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ESR and ENDOR Studies of the Hindered Internal Rotation of Higher Alkyl Groups. 2,6-Di-*t*-butyl-4-alkylphenoxyl Radicals

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Synopsis. ESR or ENDOR spectra were observed for the 2,6-di-*t*-butyl-4-methyl-, 4-ethyl-, 4-isopropyl-, and 4-cyclohexylphenoxyl radicals. From the analyses of the temperature dependence in β-proton splittings, the energy barriers to internal rotation of the alkyl group were estimated.

For a number of aromatic radicals, the restricted rotation of an alkyl group has been extensively studied by using ESR spectroscopy¹⁾ and the rotational barrier of an alkyl group has been estimated based on the statistical procedure of observed β-proton splitting and its temperature dependence, in terms of the $\cos^2\theta$ rule.²⁾

In previous papers,³⁾ the hindered rotation of the alkyl groups in the 4,4′-dialkybiphenyl anions was studied in detail. One interesting view is the fact that the secondary alkyl groups are likely to undergo a restricted rotation in a double-well potential function. In this work, the hindered internal rotation of the alkyl groups in the 2,6-di-*t*-butyl-4-alkylphenoxyl radicals was studied in order to affirm the validity of applying the ESR approach to the study on the restricted rotation of an alkyl group. The results obtained have been compared with those for the 4,4′-dialkylbiphenyl anions previously studied.³⁾

Experimental

General. The melting points and boiling point are uncorrected. The ESR and ENDOR spectra were recorded by JEOL-ME-3X and JEOL-EDX-1 spectrometers respectively. The operating conditions were similar to those described elsewhere.⁴⁾

Materials. The 2,6-di-*t*-butyl-4-methylphenol is commercially available. The other 2,6-di-*t*-butyl-4-alkylphenols were prepared by the method previously described.⁵⁾ 2,6-Di-*t*-butyl-4-ethylphenol: bp 105—110 °C/5 Torr (lit,⁵⁾ 135—138 °C/10 Torr), 2,6-di-*t*-butyl-4-isopropylphenol: mp 38.0—38.5 °C (lit,⁶⁾ 38—42 °C), 2,6-di-*t*-butyl-4-cyclohexylphenol: mp 97.0—98.2 °C (lit,⁵⁾ 98—99 °C).

Each phenoxyl radical was prepared *in vacuo* by the oxidation of the phenol with lead dioxide in toluene.

Computations. The numerical computations were carried out on the HITAC 8700 system in the Hiroshima University Computing Center.

Results and Discussion

The ESR spectra of the 2,6-di-*t*-butyl-4-methylphenoxyl (Radical-I),⁷⁾ 2,6-di-*t*-butyl-4-ethylphenoxyl (Radical-II),⁷⁾ 2,6-di-*t*-butyl-4-isopropylphenoxyl (Radical-III),⁸⁾ and 2,6-di-*t*-butyl-4-cyclohexylphenoxyl (Radical-IV)⁹⁾ radicals were observed. The ENDOR spectra of III and IV were measured in the temperature range from −100 °C to −60 °C.

The proton hyperfine coupling constants of these radicals, measured under the identical conditions, are summarized in Table 1. The alkyl β-proton splitting (A_4^β) of each radical was precisely measured as a function of the temperature. The β-proton splittings for II, III, and IV show a large temperature dependence (see Fig. 1). In addition, the experimental results indicate that both $A_2^{t\text{-Bu}}$ and A_3^{H} remain almost unchanged upon the variation of the temperature and that no important deviations of these coupling constants can be detected for these radicals.

As has been explained in detail in previous works,³⁾ the β-proton splitting at any temperature was calculated by using following equations:¹⁰⁾

$$A_4{}^\beta = B\rho_4{}^\pi\langle\cos^2\theta\rangle \qquad \theta = \alpha + \theta_0 \qquad (1)$$

TABLE 1. PROTON HYPERFINE COUPLING CONSTANTS OF THE 2,6-DI-*t*-BUTYL-4-ALKYLPHENOXYL RADICALS (G)

Alkyl		$A_2^{t\text{-Bu}}$	A_3^{H}	A_4^{γ}	A_4^{β}
Methyl^a)	ESR	—	1.63	—	11.22
Ethyl	ESR	0.06	1.60	—	8.21
Isopropyl	ENDOR	0.07	1.66	0.38	4.05
Cyclohexyl	ENDOR	0.08	1.60	0.60,0.47	4.09

The observed temperature is −60 °C. a) At −45 °C.

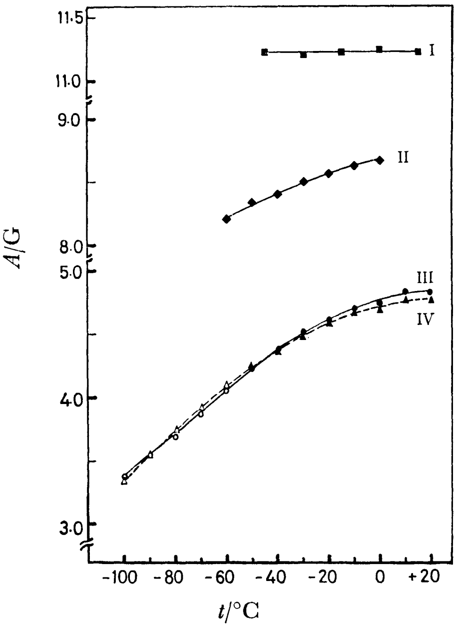

Fig. 1. Temperature dependence of the β-proton splittings observed with the 2,6-di-*t*-butyl-4-alkylphenoxyl radicals. I: Methyl, II: ethyl, III: isopropyl, IV: cyclohexyl.

■,◆,●,▲; ESR data, ○,△; ENDOR data.

$$\langle\cos^2\theta\rangle = \frac{\sum_{i=0}^{\infty}\langle\phi_i(\alpha)|\cos^2(\alpha+\theta_0)|\phi_i(\alpha)\rangle e^{-E_i/kT}}{\sum_{i=0}^{\infty}e^{-E_i/kT}} \tag{2}$$

$$-(\hbar^2/2I)(\mathrm{d}^2\phi_i/\mathrm{d}\alpha^2) + [V(\alpha) - E_i]\phi_i = 0 \tag{3}$$

where ρ_4^π is the spin density at the *p*-position and where θ is the so-called dihedral angle. The value of $B\rho_4^\pi$ was estimated to be 2×11.20 G from the methyl proton splitting of I. A free rotation is assumed for the methyl group, because the methyl proton splitting shows no detectable change throughout the entire temperature range. The moment of inertia, I, of the molecular fragment, Ar-R, can be calculated to be 5.0, 8.8, and 17 ($\times 10^{-39}$) g cm^2 for II, III, and IV respectively.

With reference to the rotational functions of the alkyl groups for the 4,4′-dialkylbiphenyl anions,[3] where the steric factor affecting the rotating alkyl groups would be identical with those considered for the alkylphenoxyl radicals, the potential barrier, $V(\alpha)$, of each alkylphenoxyl has been assumed as follows. For the ethyl group, the potential function, $V(\alpha)$, is approximately the two-fold potential (Eq. 4), and for the isopropyl and cyclohexyl groups, with a double-well potential, wherein one of the minima lies higher in energy (Eq. 5):

$$V(\alpha) = (V_0/2)((1 - \cos 2\alpha) \tag{4}$$

$$V(\alpha) = V_0\sum_{i=0}^{3} a_i \cos 2i\alpha \tag{5}$$

$$a_0 = (1/18)(9V_m/V_0+4) \qquad a_1 = -4/9$$

$$a_2 = -2/9 \qquad a_3 = (1/18)(8 - 9V_m/V_0)$$

In Eq. 4, V_0 is the energy difference between the lowest potential state (a) and the highest one (b), as displayed in Fig. 2. In Eq. 5, V_0 and V_m are the energy differences between the lowest potential at state (c) and the highest one at state (d), and between the lowest one at state (c) and the medium one at state (e), respectively, as is illustrated in Fig. 2. At the most stable conformation, each of the equilibrium dihedral angles, θ_0, is equal to $\pi/3$, $\pi/2$, and $\pi/2$ for II, III, and IV respectively (see Fig. 2). The Hamiltonian matrix $\langle i|\mathscr{H}|j\rangle$ was diagonalized by expanding the wave function into a Fourier series.

We have calculated the temperature dependence of the $\langle\cos^2\theta\rangle$ as a function of the potential barriers, V_0 and V_m, for these radicals. The best agreement between the calculated and experimental temperature dependences of $\langle\cos^2\theta\rangle$ is obtained with the choice of $V_0=1.1$, $V_0=1.6$, $V_m=0.7$, $V_0=1.6$, and $V_m=0.7$ kcal/mol as the parameters for II, III, and IV respectively. Thus, each potential barrier obtained for the phenoxyl radicals coincides with the one for the 4,4′-dialkylbiphenyl anions, furthermore, these values agree with those obtained from the calculation of the non-bonded interaction between the rotating alkyl group and the aromatic protons[3] (see Table 2).

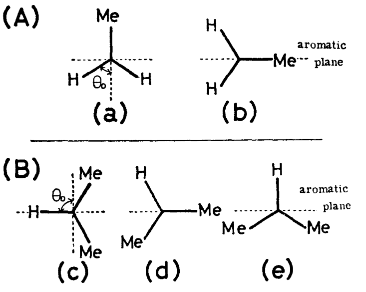

Fig. 2. Conformations of the alkyl groups in the 2,6-di-*t*-butyl-4-alkylphenoxyl radicals.
A: Ethyl, B: isopropyl, and cyclohexyl.

Table 2. The values of rotational barriers for the 2,6-di-*t*-butyl-4-alkylphenoxyl and 4,4′-dialkylbiphenyl anion radicals (kcal/mol)

	Alkyl	$\langle\cos^2\theta\rangle$	V_0	V_m
Phenoxyl	ethyl	0.37 (at −60 °C)	1.1	—
	isopropyl	0.18 (at −60 °C)	1.6	0.7
	cyclohexyl	0.18 (at −60 °C)	1.6	0.7
Biphenyl anion	ethyl	0.36 (at −90 °C)	1.0	—
	isopropyl	0.21 (at −85 °C)	1.2	0.5
	cyclohexyl	0.20 (at −85 °C)	1.2	0.6
Non-bonded interaction energy[3]	ethyl	—	1.3	—
	isopropyl	—	1.4	0.7

From the above results, we concluded that the ethyl group attached to the benzene ring may undergo a restricted rotation in the two-fold potential, which has a barrier height of 1.0—1.2 kcal/mol, and that the rotation of isopropyl and cyclohexyl groups restricted in a double-well potential, which has, as potential barrier heights, $V_0=1.2$—1.6 and $V_m=0.6$—0.7 kcal/mol. These results, furthermore, suggest that the rotational barrier of the alkyl group is mainly due to the steric repulsion between the rotating alkyl group and the neighbouring aromatic ring protons in the case of both anion and neutral free radicals.

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