

## The Crystal Structure of $\alpha$ -Sulphanilamide

BY B. H. O'CONNOR AND E. N. MASLEN

*Department of Physics, The University of Western Australia, Nedlands, Western Australia*

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The crystal structure of  $\alpha$ -sulphanilamide has been solved from Patterson and electron-density projections on the (100) plane, and by the method of generalized projections with the (1*kl*) layer of data. The parameters have been refined by the block-diagonal least-squares method with (0*kl*) (1*kl*) and (4*kl*) data. The hydrogen-bond network proposed for  $\alpha$ -sulphanilamide closely resembles that in sulphamide.

### Introduction

The structure of  $\alpha$ -sulphanilamide,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2$ , has been determined as part of a program of research on the structural properties of the aniline sulphonic acids and sulphonamides which is in progress in this laboratory. Structure analyses for sulphanilic acid monohydrate (Rae & Maslen, 1962) and metanilic acid (Hall & Maslen, 1965) have been reported, and determinations of  $\beta$ -sulphanilamide (O'Connell, 1965) and orthanilic acid (Hall, 1965) are in progress.

Four crystalline habits of sulphanilamide are known (Watanabé, 1941; Yakowitz, 1948; McLachlan, 1957) —  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\xi$ . A model for  $\alpha$ -sulphanilamide was reported earlier by Giacomello & Roverso (1941). However, atomic parameters were not listed in this publication. A two-dimensional analysis was therefore undertaken to deduce the hydrogen-bond network. The analysis has shown that the structure postulated by Giacomello & Roverso is incorrect. The hydrogen-bond system has been determined in the present work and compared with the system in sulphamide (Trueblood & Mayer, 1956). It is of interest to examine the effect on the network when the amine and sulphamide groups are substituents in a benzene ring.

### Crystal data

$\text{C}_8\text{H}_9\text{N}_2\text{O}_2\text{S}$ , *p*-aminobenzenesulphonamide.  
F.W. 172.20.

Orthorhombic:

$$a = 5.65 \pm 0.05, \quad b = 18.509 \pm 0.005, \\ c = 14.794 \pm 0.004 \text{ \AA}; \quad U = 1560 \text{ \AA}^3.$$

$Z = 8$ ,  $D_m = 1.47 \pm 0.02 \text{ g.cm}^{-3}$  by flotation,  $D_x = 1.479$ .  
Space group, *Pbca*.

Absent spectra:

$h00, 0k0, 00l$  for odd indices;  $0kl, h0l, hk0$  for  $k, l$  and  $h$  odd respectively.  
 $\mu = 28.5 \text{ cm}^{-1}$  for  $\lambda = 1.5418 \text{ \AA}$ .

### Experimental

Crystals of the  $\alpha$  form of sulphanilamide were obtained in the form of long transparent plates by evaporating a hot, saturated, aqueous alcohol solution. Examination of these plates under a polarizing microscope gave an extinction direction parallel to the long crystal axis. A crystal was mounted about this axis for the determination of cell dimensions from oscillation and back reflexion Weissenberg photographs (Rae & Maslen, 1962). Only the value of  $b$  differed significantly from the measurements of Watanabé (1941), who obtained a result of 18.61 Å.

Intensity data were collected for the (0*kl*), (1*kl*) and (4*kl*) layers with  $\text{Cu } K\alpha$  X-radiation. The zero layer was measured on a single-crystal diffractometer. A regulated Philips-1010 X-ray generator was used together with a Ni/Fe balanced filter system (Ross, 1926). The intensities for this layer were measured with a Geiger counter coupled to a decade scaler. No allowance was necessary for absorption. The (1*kl*) and (4*kl*) sets of intensities were collected on a larger specimen, using the multiple-film and multiple-exposure equi-inclination Weissenberg technique. The size of this crystal necessitated absorption corrections. These were applied with a program written by Lovell (1961) using the procedure suggested by Busing & Levy (1957) and Wells (1960).

Table 1. *Numbers of reflexions measured*

Layer	Reflexions contained in copper sphere	Reflexions measured	Reflexions with intensities above background
(0 <i>kl</i> )	182	147	120
(1 <i>kl</i> )	344	281	197
(4 <i>kl</i> )	290	232	164

Table 1 contains the number of reflexions measured in comparison with the total number available in the copper sphere.

### Solution of structure and initial refinement

#### (100) projection

The projected structure was solved by the heavy atom method, based on a sharpened Patterson projection, and refined by electron-density and difference syntheses. The four ring hydrogen atoms were included at positions expected from the molecular geometry. This gave a final  $R$  of 14.6%. For the refinement, the atomic form factors listed in *International Tables for X-ray Crystallography* (1962) were used. The final atomic parameters are listed in Table 2.

#### (1kl) generalized projection

Since there is little overlap in the (0kl) projection, this structure presents a suitable case for the solution of the  $x$  coordinates by the method of generalized projections (Cochran & Dyer, 1952).

For 1kl reflexions,

$$\frac{{}_cP_1(y_{ss}, z_{ss})}{{}_cP_0(y_{ss}, z_{ss})} = \cos 2\pi \cdot 2x_s$$

where  ${}_cP_1$  and  ${}_cP_0$  are the heights of the sulphur-sulphur peaks in the (1kl) and (0kl) Patterson syntheses.  $x_s$  represents the  $x$  coordinate of the sulphur. This modification of White & Clews's (1955) method is necessary for symmetry groups higher than monoclinic. The method yielded a value of 0.230 for  $x_s$ . The  $x$  coordinates for the other atoms were readily found by trial, and the structure was then refined by sine and cosine generalized projections to an  $R$  of 25%. Difference generalized projections then reduced  $R$  to 17.9%.

### Least-squares refinement

Positional and thermal parameters were refined by least squares with the (0kl), (1kl) and (4kl) layers of data. Mair's (1962) SFLS program for the IBM 1620

machine was used. This program makes use of the block diagonal matrix method with anisotropic thermal parameter refinement. It is quite possible that the use of incomplete data and the block diagonal approximation may have introduced strong interactions (Geller, 1961).

The weighting scheme adopted was that suggested by Hughes (1941) in which each term is given a weight which is statistically equivalent to  $1/\sigma^2 F(hkl)$  (Mills & Rollett, 1960).

Because the layers were not on a common experimental scale the  $F_0$  values had to be scaled against  $F_c$  at the completion of each structure-factor calculation. Hence those  $B_{ij}$  values which are a function of the  $h$  index may be misleading. Comparison of the  $F_0$  and  $F_c$  values suggested strong secondary extinction effects for the zero-layer data. A plot of  $I_0/I_c$  against  $I_c$  (James, 1948) gave a value of  $8 \times 10^{-6}$  for the extinction parameter  $g$ . On application of this correction the 0kl  $R$  index fell from 19% to 16%. Since, however, the first and fourth layers, which were collected on a larger crystal, did not show extinction effects it appears likely that the effect observed in the zero-layer data was caused by an underestimate in the diffractometer dead-time rating.

At the completion of the refinement the  $R$  values were 14.8%, 13.5% and 19.5% for the zero, first and fourth layers respectively. These values include the

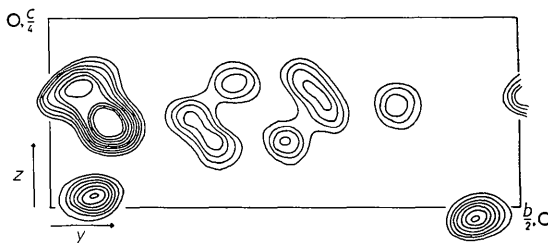


Fig. 1. Final electron-density projection on (100). The first contour is at  $3 \text{ e.}\text{\AA}^{-2}$  and the remaining contours are at  $1 \text{ e.}\text{\AA}^{-2}$ . The innermost contours of the sulphur are excluded.

Table 2. Positional and isotropic thermal parameters; least-squares plane deviations,  $\delta^*$

Atom	SFLS refinement				$\delta$ (Å)	(0kl) refinement		
	$x/a$	$y/b$	$z/c$	$B$ (Å <sup>2</sup> )		$y/b$	$z/c$	$B$ (Å <sup>2</sup> )
S	0.2484	0.0602	0.1054	—	-0.15	0.0600	0.1050	2.8
O(1)	0.2518	0.0449	0.0117	—	—	0.0460	0.0102	3.6
O(2)	0.4580	0.0444	0.1603	5.14	—	0.0425	0.1615	3.6
N(1)	0.0505	0.3741	0.1327	—	-0.03	0.3738	0.1310	4.4
N(2)	0.0355	0.0129	0.1470	4.54	—	0.0160	0.1460	4.9
C(1)	0.0972	0.3000	0.1250	4.29	-0.03	0.3025	0.1263	3.6
C(2)	0.2974	0.2719	0.1657	4.30	0.00	0.2728	0.1663	4.5
C(3)	0.3400	0.1979	0.1631	4.04	0.02	0.2000	0.1620	4.0
C(4)	0.1819	0.1515	0.1178	3.66	-0.02	0.1505	0.1162	2.1
C(5)	-0.0236	0.1801	0.0788	4.14	-0.01	0.1795	0.0778	3.7
C(6)	-0.0737	0.2530	0.0838	4.89	0.03	0.2540	0.0835	4.0
H(2)	0.4238	0.3078	0.1992	4.0	—	—	—	—
H(3)	0.5016	0.1809	0.1937	4.0	—	—	—	—
H(5)	-0.1503	0.1449	0.0464	4.0	—	—	—	—
H(6)	-0.2340	0.2738	0.0528	4.0	—	—	—	—

\* Amino- and amide-hydrogen atoms are excluded.

Table 3. *Anisotropic thermal parameters\**

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{23}$	$B_{13}$	$B_{12}$
S	0.0250	0.0029	0.0043	0.0000	-0.0004	0.0009
O(1)	0.0476	0.0038	0.0048	-0.0009	0.0045	0.0025
N(1)	0.0622	0.0042	0.0076	0.0019	0.0102	0.0000

\* Defined so that the temperature factor is  $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)$ .

effect of unobservably weak terms, using the criterion that these terms should be included only where  $|F_o|$  exceeds the observable limit;  $|F_o|$  is then set equal to this limit. The final  $(0kl)$  electron-density synthesis is shown in Fig. 1. Tables 2 and 3 list the final set of atomic parameters. A list of the observed and calculated structure factors may be obtained on application to the authors.

## Discussion

### Molecular structure

The structure proposed by Giacomello & Rivero (1941) is completely in error. The bonded distances and angles for the current analysis are shown in Fig. 2. The standard deviations vary between 0.01 and 0.02 Å for distances and 30' and 1° 30' for angles. The distances do not differ significantly from those listed by Sutton (1958) for similar structures, although it must be stressed that the standard deviations are large. The C-N bond (1.40 Å,  $\sigma=0.02$ ) is significantly shorter than the single C-N bond of 1.49 Å in sulphanic acid monohydrate. All other interatomic distances agree closely with those in sulphamide and sulphanic acid monohydrate. It is of interest to note that the O-S-O angle (119°,  $\sigma=36'$ ) is significantly greater than the tetrahedral value while the O-S-N angles are slightly less than tetrahedral. These distortions are in keeping with the values of O-S-O and O-S-N bond angles which have been reviewed by Trueblood & Mayer (1956). Recent structure determinations of metanilic acid, sulphanic acid monohydrate and dimethyl sulphone (Sands, 1963) give similar values for the O-S-O angle.

The deviations,  $\delta$ , of the carbon atoms and S and N(1) from the least-squares plane through the benzene ring are listed in Table 2. Only the deviation of S is significant.

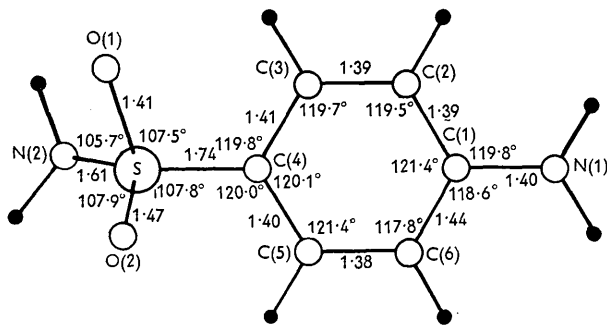


Fig. 2. Model of the molecule with observed bond distances and angles.

### Molecular packing and hydrogen bonding

The packing of the molecules and the hydrogen-bond system is illustrated in Figs. 3 and 4. The presence of the N-H...O bonds was deduced from the interatomic vectors since the nature of the refinement did not permit direct placement of the hydrogens. The molecules pack into layers parallel to the  $c$  axis. Each molecule bonds to four others in the layer by means of two strong (2.94 Å) and two very weak (3.12 Å) hydrogen bonds. The stronger bonds form a chain of molecules in the  $x$  direction and, together with the van der Waals forces in the same direction, probably give rise to the preferred growth of the crystals along the  $a$  axis. The layers of molecules are linked by weak (3.06 Å) N-H...O bonds.

The hydrogen-bond system closely resembles that found in sulphamide. In both structures each molecule bonds to four others in the same layer, although in

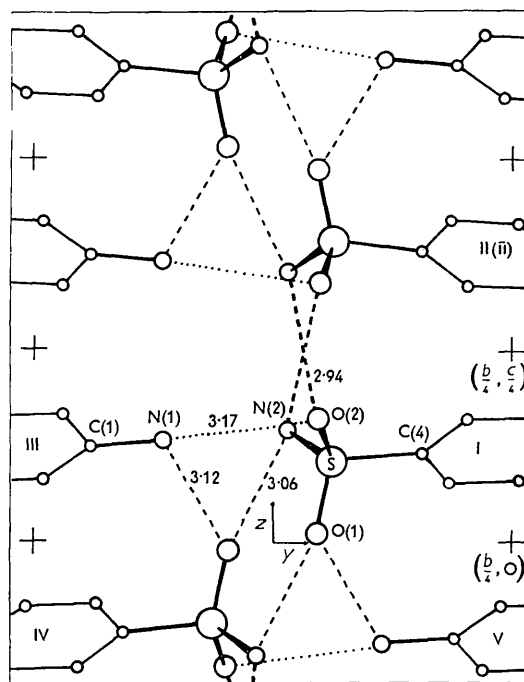


Fig. 3. Molecular packing and proposed hydrogen-bond network viewed along the  $a$  direction. Atoms are represented by circles which are approximately proportional in radius to the atomic number. The symbols I, II, III, IV, and V refer to the molecules associated with the equivalent positions  $(x, y, z)$ ,  $(\frac{1}{2}+x, y, \frac{1}{2}-z)$ ,  $(-\frac{1}{2}+x, y, \frac{1}{2}-z)$ ,  $(\frac{1}{2}-x, -\frac{1}{2}+y, z)$ ,  $(\bar{x}, \bar{y}, \bar{z})$  and  $(\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$  respectively. The distances and angles relevant to hydrogen contacts are given in Table 4.

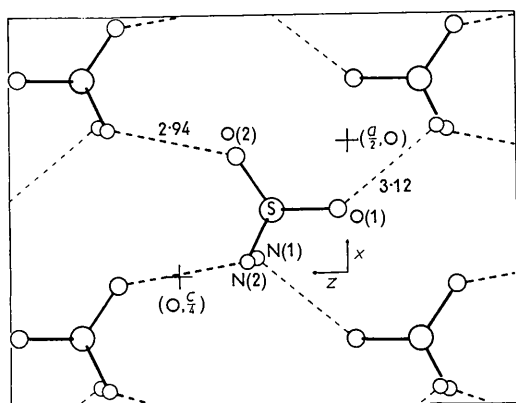


Fig. 4. A bonded layer of molecules viewed along the  $b$  direction. Atoms are represented as in Fig. 3. The carbon atoms are not shown.

sulphamide the layers are connected by weak  $N-H \cdots N$  bonds rather than the  $N-H \cdots O$  type. The packing of  $\alpha$ -sulphanilamide is comparable to that in both  $\beta$ -sulphanilamide (O'Connell, 1965) and sulphanilic acid monohydrate. The latter compound and  $\alpha$ -sulphanilamide have all hydrogen bonds packed into layers which are perpendicular to the long axes of the molecules.

Table 4. Intermolecular short contacts and angles

Contact	Distance
O(1)I $\cdots$ N(1)V	3.12 Å
O(1)I $\cdots$ N(2)IV	3.06
N(2)I $\cdots$ O(2)II	2.94
O(2)I $\cdots$ N(1)III	3.17

Contacts	Angle
C(1)III-N(1)III $\cdots$ O(1)IV	121°
C(1)III-N(1)III $\cdots$ O(2)I	169
O(2)I $\cdots$ N(1)III $\cdots$ O(1)IV	67
S(I)-O(1)I $\cdots$ N(1)V	125
S(I)-O(1)I $\cdots$ N(2)IV	144
N(1)V $\cdots$ O(1)I $\cdots$ N(2)IV	87
S(I)-N(2)I $\cdots$ O(1)IV	108
S(I)-N(2)I $\cdots$ O(2)II	112
O(1)IV $\cdots$ N(2)I $\cdots$ O(2)II	137
S(I)-O(2)I $\cdots$ N(2)II	134
S(I)-O(2)I $\cdots$ N(1)III	96
N(1)III $\cdots$ O(2)I $\cdots$ N(2)II	86

Table 4 lists the distances and angles for each  $N \cdots O$  contact. The  $S-O \cdots N$  angles associated with the amide nitrogen are considerably greater than the tetrahedral value. A similar effect is also observed in the case of sulphamide (Trueblood & Mayer, 1956). It appears that in both structures the lone pairs of electrons on the O atoms are localized and therefore

most unfavourably placed for interaction with the proton. The  $C(1)III-N(1)III \cdots O(2)I$  angle of  $169^\circ$  indicates that the  $N(1)III \cdots O(2)I$  close contact (3.17 Å) is a van der Waals attraction rather than a weak hydrogen linkage. This is most unusual in compounds of this nature. The second hydrogen of the amine group appears to participate in the weak (3.12 Å) hydrogen bond which is mentioned above. The shortest  $O \cdots O$  intermolecular contact is 3.38 Å and there is no  $N \cdots N$  approach distance less than 3.50 Å in the structure.

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