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Electron Spin Resonance and Internal Rotation of the Methyl Group in the $CH_3C(COOH)_2$ Radical

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The investigation of an x-irradiated single crystal of methyl malonic acid by means of electron spin resonance (ESR) reveals that the two main species produced by the radiation are the $CH_{3}C(COOH)_{2}$ and CH3CH(COOH) radicals. An analysis of the ESR spectra of CH3C(COOH)2 obtained at room temperature, 77°K, and 4.2°K indicates that: (a) the three methyl protons are equivalent, and the principal values of their hyperfine coupling tensor are 75.4 (along the C-CH₃ bond), 68.8 and 68.6 Mc; (b) the isotropic component of the coupling tensor (and, therefore, the spin density on the methyl protons) is positive; (c) the methyl group executes nearly free rotation about the C-C bond at 4.2°K.

INTRODUCTION

DECENT electron spin resonance (ESR) investiga- \mathbf{K} tions have established¹⁻⁸ that oriented aliphatic free radicals can be produced in organic crystals by means of x and γ irradiation. The ESR lines exhibited by these radicals arise from the hyperfine interaction of the magnetic moment of the odd electron with the magnetic moments of one or more nuclei in the radical. Detailed studies of the free radicals produced in several simple dicarboxylic acids¹⁻³ have shown that the ESR lines are due to the interaction of the protons situated in the aliphatic chain. It is convenient to classify the interacting aliphatic-chain protons as σ protons (also known as α protons) and $\pi(\beta)$ protons. Briefly, a σ proton is directly bonded to the unsaturated, "trivalent" carbon. It exhibits a decidedly anisotropic hyperfine interaction¹ and, in general, lies in the nodal plane of the odd electron's spin distribution. The odd electron has been shown to occupy essentially a $p\pi$ orbital in these radicals.^{1,4,5} A π proton is attached to a saturated carbon atom, usually one carbon removed from the "trivalent" carbon atom. In general, π protons lie above and below the nodal plane of the odd electron and possess nearly isotropic hyperfine interactions, the anisotropy being of the order of 4-8 Mc. Heller and McConnell² found that the π protons on the same methylene group in HOOC--CH--CH₂--COOH produced in irradiated succinic acid are not equivalent; i.e., the isotropic components of their hyperfine interaction are different. Similar inequivalence of π protons obtains in HOOCCHCH2CH2COOH in glutaric acid9

and in other radicals.¹⁰ This inequivalence has been ascribed² to a twist of the methylene group with respect to the backbone plane of the free radical. Such a twist increases the hyperconjugative overlap of the $p\pi$ orbital of the odd electron with the s orbital of one of the π protons of the methylene group. At the same time, it decreases the overlap with the other π proton. Since the isotropic hyperfine interaction is proportional to such an overlap, the two protons exhibit different isotropic interactions.

 π protons belonging to a methyl group which rotates or tunnels at a rate faster than the difference between the proton hyperfine couplings (up to $\approx 100 \text{ Mc}$) would be expected to be equivalent. Some confirmation for this has been found, among others, for $(CH_3)_2COH$ in irradiated polycrystalline isopropyl alcohol," CH₃CHR in irradiated alanine,⁸ and (CH₃)₂C--COOH in single crystals of dimethyl malonic acid.¹² The present paper presents a study of the structure of an oriented $CH_3C(COOH)_2$ radical produced in x-irradiated single crystals of methyl malonic acid, $CH_3CH(COOH)_2$. In particular, it provides information about the structure of the radical, the hyperfine coupling tensor of the π protons of the methyl group and the nature of the internal rotation of the methyl group about the C-C bond.

EXPERIMENTAL

Methyl malonic acid was prepared from its diethyl ester. The ester was synthesized by the reaction¹³ of ethyl propionate and ethyl oxalate and the subsequent decarbonylation of the resulting product. The methyl malonic acid thus obtained was free from malonic acid and was readily purified by several recrystallizations from ether and water. Single crystals of the acid were obtained by the very slow evaporation of aqueous solu-

¹² C. Heller and T. Cole (to be published).

^{1.} M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, J. Am. Chem. Soc. 82, 766 (1960). ² C. Heller and H. M. McConnell, J. Chem. Phys. 32, 1535 (1960).

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 ³ D. Pooley and D. H. Whiffen, Mol. Phys. 4, 81 (1961).
 ⁴ T. Cole and C. Heller, J. Chem. Phys. 34, 1085 (1961).
 ⁵ H. M. McConnell and R. W. Fessenden, J. Chem. Phys. 31, 1688 (1959).

 ⁶ N. M. Atherton and D. H. Whiffen, Mol. Phys. 3, 1 (1960).
 ⁷ D. K. Ghosh and D. H. Whiffen, Mol. Phys. 2, 285 (1959).
 ⁸ I. Miyagawa and W. Gordy, J. Chem. Phys. 32, 255 (1960).

⁹ C. Heller and T. Cole (unpublished results).

¹⁰ Y. Kurita and W. Gordy, J. Chem. Phys. **34**, 282 (1961). ¹¹ J. F. Gibson, D. J. E. Ingram, M. C. R. Symons, and M. G. Townsend, Trans. Faraday Soc. **53**, 914 (1957).

¹³ Organic Syntheses, edited by A. H. Blatt (John Wiley & Sons, Inc., New York, 1943), Vol. II, pp. 272, 279.



FIG. 1. The crystal form of methyl malonic acid and the reference set of axes employed.

tions at room temperature. Almost all the crystals obtained had the form shown in Fig. 1. Faces A, B, and C were always well developed. The angles between the normals to faces A and B, and A and C, as measured by an optical goniometer, were 87.7° and 92.3° , respectively. No information regarding the structure of methyl malonic acid is available in the literature. However, a preliminary x-ray diffraction study of the acid showed¹⁴ that its unit cell is monoclinic with the unique axis *b* along the normal to face B.

All measurements were related to an orthogonal set of axes, x, y, and z, in the crystal. This set, shown in Fig. 1, places the x axis in plane A, 2.3° from the (010) direction and perpendicular to the common edge of A and B; the y axis in plane A, 90° from the (010) direction and parallel to the common edge of A and B; and the z axis normal to plane A, 87.7° from the (010) direction. All the direction cosines (l, m, n) given in the present work are quoted with respect to the axes x, y, and z.

Crystals were x irradiated at room temperature for 1 hr, at a distance of 5 cm from a tungsten target tube operating at 50 kv and 30 ma.

ESR spectra were taken at room temperature, 77°K (liquid nitrogen), and 4.2° K (liquid helium). Room temperature spectra were obtained with an X-band spectrometer employing a TE₀₁ mode cylindrical cavity and 100-kc field modulation. The external magnetic



FIG. 2. Room temperature ESR spectrum of x-irradiated single crystal of methyl malonic acid. The external field H_0 is parallel to the z axis.



FIG. 3. Room temperature ESR spectrum of x-irradiated single crystal of methyl malonic acid. The external field H_0 is parallel to direction (0.985, 0.174, 0).

field was continuously controlled and monitored by an NMR servo. A superheterodyne X-band spectrometer was used for taking the low-temperature spectra.

Room-temperature spectra were obtained for every 10° in the three quadrants x-y, y-z, and z-x, while spectra at 77° and 4.2°K were taken only for a number of selected orientations. Initial orientations of the crystals were made by means of an optical goniometer. The uncertainty in the hyperfine splittings measured is estimated to be ± 0.3 Mc, while the uncertainty in the angles quoted is $\pm 2^{\circ}$.

The spectroscopic splitting factor g was obtained by the following relationship:

$$g = -2.0023 \times \frac{\text{frequency of cavity with sample}}{\text{frequency of center of radical spectrum}},$$

where the frequency of cavity with sample was found to be 9505.5 Mc. The absolute value of any one of the



100 Mc

¹⁴ M. E. Milberg and H. D. Blair (private communication).

FIG. 4. ESR spectrum of x-irradiated methyl malonic acid crystal taken at 4.2°K. The external field H_{θ} is parallel to direction (0.985, 0.174, 0).

g values is uncertain to ± 0.0004 , while the relative values are accurate to ± 0.0002 .

RESULTS AND ANALYSIS OF SPECTRA

Typical ESR spectra obtained at room temperature are shown in Fig. 2 $(H_0 || z \text{ axis})$, and Fig. 3 $[H_0 ||$ (0.985, 0.174, 0)]. The four lines marked P in these figures are in the ratio of 1:3:3:1. This set of lines appeared unchanged, except for small anisotropies in the line splittings and the g value, in all spectra taken. The hyperfine couplings derived from these spectra possessed a cylindrical symmetry (see below). The radical responsible for these spectra must contain three equivalent protons rotating or tunneling about a symmetry axis and, therefore, is most likely



No splittings due to the carboxyl protons could be observed, but this is in accord with results on radicals in other dicarboxylic acids.^{1,2} Likewise, no lines due to "forbidden" transitions¹ could be discerned; their expectation values in the case of this radical were calculated¹ to be $\approx 1/1000$ that of the main lines.

The radical $\dot{C}H_3$ must be ruled out as the species giving rise to set *P*. Such a radical is extremely reactive and would readily diffuse through the lattice and react with other species or molecules. Even if it existed at room temperature, it would probably tumble rapidly and give spherically symmetric (isotropic) couplings for its protons—not the cylindrically symmetric couplings observed. A nontumbling $\dot{C}H_3$ would be randomly oriented and its couplings would, again, lack cylindrical symmetry.

The five lines in the second set (marked Q) in Fig. 3 are in the ratio of 1:4:6:4:1. At other crystal orientations (see Fig. 2) this set split into additional lines. A preliminary analysis indicates that this set is due to three equivalent, nearly isotropic, protons and one anisotropic σ proton. This strongly suggests that the other free radical created in x-irradiated methyl malonic acid is CH₃ČHCOOH. For the direction (0.985, 0.174, 0) the σ proton has the same coupling as the π protons, i.e., 70.2 Mc.

Although the two radicals produced in irradiated methyl malonic acid are, therefore, identified, only a detailed study of the $CH_3\dot{C}(COOH)_2$ radical is presented here.

X-band spectra obtained at 77°K were identical with those taken at room temperature. On the other hand, there was a marked decrease in the intensity of the two central lines of $CH_3\dot{C}(COOH)_2$ (set P) in the ESR spectra taken at 4.2°K. A typical spectrum is shown in Fig. 4 for $H_0 \parallel (0.985, 0.174, 0)$. While there is no detectable change in the intensity ratio of the TABLE I. Principal elements of the hyperfine tensor A of the protons of the methyl group and the spectroscopic splitting factor g.

Tensor ^a	Principal elements	Direction cosines with respect to x , y , and z
A	$A_{11} = +68.8 \text{ Mc}$	(0.99, 0, -0.15)
	$A_{22} = +68.6 \text{ Mc}$	(0, 1.00, 0)
	$A_{33} = +75.4 \text{ Mc}$	(0.15, 0, 0.99)
g	$g_{11} = (-)2.0026$	(0.48, 0.88, 0.05)
	$g_{22} = (-)2.0034$	(0.06, -0.10, 0.99)
	$g_{33} = (-)2.0044$	(0.89, -0.44, -0.10)

^a Matrix elements for A are: $A_{xx}=69.0$, $A_{yy}=68.6$, $A_{zz}=75.2$, $A_{xy}=A_{yz}=0$, $A_{xz}=1.0$; Matrix elements for g are: $g_{xx}=2.0039$, $g_{yy}=2.0030$, $g_{zz}=2.0035$, $g_{xy}=-0.0007$, $g_{zz}=-0.0001$, $g_{yz}=0$.

lines in set Q, those in set P are nearly in the ratio of 1:1:1:1. Graphical integration of the lines of set P at several crystal orientations yielded intensity ratios varying from 1:1.3:1.3:1 to 1:1.6:1.6:1, and an average of about 1:1.45:1.45:1. The small overlap of lines due to CH₃ \dot{C} (COOH)₂ with those due to

CH₃ĊH(COOH)

prevented a more accurate intensity ratio determination, and is most likely the cause for the varying intensity ratios. On rewarming to room temperature, crystals gave the usual room-temperature spectra (Figs. 2, 3).

The observed spectra of $CH_3C(COOH)_2$ were interpreted by means of the spin Hamiltonian

$$\mathcal{K} = -\beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H}_0 + \sum_k g_N \beta_N \mathbf{I}^k \cdot \mathbf{H}_0 + \mathbf{S} \cdot \sum_k \mathbf{A} \cdot \mathbf{I}^k, \quad (1)$$

where β is the electronic Bohr magneton, **S** the electronic spin operator, **g** the spectroscopic splitting factor, and \mathbf{H}_0 the external magnetic field. g_N , β_N , \mathbf{I}^k , and **A** are the proton g factor, the Bohr magneton, the spin operator, and hyperfine tensor for proton k=1, 2, 3, respectively.

The principal elements and principal directions of the diagonalized hyperfine tensor **A** and for the electronic g value are given in Table I. It will be noted that two of the principal elements of **A** are equal within experimental uncertainty. The isotropic component of the hyperfine interaction tensor is $a=\frac{1}{3} | \text{Tr}\mathbf{A} | = 70.8$ Mc and is positive (see Discussion).

The variation of the experimental hyperfine splittings of any of the methyl group's protons with angle in the quadrants x-y and x-z are indicated by the circles in Fig. 5 (upper and lower). These variations were also calculated for quadrants x-z and y-z by means of the equation¹

$$= [(\nu_N - S_H A_{33})^2 \cos^2\theta + (\nu_N - S_H A_{22})^2 \sin^2\theta \cos^2\phi + (\nu_N - S_H A_{11})^2 \sin^2\theta \sin^2\phi]^{\frac{1}{2}}.$$
(2)



FIG. 5. Upper: Observed hyperfine splittings with the external field H_0 in the x-y quadrant. Lower: Calculated (solid and dashed lines) and observed (circles) hyperfine splittings with the external field H_0 in the z-x quadrant. In this quadrant angle θ [Eq. (2)] equals $\omega -9^{\circ}$. Solid (dashed) line gives results calculated with A_{33} and A_{11} of same (opposite) signs.

In Eq. (2) ν_N is the proton resonance frequency, i.e., 14.5 Mc, $S_H = \pm \frac{1}{2}$, A_{ii} the principal elements of tensor **A**, and θ and ϕ are the usual polar angles relating any given direction in the crystal to the principal directions of **A**. Calculations were carried out with A_{ii} having the same signs and opposite signs. The results for quadrant $x \cdot z(\phi = 90^{\circ})$ are shown in Fig. 5 (lower), where angle ω equals $\theta + 9^{\circ}$. The solid line was obtained with $A_{33} = A_{11}$, while the dashed line indicates results with $A_{33} = -A_{11}$. Clearly, A_{33} and A_{11} are of the same sign. Similarly, A_{33} and A_{22} can be shown to have the same sign.

It is to be noted that the symmetry generated by the methyl group about the C_1 — C_2 bond and the small proton-electron dipole interaction lead to a simplification of the Hamiltonian in Eq. (1). Under these conditions, the dipolar part of the Hamiltonian, hence the solid line of Fig. 5 (lower), is given to a very good approximation by the more restricted expression

$$\mathfrak{K}_{d} = -g \cdot \beta \cdot g_{N} \beta_{N} T \perp (1 - 3 \cos^{2} \alpha) S_{H} I_{H^{k}}.$$
(3)

In Eq. (3), S_H and I_{H^k} are the components of **S** and I^k along \mathbf{H}_0 , α is the angle between \mathbf{H}_0 and the symmetry axis, and $T \perp$ is the dipolar component of

$$A \perp (=A_{11} = A_{22}).$$

DISCUSSION

A. Structure of the Radical $CH_3\dot{C}(COOH)_2$

The four ESR lines due to $CH_3\dot{C}(COOH)_2$ did not split or broaden markedly for any of the crystal orientations investigated. In general, the two (or more) sites for the radical, or its C_1-C_2 bond, in a monoclinic system will be magnetically equivalent only for orientations in which H_0 is parallel or perpendicular to the twofold screw axis.² The fact that the ESR lines did

not split or broaden markedly for any orientation would suggest that the $C_1 - C_2$ bond is either perpendicular or parallel to the screw axis or glide plane. However, the possibility of two sites for the C_1 — C_2 bond differing by a small angle, e.g., $10-20^{\circ}$ (or $160-170^{\circ}$) cannot be ruled out. Such two sites would appear equivalent, since the maximum anisotropy in the hyperfine interaction (≈ 7 Mc) and in the g value (9-10 Mc)—the two factors which are sensitive to the radical's location -is of the same magnitude as the half-width of the experimental lines (5-6 Mc). The position of the $CH_3\dot{C}(COOH)_2$ radical with respect to the axes x, y, and z is shown in Fig. 6 (see below). Although this position probably represents the average of the positions of two sites of the C_1 — C_2 bond, it gives a semiquantitative estimate of the separation of these sites. The C_1 — C_2 bond makes an angle of 82° with the x axis and, therefore, 80° with the monoclinic axis (010). Hence, the C₁-C₂ bonds in the two sites differ by $\approx 160^{\circ}$ and are almost perpendicular to the (010) axis; i.e., they are very nearly magnetically equivalent.

McConnell and Robertson¹⁵ have predicted that the smallest g value should occur along a direction parallel to the symmetry axis of the odd electron's $p\pi$ orbital (perpendicular to the radical's plane). This was confirmed experimentally, with a variation of a few degrees, for several oriented free radicals.^{1,3,6} The direction of the smallest g value in the radical $CH_3C(COOH)_2$, i.e., g = 2.0026, is along (0.48, 0.88, 0.05). In addition, symmetry considerations strongly suggest that the C_1 — C_2 bond is along the axis of cylindrical symmetry of the hyperfine couplings of the protons of the methyl group, namely, along (0.15, 0, 0.99). The angle between $C_1 - C_2$ direction and the g = 2.0026 direction is, therefore, $\approx 83^{\circ}$. These facts taken together indicate that the four carbon atoms in the radical are nearly, if not actually, coplanar. The direction of the normal to this plane is close to (0.48, 0.88, 0.05), and the odd electron



FIG. 6. The position of the radical CH₃ \dot{C} (COOH)₂ and its $p\pi$ orbital with respect to the reference axes x, y, and z. The carbon of the methyl group C_1 is in the z-x plane, while C_3 and C_4 , the carbons of the carboxyl groups, are above and below the z-x plane, respectively. The axis of the $p\pi$ -orbital is nearly in the x-y plane (3° away).

¹⁶ H. M. McConnell and R. E. Robertson, J. Phys. Chem. 61, 1018 (1957).

occupies essentially a $p\pi$ orbital above and below this plane. The bonds to carbon C_2 are, therefore, nearly sp^2 in character, similar to the case of the HC(COOH)₂ radical.¹ The general form of the radical CH₃C(COOH)₂ and its position with respect to the axes x, y, and z are shown in Fig. 6.

In the previous section it was shown that the principal components of the hyperfine tensor of the π protons have the same sign. It will now be shown that the sign is positive. The theoretical equations developed by McConnell and Strathdee¹⁶ were used to evaluate the dipole-dipole contributions to the hyperfine coupling tensor of a π proton. The π proton was assumed to lie in the nodal plane of a $2p\pi$ orbital located on C₂, along the C_1 — C_2 direction [see CH₃C(COOH)₂ radical] at a distance of 2.14 A from C₂. The following dipoledipole contributions were evaluated:

- +12.6 Mc along the C_2 - C_1 -H direction
- -5.2 Mc along the direction parallel to the symmetry axis of the $2p\pi$ orbital
- -7.5 Mc along the other orthogonal direction.

In $CH_3C(COOH)_2$ the π protons do not lie along the C_1 — C_2 bond but are situated on a conical surface which makes an angle $\alpha \approx 29^{\circ}$ with the C₁--C₂ bond. In addition, there is a partial averaging out of the dipole contributions due to the methyl group's rotation about the $C_1 - C_2$ bond. However, since the remaining dipole interaction varies as $(1-3\cos^2\alpha)$, it follows that the largest positive contribution of this interaction is still along the C_1 — C_2 direction. Hence, the dipolar contributions to the hyperfine tensor are: +4.5 Mc along (0.15, 0, 0.99), the C₁—C₂ bond direction, -2.1 Mc along (0.99, 0, -0.15), and -2.3 Mc along (0, 1.00, 0).

Taking the isotropic part of the coupling tensor a = +70.9 Mc gives $A_{33} = +70.9 + 4.5 = +75.4$ Mc, $A_{22} = +70.9 - 2.3 = +68.6$ Mc, and $A_{11} = +70.9 - 2.1 =$ +68.8 Mc. On the other hand, a = -70.9 gives $A_{33} =$ -66.4 Mc, $A_{22} = -73.2$ Mc, and $A_{11} = -73.0$ Mc. A comparison with experimental results confirms the positive sign of a (and of A_{ii} in Table I). The magnitude and sign of a are in accord with theoretical predictions.^{17,18} There exists, therefore, a positive spin density at the π proton. In other words, the electronic spin angular momentum of the $p\pi$ orbital and the small spin in the σ bond at the π proton have the same sense of polarization, up or down.

It was previously suggested² that the isotropic hyperfine constant of the π proton, a, is related to the odd electron spin density ρ on the "trivalent" carbon, C₂, by the expression

$$a = R(\theta) \rho_{C_2}, \tag{4}$$

where

$$R(\theta) = B\cos^2\theta. \tag{5}$$

In Eq. (5), θ is a dihedral angle such that $\theta = 90^{\circ}$ when the C—H bond of the π proton lies in the nodal plane of the $p\pi$ orbital and $\theta = 0^{\circ}$ when it is parallel to the $p\pi$ symmetry axis. For the rotating methyl protons in $CH_3\dot{C}(COOH)_2$, $\cos^2\theta$ is averaged out, so that $\langle R(\theta) \rangle =$ $\frac{1}{2}B$. If one makes the reasonable assumption that ρ_{C_2} is equal to that found in $CH(COOH)_{2}$ and

HOOCCHCH₂(COOH),^{2,3}

namely, ≈ 0.9 , one obtains from Eq. (4) 70.9= $\langle R(\theta) \rangle 0.9$ or, $\langle R(\theta) \rangle = 78.8$ Mc, and B = 157.6 Mc. The value for $\langle R(\theta) \rangle$ compares well with the value 75.9 Mc found for π protons in freely tumbling ethyl radicals in the liquid state.¹⁹ The value B=157.6 Mc represents the largest isotropic hyperfine constant that a nonrotating π proton may assume in $p\pi$ radicals produced in dicarboxylic acids or other simple aliphatic hydrocarbon radicals. The present value of B appears to be a better choice than B = 112 Mc used previously² on the basis of results obtained for (CH₃)₂COH in polycrystalline (CH₃)₂CHOH.¹¹ A recent study of HOOCCHCH₂CH₂COOH in glutaric acid⁹ yields an isotropic coupling of 132 Mc for one of the π protons. Such a large value could be accounted for with B=157Mc, but not with B=112 Mc. The low value of B in $(CH_3)_2\dot{C}OH^{11}$ and $(CH_3)_2\dot{C}(COOH)$ $(B=120 \text{ Mc})^{12}$ may be due to a reduced spin density on the "trivalent" carbon in these radicals.

B. Internal Rotation of the Methyl Group

It was shown before that the intensity of the two central lines of the ESR spectrum of CH₃C(COOH)₂ decreased sharply when the spectrum was taken at 4.2°K. A similar decrease was reported²⁰ in the expected intensity of the proton lines in NH₂ trapped at 4.2°K in an argon matrix. McConnell²¹ suggested an explanation for this phenomenon based on the assumptions that the NH₂ radical rotates freely in the argon matrix and that there exists thermal equilibrium distribution in the various quantum states at 4.2°K. The internal rotation of the methyl group in CH₃C(COOH)₂ will be discussed here along somewhat similar lines.

X-ray diffraction studies of several dicarboxylic acids in the solid state have established²² that the carboxyl groups in these acids are bonded intermolecularly via hydrogen bonds. Such bonds also occur, in all probability, between the carboxyl groups of the $CH_3C(COOH)_2$ radical and its neighbors in the crystal

 ¹⁶ H. M. McConnell and J. Strathdee, Mol. Phys. 2, 129 (1959).
 ¹⁷ A. D. McLachlan, Mol. Phys. 1, 233 (1958).
 ¹⁸ R. Bersohn, J. Chem. Phys. 24, 1066 (1956); D. B. Chesnut,

ibid. 29, 43 (1958).

¹⁹ R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 33, 935 (1960).

 ²⁰ S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, Phys. Rev. Letters 1, 91 (1958).
 ²¹ H. M. McConnell, J. Chem. Phys. 29, 1422 (1958).
 ²² See, for example, J. A. Goedkoop and C. H. MacGillavry, Acta Cryst. 10, 125 (1957); J. D. Morrison and J. M. Robertson, J. Chem. Soc. 1949, 980, 1001.



FIG. 7. Symmetries and allowed combinations of nuclear-spin and rotational eigenfunctions for the two lowest rotational levels in CH₃C(COOH)₂. Nuclear spin functions associated with rotational level k=0 can have total $M_I = +\frac{3}{2}, +\frac{1}{2}, -\frac{3}{2}, -\frac{3}{2}$, while the nuclear spin functions associated with $k = \pm 1$ can only have total $M_I = +\frac{1}{2}$ and $-\frac{1}{2}$.

of methyl malonic acid. Hence, the only rotation which can take place in the radical is that of the methyl group about the C_1 — C_2 bond. If this internal rotation is free, its energy levels are then given by the solutions of the Schrödinger equation for rotation about a *fixed axis*.^{23,24} They are

$$W(k) = Ck^2, \tag{6}$$

where, W(k) is the energy in cm^{-1} of rotational level k, k is a quantum number having values $0, \pm 1, \pm 2 \cdots$, and

$$C = h/8\pi^2 cI. \tag{7}$$

In Eq. (7), *h* is Planck's constant, *c* is the velocity of light, and *I* is the moment of inertia of the methyl group about the C_1 — C_2 axis. If one takes the C_2 — C_1 —H angle to be 109.5° and the C_1 —H bonds to be 1.09 A, one obtains C=5.3 cm⁻¹. Hence,

$$\Delta W_{0,\pm 1} = 5.3 \text{ cm}^{-1}, \qquad \Delta W_{0,\pm 2} = 21.2 \text{ cm}^{-1}, \text{ etc.},$$

where $\Delta W_{0,\pm k}$ is the energy separation between the internal rotation levels 0 and $\pm k$.

The eigenfunctions of these rotational levels belong to the symmetry types (representations) of the rotational subgroup C_3 .^{24,25} Thus, the level k=0 is of symmetry type A, the levels k=3p, where p is an integer, are of symmetry A, and levels $k=3p\pm 1$ are of symmetry E.

In order to choose the allowed combinations of rotational and nuclear-spin eigenfunctions one must consider the total eigenfunction ψ_T for CH₃C(COOH)₂,

$$\psi_T = \psi_E \psi_V \psi_R \psi_N + \psi_{EVRN'}, \qquad (8)$$

where ψ_E , ψ_V , ψ_R , and ψ_N are the electronic, vibrational, rotational, and nuclear eigenfunctions, respectively.

 ψ_{EVRN}' is a small correction term for the interaction of the modes represented by the different eigenfunctions.²⁶ For the very low states of ψ_E , ψ_V , and ψ_R (at 4.2°K) such interaction is negligible and, therefore,

$$\psi_T = \psi_E \psi_V \psi_R \psi_N. \tag{9}$$

 ψ_T must be of symmetry A (symmetric) for the operations of subgroup C_3 , i.e., the exchange of *two pairs* of protons. It is assumed that at 4.2°K only the ground states of ψ_E and ψ_V are populated. Therefore, ψ_E is of symmetry A, since the rotation of the protons is about a σ bond (C_1 — C_2 bond) and the $p\pi$ orbital is unaffected by this rotation. Likewise, the vibrational ground state may be taken to be nondegenerate and, therefore, symmetric.²⁶ Hence, ψ_N must be of symmetry A if ψ_R is of symmetry A (since $A \times A = A$ while $A \times E = E$), while ψ_N must be of symmetry E if ψ_R is of that symmetry type $(E \times E = 2A + E)$.

The nuclear spin eigenfunctions for the protons of the methyl group and their symmetry designations are readily obtained from the character table of C_{3} .²⁷ They are

$$\psi_{N^{1}}=(\alpha\alpha\alpha), \qquad \qquad A_{+\frac{3}{2}}$$

$$\psi_N^2 = (\beta\beta\beta), \qquad A_{-1}$$

$$\psi_N^3 = (1/\sqrt{3}) \left(\alpha \alpha \beta + \alpha \beta \alpha + \beta \alpha \alpha\right), \qquad A_{+\frac{1}{2}}$$

$$\psi_N^4 = (1/\sqrt{3}) \left(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta\right), \qquad A_{-\frac{1}{2}}$$

$$\psi_{N^{5}}=(1/\sqrt{3})\left(\alpha\alpha\beta+e^{2\pi i/3}\alpha\beta\alpha+e^{4\pi i/3}\beta\alpha\alpha\right)\Big\}.$$

$$egin{aligned} \psi_N{}^6 &= (1/\sqrt{3})\left(lphalphaeta + e^{4\pi i/3}lphaeta lpha + e^{2\pi i/3}eta lpha lpha)
ight) \ \psi_N{}^7 &= (1/\sqrt{3})\left(etaeta lpha + e^{2\pi i/3}eta lpha eta + e^{4\pi i/3}lphaeta eta)
ight) \end{aligned}$$

$$\psi_{N^{8}} = (1/\sqrt{3}) \left(\beta\beta\alpha + e^{4\pi i/3}\beta\alpha\beta + e^{2\pi i/3}\alpha\beta\beta\right) \right\}. \qquad E_{-\frac{1}{2}}$$

Total $\psi_R\psi_N$ functions may be found elsewhere.²⁸ It will be noticed that for ψ_N of symmetry E, total M_I has only values of $+\frac{1}{2}$ or $-\frac{1}{2}$, while for symmetry A total M_I can have values of $+\frac{3}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$, and $-\frac{3}{2}$. The allowed combinations of ψ_R and ψ_N for the rotational levels k=0 and $k=\pm 1$ are shown schematically in Fig. 7.

The statistical weights for the rotational levels of k, taking into account the nuclear-spin eigenfunctions associated with each of these levels, $\operatorname{are}^{25} 1$ for k=0 or $k=3p\pm 1$, and 2 for $k=3p(\neq 0)$.

The introduction of a potential barrier to the internal rotation of the methyl group in CH₃C(COOH)₂ would be expected to decrease²⁴ the energy gap $\Delta W_{0,\pm 1}$ between the rotational levels k=0 and $k=\pm 1$. At a reasonably high potential (one or more kcal/mole)

²³ L. Pauling and E. B. Wilson, Jr., Introduction to Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1935), p. 271.

ρ. 271.
 ²⁴ J. S. Koehler and D. M. Dennison, Phys. Rev. 57, 1006 (1940).
 ²⁵ P. Wilser, L. J. Chem. Phys. 2, 276 (1925).

²⁵ E. B. Wilson, Jr., J. Chem. Phys. 3, 276 (1935).

²⁶ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), p. 407.
²⁷ For a table of representations of C₈ see, for example, H.

²⁷ For a table of representations of C₈ see, for example, H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 383.

Wiley & Sons, Inc., New York, 1944), p. 383. ²⁸ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 71.

these two rotational levels would actually coalesce and become part of the ground, degenerate level, v=0, of the torsional mode of vibration of the methyl group.

The energy gap $\Delta W_{0,\pm 1}$ can now be estimated. It will be assumed that the statistical distribution of the radical population in the various k levels is consistent with thermal equilibrium at 4.2°K. The only levels significantly populated at 4.2°K are k=0 and $k=\pm 1$, since the statistical weights are 1 or 2 for all levels and the energy of the levels increases as k^2 . Taking the intensity of the inner ESR lines to the outer lines in the spectrum for CH₃C(COOH)₂ to be 1.45 one obtains

$$n_1/n_0 = 0.225/1.0 = \exp(-\Delta W/kT).$$
 (10)

In Eq. (10), k is Boltzmann's constant, T is the absolute temperature, and n_1 and n_0 are the populations of rotational levels ± 1 and 0, respectively. Therefore,

$$\Delta W_{0,\pm 1} = 4.4 \text{ cm}^{-1}$$

This value is very close to that obtained above for a freely rotating methyl group (5.3 cm^{-1}) and, therefore, strongly suggests that the methyl group in

 $CH_3\dot{C}({\rm COOH})_2$

is executing nearly free, or slightly hindered, rotation about the C_1 — C_2 bond. A comparison with theoretical calculations for the rotation of the methyl group in methyl alcohol²⁴ suggests that the hindering potential in $CH_3\dot{C}(COOH)_2$ is less than 100 cal/mole of radical. A more definite assertion regarding the free rotation as well as the quantitative estimation of the small potential barrier possibly involved must await a more accurate determination of the intensities of the ESR lines of the ordinary radical, and, possibly, the deuterated one at several temperatures.

It is interesting to note that the line intensities of the

radical CH₃CHCOOH at 4.2°K give $\Delta W_{0,+1} < 0.5$ cm⁻¹ and, therefore, suggest that the methyl group in this radical is executing a decidedly hindered rotation. Since the environment of $CH_3CHCOOH$ and $CH_3C(COOH)_2$ in the crystal is the same, the pronounced difference in potential barriers to internal rotation must be caused by intramolecular conditions. The low (or zero) potential barrier in CH3C(COOH)2 may be due, in part, to the absence of a hydrogen atom on the carbon adjacent to the methyl group. Available data on barriers in various molecules indicate²⁹ that molecules with hydrogens bonded to the carbon atom adjacent to the rotating methyl group possess relatively high barriers. In addition, molecules with a sixfold symmetry for the rotation of a methyl group were found³⁰ to have very low potential barriers. The radical $CH_3\dot{C}(COOH)_2$ may possess such a symmetry, especially if the two carboxyl groups are related by a twofold rotation.

Note added in proof. A proton hyperfine coupling, similar to that reported here, has been found for the methyl group of CH₃CH(COOH) in γ -irradiated *l*-alanine [J. R. Morton and A. Horsfield, J. Chem. Phys. **35**, 1142 (1961)].

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²⁹ E. B. Wilson, Jr., Advances in Chemical Physics, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. II, p. 367; E. B. Wilson, Jr., Proc. Natl. Acad. Sci. U. S. 43, 816 (1957).

³⁰ E. Tannenbaum, R. J. Myers, and W. D. Gwinn, J. Chem. Phys. **25**, 42 (1956); R. E. Naylor, Jr., and E. B. Wilson, Jr., *ibid.* **26**, 1057 (1957).