

An Investigation of Structure and Conformation of Thiophene-2-sulphonyl Radicals

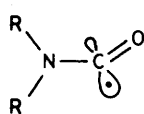
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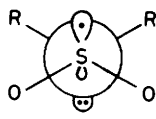
The e.s.r. spectra of a variety of photochemically generated thiophene-2-sulphonyl radicals are described. Their spin distribution is typical of σ -radicals; radicals without substituents at position 3 exhibit relatively rapid rotation about the C-S bond at all accessible temperatures while the 3-bromo-substituted ones demonstrate a marked conformational preference which has been interpreted in terms of a π -type conjugated structure. These findings are substantiated also by the results of INDO calculations carried out for the unsubstituted thiophene-2-sulphonyl radical with different relative arrangements of the SO_2 and heteroaromatic moieties.

The e.s.r. spectra of a series of arenesulphonyl,¹ alkane-sulphonyl,^{2,3} alkenesulphonyl,² and aminosulphonyl⁴ radicals have been recently reported together with the results of INDO calculations. Features of the spectra have been interpreted in terms of a σ -type species with a pyramidal radical centre at sulphur; conformational analyses have also been presented. The optical absorption spectra recorded for some of these radicals further support their σ nature.⁵ It has also been suggested that sulphonyl and acyl radicals have certain structural features in common (*cf.* the similarity between $\text{PhCO}\cdot$ and $\text{PhSO}_2\cdot$)¹ although a conformational difference has been established in $\text{R}_2\text{NCO}\cdot$ and $\text{R}_2\text{NSO}_2\cdot$,⁴ which appear to have, respectively, an in-plane structure (1) and a π -type conjugated structure (2).

We have now extended our theoretical approach and experimental study to a number of hitherto unreported thiophene-2-sulphonyl radicals; in particular we aimed to characterize them as well as to rationalize some of the unusual conformational properties observed.



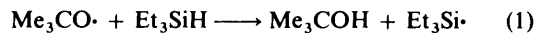
(1)



(2)

Results and Discussion

E.s.r. Results.—Sulphonyl radicals were generated by the reaction of triethylsilyl radicals, produced by photolysis of di-*t*-butyl peroxide in the presence of triethylsilane,⁶ with sulphonyl chlorides in toluene at temperatures in the range 180–230 K inside the cavity of an e.s.r. spectrometer [reactions (1) and (2)].

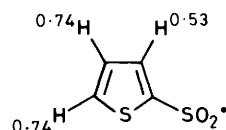
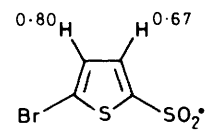
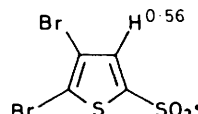
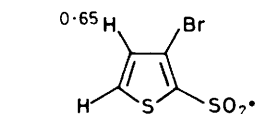
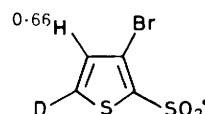
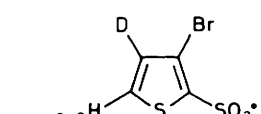
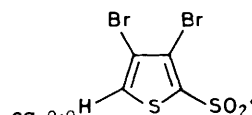
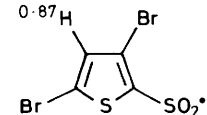


Reaction (2) is a very fast process and occurs with rate constants of *ca.* $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ at 300 K.⁷† This procedure

† In the cases of bromo-substituted thiophene-2-sulphonyl chlorides the bromine abstraction by $\text{Et}_3\text{Si}\cdot$ is also a very fast process, *ca.* $1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ (C. Chatgililoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1982, **104**, 5123). However, the resulting thienyl radical will also abstract chlorine atom from the SO_2Cl moiety with a rate constant of *ca.* $1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ (C. Chatgililoglu, *J. Org. Chem.*, in the press).

was preferred over the direct photolysis of the sulphonyl chlorides which gave in general much less intense spectra. In all cases, the detected radicals had a *g* value of *ca.* 2.005 and their hyperfine splittings enabled us to characterize them as thiophenesulphonyl radicals (see Table). In some cases there were also weak but, nevertheless, clearly detectable and reproducible

Table. E.s.r. spectra of substituted thiophene-2-sulphonyl radicals (a_{H}/G)^a

(3)^b *g* 2.0042(4)^b *g* 2.0047(5) *g* 2.0048(6)^c *g* 2.0054(7) *g* 2.0054(8) *g* 2.0053(9)^{c,d} *g* 2.0057(10) *g* 2.0058

^a Splittings $\pm 0.04 \text{ G}$; *g* value ± 0.0001 ; data refer to solution in toluene at temperatures between 180 and 230 K. ^b Spectra were also accompanied by that of the corresponding sulphonyl radical (see text). ^c ΔH_{pp} 0.15 G at 203 K. ^d Spectra were also accompanied by a very weak singlet, *g* 2.0048.

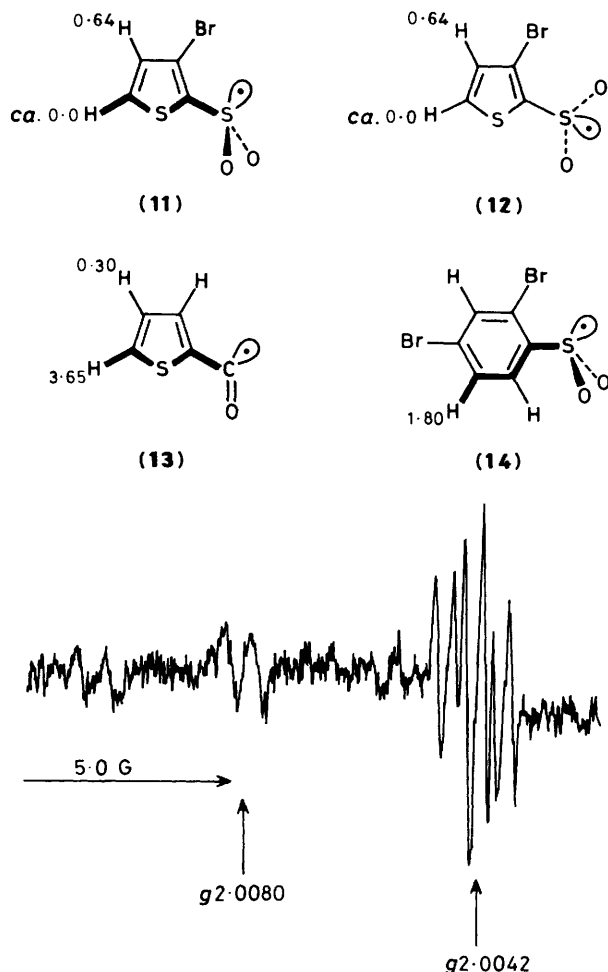
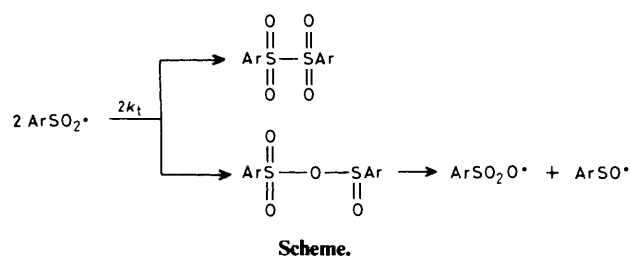


Figure 1. E.s.r. spectra from thiophene-2-sulphonyl (g 2.0042) and thiophene-2-sulphinyl (g 2.0080) radicals in toluene at 183 K

signals from thiophene-2-sulphinyl radicals ($\text{ArSO}\cdot$); their origin will be discussed later in the paper.

As far as the structural assignment of these species is concerned a distinction should be made between radicals unsubstituted in position 3 and those bearing 3-bromo substituents. The spectrum of thiophene-2-sulphonyl radical (3) contains a triplet (0.74 G), which should be associated with 4- and 5-H on the basis of the spectra from radicals (4) and (5), and a doublet (0.53 G) attributed to 3-H. In the light of the findings that these radicals show no linewidth alternation as the temperature changes ($180 \leq T \leq 230$ K) and that their spin distribution is typical of σ radicals we suggest that these species undergo rapid rotation about the C-SO₂ bond as in the cases of aren-sulphonyl radicals without *ortho*-substituents.¹

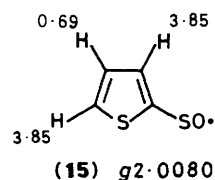
On the other hand, the spectra of the three 3-bromo-substituted radicals (6)–(8) showed unambiguously that the larger hyperfine splitting in radical (6) must be associated with the 4-H while the 5-H has a hyperfine splitting close to zero (ΔH_{pp} 0.15 G at 203 K). Consistently, also the spectra of radicals (9) and (10) indicate that the larger splitting should be attributed to 4-H. Also for radicals (6)–(10) no major variations of the spectral pattern were observed by varying the temperature. From these data we infer that the 3-bromo-substituted radicals demonstrate a marked conformational preference and in view of the bulk of the *ortho*-bromine atom, it seems likely that the oxygen atoms should lie away from it. This leaves structures (11) and (12) as the two possible alternatives. However, a structure akin to (11) may be safely ruled out



because of the observed nearly zero hyperfine splitting of 5-H; indeed, in such a fixed conformation, 5-H would lie in a W-arrangement with respect to the unpaired electron and should therefore exhibit the largest hyperfine splitting as has been shown in the case of thenoyl (13)⁸ and *o*-bromobenzenesulphonyl (14)¹ radicals (*cf.* also benzoyl radical⁹). Structure (12) accounts nicely for the vanishingly small splitting of the proton in position 5 if one considers that spin density at this proton arises from a combination of 'through-bonds' interactions (inducing a positive spin density) and 'through-space' interactions (inducing a positive spin density on C-5 and therefore a negative spin density on 5-H because of spin polarization). The differences between the possible conformations are discussed later in the light of the results of INDO calculations.

The variation of the g factors when going from radical (3) to (10) follows an expected trend and parallels the one found in aren-sulphonyl radicals by bromo-substitution.¹ Indeed g is predicted to increase when introducing atoms characterized by large spin-orbit couplings in positions of significant spin density of the radical.¹⁰ The effect of bromine substitution in position 3 is maximized because the π -type conjugative structure (12) makes 'through-space' interaction more effective.

The observed thiophene-2-sulphonyl radical (3) decayed with clean second-order kinetics and the rate constant $2k_1$ for the self-reaction was measured as 3×10^9 l mol⁻¹ s⁻¹ at 230 K in cyclopropane by kinetic e.s.r. spectroscopy.¹¹ As mentioned earlier in the paper, in some cases thiophene-2-sulphinyl radicals were detected along with the expected sulphonyl species. In Figure 1 is shown the e.s.r. spectrum obtained upon direct photolysis of thiophene-2-sulphonyl chloride; two clearly independent signals are present, the one with the lower g value (2.0042) being due to sulphonyl radical (3) and the other (g 2.0080) to sulphinyl radical (15).¹² Similarly, a weak spectrum assigned to 5-bromothiophene-2-sulphinyl radical [with $a(1\text{ H})$ 3.47, $a(1\text{ H})$ 1.30 G, g 2.0090] was observed together with radical (4) in the photolysis of 5-bromothiophene-2-sulphonyl chloride.



The formation of sulphinyl radicals is believed to occur *via* an intermediate sulphonyl sulphinyl 'anhydride' (see Scheme), decomposition of which under either thermal or photochemical conditions might be expected to yield sulphinyl radicals ($\text{ArSO}\cdot$) and oxygen-centred radicals $\text{ArSO}_2\cdot$ (which cannot be detected directly using e.s.r.). A mechanism of this type has been proposed to account for the radicals observed by e.s.r. during thermolysis or photolysis of thiosulphonates¹² as well as for the products derived from the thermolysis of sulphonyl iodides.¹³ Evidence supporting such a mechanism came from the spin-trapping experiments which excluded any possibility of direct formation of sulphinyl radicals. That is, photolysis of the

samples containing sulphonyl chloride (including PhSO_2Cl) and α -phenyl-*N*-*t*-butyl nitron (PBN) in toluene at 233 K always show two distinct species which can be assigned unambiguously to the chlorine-atom adduct [with $a(\text{N})$ 12.5, $a(\text{H})$ 0.65, $a(^{35}\text{Cl})$ 6.4, $a(^{37}\text{Cl})$ 5.3 G, g 2.0061]¹⁴ and sulphonyl radical-adduct [with $a(\text{N})$ 13.1, $a(\text{H})$ 1.9 G, g 2.0061]¹² respectively on the basis of the previous literature assignments. The signal intensities of 3-bromothiophene-2-sulphonyl radical-adducts are much weaker than those of the adducts without substituents at position 3; presumably such change in intensity reflects the relative rates of trapping rather than the quantum yield of the photolysis. The above results suggest that the primary photochemical reaction of the thiophene-2-sulphonyl chlorides is the S-Cl bond cleavage. In this respect we consider highly unlikely the previously reported finding¹⁵ that photolysis of PhSO_2Cl in the presence of α -phenyl-*N*-*t*-butyl nitron gives solely the spectrum of $\text{Ph}_2\text{CHN}(\text{O})\text{CMe}_3$, implying that C-S fission has taken place.

INDO Calculations.—INDO SCF MO calculations have been carried out for thiophene-2-sulphonyl radical in order to seek corroborative evidence for conclusions, based on the hyperfine splittings, about structure and preferred conformations. The experimental geometry of thiophene¹⁶ was adopted for the thienyl group while for the sulphonyl moiety we chose the geometrical parameters previously obtained by the best fitting of the proton hyperfine splittings constants in benzene-sulphonyl¹ and methanesulphonyl² radicals, *i.e.*, $r_{\text{S-C}}$ 1.82, $r_{\text{S-O}}$ 1.41 Å, α 130, θ 105°. The standard INDO program¹⁷ was parametrized for second-row elements according to Gregory,¹⁸ that is, the bonding parameters involving sulphur atoms were not scaled ($K = 1$) and no sulphur 3*d*-orbitals were included in the calculations.

Figure 2 indicates diagrammatically the angular dependence of thiophene-2-sulphonyl radical ring-proton hyperfine splitting

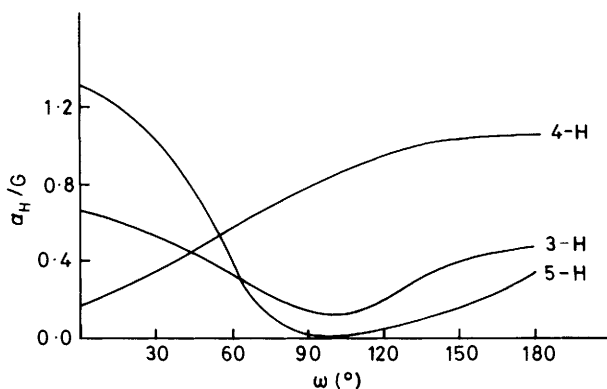


Figure 2. Calculated (INDO) angular dependence (on ω) of ring-proton hyperfine for splitting thiophene-2-sulphonyl radical see (13): α 130°, θ 105°

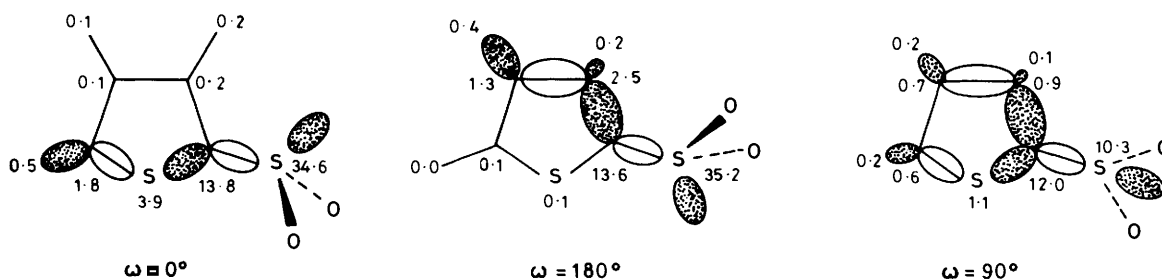
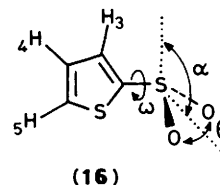


Figure 3. Spin density transmission in thiophene-2-sulphonyl radical via 'through-bonds' interactions. The numbers correspond to the electron charge in the SOMO for each atom relative to the atomic orbital lying in the molecular plane



constants on ω [where ω is the dihedral angle between the thiophene plane and the plane bisecting the OSO angle: see (16)]. It is notable that the larger hyperfine splitting derives from 4-H when ω is nearer 90°, while in the same conditions the hyperfine splitting from 5-H is close to zero.

As far as the spin density distribution is concerned, our INDO results are largely as expected for ω 0 and 180° (see Figure 3) in accordance with *W*-arrangement (*cf.* ref. 19 for other examples of this phenomenon). Indeed, the SOMO located at the SO_2 moiety interacts preferentially with the σ occupied rather than the σ^* virtual MO of the ring, since the anti-bond orbitals lie much higher in energy than do the bond and SOMO orbitals; in this case the 'principle of most negative overlap'²⁰ determines the *trans* delocalization of the unpaired electron. In fact the highest occupied MO (SOMO) will be the most out-of-phase combination of σ bond orbitals; this requirement is satisfied with a *trans* arrangement of the σ bond orbitals contributing to the SOMO.

On the other hand, when the SOMO can conjugate with the π -system (see Figure 3, ω 90°), the spin densities at 4 and 5 positions resulting from 'through-bonds' interactions are almost identical. However, in this arrangement the overall spin density derived from the sum of 'through-bonds' and 'through-space' interactions, is decreased considerably at the 5 position due to a greater negative contribution of spin polarization at this hydrogen;²¹ such spin polarization arises from the partial delocalization of the unpaired electron onto the butadiene-like MO of thiophene which has greater coefficients at C-2 and -5.²² In the light of these results it is not surprising that, as discussed earlier, radicals without a 3-bromo-substituent undergo rapid rotation at accessible temperatures.

Finally, although we realize that the conformation adopted by 3-bromo-substituted thiophene-2-sulphonyl radicals (12) differs surprisingly from that of *ortho*-bromo-substituted benzenesulphonyl radicals (14), at present we are not in a position to give a substantial explanation for this phenomenon.

Experimental

E.s.r. spectra were recorded on a Bruker ER 200 spectrometer equipped with an n.m.r. gaussmeter (field calibration), a frequency counter (g -factor determination), and a standard variable-temperature device. A 1 kW high-pressure mercury lamp was used as u.v. light source. Solution to be photolysed contained either the sulphonyl chloride or a mixture of

sulphonyl chloride, di-*t*-butyl peroxide, and triethylsilane (*ca.* 1:1:1) in toluene or cyclopropane at temperatures between 180 and 230 K; toluene was customarily employed. The samples for the spin-trapping experiments contained sulphonyl chloride and *ca.* 5×10^{-3} g of PBN in toluene or *t*-butylbenzene.

Thiophene-2-sulphonyl chloride was obtained from Kodak and was used after further purification. The following were prepared by the direct chlorosulphonation²³ of the appropriate compound: 3-bromo-, 5-bromo-, 3-bromo-4-deuterio-, 3-bromo-5-deuterio-, 3,4-dibromo-, 3,5-dibromo-, and 4,5-dibromo-thiophene-2-sulphonyl chloride; all these compounds had satisfactory analytical data (m.p.s, n.m.r. and mass spectra). 2-Bromo- and 3-bromo-thiophene were obtained from Fluka. 2,3-Dibromothiophene was prepared by bromination of 3-bromothiophene using *N*-bromosuccinimide.²⁴ 2,4-Dibromothiophene was prepared by following the previously reported method,²⁵ while 3,4-dibromothiophene was kindly provided by Dr. P. Zanirato.

3-Bromo-4-deuterio- and 3-bromo-5-deuterio-thiophene were prepared from 3,4-dibromo- and 2,4-dibromo-thiophene respectively as follows. Dibromothiophene (0.037 mol) in ether was cooled to -70°C and butyl-lithium (0.04 mol) in hexane was added dropwise; after stirring for 20 min the reaction mixture was poured into deuteriated water and worked up in the usual manner.

Acknowledgements

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