Electron Spin Resonance Study of the Interaction between Radical Ion Pairs and Macrocyclic Polyethers

By **Gian Franco Pedulli,*** Istituto di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna, Italy
Angelo Alberti, Laboratorio del C.N.R. dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, Ozzano Emilia, Italy

The alkali metal ion pairs of 2,2′-bithiazolyl, bisthiazol-2-yl ketyl, bis-2-thienyl ketyl, and of two symmetrical dithienothienyl ketyls have been studied by e.s.r. in ethereal solutions in the presence of dibenzo-18-crown-6 ether. The conformational stability of the latter three ketyls is much affected by the complexation of the ion pair by the cyclic ether. The sodium complexes show also a large enhancement of the energy barrier to the rotation of the aromatic groups. These results have been interpreted by postulating a sandwich structure for the crown complexes of the sodium ketyls.

THE structural properties of alkali metal ion pairs of radicals containing one or two binding sites as carbonyl oxygens or aromatic nitrogens have been the subject of our recent interest.[1-4] Attention has been mainly focused on the changes induced on the conformational stability of flexible radical anions by the formation of a partial bond between the organic anion and the alkali cation. For instance, in the bis-2-thienyl ketyl[1] the two observed rotational isomers are the *cis–trans* and the *trans–trans* in every condition; however the relative importance of the two conformations is greatly dependent on whether the radical is present in solution as a free ion or as an ion pair. When the ketyl is produced in alcoholic solutions as a free ion, the more stable isomer is the *cis–trans*, while the *trans–trans* becomes favoured if the alkali ion pairs[2] are formed, and the stability of the latter conformation increases with increasing size of the metal counterion. This trend has been interpreted in terms of steric interaction between the cation partially bonded to the carbonyl oxygen and the adjacent ring atoms, which should be greater in the *cis–trans* isomer because of the proximity of the bulky sulphur atom to the binding site.

Other interesting examples of flexible radical ion pairs in which the conformational stability is determined by the presence of the counterion are those derived from 2,2′-bithiazolyl and bisthiazol-2-yl ketone.[4] At variance with the behaviour shown by structurally similar derivatives such as 2,2′-bithienyl,[5] the radical ion pairs of the 2,2′-bithiazolyl exist entirely in the *cis*-conformation because of the formation of a five-membered chelated ring in which the alkali cation is partially bonded to both the aromatic nitrogens. Also in the bisthiazol-2-yl ketyl one thiazole group is prevented from rotating around the carbonyl–ring bond because of the chelation of the counterion by the lone pairs of the carbonyl oxygen and one thiazole nitrogen.

In this paper we report the results of an e.s.r. investigation on the complexation of the radical ion pairs mentioned above, with a macrocyclic polyether, dibenzo-18-crown-6. Comparison of the temperature dependence of the alkali metal splitting and of the conformational behaviour of the ion pairs of these flexible radicals with the results obtained in the absence of polyether gives useful information on the structure of the crown complexes.

EXPERIMENTAL

The preparation of the compounds used in the present work is described elsewhere.[1,4]

The radical ion pairs were produced by reduction with alkali metals in degassed tetrahydrofuran (THF), dimethoxyethane (DME), or tetrahydropyran (THP) solutions. Dibenzo-18-crown-6 ether (Fluka), contained in a side arm of the sample tube, was added to the solution after reduction had taken place.

The temperature of the samples was controlled by using standard variable temperature accessories and measured with a chromel–alumel thermocouple immediately before and after recording each spectrum.

RESULTS

Bis-2-thienyl Ketyl.—The addition of polyether to the lithium ion pair of this radical has no noticeable effects, while in the case of the sodium and potassium ion pairs significant variations are observed, with respect to the crown uncomplexed species both in the metal and proton splittings as well in the *trans–trans* : *cis–trans*-isomer ratio (see Tables 1 and 2). The sodium complex shows also a large increase

TABLE 1

Hyperfine splitting constants (G) of the alkali ion pairs of bis-2-thienyl ketyl

Counterion	Solvent	a_3	a_4	a_5
Li	THF	4.40	1.00	3.87
Li	THF + crown	4.40	1.00	3.86
Na	DME	4.39	0.99	3.86
Na	DME + crown	4.29	0.97	3.80
K	DME	4.32	0.98	3.82
K	DME + crown	4.25	0.95	3.75
Cs (free ion)	DME + crown	3.91	0.88	3.59

Crown = dibenzo-18-crown-6 ether.

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[1] M. Guerra, G. F. Pedulli, M. Tiecco, and G. Martelli, *J.C.S. Perkin II*, 1974, 562.

[2] G. F. Pedulli and A. Alberti, *Chem. Phys. Letters*, 1974, **26**, 392.

[3] G. F. Pedulli, A. Alberti, L. Testaferri, and M. Tiecco, *J.C.S. Perkin II*, 1974, 1701.

[4] G. F. Pedulli, P. Zanirato, A. Alberti, and M. Tiecco, *J.C.S. Perkin II*, 1975, 293.

[5] P. Cavalieri d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Letters*, 1969, 4179.

of the coalescence temperature, *i.e.* of the free energy of activation for the conformational interconversion.

The lithium, sodium, and potassium hyperfine splittings exhibit a positive temperature dependence indicating that they are always positive independent of the addition of crown ether.

Dissociation into free ions occurs when adding the cyclic polyether to the caesium ion pair of bis-2-thienyl ketyl; this can be deduced from the appearance in the e.s.r. spectrum of a second species, showing no alkali splitting, and whose relative concentration increases by dilution and with decreasing temperature. The effect of complexation on this ion pair could not be analysed since its amount is always very small.

TABLE 2

Relative isomer concentrations and room temperature metal splittings (G) in 2,2′-bithienyl ketyl

	Pure DME			DME + dibenzo-18-crown-6 ether		
Counterion	*trans–trans* : *cis–trans*	a_M	$\Delta G^{\ddagger}$/kcal mol^{-1}	*trans–trans* : *cis–trans*	a_M	$\Delta G^{\ddagger}$/kcal mol^{-1}
(Free ion)	0.77		7.54 ± 0.1			
Li	*ca.* 1.5	0.29		*ca.* 1.5	0.29	
Na	1.82	1.12		0.90	0.56	9.47 ± 0.2
K	3.62	0.27		1.11	0.19	
Cs	*ca.* 4.10	2.60				

2,2′-*Bithiazolyl*.—The proton and metal hyperfine splitting of the radical ion pairs of this compound are not greatly affected by the addition of the polyether. Only the metal couplings are slightly smaller, and in the case of Li in DME this temperature dependence is reversed as shown in Figure 1. When sodium and potassium are the counterions, the free anion radical can also be detected and its relative amount increases along the series DME < THF < THP for the sodium complex, while it is practically solvent independent in the case of the potassium complex. The free ion has a smaller *g* factor than the ion pairs and is favoured by dilution and by low temperatures.

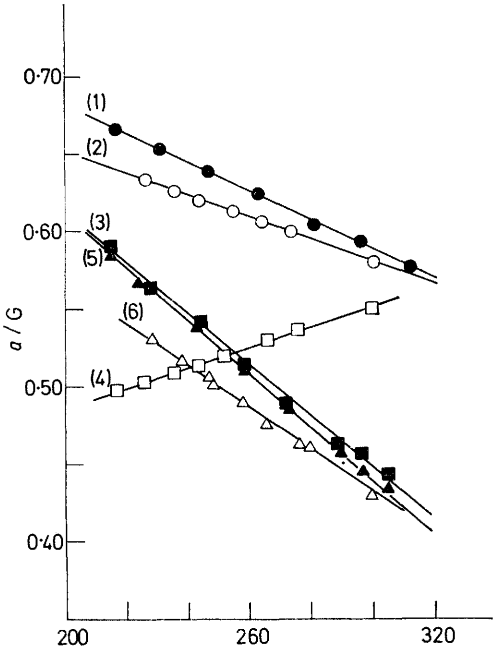

FIGURE 1 Temperature dependence of the alkali metal splitting in the radical ion pair of 2,2′-bithiazolyl: (1) THF–Li; (2) THF–Li–crown; (3) DME–Li; (4) DME–Li–crown; (5) DME–Na; (6) DME–Na–crown. Crown = dibenzo-18-crown-6 ether

Bisthiazol-2-yl Ketyl.—This anion radical could not be obtained by lithium reduction of the corresponding ketone. When using sodium or potassium as the reducing agent, the presence of the crown ether has no influence on the e.s.r. spectrum. The only observed change concerns the sodium splitting constant which is slightly smaller than in the pure solvent.

DISCUSSION

In the lithium ion pair of bis-2-thienyl ketyl, the invariance of the proton and metal splitting constants as well as of the the *trans–trans* : *cis–trans*-isomer ratio, suggests that this salt is not complexed at all or only to a very small degree by dibenzo-18-crown-6 ether. This result is not unexpected considering that the dimensions of Li^+ are too small to allow good fitting of the ion to the hole of the polyether.[6]

The behaviour of the sodium salt is totally different, which in the presence of crown ether, gives an externally complexed contact ion pair as indicated by the large decrease of the metal coupling constant and also by the non-negligible variations of the ring proton splittings. The co-ordination of the cyclic ether to the alkali cation has two main effects, reduction of the *trans–trans* : *cis–trans*-isomer ratio to a value which is only slightly larger than that observed in the free ion, and increase of the energy barrier for rotation of the thiophen rings. A correct understanding of the origin of these effects may give valuable information on the actual structure of the complexed ion pair.

The decrease of the metal hyperfine splitting suggests that the co-ordination of the sodium atom is accompanied by a weakening of its interaction with the carbonyl oxygen and therefore by a lengthening of the metal–oxygen distance. The latter factor may well account for the different isomer ratio measured in the crown complexed and uncomplexed ion pairs. Actually, if the alkali cation is located at a larger distance from the carbonyl oxygen, the steric factors responsible for the destabilization of the *cis–trans*-isomer become less important so that the stability of the two conformations should not be greatly modified with respect to the free ion. This explanation does not imply any specific hypothesis about the number of complexing crown molecules and on their spatial arrangement around the ketyl salt. On the other hand

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[6] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1970, **92**, 386.

the larger energy barrier to rotation of the thiophen rings leads to some interesting speculations on this question. Two different factors may exert their influence on the height of the rotational barrier, a conjugative factor determining stabilization of the planar ground state or a steric factor producing destabilization of the transition state. The first can be safely rejected since there are no obvious reasons why conjugation between the carbonyl group and the aromatic rings should be altered to such a large extent by complexation with the polyether; moreover a variation of this kind should also reflect on the values of the ring proton coupling constants which instead experience only small changes. The only other possibility seems therefore to be that the steric situation is drastically modified in the complexed ion pairs; to this purpose we hypothesize about their structures. There is evidence from potentiometric measurements [7] and X-ray [8] studies that alkali metals form stable 1 : 1 or 1 : 2 complexes with crown ethers. In the present case the most likely structure for a 1 : 1 complex should have the planes of the ketyl and of the cyclic ether perpendicular to each other, as exemplified in Figure 2; in this way the cation can be located close to the centre of the polyether hole making co-ordination more effective. However structure (I) does not justify the heightening of the rotational barrier since the steric interaction between the ring atoms and the crown skeleton should be in this case greater in the planar ground state than in the transition state.

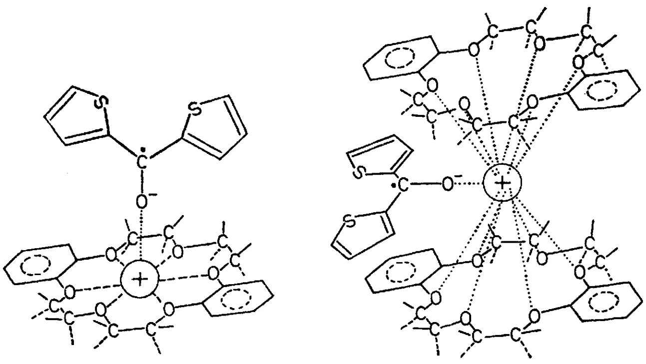
(I) (II)

Figure 2 Possible structures of the sodium bis-2-thienylketyl–dibenzo-18-crown-6 ether complex

The other possibility is that a 1 : 2 complex is being formed; in that case the simultaneous complexation of two crown molecules requires that the sodium salt of bis-2-thienyl ketyl is sandwiched between them as shown in structure (II) of Figure 2. The enhancement of the rotational energy barrier due to complexation can be satisfactorily explained in this way, because the transition state is expected to be destabilized by the steric interaction of the two crown molecules with the thiophen ring perpendicular to the plane containing the carbonyl group. The sandwich structure (II) seems therefore the most plausible to account for the experimental findings. If this is the case similar effects should also be observed in other aromatic ketyls. To test the reliability of the above interpretation we studied the sodium ion pairs of two related diaryl ketyls, *i.e.* bis-2-thieno[3,2-*b*]thienyl and bis-2-thieno[2,3-*b*]thienyl ketyl. In a previous investigation [1] on the corresponding free ions, results parallel to those found for bis-2-thienyl ketyl were obtained. Also for these derivatives, only two of the three possible rotational isomers were detected; they were identified as the *trans–trans* and the *cis–trans* on similar grounds. When producing the sodium ion pairs of these two ketyls in DME, a drastic reduction of the latter isomer is observed, as reported in Table 3. Despite the big change in the isomer ratio, the coalescence temperature is very close to that measured for the free ions. This indicates that the energy barrier to the rotation of the thienothiophen rings is scarcely affected by the formation of the ion pair. On the other hand the addition of the cyclic ether to DME solutions of the sodium ion pairs has the effect of restoring the isomer ratio to approximately the value measured for the free ions, while at the same time the coalescence temperature, *i.e.* the free energy of activation, increases by *ca.* 40°. This behaviour is similar to that shown by the crown complexed sodium ion pair of bis-2-thienyl ketyl, and gives further support to the interpretation that a 1 : 2 sandwich complex is being formed, in which steric overcrowding strongly reduces the internal motional freedom of the aromatic rings.

Table 3

Isomer ratios and activation free energies for the ketyls of condensed thiophens

Radical	Solvent	Counterion	*trans–trans* : *cis–trans*	$\Delta G^{\ddagger}$/kcal mol^{-1}
Bis-2-thieno[3,2-*b*]thienyl ketyl	CH$_3$OH	(Free ion)	1.47	8.10 ± 0.1
	DME	Na	3.1	
	DME + crown	Na	*ca.* 1.5	9.8 ± 0.2
Bis-2-thieno[2,3-*b*]thienyl ketyl	CH$_3$OH	(Free ion)	1.82	8.09 ± 0.1
	DME	Na	>4	
	DME + crown	Na	*ca.* 1.7	9.6 ± 0.2

Crown = dibenzo-18-crown-6 ether.

Analogous explanations may also be given for the potassium ion pair to justify the reduction of the alkali splitting and of the *trans–trans* : *cis–trans*-isomer ratio. However this system differs from the sodium analogue as

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[7] H. K. Frensdorff., *J. Amer. Chem. Soc.*, 1971, **93**, 600.

[8] J. Smid in ' Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley, New York, 1972, vol. 1.

no significant variations of the energy barrier to rotation have been observed after complexation. Even though a structure like (I) will satisfactorily account for this invariance, we feel that structure (II) cannot be discarded since the larger dimensions of the potassium ion with respect to sodium will produce an increase of the separation between the two crown molecules and therefore of the internal motional freedom of bis-2-thienyl ketyl.

The behaviour of the lithium ion pair of 2,2′-bithiazolyl is rather intriguing as no significant difference is observed when passing from pure THF to THF containing some dibenzo-18-crown-6 ether, whereas in DME the temperature coefficient of the lithium splitting is reversed by adding the polyether. A simple explanation of the positive temperature dependence observed in the latter case could be found by admitting that a fast equilibrium between contact and crown solvated ion pairs is taking place in solution; however this hypothesis is not substantiated by any other experimental fact and seems to contrast with what is observed for the sodium and potassium salts of this radical, which give only contact ion pairs or free ions.

TABLE 4

Hyperfine splitting constants (G) of the alkali ion pairs 2,2′-bithiazolyl in DME

Counterion	a_N	a_4	a_5
Li	2.92	0.66	3.84
Na	2.92	0.66	3.99
K	2.91	0.66	4.04
(Free ion)	2.88	0.66	4.22

The sodium salt of 2,2′-bithiazolyl in DME gives an externally co-ordinated contact ion pair, as can be deduced from the small decrease of the alkali metal splitting. The reduction of a_{Na} in this radical is not so large as in bis-2-thienyl ketyl because of chelation of the cation by the thiazole nitrogens. It is well known that chelated complexes experience only small changes in the metal splitting when changing the solvent.[9] In THF and also in THP the free ion was detected, its relative amount being greater in THP and at low temperature. With potassium the situation is quite different, as the formation of the free ion is independent of solvent, being practically the same in DME and in THP.

The behaviour of the sodium ion pair may be rationalized by admitting that complexation with the crown ether requires partial but not complete removal of the DME or THF external solvation shell around the Na^+ ion. The cation will then be externally co-ordinated both by solvent and polyether molecules; however the stability of the complex will be mainly determined by the solvating power of the medium since chelation of the cation by the nitrogen lone pairs prevents co-ordination by the cyclic ether from being very effective. The formation of free ions implies removal of these residual solvent molecules, and this process will be more difficult for DME which can more effectively compete with the macrocyclic ether as it is a more powerful solvating agent than THF which in its turn is more efficient than THP.

In the potassium ion pair on the other hand, anion and cation are less tightly bound, as can be deduced from the ring atoms splittings which are intermediate between those of the lithium and sodium complexes and those of the free ion. As a consequence the distance between the potassium ion and the dithiazolyl nitrogens will be greater than in the sodium complex; moreover the potassium ion protrudes out of the molecular plane more than sodium because of its larger dimensions. Therefore external co-ordination of the ion pair by the crown ether will be more effective than in the sodium analogue, and the role of the solvent molecule in the solvation shell will be negligible. The free ion–ion pair equilibrium constant should then be almost independent of the solvent medium. The greater dissociation observed at low temperature both in the sodium and potassium ion pairs, is expected from the known exothermicity of the solvation of radical ion pairs.[10]

In the bisthiazol-2-yl ketyl the cyclic ether gives an externally solvated contact ion pair, at least in the case of the sodium complex, as indicated by the small decrease of the sodium splitting. This variation, much smaller than that experienced by the sodium salt of bis-2-thienyl ketyl, is of the same order of magnitude of that observed in the sodium ion pair of 2,2′-bithiazolyl. This analogy further confirms that bisthiazol-2-yl ketyl has a chelate structure as suggested previously.[4]

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[9] T. Takeshita and H. Hirota, *Chem. Phys. Letters*, 1969, **4**, 369.

[10] J. T. Denison and J. B. Ramsay, *J. Amer. Chem. Soc.*, 1955, **77**, 2615.