

and C(2)N(3)C(4)N(5) and C(4)N(5)C(11)C(10). There appears, however, to be little distortion of interbond angles within this ring, the endocyclic angles at all atoms except C(4) [$126.1(2)^\circ$] differing little from those values to be expected on the basis of the bonding pattern shown in (VII).

The lengths within the oxadiazepine ring indicate that the three π -bonded systems, C(2)=N(3) [$1.268(5) \text{ \AA}$], C(4)=N(5) [$1.289(5) \text{ \AA}$] and the aromatic ring C(6)–C(11), are largely non-interacting, being separated by the C(4)–N(3) [$1.412(4) \text{ \AA}$] and C(11)–N(5) [$1.401(5) \text{ \AA}$] bonds respectively. The non-zero values of the torsion angles C(2)N(3)C(4)N(5) and C(4)N(5)C(11)C(10) support this conclusion. The difference in the lengths of C(2)=N(3) and C(4)=N(5) may possibly be considered significant, and in this respect we note two features: firstly the substituent patterns of the two bonds are

different, and secondly the values of the relevant torsion angles indicate that the first bond is relatively less distorted from planarity than the second. Other dimensions within the molecule conform to accepted values for similar bond types, and there are no abnormally short intermolecular contacts.

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Refinement of Sulphamic Acid

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Abstract. NH_3SO_3 , $M=97.1$. Orthorhombic, $a=8.115(2)$, $b=8.066(2)$, $c=9.248(2) \text{ \AA}$, $D_m=2.14$, $Z=8$, $D_c=2.13 \text{ g cm}^{-3}$, $F(000)=400$. Space group *Pbca*. Mo $K\alpha$ radiation, $\lambda=0.7107 \text{ \AA}$, $\mu(\text{Mo } K)=8.40 \text{ cm}^{-1}$. The structure has been refined by least squares to a final R of 0.027 with 793 independent diffractometer data. The length of the S–N bond is $1.772(1) \text{ \AA}$.

Introduction. Exposure of a small crystal to Zr-filtered Mo radiation on a Hilger & Watts Y290 diffractometer yielded 793 independent reflexions [$I \geq 2\sigma_I$, $\sigma_I = \sqrt{(I + B_1 + B_2)}$], measured at room temperature by the θ, ω -scan technique in the range $2\theta=0-60^\circ$. From the atomic parameters derived in an earlier neutron diffraction analysis (Sass, 1960), the structure was refined by full-matrix least squares with programs incorporated in the X-RAY 72 suite of programs. Contributions from the H atoms were included in these calculations, but their positional parameters were held constant at the values (with the estimated standard deviations) determined by Sass. Isotropic thermal parameters for the H atoms were refined in later cycles. The isotropic secondary extinction coefficient (Zachariasen, 1963; Larson, 1967) was also refined in the later cycles to $g=0.0103$. Inclusion of this parameter was observed to have a marked effect on the thermal, but not the

positional parameters. At the conclusion of the refinement, the values of R and $R' (= \sum w\Delta^2 / \sum w|F_o|^2)$ were 0.027 and 0.0016 respectively, the data having been weighted according to $w=(A+B|F_o|+C|F_o|^2)^{-1}$. The final values of A , B and C were 0.3117, -0.0220 and 0.0011 respectively. The data were not corrected for absorption, and the molecular dimensions have not been corrected for the effects of thermal motion.*

Discussion. In studies of sulphonyl-stabilized imines and of sulphonium-imines, estimations of the double-bond character of the S–N bonds are frequently made by comparison of the observed lengths with that predicted from Pauling's covalent radii, 1.74 \AA , or with the bond length in sulphamic acid. In the solid state the latter has the zwitterionic structure $\text{NH}_3^+\text{SO}_3^-$, with, on account of the quaternary N atom, a formal S–N single bond.

Previous studies of the structure of sulphamic acid have included a two-dimensional (Kanda & King, 1951) and a three-dimensional analysis (Osaki, Tado-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31595 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates and thermal parameters*

(a) Fractional coordinates and (for hydrogen) isotropic thermal parameters (\AA^2). Positional parameters and e.s.d.'s for the hydrogen atoms are those values reported by Sass (1960).

	x	y	z	U_{iso}
S	0.16665 (5)	0.09389 (5)	0.17077 (4)	—
N	0.04096 (17)	0.24085 (17)	0.08066 (15)	—
O(1)	0.05922 (18)	-0.04773 (17)	0.17735 (15)	—
O(2)	0.30448 (17)	0.07669 (17)	0.07448 (15)	—
O(3)	0.20034 (18)	0.17420 (18)	0.30607 (14)	—
H(1)	0.0947 (29)	0.3556 (35)	0.0651 (32)	0.057 (9)
H(2)	-0.0725 (19)	0.2443 (25)	0.1303 (27)	0.088 (12)
H(3)	0.0126 (27)	0.1978 (28)	-0.0202 (24)	0.060 (9)

(b) Anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	175 (2)	145 (2)	144 (2)	9 (1)	5 (1)	5 (1)
N	198 (6)	175 (6)	173 (6)	25 (5)	-16 (5)	16 (5)
O(1)	315 (7)	174 (6)	278 (7)	-66 (5)	-8 (5)	36 (5)
O(2)	229 (6)	272 (6)	272 (6)	70 (5)	75 (5)	20 (5)
O(3)	281 (7)	290 (7)	155 (6)	19 (5)	-43 (5)	38 (5)

Table 2. *Interatomic distances and angles*

(a) Bonded distances (\AA)

S-N	1.772 (1)	N-H(1)	1.033 (28)
S-O(1)	1.438 (1)	N-H(2)	1.029 (18)
S-O(2)	1.436 (1)	N-H(3)	1.022 (22)
S-O(3)	1.435 (1)		

(b) Interbond angles ($^\circ$)

N-S-O(1)	101.67 (7)	O(1)-S-O(2)	114.93 (8)
N-S-O(2)	102.78 (7)	O(1)-S-O(3)	115.91 (8)
N-S-O(3)	102.57 (6)	O(2)-S-O(3)	115.83 (8)
S-N-H(1)	115 (1)	H(1)-N-H(2)	115 (2)
S-N-H(2)	109 (1)	H(1)-N-H(3)	106 (2)
S-N-H(3)	109 (1)	H(2)-N-H(3)	102 (2)

(c) Intramolecular non-bonded distances (\AA)

O(1)···H(2)	2.62	O(2)···H(3)	2.71
O(1)···H(3)	2.72	O(3)···H(1)	2.80
O(2)···H(1)	2.82	O(3)···H(2)	2.80

koro & Nitta, 1955), both using X-ray diffraction data and refining the parameters by Fourier techniques. A neutron diffraction analysis (Sass, 1960) used least squares to refine the atomic parameters from three zonal sets of data. It is the S-N length from the latter analysis which is most often quoted [1.76 (2) \AA] in comparisons, and since the accuracy is much less than that achieved by modern X-ray analyses, it seemed desirable to carry out a refinement with data produced by current techniques.

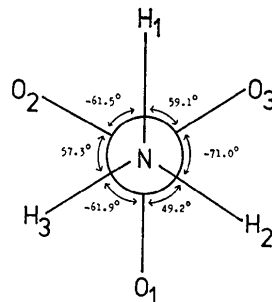


Fig. 1. The Newman projection along the N-S bond, showing torsion angles, and defining the atomic numbering.

Since undertaking the study reported here, we note that a recent investigation of sulphamic acid (Bats, Coppens & Koetzle, 1975) employed a combination of neutron diffraction and low-temperature X-ray diffraction techniques in order to investigate the electron density distribution in the molecule. Since the data-collecting conditions of this study are substantially different from our own, we present our results to permit an eventual comparison of the dimensions resulting from refinements of low-temperature and room-temperature data collected from different crystals in two laboratories.

The present refinement of the structure reveals that the S-N length is 1.772 (1) \AA , while the three S-O bonds have lengths of 1.438 (1), 1.436 (1) and 1.435 (1) \AA . The differences in the latter dimensions are probably not significant. The other feature of interest in the structure of sulphamic acid is the complex system of hydrogen bonds by which the molecules associate. This has been extensively discussed (Sass, 1960) and, since the present study utilized the H parameters derived by Sass, with no attempted modification during the refinement, we do not pursue this aspect.

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