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Abnormal Hyperfine Splitting in the ESR Spectra of $\alpha,\alpha,\gamma,\gamma$-Tetraphenylallyl-type Organic Stable Free Radicals[1]

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The ESR spectra of $\alpha,\alpha,\gamma,\gamma$-tetraphenylallyl radical have been first observed. An abnormal ESR hyperfine splitting of this radical has been compared with the ESR hyperfine splitting of other tetraphenylallyl-type radicals; it can be explained very well by introducing the idea of a twisted-allyl model of the molecule.

The history of an organic stable free radical, $\alpha,\alpha,\gamma,\gamma$-tetraphenylallyl(TPA), dates from 1923, when Ziegler published the synthetic method.[2] Observed in the course of the investigation of the magnetic properties of organic stable free radicals, the electron spin resonance(ESR) spectrum of TPA reveals an unusually large hyperfine splitting of the proton adjacent to the β-position of the allyl group, compared with the results of the familiar theoretical calculation of the spin-density distribution.[3]

The spectrum of $\alpha,\alpha,\gamma,\gamma$-bisdiphenyleneallyl(BDA) also exhibits an exceptionally large hyperfine splitting of the corresponding proton. ESR studies of the hyperfine structures of $\alpha,\alpha,\gamma,\gamma$-bisdiphenylene-$\beta$-phenylallyl(BDPA),[4,5] BDA,[4,6] $\alpha,\alpha,\gamma,\gamma$-bisdiphenylene-$\beta$-methylallyl(BDMA),[3] and $\alpha,\alpha,\gamma,\gamma$-bisdiphenylene-$\beta$-azoallyl(BDAA)[7] have already been reported by several authors, but not that of TPA; moreover, no systematic explanation of the relation between the hyperfine coupling constant of the β-position and the framework of the allyl group of these radicals has ever been given.

In the present paper, the ESR spectra of BDA and BDAA were remeasured carefully, and that of TPA was measured for the first time in diluted solutions. A possible explanation was also presented, one based on the model that *$2p_z\pi$-orbitals* of the three carbons in the allyl group of the radicals will twist one another by a certain angle with respect to the two C-C bonds. The validity of this model was examined by comparing the proton hyperfine coupling constant of TPA with those of other tetraphenylallyl-type radicals (Fig. 1).

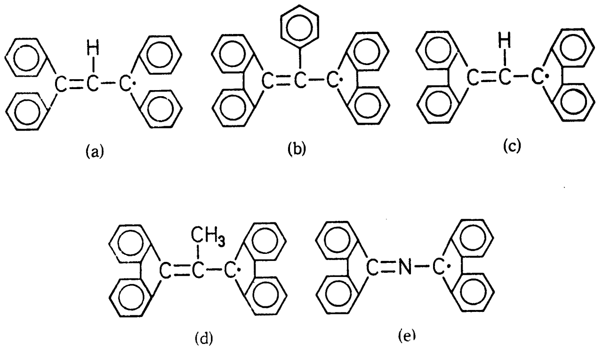

Fig. 1. Tetraphenyl-allyl type radicals.
(a) TPA (b) BDPA (c) BDA (d) BDMA (e) BDAA

Experimental

The samples were prepared following the process described in Refs. 2, 7, and 8. For the observation of the ESR spectra the solvents were well purified, dehydrated, and degassed by the usual methods.[9] An aqueous solution of peroxylamine disulfonate was used as the standard, and the value of 13.00 gauss was taken for the nitrogen coupling constants.[10] The hyperfine coupling constants were usually determined by taking the average values of two or three spectra. All the ESR spectra were obtained with a JES-ME3X-type spectrometer of the JEOL Co., equipped with a 100-kHz field modulation. The experimentally-obtained hyperfine coupling constants were then compared with the spectra reconstructed using the ESR spectrum simulator.

Results

Tetraphenylallyl. One of the observed spectra of TPA is shown in Fig. 2.

The spectrum consisted of two groups, which split further into about thirty hyperfine lines. The analysis of the hyperfine structure of the observed spectra revealed that one proton adjacent to the β-position of the allyl group (A_β^H), the eight-phenyl protons at the *ortho*-positions (A_o^H), the eight-phenyl protons at the *meta*-positions (A_m^H), and the four-phenyl protons at the *para*-positions (A_p^H) are attributable to the hyperfine structures. As a result of the reconstruction of the observed spectra by means of the ESR spectrum simulator, the proton hyperfine coupling constants for each solvent were determined to be as is shown in Table 1.

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[1] Parts of this work were presented at the 8th ESR Symposium of the Chemical Society of Japan, Hiroshima, November, 1969, and at the 9th ESR Symposium, Tokyo, October, 1970.

[2] K. Ziegler, *Ann.*, **434**, 34 (1932).

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

[4] R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 3 (1964).

[5] K. H. Hausser, *Z. Naturforsch.*, **14a**, 425 (1959).

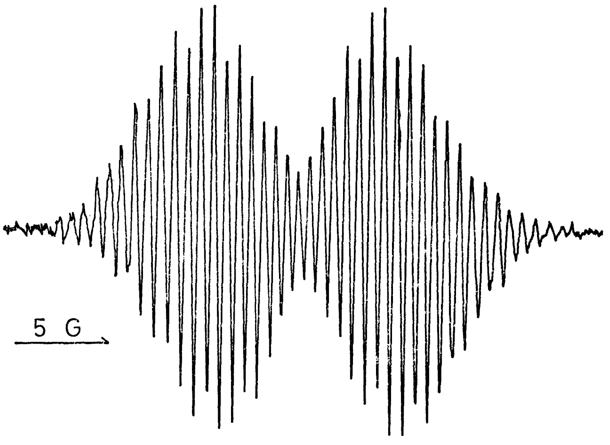
[6] K. H. Hausser, *ibid.*, **17a**, 158 (1962).

[7] R. Kuhn and F. A. Neugebauer, *Monatsh.*, **94**, 16 (1963).

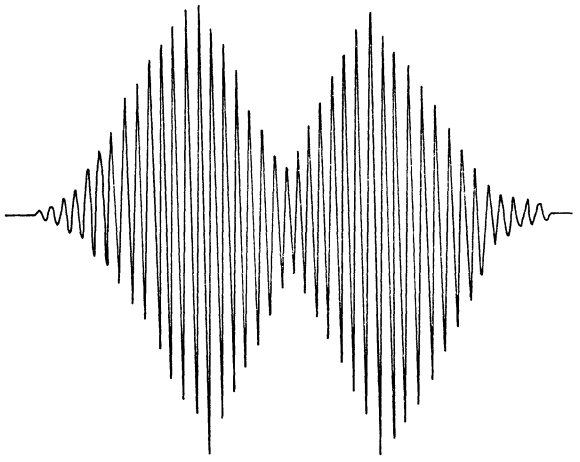
[8] R. Kuhn, H. Fischer, F. A. Neugebauer, and H. Fischer, *Ann.*, **654**, 64 (1962).

[9] Y. Deguchi, This Bulletin, **35**, 910 (1962).

[10] G. E. Pake, J. Townsend, and S. I. Weissman, *Phys. Rev.*, **85**, 683 (1952).



Simulated spectrum



Observed spectrum

Fig. 2. ESR spectrum of TPA in THF and its simulated spectrum.

Table 1. Hyperfine coupling constants for TPA at 20°C (in gauss)

Solvent	A^H_β	A^H_o	A^H_m	A^H_p
CCl_4	8.65	1.30	0.65	1.95
CS_2	8.50	1.45	0.60	1.80
n-Hexane	8.80	1.25	0.70	2.10
D.E.A.[a]	8.90	1.25	0.75	2.25
T.H.F.[b]	8.95	1.20	0.70	2.10
Ethanol	8.75	1.35	0.65	1.95

a) Diethylamine b) Tetrahydrofuran

The temperature dependence of the coupling constant (A^H_β) in the THF solution is shown in Fig. 3 as a function of the temperature. In these ESR spectra, it can be noticed that the A^H_β changes rather markedly than the others, A^H_o, A^H_m, and A^H_p.

Bisdiphenyleneallyl. The ESR hyperfine structure of BDA in diluted CS_2 solution was observed by Kuhn and Neugebauer[4] and Hausser.[6] The spectrum of BDA in a diluted CS_2 solution measured at 20°C is shown in Fig. 4.

In Table 2, the hyperfine coupling constants of the protons of BDA are also tabulated.

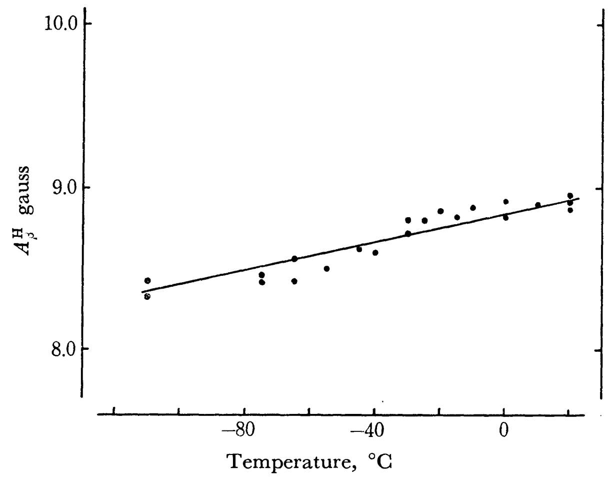


Fig. 3. Temperature dependence of the coupling constant A^H_β of TPA in THF.

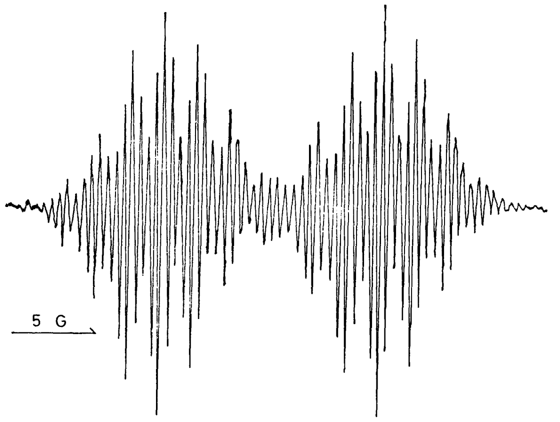


Fig. 4. ESR spectrum of BDA in CS_2.

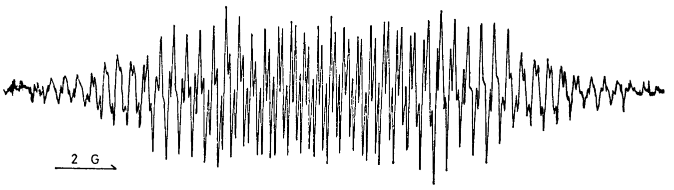
Table 2. Hyperfine coupling constants of BDA in CS_2 solution at room temperature (in gauss)

A^H_β	A^H_1	A^H_2	A^H_3	A^H_4	
13.4	1.99	1.99	0.46	—	
13.2	1.92	1.86	0.48	0.36	(Ref. 4)
13.2	1.89	1.89	0.42	0.06	(Ref. 6)

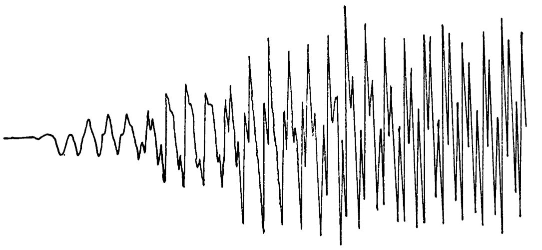
Bisdiphenyleneazoallyl. Although the ESR hyperfine structure of BDAA in a diluted benzene solution has already been observed by Kuhn and Neugebauer[7] they did not analyze the spectrum in detail. In this investigation, the ESR spectra were investigated in several organic solvents at 20°C (Fig. 5) and analyzed in detail.

Reconstructing the observed spectra by the ESR spectrum simulator, the hyperfine coupling constants for nitrogen, and each ring proton were determined, as is shown in Table 3.

From the observed ESR spectra of these tetraphenylallyl-type radicals, it can be concluded that the four phenyl groups or two biphenylene groups are equivalent.



Observed spectrum



Simulated spectrum

Fig. 5. ESR spectrum of BDAA in benzene and its simulated spectrum.

Table 3. Hyperfine coupling constants for BDAA at 20°C (in gauss)

Solvent	A^H_β	A^H_1	A^H_2	A^H_3	A^H_4
Benzene	3.38	1.69	1.61	0.44	0.40
T.H.F.[a)]	3.26	1.73	1.66	0.45	0.42
D.M.E.[b)]	3.39	1.82	1.75	0.44	0.40

a) Tetrahydrofuran b) Dimethoxyethane

Discussion

The theoretical spin densities on each carbon position were enumerated by means of McLachlan's Molecular Orbital method,[11] and also by means of the odd alternant method[12] in the case of TPA. The coupling constants calculated by means of McConnell's relation are also shown in Table 4.

Table 4 indicates that the observed hyperfine coupling constants of the ring protons are in fair agreement with the calculated hyperfine coupling constants. This coincidence indicates the validity of McLachlan's calculation. It should be noted, however, that in TPA and BDA the theoretical hyperfine coupling constants of β-protons are too small to account for the experimentally-determined hyperfine coupling constants; this is in contrast to the close agreement between the observed and the calculated values about the ring protons.

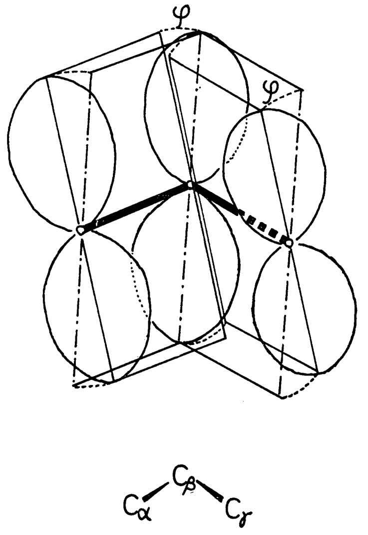


Fig. 6. Twisted allyl model.
$2p_z$ orbitals of C_α and C_γ are twisted along the C_α-C_β and C_β-C_γ bonds.

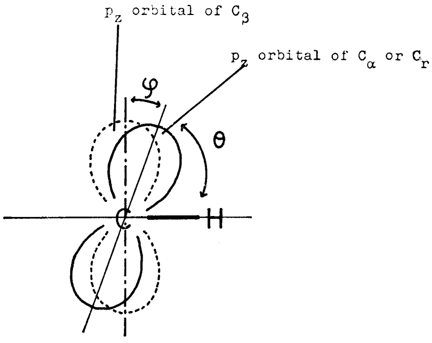


Fig. 7. Relation of the proton adjacent to C_β with *$2p_z\pi$-orbital* of C_α or C_γ.

In the ESR spectra of the allyl radical, Fessenden and Schuler[13] have observed three different hyperfine coupling constants due to protons, $A^H_\beta=4.06$ gauss, $A^H_{\alpha,\gamma}=13.93$ gauss, and $A^H_{\alpha,\gamma}=14.83$ gauss. One of them (A^H_β) is a hyperfine coupling constant of the proton adjacent to C_β; it is in satisfactory agreement with the predicted value,[14] on condition that the allyl radical has *sp^2 hybrid orbitals* where the configuration angle of C_α-C_β-C_γ is 120° and that the *$2p_z\pi$-orbitals* of each carbon situated in a C_α-C_β-C_γ plane are parallel. The substitution of phenyl groups for four hydrogen atoms attached to the end carbons, C_α and C_γ, which is the case with TPA, may affect the *$2p_z\pi$-orbital* configuration of the allyl group. The most probable situation is that the allyl group is twisted at an angle of φ, as in Fig. 6, because of the steric effect of the phenyl groups. Assuming this twisted model about the allyl group, the *$2p_z\pi$-orbitals* of C_α and C_γ will result in a nonzero spin density at the proton adjacent to C_β, as is shown in Fig. 7.

An interaction between the spin densities of C_α or C_γ and the proton adjacent to C_β can be described by the following relation[15]:

$$A'^H_\beta = (4+50\cos^2\theta)(\rho_{C\alpha}+\rho_{C\gamma}).$$

If the allyl group of TPA or BDA is twisted as in Fig. 6, the experimentally-obtained coupling constant of the proton adjacent to C_β can be estimated by

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11) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

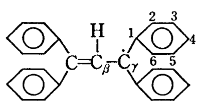
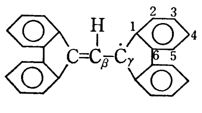
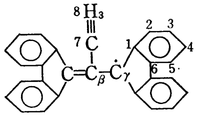
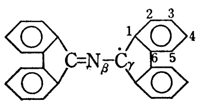
12) R. Lefebore, H. H. Dearman, and H. M. McConnell, *J. Chem. Phys.*, **32** 176 (1960).

13) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

14) H. M. McConnell, *ibid.*, **30**, 328 (1960).

15) C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960).

TABLE 4. OBSERVED AND CALCULATED COUPLING CONSTANTS

Compound		β	γ	1	2	3	4	5	6	7	8
	Observed	8.90			1.30	0.65	1.95	0.65	1.30		
	Odd. Alter.	0.74 −0.032	— +0.222	— −0.028	1.77 +0.077	0.64 −0.028	1.77 +0.077	0.64 −0.028	1.77 +0.077		
	McLachlan[a)]	1.45 −0.063	— +0.251	— −0.023	1.38 +0.060	0.53 −0.023	1.38 +0.060	0.53 −0.023	1.38 +0.060		
	Observed	13.4			1.99	0.46	1.99	—			
	Ref. 4	13.2			1.92	0.48	1.86	0.36			
	Ref. 6	13.2			1.89	0.42	1.89	0.06			
	McLachlan[b)]	2.16 −0.094	— +0.256	— −0.023	1.75 +0.076	0.35 −0.015	1.50 +0.065	0.14 −0.006	— +0.050		
	Ref. 4	1.12[c)]			1.76	0.44	1.64	0.33			
	McLachlan[b)]	2.18[d)] −0.087	— +0.260	— −0.025	1.77 +0.077	0.23 −0.010	1.50 +0.065	0.12 −0.005	+0.050	+0.001	−0.007
	Observed	3.38			1.69	0.30	1.69	0.14			
	McLachlan[b)]	4.20[e)] −0.103	— +0.254	— −0.025	1.75 +0.076	0.35 −0.015	1.50 +0.065	0.12 −0.005	+0.049		

Calculated coupling constants are obtained using the formula

$A^{H}_{CH}=Q^{H}_{CH}\cdot\rho_{Ci}$ $\quad Q^{H}_{CH}=-23.0$

a) Each phenyl group is rotated by 10° as that of triphenyl methyl and allyl group is also twisted by 28°.
b) Allyl group is twisted by 37°.
c) Methyl protons.
d) $A^{H}_{C\text{-}CH_3}=Q^{H}_{C\text{-}CH}\cdot\rho_{C\text{-}CH_3}$ $\quad Q^{H}_{C\text{-}CH_3}=+25.0$
e) $A^{N}=Q_1\cdot\rho_N+Q_2\cdot\sum\rho_{Ci}$ $\quad \rho_{Ci}$s are the spin densities of nuclei attached to the nitrogen. $Q_1=+30.9$, $Q_2=-2.$[19)]

the following equation:

$$Q^{\mathrm{H}}_{\mathrm{CH}}\cdot\rho_{\mathrm{C}\beta}+A'^{\mathrm{H}}_{\beta}$$

$$A^{\mathrm{H}}_{\beta}=Q^{\mathrm{H}}_{\mathrm{CH}}\cdot\rho_{\mathrm{C}\beta}+(4+50\cos^2\theta)(\rho_{\mathrm{C}\alpha}+\rho_{\gamma}).$$

In the case of TPA, using $\rho_{\mathrm{C}\alpha}=\rho_{\mathrm{C}\gamma}=+0.251$, $\rho_{\mathrm{C}\beta}=-0.063$, $Q^{\mathrm{CH}}_{\mathrm{H}}=-23.0$ gauss, and $\theta=62°$, A^{H}_{β} becomes 9.05 gauss. In other words, if the twisted angle is assumed to be 28°, A^{H}_{β} will become about 8.90 gauss, which is the most suitable value in this case. Similarly, the twisted angle is estimated to be 37° in the case of BDA. The twisted allyl model mentioned above can easily be applied to the other tetraphenylallyl-type radicals.

For the BDMA, the experimentally-measured hyperfine coupling constants of $A^{\mathrm{H}}_{\mathrm{CH_3}}$ are close to the theoretically calculated values, as is shown in Table 4. This fact can also be explained by this model, as is shown in Fig. 8, assuming $\rho_{\mathrm{C}\alpha}=\rho_{\mathrm{C}\gamma}=+0.260$, $\rho_{\mathrm{C}\beta}=-0.087$, $Q^{\mathrm{H}}_{\mathrm{C\text{-}CH_3}}=+25.0$ gauss, and $Q^{\mathrm{H}}_{\mathrm{C\text{-}C(CH_3)}}=0.85$ gauss;[16] thence, $A^{\mathrm{H}}_{\mathrm{CH_3}}$ becomes 2.62 gauss or 1.74 gauss.[17] Hence, the protons of the methyl group adjacent to C_β are considerably far apart from C_α or C_γ compared with the proton attached directly to C_β. Consequently, the contribution of $\rho_{\mathrm{C}\alpha}$ or $\rho_{\mathrm{C}\gamma}$ to the spin density on the methyl proton is negligibly small. On the other hand, the nitrogen nucleus of BDAA is placed at a nodal plane of the $2p_z\pi$*-orbital* of C_α or C_γ. Therefore, the hyperfine coupling constants of nitrogen (A^{N}_{β}) will not be affected directly by the spin density on C_α or C_γ.

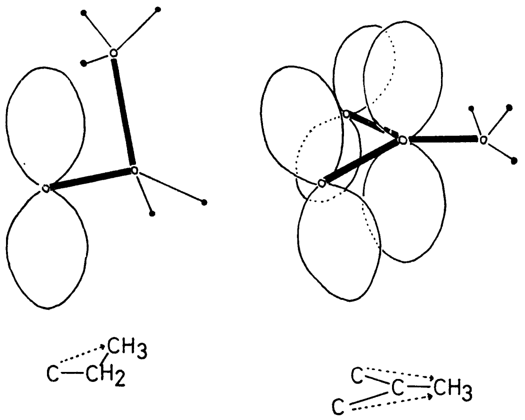


Fig. 8. Twisted allyl model for BDMA.

In addition, the temperature dependence of the coupling constant (A^{H}_{β}) of TPA can also be explained as follows: at high temperatures a vigorous wagging of the allyl group of the TPA molecule will cause the $2p_z\pi$*-orbitals* of C_α and C_γ to come nearer to the proton adjacent to C_β; thence, A^{H}_{β} will become larger, while, at low temperatures, the situation will be reversed.

In order to interpret magnitude of the C_β-proton splitting, a torsion of the phenyl rings from the molecular plane was taken into account at first. However, the spin density of C_β was, at most, the same as that of the allyl radical (the hyperfine coupling constant of the proton adjacent to C_β is only 4.06 gauss[13]). The observation of unusually large splitting of the C_β-proton in TPA or BDA can not be interpreted by means of this mechanism. The other possible explanation is that the configuration angle of C_α–C_β–C_γ is larger than a normal configuration angle of 120° because of the repulsive interaction of phenyl or biphenylene groups. Fraenkel calculated the variation in $Q^{\mathrm{H}}_{\mathrm{CH}}$ with the bond angle, taking into account the σ-π interaction of the C–H bond.[18] In view of his calculations, the configuration angle of C_α–C_β–C_γ in tetraphenylallyl-type radicals must be smaller than 120°, but this is not plausible in view of the structures of tetraphenylallyl-type radicals.

Conclusion

The abnormal hyperfine coupling constants that have been observed in TPA and BDA could be explained very well, using the method of anisotropic hyperfine interaction. Therefore, in view of the ESR spectra series of these tetraphenylallyl-type radicals, those spectra can be understood by introducing the idea of the twisted allyl model.

The authors wish to thank Professor Kazuhiko Ishizu for his helpful discussion and Mr. Hideo Hasegawa and Mr. Koichi Kubo for the treatment using the ESR spectrum simulator.

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16) K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi, and H. Takaki, *This Bulletin*, **40**, 2731 (1967).

17) $A^{\mathrm{H}}_{\mathrm{C\text{-}CH_3}}=Q^{\mathrm{H}}_{\mathrm{C\text{-}CH_3}}\cdot\rho_{\mathrm{C}\beta}+Q^{\mathrm{H}}_{\mathrm{C\text{-}C(CH_3)_3}}(\rho_{\mathrm{C}\alpha}+\rho_{\mathrm{C}\gamma})$ The sign of $Q^{\mathrm{H}}_{\mathrm{C\text{-}C(CH_3)_3}}$ has not been defined. If the signs of $Q^{\mathrm{H}}_{\mathrm{C\text{-}CH_3}}$ and $Q^{\mathrm{H}}_{\mathrm{C\text{-}C(CH_3)_3}}$ are identical, $A^{\mathrm{H}}_{\mathrm{C\text{-}CH_3}}$ will be 2.62 gauss; if the signs are the opposite, $A^{\mathrm{H}}_{\mathrm{C\text{-}CH_3}}$ will be 1.74 gauss.

18) K. Fraenkel, *J. Chem. Phys.*, **37**, 1489 (1962).

19) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).