Electron Spin Resonance Study of the Structure of the Alkali-metal Complexes of Symmetric Dithienobenzoquinones

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The formation of ion pairs was detected upon reducing the thiophen analogues of anthraquinone and phenanthraquinone with alkali-metals in ethereal solvents. Different structures of the ion pair are observed for the two classes of compounds. The thiophen analogues of phenanthraquinone give complexes where the alkali-metal is located on the molecular plane and chelated by the oxygen lone pairs. In the analogues of anthraquinone the counterion is located near only one of the carbonyl oxygen atoms at a given time. When the two carbonyl groups are non-equivalent, as in (V), the ion pair may exist in two different isomeric forms, both of which have been detected in one case.

FORMATION of ion pairs is usually observed when carbonyl compounds are reduced to the corresponding radical anions by alkali-metals in ethereal solvents. Since the alkali-cation will tend to stay in proximity to the carbonyl oxygen atom because of its greater electronegativity, a different situation may arise when two carbonyl groups are present in the same molecule, the effect being dependent on the distance apart of the groups. For instance, in ortho-semiquinones or semidiones the alkali-cation is chelated between the two oxygen atoms, its position is fixed in time, and the relative hyperfine splitting is only slightly dependent on solvent and temperature.[1-3] In para-semiquinones where

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[1] G. A. Russell and D. F. Lawson, *J. Amer. Chem. Soc.*, 1972, **94,** 1699.

[2] M. Brustolon, C. Corvaja, and L. Pasimeni, *J.C.S. Faraday II,* 1973, 403.

[3] E. Warhurst and A. M. Wilde, *Trans. Faraday Soc.,* 1969, **65,** 1413.

the two carbonyl groups are further apart the metal counterion is located near only one of them at a given time and its hyperfine splitting usually experiences marked solvent and temperature effects.[4-6] Since the metal has no preference for either of the two carbonyl oxygen atoms, it migrates between them giving rise to linewidth alternation. When the rate of migration is slow, spectral characteristics of a particular isomeric form of the ion pair are detected.

To obtain more information on the structure of ion pairs involving semiquinones and on the strength of the interaction between anion and cation, we have undertaken an e.s.r. investigation on the alkali-metal complexes of the symmetric dithienobenzoquinones (I)—VI). This class of compounds is more suitable than
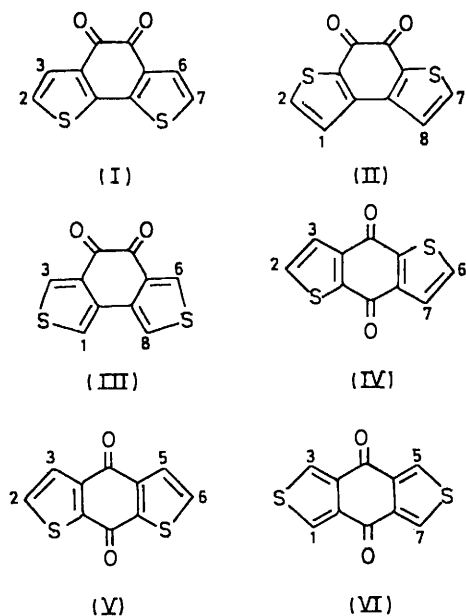
the corresponding benzene derivatives for studying the properties of the related ion pairs since the reduced number of interacting protons makes the e.s.r. spectra simpler. Furthermore the radical of (V) which contains two non-equivalent carbonyl groups is particularly interesting as it may exist in two non-degenerate forms of the ion pair.

Finally it is of interest to examine how the presence of the differently condensed thiophens affects the stability of the radicals and the magnitude of the proton and metal hyperfine splitting constants.

EXPERIMENTAL

Benzo[2,1-b;3,4-b']dithiophen-4,5-dione (I),[7] benzo-[1,2-b;4,3-b']dithiophen-4,5-dione (II),[7] benzo[1,2-c;3,4-c']dithiophen-4,5-dione (III),[7] benzo[1,2-b;4,5-b']dithiophen-4,8-dione (IV),[8] benzo[1,2-b;5,4-b']dithiophen-4,8-dione (V),[8] and benzo[1,2-c;4,5-c']dithiophen-4,8-dione (VI)[8] were prepared as reported in the literature.

[4] T. E. Gough and P. R. Hindle, Canad. J. Chem., 1971, 49, 2412.

[5] E. Warhurst and A. M. Wilde, Trans. Faraday Soc., 1971, 67, 605.

[6] K. S. Chen, T. Takeshita, K. Nakamura, and N. Hirota, J. Phys. Chem., 1973, 77, 708.

The semiquinone radicals were generated from the corresponding quinones by treatment with lithium, sodium, or potassium t-butoxide in dimethyl sulphoxide (DMSO) solution, by photolysis in methanol containing sodium methoxide, and by conventional reduction in tetrahydrofuran (THF) or dimethoxyethane (DME) with alkali-metals.

The temperature of the sample was controlled using standard variable temperature accessories and measured with a chromel–alumel thermocouple placed in the Dewar insert just above the sensitive part of the cavity.

RESULTS AND DISCUSSION

The compounds examined may be classified as thiophen analogues of phenanthraquinone [(I)—(III)] and of anthraquinone [(IV)—(VI)]. Since the properties and the spectroscopic behaviour of the related radicals are quite different, we will discuss these two classes of derivatives separately.

Thiophen Analogues of Phenanthraquinone.—Because of the similarity of the semiquinones produced from compounds (I)—(III), only one of them has been thoroughly studied, the radical from (I). By treating the quinone (I) with lithium t-butoxide in DMSO a superimposition of two spectra was detected, one showing a well defined coupling with the alkali-counterion of 0·48 G which can be attributed to the lithium complex, the other consisting of a triplet with a larger g factor which should be due to the dissociated anion since its intensity increases by dilution. When using sodium or potassium t-butoxide only the free ion could be detected. By reducing the quinones (I)—(III) with alkali-metals in THF or DME only one species showing splitting from the counterion is present; this can be identified as the contact ion pair whose proton coupling constants are only slightly modified with respect to the corresponding free ion, as shown in Table 1. The

TABLE 1

Room temperature hyperfine splitting constants (G) of the radical anions of the thiophen analogues of phenanthraquinones (I)—(III)

Compound	Solvent and counterion	a_1, a_8	a_2, a_7	a_3, a_6	a_M
(I)	DMSO, BuᵗOLi				
	(free ion)		0·45	<0·06	
	(ion pair)		0·61	0·094	0·48
	DMSO, BuᵗOK		0·45	<0·06	
	MeOH, Na		0·64	0·13	
	THF,Li		0·62	0·12	0·58
	THF, Na		0·52	<0·08	0·48
	THF, K		0·50	<0·08	0
	THF, Cs		0·50	<0·08	0·56
(II)	DMSO, BuᵗOK	0·25	1·66		
	THF, Li	0·22	1·72		0·53
	THF, Na	0·25	1·66		0·39
	THF, Cs	0·25	1·60		0·51
(III)	DMSO, BuᵗOK	0·30		2·88	
	THF, Na	0·28		2·87	0·47
	THF, Cs	0·30		2·78	0·40

assignment of these constants to the various positions has been made by analogy with the radical anions of

[7] H. Wynberg and H. J. M. Sinnige, Rec. Trav. chim., 1969, 88, 1244.

[8] D. W. H. MacDowell and J. C. Wisowaty, J. Org. Chem., 1972, 37, 1712.

similar cyclopentadithiophenones.[9] From an examination of Table 1 it appears that the proton splittings increase on going from (I) to (III); this trend can be easily explained by considering the limiting structures which can produce spin densities on the outer carbons of the thiophen rings. Structures (b) and (c) account for the relatively large coupling constants of semiquinones (II) and (III), while the much smaller splitting observed

(a)   (b)   (c)
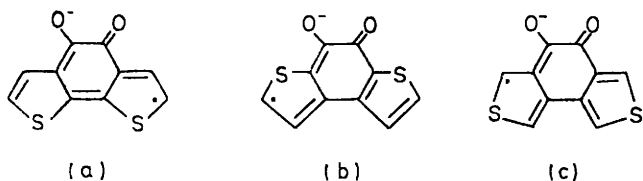
in the radical from (I) may be justified by assuming that structure (a) does not contribute appreciably to the resonance system because of the loss of aromaticity of both the thiophen rings. This means that extensive conjugation between the two thiophens is prevented and that a close similarity between the semiquinones (I)—(III) and the radical anions of dithienyl diketones should be expected. In this respect it is gratifying that the hyperfine splittings of 4- and 5-H in the semidione (VII) (0·42 and 1·66 G respectively),[10] are very close to those measured for the radical from (II) (0·25 and 1·66 G). Furthermore, the semiquinones from (I) and (III) which

(VII)
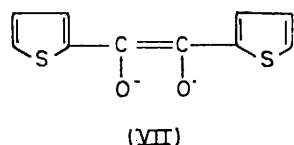
can be considered as substituted 3,3'-dithienyl diketones have almost identical room temperature sodium splittings (0·48 and 0·47 G respectively), while in the sodium complex of (II), which is formally a substituted 2,2'-dithienyl diketone, a_{Na} is only 0·37 G. In the former the reduced possibility of delocalization for the unpaired electron gives rise to larger spin densities at the carbonyl groups which reflect on the greater metal splittings.

The temperature and solvent dependence of the splitting at the alkali-counterion have also been studied for the semiquinone (I) and the results are shown in Figure 1. Although no accurate measurements have been made for the other two compounds they behave similarly to (I). The lithium splitting in DME is insensitive to changes in temperature, while in THF it has a negative temperature dependence; the latter trend is also shown by the sodium splitting in both solvents. No coupling with the potassium atom could ever be detected, while the caesium splitting increases with increasing temperature. Since it seems to be generally accepted that the temperature coefficient of

the metal hyperfine splitting constant da_M/dT is always positive,[11,12] we may then conclude that a_M is negative for Li and Na and positive for the Cs atom. If we consider the mechanisms of spin transfer from the organic anion to the alkali-cation, these findings indicate that ortho-quinones give alkali-metal chelates like other bidentate derivatives. In the case of the Li and Na complexes the most important mechanisms should be the following.

(a) Direct electron transfer, which takes place from the anion to the cation through the mixing of the aromatic MO containing the unpaired electron with the valence orbital χ_{ns} of the alkali-atom.[13] This mechanism is favoured by a low ionization potential for the anion and a high electron affinity for the cation. Since the alkali splitting can be shown to be proportional
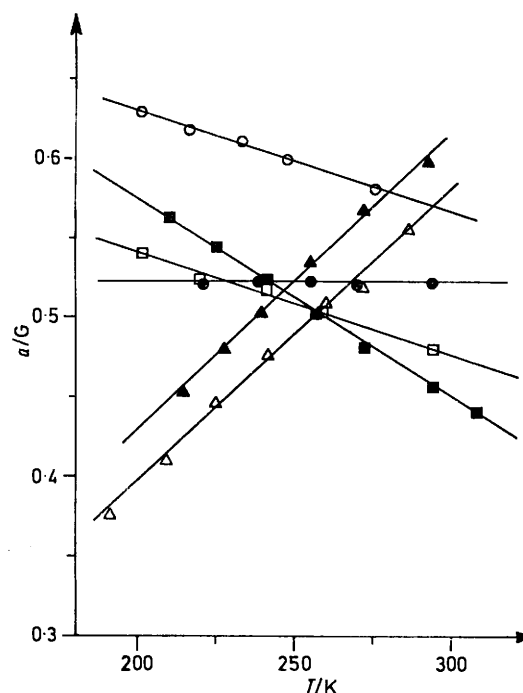

FIGURE 1   Temperature dependence of the alkali-metal splittings in the semiquinone radical from (I): O, THF–Li; ●, DME–Li; □, THF–Na; ■, DME–Na; △, THF–Cs; ▲, DME–Cs

to the overlap integrals between the $2p_z$ orbitals of the aromatic nuclei and the χ_{ns} orbital of the metal, it will be different from zero only when the cation is out of the molecular plane.

(b) Indirect spin polarization which is due to σ–π exchange;[14] this mechanism gives negative splitting constants and is particularly effective when the cation is in the molecular plane provided there is some covalent bonding between the radical and the alkali-metal. A similar mechanism is invoked to explain the way negative spin density is acquired by protons in π-radicals.

The negative metal splitting found in the Li and Na

[9] P. B. Koster, Thesis, Groningen, 1972.
[10] E. T. Strom, G. A. Russell, and J. H. Schoeb, J. Amer. Chem. Soc., 1966, 88, 2004.
[11] E. de Boer, Rec. Trav. chim., 1965, 84, 609.
[12] S. A. Al-Baldawi and T. E. Gough, Canad. J. Chem., 1970, 48, 2798.
[13] S. Aono and K. Oohashi, Progr. Theor. Phys., 1963, 30, 162.
[14] M. C. R. Symons, Nature, 1969, 224, 685.

complexes therefore indicates that the positive ion is located in the nodal plane of the organic radical and that the bonding between the metal and the oxygen lone pairs has a considerable covalent character. The low mobility of the cation in that position also explains the slight temperature dependence of a_{Li} and a_{Na}. In the case of the Cs atom the positive splitting may be due to some alternative spin transfer mechanism [15] or to the fact that the Cs ion pair has a different structure. However the most likely explanation still involves a chelate structure for this complex; because of the large size of the Cs ion, the chelation process is not so effective and the cation is less strongly bonded by the carbonyl oxygens. As a consequence the exchange mechanism is
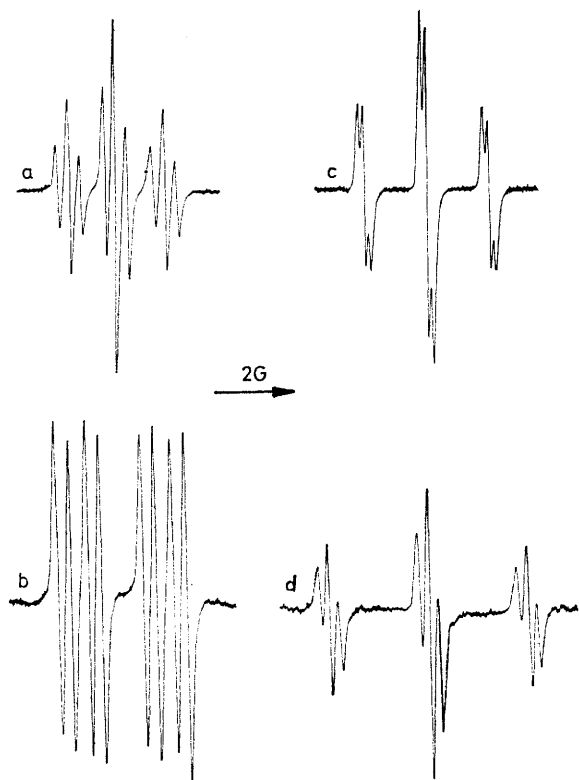

FIGURE 2 E.s.r. spectra of the semiquinone radicals from (IV) a in DMSO and b in THF–Li, and from (V) c in DMSO and d in THF–Li

less important than for smaller atoms and the acquisition of negative spin density is reduced. Furthermore the cation may oscillate more easily out of the molecular plane so positive spin density will be acquired from the π-system through direct electron transfer. These oscillations diminish on cooling and this will result in a decrease of the alkali splitting as experimentally observed.

Finally it may be interesting to point out that whenever metal chelates are formed the alkali splitting usually decreases along the series Li, Na, K, being negative for the former two and for the latter vanishingly

[15] J. L. Sommerdijk and E. de Boer, ' Ions and Ion Pairs,' ed. M. Szwarc, Wiley-Interscience, New York, 1972, ch. 8.
[16] G. F. Pedulli and M. Tiecco, to be published.

small. This trend may be extremely useful in assigning chelated structures to metal complexes of radicals which may exist in different conformations.[16]

Thiophen Analogues of Anthraquinone.—These compounds were reduced to their radical form by the methods described for (I)—(III). The semiquinones produced from (IV) and (V) are quite stable under all conditions, while e.s.r. signals from the semiquinone (VI) were not detected. After prolonged irradiation of (VI) in the presence of ethoxide ions in ethanol a quintet (1 : 4 : 6 : 4 : 1 separated by 2·37 G) was observed. This spectrum was attributed to the *p*-benzosemiquinone which shows the same coupling constant.[17]

The spectra of (IV) and (V) in DMSO are shown in Figure 2a and 2c respectively and the relative hyperfine splitting constants are reported in Table 2. We assume

TABLE 2

Room temperature hyperfine splitting constants (G) of the radical anions of the thiophen analogues of anthraquinones (IV) and (V)

Compound	Solvent and counterion	a_2, a_6	a_3, a_7	a_3, a_5	a_M
(IV)	DMSO, Bu^{t}OK	0·66	0·17		
	MeOH, Na	0·65	0·32		
	THF, Li	1·23— *ca.* 0	0·43— 0·19		0·08*
(V)	DMSO, Bu^{t}OK	0·86		0·07	
	MeOH, Na	0·82		0·22	
	THF, Li	1·44		0·18	0·11*

* a_{Li} decreases with decreasing temperature.

that in this case also the radical is present as a free ion. The small values of the proton splittings indicate that the unpaired electron is only slightly delocalized in the thiophen rings. The larger of them have been assigned to the positions adjacent to the sulphur atom by analogy with other thiophen-containing radicals.[18]

Upon reducing (IV) and (V) with lithium in THF, the spectral features are quite different from those observed in DMSO, as shown in Figures 2b and 2d. In fact the spectrum from (IV) changes from a triplet of triplets to eight lines due to three non-equivalent protons, and in the case of (V) the overall splitting becomes almost twice as large as in DMSO. This behaviour can be ascribed to the formation of the alkali-metal complexes of these two semiquinones. The counterion will tend to stay in the proximity of one of the carbonyl oxygen atoms or, more probably, to jump between them with a rate depending on solvent, temperature, and on the nature of the alkali-metal. In the case of the lithium complex in THF the rate of exchange is very low and we observe the static spectrum due to an isomeric form of the ion pair. The reason for the differences of behaviour between (IV) and (V) lies in their symmetry properties. The quinone (IV) has a centre of symmetry and hence the partial bond between the metal and each of the two oxygen atoms gives rise to equivalent ion pairs with

[17] G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, 1961, 34, 1333.
[18] L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, 101, 10.

identical spectra. We therefore observe a single e.s.r. spectrum, which however differs from that of the free ion since the loss of symmetry due to the presence of the counterion leads to the non-equivalence of all four protons. This can be easily visualized in terms of limiting structures, such as (d), where the alkali metal is partially bonded to one of the carbonyl oxygens. The absence of the fourth proton splitting only means that
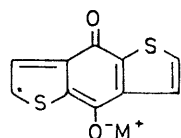

(d)

its value is smaller than the linewidth. The hyperfine splitting constants may be assigned by considering that $(a_2 + a_6)/2$ and $(a_3 + a_7)/2$ are very similar to their average values determined in the free ion. The couplings at positions 2 and 6 will then be 1·23 and *ca.* 0 G, and at positions 3 and 7 0·43 and 0·19 G, the larger values of the two groups being relative to those of the thiophen ring where the sulphur atom is adjacent to the counterion [see structure (d)]. In the Na and K complexes of (IV), the intramolecular exchange of the counterion occurs with a rate constant greater than that for lithium and causes, as usual, linewidth alternation effects which however were not analysed.

On the other hand, in the semiquinone (V) the partial bond of the alkali-cation to one or other oxygen atom will give rise, as a consequence of the lack of a centre of symmetry, to two non-equivalent isomeric ion pairs and, depending on their relative thermodynamic stability, it is possible to detect both or only one of them. When lithium is the counterion the e.s.r. spectrum shows the presence of only one species (see Figure 2d), which could have one of the following structures (A) or (B).
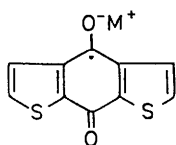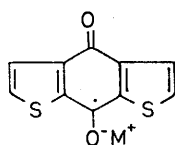
(A)   (B)

A choice between them can be made easily by considering the mesomeric systems available to the isomers. Since in (A) there is no way to delocalize the unpaired electron onto the protonated positions, a decrease in hyperfine splitting is expected with respect to the free ion. In practice a large increase in the proton couplings is observed, so possibility (A) can be ruled out. When the metal is in proximity to the oxygen adjacent to the sulphur atoms [isomer (B)], the unpaired electron can be

delocalized onto the thiophen rings and the hyperfine splitting should increase, as experimentally observed. We may then conclude that the more stable, isomeric ion pair is (B). Its greater stability with respect to (A), which seems favoured on the basis of lower steric hindrance to metal–oxygen interaction, is probably due to the more extended conjugative system with greater possibilities of delocalization for the unpaired electron. Upon increasing the size of the counterion the relative amount of (B) is expected to decrease both because this resonance stabilization should become less important as a consequence of the reduced covalent character of the metal–oxygen bond and because of the greater steric
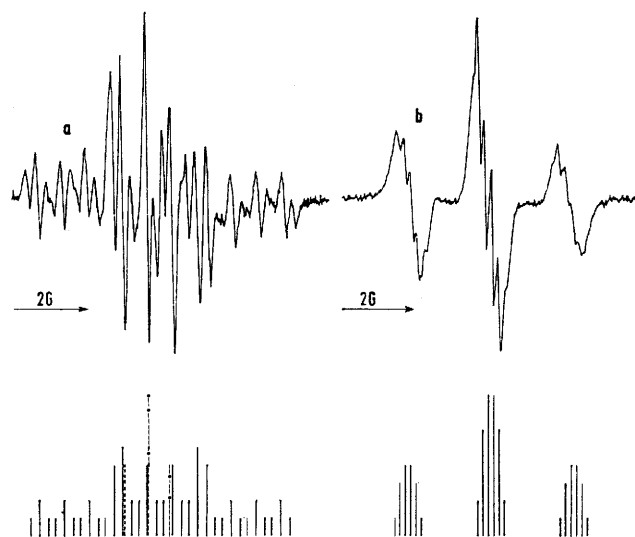

Figure 3   E.s.r. spectra of a, the Na complex at −40 °C and b, the K complex at room temperature of the semiquinone from (V together with their stick diagrams

interaction between the cation and the bulky sulphur atoms. The e.s.r. spectra of the ion pairs of semiquinone (V) with alkali-metals other than lithium show line broadening, the central peak being sharper than the outer ones as shown in Figure 3b for the potassium complex at room temperature. On reducing the temperature the spacing between the outer lines and also their width increase. These two effects of course indicate that both isomers are present although their relative amounts could not be determined. However, at least in the case of the sodium complex (Figure 3a) in THF, the slow exchange region could be reached at low temperature and the observed e.s.r. spectrum consists of a triplet of triplets due to isomer (B) ($a_{2.6}$ 1·20, $a_{3.5}$ 0·14 G) further split by sodium coupling, with a superimposed triplet (a_{H} 0·35 G) whose integrated intensity is *ca.* 1/4 of the main spectrum, which we attribute to isomer (A).