ESR Studies of Temperature Dependent Zero-field Splitting in Yang's Biradical

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Synopsis. The ESR absorptions of Yang's biradical in a few organic solvents have been studied in detail as a function of temperature, and the effect of temperature on the symmetry of the biradical molecule has been discussed on the basis of the temperature dependence of the zero-field splitting parameters.

Yang's biradical is known as a stable π-conjugated phenoxyl biradical, having a structural three-fold symmetrical axis in the molecule.[1] In the previous work, the **D**-tensor values of Yang's biradical have been determined from an analysis of its asymmetric frozen ESR spectrum.[2] The results have provided direct experimental evidence for the asymmetrical molecular distortion in Yang's biradical. On the other hand, in fluid solution the biradical molecule still retains a three-fold symmetry; the results of ESR, NMR, and ENDOR studies[3-5] in solution indicate that the six meta-ring protons are magnetically equivalent, giving a hyperfine splitting attributable to the six meta-ring protons. In the present work, the ESR absorptions of Yang's biradical in a few organic solvents have been studied in detail as a function of temperature, and the effect of temperature on the symmetry of the biradical molecule has been discussed on the basis of the temperature dependence of the zero-field splitting (ZFS) parameters.

Results and Discussion

The toluene rigid matrix ESR spectrum of Yang's biradical shows a characteristic spectrum of a non-axially symmetrical triplet, with $|D|=34.1$ G and $|E|=1.9$ G at 77 K (see Fig. 1(c)).[2] In the low temperature region between −196 and −140 °C, the ESR spectra remain almost unchanged upon variation of the temperature. When the samples were warmed to the higher temperatures, the decrease in the separation between the Z and Z′ lines and the sharpening of both the XY and X′Y′ lines have been observed until the typical triplet spectra become unobservable, as shown in Figs. 1(a) and (b). By recooling the samples to 77 K, it was confirmed that the change in the ESR spectra is reversible. A similar temperature effect on the triplet ESR spectra has also been observed in ethanol and 2-MTHF (2-methyltetrahydrofuran). The ZFS parameters $|D|$ and $|E|$ calculated from the observed spectra[2] are given in Table 1 and Fig. 2. In the low temperature region, the ZFS parameters show no detectable change. At higher temperature, the decrease in D is 10—20% and the decrease in E is 50—60% for the organic solvents used in the present work.

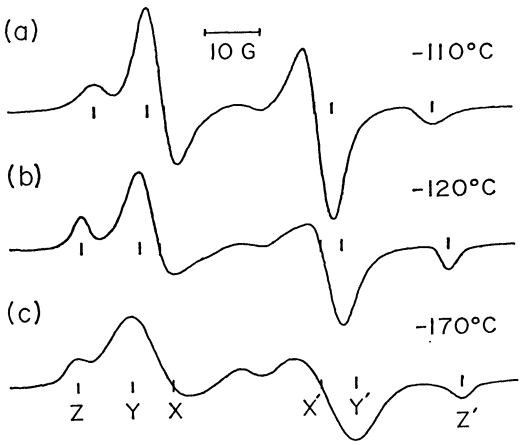


Fig. 1. Temperature dependence of the ESR absorption of Yang's biradical in toluene.
(a): −110 °C, (b): −120 °C, (c): −170 °C.

The Yang's biradical is thought to have a fixed structure in the low temperature region, because the ZFS parameters D and E show no detectable change. On warming with a consequent softening of the matrix, the D value decreases, for instance, from 34.1 G at −196 °C to 30.1 G at −110 °C in toluene. We think that one possible reason for the temperature dependence of D may be the rotation of the phenyl rings in Yang's biradical.[6] If one considers the rotation of the three phenyl rings, the average twist angle of each phenyl ring is increased as the temperature is raised. This would result in an increased average separation between the two unpaired electrons and a consequent decrease in the value of D.

At 77 K where Yang's biradical is trapped rigidly in the organic solvent matrices, the molecule has a distorted propeller structure with a non-zero E value,

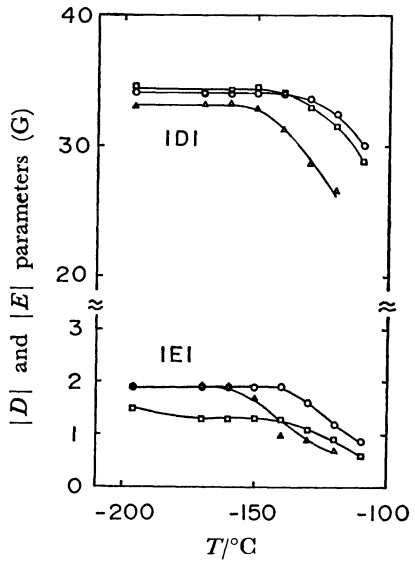
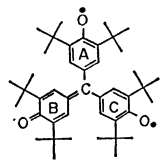


Fig. 2. Temperature dependence of the ZFS parameters $|D|$ and $|E|$ of Yang's biradical in toluene (○), ethanol (□), and 2-MTHF (△).

Table 1. The $|D|$ and $|E|$ values of Yang's biradical in toluene, ethanol and 2-MTHF at various temperatures

T/°C	Toluene		Ethanol		2-MTHF	
	$\|D\|$[a]/G	$\|E\|$[a]/G	$\|D\|$/G	$\|E\|$/G	$\|D\|$/G	$\|E\|$/G
−110	30.1	0.9	28.9	0.6	—	—
−120	32.5	1.2	31.5	0.9	26.6	0.7
−130	33.6	1.6	33.0	1.1	28.7	0.9
−140	34.0	1.9	34.1	1.3	31.3	1.0
−150	34.0	1.9	34.5	1.3	32.9	1.7
−160	34.0	1.9	34.2	1.3	33.4	1.9
−170	34.0	1.9	34.0	1.3	33.2	1.9
−196	34.1	1.9	34.6	1.5	33.1	1.9

a) The $|D|$ and $|E|$ values were calculated from the $ZZ'=2D$ and $YY'=D+3E$ separations. The E value thus calculated is smaller than the true value, considering the overlaping of the inner two pairs of lines.[2] The experimental errors in the values of $|D|$ and $|E|$ are ± 0.2 and 0.4 G, respectively. $1\,G=10^{-4}\,T$.



Yang's Biradical

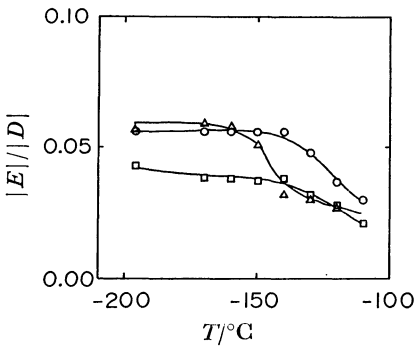


Fig. 3. Temperature dependence of the ratio of $|E|/|D|$ of Yang's biradical in toluene (○), ethanol (□), and 2-MTHF (△).

because of the asymmetric environment due to the frozen-solvent molecules. Although both the D and E values decrease with increasing temperature, the 50—60% decrease in E with increasing temperature is large compared with the 10—20% decrease in D. Among the ZFS parameters, D measures the average distance between electrons. On the other hand, E measures the deviation of the molecule from three-fold or higher symmetry weighted by this distance. Therefore, the ratio E/D provides a measure of the deviation from a structure of high symmetry. In Fig. 3, the ratio E/D is plotted as a function of temperature. The ratio E/D is constant in the low temperature region, but decreases rapidly with increasing temperature at higher temperature region (approaching the melting point of the solvent). This result may be explained by assuming that the degree of molecular asymmetry was decreased with increasing temperature. At the higher temperatures, the decrease in the rigidity of solvent matrix should allow the guest biradical molecule to assume its preferred geometry. This fact corresponds well to the fact that the molecular asymmetry of the Yang's biradical observed at the low temperature is eliminated at room temperature.[3-5]

Yang's biradical is thought to be a derivative of trimethylenemethane (TMM) $(\cdot CH_2)_2C{=}CH_2$, which also has structural three-fold symmetry. Therefore, in TMM biradical, we can expect similar temperature dependent variation in the D and E parameters. However, in the low temperature matrices, TMM shows the characteristic spectrum of an axially symmetrical triplet molecule, with $D=254$ G and $E=0$ G.[7] On the other hand, the decrease in D value of TMM with increasing temperature has been found,[8] and, in addition, the splitting of the XY lines at temperatures above 77 K has been observed,[9] using the deuterium derivative of the TMM, $(\cdot CD_2)_2C{=}CD_2$; the results suggest that the TMM molecule lacks a three-fold symmetry at the high temperature region. Recently, Claesson *et al.*[10] have proposed that the change in D value and the deviation from axial symmetry can be attributed to an anisotropic temperature dependent oscillation about a preferred axis in the TMM plane, from the results of the single crystal study of the triplet TMM molecule. Such a difference in the temperature dependence of the ZFS parameters between the small TMM molecule and the large Yang's biradical molecule is interesting.

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