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ENDOR Studies of the Hindered Internal Rotation of Alkyl Groups in the 1,4-Dialkyl Naphthalene Radical Anions

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The ENDOR spectra were measured for the anion radicals of 1,4-dimethylnaphthalene, 1,4-diethylnaphthalene, and 1,4-dipropylnaphthalene. The β-proton splittings of the alkyl groups were 3.30, 2.85, and 2.44 G at -80 °C for 1,4-dimethyl-, 1,4-diethyl-, and 1,4-dipropylnaphthalene respectively, and the positive temperature dependence of the β-proton splitting was demonstrated. Based on the Heller-McConnell relationship, $a^{\beta}_{1,4} = (B_0 + B_2 \cos^2\theta)\rho^{\pi}_{1,4}$ the β-proton splittings and their temperature dependence were interpreted in terms of a modified model of the restricted internal rotation of ethyl and propyl groups over two kinds of potential barriers. The rotational potential barriers thus estimated were 3.0 and 0.7 kcal/mol for the 1,4-diethylnaphthalene anion and 6.0 and 1.2 kcal/mol for the 1,4-dipropylnaphthalene anion. In the ENDOR spectra of potassium 1,4-diethylnaphthalene observed in THF solutions, two ENDOR lines attributed to the non-equivalent alkyl β-protons were observed at -110 °C, these lines collapsed to a single line when the temperature was raised to -70 °C. This phenomenon can be understood on the assumption that the steric effect of the solvated cation alters the rotational potential curve from a symmetric to an asymmetric one.

Based on the ESR observation, the evidence of an internal restricted rotation on the alkyl groups has now been widely established, and the temperature dependence of the alkyl β-proton splitting has been well understood in terms of the $\cos^2\theta$ rule, as has been discussed by Stone and Maki.[1] In particular, for the *para*-substituted alkylbenzene and 9-alkylanthracene, the hindered internal rotation of the ethyl group was investigated in detail. According to the ESR studies of the 4,4′-diethylbiphenyl anion radical,[2] the ethyl group may undergo a restricted rotation in the twofold-potential well, which has a barrier height of 1 kcal/mol. On the other hand, the ethyl group in 9-ethylxanthyl[3] is thought to be strongly restrained, and the ethyl β-proton is almost fixed at the most stable conformation ($\theta_0 = \pi/3$).

In this context, studies of the hindered internal rotation of the alkyl groups in 1,4-dialkylnaphthalene become very intersting, because the motion of the alkyl group in 1,4-dialkylnaphthalene is thought to be restricted by two different steric repulsions, due to the neighboring α-CH and β-CH groups of the naphthalene moiety. The former steric repulsion is similar to that restricting the motion of the alkyl group in 9-alkylxanthyl, while the other is analogous to the case in 4,4′-dialkylbiphenyl.

From the investigation of the hindered internal rotation of the alkyl group in the 1,4-dialkylnaphthalene, one can expect to obtain a revised view of the rotational potentials of the alkyl groups in the alkylated aromatic radicals previously reported. Nevertheless, the ESR spectra of 1,4-dialkylnaphthalene anion radicals have never been reported, except for the case of the 1,4-dimethylnaphthalene anion.[4]

The ESR spectra observed for the 1,4-diethyl- and 1,4-dipropylnaphthalene anion radicals revealed a poor resolution because of the superposition of the hyperfine components due to the ring 2- and ring 6-proton hyperfine couplings. Furthermore, the extra alkyl γ-proton splittings bring additional complexities to the ESR hyperfine structures. In order to determine the hyperfine coupling constants, it seemed desirable to apply the ENDOR technique.[5,6]

Experimental

The 1,4-dimethylnaphthalene was synthesized from *p*-xylene by the method previously reported by Barnet *et al.*[8] The other 1,4-dialkylnaphthalenes were prepared by the Friedel-Crafts reaction of the appropriate acylhalide and α-alkylnaphthalene, and by subsequent reduction.[9,10] The materials were purified by means of preparative fractional gas chromatography. The materials thus obtained were all recrystallized from ethanol at *ca.* -20—-30 °C.

The anion radicals were prepared by reduction with lithium, sodium, or potassium metal in several different solvents, such as tetrahydrofuran (THF), 1,2-dimethoxyethan (DME), and *N,N*-dimethylformamide (DMF).

The ESR and ENDOR spectra were recorded in the temperature ranges from $+20$ °C to -120 °C, and from -60 °C to -120 °C, respectively. The ESR and ENDOR spectrometers employed here and their operating conditions have been described in previous papers.[11,12]

Results and Discussion

ESR Spectra. The ESR spectra of the 1,4-dimethylnaphthalene anion, the reference compound of the 1,4-dialkyl derivatives, have already been reported by Gerson *et al.*[4] The spectra of the 1,4-diethylnaphthalene anion observed in DME, DMF, and THF solutions are shown in Fig. 1. The analysis of the spectra of DME and DMF solutions was hindered by the complicated overlapping of the hyperfine structures due to the alkyl γ-proton splitting (70 mG), which was detected in the temperature range between -20 °C and -50 °C. On the other hand, the ESR spectrum of the THF solution could be roughly analyzed; the results are listed in Table 1. However, the temperature dependence of the hyperfine coupling constants was not precisely determined due to line broadening. For the 1,4-dipropylnaphthalene anion, only a poorly resolved spectrum was observed everywhere, as is shown in Fig. 2; the hyperfine coupling constants could not be determined.

ENDOR Observation. The ENDOR spectra of the 1,4-dimethyl-, 1,4-diethyl-, and 1,4-dipropylnaphtha-

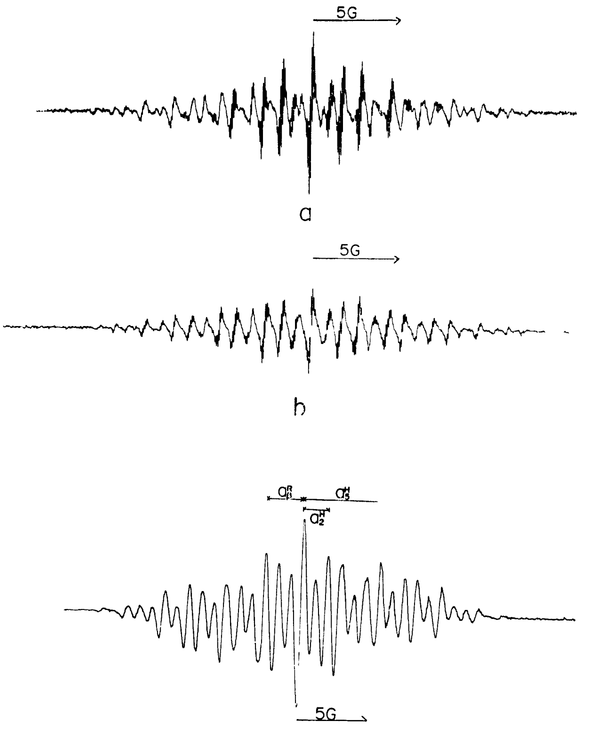

Fig. 1. The ESR spectra of the 1,4-diethylnaphthalene anion by reduction with potassium. a) DME solution at −40 °C, b) DMF solution at −40 °C, c) THF solution at +10 °C.

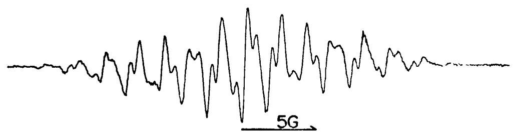

Fig. 2. The ESR spectrum of the 1,4-dipropylnaphthalene anion by reduction with potassium observed with the THF solution at +20 °C.

lene anion radicals observed in DME are shown in Fig. 3.

The spectra can be easily analyzed with reference to the ESR spectra of 1,4-dimethylnaphthalene anions. For example, 1,4-diethylnaphthalene reveals absorptions at 14.0, 16.2, 16.4, 17.9, and 21.4 MHz, which are assigned to the splitting due to the alkyl γ-, the 2,3-ring, the 6,7-ring, the alkyl β-, and the 5,8-ring protons respectively.

Of particular interest is the fact that γ-protons of the propyl group give rise to two different hyperfine coupling constants (0.17 G and 0.05 G), although the ethyl γ-protons reveal only one hyperfine coupling constant. The results are summarized in Table 1. The experimental results indicate that the coupling constants due to ring protons remain almost unchanged on the substitution of alkyl groups.

When the 1,4-dialkylnaphthalene anion radicals were prepared in THF by reduction with potassium, the alkyl β-protons exhibited anomalous hyperfine interactions. The methyl β-proton splitting of 1,4-dimethylnaphthalene showed the minimum value (3.11 G); furthermore, the methylene protons of the ethyl group exhibited non-equivalent splittings at 17.4 and 17.9 MHz below −110 °C. When the temperature was gradually elevated, the two lines of alkyl β-protons were merged into a single line (17.6 MHz), as is shown in Fig. 4. The propyl β-protons also exhibited two different signals (at 17.3 and 18.3 MHz) at −110 °C, as is

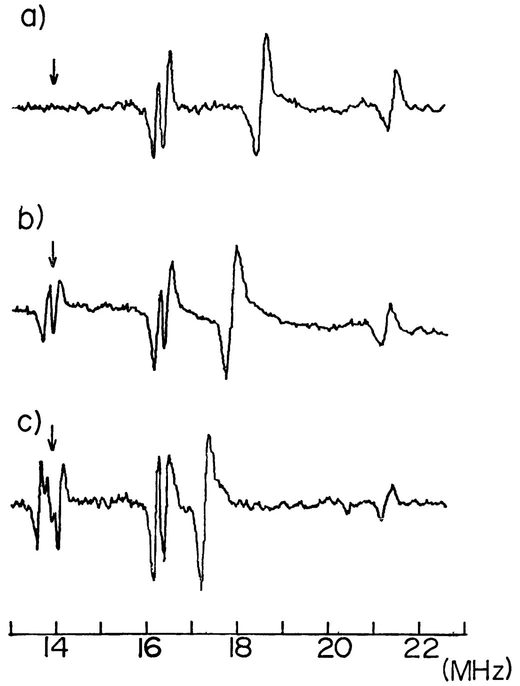

Fig. 3. The ENDOR spectra of the 1,4-dialkylnaphthalene anions by reduction with potassium observed with the DME solution at −80 °C. a) 1,4-dimethylnaphthalene, b) 1,4-diethylnaphthalene, c) 1,4-dipropylnaphthalene.

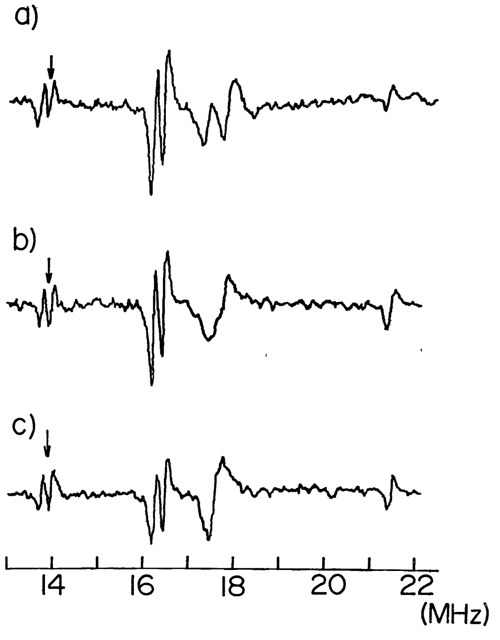

Fig. 4. The ENDOR spectra of the 1,4-diethylnaphthalene anion by reduction with potassium observed with the THF solution. a) −110 °C b) −90 °C, c) −70 °C.

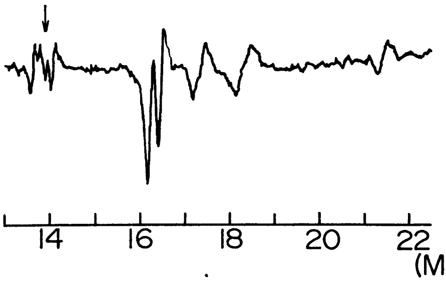

Fig. 5. The ENDOR spectrum of the 1,4-dipropylnaphthalene anion by reduction with the THF solution at −110 °C.

shown in Fig. 5, but the β-proton splittings could not be detected clearly above −110 °C.

Measurements of the β-proton splittings were extensively performed in other systems, such as DME–Na, DME–Li, THF–Na, THF–Li, and DMF–K, but the alkyl β-protons exhibited the equivalent splitting everywhere.

Table 1. Proton hyperfine coupling constants of 1,4-dialkylnaphthalene radical anions (G)

		Temp °C	a_2^H	a_6^H	a_5^H	$a^\beta_{1,4}$	$a^\gamma_{1,4}$
Methyl	K–DME[b]	−70	1.66	1.83	5.45	3.30	
	K–DME[b]		1.63	1.79	5.17	3.26	Lit. 13)
	K–DME[a]	−70	1.67	1.83	5.29	3.29	
	Li–DME[a]	−90	1.68	1.85	5.21	3.29	
	K–THF[a]	−100	1.70	1.86	5.32	3.14	
	Na–THF[a]	−100	1.65	1.82	5.32	3.41	
	Li–THF[a]	−100	1.68	1.85	5.25	3.40	
Ethyl	K–DME[a]	−80	1.68	1.86	5.27	2.87	0.09
	Li–DME[a]	−80	1.68	1.86	5.21	2.86	0.09
	K–THF[b]	−75	1.76	1.76	5.56	2.80	
	K–THF[a]	−110	1.69	1.84	5.34	2.52 2.89	0.08
	K–THF[a]	−70	1.70	1.87	5.34	2.63	0.08
	Na–THF[a]	−110	1.69	1.83	x	2.80	0.08
	Li–THF[a]	−110	1.67	1.82	5.28	2.77	0.08
Propyl	K–DME[a]	−80	1.69	1.86	5.25	2.45	0.06 0.16
	Li–DME[a]	−80	1.70	1.86	5.21	2.46	0.05 0.15
	K–THF[a]	−100	1.71	1.88	5.29	2.49 3.16	0.06 0.16
	Na–THF[a]	−100	1.67	1.85	x	2.38	0.06 0.16
	Li–THF[a]	−100	1.72	1.86	5.21	2.42	0.05 0.18

a) ENDOR, b) ESR
(x); The observation of signal was failed to.

Temperature Dependence of the Alkyl β-Proton Splittings. The ENDOR spectra in solution can be observed in only a limited temperature range because of the complicated relaxation mechanism which determines the ENDOR intensity.[17] The temperature dependences of the alkyl β-proton splittings of the 1,4-dialkylnaphthalene anions, therefore, have been examined in different solvents with various alkali metal cations.

As is shown in Fig. 6, the ethyl β- and the propyl β-proton hyperfine coupling constants show a positive temperature dependence. The slope of the temperature dependence for the propyl β-proton splitting is slightly larger than that for the ethyl β-proton splitting.

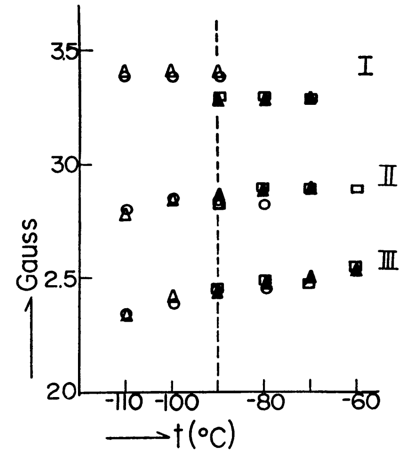

Fig. 6. Temperature dependence of the β-proton splittings observed with the 1,4-dialkylnaphthalene anions. I) 1,4-dimethylnaphthalene, II) 1,4-diethylnaphthalene, III) 1,4-dipropylnaphthalene.
□; K-DME, ▲; Li-DME, ○; Na-THF, △; Li-THF.

The reduction in the alkyl β-proton splitting from the methyl proton splitting has been successfully explained in terms of the hindered internal rotation of the alkyl group.[1,2,3,6]

To calculate the β-proton splitting as a function of the temperature, the following equations were used:[2,3,6,7]

$$Q(\theta) = B_0 + B_2 \cos^2\theta \tag{1}$$

$$a^\beta_{1.4} = \langle Q(\theta)\rangle \rho^\pi_{1.4} = B\rho^\pi_{1.4}\langle\cos^2\theta\rangle,\ \theta = \alpha + \theta_0 \tag{2}$$

$$\langle\cos^2\theta\rangle = \frac{\sum_{i=0}^{\infty}\langle\Phi_i(\alpha)|\cos^2(\alpha+\theta_0)|\Phi_i(\alpha)\rangle e^{-E_i/kT}}{\sum_{i=0}^{\infty} e^{-E_i/kT}} \tag{3}$$

Where B_0 and B_2 are the empirical parameters, $\rho^\pi_{1,4}$ is the spin density on the ring carbon atom adjacent to the alkyl group, and θ is the dihedral angle between the aliphatic C–H bond and the symmetry axis of the 2 p_z orbital on the aromatic carbon atom.[1,2] In Eq. 2, the contribution from B_0 was neglected and the value of $B\rho^\pi_{1,4}$ was estimated to be 2×3.35 G from the methyl proton splitting of the 1,4-dimethylnaphthalene anions by assuming the free rotation of the methyl group.[13] In Eq. 3, the wave function, $\Phi_i(\alpha)$, and the eigenvalue, E_i, were obtained by solving this equation:

$$-\left(\frac{\hbar^2}{2I}\right)\left(\frac{d^2\Phi_i}{d\alpha^2}\right) + [V(\alpha) - E_i]\Phi_i = 0 \tag{4}$$

where the moment of inertia, I, of the molecule fragment, Φ-R, was calculated to be 0.55×10^{-38} g·cm² for 1,4-diethylnaphthalene and 2.65×10^{-38} g·cm² for 1,4-dipropylnaphthalene, assuming that a preferred rotation of the residual group occurs about the C_1–C_4 axis of the molecule of 1,4-dialkylnaphthalenes.

In order to determine the rotational potentials, $V(\alpha)$, in Eq. 4, we assumed that the potential barrier arises from an intermolecular interaction between the alkyl group and the aromatic ring. The external barrier sources, such as a solvation of anions, were neglected, because the dependence of the β-proton splittings on the solvents and counter cations is very small, as is shown in Fig. 6.

For 1,4-diethyl- and 1,4-dipropylnaphthalene, there are two distinct steric repulsions. The major steric repulsions are those between the γ-methyl and the γ-ethyl groups, respectivery, and the 5-CH or 8-CH group of the naphthalene moiety. The other is between the γ-alkyl group and the 2-CH or 4-CH group of the naphthalene moiety. Thus, the appropriate potential function of the ethyl and propyl groups has two maxima with different heights, as is illustrated in Fig. 7. The equilibrium conformation corresponds to the (B) state given in Fig. 7. The calculation of the Lennard-Jones repulsion energy between the non-bonded ethyl and the neighboring aromatic protons supported this result. According to the above consideration, the rotational potential can be approximated as:

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

$$a_0 = \frac{1}{4}(V_a + V_c), \quad a_1 = \frac{3}{8}(V_a - V_c),$$

$$a_2 = \frac{1}{4}(V_a + V_c), \quad a_3 = \frac{1}{8}(V_a - V_c) \tag{5}$$

where V_a and V_c are the potential energies corresponding to the (A) state and the (C) state respectively, as is given in Fig. 7.

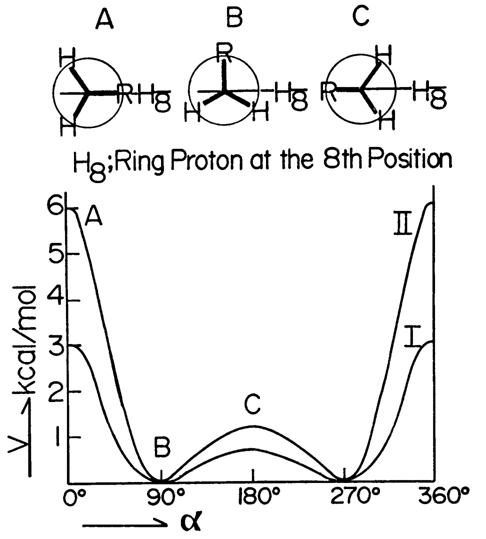

Fig. 7. Possible equilibrium conformations of the 1,4-dialkylnaphthalene anion and the rotational potential curve of the alkyl groups as a function of α. I) 1,4-diethylnaphthalene, II) 1,4-dipropylnaphthalene.

At the (A) conformation, the dihedral angle, θ_0, of the β-proton in Eq. 2 is equal to $\pi/6$. The matrix, $|\langle i|H|j\rangle|$, was diagonalized by expanding the function into a Fourier series:

$$\Phi_i(\alpha) = \sum_{j=0}^{\infty}(C_{ij} \sin j\alpha + D_{ij} \cos j\alpha) \tag{6}$$

The $\langle\cos^2\theta\rangle$ values calculated for 1,4-diethyl- and 1,4-dipropylnaphthalene in the temperature range from -120 °C to -60 °C for various values of V_a and V_c are shown in Fig. 8.

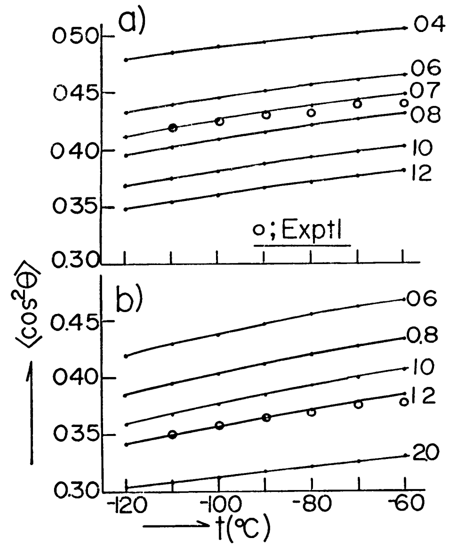

Fig. 8. Theoretical temperature dependence of $\langle\cos^2\theta\rangle$ for rotating alkyl groups. Numerical calculations were carried out by taking the potential barrier, V_c, as a variable parameter, where the barrier height, V_a, was fixed to 3 and 6 kcal/mol for 1,4-diethyl- and 1,4-dipropylnaphthalene, respectively. a) 1,4-diethylnaphthalene, b) 1,4-dipropylnaphthalene.

The best agreement between the calculated and experimental temperature dependence of $\langle\cos^2\theta\rangle$ was obtained with $V_a=3.0$, $V_c=0.7$, and $V_a=6.0$, $V_c=1.2$ kcal/mol for 1,4-diethyl- and 1,4-dipropylnaphthalene respectively.

Based on the theoretical calculation and the experimental result, it can be said that, at room temperature, the ethyl group in the 1,4-diethylnaphthalene rotates in the rotational potential in Fig. 7. On the other hand, the motion of the propyl group is thought to be a torsional oscillation around the equilibrium conformation (B) rather than a restricted rotation.

Non-equivalent Alkyl β-Proton Splittings. In the ENDOR spectra for the 1,4-diethylnaphthalene–THF–K system, two signals attributed to the non-equivalent splittings of the β-methylene protons were recorded at -110 °C. They collapsed into a single line as the temperature was raised to -70 °C (see Fig. 4.). Previous ESR and ENDOR studies[14,15] of non-equivalent alkyl β-proton splittings have established a tightly locking model of an alkyl group. The Heller-McConnell relationship gives nearly $2\pi/3$ for the sum of the two dihedral angles of the non-equivalent β-protons.[16] On the contrary, for the 1,4-diethyl- and 1,4-dipropylnaphthalene anions, the sum of the dihedral angles does not coincide with $2\pi/3$, but is much smaller. It would appear that the splitting of the methylene lines for the 1,4-diethylnaphthalene anion arises neither from rotational isomers nor from the tightly locked ethyl group.

In order to explain the anomalous non-equivalene splitting detected for the two β-methylene ENDOR lines at -110 °C, it is postulated that the steric repulsion between the solvated cation and the rotating alkyl

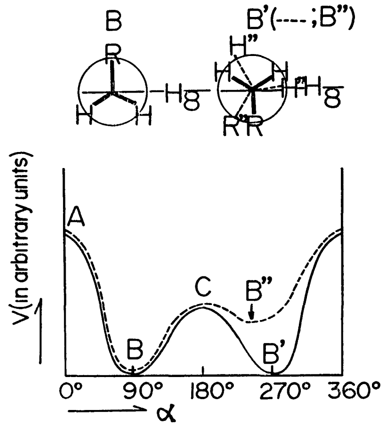

Fig. 9. Schematic diagram of the change in the potential curve due to the steric effect of the solvated-cation. (B″); Probable equilibrium conformation.

groups alters the rotational potential curve from a symmetric to an asymmetric one, where the motion of the alkyl groups take the fast rotational limit. In consequence, the averaged $\cos^2\theta$ in Eq. 3 for each alkyl β-proton may have a different value.

Based on the conductivity and ESR measurements,[18–20] it is well established that the naphthalene anions form solvent-separated ion pairs in THF solutions at low temperatures (<-70 °C) and that a potassium ion, which becomes fully coordinated with THF molecules, is located on the plane of the aromatic ring. The separation between the two opposite charges has been estimated to be 6.5—7 Å for the naphthalene anion,[21] and it has been considered to be insensitive to the aromatic moiety, as has been discussed by Chang *et al.*[19] The radius of the THF-coordinated potassium ion, which is larger than those of lithium and sodium, may be more than 4 Å[21] In 1,4-diethylnaphthalene, the ethyl substitution increases the averaged halfthickness of the aromatic moiety by about 4 Å. At the equilibrium configuration, B′, shown in Fig. 9, the γ-methyl group, which is perpendicular to the aromatic plane, gives rise to a strong steric repulsion between the alkyl group and solvated cation. If the steric repulsion due to the solvated cation is negligible, the populations at the (B) and (B′) states will be equal in a symmetric rotational potential. The steric effect of the solvated cation, however, destabilizes the (B′) state more than the (B) state and, at the same time, the (B′) state is converted into a new equilibrium conformation (B″), as is shown in Fig. 9. The rotational potential, therefore, is altered from a symmetric to an asymmetric one, and the averaged $\cos^2\theta$ for each alkyl β-proton in an asymmetric potential may take a different value. The nonequivalent alkyl β-proton splittings observed for the 1,4-dipropylnaphthalene anion may be understood on the basis of the same assumption.

At -75 °C, two signals attributed to the β-methylene protons collapsed into a single line. This means that the thermal activation energy accelerated the motion of the alkyl group; thus, the averaged thickness of the anion were increased. The distance between the paired ions becomes greater, and the asymmetry potential again approaches the original symmetric one.

The numerical calculations were carried out on the FACOM 230-75 at the Data Processing Center, Kyoto University.

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