Linewidth Alternation in the Electron Spin Resonance Spectrum of the Fluorene Radical Anion in the Presence of Dibenzo Crown Ethers

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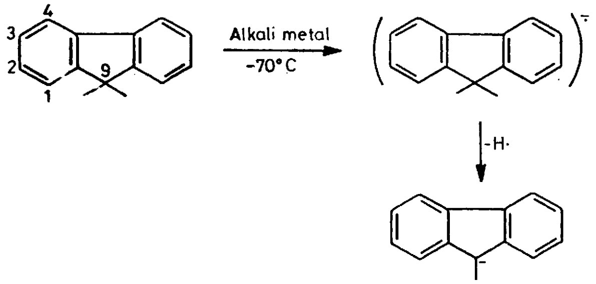
Two dibenzo crown ethers have been found to decompose slowly when in contact with alkali metals in tetrahydrofuran. Decomposition of these dibenzo crown ethers also occurs when they are brought into contact with a solution of the fluorene radical anion. The addition of the crown ethers to a solution of the radical anion has a dramatic effect upon the e.s.r. spectrum. This effect has been interpreted in terms of linewidth alternation. An intramolecular migration of the crown ether–alkali metal cation complex from one side of the radical anion plane to the other is proposed. It has been possible to examine the slow exchange region of the spectrum in the Li^+–dibenzo-18-crown-6–fluorene radical anion system. A surprising observation is that these results indicate the complexation of Li^+ by dibenzo-18-crown-6.

FLUORENE is readily reduced to the fluorenyl anion by alkali metals in ethereal solvents at room temperature. This anion has proved of great interest as it forms both contact and solvent separated ion pairs with the alkali metal counterion.[1] However at low temperatures (*ca.* −70 °C) the reduction gives a blue solution of the fluorene radical anion which decays at higher temperatures to the fluorenyl anion (Scheme).[2] The rate of decay of the fluorene radical anion to the fluorenyl anion is markedly dependent upon (i) the alkali metal counterion ($K^+ > Na^+ > Li^+$), (ii) temperature, and (iii) solvent.[2] This decay can be readily followed by studying either the changes in the visible region absorption spectrum or in the intensity of the e.s.r. spectrum of the radical anion. The results obtained employing both techniques are in precise agreement.



SCHEME

In a previous publication we reported the influence of a crown ether on the rate of the radical anion decay.[3] The purpose of the present publication is to report the influence of two crown ethers (dibenzo-14-crown-4 and dibenzo-18-crown-6) on the e.s.r. spectrum of the radical anion. In the absence of the crown ethers the e.s.r. spectrum consists of the expected pattern from five sets of two equivalent protons at all temperatures. The dibenzo crown ethers, however, have a dramatic effect upon the spectrum as a consequence of linewidth alternation associated with the two methylene protons, at the 9-position. As a preliminary to our e.s.r. investigations we investigated the possibility of the reaction between the crown ethers and the alkali metals and also between the crown ethers and the fluorene radical anion. We report the results of these investigations together with the results of our study of the influence of the dibenzo crown ethers on the e.s.r. spectrum of the fluorene radical anion.

EXPERIMENTAL

Except where otherwise stated all operations were performed using standard high vacuum techniques.

Materials.—Tetrahydrofuran was purified as described.[4] In the preliminary stages of this research it was found that commercial fluorene was contaminated with dibenzofuran and a pure sample of fluorene was therefore prepared from fluorenone as follows. Commercial fluorenone (B D.H.) was purified chromatographically on a silica gel column using light petroleum (100—120 °C) as eluant. The fluorenone was recovered from the top of the column by extraction from the silica gel with ethanol in a Soxhlet distillation. This fluorenone was then reduced with hydrazine and potassium hydroxide [5] and the resulting fluorene sublimed and then passed through a silica gel column to remove any unchanged fluorenone. After a further sublimation the purity of the fluorene was checked by mass spectroscopy and differential scanning calorimetry (d.s.c.) and was found to be >99%. The sample had a m.p. 113.5—114.8 °C.

Dibenzo-14-*crown*-4.—Two separate samples of dibenzo-14-crown-4 were used. The first was kindly supplied by Dr. H. K. Frensdorff (du Pont de Nemours and Co.). This sample was recrystallised from n-hexane before use, m.p. 145—147 °C. A second sample, prepared as described,[6] was purified by recrystallisation from methanol and then (twice) from n-hexane, m.p. 148—149 °C. The purity of this second sample was checked by d.s.c. and was found to be >97.7%.

Dibenzo-18-*crown*-6.—This crown ether, which had been prepared as described,[6a] was kindly supplied by Dr. P. Hodge of this department. It was first recrystallised from toluene and then further purified by forming the appropriate complex with sodium thiocyanate (when sodium was to be the reductant) or with potassium thiocyanate (when potassium was to be the reductant).[7] When lithium was the reductant either of these two batches was used. Both batches had m.p. 160.5—161.5 °C; their purity, checked by d.s.c., was >98.6%.

Procedure.—Tetrahydrofuran solutions of fluorene and the crown ethers were prepared as described.[2] The concentrations of these solutions were in the range 1—5 × 10^{-3}M. Sodium and potassium films were prepared as described.[4] In the case of potassium films care was taken to reduce the distillation of any sodium which may be present in the potassium as an impurity. Lithium films were prepared by the distillation of liquid NH_3 onto lithium chips. Upon dissolution the NH_3 was removed by distillation leaving behind a metal film. Solutions of the fluorene radical anion were prepared from these films as described.[2,4]

Product Analysis.—The tetrahydrofuran solution containing the reaction product was opened to air and partitioned between diethyl ether (from which alkali soluble stabilisers had been removed) and aqueous alkali. The ether layer was dried and its contents determined by u.v. absorption and mass spectroscopy. The u.v. absorption spectrum of the aqueous layer was recorded, the solution acidified, and the products extracted with diethyl ether. The ether layer was then dried and its contents determined as above. Crown ethers are sometimes soluble in aqueous alkali depending on the nature of the alkali metal cation. Care was therefore taken in each partition to select an alkali metal cation with poor solubilising properties towards the crown ether under investigation.

Spectroscopic Measurements.—All e.s.r. spectra were recorded on a Varian E3 spectrometer with 100-kHz magnetic field modulation. The magnetic field sweep was calibrated using Fremy's salt.[8] The temperature of samples was controlled by means of a Varian E4557 variable temperature unit. The temperature at which each spectrum was recorded was determined using a copper–constantan thermocouple and quoted temperatures are considered to be accurate to ± 2 K at 150 K, deteriorating to ± 3 K at 250 K. U.v.–visible absorption spectra were recorded on Unicam SP 800 spectrophotometers.

Calculations.—Computer simulations of spectra showing the alternating linewidth effect were obtained using an I.C.L. 1905F computer. The first part of the program uses the modified Bloch equations to derive the spectrum of a radical containing two protons with interchanging splitting constants and is similar to that already published.[9] The second part of the program introduces the hyperfine splitting from the remaining (non-alternating) protons and records the first derivative 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

The Reaction of Alkali Metals with Dibenzo-14-*Crown*-4 *and Dibenzo*-18-*Crown*-6.—The object of these experiments was to determine whether either of these dibenzo crown ethers reacted with alkali metals under the conditions normally used in the preparation of the fluorene radical anion. A tetrahydrofuran solution of dibenzo-14-crown-4 was allowed into contact with a potassium film at 180 K for 30 min. (This period represents a typical reaction time required in the preparation of the fluorene radical anion for the purpose of e.s.r. experiments.) The u.v. absorption spectrum of this solution remained unchanged after this period. However, in order to determine whether a reaction with the alkali metal would occur given sufficient time both the reaction time and temperature were increased. Eventually new u.v. absorptions did appear (at 257 and 306 nm, see Figure 1). Upon admitting air to the u.v. cell these absorptions slowly receded, the spectrum returning virtually to its original shape. The resulting solution was separated as described, the aqueous layer containing a substance with a molecular weight, as determined by mass spectroscopy, of 260.

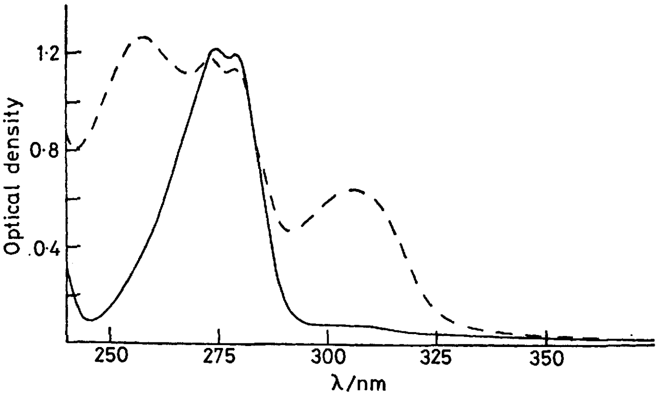
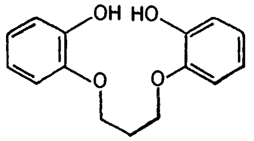


FIGURE 1 The absorption spectrum of dibenzo-14-crown-4 in tetrahydrofuran before (solid line) and after (broken line) reaction with potassium

The experiment was repeated using a sodium film. Again new u.v. absorptions (at 250 and 299 nm) eventually appeared, although more slowly than in the first experiment. Again these absorptions receded upon admitting air to the u.v. cell and again a substance with a molecular weight of 260 (determined from its mass spectrum) was obtained from the aqueous layer. Similar observations were made upon repeating the experiment using a lithium film.

On the basis of its mass spectrum the product isolated upon reaction of dibenzo-14-crown-4 with each of the alkali metals appears to be 1,3-bis-(2-hydroxyphenoxy)-propane (I). It is possible to suggest a reasonable fragmentation pathway which is in accord with the other significant peaks in the mass spectrum. The $\lambda_{max.}$ for (I) should be similar to those for the crown ether itself and this would explain why the u.v. spectrum returned almost to its original shape upon admitting air.



(I)

In order to find supporting evidence for the above proposals we selected guaiacol (2-methoxyphenol) as a suitable model compound for (I). We find the u.v. absorption spectrum of guaiacol in aqueous alkali and in alkaline tetrahydrofuran virtually identical to that of the reaction product isolated in the course of the above experiments. We therefore believe that (I) is a reasonable structure for the decomposition product.

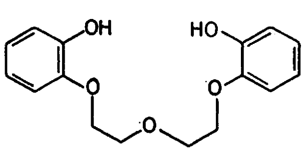
The above experiments were repeated with dibenzo-18-crown-6 and again additional absorptions appeared in the u.v. region of the spectrum upon prolonged contact with an alkali metal film. Upon admitting air to these solutions the change in these absorptions followed those observed with dibenzo-14-crown-4. It is evident that dibenzo-18-crown-6 also reacts with alkali metal films to give a 2-alkoxyphenoxide chromophore.

It would appear, therefore, that both dibenzo-14-crown-4 and dibenzo-18-crown-6 react with alkali metal films to form 2-alkoxyphenoxides. These reactions, however, are slow compared with the typical reaction times involved in the preparation of the fluorene radical anion. Despite this difference in reaction rates, however, the fluorene radical anion was prepared employing our usual procedure, filtered, and then added to a solution of the crown ether. The modified procedure was not used in the Na^+–dibenzo-14-crown-4–fluorene radical anion system. However, the extent of reaction of this crown ether with the alkali metal during the preparation of the radical anion was too small to influence the e.s.r. experiments. While the modified procedure avoids any interference from the reaction between the crown ether and the alkali metal, reaction between the fluorene radical anion and the crown ether is still possible. We have attempted to detect products from such a reaction.

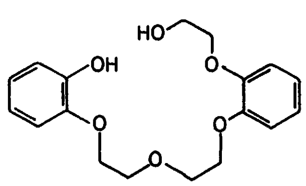
The Reaction of the Fluorene Radical Anion with Dibenzo-14-*Crown*-4 *and Dibenzo*-18-*Crown*-6.—Reaction conditions were selected which would favour reaction. A solution of the fluorene radical anion was prepared in the usual way (with lithium as the counterion), filtered, and added to a solution of dibenzo-18-crown-6. In order to encourage reaction the radical anion : crown ether ratio was set at 5 : 1 and the reaction was allowed to proceed for a period greater than that normally required to record a sequence of e.s.r. spectra. The resulting reaction mixture was then partitioned as before and the aqueous layer found to contain a reaction product with $\lambda_{max.}$ 238 and 288 nm and a molecular weight (as determined by mass spectrometry) of 290.

In order to establish the species responsible for the decomposition of the crown ether a further experiment was performed in which a solution of the fluorenyl anion, again in large excess, was added to dibenzo-18-crown-6, with Li^+ as the counterion. The solution was analysed in the usual way but no evidence could be found for any decomposition of the crown ether. It is therefore apparent that it is the radical anion and not the fluorenyl anion which attacks the crown ether. Reaction of the crown ether with the fluorenyl anion would, presumably, occur *via* proton abstraction. Since the fluorene radical anion is a weaker base than the fluorenyl anion attack by the radical anion is unlikely to be *via* proton abstraction. The most likely mechanism is the transfer of an electron from the radical anion to the crown ether. Crown ether radical anions were not observed, however, during the course of our experiments which suggests that they decompose relatively quickly.

Having gained evidence for the decomposition of the crown ether all future experiments were arranged so that the same reaction mixture was used for e.s.r. study as for the product analysis. The e.s.r. spectra were recorded on a small portion of this solution, whilst the bulk of the solution was taken through exactly the same temperature changes over exactly the same period of time. Upon completion of the e.s.r. experiments the contents of the Li^+–dibenzo-18-crown-6–fluorene radical anion solution were partitioned as before. No evidence could be obtained that the ether layer contained anything other than dibenzo-18-crown-6, fluorene, and some fluorenone (formed from the fluorenyl anion when admitting air to the solution). However a substance was obtained from the aqueous layer whose mass spectrum revealed two components with molecular weights 334 and 290. The former component was relatively unstable. Proposed structures for the two substances isolated from the aqueous layer are (II) and (III).



(II)



(III)

It is possible to suggest a fragmentation pathway of both (II) and (III) which accounts for all the remaining peaks in the mass spectrum. It was difficult to obtain an estimate of the exact amount of crown ether which had decomposed during the course of this experiment. Between 4 and 8% of the crown ether was found to have decomposed to either (II) or (III). In addition at least 80% of the crown ether was recovered from the ether layer upon completion of the experiment and this, therefore, represents the minimum amount of crown ether remaining.

When the experiment was repeated with dibenzo-14-crown-4 a green solid immediately precipitated from the mixture. It was not possible, therefore, to study the e.s.r. spectrum of the fluorene radical anion in the presence of this crown ether when Li^+ was the counterion. However, when Na^+ was the counterion this problem was not encountered and upon completion of the e.s.r. experiments the solution was again partitioned and analysed as described. Only one substance, (I), was isolated from the aqueous layer and the amount of (I) isolated corresponded to 1% of the crown ether present at the start of the experiment.

The Influence of Dibenzo Crown Ethers on the E.S.R. Spectrum of the Fluorene Radical Anion.—There is no evidence that the crown ether decomposition products described above had any influence on the e.s.r. spectrum of the radical anion. The spectrum at any given temperature was found to be independent of the previous temperature history of the sample and furthermore was also independent of the degree to which the radical anion decay reaction had proceeded.

It was not possible to record e.s.r. spectra of either of the K^+–dibenzo crown–fluorene radical anion mixtures due to the high rate of radical anion decay with this counterion. Further, when Li$^+$ was the counterion the fluorene radical anion–dibenzo-14-crown-4 mixture immediately precipitated. Consequently it was only possible to obtain a sequence of e.s.r. spectra over a temperature range for three systems: Na$^+$–dibenzo-14-crown-4–fluorene radical anion, Li$^+$–dibenzo-18-crown-6–fluorene radical anion, and Na$^+$–dibenzo-18-crown-6–fluorene radical anion. For each of these three systems spectra were recorded at 10° intervals from 183 K (the lowest temperature at which well resolved spectra could be obtained) to the highest temperature at which a reasonable concentration of the radical anion could be maintained.

To varying degrees the spectra of each of the three systems studied show the same trend. In none of these systems was a spectrum observed which was identical to that of the fluorene radical anion in the absence of a crown ether, although the similarity was closest at the highest temperature. However even at the highest temperature the amplitude of the central line was always reduced in the presence of the crown ether [see Figure 2(b)]. On cooling, the relative amplitude of this line diminished so that the spectrum was dominated by an apparent doublet [see Figure 2(c)]. On cooling further two new lines, close to and equidistant from the centre of the spectrum, appeared until eventually the spectrum was dominated by a doublet of doublets [see Figure 2(d)]. (In fact this last stage was only reached in the Li$^+$–dibenzo-18-crown-6–fluorene radical anion system.) An examination of these spectra reveals that only one of the five triplets is affected in this way, the ' pure ' lines of the remaining four triplets retain their correct 1 : 2 : 1 intensities. It is the splitting constant associated with the methylene protons which is responsible for the observed changes and these protons are not, therefore, equivalent in the presence of the dibenzo crown ethers. It is apparent that an alternating linewidth effect is present.

We have attempted a computer simulation of each spectrum assuming that it is the methylene protons whose splitting constants undergo out-of-phase modulation. The lineshape arising from these protons was computed employing the modified Bloch equations appropriate to a two jump model in which the interconverting species have equal lifetimes and spin–spin relaxation times.[9] The four remaining 1 : 2 : 1 triplet splittings were then introduced into the computation to give the simulation of the complete spectrum.

Slow exchange spectra were only obtained in one of the three systems studied. It was only possible to determine the individual values of the splitting constants (a_9 and $a_{9'}$) associated with the methylene protons for this system. In the other two systems only the sum, $a_9 + a_{9'}$, is known with any certainty. The value of τ (the mean lifetime of the species) required to obtain the simulation depends upon the individual values of these two splitting constants, and consequently it is not possible to determine the true value of τ in these two systems. Under these conditions it is the product $\tau(a_9 - a_{9'})^2$ which controls the simulation.[10] For example, exactly the same computer simuated spectrum is obtained when the methylene proton splitting constants and τ are varied but with the product remaining constant at 460×10^{-6} μT^2 s.

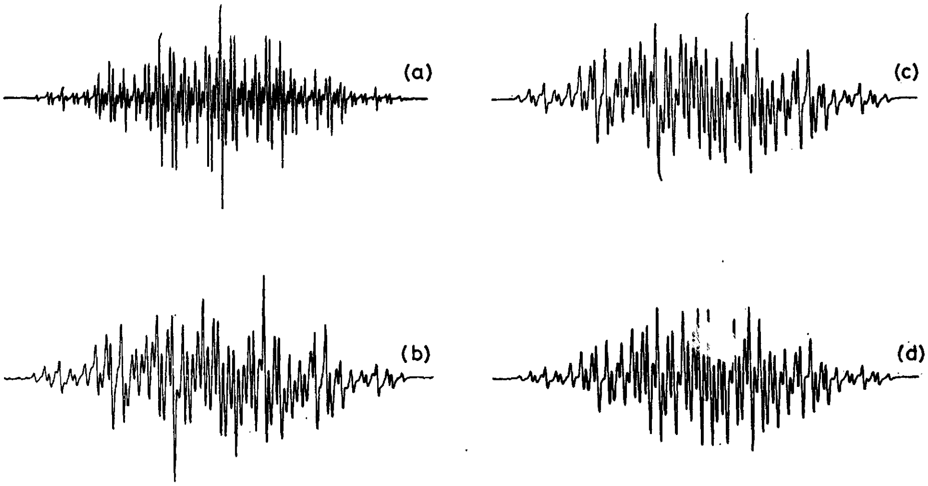


FIGURE 2 The experimental e.s.r. spectra of the fluorene radical anion in tetrahydrofuran (a) at 193 K in the absence of crown ether (Li$^+$ as the counterion) and in the presence of dibenzo-18-crown-6 at (b) 224 K, (c) 202 K, and (d) 183 K (Li$^+$ as the counterion)

For each system, at each temperature, very many computer simulations were attempted to obtain the best possible fit to the experimental spectrum. Of these various simulations two have been selected for illustration in Figure 3. We believe that the simulations have been optimised as far as is possible, and while any further modification of any of the eight parameters used in the simulation might result in an improvement of a particular feature, it does so at the expense of some other feature. The parameters used in obtaining the best possible simulation at each temperature for each system are summarised in Tables 1—3.

The effect of τ on the lineshape arising from the interaction of the unpaired electron with the methylene protons

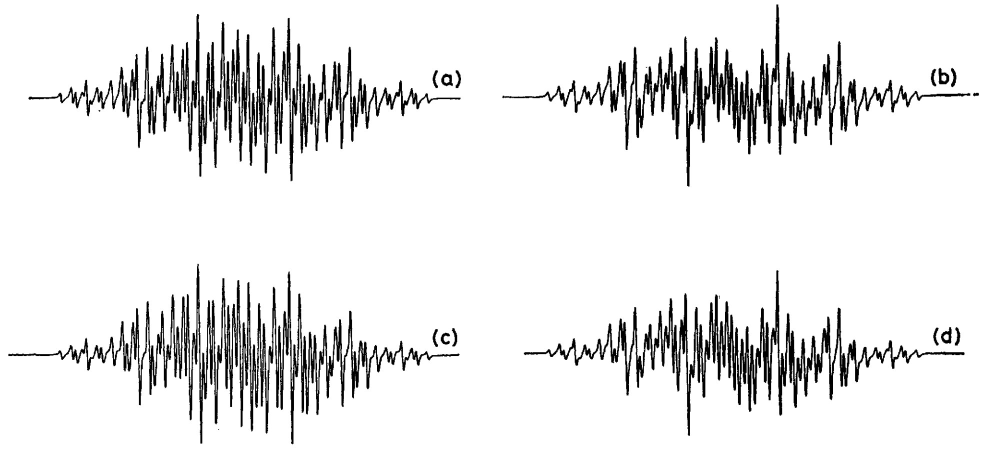


FIGURE 3 The experimental e.s.r. spectra of the Li$^+$–dibenzo-18-crown-6–fluorene radical anion system at (a) 214 K and (b) 193 K together with their computer simulations (c) and (d) respectively (parameters as given in Table 3)

is obscured by the overlapping of the many other lines arising from the ring protons. However it is possible to deconvolute the computer simulation and so examine the variation in this lineshape in the absence of the ring protons. The resulting computer deconvolutions for the system where slow exchange spectra are available (Li$^+$–dibenzo-18-crown-6) are illustrated in Figure 4. This series of deconvoluted simulations clearly shows the influence of temperature, and hence τ, on the lineshape of the lines originating from the methylene protons and at the lowest temperatures clearly reveals the doublet of doublets from which the values of a_9 and $a_{9'}$ are readily abstracted.

The essential feature common to all three systems reported in Tables 1—3 is that the two methylene protons interchange their splitting constants at a temperature dependent rate, while the remaining four pairs of ring protons retain their equivalence. This implies that the

TABLE 1

Parameters used in the computer simulation of the e.s.r. spectra of the Na$^+$–dibenzo-18-crown-6–fluorene radical anion system (splitting constants are in μT)

T/K	183	193	202	214	223	220[a]
$a_{1,8}$	124	123	120	120	120	118
$a_{2,7}$	504	499	499	499	499	494
$a_{3,6}$	86	86	88	88	88	90
$a_{4,5}$	416	416	413	413	413	410
$a_9 + a_{9'}$	735	735	735	735	735	750[b]
$\tau(a_9 - a_{9'})^2/\mu T^2$ s	1.38×10^{-3}	1.03×10^{-3}	8.27×10^{-4}	6.20×10^{-4}	6.20×10^{-4}	

[a] Na$^+$–Fluorene radical anion in tetrahydrofuran in the absence of crown ether. [b] $a_9 = a_{9'}$ in the absence of crown ether.

TABLE 2

Parameters used in the computer simulation of the e.s.r. spectra of the Na$^+$–dibenzo-14-crown-4–fluorene radical anion system (splitting constants are in μT)

T/K	183	202	214	234	253	220[a]
$a_{1,8}$	118	118	118	118	118	118
$a_{2,7}$	504	504	504	504	504	494
$a_{3,6}$	86	86	86	86	86	90
$a_{4,5}$	413	410	410	410	410	410
$a_9 + a_{9'}$	761	761	761	761	756	750[b]
$\tau(a_9 - a_{9'})^2/\mu T^2$ s	1.31×10^{-3}	1.02×10^{-3}	8.47×10^{-4}	4.59×10^{-4}	2.38×10^{-4}	

[a] Na$^+$–Fluorene radical anion in tetrahydrofuran in the absence of crown ether. [b] $a_9 = a_{9'}$ in the absence of crown ether.

TABLE 3

Parameters used in the computer simulation of the e.s.r. spectra of the Li$^+$–dibenzo-18-crown-6–fluorene radical anion system (splitting constants are in μT)

T/K	183	193	202	214	224	234	220[a]
$a_{1,8}$	121	121	121	119	119	119	118
$a_{2,7}$	496	496	496	499	499	499	494
$a_{3,6}$	90	90	90	90	90	90	90
$a_{4,5}$	416	415	415	412	412	412	410
a_9	421	421	421	422	422	422	375
$a_{9'}$	326	326	326	327	327	327	375
τ/s	5.5×10^{-7}	3.5×10^{-7}	2.1×10^{-7}	1.21×10^{-7}	7.7×10^{-8}	4.4×10^{-8}	

[a] Li$^+$–Fluorene radical anion in tetrahydrofuran in the absence of crown ether.

fluorene radical anion is involved in dynamic equilibrium between two equivalent states such that in each state the environment above and below the radical anion plane differs. Further, it can be seen from Tables 1—3, that the unpaired electron density is the same in the two six-membered rings in each state (or, any asymmetry is rapidly averaged). Since the two methylene protons are completely equivalent in the absence of the crown ether, the crown ether must be responsible for producing the different environments. It is possible that this difference results from a direct interaction between the radical anion and the crown ether (*i.e.* the alkali-metal counterion is not involved in the resulting complex). However if this were the case then the same e.s.r. spectra would be obtained at the same temperature with a particular crown ether irrespective of the nature of the counterion. In addition the decay of the radical anion to the fluorenyl anion, which is strongly dependent on the counterion in the absence of the crown ether, would become independent of the nature of the counterion in the presence of the crown ether. Neither of these two features are, however, observed. The experimental evidence therefore points to the involvement of the counterion in the resulting complex. It therefore appears that the crown ether–alkali metal counterion complex migrates from one side of the radical anion plane to the other. The difference in the methylene proton splitting constant on either side of the radical anion plane is then explicable in terms of a polar effect arising from the proximity of the alkali metal counterion–crown ether complex. If a point positive charge were positioned above the five-membered ring close to the methylene protons the delocalisation of the unpaired electron onto these protons would be accentuated by an inductive effect. Reddoch has performed calculations for four radical anions containing methylene groups (acenaphthene, pyracene, 9,10-dihydroanthracene, and benzocyclobutane) and has predicted that the methylene proton on the same side of the plane as the cation has the larger splitting constant.[11]

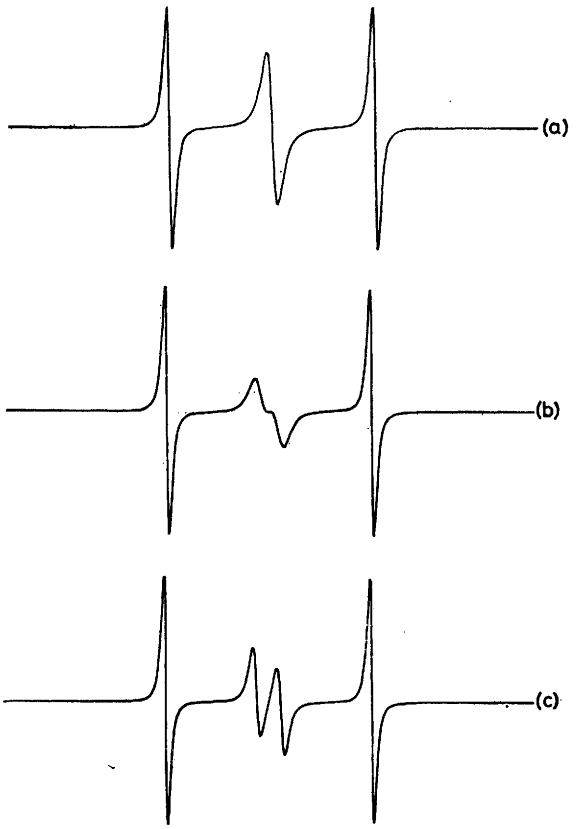


FIGURE 4 Deconvoluted computer simulations of the e.s.r. spectra of the Li$^+$–dibenzo-18-crown-6–fluorene radical anion system at (a) 224 K, (b) 202 K, and (c) 183 K

A second, but less likely, model which would produce different methylene proton splitting constants is the presence of two geometric conformers. If the presence of the complexed crown ether on one side of the plane were to distort the central ring out of the plane the splitting constant of the proton moving further out of the plane would increase whilst the other splitting constant would decrease. The distortion necessary to produce different splitting constants can be calculated from equation (1) [12] for the Li$^+$–dibenzo-18-crown-6 system where the individual values of a_9 and $a_{9'}$ have been determined. This calculation reveals that a distortion of 7° would be required to explain the observed methylene splitting constants on this model. An interpretation based upon a polar effect appears to be more acceptable.

$$a_{(\beta\text{-H})} = \rho(B_0 + B\cos^2\theta) \qquad (1)$$

Both these models require the alkali metal ion–crown ether complex to move from one side of the fluorene radical anion plane to the other. This movement could occur by either an intramolecular or an intermolecular process. A number of intermolecular processes can be proposed. For example, two radical anion complexes could interchange their complexed crown ether molecules *via* a bimolecular process: $\mathrm{Na^+CE(Fl)^{\cdot-} + Na^{+}{*}CE{*}\text{-}(Fl{*})^{\cdot-} \rightleftharpoons Na^+CE(Fl{*})^{\cdot-} + Na^{+}{*}CE{*}(Fl)^{\cdot-}}$.

If the methylene proton splitting constants are to interchange, the incoming crown ether complex must arrive on the opposite side of the radical anion plane to that occupied by the original crown ether complex. Other similar exchange processes are also possible. For example an exchange involving a fluorene radical anion and a fluorenyl anion. A further possibility could be an exchange involving an uncomplexed crown ether molecule on one hand and the radical anion–crown ether complex on the other. However the rate of all bimolecular processes of this type must depend, to some degree, upon the radical anion concentration. The experimental evidence points against this possibility as in each of the three systems studied the experimental spectra, at a particular temperature, are independent of the extent of the radical anion decay. It is also possible that the solution contains a mixture of complexed and uncomplexed radical anion pairs. A number of equilibria are possible under these circumstances which would lead to e.s.r. spectra which would be indistinguishable, in the fast exchange region, from those computed as arising from a two-jump intramolecular process. However, fortunately, slow exchange spectra are obtained in the Li^+–dibenzo-18-crown-6–fluorene radical anion system. In these spectra a contribution arising from uncomplexed radical anions would be clearly evident in a comparison between the computed and experimental spectra. There is no evidence of any uncomplexed radical anions.

We believe that the simplest and most likely mechanism is an intramolecular rearrangement of the ion pair complex. Migrations of this type have been proposed to explain the e.s.r. spectra of a number of radical anions including those of pyracene,[13] 9,10-dihydroanthracene,[14] tetra-t-butylnaphthalene,[15] benzocyclobutane,[16] acenaphthene,[17] and 5,12-dihydrotetracene.[18] If the migration is intramolecular then the first-order velocity constant is the reciprocal of the ion pair lifetime. This gives a value of k 8×10^6 s^{-1} for Li^+–dibenzo-18-crown-6–fluorene radical anion at 214 K (see Table 3). This value is comparable with those observed for the migration of the potassium cation around the radical anions of the pyracene,[19] 5,12-dihydrotetracene,[18] and benzocyclobutane [16] (10^6—10^7 s^{-1}) under similar conditions of temperature and solvent.

For the Li^+–dibenzo-18-crown-6 system, where slow exchange spectra are observed, the values of a_9 and a_9' and hence τ are known with reasonable accuracy. The resulting log k *versus* $1/T$ plot for this system is shown in Figure 5 and gives an activation energy, for this migration process of 17.6 kJ mol^{-1} and an entropy of activation of -35 J mol^{-1} K^{-1}. However, in the other two systems studied the values of τ are not known and consequently the activation energy cannot be determined using this approach. Under these circumstances it is possible to determine the activation energy from the fast exchange region spectra from the relative amplitude of the broadened central line to one of the outer lines of the appropriate triplet.[20] This approach is not particularly straightforward in the case of the fluorene radical anion spectrum due to the large degree of overlapping which occurs. It is apparent from a close inspection of the spectra (with data obtained from the computer simulations) that a minor, unbroadened, absorption occurs at the centre of the spectrum. As a consequence of this interference it is difficult to obtain the true height of the broadened line particularly when its overall intensity is relatively small. However we have attempted to obtain an estimate of the activation energy for the migration process from these data and find that, for both of these systems, it lies in the range 8—12 kJ mol^{-1}.

The negative value of $\Delta S^‡$ in the Li^+–dibenzo-18-crown-6–fluorene radical anion system is interesting. This value could arise from two separate considerations. First, it is quite possible that the transition state for this migration involves a rather specific arrangement of the crown solvated cation–radical anion ion pair. It is also possible that the solvation of the transition state by tetrahydrofuran molecules increases relative to that of the initial state. It has been proposed in two other similar intramolecular migrations that solvation increases as the migration proceeds.[10,21] In one case the solvation of the cation was proposed to have increased while in the other case it was the solvation of the anion. It is unfortunate that it has not been possible to obtain values of $\Delta S^‡$ for the two fluorene radical anion systems where Na^+ was the counterion as a comparison of these values could well have helped to distinguish between the various possibilities.

It appears that these experiments support the observation that crown ethers can 'freeze out' the intramolecular migration of cations in ion pairs.[22,23] The most dramatic influence is observed in the Li^+–dibenzo-18-crown-6–fluorene radical anion system. This observation is particularly surprising as complexation of Li^+ by dibenzo-18-crown-6 is unexpected. It is accepted that the alkali metal ions are held within the cavity of the crown ether molecule by an ion–dipole interaction between the ion and the oxygen atoms within the central crown ether ring. This interaction should be greatest when the size of the ion is matched to that of the crown ether cavity. Thus Li^+ is considered to be the appropriate size to match the cavity in dibenzo-14-crown-4 and Na^+ (and K^+) the appropriate size to match the cavity in dibenzo-18-crown-6. On the other hand the crown ether–ion interaction might be expected to be weak in the Li^+–dibenzo-18-crown-6 complex because the Li^+ is too small to match the crown ether cavity. In fact the degree of interaction in this type of situation appears rather variable. There is some evidence that the interaction can be very weak in some instances [22,24] yet reasonably strong in others.[6a,25] However we would conclude that our experiments involving the fluorene radical anion indicate a significant, if unexpected, interaction between dibenzo-18-crown-6 and the lithium cation.

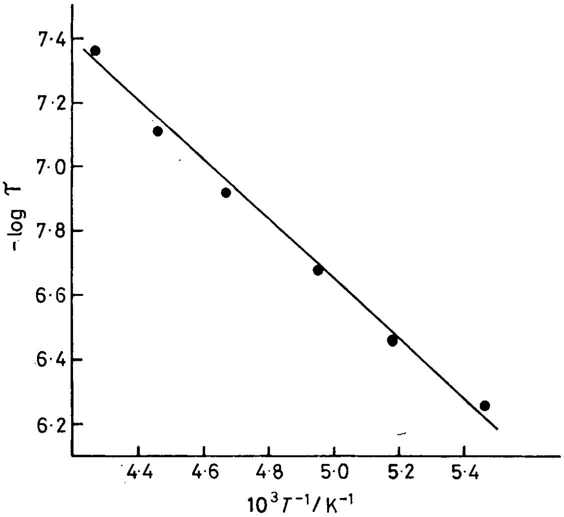


FIGURE 5 The Arrhenius plot for the Li^+–dibenzo-18-crown-6–fluorene radical anion system

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