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ESR Studies on Radical Anions of Calicene Derivatives

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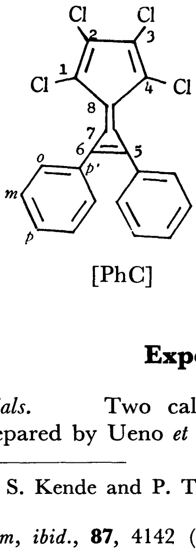
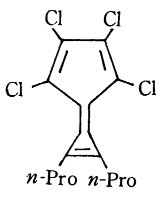
Two calicene derivatives, 1,2,3,4-tetrachloro-5,6-diphenylcalicene and 1,2,3,4-tetrachloro-5,6-di-*n*-propylcalicene, were reduced with an alkali metal in degassed tetrahydrofuran and the ESR spectra of the resluting mono-anion radicals were investigated. It was found that in both anion radicals the unpaired spin does not exist on the five-membered ring, and is localized only on the other part. In the latter anion radical, the five-membered and three-membered rings were found to be twisted toward each other at about 45°, a line width alternation caused by hindered internal rotation of two adjacent *n*-propyl groups being observed. The potential barrier for the hindered rotation was determined to be about 1.5 kcal/mol.

Cycloheptatrienecyclopentadiene, commonly called calicene, has a very unique structure consisting of unsaturated five-membered and three-membered rings bonded to each other. Its derivatives were first synthesized by Kende and Izzo,[1,2] Jones and Pyron[3] and also by Prinzbach and Fischer.[4] Since then, many derivatives have been synthesized, their physical and chemical properties being studied extensively. However, no ESR studies on their ion radicals have yet been reported.

Using two species of calicene derivatives, 1,2,3,4-tetrachloro-5,6-diphenylcalicene [PhC] and 1,2,3,4-tetrachloro-di-*n*-propylcalicene [PrC], we succeeded in preparing their anion radicals. This paper reports the details of ESR studies on these anion radicals which were briefly reported previously.[5]



[PhC]



[PrC]

Experimental

Materials. Two calicene derivatives PhC and PrC were prepared by Ueno *et al.* and Kitahara *et al.*[6,7] Tetrahydrofuran [THF] (Wako Junyaku Co.) was distilled after being refluxed over sodium wire for several hours, dehydrated with sodium-potassium alloy and degassed by freeze-thaw cycles. Sodium (Wako Junyaku Co.) and potassium (Kanto Kagaku Co.) metals were used.

Procedures. Anion radicals were prepared by bringing degassed THF solutions of calicenes into contact below −30 °C with a sodium or a potassium mirror deposited by vacuum evaporation.

In the case of PhC, the solution turned bluish green when it was warmed slowly up to room temperature. The anion radical thus obtained was very stable at room temperature giving a well resolved ESR spectrum. However, it turned reddish brown and lost the ESR signal when kept in contact with the mirror for a long time.

In the case of PrC, the ESR signals observed at low temperatures disappeared rapidly when warmed to room temperature. We therefore introduced the degassed solution previously cooled in a dry ice-methanol bath into a glass capillary also degassed, with an alkali metal mirror deposited on the wall, and immediately inserted the capillary into a low temperature apparatus attached to an ESR cavity. In this way the light yellow solution gave a stable ESR signal below −30 °C where the temperature dependence was reversible. With a gradual rise of temperature above −30 °C, the pattern of the signal changed irreversibly and finally disappeared at room temperature.

A JEOL P-10 type ESR spectrometer (X band, 100 kHz modulation) was used. A NEAC 2200 MODEL 500 Electronic Computer in the Calculation Center of Tohoku University was used for the simulation of ESR spectra and the calculation of spin densities.

Results and Discussion

Hyperfine Structure. Figure 1 shows the observed and simulated ESR spectra of PhC anion radical obtained with the use of sodium and potassium. Only

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[1] A. S. Kende and P. T. Izzo, *J. Amer. Chem. Soc.*, **87**, 1609 (1965).

[2] *idem*, *ibid.*, **87**, 4142 (1965).

[3] W. M. Jones and R. S. Pyron, *ibid.*, **87**, 1608 (1965).

[4] H. Prinzbach and U. Fischer, *Angew. Chem.*, **77**, 258 (1965).

[5] S. Niizuma, S. Konishi, H. Kokubun, and M. Koizumi, *Chem. Lett.*, **1972**, 643.

[6] M. Ueno, I. Murata, and Y. Kitahara, *Tetrahedron Lett.*, **1965**, 2967.

[7] Y. Kitahara, I. Murata, M. Ueno, K. Sato, and H. Watanabe, *Chem. Commun.*, **1966**, 180.

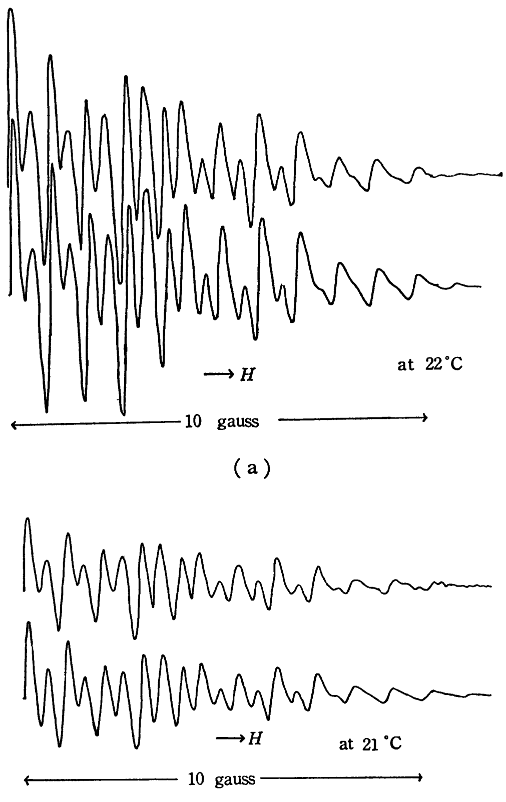

Fig. 1. ESR spectra of PhC anion radical.
(a) K reduction upper; observed
lower; simulated
(b) Na reduction upper; observed
lower; simulated

TABLE 1. OBSERVED hfs CONSTANTS AND CALCULATED SPIN DENSITIES

Position	Observed hfs const.		●	○	⊙	△
1			0	−0.005	0	−0.001
1-Cl			0	−0.001	0	−0.000
2			0	−0.004	0	−0.004
2-Cl			0	−0.001	0	−0.001
7			0	−0.032	0	−0.005
8			0	−0.003	0	−0·011
6			0.192	0.265	0.156	0.217
p′	K	Na	0.047	0.015	0.085	0.068
o	2.80	2.90	0.075	0.094	0.062	0.072
m	0.95	1.00	0.006	0.027	0.014	0.022
p	3.20	3.35	0.098	0.115	0.109	0.128

Parameters used
$\alpha_{Cl}=\alpha_C+1.8\beta$ McLachlan's in the case of bond
$\beta_{Cl}=0.8\beta$ parameter length alternation
$\alpha_{C'}=\alpha_C+0.18\beta$ $\lambda=1.0$ $\beta_{single}=0.59\beta_{double}$
$\beta_{phenyl}=0.80\beta_{double}$

●: Hückel
○: McLachlan
⊙: Hückel with bond length alternation
△: McLachlan with bond length alternation

the right halves of ESR spectra are illustrated because of their symmetry with respect to the central lines. The simulated spectra agree satisfactorily with the observed ones. Simulations were performed by assigning a set of different hfs constants to two sets of four protons and one set of two protons. These protons naturally belong to two equivalent phenyl groups. The total separation of the hyperfine structure due to the protons of the two phenyl groups is about 22 Gauss. This implies that the unpaired spin mainly exists on the two phenyl groups.

Spin Density Calculation of PhC Anion Radical. The unpaired spin densities of PhC anion radical were calculated by the simple Hückel and McLachlan methods to interpret the observed hfs constants, assuming all rings are coplanar. It has been reported that for the calculation of electronic states of PhC neutral molecule, consideration of bond length alternation[8] is desirable; accordingly a similar treatment was also taken into account in the present calculation.

The results are shown in Table 1. It is evident that the unpaired spin does not exist (simple Hückel) or scarcely exists (McLachlan) on the five-membered ring and also on the 7-carbon atom. This conclusion is quite independent of bond length alternation.

According to results from the simple Hückel method, the orbital occupied by the unpaired spin belongs to a_2, corresponding to the lowest vacant orbital of *cis*-stilbene. Thus the PhC anion radical is almost the same as the *cis*-stilbene anion radical. The ESR of the latter, however, has not yet been reported, the transform being much more stable.

The localization of the unpaired spin on two phenyl groups and on C_5 and C_6 agrees very well with the expectation based on the analysis of ESR spectra. Spin densities evaluated by the four methods are plotted against hfs constants in Fig. 2. A fairly good straight line passing through the origin can be drawn for the values obtained by McLachlan method without bond length alternation. From its slope,

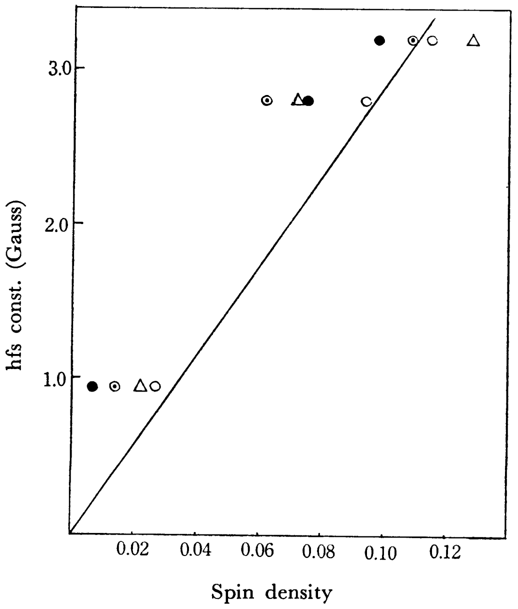

Fig. 2. A plot of hfs constants *vs.* spin densities.

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[8] T. Nakajima, S. Kohda, A. Tajiri, and S. Karasawa, *Tetrahedron*, **23**, 2189 (1967).

the ordinary McConell's Q-value of 29 Gauss is obtained. Consideration of bond length alternation does not give any improvement. A similar result was reported by Ikegami *et al.* for the case of the tropone anion radical.[9]

The observed and the simulated ESR spectra of PrC anion radical at −51 °C are shown in Fig. 3.

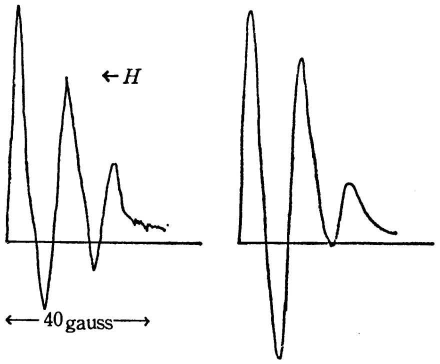

Fig. 3. ESR spectra of PrC anion radical at −51 °C.
left side; observed
right side; simulated

Under over modulation, the spectrum consists of five lines with the approximate intensity ratio 1 : 4 : 6 : 4 : 1. Thus the simulation was carried out by considering four equivalent protons. A hfs constant was found to be 14 Gauss. These must be β-protons of two *n*-propyl groups.

Generally, a hfs constant of β-protons of an alkyl group $a_\beta{}^{\mathrm{H}}$ is given by the following equation.[10]

$$a_\beta{}^{\mathrm{H}} = B\langle\cos^2\theta\rangle\rho_{\mathrm{C}}$$

where ρ_{C} is the spin density of carbon atom to which the alkyl group attaches, B is a constant in the range 40∼56 Gauss and θ is the angle between the axis of ring carbon $2p_z$ orbital and the carbon-hydrogen bond both projected on the plane perpendicular to $\mathrm{C}_\alpha-\mathrm{C}_\beta$ axis. If free rotation of the alkyl group is is allowed, $<\cos^2\theta>$ is equal to 1/2. Then from the above equation ρ_{C} becomes equal to or greater than 1/2 in the present case. Thus we can say that the spin is localized only on C_5 and C_6.

Spin Density Calculation of PrC. In calculating the unpaired spin densities of PrC, we must consider whether the three-membered and five-membered rings are coplanar or not. A molecular model for PrC demonstrates that chlorine atom bonded to C_1 or C_4 and δ-hydrogen atom of *n*-propyl groups collide with each other if free rotation is assumed for the latter group. To allow this free rotation without collision with chlorine atoms, the three-membered and five-membered rings should be twisted at an angle greater than 45°. In view of the fact that free rotation around the C_7—C_8 bond has been reported for 1-formyl-5,6-di-*n*-propylcalicene[11] at temperatures higher than room temperature on the basis of NMR data, the above geometry for PrC in our case seems to be quite reasonable although the radical is ionic and the temperature is below room temperature.

Thus, it was assumed that the five-membered and three-membered rings are not in general coplanar. In calculating the spin densities of PrC, a parameter $\cos^2\alpha$ (α is an angle between two rings) was introduced for the resonance integral between C_7 and C_8 and the calculation was made for various α-values. In the case of PhC anion radical, the unpaired spin densities were found to be independent of α, but there is no steric hindrance according to the model constructed, so that all the rings are considered to be coplanar in the PhC anion radical.

The effect of hyperconjugation was taken into account since it is generally believed that the hfs constant of an alkyl group is mainly due to this. In the actual calculation we regarded a *n*-propyl group as $-\mathrm{C}\equiv\mathrm{H_2R}$ and used the following parameters.[12,13]

$$\mathrm{C}_{5(\mathrm{or}\ 6)} \overset{1.0\beta}{\text{——}} \underset{\alpha-0.1\beta}{\mathrm{C}_\beta} \overset{2.5\beta}{\equiv} \underset{\alpha-0.5\beta}{\mathrm{H_2R}}$$

We considered that the above procedure is sufficient as a first approximation and made no use of other more refined methods.[14,15] Only the result by Hückel method is shown in Fig. 4, because McLachlan method gives an essentially similar result. When α is greater than 40°, the spin densities on C_5, C_6 and on $\mathrm{H_2R}$ are respectively 0.42 and 0.076 (Fig. 4). The latter leads to a splitting constant of a methylene proton $508\times0.076\times1/3=12.9$ Gauss which agrees fairly well with the observed value.

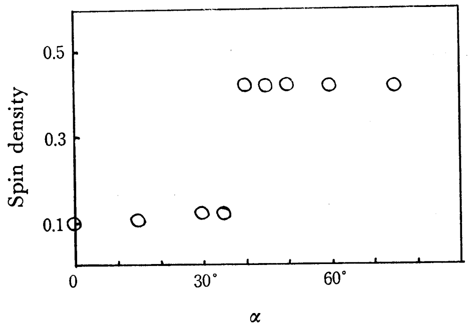

Fig. 4. A plot of spin density on position 5 or 6 *vs.* twisting angle α.

Reason for a Sudden Spin Density Change at around 40°. An unusual dependence of spin density on α appears, increasing only very little from $\alpha=0$ to $\alpha<40°$, but suddenly jumping at 40° and then remaining constant. The reason for this is as follows.

The PrC anion radical is a 21 π-electron system including hyperconjugation of two *n*-propyl so that the unpaired electron occupies the 11th orbital. According to results obtained by the simple Hückel

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[9] Y. Ikegami, H. Watanabe, and S. Seto, This Bulletin, **45**, 1976 (1972).

[10] C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

[11] A. S. Kende, P. T. Izzo, and U. Fulmor, *Tetrahedron Lett.*, **1966**, 3697.

[12] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052.

[13] R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956).

[14] J. P. Colpa and E. deBoer, *Mol. Phys.*, **7**, 333 (1963).

[15] D. H. Levy, *ibid.*, **10**, 233 (1966).

calculation the energy for two types of orbitals either depends or does not depend on angle α. These orbitals belong to b_1 and a_2 respectively, assuming PrC molecule has C_{2v} symmetry. The 11th orbital occupied by the unpaired electron at $\alpha=0$ belongs to the former and the 12th orbital to the latter. The energy of the 11th orbital increases with the increase in α, moving above the 12th level for $\alpha>40°$. Inversion occurs at 40° between 11th and 12th levels. Thus when α exceeds 40°, the unpaired electron occupies the 12th orbital (when $\alpha=0$) whose energy is independent of α. The angle α at which the inversion occurs depends slightly on the parameters of hyperconjugation. The increase of the total electronic energy due to twisting is about 0.42 β/mol which is equal to 6.9 kcal/mol at $\alpha=45°$ if resonance integral β is assumed to be 16.5 kcal/mol.[8)]

Observation of Line Width Alternation. In the ESR spectrum of PrC anion radical (Fig. 3), the second line from the right is broader than the others. We examined the temperature dependence of ESR spectra, the results for potassium and sodium reduction being given in Figs. 5 and 6. Line width changes remarkably only in the second line. The temperature dependence is almost completely reversible, and is considered to be due to the line width alternation.

Hindered Rotation as a Cause of Line Width Alternation. The line width alternation might be attributed to the hindered rotation of two n-propyl groups. The molecular model constructed shows that the free rotation of each n-propyl group around C_α–C_β, $C_{\alpha'}$–$C_{\beta'}$ axis is not allowed because of mutual steric hindrance of the two groups. It is expected that certain stable conformations exist and the transformation from one to another occurs with characteristic frequencies determined by the potential barriers between them. In the frozen state at −150 °C, PrC anion radical gives a spectrum with the intensity ratio 1 : 2 : 1, suggesting that the spectrum arises mainly from only two equivalent protons and that the other protons have fairly small hfs constants. This implies that the C_β—H or $C_{\beta'}$—H bond belonging to the former group has a small angle to the axis of $2p_z$ orbital of C_5 or C_6 and the one belonging to the latter a large angle.

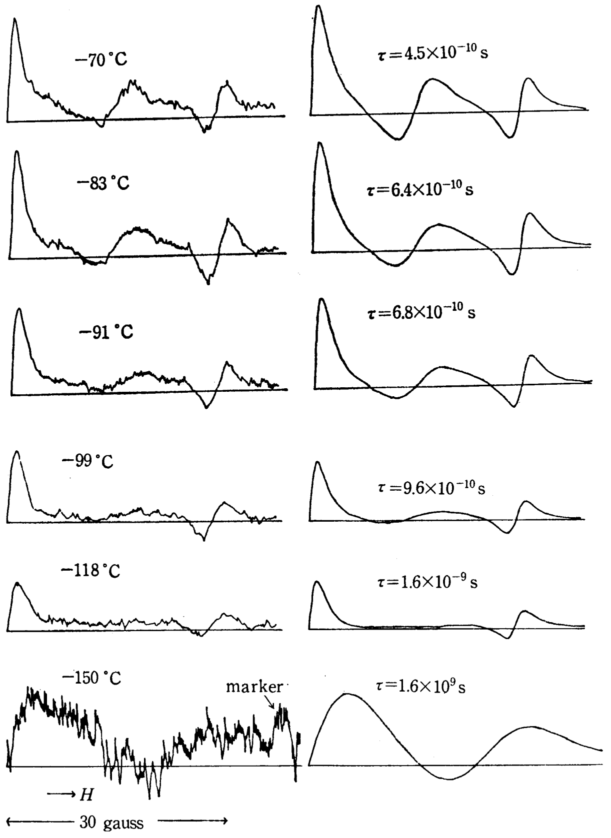

Fig. 5. ESR spectra of PrC anion radical at different temperatures (K reduction).
left side; observed
right side; simulated

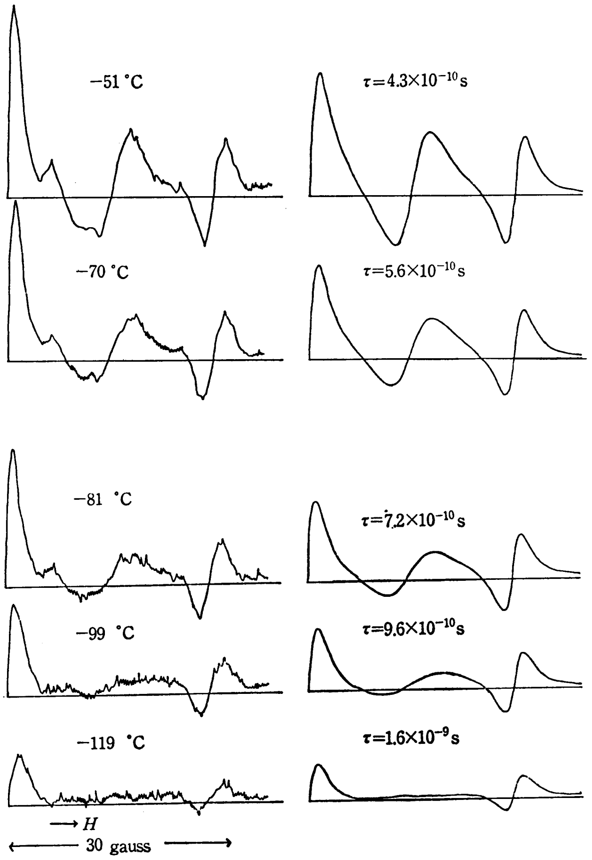

Fig. 6. ESR spectra of PrC anion radical at different temperatures (Na reduction).
left side; observed
right side; simulated

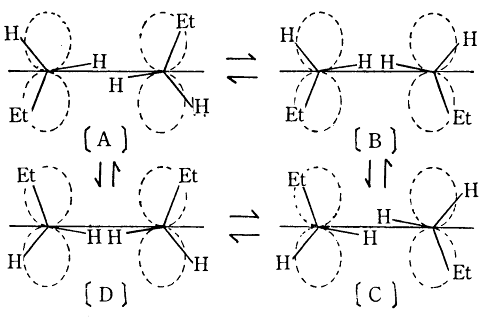

Fig. 7. Equilibrium four conformations.

The four conformations shown in Fig. 7 are most plausible as stable ones. All other conformations conceivable can be eliminated because of a strong steric hindrance between two R-groups.

Simulation Analysis of Line Width. In order to analyze the present result we made use of a theory developed and applied successfully to a similar system to ours.[16,17] According to the theory, the average magnetization to the four conformations (Fig. 7) is expressed as follows.

$$\langle\overline{G}\rangle = -i\omega_1 \mathrm{M}_0$$
$$\times \left\{ \frac{(2+3\eta\tau)(2+2\eta\tau)+\tau^2(1+\eta\tau)(\eta_\mathrm{C}\eta_\mathrm{D}+\eta_\mathrm{A}\eta_\mathrm{B})}{2\eta+3\eta^2\tau+\tau(1+2\eta\tau)(\eta_\mathrm{C}\eta_\mathrm{D}+\eta_\mathrm{A}\eta_\mathrm{B})+\tau^3\eta_\mathrm{A}\eta_\mathrm{B}\eta_\mathrm{C}\eta_\mathrm{D}} \right\}$$

where $\omega_1\mathrm{M}_0$ is a constant intensity factor, subscripts A, B, C, D refer to the four conformations and τ[18] is the lifetime of each conformation. The η's are defined by the following expression.

$$\eta_\mathrm{A} = 1/T_2 - i(\omega_0 - \omega + \omega_\mathrm{A})$$
$$2\eta = \eta_\mathrm{A} + \eta_\mathrm{B} = \eta_\mathrm{C} + \eta_\mathrm{D}$$

where $1/T_2$ is the line width in the absence of conformation change, ω_0 the Larmor precession frequency of the electron in the absence of hyperfine interaction and ω_A the shift in resonance frequency due to interactions with protons in conformation A. The imaginary part of $\langle\overline{G}\rangle$ gives an absorption spectrum. In the present case ω_A's were determined for each state of sixteen nuclear spin states and $1/T_2$ was equated to the observed line width of the end line. For simulation the absorption line was converted into the first differential by numerical differentiation for comparison with the observed spectra. Calculations were made by use of an electronic computer.

In the case of potassium reduction (Fig. 5), a constant quantity of absorption, about 1/20 of the total, should be added to the central line in order to get a good agreement with the experiment. This may be due to an impurity or a certain radical produced by some side reaction. Simulation spectra agree very well with the observed ones. Simulation was similarly made for sodium reduction (Fig. 6). For the end line and its adjacent line the agreement between observed and simulated ones is good. However, the simulated spectra differ from the observed ones in the central region where the latter is more intensive and has a small shoulder. The disagreement may be due to the same reason as in the case of potassium reduction. This is supported by the fact that strength of the central line increases and the shoulder becomes remarkable with the rise in temperature, and that this is not reversible. The best values for the hfs constants of protons are 24 and 4 Gauss for both potassium and sodium reduction and are quite consistent with the conformation in Fig. 7.

Potential Barrier Height of Hindered Rotation. The potential barrier height of the hindered rotation of *n*-propyl groups can be determined from the temperature dependence of lifetime τ or the first-order rate constant k $(=1/\tau)$. A plot of $\log_{10}(1/\tau)$ against $1/T$ is given in Fig. 8. The linearity is satisfactory. Activation energies E_A and frequency factors k_0 are determined from the slopes and the intercepts of two lines, the values being 1.6_5 kcal/mol, $1.3\times10^{11}\,\mathrm{s}^{-1}$ for potassium reduction and 1.4_1 kcal/mol, $6.2\times10^{10}\,\mathrm{s}^{-1}$ for sodium reduction. The difference in values for the two cases may be due to the difference in the perturbation by cations.

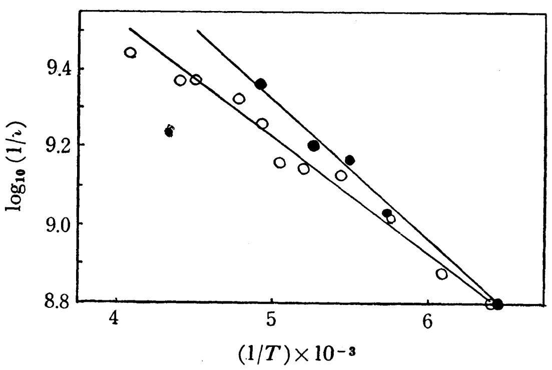

Fig. 8. A plot of $\log_{10}(1/\tau)$ *vs.* $1/T$.
○: Na reduction, ●: K reduction

Stone and Maki[19] discussed the internal rotation of an alkyl group of nitroalkane anion radical in solution from a quantum mechanical viewpoint. According to them the height of the potential barrier for internal rotation is 1.4 kcal/mol, and the spin density on nitrogen atom to which an alkyl group links is 0.7±0.1. Ishizu *et al.* also reported a similar equilibrium conformation for 2,2′-dialkylbiphenyl.[20]

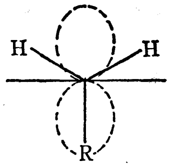

Fig. 9. Possible equilibrium conformation for $\mathrm{RCH_2}$-Ar.

The conformation is given in Fig. 9. The hindered rotation of the present system is similar to that of this compound. Miyagawa and Itoh[21] obtained 3.6±0.2 kcal/mol and $(10\pm4)\times10^{12}\,\mathrm{s}^{-1}$ as the value of E_A and k_0 respectively for rotation of a methyl group in $\mathrm{CH_3\dot{C}HCOOH}$ radical produced in a single crystal of L-alanine by γ-ray irradiation. Iwaizumi and Isobe[22] have reported on the inversion of two benzene ring planes in 4,5,9,10-tetrahydropyrene anion radical (non-planer molecule) 2.0—9.0×10^{-6} s (−90 °C)

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16) A. Carrington, *Mol. Phys.*, **5**, 425 (1962).

17) J. R. Bolton, A. Carrington, and P. F. Todd, *Mol. Phys.*, **6**, 169 (1963).

18) We defined τ as the reciprocal of the angular frequency of the transformation.

19) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

20) K. Ishizu, K. Mukai, H. Hasegawa, K. Kubo, H. Nishiguchi, and Y. Deguchi, This Bulletin, **42**, 2808 (1969).

21) I. Miyagawa and K. Itoh, *J. Chem. Phys.*, **36**, 2157 (1962).

22) M. Iwaizumi and T. Isobe, This Bulletin, **38**, 1547 (1965): Abstract of Symposium on ESR, in Kanazawa, October, p. 1 (1972).

and gave 4∼5 kcal/mol as the values of the lifetime of individual configuration and the energy barrier. The values we have obtained are reasonable as compared with the above.

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