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An Electron Spin Resonance Study of the 5,12-Dihydrotetracene Radical Anion and Its Ion Pairs with Alkali Metal Cations

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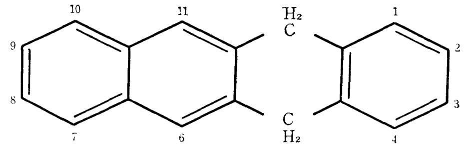
The 5,12-dihydrotetracene radical anion and its ion pairs with alkali-metal cations have been investigated by electron spin resonance (ESR). It has been found that the frequency of the inversion of the radical molecule is $\gg 10^8$ Hz and that the unpaired electron is distributed between the benzene and naphthalene rings. Such a distribution of the unpaired electron between the two conjugated systems is assumed to occur *via* a hyperconjugation mechanism. On the other hand, it was observed that the proton hyperfine splittings of the radical anion are appreciably affected by the association of an alkali-metal cation. In the case of the 5,12-dihydrotetracene-potassium ion-pair in THF, the hyperfine components of the methylene protons show an alternating line-width effect. On the basis of the observed effects of the alkali metal cations, a model of the ion-pair structure is proposed, and the alternating line-width effect is explained in terms of an intramolecular migration of the potassium ion from one side of the molecular plane to the other. The activation energy of this motion of the potassium ion has been estimated to be 3.1 ± 0.2 kcal.

In this paper we wish to report the results of an investigation of the 5,12-dihydrotetracene radical anion and of the ion pair formed between the 5,12-dihydrotetracene radical anion and alkali-metal cations. It is well known that the ESR technique provides us with interesting and important information on the spin distribution in free radicals.[1,2] It is also useful in providing information on the conformation of the molecules of free radicals, and some times allows measurements of the dynamic motions of the molecule, such as the conformational interconversion and the *cis-trans* conversion.[3–6] The 5,12-dihydrotetracene (I) treated here is an interesting molecule in that it can be considered as consisting of two conjugated systems, benzene and naphthalene rings, weakly coupled through two methylene bridges. By analogy with the 9,10-dihydroanthracene molecule, which is in a non-planar conformation,[7] it can also be considered that the conformation of the 5,12-dihydrotetracene radical anion is non-planar, which may therefore lead to an inversion process. It seemed interesting to investigate the spin distribution and the inversion process of such a molecule. In this paper we will show that the unpaired electron is distributed between the benzene and naphthalene rings by a weak coupling between the two rings, although a large portion of the spin densities exist on the naphthalene ring; the transfer of the unpaired electron between the two conjugated systems may be explained by the hyperconjugation effect of the methylene bridges. We will also show that the rate of inversion must be: $\gg 10^8$ Hz.



I

On the other hand, it has been observed that the proton hyperfine splitting constants of the 5,12-dihydrotetracene radical anion change appreciably upon the formation of the ion pair with an alkali-metal cation. For the case of the ion pair with the potassium ion in THF, the hyperfine splitting due to the methylene protons changes markedly with the temperature, and it shows an alternating line-width effect at high temperatures. It is shown that the observed effects of the cations can be explained by an ion-pair model where the alkali ion favors a situation above the naphthalene skeleton, and that

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[1] P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen, London (1967), p. 239.

[2] J. R. Bolton, "Radical Ions," ed. by E. T. Kaiser and L. Kevan, Interscience Publishers, New York, N. Y. (1968), p. 1.

[3] G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).

[4] A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

[5] D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967).

[6] P. D. Sullivan and J. R. Bolton, "Advances in Magnetic Resonance," Vol. 4, ed. by J. S. Waugh, Academic Press, New York, N. Y. (1970), p. 39.

[7] I. G. M. Campbell, C. G. LeFevre, R. J. W. LeFevre and E. E. Turner, *J. Chem. Soc.*, **1938**, 404.

the alternating line-width effect may be attributed to the migration of the potassium ion form one side of the naphthalene ring to the other. Previously, de Boer *et al.*[8] proposed an ion-pair model for the pyracene-alkali metal ion-pair, which gave us the impression that the alkyl groups have a strong affinity to the alkali ion. However, in our studies of the ion-pairs of acenaphthene[9] and 9,10-dihydroanthracene radical anions[10] with alkali ions we pointed out that an electrostatic interaction model, which predicts the ion-pair structure where an alkali ion is situated at the position of the highest negative charge, is more reliable than de Boer's model. The present result supports our prediction. This is also one of the rare sources of information about the migration of the alkali ion form one side of a molecular plane to the other.

Experimental

The anion radical of the 5,12-dihydrotetracene was prepared by reduction with lithium, sodium, and potassium. The solvents used were 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and tetrahydropyran (THP). In DME and THF, three kinds of alkali metals were used as reducing agents, while in THP only potassium was used. The 5,12-dihydrotetracene used was obtained commercially (Tokyo Kasei, G. R.) and was purified by recrystallization from benzine. The ESR spectra were measured by a Hitachi X-band ESR spectrometer, model MES 4001, employing field modulation at 100 kHz. As the radical anion was unstable above room temperature, the radical anion was prepared and the ESR spectra were measured below room temperature. Low temperatures were obtained by letting cool nitrogen gas flow through a Dewar jacket leading through the sample cavity. The temperature was controlled by adjusting the flow rate of the cool nitrogen gas, and was checked with a copper constantan thermocouple placed just below the sample. The magnetic field was calibrated by a Hitachi field marker.

Results

Representative spectra obtained in the present experiment are shown in Figs. 1 to 4. The proton

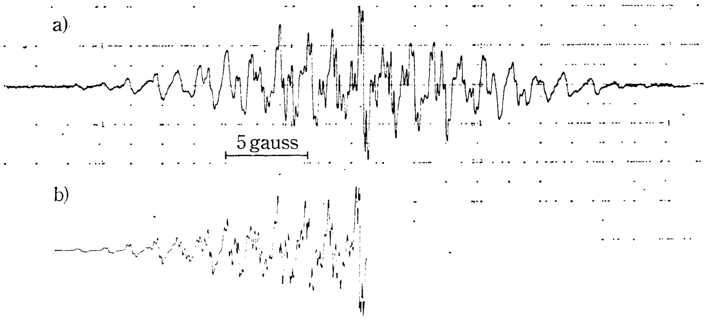

Fig. 1. ESR spectra of the 5,12-dihydrotetracene radical anion in DME with potassium as a counter ion.
a) observed spectrum at −72°C.
b) computer simulated spectrum using the hyperfine splitting constants given in Table 1.[*1]
The magnetic field increases from right to left.

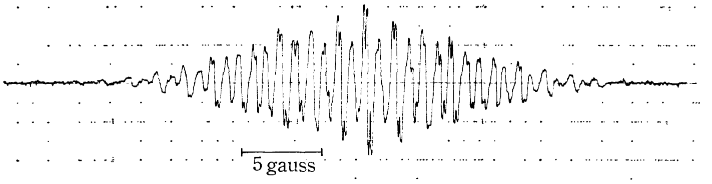

Fig. 2. ESR spectrum observed at −92°C (for) the lithium-5,12-dihydrotetracene radical - THF system.

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8) a) E. de Boer and E. L. Mackor, *J. Amer. Chem. Soc.*, **86**, 1513 (1964). b) E. de Boer, *Rec. Trav. Chim. Pays-Bas*, **84**, 609 (1965).

9) M. Iwaizumi, M. Suzuki, T. Isobe and H. Azumi, This Bulletin, **40**, 2754 (1967).

10) M. Iwaizumi and J. R. Bolton, *J. Mag. Resonance*, **2**, 278 (1970).

[*1] The line-widths at the central part of the spectra differ from those at the wings in the observed spectra. Such an effect was not taken into account in the computation of the spectrum.

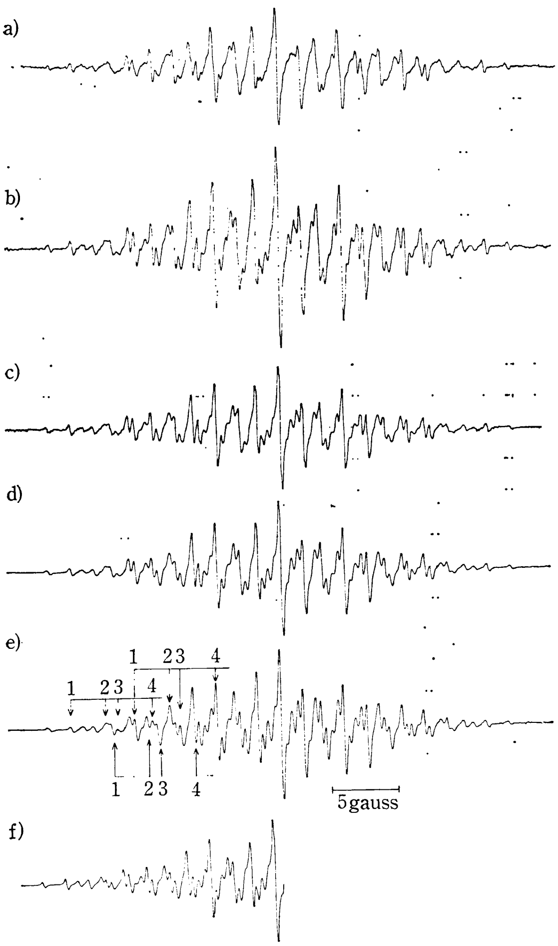
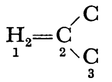


Fig. 3. ESR spectra obtained for the potassium-5,12-dihydrotetracene radical - THF system a) at −30°C, b) at −56°C, c) at −66°C, d) at −78°C and e) at −99°C. Spectrum f) is a computer simulated spectrum for d) obtained using the Bloch's two jump model with $\tau = 1.7 \times 10^{-6}$ sec.[*1] The magnetic field increases from right to left.

hyperfine splitting constants are listed in Table 1. For purposes of comparison, the hyperfine splitting constants of the *o*-xylene[11] and 2,3-dimethylnaphthalene[12] radical anions are collected, along with those of the 5,12-dihydrotetracene radical anion. All the splitting constants of the 5,12-dihydrotetracene radical anion were assigned on the basis of the Hückel molecular-orbital calculation, which is shown in Table 2, and by comparison with the hyperfine splitting constants of the *o*-xylene and 2,3-dimethylnaphthalene radical anions. In the molecular-orbital calculation, the hyperconjugation effect of the methylene bridges is included. The parameters used were as follows:

$$\delta\alpha_1 = -0.5\beta \quad \delta\alpha_2 = -0.1\beta \quad \delta\alpha_3 = -0.1\beta$$

$$\beta_{12} = 2.0\beta \quad \beta_{23} = 0.8\beta \quad \beta_{13} = 0.3\beta$$



$$\underset{1}{H_2}{=}\underset{2}{C}\begin{matrix}\diagup C \\ \diagdown \underset{3}{C}\end{matrix}$$

Here, β_{13} was introduced since the methylene protons at the axial positions must be situated in close proximity to the π-orbital in the benzene and naphthalene rings if the molecule is non-planar. The inclusion of this parameter improved the agreement between the observed hyperfine splitting constants and the calculated ones. Table 2 also lists such results of the electrostatic perturbation calculation[13,14] on the effect of the alkali ion on the proton hyperfine splittings as relate to the following discussion.

The ESR spectra observed in DME with lithium, sodium, and potassium ions as counter ions show the same hyperfine structure, and no appreciable change with the alkali ions is observed (see Table 1). Although the line width broaden and the resolution of the spectra becomes worse with an increase in the temperature, there seems to be no large change in the hyperfine splitting constants with the temperature. It may be considered, therefore, that in DME the radical anion exists as a free anion or as an ion pair bound very loosely, for there is no marked effect of the cations on the ESR spectra. It may be noted here that, in these systems, the four methylene protons show a normal quintet splitting, although they must exist as axial and equatorial protons.

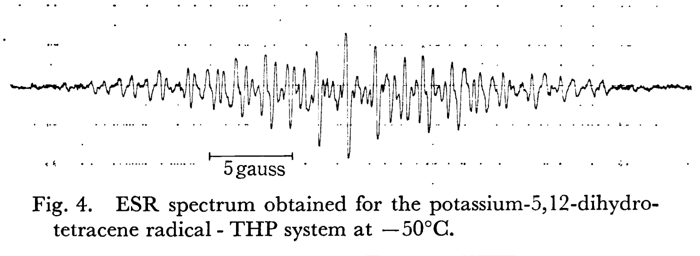


Fig. 4. ESR spectrum obtained for the potassium-5,12-dihydrotetracene radical - THP system at −50°C.

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[11] J. R. Bolton, *J. Chem. Phys.*, **41**, 2455 (1964).

[12] F. Gerson, B. Weidmann and E. Heilbronner, *Helv. Chim. Acta*, **47**, 1951 (1964).

[13] B. J. McClelland, *Trans. Faraday Soc.*, **57**, 1458 (1961).

[14] M. Iwaizumi, M. Suzuki, T. Isobe and H. Azumi, This Bulletin, **40**, 1325 (1967).

TABLE 1. OBSERVED HYPERFINE SPLITTING CONSTANTS OF THE 5,12-DIHYDROTETRACENE, 2,3-DIMETHYLNAPHTHALENE AND *o*-XYLENE RADICAL ANIONS (gauss)

a) 5,12-Dihydrotetracene radical anion

Solvent and Cation	Temperature	Position (1,4)	(2,3)	(6,11)	(7,10)	(8,9)	CH_2	Alkali-metal
DME-Li	−72°C	0.194	0.080	4.359	5.038	1.693	3.133	···
DME-Na	−72°C	0.194	0.080	4.359	5.038	1.693	3.133	···
DME-K	−72°C	0.194	0.080	4.359	5.038	1.693	3.133	···
THF-Li	−92°C	0.198	0.081	4.308	5.034	1.726	3.356	···
THF-Na	−88°C	0.196	0.080	4.022	5.082	1.636	3.448	0.868(−27°C)*1 1.168(+11°C)
THF-K	−99°C	<0.09	···	4.659	4.820	1.737	3.412, 2.651	···
THP-K	−50°C	<0.07	···	4.635	4.845	1.754	3.509, 2.495	···

b) 2,3-Dimethylnaphthalene radical anion*2

Solvent and Cation	Temperature	Position α	α′	β	CH_3	Alkali-metal
DME-Na	−70°C	4.93	4.67	1.76	1.69	···

c) *o*-Xylene radical anion*3

Solvent and Cation	Temperature	Position (3,6)	(4,5)	CH_3	Alkali-metal
DME-K	−80°C	6.93_5	1.81_5	2.00_6	···

*1 Sodium hyperfine splitting was not observed at −88°C.
*2 cited from Ref. 12.
*3 cited from Ref. 11.

TABLE 2. CALCULATED RING PROTON HYPERFINE SPLITTING CONSTANTS*1 OF 5,12-DIHYDROTETRACENE RADICAL ANION (gauss)

		Position (1,4)	(2,3)	(6,11)	(7,10)	(8,9)
Free-anion		0.110	0.040	4.018	5.018	1.812
Ion-pair*2	model A	0.049	0.040	3.577	5.027	1.923
	model B	8.160	1.944	0.302	0.119	0.071

*1 The splitting constants of the ring protons were calculated by $a_i=Q^{H}_{CH}\rho_i$ with $Q^{H}_{CH}=27$ gauss.
*2 The calculations were carried out using McClelland method[13,14] with the alkali metal placed 4.0 Å above the center of the naphthalene ring (model A) and with that placed 4.0 Å above the center of the benzene ring (model B).

When THF or THP was used as a solvent, appreciable effects of the cation were observed on the hyperfine structure of the ESR spectra. The proton hyperfine splitting constants change with the cations, and when sodium is used as a reducing agent, an additional splitting arising from the sodium nucleus is observed. In THF, this sodium hyperfine splitting has a positive temperature coefficient and disappears below a temperature of about −50°C.

The effect of the cation on the proton hyperfine splittings is especially remarkable when the cation is a potassium ion in THF and in THP. The hyperfine splittings due to the protons at 1,4 and 2,3 positions are much smaller than those in the other systems, and that of the methylene protons splits into two sets of triplets. Moreover, in THF the methylene proton hyperfine splitting changes markedly with the temperature and the two sets of triplet splittings coalesce to a quintet splitting at a higher temperature, showing the effect of the alternating line width. In Fig. 3, four of the hyperfine lines with spin states, (1,1), (1,0), (0,1), and (0,0), are numbered from 1 to 4 respectively. Here the numbers in parentheses are the magnetic index numbers[15] for the two sets of methylene protons. One can see from the figure that, as the temperature increases, the 2 and 3 lines become broad and tend to coalesce to form the quintet splitting as a result of hyperfine interaction with the methylene protons.

Discussion

Spin Distribution and Inversional Motion of the 5,12-Dihydrotetracene Radical Anion. As Table 1 shows, the unpaired electron is dis-

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15) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).

tributed between the naphthalene and benzene conjugated systems in the radical anion molecule. The distributions of the spin densities in the benzene and naphthalene rings are quite similar to those in the *o*-xylene and 2,3-dimethylnaphthalene radical anions respectively, although a large portion of the spin densities exist on the naphthalene ring. This implies that this molecule can be considered in terms of two weakly-coupled benzene and naphthalene rings. The coupling mechanism is presumably due to a hyperconjugation effect of the methylene bridges, as has also been suggested for the case of the 9,10-dihydroanthracene radical anion.16) The molecular-orbital calculation for the hyperfine splitting constants including the hyperconjugation effect of the methylene bridges, given in Table 2, well predicts the observed spin distribution.

On the other hand, as was mentioned in the preceeding section, the methylene protons show the normal quintet splitting except when there is a strong perturbation due to the alkali metal cation, as in the case of the ion-pairs with a potassium ion in THF and in THP. From the fact that the conformation of the 9,10-dihydroanthracene is nonplanar,7) it seems reasonable to consider that the 5,12-dihydrotetracene also has a non-planar conformation, which would lead to an inversion process. The methylene protons which are in axial and equatorial positions can thus be expected to exchange their positions in the inversional process with each other. The equivalence of the methylene protons in the ESR spectrum implies that the rate of the inversional motion is $\gg 10^8$ Hz.

Ion-pair Formation and Structure of the Ion Pair. As was mentioned in the previous section, the hyperfine splitting constants change with the association of the alkali ion. The effect of the potassium ion observed in THF and in THP is especially remarkable. Such cation effects provide us with very useful information about the structure of the ion pair. In such a system as two-conjugated systems weakly coupled, the spin distribution between the two conjugated systems is considered to be sensitive to the association of a cation on either of the conjugated systems.10) In the present case, it was observed that the association of the cation causes a migration of the unpaired electron density from the benzene ring to the naphthalene ring. This effect implies that the potassium ion may associate with the radical anion on the side of the naphthalene ring. The electrostatic perturbation calculations13,14) were carried out in order to establish the effect of the cation. The results given in Table 2 are for two ion-pair models, one where the cation is placed 4.0 Å above the center of the naphthalene ring (model A) and the other where the cation is placed 4.0 Å above the center of the benzene ring (model B). As may be seen from Table 2, Model A well explains the observed effect of the migration of the unpaired electron density from the benzene ring to the naphthalene ring. It is also consistent with the electrostatic interaction model, since the electron density and, hence, the negative-charge density are at maxima on the naphthalene ring.

In this ion-pair model, the two different hyperfine splittings observed for the methylene protons are attributed to the hyperfine interaction with the methylene protons on the same side of the molecular plane as the potassium ion and with those at the reverse side. Therefore, the alternating line-width effect observed in the potassium-5,12-dihydrotetracenide ion-pair in THF can be explained by the exchange of the potassium ion between the two preferred positions, above and below the molecular plane.*2

The exchange reaction mentioned above can proceed by both *inter-* and *intra*-molecular processes, (1) and (2);

$$K^+ + A^-K^{*+} \rightleftharpoons K^+A^- + K^{*+} \tag{1}$$

$$A^-K^+ \rightleftharpoons K^+A^- \tag{2}$$

where A^- stands for the radical anion. In some cases of ESR studies of ion pairs, additional alkali-metal hyperfine splittings were very useful in getting information on the life time of the ion pairs and in deducing whether exchange reactions were *inter*-molecular or *intra*-molecular in nature.8-10,17)

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16) M. Iwaizumi, T. Isobe and J. R. Bolton, to be published.

*2 The alternating line width effect can be caused also by the inversional motion of the molecule. However in the present case we do not prefer a hypothesis that the observed alternating line width effect is related to the inversional motion of the molecule. If the ratio of axial to equatorial splitting constants follows from the angular dependence of the β proton splitting constants, $a_\beta{}^H = B\cos^2\theta$, it must be about 4.0.6) However the observed ratios of the methylene proton splitting constants change with strength of association of the cation and have the values 1.287 for the potassium-5,12-dihydrotetracenide ion-pair in THF and 1.406 for that in THP. These ratios are rather close to the value observed in the methylene protons for the potassium-acenaphthenide ion-pair, 1.05. In the acenaphthene ion-pair system, two hyperfine splitting constants coming from the methylene protons were explained by the effect of the electrostatic force of the associated cation. In view of these facts it seems reasonable to attribute the present observation to the electrostatic effect of the associated cation on the proton splitting constants. It is considered that the rapid inversion process of the molecule still occur.

17) a) N. M. Atherton and A. E. Goggins, *Mol. Phys.*, **8**, 99 (1964). b) E. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.*, **62**, 269 (1966). c) T. A. Claxton, W. M. Fox and M. C. R. Symons, *ibid.*, **63**, 2570 (1967). d) D. H. Chen, E. Warhurst and A. M. Wilde, *ibid.*, **63**, 2561 (1967). e) P. S. Gill and T. E. Gough, *Can. J. Chem.*, **45**, 2112 (1967). f) J. Gendell, *J. Chem. Phys.*, **46**, 4152 (1967). g) K. Nakamura, This Bulletin, **40**, 1019 (1967).

In the present system, however, the hyperfine splitting due to the cation was not observed. It is possible that the alkali metal hyperfine splitting is averaged to zero by a rapid *inter*-molecular exchange reactoin of the alkali ion, and in some cases rapid *inter*-molecular equilibria have been concluded from the absence of cation splittings in the ESR spectra of the ion-pair systems.[18] We consider, however, that the observed reaction is the *intra*-molecular process for the following reasons.

(1) No potassium hyperfine splitting was observed, even under slow exchange conditions, such as in the potassium-5,12-dihydrotetracenide in THP, where the methylene protons showed two definite sets of triplet splittings. This implies that the potassium splitting constants are essentially too small to be resolved and that the absence of the metal splitting constant is not due to the rapid *inter*-molecular exchange of the cation. Previously, Dodson and Reddoch[19] showed that, in the naphthalene-alkali metal ion-pair system, potassium hyperfine splittings are very small, or are not observed at all, because the contributions of the hyperfine interaction with the positive and negative signs cancel each other out, although stable ion pairs are formed. It is considered that the alkali metal couplings in the present system are in a situation similar to that of the naphthalene ion-pair system.

(2) The sodium 5,12-dihydrotetracenide ion pair in THF shows a well-resolved sodium hyperfine splitting above $-30°C$, from which the lifetime of the ion pair can be estimated to be $\gg 10^{-6}$ sec. In view of the fact that the potassium ion generally has a greater tendency to associate with anion radicals than does the sodium ion,[14,18,20,21] the lifetime of the potassium-5,12-dihydrotetracenide ion pair in THF may be considered to be $\gg 10^{-6}$ sec. On the other hand, the lifetime of the static conformation of the ion pair is estimated to be about 6×10^{-7} sec from the observed alternating line-width effect in the same temperature range.

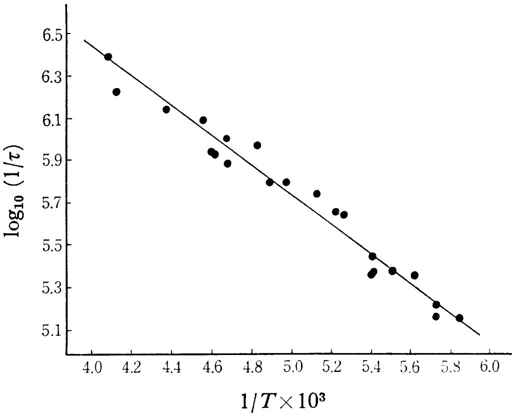

Fig. 5. Plot of $\log_{10} 1/\tau$ against $1/T \times 10^3$.

It may be concluded from these facts that the observed exchange reaction proceeds by the *intra*-molecular process. We computed spectra for different values of the lifetime of the ion-pair conformation, τ. Figure 5 shows the plot of the $\log_{10}(1/\tau)$ ($=\log_{10} k$) thus estimated against $1/T$. Here k is the rate of the exchange reaction. As is expected from the Arrhenius equation,

$$k = 1/\tau = k_0 \exp(-E_A/\boldsymbol{R}T) \qquad (3)$$

it shows a straight line. This gives a potential barrier to the migration of the potassium ion from one side of the molecular plane to the other; $E_A = 3.1 \pm 0.2$ kcal/mol, and the frequency factor, k_0, $= 1.4 \pm 0.5 \times 10^9$ sec^{-1}.

On the other hand, one can see from Table 1 that effects of the cations on the proton hyperfine splittings vary with the cations. This implies that there may be slight differences in the equilibrium positions of the cations, but the ion-pair structure is not discussed in detail here. It may also be seen from the table that, in the case of the lithium or sodium-5,12-dihydrotetracenide in THF, the effects of the cations are smaller than in the case of the potassium-5,12-dihydrotetracenide in THF or in THP, suggesting that, in the former cases, the radical anion is in a more loosely bound ion-pair state.

The numerical calculations were carried out on the NEAC 2200 Model 500 computer at the Computer Center, Tohoku University.

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[18] A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

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[20] A. C. Aten, J. Dieleman and G. J. Hoijtink, *Discuss. Faraday Soc.*, **29**, 182 (1960).

[21] N. Hirota, R. Carraway and W. Schook, *J. Amer. Chem. Soc.*, **90**, 3611 (1968).