

structure determination show this conclusion to be incorrect and further would cast some doubt on the validity (Ablov & Samus, 1975) of using this system as a model for rigidly planar biological macrocyclic chelates.

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## The Crystal and Molecular Structure of the Methanesulphonamide of Morpholine (MSM): C<sub>5</sub>H<sub>11</sub>NOSO<sub>2</sub>

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The structure of MSM has been determined by single-crystal X-ray diffraction techniques. The crystals are orthorhombic, space group  $P2_12_12_1$ , with cell parameters  $a = 13.207$ ,  $b = 10.078$  and  $c = 5.7318$  Å;  $Z = 4$ . The structure was solved with the heavy-atom method and successive Fourier syntheses. It was further refined by a least-squares technique to a final  $R$  value of 0.055 for 1051 observed reflexions, measured on an automatic four-circle diffractometer. The hetero-ring shows a chair conformation with the N-SO<sub>2</sub>-CH<sub>3</sub> group in the equatorial position. There are no intermolecular distances shorter than the sum of the van der Waals radii.

#### Introduction

The conformational equilibrium of piperidine (1) has been the subject of prolonged controversy. At present, however, there seems to be a satisfactory settlement in favour of the NH-equatorial form for the gas phase (Cook *et al.*, 1973). This conclusion appears to apply equally to a variety of C-substituted piperidines in which a ring CH<sub>2</sub> group in position 3 or 4 has been

replaced by O, S or N-H. Such a replacement in the position would not be expected to disturb greatly the equilibrium behaviour. In the present work the resolution of the crystal structure of *N*-methanesulphonylmorpholine was undertaken, following the suggestion of Dr Moreno-Mañas, in order to determine the conformation of the N-SO<sub>2</sub>-CH<sub>3</sub> group.

#### Experimental

Crystals of MSM are transparent and colourless. Accurate cell parameters were determined by least-squares calculations from 26  $\theta$  values measured on a single-crystal X-ray diffractometer with Mo  $K\alpha$  radiation. Systematic absences are compatible with the

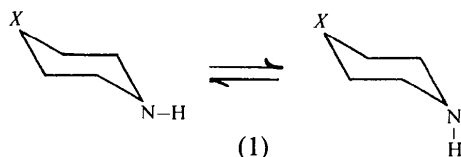


Table 1. *Crystal data*

Molecular formula $C_5H_{11}NO_3S$	
Molecular weight 165.2	
Space group $P2_12_12_1$	
$a = 13.207(1) \text{ \AA}$	$Z = 4$
$b = 10.078(1)$	$D_c = 1.426 \text{ g cm}^{-3}$
$c = 5.7318(4)$	$\mu = 3.657 \text{ cm}^{-1}$
$V = 764.430 \text{ \AA}^3$	$F(000) = 352$
Radiation $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$	
Crystal size: $0.2 \times 0.25 \times 0.2 \text{ mm}$	

space group  $P2_12_12_1$ . Cell data are summarized in Table 1. The intensities were measured on a Philips PW 1100 four-circle diffractometer operating in the  $\omega/2\theta$  scan mode. 2170 independent reflexions in the range  $2 < \theta < 30^\circ$  were recorded with graphite-monochromatized Mo  $K\alpha$  radiation. 1119 reflexions had intensities  $< 2\sigma(I)$  and were treated as unobserved and omitted from the refinement. The data were corrected for Lorentz and polarization effects but not for absorption. An overall temperature factor and scale factor were calculated from a Wilson plot and used to compute normalized structure factors (Karle & Hauptman, 1956). The statistics of the  $E$ 's confirmed a non-centrosymmetric structure.

### Structure determination and refinement

The structure was solved by the conventional heavy-atom method. The position of the S atom was determined from a three-dimensional Patterson synthesis. All the non-hydrogen atoms in the structure appeared as peaks on two subsequent Fourier syntheses. Their positions were refined by the full-matrix least-squares method. The thermal parameters were refined first isotropically and then anisotropically. All H atoms were located in a difference Fourier synthesis, and were refined with individual isotropic temperature factors. The final  $R$  value was 0.055. Anomalous dispersion corrections were applied; the values of  $\Delta f'$  and  $\Delta f''$  for S are 0.11 and 0.124 respectively (*International Tables for X-ray Crystallography*, 1974).

In the last cycles of refinement, we chose weights for the trends in  $|\Delta F_o|$  as follows (Cruickshank, 1961a,b, 1965, 1970):  $\omega = K/|f(F_o)|^2$  when  $K = 0.6027$ , and:

$$f(F_o) = 0.9096 - 0.3547 \text{ when } |F_o| < 1.1$$

$$f(F_o) = 0.3056 + 0.2256 \text{ when } 1.1 < |F_o| < 3.0$$

$$f(F_o) = 1.424 - 0.1674 \text{ when } 3.0 < |F_o| < 6.4$$

$$f(F_o) = 0.2746 + 0.0144 \text{ when } 6.4 < |F_o| < 21.8.$$

The weighting produced  $\langle \omega(F_o - F_c)^2 \rangle$  values independent of  $\sin \theta$  and the magnitudes of  $F_o$ . In the last cycle of refinement the final unweighted and weighted agreement indices were  $R = 0.055$  and  $R_w =$

Table 2. *Fractional coordinates ( $\times 10^4$  for non-hydrogen,  $\times 10^3$  for H atoms) and thermal parameters ( $\times 10^2$ ) for the hydrogen atoms*

	$x$	$y$	$z$	$U_{iso}$
S	4527 (1)	74 (1)	5551 (2)	
O(1)	4936 (3)	-48 (4)	3263 (6)	
O(2)	4067 (3)	-1059 (3)	6624 (7)	
O(3)	2513 (2)	3567 (3)	5852 (7)	
N	3662 (2)	1230 (3)	5393 (7)	
C(1)	3967 (3)	2462 (4)	4189 (9)	
C(2)	3022 (3)	3272 (5)	3734 (9)	
C(3)	2197 (4)	2375 (6)	6944 (9)	
C(4)	3089 (3)	1499 (5)	7561 (9)	
C(5)	5485 (4)	651 (4)	7420 (9)	
H(1)	422 (4)	222 (5)	271 (9)	2.2 (1.6)
H(2)	443 (3)	293 (4)	518 (9)	1.6 (1.1)
H(3)	318 (4)	406 (6)	303 (10)	3.6 (1.7)
H(4)	260 (3)	280 (4)	268 (9)	0.64 (1.1)
H(5)	186 (4)	257 (5)	834 (9)	2.01 (1.2)
H(6)	171 (4)	180 (6)	571 (11)	3.7 (1.7)
H(7)	355 (4)	192 (5)	869 (9)	2.3 (1.4)
H(8)	284 (4)	62 (5)	817 (10)	3.1 (1.4)
H(9)	522 (3)	62 (4)	890 (9)	0.97 (1.3)
H(10)	565 (4)	145 (6)	689 (11)	2.9 (1.7)
H(11)	598 (4)	4 (5)	731 (9)	3.0 (1.3)

0.0509. The final atomic parameters are given in Table 2. All the computations were performed on a Univac 1108 computer with the XRAY 70 system of crystallographic programs.\*

### Results and discussion

The MSM molecules and the numbering of the atoms are shown in Fig. 1. The morpholine ring has a chair conformation and the substituent on the N ring is in the

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32651 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

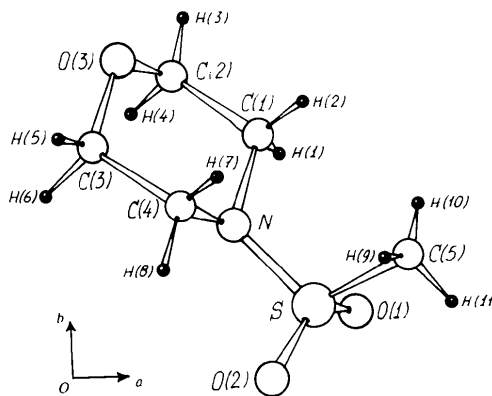


Fig. 1. MSM molecule and numbering of the atoms.

equatorial position. Bond lengths and angles are given in Table 3. The S—N bond length (1.634 Å) is shorter than that (1.76 Å) for the single S—N bond in sulphamic acid (Sass, 1960), but similar to that for the S—N bonds in methanesulphonanilide (Klug, 1968), bis(dimethylamine) sulphone (Jordan, Smith, Lohr & Lipscomb, 1963), and other sulphone compounds which are frequently described. The mean value for the S—N—C(1) and S—N—C(4) angles is 116°, which

indicates a distorted tetrahedral configuration around the N atom, although there are no steric interactions that lead one to expect the opening of this angle. On the other hand, an S—N—C angle of 119° is reported for 1-methyl-2-(*p*-tolylsulphonylamino)-2-(*p*-tolylsulphonylimino)indoline-3-spirocyclopentane where there is no steric inhibition and a short S—N bond length is present (1.62 Å) (Tickle & Prout, 1971). It would seem therefore that the short S—N bond length is a consequence of a  $d\pi-p\pi$  interaction and that an angle of 58° between the planes S—N—C(1), S—N—C(4) and O(1)—S—O(2) is suitable for such an interaction. The two S—O bond distances are 1.423 and 1.432 Å; both correspond to  $\pi$  bond orders of *ca* 0.75; the S—N bond

Table 3. *Interatomic distances (Å) and interbond angles (°) with e.s.d.'s in parentheses*

S—O(1)	1.423 (4)	O(1)—S—O(2)	119.2 (2)
S—O(2)	1.432 (3)	O(2)—S—N	107.2 (2)
S—N	1.634 (3)	O(1)—S—C(5)	108.5 (2)
S—C(5)	1.757 (5)	N—S—C(5)	107.5 (2)
C(1)—N	1.476 (5)	S—N—C(1)	115.8 (2)
C(1)—C(2)	1.514 (6)	S—N—C(4)	116.2 (3)
C(2)—O(3)	1.419 (6)	C(1)—N—C(4)	112.2 (3)
C(3)—O(3)	1.417 (6)	C(2)—O(3)—C(3)	109.8 (4)
C(3)—C(4)	1.514 (7)	N—C(1)—C(2)	108.0 (3)
C(4)—N	1.480 (6)	C(1)—C(2)—O(3)	110.9 (4)
C(1)—H(1)	0.94 (6)	C(4)—C(3)—O(3)	111.6 (4)
C(1)—H(2)	0.95 (5)	C(3)—C(4)—N	108.0 (4)
C(2)—H(3)	0.91 (6)	H(1)—C(1)—H(2)	110.9 (4.5)
C(2)—H(4)	0.95 (5)	H(3)—C(2)—H(4)	106.9 (4.8)
C(3)—H(5)	0.94 (5)	H(5)—C(3)—H(6)	111.9 (4.4)
C(3)—H(6)	1.11 (6)	H(7)—C(4)—H(8)	110.4 (4.3)
C(4)—H(7)	0.99 (5)	H(9)—C(5)—H(10)	115.6 (5.1)
C(4)—H(8)	1.01 (5)	H(10)—C(5)—H(11)	114.6 (5.1)
C(5)—H(9)	0.92 (5)		
C(5)—H(10)	0.89 (6)		
C(5)—H(11)	0.90 (5)		

Table 4. *Least-squares planes*

Plane I	Plane II	Plane III			
$\Delta$	$\Delta$	$\Delta$			
C(1)	0.005 Å	C(1)	0.000 Å	C(1)	0.000 Å
C(2)	-0.005	C(4)	0.000	C(4)	0.000
C(3)	0.005	N	0.000	S	0.000
C(4)	-0.005	S*	1.011	N*	-0.356
N*	-0.647	C(2)*	-1.193	C(2)*	-0.674
O(3)*	0.670	C(3)*	-1.181	C(3)*	-0.657
S*	-1.029				

Dihedral angles between planes (°)

Plane I—II : 51.71

Plane I—III : 26.11

Plane II—III : 25.60

\* Atom not included in definition of the plane.

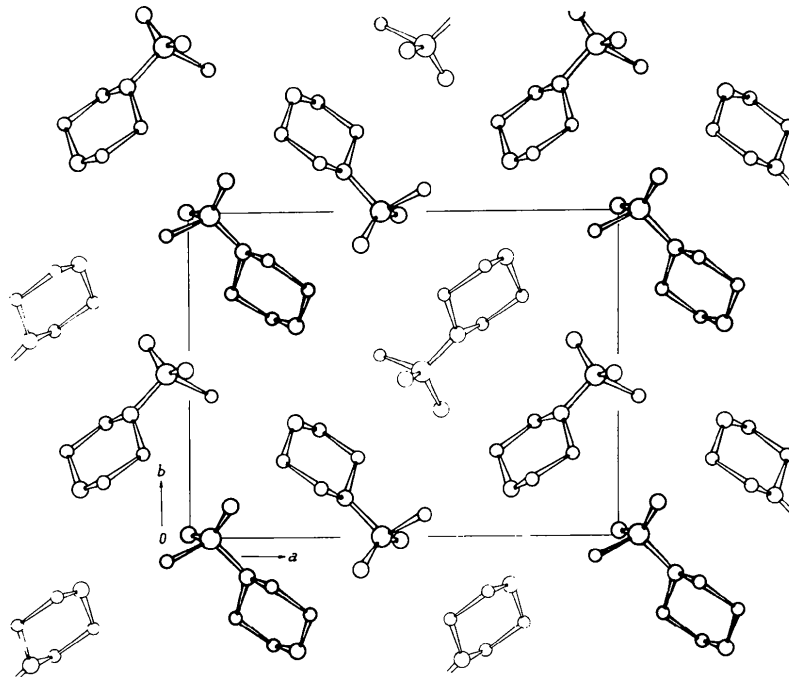


Fig. 2. The crystal structure view down *c*.

length represents a  $\pi$  bond order of *ca* 0.25, so the S—C(5) bond length of 1.75 Å should also represent a  $\pi$  bond order of 0.25 (Cruickshank, 1961*a,b*). The double-bond length between S and C in thiourea (*International Tables for X-ray Crystallography*, 1962) is 1.710 Å, and the single-bond length for these two atoms is 1.83 Å in aliphatic thiols (*International Tables for X-ray Crystallography*, 1962).

From the above evidence a double-bond character can be associated with the sulphamidic group and accordingly explained in terms of  $\pi$ -bonding molecular orbitals formed by C, N and O atoms with the 3*d*-orbitals of S.

The packing of the molecules is illustrated in Fig. 2. There are no short intermolecular distances. Least-squares planes are in Table 4.

We wish to thank Dr Moreno-Mañas for supplying the crystals used in this structural analysis and also for suggesting this work. The cooperation of the Centro de Proceso de Datos del Ministerio de Educación y Ciencia is acknowledged.

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## The Crystal and Molecular Structure of the Methanesulphonamide of *N*-Methylpiperazine (Sulfan): C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>SO<sub>2</sub>

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Crystals of the methanesulphonamide of *N*-methylpiperazine are monoclinic, space group  $P2_1/a$  with cell dimensions  $a = 15.405$ ,  $b = 8.488$ ,  $c = 6.940$  Å and  $\beta = 98.75^\circ$ . Each unit cell contains four molecules. The structural model refined to  $R = 0.064$  for 1784 observed reflexions measured on an automatic four-circle diffractometer. The results are compared with those obtained previously on the methanesulphonamide of morpholine (MSM).

### Introduction

The study of the methanesulphonamide of *N*-methylpiperazine forms part of a wider structural study on the conformational analysis of saturated heterocycles (Katritzky & Moreno-Mañas, 1974). The conformation of the N group in the ring of piperidine (Smith-Verdier, García-Blanco & Florencio, 1976), morpholine (Perales & García-Blanco, 1977) and piperazine has been recently investigated.

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### Experimental

Sulfan is a crystalline colourless solid: the material as supplied by Dr Moreno-Mañas yielded suitable crystals for study. Preliminary Weissenberg and precession photographs indicated monoclinic symmetry. Systematic absences for reflexions  $h0l$  with  $h \neq 2n$  and  $0k0$  with  $k \neq 2n$  specify space group  $P2_1/a$ . Accurate cell parameters were obtained by a least-squares procedure applied to the setting angles of 36 reflexions