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ESR Studies of the **g**- and **D**-Tensor Values of Stable *p*- and *m*-Phenylenebis(galvinoxyl) Biradicals

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The **g**- and **D**-tensor values of *p*- and *m*-phenylenebis(galvinoxyl) biradicals in several solvents have been determined from their asymmetric frozen ESR spectra. The spectra suggested that only one conformer out of two possible ones, "*propeller*" and "*anti-propeller*" structures, exists in each biradical. The **D**-tensor values were calculated for the two possible conformers, based on assumed molecular structures and spin distribution. The results indicate that the "*propeller*" structure with a 30° twist angle is preferable for the *m*-phenylenebis(galvinoxyl). In the case of the *p*-phenylenebis(galvinoxyl), a considerable accordance between the measured and calculated values for the two conformers with a 30° twist angle was obtained. Notable solvent effects in the **g**- and **D**-tensor values were observed for the *m*-phenylenebis(galvinoxyl), but not for the *p*-phenylenebis(galvinoxyl).

Recently, one of the present authors has reported the preparation of *p*- and *m*-phenylenebis(galvinoxyl) biradicals, (I) and (II), which are fairly stable phenoxyl biradicals; their structures are shown in Fig. 1.[1] The biradicals were produced by the PbO_2 oxidation of phenol precursors in 2-methyltetrahydrofuran (2-MTHF) under a vacuum. The fluid solution ESR spectra of the biradicals consist of nine lines due to eight equivalent meta-ring protons. Gierke *et al.* also obtained the biradicals from different phenol precursors by PbO_2 oxidation.[2] ESR zero-field splittings in rigid media at 77 K were observed, indicating the existence of the triplet state in the biradicals. However, no detailed analyses of the ESR spectra of the biradicals have been reported, although various types of information about the conformation, symmetry, and electronic state of triplet molecules have been obtained from the rigid matrix ESR spectra.[3–7]

In the present paper, the **g**- and **D**-tensor values of *p*- and *m*-phenylenebis(galvinoxyl) biradicals (I and II) in several solvents have been determined from their asymmetric frozen ESR spectra. The **D**-tensor values were calculated for two possible conformers in each biradical, based on the assumed molecular structures and spin distribution. On the basis of these data, the conformation and electronic structure of the biradicals and the solvent effect have been discussed. The hyperfine splittings of many stable hindered phenoxyl radicals, including several biradicals, have been studied by a number of investigators with the aid of the ESR spectra.[8] However, the **g**- and **D**-tensor values of these phenoxyl radicals have never been reported, as far as we know.

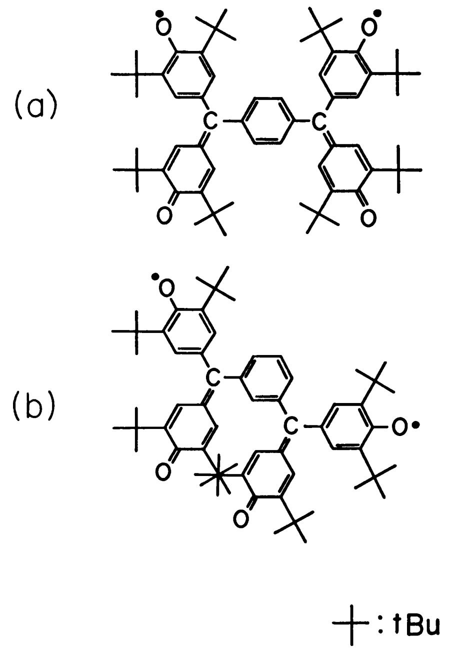

Fig. 1. Molecular structures of (a) *p*-phenylenebis(galvinoxyl) biradical (I) and (b) *m*-phenylenebis(galvinoxyl) biradical (II).

Experimental

The syntheses of *p*-bis[bis(3,5-di-*t*-butyl-4-hydroxyphenyl)methyl]benzene (mp 290—292 °C) and *m*-bis[bis(3,5-di-*t*-butyl-4-hydroxyphenyl)methyl]benzene (mp 223—224 °C) were reported previously.[1] The *p*- and *m*-phenylenebis(galvinoxyl) biradicals (I and II) were prepared by the oxidation of the above phenol precursors with PbO_2 in the 2-MTHF solvent under a nitrogen atmosphere, with the temperature kept between 5 and 10 °C, following the method of Kharash and Joshi.[9]

All the ESR measurements were carried out using a JES-ME-3X spectrometer equipped with a Takeda-Riken microwave frequency counter. The ESR splittings were determined using $(KSO_3)_2NO$ ($a^N = 13.05 \pm 0.03$ G) as a standard. The *g*-values were measured relative to the value of Li-TCNQ powder, calibrated with $(KSO_3)_2NO$ ($g = 2.0054$).[10]

Results and Discussion

ESR Spectral Analyses. The 2-MTHF solution spectra of the *p*- and *m*-phenylenebis(galvinoxyl) radicals (I and II) show nine line hyperfine splittings due to the equivalent eight *meta*-ring protons in the two galvinoxyl rings, as has been reported previously.[1] The spectra were ascribed to a biradical whose exchange energy, J, is larger than the proton coupling constant, a_m^H ($J \gg a_m^H$; $a_m^H/2 = 0.69$ G for I and II). When the solution containing the I and II biradicals is frozen into a rigid glass (77 K), one can observe some dipolar splittings, as Figs. 2 and 3 show.

The biradical in a rigid glass can be treated as a two-spin system which forms a triplet and a singlet state. The usual spin Hamiltonian[3,6] for the triplet state is:

$$H = \beta \mathbf{H} \cdot \hat{\mathbf{g}} \cdot \mathbf{S} + \mathbf{S} \cdot \hat{\mathbf{D}} \cdot \mathbf{S}, \tag{1}$$

where $\hat{\mathbf{g}}$ is the **g** tensor, $\hat{\mathbf{D}}$ is the spin-spin dipolar interaction tensor, and the other symbols have the usual meanings. When the radical has the property of a triplet without axial symmetry, we usually observe three pairs of absorption lines, from whose separations the zero-field parameters (D and E) of the dipolar electron-electron interaction can be obtained.[3,6,7] The spectrum of the I biradical can be explained as two inner pairs of lines overlapping each other, because of the small distances between zero-field absorption lines compared with the line-width of each absorption line. In the spectrum, the high-field line of the inner pair of lines is broader than the other and has a shoulder, suggesting the overlapping of two lines. A central line at $g=2$ is attributable to the monoradical impurity. In fact, in the case of the II biradical, five out of six lines theoretically expected for a non-axially symmetrical triplet are resolved, as is shown in Fig. 3.

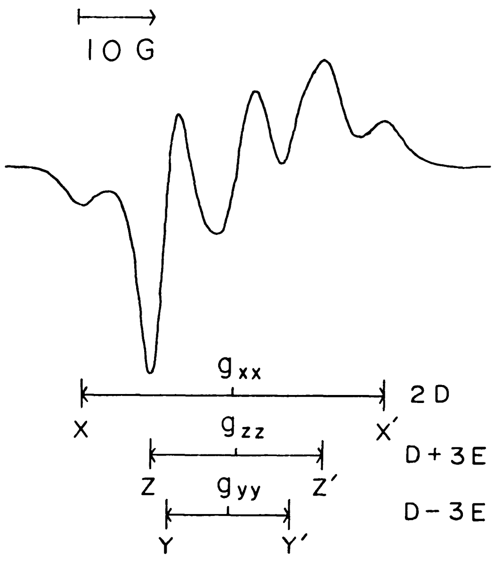

Fig. 2. ESR spectrum of the biradical (I) in 2-MTHF at 77 K.

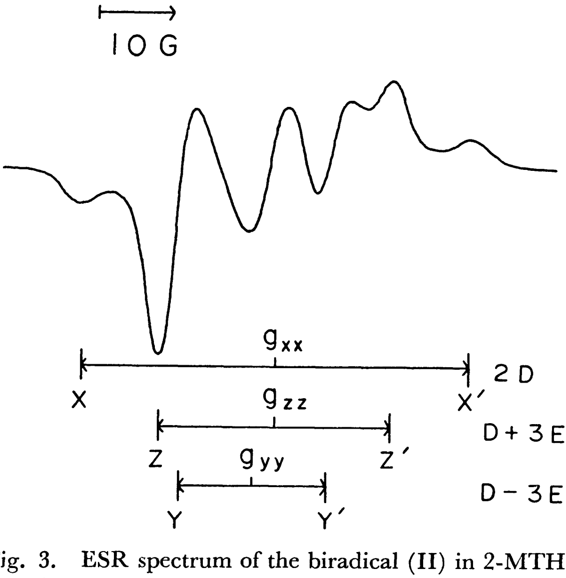

Fig. 3. ESR spectrum of the biradical (II) in 2-MTHF at 77 K.

In both the biradicals (I and II), the zero-field parameters (D and E) and the **g**-tensor values have been estimated from the positions of three pairs of turning points (XX', YY', and ZZ'), which are shown in Figs. 2 and 3, in the following way. The separation between the outer pair of lines (XX') in the spectrum of the I biradical is $2D=40.0\pm0.4$ G. Because of the localization of each unpaired electron on two galvinoxyl rings, as will be discussed later, the principal X axis of the **D** tensor, corresponding to the maximum value of $2D$, is probably parallel to the line connecting two carbon atoms bonded to the centered phenylene ring. Because of the symmetry of the biradical molecules, we can expect that the principal axes of the **D** and **g** tensors are coaxial. Consequently, the frequency center of these lines gives $g_{xx}=2.0045\pm0.0002$. The remaining pairs, ZZ' and YY', are separated by $(D+3E)=22.7\pm0.6$ G and $(D-3E)=16.0\pm0.6$ G respectively. Although, because of overlapping lines, this distance cannot be measured accurately, the value of $D=19.4\pm0.6$ G shows a considerable accordance with the value ($D=20.0\pm0.2$ G) from two external lines; thus, the E value was estimated to be $E=1.1\pm0.2$ G. The g-values from the frequency center of these two pairs of absorption lines are $g_1=2.0043\pm0.0002$ (ZZ') and $g_2=2.0049\pm0.0002$ (YY'). By comparing g_1 and g_2, the smaller, $g_1=2.0043$, was tentatively assigned to g_{zz}, and the larger, $g_2=2.0049$, to g_{yy}, as will be discussed later.* The isotropic g_{iso} value of the I biradical was measured in 2-MTHF at room temperature. The average g_{av} value of $(1/3)(g_{xx}+g_{yy}+g_{zz})=2.0045\pm0.0002$ is in agreement with the isotropic $g_{iso}=2.00441\pm0.00003$ value measured at room temperature, indicating that the **g**-tensor values obtained by the above analysis are reliable. All these values are summarized in Table 1. Similar analyses were performed for the frozen solution ESR spectrum of the II biradical in 2-MTHF. The **D**- and **g**-tensor values obtained are $D=26.1\pm0.2$ G, $E=1.9\pm0.2$ G, and $g_{xx}=2.0039\pm0.0002$, $g_{yy}=2.0056\pm0.0002$, $g_{zz}=2.0038\pm0.0002$, respectively. The average g_{av} value of $(1/3)(g_{xx}+g_{yy}+g_{zz})=2.0044\pm0.0002$ is in agreement with the isotropic $g_{iso}=2.00443\pm0.00003$ value measured in 2-MTHF at room temperature. The **D**- and **g**-tensor values obtained are listed in Table 2. Both the D and E values of the II biradical are larger than those of the I biradical.

The shift of the g value from that ($g_e=2.0023$) of the free electron is determined mainly by spin-orbit coupling, which may be large because of the presence of the nonbonding σ electrons of the oxygen atom. The energy due to the so-called n-π transitions may be low

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* This assignment was also supported by the calculations of the dipolar splitting parameters, D and E, as will be described below. The values of the D and E parameters calculated for both the "*propeller*" and "*anti-propeller*" structures of *p*-phenylenebis(galvinoxyl) biradical are negative and positive respectively. Therefore, $D_{zz}>D_{yy}>0$, where D_{zz} and D_{yy} are the principal values of the **D**-tensor; thus, the smaller, $g_1=2.0043$, is attributable to g_{zz}.[3)]

TABLE 1. **g**- AND **D**-TENSOR VALUES OF THE *p*-PHENYLENEBIS(GALVINOXYL) BIRADICAL

Solvent	$\lvert D\rvert$[a] (G)	$\lvert E\rvert$[a] (G)	g_{xx}[b]	g_{yy}	g_{zz}	g_{av}[c]	g_{iso}[d]
2-MTHF	20.0	1.1	2.0045	2.0049	2.0043	2.0045	2.00441
Toluene	19.8	1.0	2.0044	2.0048	2.0042	2.0044	2.00443
Ethyl alcohol	19.9	1.2	2.0045	2.0049	2.0040	2.0045	2.00440
Diethyl ether	20.0	1.2	2.0045	2.0047	2.0039	2.0044	2.00441

a) The experimental errors in the values of $|D|$ and $|E|$ are ±0.2 G. b) The experimental errors in the values of g_{xx}, g_{yy}, g_{zz}, and g_{av} are ±0.0002. c) The average $g_{av}=(1/3)(g_{xx}+g_{yy}+g_{zz})$. d) The experimental errors in the values of g_{iso} are ±0.00003.

TABLE 2. **g**- AND **D**-TENSOR VALUES OF THE *m*-PHENYLENEBIS(GALVINOXYL) BIRADICAL

Solvent	$\lvert D\rvert$[a] (G)	$\lvert E\rvert$[a] (G)	g_{xx}[b]	g_{yy}	g_{zz}	g_{av}[c]	g_{iso}[d]
2-MTHF	26.1	1.9	2.0039	2.0056	2.0038	2.0044	2.00443
Toluene	21.9	1.5	2.0043	2.0055	2.0039	2.0046	2.00441
Ethyl alcohol	26.0	1.9	2.0038	2.0054	2.0039	2.0044	2.00434
Diethyl ether	26.9	1.8	2.0039	2.0057	2.0041	2.0046	2.00441

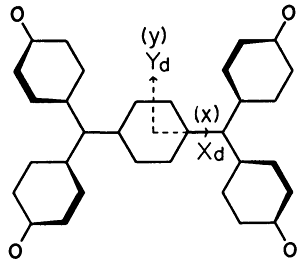
a) The experimental errors in the values of $|D|$ and $|E|$ are ±0.2 G. b) The experimental errors in the values of g_{xx}, g_{yy}, g_{zz}, and g_{av} are ±0.0002. c) The average $g_{av}=(1/3)(g_{xx}+g_{yy}+g_{zz})$. d) The experimental errors in the values of g_{iso} are ±0.00003.

in these systems; therefore, these transitions contribute strongly to the shift in the g value.[11,12] However, in the planar aromatic radicals the contribution to the g_{zz} value (perpendicular to the molecular plane) from the n-π transitions vanishes. Therefore, the value of g_{zz} should be close to the free-spin value, while g_{xx} and g_{yy} are larger than g_e. In the *p*-phenylenebis(galvinoxyl) radical, the **g**-tensor values estimated from the frozen-solution spectrum are $g_{xx}=2.0045\pm0.0002$, $g_1=2.0043\pm0.0002$, and $g_2=2.0049\pm0.0002$. By comparing g_1 and g_2, the smaller g_1 was tentatively assigned to g_{zz}, and the larger g_2, to g_{yy}. Similarly, the **g**-tensor values of the *m*-phenylenebis(galvinoxyl) radical are $g_{xx}=2.0039\pm0.0002$, $g_{yy}=2.0056\pm0.0002$, and $g_{zz}=2.0038\pm0.0002$. The g_{zz} values of both biradicals show a large deviation from that of the free electron. This is mainly due to the nonplanar character of the I and II biradicals.

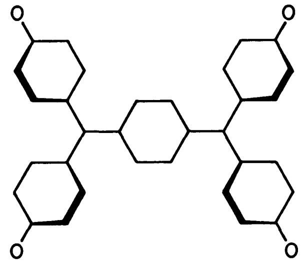
D-*Tensor Calculation with Spin Densities.* In order to clarify the molecular structures of the *p*- and *m*-phenylenebis(galvinoxyl) biradicals, and in order to determine the directions of the principal axes, X_d, Y_d, and Z_d, of the **D**-tensor in the molecules, the calculations of the dipolar splitting tensors were performed for two possible conformers in each biradical, based on the assumed molecular structures and spin distribution.

p- And *m*-phenylenebis(galvinoxyl)s (I and II) are thought to be weakly π-conjugated biradicals because of the small spin density on the central phenylene ring. The orbital containing the unpaired electron of phenylgalvinoxyl radical has, at least in the Hückel approximation, a node in the phenyl ring; in fact, a recent ENDOR study found a small hyperfine splitting ($a^{\mathrm{H}}=0.207$ G) for phenyl-ring protons.[13] In such a case, the electronic structures of the two galvinoxyl rings in these biradicals must be similar to that of the phenylgalvinoxyl. The isotropic g_{iso} values also show an excellent agreement between the phenylgalvinoxyl ($g_{iso}=2.00440\pm0.00003$), the I biradical ($g_{iso}=2.00441\pm0.00003$), and the II biradical ($g_{iso}=2.00443\pm0.00003$), supporting the above anticipation. Therefore, the dipolar magnetic system of the I and II biradicals can be adequately described as an isolated two-spin system consisting of two galvinoxyl groups, each containing one unpaired electron.

The phenylgalvinoxyl radical may, on the other hand, be considered a triphenylmethyl derivative. A molecular model indicates that the main steric interaction in phenylgalvinoxyl works between the ring protons, although weak interactions can be seen between the substituted tertiary butyl groups. Thus, the radical probably adopts a propeller configuration, the twist angle of phenyl rings being estimated to be about 30° about the methyl bond.[14] The *p*-phenylenebis(galvinoxyl) radical will have a similar configuration. Because the steric interactions between the substituted tertiary butyl groups of the two galvinoxyl rings are considered to be weak (see Fig. 1), the twist angle of phenyl rings about the methyl bond will still be about 30°. Consequently, we can expect two possible conformations, (A) and (B), in *p*-phenylenebis(galvinoxyl), in which each monoradical half is considered to have a propeller configuration. In the (A) conformation, the two $2p_z$ orbitals of two triphenylmethyl carbon atoms twist by 60° each other, while in the (B) conformation, the two $2p_z$ orbitals are parallel to each other, having a 30° twist angle to the π-orbital of the centered phenylene ring. These two conformations, (A) and (B), are shown in Fig. 4 and are named as "*propeller*" and "*anti-propeller*" structures, considering the figure as a whole molecule. Similarly, two conformations can be expected in *m*-phenylenebis(galvinoxyl). However, the Stuart molecular model indicates that the "*anti-propeller*" structure is not probable in this radical because of the strong steric interaction between two galvinoxyl rings, especially through nearest-neighboring tertiary butyl groups (see Fig. 1(b)); thus, only the "*propeller*" structure is probable (see Fig. 5).

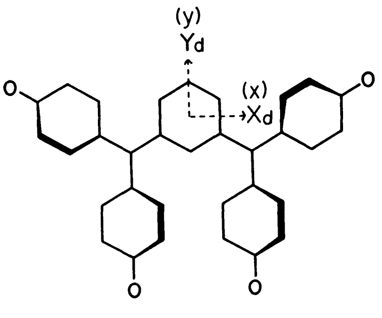


Propeller



Anti-propeller

Fig. 4. "*Propeller*" and "*anti-propeller*" structures of *p*-phenylenebis(galvinoxyl) biradical, showing the molecular axes x, y, and z and the principal axes X_d, Y_d, and Z_d of the **D**-tensor.



Propeller

Fig. 5. "*Propeller*" structure of *m*-phenylenebis(galvinoxyl) biradical, showing the molecular axes x, y, and z and the principal axes X_d, Y_d, and Z_d of the **D**-tensor.

In the "*propeller*" structure of the I and II biradicals, to achieve symmetry, the molecular z axis is chosen perpendicular to the central phenylene ring, while the x axis parallels a line connecting the two carbon atoms bonded to the central phenylene ring. On the other hand, in the "*anti-propeller*" structure of the I biradical, while the x axis is chosen similarly, the z axis is chosen perpendicular to a plane containing four oxygen atoms. We assumed that the principal axes—X_d, Y_d, and Z_d of the **D**-tensor are parallel to the molecular axes—x, y, and z, because of the symmetry of the biradical molecules, as is shown in Figs. 4 and 5. This is a favorable situation for calculating the **D**-tensor values, because, in such a case, the matrix of the **D**-tensor can be diagonalized. Therefore, the *D* and *E* parameters of the dipolar splitting can be calculated with the aid of the following equations:[15–17)]

$$D = \frac{3}{4} g_{iso}^2 \beta^2 \sum_{i,j} \frac{r_{ij}^2 - 3x_{ij}^2}{r_{ij}^5} \rho_i \rho_j \qquad (2)$$

$$E = \frac{3}{4} g_{iso}^2 \beta^2 \sum_{i,j} \frac{y_{ij}^2 - z_{ij}^2}{r_{ij}^5} \rho_i \rho_j \qquad (3)$$

where r_{ij} is the distance between the *i* and *j* atoms and where ρ_i and ρ_j are the π-spin densities on the *i* atom in one galvinoxyl group and on the *j* atom in the other galvinoxyl group in a molecule. Here we have chosen the following parameters: the twist angle of each phenyl ring to the $2p_z$ orbitals of the two triphenylmethyl carbon atoms is 30°, as has been described above; the C–O bond length is 1.27 Å, and the C–C bond length is 1.40 Å in the average, as obtained by an X-ray analysis of the galvinoxyl radical;[18)] the McLachlan spin densities were taken from Ref. 13.

Using these parameters, the calculations of the *D* and *E* values were performed for two possible conformations, the "*propeller*" and "*anti-propeller*" structures, of the I biradical, and one possible conformation, the "*propeller*" structure, of the II biradical. The results are summarized in Table 3, together with those obtained experimentally in the 2-MTHF solvent. For the I biradical, the calculated *D* and *E* parameters are 18.0 and 0.6 G for the "*propeller*" structure, and 21.7 and 1.7 G for the "*anti-propeller*" structure, while the observed ones are 20.0 and 1.1 G in 2-MTHF respectively. For the II biradical, the calculated *D* and *E* values are 27.0 and 1.3 G for the "*propeller*" structure, while the observed ones are 26.1 and 1.9 G in 2-MTHF respectively. The *p*- and *m*-phenylenebis(galvinoxyl) biradicals (I and II) are thought to be weakly π-conjugated biradicals, with a twist angle of the phenyl rings of about 30°. Therefore, the calculations of the *D* and *E* parameters were performed by assuming that the I and II biradicals consist of isolated two galvinoxyl groups, each containing one unpaired electron, as has been described above. The considerable accordance between calculated and observed values indicates that the above assumptions for the electronic structure and the twist angle of the I and II biradicals are reliable. The results also suggest that the principal X_d axis of the **D** tensor, corresponding to the maximum 2*D* value, is parallel to the molecular x axis; this is consistent with our expectations.

TABLE 3. THE *D* AND *E* PARAMETERS (IN G) OF THE DIPOLAR SPLITTING CALCULATED FOR THE "*propeller*," "*anti-propeller*," AND "*planar*" STRUCTURES OF THE *p*- AND *m*-PHENYLENEBIS(GALVINOXYL) BIRADICALS (I AND II)

	I Biradical		II Biradical	
	|*D*| (G)	|*E*| (G)	|*D*| (G)	|*E*| (G)
Propeller	18.0	0.6	27.0	1.3
Anti-propeller	21.7	1.7	—	—
Planar	22.3	1.9	94.2	4.5
Experimental[a)]	20.0	1.1	26.1	1.9

a) **D**-tensor values measured in 2-MTHF at 77 K.

The frozen-solution ESR spectrum of the I biradical in 2-MTHF (see Fig. 2) suggests that only one conformer exists in the biradical; if two conformers exist in the I biradical at the same time, we should, at least, observe a splitting in the X and/or X' absorption lines, as the results of the calculation of the D and E parameters indicate. Unfortunately, it is not possible to decide whether the I biradical molecule takes a "*propeller*" or an "*anti-propeller*" structure, because both the D and E values experimentally obtained are just the medium ones of those calculated for the two assumed conformers. By comparing the **g**-tensor values of the biradicals with those of the monoradicals, the conformations of some nitroxide biradicals have been determined recently.[5,6] The **g**-tensor values of phenoxyl monoradicals including galvinoxyl and the phenylgalvinoxyl radical have not been reported, though, as far as we know. Therefore, we can not utilize the observed **g**-tensor values of the I biradical in order to determine the conformation of the radical. The frozen-solution ESR spectrum of the II biradical in 2-MTHF (see Fig. 3) also indicates that only one conformer exists in this radical. The observed D and E parameters show a considerable accordance with those calculated for the expected "*propeller*" structure, as described above.

The discrepancy between the observed and the calculated parameters will depend mainly on the difference between the true and the presumed vector distances, that is, probably in this case, the twist angle. Therefore, calculations were also performed for the "*planar*" structure of both the biradicals for reference. In fact, in the case of the II biradical, the D and E parameters (D=94.2 and E=4.5 G) calculated for the "*planar*" structure show a large discrepancy from those (D=26.1, E=1.9 G) observed in 2-MTHF and from those (D=27.0, E=1.3 G) calculated for the "*propeller*" structure with a 30° twist angle. The results indicate that the dipolar splitting calculations are very sensitive to the twist angle, because, for instance, the nearest neighboring interatomic distances are 4.79 Å for the "*propeller*" structure and 2.42 Å for the "*planar*" structure. On the other hand, in the case of the I biradical, the dipolar splitting values are not sensitive to whether the radical molecule takes the "*planar*" or the "*non-planar*" structure, as is shown in Table 3. However, the "*planar*" structure shows the largest deviations of both the calculated D and E parameters from the experimental ones among the three structures.

Solvent Effect for the Structure of the Biradicals. Many investigations of the solvent effects of free radicals, including phenoxyl radicals, in solution have been reported.[19] The effects may be explained as a redistribution of the π-electron spin density in a radical molecule induced by the electrostatic interaction and/or the hydrogen-bond formation between radical and solvent molecules. In addition to the above effects, recent ENDOR studies of the phenylgalvinoxyl radicals in solution have provided evidence that solvent molecules may play an important role in fixing the conformation and, thus the unpaired electron distribution, of the radical molecules.[13] Based on the ENDOR data, interesting changes in conformation and symmetry for these radicals due to steric interactions and solvent effects have been discussed. Therefore, the effects of the solvent in the frozen-solution ESR spectra of the I and II biradicals have also been examined.

In the I biradical, identical spectra were obtained in frozen toluene, ethanol, and diethyl ether solutions. The observed values of the zero-field splittings, the **g** tensors, and the average g_{av} have been summarized in Table 1. The isotropic g_{iso} values of the I biradical were also measured in toluene, ethanol, and diethyl ether solvents at room temperature. In the I biradical, all these values are very close to the corresponding ones in 2-MTHF, within the limits of experimental error. This indicates that the effect of the solvent is too small to induce the change in the unpaired spin distribution and the molecular structure.

On the other hand, notable solvent dependences were observed in frozen-solution spectra of the II biradical; the results are summarized in Table 2. The observed D values are 26.1 G in 2-MTHF, 21.9 G in toluene, 26.0 G in ethanol, and 26.9±0.2 G in diethyl ether. The **g**-tensor values also appear to be slightly different from the corresponding ones in other solvents, whereas the respective average g_{av} values are close to the corresponding g_{iso} values. In addition, the g_{iso} values for the II biradical in 2-MTHF, toluene, ethanol, and diethyl ether at room temperature are 2.00443, 2.00441, 2.00434, and 2.00441±0.00003 respectively; *i. e.*, there are virtually the same, within the limits of experimental error, except for the small change in ethanol. From the values of D, the distances between the radical centers in the point-dipole approximation were estimated to be about 10.2 Å for the largest D-value in diethyl ether and 10.8 Å for the smallest D-value in toluene. These results may be explained by assuming that the twist angle between the $2p_z$ orbitals of the triphenylmethyl carbon atom and of the centered phenylene ring of the II biradical is larger in toluene than in diethyl ether.

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