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ESR Studies of a New Stable π-Conjugated Bisaryloxyl Biradical

Kazuo Mukai,* Tsukasa Hara, and Kazuhiko Ishizu
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790

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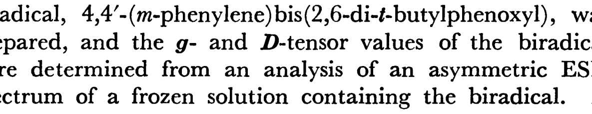
Synopsis. The new stable π-conjugated bisaryloxyl biradical, 4,4′-(*m*-phenylene)bis(2,6-di-*t*-butylphenoxyl), was prepared, and the *g*- and *D*-tensor values of the biradical were determined from an analysis of an asymmetric ESR spectrum of a frozen solution containing the biradical. A resolved hyperfine structure was observed in the ESR spectrum of a liquid solution of the biradical, giving the hyperfine splitting values theoretically expected for the triplet state of the biradical.

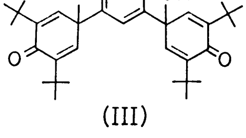
2,6-Di-*t*-butyl-4-phenylphenoxyl (aryloxyl (I)) (see Fig. 1) is a fairly stable phenoxyl radical, first prepared by Müller *et al.*, which can be separated as a solid with 90% radical concentration.[1] 4,4′,4″-(1,3,5-Benzenetriyl)tris(2,6-di-*t*-butylphenoxyl) (trisaryloxyl) is also known as a stable phenoxyl triradical prepared by Kothe *et al.*[2] The existence of a quartet state in the trisaryloxyl radical has been confirmed by ESR measurements in rigid media at 77 K.[3] These radicals can be prepared from their phenol and triphenol precursors by their PbO_2 oxidation in toluene under vacuum or nitrogen gas, respectively



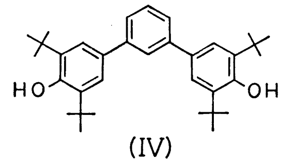
(I) (II) and (II-AB)

Fig. 1. Molecular structures of aryloxyl radical (I), bisaryloxyl biradical (II), and monoradical precursor (II-AB) of the biradical (II), and the atomic numbering system.

We have prepared the bisphenol precursor (IV) which is related to the above phenol and triphenol precursors, and have succeeded in synthesizing the corresponding π-conjugated bisaryloxyl biradical (II), 4,4′-(*m*-phenylene)bis(2,6-di-*t*-butylphenoxyl), (see Fig. 1). Zero-field splitting parameters and hyperfine splitting constants of the biradical (II) have been determined from its frozen and fluid solution ESR spectra, respectively.



(III)



(IV)

Experimental

m-*Bis(4-oxo-1-hydroxy-3,5-di-*t*-butyl-2,5-cyclohexadienyl)benzene (quinol (III)).* Quinol (III) was synthesized by a Grignard reaction of 2,6-di-*t*-butyl-*p*-benzoquinone with *m*-dibromobenzene and Mg in tetrahydrofuran (THF) under an atmosphere of nitrogen, following a method similar to that used with 4-hydroxy-2,6-di-*t*-butyl-4-phenyl-2,5-cyclohexadien-1-one.[4] The viscous reaction mixture obtained was added to an aqueous ammonia, then they were taken up in diethyl ether, washed with water, and dried over anhydrous sodium sulfate. After removal of the diethyl ether, a pasty solid remained. By adding petroleum ether (bp 50—70 °C) to the pasty residue, some white solids were precipitated. The solids were filtered off, washed with petroleum ether, and recrystallized from methyl alcohol. Mp 248—251 °C. (Found: C, 78.42; H, 9.16%. Calcd for $C_{34}H_{46}O_4$: C, 78.72; H, 8.94%). UV spectrum (λ_{max}=231 nm, log ε=4.50 in THF). NMR spectrum (δ=1.24 ppm (36 H, s, *t*Bu), 2.35 (2H, s, OH), 6.53 (4H, s, *m*-ring), 7.33 (3H, s, phenylene ring), 7.52 (1H, s, phenylene ring); δ in $CDCl_3$ with TMS as internal standard).

m-*Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)benzene (bisphenol (IV)).* Bisphenol (IV) was synthesized by reduction of quinol (III) with Zn powder and concd HCl in methyl alcohol, following the same process as that of Rieker *et al.*[4] The white solids obtained were recrystallized twice from methyl alcohol. Mp 223—225 °C. (Found: C, 82.95; H, 9.73%. Calcd for $C_{34}H_{46}O_2$: C, 83.90; H, 9.53%). UV spectrum (λ_{max}=268 nm, log ε=4.57 in THF). NMR spectrum (δ=1.53 ppm (36H, s, *t*Bu), 5.24 (2H, s, OH), 7.42 (4H, s, *m*-ring), 7.42 (3H, s, phenylene ring), 7.65 (1H, s, phenylene ring); δ in $CDCl_3$ with TMS as internal standard).

All the ESR measurements were carried out using a JES-ME-3X spectrometer equipped with a Takeda-Riken microwave frequency counter. The ESR splittings were determined using $(KSO_3)_2NO$ as a standard. The *g*-values were measured relative to the value of Li-TCNQ powder, calibrated with $(KSO_3)_2NO$ (g=2.0054).[5]

Results and Discussion

When the bisphenol precursor of the bisaryloxyl biradical (II) was oxidized with PbO_2 in toluene under vacuum, the color of the bisphenol solution immediately became purple. The ESR spectrum of this solution (see Fig. 2(a)) showed a sextet-doublet hyperfine pattern ($g_{iso}=2.00419\pm0.00003$), and we assigned the spectrum to the primary aryloxyl monoradical (II-AB) formed from the parent phenol by abstraction of a phenolic hydrogen atom. The large sextet splitting ($a^{\rm H}$=1.72±0.04 G) in the primary radical will be due to five magnetically equivalent ring protons (H_1, H_2, H_4, H_5, H_6) and the doublet splitting ($a^{\rm H}$=0.71±0.04 G) is explained by a ring proton (H_3). These hyperfine splittings and g_{iso}-value are in good agreement with those ($a^{\rm H}_{1,2,4}$=1.74±0.04, $a^{\rm H}_3$=0.74±0.04 G and g_{iso}=2.00415±0.00003) for the aryloxyl radical (I) in toluene. By further oxidation, the purple color changed to yellow-brown, and the sextet-doublet spectrum of the monoradical was altered to a twelve-line spectrum of the bisaryloxyl biradical (II) with an equivalent splitting distance of 0.86 G and with g_{iso}=2.00414±

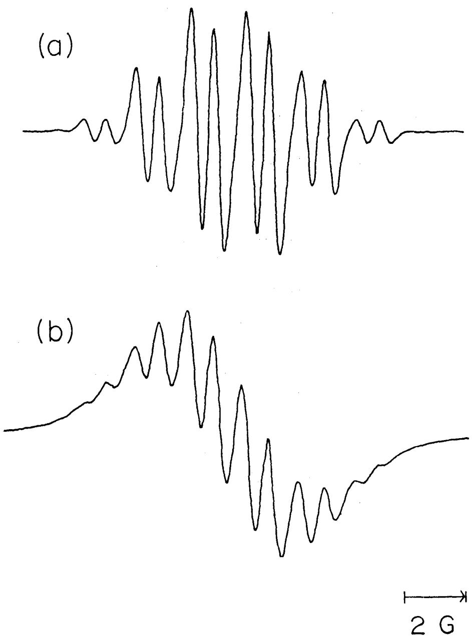


Fig. 2. (a) ESR spectrum of the monoradical precursor (II-AB) of the bisaryloxyl biradical (II) in toluene at 20 °C. (b) ESR spectrum of the bisaryloxyl biradical (II) in toluene at 20 °C.

0.00003, as shown in Fig. 2(b). The radical was stable for many weeks in toluene under vacuum at room temperature. The spectrum can be reconstructed with two sets of three and five equivalent protons ($a^H=1.72$ (3H), $a^H=0.86$ G (5H)).

Rather few triplet molecules show resolved proton hyperfine structure, because of the spin-spin dipolar broadening. The ESR spectrum of the bisaryloxyl biradical (II) shows twelve lines from the hyperfine interaction of the electrons with the eight ring protons, as described above. Kopf *et al.*[6] have proposed a simple theory to explain the hyperfine splitting of weakly π-conjugated verdazyl biradicals; their results indicate that the splitting constants of nuclei contained in rings connecting the two monoradical halves are the average of splittings from protons in corresponding positions in the monoradical, while the splitting constants for nuclei in other parts of the molecules were one-half of the monoradicals splittings. The bisaryloxyl biradical (II) is considered to be a strongly π-conjugated biradical consisting of two aryloxyl groups (AB- and BC-types) with two unpaired electrons in a molecular orbital, in which ring B is common to both monoradical-AB and -BC. Therefore, in the biradical (II), the theoretically expected values for the hyperfine splittings of the eight ring protons from those of the monoradical precursor (III-AB) are $a^H_{2,4,5}=1.72$ G (3H), $a^H_{1,6}=0.86$ G (4H), and $a^H_3=0.71$ G (1H); the observed hyperfine splittings ($a^H_{2,3,5}=1.72$ G (3H) and $a^H_{1,3,6}=0.86$ G (5H)) for the biradical (II) agree exceedingly well with the ones calculated from the monoradical precursor; this strongly supports the above explanation.

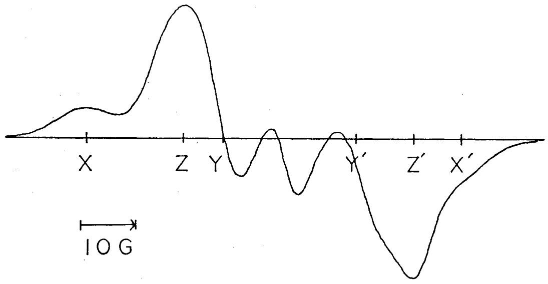


Fig. 3. ESR spectrum of the bisaryloxyl biradical (II) in toluene at 77 K.

When a solution containing the bisaryloxyl biradical (II) is frozen into glass at 77 K, one can observe dipolar splittings, as is shown in Fig. 3. A central weak line at $g=2$ is attributable to the monoradical impurity. Assuming non-axial symmetry, the zero-field splitting parameters D and E were tentatively estimated from the positions of the three pairs of turning points ZZ', YY', and XX' in Fig. 3, as performed for the bisgalvinoxyl biradicals in Refs. 7 and 8. The values are $D=34.0\pm1.0$ G and $E=3.0\pm1.0$ G. Because of the symmetry of the biradical molecule, we can expect that the principal axes of the $\boldsymbol{D}$- and $\boldsymbol{g}$-tensors are coaxial. Consequently, the frequency centers of these three pairs of absorption lines, ZZ', YY', and XX', give $g_{zz}=2.0024\pm0.0004$, $g_{yy}=2.0035\pm0.0004$, and $g_{xx}=2.0051\pm0.0004$, respectively. The average $g_{av}=1/3(g_{xx}+g_{yy}+g_{zz})=2.0037\pm0.0004$ is in agreement with the isotropic $g_{iso}=2.00414\pm0.00003$ value measured at room temperature, indicating that the $\boldsymbol{g}$-tensor values obtained by the above analysis are consistent.

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