Radical cations of Organic Sulphides and Disulphides formed by Radiolysis: an Electron Spin Resonance Study

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Exposure of dilute solutions of various organic sulphides in fluorotrichloromethane at 77 K to ^{60}Co γ-rays gave species identified by their e.s.r. spectra as the parent radical cations. The average β-proton coupling $(R_2CH\dot{S}R)^+$ of *ca.* 20 G is about half that for the corresponding ether cations, indicating greatly reduced σ–π delocalisation. However, the spread of *g*-values (*ca.* 2.032, 2.015, 2.00) is much greater than that for the ether cations. These cations readily react with other disulphide molecules to form $(R_2S \overset{\cdot}{-} SR_2)^+$ dimer cations. The spectrum for tetrahydrothiophene (tetramethylene sulphide) exhibits a large coupling to two axial protons (*ca.* 42 G) and two equatorial protons (*ca.* 19 G), the coupling constants again being about half those for tetrahydrofuran cations. However, conformational inversion did not occur below the softening point of the solids (*ca.* 160 K) in marked contrast with the ether cations. The three-and four-membered ring cations (ethylene and trimethylene sulphide cations) gave very similar spectra with $g_x = g_y$, and four equivalent protons having an isotropic coupling of *ca.* 31 G. Thus their structures are similar to the normal $R_2S\cdot^+$ cations, the equivalence of the *g*-values being interpreted in terms of effective C–$\dot{S}$–C bond angles (θ) close to 90°. This, in turn, implies that $\theta > 90°$ for the unconstrained cations. It is noteworthy that the ethylene oxide (oxirane) cation exhibits a smaller coupling to its four protons (16 G). This implies a drastic change in structure for the oxirane cation which is clearly not the case for the sulphur analogue. Disulphides of structure R–S–CH$_2$–S–R form cyclic σ^* radicals with weak S–S bonding, in marked contrast with the oxygen analogues (acetal cations) which have π-structures conferring very high spin-density onto the CH$_2$ protons. Other molecules containing two RSR units form similar cyclic σ^* radicals. Persulphides of structure RS–SR readily give the π-cations $(R\dot{S}SR)^+$, characterised by *g*-values in the region of 2.035, 2.018, 2.002. The smaller range of *g* values for $(PhS \overset{\cdot}{-} SPh)^+$ cations is interpreted in terms of *ca.* 30% spin-delocalisation into both the benzene rings.

Radical cations of ethers $(R_2O\cdot)^+$ have only recently been prepared in low-temperature matrices, and studied by e.s.r. spectroscopy.[1-4] In contrast, claims to have studied the e.s.r. spectra of various dialkyl sulphide cations $(R_2S\cdot)^+$ have been frequent during the past 15 years.[5,6] However, it is our opinion that at least some of these identifications were incorrect, the electron-loss centres in irradiated organic sulphides (R_2S) being better represented as dimer cations, $(R_2S \overset{\cdot}{-} SR_2)^+$, with a σ^* structure.[7] Despite opposition to this suggestion,[8] we still maintain that the dimer-cation formulation is correct.[9]

Possibly the first authentic $(R_2S)^+$ cation to be studied by e.s.r. spectroscopy was the di-t-butyl derivative.[9] This was prepared in a sulphuric acid matrix on annealing above 77 K, a technique which is sometimes suitable for the preparation of radical cations. However, it has recently been established that neutral solutes (S) in certain halogenated solvents such as fluorotrichloromethane (CFCl$_3$) can readily be converted into their cations (S$^+$), or into unimolecular breakdown products thereof, by exposure to ionizing radiation at low temperatures,[10-13] provided their ionization potentials are less than that of the solvent (*ca.* 11.8 eV). We therefore undertook a survey of the e.s.r. properties of organic sulphides in parallel with our studies of ether cations.[3,4] While this work was in progress, results for the dimethyl sulphide cation, $(Me_2S\cdot)^+$, prepared by this technique were published.[14] Also, we have briefly reported some of our work on cyclic disulphides.[15]

As stressed above, the σ^* dimer cations, $(R_2S \overset{\cdot}{-} SR_2)^+$, are well characterised, both in the solid state,[7,9] and in solution.[16] Furthermore, they have been extensively studied by pulse radiolysis using their intense visible absorption bands.[17-19] Some π-disulphide cations, $(RS \overset{\cdot}{-} SR)^+$ have also been prepared in sulphuric acid media,[9] and we have briefly mentioned our results for $(Bu^tS \overset{\cdot}{-} SBu^t)^+$ cations in Freon.[20] Other reports on the formation and study of $(RSSR)^+$ cations in matrices include work on $(MeS–SMe)^+$,[21] and the diamyl derivative.[22]

The aim of the present work was to prepare a range of sulphur-centred cations using CFCl$_3$ and related solvents, and to compare their structures and reactivities with those of the corresponding oxo-derivatives.

Experimental

The organic sulphur-containing samples were prepared and analysed as previously described.[4] All samples were the best available grades, except for 1,3-dithiacyclopentane which was prepared synthetically. The samples were purified, if necessary, their purities being checked by n.m.r. spectroscopy.

Solutions in redistilled CFCl$_3$ (usually 1:1000 v/v) were frozen as small spherical beads in liquid nitrogen, and exposed to ^{60}Co γ-rays at 77 K in a Vickrad cell for up to 1 h at a dose rate of *ca.* 1 Mrad h^{-1}. *X*-Band e.s.r. spectra were measured at 77 K with a Varian E-109 spectrometer calibrated with a Hewlett–Packard 5246L frequency counter and a Bruker B-H12E field probe, which were standardised with a sample of diphenylpicrylhydrazyl. Samples were annealed either using a Varian variable-temperature insert, or by decanting the nitrogen from the insert Dewar and following spectral changes, with the re-addition of liquid nitrogen whenever these were significant. *Q*-Band spectra were measured on a Bruker spectrometer at Imperial College.

Results and Discussion

In the following, we assume that the major species detected by e.s.r. spectroscopy are the parent radical cations or their unimolecular decomposition products. Spectral interpretation

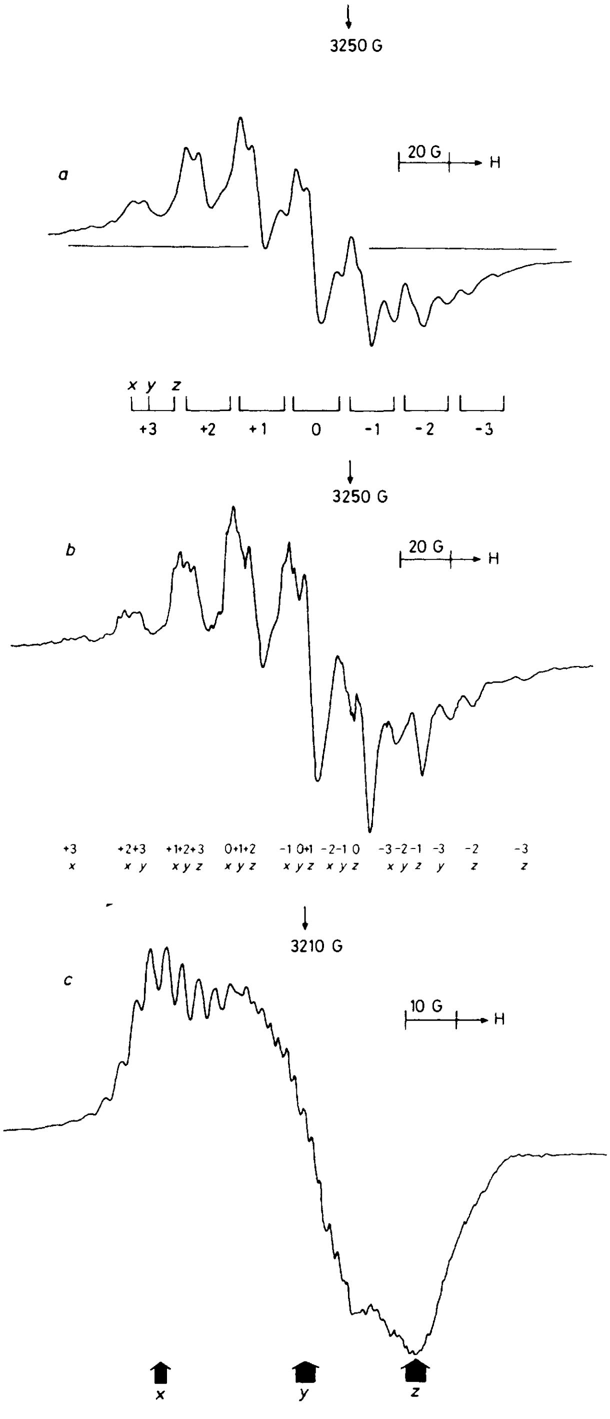
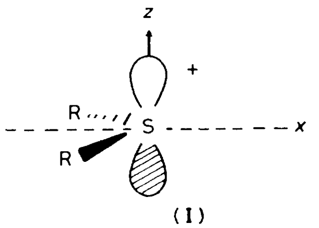


Figure 1. First-derivative *X*-band e.s.r. spectra for a dilute solution of Me_2S in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, *a* at 130 K, showing features assigned to $Me_2S^{+\cdot}$ cations; *b* at 77 K showing extra splitting assigned to chlorine; *c* for $(CD_3)_2S^{+\cdot}$ at 77 K, showing ^2H and chlorine splitting

is more difficult than for the ethers[4] since, for all the species studied, there are large positive *g*-shifts giving rise to extra features that can readily be mistaken for poorly resolved hyperfine splitting. These studies have been greatly improved and facilitated by the study of selected spectra at *Q*-band as well as *X*-band frequencies, and we are confident that the interpretations are reasonably accurate.



(I)

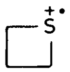
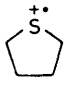
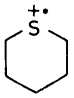
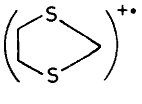
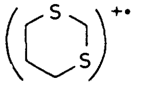
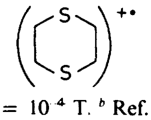
Acyclic Monosulphides.—This problem is directly illustrated by results for $Me_2S^{+\cdot}$ cations [Figure 1; structure (I)]. There can be no doubt that the two methyl groups give rise to the expected septet with $A(^1H) \approx 21$ G, but, as can be judged from these spectra, the *g*-values are less readily deduced. Those reported by Wang and Williams[14] (the values reported in ref. 14 have been corrected, the new values being those given in Table 1) refer to the cation at *ca.* 130 K, and the low value for $g_{max.}$ suggests that partial averaging occurs at this temperature, implying these are not the principal values (see Figure 1*a*). The spectrum for $Me_2S^{+\cdot}$ cations at 77 K is less readily analysed because of the appearance of some small extra splittings (Figure 1*b*) and it is not clear how to derive the correct *g*-values. The extra splitting seems to be confined to the g_x ($g_{max.}$) features, and it may be due to a weak interaction with one chlorine nucleus of a matrix molecule, of the type detected for methyl formate[23] and other radical cations in Freon[24] (see below).

To help in the spectral analysis, we also studied the perdeuteriated cation, $(CD_3)_2S^{+\cdot}$ (Figure 1*c*). In this case, the *x* features are fortuitously well resolved because the ^2H coupling (*ca.* 3.3 G) is close to the quartet splitting shown in Figure 1*b* (*ca.* 3.1 G). This gives g_x in the region of 2.032, in good agreement with our results for other $R_2S^{+\cdot}$ cations (Table 1). The g_y features, which were not resolved into sub-sets for the $(CH_3)_2S^{+\cdot}$ spectra, show a definite multiplet splitting of *ca.* 1.5 G for the $(CD_3)_2S^{+\cdot}$ spectra. Since $A_y(^2H)$ must be close to 3.0, we assign this to $^{35/37}Cl$ (separate ^{35}Cl and ^{37}Cl features would not be distinguishable under our conditions). Thus the *x* and *y* features are relatively well resolved because the two coupling constants are fortuitously close multiplets of each other. Since the *z* features in Figure 1*c* are not resolved, such coincidences cannot be occurring. From the $(CH_3)_2S^{+\cdot}$ spectra, we know that $A_z(^1H) \approx 21$ G and $A_z(Cl) \approx 1.5$ G. Hence $A(^2H)$ should be *ca.* 3.2 G: if $A_z(Cl)$ is in the region of 1.4 G, the *z* features would not be resolved for linewidths equal to those found for the *x* and *y* features. Unfortunately, we cannot be more precise than this at present.

We therefore turned to the t-butyl derivative in the expectation that there would be no proton hyperfine coupling, that weak matrix interactions would be sterically hindered, and that motional averaging would be unimportant. In fact, the 77 K *X*-band spectrum again shows extra splittings which are especially clear on the g_x ($g_{max.}$) features, which were lost reversibly on annealing, (Figures 2*a* and *b*), in close analogy with the dimethyl derivative. However, the *g*-values obtained (2.032, 2.015, 2.005) are fairly close to the maximum values observed in this study, indicating that little motional averaging can be occurring at 77 K. These conclusions are supported by the *Q*-band spectrum, which comprised three resolved sets of multiplets at *g* 2.033, 2.016, and 2.004. The *x* features appeared as an asymmetric quintet with $A \approx 9$ G. We conclude that for the acyclic $R_2S^{+\cdot}$ radicals $g_{max.}$ is *ca.* 2.032, and the data obtained for $Me_2S^{+\cdot}$ at *ca.* 130 K are motionally averaged values. The fact that $g_{int.}$ for $Me_2S^{+\cdot}$ is hardly changed at 130 K suggests marked libration about the long axis (*x*) as the source of this averaging.

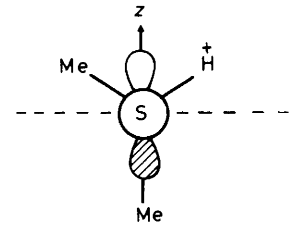
Results for the diethyl derivative are again somewhat ambiguous, although the general form of the spectrum

Table 1. E.s.r. parameters for monosulphide and disulphide cations

Cation (in CCl_3F)	T/K	^{1}H hyperfine coupling (G)[a]	g-Values			
			g_x	g_y	g_z	g_{av}
$(Me)_2S^{+\bullet}$	130	(6 H), 21	2.0190[b]	2.0145	2.0076	2.0137
$(Me)_2S^{+\bullet}$	77	*c*	2.032		2.002	
$(CD_3)_2S^{+\bullet}$	77	(6 D), 3.3	2.032	2.015	2.002	2.0163
$(Bu^t)_2S^{+\bullet}$	77	*c*	2.032	2.015	2.005	2.0160
$(Bu^t)_2S^{+\bullet}$	*ca.* 130		2.030	2.007	2.007	2.0143
$(Et)_2S^{+\bullet}$	77	(2 H), 18—20	2.032	2.016	2.002	2.0170
$(Pr^i)_2S^{+\bullet}$	77	(2 H), *ca.* 10	2.032		2.002	
	*ca.* 120	(4 H), 31	2.024	2.024	2.002	2.0166
	*ca.* 120	(4 H), 31	2.023	2.023	2.002	2.0160
	77	(2 H), 20 (2 H), 40	2.027	2.014	2.002	2.0143
	77	(2 H), 25 (2 H), 5	2.030	2.019	2.002	2.0170
	*ca.* 120	(4 or 6 H) *ca.* 6				2.0080
		≤6	2.018	*ca.* 2.008	2.002	
	77	*ca.* 4.5	2.019	*d*	2.002	

[a] G = 10^{-4} T. [b] Ref. 14 corrigendum. [c] Structure undefined (see text). [d] Uncertain.

establishes that the species is, indeed, the radical cation. The most satisfactory analysis suggests coupling to two nearly equivalent protons (giving three sets of triplets as indicated in Figure 3*a*). This gives $g_x \approx 2.032$, $g_y \approx 2.016$, and $g_z \approx 2.000$ with $A(^1H)$ 18—20 G. The Q-band spectra confirm the g-values but the proton coupling was poorly defined. There were no well defined changes on annealing prior to loss of this species. These results contrast with those for the $Et_2O^{+\bullet}$ cation, for which four equivalent protons giving the average coupling were detected.[4]



(II)

The results for the di-isopropyl derivative are readily interpreted in terms of two equivalent protons with *ca.* 10 G coupling (Figure 3*b*). The resulting g-values are very close to those for $Me_2S^{+\bullet}$ (Table 1), and the A-values suggest a conformation close to that shown in structure (**II**) for each alkyl group. However, this spectrum is remarkably similar to that for the di-t-butyl sulphide cation (Figure 2*a*), which contains no β-protons. It is possible, but unlikely, that the unexpected hyperfine features for the di-t-butyl derivative are due to chlorine. We are inclined to reject this because the coupling is greatest on the x features whereas normally $A_{max.}$ is along z, and the Q-band spectra suggest five features not four. Hence we favour ^{1}H coupling, in which case the results suggest coupling to four equivalent protons. These must be selected from the 18 γ-protons available. That this might be correct is indicated by the partially averaged spectrum shown in Figure 2*b*. Here the g-tensor has become axial, and the hyperfine coupling has been lost. Probably one proton for four of the methyl groups can adopt a W-plan structure which facilitates electron delocalisation. On annealing, rotation of the methyl groups removes this coupling.

Cyclic Monosulphides.—E.s.r. spectra for the three- and four-membered ring cations at *ca.* 120 K are almost identical, and far easier to interpret since they display axial symmetry with no

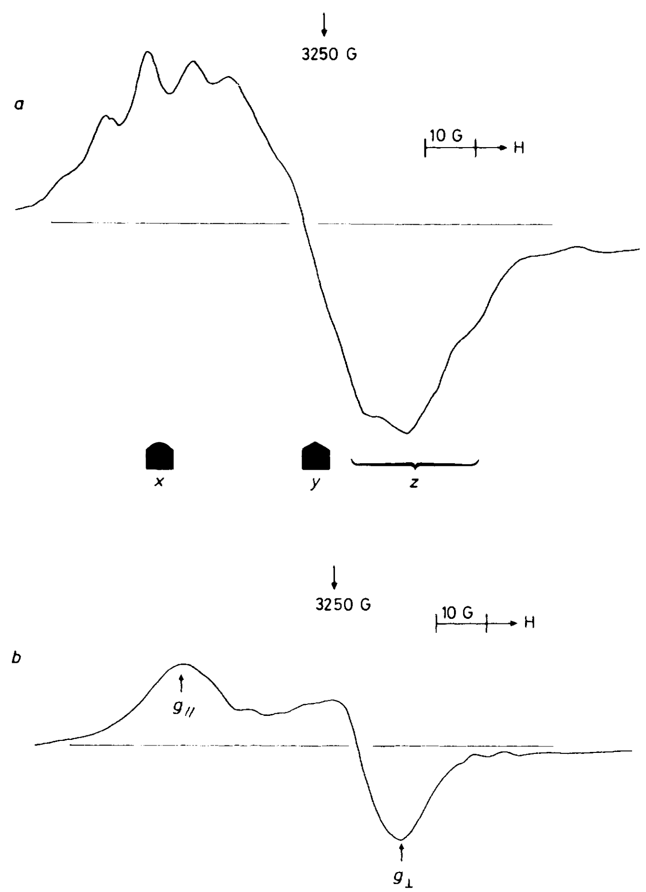


Figure 2. First-derivative *X*-band e.s.r. spectra for a dilute solution of $(Bu^t)_2S$ after exposure to ^{60}Co γ-rays at 77 K, *a* at 77 K, showing features assigned to stationary $(Bu^t)_2S^{+\bullet}$ cations and *b* at *ca.* 130 K for the librating cations

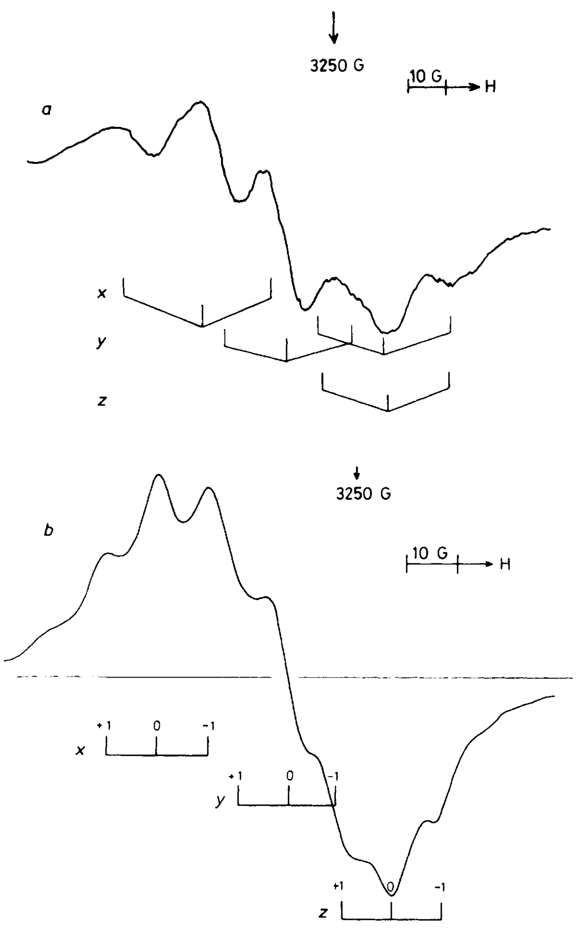
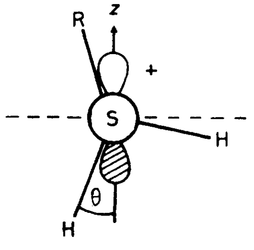
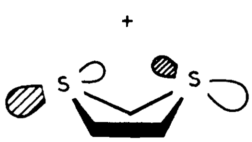


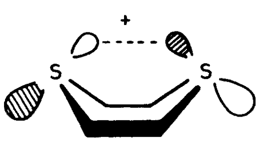
Figure 3. First-derivative *X*-band e.s.r. spectra for diethyl and di-isopropyl sulphide in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to *a* $(Et)_2S^{+\bullet}$ cations and *b* $(Me_2CH)_2S^{+\bullet}$ cations



(III)



(IV)



(V)

sign of any hyperfine interaction with matrix nuclei (Figures 4*a*, *b*). For both, the proton coupling is almost isotropic and equivalent for all four protons with $A(^1H)$ *ca.* 31 G. In both cases, the 77 K spectra were much less well defined with signs of possible matrix interactions. We have not attempted to analyse these spectra, but suggest that weak reversible solvent interaction is responsible for their complexity.

Results for the tetramethylene sulphide cation show that this now behaves like the dialkyl derivatives, with three *g*-values in the normal regions and strong coupling to two (axial) protons and relatively weak coupling to two (equatorial) protons (Table 1). On warming above 77 K, there was partial averaging of the *g*-tensor components (Figure 4*c*), but we were unable to detect any averaging of the proton hyperfine coupling constants, in marked contrast with the behaviour of the tetrahydrofuran cation.[1] This shows that the *g*-value averaging is due to some specific motion of the whole molecule, rather than to conformational averaging. Since g_x and g_y are averaged, this must be preferential rotation about the *z*-axis, that is roughly in the molecular plane.

As was found for the tetrahydropyran cation,[4] the six-membered ring derivative had a very different spectrum, with a reduced total hyperfine coupling relative to the five-membered ring cation. On annealing, the spectrum again acquired axial symmetry (Figure 4*d*) with strong coupling to two equivalent protons (25 G) and unresolved weak coupling to the other two ($\leq$ 5 G). This marked reduction in proton coupling constants is just that observed for the corresponding ether cation.[4] We suggest that the preferred conformation places two β-protons (equatorial) close to the molecular plane so that the two axial protons interact quite strongly, as indicated in structure (**III**). With this arrangement the axial proton coupling should be

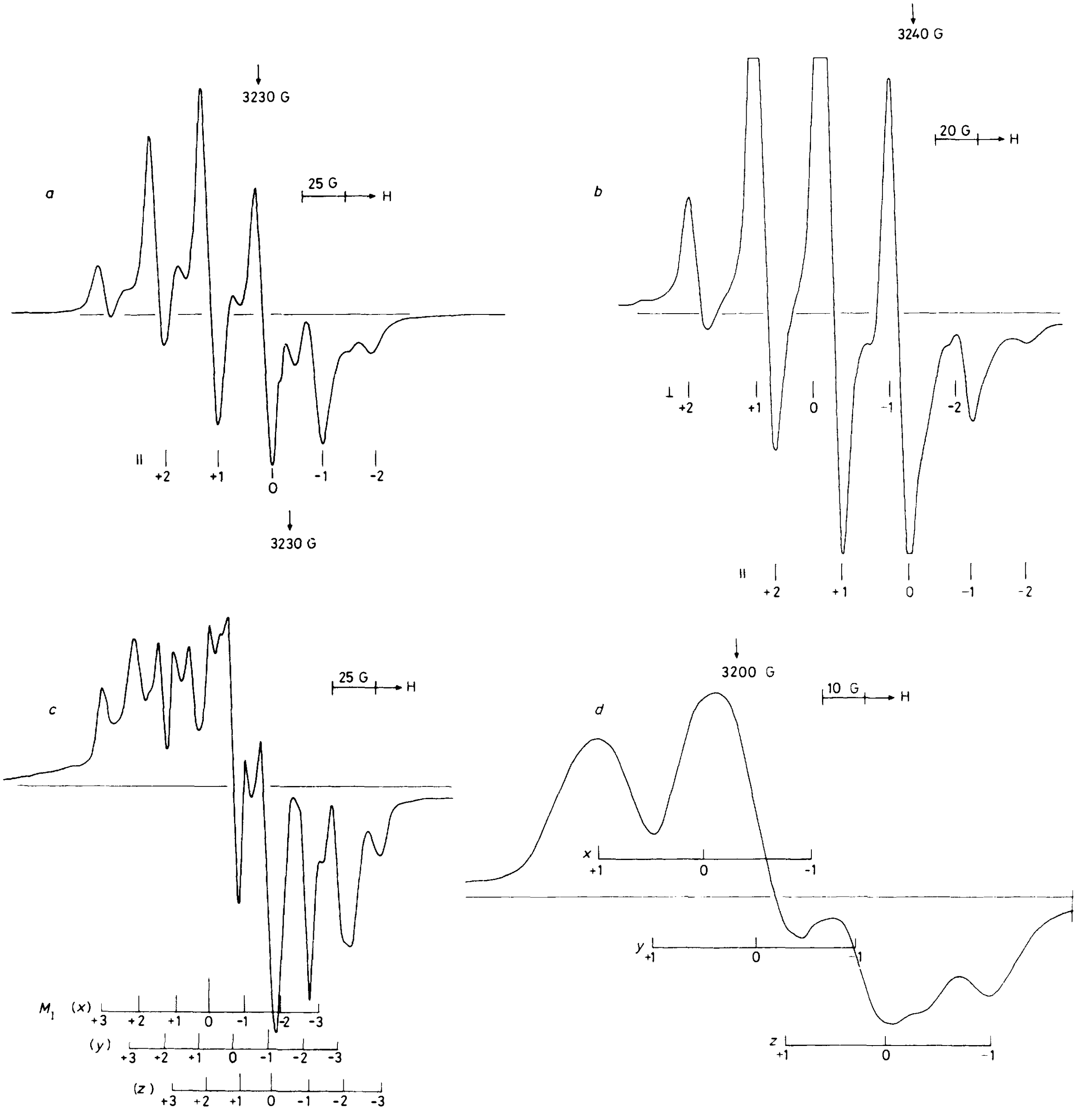


Figure 4. First-derivative *X*-band e.s.r. spectra for various cyclic sulphides in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned *a* to $(CH_2)_2S^+$ cations, *b* to $(CH_2)_3S^+$ cations, *c* to $(CH_2)_4S^+$ cations, and *d* to $(CH_2)_5S^+$ cations.

between the average of *ca.* 20 G and the value of *ca.* 30 G for θ 30°. The value of 25 G requires $\theta \approx 38°$, which is reasonable.

1,3-*Dithiacyclopentane and* 1,3-*Dithiacyclohexane Cations*.— As mentioned above, these are of particular interest since their oxygen analogues have e.s.r. spectra dominated by very large (*ca.* 150 G) triplet splittings.[3,15,25] This π-structure is clearly not that adopted by these disulphur derivatives, the maximum proton coupling being *ca.* 6 G (Figure 5). For the cyclopentane derivative the maximum *g*-value at 77 K is 2.0155 (±0.0015), the uncertainty arising because of our uncertainty in the number of hyperfine components. This is far too small for a localised $R_2S^{+\bullet}$ cation and the intense blue colour also rules out this structure. However, the $g_{max.}$ value is close to that observed for the cation of 1,3-dithiacyclohexane, which is known to form a three-electron sulphur–sulphur bond.[19] We conclude that both cations have such bonding.

This result, besides providing an interesting contrast with oxygen, is remarkable in that Asmus and his co-workers[19] were unable to detect a σ* cation of the cyclopentane derivative by optical spectroscopy. They concluded that it wasn't formed under their conditions and explained this by arguing that the structure of the cation must be π rather than the normal σ. Our results show that this is not the case at low temperatures. However, to form a σ* species, either the ring must be seriously strained or there must be 3*s*–3*p* admixture, as indicated in (**IV**). This problem is far less severe for the cyclohexane derivative and, in this case, the σ* cation (**IV**) was clearly detected by pulse-

Table 2. E.s.r. parameters for persulphide cations

Cation (in CCl_3F)	T/K	^1H hyperfine coupling (G)	g-Values			
			g_x	g_y	g_z	g_{av}
$(Me_3CSSCMe_3)^{+\bullet}$	77		2.036	2.017	2.002	2.0183
$(Me_3COOMe_3)^{+\bullet a}$	77		2.015	2.008	2.002	2.0083
$(MeSSMe)^{+\bullet b}$	77	(6 H), 8	2.036	2.017	2.002	2.0183
$(Me_2HCSSCHMe_2)^{+\bullet c}$	77	(2 H), *ca.* 11	2.035	2.018	2.003	2.0186

[a] See ref. 20. [b] Also performed in D_2SO_4 (see ref. 20). [c] See ref. 22.

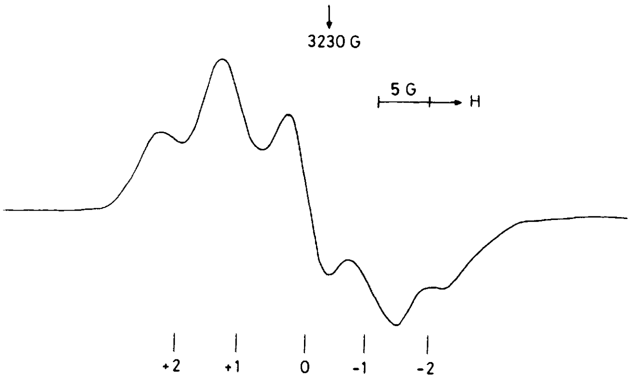


Figure 5. First-derivative X-band e.s.r. spectrum for 1,3-dithiacyclopentane in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the corresponding cation

radiolysis.[19] It is interesting that the colour changes from blue to violet on going from five- to the six-membered ring, which establishes a marked shift to high energy. (The blue colour implies a band in the near i.r.).

On annealing, the spectrum for the cyclopentane derivative cation changed reversibly to give the five-line spectrum shown in Figure 5. This has g_{av} 2.008 and A_{iso} 6 G. It is probable that there are two broad unresolved outer lines giving a septet for six equivalent protons. Otherwise, we require that only four of the six protons couple strongly.

1,4-Dithiacyclohexane Cations.—The results again require the formation of an S–S σ-bond, which is supported by the appearance of an intense red-brown colouration. The spectrum showed no proton structure in the broad x feature at *ca.* 2.019 but some resolution of the y and z features was clear with $A(^1H) \sim$ 4—5 G. We therefore agree with Asmus[19] that a boat structure must be formed, as shown in (**V**). We note that for 1,4-dioxane cations, we postulated a similar structure with weak O–O σ-bonding.

Persulphides.—We have already published our e.s.r. spectrum for the di-t-butyl derivative (Figure 1 of ref. 20). This comprises three well defined g features with no resolved hyperfine coupling, thereby fixing the g-value range to be expected. Our spectrum for the dimethyl derivative $(MeS\text{–}SMe)^+$ was identical with that shown for this cation in a sulphuric acid matrix (Figure 1 of ref. 9), with three sets of septets. This confirms our original identification. Taken together with Truby's results for the diamyl derivative,[22] we conclude that the normal range of g-values for these cations is *ca.* 2.036, 2.017, and 2.002 (Table 2).

The only corresponding oxygen derivative is, so far as we know, the di-t-butyl peroxide cation, also prepared in this manner.[20] This showed three distinct g features, the g-shifts being almost in the ratio of the spin–orbit coupling constants. Thus $g_{max.}$ $(ROOR)^+$ = 2.015 (predicted 2.015) and g_{int} = 2.0082 (predicted 2.008). Both have $g_{min.}$ close to the free-spin value.

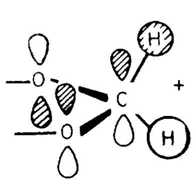
Aspects of Structure.—$R_2S^{+\bullet}$ radicals are isoelectronic with $R_2P\bullet$ radicals which have been shown to have a SOMO comprising primarily the $3p_z$ orbital on phosphorus, normal to the radical plane (z).[26] The $3s$ contribution is small (*ca.* 2—3%) and presumably arises *via* spin-polarisation of the σ-bonding electrons. Roberts and his co-workers[27] measured the isotropic ^{33}S coupling for $(Bu^t)_2S^{+\bullet}$ and this was also small, corresponding to *ca.* 3% $3s$ population.

The magnitude of the proton hyperfine coupling constants for $R_2S^{+\bullet}$ cations shows that hyperconjugative delocalisation is about half that for the corresponding ether cations, the decrease presumably reflecting the lower electron affinity of cationic sulphur and poorer overlap with the more diffuse $3p$-orbital. Nevertheless, the hyperfine coupling constants are about equal to those observed for carbon-centred radicals. The g-axes are assigned as in (**I**), the maximum shift arising *via* coupling to the formally non-bonding 'lone-pair' electrons in an s–p hybrid orbital lying along y. The intermediate g-value is then g_y, the coupling now involving mainly the σ-bonding electrons. The large difference between g_x and g_y requires that the C–$\hat{S}$–C bond angle, θ, be $>90°$, since for $\theta = 90°$ they must be equal, by symmetry. The bond angle for the parent Me_2S molecule is *ca.* $105 \pm 3°$. For the four-membered ring sulphide $g_x = g_y$, as predicted for $\theta \approx 90°$. This is also true for the three-membered ring suggesting that the $3p_x$ and $3p_y$ orbitals are used equally for bonding, with no significant s–p hybridisation.

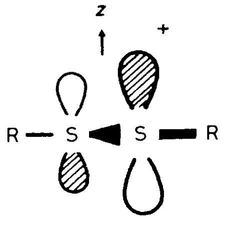
Dimerisation to form $(R_2S \overset{\centerdot}{-} SR_2)^+$ cations involves overlap between these $3p_x$ orbitals. There is a real increase in s-character for the new σ^* orbital relative to that for the parent cations,[27,28] but it remains small so that s–p hybridisation cannot be very significant. This is in marked contrast with results for $(R_3P \overset{\centerdot}{-} PR_3)^+$ σ^* dimers, which have very large ^{31}P isotropic coupling constants, indicating extensive s–p orbital hybridisation.[29] This difference is a direct result of the extra alkyl groups in the R_3P units, and is also reflected in the SOMOs for $R_3P^{+\bullet}$ and $R_2S^{+\bullet}$ cations.

It is interesting that our results strongly suggest a σ^* structure for the cyclic cation shown in (**IV**), rather than the delocalised π-structure found for the corresponding acetal [structure (**VI**)].[15,25] The ring structure should reduce the overlap for the σ^* species and might have rendered the π-structure more favourable. Our results, nevertheless, support the σ^*-structure, as does the appearance of a strong blue colour, indicating an electronic absorption in the near i.r. region. It seems that this species is much less stable than the normal σ^* dimers, since it was not detected at room temperature by pulse radiolysis.[19]

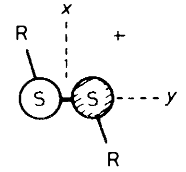
The $(RS \overset{\centerdot}{-} SR)^+$ cations have the expected π^*-structures. The fact that g_z is close to the free-spin value (2.0023) shows that the radicals must be effectively planar, as indicated in (**VII**), the π^*

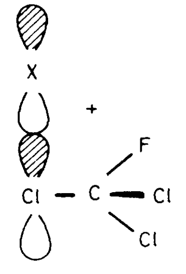


(VI)



(VII)





(VIII)

orbital being largely $|3p_z - 3p_z>$. Electron-loss is expected to favour this planar configuration. The minimum g-value should thus be along the normal (z). Both g_x and g_y should be greater than the free-spin value. The field along x should couple the SOMO mainly with the S–S σ-bonding orbital whilst the field along y will mix the SOMO mainly with the C–S orbitals. Hence g_x should be greater than g_y for the π cations. As stressed previously, the same assignments cannot be made so readily for the peroxide cations, $(ROOR)^+$.[20]

Aspects of Mechanism.—The most interesting result is the contrast in reactivity of $R_2O^{+\cdot}$ and $R_2S^{+\cdot}$ cations. The former react with parent ether molecules by hydrogen extraction as, for example, in (1), whilst the latter react to form σ* dimers as in (2). We stress that this contrast is not exclusive: oxygen radical centres *can* form σ* adducts, as is found, for example, for BrO_4^- $(BrO_4)_2^-$ and $WO_4^{-\cdot}(WO_4)_2^{3-}$ radicals,[30] but they are rare. In the special case of 1,4-dioxolane, we think that such a weak, internal σ* bond is indeed formed.[4] In this case, internal hydrogen-atom transfer cannot readily occur, and hence does not compete.

$$R_2O^{+\cdot} + R_2CHOR \longrightarrow R_2OH^+ + R_2\dot{C}OR \qquad (1)$$

$$R_2S^{+\cdot} + R_2S \longrightarrow (R_2S \overset{\cdot}{-} SR_2)^+ \qquad (2)$$

Matrix Interaction.—In our original study of bonding between radical cations (X^+) and $CFCl_3$ molecules,[24] we postulated weak σ-bonding as indicated in (**VIII**). This structure seems to be correct for strong interactions such as are observed for alkyl halide cations,[24] methyl formate,[23,24] and acetaldehyde.[24,31,32] However, there is a stringent requirement, namely, that $A_{max.}(^{35,37}Cl)$ lies along the $g_{min.}(g_z)$ direction. This is fulfilled in the above, but not in the present examples, where A_{max} (Cl) lies close to g_{max}. We therefore suggest that there is no specific σ-bonding for such very weak adducts. We recall our analysis for the alkyl radical halide ion adducts, (R•----hal$^-$) where a non-specific charge-transfer was invoked.[33] This concept might be suitable in the present case but, as stressed previously,[32] a major difficulty seems to us to be that electron donation should then be from the HOMO of $CFCl_3$, which is expected to include two, or possibly three, equivalent chlorine atoms. Another possibility is that a purely dipolar, through-space coupling is involved. This fits the absence of any isotropic coupling (as found for the R•-----hal$^-$ adducts for which $A_\perp$ was shown to be negative[33]). The magnitude of $2B$ (*ca.* 3 G) requires a separation of only *ca.* 1.2 Å on a point-dipole model, but this model is clearly incorrect, especially for the diffuse $3p$ sulphur orbital. We are inclined to favour this model for the $R_2S^{+\cdot}$----Cl-C(F)Cl_2 adducts but see no clear reason why the dipolar axis should be x. The reversible thermal loss of this weak interaction is nicely explained by our postulate of libration about the y axis.

Acknowledgements

We are grateful to Dr. J. Gibson, Imperial College, London, for allowing us to measure the Q-band spectra on his spectrometer, and for his advice and help.

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Received 21*st December* 1983; *Paper* 3/2242