

of the carbonyl bond [1.245 (3) Å]. Moreover, the C(2)–N(1)–C(13)=O(1) grouping is close to planarity [torsion angle 7.5°]. Since we have suggested minimal delocalization of the negative charge into the sulphonium-aromatic system, there should therefore be a similarity between (II) and (VII) (Cameron, Hair & Morris, 1972), in which there is no delocalization between the 'onium and imine species, in contrast to (I) where some delocalization across the S⁺–N[–] bond is postulated. Thus in (VII) the N[–]–C and C=O lengths are 1.313 (6) and 1.243 (5) Å respectively, while the corresponding values in (I) are 1.344 (3) and 1.246 (3) Å. In particular, therefore, there is an apparent progression of values for the N[–]–C(O) bonds in the three molecules, which may well reflect the degree of delocalization between the 'onium and imine groups in each case.

The major conformational features of (II) are illustrated by the Newman projections in Fig. 3. The 36° torsion about N(1)–C(2) may well arise from steric interactions involving the carbonyl group, the sulphonium-substituted aromatic ring and the sulphonium group itself [O(1)···C(3) 2.93 Å, S⁺···N(1) 2.73 Å]. As a further possible consequence of such interactions, the valence angle at N(1) [120.4 (1)°] is considerably larger than the corresponding angles in (I) [110.0 (1)°] and similar molecules, while the value of 128.2 (1)° for N(1)–C(13)–O(1) is similar to that observed elsewhere.

One interesting feature of the crystal structure of (II) is related to the large thermal motion of the terminal nitro-aromatic group, and is illustrated by the thermal ellipsoid plots in Fig. 4, which shows the over-

lap of pairs of *b*-glide related molecules viewed parallel to and perpendicular to *b*. The nature and direction of the motion thus viewed, suggests a tendency for overlapped nitrobenzene groups to associate closely in pairs by the out-of-phase flexing of adjacent molecules, to give rise to stacks of pairs of associated molecules extending throughout the crystal. Consideration of the r.m.s. amplitude of vibration in relation to the *b* spacing, indicates a closest possible approach of overlapped nitro groups of the order of 3.2–3.3 Å, such that the possibility of charge-transfer interaction cannot be excluded. However, it must be noted that although the colour of the crystals is intense orange, this colour not only persists in solution, but is solvent invariant. Whatever the exact nature of the above interaction, it would seem to be the dominant feature of the crystal packing, although several short intermolecular contacts involving the sulphonium group [S···S 3.48, S···O(1) 2.98 Å] must be noted.

References

- BAK, B., HANSEN, L. & RASTRUP-ANDERSEN, J. (1954). *J. Chem. Phys.* **22**, 2013–2017.
 CAMERON, A. F., DUNCANSON, F. D. & MORRIS, D. G. (1976). *Acta Cryst.* **B32**, 1998–2001.
 CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1972). *J. Chem. Soc. Perkin II*, pp. 1071–1076.
 CHRISTENSEN, A. T. & THOM, E. (1971). *Acta Cryst.* **B27**, 581–586.
 CHRISTENSEN, A. T. & WITMORE, W. G. (1969). *Acta Cryst.* **B25**, 73–78.
 KÁLMÁN, A., DUFFIN, B. & KUCSMAN, Á. (1971). *Acta Cryst.* **B27**, 586–594.

Acta Cryst. (1976). **B32**, 2006

The Crystal Structure of the Methanesulphonamide of Piperidine-4-spiro-1'-(2',5'-dioxolane) (C₈H₁₅NSO₄)

BY P. SMITH-VERDIER, S. GARCÍA-BLANCO AND F. FLORENCIO

Instituto 'Rocasolano', Consejo Superior de Investigaciones Científicas, Serrano 119, Madrid-6, Spain

(Received 24 December 1975; accepted 13 January 1976)

Crystals of the methanesulphonamide of piperidine-4-spiro-1'-(2',5'-dioxolane) are monoclinic, space group *P2₁/c* with *a* = 10.373 (2), *b* = 5.449 (1), *c* = 18.049 (4) Å and β = 91.87 (1)°. The structure has been refined to *R* = 0.076 for 2936 independent reflexions measured on an automatic four-circle diffractometer. The piperidine ring has a chair conformation and the S–N bond length of 1.634 Å shows a certain amount of double-bond character.

Introduction

It is difficult to carry out the conformational analysis of *N*-methylsulphonyl compounds by liquid phase methods (dipole moments and NMR) owing to (a)

the flattening at the nitrogen atom involving a not completely tetrahedral arrangement of substituents and (b) the possible existence of rotamers around the N–S bond. For these reasons Dr Moreno Mañas of Universidad Autónoma de Barcelona, suggested

that an X-ray analysis of the crystal structure of sulphonamides of cyclic amines would be useful in order to reveal their molecular conformation. The methanesulphonamide of piperidine-4-spiro-1'-(2',5'-dioxolane) was chosen as the subject of this analysis.

Experimental

Crystals of title compound were kindly supplied by Dr Moreno Mañas. The lattice constants were obtained by a least-squares analysis of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation. The unit-cell dimensions and other pertinent crystal data are included in Table 1.

The intensity data were collected from a crystal measuring $0.4 \times 0.2 \times 0.4$ mm with a Philips diffractom-

eter. Intensities were recorded in the $\omega/2\theta$ scan mode with θ between 2 and 35° ; graphite monochromatized Mo $K\alpha$ radiation was used. 2936 reflexions were measured of which 2351 had intensities greater than 2σ , σ being the standard deviation calculated from the counting statistics of the measurements. The intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied.

Solution and refinement of the structure

The sulphur position was deduced from a sharpened Patterson map using Harker peaks. An electron density map phased with sulphur revealed a chemically reasonable fragment of ten new atoms. The remainder of the structure was found in a subsequent map, phased with these eleven atoms. Full-matrix least-squares refinement using unit weights gave an R value of 0.11. A difference map clearly located all the hydrogen atoms. The structural parameters of the atoms, including isotropic hydrogen were refined by the full-matrix least-squares method minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where $w = K/(\sigma_1\sigma_2)^2$, $\sigma_1 = a + b|F_o|$ and $\sigma_2^2 = c + d \sin \theta/\lambda$ with the coefficients given in Table 2. The final unweighted and weighted agreement indices were $R = 0.096$ and $R_w = 0.076$ where $R_w = (\sum w d^2 / \sum w |F_o|^2)^{1/2}$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates and

Table 1. *Crystal data*

Standard deviations, given in parentheses, refer to the least significant digits.

$C_8H_{15}NSO_4$, M.W. 221.26	$V = 1019.5 \text{ \AA}^3$
Space group $P2_1/c$	$D_o = 1.47 \text{ g cm}^{-3}$
$a = 10.373$ (2) \AA	$D_x = 1.43$
$b = 5.449$ (1)	$F(000) = 472$
$c = 18.049$ (4)	
$\beta = 91.87$ (2) $^\circ$	
$Z = 4$	

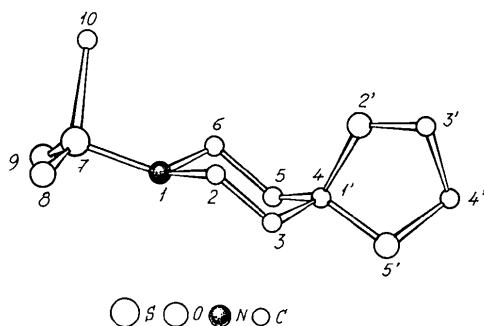


Fig. 1. Perspective drawing of the molecule viewed along the unit-cell c axis.

Table 2. *Coefficients for the weighting scheme*

	a	b
$ F_o \leq 0.50$		
$0.5 < F_o \leq 1.20$	1.244	-0.226
$1.20 < F_o \leq 2.60$	0.855	0.095
$2.60 < F_o \leq 5.30$	1.378	-0.107
$5.3 < F_o \leq 6.8$	0.494	0.059
$6.8 < F_o \leq 8.8$	0.902	0.001
$8.5 < F_o \leq 13.0$	1.022	-0.018
$13.0 < F_o $	-0.385	0.075
	c	d
$\sin \theta/\lambda < 0.50$	1.282	-1.387
$0.50 \leq \sin \theta/\lambda$	-0.980	3.158

Table 3. *Positional and thermal parameters (all $\times 10^4$) for the non-hydrogen atoms*

Standard deviations given in parentheses refer to the least significant digits. Thermal factors are those in the expression $|-2\pi^2 \sum U_{ij} a_i^* a_j^* h_i h_j|$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	1273 (3)	2603 (6)	3704 (2)	322 (13)	393 (15)	351 (14)	2 (11)	14 (11)	-2 (12)
C(2)	1988 (4)	2667 (9)	4421 (2)	406 (18)	565 (23)	357 (17)	-39 (16)	-22 (14)	-60 (16)
C(3)	3192 (4)	4219 (9)	4358 (3)	412 (19)	530 (23)	543 (22)	-34 (17)	-34 (16)	-164 (19)
C(4)≡C(1')	4009 (3)	3378 (7)	3734 (2)	344 (16)	305 (16)	613 (22)	-3 (14)	24 (15)	19 (16)
C(5)	3224 (4)	3322 (9)	3019 (2)	421 (19)	574 (25)	511 (22)	51 (18)	93 (16)	43 (19)
C(6)	2041 (4)	1698 (9)	3086 (2)	425 (19)	603 (25)	381 (18)	-26 (18)	17 (14)	-99 (17)
S(7)	-215 (1)	1627 (2)	3713 (0)	333 (4)	344 (4)	357 (4)	20 (3)	-14 (3)	13 (3)
O(8)	-789 (3)	2623 (6)	4361 (2)	381 (13)	510 (16)	515 (15)	54 (11)	89 (11)	-83 (12)
O(9)	-807 (3)	2157 (6)	3004 (2)	420 (14)	592 (18)	458 (14)	27 (12)	-109 (11)	11 (13)
C(10)	-148 (5)	-1591 (8)	3806 (2)	620 (24)	339 (18)	477 (21)	-36 (18)	-35 (18)	31 (16)
O(2')	4481 (3)	957 (6)	3877 (2)	438 (15)	375 (15)	992 (25)	71 (12)	-49 (15)	74 (16)
C(3')	5840 (5)	1103 (10)	3963 (3)	457 (22)	541 (26)	846 (33)	152 (20)	-61 (22)	-38 (25)
C(4')	6182 (5)	3380 (11)	3584 (4)	396 (21)	603 (29)	983 (38)	50 (20)	85 (22)	-124 (28)
O(5')	5107 (3)	4907 (6)	3688 (2)	369 (14)	408 (15)	973 (24)	-24 (11)	83 (14)	-31 (15)

Table 4. *Positional and thermal parameters (all $\times 10^3$) for hydrogen atoms*

Standard deviations, given in parentheses, refer to the least significant digits

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(21)	142 (6)	325 (11)	480 (3)	3.654
H(22)	216 (6)	94 (12)	459 (3)	3.654
H(31)	296 (6)	591 (13)	432 (3)	4.072
H(32)	367 (6)	422 (12)	481 (4)	4.072
H(51)	295 (7)	497 (12)	290 (4)	4.150
H(52)	368 (7)	276 (12)	265 (3)	4.150
H(61)	147 (6)	173 (11)	265 (3)	3.767
H(62)	231 (6)	3 (12)	319 (3)	3.767
H(101)	28 (7)	-200 (13)	427 (4)	4.960
H(102)	-98 (7)	-205 (14)	381 (4)	4.960
H(103)	31 (7)	-240 (14)	335 (4)	4.960
H(3'1)	596 (7)	101 (14)	445 (4)	5.436
H(3'2)	621 (7)	-28 (14)	379 (4)	5.436
H(4'1)	691 (8)	408 (15)	376 (4)	5.468
H(4'2)	630 (7)	306 (14)	301 (4)	5.468

the temperature factors for non-hydrogen and hydrogen atoms are given in Tables 3 and 4.*

The major calculations were carried out with the X-RAY System of Crystallographic Programs (Stewart, Kundell & Baldwin, 1970).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31617 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Molecular geometry*

(a) Least-squares planes defined by atomic positions and, in brackets, distances of atoms (Å) from these planes: *X*, *Y* and *Z* refer to orthogonal coordinates (Å)

Plane (1): N(1), C(2), C(3), C(4), C(5), C(6)
 $-0.2993X + 0.9305Y - 0.2111Z = -0.6531$
 [N(1) 0.2326, C(2) -0.2174, C(3) 0.2184, C(4) -0.2353, C(5) 0.2400, C(6) -0.2384]

Plane (2): C(2), C(3), C(5), C(6)
 $0.5722X - 0.7962Y + 0.1966Z = 1.4526$
 [C(2) -0.0108, C(3) 0.0108, C(5) -0.0108, C(6) 0.0108, N(1) -0.6375, C(4) 0.6604]

Plane (3): C(1'), O(2'), C(4'), O(5')
 $-0.9500X + 0.1874Y + 0.9777Z = 6.5358$
 [C(1') 0.0205, O(2') -0.0129, C(4') 0.0130, O(5') -0.0205, C(3') -0.4569]

Plane (4): C(1'), O(2'), C(3'), C(4'), O(5')
 $0.0489X + 0.2396Y + 0.9696Z = 7.2006$
 [C(1') -0.0357, O(2') 0.1394, C(3') -0.1851, C(4') 0.1601, O(5') -0.0786]

(b) Torsion angles (°)

S(7)-N(1)-C(2)-C(3)	-164.87°
C(6)-N(1)-C(2)-C(3)	-56.48
N(1)-C(2)-C(3)-C(4)	54.01
C(2)-C(3)-C(4)-C(5)	-54.98
C(3)-C(4)-C(5)-C(6)	56.50
C(4)-C(5)-C(6)-N(1)	-56.95
C(5)-C(6)-N(1)-C(2)	57.89
C(5)-C(6)-N(1)-S(7)	163.08

(c) Dihedral angle between planes 1 and 2 = 89.7°

Discussion

Fig. 1 is a drawing of the molecule looking down the unit cell *c* axis. Fig. 2 is a schematic drawing of the molecule showing the intramolecular bond lengths and angles. Further details of the molecular geometry are given in Table 5.

The piperidine ring adopts a chair conformation with the CH₃-SO₂ group substituted on the N atom in an equatorial position. According to Aroney & Le Fèvre (1960) bulky substituents on the N atom of piperidine exist mainly in this position.

The partial double-bond character of the N(1)-S(7) interaction, 1.634 (3) Å, can be explained in terms of π bonding between the sulphur 3*d* orbitals and the lone pair of electrons which are available on the nitrogen atom. In sulphamic acid SO₃(NH₃) (Sass, 1960) where the nitrogen atom has no pair of electrons available for π bonding the S-N distance is 1.76 Å, close to the 1.74 Å value for a S-N single bond given by Schoemaker & Stevenson (1941). The partial double-bond character is consistent with the opening out of the S(7)-N(1)-C(2) and S(7)-N(1)-C(6) angles to 116.6 (2) and 115.7 (3)° respectively from the tetrahedral value.

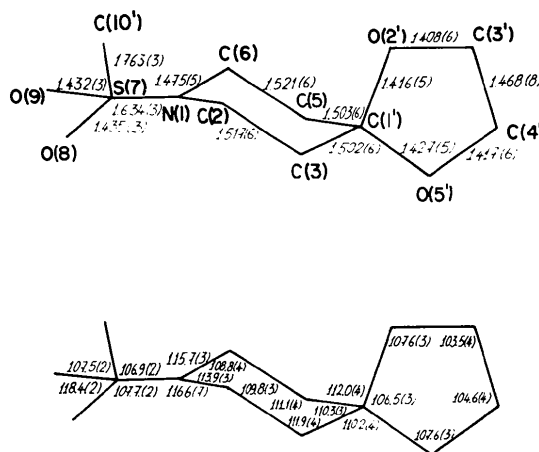


Fig. 2. Bond lengths (Å) and angles (°) with their estimated standard deviations in parentheses. Angles not shown: N(1)-S(7)-O(9) 107.6 (2), C(3)-C(1')-O(2') 109.8 (3), O(8)-S(7)-C(10) 108.4 (2), C(5)-C(1')-O(5') 108.0 (4).

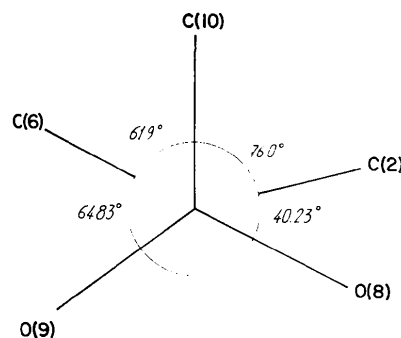
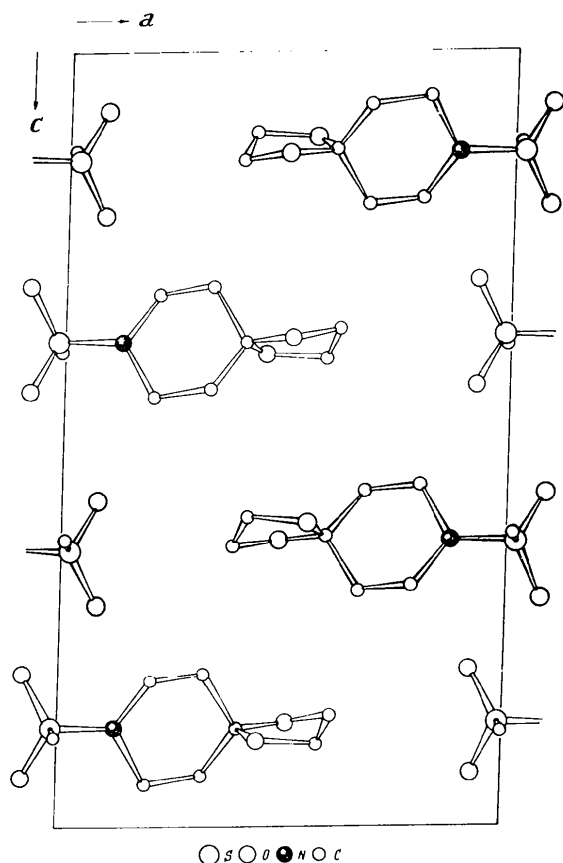


Fig. 3. Newman projection along the S(7)-N(1) bond.

Fig. 4. Projection of the structure along the *b* axis.

The third angle C(2)—N(1)—C(6) is held at 113.9 (3) by the ring geometry.

The geometry of the sulphonamide moiety is typical of that found in other sulphonamides (Karle, 1973, and references therein). The arrangement of the bonds around the sulphur atoms is a distorted tetrahedron with an O—S—O angle of 118.4°. The O(8)···O(9) distance is 2.462 Å, comparable with the values of 2.480 and 2.476 Å for O(8)···N(7) and O(9)···N(7) respectively.

C(1'), O(2'), C(4') and O(5') of the dioxolane ring lie in the same plane and C(3') is deviated from it by -0.457 Å; consequently the ring shows an envelope conformation (see Table 5). The C—O bond length averages 1.417 Å in good agreement with the accepted values for the C—O single bond. The C(3')—C(4') distance of 1.468 Å is shorter than the accepted C—C bond length (1.539 Å); this shortening would be due to the proximity of the two oxygen atoms. The planes through the piperidine and dioxolane rings make an angle of 89.9°, practically 90°, as befits a spirano compound.

The rotation of the piperidine ring about the N(1)—S(7) bond is restricted by the partial double-bond character of this bond and consequently there is only one conformer. Torsion angles about this bond are shown in Fig. 3. The bond lengths and angles involving hydrogen atoms are given in Table 6.

Table 6. Bond lengths and valence angles involving the hydrogen atoms

C(2)—H(21)	0.98 (6) Å	N(1)—C(2)—H(21)	109 (3)°
C(2)—H(22)	1.00 (7)	N(1)—C(2)—H(22)	109 (3)
		C(3)—C(2)—H(21)	113 (4)
		C(3)—C(2)—H(22)	114 (4)
		H(21)—C(2)—H(22)	101 (5)
C(3)—H(31)	0.95 (7)	C(2)—C(3)—H(31)	110 (4)
C(3)—H(32)	0.95 (6)	C(2)—C(3)—H(32)	110 (4)
		C(4)—C(3)—H(31)	113 (4)
		C(4)—C(3)—H(32)	111 (4)
		H(31)—C(3)—H(32)	100 (6)
C(5)—H(51)	0.96 (7)	C(4)—C(5)—H(51)	109 (4)
C(5)—H(52)	0.89 (7)	C(4)—C(5)—H(52)	111 (4)
		C(6)—C(5)—H(51)	109 (4)
		C(6)—C(5)—H(52)	108 (4)
		H(51)—C(5)—H(52)	108 (6)
C(6)—H(61)	0.97 (6)	C(5)—C(6)—H(61)	113 (4)
C(6)—H(62)	0.97 (7)	C(5)—C(6)—H(62)	110 (4)
		N(1)—C(6)—H(61)	106 (4)
		N(1)—C(6)—H(62)	109 (4)
		H(61)—C(6)—H(62)	110 (5)
C(10)—H(101)	0.96 (7)	S(7)—C(10)—H(101)	109 (4)
C(10)—H(102)	0.90 (8)	S(7)—C(10)—H(102)	104 (5)
C(10)—H(103)	1.06 (7)	S(7)—C(10)—H(103)	111 (4)
		H(101)—C(10)—H(102)	111 (6)
		H(101)—C(10)—H(103)	112 (6)
		H(102)—C(10)—H(103)	110 (6)
C(3')—H(3'1)	0.88 (8)	O(2')—C(3')—H(3'1)	103 (5)
C(3')—H(3'2)	0.91 (8)	O(2')—C(3')—H(3'2)	110 (5)
		C(4')—C(3')—H(3'1)	119 (5)
		C(4')—C(3')—H(3'2)	116 (5)
		H(3'1)—C(3')—H(3'2)	104 (7)
C(4')—H(4'1)	0.89 (8)	O(5')—C(4')—H(4'1)	112 (5)
C(4')—H(4'2)	1.06 (7)	O(5')—C(4')—H(4'2)	110 (4)
		C(3')—C(4')—H(4'1)	115 (5)
		C(3')—C(4')—H(4'2)	111 (4)
		H(4'1)—C(4')—H(4'2)	107 (6)

The molecular packing is shown in Fig. 4 in projection along the *b* axis. The molecules lie in layers parallel to (100) held together by van der Waals forces.

We thank Dr J. G. Rodriguez for many discussions and to the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Madrid for the facilities provided in all calculations.

References

- ARONEY, M. & LE FÈVRE, R. J. W. (1960). *J. Chem. Soc.* pp. 2161–2168.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
- KARLE, I. L. (1973). *Z. Kristallogr.* **138**, 184–195.
- SASS, R. L. (1960). *Acta Cryst.* **13**, 320–324.
- SCHOMAKER, V. & STEVENSON, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37–40.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). X-RAY 70 System, Computer Science Center, Univ. of Maryland.