

## Electron Spin Resonance Studies on the Interactions between Radical Ion Pairs and Macrocyclic Polyethers. Part 2.<sup>1</sup> Intramolecular Cation Exchange in Metal Ketyl Ion Pairs

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The effect of complexation by the polyether dibenzo-18-crown-6 of radical ion pairs from dicarbonyl derivatives has been studied by electron resonance spectroscopy. In the case of the potassium and lithium salts only small variations have been observed both in the hyperfine splitting constants and in the rate of intramolecular migration of the counterion from one carbonyl group to the other. Drastic changes, mainly in the migration rate, were however observed for the sodium salts. From a complete lineshape analysis of the e.s.r. spectra at several temperatures, the effect of complexation on the activation parameters for the intramolecular exchange was determined. In the light of these results we postulate, for the crown complexes of carbonyl derivatives, a structure more realistic than that proposed in our previous paper.

We have described previously<sup>1</sup> an e.s.r. investigation of the complexation by a macrocyclic polyether (dibenzo-18-crown-6) of a series of radical ion pairs from thiazole and thiophen derivatives. Although complexation was

<sup>1</sup> G. F. Pedulli and A. Alberti, *J.C.S. Perkin II*, 1976, 137, is considered as Part I.

revealed for sodium and potassium ion pairs by small variations in both proton and metal hyperfine splittings, in the majority of cases the presence of the crown ether was found to modify only slightly the structure and properties of the ion pair. However in the case of the sodium ketyls of thiophen and condensed thiophens,



increased, being temperature independent. To explain these results we should consider the mechanism responsible for the temperature and solvent dependence of the alkali-metal splitting in ion pairs from carbonyl

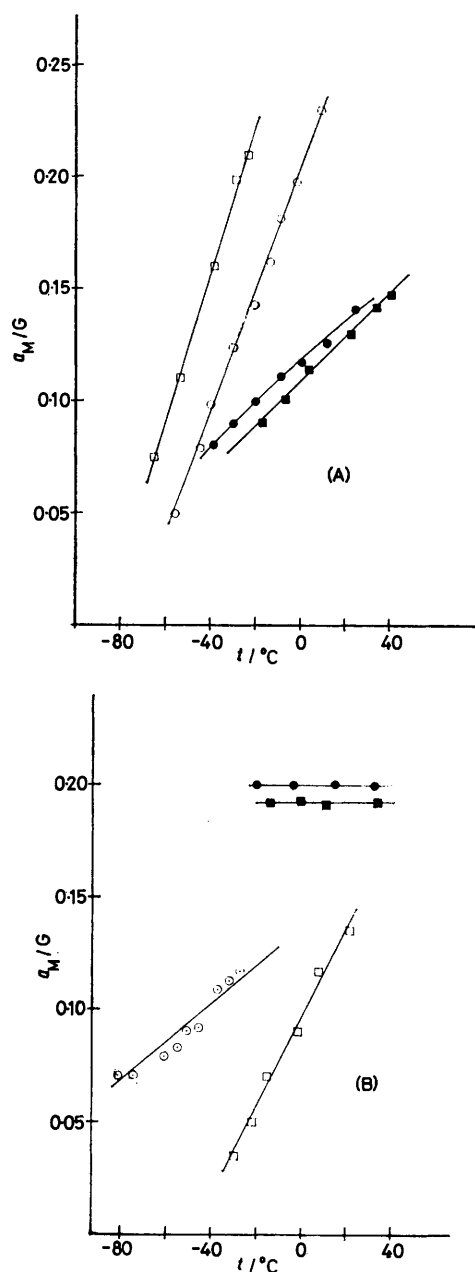


FIGURE 2 Temperature dependence of the sodium hyperfine splitting constant in the crown complexed (filled symbols) and uncomplexed (open symbols) ion pairs of thiophen-2,5-dicarbaldehyde (A) and 3,6-dimethylthieno[3,2-*b*]thiophen-2,5-dione (B); DME ●, ○; THF ■, □

derivatives. According to the results of both experimental<sup>6</sup> and theoretical<sup>7</sup> studies, the observed changes may be explained in terms of the following model. The

<sup>6</sup> K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, 1971, **93**, 6004; K. Nakamura, B. F. Wong, and N. Hirota, *ibid.*, 1973, **95**, 6919.

ion pair may exist in two stable conformations, one with the cation in the molecular plane characterized by a negative splitting constant at the metal atom, and the other with the cation above the plane approximately on the symmetry axis of the  $2p_z$  orbital of the carbonyl oxygen atom. In the latter conformation the metal splitting is positive because spin density is transferred directly from the  $\pi$ -system of the organic anion to the valence orbital of the cation.<sup>8</sup> Since these two conformations are in equilibrium, an increase of the coupling to the counterion implies a stabilization of the out-of-plane structure. The results concerning the sodium salt of the dione (2) may be explained therefore by admitting that, in the presence of cyclic ether, the metal atom is completely in the above-plane position. This is also consistent with the lack of temperature dependence of the sodium splitting. In the case of the dialdehyde (1) the interpretation of the metal splitting variation is not so straightforward; however, we believe that in both the uncomplexed and the complexed ion pair the above-plane conformation is preferred, although the in-plane conformation may still occur. The decrease of the sodium coupling after the addition of polyether may indicate a lengthening of the metal-oxygen distance and thus a weakening of the contact ion pair.

Only one potassium salt has been studied, that of the dialdehyde (1). In this case we observed after complexation a decrease of the average proton splittings (see Table 1) and of the coupling to the potassium ion. The latter becomes undetectable, whereas before complexation it ranges between 0.05 and 0.13 G in the temperature range  $-60$  to  $50$  °C.<sup>9</sup> These results provide evidence for reduction of the strength of the potassium ion pair due to complexation.

Kinetic studies of intramolecular cation transfer in the ion pairs from the dialdehyde (1)<sup>9</sup> and the dione (2)<sup>5</sup> have been reported. The factors influencing the rate constants for this process have been discussed, and in particular the important role of the solvent has been emphasized. The large negative activation entropies measured in THF and DME indicate that a considerable reorganization of solvent molecules occurs during the transfer of the cation from one carbonyl group of the organic anion to the other. The exchange process may therefore be represented as the passage between two equivalent contact ion pairs *via* a solvent-shared ion pair.

The addition of dibenzo-18-crown-6 to the lithium salt of the dione (2) has practically no effect on the exchange rate, consistent with very little complexation of the lithium ion, as mentioned previously. On the other hand for the sodium salts of both (1) and (2) the rate of migration of the counterion is drastically reduced when the polyether is added to the solution. As an

<sup>7</sup> F. Bernardi and G. F. Pedulli, *J.C.S. Perkin II*, 1975, 194; F. Bernardi, G. F. Pedulli, M. Guerra, and H. A. Schlegel, *Gazzetta*, 1975, **105**, 711.

<sup>8</sup> S. Aono and K. Ooshashi, *Progr. Theor. Phys.*, 1963, **30**, 162.

<sup>9</sup> M. Guerra, G. F. Pedulli, and M. Tiecco, *J.C.S. Perkin II*, 1973, 903.

example, Figure 3 shows this effect in the case of the dione (2); it appears that in pure THF the e.s.r. spectrum at  $-35^{\circ}\text{C}$  is characterized by some very broad

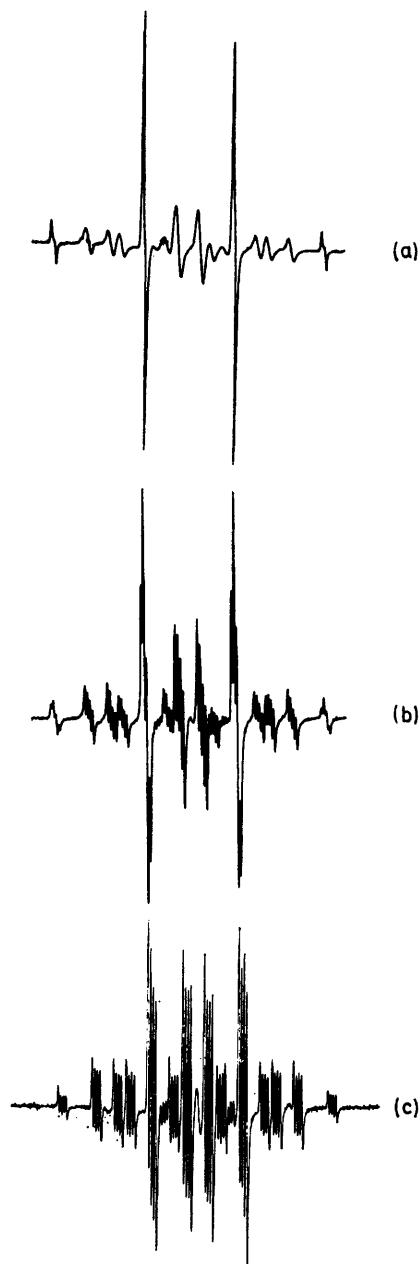


FIGURE 3 E.s.r. spectra of the sodium ion pair of (2) recorded at  $-35^{\circ}\text{C}$  in pure THF (a) and in THF containing crown ether [(b) 0.6 and (c) 1.0 mol. equiv. with respect to the radical]

lines typical of an intermediate rate of exchange, whereas in the presence of the crown ligand a sharpening of these lines is observed, indicating that the exchange is much slower than before. The large variations in the spectral shape of (2) allowed the sodium complex to be titrated. Known amounts of polyether (0.6, 1.0, and 2.0 mol. equiv. with respect to the dione) were added to the solution of the radical. The e.s.r. spectra (Figure 3) show that both complexed and uncomplexed ion pairs

are present when the molarity ratio is 0.6 : 1, but only the complexed salt can be seen when this ratio becomes 1.0 : 1; further addition of ligand leaves the spectrum unchanged. Of course these results will be meaningful only if the dione has reacted completely with the sodium to give the corresponding anion radical. To verify this point we determined by atomic absorption spectroscopy the amount of  $\text{Na}^+$  ion, and found that it was the same as that of the dione initially introduced. We may then conclude that the crown complex of the sodium ion pair of (2) (and presumably also those of the other carbonyl derivatives) has a 1 : 1 stoichiometry.

To establish whether the decrease of the sodium transfer rate is due to entropic or enthalpic factors, a complete kinetic investigation was carried out by employing established procedures;<sup>9</sup> the results are collected in Table 2 together with those previously determined<sup>5,9</sup> in the absence of crown ligand.

The potassium ion pairs do not experience significant variation in migration rates upon complexation. The activation parameters were measured only for the ion pair of (1) (Table 2).

The sodium salts behave in a completely different way from the lithium and potassium analogues, whose properties are unaffected or only slightly modified by addition of the polyether. The activation enthalpies of the crown-complexed sodium ion pairs are much greater than in the absence of ligand; on the other hand the activation entropies drop to zero, both these quantities being practically independent of solvent. The negligible small activation entropy provides evidence that the degrees of solvation of the ground and transition states in the exchange process are the same, in contrast to the situation in the absence of ligand.

Discarding for the complex the sandwich structure earlier proposed for sodium diaryl ketals<sup>1</sup> because of the determined 1 : 1 stoichiometry, we interpret these results on the basis of a structure like that depicted in Figure 4, where the planes of the anion radical and of the crown molecule are parallel to each other, the

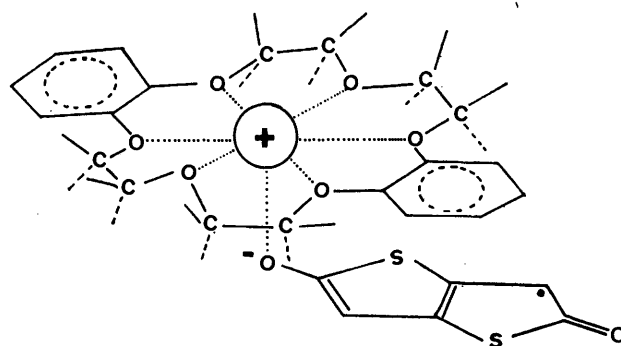


FIGURE 4 Postulated structure of the sodium ion pair of (2) complexed by dibenzo-18-crown-6

sodium ion being in the middle of the cavity in the latter. Such a structure may well explain the zero activation entropy for the intramolecular transfer since the cation, which is completely surrounded by the ether

oxygen atoms in the plane of the ligand, will be very little solvated by the medium, in either the ground or the transition state of the exchange process. This also implies that the stabilization of the transition state due to increased solvation will be lacking in the complexed salt, thus producing the observed enhancement of  $\Delta H^\ddagger$ .

disfavoured by steric crowding. Table 3 shows that (A) also remains the more stable isomer in the crown complex of the sodium ion pair and in the lithium ion pair, prepared by reduction with lithium amide. Crown complexation, on the other hand, enhances the stability of this radical at room temperature, increasing its

TABLE 2

Solvent and counterion	$E_a$ /kcal mol <sup>-1</sup>	log $A$	$\Delta H^\ddagger$ /kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ /cal mol <sup>-1</sup> K <sup>-1</sup>
Thiophen-2,5-dicarbaldehyde (1)				
THF, Na	4.79 ± 0.26	10.89 ± 0.25	4.40 ± 0.26	-10.04 ± 1.13
THF + crown, Na	9.74 ± 0.27	13.18 ± 0.21	9.20 ± 0.29	-0.05 ± 1.02
DME, Na	3.57 ± 0.09	10.04 ± 0.08	3.03 ± 0.09	-14.45 ± 0.36
DME + crown, Na	9.66 ± 0.50	13.14 ± 0.38	9.16 ± 0.52	-0.06 ± 0.11
THF, K	4.74 ± 0.11	11.76 ± 0.10	4.28 ± 0.13	-6.23 ± 0.50
THF + crown, K	4.39 ± 0.13	11.34 ± 0.12	4.03 ± 0.14	-7.78 ± 0.03
3,6-Dimethylthieno[3,2- <i>b</i> ]thiophen-2,5-dione (2)				
THF, Na	5.94 ± 0.10	11.31 ± 0.09	5.45 ± 0.09	-8.40 ± 0.37
THF + crown, Na	9.97 ± 0.37	13.12 ± 0.29	9.51 ± 0.38	-0.06 ± 1.32
DME, Na	3.63 ± 0.07	10.31 ± 0.06	3.19 ± 0.07	-12.78 ± 0.31
DME + crown, Na	9.57 ± 0.17	13.24 ± 0.13	8.98 ± 0.18	0.05 ± 0.04

TABLE 3

Proton and metal hyperfine splitting constants ( $G$ ) and ratios between isomers (A) and (B) (see text) in the radical ion pairs of 3-methylthieno[3,2-*b*]thiophen-2,5-dione (3)

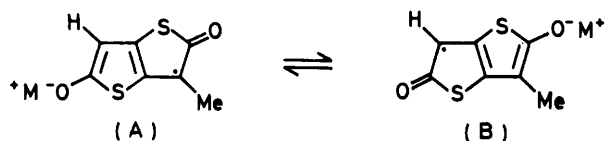
Counterion	Solvent	$t/^\circ\text{C}$	Isomer (A)			Isomer (B)			(A)/(B)
			$a_H$	$a_{CH_3}$	$a_M$	$a_H$	$a_{CH_3}$	$a_M$	
Li	THF	-68	2.18	5.33		4.71	2.57		3.3
		-27	2.08	5.35		4.73	2.50		2.6
Na	DME	-70	2.45	5.15		4.57	2.85		2.4
		-16	2.28	5.30		4.70	2.71		2.5
	THF	-90	2.88	4.85		4.29	3.37		3.5
		-43	2.77	4.95		4.35	3.30		2.4
	DME	-70	2.92	4.90		3.73	4.26		1.4
		THF + crown	-70	2.75	4.29	0.07	4.86	3.17	0.17
DME + crown	-2	2.61	4.38	0.11	4.98	3.06	0.19	3.0	
	-70	2.80	4.29	0.06	4.89	3.30	0.17	3.4	
		-6	2.67	4.39	0.11	5.03	3.16	0.18	3.4

A structure similar to that postulated in Figure 4 could also explain the greater conformational rigidity of the crown-complexed sodium ion pairs of diaryl ketyls,<sup>1</sup> as the proximity of the planes of radical and ligand will provide a strong hindrance to rotation of the aromatic rings.

In the case of the complexed potassium salts, the observation that the activation entropy is still largely negative is not surprising. The larger size of this ion presumably does not allow it to fit the cavity of the crown ligand, so that additional solvation by the medium will be possible, especially in the transition state.

The experimental data concerning the behaviour of the radical ion pair from 3-methylthieno[3,2-*b*]thiophen-2,5-dione (3) are collected in Table 3. In this case the partial bond between the carbonyl oxygen counterion gives rise to two distinct isomers, (A) and (B), which may be easily identified on the basis of relative proton hyperfine splittings. As previously found<sup>5</sup> for the sodium ion pair of (3) in THF or DME, the less stable isomer is (B). This was attributed to the fact that the approach of the cation, with its solvation shell, to the oxygen on the same side of the methyl substituent is

lifetime from a few minutes to several hours and, as in the dimethyl derivative (2), produces a drastic reduction of the 'jumping' rate of the sodium ion and an increase in its splitting. This splitting is greater for isomer (B) than for (A). Since in the former isomer the strength of



the metal-oxygen interaction is less, as indicated by its lower thermodynamic stability, the larger value of  $a_{Na}$  suggests that the above-plane position, characterized by a positive metal splitting, is more favoured for the sodium counterion than in isomer (A). This is consistent with the presence of the methyl substituent in the molecular plane in a position adjacent to the binding carbonyl group, and further supports the structure shown in Figure 4 for the complex of the sodium ion pair of the dione (2).

We thank Professor M. R. Truter for comments.