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Acta Cryst. (1976). B32, 1987

Structural Investigations of Ylides. VIII.* Crystal and Molecular Structure of a First-Row Sulphonyl-Stabilized Ylide: *N*-(Trimethylammonio)toluene-*p*-sulphonamidate

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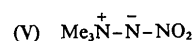
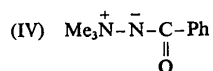
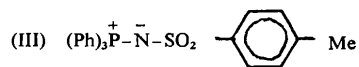
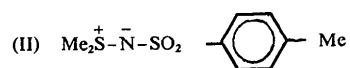
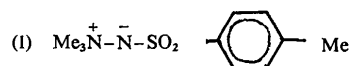
(Received 3 December 1975; accepted 5 January 1976)

The structure of the title compound has been determined from 2116 independent data collected on a diffractometer. The crystals are monoclinic, space group $P2_1/c$, with $Z=4$, $a=6.128$, $b=7.161$, $c=28.142$ Å, $\beta=93.66^\circ$. The structure was solved by direct methods, and refined by least squares to a final R of 0.007. The conformation is very similar to that of several other ylides containing the imine-sulphonyl grouping, despite the presence of water of crystallization, the latter molecules being hydrogen-bonded both to the imino-nitrogen atom and to one of the sulphonyl-oxygen atoms of the ylide molecules.

The $\overset{+}{N}-\overset{-}{N}$ and $\overset{-}{N}-\overset{-}{SO}_2$ lengths are respectively 1.472 (2) and 1.592 (2) Å, while the $\overset{+}{N}-\overset{-}{N}-\overset{-}{S}$ valence angle is 118.0 (1)°.

Introduction

Previous examples of ylides containing the imine-sulphonyl grouping, such as (II) (Cameron, Hair & Morris, 1973), (III) (Cameron, Hair & Morris, 1974) and similar molecules (Kálmán, 1967; Kálmán, Duffin & Kucsman, 1971; Kálmán & Sasvári, 1972), are all characterized by the presence of second row 'onium species which possess *d*-orbitals of energies such that delocalization is possible between the 'onium and imino-nitrogen atoms. It is plausible that such delocalization could compete with delocalization between the imino and sulphonyl species. However, in the ammonium imines (IV) and (V) (Cameron, Hair & Morris, 1972), delocalization of the formal negative charge on the imino-nitrogen may take place only *via* the stabilizing groups, and it has been shown that for these two compounds, the $\overset{+}{N}-\overset{-}{N}$ lengths are identical, no differences having been induced by the two considerably different stabilizing groups.



* Part VII: Cameron, Cameron, Campbell, & Johnson (1976).

In order to study the geometry of the imine-sulphonyl grouping in the absence of possible and competing

delocalization involving second-row 'onium species, we have determined the structure of *N*-(trimethylammonio)toluene-*p*-sulphonamide (I).

Experimental

Crystal data

N-(Trimethylammonio)toluene-*p*-sulphonamide (hydrated), C₁₀H₁₆N₂O₂S·H₂O, *M* = 246.3. Monoclinic, *a* = 6.128, *b* = 7.161, *c* = 28.142 Å, β = 93.66°, *U* = 1232.4 Å³, *D_m* = 1.30 g cm⁻³ (by flotation), *Z* = 4, *D_c* = 1.33, *F*(000) = 528. Space group *P*2₁/*c*. Mo *K*α radiation, λ = 0.7107 Å, μ(Mo *K*) = 2.57 cm⁻¹.

Crystallographic measurements

The cell parameters were initially determined photographically and subsequently refined by least squares prior to the diffractometer data collection. Intensity measurements were made on a Hilger & Watts Y290 diffractometer. A small crystal was exposed to Zr-filtered Mo radiation, and the 2θ, ω-scan technique used to record the intensities of 2116 independent reflexions [*I* > 2σ_{*I*}, σ_{*I*} = √(*I* + *B*₁ + *B*₂)] in the range 2θ 0 → 54°. The intensities were corrected with Lorentz and polarization factors, but not for absorption.

Structure determination

The structure was solved by direct phasing with the multi-symbolic approach. Triplet relationships were derived for those 160 reflexions with |*E*| > 1.78, and a solution was obtained for the 80 strongest reflexions with relationships of probability ≥ 0.8. 157 reflexions were then phased from this solution, and an *E* map based on these reflexions revealed the complete ylide molecule. A subsequent structure factor and electron density calculation improved the resolution, and suggested the presence of an additional atom close to, but not covalently bonded to, the ylide molecule. Further structure factor and electron density calculations confirmed the presence of this atom, which subsequently proved to be the O atom of a molecule of water. After each structure factor calculation, in which an overall isotropic thermal parameter *U*_{iso} = 0.05 Å² was as-

sumed, the data were placed on an approximate absolute scale by equating *k*Σ|*F_o*| and Σ|*F_c*|.

Table 2. Atomic coordinates and thermal parameters

(a) Fractional coordinates (× 10⁵)

	<i>x</i>	<i>y</i>	<i>z</i>
S	108153 (9)	57462 (8)	38918 (2)
O(1)	111765 (35)	76928 (27)	40017 (7)
O(2)	127582 (26)	46148 (30)	38586 (6)
O(3)	59155 (41)	81977 (37)	44178 (9)
N(1)	91982 (30)	50826 (27)	42790 (6)
N(2)	88108 (30)	30668 (26)	43287 (6)
C(1)	94753 (34)	56867 (30)	33109 (7)
C(2)	105574 (38)	49886 (36)	29335 (8)
C(3)	95295 (43)	49460 (38)	24789 (8)
C(4)	74175 (41)	55911 (32)	23965 (9)
C(5)	63551 (38)	62977 (38)	27781 (9)
C(6)	73597 (38)	63457 (37)	32341 (8)
C(7)	63162 (58)	55543 (50)	19004 (10)
C(8)	107594 (51)	20478 (49)	45446 (13)
C(9)	79922 (61)	21302 (42)	38801 (10)
C(10)	70394 (52)	29907 (45)	46741 (10)

(b) H atom fractional coordinates (× 10⁴) and isotropic thermal parameters (Å² × 10³)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2)	12007 (48)	4576 (44)	2984 (11)	30 (8)
H(3)	10282 (55)	4433 (49)	2212 (12)	38 (9)
H(5)	4868 (52)	6845 (46)	2732 (11)	33 (8)
H(6)	6582 (39)	6761 (34)	3475 (9)	19 (7)
H(71)	4958 (70)	5674 (63)	1948 (16)	73 (13)
H(72)	6463 (75)	6811 (73)	1748 (18)	79 (14)
H(73)	6808 (71)	4516 (69)	1699 (17)	65 (12)
H(81)	11936 (68)	2069 (59)	4314 (15)	57 (11)
H(82)	11208 (77)	2641 (70)	4803 (18)	64 (13)
H(83)	10433 (58)	832 (59)	4590 (13)	41 (9)
H(91)	7652 (46)	916 (46)	3947 (10)	23 (7)
H(92)	6792 (66)	2857 (56)	3737 (14)	45 (10)
H(93)	9168 (57)	2136 (47)	3666 (13)	37 (9)
H(101)	7537 (65)	3641 (63)	4980 (15)	59 (11)
H(102)	6666 (62)	1679 (55)	4735 (14)	52 (11)
H(103)	5689 (82)	3564 (71)	4503 (18)	76 (14)
H(O1)	6666 (91)	7375 (81)	4364 (20)	91 (20)
H(O2)	4756 (66)	8050 (58)	4286 (15)	55 (11)

(c) Anisotropic thermal parameters (Å² × 10⁴)

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
S	363	398	343	-71	-63	51
O(1)	750	454	521	-238	-90	31
O(2)	349	737	502	40	-54	134
O(3)	633	643	735	-99	-3	-137
N(1)	443	366	316	-62	-13	-3
N(2)	431	376	312	-70	-65	47
C(1)	376	340	338	-9	-19	71
C(2)	455	427	439	88	31	44
C(3)	621	456	385	69	75	2
C(4)	550	367	370	-66	-72	67
C(5)	388	545	460	23	-63	108
C(6)	402	536	381	72	34	33
C(7)	839	606	445	-122	-187	61
C(8)	586	521	760	-2	-202	220
C(9)	853	454	399	-223	-114	-38
C(10)	642	635	497	-144	129	60

Mean estimated standard deviations (Å² × 10⁴)

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
S	3	4	3	2	2	2
O	11	12	11	9	9	9
N	10	10	9	9	7	7
C	14	14	13	12	11	11

Table 1. Course of refinement

Cycles	Parameters refined	Final <i>R</i>	Final <i>R</i> '
1-4	<i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{iso} for S, O, N, and C, scale factor. Unit weights, full matrix.	0.148	0.0225
5-9	<i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{<i>ij</i>} for S, O, N, and C, scale factor. Unit weights, H atom contributions included but not refined, full matrix.	0.065	0.0052
10-13	<i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{<i>ij</i>} for S, O, N, and C, <i>x</i> , <i>y</i> , <i>z</i> for H, scale factor. Weighting scheme applied, full matrix.	0.048	0.0036
14-16	<i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{<i>ij</i>} for S, O, N, and C, <i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{iso} for H, scale factor. Weighting scheme applied, blocked matrix.	0.047	0.0035

Structure refinement

Refinement of positional, thermal and scale parameters converged after least-squares minimization, when R was 0.047 and $R' (= \sum w\Delta^2 / \sum w|F_o|^2)$ 0.0035. Details of the refinement are given in Table 1.

Difference syntheses, calculated after the preliminary cycles of refinement, revealed all 18 H atoms of the asymmetric unit, including those of the water molecule. Positional and isotropic thermal parameters for the H atoms were refined in later cycles. The weighting

Table 3. Interatomic distances and angles

(a) Bonded distances (Å)			
S—O(1)	1.442 (2)	C(1)—C(2)	1.381 (3)
S—O(2)	1.448 (2)	C(1)—C(6)	1.384 (3)
S—N(1)	1.592 (2)	C(2)—C(3)	1.390 (3)
S—C(1)	1.782 (2)	C(3)—C(4)	1.380 (3)
N(1)—N(2)	1.471 (3)	C(4)—C(5)	1.387 (3)
N(2)—C(8)	1.495 (4)	C(4)—C(7)	1.512 (4)
N(2)—C(9)	1.488 (3)	C(5)—C(6)	1.388 (3)
N(2)—C(10)	1.504 (3)	Mean O—H	0.78 (5)
Mean C—H (aryl)	0.95 (3)	Mean C—H (methyl)	0.97 (4)
(b) Interbond angles (°)			
O(1)—S—O(2)	116.1 (1)	C(8)—N(2)—C(9)	110.0 (2)
N(1)—S—O(1)	103.6 (1)	C(8)—N(2)—C(10)	108.1 (2)
N(1)—S—O(2)	115.3 (1)	C(9)—N(2)—C(10)	108.3 (2)
N(1)—S—C(1)	110.5 (1)	C(2)—C(1)—C(6)	119.6 (2)
C(1)—S—O(1)	106.0 (1)	C(1)—C(2)—C(3)	120.3 (2)
C(1)—S—O(2)	105.1 (1)	C(2)—C(3)—C(4)	120.8 (2)
S—N(1)—N(2)	118.0 (1)	C(3)—C(4)—C(5)	118.3 (2)
S—C(1)—C(2)	119.9 (2)	C(4)—C(5)—C(6)	121.5 (2)
S—C(1)—C(6)	120.5 (2)	C(3)—C(4)—C(7)	120.5 (2)
N(1)—N(2)—C(8)	112.8 (2)	C(5)—C(4)—C(7)	121.2 (2)
N(1)—N(2)—C(9)	114.2 (2)	C(5)—C(6)—C(1)	119.5 (2)
N(1)—N(2)—C(10)	103.0 (2)		
(c) Intramolecular non-bonded distances (Å)			
S·····N(2)	2.63	O(2)·····N(2)	3.04
S·····C(8)	3.22	O(2)·····C(2)	2.87
S·····C(9)	3.11	O(1)·····C(6)	3.23
O(1)·····O(2)	2.45	O(2)·····C(8)	2.98
O(1)·····N(1)	2.39	O(2)·····C(9)	3.42
O(2)·····N(1)	2.57		
(d) Intermolecular distances (Å) ≤ 3.90 Å			
O(3)·····S ⁱ	3.80	C(9)·····O(3) ⁱⁱ	3.48
O(3)·····O(2) ⁱ	3.52	C(10)·····O(3) ⁱⁱ	3.57
C(6)·····O(2) ⁱ	3.63	N(2)·····O(3) ⁱⁱ	3.93
C(9)·····O(2) ⁱ	3.66	C(10)·····O(3) ⁱⁱⁱ	3.34
C(10)·····O(2) ⁱ	3.57	C(5)·····C(4) ^{iv}	3.86
C(10)·····C(8) ⁱ	3.90	C(7)·····C(5) ^v	3.60
C(5)·····C(2) ⁱ	3.73	C(7)·····C(6) ^v	3.77
C(8)·····C(1) ⁱⁱ	3.49	C(9)·····C(7) ^v	3.51
C(9)·····O(1) ⁱⁱ	3.73		

Roman numeral superscripts refer to the following equivalent positions relative to a molecule at (x, y, z) :

(i)	$-1+x$	y	z	(ii)	x	$-1+y$	z
(iii)	$1-x$	$1-y$	$1-z$	(iv)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(v)	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$				

(e) Selected torsion angles (°) (mean e.s.d. 0.2°)

O(1)—S—N(1)—N(2)	-168.6	O(2)—S—C(1)—C(6)	168.3
O(2)—S—N(1)—N(2)	-40.7	N(1)—S—C(1)—C(2)	-137.1
C(1)—S—N(1)—N(2)	78.3	N(1)—S—C(1)—C(6)	43.3
O(1)—S—C(1)—C(2)	111.3	S—N(1)—N(2)—C(8)	70.3
O(1)—S—C(1)—C(6)	-68.3	S—N(1)—N(2)—C(9)	-56.3
O(2)—S—C(1)—C(2)	-12.1	S—N(1)—N(2)—C(10)	-173.1

scheme applied in the later stages was $w=xy$, where $x=\sin\theta/B$ if $\sin\theta < B$, else $x=1$; and $y=C/|F_o|$ if $|F_o| > C$, else $y=1$, the most suitable values of B and C finally proving to be 0.40 and 7.0 respectively.

On convergence, an electron density distribution and a difference synthesis were evaluated. Neither revealed any error in the structure, and refinement was considered complete. Final fractional coordinates and thermal parameters are given in Table 2; Table 3 contains all bond lengths, interbond angles, selected non-bonded distances, and relevant torsion angles; Table 4 gives the least-squares plane. The estimated standard deviations quoted in parentheses in Tables 2 and 3 are derived from the least-squares calculations, and should be regarded as minimum values. The atomic numbering is shown in Fig. 1.*

Table 4. Least-squares plane

(a) Equation of plane:

$$0.3660X + 0.91Y - 0.1796Z - 3.9585 = 0.$$

(X , Y and Z are orthogonal coordinates in Å.)

(b) Deviations of atoms from the plane (Å)

S	0.005*	C(1)	-0.003*	C(2)	-0.001*
C(3)	-0.001*	C(4)	-0.005*	C(5)	0.001*
C(6)	-0.003*	C(7)	0.006*		

* Denotes atom used to define the plane.

Discussion

The analysis of the present compound allows comparisons to be made both with second-row sulphonyl-stabilized ylides of the type exemplified by (II) and (III), and also with first-row ammonium ylides such as (IV) and (V). In particular, the latter comparison reveals that $N(2)-N(1)$ [1.472 (2) Å] of (I) is experimentally identical to the corresponding bonds in (IV) and (V) [respectively 1.471 (5) and 1.470 (8) Å]. This observation confirms the invariance, with change of stabilizing group, of the $N-N$ bond in ammonium imines.

Also of considerable interest, is the length of the $N(1)-S$ imine-sulphonyl bond [1.592 (2) Å], which lies within the range of values [1.581(10)–1.618(7) Å] previously observed for compounds of which (II) and (III) are typical, although the lower end of this range is poorly defined. In general, however, the shortness of these lengths in comparison with the formal $N-S$ single-bond value of 1.772 (1) Å in sulphamic acid (Cameron & Duncanson, 1975) is usually interpreted as suggesting a considerable degree of π -bond character

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31597 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

in the imine-sulphonyl bond. Moreover, whereas in molecules such as (II) and (III) there exists the possibility of delocalization of the negative charge on the central N atom onto the 'onium atom by $d_{\pi}-p_{\pi}$ interaction, which might intuitively be expected to influence or perturb the delocalization within the imine-sulphonyl systems of these molecules, no such possibility exists in the case of (I). We conclude, therefore, since the

length of N(1)-S of the present molecule is not markedly different from those values previously observed, that the effects, if any, of the potential delocalizing interactions between the 'onium and imine species do not result in gross distortions of the imine-sulphonyl bond lengths, at least in those examples reported to date.

The overall conformation of (I) is illustrated by the three Newman projections given in Fig. 2, which reveal the asymmetric dispositions of the aromatic ring and the ammonium N atom with respect to the sulphonyl group, the aromatic ring deviating from coplanarity with S=O(2) by 12.1° , and N(2)-N(1) deviating from coplanarity with S=O(1) by 11.4° . This overall conformation of the ylide moiety is very similar to the conformations observed in (II) and (III), in which the corresponding deviations for the aromatic rings are respectively 11.2 and 11.8° , and for the 'onium-imine bonds 12.8 and 12.3° . Such uniformity, when considered in conjunction with the observed lengths of the N-S(sulphonyl) bonds discussed above, suggests that the possibility or extent of $d_{\pi}-p_{\pi}$ bonding in the 'onium-imine bonds is not a major factor in determining the overall 'onium-imine-sulphonyl conformation. Moreover, it is to be noted that the conformation of the present molecule is adopted in the presence of the additional water molecule, which links sulphonyl-oxygen and imino-nitrogen atoms of adjacent molecules [O(water)-H...O(sulphonyl) 3.08 ; O(sulphonyl)...H 2.30 Å; angle O-H...O $171(5)^{\circ}$; O(water)-H...N(imino) 3.05 ; N(imino)...H 2.28 Å; angle O-H...N $172(4)^{\circ}$], while we have previously reported the geometry of a rather more complex sulphilimine (Cameron, Cameron, Campbell & Johnson, 1976) which deviates from this common conformation, apparently as the result of internal steric constraints.

Of the other features of the geometry of (I), the valence angle at the imino-nitrogen atom N(1) [$118.0(1)^{\circ}$] is intermediate in value between the values observed for the corresponding angle in (III) [$126.4(2)^{\circ}$], and the corresponding angles in sulphilimines [$113.4(5)$ - $116.2(6)^{\circ}$] and ammonium-imines [$114.2(3)$ and $115.0(5)^{\circ}$]. Other dimensions not discussed above compare well with literature values for similar bonding situations. With the exception of the hydrogen bonds mentioned previously, there are no abnormally short intermolecular contacts, and the molecular packing would appear to be largely dominated by involvement with the additional water molecules.

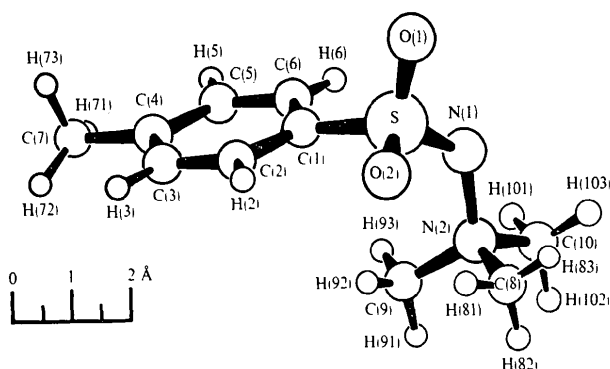


Fig. 1. A view of one molecule showing the atomic numbering.

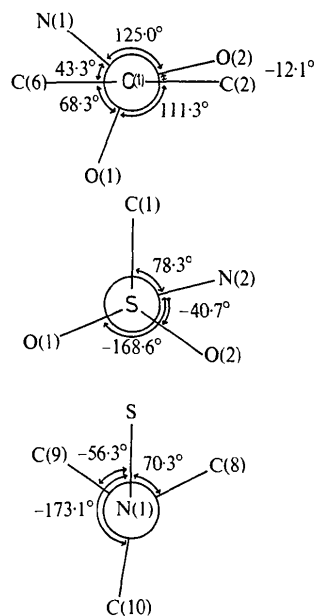


Fig. 2. Three Newman projections illustrating the molecular conformation.

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