parentheses. The enumeration of the 18 distances corresponds to the numbers in Fig. 2.

The nitrogen atoms N(13) and N(14) of molecule 1 [with carbon ring atoms C(1) through C(6)] are tetrahedrally surrounded by three Cl⁻ ions Cl(23), Cl(24) and Cl(26), with the formation of six hydrogen bonds. Two of these, 3 and 6 in Table 3 and Fig. 2, take part in a strong periodic bond chain in the general direction of the *b* axis at $z \simeq 0.1$: N(14′)–H··· Cl(26)··· H–N(13)–C(1)–C(2)–C(3)–N(14). This chain and its screw symmetric equivalent at $z = -0.1$ are connected, at $y \simeq 0$ and $y \simeq \frac{1}{2}$, by the square arrangement of hydrogen bonds 1,2,4 and 5 depicted in the *b*-axis projection at $x = 1$, $z = 0$.

The nitrogen atoms of the second molecule [with carbon ring atoms C(7) through C(12)] have a different environment: N(15) takes part in the formation of the three N–H···O hydrogen bonds 7, 8 and 9, while for N(16) spatial conditions are unfavourable for hydrogen bond formation, only distance 10 being a hydrogen

bond. In conclusion, Table 3 shows that five out of the six hydroxyl hydrogen atoms take part in O–H···Cl⁻ or O–H···O hydrogen bonds.

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References

DIJKSTRA, D. (1965). Ph. D. Thesis Delft.
FLETCHER, JR., H. G. ANDERSON, L. & LARDY, H. A. (1951). *J. Org. Chem.* 16, 1238.
MOORE, F. H. (1963). *Acta Cryst.* 16, 1169.
WOLFROM, M. L., RADELL, J., HUSBAND, R. M. & McGAS-LAND, G. E. (1957). *J. Amer. Chem. Soc.* 79, 160.

The Crystal Structure of Orthanilic Acid

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Crystals of orthanilic acid, $NH_3^+C_6H_4SO_3^-$, are monoclinic, space group $P2_1/c$, with cell dimensions $a = 7.935$, $b = 6.570$, $c = 14.225$ Å, $\beta = 105°54'$, $Z = 4$.

The structure was determined by three-dimensional X-ray techniques in order to study the N–H···O⁻ bond system, which contains a 'bifurcated' bond of intra- and inter-molecular character. The hydrogen positions were confirmed by a neutron diffraction analysis of the $0kl$ projection. The final R index on the X-ray data is 0.064. The residual electron density map contains features which are due to bonding electrons. For the majority of the C–C bonds these consist of dumbell-shaped peaks which extend approximately 1 Å above and below the plane of the benzene ring.

Introduction

The investigation of the structure of orthanilic acid was undertaken as part of the programme of research on the structural properties of the anilinesulphonic acids (Fig. 1) which is in progress in this laboratory. The three compounds are similar in constitution, differing only in the point of attachment of the ions to the benzene ring. This enables a useful comparison to be made of the molecular packing and hydrogen bonding in the structures.

Sulphanilic (aniline-*p*-sulphonic) acid and metanilic (aniline-*m*-sulphonic) acid have been investigated by Rae & Maslen (1962) and Hall & Maslen (1965). Orthanilic acid was selected for a more accurate analysis because of the possibility of the structure containing

an internal hydrogen bond. Large crystals of the material can be prepared quite readily, enabling a neutron-diffraction analysis to be carried out to confirm the hydrogen positions from the X-ray structure.

Experimental

Crystal data

Orthanilic (aniline-*o*-sulphonic) acid, $NH_3^+C_6H_4SO_3^-$
$a = 7.935 \pm 0.004$, $b = 6.570 \pm 0.006$, $c = 14.225 \pm 0.005$ Å
$\beta = 105°54' \pm 6'$, $U = 713.1$ Å³, M.W. 173.1.
$D_m = 1.617 \pm 0.010$, $Z = 4$, $D_x = 1.613 \pm 0.002$ gm.cm⁻³.
Absent reflexions: $h0l$ when l is odd, $0k0$ when k is odd.
Space group: $P2_1/c$.
Crystal habit: Colourless monoclinic prisms.
Linear absorption coefficient: $\mu = 35.84$ cm⁻¹ (Cu $K\alpha$).

X-ray data

According to the *Handbook of Chemistry and Physics* (1960) orthanilic acid crystallizes as a sesquihydrate $(NH_3^+C_6H_4SO_3^- . \frac{1}{2}H_2O)$ in one form only. When a warm aqueous solution was allowed to cool slowly under uniform conditions crystals with two habits were obtained. One form consisted of needle-like or tabular prisms and the other of diamond-shaped monoclinic prisms. Both were colourless. Crystals of the former quickly deteriorated in air to white non-crystalline matter whereas those of the latter were stable. A similar deterioration had been observed in sulphanilic acid monohydrate and this suggested that the needle-like prisms were the hydrate and that the diamond-shaped monoclinic prisms were an anhydrous form. With a polarizing microscope the directions of two unit cell axes of this form were located along the diagonals of the diamond-shaped face on the crystal. Crystals were mounted about these axes and a series of photographs were taken with a Buerger precession camera. From these the crystal symmetry was established, and the cell dimensions, corrected for film shrinkage, were measured.

Two well formed crystal specimens were selected for three-dimensional X-ray data collection. The first measured 0·19 mm in depth, and 0·36 and 0·32 mm along the *a*- and *b*-axis diagonals respectively. This was mounted and aligned about the *a* axis, and intensity data were collected for the layers 0 to 6, using multi-film, multi-exposure Weissenberg techniques with Cu *Kα* radiation.

A second crystal measuring 0·37 mm in depth, and 0·75 and 0·64 mm along the *a*- and *b*-axis diagonals respectively, was mounted and aligned about the *b* axis. Intensity data for the layers 0 to 6 were collected by procedures similar to those for the first specimen.

Both sets of data were measured visually by comparison with a calibrated intensity strip. The average film factor for common reflexions on successive packs collected at an inclination angle μ equal to zero was estimated from a large number of reflexions as 2·87. This differs from the expected value* of 2·75 for 'Ilfex' film. However, variation of film transmission factors over the years has also been observed by Morimoto & Uyeda (1963). Film factors for upper layer photographs

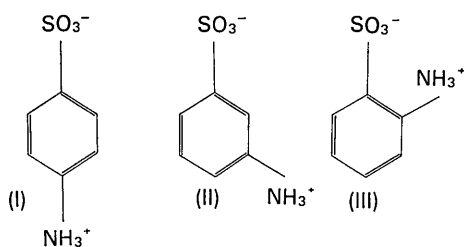*See *Acta Cryst.* (1956), **9**, 520.

Fig. 1. Chemical configuration of (I) sulphanilic acid, (II) metanilic acid and (III) orthanilic acid.

were calculated from the measured zero layer value, making allowance for the increase in effective film thickness with μ. This procedure provided more reliable film factors for short exposures than those afforded by statistical averaging of intensities on successive films. Inter-pack film factors were estimated both from exposure times and statistical averaging of common measurable reflexions.

General absorption corrections, similar to those described by Busing & Levy (1957), were applied to all reflexions. This was necessary because, although the linear absorption coefficient of the crystals was not high ($\mu = 35·8$ cm^{-1}), the large and irregularly shaped crystals resulted in a considerable range of corrections. These were applied along with the Lorentz and polarization factors in a data reduction program written by one of us (E.N.M.). In addition, this program made it possible to calculate scales between the F_o's of common (HKl)† groups. Common reflexion ratios which deviated from the mean by more than 10% and all unobserved reflexions were omitted from the scaling. The 49 (HKl) scales were then correlated in the form of a 7×7 matrix to obtain 6 layer scales relative to the first *b*-axis layer ($k = 1$) scale, which was set equal to one. The residual for the common reflections of the scaled data was 0·075, which according to the procedure of Ibers (1956) corresponds to an average $|F_o|$ standard deviation of 0·066.

Of the 1566 reflexions in the octant of the Cu *Kα* sphere, 1314 were observed and 226 were put equal to the maximum unobservable limit at that Bragg angle, $|F^u|$, and treated as described below.

Neutron data

Large crystals of orthanilic acid were grown by suspending small seed crystals in a warm aqueous solution under controlled temperature and humidity conditions. One of the more perfect crystals was shaped to form a cylinder 12 mm in length and approximately 3·5 mm in diameter, with the long axis parallel to **a**. The crystal was mounted on fine aluminum tubing and aligned on an X-ray oscillation camera.

The neutron diffraction data were collected at the Research Establishment of the Australian Atomic Energy Commission, Lucas Heights, New South Wales. The HIFAR reactor provided a primary beam of approximately 10^8 neutrons sec^{-1}cm^{-2}, which was monochromatized by reflexion from the (200) plane of a lead crystal. The monochromatic beam had an equivalent wavelength of 0·939 Å and a flux of approximately 10^5 neutrons sec^{-1}cm^{-2}. The counting apparatus consisted of a proportional BF$_3$ counter which was geared to the crystal drive in a 2:1 ratio. The scanning over an intensity peak was continuous at 6° per hour of counter movement. An arc of 3° was necessary to ensure that sufficient background was measured on either side of the peak. The counter and

† The indices H and K are constant for each group.

crystal orientations were computed prior to measurement. The neutron count rate was recorded both continuously by a chart recorder and stepwise by printout after each interval of 4·1' of counter arc (*i.e.* timing intervals of 40·9 seconds). Beam monitoring facilities were not available, but the measurement of the 002 reflexion was repeated throughout the data collection. No significant fluctuations in the level of the neutron flux were observed.

Out of a total of 201 0*kl* reflexions recorded, 86 were measurable, *i.e.* above the background level. The remainder were set at an intensity equal to the maximum unobservable limit and treated according to the unobserved reflexion criteria discussed later in this chapter. No correction for absorption or extinction was applied.

Structure determination

All non-hydrogen atoms in the structure were located from a three-dimensional Patterson synthesis sharpened for point atoms at rest. The structure was refined by least-squares procedures, using an IBM 1620 program by Mair (1963). The program uses the block diagonal approximation with a 3×3 matrix for the positional parameters and a 6×6 matrix for thermal parameters (or 1×1 if thermal motion is assumed to be isotropic) of each atom. The scale factor of observed structure factors and the overall isotropic temperature factor are refined in a 2×2 matrix and Shoemaker's corrections (Hodgson & Rollett, 1963) are applied to shifts of the thermal parameters. The weighting scheme used was $w = 1/[1 - (|F_o| - b)^2/a^2]^{\frac{1}{2}}$ (Mills & Rollett, 1960). Initially the parameters a and b in this scheme were re-evaluated after successive cycles. However in the latter stages of refinement b tended to be overestimated while a remained constant. This gave too much weight to the large structure factors. The value of b was therefore set at 4·0 electrons, which represented the most accurate value of $|F_o|$, estimated from the mean of the most reliable intensities on the first film of the film packs. Because the scheme has a maximum at $|F_o| - b$, less weight was given to reflexions with $|F_o|$ less and greater than 4·0 electrons. This is important in reducing the weights of the small $|F_o|$'s which approached the unobservable limit, $|F^u|$. Reflexions which were unobserved were given zero weight if $|F^u|$ exceeded $|F_c|$, and treated in the same way as observed reflexions if $|F^u|$ was less than $|F_c|$.

Hydrogen atoms

A three-dimensional difference synthesis phased from the structure factors after the fifth cycle of least squares showed peaks ranging in height from 0·6 to 0·8 e.Å^{-3} at or close to the expected sites of the seven hydrogen atoms in the molecule. The four benzene ring hydrogen atoms were at the positions expected from the stereochemistry of the trigonal bonds, assuming a C–H bond length of 1·085 Å. The other three hydrogen atoms were restricted to the circum-

ference of a circle of radius 0·97 Å centred at the intersection of the produced C–N bond and a plane perpendicular to it, 0·34 Å from the nitrogen. Sections of the difference syntheses in the plane of the benzene ring and in the plane of the NH$_3^+$ group hydrogens are shown in Fig.2. At this time 0*kl* neutron diffraction structure factors were calculated for all non-hydrogen atom parameters using the scattering lengths $b_{\text{sulphur}} = 0·310$, $b_{\text{oxygen}} = 0·577$, $b_{\text{nitrogen}} = 0·940$ and $b_{\text{carbon}} = 0·661 \times 10^{-12}$ cm (Bacon, 1962). The resulting structure factor residual was 0·30. A [100] projection difference synthesis phased from these structure factors showed (Fig.3) well resolved negative peaks of height ranging from $-0·75$ to $-1·75 \times 10^{-12}$ cm.Å^{-2} at the sites of the hydrogen atoms. The initial sites of the hydrogen atoms were a compromise between the values obtained from the X-ray and neutron difference syntheses.

X-ray refinement of non-hydrogen atomic parameters was continued including the hydrogen atoms in the structure factor calculation with isotropic temperature factor coefficients of 4·0 Å^{-2}. The residual decreased to 0·085 with four least-squares cycles. The
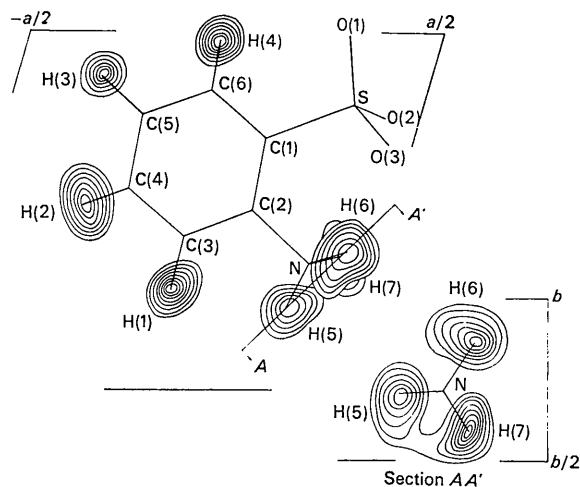
Fig.2. A three-dimensional difference synthesis projected (top left) perpendicularly to the plane of the benzene ring and (bottom right) along the C–S polar axis. Contours are from 0·1 e.Å^{-3} in intervals of 0·1 e.Å^{-3}.
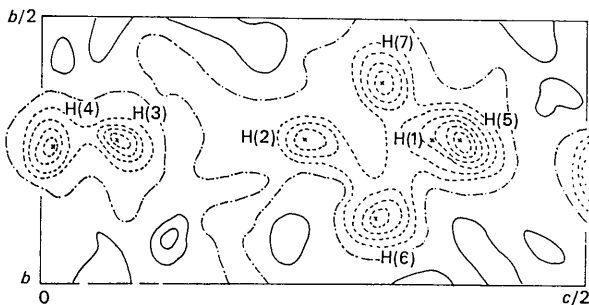

Fig.3. A [100] projection neutron difference synthesis phased from structure factors excluding the hydrogen contribution. The zero contour is chain dotted and the negative contour dashed, at intervals of 0·25 × 10^{-12} cm Å^{-2}.

pronounced anisotropy of the non-hydrogen atoms suggested, however, that the isotropic motion attributed to the hydrogens was a poor approximation. An estimate of the hydrogen atom anisotropy was made from the molecular vibrations of the non-hydrogen atoms. The translational and rotational thermal vibrational tensors, T_{ij} and ω_{ij}, were estimated as described by Cruickshank (1956a) with an origin and system of axes discussed below. The b_{ij} matrix for the benzene ring hydrogen atoms was then estimated from these tensors. Because the thermal motion of the hydrogens in the NH_3^+ group was uncertain these atoms were given the same b_{ij}'s as the nitrogen atom. Adjustments to the hydrogen positional and thermal parameters were estimated from successive cycles of neutron and X-ray structure factor and difference syntheses. Although hydrogen atoms may be expected to have a higher thermal motion than the more restricted, tighter bound non-hydrogen atoms, evidence to date indicates that hydrogen temperature factors refined from X-ray diffraction data tend to be lower than the overall value of the structure. It has been suggested (Stewart, Davidson & Simpson, 1965; Jensen, 1965) that this is a result of using the scattering factor calculated for a free hydrogen atom rather than those for the bonded case. As the hydrogen atoms contribute appreciably to the X-ray scattering only at low Bragg angles the progress of the X-ray refinement was assessed from the residual on the terms with $\sin \theta/\lambda$ less than 0.36 Å^{-1}. After four cycles of refinement no significant features remained in the synthesis, and refinement of the hydrogen atom parameters was discontinued. The residuals* of the low angle X-ray

data and neutron data were 0.054 and 0.098 respectively, compared with 0.057 and 0.240 before the start of the hydrogen atom refinement.

Secondary extinction

Examination of the structure factor agreement analysis following the inclusion of the hydrogen atoms showed that the high $|F_c|$ values were consistently larger than the corresponding $|F_o|$ values, and a plot of I_c/I_o versus I_c showed an approximately linear relationship, indicating secondary extinction effects.

The variation of the effect of secondary extinction with crystal shape and size made it necessary to correct the a- and b-axis intensity data separately. An estimate of the secondary extinction coefficient was obtained by means of the empirical relationship $I_c/I_o = \varepsilon I_c - K$ which is similar to that suggested by Hamilton (1957) for the case where I_c/I_o exceeded 1.5. The coefficient ε was calculated from this equation both by a least-squares method weighted according to I_c, and by plotting the values of I_c/I_o for integral ranges of I_c. These plots are shown in Fig. 4. There was excellent agreement between both methods, the final values of ε being 1.38×10^{-5} and 2.05×10^{-5} for the a- and b-axis data respectively. These values are consistent with the relative sizes of the crystals used in the data collection. After application of the corrections, the data reduction process described earlier was repeated. This resulted in significant improvements in the agreement of the ratio of (HKl) reflexions and lower deviations of the interlayer scales. Application of these scales reduced the residual between common reflexions to 0.073 and $\sigma|F_o|$ to 0.065. Furthermore the structure factor residual decreased by 0.01 in the two succeeding rounds of refinement, confirming the improvement in accuracy of the data. Refinement was discontinued after two further rounds of least-squares, when all shifts were less than 0.2 of the standard deviation. The final residual was 0.064.

Upper angle refinement

Although the refinement using the full data appeared to have been satisfactory it was felt advisable to conduct a second refinement using the upper angle data only, since the exact distribution of charge in the NH_3^+ and SO_3^- groups is uncertain and the neutral scattering factors are only a reasonable approximation. The procedure has the further advantage that it reduces the effect of errors due to secondary extinction and aspherical scattering, which are in general difficult to compensate for accurately in a structure analysis. However the reduction in the number of terms and angular range of the data reduces the nominal accuracy of the analysis, and especially of the thermal parameters. The scattering factor curves of neutral and ionized nitrogen, as well as those for oxygen and sulphur,
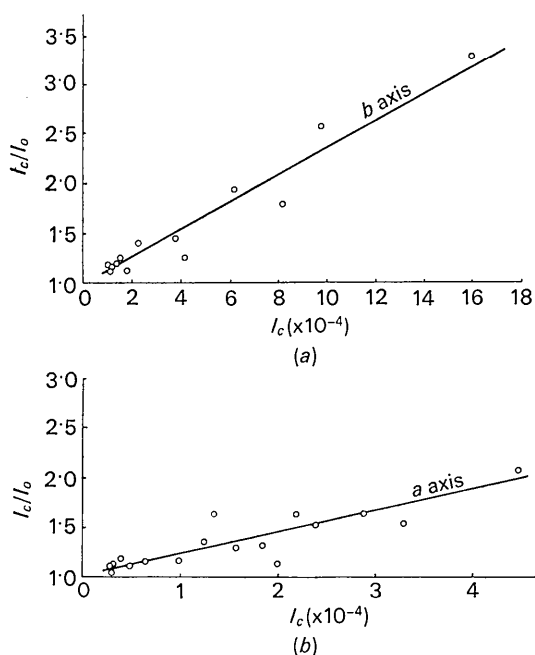
Fig. 4. Plots of I_c/I_o versus I_c for X-ray diffraction data collected about (a) the b axis and (b) the a axis showing secondary extinction effects.

* Defined as $\Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|$ for all reflexions except those unobserved, where $|F^u| > |F_c|$.

differ significantly only for sin θ/λ less than 0·4 Å^{-1}. Moreover the aspherical scattering curves for carbon (McWeeny, 1954), nitrogen, oxygen and sulphur (Dawson, 1964) do not differ significantly from the mean isotropic values above this limit. Further refinement was therefore carried out with only that part of the data with sin θ/λ greater than 0·4 Å^{-1}. After four cycles of least-squares the thermal and positional shifts did not exceed 0·2 times the standard deviations, and the refinement was discontinued. The upper and full Bragg angle data residuals were 0·068 and 0·064, respectively. A list of the observed and calculated structure factors for both the X-ray and neutron data has been deposited with the library at the University of Western Australia. Copies are available on request.

Discussion

Assessment of accuracy

The final structure factor residual of 0·064 is in close agreement with the accuracy of 0·065 estimated during the data correlation .The electron density standard deviation $\sigma(\varrho)$ was 0·13 e.Å^{-3} calculated according to Cruickshank (1949). This value is consistent with the low background obtained both in the three-dimensional difference synthesis used to locate the hydrogen atom and in the final difference synthesis used to study the valence electrons. The standard deviations of the final non-hydrogen atomic parameters were calculated from the least-squares sums. These are listed, with positional and thermal parameters refined with the upper angle data, in Tables 1 and 2. The standard deviations of the sulphur atom b_{ij}'s will be underestimated, however, because of the omission of dispersion corrections from this analysis. The hydrogen parameters are listed in Table 3. It is difficult to estimate the errors in these parameters since the refinement process involved two sets of completely independent data, X-ray and neutron. However the final shifts from difference synthesis methods indicate a coordinate standard deviation of about 0·025 Å.

In general the structural parameters refined with full angle data and upper angle data do not differ significantly. The two exceptions are the sulphur atom b_{ij}'s, which are substantially lower in the results of

the upper angle data, and the increase of the overall F_0 scale from 0·849 to 0·880. These changes appear to result from the correlation between the scale factor and the thermal parameters of all atoms, but particularly those of the sulphur atom. Although there are no significant differences in the carbon atom positional parameters (see Table 1) it is interesting to note that
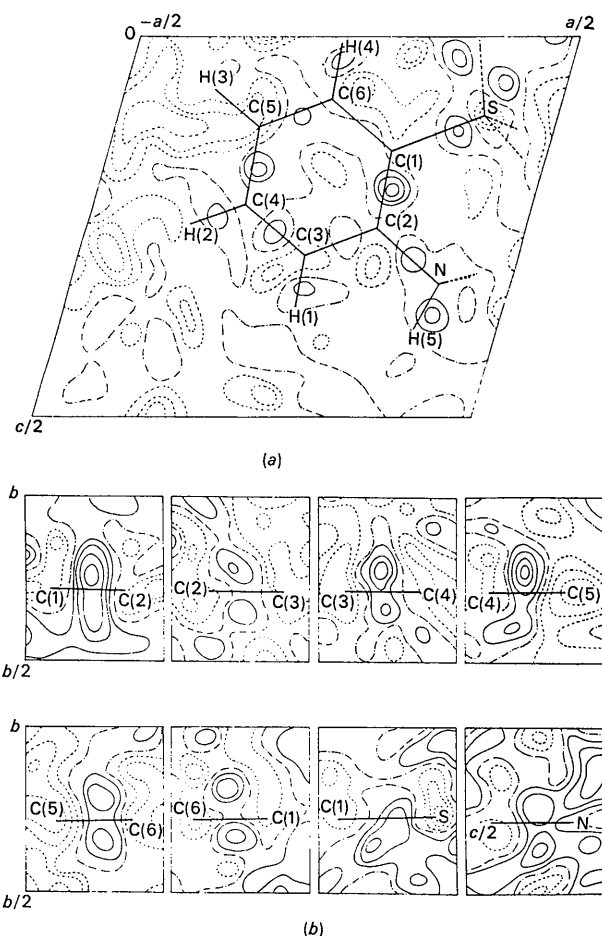

(a)

(b)

Fig. 5. (a) A section in the plane of the benzene ring of a three-dimensional difference synthesis phased from the final structure factors. (b) Sections of the final three-dimensional difference synthesis along each C–C, C–N and C–S bond perpendicular to the benzene ring. Positive contours full lines, negative contours dashed lines, at intervals of 0·1 e.Å^{-3}.

Table 1. Atomic coordinates

| | All data | | | Upper angle data | | | | | |
	x/a	y/b	z/c	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
S	0·33196	0·73142	0·10660	0·33189	0·73150	0·10658	0·00009	0·00013	0·00005
O(1)	0·26816	0·77709	0·00446	0·26789	0·77745	0·00404	0·00045	0·00090	0·00021
O(2)	0·41077	0·53527	0·12541	0·41024	0·53467	0·12509	0·00050	0·00071	0·00035
O(3)	0·43982	0·88753	0·16302	0·44119	0·88658	0·16358	0·00051	0·00078	0·00030
N	0·33546	0·71977	0·32333	0·33502	0·71957	0·32331	0·00036	0·00050	0·00019
C(1)	0·14425	0·72277	0·15185	0·14457	0·72314	0·15157	0·00038	0·00050	0·00021
C(2)	0·16129	0·71739	0·25220	0·16139	0·71707	0·25224	0·00039	0·00050	0·00021
C(3)	0·01460	0·71176	0·28655	0·01414	0·71191	0·28651	0·00043	0·00055	0·00025
C(4)	−0·15149	0·71026	0·22104	−0·15196	0·71049	0·22081	0·00045	0·00061	0·00029
C(5)	−0·16923	0·71417	0·12208	−0·16964	0·71355	0·12174	0·00044	0·00070	0·00029
C(6)	−0·02364	0·72136	0·08655	−0·02313	0·72128	0·08597	0·00046	0·00066	0·00025

the carbon–carbon bonds [Table 5(a)] are consistently longer for parameters refined with upper angle data. These increases are less than the standard deviations but their consistency suggests that this is a real effect. A section of the final three-dimensional difference syntheses in the plane of the benzene ring [Fig. 5(a)] showed only small features which could be attributed to σ-electrons. However sections along the C–C bonds, perpendicular to the plane of the benzene ring, showed peaks [Fig. 5(b)] of height ranging from 0·15 to 0·45 e.Å^{-3} at 0·5 Å above and below the bond. The peaks are not individually significant when compared

Table 2. *Thermal parameters*

The temperature factor is of the form exp $[-(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)]$

All data

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
S	0·00587	0·00055	0·00276	0·01819	0·00006	0·00174
O(1)	0·01349	0·00904	0·00495	0·05256	0·00645	0·00244
O(2)	0·01442	0·02032	0·01021	0·02947	0·00719	0·00777
O(3)	0·01542	−0·02569	0·01139	0·03679	−0·01007	0·00590
N	0·00767	−0·00016	0·00245	0·01841	−0·00003	0·00212
C(1)	0·00669	−0·00038	0·00325	0·01404	−0·00004	0·00231
C(2)	0·00693	−0·00088	0·00270	0·01277	−0·00054	0·00239
C(3)	0·00846	−0·00151	0·00504	0·01552	0·00008	0·00308
C(4)	0·00809	−0·00397	0·00508	0·01662	−0·00013	0·00420
C(5)	0·00740	−0·00064	0·00222	0·02225	0·00083	0·00410
C(6)	0·00802	−0·00100	0·00227	0·02122	−0·00098	0·00282

Upper angle data

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
S	0·00507	0·00045	0·00258	0·01719	0·00002	0·00144
O(1)	0·01229	0·00945	0·00470	0·05231	−0·00685	0·00218
O(2)	0·01332	0·02010	0·01035	0·02825	0·00739	0·00769
O(3)	0·01498	−0·02670	0·01160	0·03697	−0·01074	0·00560
N	0·00727	−0·00058	0·00202	0·01740	−0·00007	0·00176
C(1)	0·00584	0·00063	0·00297	0·01272	0·00017	0·00200
C(2)	0·00639	−0·00039	0·00265	0·01196	−0·00049	0·00197
C(3)	0·00776	−0·00143	0·00436	0·01471	−0·00000	0·00250
C(4)	0·00713	−0·00435	0·00562	0·01650	−0·00035	0·00402
C(5)	0·00565	−0·00129	0·00160	0·02209	0·00075	0·00347
C(6)	0·00772	−0·00056	0·00161	0·02067	−0·00136	0·00233

	$\sigma(b_{11})$	$\sigma(b_{12})$	$\sigma(b_{13})$	$\sigma(b_{22})$	$\sigma(b_{23})$	$\sigma(b_{33})$
S	0·00009	0·00021	0·00008	0·00018	0·00011	0·00003
O(1)	0·00049	0·00141	0·00040	0·00158	0·00070	0·00012
O(2)	0·00054	0·00125	0·00061	0·00101	0·00082	0·00024
O(3)	0·00056	0·00143	0·00056	0·00122	0·00081	0·00019
N	0·00039	0·00085	0·00034	0·00068	0·00045	0·00011
C(1)	0·00041	0·00084	0·00037	0·00066	0·00047	0·00013
C(2)	0·00042	0·00084	0·00038	0·00065	0·00046	0·00013
C(3)	0·00046	0·00095	0·00042	0·00071	0·00053	0·00014
C(4)	0·00047	0·00100	0·00048	0·00081	0·00062	0·00018
C(5)	0·00046	0·00107	0·00045	0·00096	0·00067	0·00017
C(6)	0·00048	0·00108	0·00043	0·00090	0·00059	0·00014

Table 3. *Hydrogen atom parameters*

	x/a	y/b	z/c
H(1)	0·0345	0·7132	0·3657
H(2)	−0·2594	0·7000	0·2517
H(3)	−0·3012	0·7091	0·0649
H(4)	−0·0411	0·7155	0·0063
H(5)	0·3350	0·7208	0·3922
H(6)	0·4026	0·8463	0·3142
H(7)	0·3944	0·5870	0·3170

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
H(1)	0·0162	−0·0008	0·0058	0·0322	−0·0004	0·0055
H(2)	0·0220	−0·0010	0·0053	0·0375	−0·0002	0·0062
H(3)	0·0179	−0·0015	0·0040	0·0430	−0·0002	0·0053
H(4)	0·0098	−0·0013	0·0031	0·0280	−0·0003	0·0032
H(5)	0·0096	0·0001	0·0032	0·0255	−0·0008	0·0027
H(6)	0·0080	0·0001	0·0035	0·0180	−0·0009	0·0040
H(7)	0·0120	0·0001	0·0033	0·0260	−0·0008	0·0030

Table 4(a). Thermal vibration ellipsoids

The mean square vibrational displacements are given in Å² together with their direction cosines A_{i1}, A_{i2}, A_{i3} with respect to the three axes a, b and c^*.

	B_1	B_2	B_3	A_{11}	A_{12}	A_{13}	A_{21}	A_{22}	A_{23}	A_{31}	A_{32}	A_{33}
S	1·31	2·96	0·80	−0·857	0·020	−0·514	−0·024	−0·999	0·001	−0·514	0·014	0·857
O(1)	2·71	9·30	1·27	−0·987	0·153	−0·032	−0·147	−0·980	−0·129	−0·052	−0·122	0·991
O(2)	1·63	7·22	4·31	0·852	−0·474	−0·217	0·503	0·633	0·587	0·140	0·610	−0·779
O(3)	3·06	8·63	1·54	−0·245	−0·507	−0·826	0·510	−0·792	0·334	0·824	0·339	−0·453
N	1·69	3·00	1·30	−0·991	−0·044	0·120	0·044	−0·999	−0·003	0·120	0·002	0·992
C(1)	2·20	1·60	1·10	−0·087	−0·995	−0·042	−0·697	0·091	−0·710	0·710	−0·032	−0·702
C(2)	1·58	2·07	1·27	−0·813	−0·158	−0·558	0·098	−0·985	0·135	−0·572	0·055	0·818
C(3)	2·13	2·56	1·26	−0·741	−0·198	−0·641	0·213	−0·975	0·054	−0·636	−0·096	0·765
C(4)	1·16	3·17	2·85	0·868	0·240	−0·433	0·491	−0·531	0·690	0·064	0·812	0·579
C(5)	1·30	3·84	2·68	0·998	0·050	0·014	0·052	−0·986	−0·155	0·006	0·156	−0·987
C(6)	3·60	1·96	1·62	0·108	−0·991	0·131	−0·700	0·081	0·709	0·713	0·105	0·692

Table 4(b). Molecular vibration tensors, T_{ij}, ω_{ij}

Planar part of the molecule. Origin at midpoint between sulphur and nitrogen atoms.

T_{11}	T_{22}	T_{33}	T_{12}	T_{23}	T_{13}
0·0141 (14)	0·0300 (19)	0·0193 (11)	−0·0006 (14)	0·0011 (12)	−0·0021 (10)
ω_{11}	ω_{22}	ω_{33}	ω_{12}	ω_{23}	ω_{13}
0·0009 (2)	0·0011 (2)	0·0018 (6)	−0·0000 (2)	0·0002 (4)	0·0012 (2)

Covariance (0) = 0·00000880

SO_3^- group. Origin at midpoint of three oxygen atoms

T_{11}	T_{22}	T_{33}	T_{12}	T_{23}	T_{13}
0·0141 (86)	0·0469 (51)	0·0166 (51)	−0·0041 (55)	−0·0046 (44)	0·0020 (55)
ω_{11}	ω_{22}	ω_{33}	ω_{12}	ω_{23}	ω_{13}
0·0348 (37)	0·0096 (63)	0·0090 (65)	−0·0011 (46)	0·0008 (37)	0·0136 (47)

Covariance (0) = 0·00007577
The standard deviations are given in parentheses.

Table 5(a). Bond lengths (Å)

	Length from full data	Length from upper angle data	Thermal correction	Corrected length	σ
S–O(1)	1·432	1·438	0·019	1·457	0·01
S–O(2)	1·425	1·427	0·023	1·450	0·01
S–O(3)	1·431	1·435	0·022	1·457	0·01
S–C(1)	1·778	1·773	0·001	1·774	0·003
N–C(2)	1·470	1·466	0·003	1·469	0·005
C(1)–C(2)	1·396	1·401	0·002	1·403	0·005
C(1)–C(6)	1·398	1·398	0·002	1·400	0·006
C(2)–C(3)	1·381	1·384	0·001	1·385	0·004
C(3)–C(4)	1·388	1·389	0·002	1·391	0·006
C(4)–C(5)	1·375	1·377	0·002	1·379	0·006
C(5)–C(6)	1·383	1·392	0·000	1·392	0·005

Table 5(b). Bond angles (°)

	Value from full data	Value from upper angle data	Thermal correction	Corrected value	σ
O(1)–S–O(2)	113·2	113·0	+0·4	113·4	0·3
O(1)–S–O(3)	114·0	114·4	+0·3	114·7	0·3
O(1)–S–C(1)	106·0	106·0	−0·5	105·5	0·2
O(2)–S–O(3)	112·2	111·9	0·0	111·9	0·3
O(2)–S–C(1)	105·7	105·7	−0·1	105·6	0·2
O(3)–S–C(1)	104·5	104·7	−0·1	104·6	0·2
S–C(1)–C(2)	121·0	121·0	0·0	121·0	0·3
S–C(1)–C(6)	119·9	119·8	0·0	119·8	0·3
C(2)–C(1)–C(6)	119·0	119·1	+0·1	119·2	0·3
N–C(2)–C(1)	120·7	120·7	+0·1	120·8	0·3
N–C(2)–C(3)	118·7	118·7	0·0	118·7	0·3
C(1)–C(2)–C(3)	120·5	120·5	0·0	120·5	0·3
C(2)–C(3)–C(4)	119·9	119·9	0·0	119·9	0·3
C(3)–C(4)–C(5)	119·8	119·8	0·0	119·9	0·3
C(4)–C(5)–C(6)	120·9	120·9	+0·1	121·0	0·4
C(1)–C(6)–C(5)	119·7	119·5	0·0	119·5	0·3

with the electron density standard deviation but their consistency from bond to bond suggests that they may be real.

The residual density features are in excellent agreement with the observations of O'Connell, Rae & Maslen (1966). The peaks have a maximum extension of approximately 1·0 Å above and below the plane of the ring system, compared with 0·4 Å in the plane. The peak with the greatest height in the plane is that on the bond between C(1) and C(2). This is also the least dumbell shaped. The C(1)–C(2) bond is the only C–C bond in the system which does not involve carbon atoms with hydrogen substituents. O'Connell, Rae & Maslen predict that the positions of aromatic carbon atoms with hydrogens attached are displaced towards the ring centre. This reduces the in-plane part of the residual density contributed by the bonding electrons, resulting in dumbell shaped peaks unless the thermal motions of the atoms are high enough to obscure them. The temperature factor coefficients in the orthanilic acid structure are remarkably low for an organic material, and the residual density features appear to provide strong evidence in support of O'Connell, Rae & Maslen's predictions. The observations on one structure cannot be regarded as complete confirmation, however, in view of the sensitivity of the difference synthesis to scale and temperature factor errors.

Thermal parameters

The thermal parameters of the non-hydrogen atoms in orthanilic acid are shown with their estimated standard deviations in Table 2. The thermal motions of these atoms and the steric forces influencing their anisotropy may be studied in terms of the individual atomic vibrations and molecular librations.

The magnitudes of the principle modes of the individual vibrational ellipsoids and the direction cosines of these modes to the unit cell axes a, b and c^* are listed in Table 4(a). All atoms show high anisotropy in the y direction, *i.e.* perpendicular to the plane of the molecule. There is, however, a general increase in the vibrational modes for atoms furthest from the sulphur and nitrogen atoms, indicating that the molecule oscillates about these two atoms. The thermal ellipsoids of the sulphur, nitrogen and carbon atoms are considerably less than those of the oxygen atoms. This is in agreement with the higher degree of freedom of the oxygen atoms and the concept that the SO_3^- group is largely free to rotate about the sulphur–carbon bond. The relative forms of the oxygen vibrational ellipsoids appear to be due to the molecular translational vibrations superimposed on the rotational oscillations of the SO_3^- group. The anisotropy of O(1) is larger than for the other two oxygen atoms, as is expected both from its direction of greatest freedom being parallel to the direction of largest molecular motion and the collinearity of the S–O(1) bond and the O(1)$\cdots$H(5)′–N′ hydrogen bond.

The molecular vibrational tensors, T_{ij} and ω_{ij}, are in accord with these concepts, and generally account for the b_{ij}'s within the limits of the standard deviations. If this structure contained no strong intermolecular forces the origin of the rigid body vibrations would be expected to coincide with the molecular centre of gravity. On the other hand, for a structure such as orthanilic acid, containing strong intermolecular bonds, it is expected that the molecule would tend to oscillate more nearly about the atoms involved in this bonding. A comparison of the covariance between the observed and calculated thermal motions about the centre of gravity on one hand, and the mid-point between the nitrogen and sulphur atoms on the other, indicated this was substantially the case. The results of the rigid thermal motion calculation with the origin midway between the nitrogen and sulphur atoms and the molecular axes, (1) passing through the sulphur atom site, (2) normal to the plane of the benzene ring and (3) orthogonal to axes (1) and (2), are shown in Table 4(b).

In addition to the rigid body oscillations of the planar part of the molecule it was evident from the thermal ellipsoid calculations that there was rotational oscillation of the SO_3^- group about the C–S axis. The T_{ij} and ω_{ij} tensors calculated with the origin at the centre of the three oxygen atoms and the molecular axes, (1) along the C–S axis, (2) perpendicular to the S–O (1) bond and (3) orthogonal to axes (1) and (2), are given in Table 4(b). These show that in addition to large translational vibrations perpendicular to the plane of the benzene ring there were very large oscillations about the C–S polar axis. This type of oscillation is expected in view of the high degree of freedom about this axis.

Corrections to the atomic coordinates to allow for the oscillations were calculated according to the procedure suggested by Cruickshank (1956b, 1960). The bond lengths and angles calculated from the corrected coordinates are compared with the uncorrected values in Table 5(a). The corrections, except for those involving the oxygen atoms, do not exceed the bond standard deviations.

Molecular plane

The best plane through the sulphur, nitrogen and carbon atom sites was calculated by the least-squares method. The four benzene ring hydrogen atoms were included in the calculation with zero weight. The equation of the best plane is $0·026x - 0·995y - 0·018z = 1·797$ Å. No hydrogen or non-hydrogen atoms attached to the benzene ring deviate significantly from the best plane.

Bond lengths and angles

The intramolecular bond lengths and angles are listed in Tables 5(a) and 5(b) and shown diagrammatically in Fig. 7. These values include the corrections for molecular oscillations of the non-hydrogen atoms.

The sulphur–carbon bond length of $1\cdot774\pm0\cdot003$ Å is in agreement with the values of $1\cdot77\pm0\cdot02$ and $1\cdot80\pm0\cdot02$ Å obtained for sulphanilic acid (Rae & Maslen, 1962) and metanilic acid (Hall & Maslen, 1965). Neither of the latter structures is particularly accurate, however, as their values are affected by the overlap of atomic sites in projection. The value compares closely with a similar $sp^2 - sp^3$ C–SO_3^- bond length of $1\cdot775\pm0\cdot004$ Å given by Saunderson (1965) but is considerably shorter than the more frequently quoted $sp^3 - sp^3$ C–S bond lengths of $1\cdot80\pm0\cdot01$ Å (Sutton, 1958) and $1\cdot805\pm0\cdot012$ Å (Sutherland & Young, 1963)
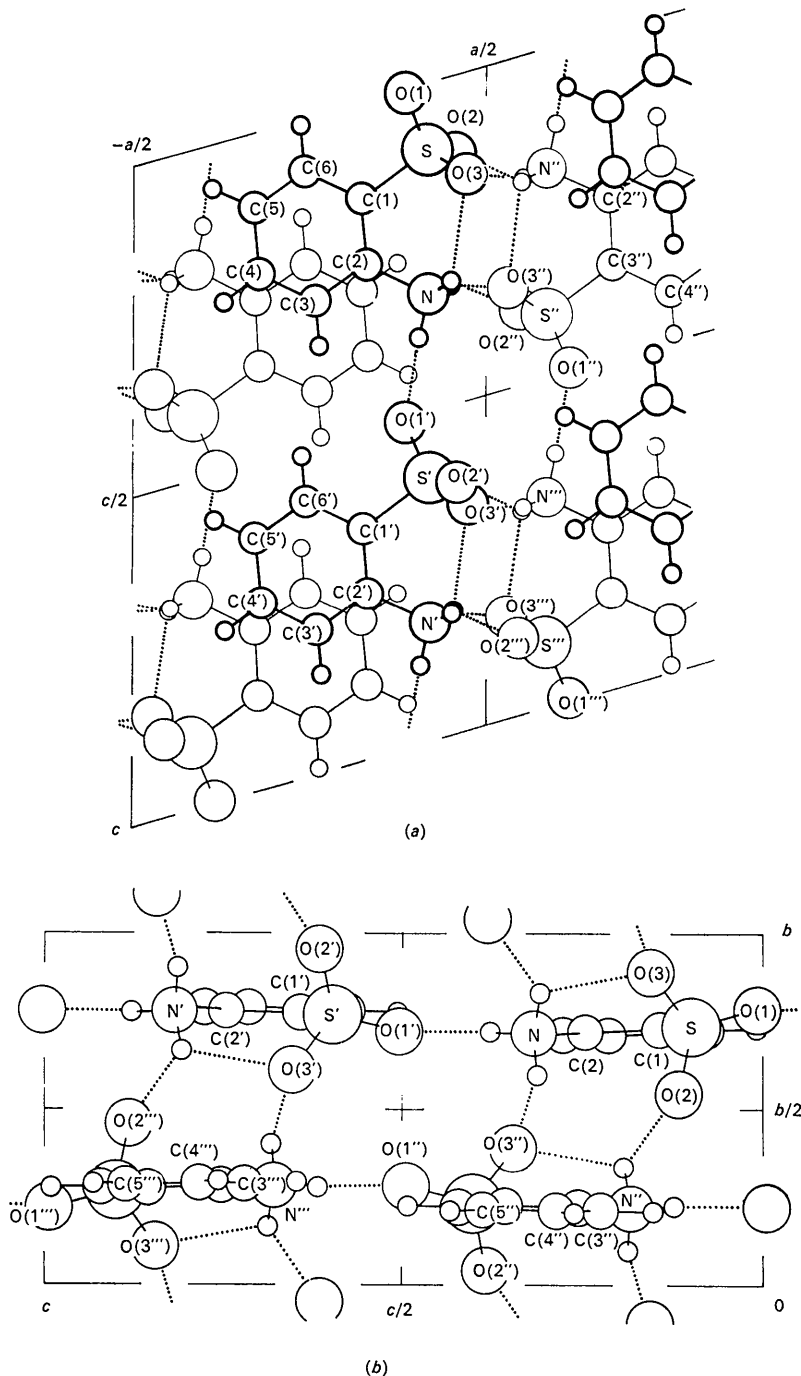
Fig. 6. A diagrammatic representation of the structure projected (a) along the b axis and (b) along the a axis. Dotted lines indicate the proposed hydrogen bonds. The superscripts ′, ″ and ‴ denote the equivalent positions at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(1 - x, 1 - y, 1 - z)$ respectively.

The difference in bond lengths is similar to those found between sp^2-sp^3 and sp^3-sp^3 C–C bonds which are discussed below.

The carbon–nitrogen bond length of $1\cdot468\pm0\cdot005$ Å is comparable with the less accurate values of $1\cdot49\pm$ $0\cdot03$ and $1\cdot44\pm0\cdot02$ Å reported for sulphanilic and metanilic acids. The accurate $C-NH_3^+$ bond lengths which are available all refer to sp^3-sp^3 single bonds rather than the sp^2-sp^3 bond type present in this structure. It is possible, however, to estimate the expected shortening from a study of equivalent C–C bonds The average sp^3 C–C bond length given by Stoicheff (1962) and Bastiansen & Traetteberg (1962) as $1\cdot536$ Å differs by about $0\cdot035$ Å from the sp^2-sp^3 C–C bond of $1\cdot501$ Å. The difference agrees closely with that of the average sp^3-sp^3 $C-NH_3^+$ bond length of $1\cdot503$ Å given by Hahn (1957) and the sp^2-sp^3 bond length of $1\cdot468\pm0\cdot005$ Å in orthanilic acid.

The aromatic carbon–carbon bond lengths do not deviate significantly from the mean value of $1\cdot395\pm$ $0\cdot003$ Å quoted by Kennard (1962). The mean C–C bond length of $1\cdot392$ Å compares favourably with this value. The deviations of the individual bond lengths, although not significant, are consistent with the steric forces which arise from the proximity of the NH_3^+ and the SO_3^- groups in the molecule. The van der Waals radii of the oxygen and hydrogen atoms should produce an orientation of the groups where there is little or no steric hindrance, but the formation of an internal hydrogen bond is favoured energetically. However, in the crystalline state the strong $N-H\cdots O^-$ bonds attached to the hydrogen atoms H(5) and H(7) restrict the position of the third atom H(6) to one where there is considerable steric hindrance between the groups. This is shown by the enlargement of the angles S–C(1)–C(2) and N–C(2)–C(1), suggesting that
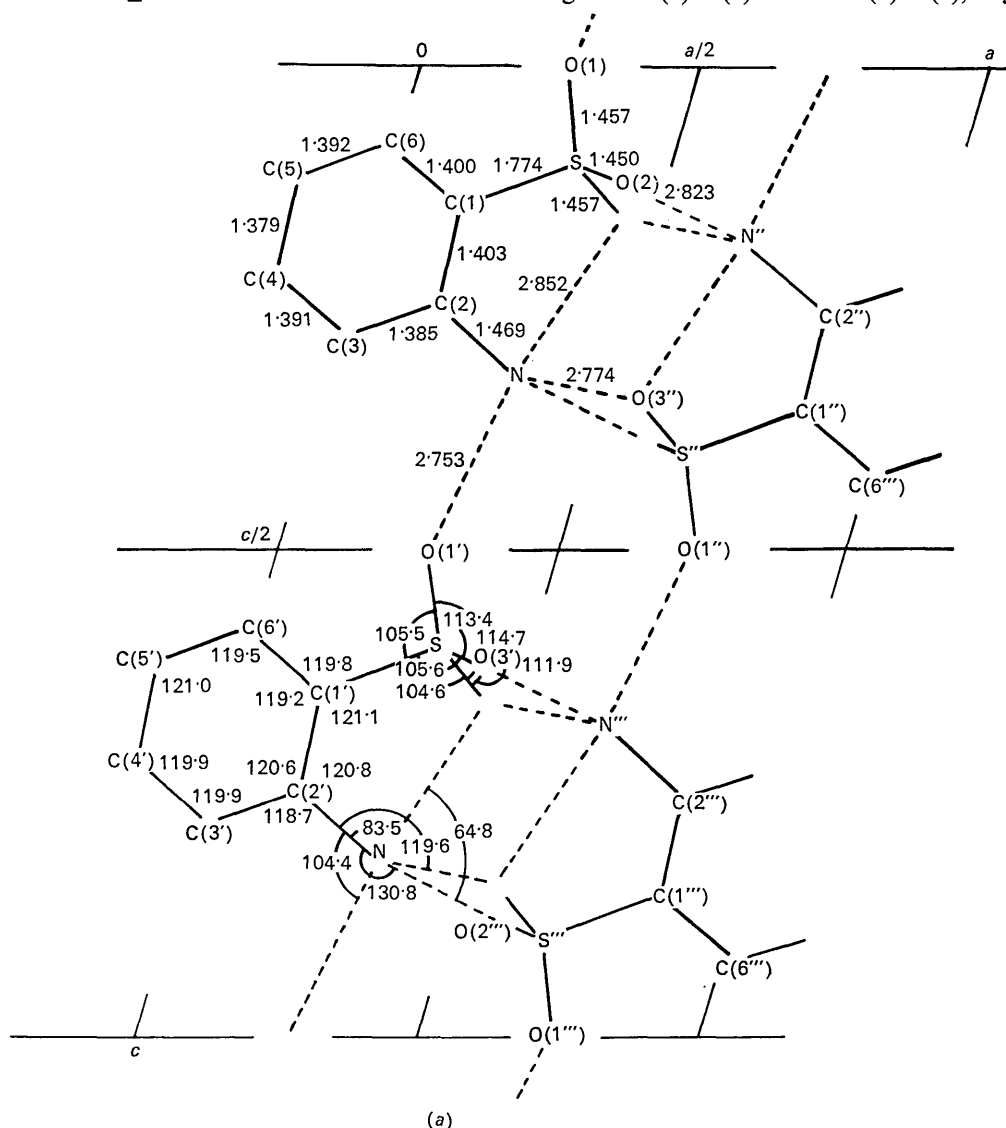

(a)

Fig. 7. (a) A diagrammatic representation of the structure showing close contacts, bond lengths and angles involving non-hydrogen atoms. Atom numbering as for Fig. 6.

the energy required for the distortion of the molecule is less than that contributed by the formation of the intermolecular N–H(5)···O(1′) and N–H(7)···O(3″)* bonds. A similar effect arising from the proximity of the CO₂ and NH₂ groups in 2-amino-3-methylbenzoic acid has been observed by Brown & Marsh (1963). This structure also contains an internal hydrogen bond. Small distortions of the C–C bond lengths in this structure and in orthanilic acid also appear to arise from the steric repulsion of the internally hydrogen bonded groups.

The average sulphur–oxygen bond length of 1·454 ± 0·005 Å agrees closely with the value of 1·45 Å given by Ondik & Smith (1962). It is slightly longer than the

* The superscripts ′, ″, ‴ and ⁱᵛ represent atoms at the equivalent positions (x,y,z), $(x,\frac{3}{2}-y,\frac{1}{2}+z)$, $(1-x,-\frac{1}{2}+y,\frac{1}{2}-z)$, $(1-x,1-y,1-z)$, $(1-x,\frac{5}{2}-y,\frac{1}{2}+z)$ in the unit cell respectively.

mean value of 1·44 Å found in metanilic, sulphanilic and sulphamic (Sass, 1960) acids and that of 1·441 ± 0·004 given by Saunderson (1965). However, these structures have not been corrected for the thermal oscillations of the SO_3^- group which are expected to be at least comparable to those in orthanilic acid.

Neither the carbon–hydrogen or nitrogen–hydrogen bonds deviate significantly from the accepted values of 1·08 ± 0·01 Å (Kennard, 1962) and 1·03 ± 0·01 Å (Ondik & Smith, 1962).

As indicated earlier, the proximity of the NH_3^+ and SO_3^- groups accounts for the increased angles S–C(1)–C(2) and N–C(2)–C(1) of 121·1° and 120·7°. No C–C–C angles deviate significantly from 120°. The C–S–O angles are consistent with values found in sulphanilic, metanilic and sulphamic (Sass, 1960) acids, showing a noticeable departure of the SO_3^- group from the regular tetrahedral configuration. It is
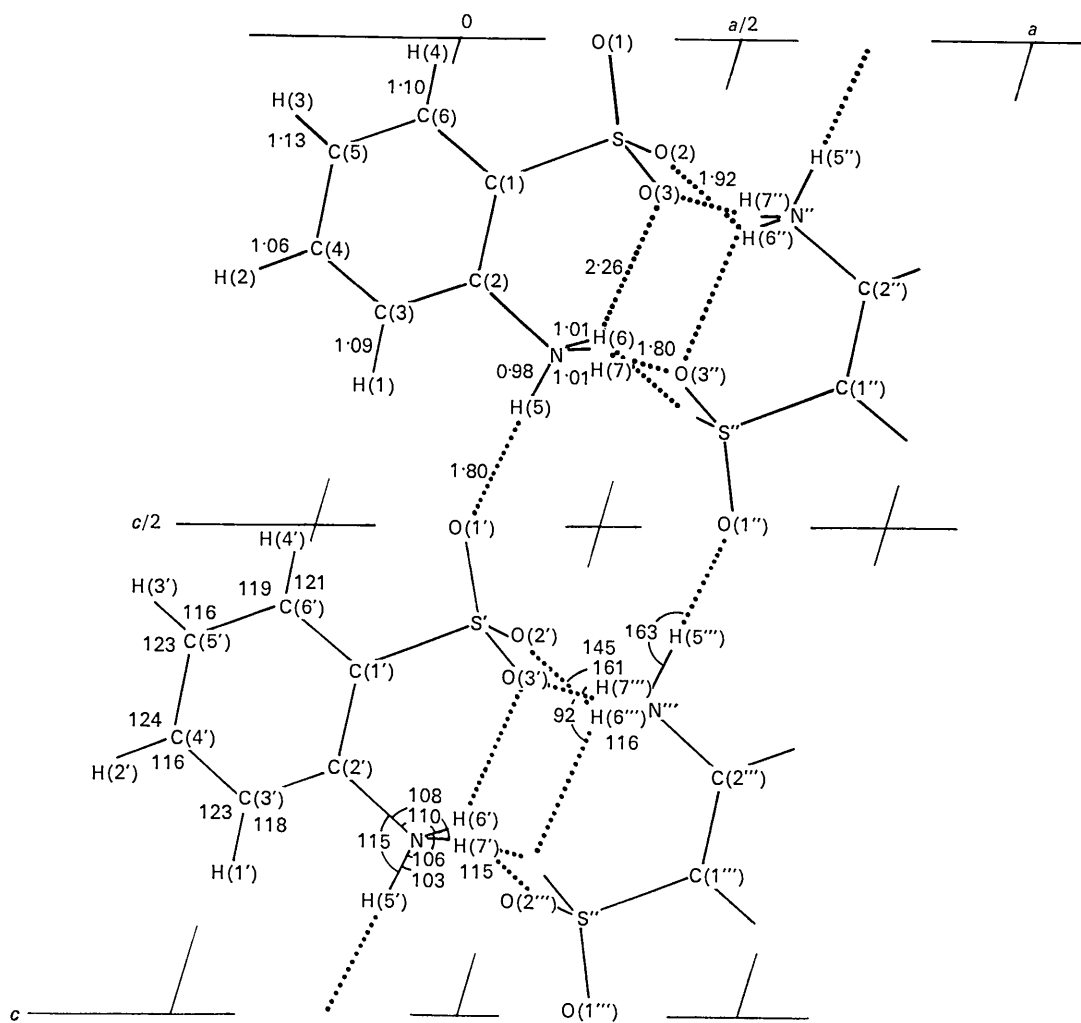
(b)

Fig.7 (cont). (b) A diagrammatic representation of the structure showing close contacts, bond lengths and angles involving hydrogen atoms. Atom numbering as for Fig.6.

interesting to note that the C(1)–C–O(3) angle of 104·6 ± 0·2° is significantly smaller than the angles C(1)–S–O(1) and C(1)–S–O(2) of 105·5° ± 0·2° and 105·6 ± 0·2°. A decrease in the C(1)–S–O(3) angle may be expected from the attachment of the internal hydrogen bond to the oxygen O(3).

The C–C–H and C–N–H bond angles conform with the expected trigonal and tetrahedral bonding configurations. There are some substantial deviations of the angles from the ideal values but in general these may be explained in terms of hydrogen bond forces or apparent shifts of atomic sites due to molecular oscillations.

Hydrogen bond lengths and angles

The hydrogen bond lengths and angles, calculated from the atomic coordinates in Tables 2 and 4, are shown diagrammatically in Fig. 6.

The shortest approach distances in the structure N···O(1′), N″···O(2), N···O(3″) and N···O(3) of 2·753, 2·823, 2·774 and 2·852 ± 0·005 Å respectively, are all close to the average N–H···O⁻ distance of 2·84 Å given by Wallwork (1962). Two of the angles formed between the nitrogen–carbon bond and these short approach distances, C(2)–N···O(1′) and C(2)–N···O(3″) are close to those expected from the tetrahedral configuration of the NH₃⁺ group, while the other two, C(2″)–N″···O(2) and C(2)–N···O(3) deviate considerably. This suggests that the NH₃⁺ group should adopt an orientation where two hydrogen atoms are collinear with the approach distances N···O(1′) and N···O(3″) with the third hydrogen atom situated somewhere between N···O(2ⁱᵛ) and N···O(3), implying that both O(3) and O(2) are acceptor atoms to a single hydrogen atom, *i.e.* a 'bifurcated' hydrogen bond. This type of bond has been reported in a number of structures, in particular in glycine (Marsh 1958; Burns & Levy, 1958) and violuric acid monohydrate (Craven & Takei, 1964) where the hydrogen parameters were refined by neutron diffraction techniques. More recently Cady & Larson (1965) and Silverman & Yannoni (1965) have reported bifurcated bonds in structures refined solely from X-ray data.

The sites of the hydrogen atoms in this structure agree closely with the hydrogen bonding system indicated by the close contacts. The N–H(5)···O(1′) and N–H(7)···O(3″) angles of 163 and 161° respectively show that the three atoms involved in these hydrogen bonds are almost collinear, while the hydrogen atom H(6) is approximately equidistant from the two acceptor atoms O(2ⁱᵛ) and O(3). The shorter N···O(1′) and N···O(3″) distances and the N″···O(2) and N···O(3) values of 2·852 Å are in accord with a hydrogen bond configuration containing two strong single and one weak bifurcated bond. The contacts H(5)···O(1′) and H(7)···O(3″) of 1·80 and 1·80 Å show that the two single hydrogen bonds are of approximately equal strength. In contrast the H(6)··· O(2ⁱᵛ) and H(6)···O(3) distances of 1·92 and 2·26 Å

differ appreciably. The difference of 0·34 Å raises some doubt about the reality of this bifurcated bond. However a similar difference was observed in the bifurcated bond in glycine. In addition the H(6)···O(3) length of 2·26 Å is considerably shorter than the 'weak' contact of 2·44 Å in glycine. The difference in 'arms' observed in these two compounds cannot be considered characteristic, however, since the H···O contacts of the bifurcated bond in the violuric acid monohydrate are almost equal. The formation of a bifurcated hydrogen bond in orthanilic acid appears to be due to the geometry of the NH₃⁺ and SO₃⁻ groups preventing a linear, single bond configuration. The hindrance of these groups limits their rotational freedom and consequently only two single hydrogen bonds may be formed without severe distortion of their tetrahedral configurations. The orientation of the third hydrogen-donor pair is a compromise between the forces maintaining the regular geometry of the NH₃⁺ and SO₃⁻ groups, and forces due to bonding with two acceptor oxygen atoms and to steric hindrance of the two hydrogen bonded groups.

References

BACON, G. E. (1962). *Neutron Diffraction.* Oxford: Clarendon Press.
BASTIANSEN, O. & TRAETTEBERG, M. (1962). *Tetrahedron,* **17,** 147.
BROWN, G. M. & MARSH, R. E. (1963). *Acta Cryst.* **16,** 191.
BURNS, J. H. & LEVY, H. A. (1958). *A.C.A. Meeting, Milwaukee, Wisconsin.*
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10,** 180.
CADY, H. H. & LARSON, A. C. (1965). *Acta Cryst.* **18,** 485.
CRAVEN, B. M. & TAKEI, W. J. (1964). *Acta Cryst.* **17,** 415.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2,** 65.
CRUICKSHANK, D. W. J. (1956a). *Acta Cryst.* **9,** 754.
CRUICKSHANK, D. W. J. (1956b). *Acta Cryst.* **9,** 757.
CRUICKSHANK, D. W. J. (1960). *Acta Cryst.* **13,** 774.
DAWSON, B. (1964). *Acta Cryst.* **17,** 997.
HAHN, T. (1957). *Z. Kristallogr.* **109,** 438.
HALL, S. R. & MASLEN, E. N. (1965). *Acta Cryst.* **18,** 301.
HAMILTON, W. C. (1957). *Acta Cryst.* **10,** 629.
Handbook of Chemistry and Physics (1960). Cleveland: Chem. Rubber Publishing Co.
HODGSON, L. I. & ROLLETT, J. S. (1963). *Acta Cryst.* **16,** 329.
IBERS, J. A. (1956). *Acta Cryst.* **9,** 652.
JENSEN, L. H. (1965). *A.C.A. Meeting, Suffern.* Paper A6.
KENNARD, O. (1962). In *International Tables for X-ray Crystallography.* Vol. III, p. 275. Birmingham: Kynoch Press.
MAIR, G. A. (1963). Private communication.
MARSH, R. E. (1958). *Acta Cryst.* **11,** 654.

MILLS, O. S. & ROLLETT, J. S. (1960). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* London: Pergamon Press.

MORIMOTO, H. & UYEDA, R. (1963). *Acta Cryst.* **16**, 1107.

McWEENY, R. (1954). *Acta Cryst.* **7**, 180.

O'CONNELL, A. M., RAE, A. I. M. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208.

ONDIK, H. & SMITH, D. (1962). In *International Tables for X-ray Crystallography.* Vol. III, p. 257. Birmingham: Kynoch Press.

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

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

SAUNDERSON, C. (1965). Private communication.

SILVERMAN, J. & YANNONI, N. F. (1965). *Acta Cryst.* **18**, 756.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *A.C.A. Meeting, Suffern.* Paper A5.

STOICHEFF, B. P. (1962). *Tetrahedron*, **17**, 135.

SUTHERLAND, H. H. & YOUNG, D. W. (1963). *Acta Cryst.* **16**, 897.

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

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

Crystal, Molecular and Electronic Structure of 1,1-Diaryl-2-halogenoethylenes. I. 2-Bromo-1,1-di-p-tolylethylene

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The crystal structure of 2-bromo-1,1-di-p-tolylethylene, $C_{16}H_{15}Br$, at room temperature, has been determined by three-dimensional methods, including anisotropic refinement by full-matrix least-squares calculations (final R value, 9·7%). There are four formula units in the orthorhombic cell, $a=16·89$, $b=13·07$, $c=6·26$ Å, with space group $P2_12_12_1$. In the molecule the atoms are distributed on three planes: the ethylene reference plane and the two tolyl rings which are rotated by 24·4° (*trans* to Br) and 67·9° (*cis* to Br). Bond lengths and angles are in the normal range; the C–Br distance is 1·87 Å. Bond angles and distances in the isolated molecule and in 'model' crystals were calculated by semi-theoretical methods and the correlation with experimental values is discussed.

Introduction

It is known that 1,1-diaryl-2-halogenoethylenes can react with sodium ethoxide following two different paths leading to nucleophilic substitution and to a Fritsch rearrangement (Beltrame & Favini, 1963; Beltrame, Carrà, Macchi & Simonetta, 1964). For the latter reaction, a geometrical and electronic model of the activated complex has been suggested (Simonetta & Carrà, 1963) in which the aryl group *trans* to the halogen lies in a plane perpendicular to the ethylenic bond. Since the geometry of the substrate might be a relevant factor in determining the relative amounts of the two possible reactions with the base, an investigation was undertaken of the crystal, molecular and electronic structure of some diarylethylenes, including 2-bromo-1,1-di-p-tolylethylene, 2-chloro-1,1-di-p-tolylethylene, 1,1-diphenylethylene and 2-bromo-1,1-diphenylprop-1-ene.

In this paper the results for 2-bromo-1,1-di-p-tolylethylene are given. The geometry of the molecule, as determined by X-ray diffraction, has been compared with the geometry of the isolated molecule calculated by semi-empirical methods and the interrelations between the two have been discussed.

Experimental

Crystal data

2-Bromo-1,1-di-p-tolylethylene, m.p. 52°C, crystallizes from isopropyl alcohol in transparent plates. The unit-cell dimensions were determined from zero-layer Weissenberg films about the b and c axes, with Cu $K\alpha$ radiation. The crystal data given below have already been published in a preliminary communication (Mariani, Mugnoli & Casalone, 1965).

2-Bromo-1,1-di-p-tolylethylene

$C_{16}H_{15}Br$ F.W. 287·2

Orthorhombic, $a=16·89\pm0·01$, $b=13·07\pm0·01$, $c=6·26\pm0·01$ Å, with λ(Cu $K\alpha_1$)=1·5405, λ(Cu $K\alpha_2$)=1·5443, λ(Cu $K\alpha$)=1·5418 Å;

$V=1381·9$ Å³; $D_m=1·37$ g.cm⁻³ (by flotation); $Z=4$; $D_c=1·38$ g.cm⁻³; $F(000)=584$; Absorption coefficient for Cu $K\alpha$ radiation, 39·1 cm⁻¹. Space group $P2_12_12_1$ (no. 19), from systematic absences: $h00$ if $h=2n+1$, $0k0$ if $k=2n+1$, $00l$ if $l=2n+1$.

Intensity measurements

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg