The Angular Dependency of the ESR Proton Hyperfine Coupling Constant of the CH_2 Group

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Recent ESR studies of organic radicals in the solid state have revealed several interesting facts on the structures of these radicals. One of these facts is that, in some radicals, the β protons--the protons in the methyl or methylene groups adjacent to the carbon atom which brings an odd electron—are chemically distinct from each other.

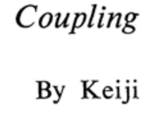

Fig. 1a

Heller and McConnell[1] have studied the ESR spectra of a γ irradiated single crystal of succinic acid, analyzing them to show that the radical produced was identified as in Fig. 1a and that the coupling constants (nearly isotropic) of the two protons, H_1 and H_2, were not equal. They concluded that the distinction was caused by a kind of deformation of the CH_2 group: the H-C-H angle was no longer bisected by the molecular plane. They assumed the following equation for the angular dependency of the coupling constant of β-protons:

$$a_H(\theta)=\rho_\alpha{}^0 K\cos^2\theta \quad (1)$$

In the equation, $a_H(\theta)$ is the isotropic hyperfine coupling constant of β protons, $\rho_\alpha{}^0$ is the spin density on the carbon (α carbon) adjacent to the methylene group, and θ is the angle between the carbon $p\pi$ orbital on the α carbon and each of the C-H bonds, both projected to a plane perpendicular to the $C_\alpha-C_\beta$ bond, as is shown in Fig. 2. In this equation they seem to have assumed that the type of deformation would be the rotation of the alkyl group around the $C_\alpha-C_\beta$ axis.

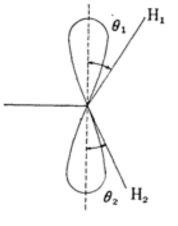

Fig. 2. Projection angles θ_1 and θ_2.

Kurita and Gordy[2] then found a similar distinction between the two protons in a CH_2 group in studying the ESR of the γ irradiated single crystal of L-glycine hydrochloride. In this case the radical was identified as that shown in Fig. 1b, and the coupling constants were $a_{H_1}=9$ gauss and $a_{H_2}=2$ gauss. If we simply applied Eq. 1 to the discussion of the a_{H_1}/a_{H_2} ratio, the deformation would have to be very large. Pooley and Whiffen[3] have also observed different coupling constants of β protons in the $HOOCCH_2\dot{C}HCOOH$ radical

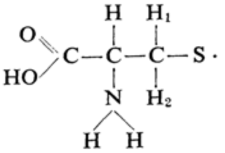

Fig. 1b

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

[2] Y. Kurita and W. Gordy, ibid., **34**, 282 (1961).

[3] D. Pooley and D. H. Whiffen, *Mol. Phys.*, **4**, 81 (1961).

from succinic acid (100 Mc and 80 Mc). Jasejà and Anderson[4] have obtained a different pair of unequal coupling constants (115 Mc and 18 Mc) in the same $HOOCCH_2\dot{C}HCOOH$ radical from aspartic acid, attributing the cause of the deformation to intermolecular forces. In both of the papers the deformation angle was discussed by the $\cos^2\theta$ rule.

Recently Ohnishi, Sugimoto and Nitta[5] have carefully studied the temperature dependency of the ESR spectra of the radical in γ-irradiated stretched polyethylene which had been assigned to the allyl-type radical shown in Fig. 1c; they have found that, at a low temperature (−180°C), the protons in CH_2 groups adjacent to the allyl group, H_1 and H_2 in the figure, give different isotropic hyperfine coupling constants, that is, 30 and 11 gauss respectively, while at a high temperature (+142°C) the distinction disappears and the both constants become 21.3 gauss. By using Eq. 1, the calculated θ values of H_1 and H_2 are obtained as 55°02′ and 18°52′. The deviation from the normal angle, 30°, seems irrationally large.

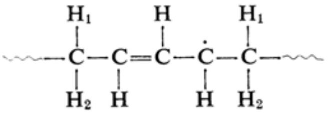

Fig. 1c

As the mechanism of deformation, the rotation would be more difficult in the case of a methylene group, CH_2R, than in the case of a methyl group, CH_3, because of the bulky group—COOH, alkyl and so forth—attached to the former. Especially in polymeric solids like stretched polyethylene, the R group being a very long chain, the rotation around the $C_\alpha-C_\beta$ axis would be almost entirely hindered. In this case the deformation would be performed by rocking, twisting, or in other ways.

In the present paper considering two typical mechanisms of deformation: one is the rotation around the $C_\alpha-C_\beta$ axis, and the other is the rocking of the CH_2 group on a plane on which normally the two C–H bonds of the CH_2 group exist, we make a valence bond calculation on the spin density on CH_2 protons for their various conformations caused by the rotation and the rocking, in order to see what angular dependency proton hyperfine coupling constants on CH_2 groups obey.

The fact that we assumed rotation and rocking as a source of non-equivalent coupling constants does not necessarily mean that the energy minimum is accomplished by these kinds of deformation. The possibility that one hydrogen is attracted to the odd p orbital, making a bent bond, might be considered, as well as a possibility of twisting. It would be very interesting to study theoretically what is the most stable conformation and why such a deformed conformation could be stable, but the calculation needed in order to explain such a slight difference in conformational energy seems to be excessively complicated, and hence this problem will not be discussed in this paper.

Method of Calculation

In calculating the ground state wave function and the spin density in the state we employed the hypothetical system, consisting of five valence electrons on the five atomic orbitals, as is shown in Fig. 3: the $2p\pi$ orbital (designated by P) on the carbon α in which an odd electron is situated, the two hybridized orbitals (σ_1 and σ_2) on the carbon β, and the two 1s orbitals (H_1 and H_2) on the two hydrogens which are bonding with the hybridized orbitals, σ_1 and σ_2 respectively. In their normal conformation, the $C_\alpha C_\beta C_\gamma$ chain is situated on the U plane and the two CH bonds are on the V plane, which is perpendicular to the U plane and which bisects the $C_\alpha C_\beta C_\gamma$ angle.

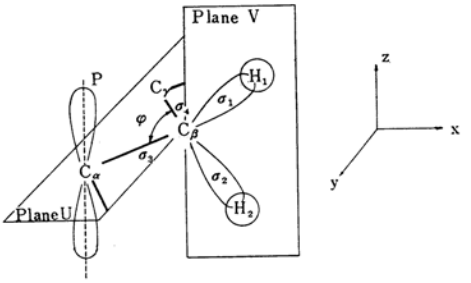

Fig. 3. The model of calculation and the notation used.

All canonical structures that have the maximum bondings, that is, five structures, are taken as the bases of the valence bond calculation, but all ionic structures were disregarded. This disregard would result in a larger spin density on hydrogen atoms, but we are going to discuss only the relative change of the spin distribution caused by the variation in conformation because of an uncertainty involved in evaluating atomic integrals that will be mentioned later, and in this the disregard does not affect the conclusion.

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[4] T. S. Jasejà and R. S. Anderson, *J. Chem. Phys.*, **36**, 2727 (1962).

[5] S. Ohnishi, S. Sugimoto and I. Nitta, ibid., **37**, 1283 (1962).

Throughout the calculations the deformation is considered to cause the corresponding change in the hybridization of the carbon orbitals making the deformed bonds, and the hydrogen atoms are always regarded as in the direction of the hybridized orbitals, with a CH bond length which is not changed by the deformation.

In treating rotating conformations, the four hybridized orbitals, σ_1, σ_2, σ_3 and σ_4, remain sp^3 hybridized. The calculation of the spin density was made for various rotated angles around the $C_\alpha-C_\beta$ axis.

In treating the rocking conformation, the hybridized orbitals on the carbon β are written with the two parameters a and b. Parameter a corresponds to the variation in the $C_\alpha C_\beta C_\gamma$ angle. The reason why we considered this kind of deformation is that, for instance, regarding the allyl type radical in oriented polyethylene mentioned above, the polyethylene main chain would be fixed, and in order to decrease the strain the allyl radical might change the angle, φ, of $C_\alpha C_\beta C_\gamma$. In our calculations the angle φ is expressed in terms of parameter a, which designates the hybrization of the orbitals, σ_3 and σ_4; a^2 is the s nature of the orbitals σ_3 and σ_4, as can be seen in the following:

$$\varphi=\cos^{-1}[a^2/(a^2-1)] \tag{2}$$

$$\left.\begin{aligned}\sigma_3&=a\psi_{\beta 2s}-\sqrt{(1-2a^2)/2}\ \psi_{\beta 2px}\\&\quad+(\sqrt{2})\ \psi_{\beta 2py}\\\sigma_4&=a\psi_{\beta 2s}-\sqrt{(1-2a^2)/2}\ \psi_{\beta 2px}\\&\quad-(1\sqrt{2})\ \psi_{\beta 2py}\end{aligned}\right\}\quad(3)$$

where $\psi_{\beta 2s}$, $\psi_{\beta 2px}$ and $\psi_{\beta 2py}$ are 2s, 2px and 2py orbitals respectively on the β carbon, the coordinates being taken as in Fig. 3.

In any conformation with a varied a value and with various magnitudes of rocking of the two CH bonds, it is assumed that the $C_\alpha C_\beta C_\gamma$ chain and, consequently, the σ_3 and σ_4 orbitals are always on the U plane, which is perpendicular to the odd p orbital, P, and that the σ_1, σ_2, H_1 and H_2 orbitals are on the V plane, parallel to P and bisecting angle φ. The other parameter, b, is utilized to stand for the hybridization of the σ_1 orbital: b^2 being the s nature of the orbital σ_1, the s nature of the orbital σ_2 is $1-2a^2-b^2$. The exact form of the σ_1 and σ_2 orbitals is written as follows:

$$\left.\begin{aligned}\sigma_1&=b\psi_{\beta 2s}+(\sqrt{2}\,ab/\sqrt{1-2a^2})\psi_{\beta 2px}\\&\quad+(\sqrt{1-2a^2-b^2}/\sqrt{1-2a^2})\psi_{\beta 2pz}\\\sigma_2&=\sqrt{1-2a^2-b^2}\ \psi_{\beta 2s}+(\sqrt{2}a\sqrt{1-2a^2-b^2}\\&\quad/\sqrt{1-2a^2})\ \psi_{\beta 2px}-(b/\sqrt{1-2a^2})\psi_{\beta 2pz}\end{aligned}\right\}\quad(4)$$

Calculations were carried out for the following three values of a:

Series 1: $a=1/2$, i.e., σ_3 and σ_4 are both sp^3 hybridized (s nature: 25%), and, consequently, the $C_\alpha C_\beta C_\gamma$ angle is 109°28′ (normal). The hybridization of σ_1 is varied from sp^3 to p, at the same time as that of σ_2 is varied from sp^3 to sp.

Series 2: $a=1/\sqrt{5}$: σ_3 and σ_4 are both sp^4 hybridized (s nature: 20%), and, consequently, the $C_\alpha C_\beta C_\gamma$ angle is 104°29′, narrower than normal.

Series 3: $a=\sqrt{3/10}$: σ_3 and σ_4 are both s^3p^7 hybridized (s nature: 30%), and the $C_\alpha C_\beta C_\gamma$ angle is 114°23′, more obtuse than normal.

The angles, θ_1 and θ_2, defined in Fig. 2 are easily connected with the parameters, a and b, as follows:

$$\left.\begin{aligned}\tan\theta_1&=ab/\sqrt{1-2a^2-b^2}\,\sqrt{1-a^2}\\\tan\theta_2&=a\sqrt{1-2a^2-b^2}/b\sqrt{1-a^2}\end{aligned}\right\}\quad(5)$$

The following relationship between the θ_1 and θ_2 angles as a function of parameter a but independent of parameter b will be used in the following section in checking the calculated results:

$$\tan\theta_1\tan\theta_2=a^2/(1-a^2) \tag{6}$$

Matrix elements between the canonical structures are reduced to those between hybridized orbitals by the usual method; they are also reduced to those between atomic orbitals by Eqs. 3 and 4.

The atomic exchange integrals requisite to the calculation are evaluated according to the methods proposed by van Vleck[6] and by

TABLE I. VALUES OF EXCHANGE INTEGRALS EMPLOYED (in unit of eV.)

Exchange integrals between C_β and H	
N_{ss}	2.00
$N_{s\sigma}$	1.82
$N_{\sigma\sigma}$	2.30
$N_{\pi\pi}$	−0.60
Exchange integrals in C_β	
$F_0(2s, 2s)-2F_0(2s, 2p)+F_0(2p, 2p)$	0.430
F_2	0.231
G_1	2.415
Exchange integrals between H_1 and H_2	
$[H_1, H_2]$	Morse function
Exchange integrals between C_β and P	
$N_{\pi ss\pi}$	0.207
$N_{\pi\sigma s\pi}$	−0.253
$N_{\pi\sigma\sigma\pi}$	0.348
$N_{\pi\pi\pi\pi}$	−1.240
$N_{\pi\pi'\pi'\pi}$	0.026

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6) J. H. van Vleck, ibid., 1, 219 (1933); 2, 20 (1934).

Karplus et al.⁷⁾ The values of the integrals employed are collected in Table I. The N_{rs}'s in the Table are the following exchange integrals between C_β and H_1 or H_2:

$$N_{rs}=-\int\psi_{\beta r}(1)\psi_{H1s}(2)\cdots H\psi_{H1s}(1)\psi_{\beta s}(2)\cdots d\tau \tag{7}$$

H: Total Hamiltonian

and are evaluated from the dissociation energy of methane and the heat of the sublimation of graphite. All N_{rs}'s between C_α and H_1 are neglected because they are small. The F_0's and F_2 and G_1 are the usual one-center atomic integrals of C_β, whose values are deduced from the spectroscopic data of a carbon atom. The exchange integral $[H_1, H_2]$ between H_1 and H_2 is calculated on the Morse function as a function of their interatomic distance. There seems no reliable method available for evaluating the exchange integrals N_{rstu} between C_α and C_β:

$$N_{rstu}=\int\psi_{\alpha r}(1)\psi_{\beta s}(2)\cdots H\psi_{\beta t}(1)\psi_{\alpha u}(2)\cdots d\tau \tag{8}$$

In this paper, except for $N_{\pi\pi\pi\pi}$, the effective two-electron Hamiltonian approximation by Karplus⁷⁾ is used, giving the following results:

$$N_{rstu}=\int\psi_{\alpha r}(1)\psi_{\beta s}(2)e^2/r_{12}\psi_{\beta t}(1)\psi_{\alpha u}(2)d\tau_1 d\tau_2 \tag{9}$$

$$\begin{pmatrix}\text{for } (r, u)=(2p\pi,\ 2p\pi) \\ s, t=2s,\ 2p\sigma,\ 2p\pi'\end{pmatrix}$$

As to $N_{\pi\pi\pi\pi}$, Altman's result⁸⁾ is adopted.

The overlap integrals between atomic orbitals are entirely disregarded in order to simplify the calculations.

Results and Discussion

The calculated spin densities on protons for rotating conformations of various angles are tabulated in Table II, together with the spin densities on β carbon hybridized orbitals. From the spin density, ρ_H, on the proton, one can calculate the coupling constant, a_H, by the following equation:

$$a_H=Q\rho_H \tag{10}$$

Q being the coupling constant of the proton when ρ_H is unity. In the normal conformation, both θ_1 and θ_2 are 30°. The spin density on a proton does not seem to be dependent only on its own projection angle, θ_1 for instance, but also on the angle of the other proton, for instance θ_2, which one can see by comparing Calculation Nos. 1 and 4, where ρ_H is different for the same θ, 30°. The situation is the same in Calculation Nos. 3 and 5. Roughly speaking, however, it varies in accord with $\cos^2\theta$, as one may see in Fig. 4. In Fig. 4 the $\rho_H=\text{const}\times\cos^2\theta$ curve is drawn so as to fit the calculated result (Calcd. No. 1) at $\theta=30°$. Accordingly, it may be said that the $\cos^2\theta$ rule may be utilized for the hyperfine coupling of CH_2 protons in the rotating conformation.

The spin density on the hybridized orbitals increases with the increased spin density on the proton of the CH bond, as is seen in Table II. Thus, as the isotropic coupling constant of the methylenic proton (deformed by rotation) becomes large, the anisotropy of the coupling will also grow large, though the magnitude of anisotropy seems to be negligibly small.

The results of the calculations for rocking

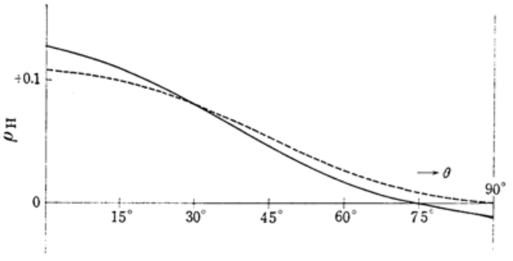

Fig. 4. Angular dependency of proton spin density for rotation.
—: Calculated; ---: const.×$\cos^2\theta$

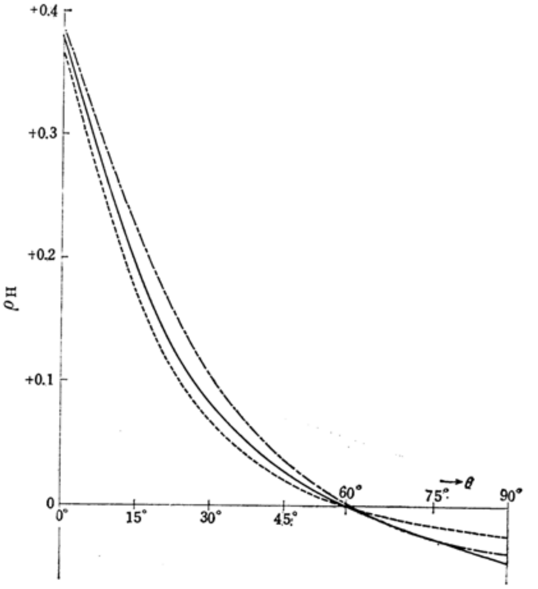

Fig. 5. Angular dependency of proton spin density for rocking.
—: Series 1; -----: Series 2; —·—: Series 3

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7) M. Karplus and D. H. Anderson, ibid., **30**, 6 (1959); M. Karplus, ibid., **30**, 11 (1959); H. S. Gutowsky, M. Karplus and D. M. Grant, ibid., **31**, 1278 (1959).

8) S. L. Altman, *Proc. Roy. Soc.*, **A210**, 327, 343 (1951-2).

TABLE II. CALCULATED SPIN DENSITY FOR VARIOUS ROTATING CONFORMATIONS

Calcd. No.	Rotation from normal site	Projection angle		Proton spin density		β Carbon spin density	
		θ_1	θ_2	ρ_{H1}	ρ_{H2}	$\rho_{\sigma1}$	$\rho_{\sigma2}$
1	0°	30°	30°	+0.0817	+0.0817	−0.0753	−0.0753
2	10°	20°	40°	+0.1039	+0.0565	−0.0941	−0.0530
3	30°	0°	60°	+0.1262	+0.0108	−0.1124	−0.0098
4	60°	30°	90°	+0.0734	−0.0108	−0.0687	+0.0113
5	90°	60°	60°	+0.0233	+0.0233	−0.0228	−0.0228

TABLE III. CALCULATED SPIN DENSITY FOR VARIOUS ROCKING CONFORMATIONS
(Series 1 : $a^2=1/4$, $\varphi=109°28'$)

Calcd. No.	Parameter b	s Nature of hybridized orbital		Projection angle		Proton spin density		β Carbon spin density	
		σ_1	σ_2	θ_1	θ_2	ρ_{H1}	ρ_{H2}	$\rho_{\sigma1}$	$\rho_{\sigma2}$
1	$1/2$	0.250	0.250	30°00′	30°00′	+0.0817	+0.0817	−0.0753	−0.0753
2	$1/\sqrt{5}$	0.200	0.300	25°14′	35°16′	+0.1097	+0.0567	−0.0988	−0.0531
3	$1/\sqrt{6}$	0.167	0.333	22°13′	39°14′	+0.1273	+0.0422	−0.1129	−0.0399
4	$1/3$	0.111	0.389	17°09′	47°12′	+0.1719	+0.0178	−0.1465	−0.0167
5	$1/\sqrt{14}$	0.071	0.429	13°16′	54°44′	+0.2094	+0.0017	−0.1723	−0.0009
6	$1/5$	0.040	0.460	9°40′	62°57′	+0.2491	−0.0119	−0.1975	+0.0129
7	0	0	0.500	0°	90°00′	+0.3829	−0.0459	−0.2662	+0.0497

TABLE IV. CALCULATED SPIN DENSITY FOR VARIOUS ROCKING CONFORMATIONS
(Series 2 : $a^2=1/5$, $\varphi=104°29'$)

Calcd. No.	Parameter b	s Nature of hybridized orbital		Projection angle		Proton spin density		β Carbon spin density	
		σ_1	σ_2	θ_1	θ_2	ρ_{H1}	ρ_{H2}	$\rho_{\sigma1}$	$\rho_{\sigma2}$
1	$\sqrt{3/10}$	0.333	0.333	26°34′	26°34′	+0.0816	+0.0816	−0.0752	−0.0752
2	$1/2$	0.250	0.350	22°54′	30°37′	+0.1035	+0.0626	−0.0936	−0.0586
3	$1/\sqrt{5}$	0.200	0.400	19°28′	35°16′	+0.1280	+0.0453	−0.1133	−0.0430
4	$1/\sqrt{6}$	0.167	0.433	17°14′	38°55′	+0.1455	+0.0348	−0.1268	−0.0333
5	$1/3$	0.111	0.489	13°24′	46°22′	+0.1827	+0.0182	−0.1538	−0.0177
6	$1/\sqrt{15}$	0.067	0.535	10°01′	54°44′	+0.2207	+0.0058	−0.1792	−0.0058
7	$1/5$	0.040	0.560	7°37′	61°52′	+0.2529	−0.0048	−0.1991	+0.0049
8	0	0	0.600	0°	90°00′	+0.3786	−0.0277	−0.2631	+0.0280

TABLE V. CALCULATED SPIN DENSITY FOR VARIOUS ROCKING CONFORMATIONS
(Series 3 : $a^2=3/10$, $\varphi=114°23'$)

Calcd. No.	Paramater b	s Nature of hybridized orbital		Projection angle		Proton spin density		β Carbon spin density	
		σ_1	σ_2	θ_1	θ_2	ρ_{H1}	ρ_{H2}	$\rho_{\sigma1}$	$\rho_{\sigma2}$
1	$1/\sqrt{5}$	0.200	0.200	33°13′	33°13′	+0.0819	+0.0819	−0.0753	−0.0753
2	$1/\sqrt{6}$	0.167	0.233	28°57′	37°46′	+0.1063	+0.0584	−0.0960	−0.0544
3	$1/3$	0.111	0.289	22°06′	46°35′	+0.1541	+0.0219	−0.1339	−0.0199
4	$1/\sqrt{15}$	0.067	0.333	16°19′	55°40′	+0.2040	−0.0031	−0.1694	+0.0050
5	$1/5$	0.040	0.360	12°18′	63°01′	+0.2433	−0.0197	−0.1948	+0.0222
6	0	0	0.400	0°	90°00′	+0.3858	−0.0371	−0.2679	+0.0403

conformations are collected in Tables III, IV and V, together with the spin densities on β carbon hybridized orbitals and the s nature of the latter. The angular dependency of proton spin densities in the case of rocking conformations is entirely different from that in the case of rotating conformations, as is illustrated in Fig. 5. It should be stressed that the $\cos^2\theta$ rule by no means applies to the proton coupling of the methylene group in the rocking conformation; the proton coupling constant varies more rapidly with the projection angle, θ. If one tries to use the $\cos^2\theta$ rule for the rocking methylene group, one will be led to a larger deformation from the normal sites than is really the case. Actually, the rotation,

TABLE VI. OBSERVED HYPERFINE COUPLING CONSTANT AND ESTIMATED PROJECTION ANGLE θ BY SEVERAL METHODS

		H_1 ($-180°C$)*	H_2 ($-180°C$)*	H_1 and H_2 ($+142°C$)*
Observed coupling constant[5]		30 gauss	11 gauss	21.3 gauss
Projection angle θ	$\cos^2\theta$ rule (21.3 gauss is assigned to 30°00′)	impossible	51°32′	30°00′ (assumed)
	$\cos^2\theta$ rule ($K=58$ gauss)	18°52′	55°02′	37°06′
	Rocking deformation ($a^2=1/4$)	24°20′	39°10′	30°00′
	Rocking deformation ($a^2=1/3$)	27°30′	41°49′	33°13′

* Observation temperature

the rocking and other kinds of deformation would take place in the methylene group, which gives unequal proton coupling constants for the two protons. Therefore, minute care should be taken in discussing the deformation angle of the methylene group on the basis of its proton coupling constants.

The proton spin density in the case of this deformation is not simply a function of θ. For instance, the negative spin density on the proton nearly on plane U (for example, -0.0459 in Calcd. No. 7 in Table III) does not seem to originate from the direct interaction of the CH bond with the odd orbital, P, but from the mixing of the interaction of the CH bond with the other CH bond and of the interaction of the latter with orbital P. This is shown by a valence bond calculation of the system consisting of the three atomic orbitals (P, σ and H orbitals of the bond in plane U) : the proton spin density in this case is calculated to be -0.0036, which is ten times smaller in magnitude than the spin density shown above.

Actually, there may occur other kinds of deformation than rotation and rocking. So far as the spin density is concerned, other deformations, twisting for instance, might be derived as a mixing of rotation and rocking in the first approximation.

The effect of the $C_\alpha C_\beta C_\gamma$ angle, φ, on the proton spin density may be seen by comparing Table III with Tables IV and V, or in Fig. 5. Generally speaking, the larger value of φ results in the larger (in absolute value) proton spin density for the same hybridization or the same b value, though the difference is relatively small. In a minute discussion this difference should be taken into consideration, but for a rough estimation of the rocking angle, the calculated spin density and its interpolation for the normal φ value (Table III) may safely be used.

The spin density on β carbon hybridized orbitals varies almost in parallel with that on the proton in the bond, as can also be seen in Tables III, IV and V. Thus, the anisotropy of the proton coupling constant becomes important for protons whose projection angle is smaller than 20°.

Application to the Allyl-Type Radical in Oriented Polyethylene

We would like to apply the results of the preceding section to the coupling constants of the two non-equivalent protons in the methylene group adjacent to the allyl-type radical in oriented polyethylene, which were observed by Ohnishi et al.[5] Application to this problem would be appropriate and rational because, as has been mentioned previously, the allyl radical, which is produced midway in an oriented polyethylene molecule, would not be able to rotate because of the long main chain of the molecule, but it would be able to rock, because rocking needs no motion of the main chain.

The coupling constants they observed are given in Table VI, where $-180°C$ is the temperature at which the deformation of the methylene group seems to be entirely frozen to the minima of the potential energy (probably double minima on either side of the normal conformation) and $+142°C$ is the one at which the transformation from one minimum to the other is perfectly free.

At first, for comparison, the $\cos^2\theta$ rule is employed to estimate the projection angle. If 21.3 gauss at $+142°C$ is assumed to correspond to $\theta=30°$, 30 gauss at $-182°C$ cannot be achieved by any θ value (Table VI). On the other hand, if an empirically deduced $K=58$ gauss and the SCF π spin density on the α carbon of allyl radical $\rho_\alpha{}^0=0.622$ are used for Eq. 1, an unexpectedly large deformation from the normal angle (30°) is obtained (Table VI).

In our valence bond calculation, an odd electron on the π carbon orbital (P) interacting with β CH bonds is treated. However, in the allyl radical, which is a conjugated system, the number of odd electrons on P is not unity but ρ_α^0. Therefore, instead of Eq. 10, Eq. 11 may be used in the first approximation:

$$a_{\rm H} = \rho_\alpha^0 \rho_{\rm H} Q \qquad (11)$$

Q is theoretically given as 507 gauss and $\rho_\alpha^0 = 0.622$, as stated above, while $a_{\rm H}$ is observed, $\rho_{\rm H}$ can then be calculated, and, consequently, the θ angle will be deduced. However, as the numerical value of the calculated proton spin density, $\rho_{\rm H}$, may include some error caused by the approximations employed, e. g., disregard of overlap integrals or of ionic structures, it seems more rational to take $\rho_{\rm H}$ as compared in its relative value. That is to say, regarding the product, $\rho_\alpha^0 Q$, as a parameter to be decided experimentally, we connect the observed $a_{\rm H}$ to $\rho_{\rm H}$ and θ and use one more relation, Eq. 6, to check the consistency of the assignment.

First we assume that the radical has the conformation where $a^2 = 0.250$, that is, $\varphi = 109°28'$. Then the coupling 21.3 gauss at $+142°$C will correspond to the normal site, $b^2 = 1/4$ and $\theta_1 = \theta_2 = 30°00'$, and from the calculated $\rho_{\rm H} = +0.0817$ of this case, $Q\rho_\alpha^0$ is obtained as 261 gauss.* Using this, and interpolating the calculated spin density in Series 1 (Table III), the values of θ in Table VI, 24°20' and 39°10', are obtained. This set of θ_1 and θ_2 comes to the relation $\tan\theta_1 \tan\theta_2 = 0.368$ and, with the aid of Eq. 6, $a^2 = 0.269$, which is larger than the assumed value, $a^2 = 0.250$.

Secondly, if the conformation of the radical is assumed to be the case, $a^2 = 0.333$, i. e., $\varphi = 114°23'$; hence we obtain the results in the last line of Table VI and $a^2 = 0.317$, which is smaller than the assumed value.

Thus, the value of a^2 in the allyl radical obtained is between 1/4 and 1/3, and therefore φ lies between 109°28' and 114°23'; a widening of the $C_\alpha C_\beta C_\gamma$ angle from the tetrahedral angle seems to take place in this allyl-type radical. The deformation from the equivalent sites derived by our rocking model is 6° to 9°, which is much smaller and more probable than 18° or more obtained by the $\cos^2\theta$ rule.

By considering the difference of the bond length between the CC single bond and the allyl CC bond, the widening of the $C_\alpha C_\beta C_\gamma$ angle is proved to be probable for the radical as a means of reducing the strain[5].

In the present paper, we applied our calculations based on the rocking conformations only to the allyl-type radical in polyethylene, but the unequal couplings of some organic radicals in single crystals and in rigid glass also seem to have to be partly reexamined in the light of this finding.

Summary

Valence-bond calculations of the angular dependency of the proton coupling constants of the methylene group in the ESR spectra have been carried out. If the rotation of the group is the only type of deformation, the $\cos^2\theta$ rule by McConnell seems to be valid. If the rocking of the group takes place, however, the angular dependency is entirely different from the $\cos^2\theta$ rule, and the deformation angle based on the rocking model is much smaller than that derived by the $\cos^2\theta$ rule. This finding has been applied to the unequal coupling constants of the two methylene protons of the allyl-type radical in polyethylene.

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* Here if $\rho_\alpha^0 = 0.622$ is applied, $Q = 420$ gauss is obtained. When we compare this with the theoretical value, 507 gauss, we recognize some effect of disregarding ionic structures, like $C^- H^+$, which makes the calculated spin density on protons larger than it is.