

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

Table 1. *Crystal data*

Molecular formula $C_6H_{14}N_2O_2S$	
Molecular weight 178.134	
Space group $P2_1/a$	
Monoclinic	$V = 896.8 (2) \text{ \AA}^3$
$a = 15.405 (2) \text{ \AA}$	$F(000) = 384$
$b = 8.488 (2)$	Radiation: $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$
$c = 6.940 (1)$	$D_c = 1.27 \text{ g cm}^{-3}$
$\beta = 98.75 (1)^\circ$	$\mu = 3.136 \text{ cm}^{-1}$

measured on a Philips four-circle diffractometer and are given in Table 1 with other crystal data. 2580 reflexions were collected on a Philips PW 1100 diffractometer operating in the  $\omega/2\theta$  scan mode with graphite-monochromated Mo  $K\alpha$  radiation. 1784 reflexions were taken as significantly above background as they were greater than  $2\sigma(I)$ . Corrections were made for Lorentz and polarization factors but not for absorption. From a Wilson plot an overall temperature factor and scale factor were calculated, and these were used to normalize the structure factors (Karle & Hauptman, 1956). The values for the statistical averages for the normalized structure factors correspond to a centrosymmetric structure.

#### Determination and refinement of the structure

The position of the S atom was deduced from a sharpened three-dimensional Patterson function. A Fourier synthesis based on the signs determined by the S only gave maxima which could easily be interpreted as the eight non-hydrogen atoms of the sulfan molecule. The  $R$  value at this stage, computed over 1200 terms, was 0.25. The refinement was carried out by a full-matrix least-squares method. Only observed experimental data were used in the refinement. Four cycles of isotropic refinement followed by three cycles of anisotropic least-squares refinement reduced the  $R$  value to 0.10. At this stage a three-dimensional difference synthesis was computed and peaks at or near the expected H positions were chosen. The H atoms were included in the refinement with isotropic thermal parameters. The weighting scheme was:  $w = Kw_1w_2$  with  $w_1 = 1/\sigma_f^2$  and  $w_2 = 1/\sigma_s^2$ , and  $\sigma_f$  and  $\sigma_s$  as follows:

$$\begin{aligned} \sigma_f &= (0.7589 + 0.0644|F_0|) & \text{if } 0 < |F_0| < 2.44, \\ \sigma_f &= (1.1948 - 0.1216|F_0|) & \text{if } 2.44 < |F_0| < 6.30, \\ \sigma_f &= (0.3982 + 0.0158|F_0|) & \text{if } 6.30 < |F_0| < 15.83, \\ \sigma_f &= (-0.2735 + 0.0480|F_0|) & \text{if } 15.83 < |F_0| < 125.86, \end{aligned}$$

$$\begin{aligned} \sqrt{\sigma_s} &= (2.3125 - 4.0609 s) & \text{if } 0 < |F_0| < 0.390, \\ \sqrt{\sigma_s} &= (-0.3723 + 2.8931 s) & \text{if } 0.390 < |F_0| < 0.4550, \\ \sqrt{\sigma_s} &= (1.8483 - 1.9380 s) & \text{if } 0.4550 < |F_0| < 0.5500, \\ \sqrt{\sigma_s} &= (-1.1953 + 3.5980 s) & \text{if } 0.5500 < |F_0| < 0.6600, \\ \sqrt{\sigma_s} &= (5.0468 - 5.7543 s) & \text{if } 0.6600 < |F_0| < 0.7000, \end{aligned}$$

where  $s$  is  $\sin \theta/\lambda$  and  $K = 1.0017$ .

Table 2. *Positional parameters ( $\times 10^4$ ) for non-hydrogen atoms*

	x	y	z
S	2268 (0)	3109 (1)	6684 (1)
O(1)	3056 (1)	3080 (4)	5838 (4)
O(2)	2161 (2)	1977 (3)	8158 (3)
N(1)	1452 (1)	2851 (3)	4917 (3)
N(2)	-78 (2)	2952 (3)	2060 (3)
C(1)	577 (2)	2602 (4)	5474 (4)
C(2)	-16 (2)	1904 (4)	3740 (5)
C(3)	794 (2)	3185 (4)	1525 (4)
C(4)	1414 (2)	3896 (4)	3198 (4)
C(5)	2144 (2)	5009 (4)	7632 (5)
C(6)	-670 (3)	2295 (5)	413 (6)

Table 3. *Hydrogen fractional coordinates ( $\times 10^3$ ), thermal parameters ( $\times 10^2$ ) and C-H bonds ( $\text{\AA}$ )*

	x	y	z	U	C-H
H(1)	33 (3)	362 (5)	579 (6)	3.4 (1.1)	0.98 (4)
H(2)	69 (2)	187 (4)	659 (6)	4.5 (1.0)	0.99 (4)
H(3)	-58 (2)	169 (4)	411 (5)	4.0 (1.0)	0.97 (4)
H(4)	21 (2)	86 (4)	334 (5)	4.4 (0.9)	1.00 (4)
H(5)	75 (2)	395 (4)	39 (4)	2.7 (0.7)	1.02 (3)
H(6)	105 (2)	223 (4)	113 (5)	3.7 (0.8)	0.96 (3)
H(7)	198 (2)	404 (4)	291 (5)	4.7 (0.9)	0.94 (4)
H(8)	122 (2)	497 (4)	357 (5)	2.6 (0.8)	1.01 (3)
H(9)	222 (2)	579 (4)	671 (4)	4.2 (0.7)	0.94 (3)
H(10)	254 (2)	509 (4)	865 (4)	3.5 (0.7)	0.86 (3)
H(11)	151 (2)	511 (4)	790 (5)	5.1 (0.8)	1.02 (4)
H(12)	-51 (4)	125 (8)	0 (9)	3.5 (2.0)	0.97 (7)
H(13)	-67 (5)	311 (9)	-71 (10)	6.1 (2.4)	1.04 (7)
H(14)	-123 (5)	218 (8)	90 (9)	5.8 (2.1)	0.98 (7)

Further cycles of anisotropic refinement of the heavy atoms with the H atoms treated isotropically gave final weighted and unweighted  $R$  values of 0.060 and 0.064 respectively [ $R_w = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$ ] with  $\langle w\Delta^2 \rangle$  showing no trends.

The atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974).

The final atomic parameters for non-hydrogen atoms are given in Table 2, and those of the H atoms together with C-H distances in Table 3.

All the calculations were performed with the XRAY 70 system of crystallographic programs and carried out on a Univac 1108 computer.\*

#### Results and discussion

The sulfan molecule, with the labelling of atoms, is shown in Fig. 1. The bond lengths and angles are

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32652 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

collected in Table 4. The piperazine ring has a chair conformation and a non-crystallographic plane of symmetry through the N(1)–N(2) atoms which is normal to the C(1)–C(2)–C(3)–C(4) chair plane. All

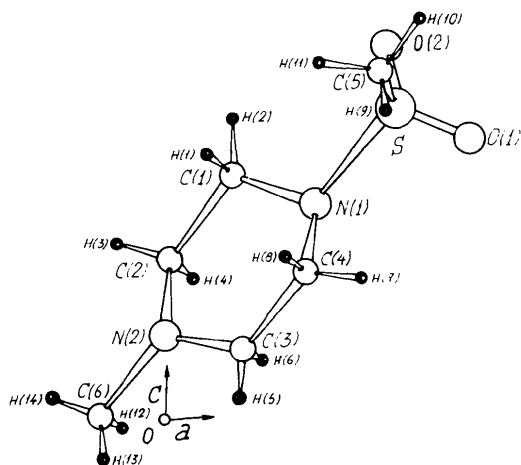


Fig. 1. A view of the sulfan molecule showing the atomic numbering.

Table 4. *Interatomic distances and angles*

S–O(1)	1.426 (2) Å	O(1)–S–O(2)	118.7 (2)°
S–O(2)	1.431 (3)	O(2)–S–N(1)	107.1 (1)
S–N(1)	1.633 (2)	O(1)–S–C(5)	108.5 (2)
S–C(5)	1.764 (3)	O(2)–S–N(1)	106.7 (1)
N(1)–C(1)	1.472 (4)	O(2)–S–C(5)	108.5 (2)
N(1)–C(4)	1.481 (4)	N(1)–S–C(5)	106.7 (1)
N(2)–C(2)	1.458 (4)	S–N(1)–C(1)	116.9 (2)
N(2)–C(3)	1.459 (4)	S–N(1)–C(4)	117.1 (2)
N(2)–C(6)	1.462 (4)	C(1)–N(1)–C(4)	111.9 (2)
C(1)–C(2)	1.517 (4)	C(2)–N(2)–C(3)	109.7 (2)
C(3)–C(4)	1.513 (4)	C(2)–N(2)–C(6)	110.5 (3)
		C(3)–N(2)–C(6)	110.0 (3)
		N(1)–C(1)–C(2)	108.3 (3)
		C(1)–C(2)–N(2)	110.7 (3)
		N(2)–C(3)–C(4)	110.9 (2)
		C(3)–C(4)–N(1)	108.8 (3)

the bond angles in this piperazine ring, except that at N(1), are close to 110° including the angle at the N(2) atom; the other outer angles at N(2) are also near this value. The average N–C distance for N(1)–C is 1.484 Å. This distance is approximately equal to that found in the dihydrochloride of piperazine (1.49 Å) where Rérat (1960) observed *I* symmetry for the piperazinium ion. The average N(2)–C distance is on the other hand 1.466 Å. This value is close to the N–C bond length 1.458 Å found in the hexahydrate of piperazine where Schwarzenbach (1968) found *2/m* symmetry for the piperazine ring. In these compounds all the bond angles in the hetero ring are near 110°. In the present work the ring has a non-crystallographic centre of symmetry. The obvious lack of a centre of symmetry could tentatively be explained as due to the difference between the two N atoms; N(2) is tetrahedral, whereas N(1) is close to trigonal. Thus, the sums of the three angles around these atoms are 346° for N(1) and 330° for N(2). The displacements of the N atoms from the plane defined by the three surrounding atoms are N(1) = –0.33 Å and N(2) = 0.47 Å (Table 5).

These results suggest that N(1) has a larger contribution from an *sp*<sup>3</sup>-hybridized configuration than from an *sp*<sup>2</sup>. This is indicated by the above mentioned displacement of the plane. Furthermore, the S–N length decreases (1.63 Å) from the observed single-bond (1.76 Å) value because of the contribution from the nitrogen lone pair, which is consistent with the opening of the S–N–C angles (117°). In a previous work (Perales & García-Blanco, 1977) the MSM molecule was found to present an identical situation. Both compounds appear to be unaffected by the eventual  $\pi$ -electron delocalization from S through N to the ring system. However, the hybridization of the N(1) atom is responsible for the relative orientation of the C–N–S and O–S–O planes. In both compounds the mean value for the angle between these two planes is 56° which is similar to 58° for the *sp*<sup>3</sup> N atoms and

Table 5. *Least-squares planes*

Plane I		Plane II		Plane III		Plane IV	
$\Delta$		$\Delta$		$\Delta$		$\Delta$	
C(1)	–0.005 Å	N(1)	0.000 Å	S	0.000 Å	C(2)	0.000 Å
C(2)	0.005	C(1)	0.000	C(1)	0.000	C(3)	0.000
C(3)	–0.005	C(4)	0.000	C(4)	0.000	C(6)	0.000
C(4)	0.005	S*	0.953	N(1)*	–0.335	N(2)*	0.472
N(1)*	0.663	C(2)*	–1.222				
N(2)*	–0.679	C(3)*	–1.207				
S*	1.157						

Dihedral angles between the planes (°)

Plane	II	III	IV
I	53.34	29.44	19.72

\* Atom not included in definition of the plane.

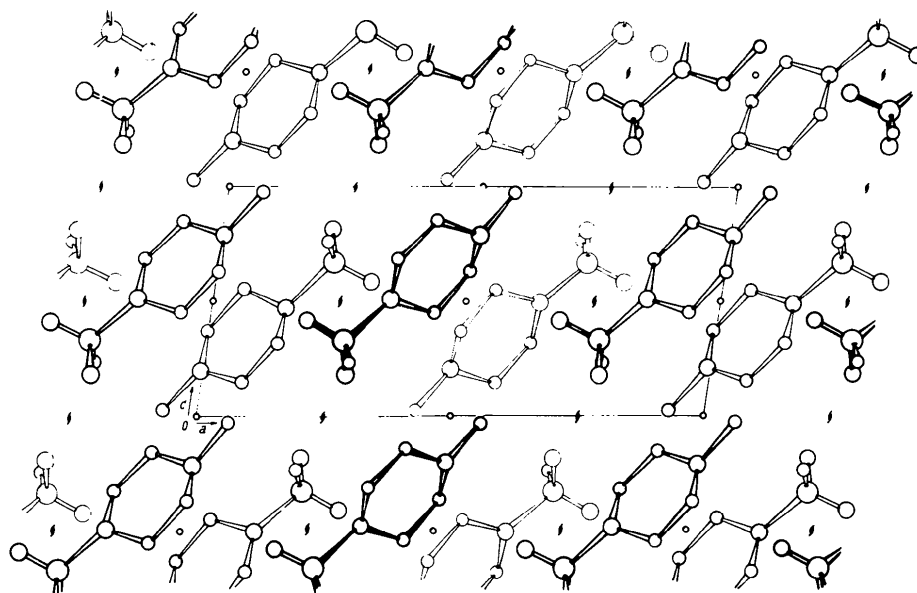


Fig. 2. The molecular packing viewed down *b*.

contrasts with the  $87^\circ$  value for the  $sp^2$  (Cameron, Prout, Denton, Spagna & White, 1975).

The conformation of the  $SO_2-CH_3$  moiety with respect to the N(1) ring is equatorial. The deviations of the N(1) and S atoms from the chair plane C(1)–C(2)–C(3)–C(4) are 0.66 and 1.16 Å respectively. This deviation is 0.5 Å larger for the S atom than for N(1) and corresponds to an angle of  $18^\circ$  with respect to the chair plane. An identical situation is found in the MSM molecule where the deviation is 0.38 Å corresponding to an angle of  $13^\circ$ .

The packing of the molecules is shown in Fig. 2. Intermolecular distances shorter than the van der Waals radii are not observed.

We wish to thank Dr Moreno-Mañas for providing the sulfan crystals. We also thank the Centro de

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