

Electron Spin Resonance of $R\dot{C}HCOR'$ Radicals in X-Irradiated Ketone-Urea Inclusion Compounds*

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(Received 30 October 1964)

Single crystals of six inclusion compounds formed between aliphatic ketones and urea were x irradiated at room temperature, and the free radicals produced were investigated by electron spin resonance. The six ketones investigated were 2-nonanone, 6-undecanone, 3-tetradecanone, 2-undecanone, 2-dodecanone, and 3-undecanone. The long-lived free radicals observed in all of these compounds ($R\dot{C}HCOR'$) are formed by the removal of one α proton from the parent ketone. The unpaired spin density in the $2p$ orbital adjacent to the carbonyl group is 0.81 ± 0.08 . A contour plot of the spin density as a function of the molecular orbital parameters is given. In qualitative agreement with the ESR results, the molecular orbital methods predict the position of maximum spin density to be adjacent to the carbonyl group.

INTRODUCTION

THE free radicals produced in a series of x-irradiated aliphatic ester-urea inclusion compounds have recently been investigated by electron spin resonance (ESR).¹ The use of an inclusion compound has the distinct advantage over a low-temperature glass or powder in that all of the guest molecules of the compound are magnetically equivalent at one or more crystalline directions. Only one ester radical ($R\dot{C}HCOOR'$) and no urea radicals were detected after x irradiation. The ester-urea single crystals were investigated as a function of temperature and of orientation in the magnetic field, and information regarding the structure and motion of the ester radical was obtained. It is of interest to investigate other aliphatic molecules by this method. In particular, the aliphatic ketone molecules are of interest because of the presence of only one oxygen atom. This simplification in structure makes possible a more quantitative investigation of the x-ray-produced ketone radicals. In this paper the radicals in a series of x-irradiated ketone-urea inclusion compounds are identified, the coupling constants are given, and the experimental and theoretical positions of maximum spin density are determined.²

EXPERIMENTAL

Single crystals of the inclusion compounds formed between urea and the aliphatic straight-chain ketones were grown from a methanol solution by either slow evaporation or by slow cooling. In all cases ketones were chosen which gave the best quality of urea inclu-

sion crystals and, therefore, the lengths of the ketone molecules studied are somewhat arbitrary. The crystals obtained were either hexagonal needles or flat hexagonal plates and were stable for several months in air at room temperature. The z axis of the Cartesian crystalline coordinate system is defined to lie along the needle axis of the urea compound, and therefore the z axis is parallel to the six faces of the hexagonal prism. The x and y axes are not specified other than that they lie in a plane perpendicular to the needle axis of the crystal. The morphology of the ketone-urea crystals is typical of the morphology of crystals formed between urea and a variety of long straight-chain molecules.³ The ketone molecules are therefore expected to exist in an extended zigzag conformation in the hollow (hexagonal) cavities formed by the urea molecules.⁴ We assume this to be the case throughout the following discussion, although no crystallographic data have been reported for the ketone-urea compounds studied in this paper.

The x-ray apparatus, X-band ESR spectrometer, modulation amplitude, and calibration standards were the same as employed in I. A conventional small Dewar connected by means of a transfer tube to a liquid helium Dewar was used to cool the crystals below room temperature. The rate of cold helium gas flow was controlled by varying the power dissipated in a resistor located inside the liquid helium Dewar. A heated nitrogen gas flow system was used to obtain temperatures above room temperature. Crystals of the 6-undecanone-urea compound were heated to $\sim 325^\circ\text{K}$ for a few minutes prior to recording the final ESR spectra to remove small quantities of additional radicals. The lines due to these radicals were not sufficiently resolved to allow identification of the radicals. The other x-irradiated ketone-urea inclusion compounds listed in Table I were not heated before obtaining the ESR spectra. For any given inclusion compound, the major lines of the ESR spectra were independent of the ratio of the ketone to urea in the methanol solution and to the length of time the crystals were x irradiated.

* Supported by the National Science Foundation under Grant No. GP-930.

† National Science Foundation Predoctoral Fellow.

‡ Contribution No. 3177.

¹ O. H. Griffith, *J. Chem. Phys.* **41**, 1093 (1964), in the following referred to as I.

² Although the ketone radical ($R\dot{C}HCOR'$) has undoubtedly been mentioned in interpretations of powder or low-temperature glass ESR spectra, we are unaware of any previous systematic investigation of this type of radical in an oriented matrix.

³ W. Schlenk, Jr., *Ann. Chem.* **565**, 204 (1949).

⁴ A. E. Smith, *Acta Cryst.* **5**, 224 (1952).

TABLE I. Proton hyperfine coupling constants of ketone radicals.^{a,b}

Radical ^a	T (°K)	a_z^α	a_{1z}^β	a_{2z}^β	a_z^ζ	a_{xy}^α	a_{1xy}^β	a_{2xy}^β
$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}(\text{CH}_2)_5\text{CH}_3$	298	76	71	47	5.4	38	68	45
$\text{CH}_3(\text{CH}_2)_4\overset{\text{O}}{\parallel}\text{CCH}(\text{CH}_2)_3\text{CH}_3$	298	76	66	48	9.1	38	63	45
$\text{CH}_3(\text{CH}_2)_{10}\overset{\text{O}}{\parallel}\text{CCHCH}_3^d$	310	~75	64	64	9.0	39	58	58
$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}(\text{CH}_2)_7\text{CH}_3$	313	77	71	53	5.0	39	68	50
$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}(\text{CH}_2)_8\text{CH}_3$	322	75	70	52	5.5	38	66	49
$\text{CH}_3(\text{CH}_2)_7\overset{\text{O}}{\parallel}\text{CCHCH}_3^d$	298	~75	65	65	9.5	38	57	57

^a a^α , a^β , and a^ζ are the coupling constants for the α proton, β protons, and the ζ protons, respectively, and xy and z denote the spectra obtained with the magnetic field in the crystalline xy or z directions. All coupling constants are reported in megacycles per second.

^b The ESR spectra of three of the radicals were recorded at temperatures above 298°K in order to improve resolution. The temperatures chosen are somewhat arbitrary. The change of resolution with temperature is caused by a slight temperature dependence of the β -proton coupling constants. The accuracy of a_z^α (~75 Mc/sec) for the third and sixth radicals is decreased to ± 3 Mc/sec by

the extensive overlapping of spectral lines. All other a^α and a^β values are estimated to be accurate to within ± 2 Mc/sec. The small a_z^ζ values should be accurate to within ± 0.7 Mc/sec.

^c These radicals are formed from the parent compound by the removal of one α proton. The parent ketones are, from top to bottom, 2-nonanone, 6-undecanone, 3-tetradecanone, 2-undecanone, 2-dodecanone, and 3-undecanone.

^d These two radicals each exhibit three magnetically equivalent β protons ($a_z^\beta = a_{1z}^\beta = a_{2z}^\beta$).

RADICAL IDENTIFICATION

The ESR spectra obtained for the x-irradiated 2-nonanone, 6-undecanone, and 3-tetradecanone-urea inclusion compounds are given in Figs. 1-3. The ESR hyperfine pattern of the 2-nonanone-urea crystal results from two nonequivalent but nearly isotropic proton coupling constants and one anisotropic proton coupling

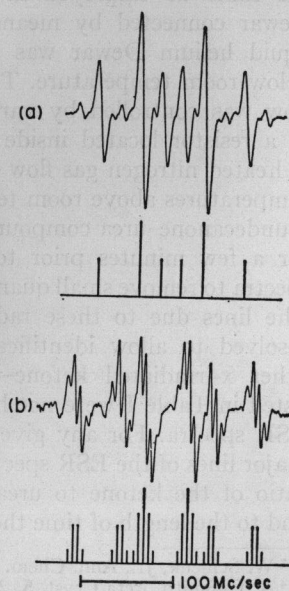


FIG. 1. The room-temperature ESR spectra of an x-irradiated 2-nonanone-urea crystal with the magnetic field vector (a) 70° from the z axis and (b) parallel to the z axis. The reconstructed "stick" spectra of the $\text{CH}_3\text{COCH}(\text{CH}_2)_5\text{CH}_3$ radical for these two orientations are given below the observed spectra.

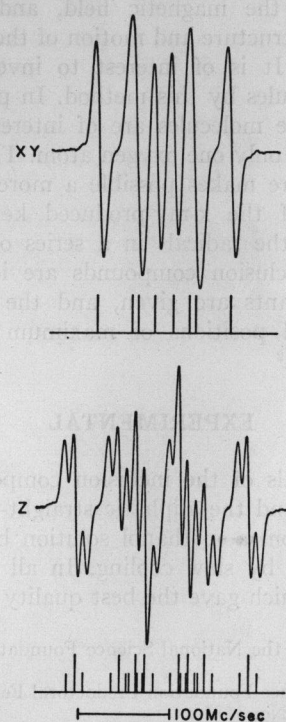


FIG. 2. The room-temperature ESR spectra of an x-irradiated 6-undecanone-urea crystal with the magnetic field parallel to the xy plane and along the z axis, respectively. The reconstructed spectra of the $\text{CH}_3(\text{CH}_2)_4\text{COCH}(\text{CH}_2)_3\text{CH}_3$ radical are given below the observed spectra.

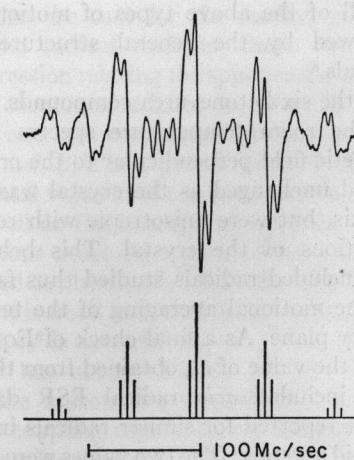
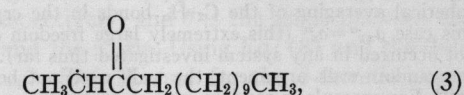
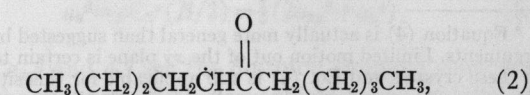
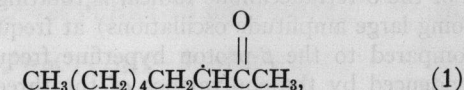


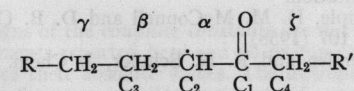
FIG. 3. The ESR spectra of an x-irradiated 3-tetradecanone-urea crystal at 310°K. The magnetic field is approximately 40° from the crystalline z axis. The reconstructed spectrum is that of the $\text{CH}_3\text{CHCOCH}_2(\text{CH}_2)_9\text{CH}_3$ radical and the remaining (major) lines are apparently due to the $\text{CH}_3\text{CH}_2\text{COCH}(\text{CH}_2)_9\text{CH}_3$ radical.

constant. The lines are further split by three small proton coupling constants which are resolved only at certain orientations of the magnetic field. The ESR spectra obtained for the 6-undecanone-urea crystal are similar except that the small splittings arise from two equivalent proton coupling constants. Finally, the ESR spectra obtained for the 3-tetradecanone-urea crystal may be constructed from three equal and nearly isotropic proton coupling constants, one anisotropic coupling constant, and two approximately equivalent coupling constants of much smaller magnitude than the other four. Therefore, the only logical choices for the radicals produced in the 2-nonanone, 6-undecanone, and 3-tetradecanone urea inclusion compounds are, respectively,



and the magnitudes and assignments of the proton coupling constants are given in Table I.⁵ In agreement with results obtained for other radicals, the β -proton

⁵ The convention for the labeling of protons (α , β , γ , ζ) and carbon atoms (C_1 , C_2 , C_3) used here is



coupling constants are very nearly isotropic and the α -proton coupling constants are anisotropic. The small splittings result from the ζ -proton coupling constants. Splittings due to the γ -protons are not resolved.

Three other ketones, 2-undecanone, 2-dodecanone, and 3-undecanone, were also investigated, and the results are summarized in Table I. The radicals observed in all ketone-urea inclusion compounds may be thought of as being formed by the removal of one hydrogen atom from the α position of the parent ketone, and there was no evidence for stable paramagnetic sites associated with the urea molecules. The g values of all six radicals were measured at room temperature and were found to be the same within experimental error. The average g values and the estimated error with the magnetic field parallel and perpendicular to the z axis, respectively, are $g(z) = 2.0040 \pm 0.0003$ and $g(xy) = 2.0044 \pm 0.0003$. As may be seen from Fig. 3, the ESR spectra of the x-irradiated 3-tetradecanone-urea compound are complicated by the presence of one or more additional radicals. All radicals present have roughly the same thermal stability, and it was not possible to greatly change the relative concentrations of the radicals by either heating the crystal or subjecting the crystal to ultraviolet light. However, the outermost unidentified doublet is split by two small and approximately equivalent coupling constants. From further considerations of the magnitudes of the various splittings it appears that all major unidentified lines can be assigned to the radical $\text{CH}_3\text{CH}_2\text{COCH}(\text{CH}_2)_9\text{CH}_3$. An analogous situation occurs in the case of the x-irradiated 3-undecanone-urea compound. We will not be concerned further with these additional radicals since a well resolved example of a nearly identical radical is present in the 6-undecanone-urea crystal.

All of the above radicals were remarkably stable. The radical concentrations remained approximately constant during the several hours of room-temperature experimentation. However, the concentrations of the radicals decreased slowly as the crystals were heated and the ESR signals disappeared at temperatures well below the melting points of the crystals.

EXPERIMENTAL DETERMINATION OF THE SPIN DENSITY ρC_2^π

a. From α -Proton Coupling-Constant Data

It is apparent from the data of Table I that the ketone radicals are very similar to the previously reported carboxylic acid⁶ and ester¹ radicals. That is, there is a large spin density associated with Carbon Atom 2, a small spin density associated with Carbon Atom 1, and presumably a small spin density associated with the oxygen atom. These are evidently π -electron spin densities and are referred to as ρC_2^π , ρC_1^π , and

⁶ H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, J. Am. Chem. Soc. **82**, 766 (1960).

ρO^π , respectively. (It is shown later that the π -electron assumption is supported by all available data.) We immediately limit the discussion to ρC_2^π since this diagonal spin-density matrix element is so much larger than the adjacent one, ρC_1^π , that the off-diagonal elements of the spin-density matrix⁷ may well dominate ρC_1^π . This means, in effect, that the estimate of ρC_1^π obtained from the coupling-constant data by the usual methods may be highly unreliable. The value of ρC_2^π , on the other hand, may be obtained by two independent methods and, therefore, ρC_2^π can be obtained with good accuracy. The procedure followed here is as follows: the value of ρC_2^π is estimated from the α -proton coupling-constant data and from the β -proton coupling-constant data; the theoretical values of ρC_2^π are obtained as a function of the molecular orbital parameters and these spin densities are then compared to the experimental ρC_2^π .

The maximum value of the α -proton coupling constant a^α occurs when the magnetic field is parallel to the z axis and the minimum value of a^α occurs with the magnetic field perpendicular to the z axis of the crystal. These two values of a^α are referred to as a_{xy}^α and a_z^α , respectively, and they are the same within experimental error for all ketone radicals studied (Table I). The first step in obtaining the spin density is to extract the isotropic contribution, a_0^α , from a_{xy}^α and a_z^α . This is somewhat more troublesome for included radicals than for radicals rapidly tumbling in solution or rigidly held in a crystal lattice, because molecular motion in the urea inclusion compounds averages a portion, but not all, of the anisotropic proton-electron hyperfine interaction.

In I, the equation

$$a_0^\alpha = \frac{1}{3}(2a_{xy}^\alpha + a_z^\alpha) \quad (4)$$

was used to obtain a_0^α from experimental values of a_{xy}^α and a_z^α . This simple relation will also be useful in obtaining an approximate value of a_0^α for the ketone radicals. In obtaining Eq. (4), the α -proton tensor elements in the xy plane are assumed to be averaged by molecular motion. This averaging can be accomplished by various types of motion. The tensor elements are obviously averaged by rapid rotation of the radicals about the crystalline z axis. They are approximately averaged if the amplitude of the radical motion in the xy plane is greater than $\sim 80^\circ$ and all bond positions in this range are equally probable (the residual few megacycles per second anisotropy would have a negligible effect on the splittings but could inhomogeneously broaden the ESR lines). The tensor averaging would also be accomplished provided that each radical executes a random walk among the orientations related by an n -fold axis of symmetry parallel to the crystalline z axis ($n \geq 3$). If $n=6$, this corresponds to a rapid jumping of the radicals between the six positions of minimum energy in the hexagonal tubular cavities of

⁷ H. M. McConnell, J. Chem. Phys. **28**, 1188 (1958).

the crystal. All of the above types of motion are, in principle, allowed by the general structure of the inclusion crystals.⁸

For each of the six ketone-urea compounds reported in Table I, the room temperature spectra recorded with the magnetic field perpendicular to the crystalline z axis remained unchanged as the crystal was rotated about the z axis, but were anisotropic with respect to arbitrary rotations of the crystal. This behavior is typical of all included radicals studied thus far and it results from the motional averaging of the tensor elements in the xy plane. As a final check of Eq. (4) for such a radical, the value of a_0 , obtained from this equation and the included *acid* radical ESR data, was compared to a_0 reported for similar radicals in "rigid" dicarboxylic acid crystals.¹ The two values were identical within experimental error and this provides a partial justification of the use of Eq. (4) for other included radicals. Assuming Eq. (4) to be valid for the ketone radicals, $a_0^\alpha = 51 \pm 2$ Mc/sec for all six ketone radicals of Table I. The π -electron spin density on Atom 2, ρC_2^π , may now be obtained from McConnell's well-known equation,⁹ $a_0^\alpha = Q\rho C^\pi$, where Q is a proportionality constant and ρC^π is the π -electron spin density on the carbon atom bonded to the α proton. A good estimate of Q is 62.7 Mc/sec. This number is the value of a_0^α reported by Fessenden and Schuler for the ethyl radical ($\text{CH}_3\dot{\text{C}}\text{H}_2$, $\rho C^\pi \approx \text{unity}$).¹⁰ Taking Q to be 62.7 Mc/sec, $\rho C_2^\pi = 0.82$.

b. From β -Proton Coupling-Constant Data

The value of ρC_2^π may also be obtained from the ketone β -proton coupling constants. The β protons undergo motion with respect to the π orbital on C_2 and the value of ρC_2^π cannot, in general, be obtained without a knowledge of the nature of the motion. However, the methyl group attached to Carbon Atom 2 of the 3-tetradecanone radical is rotating (or undergoing large amplitude oscillations) at frequencies large compared to the β -proton hyperfine frequency, as is evidenced by the equivalence of the three β protons.

⁸ Equation (4) is actually more general than suggested by these arguments. Limited motion out of the xy plane is certain to occur in these crystals and Eq. (4) is still applicable for this situation. Equation (4) would also be applicable in the limiting case of spherical averaging of the $C_2\text{-H}_\alpha$ bonds in the crystal since for this case $a_{xy}^\alpha = a_z^\alpha$ (this extremely large freedom of motion has not occurred in any system investigated thus far). Returning to the random-walk argument, the walk need not be over the full 360° . For example, a random jump between two positions in the xy plane 90° apart leads to Eq. (4). Regardless of the argument, it should be kept in mind that this equation is only an approximation; as indeed must be the case for motion as complex as that occurring in the inclusion crystals. The information regarding this motion obtained from the α -proton coupling constant is obviously restricted. The fact that the lines are broadened when the magnetic field is in the xy plane suggests that the amplitude of the $C_2\text{-H}_\alpha$ bond is large but does not correspond precisely to the case of free rotation.

⁹ See, for example, H. M. McConnell and D. B. Chesnut, J. Chem. Phys. **28**, 107 (1958).

¹⁰ R. W. Fessenden and R. H. Schuler, J. Chem. Phys. **39**, 2147 (1963).

This is also the case for the methyl group of the 3-undecanone radical and for these two radicals the usual expression relating the spin density to the β -proton coupling constants reduces to $a_0^\beta = (B/2)\rho C_2^\pi$, where a_0^β is the isotropic component of the β -proton coupling constant and $B/2$ is a proportionality constant.¹¹ The experimental value of a^β contains an anisotropic component as well as the isotropic component and these two contributions must be separated before this equation can be used to obtain ρC_2^π . Fortunately, the anisotropic component is small and, therefore, the method employed to extract a_0^β is not critical.

Heller¹² has observed that, for the $\text{CH}_3\dot{\text{C}}(\text{CO}_2\text{H})_2$ radical, the anisotropic components of the β -proton hyperfine coupling constants are adequately described by the Hamiltonian

$$\mathcal{H}_d = -g|\beta|g_N\beta_N T_\perp(1-3\cos^2\alpha)S_H I_H. \quad (5)$$

In Eq. (5) α is the angle between the magnetic field direction, \mathbf{H} , and the $\text{CH}_3\text{-}\dot{\text{C}}\text{H}$ carbon-carbon bond, S_H and I_H , are the components of S and I along \mathbf{H} , and $-g|\beta|g_N\beta_N h^{-1} T_\perp \rho C^\pi = B_d \rho C_2^\pi = (-)2.2$ Mc/sec. The isotropic value of the three β -proton coupling constants is (+) 70.9 Mc/sec for this radical. From the data reported by Morton and Horsfield¹³ for the similar radical $\text{CH}_3\dot{\text{C}}\text{HCO}_2\text{H}$, a_0^α , a_0^β , and B_d are (-)54.7, (+)70.3, and (-)3.0 Mc/sec, respectively. If we take $\rho C_2^\pi = 0.90 \pm 0.04$ for these two radicals, then a good estimate of B_d is (-)2.9 \pm 0.6 Mc/sec.

For the included radicals,¹⁴ the α -proton tensor elements are averaged in the xy plane and this requires a motional averaging of the $C_2\text{-C}_3$ bond positions in the tubular cavities. If the motions of these radicals are again taken to be free rotation, large-amplitude (equal-probability) motion or a random jumping motion, Eq. (5) yields

$$a_{xy}^\beta = \rho C_2^\pi [B_d(1 - \frac{3}{2}\sin^2\theta) + B/2], \quad (6)$$

$$a_z^\beta = \rho C_2^\pi [B_d(1 - 3\cos^2\theta) + B/2], \quad (7)$$

$$a_0^\beta = \rho C_2^\pi (B/2) = \frac{1}{3}(2a_{xy}^\beta + a_z^\beta), \quad (8)$$

where a_{xy}^β and a_z^β are the β -proton coupling constants with the magnetic field perpendicular and parallel to the z axis, respectively, and θ is the angle between the $C_2\text{-C}_3$ bond and the z axis. Using Eq. (8) and the data of Table I, $a_0^\beta = 59.6$ Mc/sec for the 3-tetradecanone and 3-undecanone radicals. For the ethyl radical, $a_0^\beta = 75.4$ Mc/sec. If B is assumed to be the same for the ketone and ethyl radicals then ρC_2^π is in excellent

¹¹ C. Heller and H. M. McConnell, J. Chem. Phys. **32**, 1535 (1960).

¹² C. Heller, J. Chem. Phys. **36**, 175 (1962).

¹³ J. R. Morton and A. Horsfield, J. Chem. Phys. **36**, 1142 (1961).

¹⁴ The signs of the coupling constants are not determined from the experiments reported here and all proton coupling constants are listed as their absolute values. The isotropic components of the α - and β -proton coupling constants of very similar radicals are known to be negative and positive, respectively.

agreement with the value of 0.82 obtained from the α -proton coupling-constant data.

From Eqs. (6) and (7) and a value for θ we may also estimate the anisotropic component of a^β . If the C-H_α bond and the axis of the $2p$ orbital on C_2 lie in the xy plane and the σ bonds involving C_2 are sp^2 hybridized, then the most probable value of θ is readily seen to be 30° . (These requirements are, of course, more stringent than those used in obtaining ρC_2^π .) Taking $\theta = 30^\circ$ and $\rho C_2^\pi = 0.79$, Eqs. (6) and (7) give $a_z^\beta \approx 62$ Mc/sec and $a_{xy}^\beta \approx 60$ Mc/sec which are in agreement with the data of Table I.¹⁵

c. Effects of Temperature Changes on the ESR Spectra

The principal question remaining is whether the above experimental value of ρC_2^π is a meaningful quantity associated with this class of aliphatic ketone radicals, or whether this spin density is a temperature-dependent function of intramolecular motion about the $C_2\text{-C}_1$ bonds. In the case of two included *ester* radicals, the ethyl heptanoate radical and the octyl propionate radical, it was possible to obtain well-resolved spectra over the wide temperature range from roughly 340° to 7°K .¹ The ester α -proton coupling constants, and hence ρC_2^π , were observed to be independent of temperature over this entire range within experimental error. The ester β -proton coupling constants changed gradually with temperature due to temperature-dependent motion about the $C_2\text{-C}_3$ bonds. For the ketone radicals it was not possible to completely resolve the ESR spectra over this wide a range of temperatures. However, some data in addition to that presented in Table I were obtained over limited temperature ranges both above and below room temperature. For example, well-resolved xy and z ESR spectra were recorded for the 3-tetradecanone-urea crystals at 313° , 323° , and 333°K . (We refer to spectra obtained with the magnetic field in the

¹⁵ The spin density on Carbon Atom 1 may be estimated by a similar procedure providing one assumes that $a^\alpha = (B/2)\rho C_1^\pi$ where B is the same for the β and ζ protons. As before, only radicals having rotating (ζ proton) methyl groups and known orientations will be useful for this purpose. From the data of Table I, the three radicals derived from 2-nonanone, 2-undecanone, and 2-dodecanone are all seen to have the three equivalent ζ -proton coupling constants characteristic of a rotating methyl group. For the most probable conformations of these radicals, the orientation of the $C_1\text{-C}_4$ bonds are inclined at approximately the same angle from the crystalline z axis (tubular axis) as are the $C_2\text{-C}_3$ bonds of all six ketone radicals. The relative isotropic and anisotropic components of the three ζ -proton coupling constants obtained from the 2-nonanone, 2-undecanone, and 2-dodecanone radicals will, therefore, be approximately the same as those of the three β -proton coupling constants obtained from the 3-tetradecanone and 3-undecanone radicals. Assuming this to be the case, ρC_1^π (ketone) $\approx \rho C_2^\pi$ (ketone) $\times a_z^\zeta$ (ketone) / a_z^β (ketone) $= \pm 0.07$. Or, from similar geometrical considerations of the previously investigated octyl propionate ester radical (for which $\rho = 0.90 \pm 0.04$), ρC_1^π (ketone) $\approx \rho C_2^\pi$ (ester) $\times a_z^\zeta$ (ketone) / a_z^β (ester) $\approx \pm 0.07$. The agreement in these two values of ρC_1^π is encouraging. A detailed knowledge of the orientations of these radicals is not necessary because the anisotropy of a^β (and a^α in this approximation) is small. The sign of ρC_1^π relative to ρC_2^π cannot be determined from these experiments. The value of ± 0.07 may be subject to revision when the effect of the off-diagonal elements of the spin-density matrix are considered.

xy and *z* crystalline directions as *xy* and *z* spectra, respectively.) Well resolved *xy* and *z* spectra were also recorded for the 6-undecanone and 2-dodecanone radicals at approximately 333°K. The α -proton coupling constants derived from these data are the same as those of Table I within the estimated experimental error of ± 2 Mc/sec. At these temperatures the spectra recorded with the magnetic field in the *xy* plane were isotropic with respect to rotations of the magnetic field in this plane, and spectra for all orientations of the magnetic field were symmetric.

The x-irradiated 6-undecanone-urea crystals were cooled from room temperature to 30°K. Both the *xy* and *z* spectra changed gradually with temperature, and the *xy* spectra began showing signs of asymmetry below 270°K. At 77°K the *xy* spectra were anisotropic with respect to rotations of the magnetic field in the *xy* plane. The features of these anisotropic spectra were repeated at intervals of 60° in the *xy* plane, and at no other orientations of the magnetic field. As with the ester radicals, this observation supports the assumption that the crystals are hexagonal and that the *z* direction lies along the crystallographic *c* axis. Although no coupling-constant data were obtained from the asymmetric *xy* ESR spectra, approximate coupling constants were measured from the symmetric 6-undecanone radical *z* spectra for temperatures down to 190°K. Over this range, a_z^α was independent of temperature within an estimated experimental error of ± 4 Mc/sec, which suggests that ρC_2^π is temperature independent (over this temperature range). Below 190°K the *z* spectra were sufficiently broadened and unresolved to prevent measurement of the coupling constants. There was, however, no indication of any major changes in the magnitude of a_z^α from 190° to 30°K. Below 50°K there was very little change in the general features of the spectra obtained with the magnetic field either parallel or perpendicular to the *z* axis of the 6-undecanone-urea crystal. All of the above temperature effects on all ketone radical spectra were reversible.

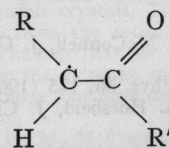
The data of Table I provide adequate evidence that the spin-density distribution is independent of the length of the ketone molecule and the exact position of the carbonyl group in the chain (and therefore of the precise conformation of these radicals in the tubular cavities). In addition, the above ESR data, recorded over a range of temperatures, strongly suggest that ρC_2^π is independent of temperature. Therefore, with reasonable certainty, the value 0.81 ± 0.08 representing the average of the values obtained from the α - and β -proton coupling-constant data may be taken to be a meaningful property of this general class of aliphatic ketone radicals. The estimated error of ± 0.08 reflects the variations among the possible choice for *B* and *Q* as well as the approximations in the formulas used and the limits of experimental accuracy.

Before proceeding to the molecular orbital calculations it is advisable to consider the π -electron assump-

tion in greater detail. McConnell, Heller, Cole, and Fessenden have shown that the radical $\dot{C}H(CO_2H)_2$ is a π -electron radical; the odd electron spin is largely localized in an orbital antisymmetric to reflection in the plane containing three carbon atoms and the α -hydrogen atom.⁶ Other dicarboxylic acid radicals and alkyl radicals having both α and β protons interacting with the unpaired spin are also known to be π -electron radicals.^{10,11} Since the magnetic properties of the ketone radicals are so similar to those of the acid and alkyl radicals, the ketone radicals are almost certainly π -electron radicals. The *g* values of the ketone radicals are quite similar to those of the acid and alkyl radicals. The isotopic coupling constants a_0^α and a_0^β are also consistent with the known π -electron proton coupling constants. Turning now to the anisotropic components of the proton coupling constants, we note that if the Carbon Atom 2 is sp^2 hybridized then the C_2-H_α bond lies in or near the crystalline *xy* plane. This follows from the fact that the "walls" of the tubular cavities restrict the possible orientations of the long straight-chain molecules. Smith⁴ has found using x-ray crystallographic techniques that the included *n*-hydrocarbons exist in a time-averaged extended zigzag conformation (this would place the C_2-H_α bond of the corresponding RĀHR π radical in the *xy* plane). In I it was shown that the C_2-H_α bonds of the carboxylic acid radicals are approximately in the *xy* plane by comparing the a_{xy}^α and a_z^α of these radicals with the known principal elements of the α -proton tensor. Extending these arguments to the ketone radicals, the ratio of a_{xy}^α (ketone)/ a_{xy}^α (acid or ester) is 0.93 and the ratio of a_z^α (ketone)/ a_z^α (acid or ester) is 0.92. These two ratios are the same within experimental error which implies a similar averaging of the tensor elements in all three radical systems. The very small ketone β -proton coupling-constant anisotropy has already been shown to be consistent with this radical orientation and hybridization. All of the data are therefore consistent with the π -electron model assumed both in obtaining the experimental value of ρC_2^π and in the following calculations.

MOLECULAR ORBITAL CALCULATIONS OF SPIN DENSITY

The spin densities were calculated using the Hückel theory¹⁶ and the method of McLachlan.¹⁷ For these molecular orbital calculations the nuclear framework of the ketone radical is represented by the structure



¹⁶ A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* (John Wiley & Sons, Inc., New York, 1961).
¹⁷ A. D. McLachlan, *Mol. Phys.* **3**, 233 (1960).

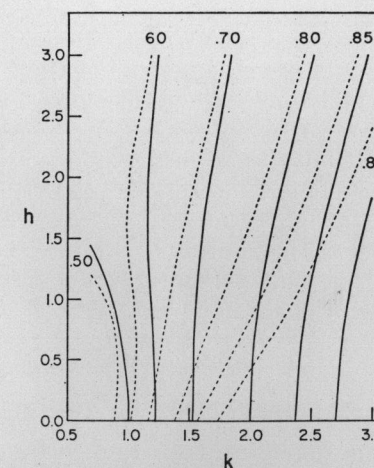


FIG. 4. The electron spin density on Carbon Atom 2 as a function of the molecular orbital parameters *h* and *k*. The solid and broken lines represent the Hückel and McLachlan ($\lambda=1.1$) values, respectively.

in which all atoms shown are coplanar. The unpaired spin density is extended over C_2 , C_1 , and the oxygen atom, and each of these three atoms contributes one electron to the π system. In the Hückel molecular orbital method the two parameters relating α_0 and β_{CO} to α_C and β_{CC} are defined by the equations $h \equiv (\alpha_0 - \alpha_C)/\beta_{CC}$ and $k \equiv \beta_{CO}/\beta_{CC}$. The one-electron wavefunctions are obtained by the usual variational procedure and the spin densities are given by the squares of the coefficients of the half-filled molecular orbital. The spin densities are, of course, a function of the two parameters *h* and *k*. In order to obtain the best over-all view of the method, the range of *h* and *k* values used here is much larger than the usual range employed in Hückel calculations.

The results for ρC_2^π are summarized by the solid lines of Fig. 4. It is interesting to note that the spin density is quite insensitive to variations in *h* and it is very sensitive to changes in *k*. Even though only one spin-density site is being considered (and hence a unique pair of *h* and *k* is not obtained), this insensitivity to *h* makes possible an estimation of *k*. If *h* is constrained to the liberal range of $0.7 \leq h \leq 2.0$ then $k \approx 2.0 \pm 0.3$. This value compares favorably with $k \approx 1.6$ reported by Vincow and Frankel¹⁸ for a series of semiquinone anion radicals. Both of these values, however, are somewhat higher than the range $0.8 \leq k \leq 1.4$ most frequently employed¹⁶ in the determination of properties

¹⁸ G. Vincow and G. K. Fraenkel, *J. Chem. Phys.* **34**, 1333 (1961). See also: P. H. Rieger and G. K. Fraenkel, *ibid.* **37**, 2811 (1962); R. Dehl and G. K. Fraenkel, *ibid.* **39**, 1793 (1963).

(other than spin densities) of compounds containing carbonyl groups.

McLachlan has obtained approximate spin-density formulas from considerations of the perturbed self-consistent field theory. In the simplest form of McLachlan's approximate method the spin density is given by

$$\rho_r^\pi = C_{r0}^2 - \lambda \sum_s \pi_{rs} C_{s0}^2, \quad (9)$$

where π_{rs} and C_{r0}^2 are the atom-atom polarizabilities and spin densities, respectively, calculated from the Hückel theory, and λ is a semiempirical constant which we will take equal to 1.10. The values of ρC_2^π obtained by this method are given by the broken lines of Fig. 4. Equation (9) has the pronounced effect of shifting ρC_2^π to lower values of *k*. A unique pair of *h* and *k* values cannot, of course, be obtained from the single experimental quantity ρC_2^π .

The ketone radical can be considered as an allyl radical in which the electron distribution is polarized by replacing one terminal carbon atom of the core by an oxygen atom. For the allyl radical, $h=0$, $k=1$ and the Hückel and McLachlan values of ρC_2^π are 0.50 and 0.60, respectively. In the ketone radical the π -electron density about the oxygen atom increases and therefore ρC_2^π increases. For example, the Hückel charge densities of the ketone radical are 0.10, 0.17, and -0.27 for C_2 , C_1 , and the oxygen atom, respectively (assuming $h=1.0$ and $k=2.0$). The Hückel spin densities for this choice of parameters are 0.78, 0.03, and 0.18 for C_2 , C_1 , and the oxygen atom, respectively. The Hückel charge densities on all three carbon atoms of the allyl radical are zero, and the Hückel spin densities are 0.50, 0.00, and 0.50 for the three carbon atoms, taken consecutively.¹⁹ This polarization effect of oxygen is so strong that the ketone radical is probably better described as an aldehyde group weakly interacting with the adjacent π electron. Further considerations of the electronic structure of this radical are of interest, and self-consistent field- and configuration-interaction calculations are currently in progress.

ACKNOWLEDGMENT

We are especially indebted to Professor Harden M. McConnell for enlightening discussions and for the use of his laboratory facilities.

¹⁹ For this choice of parameters, the McLachlan C_2 , C_1 , and oxygen spin densities for the ketone are $+0.839$, -0.008 , and $+0.170$, respectively. The McLachlan spin densities are $+0.597$, -0.194 , and $+0.597$ for the three allyl carbon atoms, taken consecutively.

