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## Crystal Structures of Acid Hydrates and Oxonium Salts. VII. Bis(methanesulphonyl)imide Monohydrate\*

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**Abstract.**  $(\text{CH}_3\text{SO}_2)_2\text{NH}\cdot\text{H}_2\text{O}$ , monoclinic,  $C2/c$ ,  $a=12.705$  (3),  $b=7.511$  (2),  $c=8.066$  (1) Å,  $\beta=97.22$  (2)°,  $Z=4$ ,  $D_m=1.657$ ,  $D_x=1.663$  g cm<sup>-3</sup>. A short  $\text{NH}\cdots\text{O}$  hydrogen bond [ $\text{N}\cdots\text{O}$  2.737 (2) Å] along a twofold crystallographic axis connects the imide with the water molecule. Both are further linked into an endless double chain by two weak, equivalent,  $\text{OH}\cdots\text{O}$  hydrogen bonds from the water molecule to two imide molecules. The atomic arrangement is similar to that of several  $\text{XY}_2$  compounds with tetrahedral Y groups.

**Introduction.** The systematic absences  $hkl$  for  $h+k$  odd and  $h0l$  for  $l$  odd led to  $C2/c$  or  $Cc$ . Cell constants were determined from diffractometric measurements. The intensities of 1683 independent reflexions with  $3.7^\circ < \theta < 35^\circ$  were measured with Zr-filtered Mo  $K\alpha$  radiation on a Siemens automatic diffractometer with a  $\theta/2\theta$  scan, 1332 reflexions having significant intensities. The data crystal had been ground to nearly spherical shape with 0.4 mm diameter. With  $\mu=6.5$  cm<sup>-1</sup> no corrections for absorption were made.

The Patterson function led to the interpretation of one S atom in  $C2/c$ . All heavy atoms were found in the following Fourier synthesis. After anisotropic refinement of these atoms ( $R=0.054$ ) a difference map showed the positions of all five H atoms as highest peaks. Nine strong reflexions of low order were omitted to decrease extinction effects. H atoms were refined anisotropically despite the known uncertainty of their

location by X-ray diffraction. The resulting thermal values seem to be acceptable, especially for the methyl H atoms.

The final  $R$  was 0.051 for all reflexions and 0.030 for the significant ones only. Atomic parameters are listed in Table 1. Atomic form factors were those of Hanson, Herman, Lea & Skillman (1964) for S, O, N, C and those of Stewart, Davidson & Simpson (1965) for H.†

An analysis of the thermal parameters of the heavy atoms was carried out assuming rigid-body motion of the imide molecule (Schomaker & Trueblood, 1968).

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30841 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters and their standard deviations

The  $B_{ij}$  in Å<sup>2</sup> are listed using the expression  $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + 2B_{23}kb^*c^* + \dots)]$ . Hydrogen atoms were refined anisotropically because a mixed-mode program was not available.

	$x$	$y$	$z$
S	0.39521 (2)	0.28642 (3)	0.15234 (3)
O(1)	0.34018 (8)	0.42088 (12)	0.05080 (12)
O(2)	0.43086 (7)	0.13080 (11)	0.07442 (11)
O(W)	0.5	0.75195 (22)	0.25
N	0.5	0.38756 (15)	0.25
C	0.31887 (10)	0.22166 (17)	0.30749 (16)
H(1)	0.5	0.5067 (58)	0.25
H(2)	0.4879 (24)	0.8206 (27)	0.3308 (29)
H(3)	0.3010 (19)	0.3316 (29)	0.3725 (26)
H(4)	0.3597 (18)	0.1221 (29)	0.3785 (31)
H(5)	0.2523 (16)	0.1818 (26)	0.2501 (32)

\* Short version of part of the dissertation of R. Attig, Technische Universität Braunschweig, Germany (BRD), 1973. For part VI of this series see Mootz & Altenburg (1971).

Table 1 (cont.)

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
S	2.29 (1)	1.91 (1)	2.21 (1)	0.17 (1)	0.34 (1)	-0.05 (1)
O(1)	3.55 (4)	3.48 (5)	3.80 (4)	0.65 (3)	-0.21 (3)	0.96 (3)
O(2)	3.77 (3)	2.86 (3)	3.50 (3)	0.32 (2)	0.53 (3)	-1.18 (2)
O(W)	13.74 (20)	2.15 (4)	3.93 (7)	0.0	3.39 (10)	0.0
N	2.43 (4)	1.55 (3)	3.74 (5)	0.0	0.30 (4)	0.0
C	3.08 (4)	3.34 (5)	3.26 (4)	-0.77 (3)	0.96 (3)	-0.08 (3)
H(1)	0.6 (8)	12.1 (23)	5.8 (15)	0.0	-0.4 (9)	0.0
H(2)	12.1 (20)	4.2 (9)	4.3 (11)	-0.9 (12)	6.1 (13)	0.5 (9)
H(3)	9.5 (16)	5.2 (10)	4.0 (10)	-4.2 (12)	3.1 (11)	-2.8 (9)
H(4)	3.9 (10)	4.7 (10)	8.1 (14)	1.0 (8)	0.1 (9)	1.4 (10)
H(5)	3.0 (9)	5.2 (11)	7.3 (13)	-2.5 (8)	-0.4 (9)	-1.0 (10)

With unit weights, the generalized index  $R_G = [\sum(U_c - U_o)^2 / \sum U_o^2]^{1/2}$  was 0.103 with a root-mean-square discrepancy of 0.0034. The results are displayed in Table 2; they have been used to apply the libration corrections to the bond lengths given in Fig. 1. These results are similar to those of the molecules  $\text{CH}_2(\text{SO}_3^-)_2$  (Truter, 1962),  $\text{NH}(\text{SO}_3^-)_2$  (Cruickshank & Jones, 1963) and  $\text{CH}_2(\text{POCl}_2)_2$  (Sheldrick, 1975).

**Discussion.** The bis(methanesulphonyl)imide molecule possesses a remarkably acid proton. The  $pK_a$  value of 2.8 (Blaschette, 1969) resembles that of monochloro-

Table 2. Rigid-body librational analysis

Centre of mass (orthogonal coordinates\*): 0.5, 0.2815, 0.1510  
(crystal coordinates): 0.5, 0.2815, 0.25

Tensors with respect to orthogonal axes and origin at the centre of mass with estimated standard deviations in parentheses

T ( $\text{\AA} \times 10^{-4}$ )	348 (12)	0	-24 (12)
		-158 (19)	0
			275 (18)
L ( $\text{rad} \times 10^{-4}$ )	124 (11)	0	-13 (4)
		-22 (5)	0
			32 (5)
S ( $\text{\AA} \cdot \text{rad} \times 10^{-4}$ )	-9 (6)	0	-13 (6)
	0	20 (5)	0
	9 (6)	0	-11 (5)

Origin (orthogonal coordinates) which gives symmetric S:  
0.5, 0.28466, 0.1510

Principal root-mean-square amplitudes and direction cosines

T ( $\text{\AA}$ )†	0.187	0.9941	0	0.1084
	0.164	0	1.0	0
	0.126	-0.1084	0	0.9941
L (rad)	0.112	0.9900	0	0.1414
	0.055	0	1.0	0
	0.047	-0.1414	0	0.9900

\* Referred to  $a \sin \beta$ ,  $b$ ,  $c$ .

† Reduced to keep  $U$  invariant.

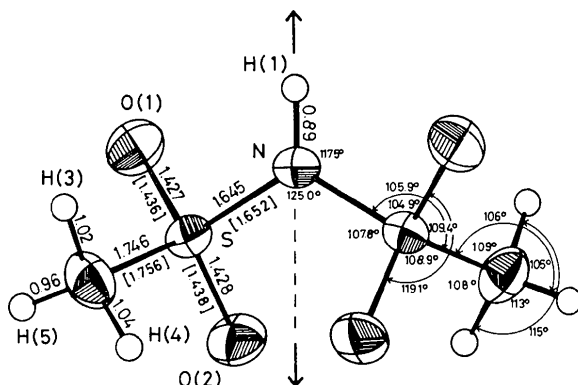


Fig. 1. The imide molecule with bond lengths and bond angles. Standard deviations: bond lengths from S 0.001 Å, to H 0.02 Å, bond angles around S and N 0.05° and around C 2°. Bond lengths in parentheses are corrected for thermal motion.

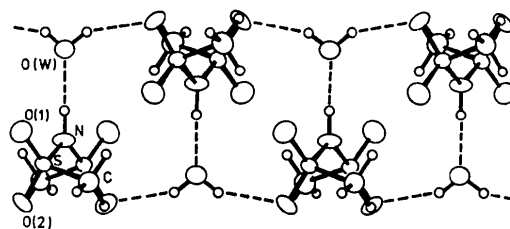


Fig. 2. Hydrogen-bonded double chain of imide and water molecules along the  $c$ -axis direction.

acetic acid and also the  $pK_a$  value of the second step of dissociation of hypodiphosphoric acid,  $\text{H}_4\text{P}_2\text{O}_6$ , which forms a dioxonium salt when crystallized with two molecules of water (Mootz & Altenburg, 1971). Despite the possible formation of an oxonium salt – not yet described for an N–H acidic compound – the title compound turned out to be a true acid hydrate with the proton at the N atom and not transferred to the water molecule. Fig. 1 shows the imide molecule with bond lengths and angles. The N–H bond lies on a crystallographic twofold axis with no evidence of statistical superposition of actual atomic displacements from this symmetry element. Therefore the configuration of the N atom is planar with  $sp^2$  hybridization. The lone pair of electrons in the remaining  $p$  orbital perpendicular to the SNS plane gives rise to  $\pi$  bonding with  $d$  orbitals of the S atoms and shortens the bond distance to 1.645 (1) Å compared to the pure single bond distance of 1.76 (2) Å in  $\text{SO}_3\text{NH}_3$  (Sass, 1960). The SN length of 1.645 (1) Å and SNS angle of 125.0 (1)° are similar to those of the salt  $\text{K}_2(\text{SO}_3)_2\text{NH}$  [1.662 (5) Å and 125.5 (5)°; Cruickshank & Jones (1963)]. The S–O mean length of 1.427 (1) Å and S–C length of 1.746 (1) Å compare well with those of other  $\text{SO}_2\text{CH}_3$  groups, e.g. in  $\text{C}_6\text{H}_5\text{NHSO}_2\text{CH}_3$  with 1.434 (3) and 1.746 (3) Å (Klug, 1968); in  $\text{C}_6\text{H}_4(\text{OH})\text{NHSO}_2\text{CH}_3$  with 1.441 (6) and 1.736 (6) Å (Klug, 1970); and in  $(\text{CH}_3)_2\text{SNSO}_2\text{CH}_3$  with 1.447 (12) and 1.749 (12) Å (Kálmán, 1967).

The water O atom is also located on the twofold axis, along which it is connected with the imide molecule through an  $\text{NH}\cdots\text{O}$  hydrogen bond. The two equivalent water H atoms are engaged in a weak hydrogen bond each to O atoms of two further imide molecules. The distance  $\text{O}(W)\text{--O}(2)$  is 2.995 (1) Å, that from H(2) to these O atoms 0.86 (2) and 2.21 (3) Å, with an angle of 152 (2)° at H(2). The resulting infinite double chains of alternating hydrogen-bonded imide and water molecules are shown in Fig. 2. The planar arrangement of hydrogen bonds around the water molecule together with its relatively free surrounding vertical to this plane causes an unusual large  $B_{11}$  value for the O atom [and even for the poorly determined H(2) atom]. No attempt was made to refine two split positions of water molecules on two sides of the twofold axis.

The arrangement of the imide molecules of this compound in the space group  $C2/c$  resembles that of sev-

Table 3. Examples of compounds with species  $XYX$  in the space group  $C2/c$  with unit-cell dimensions and geometry of the bridging groups, when known

	Ref.	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	X–Y–X	X–Y
$CH_2(SO_3K)_2$	<i>a</i>	12.55	7.75	7.30	90.5	119.7 (7)°	1.770 (7) Å
$CH_2(SO_3NH_4)_2$	<i>b</i>	12.70	7.85	7.65	92.6		
$NH(SO_3K)_2$	<i>c</i>	12.43	7.46	7.18	91.2	124.5 (5)	1.662 (5)
$NH(SO_3NH_4)_2$	<i>b</i>	12.72	7.74	7.49	92.8		
$NH(SO_3Rb)_2$	<i>b</i>	12.80	7.68	7.45	91.9		
$NH(SO_2CH_3)_2 \cdot H_2O$	<i>d</i>	12.71	7.51	8.07	97.2	125.0 (1)	1.645 (1)
$O(SO_3K)_2$	<i>e</i>	12.35	7.31	7.27	93.1	124.2 (3)	1.645 (5)
$O(CrO_3NH_4)_2$	<i>f</i>	13.26	7.54	7.74	93.2	115	1.91 (5)
$S(SO_3TI)_2$	<i>g</i>	13.20	7.45	7.58	91.0		
$CH_2(POCl_2)_2$	<i>h</i>	15.87	5.85	9.16	106.6	116.4 (4)	1.795 (4)

References: (a) Truter (1962). (b) Jones (1955). (c) Cruickshank & Jones (1963). (d) This work. (e) Lynton & Truter (1960). (f) Byström & Wilhelmi (1951). (g) Ketelaar & Sanders (1936). (h) Sheldrick (1975).

eral neutral or anionic species X–Y–X with bridging Y, such as  $CH_2$ , NH, O, S and tetrahedral groups X, with central S, P or Cr (Table 3).

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## Octamethylbicyclopentasiloxane

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**Abstract.**  $Si_5O_6C_8H_{24}$ , M.W. 365.5, m.p. 115°C, space group  $P2_1/m$ , monoclinic (from systematic absences and *E* statistics),  $a = 8.595$  (5),  $b = 14.321$  (5),  $c = 8.116$  (4) Å,  $\beta = 90.7^\circ$  (from oscillation and Weissenberg photographs),  $Z = 2$ ,  $D_x = 1.184$ ,  $D_m = 1.163$  (6) g cm<sup>-3</sup> (by flotation). The symmetry of the molecule is near to  $\bar{6}2m$ , the direction connecting Si(1) and Si(3) being the pseudotrigonal axis.

**Introduction.** Garzó, Székely, Tamás & Ujszászi (1971) isolated and identified several new polycyclic methylpolysiloxane oligomers produced by thermal decompo-

sition of branched-chain polymers. The title compound was chosen first in order to determine its structure by X-ray methods. It will be denoted as  $T_2D_3$  where T stands for the unit  $CH_3SiO_{3/2}$  and D for  $(CH_3)_2SiO_{2/2}$ . Like several cyclic methylpolysiloxanes,  $T_2D_3$  is characterized by high volatility. A crystal of the appropriate size for X-ray investigation volatilized after about 20 min at ambient pressure and temperature. The sample was sealed in a thin-walled glass capillary tube (0.3 mm in diameter). Weissenberg photographs were taken at 20–22°C with unfiltered Cu radiation around [001] (0–5 layers) and  $[\bar{1}10]$  (0–9 layers), all with the same