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# Electron Spin-Spin Interaction and Methylene Bond Angles in the Quintet Ground State of *m*-Phenylene-dimethylene Radicals

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The effect of the methylene bond angles on the electron spin-spin interaction has been semi-empirically investigated for the quintet ground states of the *m*-phenylene-dimethylene radicals, especially *m*-phenylene-bismethylene and *m*-phenylene-bisphenylmethylene. The $D$ and $E$ values calculated are compared with those observed, and the most probable structure, with a methylene bond angle near 140°, is estimated, as in the phenylmethylene radical.

Previously, the effect of the bond angle in the electron spin-spin interaction was semi-quantitatively investigated for the mono-methylene derivatives, especially the methylene and phenylmethylene radicals.[1] For these radicals, the spin Hamiltonian in the absence of the external magnetic field is expressed as:

$$\mathscr{H} = D\left[S_z^2-\frac{1}{3}S(S+1)\right] + E[S_x^2-S_y^2]. \tag{1}$$

In these derivatives, the value of $|E|/|D|$ can be used to determine the angle of the bent methylene carbon (–C–) bond by comparing the observed value with that calculated according to the following formulae:

$$D = \left(\frac{3e^2\hbar^2}{4m^2c^2}\right)\frac{2!(2S-2)!}{(2S)!}\sum_{i,j}\left\langle \phi_i(1)\phi_j(2)-\phi_j(1)\phi_i(2) \right. \times \left| \frac{r_{12}^2-3z_{12}^2}{r_{12}^5} \right| \left. \phi_i(1)\phi_j(2) \right\rangle \tag{2}$$

and:

$$E = \left(\frac{3e^2\hbar^2}{4m^2c^2}\right)\frac{2!(2S-2)!}{(2S)!}\sum_{i,j}\left\langle \phi_i(1)\phi_j(2)-\phi_j(1)\phi_i(2) \right. \times \left| \frac{y_{12}^2-x_{12}^2}{r_{12}^5} \right| \left. \phi_i(1)\phi_j(2) \right\rangle \tag{3}$$

where the $\phi_i$'s are the unpaired orbitals. This approach is possible because of the facts that the $\sigma$-electron spin density is fairly close to unity at the –C– atom and the $\pi$-electron spin distribution is insensitive to the change in the –C– bond angle. As a result, the ratio of $|E|/|D|$ is mainly determined by the *s-p* hybridization of the unpaired $\sigma$ orbital at the –C– atom. In these circumstances, the observed value of $|E|/|D|$ in phenyl derivatives can be explained by a –C– bond angle near 145°.[2]

Recently, electron spin resonance (ESR) absorption by quintet ground states of organic radicals has been reported for *m*-phenylene-bisphenylmethylene [$m$-$C_6H_4(CC_6H_5)_2$] in single crystals of benzophenone by Itoh[3] [$D/hc = \pm 0.07137\ \mathrm{cm}^{-1}$, $E/hc = \pm 0.01963\ \mathrm{cm}^{-1}$],[4] and for *m*-phenylene-bis-

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[1] J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963).

[2] J. Higuchi, to be published.

[3] K. Itoh, *Chem. Phys. Lett.*, **1**, 235 (1967).

[4] K. Itoh, private communications.

methylene [$m$-$C_6H_4(CH)_2$] [$|D|/hc=0.0844$ cm$^{-1}$, $|E|/hc=0.0233$cm$^{-1}$], $m$-phenylene-bisphenylmethylene [$|D|/hc=0.0701$ cm$^{-1}$, $|E|/hc=0.020$ cm$^{-1}$], and $m$-phenylene-dinitrene [$m$-$C_6H_4N_2$] [$|D|/hc=0.156$ cm$^{-1}$, $|E|/hc=0.029$ cm$^{-1}$] in rigid solvents by Wasserman, Murray, Yager, Trozzolo, and Smolinsky.[5] These reports are the first demonstrations of quintet states in organic radicals. Although the possibility of higher molecular spin multiplets has already been discussed for these molecular species,[6-8] and the $D$ and $E$ values theoretically calculated by assuming the linear –C– bonds,[6,7] the effect of the bent –C– bonds has not yet been treated. In the present work, therefore, such an effect will be discussed for dimethylene derivatives with a quintet ground state, especially for $m$-$C_6H_4(CH)_2$ and $m$-$C_6H_4(CC_6H_5)_2$, the observed $|E|/|D|$ values of which are 0.276 and 0.275, respectively.

The treatment adopted here is just the same as in the previous papers.[1,6,7] That is, the one-center integrals were those calculated from the self-consistent field (SCF) atomic orbitals (AO's) of the carbon atom (the $^1D$ state) expanded by Löwdin.[9] The two-center integrals were approximately evaluated as follows: the $2s$ electron was replaced by a unit point charge at the nucleus, the $2p$ electron was two half-unit point charges located to give the same quadrupole moment, and the atomic dipole effect was added as a positive and a negative charge of

$$\int_0^\infty r^2 dr \int_0^{\pi/2} \sin\theta d\theta \int_0^{2\pi} \chi_{2s}\chi_{2p\sigma} d\phi$$

located to fit the atomic dipole moment. All the methylene bonds were assumed to be coplanar with the central phenylene group. All the C–C distances were taken as 1.393 Å as in the benzene molecule,[10] and the simple LCAO-MO's were used for the $\pi$-orbitals. The unpaired $\sigma$ orbitals were assumed to be hybridized ones located at each –C– atom and directed along the bisector of the –C– bond angle. For the sake of simplicity, configuration interaction was disregarded.

## Calculation and Results

In addition to the most important contribution of the $n$-$\pi$ ($\sigma$-$\pi$) type, the spin-spin interaction in the $m$-phenylene-dimethylene radicals includes the $\pi$-$\pi$ and the $n$-$n$ types,[7] since the two $\sigma$ and two $\pi$ orbitals are occupied by unpaired electrons. As has previously been shown,[7] these two interactions should not be negligibly small compared with the $n$-$\pi$ type and should be included in any semi-quantitative discussion of the zero-field splittings of these radicals. In the present paper, therefore, the $D$ and $E$ values [*cf.* Eqs. (2) and (3)] in $m$-$C_6H_4(CH)_2$ and $m$-$C_6H_4(CC_6H_5)_2$ radicals were calculated by including all the types of interaction. The coordinate system and the –C– bond angles were taken as shown in Fig. 1.

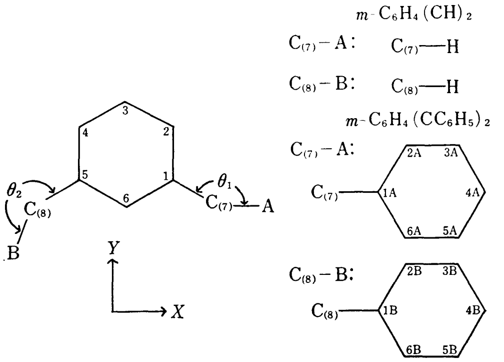

Fig. 1. Coordinate system (right-handed system) and the –C– bond angles in $m$-$C_6H_4(CX)_2$.

In the first instance, the $m$-$C_6H_4(CH)_2$ was taken as the simplest example of the ground-state quintet radicals on the assumption of the planar structure. The unpaired orbitals used were as follows:

$$\phi_1 = A_1\left[\chi_{2s7}\cot\frac{\theta_1}{2} + \left(1-\cot^2\frac{\theta_1}{2}\right)^{1/2} \times\left\{\chi_{2px7}\sin\left(\frac{\pi}{3}-\frac{\theta_1}{2}\right) - \chi_{2py7}\cos\left(\frac{\pi}{3}-\frac{\theta_1}{2}\right)\right\}\right] \tag{4}$$

$$\phi_2 = A_2\left[\chi_{2s8}\cot\frac{\theta_2}{2} - \left(1-\cot^2\frac{\theta_2}{2}\right)^{1/2} \times\left\{\chi_{2px8}\sin\left(\frac{\pi}{3}-\frac{\theta_2}{2}\right) + \chi_{2py8}\cos\left(\frac{\pi}{3}-\frac{\theta_2}{2}\right)\right\}\right] \tag{5}$$

$$\phi_3 = (3)^{-1/2}[-\chi_{2pz2}+\chi_{2pz7}+\chi_{2pz8}] \tag{6}$$

$$\phi_4 = (2)^{-1}[\chi_{2pz4}-\chi_{2pz6}+\chi_{2pz7}-\chi_{2pz8}] \tag{7}$$

where

$$A_i = \begin{cases} +1 \left(\frac{\pi}{2}<\theta_i<\pi\right) \\ -1 \left(\pi<\theta_i<\frac{3}{2}\pi\right) \end{cases} \quad (i=1, 2). \tag{8}$$

The $s$-$p$ hybridization in the $\phi_1$ and $\phi_2$ orbitals is determined by the –C– bond angles of $\theta_1$ and $\theta_2$, respectively, on the assumption that each bonding orbital of the –C– atom is equivalent and is directed along each bond. In the case of $\theta_1=\theta_2$, that is, when the radical belongs to the molecular symmetry of $C_{2v}$, the $D$ and $E$ values shown in Fig. 2 are

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[5] E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo and G. Smolinsky, *J. Amer. Chem. Soc.*, **89**, 5076 (1967).

[6] J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963).

[7] J. Higuchi, *ibid.*, **39**, 1847 (1963).

[8] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager and E. Wasserman, *J. Amer. Chem. Soc.*, **85**, 2526 (1963).

[9] P.-O. Löwdin, *Phys. Rev.*, **90**, 120 (1953).

[10] I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

obtained. A similar calculation was carried out on the assumption that $\theta_1+\theta_2=360°$, that is, when the $-C_{(8)}-H_{(8)}$ coincides with the $-C_{(7)}-H_{(7)}$ by the rotation of 120° about the center of the phenylene ring. The results thus obtained are shown in Fig. 3. The other configurations are less probable in view of the equivalence in the methylene bonds. The ratio of $E/D$ thus obtained is shown in Figs. 4 and 5, corresponding to the cases of $\theta_1=\theta_2$ and $\theta_1+\theta_2=360°$, respectively. As the observed value of $|E|/|D|$ is 0.276, one finds eight probable sets of the -C- bond angles, $\theta_1$ and $\theta_2$, where the calculated ratio coincides with the observed ratio, as given in Table 1.

Next, the $m$-$C_6H_4(CC_6H_5)_2$ radical was treated because it is the only species thus far observed in

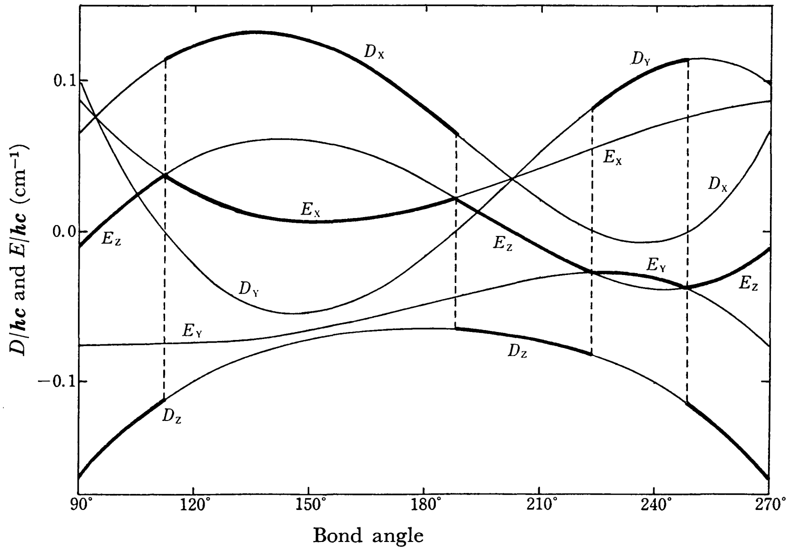

Fig. 2. $D$ and $E$ values of $m$-$C_6H_4(CH)_2$ in the case of $\theta_1=\theta_2$ (bold lines). The inferior letters, $X$, $Y$, and $Z$, on $D$ and $E$ imply that the set of axes $(x, y, z)$ in Eqs. (2) and (3) should be taken the sets of directions, respectively, $(Y, Z, X)$, $(Z, X, Y)$, and $(X, Y, Z)$ shown in Fig. 1.

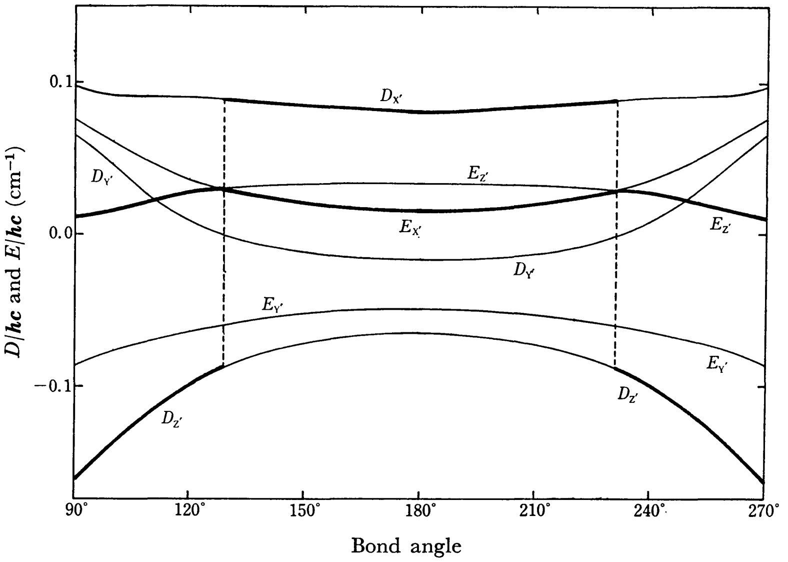

Fig. 3. $D$ and $E$ values of $m$-$C_6H_4(CH)_2$ in the case of $\theta_1+\theta_2=360°$ (bold lines). The inferior letters, $X'$, $Y'$, and $Z'$, on $D$ and $E$ imply that the set of axes $(x, y, z)$ in Eqs. (2) and (3) are close to the sets of directions, respectively, $(Y, Z, X)$, $(Z, X, Y)$, and $(X, Y, Z)$ shown in Fig. 1. In this case, the deviations of the latter directions from the former axes are seen in the text.

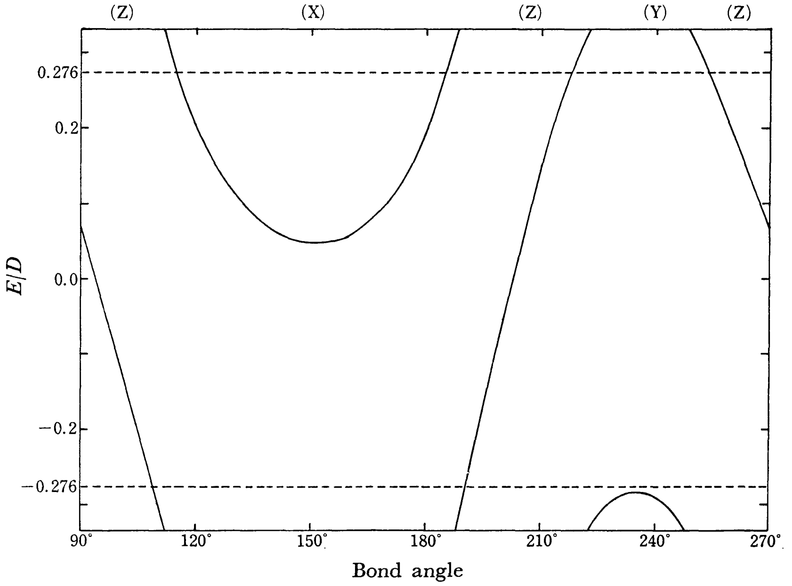

Fig. 4. The ratio of $E/D$ of $m$-$C_6H_4(CH)_2$ in the case of $\theta_1=\theta_2$. The letters on the top of the figure indicate the directions of the $z$ axis of the fine-structure tensor.

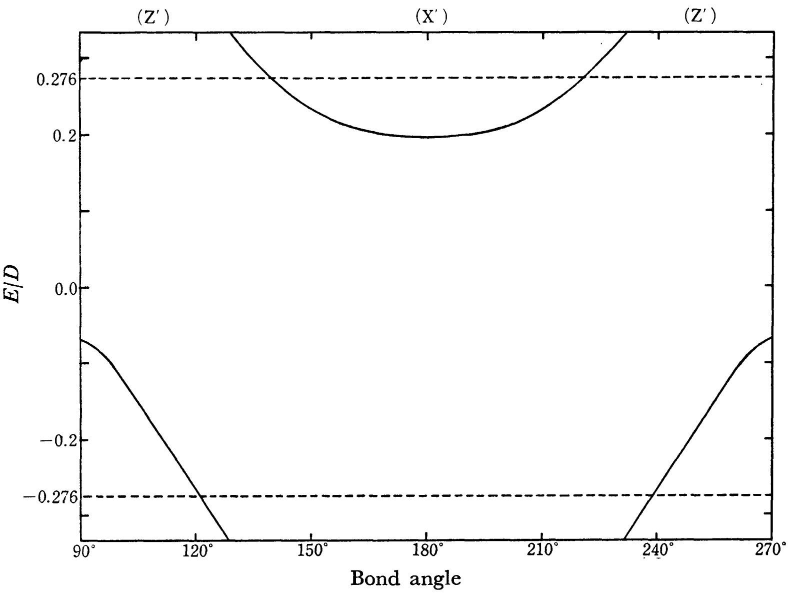

Fig. 5. The ratio of $E/D$ of $m$-$C_6H_4(CH)_2$ in the case of $\theta_1+\theta_2=360°$. The letters on the top of the figure indicates the approximate directions of the $z$ axis of the fine-structure tensor.

a single crystal. In this case, both the side phenyl groups were assumed to be either coplanar with, or perpendicular to, the central phenylene group. In the coplanar case, the treatment adopted was just the same as in the case of $m$-$C_6H_4(CH)_2$ except that the $\pi$ orbitals used were as follows:

$$\phi_3^c = (18)^{-1/2}[-2\chi_{2pz2}+2\chi_{2pz7}+2\chi_{2pz8} -\chi_{2pz2A}+\chi_{2pz4A}-\chi_{2pz6A}-\chi_{2pz2B}+\chi_{2pz4B}-\chi_{2pz6B}] \tag{9}$$

and:

$$\phi_4^c = (22)^{-1/2}[2\chi_{2pz4}-2\chi_{2pz6}+2\chi_{2pz7}-2\chi_{2pz8} -\chi_{2pz2A}+\chi_{2pz4A}-\chi_{2pz6A}+\chi_{2pz2B}-\chi_{2pz4B}+\chi_{2pz6B}]. \tag{10}$$

In the perpendicular case, the following assumption was made: the unpaired orbitals parallel to the phenylene group are given by simple LCAO forms which are constructed from the zero-energy $\pi$-orbital of phenylmethylene and the *s-p* hybridized orbital of the methylene carbon so as to give the –C– bond angle in question as follows:

$$\phi_3^{\mathrm{p}} = \left(7+\cot^2\frac{\theta_1}{2}\right)^{-1/2}\Bigg[2\left(1+\cot^2\frac{\theta_1}{2}\right)^{1/2}\phi_1 + A_1\left(1-\cot^2\frac{\theta_1}{2}\right)^{1/2}\Big\{(\chi_{2px2\mathrm{A}}-\chi_{2px4\mathrm{A}}+\chi_{2px6\mathrm{A}}) \times \sin\left(\frac{5}{6}\pi-\theta_1\right) - (\chi_{2py2\mathrm{A}}-\chi_{2py4\mathrm{A}}+\chi_{2py6\mathrm{A}}) \times \cos\left(\frac{5}{6}\pi-\theta_1\right)\Big\}\Bigg] \tag{11}$$

and:

$$\phi_3^{\mathrm{p}} = \left(7+\cot^2\frac{\theta_2}{2}\right)^{-1/2}\Bigg[2\left(1+\cot^2\frac{\theta_2}{2}\right)^{1/2}\phi_2 - A_2\left(1-\cot^2\frac{\theta_2}{2}\right)^{1/2}\Big\{(\chi_{2px2\mathrm{B}}-\chi_{2px4\mathrm{B}}+\chi_{2px6\mathrm{B}}) \times \sin\left(\frac{5}{6}\pi-\theta_2\right) + (\chi_{2py2\mathrm{B}}-\chi_{2py4\mathrm{B}}+\chi_{2py6\mathrm{B}}) \times \cos\left(\frac{5}{6}\pi-\theta_2\right)\Big\}\Bigg] \tag{12}$$

The calculation was performed in the two cases of the –C– bond angle of $\theta_1=\theta_2$ and $\theta_1+\theta_2=360°$, as in the $m$-$C_6H_4(CH)_2$ radical. The results thus obtained are quite similar to that obtained in the case of $m$-$C_6H_4(CH)_2$ shown in Figs. 4 and 5, and no significant differences can be found among these relative relationships. In each case, there are five sets of the –C– bond angles ($\theta_1$ and $\theta_2$), where the $|E|/|D|$ ratio calculated coincides with the observed value of 0.275 at larger –C– bond angles ($120° < \theta_1, \theta_2 < 240°$), as Table 1 shows.

For a structure with small –C– bond angles ($\theta_1, \theta_2 < 120°$, or $\theta_1, \theta_2 > 240°$), the ground state is not a quintet, since the orbitals,[11] $2^{-1/2}(\phi_1-\phi_2)$ and/or $2^{-1/2}(\phi_1+\phi_2)$, are doubly occupied because of the large energy difference between the $\phi_1$ (or $\phi_2$) and the $\phi_3$ (or $\phi_4$). As a result, such structures of these radicals, [I], [II], and [VI] in Table 1, are outside the scope of this discussion.

According to the recent experiment on $m$-$C_6H_4(CC_6H_5)_2$ by Itoh,[4] the radical was oriented as a substituent for the two nearest neighboring molecules in a single crystal of benzophenone.[12] Taking

TABLE 1. THE –C– BOND ANGLES WHERE $|E|/|D|$ COINCIDES WITH THE OBSERVED VALUE

| | | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|---|
| $m$-$C_6H_4(CH)_2$ | $\theta_1$ | 109° | 115° | 185° | 190° | 218° | 254° | 121° | 139° |
| | $\theta_2$ | 109° | 115° | 185° | 190° | 218° | 254° | 239° | 221° |
| | Sign of $E/D$[c] | − | + | + | − | + | + | − | + |
| | Sign of $D$ | − | + | + | − | − | − | − | + |
| | $z$ axis of fine-structure tensor | $Z$ | $X$ | $X$ | $Z$ | $Z$ | $Z$ | $Z$[d] | 27.5° from $X$ |
| $m$-$C_6H_4(CC_6H_5)_2$ (coplanar)[a] | $\theta_1$ | | | 185° | 191° | 219° | | 122° | 140° |
| | $\theta_2$ | | | 185° | 191° | 219° | | 238° | 220° |
| | Sign of $E/D$[c] | | | + | − | + | | − | + |
| | Sign of $D$ | | | + | − | − | | − | + |
| | $z$ axis of fine-structure tensor | | | $X$ | $Z$ | $Z$ | | $Z$[e] | 26.1° from $X$ |
| $m$-$C_6H_4(CC_6H_5)_2$ (perpendicular)[b] | $\theta_1$ | 109° | 115° | 185° | 191° | 218° | 254° | 122° | 140° |
| | $\theta_2$ | 109° | 115° | 185° | 191° | 218° | 254° | 238° | 220° |
| | Sign of $E/D$[c] | − | + | + | − | + | + | − | + |
| | Sign of $D$ | − | + | + | − | − | − | − | + |
| | $z$ axis of fine-structure tensor | $Z$ | $X$ | $X$ | $Z$ | $Z$ | $Z$ | $Z$[f] | 26.2° from $X$ |

a) The planar configuration.
b) The configuration with the two side phenyl groups being prependicular to the central phenylene group.
c) The sign of $E/D$ is not always chosen under the condition of $|D_x|<|D_y|<|D_z|$.
d) The $x$ axis of the fine-structure tensor makes an angle of 38.8° with the $X$ axis in Fig. 1.
e) The $x$ axis of the fine-structure tensor makes an angle of 37.4° with the $X$ axis in Fig. 1.
f) The $x$ axis of the fine-structure tensor makes an angle of 37.7° with the $X$ axis in Fig. 1.

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[11] The forms of these orbitals are not exactly correct except for the case of $\theta_1=\theta_2$, but may approximately be plausible for the present purpose.

[12] The direction cosines of the $x$, $y$, $z$ axes of the fine-structure tensor in the benzophenone crystallographic system [E. B. Fleischer, N. Sung and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968).] are as follows:

| Fine-structure axis | Crystal axis | | |
|---|---|---|---|
| | $a$ | $b$ | $c$ |
| $x$ | −0.496 | 0.110 | 0.861 |
| $y$ | 0.358 | −0.878 | 0.317 |
| $z$ | 0.792 | 0.465 | 0.396 |

TABLE 2. CALCULATED VALUES OF $D/hc$ AND $E/hc$ FOR THE PERMISSIBLE STRUCTURES ($cm^{-1}$)

| | [III] | | [VIII] | | Experimental | |
|---|---|---|---|---|---|---|
| | $D/hc$ | $E/hc$ | $D/hc$ | $E/hc$ | $D/hc$ | $E/hc$ |
| $m$-$C_6H_4(CH)_2$ | 0.0713 | 0.0196 | 0.0876 | 0.0241 | 0.0844[c] | 0.0233[c] |
| $m$-$C_6H_4(CC_6H_5)_2$ (coplanar)[a] | 0.0440 | 0.0120 | 0.0548 | 0.0151 | 0.07137[d] | 0.01963[d] |
| $m$-$C_6H_4(CC_6H_5)_2$ (perpendicular)[b] | 0.0348 | 0.0093 | 0.0493 | 0.0136 | | |

a) The planar configuration.
b) The configuration with the two side phenyl groups being perpendicular to the central phenylene group.
c) Ref. 5. d) Ref. 4.

the orientation into consideration, the $z$ axis of the fine-structure tensor does not appear to make a large angle (possibly within 30°) with the line $C_{(8)}$–$C_{(7)}$ (the $X$ axis in Fig. 1). The experimental value of $E/D$ is positive if the principal axes are chosen under the condition of $|D_x|<|D_y|<|D_z|$, as is usually done. These results appear to favor the cases [III] and [VIII] in Table 1. In these cases, the $x$ axis of the fine-structure tensor lies close to the plane of the central phenylene group. It may be noted that these results show that the phenylene group of the radical may be oriented rather perpendicularly to the *ab* plane in the benzophenone single crystal.

Although the phenyl group is substituted for the hydrogen atom, the electronic property of the methylene bond is not significantly changed, and the relative angular dependence of the $D$ and $E$ is quite similar to that of the phenyl derivatives. As a result of this, one may reasonably assume that the directions of the principal axes of the fine-structure tensor for $m$-$C_6H_4(CH)_2$ do not much deviate from those of $m$-$C_6H_4(CC_6H_5)_2$ with respect to the central phenylene group. In that case, the permissible –C– bond angles are also restricted within the cases of [III] and [VIII] in Table 1. For reference, the calculated values of $D$ and $E$ in $m$-$C_6H_4(CH)_2$ and $m$-$C_6H_4(CC_6H_5)_2$ with the probably structures, [III] and [VIII], are given in Table 2.

## Discussion

The present work includes several approximations, most of which are quite parallel to those of previous papers[1,6,7] and therefore need not be repeated here. As has been discussed already,[1] the approximations of the unpaired orbitals of $\phi_1$ and $\phi_2$, Eqs. (4) and (5), are not completely satisfactory, but they may be plausible for obtaining the trend of the $D$ and $E$ at larger –C– bond angles.[13] Although the unpaired orbitals of $\phi_1^p$ and $\phi_2^p$, Eqs. (11) and (12), were also obtained so as to give the –C– bond angle in question, the use of these orbitals corresponds to the treatment that disregards the energy difference between the $2p$ and the $s$-$p$ hybridized orbitals. In this case, the spin density at each –C– atom may be somewhat overestimated. However, the $E/D$ ratio may not be significantly changed because both the $D$ and $E$ values are approximately proportional to the spin density at the –C– atom. Consequently, the approximation of the unpaired orbitals, $\phi_1^p$ and $\phi_2^p$, may also be plausible in discussing the trend of the $E/D$ ratio at larger –C– bond angles.

The contribution of the spin-orbit interaction is important in discussing the exact values of $D$ and $E$.[14,15] Actually, the energy of this effect is predominatly due to the atomic term, while it is comparatively insensitive to the delocalization of unpaired electrons. In the case of the methylene radical, the $E/D$ ratio is scarcely change if the $D$ and $E$ values of the spin-orbit interaction calculated by Glarum[14] are added to those of the spin-spin interaction.[1,6] In view of these facts, the present results may still be valid in a semi-quantitative sense.

In the case of $\theta_1+\theta_2=360°$ ($\theta_1<\theta_2$), the directions of the principal axes of the fine-structure tensor do not always coincide with those of the coordinate axes shown in Fig. 1. That is, one of the former axes which is perpendicular to the phenylene group (the $y$ axis for $\theta_1 \geqq 129°$, or the

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13) As discussed in the previous paper (Ref. 1), the use of the hybridized orbital for the unpaired orbital (*e. g.* $\phi_1$ and $\phi_2$) is plausible, since the coefficients of the $2s$ and $2p$ orbitals are fairly close to those of the SCF-LCAO-MO of the $NH_2$ radical [J. Higuchi, *J. Chem. Phys.*, **24**, 535 (1956).] at larger bond angles. Recently, Hoffmann *et al.* [R. Hoffmann, G. D. Zeiss and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968)] showed that the contributions (gross atomic population) of the $2s$ and $2p$ orbitals are somewhat different from those of the extended Hückel orbital of the phenylmethylene radical. However, it may be too hasty to deny the validity of the present approximation from only such a calculation, since the extended Hückel orbitals depend markedly on the selection of the parameters used and are not the best approximation of the SCF-LCAO-MO's.

14) S. H. Glarum, *J. Chem. Phys.*, **39**, 3141 (1963). This is only one calculation of spin-orbit interaction which is available for knowing the effect of methylene bond angle.

15) S. J. Fogel and H. F. Hameka, *J. Chem. Phys.*, **42**, 132 (1965).

$z$ axis for $\theta_1 < 129°$) is actually parallel to the $Z$ axis of the latter system. However, the $z$ axis ($\theta_1 \geq 129°$) or the $x$ axis ($\theta_1 < 129°$) of the fine-structure tensor makes an angle of $90° - \theta_1/2$ counterclockwise with the line $C_{(8)}$–$C_{(7)}$ (the $X$ axis in Fig. 1), if only the $n$-$\pi$ interaction at each methylene carbon is taken into account. That is, the angle between the $X$ axis and the $z$ (or $x$) axis increases with decreasing the –C– bond angle. Actually, such an angle is rather large compared with that of the above one-center approximation, as can be seen in the last column [VIII] in Table 1. Apparently, this is due to the fact that other types of interaction occur in the ground-state quintet radicals.

There are many molecular species which are also expected to yield a multiplet ground state in ESR spectroscopy. Especially for the polyacene dimethylene derivatives, the $\pi$-electron distribution is fairly different from that of the present case and the spin densities at the two methylene carbons are not always equivalent. As a result, the angle between the $z$ axis of the fine-structure tensor and the line with the two methylene carbons may be changed somewhat as compared with the cases of the radicals treated here.

It may be noted that, in the case of $\theta_1 \not\doteq \theta_2$ and $\theta_1 + \theta_2 \not\doteq 360°$, there are other possible sets of –C– bond angles where the calculated ratio of $E/D$ coindcies with the observed value and where the $z$ axis of the fine-structure tensor does not make a large angle with the $X$ axis in Fig. 1. Such structures can be seen in configurations with intermediate –C– bond angles between the cases [III] and [VIII], such as $\theta_1 \simeq 160°$ and $\theta_2 \simeq 207°$. However, they may be less important for our present purposes except if a remarkable distortion of the radical in the host crystal were to occur.

The possible structure and the directions of the principal axes of the fine-structure tensor obtained in the present work do not always coincide with those estimated by Wasserman *et al.*[5] However, the details of their work are not clear in their report and comparison may be difficult because of their inclusion of some semi-empirical values.

For the triplet or quintet ground state of the methylene derivatives, the molecular structure has not been conclusively determined, since there seems to be no helpful experimental method except the magnetic resonance technique in the present situation. For the benzophenone molecule, the dihedral angle between the two phenyl groups is 56° in the single crystal.[16] This may suggest that the central phenylene group in $m$-$C_6H_4(CC_6H_5)_2$ makes some angles with the two planes of methylene bonds [$C_{(1)}$–$C_{(7)}$–$C_{(1A)}$ and $C_{(3)}$–$C_{(8)}$–$C_{(1B)}$] and also the $z$ axis of the fine-structure tensor. The calculation of the diphenylmethylene[2] showed that the $E/D$ value was almost insensitive to the change in the dihedral angle between the two phenyl groups, although it is concerned with only the small contribution of the interatomic spin-spin interaction. If only the $n$-$\pi$ interaction at each methylene carbon is taken into account, the $E/D$ ratio in $m$-$C_6H_4$-$(CC_6H_5)_2$ is changed with an increase in the dihedral angle between the central phenylene and the two planes of the methylene bonds. For the permissible structures given in Table 2, however, the deviation from the planar configuration is small at the above dihedral angles between 0° and 30°.[17] Accordingly, the results obtained for the structures with coplanar –C– bonds may still be useful in discussing the –C– bond angle semi-quantitatively.

If the absolute sign of the $D$ were to be determined by an experiment at a low temperature, one could still not choose between the cases [III] and [VIII] by the present procedure alone, since both the $D$ values calculated are positive. However, it may be possible to obtain some information on the –C– bond angles if the $^{13}C$ hyperfine splittings of the methylene carbons are obtained. On the other hand, it might also be possible to estimate the probable structure if a detailed calculation of the electronic structure is carried out. Under these circumstances, the following speculation is possible. On the assumption that the –C– bond angles are not very different from the calculated value (146°) of the phenylmethylene,[2] the case [VIII] might be the more probable,[18] although there is still a possibility of the structure [III]. At any rate, the present procedure may, in general, be useful not only for obtaining information on the molecular structures of fairly large radicals with a multiplet ground state, especially their methylene bond angles, but also in estimating their orientation in the host single crystal when that cannot be determined experimentally.

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16) E. B. Fleischer, N. Sung and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968).

17) In the benzophenone molecule, the dihedral angle between the plane of carbonyl bond [C–(C=O)–C] and the phenyl group is 30° and the above C–C–C bond angle is 122° (Ref. 16). As a result, the dihedral angle in the methylene derivatives is expected to be rather smaller than 30° because of the –C– bond angle larger than 122°.

18) A preliminary experimental result of 1,3,5-$C_6H_3$-$(CC_6H_5)_3$ radical by Itoh [private communication] is also favorable to the present assumption.