Investigations of Structure and Conformation. Part 14.[1] INDO and Electron Spin Resonance Studies of Aliphatic Sulphonyl Radicals

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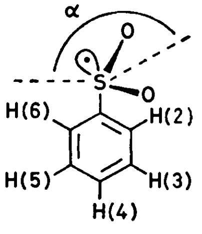
A conformational analysis is presented for a series of aliphatic sulphonyl radicals RSO$_2$·; this is based on the magnitudes of hyperfine splittings from α- and β-protons (C$_\beta$–C$_\alpha$–SO$_2$·), on the obervation of line broadening resulting from restricted rotation about both the C$_\alpha$–S and the C$_\beta$–C$_\alpha$ bonds, and on the results of molecular orbital calculations employing the INDO (Intermediate Neglect of Differential Overlap) method. The spectra and structure of the novel alkenesulphonyl radicals (*e.g.* CH$_2$=CHSO$_2$·) are also described.

THE e.s.r. spectra of a series of aromatic sulphonyl radicals (ArSO$_2$·) have been interpreted[2] in terms of a σ-type structure (1) in which the unpaired electron chiefly occupies an orbital on sulphur in the plane of the aryl ring. Interesting features of the spectra include the occurrence of the largest proton splitting from the *anti-meta* proton [H(3)] and, for hindered examples, restricted rotation about the C–S bond. On the basis of INDO calculations[3] it was suggested[2] that appropriate molecular parameters are $r_{\mathrm{S-C}}$ 0.182 and $r_{\mathrm{S-O}}$ 0.141 nm, with α *ca.* 110° and $\widehat{\mathrm{OSO}}$ *ca.* 120° [though variations in *a*(*o*-H) and *a*(*p*-H) with substituent suggest that the precise geometry of the sulphonyl group may be dependent to some extent on the steric and electronic properties of other groups present]. We have now extended our calculational approach and experimental study to a range of alkanesulphonyl, substituted alkanesulphonyl, and alkenesulphonyl radicals; in particular we aimed to rationalize some of the unusual properties of simple examples of these species [namely the order[4,5] *a*(β-H) > *a*(α-H) for –CH$_\beta$–CH$_\alpha$–SO$_2$· and the occurrence[6] of line broadening in the spectrum from MeSO$_2$·] as well as to characterize the hitherto unreported alkenesulphonyl analogues.



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RESULTS AND DISCUSSION

E.s.r. Results.—Sulphonyl radicals were generated by photolysis of solutions of di-t-butyl peroxide, triethylsilane, and sulphonyl chlorides in a variety of solvents (toluene, dimethyl ether, cyclopropane, and cyclopropane–oxiran mixtures) at temperatures in the range —30 to —130 °C in the cavity of an e.s.r. spectrometer.[2,4] In all cases radicals were detected which had *g ca.* 2.005 and hyperfine splittings[4] which enable them to be characterized as aliphatic sulphonyl radicals.

(a) *Alkanesulphonyl and Substituted Alkanesulphonyl Radicals.*—Table 1 contains the e.s.r. parameters for a variety of aliphatic radicals recorded over a range of temperature; data for RSO$_2$· (R = Me, Et, Pr, Pr$^{\mathrm{i}}$), essentially as reported previously,[4] are included here for comparison. In general, the parameters were not significantly solvent-dependent; values quoted refer mainly to solutions in cyclopropane (which generally enabled good resolution and a wide range of temperature to be obtained). In a few instances (see later) significant solvent effects were noted.

TABLE 1

E.s.r. spectra of aliphatic sulphonyl radicals[a]

Radical	T/°C	Hyperfine splittings[b] *a*(α-H)	*a*(β-H)	*a* (other)	*g*[c]
MeSO$_2$·	−50	0.055			2.0049
	−125	0.076[d]			
EtSO$_2$·	−50	0.075	0.173		2.0050
	−80	0.090[d]	0.173		
	−120	0.115[d]	0.172		
PrSO$_2$·	−40	0.070	0.212	0.070 (3H)	2.0051
	−110	0.122[d]	0.245	0.072 (3H)	
Pr$^{\mathrm{i}}$SO$_2$·	−60	0.040	0.190		2.0052
ClCH$_2$SO$_2$·	−78	0.129			2.0055
	−105	0.144[d]			
	−105[e]	0.100[d]			
	−107[f]	0.190[d]			
ClCH$_2$CH$_2$SO$_2$·[g]	−33	0.065	0.267	0.065 (1Cl)	2.0054
	−80	0.087[d]	0.300[d]	0.055 (1Cl)	
	−105	0.098[d]	0.305[d]	0.050 (1Cl)	
HOCH$_2$CH$_2$SO$_2$·	−47	0.130	0.275	0.065 (OH)	2.0052
CF$_3$CH$_2$SO$_2$	−23			0.400 (3F)	2.0047
	−94	0.035		0.383 (3F)[d]	
	−115	*d*		*d*	

[a] In cyclopropane unless indicated otherwise. [b] In mT, ±0.005. [c] ±0.0001. [d] Line-broadening observed: see text. [e] In dimethyl ether. [f] In diethyl ether. [g] In oxiran–cyclopropane.

In addition to the small size of *a*(α-H) for MeSO$_2$·, EtSO$_2$·, CF$_3$CH$_2$SO$_2$·, *etc.* and the observation that *a*(β-H) is greater than *a*(α-H) for EtSO$_2$· (assignments to α- and β-protons in substituted analogues have been made on this basis), other features are of note.

Several of the spectra showed line-broadening effects as the temperature was lowered. Thus broadening occurs for the inner lines of the 1 : 3 : 3 : 1 pattern from MeSO$_2$· (see Figure 1) and for the central line in the α-protons' 1 : 2 : 1 pattern for EtSO$_2$· (*cf.* ref. 4); these observations are consistent with restricted rotation about the C–S bond in radicals of pyramidal type [the behaviour for (2) resembles the broadening detected for the bent radical $\cdot CMe(OMe)_2$[7] and the interconversion of two conformers, *e.g.* (3) and (4), is implied[4] for $EtSO_2\cdot$]. Our calculations (see later) appear to substantiate these claims. One small but nevertheless significant solvent effect was observed for the former radical; thus, compared with solutions in diethyl ether (see Figure 1), solutions in cyclopropane showed the onset of broadening at lower temperatures [*e.g.* by —120 °C, the lowest temperature achieved in this solvent, the spectrum resembled Figure 1(b)]. This suggests that greater solvation of the SO_2 group occurs in the ethereal solvent.

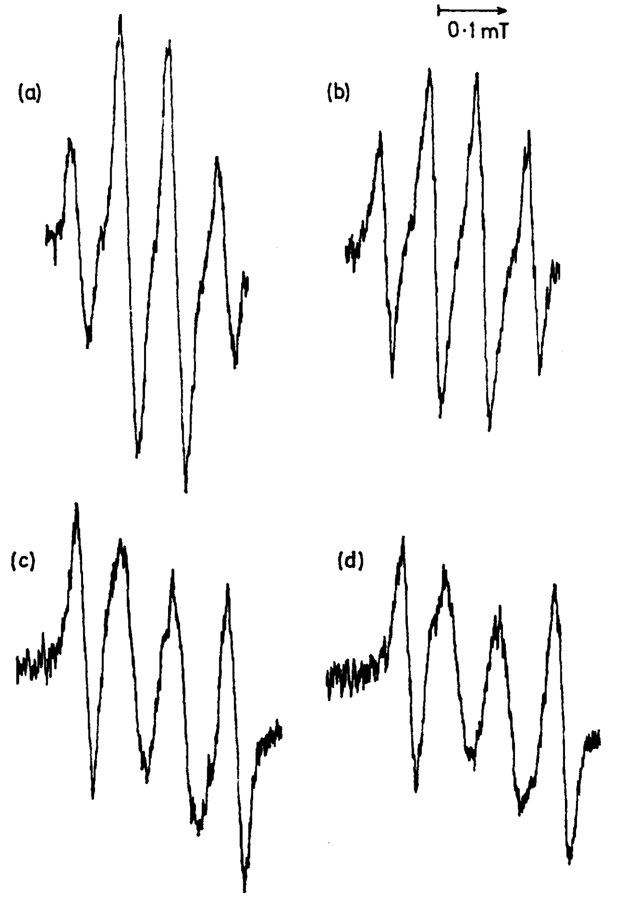
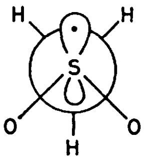


FIGURE 1 E.s.r. spectrum of $MeSO_2\cdot$ in diethyl ether: (a) —74 °C; (b) —97 °C; (c) —110 °C; (d) —120 °C



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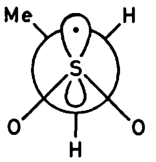

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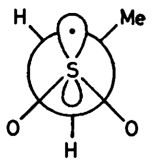

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Behaviour similar to that observed for $EtSO_2\cdot$ was also noticed for the α-proton triplets from $ClCH_2SO_2\cdot$ (the magnitude of the splitting from which was somewhat solvent dependent), $HOCH_2CH_2SO_2\cdot$, and $PrSO_2\cdot$ below *ca.* —100 °C, and more dramatic effects were detected for both $ClCH_2CH_2SO_2\cdot$ and $CF_3CH_2SO_2\cdot$. The spectrum from the former at —33 °C was satisfactorily analysed in terms of splittings of 0.065 mT from a chlorine atom and two equivalent (α) protons (separate resonances from ^{35}Cl and ^{37}Cl were not resolved) and 0.267 mT from two equivalent (β) protons. As the temperature was lowered, broadening of the central lines in both the α- and β-proton triplets occurred, and by *ca.* —100 °C these had completely disappeared (see Figure 2). This observation indicates that there is restriction to rotation not only about the C–S bond but also about the C–C bond. In the spectrum from $CF_3CH_2SO_2\cdot$ line broadening of the inner lines of the trifluoromethyl group's quartet occurred (see Figure 3), again indicating there to be restricted rotation; at the lowest temperatures employed (*ca.* —120 °C) broadening also occurred for the α-proton splitting pattern (which itself was only detectable for a limited temperature range) though detailed analysis proved impossible on account of the general broadening produced as solidification was approached. These results indicate that, as with $EtSO_2\cdot$, unsymmetrical con-

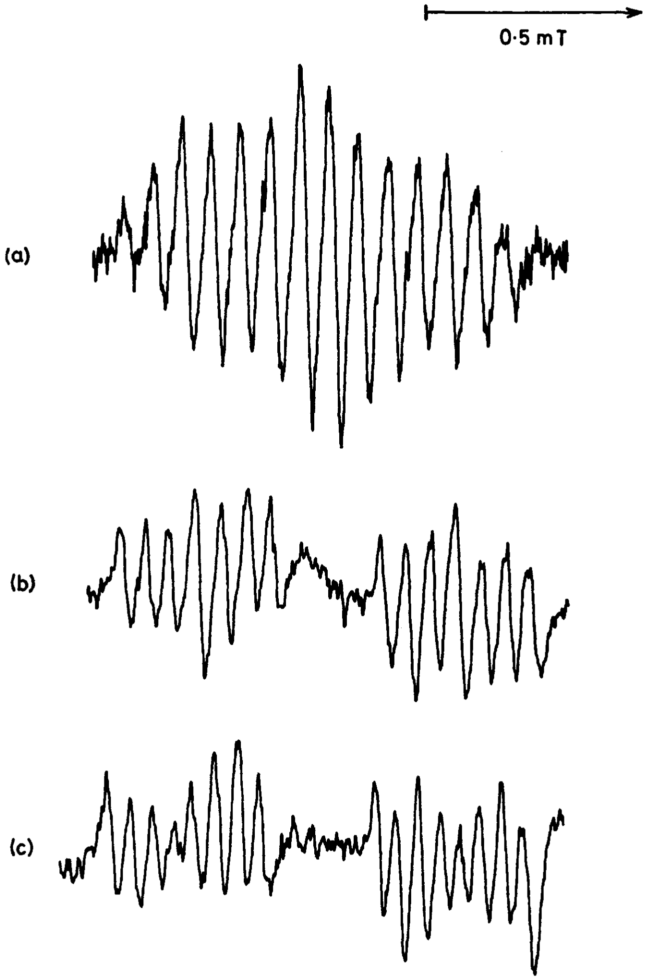


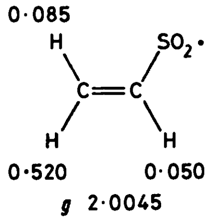
FIGURE 2 E.s.r. spectrum of $ClCH_2CH_2SO_2\cdot$ in oxiran–cyclopropane: (a) —33 °C; (b) —80 °C; (c) —105 °C

formations must be adopted [*cf.* (3) and (4)]; more detailed suggestions concerning these follow from the results of INDO calculations (see later).

Another feature of note is the general increase in $a(\alpha\text{-H})$ at lower temperatures; although in some cases this may result from changes in the weighting of different conformations as a result of motion about C_α–C_β, the change noted for $MeSO_2\cdot$ itself suggests that there may be geometrical modification of the sulphonyl group (see later). The range of both the *g* values and the α-proton splittings, and, in particular, the low value of $a(\alpha\text{-H})$ for $CF_3CH_2SO_2\cdot$, are also notable.

TABLE 2

E.s.r. spectra of alkenesulphonyl radicals[a]



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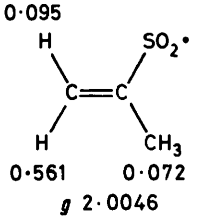

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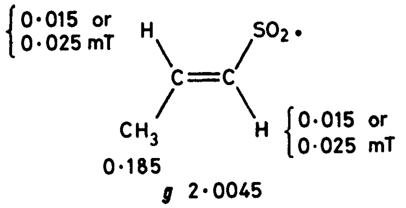

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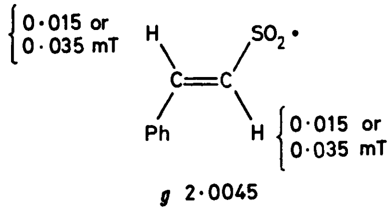

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[a] In cyclopropane at *ca.* −120 °C; splittings in mT ±0.005, *g* values ±0.0001. [b] The spectrum is somewhat dependent upon temperature and solvent; in methylbenzene at −100 °C the splittings are 0.525, 0.085, and 0.045 mT, and at −40 °C in the same solvent they are 0.510, 0.085, and 0.060 mT, respectively. [c] The spectrum from this radical was accompanied by weak resonances from another radical; no detailed analysis proved possible, but the occurrence of splittings of *ca.* 1.4 and 0.4 mT suggests that an allyl-type species is also formed.

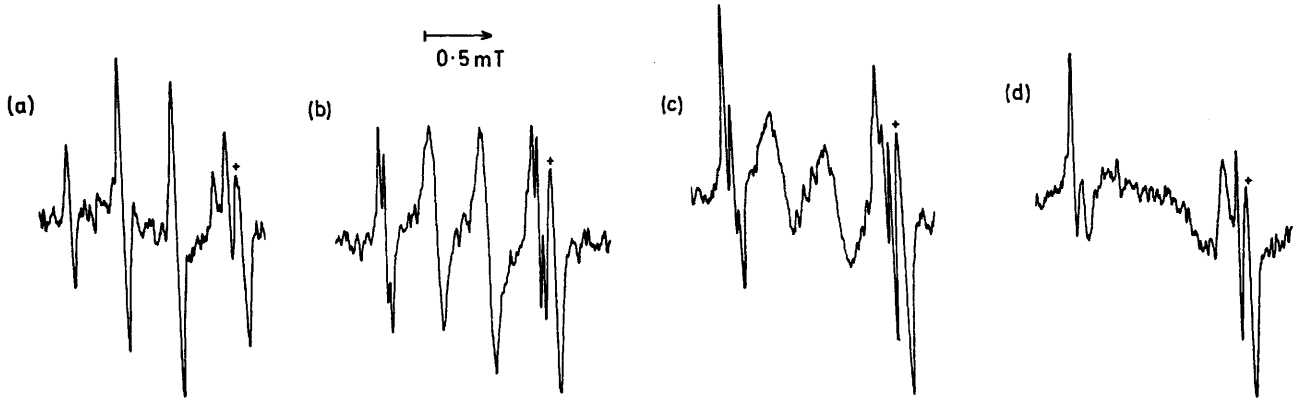
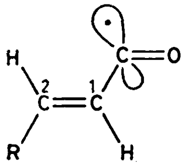


FIGURE 3 E.s.r. spectrum of $CF_3CH_2SO_2\cdot$ in cyclopropane: (a) −23 °C; (b) −85 °C; (c) −106 °C; (d) −115 °C. (The lines indicated + are from an impurity in the sample cell)

(b) *Alkenesulphonyl Radicals.*—These were generated from the reaction of alkenesulphonyl chlorides with $Et_3Si\cdot$, and their e.s.r. parameters are given in Table 2. The large proton splitting (0.52 mT) detected for the unsubstituted example is attributed to the *trans*-2-H [*cf.* (5)] on the basis of the result for the methyl- and phenyl-substituted analogues (6)—(8), and on the assumptions that no isomerization around the double bond has occurred during oxidation and that the similarities observed reflect a self-consistent pattern in a collection of radicals with more or less identical geometry around sulphur. No signals assignable to other appropriate alkenesulphonyl radicals could be detected from 1-bromoethenesulphonyl chloride and 2-phenyl-1-bromoethenesulphonyl chloride.

It is interesting to compare these results with those for some unsaturated acyl radicals which are also of σ-type[8] (the close analogy between the spin distribution in $PhSO_2$· and[9] PhCO· has previously been noted[2]). For example, the large proton-splitting of 1.98 mT in (9; R = Me) is assigned[9] to 1-H on the basis of the spectra for other substituted examples, and INDO calculations on various geometries of CH_2=CHCO· indicate that this is as expected for a σ-radical with the *s-trans* structure shown. [On the other hand, calculations for the *s-cis* structure (10) suggest that for this geometry a large splitting is expected for 1-H.*] The contrast between the assignment for (9; R = Me and those for related sulphonyl radicals suggests that, though the analogy between sulphonyl and acyl radical types may be valid in general, the conformational preferences for *s-trans* and *s-cis* structures are different in the two series. The difference is discussed further in a later section in the light of the results of INDO calculations on CH_2=CHSO_2· and substituted examples.



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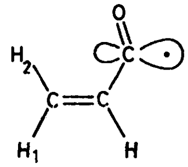

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INDO Calculations.—We have carried out INDO calculations[3] on a variety of possible structures and conformations of the radical $MeSO_2$·. We chose initially a geometry [see (11)] with $r_{\text{S–C}}$ 0.180, $r_{\text{C–H}}$ 0.108, and $r_{\text{S–O}}$ 0.143 nm, tetrahedral geometry at carbon, and the staggered conformation with the dihedral angle θ [defined as that between the half-filled orbital and the downward pointing C–H bond as shown in (11)] = 0, and we varied the angles 2ψ and α in the ranges 110—100 and 130—120° respectively (chosen on the basis of our previous calculation[2] on $C_6H_5SO_2$·).

Table 3

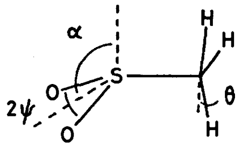
INDO Calculations on $MeSO_2$·[a]

$r_{\text{C–S}}$	α	2ψ	a(H) (average)/mT	ρ_{3s}
0.180	130	100	0.188	0.062
0.180	130	105	0.208	0.061
0.180	130	110	0.229	0.061
0.180	125	100	0.227	0.062
0.180	125	105	0.252	0.061
0.180	120	100	0.276	0.061
0.180	120	105	0.297	0.059
0.184	130	105	0.208	0.061
0.188	130	105	0.077	0.064
0.188	130	110	0.106	0.062
0.188	135	105	0.052	0.062
0.188	140	105	0.039	0.060

[a] For other parameters see text; calculations performed on the staggered conformation (11).

It is encouraging to find that, as indicated in Table 3 (which contains a sample of our results), the average α-proton splitting of *ca.* 0.2 mT is reasonably close to the values observed for radicals of this type and the calculated spin density in the sulphur 3*s* orbital is close to that expected [anisotropic data for ^{33}S splittings in solid-state spectra from[10] $MeSO_2$· and both[11] $PhSO_2$· and $PhCH_2SO_2$· suggest a value of ρ(3*s*) *ca.* 8%]. As α was raised and 2ψ was lowered, the value of *a*(H) decreased towards that observed for $MeSO_2$· [with ρ(3*s*), at *ca.* 6%, relatively insensitive to these changes]. For a combination of values 2ψ 105 and α 130° we varied somewhat the value of $r_{\text{S–C}}$ and found that a longer bond length led to the required further reduction in *a*(H), as well as to a slight increase in ρ(3*s*). With $r_{\text{C–S}}$ 0.188, calculations were carried out for α 130, 135, and 140 and 2ψ 105 and 100°; optimum agreement for $MeSO_2$· was obtained for α 130, 2ψ 105° (see Table 3). It is interesting to note that for all calculations on the fixed conformation with θ = 0, 1-H is calculated to have a significant positive splitting and that 2- and 3-H are predicted to have negative splittings [see *e.g.* (12), for α 130, 2ψ 105° and $r_{\text{C–S}}$ 0.188 nm].

Figure 4 indicates diagrammatically the angular dependence of *a*(H) as θ was altered for a selection of geometries. These results are largely as expected if for the regions with θ *ca.* 0 and 180° the splitting is essentially governed by a hyperconjugative $B\cos^2\theta$ type interaction with the *p*-containing orbital on sulphur, and that when θ is nearer 90°, so that this contribution is small, a through-bond spin-polarisation mechanism, giving negative spin density at the protons, is dominant. These conclusions must remain tentative, since we have been unable to 'freeze out' rotation around the C–S bonds in $MeSO_2$· or related radicals, and the solid-state spectra for $MeSO_2$· do not yield resolvable proton splittings.[10] However, it is notable that the form of the calculated angular dependence for the β-proton splitting in MeCO· resembles[12] that found here for $MeSO_2$·, and also that in Bu^t_2CHCO·, for which a conformation is proposed in which the β-hydrogen eclipses the carbonyl group [and is hence *trans* to the orbital of the unpaired electron, as in (12)], a large proton splitting of *ca.* 1.1 mT is reported.[8]



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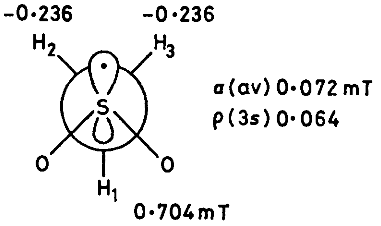

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Use of the *calculated* splittings for (12) in conjunction with a spectrum simulation programme in which exchange effects were incorporated led to simulation of the line-broadening for $MeSO_2$· at various temperatures (*e.g.* simulation of the spectrum for −110 °C in diethyl ether was achieved with k 0.8 × 10^9 s^{-1}). A value of the activation energy for this process of *ca.* 15 kJ mol^{-1} (with

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* We have been informed (Professor A. G. Davies, personal communication) that the calculated splittings for the β-protons in the results of the INDO calculations on each of radicals (9; R = H) and (10) in ref. 8 should be reversed.

A 0.8 × 10^{13} s^{-1}) was obtained, though in view of the uncertainties involved this should only be regarded as an indication of its magnitude.

Our calculations suggest that particularly low average α-proton splittings may arise when α, the degree of bending at sulphur, becomes larger (*e.g.* 130—140°); this may be reflected in the experimental observations by the decrease in *a*(H) for $MeSO_2\cdot$ as the temperature is raised (*e.g.* due to increased amplitude of bending vibration, though C–S bond stretching may also become important).

TABLE 4

INDO Calculations on $CH_3CH_2SO_2\cdot$ [a,b]

ω [c]	*a*[α-H(1)]	*a*[α-H(2)]	*a*(α-average)	*a*[β-H(3)]	*a*[β-H(4)]	*a*[β-H(5)]	*a*(β-average)
180	0.429	−0.080	0.174	0.250	0.055	0.036	0.114
170	0.410	−0.077	0.167	0.250	0·030	0.071	0.117
160	0.391	−0.079	0.156	0.231	0·014	0.109	0·118
150	0.373	−0.086	0.144	0.193	0·010	0.139	0·114
140	0.368	−0.097	0.136	0.160	0·010	0·175	0·118
130	0.371	−0.106	0.133	0.113	0·038	0·188	0.113
120	0.385	−0.112	0.136	0.074	0·065	0.194	0.110
110	0.409	−0.119	0.145	0.044	0.106	0.203	0.117
100	0.427	−0.114	0.157	0.017	0.141	0.180	0.113
90	0.443	−0.108	0.168	0.003	0.183	0.157	0.114
80	0.447	−0.097	0.175	0.001	0.213	0.122	0.119
70	0.442	−0.087	0.178	0.013	0.237	0.087	0.112
60	0.428	−0.080	0.174	0.036	0.250	0.055	0.113

[a] With r_{C-H} 0.108, r_{C-C} 0.154, r_{C-S} 0.188, r_{S-O} 0.140 nm, α 130, 2ψ 105, θ 40° [see (12)]. [b] Splitting in mT. [c] See (13)

We have also carried out calculations on the radical $EtSO_2\cdot$ with particular attention to the conformations having non-equivalently placed α-protons (as suggested by the detection of line-broadening in several examples, see earlier), *cf.* (13). Parameters chosen were as follows: α 130, 2ψ 105°, r_{C-S} 0.188 nm (*i.e.* from the results of our calculations for $MeSO_2\cdot$) together with tetrahedral geometry around each carbon, r_{C-H} 0.108 nm, and various values of θ and ω [see (14)]. In particular, we aimed to determine whether or not realistic conformations could be found in which the average α-proton splitting was calculated to be significantly less than the β-proton splitting and, if so, to learn something of the angular dependence of spin transmission to β-protons and the preferred conformation(s) adopted by CH_2X groups (for example, X = Me or Cl).

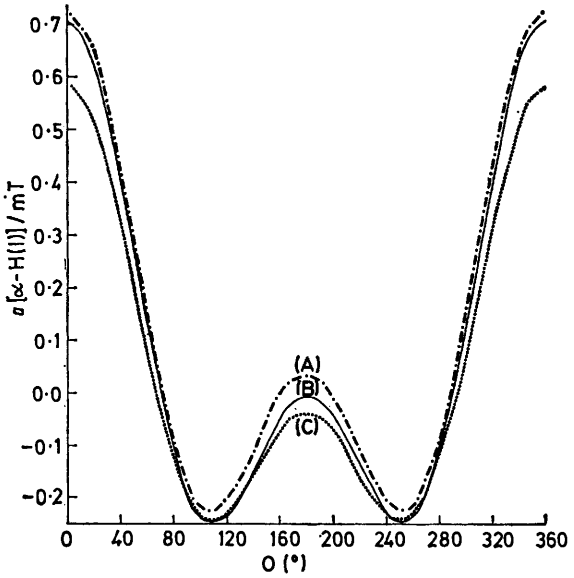
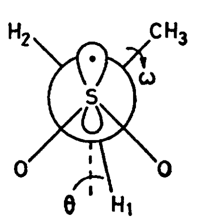


FIGURE 4 Calculated (INDO) angular dependence (on θ) of α-proton splittings for $CH_3SO_2\cdot$ [see (11)]: (A), α 130, 2ψ 110°; (B), α 140° 2ψ 105°; (C), α 130°, 2ψ 105°

We varied θ in the range 0—60° and, for each value of θ, varied ω from 60 to 180° in 10° intervals. For a given value of θ the *average* α-proton splitting and *average* β-proton splitting proved relatively insensitive to the angle of rotation ω, and no significant trends were observed for different values of θ. Our results are typified by those for θ = 40°, listed in Table 4. As can be seen, the individual α-proton splittings are found to be quite different (as required to account for the marked line-broadening observed in some cases) with an average value (*ca.* 0.16 mT) somewhat greater than for $MeSO_2\cdot$ (as is observed for $PrSO_2\cdot$, $EtSO_2\cdot$, and $ClCH_2CH_2SO_2\cdot$). For the freely rotating β-Me group in $EtSO_2\cdot$ the calculated average (0.11 mT) is reasonably close to that observed (0.174 mT). However, individual β-proton splittings are calculated to be considerably larger than this for certain values of ω (the angular dependence of this is shown in Figure 5, from which it appears that a *B*cos²ω type relationship is followed). Thus individual values as high as 0.25 mT are calculated. The observation that, for the β-substituted radicals $XCH_2CH_2SO_2\cdot$ (X = Me, Cl, or OH), the β-splitting is greater than that for $CH_3CH_2SO_2\cdot$ suggests that the substituted radicals preferentially occupy conformations with the substituent occupying a position associated with a *low* splitting in the unsubstituted analogue, *i.e.* with ω *ca.* 90° and X replacing 3-H (see Table 4). This is shown for X = Cl in structure (15),



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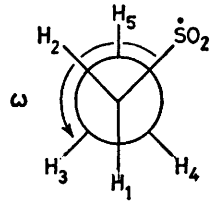


(14)

together with calculated α- and β-proton splittings for the parent. As models show, this preference would appear to result from the avoidance of eclipsing interactions between the S–O bonds and the α-C–H and, particularly, C_α–C_β bonds, together with a preference at the β-carbon for a geometry in which the chlorine atom avoids the bulky SO_2 group. A variety of calculations for $CF_3CH_2SO_2\cdot$ [with geometry as for $CH_3CH_2SO_2$. (as above) with r_{C-F} 0.135 nm, and various values of θ and ω] has also been performed. Results were essentially as described above for $CH_3CH_2SO_2\cdot$, with similar values of ρ(3*s*), with the following notable differences: the averaged α-proton splittings for any particular conformation are *ca.* 50% of those for $CH_3CH_2SO_2\cdot$, and large β-fluorine splittings (up to *ca.* 1.2 mT) are calculated [the angular dependence on ω having a maximum at ω 180°; see *e.g.* (16)]. Another conclusion based on the results of INDO calculations is that $Me_2CHSO_2\cdot$ exists in a preferred conformation (17) rather than (18) (for which a large α-proton splitting would be expected; *cf.* $Bu^t{}_2CHCO\cdot$).

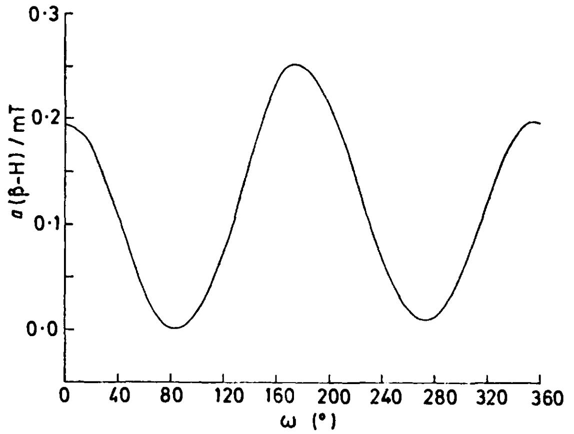
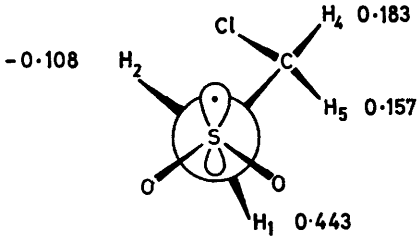
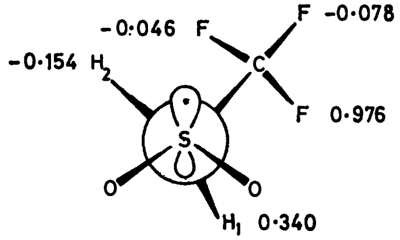


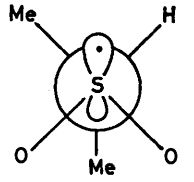
FIGURE 5 Calculated (INDO) angular dependence (on ω) of β-proton splittings for $CH_3CH_2SO_2\cdot$ [with θ 40°, see (13) and (14)]



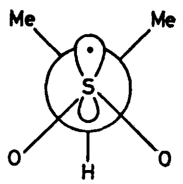
(15)



(16)



(17)



(18)

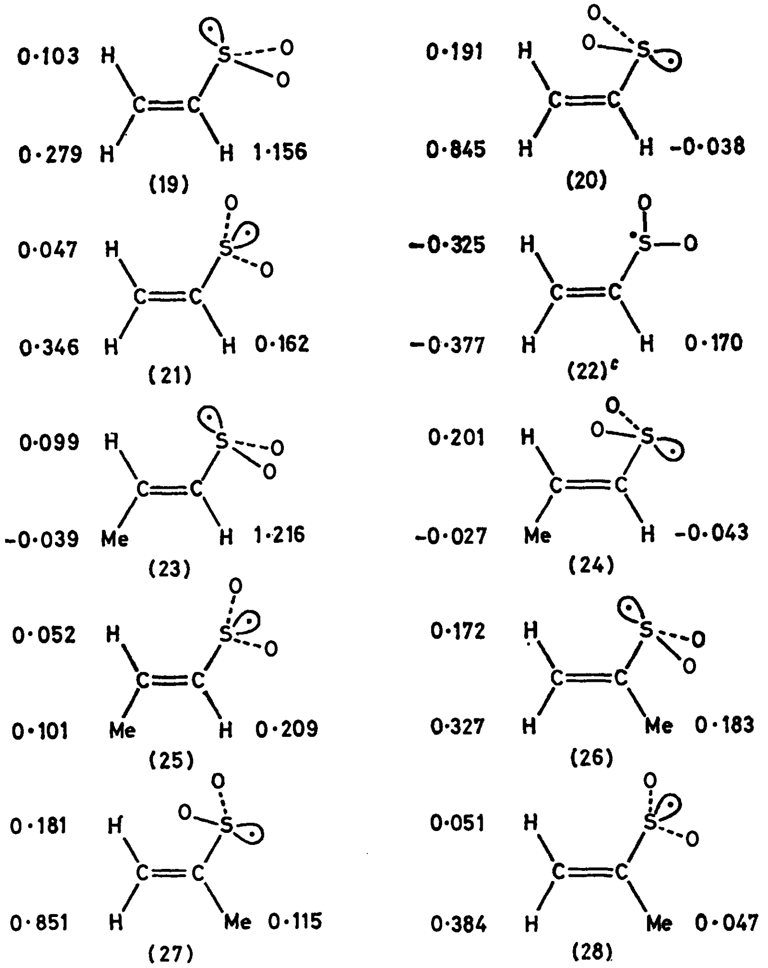
Table 5 contains the results of a set of INDO calculations on the ethenesulphonyl radical $CH_2{=}CHSO_2\cdot$, employing parameters chosen on the basis of our findings for $PhSO_2\cdot$ (r_{C-S} 0.182, r_{S-O} 0.141 nm, $\widehat{CCS}$ 120, α 130, 2ψ 105°; with r_{C-H} 0.108, r_{C-C} 0.134 nm). We studied 'bisected' conformations with the in-plane orbital containing the unpaired electron on sulphur either *syn* or *anti* to the double bond [*i.e.* (19) and (20)], as well as the geometry (21) which formally allows conjugation between the unpaired electron and the *p*-electrons in the double bond [the allyl-type radical with all the atoms in a plane (22) was also examined].

As can be seen, the observations that 2-H *trans* to sulphur has the significant coupling (of *ca.* 0.5 mT) and that the splittings from 1-H and *cis*-2-H are much smaller are in reasonable accord with calculations both for the bisected *s-cis* form (20) and for the formally conjugated structure (21) [the large difference between the two β-proton splittings for the latter, and their positive sign, indicates that through-bond spin transmission is evidently more effective than *p*–π conjugation; *cf.* the 'expected' behaviour for (22)]. The clear analogy between INDO calculations [8] on the *s-trans* and *s-cis* forms of $CH_2{=}CHCO\cdot$ and those of $CH_2{=}CHSO_2\cdot$ is notable, as is the observation that for both sets of calculations for the *s-cis* form [in (10) and (20)] the large long-range coupling derives from the proton held in a W relationship with the orbital of the unpaired electron (see, *e.g.* ref. 13 for other examples of this phenomenon). It is also notable that for slight geometric modification of the SO_2 group in (20), improved agreement with experiment is obtained (for 2ψ 120, α 130°, for example, splittings calculated for *cis*-2-H, *trans*-2-H, and 1-H are 0.132, 0.675, and 0.019 mT, respectively). For (21) slight improvements result from lowering 2ψ and increasing α.

We conclude on the basis of these calculations that unlike radicals $CHR{=}CHCO\cdot$, which apparently prefer the *s-trans* structure (9), $CH_2{=}CHSO_2\cdot$ prefers either (20) or (21). Although rotation around $C-SO_2\cdot$ is presumably rapid under the conditions employed (*cf.* $PhSO_2\cdot$, in which rotation around the $C-SO_2$ bond is still in the fast exchange region at *ca.* −120°), it seems likely, at least on the basis of a lack of a significant temperature dependence of the splittings, that one of the two conformations is heavily weighted, so that the radical is effectively locked in one of them. It is not clear why, if an in-plane σ-type structure for $CH_2{=}CHSO_2\cdot$ is preferred (*cf.* $PhSO_2\cdot$), it is the *s-cis* form (20) rather than the apparently less hindered *s-trans* form (19) that is favoured (though this might be understandable for the 1-methyl-substituted radical). It is thus tempting to speculate that the radicals may preferentially adopt the σ-form (21) in which the unpaired electron is delocalized, to some extent at least, into the π-system. This suggestion receives some support from the results of our INDO calculations on methyl-containing radicals (see Table 5). Thus the significant long-range interaction with the *trans*-2-methyl group protons in (7) (0.189 mT) is approached by that calculated for (25), but not (23) or (24), and the very small methyl-proton splitting in (6) is reflected by calculations on (28), but not (26) or (27).

TABLE 5

INDO Calculations on alkenesulphonyl radicals [a,b]



[a] For parameters see text. [b] Splittings in mT. [c] As (21), but with α 90°.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E-104 X-band spectrometer employing 100 kHz modulation. Details of the procedure for measuring and calibrating spectra, the photolytic apparatus, and the programs employed have been described previously.[2,14] Solutions to be photolysed contained a mixture of sulphonyl chloride, di-t-butyl peroxide, and triethylsilane (*ca.* 1 : 1 : 1) in toluene, cyclopropane, cyclopropane–oxiran, dimethyl ether, or diethyl ether; cyclopropane was customarily employed.

The following reagents were commerical products and were used without further purification: chloromethanesulphonyl chloride and 2-chloroethanesulphonyl chloride (Lancaster Syntheses Ltd.), 2,2,2-trifluoroethanesulphonyl chloride (Fluka), methanesulphonyl chloride (B.D.H.), propanesulphonyl chloride (Eastman), and 2-phenylethenesulphonylchloride (Aldrich). Ethanesulphonyl chloride and 1-methylethanesulphonyl chloride were prepared by chlorination of the appropriate mercaptan.[15] Ethenesulphonyl chloride, 1-bromoethenesulphonyl chloride, and 2-phenyl-1-bromoethenesulphonyl chloride were prepared by the method of Rondestvedt,[16] and 1-methylethenesulphonyl chloride and prop-1-enesulphonyl chloride were prepared by the methods of Stewart and Cordts.[17] All compounds prepared had satisfactory analytical data (n.m.r. and mass spectra, b.p.s or m.p.s); the ^{1}H n.m.r. spectra of 2-phenylethenesulphonyl chloride [$\delta(CDCl_3)$ 7.56 (5 H, s), 7.28 (1 H, d, J 16 Hz), and 7.78 (1 H, d, J 16 Hz)] and prop-1-enesulphonyl chloride [$\delta(CDCl_3)$ 2.04 (3 H, d, 7 Hz), 6.64 (1 H, d, 15 Hz), and 7.0 (1 H, dq, 15 Hz, 7 Hz)] indicated that these compounds possess the *trans* (*E*) configuration.

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