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Electron Spin-Spin Interaction in the Multiplet Ground State of Non-planar Methylene Derivatives

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The effect of deviation from the planar structure in electron spin-spin interaction has been semiempirically investigated for spin multiplet ground state of radicals with methylene bonds. If these bonds are not coplanar, a significant influence occasionally appears on the values of D and E, while the influence is very small if the relative orientation among the methylene bonds still does not change.

In previous papers,[1-3] the electron spin-spin interaction of the methylene derivatives was investigated by assuming coplanar methylene bonds with the central benzene ring. From the non-planar structure of the benzophenone molecule (the dihedral angle between the plane of the carbonyl bond [C–(C=O)–C] and that of the phenyl group (α) is 30°, and the bond angle at the carbonyl carbon atom (θ) is 122°),[4] the above assumption does not seem always adequate for higher molecular spin multiplet radicals with several phenyl groups. In the present paper, a semi-quantitative study will be reported on the relation between the electron spin-spin interaction and the molecular structure, especially concerning the influence on the deviation from the planar structure.

The ratio of E/D is used for a measure which can be compared with the observed value, since this ratio may be largely affected by the molecular structure but subject to minor influence on the spin density at the methylene carbon –C–. The values of D and E were evaluated according to the formulas

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

and

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

where ϕ_i's are the unpaired orbitals. Details of the

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[1] J. Higuchi, *J. Chem. Phys.*, **38**, 1237; **39**, 1847 (1963).

[2] J. Higuchi, *ibid.*, **39**, 1339 (1963). The revised result is given in Appendix of the present paper.

[3] J. Higuchi, This Bulletin, **43**, 3773 (1970).

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

calculation are the same as those in previous papers.[5]

Radicals with Only One Methylene Bond

Diphenylmethylene $(C_6H_5)_2C$ is taken as the simplest example of non-planar triplet radicals with only one methylene bond assuming the symmetry of C_2. In this case, the unpaired orbitals may be expressed as

$$\phi_1 = (4-6\sin^2\alpha\cos\theta)^{-1/2}[2\chi_{l0}-\sin\alpha\,(-\cos\theta)^{1/2} \times(\chi_2-\chi_4+\chi_6-\chi_{2'}+\chi_{4'}-\chi_{6'})] \tag{3}$$

and

$$\phi_2 = (4+6\cos^2\alpha)^{-1/2} \times[2\chi_{\pi 0}-\cos\alpha(\chi_2-\chi_4+\chi_6+\chi_{2'}-\chi_{4'}+\chi_{6'})]. \tag{4}$$

Here, θ and α are, respectively, the –C– bond angle and the dihedral angle between the plane of the –C– bond and that of the phenyl group, χ_{l0} is the *s*–*p* hybridized orbital of the –C– atom (0):

$$\chi_{l0} = [(1+\cos\theta)/(1-\cos\theta)]^{1/2}\chi_{2s0} + [-2\cos\theta/(1-\cos\theta)]^{1/2}\chi_{2px0} \tag{5}$$

(x is the symmetry axis of the molecule),

$\chi_{\pi 0}$ is the p orbital of the –C– atom which is perpendicular to the –C– bond plane, and χ_i's $(i\neq 0)$ are the p orbitals of atom C_i's which are perpendicular to the phenyl plane concerned.

Figure 1 shows the calculated D and E values of diphenylmethylene as a function of the –C– bond angle (θ) assuming the planar structure ($\alpha=0°$) and the structure with the two phenyl groups to be perpendicular to the plane of the –C– bond ($\alpha=90°$). Similar calculations were carried out at various dihedral angles of α. The deviation of D and E values from those of the planar structure with the same –C– angle is fairly small at angles of α within 60°. In these calculations, we obtain various sets of angles, θ and α, where the ratio of E/D coincides with the observed value of 0.04735 [$D/hc=\pm 0.40505\ \text{cm}^{-1}$, $E/hc=\pm 0.01918\ \text{cm}^{-1}$][6] as shown in Fig. 2. As a result, the probable –C– bond angles are found over a range between 144° and 150°. It should be noted here that the electron spin resonance experiment of diphenylmethylene by Brandon *et al.*[6] was carried out using a host crystal of benzophenone molecule. From the dihedral angle of $\alpha=30°$ in the host molecule with $\theta=122°$, the value of α in the diphenylmethylene might be slightly smaller than 30°, since the steric hindrance is expected to be smaller than that of the benzophenone because of its larger θ value. In view of these facts, the most probable –C– bond angle can be estimated to be 145°±1° as in the phenylmethylene (see Appendix). In this case, the influence of non-planar structure does not appear remarkably, although the D and E values increase with increasing dihedral angle of α. This is apparently due to the fact that the terms with α almost cancel each other in the ratio of E/D, since the atomic contribution in D is approximatley proportional to that of E. Similarly, the influence of non-planar structure on the ratio of E/D is expected to be very small for other triplet radicals with only one methylene bond, because of the slight change of their atomic term which has a large contribution to the energy. This is similar to the case of *m*-phenylene-*bis*-phenylmethylene where the change in the orientation of only the side phenyl groups does not significantly affect the relative values of D and E[3].

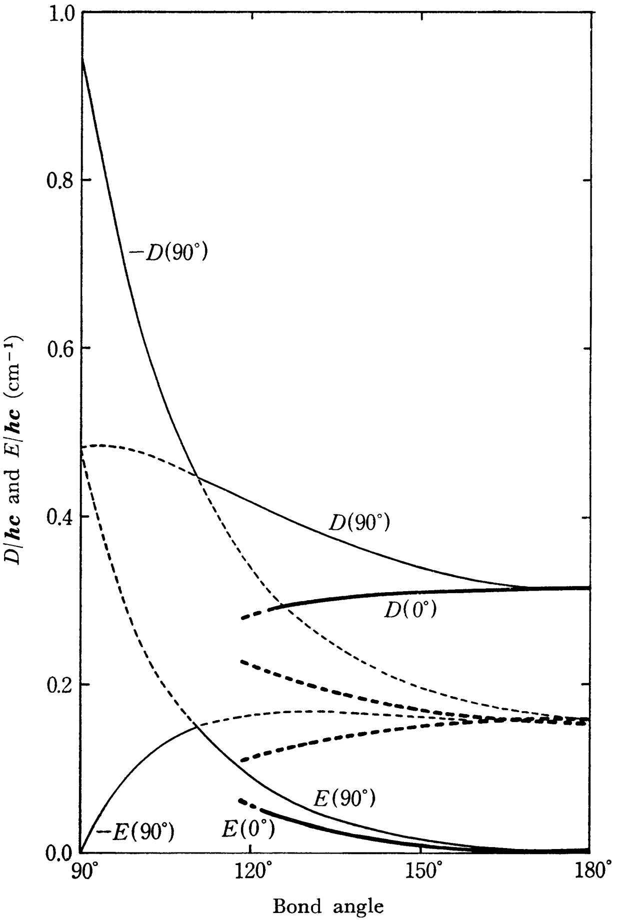

Fig. 1. D and E values of diphenylmethylene with planar structure ($\alpha=0°$) (bold lines) and that with the two phenyl groups perpendicular to the plane of the –C– bond ($\alpha=90°$) (fine lines). For large (small) –C– bond angles, the principal axes of fine-structure tensor [or Eqs. (1) and (2)] are as follows: the x axis is the symmetry axis of the molecule, the y (z) axis is perpendicular to the plane of the –C– bond, and the z (y) axis is perpendicular to the other axis. Fine dotted lines are the extensions in the case of $\alpha=90°$. Bold dotted lines correspond to the case where the z axis in Eq. (1) is taken to be perpendicular to the molecular plane ($\alpha=0°$).

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[5] The one-center integrals were those calculated from the self-consistent field atomic orbitals. The two-center integrals were approximately evaluated as follows: the 2*s* electron was replaced by a unit point charge at the nucleus, the 2*p* electron was two half-unit charges located to give the same quadrupole moment, and the atomic dipole effect was added. All the C–C distances were taken to be 1.393 Å as in benzene molecule. Simple LCAO-MO's were used for the π-orbitals. The unpaired σ 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. [Refs. 2 and 3].

[6] R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *J. Chem. Phys.*, **43**, 2006 (1965). The x and the y axes of this paper correspond to, respectively, the y and the x axes of the present work.

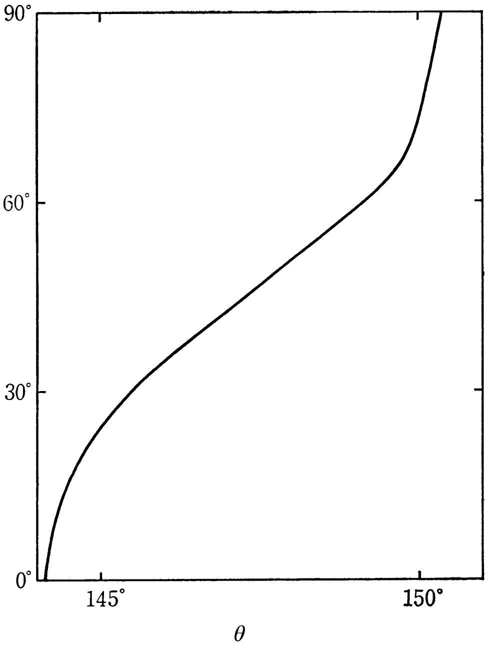

Fig. 2. The -C- bond angle (θ) and the dihedral angle between the plane of the -C- bond and that of the phenyl groups (α) in the diphenylmethylene with the structure where E/D coincides with the experimental value.

Radicals with Several Methylene Bonds

For spin multiplet radicals with more than one methylene bond such as *m*-phenylene-dimethylene, the approximation of the planar structure might not always be adequate for discussing the spin-spin interaction, since the relative orientation of these bonds is expected to have a great influence on the ratio of E/D. In the spin quintet radicals with coplanar methylene bonds, the bond angular dependence of D and E does not differ much between the calculation with all the spin-spin interactions and that with only the atomic contribution.[7] This means that approximation without interatomic interactions might be used for knowing the general tendency of *m*-phenylene-dimethylene radicals, because the main contribution of the D and the E values is due to the atomic term. In view of these facts, a simplified calculation of the D and the E values for only the atomic contribution is carried out by changing dihedral angles between the plane of the central phenylene group and that of each side methylene bond. Hereafter, such angles are denoted by α_1 and α_2, corresponding to the methylene bond with C_7 and that with C_8, respectively. (Fig. 3).

The result obtained for *m*-phenylene-dimethylene shows that the relative orientation of two methylene bonds has a significant influence on the D and E values. In some sets of the –C– bond angles, all the possible values of $|E|/|D|$ appear by changing α_1 and α_2 [*e.g.* in the case of $\theta_1=\theta_2=210°$, the $|E|/|D|$ changes from 0 to 1/3 by varying α_i ($\alpha_1=\alpha_2$) from 0° to 60°]. In such cases, one cannot estimate the –C– bond angles from only the absolute value of E/D, although the possibility of α_i values larger than 45° may be very small. On the other hand, it is not always very easy to calculate the D and E values which can be compared with the experimental values in a quantitative sense. A similar result is obtained for the septet ground state of 1,3,5-$C_6H_3(CX)_3$ without a C_3 axis.

As an example, Figs. 4 and 5 show the ratio of $|E|/|D|$ thus obtained for *m*-phenylene-dimethylene at the dihedral angles of $\alpha_1=30°$ and $\alpha_2=\pm 30°$ in the cases of $\theta_1=\theta_2$ and $\theta_1+\theta_2=360°$, respectively. Such dihedral angles might have probable values when the host crystal used is the benzophenone (with $\alpha=30°$). We see that the uncertainty of the –C– bond angles due to the change of $\Delta\alpha_i=\pm 30°$ is larger than 10° for some values of E/D. For *m*-phenylene-*bis*-phenylmethylene and *m*-phenylene-*bis*-methylene, however, the direction of principal axes in the fine-structure tensor [or those in Eqs. (1) and (2)] differ from those of the cases where all the possible values

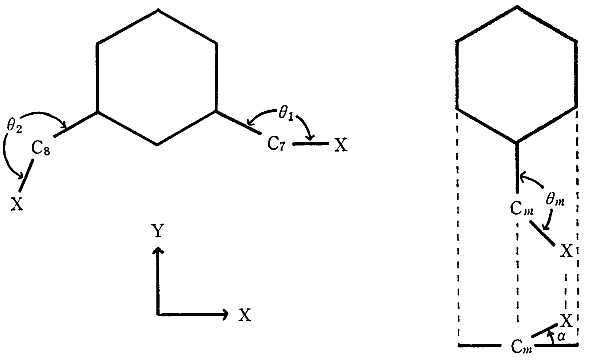

Fig. 3. Coordinate system (right-handed system), the methylene bond angles (θ_i's), and the dihedral angles between the central phenylene group and that of a side methylene bond (α_i's) in m-$C_6H_4(CX)_2$.

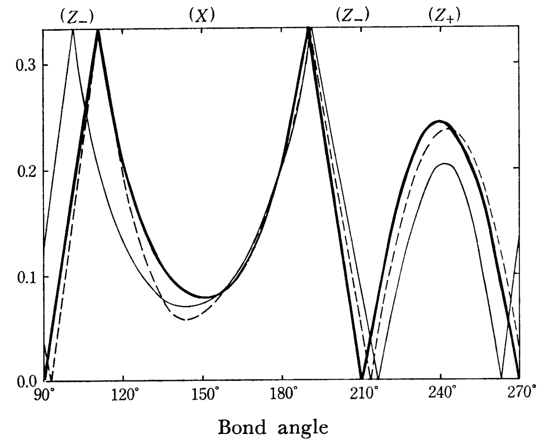

Fig. 4. The ratio of E/D of m-$C_6H_4(CX)_2$ calculated with only the intratomic interaction with $\theta_1=\theta_2$ in the cases of $\alpha_1=\alpha_2=0°$ (bold full line), $\alpha_1=\alpha_2=30°$ (fine full line), and $\alpha_1=-\alpha_2=30°$ (fine broken line). The letters X, Z_+, and Z_- on the top of the figure imply that the set of axes (x, y, z) in Eqs. (1) and (2) should take the sets of directions, respectively, (Y, Z, X), (X, Y, Z), and (Y, X, Z) shown in Fig. 3.

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[7] For example, compare Figs. 4 and 5 of Ref. 3 with the bold lines in Figs. 4 and 5 of this paper.

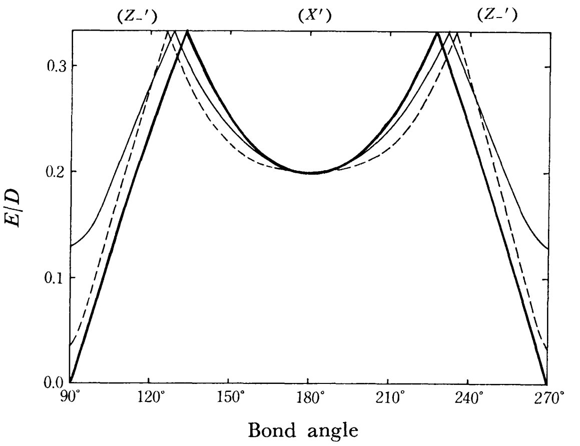

Fig. 5. The ratio of E/D of m-$C_6H_4(CX)_2$ calculated with only the intratomic interaction when $\theta_1+\theta_2=360°$ in the cases of $\alpha_1=\alpha_2=0°$ (bold full line), $\alpha_1=\alpha_2=30°$ (fine full line), and $\alpha_1=-\alpha_2=30°$ (fine broken line). The letters X' and Z_-' on the top of the figure imply that the set of axes (x, y, z) in Eqs. (1) and (2) are close to the sets of directions, (Y, Z, X) and (Y, X, Z) respectively, shown in Fig. 3. In the case of $\alpha_1=\alpha_2=0°$, the z axis ($\theta_1 \gtrsim 129°$) or the x axis ($\theta_1 < 129°$) makes angle of $90°-\theta_1/2$ counter-clockwise with the X axis in Fig. 3.

of $|E|/|D|$ appear by changing α_1 and α_2 under the conditions of $|D| \gtrsim 3|E|$ and $E/D \gtrsim 0$. In these cases, the uncertainty is not large near the observed ratio of E/D ($\simeq 0.275$) [*i.e.* $\theta_1=\theta_2\simeq 185°$ and $\theta_1\simeq 140°$, $\theta_2\simeq 220°$]. This might show that the conclusion obtained in the previous work[3] on the spin quintet radicals is fairly reasonable. In general, however, one should take the influence of the relative orientation among methylene bonds into consideration for discussing the electron spin-spin interaction in molecular multiplets with several methylene bonds.

Some Remarks

Recently, Bernheim *et al.*[8] reported values of D and E for the methylene radical (CH_2) in matrix [$|D|/hc=0.69\ \mathrm{cm}^{-1}$, $|E|/hc=0.003\ \mathrm{cm}^{-1}$]. A similar result was also obtained by Wasserman *et al.*[9] If the present procedure is applied to these values, the -C- bond angle may be near 170° which is much larger than the estimated values of the triplet ground states of phenylmethylene and diphenylmethylene (~145°) and the quintet ground states of *m*-phenylene-*bis*-methylene and *m*-phenylene-*bis*-phenylmethylene (~140°). Wasserman *et al.*[9] showed that if the effect of the partial rotation in the matrix is included the -C- bond angle is 136° which is fairly close to that of these radicals. Further, they reported that the D and especially the E value considerably decrease by such a partial rotation and that the extrapolated D/hc value yields $0.93\ \mathrm{cm}^{-1}$ for an immobile methylene radicals. These evidences do not contradict the results we obtained, and suggest the necessity of further investigations of spin multiplet radicals with methylene bonds.

Most of the numerical calculations were carried out on HITAC 5020E at the Computer Centre, The University of Tokyo.

Appendix

Spin-Spin Interaction in Phenylmethylene. There were some numerical errors in the calculation of planar phenylmethylene in a previous paper.[2] The revised result given herewith is closely connected with the present work on diphenylmethylene. As can be seen in Fig. 6, the general tendency of the angular dependence of D and E values does not differ much from the previous result. However, the most possible -C- bond angle is obtained near $\theta=145°$ where the calculated E/D value coincides with the observed ratio of $|E|/|D|=0.046$.[10] For large (small) -C- bond angles, the principal axes of fine-structure tensor [or those in Eqs. (1) and (2)] are as follows: the x axis is closely directed to the bisector of the -C- bond angle, the y (z) axis is perpendicular to the molecular plane, and the z (y) axis is perpendicular to the other axes. The deviation from the z (y) axis from the symmetry axis of the carbon skeleton in the phenylmethylene is given in Table 1.

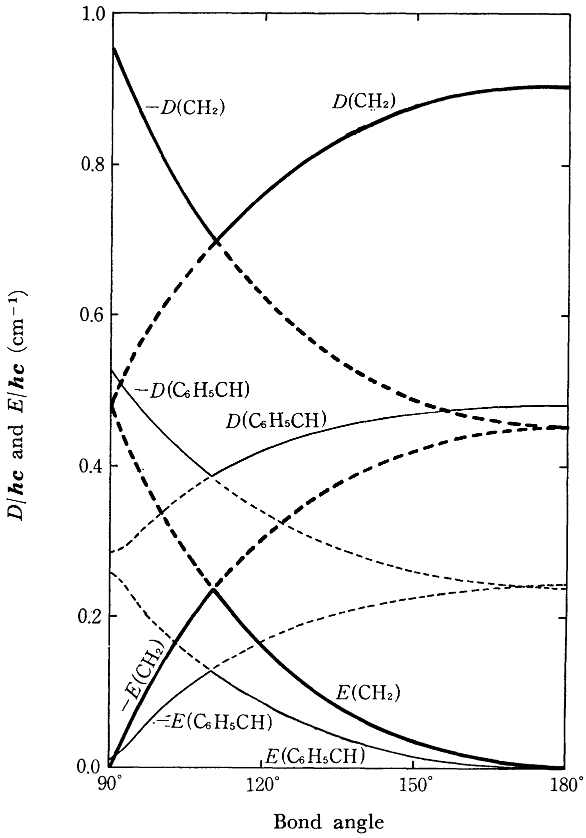

Fig. 6. D and E values of methylene (bold lines) and of phenylmethylene (fine lines). For large (small) -C- bond angles, the y (z) axis of fine-structure tensor [or Eqs. (1) and (2)] is perpendicular to the molecular plane. Dotted lines show their extensions [the revised figure of Fig. 1 in Ref. 2].

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8) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970).

9) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970).

10) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Amer. Chem. Soc.*, **84**, 4990 (1962).

TABLE 1. DEVIATION OF z[a] (OR y[b]) AXIS FROM THE SYMMETRY AXIS OF THE CARBON SKELETON IN THE PHENYLMETHYLENE[c]

-C- bond angle	180°	165°	150°	135°	120°	105°	90°
Deviation	0.0°	8.0°	16.0°	24.0°	32.0°	40.6°	0.0°

a) For large -C- bond angles.
b) For small -C- bond angles.
c) The revised table of Table 1 in Ref. 2.