3793(3) 0.01502(17) -0.08218(13) 0.0508(5) Uani 1 1 d . . .
C2 C 0.3250(3) 0.10723(17) -0.05190(13) 0.0493(5) Uani 1 1 d . . .
C3 C 0.1864(2) 0.13668(17) 0.03520(11) 0.0473(5) Uani 1 1 d . . .
C4 C 0.2204(3) 0.2953(2) 0.10264(14) 0.0611(6) Uani 1 1 d . . .
C5 C 0.3383(4) 0.2939(3) 0.16170(15) 0.0810(9) Uani 1 1 d . . .
```

H5A H 0.3504 0.2258 0.1805 0.122 Uiso 1 1 calc R . .
H5B H 0.3203 0.3402 0.1968 0.122 Uiso 1 1 calc R . .
H5C H 0.4216 0.3146 0.1464 0.122 Uiso 1 1 calc R . .
C6 C 0.1968(6) 0.4001(3) 0.0715(2) 0.1147(16) Uani 1 1 d . . .
H6A H 0.1193 0.3982 0.0330 0.172 Uiso 1 1 calc R . .
H6B H 0.2789 0.4220 0.0556 0.172 Uiso 1 1 calc R . .
H6C H 0.1771 0.4472 0.1059 0.172 Uiso 1 1 calc R . .
C7 C 0.2572(2) 0.01982(16) -0.19927(11) 0.0447(5) Uani 1 1 d . . .
C8 C 0.1197(3) -0.00324(17) -0.24342(11) 0.0492(5) Uani 1 1 d . . .
C9 C -0.0427(2) 0.11528(16) -0.20713(10) 0.0414(4) Uani 1 1 d . . .
C10 C -0.1940(3) 0.2169(3) -0.14897(18) 0.0793(10) Uani 1 1 d . . .
C11 C -0.1228(4) 0.2702(3) -0.0862(3) 0.1103(14) Uani 1 1 d . . .
H11A H -0.0315 0.2909 -0.0920 0.165 Uiso 1 1 calc R . .
H11B H -0.1146 0.2250 -0.0470 0.165 Uiso 1 1 calc R . .
H11C H -0.1757 0.3296 -0.0785 0.165 Uiso 1 1 calc R . .
C12 C -0.3365(5) 0.1870(5) -0.1408(4) 0.192(3) Uani 1 1 d . . .
H12A H -0.3833 0.1525 -0.1820 0.288 Uiso 1 1 calc R . .
H12B H -0.3881 0.2473 -0.1334 0.288 Uiso 1 1 calc R . .
H12C H -0.3303 0.1421 -0.1016 0.288 Uiso 1 1 calc R . .
C13 C 0.3133(2) -0.13925(15) -0.14248(11) 0.0424(5) Uani 1 1 d . . .
C14 C 0.2626(3) -0.20562(15) -0.09174(12) 0.0474(5) Uani 1 1 d . . .
C15 C 0.3649(2) -0.37487(14) -0.07061(10) 0.0369(4) Uani 1 1 d . A .
C16 C 0.2798(2) -0.51346(15) -0.15280(11) 0.0490(5) Uani 0.473(6) 1 d P A 1
H16A H 0.2416 -0.4593 -0.1856 0.059 Uiso 0.473(6) 1 calc PR A 1
C17 C 0.3599(9) -0.5868(7) -0.1869(4) 0.099(3) Uani 0.473(6) 1 d P A 1
H17A H 0.4196 -0.5498 -0.2117 0.148 Uiso 0.473(6) 1 calc PR A 1
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H17C H 0.4156 -0.6295 -0.1524 0.148 Uiso 0.473(6) 1 calc PR A 1
C18 C 0.1658(7) -0.5636(6) -0.1258(3) 0.077(2) Uani 0.473(6) 1 d P A 1
H18A H 0.1037 -0.5123 -0.1142 0.116 Uiso 0.473(6) 1 calc PR A 1
H18B H 0.2042 -0.6024 -0.0850 0.116 Uiso 0.473(6) 1 calc PR A 1
H18C H 0.1153 -0.6085 -0.1606 0.116 Uiso 0.473(6) 1 calc PR A 1
C16A C 0.2798(2) -0.51346(15) -0.15280(11) 0.0490(5) Uani 0.527(6) 1 d P A 2
H16B H 0.1909 -0.4766 -0.1637 0.059 Uiso 0.527(6) 1 calc PR A 2
C17A C 0.3562(6) -0.5000(5) -0.2109(3) 0.0671(17) Uani 0.527(6) 1 d P A 2
H17D H 0.3725 -0.4283 -0.2172 0.101 Uiso 0.527(6) 1 calc PR A 2
H17E H 0.3015 -0.5276 -0.2529 0.101 Uiso 0.527(6) 1 calc PR A 2
H17F H 0.4439 -0.5353 -0.2001 0.101 Uiso 0.527(6) 1 calc PR A 2
C18A C 0.2527(7) -0.6243(4) -0.1422(3) 0.073(2) Uani 0.527(6) 1 d P A 2
H18D H 0.1841 -0.6309 -0.1135 0.110 Uiso 0.527(6) 1 calc PR A 2
H18E H 0.3376 -0.6570 -0.1198 0.110 Uiso 0.527(6) 1 calc PR A 2
H18F H 0.2188 -0.6562 -0.1863 0.110 Uiso 0.527(6) 1 calc PR A 2
H2N H 0.173(3) 0.032(2) -0.0254(15) 0.069(9) Uiso 1 1 d . . .
H3N H 0.314(3) 0.2410(19) 0.0279(13) 0.051(7) Uiso 1 1 d . . .
H4N H -0.008(3) -0.013(2) -0.1821(14) 0.052(7) Uiso 1 1 d . . .
H5N H -0.124(3) 0.083(2) -0.1386(14) 0.051(7) Uiso 1 1 d . . .
H6N H 0.229(3) -0.3294(19) -0.1398(14) 0.052(7) Uiso 1 1 d . . .
H7N H 0.414(3) -0.5066(19) -0.0695(13) 0.048(7) Uiso 1 1 d . . .
H1A H 0.405(3) -0.034(2) -0.0458(14) 0.058(7) Uiso 1 1 d . . .
H1B H 0.460(3) 0.0334(18) -0.0988(12) 0.048(6) Uiso 1 1 d . . .
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H2B H 0.399(3) 0.138(2) -0.0229(14) 0.064(8) Uiso 1 1 d . . .
H4 H 0.145(3) 0.266(3) 0.1203(17) 0.085(10) Uiso 1 1 d . . .

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H7B H 0.260(2) 0.0885(18) -0.1897(11) 0.042(6) Uiso 1 1 d . . .
H8A H 0.114(2) -0.074(2) -0.2542(12) 0.052(7) Uiso 1 1 d . . .
H8B H 0.109(2) 0.0358(19) -0.2851(13) 0.055(7) Uiso 1 1 d . . .
H10 H -0.221(4) 0.248(3) -0.1877(19) 0.096(12) Uiso 1 1 d . . .
H13A H 0.407(3) -0.1478(18) -0.1391(12) 0.049(6) Uiso 1 1 d . . .
H13B H 0.274(3) -0.1591(19) -0.1846(13) 0.050(7) Uiso 1 1 d . . .
H14A H 0.165(3) -0.1928(19) -0.0947(13) 0.053(7) Uiso 1 1 d . . .
H14B H 0.313(3) -0.1922(19) -0.0465(14) 0.057(7) Uiso 1 1 d . . .

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N3 0.0563(12) 0.0528(11) 0.0558(12) -0.0107(9) 0.0209(10) -0.0091(9)
N4 0.0550(11) 0.0402(9) 0.0420(10) 0.0138(8) -0.0004(8) -0.0043(8)
N5 0.0644(14) 0.0715(15) 0.0746(15) 0.0330(13) 0.0293(12) 0.0168(12)
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N7 0.0594(11) 0.0288(8) 0.0474(10) -0.0007(7) -0.0215(9) 0.0044(8)
C1 0.0508(13) 0.0367(11) 0.0586(14) -0.0088(10) -0.0048(11) -0.0042(9)
C2 0.0586(14) 0.0346(11) 0.0524(12) -0.0081(9) 0.0050(10) -0.0096(10)
C3 0.0485(12) 0.0435(11) 0.0467(11) 0.0103(9) 0.0017(9) -0.0019(9)
C4 0.0670(16) 0.0617(15) 0.0596(15) -0.0106(12) 0.0248(13) 0.0033(13)
C5 0.090(2) 0.096(2) 0.0594(16) -0.0269(16) 0.0205(15) 0.0086(18)
C6 0.193(5) 0.074(2) 0.089(2) -0.0002(19) 0.056(3) 0.055(3)
C7 0.0570(13) 0.0297(10) 0.0474(12) 0.0045(8) 0.0102(10) 0.0027(9)
C8 0.0710(15) 0.0363(11) 0.0366(11) 0.0036(9) 0.0017(10) 0.0060(10)
C9 0.0346(10) 0.0469(11) 0.0380(10) 0.0091(8) -0.0042(8) -0.0023(8)
C10 0.0685(19) 0.101(3) 0.073(2) 0.0218(18) 0.0252(16) 0.0357(18)
C11 0.085(3) 0.075(2) 0.170(5) -0.009(3) 0.023(3) 0.0038(19)
C12 0.069(3) 0.267(8) 0.244(7) -0.136(6) 0.042(4) 0.007(4)
C13 0.0493(12) 0.0297(9) 0.0434(11) -0.0032(8) -0.0027(9) 0.0042(8)
C14 0.0635(15) 0.0289(10) 0.0447(12) 0.0014(8) -0.0024(10) 0.0066(9)
C15 0.0408(10) 0.0283(9) 0.0374(9) 0.0027(7) -0.0022(8) -0.0034(7)
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C17 0.117(6) 0.099(7) 0.069(4) -0.040(4) -0.008(4) 0.028(5)
C18 0.068(4) 0.077(5) 0.070(4) -0.002(3) -0.025(3) -0.021(3)
C16A 0.0591(13) 0.0316(10) 0.0446(11) -0.0021(8) -0.0186(10) 0.0011(9)
C17A 0.078(3) 0.065(4) 0.052(3) -0.012(2) -0.004(2) 0.002(3)
C18A 0.092(5) 0.040(3) 0.069(3) -0.004(2) -0.031(3) -0.022(3)

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 All esds (except the esd in the dihedral angle between two l.s. planes)

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 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C7 1.466(3) . ?
N1 C13 1.467(2) . ?
N2 C3 1.331(3) . ?
N2 C2 1.443(3) . ?
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N3 C3 1.329(3) . ?
N3 C4 1.474(3) . ?
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N4 C9 1.344(3) . ?
N4 C8 1.443(3) . ?
N4 H4N 0.78(3) . ?
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N5 C10 1.448(4) . ?
N5 H5N 0.75(3) . ?
N6 C15 1.324(3) . ?
N6 C14 1.448(3) . ?
N6 H6N 0.79(3) . ?
N7 C15 1.327(3) . ?
N7 C16 1.464(3) . ?
N7 H7N 0.78(3) . ?
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C1 H1A 0.98(3) . ?
C1 H1B 0.96(2) . ?
C2 H2A 0.97(3) . ?
C2 H2B 0.94(3) . ?
C4 C5 1.497(4) . ?
C4 C6 1.528(4) . ?
C4 H4 0.98(3) . ?
C5 H5A 0.9800 . ?
C5 H5B 0.9800 . ?
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C6 H6C 0.9800 . ?
C7 C8 1.511(3) . ?
C7 H7A 0.98(3) . ?
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H2A C2 H2B 107(2) . . ?
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H8A C8 H8B 110(2) . . ?
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H18A C18 H18B 109.5 . . ?
C16 C18 H18C 109.5 . . ?

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H18B C18 H18C 109.5 . . ?
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H17E C17A H17F 109.5 . . ?
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N3 H3N S3  0.89(3) 2.67(3) 3.520(2) 159(2) 3_655
N4 H4N S1  0.78(3) 2.56(3) 3.325(2) 167(2) 3
N5 H5N S1  0.75(3) 2.72(3) 3.435(3) 159(3) 3
N6 H6N S2  0.79(3) 2.68(3) 3.3812(19) 149(2) 2_544
N7 H7N S3  0.78(3) 2.58(3) 3.3477(19) 167(2) 3_645

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 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
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_symmetry_cell_setting           Monoclinic
_symmetry_space_group_name_H-M    P2(1)/c

loop_
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 'x, y, z'
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'-x, y+1/2, -z+1/2'

'-x, -y, -z'

'x, -y-1/2, z-1/2'

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_cell_length_b 12.8236(8)

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_cell_angle_beta 101.6040(10)

_cell_angle_gamma 90.00

_cell_volume 2868.8(3)

_cell_formula_units_Z 4

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_cell_measurement_reflns_used 3106

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_exptl_crystal_F_000 1072

_exptl_absorpt_coefficient_mu 0.279

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_exptl_absorpt_process_details SADABS

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_diffrn_ambient_temperature 173(2)

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_diffrn_measurement_method 'phi and omega scans'

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_diffrn_reflns_number 23083

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_diffrn_reflns_theta_min 1.86

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_computing_publication_material 'Bruker SHELXTL'

_refine_special_details

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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-

factors based on ALL data will be even larger.

;

_refine_ls_structure_factor_coef Fsqd

_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0472P)^2^+0.1577P] where P=(Fo^2^+2Fc^2^)/3'

_atom_sites_solution_primary direct

_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens geom

_refine_ls_hydrogen_treatment refall

_refine_ls_extinction_method none

_refine_ls_extinction_coef ?

_refine_ls_number_reflns 6251

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_refine_ls_goodness_of_fit_ref 1.040

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loop_

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S1 S 0.08445(5) 0.36869(4) 0.55968(3) 0.03233(15) Uani 1 1 d . . .

S2 S -0.05847(5) 0.30676(4) 0.25954(3) 0.03100(15) Uani 1 1 d . . .

S3 S 0.44265(5) 0.84265(3) 0.48805(2) 0.02594(14) Uani 1 1 d . . .

N1 N 0.26277(14) 0.54628(10) 0.37575(7) 0.0227(4) Uani 1 1 d . . .

N2 N 0.29668(16) 0.36510(12) 0.50775(8) 0.0281(4) Uani 1 1 d . . .

N3 N 0.30228(16) 0.24441(12) 0.58188(9) 0.0292(4) Uani 1 1 d . . .

N4 N 0.00062(15) 0.49434(12) 0.30855(9) 0.0271(4) Uani 1 1 d . . .

N5 N -0.14954(17) 0.40463(14) 0.34955(9) 0.0327(5) Uani 1 1 d . . .

N6 N 0.26079(16) 0.83752(11) 0.38467(9) 0.0268(4) Uani 1 1 d . . .

N7 N 0.35280(15) 0.99884(11) 0.41394(8) 0.0258(4) Uani 1 1 d . . .

C1 C 0.32986(19) 0.49433(15) 0.43113(10) 0.0272(5) Uani 1 1 d . . .

C2 C 0.22983(19) 0.43004(15) 0.45746(10) 0.0276(5) Uani 1 1 d . . .

C3 C 0.23469(18) 0.32274(13) 0.55005(9) 0.0247(5) Uani 1 1 d . . .

C4 C 0.2672(2) 0.17969(16) 0.63118(10) 0.0341(5) Uani 1 1 d . . .

C5 C 0.2590(3) 0.2457(2) 0.68663(13) 0.0487(7) Uani 1 1 d . . .

C6 C 0.1390(3) 0.1188(2) 0.60763(16) 0.0468(7) Uani 1 1 d . . .

C7 C 0.3833(3) 0.1025(2) 0.64829(16) 0.0519(8) Uani 1 1 d . . .

C8 C 0.24416(19) 0.48172(14) 0.32086(10) 0.0254(5) Uani 1 1 d . . .

C9 C 0.11266(19) 0.50763(16) 0.27826(10) 0.0279(5) Uani 1 1 d . . .

C10 C -0.07045(17) 0.40517(14) 0.30897(9) 0.0248(5) Uani 1 1 d . . .

C11 C -0.24445(19) 0.32532(15) 0.36385(10) 0.0339(5) Uani 1 1 d . . .

C12 C -0.3003(3) 0.3721(2) 0.41575(16) 0.0519(7) Uani 1 1 d . . .

C13 C -0.3565(3) 0.3092(3) 0.30846(16) 0.0592(8) Uani 1 1 d . . .

C14 C -0.1735(4) 0.2242(2) 0.3856(2) 0.0622(9) Uani 1 1 d . . .

C15 C 0.31043(19) 0.65189(13) 0.36674(11) 0.0248(5) Uani 1 1 d . . .

C16 C 0.22806(18) 0.72917(13) 0.39474(11) 0.0250(5) Uani 1 1 d . . .

C17 C 0.34423(17) 0.89652(13) 0.42429(9) 0.0232(4) Uani 1 1 d . . .

C18 C 0.27412(19) 1.06502(13) 0.36520(10) 0.0306(5) Uani 1 1 d . . .

C19 C 0.3072(3) 1.03939(18) 0.30346(12) 0.0400(6) Uani 1 1 d . . .

C20 C 0.3166(3) 1.17686(16) 0.38200(15) 0.0517(8) Uani 1 1 d . . .

C21 C 0.1248(2) 1.0554(2) 0.36334(17) 0.0456(7) Uani 1 1 d . . .

H2N H 0.365(2) 0.3351(16) 0.5028(10) 0.039(6) Uiso 1 1 d . . .

H3N H 0.366(2) 0.2233(15) 0.5675(10) 0.032(6) Uiso 1 1 d . . .

H4N H 0.0007(19) 0.5342(15) 0.3377(10) 0.024(6) Uiso 1 1 d . . .

H5N H -0.146(2) 0.4524(17) 0.3701(11) 0.033(7) Uiso 1 1 d . . .

H6N H 0.2204(17) 0.8634(13) 0.3526(9) 0.014(5) Uiso 1 1 d . . .

H7N H 0.406(2) 1.0276(15) 0.4395(9) 0.027(6) Uiso 1 1 d . . .

H1A H 0.3690(19) 0.5455(15) 0.4614(10) 0.032(6) Uiso 1 1 d . . .

H1B H 0.405(2) 0.4501(15) 0.4248(9) 0.035(6) Uiso 1 1 d . . .

H2A H 0.1735(18) 0.4752(14) 0.4717(9) 0.021(5) Uiso 1 1 d . . .

H2B H 0.1778(17) 0.3860(13) 0.4246(9) 0.018(5) Uiso 1 1 d . . .

H5A H 0.347(3) 0.280(2) 0.7005(12) 0.077(9) Uiso 1 1 d . . .

H5B H 0.239(3) 0.200(2) 0.7202(13) 0.068(8) Uiso 1 1 d . . .

H5C H 0.191(2) 0.2977(19) 0.6772(11) 0.050(7) Uiso 1 1 d . . .

H6A H 0.128(2) 0.072(2) 0.6408(13) 0.069(8) Uiso 1 1 d . . .

H6B H 0.147(3) 0.084(2) 0.5703(13) 0.068(9) Uiso 1 1 d . . .

H6C H 0.063(3) 0.163(2) 0.5975(12) 0.069(8) Uiso 1 1 d . . .

H7A H 0.385(2) 0.0559(18) 0.6126(12) 0.052(8) Uiso 1 1 d . . .

H7B H 0.467(3) 0.1384(18) 0.6609(11) 0.060(8) Uiso 1 1 d . . .

H7C H 0.366(2) 0.060(2) 0.6808(13) 0.063(8) Uiso 1 1 d . . .

H8A H 0.316(2) 0.4896(16) 0.2982(10) 0.039(6) Uiso 1 1 d . . .

H8B H 0.2432(18) 0.4084(15) 0.3340(9) 0.030(5) Uiso 1 1 d . . .

H9A H 0.0981(18) 0.4619(15) 0.2436(9) 0.026(5) Uiso 1 1 d . . .

H9B H 0.1152(17) 0.5783(15) 0.2662(8) 0.024(5) Uiso 1 1 d . . .

H12A H -0.363(2) 0.3228(18) 0.4268(11) 0.051(7) Uiso 1 1 d . . .

H12B H -0.348(2) 0.4350(19) 0.4007(11) 0.056(8) Uiso 1 1 d . . .

H12C H -0.231(3) 0.386(2) 0.4500(14) 0.080(10) Uiso 1 1 d . . .

H13A H -0.324(3) 0.276(2) 0.2749(14) 0.073(10) Uiso 1 1 d . . .

H13B H -0.408(4) 0.375(3) 0.2976(16) 0.114(13) Uiso 1 1 d . . .

H13C H -0.414(3) 0.260(2) 0.3196(12) 0.071(8) Uiso 1 1 d . . .

H14A H -0.143(3) 0.193(2) 0.3507(13) 0.069(9) Uiso 1 1 d . . .

H14B H -0.106(3) 0.239(2) 0.4185(15) 0.085(12) Uiso 1 1 d . . .

H14C H -0.238(3) 0.176(2) 0.3999(12) 0.067(8) Uiso 1 1 d . . .

H15A H 0.2979(18) 0.6667(14) 0.3228(10) 0.022(5) Uiso 1 1 d . . .

H15B H 0.4038(18) 0.6593(13) 0.3824(8) 0.021(5) Uiso 1 1 d . . .

H16A H 0.2382(18) 0.7184(14) 0.4380(10) 0.022(5) Uiso 1 1 d . . .

H16B H 0.1376(18) 0.7178(13) 0.3761(8) 0.018(4) Uiso 1 1 d . . .

H19A H 0.258(2) 1.0819(16) 0.2729(10) 0.039(6) Uiso 1 1 d . . .

H19B H 0.399(3) 1.0539(18) 0.3022(12) 0.063(8) Uiso 1 1 d . . .

H19C H 0.288(2) 0.9672(18) 0.2907(10) 0.044(6) Uiso 1 1 d . . .

H20A H 0.410(3) 1.1847(19) 0.3867(12) 0.064(9) Uiso 1 1 d . . .

H20B H 0.271(2) 1.221(2) 0.3514(12) 0.062(8) Uiso 1 1 d . . .

H20C H 0.289(2) 1.1935(19) 0.4213(13) 0.059(9) Uiso 1 1 d . . .

H21A H 0.110(2) 1.0660(19) 0.4014(13) 0.056(9) Uiso 1 1 d . . .

H21B H 0.082(2) 1.1076(19) 0.3355(11) 0.052(7) Uiso 1 1 d . . .

H21C H 0.090(2) 0.9888(19) 0.3465(11) 0.054(7) Uiso 1 1 d . . .

loop_

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_atom_site_aniso_U_22

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S2 0.0387(3) 0.0259(2) 0.0290(4) -0.0055(2) 0.0082(2) -0.00277(19)

S3 0.0312(2) 0.0193(2) 0.0245(3) 0.0026(2) -0.0011(2) -0.00067(17)

N1 0.0309(8) 0.0170(7) 0.0190(10) 0.0009(7) 0.0021(7) -0.0021(6)

N2 0.0273(8) 0.0290(8) 0.0298(12) 0.0081(8) 0.0098(8) 0.0062(7)

N3 0.0283(9) 0.0303(9) 0.0316(12) 0.0092(8) 0.0125(8) 0.0063(7)

N4 0.0298(8) 0.0264(8) 0.0253(11) -0.0095(8) 0.0064(8) -0.0047(6)

N5 0.0373(10) 0.0288(9) 0.0352(13) -0.0094(9) 0.0149(9) -0.0058(7)

N6 0.0326(9) 0.0177(7) 0.0259(11) 0.0046(7) -0.0045(8) -0.0022(6)

N7 0.0283(8) 0.0166(7) 0.0277(11) 0.0003(7) -0.0062(8) -0.0027(6)

C1 0.0295(10) 0.0246(9) 0.0258(14) 0.0045(9) 0.0011(9) 0.0003(8)

C2 0.0287(10) 0.0265(10) 0.0270(14) 0.0039(9) 0.0040(9) 0.0040(8)

C3 0.0277(9) 0.0224(9) 0.0237(13) -0.0012(8) 0.0045(9) -0.0024(7)

C4 0.0383(11) 0.0360(11) 0.0316(15) 0.0129(10) 0.0158(10) 0.0035(9)

C5 0.0586(16) 0.0576(16) 0.0323(18) 0.0062(14) 0.0146(14) 0.0065(13)

C6 0.0490(14) 0.0402(13) 0.054(2) 0.0112(14) 0.0166(14) -0.0051(11)

C7 0.0497(15) 0.0530(16) 0.057(2) 0.0327(16) 0.0204(15) 0.0151(12)

C8 0.0319(10) 0.0214(9) 0.0240(13) -0.0025(9) 0.0080(9) 0.0005(7)

C9 0.0336(10) 0.0275(10) 0.0229(14) -0.0013(10) 0.0066(9) -0.0058(8)

C10 0.0230(9) 0.0264(9) 0.0229(13) 0.0013(8) -0.0007(9) 0.0014(7)

C11 0.0349(11) 0.0331(11) 0.0367(15) -0.0011(10) 0.0145(10) -0.0062(8)

C12 0.0587(17) 0.0487(15) 0.059(2) -0.0038(15) 0.0378(16) -0.0113(13)

C13 0.0414(14) 0.082(2) 0.053(2) -0.0026(18) 0.0086(14) -0.0265(15)

C14 0.075(2) 0.0457(15) 0.076(3) 0.0219(17) 0.039(2) 0.0114(14)

C15 0.0272(10) 0.0211(9) 0.0254(14) 0.0011(9) 0.0039(9) -0.0050(7)

C16 0.0271(10) 0.0175(8) 0.0284(15) 0.0007(9) 0.0008(9) -0.0050(7)

C17 0.0243(9) 0.0205(9) 0.0243(13) -0.0013(8) 0.0040(8) -0.0006(7)

C18 0.0354(10) 0.0190(9) 0.0315(15) 0.0016(9) -0.0074(9) 0.0016(7)

C19 0.0474(14) 0.0332(12) 0.0343(17) 0.0124(11) -0.0043(12) -0.0034(10)

C20 0.0725(19) 0.0189(10) 0.050(2) 0.0069(11) -0.0209(16) 0.0006(11)

C21 0.0384(12) 0.0404(14) 0.052(2) -0.0009(13) -0.0045(13) 0.0130(10)

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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_geom_bond_atom_site_label_2
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S1 C3 1.6988(19) . ?
S2 C10 1.697(2) . ?
S3 C17 1.7151(19) . ?
N1 C1 1.450(2) . ?
N1 C8 1.460(3) . ?
N1 C15 1.467(2) . ?
N2 C3 1.353(3) . ?
N2 C2 1.454(2) . ?
N2 H2N 0.82(2) . ?
N3 C3 1.339(2) . ?
N3 C4 1.480(3) . ?
N3 H3N 0.83(2) . ?

N4 C10 1.356(2) . ?

N4 C9 1.453(3) . ?

N4 H4N 0.83(2) . ?

N5 C10 1.331(3) . ?

N5 C11 1.484(3) . ?

N5 H5N 0.76(2) . ?

N6 C17 1.334(2) . ?

N6 C16 1.457(2) . ?

N6 H6N 0.821(18) . ?

N7 C17 1.338(2) . ?

N7 C18 1.483(2) . ?

N7 H7N 0.80(2) . ?

C1 C2 1.521(3) . ?

C1 H1A 0.97(2) . ?

C1 H1B 0.98(2) . ?

C2 H2A 0.917(18) . ?

C2 H2B 0.992(18) . ?

C4 C5 1.516(3) . ?

C4 C6 1.525(3) . ?

C4 C7 1.534(3) . ?

C5 H5A 0.99(3) . ?

C5 H5B 1.01(3) . ?

C5 H5C 0.95(2) . ?

C6 H6A 0.98(3) . ?

C6 H6B 0.97(3) . ?

C6 H6C 0.95(3) . ?

C7 H7A 1.00(3) . ?

C7 H7B 0.96(3) . ?

C7 H7C 0.95(3) . ?

C8 C9 1.519(3) . ?

C8 H8A 0.97(2) . ?

C8 H8B 0.986(19) . ?

C9 H9A 0.96(2) . ?

C9 H9B 0.947(19) . ?

C11 C12 1.516(3) . ?

C11 C14 1.517(3) . ?

C11 C13 1.522(3) . ?

C12 H12A 0.96(2) . ?

C12 H12B 0.97(2) . ?

C12 H12C 0.95(3) . ?

C13 H13A 0.98(3) . ?

C13 H13B 1.00(4) . ?

C13 H13C 0.93(3) . ?

C14 H14A 0.98(3) . ?

C14 H14B 0.92(3) . ?

C14 H14C 1.00(3) . ?

C15 C16 1.515(3) . ?

C15 H15A 0.98(2) . ?

C15 H15B 0.953(18) . ?

C16 H16A 0.96(2) . ?

C16 H16B 0.946(18) . ?

C18 C19 1.521(3) . ?

C18 C20 1.524(3) . ?

C18 C21 1.524(3) . ?

C19 H19A 0.94(2) . ?

C19 H19B 0.96(3) . ?

C19 H19C 0.98(2) . ?

C20 H20A 0.94(3) . ?

C20 H20B 0.93(3) . ?

C20 H20C 1.00(3) . ?

C21 H21A 0.90(3) . ?

C21 H21B 0.96(2) . ?

C21 H21C 0.97(2) . ?

loop_

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C10 N4 C9 125.17(18) . . ?

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C17 N6 H6N 119.5(12) . . ?

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N2 H2N S3 0.82(2) 2.99(2) 3.7561(17) 155.6(19) 3_666

N7 H7N S3 0.80(2) 2.60(2) 3.3847(17) 167.9(18) 3_676

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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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H9 H 0.1312(16) 0.4680(16) 0.5974(8) 0.044(7) Uiso 1 1 d . . .
H10A H 0.4228(14) 0.2931(14) 0.7006(7) 0.029(6) Uiso 1 1 d . . .
H10B H 0.4060(15) 0.3223(14) 0.7538(8) 0.031(6) Uiso 1 1 d . . .
H11A H 0.3384(16) 0.1752(16) 0.7370(8) 0.039(6) Uiso 1 1 d . . .
H11B H 0.2500(15) 0.2451(14) 0.7426(7) 0.026(5) Uiso 1 1 d . . .
H14 H 0.1258(15) 0.1180(15) 0.5266(7) 0.037(6) Uiso 1 1 d . . .
H15 H -0.0091(17) 0.0937(18) 0.4695(9) 0.057(8) Uiso 1 1 d . . .
H16 H -0.1673(17) 0.1194(17) 0.4882(8) 0.047(7) Uiso 1 1 d . . .
H17 H -0.1890(17) 0.1728(15) 0.5663(8) 0.041(7) Uiso 1 1 d . . .
H18 H -0.0511(17) 0.1951(17) 0.6209(9) 0.051(8) Uiso 1 1 d . . .
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H19B H 0.3166(15) 0.4924(16) 0.7557(7) 0.037(6) Uiso 1 1 d . . .
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H20B H 0.1583(17) 0.5375(17) 0.7441(9) 0.054(7) Uiso 1 1 d . . .
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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_cell_length_c                    9.7837(7)
_cell_angle_alpha                 69.1930(10)
_cell_angle_beta                  66.8720(10)
_cell_angle_gamma                 65.6220(10)
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;

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_computing_molecular_graphics     'Bruker SHELXTL'
_computing_publication_material   'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
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_atom_sites_solution_hydrogens    geom
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 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
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 _atom_site_disorder_group
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N1 N 0.8447(3) 0.4522(3) 0.1267(3) 0.0462(6) Uani 1 1 d . . .
N2 N 0.6594(4) 0.2073(3) 0.1808(3) 0.0515(7) Uani 1 1 d . . .
N3 N 0.7064(3) 0.1080(3) -0.0213(3) 0.0472(6) Uani 1 1 d . . .
C1 C 0.9575(4) 0.6115(4) -0.1338(3) 0.0550(8) Uani 1 1 d . . .
H1A H 0.9393 0.5370 -0.1777 0.066 Uiso 1 1 calc R . .
H1B H 0.9334 0.7259 -0.2020 0.066 Uiso 1 1 calc R . .
C2 C 0.8152(4) 0.6193(4) 0.0216(4) 0.0570(8) Uani 1 1 d . . .
H2A H 0.8290 0.6982 0.0634 0.068 Uiso 1 1 calc R . .
H2B H 0.6829 0.6633 0.0125 0.068 Uiso 1 1 calc R . .
C3 C 0.7054(5) 0.4662(4) 0.2787(3) 0.0617(9) Uani 1 1 d . . .
H3A H 0.5799 0.5470 0.2650 0.074 Uiso 1 1 calc R . .
H3B H 0.7502 0.5135 0.3305 0.074 Uiso 1 1 calc R . .
C4 C 0.6768(6) 0.3050(5) 0.3786(4) 0.0706(10) Uani 1 1 d . . .
H4A H 0.6079 0.3212 0.4839 0.085 Uiso 1 1 calc R . .
H4B H 0.8048 0.2201 0.3797 0.085 Uiso 1 1 calc R . .
C5 C 0.5665(5) 0.2328(5) 0.3360(3) 0.0599(9) Uani 1 1 d . . .
H5A H 0.5593 0.1236 0.4085 0.072 Uiso 1 1 calc R . .
H5B H 0.4336 0.3111 0.3442 0.072 Uiso 1 1 calc R . .
C6 C 0.6161(4) 0.1147(3) 0.1255(3) 0.0404(6) Uani 1 1 d . . .
C7 C 0.8386(4) 0.1998(4) -0.1276(3) 0.0500(7) Uani 1 1 d . . .
H7A H 0.9471 0.1697 -0.0869 0.060 Uiso 1 1 calc R . .
H7B H 0.7713 0.3227 -0.1383 0.060 Uiso 1 1 calc R . .
C8 C 0.9154(5) 0.1587(5) -0.2818(3) 0.0644(9) Uani 1 1 d . . .
H8A H 0.9793 0.0353 -0.2697 0.077 Uiso 1 1 calc R . .
H8B H 0.8062 0.1902 -0.3220 0.077 Uiso 1 1 calc R . .
C9 C 1.0548(6) 0.2472(6) -0.3951(4) 0.0857(13) Uani 1 1 d . . .
H9A H 1.1002 0.2146 -0.4924 0.129 Uiso 1 1 calc R . .
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H9B H 1.1644 0.2155 -0.3569 0.129 Uiso 1 1 calc R . .
H9C H 0.9913 0.3696 -0.4105 0.129 Uiso 1 1 calc R . .
H2N H 0.731(5) 0.271(4) 0.121(4) 0.063(10) Uiso 1 1 d . . .
H3N H 0.660(4) 0.064(4) -0.054(3) 0.049(8) Uiso 1 1 d . . .

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 _atom_site_aniso_U_12
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N1 0.0478(14) 0.0497(14) 0.0440(13) -0.0145(11) -0.0034(11) -0.0243(11)
N2 0.0669(17) 0.0682(17) 0.0345(13) -0.0120(12) -0.0027(11) -0.0467(15)
N3 0.0547(15) 0.0661(16) 0.0372(13) -0.0149(11) -0.0072(11) -0.0378(13)
C1 0.0597(19) 0.0556(18) 0.0514(17) -0.0044(14) -0.0175(15) -0.0251(15)
C2 0.0452(17) 0.0520(18) 0.064(2) -0.0108(15) -0.0074(15) -0.0159(14)
C3 0.070(2) 0.072(2) 0.0518(18) -0.0274(16) 0.0044(16) -0.0404(18)
C4 0.096(3) 0.092(3) 0.0418(17) -0.0238(17) 0.0004(17) -0.059(2)
C5 0.076(2) 0.084(2) 0.0362(15) -0.0205(15) 0.0038(14) -0.0546(19)
C6 0.0441(15) 0.0486(15) 0.0349(14) -0.0069(11) -0.0123(11) -0.0223(12)
C7 0.0567(18) 0.0670(19) 0.0370(15) -0.0121(14) -0.0065(13) -0.0361(15)
C8 0.072(2) 0.094(3) 0.0449(17) -0.0240(17) -0.0037(16) -0.049(2)
C9 0.096(3) 0.125(4) 0.050(2) -0.022(2) 0.0060(19) -0.072(3)

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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C1 1.461(4) 2_765 ?
N1 C2 1.467(4) . ?
N1 C3 1.477(4) . ?
N2 C6 1.340(3) . ?
N2 C5 1.460(4) . ?
N2 H2N 0.87(3) . ?
N3 C6 1.340(3) . ?
N3 C7 1.454(3) . ?
N3 H3N 0.83(3) . ?

C1 N1 1.461(4) 2_765 ?
C1 C2 1.503(4) . ?
C1 H1A 0.9900 . ?
C1 H1B 0.9900 . ?
C2 H2A 0.9900 . ?
C2 H2B 0.9900 . ?
C3 C4 1.476(4) . ?
C3 H3A 0.9900 . ?
C3 H3B 0.9900 . ?
C4 C5 1.519(4) . ?
C4 H4A 0.9900 . ?
C4 H4B 0.9900 . ?
C5 H5A 0.9900 . ?
C5 H5B 0.9900 . ?
C7 C8 1.506(4) . ?
C7 H7A 0.9900 . ?
C7 H7B 0.9900 . ?
C8 C9 1.491(4) . ?
C8 H8A 0.9900 . ?
C8 H8B 0.9900 . ?
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C9 H9B 0.9800 . ?
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C1 N1 C3 111.3(2) 2_765 . ?
C2 N1 C3 109.5(2) . . ?
C6 N2 C5 123.3(2) . . ?
C6 N2 H2N 122(2) . . ?
C5 N2 H2N 114(2) . . ?
C6 N3 C7 125.6(2) . . ?
C6 N3 H3N 113(2) . . ?
C7 N3 H3N 120(2) . . ?
N1 C1 C2 111.5(3) 2_765 . ?
N1 C1 H1A 109.3 2_765 . ?
C2 C1 H1A 109.3 . . ?
N1 C1 H1B 109.3 2_765 . ?
C2 C1 H1B 109.3 . . ?
H1A C1 H1B 108.0 . . ?
N1 C2 C1 111.3(2) . . ?
N1 C2 H2A 109.4 . . ?
C1 C2 H2A 109.4 . . ?
N1 C2 H2B 109.4 . . ?
C1 C2 H2B 109.4 . . ?
H2A C2 H2B 108.0 . . ?

N1 C3 C4 114.3(3) . . ?
N1 C3 H3A 108.7 . . ?
C4 C3 H3A 108.7 . . ?
N1 C3 H3B 108.7 . . ?
C4 C3 H3B 108.7 . . ?
H3A C3 H3B 107.6 . . ?
C3 C4 C5 116.3(3) . . ?
C3 C4 H4A 108.2 . . ?
C5 C4 H4A 108.2 . . ?
C3 C4 H4B 108.2 . . ?
C5 C4 H4B 108.2 . . ?
H4A C4 H4B 107.4 . . ?
N2 C5 C4 111.1(2) . . ?
N2 C5 H5A 109.4 . . ?
C4 C5 H5A 109.4 . . ?
N2 C5 H5B 109.4 . . ?
C4 C5 H5B 109.4 . . ?
H5A C5 H5B 108.0 . . ?
N3 C6 N2 117.0(2) . . ?
N3 C6 S1 120.5(2) . . ?
N2 C6 S1 122.4(2) . . ?
N3 C7 C8 110.9(2) . . ?
N3 C7 H7A 109.5 . . ?
C8 C7 H7A 109.5 . . ?
N3 C7 H7B 109.5 . . ?
C8 C7 H7B 109.5 . . ?
H7A C7 H7B 108.0 . . ?
C9 C8 C7 113.3(3) . . ?
C9 C8 H8A 108.9 . . ?
C7 C8 H8A 108.9 . . ?
C9 C8 H8B 108.9 . . ?
C7 C8 H8B 108.9 . . ?
H8A C8 H8B 107.7 . . ?
C8 C9 H9A 109.5 . . ?
C8 C9 H9B 109.5 . . ?
H9A C9 H9B 109.5 . . ?
C8 C9 H9C 109.5 . . ?
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C1 N1 C3 C4 -79.6(4) 2_765 . . . ?
C2 N1 C3 C4 161.0(3) . . . . ?
N1 C3 C4 C5 -71.7(4) . . . . ?
C6 N2 C5 C4 166.0(3) . . . . ?
C3 C4 C5 N2 57.4(4) . . . . ?
C7 N3 C6 N2 -3.7(4) . . . . ?
C7 N3 C6 S1 177.6(2) . . . . ?
C5 N2 C6 N3 177.1(3) . . . . ?
C5 N2 C6 S1 -4.2(4) . . . . ?
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N2 H2N N1  0.87(3) 2.18(3) 2.911(3) 142(3) .

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'H'  'H'   0.0000   0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N'  'N'   0.0061   0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'S'  'S'   0.1246   0.1234
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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 _symmetry_equiv_pos_as_xyz
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 '-x, -y, -z'

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_cell_length_c                   9.4581(12)
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_cell_angle_beta                 76.883(2)
_cell_angle_gamma                 82.603(2)
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_exptl_special_details
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;

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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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_atom_sites_solution_hydrogens    geom
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 _atom_site_fract_z
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 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
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 _atom_site_refinement_flags
 _atom_site_disorder_assembly
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S1 S 0.19140(6) 0.56239(4) 0.29176(4) 0.03720(15) Uani 1 1 d . . .
N1 N 0.13615(16) 0.09888(13) -0.01088(12) 0.0269(3) Uani 1 1 d . . .
N2 N 0.12567(18) 0.37221(14) 0.12038(14) 0.0315(3) Uani 1 1 d . . .
N3 N -0.08475(18) 0.40433(14) 0.33429(15) 0.0327(3) Uani 1 1 d . . .
C1 C -0.1552(2) 0.04375(17) -0.05910(17) 0.0307(3) Uani 1 1 d . . .
C2 C 0.0306(2) 0.09390(17) -0.12345(16) 0.0303(3) Uani 1 1 d . . .
C3 C 0.3196(2) 0.14434(18) -0.07466(18) 0.0341(4) Uani 1 1 d . . .
C4 C 0.3153(2) 0.30339(18) -0.11601(17) 0.0357(4) Uani 1 1 d . . .
C5 C 0.2941(2) 0.39593(18) 0.01334(17) 0.0346(4) Uani 1 1 d . . .
C6 C 0.0715(2) 0.43834(15) 0.24626(16) 0.0287(3) Uani 1 1 d . . .
C7 C -0.1987(2) 0.30277(17) 0.30236(17) 0.0308(3) Uani 1 1 d . . .
C8 C -0.3793(2) 0.30532(19) 0.41329(19) 0.0347(4) Uani 1 1 d . . .
C9 C -0.5038(2) 0.20519(18) 0.37778(17) 0.0320(3) Uani 1 1 d . . .
C10 C -0.6816(2) 0.2003(2) 0.49173(19) 0.0374(4) Uani 1 1 d . . .
C11 C -0.8081(3) 0.1026(2) 0.4550(2) 0.0451(4) Uani 1 1 d . . .
H2N H 0.079(2) 0.2996(19) 0.1085(18) 0.036(5) Uiso 1 1 d . . .
H3N H -0.107(2) 0.4304(18) 0.416(2) 0.034(5) Uiso 1 1 d . . .
H1A H -0.223(2) 0.0399(16) -0.1344(17) 0.028(4) Uiso 1 1 d . . .
H1B H -0.230(2) 0.1154(17) 0.0126(18) 0.031(4) Uiso 1 1 d . . .
H2A H 0.013(2) 0.1832(18) -0.1678(17) 0.029(4) Uiso 1 1 d . . .
H2B H 0.100(2) 0.0286(17) -0.1987(17) 0.028(4) Uiso 1 1 d . . .
H3A H 0.392(2) 0.1220(17) -0.0010(18) 0.032(4) Uiso 1 1 d . . .
H3B H 0.376(2) 0.0847(18) -0.158(2) 0.041(5) Uiso 1 1 d . . .
H4A H 0.424(3) 0.3198(18) -0.1802(19) 0.036(4) Uiso 1 1 d . . .
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H4B H 0.218(3) 0.3346(18) -0.1689(19) 0.042(5) Uiso 1 1 d . . .
H5A H 0.288(2) 0.498(2) -0.0198(19) 0.041(5) Uiso 1 1 d . . .
H5B H 0.402(2) 0.3713(18) 0.0604(18) 0.037(4) Uiso 1 1 d . . .
H7A H -0.132(2) 0.2077(19) 0.2993(18) 0.036(4) Uiso 1 1 d . . .
H7B H -0.223(2) 0.3261(18) 0.2069(19) 0.039(5) Uiso 1 1 d . . .
H8A H -0.349(3) 0.2779(19) 0.509(2) 0.045(5) Uiso 1 1 d . . .
H8B H -0.440(3) 0.397(2) 0.419(2) 0.051(5) Uiso 1 1 d . . .
H9A H -0.443(2) 0.1055(18) 0.3691(17) 0.033(4) Uiso 1 1 d . . .
H9B H -0.534(2) 0.2324(18) 0.2801(19) 0.040(5) Uiso 1 1 d . . .
H10A H -0.746(3) 0.299(2) 0.500(2) 0.053(5) Uiso 1 1 d . . .
H10B H -0.651(3) 0.1666(19) 0.588(2) 0.047(5) Uiso 1 1 d . . .
H11A H -0.830(3) 0.130(2) 0.357(2) 0.051(5) Uiso 1 1 d . . .
H11B H -0.745(3) 0.002(2) 0.444(2) 0.052(6) Uiso 1 1 d . . .
H11C H -0.922(3) 0.105(2) 0.528(2) 0.068(7) Uiso 1 1 d . . .

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 _atom_site_aniso_U_13
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N1 0.0248(6) 0.0295(6) 0.0271(6) -0.0036(5) -0.0045(5) -0.0060(5)
N2 0.0320(7) 0.0324(7) 0.0311(7) -0.0051(5) -0.0021(5) -0.0138(6)
N3 0.0319(7) 0.0342(7) 0.0323(7) -0.0113(6) -0.0016(6) -0.0098(6)
C1 0.0299(8) 0.0322(8) 0.0321(8) -0.0025(6) -0.0108(7) -0.0035(6)
C2 0.0345(8) 0.0298(8) 0.0276(8) -0.0016(6) -0.0072(6) -0.0065(6)
C3 0.0265(8) 0.0411(9) 0.0335(8) -0.0075(7) -0.0005(7) -0.0068(7)
C4 0.0328(8) 0.0447(10) 0.0287(8) -0.0007(7) 0.0009(7) -0.0155(7)
C5 0.0339(9) 0.0365(9) 0.0334(8) 0.0007(7) -0.0020(7) -0.0149(7)
C6 0.0298(8) 0.0248(7) 0.0322(8) -0.0018(6) -0.0072(6) -0.0049(6)
C7 0.0291(8) 0.0318(8) 0.0323(8) -0.0081(6) -0.0041(6) -0.0075(6)
C8 0.0300(8) 0.0351(9) 0.0385(9) -0.0109(7) -0.0014(7) -0.0081(7)
C9 0.0297(8) 0.0340(9) 0.0330(8) -0.0060(7) -0.0058(6) -0.0056(7)
C10 0.0337(9) 0.0429(10) 0.0361(9) -0.0047(7) -0.0040(7) -0.0107(7)
C11 0.0384(10) 0.0520(12) 0.0488(11) 0.0025(9) -0.0120(9) -0.0181(9)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

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N1 C2 1.4707(19) . ?
N1 C3 1.4777(18) . ?
N2 C6 1.3397(19) . ?
N2 C5 1.4607(19) . ?
N2 H2N 0.834(18) . ?
N3 C6 1.337(2) . ?
N3 C7 1.4543(19) . ?
N3 H3N 0.807(18) . ?
C1 N1 1.4628(19) 2 ?
C1 C2 1.512(2) . ?
C1 H1A 0.970(16) . ?
C1 H1B 1.013(17) . ?
C2 H2A 0.922(16) . ?
C2 H2B 0.986(16) . ?
C3 C4 1.524(2) . ?
C3 H3A 0.972(17) . ?
C3 H3B 0.982(18) . ?
C4 C5 1.522(2) . ?
C4 H4A 0.925(18) . ?
C4 H4B 0.983(19) . ?
C5 H5A 0.994(18) . ?
C5 H5B 1.004(18) . ?
C7 C8 1.513(2) . ?
C7 H7A 0.970(17) . ?
C7 H7B 0.967(18) . ?
C8 C9 1.516(2) . ?
C8 H8A 0.993(19) . ?
C8 H8B 0.92(2) . ?
C9 C10 1.517(2) . ?
C9 H9A 0.993(17) . ?
C9 H9B 1.009(18) . ?
C10 C11 1.516(2) . ?
C10 H10A 0.99(2) . ?
C10 H10B 1.005(19) . ?
C11 H11A 0.99(2) . ?
C11 H11B 1.01(2) . ?
C11 H11C 0.97(2) . ?

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C1 N1 C3 110.21(12) 2 . ?
C2 N1 C3 110.93(12) . . ?
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C6 N2 C5 123.54(13) . . ?
C6 N2 H2N 120.1(12) . . ?
C5 N2 H2N 114.6(12) . . ?
C6 N3 C7 124.79(13) . . ?
C6 N3 H3N 116.9(13) . . ?
C7 N3 H3N 117.2(13) . . ?
N1 C1 C2 111.34(12) 2 . ?
N1 C1 H1A 108.1(9) 2 . ?
C2 C1 H1A 110.3(9) . . ?
N1 C1 H1B 110.9(9) 2 . ?
C2 C1 H1B 109.0(9) . . ?
H1A C1 H1B 107.2(13) . . ?
N1 C2 C1 111.04(12) . . ?
N1 C2 H2A 110.3(10) . . ?
C1 C2 H2A 108.8(10) . . ?
N1 C2 H2B 109.4(9) . . ?
C1 C2 H2B 109.5(9) . . ?
H2A C2 H2B 107.7(13) . . ?
N1 C3 C4 113.77(13) . . ?
N1 C3 H3A 106.3(10) . . ?
C4 C3 H3A 108.6(10) . . ?
N1 C3 H3B 107.4(10) . . ?
C4 C3 H3B 112.4(10) . . ?
H3A C3 H3B 108.0(14) . . ?
C5 C4 C3 113.34(14) . . ?
C5 C4 H4A 107.5(11) . . ?
C3 C4 H4A 109.2(11) . . ?
C5 C4 H4B 110.2(10) . . ?
C3 C4 H4B 110.5(10) . . ?
H4A C4 H4B 105.6(14) . . ?
N2 C5 C4 110.07(13) . . ?
N2 C5 H5A 109.1(10) . . ?
C4 C5 H5A 109.6(10) . . ?
N2 C5 H5B 108.8(10) . . ?
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H5A C5 H5B 109.1(14) . . ?
N3 C6 N2 116.76(13) . . ?
N3 C6 S1 121.08(11) . . ?
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N3 C7 C8 111.37(12) . . ?
N3 C7 H7A 109.5(10) . . ?
C8 C7 H7A 110.5(10) . . ?
N3 C7 H7B 109.2(10) . . ?
C8 C7 H7B 109.2(10) . . ?
H7A C7 H7B 107.0(14) . . ?
C7 C8 C9 112.12(13) . . ?
C7 C8 H8A 107.0(11) . . ?
C9 C8 H8A 110.8(11) . . ?
C7 C8 H8B 110.2(12) . . ?
C9 C8 H8B 109.4(12) . . ?
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C8 C9 C10 113.02(13) . . ?
C8 C9 H9A 111.8(10) . . ?

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C10 C9 H9A 106.6(9) . . ?
C8 C9 H9B 110.9(10) . . ?
C10 C9 H9B 109.1(10) . . ?
H9A C9 H9B 105.0(13) . . ?
C11 C10 C9 113.16(14) . . ?
C11 C10 H10A 109.3(11) . . ?
C9 C10 H10A 107.8(12) . . ?
C11 C10 H10B 108.9(10) . . ?
C9 C10 H10B 108.8(11) . . ?
H10A C10 H10B 108.8(15) . . ?
C10 C11 H11A 109.0(11) . . ?
C10 C11 H11B 110.5(11) . . ?
H11A C11 H11B 103.4(16) . . ?
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C3 N1 C2 C1 178.54(13) . . . . ?
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C1 N1 C3 C4 -165.53(13) 2 . . . ?
C2 N1 C3 C4 74.70(17) . . . . ?
N1 C3 C4 C5 78.06(18) . . . . ?
C6 N2 C5 C4 179.49(15) . . . . ?
C3 C4 C5 N2 -57.95(19) . . . . ?
C7 N3 C6 N2 -0.5(2) . . . . ?
C7 N3 C6 S1 178.16(12) . . . . ?
C5 N2 C6 N3 -179.14(14) . . . . ?
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C6 N3 C7 C8 -171.42(15) . . . . ?
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C8 C9 C10 C11 178.83(16) . . . . ?

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 _geom_hbond_distance_DH
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 _geom_hbond_distance_DA
 _geom_hbond_angle_DHA
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N3 H3N S1  0.807(18) 2.691(18) 3.4726(15) 163.5(16) 2_566

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 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
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_symmetry_space_group_name_H-M    P2(1)/n

loop_
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 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'
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_cell_length_c                  13.8136(15)
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_cell_angle_beta                 102.1330(10)
_cell_angle_gamma                90.00
_cell_volume                    2237.0(4)
_cell_formula_units_Z            4
_cell_measurement_temperature     173(2)
_cell_measurement_reflns_used     8911
_cell_measurement_theta_min       2.29
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_exptl_special_details
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_diffrn_radiation_monochromator   graphite
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_diffrn_measurement_method        'phi and omega scans'
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_computing_cell_refinement       'Bruker SMART'
_computing_data_reduction        'Bruker SAINT'
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_computing_molecular_graphics    'Bruker SHELXTL'
_computing_publication_material  'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_scheme      calc
_refine_ls_weighting_details
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_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   geom
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_refine_ls_extinction_method     none
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_refine_ls_number_reflns         4886
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_refine_ls_wR_factor_ref         0.0968
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 _atom_site_type_symbol
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_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group
S1 S 0.79202(3) 1.08159(2) 0.44760(2) 0.02840(10) Uani 1 1 d . . .
S2 S 0.43841(3) 0.19507(3) 0.30954(3) 0.04129(12) Uani 1 1 d . . .
N1 N 0.74232(10) 0.69141(8) 0.40897(8) 0.0295(2) Uani 1 1 d . . .
N2 N 0.53367(9) 0.57648(7) 0.34197(7) 0.0268(2) Uani 1 1 d . . .
N3 N 0.75910(9) 0.89746(8) 0.42469(8) 0.0289(2) Uani 1 1 d . . .
N4 N 0.60245(9) 0.99130(8) 0.35477(8) 0.0288(2) Uani 1 1 d . . .
N5 N 0.49568(9) 0.37537(8) 0.30782(8) 0.0287(2) Uani 1 1 d . . .
N6 N 0.63072(10) 0.28029(8) 0.40694(8) 0.0293(2) Uani 1 1 d . . .
C1 C 0.72318(12) 0.63706(10) 0.31714(10) 0.0333(3) Uani 1 1 d . . .
C2 C 0.59344(12) 0.62621(10) 0.27354(10) 0.0321(3) Uani 1 1 d . . .
C3 C 0.55343(13) 0.62967(10) 0.43522(10) 0.0339(3) Uani 1 1 d . . .
C4 C 0.68298(13) 0.64358(10) 0.47873(10) 0.0353(3) Uani 1 1 d . . .
C5 C 0.86955(12) 0.70161(10) 0.45039(12) 0.0369(3) Uani 1 1 d . . .
C6 C 0.89845(13) 0.78472(10) 0.52017(11) 0.0377(3) Uani 1 1 d . . .
C7 C 0.88296(11) 0.87903(10) 0.46784(11) 0.0325(3) Uani 1 1 d . . .
C8 C 0.71337(10) 0.98320(9) 0.40678(8) 0.0242(2) Uani 1 1 d . . .
C9 C 0.51882(11) 0.91544(9) 0.32150(10) 0.0289(3) Uani 1 1 d . . .
C10 C 0.45099(14) 0.89081(12) 0.40092(12) 0.0412(3) Uani 1 1 d . . .
C11 C 0.43651(13) 0.94525(12) 0.22542(11) 0.0382(3) Uani 1 1 d . . .
C12 C 0.40615(12) 0.56927(10) 0.29991(10) 0.0321(3) Uani 1 1 d . . .
C13 C 0.37669(12) 0.49941(10) 0.21472(10) 0.0323(3) Uani 1 1 d . . .
C14 C 0.38038(12) 0.39769(10) 0.24621(10) 0.0325(3) Uani 1 1 d . . .
C15 C 0.52675(11) 0.28967(9) 0.34266(9) 0.0280(3) Uani 1 1 d . . .
C16 C 0.71897(11) 0.35359(9) 0.43542(9) 0.0282(3) Uani 1 1 d . . .
C17 C 0.79060(15) 0.36754(13) 0.35661(13) 0.0444(4) Uani 1 1 d . . .
C18 C 0.79661(13) 0.32778(11) 0.53490(11) 0.0373(3) Uani 1 1 d . . .
H3N H 0.7195(14) 0.8503(12) 0.4054(11) 0.039(4) Uiso 1 1 d . . .
H4N H 0.5747(14) 1.0468(12) 0.3503(11) 0.037(4) Uiso 1 1 d . . .
H5N H 0.5365(14) 0.4215(11) 0.3299(11) 0.035(4) Uiso 1 1 d . . .
H6N H 0.6539(13) 0.2275(12) 0.4185(11) 0.036(4) Uiso 1 1 d . . .
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H1B H 0.7592(14) 0.6694(11) 0.2718(11) 0.039(4) Uiso 1 1 d . . .
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H2B H 0.5822(13) 0.5933(11) 0.2135(12) 0.036(4) Uiso 1 1 d . . .
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H3B H 0.5178(13) 0.5945(11) 0.4799(11) 0.034(4) Uiso 1 1 d . . .
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H4B H 0.6910(13) 0.6809(12) 0.5393(11) 0.038(4) Uiso 1 1 d . . .
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H5B H 0.8990(14) 0.6434(12) 0.4829(11) 0.040(4) Uiso 1 1 d . . .
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H7B H 0.9103(14) 0.9275(11) 0.5110(11) 0.037(4) Uiso 1 1 d . . .
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C5 0.0304(7) 0.0301(7) 0.0455(8) -0.0017(6) -0.0028(6) 0.0064(5)
C6 0.0313(7) 0.0387(8) 0.0371(7) -0.0037(6) -0.0067(6) 0.0055(6)
C7 0.0225(6) 0.0312(7) 0.0399(7) -0.0061(6) -0.0024(5) 0.0018(5)
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C9 0.0213(6) 0.0281(6) 0.0357(7) -0.0056(5) 0.0026(5) 0.0002(5)
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C16 0.0231(6) 0.0266(6) 0.0337(6) -0.0037(5) 0.0034(5) 0.0013(5)
C17 0.0373(8) 0.0480(9) 0.0513(9) 0.0072(7) 0.0170(7) 0.0032(7)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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 on F^2^ are statistically about twice as large as those based on F, and R-
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H2B H 0.377(2) 1.240(2) 0.367(2) 0.027(5) Uiso 1 1 d . . .
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H8B H 0.689(3) 0.875(3) 0.039(3) 0.047(6) Uiso 1 1 d . . .
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H10B H 0.860(3) 0.565(3) 0.085(3) 0.041(6) Uiso 1 1 d . . .
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N2 0.0146(6) 0.0268(7) 0.0251(7) -0.0149(6) 0.0015(5) -0.0055(5)
N3 0.0179(7) 0.0282(7) 0.0326(8) -0.0209(7) 0.0019(6) -0.0045(6)
C1 0.0280(9) 0.0332(9) 0.0237(8) -0.0129(7) 0.0045(7) -0.0146(8)
C2 0.0302(9) 0.0248(8) 0.0219(8) -0.0084(7) -0.0005(7) -0.0095(7)
C3 0.0213(8) 0.0275(9) 0.0299(9) -0.0162(8) -0.0008(7) -0.0002(7)
C4 0.0158(8) 0.0348(9) 0.0306(9) -0.0180(8) 0.0042(6) -0.0046(7)
C5 0.0149(8) 0.0320(9) 0.0296(9) -0.0170(8) 0.0025(6) -0.0061(7)
C6 0.0198(8) 0.0222(8) 0.0222(8) -0.0088(6) 0.0023(6) -0.0074(6)
C7 0.0178(8) 0.0243(8) 0.0269(8) -0.0135(7) 0.0015(6) -0.0053(6)
C8 0.0238(9) 0.0298(9) 0.0434(11) -0.0199(9) 0.0099(8) -0.0097(7)
C9 0.0279(10) 0.0383(11) 0.0273(9) -0.0128(8) -0.0012(7) -0.0032(8)
C10 0.0184(8) 0.0340(10) 0.0430(11) -0.0226(9) 0.0015(7) -0.0027(7)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 C5 1.4639(19) . ?
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N3 C6 1.350(2) . ?
N3 C7 1.483(2) . ?
N3 H3N 0.802(18) . ?
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C3 H3B 1.016(17) . ?
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C7 C10 1.529(2) . ?
C8 H8A 0.98(2) . ?
C8 H8B 0.97(2) . ?
C8 H8C 0.964(19) . ?
C9 H9A 0.94(2) . ?
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C1 N1 C3 109.78(13) 2_676 . ?
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C6 N2 C5 122.05(13) . . ?
C6 N2 H2N 119.5(11) . . ?
C5 N2 H2N 118.4(11) . . ?
C6 N3 C7 130.44(14) . . ?
C6 N3 H3N 114.4(14) . . ?
C7 N3 H3N 115.1(14) . . ?
N1 C1 C2 112.19(14) 2_676 . ?
N1 C1 H1A 107.7(11) 2_676 . ?
C2 C1 H1A 110.1(11) . . ?
N1 C1 H1B 109.3(10) 2_676 . ?
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H1A C1 H1B 108.3(15) . . ?
N1 C2 C1 111.90(14) . . ?
N1 C2 H2A 108.1(10) . . ?
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H2A C2 H2B 109.7(14) . . ?
N1 C3 C4 113.92(14) . . ?
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'-x, -y, -z'

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_reflns_threshold_expression     >2sigma(I)

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_computing_cell_refinement       'Bruker SMART'
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_computing_molecular_graphics    'Bruker SHELXTL'
_computing_publication_material  'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;
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_refine_ls_structure_factor_coef Fsqd

_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0618P)^2^+0.1351P] where P=(Fo^2^+2Fc^2^)/3'

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_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens difmap

_refine_ls_hydrogen_treatment refall

_refine_ls_extinction_method none

_refine_ls_extinction_coef ?

_refine_ls_number_reflns 2842

_refine_ls_number_parameters 230

_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.0412

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N1 N 0.35822(15) 0.92005(14) 0.54521(11) 0.0220(2) Uani 1 1 d . . .

N2 N 0.18894(18) 0.60222(16) 0.52342(12) 0.0289(3) Uani 1 1 d . . .

N3 N 0.28742(16) 0.79089(14) 0.34698(12) 0.0243(3) Uani 1 1 d . . .

C1 C 0.68384(19) 0.90165(17) 0.51718(15) 0.0261(3) Uani 1 1 d . . .

C2 C 0.51998(19) 0.86426(18) 0.61371(14) 0.0245(3) Uani 1 1 d . . .

C3 C 0.1955(2) 0.88913(19) 0.63825(15) 0.0283(3) Uani 1 1 d . . .

C4 C 0.2243(2) 0.7071(2) 0.70655(15) 0.0305(3) Uani 1 1 d . . .

C5 C 0.3085(2) 0.58911(18) 0.61446(14) 0.0276(3) Uani 1 1 d . . .

C6 C 0.19286(18) 0.68268(17) 0.39356(14) 0.0241(3) Uani 1 1 d . . .

C7 C 0.3029(2) 0.88962(17) 0.20854(14) 0.0264(3) Uani 1 1 d . . .

C8 C 0.46963(19) 0.80663(16) 0.11929(13) 0.0245(3) Uani 1 1 d . . .

C9 C 0.6459(2) 0.80378(18) 0.12495(15) 0.0292(3) Uani 1 1 d . . .

C10 C 0.7992(2) 0.7260(2) 0.04439(16) 0.0332(3) Uani 1 1 d . . .

C11 C 0.7773(2) 0.64946(19) -0.04283(15) 0.0323(3) Uani 1 1 d . . .

C12 C 0.6031(2) 0.65287(19) -0.05037(14) 0.0313(3) Uani 1 1 d . . .

C13 C 0.4497(2) 0.73164(18) 0.02984(14) 0.0285(3) Uani 1 1 d . . .

H2N H 0.126(3) 0.542(2) 0.5513(18) 0.036(5) Uiso 1 1 d . . .

H3N H 0.328(2) 0.813(2) 0.4014(17) 0.024(4) Uiso 1 1 d . . .

H1A H 0.790(2) 0.8650(19) 0.5634(15) 0.024(4) Uiso 1 1 d . . .

H1B H 0.721(2) 0.838(2) 0.4475(16) 0.026(4) Uiso 1 1 d . . .

H2A H 0.556(2) 0.744(2) 0.6467(16) 0.029(4) Uiso 1 1 d . . .

H2B H 0.494(2) 0.918(2) 0.6868(17) 0.031(4) Uiso 1 1 d . . .

H3A H 0.098(2) 0.930(2) 0.5857(18) 0.033(4) Uiso 1 1 d . . .

H3B H 0.158(2) 0.955(2) 0.7046(17) 0.031(4) Uiso 1 1 d . . .

H4A H 0.105(3) 0.695(2) 0.7530(19) 0.044(5) Uiso 1 1 d . . .

H4B H 0.308(2) 0.668(2) 0.7733(18) 0.037(5) Uiso 1 1 d . . .

H5A H 0.335(2) 0.475(2) 0.6710(18) 0.034(4) Uiso 1 1 d . . .

H5B H 0.426(2) 0.6056(19) 0.5612(16) 0.024(4) Uiso 1 1 d . . .

H7A H 0.311(2) 0.996(2) 0.2128(16) 0.029(4) Uiso 1 1 d . . .

H7B H 0.193(2) 0.915(2) 0.1721(16) 0.026(4) Uiso 1 1 d . . .

H9 H 0.662(2) 0.855(2) 0.1835(19) 0.041(5) Uiso 1 1 d . . .

H10 H 0.921(3) 0.728(2) 0.0510(19) 0.042(5) Uiso 1 1 d . . .

H11 H 0.882(3) 0.594(2) -0.0971(19) 0.040(5) Uiso 1 1 d . . .

H12 H 0.588(3) 0.602(2) -0.1096(19) 0.041(5) Uiso 1 1 d . . .

H13 H 0.331(3) 0.730(2) 0.0258(18) 0.038(5) Uiso 1 1 d . . .

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N1 0.0198(5) 0.0243(6) 0.0230(6) -0.0052(4) -0.0023(4) -0.0092(4)

N2 0.0323(7) 0.0308(7) 0.0296(6) -0.0031(5) -0.0045(5) -0.0201(5)

N3 0.0261(6) 0.0280(6) 0.0229(6) -0.0069(5) -0.0039(5) -0.0125(5)

C1 0.0221(7) 0.0244(7) 0.0320(7) -0.0065(6) -0.0074(6) -0.0057(5)

C2 0.0256(7) 0.0243(7) 0.0257(7) -0.0045(5) -0.0071(5) -0.0095(5)

C3 0.0236(7) 0.0359(8) 0.0285(7) -0.0124(6) 0.0017(6) -0.0127(6)

C4 0.0316(8) 0.0394(8) 0.0235(7) -0.0047(6) 0.0004(6) -0.0200(7)

C5 0.0304(7) 0.0246(7) 0.0281(7) 0.0001(6) -0.0074(6) -0.0125(6)

C6 0.0213(6) 0.0248(7) 0.0282(7) -0.0109(5) -0.0004(5) -0.0080(5)

C7 0.0292(7) 0.0240(7) 0.0263(7) -0.0050(5) -0.0069(6) -0.0081(6)

C8 0.0297(7) 0.0217(6) 0.0208(6) 0.0006(5) -0.0066(5) -0.0098(5)

C9 0.0342(8) 0.0297(7) 0.0267(7) -0.0036(6) -0.0071(6) -0.0145(6)

C10 0.0289(8) 0.0359(8) 0.0334(8) -0.0014(6) -0.0051(6) -0.0142(6)

C11 0.0331(8) 0.0319(8) 0.0262(7) -0.0029(6) 0.0014(6) -0.0110(6)

C12 0.0410(9) 0.0322(8) 0.0221(7) -0.0048(6) -0.0030(6) -0.0159(7)

C13 0.0307(8) 0.0320(8) 0.0249(7) -0.0039(6) -0.0057(6) -0.0140(6)

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All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles

and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

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N1 C1 1.4679(18) 2_676 ?

N1 C2 1.4679(17) . ?

N1 C3 1.4731(17) . ?

N2 C6 1.3452(19) . ?

N2 C5 1.4596(19) . ?

N2 H2N 0.808(19) . ?

N3 C6 1.3380(17) . ?

N3 C7 1.4670(18) . ?

N3 H3N 0.824(17) . ?

C1 N1 1.4679(18) 2_676 ?

C1 C2 1.5131(19) . ?

C1 H1A 0.969(16) . ?

C1 H1B 0.999(16) . ?

C2 H2A 0.972(17) . ?

C2 H2B 0.979(17) . ?

C3 C4 1.518(2) . ?

C3 H3A 0.953(19) . ?

C3 H3B 0.982(17) . ?

C4 C5 1.526(2) . ?

C4 H4A 0.977(19) . ?

C4 H4B 0.979(19) . ?

C5 H5A 0.988(18) . ?

C5 H5B 0.998(16) . ?

C7 C8 1.513(2) . ?

C7 H7A 0.998(17) . ?

C7 H7B 0.958(17) . ?

C8 C13 1.390(2) . ?

C8 C9 1.393(2) . ?

C9 C10 1.387(2) . ?

C9 H9 0.93(2) . ?

C10 C11 1.387(2) . ?

C10 H10 0.98(2) . ?

C11 C12 1.380(2) . ?

C11 H11 0.951(19) . ?

C12 C13 1.389(2) . ?

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C13 H13 0.953(19) . ?

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C1 N1 C2 108.68(11) 2_676 . ?

C1 N1 C3 109.47(11) 2_676 . ?

C2 N1 C3 111.62(11) . . ?

C6 N2 C5 127.33(12) . . ?

C6 N2 H2N 116.5(13) . . ?

C5 N2 H2N 115.3(13) . . ?

C6 N3 C7 124.16(12) . . ?

C6 N3 H3N 117.8(11) . . ?

C7 N3 H3N 117.5(11) . . ?

N1 C1 C2 111.23(11) 2_676 . ?

N1 C1 H1A 108.8(9) 2_676 . ?

C2 C1 H1A 110.1(9) . . ?

N1 C1 H1B 110.3(9) 2_676 . ?

C2 C1 H1B 109.8(9) . . ?

H1A C1 H1B 106.5(13) . . ?

N1 C2 C1 110.75(11) . . ?

N1 C2 H2A 108.5(10) . . ?

C1 C2 H2A 106.4(10) . . ?

N1 C2 H2B 111.4(10) . . ?

C1 C2 H2B 108.9(10) . . ?

H2A C2 H2B 110.8(14) . . ?

N1 C3 C4 113.49(12) . . ?

N1 C3 H3A 105.7(10) . . ?

C4 C3 H3A 109.5(11) . . ?

N1 C3 H3B 110.1(10) . . ?

C4 C3 H3B 110.6(10) . . ?

H3A C3 H3B 107.1(14) . . ?

C3 C4 C5 115.33(12) . . ?

C3 C4 H4A 108.4(11) . . ?

C5 C4 H4A 108.6(11) . . ?

C3 C4 H4B 110.8(10) . . ?

C5 C4 H4B 105.7(10) . . ?

H4A C4 H4B 107.7(15) . . ?

N2 C5 C4 115.31(13) . . ?

N2 C5 H5A 105.6(10) . . ?

C4 C5 H5A 107.8(10) . . ?

N2 C5 H5B 108.8(9) . . ?

C4 C5 H5B 109.9(9) . . ?

H5A C5 H5B 109.3(14) . . ?

N3 C6 N2 117.58(12) . . ?

N3 C6 S1 122.97(11) . . ?

N2 C6 S1 119.45(10) . . ?

N3 C7 C8 113.42(11) . . ?

N3 C7 H7A 105.9(9) . . ?

C8 C7 H7A 110.1(9) . . ?

N3 C7 H7B 110.1(9) . . ?

C8 C7 H7B 109.6(9) . . ?

H7A C7 H7B 107.5(14) . . ?

C13 C8 C9 118.65(13) . . ?

C13 C8 C7 120.59(13) . . ?

C9 C8 C7 120.76(13) . . ?

C10 C9 C8 120.85(14) . . ?

C10 C9 H9 119.4(11) . . ?

C8 C9 H9 119.8(11) . . ?

C9 C10 C11 119.79(14) . . ?

C9 C10 H10 118.2(11) . . ?

C11 C10 H10 122.0(11) . . ?

C12 C11 C10 119.92(15) . . ?

C12 C11 H11 119.5(11) . . ?

C10 C11 H11 120.5(11) . . ?

C11 C12 C13 120.18(14) . . ?

C11 C12 H12 120.2(12) . . ?

C13 C12 H12 119.7(12) . . ?

C12 C13 C8 120.60(14) . . ?

C12 C13 H13 119.3(11) . . ?

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C1 N1 C2 C1 -57.54(16) 2_676 . . . ?

C3 N1 C2 C1 -178.37(11) . . . . ?

N1 C1 C2 N1 59.03(16) 2_676 . . . ?

C1 N1 C3 C4 179.10(12) 2_676 . . . ?

C2 N1 C3 C4 -60.53(15) . . . . ?

N1 C3 C4 C5 -47.60(18) . . . . ?

C6 N2 C5 C4 99.95(17) . . . . ?

C3 C4 C5 N2 -69.27(17) . . . . ?

C7 N3 C6 N2 -179.23(12) . . . . ?

C7 N3 C6 S1 0.46(19) . . . . ?

C5 N2 C6 N3 -15.1(2) . . . . ?

C5 N2 C6 S1 165.18(12) . . . . ?

C6 N3 C7 C8 -91.41(16) . . . . ?

N3 C7 C8 C13 103.43(15) . . . . ?

N3 C7 C8 C9 -76.59(16) . . . . ?

C13 C8 C9 C10 -0.8(2) . . . . ?

C7 C8 C9 C10 179.19(13) . . . . ?

C8 C9 C10 C11 -0.2(2) . . . . ?

C9 C10 C11 C12 0.8(2) . . . . ?

C10 C11 C12 C13 -0.5(2) . . . . ?

C11 C12 C13 C8 -0.5(2) . . . . ?

C9 C8 C13 C12 1.2(2) . . . . ?

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N2 H2N S1  0.808(19) 2.649(19) 3.4361(13) 164.9(17) 2_566
N3 H3N N1  0.824(17) 2.144(18) 2.9461(17) 164.2(15) .


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'-x, -y, -z'
'x, -y-1/2, z-1/2'

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
```

```
 factors based on ALL data will be even larger.
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S2 S 0.27852(8) 0.298352(19) 0.90440(6) 0.02877(15) Uani 1 1 d . . .
N1 N -0.1241(2) 0.51460(6) 0.35463(16) 0.0196(3) Uani 1 1 d . . .
N2 N 0.0164(3) 0.59114(6) 0.18200(18) 0.0248(4) Uani 1 1 d . . .
N3 N 0.3428(3) 0.63504(6) 0.26898(16) 0.0232(4) Uani 1 1 d . . .
C1 C -0.2308(3) 0.50509(8) 0.4638(2) 0.0216(4) Uani 1 1 d . . .
C2 C -0.0753(3) 0.51610(8) 0.6126(2) 0.0224(4) Uani 1 1 d . . .
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C4 C -0.2022(3) 0.51669(8) 0.0889(2) 0.0246(4) Uani 1 1 d . . .
C5 C -0.1774(3) 0.57101(8) 0.0723(2) 0.0269(5) Uani 1 1 d . . .
C6 C 0.1785(3) 0.61656(7) 0.1561(2) 0.0206(4) Uani 1 1 d . . .
C7 C 0.3692(3) 0.63345(7) 0.41794(19) 0.0195(4) Uani 1 1 d . . .
C8 C 0.5819(3) 0.62504(7) 0.5122(2) 0.0228(4) Uani 1 1 d . . .
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C9 C 0.6226(3) 0.62601(8) 0.6587(2) 0.0260(4) Uani 1 1 d . . .
C10 C 0.4505(3) 0.63480(8) 0.7130(2) 0.0261(4) Uani 1 1 d . . .
C11 C 0.2392(3) 0.64323(7) 0.6195(2) 0.0238(4) Uani 1 1 d . . .
C12 C 0.1966(3) 0.64341(7) 0.4723(2) 0.0213(4) Uani 1 1 d . . .
O1S O 0.3005(2) 0.30789(6) 0.75885(15) 0.0346(4) Uani 1 1 d . . .
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C2S C 0.0518(5) 0.25669(11) 0.8726(4) 0.0494(7) Uani 1 1 d . . .
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H1B H -0.277(3) 0.4700(8) 0.461(2) 0.019(5) Uiso 1 1 d . . .
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H2B H -0.031(3) 0.5514(8) 0.623(2) 0.022(5) Uiso 1 1 d . . .
H3A H -0.320(3) 0.4663(9) 0.207(2) 0.028(6) Uiso 1 1 d . . .
H3B H -0.421(3) 0.5206(8) 0.202(2) 0.023(5) Uiso 1 1 d . . .
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H5B H -0.154(3) 0.5792(8) -0.018(2) 0.031(6) Uiso 1 1 d . . .
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H9 H 0.765(4) 0.6215(8) 0.721(2) 0.025(6) Uiso 1 1 d . . .
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H12 H 0.053(3) 0.6514(7) 0.410(2) 0.021(5) Uiso 1 1 d . . .
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H1SB H 0.470(5) 0.2467(11) 1.079(3) 0.067(9) Uiso 1 1 d . . .
H1SC H 0.491(4) 0.2311(11) 0.928(3) 0.052(8) Uiso 1 1 d . . .
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H2SB H -0.079(5) 0.2722(11) 0.818(3) 0.057(8) Uiso 1 1 d . . .
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S2 0.0314(3) 0.0224(3) 0.0378(3) 0.0042(2) 0.0184(2) 0.0001(2)
N1 0.0180(7) 0.0242(9) 0.0169(8) 0.0013(6) 0.0059(6) -0.0012(6)
N2 0.0260(9) 0.0312(10) 0.0158(8) 0.0026(7) 0.0049(7) -0.0084(7)
N3 0.0224(8) 0.0310(10) 0.0177(8) -0.0006(7) 0.0086(7) -0.0087(7)
C1 0.0192(9) 0.0242(11) 0.0234(10) 0.0016(8) 0.0097(8) 0.0001(8)
C2 0.0206(9) 0.0275(11) 0.0214(10) 0.0011(8) 0.0099(8) 0.0013(8)
C3 0.0228(10) 0.0285(12) 0.0213(10) -0.0002(9) 0.0048(8) -0.0064(9)
C4 0.0241(10) 0.0309(12) 0.0166(9) -0.0030(8) 0.0035(8) -0.0070(9)
C5 0.0210(10) 0.0348(13) 0.0211(10) 0.0045(9) 0.0016(8) -0.0053(9)
C6 0.0215(9) 0.0198(10) 0.0214(9) 0.0019(8) 0.0080(8) 0.0009(8)
C7 0.0225(9) 0.0181(9) 0.0182(9) -0.0001(7) 0.0070(7) -0.0048(7)
C8 0.0219(9) 0.0231(11) 0.0252(10) -0.0005(8) 0.0101(8) -0.0007(8)
C9 0.0229(10) 0.0279(11) 0.0239(10) 0.0019(9) 0.0029(9) 0.0010(9)

C10 0.0341(11) 0.0270(11) 0.0166(9) 0.0003(8) 0.0072(9) -0.0032(9)
C11 0.0277(10) 0.0215(10) 0.0265(10) -0.0019(8) 0.0145(9) -0.0008(8)
C12 0.0188(9) 0.0211(10) 0.0232(10) 0.0005(8) 0.0056(8) -0.0014(8)
O1S 0.0306(8) 0.0410(10) 0.0324(8) 0.0072(7) 0.0105(7) -0.0093(7)
C1S 0.0426(14) 0.0305(13) 0.0442(15) 0.0088(12) 0.0119(12) 0.0045(11)
C2S 0.0409(15) 0.0409(16) 0.074(2) 0.0110(15) 0.0291(15) -0.0077(12)

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C1 1.467(2) . ?
N1 C2 1.470(2) 3_566 ?
N1 C3 1.473(2) . ?
N2 C6 1.336(2) . ?
N2 C5 1.460(2) . ?
N2 H2N 0.79(2) . ?
N3 C6 1.355(2) . ?
N3 C7 1.422(2) . ?
N3 H3N 0.85(2) . ?
C1 C2 1.510(3) . ?
C1 H1A 0.98(2) . ?
C1 H1B 1.00(2) . ?
C2 N1 1.470(2) 3_566 ?
C2 H2A 0.97(2) . ?
C2 H2B 1.00(2) . ?
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C3 H3B 0.99(2) . ?
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C5 H5A 0.99(2) . ?
C5 H5B 0.97(2) . ?
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C7 C12 1.396(3) . ?
C8 C9 1.381(3) . ?

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C8 H8 0.94(2) . ?
C9 C10 1.386(3) . ?
C9 H9 0.92(2) . ?
C10 C11 1.382(3) . ?
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C11 C12 1.386(3) . ?
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C12 H12 0.95(2) . ?
C1S H1SA 0.93(3) . ?
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C1S H1SC 0.95(3) . ?
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N1 C1 C2 111.20(15) . . ?
N1 C1 H1A 107.3(11) . . ?
C2 C1 H1A 109.5(11) . . ?
N1 C1 H1B 110.4(11) . . ?
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N1 C2 H2A 109.6(11) 3_566 . ?
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H2A C2 H2B 108.5(16) . . ?
N1 C3 C4 113.54(16) . . ?
N1 C3 H3A 110.3(12) . . ?
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N2 C5 H5A 106.4(12) . . ?
C4 C5 H5A 111.0(12) . . ?
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C4 C5 H5B 112.3(13) . . ?
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C8 C7 N3 117.32(16) . . ?
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C1 N1 C3 C4 172.90(18) . . . . ?
C2 N1 C3 C4 -68.6(2) 3_566 . . . ?
N1 C3 C4 C5 -65.5(2) . . . . ?
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C3 C4 C5 N2 73.9(2) . . . . ?
C5 N2 C6 N3 176.82(19) . . . . ?
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C6 N3 C7 C12 -45.4(3) . . . . ?
C12 C7 C8 C9 0.7(3) . . . . ?
N3 C7 C8 C9 175.98(18) . . . . ?
C7 C8 C9 C10 0.8(3) . . . . ?
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N3 H3N O1S  0.85(2) 2.01(2) 2.842(2) 165(2) 3_666
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 'x-1/2, -y-1/2, z-1/2'

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_cell_length_b                  15.9450(13)
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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N1 N 0.18108(16) -0.11716(9) 0.01326(13) 0.0370(3) Uani 1 1 d . . .
N2 N 0.22310(13) -0.07109(8) 0.29189(13) 0.0277(3) Uani 1 1 d . . .
N3 N 0.02057(14) -0.08557(8) 0.36162(13) 0.0292(3) Uani 1 1 d . . .
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C3 C 0.2224(2) -0.20407(12) -0.00481(17) 0.0445(4) Uani 1 1 d . . .
C4 C 0.0854(3) -0.25957(12) -0.04777(19) 0.0518(5) Uani 1 1 d . . .
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C6 C 0.4193(2) -0.06877(13) 0.18966(19) 0.0429(4) Uani 1 1 d . . .
C7 C 0.36481(18) -0.03331(11) 0.29677(19) 0.0356(4) Uani 1 1 d . . .
C8 C 0.15253(15) -0.04837(8) 0.37486(14) 0.0251(3) Uani 1 1 d . . .
C9 C -0.04422(16) -0.15864(9) 0.28724(14) 0.0266(3) Uani 1 1 d . . .
C10 C 0.0379(2) -0.23161(10) 0.29630(17) 0.0361(4) Uani 1 1 d . . .
C11 C -0.0360(3) -0.30348(12) 0.2319(2) 0.0497(5) Uani 1 1 d . . .
C12 C -0.1889(3) -0.30295(13) 0.1599(2) 0.0545(6) Uani 1 1 d . . .
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H2N H 0.178(2) -0.0992(12) 0.2252(18) 0.031(4) Uiso 1 1 d . . .
H3N H -0.026(2) -0.0658(11) 0.4043(18) 0.030(4) Uiso 1 1 d . . .
H1A H -0.146(3) -0.1307(15) -0.237(2) 0.066(7) Uiso 1 1 d . . .
H1B H -0.112(2) -0.1454(13) -0.081(2) 0.051(6) Uiso 1 1 d . . .
H2A H 0.036(3) -0.0314(16) -0.097(2) 0.072(7) Uiso 1 1 d . . .
H2B H 0.108(3) -0.0918(15) -0.187(2) 0.061(6) Uiso 1 1 d . . .
H3A H 0.294(3) -0.2262(14) 0.081(2) 0.062(6) Uiso 1 1 d . . .
H3B H 0.272(2) -0.2067(14) -0.070(2) 0.054(6) Uiso 1 1 d . . .
H4A H 0.112(3) -0.3159(16) -0.062(2) 0.066(7) Uiso 1 1 d . . .
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H6B H 0.446(2) -0.1305(15) 0.205(2) 0.057(6) Uiso 1 1 d . . .
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H13 H -0.379(3) -0.2310(14) 0.105(2) 0.060(6) Uiso 1 1 d . . .
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O1 0.0559(8) 0.0454(7) 0.0340(6) -0.0069(5) 0.0020(6) 0.0087(6)
N1 0.0398(7) 0.0404(8) 0.0332(7) -0.0009(6) 0.0159(6) 0.0027(6)
N2 0.0242(6) 0.0300(6) 0.0295(6) -0.0064(5) 0.0105(5) -0.0035(5)
N3 0.0272(6) 0.0293(6) 0.0356(7) -0.0115(5) 0.0166(5) -0.0041(5)
C1 0.0480(11) 0.0544(11) 0.0472(11) -0.0060(9) 0.0071(9) 0.0172(9)
C2 0.0602(12) 0.0411(10) 0.0427(10) 0.0064(8) 0.0141(9) 0.0144(9)
C3 0.0500(10) 0.0498(11) 0.0294(8) 0.0016(7) 0.0087(8) 0.0186(8)
C4 0.0757(14) 0.0363(10) 0.0331(9) 0.0008(7) 0.0066(9) 0.0070(9)

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C5 0.0498(10) 0.0540(11) 0.0468(10) 0.0071(9) 0.0248(9) -0.0018(9)
C6 0.0333(8) 0.0530(11) 0.0481(10) -0.0030(8) 0.0213(8) -0.0012(8)
C7 0.0282(8) 0.0356(9) 0.0471(10) -0.0079(7) 0.0184(7) -0.0046(6)
C8 0.0241(6) 0.0225(6) 0.0274(7) -0.0017(5) 0.0076(5) 0.0013(5)
C9 0.0304(7) 0.0280(7) 0.0243(6) -0.0056(5) 0.0133(6) -0.0058(6)
C10 0.0423(9) 0.0305(8) 0.0367(8) -0.0034(6) 0.0154(7) 0.0008(7)
C11 0.0749(14) 0.0295(9) 0.0563(11) -0.0106(8) 0.0375(10) -0.0049(9)
C12 0.0742(14) 0.0523(11) 0.0504(11) -0.0290(9) 0.0386(10) -0.0355(11)
C13 0.0409(10) 0.0732(14) 0.0388(9) -0.0229(9) 0.0172(8) -0.0250(9)
C14 0.0297(7) 0.0469(9) 0.0330(8) -0.0080(7) 0.0129(6) -0.0048(7)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C2 1.468(2) . ?
N1 C3 1.471(2) . ?
N1 C5 1.474(2) . ?
N2 C8 1.3302(18) . ?
N2 C7 1.4582(19) . ?
N2 H2N 0.817(19) . ?
N3 C8 1.3477(18) . ?
N3 C9 1.4180(18) . ?
N3 H3N 0.798(19) . ?
C1 C2 1.495(3) . ?
C1 H1A 0.98(2) . ?
C1 H1B 0.97(2) . ?
C2 H2A 1.00(3) . ?
C2 H2B 1.00(2) . ?
C3 C4 1.503(3) . ?
C3 H3A 0.99(2) . ?
C3 H3B 0.96(2) . ?
C4 H4A 0.96(3) . ?
C4 H4B 0.95(2) . ?
C5 C6 1.512(3) . ?
C5 H5A 0.99(2) . ?
C5 H5B 1.10(3) . ?
C6 C7 1.513(2) . ?
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C6 H6A 1.00(2) . ?
C6 H6B 1.01(2) . ?
C7 H7A 0.96(2) . ?
C7 H7B 0.96(2) . ?
C9 C10 1.385(2) . ?
C9 C14 1.388(2) . ?
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C10 H10 0.98(2) . ?
C11 C12 1.379(3) . ?
C11 H11 0.90(2) . ?
C12 C13 1.366(3) . ?
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C3 N1 C5 112.30(15) . . ?
C8 N2 C7 122.62(13) . . ?
C8 N2 H2N 119.3(13) . . ?
C7 N2 H2N 116.7(13) . . ?
C8 N3 C9 128.54(12) . . ?
C8 N3 H3N 116.5(13) . . ?
C9 N3 H3N 114.9(13) . . ?
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O1 C1 H1A 106.3(14) . . ?
C2 C1 H1A 111.3(14) . . ?
O1 C1 H1B 110.5(13) . . ?
C2 C1 H1B 108.5(13) . . ?
H1A C1 H1B 108.7(19) . . ?
N1 C2 C1 110.80(16) . . ?
N1 C2 H2A 106.1(14) . . ?
C1 C2 H2A 111.3(15) . . ?
N1 C2 H2B 108.0(13) . . ?
C1 C2 H2B 108.5(13) . . ?
H2A C2 H2B 112.1(19) . . ?
N1 C3 C4 110.60(16) . . ?
N1 C3 H3A 110.3(13) . . ?
C4 C3 H3A 108.0(13) . . ?
N1 C3 H3B 110.7(13) . . ?
C4 C3 H3B 110.2(13) . . ?
H3A C3 H3B 106.8(19) . . ?
O1 C4 C3 112.14(16) . . ?

O1 C4 H4A 108.1(14) . . ?
C3 C4 H4A 110.7(14) . . ?
O1 C4 H4B 107.6(14) . . ?
C3 C4 H4B 108.4(13) . . ?
H4A C4 H4B 109.8(19) . . ?
N1 C5 C6 112.90(15) . . ?
N1 C5 H5A 109.9(13) . . ?
C6 C5 H5A 106.4(13) . . ?
N1 C5 H5B 110.8(13) . . ?
C6 C5 H5B 101.9(13) . . ?
H5A C5 H5B 114.7(18) . . ?
C7 C6 C5 115.07(16) . . ?
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C5 C6 H6A 107.4(12) . . ?
C7 C6 H6B 112.2(13) . . ?
C5 C6 H6B 107.3(13) . . ?
H6A C6 H6B 109.4(17) . . ?
N2 C7 C6 112.10(14) . . ?
N2 C7 H7A 107.2(13) . . ?
C6 C7 H7A 108.8(13) . . ?
N2 C7 H7B 109.4(13) . . ?
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H7A C7 H7B 109.3(18) . . ?
N2 C8 N3 118.65(13) . . ?
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C9 C10 C11 119.04(17) . . ?
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C12 C11 C10 120.98(18) . . ?
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C10 C11 H11 116.6(15) . . ?
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C11 C12 H12 117.5(17) . . ?
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C14 C13 H13 119.4(14) . . ?
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O1 C1 C2 N1 -59.8(2) . . . . ?
C2 N1 C3 C4 -55.60(19) . . . . ?
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C2 N1 C5 C6 165.76(16) . . . . ?
C3 N1 C5 C6 -74.53(19) . . . . ?
N1 C5 C6 C7 -73.6(2) . . . . ?
C8 N2 C7 C6 -178.63(14) . . . . ?
C5 C6 C7 N2 57.9(2) . . . . ?
C7 N2 C8 N3 178.81(14) . . . . ?
C7 N2 C8 S1 -0.4(2) . . . . ?
C9 N3 C8 N2 13.4(2) . . . . ?
C9 N3 C8 S1 -167.40(12) . . . . ?
C8 N3 C9 C10 47.7(2) . . . . ?
C8 N3 C9 C14 -138.30(16) . . . . ?
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C9 C10 C11 C12 -0.1(3) . . . . ?
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N3 H3N S1  0.798(19) 2.535(19) 3.3161(13) 166.1(17) 3_556

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 'x, -y-1/2, z-1/2'

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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S2 S 0.02549(5) 0.12626(2) 0.23756(2) 0.03207(12) Uani 1 1 d . . .
N1 N 0.37817(18) 0.55680(8) 0.28810(7) 0.0290(3) Uani 1 1 d . . .
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N2 N 0.62067(17) 0.51185(8) 0.35866(7) 0.0267(3) Uani 1 1 d . . .
N3 N 0.74027(16) 0.35961(7) 0.31837(7) 0.0243(3) Uani 1 1 d . . .
N4 N 0.23033(17) 0.23683(8) 0.18171(7) 0.0269(3) Uani 1 1 d . . .
N5 N -0.01650(18) 0.19969(8) 0.10889(7) 0.0296(3) Uani 1 1 d . . .
C1 C 0.5719(2) 0.51161(9) 0.18997(9) 0.0276(3) Uani 1 1 d . . .
C2 C 0.5877(2) 0.47473(10) 0.12187(9) 0.0323(4) Uani 1 1 d . . .
C3 C 0.4402(2) 0.44272(10) 0.08370(9) 0.0339(4) Uani 1 1 d . . .
C4 C 0.2749(2) 0.44758(9) 0.11405(9) 0.0309(3) Uani 1 1 d . . .
C5 C 0.2574(2) 0.48365(9) 0.18240(9) 0.0268(3) Uani 1 1 d . . .
C6 C 0.40600(19) 0.51597(8) 0.22098(8) 0.0239(3) Uani 1 1 d . . .
C7 C 0.48312(19) 0.56058(8) 0.35144(8) 0.0240(3) Uani 1 1 d . . .
C8 C 0.7434(2) 0.50894(9) 0.42400(9) 0.0297(3) Uani 1 1 d . . .
C9 C 0.8922(2) 0.44958(10) 0.41151(10) 0.0329(4) Uani 1 1 d . . .
C10 C 0.8252(2) 0.36553(9) 0.39376(9) 0.0305(4) Uani 1 1 d . . .
C11 C 0.6188(2) 0.29126(9) 0.31327(9) 0.0296(3) Uani 1 1 d . . .
C12 C 0.5035(2) 0.29052(10) 0.24159(9) 0.0288(3) Uani 1 1 d . . .
C13 C 0.3478(2) 0.23484(10) 0.24845(9) 0.0291(3) Uani 1 1 d . . .
C14 C 0.08569(19) 0.19157(8) 0.17212(8) 0.0246(3) Uani 1 1 d . . .
C15 C 0.0052(2) 0.25682(9) 0.05171(8) 0.0269(3) Uani 1 1 d . . .
C16 C -0.1371(2) 0.30678(10) 0.03274(9) 0.0334(4) Uani 1 1 d . . .
C17 C -0.1235(3) 0.36129(11) -0.02450(10) 0.0423(4) Uani 1 1 d . . .
C18 C 0.0315(3) 0.36606(11) -0.06232(9) 0.0428(4) Uani 1 1 d . . .
C19 C 0.1725(3) 0.31605(11) -0.04374(9) 0.0390(4) Uani 1 1 d . . .
C20 C 0.1601(2) 0.26030(10) 0.01297(9) 0.0316(3) Uani 1 1 d . . .
C21 C 0.8758(2) 0.35393(13) 0.26318(11) 0.0387(4) Uani 1 1 d . . .
H1N H 0.279(2) 0.5814(11) 0.2894(9) 0.033(5) Uiso 1 1 d . . .
H2N H 0.635(2) 0.4739(11) 0.3275(10) 0.034(5) Uiso 1 1 d . . .
H4N H 0.256(2) 0.2694(11) 0.1491(10) 0.033(5) Uiso 1 1 d . . .
H5N H -0.118(3) 0.1761(11) 0.1088(10) 0.039(5) Uiso 1 1 d . . .
H1 H 0.673(2) 0.5338(10) 0.2155(9) 0.029(4) Uiso 1 1 d . . .
H2 H 0.700(2) 0.4733(10) 0.1015(9) 0.033(5) Uiso 1 1 d . . .
H3 H 0.449(2) 0.4185(11) 0.0377(10) 0.039(5) Uiso 1 1 d . . .
H4 H 0.169(2) 0.4263(10) 0.0878(9) 0.036(5) Uiso 1 1 d . . .
H5 H 0.147(2) 0.4882(10) 0.2028(9) 0.030(4) Uiso 1 1 d . . .
H8A H 0.793(2) 0.5634(10) 0.4338(9) 0.031(4) Uiso 1 1 d . . .
H8B H 0.676(2) 0.4929(10) 0.4661(10) 0.036(5) Uiso 1 1 d . . .
H9A H 0.966(2) 0.4459(11) 0.4572(11) 0.044(5) Uiso 1 1 d . . .
H9B H 0.970(2) 0.4682(11) 0.3732(11) 0.041(5) Uiso 1 1 d . . .
H10A H 0.927(2) 0.3278(11) 0.3994(9) 0.037(5) Uiso 1 1 d . . .
H10B H 0.736(2) 0.3511(10) 0.4298(10) 0.033(5) Uiso 1 1 d . . .
H11A H 0.540(2) 0.2945(10) 0.3563(10) 0.038(5) Uiso 1 1 d . . .
H11B H 0.683(2) 0.2411(11) 0.3201(9) 0.033(4) Uiso 1 1 d . . .
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H18 H 0.037(3) 0.4052(13) -0.1012(12) 0.054(6) Uiso 1 1 d . . .
H19 H 0.277(3) 0.3154(12) -0.0691(11) 0.046(5) Uiso 1 1 d . . .
H20 H 0.251(2) 0.2255(11) 0.0241(9) 0.034(5) Uiso 1 1 d . . .
H21A H 0.953(3) 0.4015(14) 0.2697(12) 0.062(6) Uiso 1 1 d . . .
H21B H 0.948(3) 0.3066(14) 0.2720(12) 0.065(7) Uiso 1 1 d . . .

H21C H 0.825(2) 0.3564(11) 0.2129(11) 0.040(5) Uiso 1 1 d . . .

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C3 0.0473(10) 0.0323(8) 0.0220(8) -0.0039(7) 0.0000(7) -0.0013(7)
C4 0.0366(9) 0.0271(8) 0.0280(8) -0.0011(6) -0.0088(7) -0.0025(7)
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C8 0.0339(9) 0.0283(8) 0.0260(8) -0.0035(6) -0.0087(7) 0.0026(7)
C9 0.0316(8) 0.0318(8) 0.0338(9) -0.0040(7) -0.0131(7) 0.0018(7)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 C8 1.4637(18) . ?
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N4 C13 1.4598(19) . ?
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N5 C15 1.4233(19) . ?
N5 H5N 0.857(19) . ?
C1 C2 1.386(2) . ?
C1 C6 1.392(2) . ?
C1 H1 0.945(17) . ?
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C7 N1 C6 C5 144.98(16) . . . . ?
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N5 H5N S1  0.857(19) 2.516(19) 3.3548(14) 166.3(16) 2_545

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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 are estimated using the full covariance matrix. The cell esds are taken
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 used when they are defined by crystal symmetry. An approximate (isotropic)
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N3 C6 1.3235(15) . ?
N3 C7 1.4581(14) . ?
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 '-x, -y, -z'

_cell_length_a                   6.0154(7)
_cell_length_b                   7.5525(8)
_cell_length_c                   14.9498(16)
_cell_angle_alpha                 81.922(2)
_cell_angle_beta                 83.826(2)
_cell_angle_gamma                  76.145(2)
_cell_volume                     650.95(12)
_cell_formula_units_Z            1
_cell_measurement_temperature     173(2)
_cell_measurement_reflns_used     2601
_cell_measurement_theta_min       2.76
_cell_measurement_theta_max       28.19

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_exptl_crystal_colour             colorless
_exptl_crystal_size_max           0.26
_exptl_crystal_size_mid           0.12
_exptl_crystal_size_min           0.08
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.344
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              280
_exptl_absorpt_coefficient_mu     0.241
_exptl_absorpt_correction_type    'multi-scan'
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_exptl_absorpt_correction_T_max   0.9810
_exptl_absorpt_process_details    SADABS

_exptl_special_details
;
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;

_diffrn_ambient_temperature       173(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
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_diffrn_measurement_method        'phi and omega scans'
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_diffrn_reflns_av_sigmaI/netI     0.0229
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_diffrn_reflns_limit_k_min       -8
_diffrn_reflns_limit_k_max        8
_diffrn_reflns_limit_l_min       -17
_diffrn_reflns_limit_l_max        17
_diffrn_reflns_theta_min         1.38
_diffrn_reflns_theta_max         25.00
_reflns_number_total             2263
_reflns_number_gt                2054
_reflns_threshold_expression      >2sigma(I)

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_computing_cell_refinement        'Bruker SMART'
_computing_data_reduction         'Bruker SAINT'
_computing_structure_solution     'Bruker SHELXTL'
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_computing_publication_material   'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0439P)^2^+0.9183P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    difmap
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_refine_ls_extinction_method      none
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_refine_ls_goodness_of_fit_ref   1.121
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 _atom_site_symmetry_multiplicity
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 _atom_site_refinement_flags
 _atom_site_disorder_assembly
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O1 O -0.3042(3) 0.2008(3) 0.06767(13) 0.0404(5) Uani 1 1 d . . .
N1 N -0.3992(4) 0.3747(3) 0.43432(15) 0.0312(5) Uani 1 1 d . . .
N2 N -0.1337(4) 0.0302(3) 0.22417(15) 0.0272(5) Uani 1 1 d . . .
N3 N 0.0710(4) 0.1374(3) 0.09625(16) 0.0303(5) Uani 1 1 d . . .
C1 C -0.5986(6) 0.6843(4) 0.4688(2) 0.0405(8) Uani 1 1 d . . .
C2 C -0.5983(6) 0.5262(5) 0.4171(2) 0.0419(8) Uani 1 1 d . . .
C3 C -0.3988(5) 0.2257(4) 0.3818(2) 0.0333(7) Uani 1 1 d . . .
C4 C -0.1834(5) 0.0724(4) 0.38783(19) 0.0314(6) Uani 1 1 d . . .
C5 C -0.1605(5) -0.0583(4) 0.31682(18) 0.0303(6) Uani 1 1 d . . .
C6 C 0.0662(5) 0.0516(4) 0.18486(18) 0.0269(6) Uani 1 1 d . . .
C7 C -0.1074(5) 0.2115(4) 0.04308(18) 0.0295(6) Uani 1 1 d . . .
C8 C -0.0468(5) 0.3066(4) -0.04797(18) 0.0284(6) Uani 1 1 d . . .
C9 C 0.1761(5) 0.2891(4) -0.08688(19) 0.0329(6) Uani 1 1 d . . .
C10 C 0.2166(6) 0.3814(4) -0.1720(2) 0.0402(7) Uani 1 1 d . . .
C11 C 0.0371(6) 0.4902(4) -0.2192(2) 0.0395(7) Uani 1 1 d . . .
C12 C -0.1853(6) 0.5066(5) -0.1799(2) 0.0426(8) Uani 1 1 d . . .
C13 C -0.2271(5) 0.4151(4) -0.0950(2) 0.0366(7) Uani 1 1 d . . .
H2N H -0.241(5) 0.060(4) 0.198(2) 0.026(8) Uiso 1 1 d . . .
H3N H 0.196(6) 0.158(4) 0.075(2) 0.036(9) Uiso 1 1 d . . .
H1A H -0.737(6) 0.792(5) 0.457(2) 0.041(9) Uiso 1 1 d . . .
H1B H -0.452(6) 0.731(4) 0.449(2) 0.044(9) Uiso 1 1 d . . .
H2A H -0.604(7) 0.567(5) 0.360(3) 0.063(11) Uiso 1 1 d . . .
H2B H -0.733(5) 0.479(4) 0.439(2) 0.028(8) Uiso 1 1 d . . .
H3A H -0.416(6) 0.283(5) 0.320(2) 0.047(9) Uiso 1 1 d . . .
H3B H -0.534(6) 0.174(4) 0.400(2) 0.039(9) Uiso 1 1 d . . .
H4A H -0.178(5) -0.001(4) 0.445(2) 0.032(8) Uiso 1 1 d . . .
H4B H -0.052(5) 0.120(3) 0.3797(17) 0.016(6) Uiso 1 1 d . . .
H5A H -0.291(5) -0.111(4) 0.3210(18) 0.025(7) Uiso 1 1 d . . .
H5B H -0.028(5) -0.161(4) 0.3248(19) 0.026(7) Uiso 1 1 d . . .
```

```
H9 H 0.293(6) 0.215(5) -0.057(2) 0.048(10) Uiso 1 1 d . . .
H10 H 0.372(6) 0.370(5) -0.199(2) 0.053(10) Uiso 1 1 d . . .
H11 H 0.067(6) 0.547(5) -0.276(2) 0.049(10) Uiso 1 1 d . . .
H12 H -0.305(7) 0.589(5) -0.211(3) 0.061(11) Uiso 1 1 d . . .
H13 H -0.368(6) 0.412(5) -0.065(2) 0.050(10) Uiso 1 1 d . . .

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 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
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O1 0.0285(11) 0.0568(14) 0.0320(11) 0.0071(10) -0.0055(9) -0.0079(9)
N1 0.0356(13) 0.0350(13) 0.0204(11) -0.0024(9) -0.0044(9) -0.0021(10)
N2 0.0238(12) 0.0355(13) 0.0215(12) 0.0002(10) -0.0060(10) -0.0051(10)
N3 0.0242(13) 0.0371(13) 0.0287(13) -0.0026(10) 0.0007(10) -0.0074(10)
C1 0.054(2) 0.0386(17) 0.0236(15) 0.0001(13) -0.0043(14) -0.0010(16)
C2 0.052(2) 0.0428(18) 0.0243(16) -0.0040(13) -0.0114(14) 0.0057(15)
C3 0.0357(16) 0.0396(17) 0.0234(15) -0.0046(12) -0.0038(12) -0.0052(13)
C4 0.0336(16) 0.0376(16) 0.0205(14) 0.0004(12) -0.0037(12) -0.0049(13)
C5 0.0314(15) 0.0348(16) 0.0232(14) 0.0020(11) -0.0034(11) -0.0074(13)
C6 0.0281(14) 0.0271(14) 0.0254(14) -0.0053(11) -0.0035(11) -0.0040(11)
C7 0.0338(16) 0.0296(14) 0.0251(14) -0.0056(11) -0.0025(11) -0.0059(12)
C8 0.0350(15) 0.0263(14) 0.0255(14) -0.0066(11) -0.0041(11) -0.0070(11)
C9 0.0332(16) 0.0358(16) 0.0274(15) -0.0016(12) -0.0015(12) -0.0050(13)
C10 0.0443(19) 0.0460(18) 0.0310(16) -0.0042(13) 0.0040(14) -0.0146(15)
C11 0.059(2) 0.0370(17) 0.0270(16) 0.0038(13) -0.0092(14) -0.0203(15)
C12 0.049(2) 0.0405(18) 0.0389(18) 0.0071(14) -0.0166(15) -0.0127(15)
C13 0.0357(17) 0.0407(17) 0.0343(16) -0.0010(13) -0.0073(13) -0.0105(14)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

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O1 C7 1.220(3) . ?
N1 C1 1.453(4) 2_466 ?
N1 C3 1.459(4) . ?
```

N1 C2 1.462(4) . ?
N2 C6 1.316(4) . ?
N2 C5 1.461(3) . ?
N2 H2N 0.76(3) . ?
N3 C7 1.366(4) . ?
N3 C6 1.391(4) . ?
N3 H3N 0.82(3) . ?
C1 N1 1.453(4) 2_466 ?
C1 C2 1.510(5) . ?
C1 H1A 1.02(3) . ?
C1 H1B 1.03(3) . ?
C2 H2A 0.87(4) . ?
C2 H2B 0.97(3) . ?
C3 C4 1.518(4) . ?
C3 H3A 0.97(4) . ?
C3 H3B 0.98(3) . ?
C4 C5 1.523(4) . ?
C4 H4A 0.95(3) . ?
C4 H4B 0.93(3) . ?
C5 H5A 0.96(3) . ?
C5 H5B 0.97(3) . ?
C7 C8 1.499(4) . ?
C8 C13 1.385(4) . ?
C8 C9 1.386(4) . ?
C9 C10 1.389(4) . ?
C9 H9 0.90(4) . ?
C10 C11 1.383(5) . ?
C10 H10 0.97(4) . ?
C11 C12 1.386(5) . ?
C11 H11 0.92(4) . ?
C12 C13 1.387(4) . ?
C12 H12 0.94(4) . ?
C13 H13 0.92(4) . ?

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C1 N1 C3 112.5(2) 2_466 . ?
C1 N1 C2 108.6(2) 2_466 . ?
C3 N1 C2 110.6(2) . . ?
C6 N2 C5 122.7(2) . . ?
C6 N2 H2N 120(2) . . ?
C5 N2 H2N 117(2) . . ?
C7 N3 C6 129.0(2) . . ?
C7 N3 H3N 115(2) . . ?
C6 N3 H3N 115(2) . . ?
N1 C1 C2 110.7(3) 2_466 . ?
N1 C1 H1A 108.3(18) 2_466 . ?

C2 C1 H1A 112.4(18) . . ?
N1 C1 H1B 108.0(19) 2_466 . ?
C2 C1 H1B 109.1(18) . . ?
H1A C1 H1B 108(3) . . ?
N1 C2 C1 111.5(3) . . ?
N1 C2 H2A 112(3) . . ?
C1 C2 H2A 108(3) . . ?
N1 C2 H2B 106.7(17) . . ?
C1 C2 H2B 107.8(17) . . ?
H2A C2 H2B 110(3) . . ?
N1 C3 C4 113.7(2) . . ?
N1 C3 H3A 106(2) . . ?
C4 C3 H3A 111(2) . . ?
N1 C3 H3B 111.0(18) . . ?
C4 C3 H3B 109.3(18) . . ?
H3A C3 H3B 106(3) . . ?
C3 C4 C5 112.8(2) . . ?
C3 C4 H4A 112.6(18) . . ?
C5 C4 H4A 106.2(18) . . ?
C3 C4 H4B 110.9(16) . . ?
C5 C4 H4B 107.2(16) . . ?
H4A C4 H4B 107(2) . . ?
N2 C5 C4 113.0(2) . . ?
N2 C5 H5A 107.4(17) . . ?
C4 C5 H5A 111.4(17) . . ?
N2 C5 H5B 106.9(17) . . ?
C4 C5 H5B 111.5(17) . . ?
H5A C5 H5B 106(2) . . ?
N2 C6 N3 117.6(2) . . ?
N2 C6 S1 124.1(2) . . ?
N3 C6 S1 118.2(2) . . ?
O1 C7 N3 122.3(3) . . ?
O1 C7 C8 121.7(2) . . ?
N3 C7 C8 115.9(2) . . ?
C13 C8 C9 119.4(3) . . ?
C13 C8 C7 116.9(3) . . ?
C9 C8 C7 123.7(2) . . ?
C8 C9 C10 119.8(3) . . ?
C8 C9 H9 119(2) . . ?
C10 C9 H9 121(2) . . ?
C11 C10 C9 120.9(3) . . ?
C11 C10 H10 119(2) . . ?
C9 C10 H10 120(2) . . ?
C10 C11 C12 118.9(3) . . ?
C10 C11 H11 119(2) . . ?
C12 C11 H11 122(2) . . ?
C11 C12 C13 120.5(3) . . ?
C11 C12 H12 118(2) . . ?
C13 C12 H12 121(2) . . ?
C8 C13 C12 120.4(3) . . ?
C8 C13 H13 112(2) . . ?
C12 C13 H13 127(2) . . ?

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 _geom_torsion_site_symmetry_2
 _geom_torsion_site_symmetry_3
 _geom_torsion_site_symmetry_4
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C1 N1 C2 C1 57.7(4) 2_466 . . . ?
C3 N1 C2 C1 -178.4(3) . . . . ?
N1 C1 C2 N1 -58.9(4) 2_466 . . . ?
C1 N1 C3 C4 -64.9(3) 2_466 . . . ?
C2 N1 C3 C4 173.5(3) . . . . ?
N1 C3 C4 C5 -166.8(2) . . . . ?
C6 N2 C5 C4 84.1(3) . . . . ?
C3 C4 C5 N2 64.2(3) . . . . ?
C5 N2 C6 N3 179.8(2) . . . . ?
C5 N2 C6 S1 -0.6(4) . . . . ?
C7 N3 C6 N2 2.7(4) . . . . ?
C7 N3 C6 S1 -176.9(2) . . . . ?
C6 N3 C7 O1 -4.4(5) . . . . ?
C6 N3 C7 C8 175.9(2) . . . . ?
O1 C7 C8 C13 13.5(4) . . . . ?
N3 C7 C8 C13 -166.8(3) . . . . ?
O1 C7 C8 C9 -165.6(3) . . . . ?
N3 C7 C8 C9 14.2(4) . . . . ?
C13 C8 C9 C10 0.5(4) . . . . ?
C7 C8 C9 C10 179.5(3) . . . . ?
C8 C9 C10 C11 -0.4(5) . . . . ?
C9 C10 C11 C12 0.2(5) . . . . ?
C10 C11 C12 C13 -0.2(5) . . . . ?
C9 C8 C13 C12 -0.5(4) . . . . ?
C7 C8 C13 C12 -179.6(3) . . . . ?
C11 C12 C13 C8 0.3(5) . . . . ?

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 _geom_hbond_distance_HA
 _geom_hbond_distance_DA
 _geom_hbond_angle_DHA
 _geom_hbond_site_symmetry_A
N2 H2N O1  0.76(3) 2.11(3) 2.687(3) 133(3) .
N2 H2N S1  0.76(3) 2.86(3) 3.412(3) 132(3) 1_455

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;
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 'C14 H12 N4 O3 S'
_chemical_formula_weight         316.34

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 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M    P2(1)/n

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 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

_cell_length_a                   7.9095(18)
_cell_length_b                   9.972(2)
_cell_length_c                   17.615(4)
_cell_angle_alpha                 90.00
_cell_angle_beta                  92.752(4)
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_cell_volume                     1387.7(5)
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_exptl_special_details
;
 ?
;

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_diffrn_reflns_av_sigmaI/netI    0.0342
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_computing_publication_material   'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0537P)^2^+0.3370P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
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O1 O 0.53862(17) 0.29929(12) 0.10718(9) 0.0372(4) Uani 1 1 d . . .
O2 O 1.09188(18) 0.19547(14) 0.21914(9) 0.0413(4) Uani 1 1 d . . .
O3 O 1.27694(17) 0.35309(14) 0.23993(9) 0.0389(4) Uani 1 1 d . . .
N1 N 0.41003(17) 0.78336(13) 0.08176(8) 0.0214(3) Uani 1 1 d . . .
N2 N 0.20261(19) 0.61928(14) 0.04985(9) 0.0229(3) Uani 1 1 d . . .
N3 N 0.45128(18) 0.51794(14) 0.09099(8) 0.0214(3) Uani 1 1 d . . .
N4 N 1.13402(19) 0.31432(16) 0.22185(9) 0.0294(4) Uani 1 1 d . . .
C1 C 0.6374(2) 0.94374(19) 0.10653(13) 0.0281(4) Uani 1 1 d . . .
C2 C 0.4527(2) 0.91412(16) 0.09293(10) 0.0223(4) Uani 1 1 d . . .
C3 C 0.3314(2) 1.01469(17) 0.09173(11) 0.0261(4) Uani 1 1 d . . .
C4 C 0.1625(2) 0.98049(18) 0.07901(11) 0.0283(4) Uani 1 1 d . . .
C5 C 0.1179(2) 0.84851(17) 0.06550(11) 0.0258(4) Uani 1 1 d . . .
C6 C 0.2473(2) 0.75328(16) 0.06694(10) 0.0213(4) Uani 1 1 d . . .
C7 C 0.2907(2) 0.50316(16) 0.05907(10) 0.0196(4) Uani 1 1 d . . .
C8 C 0.5641(2) 0.41783(16) 0.11563(10) 0.0223(4) Uani 1 1 d . . .
C9 C 0.7245(2) 0.46883(16) 0.15414(10) 0.0206(4) Uani 1 1 d . . .
C10 C 0.8505(2) 0.37397(17) 0.17007(10) 0.0219(4) Uani 1 1 d . . .
C11 C 1.0025(2) 0.41580(17) 0.20336(10) 0.0229(4) Uani 1 1 d . . .
C12 C 1.0374(2) 0.54838(18) 0.22113(10) 0.0254(4) Uani 1 1 d . . .
C13 C 0.9100(2) 0.64170(18) 0.20729(11) 0.0278(4) Uani 1 1 d . . .
C14 C 0.7550(2) 0.60240(17) 0.17435(11) 0.0252(4) Uani 1 1 d . . .
H1A H 0.679(3) 0.923(2) 0.1567(14) 0.041(6) Uiso 1 1 d . . .
H1B H 0.659(3) 1.035(3) 0.0960(14) 0.052(7) Uiso 1 1 d . . .
H1C H 0.705(3) 0.890(2) 0.0708(13) 0.043(6) Uiso 1 1 d . . .
H2N H 0.101(3) 0.6110(19) 0.0339(11) 0.025(5) Uiso 1 1 d . . .
H3 H 0.364(3) 1.106(2) 0.0985(12) 0.035(5) Uiso 1 1 d . . .
H3N H 0.478(3) 0.599(2) 0.0952(11) 0.027(5) Uiso 1 1 d . . .
H4 H 0.078(3) 1.049(2) 0.0784(11) 0.032(5) Uiso 1 1 d . . .
H5 H 0.006(3) 0.8211(19) 0.0561(11) 0.030(5) Uiso 1 1 d . . .
H10 H 0.835(3) 0.284(2) 0.1575(12) 0.035(6) Uiso 1 1 d . . .
H12 H 1.144(3) 0.573(2) 0.2427(12) 0.035(6) Uiso 1 1 d . . .
H13 H 0.929(3) 0.735(2) 0.2211(11) 0.033(5) Uiso 1 1 d . . .
H14 H 0.673(3) 0.664(2) 0.1666(11) 0.031(5) Uiso 1 1 d . . .

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O1 0.0264(7) 0.0182(6) 0.0652(10) -0.0030(6) -0.0175(7) 0.0007(5)
O2 0.0330(8) 0.0288(7) 0.0609(10) 0.0034(7) -0.0095(7) 0.0083(6)
O3 0.0184(7) 0.0483(9) 0.0488(9) -0.0061(7) -0.0107(6) 0.0065(6)
N1 0.0191(7) 0.0186(7) 0.0262(8) -0.0010(6) -0.0027(6) -0.0009(5)
```

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N2 0.0145(8) 0.0180(7) 0.0352(9) -0.0013(6) -0.0077(6) -0.0002(5)
N3 0.0178(7) 0.0144(7) 0.0312(9) -0.0016(6) -0.0061(6) -0.0011(5)
N4 0.0226(8) 0.0338(9) 0.0314(9) -0.0017(7) -0.0041(7) 0.0061(7)
C1 0.0248(10) 0.0233(9) 0.0358(11) 0.0002(8) -0.0023(8) -0.0058(7)
C2 0.0248(9) 0.0199(8) 0.0219(9) 0.0007(7) -0.0024(7) -0.0025(7)
C3 0.0312(10) 0.0174(8) 0.0290(10) -0.0004(7) -0.0055(8) -0.0015(7)
C4 0.0288(10) 0.0216(9) 0.0337(11) -0.0028(8) -0.0075(8) 0.0064(7)
C5 0.0198(9) 0.0220(8) 0.0347(10) -0.0012(7) -0.0067(8) 0.0011(7)
C6 0.0223(9) 0.0181(8) 0.0231(9) 0.0003(7) -0.0037(7) 0.0008(6)
C7 0.0164(8) 0.0196(8) 0.0227(9) 0.0002(7) -0.0019(7) 0.0001(6)
C8 0.0183(9) 0.0190(8) 0.0293(10) 0.0004(7) -0.0030(7) -0.0002(6)
C9 0.0182(9) 0.0191(8) 0.0243(9) 0.0002(7) -0.0022(7) -0.0014(6)
C10 0.0203(9) 0.0198(8) 0.0255(9) -0.0008(7) -0.0015(7) 0.0017(7)
C11 0.0171(8) 0.0274(9) 0.0240(9) 0.0015(7) -0.0006(7) 0.0045(7)
C12 0.0197(9) 0.0307(9) 0.0252(9) 0.0004(8) -0.0047(7) -0.0035(7)
C13 0.0255(10) 0.0234(9) 0.0339(11) -0.0023(8) -0.0065(8) -0.0039(7)
C14 0.0212(9) 0.0205(8) 0.0332(10) -0.0009(7) -0.0063(7) 0.0024(7)

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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O2 N4 1.231(2) . ?
O3 N4 1.222(2) . ?
N1 C6 1.335(2) . ?
N1 C2 1.359(2) . ?
N2 C7 1.357(2) . ?
N2 C6 1.411(2) . ?
N2 H2N 0.84(2) . ?
N3 C7 1.372(2) . ?
N3 C8 1.394(2) . ?
N3 H3N 0.84(2) . ?
N4 C11 1.477(2) . ?
C1 C2 1.499(3) . ?
C1 H1A 0.95(2) . ?
C1 H1B 0.95(3) . ?
C1 H1C 1.00(2) . ?
C2 C3 1.387(2) . ?
C3 C4 1.386(3) . ?
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C3 H3 0.95(2) . ?
C4 C5 1.380(2) . ?
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C5 C6 1.395(2) . ?
C5 H5 0.93(2) . ?
C8 C9 1.499(2) . ?
C9 C10 1.393(2) . ?
C9 C14 1.397(2) . ?
C10 C11 1.376(2) . ?
C10 H10 0.93(2) . ?
C11 C12 1.383(2) . ?
C12 C13 1.385(3) . ?
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C7 N2 C6 131.34(15) . . ?
C7 N2 H2N 115.6(13) . . ?
C6 N2 H2N 112.9(13) . . ?
C7 N3 C8 128.06(14) . . ?
C7 N3 H3N 111.5(14) . . ?
C8 N3 H3N 120.4(14) . . ?
O3 N4 O2 124.03(16) . . ?
O3 N4 C11 118.28(15) . . ?
O2 N4 C11 117.67(15) . . ?
C2 C1 H1A 113.3(14) . . ?
C2 C1 H1B 109.8(15) . . ?
H1A C1 H1B 110(2) . . ?
C2 C1 H1C 109.8(13) . . ?
H1A C1 H1C 107.3(19) . . ?
H1B C1 H1C 106.8(19) . . ?
N1 C2 C3 121.65(16) . . ?
N1 C2 C1 116.46(15) . . ?
C3 C2 C1 121.88(16) . . ?
C4 C3 C2 119.01(16) . . ?
C4 C3 H3 120.5(13) . . ?
C2 C3 H3 120.5(13) . . ?
C5 C4 C3 119.89(17) . . ?
C5 C4 H4 120.6(12) . . ?
C3 C4 H4 119.5(12) . . ?
C4 C5 C6 117.71(17) . . ?
C4 C5 H5 122.9(12) . . ?
C6 C5 H5 119.4(12) . . ?

N1 C6 C5 123.37(16) . . ?
N1 C6 N2 118.94(15) . . ?
C5 C6 N2 117.68(16) . . ?
N2 C7 N3 114.66(14) . . ?
N2 C7 S1 119.19(13) . . ?
N3 C7 S1 126.15(13) . . ?
O1 C8 N3 124.22(16) . . ?
O1 C8 C9 121.38(15) . . ?
N3 C8 C9 114.40(14) . . ?
C10 C9 C14 118.87(16) . . ?
C10 C9 C8 116.29(15) . . ?
C14 C9 C8 124.84(15) . . ?
C11 C10 C9 118.80(16) . . ?
C11 C10 H10 119.5(13) . . ?
C9 C10 H10 121.6(13) . . ?
C10 C11 C12 123.16(16) . . ?
C10 C11 N4 118.55(15) . . ?
C12 C11 N4 118.29(16) . . ?
C13 C12 C11 117.81(17) . . ?
C13 C12 H12 121.5(13) . . ?
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C12 C13 C14 120.31(17) . . ?
C12 C13 H13 119.6(12) . . ?
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C1 C2 C3 C4 -179.86(18) . . . . ?
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C3 C4 C5 C6 1.4(3) . . . . ?
C2 N1 C6 C5 -2.8(3) . . . . ?
C2 N1 C6 N2 175.51(15) . . . . ?
C4 C5 C6 N1 1.1(3) . . . . ?
C4 C5 C6 N2 -177.28(17) . . . . ?
C7 N2 C6 N1 14.6(3) . . . . ?
C7 N2 C6 C5 -166.99(18) . . . . ?
C6 N2 C7 N3 0.4(3) . . . . ?
C6 N2 C7 S1 -179.87(15) . . . . ?

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C8 N3 C7 N2 171.78(16) . . . . ?
C8 N3 C7 S1 -7.9(3) . . . . ?
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C7 N3 C8 C9 -174.95(16) . . . . ?
O1 C8 C9 C10 8.4(3) . . . . ?
N3 C8 C9 C10 -171.27(15) . . . . ?
O1 C8 C9 C14 -171.82(18) . . . . ?
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C14 C9 C10 C11 -1.7(3) . . . . ?
C8 C9 C10 C11 178.10(16) . . . . ?
C9 C10 C11 C12 -0.8(3) . . . . ?
C9 C10 C11 N4 178.50(15) . . . . ?
O3 N4 C11 C10 168.50(17) . . . . ?
O2 N4 C11 C10 -12.6(2) . . . . ?
O3 N4 C11 C12 -12.2(2) . . . . ?
O2 N4 C11 C12 166.77(17) . . . . ?
C10 C11 C12 C13 2.7(3) . . . . ?
N4 C11 C12 C13 -176.62(16) . . . . ?
C11 C12 C13 C14 -2.0(3) . . . . ?
C12 C13 C14 C9 -0.4(3) . . . . ?
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C8 C9 C14 C13 -177.50(17) . . . . ?

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N3 H3N N1  0.84(2) 1.93(2) 2.671(2) 147.2(19) .

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'N'  'N'   0.0061   0.0033
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'O'  'O'   0.0106   0.0060
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'S'  'S'   0.1246   0.1234
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 '-x, -y, -z'

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_computing_publication_material  'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
```

on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type   full
_refine_ls_weighting_scheme   calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.1079P)^2^+0.1797P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary   direct
_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   geom
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_refine_ls_extinction_method   none
_refine_ls_extinction_coef   ?
_refine_ls_number_reflns   2394
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_refine_ls_number_restraints   0
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_refine_ls_wR_factor_ref   0.1806
_refine_ls_wR_factor_gt   0.1482
_refine_ls_goodness_of_fit_ref   1.052
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S1 S 0.1804(2) 0.48502(7) 0.38381(6) 0.0302(3) Uani 1 1 d . . .
O1 O 0.5733(8) 0.8644(2) 0.45784(16) 0.0413(7) Uani 1 1 d . . .
O2 O 0.4179(9) 0.6743(3) 0.81125(18) 0.0578(9) Uani 1 1 d . . .
O3 O 0.7991(9) 0.7903(3) 0.89686(18) 0.0639(10) Uani 1 1 d . . .
N1 N 0.2750(7) 0.7626(2) 0.21137(18) 0.0264(7) Uani 1 1 d . . .
N2 N 0.2559(8) 0.6971(3) 0.34156(19) 0.0293(7) Uani 1 1 d . . .
N3 N 0.4431(8) 0.6801(3) 0.48173(19) 0.0265(7) Uani 1 1 d . . .
N4 N 0.6523(9) 0.7550(3) 0.8250(2) 0.0361(8) Uani 1 1 d . . .
C1 C 0.3473(10) 0.8527(3) 0.0814(2) 0.0361(9) Uani 1 1 d . . .
H1A H 0.4865 0.9110 0.1250 0.054 Uiso 1 1 calc R . .
H1B H 0.1580 0.8853 0.0556 0.054 Uiso 1 1 calc R . .
H1C H 0.4956 0.8263 0.0353 0.054 Uiso 1 1 calc R . .

C2 C 0.1967(9) 0.7539(3) 0.1249(2) 0.0283(8) Uani 1 1 d . . .
C3 C -0.0123(10) 0.6586(3) 0.0782(2) 0.0328(9) Uani 1 1 d . . .
C4 C -0.1466(11) 0.5707(4) 0.1219(3) 0.0348(9) Uani 1 1 d . . .
C5 C -0.0691(10) 0.5787(3) 0.2106(2) 0.0321(9) Uani 1 1 d . . .
C6 C 0.1463(9) 0.6753(3) 0.2514(2) 0.0260(8) Uani 1 1 d . . .
C7 C 0.2923(9) 0.6258(3) 0.3995(2) 0.0254(8) Uani 1 1 d . . .
C8 C 0.5719(9) 0.7936(3) 0.5075(2) 0.0282(8) Uani 1 1 d . . .
C9 C 0.7138(9) 0.8298(3) 0.6004(2) 0.0256(8) Uani 1 1 d . . .
C10 C 0.6172(9) 0.7704(3) 0.6683(2) 0.0244(8) Uani 1 1 d . . .
C11 C 0.7567(9) 0.8159(3) 0.7519(2) 0.0268(8) Uani 1 1 d . . .
C12 C 0.9862(10) 0.9173(3) 0.7701(2) 0.0291(8) Uani 1 1 d . . .
C13 C 1.0754(10) 0.9759(3) 0.7029(2) 0.0303(9) Uani 1 1 d . . .
C14 C 0.9411(10) 0.9336(3) 0.6183(2) 0.0300(9) Uani 1 1 d . . .
H2N H 0.346(10) 0.768(3) 0.358(2) 0.035(11) Uiso 1 1 d . . .
H3N H 0.472(11) 0.637(4) 0.517(3) 0.050(14) Uiso 1 1 d . . .
H3 H -0.050(9) 0.654(3) 0.019(2) 0.033(10) Uiso 1 1 d . . .
H4 H -0.249(12) 0.507(4) 0.091(3) 0.060(15) Uiso 1 1 d . . .
H5 H -0.152(9) 0.524(3) 0.237(2) 0.027(10) Uiso 1 1 d . . .
H10 H 0.458(10) 0.707(3) 0.664(3) 0.039(11) Uiso 1 1 d . . .
H12 H 1.085(9) 0.943(3) 0.834(2) 0.033(10) Uiso 1 1 d . . .
H13 H 1.208(10) 1.038(4) 0.708(3) 0.038(12) Uiso 1 1 d . . .
H14 H 1.006(9) 0.973(3) 0.570(2) 0.036(11) Uiso 1 1 d . . .

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O1 0.065(2) 0.0274(15) 0.0288(14) 0.0064(12) -0.0100(13) -0.0009(13)
O2 0.082(2) 0.0427(19) 0.0387(17) 0.0075(14) -0.0005(16) -0.0221(18)
O3 0.076(2) 0.081(3) 0.0258(16) 0.0094(15) -0.0119(16) -0.0157(19)
N1 0.0261(16) 0.0270(17) 0.0264(16) 0.0021(12) -0.0014(13) 0.0075(13)
N2 0.0386(19) 0.0233(18) 0.0236(16) 0.0017(13) -0.0059(14) 0.0010(14)
N3 0.0340(17) 0.0210(17) 0.0231(16) 0.0027(13) -0.0044(13) 0.0022(13)
N4 0.044(2) 0.036(2) 0.0279(18) 0.0016(14) 0.0016(15) 0.0066(16)
C1 0.036(2) 0.040(2) 0.032(2) 0.0052(17) -0.0012(17) 0.0053(18)
C2 0.0269(19) 0.034(2) 0.0248(18) 0.0014(15) -0.0009(15) 0.0126(16)
C3 0.037(2) 0.036(2) 0.024(2) 0.0012(16) -0.0044(17) 0.0103(17)
C4 0.036(2) 0.032(2) 0.033(2) -0.0029(18) -0.0090(18) 0.0064(18)
C5 0.037(2) 0.026(2) 0.033(2) 0.0052(17) -0.0028(17) 0.0041(17)
C6 0.0264(18) 0.026(2) 0.0258(18) 0.0022(15) -0.0034(15) 0.0071(15)
C7 0.0197(17) 0.031(2) 0.0259(18) 0.0019(15) 0.0025(15) 0.0075(15)
C8 0.0295(19) 0.027(2) 0.0274(19) 0.0025(16) 0.0013(16) 0.0023(16)
C9 0.0291(19) 0.0222(19) 0.0258(18) 0.0006(14) -0.0022(15) 0.0088(15)
C10 0.0230(18) 0.0202(19) 0.0294(19) -0.0006(15) 0.0009(15) 0.0058(15)
C11 0.031(2) 0.027(2) 0.0240(18) 0.0023(15) 0.0004(15) 0.0099(16)
C12 0.0293(19) 0.029(2) 0.0263(19) -0.0049(15) -0.0045(16) 0.0077(16)
C13 0.028(2) 0.025(2) 0.035(2) 0.0000(16) 0.0002(17) 0.0021(17)
C14 0.034(2) 0.026(2) 0.030(2) 0.0022(16) 0.0020(17) 0.0042(16)

```
_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O1 C8 1.222(4) . ?
O2 N4 1.216(4) . ?
O3 N4 1.218(4) . ?
N1 C6 1.335(4) . ?
N1 C2 1.346(4) . ?
N2 C7 1.341(4) . ?
N2 C6 1.418(4) . ?
N2 H2N 0.87(4) . ?
N3 C8 1.374(5) . ?
N3 C7 1.405(4) . ?
N3 H3N 0.82(4) . ?
N4 C11 1.470(5) . ?
C1 C2 1.500(5) . ?
C1 H1A 0.9800 . ?
C1 H1B 0.9800 . ?
C1 H1C 0.9800 . ?
C2 C3 1.390(5) . ?
C3 C4 1.382(6) . ?
C3 H3 0.92(4) . ?
C4 C5 1.379(5) . ?
C4 H4 0.87(4) . ?
C5 C6 1.379(5) . ?
C5 H5 0.85(4) . ?
C8 C9 1.499(5) . ?
C9 C10 1.384(5) . ?
C9 C14 1.401(5) . ?
C10 C11 1.384(5) . ?
C10 H10 0.90(4) . ?
C11 C12 1.385(5) . ?
C12 C13 1.364(5) . ?
C12 H12 1.03(4) . ?
C13 C14 1.385(5) . ?
C13 H13 0.84(4) . ?
C14 H14 0.97(4) . ?
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C6 N1 C2 117.5(3) . . ?
C7 N2 C6 131.1(3) . . ?
C7 N2 H2N 116(3) . . ?
C6 N2 H2N 112(3) . . ?
C8 N3 C7 128.4(3) . . ?
C8 N3 H3N 117(3) . . ?
C7 N3 H3N 114(3) . . ?
O3 N4 O2 123.4(3) . . ?
O3 N4 C11 118.0(3) . . ?
O2 N4 C11 118.5(3) . . ?
C2 C1 H1A 109.5 . . ?
C2 C1 H1B 109.5 . . ?
H1A C1 H1B 109.5 . . ?
C2 C1 H1C 109.5 . . ?
H1A C1 H1C 109.5 . . ?
H1B C1 H1C 109.5 . . ?
N1 C2 C3 121.8(3) . . ?
N1 C2 C1 116.4(3) . . ?
C3 C2 C1 121.7(3) . . ?
C4 C3 C2 119.1(4) . . ?
C4 C3 H3 122(2) . . ?
C2 C3 H3 119(2) . . ?
C5 C4 C3 119.6(4) . . ?
C5 C4 H4 121(3) . . ?
C3 C4 H4 118(3) . . ?
C4 C5 C6 117.4(4) . . ?
C4 C5 H5 119(2) . . ?
C6 C5 H5 123(2) . . ?
N1 C6 C5 124.5(3) . . ?
N1 C6 N2 110.5(3) . . ?
C5 C6 N2 125.0(3) . . ?
N2 C7 N3 114.2(3) . . ?
N2 C7 S1 127.3(3) . . ?
N3 C7 S1 118.6(3) . . ?
O1 C8 N3 122.6(3) . . ?
O1 C8 C9 119.8(3) . . ?
N3 C8 C9 117.6(3) . . ?
C10 C9 C14 119.6(3) . . ?
C10 C9 C8 123.8(3) . . ?
C14 C9 C8 116.5(3) . . ?
C11 C10 C9 117.9(3) . . ?
C11 C10 H10 116(3) . . ?
C9 C10 H10 125(3) . . ?
C10 C11 C12 123.0(3) . . ?
C10 C11 N4 118.7(3) . . ?
```

C12 C11 N4 118.3(3) . . ?
C13 C12 C11 118.5(3) . . ?
C13 C12 H12 124(2) . . ?
C11 C12 H12 118(2) . . ?
C12 C13 C14 120.4(4) . . ?
C12 C13 H13 125(3) . . ?
C14 C13 H13 115(3) . . ?
C13 C14 C9 120.6(3) . . ?
C13 C14 H14 121(2) . . ?
C9 C14 H14 118(2) . . ?

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 _geom_torsion_site_symmetry_4
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C6 N1 C2 C3 0.5(5) . . . . ?
C6 N1 C2 C1 -179.5(3) . . . . ?
N1 C2 C3 C4 0.7(5) . . . . ?
C1 C2 C3 C4 -179.3(3) . . . . ?
C2 C3 C4 C5 -0.5(6) . . . . ?
C3 C4 C5 C6 -0.9(6) . . . . ?
C2 N1 C6 C5 -2.0(5) . . . . ?
C2 N1 C6 N2 179.3(3) . . . . ?
C4 C5 C6 N1 2.2(6) . . . . ?
C4 C5 C6 N2 -179.2(3) . . . . ?
C7 N2 C6 N1 -155.3(4) . . . . ?
C7 N2 C6 C5 26.0(6) . . . . ?
C6 N2 C7 N3 173.7(3) . . . . ?
C6 N2 C7 S1 -6.3(6) . . . . ?
C8 N3 C7 N2 -3.9(5) . . . . ?
C8 N3 C7 S1 176.1(3) . . . . ?
C7 N3 C8 O1 -1.0(6) . . . . ?
C7 N3 C8 C9 178.8(3) . . . . ?
O1 C8 C9 C10 155.9(4) . . . . ?
N3 C8 C9 C10 -24.0(5) . . . . ?
O1 C8 C9 C14 -20.2(5) . . . . ?
N3 C8 C9 C14 159.9(3) . . . . ?
C14 C9 C10 C11 -1.2(5) . . . . ?
C8 C9 C10 C11 -177.2(3) . . . . ?
C9 C10 C11 C12 0.1(5) . . . . ?
C9 C10 C11 N4 179.0(3) . . . . ?
O3 N4 C11 C10 173.8(3) . . . . ?
O2 N4 C11 C10 -8.3(5) . . . . ?
O3 N4 C11 C12 -7.3(5) . . . . ?
O2 N4 C11 C12 170.6(3) . . . . ?
C10 C11 C12 C13 0.9(5) . . . . ?

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N4 C11 C12 C13 -178.0(3) . . . . ?
C11 C12 C13 C14 -0.7(5) . . . . ?
C12 C13 C14 C9 -0.4(6) . . . . ?
C10 C9 C14 C13 1.4(5) . . . . ?
C8 C9 C14 C13 177.7(3) . . . . ?

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 _geom_hbond_distance_DA
 _geom_hbond_angle_DHA
 _geom_hbond_site_symmetry_A
N2 H2N O1  0.87(4) 1.89(4) 2.614(4) 139(4) .
N3 H3N S1  0.82(4) 2.72(5) 3.490(4) 158(4) 2_666

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_refine_diff_density_max    0.485
_refine_diff_density_min   -0.417
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#                           CCDC
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2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
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_cell_length_b                 19.570(5)
_cell_length_c                 10.609(3)
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_cell_angle_beta                95.509(4)
_cell_angle_gamma                 90.00
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_atom_site_fract_z
S1 S 0.12268(6) 0.57549(2) 0.39854(4)
O1 O 0.27979(16) 0.62347(6) 0.17230(11)
N1 N 0.08728(16) 0.38415(7) 0.14247(12)
N2 N 0.04436(16) 0.45217(7) 0.32015(13)
N3 N 0.17931(16) 0.51391(7) 0.17820(12)
C1 C 0.01651(18) 0.39148(7) 0.24941(14)
C2 C -0.0823(2) 0.34198(8) 0.29731(15)
C3 C -0.1057(2) 0.28166(9) 0.23051(17)
C4 C -0.0314(2) 0.27289(9) 0.11995(17)
C5 C 0.06297(19) 0.32496(8) 0.07739(15)
C6 C 0.1433(2) 0.31887(10) -0.04331(18)
C7 C 0.11715(18) 0.51189(8) 0.29299(14)
C8 C 0.25498(18) 0.56838(8) 0.12206(14)
C9 C 0.30427(18) 0.55320(8) -0.00695(14)
C10 C 0.2498(2) 0.49672(9) -0.07875(15)
C11 C 0.3015(2) 0.48594(9) -0.19781(16)
C12 C 0.4078(2) 0.53165(10) -0.24600(16)
C13 C 0.4620(2) 0.58812(10) -0.17604(17)
C14 C 0.4106(2) 0.59922(9) -0.05708(16)
H2N H 0.005(2) 0.4527(10) 0.388(2)
H3N H 0.172(2) 0.4766(11) 0.1404(19)
H2 H -0.132(2) 0.3505(10) 0.3743(19)
H3 H -0.170(3) 0.2473(11) 0.2610(19)
H4 H -0.044(2) 0.2325(12) 0.074(2)
H6A H 0.081(3) 0.3436(12) -0.112(2)
H6B H 0.255(3) 0.3367(12) -0.035(2)
H6C H 0.152(3) 0.2711(12) -0.066(2)
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H10 H 0.175(2) 0.4648(10) -0.0458(18)
H11 H 0.260(3) 0.4477(11) -0.246(2)
H12 H 0.440(2) 0.5231(11) -0.326(2)
H13 H 0.538(3) 0.6186(12) -0.210(2)
H14 H 0.446(2) 0.6368(11) -0.0070(19)
C1S C 0.5115(2) 0.66157(9) 0.42016(15)
Cl1S Cl 0.43116(6) 0.71511(2) 0.53195(5)
Cl2S Cl 0.60946(8) 0.70997(3) 0.31089(5)
Cl3S Cl 0.64925(8) 0.60358(3) 0.49808(5)
H1S H 0.424(3) 0.6376(11) 0.377(2)

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3 1/2+x,1/2+y,1/2+z
4 -x,1/2+y,1/2-z

5 -x,-y,-z
6 1/2+x,-y,z
7 1/2-x,1/2-y,1/2-z
8 x,1/2-y,1/2+z
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S1 S 0.325530(17) 0.07044(6) 0.089343(16)
O1 O 0.45200(4) -0.19130(18) -0.01226(5)
N1 N 0.52757(5) 0.2242(2) 0.15298(5)
N2 N 0.43544(6) 0.1194(2) 0.06708(5)
N3 N 0.35631(6) -0.1374(2) 0.00223(5)
C1 C 0.63022(8) 0.3008(3) 0.23902(8)
C2 C 0.56117(7) 0.3735(3) 0.19990(6)
C3 C 0.53387(7) 0.5835(3) 0.21147(7)
C4 C 0.47043(7) 0.6418(3) 0.17296(7)
C5 C 0.43515(7) 0.4896(3) 0.12476(7)
C6 C 0.46631(6) 0.2829(2) 0.11719(6)
C7 C 0.37622(6) 0.0224(2) 0.05191(6)
C8 C 0.39415(6) -0.2414(2) -0.02676(6)
C9 C 0.36042(6) -0.4242(2) -0.07530(6)
C10 C 0.39849(7) -0.6088(3) -0.08405(6)
C11 C 0.36993(7) -0.7871(3) -0.12754(7)
C12 C 0.30314(7) -0.7813(3) -0.16301(7)
C13 C 0.26499(7) -0.5955(3) -0.15534(7)
C14 C 0.29322(7) -0.4169(3) -0.11166(6)
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H1B H 0.6596(10) 0.316(4) 0.2159(10)
H1C H 0.6469(11) 0.381(4) 0.2757(12)
H3 H 0.5588(9) 0.682(4) 0.2453(9)
H4 H 0.4514(8) 0.790(3) 0.1791(8)
H5 H 0.3904(8) 0.522(3) 0.0969(8)
H10 H 0.4433(8) -0.608(3) -0.0590(8)
H11 H 0.3942(8) -0.908(3) -0.1333(8)
H12 H 0.2827(9) -0.905(3) -0.1932(9)
H13 H 0.2173(9) -0.591(3) -0.1802(9)
H14 H 0.2672(8) -0.289(3) -0.1061(7)
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H1S H 0.2667(11) 0.435(4) 0.0311(10)
H1S H 0.2333(11) 0.435(4) -0.0311(10)
S1 S 0.174470(17) 0.07044(6) -0.089343(16)

O1 O 0.04800(4) -0.19130(18) 0.01226(5)
N1 N -0.02757(5) 0.2242(2) -0.15298(5)
N2 N 0.06456(6) 0.1194(2) -0.06708(5)
N3 N 0.14369(6) -0.1374(2) -0.00223(5)
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C2 C -0.06117(7) 0.3735(3) -0.19990(6)
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C6 C 0.03369(6) 0.2829(2) -0.11719(6)
C7 C 0.12378(6) 0.0224(2) -0.05191(6)
C8 C 0.10585(6) -0.2414(2) 0.02676(6)
C9 C 0.13958(6) -0.4242(2) 0.07530(6)
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C12 C 0.19686(7) -0.7813(3) 0.16301(7)
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H1C H -0.1469(11) 0.381(4) -0.2757(12)
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H1C H 0.3531(11) -0.381(4) -0.2757(12)
H3 H 0.4412(9) -0.682(4) -0.2453(9)
H4 H 0.5486(8) -0.790(3) -0.1791(8)
H5 H 0.6096(8) -0.522(3) -0.0969(8)
H10 H 0.5567(8) 0.608(3) 0.0590(8)
H11 H 0.6058(8) 0.908(3) 0.1333(8)
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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O3 O 0.88022(19) -0.07368(15) 0.84686(16) 0.0468(4) Uani 1 1 d . . .
N1 N 0.83940(17) 0.61957(14) 1.14964(15) 0.0242(3) Uani 1 1 d . . .
N2 N 0.65499(18) 0.81179(16) 1.05434(16) 0.0252(3) Uani 1 1 d . . .
N3 N 0.59347(18) 0.61951(15) 0.89178(16) 0.0247(3) Uani 1 1 d . . .
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N3 0.0226(7) 0.0258(8) 0.0216(7) 0.0030(6) -0.0004(6) 0.0079(6)
N4 0.0273(8) 0.0288(8) 0.0359(9) -0.0023(7) 0.0041(7) 0.0044(6)
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C7 0.0234(8) 0.0227(8) 0.0221(8) 0.0038(6) 0.0054(7) 0.0041(6)
C8 0.0227(8) 0.0270(9) 0.0221(8) 0.0030(7) 0.0042(7) 0.0034(7)
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C11 0.0288(9) 0.0317(10) 0.0258(9) -0.0033(7) 0.0040(7) -0.0004(7)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
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 used when they are defined by crystal symmetry.  An approximate (isotropic)
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N1 C2 1.355(2) . ?
N2 C7 1.357(2) . ?
N2 C6 1.413(2) . ?
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N3 C7 1.375(2) . ?
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C1 H1C 0.99(2) . ?
C2 C3 1.384(2) . ?
C3 C4 1.385(3) . ?
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C4 C5 1.381(2) . ?
C4 H4 0.971(19) . ?
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C5 H5 0.92(2) . ?
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C9 C14 1.392(2) . ?
C9 C10 1.395(2) . ?
C10 C11 1.381(3) . ?
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C11 C12 1.379(2) . ?
C11 H11 0.96(2) . ?
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C14 H14 0.95(2) . ?

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C7 N3 C8 127.90(14) . . ?
C7 N3 H3N 114.5(12) . . ?
C8 N3 H3N 117.6(12) . . ?
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O3 N4 C12 118.08(15) . . ?
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C2 C1 H1B 107.8(13) . . ?
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H1B C1 H1C 111.0(17) . . ?
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C3 C2 C1 121.69(16) . . ?

C2 C3 C4 119.39(16) . . ?
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C4 C3 H3 119.4(12) . . ?
C5 C4 C3 119.47(17) . . ?
C5 C4 H4 120.1(12) . . ?
C3 C4 H4 120.5(12) . . ?
C4 C5 C6 117.73(17) . . ?
C4 C5 H5 122.0(13) . . ?
C6 C5 H5 120.3(12) . . ?
N1 C6 C5 123.59(15) . . ?
N1 C6 N2 118.71(15) . . ?
C5 C6 N2 117.70(15) . . ?
N2 C7 N3 114.78(14) . . ?
N2 C7 S1 119.62(13) . . ?
N3 C7 S1 125.60(13) . . ?
O1 C8 N3 124.23(16) . . ?
O1 C8 C9 121.31(15) . . ?
N3 C8 C9 114.46(14) . . ?
C14 C9 C10 119.29(16) . . ?
C14 C9 C8 123.79(15) . . ?
C10 C9 C8 116.92(15) . . ?
C11 C10 C9 120.79(16) . . ?
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C12 C11 H11 120.5(13) . . ?
C10 C11 H11 121.4(13) . . ?
C11 C12 C13 122.98(17) . . ?
C11 C12 N4 118.66(16) . . ?
C13 C12 N4 118.35(15) . . ?
C14 C13 C12 118.00(16) . . ?
C14 C13 H13 120.7(13) . . ?
C12 C13 H13 121.3(13) . . ?
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C6 N1 C2 C1 178.25(15) . . . . ?
N1 C2 C3 C4 1.3(3) . . . . ?
C1 C2 C3 C4 -177.70(17) . . . . ?
C2 C3 C4 C5 -1.0(3) . . . . ?

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C2 N1 C6 C5 0.0(2) . . . . ?
C2 N1 C6 N2 179.88(14) . . . . ?
C4 C5 C6 N1 0.3(3) . . . . ?
C4 C5 C6 N2 -179.55(16) . . . . ?
C7 N2 C6 N1 5.1(3) . . . . ?
C7 N2 C6 C5 -175.02(17) . . . . ?
C6 N2 C7 N3 -0.2(3) . . . . ?
C6 N2 C7 S1 179.21(14) . . . . ?
C8 N3 C7 N2 177.18(15) . . . . ?
C8 N3 C7 S1 -2.2(3) . . . . ?
C7 N3 C8 O1 -2.6(3) . . . . ?
C7 N3 C8 C9 176.98(15) . . . . ?
O1 C8 C9 C14 -167.42(16) . . . . ?
N3 C8 C9 C14 13.0(2) . . . . ?
O1 C8 C9 C10 12.6(2) . . . . ?
N3 C8 C9 C10 -166.95(15) . . . . ?
C14 C9 C10 C11 -1.8(3) . . . . ?
C8 C9 C10 C11 178.17(16) . . . . ?
C9 C10 C11 C12 2.0(3) . . . . ?
C10 C11 C12 C13 -0.7(3) . . . . ?
C10 C11 C12 N4 -179.33(15) . . . . ?
O2 N4 C12 C11 6.8(2) . . . . ?
O3 N4 C12 C11 -172.82(16) . . . . ?
O2 N4 C12 C13 -171.87(16) . . . . ?
O3 N4 C12 C13 8.5(2) . . . . ?
C11 C12 C13 C14 -0.6(3) . . . . ?
N4 C12 C13 C14 177.97(15) . . . . ?
C12 C13 C14 C9 0.8(3) . . . . ?
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C8 C9 C14 C13 -179.58(15) . . . . ?

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N3 H3N N1  0.86(2) 1.923(19) 2.658(2) 142.9(17) .

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'S' 'S' 0.1246 0.1234

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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loop_

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'-x, -y, -z'

'x, -y-1/2, z-1/2'

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_cell_length_b 20.077(2)

_cell_length_c 9.8693(10)

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_cell_angle_gamma 90.00

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_cell_measurement_reflns_used 4612

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_exptl_absorpt_process_details SADABS

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_diffrn_radiation_source 'fine-focus sealed tube'

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_reflns_number_gt 2699

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_computing_molecular_graphics 'Bruker SHELXTL'

_computing_publication_material 'Bruker SHELXTL'

_refine_special_details

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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

;

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_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0596P)^2^+0.3108P] where P=(Fo^2^+2Fc^2^)/3'

_atom_sites_solution_primary direct

_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens difmap

_refine_ls_hydrogen_treatment refall

_refine_ls_extinction_method none

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loop_

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O1 O 0.81340(13) 0.46964(6) 0.31452(12) 0.0365(3) Uani 1 1 d . . .

O2 O 0.30177(13) 0.54738(5) 0.23649(12) 0.0357(3) Uani 1 1 d . . .

N1 N 0.90015(16) 0.31410(6) 0.10090(12) 0.0298(3) Uani 1 1 d . . .

N2 N 0.68180(16) 0.38827(6) 0.09377(13) 0.0290(3) Uani 1 1 d . . .

N3 N 0.51742(16) 0.46363(6) 0.17299(13) 0.0286(3) Uani 1 1 d . . .

C1 C 0.73431(18) 0.33494(7) 0.02422(14) 0.0273(3) Uani 1 1 d . . .

C2 C 0.6309(2) 0.30839(8) -0.10894(16) 0.0326(3) Uani 1 1 d . . .

C3 C 0.7070(2) 0.25756(8) -0.16261(17) 0.0366(4) Uani 1 1 d . . .

C4 C 0.8769(2) 0.23413(8) -0.08351(17) 0.0367(4) Uani 1 1 d . . .

C5 C 0.9707(2) 0.26345(7) 0.04916(16) 0.0332(3) Uani 1 1 d . . .

C6 C 1.1551(3) 0.24067(10) 0.1410(2) 0.0468(4) Uani 1 1 d . . .

C7 C 0.51777(19) 0.41176(7) 0.07928(15) 0.0281(3) Uani 1 1 d . . .

C8 C 0.65784(18) 0.48925(7) 0.28633(15) 0.0275(3) Uani 1 1 d . . .

C9 C 0.61289(18) 0.54056(7) 0.37792(15) 0.0266(3) Uani 1 1 d . . .

C10 C 0.75659(19) 0.56142(7) 0.49913(16) 0.0301(3) Uani 1 1 d . . .

C11 C 0.7333(2) 0.60621(8) 0.59678(17) 0.0345(3) Uani 1 1 d . . .

C12 C 0.5630(2) 0.63210(8) 0.57321(18) 0.0384(4) Uani 1 1 d . . .

C13 C 0.4178(2) 0.61335(8) 0.45378(18) 0.0359(4) Uani 1 1 d . . .

C14 C 0.44041(18) 0.56751(7) 0.35617(15) 0.0287(3) Uani 1 1 d . . .

C15 C 0.1206(2) 0.56834(10) 0.2178(2) 0.0441(4) Uani 1 1 d . . .

H2N H 0.765(2) 0.4068(9) 0.162(2) 0.041(5) Uiso 1 1 d . . .

H3N H 0.408(3) 0.4806(9) 0.164(2) 0.045(5) Uiso 1 1 d . . .

H2 H 0.522(2) 0.3247(9) -0.1588(19) 0.040(5) Uiso 1 1 d . . .

H3 H 0.640(2) 0.2385(9) -0.257(2) 0.045(5) Uiso 1 1 d . . .

H4 H 0.932(2) 0.1983(9) -0.1147(19) 0.044(5) Uiso 1 1 d . . .

H6A H 1.248(4) 0.2674(15) 0.131(3) 0.112(11) Uiso 1 1 d . . .

H6B H 1.172(3) 0.2410(12) 0.244(3) 0.075(7) Uiso 1 1 d . . .

H6C H 1.182(3) 0.1964(14) 0.125(3) 0.088(8) Uiso 1 1 d . . .

H10 H 0.870(2) 0.5438(8) 0.5087(19) 0.042(5) Uiso 1 1 d . . .

H11 H 0.826(3) 0.6182(9) 0.677(2) 0.040(5) Uiso 1 1 d . . .

H12 H 0.546(2) 0.6634(9) 0.640(2) 0.043(5) Uiso 1 1 d . . .

H13 H 0.301(3) 0.6323(9) 0.4407(19) 0.046(5) Uiso 1 1 d . . .

H15A H 0.052(3) 0.5454(10) 0.133(2) 0.056(6) Uiso 1 1 d . . .

H15B H 0.087(3) 0.5538(10) 0.298(2) 0.050(5) Uiso 1 1 d . . .

H15C H 0.107(2) 0.6185(10) 0.2050(19) 0.043(5) Uiso 1 1 d . . .

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O1 0.0212(5) 0.0451(6) 0.0382(6) -0.0103(5) 0.0038(4) 0.0054(4)

O2 0.0200(5) 0.0412(6) 0.0412(6) -0.0005(5) 0.0044(4) 0.0061(4)

N1 0.0314(6) 0.0308(6) 0.0263(6) 0.0010(5) 0.0087(5) 0.0027(5)

N2 0.0237(6) 0.0328(7) 0.0267(6) -0.0045(5) 0.0038(5) -0.0006(5)

N3 0.0210(6) 0.0324(6) 0.0298(6) -0.0005(5) 0.0056(5) 0.0020(5)

C1 0.0291(7) 0.0274(7) 0.0260(7) 0.0022(6) 0.0103(5) -0.0032(5)

C2 0.0323(8) 0.0354(8) 0.0281(7) -0.0002(6) 0.0079(6) -0.0036(6)

C3 0.0416(9) 0.0394(8) 0.0287(7) -0.0060(6) 0.0120(7) -0.0079(7)

C4 0.0452(9) 0.0325(8) 0.0350(8) -0.0050(6) 0.0173(7) -0.0005(7)

C5 0.0377(8) 0.0323(8) 0.0310(7) 0.0016(6) 0.0136(6) 0.0033(6)

C6 0.0454(10) 0.0474(10) 0.0427(10) -0.0030(8) 0.0088(8) 0.0176(8)

C7 0.0265(7) 0.0293(7) 0.0271(7) 0.0032(6) 0.0077(5) -0.0006(5)

C8 0.0219(7) 0.0303(7) 0.0288(7) 0.0035(6) 0.0067(5) 0.0007(5)

C9 0.0243(7) 0.0269(7) 0.0286(7) 0.0037(5) 0.0091(5) 0.0008(5)

C10 0.0259(7) 0.0306(7) 0.0319(7) 0.0024(6) 0.0078(6) 0.0014(6)

C11 0.0368(8) 0.0329(8) 0.0308(8) -0.0021(6) 0.0078(7) -0.0017(6)

C12 0.0460(9) 0.0336(8) 0.0390(9) -0.0015(7) 0.0189(7) 0.0039(7)

C13 0.0343(8) 0.0348(8) 0.0416(9) 0.0053(7) 0.0170(7) 0.0079(6)

C14 0.0257(7) 0.0277(7) 0.0321(7) 0.0064(6) 0.0092(6) 0.0026(5)

C15 0.0218(8) 0.0486(10) 0.0597(12) 0.0064(9) 0.0112(8) 0.0074(7)

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All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles

and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

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O1 C8 1.2283(16) . ?

O2 C14 1.3655(17) . ?

O2 C15 1.4420(18) . ?

N1 C1 1.3344(18) . ?

N1 C5 1.3428(19) . ?

N2 C7 1.3404(18) . ?

N2 C1 1.4096(18) . ?

N2 H2N 0.847(19) . ?

N3 C8 1.3745(18) . ?

N3 C7 1.3935(19) . ?

N3 H3N 0.905(19) . ?

C1 C2 1.392(2) . ?

C2 C3 1.380(2) . ?

C2 H2 0.895(18) . ?

C3 C4 1.382(2) . ?

C3 H3 0.978(18) . ?

C4 C5 1.392(2) . ?

C4 H4 0.946(18) . ?

C5 C6 1.497(2) . ?

C6 H6A 0.94(3) . ?

C6 H6B 0.98(2) . ?

C6 H6C 0.94(3) . ?

C8 C9 1.492(2) . ?

C9 C10 1.399(2) . ?

C9 C14 1.4129(19) . ?

C10 C11 1.376(2) . ?

C10 H10 0.941(18) . ?

C11 C12 1.385(2) . ?

C11 H11 0.905(19) . ?

C12 C13 1.383(2) . ?

C12 H12 0.957(18) . ?

C13 C14 1.388(2) . ?

C13 H13 0.966(19) . ?

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C15 H15C 1.016(19) . ?

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C1 N1 C5 118.54(13) . . ?

C7 N2 C1 130.72(13) . . ?

C7 N2 H2N 113.0(12) . . ?

C1 N2 H2N 116.0(12) . . ?

C8 N3 C7 129.29(12) . . ?

C8 N3 H3N 114.4(12) . . ?

C7 N3 H3N 116.1(12) . . ?

N1 C1 C2 123.82(14) . . ?

N1 C1 N2 111.05(12) . . ?

C2 C1 N2 125.09(13) . . ?

C3 C2 C1 116.98(14) . . ?

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C1 C2 H2 121.3(11) . . ?

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C2 C3 H3 119.5(11) . . ?

C4 C3 H3 120.3(11) . . ?

C3 C4 C5 118.99(15) . . ?

C3 C4 H4 122.9(11) . . ?

C5 C4 H4 118.1(11) . . ?

N1 C5 C4 121.44(14) . . ?

N1 C5 C6 116.54(14) . . ?

C4 C5 C6 122.02(15) . . ?

C5 C6 H6A 113.3(18) . . ?

C5 C6 H6B 112.6(13) . . ?

H6A C6 H6B 106(2) . . ?

C5 C6 H6C 114.6(16) . . ?

H6A C6 H6C 107(2) . . ?

H6B C6 H6C 102.7(19) . . ?

N2 C7 N3 114.59(12) . . ?

N2 C7 S1 128.23(11) . . ?

N3 C7 S1 117.17(10) . . ?

O1 C8 N3 121.87(13) . . ?

O1 C8 C9 120.92(12) . . ?

N3 C8 C9 117.17(12) . . ?

C10 C9 C14 118.10(13) . . ?

C10 C9 C8 115.56(12) . . ?

C14 C9 C8 126.30(12) . . ?

C11 C10 C9 121.89(14) . . ?

C11 C10 H10 122.1(11) . . ?

C9 C10 H10 116.0(11) . . ?

C10 C11 C12 119.04(15) . . ?

C10 C11 H11 121.1(12) . . ?

C12 C11 H11 119.8(12) . . ?

C13 C12 C11 120.85(15) . . ?

C13 C12 H12 119.6(11) . . ?

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C12 C13 H13 118.7(11) . . ?

C14 C13 H13 121.0(11) . . ?

O2 C14 C13 122.63(13) . . ?

O2 C14 C9 117.51(13) . . ?

C13 C14 C9 119.86(14) . . ?

O2 C15 H15A 102.3(12) . . ?

O2 C15 H15B 110.5(11) . . ?

H15A C15 H15B 110.1(17) . . ?

O2 C15 H15C 111.2(11) . . ?

H15A C15 H15C 111.6(15) . . ?

H15B C15 H15C 110.9(16) . . ?

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C5 N1 C1 N2 -179.86(12) . . . . ?

C7 N2 C1 N1 -159.20(14) . . . . ?

C7 N2 C1 C2 22.7(2) . . . . ?

N1 C1 C2 C3 0.0(2) . . . . ?

N2 C1 C2 C3 177.87(13) . . . . ?

C1 C2 C3 C4 1.5(2) . . . . ?

C2 C3 C4 C5 -1.3(2) . . . . ?

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C1 N1 C5 C6 -178.41(15) . . . . ?

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C3 C4 C5 C6 179.89(16) . . . . ?

C1 N2 C7 N3 176.58(13) . . . . ?

C1 N2 C7 S1 -2.3(2) . . . . ?

C8 N3 C7 N2 -7.2(2) . . . . ?

C8 N3 C7 S1 171.81(12) . . . . ?

C7 N3 C8 O1 4.2(2) . . . . ?

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O1 C8 C9 C10 -3.0(2) . . . . ?

N3 C8 C9 C10 174.88(12) . . . . ?

O1 C8 C9 C14 179.38(13) . . . . ?

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C8 C9 C10 C11 -176.99(13) . . . . ?

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C11 C12 C13 C14 0.7(2) . . . . ?

C15 O2 C14 C13 -7.1(2) . . . . ?

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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 factors based on ALL data will be even larger.
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O2 O 0.29937(14) 0.29542(13) 1.14630(9) 0.0312(2) Uani 1 1 d . . .
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H1C H -0.386(4) 0.113(3) 0.687(2) 0.073(7) Uiso 1 1 d . . .
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H10 H 0.408(2) 0.799(2) 1.0590(14) 0.030(4) Uiso 1 1 d . . .
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H13 H 0.124(3) 0.249(2) 0.9255(16) 0.041(5) Uiso 1 1 d . . .
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H15B H 0.075(3) 0.082(2) 1.1011(15) 0.038(4) Uiso 1 1 d . . .
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O2 0.0341(5) 0.0293(5) 0.0282(5) 0.0071(4) -0.0063(4) 0.0120(4)
N1 0.0243(5) 0.0200(5) 0.0213(5) 0.0023(4) -0.0004(4) 0.0079(4)
N2 0.0279(6) 0.0187(5) 0.0239(5) 0.0044(4) -0.0042(4) 0.0070(4)
N3 0.0251(5) 0.0179(5) 0.0216(5) 0.0021(4) -0.0040(4) 0.0056(4)
C1 0.0402(8) 0.0217(7) 0.0301(7) 0.0031(6) -0.0047(6) 0.0094(6)
C2 0.0257(6) 0.0209(6) 0.0235(6) 0.0006(5) 0.0000(5) 0.0084(5)
C3 0.0301(7) 0.0215(7) 0.0285(7) -0.0026(5) -0.0028(5) 0.0065(5)
C4 0.0302(7) 0.0297(7) 0.0228(6) -0.0026(5) -0.0055(5) 0.0112(6)
C5 0.0294(7) 0.0256(7) 0.0223(6) 0.0036(5) -0.0016(5) 0.0119(5)
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C9 0.0220(6) 0.0239(6) 0.0207(6) 0.0020(5) -0.0005(5) 0.0079(5)
C10 0.0265(6) 0.0230(7) 0.0224(6) -0.0020(5) -0.0029(5) 0.0068(5)
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 are estimated using the full covariance matrix. The cell esds are taken
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N1 C2 1.3499(17) . ?
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N3 H3N 0.882(18) . ?
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N2 C7 N3 115.81(11) . . ?
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O2 C15 H15B 110.8(10) . . ?

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N1 C2 C3 C4 1.0(2) . . . . ?
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C4 C5 C6 N2 -178.88(12) . . . . ?
C7 N2 C6 N1 7.2(2) . . . . ?
C7 N2 C6 C5 -172.83(13) . . . . ?
C6 N2 C7 N3 -5.5(2) . . . . ?
C6 N2 C7 S1 173.85(11) . . . . ?
C8 N3 C7 N2 176.82(12) . . . . ?
C8 N3 C7 S1 -2.5(2) . . . . ?
C7 N3 C8 O1 3.9(2) . . . . ?
C7 N3 C8 C9 -176.65(12) . . . . ?
O1 C8 C9 C14 -165.73(15) . . . . ?
N3 C8 C9 C14 14.80(19) . . . . ?
O1 C8 C9 C10 12.6(2) . . . . ?
N3 C8 C9 C10 -166.87(11) . . . . ?
C14 C9 C10 C11 -1.17(19) . . . . ?
C8 C9 C10 C11 -179.61(12) . . . . ?
C9 C10 C11 C12 0.9(2) . . . . ?
C15 O2 C12 C13 0.6(2) . . . . ?
C15 O2 C12 C11 -178.96(12) . . . . ?
C10 C11 C12 O2 179.58(12) . . . . ?
C10 C11 C12 C13 0.0(2) . . . . ?
O2 C12 C13 C14 179.85(12) . . . . ?
C11 C12 C13 C14 -0.6(2) . . . . ?
C10 C9 C14 C13 0.6(2) . . . . ?
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N3 H3N N1  0.882(18) 1.945(17) 2.6973(16) 142.2(15) .

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
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 factors based on ALL data will be even larger.
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N1 N 0.44353(12) 0.65239(12) 0.83835(11) 0.0218(2) Uani 1 1 d . . .
N2 N 0.44146(13) 0.46127(13) 0.75961(11) 0.0226(2) Uani 1 1 d . . .
N3 N 0.49487(13) 0.30198(13) 0.61456(11) 0.0223(2) Uani 1 1 d . . .
O1 O 0.72572(11) 0.32596(12) 0.62081(10) 0.0287(2) Uani 1 1 d . . .
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C3 C 0.18018(17) 0.66498(17) 1.03608(14) 0.0295(3) Uani 1 1 d . . .
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C6 C 0.4787(2) 0.8522(2) 0.90219(18) 0.0351(3) Uani 1 1 d . . .
C7 C 0.38516(15) 0.38409(14) 0.71238(13) 0.0214(2) Uani 1 1 d . . .
C8 C 0.65672(15) 0.27222(14) 0.57691(13) 0.0206(2) Uani 1 1 d . . .
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C12 C 0.91734(16) -0.01792(16) 0.28844(14) 0.0268(3) Uani 1 1 d . . .
C13 C 0.78623(16) -0.03859(15) 0.37589(14) 0.0260(3) Uani 1 1 d . . .
C14 C 0.69944(15) 0.05423(15) 0.47033(13) 0.0229(3) Uani 1 1 d . . .
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H3 H 0.088(2) 0.671(2) 1.1038(18) 0.033(4) Uiso 1 1 d . . .
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H6B H 0.557(3) 0.803(3) 0.961(3) 0.086(8) Uiso 1 1 d . . .
H6C H 0.538(4) 0.856(3) 0.818(3) 0.096(9) Uiso 1 1 d . . .
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H12 H 0.977(2) -0.082(2) 0.2237(19) 0.036(4) Uiso 1 1 d . . .
H13 H 0.757(2) -0.118(2) 0.3710(17) 0.030(4) Uiso 1 1 d . . .
H14 H 0.611(2) 0.0353(18) 0.5309(16) 0.027(4) Uiso 1 1 d . . .
H1OS H 0.591(2) 0.695(2) 0.660(2) 0.035(5) Uiso 1 1 d . . .
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H1SA H 0.839(2) 0.508(3) 0.640(2) 0.050(5) Uiso 1 1 d . . .
H1SB H 0.836(3) 0.635(3) 0.692(2) 0.056(6) Uiso 1 1 d . . .
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S1 0.02274(18) 0.0426(2) 0.0417(2) -0.02409(16) 0.00819(14) -0.01911(15)
N1 0.0195(5) 0.0258(5) 0.0211(5) -0.0094(4) 0.0001(4) -0.0092(4)
N2 0.0180(5) 0.0281(5) 0.0250(5) -0.0134(4) 0.0033(4) -0.0107(4)
N3 0.0191(5) 0.0267(5) 0.0254(5) -0.0134(4) 0.0008(4) -0.0101(4)
O1 0.0219(5) 0.0360(5) 0.0363(5) -0.0213(4) 0.0027(4) -0.0137(4)
C1 0.0247(6) 0.0265(6) 0.0256(6) -0.0108(5) -0.0020(5) -0.0097(5)
C2 0.0288(7) 0.0336(7) 0.0270(7) -0.0171(6) 0.0024(5) -0.0099(6)
C3 0.0245(6) 0.0373(7) 0.0240(6) -0.0116(6) 0.0055(5) -0.0119(6)
C4 0.0246(6) 0.0314(7) 0.0232(6) -0.0093(5) 0.0020(5) -0.0134(5)
C5 0.0194(6) 0.0236(6) 0.0197(6) -0.0082(5) -0.0012(5) -0.0073(5)
C6 0.0369(8) 0.0398(8) 0.0400(9) -0.0213(7) 0.0034(7) -0.0215(7)
C7 0.0200(6) 0.0218(6) 0.0219(6) -0.0071(5) -0.0003(5) -0.0080(5)
C8 0.0197(6) 0.0201(5) 0.0219(6) -0.0063(5) -0.0013(5) -0.0078(5)
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C1S 0.0248(7) 0.0324(7) 0.0344(8) -0.0081(6) -0.0038(6) -0.0136(6)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
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 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 C5 1.4127(16) . ?
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C10 C11 1.3822(18) . ?
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C3 C4 C5 117.09(13) . . ?
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N1 C5 N2 111.01(11) . . ?
C4 C5 N2 125.44(12) . . ?
N2 C7 N3 114.12(11) . . ?
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C10 C11 Cl1 119.41(10) . . ?

C12 C11 Cl1 118.96(10) . . ?
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C8 N3 C7 S1 -171.01(10) . . . . ?
C7 N3 C8 O1 -5.1(2) . . . . ?
C7 N3 C8 C9 174.96(11) . . . . ?
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C9 C10 C11 Cl1 179.58(9) . . . . ?
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Cl1 C11 C12 C13 178.73(10) . . . . ?
C11 C12 C13 C14 1.4(2) . . . . ?
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N3 H3N O1S  0.832(17) 2.054(17) 2.8551(15) 161.4(16) 2_666
O1S H1OS N1  0.79(2) 2.06(2) 2.8496(15) 177.3(18) .

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 'N'  'N'   0.0061   0.0033
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 'O'  'O'   0.0106   0.0060
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 'S'  'S'   0.1246   0.1234
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 'Cl'  'Cl'   0.1484   0.1585
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_symmetry_cell_setting           Monoclinic
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 'x+1/2, y+1/2, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y, z-1/2'
 '-x+1/2, -y+1/2, -z'
 'x+1/2, -y+1/2, z-1/2'

_cell_length_a                 28.847(6)
_cell_length_b                 3.8548(7)
_cell_length_c                 24.769(5)
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_cell_angle_beta               105.929(3)
_cell_angle_gamma              90.00
_cell_volume                   2648.5(9)
_cell_formula_units_Z          8
_cell_measurement_temperature    173(2)
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_computing_cell_refinement        'Bruker SAINT'
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0591P)^2^+0.7089P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
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_refine_ls_hydrogen_treatment     refall
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N1 N 0.16128(6) 0.3754(4) 0.09590(7) 0.0257(4) Uani 1 1 d . . .
N2 N 0.10297(6) 0.4174(5) 0.14023(7) 0.0244(4) Uani 1 1 d . . .
N3 N 0.03299(6) 0.5989(4) 0.15821(7) 0.0223(4) Uani 1 1 d . . .
O1 O 0.02970(5) 0.6779(4) 0.06595(6) 0.0352(4) Uani 1 1 d . . .
C1 C 0.20514(8) 0.2855(6) 0.09270(9) 0.0301(5) Uani 1 1 d . . .
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C3 C 0.22566(8) 0.0385(6) 0.18339(9) 0.0298(5) Uani 1 1 d . . .
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C5 C 0.15012(7) 0.3003(5) 0.14357(8) 0.0224(4) Uani 1 1 d . . .
C6 C 0.07925(7) 0.4616(5) 0.17917(8) 0.0205(4) Uani 1 1 d . . .
C7 C 0.00981(7) 0.6954(5) 0.10346(8) 0.0232(4) Uani 1 1 d . . .
C8 C -0.04070(7) 0.8190(5) 0.09233(8) 0.0206(4) Uani 1 1 d . . .
C9 C -0.06939(7) 0.7627(5) 0.12872(8) 0.0227(4) Uani 1 1 d . . .
C10 C -0.11673(7) 0.8738(5) 0.11455(9) 0.0245(4) Uani 1 1 d . . .
C11 C -0.13523(7) 1.0390(5) 0.06367(8) 0.0230(4) Uani 1 1 d . . .
C12 C -0.10791(7) 1.0983(5) 0.02655(8) 0.0250(4) Uani 1 1 d . . .
C13 C -0.06054(7) 0.9855(5) 0.04120(8) 0.0242(4) Uani 1 1 d . . .
O1S O 0.0000 -0.0586(6) 0.2500 0.0291(5) Uani 1 2 d S . .
H1 H 0.2122(8) 0.332(6) 0.0588(10) 0.030(6) Uiso 1 1 d . . .
H2 H 0.2688(8) 0.066(6) 0.1303(10) 0.037(6) Uiso 1 1 d . . .
H2N H 0.0881(9) 0.481(6) 0.1087(10) 0.036(7) Uiso 1 1 d . . .
H3 H 0.2474(8) -0.097(6) 0.2141(9) 0.030(6) Uiso 1 1 d . . .
H3N H 0.0197(8) 0.655(6) 0.1818(9) 0.024(6) Uiso 1 1 d . . .
H4 H 0.1730(7) 0.070(6) 0.2187(9) 0.022(5) Uiso 1 1 d . . .
H9 H -0.0586(8) 0.644(6) 0.1618(10) 0.031(6) Uiso 1 1 d . . .
H10 H -0.1365(8) 0.836(5) 0.1373(9) 0.027(6) Uiso 1 1 d . . .
H12 H -0.1219(8) 1.209(6) -0.0084(10) 0.031(6) Uiso 1 1 d . . .
H13 H -0.0409(8) 1.017(6) 0.0166(9) 0.029(6) Uiso 1 1 d . . .
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H1S H 0.0234(9) 0.071(7) 0.2535(12) 0.055(9) Uiso 1 1 d . . .

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Cl1 0.0199(3) 0.0402(3) 0.0353(3) 0.0007(2) 0.0055(2) 0.0062(2)
N1 0.0246(9) 0.0308(9) 0.0222(9) -0.0004(7) 0.0075(7) 0.0007(7)
N2 0.0197(8) 0.0348(10) 0.0182(9) 0.0031(7) 0.0045(7) 0.0038(7)
N3 0.0198(8) 0.0295(9) 0.0188(8) 0.0022(7) 0.0075(7) 0.0035(7)
O1 0.0255(8) 0.0597(11) 0.0225(8) 0.0101(7) 0.0102(6) 0.0121(7)
C1 0.0270(11) 0.0369(12) 0.0298(12) -0.0036(9) 0.0139(9) -0.0002(9)
C2 0.0245(11) 0.0343(12) 0.0369(12) -0.0060(9) 0.0116(10) 0.0041(9)
C3 0.0268(11) 0.0292(11) 0.0309(12) -0.0014(9) 0.0033(9) 0.0081(9)
C4 0.0289(11) 0.0283(11) 0.0227(11) 0.0012(9) 0.0083(9) 0.0035(8)
C5 0.0202(10) 0.0222(10) 0.0245(10) -0.0039(8) 0.0058(8) -0.0006(8)
C6 0.0207(9) 0.0189(9) 0.0219(10) -0.0017(7) 0.0058(8) -0.0010(7)
C7 0.0224(10) 0.0256(10) 0.0210(10) 0.0026(8) 0.0051(8) 0.0000(8)
C8 0.0184(9) 0.0232(10) 0.0191(10) -0.0001(7) 0.0032(8) -0.0003(7)
C9 0.0232(10) 0.0257(10) 0.0187(10) 0.0022(8) 0.0048(8) -0.0022(8)
C10 0.0215(10) 0.0308(11) 0.0231(10) -0.0026(8) 0.0092(8) -0.0035(8)
C11 0.0172(9) 0.0239(10) 0.0266(10) -0.0038(8) 0.0037(8) 0.0003(8)
C12 0.0251(10) 0.0274(11) 0.0206(10) 0.0020(8) 0.0031(8) 0.0024(8)
C13 0.0234(10) 0.0295(11) 0.0206(10) 0.0019(8) 0.0076(8) -0.0009(8)
O1S 0.0223(11) 0.0387(13) 0.0268(11) 0.000 0.0073(9) 0.000

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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Cl1 C11 1.7400(19) . ?
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N1 C5 1.338(3) . ?
N2 C6 1.338(2) . ?
N2 C5 1.414(2) . ?

N2 H2N 0.82(2) . ?
N3 C7 1.388(2) . ?
N3 C6 1.396(2) . ?
N3 H3N 0.81(2) . ?
O1 C7 1.220(2) . ?
C1 C2 1.378(3) . ?
C1 H1 0.93(2) . ?
C2 C3 1.377(3) . ?
C2 H2 0.94(2) . ?
C3 C4 1.381(3) . ?
C3 H3 0.99(2) . ?
C4 C5 1.381(3) . ?
C4 H4 0.87(2) . ?
C7 C8 1.485(3) . ?
C8 C13 1.395(3) . ?
C8 C9 1.398(3) . ?
C9 C10 1.381(3) . ?
C9 H9 0.92(2) . ?
C10 C11 1.382(3) . ?
C10 H10 0.92(2) . ?
C11 C12 1.384(3) . ?
C12 C13 1.384(3) . ?
C12 H12 0.95(2) . ?
C13 H13 0.95(2) . ?
O1S H1S 0.83(2) . ?

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C6 N2 C5 132.27(18) . . ?
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C7 N3 C6 128.30(17) . . ?
C7 N3 H3N 115.8(16) . . ?
C6 N3 H3N 115.2(16) . . ?
N1 C1 C2 123.5(2) . . ?
N1 C1 H1 116.6(14) . . ?
C2 C1 H1 119.9(14) . . ?
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C2 C3 H3 121.1(13) . . ?
C4 C3 H3 118.6(13) . . ?
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N1 C5 N2 109.87(17) . . ?
C4 C5 N2 126.28(18) . . ?
N2 C6 N3 113.94(17) . . ?
N2 C6 S1 127.56(15) . . ?
N3 C6 S1 118.50(14) . . ?
O1 C7 N3 121.86(18) . . ?
O1 C7 C8 121.24(18) . . ?
N3 C7 C8 116.90(16) . . ?
C13 C8 C9 119.27(18) . . ?
C13 C8 C7 116.97(17) . . ?
C9 C8 C7 123.69(17) . . ?
C10 C9 C8 120.45(18) . . ?
C10 C9 H9 117.0(14) . . ?
C8 C9 H9 122.5(14) . . ?
C9 C10 C11 118.82(19) . . ?
C9 C10 H10 122.1(14) . . ?
C11 C10 H10 119.0(14) . . ?
C10 C11 C12 122.29(18) . . ?
C10 C11 Cl1 118.86(15) . . ?
C12 C11 Cl1 118.86(15) . . ?
C13 C12 C11 118.35(19) . . ?
C13 C12 H12 121.4(13) . . ?
C11 C12 H12 120.2(13) . . ?
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C12 C13 H13 120.8(13) . . ?
C8 C13 H13 118.3(13) . . ?

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N1 C1 C2 C3 1.6(3) . . . . ?
C1 C2 C3 C4 -1.5(3) . . . . ?
C2 C3 C4 C5 -0.3(3) . . . . ?
C1 N1 C5 C4 -2.2(3) . . . . ?
C1 N1 C5 N2 179.07(17) . . . . ?
C3 C4 C5 N1 2.2(3) . . . . ?
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C6 N2 C5 C4 15.5(3) . . . . ?
C5 N2 C6 N3 177.39(19) . . . . ?
C5 N2 C6 S1 -3.0(3) . . . . ?
C7 N3 C6 N2 -0.8(3) . . . . ?
C7 N3 C6 S1 179.50(16) . . . . ?

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C6 N3 C7 O1 -2.4(3) . . . . ?
C6 N3 C7 C8 177.07(18) . . . . ?
O1 C7 C8 C13 -14.0(3) . . . . ?
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O1 C7 C8 C9 162.86(19) . . . . ?
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C9 C10 C11 Cl1 179.74(15) . . . . ?
C10 C11 C12 C13 0.4(3) . . . . ?
Cl1 C11 C12 C13 -179.69(15) . . . . ?
C11 C12 C13 C8 -0.6(3) . . . . ?
C9 C8 C13 C12 0.7(3) . . . . ?
C7 C8 C13 C12 177.76(18) . . . . ?

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 _geom_hbond_distance_DA
 _geom_hbond_angle_DHA
 _geom_hbond_site_symmetry_A
N2 H2N O1  0.82(2) 1.88(2) 2.593(2) 144(2) .
N3 H3N O1S  0.81(2) 2.22(2) 3.001(2) 162(2) 1_565
O1S H1S S1  0.83(2) 2.50(2) 3.3063(14) 166(3) .

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'N'  'N'   0.0061   0.0033
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'O'  'O'   0.0106   0.0060
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_symmetry_space_group_name_H-M    P-1

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 'x, y, z'
 '-x, -y, -z'

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_cell_angle_gamma                   81.197(2)
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_diffrn_reflns_av_sigmaI/netI     0.0336
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_diffrn_reflns_limit_l_min        -18
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_reflns_number_gt                 4825
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_computing_data_collection        'Bruker SMART'
_computing_cell_refinement        'Bruker SAINT'
_computing_data_reduction         'Bruker SAINT'
_computing_structure_solution     'Bruker SHELXTL'
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_computing_molecular_graphics     'Bruker SHELXTL'
_computing_publication_material   'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
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_refine_ls_matrix_type           full
_refine_ls_weighting_scheme      calc
_refine_ls_weighting_details
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_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   difmap
_refine_ls_hydrogen_treatment    refall
_refine_ls_extinction_method     none
_refine_ls_extinction_coef       ?
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_refine_ls_R_factor_all          0.0661
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_refine_ls_wR_factor_ref         0.1558
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_refine_ls_goodness_of_fit_ref   1.037
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O1 O 0.24575(17) 0.72622(12) 0.17972(11) 0.0279(3) Uani 1 1 d . . .
N1 N 0.51838(19) 1.07189(13) 0.11236(11) 0.0211(3) Uani 1 1 d . . .
N2 N 0.2349(2) 1.06869(14) 0.18394(12) 0.0227(4) Uani 1 1 d . . .
N3 N 0.3566(2) 0.88948(13) 0.17481(12) 0.0199(3) Uani 1 1 d . . .
N4 N 1.1691(2) 0.50978(15) 0.09090(14) 0.0332(4) Uani 1 1 d . . .
C1 C 0.6520(2) 1.12965(17) 0.07302(13) 0.0228(4) Uani 1 1 d . . .
C2 C 0.6436(3) 1.24565(18) 0.06377(15) 0.0266(4) Uani 1 1 d . . .
C3 C 0.4924(3) 1.30330(18) 0.09364(15) 0.0280(4) Uani 1 1 d . . .
C4 C 0.3543(3) 1.24555(16) 0.13314(15) 0.0249(4) Uani 1 1 d . . .
C5 C 0.3741(2) 1.12856(16) 0.14172(13) 0.0202(4) Uani 1 1 d . . .
C6 C 0.2168(2) 0.95615(15) 0.20348(13) 0.0191(4) Uani 1 1 d . . .
C7 C 0.3669(2) 0.77542(16) 0.17275(13) 0.0196(4) Uani 1 1 d . . .
C8 C 0.5454(2) 0.72032(15) 0.15795(13) 0.0189(4) Uani 1 1 d . . .
C9 C 0.5645(2) 0.61635(16) 0.13383(15) 0.0237(4) Uani 1 1 d . . .
C10 C 0.7248(3) 0.56056(17) 0.11788(15) 0.0255(4) Uani 1 1 d . . .
C11 C 0.8664(2) 0.60827(16) 0.12633(13) 0.0215(4) Uani 1 1 d . . .
```

C12 C 0.8487(2) 0.71013(17) 0.15296(15) 0.0258(4) Uani 1 1 d . . .
C13 C 0.6869(2) 0.76538(17) 0.16851(15) 0.0247(4) Uani 1 1 d . . .
C14 C 1.0347(2) 0.55215(16) 0.10742(14) 0.0245(4) Uani 1 1 d . . .
C15 C 0.8113(3) 1.0619(2) 0.04102(17) 0.0321(5) Uani 1 1 d . . .
S1' S 0.91676(6) 0.26863(4) 0.24391(4) 0.02572(16) Uani 1 1 d . . .
O1' O 0.70998(17) 0.43732(13) 0.34877(12) 0.0334(4) Uani 1 1 d . . .
N1' N 0.43230(19) 0.10476(13) 0.38183(11) 0.0197(3) Uani 1 1 d . . .
N2' N 0.7142(2) 0.11003(13) 0.30908(12) 0.0208(3) Uani 1 1 d . . .
N3' N 0.5955(2) 0.28490(13) 0.33100(12) 0.0210(3) Uani 1 1 d . . .
N4' N -0.2107(2) 0.67378(15) 0.41023(14) 0.0319(4) Uani 1 1 d . . .
C1' C 0.3020(2) 0.04616(16) 0.42495(13) 0.0205(4) Uani 1 1 d . . .
C2' C 0.3122(2) -0.07031(17) 0.43564(15) 0.0239(4) Uani 1 1 d . . .
C3' C 0.4615(2) -0.12726(17) 0.40165(15) 0.0256(4) Uani 1 1 d . . .
C4' C 0.5964(2) -0.06744(16) 0.35834(14) 0.0214(4) Uani 1 1 d . . .
C5' C 0.5761(2) 0.04854(15) 0.35081(13) 0.0185(4) Uani 1 1 d . . .
C6' C 0.7347(2) 0.22096(15) 0.29833(13) 0.0194(4) Uani 1 1 d . . .
C7' C 0.5877(2) 0.39365(16) 0.34551(13) 0.0204(4) Uani 1 1 d . . .
C8' C 0.4101(2) 0.45112(15) 0.35849(13) 0.0185(4) Uani 1 1 d . . .
C9' C 0.3881(2) 0.54664(16) 0.39574(14) 0.0229(4) Uani 1 1 d . . .
C10' C 0.2285(3) 0.60366(16) 0.40914(14) 0.0242(4) Uani 1 1 d . . .
C11' C 0.0894(2) 0.56696(15) 0.38493(13) 0.0202(4) Uani 1 1 d . . .
C12' C 0.1095(2) 0.47296(16) 0.34692(14) 0.0226(4) Uani 1 1 d . . .
C13' C 0.2708(2) 0.41595(16) 0.33391(14) 0.0219(4) Uani 1 1 d . . .
C14' C -0.0782(2) 0.62687(16) 0.39883(14) 0.0232(4) Uani 1 1 d . . .
C15' C 0.1461(3) 0.11306(19) 0.46136(17) 0.0289(5) Uani 1 1 d . . .
H2 H 0.735(3) 1.286(2) 0.0352(19) 0.042(7) Uiso 1 1 d . . .
H2' H 0.225(3) -0.111(2) 0.4682(18) 0.035(6) Uiso 1 1 d . . .
H2N H 0.142(3) 1.115(2) 0.2022(18) 0.039(7) Uiso 1 1 d . . .
H2N' H 0.801(3) 0.075(2) 0.2901(17) 0.027(6) Uiso 1 1 d . . .
H3 H 0.472(3) 1.388(2) 0.0871(19) 0.046(7) Uiso 1 1 d . . .
H3' H 0.479(3) -0.212(2) 0.4048(16) 0.029(6) Uiso 1 1 d . . .
H3N H 0.443(3) 0.9220(19) 0.1491(16) 0.023(6) Uiso 1 1 d . . .
H3N' H 0.503(3) 0.247(2) 0.3497(17) 0.034(6) Uiso 1 1 d . . .
H4 H 0.250(3) 1.284(2) 0.1485(17) 0.033(6) Uiso 1 1 d . . .
H4' H 0.694(3) -0.1041(19) 0.3378(16) 0.025(6) Uiso 1 1 d . . .
H9 H 0.464(3) 0.581(2) 0.1337(17) 0.034(6) Uiso 1 1 d . . .
H9' H 0.487(3) 0.569(2) 0.4113(17) 0.036(6) Uiso 1 1 d . . .
H10 H 0.743(3) 0.487(2) 0.0989(17) 0.035(6) Uiso 1 1 d . . .
H10' H 0.213(3) 0.668(2) 0.4365(17) 0.033(6) Uiso 1 1 d . . .
H12 H 0.946(3) 0.7410(19) 0.1628(16) 0.030(6) Uiso 1 1 d . . .
H12' H 0.013(3) 0.4503(18) 0.3270(15) 0.022(5) Uiso 1 1 d . . .
H13 H 0.676(3) 0.832(2) 0.1899(18) 0.041(7) Uiso 1 1 d . . .
H13' H 0.290(3) 0.354(2) 0.3054(18) 0.039(7) Uiso 1 1 d . . .
H15A H 0.873(4) 1.032(2) 0.095(2) 0.056(8) Uiso 1 1 d . . .
H15B H 0.872(4) 1.106(3) -0.015(2) 0.057(8) Uiso 1 1 d . . .
H15C H 0.774(4) 0.993(3) 0.022(2) 0.064(9) Uiso 1 1 d . . .
H15D H 0.070(4) 0.132(2) 0.419(2) 0.048(8) Uiso 1 1 d . . .
H15E H 0.090(4) 0.069(2) 0.525(2) 0.053(8) Uiso 1 1 d . . .
H15F H 0.182(3) 0.181(2) 0.4748(19) 0.045(7) Uiso 1 1 d . . .

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S1 0.0133(2) 0.0205(3) 0.0359(3) -0.0091(2) 0.00683(19) -0.00132(19)
O1 0.0170(7) 0.0242(7) 0.0440(9) -0.0133(6) 0.0003(6) -0.0023(6)
N1 0.0150(7) 0.0215(8) 0.0246(8) -0.0054(6) 0.0008(6) 0.0011(6)
N2 0.0134(7) 0.0191(8) 0.0342(9) -0.0099(7) 0.0048(6) 0.0006(6)
N3 0.0110(7) 0.0182(8) 0.0295(9) -0.0080(6) 0.0023(6) 0.0006(6)
N4 0.0223(9) 0.0298(9) 0.0456(11) -0.0137(8) 0.0012(8) 0.0056(7)
C1 0.0174(9) 0.0269(10) 0.0207(9) -0.0016(7) -0.0008(7) -0.0012(8)
C2 0.0188(9) 0.0281(10) 0.0298(11) -0.0021(8) 0.0000(8) -0.0056(8)
C3 0.0271(10) 0.0224(10) 0.0334(11) -0.0059(8) -0.0009(8) -0.0041(8)
C4 0.0196(9) 0.0203(9) 0.0340(11) -0.0098(8) 0.0019(8) 0.0003(8)
C5 0.0163(9) 0.0211(9) 0.0224(9) -0.0056(7) -0.0002(7) -0.0011(7)
C6 0.0139(8) 0.0200(9) 0.0230(9) -0.0065(7) -0.0016(7) 0.0009(7)
C7 0.0155(9) 0.0202(9) 0.0224(9) -0.0069(7) -0.0019(7) 0.0027(7)
C8 0.0169(9) 0.0180(9) 0.0201(9) -0.0041(7) -0.0026(7) 0.0025(7)
C9 0.0186(9) 0.0202(9) 0.0325(11) -0.0078(8) -0.0018(8) -0.0016(8)
C10 0.0227(10) 0.0186(9) 0.0347(11) -0.0088(8) -0.0022(8) 0.0016(8)
C11 0.0172(9) 0.0206(9) 0.0235(9) -0.0043(7) -0.0007(7) 0.0032(7)
C12 0.0158(9) 0.0260(10) 0.0377(11) -0.0135(8) -0.0029(8) 0.0006(8)
C13 0.0191(9) 0.0226(10) 0.0349(11) -0.0138(8) -0.0041(8) 0.0022(8)
C14 0.0211(10) 0.0206(9) 0.0301(10) -0.0062(8) -0.0001(8) -0.0006(8)
C15 0.0177(10) 0.0347(12) 0.0343(12) -0.0001(10) 0.0041(8) 0.0032(9)
S1' 0.0139(2) 0.0214(3) 0.0393(3) -0.0086(2) 0.00576(19) -0.00131(18)
O1' 0.0153(7) 0.0339(8) 0.0580(10) -0.0249(7) -0.0022(6) -0.0022(6)
N1' 0.0126(7) 0.0203(8) 0.0255(8) -0.0070(6) -0.0009(6) 0.0009(6)
N2' 0.0132(7) 0.0177(8) 0.0294(9) -0.0082(6) 0.0034(6) 0.0027(6)
N3' 0.0124(7) 0.0173(8) 0.0327(9) -0.0084(6) 0.0014(6) -0.0003(6)
N4' 0.0234(9) 0.0242(9) 0.0446(11) -0.0094(8) 0.0004(8) 0.0053(7)
C1' 0.0125(8) 0.0242(9) 0.0243(9) -0.0063(7) -0.0010(7) -0.0014(7)
C2' 0.0167(9) 0.0247(10) 0.0302(10) -0.0069(8) 0.0004(8) -0.0053(8)
C3' 0.0224(10) 0.0207(10) 0.0339(11) -0.0080(8) -0.0022(8) -0.0024(8)
C4' 0.0155(9) 0.0206(9) 0.0289(10) -0.0110(8) 0.0008(7) 0.0008(7)
C5' 0.0136(8) 0.0208(9) 0.0212(9) -0.0064(7) -0.0019(7) -0.0003(7)
C6' 0.0142(8) 0.0201(9) 0.0228(9) -0.0055(7) -0.0024(7) 0.0017(7)
C7' 0.0141(9) 0.0215(9) 0.0255(9) -0.0078(7) -0.0005(7) 0.0005(7)
C8' 0.0140(8) 0.0176(9) 0.0222(9) -0.0057(7) 0.0012(7) 0.0012(7)
C9' 0.0191(9) 0.0204(9) 0.0304(10) -0.0083(8) -0.0046(8) -0.0015(7)
C10' 0.0236(10) 0.0178(9) 0.0323(11) -0.0105(8) -0.0020(8) 0.0004(8)
C11' 0.0176(9) 0.0163(8) 0.0227(9) -0.0019(7) 0.0000(7) 0.0022(7)
C12' 0.0152(9) 0.0235(10) 0.0295(10) -0.0088(8) -0.0025(7) -0.0001(7)
C13' 0.0184(9) 0.0196(9) 0.0289(10) -0.0105(8) -0.0021(7) 0.0016(7)
C14' 0.0220(10) 0.0182(9) 0.0267(10) -0.0035(7) -0.0005(8) -0.0006(8)
C15' 0.0146(9) 0.0298(11) 0.0397(12) -0.0102(9) 0.0042(8) 0.0012(8)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
```

and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

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O1 C7 1.200(2) . ?
N1 C5 1.334(2) . ?
N1 C1 1.348(2) . ?
N2 C6 1.362(2) . ?
N2 C5 1.405(2) . ?
N2 H2N 0.92(3) . ?
N3 C6 1.369(2) . ?
N3 C7 1.401(2) . ?
N3 H3N 0.84(2) . ?
N4 C14 1.146(3) . ?
C1 C2 1.389(3) . ?
C1 C15 1.502(3) . ?
C2 C3 1.384(3) . ?
C2 H2 0.94(3) . ?
C3 C4 1.377(3) . ?
C3 H3 1.01(3) . ?
C4 C5 1.397(3) . ?
C4 H4 0.93(2) . ?
C7 C8 1.501(2) . ?
C8 C13 1.383(3) . ?
C8 C9 1.398(3) . ?
C9 C10 1.382(3) . ?
C9 H9 0.97(2) . ?
C10 C11 1.393(3) . ?
C10 H10 1.00(2) . ?
C11 C12 1.392(3) . ?
C11 C14 1.444(3) . ?
C12 C13 1.389(3) . ?
C12 H12 0.96(2) . ?
C13 H13 0.95(3) . ?
C15 H15A 0.96(3) . ?
C15 H15B 0.96(3) . ?
C15 H15C 1.06(3) . ?
S1' C6' 1.6670(18) . ?
O1' C7' 1.202(2) . ?
N1' C5' 1.337(2) . ?
N1' C1' 1.342(2) . ?
N2' C6' 1.364(2) . ?
N2' C5' 1.408(2) . ?
N2' H2N' 0.82(2) . ?
N3' C6' 1.369(2) . ?

N3' C7' 1.401(2) . ?
N3' H3N' 0.91(3) . ?
N4' C14' 1.142(2) . ?
C1' C2' 1.390(3) . ?
C1' C15' 1.501(3) . ?
C2' C3' 1.389(3) . ?
C2' H2' 0.92(3) . ?
C3' C4' 1.380(3) . ?
C3' H3' 1.02(2) . ?
C4' C5' 1.387(3) . ?
C4' H4' 0.89(2) . ?
C7' C8' 1.501(2) . ?
C8' C13' 1.386(3) . ?
C8' C9' 1.402(3) . ?
C9' C10' 1.377(3) . ?
C9' H9' 0.95(3) . ?
C10' C11' 1.392(3) . ?
C10' H10' 0.96(2) . ?
C11' C12' 1.393(3) . ?
C11' C14' 1.446(2) . ?
C12' C13' 1.388(3) . ?
C12' H12' 0.97(2) . ?
C13' H13' 0.95(3) . ?
C15' H15D 0.90(3) . ?
C15' H15E 1.02(3) . ?
C15' H15F 1.00(3) . ?

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C6 N2 C5 131.30(16) . . ?
C6 N2 H2N 116.0(16) . . ?
C5 N2 H2N 112.7(16) . . ?
C6 N3 C7 127.25(16) . . ?
C6 N3 H3N 116.9(15) . . ?
C7 N3 H3N 115.4(15) . . ?
N1 C1 C2 121.66(17) . . ?
N1 C1 C15 116.63(18) . . ?
C2 C1 C15 121.70(18) . . ?
C3 C2 C1 118.80(19) . . ?
C3 C2 H2 119.2(16) . . ?
C1 C2 H2 121.9(16) . . ?
C4 C3 C2 120.15(19) . . ?
C4 C3 H3 115.0(15) . . ?
C2 C3 H3 124.8(15) . . ?
C3 C4 C5 117.55(18) . . ?
C3 C4 H4 120.9(15) . . ?

C5 C4 H4 121.3(15) . . ?
N1 C5 C4 123.06(17) . . ?
N1 C5 N2 119.09(16) . . ?
C4 C5 N2 117.85(16) . . ?
N2 C6 N3 114.85(16) . . ?
N2 C6 S1 119.63(13) . . ?
N3 C6 S1 125.48(14) . . ?
O1 C7 N3 123.96(16) . . ?
O1 C7 C8 122.52(17) . . ?
N3 C7 C8 113.49(15) . . ?
C13 C8 C9 119.87(17) . . ?
C13 C8 C7 123.92(17) . . ?
C9 C8 C7 116.20(17) . . ?
C10 C9 C8 119.91(18) . . ?
C10 C9 H9 120.8(14) . . ?
C8 C9 H9 119.1(14) . . ?
C9 C10 C11 119.66(18) . . ?
C9 C10 H10 122.1(14) . . ?
C11 C10 H10 118.2(14) . . ?
C12 C11 C10 120.91(17) . . ?
C12 C11 C14 118.99(17) . . ?
C10 C11 C14 120.11(17) . . ?
C13 C12 C11 118.77(18) . . ?
C13 C12 H12 120.0(13) . . ?
C11 C12 H12 121.2(14) . . ?
C8 C13 C12 120.84(18) . . ?
C8 C13 H13 120.9(16) . . ?
C12 C13 H13 118.1(16) . . ?
N4 C14 C11 178.5(2) . . ?
C1 C15 H15A 106.8(18) . . ?
C1 C15 H15B 111.1(18) . . ?
H15A C15 H15B 116(2) . . ?
C1 C15 H15C 106.9(17) . . ?
H15A C15 H15C 108(2) . . ?
H15B C15 H15C 108(2) . . ?
C5' N1' C1' 118.75(16) . . ?
C6' N2' C5' 131.16(16) . . ?
C6' N2' H2N' 111.1(16) . . ?
C5' N2' H2N' 117.6(17) . . ?
C6' N3' C7' 127.47(16) . . ?
C6' N3' H3N' 112.8(15) . . ?
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H14 H 0.523(3) 0.332(3) 0.460(3)
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H3N H 1.223(3) 1.413(2) -0.050(2)
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H1C H 1.303(3) 1.566(3) 0.341(3)
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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N2 C6 N3 114.09(16) . . ?
N2 C6 S1 128.45(15) . . ?
N3 C6 S1 117.44(13) . . ?
O1 C7 N3 122.93(17) . . ?
O1 C7 C8 122.29(17) . . ?
N3 C7 C8 114.78(16) . . ?
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C10 C9 Br1 117.92(17) . . ?
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C10 C11 C12 121.0(2) . . ?
C10 C11 H11 118.3(19) . . ?
C12 C11 H11 120.6(19) . . ?
C11 C12 C13 119.6(2) . . ?
C11 C12 H12 120.8(17) . . ?
C13 C12 H12 119.6(17) . . ?
C12 C13 C8 120.4(2) . . ?
C12 C13 H13 120.1(13) . . ?
C8 C13 H13 119.6(13) . . ?
C1 C14 H14A 113(2) . . ?
C1 C14 H14B 109(2) . . ?
H14A C14 H14B 110(3) . . ?
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C1 C2 C3 C4 0.2(3) . . . . ?
C2 C3 C4 C5 -0.7(3) . . . . ?
C1 N1 C5 C4 -0.1(3) . . . . ?
C1 N1 C5 N2 178.79(17) . . . . ?
C3 C4 C5 N1 0.7(3) . . . . ?
C3 C4 C5 N2 -178.10(19) . . . . ?
C6 N2 C5 N1 175.2(2) . . . . ?
C6 N2 C5 C4 -5.9(3) . . . . ?
C5 N2 C6 N3 -177.10(18) . . . . ?
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C7 N3 C6 S1 178.91(16) . . . . ?
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C6 N3 C7 C8 178.20(17) . . . . ?
O1 C7 C8 C13 -125.7(2) . . . . ?
N3 C7 C8 C13 54.0(2) . . . . ?
O1 C7 C8 C9 53.8(3) . . . . ?
N3 C7 C8 C9 -126.58(19) . . . . ?
C13 C8 C9 C10 0.4(3) . . . . ?
C7 C8 C9 C10 -179.02(19) . . . . ?
C13 C8 C9 Br1 -177.38(14) . . . . ?
C7 C8 C9 Br1 3.2(3) . . . . ?
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Br1 C9 C10 C11 178.13(19) . . . . ?
C9 C10 C11 C12 -0.7(4) . . . . ?
C10 C11 C12 C13 0.5(4) . . . . ?
C11 C12 C13 C8 0.2(3) . . . . ?
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N3 H3N O1  0.83(2) 2.00(3) 2.831(2) 177(2) 4_575

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_cell_length_c                  11.7435(16)
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0735P)^2^+0.2907P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    difmap
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O1 O 0.5632(2) 0.06586(7) 0.63316(10) 0.0465(3) Uani 1 1 d . . .
N1 N 0.0789(3) 0.20415(8) 0.67727(13) 0.0526(4) Uani 1 1 d . . .
N2 N 0.2952(3) 0.12989(7) 0.78058(11) 0.0348(3) Uani 1 1 d . . .
N3 N 0.5760(3) 0.04738(6) 0.82481(11) 0.0311(3) Uani 1 1 d . . .
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C2 C -0.2448(4) 0.27438(10) 0.7495(2) 0.0551(5) Uani 1 1 d . . .
C3 C -0.2140(4) 0.24757(10) 0.85570(19) 0.0530(5) Uani 1 1 d . . .
C4 C -0.0363(4) 0.19877(10) 0.87347(17) 0.0445(4) Uani 1 1 d . . .
C5 C 0.1059(3) 0.17861(8) 0.78089(14) 0.0340(4) Uani 1 1 d . . .
C6 C 0.3923(3) 0.09143(7) 0.86210(13) 0.0309(3) Uani 1 1 d . . .
C7 C 0.6504(3) 0.03498(8) 0.71398(13) 0.0324(3) Uani 1 1 d . . .
C8 C 0.8400(3) -0.01810(7) 0.69713(13) 0.0305(3) Uani 1 1 d . . .
C9 C 1.0211(3) -0.03535(8) 0.77843(15) 0.0355(4) Uani 1 1 d . . .
C10 C 1.2016(3) -0.08271(9) 0.75274(18) 0.0433(4) Uani 1 1 d . . .
C11 C 1.2007(3) -0.11267(9) 0.64714(17) 0.0445(4) Uani 1 1 d . . .
C12 C 1.0193(4) -0.09632(9) 0.56654(16) 0.0418(4) Uani 1 1 d . . .
C13 C 0.8401(3) -0.04909(8) 0.59092(14) 0.0367(4) Uani 1 1 d . . .
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H3N H 0.626(3) 0.0217(10) 0.8751(17) 0.039(5) Uiso 1 1 d . . .
H1 H -0.119(5) 0.2675(13) 0.582(2) 0.080(8) Uiso 1 1 d . . .
H2 H -0.361(4) 0.3077(12) 0.7353(19) 0.065(7) Uiso 1 1 d . . .
H3 H -0.310(5) 0.2647(12) 0.916(2) 0.068(7) Uiso 1 1 d . . .
H4 H -0.013(4) 0.1782(11) 0.9437(19) 0.054(6) Uiso 1 1 d . . .
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H12 H 1.016(4) -0.1185(11) 0.494(2) 0.055(6) Uiso 1 1 d . . .
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O1 0.0584(8) 0.0572(8) 0.0241(6) 0.0115(5) 0.0089(5) 0.0208(6)
N1 0.0761(11) 0.0519(9) 0.0297(8) 0.0009(7) 0.0001(7) 0.0279(8)
N2 0.0454(8) 0.0363(7) 0.0229(7) 0.0019(5) 0.0043(5) 0.0064(6)
N3 0.0421(7) 0.0308(7) 0.0205(6) 0.0021(5) -0.0013(5) 0.0028(5)
C1 0.0907(16) 0.0601(13) 0.0382(11) 0.0036(9) -0.0040(10) 0.0356(12)
C2 0.0580(12) 0.0472(11) 0.0602(13) 0.0005(9) 0.0004(10) 0.0202(9)
C3 0.0557(11) 0.0470(11) 0.0567(12) 0.0020(9) 0.0204(10) 0.0100(9)
C4 0.0511(10) 0.0432(10) 0.0393(10) 0.0055(8) 0.0122(8) 0.0062(8)
C5 0.0409(8) 0.0308(8) 0.0304(8) -0.0005(6) -0.0002(6) 0.0006(6)
C6 0.0420(8) 0.0276(7) 0.0229(7) -0.0026(5) -0.0018(6) -0.0029(6)
C7 0.0364(8) 0.0362(8) 0.0246(8) 0.0028(6) 0.0041(6) -0.0011(6)
C8 0.0309(7) 0.0325(8) 0.0281(7) 0.0046(6) 0.0048(6) -0.0038(6)
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C11 0.0366(9) 0.0388(9) 0.0581(12) 0.0019(8) 0.0110(8) 0.0002(7)
C12 0.0475(10) 0.0404(9) 0.0378(10) 0.0003(7) 0.0139(8) -0.0007(7)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 C6 1.336(2) . ?
N2 C5 1.407(2) . ?
N2 H2N 0.86(2) . ?
N3 C7 1.3849(19) . ?
N3 C6 1.392(2) . ?
N3 H3N 0.83(2) . ?
C1 C2 1.374(3) . ?
C1 H1 1.02(3) . ?
C2 C3 1.370(3) . ?
C2 H2 0.93(2) . ?
C3 C4 1.380(3) . ?
C3 H3 0.94(2) . ?
C4 C5 1.386(2) . ?
C4 H4 0.93(2) . ?
C7 C8 1.485(2) . ?
C8 C9 1.391(2) . ?
C8 C13 1.397(2) . ?
C9 C10 1.389(3) . ?
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C10 H10 0.92(2) . ?
C11 C12 1.382(3) . ?
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C12 H12 0.97(2) . ?
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C7 N3 C6 127.91(14) . . ?
C7 N3 H3N 117.6(13) . . ?
C6 N3 H3N 113.5(13) . . ?
N1 C1 C2 123.61(19) . . ?
N1 C1 H1 115.7(15) . . ?
C2 C1 H1 120.6(15) . . ?
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C3 C2 H2 121.9(14) . . ?
C1 C2 H2 120.1(14) . . ?
C2 C3 C4 120.04(18) . . ?
C2 C3 H3 118.6(15) . . ?
C4 C3 H3 121.3(15) . . ?
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C5 C4 H4 119.4(14) . . ?
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N1 C5 N2 110.14(14) . . ?
C4 C5 N2 126.70(15) . . ?
N2 C6 N3 114.56(14) . . ?
N2 C6 S1 127.02(13) . . ?
N3 C6 S1 118.41(11) . . ?
O1 C7 N3 121.87(15) . . ?
O1 C7 C8 121.24(14) . . ?
N3 C7 C8 116.89(13) . . ?
C9 C8 C13 119.65(15) . . ?
C9 C8 C7 123.48(14) . . ?
C13 C8 C7 116.79(14) . . ?
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N1 C1 C2 C3 0.2(4) . . . . ?
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C2 C3 C4 C5 -0.1(3) . . . . ?
C1 N1 C5 C4 -0.2(3) . . . . ?
C1 N1 C5 N2 179.94(19) . . . . ?
C3 C4 C5 N1 0.2(3) . . . . ?
C3 C4 C5 N2 -179.91(17) . . . . ?
C6 N2 C5 N1 179.00(17) . . . . ?
C6 N2 C5 C4 -0.9(3) . . . . ?
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C7 N3 C6 N2 -6.5(2) . . . . ?
C7 N3 C6 S1 172.61(12) . . . . ?
C6 N3 C7 O1 3.5(3) . . . . ?
C6 N3 C7 C8 -175.98(14) . . . . ?
O1 C7 C8 C9 151.60(17) . . . . ?
N3 C7 C8 C9 -28.9(2) . . . . ?
O1 C7 C8 C13 -25.0(2) . . . . ?
N3 C7 C8 C13 154.55(14) . . . . ?
C13 C8 C9 C10 0.6(2) . . . . ?
C7 C8 C9 C10 -175.85(15) . . . . ?
C8 C9 C10 C11 -0.2(2) . . . . ?
C9 C10 C11 C12 -0.6(3) . . . . ?
C10 C11 C12 C13 1.0(3) . . . . ?
C11 C12 C13 C8 -0.5(2) . . . . ?
C9 C8 C13 C12 -0.3(2) . . . . ?
C7 C8 C13 C12 176.44(15) . . . . ?

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 _geom_hbond_atom_site_label_H
 _geom_hbond_atom_site_label_A
 _geom_hbond_distance_DH
 _geom_hbond_distance_HA
 _geom_hbond_distance_DA
 _geom_hbond_angle_DHA
 _geom_hbond_site_symmetry_A
N2 H2N O1  0.86(2) 1.85(2) 2.5926(18) 143.1(19) .
N3 H3N S1  0.83(2) 2.74(2) 3.5308(14) 160.8(17) 3_657
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_diffrn_reflns_theta_full              27.00
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data_30O

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 'C13 H10 N4 O3 S'
_chemical_formula_weight         302.31

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 'H'  'H'   0.0000   0.0000
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 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M    P2(1)/n

loop_
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 'x, y, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

_cell_length_a                   3.8902(12)
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_cell_length_c                  22.813(7)
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_diffrn_reflns_av_sigmaI/netI     0.0324
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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 'calc w=1/[\s^2^(Fo^2^)+(0.0777P)^2^+1.3202P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   difmap
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_refine_ls_wR_factor_ref         0.1359
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_refine_ls_goodness_of_fit_ref   1.031
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 _atom_site_symmetry_multiplicity
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 _atom_site_refinement_flags
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O1 O 0.0654(6) 0.40185(14) 0.81583(9) 0.0346(6) Uani 1 1 d . . .
O2 O 0.2362(7) 0.81007(16) 0.89720(10) 0.0452(7) Uani 1 1 d . . .
O3 O -0.0406(7) 0.88453(15) 0.82940(11) 0.0484(7) Uani 1 1 d . . .
N1 N 0.3827(6) 0.16070(16) 0.87034(10) 0.0246(6) Uani 1 1 d . . .
N2 N 0.3385(7) 0.30839(16) 0.90278(11) 0.0242(6) Uani 1 1 d . . .
N3 N 0.1225(6) 0.45665(16) 0.90921(10) 0.0215(5) Uani 1 1 d . . .
N4 N 0.0483(7) 0.81242(17) 0.85357(10) 0.0293(6) Uani 1 1 d . . .
C1 C 0.4792(8) 0.0722(2) 0.87611(13) 0.0261(6) Uani 1 1 d . . .
C2 C 0.6487(8) 0.0378(2) 0.92509(13) 0.0268(7) Uani 1 1 d . . .
C3 C 0.7273(8) 0.0988(2) 0.96997(13) 0.0266(7) Uani 1 1 d . . .
C4 C 0.6317(7) 0.1904(2) 0.96554(12) 0.0231(6) Uani 1 1 d . . .
C5 C 0.4545(7) 0.21746(18) 0.91499(11) 0.0201(6) Uani 1 1 d . . .
C6 C 0.2547(7) 0.37843(18) 0.93820(12) 0.0204(6) Uani 1 1 d . . .
C7 C 0.0402(7) 0.46621(19) 0.85062(12) 0.0230(6) Uani 1 1 d . . .
C8 C -0.0755(7) 0.55915(19) 0.82937(11) 0.0209(6) Uani 1 1 d . . .
C9 C 0.0240(7) 0.64203(19) 0.85595(12) 0.0214(6) Uani 1 1 d . . .
C10 C -0.0703(7) 0.72389(19) 0.82815(12) 0.0230(6) Uani 1 1 d . . .
C11 C -0.2596(8) 0.7267(2) 0.77622(12) 0.0255(7) Uani 1 1 d . . .
C12 C -0.3598(8) 0.6437(2) 0.75097(12) 0.0253(6) Uani 1 1 d . . .
C13 C -0.2679(7) 0.5605(2) 0.77661(12) 0.0240(6) Uani 1 1 d . . .
H1 H 0.421(8) 0.031(2) 0.8436(15) 0.033(9) Uiso 1 1 d . . .
H2 H 0.709(7) -0.023(2) 0.9285(13) 0.026(8) Uiso 1 1 d . . .
H2N H 0.268(9) 0.315(3) 0.8707(17) 0.039(10) Uiso 1 1 d . . .
H3 H 0.841(8) 0.076(2) 1.0045(14) 0.028(8) Uiso 1 1 d . . .
H3N H 0.067(8) 0.502(2) 0.9295(14) 0.029(9) Uiso 1 1 d . . .
H4 H 0.684(8) 0.231(2) 0.9909(14) 0.029(9) Uiso 1 1 d . . .
H9 H 0.156(8) 0.645(2) 0.8899(15) 0.025(8) Uiso 1 1 d . . .
H11 H -0.322(8) 0.784(2) 0.7613(14) 0.031(8) Uiso 1 1 d . . .
H12 H -0.490(8) 0.645(2) 0.7153(15) 0.029(8) Uiso 1 1 d . . .
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O1 0.0631(15) 0.0247(11) 0.0154(11) -0.0032(9) -0.0117(10) 0.0087(10)
O2 0.0787(18) 0.0296(12) 0.0262(12) -0.0017(10) -0.0228(12) -0.0062(12)
O3 0.0836(19) 0.0209(12) 0.0398(15) 0.0029(10) -0.0167(13) 0.0054(12)
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N1 0.0383(14) 0.0215(12) 0.0138(12) -0.0029(9) -0.0029(10) 0.0024(10)
N2 0.0416(15) 0.0207(13) 0.0102(12) 0.0003(10) -0.0062(10) 0.0052(11)
N3 0.0348(14) 0.0173(12) 0.0121(12) -0.0004(10) -0.0046(9) 0.0024(10)
N4 0.0460(16) 0.0222(13) 0.0196(13) -0.0006(10) -0.0024(11) 0.0015(11)
C1 0.0376(16) 0.0204(15) 0.0202(15) -0.0046(12) -0.0026(12) 0.0010(12)
C2 0.0363(17) 0.0184(15) 0.0256(16) -0.0010(12) -0.0024(12) 0.0057(12)
C3 0.0327(16) 0.0264(15) 0.0204(15) 0.0011(12) -0.0065(12) 0.0050(13)
C4 0.0301(15) 0.0234(15) 0.0154(14) -0.0029(12) -0.0063(11) 0.0015(12)
C5 0.0268(14) 0.0176(13) 0.0158(14) 0.0002(10) -0.0001(11) 0.0015(11)
C6 0.0269(14) 0.0183(13) 0.0158(14) 0.0001(11) -0.0036(11) -0.0003(11)
C7 0.0318(15) 0.0223(15) 0.0146(14) -0.0005(11) -0.0037(11) 0.0006(12)
C8 0.0284(14) 0.0222(15) 0.0120(13) 0.0001(11) -0.0014(11) 0.0025(11)
C9 0.0280(15) 0.0259(15) 0.0100(13) 0.0012(11) -0.0027(11) 0.0027(12)
C10 0.0333(16) 0.0202(14) 0.0155(14) 0.0006(11) 0.0007(11) 0.0014(12)
C11 0.0357(17) 0.0253(16) 0.0153(14) 0.0053(12) -0.0013(12) 0.0080(13)
C12 0.0307(15) 0.0301(16) 0.0148(14) 0.0015(12) -0.0056(12) 0.0032(12)
C13 0.0312(16) 0.0258(16) 0.0149(14) -0.0019(12) -0.0025(11) 0.0002(12)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O1 C7 1.224(3) . ?
O2 N4 1.223(3) . ?
O3 N4 1.220(3) . ?
N1 C5 1.330(3) . ?
N1 C1 1.332(4) . ?
N2 C6 1.336(4) . ?
N2 C5 1.409(4) . ?
N2 H2N 0.78(4) . ?
N3 C7 1.375(3) . ?
N3 C6 1.397(3) . ?
N3 H3N 0.83(3) . ?
N4 C10 1.469(4) . ?
C1 C2 1.377(4) . ?
C1 H1 0.97(3) . ?
C2 C3 1.377(4) . ?
C2 H2 0.91(3) . ?
C3 C4 1.371(4) . ?
C3 H3 0.95(3) . ?
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C4 C5 1.387(4) . ?
C4 H4 0.84(3) . ?
C7 C8 1.487(4) . ?
C8 C9 1.388(4) . ?
C8 C13 1.404(4) . ?
C9 C10 1.382(4) . ?
C9 H9 0.92(3) . ?
C10 C11 1.382(4) . ?
C11 C12 1.377(4) . ?
C11 H11 0.92(3) . ?
C12 C13 1.376(4) . ?
C12 H12 0.95(3) . ?
C13 H13 0.95(3) . ?

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C6 N2 C5 131.4(2) . . ?
C6 N2 H2N 113(3) . . ?
C5 N2 H2N 114(3) . . ?
C7 N3 C6 128.1(2) . . ?
C7 N3 H3N 114(2) . . ?
C6 N3 H3N 118(2) . . ?
O3 N4 O2 123.4(3) . . ?
O3 N4 C10 118.3(2) . . ?
O2 N4 C10 118.4(2) . . ?
N1 C1 C2 123.5(3) . . ?
N1 C1 H1 116.2(19) . . ?
C2 C1 H1 120.3(19) . . ?
C1 C2 C3 118.0(3) . . ?
C1 C2 H2 122.2(19) . . ?
C3 C2 H2 119.8(19) . . ?
C4 C3 C2 120.0(3) . . ?
C4 C3 H3 121.1(19) . . ?
C2 C3 H3 118.8(19) . . ?
C3 C4 C5 117.4(3) . . ?
C3 C4 H4 124(2) . . ?
C5 C4 H4 119(2) . . ?
N1 C5 C4 123.9(3) . . ?
N1 C5 N2 110.9(2) . . ?
C4 C5 N2 125.2(2) . . ?
N2 C6 N3 114.4(2) . . ?
N2 C6 S1 126.7(2) . . ?
N3 C6 S1 118.9(2) . . ?
O1 C7 N3 122.3(3) . . ?
O1 C7 C8 119.7(2) . . ?
N3 C7 C8 118.0(2) . . ?

C9 C8 C13 120.1(3) . . ?
C9 C8 C7 123.3(2) . . ?
C13 C8 C7 116.3(2) . . ?
C10 C9 C8 117.5(3) . . ?
C10 C9 H9 119.4(19) . . ?
C8 C9 H9 123.1(19) . . ?
C11 C10 C9 123.3(3) . . ?
C11 C10 N4 118.1(2) . . ?
C9 C10 N4 118.6(2) . . ?
C12 C11 C10 118.3(3) . . ?
C12 C11 H11 123(2) . . ?
C10 C11 H11 118(2) . . ?
C11 C12 C13 120.4(3) . . ?
C11 C12 H12 119.1(18) . . ?
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C8 C13 H13 119(2) . . ?

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N1 C1 C2 C3 -1.1(5) . . . . ?
C1 C2 C3 C4 1.2(5) . . . . ?
C2 C3 C4 C5 0.4(4) . . . . ?
C1 N1 C5 C4 2.2(4) . . . . ?
C1 N1 C5 N2 179.9(3) . . . . ?
C3 C4 C5 N1 -2.1(4) . . . . ?
C3 C4 C5 N2 -179.6(3) . . . . ?
C6 N2 C5 N1 155.9(3) . . . . ?
C6 N2 C5 C4 -26.4(5) . . . . ?
C5 N2 C6 N3 -175.0(3) . . . . ?
C5 N2 C6 S1 5.4(5) . . . . ?
C7 N3 C6 N2 6.7(4) . . . . ?
C7 N3 C6 S1 -173.7(2) . . . . ?
C6 N3 C7 O1 2.6(5) . . . . ?
C6 N3 C7 C8 -176.0(3) . . . . ?
O1 C7 C8 C9 -150.9(3) . . . . ?
N3 C7 C8 C9 27.7(4) . . . . ?
O1 C7 C8 C13 23.0(4) . . . . ?
N3 C7 C8 C13 -158.4(3) . . . . ?
C13 C8 C9 C10 -0.7(4) . . . . ?
C7 C8 C9 C10 173.0(3) . . . . ?
C8 C9 C10 C11 0.7(4) . . . . ?

C8 C9 C10 N4 -176.6(2) . . . . ?
O3 N4 C10 C11 3.8(4) . . . . ?
O2 N4 C10 C11 -174.9(3) . . . . ?
O3 N4 C10 C9 -178.8(3) . . . . ?
O2 N4 C10 C9 2.5(4) . . . . ?
C9 C10 C11 C12 0.1(5) . . . . ?
N4 C10 C11 C12 177.5(3) . . . . ?
C10 C11 C12 C13 -1.0(4) . . . . ?
C11 C12 C13 C8 1.1(4) . . . . ?
C9 C8 C13 C12 -0.2(4) . . . . ?
C7 C8 C13 C12 -174.3(3) . . . . ?

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N2 H2N O1 0.78(4) 1.92(4) 2.603(3) 145(4) .
N3 H3N S1 0.83(3) 2.61(3) 3.401(3) 162(3) 3_567

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'C13 H10 N4 O3 S'

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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M P2(1)/n

loop_

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'-x+1/2, y+1/2, -z+1/2'

'-x, -y, -z'

'x-1/2, -y-1/2, z-1/2'

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_cell_length_b 13.2760(16)

_cell_length_c 19.753(2)

_cell_angle_alpha 90.00

_cell_angle_beta 94.136(2)

_cell_angle_gamma 90.00

_cell_volume 1302.4(3)

_cell_formula_units_Z 4

_cell_measurement_temperature 173(2)

_cell_measurement_reflns_used 1577

_cell_measurement_theta_min 2.57

_cell_measurement_theta_max 23.64

_exptl_crystal_description needle

_exptl_crystal_colour yellow

_exptl_crystal_size_max 0.35

_exptl_crystal_size_mid 0.05

_exptl_crystal_size_min 0.04

_exptl_crystal_density_meas 0

_exptl_crystal_density_diffrn 1.542

_exptl_crystal_density_method 'not measured'

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_exptl_absorpt_coefficient_mu     0.265
_exptl_absorpt_correction_type    'multi-scan'
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_exptl_absorpt_correction_T_max   0.9895
_exptl_absorpt_process_details    SADABS

_exptl_special_details
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_diffrn_ambient_temperature       173(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   'CCD area detector Bruker Apex'
_diffrn_measurement_method        'phi and omega scans'
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_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             12585
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_diffrn_reflns_av_sigmaI/netI     0.0472
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_diffrn_reflns_limit_h_max 6

_diffrn_reflns_limit_k_min -16

_diffrn_reflns_limit_k_max 16

_diffrn_reflns_limit_l_min -25

_diffrn_reflns_limit_l_max 25

_diffrn_reflns_theta_min 1.85

_diffrn_reflns_theta_max 27.00

_reflns_number_total 2855

_reflns_number_gt 2029

_reflns_threshold_expression >2sigma(I)

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_computing_molecular_graphics 'Bruker SHELXTL'

_computing_publication_material 'Bruker SHELXTL'

_refine_special_details

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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and

goodness of fit S are based on F^2^, conventional R-factors R are based

on F, with F set to zero for negative F^2^. The threshold expression of

F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is

not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

;

_refine_ls_structure_factor_coef Fsqd

_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0523P)^2^+0.1644P] where P=(Fo^2^+2Fc^2^)/3'

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_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens difmap

_refine_ls_hydrogen_treatment refall

_refine_ls_extinction_method none

_refine_ls_extinction_coef ?

_refine_ls_number_reflns 2855

_refine_ls_number_parameters 230

_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.0776

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_refine_ls_goodness_of_fit_ref 1.042

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_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

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_atom_site_symmetry_multiplicity

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_atom_site_refinement_flags

_atom_site_disorder_assembly

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S1 S -0.39764(12) 0.14814(4) 0.22989(3) 0.0339(2) Uani 1 1 d . . .

O1 O -0.0947(3) -0.04278(11) 0.26825(8) 0.0322(4) Uani 1 1 d . . .

O2 O 0.9176(3) -0.29376(12) 0.45361(9) 0.0430(5) Uani 1 1 d . . .

O3 O 1.0435(3) -0.15487(13) 0.50330(9) 0.0440(5) Uani 1 1 d . . .

N1 N 0.2920(4) 0.26283(14) 0.37867(10) 0.0291(5) Uani 1 1 d . . .

N2 N -0.0894(4) 0.27428(14) 0.30108(10) 0.0274(5) Uani 1 1 d . . .

N3 N 0.0353(4) 0.10857(14) 0.31683(11) 0.0272(5) Uani 1 1 d . . .

N4 N 0.8957(4) -0.20305(15) 0.46284(10) 0.0316(5) Uani 1 1 d . . .

C1 C 0.4824(5) 0.30993(19) 0.41916(13) 0.0329(6) Uani 1 1 d . . .

C2 C 0.4957(5) 0.41245(19) 0.42632(14) 0.0368(6) Uani 1 1 d . . .

C3 C 0.3034(5) 0.4710(2) 0.39030(14) 0.0395(7) Uani 1 1 d . . .

C4 C 0.1078(5) 0.42522(17) 0.34894(13) 0.0335(6) Uani 1 1 d . . .

C5 C 0.1107(4) 0.32053(16) 0.34425(12) 0.0261(5) Uani 1 1 d . . .

C6 C -0.1403(4) 0.17585(16) 0.28439(11) 0.0250(5) Uani 1 1 d . . .

C7 C 0.0543(4) 0.00559(16) 0.30682(12) 0.0245(5) Uani 1 1 d . . .

C8 C 0.2805(4) -0.04447(16) 0.34935(11) 0.0234(5) Uani 1 1 d . . .

C9 C 0.4606(5) 0.00649(18) 0.39460(12) 0.0283(5) Uani 1 1 d . . .

C10 C 0.6611(5) -0.04555(18) 0.43179(12) 0.0294(5) Uani 1 1 d . . .

C11 C 0.6792(4) -0.14822(16) 0.42343(11) 0.0251(5) Uani 1 1 d . . .

C12 C 0.5054(5) -0.20060(18) 0.37909(13) 0.0295(6) Uani 1 1 d . . .

C13 C 0.3062(4) -0.14803(17) 0.34207(13) 0.0294(5) Uani 1 1 d . . .

H2N H -0.192(5) 0.3176(18) 0.2837(12) 0.031(7) Uiso 1 1 d . . .

H3N H 0.157(5) 0.1390(19) 0.3413(13) 0.040(8) Uiso 1 1 d . . .

H1 H 0.602(5) 0.2673(18) 0.4421(12) 0.032(7) Uiso 1 1 d . . .

H2 H 0.632(5) 0.4413(19) 0.4558(14) 0.052(8) Uiso 1 1 d . . .

H3 H 0.314(5) 0.541(2) 0.3948(14) 0.051(8) Uiso 1 1 d . . .

H4 H -0.027(5) 0.4595(18) 0.3233(13) 0.040(7) Uiso 1 1 d . . .

H9 H 0.443(5) 0.0746(18) 0.4012(12) 0.034(7) Uiso 1 1 d . . .

H10 H 0.777(4) -0.0105(17) 0.4620(12) 0.031(6) Uiso 1 1 d . . .

H12 H 0.527(5) -0.2709(18) 0.3733(12) 0.033(7) Uiso 1 1 d . . .

H13 H 0.187(5) -0.1829(17) 0.3119(12) 0.034(7) Uiso 1 1 d . . .

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_atom_site_aniso_U_33

_atom_site_aniso_U_23

_atom_site_aniso_U_13

_atom_site_aniso_U_12

S1 0.0287(3) 0.0244(3) 0.0457(4) 0.0009(3) -0.0164(3) -0.0006(3)

O1 0.0302(9) 0.0266(9) 0.0376(10) -0.0039(7) -0.0131(7) 0.0005(7)

O2 0.0464(11) 0.0278(10) 0.0528(12) 0.0030(9) -0.0090(9) 0.0136(8)

O3 0.0372(10) 0.0394(10) 0.0518(12) 0.0023(9) -0.0224(9) 0.0020(8)

N1 0.0252(10) 0.0278(11) 0.0332(12) -0.0020(9) -0.0054(9) 0.0018(8)

N2 0.0241(10) 0.0202(10) 0.0363(12) 0.0024(9) -0.0093(9) 0.0012(8)

N3 0.0222(10) 0.0214(10) 0.0365(12) 0.0003(9) -0.0082(9) 0.0001(8)

N4 0.0272(10) 0.0327(12) 0.0341(12) 0.0055(10) -0.0046(9) 0.0041(9)

C1 0.0268(12) 0.0351(14) 0.0352(15) -0.0017(12) -0.0088(11) 0.0035(11)

C2 0.0321(13) 0.0387(15) 0.0381(16) -0.0073(12) -0.0085(12) -0.0046(11)

C3 0.0446(16) 0.0243(13) 0.0479(17) -0.0014(12) -0.0093(13) -0.0057(11)

C4 0.0367(14) 0.0233(13) 0.0387(16) 0.0021(11) -0.0107(12) -0.0014(10)

C5 0.0226(11) 0.0262(12) 0.0287(13) -0.0007(10) -0.0021(10) -0.0007(9)

C6 0.0211(11) 0.0222(11) 0.0310(13) 0.0046(10) -0.0024(10) 0.0018(8)

C7 0.0202(11) 0.0227(11) 0.0302(13) 0.0023(10) -0.0015(10) -0.0014(9)

C8 0.0201(11) 0.0235(11) 0.0262(13) 0.0004(10) -0.0018(9) 0.0003(9)

C9 0.0288(12) 0.0204(12) 0.0343(14) -0.0014(10) -0.0061(10) 0.0004(10)

C10 0.0280(12) 0.0278(13) 0.0307(14) -0.0021(11) -0.0093(11) -0.0002(10)

C11 0.0202(11) 0.0265(12) 0.0281(13) 0.0025(10) -0.0015(9) 0.0050(9)

C12 0.0274(12) 0.0219(12) 0.0387(15) -0.0005(11) -0.0015(11) 0.0028(10)

C13 0.0244(11) 0.0241(12) 0.0384(15) -0.0019(11) -0.0058(10) -0.0018(10)

_geom_special_details

;

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

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S1 C6 1.654(2) . ?
O1 C7 1.209(3) . ?
O2 N4 1.224(2) . ?
O3 N4 1.227(2) . ?
N1 C5 1.333(3) . ?
N1 C1 1.349(3) . ?
N2 C6 1.367(3) . ?
N2 C5 1.405(3) . ?
N2 H2N 0.83(2) . ?
N3 C6 1.376(3) . ?
N3 C7 1.386(3) . ?
N3 H3N 0.85(3) . ?
N4 C11 1.475(3) . ?
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C1 C2 1.370(3) . ?

C1 H1 0.92(2) . ?

C2 C3 1.389(4) . ?

C2 H2 0.94(3) . ?

C3 C4 1.368(3) . ?

C3 H3 0.94(3) . ?

C4 C5 1.393(3) . ?

C4 H4 0.93(2) . ?

C7 C8 1.510(3) . ?

C8 C13 1.389(3) . ?

C8 C9 1.395(3) . ?

C9 C10 1.381(3) . ?

C9 H9 0.92(2) . ?

C10 C11 1.377(3) . ?

C10 H10 0.93(2) . ?

C11 C12 1.375(3) . ?

C12 C13 1.379(3) . ?

C12 H12 0.95(2) . ?

C13 H13 0.93(2) . ?

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C5 N1 C1 117.2(2) . . ?

C6 N2 C5 132.5(2) . . ?

C6 N2 H2N 117.8(17) . . ?

C5 N2 H2N 109.8(17) . . ?

C6 N3 C7 128.4(2) . . ?

C6 N3 H3N 111.0(17) . . ?

C7 N3 H3N 119.8(17) . . ?

O2 N4 O3 123.67(19) . . ?

O2 N4 C11 118.45(19) . . ?

O3 N4 C11 117.89(18) . . ?

N1 C1 C2 123.3(2) . . ?

N1 C1 H1 114.2(15) . . ?

C2 C1 H1 122.5(15) . . ?

C1 C2 C3 118.5(2) . . ?

C1 C2 H2 119.6(16) . . ?

C3 C2 H2 121.9(16) . . ?

C4 C3 C2 119.5(2) . . ?

C4 C3 H3 122.0(17) . . ?

C2 C3 H3 118.5(17) . . ?

C3 C4 C5 118.2(2) . . ?

C3 C4 H4 124.2(15) . . ?

C5 C4 H4 117.6(15) . . ?

N1 C5 C4 123.3(2) . . ?

N1 C5 N2 118.90(19) . . ?

C4 C5 N2 117.8(2) . . ?

N2 C6 N3 114.07(19) . . ?

N2 C6 S1 119.40(16) . . ?

N3 C6 S1 126.53(17) . . ?

O1 C7 N3 124.7(2) . . ?

O1 C7 C8 121.1(2) . . ?

N3 C7 C8 114.25(18) . . ?

C13 C8 C9 119.1(2) . . ?

C13 C8 C7 116.66(19) . . ?

C9 C8 C7 124.2(2) . . ?

C10 C9 C8 120.3(2) . . ?

C10 C9 H9 119.3(15) . . ?

C8 C9 H9 120.4(15) . . ?

C11 C10 C9 118.9(2) . . ?

C11 C10 H10 122.1(14) . . ?

C9 C10 H10 119.0(14) . . ?

C12 C11 C10 122.2(2) . . ?

C12 C11 N4 119.3(2) . . ?

C10 C11 N4 118.5(2) . . ?

C11 C12 C13 118.5(2) . . ?

C11 C12 H12 120.2(15) . . ?

C13 C12 H12 121.3(15) . . ?

C12 C13 C8 120.9(2) . . ?

C12 C13 H13 119.2(15) . . ?

C8 C13 H13 119.9(14) . . ?

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C5 N1 C1 C2 0.3(4) . . . . ?

N1 C1 C2 C3 0.2(4) . . . . ?

C1 C2 C3 C4 -0.1(4) . . . . ?

C2 C3 C4 C5 -0.4(4) . . . . ?

C1 N1 C5 C4 -0.8(4) . . . . ?

C1 N1 C5 N2 179.4(2) . . . . ?

C3 C4 C5 N1 0.9(4) . . . . ?

C3 C4 C5 N2 -179.3(2) . . . . ?

C6 N2 C5 N1 -1.5(4) . . . . ?

C6 N2 C5 C4 178.8(2) . . . . ?

C5 N2 C6 N3 1.2(4) . . . . ?

C5 N2 C6 S1 -179.3(2) . . . . ?

C7 N3 C6 N2 -173.7(2) . . . . ?

C7 N3 C6 S1 6.9(4) . . . . ?

C6 N3 C7 O1 -3.2(4) . . . . ?

C6 N3 C7 C8 177.3(2) . . . . ?

O1 C7 C8 C13 -0.4(3) . . . . ?

N3 C7 C8 C13 179.1(2) . . . . ?

O1 C7 C8 C9 179.7(2) . . . . ?

N3 C7 C8 C9 -0.8(3) . . . . ?

C13 C8 C9 C10 -0.2(4) . . . . ?

C7 C8 C9 C10 179.7(2) . . . . ?

C8 C9 C10 C11 -0.1(4) . . . . ?

C9 C10 C11 C12 0.3(4) . . . . ?

C9 C10 C11 N4 179.4(2) . . . . ?

O2 N4 C11 C12 1.6(3) . . . . ?

O3 N4 C11 C12 -178.2(2) . . . . ?

O2 N4 C11 C10 -177.4(2) . . . . ?

O3 N4 C11 C10 2.8(3) . . . . ?

C10 C11 C12 C13 -0.2(4) . . . . ?

N4 C11 C12 C13 -179.2(2) . . . . ?

C11 C12 C13 C8 -0.1(4) . . . . ?

C9 C8 C13 C12 0.3(4) . . . . ?

C7 C8 C13 C12 -179.5(2) . . . . ?

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_geom_hbond_atom_site_label_A

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_geom_hbond_distance_HA

_geom_hbond_distance_DA

_geom_hbond_angle_DHA

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 _geom_hbond_site_symmetry_A
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N3 H3N N1  0.85(3) 1.90(3) 2.664(3) 148(2) .

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;
_chemical_name_common            ?
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'H'  'H'   0.0000   0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N'  'N'   0.0061   0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'O'  'O'   0.0106   0.0060
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'S'  'S'   0.1246   0.1234
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M    P2(1)/c

loop_
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 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'
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_cell_length_c 10.3383(11)

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_cell_angle_gamma 90.00

_cell_volume 1352.0(2)

_cell_formula_units_Z 4

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_cell_measurement_reflns_used 7399

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_cell_measurement_theta_max 28.17

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_exptl_absorpt_process_details SADABS

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_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   'CCD area detector Bruker Apex'
_diffrn_measurement_method        'phi and omega scans'
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_computing_cell_refinement       'Bruker SMART'
_computing_data_reduction        'Bruker SAINT'
_computing_structure_solution    'Bruker SHELXTL'
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_computing_molecular_graphics    'Bruker SHELXTL'
_computing_publication_material  'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
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_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0542P)^2^+0.3992P] where P=(Fo^2^+2Fc^2^)/3'

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_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens difmap

_refine_ls_hydrogen_treatment refall

_refine_ls_extinction_method none

_refine_ls_extinction_coef ?

_refine_ls_number_reflns 2958

_refine_ls_number_parameters 233

_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.0363

_refine_ls_R_factor_gt 0.0331

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_refine_ls_wR_factor_gt 0.0907

_refine_ls_goodness_of_fit_ref 1.043

_refine_ls_restrained_S_all 1.043

_refine_ls_shift/su_max 0.001

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_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

_atom_site_occupancy

_atom_site_symmetry_multiplicity

_atom_site_calc_flag

_atom_site_refinement_flags

_atom_site_disorder_assembly

_atom_site_disorder_group

S1 S 0.95326(4) 0.06520(2) 0.64878(4) 0.03324(12) Uani 1 1 d . . .

O1 O 0.66421(11) -0.01429(6) 0.90967(10) 0.0300(2) Uani 1 1 d . . .

O2 O 1.04737(11) 0.15228(6) 1.05914(9) 0.0305(2) Uani 1 1 d . . .

N1 N 0.54061(13) -0.13064(7) 0.54656(11) 0.0292(2) Uani 1 1 d . . .

N2 N 0.71309(13) -0.02994(7) 0.67378(11) 0.0251(2) Uani 1 1 d . . .

N3 N 0.85371(13) 0.05827(7) 0.85578(11) 0.0251(2) Uani 1 1 d . . .

C1 C 0.46747(17) -0.17527(9) 0.42974(14) 0.0321(3) Uani 1 1 d . . .

C2 C 0.50074(17) -0.16521(9) 0.31026(14) 0.0313(3) Uani 1 1 d . . .

C3 C 0.61506(16) -0.10587(9) 0.31181(14) 0.0306(3) Uani 1 1 d . . .

C4 C 0.69331(16) -0.05854(8) 0.43115(14) 0.0279(3) Uani 1 1 d . . .

C5 C 0.65088(14) -0.07328(8) 0.54565(13) 0.0243(3) Uani 1 1 d . . .

C6 C 0.83214(14) 0.02740(8) 0.72316(13) 0.0239(3) Uani 1 1 d . . .

C7 C 0.76935(14) 0.04037(8) 0.93966(13) 0.0235(2) Uani 1 1 d . . .

C8 C 0.80759(14) 0.09323(8) 1.06826(12) 0.0231(2) Uani 1 1 d . . .

C9 C 0.69844(16) 0.08706(8) 1.13524(13) 0.0269(3) Uani 1 1 d . . .

C10 C 0.71896(17) 0.13208(9) 1.25567(14) 0.0307(3) Uani 1 1 d . . .

C11 C 0.85170(18) 0.18449(9) 1.31102(14) 0.0343(3) Uani 1 1 d . . .

C12 C 0.96177(17) 0.19288(9) 1.24695(14) 0.0314(3) Uani 1 1 d . . .

C13 C 0.94103(14) 0.14756(8) 1.12574(13) 0.0253(3) Uani 1 1 d . . .

C14 C 1.17947(17) 0.21097(10) 1.10959(16) 0.0343(3) Uani 1 1 d . . .

H2N H 0.6642(19) -0.0417(10) 0.7311(17) 0.034(4) Uiso 1 1 d . . .

H3N H 0.927(2) 0.0933(10) 0.8846(16) 0.028(4) Uiso 1 1 d . . .

H1 H 0.387(2) -0.2151(10) 0.4322(17) 0.035(4) Uiso 1 1 d . . .

H2 H 0.446(2) -0.2005(11) 0.2298(18) 0.038(4) Uiso 1 1 d . . .

H3 H 0.640(2) -0.0966(11) 0.2302(18) 0.037(4) Uiso 1 1 d . . .

H4 H 0.7676(19) -0.0175(10) 0.4357(16) 0.032(4) Uiso 1 1 d . . .

H9 H 0.6127(19) 0.0516(10) 1.0964(16) 0.030(4) Uiso 1 1 d . . .

H10 H 0.644(2) 0.1276(10) 1.3002(18) 0.038(4) Uiso 1 1 d . . .

H11 H 0.869(2) 0.2170(11) 1.3954(19) 0.045(5) Uiso 1 1 d . . .

H12 H 1.052(2) 0.2278(11) 1.2847(18) 0.039(4) Uiso 1 1 d . . .

H14A H 1.238(2) 0.2038(11) 1.0466(19) 0.044(5) Uiso 1 1 d . . .

H14B H 1.142(2) 0.2680(12) 1.1021(18) 0.044(5) Uiso 1 1 d . . .

H14C H 1.249(2) 0.1952(10) 1.2026(18) 0.036(4) Uiso 1 1 d . . .

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O1 0.0274(5) 0.0335(5) 0.0305(5) -0.0059(4) 0.0123(4) -0.0104(4)

O2 0.0238(5) 0.0362(5) 0.0302(5) -0.0046(4) 0.0084(4) -0.0114(4)

N1 0.0260(6) 0.0318(6) 0.0289(6) -0.0034(4) 0.0092(5) -0.0033(4)

N2 0.0235(5) 0.0287(5) 0.0237(5) -0.0021(4) 0.0096(4) -0.0026(4)

N3 0.0220(5) 0.0274(5) 0.0255(5) -0.0030(4) 0.0084(4) -0.0062(4)

C1 0.0284(7) 0.0323(7) 0.0328(7) -0.0049(5) 0.0081(6) -0.0046(5)

C2 0.0291(7) 0.0317(7) 0.0275(6) -0.0052(5) 0.0040(5) 0.0045(5)

C3 0.0312(7) 0.0338(7) 0.0262(6) 0.0009(5) 0.0098(5) 0.0076(5)

C4 0.0261(6) 0.0289(6) 0.0285(6) 0.0006(5) 0.0100(5) 0.0017(5)

C5 0.0205(6) 0.0242(6) 0.0256(6) -0.0007(4) 0.0055(5) 0.0033(4)

C6 0.0204(6) 0.0253(6) 0.0252(6) 0.0009(5) 0.0075(5) 0.0020(4)

C7 0.0196(6) 0.0250(6) 0.0241(6) 0.0010(5) 0.0059(5) -0.0001(4)

C8 0.0217(6) 0.0233(6) 0.0217(5) 0.0022(4) 0.0048(5) 0.0005(4)

C9 0.0258(6) 0.0270(6) 0.0272(6) 0.0016(5) 0.0092(5) -0.0021(5)

C10 0.0345(7) 0.0312(7) 0.0284(6) 0.0022(5) 0.0142(6) 0.0021(5)

C11 0.0425(8) 0.0320(7) 0.0257(6) -0.0034(5) 0.0097(6) 0.0003(6)

C12 0.0314(7) 0.0297(7) 0.0278(7) -0.0030(5) 0.0049(5) -0.0055(5)

C13 0.0240(6) 0.0252(6) 0.0239(6) 0.0028(5) 0.0057(5) -0.0007(5)

C14 0.0264(7) 0.0356(8) 0.0348(8) 0.0012(6) 0.0043(6) -0.0118(6)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles

and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

;

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_geom_bond_atom_site_label_2

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O1 C7 1.2268(15) . ?

O2 C13 1.3691(15) . ?

O2 C14 1.4371(15) . ?

N1 C1 1.3388(17) . ?

N1 C5 1.3402(16) . ?

N2 C6 1.3440(16) . ?

N2 C5 1.4075(16) . ?

N2 H2N 0.877(17) . ?

N3 C7 1.3744(16) . ?

N3 C6 1.3986(16) . ?

N3 H3N 0.821(17) . ?

C1 C2 1.383(2) . ?

C1 H1 0.962(17) . ?

C2 C3 1.381(2) . ?

C2 H2 0.968(18) . ?

C3 C4 1.3875(19) . ?

C3 H3 0.962(17) . ?

C4 C5 1.3906(18) . ?

C4 H4 0.915(16) . ?

C7 C8 1.4958(17) . ?

C8 C9 1.3956(17) . ?

C8 C13 1.4084(17) . ?

C9 C10 1.3839(19) . ?

C9 H9 0.913(17) . ?

C10 C11 1.384(2) . ?

C10 H10 0.950(17) . ?

C11 C12 1.383(2) . ?

C11 H11 0.973(18) . ?

C12 C13 1.3927(18) . ?

C12 H12 0.933(18) . ?

C14 H14A 0.984(18) . ?

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C14 H14C 0.964(18) . ?

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C13 O2 C14 119.02(11) . . ?

C1 N1 C5 117.48(11) . . ?

C6 N2 C5 131.54(11) . . ?

C6 N2 H2N 114.2(11) . . ?

C5 N2 H2N 114.3(11) . . ?

C7 N3 C6 129.75(11) . . ?

C7 N3 H3N 117.2(11) . . ?

C6 N3 H3N 113.0(11) . . ?

N1 C1 C2 123.37(13) . . ?

N1 C1 H1 115.9(10) . . ?

C2 C1 H1 120.7(10) . . ?

C3 C2 C1 118.15(12) . . ?

C3 C2 H2 122.2(10) . . ?

C1 C2 H2 119.6(10) . . ?

C2 C3 C4 120.01(13) . . ?

C2 C3 H3 120.4(10) . . ?

C4 C3 H3 119.6(10) . . ?

C3 C4 C5 117.39(13) . . ?

C3 C4 H4 122.8(10) . . ?

C5 C4 H4 119.8(10) . . ?

N1 C5 C4 123.59(12) . . ?

N1 C5 N2 110.76(11) . . ?

C4 C5 N2 125.63(12) . . ?

N2 C6 N3 113.98(11) . . ?

N2 C6 S1 128.96(10) . . ?

N3 C6 S1 117.06(9) . . ?

O1 C7 N3 122.30(11) . . ?

O1 C7 C8 120.99(11) . . ?

N3 C7 C8 116.68(11) . . ?

C9 C8 C13 118.29(11) . . ?

C9 C8 C7 115.53(11) . . ?

C13 C8 C7 126.18(11) . . ?

C10 C9 C8 121.83(12) . . ?

C10 C9 H9 121.2(10) . . ?

C8 C9 H9 117.0(10) . . ?

C11 C10 C9 118.90(13) . . ?

C11 C10 H10 119.9(10) . . ?

C9 C10 H10 121.2(10) . . ?

C10 C11 C12 120.97(13) . . ?

C10 C11 H11 120.8(11) . . ?

C12 C11 H11 118.3(11) . . ?

C11 C12 C13 120.10(13) . . ?

C11 C12 H12 121.0(11) . . ?

C13 C12 H12 118.9(11) . . ?

O2 C13 C12 122.66(11) . . ?

O2 C13 C8 117.42(11) . . ?

C12 C13 C8 119.91(12) . . ?

O2 C14 H14A 104.9(11) . . ?

O2 C14 H14B 111.0(11) . . ?

H14A C14 H14B 108.3(15) . . ?

O2 C14 H14C 109.7(10) . . ?

H14A C14 H14C 108.9(15) . . ?

H14B C14 H14C 113.7(15) . . ?

loop_

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C5 N1 C1 C2 0.3(2) . . . . ?

N1 C1 C2 C3 -0.2(2) . . . . ?

C1 C2 C3 C4 0.2(2) . . . . ?

C2 C3 C4 C5 -0.39(19) . . . . ?

C1 N1 C5 C4 -0.51(19) . . . . ?

C1 N1 C5 N2 178.20(11) . . . . ?

C3 C4 C5 N1 0.55(19) . . . . ?

C3 C4 C5 N2 -177.96(12) . . . . ?

C6 N2 C5 N1 174.48(12) . . . . ?

C6 N2 C5 C4 -6.8(2) . . . . ?

C5 N2 C6 N3 177.75(12) . . . . ?

C5 N2 C6 S1 -2.2(2) . . . . ?

C7 N3 C6 N2 -1.90(19) . . . . ?

C7 N3 C6 S1 178.04(10) . . . . ?

C6 N3 C7 O1 6.2(2) . . . . ?

C6 N3 C7 C8 -171.66(11) . . . . ?

O1 C7 C8 C9 -11.24(17) . . . . ?

N3 C7 C8 C9 166.63(11) . . . . ?

O1 C7 C8 C13 168.95(12) . . . . ?

N3 C7 C8 C13 -13.18(18) . . . . ?

C13 C8 C9 C10 -0.47(19) . . . . ?

C7 C8 C9 C10 179.71(12) . . . . ?

C8 C9 C10 C11 -0.1(2) . . . . ?

C9 C10 C11 C12 0.7(2) . . . . ?

C10 C11 C12 C13 -0.7(2) . . . . ?

C14 O2 C13 C12 -4.81(18) . . . . ?

C14 O2 C13 C8 176.15(11) . . . . ?

C11 C12 C13 O2 -178.91(12) . . . . ?

C11 C12 C13 C8 0.1(2) . . . . ?

C9 C8 C13 O2 179.53(11) . . . . ?

C7 C8 C13 O2 -0.67(18) . . . . ?

C9 C8 C13 C12 0.46(18) . . . . ?

C7 C8 C13 C12 -179.74(12) . . . . ?

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N3 H3N O2  0.821(17) 1.959(16) 2.6277(14) 138.1(14) .


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 'N'  'N'   0.0061   0.0033
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 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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'-x, y+1/2, -z+1/2'
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'x, -y-1/2, z-1/2'

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_cell_angle_gamma 90.00
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_cell_measurement_theta_max 28.18

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_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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S1 S 0.50976(3) 0.37554(2) 0.11052(5) 0.04340(13) Uani 1 1 d . . .
O1 O 0.14308(7) 0.44444(6) 0.12990(14) 0.0432(2) Uani 1 1 d . . .
O2 O 0.15303(9) 0.85182(6) 0.13355(14) 0.0461(3) Uani 1 1 d . . .
N1 N 0.20751(10) 0.19875(8) 0.17714(18) 0.0459(3) Uani 1 1 d . . .
N2 N 0.29597(9) 0.32411(7) 0.12890(15) 0.0364(2) Uani 1 1 d . . .
N3 N 0.32996(8) 0.46897(7) 0.11696(15) 0.0337(2) Uani 1 1 d . . .
C1 C 0.20323(15) 0.11308(10) 0.1851(2) 0.0526(4) Uani 1 1 d . . .
C2 C 0.29231(15) 0.06024(10) 0.1498(2) 0.0530(4) Uani 1 1 d . . .
C3 C 0.39103(15) 0.09872(10) 0.1043(2) 0.0535(4) Uani 1 1 d . . .
C4 C 0.39899(13) 0.18702(10) 0.0945(2) 0.0463(3) Uani 1 1 d . . .
C5 C 0.30473(11) 0.23399(8) 0.13365(17) 0.0363(3) Uani 1 1 d . . .
C6 C 0.37241(10) 0.38614(8) 0.11814(17) 0.0326(3) Uani 1 1 d . . .
C7 C 0.22053(9) 0.49587(8) 0.12652(16) 0.0333(3) Uani 1 1 d . . .
C8 C 0.20380(9) 0.58933(8) 0.13098(16) 0.0318(3) Uani 1 1 d . . .
C9 C 0.10163(10) 0.62166(8) 0.07094(18) 0.0350(3) Uani 1 1 d . . .
C10 C 0.08061(10) 0.70878(9) 0.07039(18) 0.0371(3) Uani 1 1 d . . .
C11 C 0.16276(10) 0.76510(8) 0.13100(16) 0.0353(3) Uani 1 1 d . . .
C12 C 0.26443(11) 0.73357(9) 0.19459(18) 0.0383(3) Uani 1 1 d . . .
C13 C 0.28453(10) 0.64702(9) 0.19478(18) 0.0354(3) Uani 1 1 d . . .
C14 C 0.04913(16) 0.88695(12) 0.0747(3) 0.0561(4) Uani 1 1 d . . .
H2N H 0.2275(16) 0.3425(12) 0.134(3) 0.062(5) Uiso 1 1 d . . .
H3N H 0.3790(13) 0.5084(11) 0.094(2) 0.044(4) Uiso 1 1 d . . .
H1 H 0.1319(16) 0.0890(13) 0.219(3) 0.067(5) Uiso 1 1 d . . .
H2 H 0.2858(14) 0.0002(13) 0.159(2) 0.059(5) Uiso 1 1 d . . .
H3 H 0.4527(18) 0.0685(14) 0.076(3) 0.073(6) Uiso 1 1 d . . .
H4 H 0.4634(15) 0.2137(11) 0.060(2) 0.057(5) Uiso 1 1 d . . .
H9 H 0.0467(13) 0.5816(10) 0.025(2) 0.044(4) Uiso 1 1 d . . .
H10 H 0.0097(14) 0.7284(10) 0.023(2) 0.046(4) Uiso 1 1 d . . .
H12 H 0.3183(14) 0.7728(11) 0.238(2) 0.047(4) Uiso 1 1 d . . .
H13 H 0.3553(15) 0.6274(10) 0.240(2) 0.047(4) Uiso 1 1 d . . .
H14A H 0.052(2) 0.9464(17) 0.093(3) 0.095(7) Uiso 1 1 d . . .
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H14B H 0.0356(17) 0.8702(11) -0.056(3) 0.064(5) Uiso 1 1 d . . .
H14C H -0.0090(17) 0.8686(11) 0.150(3) 0.057(5) Uiso 1 1 d . . .

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O1 0.0264(4) 0.0392(5) 0.0640(6) 0.0032(4) 0.0023(4) -0.0032(4)
O2 0.0507(6) 0.0372(5) 0.0505(6) -0.0048(4) 0.0030(4) 0.0083(4)
N1 0.0433(6) 0.0406(6) 0.0536(7) 0.0078(5) -0.0035(5) -0.0059(5)
N2 0.0289(5) 0.0343(6) 0.0458(6) 0.0034(4) -0.0006(4) 0.0004(4)
N3 0.0243(5) 0.0333(5) 0.0434(6) 0.0032(4) 0.0016(4) -0.0008(4)
C1 0.0558(9) 0.0419(8) 0.0599(9) 0.0095(7) -0.0074(7) -0.0097(7)
C2 0.0699(10) 0.0347(7) 0.0539(8) 0.0046(6) -0.0167(7) -0.0036(7)
C3 0.0599(10) 0.0417(8) 0.0588(9) -0.0054(7) -0.0088(7) 0.0093(7)
C4 0.0454(8) 0.0403(7) 0.0531(8) -0.0018(6) -0.0013(6) 0.0021(6)
C5 0.0398(7) 0.0353(6) 0.0338(6) 0.0033(5) -0.0053(5) -0.0009(5)
C6 0.0291(6) 0.0349(6) 0.0340(6) 0.0034(5) 0.0004(4) 0.0009(4)
C7 0.0252(6) 0.0401(6) 0.0347(6) 0.0012(5) 0.0018(4) -0.0002(5)
C8 0.0257(5) 0.0375(6) 0.0321(6) -0.0014(5) 0.0035(4) 0.0010(5)
C9 0.0248(6) 0.0417(7) 0.0385(6) -0.0011(5) 0.0014(5) -0.0003(5)
C10 0.0284(6) 0.0445(7) 0.0383(6) 0.0004(5) 0.0019(5) 0.0056(5)
C11 0.0384(6) 0.0357(6) 0.0320(6) -0.0032(5) 0.0070(5) 0.0038(5)
C12 0.0332(6) 0.0403(7) 0.0414(7) -0.0083(5) 0.0003(5) -0.0023(5)
C13 0.0264(6) 0.0425(7) 0.0371(6) -0.0047(5) -0.0010(5) 0.0023(5)
C14 0.0608(10) 0.0472(9) 0.0603(10) -0.0038(7) -0.0029(8) 0.0202(8)

_geom_special_details
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O1 C7 1.2319(15) . ?
O2 C11 1.3579(16) . ?
O2 C14 1.429(2) . ?
N1 C5 1.3360(17) . ?
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N1 C1 1.3387(19) . ?
N2 C6 1.3395(16) . ?
N2 C5 1.4103(17) . ?
N2 H2N 0.88(2) . ?
N3 C7 1.3878(15) . ?
N3 C6 1.3898(16) . ?
N3 H3N 0.871(17) . ?
C1 C2 1.380(2) . ?
C1 H1 0.97(2) . ?
C2 C3 1.377(3) . ?
C2 H2 0.94(2) . ?
C3 C4 1.383(2) . ?
C3 H3 0.91(2) . ?
C4 C5 1.385(2) . ?
C4 H4 0.919(18) . ?
C7 C8 1.4722(18) . ?
C8 C9 1.3968(17) . ?
C8 C13 1.4007(17) . ?
C9 C10 1.3826(19) . ?
C9 H9 0.967(16) . ?
C10 C11 1.3918(18) . ?
C10 H10 0.967(16) . ?
C11 C12 1.3950(18) . ?
C12 C13 1.3717(19) . ?
C12 H12 0.945(17) . ?
C13 H13 0.962(17) . ?
C14 H14A 0.94(3) . ?
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C6 N2 C5 132.08(11) . . ?
C6 N2 H2N 114.6(13) . . ?
C5 N2 H2N 113.3(13) . . ?
C7 N3 C6 129.16(11) . . ?
C7 N3 H3N 116.4(11) . . ?
C6 N3 H3N 114.0(11) . . ?
N1 C1 C2 123.90(15) . . ?
N1 C1 H1 115.5(12) . . ?
C2 C1 H1 120.6(12) . . ?
C3 C2 C1 117.46(15) . . ?
C3 C2 H2 121.5(11) . . ?
C1 C2 H2 121.0(11) . . ?
C2 C3 C4 120.48(16) . . ?

C2 C3 H3 122.8(14) . . ?
C4 C3 H3 116.7(14) . . ?
C3 C4 C5 117.33(15) . . ?
C3 C4 H4 121.6(11) . . ?
C5 C4 H4 121.0(11) . . ?
N1 C5 C4 123.75(13) . . ?
N1 C5 N2 110.50(11) . . ?
C4 C5 N2 125.74(12) . . ?
N2 C6 N3 114.71(11) . . ?
N2 C6 S1 127.99(10) . . ?
N3 C6 S1 117.28(9) . . ?
O1 C7 N3 121.75(12) . . ?
O1 C7 C8 122.70(11) . . ?
N3 C7 C8 115.55(10) . . ?
C9 C8 C13 118.60(12) . . ?
C9 C8 C7 118.12(11) . . ?
C13 C8 C7 123.26(11) . . ?
C10 C9 C8 121.13(12) . . ?
C10 C9 H9 120.6(9) . . ?
C8 C9 H9 118.2(9) . . ?
C9 C10 C11 119.32(12) . . ?
C9 C10 H10 118.3(10) . . ?
C11 C10 H10 122.4(10) . . ?
O2 C11 C10 124.87(12) . . ?
O2 C11 C12 115.00(12) . . ?
C10 C11 C12 120.13(12) . . ?
C13 C12 C11 120.15(12) . . ?
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C12 C13 C8 120.65(12) . . ?
C12 C13 H13 118.1(9) . . ?
C8 C13 H13 121.3(9) . . ?
O2 C14 H14A 108.0(15) . . ?
O2 C14 H14B 108.6(11) . . ?
H14A C14 H14B 113.5(17) . . ?
O2 C14 H14C 111.6(12) . . ?
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N1 C1 C2 C3 0.2(2) . . . . ?
C1 C2 C3 C4 -0.2(2) . . . . ?

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C1 N1 C5 C4 0.9(2) . . . . ?
C1 N1 C5 N2 179.39(12) . . . . ?
C3 C4 C5 N1 -1.0(2) . . . . ?
C3 C4 C5 N2 -179.19(13) . . . . ?
C6 N2 C5 N1 169.20(13) . . . . ?
C6 N2 C5 C4 -12.4(2) . . . . ?
C5 N2 C6 N3 -179.98(12) . . . . ?
C5 N2 C6 S1 -1.3(2) . . . . ?
C7 N3 C6 N2 0.47(19) . . . . ?
C7 N3 C6 S1 -178.34(10) . . . . ?
C6 N3 C7 O1 -3.2(2) . . . . ?
C6 N3 C7 C8 177.19(11) . . . . ?
O1 C7 C8 C9 -23.53(18) . . . . ?
N3 C7 C8 C9 156.06(11) . . . . ?
O1 C7 C8 C13 155.52(12) . . . . ?
N3 C7 C8 C13 -24.89(17) . . . . ?
C13 C8 C9 C10 1.31(18) . . . . ?
C7 C8 C9 C10 -179.59(11) . . . . ?
C8 C9 C10 C11 -0.09(19) . . . . ?
C14 O2 C11 C10 2.03(19) . . . . ?
C14 O2 C11 C12 -178.23(13) . . . . ?
C9 C10 C11 O2 178.60(11) . . . . ?
C9 C10 C11 C12 -1.12(18) . . . . ?
O2 C11 C12 C13 -178.66(12) . . . . ?
C10 C11 C12 C13 1.08(19) . . . . ?
C11 C12 C13 C8 0.18(19) . . . . ?
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C7 C8 C13 C12 179.60(12) . . . . ?

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N2 H2N O1  0.88(2) 1.89(2) 2.6318(15) 141.6(18) .
N3 H3N S1  0.871(17) 2.703(17) 3.5214(12) 157.0(13) 3_665

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data_34
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_symmetry_space_group_name_H-M    P2(1)/n

loop_
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 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

_cell_length_a                   3.9319(6)
_cell_length_b                   14.423(2)
_cell_length_c                   22.706(4)
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_cell_angle_beta                  92.806(3)
_cell_angle_gamma                 90.00
_cell_volume                     1286.1(3)
_cell_formula_units_Z             4
_cell_measurement_temperature     173(2)
_cell_measurement_reflns_used     1195
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_atom_sites_solution_secondary    difmap
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S1 S 0.28286(18) 0.62260(5) 1.00999(3) 0.02495(19) Uani 1 1 d . . .
O1 O 0.0756(6) 0.58928(13) 0.81275(8) 0.0378(6) Uani 1 1 d . . .
N1 N 0.3627(6) 0.83736(15) 0.86703(10) 0.0274(5) Uani 1 1 d . . .
N2 N 0.3327(6) 0.68961(16) 0.90021(11) 0.0262(6) Uani 1 1 d . . .
N3 N 0.1301(6) 0.54077(16) 0.90849(10) 0.0244(5) Uani 1 1 d . . .
C1 C 0.4568(8) 0.9257(2) 0.87247(13) 0.0297(7) Uani 1 1 d . . .
C2 C 0.6307(7) 0.9617(2) 0.92167(13) 0.0284(7) Uani 1 1 d . . .
C3 C 0.7184(7) 0.9012(2) 0.96702(13) 0.0288(7) Uani 1 1 d . . .
C4 C 0.6267(7) 0.8087(2) 0.96294(13) 0.0270(6) Uani 1 1 d . . .
C5 C 0.4446(7) 0.78102(18) 0.91216(11) 0.0229(6) Uani 1 1 d . . .
C6 C 0.2524(6) 0.62097(18) 0.93671(12) 0.0220(6) Uani 1 1 d . . .
C7 C 0.0552(7) 0.52714(19) 0.84870(12) 0.0246(6) Uani 1 1 d . . .
C8 C -0.0472(6) 0.43156(18) 0.83072(11) 0.0219(6) Uani 1 1 d . . .
C9 C 0.0652(7) 0.35278(18) 0.86122(12) 0.0226(6) Uani 1 1 d . . .
C10 C -0.0177(7) 0.26685(18) 0.83851(12) 0.0251(6) Uani 1 1 d . . .
C11 C -0.2124(7) 0.2564(2) 0.78626(13) 0.0281(7) Uani 1 1 d . . .
C12 C -0.3252(7) 0.3351(2) 0.75650(13) 0.0290(7) Uani 1 1 d . . .
C13 C -0.2425(7) 0.4219(2) 0.77798(12) 0.0249(6) Uani 1 1 d . . .
H1 H 0.406(6) 0.9632(18) 0.8398(12) 0.024(7) Uiso 1 1 d . . .
H2 H 0.687(8) 1.025(2) 0.9220(13) 0.045(9) Uiso 1 1 d . . .
H3 H 0.852(7) 0.9231(19) 1.0011(13) 0.036(8) Uiso 1 1 d . . .
H4 H 0.682(7) 0.765(2) 0.9937(14) 0.044(9) Uiso 1 1 d . . .
H9 H 0.200(7) 0.3573(18) 0.8952(13) 0.027(8) Uiso 1 1 d . . .
H11 H -0.260(7) 0.193(2) 0.7720(12) 0.035(8) Uiso 1 1 d . . .
H12 H -0.457(8) 0.3250(19) 0.7204(14) 0.040(9) Uiso 1 1 d . . .
H13 H -0.309(6) 0.4761(17) 0.7572(11) 0.019(7) Uiso 1 1 d . . .
H2N H 0.279(8) 0.681(2) 0.8651(15) 0.046(10) Uiso 1 1 d . . .
H3N H 0.071(7) 0.4986(19) 0.9314(13) 0.029(8) Uiso 1 1 d . . .

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S1 0.0312(4) 0.0258(4) 0.0175(4) -0.0003(3) -0.0023(3) -0.0057(3)
O1 0.0673(16) 0.0264(11) 0.0188(11) 0.0046(9) -0.0088(10) -0.0098(10)
N1 0.0371(14) 0.0231(13) 0.0217(13) 0.0028(10) -0.0014(10) -0.0015(10)
N2 0.0404(15) 0.0207(13) 0.0171(14) 0.0019(10) -0.0035(10) -0.0056(10)
N3 0.0372(14) 0.0187(12) 0.0168(12) 0.0016(10) -0.0024(10) -0.0044(10)
C1 0.0392(18) 0.0248(16) 0.0254(17) 0.0052(13) 0.0036(13) -0.0005(13)
C2 0.0317(16) 0.0203(15) 0.0331(17) -0.0015(13) 0.0008(13) -0.0058(13)
C3 0.0296(16) 0.0306(16) 0.0260(16) -0.0020(13) -0.0017(12) -0.0079(13)
C4 0.0313(16) 0.0246(15) 0.0246(16) 0.0008(12) -0.0037(12) -0.0035(12)
C5 0.0250(14) 0.0228(15) 0.0207(15) -0.0008(11) 0.0011(11) -0.0009(11)
C6 0.0220(14) 0.0201(14) 0.0237(15) -0.0012(11) -0.0025(11) 0.0006(11)
C7 0.0299(15) 0.0251(15) 0.0182(15) 0.0015(12) -0.0042(11) -0.0006(12)
C8 0.0235(14) 0.0249(15) 0.0174(14) -0.0021(11) 0.0019(10) -0.0031(11)
C9 0.0273(15) 0.0252(15) 0.0151(14) 0.0003(11) -0.0019(11) -0.0025(11)
C10 0.0293(15) 0.0226(15) 0.0238(15) 0.0033(12) 0.0042(11) -0.0021(12)

C11 0.0339(17) 0.0260(16) 0.0244(16) -0.0057(12) 0.0022(12) -0.0079(13)
C12 0.0291(16) 0.0360(17) 0.0215(16) -0.0047(13) -0.0029(12) -0.0074(13)
C13 0.0291(15) 0.0277(16) 0.0174(14) 0.0026(12) -0.0049(11) -0.0019(12)

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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S1 C6 1.662(3) . ?
O1 C7 1.218(3) . ?
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N1 C5 1.335(3) . ?
N2 C6 1.339(3) . ?
N2 C5 1.412(3) . ?
N2 H2N 0.82(3) . ?
N3 C7 1.389(3) . ?
N3 C6 1.396(3) . ?
N3 H3N 0.84(3) . ?
C1 C2 1.382(4) . ?
C1 H1 0.93(3) . ?
C2 C3 1.380(4) . ?
C2 H2 0.94(3) . ?
C3 C4 1.385(4) . ?
C3 H3 0.97(3) . ?
C4 C5 1.386(4) . ?
C4 H4 0.95(3) . ?
C7 C8 1.488(4) . ?
C8 C9 1.392(4) . ?
C8 C13 1.397(3) . ?
C9 C10 1.375(4) . ?
C9 H9 0.92(3) . ?
C10 C11 1.388(4) . ?
C11 C12 1.382(4) . ?
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C13 H13 0.94(3) . ?

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C1 N1 C5 117.1(2) . . ?
C6 N2 C5 130.7(2) . . ?
C6 N2 H2N 116(2) . . ?
C5 N2 H2N 113(2) . . ?
C7 N3 C6 128.1(2) . . ?
C7 N3 H3N 117(2) . . ?
C6 N3 H3N 115(2) . . ?
N1 C1 C2 124.0(3) . . ?
N1 C1 H1 115.8(17) . . ?
C2 C1 H1 120.2(17) . . ?
C3 C2 C1 117.5(3) . . ?
C3 C2 H2 123.9(19) . . ?
C1 C2 H2 118.6(19) . . ?
C2 C3 C4 120.3(3) . . ?
C2 C3 H3 119.9(17) . . ?
C4 C3 H3 119.8(17) . . ?
C3 C4 C5 117.1(3) . . ?
C3 C4 H4 122.2(19) . . ?
C5 C4 H4 120.7(19) . . ?
N1 C5 C4 124.0(3) . . ?
N1 C5 N2 111.1(2) . . ?
C4 C5 N2 124.9(2) . . ?
N2 C6 N3 114.5(2) . . ?
N2 C6 S1 127.0(2) . . ?
N3 C6 S1 118.5(2) . . ?
O1 C7 N3 122.2(2) . . ?
O1 C7 C8 121.6(2) . . ?
N3 C7 C8 116.2(2) . . ?
C9 C8 C13 119.5(2) . . ?
C9 C8 C7 123.0(2) . . ?
C13 C8 C7 117.2(2) . . ?
C10 C9 C8 119.0(3) . . ?
C10 C9 H9 119.8(17) . . ?
C8 C9 H9 121.1(17) . . ?
C9 C10 C11 121.9(3) . . ?
C9 C10 Cl1 119.1(2) . . ?
C11 C10 Cl1 119.0(2) . . ?
C12 C11 C10 118.6(3) . . ?
C12 C11 H11 123.3(17) . . ?
C10 C11 H11 118.1(17) . . ?
C13 C12 C11 120.6(3) . . ?
C13 C12 H12 123.3(17) . . ?
C11 C12 H12 116.1(18) . . ?
C12 C13 C8 120.3(3) . . ?
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C8 C13 H13 118.3(16) . . ?

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N1 C1 C2 C3 1.7(4) . . . . ?
C1 C2 C3 C4 -1.3(4) . . . . ?
C2 C3 C4 C5 -0.4(4) . . . . ?
C1 N1 C5 C4 -1.6(4) . . . . ?
C1 N1 C5 N2 -179.4(2) . . . . ?
C3 C4 C5 N1 1.9(4) . . . . ?
C3 C4 C5 N2 179.4(3) . . . . ?
C6 N2 C5 N1 -154.0(3) . . . . ?
C6 N2 C5 C4 28.3(5) . . . . ?
C5 N2 C6 N3 176.2(3) . . . . ?
C5 N2 C6 S1 -3.6(4) . . . . ?
C7 N3 C6 N2 -6.2(4) . . . . ?
C7 N3 C6 S1 173.6(2) . . . . ?
C6 N3 C7 O1 -3.6(5) . . . . ?
C6 N3 C7 C8 175.5(2) . . . . ?
O1 C7 C8 C9 150.2(3) . . . . ?
N3 C7 C8 C9 -29.0(4) . . . . ?
O1 C7 C8 C13 -24.5(4) . . . . ?
N3 C7 C8 C13 156.4(2) . . . . ?
C13 C8 C9 C10 0.3(4) . . . . ?
C7 C8 C9 C10 -174.2(2) . . . . ?
C8 C9 C10 C11 -0.5(4) . . . . ?
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C9 C10 C11 C12 0.0(4) . . . . ?
Cl1 C10 C11 C12 -178.5(2) . . . . ?
C10 C11 C12 C13 0.7(4) . . . . ?
C11 C12 C13 C8 -0.9(4) . . . . ?
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C7 C8 C13 C12 175.2(3) . . . . ?

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N3 H3N S1  0.84(3) 2.63(3) 3.451(3) 164(2) 3_567
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'x, -y, z-1/2'
'-x+1/2, -y+1/2, -z'
'x+1/2, -y+1/2, z-1/2'

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_cell_length_b                 3.8548(7)
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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Cl1 Cl -0.194918(18) 1.17748(14) 0.04565(2) 0.03223(17) Uani 1 1 d . . .
N1 N 0.16128(6) 0.3754(4) 0.09590(7) 0.0257(4) Uani 1 1 d . . .
N2 N 0.10297(6) 0.4174(5) 0.14023(7) 0.0244(4) Uani 1 1 d . . .
N3 N 0.03299(6) 0.5989(4) 0.15821(7) 0.0223(4) Uani 1 1 d . . .
O1 O 0.02970(5) 0.6779(4) 0.06595(6) 0.0352(4) Uani 1 1 d . . .
C1 C 0.20514(8) 0.2855(6) 0.09270(9) 0.0301(5) Uani 1 1 d . . .
C2 C 0.23870(8) 0.1212(6) 0.13547(10) 0.0313(5) Uani 1 1 d . . .
C3 C 0.22566(8) 0.0385(6) 0.18339(9) 0.0298(5) Uani 1 1 d . . .
C4 C 0.18058(7) 0.1272(5) 0.18820(9) 0.0264(5) Uani 1 1 d . . .
C5 C 0.15012(7) 0.3003(5) 0.14357(8) 0.0224(4) Uani 1 1 d . . .
C6 C 0.07925(7) 0.4616(5) 0.17917(8) 0.0205(4) Uani 1 1 d . . .
C7 C 0.00981(7) 0.6954(5) 0.10346(8) 0.0232(4) Uani 1 1 d . . .
C8 C -0.04070(7) 0.8190(5) 0.09233(8) 0.0206(4) Uani 1 1 d . . .
C9 C -0.06939(7) 0.7627(5) 0.12872(8) 0.0227(4) Uani 1 1 d . . .
C10 C -0.11673(7) 0.8738(5) 0.11455(9) 0.0245(4) Uani 1 1 d . . .
C11 C -0.13523(7) 1.0390(5) 0.06367(8) 0.0230(4) Uani 1 1 d . . .
C12 C -0.10791(7) 1.0983(5) 0.02655(8) 0.0250(4) Uani 1 1 d . . .
C13 C -0.06054(7) 0.9855(5) 0.04120(8) 0.0242(4) Uani 1 1 d . . .
O1S O 0.0000 -0.0586(6) 0.2500 0.0291(5) Uani 1 2 d S . .
H1 H 0.2122(8) 0.332(6) 0.0588(10) 0.030(6) Uiso 1 1 d . . .
H2 H 0.2688(8) 0.066(6) 0.1303(10) 0.037(6) Uiso 1 1 d . . .
H2N H 0.0881(9) 0.481(6) 0.1087(10) 0.036(7) Uiso 1 1 d . . .
H3 H 0.2474(8) -0.097(6) 0.2141(9) 0.030(6) Uiso 1 1 d . . .
H3N H 0.0197(8) 0.655(6) 0.1818(9) 0.024(6) Uiso 1 1 d . . .
H4 H 0.1730(7) 0.070(6) 0.2187(9) 0.022(5) Uiso 1 1 d . . .
H9 H -0.0586(8) 0.644(6) 0.1618(10) 0.031(6) Uiso 1 1 d . . .
H10 H -0.1365(8) 0.836(5) 0.1373(9) 0.027(6) Uiso 1 1 d . . .
H12 H -0.1219(8) 1.209(6) -0.0084(10) 0.031(6) Uiso 1 1 d . . .
H13 H -0.0409(8) 1.017(6) 0.0166(9) 0.029(6) Uiso 1 1 d . . .
H1S H 0.0234(9) 0.071(7) 0.2535(12) 0.055(9) Uiso 1 1 d . . .

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N1 0.0246(9) 0.0308(9) 0.0222(9) -0.0004(7) 0.0075(7) 0.0007(7)
N2 0.0197(8) 0.0348(10) 0.0182(9) 0.0031(7) 0.0045(7) 0.0038(7)
N3 0.0198(8) 0.0295(9) 0.0188(8) 0.0022(7) 0.0075(7) 0.0035(7)
O1 0.0255(8) 0.0597(11) 0.0225(8) 0.0101(7) 0.0102(6) 0.0121(7)
C1 0.0270(11) 0.0369(12) 0.0298(12) -0.0036(9) 0.0139(9) -0.0002(9)
C2 0.0245(11) 0.0343(12) 0.0369(12) -0.0060(9) 0.0116(10) 0.0041(9)
C3 0.0268(11) 0.0292(11) 0.0309(12) -0.0014(9) 0.0033(9) 0.0081(9)
C4 0.0289(11) 0.0283(11) 0.0227(11) 0.0012(9) 0.0083(9) 0.0035(8)
C5 0.0202(10) 0.0222(10) 0.0245(10) -0.0039(8) 0.0058(8) -0.0006(8)
C6 0.0207(9) 0.0189(9) 0.0219(10) -0.0017(7) 0.0058(8) -0.0010(7)
C7 0.0224(10) 0.0256(10) 0.0210(10) 0.0026(8) 0.0051(8) 0.0000(8)
C8 0.0184(9) 0.0232(10) 0.0191(10) -0.0001(7) 0.0032(8) -0.0003(7)
C9 0.0232(10) 0.0257(10) 0.0187(10) 0.0022(8) 0.0048(8) -0.0022(8)
C10 0.0215(10) 0.0308(11) 0.0231(10) -0.0026(8) 0.0092(8) -0.0035(8)
C11 0.0172(9) 0.0239(10) 0.0266(10) -0.0038(8) 0.0037(8) 0.0003(8)
C12 0.0251(10) 0.0274(11) 0.0206(10) 0.0020(8) 0.0031(8) 0.0024(8)
C13 0.0234(10) 0.0295(11) 0.0206(10) 0.0019(8) 0.0076(8) -0.0009(8)
O1S 0.0223(11) 0.0387(13) 0.0268(11) 0.000 0.0073(9) 0.000

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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 C6 1.338(2) . ?
N2 C5 1.414(2) . ?
N2 H2N 0.82(2) . ?
N3 C7 1.388(2) . ?
N3 C6 1.396(2) . ?
N3 H3N 0.81(2) . ?
O1 C7 1.220(2) . ?
C1 C2 1.378(3) . ?
C1 H1 0.93(2) . ?
C2 C3 1.377(3) . ?
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C2 H2 0.94(2) . ?
C3 C4 1.381(3) . ?
C3 H3 0.99(2) . ?
C4 C5 1.381(3) . ?
C4 H4 0.87(2) . ?
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C8 C13 1.395(3) . ?
C8 C9 1.398(3) . ?
C9 C10 1.381(3) . ?
C9 H9 0.92(2) . ?
C10 C11 1.382(3) . ?
C10 H10 0.92(2) . ?
C11 C12 1.384(3) . ?
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C7 N3 C6 128.30(17) . . ?
C7 N3 H3N 115.8(16) . . ?
C6 N3 H3N 115.2(16) . . ?
N1 C1 C2 123.5(2) . . ?
N1 C1 H1 116.6(14) . . ?
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O1 C7 N3 121.86(18) . . ?
O1 C7 C8 121.24(18) . . ?

N3 C7 C8 116.90(16) . . ?
C13 C8 C9 119.27(18) . . ?
C13 C8 C7 116.97(17) . . ?
C9 C8 C7 123.69(17) . . ?
C10 C9 C8 120.45(18) . . ?
C10 C9 H9 117.0(14) . . ?
C8 C9 H9 122.5(14) . . ?
C9 C10 C11 118.82(19) . . ?
C9 C10 H10 122.1(14) . . ?
C11 C10 H10 119.0(14) . . ?
C10 C11 C12 122.29(18) . . ?
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C12 C11 Cl1 118.86(15) . . ?
C13 C12 C11 118.35(19) . . ?
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C11 C12 H12 120.2(13) . . ?
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C2 C3 C4 C5 -0.3(3) . . . . ?
C1 N1 C5 C4 -2.2(3) . . . . ?
C1 N1 C5 N2 179.07(17) . . . . ?
C3 C4 C5 N1 2.2(3) . . . . ?
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C6 N2 C5 C4 15.5(3) . . . . ?
C5 N2 C6 N3 177.39(19) . . . . ?
C5 N2 C6 S1 -3.0(3) . . . . ?
C7 N3 C6 N2 -0.8(3) . . . . ?
C7 N3 C6 S1 179.50(16) . . . . ?
C6 N3 C7 O1 -2.4(3) . . . . ?
C6 N3 C7 C8 177.07(18) . . . . ?
O1 C7 C8 C13 -14.0(3) . . . . ?
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N3 H3N O1S  0.81(2) 2.22(2) 3.001(2) 162(2) 1_565
O1S H1S S1  0.83(2) 2.50(2) 3.3063(14) 166(3) .

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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O2 O 0.8699(3) 0.30339(9) 0.32621(5) 0.0403(4) Uani 1 1 d . . .
N1 N 0.6485(4) 0.45463(10) 0.10165(6) 0.0376(4) Uani 1 1 d . . .
N2 N 0.4490(4) 0.40487(10) 0.17387(6) 0.0308(4) Uani 1 1 d . . .
N3 N 0.3161(4) 0.39644(9) 0.25688(6) 0.0281(4) Uani 1 1 d . . .
N4 N 0.0327(5) 0.38152(12) 0.47643(6) 0.0505(5) Uani 1 1 d . . .
N5 N 0.5527(4) 0.19253(10) 0.35094(6) 0.0348(4) Uani 1 1 d . . .
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H2 H 0.684(5) 0.3769(13) -0.0104(9) 0.057(7) Uiso 1 1 d . . .
H2N H 0.526(5) 0.4529(14) 0.1831(7) 0.045(6) Uiso 1 1 d . . .
H3 H 0.424(5) 0.2616(13) 0.0306(8) 0.042(6) Uiso 1 1 d . . .
H3N H 0.208(5) 0.3675(12) 0.2788(7) 0.037(6) Uiso 1 1 d . . .
H4 H 0.310(5) 0.2737(12) 0.1138(7) 0.038(6) Uiso 1 1 d . . .
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H12 H 0.700(5) 0.6504(14) 0.3927(8) 0.049(6) Uiso 1 1 d . . .
H13 H 0.714(5) 0.6032(12) 0.3108(7) 0.040(6) Uiso 1 1 d . . .
H15 H 0.695(5) 0.2167(12) 0.2837(8) 0.044(6) Uiso 1 1 d . . .
H16A H 0.664(7) 0.1698(18) 0.4205(10) 0.083(9) Uiso 1 1 d . . .
H16B H 0.337(7) 0.2277(16) 0.4136(10) 0.071(8) Uiso 1 1 d . . .
H16C H 0.692(6) 0.2662(16) 0.4054(9) 0.069(8) Uiso 1 1 d . . .
H17A H 0.161(6) 0.1170(13) 0.3503(8) 0.057(7) Uiso 1 1 d . . .
H17B H 0.497(5) 0.0641(14) 0.3533(7) 0.047(6) Uiso 1 1 d . . .
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C7 0.0337(11) 0.0238(9) 0.0283(10) 0.0008(7) 0.0017(8) 0.0038(8)
C8 0.0294(10) 0.0243(9) 0.0276(10) 0.0008(7) -0.0007(8) 0.0044(8)
C9 0.0344(11) 0.0274(10) 0.0275(10) -0.0013(8) -0.0015(8) 0.0010(9)
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C13 0.0379(12) 0.0270(10) 0.0334(11) 0.0017(8) 0.0015(9) 0.0036(9)
C14 0.0456(13) 0.0401(12) 0.0246(10) -0.0048(9) -0.0011(9) 0.0013(10)
C15 0.0333(11) 0.0310(11) 0.0351(12) 0.0032(9) 0.0001(9) 0.0013(9)
C16 0.0514(16) 0.0617(17) 0.0434(14) 0.0073(12) 0.0114(12) -0.0010(14)
C17 0.0381(14) 0.0313(12) 0.0660(17) 0.0038(11) 0.0105(12) -0.0032(10)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C1 1.332(2) . ?
N1 C5 1.335(2) . ?
N2 C6 1.347(2) . ?
N2 C5 1.400(2) . ?
N2 H2N 0.86(2) . ?
N3 C7 1.371(2) . ?
N3 C6 1.399(2) . ?
N3 H3N 0.865(19) . ?
N4 C14 1.138(2) . ?
N5 C15 1.329(2) . ?
N5 C16 1.445(3) . ?
N5 C17 1.450(3) . ?
C1 C2 1.371(3) . ?
C1 H1 0.94(2) . ?
C2 C3 1.366(3) . ?
C2 H2 0.98(2) . ?
C3 C4 1.378(3) . ?
C3 H3 0.95(2) . ?
C4 C5 1.384(3) . ?
C4 H4 0.89(2) . ?
C7 C8 1.496(2) . ?
C8 C9 1.385(2) . ?
C8 C13 1.389(3) . ?
C9 C10 1.395(2) . ?
C9 H9 0.934(19) . ?
C10 C11 1.386(3) . ?
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C11 H11 0.951(18) . ?
C12 C13 1.381(3) . ?
C12 H12 0.91(2) . ?
C13 H13 0.97(2) . ?
C15 H15 0.97(2) . ?
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C16 H16A 0.97(3) . ?
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C7 N3 C6 128.28(16) . . ?
C7 N3 H3N 119.3(13) . . ?
C6 N3 H3N 112.3(13) . . ?
C15 N5 C16 120.83(19) . . ?
C15 N5 C17 121.43(19) . . ?
C16 N5 C17 117.69(19) . . ?
N1 C1 C2 124.1(2) . . ?
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C2 C3 H3 122.0(13) . . ?
C4 C3 H3 118.2(13) . . ?
C3 C4 C5 118.1(2) . . ?
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C4 C5 N2 126.43(17) . . ?
N2 C6 N3 114.20(16) . . ?
N2 C6 S1 127.46(14) . . ?
N3 C6 S1 118.34(13) . . ?
O1 C7 N3 122.45(17) . . ?
O1 C7 C8 119.38(16) . . ?
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C8 C13 H13 117.6(11) . . ?
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N5 C17 H17B 109.7(12) . . ?
H17A C17 H17B 107.3(18) . . ?
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C1 C2 C3 C4 0.1(3) . . . . ?
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C1 N1 C5 C4 0.1(3) . . . . ?
C1 N1 C5 N2 -179.96(18) . . . . ?
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C6 N2 C5 C4 -0.5(3) . . . . ?
C5 N2 C6 N3 177.82(17) . . . . ?
C5 N2 C6 S1 -2.7(3) . . . . ?
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N3 C7 C8 C13 -173.91(17) . . . . ?
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C8 C9 C10 C11 -0.5(3) . . . . ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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O1 O 0.22722(5) -0.0750(5) 0.06231(7) 0.0324(4) Uani 1 1 d . . .
N1 N 0.10964(5) -0.2028(5) 0.04709(8) 0.0283(4) Uani 1 1 d . . .
N2 N 0.16711(5) 0.0303(5) 0.11161(8) 0.0232(4) Uani 1 1 d . . .
N3 N 0.23560(5) 0.1985(5) 0.15158(8) 0.0228(4) Uani 1 1 d . . .
N4 N 0.45170(6) 0.4029(7) 0.10654(10) 0.0470(6) Uani 1 1 d . . .
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C1 C 0.06889(7) -0.2835(7) 0.02904(10) 0.0325(5) Uani 1 1 d . . .
C2 C 0.04164(7) -0.2071(6) 0.06177(10) 0.0311(5) Uani 1 1 d . . .
C3 C 0.05716(7) -0.0390(7) 0.11605(11) 0.0323(5) Uani 1 1 d . . .
C4 C 0.09928(7) 0.0453(6) 0.13651(10) 0.0290(5) Uani 1 1 d . . .
C5 C 0.12394(6) -0.0402(5) 0.09976(9) 0.0225(4) Uani 1 1 d . . .
C6 C 0.19501(6) 0.1794(5) 0.15800(9) 0.0205(4) Uani 1 1 d . . .
C7 C 0.24981(6) 0.0819(5) 0.10535(9) 0.0213(4) Uani 1 1 d . . .
C8 C 0.29436(6) 0.1578(5) 0.10875(9) 0.0199(4) Uani 1 1 d . . .
C9 C 0.30727(7) 0.0621(6) 0.05905(9) 0.0245(4) Uani 1 1 d . . .
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C12 C 0.36317(7) 0.3783(6) 0.15721(10) 0.0251(4) Uani 1 1 d . . .
C13 C 0.32242(6) 0.3162(5) 0.15774(9) 0.0219(4) Uani 1 1 d . . .
C14 C 0.41811(7) 0.3492(7) 0.10685(10) 0.0326(5) Uani 1 1 d . . .
Cl1S Cl 0.45627(3) 0.9717(2) 0.25202(4) 0.0594(2) Uani 1 1 d D . .
C1S C 0.5027(3) 0.785(2) 0.2712(5) 0.112(5) Uani 0.50 1 d PD . 1
H2N H 0.1772(8) -0.038(7) 0.0840(12) 0.034(7) Uiso 1 1 d . . .
H3N H 0.2533(8) 0.277(8) 0.1825(13) 0.039(8) Uiso 1 1 d . . .
H1 H 0.0576(8) -0.395(7) -0.0102(11) 0.029(6) Uiso 1 1 d . . .
H2 H 0.0133(8) -0.261(7) 0.0447(11) 0.032(6) Uiso 1 1 d . . .
H3 H 0.0383(8) 0.010(7) 0.1383(12) 0.038(7) Uiso 1 1 d . . .
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H10 H 0.3551(8) 0.059(7) 0.0249(12) 0.031(6) Uiso 1 1 d . . .
H12 H 0.3813(8) 0.493(7) 0.1887(12) 0.032(7) Uiso 1 1 d . . .
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N1 0.0233(9) 0.0378(11) 0.0245(9) -0.0049(8) 0.0082(7) -0.0052(8)
N2 0.0196(8) 0.0336(10) 0.0182(8) -0.0029(7) 0.0080(7) -0.0019(7)
N3 0.0188(8) 0.0319(10) 0.0181(8) -0.0035(7) 0.0060(7) -0.0020(7)
N4 0.0255(10) 0.0736(17) 0.0456(13) -0.0056(12) 0.0161(9) -0.0097(11)
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C2 0.0199(10) 0.0390(13) 0.0343(12) -0.0004(10) 0.0075(9) -0.0055(9)
C3 0.0240(11) 0.0415(14) 0.0358(12) -0.0028(10) 0.0155(9) -0.0007(10)
C4 0.0232(10) 0.0390(13) 0.0268(11) -0.0051(10) 0.0102(9) -0.0021(9)
C5 0.0196(9) 0.0261(11) 0.0224(10) 0.0016(8) 0.0069(8) -0.0012(8)
C6 0.0203(9) 0.0222(10) 0.0198(9) 0.0030(8) 0.0070(7) 0.0010(8)
C7 0.0203(9) 0.0251(10) 0.0187(9) 0.0003(8) 0.0061(7) 0.0006(8)
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C9 0.0239(10) 0.0303(11) 0.0197(10) -0.0029(8) 0.0070(8) -0.0017(9)
C10 0.0275(11) 0.0337(12) 0.0221(10) -0.0020(9) 0.0118(8) 0.0008(9)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

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N1 C1 1.341(3) . ?
N2 C6 1.335(3) . ?
N2 C5 1.415(3) . ?
N2 H2N 0.85(3) . ?
N3 C7 1.371(3) . ?
N3 C6 1.409(2) . ?
N3 H3N 0.84(3) . ?
N4 C14 1.144(3) . ?
C1 C2 1.377(3) . ?
C1 H1 0.98(3) . ?
C2 C3 1.381(3) . ?
C2 H2 0.94(3) . ?
C3 C4 1.388(3) . ?
C3 H3 0.94(3) . ?
C4 C5 1.388(3) . ?
C4 H4 0.90(3) . ?
C7 C8 1.497(3) . ?
C8 C13 1.390(3) . ?
C8 C9 1.395(3) . ?
C9 C10 1.381(3) . ?
C9 H9 0.93(3) . ?
C10 C11 1.394(3) . ?
C10 H10 0.91(3) . ?
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C11 C14 1.446(3) . ?
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C12 H12 0.92(3) . ?
C13 H13 0.89(3) . ?
Cl1S C1S 1.654(9) . ?

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C1S C1S 0.95(2) 2_655 ?
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C6 N2 C5 132.43(18) . . ?
C6 N2 H2N 114.1(18) . . ?
C5 N2 H2N 113.5(18) . . ?
C7 N3 C6 128.92(18) . . ?
C7 N3 H3N 118.0(18) . . ?
C6 N3 H3N 112.8(18) . . ?
N1 C1 C2 123.5(2) . . ?
N1 C1 H1 118.4(15) . . ?
C2 C1 H1 118.1(15) . . ?
C1 C2 C3 118.2(2) . . ?
C1 C2 H2 117.8(15) . . ?
C3 C2 H2 123.9(16) . . ?
C2 C3 C4 120.0(2) . . ?
C2 C3 H3 117.5(16) . . ?
C4 C3 H3 122.5(16) . . ?
C5 C4 C3 117.2(2) . . ?
C5 C4 H4 121.5(16) . . ?
C3 C4 H4 121.1(16) . . ?
N1 C5 C4 123.92(19) . . ?
N1 C5 N2 110.07(17) . . ?
C4 C5 N2 126.01(19) . . ?
N2 C6 N3 113.93(17) . . ?
N2 C6 S1 128.92(15) . . ?
N3 C6 S1 117.15(15) . . ?
O1 C7 N3 122.12(18) . . ?
O1 C7 C8 120.59(18) . . ?
N3 C7 C8 117.28(17) . . ?
C13 C8 C9 119.87(18) . . ?
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C9 C8 C7 116.44(18) . . ?
C10 C9 C8 120.60(19) . . ?
C10 C9 H9 118.6(17) . . ?
C8 C9 H9 120.7(17) . . ?
C9 C10 C11 119.11(19) . . ?
C9 C10 H10 118.4(16) . . ?
C11 C10 H10 122.5(16) . . ?
C12 C11 C10 120.84(19) . . ?
C12 C11 C14 119.31(19) . . ?
C10 C11 C14 119.85(19) . . ?
C13 C12 C11 119.53(19) . . ?
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C13 C12 H12 120.0(16) . . ?
C11 C12 H12 120.4(16) . . ?
C12 C13 C8 120.05(19) . . ?
C12 C13 H13 116.7(16) . . ?
C8 C13 H13 123.3(16) . . ?
N4 C14 C11 179.8(3) . . ?
C1S Cl1S C1S 31.9(7) . 2_655 ?
C1S C1S Cl1S 80.7(10) 2_655 . ?
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C1 C2 C3 C4 -0.6(4) . . . . ?
C2 C3 C4 C5 1.3(4) . . . . ?
C1 N1 C5 C4 0.7(3) . . . . ?
C1 N1 C5 N2 -179.1(2) . . . . ?
C3 C4 C5 N1 -1.3(4) . . . . ?
C3 C4 C5 N2 178.4(2) . . . . ?
C6 N2 C5 N1 -178.6(2) . . . . ?
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C5 N2 C6 N3 180.0(2) . . . . ?
C5 N2 C6 S1 -1.2(4) . . . . ?
C7 N3 C6 N2 -1.0(3) . . . . ?
C7 N3 C6 S1 179.98(18) . . . . ?
C6 N3 C7 O1 -3.0(4) . . . . ?
C6 N3 C7 C8 176.21(19) . . . . ?
O1 C7 C8 C13 -176.0(2) . . . . ?
N3 C7 C8 C13 4.8(3) . . . . ?
O1 C7 C8 C9 4.3(3) . . . . ?
N3 C7 C8 C9 -174.92(19) . . . . ?
C13 C8 C9 C10 0.1(3) . . . . ?
C7 C8 C9 C10 179.8(2) . . . . ?
C8 C9 C10 C11 -0.2(3) . . . . ?
C9 C10 C11 C12 0.3(3) . . . . ?
C9 C10 C11 C14 -179.7(2) . . . . ?
C10 C11 C12 C13 -0.3(3) . . . . ?
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C11 C12 C13 C8 0.2(3) . . . . ?
C9 C8 C13 C12 -0.1(3) . . . . ?
C7 C8 C13 C12 -179.77(19) . . . . ?
C12 C11 C14 N4 -40(100) . . . . ?

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N2 H2N O1  0.85(3) 1.89(3) 2.617(2) 143(2) .

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 '-x, -y, -z'

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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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O1 O 0.48195(12) 0.38818(8) 0.38294(8) 0.0336(2) Uani 1 1 d . . .
N1 N 0.28615(14) 0.41826(10) 0.12405(10) 0.0314(3) Uani 1 1 d . . .
N2 N 0.37501(13) 0.28479(10) 0.25718(9) 0.0246(2) Uani 1 1 d . . .
N3 N 0.53095(13) 0.19782(10) 0.38288(9) 0.0241(2) Uani 1 1 d . . .
N4 N 0.98326(19) 0.26769(14) 0.81492(13) 0.0504(4) Uani 1 1 d . . .
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C3 C 0.15153(16) 0.27442(13) 0.04060(12) 0.0323(3) Uani 1 1 d . . .
C4 C 0.22648(16) 0.23452(12) 0.13044(12) 0.0287(3) Uani 1 1 d . . .
C5 C 0.29382(14) 0.30983(11) 0.16723(10) 0.0236(3) Uani 1 1 d . . .
C6 C 0.45167(14) 0.18795(11) 0.30022(10) 0.0228(3) Uani 1 1 d . . .
C7 C 0.54400(15) 0.29517(11) 0.41966(10) 0.0235(3) Uani 1 1 d . . .
C8 C 0.63931(14) 0.28211(11) 0.50782(10) 0.0221(3) Uani 1 1 d . . .
C9 C 0.67463(15) 0.18148(11) 0.57705(11) 0.0243(3) Uani 1 1 d . . .
C10 C 0.76377(16) 0.17667(12) 0.65682(11) 0.0271(3) Uani 1 1 d . . .
C11 C 0.81697(15) 0.27293(12) 0.66694(11) 0.0266(3) Uani 1 1 d . . .
C12 C 0.78106(16) 0.37456(12) 0.59819(11) 0.0280(3) Uani 1 1 d . . .
C13 C 0.69136(15) 0.37857(11) 0.51956(11) 0.0256(3) Uani 1 1 d . . .
C14 C 0.90958(18) 0.26943(13) 0.74964(13) 0.0346(3) Uani 1 1 d . . .
S1' S 0.81923(5) 0.96531(3) 0.43669(3) 0.03656(12) Uani 1 1 d . . .
O1' O 0.72968(12) 0.62916(8) 0.38013(8) 0.0319(2) Uani 1 1 d . . .
N1' N 0.94889(13) 0.60776(10) 0.62205(9) 0.0270(2) Uani 1 1 d . . .
N2' N 0.84390(13) 0.73998(10) 0.49547(9) 0.0256(2) Uani 1 1 d . . .
N3' N 0.70833(13) 0.82082(10) 0.35542(9) 0.0240(2) Uani 1 1 d . . .
N4' N 0.30785(18) 0.72593(14) -0.09640(12) 0.0491(4) Uani 1 1 d . . .
C1' C 1.03464(16) 0.57170(13) 0.70122(11) 0.0296(3) Uani 1 1 d . . .
C2' C 1.10783(16) 0.64183(13) 0.74073(11) 0.0301(3) Uani 1 1 d . . .
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C10' C 0.50822(17) 0.82392(13) 0.06959(12) 0.0299(3) Uani 1 1 d . . .
C11' C 0.44887(15) 0.72928(12) 0.06422(11) 0.0281(3) Uani 1 1 d . . .
C12' C 0.46687(16) 0.63411(13) 0.14293(12) 0.0302(3) Uani 1 1 d . . .
C13' C 0.54454(16) 0.63447(12) 0.22760(11) 0.0276(3) Uani 1 1 d . . .
C14' C 0.36947(18) 0.72810(14) -0.02548(13) 0.0352(3) Uani 1 1 d . . .
O1S O 0.1993(4) 0.9876(3) 0.0488(5) 0.1105(17) Uani 0.50 1 d PD . .
C1S C 0.0859(5) 0.9920(3) 0.0130(6) 0.0737(15) Uani 0.50 1 d PD . .
C2S C -0.0644(4) 1.0178(3) 0.0921(3) 0.1018(10) Uani 1 1 d D . .
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H9 H 0.6376(18) 0.1157(15) 0.5717(14) 0.032(4) Uiso 1 1 d . . .
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H13 H 0.6668(19) 0.4444(16) 0.4734(15) 0.036(5) Uiso 1 1 d . . .
H2N' H 0.817(2) 0.6759(17) 0.4787(15) 0.045(5) Uiso 1 1 d . . .
H3N' H 0.668(2) 0.8816(17) 0.3240(15) 0.037(5) Uiso 1 1 d . . .
H1' H 1.0435(19) 0.4865(15) 0.7290(14) 0.036(5) Uiso 1 1 d . . .
H2' H 1.171(2) 0.6120(16) 0.7977(15) 0.043(5) Uiso 1 1 d . . .
H3' H 1.140(2) 0.8044(16) 0.7271(15) 0.039(5) Uiso 1 1 d . . .
H4' H 0.9873(19) 0.8691(15) 0.5836(14) 0.032(4) Uiso 1 1 d . . .
H9' H 0.6283(18) 0.8878(15) 0.1554(13) 0.030(4) Uiso 1 1 d . . .
H10' H 0.4983(18) 0.8840(15) 0.0132(14) 0.033(4) Uiso 1 1 d . . .
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N2 0.0302(6) 0.0199(5) 0.0252(6) -0.0044(4) -0.0108(5) -0.0016(4)
N3 0.0293(6) 0.0185(5) 0.0255(6) -0.0019(4) -0.0111(5) -0.0014(5)
N4 0.0581(10) 0.0514(9) 0.0497(9) -0.0048(7) -0.0306(7) -0.0134(7)
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C2 0.0340(8) 0.0406(8) 0.0271(7) -0.0006(6) -0.0132(6) -0.0023(6)
C3 0.0318(7) 0.0349(8) 0.0334(8) -0.0100(6) -0.0125(6) -0.0026(6)
C4 0.0305(7) 0.0261(7) 0.0304(7) -0.0042(6) -0.0098(6) -0.0024(6)
C5 0.0245(6) 0.0239(6) 0.0216(6) -0.0029(5) -0.0067(5) 0.0004(5)
C6 0.0252(6) 0.0218(6) 0.0220(6) -0.0017(5) -0.0054(5) -0.0048(5)
C7 0.0277(7) 0.0211(6) 0.0219(6) -0.0034(5) -0.0053(5) -0.0030(5)

C8 0.0243(6) 0.0217(6) 0.0206(6) -0.0041(5) -0.0047(5) -0.0022(5)
C9 0.0288(7) 0.0203(6) 0.0251(6) -0.0038(5) -0.0059(5) -0.0052(5)
C10 0.0316(7) 0.0236(7) 0.0258(7) -0.0005(5) -0.0091(5) -0.0027(5)
C11 0.0265(7) 0.0295(7) 0.0255(7) -0.0060(5) -0.0067(5) -0.0043(5)
C12 0.0323(7) 0.0251(7) 0.0293(7) -0.0058(5) -0.0057(6) -0.0081(6)
C13 0.0320(7) 0.0198(6) 0.0251(6) -0.0023(5) -0.0058(5) -0.0041(5)
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O1' 0.0426(6) 0.0213(5) 0.0350(6) -0.0011(4) -0.0182(5) -0.0058(4)
N1' 0.0304(6) 0.0246(6) 0.0271(6) -0.0024(5) -0.0094(5) -0.0040(5)
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N4' 0.0582(9) 0.0582(10) 0.0392(8) -0.0014(7) -0.0238(7) -0.0226(8)
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C13' 0.0333(7) 0.0245(7) 0.0263(7) -0.0021(5) -0.0066(5) -0.0078(6)
C14' 0.0391(8) 0.0383(8) 0.0317(8) -0.0030(6) -0.0101(6) -0.0127(7)
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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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C1 H1 1.02(2) . ?
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C8 C9 1.3937(18) . ?
C8 C13 1.3963(19) . ?
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C8' C13' H13' 120.2(11) . . ?
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C2S C1S C2S 113.9(4) 2_575 . ?
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;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.

 In the crystal structure there are chloroform, CHCl3, solvent molecule
 disordered around an inversion center. It was treated by SQUEEZE
 [Van der Sluis,P. & Spek, A.L. (1990) Acta Cryst., Sect.A,A46,194-201.].
 Corrections of the X-ray data by SQUEEZE  (63 electron/cell) was close to
 the required values (58 electron/cell) for one CHCl3 molecule per
 the unit cell.

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N3 N 0.5315(2) 0.69851(16) 0.38399(15) 0.0248(4) Uani 1 1 d . . .
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 are estimated using the full covariance matrix.  The cell esds are taken
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N2 C5 1.417(3) . ?
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N3 C7 1.382(3) . ?
N3 C6 1.403(3) . ?
N3 H3N 0.82(2) . ?
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C9 C10 1.385(3) . ?
C9 H9 0.93(2) . ?
C10 C11 1.390(3) . ?
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C11 C12 1.392(3) . ?
C11 C14 1.450(3) . ?
C12 C13 1.379(3) . ?
C12 H12 1.00(3) . ?
C13 H13 0.94(3) . ?
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O1' C7' 1.222(2) . ?
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N1' C5' 1.342(3) . ?
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O1 C7 C8 120.52(19) . . ?
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N2' C6' N3' 114.27(19) . . ?
N2' C6' S1' 127.75(17) . . ?
N3' C6' S1' 117.98(16) . . ?
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C9' C8' C13' 119.8(2) . . ?
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C9' C10' C11' 119.8(2) . . ?
C9' C10' H10' 123.2(14) . . ?
C11' C10' H10' 117.0(14) . . ?
C10' C11' C12' 120.5(2) . . ?
C10' C11' C14' 120.3(2) . . ?
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C13' C12' C11' 119.1(2) . . ?
C13' C12' H12' 120.4(15) . . ?
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C12' C13' C8' 120.7(2) . . ?
C12' C13' H13' 117.7(18) . . ?
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N4' C14' C11' 179.5(3) . . ?

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N1 C1 C2 C3 1.5(4) . . . . ?
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C2 C3 C4 C5 -0.4(4) . . . . ?
C1 N1 C5 C4 -2.4(4) . . . . ?
C1 N1 C5 N2 179.7(2) . . . . ?
C3 C4 C5 N1 2.4(4) . . . . ?
C3 C4 C5 N2 -179.9(2) . . . . ?
C6 N2 C5 N1 -151.9(2) . . . . ?
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C7' N3' C6' N2' 7.6(3) . . . . ?
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O1' C7' C8' C13' -18.0(3) . . . . ?
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C13' C8' C9' C10' -1.5(3) . . . . ?

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N2' H2N' O1'  0.87(3) 1.87(2) 2.612(2) 142(2) .
N3 H3N S1'  0.82(2) 2.79(3) 3.594(2) 169(2) 2_666
N3' H3N' S1  0.79(3) 2.78(3) 3.530(2) 160(3) 2_666

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'H'  'H'   0.0000   0.0000
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'-x, y+1/2, -z+1/2'
'-x, -y, -z'
'x, -y-1/2, z-1/2'

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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Cl2 Cl 0.03954(6) -0.31632(18) 0.29827(2) 0.02814(19) Uani 1 1 d . . .
S1 S 0.51838(5) 0.29183(17) 0.56322(2) 0.02149(18) Uani 1 1 d . . .
O1 O 0.14386(15) 0.2721(6) 0.51719(7) 0.0339(5) Uani 1 1 d . . .
N1 N 0.23292(18) 0.6343(6) 0.64152(8) 0.0284(5) Uani 1 1 d . . .
N2 N 0.31145(18) 0.4507(6) 0.58002(7) 0.0222(5) Uani 1 1 d . . .
N3 N 0.32595(19) 0.2030(6) 0.50840(8) 0.0217(5) Uani 1 1 d . . .
C1 C 0.2367(2) 0.7696(8) 0.68461(10) 0.0305(7) Uani 1 1 d . . .
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C5 C 0.3302(2) 0.5914(6) 0.62581(8) 0.0196(5) Uani 1 1 d . . .
C6 C 0.3804(2) 0.3231(6) 0.55208(9) 0.0190(5) Uani 1 1 d . . .
C7 C 0.2134(2) 0.1844(7) 0.49266(9) 0.0221(5) Uani 1 1 d . . .
C8 C 0.1769(2) 0.0547(7) 0.44407(9) 0.0206(5) Uani 1 1 d . . .
C9 C 0.2396(2) 0.0965(6) 0.40782(9) 0.0188(5) Uani 1 1 d . . .
C10 C 0.1978(2) -0.0164(6) 0.36314(9) 0.0197(5) Uani 1 1 d . . .
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C11 C 0.0928(2) -0.1713(6) 0.35409(9) 0.0211(5) Uani 1 1 d . . .
C12 C 0.0297(2) -0.2126(7) 0.38974(9) 0.0237(6) Uani 1 1 d . . .
C13 C 0.0716(2) -0.0993(7) 0.43451(9) 0.0245(6) Uani 1 1 d . . .
H1 H 0.163(3) 0.794(8) 0.6958(11) 0.046(9) Uiso 1 1 d . . .
H2 H 0.332(3) 0.958(8) 0.7393(12) 0.039(9) Uiso 1 1 d . . .
H3 H 0.505(2) 0.884(7) 0.7153(9) 0.023(7) Uiso 1 1 d . . .
H4 H 0.493(3) 0.646(8) 0.6405(10) 0.030(8) Uiso 1 1 d . . .
H9 H 0.302(2) 0.195(7) 0.4113(9) 0.013(7) Uiso 1 1 d . . .
H12 H -0.041(2) -0.325(7) 0.3814(9) 0.025(7) Uiso 1 1 d . . .
H13 H 0.029(2) -0.129(7) 0.4592(9) 0.020(7) Uiso 1 1 d . . .
H2N H 0.238(2) 0.429(7) 0.5680(10) 0.026(8) Uiso 1 1 d . . .
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Cl2 0.0321(4) 0.0333(4) 0.0166(3) -0.0042(3) -0.0040(3) -0.0031(3)
S1 0.0177(3) 0.0271(3) 0.0191(3) -0.0035(3) 0.0012(2) 0.0003(3)
O1 0.0190(10) 0.0620(14) 0.0218(10) -0.0119(10) 0.0063(8) -0.0035(9)
N1 0.0241(12) 0.0365(13) 0.0250(13) -0.0089(10) 0.0057(10) -0.0016(10)
N2 0.0161(11) 0.0341(12) 0.0163(11) -0.0040(9) 0.0022(9) -0.0012(9)
N3 0.0193(11) 0.0299(12) 0.0167(12) -0.0038(10) 0.0053(9) 0.0001(10)
C1 0.0300(16) 0.0383(16) 0.0252(15) -0.0095(12) 0.0105(12) -0.0008(13)
C2 0.0388(17) 0.0281(14) 0.0158(14) -0.0042(11) 0.0079(12) -0.0031(12)
C3 0.0285(15) 0.0298(14) 0.0173(13) -0.0028(11) 0.0008(11) -0.0053(12)
C4 0.0233(14) 0.0283(13) 0.0193(14) -0.0031(11) 0.0044(11) -0.0025(11)
C5 0.0229(13) 0.0221(12) 0.0142(12) -0.0014(10) 0.0040(10) -0.0016(10)
C6 0.0194(12) 0.0201(12) 0.0169(13) 0.0005(10) 0.0012(10) -0.0032(10)
C7 0.0191(13) 0.0283(13) 0.0188(13) 0.0000(11) 0.0028(10) -0.0032(11)
C8 0.0170(12) 0.0273(13) 0.0170(13) -0.0013(11) 0.0010(10) 0.0009(10)
C9 0.0151(13) 0.0203(12) 0.0205(13) -0.0012(10) 0.0009(10) -0.0012(10)
C10 0.0205(13) 0.0213(12) 0.0178(13) 0.0021(10) 0.0047(10) 0.0017(10)
C11 0.0241(13) 0.0214(12) 0.0153(13) -0.0003(10) -0.0045(10) -0.0002(10)
C12 0.0195(13) 0.0301(14) 0.0205(14) -0.0018(11) 0.0003(10) -0.0045(11)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
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 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C5 1.339(3) . ?
N1 C1 1.340(3) . ?
N2 C6 1.340(3) . ?
N2 C5 1.412(3) . ?
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N3 C7 1.374(3) . ?
N3 C6 1.407(3) . ?
N3 H3N 0.71(3) . ?
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C1 H1 1.00(3) . ?
C2 C3 1.384(4) . ?
C2 H2 0.85(3) . ?
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C4 C5 1.383(4) . ?
C4 H4 0.85(3) . ?
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C8 C9 1.392(3) . ?
C8 C13 1.398(4) . ?
C9 C10 1.379(4) . ?
C9 H9 0.84(3) . ?
C10 C11 1.394(4) . ?
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C7 N3 H3N 115(3) . . ?
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C5 C4 H4 121(2) . . ?
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C4 C5 N2 126.5(2) . . ?
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O1 C7 C8 120.1(2) . . ?
N3 C7 C8 117.7(2) . . ?
C9 C8 C13 119.3(2) . . ?
C9 C8 C7 123.3(2) . . ?
C13 C8 C7 117.3(2) . . ?
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C2 C3 C4 C5 1.0(4) . . . . ?

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C1 N1 C5 N2 -179.4(2) . . . . ?
C3 C4 C5 N1 -0.1(4) . . . . ?
C3 C4 C5 N2 178.6(2) . . . . ?
C6 N2 C5 N1 -170.5(3) . . . . ?
C6 N2 C5 C4 10.6(5) . . . . ?
C5 N2 C6 N3 179.2(2) . . . . ?
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C7 N3 C6 N2 -3.8(4) . . . . ?
C7 N3 C6 S1 176.0(2) . . . . ?
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Cl2 C11 C12 C13 179.7(2) . . . . ?
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N3 H3N S1 0.71(3) 2.85(3) 3.554(2) 175(3) 3_656

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_symmetry_space_group_name_H-M    P2(1)/c

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 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
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 factors based on ALL data will be even larger.
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N1 N 0.0298(5) 0.40539(9) 1.27294(11) 0.0309(4) Uani 1 1 d . . .
N2 N -0.0923(5) 0.36135(10) 1.14050(11) 0.0284(4) Uani 1 1 d . . .
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C5 C -0.1303(5) 0.35685(10) 1.22970(13) 0.0260(4) Uani 1 1 d . . .
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O1 0.0565(11) 0.0366(9) 0.0240(8) -0.0032(6) 0.0045(8) -0.0149(8)
N1 0.0380(11) 0.0305(10) 0.0243(9) -0.0003(7) 0.0025(8) 0.0036(8)
N2 0.0352(11) 0.0291(10) 0.0211(9) 0.0029(7) 0.0031(8) -0.0046(9)
N3 0.0349(11) 0.0340(10) 0.0182(9) -0.0015(7) 0.0008(8) -0.0068(8)
C1 0.0426(14) 0.0366(13) 0.0246(11) -0.0055(9) 0.0020(10) 0.0029(11)
C2 0.0399(14) 0.0441(14) 0.0205(10) -0.0002(9) 0.0052(10) 0.0078(11)
C3 0.0396(14) 0.0354(13) 0.0268(11) 0.0052(9) 0.0090(10) 0.0068(10)
C4 0.0350(13) 0.0307(12) 0.0245(10) 0.0018(9) 0.0039(9) 0.0025(10)
C5 0.0301(12) 0.0276(11) 0.0202(10) 0.0018(8) 0.0022(9) 0.0079(9)
C6 0.0274(11) 0.0304(11) 0.0220(10) 0.0030(8) 0.0032(9) 0.0032(9)
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C8 0.0268(11) 0.0262(11) 0.0209(10) 0.0002(8) 0.0000(8) 0.0012(8)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C5 1.337(3) . ?
N2 C6 1.340(3) . ?
N2 C5 1.409(3) . ?
N2 H2N 0.75(2) . ?
N3 C7 1.373(3) . ?
N3 C6 1.401(3) . ?
N3 H3N 0.81(3) . ?
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C1 H1 0.93(2) . ?
C2 C3 1.374(4) . ?
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C4 H4 1.01(3) . ?
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C8 C13 1.390(3) . ?
C8 C9 1.395(3) . ?
C9 C10 1.390(3) . ?
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C6 N3 H3N 110.6(18) . . ?
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C2 C1 H1 122.5(15) . . ?
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C2 C3 C4 120.1(2) . . ?
C2 C3 H3 121.3(14) . . ?
C4 C3 H3 118.6(14) . . ?
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C5 C4 H4 120.7(14) . . ?
C3 C4 H4 122.0(14) . . ?
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N1 C5 N2 110.66(18) . . ?
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N3 C6 S1 117.20(16) . . ?
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O1 C7 C8 121.68(19) . . ?
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C13 C8 C9 118.96(19) . . ?
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C11 C12 H12 122.2(13) . . ?
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C7 N3 C6 S1 -172.54(19) . . . . ?
C6 N3 C7 O1 -6.2(4) . . . . ?
C6 N3 C7 C8 173.9(2) . . . . ?
O1 C7 C8 C13 -9.0(3) . . . . ?
N3 C7 C8 C13 170.9(2) . . . . ?
O1 C7 C8 C9 171.4(2) . . . . ?
N3 C7 C8 C9 -8.7(3) . . . . ?
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C7 C8 C9 C10 178.2(2) . . . . ?
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C11 C12 C13 C8 0.3(3) . . . . ?
C9 C8 C13 C12 1.0(3) . . . . ?
C7 C8 C13 C12 -178.6(2) . . . . ?

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 _geom_hbond_atom_site_label_H
 _geom_hbond_atom_site_label_A
 _geom_hbond_distance_DH
 _geom_hbond_distance_HA
 _geom_hbond_distance_DA
 _geom_hbond_angle_DHA
 _geom_hbond_site_symmetry_A
N2 H2N O1  0.75(2) 2.00(2) 2.645(2) 144(2) .
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_diffrn_reflns_theta_full              27.00
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_refine_diff_density_min   -0.216
_refine_diff_density_rms    0.066

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data_41

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;
_chemical_name_common            ?
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_chemical_formula_moiety         ?
_chemical_formula_sum
 'C13 H10 Br N3 O S'
_chemical_formula_weight         336.21

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 _atom_type_scat_source
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 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
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 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Br'  'Br'  -0.2901   2.4595
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M    Pbca

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 _symmetry_equiv_pos_as_xyz
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 '-x+1/2, -y, z+1/2'
 '-x, y+1/2, -z+1/2'
 'x+1/2, -y+1/2, -z'
 '-x, -y, -z'
```

'x-1/2, y, -z-1/2'
'x, -y-1/2, z-1/2'
'-x-1/2, y-1/2, z'

_cell_length_a 14.2904(10)
_cell_length_b 9.2601(6)
_cell_length_c 20.4694(14)
_cell_angle_alpha 90.00
_cell_angle_beta 90.00
_cell_angle_gamma 90.00
_cell_volume 2708.7(3)
_cell_formula_units_Z 8
_cell_measurement_temperature 173(2)
_cell_measurement_reflns_used 5325
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_exptl_crystal_size_mid 0.26
_exptl_crystal_size_min 0.20
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_exptl_crystal_F_000 1344
_exptl_absorpt_coefficient_mu 3.184
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_exptl_special_details
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_diffrn_ambient_temperature 173(2)
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_diffrn_radiation_monochromator graphite
_diffrn_measurement_device_type 'CCD area detector'
_diffrn_measurement_method 'phi and omega scans'
_diffrn_detector_area_resol_mean ?
_diffrn_standards_number ?
_diffrn_standards_interval_count ?
_diffrn_standards_interval_time ?
_diffrn_standards_decay_% ?
_diffrn_reflns_number 28361
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_diffrn_reflns_av_sigmaI/netI 0.0133
_diffrn_reflns_limit_h_min -18

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_diffrn_reflns_theta_min         1.99
_diffrn_reflns_theta_max         27.00
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_reflns_number_gt                2667
_reflns_threshold_expression     >2sigma(I)

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_computing_cell_refinement       'Bruker SMART'
_computing_data_reduction        'Bruker SAINT'
_computing_structure_solution    'Bruker SHELXTL'
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_computing_molecular_graphics    'Bruker SHELXTL'
_computing_publication_material  'Bruker SHELXTL'

_refine_special_details
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Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
goodness of fit S are based on F^2^, conventional R-factors R are based
on F, with F set to zero for negative F^2^. The threshold expression of
F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement.  R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

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_refine_ls_weighting_scheme      calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.0394P)^2^+1.0329P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary     direct
_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   difmap
_refine_ls_hydrogen_treatment    refall
_refine_ls_extinction_method     none
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_refine_ls_restrained_S_all      1.053
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_refine_ls_shift/su_mean         0.000
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 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
Br1 Br 0.408962(14) 1.02584(2) 0.742385(9) 0.03424(8) Uani 1 1 d . . .
S1 S 0.19463(3) 0.98678(5) 0.52059(2) 0.02883(11) Uani 1 1 d . . .
O1 O 0.33111(8) 0.68339(14) 0.66816(6) 0.0331(3) Uani 1 1 d . . .
N1 N 0.05278(9) 0.62729(14) 0.57141(6) 0.0223(3) Uani 1 1 d . . .
N2 N 0.17783(9) 0.77002(15) 0.60602(7) 0.0230(3) Uani 1 1 d . . .
N3 N 0.32443(9) 0.87219(15) 0.59573(6) 0.0212(3) Uani 1 1 d . . .
C1 C -0.03956(11) 0.61123(18) 0.56060(8) 0.0249(3) Uani 1 1 d . . .
C2 C -0.10460(11) 0.7184(2) 0.57211(8) 0.0262(3) Uani 1 1 d . . .
C3 C -0.07445(11) 0.84790(19) 0.59816(9) 0.0271(3) Uani 1 1 d . . .
C4 C 0.02022(11) 0.86670(18) 0.61015(8) 0.0259(3) Uani 1 1 d . . .
C5 C 0.07993(10) 0.75462(17) 0.59470(8) 0.0214(3) Uani 1 1 d . . .
C6 C 0.23096(10) 0.86944(16) 0.57685(7) 0.0203(3) Uani 1 1 d . . .
C7 C 0.36842(11) 0.78348(16) 0.63959(8) 0.0217(3) Uani 1 1 d . . .
C8 C 0.47027(10) 0.81717(17) 0.64947(8) 0.0217(3) Uani 1 1 d . . .
C9 C 0.49941(11) 0.91488(18) 0.69671(8) 0.0254(3) Uani 1 1 d . . .
C10 C 0.59334(13) 0.9380(2) 0.70929(10) 0.0354(4) Uani 1 1 d . . .
C11 C 0.65895(12) 0.8632(3) 0.67276(11) 0.0419(5) Uani 1 1 d . . .
C12 C 0.63144(13) 0.7691(2) 0.62408(10) 0.0378(4) Uani 1 1 d . . .
C13 C 0.53724(12) 0.74595(19) 0.61219(9) 0.0282(4) Uani 1 1 d . . .
H1 H -0.0569(15) 0.521(2) 0.5459(10) 0.026(5) Uiso 1 1 d . . .
H2 H -0.1686(13) 0.701(2) 0.5631(8) 0.022(4) Uiso 1 1 d . . .
H3 H -0.1186(13) 0.923(2) 0.6085(9) 0.025(5) Uiso 1 1 d . . .
H4 H 0.0445(15) 0.951(2) 0.6291(10) 0.033(5) Uiso 1 1 d . . .
H10 H 0.614(2) 1.000(3) 0.7386(13) 0.047(7) Uiso 1 1 d . . .
H11 H 0.7241(16) 0.878(2) 0.6820(11) 0.051(6) Uiso 1 1 d . . .
H12 H 0.6759(15) 0.721(2) 0.5966(10) 0.038(6) Uiso 1 1 d . . .
H13 H 0.5194(14) 0.688(2) 0.5780(10) 0.036(5) Uiso 1 1 d . . .
H2N H 0.2054(14) 0.712(2) 0.6279(10) 0.032(5) Uiso 1 1 d . . .
H3N H 0.3554(15) 0.940(2) 0.5804(10) 0.032(5) Uiso 1 1 d . . .

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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
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Br1 0.03966(13) 0.03700(13) 0.02607(11) -0.00544(7) 0.00203(7) 0.00354(8)
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S1 0.0249(2) 0.0324(2) 0.0292(2) 0.01041(17) -0.00471(16) 0.00147(16)
O1 0.0232(6) 0.0335(7) 0.0428(7) 0.0163(6) -0.0095(5) -0.0073(5)
N1 0.0174(6) 0.0217(6) 0.0276(7) 0.0007(5) -0.0007(5) -0.0003(5)
N2 0.0166(6) 0.0218(7) 0.0306(7) 0.0043(6) -0.0066(5) -0.0011(5)
N3 0.0179(6) 0.0215(6) 0.0243(7) 0.0038(5) -0.0022(5) -0.0031(5)
C1 0.0211(8) 0.0249(8) 0.0286(8) -0.0008(6) -0.0022(6) -0.0032(6)
C2 0.0154(7) 0.0359(9) 0.0273(8) 0.0024(7) -0.0017(6) 0.0001(6)
C3 0.0220(7) 0.0294(9) 0.0300(9) 0.0019(7) 0.0001(6) 0.0067(7)
C4 0.0249(8) 0.0223(8) 0.0304(8) -0.0025(7) -0.0032(6) 0.0007(6)
C5 0.0174(7) 0.0238(8) 0.0230(8) 0.0040(6) -0.0026(6) -0.0011(6)
C6 0.0195(7) 0.0204(7) 0.0212(7) -0.0011(6) -0.0019(6) 0.0008(6)
C7 0.0190(7) 0.0217(7) 0.0245(7) 0.0001(6) -0.0025(6) -0.0008(6)
C8 0.0182(7) 0.0217(7) 0.0253(8) 0.0036(6) -0.0040(6) -0.0013(6)
C9 0.0234(8) 0.0280(8) 0.0247(8) 0.0015(7) -0.0008(6) -0.0006(6)
C10 0.0293(9) 0.0417(11) 0.0351(10) 0.0004(8) -0.0102(7) -0.0111(8)
C11 0.0174(8) 0.0547(13) 0.0538(12) 0.0090(10) -0.0047(8) -0.0066(8)
C12 0.0228(8) 0.0422(11) 0.0484(11) 0.0048(9) 0.0072(8) 0.0040(8)
C13 0.0267(8) 0.0265(8) 0.0315(9) 0.0013(7) 0.0028(7) 0.0002(7)

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;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

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_geom_bond_distance
_geom_bond_site_symmetry_2
_geom_bond_publ_flag
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S1 C6 1.6662(15) . ?
O1 C7 1.219(2) . ?
N1 C5 1.330(2) . ?
N1 C1 1.346(2) . ?
N2 C6 1.334(2) . ?
N2 C5 1.4253(18) . ?
N2 H2N 0.80(2) . ?
N3 C7 1.370(2) . ?
N3 C6 1.3908(19) . ?
N3 H3N 0.83(2) . ?
C1 C2 1.380(2) . ?
C1 H1 0.92(2) . ?
C2 C3 1.382(3) . ?
C2 H2 0.946(18) . ?
C3 C4 1.386(2) . ?
C3 H3 0.96(2) . ?
C4 C5 1.380(2) . ?

C4 H4 0.93(2) . ?
C7 C8 1.502(2) . ?
C8 C9 1.388(2) . ?
C8 C13 1.390(2) . ?
C9 C10 1.383(2) . ?
C10 C11 1.385(3) . ?
C10 H10 0.88(3) . ?
C11 C12 1.381(3) . ?
C11 H11 0.96(2) . ?
C12 C13 1.385(3) . ?
C12 H12 0.96(2) . ?
C13 H13 0.92(2) . ?

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 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
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 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
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C6 N2 C5 123.70(14) . . ?
C6 N2 H2N 115.6(14) . . ?
C5 N2 H2N 120.3(14) . . ?
C7 N3 C6 127.74(14) . . ?
C7 N3 H3N 117.3(15) . . ?
C6 N3 H3N 114.8(15) . . ?
N1 C1 C2 123.56(16) . . ?
N1 C1 H1 114.7(13) . . ?
C2 C1 H1 121.7(13) . . ?
C1 C2 C3 118.69(14) . . ?
C1 C2 H2 120.0(11) . . ?
C3 C2 H2 121.3(11) . . ?
C2 C3 C4 118.81(15) . . ?
C2 C3 H3 120.4(12) . . ?
C4 C3 H3 120.8(12) . . ?
C5 C4 C3 117.93(15) . . ?
C5 C4 H4 119.3(13) . . ?
C3 C4 H4 122.7(13) . . ?
N1 C5 C4 124.65(14) . . ?
N1 C5 N2 115.68(14) . . ?
C4 C5 N2 119.63(14) . . ?
N2 C6 N3 115.76(13) . . ?
N2 C6 S1 125.59(12) . . ?
N3 C6 S1 118.65(11) . . ?
O1 C7 N3 124.74(14) . . ?
O1 C7 C8 121.15(14) . . ?
N3 C7 C8 114.10(13) . . ?
C9 C8 C13 119.02(15) . . ?
C9 C8 C7 121.31(14) . . ?
C13 C8 C7 119.64(15) . . ?
C10 C9 C8 121.43(16) . . ?

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C10 C9 Br1 119.04(14) . . ?
C8 C9 Br1 119.47(11) . . ?
C9 C10 C11 118.64(18) . . ?
C9 C10 H10 124(2) . . ?
C11 C10 H10 117(2) . . ?
C12 C11 C10 120.82(17) . . ?
C12 C11 H11 120.7(14) . . ?
C10 C11 H11 118.5(14) . . ?
C11 C12 C13 120.09(18) . . ?
C11 C12 H12 121.8(13) . . ?
C13 C12 H12 118.1(13) . . ?
C12 C13 C8 119.95(17) . . ?
C12 C13 H13 119.6(13) . . ?
C8 C13 H13 120.3(13) . . ?

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 _geom_torsion_site_symmetry_2
 _geom_torsion_site_symmetry_3
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N1 C1 C2 C3 -2.2(3) . . . . ?
C1 C2 C3 C4 1.7(3) . . . . ?
C2 C3 C4 C5 0.6(2) . . . . ?
C1 N1 C5 C4 2.3(2) . . . . ?
C1 N1 C5 N2 179.89(13) . . . . ?
C3 C4 C5 N1 -2.7(3) . . . . ?
C3 C4 C5 N2 179.71(15) . . . . ?
C6 N2 C5 N1 120.17(17) . . . . ?
C6 N2 C5 C4 -62.1(2) . . . . ?
C5 N2 C6 N3 177.59(14) . . . . ?
C5 N2 C6 S1 -2.8(2) . . . . ?
C7 N3 C6 N2 1.4(2) . . . . ?
C7 N3 C6 S1 -178.27(12) . . . . ?
C6 N3 C7 O1 2.0(3) . . . . ?
C6 N3 C7 C8 -179.23(14) . . . . ?
O1 C7 C8 C9 -91.9(2) . . . . ?
N3 C7 C8 C9 89.34(18) . . . . ?
O1 C7 C8 C13 86.0(2) . . . . ?
N3 C7 C8 C13 -92.81(18) . . . . ?
C13 C8 C9 C10 -2.8(2) . . . . ?
C7 C8 C9 C10 175.03(16) . . . . ?
C13 C8 C9 Br1 174.26(12) . . . . ?
C7 C8 C9 Br1 -7.9(2) . . . . ?
C8 C9 C10 C11 1.2(3) . . . . ?
Br1 C9 C10 C11 -175.91(15) . . . . ?
C9 C10 C11 C12 1.0(3) . . . . ?
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C10 C11 C12 C13 -1.5(3) . . . . ?
C11 C12 C13 C8 -0.2(3) . . . . ?
C9 C8 C13 C12 2.3(2) . . . . ?
C7 C8 C13 C12 -175.59(15) . . . . ?

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 _geom_hbond_atom_site_label_A
 _geom_hbond_distance_DH
 _geom_hbond_distance_HA
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 _geom_hbond_angle_DHA
 _geom_hbond_site_symmetry_A
N3 H3N N1  0.83(2) 2.18(2) 2.9846(19) 162.4(19) 8_665
N2 H2N O1  0.80(2) 1.99(2) 2.6570(18) 139.6(19) .

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_diffrn_reflns_theta_full              27.00
_diffrn_measured_fraction_theta_full   1.000
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 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Cl'  'Cl'   0.1484   0.1585
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M    P2(1)/n

loop_
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 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

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_cell_length_b                    8.3644(9)
_cell_length_c                    16.6231(19)
_cell_angle_alpha                 90.00
_cell_angle_beta                  101.726(2)
_cell_angle_gamma                 90.00
_cell_volume                      1469.7(3)
_cell_formula_units_Z             4
_cell_measurement_temperature     173(2)
_cell_measurement_reflns_used     9988
_cell_measurement_theta_min       2.50
_cell_measurement_theta_max       28.26

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_exptl_crystal_size_max           0.38
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_exptl_crystal_density_diffrn     1.538
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_exptl_crystal_F_000              696
_exptl_absorpt_coefficient_mu     0.584
_exptl_absorpt_correction_type    'multi-scan'
_exptl_absorpt_correction_T_min   0.8085
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_exptl_special_details
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_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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 'calc w=1/[\s^2^(Fo^2^)+(0.0463P)^2^+0.5136P] where P=(Fo^2^+2Fc^2^)/3'
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S1 S 0.70644(3) 0.47826(4) 0.196371(19) 0.02777(10) Uani 1 1 d . . .
O1 O 0.51830(9) 0.24047(11) 0.24331(5) 0.0251(2) Uani 1 1 d . . .
N1 N 0.78282(10) 0.51358(13) 0.47972(6) 0.0220(2) Uani 1 1 d . . .
N2 N 0.81188(10) 0.56905(13) 0.34519(6) 0.0214(2) Uani 1 1 d . . .
N3 N 0.65569(10) 0.38116(13) 0.34243(6) 0.0209(2) Uani 1 1 d . . .
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C3 C 0.96613(13) 0.73671(17) 0.54290(8) 0.0254(3) Uani 1 1 d . . .
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C6 C 0.93464(16) 0.6817(2) 0.68731(8) 0.0323(3) Uani 1 1 d . . .
C7 C 0.72402(12) 0.47344(14) 0.29792(7) 0.0196(2) Uani 1 1 d . . .
C8 C 0.55402(11) 0.28268(14) 0.31415(7) 0.0200(2) Uani 1 1 d . . .
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H2N H 0.8510(17) 0.629(2) 0.3182(11) 0.033(4) Uiso 1 1 d . . .
H3 H 1.0270(16) 0.815(2) 0.5644(10) 0.033(4) Uiso 1 1 d . . .
H3N H 0.6772(16) 0.399(2) 0.3953(11) 0.031(4) Uiso 1 1 d . . .
H4 H 0.9805(16) 0.764(2) 0.4233(10) 0.030(4) Uiso 1 1 d . . .
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H6B H 0.860(2) 0.669(3) 0.7105(13) 0.057(6) Uiso 1 1 d . . .
H6C H 0.989(2) 0.605(3) 0.7135(13) 0.059(6) Uiso 1 1 d . . .
H10 H 0.3675(16) 0.086(2) 0.3029(11) 0.029(4) Uiso 1 1 d . . .
H12 H 0.3102(17) 0.069(2) 0.5378(11) 0.035(4) Uiso 1 1 d . . .
H14 H 0.5824(14) 0.353(2) 0.4790(9) 0.023(4) Uiso 1 1 d . . .

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Cl2 0.0398(2) 0.0383(2) 0.02022(17) 0.00329(13) 0.01187(13) 0.00860(14)
S1 0.03664(19) 0.03184(19) 0.01537(16) -0.00029(12) 0.00655(13) -0.00688(13)
O1 0.0257(4) 0.0305(5) 0.0192(4) -0.0053(4) 0.0051(3) -0.0018(4)
N1 0.0248(5) 0.0239(5) 0.0179(5) 0.0008(4) 0.0057(4) -0.0016(4)
N2 0.0244(5) 0.0239(5) 0.0174(5) 0.0014(4) 0.0073(4) -0.0040(4)
N3 0.0248(5) 0.0234(5) 0.0155(5) -0.0018(4) 0.0063(4) -0.0035(4)
C1 0.0281(6) 0.0268(6) 0.0183(6) 0.0029(5) 0.0064(5) 0.0011(5)
C2 0.0275(6) 0.0259(6) 0.0181(6) 0.0008(5) 0.0016(5) 0.0042(5)
C3 0.0236(6) 0.0273(6) 0.0239(6) -0.0012(5) 0.0013(5) -0.0026(5)
C4 0.0217(6) 0.0261(6) 0.0222(6) 0.0019(5) 0.0050(5) -0.0017(5)
C5 0.0196(5) 0.0221(6) 0.0179(6) 0.0004(4) 0.0043(4) 0.0024(4)
C6 0.0404(8) 0.0361(8) 0.0180(6) -0.0010(6) 0.0006(6) -0.0005(7)
C7 0.0218(6) 0.0194(6) 0.0185(5) -0.0002(4) 0.0064(4) 0.0019(4)
C8 0.0211(6) 0.0194(6) 0.0202(6) -0.0011(4) 0.0061(5) 0.0028(4)
C9 0.0208(5) 0.0194(6) 0.0220(6) 0.0003(4) 0.0072(5) 0.0025(4)
C10 0.0236(6) 0.0228(6) 0.0289(7) -0.0042(5) 0.0078(5) 0.0001(5)
C11 0.0221(6) 0.0212(6) 0.0427(8) -0.0010(5) 0.0116(5) -0.0016(5)
C12 0.0275(6) 0.0243(6) 0.0361(7) 0.0066(5) 0.0172(6) 0.0052(5)
C13 0.0267(6) 0.0244(6) 0.0214(6) 0.0035(5) 0.0094(5) 0.0074(5)
C14 0.0232(6) 0.0213(6) 0.0224(6) 0.0006(5) 0.0074(5) 0.0010(5)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C1 1.3462(16) . ?
N2 C7 1.3614(16) . ?
N2 C5 1.4023(15) . ?
N2 H2N 0.840(19) . ?
N3 C8 1.3764(16) . ?
N3 C7 1.3818(16) . ?
N3 H3N 0.875(18) . ?
C1 C2 1.3789(19) . ?
C1 H1 1.002(18) . ?
C2 C3 1.3989(19) . ?
C2 C6 1.5021(17) . ?
C3 C4 1.3770(18) . ?
C3 H3 0.944(18) . ?
C4 C5 1.3967(18) . ?
C4 H4 0.961(17) . ?
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C6 H6B 0.96(2) . ?
C6 H6C 0.92(2) . ?
C8 C9 1.5104(17) . ?
C9 C14 1.3922(18) . ?
C9 C10 1.3941(18) . ?
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C7 N3 H3N 112.4(11) . . ?
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C1 C2 C3 116.65(12) . . ?
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C1 C2 C6 121.65(12) . . ?
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C4 C5 N2 117.75(11) . . ?
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C2 C6 H6B 111.0(13) . . ?
H6A C6 H6B 101(2) . . ?
C2 C6 H6C 110.7(14) . . ?
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H6B C6 H6C 103.8(19) . . ?
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N3 C7 S1 126.50(10) . . ?
O1 C8 N3 125.38(11) . . ?
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'x, -y, z-1/2'

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_computing_molecular_graphics    'Bruker SHELXTL'
_computing_publication_material  'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0505P)^2^+3.6505P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens difmap

_refine_ls_hydrogen_treatment refall

_refine_ls_extinction_method none

_refine_ls_extinction_coef ?

_refine_ls_number_reflns 2919

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_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.0507

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_refine_ls_goodness_of_fit_ref 1.045

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_refine_ls_shift/su_mean 0.000

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O1 O 0.34303(5) 0.68089(19) 0.87988(12) 0.0449(4) Uani 1 1 d . . .

N1 N 0.46810(7) 0.2949(3) 0.87905(14) 0.0462(5) Uani 1 1 d . . .

N2 N 0.39381(6) 0.4104(2) 0.95039(12) 0.0359(4) Uani 1 1 d . . .

N3 N 0.29960(6) 0.4434(2) 0.93037(11) 0.0317(4) Uani 1 1 d . . .

C1 C 0.51839(9) 0.2233(4) 0.8836(2) 0.0522(6) Uani 1 1 d . . .

C2 C 0.54660(8) 0.1801(3) 0.9680(2) 0.0505(6) Uani 1 1 d . . .

C3 C 0.52224(8) 0.2113(3) 1.05142(19) 0.0474(5) Uani 1 1 d . . .

C4 C 0.46992(8) 0.2846(3) 1.05124(15) 0.0394(5) Uani 1 1 d . . .

C5 C 0.44557(7) 0.3221(3) 0.96137(15) 0.0355(4) Uani 1 1 d . . .

C6 C 0.44297(11) 0.3217(5) 1.1422(2) 0.0599(8) Uani 1 1 d . . .

C7 C 0.34423(7) 0.3417(2) 0.95970(13) 0.0306(4) Uani 1 1 d . . .

C8 C 0.30032(7) 0.6010(3) 0.88930(13) 0.0329(4) Uani 1 1 d . . .

C9 C 0.24553(7) 0.6709(3) 0.85561(13) 0.0314(4) Uani 1 1 d . . .

C10 C 0.20464(7) 0.5696(3) 0.81058(13) 0.0339(4) Uani 1 1 d . . .

C11 C 0.15595(8) 0.6437(3) 0.77407(14) 0.0392(5) Uani 1 1 d . . .

C12 C 0.14774(8) 0.8158(3) 0.78416(15) 0.0412(5) Uani 1 1 d . . .

C13 C 0.18793(8) 0.9159(3) 0.83026(15) 0.0402(5) Uani 1 1 d . . .

C14 C 0.23737(8) 0.8441(3) 0.86473(14) 0.0357(4) Uani 1 1 d . . .

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H3N H 0.2720(9) 0.406(3) 0.9415(15) 0.034(6) Uiso 1 1 d . . .

H1 H 0.5317(11) 0.204(3) 0.8238(19) 0.052(7) Uiso 1 1 d . . .

H2 H 0.5813(11) 0.129(3) 0.9672(19) 0.060(7) Uiso 1 1 d . . .

H3 H 0.5382(10) 0.188(3) 1.1118(18) 0.051(7) Uiso 1 1 d . . .

H6C H 0.4658(16) 0.368(5) 1.187(3) 0.103(12) Uiso 1 1 d . . .

H6B H 0.4209(18) 0.414(6) 1.135(3) 0.125(15) Uiso 1 1 d . . .

H6A H 0.424(2) 0.235(6) 1.163(4) 0.146(19) Uiso 1 1 d . . .

H10 H 0.2115(9) 0.452(3) 0.8030(15) 0.040(6) Uiso 1 1 d . . .

H11 H 0.1288(11) 0.568(3) 0.7428(18) 0.057(7) Uiso 1 1 d . . .

H12 H 0.1147(10) 0.867(3) 0.7588(17) 0.048(6) Uiso 1 1 d . . .

H13 H 0.1845(10) 1.035(3) 0.8378(16) 0.048(7) Uiso 1 1 d . . .

H14 H 0.2639(9) 0.914(3) 0.8940(16) 0.041(6) Uiso 1 1 d . . .

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O1 0.0228(7) 0.0439(8) 0.0672(10) 0.0092(7) -0.0040(6) -0.0023(6)

N1 0.0216(8) 0.0644(12) 0.0526(11) 0.0046(9) 0.0031(7) 0.0008(8)

N2 0.0182(7) 0.0402(10) 0.0487(10) 0.0068(8) -0.0031(6) 0.0008(7)

N3 0.0149(7) 0.0417(9) 0.0384(9) 0.0032(7) 0.0001(6) 0.0006(6)

C1 0.0234(10) 0.0720(17) 0.0618(15) -0.0051(13) 0.0090(9) 0.0029(10)

C2 0.0179(9) 0.0528(14) 0.0804(17) 0.0004(12) 0.0002(10) 0.0043(9)

C3 0.0253(10) 0.0528(13) 0.0625(14) 0.0086(11) -0.0113(9) -0.0004(9)

C4 0.0231(9) 0.0453(12) 0.0489(11) 0.0003(9) -0.0062(8) -0.0010(8)

C5 0.0158(8) 0.0427(11) 0.0475(11) 0.0028(9) -0.0016(7) -0.0021(7)

C6 0.0385(13) 0.093(2) 0.0464(14) -0.0085(14) -0.0090(11) 0.0072(14)

C7 0.0198(8) 0.0407(10) 0.0309(9) -0.0016(8) -0.0012(6) 0.0016(7)

C8 0.0225(9) 0.0404(11) 0.0353(10) 0.0003(8) -0.0014(7) 0.0018(7)

C9 0.0223(8) 0.0425(11) 0.0294(9) 0.0032(8) 0.0026(7) 0.0023(7)

C10 0.0239(9) 0.0443(12) 0.0338(10) 0.0000(8) 0.0031(7) 0.0011(8)

C11 0.0236(9) 0.0591(13) 0.0345(10) 0.0023(9) -0.0003(7) -0.0020(9)

C12 0.0246(9) 0.0602(14) 0.0386(11) 0.0113(9) 0.0015(8) 0.0110(9)

C13 0.0334(10) 0.0432(12) 0.0444(11) 0.0056(9) 0.0050(8) 0.0084(9)

C14 0.0278(9) 0.0434(11) 0.0357(10) 0.0022(8) 0.0007(8) 0.0008(8)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles

and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

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O1 C8 1.229(2) . ?

N1 C5 1.325(3) . ?

N1 C1 1.344(3) . ?

N2 C7 1.335(2) . ?

N2 C5 1.438(2) . ?

N2 H2N 0.86(3) . ?

N3 C8 1.372(3) . ?

N3 C7 1.391(2) . ?

N3 H3N 0.76(2) . ?

C1 C2 1.373(4) . ?

C1 H1 0.93(3) . ?

C2 C3 1.365(4) . ?

C2 H2 0.93(3) . ?

C3 C4 1.397(3) . ?

C3 H3 0.93(3) . ?

C4 C5 1.390(3) . ?

C4 C6 1.497(3) . ?

C6 H6C 0.89(4) . ?

C6 H6B 0.91(5) . ?

C6 H6A 0.89(5) . ?

C8 C9 1.491(2) . ?

C9 C14 1.389(3) . ?

C9 C10 1.396(3) . ?

C10 C11 1.389(3) . ?

C10 H10 0.95(2) . ?

C11 C12 1.382(3) . ?

C11 H11 0.98(3) . ?

C12 C13 1.385(3) . ?

C12 H12 0.95(2) . ?

C13 C14 1.388(3) . ?

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C5 N1 C1 116.7(2) . . ?

C7 N2 C5 125.49(18) . . ?

C7 N2 H2N 116.2(16) . . ?

C5 N2 H2N 116.7(16) . . ?

C8 N3 C7 128.15(16) . . ?

C8 N3 H3N 118.5(17) . . ?

C7 N3 H3N 113.3(17) . . ?

N1 C1 C2 123.3(2) . . ?

N1 C1 H1 113.1(16) . . ?

C2 C1 H1 123.5(16) . . ?

C3 C2 C1 118.3(2) . . ?

C3 C2 H2 121.8(16) . . ?

C1 C2 H2 120.0(16) . . ?

C2 C3 C4 121.1(2) . . ?

C2 C3 H3 124.6(16) . . ?

C4 C3 H3 114.4(16) . . ?

C5 C4 C3 115.2(2) . . ?

C5 C4 C6 123.1(2) . . ?

C3 C4 C6 121.7(2) . . ?

N1 C5 C4 125.39(18) . . ?

N1 C5 N2 113.02(17) . . ?

C4 C5 N2 121.38(18) . . ?

C4 C6 H6C 113(2) . . ?

C4 C6 H6B 110(3) . . ?

H6C C6 H6B 95(3) . . ?

C4 C6 H6A 114(3) . . ?

H6C C6 H6A 114(4) . . ?

H6B C6 H6A 110(4) . . ?

N2 C7 N3 115.36(17) . . ?

N2 C7 S1 124.86(14) . . ?

N3 C7 S1 119.77(14) . . ?

O1 C8 N3 122.95(17) . . ?

O1 C8 C9 121.27(18) . . ?

N3 C8 C9 115.77(16) . . ?

C14 C9 C10 120.30(18) . . ?

C14 C9 C8 117.74(17) . . ?

C10 C9 C8 121.83(18) . . ?

C11 C10 C9 119.4(2) . . ?

C11 C10 H10 121.4(13) . . ?

C9 C10 H10 119.1(13) . . ?

C12 C11 C10 120.1(2) . . ?

C12 C11 H11 123.6(16) . . ?

C10 C11 H11 116.3(16) . . ?

C11 C12 C13 120.46(19) . . ?

C11 C12 H12 120.4(15) . . ?

C13 C12 H12 119.1(15) . . ?

C12 C13 C14 120.0(2) . . ?

C12 C13 H13 123.5(14) . . ?

C14 C13 H13 116.4(15) . . ?

C13 C14 C9 119.7(2) . . ?

C13 C14 H14 118.2(14) . . ?

C9 C14 H14 122.1(14) . . ?

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N1 C1 C2 C3 0.1(4) . . . . ?

C1 C2 C3 C4 0.2(4) . . . . ?

C2 C3 C4 C5 0.0(3) . . . . ?

C2 C3 C4 C6 -179.2(3) . . . . ?

C1 N1 C5 C4 0.8(3) . . . . ?

C1 N1 C5 N2 175.5(2) . . . . ?

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C6 C4 C5 N1 178.6(3) . . . . ?

C3 C4 C5 N2 -174.83(19) . . . . ?

C6 C4 C5 N2 4.3(4) . . . . ?

C7 N2 C5 N1 106.8(2) . . . . ?

C7 N2 C5 C4 -78.3(3) . . . . ?

C5 N2 C7 N3 -169.64(17) . . . . ?

C5 N2 C7 S1 10.7(3) . . . . ?

C8 N3 C7 N2 3.3(3) . . . . ?

C8 N3 C7 S1 -177.02(15) . . . . ?

C7 N3 C8 O1 -6.2(3) . . . . ?

C7 N3 C8 C9 173.49(17) . . . . ?

O1 C8 C9 C14 -36.1(3) . . . . ?

N3 C8 C9 C14 144.24(18) . . . . ?

O1 C8 C9 C10 139.8(2) . . . . ?

N3 C8 C9 C10 -39.9(2) . . . . ?

C14 C9 C10 C11 0.7(3) . . . . ?

C8 C9 C10 C11 -175.08(17) . . . . ?

C9 C10 C11 C12 -1.3(3) . . . . ?

C10 C11 C12 C13 0.3(3) . . . . ?

C11 C12 C13 C14 1.5(3) . . . . ?

C12 C13 C14 C9 -2.2(3) . . . . ?

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N3 H3N S1 0.76(2) 2.76(2) 3.4941(17) 166(2) 7_557

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_symmetry_space_group_name_H-M    P2(1)/n

loop_
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 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

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_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_scheme       calc
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O1 O 0.39192(10) 0.11562(8) 0.03443(8) 0.0311(2) Uani 1 1 d . . .
O2 O 0.15257(10) 0.23317(10) -0.59097(8) 0.0339(2) Uani 1 1 d . . .
O3 O 0.28956(10) 0.09002(10) -0.57085(9) 0.0365(2) Uani 1 1 d . . .
N1 N 0.55959(10) 0.19844(10) 0.39850(10) 0.0260(2) Uani 1 1 d . . .
N2 N 0.43373(10) 0.26882(10) 0.21435(9) 0.0224(2) Uani 1 1 d . . .
N3 N 0.42076(10) 0.31782(10) 0.02257(9) 0.0208(2) Uani 1 1 d . . .
N4 N 0.23611(11) 0.16533(10) -0.53010(9) 0.0266(2) Uani 1 1 d . . .
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C2 C 0.55432(13) 0.28100(13) 0.58157(11) 0.0278(3) Uani 1 1 d . . .
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C6 C 0.30362(13) 0.43840(12) 0.32635(12) 0.0262(3) Uani 1 1 d . . .
C7 C 0.45753(11) 0.35032(11) 0.14244(10) 0.0199(2) Uani 1 1 d . . .
C8 C 0.38918(12) 0.20496(11) -0.02524(11) 0.0223(2) Uani 1 1 d . . .
C9 C 0.35089(11) 0.19850(11) -0.15778(10) 0.0209(2) Uani 1 1 d . . .
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C11 C 0.23587(12) 0.27567(11) -0.35310(11) 0.0230(3) Uani 1 1 d . . .
C12 C 0.27579(12) 0.17605(11) -0.39952(10) 0.0220(2) Uani 1 1 d . . .
C13 C 0.35285(12) 0.08770(11) -0.32982(11) 0.0243(3) Uani 1 1 d . . .
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H2N H 0.4144(17) 0.1995(17) 0.1847(16) 0.036(4) Uiso 1 1 d . . .
H3 H 0.4231(14) 0.4185(14) 0.5600(13) 0.026(4) Uiso 1 1 d . . .
H3N H 0.4307(15) 0.3695(15) -0.0217(14) 0.025(4) Uiso 1 1 d . . .
H6A H 0.2369(19) 0.3901(17) 0.2739(17) 0.047(5) Uiso 1 1 d . . .
H6B H 0.2669(18) 0.4783(17) 0.3778(18) 0.046(5) Uiso 1 1 d . . .
H6C H 0.3287(17) 0.4952(17) 0.2791(16) 0.042(5) Uiso 1 1 d . . .
H10 H 0.2461(15) 0.3540(14) -0.1989(13) 0.026(4) Uiso 1 1 d . . .
H11 H 0.1836(15) 0.3360(15) -0.4018(14) 0.027(4) Uiso 1 1 d . . .
H13 H 0.3804(15) 0.0231(15) -0.3625(14) 0.029(4) Uiso 1 1 d . . .
H14 H 0.4416(15) 0.0402(15) -0.1572(14) 0.028(4) Uiso 1 1 d . . .

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O1 0.0503(6) 0.0219(5) 0.0214(4) 0.0008(4) 0.0126(4) -0.0025(4)
O2 0.0364(5) 0.0394(6) 0.0207(4) 0.0027(4) 0.0030(4) -0.0048(4)
O3 0.0452(6) 0.0412(6) 0.0246(5) -0.0118(4) 0.0138(4) -0.0045(5)
N1 0.0281(5) 0.0292(6) 0.0221(5) 0.0033(4) 0.0104(4) 0.0020(4)
N2 0.0308(5) 0.0205(5) 0.0167(5) -0.0015(4) 0.0092(4) -0.0027(4)
N3 0.0277(5) 0.0204(5) 0.0149(5) 0.0008(4) 0.0080(4) -0.0015(4)
N4 0.0295(6) 0.0299(6) 0.0201(5) -0.0046(4) 0.0081(4) -0.0110(4)
C1 0.0277(6) 0.0337(7) 0.0222(6) 0.0064(5) 0.0063(5) 0.0016(5)
C2 0.0324(7) 0.0328(7) 0.0167(6) 0.0016(5) 0.0064(5) -0.0072(5)
C3 0.0312(6) 0.0239(6) 0.0202(6) -0.0026(5) 0.0114(5) -0.0071(5)

C4 0.0252(6) 0.0204(6) 0.0197(6) 0.0007(4) 0.0090(5) -0.0037(5)
C5 0.0248(6) 0.0230(6) 0.0167(5) 0.0003(4) 0.0080(5) -0.0039(5)
C6 0.0305(7) 0.0264(6) 0.0227(6) 0.0009(5) 0.0103(5) 0.0022(5)
C7 0.0209(5) 0.0223(6) 0.0170(5) -0.0004(4) 0.0070(4) 0.0022(4)
C8 0.0256(6) 0.0228(6) 0.0193(6) -0.0011(5) 0.0086(5) 0.0001(5)
C9 0.0236(6) 0.0214(6) 0.0182(6) -0.0019(4) 0.0076(4) -0.0038(4)
C10 0.0230(6) 0.0215(6) 0.0223(6) -0.0029(5) 0.0090(5) -0.0019(5)
C11 0.0219(6) 0.0241(6) 0.0218(6) 0.0015(5) 0.0058(5) -0.0019(5)
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C13 0.0294(6) 0.0215(6) 0.0243(6) -0.0050(5) 0.0122(5) -0.0034(5)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C5 1.3298(16) . ?
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N2 H2N 0.848(18) . ?
N3 C8 1.3801(16) . ?
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N3 H3N 0.816(17) . ?
N4 C12 1.4756(15) . ?
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C8 N3 H3N 116.8(11) . . ?
C7 N3 H3N 115.1(11) . . ?
O3 N4 O2 124.14(11) . . ?
O3 N4 C12 117.85(11) . . ?
O2 N4 C12 118.00(11) . . ?
N1 C1 C2 122.89(12) . . ?
N1 C1 H1 115.9(10) . . ?
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C1 C2 C3 118.34(12) . . ?
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C5 C4 C6 123.46(11) . . ?
C3 C4 C6 121.13(11) . . ?
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N1 C5 N2 113.14(11) . . ?
C4 C5 N2 121.31(11) . . ?
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C4 C6 H6B 111.6(12) . . ?
H6A C6 H6B 106.1(16) . . ?
C4 C6 H6C 111.1(11) . . ?
H6A C6 H6C 107.8(16) . . ?
H6B C6 H6C 110.3(16) . . ?
N2 C7 N3 115.41(11) . . ?
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O1 C8 N3 123.58(11) . . ?
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O1 C8 C9 C14 -37.01(17) . . . . ?
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O2 N4 C12 C11 -12.40(16) . . . . ?
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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S1A S 0.79379(15) 0.50684(8) 0.75461(6) 0.0267(2) Uani 1 1 d . . .
O1A O 0.8466(4) 0.9085(2) 0.55419(15) 0.0304(6) Uani 1 1 d . . .
N1A N 0.8449(4) 0.5199(3) 0.51706(18) 0.0251(7) Uani 1 1 d . . .
N2A N 0.9132(5) 0.6554(3) 0.59454(19) 0.0222(7) Uani 1 1 d . . .
N3A N 0.7712(5) 0.7631(3) 0.68783(19) 0.0216(6) Uani 1 1 d . . .
C1A C 0.9023(6) 0.4260(4) 0.4833(2) 0.0291(8) Uani 1 1 d . . .
C2A C 1.0876(6) 0.3597(4) 0.4956(3) 0.0312(9) Uani 1 1 d . . .
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C4A C 1.1663(6) 0.4869(3) 0.5841(2) 0.0236(8) Uani 1 1 d . . .
C5A C 0.9755(5) 0.5478(3) 0.5657(2) 0.0212(7) Uani 1 1 d . . .
C6A C 1.3079(7) 0.5269(5) 0.6367(3) 0.0327(10) Uani 1 1 d . . .
C7A C 0.8307(5) 0.6458(3) 0.6737(2) 0.0198(7) Uani 1 1 d . . .
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C8A C 0.7734(5) 0.8855(3) 0.6289(2) 0.0210(7) Uani 1 1 d . . .
C9A C 0.6864(6) 0.9902(3) 0.6641(2) 0.0217(7) Uani 1 1 d . . .
C10A C 0.8240(7) 1.0927(4) 0.6572(2) 0.0313(9) Uani 1 1 d . . .
C11A C 0.7557(7) 1.1931(4) 0.6884(3) 0.0356(10) Uani 1 1 d . . .
C12A C 0.5489(8) 1.1916(4) 0.7252(3) 0.0389(10) Uani 1 1 d . . .
C13A C 0.4104(7) 1.0930(4) 0.7300(3) 0.0345(9) Uani 1 1 d . . .
C14A C 0.4804(6) 0.9911(3) 0.6994(2) 0.0266(8) Uani 1 1 d . . .
Br1B Br 1.22045(5) 0.45282(4) 0.91283(3) 0.04392(12) Uani 1 1 d . . .
S1B S 0.65851(17) 0.79871(9) 0.88022(6) 0.0311(2) Uani 1 1 d . . .
O1B O 0.7016(4) 0.4038(2) 1.08429(15) 0.0315(6) Uani 1 1 d . . .
N1B N 0.6167(5) 0.7937(3) 1.11794(19) 0.0258(7) Uani 1 1 d . . .
N2B N 0.5751(5) 0.6491(3) 1.04299(18) 0.0217(6) Uani 1 1 d . . .
N3B N 0.7218(5) 0.5458(3) 0.9477(2) 0.0225(6) Uani 1 1 d . . .
C1B C 0.5453(6) 0.8886(4) 1.1494(2) 0.0314(9) Uani 1 1 d . . .
C2B C 0.3558(6) 0.9468(4) 1.1352(2) 0.0293(8) Uani 1 1 d . . .
C3B C 0.2300(6) 0.9032(4) 1.0869(2) 0.0298(8) Uani 1 1 d . . .
C4B C 0.2965(5) 0.8056(3) 1.0533(2) 0.0256(8) Uani 1 1 d . . .
C5B C 0.4944(5) 0.7564(3) 1.0704(2) 0.0202(7) Uani 1 1 d . . .
C6B C 0.1579(7) 0.7540(5) 1.0040(3) 0.0388(10) Uani 1 1 d . . .
C7B C 0.6482(5) 0.6599(3) 0.9623(2) 0.0215(7) Uani 1 1 d . . .
C8B C 0.7446(5) 0.4258(3) 1.0067(2) 0.0224(7) Uani 1 1 d . . .
C9B C 0.8196(6) 0.3209(3) 0.9704(2) 0.0233(7) Uani 1 1 d . . .
C10B C 0.6781(7) 0.2167(4) 0.9820(3) 0.0334(9) Uani 1 1 d . . .
C11B C 0.7381(8) 0.1160(4) 0.9502(3) 0.0388(10) Uani 1 1 d . . .
C12B C 0.9354(8) 0.1151(4) 0.9094(3) 0.0416(11) Uani 1 1 d . . .
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C14B C 1.0195(6) 0.3179(4) 0.9287(2) 0.0285(8) Uani 1 1 d . . .
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O1C O 0.8855(3) 0.0231(2) 0.24682(14) 0.0242(5) Uani 1 1 d . . .
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N3C N 0.8225(5) 0.0610(3) 0.37555(19) 0.0213(6) Uani 1 1 d . . .
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C3C C 0.2582(6) 0.4714(4) 0.2208(2) 0.0299(8) Uani 1 1 d . . .
C4C C 0.4261(5) 0.4008(3) 0.2560(2) 0.0222(7) Uani 1 1 d . . .
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C7C C 0.6575(5) 0.1483(3) 0.3627(2) 0.0210(7) Uani 1 1 d . . .
C8C C 0.9238(5) 0.0011(3) 0.3196(2) 0.0199(7) Uani 1 1 d . . .
C9C C 1.0853(5) -0.0937(3) 0.3574(2) 0.0205(7) Uani 1 1 d . . .
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C11C C 1.3831(6) -0.1438(4) 0.4388(2) 0.0298(8) Uani 1 1 d . . .
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H3A H 1.334(6) 0.347(4) 0.557(2) 0.031(11) Uiso 1 1 d . . .
H10A H 0.960(6) 1.104(3) 0.629(2) 0.024(10) Uiso 1 1 d . . .
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H12A H 0.495(6) 1.252(4) 0.748(3) 0.046(12) Uiso 1 1 d . . .

H13A H 0.257(6) 1.093(4) 0.749(2) 0.031(10) Uiso 1 1 d . . .
H6AA H 1.262(7) 0.484(4) 0.695(3) 0.053(14) Uiso 1 1 d . . .
H6AB H 1.312(6) 0.618(4) 0.627(2) 0.033(11) Uiso 1 1 d . . .
H6AC H 1.431(7) 0.501(4) 0.628(2) 0.029(11) Uiso 1 1 d . . .
H1B H 0.628(6) 0.920(4) 1.186(2) 0.032(10) Uiso 1 1 d . . .
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H6BA H 0.162(6) 0.659(4) 1.021(3) 0.046(13) Uiso 1 1 d . . .
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H6BC H 0.201(6) 0.797(4) 0.944(2) 0.024(10) Uiso 1 1 d . . .
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H13C H 1.268(5) -0.370(3) 0.3718(19) 0.006(8) Uiso 1 1 d . . .
H6CA H 0.593(7) 0.565(5) 0.261(3) 0.056(13) Uiso 1 1 d . . .
H6CB H 0.531(8) 0.454(5) 0.358(3) 0.077(16) Uiso 1 1 d . . .
H6CC H 0.711(6) 0.422(3) 0.286(2) 0.022(9) Uiso 1 1 d . . .
H2NA H 0.909(5) 0.730(4) 0.554(2) 0.019(9) Uiso 1 1 d . . .
H3NA H 0.728(5) 0.755(3) 0.737(2) 0.022(10) Uiso 1 1 d . . .
H2NB H 0.580(6) 0.577(4) 1.082(3) 0.031(11) Uiso 1 1 d . . .
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H2NC H 0.663(5) 0.153(3) 0.252(2) 0.018(9) Uiso 1 1 d . . .
H3NC H 0.839(6) 0.027(4) 0.426(3) 0.031(11) Uiso 1 1 d . . .

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N3A 0.0302(17) 0.0197(15) 0.0155(15) -0.0076(12) -0.0009(13) 0.0054(12)
C1A 0.029(2) 0.033(2) 0.030(2) -0.0153(17) -0.0054(16) -0.0026(17)
C2A 0.040(2) 0.025(2) 0.032(2) -0.0172(17) 0.0005(17) 0.0033(17)
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C4A 0.0286(19) 0.0193(17) 0.0229(18) -0.0082(14) 0.0003(15) 0.0035(15)
C5A 0.0233(18) 0.0200(18) 0.0199(17) -0.0068(14) -0.0012(14) 0.0036(14)
C6A 0.028(2) 0.040(3) 0.034(2) -0.017(2) -0.0077(19) 0.010(2)
C7A 0.0176(16) 0.0197(17) 0.0253(17) -0.0116(14) -0.0040(13) 0.0031(13)
C8A 0.0191(17) 0.0208(18) 0.0224(18) -0.0050(14) -0.0052(14) 0.0054(14)

C9A 0.034(2) 0.0175(17) 0.0158(16) -0.0075(14) -0.0070(15) 0.0057(15)
C10A 0.035(2) 0.027(2) 0.027(2) -0.0065(16) 0.0058(18) -0.0034(17)
C11A 0.055(3) 0.019(2) 0.032(2) -0.0073(17) -0.003(2) -0.0015(19)
C12A 0.061(3) 0.024(2) 0.035(2) -0.0167(18) 0.0021(19) 0.0111(19)
C13A 0.036(2) 0.034(2) 0.037(2) -0.0161(19) -0.0051(18) 0.0107(19)
C14A 0.0282(19) 0.0261(19) 0.0279(19) -0.0106(16) -0.0070(15) 0.0055(15)
Br1B 0.0252(2) 0.0527(3) 0.0601(3) -0.0284(2) -0.00031(19) -0.00387(19)
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O1B 0.0462(16) 0.0261(14) 0.0203(13) -0.0072(11) 0.0000(11) 0.0108(12)
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N2B 0.0296(16) 0.0193(16) 0.0165(14) -0.0064(13) -0.0023(12) 0.0026(13)
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C2B 0.044(2) 0.0195(19) 0.0259(19) -0.0114(16) 0.0011(17) 0.0041(16)
C3B 0.027(2) 0.033(2) 0.030(2) -0.0127(17) 0.0009(16) 0.0065(17)
C4B 0.0219(18) 0.0257(19) 0.0267(18) -0.0050(15) -0.0021(14) -0.0014(14)
C5B 0.0251(18) 0.0218(18) 0.0147(16) -0.0084(14) 0.0001(13) 0.0010(14)
C6B 0.030(2) 0.043(3) 0.051(3) -0.023(2) -0.013(2) 0.003(2)
C7B 0.0214(17) 0.0231(18) 0.0221(17) -0.0102(15) -0.0029(14) -0.0004(14)
C8B 0.0218(17) 0.0236(19) 0.0224(18) -0.0083(15) -0.0030(14) 0.0025(14)
C9B 0.0272(19) 0.0221(18) 0.0202(17) -0.0049(14) -0.0066(14) 0.0051(15)
C10B 0.044(3) 0.022(2) 0.033(2) -0.0086(17) 0.0015(18) -0.0026(17)
C11B 0.056(3) 0.023(2) 0.038(2) -0.0114(18) -0.004(2) -0.002(2)
C12B 0.065(3) 0.028(2) 0.032(2) -0.0127(19) -0.001(2) 0.014(2)
C13B 0.038(3) 0.041(3) 0.035(2) -0.017(2) 0.004(2) 0.010(2)
C14B 0.033(2) 0.029(2) 0.0281(19) -0.0145(16) -0.0070(16) 0.0077(16)
Br1C 0.0324(2) 0.02525(19) 0.0400(2) -0.01745(16) -0.00816(16) 0.00336(15)
S1C 0.0307(5) 0.0279(5) 0.0252(4) -0.0144(4) -0.0031(4) 0.0086(4)
O1C 0.0276(13) 0.0245(13) 0.0244(13) -0.0121(10) -0.0079(10) 0.0077(10)
N1C 0.0285(16) 0.0231(16) 0.0313(16) -0.0056(13) -0.0096(13) 0.0003(13)
N2C 0.0232(15) 0.0225(16) 0.0242(15) -0.0136(13) -0.0050(12) 0.0078(12)
N3C 0.0256(16) 0.0209(16) 0.0200(15) -0.0088(13) -0.0072(13) 0.0058(13)
C1C 0.028(2) 0.036(2) 0.032(2) -0.0022(17) -0.0108(16) -0.0019(17)
C2C 0.023(2) 0.035(2) 0.033(2) -0.0051(18) -0.0069(17) 0.0070(17)
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C5C 0.0222(17) 0.0237(18) 0.0184(16) -0.0039(13) -0.0033(13) 0.0034(14)
C6C 0.039(2) 0.019(2) 0.043(2) -0.0144(18) -0.0130(19) 0.0080(17)
C7C 0.0226(17) 0.0175(17) 0.0244(17) -0.0083(14) -0.0045(14) -0.0010(13)
C8C 0.0183(16) 0.0199(17) 0.0207(17) -0.0064(14) 0.0001(13) -0.0018(13)
C9C 0.0221(18) 0.0178(17) 0.0211(17) -0.0064(14) -0.0007(14) 0.0015(14)
C10C 0.0241(18) 0.027(2) 0.0259(18) -0.0083(15) -0.0032(14) -0.0002(15)
C11C 0.0223(19) 0.036(2) 0.028(2) -0.0050(17) -0.0036(16) -0.0027(16)
C12C 0.024(2) 0.035(2) 0.034(2) 0.0005(18) -0.0038(17) 0.0056(17)
C13C 0.035(2) 0.022(2) 0.028(2) -0.0074(17) -0.0009(16) 0.0071(16)
C14C 0.0227(17) 0.0212(17) 0.0249(18) -0.0084(14) -0.0017(14) 0.0005(14)

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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not relevant to the choice of reflections for refinement. R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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S1 S 0.38582(15) 0.52857(7) 0.23282(3) 0.0479(2) Uani 1 1 d . . .
O1 O 0.1916(5) 0.3002(2) 0.27198(10) 0.0778(8) Uani 1 1 d . . .
O2 O 0.8891(4) 0.45704(15) 0.39660(8) 0.0451(5) Uani 1 1 d . . .
N1 N 0.5081(5) 0.3932(2) 0.32539(11) 0.0407(6) Uani 1 1 d . . .
N2 N 0.7488(4) 0.55707(18) 0.31552(9) 0.0341(5) Uani 1 1 d . . .
C1 C 0.0986(7) 0.1502(3) 0.36440(17) 0.0619(9) Uani 1 1 d . . .
C2 C 0.0565(8) 0.0740(3) 0.41014(19) 0.0720(12) Uani 1 1 d . . .
C3 C 0.2130(7) 0.0759(2) 0.46059(16) 0.0530(8) Uani 1 1 d . . .

C4 C 0.4060(7) 0.1556(2) 0.46563(16) 0.0539(8) Uani 1 1 d . . .
C5 C 0.4468(6) 0.2325(3) 0.41992(14) 0.0487(8) Uani 1 1 d . . .
C6 C 0.2920(5) 0.2303(2) 0.36870(13) 0.0396(7) Uani 1 1 d . . .
C7 C 0.3208(6) 0.3086(2) 0.31709(13) 0.0451(7) Uani 1 1 d . . .
C8 C 0.5468(5) 0.4876(2) 0.29221(11) 0.0340(6) Uani 1 1 d . . .
C9 C 0.9061(5) 0.5413(2) 0.36519(11) 0.0330(5) Uani 1 1 d . . .
C10 C 1.1008(5) 0.63068(19) 0.38047(11) 0.0307(5) Uani 1 1 d . . .
C11 C 1.1350(7) 0.7289(2) 0.34832(14) 0.0483(8) Uani 1 1 d . . .
C12 C 1.3237(8) 0.8061(3) 0.36609(15) 0.0574(9) Uani 1 1 d . . .
C13 C 1.4760(6) 0.7872(3) 0.41557(14) 0.0492(8) Uani 1 1 d . . .
C14 C 1.4419(6) 0.6913(2) 0.44859(14) 0.0415(7) Uani 1 1 d . . .
C15 C 1.2584(6) 0.6134(2) 0.43078(12) 0.0372(6) Uani 1 1 d . . .
H1N H 0.609(7) 0.386(2) 0.3542(13) 0.056(10) Uiso 1 1 d . . .
H2N H 0.767(4) 0.6186(18) 0.2929(10) 0.016(6) Uiso 1 1 d . . .
H1 H 0.003(8) 0.148(3) 0.3313(17) 0.089(13) Uiso 1 1 d . . .
H2 H -0.053(9) 0.024(3) 0.4027(18) 0.099(14) Uiso 1 1 d . . .
H3 H 0.186(6) 0.022(2) 0.4928(13) 0.061(9) Uiso 1 1 d . . .
H4 H 0.504(7) 0.164(3) 0.5021(17) 0.092(13) Uiso 1 1 d . . .
H5 H 0.566(7) 0.289(3) 0.4253(13) 0.063(10) Uiso 1 1 d . . .
H11 H 1.044(6) 0.740(2) 0.3163(14) 0.059(10) Uiso 1 1 d . . .
H12 H 1.330(7) 0.870(2) 0.3440(13) 0.072(11) Uiso 1 1 d . . .
H13 H 1.606(7) 0.835(2) 0.4273(12) 0.056(9) Uiso 1 1 d . . .
H14 H 1.539(6) 0.676(2) 0.4817(13) 0.056(9) Uiso 1 1 d . . .
H15 H 1.227(5) 0.548(2) 0.4522(12) 0.046(8) Uiso 1 1 d . . .

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O1 0.0848(18) 0.0995(17) 0.0492(13) 0.0055(13) -0.0301(14) -0.0407(14)
O2 0.0451(11) 0.0474(10) 0.0429(11) 0.0119(9) -0.0153(9) -0.0098(11)
N1 0.0343(13) 0.0540(14) 0.0337(14) 0.0026(12) -0.0074(12) -0.0065(11)
N2 0.0313(12) 0.0425(12) 0.0284(12) 0.0064(10) -0.0006(10) -0.0009(11)
C1 0.060(2) 0.074(2) 0.052(2) -0.0033(19) -0.001(2) -0.027(2)
C2 0.074(3) 0.067(2) 0.075(3) -0.008(2) 0.007(2) -0.038(2)
C3 0.059(2) 0.0482(17) 0.052(2) 0.0008(17) 0.0201(17) -0.0049(16)
C4 0.053(2) 0.0556(18) 0.053(2) 0.0105(16) 0.0003(19) -0.0079(18)
C5 0.0436(19) 0.0524(18) 0.0501(19) 0.0020(16) -0.0051(15) -0.0142(16)
C6 0.0328(15) 0.0467(14) 0.0393(16) -0.0091(13) 0.0033(13) -0.0068(13)
C7 0.0440(19) 0.0553(16) 0.0360(16) -0.0049(15) -0.0058(14) -0.0105(14)
C8 0.0261(13) 0.0464(14) 0.0294(13) -0.0001(12) 0.0056(10) 0.0041(12)
C9 0.0259(12) 0.0451(14) 0.0279(13) 0.0022(12) 0.0022(11) 0.0044(13)
C10 0.0271(13) 0.0370(12) 0.0279(13) -0.0009(11) 0.0035(12) 0.0021(12)
C11 0.0516(19) 0.0545(17) 0.0388(17) 0.0065(15) -0.0055(17) -0.0040(18)
C12 0.074(3) 0.0464(16) 0.052(2) 0.0117(17) -0.0004(19) -0.0173(17)
C13 0.0442(19) 0.0525(19) 0.051(2) -0.0080(16) 0.0062(16) -0.0119(16)
C14 0.0326(17) 0.0481(16) 0.0438(18) -0.0028(14) -0.0077(14) -0.0010(14)
C15 0.0295(15) 0.0410(14) 0.0412(16) 0.0032(14) -0.0023(13) 0.0005(13)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O1 C7 1.203(3) . ?
O2 C9 1.233(3) . ?
N1 C8 1.367(3) . ?
N1 C7 1.399(3) . ?
N1 H1N 0.82(3) . ?
N2 C9 1.375(3) . ?
N2 C8 1.415(3) . ?
N2 H2N 0.90(2) . ?
C1 C6 1.374(4) . ?
C1 C2 1.386(5) . ?
C1 H1 0.88(4) . ?
C2 C3 1.374(5) . ?
C2 H2 0.83(4) . ?
C3 C4 1.369(4) . ?
C3 H3 0.98(3) . ?
C4 C5 1.390(4) . ?
C4 H4 0.96(4) . ?
C5 C6 1.383(4) . ?
C5 H5 0.91(3) . ?
C6 C7 1.493(4) . ?
C9 C10 1.494(3) . ?
C10 C11 1.391(4) . ?
C10 C15 1.390(4) . ?
C11 C12 1.386(4) . ?
C11 H11 0.86(3) . ?
C12 C13 1.363(5) . ?
C12 H12 0.92(3) . ?
C13 C14 1.376(4) . ?
C13 H13 0.91(3) . ?
C14 C15 1.374(4) . ?
C14 H14 0.90(3) . ?
C15 H15 0.93(3) . ?

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C8 N1 H1N 115(2) . . ?
C7 N1 H1N 116(2) . . ?
C9 N2 C8 129.0(2) . . ?
C9 N2 H2N 120.4(14) . . ?
C8 N2 H2N 110.6(14) . . ?
C6 C1 C2 121.3(4) . . ?
C6 C1 H1 118(2) . . ?
C2 C1 H1 121(2) . . ?
C3 C2 C1 120.2(3) . . ?
C3 C2 H2 124(3) . . ?
C1 C2 H2 116(3) . . ?
C4 C3 C2 119.2(3) . . ?
C4 C3 H3 120.2(18) . . ?
C2 C3 H3 120.6(18) . . ?
C3 C4 C5 120.6(3) . . ?
C3 C4 H4 120(2) . . ?
C5 C4 H4 119(2) . . ?
C6 C5 C4 120.6(3) . . ?
C6 C5 H5 119.6(19) . . ?
C4 C5 H5 119.5(19) . . ?
C1 C6 C5 118.1(3) . . ?
C1 C6 C7 117.1(3) . . ?
C5 C6 C7 124.7(2) . . ?
O1 C7 N1 122.5(3) . . ?
O1 C7 C6 122.6(3) . . ?
N1 C7 C6 114.9(2) . . ?
N1 C8 N2 113.1(2) . . ?
N1 C8 S1 128.2(2) . . ?
N2 C8 S1 118.63(19) . . ?
O2 C9 N2 122.0(2) . . ?
O2 C9 C10 120.3(2) . . ?
N2 C9 C10 117.7(2) . . ?
C11 C10 C15 118.1(3) . . ?
C11 C10 C9 125.0(3) . . ?
C15 C10 C9 116.9(2) . . ?
C12 C11 C10 120.3(3) . . ?
C12 C11 H11 120(2) . . ?
C10 C11 H11 119(2) . . ?
C13 C12 C11 120.5(3) . . ?
C13 C12 H12 124(2) . . ?
C11 C12 H12 116(2) . . ?
C12 C13 C14 120.1(3) . . ?
C12 C13 H13 122.1(18) . . ?
C14 C13 H13 117.8(18) . . ?
C15 C14 C13 119.9(3) . . ?
C15 C14 H14 117.8(18) . . ?

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C13 C14 H14 122.3(18) . . ?
C14 C15 C10 121.1(3) . . ?
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C1 C2 C3 C4 1.6(5) . . . . ?
C2 C3 C4 C5 -1.1(5) . . . . ?
C3 C4 C5 C6 0.4(5) . . . . ?
C2 C1 C6 C5 0.6(5) . . . . ?
C2 C1 C6 C7 -179.8(3) . . . . ?
C4 C5 C6 C1 -0.1(5) . . . . ?
C4 C5 C6 C7 -179.7(3) . . . . ?
C8 N1 C7 O1 12.4(5) . . . . ?
C8 N1 C7 C6 -167.1(2) . . . . ?
C1 C6 C7 O1 -3.6(5) . . . . ?
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C1 C6 C7 N1 175.9(3) . . . . ?
C5 C6 C7 N1 -4.6(4) . . . . ?
C7 N1 C8 N2 177.4(3) . . . . ?
C7 N1 C8 S1 -0.4(4) . . . . ?
C9 N2 C8 N1 0.6(3) . . . . ?
C9 N2 C8 S1 178.66(19) . . . . ?
C8 N2 C9 O2 1.4(4) . . . . ?
C8 N2 C9 C10 -178.4(2) . . . . ?
O2 C9 C10 C11 -179.7(3) . . . . ?
N2 C9 C10 C11 0.1(4) . . . . ?
O2 C9 C10 C15 0.2(4) . . . . ?
N2 C9 C10 C15 -179.9(2) . . . . ?
C15 C10 C11 C12 0.7(4) . . . . ?
C9 C10 C11 C12 -179.4(3) . . . . ?
C10 C11 C12 C13 -0.7(5) . . . . ?
C11 C12 C13 C14 -0.5(5) . . . . ?
C12 C13 C14 C15 1.6(4) . . . . ?
C13 C14 C15 C10 -1.5(4) . . . . ?
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C9 C10 C15 C14 -179.5(2) . . . . ?

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N2 H2N O1  0.90(2) 2.62(2) 3.523(3) 178.5(19) 3_655

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data_49



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'N' 'N' 0.0061 0.0033

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'O' 'O' 0.0106 0.0060

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'S' 'S' 0.1246 0.1234

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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'-x, y+1/2, -z+1/2'

'x+1/2, -y+1/2, -z'

'-x, -y, -z'

'x-1/2, y, -z-1/2'

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_cell_angle_beta 90.00

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_computing_cell_refinement       'Bruker SAINT'
_computing_data_reduction        'Bruker SAINT'
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_computing_molecular_graphics    'Bruker SHELXTL'
_computing_publication_material  'Bruker SHELXTL'

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0535P)^2^+1.3875P] where P=(Fo^2^+2Fc^2^)/3'

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_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens difmap

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_refine_ls_extinction_method none

_refine_ls_extinction_coef ?

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_atom_site_fract_z

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O1 O 0.94202(12) 0.12749(18) 0.33323(7) 0.0444(4) Uani 1 1 d . . .

O2 O 0.73032(19) 0.3936(3) 0.19480(10) 0.0901(9) Uani 1 1 d . . .

O3 O 0.56515(17) 0.3968(3) 0.20442(11) 0.0834(8) Uani 1 1 d . . .

O4 O 0.40258(11) 0.15597(16) 0.36404(8) 0.0395(4) Uani 1 1 d . . .

O5 O 0.49076(11) 0.01598(17) 0.41940(7) 0.0391(4) Uani 1 1 d . . .

N1 N 1.13928(12) -0.06916(17) 0.43575(7) 0.0263(4) Uani 1 1 d . . .

N2 N 0.97702(12) -0.14713(17) 0.45765(8) 0.0279(4) Uani 1 1 d . . .

N3 N 0.86282(13) -0.02366(18) 0.39726(8) 0.0274(4) Uani 1 1 d . . .

N4 N 0.65071(19) 0.3556(2) 0.21816(10) 0.0522(6) Uani 1 1 d . . .

N5 N 0.48328(13) 0.09906(18) 0.37831(8) 0.0304(4) Uani 1 1 d . . .

C1 C 1.24399(16) -0.0673(2) 0.44058(10) 0.0306(5) Uani 1 1 d . . .

C2 C 1.29082(17) -0.1563(2) 0.47859(10) 0.0334(5) Uani 1 1 d . . .

C3 C 1.23169(16) -0.2483(2) 0.51265(10) 0.0333(5) Uani 1 1 d . . .

C4 C 1.12690(16) -0.2485(2) 0.50824(10) 0.0308(5) Uani 1 1 d . . .

C5 C 1.07950(15) -0.1562(2) 0.46837(9) 0.0255(4) Uani 1 1 d . . .

C6 C 0.95789(15) -0.0540(2) 0.41624(9) 0.0267(4) Uani 1 1 d . . .

C7 C 0.86215(16) 0.0735(2) 0.35474(9) 0.0317(5) Uani 1 1 d . . .

C8 C 0.75890(16) 0.1206(2) 0.33369(9) 0.0304(5) Uani 1 1 d . . .

C9 C 0.75274(18) 0.2111(2) 0.28545(9) 0.0349(5) Uani 1 1 d . . .

C10 C 0.65728(18) 0.2577(2) 0.26837(9) 0.0355(5) Uani 1 1 d . . .

C11 C 0.56754(17) 0.2219(2) 0.29675(10) 0.0335(5) Uani 1 1 d . . .

C12 C 0.57661(15) 0.1336(2) 0.34475(9) 0.0282(5) Uani 1 1 d . . .

C13 C 0.67008(15) 0.0812(2) 0.36332(9) 0.0271(4) Uani 1 1 d . . .

H1 H 1.2760(17) -0.004(2) 0.4168(10) 0.032(6) Uiso 1 1 d . . .

H2 H 1.3641(19) -0.158(2) 0.4815(10) 0.037(6) Uiso 1 1 d . . .

H3 H 1.2633(18) -0.309(3) 0.5385(10) 0.039(7) Uiso 1 1 d . . .

H4 H 1.0848(17) -0.308(2) 0.5307(10) 0.032(6) Uiso 1 1 d . . .

H9 H 0.8109(19) 0.235(3) 0.2665(11) 0.045(7) Uiso 1 1 d . . .

H11 H 0.5039(17) 0.253(2) 0.2874(10) 0.034(6) Uiso 1 1 d . . .

H13 H 0.6719(17) 0.020(2) 0.3955(10) 0.034(6) Uiso 1 1 d . . .

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O1 0.0281(8) 0.0553(11) 0.0498(10) 0.0219(8) 0.0072(7) 0.0049(7)

O2 0.0785(16) 0.118(2) 0.0736(15) 0.0638(15) 0.0253(13) 0.0246(15)

O3 0.0659(14) 0.0846(16) 0.0998(18) 0.0588(15) -0.0354(13) -0.0084(12)

O4 0.0245(8) 0.0378(9) 0.0563(10) -0.0038(8) -0.0076(7) 0.0036(7)

O5 0.0304(8) 0.0422(9) 0.0447(9) 0.0090(8) 0.0011(7) -0.0013(7)

N1 0.0224(8) 0.0266(9) 0.0300(9) 0.0001(7) 0.0013(7) 0.0015(7)

N2 0.0227(9) 0.0283(9) 0.0327(9) 0.0039(7) 0.0022(7) 0.0019(7)

N3 0.0224(8) 0.0279(9) 0.0319(9) 0.0037(7) 0.0010(7) 0.0044(7)

N4 0.0621(15) 0.0518(14) 0.0426(12) 0.0173(10) -0.0095(11) 0.0035(11)

N5 0.0233(9) 0.0285(9) 0.0395(11) -0.0039(8) -0.0051(7) -0.0001(7)

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C2 0.0233(11) 0.0387(13) 0.0381(12) -0.0043(10) -0.0024(9) 0.0016(9)

C3 0.0325(11) 0.0320(12) 0.0355(12) -0.0017(10) -0.0075(9) 0.0034(9)

C4 0.0304(11) 0.0271(10) 0.0349(12) 0.0027(9) -0.0002(9) -0.0002(9)

C5 0.0237(10) 0.0240(10) 0.0288(10) -0.0018(8) 0.0012(8) 0.0000(8)

C6 0.0241(10) 0.0267(11) 0.0291(11) -0.0020(8) 0.0056(8) -0.0003(8)

C7 0.0267(11) 0.0362(12) 0.0322(11) 0.0037(9) 0.0045(9) 0.0048(9)

C8 0.0293(11) 0.0321(11) 0.0298(11) 0.0005(9) -0.0005(9) 0.0055(9)

C9 0.0348(12) 0.0399(13) 0.0300(11) 0.0061(10) 0.0039(10) 0.0031(10)

C10 0.0456(13) 0.0321(12) 0.0288(11) 0.0070(9) -0.0067(9) 0.0028(10)

C11 0.0312(12) 0.0325(12) 0.0370(12) 0.0010(9) -0.0114(10) 0.0025(9)

C12 0.0261(10) 0.0282(11) 0.0304(11) -0.0032(8) -0.0044(8) 0.0004(8)

C13 0.0281(11) 0.0265(10) 0.0266(10) 0.0016(9) -0.0030(8) 0.0030(8)

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All esds (except the esd in the dihedral angle between two l.s. planes)

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 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O3 N4 1.221(3) . ?
O4 N5 1.226(2) . ?
O5 N5 1.228(2) . ?
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N1 C1 1.365(3) . ?
N2 C6 1.319(3) . ?
N2 C5 1.357(3) . ?
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N3 C7 1.340(3) . ?
N4 C10 1.476(3) . ?
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N5 C12 1.468(3) . ?

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C1 H1 0.91(2) . ?

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C3 C4 1.366(3) . ?

C3 H3 0.92(2) . ?

C4 C5 1.406(3) . ?

C4 H4 0.94(2) . ?

C7 C8 1.494(3) . ?

C8 C13 1.386(3) . ?

C8 C9 1.397(3) . ?

C9 C10 1.374(3) . ?

C9 H9 0.90(2) . ?

C10 C11 1.374(3) . ?

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C11 H11 0.90(2) . ?

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N1 S1 C6 85.94(9) . . ?

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C6 N2 C5 110.79(17) . . ?

C6 N3 C7 112.74(17) . . ?

O2 N4 O3 124.5(2) . . ?

O2 N4 C10 118.3(2) . . ?

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C2 C1 N1 119.3(2) . . ?

C2 C1 H1 126.1(14) . . ?

N1 C1 H1 114.6(14) . . ?

C1 C2 C3 120.0(2) . . ?

C1 C2 H2 120.1(14) . . ?

C3 C2 H2 119.9(14) . . ?

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C4 C3 H3 119.4(15) . . ?

C2 C3 H3 120.2(15) . . ?

C3 C4 C5 118.9(2) . . ?

C3 C4 H4 122.9(14) . . ?

C5 C4 H4 118.3(14) . . ?

N2 C5 N1 115.16(17) . . ?

N2 C5 C4 125.77(19) . . ?

N1 C5 C4 119.04(18) . . ?

N2 C6 N3 123.24(18) . . ?

N2 C6 S1 115.90(15) . . ?

N3 C6 S1 120.86(15) . . ?

O1 C7 N3 124.00(19) . . ?

O1 C7 C8 119.55(19) . . ?

N3 C7 C8 116.43(18) . . ?

C13 C8 C9 119.88(19) . . ?

C13 C8 C7 120.80(18) . . ?

C9 C8 C7 119.24(19) . . ?

C10 C9 C8 118.3(2) . . ?

C10 C9 H9 122.8(16) . . ?

C8 C9 H9 118.9(16) . . ?

C11 C10 C9 123.6(2) . . ?

C11 C10 N4 117.9(2) . . ?

C9 C10 N4 118.4(2) . . ?

C10 C11 C12 116.55(19) . . ?

C10 C11 H11 125.8(14) . . ?

C12 C11 H11 117.6(15) . . ?

C11 C12 C13 122.5(2) . . ?

C11 C12 N5 118.21(18) . . ?

C13 C12 N5 119.22(18) . . ?

C12 C13 C8 119.12(19) . . ?

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C8 C13 H13 121.7(14) . . ?

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S1 N1 C1 C2 -176.19(16) . . . . ?

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C2 C3 C4 C5 0.9(3) . . . . ?

C6 N2 C5 N1 0.7(3) . . . . ?

C6 N2 C5 C4 -177.6(2) . . . . ?

C1 N1 C5 N2 -178.87(18) . . . . ?

S1 N1 C5 N2 -1.4(2) . . . . ?

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S1 N1 C5 C4 176.94(15) . . . . ?

C3 C4 C5 N2 177.8(2) . . . . ?

C3 C4 C5 N1 -0.4(3) . . . . ?

C5 N2 C6 N3 -179.69(19) . . . . ?

C5 N2 C6 S1 0.4(2) . . . . ?

C7 N3 C6 N2 -179.62(19) . . . . ?

C7 N3 C6 S1 0.3(3) . . . . ?

N1 S1 C6 N2 -1.00(16) . . . . ?

N1 S1 C6 N3 179.10(17) . . . . ?

C6 N3 C7 O1 2.4(3) . . . . ?

C6 N3 C7 C8 -176.13(18) . . . . ?

O1 C7 C8 C13 -168.8(2) . . . . ?

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O1 C7 C8 C9 7.8(3) . . . . ?

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C7 C8 C9 C10 -177.3(2) . . . . ?

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O4 N5 C12 C11 -3.8(3) . . . . ?

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O4 N5 C12 C13 173.97(19) . . . . ?

O5 N5 C12 C13 -5.3(3) . . . . ?

C11 C12 C13 C8 1.4(3) . . . . ?

N5 C12 C13 C8 -176.21(18) . . . . ?

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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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O1 O 0.07935(13) 0.62429(6) 0.07880(3) 0.0258(2) Uani 1 1 d . . .
O2 O 0.17264(13) 0.97030(6) -0.06602(3) 0.0256(2) Uani 1 1 d . . .
N1 N 0.05254(14) 0.52217(8) 0.21433(4) 0.0227(2) Uani 1 1 d . . .
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N3 N 0.13546(16) 0.73595(7) 0.13810(4) 0.0254(2) Uani 1 1 d . . .
C1 C -0.0168(2) 0.35881(10) 0.19561(6) 0.0320(3) Uani 1 1 d . . .
C2 C 0.01189(18) 0.43516(9) 0.23249(5) 0.0253(3) Uani 1 1 d . . .
C3 C 0.0020(2) 0.42416(10) 0.28368(5) 0.0297(3) Uani 1 1 d . . .
C4 C 0.03583(19) 0.49947(11) 0.31585(5) 0.0310(3) Uani 1 1 d . . .
C5 C 0.0800(2) 0.58524(11) 0.29695(5) 0.0303(3) Uani 1 1 d . . .
C6 C 0.08670(18) 0.59687(9) 0.24443(5) 0.0252(3) Uani 1 1 d . . .
C7 C 0.11205(18) 0.66702(9) 0.17105(5) 0.0238(3) Uani 1 1 d . . .
C8 C 0.11364(17) 0.70819(8) 0.09014(5) 0.0218(2) Uani 1 1 d . . .
C9 C 0.12950(17) 0.77907(8) 0.05013(4) 0.0207(2) Uani 1 1 d . . .
C10 C 0.07442(17) 0.75778(9) 0.00106(5) 0.0224(2) Uani 1 1 d . . .
C11 C 0.08979(18) 0.82301(9) -0.03671(5) 0.0232(3) Uani 1 1 d . . .
C12 C 0.16275(17) 0.91108(8) -0.02639(5) 0.0213(2) Uani 1 1 d . . .
C13 C 0.21724(17) 0.93357(8) 0.02255(5) 0.0218(2) Uani 1 1 d . . .
C14 C 0.19912(17) 0.86755(8) 0.06026(5) 0.0221(3) Uani 1 1 d . . .
C15 C 0.2593(2) 1.05828(9) -0.05709(5) 0.0278(3) Uani 1 1 d . . .
H1A H -0.058(3) 0.3054(15) 0.2125(7) 0.053(5) Uiso 1 1 d . . .
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H1B H -0.111(3) 0.3753(14) 0.1711(8) 0.053(5) Uiso 1 1 d . . .
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H3 H -0.027(2) 0.3653(13) 0.2961(6) 0.037(4) Uiso 1 1 d . . .
H4 H 0.029(2) 0.4943(12) 0.3527(6) 0.034(4) Uiso 1 1 d . . .
H5 H 0.105(2) 0.6364(12) 0.3173(6) 0.032(4) Uiso 1 1 d . . .
H10 H 0.020(2) 0.7001(11) -0.0055(6) 0.026(4) Uiso 1 1 d . . .
H11 H 0.052(2) 0.8097(11) -0.0693(6) 0.028(4) Uiso 1 1 d . . .
H13 H 0.265(2) 0.9932(11) 0.0308(6) 0.027(4) Uiso 1 1 d . . .
H14 H 0.236(2) 0.8840(10) 0.0943(6) 0.027(4) Uiso 1 1 d . . .
H15A H 0.251(2) 1.0909(11) -0.0888(7) 0.037(4) Uiso 1 1 d . . .
H15B H 0.391(2) 1.0508(10) -0.0467(6) 0.029(4) Uiso 1 1 d . . .
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O1 0.0343(5) 0.0194(4) 0.0235(4) -0.0001(3) -0.0004(4) -0.0018(4)
O2 0.0306(5) 0.0233(4) 0.0228(4) 0.0032(3) -0.0005(4) -0.0023(4)
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N2 0.0368(6) 0.0242(5) 0.0225(5) -0.0007(4) -0.0009(5) 0.0001(5)
N3 0.0335(6) 0.0202(5) 0.0224(5) -0.0002(4) 0.0000(4) -0.0016(4)
C1 0.0421(8) 0.0243(7) 0.0295(7) 0.0042(6) 0.0027(6) -0.0016(6)
C2 0.0232(6) 0.0242(6) 0.0286(7) 0.0044(5) 0.0011(5) 0.0030(5)
C3 0.0286(7) 0.0321(7) 0.0283(7) 0.0082(6) 0.0020(5) 0.0030(6)
C4 0.0305(7) 0.0404(8) 0.0222(6) 0.0060(6) -0.0003(5) 0.0066(6)
C5 0.0341(7) 0.0340(7) 0.0227(6) -0.0018(5) -0.0020(5) 0.0036(6)
C6 0.0254(6) 0.0262(6) 0.0239(6) -0.0009(5) -0.0006(5) 0.0025(5)
C7 0.0254(6) 0.0198(6) 0.0264(6) -0.0033(5) -0.0009(5) 0.0003(5)
C8 0.0205(6) 0.0209(6) 0.0239(6) -0.0003(5) 0.0009(5) 0.0010(5)
C9 0.0200(5) 0.0201(6) 0.0221(6) 0.0001(4) 0.0016(4) 0.0015(4)
C10 0.0218(6) 0.0199(6) 0.0255(6) -0.0031(5) 0.0002(5) -0.0007(5)
C11 0.0253(6) 0.0246(6) 0.0198(6) -0.0032(5) -0.0018(5) -0.0002(5)
C12 0.0193(5) 0.0218(6) 0.0227(6) 0.0015(5) 0.0018(4) 0.0024(5)
C13 0.0224(6) 0.0185(5) 0.0245(6) -0.0026(5) 0.0001(5) -0.0005(5)
C14 0.0235(6) 0.0220(6) 0.0210(6) -0.0020(4) -0.0009(5) 0.0014(5)
C15 0.0299(7) 0.0233(6) 0.0303(7) 0.0036(5) 0.0034(6) -0.0026(5)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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S1 O1 2.1419(10) . ?
O1 C8 1.2680(15) . ?
O2 C12 1.3570(15) . ?
O2 C15 1.4298(16) . ?
N1 C6 1.3622(17) . ?
N1 C2 1.3728(16) . ?
N2 C7 1.3220(17) . ?
N2 C6 1.3512(17) . ?
N3 C7 1.3338(16) . ?
N3 C8 1.3457(16) . ?
C1 C2 1.4867(19) . ?
C1 H1A 0.94(2) . ?
C1 H1B 0.97(2) . ?
C1 H1C 0.98(2) . ?
C2 C3 1.3723(19) . ?
C3 C4 1.402(2) . ?
C3 H3 0.932(18) . ?
C4 C5 1.369(2) . ?
C4 H4 0.983(16) . ?
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C8 C9 1.4779(17) . ?
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C9 C10 1.3975(17) . ?
C10 C11 1.3790(18) . ?
C10 H10 0.934(16) . ?
C11 C12 1.3980(17) . ?
C11 H11 0.927(16) . ?
C12 C13 1.3969(17) . ?
C13 C14 1.3872(17) . ?
C13 H13 0.951(15) . ?
C14 H14 0.973(15) . ?
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C12 O2 C15 116.70(10) . . ?
C6 N1 C2 123.41(11) . . ?
C6 N1 S1 111.43(9) . . ?
C2 N1 S1 125.14(9) . . ?
C7 N2 C6 111.10(11) . . ?
C7 N3 C8 112.80(11) . . ?
C2 C1 H1A 109.5(12) . . ?
C2 C1 H1B 111.1(12) . . ?
H1A C1 H1B 107.5(17) . . ?
C2 C1 H1C 112.0(11) . . ?
H1A C1 H1C 108.5(16) . . ?
H1B C1 H1C 108.0(16) . . ?
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N1 C2 C1 118.09(12) . . ?
C3 C2 C1 124.19(13) . . ?
C2 C3 C4 120.48(13) . . ?
C2 C3 H3 117.9(11) . . ?
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C5 C4 C3 120.83(13) . . ?
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C3 C4 H4 122.7(10) . . ?
C4 C5 C6 118.63(13) . . ?
C4 C5 H5 123.0(10) . . ?
C6 C5 H5 118.4(10) . . ?
N2 C6 N1 115.71(11) . . ?
N2 C6 C5 125.37(13) . . ?
N1 C6 C5 118.90(12) . . ?
N2 C7 N3 123.95(12) . . ?
N2 C7 S1 116.12(10) . . ?
N3 C7 S1 119.93(10) . . ?
O1 C8 N3 122.03(11) . . ?
O1 C8 C9 120.02(11) . . ?
N3 C8 C9 117.95(11) . . ?
C14 C9 C10 118.82(11) . . ?
C14 C9 C8 121.23(11) . . ?
C10 C9 C8 119.95(11) . . ?
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C9 C10 H10 119.2(9) . . ?
C10 C11 C12 120.23(11) . . ?
C10 C11 H11 121.1(10) . . ?
C12 C11 H11 118.7(10) . . ?
O2 C12 C11 115.85(11) . . ?
O2 C12 C13 124.30(11) . . ?
C11 C12 C13 119.85(11) . . ?
C14 C13 C12 119.26(11) . . ?
C14 C13 H13 119.0(9) . . ?
C12 C13 H13 121.8(9) . . ?
C13 C14 C9 121.27(11) . . ?
C13 C14 H14 118.7(9) . . ?

C9 C14 H14 120.0(9) . . ?
O2 C15 H15A 104.9(10) . . ?
O2 C15 H15B 111.4(9) . . ?
H15A C15 H15B 110.8(13) . . ?
O2 C15 H15C 111.7(9) . . ?
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O1 S1 N1 C2 173.77(15) . . . . ?
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C7 N2 C6 C5 -177.71(13) . . . . ?
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C4 C5 C6 N2 177.67(13) . . . . ?
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C6 N2 C7 S1 -0.94(15) . . . . ?
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S1 O1 C8 N3 1.71(14) . . . . ?
S1 O1 C8 C9 -177.86(9) . . . . ?
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C14 C9 C10 C11 0.40(18) . . . . ?
C8 C9 C10 C11 -179.50(11) . . . . ?
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C15 O2 C12 C11 -175.58(11) . . . . ?
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#
#               Cambridge Crystallographic Data Centre
#                           CCDC
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C12 C 0.5347(4) 0.4486(4) 0.6653(2)
C13 C 0.7093(4) 0.5296(4) 0.7448(2)
C14 C 0.1597(4) 0.3517(4) 0.5989(2)
F1 F 0.2011(3) 0.4023(5) 0.51174(16)
F2 F 0.0147(4) 0.4095(4) 0.61655(17)
F3 F 0.0665(4) 0.1588(3) 0.5781(2)
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H2 H 1.846(6) 1.086(5) 1.329(3)
H3 H 1.675(6) 1.158(5) 1.447(3)
H4 H 1.324(5) 1.071(5) 1.386(3)
H9 H 0.494(5) 0.622(5) 0.933(3)
H10 H 0.194(5) 0.493(5) 0.802(3)
H12 H 0.545(5) 0.405(5) 0.597(3)
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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_atom_site_fract_z

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N1 N 0.55397(15) -0.02172(6) 0.73894(11) 0.0263(2) Uani 1 1 d . . .

N2 N 0.86368(14) -0.01417(6) 0.69958(11) 0.0249(2) Uani 1 1 d . . .

N3 N 1.00824(14) 0.06866(6) 0.87043(11) 0.0248(2) Uani 1 1 d . . .

C1 C 0.37190(19) -0.04437(8) 0.71399(15) 0.0317(3) Uani 1 1 d . . .

C2 C 0.3234(2) -0.09075(8) 0.60368(15) 0.0351(3) Uani 1 1 d . . .

C3 C 0.4606(2) -0.11405(8) 0.51900(15) 0.0333(3) Uani 1 1 d . . .

C4 C 0.64462(18) -0.09157(7) 0.54423(13) 0.0282(3) Uani 1 1 d . . .

C5 C 0.69099(18) -0.04326(7) 0.65987(13) 0.0249(3) Uani 1 1 d . . .

C6 C 0.7940(2) -0.11574(9) 0.45627(15) 0.0347(3) Uani 1 1 d . . .

C7 C 0.85942(17) 0.03107(7) 0.80859(13) 0.0238(2) Uani 1 1 d . . .

C8 C 0.96330(18) 0.11130(7) 0.97706(13) 0.0255(3) Uani 1 1 d . . .

C9 C 1.11005(18) 0.15828(7) 1.05555(12) 0.0257(3) Uani 1 1 d . . .

C10 C 1.29076(19) 0.16171(8) 1.01635(14) 0.0303(3) Uani 1 1 d . . .

C11 C 1.4267(2) 0.20573(8) 1.09141(16) 0.0357(3) Uani 1 1 d . . .

C12 C 1.3817(2) 0.24709(8) 1.20572(15) 0.0359(3) Uani 1 1 d . . .

C13 C 1.2018(2) 0.24402(8) 1.24517(14) 0.0358(3) Uani 1 1 d . . .

C14 C 1.0662(2) 0.19976(8) 1.17114(14) 0.0310(3) Uani 1 1 d . . .

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H2 H 0.197(3) -0.1057(10) 0.5845(17) 0.042(4) Uiso 1 1 d . . .

H3 H 0.424(2) -0.1450(10) 0.4419(18) 0.039(4) Uiso 1 1 d . . .

H6A H 0.882(2) -0.1531(10) 0.5061(18) 0.044(5) Uiso 1 1 d . . .

H6B H 0.737(3) -0.1405(11) 0.376(2) 0.057(5) Uiso 1 1 d . . .

H6C H 0.872(3) -0.0755(12) 0.4292(19) 0.052(5) Uiso 1 1 d . . .

H10 H 1.320(2) 0.1332(9) 0.9379(17) 0.035(4) Uiso 1 1 d . . .

H11 H 1.554(3) 0.2072(10) 1.0650(18) 0.047(5) Uiso 1 1 d . . .

H12 H 1.478(2) 0.2777(9) 1.2568(17) 0.038(4) Uiso 1 1 d . . .

H13 H 1.174(2) 0.2722(10) 1.3218(19) 0.044(5) Uiso 1 1 d . . .

H14 H 0.942(2) 0.1949(9) 1.1974(16) 0.034(4) Uiso 1 1 d . . .

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O1 0.0297(5) 0.0363(5) 0.0310(5) -0.0023(4) 0.0078(4) 0.0008(4)

N1 0.0233(5) 0.0290(5) 0.0267(5) 0.0058(4) 0.0032(4) -0.0001(4)

N2 0.0232(5) 0.0257(5) 0.0259(5) 0.0013(4) 0.0034(4) 0.0004(4)

N3 0.0241(5) 0.0256(5) 0.0250(5) 0.0008(4) 0.0042(4) -0.0001(4)

C1 0.0225(6) 0.0387(7) 0.0342(7) 0.0100(5) 0.0042(5) -0.0010(5)

C2 0.0248(7) 0.0402(8) 0.0393(7) 0.0091(6) -0.0015(5) -0.0051(6)

C3 0.0325(7) 0.0317(7) 0.0340(7) 0.0023(6) -0.0050(6) -0.0034(5)

C4 0.0288(6) 0.0261(6) 0.0289(6) 0.0037(5) -0.0008(5) 0.0013(5)

C5 0.0241(6) 0.0245(6) 0.0262(6) 0.0062(5) 0.0031(5) 0.0020(4)

C6 0.0335(8) 0.0373(8) 0.0329(7) -0.0064(6) 0.0017(6) 0.0020(6)

C7 0.0229(6) 0.0248(6) 0.0245(6) 0.0061(4) 0.0063(5) 0.0026(4)

C8 0.0274(6) 0.0248(6) 0.0249(6) 0.0051(5) 0.0054(5) 0.0030(5)

C9 0.0322(7) 0.0217(6) 0.0233(6) 0.0031(4) 0.0035(5) 0.0030(5)

C10 0.0324(7) 0.0281(6) 0.0311(7) -0.0040(5) 0.0059(5) 0.0011(5)

C11 0.0333(7) 0.0326(7) 0.0412(8) -0.0035(6) 0.0046(6) -0.0020(6)

C12 0.0433(8) 0.0285(7) 0.0342(7) -0.0021(5) -0.0032(6) -0.0026(6)

C13 0.0517(9) 0.0293(7) 0.0264(6) -0.0033(5) 0.0048(6) 0.0021(6)

C14 0.0378(8) 0.0291(7) 0.0271(6) 0.0010(5) 0.0076(5) 0.0033(5)

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All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles

and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

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S1 C7 1.7718(13) . ?

S1 O1 2.0980(10) . ?

O1 C8 1.2741(16) . ?

N1 C5 1.3606(16) . ?

N1 C1 1.3629(17) . ?

N2 C7 1.3231(16) . ?

N2 C5 1.3583(16) . ?

N3 C8 1.3410(16) . ?

N3 C7 1.3420(17) . ?

C1 C2 1.358(2) . ?

C1 H1 0.940(17) . ?

C2 C3 1.405(2) . ?

C2 H2 0.943(18) . ?

C3 C4 1.3757(19) . ?

C3 H3 0.936(17) . ?

C4 C5 1.4151(18) . ?

C4 C6 1.4976(19) . ?

C6 H6A 1.001(18) . ?

C6 H6B 0.94(2) . ?

C6 H6C 0.96(2) . ?

C8 C9 1.4834(18) . ?

C9 C10 1.3898(19) . ?

C9 C14 1.3971(18) . ?

C10 C11 1.389(2) . ?

C10 H10 0.951(16) . ?

C11 C12 1.388(2) . ?

C11 H11 0.973(19) . ?

C12 C13 1.385(2) . ?

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C14 H14 0.956(16) . ?

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N1 S1 O1 166.84(5) . . ?

C7 S1 O1 81.09(5) . . ?

C8 O1 S1 105.38(8) . . ?

C5 N1 C1 123.72(12) . . ?

C5 N1 S1 111.96(9) . . ?

C1 N1 S1 124.29(10) . . ?

C7 N2 C5 110.79(11) . . ?

C8 N3 C7 111.94(11) . . ?

C2 C1 N1 118.46(13) . . ?

C2 C1 H1 126.2(10) . . ?

N1 C1 H1 115.3(10) . . ?

C1 C2 C3 119.61(13) . . ?

C1 C2 H2 118.9(10) . . ?

C3 C2 H2 121.5(10) . . ?

C4 C3 C2 122.09(13) . . ?

C4 C3 H3 119.2(10) . . ?

C2 C3 H3 118.7(10) . . ?

C3 C4 C5 117.02(12) . . ?

C3 C4 C6 123.29(13) . . ?

C5 C4 C6 119.69(12) . . ?

N2 C5 N1 115.35(11) . . ?

N2 C5 C4 125.53(12) . . ?

N1 C5 C4 119.11(12) . . ?

C4 C6 H6A 111.8(10) . . ?

C4 C6 H6B 108.8(12) . . ?

H6A C6 H6B 106.4(15) . . ?

C4 C6 H6C 114.5(11) . . ?

H6A C6 H6C 105.3(15) . . ?

H6B C6 H6C 109.7(16) . . ?

N2 C7 N3 124.56(11) . . ?

N2 C7 S1 116.10(9) . . ?

N3 C7 S1 119.34(9) . . ?

O1 C8 N3 122.24(12) . . ?

O1 C8 C9 118.43(11) . . ?

N3 C8 C9 119.33(11) . . ?

C10 C9 C14 119.31(12) . . ?

C10 C9 C8 121.20(11) . . ?

C14 C9 C8 119.49(12) . . ?

C11 C10 C9 120.44(13) . . ?

C11 C10 H10 120.5(10) . . ?

C9 C10 H10 119.0(10) . . ?

C12 C11 C10 119.91(14) . . ?

C12 C11 H11 119.8(11) . . ?

C10 C11 H11 120.3(11) . . ?

C13 C12 C11 119.94(13) . . ?

C13 C12 H12 121.2(10) . . ?

C11 C12 H12 118.9(10) . . ?

C12 C13 C14 120.33(13) . . ?

C12 C13 H13 118.7(11) . . ?

C14 C13 H13 121.0(11) . . ?

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O1 S1 N1 C5 3.7(3) . . . . ?

C7 S1 N1 C1 -178.66(11) . . . . ?

O1 S1 N1 C1 -174.48(17) . . . . ?

C5 N1 C1 C2 -0.36(19) . . . . ?

S1 N1 C1 C2 177.64(10) . . . . ?

N1 C1 C2 C3 0.1(2) . . . . ?

C1 C2 C3 C4 0.2(2) . . . . ?

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C2 C3 C4 C6 179.72(13) . . . . ?

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C7 N2 C5 C4 177.71(11) . . . . ?

C1 N1 C5 N2 179.16(11) . . . . ?

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S1 N1 C5 C4 -177.87(9) . . . . ?

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C5 N2 C7 N3 -179.30(11) . . . . ?

C5 N2 C7 S1 0.64(13) . . . . ?

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N1 S1 C7 N3 179.83(10) . . . . ?

O1 S1 C7 N3 0.79(9) . . . . ?

S1 O1 C8 N3 0.09(14) . . . . ?

S1 O1 C8 C9 179.17(9) . . . . ?

C7 N3 C8 O1 0.49(17) . . . . ?

C7 N3 C8 C9 -178.58(10) . . . . ?

O1 C8 C9 C10 -175.95(11) . . . . ?

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O1 C8 C9 C14 4.16(17) . . . . ?

N3 C8 C9 C14 -176.73(11) . . . . ?

C14 C9 C10 C11 0.2(2) . . . . ?

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C9 C10 C11 C12 -0.5(2) . . . . ?

C10 C11 C12 C13 0.4(2) . . . . ?

C11 C12 C13 C14 0.1(2) . . . . ?

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
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N1 N 0.37421(14) -0.13187(14) -0.11162(8) 0.0373(3) Uani 1 1 d . . .
N2 N 0.97825(13) 0.12945(12) -0.09007(7) 0.0320(3) Uani 1 1 d . . .
N3 N 1.13051(13) 0.32606(12) -0.05304(7) 0.0303(2) Uani 1 1 d . . .
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C3 C 0.11996(18) 0.01110(18) -0.29105(10) 0.0456(4) Uani 1 1 d . . .
C4 C 0.23072(19) 0.10255(18) -0.32007(10) 0.0444(4) Uani 1 1 d . . .
C5 C 0.38116(17) 0.11022(16) -0.28094(9) 0.0363(3) Uani 1 1 d . . .
C6 C 0.42121(15) 0.02505(14) -0.21065(8) 0.0297(3) Uani 1 1 d . . .
C7 C 0.56062(15) 0.01032(14) -0.15385(8) 0.0305(3) Uani 1 1 d . . .
C8 C 0.52563(17) -0.08443(15) -0.09474(9) 0.0348(3) Uani 1 1 d . . .
C9 C 0.71167(16) 0.08794(16) -0.15887(9) 0.0349(3) Uani 1 1 d . . .
C10 C 0.83885(15) 0.04005(14) -0.09246(9) 0.0327(3) Uani 1 1 d . . .
C11 C 0.99871(15) 0.25324(13) -0.04779(8) 0.0284(3) Uani 1 1 d . . .
C12 C 1.24784(16) 0.28749(17) -0.10626(9) 0.0355(3) Uani 1 1 d . . .
C13 C 1.3823(2) 0.3910(2) -0.09501(16) 0.0592(5) Uani 1 1 d . . .
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H4 H 0.200(2) 0.157(2) -0.3656(12) 0.058(5) Uiso 1 1 d . . .
H5 H 0.4577(19) 0.1731(18) -0.3021(10) 0.041(4) Uiso 1 1 d . . .
H8 H 0.5858(18) -0.1170(18) -0.0485(10) 0.038(4) Uiso 1 1 d . . .
H9A H 0.748(2) 0.076(2) -0.2122(11) 0.052(5) Uiso 1 1 d . . .
H9B H 0.6942(18) 0.1925(18) -0.1539(10) 0.038(4) Uiso 1 1 d . . .
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H12B H 1.2020(18) 0.2899(17) -0.1613(10) 0.036(4) Uiso 1 1 d . . .
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H13B H 1.463(3) 0.368(3) -0.1332(14) 0.083(7) Uiso 1 1 d . . .
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N3 0.0319(6) 0.0256(6) 0.0349(6) -0.0064(5) 0.0105(5) -0.0050(4)
C1 0.0342(7) 0.0297(6) 0.0344(7) -0.0098(5) 0.0115(5) -0.0046(5)
C2 0.0327(7) 0.0395(8) 0.0487(8) -0.0161(7) 0.0115(6) -0.0077(6)
C3 0.0347(8) 0.0528(9) 0.0480(9) -0.0179(7) -0.0004(6) 0.0012(7)
C4 0.0472(9) 0.0495(9) 0.0356(8) -0.0032(7) 0.0010(7) 0.0072(7)
C5 0.0387(7) 0.0380(7) 0.0332(7) -0.0022(6) 0.0086(6) 0.0002(6)
C6 0.0304(6) 0.0297(6) 0.0303(6) -0.0070(5) 0.0090(5) -0.0027(5)
C7 0.0313(7) 0.0297(6) 0.0314(6) -0.0027(5) 0.0078(5) -0.0042(5)
C8 0.0376(7) 0.0336(7) 0.0336(7) 0.0001(5) 0.0055(6) -0.0066(6)
C9 0.0333(7) 0.0362(8) 0.0360(7) 0.0027(6) 0.0074(6) -0.0080(6)
C10 0.0319(7) 0.0244(6) 0.0418(7) -0.0034(5) 0.0045(6) -0.0039(5)

C11 0.0306(6) 0.0250(6) 0.0298(6) 0.0007(5) 0.0044(5) -0.0016(5)
C12 0.0309(7) 0.0370(7) 0.0400(8) -0.0069(6) 0.0103(6) -0.0015(6)
C13 0.0453(10) 0.0493(10) 0.0887(15) -0.0171(10) 0.0319(10) -0.0137(8)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 C10 1.4588(17) . ?
N2 H2N 0.880(17) . ?
N3 C11 1.3355(16) . ?
N3 C12 1.4544(17) . ?
N3 H3N 0.826(18) . ?
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C2 C3 1.377(2) . ?
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C2 C3 H3 119.8(11) . . ?
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C5 C4 C3 121.23(15) . . ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
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N2 N 0.11411(14) 0.20465(18) 0.3769(2) 0.0303(5) Uani 1 1 d . . .
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C7 C 0.23055(15) 0.10122(19) 0.6695(2) 0.0277(5) Uani 1 1 d . . .
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C9 C 0.26184(17) 0.1513(2) 0.5420(3) 0.0324(6) Uani 1 1 d . . .
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H16B H -0.450(3) 0.300(4) -0.133(5) 0.115(16) Uiso 1 1 d . . .
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N2 0.0382(13) 0.0315(12) 0.0204(11) -0.0065(9) 0.0054(9) 0.0009(9)
N3 0.0372(13) 0.0468(14) 0.0264(12) -0.0086(11) 0.0059(10) 0.0027(11)
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C2 0.060(2) 0.0363(15) 0.0318(15) 0.0055(12) 0.0161(15) 0.0079(14)
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C8 0.0338(15) 0.0283(13) 0.0284(13) -0.0020(10) 0.0071(12) 0.0009(11)
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C10 0.0372(15) 0.0362(15) 0.0235(13) -0.0035(11) 0.0088(11) 0.0002(12)
C11 0.0344(14) 0.0275(12) 0.0222(12) 0.0011(9) 0.0106(11) -0.0048(10)
C12 0.0389(16) 0.057(2) 0.0313(15) 0.0009(14) 0.0037(13) 0.0055(14)
C13 0.0393(16) 0.0380(16) 0.0399(16) -0.0060(13) 0.0086(13) 0.0014(12)
C14 0.0415(17) 0.0473(19) 0.0471(18) -0.0004(15) 0.0033(14) 0.0003(14)
C15 0.0430(19) 0.074(3) 0.065(2) -0.012(2) 0.0068(17) 0.0033(17)
C16 0.042(2) 0.084(3) 0.091(3) -0.009(3) -0.004(2) 0.003(2)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

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N2 C11 1.328(3) . ?
N2 C10 1.459(3) . ?
N2 H2N 0.76(3) . ?
N3 C11 1.338(3) . ?
N3 C12 1.458(3) . ?
N3 H3N 0.79(3) . ?
C1 C2 1.393(3) . ?
C1 C6 1.405(3) . ?
C2 C3 1.372(4) . ?
C2 H2 0.92(3) . ?
C3 C4 1.394(4) . ?
C3 H3 0.97(3) . ?
C4 C5 1.372(4) . ?
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C5 C6 1.398(3) . ?
C5 H5 0.94(3) . ?
C6 C7 1.440(3) . ?
C7 C8 1.362(3) . ?
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C8 H8 0.95(2) . ?
C9 C10 1.514(3) . ?
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C10 H10A 0.99(3) . ?
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C14 C15 1.505(4) . ?
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C15 C16 1.515(5) . ?
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C2 C3 C4 121.7(3) . . ?
C2 C3 H3 118.4(17) . . ?
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C5 C4 C3 120.9(3) . . ?
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C8 C7 C6 105.8(2) . . ?
C8 C7 C9 129.6(2) . . ?
C6 C7 C9 124.6(2) . . ?
C7 C8 N1 110.2(2) . . ?
C7 C8 H8 131.1(14) . . ?
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C7 C9 C10 115.7(2) . . ?
C7 C9 H9A 108.6(14) . . ?
C10 C9 H9A 110.6(13) . . ?
C7 C9 H9B 108.5(13) . . ?
C10 C9 H9B 107.0(14) . . ?
H9A C9 H9B 106.0(18) . . ?
N2 C10 C9 111.4(2) . . ?
N2 C10 H10A 110.9(14) . . ?
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C9 C10 H10B 110.6(14) . . ?
H10A C10 H10B 110(2) . . ?
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C4 C5 C6 C1 -0.6(4) . . . . ?

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N3 H3N S1  0.79(3) 2.74(3) 3.500(2) 161(3) 4_566
N1 H1N S1  0.80(2) 2.61(3) 3.408(2) 177(2) 3_556

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 '-x, -y, -z'

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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Cl2 Cl 0.66436(6) 0.45378(5) 0.70274(5) 0.04702(15) Uani 1 1 d . . .
S1 S 0.75615(5) -0.20602(4) -0.11224(4) 0.03433(12) Uani 1 1 d . . .
S2 S 0.01787(6) 0.90363(5) 0.21368(4) 0.04386(14) Uani 1 1 d . . .
O1 O 0.66837(14) 0.19740(11) 0.08330(11) 0.0353(3) Uani 1 1 d . . .
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N3 N 0.78898(17) 0.01834(13) 0.04978(13) 0.0281(3) Uani 1 1 d . . .
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C9 C 0.85632(19) 0.33008(16) 0.29349(15) 0.0293(4) Uani 1 1 d . . .
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C20 C 0.29401(19) 0.43230(16) 0.91650(15) 0.0290(4) Uani 1 1 d . . .
C21 C 0.0978(2) 0.78563(18) 0.12796(18) 0.0362(4) Uani 1 1 d . . .
H1 H 0.278(2) 0.0500(19) -0.3465(17) 0.036(5) Uiso 1 1 d . . .
H2N H 0.606(2) 0.0695(19) -0.0756(17) 0.028(5) Uiso 1 1 d . . .
H3 H 0.542(2) -0.2174(19) -0.4976(18) 0.036(5) Uiso 1 1 d . . .
H3N H 0.848(2) -0.0137(19) 0.0832(18) 0.033(5) Uiso 1 1 d . . .
H4 H 0.683(2) -0.1773(17) -0.3158(16) 0.027(5) Uiso 1 1 d . . .
H4N H 0.301(2) 0.605(2) 0.9404(19) 0.043(6) Uiso 1 1 d . . .
H5NA H 0.153(3) 0.504(3) 1.019(2) 0.059(7) Uiso 1 1 d . . .
H5NB H 0.157(3) 0.369(2) 0.991(2) 0.051(7) Uiso 1 1 d . . .
H8A H 0.850(2) 0.148(2) 0.2770(19) 0.043(6) Uiso 1 1 d . . .
H8B H 0.966(3) 0.178(2) 0.2088(19) 0.043(6) Uiso 1 1 d . . .
H10 H 0.685(3) 0.313(2) 0.385(2) 0.052(6) Uiso 1 1 d . . .
H11 H 0.665(2) 0.525(2) 0.483(2) 0.047(6) Uiso 1 1 d . . .
H13 H 1.006(2) 0.6008(19) 0.3286(17) 0.035(5) Uiso 1 1 d . . .
H14 H 1.021(3) 0.397(2) 0.233(2) 0.047(6) Uiso 1 1 d . . .
H15A H 1.020(3) 0.778(2) 0.5079(19) 0.047(6) Uiso 1 1 d . . .
H15B H 0.923(2) 0.802(2) 0.401(2) 0.052(7) Uiso 1 1 d . . .
H15C H 0.894(2) 0.869(2) 0.535(2) 0.045(6) Uiso 1 1 d . . .
H16 H 0.479(2) 0.6266(19) 0.8408(17) 0.035(5) Uiso 1 1 d . . .
H18 H 0.534(2) 0.2617(19) 0.7606(18) 0.036(5) Uiso 1 1 d . . .
H19 H 0.336(2) 0.255(2) 0.8724(19) 0.045(6) Uiso 1 1 d . . .

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S2 0.0518(3) 0.0458(3) 0.0313(2) 0.0095(2) 0.0021(2) 0.0234(2)
O1 0.0407(7) 0.0255(6) 0.0341(7) 0.0046(5) -0.0013(5) 0.0104(5)
O2 0.0434(8) 0.0262(6) 0.0454(8) 0.0023(6) 0.0146(6) 0.0061(6)
N1 0.0344(8) 0.0273(7) 0.0294(7) 0.0087(6) 0.0058(6) 0.0092(6)
N2 0.0358(8) 0.0197(7) 0.0275(7) 0.0048(6) 0.0033(6) 0.0074(6)
N3 0.0336(8) 0.0229(7) 0.0280(7) 0.0094(6) 0.0012(6) 0.0071(6)
N4 0.0311(8) 0.0222(7) 0.0323(8) 0.0060(6) 0.0029(6) 0.0055(6)
N5 0.0404(10) 0.0346(9) 0.0474(10) 0.0138(8) 0.0149(8) 0.0040(8)
N6 0.0654(13) 0.0411(10) 0.0773(14) 0.0147(10) 0.0327(11) 0.0162(9)
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C3 0.0321(9) 0.0250(8) 0.0290(9) 0.0074(7) 0.0077(7) 0.0038(7)
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C9 0.0310(9) 0.0254(8) 0.0288(9) 0.0080(7) -0.0030(7) 0.0018(7)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O1 C7 1.223(2) . ?
O2 C12 1.372(2) . ?
O2 C15 1.419(2) . ?
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N5 H5NB 0.83(3) . ?
N6 C21 1.152(3) . ?
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C3 C4 1.384(2) . ?
C3 H3 0.89(2) . ?
C4 C5 1.398(2) . ?
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C7 C8 1.507(2) . ?
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C8 H8A 0.94(2) . ?
C8 H8B 0.93(2) . ?
C9 C14 1.381(3) . ?
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C10 C11 1.386(3) . ?
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C15 H15B 0.99(2) . ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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_atom_sites_solution_secondary    difmap
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_refine_ls_goodness_of_fit_ref    1.031
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Cl1 Cl 0.40934(5) -0.40220(4) 0.69812(4) 0.03852(12) Uani 1 1 d . . .
S1 S 0.14973(6) 0.30800(4) 0.59894(3) 0.03529(12) Uani 1 1 d . . .
O1 O 0.11217(15) 0.33930(10) 0.19926(9) 0.0277(2) Uani 1 1 d . . .
O2 O 0.77010(15) 0.88659(11) 0.03020(10) 0.0316(2) Uani 1 1 d . . .
N1 N 0.27614(16) -0.03336(12) 0.44044(11) 0.0248(2) Uani 1 1 d . . .
N2 N 0.17241(16) 0.17995(12) 0.43394(11) 0.0210(2) Uani 1 1 d . . .
N3 N 0.08547(16) 0.41381(12) 0.36116(10) 0.0222(2) Uani 1 1 d . . .
C1 C 0.3299(2) -0.16721(15) 0.49936(14) 0.0277(3) Uani 1 1 d . . .
C2 C 0.33537(19) -0.22854(14) 0.62710(14) 0.0277(3) Uani 1 1 d . . .
C3 C 0.2805(2) -0.15092(16) 0.69722(14) 0.0304(3) Uani 1 1 d . . .
C4 C 0.2237(2) -0.01270(15) 0.63795(13) 0.0271(3) Uani 1 1 d . . .
C5 C 0.22630(18) 0.04164(14) 0.50899(12) 0.0216(3) Uani 1 1 d . . .
C6 C 0.13592(18) 0.29386(14) 0.46145(12) 0.0218(3) Uani 1 1 d . . .
C7 C 0.08196(18) 0.43404(14) 0.23762(12) 0.0214(3) Uani 1 1 d . . .
C8 C 0.0481(2) 0.58430(14) 0.15131(13) 0.0239(3) Uani 1 1 d . . .
C9 C 0.24236(19) 0.66364(13) 0.11785(12) 0.0221(3) Uani 1 1 d . . .
C10 C 0.3025(2) 0.74934(15) 0.17955(13) 0.0280(3) Uani 1 1 d . . .
C11 C 0.4790(2) 0.82143(16) 0.14903(14) 0.0294(3) Uani 1 1 d . . .
C12 C 0.6002(2) 0.80929(14) 0.05527(13) 0.0249(3) Uani 1 1 d . . .
C13 C 0.5445(2) 0.72252(15) -0.00578(13) 0.0255(3) Uani 1 1 d . . .
C14 C 0.3664(2) 0.64996(14) 0.02675(12) 0.0248(3) Uani 1 1 d . . .
C15 C 0.8772(2) 0.90134(17) -0.08157(15) 0.0319(3) Uani 1 1 d . . .
H1 H 0.366(2) -0.2189(18) 0.4485(15) 0.026(4) Uiso 1 1 d . . .
H2N H 0.167(2) 0.1941(17) 0.3561(17) 0.028(4) Uiso 1 1 d . . .
H3 H 0.281(3) -0.1910(19) 0.7842(17) 0.037(5) Uiso 1 1 d . . .
H3N H 0.056(2) 0.4827(18) 0.3798(15) 0.026(4) Uiso 1 1 d . . .
H4 H 0.185(2) 0.0429(17) 0.6832(15) 0.027(4) Uiso 1 1 d . . .
H8A H -0.044(2) 0.6304(17) 0.1908(15) 0.026(4) Uiso 1 1 d . . .
H8B H -0.008(2) 0.5778(17) 0.0798(15) 0.025(4) Uiso 1 1 d . . .
H10 H 0.220(2) 0.7618(18) 0.2409(16) 0.032(4) Uiso 1 1 d . . .
H11 H 0.516(3) 0.880(2) 0.1886(17) 0.039(5) Uiso 1 1 d . . .
H13 H 0.622(2) 0.7121(18) -0.0670(16) 0.031(4) Uiso 1 1 d . . .
H14 H 0.330(2) 0.5895(18) -0.0147(15) 0.031(4) Uiso 1 1 d . . .
H15A H 0.980(3) 0.969(2) -0.0913(19) 0.053(6) Uiso 1 1 d . . .
H15B H 0.934(2) 0.8118(19) -0.0791(16) 0.033(4) Uiso 1 1 d . . .
H15C H 0.791(3) 0.9351(19) -0.1528(17) 0.037(5) Uiso 1 1 d . . .

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S1 0.0523(2) 0.0317(2) 0.02474(19) -0.01337(15) -0.00844(16) 0.01433(17)
O1 0.0363(5) 0.0227(5) 0.0244(5) -0.0095(4) 0.0027(4) -0.0016(4)
O2 0.0288(5) 0.0348(6) 0.0336(6) -0.0159(5) 0.0041(4) -0.0104(4)
N1 0.0217(5) 0.0226(6) 0.0282(6) -0.0076(5) 0.0005(4) 0.0003(4)
N2 0.0224(5) 0.0196(5) 0.0191(5) -0.0052(4) 0.0007(4) -0.0003(4)
N3 0.0244(6) 0.0192(6) 0.0228(5) -0.0078(4) 0.0001(4) 0.0027(4)
C1 0.0219(6) 0.0227(7) 0.0367(8) -0.0092(6) 0.0004(6) 0.0015(5)
C2 0.0162(6) 0.0194(6) 0.0387(8) -0.0006(6) -0.0025(5) -0.0003(5)
C3 0.0266(7) 0.0282(7) 0.0288(8) -0.0017(6) -0.0033(6) -0.0035(6)
C4 0.0276(7) 0.0254(7) 0.0255(7) -0.0064(6) 0.0001(5) -0.0013(5)
C5 0.0153(6) 0.0207(6) 0.0259(6) -0.0055(5) 0.0001(5) -0.0015(5)
C6 0.0172(6) 0.0225(6) 0.0240(6) -0.0069(5) 0.0006(5) 0.0006(5)
C7 0.0169(6) 0.0225(6) 0.0230(6) -0.0067(5) 0.0016(5) -0.0028(5)
C8 0.0238(6) 0.0226(7) 0.0222(6) -0.0047(5) -0.0011(5) 0.0005(5)
C9 0.0242(6) 0.0180(6) 0.0198(6) -0.0019(5) -0.0019(5) 0.0006(5)
C10 0.0315(7) 0.0284(7) 0.0252(7) -0.0116(6) 0.0040(6) -0.0016(6)
C11 0.0334(8) 0.0289(7) 0.0294(7) -0.0151(6) -0.0004(6) -0.0043(6)
C12 0.0250(6) 0.0217(6) 0.0249(7) -0.0052(5) -0.0014(5) -0.0022(5)
C13 0.0278(7) 0.0251(7) 0.0230(7) -0.0083(5) 0.0026(5) -0.0006(5)
C14 0.0296(7) 0.0212(6) 0.0231(6) -0.0078(5) -0.0012(5) -0.0025(5)
C15 0.0301(8) 0.0311(8) 0.0356(8) -0.0142(6) 0.0060(6) -0.0075(6)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

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S1 C6 1.6658(14) . ?
O1 C7 1.2239(16) . ?
O2 C12 1.3681(16) . ?
O2 C15 1.4313(18) . ?
N1 C5 1.3347(18) . ?
N1 C1 1.3379(18) . ?
N2 C6 1.3397(17) . ?
N2 C5 1.4116(17) . ?
N2 H2N 0.864(18) . ?
N3 C7 1.3755(17) . ?
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N3 C6 1.3923(17) . ?
N3 H3N 0.834(17) . ?
C1 C2 1.383(2) . ?
C1 H1 0.957(17) . ?
C2 C3 1.379(2) . ?
C3 C4 1.382(2) . ?
C3 H3 0.940(18) . ?
C4 C5 1.3921(19) . ?
C4 H4 0.940(17) . ?
C7 C8 1.5108(18) . ?
C8 C9 1.5206(18) . ?
C8 H8A 0.987(16) . ?
C8 H8B 0.952(16) . ?
C9 C14 1.3854(19) . ?
C9 C10 1.3944(19) . ?
C10 C11 1.382(2) . ?
C10 H10 0.942(17) . ?
C11 C12 1.392(2) . ?
C11 H11 0.923(19) . ?
C12 C13 1.3883(19) . ?
C13 C14 1.3942(19) . ?
C13 H13 0.914(17) . ?
C14 H14 0.953(17) . ?
C15 H15A 0.96(2) . ?
C15 H15B 0.984(18) . ?
C15 H15C 0.984(19) . ?

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C5 N1 C1 117.90(12) . . ?
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C5 N2 H2N 113.9(11) . . ?
C7 N3 C6 129.08(12) . . ?
C7 N3 H3N 116.7(11) . . ?
C6 N3 H3N 114.2(11) . . ?
N1 C1 C2 122.25(14) . . ?
N1 C1 H1 116.6(10) . . ?
C2 C1 H1 121.1(10) . . ?
C3 C2 C1 119.42(13) . . ?
C3 C2 Cl1 120.49(12) . . ?
C1 C2 Cl1 120.08(12) . . ?
C2 C3 C4 119.11(14) . . ?
C2 C3 H3 120.9(11) . . ?
C4 C3 H3 120.0(11) . . ?
C3 C4 C5 117.72(14) . . ?

C3 C4 H4 121.1(10) . . ?
C5 C4 H4 121.2(10) . . ?
N1 C5 C4 123.57(13) . . ?
N1 C5 N2 111.24(11) . . ?
C4 C5 N2 125.17(12) . . ?
N2 C6 N3 114.82(12) . . ?
N2 C6 S1 127.59(10) . . ?
N3 C6 S1 117.57(10) . . ?
O1 C7 N3 122.93(12) . . ?
O1 C7 C8 122.09(12) . . ?
N3 C7 C8 114.91(11) . . ?
C7 C8 C9 109.56(11) . . ?
C7 C8 H8A 110.0(9) . . ?
C9 C8 H8A 111.0(9) . . ?
C7 C8 H8B 105.6(10) . . ?
C9 C8 H8B 110.7(9) . . ?
H8A C8 H8B 109.9(13) . . ?
C14 C9 C10 118.23(12) . . ?
C14 C9 C8 120.63(12) . . ?
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C11 C10 C9 121.07(13) . . ?
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C10 C11 H11 120.6(11) . . ?
C12 C11 H11 119.3(11) . . ?
O2 C12 C13 124.46(13) . . ?
O2 C12 C11 115.80(12) . . ?
C13 C12 C11 119.74(13) . . ?
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C9 C14 H14 119.5(10) . . ?
C13 C14 H14 119.0(10) . . ?
O2 C15 H15A 106.6(12) . . ?
O2 C15 H15B 112.5(10) . . ?
H15A C15 H15B 109.9(16) . . ?
O2 C15 H15C 110.4(10) . . ?
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H15B C15 H15C 107.4(14) . . ?

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C5 N1 C1 C2 -0.1(2) . . . . ?
N1 C1 C2 C3 1.2(2) . . . . ?
N1 C1 C2 Cl1 -179.20(10) . . . . ?
C1 C2 C3 C4 -0.9(2) . . . . ?
Cl1 C2 C3 C4 179.56(11) . . . . ?
C2 C3 C4 C5 -0.5(2) . . . . ?
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C1 N1 C5 N2 -179.68(11) . . . . ?
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C6 N2 C5 N1 -170.80(12) . . . . ?
C6 N2 C5 C4 10.8(2) . . . . ?
C5 N2 C6 N3 -179.82(12) . . . . ?
C5 N2 C6 S1 1.9(2) . . . . ?
C7 N3 C6 N2 -5.26(19) . . . . ?
C7 N3 C6 S1 173.24(11) . . . . ?
C6 N3 C7 O1 5.5(2) . . . . ?
C6 N3 C7 C8 -171.51(12) . . . . ?
O1 C7 C8 C9 -90.95(15) . . . . ?
N3 C7 C8 C9 86.08(14) . . . . ?
C7 C8 C9 C14 80.70(15) . . . . ?
C7 C8 C9 C10 -97.85(15) . . . . ?
C14 C9 C10 C11 1.4(2) . . . . ?
C8 C9 C10 C11 -179.97(13) . . . . ?
C9 C10 C11 C12 0.0(2) . . . . ?
C15 O2 C12 C13 13.2(2) . . . . ?
C15 O2 C12 C11 -166.84(13) . . . . ?
C10 C11 C12 O2 178.85(13) . . . . ?
C10 C11 C12 C13 -1.2(2) . . . . ?
O2 C12 C13 C14 -179.23(13) . . . . ?
C11 C12 C13 C14 0.8(2) . . . . ?
C10 C9 C14 C13 -1.8(2) . . . . ?
C8 C9 C14 C13 179.58(12) . . . . ?
C12 C13 C14 C9 0.7(2) . . . . ?

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 _geom_hbond_angle_DHA
 _geom_hbond_site_symmetry_A
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N3 H3N S1 0.834(17) 2.642(18) 3.4372(12) 160.1(15) 2_566

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 'O'  'O'   0.0106   0.0060
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 'Cl'  'Cl'   0.1484   0.1585
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M    Pbca

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 '-x, y+1/2, -z+1/2'
 'x+1/2, -y+1/2, -z'
 '-x, -y, -z'
 'x-1/2, y, -z-1/2'
 'x, -y-1/2, z-1/2'
 '-x-1/2, y-1/2, z'

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_cell_length_c                   21.622(2)
_cell_angle_alpha                90.00
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_cell_angle_gamma                90.00
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_exptl_crystal_size_mid          0.14
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_exptl_crystal_density_diffrn    1.622
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_exptl_crystal_F_000             1456
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_computing_molecular_graphics    'Bruker SHELXTL'
_computing_publication_material  'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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Cl3 Cl 0.35220(5) 0.75551(7) 0.72740(2) 0.05416(19) Uani 1 1 d . . .
Cl4 Cl 0.47048(4) 0.42703(5) 0.91751(3) 0.04275(16) Uani 1 1 d . . .
O1 O 0.20833(8) 1.05279(12) 1.05783(5) 0.0263(3) Uani 1 1 d . . .
O2 O 0.29456(8) 1.04855(12) 0.94442(5) 0.0258(3) Uani 1 1 d . . .
N1 N 0.24996(9) 0.84717(17) 1.00199(6) 0.0238(3) Uani 1 1 d . . .
C1 C 0.20611(10) 0.91925(17) 1.04953(7) 0.0214(3) Uani 1 1 d . . .
C2 C 0.15651(10) 0.81717(17) 1.09150(8) 0.0217(3) Uani 1 1 d . . .
C3 C 0.15257(11) 0.85519(19) 1.15371(8) 0.0263(4) Uani 1 1 d . . .
C4 C 0.10805(12) 0.7617(2) 1.19378(8) 0.0300(4) Uani 1 1 d . . .
C5 C 0.06731(12) 0.6329(2) 1.17333(8) 0.0291(4) Uani 1 1 d . . .
C6 C 0.07147(11) 0.59925(18) 1.11113(8) 0.0250(3) Uani 1 1 d . . .
C7 C 0.11514(11) 0.68990(18) 1.06945(8) 0.0229(3) Uani 1 1 d . . .
C8 C 0.29318(10) 0.91513(17) 0.95326(7) 0.0211(3) Uani 1 1 d . . .
C9 C 0.33600(10) 0.80702(17) 0.91013(8) 0.0222(3) Uani 1 1 d . . .
C10 C 0.32751(11) 0.8316(2) 0.84705(8) 0.0270(4) Uani 1 1 d . . .
C11 C 0.36223(12) 0.7282(2) 0.80656(8) 0.0324(4) Uani 1 1 d . . .
C12 C 0.40607(13) 0.6022(2) 0.82760(9) 0.0337(4) Uani 1 1 d . . .
C13 C 0.41564(11) 0.58334(18) 0.89061(9) 0.0279(4) Uani 1 1 d . . .
C14 C 0.38139(11) 0.68416(18) 0.93270(8) 0.0242(3) Uani 1 1 d . . .
H1N H 0.2503(12) 0.763(3) 1.0019(8) 0.026(5) Uiso 1 1 d . . .
H3 H 0.1834(14) 0.939(2) 1.1685(10) 0.040(6) Uiso 1 1 d . . .
H5 H 0.0371(13) 0.572(2) 1.2013(10) 0.035(6) Uiso 1 1 d . . .
H7 H 0.1162(12) 0.665(2) 1.0277(9) 0.023(5) Uiso 1 1 d . . .
H10 H 0.2937(14) 0.910(2) 0.8314(10) 0.037(6) Uiso 1 1 d . . .
H12 H 0.4297(14) 0.533(3) 0.7988(11) 0.040(6) Uiso 1 1 d . . .
H14 H 0.3898(13) 0.668(2) 0.9753(9) 0.027(5) Uiso 1 1 d . . .

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Cl2 0.0466(3) 0.0240(2) 0.0432(3) -0.00013(18) 0.0015(2) -0.01439(19)
Cl3 0.0784(4) 0.0583(4) 0.0257(3) -0.0042(2) 0.0008(2) 0.0171(3)
Cl4 0.0520(3) 0.0232(2) 0.0531(3) 0.00193(19) 0.0065(2) 0.0148(2)
O1 0.0329(6) 0.0159(6) 0.0301(6) -0.0015(5) 0.0064(5) -0.0025(4)
O2 0.0311(6) 0.0161(6) 0.0301(6) 0.0022(5) 0.0054(5) 0.0016(4)
N1 0.0303(7) 0.0113(7) 0.0298(8) 0.0000(5) 0.0070(6) 0.0003(5)
C1 0.0217(7) 0.0176(7) 0.0248(8) 0.0009(6) 0.0001(6) -0.0001(6)
C2 0.0225(8) 0.0172(7) 0.0253(8) 0.0024(6) 0.0016(6) 0.0012(6)
C3 0.0313(9) 0.0211(8) 0.0266(8) -0.0010(7) 0.0008(7) -0.0017(7)
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C4 0.0371(9) 0.0303(9) 0.0227(8) 0.0010(7) 0.0036(7) -0.0008(8)
C5 0.0327(9) 0.0264(9) 0.0281(8) 0.0075(7) 0.0049(7) -0.0023(7)
C6 0.0250(8) 0.0172(7) 0.0327(9) 0.0017(6) -0.0007(7) -0.0020(6)
C7 0.0259(8) 0.0182(8) 0.0245(8) 0.0005(6) 0.0017(6) 0.0010(6)
C8 0.0204(7) 0.0179(7) 0.0251(8) 0.0001(6) 0.0005(6) 0.0005(6)
C9 0.0216(7) 0.0164(7) 0.0287(8) -0.0018(6) 0.0039(6) -0.0016(6)
C10 0.0284(8) 0.0240(8) 0.0287(8) 0.0019(7) 0.0018(7) 0.0008(7)
C11 0.0380(9) 0.0336(10) 0.0255(9) -0.0026(7) 0.0024(7) 0.0006(8)
C12 0.0399(10) 0.0267(9) 0.0346(9) -0.0081(8) 0.0088(8) 0.0031(8)
C13 0.0283(8) 0.0169(8) 0.0384(9) -0.0001(7) 0.0049(7) 0.0025(6)
C14 0.0270(8) 0.0180(8) 0.0275(9) 0.0003(6) 0.0038(7) -0.0003(6)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O1 C1 1.2119(19) . ?
O2 C8 1.2123(19) . ?
N1 C8 1.386(2) . ?
N1 C1 1.388(2) . ?
N1 H1N 0.76(3) . ?
C1 C2 1.497(2) . ?
C2 C3 1.389(2) . ?
C2 C7 1.390(2) . ?
C3 C4 1.385(2) . ?
C3 H3 0.95(2) . ?
C4 C5 1.386(3) . ?
C5 C6 1.380(2) . ?
C5 H5 0.94(2) . ?
C6 C7 1.386(2) . ?
C7 H7 0.929(19) . ?
C8 C9 1.497(2) . ?
C9 C10 1.388(2) . ?
C9 C14 1.392(2) . ?
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C10 H10 0.94(2) . ?
C11 C12 1.391(3) . ?
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O1 C1 N1 123.82(15) . . ?
O1 C1 C2 121.97(15) . . ?
N1 C1 C2 114.20(14) . . ?
C3 C2 C7 120.92(15) . . ?
C3 C2 C1 117.32(15) . . ?
C7 C2 C1 121.75(15) . . ?
C4 C3 C2 118.58(16) . . ?
C4 C3 H3 121.2(13) . . ?
C2 C3 H3 120.1(13) . . ?
C3 C4 C5 121.81(16) . . ?
C3 C4 Cl1 119.25(14) . . ?
C5 C4 Cl1 118.94(14) . . ?
C6 C5 C4 118.18(16) . . ?
C6 C5 H5 121.6(13) . . ?
C4 C5 H5 120.2(13) . . ?
C5 C6 C7 121.86(16) . . ?
C5 C6 Cl2 118.72(13) . . ?
C7 C6 Cl2 119.42(13) . . ?
C6 C7 C2 118.62(16) . . ?
C6 C7 H7 119.9(13) . . ?
C2 C7 H7 121.5(13) . . ?
O2 C8 N1 124.23(15) . . ?
O2 C8 C9 122.26(15) . . ?
N1 C8 C9 113.46(14) . . ?
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C10 C9 C8 117.93(15) . . ?
C14 C9 C8 120.91(15) . . ?
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C11 C10 H10 119.2(13) . . ?
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C10 C11 C12 121.60(17) . . ?
C10 C11 Cl3 119.74(15) . . ?
C12 C11 Cl3 118.66(14) . . ?
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C12 C13 C14 121.84(16) . . ?

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C14 C13 Cl4 119.38(14) . . ?
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O1 C1 C2 C3 -33.6(2) . . . . ?
N1 C1 C2 C3 145.09(15) . . . . ?
O1 C1 C2 C7 145.82(17) . . . . ?
N1 C1 C2 C7 -35.5(2) . . . . ?
C7 C2 C3 C4 1.4(3) . . . . ?
C1 C2 C3 C4 -179.17(15) . . . . ?
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C2 C3 C4 Cl1 179.34(13) . . . . ?
C3 C4 C5 C6 -0.4(3) . . . . ?
Cl1 C4 C5 C6 179.83(14) . . . . ?
C4 C5 C6 C7 0.3(3) . . . . ?
C4 C5 C6 Cl2 179.76(14) . . . . ?
C5 C6 C7 C2 0.7(3) . . . . ?
Cl2 C6 C7 C2 -178.78(12) . . . . ?
C3 C2 C7 C6 -1.6(2) . . . . ?
C1 C2 C7 C6 179.04(15) . . . . ?
C1 N1 C8 O2 -3.7(3) . . . . ?
C1 N1 C8 C9 178.64(15) . . . . ?
O2 C8 C9 C10 -41.4(2) . . . . ?
N1 C8 C9 C10 136.28(16) . . . . ?
O2 C8 C9 C14 139.82(17) . . . . ?
N1 C8 C9 C14 -42.5(2) . . . . ?
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C8 C9 C10 C11 -176.26(16) . . . . ?
C9 C10 C11 C12 -0.8(3) . . . . ?
C9 C10 C11 Cl3 179.71(13) . . . . ?
C10 C11 C12 C13 -1.1(3) . . . . ?
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C11 C12 C13 Cl4 -179.79(14) . . . . ?
C12 C13 C14 C9 0.2(3) . . . . ?
Cl4 C13 C14 C9 -178.61(13) . . . . ?
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N1 H1N O2  0.76(3) 2.39(2) 3.0317(19) 143.5(18) 8_655

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 'S'  'S'   0.1246   0.1234
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 '-x+1/2, y+1/2, -z+1/2'
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 'x-1/2, -y-1/2, z-1/2'

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_cell_length_b                  7.5855(5)
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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O1 O 0.32020(9) 0.19181(13) 0.12478(5) 0.0302(2) Uani 1 1 d . . .
N1 N 0.50848(10) 0.62846(13) 0.12725(6) 0.0215(2) Uani 1 1 d . . .
N2 N 0.59194(10) 0.34449(13) 0.16751(6) 0.0209(2) Uani 1 1 d . . .
N3 N 0.44406(10) 0.29492(13) 0.04182(6) 0.0197(2) Uani 1 1 d . . .
C1 C 0.44280(13) 0.77526(16) 0.14035(8) 0.0248(3) Uani 1 1 d . . .
C2 C 0.38506(13) 0.79431(17) 0.20434(8) 0.0272(3) Uani 1 1 d . . .
C3 C 0.39328(13) 0.65523(19) 0.25739(8) 0.0287(3) Uani 1 1 d . . .
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C5 C 0.51520(11) 0.49638(15) 0.17917(7) 0.0197(2) Uani 1 1 d . . .
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C13 C 0.07580(14) 0.2158(2) 0.00125(9) 0.0366(3) Uani 1 1 d . . .
C14 C 0.70233(14) 0.28686(19) 0.23591(8) 0.0297(3) Uani 1 1 d . . .
H1 H 0.4422(16) 0.868(2) 0.1033(10) 0.028(4) Uiso 1 1 d . . .
H2 H 0.3417(17) 0.902(2) 0.2110(10) 0.033(4) Uiso 1 1 d . . .
H3 H 0.3553(17) 0.664(2) 0.3033(11) 0.038(4) Uiso 1 1 d . . .
H3N H 0.4436(15) 0.303(2) -0.0066(10) 0.028(4) Uiso 1 1 d . . .
H4 H 0.4669(16) 0.403(2) 0.2789(10) 0.028(4) Uiso 1 1 d . . .
H9 H 0.272(2) 0.481(3) -0.0628(12) 0.062(6) Uiso 1 1 d . . .
H10 H 0.067(2) 0.559(3) -0.1526(14) 0.071(7) Uiso 1 1 d . . .
H11 H -0.131(2) 0.423(3) -0.1460(12) 0.053(5) Uiso 1 1 d . . .
H12 H -0.131(2) 0.210(3) -0.0498(13) 0.062(6) Uiso 1 1 d . . .
H13 H 0.078(2) 0.133(3) 0.0409(13) 0.052(5) Uiso 1 1 d . . .
H14A H 0.788(2) 0.286(3) 0.2230(12) 0.054(6) Uiso 1 1 d . . .
H14B H 0.6853(19) 0.168(3) 0.2489(12) 0.048(5) Uiso 1 1 d . . .
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N1 0.0204(5) 0.0228(5) 0.0207(5) 0.0001(4) 0.0041(4) 0.0007(4)
N2 0.0203(5) 0.0210(5) 0.0196(5) 0.0005(4) 0.0022(4) 0.0018(4)
N3 0.0182(5) 0.0234(5) 0.0173(5) -0.0005(4) 0.0042(4) 0.0003(4)
C1 0.0240(6) 0.0229(6) 0.0254(6) -0.0005(5) 0.0026(5) 0.0019(5)
C2 0.0216(6) 0.0277(6) 0.0305(6) -0.0084(5) 0.0035(5) 0.0023(5)
C3 0.0258(6) 0.0369(7) 0.0254(6) -0.0076(5) 0.0100(5) -0.0028(5)
C4 0.0284(6) 0.0287(6) 0.0220(6) -0.0003(5) 0.0078(5) -0.0032(5)
C5 0.0169(5) 0.0215(5) 0.0191(5) -0.0020(4) 0.0019(4) -0.0014(4)
C6 0.0186(5) 0.0190(5) 0.0217(5) 0.0015(4) 0.0052(4) -0.0012(4)
C7 0.0211(6) 0.0180(5) 0.0233(6) -0.0026(4) 0.0064(4) -0.0020(4)
C8 0.0192(5) 0.0211(5) 0.0229(5) -0.0035(4) 0.0058(4) 0.0000(4)
C9 0.0210(6) 0.0415(8) 0.0466(8) 0.0179(7) 0.0067(6) 0.0010(6)
C10 0.0297(7) 0.0526(10) 0.0521(9) 0.0259(8) 0.0041(7) 0.0066(7)
C11 0.0220(6) 0.0432(8) 0.0353(7) -0.0035(6) -0.0002(5) 0.0065(5)
C12 0.0212(7) 0.0569(10) 0.0428(8) 0.0017(7) 0.0014(6) -0.0118(6)
C13 0.0264(7) 0.0460(8) 0.0348(7) 0.0088(6) 0.0032(5) -0.0104(6)
C14 0.0289(7) 0.0309(7) 0.0237(6) 0.0005(5) -0.0033(5) 0.0065(5)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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O1 C7 C8 C9 155.33(13) . . . . ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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O1 O 0.83440(11) 0.6743(3) 0.47306(6) 0.0403(3) Uani 1 1 d . . .
O2 O 0.71426(10) 0.6723(2) 0.37138(5) 0.0294(3) Uani 1 1 d . . .
N1 N 0.80184(11) -0.0574(3) 0.22925(6) 0.0250(3) Uani 1 1 d . . .
N2 N 0.83303(11) 0.2351(3) 0.32684(6) 0.0240(3) Uani 1 1 d . . .
N3 N 0.97565(13) 0.2746(3) 0.41876(7) 0.0324(3) Uani 1 1 d . . .
C1 C 0.73673(14) -0.1463(3) 0.16939(8) 0.0306(3) Uani 1 1 d . . .
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C2 C 0.62971(15) -0.0357(4) 0.14696(8) 0.0339(4) Uani 1 1 d . . .
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C4 C 0.65507(14) 0.2586(3) 0.24668(8) 0.0281(3) Uani 1 1 d . . .
C5 C 0.76547(12) 0.1418(3) 0.26799(7) 0.0228(3) Uani 1 1 d . . .
C6 C 0.94043(13) 0.1453(3) 0.36011(7) 0.0236(3) Uani 1 1 d . . .
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C8 C 0.65695(14) 0.9224(3) 0.46423(8) 0.0290(3) Uani 1 1 d . . .
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F3 F 0.56260(10) 0.7764(3) 0.47525(6) 0.0480(3) Uani 1 1 d . . .
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H2 H 0.5820(19) -0.095(4) 0.1071(11) 0.040(5) Uiso 1 1 d . . .
H2N H 0.8016(17) 0.371(4) 0.3446(10) 0.033(5) Uiso 1 1 d . . .
H3 H 0.5154(18) 0.252(4) 0.1732(10) 0.035(5) Uiso 1 1 d . . .
H3NA H 0.9316(19) 0.410(5) 0.4316(11) 0.042(6) Uiso 1 1 d . . .
H3NB H 1.043(2) 0.231(5) 0.4425(12) 0.047(6) Uiso 1 1 d . . .
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O2 0.0299(6) 0.0343(6) 0.0228(5) -0.0042(4) -0.0003(4) 0.0049(5)
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N2 0.0221(6) 0.0264(6) 0.0227(6) -0.0043(5) -0.0002(5) 0.0030(5)
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C2 0.0309(8) 0.0410(9) 0.0269(7) -0.0051(7) -0.0066(6) -0.0038(7)
C3 0.0237(7) 0.0407(9) 0.0299(8) 0.0014(7) -0.0035(6) 0.0018(7)
C4 0.0245(7) 0.0323(8) 0.0270(7) -0.0027(6) 0.0012(6) 0.0025(6)
C5 0.0217(7) 0.0257(7) 0.0209(6) 0.0005(5) 0.0019(5) -0.0035(5)
C6 0.0213(7) 0.0252(7) 0.0233(7) 0.0003(6) 0.0001(5) -0.0014(5)
C7 0.0234(7) 0.0264(7) 0.0251(7) -0.0014(6) 0.0015(5) -0.0003(6)
C8 0.0299(8) 0.0341(8) 0.0222(7) -0.0014(6) 0.0006(6) 0.0047(6)
F1 0.0554(7) 0.0657(8) 0.0373(6) -0.0248(6) -0.0057(5) 0.0162(6)
F2 0.0557(7) 0.0421(6) 0.0441(6) 0.0121(5) 0.0133(5) 0.0232(5)
F3 0.0390(6) 0.0543(7) 0.0549(7) -0.0013(5) 0.0220(5) -0.0009(5)

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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

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O1 C7 1.2307(19) . ?
O2 C7 1.2469(18) . ?
N1 C5 1.340(2) . ?
N1 C1 1.360(2) . ?
N1 H1N 0.92(2) . ?
N2 C5 1.3653(18) . ?
N2 C6 1.3820(19) . ?
N2 H2N 0.86(2) . ?
N3 C6 1.3158(19) . ?
N3 H3NA 0.90(2) . ?
N3 H3NB 0.87(2) . ?
C1 C2 1.359(2) . ?
C1 H1 0.94(2) . ?
C2 C3 1.397(2) . ?
C2 H2 0.93(2) . ?
C3 C4 1.370(2) . ?
C3 H3 0.94(2) . ?
C4 C5 1.401(2) . ?
C4 H4 0.88(2) . ?
C7 C8 1.542(2) . ?
C8 F1 1.3243(18) . ?
C8 F2 1.3273(19) . ?
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C5 N1 C1 122.46(14) . . ?
C5 N1 H1N 115.3(14) . . ?
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C5 N2 C6 130.21(13) . . ?
C5 N2 H2N 112.2(13) . . ?
C6 N2 H2N 117.6(13) . . ?
C6 N3 H3NA 119.1(14) . . ?
C6 N3 H3NB 118.6(15) . . ?
H3NA N3 H3NB 122(2) . . ?
C2 C1 N1 120.41(15) . . ?
C2 C1 H1 125.7(12) . . ?
N1 C1 H1 113.8(12) . . ?

C1 C2 C3 118.59(15) . . ?
C1 C2 H2 122.6(13) . . ?
C3 C2 H2 118.7(13) . . ?
C4 C3 C2 120.45(15) . . ?
C4 C3 H3 118.0(12) . . ?
C2 C3 H3 121.6(12) . . ?
C3 C4 C5 119.50(15) . . ?
C3 C4 H4 122.4(12) . . ?
C5 C4 H4 118.0(13) . . ?
N1 C5 N2 122.00(13) . . ?
N1 C5 C4 118.58(13) . . ?
N2 C5 C4 119.42(14) . . ?
N3 C6 N2 113.08(14) . . ?
N3 C6 S1 122.40(12) . . ?
N2 C6 S1 124.52(11) . . ?
O1 C7 O2 129.25(15) . . ?
O1 C7 C8 116.52(13) . . ?
O2 C7 C8 114.17(13) . . ?
F1 C8 F2 107.97(14) . . ?
F1 C8 F3 106.20(13) . . ?
F2 C8 F3 106.35(13) . . ?
F1 C8 C7 113.83(13) . . ?
F2 C8 C7 112.58(13) . . ?
F3 C8 C7 109.46(13) . . ?

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N1 C1 C2 C3 -0.3(3) . . . . ?
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C2 C3 C4 C5 -0.2(3) . . . . ?
C1 N1 C5 N2 -177.98(14) . . . . ?
C1 N1 C5 C4 1.4(2) . . . . ?
C6 N2 C5 N1 -4.4(2) . . . . ?
C6 N2 C5 C4 176.19(15) . . . . ?
C3 C4 C5 N1 -0.8(2) . . . . ?
C3 C4 C5 N2 178.57(15) . . . . ?
C5 N2 C6 N3 -175.68(15) . . . . ?
C5 N2 C6 S1 4.2(2) . . . . ?
O1 C7 C8 F1 13.3(2) . . . . ?
O2 C7 C8 F1 -169.20(14) . . . . ?
O1 C7 C8 F2 136.55(16) . . . . ?
O2 C7 C8 F2 -45.90(19) . . . . ?
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N1 H1N S1  0.92(2) 2.18(2) 2.9622(13) 142.9(18) .
N3 H3NB O1  0.87(2) 2.06(2) 2.8149(18) 145(2) 3_766
N3 H3NA O1  0.90(2) 1.96(2) 2.8485(19) 171(2) .

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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and

goodness of fit S are based on F^2^, conventional R-factors R are based

on F, with F set to zero for negative F^2^. The threshold expression of

F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is

not relevant to the choice of reflections for refinement. R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

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S2 S 0.59704(4) -0.08413(7) 0.158849(14) 0.02813(15) Uani 1 1 d . . .

N1 N 0.51548(12) 0.0785(2) 0.08621(4) 0.0223(4) Uani 1 1 d . . .

N2 N 0.36104(12) 0.1449(2) 0.07808(4) 0.0223(4) Uani 1 1 d . . .

N3 N 0.65794(12) 0.1991(2) 0.12983(4) 0.0214(4) Uani 1 1 d . . .

N4 N 0.61917(13) 0.2173(2) 0.18652(5) 0.0238(4) Uani 1 1 d . . .

O1 O 0.37538(10) 0.0011(2) 0.12746(4) 0.0296(4) Uani 1 1 d . . .

O2 O 0.19143(10) 0.2242(2) 0.06003(4) 0.0318(4) Uani 1 1 d . . .

O3 O 0.66247(12) 0.4755(2) 0.16693(4) 0.0312(4) Uani 1 1 d . . .

O4 O 0.58554(11) 0.2053(2) 0.25253(4) 0.0300(4) Uani 1 1 d . . .

C1 C 0.61064(14) 0.0601(3) 0.07699(5) 0.0213(4) Uani 1 1 d . . .

C2 C 0.63508(16) -0.0186(3) 0.04704(6) 0.0266(5) Uani 1 1 d . . .

C3 C 0.72726(17) -0.0380(3) 0.03861(6) 0.0306(5) Uani 1 1 d . . .

C4 C 0.79605(17) 0.0205(3) 0.05989(6) 0.0308(5) Uani 1 1 d . . .

C5 C 0.77210(15) 0.0966(3) 0.09018(6) 0.0262(5) Uani 1 1 d . . .

C6 C 0.67977(14) 0.1153(3) 0.09898(5) 0.0207(4) Uani 1 1 d . . .

C7 C 0.45215(14) 0.1553(3) 0.06699(5) 0.0211(4) Uani 1 1 d . . .

C8 C 0.32543(14) 0.0654(3) 0.10608(5) 0.0212(4) Uani 1 1 d . . .

C9 C 0.22234(14) 0.0596(3) 0.10904(5) 0.0206(4) Uani 1 1 d . . .

C10 C 0.18766(16) -0.0343(3) 0.13621(6) 0.0251(5) Uani 1 1 d . . .

C11 C 0.09417(16) -0.0553(3) 0.14130(6) 0.0284(5) Uani 1 1 d . . .

C12 C 0.03229(16) 0.0204(3) 0.11940(6) 0.0304(5) Uani 1 1 d . . .

C13 C 0.06378(15) 0.1138(3) 0.09225(6) 0.0286(5) Uani 1 1 d . . .

C14 C 0.15814(14) 0.1324(3) 0.08667(5) 0.0230(4) Uani 1 1 d . . .

C15 C 0.13001(18) 0.2566(3) 0.03216(6) 0.0320(5) Uani 1 1 d . . .

C16 C 0.62663(14) 0.1192(3) 0.15723(5) 0.0219(4) Uani 1 1 d . . .

C17 C 0.64167(14) 0.3851(3) 0.19081(5) 0.0227(4) Uani 1 1 d . . .

C18 C 0.64042(14) 0.4553(3) 0.22596(5) 0.0235(4) Uani 1 1 d . . .

C19 C 0.66912(15) 0.6233(3) 0.22867(6) 0.0286(5) Uani 1 1 d . . .

C20 C 0.67428(17) 0.7035(3) 0.25959(7) 0.0340(5) Uani 1 1 d . . .

C21 C 0.65031(18) 0.6153(4) 0.28859(7) 0.0369(6) Uani 1 1 d . . .

C22 C 0.62039(17) 0.4508(3) 0.28674(6) 0.0317(5) Uani 1 1 d . . .

C23 C 0.61511(14) 0.3690(3) 0.25560(5) 0.0249(5) Uani 1 1 d . . .

C24 C 0.57470(18) 0.1100(3) 0.28318(6) 0.0321(5) Uani 1 1 d . . .

H1N H 0.4965(19) 0.036(3) 0.1045(7) 0.039(8) Uiso 1 1 d . . .

H2N H 0.3236(17) 0.189(3) 0.0644(7) 0.030(7) Uiso 1 1 d . . .

H3N H 0.6740(18) 0.298(4) 0.1330(7) 0.036(8) Uiso 1 1 d . . .

H4N H 0.6054(19) 0.161(4) 0.2035(7) 0.041(8) Uiso 1 1 d . . .

H2 H 0.5889(16) -0.055(3) 0.0317(6) 0.023(6) Uiso 1 1 d . . .

H3 H 0.7406(19) -0.092(3) 0.0182(6) 0.035(7) Uiso 1 1 d . . .

H4 H 0.860(2) 0.005(3) 0.0534(7) 0.043(8) Uiso 1 1 d . . .

H5 H 0.8171(18) 0.141(3) 0.1038(7) 0.035(7) Uiso 1 1 d . . .

H10 H 0.2302(17) -0.085(3) 0.1501(6) 0.030(7) Uiso 1 1 d . . .

H11 H 0.0695(19) -0.128(4) 0.1583(7) 0.040(7) Uiso 1 1 d . . .

H12 H -0.0319(18) 0.008(3) 0.1225(6) 0.034(7) Uiso 1 1 d . . .

H13 H 0.0199(17) 0.168(3) 0.0765(6) 0.032(7) Uiso 1 1 d . . .

H15A H 0.1684(17) 0.311(3) 0.0142(6) 0.032(7) Uiso 1 1 d . . .

H15B H 0.0827(18) 0.337(3) 0.0386(6) 0.036(7) Uiso 1 1 d . . .

H15C H 0.1019(18) 0.148(4) 0.0233(7) 0.042(8) Uiso 1 1 d . . .

H19 H 0.6852(18) 0.677(3) 0.2082(7) 0.036(7) Uiso 1 1 d . . .

H20 H 0.6955(17) 0.818(4) 0.2608(6) 0.036(7) Uiso 1 1 d . . .

H21 H 0.6558(17) 0.665(3) 0.3104(7) 0.035(7) Uiso 1 1 d . . .

H22 H 0.6025(18) 0.396(3) 0.3061(7) 0.037(7) Uiso 1 1 d . . .

H24A H 0.5603(18) -0.002(4) 0.2751(6) 0.032(7) Uiso 1 1 d . . .

H24B H 0.634(2) 0.108(4) 0.2955(7) 0.045(8) Uiso 1 1 d . . .

H24C H 0.5234(19) 0.159(4) 0.2974(7) 0.042(7) Uiso 1 1 d . . .

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S2 0.0367(3) 0.0247(3) 0.0229(3) 0.0034(2) 0.0016(2) -0.0041(2)

N1 0.0205(9) 0.0301(10) 0.0163(8) 0.0007(8) 0.0005(7) -0.0002(8)

N2 0.0201(9) 0.0277(10) 0.0190(9) 0.0010(7) -0.0013(7) 0.0014(8)

N3 0.0239(9) 0.0222(9) 0.0180(9) 0.0011(7) 0.0001(7) 0.0001(7)

N4 0.0282(10) 0.0266(10) 0.0165(9) 0.0018(7) 0.0007(7) -0.0014(8)

O1 0.0223(8) 0.0422(10) 0.0243(8) 0.0094(7) -0.0021(6) 0.0033(7)

O2 0.0241(8) 0.0438(10) 0.0274(8) 0.0147(7) -0.0034(6) -0.0004(7)

O3 0.0429(10) 0.0274(8) 0.0232(8) 0.0034(7) -0.0001(7) -0.0014(7)

O4 0.0386(9) 0.0328(9) 0.0187(7) 0.0012(7) 0.0017(7) -0.0056(7)

C1 0.0196(10) 0.0226(10) 0.0216(10) 0.0033(8) 0.0030(8) 0.0023(8)

C2 0.0315(12) 0.0255(11) 0.0227(11) -0.0015(9) 0.0002(9) 0.0016(9)

C3 0.0373(14) 0.0288(12) 0.0256(12) -0.0002(9) 0.0105(10) 0.0084(10)

C4 0.0266(12) 0.0330(12) 0.0328(13) 0.0070(10) 0.0083(10) 0.0068(10)

C5 0.0223(11) 0.0284(12) 0.0279(11) 0.0070(9) -0.0004(9) 0.0004(9)

C6 0.0235(10) 0.0199(10) 0.0188(10) 0.0035(8) 0.0009(8) 0.0023(8)

C7 0.0224(10) 0.0223(10) 0.0185(10) -0.0046(8) 0.0003(8) -0.0016(8)

C8 0.0220(10) 0.0229(10) 0.0188(10) -0.0030(8) -0.0001(8) 0.0011(8)

C9 0.0199(10) 0.0215(10) 0.0204(10) -0.0025(8) 0.0002(8) -0.0002(8)

C10 0.0253(11) 0.0284(11) 0.0215(11) -0.0014(9) 0.0020(9) 0.0003(9)

C11 0.0280(12) 0.0307(12) 0.0265(11) 0.0011(10) 0.0066(9) -0.0040(10)

C12 0.0191(11) 0.0380(13) 0.0341(13) -0.0031(10) 0.0039(9) -0.0035(10)

C13 0.0218(11) 0.0334(13) 0.0305(12) 0.0009(10) -0.0042(9) 0.0019(9)

C14 0.0226(11) 0.0244(11) 0.0219(10) 0.0003(8) 0.0010(8) -0.0001(8)

C15 0.0329(13) 0.0381(14) 0.0251(12) 0.0045(11) -0.0047(10) 0.0095(11)

C16 0.0182(10) 0.0266(11) 0.0209(10) 0.0012(8) -0.0019(8) 0.0013(8)

C17 0.0199(10) 0.0270(11) 0.0212(10) 0.0013(9) -0.0014(8) 0.0035(8)

C18 0.0198(10) 0.0285(11) 0.0223(10) -0.0017(9) -0.0018(8) 0.0023(9)

C19 0.0235(11) 0.0309(12) 0.0312(12) -0.0013(10) 0.0020(9) 0.0008(9)

C20 0.0289(12) 0.0321(13) 0.0410(14) -0.0120(11) 0.0027(10) -0.0027(10)

C21 0.0333(13) 0.0459(15) 0.0315(13) -0.0152(12) 0.0019(10) -0.0003(11)

C22 0.0285(12) 0.0423(14) 0.0243(12) -0.0052(10) 0.0032(10) 0.0011(10)

C23 0.0198(10) 0.0309(11) 0.0240(11) -0.0026(9) -0.0010(8) 0.0011(9)

C24 0.0348(14) 0.0387(14) 0.0226(12) 0.0055(10) 0.0027(10) -0.0049(11)

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;

All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles

and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

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S2 C16 1.664(2) . ?

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N1 C1 1.431(3) . ?

N1 H1N 0.85(3) . ?

N2 C8 1.375(3) . ?

N2 C7 1.391(3) . ?

N2 H2N 0.84(3) . ?

N3 C16 1.334(3) . ?

N3 C6 1.425(3) . ?

N3 H3N 0.83(3) . ?

N4 C17 1.376(3) . ?

N4 C16 1.399(3) . ?

N4 H4N 0.83(3) . ?

O1 C8 1.223(2) . ?

O2 C14 1.368(3) . ?

O2 C15 1.440(3) . ?

O3 C17 1.223(3) . ?

O4 C23 1.368(3) . ?

O4 C24 1.437(3) . ?

C1 C2 1.385(3) . ?

C1 C6 1.396(3) . ?

C2 C3 1.383(3) . ?

C2 H2 0.95(2) . ?

C3 C4 1.383(4) . ?

C3 H3 0.93(3) . ?

C4 C5 1.386(3) . ?

C4 H4 0.97(3) . ?

C5 C6 1.388(3) . ?

C5 H5 0.92(3) . ?

C8 C9 1.496(3) . ?

C9 C10 1.400(3) . ?

C9 C14 1.406(3) . ?

C10 C11 1.377(3) . ?

C10 H10 0.92(3) . ?

C11 C12 1.382(3) . ?

C11 H11 0.96(3) . ?

C12 C13 1.381(3) . ?

C12 H12 0.94(3) . ?

C13 C14 1.390(3) . ?

C13 H13 0.99(3) . ?

C15 H15A 1.00(3) . ?

C15 H15B 0.97(3) . ?

C15 H15C 1.01(3) . ?

C17 C18 1.499(3) . ?

C18 C19 1.395(3) . ?

C18 C23 1.406(3) . ?

C19 C20 1.380(3) . ?

C19 H19 0.94(3) . ?

C20 C21 1.387(4) . ?

C20 H20 0.95(3) . ?

C21 C22 1.372(4) . ?

C21 H21 0.95(3) . ?

C22 C23 1.394(3) . ?

C22 H22 0.92(3) . ?

C24 H24A 0.96(3) . ?

C24 H24B 0.99(3) . ?

C24 H24C 1.01(3) . ?

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C7 N1 H1N 116.6(19) . . ?

C1 N1 H1N 119.3(19) . . ?

C8 N2 C7 129.52(19) . . ?

C8 N2 H2N 117.9(17) . . ?

C7 N2 H2N 112.5(17) . . ?

C16 N3 C6 123.52(19) . . ?

C16 N3 H3N 114.8(19) . . ?

C6 N3 H3N 120.6(19) . . ?

C17 N4 C16 128.16(19) . . ?

C17 N4 H4N 118(2) . . ?

C16 N4 H4N 113(2) . . ?

C14 O2 C15 117.93(18) . . ?

C23 O4 C24 117.02(18) . . ?

C2 C1 C6 119.4(2) . . ?

C2 C1 N1 120.61(19) . . ?

C6 C1 N1 119.89(18) . . ?

C3 C2 C1 120.2(2) . . ?

C3 C2 H2 119.4(14) . . ?

C1 C2 H2 120.4(14) . . ?

C2 C3 C4 120.6(2) . . ?

C2 C3 H3 117.3(17) . . ?

C4 C3 H3 122.1(17) . . ?

C3 C4 C5 119.5(2) . . ?

C3 C4 H4 119.1(17) . . ?

C5 C4 H4 121.4(17) . . ?

C4 C5 C6 120.3(2) . . ?

C4 C5 H5 120.0(16) . . ?

C6 C5 H5 119.6(16) . . ?

C5 C6 C1 120.0(2) . . ?

C5 C6 N3 118.55(19) . . ?

C1 C6 N3 121.41(18) . . ?

N1 C7 N2 116.27(18) . . ?

N1 C7 S1 126.61(16) . . ?

N2 C7 S1 117.12(16) . . ?

O1 C8 N2 121.78(19) . . ?

O1 C8 C9 121.45(19) . . ?

N2 C8 C9 116.77(18) . . ?

C10 C9 C14 117.66(19) . . ?

C10 C9 C8 115.68(19) . . ?

C14 C9 C8 126.60(19) . . ?

C11 C10 C9 121.9(2) . . ?

C11 C10 H10 121.2(16) . . ?

C9 C10 H10 116.9(16) . . ?

C10 C11 C12 119.5(2) . . ?

C10 C11 H11 122.8(16) . . ?

C12 C11 H11 117.5(16) . . ?

C13 C12 C11 120.4(2) . . ?

C13 C12 H12 118.9(16) . . ?

C11 C12 H12 120.7(16) . . ?

C12 C13 C14 120.3(2) . . ?

C12 C13 H13 120.8(15) . . ?

C14 C13 H13 118.9(15) . . ?

O2 C14 C13 121.61(19) . . ?

O2 C14 C9 118.05(18) . . ?

C13 C14 C9 120.3(2) . . ?

O2 C15 H15A 106.2(14) . . ?

O2 C15 H15B 110.6(15) . . ?

H15A C15 H15B 108(2) . . ?

O2 C15 H15C 111.1(16) . . ?

H15A C15 H15C 110(2) . . ?

H15B C15 H15C 111(2) . . ?

N3 C16 N4 115.98(19) . . ?

N3 C16 S2 125.14(17) . . ?

N4 C16 S2 118.88(16) . . ?

O3 C17 N4 121.7(2) . . ?

O3 C17 C18 120.3(2) . . ?

N4 C17 C18 117.95(18) . . ?

C19 C18 C23 118.4(2) . . ?

C19 C18 C17 114.9(2) . . ?

C23 C18 C17 126.8(2) . . ?

C20 C19 C18 121.4(2) . . ?

C20 C19 H19 123.0(17) . . ?

C18 C19 H19 115.6(17) . . ?

C19 C20 C21 119.3(2) . . ?

C19 C20 H20 119.6(16) . . ?

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C21 C22 H22 119.5(17) . . ?

C23 C22 H22 120.2(17) . . ?

O4 C23 C22 122.3(2) . . ?

O4 C23 C18 117.78(19) . . ?

C22 C23 C18 119.9(2) . . ?

O4 C24 H24A 103.0(15) . . ?

O4 C24 H24B 109.4(17) . . ?

H24A C24 H24B 110(2) . . ?

O4 C24 H24C 110.6(16) . . ?

H24A C24 H24C 112(2) . . ?

H24B C24 H24C 112(2) . . ?

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C7 N1 C1 C6 126.3(2) . . . . ?

C6 C1 C2 C3 -1.8(3) . . . . ?

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C3 C4 C5 C6 -0.5(3) . . . . ?

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C4 C5 C6 N3 -178.0(2) . . . . ?

C2 C1 C6 C5 2.3(3) . . . . ?

N1 C1 C6 C5 179.58(19) . . . . ?

C2 C1 C6 N3 179.07(19) . . . . ?

N1 C1 C6 N3 -3.7(3) . . . . ?

C16 N3 C6 C5 -107.2(2) . . . . ?

C16 N3 C6 C1 76.0(3) . . . . ?

C1 N1 C7 N2 172.99(18) . . . . ?

C1 N1 C7 S1 -6.5(3) . . . . ?

C8 N2 C7 N1 -0.6(3) . . . . ?

C8 N2 C7 S1 178.95(17) . . . . ?

C7 N2 C8 O1 6.5(3) . . . . ?

C7 N2 C8 C9 -172.99(19) . . . . ?

O1 C8 C9 C10 -4.6(3) . . . . ?

N2 C8 C9 C10 174.79(18) . . . . ?

O1 C8 C9 C14 178.2(2) . . . . ?

N2 C8 C9 C14 -2.4(3) . . . . ?

C14 C9 C10 C11 -0.3(3) . . . . ?

C8 C9 C10 C11 -177.7(2) . . . . ?

C9 C10 C11 C12 -1.1(3) . . . . ?

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C11 C12 C13 C14 0.1(4) . . . . ?

C15 O2 C14 C13 -19.2(3) . . . . ?

C15 O2 C14 C9 162.3(2) . . . . ?

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C12 C13 C14 C9 -1.5(3) . . . . ?

C10 C9 C14 O2 -179.91(19) . . . . ?

C8 C9 C14 O2 -2.8(3) . . . . ?

C10 C9 C14 C13 1.6(3) . . . . ?

C8 C9 C14 C13 178.6(2) . . . . ?

C6 N3 C16 N4 172.64(18) . . . . ?

C6 N3 C16 S2 -7.1(3) . . . . ?

C17 N4 C16 N3 -1.3(3) . . . . ?

C17 N4 C16 S2 178.47(17) . . . . ?

C16 N4 C17 O3 8.5(3) . . . . ?

C16 N4 C17 C18 -171.25(19) . . . . ?

O3 C17 C18 C19 -3.3(3) . . . . ?

N4 C17 C18 C19 176.42(19) . . . . ?

O3 C17 C18 C23 177.7(2) . . . . ?

N4 C17 C18 C23 -2.5(3) . . . . ?

C23 C18 C19 C20 1.0(3) . . . . ?

C17 C18 C19 C20 -178.0(2) . . . . ?

C18 C19 C20 C21 -0.1(4) . . . . ?

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C24 O4 C23 C22 -10.3(3) . . . . ?

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C21 C22 C23 O4 -179.9(2) . . . . ?

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C19 C18 C23 O4 178.87(19) . . . . ?

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N2 H2N O2  0.84(3) 1.94(3) 2.631(2) 139(2) .

N3 H3N O3  0.83(3) 1.95(3) 2.633(2) 140(3) .

N4 H4N O4  0.83(3) 1.99(3) 2.660(2) 137(3) .


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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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S2 S 0.18801(4) 0.638912(18) 0.18093(3) 0.03003(11) Uani 1 1 d . . .
O1 O 0.5887(2) 0.56814(5) 0.34801(8) 0.0549(4) Uani 1 1 d . . .
O2 O 0.81700(16) 0.42184(5) 0.51512(7) 0.0392(3) Uani 1 1 d . . .
O3 O 0.76232(14) 0.66164(5) 0.17171(8) 0.0364(3) Uani 1 1 d . . .
O4 O 0.56701(13) 0.72870(5) 0.39782(7) 0.0292(2) Uani 1 1 d . . .
N1 N 0.45914(17) 0.49133(6) 0.21261(8) 0.0288(3) Uani 1 1 d . . .
N2 N 0.62073(18) 0.46261(6) 0.35663(9) 0.0305(3) Uani 1 1 d . . .
N3 N 0.46652(15) 0.60027(5) 0.11430(8) 0.0222(2) Uani 1 1 d . . .
N4 N 0.50801(15) 0.68386(5) 0.21973(8) 0.0232(2) Uani 1 1 d . . .
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C2 C 0.27030(19) 0.44191(7) 0.07441(10) 0.0284(3) Uani 1 1 d . . .
C3 C 0.18324(18) 0.44739(7) -0.01871(10) 0.0294(3) Uani 1 1 d . . .
C4 C 0.19364(19) 0.50183(7) -0.06904(10) 0.0309(3) Uani 1 1 d . . .
C5 C 0.28691(18) 0.55260(7) -0.02551(10) 0.0268(3) Uani 1 1 d . . .
C6 C 0.37104(16) 0.54806(6) 0.06812(9) 0.0219(3) Uani 1 1 d . . .
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C9 C 0.7332(2) 0.52805(7) 0.49511(10) 0.0297(3) Uani 1 1 d . . .
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C11 C 0.8134(2) 0.60149(9) 0.62445(12) 0.0431(4) Uani 1 1 d . . .
C12 C 0.8943(3) 0.55395(9) 0.68085(11) 0.0461(4) Uani 1 1 d . . .
C13 C 0.8967(2) 0.49376(8) 0.64657(11) 0.0412(4) Uani 1 1 d . . .
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C15 C 0.9042(3) 0.37223(8) 0.57264(13) 0.0453(4) Uani 1 1 d . . .
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C18 C 0.78131(17) 0.73201(6) 0.30015(9) 0.0227(3) Uani 1 1 d . . .
C19 C 0.94113(18) 0.75416(6) 0.28371(10) 0.0268(3) Uani 1 1 d . . .
C20 C 1.0484(2) 0.79117(7) 0.34915(11) 0.0326(3) Uani 1 1 d . . .
C21 C 0.9982(2) 0.80468(7) 0.43428(11) 0.0332(3) Uani 1 1 d . . .
C22 C 0.83934(19) 0.78368(7) 0.45293(10) 0.0289(3) Uani 1 1 d . . .
C23 C 0.72780(17) 0.74888(6) 0.38529(9) 0.0235(3) Uani 1 1 d . . .
C24 C 0.5065(2) 0.74885(9) 0.48089(12) 0.0401(4) Uani 1 1 d . . .
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H15C H 0.892(2) 0.3370(10) 0.5301(14) 0.045(5) Uiso 1 1 d . . .
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C4 0.0273(7) 0.0387(8) 0.0237(7) -0.0088(6) -0.0028(5) 0.0070(6)
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C23 0.0255(7) 0.0187(6) 0.0257(6) -0.0004(5) 0.0028(5) 0.0021(5)
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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 H2N O2  0.822(19) 1.952(19) 2.6398(16) 140.7(17) .
N3 H3N O3  0.855(18) 1.974(18) 2.6438(15) 134.4(16) .
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