The Influence of Crown Ethers on Cation Migration Processes. Part 5.[1] The Acenaphthene Radical Anion

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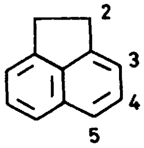
The radical anion of acenaphthene has been prepared in tetrahydrofuran and in tetrahydrofuran in the presence of dibenzo-18-crown-6, 18-crown-6, or [2.2.2]cryptand as cation complexing agent, with either Li^+, Na^+, or K^+ as counterion. Linewidth alternation has been observed in the K^+/(acenaphthene)$^{-\bullet}$/tetrahydrofuran system as a result of cation migration from one side of the molecular plane to the other. The activation energy for this process has been determined (6.6 kJ mol^{-1}) by a procedure which does not require a knowledge of the methylene proton splitting constants in the 'slow' exchange limit. Linewidth alternation is not observed in this system upon addition of any one of the foregoing cation complexing agents. However, equilibria between contact (or 'tight') and solvent-separated (or 'loose') ion pairs have been observed in the Na^+/(acenaphthene)$^{-\bullet}$/tetrahydrofuran and K^+/(acenaphthene)$^{-\bullet}$/18-crown-6/tetrahydrofuran systems (ΔH° 10.2 and 14.1 kJ mol^{-1}, respectively). Values of da/dT, determined for each system, appear to be significantly influenced by the counterion. In particular da(4-H)/dT is positive in pure tetrahydrofuran but negative in the presence of the cation complexing agents.

Ion pairs formed following the reaction of alkali metals with acenaphthene (1) have been of considerable interest in the past.[2–4] An e.s.r. study of the acenaphthene radical anion in a range of ether-related solvents has shown that two different alternating linewidth effects can occur.[3] First, it appears that the alkali metal counterion can, under certain conditions, migrate from one side of the molecular plane to the other. This process affects the relative widths of the lines resulting from the interaction of the unpaired electron with the methylene protons, with the $\Sigma M_I = \pm 1$ lines broadening but the $\Sigma M_I = 0$ and ± 2 lines remaining sharp. We have observed similar cation-migration processes in the 5,12-dihydrotetracene[5,6] and fluorene[7] radical anion systems and find that the addition of various crown ethers can have a significant influence on the rate of cation migration. Secondly, it appears that in the acenaphthene radical anion the cation can also oscillate between two sites on the same side of the molecular plane. This process also affects the widths of the hyperfine lines associated with the four methylene protons. Here the methylene protons fall into two sets of two equivalent nuclei with the central line of each resulting 1:2:1 triplet broadening at low temperatures.

We have been particularly interested in the influence of crown ethers on the rate of cation migration processes and have observed significant effects in several systems.[1,5–7] Similar effects have been reported for the radical anions of pyrazine[8] and tetramethylbenzosemiquinone.[9,10] We hoped that such effects might be observed upon addition of cation complexing agents to the acenaphthene radical anion system. We selected tetrahydrofuran rather than 1,2-dimethoxyethane as the solvent for this study as the latter has solvation properties similar to those of the various crown ethers.[1] We found, however, that the addition of crown ethers to solutions of the radical anion did not induce linewidth alternation with any of the various alkali metal counterions. Nevertheless we have attempted to computer-simulate the linewidth alternation observed for the acenaphthene radical anion, with K^+ as counterion, in tetrahydrofuran but in the absence of any cation complexing agents. The spectrum simulation method is explained later and appears to be successful despite the fact that even at the lowest temperature at which spectra could be recorded the 'slow exchange' methylene splitting constants are not available. We also report several systems in which equilibria between different



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types of ion pair are present. In addition we report the results of a detailed study of the temperature dependence of the hyperfine splitting constants for the radical anion (in tetrahydrofuran) in the presence of dibenzo-18-crown-6, 18-crown-6, and [2.2.2]cryptand as cation complexing agents.

Experimental

All vacuum operations were performed by use of standard high-vacuum techniques.

Materials.—Tetrahydrofuran (B.D.H.) was purified as described previously[11] and stored over sodium–potassium alloy. Acenaphthene (Aldrich), dibenzo-18-crown-6 (Lancaster Synthesis), and 18-crown-6 (Lancaster Synthesis) were all purified by repeated recrystallisation before use. [2.2.2]Cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Fluka) was used as supplied, and the alkali metals were washed in light petroleum before use.

Procedure.—Solutions of acenaphthene in tetrahydrofuran were prepared by the standard methods described previously.[12] The concentrations of acenaphthene and of the cation complexing agent were arranged to be as near as possible the same as one another, and were in the range 2—3 × 10^{-3} mol dm^{-3}. The radical anion was prepared from these solutions as described previously,[12] by using metal films in the experiments involving sodium or potassium and small pieces of metal in the experiments involving lithium.

Spectroscopic Measurements.—All e.s.r. spectra were recorded with a Varian E3 spectrometer, the magnetic field sweep of which was calibrated with Fremy's salt.[13] The temperature of the samples was controlled by means of a Varian E4557 variable-temperature unit.

Table 1. Hyperfine splitting constants (in μT) for the acenaphthene radical anion in tetrahydrofuran, with Li$^+$ or Na$^+$ as the counterion, taken as least-squares values from *a vs. T* plots

T/K	*a*(2-H)	*a*(3-H)	*a*(4-H)	*a*(5-H)	*a*(^{23}Na)
Lithium					
150*	751	108	236	420	
200	744	109	238	412	
250	737	111	241	405	
300	730	112	244	397	
Sodium (species A)					
150*	756	106	237	419	
200	752	107	239	415	
250	749	107	241	412	
300	746	108	243	408	
Sodium (species B)					
150*	758	104	240	422	19
200	754	105	239	418	51
250	749	106	239	415	83
300	744	108	239	412	116

* Values lie slightly outside the temperature range covered experimentally.

Table 2. Hyperfine splitting constants (in μT) for the acenaphthene radical anion in tetrahydrofuran, with K$^+$ as the counterion, taken from best-fit computer simulations (x = 30; see text)

T/K	*a*(2-H)	*a*(3-H)	*a*(4-H)	*a*(5-H)	$10^8\ \tau$/s
182	728,788	108	241	417	15
190	725,785	109	241	417	12.5
200	725,785	109	240	416	10.2
213	723,783	109	240	415	8.2
223	720,780	109	241	414	6.7
234	720,780	109	241	413	5.9
244	720,780	110	242	413	4.9

Computer Simulation of E.s.r. Spectra.—Computer simulations of e.s.r. spectra were obtained using a Data General Nova 1220 computer on line to the spectrometer. The program used in the simulation of spectra exhibiting an alternating linewidth effect employed the modified Bloch equations appropriate to a two-jump process in which two pairs of two equivalent protons interchange their splitting constants. The hyperfine splitting constants quoted from these simulations are considered accurate to within $\pm 1\ \mu$T. Spectra not exhibiting linewidth alternation were computer-simulated employing a conventional spectrum simulation program. The hyperfine splitting constants obtained from these latter simulations are also considered accurate to within $\pm 1\ \mu$T. The temperature coefficients da/dT, for the variation of the hyperfine splitting constants with temperature, were obtained by a least-squares analysis and are considered accurate to within $\pm 0.5 \times 10^{-2}\ \mu$T K^{-1}. (The absolute magnitude of a was used to calculate the values of da/dT quoted in this paper.) The magnitude of each hyperfine splitting constant, in each system, is presented in the text at four temperatures (150, 200, 250, and 300 K). These latter values were obtained using a least-squares analysis of the splitting constants obtained from the best-fit computer simulation of each experimental spectrum. The resulting least-squares splitting constants are quoted in Tables 1, 3, 4, and 5, an asterisk indicating that at that particular temperature the least-squares values lie slightly outside the temperature range covered experimentally.

Results

The Acenaphthene Radical Anion/Tetrahydrofuran System.—We describe first the results obtained for the acenaphthene radical anion in tetrahydrofuran in the absence of any cation complexing agents. Acenaphthene was readily reduced by all three alkali metals to give a green solution of the radical anion. When lithium was the counterion the spectra obtained were consistent with the presence of a single species. However, when sodium was the counterion the spectra indicated a mixture of two species, one of which exhibited additional splitting from the counterion. The alternating linewidth effect was observed when potassium was the counterion. This effect has been reported for this system previously by Iwaizumi *et al.*,[3] and we have computer-simulated these latter spectra as described in detail later.

Lithium. E.s.r. spectra were recorded at approximately 10 K intervals from 181 to 305 K and computer-simulated. The plots of a *vs.* T are linear over this temperature range for each hyperfine splitting constant and the resulting values of da/dT obtained from these plots are summarised in Table 6. Hyperfine coupling to ^{7}Li was observed in the spectra recorded at 296 and 305 K (20 and 29 μT, respectively). Values of a at four temperatures (150, 200, 250, and 300 K) were determined from the a *vs.* T plots and are reported in Table 1.

Sodium. It is apparent from the spectra obtained for this system (recorded over the temperature range 181—307 K) that two species are present. The dominant species (species B) exhibits additional hyperfine structure resulting from the interaction of the unpaired electron with the ^{23}Na nucleus. [The other species (A) does not exhibit additional splitting.] These spectra have been computer-simulated as those of mixtures of two species. However, below 217 K accurate splitting constants could only be obtained for species A. Plots of a *vs.* T for each splitting constant were all linear and the resulting values of da/dT for both species are summarised in Table 6. The values of a at 150, 200, 250, and 300 K obtained from these plots are summarised in Table 1. The best-fit computer simulations of the experimental spectra also reveal the relative equilibrium proportions of both species at each temperature. From these data, and the resulting ln K *vs.* $1/T$ plot, a value for ΔH° of 10.2 $\pm$ 2 kJ mol^{-1} was obtained.

Potassium. When potassium is the counterion the alternating linewidth effect is observed over the temperature range 182—244 K. This alternation affects the relative intensities of the $\Sigma M_{\mathrm{I}} = \pm 1$ lines arising from the interaction of the unpaired electron with the four methylene protons. Unfortunately, at the lowest temperature at which a reasonable spectrum could be recorded (182 K) the lifetime of the species was still too small for the methylene proton splitting constants in the 'slow exchange' region to be individually determined. Their mean value, a, can be determined by computer simulation of the spectrum at each temperature. The problem is, however, how to proportionate this mean value between the two (triplet) hyperfine couplings. We have therefore selected a (2H) values of $\bar{a} \pm x$ (x = 20, 30, or 40 μT) and undertaken a simulation of each spectrum with these assumed values. Obviously the value of τ (the average lifetime of the counterion on either one of the equivalent sites) required to obtain the best computer fit at each temperature varies with x. However, all three sets of simulations give ln τ *vs.* $1/T$ plots which run exactly parallel. We have therefore concluded that, if an absolute value of τ is not necessarily essential, the activation energy obtained from the Arrhenius plot is independent of the selected value of x. Figure 1 illustrates two typical computer simulations obtained (with x = 30) and

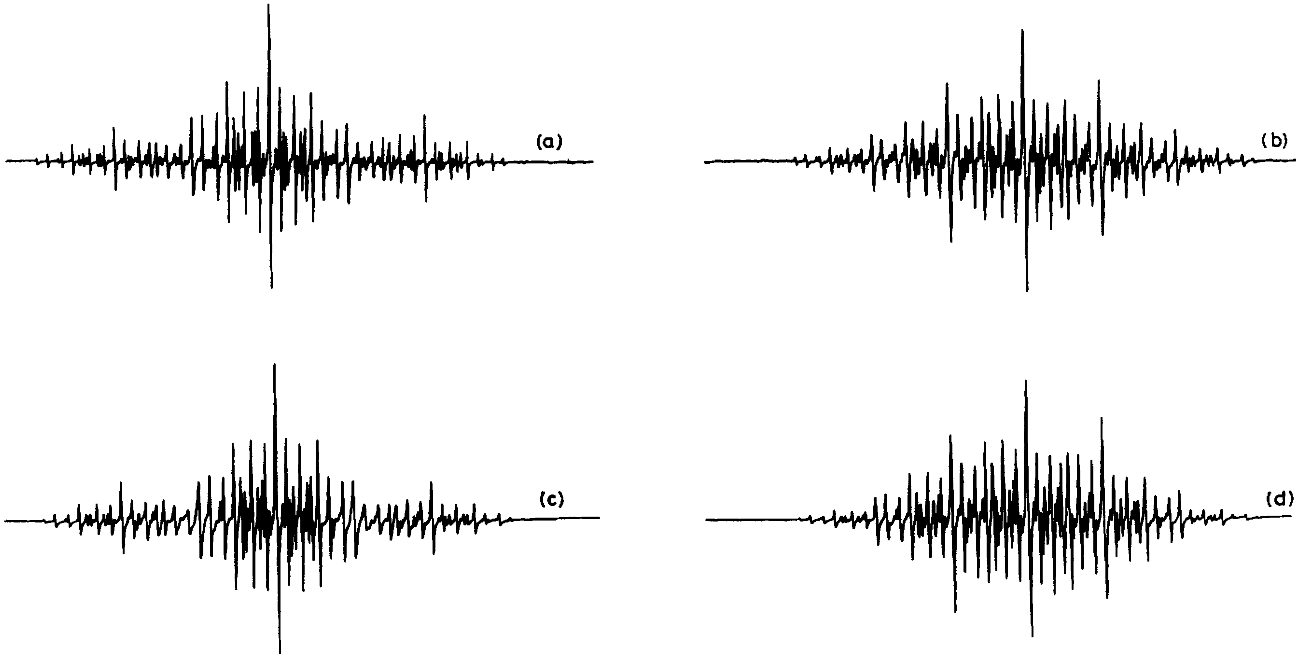

Figure 1. Experimental e.s.r. spectra of the K^+/(acenaphthene)$^{-\cdot}$ system in tetrahydrofuran at (a) 182 K and (b) 277 K together with their computer simulations (c) (x = 30 μT) and (d), respectively (parameters as Table 2)

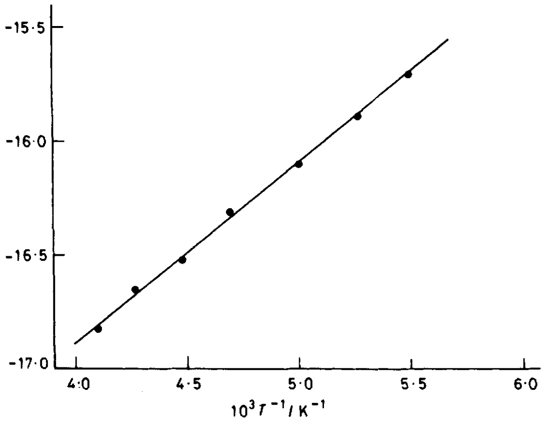

Figure 2. Arrhenius plot for the K^+/(acenaphthene)$^{-\cdot}$ system in tetrahydrofuran

Figure 2 the resulting Arrhenius plot (E_a = 6.6 ± 0.5 kJ mol^{-1}). The various parameters obtained from these simulations are summarised in Table 2.

The Acenaphthene Radical Anion/Dibenzo-18-*crown*-6/*Tetrahydrofuran System*.—Again acenaphthene was readily reduced with all three alkali metals to give a green solution of the radical anion. In several other systems the addition of dibenzo-18-crown-6 to a tetrahydrofuran solution of a radical anion induces linewidth alternation.[1,5–10] We hoped this would also be the case with the acenaphthene radical anion. However, the spectra obtained with each alkali metal counterion are consistent with the presence of a single species, and the alternating linewidth effect observed in the absence of the crown ether when K^+ is the counterion is no longer observed upon the addition of the crown ether. A computer simulation was obtained for each spectrum at each temperature. The highest temperature at which spectra were recorded was dependent upon the decay of the radical anion as the temperature was increased. (It is interesting in this respect that the stability varied: $Li^+ < Na^+ < K^+$.) Plots of *a vs. T* were linear for each hyperfine splitting constant in each system over the temperature range available; the least-squares fit values at 150, 200, 250, and 300 K are summarised in Table 3. The resulting values of d*a*/d*T* obtained from these plots are summarised in Table 6.

Table 3. Hyperfine splitting constants (in μT) for the acenaphthene radical anion in tetrahydrofuran, with Li^+, Na^+, or K^+ as the counterion in the presence of dibenzo-18-crown-6, taken as least-squares values from *a vs. T* plots

T/K	*a*(2-H)	*a*(3-H)	*a*(4-H)	*a*(5-H)
Lithium				
150*	757	105	239	420
200	748	108	235	417
250	739	112	230	414
300*	730	115	226	411
Sodium				
150	755	107	235	419
200	747	109	232	417
250	739	111	230	415
300*	731	112	228	413
Potassium				
150	749	105	234	419
200	746	107	232	414
250	743	109	230	408
300*	739	111	229	403

* Values lie slightly outside the temperature range covered experimentally.

The Acenaphthene Radical Anion/18-*Crown*-6/*Tetrahydrofuran System*.—*Lithium and sodium*. When either Li^+ or Na^+ was the counterion the e.s.r. spectra obtained for this system were again consistent with the presence of a single species only. Hyperfine structure arising from the interaction of the unpaired

Table 4. Hyperfine splitting constants (in μT) for the acenaphthene radical anion in tetrahydrofuran, with Li$^+$, Na$^+$, or K$^+$ as the counterion in the presence of 18-crown-6, taken as least-squares values from *a vs. T* plots

T/K	*a*(2-H)	*a*(3-H)	*a*(4-H)	*a*(5-H)
Lithium				
150*	753	104	234	421
200	744	108	232	417
250	736	112	230	414
300	728	116	229	410
Sodium				
150	749	104	233	420
200	740	107	231	417
250	733	111	229	414
300	724	114	227	412
Potassium (species A)				
150	749	106	238	418
200	745	108	236	416
250	740	110	234	414
300*	737	112	232	412
Potassium (species B)				
150	757	103	243	423
200	751	104	240	420
250	745	105	237	418
300*	738	106	235	415

* Values lie slightly outside the temperature range covered experimentally.

electron with the alkali metal counterion was not observed for either alkali metal ion. A best-fit computer simulation of each spectrum was obtained at each temperature at which spectra were recorded (*ca.* 10 K intervals). Plots of *a vs. T* all gave good straight lines for each splitting constant when either Li$^+$ or Na$^+$ was present as the counterion. The least-squares fit values for each hyperfine splitting constant at 150, 200, 250, and 300 K are summarised in Table 4 and the corresponding values of d*a*/d*T* are summarised in Table 6.

Potassium. When K$^+$ was the counterion the e.s.r. spectra (over the temperature range 152—248 K) indicated the presence of two species. Hyperfine coupling to the counterion was not evident in the spectra of either species. Each experimental spectrum was computer-simulated in terms of two species (A and B) in equilibrium with one another. Species A predominated at the low end of the temperature range and species B at the high end. The resulting plots of *a vs. T* were all linear and the values of *a* at 150, 200, 250, and 300 K for both species are summarised in Table 4. The values of d*a*/d*T* taken from these plots are summarised in Table 6. The equilibrium constant for the equilibrium between the two species was obtained over the temperature range 152—248 K from the relative proportions of the two species present (in the best-fit computer simulations). From the resulting ln *K vs.* 1/*T* plot the value for ΔH° of 14.1 ± 1 kJ mol^{-1} was obtained.

The Acenaphthene Radical Anion/[2.2.2]*Cryptand/Tetrahydrofuran System.*—A green solution of the radical anion was again obtained when acenaphthene was reduced with each of the three alkali metals. All the spectra recorded for this system were readily interpreted in terms of single species without coupling to the appropriate alkali metal counterion. A best-fit computer simulation was obtained for each spectrum and the values of *a* at 150, 200, 250, and 300 K, taken from *a vs. T* plots, are reported in Table 5. The values of d*a*/d*T* obtained from these plots are summarised in Table 6.

Table 5. Hyperfine splitting constants (in μT) for the acenaphthene radical anion in tetrahydrofuran, with Li$^+$, Na$^+$, or K$^+$ as the counterion in the presence of [2.2.2]cryptand, taken as least-squares values from *a vs. T* plots

T/K	*a*(2-H)	*a*(3-H)	*a*(4-H)	*a*(5-H)
Lithium				
150	754	106	241	423
200	745	109	238	418
250	736	111	235	413
300	728	114	232	408
Sodium				
150	752	106	242	420
200	743	109	239	416
250	733	113	235	412
300	724	116	232	409
Potassium				
150	750	107	239	417
200	742	110	235	411
250	733	114	232	405
300*	724	118	228	400

* Values lie slightly outside the temperature range covered experimentally.

Discussion

Linewidth Alternation in the Potassium/Acenaphthene Radical Anion/Tetrahydrofuran System.—The linewidth alternation observed in this system results in broadening of the $\Sigma M_I = \pm 1$ lines of the quintet arising from the interaction of the unpaired electron with the four methylene protons. In the slow-exchange limit this would lead to two sets of two equivalent protons with the two protons on the same side of the molecular plane as the cation having different hyperfine splitting constants from the two protons on the other side of the molecular plane. We believe, therefore, that cation migration from one side of the molecular plane to the other is responsible for the linewidth alternation observed in this system. The alternative oscillation of the cation between two equivalent sites on the same side of the molecular plane would also result in linewidth alternation but this latter alternation would be observed at much lower temperatures. Additionally the slow exchange situation for this latter migration would result in different hyperfine splitting constants for all four methylene protons whilst the fast exchange situation would result in two pairs of two equivalent protons.

We have observed cation migration between equivalent sites on the two sides of the molecular plane in two other systems. In the fluorene radical anion this results in a difference between the methylene hyperfine splitting constants of *ca.* ±50 μT,[7] and in the 5,12-dihydrotetracene radical anion of *ca.* ±45 μT.[5,6] Unfortunately the slow exchange situation is not observed in the K$^+$/(acenaphthene)$^{-\bullet}$/tetrahydrofuran system, but we have attempted computer simulation of these spectra assuming a similar difference in methylene proton splitting constants. [In fact the 'slow' exchange values are available in the K$^+$/(acenaphthene)$^{-\bullet}$/tetrahydropyran system and give a difference between the methylene hyperfine splitting constants of *ca.* ±17 μT.[3]] The three values selected for *x* of ±20, ±30, and ±40 μT require different values to achieve the same computer

Table 6. Values of 10^2 (da/dT)/μT K^{-1} for the acenaphthene radical anion in tetrahydrofuran and in tetrahydrofuran in the presence of various cation complexing agents

Counterion	da(2-H)/dT	da(3-H)/dT	da(4-H)/dT	da(5-H)/dT	da(^{23}Na/dT)
Tetrahydrofuran					
Li^+	−13.6	+2.9	+5.4	−15.0	
Na^+ (species A)	−6.9	+1.2	+3.6	−7.3	
Na^+ (species B)	−9.8	+2.5	0.0	−6.9	+64.5
K^+	−13.1	+2.0	+1.4	−7.4	
Dibenzo-18-crown-6/tetrahydrofuran					
Li^+	−18.3	+6.9	−8.6	−6.1	
Na^+	−15.9	+3.5	−5.2	−3.8	
K^+	−6.4	+3.9	−3.9	−10.8	
18-Crown-6/tetrahydrofuran					
Li^+	−16.6	+7.9	−3.2	−7.0	
Na^+	−16.4	+6.8	−3.5	−5.7	
K^+ (species A)	−7.9	+3.9	−3.7	−4.1	
K^+ (species B)	−12.5	+2.3	−5.5	−5.0	
[2.2.2]Cryptand/tetrahydrofuran					
Li^+	−17.6	+5.1	−5.9	−10.0	
Na^+	−18.4	+7.4	−6.6	−7.3	
K^+	−17.2	+7.3	−6.9	−11.1	

simulation. However, the corresponding ln τ *vs.* $1/T$ plots for each value of x gave three exactly parallel plots and we have therefore concluded that the activation energy obtained for this system (6.6 kJ mol^{-1}) is realistic. This is the lowest activation energy we have observed for a cation migration process of this type. We believe that this is probably a result of the oscillation of the cation between two equivalent sites on the same side of the molecular plane facilitating the migration.

It is perhaps surprising that linewidth alternation is not observed when either Li^+ or Na^+ is the counterion. This could well be a consequence of a stronger cation–solvent interaction in the case of these latter two ions resulting in a different environment of the counterion with respect to the radical anion. It is interesting, in this respect, that the addition of specific solvating agents to solutions of the radical anion changes the sign of da(4-H)/dT. (This feature is discussed in more detail later.) It seems likely, therefore, that the environment of the counterion relative to the radical anion also changes in the presence of specific solvating agents and that this change facilitates cation migration.

*Equilibria in the Sodium/Acenaphthene Radical Anion/Tetrahydrofuran and Potassium/Acenaphthene Radical Anion/*18-*Crown*-6/*Tetrahydrofuran Systems.*—The proton hyperfine splitting constants of the two species present in the Na^+/(acenaphthene)$^{-\bullet}$/tetrahydrofuran system are remarkably similar (see Table 1). However, the two species are readily distinguished by the additional hyperfine coupling to the ^{23}Na nucleus observed in species B. This species predominates in the temperature range studied (181—307 K) and is favoured at higher temperatures. We identify this species, therefore, as a contact ion pair. Hyperfine coupling to the alkali metal ion is not observed in either species in the K^+/(acenaphthene)$^{-\bullet}$/18-crown-6/tetrahydrofuran system. However, in this system the hyperfine splitting constants of the two species differ significantly, particularly at low temperatures (Table 4). Species B is favoured at high temperatures and this species is therefore identified as a contact or 'tight' ion pair.

It is interesting that both of these equilibrium systems give large positive $\Delta S°$ values. The values calculated at 233 K for the Na^+/(acenaphthene)$^{-\bullet}$/tetrahydrofuran and K^+/(acenaphthene)$^{-\bullet}$/18-crown-6/tetrahydrofuran systems are 59 and 68 J mol^{-1} K^{-1}, respectively. These significant positive values, in going from the solvent-separated (or 'loose') ion pair to the contact (or 'tight') ion pair, presumably result as a consequence of the release of solvent molecules in moving from the former to the latter type of ion pair.

Hyperfine Parameters.—The values of da/dT for the various systems are collected in Table 6. Two features are noteworthy. First, the values of da(2-H)/dT and da(5-H)/dT are negative in all systems, but values of da(3-H)/dT are positive. Secondly, the values of da(4-H)/dT are positive in tetrahydrofuran but negative in the presence of the various cation complexing agents.

We consider first the (acenaphthene)$^{-\bullet}$/tetrahydrofuran system. In the radical anions of planar aromatic hydrocarbons a positive spin density on a particular carbon atom invariably leads to a negative value of da(H)/dT for the attached proton.[14] Conversely, a negative spin density on a particular carbon atom almost invariably leads to a positive da(H)/dT. The positive values for da(3-H)/dT in tetrahydrofuran and da(4-H)/dT in tetrahydrofuran are therefore unexpected. There can be little doubt that there is a positive spin density on C-4, but there is some ambiguity concerning the sign of the spin density on C-3. A simple Huckel calculation employing a methylene group inductive parameter (h) of −0.25 and a McLachlan parameter (λ) of 0.001 predicts a positive spin density with a magnitude consistent with the experimental splitting constant.[2] However, we have undertaken a calculation with values for h and λ of −0.50 and 1.0, respectively and find a negative spin density, of approximately the correct magnitude, predicted at this position. It is, therefore, a little uncertain whether the spin density on C-3 is positive or negative. However, the positive da(4-H)/dT values observed must be due to the alkali metal counterion perturbing the spin distribution on C-4 as a function of temperature. An increase in temperature would favour a 'tighter' ion pair and therefore the magnitude of the counterion perturbation would increase with temperature. The positive counterion would attract spin density to the carbon atoms within its vicinity. We would therefore expect da/dT to become more positive for those protons close to the counterion, and more negative for those protons more distant. This leads us to suggest that the counterion is located within the general vicinity of C-4. Calculations by Iwaizumi suggested a site nearer to the methylene bridge.[3] However we are encouraged to believe that the site of the counterion is further away from the methylene bridge in (acenaphthene)$^{-\bullet}$ than in (fluorene)$^{-\bullet}$ or (5,12-dihydrotetracene)$^{-\bullet}$ as the perturbation of the methylene proton hyperfine splitting constants by the counterion is much smaller in the first of these (*ca.* ± 17 μT) than in the latter two (*ca.* ± 50 and *ca.* ± 45 μT, respectively).

The addition of cation complexing agents to the solution of the radical anion results in a change of sign of $\mathrm{d}a(4\text{-H})/\mathrm{d}T$. By the logic of the foregoing argument therefore, these complexing agents move the position of the cation away from its favoured site in tetrahydrofuran. Although there are exceptions, values of $\mathrm{d}a/\mathrm{d}T$ are larger in the presence of the complexing agents, with the influence of [2.2.2]cryptand most noticeable in this respect. This increase in magnitude of $\mathrm{d}a/\mathrm{d}T$ could be a result of a much greater range of complexed-cation radical anion separations than in pure tetrahydrofuran.

References

1 Part 4, N. J. Flint and B. J. Tabner, *J. Chem. Soc., Perkin Trans. 2,* 1984, 569.
2 A. M. Hermann, A. Rembaum, and W. R. Carper, *J. Phys. Chem.*, 1967, **71**, 2661.
3 M. Iwaizumi, M. Suzuki, T. Isobe, and H. Azumi, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2754.
4 A. H. Reddoch, *J. Magn. Reson.*, 1974, **15**, 75.
5 B. J. Tabner and T. Walker, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1508.
6 A. J. Burke and B. J. Tabner, *J. Chem. Soc., Perkin Trans. 2*, 1983, 205.
7 E. J. Rothwell and B. J. Tabner, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1384.
8 G. F. Pedulli and A. Alberti, *Chem. Phys. Lett.*, 1977, **48**, 72.
9 M. P. Eastman, G. V. Bruno, C. A. McGuyer, A. R. Gutierrez, and J. M. Shannon, *J. Phys. Chem.*, 1979, **83**, 2523.
10 S. Konishi, S. Niizuma, and H. Kokubun, *Chem. Phys. Lett.*, 1980, **71**, 164.
11 D. Casson and B. J. Tabner, *J. Chem. Soc. B*, 1969, 572.
12 D. Casson and B. J. Tabner, *J. Chem. Soc. B*, 1969, 887.
13 R. J. Faber and G. E. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 246.
14 P. D. Sullivan and E. M. Menger, *Adv. Magn. Reson.*, 1977, **9**, 1.

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