Sulphone Structures. Part II.[1] Crystal and Molecular Structure of *N*-*p*-Tolylsulphonylbenzylamine, 1-Methyl-3-*p*-tolylsulphonylaminoindole, 1-Methyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane, and 1,2,3,4-Tetrahydro-1,2,4-trimethyl-4-*p*-tolylsulphonylamino-3-*p*-tolylsulphonyliminoquinoline

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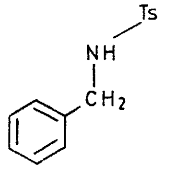
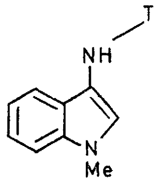
The crystal and molecular structures of the four title compounds have been determined by heavy-atom methods. (I): *N*-*p*-Tolylsulphonylbenzylamine, triclinic, a = 9·686, b = 9·156, c = 9·749 Å (all ±0·003 Å), α = 68·1, β = 64·5, γ = 60·5° (all ±0·1°), space group $P\bar{1}$, Z = 2. Four-circle diffractometer data, R 0·066 for 2515 independent reflections. (II): 1-Methyl-3-*p*-tolylsulphonylaminoindole, monoclinic, a = 20·69, b = 17·39, c = 9·53 Å (all ±0·01 Å), β = 118·25° ± 0·03°, space group $C2/c$, Z = 8, linear diffractometer data, R 0·065 for 1948 independent reflections. (III): 1-Methyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane, monoclinic, a = 16·08, b = 11·42, c = 20·51 Å (all ±0·01Å), β = 105·0° ± 0·1°, space group $C2/c$, Z = 8, Linear diffractometer data, R 0·055 for 1448 independent reflections. (IV): 1,2,3,4-Tetrahydro-1,2,4-trimethyl-4-*p*-tolylsulphonylamino-3-*p*-tolylsulphonyliminoquinoline, triclinic, a = 7·67 ± 0·01, b = 13·71 ± 0·02, c = 13·57 ± 0·02 Å, α = 110·4 ± 0·1, β = 109·2 ± 0·1, γ = 92·8 ± 0·2°, space group $P\bar{1}$, Z = 2. Visually estimated data, R 0·103 for 1481 independent reflections. In the four compounds the bond lengths and interbond angles at any sulphur atom are unaffected by the substituents at the nitrogen atom bonded to the sulphur atom. The bond lengths, but not the interbond angles, are the same for an sp^2 and an sp^3 nitrogen atom and the angle between the planes through the O–S–O sulphonyl atoms and through the S–N–C atoms is restricted to the range 53—65 for an sp^3 and 83—88° for an sp^2 nitrogen atom.

THE co-ordination sphere about the sulphur atom in *p*-tolylsulphonylamino- and *p*-tolylsulphonylimino-groups appears to be affected[1] by the conjugation of the nitrogen atom with an aromatic system. We report the crystal structures of four compounds which each contain one or more of these sulphonyl groups: (I) N-*p*-tolylsulphonylbenzylamine, (II) 1-methyl-3-*p*-tolylsulphonylaminoindole, (III) 1-methyl-3-*p*-tolylsulphonyliminoindoline-2-spirocyclopentane, and (IV) 1,2,3,4-tetrahydro-1,2,4-trimethyl-4-*p*-tolylsulphonylamino-3-*p*-tolylsulphonyliminoquinoline.



(I)



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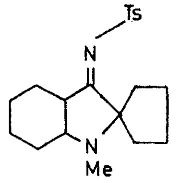
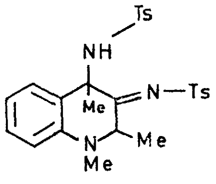
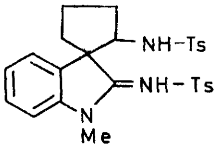


(III)



(IV)



(V)

RESULTS AND DISCUSSION

Interatomic distances and interbond angles for the four compounds are given in Tables 1 and 2 and selected interplane angles are in Table 3. The atom numbering system used in the crystal analysis of the four compounds is given in Figures 1—4 and the packing of these molecules in Figures 5—8.

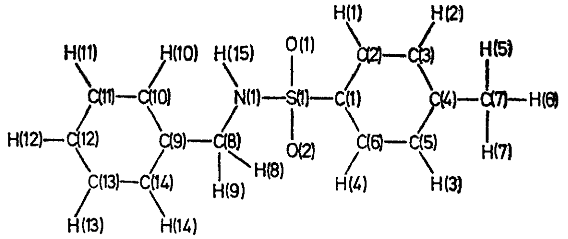


FIGURE 1 Atom numbering for (I)

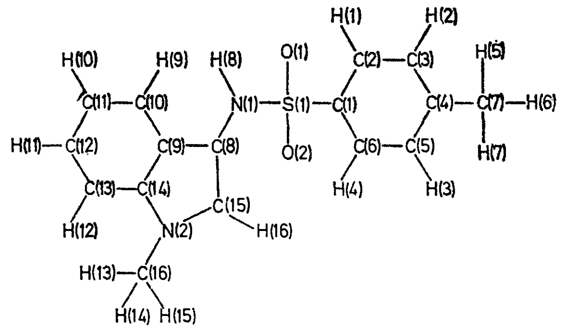


FIGURE 2 Atom numbering for (II)

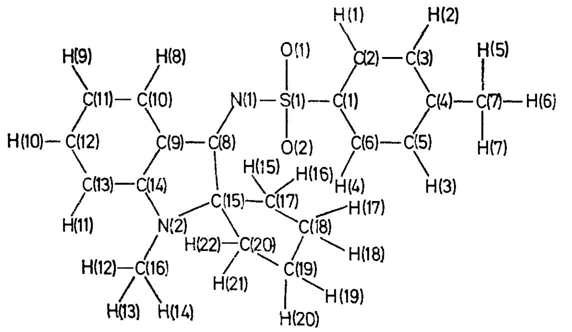


FIGURE 3 Atom numbering for (III)

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[1] Part I, J. Tickle and C. K. Prout, *J. Chem. Soc.* (*C*), 1971, 3401.

TABLE 1

Interatomic distances (Å) for compounds (I)—(IV)

	(I)	(II)	(III)	(IV)
S(1)–O(1)	1·429(2)	1·453(3)	1·435(3)	1·465(7)
S(1)–O(2)	1·432(2)	1·436(3)	1·444(4)	1·427(7)
S(1)–C(1)	1·763(3)	1·771(4)	1·764(4)	1·736(10)
S(1)–N(1)	1·619(2)	1·630(4)	1·619(4)	1·635(8)
S(2)–O(3)				1·418(8)
S(2)–O(4)				1·431(8)
S(2)–C(21)				1·758(10)
S(2)–N(3)				1·646(8)
C(1)–C(2)	1·381(4)	1·374(7)	1·378(7)	1·37(1)
C(1)–C(6)	1·385(4)	1·395(6)	1·386(7)	1·40(1)
C(2)–C(3)	1·384(4)	1·392(7)	1·400(6)	1·39(1)
C(3)–C(4)	1·396(5)	1·385(7)	1·382(8)	1·40(1)
C(4)–C(5)	1·377(5)	1·364(9)	1·348(8)	1·37(2)
C(5)–C(6)	1·380(4)	1·390(7)	1·397(6)	1·36(1)
C(4)–C(7)	1·506(5)	1·530(7)	1·533(7)	1·52(1)
N(1)–C(8)	1·475(3)	1·441(4)	1·304(5)	1·465(13)
C(8)–C(9)	1·499(4)	1·424(5)	1·442(5)	1·511(15)
C(9)–C(10)	1·388(4)	1·409(6)	1·402(6)	1·360(16)
C(9)–C(14)	1·391(4)	1·429(4)	1·396(6)	1·443(16)
C(10)–C(11)	1·391(4)	1·388(6)	1·388(7)	1·386(19)
C(11)–C(12)	1·385(5)	1·416(6)	1·374(9)	1·404(22)
C(12)–C(13)	1·372(5)	1·382(7)	1·376(8)	1·367(19)
C(13)–C(14)	1·380(4)	1·404(5)	1·419(6)	1·335(16)
C(14)–N(2)		1·367(5)	1·356(5)	1·377(13)
N(3)–C(17)				1·225(13)
C(8)–C(15)		1·383(5)	1·514(6)	
C(15)–C(17)			1·559(7)	1·558(16)
N(2)–C(15)		1·387(5)	1·462(6)	1·432(14)
N(2)–C(16)		1·474(5)	1·465(8)	1·509(16)
C(15)–C(20)			1·557(7)	
C(17)–C(18)			1·506(8)	
C(18)–C(19)			1·456(12)	
C(19)–C(20)			1·478(9)	
C(8)–C(17)				1·486(13)
C(8)–C(19)				1·553(16)
C(15)–C(18)				1·598(18)
C(21)–C(22)				1·37(1)
C(21)–C(26)				1·33(2)
C(22)–C(23)				1·42(1)
C(23)–C(24)				1·34(2)
C(24)–C(25)				1·39(1)
C(25)–C(26)				1·40(1)
C(24)–C(26)				1·56(1)
O(1)–N(1′)		2·983(5)		3·004(9)

Primed atom is at equivalent position $(-x, -y, -z)$.

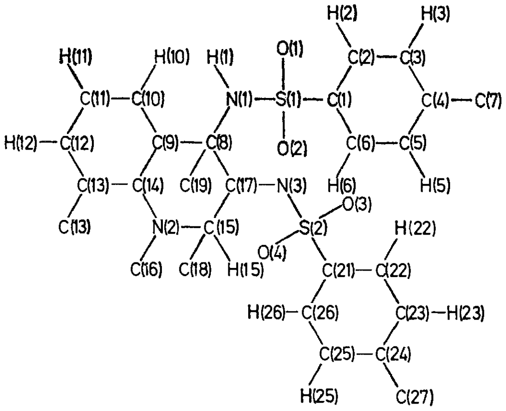

FIGURE 4 Atom numbering for (IV)

Compound (I).—The crystal contains isolated molecules which have configuration and dimensions consistent with formula (I). There is no hydrogen bond formed by the amine hydrogen atom H(15), and the sulphonyl oxygen atoms. The closest approach across the symmetry centre is 2·24 Å between H(15) and O(2).

The planes of the two phenyl groups are almost perpendicular so that the hydrogen atom H(1), bonded to carbon atom C(2), lies in the angle between the two methylene hydrogen atoms H(8) and H(9) and makes contacts of 2·64 and 2·74 Å respectively. The

TABLE 2

Interbond angles (deg.) for compounds (I)—(IV)

	(I)	(II)	(III)	(IV)
O(1)–S(1)–O(2)	119·0(2)	118·5(4)	116·5(4)	118·5(5)
O(1)–S(1)–N(1)	107·9(3)	104·7(5)	111·7(5)	107·2(5)
O(1)–S(1)–C(1)	108·3(3)	107·1(4)	108·1(4)	105·0(6)
O(2)–S(1)–N(1)	105·5(3)	108·8(4)	111·9(4)	110·1(4)
O(2)–S(1)–C(1)	108·3(3)	107·9(5)	107·5(5)	107·5(6)
N(1)–S(1)–C(1)	107·4(3)	109·7(4)	99·6(5)	107·9(5)
O(3)–S(2)–O(4)				117·8(5)
O(3)–S(2)–N(3)				110·0(5)
O(3)–S(2)–C(21)				108·6(5)
O(4)–S(2)–N(3)				110·7(5)
N(3)–S(2)–C(21)				100·3(5)
S(1)–N(1)–C(8)	119·5(4)	122·2(5)	125·9(6)	124·7(7)
S(1)–C(1)–C(2)	119·8(4)	120·3(8)	118·4(9)	118·8(9)
S(1)–C(1)–C(6)	119·8(4)	119·4(8)	120·3(9)	119·7(9)
C(2)–C(1)–C(6)	120·4(5)	120·1(7)	121·1(7)	121·4(10)
C(1)–C(2)–C(3)	119·0(6)	120·2(8)	119·9(8)	119·1(11)
C(2)–C(3)–C(4)	121·6(6)	120·5(11)	119·4(11)	119·8(11)
C(3)–C(4)–C(5)	118·6(6)	118·4(10)	119·4(9)	119·5(11)
C(3)–C(4)–C(7)	120·8(6)	120·2(9)	117·7(10)	119·7(11)
C(5)–C(4)–C(7)	120·0(6)	121·4(8)	122·9(7)	120·6(10)
C(4)–C(5)–C(6)	121·1(5)	122·7(8)	123·3(7)	121·4(10)
C(5)–C(6)–C(1)	119·8(6)	118·1(10)	116·9(10)	118·7(10)
N(1)–C(8)–C(9)	111·8(5)	125·8(6)	135·1(5)	108·8(8)
N(1)–C(8)–C(15)		126·2(6)	117·4(7)	
C(9)–C(8)–C(15)		107·9(7)	107·5(9)	
N(1)–C(8)–C(17)				110·5(8)
N(1)–C(8)–C(19)				101·9(8)
C(9)–C(8)–C(17)				113·1(9)
C(9)–C(8)–C(19)				111·2(9)
C(17)–C(8)–C(19)				110·8(9)
C(8)–C(9)–C(10)	122·7(5)	134·6(5)	132·1(7)	119·3(10)
C(8)–C(9)–C(14)	118·8(5)	106·4(7)	106·7(10)	119·9(10)
C(10)–C(9)–C(14)	118·4(5)	119·0(6)	121·2(8)	120·8(11)
C(9)–C(10)–C(11)	120·8(6)	118·6(8)	117·2(10)	121·7(14)
C(10)–C(11)–C(12)	119·6(7)	121·7(8)	121·0(11)	113·9(14)
C(11)–C(12)–C(13)	120·0(6)	120·8(9)	123·8(9)	126·4(14)
C(12)–C(13)–C(14)	120·3(5)	118·0(7)	115·8(9)	118·0(12)
C(13)–C(14)–C(9)	120·8(6)	121·8(7)	121·0(7)	118·8(10)
C(13)–C(14)–N(2)		130·6(5)	126·4(7)	119·6(10)
C(9)–C(14)–N(2)		107·6(6)	112·6(9)	121·6(10)
C(14)–N(2)–C(15)		109·8(6)	109·6(8)	117·0(9)
C(14)–N(2)–C(16)		125·4(5)	125·0(9)	121·0(9)
C(15)–N(2)–C(16)		124·6(7)	124·7(8)	111·9(9)
N(2)–C(15)–C(8)		108·3(3)	103·4	
N(2)–C(15)–C(17)			113·4(8)	107·8(9)
N(2)–C(15)–C(18)				115·7(9)
C(17)–C(15)–C(18)				110·7(9)
N(3)–C(17)–C(8)				120·1(9)
N(3)–C(17)–C(15)				124·1(9)
C(8)–C(17)–C(15)				115·5(8)
N(2)–C(15)–C(20)			112·3(10)	
C(8)–C(15)–C(17)			112·0(11)	
C(8)–C(15)–C(20)			111·9(8)	
C(17)–C(15)–C(20)			104·1(9)	
C(15)–C(17)–C(18)			104·7(12)	
C(17)–C(18)–C(19)			106·6(17)	
C(18)–C(19)–C(20)			109·5(11)	
C(19)–C(20)–C(15)			106·8(15)	
S(2)–N(3)–C(17)				122·5(8)
S(2)–C(21)–C(22)				118·9(8)
S(2)–C(21)–C(26)				117·3(8)
C(22)–C(21)–C(26)				123·8(9)
C(21)–C(22)–C(23)				118·9(10)
C(22)–C(23)–C(24)				116·7(11)
C(23)–C(24)–C(25)				124·2(11)
C(23)–C(24)–C(27)				117·1(10)
C(25)–C(24)–C(27)				118·6(10)
C(24)–C(25)–C(26)				118·1(10)
C(21)–C(26)–C(25)				118·6(9)

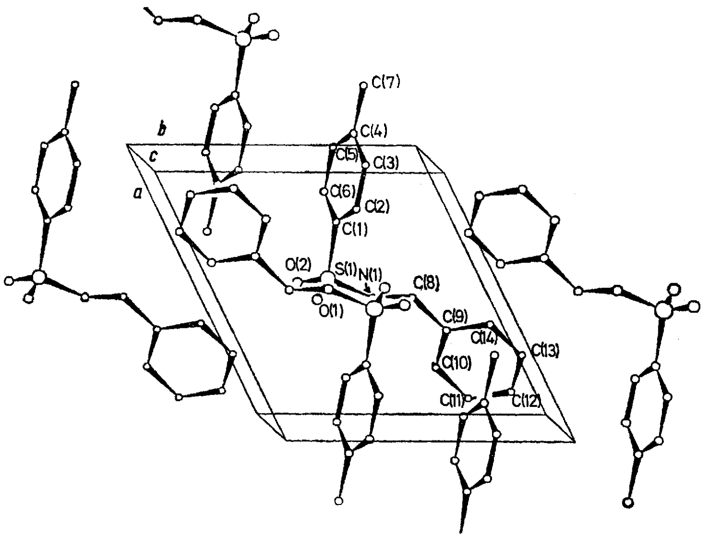

FIGURE 5 Compound (I), viewed so that axis c is 7·1° to the perpendicular to the page

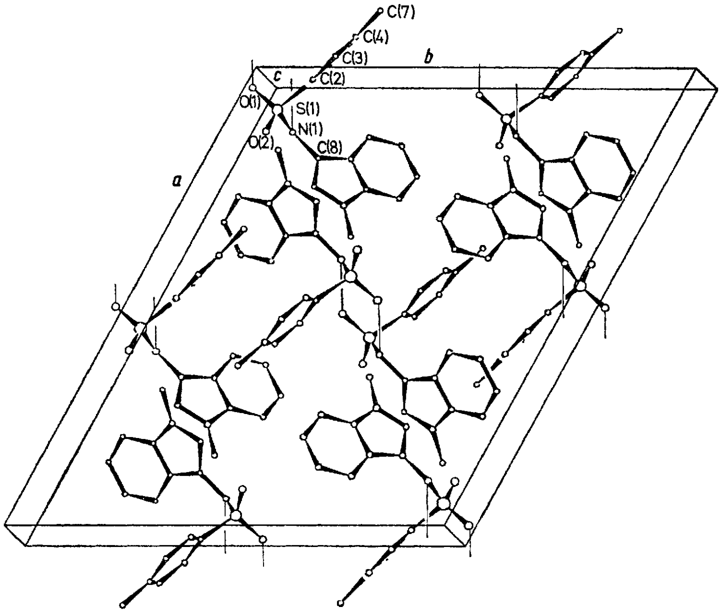

FIGURE 6 Compound (II), axis viewed so that c is at 7·1° to the perpendicular to the page

S(1)–N(1) bond length (1·619 Å) is shorter than that (1·76 Å) for the formal single S–N bond in the zwitterion form of sulphamic acid,[2] but very close to that (1·623 Å) for the two equivalent S–N bonds in bisdimethylamino sulphone.[3] The S(1)–N(1)–C(8) angle is 119·5°, and though the opening of this angle from that expected for an sp^3 nitrogen atom could be due to the steric interaction between hydrogen atom H(1) and atoms H(8) and H(9) (see earlier), an effectively identical S–N–C angle of 119·4(6) is reported[1] for 1-methyl-2′-(p-tolylsulphonylamino)-2-(p-tolylsulphonylimino)indoline-3-spirocyclopentane (V) where there is no steric inhibition and where the analogous S–N bond length is also 1·619 Å. It would seem therefore that this short S–N bond length is a consequence of a d_π–p_π interaction and that the angle of 59·5° between the planes C(8),

TABLE 3

Selected interplane angles (deg.)

Compound	Planes through atoms	Type of N	Angle
(I)	O(1), S(1), O(2) C(8), N(1), S(1)	Amino	59·5
(II)	O(1), S(1), O(2) C(8), N(1), S(1)	Amino	65·0
(III)	O(1), S(1), O(2) C(8), N(1), S(1)	Imino	83·4
(IV)	O(1), S(1), O(2) C(15), N(1), S(1)	Amino	53·6
(IV)	O(3), S(2), O(4) C(17), N(3), S(2)	Imino	88·3
(V) *	O(1), S(1), O(2) C(15), N(1), S(1)	Imino	97·7
(V) *	O(3), S(2), O(4) C(27), N(2), S(2)	Amino	53·7

* From ref. 1.

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[2] R. L. Sass, *Acta Cryst.*, 1960, **13**, 320.

[3] T. Jordan, H. W. Smith, L. L. Lohr, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1963, **85**, 846.

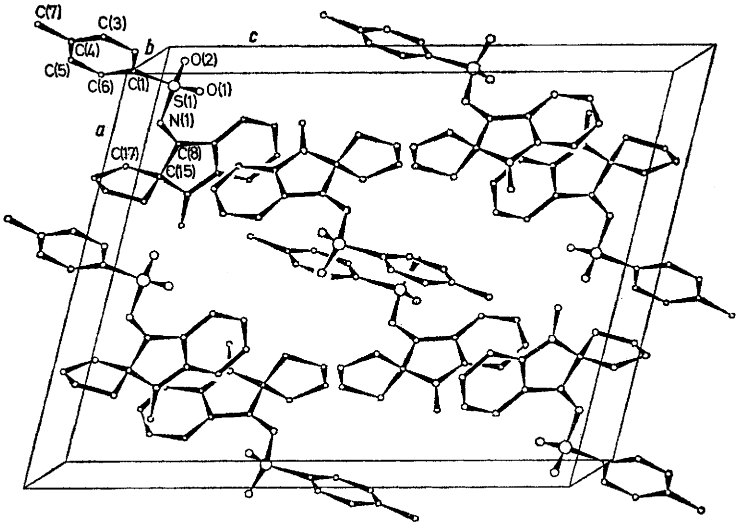

FIGURE 7 Compound (III), viewed so that axis *b* is at 9·5° to the perpendicular to the page

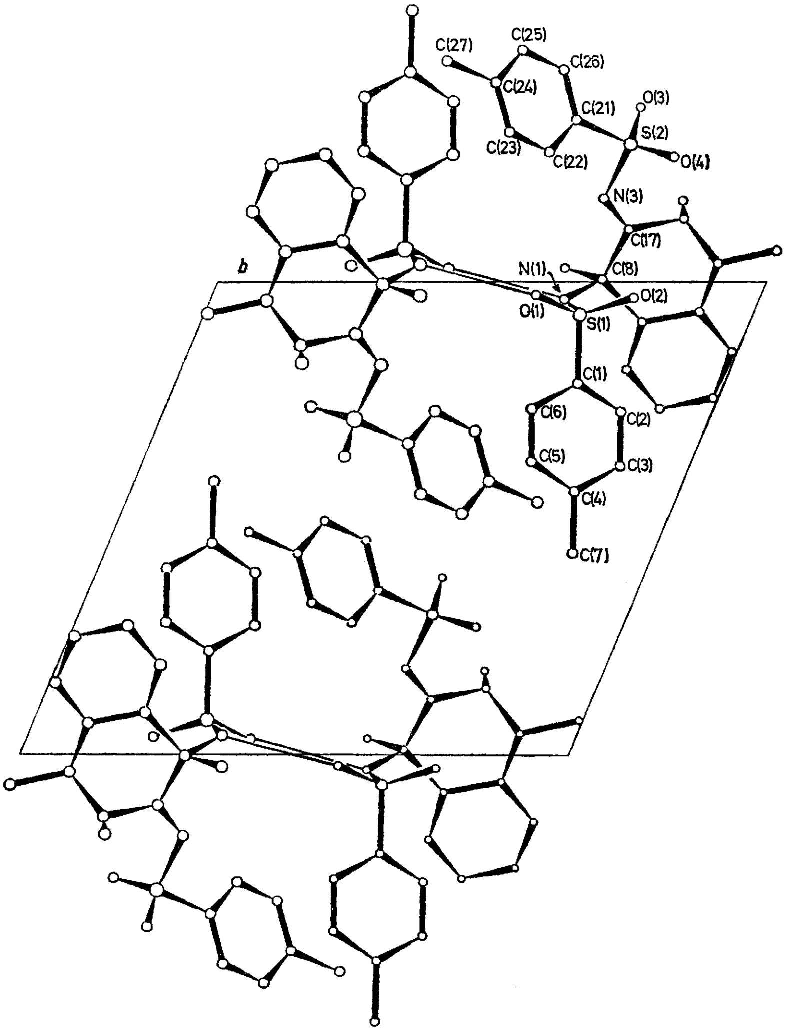

FIGURE 8 Compound (IV), projected along (100)

N(1), S(1) and O(1), S(1), O(2) is suitable for such an interaction. The two sulphur–oxygen bond lengths [S(1)–O(1) 1·429 and S(1)–O(2) 1·432 Å] both correspond [4] to π bond-orders of *ca.* 0·75; the S–N bond lengths represents [4] a π bond-order of *ca.* 0·25, so the S(1)–C(1) bond length of 1·763 Å should also represent a π bond-order of 0·25. The double-bond length between a carbon and a sulphur atom in thiourea [5] is 1·710 Å and the corresponding single bond in an aliphatic thiol [5] is 1·83 Å. The shortening of the S–C bond in (I) is too large to be attributed only to the difference in radii between an sp^2 and an sp^3 carbon atom,[6] and is consistent with an increased π bond-order.

The methylene group at carbon atom C(8) precludes any electron delocalisation from the sulphur atom to the phenyl group and the C(8)–N(1) bond length of 1·475 Å is in agreement with the expected [5] length for an aliphatic C–N bond.

Compound (II).—The crystal is formed from dimers at symmetry centres in which hydrogen bonds of 2·983 Å link the oxygen atom O(1) of one molecule of (II) to the nitrogen atom N(1) in the second molecule. The sulphonylamino-group in (II) is conjugated through N(1) both to a phenyl group and to N(2). The S(1)–N(1) bond (1·630 Å) is longer and N(1)–C(8) shorter than the comparable distances in compound (I). Atom C(8) in (I) is an sp^3 and in compound (II) an sp^2 carbon atom, and the shortening of N(1)–C(8) represents no more than the difference in radii between the two types.[6] The S(1)–N(1)–C(8) angle is 122·2° and the torsional angle between the N(1)–C)8) bond is 39·2°. This twist about the N–C bond is required to relieve the steric interaction between hydrogen atoms H(8) and H(9). The angle (65·0°) between the C(8), N(1), S(1) and O(1), S(1), O(2) planes is similar to that observed for compound (I). The very small decrease in the N–C bond length coupled with the twist about it, rather than deformation of the C–N–S bond angle, suggests that the d_π–p_π interaction between the sulphur and nitrogen atoms is the dominant effect rather than electron delocalisation from this nitrogen atom into the indole fragment. The two sulphur–oxygen bonds are non-equivalent [S(1)–O(1) 1·453, and S(1)–O(2) 1·436 Å]; the greater length of S(1)–O(1) may be a consequence of the hydrogen bond formed by O(1). The dimensions of the 1-methylindole and tolyl fragments are much as expected; the steric strain of bonding a five- to a six-membered ring causes the bond between atoms C(9) and C(14) to increase somewhat from the usual [5] aromatic C–C bond length, and the bond lengths C(9)–C(8) (1·424 Å) and C(8)–C(15) (1·385 Å) indicate that some of the formal double-bond character is retained by bond C(8)–C(15).

Compound (III).—The crystal is constructed from isolated molecules which corresponded to formula (III). This molecule differs from (I) and (II) in that it contains a sulphonylimino-group. This group is conjugated with the adjacent phenyl group and, through the phenyl group, to nitrogen atom N(2). The spiro-carbon atom C(15) isolates the two nitrogen atoms from any further π electron interaction.

The plane through atoms S(1), N(1), C(8) passes through carbon atom C(15) and approximately bisects the bond between C(18) and C(19). Hydrogen atom H(8) lies in the angle O(1)–S(1)–O(2) between the two sulphonyl oxygen atoms, 2·6 Å from O(1) and 2·8 Å from O(2); examination of a 'space-filling' model of the molecule suggests that in this conformation the hydrogen atom would hinder rotation of the sulphonyl group about the N(1)–S(1) bond. The C(8)–N(1) bond length (1·304 Å) is almost exactly intermediate between that for the C≡N bond (1·13 Å) in tetracyanobenzene [7] and the formal C–N single-bond (1·475 Å) in (I). It is therefore a reasonable value for a C=N double bond, for carbon bonded to an aromatic ring. The distances between the sulphur atom S(1) and the four atoms bonded to it, are not essentially different from the equivalent distance in (I), but in (III) the interbond angles O(1)–S(1)–O(2) (116·5°) and N(1)–S(1)–C(1) (99·6°) are both significantly smaller than the equivalent angles in the other compounds: (I) 119·0 and 107·4, (II) 118·5 and 107·4, and (IV) 118·2 and 104·6°. However the corresponding angles [117·7(4) and 101·2(3)°] in the sulphonylimino-group [1] of compound (V) are in close agreement with those of compound (III). The angle between the plane through atoms C(8), N(1), S(1) and O(1), S(1), O(2) is 83·4°, *ca.* 20° larger than the angle between the equivalent planes in compounds (I) and (II). The nitrogen atom N(1) has two atomic orbitals available for a π electron interaction with the sulphonyl group, but since the S(1)–N(1) bond length is unaltered between compounds (I) and (III), the overall effect of the d_π–p_π interaction along this bond must be unaltered; however, since the relative orientation of the C–N–S plane and the tetrahedron of atoms bonded to the sulphur atoms is altered, the combinations of *d* orbitals in the interaction must also be altered. This in turn will affect the π electron molecular orbital about the sulphur atom which is reflected in the change in bond angle exhibited in the co-ordination sphere of the sulphur atom. A similar effect is observed [1] in compound (V) where at the sulphonylimino-group the angle between the C–N–S plane and the O–S–O plane is 97·7° while at the sulphonylamino-group this angle is 53·7°.

The very short S–N bond (1·553 Å) exhibited [1] at the sulphonylimino-groups in compound (V) was explained in terms of contributions to the structure from valence-bond structures (VI) and (VII) where there was a charge separation between atoms in close proximity. In compound (III) it is possible to write a single valence-bond structure (VIII), but here the charged atoms

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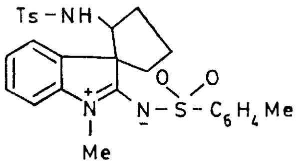
[4] D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.

[5] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1969.

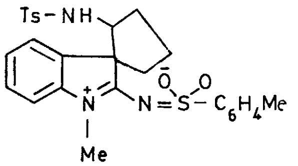
[6] C. A. Coulson, 'Valence,' Oxford University Press, London, 1961, p. 210.

[7] H. Tsuchiya, F. Morumo, and Y. Saito, *Acta Cryst.*, 1972, **B28**, 1935.

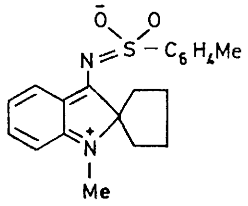
are more widely separated and their effect upon the intervening bond lengths is greatly diminished.



(VI)



(VII)



(VIII)

The dimensions within the rest of the molecule are as expected; of the three C–C bond lengths at the spiro-carbon C(15), those to the cyclopentane group [C(15)–C(17), C(15)–C(20) mean 1·558 Å] are equal, but the third [C(15)–C(18) 1·574 Å] is shorter. This difference probably represents no more than the smaller covalent radius of the sp^2 carbon C(18), relative to those of the sp^3 carbons [6] C(17) and C(20). A similar shortening has been observed [8] in (—)-(*S*)-spiro[4.4]nonane-1,6-dione.

Compound (IV).—The crystal is formed from dimers at symmetry centres in which hydrogen bonds of length 3·004 Å link oxygen O(1) of one molecule of (IV) with nitrogen N(1) of a second molecule.

Hydrogen H(15) lies in the angle O(3)–S(1)–O(4) and is 2·5 Å from both oxygen atoms. Oxygen O(3) must also be close to the methyl hydrogen atoms bonded to carbon C(15).

The molecule contains two *p*-tolylsulphonyl groups, one bonded to an amino- and the other to an imino-nitrogen atom. The π electrons of both nitrogen atoms are isolated from each other and from the aromatic ring by sp^3 carbon atoms.

In the sulphonyl group bonded to the amino-nitrogen atom, the S(1)–N(1) bond length is not significantly different from the S–N bond lengths in compounds (I)—(III). The two sulphur–oxygen bonds however are distinguishable, S(1)–O(1) (1·465 Å), where atom O(1) forms part of a hydrogen bond (see earlier), being longer than S(1)–O(2) (1·427 Å). The angle between the C(15), N(1), S(1) and O(1), S(1), O(2) plane is 53·6°.

In the other sulphonyl group that bonded to the imino-nitrogen atom the S(2)–N(3) (1·646 Å) is significantly longer and the N(3)–C(17) bond length (1·225 Å) significantly shorter than the corresponding lengths discussed so far. Equivalent S–N bond lengths in compounds (III) and (V) are 1·619 and 1·553 Å, and the C–N bond lengths are 1·304 and 1·294 Å. In (III) and (V) the π system of the aromatic group can be extended to the S–N bond (see above), while in compound (IV) no such extension is possible and the π electrons of the C=N bond are more restricted with a consequent shortening of the bond. In addition, angle N(3)–C(17)–C(15) (124·1°) is larger than the N(3)–C(17)–C(8) (120·1°). Hydrogen H(15) bonded to C(15) is not only 2·5 Å from each of these sulphonyl oxygen atoms, but is also only 2·5 Å from the sulphur atom itself, and protrudes into the plane through atoms O(3), S(2), O(4) from the same side and with a maximum steric repulsion in the same direction as the S(2)–N(3) bond. The slightly longer S–N bond is probably a consequence of this steric interaction. Similarly the unusually long aliphatic C(15)–C(18) bond (1·598 Å) is possibly caused by oxygen O(3), which appears to be forced into the gap between hydrogen atom H(15) and the methyl hydrogen atoms bonded to C(18). An examination of a molecular model suggests that there are less sterically unfavourable conformations available to the sulphonyl group and the present arrangement must be required either by crystal packing forces or more likely by the requirement to keep the value of the angle between the C(17), N(3), S(2) and O(3), S(2), O(4) planes within a certain range. In this case the angle is 88·8°, intermediate between that observed in compound (III) and that observed for the sulphonyl-imino-group of (V). The interbond angles O(3)–S(2)–O(4) (117·8°) and N(3)–S(2)–C(21) (100·3°) are, as in compound (III), smaller than those between equivalent bonds in the sulphonylamino-groups of the other compounds.

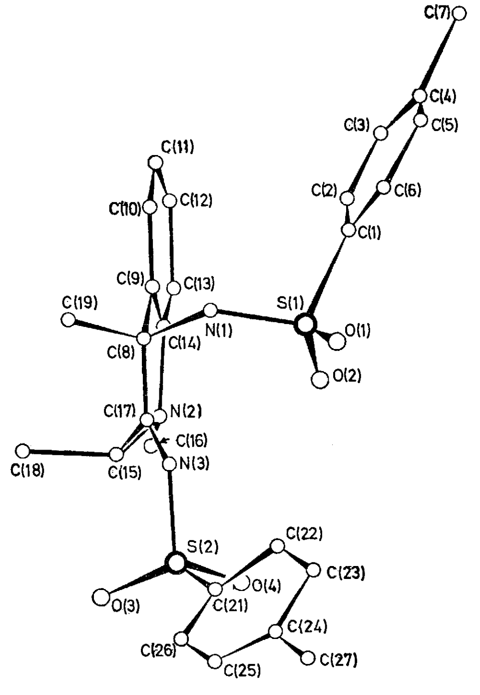


FIGURE 9 Compound (IV) projected along (0,1,0)

The bond lengths and angles in the rest of the molecule are much as would be expected. In the non-aromatic six-membered ring (Figure 9), methyl groups

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[8] C. Altona, R. A. G. de Graaff, C. H. Leeuwestein, and C. Romers, *Chem. Comm.*, 1971, 1305.

TABLE 4

Final atomic parameters * ($\times 10^4$) for compound (I)

	x	y	z	U_{11} †	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	4677(1)	4572(1)	2594(1)	467	411	537	−120	−200	−164
O(1)	14659(3)	3788(3)	3866(2)	651	564	699	−75	−395	−165
O(2)	4917(3)	3513(3)	1672(3)	682	518	698	−238	−217	−229
N(1)	14470(3)	14094(3)	1392(3)	531	570	549	−179	−158	−262
C(1)	2513(3)	14226(3)	3316(3)	492	480	477	−64	−179	−250
C(2)	1913(4)	13370(4)	4493(3)	573	686	539	−182	−163	−268
C(3)	227(4)	12336(4)	4969(4)	618	681	546	−186	−109	−220
C(4)	−874(4)	12190(4)	4317(4)	478	597	612	−7	−118	−244
C(5)	−247(4)	13073(4)	3165(4)	536	639	737	−70	−279	−257
C(6)	1433(4)	14088(4)	2656(4)	574	580	625	−134	−255	−252
C(7)	−2703(5)	11053(7)	4837(6)	549	894	931	−136	−122	−162
C(8)	14557(4)	12761(4)	1966(4)	529	559	640	−277	−132	−256
C(9)	13229(3)	12086(3)	902(3)	465	496	532	−116	−201	−198
C(10)	11744(4)	13024(4)	−90(4)	587	673	641	−258	−96	−308
C(11)	9491(4)	12381(5)	−998(4)	583	850	652	−234	−86	−326
C(12)	9233(4)	9216(5)	−917(4)	695	744	674	36	−249	−440
C(13)	12233(4)	10155(4)	57(4)	721	513	912	4	−374	−308
C(14)	13464(4)	9524(4)	947(4)	523	457	767	−118	−273	−165
H(1)	2706(5)	13376(52)	4912(45)	537					
H(2)	−108(49)	11816(51)	14158(47)	531					
H(3)	−905(48)	13139(50)	2621(44)	496					
H(4)	1976(55)	14865(58)	1910(52)	666					
H(5)	−2953(89)	11019(91)	14182(95)	352					
H(6)	−2848(76)	9945(88)	4024(75)	99					
H(7)	−3266(83)	11743(87)	4915(95)	142					
H(8)	14356(44)	13320(46)	3014(42)	441					
H(9)	4304(45)	11694(47)	2192(41)	434					
H(10)	11622(53)	14151(56)	−69(47)	614					
H(11)	10479(57)	13113(57)	−1622(51)	682					
H(12)	10226(60)	9530(60)	−1609(53)	726					
H(13)	12349(54)	11283(58)	114(49)	645					
H(14)	14483(47)	10329(48)	1588(42)	464					
H(15)	14548(55)	13819(58)	532(54)	578					

* The temperature factor $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^* + U_{13}hla^*c^* + U_{12}hka^*b^*)]$. † U_{iso} for H atoms.

TABLE 5

Final atomic parameters * ($\times 10^4$) for compound (II)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	570(04)	2127(1)	438(05)	414	646	406	33	132	−24
O(1)	71(1)	1627(4)	−433(2)	551	878	384	−3	119	9
O(2)	1098(1)	3183(4)	536(2)	465	814	658	86	222	−111
N(1)	1004(2)	727(5)	971(2)	455	640	449	−31	107	−17
N(2)	2618(1)	1212(4)	3087(2)	371	854	491	45	108	−27
C(1)	22(2)	2791(5)	889(2)	455	618	428	47	153	−9
C(2)	6(2)	4207(6)	1030(3)	775	587	761	−10	419	−61
C(3)	−485(3)	4746(7)	1287(4)	963	654	863	10	502	34
C(4)	−944(2)	3859(6)	1438(3)	670	756	603	129	310	163
C(5)	−912(2)	2455(7)	1307(3)	664	847	898	98	459	21
C(6)	−436(2)	1882(6)	1034(3)	656	693	793	65	395	−9
C(7)	−1487(4)	4460(10)	1717(5)	966	185	1882	174	555	327
C(8)	1561(1)	779(5)	1872(2)	379	662	438	−1	133	17
C(9)	1547(1)	34(4)	2574(2)	377	587	477	−2	151	37
C(10)	1032(2)	−835(5)	2655(3)	462	697	617	10	224	7
C(11)	1202(2)	−1362(6)	3473(3)	621	746	775	132	362	30
C(12)	1880(2)	−1069(6)	4217(3)	682	887	595	211	291	162
C(13)	2400(2)	−238(6)	4152(3)	491	874	526	101	147	121
C(14)	2228(1)	328(5)	3332(2)	376	761	460	30	119	−66
C(15)	2222(1)	1487(5)	2200(2)	423	765	510	51	176	4
C(16)	3329(2)	1859(8)	3681(3)	427	26	1681	40	51	−123
H(1)	239(23)	4864(6)	817(31)	519					
H(2)	−477(36)	14347(97)	1450(46)	970					
H(3)	−1147(27)	1688(76)	1460(35)	578					
H(4)	−398(33)	717(94)	952(43)	748					
H(5)	−1597(42)	3726(108)	2020(54)	1118					
H(6)	−1265(40)	4919(124)	2392(59)	1060					
H(7)	−1788(37)	14885(111)	1276(51)	829					
H(8)	781(22)	66(63)	795(29)	525					
H(9)	526(33)	−1014(86)	2143(44)	802					
H(10)	885(27)	−2039(69)	3594(34)	621					
H(11)	1996(22)	−1554(61)	4792(31)	454					
H(12)	2887(35)	128(101)	4720(47)	1010					
H(13)	3560(35)	2451(101)	3372(48)	1012					
H(14)	3644(35)	1082(92)	4072(45)	841					
H(15)	3304(27)	2598(75)	4081(37)	703					
H(16)	2381(22)	2020(55)	1876(28)	314					

* Temperature factor (T) defined in Table 4. † U_{iso} for H atoms.

at carbon atoms C(18) and C(19) are both on the same side of this ring but do not come any closer to each other than a van der Waals separation. The ring-closing at atoms C(9) and C(14), however, causes some strain on the C(9)–C(14) bond, lengthening it to 1·443 Å, greater than the usual value[5] for an aromatic C–C bond.

Conclusions.—The S–N bond lengths in the four compounds appear to be unaffected by the opportunity for π electron delocalisation from sulphur through nitrogen to an aromatic system, but the hybridisation of the nitrogen atom imposes restrictions on the relative orientations of the C–N–S and O–S–O planes. The angles between these planes are *ca.* 87 for sp^2 and 58° for sp^3 nitrogen atoms. A shortened S–N bond length seems to require a charge separation across the bond, but the effect of this separation decreases rapidly as the number of intervening atoms increases.

EXPERIMENTAL

Crystals were all prepared as described in ref. 9.

Each of the four structures was determined by the heavy-atom method. The positions of the sulphur atom(s) were found from three-dimensional unsharpened Patterson functions, and the locations of the remaining non-hydrogen atoms were derived from successive F_0 and difference syntheses. The preliminary atomic parameters were refined by full-matrix least-squares, first with individual isotropic temperature factors and unit weights and subsequently with anisotropic temperature factors and individual weights (w) calculated for each reflection. For compounds (I)—(III) the weights were calculated from a truncated Chebyshev series: $w = [\sum_{i=1}^{n} a_i T_i(x)]^{-1}$, where $x = F_0/F_{\max.}$, and for compound (IV) $w = \{1 + [(|F_0| - 23{\cdot}0)/30{\cdot}0]^2\}^{-1}$. When the refinement appeared to be almost converged, *i.e.* when Σ(parameter shifts/parameter $\sigma)^2 \simeq 5$, the positions of the hydrogen atoms were determined geometrically.

TABLE 6

Final atomic parameters * ($\times 10^4$) for compound (III)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	427(1)	1934(1)	793(04)	435	584	421	8	35	6
O(1)	-223(2)	1174(4)	922(1)	497	877	568	61	161	24
O(2)	633(2)	2961(4)	1215(1)	798	667	533	−102	−74	6
N(1)	1283(2)	1216(4)	759(2)	478	786	491	135	112	107
N(2)	2859(2)	−750(5)	1702(2)	612	849	531	92	70	246
C(1)	853(2)	2413(5)	−52(2)	414	537	442	−12	21	−31
C(2)	−301(3)	3495(5)	−179(2)	679	539	517	−24	42	84
C(3)	−643(3)	3865(6)	−846(2)	759	626	592	61	22	197
C(4)	−582(3)	3138(6)	−1370(2)	569	794	465	87	48	39
C(5)	−203(3)	2083(6)	−1231(2)	677	677	487	−33	68	20
C(6)	131(3)	1667(5)	−575(2)	612	522	552	−17	31	69
C(7)	−973(5)	3570(9)	−2092(3)	1109	1268	479	199	38	205
C(8)	1738(2)	541(5)	1231(2)	428	677	377	13	11	2
C(9)	1706(2)	221(4)	1904(2)	480	603	358	−11	19	−63
C(10)	1159(3)	565(6)	2303(2)	631	742	431	−70	65	7
C(11)	1293(4)	51(6)	2935(2)	930	907	426	−31	209	1
C(12)	1948(4)	740(7)	3163(2)	1025	1064	342	82	72	5
C(13)	2504(4)	−1094(6)	2792(2)	780	884	485	103	−28	104
C(14)	2377(3)	−570(5)	2146(2)	582	681	389	7	3	47
C(15)	2479(2)	−122(5)	1075(2)	494	754	394	−6	62	53
C(16)	3565(5)	−1595(9)	1793(4)	951	1249	863	155	196	527
C(17)	3124(3)	714(6)	854(3)	525	801	751	−145	170	−92
C(18)	2858(4)	681(8)	95(3)	836	1268	730	111	384	137
C(19)	2482(6)	−477(10)	−96(3)	1415	1590	705	−411	580	−684
C(20)	2168(4)	−965(6)	464(2)	756	816	530	−43	134	−14
H(1)	−351(31)	4129(57)	237(24)	439					
H(2)	−955(26)	4547(50)	−897(19)	288					
H(3)	−160(32)	1600(64)	−1527(27)	475					
H(4)	422(31)	1121(55)	−513(22)	386					
H(5)	−817(55)	3254(100)	−2273(45)	936					
H(6)	−737(45)	4397(82)	−2087(35)	507					
H(7)	−1593(40)	3739(65)	−2152(29)	661					
H(8)	678(33)	1123(51)	2159(24)	204					
H(9)	940(32)	73(61)	3252(26)	407					
H(10)	2043(38)	−1079(70)	3561(32)	636					
H(11)	2985(33)	−1538(57)	2926(25)	546					
H(12)	3825(45)	−1616(85)	1458(40)	851					
H(13)	4006(56)	−1759(97)	2291(47)	1014					
H(14)	3339(75)	−2468(156)	1819(54)	1686					
H(15)	3743(46)	413(78)	1006(30)	811					
H(16)	3132(29)	1396(62)	1094(26)	316					
H(17)	3342(39)	878(61)	94(27)	599					
H(18)	2378(66)	1217(106)	180(45)	1417					
H(19)	2925(105)	−1210(167)	31(82)	1325					
H(20)	2303(56)	806(89)	529(46)	957					
H(21)	2218(11)	−1790(69)	589(27)	879					
H(22)	1605(60)	−937(90)	305(41)	1160					

* Temperature factor (T) defined in Table 4. † U_{iso} for H atoms.

For compounds (I)—(III) these hydrogen atom parameters, with individual isotropic temperature factors, were included amongst those to be refined, while for compound *(IV) they* were included in the calculations but not altered in the refinement, which for all four compounds was then continued to convergence.

TABLE 7

Final atomic parameters * ($\times 10^4$) for compound (IV)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{11}	U_{12}
S(1)	1219(6)	6843(3)	696(3)	282	49	71	59	119	88
S(2)	−1855(6)	6453(3)	−2931(4)	324	74	76	74	147	130
O(1)	2006(15)	5898(7)	286(9)	271	64	117	81	198	153
O(2)	1468(16)	7685(7)	339(8)	399	48	75	73	103	43
O(3)	−3681(17)	6358(9)	−3712(9)	391	95	88	72	112	198
O(4)	−463(16)	7336(8)	−2662(9)	328	74	119	88	222	136
N(1)	−1016(16)	6447(8)	372(9)	244	43	65	60	84	93
N(2)	−2271(21)	8973(10)	−386(12)	403	60	114	99	160	188
N(3)	−1983(16)	6383(9)	−1770(10)	221	59	83	71	139	112
C(1)	2309(27)	7339(12)	2159(13)	456	54	77	65	210	125
C(2)	2268(28)	8362(12)	2770(14)	496	58	82	81	152	102
C(3)	3117(27)	8759(13)	3944(14)	412	64	83	54	99	102
C(4)	4022(27)	8117(14)	4478(14)	381	103	82	116	148	147
C(5)	3977(22)	7081(11)	3841(13)	257	48	90	57	116	114
C(6)	3107(24)	6669(13)	2693(13)	321	89	69	110	115	168
C(7)	4906(32)	8547(15)	5762(15)	576	99	77	100	148	147
C(8)	−2514(22)	6982(10)	−63(11)	310	41	61	51	106	96
C(9)	−2324(23)	8040(12)	861(14)	303	65	103	80	134	184
C(10)	−2317(31)	8074(15)	1875(14)	554	110	67	37	220	266
C(11)	−2149(36)	9021(17)	2751(18)	620	126	128	112	231	308
C(12)	−1878(32)	9920(16)	2509(17)	502	113	125	29	154	304
C(13)	−1896(28)	9927(13)	1501(16)	402	66	118	39	81	234
C(14)	−2196(23)	8997(11)	650(12)	291	54	62	15	33	127
C(15)	−3272(25)	8026(11)	−1355(13)	397	60	78	98	140	179
C(16)	−2465(29)	9948(13)	−661(18)	442	64	180	157	210	178
C(17)	−2473(21)	7075(11)	−1114(12)	224	65	87	86	120	155
C(18)	−5506(26)	7829(13)	−1731(14)	332	69	109	86	50	164
C(19)	−4303(24)	6209(12)	−322(15)	272	64	157	99	283	109
C(21)	−998(21)	5290(11)	−3443(12)	185	59	65	8	87	112
C(22)	523(23)	5085(14)	−2715(14)	223	101	86	17	112	79
C(23)	1278(26)	4174(13)	−3143(14)	352	74	91	14	139	110
C(24)	380(25)	3545(13)	−4238(14)	322	79	92	53	190	85
C(25)	−1140(25)	3762(13)	−4973(14)	309	81	86	51	149	44
C(26)	−1848(23)	4670(12)	−4535(13)	250	60	91	66	122	52
C(27)	1061(28)	2481(14)	−4687(15)	368	90	112	31	205	188
H(1)	−1524	5802	448						
H(2)	1632	8809	2368						
H(3)	3077	9503	4401						
H(5)	4594	6615	4222						
H(6)	3056	5903	2259						
H(10)	−2438	7390	1979						
H(11)	−2218	9054	3484						
H(12)	−1646	10634	3123						
H(13)	−1693	10560	1388						
H(15)	−2998	8047	−2019						
H(22)	1062	5582	−1902						
H(23)	2414	3981	−2683						
H(25)	−1706	3280	−5791						
H(26)	−2960	4875	−5001						

* Temperature factor (T) defined in Table 4.

Crystal Data (I).—$C_{14}H_{15}NO_2S$, M = 261·3. Triclinic, a = 9·668 ± 0·003, b = 9·156 ± 0·003, c = 9·749 ± 0·003 Å, α = 68·1 ± 0·1°, β = 64·5 ± 0·1°, γ = 60·5 ± 0·1°, U = 629·0 Å^3, D_m = 1·378 g cm^{-3}, Z = 2, D_c = 1·379 g cm^{-3}, $F(000)$ = 138. Space group $P\bar{1}$ (C_i^1, No. 2). Hilger and Watts four-circle diffractometer data, monochromatic Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 2·49 cm^{-1}.

Unit-cell dimensions were determined during the calculation[10] of the crystal axes orientation matrix which was used for the measurement, by the ordinate analysis technique,[11] of 2515 independent reflections with $I > 3\sigma$. Data were not corrected for absorption. The crystals were exceptionally good scatterers of X-rays and a small well formed crystal was selected so that even on the strongest reflections there was no risk of saturating the diffractometer scintillation counter. After three cycles of refinement with isotropic temperature factors, R was 0·24, the hydrogen atom positions were determined after three cycles of anisotropic refinement, with R then 0·087. 27 reflections having very large values of both F_0 and F_c, but where the measurement of F_0 (because of its large value) was suspect, were removed and the refinement converged at R 0·066. Weighting function parameters were: n = 4, a_0 = 2118·7, a_1 = 2109·0, a_2 = 5·6, a_3 = 44·7, and a_4 = 161·2; $F_{\text{max.}}$ = 370.

Crystal Data (II).—$C_{16}H_{16}N_2O_2S$, M = 300·4. Monoclinic, a = 20·69 ± 0·01, b = 9·53 ± 0·01, c = 17·39 ± 0·01 Å, β = 118·25 ± 0·03°, U = 3020·5 Å^3, D_m = 1·330 g

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[9] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc. (C)*, 1971, 3769, and references therein.

[10] M. Dobler and B. Duerr, 1969, personal communication.

[11] H. C. Watson, D. M. Shatton, J. M. Cobe, and H. Muirhead, *Nature*, 1970, **225**, 806.

cm^{-3}, $Z =$, $D_c =8$ 1·321 g cm^{-3}, $F(000) = 158$. Space group $C2/c$ (C_{2h}^6, No. 15). Hilger and Watts linear diffractometer data, Mo-K_α radiation; μ(Mo-K_α) = 2·20 cm^{-1}.

Unit-cell dimensions were determined from the diffractometer slide settings, and 1948 independent reflections were measured having $I > 3\sigma$. Data were corrected for Lorentz and polarisation effects but not for absorption. After four cycles of refinement with isotropic temperature factors R was 0·15; three cycles with anisotropic temperature factors reduced R to 0·93. After the hydrogen atoms had been included refinement converged at R 0·065. The weighting function parameters were: $n = 4$, $a_0 = 27·8$, $a_1 = 37·7$, $a_2 = 16·8$, $a_3 = 8·0$, and $a_4 = 2·716$; $F_{\text{max.}} = 37·0$.

Crystal Data (III).—$C_{20}H_{22}N_2O_2S$, $M = 354·5$. Monoclinic, $a = 16·08 \pm 0·01$, $b = 11·42 \pm 0·01$, $c = 20·51 \pm 0·01$ Å, $\beta = 105·0 \pm 0·1°$, $U = 3638·0$ Å^3, $D_m = 1·301$ g cm^{-3}, $Z = 8$, $D_c = 1·294$ g cm^{-3}, $F(000) = 188$. Space group $C2/c$ (C_{2h}^6, No. 15). Hilger and Watts linear diffractometer data, Mo-K_α radiation; μ(Mo-K_α) = 1·92 cm^{-1}.

Unit-cell dimensions were determined as for (II) and 1448 independent reflections were measured having $I > 3\sigma$. Data were corrected for Lorentz and polarisation effects but not for absorption.

After three cycles of refinement with isotropic temperature factors R 0·24, and was reduced to 0·088 after three cycles with anisotropic temperature factors. Three further cycles after inclusion of hydrogen atom parameters resulted in convergence at R 0·055. Parameters for the weighting function were: $n = 3$, $a_0 = 5·4$, $a_1 = 2·4$, $a_2 = 0·67$, and $a_3 = -0·51$; $F_{\text{max.}} = 1317$.

Crystal Data (IV).—$C_{26}H_{28}N_3O_4S_2$, $M = 510·7$. Triclinic, $a = 7·67 \pm 0·01$, $b = 13·71 \pm 0·02$, $c = 13·57 \pm 0·02$ Å, $\alpha = 110·4 \pm 0·1$, $\beta = 109·2 \pm 0·1$, $\gamma = 92·8 \pm 0·2°$, $U = 1261·6$ Å^3, $D_m = 1·345$ g cm^{-3}, $Z = 2$, $D_c = 1·344$ g cm^{-3}, $F(000) = 269$. Space group $P\bar{1}$ (C_i^1, No. 2). Equi-inclination Weissenberg photographs, Cu-K_α radiation, $\lambda = 1·54178$ Å; μ(Cu-K_α) = 21·6 cm^{-1}.

Unit-cell dimensions were measured from zero-layer Weissenberg photographs and the intensities of 1967 independent reflections were estimated visually from equi-inclination Weissenberg photographs for the layers 0—6 *kl*. Data were corrected for Lorentz and polarisation effects but not for absorption.

The refinement with isotropic temperature factors concluded after four cycles with R 0·21; after two cycles with anisotropic temperature factors hydrogen atom parameters were included and R was then 0·157. Three cycles then brought the refinement to convergence with R 0·103.

Observed structure amplitudes and the structure factors calculated from the final atomic parameters in Tables 4—7 are deposited * at the New University of Ulster Library. Atomic scattering factors were those for neutral atoms [5] and were corrected for the real part of the anomalous dispersion.

For compounds (I)—(III) computations were made by use of Carruthers' crystallographic program,[12] and for compound (IV) by use of the N.U.U. Crystal System.[13] Diagrams were drawn by use of STRPL.[13]

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[13] T. S. Cameron, University of Ulster Internal Report I, 1973.

* Catalogue number QD 921.C32. Copies may be obtained on application to the Librarian for Science. The Tables are also listed in Supplementary Publication No. SUP 21145 (38 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.