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An ENDOR Study of the Hindered Internal Rotation of the Cyclopropyl Group in the 2,6-Di-*t*-butyl-4-cyclopropylphenoxyl Radical

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The ESR and ENDOR spectra were observed for the 2,6-di-*t*-butyl-4-cyclopropylphenoxyl radical. The assignments of the proton hyperfine coupling constants were confirmed with reference to those of the 2,6-di-*t*-butyl-4-methyl- and 4-(1-deuteriocyclopropyl)phenoxyl radicals. The β-proton hyperfine coupling constant for the cyclopropyl group and its temperature dependence were precisely determined. Of particular interest is the fact that the observed cyclopropyl β-proton splitting is smaller than the γ-proton splittings (A_4^β: 0.72, $A_4^{\gamma_1}$: 0.83, $A_4^{\gamma_2}$: 1.44 G at −70 °C). Based on the modified $\cos^2\theta$ rule, $A_4^\beta=(1.85\langle\cos^2\theta\rangle-0.10)\times A_4^{Me}$, where the conjugative interaction between the π-system and the cyclopropyl pseudo π-orbital was incorporated, as proposed by Hudson and Bauld, the β-proton splitting was evaluated. The magnitude of the β-proton splitting and its temperature dependence were interpreted in terms of the restricted rotation of the cyclopropyl group in a two-fold potential; the stable conformation was the bisected one. The rotational barrier height, which corresponds to the difference in energy between the bisected and perpendicular conformations, was estimated to be 2.6 kcal/mol. The rotational barrier was attributed to the stabilization of the bisected conformation arising from the conjugative interaction of the aromatic and cyclopropyl moieties.

It has been well-known for a long time that a cyclopropyl group has a stronger π-conjugative ability than the other alkyl groups,[1] and so the behaviour of a cyclopropyl group in chemical reactions has been of interest. For example, accelerations by a cyclopropyl group have been observed in the reactions which proceed *via* a cationic intermediate.[2] The results have been explained in terms of the conjugative stabilization effect of a cyclopropyl group for the intermediate. This effect is greatly affected by the conformation of the cyclopropyl group.[3] On the other hand, the double-bond character of a cyclopropane ring and its electronic structure have been investigated in detail. Several models of the bond system in cyclopropane have been proposed by several authors.[4] The Walsh model of the chemical bonds in cyclopropane, which is a typical model, suggests that the conjugative interaction between the pseudo π-orbital of the cyclopropyl ring and the phenyl π-system is at its maximum when the molecule adopts the bisected conformation in which C_1–H_β bond of the cyclopropyl ring lies on the aromatic plane (Fig. 1). Indeed, the conformational investigations of the cyclopropylbenzene by using NMR spectroscopy support the above expectation.[5]

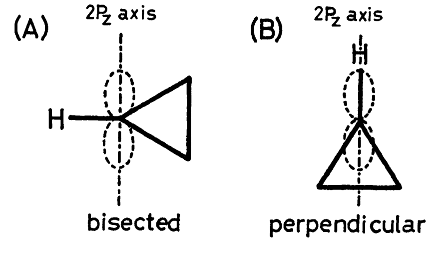

Fig. 1. Conformations of the cyclopropyl group in the 2,6-di-*t*-butyl-4-cyclopropylphenoxyl radical.
(A) Bisected conformation, (B) perpendicular conformation.

It has been established that the internal rotation of an alkyl group can be studied for the various free radicals on the basis of the ESR and ENDOR techniques. For a number of aromatic radicals, the rotational barrier of an alkyl group has been estimated by the Heller-McConnell relationship[6] with the aid of some statistic procedures treating the observed β-proton splitting and its temperature dependence. Particularly, the hindered internal rotations of alkyl groups in the 4,4′-dialkylbiphenyl anion radicals[7] and the 2,6-di-*t*-butyl-4-alkylphenoxyl radicals[8] have been reported in previous papers.

In the present paper, from an analysis of the temperature dependence of the β-proton splitting on the basis of the modified $\cos^2\theta$ rule,[9] the hindered internal rotation of the cyclopropyl group in the 2,6-di-*t*-butyl-4-cyclopropylphenoxyl radical has been studied. The comparison of the results thus obtained with those for the other 2,6-di-*t*-butyl-4-alkylphenoxyl radicals[8] has been made with the purpose of examining the effect of the cyclopropyl group on the aromatic neutral radical. In this radical series, the spin density on the carbon atom of the phenoxyl moiety to which an alkyl group is attached is expected to be generally high. If this is so, the cyclopropyl β-proton splitting as well as its temperature dependence may be precisely determined. Therefore, this phenoxyl radical may be adequate for this study.

Results

ESR Spectra. The ESR spectra of the 2,6-di-*t*-butyl-4-cyclopropylphenoxyl radical (Radical-H) and the 2,6-di-*t*-butyl-4-(1-deuteriocyclopropyl)phenoxyl radical (Radical-D), generated by the lead-dioxide oxidation of the corresponding phenols,[10] in toluene were observed in the temperature range from −80 °C to 20 °C. As is shown in Fig. 2, the pattern of the ESR spectrum observed for the Radical-H varied with the change in the temperature, while that for the Radical-D remained unchanged. These results imply that the magnitude of the cyclopropyl β-proton hy-

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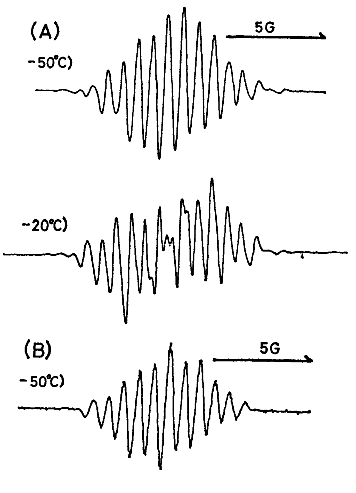


Fig. 2. ESR spectra of the Radical-H and Radical-D. (A) Radical-H, (B) Radical-D.

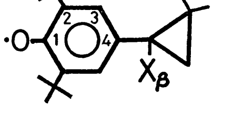
perfine coupling constant is strongly dependent on the temperature. The hyperfine coupling constants, however, could not be determined precisely because of the poorly resolved ESR spectrum.

ENDOR Spectra. The ENDOR spectrum of the Radical-H at −70 °C, shown in Fig. 3 (A), was composed of five signals in the upper half of the spectrum. With reference to the hyperfine splittings for the 2,6-di-*t*-butyl-4-alkylphenoxyl radicals,[8] the signals at 13.91 and 16.21 MHz could be assigned to the splittings due to the *t*-butyl protons and two protons at the 3-positions of the phenoxyl moiety respectively. The signal corresponding to the cyclopropyl β-proton splitting, at 14.84 MHz, was easily assigned with reference to the ENDOR spectrum of the Radical-D, as is shown in Fig. 3 (B). The other signals, at 15.01 and 15.81 MHz, were then assigned to those due to the non-equivalent pair of cyclopropyl γ-proton splittings. The analyzed hyperfine coupling constants of the Radical-H, Radical-D, and related phenoxyl radicals are summarized in Table 1. As may be seen in Fig. 3 (A), the β-proton splitting for the Radical-H showed a large positive temperature dependence. The temperature dependence of these hyperfine coupling constants for the Radical-H is depicted in Fig. 4.

In comparing the coupling constants for the Radical-H with those for the 2,6-di-*t*-butyl-4-alkylphenoxyl radicals,[8] the following interesting facts may be pointed out:

(1) The magnitude of the β-proton coupling constant for the cyclopropyl group was much smaller than those for the other alkyl groups, but its temperature dependence was considerably large.

(2) The magnitudes of the non-equivalent γ-proton coupling constants were several times as large as that for the 2,6-di-*t*-butyl-4-isopropylphenoxyl (isopropylphenoxyl) radical.



Radical-H (X_β=H)
Radical-D (X_β=D)

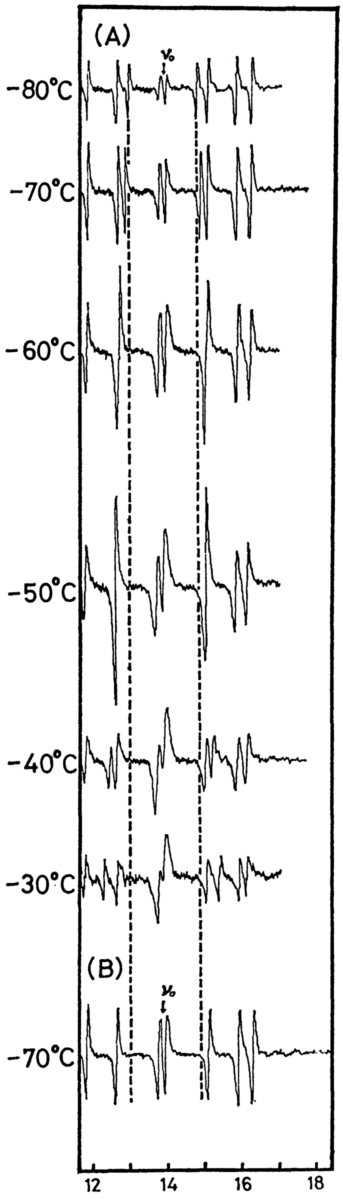


Fig. 3. ENDOR spectra of the Radical-H and Radical-D; the free proton frequency is designated with ν_0. The ENDOR signal arising from the β-proton is lost in the spectrum (B).

Discussion

Magnitude of the β-Proton Splitting. In the previous works on the 4,4′-dialkylbiphenyl radical anions and the 2,6-di-*t*-butyl-4-alkylphenoxyl (alkylphenoxyl) radicals, the magnitude of the β-proton splitting was interpreted in connection with the steric interaction between the aromatic ring protons and the rotating alkyl group.[7,8] From this point of view, the β-proton splitting for the Radical-H may resemble to that for the isopropylphenoxyl radical, because both the skeletal composition and the size of a cyclopropyl group seem to be similar to those of an isopropyl group. In fact, the β-proton splitting for the 4,4′-dicyclopropylbiphenyl anion was 3.31 G[11,12] (1 G$=10^{-4}$ T) and that for the 4,4′-diisopropylbiphenyl anion was 2.78 G[7] at −90

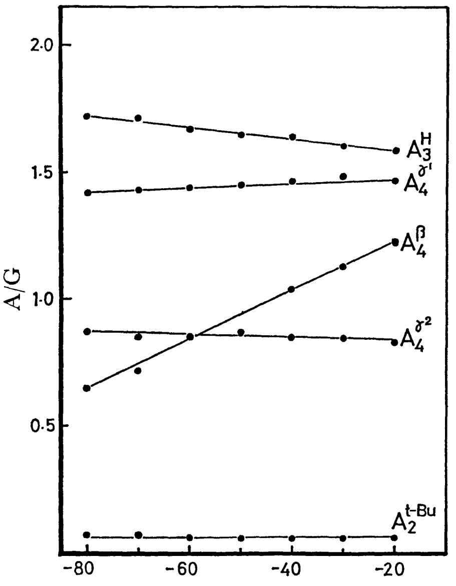


Fig. 4. Temperature dependence of the hyperfine coupling constants for the Radical-H.

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^{β}	$A_4^{\gamma1}$	$A_4^{\gamma2}$	A_4^{β}/A_4^{Me}	Ref.
Me	—	1.63	11.22	—	—	1.00	8
Et	0.06	1.60	8.21	—	—	0.73	8
i-Pr	0.07	1.66	4.05	0.38	—	0.36	8
c-He	0.08	1.60	4.09	0.60	0.47	0.36	8
c-Pr	0.07	1.70	0.83	1.44	0.83	0.07	
c-Pr-d_1	0.06	1.68	a)	1.43	0.86	—	

The Data at −60 °C.
a) The ENDOR signal disappeared.

°C. The results were in line with the above expectation. However, the observed β-proton splitting for the Radical-H deviated greatly from the expectation, as has been described in the previous section (see Table 1). This discrepancy could not be explained solely in terms of the steric interaction model.

The small value of the β-proton splitting, which is remarkably distinct from that for the 4,4′-dicyclopropylbiphenyl anion, suggests that the cyclopropyl group in the Radical-H strongly prefers the bisected conformation (Fig. 1-A). That may be attributed to the conjugative interaction between the aromatic and cyclopropyl moieties.

Similar observations have been reported in earlier works. In the semidiones, the β-proton splitting of the cyclopropyl group was one-tenth as large as that of the methyl group.[13] For the cyclopropylmethyl radicals, the β-proton splitting was much smaller than that for the methyl substituent.[14] In aromatic radicals, the β-proton splitting for the 4,4′,4″-tricyclopropyltriphenylmethyl radical was one-sixth that of methyl-substituted analogue.[11] These observations were interpreted in terms of the propensity of the bisected conformation for the cyclopropyl group.

Temperature Dependence of the β-Proton Splitting. The magnitude of a β-proton splitting is often calculated using the following equations:

$$A^{\beta} = \langle Q(\theta)\rangle \rho^{\pi}, \tag{1}$$

and:

$$Q(\theta) = B_0 + B_2 \cos^2\theta, \tag{2}$$

where B_0 and B_2 are empirical parameters, ρ^{π} is the spin density on the aromatic-ring carbon attached to an alkyl group, and θ is the angle between the axis of the $2p_z$ orbital and the C–H$_{\beta}$ bond of the alkyl group, both projected on the plane perpendicular to the bond between the methine carbon of the alkyl group and the aromatic carbon. The term of $\langle\cos^2\theta\rangle$ is the quantum mechanical average of $\cos^2\theta$ over the appropriate rotational wave functions.

For the cases of the alkylphenoxyl radicals (alkyl; Et, *i*-Pr, and *c*-He), Eq. 1 was successfully approximated to Eq. 3 on the basis of the following assumptions:[8] (1) The values of $A_2^{t\text{-Bu}}$ (*t*-butyl proton splitting) and A_3^{H} (phenoxyl-ring proton splitting) for the above phenoxyl radicals were nearly the same as that for the 2,6-di-*t*-butyl-4-methylphenoxyl (methylphenoxyl) radical; hence, each spin density on the 4-carbon of the phenoxyl ring among these alkylphenoxyl radicals was much like that for the methylphenoxyl. (2) If the methyl group in the methylphenoxyl radical is assumed to rotate freely, the value of the $\langle\cos^2\theta\rangle$ is one-half it, since the methyl-proton splitting for this radical remains almost unchanged from −45 °C to 15 °C. Therefore, $B_2\rho_4^{\pi}$ was assumed to be $2\times A_4^{Me}$. A_4^{Me} is the methyl-proton splitting for the methylphenoxyl radical. (3) The B_0 term being smaller than the $B_2\langle\cos^2\theta\rangle$ term, the B_0 term was neglected in Eq. 2:

$$A_4^{\beta} = 2 \times A_4^{Me}\langle\cos^2\theta\rangle. \tag{3}$$

Although the first assumption may be appropriate for the Radical-H, the latter two assumptions may be no longer valid for any cyclopropyl-substituted radicals. There are two difficulties with the above simple model:

(1) Because of the conjugative interaction between the aromatic π-system and the cyclopropyl pseudo π-orbital, the mechanism which induces spin density on the β-hydrogen atom may be different. Therefore, the B_0 and B_2 terms for the cyclopropyl-substituted radical systems may not be identical to those for the cases of the normal alkyl-substituted radicals.

(2) The propensity of the cyclopropyl group to take the bisected conformation makes the $\langle\cos^2\theta\rangle$ value small in Eq. 2. When the $\langle\cos^2\theta\rangle$ value is small, the contribution of the B_0 term is no longer negligible.[15] To avoid the above difficulties, Hudson and Bauld added a third term, one which resulted from the conjugative interaction between the cyclopropyl group and the π-system, to the conventional Heller-McConnell relationship.[6] They divided the third term into conformational-dependent and -independent parts, which they then added to the B_0 and B_2 terms respectively of the normal $\cos^2\theta$ rule. From the comparative study of the 4-(2-cyclopropyl-1-ethynyl)nitrobenzene and the 4-(1-propynyl)nitrobenzene anion radicals, they sug-

gested that the conjugative effect produced a negative spin density at the β-hydrogen atom and proposed Eq. 4 for the conformational analysis of a cyclopropyl group in a radical system:[9)]

$$A_4^{\beta} = [1.85\langle\cos^2\theta\rangle - 0.10] \times A_4^{\mathrm{Me}}. \tag{4}$$

The β-proton splitting of the methylphenoxyl radical, A_4^{Me}, was 11.20 G.[8)] With the aid of the Boltzmann statistics, the β-proton splitting of the Radical-H as a function of the temperature was calculated based on Eqs. 4 and 6.

$$\theta = \alpha + \theta_0 \tag{5}$$

$$\langle\cos^2\theta\rangle = \frac{\sum\limits_{i=0} \langle\psi_i(\alpha)\,|\cos^2(\alpha+\theta_0)|\,\psi_i(\alpha)\rangle e^{-E_i/kT}}{\sum\limits_{i=0} e^{-E_i/kT}} \tag{6}$$

Here, the wave functions, $\psi_i(\alpha)$, and the eigen values, E_i, are obtained by solving the following equation:

$$-\frac{\hbar^2}{2I}\left(\frac{d^2\psi_i}{d\alpha^2}\right) + [V_{(\alpha)} - E_i]\psi_i = 0. \tag{7}$$

In Eq. 7, the moment of inertia, I, of the molecular fragment aryl-cyclopropyl may be calculated to be 7.8×10^{-39} g cm^2 for the Radical-H, assuming that the preferred rotation of the residual group occurs about the long axis of this radical. In Eq. 7, $V_{(\alpha)}$ is the potential function to the internal rotation of the cyclopropyl group in this radical. In order to solve Eq. 7, the precise potential function must be assumed. Sorriso *et al.* and Collet *et al.*[16)] theoretically calculated the angular dependence of the rotational barrier in the cyclopropylbenzene by means of the molecular orbital theory. By reference to these results, the potential function was approximated as follows:

$$V_{(\alpha)} = \frac{V_0}{2}(1 - \cos 2\alpha). \tag{8}$$

In Eq. 8, V_0 is the difference in energy between the lowest energy state, the bisected conformation, and the highest one, the perpendicular. The α value is the dihedral angle between the β-proton and the aromatic plane, so it is equal to zero in the bisected conformation and $\pi/2$ in the perpendicular. The θ_0 value in Eq. 5 becomes equal to $\pi/2$. The Hamiltonian matrix, $<i|H|j>$, was diagonalized by expanding the wave function in a Fourier series:

$$\psi_i(\alpha) = \sum_{j=0} (A_{ij}\cos j\alpha + B_{ij}\sin j\alpha). \tag{9}$$

The temperature dependences of $<\cos^2\theta>$ as a function of V_0 for the Radical-H have also been calculated. The results calculated in the temperature range from -80 °C to 0 °C for the various values of V_0 are shown in Fig. 5. The best agreement between the calculated and the experimental temperature dependence, evaluated by means of Eq. 4, was obtained with $V_0 = 2.6$ kcal/mol (1 kcal=4.184 kJ). On the other hand, the magnitudes $<\cos^2\theta>$ evaluated from Eq. 3 were very small. In this case, the potential barrier calculated was 5.0—7.5 kcal/mol, although the observed temperature dependence of the β-proton splitting could not be adequately explained. The latter value of the potential barrier, which corresponds to the energy difference between the bisected and perpendicular conformation (Fig. 1), may be comparable to the conjugative energy between two phenyl rings for the biphenyl molecule when the molecule is coplanar (about 6 kcal/mol).[17)] Then, the potential barrier of 5.0—7.5 kcal/mol may not be adequate for the internal rotation of the cyclopropyl group in the Radical-H. However, the former value, 2.6 kcal/mol, is more appropriate for this radical. This result is compatible with the results of other investigations of the cyclopropylbenzene made using several techniques. Parr and Schaefer have reported on the basis of their NMR measurements, that the rotational barrier of the cyclopropyl group in the cyclopropylbenzene (assuming a two-fold potential) was 2.0±0.3 kcal/mol.[5)] Based on the molecular orbital calculations for the cyclopropylbenzene,[16)] the energy difference between the bisected and perpendicular conformations was reported to be 11.7 kJ (2.8 kcal/mol; CNDO/2) or 3.67×10^{-2} au. (2.3 kcal/mol; INDO). The compatibility with the other results implies the validity of the adoption of Eq. 4 to estimate the $<\cos^2\theta>$ for the Radical-H.

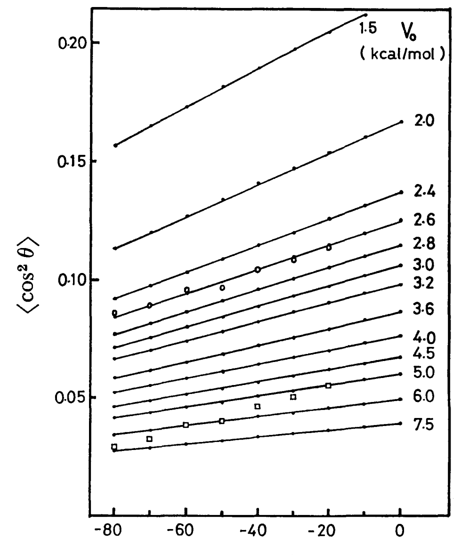


Fig. 5. The theoretically calculated and experimental temperature dependence of $\langle\cos^2\theta\rangle$ for the Radical-H. The numerical calculations were carried out with various values of V_0, which was the energy difference between the bisected and perpendicular conformation. —●—; Theoretically calculated values of $\langle\cos^2\theta\rangle$, ○; $\langle\cos^2\theta\rangle$ vaules evaluated from Eq. 4, □; $\langle\cos^2\theta\rangle$ values evaluated from Eq. 3.

In previous papers, the potential barriers to the internal rotation of the alkyl group in the alkyl-substituted biphenyl anion and phenoxyl radicals have been reported. As is shown in Table 2, in the 4,4′-dialkylbiphenyl radical anion series[7)] the rotational barriers were 1.0, 1.2, and 1.2 kcal/mol for the 4,4′-diethyl-, 4,4′-diisopropyl-, and 4,4′-dicyclohexylbiphenyl anions respectively. In the phenoxyl series,[8)] those for the 2,6-di-*t*-butyl-4-ethyl-, -4-isopropyl-, and -4-cyclohexylphenoxyl radicals were 1.1, 1.6, and 1.6 kcal/mol respectively. In both cases, the rotational

TABLE 2. THE VALUES OF THE 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	Ref.
Phenoxyl	Et	0.37 (at −60 °C)	1.1		8
	i-Pr	0.18 (at −60 °C)	1.6	0.7	8
	c-He	0.18 (at −60 °C)	1.6	0.7	8
	c-Pr	0.09 (at −60 °C)[a]	2.6		
Biphenyl anion	Et	0.36 (at −90 °C)	1.0		7
	i-Pr	0.21 (at −85 °C)	1.2	0.5	7
	c-He	0.20 (at −85 °C)	1.2	0.6	7
	c-Pr	0.37 (at −80 °C)[a]	0.46		9

The V_0 values show the highest values for the two-fold potential (Et, *c*-Pr) or the double-well potential (*i*-Pr, *c*-He). The V_m values show the medium value for the double-well potential (*i*-Pr, *c*-He). For particulars, see Refs. 7 and 8. a) The $\langle\cos^2\theta\rangle$ values were estimated based on Eq. 4.

barriers obtained were very similar to each other for the same alkyl groups, and in both they were interpreted in terms of the steric repulsion between the rotating alkyl group and the aromatic protons. However, the rotational barrier of the cyclopropyl group in the Radical-H deviated remarkably from the above alkylphenoxyl radical series. Based on the magnitudes of $\langle\cos^2\theta\rangle$ at -90 °C as evaluated with Eq. 4, Hudson and Bauld estimated the rotational barrier of the cyclopropyl group in the 4,4′-dicyclopropylbiphenyl radical anion to be 0.46 kcal/mol, assuming a two-fold potential in which the bisected conformation was more stable than the perpendicular one.[9] The present conclusion that the rotational barrier of the cyclopropyl group in the Radical-H is 2.6 kcal/mol is not compatible with their result. Because the steric factors are nearly comparable with the two cases, the difference in the rotational barriers for these radicals may be mainly correlated to the proportion of the contribution of the conjugative interaction between the cyclopropyl and aromatic moieties. The difference may not be expected from the solvent effects or the difference in the moment of inertia.[15] Therefore, the conjugative interaction in the Radical-H may be anticipated to be considerably important.

The Conjugative Interaction. The conclusion obtained in the previous section indicates that the contribution of the π-type conjugation between the cyclopropyl group and the π-system is more significant in the Radical-H than in the 4,4′-dicyclopropylbiphenyl anion radical. This difference may be well understood in terms of the perturbational molecular orbital theory.[18]

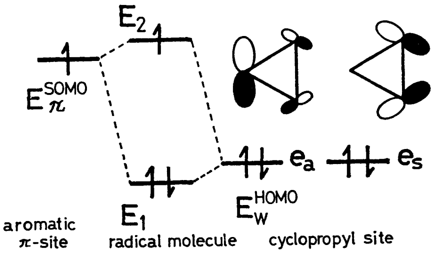


Fig. 6. Energy diagram: left-handed and right-handed are schemes of the cyclopropyl site and aromatic π-site respectively, before a perturbational interaction. The central one is the energy diagram after the interaction. E_π^{SOMO}; the energy level of the SOMO for the aromatic π-system, which contains unpaired electron, E_W^{HOMO}; the energy levels of the HOMO for the cyclopropyl system. E_1 and E_2; the energy levels of the radical molecule after the perturbational interaction between the aromatic and the cyclopropyl system. The right-handed pictures are the outline for the HOMO of the Walsh-type molecular orbitals for the cyclopropyl system, the symmetry labels refer to the C_s point group.

On the basis of the perturbational molecular orbital theory, Hoffmann *et al.* have discussed the stabilization of the cyclopropyl carbinyl cation arising from the interaction of the cyclopropyl group and the vacant carbonium $2p_z$ orbital.[19] The stabilization energy, E_s, of a molecule arising from the conjugative interaction between the cyclopropyl pseudo-π-orbital and the aromatic π-system may be approximately comprehended in terms of the following equations and the energetic picture shown in Fig. 6:

$$E_s = \frac{|H_{ij}|^2}{\Delta E}, \qquad \Delta E = E_\pi^{SOMO} - E_W^{HOMO}, \tag{10}$$

$$|H_{ij}|^2 = (C_i^\pi)^2(C_j^W)^2\beta^2, \tag{11}$$

where H_{ij} is the matrix element of the perturbational interaction and where ΔE is the energy difference between the SOMO (Singly Occupied Molecular Orbital) of the π-system, E_π^{SOMO}, and the HOMO (Highest Occupied Molecular Orbital) of the cyclopropyl Walsh orbital, E_W^{HOMO} (see Fig. 6). The $|H_{ij}|^2$ term contains the square of the coefficients of the corresponding AO's (Atomic Orbitals) at the carbon atoms, attached to each other, for the HOMO of the cyclopropyl and the SOMO of the aromatic moieties; β is the resonance integral between the aromatic π-system and the cyclopropyl group. Only one orbital in the HOMO's of the cyclopropane which interacts with the π-system is denoted as e_a, because the Walsh-type orbital denoted e_s has a node on the plane of the three-membered ring at the cyclopropyl-1-carbon atom (Fig. 6). The resonance integral, β, should be dependent on the conformation of the cyclopropyl group, because the Walsh-type orbital denoted as e_a spreads on the plane of the three-membered ring. The terms of $(C_j^W)^2\beta^2$ in Eq. 11 for the Radical-H and the 4,4′-dicyclopropylbiphenyl anion being assumed to be equal, the stablization energy arising from the conjugative interaction, E_s, may be proportional to the square of the coefficient of the SOMO-AO on the aromatic carbon attached to the cyclopropyl group. On the other hand, the stabilization energy, E_s, is inversely proportional to the energetic separation between the SOMO of the π-system and the HOMO of the cyclopropyl group.

The results of the HMO calculation, summarised in Table 3, suggest that the contribution of the conjugative interaction in the Radical-H is larger than that of the 4,4′-dicyclopropylbiphenyl radical anion. When the molecule adopts the bisected conformation,

TABLE 3. THE CALCULATED SOMO ENERGIES AND COEFFICIENTS AT THE AROMATIC 4-POSITIONS[20)]

	Biphenyl anion[a)]	Phenoxyl[b)]
Aromatic SOMO energy	$\alpha-0.705\beta$	$\alpha+0.894\beta$
Aromatic SOMO coefficient	0.398	0.545

a) Data from Ref. 20a. b) The values of the parameters, α_O as the Coulomb integral and β_{C-O} as the resonance integral, for the 2,6-di-*t*-butylphenoxyl radical were $\alpha+2\beta$ and 0.6β respectively.[20b)] The HMO calculation was carried out by neglecting the contributions from the two *t*-butyl groups.

the overlapping between the π-orbital of the phenoxyl and the cyclopropyl pseudo-π-orbital is at its maximum, therefore, the stabilization effect is the most. On the contrary, the overlapping is at its minimum, and the effect is least in the perpendicular conformation. The large potential barrier estimated for the Radical-H can be understood from this point of view.

Experimental

General. All the melting points are uncorrected. The IR spectra were obtained on a Hitachi 215 spectrometer; the Mass spectra, on a Hitachi RMS-4 and RMU-6L spectrometer; the NMR spectra, on a Varian T-60 spectrometer, and the UV spectrum, on a Hitachi 124 spectrophotometer. The chemical shifts of the NMR spectra are given in ppm (δ), with tetramethylsilane as the internal standard. The ESR spectra were measured on a JEOL-ME-3X spectrometer operating with a 100 kHz magnetic-field modulation. The ENDOR spectra were measured in the temperature range from −80 °C to −20 °C using a JEOL-EDX-1 spectrometer operating with a 80 Hz magnetic-field modulation. About 150 W of continuous radiowaves (frequency modulated at 6.5 kHz) were present in the cavity for NMR excitation.

Materials. *2,6-Di-*t*-butyl-4-acetylphenyl Acetate*: Into a cold mixture of anhydrous aluminum chloride (67 g, 0.5 mol) and acetyl chloride (31 ml, 0.4 mol) in carbon disulfide (150 ml), was added a solution of the commercial 2,6-di-*t*-butylphenol (31 g, 0.15 mol) in the same solvent (70 ml) below 5 °C[21)] over a 2-h period. After being stirred for an hour at room temperature, the mixture was heated under reflux for 2 h. Then, the mixture was poured into an ice-cold 1 mol dm^{-3} HCl solution, the organic layer was separated, and the aqueous layer was extracted with a solvent. The combined organic layer was washed with water, an aqueous sodium hydrogencarbonate solution, and water, successively. The subsequent evaporation of the solvent, after being dried with anhydrous calcium chloride, gave a solid residue, which was then recrystallized from hexane to give colorless prisms (35 g) in an 80% yield.

Mp 100.5—101.2 °C. NMR (CCl_4) 7.83 (s, 2H), 2.50 (s, 3H), 2.29 (s, 3H), 1.37 (s, 18H). IR (nujol) 1765 cm^{-1} and 1680 cm^{-1}. Found: C, 74.60; H, 9.15%; M$^+$, 290. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02%; M, 290.

*2,6-Di-*t*-butyl-4-(1-hydroxyethyl)phenyl Acetate*: A solution of the above acetate (20 g, 0.07 mol) dissolved in 2-propanol (120 ml) was gradually stirred into a suspension of sodium borohydride (1.3 g, 0.03 mol) in 2-propanol (50 ml) at room temperature. After being stirred for 2 d at room temperature, the solvent was removed *in vacuo*. The residue was slowly poured into a cold 1 mol dm^{-3} HCl solution; then the aqueous layer was extracted with ether three times. The organic layer was washed with a saturated solution of sodium hydrogencarbonate and water. After the solution had been dried over anhydrous sodium sulfate, the concentration of the solution *in vacuo* gave a solid residue, which was subsequently recrystallized from cyclohexane to afford colorless plates (15 g, 74%).

Mp 103.4—104.0 °C, NMR (CCl_4) 7.25 (d, 1H, J=2 Hz), 7.18 (d, 1H, J=2 Hz), 4.68 (q, 1H, J=6 Hz), 2.24 (s, 3H), 2.13 (s, 1H, OH), 1.40, 1.33 (d, J=6 Hz, s, 21H), IR (nujol) 3550 and 1740 cm^{-1}. Found: C, 74.12; H, 9.75%; M$^+$, 292. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65%; M, 292.

*2,6-Di-*t*-butyl-4-ethenylphenyl Acetate*: Into concd phosphoric acid (6 g) was added a solution of the above hydroxy ester (8.8 g, 0.03 mol) dissolved in benzene (60 ml). The mixture was heated under a gentle reflux of benzene for 3 h, until no more water was taken off as an azeotropic mixture. The organic layer was then washed with water and an aqueous sodium hydrogencarbonate solution. The evaporation of the solvent *in vacuo* left a colorless oil (7 g), which was employed as the reactant of the following experiment without any further purification. The NMR and IR data were as follows: NMR (CCl_4) 7.33 (s, 2H), 6.68 (dd, 1H, J=11 Hz, 17 Hz), 5.64 (d, 1H, J=17 Hz), 5.16 (d, 1H, J=11 Hz), 2.22 (s, 3H), 1.37 (s, *t*-Bu), and IR (nujol) 1775 cm^{-1}.

*2,6-Di-*t*-butyl-4-cyclopropylphenyl Acetate*: Into a mixture of palladium acetate (10 mg) and a solution of the above crude oil (7 g) dissolved in ether (30 ml) was added an ethereal solution of diazomethane,[22)] prepared from 45 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide according to a previously reported method[23)] in an ice–salt bath over a 3-h period. Since the yellow color which is indicative of the presence of diazomethane remained unchanged, additional palladium acetate (10 mg) was added. The mixture was stirred overnight at room temperature and then washed with cold 1 mol dm^{-3} HCl and water. After the mixture has been dried, the removal of the solvent *in vacuo* gave a pale yellow oil. If the olefinic absorptions (6.8—5.0 ppm) were found upon NMR observation, the above procedure was done over again. The product was purified by alumina-column chromatography, using cyclohexane and benzene as eluents. The product (5.9 g) was eluted in the fraction of the mixed solvent (5—10% benzene and 90—95% cyclohexane). The NMR and IR data were as follows: NMR (CCl_4) 6.93 (d, 2H), 2.24 (s, 3H), 1.35 (*t*-Bu), 0.55—0.98 (m, 4H), and IR (neat) 1770 cm^{-1}.

*2,6-Di-*t*-butyl-4-cyclopropylphenol*: To an ethereal suspension of lithium aluminum hydride (0.6 g, 0.02 mol), was added a solution of the above acetate (5.9 g, 0.02 mol) in ether (10 ml) below 10 °C over period of an hour. After the mixture had been stirred at room temperature for an hour, it was heated under reflux for 2 h. Then, cold water was added to the mixture and it was poured into an ice-cooled 1 mol dm^{-3} HCl solution, the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was washed with water, an aqueous sodium hydrogencarbonate solution, and water. After the organic layer had been dried, the solvent was removed off *in vacuo* to leave a yellow, crystalline substance. It was chromatographed on silica gel, using light petroleum ether as the eluent. The first fraction gave white crystals. Recrystallization from pentane gave 2.4 g of white plate crystals. The total yield of the product from the 2,6-di-*t*-butyl-4-(1-

hydroxyethyl)phenyl acetate was 32%.

Mp 63.5—65.0 °C, NMR (CCl_4) 6.80 (s, 2H), 4.82 (s, 1H), 1.52—1.80 (m, 1H), 1.43 (s, 18H), 0.46—0.88 (m, 4H). IR (nujol) 3660 cm^{-1}. Found: C, 82.72; H, 10.75%; M$^+$, 246. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64%; M, 246. UV$_{max}$ (hexane) 224 nm (log ε: 3.6).

The desired deuterio compound was prepared from the 2,6-di-*t*-butyl-4-acetylphenyl acetate in a manner similar to that used in the preparation of the 2,6-di-*t*-butyl-4-cyclopropylphenol. Deuterium was introduced by means of sodium borodeuteride reduction.

*2,6-Di-*t*-butyl-4-(1-deuterio-1-hydroxyethyl)phenyl Acetate*: To a suspension of sodium borodeuteride (0.4 g, 0.01 mol) in 2-propanol (20 ml), a saturated solution of the 2,6-di-*t*-butyl-4-acetylphenyl acetate (5.6 g, 0.02 mol) in the same solvent was added. Thereafter, the procedure described above was employed. The spectral data of the product; mp 102.6—103.3 °C (4.5 g, 81% yield) are as follows: NMR (CCl_4) 7.23 (d, 1H, J=2 Hz), 7.18 (d, 1H, J=2 Hz), 2.23 (s, 3H), 2.17 (s, 1H, OH), 1.37, 1.33 (s, s, 21H); IR (nujol) 3530 and 1740 cm^{-1}; M$^+$ 293.

*2,6-Di-*t*-butyl-4-(1-deuterioethenyl)phenyl Acetate*: A solution of the above acetate (4 g, 0.01 mol) dissolved in benzene (30 ml) was added to a suspension of concd phosphoric acid (4 g) in benzene (20 ml). The further procedure, described above, gave an oily product. The NMR data were as follows: NMR (CCl_4) 7.25 (s), 5.59 (m), 5.15 (s), 2.26 (s), 1.36 (*t*-Bu).

*2,6-Di-*t*-butyl-4-(1-deuteriocyclopropyl)phenyl Acetate*: Into a mixture of palladium acetate (10 mg) and a solution of the above crude oil dissolved in ether (20 ml) was added an excess of an ethereal solution of diazomethane in an ice–salt bath over a 3-h period. The further procedure was as has been described above; it gave 3.5 g of an oily product. The NMR data were as follows: NMR (CCl_4) 6.96 (s), 2.23 (s), 1.32 (*t*-Bu), 0.56—0.93 (m).

*2,6-Di-*t*-butyl-4-(1-deuteriocyclopropyl)phenol*: Into a suspension of lithium aluminum hydride (0.5 g, 0.01 mol) in ether (10 ml), a solution of the above acetate (3.5 g) in the same solvent (10 ml) was added below 10 °C for 1 h. Subsequent treatment as above gave white crystalline plates (1.0 g, 0.004 mol).

The total yield of the product from the 2,6-di-*t*-butyl-4-(1-deuterio-1-hydroxyethyl)phenyl acetate was 28%. Mp 60.5—63.0 °C, NMR (CCl_4) 6.78 (s, 2H), 4.80 (s, 1H), 1.45 (s, 18H), 0.49—0.86 (m, 4H); IR (nujol) 3650 cm^{-1}; M$^+$, 247.

Preparation of the Radicals. *In vacuo*, both phenoxyl radicals were prepared by the oxidation of the corresponding phenols with lead dioxide (PbO_2) in toluene.[10] Both solutions of the radicals were slightly blue.[24]

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

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