# NOTES

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## ESR Study of the *t*-Pentyl Derivative of Yang's Biradical

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**Synopsis.** An asymmetrical *t*-pentyl derivative of Yang's biradical was prepared, and the ***g***- and ***D***-tensor values of the biradical were determined from an analysis of an asymmetric ESR spectrum of a frozen solution containing the biradical. The result may be understood by assuming that the benzene ring onto which two pentyl groups are substituted is twisted more than the other two benzene rings. On the other hand, the fluid solution ESR spectrum shows seven hyperfine splittings due to six equivalent meta ring protons in the three benzene rings of the pentyl derivative.

Yang's biradical (I) is a ground-state triplet molecule which has structural three-fold symmetry and degenerate partially-filled levels.[1,2] The evidence for the triplet state (S=1) has been demonstrated by the ESR observation of zero-field splitting in rigid media.[3,4] The triplet ground state has actually been confirmed by susceptibility measurements,[5] that is, the susceptibility of powder samples of Yang's biradical follows the Curie-Weiss law with a paramagnetic Curie constant of 1.0 K·emu/mol and a Weiss constant of −4 K in the temperature region between 4.2 and 300 K. In a previous paper, Mukai *et al.* analyzed the toluene rigid-matrix ESR spectrum of Yang's biradical, obtained with $D=34.1$ G and $E=2.3$ G,[6] as the characteristic spectrum of a non-axially symmetrical triplet. This result was explained by assuming that at least one of the twist angles of the three benzene rings is different from the other two rings in the low-temperature rigid matrix. It was suggested that both Jahn-Teller distortion and the asymmetric environment due to frozen solvent molecules may contribute to such a molecular distortion in Yang's biradical. In that publication, the effect of asymmetric deuterium substitution on molecular distortion in Yang's biradical was also reported, indicating that the effect is negligible.

In work reported here, for the purpose of obtaining further information about the molecular distortion, a less symmetrical di-*t*-pentyl derivative (see Fig. 1(a)) of Yang's biradical was synthesized, and the effect of the pentyl substitution on the unpaired spin distribution and symmetry of Yang's biradical was studied.

### Experimental

2,6-Di-*t*-butylphenol is commercially available. 2,6-Di-*t*-pentylphenol (bp 100—110 °C/2 mmHg) was synthesized by the reaction of phenol with 2-methyl-2-butene in the presence of aluminium phenoxide as a catalyst in an autoclave according to the method of Kolka *et al.*[7] The bisphenol precursor of the di-*t*-pentyl derivative (see Fig. 1(a)) of Yang's biradical was synthesized from 2,6-di-*t*-butylphenol and 2,6-di-*t*-pentylphenol, following a method similar to that used with the bisphenol precursor of Yang's biradical.[1] Mp 245—247 °C. Found: C, 82.55; H, 10.15%. Calcd for $C_{45}H_{66}O_3$: C, 82.53; H, 10.16%. UV spectrum ($\lambda_{max}=266$ nm, $\log\varepsilon=4.24$; 412 nm, $\log\varepsilon=4.57$ in cyclohexane).

ESR spectra were obtained in the X band using a JES-ME-3X spectrometer equipped with a Takeda-Riken microwave frequency counter, which was used 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 $(KSO_3)_2NO$ ($g=2.0054$).[8]

### Results and Discussion

The initial slight oxidation of the bisphenol precursor of the di-*t*-pentyl derivative of Yang's biradical in toluene gives a five line hyperfine pattern ($a^H_m=1.30\pm0.04$ G and $g_{iso}=2.00442\pm0.00003$) due to the equivalent four meta ring protons of the monoradical precursor. As the oxidation process proceeds further, the spectrum of the monoradical is altered to a seven-line spectrum with an equivalent splitting constant of $a=0.86\pm0.04$ G and with $g_{iso}=2.00447\pm0.00003$, as shown in Fig. 1(b). This spectrum is believed to be due to the magnetically equivalent six meta ring protons of the di-*t*-pentyl derivative of Yang's biradical. The $g_{iso}$-value for the pentyl derivative is in good agreement with that ($g_{iso}=2.00451\pm0.00003$) for Yang's biradical.[6] The hyperfine splitting constant ($a^H_m$) due to the meta ring hydrogen atoms of the pentyl derivative is also the same as that ($a^H_m=0.91\pm0.04$) for Yang's biradical, to within experimental error.

When a solution containing the biradical is frozen into rigid glass at 77 K, one can observe dipolar splittings, as is shown in Fig. 2. Assuming non-axial symmetry, the zero-field splitting parameters *D* and *E* and the ***g***-tensor values were tentatively estimated from the

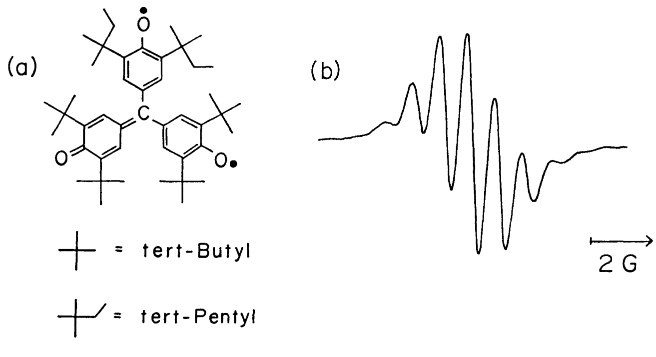

Fig. 1. (a) Molecular structure of the di-*t*-pentyl derivative of Yang's biradical, and (b) ESR spectrum of the biradical in toluene at 20 °C.

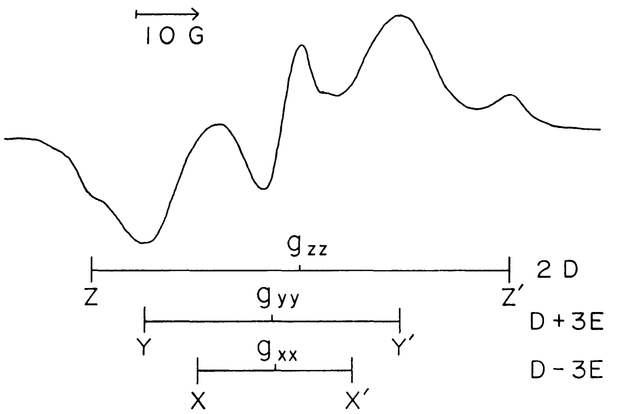

Fig. 2. ESR spectrum of the di-*t*-pentyl derivative of Yang's biradical in toluene at 77 K.

positions of the three pairs of turning points $ZZ'$, $YY'$, and $XX'$ in Fig. 2, as performed for Yang's biradical in Ref. 6. The separation of the two outermost lines ($ZZ'$) is $2D=66.6\pm0.4$ G. Due to the delocalization of each unpaired electron, the principal $Z$-axis of the $\boldsymbol{D}$-tensor, corresponding to a maximum separation $2D$, is probably parallel to the $2p_z$ orbital of the center triphenylmethyl carbon atom. The remaining pairs, $YY'$ and $XX'$ ,are separated by $(D+3E)=40.6\pm1.2$ G, and $(D-3E)=24.5\pm1.2$ G, respectively. The $E$ values calculated from the separations ,$YY'$ and $XX'$, assuming $D=33.3$ G, are 2.4 and 2.9 G, respectively. These values will give lower and higher limits of the $E$ value, considering the overlapping of the two inner pairs of lines. The average value is $E=2.7\pm0.4$ G. Corresponding separations for Yang's biradical are $ZZ'=68.3\pm0.4$ G, $YY'=40.0\pm1.2$ G, and $XX'=26.0\pm1.2$ G, respectively.[6] The experimental errors in the absolute values of these separations were estimated by considering the overlapping of the lines. On the other hand, comparing the rigid-matrix ESR spectra of Yang's biradical and its pentyl derivative, the relative decrease in the $ZZ'=2D$ separation and the relatively small increase in the $YY'=D+3E$ separation in the pentyl derivative compared to those of Yang's biradical are obvious. Therefore, it appears reliable that the values, $D=33.3$ G and $E=2.7$ G, show a relatively small decrease and increase, respectively, compared with the values ($D=34.1$ G and $E=2.3$ G) for Yang's biradical reported previously. The frequency centers of these three pairs of absorption lines, $ZZ'$, $YY'$, and $XX'$, give $g_{zz}=2.0025\pm0.0002$, $g_{yy}=2.0053\pm0.0002$, and $g_{xx}=2.0050\pm0.0002$, respectively. The average $g_{\rm av}=1/3(g_{xx}+g_{yy}+g_{zz})=2.0043\pm0.0002$ is in agreement with the isotropic $g_{\rm iso}=2.00447\pm0.00003$ value measured at room temperature, indicating that the $\boldsymbol{g}$-tensor values obtained by the above analysis are consistent.

Yang's biradical may be considered to be triphenylmethyl derivatives. A molecular model indicates that the main steric interaction in Yang's biradical operates between the ring protons, although weak interactions can be seen between the substituted tertiary butyl groups. Thus, the radical most probably adopts a propeller configuration, with a twist angle of about 30°.[2] By substituting a tertiary pentyl group for the tertiary butyl group, the steric interaction between the substituted groups increases to some extent. Consequently, the benzene ring onto which the pentyl groups are substituted will be twisted more than the other two benzene rings. This results in a decrease in the $D$-parameter and an increase in the $E$-parameter in the pentyl derivative in comparison to those for Yang's biradical. Therefore, in addition to both Jahn-Teller distortion and the asymmetric environment due to the frozen solvent molecules, as is observed for Yang's biradical, the asymmetric pentyl substitution may also contribute to the molecular distortion found for the pentyl derivative of Yang's biradical in the low-temperature rigid matrix.

On the other hand, the fluid-solution ESR spectrum of Yang's biradical exhibits seven equally-spaced lines due to the six equivalent protons in the biradical.[3,6] The results of NMR and ENDOR studies[4,9] in solution also indicate that the six ring protons are magnetically equivalent, resulting in a hyperfine splitting for the six meta ring protons. The ESR spectrum of the pentyl derivative at 20 °C also appears to correspond to the hyperfine interaction with six equivalent meta ring protons. The difference in the proton splittings for the pentyl derivative is expected to be less than the line widths.

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