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ESR Studies of the Ion-pairs of the Acenaphthylene Radical Anion and Alkali Metal Cations*[1]

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Two types of temperature dependence of the proton hyperfine splitting constants of the acenaphthylene radical anion are described. One is that for the radical anions which are in a state of rapid exchange between the ion-paired form and the free radical anion, and the other is that for the radical anions which exist as stable ion pairs with a relatively long lifetime. From the examination of the effects of the alkali ions in terms of the molecular orbital method, it is concluded that the most favored ion-pair configuration is that in which the alkali ion is placed above the five-membered ring. The equilibrium position of the alkali ion moves toward the position 11 with an increase in the radius of the alkali ion. In relation to this ion-pair structure, the temperature dependence of alkali-metal hyperfine splittings is also discussed.

It is now well established that the radical anions formed by alkali-metal reduction in ether-type solvents associate with alkali ions to form ion pairs

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*[1] The theoretical section was presented at the symposium on Electron Spin Resonance, Nagoya, October, 1965.

under some conditions, conditions which can be characterized in terms of solvents, alkali ions, the concentration, and the temperature. In ESR, the formation of the ion pairs is usually evidenced by the appearance of extra hyperfine splittings due to the associated alkali metals. The examination of these alkali-metal hyperfine splittings has been very useful in providing valuable information on the ion pairs.1) On the other hand, several examples which show notable changes in the hyperfine splitting constants upon the formation of the ion pairs have been reported for the radical anions of benzophenone,2) nitroaromatics,3) nitrogen heterocycles,4) and a few hydrocarbons.5) Our previous findings with ESR studies of the acenaphthylene radical anion also showed that the proton hyperfine splitting constants are notably affected by the ion-pair formation.1d,6) These changes in the hyperfine splitting constants with the cations as well as with the alkali-metal hyperfine splittings seem very useful in getting information on the ion pairing. The present work has aimed chiefly at obtaining more detailed knowledge of the ion-pair formation of the acenaphthylene radical anion through an examination of the effects of the alkali ions on the proton hyperfine splitting constants. The effects of the alkali ions were observed as a function of the temperature. In relation to the structure of the ion pair estimated from these studies, the temperature dependence of the alkali-metal hyperfine splittings is also discussed.

Experimental

The radical anions of acenaphthylene were prepared by alkali-metal reduction, using lithium, sodium, potassium, and cesium as reducing agents, and 1, 2-dimethoxyethane (DME), tetrahydrofuran (THF), and tetrahydropyrane (THP) as solvents. The ESR spectra were measured at various temperatures by the use of a Hitachi MPU 3B-type X-band ESR spectrometer equipped with 100 kc field modulation. The low temperatures were obtained by letting dry and cool air flow through a Dewar jacket leading through the sample cavity. The temperature was controlled by adjusting the flow rate of the cool air. For higher temperatures an electric heater was inserted into a constant flow of the air. The temperature was measured with a copper-constantan thermocouple.

Results and Discussion

Temperature Dependence of the Proton Hyperfine Splittings. As has been established in a previous paper,6) the proton hyperfine splittings of the acenaphthylene radical anion change notably with alkali ions, even when no alkali-metal hyperfine splitting is observed. When no alkali-metal hyperfine splitting is observed, the proton hyperfine splittings vary markedly with the temperature and also with the concentration, except for a few exceptions which will be presented later. Typical examples which show such marked changes in the proton hyperfine splittings with the temperature or with the concentration are the radical anions

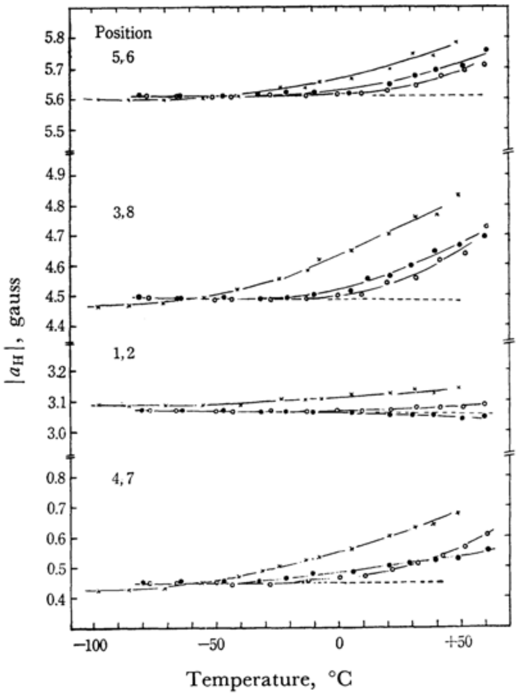

Fig. 1. Temperature dependence of proton hyperfine splittings (a_H) of the acenaphthylene anion radical.

—○—: Plots for the radical anion produced with lithium in DME.

—●—: Plots for the radical anion produced with sodium in DME.

—×—: Plots for the radical anion produced with lithium in THF.

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1) For example, a) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961). b) N. Hirota and S. I. Weissman, *ibid.*, **82**, 4424 (1960); *ibid.*, **86**, 2538 (1964). c) R. L. Ward, *J. Chem. Phys.*, **36**, 1405 (1962). d) E. de Boer and E. L. Mackor, *Proc. Chem. Soc.*, **1963**, 23; *J. Am. Chem. Soc.*, **86**, 1513 (1964). e) H. Nishiguchi, Y. Nakai, K. Nakamura, Y. Deguchi and H. Takaki, *J. Chem. Phys.*, **40**, 241 (1964); H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takaki, *Mol. Phys.*, **9**, 153 (1965). f) G. R. Luckhurst, *ibid.*, **9**, 179 (1965).

2) a) N. Hirota, *J. Chem. Phys.*, **37**, 1884 (1962). b) P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, **1963**, 5412.

3) a) R. L. Ward, *J. Chem. Phys.*, **32**, 410 (1960); *J. Am. Chem. Soc.*, **83**, 1296 (1961). b) T. Kitagawa, T. Layloff and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964).

4) a) N. M. Atherton, F. Gerson and J. N. Murrell, *Mol. Phys.*, **6**, 265 (1963). b) N. M. Atherton and A. E. Goggins, *ibid.*, **8**, 99 (1964); *Trans. Faraday Soc.*, **61**, 1399 (1965). c) J. dos Santos-Veiga and A. F. Neiva-Correia, *Mol. Phys.*, **9**, 395 (1965).

5) a) A. H. Reddoch, *J. Chem. Phys.*, **41**, 444 (1964); *ibid.*, **43**, 225 (1965). b) J. R. Bolton and G. K. Fraenkel, *ibid.*, **40**, 3307 (1964). c) M. Iwaizumi and T. Isobe, This Bulletin, **38**, 1547 (1965).

6) M. Iwaizumi and T. Isobe, This Bulletin, **37**, 1651 (1964).

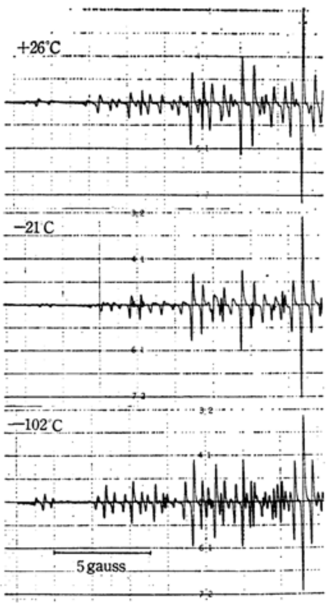

Fig. 2. ESR spectra of the acenaphthylene radical anion produced with lithium in THF. Half of each spectrum is shown.

with the lithium or the sodium ion in DME and with the lithium ion in THF. Figures 1 and 2 show the temperature dependence of the proton hyperfine splittings of the typical samples. At low temperatures, *i. e.,* below about −10°C for the radical anion with the lithium ion in DME, about −25°C for that with the sodium ion in DME, and about −100°C for that with the lithium ion in THF, the hyperfine splitting constants of these radical anions become approximately the same as those observed in dimethylformamide, which have been regarded in the previous paper⁶⁾ as coming from the free anion. In such a state, all the hyperfine lines show almost the same line width. However, as the temperature rises, the lines broaden abnormally with the changes in the proton hyperfine splitting constants: the lines which show a larger deviation in position from those observed at low temperatures become broader. This behavior of the hyperfine structure is quite similar to that found in the system of the azulene-lithium ion in DME⁵ᵃ⁾ and may be interpreted by assuming that, at the low temperatures, almost all the radical anions exist as free anions, while as the temperature increases the formation of ion pairs occurs. The ion-paired radicals and the free anion must have different coupling constants and must rapidly interconvert. The observed hyperfine splitting constants in such equilibrium states are the averages of the hyperfine splittings of the ion-paired radicals and the free anion weighted according to their relative concentrations.

The radical anions with the potassium ion in DME and with the sodium ion in THF show no alkali metal hyperfine splitting. However, above room temperature, the proton hyperfine splittings are scarcely affected by the temperature, in contrast to the examples mentioned above. In these systems almost all the radicals may be considered to occur in the ion-paired form at room temperature or higher, though no alkali metal hyperfine splitting is observed. The alkali-metal hyperfine splittings may be too small to be resolved, or the ion-pairs may participate in the rapid exchange of the cation. Previously Aten *et al.*⁷⁾ pointed out that ion-pair formation is favored by the large radius of the cations. Our observations seem to follow this rule. For example, as has just been noted, the radical anion with the potassium ion in DME may occur mostly as an ion pair above room temperature, but the radical anion with the sodium or lithium ion in DME is in the equilibrium state between the ion-paired form and the free anion at all the temperatures observed. Further, from the fact that, in these solutions, the apparent perturbation of the proton hyperfine splittings with the sodium ion is larger than that with the lithium ion, we can see that the radical anion associates with the sodium ion to a greater extent than with the lithium ion. The radical anion with the potassium ion in DME, of course, shows a larger perturbation of the proton hyperfine splittings than that with the sodium or lithium ion in DME.

On the other hand, when the radical anions are prepared in solvents with lower dielectric constants,

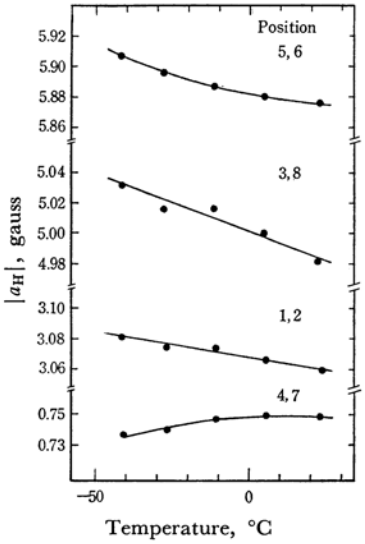

Fig. 3. Temperature dependenc of proton hyperfine splittings (a_H) of the acenaphthylene radical anion prodced with sodium in THP.

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

like THP, the radical anions show extra alkali-metal hyperfine splittings and may be considered to occur as stable ion pairs with relatively long lifetimes. As is apparent from a comparison between Figs. 1 and 3, the temperature coefficients of the proton hyperfine splitting constants of these ion-paired radicals are very small and have signs opposite to those of the radicals in the equilibrium state; *i. e.*, the apparent effects of the alkali ions increase only slightly when the temperature is lowered. The proton hyperfine splitting constants are scarcely affected either by the change in the concentration. Here, we assume that the alkali ion is oscillating in the field of the negative charge of the radical anions in the ion-pair. The alkali ion will then stay longer in the vicinity of the potential minimum point as the temperature decreases. At low temperatures, further, the solvent sheath may become more compact. It seems that these effects may be important in determining the temperature dependence of the proton hyperfine splittings observed for the stable ion pairs.

Figures 1 and 4 clearly show that the effects of the alkali ion on the proton hyperfine splitting constants of the acenaphthylene radical anion are large for the protons belonging to the six-membered ring, especially for the protons at positions 3 and 8, but not for those at positions 1 and 2. Here it seems worthwhile to note also that the changes in the proton hyperfine splittings differ slightly in the radicals with different alkali ions. For example, the proton hyperfine splittings at positions 1 and 2 increase slightly upon ion-pair formation with the lithium ion, while they decrease upon ion-pairing with alkali ions having a larger radius. Recently Reddoch reported(5a) that, in the anthracene-alkali ion or azulene-alkali ion system, the relative magnitude of the perturbation of each proton hyperfine splitting is independent of the solvent, the cations, and the concentration, with a few exceptions. However, in the present work, as has just been noted, it changes with the cations, though it is roughly independent of the solvents. This observation may imply, as will be discussed later, that the ion-pair configuration changes with the alkali ions, but is not affected so extensively by solvents as it is affected by the alkali ions.

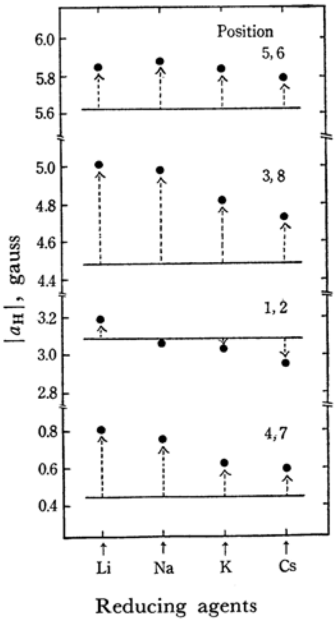

Fig. 4. Proton hyperfine splitting constants (a_H) of acenaphthylene radical anion observed in THP.
●: The values for the ion pairs at 23°C.
Horizontal lines indicate the values for the free anion, which were observed at −58°C for radical anion with lithium ion in THP.

Molecular Orbital Treatment for the Effects of the Alkali Metal Cations. An attempt has been made to obtain information on the structure of the ion pairs through an examination of the effects of the alkali ions in terms of the molecular orbital theory. The method consisted of calculations of the proton hyperfine splitting constants in the presence of the alkali ions and the interaction energies between the radical anion and the alkali ion for the various ion-pair configurations.

In the calculations, the electrostatic interaction model was adopted, and no allowance for the resonance effect arising from electron-sharing between the radical anion and the alkali ion was made. The resonance effect must be less important in the present case, because the odd-electron population in the alkali ion is about 0.002 or less. The method of calculation was about the same as those used by McClelland,(8) Buschow,(9) Dieleman,(10) Hush,(11) and Reddoch.(5a)

Now, a one-electron Hamiltonian for the π-electron in the presence of the alkali ion, H, may be represented in the form:

$$H = H^{\circ} - e^2/r \tag{1}$$

where H° is the Hamiltonian for the free anion and r is the distance between the center of the alkali ion and the electron. The molecular orbitals for the ion-paired radical anion,

$$\Psi_i = \sum_{\mu=1}^{2N} C_{i\mu}\phi_\mu \quad (i = 1, 2, \cdots, 2N),$$

are obtained from the secular equation,

$$\det|H_{\mu\nu} - ES_{\mu\nu}| = 0 \tag{2}$$

where:

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8) B. J. McClelland, *Trans. Faraday Soc.*, **57**, 1458 (1961).
9) K. H. J. Buschow, thesis, Amsterdam, 1963.
10) J. Dieleman, thesis, Amsterdam, 1962.
11) N. S. Hush and J. R. Rowlands, *Mol. Phys.*, **6**, 201 (1963).

$$H_{\mu\nu} = \int \phi_\mu H \phi_\nu \mathrm{d}\tau = H^\circ_{\mu\nu} - e^2 \int (\phi_\mu \phi_\nu / r)\mathrm{d}\tau, \tag{3}$$

$$S_{\mu\nu} = \int \phi_\mu \phi_\nu \mathrm{d}\tau\,. \tag{4}$$

According to McClelland, the $\int(\phi_\mu\phi_\nu/r)\mathrm{d}\tau$ term may be approximated as follows;

$$\int (\phi_\mu \phi_\nu / r)\mathrm{d}\tau = 2S_{\mu\nu}/(r_\mu + r_\nu)\,. \tag{5}$$

The spin distribution in the radical anion in the presence of the alkali ion can be calculated straightforwardly from the lowest antibonding orbital of acenaphthylene. However, as was stated in the previous paper,⁶⁾ negative spin densities may occur in this radical. It is well known that a simple molecular orbital treatment cannot explain the negative spin density. Therefore, we applied the correction to the spin densities, obtained from Hückel method, by using the McLachlan method¹²⁾ with the value of $\lambda=1$.

On the other hand, the electrostatic interaction energies between the radical anion and the alkali ions are calculated by the following equation:

$$\varepsilon = 2\sum_{i=1}^{N}(E_i - E^\circ_i) + E_{N+1} - E^\circ_{N+1} + \sum_{\mu=1}^{2N} e^2/r_\mu \tag{6}$$

where E and E° are eigen values obtained from the secular equation for the ion-paired radical and the free radical anion respectively. The final summation of this equation arises from the Coulomb repulsion between the 2 N nuclei, each of which has an effective charge of $+e$, and the alkali ion. In the above calculation we assumed that all the bond lengths were 1.39 Å and that $\beta=-2.5$ eV.

The calculations for the hyperfine splitting constants have been carried out for the various ion-pair configurations. Figure 5 shows the results which give the best fit with the experimental values; the solid lines show the results calculated for the configuration where the alkali ion is placed just above the position marked A in Fig. 6, while the dotted lines do so for the B position, which is located nearer to the 11 position. As may be seen from this figure, the calculation for the solid lines predicts well the relative magnitude of the change in each proton hyperfine splitting of the radical anion with the lithium ion, while the calculation for the dotted lines does so for the radical anion with the potassium or cesium ion, even though the thermal motion of the alkali ion in the field of the radical anion, as has been pointed out by Weissman *et al.*,¹ᵃ⁾ is disregarded.

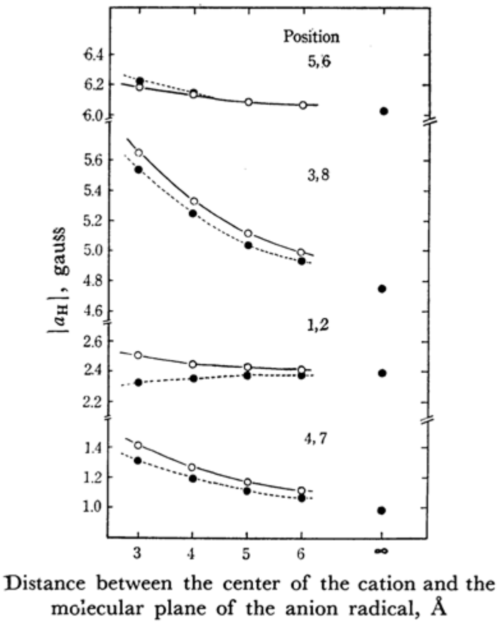

Fig. 5. Calculated values of the proton hyperfine splittings (a_H) of the acenaphthylene radical anion.
—○— and ···●··· are the values for the ion pair configurations where the alkali ions are placed just above the positions marked A and B in Fig. 6 respectively.

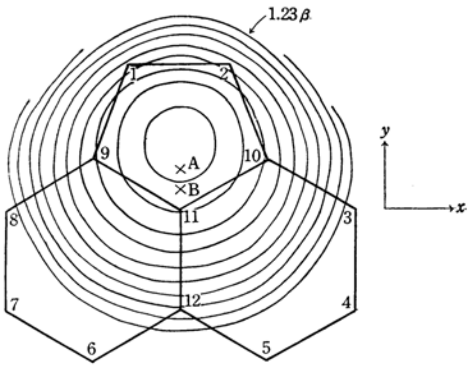

Fig. 6. Electrostatic potential energy map for an alkali ion moving at a distance of 4 Å above the molecular plane of the acenaphthylene radical anion.
The contour lines are drawn at intervals of 0.01β.

The calculations of electrostatic interaction energies, using Eq. (6), predict the same ion-pair configuration. Figure 6 shows the potential energy map calculated for the cation, which lies on the plane 4 Å above the molecular plane. It is apparent from this map that the cation may be located near region of the five-membered ring. However, it should also be noticed that this potential minimum position changes slightly with the distance between

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12) A. D. McLachlan, *ibid.*, **3**, 233 (1960).

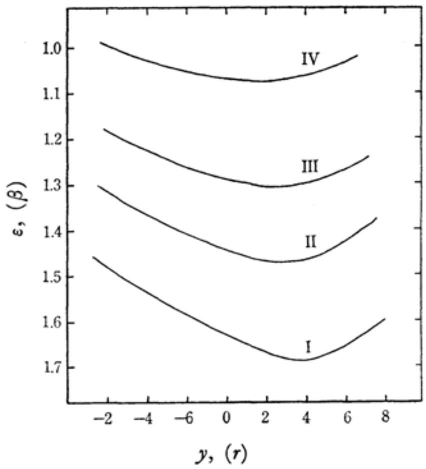

Fig. 7. Electrostatic potential energy (ε) for various ion-pair configurations.
The alkali ion is placed above the symmetry axis passing through the positions 11 and 12 and at distances of I: 3.0 Å, II: 3.5 Å, III: 4 Å, and IV: 5 Å from the molecular plane respectively. r is the C–C bond length and the origin of the y coordinate is at the position 11.

TABLE 1. OBSERVED AND CALCULATED VALUES FOR THE PERTURBATION OF THE PROTON HYPERFINE SPLITTINGS OF RADICAL ANIONS OF NAPHTHALENE, ANTHRACENE AND ACENAPHTHYLENE CAUSED BY ION PAIR FORMATION

Compound	Position	Observation*1 (gauss)	Calculation*2 (gauss)
Naphthalene	α	−0.015*3	−0.149
	β	+0.032	+0.143
Anthracene	1	−0.143*3	−0.672
	2	+0.025	+0.111
	9	+0.122	+0.730
Acenaphthylene	1, 2	−0.029*4	−0.047
	3, 8	+0.498	+0.490
	4, 7	+0.303	+0.198
	5, 6	+0.248	+0.101

*1 The values for radical anions with sodium ion in THP.

*2 For naphthalene and anthracene radical anions, the alkali ion is placed above the center of symmetry and for acenaphthylene radical anion it is placed above the position B in Fig. 6. The distance between the cation and the radical anion is taken to be 4 Å in each case.

*3 The perturbation is taken as the difference from the value in DMF in which the radical may be considered to exist as a free anion; $|a_{\mathrm{THP}}| - |a_{\mathrm{DMF}}|$.

*4 The perturbation is taken as the difference between the value at 23°C and that at −58°C. Refer to Fig. 5.

the cation and the radical anion. Figure 7 shows the variation in the electrostatic interaction energy with the ion-pair configuration, and it indicates that the potential minimum position moves toward the position 11 with an increase in the distance between the two ions or, in other words, with an increase in the radius of the alkali ion. These results agree well with the prediction obtained from the calculation of the effects of the alkali ions on the proton hyperfine splittings. It may be concluded, therefore, that the most likely structure of the ion-pair may be that in which the alkali ion is located in the vicinity of the five-membered ring, but the most favored position of the alkali ion may change slightly with the distance between the two ions, *i. e.,* the position may move toward the position 11 with an increase in the radius of the alkali ion. Our observation concerning the effect of the solvents mentioned above may imply that the distance between the radical anion and the alkali ion does not change very extensively with the solvents, suggesting that the ion-pair may be, rather, a contact pair.

The observed changes of the proton hyperfine splittings of acenaphthylene radical anion are strikingly larger than those of the other common aromatic hydrocarbon radical anions. The changes in the acenaphthylene radical anion amount to about 10%, while those in naphthalene or anthracene radical anions are only 3% or less. Table 1 shows the observed and calculated results on the changes in the proton hyperfine splittings in the presence of the alkali ions for naphthalene, anthracene and acenaphthylene radical anions.

The calculations in Table 1 indicate that the proton hyperfine splittings of the acenaphthylene radical anion may be more sensitive than those of the naphthalene radical anion in the presence of the alkali ion, but not much more sensitive than those of the anthracene radical anion.

Let us now consider the interaction energies between the radical anions and the cation. Previously Buschow *et al.*13) pointed out that the interaction energy between radical anions and the alkali ion depends on the size of the radical anion; *i. e.,* the tendency toward the formation of the ion-pair may decrease with the larger size of the hydrocarbon radical anion. However, the interaction energy between the two ions may be considered to depend also on the charge distribution in the radical anion. In a radical anion with a high negative charge located in a small portion of it, the tendency toward the formation of the ion-pair will increase. Figure 8 shows the electrostatic potential energy map calculated for the cation in the field of the anthracene radical anion. A comparison between Figs. 6 and 8 clearly shows that a steeper

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13) K. H. J. Buschow, J. Dieleman and G. J. Hoijtink, *J. Chem. Phys.,* **42**, 1993 (1965).

and deeper potential valley exists in the acenaphthylene radical anion. It may be expected, therefore, that the acenaphthylene radical anion will form more compact ion-pairs with the alkali ions, and that the amplitude of the thermal oscillational motion of the alkali ion in the ion-pairs will be smaller than in anthracene-alkali ion system. Therefore, it seems likely that these situations may cause the larger perturabation of the proton hyperfine splittings observed in the acenaphthylene radical anion.

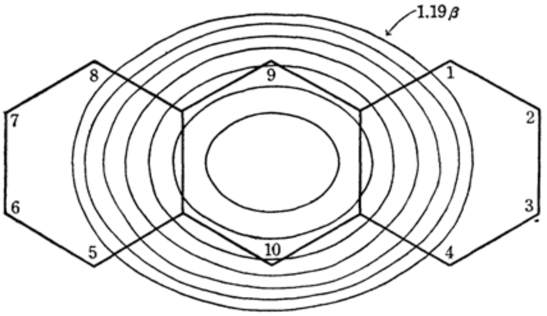

Fig. 8. Electrostatic potential energy map for an alkali ion moving at a distance of 4 Å above the molecular plane of the anthracene radical anion. The contour lines are drawn at intervals of 0.01β.

Temperature Dependence of Alkali Metal Hyperfine Splitting Constants. Atherton *et al.*[1a] found that, in the naphthalene-sodium ion system, the hyperfine splittings due to the sodium metal decrease as the temperature decreases. Similar positive temperature coefficients of the alkali metal hyperfine splittings have been observed in the pyracene-alkali ion system, too.[1d] In these cases, the positive temperature coefficient has been explained by assuming that the alkali ions reside near the nodal plane of the lowest antibonding π-orbital of the respective molecules at low temperatures. In view of these results, a similar positive temperature coefficient may be expected in the present case, because the most likely position for the alkali ion is considered to be on the nodal plane, which passes through the 11—12 bond, of the lowest antibonding π-orbital of acenaphthylene. However, in the present case both negative and positive temperature coefficients were observed.

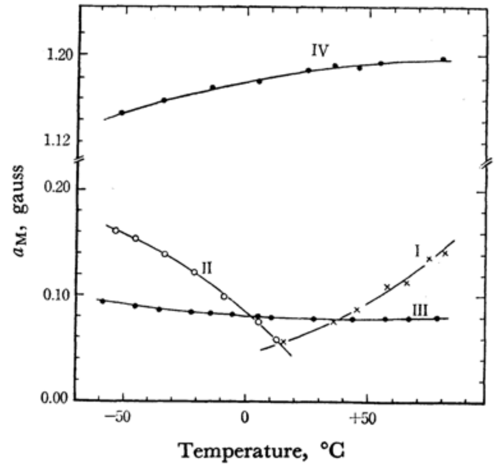

Fig. 9. Temperature dependence of the alkali metal hyperfine splittings (a_M) for acenaphthylene-alkali ion system in THP; I: lithium, II: sodium, III: potassium and IV: cesium.

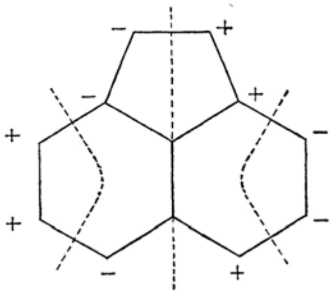

Fig. 10. Nodes in the lowest antibonding π-orbital of acenaphthylene.

The temperature dependence of the alkali mtal hyperfine splittings in THP is shown in Fig. 9. The figure shows that lithium and cesium hyperfine splittings have a positive temperature coefficient, while sodium and potassium hyperfine splittings have a negative coefficient. Here, we assume the charge transfer model to be the most important mechanism producing alkali metal hyperfine splittings, as treated in the above examples. The contribution to the alkali metal hyperfine splittings arising from this mechanism will strongly depend on the overlap between the vacant *s* orbital of the alkali ion and the orbital occupied by the unpaired electron in the radical anion. In the case of the acenaphthylene radical anion, the lowest antibonding π-orbital, occupied by the unpaired electron in the first-order approximation, has nodes on the symmetry plane passing through the positions 11 and 12, the planes intersecting the 3—10 and 4—5 bonds and the 6—7 and 8—9 bonds, as is shown in Fig. 10. Therefore, it is desirable that the alkali ion be situated near the 1—9, 2—10, 3—4 and 7—8 bonds and the positions 5 and 6 in order to show the extra alkali metal hyperfine splittings. If it is assumed that the alkali ion is oscillating around the potential minimum point existing above the five-membered ring, it may be considered that the regions of the 1—9 and 2—10 bonds make the largest contribution to the overlap between the two orbitals. Since these two regions of high overlap are located relatively close to the potential minimum position, it may be expected that, for the large cations, there is still a contribution from these two regions at low temperatures. It even seems possible that the overlap between the two orbitals may rather tend to increase as the alkali ion settles above the five-membered ring with a decrease in the temperature. Moreover, taking into account the fact that the solvent sheath may become more compact on a lowering of the temperature, it seems reasonable to consider that the overlap between the two orbitals may increase on a lowering of the temperature and that thus the spectra will show a negative temperature coefficient of the alkali metal hyperfine splittings, as was observed for sodium and potassium hyperfine splittings.

In the case of the smaller cation, because of the shorter distance between the cation and the radical anion, the thermal motion may be restricted to the smaller region around the potential minimum point by the stronger negative field of the radical anion; further, because of the smaller size of the cation, the contribution of the regions of the 1—9 and 2—10 bonds to the overlap between the two orbitals may become less important at low temperatures. The positive temperature coefficient of lithium hyperfine splittings may be explained by assuming such a situation. Meanwhile, if the potential minimum point is placed near the 11—12 bond, the situation may become similar to that in the naphthalene-alkali ion system, and the negative temperature coefficient will probably become impossible. The positive temperature coefficient observed for the cesium hyperfine splitting may imply that the equilibrium position of the cesium ion is nearer to the 11—12 bond than that of sodium or potassium ion, in accordance with the prediction in the preceding section.

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.