Structural Investigations of Ylides. Part III.† Crystal and Molecular Structure of *N*-(Dimethylsulphonio)toluene-*p*-sulphonamidate [1]

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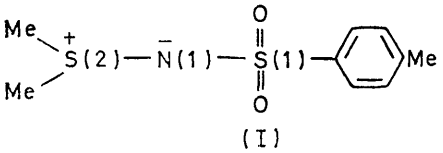
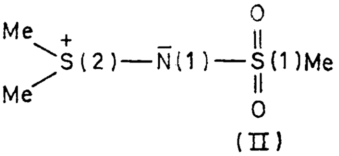
The crystal and molecular structure of the title compound has been determined from *X*-ray photographic data. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 12{\cdot}93(2)$, $b = 7{\cdot}17(1)$, $c = 12{\cdot}50(2)$ Å, $\beta = 104{\cdot}2(1)°$. The structure was solved by the heavy atom technique and refined by least-squares calculations to R 0·107 for 1085 independent data. The molecular geometry is compared with those of other similar ylides in relation to the possibility of *d*-orbital involvement within the S–N–S bonding system.

FOR ylides (X^+–Y^-) in which the 'onium group (X^+) is a second or higher-row element, it has been suggested that an additional bonding interaction, formally of the d_π–p_π type, may occur between the empty *d*-orbitals of the 'onium group (X^+) and a lone-pair of electrons on the vicinal atom (Y^-). Despite the stabilising effect which such an interaction would be expected to confer on the X^+–Y^- system, many examples, with the notable exception of the sulphoxides (X = S, Y = O) and the phosphine oxides (X = P, Y = O), require that an electron-withdrawing group (*e.g.* $-CO_2R$, $-COR$, or $-SO_2R$) be attached to the atom Y to provide further stabilisation. In cases where a sulphonyl grouping provides the additional stability, there is also the possibility of d_π–p_π bonding both in the X^+–Y^- and the Y^-–SO_2R moieties.

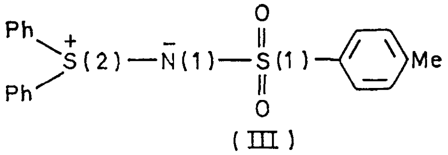
As part of a more general study of the bonding and conformations of second-row ylides, we have determined the crystal and molecular structure of (I), which is representative of the class of ylides (X = S, Y = N) stabilised by a sulphonyl function. Our choice of this compound for study was influenced by the recent analyses of the related compounds (II) [2] and (III),[3] with which geometrical comparisons may be made.



(I)



(II)



(III)

EXPERIMENTAL

Crystal Data.—(I) $C_9H_{13}NO_2S_2$, $M = 231{\cdot}3$. Monoclinic, $a = 12{\cdot}93(2)$, $b = 7{\cdot}17(1)$, $c = 12{\cdot}50(2)$ Å, $\beta = 104{\cdot}2(1)°$, $U = 1123{\cdot}4$ Å^3, $D_m = 1{\cdot}34$ (by flotation in aqueous KI), $Z = 4$, $D_c = 1{\cdot}37$, $F(000) = 488$. Space group $P2_1/c$ (C^5_{2h}). Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å), μ(Cu-K_α) = 47·5 cm^{-1}.

Crystallographic Measurements.—Unit-cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation. The space group is uniquely determined by systematic absences.

A small crystal, rotating about the needle axis *b*, was exposed to Cu-K_α radiation, and 1085 independent reflexions from the reciprocal-lattice nets $h0$—$6l$ were recorded on equatorial and equi-inclination Weissenberg photographs by the multiple-film technique. Intensities, measured visually by comparison with a calibrated strip, were corrected for the appropriate Lorentz and polarisation factors, and were subsequently placed on an approximate absolute scale by making $k\Sigma|F_o| = \Sigma|F_c|$ for each layer. Absorption effects were not considered.

Structure Determination.—The positions of both sulphur atoms were determined by inspection of the three-dimensional Patterson function, and the analysis thereafter proceeded on the basis of the phase-determining heavy-atom method. The entire structure was revealed after one set of structure-factor and electron-density calculations, three further rounds of such calculations effecting a preliminary refinement of positional parameters prior to the least-squares process. In each of the above computations an overall isotropic thermal parameter U_{iso} 0·05 Å^2 was assumed, and after each cycle the data were scaled as before.

Structure Refinement.—The refinement of positional, vibrational, and scale parameters by three-dimensional least-squares calculations converged after 12 cycles, when R was 0·107, and R' ($= \Sigma w\Delta^2/\Sigma w|F_o|^2$) was 0·019. After cycle 5, the data were converted to an overall absolute scale by means of the refined values of the individual scale factors, and in subsequent cycles an overall scale factor was refined. Although the initial least-squares refinement was by full-matrix calculations, inclusion of anisotropic thermal parameters in cycle 7 necessitated the use of the block-diagonal approximation to the normal-equation matrix as a result of computer-store limitations.

A weighting scheme of the form: $\sqrt{w} = [\{1 - \exp[-p_1(\sin\theta/\lambda)^2]\}/[1 + p_2|F_o| + p_3|F_o|^2]]^{\frac{1}{2}}$, was applied in all cycles, the initial values of the p parameters being chosen to give unit weights to all reflexions. In later cycles they were varied according to an ($|F_o|$ and $\sin\theta/\lambda$) analysis of $w\Delta^2$, the final values being p_1 100, p_2 0·001, and p_3 = 0·01.

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† Part II, ref. 9.

[1] Preliminary communication, A. F. Cameron, N. J. Hair, and D. G. Morris, *Chem. Comm.*, 1971, 918.

[2] A. Kálmán, *Acta Cryst.*, 1967, **22**, 501.

[3] A. Kálmán, B. Duffin, and Á. Kucsman, *Acta Cryst.*, 1971, *B*, **27**, 586.

On convergence of the least-squares refinement, an electron-density distribution and difference-Fourier synthesis were evaluated, neither of which revealed any errors in the structure. Although there were diffuse peaks evident in the difference synthesis in positions stereochemically acceptable for hydrogen atoms, it proved impossible to determine their co-ordinates with any accuracy. The refinement was therefore considered complete.

In all the previous structure-factor calculations, atomic scattering factors were taken from ref. 4. Final values of observed and calculated structure factors appear in Supplementary Publication No. SUP 20782 (2 pp).* Table 1 contains the final fractional co-ordinates and anisotropic thermal parameters, while all bond-lengths, valence angles, and pertinent intra- and inter-molecular non-bonded distances are given in Table 2. The appropriate estimated standard deviations derived from the inverse of the least-squares normal-equation matrix are included in Tables 1 and 2, the mean values for S–O, S–N, S–C, and C–C

TABLE 1

Fractional co-ordinates and anisotropic thermal parameters

(*a*) Fractional co-ordinates

	x/*a*	*y*/*b*	*z*/*c*
S(1)	0·79981(17)	0·32531(35)	0·31025(19)
S(2)	0·85792(18)	0·67855(36)	0·37083(20)
O(1)	0·7809(5)	0·3958(10)	0·1995(5)
O(2)	0·8436(6)	0·1431(10)	0·3332(7)
N(1)	0·8764(6)	0·4561(11)	0·3980(7)
C(1)	0·6761(6)	0·3217(12)	0·3445(7)
C(2)	0·5870(7)	0·4113(14)	0·2760(8)
C(3)	0·4898(7)	0·4061(15)	0·3035(9)
C(4)	0·4777(7)	0·3173(14)	0·3968(9)
C(5)	0·5663(8)	0·2277(16)	0·4652(8)
C(6)	0·6655(7)	0·2312(14)	0·4374(7)
C(7)	0·3713(9)	0·3124(18)	0·4263(12)
C(8)	0·9782(11)	0·7524(17)	0·3348(10)
C(9)	0·8838(8)	0·7790(17)	0·5063(9)

(*b*) Anisotropic thermal parameters (Å^2 × 10^4) *

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S(1)	435	546	571	−34	210	29
S(2)	458	553	590	60	5	33
O(1)	672	870	522	66	457	−110
O(2)	689	510	1231	−82	602	160
N(1)	440	544	730	200	−230	−105
C(1)	421	445	484	−89	27	−177
C(2)	449	577	609	171	26	133
C(3)	421	621	778	85	83	76
C(4)	478	555	819	−377	250	−234
C(5)	566	821	527	103	183	−256
C(6)	548	581	504	92	135	−119
C(7)	589	951	1276	−854	805	−576
C(8)	1075	722	928	100	1195	−401
C(9)	565	829	776	−451	326	−42

* The anisotropic temperature factor is in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hk^*b^*)]$.

(*c*) Estimated standard deviations (× 10^4) for anisotropic thermal parameters

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S	12	16	12	23	19	23
O	42	47	50	77	73	74
N	38	51	49	80	69	74
C	56	73	73	107	96	102

TABLE 2

Bonded distances, valency angles, and relevant intra- and inter-molecular non-bonded distances

(*a*) Bonded distances (Å)

S(1)–O(1)	1·438(7)	C(1)–C(2)	1·411(12)
S(1)–O(2)	1·425(8)	C(1)–C(6)	1·366(13)
S(1)–N(1)	1·591(8)	C(2)–C(3)	1·382(13)
S(1)–C(1)	1·755(8)	C(3)–C(4)	1·371(15)
S(2)–N(1)	1·636(8)	C(4)–C(5)	1·406(14)
S(2)–C(8)	1·801(13)	C(4)–C(7)	1·510(15)
S(2)–C(9)	1·794(12)	C(5)–C(6)	1·409(13)

(*b*) Valency angles (°)

O(1)–S(1)–O(2)	118·8(5)	S(1)–C(1)–C(2)	120·2(7)
O(1)–S(1)–N(1)	112·8(4)	S(1)–C(1)–C(6)	120·1(7)
O(1)–S(1)–C(1)	106·9(4)	C(2)–C(1)–C(6)	119·7(8)
O(2)–S(1)–N(1)	104·6(4)	C(1)–C(2)–C(3)	119·6(9)
O(2)–S(1)–C(1)	106·2(4)	C(2)–C(3)–C(4)	121·7(9)
N(1)–S(1)–C(1)	106·9(4)	C(3)–C(4)–C(5)	118·9(9)
N(1)–S(2)–C(8)	104·3(5)	C(3)–C(4)–C(7)	121·3(9)
N(1)–S(2)–C(9)	102·2(5)	C(5)–C(4)–C(7)	119·8(9)
C(8)–S(2)–C(9)	98·4(5)	C(4)–C(5)–C(6)	119·9(9)
S(1)–N(1)–S(2)	113·4(5)	C(5)–C(6)–C(1)	120·3(9)

(*c*) Intramolecular non-bonded distances (Å)

S(1) · · · C(8)	3·80	O(2) · · · C(6)	2·98
S(2) · · · O(1)	2·94	N(1) · · · C(2)	3·69
S(2) · · · O(2)	3·87	N(1) · · · C(6)	3·31
S(2) · · · C(1)	3·44	C(1) · · · C(4)	2·80
S(2) · · · C(2)	3·91	C(2) · · · C(5)	2·78
O(1) · · · C(2)	2·90	C(2) · · · C(7)	3·79
O(1) · · · C(6)	3·83	C(3) · · · C(6)	2·77
O(1) · · · C(8)	3·71	C(6) · · · C(7)	3·82
O(2) · · · C(2)	3·75		

(*d*) Intermolecular distances (Å)

S(2) · · · O(2$^{\mathrm{I}}$)	3·36	O(2) · · · C(4$^{\mathrm{III}}$)	3·60
O(1) · · · C(5$^{\mathrm{II}}$)	3·62	C(4) · · · C(4$^{\mathrm{V}}$)	3·62
O(1) · · · C(6$^{\mathrm{II}}$)	3·37	C(4) · · · C(5$^{\mathrm{V}}$)	3·80
O(1) · · · C(7$^{\mathrm{III}}$)	3·71	C(4) · · · C(7$^{\mathrm{V}}$)	3·69
O(2) · · · C(8$^{\mathrm{IV}}$)	3·29	C(5) · · · C(7$^{\mathrm{V}}$)	3·58
O(2) · · · C(9$^{\mathrm{IV}}$)	3·35	C(6) · · · C(7$^{\mathrm{V}}$)	3·77
C(2) · · · C(3$^{\mathrm{III}}$)	3·75	C(7) · · · C(9$^{\mathrm{V}}$)	3·66

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $x,\ 1 + y,\ z$
II $x,\ 1/2 - y,\ -1 + z$
III $1 - x,\ 3/2 + y,\ 3/2 - z$
IV $x,\ -1 + y,\ z$
V $1 + x,\ 1 + y,\ 1 + z$

TABLE 3

Least-squares planes given in the form $lX' + mY' + nZ' = d$, where X', Y' and Z' are co-ordinates in Å

(*a*) Plane equations

Plane (1): $-0{\cdot}2373X' - 0{\cdot}8437Y' - 0{\cdot}4815Z' = -4{\cdot}9956$
Plane (2): $0{\cdot}6806X' - 0{\cdot}0301Y' - 0{\cdot}7321Z' = 5{\cdot}7711$
Plane (3): $-0{\cdot}4542X' + 0{\cdot}8439Y' - 0{\cdot}2857Z' = -1{\cdot}3259$

(*b*) Deviation of atoms (Å) from planes

Plane (1):
S(1) 0·003, O(1)* 0·271, O(1) − 0·003, C(2) − 0·003, C(3) 0·003, C(4) − 0·004, C(5) − 0·001, C(6) 0·001, C(7) 0·003

Plane (2):
S(1) 0·000, S(2) 0·000, N(1) 0·000

Plane (3):
S(2) 0·000, C(8) 0·000, C(9) 0·000

(*c*) Dihedral angles (°) between planes

(1)–(2) 77·5, (1)–(3) 62·2, (2)–(3) 82·8

* Not used in definition of plane.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

bonds being 0·007, 0·008, 0·011, and 0·013 Å, and for valence angles 0·6°. These are best regarded as minimum values. Details of least-squares planes calculated for various portions of the molecular framework are included in Table 3.

The atomic numbering system used and the molecular packing viewed down *b* are illustrated in Figures 1 and 2 respectively.

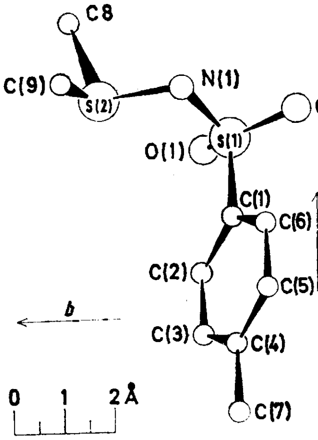


FIGURE 1 A view of the molecule showing the atomic numbering system used

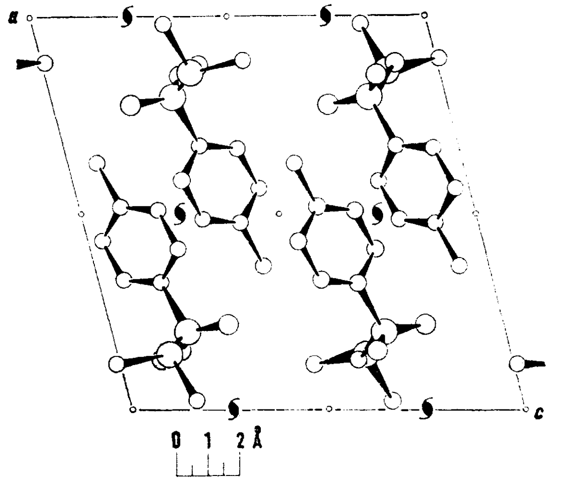
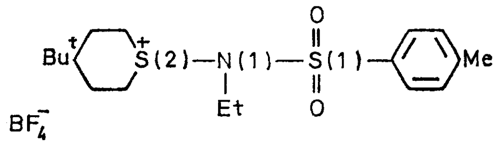


FIGURE 2 The molecular packing viewed along *b*

DISCUSSION

The dimensions of (I) [S(1)–N(1) 1·591(8), S(2)–N(1) 1·636(8) Å] may be compared directly with those of (II)[2] [S(1)–N(1) 1·581(10), S(2)–N(1) 1·633(9) Å] and (III)[3] [S(1)–N(1) 1·598(8), S(2)–N(1) 1·628(7) Å], revealing that there is no significant variation in the values of the sulphur–nitrogen bonds throughout the three molecules. We may conclude, therefore, that interchange of the respective aliphatic (methyl) and aromatic (phenyl) substituents produces no discernible effect in the bonding of $\overset{+}{S}$–$\overset{-}{N}$–S(sulphonyl) systems. It is also noticeable that in each case the S(1)–N(1) bond is significantly shorter than the S(2)–N(1) bond, although the different oxidation states of S(1) and S(2) render difficult any direct comparison of these bonds. However, both the S(1)–N(1) and S(2)–N(1) bonds are shorter than the value which might possibly be expected for a sulphur–nitrogen single-bond [1·76(2) for sulphamic acid,[5] 1·74 Å from Pauling's covalent radii[6]], and thus, to the extent that such comparisons are valid, the dimensions of (I)—(III) are consistent with some level of *d*-orbital involvement in the delocalisation of the nitrogen lone-pair electrons.



(IV)

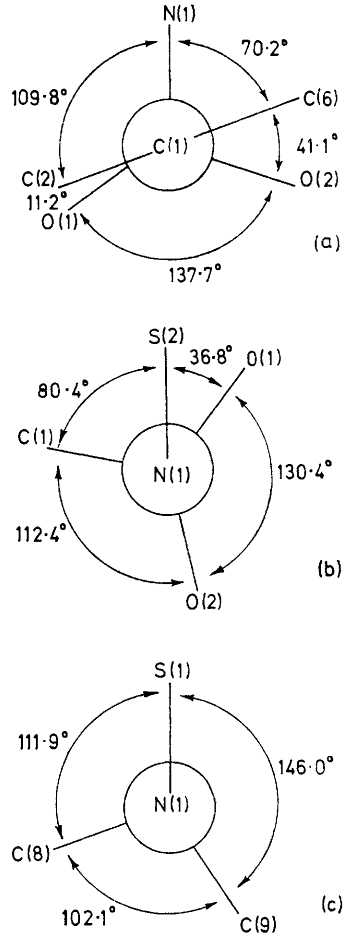


FIGURE 3 Newman projections along (a) C(1)–S(1), (b) N(1)–S(1), and (c) N(1)–S(2) bonds

Consideration of the *N*-alkylated derivative (IV),[7] reveals that in this case the S(1)–N(1) [1·681(5) Å] bond

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

[6] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

[7] R. E. Cook, M. D. Glick, J. J. Rigau, and C. R. Johnson, *J. Amer. Chem. Soc.*, 1971, **93**, 924.

is significantly longer than the S(1)–N(1) bonds of (I)—(III), while the S(2)–N(1) bond [1·644(5) Å] is experimentally identical to the corresponding bonds in the other three molecules. While there are fundamental differences between (IV) and (I)—(III) which make direct comparison difficult [*e.g.* (IV) is formally a charged species, whereas (I)—(III) are not], we nevertheless note that whereas the nitrogen atom of (IV) has only one lone-pair of electrons which may be considered initially in a *p*-type orbital approximately perpendicular to the S–N–S plane, the nitrogen atoms of (I)—(III) all bear two lone-pairs of electrons. The removal of one of these lone-pairs of electrons by *N*-alkylation, apparently produces a marked effect in the S(1)–N(1), but not in the S(2)–N(1) bond.

The solid-state conformation of (I) is best described in terms of the three Newman projections (see Figure 3) along the C(1)–S(1), S(1)–N(1), and S(2)–N(2) bonds, and is very similar to the conformations of (II) and (III). The C(1)–S(1) projection is characterised by the asymmetric dispositions of the aromatic and sulphonyl groups, the torsion angle C(2)–C(1)–S(1)–O(1) being −11·2°. It is possible that this conformation is favoured to reduce steric interaction between C(2) and S(2) [C(2) · · · S(2) 3·91 Å]. There is considerable interest, however, in the *semi-gauche* relationship of O(1) and S(2), demonstrated by the projection along the S(1)–N(1) bond. That the value of 36·8° for the torsion angle S(2)–N(1)–S(1)–O(1) is similar to those of 31·7 and 34·0° for this same angle in (II) and (III), is remarkable in view of the different substituent patterns and crystal environments of the three molecules, and it may be that the value of this torsion angle in these three molecules is related to the bonding within the S–N–S systems. The S(2)–N(1) projection reveals that the methyl substituents on S(2) are staggered with respect to the S(1)–N(1) bond, possibly as a result of steric effects.

Other features of the geometry of (I), are the approximately tetrahedral and pyramidal stereochemistries of S(1) and S(2) respectively, which are similar to the geometries previously observed for sulphur atoms in comparable environments.[3,4] Apart from the S(2) · · · C(2) short contact mentioned, the only other intramolecular contact of interest is that between S(2) and O(1) [2·94 Å]. Although this distance is less than the sum of the respective van der Waals' radii, the interaction is probably of much less significance than the corresponding short contacts observed in first-row ylides.[8,9] There are no abnormally short intermolecular contacts.

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[3/646 *Received*, *27th March*, 1973]

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[8] A. F. Cameron, N. J. Hair, and D. G. Morris, *J.C.S. Perkin II*, 1972, 1071.

[9] A. F. Cameron, N. J. Hair, and D. G. Morris, *J.C.S. Perkin II*, 1972, 1331.