The Geometry at Nitrogen in *N*-Phenylsulphonyl-pyrroles and -indoles. The Geometry of Sulphonamides

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The structures of 1-phenylsulphonylpyrrole, 1-phenylsulphonylindole, 4,5,6,7-tetrahydro-1-phenylsulphonylindole, and 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole have been determined by *X*-ray crystallography. The heterocyclic nitrogen is planar in some and pyramidal in others. A preferred geometry for the $PhSO_2N$ unit emerged from the structures; it is compared with available data for sulphonamides.

It is generally accepted that the ring nitrogen in pyrroles and indoles, and indeed in the analogous situation in azoles in general, is planar to allow maximal interaction between an orthogonal lone pair of electrons on the nitrogen and the π electrons generating 6- and 10-π-electron aromatic systems.

We report here that this view can be largely substantiated by an examination of the available crystal structure data[1] for *N*-substituted pyrroles and indoles.

Pyrroles.—There are data for 26† *N*-substituted pyrroles where the pyrrole ring is not imbedded in any other ring system. Significantly, these examples include a large variety of *N*-substituent types: carbon as simple alkyl, aryl, and heteroaryl, and as thio- and dithio-carboxylate, nitrogen as arylamino, imide, and as another pyrrole, and mercury(II) and phosphorus(III).

The internal angles for these non-imbedded pyrroles fall within a range 105.1—111.1°, giving an average figure for this angle of 108.6°, where 20 of the 26 examples have values lying in a 3° range between 107 and 110°.

Greater variation is found in the two angles external to the pyrrole ring, the smallest recorded being 120.4 and the largest 130.7°, but 41 of the 52 angles lie in a 5° range between 123 and 128°. Inspection of the structures shows that this external angle variation depends on the presence and size of the α-substituent.

Importantly, despite these angular variations, there is great consistency in values for the sum of the three angles at nitrogen: the farthest from the 360° figure which corresponds to a perfectly planar situation, being 356.4°. However in 22 of the 26 examples the three nitrogen angles total between 359.5 and 360°.

Turning to *N*-substituted pyrroles in which the ring *is* imbedded in another ring system, rather larger variations in angles are found, though the sums of the three angles still amass near to 360°. The 26 examples‡ for which data are available include, as *N*-substituents, carbon as alkyl (including examples both where the *N*-alkyl substituent is and is not part of a carbocyclic ring to the pyrrole α-position), and iron(III), palladium(II), zinc(II), manganese(III) and (V), copper(II), cobalt(II), and nickel(II) and (III), in each case as part of a ring also involving co-ordination to a pyrrole α-substituent.

The internal angles fall within a range 103.9—113.2°, giving an average figure of 109.1°, closely similar to that for the non-imbedded pyrroles, with 19 of the 26 lying between 105.0 and 109.0°.

The greater variation of external angle noted above for non-imbedded pyrroles is further extended in the imbedded set, particularly but not always where there is a steric constraint in the form of a ring from nitrogen to a pyrrole α-position. This larger total range then is from 109.7—145.6°. Invariably, of the two angles external to the pyrrole, that which is also internal to an extra ring at a pyrrole α-position is the smaller.

The key observation however is that again, despite this wider variation in external angles, summation of the three angles at nitrogen produces figures very close to 360°. Thus, the N angle sum farthest from this figure is 356.0° but 22 of the 26 values lie between 359.3 and 360°.

Indoles.—There are 21 *N*-substituted indoles for which data are available in the Cambridge file and which are not imbedded in another ring system. The nitrogen substituents are less varied than those encountered in the pyrroles, but do include carbon as alkyl, aryl, acyl, and aroyl, and oxygen as alkoxyl.

The range of internal angles at nitrogen spans some 8° from 105.0—112.6°. The mean of these values is 108.6° and 17 of the 21 lie within 1.5° on either side of this value. It is to be noted that this average figure is identical with the corresponding value for the group of non-imbedded pyrroles.

The two external angles in the non-imbedded indoles group can usefully be assessed separately and what emerges is that the averages for the two are virtually identical (125.3 and 125.6). The ranges similarly are parallel, 122.2—128.8° for the 7a-1-substituent angle and 121.7—127.9° for the 2-1-substituent angle.

In summing the three angles at nitrogen as an assessment of planarity it is found that only 2 of the 21 lie outside the range 359.0—360°, the farthest from the perfectly planar situation being 357.2°.

The stereochemical constraints imposed by imbedding the indole within another ring system lead to some large variations in angles and also to a somewhat larger number of examples with distortion from planarity at nitrogen. Of the 27 for which data are available, 22 have internal angles within 1.5° either way of the mean value of 108.4°, again virtually identical with non-imbedded pyrroles and indoles. There are however two examples

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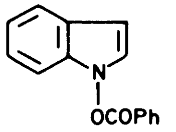
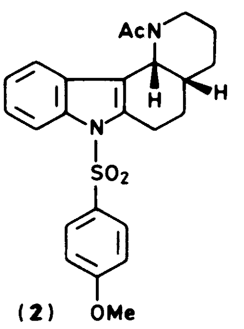
† In analysing the pyrrole-containing structures, from symmetrical structures containing more than one pyrrole ring of identical dimensions, only one of these has been counted. In structures with more than one pyrrole ring, but in which the heterocyclic nuclei have different bond angles, each different pyrrole ring has been counted as a separate example.

‡ Omitted from this total are 6 structures, 5 porphyrin and one corrin macrocycle, in which the geometry of the system, particularly in four of these which also still contain a central metal atom, places such severe restraint on a pyrrole alkyl group as to force it out of the plane of the macrocycles and therefore of the pyrrole concerned.



(1)



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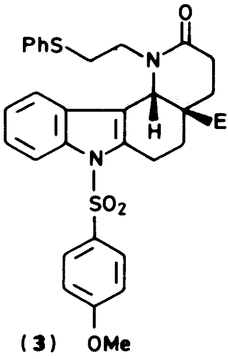

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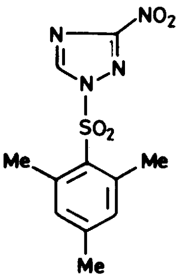

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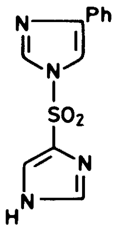

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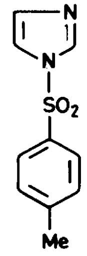

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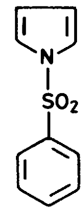

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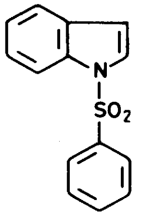

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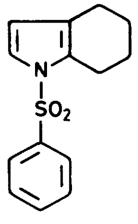

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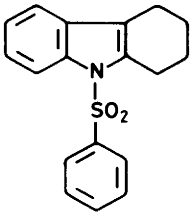

(10)

at great variance with this average, having values of 99.6 and 123.0° (however, see later).

A greater spread is also found for the angles external to indole nitrogen. Considering the 7a–1-substituent angles first, a range of 121.0—138.2° is found leading to a mean value of 127.8°. For 2–1-substituent angles an even bigger spread is found, from 106.9—133.2°, the average value being 123.2°.

Considering finally the sum of the angles at nitrogen in the imbedded group of indoles, it is found that 21 of the 27 lie between 359.0 and 360° while the farthest from planarity corresponds to a value of 356.1°. It is significant that the extreme values for the component angles noted above, 99.6 (internal) with 133.2 (external) and 123.0 (internal) with 106.9 (external), are nevertheless part of planar indoles, with sums of 359.9 and 360° respectively. It is also relevant to note that all of the values (six) less than 359 correspond to structures in which there is a ring between the indole α-position and the nitrogen; however, there are several examples with this structural feature but which nevertheless have planar nitrogen.

Recently, in a report[2] appearing after the completion of the work described herein, Acheson *et al.* described the crystal structure of 1-benzoyloxyindole (**1**) which showed the nitrogen to be pyramidal to the extent that the bond angles at nitrogen sum to 355.0°.

N-Arylsulphonylazoles.—With this background it seemed to us surprising that the *N*-4-methoxyphenylsulphonylindoles (**2**)[3] and (**3**)[4] were shown by *X*-ray crystallography to have substantially non-planar indole nitrogen atoms, since there was no obvious steric reason why the nitrogen should not be typically planar. The sum of the N angles in (**3**) is 354.1°. The novelty of the nitrogen situation in these *N*-arylsulphonylindoles is further emphasised by comparison with the *N*-mesitylsulphonyl-1,2,4-triazole (**4**)[5], the *N*-(4-imidazolylsulphonyl)-imidazole (**5**)[6], and 1-tosylimidazole (**6**)[7] in each of which the arylsulphonyl-bearing nitrogen had been shown to be planar, with N angle sums of 360, 359.4, and 359.6°, respectively.

It did not seem possible to us that the stereochemical demands of the 1,2,3,4-tetrahydrocarbazole ring system imbedded in both (**2**) and (**3**) could be influencing the situation sufficiently to tip the balance of conjugative and steric effects in favour of a pyramidal ring nitrogen. Accordingly, in order to examine this question we have now determined the *X*-ray structures of 1-phenylsulphonylpyrrole (**7**)[8] and 1-phenylsulphonylindole (**8**)[9] and have prepared and determined the structures of 4,5,6,7-tetrahydro-1-phenylsulphonylindole (**9**) and, as closest analogue of (**2**) and (**3**), 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole (**10**).

Results

Each of the *N*-phenylsulphonyl heterocycles was prepared by the catalytic two-phase method[10] and their preparation is exemplified for 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole (**10**).

1,2,3,4-*Tetrahydro-9-phenylsulphonylcarbazole*.—To 1,2,3,4-tetrahydrocarbazole (2 g) in solution in tetrahydrofuran (30 ml) containing tetrabutylammonium hydroxide solution (6 drops, 40%) was added aqueous sodium hydroxide (10 ml, 50%) with vigorous stirring. After 5 min a solution of benzenesulphonyl chloride (4 g) in tetrahydrofuran (10 ml) was added dropwise over 10 min. The mixture was then stirred for a further 30 min. The organic phase was separated, and the aqueous phase washed with ethyl acetate (× 2). The combined organic phases were evaporated under reduced pressure then dissolved in chloroform, washed twice with water, dried, and evaporated to give a brown crystalline material, which recrystallised from methanol to give pale brown crystals of the *phenylsulphonyl derivative* (**10**) (3.35 g, 92%). 1-Phenylsulphonylpyrrole (**7**) had m.p. 86—87 °C (ethanol) (lit.,[8] 89—89.5 °C). 1-Phenylsulphonylindole (**8**) had m.p. 76—77 °C (ethanol) (lit.,[9] 77.5—79 °C). 4,5,6,7-*Tetrahydro*-1-*phenylsulphonylindole* (**9**) had m.p. 50—51 °C (ethanol) (Found: C, 63.9; H, 5.8; N, 5.1; S, 12.0. $C_{14}H_{15}NO_2S$ requires C, 64.4; H, 5.7; N, 5.4; S, 12.3%). 1,2,3,4-*Tetrahydro-9-phenylsulphonylcarbazole* (**10**) formed triclinic crystals, m.p. 107—109 °C (methanol). Crystallised from ethanol, (**10**) formed orthorhombic crystals, m.p. 107—109 °C (Found: C, 69.8; H, 5.6; N, 4.4; S, 10.2. $C_{18}H_{17}NO_2S$ requires C, 69.5; H, 5.5; N, 4.5; S, 10.3%).

X-*Ray Structure Determination of Compounds* (**7**)—(**10**).—In each case intensity data were collected on an Enraf–Nonius CAD-4 computer-controlled Kappa axis single-crystal diffractometer and the structures were solved by direct methods with the MULTAN-80 suite of programs. Thermal parameters are given in Supplementary Publication SUP No. 56525 (6 pp.).*

1-*Phenylsulphonylpyrrole* (**7**). *Crystal data*. $C_{10}H_9NO_2S$, $M = 207$, monoclinic, $a = 11.701(4)$, $b = 7.872(1)$, $c = 11.085(1)$ Å; $\beta = 101.83(2)°$; $U = 999$ Å^3, $Z = 4$, $\rho_c = 1.38$, $\mu(\text{Mo-}K_\alpha) = 3.12$ cm^{-1}, space group $P2_1/c$ (No. 14), 1 109 unique reflexions with $F > 3\sigma(F)$, $R = 4.6\%$.

The crystals were clear, colourless blocks with six faces and slightly elongated, and precession photography revealed the unambiguous space group. Intensity data were collected, from a specimen of dimensions 0.3 × 0.16 × 0.35 mm cleaved from a typical block, out to $\theta = 25°$. No absorption correction was applied as $\mu R < 0.11$. There was no significant intensity variation during standard reflexion monitoring. The partial solution obtained using the MULTAN program was completed using difference Fourier methods. Hydrogen atoms were assigned and then refined using isotropic temperature factors. These and the 14 non-hydrogen atom positions and anisotropic thermal parameters were taken to convergence at $R = 4.6\%$. The weighting scheme $w^{-1} = (0.5 - 0.015F + 0.0009F^2)$ was used to obtain uniform $w \times \Delta F^2$ over the F range.

A stereoscopic drawing of the molecule is shown in Figure 1, a list of positional co-ordinates is given in Table 1, and Tables 2—4 list bond lengths, bond angles, and torsions angles in (**7**).

1-*Phenylsulphonylindole* (**8**). *Crystal data*. $C_{14}H_{11}NO_2S$, $M = 257$, monoclinic, $a = 6.350(1)$, $b = 11.229(1)$, $c = 17.681(6)$ Å; $\beta = 104.16(2)$; $U = 1\,222$ Å^3, $Z = 4$, $\rho_c = 1.40$, $\mu(\text{Mo-}K_\alpha) = 2.73$ cm^{-1}, space group $P2_1/c$ (No. 14), 1 765 unique reflexions with $F > 3\sigma(F)$, $R = 3.27\%$.

Table 1. Atomic co-ordinates for 1-phenylsulphonylpyrrole (7)

Atom	x	y	z
N(1)	0.118 6(3)	0.176 5(4)	0.360 6(3)
C(2)	0.030 9(4)	0.080 4(6)	0.291 6(4)
C(3)	−0.070 7(5)	0.115 2(8)	0.342 4(7)
C(4)	−0.033 6(5)	0.232 6(8)	0.443 9(6)
C(5)	0.082 3(4)	0.265 1(6)	0.452 6(4)
S(6)	0.259 8(1)	0.162 5(1)	0.349 0(1)
O(7)	0.312 6(3)	0.319 9(4)	0.390 4(3)
O(8)	0.260 5(3)	0.101 3(5)	0.228 5(3)
C(9)	0.317 9(3)	0.005 5(5)	0.453 5(3)
C(10)	0.312 6(4)	−0.161 6(6)	0.418 6(4)
C(11)	0.354 8(5)	−0.281 7(6)	0.502 8(6)
C(12)	0.399 4(5)	−0.237 2(9)	0.616 2(6)
C(13)	0.404 7(4)	−0.078 3(7)	0.652 8(5)
C(14)	0.364 6(4)	0.046 6(5)	0.573 4(4)
H(2)	0.048 1(38)	0.011 2(61)	0.225 8(40)
H(3)	−0.100 2(29)	0.075 6(44)	0.299 5(29)
H(4)	−0.054 1(31)	0.265 9(46)	0.485 4(32)
H(5)	0.124 0(35)	0.334 6(53)	0.505 0(36)
H(10)	0.275 6(35)	−0.185 6(52)	0.336 0(35)
H(11)	0.341 3(50)	−0.409 2(79)	0.461 4(53)
H(12)	0.420 2(50)	−0.342 4(75)	0.692 7(51)
H(13)	0.429 3(50)	−0.047 5(79)	0.750 2(51)
H(14)	0.364 8(35)	0.162 2(51)	0.594 8(35)

The numbering of atoms is that given in Figure 1.

Table 2. Bond distances (Å) for (7) with estimated standard deviations in parentheses

N(1)–C(2)	1.374(5)	S(6)–C(9)	1.735(4)
C(2)–C(3)	1.443(8)	C(9)–C(10)	1.369(5)
C(3)–C(4)	1.452(9)	C(10)–C(11)	1.349(6)
C(4)–C(5)	1.365(7)	C(11)–C(12)	1.306(7)
C(5)–N(1)	1.373(5)	C(12)–C(13)	1.313(8)
S(6)–N(1)	1.686(3)	C(13)–C(14)	1.339(6)
S(6)–O(7)	1.418(3)	C(14)–C(9)	1.368(5)
S(6)–O(8)	1.422(3)		

Numbering of atoms is that given in Figure 1. In the room-temperature structure of (7), atoms C(3) and C(4) and also C(11), C(12), and C(13) display considerable anisotropic thermal motion and the differences in bond-lengths between equivalent bonds were ascribed solely to this. A further study, at −80 °C, whilst exhibiting smaller thermal ellipsoids, nevertheless retained the main features of the discrepancies recorded above.

The crystals were colourless and transparent with a dominant bi-pyramidal habit. Intensity data were collected, from a sample of dimensions 0.4 × 0.4 × 0.55 mm, out to $\theta = 25°$. No absorption correction was applied as $\mu R < 0.17$. There was no significant intensity variation during standard reflexion monitoring. The positions of the 18 non-hydrogen atoms and isotropic temperature factors were refined by least squares to $R = 11.6\%$. A difference Fourier synthesis confirmed the structure and allowed assignment of the hydrogen atom positions. All atomic positions were refined to convergence at $R = 3.27\%$. The weighting scheme $w^{-1} = (0.15 - 0.008F + 0.0008F^2)$ was used in the final cycles to obtain a uniform $w \times \Delta F^2$ over the F range.

A stereoscopic drawing of the molecule is shown in Figure 2, a list of positional co-ordinates is given in Table 5, and Tables 6—8 list bond lengths, bond angles, and torsion angles in (**8**).

4,5,6,7-*Tetrahydro*-1-*phenylsulphonylindole* (**9**). *Crystal data*. $C_{14}H_{15}NO_2S$, $M = 261$, triclinic, $a = 8.026(6)$, $b = 8.287(7)$, $c = 10.078(7)$ Å; $\alpha = 94.26(6)°$, $\beta = 90.90(6)°$, $\gamma = 108.85(6)°$; $U = 632$ Å^3, $Z = 2$, $\rho_c = 1.37$, $\mu(\text{Mo-}K_\alpha) = 2.63$ cm^{-1}, space group $P\bar{1}$ (No. 2), 1 935 unique reflexions with $F > 3\sigma(F)$, $R = 5.39\%$.

The colourless, transparent crystals became pink on pro-

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* For details of Supplementary Publications see Instructions for Authors (1986), in *J. Chem. Soc., Perkin Trans. 2*, 1986, Issue 1. Structure factors are available on request from the editorial office.

Table 3. Bond angles (°) for (**7**) with estimated standard deviations in parentheses

N(1)–C(2)–C(3)	105.1(4)	C(9)–S(6)–O(8)	108.0(2)
C(2)–C(3)–C(4)	106.5(4)	O(7)–S(6)–O(8)	120.9(2)
C(3)–C(4)–C(5)	108.0(4)	S(6)–C(9)–C(10)	120.5(3)
C(4)–C(5)–N(1)	107.9(4)	S(6)–C(9)–C(14)	120.3(3)
C(5)–N(1)–C(2)	112.6(4)	C(9)–C(10)–C(11)	119.2(4)
C(2)–N(1)–S(6)	123.6(3)	C(10)–C(11)–C(12)	119.7(5)
C(5)–N(1)–S(6)	123.1(3)	C(11)–C(12)–C(13)	122.5(6)
N(1)–S(6)–O(7)	106.7(2)	C(12)–C(13)–C(14)	120.5(5)
N(1)–S(6)–O(8)	106.7(2)	C(13)–C(14)–C(9)	118.8(4)
N(1)–S(6)–C(9)	104.6(2)	C(14)–C(9)–C(10)	119.2(4)
C(9)–S(6)–O(7)	108.7(2)		

Numbering of atoms is that given in Figure 1.

longed exposure to light and air; a clear, colourless specimen of 0.20 × 0.40 × 0.70 mm was used for data collection at −177 °C with measurements out to $\theta = 25°$. No absorption correction was applied as $\mu R < 0.18$. Standard reflexion monitoring showed no crystal deterioration.

Table 4. Torsion angles (°) for (**7**)

N(1)–C(2)–C(3)–C(4)	−1
C(2)–C(3)–C(4)–C(5)	0
C(3)–C(4)–C(5)–N(1)	1
C(4)–C(5)–N(1)–C(2)	−2
C(5)–N(1)–C(2)–C(3)	2
C(9)–C(10)–C(11)–C(12)	0
C(10)–C(11)–C(12)–C(13)	0
C(11)–C(12)–C(13)–C(14)	−1
C(12)–C(13)–C(14)–C(9)	0
C(13)–C(14)–C(9)–C(10)	1
C(14)–C(9)–C(10)–C(11)	−1
C(4)–C(5)–N(1)–S(6)	−172
C(3)–C(2)–N(1)–S(6)	172
C(5)–N(1)–S(6)–O(7)	−35
C(5)–N(1)–S(6)–O(8)	−165
C(5)–N(1)–S(6)–C(9)	81
N(1)–S(6)–C(9)–C(10)	88
S(6)–C(9)–C(10)–C(11)	−178

Numbering of atoms is that given in Figure 1.

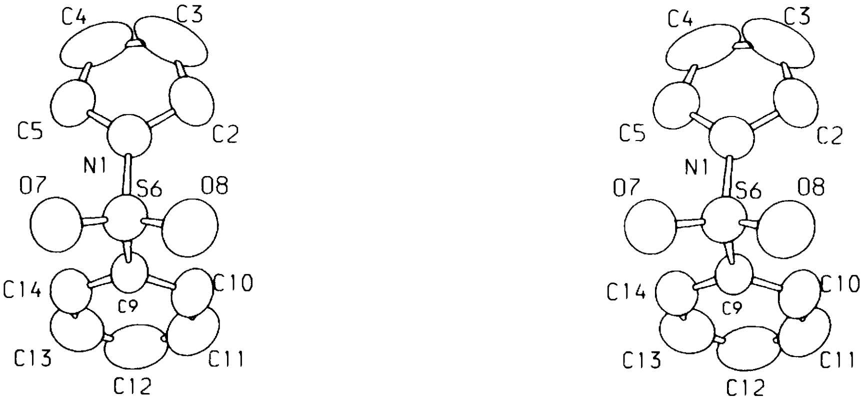


Figure 1. Stereoscopic drawing of 1-phenylsulphonylpyrrole (**7**)

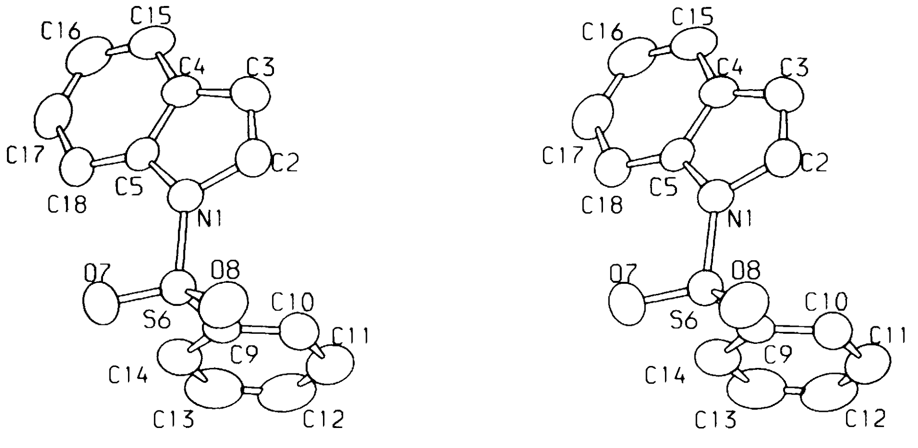


Figure 2. Stereoscopic drawing of 1-phenylsulphonylindole (**8**)

Difference Fourier syntheses after the heavy atom had been placed led to hydrogen-atom-position assignment and these, with isotropic B values, were refined in addition to the 18 non-hydrogen positions and anisotropic temperature factors to $R = 5.39\%$. A weighting scheme $w^{-1} = (0.4 + 0.0016F^2)$ was used in final cycles to give a uniform $w \times \Delta F^2$ over the range of F.

Measurements of unit cell dimensions at room temperature and at −177 °C showed differences consistent with uniform expansion.

A stereoscopic drawing of the molecule is shown in Figure 3, a list of positional co-ordinates is given in Table 9, and Tables 10—12 list bond lengths, bond angles, and torsion angles in (**9**).

1,2,3,4-*Tetrahydro-9-phenylsulphonylcarbazole* (**10**) (*triclinic form*). *Crystal data.* $C_{18}H_{17}NO_2S$, $M = 311$, triclinic, $a =$

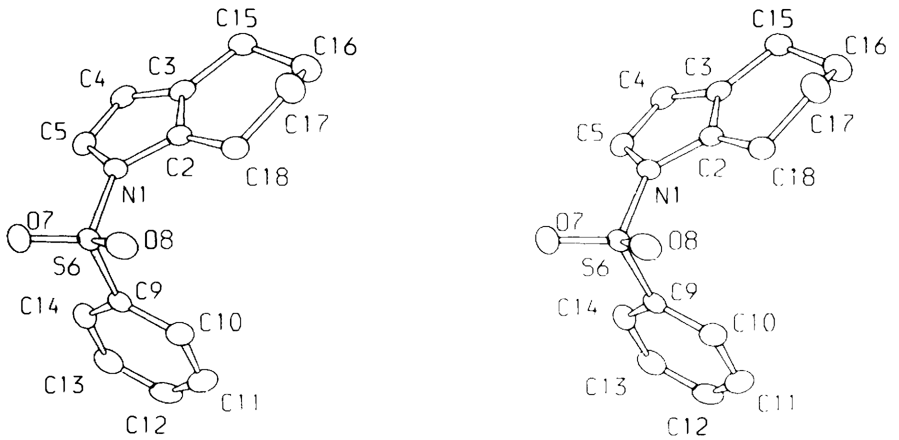


Figure 3. Stereoscopic drawing of 4,5,6,7-tetrahydro-1-phenylsulphonylindole (**9**)

Table 5. Atomic co-ordinates for 1-phenylsulphonylpyrrole (**8**)

Atom	*x*	*y*	*z*
N(1)	0.244 7(2)	0.326 4(1)	0.377 3(1)
C(2)	0.441 5(3)	0.373 0(2)	0.365 5(1)
C(3)	0.480 5(3)	0.325 2(2)	0.301 1(1)
C(4)	0.312 5(3)	0.241 3(2)	0.269 9(1)
C(5)	0.168 8(3)	0.241 7(1)	0.318 5(1)
S(6)	0.186 5(1)	0.334 1(0)	0.463 3(0)
O(7)	−0.035 7(2)	0.302 8(2)	0.450 4(1)
O(8)	0.262 6(2)	0.447 6(1)	0.494 1(1)
C(9)	0.345 4(3)	0.223 6(2)	0.520 4(1)
C(10)	0.564 6(3)	0.244 7(2)	0.551 4(1)
C(11)	0.686 1(4)	0.159 6(2)	0.598 9(1)
C(12)	0.590 8(5)	0.056 2(2)	0.615 0(1)
C(13)	0.375 4(5)	0.035 5(2)	0.583 2(1)
C(14)	0.248 3(4)	0.119 4(2)	0.535 7(1)
C(15)	0.272 9(4)	0.165 4(2)	0.205 4(1)
C(16)	0.094 4(4)	0.094 2(2)	0.191 6(1)
C(17)	−0.047 1(4)	0.096 0(2)	0.240 0(1)
C(18)	−0.013 6(3)	0.170 1(2)	0.304 3(1)
H(2)	0.515 0(29)	0.429 5(16)	0.399 4(11)
H(3)	0.602 9(34)	0.346 5(18)	0.280 1(13)
H(10)	0.631 9(33)	0.319 7(18)	0.539 2(13)
H(11)	0.838 5(43)	0.176 1(23)	0.623 0(16)
H(12)	0.687 7(42)	−0.000 7(24)	0.649 8(16)
H(13)	0.304 5(45)	−0.029 7(26)	0.593 8(17)
H(14)	0.089 8(36)	0.109 9(21)	0.513 0(14)
H(15)	0.376 9(38)	0.164 7(21)	0.169 9(14)
H(16)	0.067 8(38)	0.041 2(22)	0.146 5(14)
H(17)	−0.168 1(40)	0.044 8(21)	0.229 5(15)
H(18)	−0.107 2(31)	0.173 5(17)	0.336 8(12)

The numbering of atoms is that given in Figure 2.

Table 6. Bond distances (Å) for (**8**) with estimated standard deviations in parentheses

C(5)–N(1)	1.408(2)	S(6)–N(1)	1.660(1)
N(1)–C(2)	1.400(2)	S(6)–O(7)	1.418(1)
C(2)–C(3)	1.336(3)	S(6)–O(8)	1.423(1)
C(3)–C(4)	1.429(3)	S(6)–C(9)	1.755(2)
C(4)–C(5)	1.398(3)	C(9)–C(10)	1.386(3)
C(4)–C(15)	1.397(3)	C(10)–C(11)	1.378(3)
C(15)–C(16)	1.359(3)	C(11)–C(12)	1.371(4)
C(16)–C(17)	1.384(4)	C(12)–C(13)	1.365(4)
C(17)–C(18)	1.383(3)	C(13)–C(14)	1.384(4)
C(18)–C(5)	1.382(3)	C(14)–C(9)	1.379(3)

Numbering of atoms is that given in Figure 2.

Table 7. Bond angles (°) for (**8**) with estimated standard deviations in parentheses

N(1)–C(2)–C(3)	109.3(2)	N(1)–S(6)–O(7)	106.7(1)
C(2)–C(3)–C(4)	108.5(2)	N(1)–S(6)–O(8)	105.3(1)
C(3)–C(4)–C(5)	107.4(2)	N(1)–S(6)–C(9)	105.0(1)
C(4)–C(5)–N(1)	106.8(2)	C(9)–S(6)–O(7)	109.0(1)
C(5)–N(1)–C(2)	108.0(1)	C(9)–S(6)–O(8)	108.6(1)
C(4)–C(15)–C(16)	118.7(2)	O(7)–S(6)–O(8)	121.0(1)
C(15)–C(16)–C(17)	121.3(2)	S(6)–C(9)–C(10)	119.1(1)
C(16)–C(17)–C(18)	121.6(2)	S(6)–C(9)–C(14)	119.4(2)
C(17)–C(18)–C(5)	116.9(2)	C(9)–C(10)–C(11)	118.8(2)
C(18)–C(5)–C(4)	122.0(2)	C(10)–C(11)–C(12)	120.3(2)
C(5)–C(4)–C(15)	119.3(2)	C(11)–C(12)–C(13)	120.5(2)
C(3)–C(4)–C(15)	133.3(2)	C(12)–C(13)–C(14)	120.7(2)
N(1)–C(5)–C(18)	131.2(2)	C(13)–C(14)–C(9)	118.3(2)
C(2)–N(1)–S(6)	121.9(1)	C(14)–C(9)–C(10)	121.4(2)
C(5)–N(1)–S(6)	126.2(1)		

Numbering of atoms is that given in Figure 2.

Table 8. Torsion angles (°) for (**8**)

N(1)–C(2)–C(3)–C(4)	−2
C(2)–C(3)–C(4)–C(5)	1
C(3)–C(4)–C(5)–N(1)	1
C(4)–C(5)–N(1)–C(2)	−2
C(5)–N(1)–C(2)–C(3)	2
C(4)–C(15)–C(16)–C(17)	0
C(15)–C(16)–C(17)–C(18)	0
C(16)–C(17)–C(18)–C(5)	0
C(17)–C(18)–C(5)–C(4)	1
C(18)–C(5)–C(4)–C(15)	−1
C(5)–C(4)–C(15)–C(16)	0
C(9)–C(10)–C(11)–C(12)	0
C(10)–C(11)–C(12)–C(13)	1
C(11)–C(12)–C(13)–C(14)	−1
C(12)–C(13)–C(14)–C(9)	1
C(13)–C(14)–C(9)–C(10)	0
C(14)–C(9)–C(10)–C(11)	−1
C(2)–C(3)–C(4)–C(15)	−179
C(2)–N(1)–C(5)–C(18)	179
C(18)–C(5)–N(1)–S(6)	21
C(3)–C(2)–N(1)–S(6)	162
C(5)–N(1)–S(6)–O(7)	−37
C(5)–N(1)–S(6)–O(8)	−167
C(5)–N(1)–S(6)–C(9)	79
N(1)–S(6)–C(9)–C(10)	77
S(6)–C(9)–C(10)–C(11)	177

Numbering of atoms is that given in Figure 2.

Table 9. Atomic co-ordinates for 4,5,6,7-tetrahydro-1-phenylsulphonylindole (**9**)

Atom	x	y	z
N(1)	0.073 3(4)	0.167 5(4)	0.780 1(3)
C(2)	0.057 8(4)	0.217 2(4)	0.915 2(3)
C(3)	−0.117 9(4)	0.196 4(4)	0.929 5(3)
C(4)	−0.209 2(4)	0.136 9(4)	0.804 3(4)
C(5)	−0.090 6(4)	0.120 4(4)	0.713 7(3)
S(6)	0.257 9(1)	0.200 1(1)	0.697 5(1)
O(7)	0.213 0(3)	0.077 6(3)	0.584 3(3)
O(8)	0.394 6(3)	0.205 3(3)	0.790 3(3)
C(9)	0.299 3(4)	0.405 1(4)	0.640 8(3)
C(10)	0.416 1(4)	0.544 1(5)	0.714 5(4)
C(11)	0.448 8(5)	0.704 3(5)	0.669 8(4)
C(12)	0.363 5(5)	0.722 8(5)	0.554 2(4)
C(13)	0.246 9(5)	0.582 7(5)	0.481 3(4)
C(14)	0.214 6(5)	0.422 2(5)	0.524 5(4)
C(15)	−0.188 1(5)	0.234 8(5)	1.060 9(4)
C(16)	−0.039 9(5)	0.344 9(5)	1.156 1(4)
C(17)	0.116 5(5)	0.280 3(5)	1.156 4(4)
C(18)	0.200 2(4)	0.281 3(4)	1.020 6(4)
H(4)	−0.342 6(43)	0.111 6(42)	0.781 8(32)
H(5)	−0.111 5(44)	0.078 9(43)	0.614 9(33)
H(10)	0.462 1(53)	0.536 4(52)	0.788 3(40)
H(11)	0.528 9(59)	0.791 8(59)	0.730 8(45)
H(12)	0.389 5(53)	0.834 9(52)	0.522 5(40)
H(13)	0.187 9(56)	0.591 9(55)	0.396 8(42)
H(14)	0.128 7(57)	0.336 1(56)	0.467 8(43)
H(151)	−0.251 6(56)	0.125 5(55)	1.096 0(43)
H(152)	−0.275 5(59)	0.299 7(58)	1.045 0(45)
H(161)	−0.079 3(55)	0.335 4(53)	1.253 9(41)
H(162)	0.005 6(61)	0.476 4(60)	1.123 1(46)
H(171)	0.058 9(60)	0.143 8(59)	1.189 6(45)
H(172)	0.213 7(41)	0.347 8(41)	1.227 8(31)
H(181)	0.271 0(50)	0.207 4(49)	1.021 0(37)
H(182)	0.277 0(51)	0.400 0(51)	1.003 0(39)

The numbering of atoms is that given in Figure 3.

Table 10. Bond distances (Å) for (**9**) with estimated standard deviations in parentheses

N(1)–C(2)	1.412(4)	S(6)–N(1)	1.666(3)
C(2)–C(3)	1.376(5)	S(6)–O(7)	1.428(3)
C(3)–C(4)	1.420(5)	S(6)–O(8)	1.418(3)
C(4)–C(5)	1.360(5)	S(6)–C(9)	1.763(4)
C(5)–N(1)	1.390(4)	C(9)–C(10)	1.382(5)
C(3)–C(15)	1.500(5)	C(10)–C(11)	1.379(6)
C(15)–C(16)	1.517(5)	C(11)–C(12)	1.385(6)
C(16)–C(17)	1.516(5)	C(12)–C(13)	1.383(6)
C(17)–C(18)	1.533(5)	C(13)–C(14)	1.376(5)
C(18)–C(2)	1.485(5)	C(14)–C(9)	1.385(5)

Numbering of atoms is that given in Figure 3.

Table 11. Bond angles ( ) for (**9**) with estimated standard deviations in parentheses.

N(1)–C(2)–C(3)	105.7(3)	N(1)–S(6)–O(7)	105.6(2)
C(2)–C(3)–C(4)	108.9(3)	N(1)–S(6)–O(8)	107.7(1)
C(3)–C(4)–C(5)	108.2(3)	N(1)–S(6)–C(9)	104.2(1)
C(4)–C(5)–N(1)	107.5(3)	C(9)–S(6)–O(7)	108.1(2)
C(5)–N(1)–C(2)	109.7(3)	C(9)–S(6)–O(8)	109.0(2)
C(3)–C(15)–C(16)	110.7(3)	O(7)–S(6)–O(8)	121.0(2)
C(15)–C(16)–C(17)	112.1(3)	S(6)–C(9)–C(10)	118.6(3)
C(16)–C(17)–C(18)	113.3(3)	S(6)–C(9)–C(14)	119.3(3)
C(17)–C(18)–C(2)	108.8(3)	C(9)–C(10)–C(11)	118.5(4)
C(18)–C(2)–C(3)	126.5(3)	C(10)–C(11)–C(12)	119.8(4)
C(2)–C(3)–C(15)	121.9(3)	C(11)–C(12)–C(13)	121.1(4)
C(4)–C(3)–C(15)	129.2(3)	C(12)–C(13)–C(14)	119.5(4)
N(1)–C(2)–C(18)	127.8(3)	C(13)–C(14)–C(9)	119.0(4)
C(2)–N(1)–S(6)	127.4(2)	C(14)–C(9)–C(10)	122.1(3)
C(5)–N(1)–S(6)	121.5(2)		

Numbering of atoms is that given in Figure 3.

Table 12. Torsion angles (°) for (**9**)

N(1)–C(2)–C(3)–C(4)	−1
C(2)–C(3)–C(4)–C(5)	0
C(3)–C(4)–C(5)–N(1)	0
C(4)–C(5)–N(1)–C(2)	−1
C(5)–N(1)–C(2)–C(3)	1
C(3)–C(15)–C(16)–C(17)	−46
C(15)–C(16)–C(17)–C(18)	61
C(16)–C(17)–C(18)–C(2)	−42
C(17)–C(18)–C(2)–C(3)	14
C(18)–C(2)–C(3)–C(15)	−1
C(2)–C(3)–C(15)–C(16)	17
C(9)–C(10)–C(11)–C(12)	1
C(10)–C(11)–C(12)–C(13)	−1
C(11)–C(12)–C(13)–C(14)	0
C(12)–C(13)–C(14)–C(9)	0
C(13)–C(14)–C(9)–C(10)	0
C(14)–C(9)–C(10)–C(11)	0
C(5)–C(4)–C(3)–C(15)	−180
C(5)–N(1)–C(2)–C(18)	−178
C(18)–C(2)–N(1)–S(6)	−12
C(4)–C(5)–N(1)–S(6)	−168
C(5)–N(1)–S(6)–O(7)	−36
C(5)–N(1)–S(6)–O(8)	−166
C(5)–N(1)–S(6)–C(9)	78
N(1)–S(6)–C(9)–C(10)	97
S(6)–C(9)–C(10)–C(11)	180

Numbering of atoms is that given in Figure 3.

8.140(2), $b = 9.504(2)$, $c = 10.699(5)$ Å; $\alpha = 76.55(3)°$, $\beta = 81.16(3)°$, $\gamma = 74.02(2)°$; $U = 770$ Å^3, $Z = 2$, $\rho_c = 1.34$, μ(Mo-K_α) = 2.31 cm^{-1}, space group $P\bar{1}$ (No. 2), 3 488 unique reflexions with $F > 3\sigma(F)$, $R = 6.35\%$.

The crystals were multi-faceted, equidimensional blocks. A specimen of dimensions 0.3 × 0.3 × 0.5 mm was coated in grease and used for collection of data out to $\theta = 30°$. Standard reflexion monitoring showed no significant deterioration to occur. No absorption correction was applied as $\mu R < 0.15$. The structure was solved and the 22 non-hydrogen-atoms positions confirmed by difference Fourier synthesis and the 17 hydrogen atoms assigned. Least-squares refinement of the non-hydrogen positional and anisotropic temperature parameters converged at $R = 8.5\%$. Problems associated with disorder, indicated by abnormally high thermal parameters and short bond lengths, were resolved using half occupancy parameters at alternative sites. After experimentation with various constraints on the parameters of the disordered atoms C(31), C(32), C(41), and C(42), positions were chosen to be symmetrical and were not subsequently refined. Refinement then continued to $R = 6.35\%$. The weighting scheme $w^{-1} = (0.084 + 0.022F + 0.000\,27F^2)$ was used in the final stages to obtain a uniform $w \times \Delta F^2$ distribution over the F range.

A stereoscopic drawing of the molecule is shown in Figure 4, a list of positional co-ordinates is given in Table 13, and Tables 14—16 list bond lengths, bond angles, and torsion angles in (**10**) (triclinic form).

1,2,3,4-*Tetrahydro*-9-*phenylsulphonylcarbazole* (**10**) (*orthorhombic form*). *Crystal data* $C_{18}H_{17}NO_2S$, $M = 311$, orthorhombic, $a = 9.269(1)$, $b = 22.072(2)$, $c = 14.779(1)$ Å; $U = 3\,024$ Å^3, $Z = 8$, $\rho_c = 1.37$, μ(Mo-K_α) = 2.36 cm^{-1}, space group $Pbca$ (No. 61), 2 557 unique reflexions with $F > 3\sigma(F)$, $R = 4.86\%$.

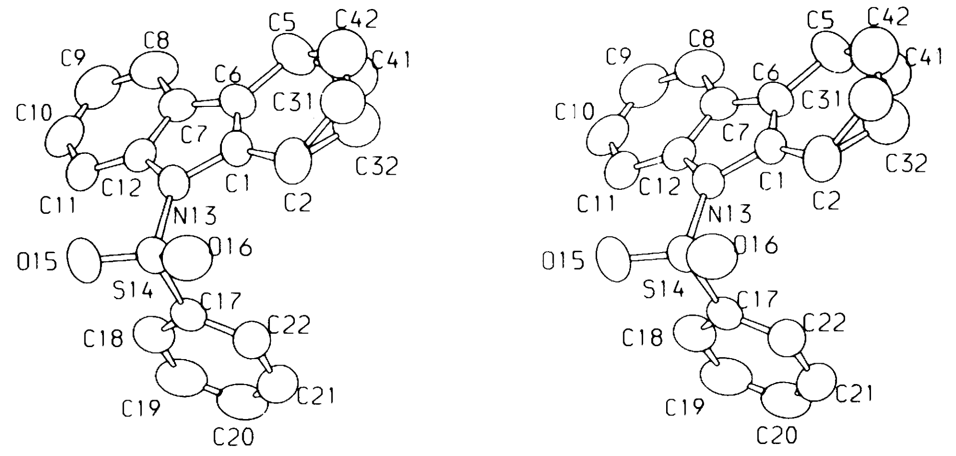


Figure 4. Stereoscopic drawing of 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole (**10**) (triclinic form)

Table 13. Atomic co-ordinates for 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole (**10**) (triclinic modification)

Atom	*x*	*y*	*z*
C(1)	0.256 8(3)	0.127 3(3)	0.439 1(2)
C(2)	0.216 9(4)	0.268 9(4)	0.486 2(3)
C(31)	0.2064	0.2348	0.6298
C(32)	0.1253	0.2483	0.6181
C(41)	0.1153	0.1146	0.6928
C(42)	0.1965	0.1011	0.7045
C(5)	0.194 3(5)	−0.031 3(5)	0.654 6(3)
C(6)	0.247 4(3)	−0.006 6(3)	0.513 2(2)
C(7)	0.297 8(3)	−0.116 5(3)	0.434 1(3)
C(8)	0.315 6(5)	−0.271 3(4)	0.460 0(4)
C(9)	0.366 7(5)	−0.345 1(3)	0.358 5(4)
C(10)	0.398 0(4)	−0.271 6(3)	0.234 9(4)
C(11)	0.386 1(4)	−0.120 8(3)	0.206 6(3)
C(12)	0.335 8(3)	−0.044 8(2)	0.308 5(2)
C(13)	0.316 7(3)	0.107 5(2)	0.310 8(2)
C(14)	0.314 4(1)	0.241 6(1)	0.180 5(1)
C(15)	0.429 1(3)	0.177 8(3)	0.083 2(2)
C(16)	0.343 8(3)	0.365 0(2)	0.219 6(2)
C(17)	0.104 3(3)	0.288 6(3)	0.135 8(2)
C(18)	0.062 9(4)	0.210 2(3)	0.057 1(3)
C(19)	−0.103 2(5)	0.248 0(4)	0.024 3(4)
C(20)	−0.224 8(4)	0.361 7(5)	0.069 5(4)
C(21)	−0.180 0(5)	0.440 4(4)	0.145 8(4)
C(22)	−0.015 4(4)	0.405 2(3)	0.179 8(3)
H(21)	0.1068	0.3324	0.4578
H(22)	0.3077	0.3210	0.4514
H(311)	0.1459	0.3263	0.6610
H(312)	0.3233	0.2034	0.6561
H(321)	0.0045	0.2565	0.6103
H(322)	0.1312	0.3288	0.6589
H(411)	−0.0035	0.1484	0.6705
H(412)	0.1141	0.1003	0.7866
H(421)	0.1291	0.0978	0.7888
H(422)	0.3154	0.0953	0.7162
H(51)	0.1107	−0.0924	0.6751
H(52)	0.2951	−0.0830	0.7018
H(8)	0.2921	−0.3255	0.5480
H(9)	0.3811	−0.4535	0.3755
H(10)	0.4295	−0.3277	0.1650
H(11)	0.4118	−0.0687	0.1183
H(18)	0.1499	0.1291	0.0250
H(19)	−0.1348	0.1933	−0.0316
H(20)	−0.3432	0.3866	0.0473
H(210)	−0.2666	0.5226	0.1765
H(220)	0.0165	0.4617	0.2341

The numbering of atoms is that given in Figure 4.

Table 14. Bond distances (Å) for (**10**) (triclinic) with estimated standard deviations in parentheses

C(1)–C(2)	1.482(4)	C(12)–C(7)	1.388(3)
C(2)–C(31)	1.489(3)	C(6)–C(7)	1.430(4)
C(2)–C(32)	1.489(3)	C(1)–N(13)	1.421(3)
C(31)–C(41)	1.505(5)	C(12)–N(13)	1.419(3)
C(32)–C(42)	1.505(5)	N(13)–S(14)	1.654(2)
C(41)–C(5)	1.481(4)	S(14)–O(15)	1.417(2)
C(42)–C(5)	1.481(4)	S(14)–O(16)	1.422(2)
C(5)–C(6)	1.490(4)	S(14)–C(17)	1.756(3)
C(6)–C(1)	1.349(4)	C(17)–C(18)	1.378(4)
C(7)–C(8)	1.403(4)	C(18)–C(19)	1.378(5)
C(8)–C(9)	1.378(5)	C(19)–C(20)	1.375(6)
C(9)–C(10)	1.366(6)	C(20)–C(21)	1.372(6)
C(10)–C(11)	1.373(4)	C(21)–C(22)	1.374(5)
C(11)–C(12)	1.395(3)	C(22)–C(17)	1.380(4)

Numbering of atoms is that given in Figure 4.

Table 15. Bond angles (°) for (**10**) (triclinic) with estimated standard deviations in parentheses

C(1)–C(2)–C(31)	109.1(3)	N(13)–C(1)–C(2)	126.4(2)
C(1)–C(2)–C(32)	109.1(3)	N(13)–C(12)–C(11)	130.6(2)
C(2)–C(31)–C(41)	114.3(1)	C(5)–C(6)–C(7)	127.1(3)
C(2)–C(32)–C(42)	114.3(1)	C(6)–C(7)–C(8)	133.3(3)
C(31)–C(41)–C(5)	114.3(1)	N(13)–S(14)–O(15)	106.9(1)
C(32)–C(42)–C(5)	114.3(1)	N(13)–S(14)–O(16)	106.7(1)
C(41)–C(5)–C(6)	109.5(3)	N(13)–S(14)–O(17)	104.9(1)
C(42)–C(5)–C(6)	109.5(3)	O(15)–S(14)–O(16)	119.2(1)
C(5)–C(6)–C(1)	124.1(3)	O(15)–S(14)–C(17)	108.9(2)
C(6)–C(1)–C(2)	125.1(3)	O(16)–S(14)–C(17)	109.2(1)
C(1)–C(6)–C(7)	108.8(2)	S(14)–C(17)–C(18)	119.6(2)
C(6)–C(7)–C(12)	107.8(2)	S(14)–C(17)–C(22)	118.8(2)
C(7)–C(12)–N(13)	107.2(2)	C(17)–C(18)–C(19)	118.7(3)
C(12)–N(13)–C(1)	107.6(2)	C(18)–C(19)–C(20)	120.5(3)
N(13)–C(1)–C(6)	108.4(2)	C(19)–C(20)–C(21)	119.8(3)
C(7)–C(8)–C(9)	118.2(3)	C(20)–C(21)–C(22)	120.9(3)
C(8)–C(9)–C(10)	121.9(3)	C(21)–C(22)–C(17)	118.6(3)
C(9)–C(10)–C(11)	121.4(3)	C(22)–C(17)–C(18)	121.6(3)
C(10)–C(11)–C(12)	117.3(3)	S(14)–N(13)–C(1)	126.3(2)
C(11)–C(12)–C(7)	122.2(3)	S(14)–N(13)–C(12)	124.3(2)
C(12)–C(7)–C(8)	118.9(3)		

Numbering of atoms is that given in Figure 4.

The crystals were transparent, with a slight brown tinge, and rod-shaped. A specimen of typical hexagonal prismatic habit, dimensions 0.2 × 0.26 × 0.5 mm, was used for data collection out to θ = 30°. Standard reflexion monitoring showed no

Table 16. Torsion angles (°) for (**10**) (triclinic)

C(6)-C(1)-C(2)-C(31)	14
C(6)-C(1)-C(2)-C(32)	-14
C(1)-C(2)-C(31)-C(41)	-41
C(1)-C(2)-C(32)-C(42)	41
C(2)-C(31)-C(41)-C(5)	59
C(2)-C(32)-C(42)-C(5)	-59
C(31)-C(41)-C(5)-C(6)	-41
C(32)-C(42)-C(5)-C(6)	41
C(41)-C(5)-C(6)-C(1)	14
C(42)-C(5)-C(6)-C(1)	-14
C(5)-C(6)-C(1)-C(2)	0
N(13)-C(1)-C(6)-C(7)	-1
C(1)-C(6)-C(7)-C(12)	-1
C(6)-C(7)-C(12)-N(13)	3
C(7)-C(12)-N(13)-C(1)	-3
C(12)-N(13)-C(1)-C(6)	3
C(12)-C(7)-C(8)-C(9)	-1
C(7)-C(8)-C(9)-C(10)	-1
C(8)-C(9)-C(10)-C(11)	2
C(9)-C(10)-C(11)-C(12)	-2
C(10)-C(11)-C(12)-C(7)	0
C(11)-C(12)-C(7)-C(8)	2
C(11)-C(12)-N(13)-S(14)	13
C(22)-C(17)-C(18)-C(19)	-1
C(17)-C(18)-C(19)-C(20)	0
C(18)-C(19)-C(20)-C(21)	1
C(19)-C(20)-C(21)-C(22)	-1
C(20)-C(21)-C(22)-C(17)	0
C(21)-C(22)-C(17)-C(18)	1
C(41)-C(5)-C(6)-C(7)	-167
C(42)-C(5)-C(6)-C(7)	165
C(5)-C(6)-C(7)-C(8)	-1
C(6)-C(7)-C(8)-C(9)	179
C(10)-C(11)-C(12)-N(13)	178
C(11)-C(12)-N(13)-C(1)	178
C(12)-N(13)-C(1)-C(2)	-179
N(13)-C(1)-C(2)-C(31)	-164
N(13)-C(1)-C(2)-C(32)	169
C(12)-N(13)-S(14)-O(15)	-35
C(12)-N(13)-S(14)-O(16)	-163
C(12)-N(13)-S(14)-C(17)	81
N(13)-S(14)-C(17)-C(18)	-87
S(14)-C(17)-C(18)-C(19)	179

Numbering of atoms is that given in Figure 4.

crystal deterioration. No absorption correction was applied as $\mu R < 0.12$.

The 22 non-hydrogen atoms were confirmed by Fourier methods and the 17 hydrogen atoms assigned. Least-squares refinement of all positional parameters and of non-hydrogen atom anisotropic thermal parameters proceeded to $R = 4.86\%$. During final cycles the weighting scheme $w^{-1} = (1.7 - 0.05F + 0.001F^2)$ produced a uniform $w \times \Delta F^2$ distribution over the F range.

A stereoscopic drawing of the molecule is shown in Figure 5, a list of positional co-ordinates is given in Table 17, and Tables 18—20 list bond lengths, bond angles, and torsion angles for (**10**) (orthorhombic form).

Discussion

Of the compounds here examined, in all save the orthorhombic form (see below) of 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole (**10**), the pyrrole ring nitrogen proved to be essentially planar with N angle sums of 359.3, 358.5, 358.1, and 356.1°, there being a drift away from planarity in the order (**7**), (**9**), triclinic (**10**), and (**8**).

Noting that the crystallographic determinations [3,4] of (**2**) and (**3**) were carried out at −160 °C; the structure of 1-phenylsulphonylpyrrole was re-determined at −80 °C. There was no significant difference in the nitrogen geometry at the lower temperature. Further, the *X*-ray determination of (**9**) was in fact conducted at −177 °C, because of its low m.p. and relative instability, and as indicated above, the nitrogen proved to be substantially planar.

Table 17. Atomic co-ordinates for 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole (**10**) (orthorhombic modification)

Atom	*x*	*y*	*z*
C(1)	-0.127 7(2)	0.118 4(1)	0.109 4(2)
C(2)	-0.247 4(3)	0.163 5(1)	0.103 9(2)
C(3)	-0.392 1(3)	0.130 3(2)	0.107 0(3)
C(4)	-0.394 5(3)	0.074 3(2)	0.050 7(3)
C(5)	-0.282 9(3)	0.028 0(1)	0.080 4(2)
C(6)	-0.142 7(3)	0.058 0(1)	0.102 0(2)
C(7)	-0.005 9(3)	0.030 2(1)	0.121 4(2)
C(8)	0.036 2(3)	-0.030 3(1)	0.127 3(2)
C(9)	0.175 8(4)	-0.042 8(2)	0.153 1(2)
C(10)	0.272 5(3)	0.003 1(2)	0.171 0(2)
C(11)	0.234 5(3)	0.063 3(1)	0.165 2(2)
C(12)	0.092 7(3)	0.076 0(1)	0.140 0(2)
N(13)	0.018 3(2)	0.132 2(1)	0.134 6(1)
S(14)	0.099 1(1)	0.195 2(0)	0.099 4(0)
O(15)	0.238 6(2)	0.195 7(1)	0.140 5(1)
O(16)	0.001 9(2)	0.243 9(1)	0.115 6(1)
C(17)	0.119 3(3)	0.186 1(1)	-0.018 0(2)
C(18)	0.240 1(3)	0.157 3(1)	-0.052 1(2)
C(19)	0.255 2(4)	0.152 2(1)	-0.144 5(2)
C(20)	0.153 1(4)	0.175 9(1)	-0.201 4(2)
C(21)	0.032 6(4)	0.204 5(1)	-0.167 1(2)
C(22)	0.015 2(3)	0.210 0(1)	-0.075 3(2)
H(21)	-0.240 1(36)	0.185 8(14)	0.046 1(22)
H(22)	-0.244 6(37)	0.192 6(14)	0.155 7(22)
H(31)	-0.463 1(35)	0.156 5(15)	0.085 6(23)
H(32)	-0.412 5(34)	0.112 2(15)	0.174 4(22)
H(41)	-0.367 2(33)	0.090 9(14)	-0.016 2(23)
H(42)	-0.495 0(35)	0.055 1(15)	0.051 5(22)
H(51)	-0.267 7(36)	-0.001 1(15)	0.033 2(21)
H(52)	-0.319 2(35)	0.005 1(15)	0.132 1(22)
H(8)	-0.032 3(35)	-0.059 6(15)	0.116 6(23)
H(9)	0.204 7(35)	-0.083 4(15)	0.158 0(23)
H(10)	0.360 9(34)	-0.006 6(15)	0.188 3(21)
H(11)	0.295 1(35)	0.092 7(15)	0.179 3(22)
H(18)	0.306 7(34)	0.140 8(15)	-0.009 2(22)
H(19)	0.335 2(34)	0.131 1(15)	-0.167 8(22)
H(20)	0.172 3(35)	0.172 2(14)	-0.262 0(23)
H(210)	-0.037 5(35)	0.222 5(14)	-0.209 0(21)
H(220)	-0.067 5(34)	0.230 4(15)	-0.050 4(21)

The numbering of atoms is that given in Figure 5.

Table 18. Bond distances (Å) for (**10**) (orthorhombic) with estimated standard deviations in parentheses

C(1)-C(2)	1.494(4)	C(1)-N(13)	1.437(3)
C(2)-C(3)	1.530(4)	C(12)-N(13)	1.421(3)
C(3)-C(4)	1.490(5)	N(13)-S(14)	1.663(2)
C(4)-C(5)	1.519(4)	S(14)-O(15)	1.428(2)
C(5)-C(6)	1.493(4)	S(14)-O(16)	1.422(2)
C(6)-C(1)	1.343(4)	S(14)-C(17)	1.757(3)
C(7)-C(8)	1.394(4)	C(17)-C(18)	1.383(4)
C(8)-C(9)	1.377(5)	C(18)-C(19)	1.377(4)
C(9)-C(10)	1.379(5)	C(19)-C(20)	1.370(4)
C(10)-C(11)	1.377(4)	C(20)-C(21)	1.379(5)
C(11)-C(12)	1.395(4)	C(21)-C(22)	1.371(4)
C(12)-C(7)	1.391(4)	C(22)-C(17)	1.388(4)
C(6)-C(7)	1.438(4)		

Numbering of atoms is that given in Figure 5.

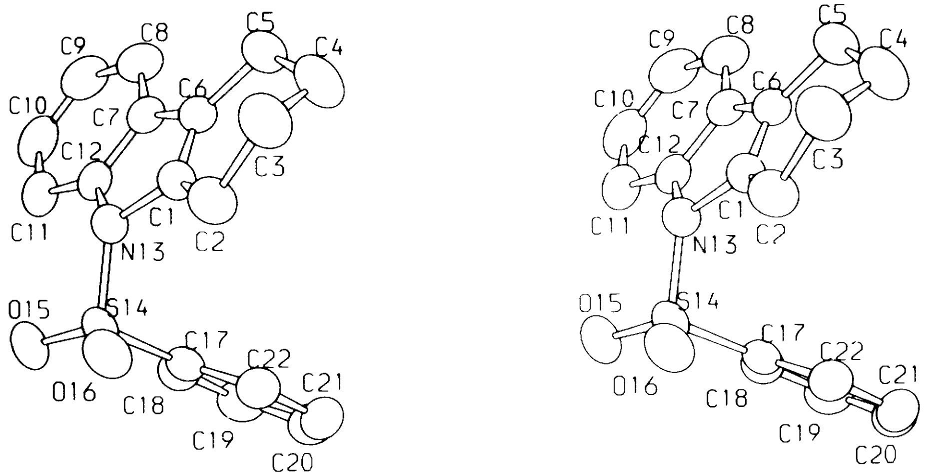


Figure 5. Stereoscopic drawing of 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole (**10**) (orthorhombic form)

Table 19. Bond angles (°) for (**10**) (orthorhombic) with estimated standard deviations in parentheses

C(1)–C(2)–C(3)	109.2(2)	C(5)–C(6)–C(7)	128.3(2)
C(2)–C(3)–C(4)	113.2(3)	C(6)–C(7)–C(8)	132.0(3)
C(3)–C(4)–C(5)	112.7(3)	N(13)–S(14)–O(15)	106.3(1)
C(4)–C(5)–C(6)	110.9(3)	N(13)–S(14)–O(16)	107.1(1)
C(5)–C(6)–C(1)	123.2(3)	N(13)–S(14)–C(17)	105.1(1)
C(6)–C(1)–C(2)	125.5(2)	O(15)–S(14)–O(16)	119.8(1)
C(1)–C(6)–C(7)	108.4(2)	O(15)–S(14)–C(17)	108.9(1)
C(6)–C(7)–C(12)	107.9(2)	O(16)–S(14)–C(17)	108.7(1)
C(7)–C(12)–N(13)	107.8(2)	S(14)–C(17)–C(18)	120.0(2)
C(12)–N(13)–C(1)	106.6(2)	S(14)–C(17)–C(22)	119.0(2)
N(13)–C(1)–C(6)	109.3(2)	C(17)–C(18)–C(19)	118.8(3)
C(7)–C(8)–C(9)	118.2(3)	C(18)–C(19)–C(20)	120.5(3)
C(8)–C(9)–C(10)	121.1(3)	C(19)–C(20)–C(21)	120.6(3)
C(9)–C(10)–C(11)	122.1(3)	C(20)–C(21)–C(22)	120.0(3)
C(10)–C(11)–C(12)	116.8(3)	C(21)–C(22)–C(17)	119.2(3)
C(11)–C(12)–C(7)	121.7(3)	C(22)–C(17)–C(18)	121.0(3)
C(12)–C(7)–C(8)	120.0(3)	S(14)–N(13)–C(1)	121.4(2)
N(13)–C(1)–C(2)	124.9(2)	S(14)–N(13)–C(12)	122.0(2)
N(13)–C(12)–C(11)	130.4(3)		

Numbering of atoms is that given in Figure 5.

Table 20. Torsion angles (°) for (**10**) (orthorhombic)

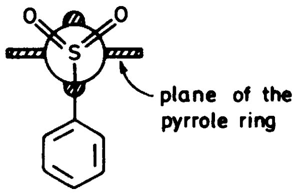
C(6)–C(1)–C(2)–C(3)	11
C(1)–C(2)–C(3)–C(4)	-42
C(2)–C(3)–C(4)–C(5)	60
C(3)–C(4)–C(5)–C(6)	-42
C(4)–C(5)–C(6)–C(1)	11
C(5)–C(6)–C(1)–C(2)	5
N(13)–C(1)–C(6)–C(7)	-1
C(1)–C(6)–C(7)–C(12)	-1
C(6)–C(7)–C(12)–N(13)	1
C(7)–C(12)–N(13)–C(1)	-2
C(12)–N(13)–C(1)–C(6)	1
C(12)–C(7)–C(8)–C(9)	1
C(7)–C(8)–C(9)–C(10)	-1
C(8)–C(9)–C(10)–C(11)	1
C(9)–C(10)–C(11)–C(12)	0
C(10)–C(11)–C(12)–C(7)	0
C(11)–C(12)–C(7)–C(8)	0
C(22)–C(17)–C(18)–C(19)	-1
C(17)–C(18)–C(19)–C(20)	1
C(18)–C(19)–C(20)–C(21)	-1
C(19)–C(20)–C(21)–C(22)	1
C(20)–C(21)–C(22)–C(17)	-1
C(21)–C(22)–C(17)–C(18)	0
C(4)–C(5)–C(6)–C(7)	-172
C(5)–C(6)–C(7)–C(8)	-1
C(6)–C(7)–C(8)–C(9)	-176
C(10)–C(11)–C(12)–N(13)	175
C(11)–C(12)–N(13)–C(1)	-177
C(12)–N(13)–C(1)–C(2)	174
N(13)–C(1)–C(2)–C(3)	-161
C(11)–C(12)–N(13)–S(14)	37
C(12)–N(13)–S(14)–O(15)	-42
C(12)–N(13)–S(14)–O(16)	-171
C(12)–N(13)–S(14)–C(17)	73
N(13)–S(14)–C(17)–C(18)	-88
S(14)–C(17)–C(18)–C(19)	-178

Numbering of atoms is that given in Figure 5.

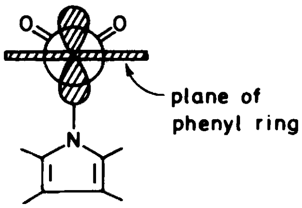
These determinations reinforce the view that there is a substantial tendency for the nitrogen atom in pyrroles and indoles to be planar. However, the most fascinating aspect to emerge from this study is the ability of 1,2,3,4-tetrahydro-9-phenylsulphonylcarbazole to crystallise in two modifications, in one of which (triclinic) the nitrogen is essentially planar, but in the other (orthorhombic) it is pyramidal to the extent that the nitrogen angles sum only to 350.0°. It is thus the most non-planar indole yet reported.

There are two points which emerge from a consideration of these observations. The first is that although there is a marked tendency for the nitrogen atom in pyrroles and indoles to be planar, this tendency can be overcome by other factors and that at least in the case of arylsulphonylindoles these other factors (see also below) can be no more than the forces involved in crystal packing.

Secondly, it seems likely that the difference in energy between planar and pyramidal forms of *N*-arylsulphonyl-substituted azoles is smaller than in situations where the heterocycle carries a simpler substituent and that an electronic interaction between the nitrogen lone pair and the sulphur substituent is responsible for reducing the energy difference between the two forms. It is, we believe, significant that in each of the crystalline compounds described here the sulphonyl group is orientated in such a way as to have both the nitrogen lone pair and the *p* orbital at the sulphur-bearing aromatic carbon nearly coplanar, the plane in question bisecting the O–S–O angle. The Newman projections



(11)



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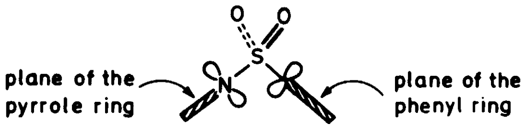

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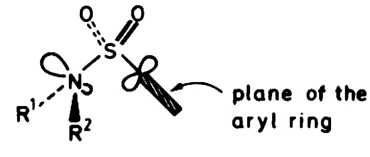

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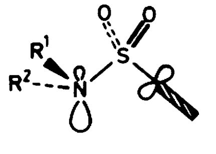

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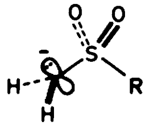
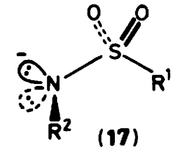


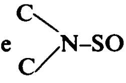
(16)



(17)

(**11**) (along S–N) and (**12**) (along C–S) and the side view (**13**) aim to illustrate the idealised situation.

As a quantitative measure of this coplanarity and assuming that the nitrogen lone pair is orientated in a plane which bisects the C–N–C angle and is perpendicular to the pyrrole ring, one may examine the dihedral angle between that plane and the N–S–C plane: the values are 171, 169, 168, 171, and 163° for (**7**), (**8**), (**9**), triclinic (**10**), and orthorhombic (**10**), respectively. Similarly, an examination of the dihedral angles between the N–S–C plane and the *p*-orbital at the sulphur-bearing aromatic carbon, assumed to be perpendicular to the plane of the benzene ring, produces values of 178, 167, 173, 177, and 178°, respectively.

In the light of the preferences highlighted above and idealised in (**11**), (**12**), and (**13**), we have also examined the available *X*-ray crystal structures of molecules containing the sulphonamide group. A search of the Cambridge Crystallographic Data File for structures containing the  $\mathrm{C_2N{-}SO_2{-}C}$ fragment, in which the N–S bond was not part of a ring, yielded 49 examples for which co-ordinates were available. Fragments which were not symmetry-related in structures containing more than one sulphonamide unit were taken as separate examples.

The 49 *N,N*-distributed sulphonamides contain a range of nitrogen types, including cyclic and acyclic aliphatic, aromatic, amide, monothioimide, enamine, and amidine. The geometry at nitrogen is correspondingly variable, ranging from distinctly pyramidal, with sum of angles at nitrogen of 340.2°, to near planar. We have assumed that the nitrogen lone pair lies on an extension, through the nitrogen, of the normal to the plane of its ligands (C, C, and S), and determined dihedral angles between this plane and the sulphonyl $\mathrm{N{-}S{-}C_{Ar}}$ plane. Of the 49 samples, 32 have dihedral angles within 20° of 180° and 39 have values within 30° of 180°, a distribution which shows a clear preference for the nitrogen lone pair to lie anti-coplanar to the S–C bond.

A subset of 43 examples were arylsulphonamides, and we have also examined dihedral angles between the normal to the aromatic ring through its linking C-atom and the N–S–C plane at the sulphonyl group. For 39 of the 43, the dihedral angles fall within 20° of zero. Again, the distribution indicates a clear conformational preference, in this case, for the plane, which presumably contains an aromatic *p*-orbital, to eclipse the N–S bond.

The preferred conformation for arylsulphonamides is thus indicated as (**14**), with both the nitrogen lone pair and the aromatic *p*-orbital lying on the bisector of the O–S–O internuclear angle. Unfortunately, there are few data from solution-phase measurement to support the results of the crystal-structure survey. Polarised i.r. and Raman spectroscopy of some *N,N*-dimethyl sulphonamides have been reported[11] and the data are said to be consistent with a *'trans'* conformation, with a barrier to rotation about the N–S bond of 5—6 kcal $\mathrm{mol^{-1}}$. It is not clear, however, what is meant by *'trans'* in this work.

It is not easy to rationalise the conformational preferences in terms of minimisation of non-bonded repulsions between the various substituents on the basic N–S–C system, and we suggest that they may be a manifestation of bonding between a sulphur *d*-orbital and the nitrogen lone pair, and, in the case of the aryl sulphonamides, of bonding between the same *d*-orbital and a π-orbital on the aromatic ring. Molecular-orbital calculations on benzenesulphonamide, using an STO-3G basis set including sulphur *d*-orbitals, have been reported,[12] and the results are consistent with this idea. Although a full geometry minimisation was not carried out, torsional angles about both the N–S and S–C bonds were varied and the minimum-energy conformation corresponded to (**14**) with $R^1 = R^2 = H$. Interestingly, the conformation corresponding to (**15**) was calculated to be only 0.026 kcal $\mathrm{mol^{-1}}$ higher and this is not found in any of the crystal structures. Sulphonamides are isoelectronic with sulphonyl-stabilised carbanions, and recent calculations[13] using 3-21G* and 3-21G basis sets with and without *d*-orbitals have demonstrated the importance of including the *d*-orbitals in achieving a proper description of the bonding in these anions. Inclusion of the *d*-orbitals results in shortening of the S–carbanion bond in the minimised structures, and the minimum-energy conformation (**16**) has the carbanionic lone pair in a plane bisecting the O–S–O angle, in complete agreement with the preference revealed by the crystal-structure survey.

It seems very likely, in the light of the discussion above, that the well known acidity of primary and secondary sulphonamides can be ascribed to interaction between the negative charge on nitrogen and the sulphur in a way which parallels the lone pair/sulphur interactions discussed above, *i.e.* that such an anion would be orientated as shown in (**17**). Some elementary text books have ascribed sulphonamide acidity to an enolate-like interaction with an S=O bond; this seems to be less likely.

Acknowledgements

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