Electron Spin Resonance and Molecular Motion of the $\text{RCH}_2\dot{\text{C}}\text{HCOOR}'$ Radicals in X-Irradiated Ester-Urea Inclusion Compounds*

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Single crystals of the inclusion compounds formed between long-chain alkyl esters and urea were x irradiated at room temperature, and the free radicals produced were investigated by electron spin resonance. The 11 esters studied were diethyl adipate and the methyl, ethyl, hexyl, and octyl esters of monocarboxylic acids. The long-lived free radicals observed in all of these compounds are of the type $\text{RCH}_2\dot{\text{C}}\text{HCOOR}'$. These are π -electron radicals with the unpaired electron largely localized on one carbon $2p$ orbital. The coupling constants of the alcohol protons (R') were resolved in the spectra of several radicals and the values ranged from 3 to 6 Mc/sec. The ester radicals undergo motion in the tubular cavities formed by the urea molecules of the crystal, and this affects the magnitudes of the proton coupling constants. The dependence of the α - and β -proton coupling constants on this motion is briefly considered. From the ethyl heptanoate radical ESR data, recorded over the range of 352° to $7^\circ \pm 3^\circ\text{K}$, and from the room-temperature ESR data of all eleven ester radicals, information is obtained regarding the motions and orientations of the ester radicals. In addition, two carboxylic-acid-urea inclusion compounds were investigated, and the orientations and motions of the well-known radicals produced in these systems ($\text{RCH}_2\dot{\text{C}}\text{HCOOH}$) are compared to those of the ester radicals. Approximate equations are given which relate the observed α -proton coupling constants and spectroscopic splitting factors to the diagonal elements of the α -proton tensors and g tensors of all radicals investigated.

INTRODUCTION

THE inclusion compounds formed between urea and the n hydrocarbons or their derivatives have been extensively studied.¹⁻⁴ Crystallographic data have been reported on the crystals formed between urea and acids, alcohols, halides, ethers, and several n hydrocarbons. By comparing x-ray powder diffraction patterns, it has been concluded that all of these systems have similar hexagonal crystal structures.^{5,6} Furthermore, Smith⁷ has completed a detailed crystallographic investigation of the n -hexadecane-urea compound. Long crystals, hexagonal in cross section, were formed by the addition of hexadecane to a solution containing urea and isopropyl alcohol. The unit cell is hexagonal ($a_0 = 8.230 \text{ \AA}$ and $c_0 = 11.005 \text{ \AA}$), and there are six urea molecules per unit cell. The hexadecane molecules are in an extended planar zigzag configuration with their long axes parallel to the c axis, and are enclosed in tubular cavities formed by spirals of hy-

drogen-bonded urea molecules. The time-average positions of the plane of the hydrocarbon molecules are either perpendicular to the a axis, or are at multiples of 60° to this position. The view along the c axis of a long-chain hydrocarbon-urea compound is given in Fig. 1.

In addition to the crystallographic work, dielectric absorption⁸ and nuclear magnetic resonance⁹ investigations of several urea inclusion compounds have been reported. Results from all of these investigations support the conclusion that the hydrocarbon molecules (or their derivatives) fit only loosely in the tubular cavities, and thus may undergo a large degree of molecular motion.

Because of the simplifying effects of ordered structure and molecular motion, these compounds provide a convenient medium for electron spin resonance (ESR) studies of certain x-ray-produced free radicals. A preliminary account of this technique has been published.¹⁰ In this paper we are concerned with the identification, orientation, and molecular motion of the free radicals produced by the x irradiation of the ester-urea crystals.

PROTON COUPLING CONSTANTS

Apparently, no crystal-structure data have been published on the compounds formed between urea and the straight-chain ester molecules. However, considering the data reported above, it is highly plausible that these compounds have hexagonal crystal structures.

* R. J. Meakins, Trans. Faraday Soc. **51**, 953 (1955).

† D. F. R. Gilson and C. A. McDowell, Mol. Phys. **4**, 125 (1961).

‡ O. H. Griffith and H. M. McConnell, Proc. Natl. Acad. Sci. (U.S.) **48**, 1877 (1962).

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‡ Contribution No. 3095.

¹ O. Redlich, C. M. Gable, A. K. Dunlop, and R. W. Millar, J. Am. Chem. Soc. **72**, 4153 (1950).

² K. A. Kobe and W. G. Domask, Petroleum Refiner **31**, No. 3, 106 (1952).

³ W. Schlenk, Jr., Fortsch. Chem. Forsch. **2**, 92 (1951).

⁴ Other terms often used to describe these crystals are occlusion compounds, adducts, complexes, and canal complexes. The nomenclature is somewhat unfortunate as these systems are neither compounds nor complexes. They are simply crystalline structures in which one of the components fits into cavities formed by the other. There exist no chemical bonds between the two components (other than perhaps hydrogen bonds).

⁵ W. Schlenk, Jr., Ann. **565**, 204 (1949).

⁶ A. E. Smith, J. Chem. Phys. **18**, 150 (1950).

⁷ A. E. Smith, Acta Cryst. **5**, 224 (1952).

Here we assume this to be the case, and later provide ESR data supporting this assumption. Anticipating the experimental results, we assume that the only stable radical formed is the one obtained by removal of one of the α protons¹¹ from the ester molecule. Therefore we have a model in which there are six orientations of one radical. As in the case of the hexadecane-urea crystal, the esters are taken to be in an extended all-*trans* configuration with the time-average position of the plane containing the carbon atoms perpendicular to the tubular axis. The six orientations are related by the sixfold symmetry axis of the tubular cavity.¹²

The ester radical is expected to be very similar in electronic structure to the extensively studied radical $\text{RCH}_2\dot{\text{C}}\text{HCO}_2\text{H}$ formed by the x irradiation of aliphatic dicarboxylic acids.¹³⁻¹⁵ Therefore, as in the acid case, the spin density is largely localized on the π orbital of Carbon Atom 2 and the problem becomes primarily one involving two isotropic β protons and one anisotropic α proton. The coupling constants of both α and β protons have been investigated in detail by McConnell and co-workers^{13,16-18} and by others.^{14,15} We briefly consider here the aspects of the dependence of the α - and β -proton coupling constants on the motion and orientations encountered in the experimental work reported below (as represented by the above model). The six possible orientations of the radical have a negligible effect on the coupling constants of the β protons, but

¹¹ The convention for the labeling of protons (α , β , γ , ζ) and carbon atoms (C_1 , C_2 , C_3) used here is

¹² The choice of the number of orientations of the ester radicals needs to be qualified. For the purpose of this footnote, the carbon nuclei are assumed to be in a planar zigzag conformation. Therefore, there are presumably 12 orientations; the six mentioned above, and six more related to the first six by twofold rotations about the c axis. Even more orientations may exist if the ester molecules stack in a head-to-head fashion in the tubular cavities, rather than in a head-to-tail fashion. In any case, if we assume that the molecular x' and z' axes lie in the crystalline xy plane there are only three magnetically distinguishable orientations (see Fig. 2 for the definitions of the axes). We refer to the existence of six orientations rather than to three (or some other number) to emphasize the hexagonal structure of the crystal. Of course, the lengths of the hydrocarbon derivatives are not integral multiples of the urea spiral repeat distance (except by accident). As pointed out by Smith,⁷ this causes a one-dimensional disorder along the c axis of the crystal. However, all orientations may be obtained from the above-mentioned orientations by simple translations along the c axis, and therefore the disorder does not affect the ESR spectra, proving the carbon nuclei are in a planar zigzag configuration.

¹³ C. Heller and H. M. McConnell, *J. Chem. Phys.* **32**, 1535 (1960).

¹⁴ D. Pooley and D. H. Whiffen, *Mol. Phys.* **4**, 81 (1961).

¹⁵ J. R. Morton and A. Horsfield, *Mol. Phys.* **4**, 219 (1961).

¹⁶ H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Am. Chem. Soc.* **82**, 766 (1960).

¹⁷ H. M. McConnell and R. W. Fessenden, *J. Chem. Phys.* **31**, 1688 (1959).

¹⁸ H. M. McConnell and J. Strathdee, *Mol. Phys.* **2**, 129 (1959).

are important to the discussion of the α -proton coupling constants.

β -Proton Coupling Constants

Theoretical studies¹⁹⁻²¹ suggest that the isotropic coupling constants of the β protons, a^β , are related to the spin density in the p_x orbital on Carbon Atom 2, ρ_c^π , by the linear equation

$$a^\beta = R(\theta)\rho_c^\pi. \quad (1)$$

Heller and McConnell^{13,22} have suggested that $R(\theta)$ be approximated by the relation

$$R(\theta) = B^0 \cos^2 \theta, \quad (2)$$

where θ is the angle between the axis of the p_x orbital on C_2 and the projection of the $\text{C}_3\text{-H}_\beta$ bond onto a plane which is perpendicular to the $\text{C}_2\text{-C}_3$ bond.

For radicals containing two β protons attached to the same carbon atom, the two values of θ_0 are $30^\circ \mp \gamma$ or $60^\circ \mp \gamma$, depending on the conformation of the molecule. Equation (2) then becomes

$$R_{1,2}(\theta) = B^0 \cos^2(30^\circ \mp \gamma), \quad (3)$$

or

$$R_{1,2}(\theta) = B^0 \cos^2(60^\circ \mp \gamma). \quad (4)$$

The upper and lower signs refer to the positions of Protons 1 and 2, respectively, and γ is called the angle of twist (Fig. 2). In the special case that $\gamma = 0$, the two protons will have identical coupling constants. Equation (2) has been justified by valence-bond theory,²¹ and Eqs. (2) and (3) have been used in numerous experimental studies of free radicals containing β protons.¹³⁻¹⁵

If the β protons undergo motion with respect to the axis of the p_x orbital, $R(\theta)$ must be replaced by an

¹⁹ H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.* **28**, 107 (1958).

²⁰ A. D. McLachlan, H. Dearman, and R. Lefebvre, *J. Chem. Phys.* **33**, 65 (1960).

²¹ A. D. McLachlan, *Mol. Phys.* **1**, 233 (1958).

²² The actual relation suggested by Heller and McConnell is $R(\theta) = A^0 + B^0 \cos^2 \theta$. As noted by these authors, the constant A^0 is expected to be zero on theoretical grounds.^{21,23} A^0 is found to be negligible within the limits of experimental error for the radicals discussed here. (For example, assume that either $B^0(\text{CH}_2) = B^0(\text{CH}_3)$ or that the ethyl heptanoate radical at 298°K is undergoing complete averaging of the β -proton positions with respect to the α proton. One may then solve the three equations involving the completely averaged room-temperature β -proton data and the $7^\circ \pm 3^\circ\text{K}$ ethyl heptanoate radical data for the three unknowns A^0 , B^0 , and γ . A^0 is found to be zero within the limits of ± 5 Mc/sec). It may be noted that all proton coupling constants are listed as their absolute values. The α - and β -proton coupling constants of very similar radicals have been found to be negative¹⁶ and positive,²⁸ respectively.

²³ P. G. Lykos, *J. Chem. Phys.* **32**, 625 (1960).

FIG. 1. A long-chain hydrocarbon (*n*-hexadecane)-urea inclusion compound. The contents of the unit cell are projected onto the (001) plane and show the packing arrangement. This figure was reproduced from the crystal structure work⁹ of Smith with his kind permission.

average value $\langle R(\theta) \rangle$. For example, if all values of θ are equally likely (e.g., free rotation about the $\text{C}_2\text{-C}_3$ bond) and the frequency associated with the motion is large compared to the hyperfine frequency,²⁴ then

$$\langle R(\theta) \rangle / B^0 = \frac{1}{2}. \quad (5)$$

In general, the values of θ will not all be equally likely, and the probability density function describing the motion must be determined in order to evaluate $\langle R(\theta) \rangle$. Stone and Maki²⁶ have used the harmonic oscillator and free-rotor approximations to evaluate $\langle R(\theta) \rangle$. Several other authors have also considered the effects of molecular motion on β -proton coupling constants.²⁷⁻²⁹

²⁴ This is perhaps too stringent a requirement on the frequency of the motion. Arguments based on rapidly fluctuating magnetic environments²⁶ suggest that the criterion is that the frequency of the motion should be large compared to the difference in the hyperfine frequencies considered. This argument applies to the α - as well as to the β -proton hyperfine interactions. This distinction does not affect significantly our qualitative arguments involving the motion of the protons.

²⁶ P. W. Anderson and P. R. Weiss, *Rev. Mod. Phys.* **25**, 269 (1953).

²⁷ E. W. Stone and A. H. Maki, *J. Chem. Phys.* **37**, 1326 (1962).

²⁸ S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Chem. Phys.* **37**, 1283 (1962).

²⁹ C. Heller, *J. Chem. Phys.* **36**, 175 (1962).

³⁰ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **39**, 2147 (1963).

In the case of the ester-urea crystals, the urea molecules restrict the internal motion of the ester molecules and create an essentially infinite barrier to complete rotation about the $\text{C}_2\text{-C}_3$ bonds. However, restricted motion about the $\text{C}_2\text{-C}_3$ bond is allowed. It is reasonable to assume this motion occurs about some equilibrium position described by the angle $\theta = \theta_0$. The effects of motion may then be readily estimated assuming various probability distribution functions.

If the motion is taken to be constrained between the extreme values of $\theta_0 \pm \alpha$, and all angles between the extreme values are assumed to be equally probable, then by direct integration of Eq. (2) one obtains

$$\langle R(\theta) \rangle / B^0 = \frac{1}{2} + (\cos^2 \theta_0 - \frac{1}{2}) (\sin 2\alpha / 2\alpha). \quad (6)$$

Or, if the motion is described as a simple harmonic oscillation between $\theta_0 + \alpha$ and $\theta_0 - \alpha$, then from Eq. (2) and the probability distribution function for a classical harmonic oscillator one obtains

$$\langle R(\theta) \rangle / B^0 = \frac{1}{2} + (\cos^2 \theta_0 - \frac{1}{2}) J_0(2\alpha), \quad (7)$$

where $J_0(2\alpha)$ is a Bessel's function of the first kind.

Finally, the motion could be approximated by a quantum mechanical harmonic oscillator. Assuming

FIG. 2. (a) The definition of the molecular Cartesian coordinate system with respect to the C_2-H_α bond and the p_z orbital (perpendicular to plane of paper) on C_2 . The origin is at the C_2 nucleus and the positive x' axis extends into the paper (see Footnote 11 for the labeling of protons and carbon atoms). (b) The view along the y' molecular axis showing one possible geometrical configuration of the free radical β protons. The solid line and dashed line represent the axis of the $2p_z$ orbital and the radical plane, respectively.

Boltzmann statistics, one obtains

$$\frac{\langle R(\theta) \rangle}{B^0} = \frac{1}{2} + \left(\cos^2 \theta_0 - \frac{1}{2} \right) \left[1 - \exp\left(-\frac{E}{kT}\right) \right] \times \sum_{n=0}^{\infty} \sum_{\nu=0}^n \frac{(-2)^{\nu} n!}{(\nu!)^2 b^{\nu} (n-\nu)!} \exp\left(-\frac{nE}{kt} - b^{-1}\right), \quad (8)$$

where

$$E = \hbar(V_0/I)^{1/2} \quad \text{and} \quad b = (IV_0)^{1/2}/\hbar,$$

$\alpha^2 V_0/2$ is the potential-energy term of the harmonic oscillator Hamiltonian, and I is the reduced moment of inertia for motion about the C_2-C_3 bond. Equation (8) may, in principle, be used to obtain a value for V_0 , providing I is known and the torsional motion about the C_2-C_3 bond is not coupled to the other motions of the molecule. Of course, all three equations [(5)-(7)] assume that the frequency associated with the motion is large compared to the β -proton hyperfine frequency.

The limiting behavior (for small α or low temperatures) of Eqs. (5)-(7) are qualitatively the same. The dependence of $\langle R(\theta) \rangle$ on the motion in all three of these equations is of the form

$$\langle R(\theta) \rangle / B^0 = \frac{1}{2} + (\cos^2 \theta_0 - \frac{1}{2}) F, \quad (9)$$

where F depends on the motion. This same algebraic form is obtained with any potential function which is symmetric about the equilibrium position θ_0 . For example, if one includes the anharmonic potential $V_1 = c_1 \alpha^4 + c_2 \alpha^8 + \dots$ as a first-order perturbation of the harmonic oscillator, Eq. (9) is modified only by a change

in F . The form of Eq. (9) is also retained if the motion is harmonic and is coupled to other harmonic oscillations. We have omitted from Eq. (9) a correction term of the form $G \sin 2\theta_0$ resulting from antisymmetric potential terms. This correction could arise, for example, from the perturbation of the harmonic oscillator by an anharmonic potential of the form $V_1 = d_1 \alpha^3 + d_2 \alpha^5 + \dots$ the motions of the ester radicals in the urea inclusion compounds are expected to be complex. Therefore, we only attempt to compare qualitatively the degree of motion of the β protons in the different radicals, and we neglect the correction term $G \sin 2\theta_0$.³⁰

Rewriting θ_0 as $30 \pm \gamma$, Eqs. (5)-(9) may be written in the form

$$\langle R_{1,2}(\theta) \rangle = A + B \cos^2(30 \mp \gamma), \quad (10a)$$

where

$$A = (B^0 - B)/2 \quad (10b)$$

and A and B depend on the motion and do not contain γ . As the motion decreases, B approaches B^0 and A approaches zero. As the motion becomes large, Eqs. (7) and (8) would not apply, but the B and A obtained from Eq. (6) approaches 0 and $B^0/2$, respectively, and therefore Eq. (10a) for this angular dependence approach Eq. (5) (as expected). The ester and acid radicals reported below cover the complete range of possible values of A and B .

If the presence of motion is ignored, then one value of B' and one value of γ' may still be found from Eq. (3) which yield the experimental values of the two β -proton coupling constants (throughout this section we denote by primes the values of B and γ obtained from Eq. (3) and the ESR data of a radical undergoing motion). However, the values of B' and γ' will be lower than B^0 and γ . In general, to obtain B^0 the system must be cooled to a temperature at which motion about the C_2-C_3 bond becomes negligible. The values of γ obtained with B^0 from the low temperature is not necessarily the same as the room-temperature value of γ since θ_0 may be a function of temperature.

α -Proton Coupling Constant

The approximate spin Hamiltonian for a system of one proton (I) interacting with one electron (S) in a

³⁰ It is difficult to estimate the correction term. However, the quantity G must approach zero as the amplitudes of oscillation become small. For large-amplitude oscillations the motion will be complex, and one must decide to what extent the resultant motion may be described as a symmetric movement about an equilibrium position. For very large oscillations (e.g., $\geq 90^\circ$) one expects qualitatively that the values of the β -proton coupling constants would be nearly independent of the angle of twist. In other words, the effect of the B and G terms of Eq. (10a) are expected to become negligible with respect to $B^0/2$, and thus Eq. (10a) should approach Eq. (5). This is experimentally observed to be the case for the ethyl heptanoate radical motion. We will proceed to use equations based on Eqs. (10a), but it should be remembered that we are only attempting to estimate the effects of complex motion on the β -proton coupling constants qualitatively.

magnetic field ($\mathbf{H}$) is¹⁶

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_{hF}, \quad (11)$$

where

$$\mathcal{H}_s = |\beta| \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} \quad (12)$$

and

$$\mathcal{H}_{hF} = hA S_x I_{x'} + hB S_x I_{x'} + hC S_y I_{y'}; \quad (13)$$

β is the electronic Bohr magneton; $\mathbf{g}$ is the spectroscopic splitting factor tensor; and A , B , C are the diagonal elements of the α -proton nuclear hyperfine coupling constant tensor. The nuclear Zeeman term has been neglected. In Eq. (11) the molecular Cartesian coordinate system (x' , y' , z') is used in which the α proton hyperfine tensor is diagonal. This right-handed coordinate system is assumed to bear the same relation to the geometry of the ester radical as it does to that of the corresponding carboxylic acid radical¹⁶ (Fig. 2).

In our model, the molecular y' axis is approximately parallel to the c axis (tubular axis) of the urea compound. If we consider frequencies of motion in a plane perpendicular to the c axis sufficiently large to produce an isotropic α -proton splitting in that plane, and assume further that all orientations of x' and z' in that plane are equally likely, then Eq. (13) reduces to the axially symmetric form

$$\mathcal{H}_{hF} = hD S_x I_{x'} + hD S_x I_{x'} + hC S_y I_{y'}, \quad (14)$$

where

$$D = (A + B)/2.$$

Using Eq. (14) in place of Eq. (13) and assuming that the anisotropy of g is small, the α -proton coupling constant, a^α , as a function of the angle, Φ , between the magnetic field vector and the crystalline c axis is¹⁶

$$a^\alpha = [D^2 + (C^2 - D^2) \cos^2 \Phi]^{\frac{1}{2}}. \quad (15)$$

Furthermore, the isotropic value a_0^α is

$$a_0^\alpha = \frac{1}{3}(A + B + C) = \frac{1}{3}(2D + C). \quad (16)$$

If the motion is not of sufficient amplitude or frequency to justify the use of Eq. (12), then the ESR spectra perpendicular to the c axis will be anisotropic and asymmetric. However, because of the crystal symmetry, the ESR spectra recorded with the magnetic field parallel to the crystalline c axis will remain symmetric even in the absence of molecular motion. It may be noted that since the β -proton coupling constant is a function of the motion about the $\text{C}_2\text{--C}_3$ bond and the α -proton coupling constant is a function of the orientation of the $\text{C}_2\text{--H}_\alpha$ bond with respect to the crystal coordinate system, the ESR data gives information regarding both the internal motion of the radical and motion of the radical with respect to the laboratory coordinate system.

EXPERIMENTAL

During the preliminary identification of radicals, the chemicals used were purified by distillation or recrystallization. For the majority of the work, standard commercial grade chemicals were used. Crystals of all of the acid and ester urea inclusion compounds used to obtain the data of Table I and Fig. 5 were grown from methanol by slow evaporation. A few crystals of some of the compounds were also grown from ethyl alcohol and from isopropyl alcohol, and yielded the same ESR spectra as the crystals grown from methanol. Thus, although the possibility that solvent molecules are present in the crystals has not been eliminated, if present, their effects on the ESR spectra appear to be negligible.

The crystals were obtained in the form of hexagonal needles (angles measured to $\pm 15^\circ$). The z axis of the crystalline coordinate system is defined to lie along the needle axis of the urea compound. It will not be necessary to specify the x and y axes other than that they lie in a plane perpendicular to the z axis, and hence perpendicular to the basal plane. The morphology of these compounds is the same as that of the hexagonal hexadecane-urea adduct, and this fact suggests that all of these compounds have hexagonal crystal structures and that the z axis lies along the crystalline c axis. This point is considered later in connection with the low-temperature ESR data for the x-irradiated ethyl heptanoate-urea crystal.

The crystals were subjected to 30-kV x rays from a Machlett AEG-505 x-ray tube for two to ten hours at room temperature. A Varian X-band spectrometer was used to obtain the ESR data, and the modulation amplitude was approximately 1 Mc/sec. Crystals studied at room temperature were mounted on a Teflon plug in the microwave cavity with the aid of a microscope. An average of several spectra of three or more crystals was used to obtain each value reported in Table I. The crystals were mounted in a metal Dewar system to obtain spectra recorded below room temperature and they were placed in a heated gas-flow system for temperatures above room temperature. The uncertainty in temperature measurements decreased from $\pm 3^\circ\text{K}$ near liquid-helium temperatures to $\pm 1^\circ\text{K}$ above 30°K , and all temperatures listed without an uncertainty may be taken to be $\pm 1^\circ\text{K}$. Peroxylamine disulphonate and diphenylpicrylhydrazyl (solvent-free DPPH, Eastman Company) were used for the scan calibration and g -value standard, respectively. The total width of the peroxylamine disulphonate spectrum was taken to be 72.9 Mc/sec³¹ (26.0 G) and the g value of DPPH as 2.0036.³² For any given urea compound, the major features of the ESR spectra were independent of the source and purity of the chemicals,

³¹ J. J. Windle and A. K. Wiersema, J. Chem. Phys. **39**, 1139 (1963).

³² R. T. Weidner and C. A. Whitmer, Phys. Rev. **91**, 1279 (1953).

TABLE I. Summary of proton hyperfine coupling constants for acid and ester radicals.^{a-d}

Parent compound	a_z^α	a_{1z}^β	a_{2z}^β	a_{xy}^α	a_{1xy}^β	a_{2xy}^β
Ethyl hexanoate	82	75	63	40.7	72.6	61.5
Ethyl heptanoate	84.8	68.3	68.3	40.6	65.4	65.4
Ethyl octanoate	82	78	69	40.6	74.7	67.2
Ethyl nonanoate	...	...	...	40.6	$\sim \frac{1}{2}(136)$	$\sim \frac{1}{2}(136)$
Ethyl decanoate	...	...	...	41.0	$\sim \frac{1}{2}(146)$	$\sim \frac{1}{2}(146)$
Ethyl undecanoate	83	79	66	41.3	78.0	65.3
Ethyl dodecanoate	...	...	...	40.8	$\sim \frac{1}{2}(148)$	$\sim \frac{1}{2}(148)$
Methyl octanoate	83	89	66.5	41.1	87.4	64.4
Hexyl octanoate	82	76	59	41.0	72.4	57.2
Octyl propionate ^e	84.4	71.7	71.7	41.9	65.1	65.1
Diethyl adipate	84	67	67	41.0	64.5	64.5
Decanoic acid	...	...	...	42.4	$\sim \frac{1}{2}(178)$	$\sim \frac{1}{2}(178)$
Sebacic acid	81.8	90.4	90.4	42.4	87.2	87.2

^a All values are reported in megacycles per second.

^b The radicals are those formed by the removal of one α proton from the parent compound.

^c a^α , a_1^β , a_2^β are the coupling constants for the α proton and two β protons, respectively, and xy and z denote the spectra recorded with the magnetic field in the crystalline xy or z directions.

^d The limits of experimental error varied with the orientation of the crystals and the extent of overlap of the individual lines. Numbers reported to two and three digits are accurate to ± 1.5 Mc/sec and ± 3 Mc/sec, respectively. The β -proton coupling constants listed as approximately one half a given number indicate that the sum of the two coupling constants is known to ± 2 Mc/sec and their difference is only a few megacycles per second, but the two individual values are not accurately known. Some values are omitted (...) due to poor accuracy caused by the extensive overlapping of lines. There was nothing unusual about these overlapped spectra and the α - and β -proton coupling constants were in the same range as those reported in Table I. The decanoic acid radical, for example, gave a four-line z spectrum of approximate (but not exact) intensity ratio 1:3:3:1, which is due to three nearly equivalent protons [$a \sim \frac{1}{3}(252)$ Mc/sec].

^e The radical derived from octyl propionate exhibits three magnetically equivalent β protons ($a_1^\beta = a_2^\beta = a_3^\beta$).

the ratio of the hydrocarbon derivative to urea in the alcohol solution, and the length of time the crystals were x irradiated. The resolution of the proton splittings depended slightly on the history of the crystal, but this variation was not given any further study.

For each of the urea inclusion compounds reported in Table I, the room-temperature spectrum recorded with the magnetic field in the crystalline xy plane remained unchanged as the crystal was rotated about the z axis. Otherwise, the ESR spectra were anisotropic with respect to arbitrary rotations of the crystal.

IDENTIFICATION OF THE ESTER RADICALS

The room-temperature (298°K) ESR spectra of the x -irradiated ethyl-heptanoate-urea crystal are shown in Fig. 3, where xy and z indicate that the magnetic field is perpendicular or parallel, respectively, to the z axis of the crystal. The proton coupling constants obtained from those and other room-temperature spectra are given in Table I. The room-temperature ethyl heptanoate-urea spectrum for the xy orientation clearly consists of six lines of relative intensities 1:1:2:2:1:1 and is due to the interaction of two equivalent protons ($a=65$ Mc/sec) and a third proton ($a=41$ Mc/sec). The z spectrum of ethyl-heptanoate-urea consists of six lines of relative intensities 1:2:1:1:2:1, and results from the interaction of two equivalent protons ($a=84$

Mc/sec) and a third proton ($a=68$ Mc/sec). Furthermore, a small splitting of each line of the outside doublet into three lines is barely visible. This splitting,

FIG. 3. The ESR spectra of the ethyl heptanoate radical as a function of temperature. (The extremely small lines in the center of the z orientation, 298°K spectra, are due to an exciton impurity in the microwave cavity.)

and similar splittings of the inner lines, were slightly better resolved in some of the ESR spectra.

Spectra of the radicals formed in the systems methyl-octanoate-urea and octyl-propionate-urea are shown in Fig. 4. The eight-line equal-intensity spectrum for the xy orientation of the methyl-octanoate-urea crystal arises from the interaction of three nonequivalent protons ($a=41, 64, 87$ Mc/sec). The z spectrum of the methyl-octanoate-urea crystal is approximately a six-line spectrum (1:1:2:2:1:1) split further by three approximately equally coupled protons. The spectrum is adequately reconstructed if the four proton coupling constants are chosen to be 89, 83, 66, and 3 Mc/sec. The xy spectrum of the octyl-propionate-urea crystal consists of eight lines of relative intensities 1:1:3:3:3:3:1:1, and is due to three equivalent protons ($a=65$ Mc/sec) and a fourth proton ($a=42$ Mc/sec). On closer examination it is seen that each line is further split by the interaction of two approximately equivalent protons ($a \approx 1-3$ Mc/sec). Finally, the z spectrum of the octyl-propionate-urea crystal consists of approximately five lines split further by two protons ($a=6$ Mc/sec). The approximately five-line spectrum is due to three equivalent protons ($a=72$ Mc/sec) and one proton ($a=84$ Mc/sec).

In view of these data, the only reasonable choices for the radicals produced in ethyl-heptanoate-urea, methyl-octanoate-urea, and octyl-propionate-urea crystals are, respectively,

The α - and β -proton coupling constant assignments are given in Table I. The small coupling constants are due to the ζ -protons,³³ and splittings due to the γ protons are not observed.

³³ We have observed radicals formed by the removal of one α proton from several other hydrocarbon derivatives. For example, many alkyl ketones and ethers yielded radicals of the form

respectively. Other examples are the radicals formed from sulfides and unsaturated compounds (both alkenes and alkynes). The ζ -proton splittings of the ester radicals are being considered further in connection with the current work on these and other radicals formed by the x irradiation of urea inclusion compounds. Similar studies are also in progress using x-ray techniques and the inclusion compounds of *trans-anti-trans-anti-trans*-perhydrotriphenylene, which were recently reported by M. Farina, G. Allegra, and G. Natta, J. Am. Chem. Soc. **86**, 517 (1964).

FIG. 4. The room-temperature ESR spectra recorded with the magnetic field in the xy plane and along the z axis of two ester-urea crystals. The spectra A and B are of the methyl octanoate radical and the octyl propionate radical, respectively.

As expected, the α -proton coupling constants exhibit large anisotropies. These anisotropies were examined in detail for the systems ethyl-heptanoate-urea and octyl-propionate-urea at room temperature. If D is taken to be $a_{xy}\alpha$ and C is taken to be $a_z\alpha$, Eq. (15) reproduces the anisotropy within experimental error for all values of the angle Φ (for the limits of experimental errors see Table I). In contrast, and again as expected, the β -proton coupling constants are very nearly isotropic. The maximum and minimum values of a^β occur in the z and xy directions, respectively, and the two values differ by only a few megacycles per second.

The three β protons of the octyl propionate radical have equal coupling constants, which indicates that the methyl group is rotating (or undergoing large amplitude oscillations) at room temperature. From Eqs. (1) and (5), the values of $\rho_c^\pi B^0(\text{CH}_3)$ are

$$\rho_c^\pi B^0(\text{CH}_3)_{xy} = 2a_{xy}\beta = 130 \text{ Mc/sec},$$

$$\rho_c^\pi B^0(\text{CH}_3)_z = 2a_z\beta = 143 \text{ Mc/sec}.$$

The two values differ because of the anisotropy of the β -proton coupling constants. Only the product and not the individual values of ρ_c^π and $B^0(\text{CH}_3)$ are determined from these data. (To avoid unnecessary subscripts, the spin densities on Carbon Atom 2 of all radicals are written simply as ρ_c^π . This does not imply that all of the spin densities are equal, although evidence for this equality is presented later, and each value of ρ_c^π is to be identified with the particular radical being considered.)

In the case of the ethyl heptanoate radical, the two β protons are also equivalent, but it is not possible to determine from the room-temperature data whether

this is due to stationary equivalent 30° or 60° positions, small oscillations about one of these positions, or a complete averaging of the angle θ as given by Eq. (5). If one assumes that the last explanation is correct, the values of $\rho_c^\pi B^0(\text{CH}_2)$ are

$$\beta_c^\pi B^0(\text{CH}_2)_{xy} = 2a_{xy}^\beta = 131 \text{ Mc/sec},$$

$$\beta_c^\pi B^0(\text{CH}_2)_z = 2a_z^\beta = 137 \text{ Mc/sec}.$$

These values are approximately the same as those for $\rho_c^\pi B^0(\text{CH}_3)$, and this provides partial verification of the assumption of complete averaging of the angle θ . A further discussion of the ethyl-heptanoate-urea crystal is given in the following section.

The two β protons of the methyl octanoate radical are not equivalent. Using the two a_{xy}^β values and Eqs. (1), (3) [or Eq. (10a) with $A=0$], the values of $\rho_c^\pi B'(\text{CH}_2)_{xy}$ and γ' are found to be 102 Mc/sec and 7.5° , whereas using Eqs. (1) and (4), the values are 302 Mc/sec and 2.5° . Any set of two β -proton coupling constants must satisfy both Eq. (3) and Eq. (4), and further data are needed to decide which conformation is correct. By arguments given above,

$$B \gg B' \gg B/2,$$

where the prime indicates motion about the $\text{C}_2\text{-C}_3$ bond. Noting that for the very similar octyl propionate radical $\rho_c^\pi B(\text{CH}_3) = 130$ Mc/sec, the second set of values for $\rho_c^\pi B'(\text{CH}_2)$ and γ may be discarded. It is, therefore, concluded that the β protons of the methyl octanoate radical are undergoing oscillations with respect to the α proton about positions shifted from the 30° symmetry positions (Fig. 2). The β -proton coupling constants of these radicals are discussed further below.

TEMPERATURE VARIATIONS OF THE ETHYL HEPTANOATE RADICAL SPECTRA

X-irradiated single crystals of the ethyl-heptanoate-urea compound were investigated at temperatures above and below room temperature. The spectra at elevated temperatures for both the xy and z orientations were similar to the room-temperature spectra. The intensities of the spectra decreased markedly above 345°K , and the highest temperature for which spectra were recorded was 352°K . Below room temperature, spectra were recorded down to $7^\circ \pm 3^\circ\text{K}$, and a few of these spectra are given in Fig. 3. The xy spectrum gradually changed from a six-line to an eight-line spectrum, and the eight lines became unsymmetrical at lower temperatures ($\sim 150^\circ\text{K}$) due to incomplete averaging of the six orientations of the radical. Rotation of the crystal about the z axis, while maintaining the magnetic field in the xy plane, produced marked changes in the spectra at 77°K . The features of the spectra were reproducible at intervals of about 60° and at no other angles. This data supports the

assumption that the crystal structure is hexagonal and that the c axis lies along the z direction of the crystal.

Spectra recorded with the magnetic field along the z axis also changed gradually with decreasing temperature, and all temperature effects at all orientations were reversible. Due to the overlap of lines in both the xy and z orientations, values of the coupling constants were obtained only over certain temperature regions. Fortunately, these regions were complementary, and either the xy or z coupling constants were obtained for most temperatures.

The a_{xy}^α coupling constant of the ethyl heptanoate radical was measured down to 150°K , and the a_z^α coupling constant was measured from 298° to 220°K and from 135° to $7^\circ \pm 3^\circ\text{K}$. The values of the α -proton coupling constant for both orientations were found to be approximately independent of temperature. The value of a_z^α decreased approximately 3 Mc/sec in going from $7^\circ \pm 3^\circ\text{K}$ to 298°K , and a_{xy}^α remained unchanged over the range 298° to 150°K . Three effects which in principle could change the value of a^α with a change in temperature are: (1) a change in the value of ρ_c^π due to motion about the $\text{C}_1\text{-C}_2$ bond, (2) motion of the α proton in the xz or yz planes, and (3) reorientation of the molecule with respect to the crystalline z axis. Barring the highly unlikely cancellation of these effects, one may conclude that ρ_c^π is independent of temperature, that the molecular motion (at frequencies greater than the hyperfine frequency) of the α proton occurs primarily in the xy plane, and that there are no major reorientations of the molecular axes with respect to the crystalline z axis over the temperature range investigated. Since the unpaired spin density is largely localized on Carbon Atom 2, motion about the $\text{C}_1\text{-C}_2$ bond would not be expected to have a large effect on ρ_c^π , and therefore no conclusions about this motion may be drawn from the above data.

The β -proton coupling constant data over the range $7^\circ \pm 3^\circ$ to 250°K is presented in Fig. 5. Above 250°K the values of a_{xy}^β and a_z^β decreased gradually to the room-temperature values, a change of approximately 1 to 3 Mc/sec in 50°K . The two sets of curves in Fig. 5 would, of course, coincide if the β -proton hyperfine interaction were completely isotropic. Below 250°K the β protons became magnetically nonequivalent, causing the gradual transition from a six- to an eight-line spectrum. Using the same arguments as for the methyl octanoate radical room-temperature data, it is found that Eq. (3) and not (4) lead to acceptable values of $\rho_c^\pi B'(\text{CH}_2)$ for all data derived from the eight-line spectra.

The values of γ' and $\rho_c^\pi B'$ obtained from Eq. (3) increase with decreasing temperature. Taking 131 and 50 Mc/sec as the low-temperature limiting values of a_{1z}^β and a_{2z}^β , the values of γ and $\rho_c^\pi B^0(\text{CH}_2)_z$ are found to be 22° and 133 Mc/sec. The low-temperature limiting value of $\rho_c^\pi B^0(\text{CH}_2)_z$ may be compared to the

values 143 Mc/sec for $\rho_c^\pi B^0(\text{CH}_3)_2$ and 137 Mc/sec for $\rho_c^\pi B^0(\text{CH}_2)_2$ obtained from Eq. (5) and the room-temperature octyl propionate radical data and ethyl heptanoate radical data, respectively. The experimental uncertainties in these values are roughly ± 6 Mc/sec, and are large due to the doubling of the experimentally observed values of the room-temperature data to obtain $\rho_c^\pi B^0(\text{CH}_2)_2$ and $\rho_c^\pi B^0(\text{CH}_3)_2$ and due to uncertainties in the measurements of the broader lines of the low-temperature spectra. Within the limits of experimental error these three values of $\rho_c^\pi B$ are approximately equal. And since the values of B and the values of ρ_c^π are expected to be nearly equal, this again supports the assumption of complete averaging of the β -proton positions in the ethyl heptanoate radical at room temperature.

Further qualitative information about the β -proton motion may be obtained from Eqs. (8) and (10a) and the data of Fig. 5. By combining Eqs. (1) and (10a) one obtains

$$\frac{2a_1^\beta - \rho_c^\pi B^0}{2a_2^\beta - \rho_c^\pi B^0} = \frac{\cos^2(30^\circ - \gamma) - \frac{1}{2}}{\cos^2(30^\circ + \gamma) - \frac{1}{2}} \quad (17)$$

With a known value of B^0 this equation may be used to estimate γ . Eq. (17) is double-valued in the sense that if γ_1 is a solution so is the angle $90^\circ - \gamma_1$.³⁴ However, only one of these angles yields the experimental coupling constants by Eq. (10a), and the choice of angles is made by comparing the low-temperature results of Eqs. (10a) and (17). Over the temperature range $7^\circ \pm 3^\circ$ to 130°K , γ for the ethyl heptanoate radical is found to be approximately constant and equal to $22^\circ \pm 4^\circ$. Above 130°K the values of γ obtained from Eq. (17) decrease slowly with increasing temperature, but this change may not be significant. Once γ (hence θ_0) has been shown to be constant, Eq. (8) may in principle be used to estimate V_0 . Ignoring anharmonicities, Eq. (8) would be applicable providing at the temperatures of interest all motions which might couple with the torsional motion about the $\text{C}_2\text{--C}_3$ bond are negligible. This is equivalent to requiring that V_0 be much less than the potential barriers associated with motion about other bonds in the radical. If, as a gross approximation, the groups attached to C_2 and C_3 are allowed to undergo motion and the radical is assumed to be in a planar zigzag conformation, then $I \sim 1.7$ (10)⁻³⁸ g cm² for the ethyl heptanoate radical. From Eq. (8) and the β -proton coupling constant data in the temperature range $7^\circ \pm 3^\circ$ to 40°K , V_0 is found to

³⁴ Actually, of course, if γ_1 is a solution to Eq. (17), so are the angles $\gamma = \gamma_1 \pm n90^\circ$ ($n=0, 1, 2, \dots$). These angles fall into two sets, those corresponding to even values of n and those corresponding to odd values of n . Only one set yields the correct values of the coupling constants by Eq. (10a), and all of the members of each set are magnetically equivalent. Similar arguments hold for Eq. (3a). If α is a solution to (3a), so are the angles $\alpha = \pm \alpha_1 \pm n180^\circ$. These angles correspond to magnetically equivalent orientations of the β protons and for our purposes are considered to be the same.

FIG. 5. The two β -proton coupling constants of the ethyl heptanoate radical as a function of temperature.

be in the neighborhood of 1–3 kcal/mole. Other reasonable values of I yield similar values of V_0 , and these values of V_0 are of course merely order-of-magnitude estimates of V_0 . Since potential barriers associated with other bonds in the ester radical cannot be assumed to be much less than 1 kcal/mole,^{35,36} and since the exact value of I is not known, a reliable value of V_0 cannot be obtained from the ESR data of Fig. 5.

Preliminary spectra of the octyl propionate radical have also been recorded over the temperature range 298° to $7^\circ \pm 3^\circ\text{K}$. As in the case of the ethyl heptanoate radical, a_z^α is independent of temperature. However, the methyl group of the octyl propionate radical is apparently still undergoing rotation or large amplitude oscillations at $7^\circ \pm 3^\circ\text{K}$. This behavior is similar to that reported for the $\text{CH}_3\dot{\text{C}}(\text{COOH})_2$ radical, which is formed by the x irradiation of methylmalonic acid.²⁸

DISCUSSION OF THE ROOM-TEMPERATURE ESTER RADICAL SPECTRA

In addition to ethyl heptanoate, octyl propionate, and methyl octanoate, several other esters were investigated at room temperature. After x irradiation, each of these systems exhibited the radical formed by the removal of one α proton from the ester molecule. The β -proton coupling constants were resolved in the z spectra of several ester radicals, and they ranged from 3 to 6 Mc/sec. The α - and β -proton coupling-constant data are summarized in Table I. Within the limits of

³⁵ D. J. Millen, *Progr. Stereochem.* **3**, 138 (1962).

³⁶ E. B. Wilson, *Advan. Chem. Phys.* **2**, 367 (1959).

FIG. 6. The room-temperature ESR spectra recorded with the magnetic field in the xy and z directions of an x -irradiated sebacic acid-urea crystal.

experimental accuracy, all of the ester radicals have the same values of a_z^α and a_{xy}^α . This suggests that all of the ester radicals have the same spin density, ρ_c^π , and the same orientation of the α proton with respect to the crystalline z axis.

Of the ester radicals reported in Table I, only those derived from ethyl heptanoate, octyl propionate, and diethyl adipate exhibit magnetically equivalent β protons, and the coupling constants are the same for all three radicals. Therefore, as in the case of the ethyl heptanoate and octyl propionate radicals, the β protons of the diethyl adipate radical are undergoing complete averaging as given by Eq. (5). The radicals derived from either ethyl nonanoate, ethyl decanoate, or ethyl dodecanoate have two β -proton coupling constants that differ by only a few megacycles, and therefore the spectra are not completely resolved. However, the sum of the two coupling constants, a_{xy1}^β and a_{xy2}^β , is easily measured to within 2 Mc/sec, and in Table I the values of these coupling constants are listed as approximately one-half of this sum. The fact that the β -proton coupling constants are nearly equal to those of the ethyl heptanoate radical implies that oscillations about the C_2 - C_3 bonds in these three radicals are of nearly the same amplitude as in the ethyl heptanoate radical.

For the remainder of the ester radicals listed in Table I, the two β -proton coupling constants differ sufficiently to produce well-resolved eight-line spectra, and it is again found that Eq. (3) and not (4) leads to acceptable values of B' . From Eq. (17) and the data of Table I, values of γ_1 and $\gamma_1 - 90^\circ$ are readily

obtained. In the absence of low-temperature data, A and B must be evaluated in order to determine which of the two angles is correct. By subtracting one of the equations (10a) from the other and simplifying the resulting equation, one obtains

$$\rho_c^\pi B = 2(a_1^\beta - a_2^\beta)/\sqrt{3} |\sin 2\gamma|. \quad (18)$$

In Eq. (18), both angles yield the same value of $\rho_c^\pi B$. The value of $\rho_c^\pi A$ is determined from Eq. (10d), $\rho_c^\pi B$, and a known value of $\rho_c^\pi B^0(\text{CH}_2)$. Since ρ_c^π is apparently a constant, the value of $\rho_c^\pi B^0(\text{CH}_2)$ is the same for all ester radicals having two β protons, and is approximately the same as that of $\rho_c^\pi B^0(\text{CH}_3)$. Here we will take the value of $\rho_c^\pi B_{xy}^0$ to be 131 Mc/sec. Upon substituting $\rho_c^\pi A$, $\rho_c^\pi B$, and the two angles into Eq. (10), only one of the two angles yields the experimentally observed β -proton coupling constants and the other angle is discarded. By this procedure, the values of γ for ethyl hexanoate, ethyl octanoate, ethyl undecanoate, methyl octanoate, and hexyl octanoate are determined to be 30° , 10° , 15° , 15° , and 45° , respectively (all angles $\pm 8^\circ$). These angles may be compared to the values of γ' , 4° , 3° , 4° , 7° , and 6° , respectively, obtained for the same radicals from Eq. (3).

The amplitudes of oscillation about the C_2 - C_3 bonds may be estimated with the above values of γ and Eq. (6) or Eq. (7). Since the oscillations are large, Eq. (6) and not Eq. (7) is used here, although it may be noted that the equations give the same result for small angles. For instance, taking B^0 and γ to be 131 Mc/sec and 22° , the two values of $\langle R_1(\theta) \rangle$ and of $\langle R_2(\theta) \rangle$ obtained from Eqs. (6) and (7) differ by only 5% and 2.5%, respectively, for an oscillation amplitude of 30° . Using Eq. (6), the amplitudes of oscillation for the above six radicals fall in the range of 70° to 80° . By the same equation, the values of α of the other ester radicals are at least 80° to 90° , and therefore there exists large amplitudes of oscillation about the C_2 - C_3 bonds of all ester radicals reported in Table I.

By this point it is obvious that the assumption of a time average planar zigzag conformation of the ester radicals is an approximation. For such a conformation, γ would be zero and the equilibrium angle θ_0 of the two β protons would be 30° . The angles of twist for the radicals exhibiting magnetically equivalent (or nearly equivalent) β protons cannot be obtained from the ESR data. However, the room-temperature values of γ for the six ester radicals exhibiting eight resolved lines, and the low-temperature value of γ for the ethyl heptanoate radical are significant. Considering the constraints imposed by the van der Waals radius of the tubular cavity, this implies twisting about other bonds besides the C_2 - C_3 bond. From Fig. 1, or by use of molecular models, it is seen that a molecule with an angle or twist about the C_2 - C_3 bond is most easily accommodated by the tubular cavity if there exist

also similar out-of-plane adjustments in adjacent bonds of the ester molecule. (This same argument applies to oscillations about the $\text{C}_2\text{-C}_3$ bond since a cooperative motion is required in order to achieve the large amplitude oscillations of the β protons.) It is clear, however, that all radicals in a given ester-urea compound have approximately the same angle of twist γ and the same degree of molecular motion. Otherwise the ESR spectra would be a superposition of lines from each nonequivalent radical, and the spectra would be complex.³⁷ Of course, whether or not the undamaged molecules exist in a time average planar zigzag configuration cannot be determined from the ESR data.

CARBOXYLIC ACID-UREA INCLUSION COMPOUNDS

Of the two acids investigated, one (decanoic acid) is a monocarboxylic acid, and the other (sebacic acid) is a dicarboxylic acid. The radicals produced by x irradiation of these acid-urea crystals are

and are formed by removal of one α proton from the corresponding acid molecule. Typical room-temperature

³⁷ Although there is no obvious trend in the ester radical conformations of the series beginning with the ethyl hexanoate radical and ending with the ethyl dodecanoate radical, there are differences in the conformations of these and the other radicals reported in Table I. The van der Waals radius of the tubular cavity is necessarily nonuniform, and it is tempting to suggest that this is related to the differences in the angles of twist of the ester radicals. However, the lengths of the ester molecules are not, in general, integral multiples of the urea spiral repeat distance, and therefore the positions of the urea molecules relative to the $\text{C}_2\text{-C}_3$ bonds would not be expected to be identical for all ester radicals of a given crystal. Thus, one might expect that if the nonuniformity of the van der Waals radii caused the variations in the angles of twist, then the radicals of a given crystal would not all have the same angle of twist. This argument assumes that there do not exist unoccupied spaces in the tubular cavities. If there are spaces between the ester molecules, then the non-uniformity of the cavities, hydrogen bonding of the ester group with the urea molecules, or distortions of the lattice caused by the ester functional groups would readily explain the above observations. Another possible explanation is the existence of a cooperative effect among the ester molecules. In any case, the structures appear to be highly ordered, since the radicals of a given inclusion compound do have the same angle of twist. (This also suggests that the ester radicals are not rotating in the tubular cavities.) In all of these arguments we are, of course, ignoring the remote possibility that although all stable radicals in one crystal have a given conformation, there exist other conformations corresponding to radicals which are unstable and are therefore not observed.

Others have observed deviations from planar zigzag conformations. Smith⁷ has found that in the *n*-hexadecane-urea crystal the hydrocarbon chain length is slightly shorter than that calculated for an extended planar configuration. This is supported by the observation that the urea/hydrocarbon ratio for this crystal is lower than expected for an extended planar configuration.^{1,5,7} However, Smith⁷ found that two other compounds, *n*-dodecane and decamethylene dibromide, do exist in planar extended zigzag configurations in the urea inclusion compounds.

ESR spectra are given in Fig. 6. The above sebacic acid radical has also been found in x-irradiated single crystals of sebacic acid,³⁸ and this general type of radical has been observed in many other crystalline dicarboxylic acids.¹³⁻¹⁶ The above two carboxylic acid radicals are briefly investigated here primarily as a test of the model chosen to represent the radicals in the urea inclusion compounds. The α -proton coupling constants of the acid radicals are given in Table I, and are approximately the same as those of the ester radicals. As with the esters, taking D to be a_{xy}^α and C to be a_z^α , Eq. (15) reproduces the a^α anisotropy to within ± 2 Mc/sec for both the sebacic acid radical and the decanoic acid radical. The values, in megacycles per second of C , D , a_0^α are 82, 42, 56 and 84, 42, 56 for the sebacic acid radical and the decanoic acid radical, respectively.

To compare these results, the diagonal a^α tensor elements for the radicals in pure dicarboxylic acids are needed, and there are differences in the values reported for these tensor elements. Two examples are the values for the succinic acid radical¹⁴ and the sebacic acid radical.³⁸ The diagonal values of the a^α tensor, C , B , A for these two radicals are 92, 59, 30 and 88, 56, 27 Mc/sec, respectively. From these tensor elements, the values of C , D , a_0^α are 92, 44, 60 and 88, 41, 57, respectively. The agreement between these values and those for the acid-urea crystals is satisfactory. The values of D and a_0^α for all four systems are essentially identical, and the C values of the radicals in the urea adducts are slightly below those of the radicals in the pure acid crystals. The difference in C values may be caused by the molecular y' axis being tilted away from the crystalline z axis. Besides decreasing the apparent value of C , this shift would, of course, also increase the value of D obtained from a_{xy}^α over the one derived from the average of the diagonal tensor elements.

The a_z^α and a_{xy}^α of the acid radicals are approximately equal to those of the ester radicals (Table I). This is an indication that the spin densities ρ_e^π and the orientations of the radicals with respect to the molecular z axis are approximately the same for the acid and ester radicals. The value of ρ_e^π is nearly unity, as may be seen by comparison of the above values of a_0^α with the range of a_0^α values, 59 to 64 Mc/sec, recently reported for transient alkyl radicals.²⁹ (Note: $a_0^\alpha = Q\rho_e^\pi$, where Q is a constant.^{19,20} The fact that ρ_e^π is nearly unity in the case of the carboxyl radicals has already been established.¹⁶) Although no detailed temperature investigations of the acid spectra were undertaken, the spectra of both acid radicals changed gradually and reversibly with temperature. Splittings due to the carboxyl proton or the γ protons were not resolved in any spectrum of either acid radical.

³⁸ F. B. Booth, Ph.D. thesis, California Institute of Technology (1963).

The two β protons of the sebacic radical are magnetically equivalent, and a^β for these two protons is found to be equal to 87 Mc/sec. The two β protons of the decanoic acid radical are nearly equivalent ($\pm 1-3$ Mc/sec) and the values of the two β -proton coupling constants are approximately the same as those of the sebacic acid radical. From Eqs. (3) and (4), and using the more accurate a^β of the sebacic acid radical, the values of $\rho_c^\pi B_{xy}'$ are 116 and 349 Mc/sec for equilibrium angles of 30° and 60° , respectively, and again the value 349 Mc/sec is discarded. The value of 116 ± 2 Mc/sec is slightly below the $\rho_c^\pi B_{xy}^0$ values for the octyl propionate radical (130 ± 3 Mc/sec) and the ethyl heptanoate radical (131 ± 3 Mc/sec), suggesting that the β protons of the acid radicals are undergoing limited motion about the 30° equilibrium position. Taking B^0 to be 130 Mc/sec, the angle of oscillation γ for the sebacic acid radical lies in the range 30° to 45° . It should be stressed here that Eq. (6) is being used only to compare, *qualitatively*, motion about the C_2-C_3 bond. However, it is clear that the degree of motion about the C_2-C_3 bond is much larger in the ester radicals than it is in the acid radicals.

One major difference between the ester and the acid radicals is the possibility of forming hydrogen bonds involving the carboxylic protons. X-ray diffraction studies of several pure crystalline dicarboxylic acids have established that the acid molecules are bonded end to end by intermolecular hydrogen bonds.^{39,40} It has been suggested that the acid molecules in the acid-urea crystals are bonded together in the same manner.⁴¹ The hydrogen bonding in either the monocarboxylic or dicarboxylic acids would effectively hinder oscillations about the C_2-C_3 bond (as is readily seen by use of molecular models). Another possible, although less likely, explanation of the reduced motion in the acids is hydrogen bonding between the acid molecules and the urea molecules. The $O-H \cdots N$ bond is known,⁴² and hydrogen bonding is observed between molecules of urea and oxalic acid in the monoclinic urea-oxalic acid crystals.⁴³ Hydrogen bonding involving the urea protons may also occur in both the acid and ester molecules, but this bonding would not easily explain the difference in molecular motion in the two cases.

The above discussion is relevant to the question of possible complete rotation (or rapid reorientation among the six radical positions) of the hydrocarbon derivatives in the tubular cavities. The room-temperature ESR spectra of both the acid and ester radicals could result from large amplitude oscillations of the α proton in the xy plane or from rotation of the entire molecule about the crystalline z axis. The gradual and

continuous changes of the spectra with temperature require the presence of large oscillations of the α proton but do not rule out entirely the possibility of complete rotation at room temperature. However, because of the formation of the $C-O \cdots X$ hydrogen bonds mentioned above it is very unlikely that the dicarboxylic acids undergo rotation at room temperature. Hydrogen bonding between the dicarboxylic acid molecules would create molecular units of essentially infinite length, and hydrogen bonding between the acid molecules and the urea molecules would create a barrier to rotation of the carboxyl groups.

An estimation of the lower limits of the frequency and amplitude associated with the α -proton motion may be obtained from Eqs. (11)–(13) and the acid radical tensor elements quoted above. If the radicals are freely rotating in the tubular cavities, then the only condition necessary to obtain an isotropic splitting in the xy plane is that the rotational frequency be large compared to the hyperfine frequency (motional frequency $\gg 60$ Mc/sec for the acid and ester radicals). If instead of rotating freely, the α proton is oscillating in the xy plane with an amplitude δ about some equilibrium position, then the amplitude of oscillation is also important. From Eqs. (11)–(13) one may obtain the very approximate relation

$$\Delta a_{xy}^\alpha \sim (A - B) \left[(\cos^2 \phi_0) - \frac{1}{2} \right] (\sin 2\delta / 2\delta), \quad (19)$$

where Δa_{xy}^α is a measure of the α -proton anisotropy in the xy plane, and ϕ_0 is the angle between the magnetic field (in the xy plane) and either the x' or z' molecular axes. For the ester and acid radicals the difference between A and B is evidently ~ 29 Mc/sec, and if δ is taken to be greater than 80° , then: $0 \geq \Delta a_{xy}^\alpha \geq 3$ Mc/sec. Since there are six radical orientations (in general, three different values of ϕ_0) that contribute to the ESR spectra, an anisotropy of a few megacycles per second would only contribute to the broadening of the ESR lines and would not produce a measurable effect on the splittings in the xy plane.

SPECTROSCOPIC SPLITTING-FACTOR DATA

The g values of the ester radicals reported in Table I are identical within experimental error. The averages of the values measured with the magnetic field in the crystalline xy and z directions are $g(xy) = 2.0031$ and $g(z) = 2.0036$, respectively. The values of the two acid radicals are also the same and are given by $g(xy) = 2.0025$ and $g(z) = 2.0041$. The experimental uncertainty in all g -value measurements is ± 0.0003 (relative to the g value assumed for DPPH). As in the case of most organic free radicals, the anisotropy of the g value is small, and therefore the electron spin vector is aligned along the magnetic field direction. This was assumed in calculating the proton coupling constants from the ESR data.

It is desirable to relate the measured g -value data to the isotropic g value g_0 . It cannot be assumed that

³⁹ J. D. Morrison and J. M. Robertson, J. Chem. Soc. **1949**, 980.

⁴⁰ J. M. Robertson and J. D. Morrison, J. Chem. Soc. **1949**, 993.

⁴¹ L. C. Fetterley, Ph.D. thesis, University of Washington, 1950.

⁴² J. Donohue, J. Phys. Chem. **56**, 502 (1952).

⁴³ J. H. Sturdivant (private communication).

the principal elements of the g tensor correspond to the molecular x' , y' , z' directions. (The minimum element evidently lies along the z' direction.^{14,44}) However, we have shown that the large amplitude motions of the molecular x' and z' axes occur in the crystalline xy plane. For this situation the isotropic g value is given to a good approximation by the relation $g_0 \approx \frac{1}{3}[2g(xy) + g(z)]$, regardless of the orientations of the principal values of the g tensor in the molecular coordinate system. From this formula and the above data, g_0 for the ester and acid radicals are 2.0033 and 2.0030, respectively. These values of g_0 are essentially identical to those reported for the adipic acid radical (2.0031) and the succinic acid radical (2.0030). (g -value data have not been reported for the sebacic acid radical produced in crystalline sebacic acid.)

SUMMARY

The long-lived free radicals observed in all of the aliphatic ester-urea crystals investigated were of the type $\text{RCH}_2\dot{\text{C}}\text{HCOOR}'$. These radicals are similar to the well-known free radicals produced in x-irradiated dicarboxylic acids, except that the splittings due to the alcohol protons (of R') are present in the ESR spectra of the ester radicals. These previously unobserved splittings provide evidence that a small fraction of the unpaired spin density is distributed on the carboxyl group of the ester radical. The room-temperature study of the ester radicals shows that (a) the orientation of the axis of the $2p$ orbital on C_2 with respect to the crystalline c axis (tubular axis) is the same for all radicals studied; (b) there exist motions of the α and β protons at frequencies greater than 10–100 Mc/sec; (c) the amplitude of the α -proton motion in a plane perpendicular to the c axis is greater than $\approx 80^\circ$, and the anisotropy of the α -proton coupling constant is adequately described by an axially symmetric spin Hamiltonian; (d) the amplitudes of oscillation of the β -protons with respect to the α protons are large for all ester radicals, but the β -proton positions are completely averaged only for a few of the radicals studied; (e) there exist significant deviations from time-average planar zigzag configurations in many ester radicals (causing nonequivalence of the β protons); and (f) all radicals of a given ester-urea crystal have the same time-average configuration and approximately the same degree of molecular motion (indicating a high degree of order in the ester-urea crystals).

In addition to the room-temperature study of the eleven ester radicals, the ethyl heptanoate radical was

also investigated over the temperature range 352° to $7^\circ \pm 3^\circ\text{K}$, and it was found that (a) over this range there is no significant reorientation of the axis of the $2p$ orbital on C_2 with respect to the crystalline c axis; (b) the α -proton motion occurs primarily in a plane perpendicular to the c axis; (c) the β -proton angle of twist is approximately independent of temperature over the range 130° to $7^\circ \pm 3^\circ\text{K}$; (d) the large amplitude oscillations about the $\text{C}_2\text{--C}_3$ bonds decrease continuously with decreasing temperature; and (e) both the anisotropy of the low-temperature ESR spectra and the morphology of the crystals suggest that the ester-urea crystals have hexagonal structures. All temperature effects are reversible. Considering the constraints imposed by the tubular cavities, the large amplitude oscillations about the $\text{C}_2\text{--C}_3$ bonds strongly suggest that the intramolecular motions of the ester radicals are cooperative.

Two acid-urea crystals, decanoic-acid-urea and sebacic-acid-urea were also studied, and the ESR data showed that (a) the long-lived radicals are of the type $\text{RCH}_2\dot{\text{C}}\text{HCOOH}$; (b) the acid radical α -proton motion and orientation are similar to the ester radical motion and orientation; and (c) there exists motion of the β protons of similar frequency (i.e., above 10–100 Mc/sec) but much lower amplitude than in the ester radicals. This decrease in motion is evidently caused by hydrogen bonds involving the carboxyl protons of the acid radicals. For both the acid and ester radicals, one may obtain the approximate values for one α -proton hyperfine (principal) tensor element, the average of the other two elements, the isotropic α -proton coupling constant, and the isotropic g value g_0 .

Note added in proof: It has come to our attention that Radell and Connolly [J. Radell and J. W. Connolly, *Advan. X-Ray Anal.* **4**, 140 (1960)] have investigated several ester-urea inclusion compounds by x-ray powder diffraction techniques and report that the ester-urea compounds have hexagonal crystal structures. This observation supports our assumptions regarding the orientations of the ester molecules in the urea lattice and is in agreement with the ESR results reported above.

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⁴⁴ H. M. McConnell and R. E. Robertson, *J. Phys. Chem.* **61**, 1018 (1957).