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ESR Studies of the Alkali Metal-Acenaphthene Ion Pairs*[1]

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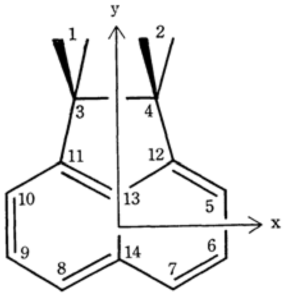
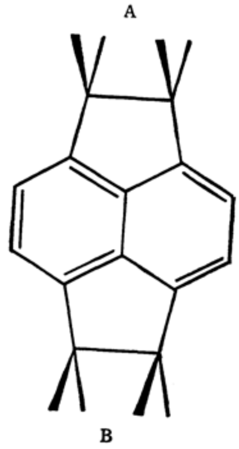
Ion pairs formed by alkali metals with acenaphthene in ether-type solvents have been investigated by means of electron spin resonance (ESR). The ESR spectra of the ion pairs were found to show phenomena quite analogous to those found by de Boer *et al.* in the pyracene-alkali ion system; similar two-line-width alternation effects were also observed in the present work. These observations were contrary to the expectations formed by a consideration of the pyracene-alkali metal ion pair, where the phenomena have been explained on the basis of the assumption that a potential well exists near the two ethylene bridges. This paper shows that, in the acenaphthene-alkali metal ion pairs, the alkali ion may be situated above the naphthalene skeleton rather than near the ethylene bridge. One of the line-width alternation effects is explained in terms of the exchange reaction between two ion-pair conformations in which the alkali ion is situated above and under the molecular plane respectively, while the other is ascribed to the oscillation of the cation in the potential well above either side of the molecular plane.

Previously, de Boer *et al.*[1] found two-line-width alternation effects in the ESR spectra of the ion pair formed by alkali metals with pyracene (II). They postulated that, in the most likely ion-pair conformation, the alkali ion is placed near the ethylene bridges, *i. e.*, at A and B, and they explained these two line-width alternation effects in terms of the intramolecular hopping motion of the cation from the A to the B position and *vice versa*, and the oscillation of the cation in either of the potential wells, at A or B.

In the present study, we have examined the ESR spectra of the ion pairs formed by alkali metals with acenaphthene (I), and have found that the ESR spectra show phenomena quite similar to those observed in the pyracene-alkali ion system; similar two-line-width alternation effects were also observed, in spite of the fact that there is only one ethylene bridge. We will discuss here the structure of the acenaphthene-alkali metal ion pair on the basis of such observations and will examine the interaction between the two ions by the molecular orbital method.



(I)



(II)

Experimental

The radical anion of acenaphthene was prepared by the usual method of alkali metal reduction, using lithium, sodium, and potassium as the reducing agents. The solvents used were purified by distillation after refluxing them with potassium and with lithium aluminum hydride. As the radical anion was unstable above about $-10°C$, the radical anions were prepared below $-10°C$. The spectra were measured at different temperatures, lower than room temperature, by the

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*[1] A part of this paper was presented at symmposium on Electron Spin Resonance, Sendai, September, 1966.

[1] a) E. de Boer and E. L. Mackor, *Proc. Chem. Soc.*, **1963**, 23; *J. Am. Chem. Soc.*, **86**, 1513 (1964). b) E. de Boer, *Rec. Trav. Chim.*, **84**, 609 (1965).

used of a Hitachi MPU 3B-type X-band ESR spectrometer with a 100 kc field modulation. Above about −10°C, a gradual decrease in the signal intensity was observed during the measurement of the spectrum.

Results and Discussion

ESR Spectra of the Acenaphthene-Alkali Metal Ion Pairs. Previously Aten *et al.*[2] pointed out that the tendency of radical anions toward ion-pair formation should increase with increases in the temperature and in the radius of the alkali ion and with a decrease in the dielectric constant of the solvent. Our observations seem to support this rule; the ESR spectrum attributed to a "free" anion was obtained from the radical anion produced with lithium in 1, 2-dimethoxyethane (DME), or when the solutions of the radical anions produced with sodium or potassium in DME and produced with lithium or sodium in tetrahydrofuran (THF) were cooled. Figure 1 shows the ESR spectrum of the "free" radical anion obtained from the solution with the lithium ion as a cation in DME.

On the other hand, notable changes in the proton hyperfine splittings, especially of the methylene protons, were observed on the formation of the ion pair. Figures 2 and 7 show the ESR spectra of the radical anions produced with potassium in tetrahydropyran (THP) and in diethylether (DEE) respectively. These radical anions may be considered to exist as strong ion-pairs, and the spectra show quite a different hyperfine structure from that of the "free" radical anion; *i. e.*, besides the extra potassium hyperfine splittings in Fig. 7, the four methylene protons are seen to be no longer equivalent and the hyperfine splittings due to the methylene protons are seen to be composed of two sets of triplet splittings.

In some cases, however, the hyperfine splittings due to the methylene protons do not show a clear separation into two sets of triplet splittings, although characteristic line-width-broadening effects are observed. Figures 3—6 show typical examples of such line-width-broadening effects. Among them, the effect observed for the radical anion produced with potassium in DME is different in nature from the others. In this case the hyperfine lines due to the methylene protons with $M_{\mathrm{CH}_2}=\pm 2$, where M_{CH_2} is the quantum number for the total angular momentum of the four methylene protons, are broader than those with $M_{\mathrm{CH}_2}=0$ or ± 1; the broadening effect increases in this order: the lines with $M_{\mathrm{CH}_2}=0<$ those with $\pm 1<$ those with ± 2, and the intensities of the lines at both wings of the spectrum diminish extensively compared to those to be expected from the normal hyperfine interaction. As the temperature decreases, however, the line-width-broadening effect disappears and the hyperfine structure changes to that of the "free" radical anion. This line-width-broadening effect is quite analogous to that observed in the azulene-[3] and acenaphthylene-[4] alkali ion systems, and may be explained by assuming that the radical anion is in the equilibrium state between the "free" radical anion and ion-paired forms, and that they rapidly interconvert.

The line-width broadening shown in Figs. 4—6 is a typical phenomenon of the alternating line-width; the hyperfine lines of the methylene protons with $M_{\mathrm{CH}_2}=\pm 1$ are broad, but those with $M_{\mathrm{CH}_2}=0$ and ± 2 are sharp. Hence, in this case too, the hyperfine lines do not show the normal intensity ratio of 1 : 4 : 6 : 4 : 1 which would come from interaction with four equivalent protons.

Interestingly, the line-width alternation effect was also observed in the case of the radical anions which show the hyperfine splittings due to the methylene protons fallen distinctly apart into two sets of triplet splittings at low temperatures; *i. e,*

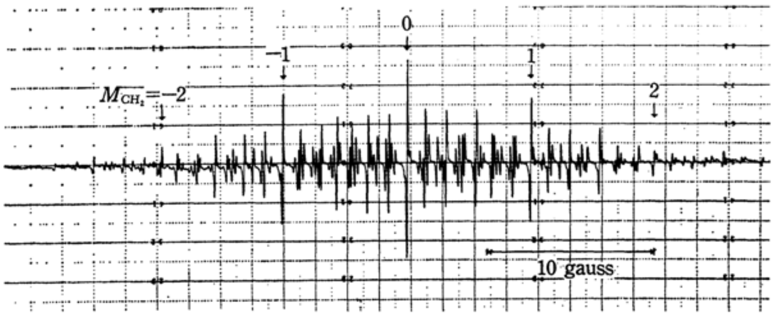

Fig. 1. ESR spectrum of the acenaphthene radical anion, produced with lithium in DME, at −74°C.
The vertical arrows mark the lines corresponding to one of the sets of quintet splittings due to four methylene protons.

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

[3] A. H. Reddoch, *J. Chem. Phys.*, **41**, 444 (1964).

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

as Fig. 7 shows, the hyperfine lines corresponding to $M_{CH_2}'=0$, where M_{CH_2}' is the quantum number for the nuclear spin angular momentum of the methylene protons with the larger splitting constant of the two sets, become broader than those for $M_{CH_2}'=\pm 1$ as the temperature decreases.

These phenomena observed in the acenaphthene-alkali ion system are quite analogous to those found by de Boer *et al.*[1] in the pyracene-alkali metal ion pairs. Namely, the ESR spectrum of the pyracene radical anion with the sodium ion in THF show the phenomenon of the alternating line-width in the nonet splittings due to the eight methylene protons at certain temperatures. On

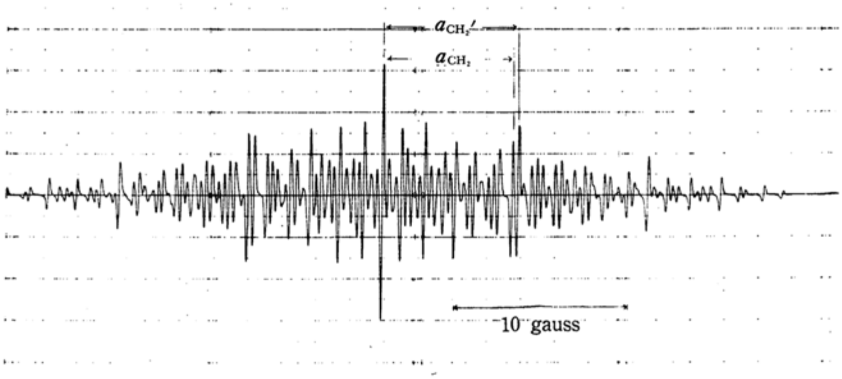

Fig. 2. ESR spectrum of the acenaphthene-potassium ion pair in THP at −56°C.

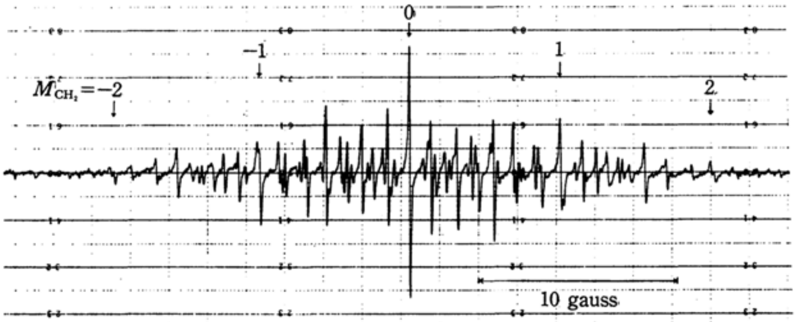

Fig. 3. ESR spectrum of the acenaphthene radical anion, produced with potassium in DME, at −56°C.
The vertical arrows mark the lines corresponding to one of the sets of quintet splittings due to four methylene protons.

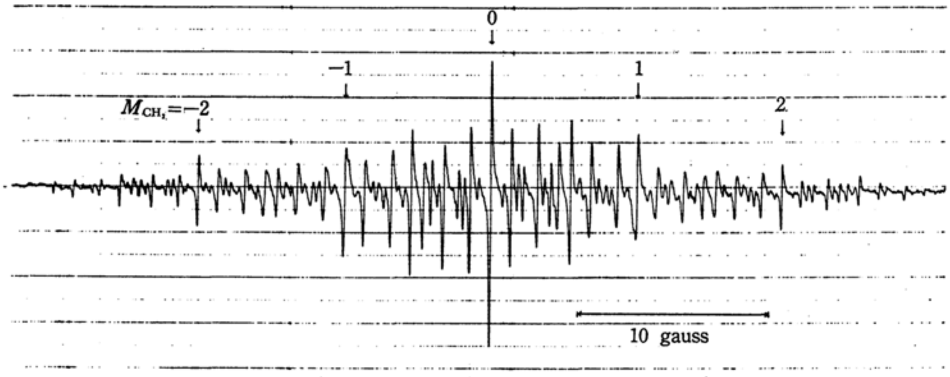

Fig. 4. ESR spectrum of the acenaphthene-potassium ion pair in THF at −88°C.
The vertical arrows mark the lines corresponding to one of the sets of quintet splittings due to four methylene protons.

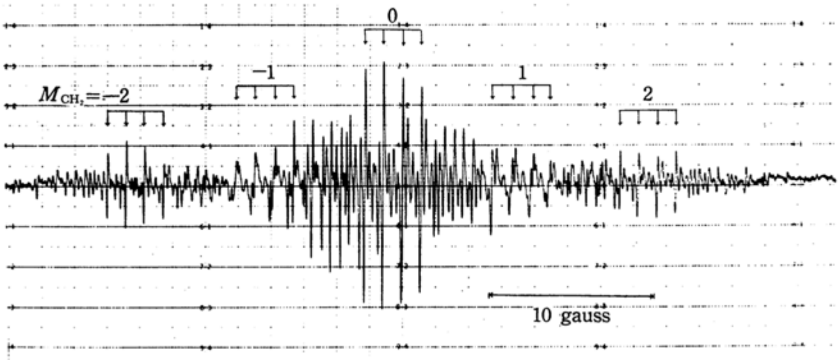

Fig. 5. ESR spectrum of the acenaphthene-sodium ion pair in an equal volume mixture of THF and THP at −3°C.
The vertical arrows mark the lines corresponding to one of the sets of quintet splittings due to four methylene protons.

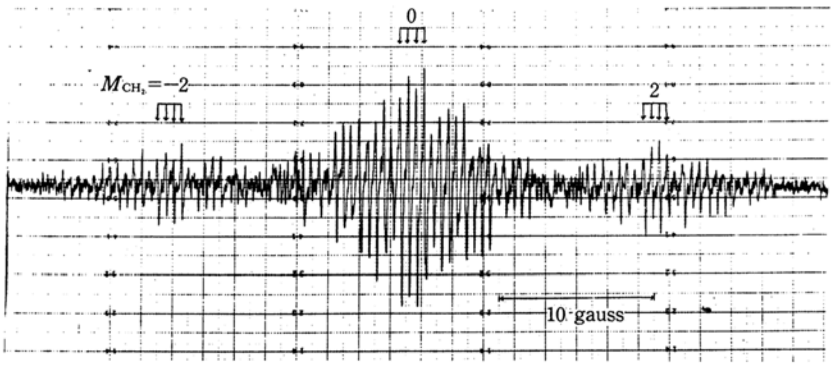

Fig. 6. ESR spectrum of the acenaphthene-lithium ion pair in 2-MeTHF at +17°C. The vertical arrows mark the lines corresponding to one of the sets of quintet splittings due to four methylene protons.

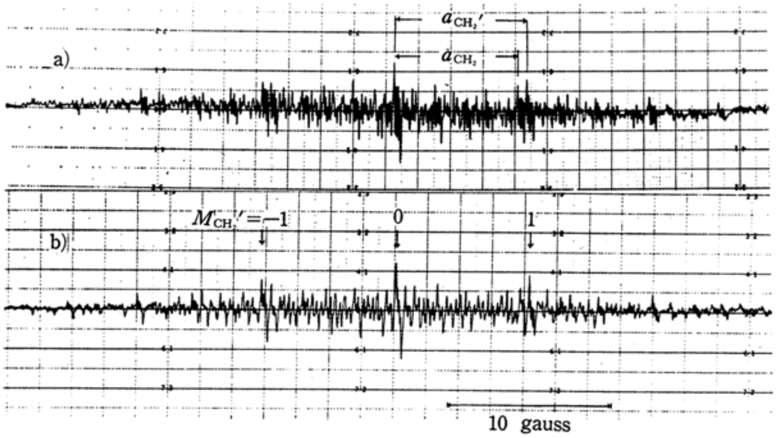

Fig. 7. ESR spectra of the acenaphthene-potassium ion pair in DEE.
a) at −47°C b) at −88°C
The vertical arrows mark the lines corresponding to one of the sets of quintet splittings due to two methylene protons with larger splitting constant.

the other hand, in the ESR spectra of the radical anion with the potassium or sodium ion in 2-methyltetrahydrofuran (2-MeTHF), the hyperfine splittings due to the methylene protons are composed of two sets of quintet splittings, and when these solutions were cooled, another line-width-alternation effect is observed in the hyperfine lines due to the four methylene protons with the larger splitting constant of two sets of quintet splittings. To explain these phenomena de Boer *et al.* assumed that the most likely conformation of the ion pair is that in which the alkali ion is placed near the ethylene bridges, *i. e.,* at A and B; they attributed the two-line-width alternation effects to the modulation effects of the jumping of an alkali ion from one site (A) to another (B), and to the oscillation of the alkali ion in either of the potential wells, at A or B.

The line-width alternation effects observed in the present work may be explained by assuming the rapid exchange of the cation between its possible equilibrium positions within the ion pair. However, it seems very interesting that quite similar two-line-width alternation effects were observed, even though there is only one ethylene bridge, in the acenaphthene molecule. To explain this observation, we may assume that the alkali ion favors a position above the molecular plane, so that the hyperfine splittings due to the methylene protons are divided into two sets, the triplet splittings coming from the protons on the same side as the alkali ion and those from the protons on the reverse side. Then the line-width alternation effect observed in the quintet splittings due to four methylene protons may be attributed to the rapid exchange between the two ion pair conformations, in which the alkali ion is situated above and under the molecular plane. Since the resolved alkali metal hyperfine splittings were observed in the spectra of the ion pairs with the sodium or lithium ion, as Figs. 5 and 6 show, it may be concluded that the exchange reaction in these cases is intramolecular in nature, as in the cases of the pyracene-1) and pyrazine-5) alkali ion systems. At still lower temperatures, or when the radical anion exists as a more tightly-bound ion pair, the exchange of the alkali ion between the one side of the molecular plane and the other slows down, and the phenomenon which reflects such an exchange of the alkali ion should become unobservable. The ESR spectra shown in Figs. 2 and 7a correspond to such a situation.

As will be discussed in the following section, the most likely position of the alkali ion is above the naphthalene skeleton rather than near the ethylene bridge. Further, it will be shown in the following section that double minima may occur along the x axis in the potential well for the cation as the distance between the molecular plane of the radical anion and the alkali ion decreases. Therefore, the line-width alternation effect shown in Fig. 7 may be ascribed to the movement of the alkali ion from the one minimum of the double potential minima to the other in the potential well above either side of the molecular plane. Such a motion of the alkali ion will introduce the out-of-phase modulation in the isotropic hyperfine splittings for each set of protons at the positions symmetric to the y axis of the molecule. However, it seems likely that such a modulation in the coupling constants will be most appreciable for the protons which are subjected to the largest change in the hyperfine splittings on the formation of the ion pair. Namely, the modulation effect may be the largest for the methylene protons with the larger splitting constant of the two sets, the constant which is most perturbed on the formation of the ion pair, as is shown in Fig. 8. Thus, the line-width alternation will become most appreciable in the hyperfine splittings coming from those methylene protons.

Molecular Orbital Treatment of the Interaction between the Acenaphthene Radical Anion and the Alkali Metal Cations. We made an attempt to obtain information on the most favored structure of the ion pair through an examination of the interaction between the two ions by means of the molecular orbital theory. The method consists of calculations of the effect of the alkali ion on the proton hyperfine splittings and for the electrostatic interaction energies between the two ions. The details of the method of calculation have been described in a previous paper.4) In the present calculations, only the structure of the ion pair in which the alkali ion is placed above the molecular plane has been treated on the basis of the results presented in the preceding section. The dimensions of the radical anion and the parameter for the Coulomb and exchange integrals were assumed to be as follows:

C–C bond length (in the aromatic part) = 1.39 Å

C–C bond length (in the aliphatic part) = 1.54 Å

C–H bond length = 1.09 Å

$\angle$HCH = 109°28′

$\angle$H(1)C(3)C(4) (projected on the molecular plane) = 129°

$$\alpha_1 = -0.5\beta, \qquad \alpha_3 = -0.1\beta,$$
$$\beta_{1,3} = 2.5\beta, \qquad \beta_{3,4} = \beta_{3,11} = 0.8\beta,$$
$$\beta_{1,4} = \beta_{1,11} = 0.3\beta$$

where the exchange integrals were derived by correcting the values obtained by assuming proportionality between the overlap integral and the exchange integral, so as to be more suitable for

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5) a) N. M. Atherton and A. E. Goggins, *Mol. Phys.,* **8,** 99 (1964); *Trans. Faraday Soc.,* **61,** 1399 (1965); *ibid.,* **62,** 1702, 1707 (1966). b) J. dos Santos-Veiga and A. F. Neiva-Correia, *Mol. Phys.,* **9,** 395 (1965).

reproducing the experimental value of the hyperfine splitting constants. The overlap integrals, $S_{i,j}$, where $i \neq j$, are assumed to be 0. In the present work, the inclusion of the exchange integrals, $\beta_{1,4}$ and $\beta_{1,11}$, fairly well improved the agreement of the hyperfine splitting constants with the observed values.

The calculations of the hyperfine splitting constants of the ring protons were carried out by the following relation, proposed by Colpa and Bolton⁶⁾:

$$a_{\mathrm{H}} = -(Q+K\varepsilon)\rho$$

where Q and K are constants and are taken to be 31.2 and 17 gauss respectively, and where ρ and ε are the spin density and the excess charge density on the neighboring carbon atom. On the other hand, the hyperfine splitting constants of the methylene protons were calculated by this relation:

$$a_{\mathrm{CH_2}} = 327C_{\mathrm{H}}^2 + 19.8C_{\mathrm{C}}^2$$

according to Levy *et al.*⁷⁾ In this equation C_{H} and C_{C} are the coefficients of the pseudo π orbital for the methylene protons and of the atomic orbital for the methylene carbon in the molecular orbital occupied by an odd electron.

Figure 9 shows the proton hyperfine splitting constants calculated for several ion-pair configurations in which the alkali ion is placed above the y axis of the radical anion. It is clear, from a

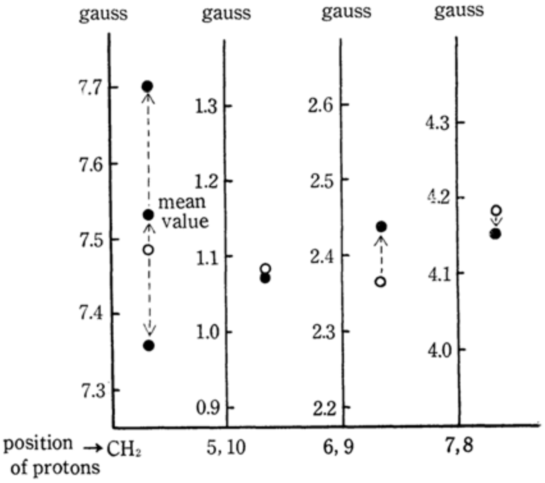


Fig. 8. The proton hyperfine splitting constants of the acenaphthene radical anion.

○: The values for the "free" radical anion obtained from the solution with lithium ion in DME.

●: The values for the acenaphthene-potassium ion pair in THP.

The arrows indicate the direction and magnitude of change of the hyperfine splitting constants with formation of the ion pair.

The assignment of the hyperfine splitting constants followed Copa *et al.*⁸⁾

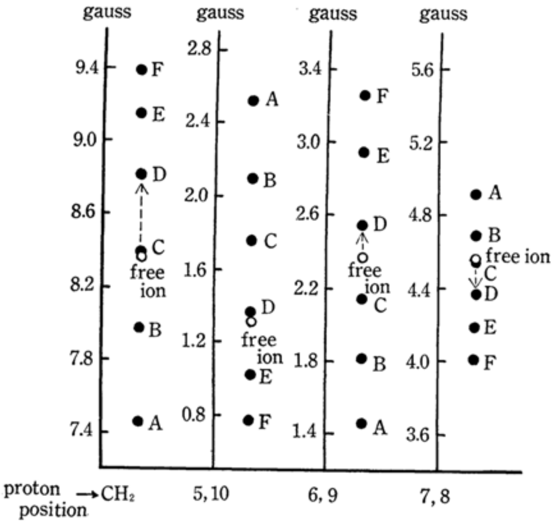
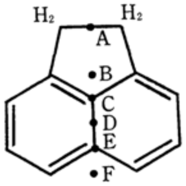


Fig. 9. The proton hyperfine splitting constants calculated for several ion pair configurations.



The alkali ion is situated just above the positions A, B, C,⋯, F, and at distance of 4 Å from the molecular plane respectively.

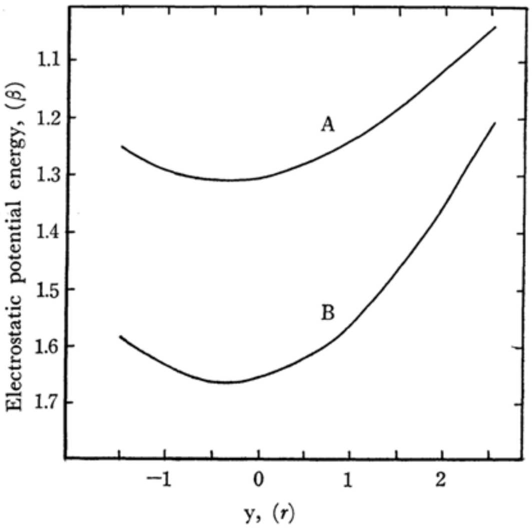


Fig. 10. Variation of the electrostatic potential energy as the cation moves along y axis. The cation is placed at distance of 3 Å (A) and 4 Å (B) from the molecular plane respectively. *r* is the bond length in aromatic part.

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6) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

7) D. H. Levy, *ibid.*, **10**, 233 (1966).

8) J. P. Colpa and E. de Boer, *ibid.*, **7**, 333 (1964).

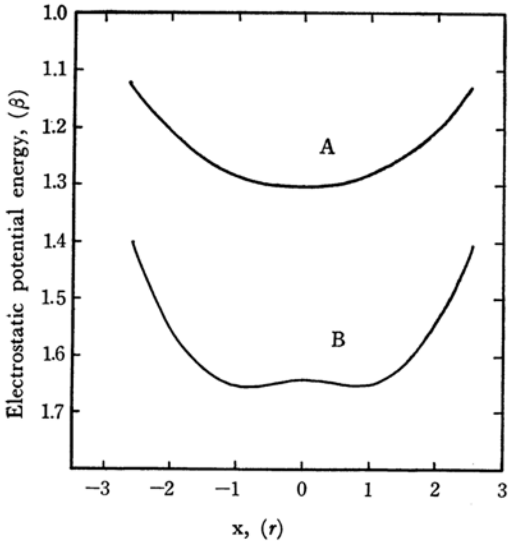

Fig. 11. Variation of the electrostatic potential energy as the cation moves along x axis. The cation is placed at distance of 3 Å (A) and 4 Å (B) from the molecular plane respectively. r is the bond length in aromatic part.

comparison of this figure with the observation shown in Fig. 8, that the ion-pair configuration in which the alkali ion is placed above the mid-point of the 11—12 bond predicts well the observed effect of the alkali ion. This ion-pair configuration is shown to be most favorable also by the calculation of the electrostatic interaction energies between the two ions. Figure 10 shows the variation in the electrostatic interaction energy as the cation moves along the y axis. It may be seen from this figure that the potential minimum point is above the vicinity of the mid-point of the 11—12 bond or above the 14 position. Further, Fig. 11 shows that the double minima occur in the potential well along the x axis as the distance between the two ions decreases. In view of these results, it may be concluded that the most likely equilibrium position of the alkali ion is above the naphthalene skeleton, rather than near the ethylene bridge.

In the above calculations the protons in the methylene group have been treated as a pseudo π orbital:

$$\Psi_\pi = N_\pi\{(1\mathrm{S_u}) - (1\mathrm{S_l})\}$$

where N_π are normarization constants, and where $1\mathrm{S_u}$ and $1\mathrm{S_l}$ are 1S atmoic orbitals of the upper and lower atoms. However, we observed different splitting constants for the methylene protons situated on the upper and lower sides of the molecular plane in the presence of the alkali ion. Let us now consider the function Ψ_π in the presence of the alkali metal cation. Let us assume that the alkali metal cation is placed nearer to the proton $\mathrm{H_u}$ on the upper side than to the proton $\mathrm{H_l}$ on the lower side. Then the integral $\int(1\mathrm{S_u})H(1\mathrm{S_u})d\tau$ becomes larger than $\int(1\mathrm{S_l})H(1\mathrm{S_l})d\tau$, and we obtain the function:

$$\Psi'_\pi = N_\pi\{a(1\mathrm{S_u}) - b(1\mathrm{S_l})\}$$

where $a<b$. It may be seen from this function that the methylene protons on the side reverse to the alkali ion may have larger splitting constants than the protons on the same side.

The numerical calculations were carried out on the NEAC 2230 at the Computation Center, Tohoku University.

The authors wish to express their appreciation to Miss Akie Sakai for her help throughout this work.