An Electron Spin Resonance Investigation of the Radical Cations from Poly(alkylthio)benzenes

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The radical cations of some poly(methylthio)- and poly(isopropylthio)-benzenes have been investigated by e.s.r. spectroscopy. Discrimination between the couplings due to the aryl and alkyl protons, when the assignment is not straightforward, has been made by hydrogen–deuterium exchange of the acidic aryl protons. Oxidation of the title compounds did not lead in all cases to the corresponding cation radicals, and in some instances secondary species were observed arising from the fragmentation of the initially formed radicals. The conformational preference of the alkylthio and of the isopropyl groups is discussed.

Radical cations of alkylthiobenzenes have been reported so far only in the cases of 1,4-bis(methylthio), 1,4-bis(ethylthio),[1] and 1,2,4,5-tetrakis(methylthio)[2] derivatives. The recent report by some of us[3] of a simple and reliable synthetic method for preparing poly(alkylthio)benzenes prompted us to undertake an e.s.r. investigation of the properties of the related cation radicals.

We have studied hexakis-, pentakis-, tetrakis-, tris-, and bis-(methylthio)- and -(isopropylthio)-benzenes. The oxidation of these compounds either with sulphuric acid or with AlCl$_3$–SbCl$_3$ in CH$_2$Cl$_2$ gives rise in several cases to the corresponding radical cations. However, with methylthio-derivatives, in a few instances fragmentation of the initially formed radical cations, leading to the ultimate formation of a more stable radical, has been observed.

The magnitude of the hyperfine splitting constants enabled us to establish the symmetry of the singly occupied molecular orbital. Evidence for restricted rotation of the SR group was also obtained, and with the radical from 1,4-bis(isopropylthio)benzene the *cis*- and *trans*-isomers were actually resolved. The conformational preference of the isopropyl groups in the variously substituted derivatives was also investigated.

Experimental

The title compounds were synthesized as described previously.[3] The radical cations were generated in degassed solutions of CH$_2$Cl$_2$ by treatment with sulphuric acid or with aluminium trichloride–antimony trichloride (3 : 1). The latter system was found to be a more effective oxidation agent than each individual chloride and gave rise to better resolved spectra, whose quality generally improved by lowering the temperature to *ca.* −50 °C. The same cations were alternatively obtained by oxidation with Bu^{t}OH$^{+\cdot}$ radicals, produced by photolysis of degassed solutions of CH$_2$Cl$_2$ containing di-t-butyl peroxide and trifluoroacetic acid.[4]

Temperature control was achieved by means of standard devices. The *g* factors were measured with respect to a solid sample of diphenylpicrylhydrazyl (*g* 2.0037). McLachlan spin density calculations have been performed by using the following parameters:[5] h_S 1.2, k_{CS} 0.65, and λ 1.2.

Results and Discussion

The compounds examined are poly(methylthio)- (Ia)—(IXa) and poly(isopropylthio)-benzenes (Ib)—(IXb). As mentioned in the Introduction, the oxidation of compounds (I)—(IX)
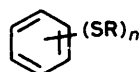
(I) $n = 6$
(II) $n = 5$
(III) $n = 4$ (1,2,3,4)
(IV) $n = 4$ (1,2,3,5)
(V) $n = 4$ (1,2,4,5)
(VI) $n = 3$ (1,2,3)
(VII) $n = 3$ (1,2,4)
(VIII) $n = 3$ (1,3,5)
(IX) $n = 2$ (1,4)

a; R = Me
b; R = CHMe$_2$

did not lead in all cases to the corresponding radical cations. These could actually be obtained only with (Ia, b), (IIIa, b), (Va, b), (VIIa, b), and (IXa, b). The spectra of pentakis- (IIa), tetrakis- (IVa), and tris-(methylthio)benzenes (VIa) could not be observed even at low temperature. Oxidation of these compounds leads to the formation of the radical cation of 1,2,4,5-tetrakis(methylthio)benzene (Va). Under the same conditions (at or below room temperature) compounds (IIIa) and (VIIa) gave the corresponding radical cations. However, if the oxidation was carried out above room temperature these two radicals also gave rise to the formation of the radical cation of (Va). The formation of (Va) from (IIa), (IIIa), (IVa), (VIa), and (VIIa) cannot find a straightforward interpretation but it clearly indicates that the radical cations of these (methylthio)benzenes suffer fragmentation at the aryl-sulphur bond. It can be tentatively suggested that the fragmentation gives rise to an SR cation and an aryl radical which can abstract hydrogen from the solvent. The new (methylthio)benzene so formed can then suffer substitution by the SR cation eventually to give compound (Va). Other products can be formed together with (Va) which cannot be detected because their radical cations are not sufficiently stable.

In contrast with what it has been observed to occur with (IIa) and (IVa), the oxidation of the corresponding iso-propylthio derivatives (IIb) and (IVb) did not give rise to an e.s.r. signal. The mass spectra of the (isopropylthio)benzenes indicate that in this case the largely preferred fragmentation of the radical cations involves the alkyl-sulphur bond, with elimination of propene, and formation of the thiophenol radical cation.[3] If this also occurs in solution, then the observed different behaviour of the (methylthio)benzene and (iso-propylthio)benzene radical cations can be attributed to their different ways of fragmentation. This hypothesis must be con-

Table E.s.r. spectral parameters of the radical cations from poly-(alkylthio)benzenes ($G = 10^{-4}$ T)

Compound		a^H_{Ar}/G	a^H_{SR}/G	g	T/K
(Ia)			2.55 (18 H)	2.0070	298
(Ib)			3.79 (6 H)[a]	2.0076	213
(IIIa)		1.47 (2 H)	5.01 (6 H)	2.0089	263
(IIIb)		1.42 (2 H)	3.28 (2 H)		298
(Va)		0.73 (2 H)	2.59 (12 H)	2.0077	298
(Vb)		0.69 (2 H)	1.93 (4 H)[b]	2.0077	213
(VIIa)		2.9 (1 H)	1.6 (3 H)	2.0082	233
		<0.2 (2 H)	4.4 (6 H)		
(VIIb)		3.0 (1 H)	1.1 (1 H)	2.0082	233
		<0.2 (2 H)	3.0 (2 H)		
(IXa)[c]	cis	1.12 (2 H)	5.31 (6 H)	2.0087_4	235
		1.69 (2 H)			
	trans	1.03 (2 H)	5.44 (6 H)	2.0087_2	235
		1.79 (2 H)			
(IXb)	cis	1.09 (2 H)	3.36 (2 H)	2.0087	228
		1.62 (2 H)	0.11 (12 H)		
	trans	0.98 (2 H)	3.48 (2 H)	2.0087	228
		1.79 (2 H)	0.11 (12 H)		

[a] da/dT −3.5 mG K⁻¹. [b] da/dT −1.2 mG K⁻¹. [c] Data from ref. 1.

(III a)

(III b)

(VII a)

(VII b)

firmed by more chemical and spectroscopic evidence which we are currently attempting to accumulate.

In the case of (IVb) an as yet unidentified and very long lived paramagnetic species is formed after a while, whose e.s.r. spectrum consists of a 1 : 2 : 1 triplet separated by 1.12 G and centred at g 2.0149, the principal components of the g tensor being g_1 2.0245, g_2 2.0174, and g_3 2.0028.*

The hyperfine splitting constants and g factors of the radicals which could be observed are reported in the Table. A distinction between the couplings due to aryl and alkyl protons could be made on the basis of the fact that the former readily undergo hydrogen–deuterium exchange by mildly heating D_2SO_4 solutions of the samples. From the data in the Table several points emerge which deserve discussion. The first concerns the removal of the degeneracy of the two highest occupied MOs of benzene upon substitution. It is well known that these two degenerate orbitals are characterized by different symmetry, one being symmetric (S) and the other antisymmetric (A) with respect to a plane perpendicular to the ring and containing two opposite carbons, with electron distribution as shown.

Electron-donating substituents, such as alkylthio groups, are bound to destabilize the orbital in which they occupy positions of higher electron density. For instance, destabilization of orbital (S) is expected in the 1,4-bis(alkylthio)-benzenes where, owing to the molecular symmetry, the two substituents are linked to the two strongly charged carbon atoms. On the other hand the energy of orbital (A) should not be affected, to a first approximation, upon 1,4-disubstitution.

* *Note added in proof:* The e.s.r. parameters of the secondary radical obtained from (IVb) suggest that this is in fact the cation radical of benzodithiete for which g 2.0150 and a(2H) 1.15 G have been reported (J. Giordan and H. Bock, *Chem. Ber.*, 1982, **115**, 2548).
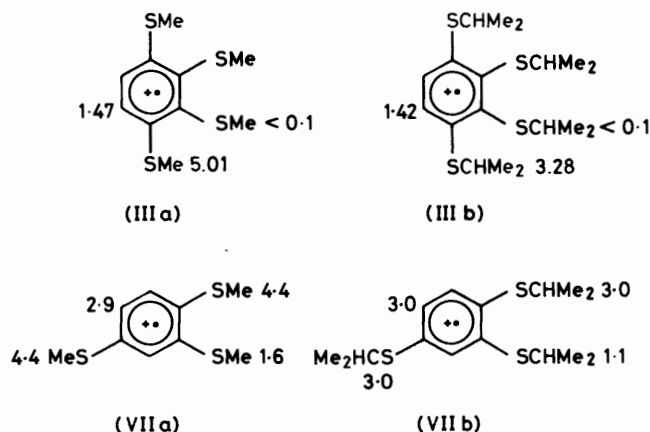
Therefore, in the corresponding radical cation, the singly occupied MO should be the symmetric one. On the same basis, it can be inferred that the unpaired electron will occupy orbital (A) in the 1,2,4,5-tetrakis(alkylthio) derivatives, and (S) in the 1,2,3,4-tetrasubstituted benzenes. No removal of the degeneracy is expected for the hexakis(alkylthio)benzenes.

The symmetry of the SOMO can be established experimentally from the magnitude of the aryl proton splittings which reflect the spin density on the adjacent carbon atom. Thus, a_H values of ca. 1 and ca. 4—5 G are expected for hydrogens bonded to carbons characterized by low and high spin density, respectively. The data in the Table prove the above predictions as the SOMO has A symmetry in the cations from (V) and S symmetry in those from (IX) and (III).

In the cations from (IIIa and b) the protons of only two of the four alkyl groups are coupled with the unpaired electron which, because of the S symmetry of the SOMO, should be those linked to positions 1 and 4. McLachlan MO calculations are in agreement with this assignment.

The same kind of calculations also suggests A symmetry for the SOMO in the radical cations from (VIIa and b) with the assignment shown for the hyperfine splittings.

Conformational Isomerism.—All these radicals may in principle exist in several spatial arrangements since conformational isomers may arise from restricted rotation of the alkyl groups around the Ar–S bonds. The most favourable case is represented by 1,4-bis(alkylthio)benzenes; cis- and trans-isomers have actually been detected by Forbes and Sullivan in the radical cations of 1,4-bis(methylthio)- and 1,4-bis(ethylthio)-benzene.[1] Accordingly, also the e.s.r. spectrum of the radical from 1,4-bis(isopropylthio)benzene (IXb) (Figure 1) shows the presence of two species which can be identified as the isomers of this cation. The hyperfine splittings were assigned by analogy with Forbes and Sullivan.

The lack of any selective broadening of the spectral lines up to 330 K indicates that the energy barrier for the rotation around the Ar–S bond is >10 kcal mol⁻¹. This implies a significant conjugative interaction between the π-system of the aromatic ring and the sulphur lone pair, which keeps the isopropyl group on the molecular plane despite its bulk. This behaviour is peculiar to the radical cations of alkylthio-derivatives since in related diamagnetic compounds[6] or radical anions[7] the alkyl group tends to deviate from coplanarity more and more by increasing its size and in any case is characterized by a much lower rotational barrier.

The presence of distinct conformational isomers can also be inferred from the asymmetric shape of the e.s.r. spectrum of the cations from the 1,2,4-trisubstituted derivatives (VIIa
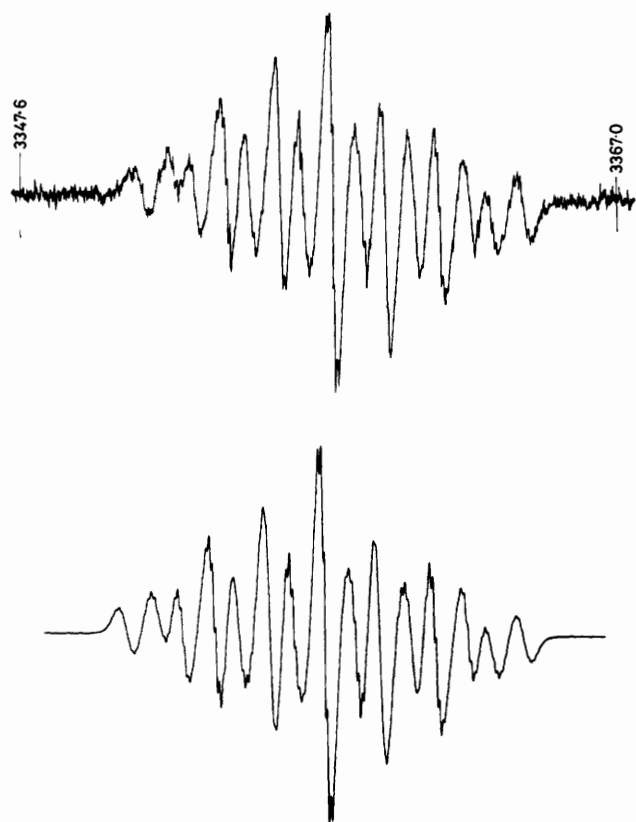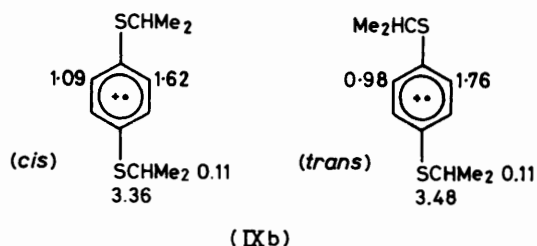
Figure 1. Room temperature experimental (top) and simulated (bottom) e.s.r. spectrum of the *cis*- and *trans*-isomers of the radical cation from 1,4-bis(isopropylthio)benzene


and b). However, we have not been able to achieve a full interpretation of these spectra because of their complexity and line overlap.

Conformational isomerism is, of course, also possible in the tetrasubstituted benzenes (IIIa, b) and (Va, b), which may exist in ten and seven distinguishable forms, respectively. In the case of the cation from 1,2,4,5-tetrakis(methylthio)-benzene (Va) the sharpness of the spectral lines and the absence of signals not belonging to the main spectrum indicate that one of the seven possible isomers is by far the most stable. If we discard on steric grounds all the structures where two adjacent methyl groups point towards each other, the equivalence of the aryl protons and that of the four methyl groups can be accounted for only by conformation (X).

The radical cation from (IIIa) was also found to exist in a single conformation which is probably (XI), as it is characterized by a plane of symmetry bisecting the bonds C(2)–C(3) and C(5)–C(6).

In the cation of the hexakis(methylthio)-derivative (Ia), despite the considerable steric crowding, the magnitude of the hyperfine splittings suggests that if deviation of the methyl groups from coplanarity with the aryl ring exists, it is in fact
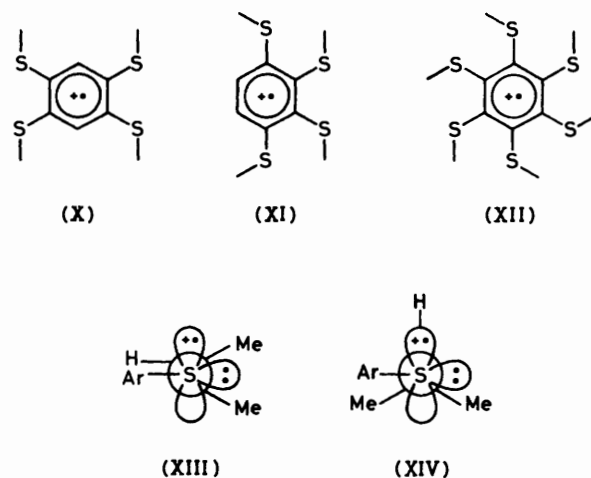
rather small. The conjugative interaction of the sulphur lone pair with the π-system seems therefore strong enough to overcome steric repulsion between the alkylthio-groups, and the conformation adopted by this cation should be (XII).

The e.s.r. spectra of the radicals from the (isopropylthio)-benzenes (Ib), (IIIb), and (Vb) are not resolved to the same extent; however, from the symmetry of the spectral pattern it can be inferred that they too exist in a single conformation, presumably the same as that of the corresponding methylthio-derivative.

A further point of interest concerns the conformation adopted by the isopropyl groups in these cations. The conformational preference of a proton in the β-position with respect to a radical site (in the present case the sulphur atom) may be established by means of the usual relation (1) where

$$a(H_\beta) = A + B\langle\cos^2\theta\rangle \qquad (1)$$

θ is the dihedral angle between the symmetry axis of the p_z orbital on sulphur and the C_β–H_β bond. The constant A is usually neglected while B is assumed to be twice the methyl proton coupling in the corresponding methyl-substituted radical, where $\langle\cos^2\theta\rangle$ is $\frac{1}{2}$.

In the radical cations of the isopropylthio-derivatives two limiting conformations can be envisaged, in which the iso-propyl hydrogen lies either in the nodal plane of the sulphur $3p_z$ orbital (XIII) or in an eclipsed position with respect to it (XIV). Because of the torsional oscillations about the equilibrium position $a(H_\beta)$ is expected to be intermediate between 0 and $B/2$ in the former case, and between $B/2$ and B in the latter one.

The e.s.r. data for the tetrasubstituted (III) and (V), tri-substituted (VII), and disubstituted (IX) compounds show that the ratio a^H_{Pri}/a^H_{Me} is < 1, *i.e.* the conformation adopted by the isopropyl group is (XIII). This suggests a stronger hyperconjugative interaction between sulphur and the C_β–Me than with the C_β–H bond, and is consistent with the reported conformational preference of the ethyl group in the radical cation of 1,4-bis(ethylthio)benzene[1] where the methyl is eclipsed with the sulphur $3p_z$ orbital.

On the other hand, the ratio of $a^H_{Pri}/a^H_{Me} > 1$ found in the cations from hexakis(alkylthio)benzenes (I) indicates that the isopropyl groups adopt preferentially conformation (XIV), this providing evidence that the stabilization due to hyper-conjugation cannot counterbalance the now dramatic re-pulsion between the alkylthio-groups. An examination of molecular models suggests the most stable geometry of this radical to be (XV), where half of the isopropyl groups have

(XV)

Scheme.
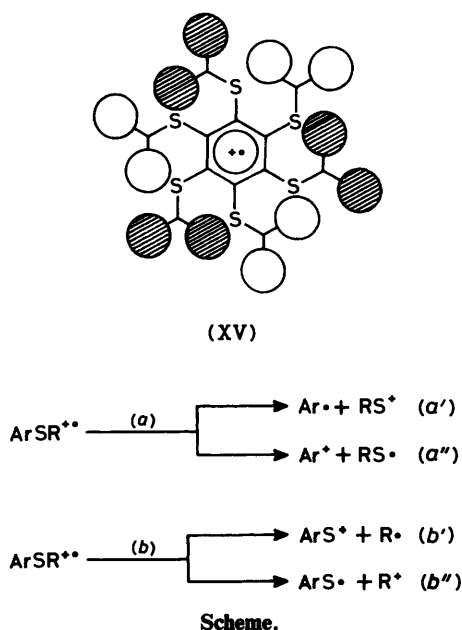
methyls above and the other half below the plane of the aromatic ring.

PMO Interpretation of the Fragmentation Processes.—The fragmentation reactions of radical cations of poly(alkylthio)-benzenes can be qualitatively rationalized in terms of the Perturbational Molecular Orbital (PMO) method, following an approach similar to that recently discussed by Rossi to describe the decomposition of certain radical anions.[8]

In principle the fragmentation of an ArSR$^{+\cdot}$ cation may occur in several different ways involving the rupture of either the Ar—SR (*a*) or the ArS—R (*b*) bond as shown in the Scheme.

The e.s.r. data provide evidence that route (*a*) is preferred for the methylthio-derivatives while they do not give any indication about the fragmentation of the poly(isopropylthio)-benzene cations. Since the reaction co-ordinate for the decomposition of ArSR$^{+\cdot}$ into a neutral radical and a positive ion has to be the same as for the combination of these species, we shall consider for simplicity the pathway for the latter reaction. The MOs that will be taken into account are σ of the coupling species and π of the aryl group. These are schematically represented in Figure 2 where the ordering of the nonbonding σ orbitals of the various fragments is based on the ionization potentials of the corresponding radicals, *i.e.* 9.2,[9] 8.06,[10] 9.85,[11] 8.63,[10] and 7.5 eV [12] for Ph·, MeS·, Me·, PhS·, and Me$_2$CH·, respectively.

During the coupling process the σ and σ* orbitals of the bond being formed become increasingly separated while the energy of the other orbitals changes only slightly. Since in the resulting radical cations the unpaired electron has been found to occupy an MO of π-symmetry, in the reaction co-ordinate there must be a crossing point between the incipient σ molecular orbital and the π orbital, from which the unpaired electron is transferred to the π orbital. The two pathways corresponding to the reverse of the fragmentation reactions (*a*) and (*b*) are shown in Figure 2.

The stability of the radical cations toward fragmentation depends on the energy gap between the π and the Ar—SR or ArS—R σ MOs. If the gap is small, promotion of one electron into the π orbital will produce weakening of a single bond and will lead eventually to fragmentation, following the same
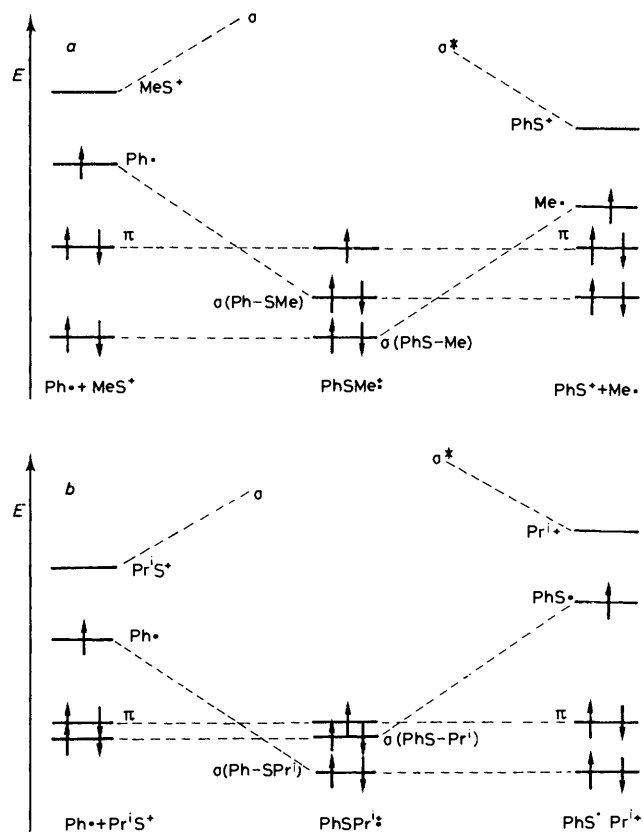

Figure 2. Changes in energy during the coupling process of *a* a phenyl radical with a MeS$^+$ cation (left) or a PhS$^+$ cation with a methyl radical (right); and *b* a phenyl radical with a Pr^{i}S$^+$ cation (left) or a Pr^{i+} cation with a phenylthiyl radical (right), to give an alkylthiobenzene radical cation

reaction co-ordinate as for the reverse combination reaction. The e.s.r. data suggest that this extra energy needed by the π radical to become a σ radical can be easily gained by molecular collisions. If this interpretation is correct Figures 2a and b show that different fragmentation paths are expected for the methylthio- and isopropylthio-derivatives, since the highest doubly occupied molecular orbital (HOMO), and thus closest to the π SOMO, is the σ MO of the Ar—SMe bond and of the ArS—Pr^i bond, respectively. Therefore the easier pathway for decomposition should be (*a'*) for the poly(methylthio)benzene and (*b'*) for the poly(isopropylthio)benzene radical cations. In the former case the nature of the secondary radicals observed in some instances is consistent with the predicted fragmentation pattern; on the other hand, the failure to detect secondary radicals for the isopropylthio-compounds suggests that these fragment in a different fashion than their methylthio-analogues, although there is no experimental evidence that the chosen route is (*b'*).

Another factor determining the ease of decomposition is the low spin density at the sulphur suffering fragmentation. For instance, on energy grounds only the 1,4-bis(methylthio)-benzene cation (IXa) should fragment more easily than the pentakis(methylthio)-analogue (IIa), since in the latter one the SOMO π orbital is higher in energy and therefore more distant from the σ of the Ar—SMe bond. The experimental data however show that the former cation is fairly stable while that from (IIa) is not. Since in (IXa) the spin density is essentially localized on the sulphur atoms and on the linked C(1) and C(4), it seems that the elimination of an RS$^+$ cation

is made more difficult by this excess of electron density. On the other hand, in the cation from (IXa) MO calculations show that the SOMO has a node at C(3), and in fact the linked SR group may easily fragment to give (Va). Similarly, the cation from 1,2,3,4-tetrakis(methylthio)benzene (IIIa) should undergo fragmentation at the 2 or 3 position, *i.e.* at a sulphur with a very small unpaired electron density, to be able to give (Va) eventually.

Acknowledgements

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