Acta Cryst. (1965). **18**, 301

The Crystal Structure of Metanilic Acid

By S. R. Hall* and E. N. Maslen

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

(*Received* 4 *March* 1964 *and in revised form* 20 *April* 1964)

The crystal structure of metanilic acid, $NH_3^+C_6H_4SO_3^-$, has been determined by two-dimensional X-ray diffraction methods. The structure is unusual in that the benzene ring lies in the $xy\frac{1}{4}$ mirror plane, with the SO_3^- and NH_3^+ groups arranged symmetrically across this plane. There is a strong $N^+–H–O^-$ bond system and close packing which accounts for the high density of the crystal.

Introduction

An investigation of the structure of metanilic acid was undertaken as part of the programme of research on the structural properties of the anilinesulphonic acids which is in progress in this laboratory. Rae & Maslen (1962) have determined the structure of sulphanilic acid monohydrate, and work on orthanilic acid is in progress. The principal aim of this programme is a comparative study of the hydrogen-bond systems in these compounds. A satisfactory analysis of metanilic acid has been obtained by solving two projections of the structure.

Experimental

Crystal data

Metanilic (aniline-*m*-sulphonic) acid $NH_3^+C_6H_4SO_3^-$. M.W. 173·1.

$$a=8\cdot500\pm1,\ b=11\cdot944\pm1,\ c=6\cdot756\pm5\ \text{Å}\ .$$

$Z=4$, $V=685\cdot9$ Å^3.

$D_m=1\cdot69\pm2$, $D_x=1\cdot677\pm1$ g.cm^{-3}.

Crystal habit:

colourless orthorhombic needles elongated in the *c* direction.

Linear absorption coefficient,

$$\mu=37\cdot1\ \text{cm}^{-1}\ (\text{Cu}\ K\alpha),\ \mu=4\cdot1\ \text{cm}^{-1}\ (\text{Mo}\ K\alpha)\ .$$

Metanilic acid crystallizes in two forms, anhydrous orthorhombic needles and sesquihydrate triclinic prisms (*Handbook of Physics and Chemistry*, 1960). The anhydrous crystals required for this analysis were grown by allowing a warm aqueous solution to cool and evaporate under uniform conditions. Several recrystallizations, with seeding, were necessary before crystals of a size suitable for X-ray data collection were obtained. The *a* and *b* cell dimensions were measured by the back-reflexion Weissenberg method. The *c* cell dimension was determined from a Buerger precession photograph, after correction for film shrinkage. The density measured by flotation agreed with the theoretical density calculated assuming that there were four molecules per unit cell.

Space group

Systematic absences in the *hk*0, 0*kl*, *h*00 and 00*l* reflexions recorded on precession photographs limited the space group to either $Pna2_1$ (C_{2v}^9), which is non-centrosymmetric with four asymmetric units per cell, or *Pnam* (D_{2h}^{16}), which is centrosymmetric with eight asymmetric units per cell. Tests on the crystals for piezoelectricity failed to produce a positive result and could not resolve the ambiguity.

If the space group is *Pnam* the asymmetric unit contains only half a molecule, since there are only four molecules per unit cell. This is possible only if the benzene ring lies exactly in the plane $z/c=0\cdot25$, with the SO_3^- and NH_3^+ groups mirrored across it. If the space group is $Pna2_1$, on the other hand, there is a degree of freedom in the choice of origin of the z/c coordinates. Since the structure was to be solved by the heavy atom method, the z/c coordinate of the sulphur atom could be arbitrarily set equal to 0·25. By adopting $Pna2_1$ as a tentative space group the analysis could proceed without any invalid restrictions on the trial structures. If this initial choice had been correct the solution would have yielded a non-centrosymmetric structure. However, it was found that the analysis added the mirror plane along $z/c=0\cdot25$ showing *Pnam* to be the correct space group.

Intensity data

Multi-film Weissenberg methods with Cu $K\alpha$ radiation and precession techniques with Mo $K\alpha$ radiation were used to collect the *hk*0 and 0*kl* intensity data respectively. Intensities were estimated by visual comparison with a calibrated intensity strip and corrected for Lorentz and polarization factors. Absorption corrections were not required because of the uniform crystal cross-section and the low linear absorption coefficients. Secondary extinction was not allowed for at this stage but empirical corrections were applied during refinement.

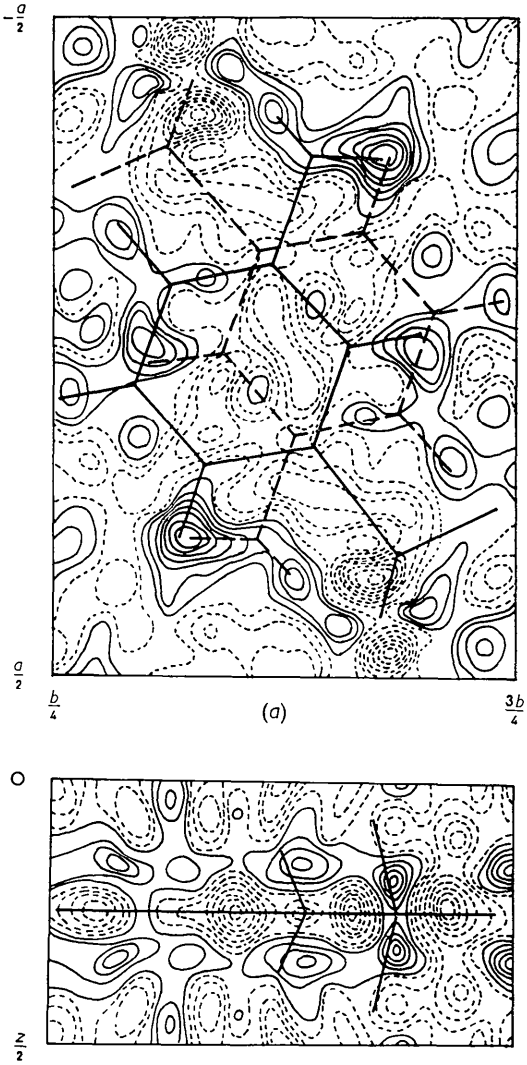
Present address: Division of Pine Physics, National Research Council, Ottawa, Canada.

Of the 134 theoretically observable reflexions in the *hk*0 zone, 111 were measured and of the remainder, 20 were given the maximum unobservable value for that Bragg angle. 45 of the 58 theoretical observable intensities were measured in the 0*kl* zone and 12 were given the maximum unobservable value.

Solution of the structure

A (001) projection Patterson synthesis was calculated* from data modified by the function $(1/f^2).\exp(2B\sin^2\theta/\lambda^2)$ which has properties described by Abrahamsson & Maslen (1960, 1962). Patterson peaks corresponding to the sulphur atom at $x/a=0{\cdot}305$ and $y/b=0{\cdot}625$ were easily identified. A (001) projection Fourier synthesis was calculated and this enabled all non-hydrogen atoms except the oxygens O(2) and O(3) to be located. Structure factors were evaluated from these atoms with the atomic scattering factors of Dawson (1960) for sulphur and of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen and carbon. A further Fourier synthesis calculated with these phases indicated the sites of O(2) and O(3). With coordinate shifts from two rounds of difference syntheses the *R* index of the *hk*0 data decreased to 0·27.

From the projection on (001) it was apparent that all atoms except O(2) and O(3) were close to the $xy\frac{1}{4}$ plane. 0*kl* structure factors were calculated assuming the molecule to lie exactly on this plane. A (100) projection Fourier synthesis phased from this calculation enabled the two oxygen atoms to be positioned. This Fourier and a subsequent difference synthesis also showed small *z*-coordinate shifts off the $xy\frac{1}{4}$ plane for the carbon and nitrogen atoms. The magnitude of these shifts was doubtful because of the effect of inverse overlap (Rae & Maslen, 1963). Nevertheless they were included in a trial round of structure factors in order to resolve any false symmetry. *R* decreased slightly to a value of 0·21.



(*a*)

(*b*)

Fig. 1. Difference synthesis projection (*a*) along the *c* axis and (*b*) along the *a* axis showing features due to thermal anisotropy and hydrogen contribution. Zero and negative contours are broken. The contour interval is 0·2 e.Å^{-3} except near mirror plane in (*b*) where the interval is 0·4 e.Å^{-4}.

All subsequent refinement of the basic structure was carried out simultaneously on both sets of data by Fourier and difference synthesis methods. With isotropic temperature factors the *hk*0 data refined quickly to an *R* value of 0·14 whereas the 0*kl* data refined more slowly to 0·19. It was clear from the 0*kl* difference synthesis that anisotropic temperature factor coefficients would be required for most atoms for further refinement of this projection. Application of anisotropic coefficients reduced *R* to 0·12. The appearance of the difference maps at this stage was rather confused, as they contained features near the atomic sites which could not be explained simply in terms of temperature factor errors. These could be accounted for in terms of combined coordinate and temperature factor adjustments, however, if it were assumed that the molecule was mirrored across the $xy\frac{1}{4}$ plane. Moreover intermolecular distance and angle calculations showed that the oxygen–nitrogen contacts with distances close to the N^+–H–O^- bond length of 2·84 Å (Wallwork, 1962) were arranged in a tetrahedron placed symmetrically across the plane, and the packing in the remainder of the structure showed the same symmetry. There appeared to be no reason why intermolecular forces should constrain the molecule to deviate from the orientation which was symmetrical across the $xy\frac{1}{4}$ plane. Accordingly structure factors were calculated assuming the space group *Pnam*. The *R* values for both projections

---

* This calculation was carried out on the SILLIAC computer, University of Sydney. All subsequent calculations were performed on an IBM 1620 computer, University of Western Australia.

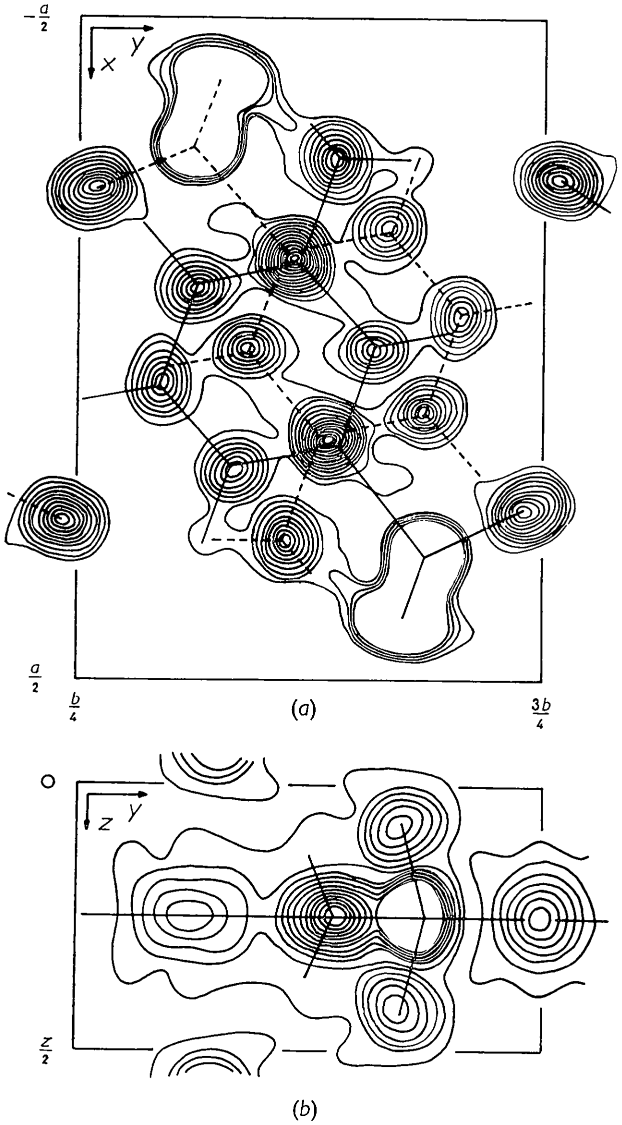


Fig. 2. F_o-Fourier synthesis projection (a) along the c axis and (b) along the a axis phased from final structure factors. The contour interval is 1 e.Å^{-3} starting from 2 e.Å^{-3}.

increased slightly, but the subsequent difference syntheses were greatly simplified. A large negative peak at the oxygen sites O(2) and O(3) in the *hk*0 projection was now resolved into peaks characteristic of thermal anisotropy (Fig. 1(*a*)) and in the 0*kl* projection the principal features were clearly due to anisotropy. It was now clear that the previous coordinate shifts from the $xy\frac{1}{4}$ plane in this projection were due to a misinterpretation of features in the difference synthesis resulting from temperature factor errors. The application of coordinate and temperature factor shifts in three successive rounds of refinement lowered the R values to about 0·10.

*hk*0 structure factors now showed the high F_c terms to be consistently larger than equivalent F_o values, indicating secondary extinction effects. The secondary extinction coefficient (ε) was estimated by plotting I_c/I_o *versus* I_c to be $1{\cdot}2 \times 10^{-5}$. Application of this value of ε to the observed structure factors considerably improved the overall agreement. In the 0*kl* data only the strongest reflection (002) showed any effects of secondary extinction and this was corrected accordingly.

The (001) projection difference synthesis now showed (Fig. 1(*a*)) well defined peaks where the four benzene-ring hydrogen atoms were expected, assuming a C–H bond length of 1·09 Å. Peaks corresponding to the three hydrogen atoms of the NH_3^+ group were also evident. These three hydrogen atoms were positioned assuming a tetrahedral configuration with the nitrogen and an N–H bond length of 1·03 Å. Structure factors were evaluated including these hydrogen atoms with isotropic temperature factor coefficients 1·5 times those of the atoms to which they were attached. Considering the low hydrogen atom contribution to the total scattering of the structure, the decrease of 0·01 in both R values was satisfactory.

Table 1. *Observed and calculated structure factors*

(×10)

H	K	L	F_o	F_c
0	2	0	650	726
0	4	0	580	548–
0	6	0	300	288–
0	8	0	465	475
0	10	0	109	122
0	12	0	117	116–
0	14	0	74	69–
1	1	0	180	159–
1	2	0	722	721–
1	3	0	156	130–
1	4	0	52	40
1	5	0	364	376–
1	6	0	358	355
1	7	0	68	49–
1	8	0	195	200
1	9	0	196	186
1	10	0	344	364–
1	11	0	24*	9
1	12	0	24*	20–
1	13	0	121	110–
1	14	0	117	122
1	15	0	7*	24–
2	0	0	465	524–
2	1	0	494	515–
2	2	0	51	46
2	3	0	524	539–
2	4	0	191	168–
2	5	0	286	272
2	6	0	67	49
2	7	0	410	439
2	8	0	318	319–
2	9	0	164	174
2	10	0	37	25–
2	11	0	24*	1–
2	12	0	159	169
2	13	0	21*	12
2	14	0	77	69
2	15	0	63	60
3	1	0	346	367–
3	2	0	303	284–
3	3	0	344	352
3	4	0	490	481–
3	5	0	360	347
3	6	0	46	49
3	7	0	134	125–
3	8	0	46	36
3	9	0	77	75–
3	10	0	25*	17
3	11	0	137	136
3	12	0	166	170–
3	13	0	137	136
3	14	0	37	29–
4	0	0	211	210–
4	1	0	25	38
4	2	0	336	327–
4	3	0	166	158
4	4	0	233	233
4	5	0	306	287–
4	6	0	79	60–
4	7	0	300	307–
4	8	0	137	131–
4	9	0	67	79
4	10	0	177	182–
4	11	0	139	155
4	12	0	21*	0
4	13	0	163	156–
4	14	0	36	35
5	1	0	117	105
5	2	0	171	173
5	3	0	67	67–
5	4	0	45	42
5	5	0	106	87
5	6	0	58	67–
5	7	0	380	408
5	8	0	212	208
5	9	0	159	153
5	10	0	90	79
5	11	0	202	196–
5	12	0	106	85
5	13	0	180	186–
6	0	0	23*	3
6	1	0	126	121–
6	2	0	182	176
6	3	0	141	139–
6	4	0	92	89–
6	5	0	196	213
6	6	0	62	61
6	7	0	51	47
6	8	0	24*	13
6	9	0	96	109–
6	10	0	21*	0–
6	11	0	74	66–
6	12	0	74	88–
7	1	0	308	285–
7	2	0	82	76
7	3	0	127	134–
7	4	0	76	73
7	5	0	63	63
7	6	0	126	129
7	7	0	37	31–
7	8	0	104	107–
7	9	0	63	55–
7	10	0	111	113–
7	11	0	15*	6
8	0	0	120	116–
8	1	0	23*	21–
8	2	0	25	23
8	3	0	82	73
8	4	0	296	310
8	5	0	23*	1
8	6	0	22*	28–
8	7	0	45	37–
8	8	0	92	108–
8	9	0	51	59–
8	10	0	15*	9–
9	1	0	37	28
9	2	0	226	231
9	3	0	21*	15
9	4	0	21*	23
9	5	0	18*	8–
9	6	0	273	271–
9	7	0	17*	26–
9	8	0	69	63–
10	0	0	225	221
10	1	0	125	127
10	2	0	93	89
10	3	0	104	94
10	4	0	246	251–
10	5	0	15*	14–
10	6	0	109	95–
0	2	0	736	721
0	4	0	579	550–
0	6	0	318	305–
0	8	0	504	488
0	10	0	142	135
0	12	0	153	120–
0	14	0	91	90–
0	16	0	78*	56
0	1	1	502	522
0	3	1	427	424
0	5	1	392	344
0	7	1	219	210–
0	9	1	247	239
0	11	1	228	228
0	13	1	91	77–
0	15	1	88*	118–
0	0	2	1700	1710–
0	2	2	296	273–
0	4	2	61*	25
0	6	2	119	123–
0	8	2	360	349–
0	10	2	84*	78
0	12	2	156	183
0	14	2	90*	19
0	16	2	97	110–
0	1	3	66*	28–
0	3	3	136	111
0	5	3	177	159–
0	7	3	77*	88–
0	9	3	301	309–
0	11	3	154	132–
0	13	3	181	153
0	15	3	137	112
0	0	4	808	858
0	2	4	198	188
0	4	4	154	135–
0	6	4	80*	42
0	8	4	268	247
0	10	4	88*	16–
0	12	4	127	116–
0	1	5	231	207
0	3	5	262	276
0	5	5	84*	57
0	7	5	122	126–
0	9	5	88	105
0	11	5	153	153
0	0	6	527	575–
0	2	6	194	172–
0	4	6	196	198
0	6	6	88*	55
0	8	6	198	172–
0	1	7	88	79–
0	3	7	125	114–
0	5	7	88*	13–
0	0	8	212	178
0	2	8	86	68

* indicates the maximum unobservable F_o for that Bragg angle.

Refinement was continued until no significant coordinate or temperature factor shifts were indicated by the difference syntheses. The final R values were 0·059 for the *hk*0 data and 0·065 for the 0*kl* data. The (001) and (100) projection Fourier syntheses phased from the final structure factors (Table 1) are shown on Fig. 2.

Discussion

General

A diagrammatic representation of the structure of metanilic acid with the hydrogen-bond system is shown in Fig. 3. In evaluating the accuracy of this structure it is important to consider two factors. First, the z/c coordinate of the majority of atoms in the structure is restricted by symmetry to 0·25, and the thermal vibrations of these atoms are also confined on or perpendicular to the $xy\frac{1}{4}$ plane. This increases the proportion of structure factors to unknown parameters, and results in lower atomic coordinate standard deviations than those obtained when there are no symmetry restrictions. Secondly only two atomic sites in the structure are subject to overlap. These are the atomic sites of the carbon atoms C(1) and C(5), which fortunately may be determined from the remaining atomic positions using the hexagonal symmetry of the benzene ring. Since the main purpose of this analysis is the study of the hydrogen bond

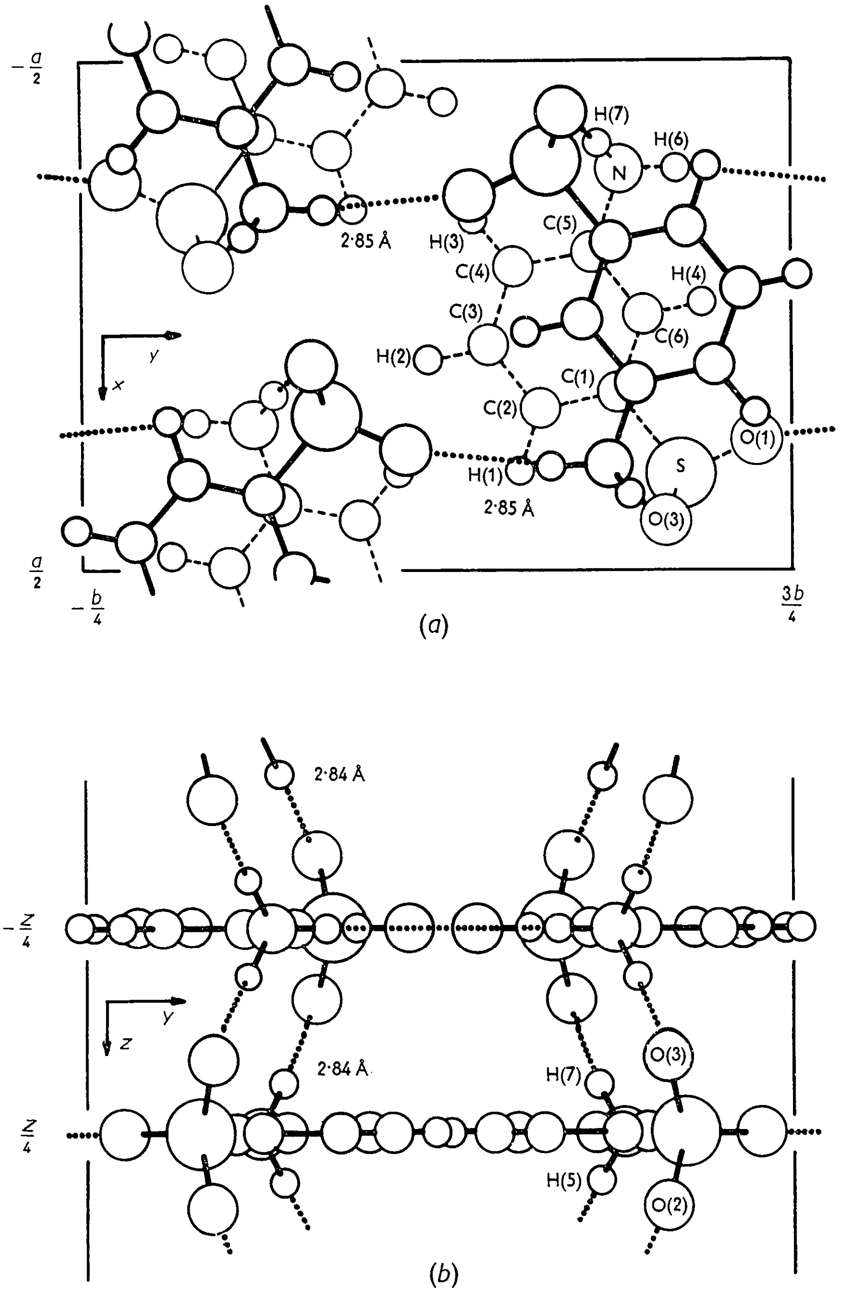


Fig. 3. Diagrammatic representation of structure projected (*a*) along the *c* axis and (*b*) along the *a* axis, showing the hydrogen-bond system (dotted lines).

system which does not involve C(1) and C(5), the relatively larger errors in their coordinates are unimportant. Moreover, as shown below, the thermal motion is entirely in accordance with what is expected, on physical grounds, in this system. These factors, with the close agreement of the final observed and calculated structure factors, indicate that the accuracy of this analysis is superior to that usually achieved in a two-dimensional study.

Possibly the most interesting feature of this analysis is the space group of the structure. This symmetry is extremely uncommon in an organic structure of this type, since it requires that the benzene ring lies exactly in the mirror plane and the NH_3^+ and SO_3^- groups symmetrical about it. The low rate of crystallization is probably a result of the latter condition since both groups, which are freely rotating in solution, must adopt this restricted orientation before solidification occurs.

The close packing of the structure with parallel planes of molecules, 3·38 Å apart, accounts for the fine needle-like habit of the crystal. Unlike sulphanilic acid monohydrate (Rae & Maslen, 1962) which has a similar interplanar distance (3·42 Å), metanilic acid is also closely packed within these planes. This explains the unusually high density of the crystals.

Intramolecular bonds and angles

The intramolecular bonds and angles listed in Table 4 are calculated from the final atomic coordinates shown in Table 2. The bond and angle standard deviations are estimated according to Cruickshank's (1949) formulae. Bonds involving hydrogen atoms are not listed since these were assumed in deriving the hydrogen positions.

The C–S and C–N bond lengths of 1·80 ± 1 and 1·44 ± 1 Å agree closely with the values of 1·80 ± 1 and 1·47 ± 1 Å given by Sutton (1958). The average C–C partial double bond length of 1·385 Å is in good agreement with the usual value of 1·395 Å. Neither C–C bonds or C–C–C angles deviate significantly from the accepted values.

The mean S–O bond length of 1·44 ± 1 Å is close to the average value of 1·45 Å given by Ondik & Smith (1962) and identical with values found in sulphanilic acid monohydrate by Rae & Maslen (1962), and in sulphamic acid by Sass (1960) and Jeffrey & Stadler (1951). The O–S–C angles are consistently less than the 109·3° and correspond to a general flattening of the SO_3^- group similar to that found by the above mentioned workers.

Table 2. *Atomic coordinates and isotropic temperature factors*

Atom	x/a	y/b	z/c	$B(hk0)$	$B(0kl)$
S	0·3114	0·6226	0·2500	—	—
O(1)	0·2400	0·7320	0·2500	1·7	—
O(2)	0·4000	0·5990	0·4270	—	2·7
O(3)	0·4000	0·5990	0·0730	—	2·7
N	−0·2880	0·5300	0·2500	2·2	—
C(1)	0·1460	0·5280	0·2500	2·1	—
C(2)	0·1790	0·4120	0·2500	2·1	—
C(3)	0·0560	0·3380	0·2500	2·1	—
C(4)	−0·0970	0·3760	0·2500	1·6	—
C(5)	−0·1270	0·4920	0·2500	2·1	—
C(6)	−0·0060	0·5670	0·2500	2·0	—
H(1)	0·2960	0·3830	0·2500	2·5	4·0
H(2)	0·0820	0·2520	0·2500	2·5	4·0
H(3)	−0·1890	0·3160	0·2500	2·5	4·0
H(4)	−0·0290	0·6520	0·2500	2·5	4·0
H(5)	−0·3410	0·5000	0·3650	3·0	4·0
H(6)	−0·2890	0·6140	0·2500	2·5	4·0
H(7)	−0·3410	0·5000	0·1350	3·0	4·0

The agreement of these bond lengths and angles with standard values within the limits of error confirms the unusually high accuracy of the projection analysis, and indicates that it may be used with confidence for the study of the hydrogen bond system.

Intermolecular bonding

From the close approach distances shown in Fig. 3 it is apparent that hydrogen bonds form the basis of the intermolecular bonding system. The distances of O(1)–N, O(2)–N and O(3)–N of 2·85, 2·84 and 2·84 Å agree closely with the normal N^+–H–O^- bond length of 2·83 Å given by Wallwork (1962) but differ significantly from the average N–H–O bond length of 2·93 Å. The angles O(1)–N–C(5), O(2)–N–C(5) and O(3)–N–C(5) of 104°, 99° and 99° and the angles O(1)–N–O(2), O(2)–N–O(3) and O(1)–N–O(3) of 125°, 101° and 125° agree roughly with a tetrahedral configuration. This and the apparent N^+–H–O^- bond

Table 3. *Anisotropic temperature factor coefficients*

	*hk*0			0*kl*		
	B_{11}	B_{12}	B_{22}	B_{22}	B_{23}	B_{33}
S	0·0042	0·0000	0·0032	0·0021	0·0000	0·0153
O(1)	—	—	—	0·0028	0·0000	0·0548
O(2)	0·0070	−0·0032	0·0063	—	—	—
O(3)	0·0070	−0·0032	0·0063	—	—	—
N	—	—	—	0·0018	0·0000	0·0131
C(1)	—	—	—	0·0026	0·0000	0·0181
C(2)	—	—	—	0·0045	0·0000	0·0240
C(3)	—	—	—	0·0035	0·0000	0·0240
C(4)	—	—	—	0·0032	0·0000	0·0230
C(5)	—	—	—	0·0023	0·0000	0·0169
C(6)	—	—	—	0·0026	0·0000	0·0180

system are in accord with the zwitterion configuration of the structure.

Thermal motion

The isotropic and anisotropic temperature factor coefficients are listed in Tables 2 and 3 respectively. These thermal parameters were refined independently because the two sets of intensity data had been collected from different crystals and under different conditions. Since temperature factor refinement from projection data is usually unreliable, the coefficients listed are not likely to have more than qualitative significance.

Table 4. *Intramolecular bond lengths and angles*

Bond	Length	e.s.d.
S–O(1)	1·44 Å	0·01 Å
S–O(2)	1·44	0·01
S–O(3)	1·44	0·01
S–C(1)	1·80	0·01
N–C(5)	1·44	0·02
C(1)–C(2)	1·41	0·02
C(2)–C(3)	1·37	0·02
C(3)–C(4)	1·38	0·02
C(4)–C(5)	1·41	0·02
C(5)–C(6)	1·36	0·02
C(6)–C(1)	1·37	0·02

Bonds	Angle	e.s.d.
O(1)–S–O(2)	113·4°	1·5°
O(1)–S–O(3)	113·4	1·5
O(2)–S–O(3)	112·2	1·5
O(1)–S–C(1)	103·9	2·0
O(2)–S–C(1)	106·5	2·0
O(3)–S–C(1)	106·5	2·0
S–C(1)–C(2)	117·3	2·0
S–C(1)–C(6)	121·4	2·0
N–C(5)–C(4)	118·8	2·0
N–C(5)–C(6)	120·6	2·0
C(1)–C(2)–C(3)	118·8	2·0
C(2)–C(3)–C(4)	120·6	2·0
C(3)–C(4)–C(5)	119·7	2·0
C(4)–C(5)–C(6)	120·6	2·0
C(5)–C(6)–C(1)	119·1	2·0
C(6)–C(1)–C(2)	121·3	2·0

The e.s.d. of the bonds and angles involving the atoms C(1) and C(5) may be underestimated owing to overlap of these sites.

Nevertheless these values correspond closely to what is expected on physical grounds. With the hydrogen-bond system in the structure, three major types of thermal vibration may be expected. Firstly, the molecule as a whole should preferentially vibrate perpendicular to the plane of the benzene ring, since there is greatest freedom in this direction. A similar motion has been observed in sulphanilic acid by Rae & Maslen (1962). Secondly the benzene ring should execute rigid body oscillations about the tightly bound sulphur and nitrogen atoms. This would give rise to significantly larger anisotropic coefficients in the $0kl$ projection for the carbons C(2), C(3) and C(4) as compared with C(1) and C(5). Thirdly, the thermal motion of the oxygen atoms would be expected to be largest perpendicular to both the attached hydrogen-bonds and the S–O bond, that is, in the direction of greatest freedom. This motion would be particularly large in the case of the oxygen atom O(1) where the two bonds, N–H–O(1) and S–O(1), are collinear and are both perpendicular to the general molecular vibration.

The temperature factor coefficients are consistent with these vibrations. In the case of the thermal motion of oxygen atoms O(2) and O(3), this is superimposed on the molecular vibration so that the overall effect appears as a high isotropic temperature factor in the $0kl$ projection and as anisotropy at 20° to the y direction in the $hk0$ projection (Fig. 1(*a*)).

One of us (S. R. H.), gratefully acknowledges the receipt of a Commonwealth Postgraduate Award.

References

Abrahamsson, S. & Maslen, E. N. (1960). *Acta Cryst.* **13**, 1001.

Abrahamsson, S. & Maslen, E. N. (1962). *Z. Kristallogr.* **118**, 1.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Dawson, B. (1960). *Acta Cryst.* **13**, 403.

Handbook of Physics and Chemistry (1960). p. 1090. Cleveland: Chem. Rubber Publishing Co.

Jeffrey, G. A. & Stadler, H. P. (1951). *J. Chem. Soc.* p. 1467.

Ondik, H. & Smith, D. (1962). In *International Tables for X-ray Crystallography*. Vol. III, p. 272.

Rae, A. I. M. & Maslen, E. N. (1962). *Acta Cryst.* **15**, 1285.

Rae, A. I. M. & Maslen, E. N. (1963). *Acta Cryst.* **16**, 703.

Sass, R. L. (1960). *Acta Cryst.* **13**, 320.

Sutton, L. E. (1958). *Tables of Interatomic Distances and Configurations in Ions and Molecules.* Special Publ. No. 11. London: The Chemical Society.

Wallwork, S. C. (1962). *Acta Cryst.* **15**, 758.