Acta Cryst. (1975). B**31**, 2508

The Crystal Structures of a Series of Salts of Phthalic Acid. IV. The Crystal Structure of Ammonium Hydrogen Phthalate

By R. A. Smith

Department of Geology, University of Alberta, Edmonton, Alberta, Canada

(*Received* 23 *May* 1975; *accepted* 26 *May* 1975)

Abstract. $NH_4(HOOC.C_6H_4.COO)$, orthorhombic, $a=6{\cdot}430$ (3), $b=10{\cdot}240$ (6), $c=26{\cdot}130$ (9) Å, $Z=8$, *Pcab*. The previously reported gross structure was refined to $R=6{\cdot}4\%$ for 504 counter reflexions. The carboxyl groups are joined to each other only by intermolecular hydrogen bonds.

Introduction. The purpose of this series of structure determinations is to attempt to explain certain anomalous physical properties of some salts of phthalic acid in terms of their structures. Details of the problem were given in part I of this series (Smith, 1975). The gross structure of ammonium hydrogen phthalate was reported by Okaya & Pepinsky (1957) who suggested that the two carboxyl groups were joined by an intramolecular hydrogen bond. Such bonds have been found in salts of phthalic acid by Cingi, Guastini, Musatti & Nardelli (1969) and by Gonschorek & Küppers (1975), but the packing diagram suggested that any hydrogen bonds between carboxyl groups in this case would be intermolecular. This anomaly warranted redetermination of the structure.

Ammonium hydroxide and a large excess of phthalic acid solution were mixed and allowed to evaporate. In addition to unreacted phthalic acid at least two other products were obtained and preliminary photographic data were obtained for each. Cell data for one of the products were consistent with those reported for ammonium hydrogen phthalate by Okaya & Pepinsky (1957). The remaining product is currently under investigation.

The crystal, of maximum dimension 0·1 mm, was mounted about **a** on a Pailred diffractometer and cell dimensions obtained from several intense high-angle reflexions (Cu $K\alpha_1$ radiation, graphite monochromator). Intensities for two octants in the ranges: $3° \leq$ detector elevation $\leq 114°$; $0° \leq$ equi-inclination angle $\leq 43°$ were collected by the ω scan technique. Systematically absent reflexions and those with a ratio of greater than three for the background counts obtained on either side of the peak were removed leaving 1237 measured reflexions. These data were reduced to $|F|$ and σF (Doedens & Ibers, 1967); 504 satisfied the criterion $I \geq 3\sigma I$ and were used in subsequent calculations. No absorption correction was applied [$\mu(\text{Cu } K\alpha) = 9 \text{ cm}^{-1}$].

The final parameters for the heavy atoms, as reported by Okaya & Pepinsky (1957), were used as a starting model. Scattering factors were obtained from Cromer's (1968) coefficients and the model was refined with the program *SFLS*5. The positional parameters of all H atoms were obtained from a difference synthesis and included with the scattering factor of Mason & Robertson (1966). R was reduced to 6·4%. A scale factor was used for each layer to allow for systematic error in F_o as a function of equi-inclination angle (Bennett, 1974).

The refined positional and thermal parameters are given in Table 1. The dimensions of the phthalate ion are given in Fig. 1 and are as expected. Fig. 2 is a packing diagram seen down **a**. The H atom on the carboxyl group is involved in an intermolecular bond between O(4) and O(2) and not in an intramolecular bond be-

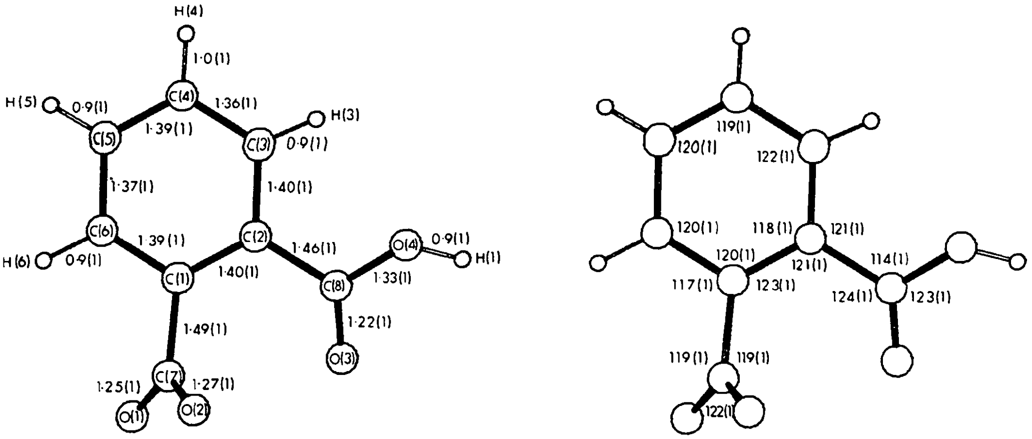

Fig. 1. Bond angles and distances in the phthalate ion.

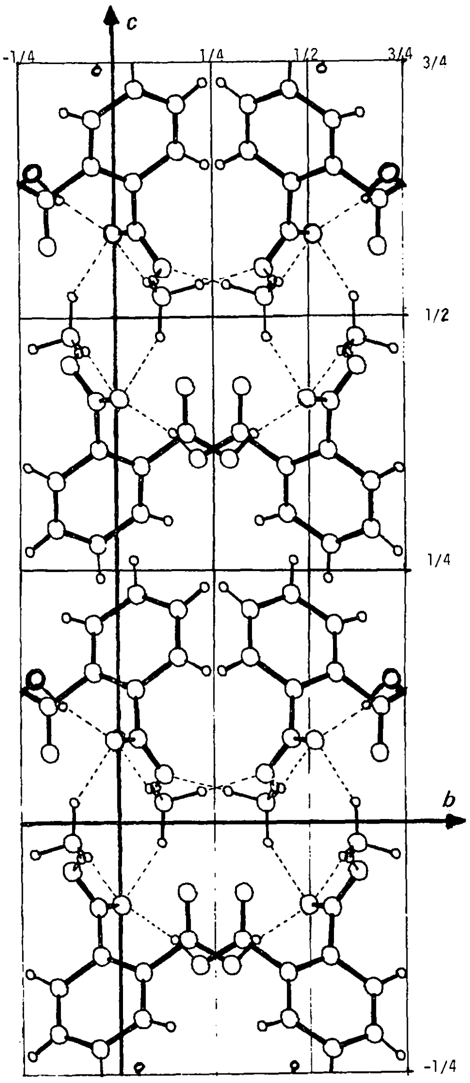

Fig. 2. A packing diagram for ammonium acid phthalate seen down **a**.

tween O(3) and O(2) as suggested by Okaya & Pepinsky (1957). All hydrogen bonds are listed in Table 2. The planes of the ionized and un-ionized carboxyl groups make angles of 74 and 26° respectively with that of the benzene ring.*

Discussion. Discussion of the anomalous physical properties reported for these salts by Mattson & Ehlert (1966) will be deferred, pending completion of the structure of the remaining product of the reaction, which will form the fifth and last paper in this series.

Table 1. *Positional and thermal parameters*

Standard deviations in parentheses.
U is in the form $\exp[-2\pi^2U(2\sin\theta/\lambda)^2]$.

(*a*) Heavy atoms

	x	y	z	U (Å^2)
N	0·216 (2)	−0·118 (1)	0·0202 (3)	0·060 (3)
O(1)	0·659 (1)	−0·120 (1)	0·0485 (2)	0·057 (2)
O(2)	0·897 (1)	0·009 (1)	0·0818 (2)	0·051 (2)
O(3)	0·503 (1)	0·177 (1)	0·0697 (2)	0·059 (2)
O(4)	0·447 (1)	0·290 (1)	0·1414 (2)	0·050 (2)
C(7)	0·724 (1)	−0·052 (1)	0·0846 (4)	0·049 (2)
C(8)	0·481 (1)	0·180 (1)	0·1158 (3)	0·044 (2)
C(1)	0·602 (1)	−0·047 (1)	0·1329 (3)	0·037 (2)
C(2)	0·492 (1)	0·065 (1)	0·1483 (3)	0·039 (2)
C(3)	0·386 (1)	0·059 (1)	0·1953 (4)	0·047 (3)
C(4)	0·391 (1)	−0·048 (1)	0·2256 (4)	0·053 (3)
C(5)	0·504 (1)	−0·157 (1)	0·2100 (3)	0·058 (3)
C(6)	0·606 (1)	−0·157 (1)	0·1639 (3)	0·045 (2)

(*b*) Hydrogen atoms. U fixed at 0·051 (Å^2)

	x	y	z
H(N)1	0·19 (2)	−0·076 (8)	0·042 (3)
H(N)2	0·20 (1)	−0·108 (7)	−0·010 (3)
H(N)3	0·36 (1)	−0·098 (7)	0·035 (3)
H(N)4	0·20 (1)	−0·215 (7)	0·031 (2)
H(1)	0·46 (1)	0·346 (7)	0·117 (3)
H(3)	0·32 (1)	0·133 (7)	0·204 (2)
H(4)	0·33 (1)	−0·044 (6)	0·260 (3)
H(5)	0·52 (1)	−0·227 (7)	0·234 (2)
H(6)	0·66 (1)	−0·233 (7)	0·151 (2)

Table 2. *Hydrogen bonding in ammonium acid phthalate*

	Distance (Å)	Angle (°)
N——H(N)1···O(2)$[1-x,y,z]$	2·91 (1)	139
N——H(N)2···O(2)$[1-x,\bar{y},\bar{z}]$	2·98 (1)	157
N——H(N)3···O(1)$[x,y,z]$	2·94 (1)	159
N——H(N)4···O(1)$[x-\frac{1}{2},-\frac{3}{2}-y,z]$	2·80 (1)	179
O(4)–H(1)·····O(2)$[x-\frac{1}{2},\frac{1}{2}-y,z]$	2·61 (1)	156

The author thanks the University of Alberta for providing research funds, Grant no. 55-32634.

References

Bennett, M. J. (1974). Private communication.
Cingi, M. B., Guastini, C., Musatti, A. & Nardelli, M. (1969). *Acta Cryst.* **B25**, 1833–1840.
Cromer, D. T. (1968). *Acta Cryst.* **A24**, 321–324.
Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 204–210.
Gonschorek, W. & Küppers, H. (1975). *Acta Cryst.* **B31**, 1068–1072.
Mason, R. & Robertson, G. B. (1966). *Advanc. Struct. Res. Diffraction Meth.* **2**, 35–73.
Mattson, R. A. & Ehlert, R. C. (1966). *Advanc. X-ray Anal.* **9**, 471–486.
Okaya, Y. & Pepinsky, R. (1957). *Acta Cryst.* **10**, 324–328.
Smith, R. A. (1975). *Acta Cryst.* **B31**, 1773–1775.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31153 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.