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The Crystal Structures of a Series of Salts of Phthalic Acid. II.* The Crystal Structure of Sodium Acid Phthalate Hemihydrate

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Abstract. In an attempt to grow crystals of sodium acid phthalate the hemihydrate was obtained. $\mathrm{Na(HOOC.C_6H_4.COO).\frac{1}{2}H_2O}$ is orthorhombic, $a=6{\cdot}75(1)$, $b=9{\cdot}31(1)$, $c=26{\cdot}60(3)$ Å, $B2ab$, $Z=8$. The structure was solved by direct methods and refined to $R=4{\cdot}5\%$ for 323 counter reflexions. The water of crystallization occupies a position of site symmetry 2 and is hydrogen bonded to two O atoms of ionized carboxyl groups. The O–H···O distance is 2·80(1) Å and the O–H–O angle 154°.

Introduction. The structure analysis of sodium acid phthalate hemihydrate was undertaken as part of an investigation of a series of salts of phthalic acid. The aim of the investigation was to attempt to correlate structural features and anomalous properties observed in these compounds by Mattson & Ehlert (1966). A discussion of the problem appeared in part I of this series (Smith, 1975).

Sodium acid phthalate hemihydrate was obtained by dissolving stoichiometric amounts of sodium bicarbonate and phthalic acid in water. Large rhombic bipyramidal crystals formed on evaporation as the major product. These crystals were elongated in the [100] direction (Lasheen & Abdeen, 1972). The density was determined to be 1·566 g cm^{-3} by flotation. Preliminary photographs indicated space group $B2ab$, a non-standard setting of $Aba2$, and cell dimensions similar to those reported by Okaya & Pepinsky (1957). The general positions for $B2ab$ are $(0,0,0;\ \frac{1}{2},0,\frac{1}{2})+$ $(x,y,z;\ x,\bar{y},\bar{z};\ x,\frac{1}{2}+y,\frac{1}{2}-z;\ x,\frac{1}{2}-y,\frac{1}{2}+z)$. The calculated density on the basis of eight $\mathrm{Na(HOOC.C_6H_4.COO)}$ per cell is only 1·49 g cm^{-3} and the difference between this and the observed density is equivalent to an additional 9 a.m.u. per asymmetric unit. The crystals were observed to effloresce after lengthy exposure to the air and had a different powder pattern thereafter. The original product was obtained upon recrystallization and hence the compound is a hemihydrate.

An equant fragment of maximum dimension 0·1 mm was cleaved from a large crystal and mounted about **a** on a Pailred diffractometer. Cell dimensions were

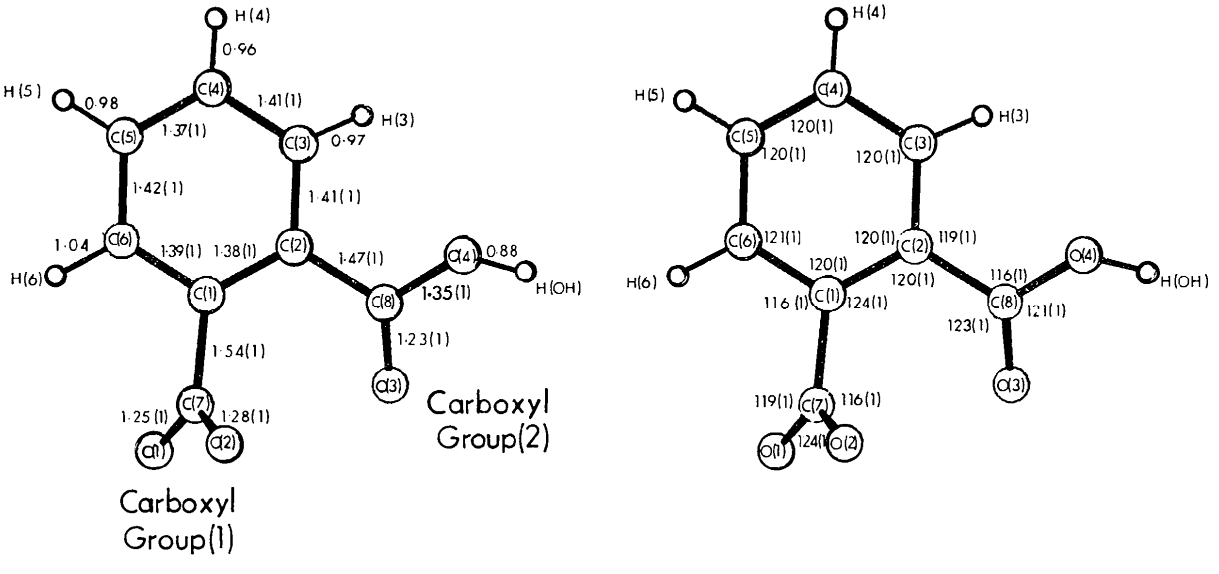

Fig. 1. Bond angles and distances in the phthalate ion. The planes of carboxyl groups (1) and (2) make angles of 67° and 27° respectively with that of the aromatic ring.

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derived from careful centring of several high-angle reflexions and data out to a $\sin \theta/\lambda$ limit of 0·495 were collected with the ω scan technique, Cu $K\alpha$ radiation and a graphite monochromator. Backgrounds were measured on either side of the peak. The data were reduced to $|F|$ and σF by the method of Doedens & Ibers (1967). 483 unique reflexions were accessible in principle and of these 480 were actually measured (reflexions of the form $h00$ were unavailable without remounting the crystal). 323 satisfied the criterion $I \geq 3\sigma I$ and were used in subsequent calculations. No absorption correction was made (μ(Cu $K\alpha$) = 12 cm^{-1}).

The structure was solved with *MAGIC* (Dewar & Stone, 1968). Scattering factors for neutral atoms and for Na$^+$ were obtained from Cromer (1968). The structure was refined with *SFLS5* (Prewitt, 1966). The final R was 4·5% with all heavy atoms isotropic. The positions of the six H atoms were determined from a difference synthesis and were not varied.

The atomic coordinates and thermal parameters are listed in Table 1.*

Table 1. *Atomic parameters*

(*a*) Atomic parameters and their standard deviations for the heavy atoms

U in the form $\exp[-2\pi^2 U(1/d^2_{hkl})]$

	x	y	z	U (Å^2)
Na	0·440*	0·3304 (4)	−0·0031 (1)	0·029 (1)
O(1)	0·626 (1)	−0·1659 (7)	0·0467 (2)	0·031 (2)
O(2)	0·828 (1)	0·0110 (7)	0·0699 (2)	0·025 (2)
O(3)	0·438 (1)	0·1684 (6)	0·0656 (2)	0·030 (2)
O(4)	0·416 (1)	0·3061 (7)	0·1347 (2)	0·035 (2)
O(5)	0·213 (1)	0*	0*	0·028 (3)
C(7)	0·681 (2)	−0·073 (1)	0·0772 (4)	0·030 (3)
C(8)	0·446 (2)	0·179 (1)	0·1118 (3)	0·030 (3)
C(1)	0·579 (2)	−0·063 (1)	0·1287 (3)	0·019 (2)
C(2)	0·478 (2)	0·056 (1)	0·1454 (3)	0·017 (3)
C(3)	0·393 (2)	0·059 (1)	0·1936 (4)	0·030 (3)
C(4)	0·442 (2)	−0·059 (1)	0·2263 (3)	0·029 (3)
C(5)	0·524 (2)	−0·177 (1)	0·2097 (3)	0·029 (3)
C(6)	0·599 (2)	−0·181 (1)	0·1600 (3)	0·028 (3)

(*b*) Atomic parameters for the hydrogen atoms (U = 0·032 Å^2)

	x	y	z
H(3)	0·322	0·145	0·203
H(4)	0·370	−0·053	0·260
H(5)	0·551	−0·259	0·232
H(6)	0·685	−0·268	0·149
H(O)	0·365	0·388	0·121
H(H_2O)	0·302	0·085	0·010

* Denotes parameter not varied.

Discussion. Sodium acid phthalate hemihydrate consists of sodium ions, phthalate ions and water molecules. The bond angles and distances are as expected, with those of the phthalate ion given in Fig. 1. The Na$^+$ ion is surrounded by six O atoms, four from the ionized carboxyl groups, one from an un-ionized carboxyl group and one from the water molecule at distances of 2·30(1), 2·43(1), 2·56(1), 2·56(1), 2·37(1) and 2·43(1) Å respectively. The water molecule occupies a special position of site symmetry 2 and is hydrogen bonded to two O atoms of the ionized carboxyl group with an O–H···O distance of 2·80(1) Å, an O–H–O angle of 154°, an O–H distance of 1·03 Å and an H–O–H angle of 107°. The planes of the ionized and un-ionized carboxyl groups make angles of 67° and 27° respectively with that of the aromatic ring. A packing diagram down **a** was obtained with *ORTEP* (Johnson, 1965) and appears in Fig. 2.

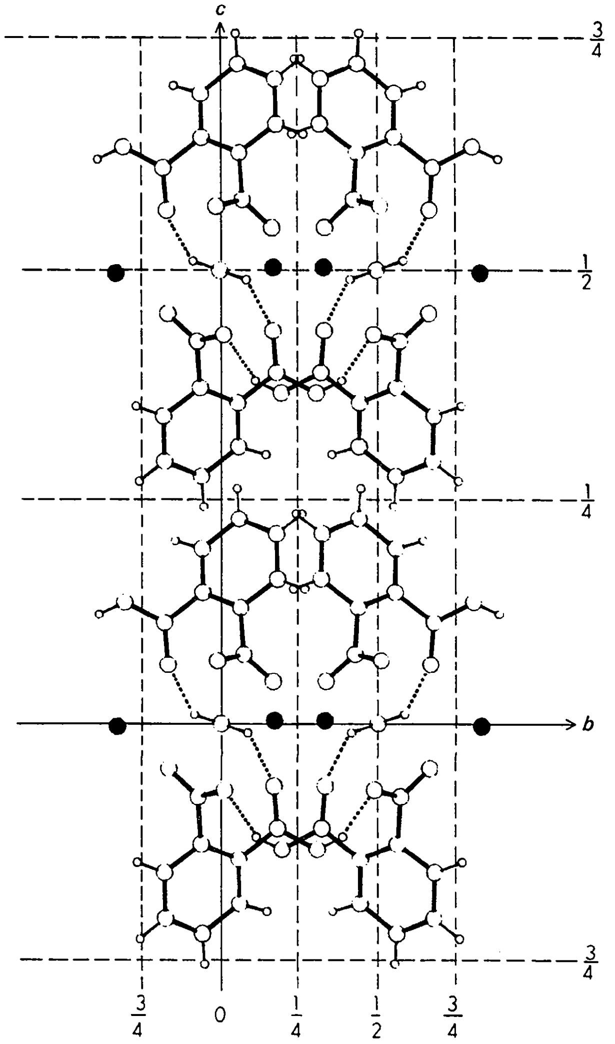

Fig. 2. A packing diagram down **a**. The sodium ions are indicated by solid circles.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31075 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The pattern of bond lengths and angles in the un-ionized carboxyl group is as expected with the C–O distance involving the O bonded to the proton 0·12(1) Å longer than the other. The differences in C–O lengths of un-ionized carboxyl groups in light-atom structures is 0·11 Å as in the structure of D-tartaric acid (Okaya, Kay & Stemple, 1966). The difference in C–O distances is around 0·07 Å where the carboxyl group is 'half ionized' (Ferguson, Sime, Speakman & Young, 1968) and the difference is expected to be zero for fully ionized carboxyl groups and, indeed, the two C–O distances on the ionized carboxyl group are not significantly different in this case. The presence of water of crystallization in sodium acid phthalate hemihydrate renders it unsuitable for general use as a monochromator crystal in X-ray fluorescence analysis because of its tendency to effloresce in air or *in vacuo*.

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References

CROMER, D. T. (1968). *Acta Cryst.* A**24**, 321–324.

DEWAR, R. B. K. & STONE, A. L. (1968). *MAGIC. Use of Computers in the X-ray Phase Problem.* In R. B. K. DEWAR, Ph.D. Dissertation, Univ. of Chicago.

DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 204–210.

FERGUSON, G., SIME, J. G., SPEAKMAN, J. C. & YOUNG, R. (1968). *Chem. Commun.* p. 162.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

LASHEEN, M. A. & ABDEEN, A. M. (1972). *Acta Cryst.* A**28**, 245–249.

MATTSON, R. A. & EHLERT, R. C. (1966). *Advanc. X-ray Anal.* **9**, 471–486.

OKAYA, Y., KAY, M. I. & STEMPLE, N. R. (1966). *Acta Cryst.* **21**, 237–243.

OKAYA, Y. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 324–328.

PREWITT, C. (1966). *SFLS5*. An unpublished least-squares program.

SMITH, R. A. (1975). *Acta Cryst.* B**31**, 1773–1775.

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The Crystal Structures of a Series of Salts of Phthalic Acid.
III. The Crystal Structure of Rubidium Acid Phthalate

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Abstract. Rb(HOOC.C_6H_4.COO) is orthorhombic, $a=6·561(1)$, $b=10·064(2)$, $c=13·068(2)$ Å, $P2_1ab$, $\varrho_{\rm obs}=1·94$, $\varrho_{\rm calc}=1·93$ g cm^{-3}, $Z=4$. The structure was solved by assuming isomorphism with the K salt (Okaya. *Acta Cryst.* (1965). **19**, 879–882). The final R for 333 counter reflexions was 4·6% and the structure shows no unusual features.

Introduction. The structure analysis of rubidium acid phthalate was undertaken as part of an investigation of a series of salts of phthalic acid. Anomalous properties had been observed in these compounds by Mattson & Ehlert (1966). Details are given in part I of this series (Smith, 1975).

Rubidium carbonate and phthalic acid in stoichiometric amounts for the formation of the acid salt were dissolved in water. Large rhombic bipyramidal crystals possessing perfect cleavage in the plane of the largest face formed and were the sole product upon complete evaporation of the water. Preliminary photographs indicated that rubidium acid phthalate crystallized in space group $P2_1ab$ and was isomorphous with the K salt (Okaya, 1965). General positions for this space group, a non-standard setting of $Pca2_1$ (No. 29), are x,y,z; $\frac{1}{2}+x,\bar{y},\bar{z}$; $x,\frac{1}{2}+y,\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,z$.

A fresh well formed crystal, $0·15\times0·15\times0·05$ mm, was taken and mounted about **a** on a manual Picker four-circle diffractometer. 12 high-angle intense reflexions were carefully centred in 2θ with Cu $K\alpha_1$ radiation (no monochromator) and from these values cell dimensions were derived as $a=6·561(1)$, $b=10·064(2)$, $c=13·068(2)$ Å at 22°C. Intensities were collected for one octant by the coupled θ–2θ scan method. Of the 446 unique reflexions available within the limit $3°\le2\theta\le90°$, 56 were systematically absent and the intensities of the remaining 390 reflexions were measured and reduced to $|F|$ and σF by the method of Doedens & Ibers (1967). The criterion for observation was $I\ge3\sigma I$; 333 reflexions satisfied this condition and were used in subsequent calculations. In view of the tabular nature of the crystal and the high absorption coefficient ($\mu=84$ cm^{-1} with Cu $K\alpha$ radiation) corrections were applied with a local version of the program originally written by Coppens, Leiserowitz & Rabinovich (1965). Transmission factors ranged from 0·555 to 0·813.

The structure was solved by assuming that the Rb was isomorphous with the K salt (Okaya, 1965). With anisotropic temperature factors for Rb^+ the structure was refined to $R=4·8$%. Scattering factors were from