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Environment Effect on the Symmetry of Yang's Biradical

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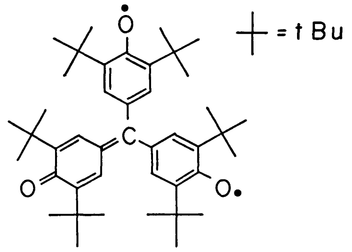
Synopsis. The ESR spectrum of Yang's biradical, which has a structural three-fold symmetry and degenerate, partially filled levels, has been measured in several solvents at 77 K. The results of the analyses of the ESR spectra have shown that Yang's biradical must lack a three-fold symmetry in frozen solutions. The notable solvent effects observed for the zero-field splitting parameters (D and E) suggest that the asymmetric environment due to frozen-solvent molecules contributes to the molecular distortion found for Yang's biradical.

Yang and Castro have reported the preparation of a fairly stable phenoxyl biradical, which is known as Yang's biradical (I).[1)] Yang's biradical is a ground-state triplet molecule which has a structural three-fold symmetry and degenerate, partially filled levels.[2–4)] However, recently, the toluene rigid matrix ESR spectrum of Yang's biradical was reported to be a characteristic spectrum of a non-axially symmetrical triplet, with $D=34.1$ and $E=2.3$ G.[5)] This result may be explained by assuming that at least one of the twist angles of the three phenyl rings is different from the other two rings in the low-temperature rigid matrix. It is probable that the Jahn-Teller effect induces such molecular distortion in Yang's biradical, thus splitting the degenerate, partially filled levels. In addition to the above Jahn-Teller distortion, the asymmetric environment due to frozen solvent molecules may contribute to the molecular distortion found for Yang's biradical in the low-temperature rigid matrix. In fact, recent ENDOR studies[6)] of phenylgalvinoxyl and some of its derivatives in fluid solutions and ESR studies[7)] of *p*- and *m*-phenylenebis(galvinoxyl) biradicals in frozen solutions have given evidence that solvent molecules may play an important role in fixing the conformation and symmetry of the radical in both fluid and frozen solutions.



Yang's Biradical (I)

On the other hand, the fluid-solution ESR spectrum of Yang's biradical shows seven equally spaced lines, due to the six equivalent protons in the biradical.[5)] The results of NMR and ENDOR studies[8,9)] in solution also indicate that the six ring protons are magnetically equivalent, giving a hyperfine splitting for the six meta-ring protons. The expected inequivalence of the proton splitting was not observed in these measurements.

In the present work, in order to obtain further information on such molecular distortion, we have measured the ESR spectra of Yang's biradical in five solvents— ethanol, toluene, 2-methyltetrahydrofuran (2-MTHF), diethyl ether, and diglyme, and have studied the effect of solvents on the unpaired spin distribution and symmetry of Yang's biradical.

Experimental

Yang's biradical was prepared by the oxidation of the corresponding bisphenol (mp 276—278 °C) (lit, mp 278—279 °C)[1)] with alkaline potassium hexacyanoferrate (III) in diethyl ether under a nitrogen atmosphere, with the temperature kept between 5 and 10 °C, according to the method of Yang and Castro.[1)] A deep purple crystalline compound with a metallic luster was isolated from the diethyl ether layer. The ESR spectra were obtained at the X band using a JES-ME-3X spectrometer equipped with a Takeda-Riken microwave frequency counter to measure the klystron frequency. The ESR splittings were determined using $(KSO_3)_2NO$ ($a^N=13.05\pm0.03$ 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

When the solution containing the biradical is frozen into a rigid glass (77 K), one can observe some dipolar splittings. The zero-field parameters (D and E) and $\boldsymbol{g}$-tensor values have been tentatively estimated from the positions of the three pairs of turning points (ZZ′, YY′, XX′), as performed in a previous paper.[5)] Notable solvent dependences of the zero-field splitting parameters were observed in the frozen-solution spectra of the biradical; the results are summarized in Table 1. The observed D and E values are 34.6 and 1.5 G in ethanol, 34.1 and 1.9 G in toluene, 33.1 and 1.9 G in 2-MTHF, 32.7 and 4.7 G in diethyl ether, and 32.1 and 3.6 G in diglyme, respectively. The $\boldsymbol{g}$-tensor values also appear to be slightly solvent-dependent, while the observed change in the g_{iso} value of the biradical at 20 °C is negligible, as is shown in Table 1.

Since the axial spectra, *i.e.*, the spectra characterized by only one zero-field splitting parameter, D, could not be observed in any of the solvents used, Yang's biradical must lack a three-fold symmetry in these frozen solutions. In a previous paper,[5)] it was suggested that both Jahn-Teller distortion and the asymmetric environment due to the frozen-solvent molecules may contribute to such molecular distortion in Yang's biradical. The notable solvent effect observed for the zero-field param-

Table 1. $\boldsymbol{D}$- and $\boldsymbol{g}$-tensor values of Yang's biradical (I) in several solvents at 77 K

	$\lvert D\rvert^{a)}$ (G)	$\lvert E\rvert^{a)}$ (G)	$g_{zz}{}^{b)}$	g_{yy}	g_{xx}	$g_{av}{}^{c)}$	$g_{iso}{}^{d)}$
Ethanol	34.6	1.5	2.0025	2.0057	—e)	—	2.00441
Toluene	34.1	1.9	2.0026	2.0054	2.0054	2.0045	2.00451
2-MTHF	33.1	1.9	2.0025	2.0054	2.0058	2.0046	2.00443
Diethyl ether	32.7	4.7	2.0032	2.0060	—	—	2.00446
Diglyme	32.1	3.6	2.0033	2.0061	—	—	2.00442

a) The $\lvert D\rvert$ and $\lvert E\rvert$ values were calculated from the $ZZ'=2D$ and $YY'=D+3E$ separations, because the turning points, X and X', are not obvious as a result of overlapping with the central monoradical signal. The E value thus calculated is smaller than the true value, considering the overlapping of the inner two pairs of lines.[5] The experimental errors in the values of $\lvert D\rvert$ and $\lvert E\rvert$ are ±0.3 and 0.5 G respectively. b) The experimental errors in the values of g_{zz}, g_{yy}, g_{xx}, and g_{av} are ±0.0003. c) The average $g_{av}=1/3(g_{zz}+g_{yy}+g_{xx})$. d) The isotropic g_{iso}-values measured at 20 °C. The experimental errors in the values of g_{iso} are ±0.00003. e) In ethanol, diethyl ether, and diglyme solvents, the g_{xx} values could not be determined because of overlap with the central monoradical signal.

eters of Yang's biradical indicates that solvent molecules may contribute remarkably to a change in the steric structure of the radical molecule. In addition, it is interesting that this solvent effect on the symmetry of Yang's biradical is larger than the effects due to the asymmetric deuterium[5] and tertiary pentyl[11] substitutions. Yang's biradical may be considered to have a propeller configuration, with a twist angle of about 30°. Due to the delocalization of each unpaired electron, the principal Z axis of the $\boldsymbol{D}$-tensor, corresponding to the maximum $2D$ value (ZZ′), is probably parallel to the $2p_z$ orbital of the center triphenylmethyl carbon atom. Therefore, in Yang's biradical with a non-zero E value, at least one of the twist angles of the three phenyl rings is different from the other two rings in the low-temperature rigid matrices. Upon an increase in these twist angles, the D parameter will decrease and, inversely, the E parameter will increase. In fact, it can be seen from Table 1 that the decrease in the D parameter results in the increase in the E parameter.

On the other hand, the fluid solution ESR spectra of Yang's biradical in the above solvents at 20 °C appear to correspond to hyperfine interaction with the six equivalent meta-ring protons. This result can be explained as follows: (i) the biradical apparently shows an equivalent hyperfine splitting due to the rapid exchange between distorted structures, or (ii) the radical molecule retains a three-fold symmetry in fluid solutions, because the asymmetric environment due to frozen solvent molecules disappears in fluid solutions.

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