Investigations of Structure and Conformation. Part 12.[1] The Structure of Aromatic Sulphonyl Radicals: An E.s.r. and INDO Molecular Orbital Study

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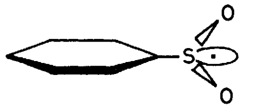
The e.s.r. spectra are described of a variety of arenesulphonyl radicals ($ArSO_2\cdot$) which have been generated photolytically over a wide range of temperature. It is shown that the spin distribution in these σ-radicals resembles that in the benzoyl radical; radicals without *ortho*-substituents, which undergo relatively rapid rotation about the C–S bond at all accessible temperatures, have $a(m\text{-H}) > a(o\text{-H}), a(p\text{-H})$. For some di-*ortho*-substituted radicals, rotation around C–S is slow at low temperature (barriers to rotation have been determined for some examples) and some mono-*ortho*-substituted radicals demonstrate marked conformational preferences; analysis shows that the largest proton-splitting (*ca.* 0.2 mT) derives from the *meta*-proton *anti* to the orbital of the unpaired electron on sulphur. INDO calculations yield results in good agreement with these findings.

E.S.R. spectroscopy has been previously employed to characterize the formation of alkanesulphonyl ($RSO_2\cdot$) radicals in a variety of processes, including the reactions of sulphonyl halides with $Et_3Si\cdot$,[2] of sulphinic acids with $Bu^tO\cdot$,[2] and of dialkyl sulphoxides with $\cdot OH$,[3] and the photolysis of sulphones.[4,5] Features of the spectra [*e.g.* the anisotropy of the ^{33}S-splitting for [5] $MeSO_2\cdot$ and the ordering [2] $|a(\beta\text{-H})| > |a(\alpha\text{-H})|$ for $-CH(\beta)-CH(\alpha)-SO_2\cdot$] are interpretable in terms of a σ-type species with a pyramidal radical centre at sulphur.

The spectra of aromatic analogues, prepared by cerium(IV) oxidation of sulphinic acids in an aqueous flow system [6] and by reaction of arenesulphonyl halides with [2] $Et_3Si\cdot$, show several unusual features. For example, the relative magnitudes of the splittings are different from those typical of planar π-radicals; for $C_6H_5SO_2\cdot$, the proposed assignment [2,6] of splittings is $a(o\text{-H}) > a(p\text{-H}) > a(m\text{-H})$ (with values 0.106, 0.050, and 0.033 mT, respectively). On this basis, and on the evidence of non-equivalence between two splittings assigned to the *ortho*-protons in 4-chlorobenzenesulphonyl, a σ-structure of the type (1) in which the singly occupied orbital is in the plane of the benzene ring, rather than (2), was proposed.[2]



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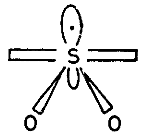


(2)

Further evidence for a structure of the type (1) derives [7] from the kinetic and u.v. spectroscopic behaviour of aromatic sulphonyl radicals generated during the flash-photolysis of sulphones; [7] these radicals have $2k_t$ *ca.* 5×10^8 l mol^{-1} s^{-1} and $\lambda_{max.}$ *ca.* 330 nm, with little dependence of either of these properties on the nature of substituents in the ring, and it is argued that there is no π-type delocalization of the unpaired electron. In contrast, thermodynamic arguments [8] suggest a value of 58.5 ± 5 kJ mol^{-1} as the stabilization energy in $C_6H_5SO_2\cdot$, implying π-type delocalization as would be expected for (2).

We have carried out a series of INDO [9] calculations on a variety of assumed geometries for $C_6H_5SO_2\cdot$ and have found that calculations on structures of the type (1) lead to an estimated spin distribution such that the largest splittings derive from the *meta*-protons, in a way which closely resembles the experimental and calculated [10] splittings for the analogous σ-type benzoyl radical $C_6H_5CO\cdot$ [where the unpaired electron occupies an in-plane orbital like that depicted for (1)]. Here we describe these results together with the e.s.r. spectra of a variety of substituted sulphonyl radicals, chosen so as to allow an unambiguous assignment of ring-proton splittings to be made.

RESULTS AND DISCUSSION

E.s.r. Results.—Sulphonyl radicals were generated by photolysis of solutions of di-t-butyl peroxide, triethylsilane, and arenesulphonyl chlorides in a variety of solvents (toluene, *m*-xylene, and cyclopropane–oxiran) and also by direct photolysis of the arenesulphonyl chlorides in toluene, at temperatures between −10 and −90 °C in the cavity of an e.s.r. spectrometer. In all cases, radicals were detected which had *g ca.* 2.005 and, usually, hyperfine splittings which enable them to be characterized as arenesulphonyl radicals. In some cases there were also weak but, nevertheless, clearly detectable and reproducible signals from arenesulphinyl radicals ($ArSO\cdot$; *g ca.* 2.009, *cf.* ref. 11); it seems possible that these radicals arise from the decay of $ArSO_2\cdot$, *via* $ArSO_2OS(O)Ar$, to $ArSO\cdot$ and $ArSO_3\cdot$.[12] Their origin will not be discussed further here.

Sulphonyl Radicals without ortho-*Substituents.*—Table 1 contains details of the analyses and assignments of the e.s.r. spectra from the benzenesulphonyl radical and some *meta*- and *para*-substituted derivatives.

Details of the spectra of the unsubstituted radical and the 4-methyl- and 4-bromo-derivatives were found to be essentially as described previously [2] (*i.e.* each radical's spectrum showed two sets of triplet splittings of *ca.* 0.10 and 0.03 mT; interaction was also detected with the 4-proton in $C_6H_5SO_2\cdot$ and with the protons of the 4-methyl group in $4\text{-}MeC_6H_4SO_2\cdot$). The spectrum from 4-t-butylbenzenesulphonyl is analysed similarly.

TABLE 1

E.s.r. spectra of arenesulphonyl radicals ($ArSO_2\cdot$) without *ortho*-substituents [a]

Radical	Hyperfine splittings (mT) [b]			g [c]
(Ar =)	$a(o\text{-H})$	$a(m\text{-H})$	$a(p\text{-X})$	
C_6H_5	0.033	0.113	0.052	2.0045
$4\text{-Me-}C_6H_4$	0.032	0.118	0.065	2.0045
$4\text{-Br-}C_6H_4$	0.031	0.095		2.0047
$4\text{-Bu}^t\text{-}C_6H_4$	0.028	0.103		2.0045
$4\text{-Cl-}C_6H_4$	0.032	0.096		2.0045
	0.032	0.096	0.012 (^{35}Cl), 0.010 (^{37}Cl) [d]	2.0045
$4\text{-F-}C_6H_4$	0.031	0.090	0.175 (^{19}F)	2.0044
$3,5\text{-di-}CF_3\text{-}C_6H_3$	0.055		0.055	2.0043
$3\text{-Me-4-Br-}C_6H_3$	0.030	0.100		2.0046
$3\text{-Me-4-Cl-}C_6H_3$	0.030	0.100		2.0046

[a] Data refer to solutions in toluene at low temperatures (*ca.* −80 °C); proton splittings except where indicated otherwise. [b] Typically ±0.005 mT. [c] Typically ±0.0001. [d] At *ca.* −60°.

Clear indication that it is the *meta*-protons in these radicals which are responsible for the larger of the two sets of triplet splittings derives from the spectra from 3-methyl-4-bromo- and 3-methyl-4-chloro-benzenesulphonyl, for each of which only one large splitting of 0.100 mT was detected, and from 3,5-bis(trifluoromethyl)benzenesulphonyl, in which both the *meta*-positions are blocked and for which only a small quartet splitting (0.055 mT), from the *ortho*- and *para*-protons, was detected.

The equivalence of the pairs of *ortho*-proton splittings in all these radicals, and of the pairs of *meta*-protons in the radicals which only possess a *para*-substituent, suggests that either these species are undergoing rapid rotation about the $C-SO_2\cdot$ bond or the spin distribution is symmetrical (*e.g.* as would be expected for a planar π-type radical). The finding that the *meta*-proton splittings are larger than those from the *ortho*-protons points strongly to a structure in which the half-filled orbital is in, or close to, the plane of the benzene ring, and analogy with benzoyl then leads us to expect an asymmetric distribution of spin density. It therefore seems likely that rotation around $C-SO_2\cdot$ is indeed rapid, which then makes it surprising that for 4-chlorobenzenesulphonyl two non-equivalent splittings of *ca.* 0.1 mT (0.090 and 0.120 mT) have been reported [2] and that the spectrum from 4-fluorobenzenesulphonyl has similarly been analysed.

We resolved this apparent anomaly by a detailed study of 4-chlorobenzenesulphonyl in a range of solvents and at various temperatures. Figure 1(a) shows the spectrum obtained at −86 °C in toluene; it is typical of the low-temperature spectra in a variety of solvents and shows splittings from two pairs of protons (0.096 and 0.032 mT) but no extra resolvable interaction. Figure 1(b) shows the spectrum obtained in toluene at −60 °C; it can be seen that each of the central lines of the main triplet now shows a further interaction which is apparently a doublet, an effect which becomes more marked at higher temperature [Figure 1(c)]. This extra splitting does not simply appear on the central line, which would be the case if the two larger splittings become non-equivalent, and we believe that it originates in the partial resolution of a small chlorine splitting; it can be effectively simulated [see, *e.g.* Figure 1(d)] by superposition of spectra with appropriate splittings from ^{35}Cl and ^{37}Cl (relative intensities 3 : 1; splittings in the ratio of the ^{35}Cl and ^{37}Cl nuclear magnetic moments, 0.820 1 : 0.683 3). The low-temperature spectra are best simulated by the incorporation of a small unresolved chlorine splitting (*e.g.* 0.009 mT for ^{35}Cl, 0.007 5 mT for ^{37}Cl).

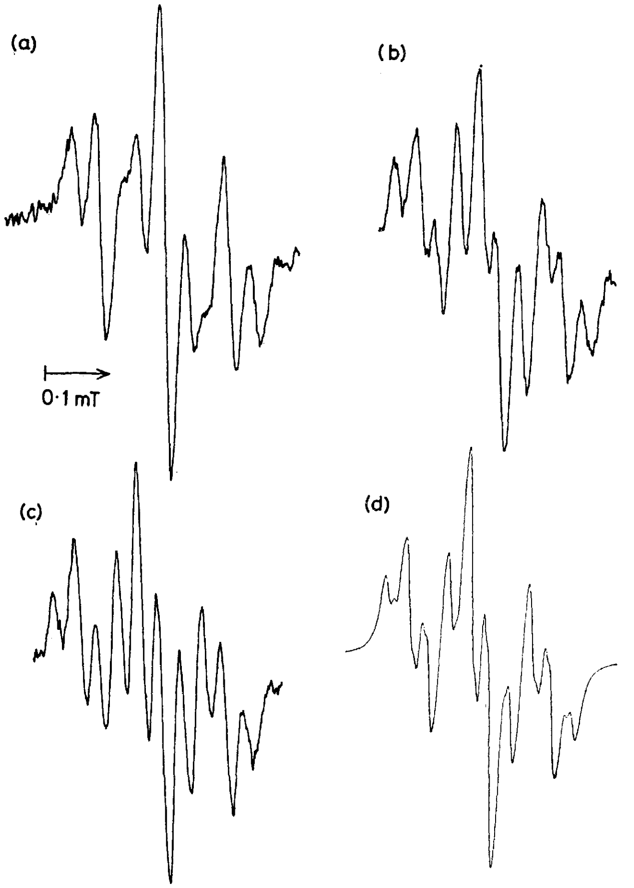


FIGURE 1 E.s.r. spectrum from the 4-chlorobenzenesulphonyl radical: (a) in toluene at −86 °C, (b) in toluene at −60 °C, (c) in toluene at −45 °C, and (d) simulated using the following splittings: a(2H) 0.032, a(2H) 0.096, $a(^{35}Cl)$ 0.012 $a(^{37}Cl)$ 0.010 mT (with line-width 0.012 mT)

We infer, then, that at all accessible temperatures the 4-chlorobenzenesulphonyl radical is undergoing rapid rotation about C–S (to give pairs of equivalent *ortho*- and *meta*-proton splittings) and that a slight increase in the interaction with chlorine as the temperature is raised accounts for the observed changes. The mechanism by which this operates is not clear but it seems likely that geometrical modifications increase the spin density at chlorine.

For the 4-fluorobenzenesulphonyl radical we find that the spectrum is satisfactorily analysed in terms of two sets of equivalent splittings similar to those for other

4-substituted radicals [0.031 and 0.090 mT, evidently from *ortho*- and *meta*-protons, respectively]; the extra doublet splitting (0.175 mT) is attributed to interaction of the unpaired electron with ^{19}F.*

It is impossible at this stage to be more specific about the magnitude of the *individual ortho*- and *meta*-proton splittings in these arenesulphonyl radicals because the observed values are averaged quantities for various conformations. It is also notable that the average values themselves are to a certain extent dependent upon the electronic effects of the substituents [*cf.* the *ortho*-proton splittings of 0.016 (see ref. 2), 0.032, and 0.055 mT for 4-methoxy-, 4-methyl-, and 3,5-bis(trifluoromethyl)-benzenesulphonyl, respectively]. These effects are discussed later in the light of the results of INDO calculations.

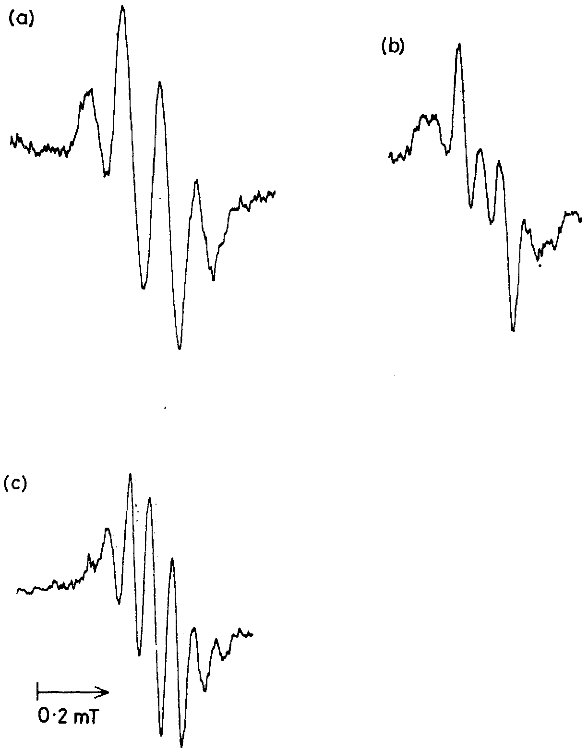
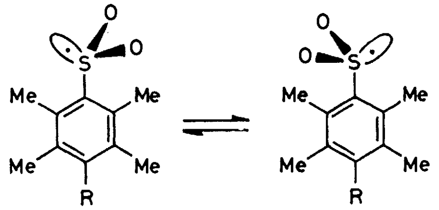


FIGURE 2 E.s.r. spectrum from the pentamethylbenzenesulphonyl radical in toluene: (a) at -80 °C, (b) at -47 °C, and (c) at -32 °C

Sulphonyl Radicals with ortho-*Substituents*.—The e.s.r. spectra and assignments for a variety of *ortho*-substituted arenesulphonyl radicals are shown in Table 2; the assignments are justified in the following analysis.

The spectrum of the 2,4,6-trimethylbenzenesulphonyl radical (3) contains a triplet (0.107 mT), which must clearly be associated with the *meta*-protons (*cf.* the unhindered analogues discussed above) and a septet (0.075 mT), which, on the basis of the spectra from (4; R = H, Me) is associated with the *ortho*-methyl groups' protons. This spectrum showed no significant alteration as the temperature was changed. In contrast, the spectra of (4; R = H, Me) showed alternating line-width effects which were temperature-dependent (see Figure 2). Thus for both (4; R = H) and (4; R = Me) the high-temperature spectrum (above -30 °C) had a(6H) 0.060 mT [evidently from the *ortho* methyl group-protons, *cf.* (3)] whereas at -80 °C interaction with only three protons [a(3H) 0.100 mT] could be detected; spectra at intermediate temperatures showed alternating line-broadening and were satisfactorily simulated with a two-jump exchange process with interchange of two sets of methyl-group splittings of 0.100 and 0.020 mT (the latter chosen to give the high-temperature average of 0.060 mT), and ΔH 0.035 mT. The resultant kinetic data (for example, values of k at -80 and -35 °C are 0.9×10^6 and 12×10^7 s^{-1}, respectively) lead to a value for the activation energy for the interconversion process (presumably hindered rotation around C–S) of 22.2 kJ mol^{-1}.

The spectrum from (5), like that from (3), showed a septet attributed to the six *ortho*-methyl-group protons, in addition to a doublet from the single *meta*-proton; this spectrum was invariant with temperature. We believe that the radicals (3)—(5) possess an asymmetric distribution of spin-density, as judged by the low-temperature data for (4; R = H, Me), but that in (3) and (5) rotation around C–S is rapid at all accessible temperatures, whereas the rotation is slower for (4; R = H, Me). This evidently reflects increased steric hindrance to rotation of the sulphonyl group [*e.g.* (6) $\rightleftharpoons$ (7)] by the *ortho*-methyl groups in (4; R = H, Me), presumably on account of the ' buttressing ' effect of the 3- and 5-methyl groups (*cf.*, for example, similar conclusions based on the e.s.r. spectra from the 2,3,5,6-tetraisopropylnitrobenzene anion-radical [13]). In the light of these results it is not surprising that, as discussed earlier, radicals without *ortho*-substituents undergo fast exchange at accessible temperatures.



(6) (7)

Another arenesulphonyl radical which showed evidence of restricted rotation was the 2,4,6-trichloro-derivative (8); at high temperatures (*ca.* -30 °C) this showed a(2H) = a(2Cl) = 0.07 mT (separate ^{35}Cl and ^{37}Cl resonances were not resolved) whereas at low temperatures (*ca.* -80 °C) only one proton and one chlorine gave a detectable interaction (a 0.140 mT each). At intermediate temperatures line-broadening occurred. We conclude that the radical exists in a unique conformation

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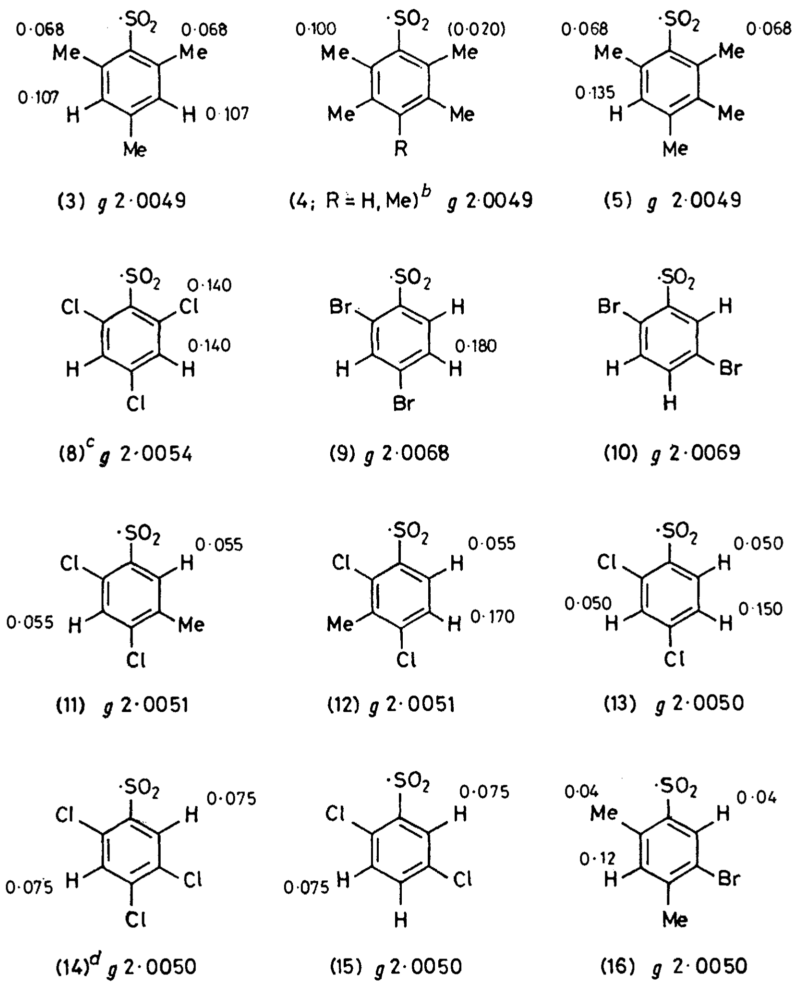
* The spectrum previously assigned [2] to 4-FC$_6$H$_4$SO$_2$· was in fact due to C$_6$F$_5$SO$_2$· and that assigned to C$_6$F$_5$SO$_2$· was due to 4-F-C$_6$H$_4$SO$_2$· (B. P. Roberts, personal communication); the spectrum from C$_6$F$_5$SO$_2$· shows fluorine splittings of 0.175 mT (2F) and 0.03 mT (3F), the larger splittings presumably being from the *meta* fluorines in a radical undergoing rapid rotation about C–S.

at low temperatures (justification for assignment of splittings to the chlorine and hydrogen *anti* to the unpaired electron is presented later) and that at higher temperatures the rate of restricted rotation increases until the two *ortho*-chlorines (and the two *meta*-protons) appear equivalent. We estimate from spectrum simulation that k is *ca.* 10^7 s^{-1} at -50 °C. Again, evidence is provided for asymmetric spin distribution in the ring, with one *meta*-proton splitting being much greater than the other.

TABLE 2

E.s.r. spectra of *ortho*-substituted arenesulphonyl radicals (a_H/mT) [a]



[a] Splittings ±0.005 mT; g-values ±0.0001; data refer to low temperatures (*ca.* -80 °C) and to proton splittings except where stated otherwise. [b] Line-width alternation detected: see text; at -30 °C, analysis has a(6H) 0.060 mT. The smaller indicated methyl-proton splitting in the low-temperature spectra is not resolved but is calculated from the averaged splitting. [c] Line-width alternation detected, see text; at -30 °C, a(2H) = a(2Cl) = 0.07 mT. [d] A chlorine splitting became resolved above -40 °C; see text.

Spectra from (8) were also accompanied by a singlet, g *ca.* 2.004 6, which became prominent at very low temperature; a similar singlet was the only signal detected from photolysis of 2,4,6-tribromobenzenesulphonyl chloride and also from the photolysis of SO_2Cl_2. It seems possible that this is from $\cdot SO_2Cl$, produced from the arenesulphonyl chlorides by C–S homolysis in very hindered radicals. The spectrum from 2,4,6-tri-isopropylbenzenesulphonyl comprised a complex multiplet (g 2.055 0) which could not be analysed or assigned unambiguously.

The spectra of the two bromine-substituted radicals (9) and (10) which have only one *ortho*-substituent enable us to pinpoint what we believe to be the position of the largest individual splitting in the ring in arenesulphonyl radicals. Thus (9) gives a large doublet (0.18 mT) which is not present in the 5-substituted analogue (10) (other small splittings, *ca.* 0.03 mT, were present, but resolution was not sufficiently good for unambiguous analysis). In view of the bulk of the *ortho*-bromine atom, it seems likely that the oxygen atoms lie *anti* to this, so that the preferred conformations occupied are as indicated (with the large *meta*-proton splitting *anti* to the orbital of the unpaired electron, *cf.* calculations for benzoyl). The fact that a(m-H) for (9) is nearly twice that for (3) and for other unhindered arenesulphonyls suggests that (9) is effectively locked in the conformation indicated and that the two *meta*-protons have splittings of *ca.* 0.18 mT and nearly zero.

A similar conclusion is reached from inspection of the splittings of radicals (11)—(13), in each of which we believe that the sulphonyl oxygens avoid the *ortho*-chlorine substituents. We note then that an arenesulphonyl radical evidently needs *two ortho*-substituents *and* low temperatures before conformational 'locking' is achieved [*i.e.*, as in (4) and (8)]; however, though rotation about C–S is, therefore, expected to be rapid in (11) and related radicals (and, as expected, no temperature effects were discerned), nevertheless the e.s.r. spectra will reflect the weighted average of all possible conformations (*e.g.* with Cl and SO_2 both *syn* and *anti*) and hence will presumably reflect to a large degree the splittings for the *anti*-conformer. Again, the assignment to the *anti meta*-proton of the large splitting (0.15—0.17 mT) follows. The lack of a chlorine splitting in these examples also indicates that the chlorine splitting in (8) derives from the chlorine atom *anti* to the unpaired electron. The assignment of the simple triplet observed for (14) at −60 °C is unambiguous; at higher temperatures a small chlorine splitting (*ca.* 0.03 mT at −35 °C) became resolved [*cf.* 4-chlorobenzenesulphonyl]. The radical (15) had a similar low-temperature spectrum but modifications as the temperature was raised could not be analysed unambiguously, though chlorine splittings are presumably involved.

TABLE 3

INDO calculations on the benzenesulphonyl radical [a]

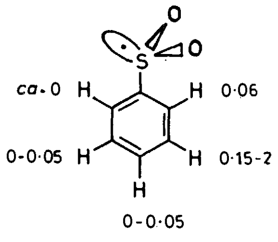
Geometry [b]		Hyperfine splittings/mT					
θ	α	$a(H_2)$	$a(H_3)$	$a(H_4)$	$a(H_5)$	$a(H_6)$	ρ_{3s}(sulphur)
130	140	0.047 94	0.087 53	0.010 83	0.001 07	0.062 68	0.056
	130	0.045 73	0.093 31	0.010 13	0.000 38	0.058 61	0.053
	120	0.035 01	0.095 19	0.007 99	−0.000 65	0.046 56	0.046
	110	0.004 09	0.080 70	0.003 84	−0.001 41	0.011 98	0.034
	100	−0.029 08	0.060 78	−0.000 96	0.002 63	−0.023 24	0.019
120	130	0.091 44	0.121 11	0.015 19	0.007 75	0.110 47	0.056
	120	0.061 52	0.106 57	0.012 41	0.001 57	0.073 52	0.049
	110	0.034 67	0.101 44	0.007 66	−0.000 68	0.045 73	0.038
	100	−0.019 15	0.069 56	0.000 24	0.000 82	−0.012 53	0.021
110	120	0.099 62	0.124 65	0.017 99	0.006 98	0.113 73	0.052
	110	0.063 93	0.116 35	0.011 99	0.002 19	0.075 97	0.042
	100	−0.003 88	0.081 36	0.002 23	−0.000 56	0.004 43	0.023
105	120	0.126 04	0.140 90	0.020 67	0.012 32	0.143 10	0.054
	110	0.080 56	0.124 43	0.014 44	0.004 33	0.093 10	0.044
	105	0.047 26	0.110 70	0.009 45	0.000 72	0.058 42	0.035
	100	0.008 31	0.091 61	0.003 66	−0.001 45	0.018 44	0.025

[a] For calculational details, see text. [b] For definition of θ and α, see (18). Other parameters employed: S–O 0.1410, C–C 0.1394, C–S 0.1820, C–H 0.1080 nm.

The splittings for (16) [a(4H) 0.04 mT, a(1H) 0.12 mT] are assigned as indicated, although this analysis is not unambiguous; the occurrence of a *meta*-proton splitting (0.12 mT) lower than those for (8), (9), (12), and (13) suggests that the conformational preference for SO_2 and Me *anti* is not so clearly established as for those examples where the *ortho*-substituent is chlorine or bromine.

We note that the sterically-hindered radicals have, in general, *g*-values somewhat greater than those of their unhindered counterparts. Other differences between the two categories of radical include the resolution of *para*-H and *para*-CH_3 proton splittings for the unhindered radicals described in Table 1 but a lack of such detectable interaction for the hindered varieties in Table 2. Although this suggests that there are structural variations possible in the arenesulphonyl radicals, it nevertheless seems highly likely that all the radicals possess *essentially* the same σ-structure (17), with the associated large *anti meta*-proton coupling and other splittings as indicated. Such a set of splittings accounts for the low-temperature spectra of very hindered radicals and the radicals which are conformationally 'locked' with a large *ortho*-substituent, as well as the averaged values observed for unhindered rapidly-equilibrating examples.

INDO Calculations.—We have carried out INDO calculations on a variety of assumed geometries for the benzenesulphonyl radical itself, based on the 'bisected' σ-structure (18) [*cf.* structure (1)]: clearly a structure akin to (2) must be ruled out because of the observed non-equivalence within the pairs of *ortho*- and *meta*-proton couplings. We varied the angles α and θ ($\widehat{OSO}$) as defined in (18) and have used other geometric parameters as shown in Table 3. We employed a modification of the standard INDO program [9] which includes [14] the CNDO/2 parametrization for second-row elements [15] and the Slater and Condon parameters suggested by Benson and Hudson [16] for second-row elements.



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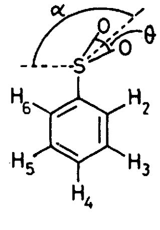

(18)

The results of the calculations for a range of values of α and θ resemble quite closely those for benzoyl[10] and it is gratifying to find that trends in the experimental spectra can be reproduced. For example, for geometries with α in the range 100—130° and θ in the range 105—130°, the largest calculated splitting is generally found to be that from the *meta*-hydrogen *anti* to the orbital of the unpaired electron on sulphur, with a calculated value *ca.* 0.1 mT. There are values of α and θ for which the *para*- and *ortho*-proton splittings are, as expected, much smaller (see, *e.g.* α 100—110° with θ 105—130°) and it is also interesting to note that in the region α 100—110° the a(*o*-H) values are particularly sensitive to small changes in this angle of bending. Such minor modifications of geometry (*e.g.* as brought about by the introduction of *ortho*-substituents which may exert a steric effect or *para*-substituents which will, to some extent at least, be conjugated with the sulphonyl group) may well account for the observed variations with substituents of *ortho*- and *para*-splittings. We also note that, for geometries with α 110—120° and θ 105—130°, the calculated values of the spin density in the sulphur 3*s*-orbital are *ca.* 0.04—0.05 which is close to the value (0.074) for $MeSO_2\cdot$ derived[5] from the ^{33}S splitting in this species.

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 previously been described;[17] the programs have been executed on a DEC KL10 computer at the University of York.

Solutions to be photolysed contained either the arenesulphonyl chloride or a mixture of arenesulphonyl chloride, di-t-butyl peroxide, and triethylsilane (*ca.* 1 : 1 : 1) in toluene, *m*-xylene, or cyclopropane–oxiran; toluene was customarily employed. The direct photolysis method gave, in general, less intense spectra than did the peroxide-triethylsilane method, which was usually preferred.

The following reagents were commercial products purified before use by recrystallization from light petroleum: 4-fluoro- and 2,4,5-trichloro-benzenesulphonyl chloride and 2-mesitylenesulphonyl chloride (Aldrich), 4-chlorobenzenesulphonyl chloride (Koch–Light Ltd.), and 3,5-bis(trifluoromethyl)benzenesulphonyl chloride (Lancaster Syntheses Ltd.). Benzenesulphonyl chloride was obtained from Koch–Light Ltd. and was used without further purification. The following were prepared by the direct chlorosulphonation[18] of the appropriate compounds and were characterized on the basis of previously-reported data: 5-bromo-2,4-dimethylbenzenesulphonyl chloride,[18] 4-chloro-3-methyl-, 4-bromo-3-methyl-, 2,4-dibromo-, 2,5-dibromo-, 2,4-dichloro-, 2,5-dichloro-, 2,4-dichloro-3-methyl-, 2,4-dichloro-5-methyl-, 2,4,6-trichloro-, and 2,4,6-tribromo-benzenesulphonyl chloride (*cf.* ref. 19), and 4-t-butyl-, 2,3,5,6-tetramethyl-, 2,3,4,6-tetramethyl-, and pentamethylbenzenesulphonyl chloride (*cf.* ref. 20).

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