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ENDOR Studies of Alkylated Biphenyl Anion Radicals in Solution. Relation between Molecular Size and Optimum Temperature of ENDOR Enhancement

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The ENDOR spectra of several alkylated biphenyl anions with *para-* and *meta*-substitutions were observed, and the relation between the molecular size and the optimum temperature of *ortho*-proton ENDOR were investigated in terms of the electron-nuclear dipole-dipole interaction. On the basis of the Stokes-Einstein model, a linear relation was found between the inverse of the effective radius and the cubic root of the η/T value at the optimum temperature of the *ortho*-proton ENDOR, under the assumption that the radical anion undergoes rotation accompanied by the solvent shell. In this situation, the separation between the radical anion and the counter cation thus estimated is more than 8.3 Å and the ion pair exists as a solvent-separated ion pair.

It is known that the optimum ENDOR enhancement in a solution can usually be observed in the temperature region close to the freezing point of the solvent. In identical physico-chemical environments, the optimum temperature varies with the proton species, *e.g.*, the aromatic protons and the aliphatic protons; the electron-nuclear hyperfine interaction affects a shift of the optimum temperature. A larger spin density on aromatic carbon usually displaces the optimum enhancement toward higher temperatures. Such an effect is successfully interpreted under the assumption that the electron-nuclear dipole-dipole interaction (END) plays the dominant role in the relaxation process, when the Heisenberg spin-exchange interaction in negligible in dilute solution systems;1) that is, the desaturation of the ESR by NMR exciation is most effectively established when the lattice-induced nuclear-spin transition probability, W_n, has a certain value comparable to the lattice-induced electron-spin transition probability, W_e. W_n is proportional to the molecular rotational correlation time, τ_R, and the square of spin density. The τ_R value can be also related to the molecular volume and, therefore, the molecular volume, as well as the spin density, should affect the optimum temperature for ENDOR enhancement.

Alkylated biphenyls with *meta-* or *para*-substituents are some of the most suitable systems for investigating this point, because the spin densities at the *ortho*-position are only slightly perturbed by alkyl substitution,2) and ENDOR observation has already been established.3–5) In the present paper, the relation between the molecular radius and the temperature dependence of the ENDOR enhancement is investigated for anion radicals such as biphenyl (BP), 4,4′-bitolyl (*p*-Me), 4,4′-diethylbiphenyl (*p*-Et), 4,4′-di-*t*-butylbiphenyl (*p*-Bu), 3,3′,5,5′-tetramethylbiphenyl (*m*-Me), and 3,3′,5,5′-tetra-*t*-butylbiphenyl (*m*-Bu). The effective radii of the solvated radical anions are estimated and the structures of the ion-pairs are discussed.

Experimental

Commercial biphenyl was recrystallized from ethanol and the alkylbiphenyls employed was synthesized and purified in the manner described in a previous paper.6)

The anion radicals were prepared by reduction with potassium metal in 1,2-dimethoxyethane (DME). The ENDOR spectra were recorded using a JEOL-type ES-EDX-1 spectrometer for a constant rate of microwave output (3.2 mW) from a JES-ME3-ESR spectrometer. The operating power of NMR excitation was maintained constant (120 W). The viscosity of the solvent for all temperatures was calculated using the formula given in the table.7)

Results and Discussion

Hyperfine Coupling Constants and Optimum Temperature of the ENDOR Signal Intensity. Figure 1 shows the ENDOR spectra of biphenyl and the 3,3′,5,5′-tetra-*t*-butylbiphenyl anion radical. With reference to the previous work, the signals for the biphenyl anion radical observed at 14.43, 17.63, and 21.46 MHz can be easily assigned to the *meta-*, *ortho-*, and *para*-ring protons. The ENDOR spectrum of the 3,3′,5,5′-tetra-*t*-butylbiphenyl anions clearly resolved the *t*-butyl proton splittings, which have never been detected in previous ESR studies.8) The proton hyperfine splittings for the alkylbiphenyls determined in the same manner are summarized in Table 1, where it is seen that the magnitude of the *ortho*-ring proton splitting more or less close to that of the biphenyl anion radicals. A typical example of the temperature dependence of the ENDOR intensities (F) are shown in Fig. 2. For biphenyl anion radicals, the maximum ENDOR signals for the *meta-*, *ortho-*, and *para*-ring protons appear at −95, −90, and −80 °C, respectively, in order of increasing spin densities; that is, $\rho_m < \rho_o < \rho_p$.

For 9,10-anthraquinone, similar effects due to the different spin densities have already been studied by Kotake and Kuwata, who demonstrated the importance

Table 1. Proton hyperfine coupling constants for alkylbiphenyl anion radicals (in G)

	o	*m*	*p*
BP	2.66	0.41	5.31
p-Me	2.73	0.47	5.76a)
p-Et	2.70	0.44	3.76b)
p-Bu	2.71	0.46	0.11c)
m-Me	2.53	0.31a)	4.90
m-Bu	2.59	0.06c)	5.14

a) Methyl proton. b) Ethyl proton. c) Butyl proton.

of the END mechanism.[9] A similar tendency was also seen for the *para*- and *ortho*-positions of the 3,3′,5,5′-tetra-*t*-butylbiphenyl anion radical, except for the anomalous optimum temperature of the *t*-butyl proton, which has often been reported for the hindered phenoxyl radicals.[10] In the case of 3,3′,5,5′-tetra-*t*-butylbiphenyl, however, the optimum temperatures for both the *para*- and *ortho*-positions (−40 °C, −73 °C) were displaced to higher temperatures in comparison with those (−80 °C, −95 °C) for biphenyl. Actually, the ENDOR of the *para*-ring proton of biphenyl anion radicals was clearly recorded at −78 °C, but that of 3,3′,5,5′-tetra-*t*-butylbiphenyl could hardly be detected and the signal intensity gradually increased with elevation of the observing temperature, up to −40 °C.

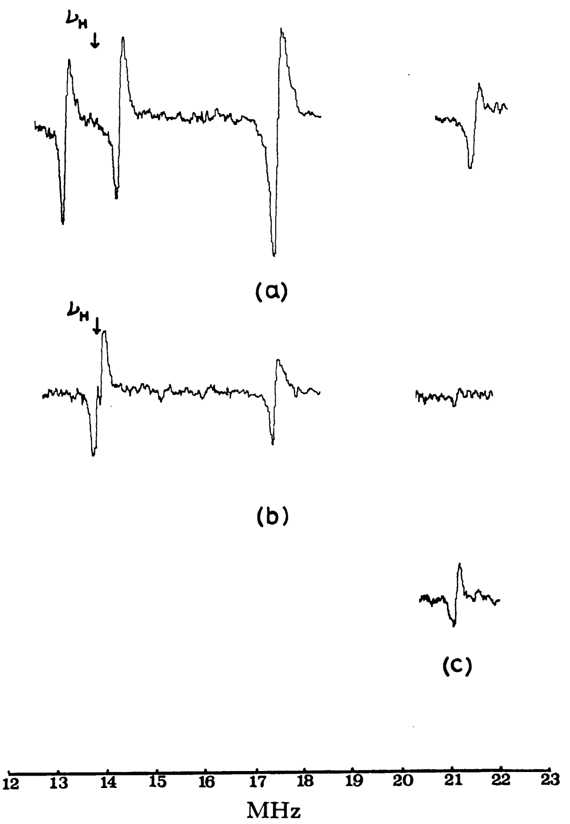

Fig. 1. The ENDOR spectra of biphenyl (a) and 3,3′,-5,5′-tetra-*t*-butylbiphenyl anion radical (b). (a) and (b) were observed at −78 °C. (c) is the ENDOR of *para*-protons of 3,3′,5,5′-tetra-*t*-butylbiphenyl observed at −40 °C.

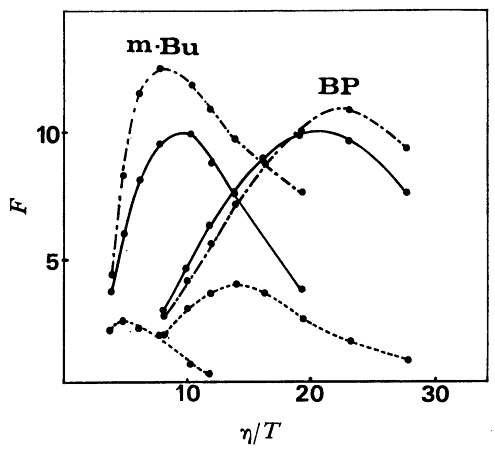

Fig. 2. Temperature dependence of the ENDOR enhancement for biphenyl and 3,3′,5,5′-tetra-*t*-butylbiphenyl anion radicals.
------: *para*, ——: *ortho*, -·-·-: *meta*.
F denotes the ENDOR enhancement calculated to be $F=I_{\mathrm{ENDOR}}/I_{\mathrm{ESR}}$, where I_{ENDOR} and I_{ESR} are the peak height of the ENDOR and ESR signal at any temperature.

Because the spin densities on the *para*- and the *ortho*-positions are close together in both radicals, alterations of the optimum temperature could be attributed to the differences of the molecular radii. This is true, because the optimum temperature of the *ortho*-proton ENDOR increases with an increase in the number of substituents and their spherical bulkiness as shown in Table 2.

TABLE 2. OPTIMUM TEMPERATURES (°C) OF *ortho*-PROTON ENDOR

BP	*p*-Bu	*p*-Me	*m*-Me	*p*-Et	*m*-Bu
−95	−79	−87	−86	−86	−73

Molecular Radius and Optimum Temperature. Under ordinary ENDOR conditions in solution, the electron-spin transition probability, W_e, and that of the nuclear spin, W_n, can be expressed as functions of the rotational correlation time, τ_R, as follows:[1]

$$W_e = A(1/\tau_R), \tag{1}$$

$$W_n = B\tau_R \tag{2}$$

Where A is the constant related to the magnitude of the g-factor and hyperfine anisotropies, and B is related to that of hyperfine anisotopy only. According to the END approximation, optimum ENDOR enhancement is observed when the ratio

$$b = W_n/W_e = (B/A)\tau_R^2 \tag{3}$$

has a certain value. Because B is proportional to the expectation value of the END term over the molecular wave function, the rotational correlation time at the optimum ENDOR enhancement, τ_R^{opt}, should become shorter for an increase of the spin density on the carbon atom to which the observing proton is bonded. In alkylbiphenyl anion radicals studied here, τ_R^{opt}, corresponding to the optimum ENDOR of the *ortho*-ring proton may have a constant value for each anion radical, because the spin densities, ρ_2^{π}, at the *ortho*-position have more or less the same values regardless of the alkyl substitutions. On the other hand, τ_R^{opt}, can be expressed by the Stokes-Einstein relationship:

$$\tau_R^{\mathrm{opt}} = \frac{4\pi r^3}{3k}(\eta/T)_{\mathrm{opt}}. \tag{4}$$

One may thus expect that a linear relation holds between the inverse of the effective radius, $1/r$, and the cubic root of the (η/T) value calculated for the optimum temperature of the *ortho*-proton ENDOR. If the radical ions are subject to a tumbling motion accompanied by the solvent shell, which has an averaged thickness, r_s, the following relation can be derived;

$$(r'+r_s)/(r+r_s) = (\eta'/T')^{-1/3}/(\eta/T)^{-1/3}, \tag{5}$$

Where r and r' are the averaged radius of the alkylbiphenyl and the biphenyl anion radical, respectively, and η and η' are the viscosity coefficient at the optimum ENDOR temperature for the derivative (T') and for the biphenyl anion radical (T). The averaged radii, r, of the alkylated biphenyl, which is regarded to be an ellipsoid, were calculated by taking the geometrical average of the three axes a, b, and c. The length of each axis was estimated using the following interatomic bond distances R and bond angles θ:[11]

$$R_{\mathrm{C-C}}(\text{aromatic}) = 1.40\ \text{Å},\quad R_{\mathrm{C_1-C_1'}}(\text{bridgehead}) = 1.49\ \text{Å},$$
$$R_{\mathrm{C-C}}(\text{aliphatic}) = 1.54\ \text{Å},\quad R_{\mathrm{C-H}} = 1.08\ \text{Å},$$
$$\theta_{\mathrm{sp^2}} = 120° \text{ and } \theta_{\mathrm{sp^3}} = 109°.$$

The total length of each shorter and longer axes a and b was estimated by summing the Van der Waals radii of the ring, the aliphatic (1.20 Å) and terminal methyl protons (2.00 Å), and the thickness of the phenyl group, c, was assumed to be 3.40 Å. As is shown in Fig. 3, a linear rotation can be seen between the (r/r') and the $[(\eta/T)/(\eta'/T')]^{1/3}$ values of each derivative, and r_s is thus estimated to be 2.4 Å, as calculated from the slope of the plot. The rotational correlation times of the anions at the optimum ENDOR, τ_R^{opt}, calculated using the effective radius $r+r_s$ have more or less constant values, which are close to 1.0×10^{-9} s, as summarized in Table 3.

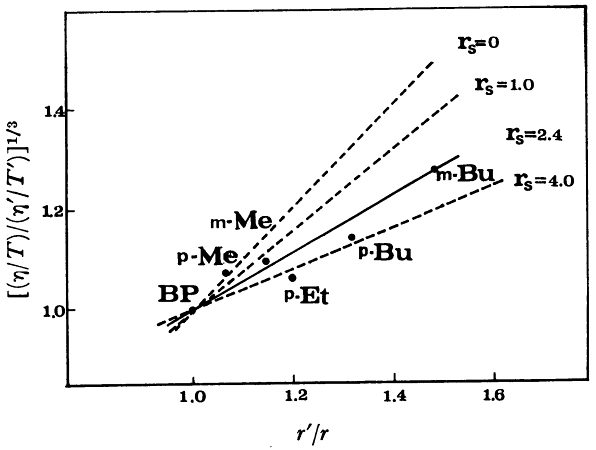

Fig. 3. Relation between the molecular radii and the cubic root of η/T value.

Table 3. Molecular radii, molecular volumes and rotational correlation times at optimum ENDOR enhancement

	BP	*p*-Me	*p*-Et	*p*-Bu	*m*-Me	*m*-Bu
r (10^{-8} cm)	3.16	3.36	3.79	4.16	3.60	4.69
V (10^{-24} cm)	132	159	228	307	200	432
τ_R^{opt} (10^{-9} s)	1.08	0.98	1.28	1.19	1.05	1.07

The τ_R^{opt} values were calculated assuming that the thickness of the solvent shell is 2.4 Å

Since the τ_R^{opt} value thus determined may contain inaccuracies attributable to the crude estimation of the molecular volume and neglect of the contribution due to the anisotropic rotational diffusion,[12] the numerical values cannot be taken too seriously. Nevertheless, the large effective radius of the anion radical demonstrated here, is quite interesting, because this suggests that the distance between the radical anion and the alkali metal cation should be large, at least 8.3 Å in the case of biphenyl$^-$–K$^+$ system, in which case the radius of K$^+$ is assumed to be 1.5 Å.[13] Previous NMR studies of the biphenyl$^-$–K$^+$ system confirmed that the interaction between the anion and the cation is rather weak in DME, and the ion pair is considered to be a solvent separated ion pair.[14] According to conductance studies of biphenyl$^-$–Na$^+$ ion pairs in DME, the dissociation energy is reduced by lowering the temperature, that is, $\Delta H_{20\,°\mathrm{C}} = -2.5$ kcal and $\Delta H_{-55\,°\mathrm{C}} = 0$ kcal.[15] This means that the cation and the anion are completely separated by the solvent molecules at low temperature. Indeed, no important change was observed in the temperature dependence of the ENDOR enhancement for the biphenyl anion radical, even through the alkali metal cation is replaced by sodium in the present investigation.

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