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ESR Studies of a New Stable π-Conjugated 4,4′-(Biphenyl-3,3′-diyl)bis(aryloxyl) Biradical

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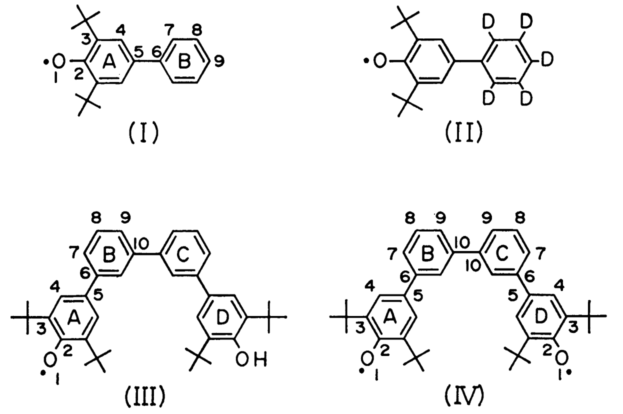
ENDOR observations were carried out for 2,6-di-*t*-butyl-4-phenylphenoxyl and some of its derivatives. Based on the proton hyperfine splittings, the structure of the aryloxyl monoradicals was investigated in terms of the McLachlan MO calculation. A new stable π-conjugated bis(aryloxyl) biradical, 4,4′-(biphenyl-3,3′-diyl)-bis(2,6-di-*t*-butylphenoxyl), was prepared, and the $\boldsymbol{g}$- and $\boldsymbol{D}$-tensor values of the biradical in toluene have been determined from its asymmetric frozen ESR spectrum. The $\boldsymbol{D}$-tensor values were calculated for the twisted "cis" and "trans" conformers of the biradical molecule, using the McLachlan spin densities of 2,6-di-*t*-butyl-4-phenylphenoxyl, which is a monoradical half of the biradical.

2,6-Di-*t*-butyl-4-phenylphenoxyl (aryloxyl radical (I)) (Fig. 1) is a fairly stable phenoxyl radical, which can be purely separated as a solid.[1] ESR[2] and NMR[3] studies of the aryloxyl radical (I) and some of its derivatives were already reported. In a recent paper, a report was given on the preparation of a new stable π-conjugated *m*-phenylenebis(aryloxyl) biradical, 4,4′-(*m*-phenylene)bis(2,6-di-*t*-butylphenoxyl), in which two aryloxyl monoradical parts strongly conjugated each other through the meta-position of central benzene ring.[4] Kothe *et al.*[5] prepared a stable benzene-1,3,5-tris(aryloxyl) triradical, 4,4′,4″-(1,3,5-benzenetriyl)tris-(2,6-di-*t*-butylphenoxyl), which is related to the *m*-phenylenebis(aryloxyl) biradical. The existence of triplet and quartet states in the bis and tris(aryloxyl) radicals, respectively, has been confirmed by ESR measurements in rigid media at 77 K.[4,6] However, no detailed study of the electronic and molecular structure of these bi- and tri-radicals seems to have been carried out so far.

First, ENDOR measurements were carried out in order to study the three aryloxyl monoradicals (I), (II), and (III) (Fig. 1), the detailed proton hyperfine splittings of the radicals being determined. The structure of the aryloxyl radicals was investigated by means of McLachlan MO calculation of the spin densities. The aryloxyl radical (I) is a monoradical half of the bis(aryloxyl) biradical (IV) (Fig. 1), and the aryloxyl radical (III) a monoradical precursor of the bis-(aryloxyl) biradical (IV).



(I) (II) (III) (IV)

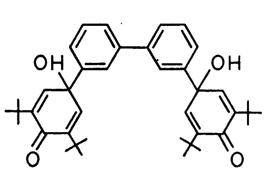
Fig. 1. Molecular structures of aryloxyl radicals (I), (II), (III), and (IV), and the atomic numbering system.

Secondly, we have prepared a new stable π-conjugated 4,4′-(biphenyl-3,3′-diyl)bis(aryloxyl) biradical (IV), and succeeded in observing the zero-field ESR spectrum in toluene rigid glass. The ESR spectrum at 77 K can be clearly analyzed as the characteristic spectrum of a non-axially symmetrical triplet, with $|D|=35.4\pm0.3$ G and $|E|=2.6\pm0.3$ G, and $g_{xx}=2.0045\pm0.0002$, $g_{yy}=2.0051\pm0.0002$ and $g_{zz}=2.0024\pm0.0002$. The D and E parameters were calculated for the assumed molecular structures, using McLachlan spin densities of the aryloxyl (I) which is a monoradical half of the biradical (IV). From the results, the conformation and electronic structure of the biradical have been discussed.

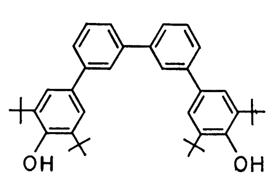
Experimental

Measurements. ESR measurements were carried out using a JES-ME-3X spectrometer equipped with a Takeda-Riken microwave frequency counter. The ENDOR spectra were recorded on a JEOL-type ES-EDX-1 spectrometer, operated with 80 Hz magnetic field modulation. About 150 W of the continuous radio wave frequency modulated at 6.5 kHz were running inside the cavity for NMR excitation. The ESR splittings were determined using $(KSO_3)_2NO$ or Mn^{+2} in MgO as a standard. The *g*-values were measuted relative to the value of Li–TCNQ powder, calibrated with $(KSO_3)_2NO$ ($g=2.0054$).[7] The aryloxyl radicals (I)—(IV) were prepared by the oxidation of the corresponding phenols with PbO_2 in toluene under a vacuum.

Preparation of Specimens. Rieker and Scheffler[2] reported the syntheses and physical properties of the phenol precursors of the aryloxyl radicals (I) and (II). Quinol (V) was synthesized by the reaction of the dimagnesium derivative of 3,3′-dibromobiphenyl with 2,6-di-*t*-butyl-*p*-benzoquinone;[8] the highly reactive magnesium investigated by Rieke and Bales[9] allows the ready preparation of many Grignard reagents which were heretofore not easily prepared or could not be prepared at all. Using their method, we have prepared the dimagnesium derivative of 3,3′-dibromobiphenyl at 20 °C.



(V)



(VI)

4,4′-(biphenyl-3,3′-diyl)bis(4-hydroxy-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one) (quinol (V)). Freshly cut potassium (2.81 g, 0.072 mol), $MgCl_2$ (3.81 g, 0.040 mol), KI (3.32 g, 0.020 mol), and THF (tetrahydrofuran) (90 ml) were placed in an 100 ml four-necked flask equipped with reflux condensor, dropping funnel, thermometer, heating mantle, and magnetic stirrer under nitrogen atmosphere. The mixture was refluxed for 3 h with stirring, and was then left to stand at 30 °C for 0.5 h. A THF solution of 3,3′-dibromobiphenyl (3.12 g, 0.010 mol) was added dropwise below 30 °C, and the mixture was reacted for 0.5 h at 30 °C. In the same way, a THF solution of 2,6-di-*t*-butyl-*p*-benzoquinone (4.41 g, 0.020 mol) was added slowly below 30 °C, and then the reaction mixture was refluxed for 1.5 h under stirring. The grayish black solids precipitated were quickly filtered off and hydrolyzed in saturated NH_4Cl solution (200 ml). They were then taken up in diethyl ether, washed with water, and dried over anhydrous sodium sulfate. After removal of the diethyl ether, viscous oil was remained. By adding petroleum ether (bp 50—70 °C) to the viscous oil, white solids (1.5 g, 0.0025 mol) precipitated. The solids obtained were recrystallized first from ligroin (bp 90—105 °C), and then from dioxane, and finally heated at 180 °C for 11 h under vacuum (5×10^{-3} Torr; 1 Torr=133.322 Pa) in order to completely remove the dioxane solvent included in the crystal. Mp 246—248 °C. (Found: C, 80.21; H, 8.88%. Calcd for $C_{40}H_{50}O_4$: C, 80.77; H, 8.47%). UV spectrum ($\lambda_{max}=228$ nm, log $\varepsilon=4.80$ in THF). NMR spectrum ($\delta=1.27$ ppm (36H, s, *t*Bu), 2.30 (2H, s, OH), 6.58 (4H, s, *m*-ring), 7.12—7.83 (8H, multiplet, biphenylene ring); δ in $CDCl_3$ with TMS as internal standard).

*3,3′-Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)biphenyl (Bisphenol (VI)).* Bisphenol (VI) was synthesized by the reduction of quinol (V) (1.0 g, 0.0017 mol) with Zn powder (1.3 g, 0.020 mol) and concd HCl (15 ml) in methyl alcohol (60 ml) at 55 °C for 2 h, by a process similar to that of Rieker and Scheffler.[2] The white solid (0.75 g, 0.0013 mol) obtained was first washed with hot methyl alcohol, and then recrystallized from dioxane, and heated at 175 °C for 7 h under vacuum (5×10^{-3} Torr) in order to completely remove the dioxane solvent included in the crystal. Mp 213—215 °C. (Found: C, 85.05; H, 9.13%. Calcd for $C_{40}H_{50}O_2$: C, 85.36; H, 8.95%). UV spectrum ($\lambda_{max}=217$ nm, log $\varepsilon=4.80$, $\lambda_{max}=263$ nm, log $\varepsilon=4.76$ in THF). NMR spectrum ($\delta=1.48$ ppm (36H, s, *t*Bu), 5.02 (2H, s, OH), 7.28 (4H, s, *m*-ring), 7.28, 7.38, 7.58 (8H, multiplet, biphenylene ring); δ in CCl_4 with TMS as an internal standard).

Results

ENDOR Spectra of Aryloxyl Monoradicals (I), (II), and (III). The ESR spectra of the aryloxyl radicals (I) and (II) have been reported by Rieker and Scheffler.[2] The spectrum of the aryloxyl radical (III) shows a sextet-doublet hyperfine pattern. Both the ring proton hyperfine splittings and the g_{iso}-values of the radicals observed in toluene at 20 °C are given in Table 1.

The ENDOR spectrum of aryloxyl radical (I) in toluene at −85 °C (Fig. 2(a)) clearly shows five different proton hyperfine splittings (1.872, 1.752, 1.620, 0.672, and 0.064 G). On the other hand, the ENDOR spectrum of deuterated aryloxyl radical (II) in toluene at −87 °C shows only two different hyperfine splittings (Fig. 2(b)). The splitting of 1.638 G in (II) is easily assigned to the two meta protons of the phenyl ring A, and that of 0.069 G to the *t*-butyl protons. Comparing

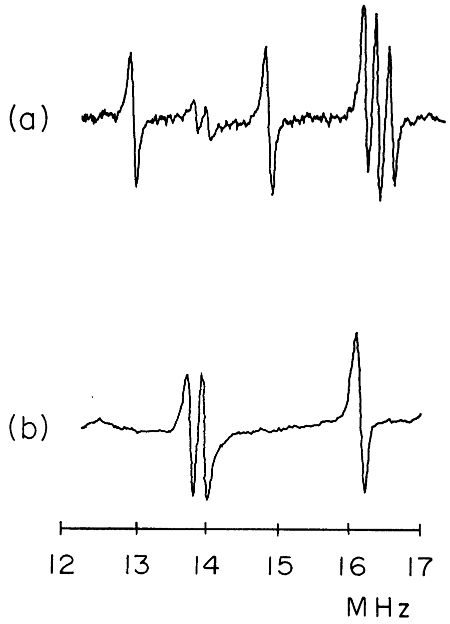


Fig. 2. ENDOR spectra of (a) aryloxyl radical (I) (at −85 °C) and (b) aryloxyl radical (II) (at −87 °C) in toluene.

Table 1. Hyperfine couplings (a_i^H) (in G), g_{iso}-values, and spin densities (ρ_i) of aryloxyl radicals (I), (II), and (III)

		a_4^H	a_7^H	a_8^H	a_9^H	a_{tBu}^H	g_{iso}
I	ESR	1.74[a]	1.74	0.74	1.74	—	2.00415[c]
	ENDOR	1.620[b]	1.752	0.672	1.872	0.064	—
	ρ(Exptl)	−0.0600	0.0649	−0.0249	0.0693	0.228	—
	ρ(Calcd)	−0.0519	0.0629	−0.0301	0.0594	0.2211	($\theta_{AB}=0°$)
II	ESR	1.65	—	—	—	—	2.00414
	ENDOR	1.638	—	—	—	0.069	—
III	ESR	1.76	1.76	0.69	1.76	—	2.00414
	ENDOR	1.673	1.766	0.683	1.902	0.070	—
	ρ(Exptl)	−0.0620	0.0654	−0.0253	0.0704	0.250	—
	ρ(Calcd)	−0.0511	0.0621	−0.0307	0.0592	0.2216	($\theta_{AB}=\theta_{CD}=0°$, $\theta_{BC}=30°$)

a) Experimental errors ±0.04 G. 1 G=10^{-4} T. b) Experimental errors ±0.010 G. c) Experimental errors ±0.00003.

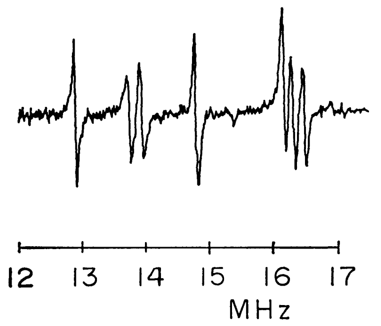


Fig. 3. ENDOR spectrum of aryloxyl radical (III) (at −65 °C) in toluene.

the ENDOR spectrum of aryloxyl radical (I) with that of aryloxyl (II), the hyperfine splittings of 1.872, 1.752, and 0.672 G of the former, which have never been observed in the latter, can clearly be identified as the proton hyperfine splittings in the substituted phenyl ring B. Of these three splittings, the smallest, 0.672 G, is also easily assigned to the two meta protons of the phenyl ring B, taking their ESR hyperfine splittings into account. In this case, we cannot distinguish the splitting due to ortho- and para-protons of the phenyl ring B. A tentative assignment was made, however, with reference to the analogous splitting of the aryloxyl radical (I) obtained by NMR measurements[3] (Table 1). The monoradical precursor (III) of the biradical (IV) shows a spectrum similar to that of aryloxyl radical (I) (Fig. 3). The value of each hyperfine splitting is very close to the corresponding value of aryloxyl radical (I). This indicates that the effects of the meta-substituion of the phenyl ring by biphenyl group are very small to induce a change in the unpaired spin distribution or molecular structure. The experimental values of the spin densities were estimated using the relation, $a_i^H = Q^H \cdot \rho_i$ and $a_{tBu}^H = Q^{tBu} \cdot \rho_i$, where Q^H and Q^{tBu} were taken to be 27 and 0.28 G[10] respectively. The proton hyperfine splittings and the experimental spin densities ρ(Exp.) are summarized in Table 1.

Triplet ESR Spectrum of 4,4′-(Biphenyl-3,3′-diyl)bis(aryloxyl) Biradical (IV). When the bisphenol precursor (VI) of bis(aryloxyl) biradical (IV) was slightly oxidized with PbO_2 in toluene under vacuum, the color of the phenol solution immediately became violet. The ESR spectrum of this solution showed a sextet-doublet hyperfine pattern ($a^H = 1.76 \pm 0.04$ G, $a^H = 0.69 \pm 0.04$ G, $g_{iso} = 2.00414 \pm 0.00003$) due to the six ring protons of the monoradical precursor (III). By further oxidation, the color turned pink, a broad absorption due to the biradical being superposed on the hyperfine spectrum of the monoradical. By freezing the pink solution containing the biradical (IV) into a rigid glass (77 K), one can observe dipolar splittings as shown in Fig. 4.

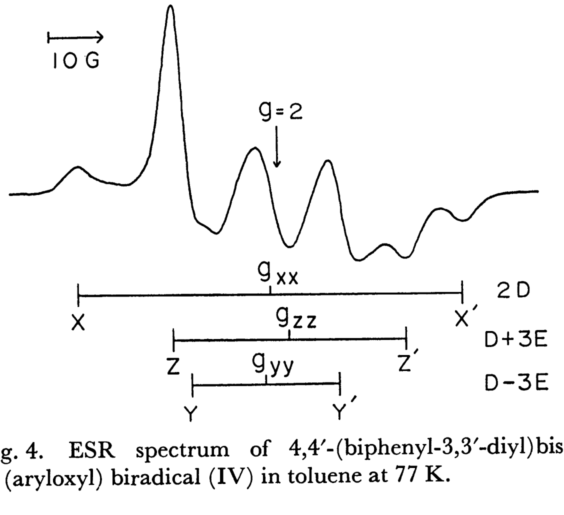


Fig. 4. ESR spectrum of 4,4′-(biphenyl-3,3′-diyl)bis(aryloxyl) biradical (IV) in toluene at 77 K.

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 for the triplet state is

$$H = \beta \boldsymbol{H} \cdot \hat{\boldsymbol{g}} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \hat{\boldsymbol{D}} \cdot \boldsymbol{S} \qquad (1)$$

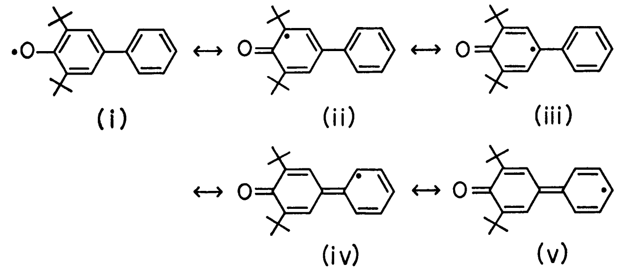
$$= \beta \boldsymbol{H} \cdot \hat{\boldsymbol{g}} \cdot \boldsymbol{S} - XS_x^2 - YS_y^2 - ZS_z^2 \quad (S = 1) \qquad (2)$$

where $\boldsymbol{g}$ is the $\hat{\boldsymbol{g}}$ tensor, and $\hat{\boldsymbol{D}}$ the fine structure tensor with principal values of $-X$, $-Y$, and $-Z$, the other symbols having their usual meanings. When the radical has the property of a triplet having no axial symmetry, we usually observe three pairs of absorption lines, from whose separations the zero-field parameters (D and E) of the spin-spin dipolar interaction can be obtained.[11] In the case of biradical (IV), five out of the six lines theoretically expected for a non-axially symmetrical triplet are resolved (Fig. 4). In the spectrum, the intensity of the low-field line of the inner pair of lines is higher than the other, suggesting the overlapping of two lines. A central line at $g = 2$ is attributable to the monoradical impurity, since the relative intensity of central line decreases when the PbO_2 oxidation proceeds from monoradical to biradical. Separation values between the three pairs of turning points (X, X'; Y, Y'; and Z, Z') in the spectrum of the biradical are 70.8 ± 0.6, 42.6 ± 0.6, and 27.0 ± 0.6 G, respectively. They correspond to $2D$, $D+3E$, and $D-3E$. The D and E values were estimated to be $D = 35.4 \pm 0.3$ G and $E = 2.6 \pm 0.3$ G, respectively. Assuming that the principal axes of the $\boldsymbol{D}$- and $\boldsymbol{g}$-tensors are coaxial, $\boldsymbol{g}$-tensor values have been estimated from the positions of three pairs of turning points (X, X'; Y, Y'; and Z, Z').[11–13] They are $g_{xx} = 2.0045 \pm 0.0002$ (X, X'), $g_{yy} = 2.0051 \pm 0.0002$ (Y, Y'), and $g_{zz} = 2.0024 \pm 0.0002$ (Z, Z'). The average g_{av} value of $1/3(g_{xx} + g_{yy} + g_{zz}) = 2.0040 \pm 0.0002$ agrees with the isotropic g_{iso}-value (2.00414 ± 0.00003) measured at 20 °C, indicating that the $\boldsymbol{g}$-tensor values obtained by the above analyses are reliable.

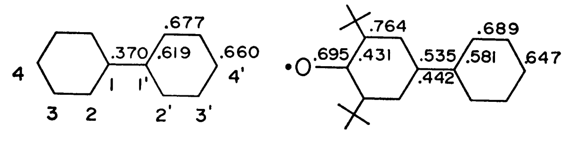
Discussion

The Structure of Aryloxyl Monoradicals. McLachlan spin densities (ρ_i) of the aryloxyl radical (I) were calculated, varying the twist angle θ_{AB} between the phenyl rings A and B. The MO parameters were given the values $\alpha_O = \alpha + 1.3\beta$, $\beta_{CO} = 1.5\beta$, and $\lambda = 1.2$.[14] The results are shown in Fig. 5. Comparing these spin densities and the experimental values calculated from the hyperfine splittings, the best accordance was found for the twist angle $\theta_{AB}=0°$ (Table 1). Thus, spin densities (ρ_i) were calculated, in the case of the aryloxyl radical (III), holding one twist angle θ_{AB} at 0° and varying the other twist angles θ_{BC} and θ_{CD}; here we used the same MO parameters, $\alpha_O=\alpha+1.3\beta$, $\beta_{C-O}=1.5\beta$, for the oxygen atom (O_1), and the parameters $\alpha_{OH}=\alpha+0.9\beta$, $\beta_{C-OH}=0.4\beta$ for the oxygen atom of the OH group.[15] The results show that a very small unpaired spin density (lower than 1.5%) exists in the C and D rings, the spin density distribution not being sensitively affected by varying the twist angles θ_{BC} and θ_{CD}. The spin densities obtained for the structure $\theta_{AB}=\theta_{CD}=0°$, $\theta_{BC}=30°$ of the radical molecule (III) (Table 1) also show good agreement with those obtained from the hyperfine splittings of the radical (III).

The aryloxyl radical (I) may be considered to be a biphenyl derivative; the molecule of biphenyl is planar or nearly so in both the solid and triplet state, but twisted 30—40° around the central single bond in the vapor phase and in solution.[16] Thus, the degree of twisting of biphenyl molecule is clearly due to a delicate balance of non-bonded repulsion and conjugation. On the other hand, it is obvious that the inter-ring bond acquires some double-bond character in the aryloxyl radical (I) in view of a valence-bond. This is apparent in the quinoid valence structures (iv) and (v) for the aryloxyl radical (I):



We reach a similar conclusion by calculating the bond orders due to the Hückel molecular-orbital, the result for aryloxyl radical (I) indicating that the 1—1′ and 2—3 bonds are strengthened and the 1—2 and 3—4 bonds weakened as compared to biphenyl molecule.



All the results indicate that the aryloxyl radical (I) has planar character.

***D*-Tensor Calculation with Spin Densities.** In order to clarify the molecular structure of the 4,4′-(biphenyl-3,3′-diyl)bis(aryloxyl) biradical (IV), and determine the directions of the principal axes, X_d, Y_d, and Z_d, of the **D**-tensor in the molecule (Figs. 6 and 8), calculations of the dipolar splitting tensors were performed for the assumed molecular structures using McLachlan spin densities of the aryloxyl radical (I).

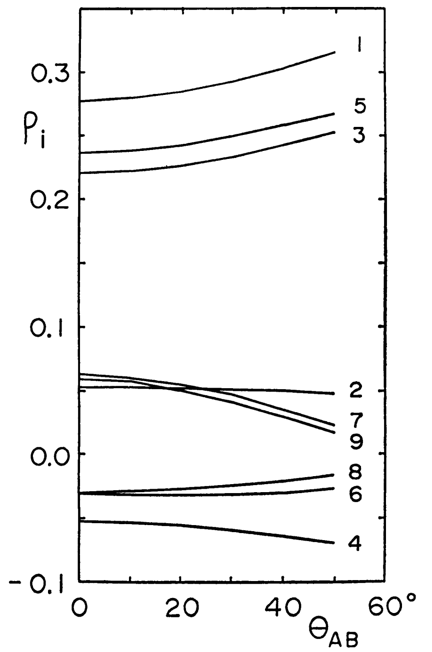


Fig. 5. Dependence of McLachlan MO spin densities (ρ_i) of carbon and oxygen atoms in aryloxyl radical (I) on twist angle θ_{AB}.

Bis(aryloxyl) (IV) is thought to be a weakly π-conjugated biradical consisting of two aryloxyl monoradical parts. The values of the hyperfine splittings of the ring protons and the isotropic g_{iso} value of the monoradical precursor (III) of the bis(aryloxyl) show an excellent agreement with the corresponding values of the aryloxyl (I), that is, a monoradical half of the biradical (Table 1). No hyperfine splitting arising from the protons in C and D rings was observed even by the ENDOR measurement with resolution higher than that of ESR measurement.[17] The results of McLachlan MO calculation of the radical (III) also supported the above anticipation, showing the existence of very small unpaired electron density (1.0—1.5%) in the C and D rings. Therefore, the dipolar magnetic system of the bis(aryloxyl) biradical may be adequately described as

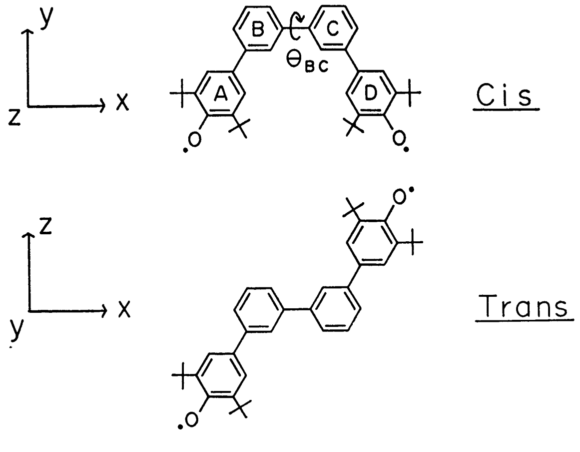


Fig. 6. Molecular structures and the coordinate systems (right-handed systems) chosen for "cis" and "trans" conformations of the 4,4′-(biphenyl-3,3′-diyl)bis(aryloxyl) biradical (IV).

an isolated two-spin system consisting of two aryloxyl groups, each containing one unpaired electron.

Aryloxyl monoradical parts of the bis(aryloxyl) (IV) seem to be planar in solution. Thus, as a most plausible case, the ***D***-tensor values have been calculated, assuming that $\theta_{AB}=\theta_{CD}=0°$ and varying θ_{BC}. Molecular structures and the coordinate systems (x, y, and z) chosen for "cis" and "trans" conformations of the bis(aryloxyl) biradical (IV) are shown in Fig. 6, where $\theta_{BC}=0°$ corresponds to a planar "cis" conformation, and $\theta_{BC}=180°$ is a planar "trans" conformer. In the planar "cis" conformation, 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 molecule[13,18] (Fig. 8). By varying the twist angle θ_{BC}, we can expect that the Y_d axis still coincides with the molecular y axis, but the X_d axis is parallel to the line inclined θ_x from the molecular x axis within xz plane.

In such a case, the ***D***-tensor components of the dipolar splitting can be calculated with the aid of the following equations.[13,19,20]

$$D_{mm} = (1/2)g^2\beta^2\sum_{i,j}\rho_i\rho_j(r_{ij}^2-3m_{ij}^2)/r_{ij}^5, \qquad (3)$$

$$(m = x, y, z)$$

$$D_{mn} = (1/2)g^2\beta^2\sum_{i,j}\rho_i\rho_j(-3m_{ij}n_{ij})/r_{ij}^5, \qquad (4)$$

$$(m, n = x, y, z;\ \text{but}\ m \neq n)$$

where r_{ij} is the distance between the i and j atoms, and ρ_i and ρ_j are the McLachlan π-spin densities on the i atom in one aryloxyl group and the j atom in the other aryloxyl group, respectively, in a molecule. Here we have chosen the following parameters: the C–O bond length is 1.27 Å, and the C–C bond length is 1.40 Å on the average, as obtained by an X-ray analysis of the galvinoxyl radical.[21] The resulting tensor is then diagonalized, giving the principal values *X*, *Y*, and *Z* and their directions.

Several authors have carried out such calculations for the radical pairs[19,20] and the weakly π-conjugated biradicals,[13,18,22] and obtained good agreement with experiment. However, the agreement was not satisfactory[13] when the internuclear distances between two monoradical parts are small. The discrepancy between observed and calculated zero-field splitting values depends mainly on the difference between the true and the calculated zero-field splitting values for short interatomic distances. In such a case, the electron distribution within a $2p_z$ orbital has to be represented by two half-charges located above and below the plane containing the atom. This approximation has been shown to be quite good if the separation between the half-charges is 1.4 Å even when the internuclear distances are as small as 1.6 Å.[23,24]

Therefore, we calculated the ***D***-tensor values of the bis(aryloxyl) (IV), using the above approximations ((a) "point-charge" and (b) "half-charge" approximations), and compared the results obtained. How the principal values *X*, *Y*, and *Z* of the zero-field splitting and the value of the direction cosine (cos θ_x) of the principal axis-X_d of the zero-field splitting tensor to the molecular axis-x vary as a function of θ_{BC} is shown in Figs. 7 and 8, respectively. The results indicate that, in the above two kinds of approximations, $|X|$ is the largest component of the zero-field splitting tensor and is consistent with our expectation. Thus, the zero-field parameters *D* and *E* are given by

$$D = -3X/2, \quad E = -(Y-Z)/2. \qquad (5)$$

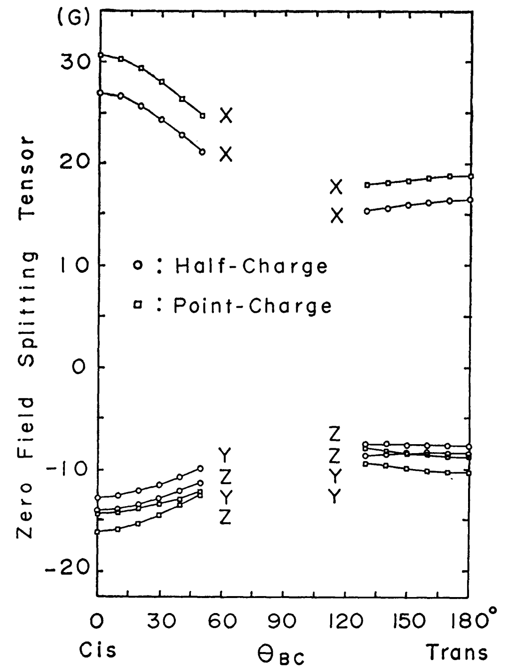


Fig. 7. The variation of the principal components of the zero-field splitting tensor as a function of the twist angle θ_{BC}.

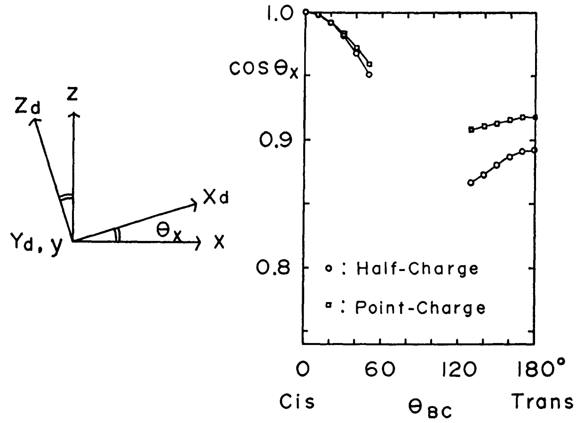


Fig. 8. The variation of the direction cosine (cos θ_x) of the pricipal axis-X_d of the zero-field splitting tensor to the molecular axis-x as a function of the twist angle θ_{BC}.

Figure 9 shows how the *D* and *E* parameters vary as functions of θ_{BC}. By comparing the observed *D*-parameter ($|D|=35.4$ G) with the calculated ones, the agreements were observed for the cases of $\theta_{BC}=35°$ in the "half-charge" approximation and $\theta_{BC}=57°$ in the "point-charge" approximation, where the θ_x values are 13° and 18°, respectively. On the other hand, in both the approximations, the absolute values of all the calculated *E*-parameters are smaller than the observed one ($|E|=2.6$ G). The absolute values of all the *D*-parameters calculated by the "point-charge" approximations are 3.6—5.4 G larger than those calculated by the "half-charge" approximation for the corresponding

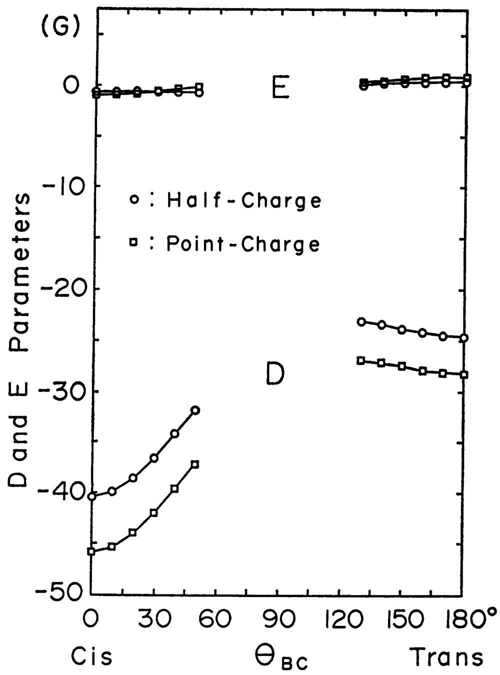


Fig. 9. The variation of the zero-field splitting parameters D and E as a function of the twist angle θ_{BC}.

twist angle θ_{BC}. For instance, in a planar "cis" conformer ($\theta_{BC}=0°$), the total D-parameters calculated are -45.8 G for the "point-charge" approximation and -40.4 G for the "half-charge" approximation, where the values of the D-parameter calculated for the nearest neighboring atoms ($C_{10B}-C_{10C}$) (Fig. 1) are -9.2 G for the former and -5.0 G for the latter. The difference (5.4 G) between the total D-parameters of the two approximations could be attributed to the difference (4.2 G) obtained for the nearest neighboring atoms (C_{10B}-C_{10C}). The results indicate that the "point-charge" approximation is unsatisfactory for the calculation of **D**-tensor value of the radical molecule with short interatomic distance, such as 1.4 Å, and the "half-charge" approximation improves the calculation considerably.

Two sets of ESR spectra of the lowest excited triplet state of 2,2′-bipyridyl in poly(vinyl alcohol) (PVA) films have been observed.[25] They are interpreted to be due to its "cis" and "trans" conformations from the experimental and theoretical viewpoints, since the molecular structure in the triplet state is considered to be planar. Similar phenomena have also been observed for 3,3′-dimethylbiphenyl and 3,3′-difluorobiphenyl in rigid glass.[26,27] On the other hand, the bis(aryloxyl) biradical (IV) is considered to be a biphenyl (B and C rings) derivative. Thus, we can expect similar conformations, "cis" and "trans" forms, in the bis(aryloxyl) biradical (VI). However, the frozen-solution ESR spectrum of the bis(aryloxyl) in toluene (Fig. 4) suggests that only one conformer exists in the biradical. If two conformers exist in the aryloxyl biradical at the same time, we should, at least, observe a splitting in the X and/or X′ absorption lines as the results of calculation of the D and E parameters indicate. Although the **D**-tensor calculation presented here is of a very approximate nature for the bis(aryloxyl) biradical, the result indicates that the bis(aryloxyl) biradical has "cis" conformation rather than "trans."

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