Effect of Methyl Substitution on the Electron Spin Resonance Spectra of Yang's Biradical

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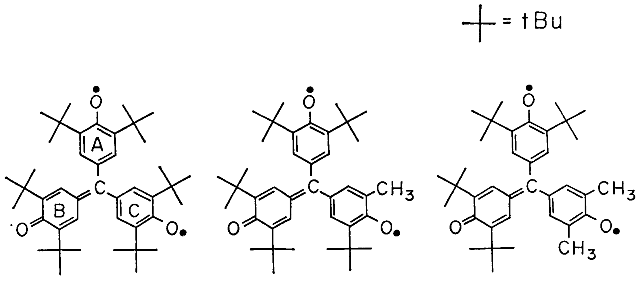
Mono- and dimethyl derivatives (II) and (III) of Yang's biradical (I) were prepared, and the methyl-substitution effects on the molecular symmetry and spin-density distribution of Yang's biradical have been studied. Resolved hyperfine structures were observed in the ESR spectra of liquid solutions of the biradicals (II) and (III), giving the hyperfine splitting values theoretically expected for their triplet states. In a fluid solution, the biradical molecules retain a three-fold symmetry, as has been reported for Yang's biradical, and the expected methyl-substitution effect is too small to induce any asymmetric, unpaired spin distribution. The **g**- and **D**-tensor values of the (II) and (III) biradicals were determined from analyses of the asymmetric ESR spectra of frozen solutions containing the biradicals. The results suggest that these biradicals must also lack a three-fold symmetry in a frozen solution, as has been observed for Yang's biradical. Essentially the same **g**- and **D**-tensor values as those of Yang's biradical are observed for the monomethyl derivative (II). On the other hand, the dimethyl derivative (III) shows quite different **g**- and **D**-tensor values.

Yang's biradical (I) is known as a fairly stable phenoxyl biradical; it has a structural three-fold symmetry and doubly degenerate non-bonding orbitals, each being half-filled.[1,2] This implies the possible existence of a triplet ground state ($S=1$), which has actually been confirmed by susceptibility measurements.[3] The fluid-solution ESR spectrum shows seven hyperfine splitting due to six equivalent *meta*-ring protons in the three benzene rings of the biradical.[4] The results of NMR[5] and ENDOR[6] studies in solution also indicate that the six *meta*-ring protons are magnetically equivalent, giving a hyperfine splitting attributable to the six *meta*-ring protons. However, the toluene rigid matrix ESR spectrum of Yang's biradical was recently reported to be a characteristic spectrum of a non-axially symmetrical triplet, with $|D|=34.1$ and $|E|=2.3$ G.[7] This result may be 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. 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.[8] In the previous papers, the effects of asymmetric deuterium and *t*-pentyl substitution on molecular distortion in Yang's biradical were also reported, indicating that the effects are negligible for the former and small for the latter.[7,9]



Yang's Biradical 1Me-Yang's Biradical 2Me-Yang's Biradical

Fig. 1. Molecular structures of Yang's biradical (I), 1Me-Yang's biradical (II), and 2Me-Yang's biradical (III).

In the present work, in order to obtain further information on such molecular distortion, we have prepared the two methyl derivatives (hereafter called as the 1Me- and 2Me-Yang's biradicals (II) and (III); see Fig. 1) of Yang's biradical by the PbO$_2$ oxidation in toluene of the corresponding bisphenol precursors. The isotropic hyperfine splittings and **g**- and **D**-tensor values of these biradicals have been determined from their solution and asymmetric frozen ESR spectra respectively. The results provide direct experimental evidence for the symmetry and electronic structure of these radicals. The isotropic hyperfine splittings of the monoradical precursors of the (I), (II), and (III) biradicals have also been determined by means of their solution ESR spectra and compared with those of the corresponding biradicals.

In general, the effect of the methyl substitution on the unpaired spin distribution in free radicals, including phenoxyl radicals, is very small. However, as has been shown in ESR[10] and NMR[11] studies of the benzene anion and its methyl derivatives, the effect can be significant if the orbital ground state of the parent free radical is two-fold degenerate and if methyl substitution, by lowering the symmetry, removes the degeneracy. A notable methyl substitution effect has also been observed in ENDOR studies[12] of the pentaphenylcyclopentadienyl neutral radical, which has doubly degenerate non-bonding orbitals. By the asymmetric methyl substitution of Yang's biradical, therefore, we can expect a change in the unpaired spin distribution (the asymmetric spin distribution) and a lifting of the degeneracy.

Results and Discussion

Solution ESR Spectra of 1Me- and 2Me-Yang's Biradicals (II) and (III). As has been described in previous papers,[7–9] the oxidation product of the bisphenol precursor (bisphenol (I)) of Yang's biradical with PbO$_2$ in toluene in a sealed, degassed system initially gives a quintet ESR spectrum ($a_m^H=1.32\pm 0.04$ G) attributable to the four equivalent *meta*-ring protons of the monoradical precursor. After further

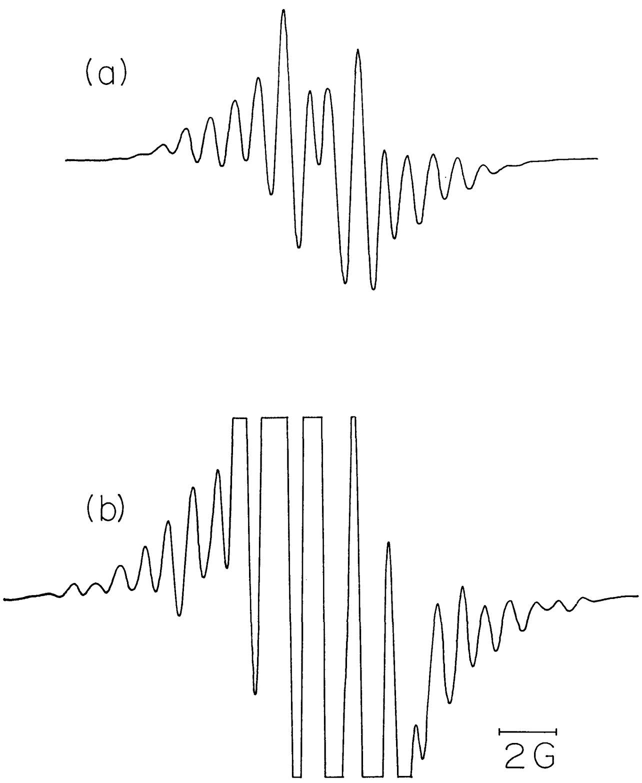


Fig. 2. Solution ESR spectra of (a) 1Me-Yang's biradical (II) and (b) 2Me-Yang's biradical (III) in toluene at 20 °C. Each spectrum includes a quintet signal due to remaining monoradical impurity.

oxidation, a five-line spectrum of the monoradical is altered to a seven-line spectrum of Yang's biradical, with an equivalent splitting constant of $a_{\rm m}^{\rm H}=0.91\pm 0.04$ G.[4,7]

The initial partial oxidation of the bisphenol (II), the bisphenol precursor of the 1Me-Yang's biradical (II), gives ESR spectra consisting of (i) a central strong quintet and (ii) weak quartet-quintet patterns on both sides of the central quintet. The spectra are thought to be attributable to the two kinds of monoradicals (AB- and BC-types) produced when the oxidation proceeds from the A and C hydroxyphenyl rings in the bisphenol precursor respectively; the former monoradical is very stable, while the latter is unstable, disappearing within about 30 minutes at 20 °C. The spectra are readily analyzed, giving $a_{\rm m}^{\rm H}=1.30\pm0.04$ G for the (II-AB) monoradical and $a_{\rm CH_3}^{\rm H}=4.07\pm0.04$ G and $a_{\rm m}^{\rm H}=1.36\pm0.04$ G for the (II-BC) monoradical. As the oxidation proceeds further, the spectra of the two monoradicals are altered into a sixteen-line absorption signal which may be attributed to the 1Me-Yang's biradical (II). As this biradical is unstable, ESR measurements were performed on several samples, under slightly different conditions of oxidation, in order to obtain a better ESR spectrum. The best spectrum obtained is shown in Fig. 2(a). However, the spectrum indicates that a quintet signal caused by a monoradical impurity still remains. The sixteen-line absorption signal of the (II) biradical may be explained by three protons ($a_{\rm CH_3}^{\rm H}=2.59\pm0.04$ G) of a methyl group and six equivalently interacting protons ($a_{\rm m}^{\rm H}=0.86\pm0.04$ G) at the meta positions.

Table 1. Hyperfine splittings of Yang's biradical (I), the 1Me-Yang's biradical (II), and the 2Me-Yang's biradical (III), and their monoradical precursors (AB- and BC-types) in toluene at 20 °C (G)

	Biradical		Monoradical precursors		
			AB-type	BC-type	
	$a_{\rm m}^{\rm H}$ a)	$a_{\rm CH_3}^{\rm H}$	$a_{\rm m}^{\rm H}$	$a_{\rm m}^{\rm H}$	$a_{\rm CH_3}^{\rm H}$
Yang's (I)	0.91	—	1.32	1.32	—
1Me-Yang's (II)	0.86	2.59	1.30	1.36	4.07
2Me-Yang's (III)	0.86	2.58	1.31	1.30	4.05

a) The experimental errors in the values of $a_{\rm m}^{\rm H}$ and $a_{\rm CH_3}^{\rm H}$ are ±0.04 G.

Similarly, the oxidation of bisphenol (III), the bisphenol precursor of the 2Me-Yang's biradical (III), initially gives ESR spectra consisting of (i) a strong quintet and (ii) a weak septet-quintet splitting; the spectra are attributable to the two kinds of monoradicals (III-AB and -BC) produced when the oxidation proceeds from the A and C hydroxyphenyl rings in the bisphenol precursor respectively. The hyperfine splittings ($a_{\rm m}^{\rm H}=1.31\pm0.04$ G) and ($a_{\rm CH_3}^{\rm H}=4.05\pm 0.04$ G, $a_{\rm m}^{\rm H}=1.30\pm0.04$ G) were observed for the (III-AB) and (III-BC) monoradicals respectively. After further oxidation, the ESR spectra of the two monoradicals were altered to an ESR spectrum, as is shown in Fig. 2(b). This spectrum may be explained by considering the contribution from both an absorption signal of the (III) biradical and a central strong quintet signal of the remaining monoradical. The stability of the (III) biradical with two methyl groups is even less than is the case for the (II) biradical, which has one methyl group, disappearing within about 20 minutes at 20 °C. The hyperfine splittings obtained for the (III) biradical are $a_{\rm CH_3}^{\rm H}=2.58\pm0.04$ G and $a_{\rm m}^{\rm H}=0.86\pm0.04$ G, arising from six protons of two methyl groups and six magnetically equivalent *meta*-ring protons respectively. All the hyperfine splittings are listed in Table 1. The *g*-values ($g_{\rm iso}$) of these biradicals in toluene were also measured; they are listed in the last column of Table 2.

As is clear from the results listed in Table 1, the hyperfine splittings obtained for the monoradical precursors (AB- and BC-types) of Yang's biradical and its methyl derivatives in solution are equivalent to each other as resolved by the ESR experiments. The hyperfine splitting constants of Yang's biradical and its methyl derivatives in a fluid solution also show a good agreement with each other within the limits of experimental error. As has been observed for the benzene anion and its methyl derivatives,[10,11] the methyl-substitution effect can be significant if the two-fold degeneracy of the parent free radical is lifted by asymmetrical methyl substitution. Yang's biradical (I) has a structural three-fold symmetry and is orbitally degenerate.[2] By asymmetric methyl substitution, therefore, we can expect a lifting of the degeneracy, and thus a change in the unpaired spin dis-

Table 2. *D*- and *g*-tensor values of Yang's biradical (I), the 1Me-Yang's biradical (II), and the 2Me-Yang's biradical (III) in toluene at 77 K

	$\lvert D\rvert$[a)]/G	$\lvert E\rvert$[a)]/G	g_{xx}[b)]	g_{yy}	g_{zz}	g_{av}[c)]	g_{iso}[d)]
Yang's (I)	34.1	2.3	2.0054	2.0054	2.0026	2.0045	2.00451
1Me-Yang's (II)	34.2	2.2	2.0052	2.0055	2.0030	2.0046	2.00447
2Me-Yang's (III)	23.3	1.4	2.0046	2.0041	2.0035	2.0040	2.00457

a) The experimental errors in the values of $\lvert D\rvert$ and $\lvert E\rvert$ are ±0.2 and 0.4 G respectively. 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 ±0.00005.

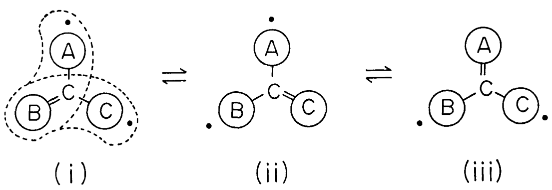


Fig. 3. Schematic representation of three valence-bond structures (i), (ii), and (iii) of the biradicals.

tribution (an asymmetric spin distribution). However, the present experimental results indicate that the expected methyl-substitution effect is too small to induce any asymmetric unpaired spin distribution in a fluid solution.

The hyperfine splitting ($a^{H}_{m}=0.91$ G) of the *meta*-ring protons of Yang's biradical is nearly two-thirds of the splitting ($a^{H}_{m}=1.32$ G) observed for the monoradical precursor. Similar results were observed for the 1Me- and 2Me-Yang's biradicals, (II) and (III). For instance, in the (III) biradical, the predicted values for the hyperfine splittings of the *meta*-ring protons and methyl protons from those of the monoradical precursor (III-BC) are 0.87 G and 2.70 G, while the observed values are 0.86 G and 2.58 G, respectively. The relative ratio (2/3) of the hyperfine splitting constants of the biradicals to the monoradicals can be predicted on the basis of simple resonance theory, as follows: one can, in principle, schematically draw three valence-bond structures, (i), (ii), and (iii) (see Fig. 3) for each biradical under study. The (i) structure is considered to be a strongly π-conjugated biradical consisting of two galvinoxyl groups (AB- and BC-types), with two unpaired electrons in a molecular orbital, in which the B ring is common to both monoradical-AB and -BC. If the nucleus, X, is in the B ring, the splitting constant ($a^{bi}_{i\text{-}B}$) in the biradical will be the arithmetic average of the splitting constants from the monoradical-AB and -BC, as was proposed by Kopf *et al.*:[13)]

$$a^{bi}_{i\text{-}B}=\frac{1}{2}(a^{mono}_{AB}+a^{mono}_{BC})$$

If X is in the A ring (which is not included in the monoradical-BC), $a^{mono}_{BC}=0$, thus:

$$a^{bi}_{i\text{-}A}=\frac{1}{2}a^{mono}_{AB}$$

Similarly, for the splitting constant ($a^{bi}_{i\text{-}C}$) of the C ring,

$$a^{bi}_{i\text{-}C}=\frac{1}{2}a^{mono}_{BC}$$

For the (ii) and (iii) structures, the hyperfine splittings may be similarly represented, using the hyperfine splittings of the monoradical. If the (i), (ii), and (iii) structures are equally probable, the hyperfine splitting (for instance, a^{bi}_{A}) of a given nucleus, X, in the A ring of the biradical may be represented, taking the contribution from the three valence-bond structures, as:

$$\begin{aligned}a^{bi}_{i\text{-}A}&=\frac{1}{3}(a^{bi}_{i\text{-}A}+a^{bi}_{ii\text{-}A}+a^{bi}_{iii\text{-}A})\\&=\frac{1}{3}\left\{\frac{1}{2}a^{mono}_{AB}+\frac{1}{2}a^{mono}_{AC}+\frac{1}{2}(a^{mono}_{AB}+a^{mono}_{AC})\right\}\\&=\frac{2}{3}a^{mono}_{AB}\end{aligned}$$

This is what is experimentally observed for the methyl and *meta*-ring protons of the (I), (II), and (III) biradicals, as has been described above; the observed hyperfine splittings for the biradicals agree exceedingly well with those calculated from the corresponding monoradicals, thus strongly supporting the above explanation.

Rigid Matrix ESR Spectra of the 1Me- and 2Me-Yang's Biradicals (II) and (III). The observation and detailed analysis of the rigid matrix ESR spectrum of Yang's biradical have been reported in a previous paper.[7)] When the bisphenol precursor (bisphenol (II)) of the 1Me-Yang's biradical (II) was oxidized with PbO_2 in toluene under a vacuum, the yellow-brown color of the phenol solution immediately became the yellow-orange of the (II-AB) and (II-BC) monoradicals. Upon further oxidation, the color was changed to yellow-green. By quickly freezing the yellow-green solution containing the (II) biradical into a rigid glass (77 K), one can observe some dipolar splittings, as is shown in Fig. 4(b). The spectrum consists of two pairs of lines disposed about $g=2$ and a weak line at $g=2$ from the monoradicals. As has been described in a previous section, the (II) biradical is unstable at 20 °C; thus, the ESR observations were performed for several samples in order to minimize the central monoradical signal and in order to get a better spectrum. The best spectrum obtained is shown in Fig. 4(b). This spectrum remained unchanged after a period of several hours at 77 K. Upon annealing at 20 °C for 30 min, however, the yellow-green color disappeared along with the biradical signal. The spectrum of the 1Me-Yang's biradical shows a shape essentially the same as that of Yang's biradical (see Fig. 4(a)), except for the difference

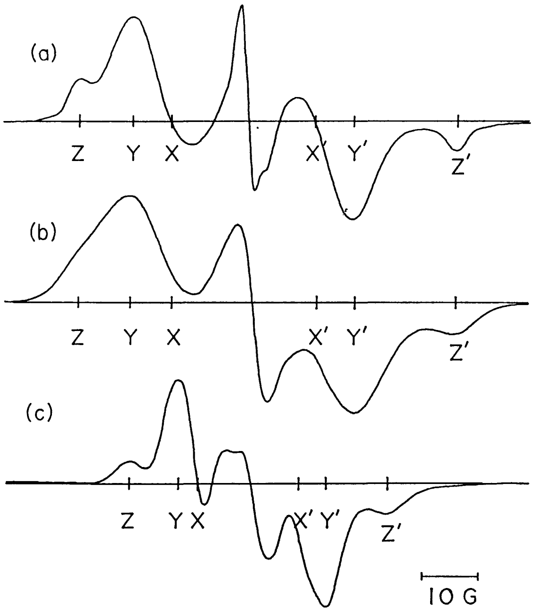


Fig. 4. Rigid matrix ESR spectra of (a) Yang's biradical (I), (b) 1Me-Yang's biradical (II), and (c) 2Me-Yang's biradical (III) in toluene at 77 K.

in the central monoradical intensity and the increase in the linewidth of each absorption line. The position and separation of the signals of the 1Me-Yang's biradical are quite similar to those of Yang's biradical. The zero-field splitting 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', and XX'), as performed for Yang's biradical in a previous paper. These values are $D=34.2\pm0.2$ G, $E=2.2\pm0.4$ G, $g_{zz}=2.0030\pm0.0002$, $g_{yy}=2.0055\pm0.0002$, and $g_{xx}=2.0052\pm0.0002$. The average, $g_{av}=1/3(g_{xx}+g_{yy}+g_{zz})=2.0046\pm0.0002$, is in agreement with the isotropic $g_{iso}=2.00447\pm0.00005$ value measured at room temperature, indicating that the $\boldsymbol{g}$-tensor values obtained by the above analysis are consistent. Similarly, the toluene rigid-matrix ESR spectrum of the 2Me-Yang's biradical (III) has been measured. The ESR spectrum of the 2Me-Yang's biradical at 77 K is very different from those of Yang's biradical and the 1Me-Yang's biradical, as is shown in Fig. 4(c). The zero-field parameters and $\boldsymbol{g}$-tensor values were similarly estimated from the three pairs of turning points (ZZ', YY', and XX'), giving the values of $D=23.3\pm0.2$ G, $E=1.4\pm0.4$ G, $g_{zz}=2.0035\pm0.0002$, $g_{yy}=2.0041\pm0.0002$, $g_{xx}=2.0046\pm0.0002$, and $g_{av}=2.0040\pm0.0002$. The observed $\boldsymbol{D}$- and $\boldsymbol{g}$-tensor values of these biradicals, (II) and (III), are summarized in Table 2, together with those of Yang's biradical.

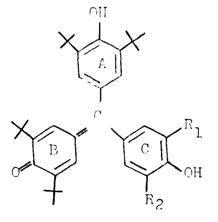
As has been described in a previous section, the results of the measurements of the solution ESR spectra of Yang's biradical (I) and its methyl derivatives (II) and (III) suggest that these radical molecules retain a three-fold symmetry in a fluid solution and show similar unpaired-spin distributions. On the other hand, since the axial spectra, *i.e.*, the spectra characterized by only one zero-field splitting parameter, D, could not be observed in any of these biradicals, (I), (II), or (III), these biradicals must lack a three-fold symmetry in a frozen solution. Yang's biradical and its methyl derivatives may be considered to have a propeller configuration, with a twist angle of about 30° in solution. 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 central triphenylmethyl carbon atom. Therefore, in the (I), (II), and (III) biradicals with non-zero E values, at least one of the twist angles of the three phenyl rings is different from those of the other two rings in the low-temperature rigid matrix. By substituting the methyl group for the tertiary butyl group, the steric interaction between the substituents will decrease to some extent. Consequently, the benzene ring into which the methyl groups are substituted will be twisted less than the other two benzene rings. Therefore, we can expect an increase in the D-parameter of the methyl derivatives in comparison with that of Yang's biradical.[14,15] However, in the 1Me-Yang's biradical, both the $\boldsymbol{g}$- and $\boldsymbol{D}$-tensor values are in good agreement with those of Yang's biradical. This, together with the results obtained in solution ESR spectra, gives further accurate evidence that monomethyl-substitution effects for molecular symmetry and spin-density distribution are negligible in Yang's biradical.

On the other hand, in the dimethyl derivative (III) of Yang's biradical, the change in the $\boldsymbol{D}$- and $\boldsymbol{g}$-tensor values is very remarkable. However, in contrast to the above expectation (an increase in the D-parameter), the D-parameter decreased 10.8 G compared to that (34.1 G) of Yang's biradical, suggesting an increase in the twist angle. In fact, the increase in the g_{zz} value and the decreases in the g_{yy} and g_{xx} values observed for the 2Me-Yang's biradical may also be explained by the increase in the twist angle. A notable solvent effect has been observed for the zero-field parameters of Yang's biradical; for instance, the D- and E-parameters vary from $D=34.6$ G and $E=1.5$ G in ethyl alcohol to $D=32.1$ G and $E=3.6$ G in diglyme.[8] The results suggest that the asymmetric environment due to frozen solvent molecules may contribute remarkably to a change in the conformation of the radical molecule. However, the change in the D-parameter of the 2Me-Yang's biradical is more remarkable than that due to the solvent effect. The reason why dimethyl-substitution effects are negligible in a fluid solution, while they are very remarkable in a frozen solution, is not clear at present.

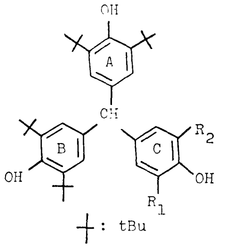
Experimental

Measurements. The 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 $(KSO_3)_2NO$ ($g=2.0054$).[16] The proton magnetic resonance spectra were recorded on a JEOLCO 4H-100 100 MHz spectrometer. The NMR spectra were measured in a C_6D_6 solvent, with tetramethylsilane as the internal standard.

Preparation of Specimens. The bisphenol and trisphenol precursors of Yang's biradical (I) and its methyl derivatives (II) and (III) were prepared according to a procedure similar to that used by Yang and Castro.[1] The condensation of 2,6-di-*t*-butylphenol, 2-*t*-butyl-6-methylphenol, and 2,6-dimethylphenol with 2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-hydroxybenzylidene)-2,5-cyclohexadien-1-one[17,18] in H_2SO_4–CH_3COOH gave a solid mixture of the bisphenol and the trisphenol, respectively. The mixture was separated by silica-gel-column chromatography (using benzene as the eluent). The subsequent removal of the benzene from bisphenol solution left a brick-red crystalline solid; this was heated at 160 °C for 5 h under a vacuum (0.1 Torr) to remove the solvent completely. The evaporation of the benzene from the trisphenol solution left pale yellow crystals, which were subsequently recrystallized twice from ethyl alcohol.



Bisphenol (I), $R_1=R_2=t$Bu
Bisphenol (II), $R_1=t$Bu, $R_2=CH_3$
Bisphenol (III), $R_1=R_2=CH_3$



Trisphenol (I), $R_1=R_2=t$Bu
Trisphenol (II), $R_1=t$Bu, $R_2=CH_3$
Trisphenol (III), $R_1=R_2=CH_3$

Bisphenol (I). Mp 278.5—280.5 °C, brick red crystals; UV max 434 nm (log ε 4.50) in tetrahydrofuran; NMR 1.32 (36 H, s, *t*Bu, rings A and C), 1.54 (18 H, s, *t*Bu, ring B), 5.30 (2 H, s, OH), 7.53 (4H, s, aromatic H, rings A and C), 7.77 ppm (2H, s, aromatic H, ring B). Found: C, 82.30; H, 10.10%. Calcd for $C_{43}H_{62}O_3$: C, 82.83; H, 9.97%.

Trisphenol (I). Mp 241.0—242.0 °C, pale yellow crystals; UV max 278 nm (log ε 3.77) in cyclohexane; NMR 1.35 (54 H, s, *t*Bu), 4.87 (3 H, s, OH), 5.70 (1 H, s, CH), 7.43 ppm (6H, s, aromatic H). Found: C, 81.61; H, 10.54%. Calcd for $C_{43}H_{64}O_3$: C, 82.11; H, 10.26%.

Bisphenol (II). Mp 269.0—271.0 °C, brick red crystals; UV max 432 nm (log ε 4.46) in tetrahydrofuran; NMR 1.32 (18 H, s, *t*Bu, ring A), 1.47 (9 H, s, *t*Bu, ring C), 1.53 (18 H, s, *t*Bu, ring B), 1.59 (3 H, s, CH_3), 4.58 (1H, s, OH, ring C), 5.30 (1 H, s, OH, ring A), 7.10 (1 H, s, aromatic H neighboring the methyl group), 7.52 (2 H, s, aromatic H, ring A), 7.55(1 H, s, aromatic H neighboring the *t*-butyl group, ring C), 7.73 ppm (2 H, s, aromatic H, ring B). Found: : C, 82.04; H, 9.79%. Calcd for $C_{40}H_{56}O_3$: C, 82.14; H, 9.65%.

Trisphenol (II). Mp 213.5—214.5 °C, pale yellow crystals; UV max 278 nm (log ε 3.78) in cyclohexane; NMR 1.37 (36 H, s, *t*Bu, rings A and B), 1.51 (9H, s, *t*Bu, ring C), 1.64 (3H, s, CH_3), 4.12 (1 H, s, OH, ring C), 4.87 (2 H, s, OH, rings A and B), 5.62 (1 H, s, CH), 7.02 (1 H, s, aromatic H neighboring the methyl group, ring C), 7.38 (1 H, s, aromatic H neighboring the *t*-butyl group, ring C), 7.40 ppm (4H, s, aromatic H, rings A and B). Found; C, 81.60; H, 10.12%. Calcd for $C_{40}H_{58}O_3$: C, 81.86; H, 9.96%.

Bisphenol (III). Mp 270.0—271.5 °C, brick red crystals; UV max 430 nm (log ε 4.44) in tetrahydrofuran; NMR 1.33 (18 H, s, *t*Bu, ring A), 1.51 (9 H, s, *t*Bu, ring B), 1.53 (9H, s, *t*Bu, ring B), 1.90 (6 H, s, CH_3, ring C), 4.37 (1 H, s, OH, ring C), 5.28 (1 H, s, OH, ring A), 7.11 (2H, s, aromatic H, ring C), 7.50 (2 H, s, aromatic H, ring A), 7.70 ppm (2 H, s, aromatic H, ring B). Found: C, 81.77; H, 9.52%. Calcd for $C_{37}H_{50}O_3$: C, 81.87; H, 9.29%.

Trisphenol (III). Mp 170.5—172.0 °C, pale yellow crystals; UV max 278 nm (log ε 3.77) in cyclohexane; NMR 1.37 (36 H, s, *t*Bu, rings A and B), 1.91 (6 H, s, CH_3), 3.95 (1H, s, OH, ring C), 4.88 (2 H, s, OH, rings A and B), 5.59 (1 H, s, CH), 7.05 (2 H, s, aromatic H, ring C), 7.38 ppm (4H, s, aromatic H, rings A and B). Found: C. 81.58; H, 9.83%. Calcd for $C_{37}H_{52}O_3$: C, 81.57; H, 9.62%.

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