

## An Electron Spin Resonance Study of the Fluorene Radical Anion in the Presence of 18-Crown-6 and Dicyclohexyl-18-crown-6

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The e.s.r. spectrum of the fluorene radical anion has been studied in tetrahydrofuran solution in the presence of dicyclohexyl-18-crown-6 and 18-crown-6. Two superimposed spectra of the radical anion (with slightly different splitting constants) were noticeable at low temperature, particularly in the Li<sup>+</sup>-dicyclohexyl-18-crown-6 system. Two other effects were also observed in the low temperature spectra but to differing extents in the various systems. One of these effects may be a consequence of linewidth alternation. These results reveal the presence of a complex set of equilibria involving a variety of radical anion 'species' and also indicate complexation of Li<sup>+</sup> by 18-crown-6 type polyethers.

The complexing of alkali-metal ions by crown ethers has aroused considerable interest and has been widely studied.<sup>1,2</sup> In comparison, however, the influence of crown ethers on radical anions and their reactions appears to have attracted less attention. In a previous publication, we reported that crown ethers can influence not only the rate but also the order of the decay of the fluorene radical anion.<sup>3</sup>

Recently Eastman *et al.*<sup>4</sup> presented evidence that crown ethers can profoundly influence the rate of cation migration in the durosemiquinone radical anion and these observations have been confirmed by Konishi *et al.*<sup>5</sup> Two further examples of this influence, involving the fluorene<sup>6</sup> and 5,12-dihydro-tetracene<sup>7</sup> radical anions, have been observed in these laboratories. In both cases linewidth alternation can be observed in the e.s.r. spectrum of the radical anion upon addition of a crown ether.

In a previous publication we reported the influence of two dibenzocrown ethers on the e.s.r. spectrum of the fluorene radical anion.<sup>6</sup> As a preliminary to this work the reaction of these dibenzocrown ethers with alkali-metals and with the fluorene radical anion was also investigated. The extent of these reactions was found to be relatively insignificant under the conditions normally required to record the e.s.r. spectra. In addition we found that there was no evidence to suggest that the products of these reactions influenced the e.s.r. spectra.

We have now extended our investigations to include two non-benzenoid crown ethers (dicyclohexyl-18-crown-6 and 18-crown-6). Again we have briefly examined the reactions of the crown ethers with lithium, sodium, and potassium films as a preliminary to our study of their influence 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 and fluorene were purified as described.<sup>6,8</sup>

**Dicyclohexyl-18-crown-6.** This crown ether (Aldrich) was obtained as an oily, impure mixture of two isomers (*cis-syn-cis* and *cis-anti-cis*) from which a crystalline solid, m.p. 46–51.5 °C, and a yellow wax were isolated using a published procedure.<sup>9</sup> The solid was found to be a mixture of isomers but was used for these experiments without further purification.

**18-Crown-6.** This crown ether (Lancaster Synthesis) was recrystallised from light petroleum (b.p. 40–60 °C) and then purified *via* its acetonitrile complex.<sup>10</sup> The resulting product had m.p. 38.5–40.5 °C.

**Procedure.**—Tetrahydrofuran solutions of fluorene and crown ether were prepared as described.<sup>11</sup> The concentrations of these solutions were in the range 1–5 × 10<sup>-3</sup>M. Sodium and potassium films were prepared as described.<sup>8</sup> In the case of potassium films care was taken to reduce distillation of any sodium which may be present in the potassium as an impurity. Lithium films were prepared by the distillation of liquid ammonia onto lithium chips. Upon lithium dissolution the ammonia was removed by distillation leaving behind a lithium film. Solutions of the fluorene radical anion were prepared from these films using our 'unmodified' procedure.<sup>6</sup>

**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.<sup>12</sup> The temperature of the samples was controlled by means of a Varian E4457 variable temperature unit and the temperature at which each spectrum was recorded was determined using a copper-constantan thermocouple. 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.

**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 ICL 1905F computer. The first part of the program uses the modified Bloch equations appropriate to a two-jump model in which the interconverting species have equal lifetimes and spin-spin relaxation times, and is similar to that already published.<sup>13</sup> The resulting line-shape 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

**The Reaction of Alkali-metals with Dicyclohexyl-18-crown-6.**—The reaction between alkali-metals and dicyclohexyl-18-crown-6 has been studied previously.<sup>2</sup> Most of these previous

Hyperfine splitting constants (in  $\mu\text{T}$ ), obtained by computer simulation of the experimental e.s.r. spectra, for the fluorene radical anion in tetrahydrofuran in the presence of various alkali-metal counterions and crown ethers

	$T/\text{K}$	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	$a_9$
Li <sup>+</sup> -Dicyclohexyl-18-crown-6	233	122	505	90	414	385
primary species	183	122	507	90	414	385
secondary species	183	114	512	90	420	401
Na <sup>+</sup> -Dicyclohexyl-18-crown-6	233	121	503	88	409	377
	183	123	504	88	412	378
Li <sup>+</sup> -18-Crown-6	233	120	503	88	411	377
	183	120	508	88	415	386
Na <sup>+</sup> or Li <sup>+</sup> (no crown ether) <sup>a</sup>	220	118	494	90	410	375

<sup>a</sup> Taken from ref. 6.

studies have been carefully designed with the object of obtaining absorption spectra of the alkali-metal anions and of solvated electrons.<sup>2,14</sup> The e.s.r. spectrum of the latter has also been observed.<sup>2</sup> We were concerned that any such reactions should not prove a hindrance to our experiments involving the fluorene radical anion. We therefore repeated these experiments in a Pyrex apparatus typical of those used in the preparation of radical anions for e.s.r. study.

When a tetrahydrofuran solution of dicyclohexyl-18-crown-6 was brought into contact with a potassium film at room temperature a blue colour immediately developed. The visible-near i.r. spectrum of the blue solution showed a broad absorption at 910 nm but this feature was eventually replaced by a broad absorption at 750 nm at room temperature. No colouration was observed when the experiment was repeated with sodium or lithium films.

The absorption maximum for K<sup>-</sup> has been reported to be *ca.* 890 nm in tetrahydrofuran at 298 K in the presence of the crown ether.<sup>2</sup> In contrast Na<sup>-</sup> has an absorption maximum at *ca.* 740 nm at 298 K.<sup>2</sup> The species peaking at 750 nm in our experiments, therefore, appears to be Na<sup>-</sup>. In retrospect this is not too surprising as there is ample evidence to show that sodium can be leached out of Pyrex glass under the conditions of these experiments.<sup>15</sup> The spectrum of the K<sup>-</sup> ion is only obtained free from interference from the Na<sup>-</sup> ion if an all silica apparatus is used.<sup>2</sup> What is surprising, however, is that the blue colour was not observed when the experiment was repeated employing a sodium film. This implies that it is somewhat easier to form the sodium anion in the presence of an excess of potassium.

The e.s.r. spectrum of the blue solution formed in the presence of the crown ether employing a potassium film consisted of two signals. The major spectrum was a singlet ( $g$   $2.0024 \pm 0.0004$  at 235 K,  $\Delta B_{pp}$   $5.3 \pm 0.5 \mu\text{T}$ ). This spectrum decayed irreversibly when the solution was warmed to room temperature and can be assigned to solvated electrons.<sup>2</sup> The second, rather weak spectrum was a multiplet [ $a(6\text{H})$   $370 \pm 10 \mu\text{T}$ ] and has been assigned to the benzene radical anion present as a trace impurity.<sup>16,17</sup>

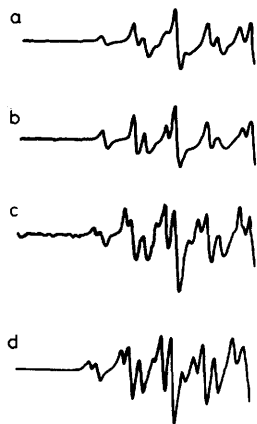
Neither e.s.r. spectrum described above were observed under any conditions when the solutions also contained the fluorene radical anion. However, in our experiments with two dibenzocrown ethers decomposition of the crown ether when in contact with the alkali metal was observed.<sup>6</sup> Upon completion of the e.s.r. measurements on the Na<sup>+</sup>-dicyclohexyl-18-crown-6-fluorene radical anion system the resulting solutions were analysed as described<sup>6</sup> to determine if decomposition of the crown ether had occurred. No evidence could be found for the decomposition of this crown ether. In a previous publication we proposed that the attack of the fluorene

radical anion on the dibenzocrown ethers occurred *via* an electron transfer reaction to the aromatic ring of the crown ether.<sup>6</sup> This mechanism would not be possible for dicyclohexyl-18-crown-6.

*E.s.r. Spectra.*—E.s.r. spectra were recorded for the following systems: Li<sup>+</sup>-18-crown-6-, Li<sup>+</sup>-dicyclohexyl-18-crown-6-, and Na<sup>+</sup>-dicyclohexyl-18-crown-6-fluorene radical anion. For each of these systems spectra were recorded at 10° intervals from the highest temperature at which a steady radical anion concentration could be maintained to the lowest temperature at which well resolved spectra could be recorded (usually *ca.* 173 K). In none of these systems was there evidence for decomposition of the crown ether and none of the reactions noted in the absence of the fluorene radical anion were observed in its presence.

The e.s.r. spectra obtained for each of the three systems were similar in several respects. For example, at temperatures above *ca.* 213 K all three systems gave spectra which were identical with those obtained in the absence of the crown ether (apart from minor differences in the values of individual splitting constants, see Table). All lines in a particular spectrum therefore retain relative intensities consistent with a single spectral linewidth. However at temperatures below *ca.* 213 K several changes were observed in the spectra although to varying degrees in each of the three systems studied. First, a set of hyperfine lines from a second species were observed in the wings of the spectrum. Secondly, an asymmetry in the intensity of corresponding high and low field lines was observed. Thirdly, the relative intensity of the central line in the spectrum decreased, possibly as a result of a linewidth alternation. These observations contrast with the results obtained in the presence of the dibenzocrown ethers where linewidth alternation was observed for each of the three systems studied, even at the highest temperatures at which spectra could be recorded.<sup>6</sup>

The first of these features, the additional hyperfine lines from a second species, was especially noticeable in the Li<sup>+</sup>-dicyclohexyl-18-crown-6-fluorene radical anion system. This feature, observed in spectra recorded below 193 K, is particularly noticeable in the 'wings' of the spectrum but can also be observed, usually as minor shoulders, elsewhere. A series of spectra showing the growth of this feature with decrease in temperature is featured in the Figure. The Figure features the low field wing of the spectrum (originating from the two smallest triplet splitting constants) for the Li<sup>+</sup>-dicyclohexyl-18-crown-6-fluorene radical anion system. Figure a, recorded at 263 K, shows the anticipated triplet of triplets. However in Figures b and c the growth of the additional lines into this hyperfine pattern is clearly seen. A computer simulation,



The low field wing of the experimental e.s.r. spectrum of the  $\text{Li}^+$ –dicyclohexyl-18-crown-6–fluorene radical anion system in tetrahydrofuran at 263 a, 214 b, and 183 K c, together with a computer simulation d (based on the splitting constants given in the Table) of the experimental spectrum at 183 K

Figure d, reveals that the new pattern is also a triplet of triplets with splitting constants similar to the original pattern but offset to low field. These features are mirrored in the high field wing of the spectrum. Since the new spectrum is present only as a secondary feature a detailed identification of its complete hyperfine pattern is difficult. However it is apparent that this secondary species can again be assigned to the fluorene radical anion but with a different set of splitting constants to those associated with the major spectrum (see Table).

It therefore appears that more than one fluorene radical anion species is present, the secondary species increasing in importance with decreasing temperature. This secondary species is only observed in the presence of the non-benzenoid crown ethers and is most noticeable when  $\text{Li}^+$  is the counterion in the presence of dicyclohexyl-18-crown-6. It is possible to assign this secondary spectrum to several different species. For example, it could arise from an unassociated radical anion. If the unassociated radical anion was present, but the appropriate equilibrium was not time averaged, then it could be observed as a discrete spectrum. Alternatively, both the primary and secondary spectra could arise from different types of ion pair. Nakamura has investigated this possibility in the fluorenone radical anion with  $\text{K}^+$  and  $\text{Na}^+$  as the counterion in the presence of 18-crown-6.<sup>18</sup> He concluded that two different crown contact ion pairs, one of which involved a solvent molecule and one of which did not, and a crown separated ion pair (in which the crown ether and a solvent molecule both solvate the counterion) were present. Presumably each of these different types of ion pair could give rise to different splitting constants and could contribute separately to the observed spectrum if they are not time averaged. However there are further possibilities with dicyclohexyl-18-crown-6 where two isomers are present in the sample of crown ether used. In the case of the *cis-syn-cis* isomer two arrangements of the cation–crown ether complex are possible with the alicyclic crown ether substituents pointing either away from or towards the radical anion. It is possible that each of the three consequent crown ether–cation complexes may have different associating characteristics towards the fluorene radical anion.

The second feature, revealed by a careful examination of the low temperature spectra, is an asymmetry in the intensity of the hyperfine pattern. Lines in the high field half of the

spectrum have a greater intensity than their low field counterparts. This effect is most noticeable when  $\text{Na}^+$  is the counterion in the presence of dicyclohexyl-18-crown-6. The secondary species observed at low temperature when  $\text{Li}^+$  is the counterion in the presence of dicyclohexyl-18-crown-6 is not, apparently, responsible for this effect. These spectra are not particularly asymmetric and it would appear that the primary and secondary species have essentially the same  $g$  value. It appears, therefore, that the asymmetry in the low temperature spectra might arise from an ion pair equilibrium but that the secondary species is a separate feature. Alternatively it is possible that the asymmetry results from slow molecular tumbling which might seem plausible in view of the large size of the radical anion–crown ether, counterion system. However this effect is not observed in the presence of the dibenzocrown ethers where the corresponding system must have a similar size. The complex nature of these spectra prevents a more exhaustive examination of this feature.

The third feature is a diminution in the intensity of the central line compared with other key lines in the spectrum. This feature is not apparent at higher temperatures. It is possible that an ion pair equilibrium between two species having different  $g$  values (and, perhaps, slightly different splitting constants) is responsible for this effect. The lifetime of the species involved in the equilibrium would have to be greater than that required to give 'fast exchange' conditions but still small enough to give a single spectrum. However linewidth alternation could also be responsible for this effect and could be occurring in any of the species present.

In order to test the suggestion that linewidth alternation could provide an explanation of this feature we attempted a computer simulation of the spectrum due to the primary species assuming that it is the methylene protons whose splitting constants undergo out-of-phase modulation. In none of the three systems is the 'slow' exchange region approached and hence it has not been possible to determine the individual values of  $a_o$  and  $a_s$  required for the simulation. Consequently, for the purpose of the computer simulations, the value of  $a_o + a_s$  was proportioned between  $a_o$  and  $a_s$  in the ratio 1 : 1.3. This value for the ratio was selected as it is that found for the  $\text{Li}^+$ –dibenzo-18-crown-6–fluorene radical anion,<sup>6</sup> and also for a similar cation migration process in the  $\text{Na}^+$ –dibenzo-18-crown-6-5,12-dihydrotriacene radical anion system.<sup>7</sup> An error in this ratio would influence the absolute but not the relative values of  $\tau$ . Simulations of the various spectra can be found using this procedure which agree reasonably well with the relative line intensities of the principal species. Unfortunately the matching of the simulated and experimental spectra is complicated by interference from the features described above.

Because of the complicated nature of these spectra in the low temperature region, and of the possibility of alternative explanations for the diminution in the relative intensity of the central line, we have not attempted to obtain a value for the activation energy for the cation migration. However, it is possible to conclude that if linewidth alternation, due to cation migration, is present in these systems then the velocity constant for this process, at a particular temperature, is considerably greater in the presence of these non-benzenoid crown ethers than in the presence of the benzenoid crown ethers studied previously.

We conclude from these results that 18-crown-6 and dicyclohexyl-18-crown ether are associated with the fluorene radical anion and the alkali-metal counterion producing (at least) a three-membered entity. On reaching a similar conclusion for dibenzo-18-crown-6 we discounted the possibility that a purely anion–molecule interaction between the radical anion and the crown ether was binding the crown ether to the ion

pair.<sup>6</sup> We argued that the dependence of the e.s.r. spectrum and of the kinetics of the radical anion decay upon the nature of the alkali-metal counterion made such an explanation unlikely. We now have further evidence that the crown molecule binds to the ion pair when the aromatic substituents (the most likely origin of an anion-molecule interaction) are saturated or removed. Thus we postulated complexation of the lithium counterion by 18-crown-6 type crown ethers through an ion-dipole interaction.

A recent review of the already numerous examples of cation-crown ether interactions<sup>1a</sup> concluded that all crown ethers with a ring larger than 14-crown-4 reject lithium under most conditions. Certainly, from the criterion of size compatibility, 18-crown-6 crown ethers would not be expected to complex the relatively small Li<sup>+</sup> cation strongly. But, as these reviewers and others<sup>19</sup> have indicated factors such as the flexibility of the crown ether, and the stabilisation of the cation resulting from the replacement of a solvation shell by a crown ether macrocycle, also influence complexation. For example, the complexation of lithium iodide by 18-crown-6 in acetonitrile has been reported.<sup>20</sup> We do not suggest that our results indicate the normal selectivity sequence for these crown ethers (*i.e.* K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup>) has been reversed, but that they provide additional examples of significant complexation constants for Li<sup>+</sup>. (For Li<sup>+</sup>-dibenzo-18-crown-6-fluorene radical anion at 180 K we estimate  $K_{eq} \geq 10^4$  l mol<sup>-1</sup>). The structure of the Li<sup>+</sup>-crown ether complex in tetrahydrofuran is unclear and remains an interesting question.

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