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The Crystal Structure of Sulphanilic Acid Mono-Hydrate

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The crystal structure of sulphanilic acid mono-hydrate has been solved by a combination of Patterson and Fourier syntheses on two projections. These have been refined using difference syntheses to accuracies of 12.3% (*hk0*) and 14.6% (*0kl*) in *R*. The molecules have been shown to pack with their benzeno rings in parallel layers 3.4 Å apart. The charged groups and water molecule are connected by a series of hydrogen bonds and this system is compared with that existing in sulphamic acid.

1. Introduction

The crystal structure of sulphanilic acid mono-hydrate, $\text{NH}_3^+\text{C}_6\text{H}_4\text{SO}_3^-\cdot\text{H}_2\text{O}$, is of interest in relation to a programme of work on the structural properties of charged groups which is in progress in this laboratory. That sulphanilic acid exists in the zwitterion configuration in solution is known from a variety of chemical evidence, of which the work on dissociation constants by Kumler (1955) is perhaps the most conclusive. It is reasonable in the light of work on similar structures—particularly sulphamic acid—to presume that this configuration persists in the solid state.

Structural investigations on sulphamic acid ($\text{NH}_3^+\text{SO}_3^-$), by X-ray diffraction (Kanda & King, 1951; Osaki *et al.*, 1955) and neutron diffraction (Sass, 1960) have revealed the interactions of the charged groups and the details of the hydrogen bond system in that molecule.

The present work was undertaken in order to investigate the changes, if any, which take place in these interactions when the charged groups are separated by a benzene ring.

2. Experimental

Two crystalline habits for sulphanilic acid have been reported (Hodgman *et al.*, 1955)—elongated monoclinic laths and rhombic plates. Crystals of the first form were obtained by precipitation from a hot saturated aqueous solution and the rhombic crystals when a cold solution was allowed to evaporate. Both forms were initially transparent, but decomposed quickly to white microcrystalline aggregates when exposed to air.

Although Hodgman *et al.* (1955) indicate that the monoclinic crystals contain two molecules of water of crystallization per molecule compared with one for the rhombic form, X-ray photography showed that both forms are chemically identical. They have the same space group, cell dimensions and distribution of intensities, differing only in the development of their crystal faces. A density measurement—see below—showed that the crystals contain one molecule of water per molecule.

The cell dimensions were measured using the back-reflection technique, modified for the Weissenberg camera. A crystal, mounted about a non-unique axis,

was oriented so that it oscillated through about 20° on each side of a central lattice line. A slot about 3 cm. long was cut in a film which was then placed in the Weissenberg Camera so that the collimator passed through the slot. The resulting photograph gave identical sets of reflections on either side of the film. The parameters were then measured and extrapolation techniques applied in a way similar to that described by Farquhar & Lipson (1946), but the back-reflection Weissenberg photograph is more easily indexed than the oscillation photograph employed by them. The method differs from that of Buerger (1942) in that a specially modified camera is not used.

The angle β was evaluated by measuring the distance between the $h00$ and $00l$ lines of an $h0l$ Weissenberg film. Shrinkage was allowed for by measuring the distance between two lattice lines 180° apart.

The resulting cell dimensions are:

$$a = (6.473 \pm 0.001), \quad b = (18.308 \pm 0.002), \\ c = (6.812 \pm 0.001) \text{ \AA}; \quad \beta = 93^\circ 38' \pm 6'.$$

Examination of the systematic absences in the $hk0$, $hk1$, $hk2$ and $0kl$ reflections determined the space-group uniquely as $P2_1/c$. The assumption of four molecules of sulphanic acid and four water molecules in the cell, gives a calculated density of $1.576 \pm 0.001 \text{ g.cm.}^{-3}$. This compares with the value of $1.55 \pm 0.02 \text{ g.cm.}^{-3}$ obtained by flotation in a mixture of carbon tetrachloride and chloroform; this value is slightly low, probably because the crystals had partially dried out.

Intensity data for the $hk0$ and $0kl$ zones were collected using Cu $K\alpha$ radiation and multiple-film and multiple-exposure Weissenberg techniques. The crystals were lath-like and they were coated with shellac to prevent degradation. The intensities of each zone were measured by visual comparison with a calibrated intensity strip. They were corrected for Lorentz and polarization factors, but no allowance was made for absorption. Extinction was allowed for in the course of the structure refinement. The reflection sphere for Cu $K\alpha$ contains 162 independent $hk0$ and 167 independent $0kl$ reflections. Of these, 135 and 133 respectively were observed. The reflections which were too weak to be recorded were given an F value equal to half the minimum measurable F value appropriate to the particular Bragg angle for the reflection.

3. Solution of the structure

Projection on (001)

A Patterson synthesis projected on (001) was calculated* using data modified by the function $1/\bar{f}^2 \exp(2B \sin^2 \theta/\lambda^2)$ where \bar{f} is the average unitary scattering factor for the molecule and B is a mean temperature factor coefficient which was determined

* This and subsequent calculations were performed on the University of Sydney's Silliac I computer.

from a Wilson plot to be 4.0 \AA^2 . The properties of this modification function are discussed by Abrahamsson & Maslen (1960, 1962).

Patterson peaks, readily identifiable as sulphur-sulphur vectors, were observed corresponding to a sulphur position of $x/a = 0.250$, $y/b = 0.141$. An atom with one coordinate exactly equal to one quarter of the unit-cell edge contributes to only half the reflections and an electron-density map based on this position will contain false mirror lines along one quarter and three quarters of the cell edge. If, however, the coordinate is slightly different from one quarter, the vector overlap in the Patterson projection is such that the atom will appear to lie exactly on the quarter line, but the vector peaks will be extended in the direction of the displacement. The sulphur-sulphur peaks in the (001) Patterson projection of sulphanic acid were extended in this manner and an approximate calculation, using the amount of extension, gave an x/a coordinate of 0.234. (The final value was 0.2358 (Table 2)).

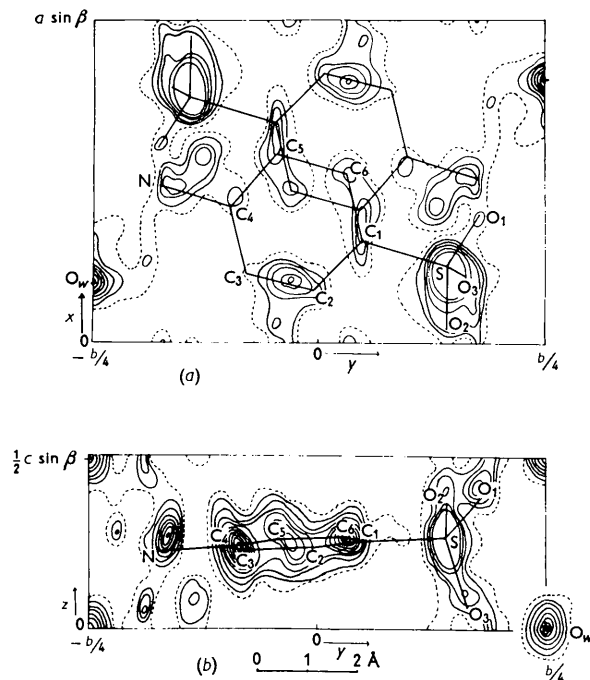


Fig. 1. (a) Electron density projected on (001) based on phases from the sulphur atom alone, (b) projected on (100), based on phases from sulphur and six carbons. First contour (broken) at $3 \text{ e.}\text{\AA}^{-2}$; contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$ thereafter. 24 contours in (a) and 20 contours in (b) are omitted at the centre of the sulphur peaks. Two asymmetric units are shown in (a). The molecular skeletons do not show hydrogen positions.

A Fourier synthesis was evaluated with signs corresponding to this sulphur position and is shown in Fig. 1(a). The pseudo-symmetry has been almost entirely eliminated and, although there are several spurious peaks, it was possible to postulate positions for all the atoms except hydrogen.

Structure factors based on these positions were calculated using the scattering factor curve of Viervoll & Øgrim (1949) for sulphur and those of Berghuis *et al.* (1955) for carbon, nitrogen and oxygen, and the temperature factor of 4.0 \AA^2 obtained from the Wilson plot. (These scattering factor curves were also used in all subsequent structure-factor calculations.) The R -factor at this stage was 46%. When one oxygen position had been corrected by $\frac{1}{4} \text{ \AA}$ and some smaller adjustments made to the positions of the other atoms, the R -factor fell to 33%.

Projection on (100)

The modification function used for the $hk0$ zone was also applied to the $0kl$ data and a sharpened Patterson projection on (100) was evaluated. Several peaks of similar height were observed, but prior knowledge of the y coordinate of the sulphur atom from the (001) projection enabled the sulphur-sulphur vectors to be identified.

The z -coordinate of the sulphur atom was also very close to $\frac{1}{4}$. The z coordinates of the light atoms relative to the sulphur were obtained from a comparison of the x, y coordinates and the bond lengths expected from the covalent radii of the atoms. Structure factors were calculated based on the positions of the sulphur, nitrogen and six carbon atoms, which were the only atoms that could be definitely fixed by these methods. The R -factor was 50%.

The resulting Fourier synthesis is shown in Fig. 1(b). The pseudo-symmetry has been largely eliminated although the outer carbons of the benzene ring lie much nearer $z/c = \frac{1}{4}$ than had first been thought. Nevertheless, the oxygen peaks are quite prominent and a full structure could be postulated. After several cycles of Fourier and error syntheses the R -factor fell to 33%.

4. Refinement of the structure

Atomic coordinates and temperature factors were refined through about ten cycles of structure-factor calculations and difference syntheses on each projection. The scale of the data was adjusted after each calculation by comparison of the sums of the moduli of the observed and calculated structure factors.

When the R -factors had reached about 25%, the four hydrogen atoms attached to the benzene ring were included at positions deduced from the molecular symmetry of the ring, assuming C-H bond lengths of 1.09 \AA . All these positions coincided with regions of positive electron density in the difference maps. The hydrogen scattering factor used in the structure factor calculations was that of Berghuis *et al.* (1955). Inclusion of the four hydrogen atoms lowered the R -factors by about 2%.

During the later stages of the refinement, the difference maps yielded considerable evidence for anisotropic thermal motion of the sulphur atom.

When R had reached about 21%, allowance was made for this and the anisotropic parameters were refined in subsequent calculations. Evidence was also obtained for light-atom anisotropy, but it was considered that the amount and accuracy of the data did not justify the introduction of the additional parameters required to make allowance for this.

Comparison of the observed and calculated structure factors, when the structure had attained an accuracy of about 17% in R , revealed discrepancies in the large terms consistent with secondary extinction. Independent plots of I_o/I_c against I_o were made in each projection to determine the extinction parameter g (James, 1948). The values obtained were 6×10^{-6} and 3×10^{-6} for the $hk0$ and $0kl$ sets of data respectively. The observed structure factors were then corrected using these results. Use of the corrected data lowered the R -factors by about 1%.

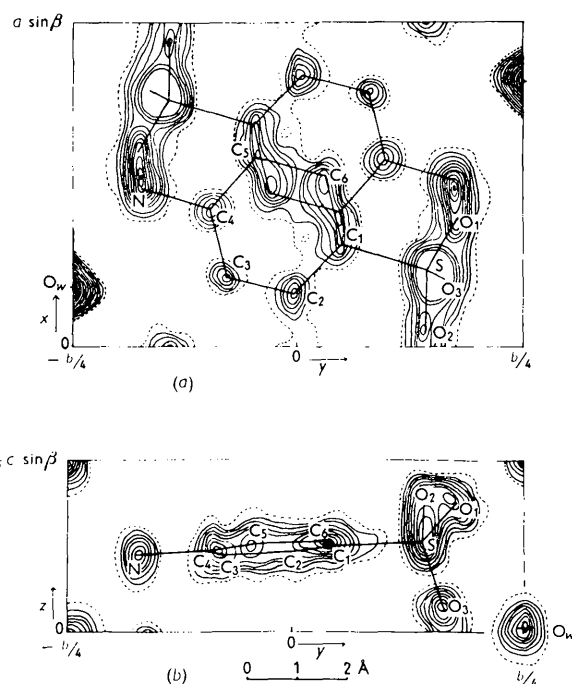


Fig. 2. Final electron-density projected on (001), (a) and (100), (b). First contour (broken) at 3 e. \AA^{-2} ; contours at intervals of 1 e. \AA^{-2} thereafter. 21 contours in (a) and 20 contours in (b) omitted from the centres of the sulphur peaks. Two asymmetric units are shown in (a). The molecular skeletons do not show hydrogen positions.

Refinement was continued until no further significant changes in the atomic coordinates and thermal parameters could be deduced from the difference maps. The R -factors in the $hk0$ and $0kl$ zones were then 13.0% and 15.2% respectively. Fourier and difference syntheses calculated at this stage are shown in Figs. 2 and 3. The only factor for which allowance had not been made, other than light-atom anisotropy, was the contribution of the five remaining hydrogen atoms. The positions of four of these could be postu-

lated from the hydrogen-bond system discussed below. They all occur at or near peaks in the difference syntheses (Figs. 3(a), (b)). Inclusion of these hydrogen atoms in the structure factor calculations lowered the R -factors to 12.3% ($hk0$) and 14.6% ($0kl$). The final values for the observed and calculated structure factors are given in Table 1.

5. Discussion

The final atomic coordinates are listed in Table 2, and the bond lengths and angles derived from them are shown in Table 3 along with corresponding standard deviations calculated using Cruickshank's (1949) method. Bond lengths and angles involving

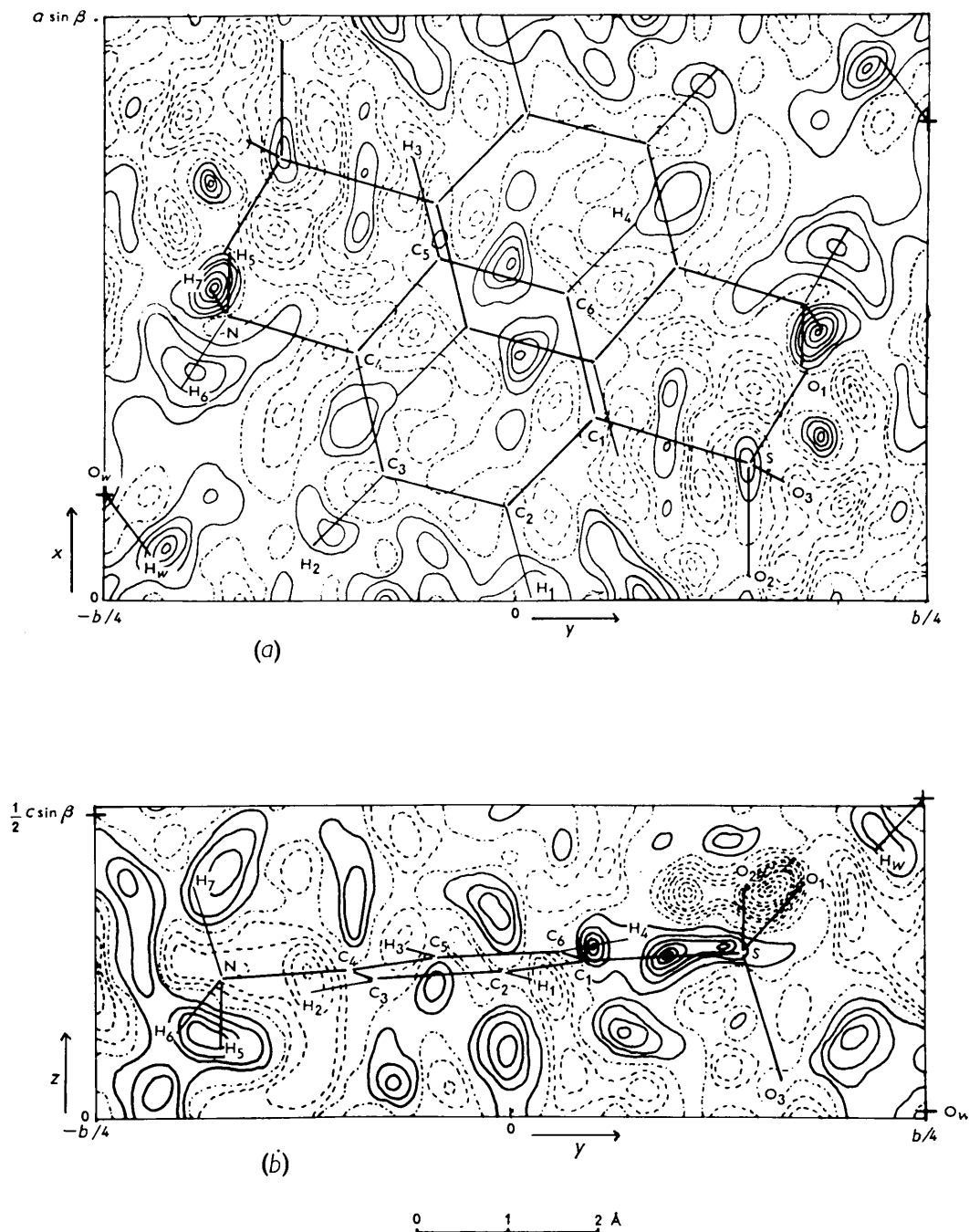


Fig. 3. Final difference maps projected on (001), (a) and (100), (b). Zero contour 'dot-dash', positive contours solid and negative contours broken. The contour interval is $\frac{1}{4} e \cdot \text{\AA}^{-2}$. Two asymmetric units are shown in (a). Full molecular skeletons, including hydrogen positions are superposed.

Table I. Observed and calculated structure factors

| h | k | l | $ F_o $ | F_c | h | k | l | $ F_o $ | F_c | h | k | l | $ F_o $ | F_c | h | k | l | $ F_o $ | F_c | h | k | l | $ F_o $ | F_c | | | |
|---|----|---|---------|-------|---|----|---|---------|-------|------|----|---|---------|-------|--------|----|----|---------|-------|-------|----|----|---------|-------|-------|------|------|
| 0 | 4 | 0 | 42.6 | -45.3 | 3 | 4 | 0 | 12.9 | -15.1 | 6 | 4 | 0 | 19.5 | 20.8 | 0 | 1 | 2 | 30.8 | 41.1 | 0 | 18 | 4 | 9.9 | -12.4 | | | |
| | 6 | | 59.9 | 65.1 | | 5 | | 31.4 | -26.2 | | 5 | | 18.3 | 18.7 | | 2 | | 31.2 | -65.4 | | 19 | | 3.0 | 2.0 | | | |
| | 8 | | 11.1 | 9.1 | | 6 | | 13.3 | -10.0 | | 6 | | < 1.6 | 2.9 | | 3 | | 19.7 | 17.9 | | 20 | | 9.4 | 6.8 | | | |
| | 10 | | 50.0 | -51.6 | | 7 | | 8.7 | -9.3 | | 7 | | 4.8 | -8.4 | | 4 | | 38.4 | 38.0 | | | | | | | | |
| | 12 | | 20.4 | 18.1 | | 8 | | 16.3 | -14.4 | | 8 | | < 1.6 | -1.5 | | 5 | | 22.9 | -24.6 | | 0 | 1 | 5 | < 2.4 | 5.9 | | |
| | 14 | | 1.4 | -1.2 | | 9 | | 19.1 | 19.0 | | 9 | | 7.4 | -7.0 | | 6 | | 28.2 | -30.4 | | 2 | | 13.8 | -6.3 | | | |
| | 16 | | 3.7 | 1.9 | | 10 | | 4.6 | 1.7 | | 10 | | 3.1 | 3.6 | | 7 | | 11.5 | 9.8 | | 3 | | 2.9 | -3.2 | | | |
| | 18 | | 18.3 | -17.0 | | 11 | | 3.6 | 3.5 | | 11 | | 3.8 | -1.9 | | 8 | | 3.6 | 2.0 | | 4 | | 7.2 | 5.8 | | | |
| | 20 | | 7.2 | 6.3 | | 12 | | 19.0 | -21.8 | | 12 | | 9.3 | 7.4 | | 9 | | < 2.0 | 0.3 | | 5 | | < 2.4 | 2.4 | | | |
| | 22 | | 25.4 | 17.2 | | 13 | | 13.3 | -11.5 | | 13 | | < 1.2 | -0.1 | | 10 | | 9.7 | 9.2 | | 6 | | 11.5 | 8.9 | | | |
| | | | | | | 14 | | 1.9 | 3.5 | | 14 | | 8.3 | -7.1 | | 11 | | < 2.2 | 0.6 | | 7 | | 8.5 | -6.5 | | | |
| 1 | 0 | 0 | 43.9 | -48.4 | | 15 | | 14.5 | 12.9 | | 15 | | 4.7 | -2.5 | | 12 | | 19.3 | 18.7 | | 8 | | 19.9 | -16.6 | | | |
| | 1 | | 41.0 | -48.2 | | 16 | | < 1.6 | -2.4 | | | | | | | 13 | | 3.8 | -2.2 | | 9 | | < 2.6 | -0.1 | | | |
| | 2 | | 20.8 | -22.1 | | 17 | | 2.2 | 2.6 | | 7 | 0 | 0 | 4.9 | -7.6 | | 14 | | 19.5 | -19.6 | | 10 | | 14.2 | -13.6 | | |
| | 3 | | 40.5 | -42.0 | | 18 | | 4.4 | 5.7 | | 1 | | 10.6 | 10.1 | | 15 | | < 2.6 | 2.3 | | 11 | | 10.9 | 13.2 | | | |
| | 4 | | 9.1 | -8.4 | | 19 | | 11.1 | -7.7 | | 2 | | 6.6 | 7.5 | | 16 | | 4.8 | 4.6 | | 12 | | 13.1 | 15.4 | | | |
| | 5 | | 84.3 | 87.4 | | 20 | | 4.4 | 3.5 | | 3 | | < 1.6 | -1.7 | | 17 | | 7.9 | 5.4 | | 13 | | < 2.4 | 1.4 | | | |
| | 6 | | 14.1 | -12.5 | | | | | | | 4 | | 7.1 | 7.1 | | 18 | | 15.0 | 15.7 | | 14 | | 4.0 | 4.3 | | | |
| | 7 | | 58.2 | -59.9 | 4 | 0 | 0 | 31.9 | 29.3 | | 5 | | 3.8 | -3.5 | | 19 | | 2.8 | -2.1 | | 15 | | 5.4 | -3.4 | | | |
| | 8 | | 55.6 | 56.8 | | 1 | | 8.7 | -8.2 | | 6 | | 3.5 | -5.2 | | 20 | | 4.7 | -4.4 | | 16 | | 8.8 | -9.9 | | | |
| | 9 | | 57.0 | -54.7 | | 2 | | 4.6 | -4.2 | | 7 | | < 1.2 | 2.8 | | 21 | | 7.8 | -3.8 | | 17 | | 4.4 | 5.0 | | | |
| | 10 | | 12.4 | -10.4 | | 3 | | 3.5 | -4.9 | | 8 | | < 1.2 | 0.3 | | 22 | | 25.2 | -19.6 | | 18 | | 4.6 | 3.1 | | | |
| | 11 | | 11.1 | 8.9 | | 4 | | 26.1 | -25.7 | | 9 | | 9.7 | 8.1 | | | | | | 0 | 1 | 3 | 8.5 | 10.5 | | | |
| | 12 | | < 1.4 | 3.4 | | 5 | | 25.4 | -26.2 | | 10 | | 5.4 | 4.5 | | 2 | | 16.4 | -21.9 | | 0 | 0 | 6 | 33.5 | -31.5 | | |
| | 13 | | 34.1 | 34.2 | | 6 | | 17.1 | 14.5 | | 11 | | < 1.0 | -1.2 | | 3 | | 23.8 | -26.7 | | 1 | | 4.7 | 0.5 | | | |
| | 14 | | 33.7 | 31.1 | | 7 | | 13.3 | 16.1 | | 12 | | 1.3 | -3.3 | | 4 | | 13.3 | 12.1 | | 2 | | 13.3 | -13.7 | | | |
| | 15 | | 3.6 | -3.2 | | 8 | | 10.4 | 9.2 | | | | | | | 5 | | 5.4 | 5.5 | | 3 | | 11.9 | 9.6 | | | |
| | 16 | | 8.1 | 7.5 | | 9 | | < 1.6 | -1.5 | | 8 | 0 | 0 | 2.9 | 0.1 | | 6 | | 16.4 | -13.9 | | 4 | | 13.3 | 10.8 | | |
| | 17 | | 3.1 | 3.7 | | 10 | | 17.8 | -18.3 | | 1 | | 1.6 | -0.7 | | 6 | | 16.4 | -13.9 | | 5 | | 4.0 | 0.7 | | | |
| | 18 | | 6.6 | -5.0 | | 11 | | < 1.6 | 0.3 | | 2 | | 3.7 | -3.9 | | 7 | | 16.6 | 17.9 | | 6 | | 11.3 | -12.5 | | | |
| | 19 | | 2.4 | 10.3 | | 12 | | 3.6 | -4.0 | | 3 | | 1.6 | -1.3 | | 8 | | 16.8 | 14.0 | | 7 | | < 2.6 | -1.3 | | | |
| | 20 | | 7.1 | 5.8 | | 13 | | 10.5 | -11.5 | | 4 | | 7.6 | -5.8 | | 9 | | 7.4 | -9.7 | | 8 | | < 2.6 | -0.7 | | | |
| | 21 | | 10.6 | 6.6 | | 14 | | 12.4 | 11.0 | | 5 | | 6.9 | -4.8 | | 10 | | 32.8 | 35.4 | | 9 | | < 2.4 | -0.9 | | | |
| | 22 | | 6.5 | -4.7 | | 15 | | < 1.6 | 0.3 | | 6 | | 5.3 | 8.0 | | 11 | | 12.4 | -13.2 | | 10 | | 9.9 | 7.8 | | | |
| | 23 | | 16.5 | -11.1 | | 16 | | 2.8 | -3.0 | | | | | | | 12 | | 21.8 | -22.6 | | 11 | | 2.8 | 2.2 | | | |
| | | | | | | 17 | | 4.5 | -2.7 | | | | | | | 13 | | < 2.4 | 1.1 | | 12 | | 5.9 | -2.7 | | | |
| | | | | | | 18 | | 18.0 | -12.1 | | | | | | | 14 | | 15.6 | -15.9 | | 13 | | 3.3 | -0.7 | | | |
| | | | | | | 19 | | 2.7 | 1.5 | | | | | | | 15 | | < 2.6 | 2.2 | | 14 | | 4.0 | -5.5 | | | |
| | | | | | | 20 | | 6.4 | -4.5 | | | | | | | 16 | | 19.7 | 20.5 | | 15 | | 5.0 | 4.4 | | | |
| 2 | 0 | 0 | 26.5 | -28.2 | | | | | | | 0 | 1 | 1 | < 0.8 | 2.3 | | 17 | | < 2.4 | -3.7 | | 16 | | 5.1 | 3.4 | | |
| | 1 | | 14.6 | 14.6 | | | | | | | 2 | | 45.7 | -44.1 | | 18 | | 5.1 | -4.0 | | | | | | | | |
| | 2 | | 14.1 | 9.8 | | | | | | | 3 | | 6.3 | 6.0 | | 19 | | 4.1 | -1.9 | | 0 | 1 | 7 | < 2.4 | -5.0 | | |
| | 3 | | 18.5 | -19.0 | | | | | | | 4 | | 41.9 | 42.0 | | 20 | | 12.9 | -13.7 | | 2 | | 7.7 | 5.5 | | | |
| | 4 | | 14.4 | 12.7 | 5 | 0 | 0 | 24.5 | 26.1 | | 5 | | 5.3 | 1.2 | | 21 | | 3.8 | 2.7 | | 3 | | < 2.4 | 4.3 | | | |
| | 5 | | 46.6 | 46.0 | | 1 | | 15.5 | -14.0 | | 6 | | 36.3 | 33.4 | | 22 | | 6.1 | 6.6 | | 4 | | < 2.4 | -3.0 | | | |
| | 6 | | 17.3 | 16.4 | | 2 | | 7.4 | -7.8 | | 7 | | 8.6 | -2.7 | | | | | | 0 | 0 | 4 | 66.5 | 68.2 | | | |
| | 7 | | 17.8 | 16.8 | | 3 | | < 1.6 | -0.8 | | 8 | | 57.9 | -59.9 | | 1 | | 28.9 | -30.9 | | 5 | | 5.0 | 2.3 | | | |
| | 8 | | 28.7 | -27.3 | | 4 | | 7.9 | -8.9 | | 9 | | 3.4 | -4.2 | | 2 | | 22.2 | 21.8 | | 6 | | 6.8 | 7.6 | | | |
| | 9 | | < 1.0 | 1.7 | | 5 | | 16.1 | 15.4 | | 10 | | 33.5 | -33.4 | | 3 | | 9.9 | -9.5 | | 7 | | 2.9 | 2.4 | | | |
| | 10 | | 27.5 | 27.4 | | 6 | | 4.0 | -4.7 | | 11 | | 9.0 | 7.7 | | 4 | | < 2.0 | 4.9 | | 8 | | 6.2 | 6.7 | | | |
| | 11 | | 3.7 | -5.7 | | 7 | | < 1.6 | 4.3 | | 12 | | 35.8 | 35.9 | | 5 | | 13.7 | 14.1 | | 9 | | 11.2 | -9.8 | | | |
| | 12 | | 5.7 | -3.5 | | 8 | | 9.5 | 8.9 | | 13 | | 8.4 | 5.8 | | 6 | | 5.1 | -4.4 | | 10 | | 6.2 | -6.8 | | | |
| | 13 | | 8.9 | 7.1 | | 9 | | 19.7 | -21.6 | | 14 | | 17.9 | 12.8 | | 7 | | 6.9 | -5.4 | | 11 | | 0 | 0 | 8 | 16.3 | 16.0 |
| | 14 | | 24.7 | -28.7 | | 10 | | 4.4 | -3.2 | | 15 | | 12.4 | -7.0 | | 8 | | 17.0 | 16.1 | | 1 | | 9.3 | -7.5 | | | |
| | 15 | | 18.7 | -15.9 | | 11 | | 4.8 | 5.1 | | 16 | | 23.7 | -23.2 | | 9 | | 6.9 | -6.4 | | 2 | | 4.6 | 3.7 | | | |
| | 16 | | 6.6 | -7.3 | | 12 | | 10.6 | 9.0 | | 17 | | < 2.6 | 2.2 | | 10 | | 20.3 | -20.3 | | 3 | | 5.4 | -3.7 | | | |
| | 17 | | 2.2 | 2.0 | | 13 | | 13.6 | 12.9 | | 18 | | 4.7 | 4.8 | | 11 | | 9.4 | 9.7 | | 4 | | < 1.8 | -1.1 | | | |
| | 18 | | 13.8 | 13.3 | | 14 | | 6.2 | 5.7 | | 19 | | 7.2 | 3.5 | | 12 | | 4.8 | -1.8 | | 5 | | 3.1 | 1.3 | | | |
| | 19 | | 3.5 | 1.9 | | 15 | | 3.5 | -4.3 | | 20 | | 17.4 | 16.7 | | 13 | | 5.6 | -5.0 | | 6 | | < 1.6 | 2.0 | | | |
| | 20 | | 11.9 | -10.1 | | 16 | | 2.5 | 1.1 | | 21 | | 4.4 | -2.8 | | 14 | | 6.0 | 5.8 | | 7 | | < 1.6 | -0.4 | | | |
| | 21 | | < 1.0 | 0.4 | | 17 | | 11.9 | -7.5 | | 22 | | 7.7 | -7.9 | | 15 | | < 2.4 | -4.8 | | 8 | | 3.0 | 3.5 | | | |
| | 22 | | 6.6 | -5.1 | | 18 | | 7.0 | -5.6 | | 23 | | 2.2 | -0.2 | | 16 | | 3.7 | -0.8 | | 9 | | 6.1 | -1.6 | | | |
| 3 | 0 | 0 | 48.4 | -50.4 | | 6 | 0 | 0 | 5.8 | -4.5 | 0 | 0 | 2 | 126.5 | -128.6 | | 17 | | 3.1 | -2.3 | | | | | | | |
| | 1 | | 13.8 | 9.5 | | 1 | | 6.8 | -9.2 | | | | | | | | | | | | | | | | | | |
| | 2 | | 11.9 | 10.7 | | 2 | | < 1.6 | 0.4 | | | | | | | | | | | | | | | | | | |
| | 3 | | 17.7 | 18.2 | | 3 | | 3.5 | -2.1 | | | | | | | | | | | | | | | | | | |

hydrogen atoms are not quoted as they were assumed in deriving the hydrogen positions. The mean S-O bond length is 1.44 Å identical with that found by Sass (1960) and by Jeffrey & Stadler (1955), and none

of the individual values deviate significantly from the mean. The C-S distance of 1.77 Å and the C-N distance of 1.49 Å are close to the average single bond lengths quoted by Sutton (1958). The average C-C

Table 2. Atomic positions, temperature factors and deviations from least squares plane

| Atom | x/a | y/b | z/c | $B(hk0)$ | $B(0kl)$ | δ^* |
|----------------|--------|---------|--------|---------------------|--------------------|------------|
| S | 0.2358 | 0.1402 | 0.2610 | — | — | 0.016 |
| C ₁ | 0.3119 | 0.0474 | 0.2501 | 2.65 Å ² | 3.4 Å ² | 0.012 |
| C ₂ | 0.1633 | -0.0060 | 0.2351 | 2.65 | 3.4 | -0.017 |
| C ₃ | 0.2160 | -0.0804 | 0.2204 | 2.65 | 3.4 | 0.017 |
| C ₄ | 0.4215 | -0.0967 | 0.2351 | 2.65 | 3.4 | -0.011 |
| C ₅ | 0.5828 | -0.0443 | 0.2528 | 2.65 | 3.4 | 0.005 |
| C ₆ | 0.5215 | 0.0289 | 0.2633 | 2.65 | 3.4 | -0.006 |
| N | 0.4892 | -0.1740 | 0.2234 | 1.85 | 3.0 | 0.006 |
| O ₁ | 0.3947 | 0.1776 | 0.3736 | 4.1 | 6.0 | — |
| O ₂ | 0.0445 | 0.1415 | 0.3626 | 6.0 | 6.0 | — |
| O ₃ | 0.2028 | 0.1628 | 0.0588 | 6.0 | 4.5 | — |
| O _w | 0.1842 | -0.2510 | 0.4867 | 3.5 | 4.3 | — |
| H ₁ | 0.0000 | 0.0082 | 0.2210 | 4.0 | 4.5 | — |
| H ₂ | 0.0976 | -0.1218 | 0.1982 | 4.0 | 4.5 | — |
| H ₃ | 0.7461 | -0.0582 | 0.2717 | 4.0 | 4.5 | — |
| H ₄ | 0.6408 | 0.0710 | 0.2841 | 4.0 | 4.5 | — |
| H ₅ | 0.5898 | -0.1747 | 0.1101 | 4.0 | 4.5 | — |
| H ₆ | 0.3653 | -0.2021 | 0.1322 | 4.0 | 4.5 | — |
| H ₇ | 0.5279 | -0.1912 | 0.3675 | 4.0 | 4.5 | — |
| H _w | 0.0780 | -0.2212 | 0.5734 | 4.0 | 4.5 | — |

* δ is the deviation from the least squares plane.

bond length is (1.39 ± 0.01) Å in excellent agreement with the value of 1.395 Å for benzene (Sutton, 1958) and again none of the individual deviations is significant. The angles in the benzene ring do not agree so well with standard values, but none of the discrepancies amount to more than twice the corresponding standard deviation. In the SO₃ group, the average C-S-O angle is 106° and the average O-S-O angle is 113°. Although these are not very significantly different from the tetrahedral angle of 109.5°, a slight flattening of the SO₃⁻ group would be consistent with the results of Sass (1960) and Jeffrey & Stadler (1955).

Table 3. Intramolecular bond lengths and angles

| Bond | Length | σ | Bonds | Angle | σ |
|--------------------------------|--------|----------|--|-------|----------|
| S-O ₁ | 1.42 Å | 0.02 Å | C ₁ -S-O ₁ | 107° | 2° |
| S-O ₂ | 1.46 | 0.02 | C ₁ -S-O ₂ | 106 | 2 |
| S-O ₃ | 1.44 | 0.02 | C ₁ -S-O ₃ | 105 | 2 |
| S-C ₁ | 1.77 | 0.02 | O ₁ -S-O ₂ | 110 | 2 |
| C ₁ -C ₂ | 1.37 | 0.03 | O ₂ -S-O ₃ | 112 | 2 |
| C ₂ -C ₃ | 1.41 | 0.03 | O ₃ -S-O ₁ | 116 | 2 |
| C ₃ -C ₄ | 1.36 | 0.03 | C ₆ -C ₁ -C ₂ | 120 | 2½ |
| C ₄ -C ₅ | 1.42 | 0.03 | C ₁ -C ₂ -C ₃ | 122 | 2½ |
| C ₅ -C ₆ | 1.40 | 0.03 | C ₂ -C ₃ -C ₄ | 117 | 2½ |
| C ₆ -C ₁ | 1.40 | 0.03 | C ₃ -C ₄ -C ₅ | 125 | 2½ |
| C ₄ -N | 1.49 | 0.03 | C ₄ -C ₅ -C ₆ | 117 | 2½ |
| | | | C ₅ -C ₆ -C ₁ | 120 | 2½ |

The equation of the best least-squares plane derived from the positions of the carbon atoms is $z' = 1.522 + 0.0696x + 0.0663y$ where x and y coincide with the a and b axes of the unit cell and z' is perpendicular to the ab plane, giving an orthogonal set of coordinates. The deviations of the carbons from the plane along with those of the sulphur and nitrogen atoms are given in Table 2. None are significant compared with the standard deviation in position of 0.02 Å.

The final isotropic temperature factors obtained from the refinement of both projections are given in Table 2. The best isotropic temperature factor for the

carbon atoms is 3.4 Å² in the (100) projection compared with 2.65 Å² in the (001) projection. This may indicate that the ring is vibrating preferentially in a direction perpendicular to its plane. However there is little evidence for this in the difference maps and the discrepancy may be due simply to inaccuracy arising from poor resolution. The discrepancy in the temperature factors of the nitrogen is more pronounced and the (100) difference map indicates that this atom is vibrating preferentially in a direction perpendicular to the plane of the ring. Comparison of the isotropic temperature factors of the SO₃ oxygens in the two projections together with an examination of the difference map indicate that there is probably an oscillatory motion of the group about the C-S bond combined with a vibration, again in a direction perpendicular to the benzene ring. Analysis of the motion of the sulphur atom shows that it too is moving principally in that direction. The postulated anisotropic parameters of the sulphur atom are $B_{11} = 0.0216$, $B_{12} = 0.0010$, $B_{22} = 0.0016$ in the (001) projection, where the temperature factor is $\exp[-(B_{11}h^2 + B_{12}hk + B_{22}k^2)]$, and $B_{22} = 0.0010$, $B_{23} = 0$, $B_{33} = 0.0211$ in the (0kl) projection using a similar notation. The poor agreement between the values of B_{22} obtained from each projection only serves to emphasize the fact that values for thermal parameters derived from projection data, particularly where there is overlap, have no more than qualitative significance.

The benzene rings pack in sheets perpendicular to the c -axis. The closest distance of approach of two rings in the same plane is a hydrogen-hydrogen distance of 2.13 Å and no two carbon atoms approach closer than 3.9 Å in this direction. The perpendicular distance between the rings is 3.41 Å and the closest contacts in this direction are a carbon-hydrogen distance of 3.41 Å and a carbon-carbon distance of 3.42 Å.

6. Hydrogen-bond system

Fig. 4 shows the probable hydrogen-bond system and other close contacts with the relevant distances and angles indicated. The distances $N(1) \cdots O_1(6)$, $N(1) \cdots O_3(2)$, and $N(1) \cdots O_w(1)$ all lie between 2.80 Å and 2.86 Å and are thus appropriate for N-H \cdots O bonds. The angle $C_4(1)-N(1) \cdots O_w(1)$ is nearly equal to the tetrahedral angle, but the angles $C_4(1)-N(1) \cdots O_1(6)$ and $C_4(1)-N(1) \cdots O_3(2)$ are respectively 17° and 9° less than the tetrahedral angle. If it is assumed that the N-H \cdots O_w bond is linear and the others are distorted from the linear by up to 18°, then the bond system is perfectly compatible with a tetrahedral configuration of the hydrogen atoms. The atoms H_5 , H_6 and H_7 were placed on this basis assuming N-H bond lengths of 1.03 Å.

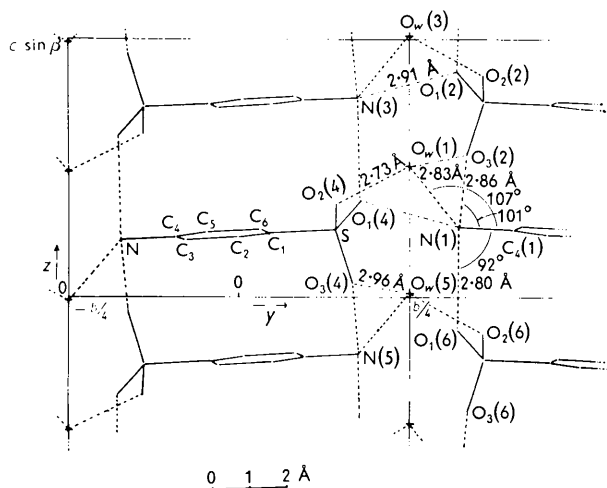


Fig. 4. A diagram of the hydrogen-bond system projected on (100). Broken lines show hydrogen bonds and 'dot-dash' lines unbonded close contacts. Hydrogen positions are not shown.

The $O_w(1) \cdots O_2(4)$ distance of 2.73 Å implies the existence of a hydrogen bond between these two atoms and H_w was placed assuming this bond to be nearly linear and an O-H bond length of 0.96 Å. There are no other atoms within hydrogen-bonding distance of the water oxygen, but the distance $O_w(1) \cdots O_3(2)$ is 2.97 Å and the angle $O_2(4) \cdots O_w(1) \cdots O_3(2) = 88^\circ$ compared with the average H-O-H angle of 105° . The remaining water hydrogen may, therefore, point approximately towards O_3 , possibly forming a weak attachment. This would be consistent with the evidence from the difference maps.

Comparison of the hydrogen-bond system with that existing in sulphamic acid (Sass, 1960) shows that the environment of the nitrogen atom is similar in both structures being hydrogen-bonded to three tetrahedrally disposed oxygens. Similarly all the SO_3 oxygens

bond to neighbouring hydrogens. In sulphanic acid, however, the presence of the water molecule gives rise to an additional O-H \cdots O bond.

The hydrogen-bond system is in complete accord with the expected zwitterion configuration of the molecule and, although the standard deviation on electron density is $0.5 \text{ e.}\text{\AA}^{-2}$, the evidence from the difference maps for the three hydrogens being bonded to the nitrogen is quite strong. A neutron-diffraction study would be useful in providing final confirmation, but there is little doubt that the postulated configuration is basically correct.

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