

Fig. 3. View of (II) along **b** showing molecular packing and hydrogen bonding.

between the bonds and angles in the two molecules at a significance level of 3σ . There are minor differences in the comparative values of some of the torsion angles in the two molecules.* However, the following conformational details apply to both molecules. Ring *A* is planar within experimental error as is the enol side chain. Rings *B* and *C* have chair conformations. Ring

* See deposition footnote.

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Anthranilic Acid I,* $C_7H_7NO_2$, by Neutron Diffraction

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Abstract. $M_r = 137.14$, orthorhombic, $P2_1cn$ (non-standard setting of $Pna2_1$), $a = 12.864$ (2), $b = 10.790$ (2), $c = 9.314$ (1) Å, $V = 1292.81$ Å³, $Z = 8$, $D_m = 1.405$ (1), $D_x = 1.409$ Mg m⁻³, $\lambda = 1.168$ Å, $\mu = 0.17$ mm⁻¹, $F(000) = 576$, $T = 293$ K, $R = 0.048$ for 1207 observed [$I > \sigma(I)$] reflexions. There are two molecules per asymmetric unit, one is neutral and the other a zwitterion $C_6H_4.NH_3^+.COO^-$, confirming the X-ray results [Brown (1968). *Proc. R. Soc. London Ser. A*, **302**, 185–199] with significant differences in the C–N and C–O bond lengths in the two molecules. The molecules are linked three-dimensionally in the crystal by a set of six hydrogen bonds of lengths 2.497 (7)–2.894 (6) Å. The H-atom parameters have been refined, giving O–H 1.039 (12), mean C–H 1.081 (11) and mean N–H 1.048 (9) Å.

* 2-Aminobenzoic acid, low-temperature form.

D is a C(13) envelope. The ring junctions *A/B*, *B/C*, *C/D* are all *trans*. These structures are in all respects very similar to that of the closely related dexamethasone acetate (Terzis & Theophanides, 1975).

Hydrogen bonding: (I): O(3)⋯O(17)($-x, y + \frac{1}{2}, -z$), 2.77 (2) Å; (II): O(3)⋯O(17)($-x, y - \frac{1}{2}, -z$), 2.75 (2), O(3)⋯O(11)($x, y, z - 1$), 2.82 (2) Å. Figs. 2 and 3 show the hydrogen bonding and molecular packing of compounds (I) and (II) respectively.

References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for torsion-angle, mean-plane, and libration-correction calculations. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- TERZIS, A. & THEOPHANIDES, T. (1975). *Acta Cryst.* **B31**, 796–801.

Introduction. The structure of the title compound has already been determined by X-rays (Brown, 1968), and this work was undertaken principally to confirm the suggested positions of the H atoms which had indicated the novel coexistence of neutral molecules and zwitterions in the same crystal.

Experimental. Large brown triangular crystals approx. $5 \times 6 \times 3$ mm from cold ethanol. Density by flotation in NaI solution. Lattice parameters from 20 high-angle reflexions on a 57.3 mm radius camera. Intensities on a modified Hilger & Watts diffractometer at UKAEA, Harwell, 1207 reflexions observed out of 1264 counted. Corrections for Lp and absorption, transmission factors between 50 and 100% based on calculated path length. Empirical extinction for seven strong reflexions during refinement. Two standard reflexions, no variation other than that due to changes in neutron beam flux (< 5%).

Table 1. Final atomic parameters and e.s.d.'s

$$B_{eq} = \frac{1}{3}[(\beta_{11}/a^2) + (\beta_{22}/b^2) + (\beta_{33}/c^2)].$$

Molecule 'A'	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	0.1358	0.0873 (3)	0.2036 (3)	2.33 (5)
C(2)	0.1690 (3)	0.0452 (4)	0.3398 (4)	3.22 (6)
C(3)	0.1656 (3)	-0.0824 (4)	0.3752 (3)	3.34 (6)
C(4)	0.1329 (3)	-0.1699 (3)	0.2696 (4)	2.69 (5)
C(5)	0.1015 (3)	-0.1276 (3)	0.1396 (4)	2.37 (5)
C(6)	0.1013 (3)	-0.0013 (3)	0.1023 (3)	1.98 (4)
C(7)	0.0609 (3)	0.0367 (3)	-0.0410 (3)	2.07 (4)
N(1)	0.1411 (2)	0.2135 (2)	0.1767 (2)	2.79 (4)
O(1)	0.0681 (5)	0.1431 (4)	-0.0808 (5)	3.85 (7)
O(2)	0.0234 (4)	-0.0498 (4)	-0.1228 (4)	3.31 (6)
H(2) C(2)	0.1897 (10)	0.1054 (13)	0.4133 (14)	6.39 (21)
H(3) C(3)	0.1899 (11)	-0.1068 (15)	0.4816 (12)	6.87 (21)
H(4) C(4)	0.1282 (10)	-0.2620 (8)	0.2993 (11)	4.04 (16)
H(5) C(5)	0.0736 (7)	-0.1976 (7)	0.0607 (9)	4.04 (12)
H(6) N(1)	0.1000 (8)	0.2379 (9)	0.0823 (8)	4.28 (14)
H(7) N(1)	0.1142 (7)	0.2624 (7)	0.2631 (7)	3.82 (11)
H(8) O(2)	-0.0005 (8)	-0.0160 (7)	-0.2219 (10)	4.46 (14)

Molecule 'B'	x	y	z	$B_{eq}(\text{\AA}^2)$
C(11)	0.3609 (2)	0.4176 (2)	0.2022 (3)	1.80 (4)
C(12)	0.3274 (2)	0.4626 (3)	0.3348 (3)	2.20 (4)
C(13)	0.3305 (3)	0.5872 (3)	0.3607 (4)	2.83 (5)
C(14)	0.3701 (3)	0.6684 (3)	0.2581 (4)	2.86 (5)
C(15)	0.4021 (3)	0.6226 (3)	0.1261 (3)	2.32 (5)
C(16)	0.3968 (2)	0.4952 (2)	0.0965 (3)	1.75 (4)
C(17)	0.4296 (2)	0.4505 (2)	-0.0483 (2)	1.82 (4)
N(11)	0.3563 (2)	0.2844 (2)	0.1783 (2)	2.44 (3)
O(11)	0.4241 (3)	0.3360 (3)	-0.0778 (3)	2.43 (5)
O(12)	0.4646 (4)	0.5302 (4)	-0.1392 (4)	3.58 (7)
H(12) C(12)	0.2978 (9)	0.3992 (6)	0.4162 (7)	4.19 (11)
H(13) C(13)	0.3055 (9)	0.6322 (9)	0.4675 (8)	5.16 (14)
H(14) C(14)	0.3717 (9)	0.7723 (9)	0.2792 (11)	5.16 (16)
H(15) C(15)	0.4268 (7)	0.6835 (7)	0.0421 (7)	4.00 (12)
H(16) N(11)	0.3888 (6)	0.2682 (5)	-0.0778 (8)	3.03 (10)
H(17) N(11)	0.3910 (7)	0.2331 (8)	0.2611 (10)	4.23 (14)
H(18) N(11)	0.2783 (7)	0.2506 (6)	0.1736 (8)	3.82 (12)

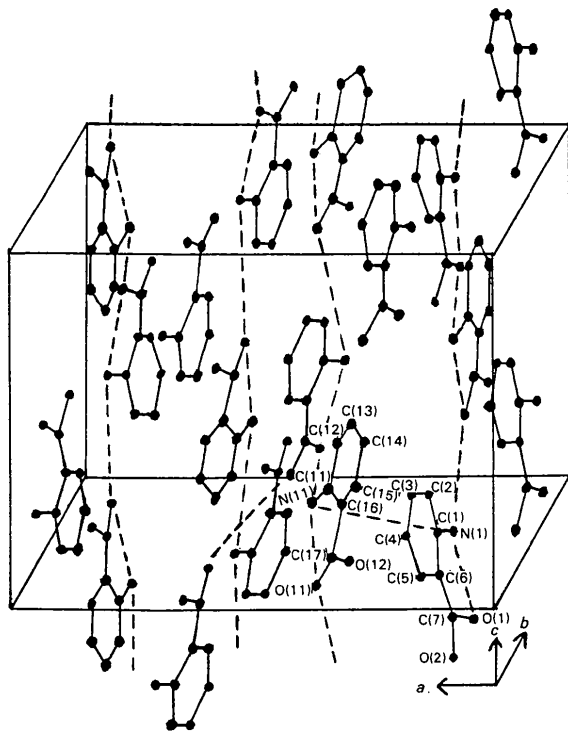


Fig. 1. Unit cell showing atom numbering and arrangement of molecules. Representative hydrogen bonds are shown by dashed lines.

Index range h 0–15, k 0–13, l 0–11. $\theta_{\max} = 45^\circ$. Structure previously solved from X-ray data. Refinement by least squares on F commencing with X-ray results using *NRC* programs (Ahmed, Hall, Pippy & Huber, 1970) on the London Polytechnic's ICL 1905E computer. β_{ij} refined for all atoms including H with $\sqrt{w} = 1/F_o$ until shifts were all $< 0.25\sigma$. Max. values in final difference Fourier map $< \pm 0.1 \times 10^{-12}$ cm. Scattering cross-sections C 6.61, N 9.40, O 5.77, H -3.78 fm (*International Tables for X-ray Crystallography*, 1962). $R_w = 0.093$.

Table 2. Bond lengths (Å), bond angles ($^\circ$) and H-bonding details

Molecule 'A'		Molecule 'B'	
C(1)–C(2)	1.414 (4)	C(11)–C(12)	1.396 (4)
C(1)–C(6)	1.414 (3)	C(11)–C(16)	1.372 (4)
C(2)–C(3)	1.416 (7)	C(12)–C(13)	1.367 (5)
C(3)–C(4)	1.427 (6)	C(13)–C(14)	1.393 (6)
C(4)–C(5)	1.356 (5)	C(14)–C(15)	1.388 (5)
C(5)–C(6)	1.406 (5)	C(15)–C(16)	1.404 (4)
C(6)–C(7)	1.490 (4)	C(16)–C(17)	1.493 (4)
C(7)–O(1)	1.211 (6)	C(17)–O(11)	1.268 (5)
C(7)–O(2)	1.298 (6)	C(17)–O(12)	1.288 (8)
C(1)–N(1)	1.386 (3)	C(11)–N(11)	1.455 (4)
C(2)–H(2)	0.980 (16)	C(12)–H(12)	1.090 (9)
C(3)–H(3)	1.072 (14)	C(13)–H(13)	1.153 (10)
C(4)–H(4)	1.033 (10)	C(14)–H(14)	1.138 (12)
C(5)–H(5)	1.113 (10)	C(15)–H(15)	1.070 (9)
N(1)–H(6)	1.059 (9)	N(11)–H(16)	1.039 (8)
N(1)–H(7)	1.022 (9)	N(11)–H(17)	1.049 (10)
O(2)–H(8)	1.039 (12)	N(11)–H(18)	1.069 (10)
C(2)–C(1)–C(6)	118.4 (2)	C(12)–C(11)–C(16)	121.8 (3)
C(2)–C(1)–N(1)	117.6 (2)	C(12)–C(11)–N(11)	117.8 (3)
C(6)–C(1)–N(1)	124.0 (2)	C(16)–C(11)–N(11)	120.4 (3)
C(1)–C(2)–C(3)	120.8 (4)	C(11)–C(12)–C(13)	119.3 (3)
C(1)–C(2)–H(2)	119.7 (9)	C(11)–C(12)–H(12)	120.3 (6)
C(3)–C(2)–H(2)	119.3 (10)	C(13)–C(12)–H(12)	120.4 (6)
C(2)–C(3)–C(4)	119.5 (4)	C(12)–C(13)–C(14)	120.6 (4)
C(2)–C(3)–H(3)	116.5 (9)	C(12)–C(13)–H(13)	123.9 (7)
C(4)–C(3)–H(3)	124.0 (9)	C(13)–C(14)–H(14)	115.4 (6)
C(3)–C(4)–C(5)	118.7 (4)	C(13)–C(14)–C(15)	119.5 (4)
C(3)–C(4)–H(4)	118.0 (7)	C(13)–C(14)–H(14)	120.5 (6)
C(5)–C(4)–H(4)	123.1 (8)	C(15)–C(14)–H(14)	119.9 (7)
C(4)–C(5)–C(6)	123.2 (3)	C(14)–C(15)–C(16)	120.5 (3)
C(4)–C(5)–H(5)	117.2 (6)	C(14)–C(15)–H(15)	121.2 (6)
C(6)–C(5)–H(5)	119.6 (6)	C(16)–C(15)–H(15)	118.2 (6)
C(5)–C(6)–C(1)	119.2 (3)	C(15)–C(16)–C(17)	118.7 (3)
C(5)–C(6)–C(1)	119.4 (3)	C(15)–C(16)–C(11)	118.2 (3)
C(7)–C(6)–C(1)	121.4 (3)	C(17)–C(16)–C(11)	123.1 (3)
C(6)–C(7)–O(1)	120.6 (4)	C(16)–C(17)–O(11)	119.6 (3)
C(6)–C(7)–O(2)	117.2 (4)	C(16)–C(17)–O(12)	118.5 (3)
O(1)–C(7)–O(2)	122.1 (4)	O(11)–C(17)–O(12)	121.9 (4)
C(1)–N(1)–H(6)	111.6 (6)	C(11)–N(11)–H(16)	106.7 (5)
C(1)–N(1)–H(7)	110.4 (5)	C(11)–N(11)–H(17)	113.0 (6)
H(6)–N(1)–H(7)	110.9 (8)	H(16)–N(11)–H(17)	113.8 (7)
C(7)–O(2)–H(8)	112.2 (7)	C(11)–N(11)–H(18)	112.4 (5)
		H(16)–N(11)–H(18)	106.5 (7)
		H(17)–N(11)–H(18)	104.4 (7)
		C(17)–O(12)–H(8)	117.6 (6)

Hydrogen bonding

X–H...A	X–H (Å)	H...A (Å)	X...A (Å)	\angle X–H...A ($^\circ$)
O(2)–H(8)–O(12)	1.039 (12)	1.458 (12)	2.497 (7)	179.1 (1.1)
N(1)–H(6)–O(1)	1.059 (9)	1.876 (10)	2.686 (6)	130.2 (8)
N(1)–H(7)–O(1 ⁱⁱ)	1.022 (9)	1.872 (10)	2.894 (6)	177.9 (8)
N(11)–H(18)–N(1)	1.069 (10)	1.810 (10)	2.872 (5)	172.1 (8)
N(11)–H(16)–O(11)	1.039 (8)	1.685 (8)	2.599 (6)	144.0 (7)
N(11)–H(17)–O(11 ⁱⁱ)	1.049 (10)	1.729 (11)	2.759 (4)	166.0 (9)

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Discussion. The final positional and equivalent isotropic thermal parameters are in Table 1,* and bond lengths and interbond angles in Table 2. The numbering of the atoms and packing arrangement of the molecules showing the H-bond system are in Fig. 1. The phenyl rings of the molecules are effectively planar, r.m.s. displacements of the atoms being 0.011 (4) Å for molecule 'A' and 0.012 (4) Å for molecule 'B'. The carboxyl groups are rotated by +5.38 (5) and +1.71 (5)° respectively from the planes of their rings. The two phenyl rings make an angle of +138.85 (5)°.

Comparison of the neutron and X-ray results shows some quite appreciable differences, which may be due

* Lists of structure factors, anisotropic thermal parameters and mean-planes' details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39884 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

to the lower accuracy of the X-ray intensity data. However, the properties being measured are not the same by the two methods, the centre of gravity of the diffracting electrons by X-rays, and the position of the atomic nucleus by neutrons. Nevertheless, variations of up to 0.07 Å in bond lengths are more than might be expected, and difficult to account for convincingly. A re-determination of the X-ray structure might clarify the discrepancies.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1970). NRC crystallographic programs for the IBM/360 system. National Research Council, Ottawa, Canada.
 BROWN, C. J. (1968). *Proc. R. Soc. London Ser. A*, **302**, 185–199.
International Tables for X-ray Crystallography (1962). Vol. III, p. 229. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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Refinement of 4-Methyl-5-sulfosalicylic Acid Tetrahydrate, $C_8H_8O_6S \cdot 4H_2O$ *

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Abstract. $M_r = 304.27$, monoclinic, $P2_1/c$, $a = 7.425$ (1), $b = 25.353$ (3), $c = 8.291$ (2) Å, $\beta = 118.09$ (1)°, $V = 1377$ (1) Å³, $Z = 4$, $D_x = 1.467$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.255$ mm⁻¹, $F(000) = 640$, $T = 295$ K. Refinement based on 2860 reflexions gave a final $wR(F^2)$ value of 0.074. The molecular structure can best be formulated as the diaquaonium salt $H_7O_3^+ \cdot CH_3C_6H_2COOH(OH)SO_3^- \cdot H_2O$. The salicylic acid molecules are linked by hydrogen bonds *via* the H_2O molecule and the disordered $H_7O_3^+$ complex.

Introduction. A large number of papers dealing with the geometry of water–proton complexes have been published. The different types of complexes occurring in such systems were identified by Lundgren (1974) and Lundgren & Olovsson (1976). Taesler (1981) showed that the type of complex formed in one specific compound is governed mainly by the water/proton ratio and the type of anion.

The structure of 4-methyl-5-sulfosalicylic acid (4,5-MSSA) (Vyas, Sakore & Biswas, 1978) showed some

unexpected features in the water–proton system, both regarding the nature and the geometry of the complex. They described the molecular structure as $H_7O_3^+ \cdot H_3O^+ \cdot CH_3C_6H_2COO^- \cdot (OH)SO_3^-$. One of the internal hydrogen bonds in the $H_7O_3^+$ ion was 2.40 (3) Å which is 0.1 Å shorter than expected. This could have been caused by an unresolved disorder in the $H_7O_3^+$ ion. The oxygen–oxygen distances from the H_3O^+ ion are 2.55, 2.81 and 3.00 ($\sigma \sim 0.03$) Å. The expected mean value is 2.57 Å. The structure has been redetermined to clarify these points.

Experimental. Crystals obtained by treating 4-methylsalicylic acid with conc. sulfuric acid, followed by recrystallization from aqueous solution; crystal 0.4 × 0.3 × 0.1 mm, in glass capillary. CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Cell parameters (significantly different from values of Vyas *et al.*) from 20 reflexions ($16 < \theta < 19^\circ$). 2900 reflexions collected for $\sin\theta/\lambda \leq 0.62$ Å⁻¹, $0 \leq h \leq 9$, $-31 \leq k \leq 0$, $-9 \leq l \leq 9$, 40 excluded due to overlap. Profiles corrected for background (Lehmann & Larsen, 1974). Variations in five test reflexions were not significant, $\sigma^2(I_o) = [\sigma_e^2 +$

* Hydrogen Bond Studies. 150.