The Influence of Crown Ethers on Cation Migration Processes. Part 3.[1] The 5,12-Dihydrotetracene Radical Anion with Lithium or Potassium as Counterion

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The addition of dibenzo-18-crown-6 to a solution of 5,12-dihydrotetracene in tetrahydrofuran has been found to reduce dramatically the rate of cation migration when Li^+ is the counterion. The resulting e.s.r. spectra, which exhibit linewidth alternation, have been computer-simulated employing modified Bloch equations. The activation energy for this process has been found to be 13.5 kJ mol^{-1}. Linewidth alternation is also present when K^+ is the counterion, and is accompanied by a significant change in the various splitting constants as the ' fast exchange ' region is approached.

In a number of radical anions there are two equivalent cation binding sites between which intramolecular cation migration can occur. Unfortunately in very many cases this migration is too fast to be measured by e.s.r. It is not surprising, however, that the addition to the solution of a cation-binding agent, such as a crown ether, can have a significant influence upon the rate of migration. Examples of this influence have been reported for the radical anions of pyrazine[2] and durosemiquinone.[3] In some radical anions, for example those of fluorene[4] and 5,12-dihydrotetracene (1),[5] the cation appears to migrate from one side of the radical anion plane to the other. This rate of migration is also significantly influenced by the addition of a crown ether.[1] The magnitude of this effect not only depends upon solvent, counterion, and temperature but also upon the compatibility of the alkali metal counterion with the binding site in a particular crown ether.

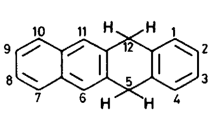
In an earlier publication we reported that the addition of dibenzo-18-crown-6 to a solution of Na^+-5,12-dihydrotetracene radical anion in tetrahydrofuran reduced the rate of cation migration such that linewidth alternation was observed in the e.s.r. spectrum.[1] An examination of this effect showed that it was the methylene protons whose splitting constants were undergoing the out-of-phase modulation. We have now extended our study to include the Li^+- and K^+-5,12-dihydrotetracene radical anion systems. This enables a comparison to be made amongst the various alkali metal ions in cation–crown ether interactions. Of particular interest is the influence of the crown ether on the K^+-5,12-dihydrotetracene radical system, as linewidth alternation is observed in this system in the absence of the crown ether.[5]

Experimental

All operations were performed employing high vacuum techniques.

Materials.—Tetrahydrofuran and 5,12-dihydrotetracene were purified as described.[6] Dibenzo-18-crown-6, prepared as described,[7] was supplied by Dr. P. Hodge of this Department and was purified as described.[4] Lithium and potassium were washed in light petroleum before use.

Procedure.—Solutions of 5,12-dihydrotetracene and dibenzo-18-crown-6 in tetrahydrofuran were prepared by the methods described previously.[1] In each experiment the concentration of the crown ether was 3.3×10^{-3} mol l^{-1} and of 5,12-dihydrotetracene was in the range 2.6—3.2×10^{-3} mol l^{-1}. The radical anion was prepared from these solutions as described.[1]



(1)

Spectroscopic Measurements.—All e.s.r. spectra were recorded with a Varian E3 spectrometer, the magnetic field sweep of which was calibrated using Fremy's salt.[8] The temperature of the samples was controlled by means of a Varian E4557 variable-temperature unit.

Simulation of E.s.r. Spectra.—Computer simulations of e.s.r. spectra in which the alternating linewidth effect was present were obtained using an I.C.L. 2960 computer. The first part of the program uses the modified Bloch equations appropriate to a two-jump model in which two pairs of two equivalent protons interchange their splitting constants. This part of the program is similar to that already published.[9] The resulting lineshape is then utilised in the second part of the program which introduces the hyperfine splitting from the remaining (non-alternating) protons and records the first derivative of the resulting spectrum on a Calcomp plotter. A second program, which simulates spectra without selective line broadening, was used in conjunction with a Data General Nova 1220 computer on line to the e.s.r. spectrometer.

Results and Discussion

Lithium.—In the absence of a crown ether the e.s.r. spectrum of the 5,12-dihydrotetracene radical anion in tetrahydrofuran solution is readily interpreted when Li^+ is the counterion.[1,5] The interpretation requires four 1 : 2 : 1 triplets and a 1 : 4 : 6 : 4 : 1 quintet, with a fifth 1 : 2 : 1 triplet barely discernible within the linewidth of the spectrum. The computer simulation of this spectrum shows that linewidth alternation is not present over the temperature range 203—273 K.

The e.s.r. spectrum of the radical anion in the presence of dibenzo-18-crown-6 at 269 K is similar to that obtained in the absence of the crown ether (apart from minor differences in the various splitting constants). E.s.r. spectra were recorded at approximately 10 K intervals over the temperature range 173—269 K, the spectrum changing dramatically as the temperature decreased. These changes concern the amplitudes of certain lines in the spectrum, which decrease with temperature until at the lowest temperatures new lines, of relatively low amplitude, become apparent. Again an examination of these spectra reveals that it is the lines associated with the methylene protons whose splitting constants are involved in

Table 1. Parameters used in the computer simulation of the e.s.r. spectra of the Li^+–dibenzo-18-crown-6–5,12-dihydrotetracene radical anion system in tetrahydrofuran (splitting constants in μT)

T/K	173	180	194	203	213	222	233	243	253	261	269
$a_{1,4}$	20	20	20	20	20	20	20	20	20	20	20
$a_{2,3}$											
$a_{6,11}$	434	434	432	432	432	430	428	426	425	425	425
$a_{7,10}$	509	507	507	507	507	507	507	505	503	504	504
$a_{8,9}$	169	170	169	169	169	169	169	169	168	168	168
$a_{5,12}$	387	387	387	386	386	386	386	383	381	379	379
$a_{5',12'}$	279	277	277	276	276	276	276	273	271	270	270
10^8 τ/s	80.0	60.0	30.0	20.0	15.0	11.0	9.0	6.0	5.0	3.5	2.75

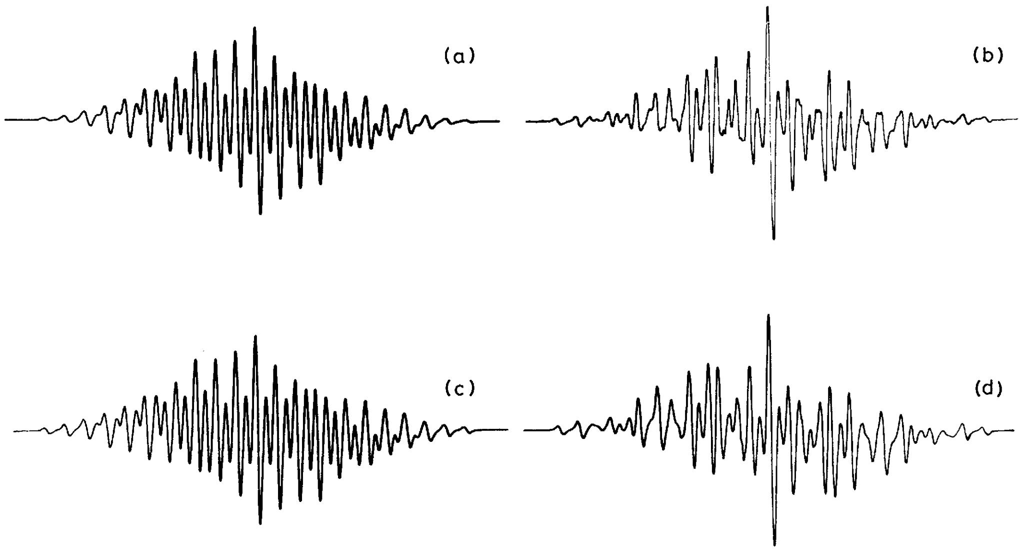


Figure 1. The experimental e.s.r. spectra of the Li^+–dibenzo-18-crown-6–5,12-dihydrotetracene radical anion system in tetrahydrofuran at (a) 261 K, and (b) 194 K together with their computer simulations (c) and (d) respectively (parameters as given in Table 1)

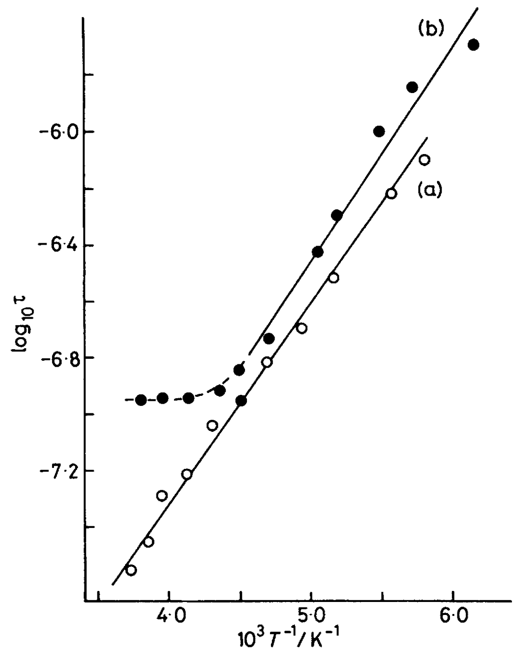


Figure 2. The Arrhenius plot for the dibenzo-18-crown-6–5,12-dihydrotetracene radical anion system in tetrahydrofuran with (a) Li^+ and (b) K^+ as the counterion

this process whilst the ' pure ' lines of the 1 : 2 : 1 triplets retain their correct relative intensities. This is precisely the same effect as we reported for the Na^+–5,12-dihydrotetracene radical anion in the presence of dibenzo-18-crown-6.[1]

A computer simulation has been obtained for each spectrum. Each simulation has been optimised as far as possible and the various parameters obtained for the best fit simulation are reported in Table 1. (Typical spectra and their computer simulations are illustrated in Figure 1.) At the very lowest temperatures ' slow exchange ' conditions prevail and it has been possible to obtain values of $a_{5,12}$ and $a_{5',12'}$ directly from these spectra. However at higher temperatures, as the ' fast exchange ' conditions is approached, only the sum, $a_{5,12} + a'_{5,12'}$, can be determined accurately. Where this sum drifts with temperature the individual values of $a_{5,12}$ and $a_{5',12'}$ have been obtained for the purpose of the computer simulation by proportioning their sum in the same ratio as that which appertained in the slow exchange region.

The process responsible for the linewidth alternation in this system appears to be the migration of the cation between two equivalent sites on either side of the radical anion plane. Iwaizume and Isobe proposed this migration process to account for the linewidth alternation observed in the K^+–5,12-dihydrotetracene radical anion in the absence of the crown ether.[5] A similar explanation seems to hold for the linewidth alternation observed in the fluorene radical anion in the presence of crown ethers.[4] Figure 2(a) shows the log τ *vs.* 1/T plot for the migration process in the Li^+–dibenzo-

Table 2. Parameters used in the computer simulation of the e.s.r. spectra of the K$^+$–dibenzo-18-crown-6–5,12-dihydrotetracene radical anion system in tetrahydrofuran (splitting constants in μT)

T/K	163	175	183	193	199	213	223	230	242	253	263	268	283	293
$a_{1,4}$	20	20	20	20	20	20	20	20	20	15	12	10	10	10
$a_{2,3}$														
$a_{6,11}$	434	432	432	429	429	427	427	427	429	426	428	429	434	434
$a_{7,10}$	512	506	506	503	503	503	503	502	502	500	500	498	497	497
$a_{8,9}$	172	171	172	171	171	169	169	169	170	169	169	169	169	169
$a_{5,12}$	372	372	372	369	369	371	371	370	646	638	638	609	609	609
$a_{5',12'}$	282	282	282	280	280	282	282	281						
$10^8\ \tau$/s	200	140	100	50.0	35.0	18.0	14.0	12.0	[a]	[a]	[a]	[a]	[a]	[a]

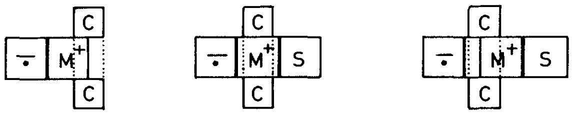
[a] Values of τ appear to remain unchanged in the range 11.0—12.0 (× 10^{-8}) s.

18-crown-6-5,12-dihydrotetracene radical anion system from which an activation energy of 13.5 kJ mol^{-1} has been obtained.

Potassium.—The e.s.r. spectrum of the 5,12-dihydrotetracene radical anion in tetrahydrofuran is particularly interesting in the absence of the crown ether when K$^+$ is the counterion. Linewidth alternation is observed and the activation energy for the cation migration process has been determined.[5] The addition of dibenzo-18-crown-6 to this system is therefore of considerable interest as it provides an opportunity to study the influence of the crown ether on the cation migration process.

The e.s.r. spectrum of the 5,12-dihydrotetracene radical anion in the presence of dibenzo-18-crown-6 was recorded at approximately 10 K intervals from 163 to 293 K. Superficially these spectra follow the same trends as observed in the presence of the crown ether when either Li$^+$ or Na$^+$ is the counterion. Linewidth alternation is again present and can be associated, as before, with a loss of equivalence of the methylene protons. A computer simulation of each spectrum has been obtained and with ' slow exchange ' conditions again prevailing at the lowest temperatures the simulation of the low temperature spectra presents no particular problem. However for the spectra recorded in the range *ca.* 230—293 K the simulations indicate an unexpected feature in that little further change in the value of the species lifetime (τ) appears to be required. Further, a change in the value of $a_5 + a_{12}$ occurs in this temperature region (see Table 2) which is significantly greater than that observed when either Li$^+$ or Na$^+$ is the counterion in the presence of the crown ether or when K$^+$ is the counterion in the absence of the crown ether.

One possible explanation of the above observation is that the rate of cation migration increases with temperature but then reaches a maximum value. However it is difficult to find plausible reasons for such an effect and an alternative explanation of this feature may be possible. When the rate of exchange increases above that appropriate to ' slow exchange ' the sum $a_5 + a_{12}$ can be determined accurately but not the individual values of a_5 and a_{12}. Under these conditions it is the product $\tau(a_5 - a_{12})^2$ which controls the computer simulation.[10] Consequently an increase in τ can be counterbalanced by a corresponding decrease in $(a_5 - a_{12})^2$. At these higher temperatures there is quite a significant change in the value of $a_5 + a_{12}$ and the apparently constant value of τ could be a consequence of an increase in the difference between the values of a_5 and $a_{5'}$ (and between a_{12} and $a_{12'}$). Figure 2 (b) shows the log τ *vs.* $1/T$ plot for this system assuming that the values of $a_{5,12}$ and $a_{5',12'}$ remain a constant proportion of their sum. The dashed line indicates the section of the plot where deviation from linearity becomes significant. It is perhaps of interest that in order for a straight line plot to have been maintained at, for example, 263 K the required difference between $a_{5,12}$ and $a_{5',12'}$ would be *ca.* 140 μT.



(a) (b) (c)

Figure 3. A schematic representation of possible crown contact [(a) and (b)] and crown separated (c) ion pairs (C represents the crown ether and S the solvent)

The values of the various splitting constants change very little in the presence of the crown ether when Na$^+$ is the counterion and although they do vary with temperature when Li$^+$ is the counterion the trend is still much less marked than that observed when K$^+$ is the counterion. The interaction between the alkali metal counterion and the crown ether has been reported to be greatest for K$^+$,[11] and the marked temperature dependence of the hyperfine splitting constants indicates that this complex interacts strongly with the radical anion. Nakamura has identified three different types of ion pair in radical anion–crown ether–alkali metal ion systems.[12] Two of these are contact ion pairs, one of which involves a solvent molecule [Figure 3 (b)] and one of which does not [Figure 3 (a)], and a crown-separated ion pair in which the crown ether and the solvent both solvate the counterion [Figure 3 (c)]. The significant interaction between the crown ether–K$^+$ complex and the 5,12-dihydrotetracene radical anion suggests that, in the 230—293 K temperature region, a contact ion pair predominates. The decrease in the overall values of the individual splitting constants in the radical anion over this temperature region indicates an increasing unpaired electron density on the crown ether–K$^+$ complex. It is possible to explain the difference in the methylene proton splitting constants on either side of the radical anion plane in terms of a polar effect arising from the proximity of the crown ether–K$^+$ complex. Calculations on four similar radical anions (acenaphthene, pyracene, 9,10-dihydroanthracene, and 1,2-dihydrobenzocyclobutene) predict that the methylene proton(s) on the same side of the radical anion plane as the cation has the larger splitting constant.[13] It therefore seems reasonable to propose that an increasing unpaired electron density on the crown ether–K$^+$ complex, indicating a greater interaction with the radical anion, could accentuate the difference between the environment of the methylene protons on either side of the radical anion plane.

Activation Parameters.—Unfortunately, owing to the unusual features observed when K$^+$ is the counterion, it has not been possible to obtain reliable values for ΔG‡, Δ$H^‡$, and Δ$S^‡$ for this system. However a comparison of the values obtained when either Na$^+$ or Li$^+$ is the counterion in the presence of dibenzo-18-crown-6 is possible. The variation in these parameters may be explicable in terms of the changing nature of the ion pair with complexation of the counterion by the crown ether. Solvent molecules are more likely to compete with the crown ether for the 'solvation' of the counterion when Li^+ is the counterion. The resulting weaker interaction with the crown ether may explain the lower value of $\Delta H^\ddagger$ observed in the presence of this counterion ($\Delta H^\ddagger$ increases from 11.5 kJ mol^{-1} when Li^+ is the counterion to 17.3 kJ mol^{-1} when Na^+ is the counterion). The negative values of $\Delta S^\ddagger$ (−57 2 J mol^{-1} K^{-1} when Li^+ is the counterion and −39 9 J mol^{-1} K^{-1} when Na^+ is the counterion) indicate a specific arrangement of the radical anion–crown ether–counterion complex in the transition state A better understanding of these parameters may be gained from a study of a system where linewidth alternation is present for all three counterions both in the presence and in the absence of the crown ether.

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