Structure of Sulphamic Acid Molecule from a Three-dimensional Fourier Analysis

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Introduction

Physical and chemical properties of sulphamic acid, or aminosulphonic acid HSO_3NH_2, stand in highly interesting contrast with those of sulphuric and other sulphonic acids. A crystal structure investigation of sulphamic acid has recently been undertaken by Brown, Cox and Llewellyn[1] who determined the dimensions of the unit cell as well as the space group but did not give any further detailed account of the structure. As it is of significance to know the molecular structure and arrangement in crystals of this substance, we have carried out the determination of atomic parameters by means of the three-dimensional Fourier syntheses. The present paper, of which an abstract was sent to the Stockholm Congress of the International Union of Crystallography in 1951, deals with some account of this investigation. After having sent our abstract we were informed of the paper by Kanda and King[2] of the determination of sulphamic acid and on later study of their paper we found that our results were in general agreement with theirs. However, as to the detailed structure of the molecule, there are some points of difference, which seem to be worth discussing here.

Determination of the Structure

Crystal Data.—Sulphamic acid, HSO_3NH_2; molecular weight, 97.09; the dimensions of the unit cell, from a series of symmetrical back-reflexion photographs, $a=8.066\pm0.001$ Å, $b=8.115\pm0.001$ Å, $c=9.255\pm0.003$ Å (Cu $K\alpha_1$, $\lambda=1.5405$ Å);* density, calculated 2.129, observed 2.126 gm/cm³ (in toluene at 25°C) 2.03 gm/cm³ (in ether at 12°C) (Cupery)[3]; eight molecules per unit cell, space group $D_{2h}^{15}-Pcab$.

In view of the conflicting circumstances in the Patterson projections of this space group, we computed the three-dimensional Patterson function $P(u\,v\,w)$ near the origin besides its sections at $w=0$, $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{3}{4}$. Comparison among these functions together with ordinary Patterson projections immediately led us to an unambiguous solution of the spatial arrangement of the molecules, of which the structure was preliminarily assumed to be a regular tetrahedron similar to the SO_4-ion. Parameters thus obtained were improved through the calculation of structure factors and Fourier projections on the principal planes. As the refinement seemed insufficient, we calculated electron densities about each

TABLE I

ATOMIC PARAMETERS

	x/a	y/b	z/c	x(in Å)	y(in Å)	z(in Å)
S	0.0940	0.1668	0.1719	0.758	1.354	1.591
				(−0.003)	(−0.004)	(0.007)
O_I	−0.0486	0.0601	0.1767	−0.392	0.488	1.635
				(0.001)	(0.011)	(0.002)
O_{II}	0.0750	0.3057	0.0757	0.605	2.481	0.701
				(−0.002)	(0.015)	(0.015)
O_{III}	0.1758	0.2025	0.3055	1.418	1.643	2.827
				(−0.001)	(0.021)	(0.011)
N	0.2377	0.0438	0.0790	1.917	0.355	0.731
				(−0.046)	(0.036)	(−0.024)

Atomic parameters listed here are already corrected for finite series summation by the values in brackets.

1) C.J. Brown, E.G. Cox and F.J. Llewellyn, *J. Chem. Soc.*, **1940**, 1.

2) F.A. Kanda and A.J. King, *J. Am. Chem. Soc.*, **73**, 2315 (1951).

* Tne data of Kanda and King, if multiplied by the factor 1.0020, become $a=8.116$Å, $b=8.065$Å, $c=9.246$Å, *Pbca*, in good agreement with our values.

3) M.E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

atomic centre using three-dimensional data. After two stages of refinement, F_c-corrections were introduced, the effect of which was considerable as given in brackets in Table I of the corrected parameters.

The nitrogen atom was first recognized in our case from the presence of single atom at a particularly larger distance~1.7 Å from the central sulphur atom, while the other three are at essentially same distance~1.4 Å. This choice was later verified by the electron density plot using the three-dimensional data; namely the peak corresponding to the nitrogen atom was found to be sensibly lower and broader than those for oxygen atoms (Fig. 1).

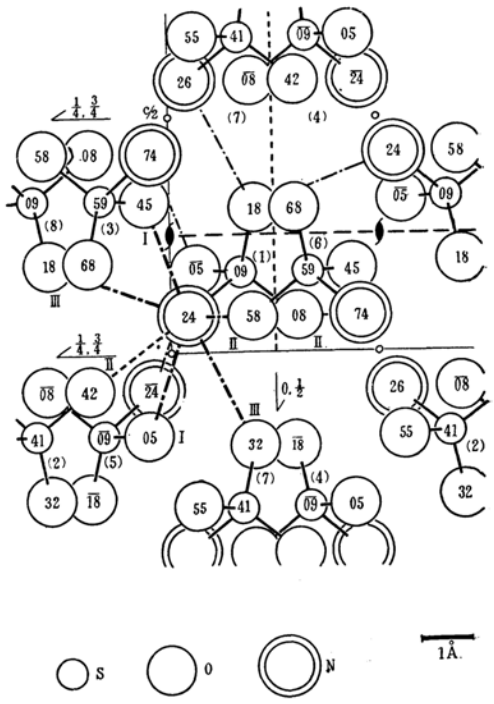

Fig. 2. Projection of part of unit cell upon (100). N-H·····O bonds only between molecule (1) and its neighbours are shown in chain lines, while dotted one show another close approach (2.84 Å) between O and N.

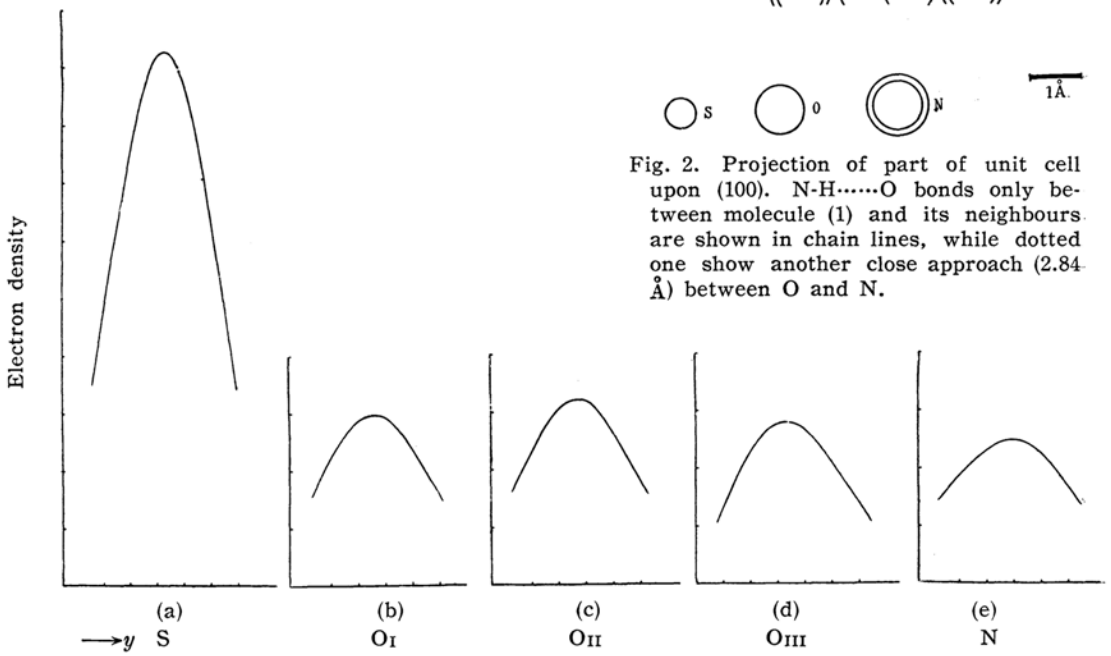

Fig. 1. Electron density plot along lines through atomic positions. Only curves along *b*-axis are shown.

Description of the Structure

The one nitrogen and the three oxygen atoms in the molecule of sulphamic acid constitute a nearly regular tetrahedron, and such tetrahedra are linked three-dimensionally to each other through hydrogen bonds of the type N-H·····O as shown partially in Fig. 2. The nitrogen atom of the molecule (1) (see Fig. 2) is surrounded, besides the three oxygen atoms of the same molecule, by six oxygen atoms, each from one of the neighbouring molecules, five being at distances ranging from 2.93 to 3.01 Å and the sixth at a distance of 2.84 Å. In spite of such a short distance, the sixth atom does not seem to be concerned with the hydrogen bond formation subst antially, because it lies rather in the extended direction of the sulphur-nitrogen axis of the molecule. The arrangement of the oxygen atoms around the nitrogen is illustrated by Fig. 3, in which the atoms are projected upon the plane of three oxygen atoms of the molecule (1). The five N-O directions except the sixth all make angles ranging from 100° to 114° with the N-S axis and this would

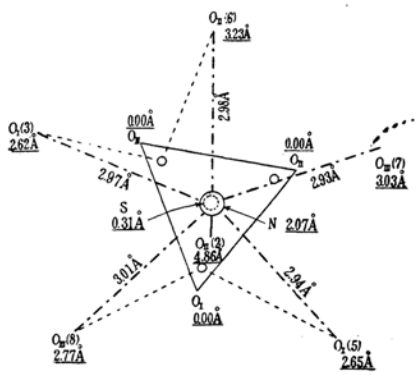

Fig. 3. Arrangement of the oxygen atoms surrounding a nitrogen atom of molecule (1), projected on the plane O_I O_{II} O_{III}. Underlined figures show the height of corresponding atoms measured from the plane of projection. Chain lines indicate the atom pairs linked by N-H·····O bonds.

suggest that all these N·····O pairs take part in the hydrogen bonding. A tentative location of three hydrogen atoms, which leads to one single and two bifurcated hydrogen bonds, are indicated in Fig. 3.* As for the non-hydrogen bonded nature of the sixth N·····O distance, it may be added that, in the case of potassium sulphamate crystal determined by Brown, Cox and Llewellyn[1] and by Jeffrey and Stadler[4] they have already found a short N·····O distance 3.04 Å, which they did not consider to be hydrogen bonded. Another instance is found in the case of orthorhombic hydrazonium sulphate[5], where a similarly disposed oxygen atom was not considered to be hydrogen bonded in spite of a shorter distance of 2.82 Å.

Discussion of the Molecular Structure

Though further refinements of atomic coordinates have not been carried out, the values of standard deviations σ listed in Table II seem to indicate already that we may discuss the molecular structure in some detail. The determined dimensions of the molecule are listed in Table III.

TABLE II
STANDARD DEVIATIONS

	S		O(average)	N
$\sigma(r)$	0.008Å		0.024Å	0.028Å
	S-O	S-N	O-O	O-N
σ(distance)	0.025Å	0.029Å	0.034Å	0.037Å

As to the shape of the NO_3 tetrahedron, the mutual deviations observed within the values of the three O-O's, or within those of the three O-N edges (see Table III) will be regarded as insignificant, whereas there is observed significant difference between the averaged values for the set of O-O and that for O-N. Thus we have in this crystal a somewhat elongated, but nearly regular tetrahedron.

The observed differences within three S-O distances are also insignificant and their mean value comes out 1.44 Å,* which deviates considerably from those given by Kanda and King[2], but agrees perfectly with the refined values obtained by Jeffrey and Stadler[4] in the case of potassium sulphamate.

TABLE III
BOND LENGTHS AND BOND ANGLES

Substances	S-N	S-O	O-O	N-O	∠NSO	∠OSO
Sulphamic acid						
present work	1.75_5	1.43	2.42	2.48	102°	114°
		1.44	2.42	2.50	102°	115°
		1.45	2.46	2.51	103°	118°
Kanda & King[2]	1.73	1.47	2.54	2.33	92°	114°
		1.48	2.57	2.49	100°	117°
		1.49	2.60	2.53	102°	119°
NH_4O_3S-NO·NO	1.791	1.464			102.2°	114.2°
Jeffrey & Stadley[4]		1.434			102.2°	114.2°
		1.434			105.7°	116.0°
KO_3S·NH_2	1.60	1.42	2.38	2.45	107°	111°
Jeffery & Stadler[4]		1.45	2.38	2.49	107°	112°
		1.45	2.38	2.49	108°	112°
β-isoprene sulphone Jeffery[6]		1.436	2.403			113.7°
SO_2 (microwave spectroscopy)[17]		1.433				

* This location turned out to be similar to that obtained by Kanda and King.

4) G.A. Jeffrey and H.P. Stadler, *J. Chem. Soc.*, 1951, 1467.

5) I. Nitta, K. Sakurai and Y. Tomiie, *Acta Cryst.*, 4, 289 (1951).

6) G.A. Jeffrey, *Acta Cryst.*, 4, 58 (1951).

The mean value of the three bond angles O-S-O is 116° which is considerably greater than the tetrahedral angle.

Our determined value of the S-N bond length is 1.75_5 Å in rather good agreement with that found by Kanda and King[2]. On the other hand Jeffrey and Stadler[4] have obtained a value 1.791 Å for the S-N distance in the dinitrososulphite ion and 1.60 Å for that in the sulphamate ion, of which the former was regarded by them to correspond very closely to the length of a pure single σ bond and the latter to that associated with a double bond. They discussed the accordance of their value 1.79 Å for N^+-S with that calculated from the well established values C-N=1.48 Å, C-S=1.81 Å and N-N=1.48 Å. A similar discussion to that of the case of dinitrososulphite ion will also be applied to the present case, although here the bond length is somewhat shorter and there are some differences in the distribution of valence forces around the nitrogen atom; for example, this is more or less tetrahedral and the configuration of three oxygen and three hydrogen atoms seems to be such as to form a trigonal prism, as shown in Fig. 3. As shown in Table III the observed N-S-O bond angles are nearly equal to each other and their mean value 102° is sensibly smaller than that 107° found by Jeffrey and Stadler[4] in the case of potassium sulphamate, of which the latter is more close to the tetrahedral angle 109.5°.

As to the bonding characteristics of the molecule as a whole, there are two extreme ideal structures conceivable; the one containing a hydroxyl and an amino group, $(H_2N)-SO_2-(OH)$, and the other of a zwitterion type, $(H_3N)^+-(SO_3)^-$. In the former case the lone pair of $2p$ electrons on the neutral amine nitrogen atom will be expected to possess a tendency to form a linkage of a partial double bond character with the central sulphur atom, as actually observed by Brown and Cox[1] and by Jeffrey and Stadler[4] in the case of sulphamate ion $(H_2NSO_3)^-$ in the potassium and ammonium salts. In the other case of zwitterion structure, on the contrary, the absence of such a lone pair of electrons will prevent double bond formation with the sulphur atom. The observed value 1.75_5 Å of the S-N bond distance, which corresponds more closely to a single covalent $S-N^+$ bond, will thus be accounted for essentially by the zwitterion structure $(H_3N)^+-(SO_3)^-$. In this respect our conclusion is in agreement with that of Kanda and King[2]. The location of three hydrogen atoms around the ammonium nitrogen was not determined directly. However, assuming that they are arranged so that the bond angles S-N-H and H-N-H form approximately tetrahedral angles and that they are all linked by forming hydrogen bonds with adjacent oxygen atoms of the surrounding molecules, it is possible to assign probable positions for them which are shown in Fig. 3 as already mentioned. It may be added that such assignment makes one hydrogen atom H_{II} lie on the line connecting the central nitrogen and an oxygen $O_{III}(7)$ and each of the other two, H_I or H_{III}, on the plane of $NO_I(5)O_{III}(8)$ or $NO_I(3)O_{II}(6)$, thus the latter H_I or H_{III} forming bifurcated bonds. Moreover, such configuration of the hydrogen atoms may be an electrostatically stable one because each hydrogen atom comes very near to each of the three oxygen atoms in the molecule.* Turning to the part SO_3, it has already been remarked that the S-O bond length found is in the mean to be 1.44Å, which is consistent with the remarkably constant values reported for S-O bonds in various molecules, and a similar discussion on the nature of the bond to that given by Jeffrey and Stadler[4] will also apply to the present case. Only it will be of some interest to notice that this zwitterion type of sulphamic acid molecule may be regarded as an addition compound of pyramidal ammonia molecule NH_3 and planar sulphur trioxide SO_3, as in the cases of NH_3-BF_3 and the like which have been extensively studied by Hoard, Geller and others.[7-14] The flat shape of the SO_3 pyramid may suggest a considerable contribution of the π-bond

* The values given in the Abstracts of the Second International Congress (I.U.C., 1951) are those before the correction for finite series and refinement of lattice parameters.

* Quite recently (at a meeting of the Physical Society of Japan held in Nagoya in April, 1955) K. Sano of the Yamanashi University, Japan, reported his nuclear magnetic resonance absorption experiment of this crystal. In this connection it is remarked that the above-mentioned location of the three hydrogen atoms as forming a regular triangle is only a tentative one and the possibility of a deviation from such a regular arrangement is not excluded.

7) S. Geller and J.L. Hoard, *Acta. Cryst.*, 3, 121 (1950).

8) J. L. Hoard, T. B. Owen, A. Buzzell and O. N. Salmon, *Acta Cryst.*, 3, 130 (1950).

9) S. Geller and O.N. Salmon, *Acta Cryst.*, 4, 379 (1951).

10) S. Geller, R. E. Hughes and J. L. Hoard, *Acta Cryst.*, 4, 380 (1951).

11) S. Geller and M.E. Miberg, *Acta Cryst.*, 4, 381 (1951).

12) J. L. Hoard, S. Geller and W. M. Cashin, *Acta Cryst.*, 4, 396 (1951).

13) S. Geller and J.L. Hoard, *Acta Cryst.*, 4, 399 (1951).

14) J. L. Hoard, S. Geller and T. B. Owen, *Acta Cryst.*, 4, 405 (1951).

nature in the S-O linkage. Recently Pauling[15] gave an interesting discussion on the interatomic distances and bond character in the oxygen acids and related substances. He gave for the S-O distance in the flat molecule of SO_3 the calculated value of 1.44Å, which also suggest the view that the nature of the S-O bond in sulphamic acid molecule is not very different from that in SO_3 molecule.

In order to obtain some further information on the structure of the molecule, we have carried out a dielectric measurement of this crystal at various temperatures using the alternating field of the frequency of 3 Mc. The results are $\varepsilon_a=5.2$, $\varepsilon_b=5.2$ and $\varepsilon_c=5.0$ (at 12~15°C), which are sensibly constant at various temperatures. By combining these data, comparable with those of ordinary ionic crystals of NaCl type, with those of refractive indices $n_a=1.568$, $n_b=1.563$ and $n_c=1.553$ (at 25±3°C) for 5461 Å of this crystal given by Bryant,[16] it is obvious that the infrared polarisabilities are fairly large, by far larger than ordinary molecular crystals containing amino or hydroxyl group, standing thus not in contradiction to the view of the zwitterion structure of the molecule in the crystalline state.

15) L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

16) W. M. D. Bryant, *J. Am. Chem. Soc.*, **61**, 2551 (1939).

17) B. P. Dailey, S. Golden and E. B. Wilson, Jr., *Phys. Rev.*, **72**, 871 (1947).

Experimental Remarks

Crystals obtained from neutral aqueous solution were ground into thin rods of cylindrical shape as far as possible, the cross sections being 0.24×0.31 mm. for [100], 0.27×0.25 mm. for [010], 0.12×0.10 mm. for [001].

Oscillation photographs were taken using the multiple film technique with the Cu-K radiations. Intensities were estimated by comparing with standard density scales. Atomic scattering factors for S^{+6}, O^{-2}, N^{-2} were taken from the International Tables. The effect of outer electrons was found to be small when all (hkl) data were taken into account. Three-dimensional Fourier summations were carried out along lines parallel to the three principal axes using 120-section cosine tables, these lines passing in no case more than 0.10 Å apart from the peak obtained.

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