Semiempirical SCF-MO Study of the Molecular and Electronic Structures of Radicals derived from Thiols, Sulphides, and Disulphides

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Molecular and electronic structures have been calculated, using the MNDO method, for a range of radical species, but particularly cation radicals, derived from a number of simple thiols, sulphides, and disulphides. The calculations on the disulphur neutral radicals, alternatively formulated as $RSS^{\cdot}$ or $RSSR_2^{\cdot}$, lend support to the $RSSR_2^{\cdot}$ formulation and effectively exclude the alternative $RSS^{\cdot}$.

Radicals derived by radiolysis of thiols, sulphides, and disulphides have been the subject of extensive experimental studies in recent years.[1-5] Attention has focused on a number of points: the geometric and electronic structures of the radicals, in particular the nature of the SOMO; the magnitude of the proton hyperfine coupling; and the identity of the family of radicals having g values of 2.058, 2.025, and 2.001, previously denoted [1,2] X, which are formed from many thiols and disulphides and from methionine [1,2,6] and which have been identified variously as $RS^{\cdot}$,[6-8] $RSS^{\cdot}$,[9,10] and $RSSR_2^{\cdot}$.[1,2] Here we report the results of MNDO [11,12] calculations relevant to some of these questions

Calculations

All calculations were made using MNDO,[11,12] with the published parameters for sulphur,[13] implemented on a VAX 11/780 computer. UHF wavefunctions were used for open-shell species, and all geometries were completely optimised throughout, except where specifically stated otherwise.

Results and Discussion

It is convenient to discuss in turn radical species derived from thiols, dialkyl sulphides, dialkyl disulphides, and cyclic polysulphur species, before turning to the radicals denoted [1,2] X.

Radicals from Thiols.—Thiyl radicals, $RS^{\cdot}$, have been detected [1] in frozen solutions, both in the parent thiol RSH and in various alcohols. Hyperfine coupling was not resolved, and this failure was ascribed to the variation, in both strength and direction, of the hydrogen bonding in the glassy medium. However the hyperfine coupling to ^{33}S in the thiyl derived from *N*-acetyl-L-cysteine indicated [14] that, in this radical at least, the SOMO had π rather than σ character.

For the simplest thiyl radicals, $CH_3S^{\cdot}$ and $C_2H_5S^{\cdot}$, each of C_s symmetry, the SOMO is calculated to be localised primarily on the sulphur, to have A' symmetry, and to be perpendicular to the C–S bond. This accords with the experimental deduction of a π SOMO, although in radicals of this type σ and π are not strictly separable.

The hydrogen atom shift reactions [equations (1) and (2)]

$$CH_3S^{\cdot} \longrightarrow \dot{C}H_2SH \quad (1)$$

$$CH_3CH_2S^{\cdot} \longrightarrow CH_3\dot{C}HSH \quad (2)$$

are both calculated to be exothermic, for isolated species, by 0.6 kJ mol^{-1} for $CH_3S^{\cdot}$ and 26.4 kJ mol^{-1} for $C_2H_5S^{\cdot}$. The resulting rearranged radicals both have C_s symmetry, with the SOMO of A'' symmetry, being a C–S π^* orbital perpendicular to the CSH plane.

The calculated spin densities and observed A values for these, and other radicals, are collected in Table 1: in accord with the π character of the SOMO, both CH_2SH and CH_3CHSH exhibit essentially zero spin density on the thiol hydrogen.

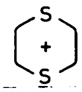
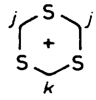
Both $MeSH^+$ and $MeSH^-$ have been reported [8] to be formed on irradiation of solid MeSH, although this interpretation of the experimental data has been doubted.[1] It was suggested [1] alternatively that the radical described [8] as $MeSH^+$ was in fact the dimeric species $(MeSH)_2^+$. The calculated $\Delta H_f^{\ominus}$ values indicate that formation of such a dimeric species from MeSH and $MeSH^+$ is exothermic by 143 kJ mol^{-1} (*cf.* 116 kJ mol^{-1} for formation [15] of the analogous $Me_4S_2^+$): the calculated spin density for methyl hydrogens is certainly consistent with this interpretation. (We discuss later the question of the scale factor between A and ρ, appropriate to the MNDO parameterisation.) A second possibility is the radical (Me′)SH–S(Me″), where the calculated hydrogen spin density is much greater for Me″ than for Me′.

For both $(MeSH)_2^+$ and MeSH–SMe, the SOMO is primarily an S–S antibonding orbital, the major component of which is parallel to the S–S direction: however there is in each case a contribution from p orbitals perpendicular to the S–S direction. The consequences of this SOMO structure are: (*a*) the calculated barrier to rotation about the S–S bond is small; (*b*) the calculated spin density at S–*H* is very dependent on conformation, approaching zero near a node of the perpendicular SOMO components. While the very small coupling to S–*H* found [1] in both $(RSH)_2^+$ and RSH–SR types of radical may be due to other factors, it is at least possible that preferred conformations may exist in the particular media employed.

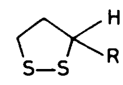
Although $MeSH^-$ is calculated to be bound, as an isolated species, with C–S 1.712 Å, and to be similarly stable with respect to dissociation into $CH_3^{\cdot}$ and SH^-, its SOMO is calculated to be σ^*, localised in the S–H bond, with a very high spin density at S–*H*, and a rather small density at C–*H* (Table). Its e.s.r. spectrum should therefore be highly characteristic. We note also that $MeSH_2$ is calculated to have its SOMO localised primarily in the S–H bonds, with again a very high spin density at S–*H*.

Radicals from Dialkyl Sulphides.—The calculated spin densities, together with the SOMO type, for simple radicals of type R_2S^+ are given in the Table. While only Me_2S^+ of these species appears to have been identified hitherto, the parent sulphides are all readily available and hence the calculated spin densities should be of value in the identification of these radicals. It has been convincingly argued [2] that many of the radicals previously identified as R_2S^+ are in fact of the type $R_4S_2^+$: the changes in $\rho(^1H)$ consequent on the conversion of Me_2S^+ into $Me_4S_2^+$ have been discussed.[15] We note here that the calculated spin densities at α-H in radicals R_2S^+ are in the

Table. Observed hydrogen hyperfine splittings, and calculated spin densities and SOMO types

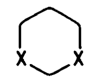
Radical	$A(^1H)/G$[a]	$\rho(^1H)$	SOMO
CH_3S	*b*	0.023 (× 3)	S(*p*π)
EtS	*b*	0.033 (× 2) −0.001 (× 3)	S(*p*π)
CH_2SH	21[c]	*ca.* 0 (S*H*) −0.051 (× 2)	(C–S)π*
CH_3CHSH	*b*	*ca.* 0 (S*H*) −0.050 (× 1) 0.022 (× 3)	(C–S)π*
CH_3SH^+	*d*	−0.041 (S*H*) 0.026 (× 3)	(C–S)π
$(CH_3SH)_2^+$	*ca.* 0[c] 5 (× 6)[c]	−0.010 (S*H*)[e] 0.005 (× 6)	(S–S)a . b[f]
$(CH_3')SH{-}S(CH_3'')$		(S*H*)[e] 0.001 (CH_3') 0.009 (CH_3'')	(S–S)*a* . *b*[f]
CH_3SH^-	*d*	0.538 (S*H*) −0.002 (× 3)	(S–H)σ*
CH_3SH_2		0.267 (× 2, S*H*) −0.010 (× 3)	(S–H)σ*
Me_2S^+	20.4[g]	0.021 (× 6)	(C–S)π*
Et_2S^+		0.029 (× 4) −0.001 (× 6)	(C–S)π*
		0.016 (× 4)	S(*p*π)
		0.027 (× 4) −0.001 (× 2)	(C–S)π*
		0.032 (× 4) −0.001 (× 4)	A_2, mainly on β-carbons
CH_3SCH_2	17 (× 2) 3 (× 3)	−0.051 (× 2) *ca.* 0 (× 3)	[S–C(H₂)]π*
CH_3SSCH_2		−0.051 (× 2) *ca.* 0 (× 3)	[S–C(H₂)]π*
Me_2S^-		−0.017 (× 6)	(C–S–C)σ*
$Me_2S_2^+$	9.1[h]	0.008 (× 6)	(S–S)π*
$Bu^t{}_2S_2^+$	Small[i]	−0.001 (× 18)	(S–S)π*
$Me_2S_2^-$	5.0[h]	0.007 (× 6)	*f*
		0.011 (× 4, α) −0.001 (× 2, β)	(S–S)π*
		0.005 (× 2, α, *ax*) 0.006 (× 2, α, *eq*) −0.002 (× 2, β)	(S–S)σ*
		See text	
		0.010 (× 2, α, *ax*) 0.012 (× 2, α, *eq*) *ca.* 0 (× 4, β)	(S–S)*
		See text	
		0.020 (× 4, *ax*) −0.001 (× 4, *eq*)	(S–S)π*
		0.042 (× 2, *j*, *ax*) 0.009 (× 2, *j*, *eq*) 0.002 (× 2, *k*)	*f*

[a] 1 G = 10^{-4} T. [b] Coupling either not resolved, or not reported: ref. 1. [c] Ref. 1. [d] Identification uncertain, ref. 8. [e] ρ(S*H*) very dependent on conformation; see text. [f] SOMO contains components both parallel and perpendicular to S–S direction. [g] Ref. 4. [h] Ref. 8. [i] Ref. 5.

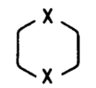


(1) a; R = H
b; R = [CH$_2$]$_4$CO$_2$H

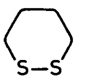
(2)



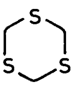
(3) a; X = S
b; X = O



(4) a; X = S
b; X = O



(5)



(6)

range 0.016—0.032, whereas in $Me_4S_2^+$ the value is only 0.005.

γ-Irradiation of pure Me_2S yields [2] the radical $CH_3SCH_2^{\cdot}$: the conformation of lowest calculated $\Delta H_f^{\ominus}$ has the CH_2 group coplanar with CSC, when the SOMO is localised primarily in the S–C(H$_2$) bond, and is of π^* character perpendicular to the $CSCH_2$ plane.

Although anion radicals of type R_2S^- have never been definitely identified, Me_2S^- is calculated to be a bound species in which the SOMO is a (C–S–C) σ^* orbital. The calculated spin density at sulphur in Me_2S^- is 0.085, whereas in $Me_2S_2^-$ and $MeS^{\cdot}$ the corresponding values are much lower (0.036 and 0.006, respectively): this again may be of value in the identification of such radicals.

Radicals from Dialkyl Disulphides.—The cation radicals $R_2S_2^+$ derived from Me_2S_2 and $Bu^t_2S_2$ (and from H_2S_2) are calculated to have planar skeletons of local C_{2h} symmetry, as suggested from experimental data.[5,8] In each species the SOMO has B_u symmetry and is a π^* orbital localised primarily on the sulphur atoms, perpendicular to the skeletal plane. Me_2S_2 undergoes electron capture, as well as electron loss upon γ-irradiation, to yield [2,8] $Me_2S_2^-$: this radical is calculated to have C_2 symmetry with a torsion angle CSSC of 100.0° [*cf.* 100.2° calculated for Me_2S_2, experimental values: 83.9(9)°,[16] 85.3(37)° [17]]. The SOMO is an antibonding, primarily S–S orbital: it contains a major contribution from *p* orbitals parallel to the S–S direction and a minor contribution from orbitals perpendicular to this direction.

Radicals from Dithiolanes, Dithianes, and 1,3,5-*Trithiane*.—1,2-Dithiolane (1a) is a simple model for lipoic acid (1b), the anion radical of which adopts a conformation such that only one of the three α-hydrogens is coupled to the unpaired electron.[2] The minimum energy conformation of the anion radical of (1a) is calculated to have C_s symmetry, with the β-carbon out of the plane of the other heavy atoms, and with spin densities as given in the Table. Variation of the CSSC torsion angle from 0° at the energy minimum to 15° requires the expenditure of only some 3 kJ mol^{-1}, and causes a major difference in the spin densities at the α-hydrogens. The pseudoaxial hydrogens have in this conformation a calculated spin density of less than 0.001 whilst the pseudoequatorial hydrogens have a value of 0.012. Such a value is consistent with the observed 10 G coupling observed [2] for the radical anion of (1b): we conclude that the preferred conformation of this (1b) anion has a CSSC torsion angle close to 15°, with the side chain in a pseudoequatorial site. In contrast the radical cation derived from (1a) is calculated to have C_{2v} symmetry.

For 1,3-dithiolane (2) the neutral parent is calculated to have C_{2v} symmetry with the HOMO, a B_1 orbital, localised on the two sulphur atoms. All optimisations for the cation radical of (2) gave electronic structures having the SOMO localised almost entirely on one of the sulphurs. This is in complete contrast to both the observed [18,19] and calculated [20] electronic structure of the analogous 1,3-dioxolane. Whilst the calculated electronic structure of the (2) cation radical may be a computational artefact (for which we can provide no explanation) we note that in the cation radical of *p*-benzoquinone, the SOMO is found [21] to be localised almost entirely on only one of the oxygens.

The cation derived from 1,3-dithiane (3a) is potentially of interest, since the cation of the oxygen analogue [19] (3b) is calculated [20] to have a structure which contains a planar COCOC fragment with the sixth ring atom displaced from the plane, in accord with the observed [19] e.s.r. spectrum. Although the structure of the parent molecule (3a) optimises to a chair conformation, consistent with the major conformer observed experimentally,[22] the structure of the cation radical is analogous to that calculated earlier [20] for the cation of (3b): five of the skeletal atoms, CSCSC, again define a plane with the remaining carbon atom displaced from this plane by *ca.* 0.61 Å. However, as with the cation derived from (2), but unlike that from (3b), the SOMO in the cation of (3a) is calculated to be localised almost entirely on one of the sulphur atoms.

The energies calculated for the two conformers, chair and boat, of the cation radical derived from (4a) are very similar: the $\Delta H_f^{\ominus}$ values are +862.4 and +864.7 kJ mol^{-1}. For the chair conformer, the axial hydrogens have a much higher spin density than the equatorial hydrogens, just as found [20] for the oxygen analogue cation derived from (4b). In the cation radical derived from (5), the ring has C_2 symmetry, with a calculated torsion angle CSSC of *ca.* 8°.

The structure of the trithiane (6) is calculated to have a chair conformation of C_{3v} symmetry, with a HOMO of E symmetry, localised primarily on the sulphur atoms. Ionisation to form the cation radical consequently yields a Jahn–Teller-sensitive species, and the calculated structure for this species has only C_s symmetry. Two sulphur atoms and two carbon atoms define a plane normal to the symmetry plane, and the SOMO is strongly localised on these two sulphurs: relative to the vector between these atoms, the SOMO has both parallel and perpendicular components, both of which are antibonding. The major hydrogen spin density resides on the pseudoaxial hydrogens bonded to the two carbon atoms defining the SCCS plane. This cation has a molecular and electronic structure entirely different from its oxygen analogue.[19,20]

Magnitude of the MNDO Scale Factor.—We have previously found that the approximate values of the scale factor appropriate for the MNDO parameterization, relating the calculated spin density at hydrogen and the observed hyperfine coupling, appear to be *ca.* 1 100 G for carbon-centred radicals [15] and 850—900 G for oxygen-centred radicals.[20] The limited data of the Table again suggest an approximate correlation between ρ and $A(^1H)$, although the observed and calculated parameters for CH_3SCH_2 are seriously inconsistent with the remainder: no improvement is effected for this radical if its identification is changed from CH_3SCH_2 to the alternative possibility CH_3SSCH_2 (see Table).

The limited data available suggest that the scale factor for sulphur radicals is *ca.* 1 000 G; the differing values which appear, from experimental data for a comparatively small number of radicals, to be appropriate for series containing differing heteroatoms, suggest the possibility that the MNDO parameterization yields a systematic variation in scale factor with *e.g.* the electronegativity of the heteroatom. However this possibility remains to be tested.

We note however that the MNDO approximation appears to give very poor calculated $\rho(^1H)$ values for a wide range of planar π-radicals. As relevant examples, we cite the recently observed[23] cation radicals of furan and thiophene: the observed α and β hydrogen couplings are, in the furan cation, 14 and 3.5 G, and in the thiophene cation, 13 and 2.5 G, giving $\alpha:\beta$ ratios of 4.0 and 5.2 : 1, respectively. The corresponding calculated spin densities are −0.029 and −0.001 in the furan cation, and −0.030 and +0.001 in the thiophene cation, with $|\alpha:\beta|$ ratios of 29 and 30 : 1, respectively.

Identity of the Disulphur Radicals X.—These radicals contain two non-equivalent sulphur atoms,[9] and both formulations $RSS^\cdot$ and $RSSR_2^\cdot$ are possible. The experimental evidence for each possibility has been discussed very thoroughly;[1] here we comment simply on the observed hyperfine couplings and the calculated spin densities in the two simplest cases (R = CH_3 or C_2H_5).

The radical X derived from CH_3SH exhibits[1] hyperfine coupling to three equivalent hydrogens with *a* 7.2 G. The calculated hydrogen spin density in $CH_3SS^\cdot$ is 0.003, while in the alternative $CH_3S\dot{S}(CH_3)_2$ the hydrogen spin density for the unique methyl group is 0.009, and for the pair of methyl groups it is 0.000 5. The densities for $CH_3S\dot{S}(CH_3)_2$ indicate that no splitting should be observed from the $S(CH_3)_2$ group, and the observed hyperfine coupling to three hydrogens is readily reconciled, adopting a scale factor of around 1 000 G, with the calculated spin density in $CH_3S\dot{S}(CH_3)_2$, but not with that in $CH_3SS^\cdot$.

In the radical X derived from EtSH, hyperfine coupling to a single hydrogen atom is observed[1] with *a* 8 G. In $EtSS^\cdot$, the energies calculated for free optimisations at a range of fixed values for the torsion angle CCSS indicate that the height of the conformation barrier about the C–S bond is no more than 1 kJ mol^{-1}. At all conformations the SOMO is an (S–S)π orbital and when the torsion angle CCSS is 120°, one of the CH_2 hydrogens is almost in the nodal plane of the SOMO. The calculated spin densities for the two CH_2 hydrogens at this conformation are 0.000_2 (in plane H), and 0.004: this latter is the biggest spin density at a CH_2 hydrogen which was found for any conformation.

In the alternative $EtSSEt_2^\cdot$ formulation, there is again almost free rotation about the C–S bond of the EtSS fragment. In a range of conformations, the calculated spin densities at the CH_2 hydrogens in the SEt_2 fragment are always *ca.* −0.005. For a conformer having one CH_2 hydrogen of the EtSS portion fixed in the $C_\alpha SS$ plane, and *trans* to the SS bond, the calculated spin densities at these two hydrogens are 0.023 (in-plane H), and 0.002: for other conformations the values are more similar. Thus for a hydrogen fixed in the $C_\alpha SS$ plane but *cis* to the SS bond, the values are 0.012 (in-plane H) and 0.007. It seems clear that there will exist a conformation of $EtSSEt_2^\cdot$ in which a single hydrogen can have a large enough spin density to give rise to an observed hyperfine coupling of 8 G: there is no conformation of EtSS which can explain such a coupling.

For both $MeSSMe_2^\cdot$ and $EtSSEt_2^\cdot$ the SOMO is strongly localised on the two sulphur atoms: the major component is an antibonding combination parallel to the S–S direction (σ^*) with a minor bonding combination perpendicular to this direction (π). Nelson *et al.* have argued[1] that an essentially σ^* electronic structure is required to interpret the observed *g* tensor in terms of a structure of type $RSSR_2^\cdot$: the forms of the SOMO found here for $RSSR_2^\cdot$ when R = Me or Et give strong support to this argument. Both the forms of the SOMO and the calculated spin densities lend support to the formulation $RSSR_2^\cdot$ but are inconsistent with the alternative formulation $RSS^\cdot$.

It has been demonstrated[1] that at temperatures above 77 K, the radicals X can give rise to $RS^\cdot$, detected by spin trapping. This implies that, if X is $RSSR_2^\cdot$, the S–S bond is relatively weak. Calculated $\Delta H_f^\ominus$ values for the various components yield S–S bond dissociation energies of 23 and 17 kJ mol^{-1} for $RSSR_2^\cdot$ when R = Me or Et respectively, indicating that the radicals $RSSR_2^\cdot$ are bound species, but readily dissociate to $RS^\cdot$ and R_2S. In contrast the calculated S–S bond dissociation energy for $Me_2S_2^-$ (yielding RS and RS^-) is 142 kJ mol^{-1}; and that for Me_2S_2 is 250 kJ mol^{-1}.

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