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The Crystal Structures of a Series of Salts of Phthalic Acid. Diammonium Phthalate $(NH_4)_2(OOC.C_6H_4.COO)$

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Abstract. In an attempt to grow crystals of ammonium acid phthalate with the aim of refining the previously reported gross structure, the diammonium salt was obtained. $(NH_4)_2(OOC.C_6H_4.COO)$, orthorhombic, $a=6{\cdot}839$ (14), $b=13{\cdot}041$ (4), $c=22{\cdot}118$ (8) Å, *Pcab*, $\varrho_{obs}=1{\cdot}34$ $\varrho_{calc}=1{\cdot}34$ g cm^{-3}, $Z=8$. The structure was solved by direct methods and refined to an R of 5·0% for 875 counter reflexions. Each NH_4^+ ion is hydrogen bonded to four O atoms. N–H···O distances range from 2·754 (4) to 3·152 (5) Å with seven of the eight N–H···O angles greater than 155°. The planes of the two carboxyl groups are inclined to that of the aromatic ring at angles of 32° and 71°.

Introduction. The structure of ammonium acid phthalate was solved in projection by Okaya & Pepinsky (1957) who also reported cell dimensions, space groups and densities for several acid phthalates (Table 1).

Although projection data for the Rb^+ salt were used as a phasing model for the NH_4^+ salt no positional parameters were given for the former.

Table 1. *Cell constants, space groups and observed densities for several acid phthalates,* $C_6H_4(COOH)(COO)M$

M	a (Å)	b (Å)	c (Å)	Density g cm^{-3}	Space group
Na^+	6·76	9·31	26·42	1·504	*B2ab*
K^+	6·47	9·61	13·26	1·636	$P2_12_12$
NH_4^+	6·40	10·23	26·14	1·415	*Pcab*
Rb^+	6·55	10·02	12·99	1·933	$P2_12_12$

The structure of potassium acid phthalate was later reported by Okaya (1965) with $c=13{\cdot}857$ Å, space group $P2_1ab$ (a non-standard setting of $Pca2_1$), with no density quoted. In recent years several salts of monoprotonated phthalic acid have found application as monochromator crystals in X-ray fluorescence analysis and workers in this field have generally used a $2d$ spacing of 26·63 Å for the 001 reflexion from potassium acid phthalate (Norrish, 1974). This implies a c dimension of 13·315 Å for this salt, a value close to that in Table 1.

When these acid phthalate crystals are used in X-ray fluorescence analysis spurious reflectivity spikes have been observed at about 531 eV, close to the energy of the K_α radiation of oxygen. The relative heights of these peaks have been reported by Mattson & Ehlert (1966) for a series of monochromator crystals. In an attempt to correlate the height of the reflectivity spike with the contribution from the O atoms to the overall intensity of the 001 reflexion, the data in Table 1 were re-examined to verify the assumption of Okaya & Pepinsky (1957) that the salts were isomorphous. Earlier work of Muthmann & Ramsay (1890), Zirngiebl (1902) and Groth (1917) had suggested that this was so.

The Na^+ salt has a density of 1·566 g cm^{-3} and is a hemi-hydrate, the Rb^+ salt has space group $P2_1ab$, the NH_4^+ salt is as reported in Table 1 and the K^+ salt has $c=13{\cdot}315$ Å. The c dimension given by Okaya (1965) is erroneous and internally inconsistent with the reported atomic coordinates and derived bond lengths, but the structure is otherwise correct and has not been investigated further. The other three salts form the basis of subsequent papers in this series.

Ammonium carbonate and phthalic acid in stoichiometric amounts for formation of ammonium acid phthalate were dissolved in water. Large colourless rhombic bipyramidal crystals possessing perfect cleavage in the plane of the largest face formed upon evaporation and were separated from the other crystals present. Preliminary photographs indicated space group *Pcab* with absences $h0l$ for $h=2n$; $0kl$ for $l=2n$; $hk0$ for $k=2n$ and is a non-standard setting of *Pbca* (No. 61) with general positions $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,z;\ \frac{1}{2}-x,y,\frac{1}{2}+z;\ x,\frac{1}{2}+y,\frac{1}{2}-z)$. *Pcab* was retained to facilitate comparison with the space groups in Table 1 although the cell dimensions given for the NH_4^+ salt are grossly dissimilar. The density of 1·34 g cm^{-3}, measured by flotation, coupled with the cell volume gave an X-ray molecular weight of 199, some 16 a.m.u. more than that for a molecule of ammonium acid phthalate. Chemical analysis indicated 11·2% by weight of N suggesting a reaction of more than one molecule of ammonia with one molecule of phthalic acid. Although no data had been reported by Mattson & Ehlert (1966) for the diammonium salt, the crystals possessed, in principle, the attributes essential for a monochromator crystal in X-ray fluorescence and the crystal structure was therefore determined.

A fragment (0·09 × 0·09 × 0·10 mm) was cleaved from a large crystal, mounted about **a** on a Pailred diffractometer and cell dimensions determined from several high-angle reflexions with Cu $K\alpha$ radiation. Intensities for two octants were collected with an ω-scan technique, Cu $K\alpha$ radiation, and a graphite (002) monochromator. Backgrounds were measured on either side of the peak with the crystal and counter stationary. Of the 1678 unique reflexions available within the ranges: $3° \leq$ detector elevation $\leq 93°$; $0 \leq$ inclination angle $< 45°$, 675 were either systematically absent, within the small cone of reciprocal space unavailable with this diffractometer, or rejected on the basis of a ratio of background counts greater than 3·0. The remaining 1003 measured reflexions were reduced to $|F|$ and $\sigma(F)$ (Doedens & Ibers, 1967). Of the 1003 measured reflexions 875 obeyed the condition $I \geq 3\sigma(I)$ and were used in subsequent calculations. The low detector elevation maximum was chosen to avoid bias in the data since the maximum inclination angle available on the local Pailred diffractometer is 43°. No absorption correction was made [μ(Cu $K\alpha$) = 9 cm^{-1}].

The structure was solved by direct methods with *MAGIC*. Scattering factors for neutral atoms were obtained from Cromer (1968). The model was refined with anisotropic heavy atoms with a locally modified version of *SFLS5*. A scale factor for each layer of data was employed to allow for a systematic error in F_{obs} as a function of the inclination angle (Bennett, 1974). The positional parameters of all H atoms were determined from a difference synthesis, but were not refined. The final R for the 875 observed reflexions was 5·0% and the molecule is seen to be diammonium phthalate. The atomic coordinates and thermal parameters are listed in Table 2.*

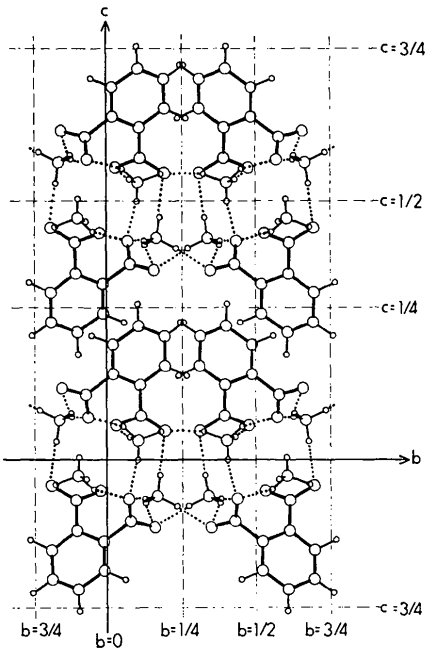

Fig. 2. Packing diagram seen down a. Hydrogen bonds are shown by a dotted line.

Discussion. The structure consists of NH_4^+ and phthalate ions. Bond distances and angles are shown in Fig. 1, and are all normal. The hydrogen bonds are listed in Table 3. Each NH_4^+ ion is hydrogen bonded to four O atoms with average N–H···O distances of 2·866 (5) Å and a range of distances from 2·754 (5) to 3·152 (5) Å in good agreement with those reported for ammonium hydrogen terephthalate by Cobbledick & Small (1972). The N–H···O angles range from 137° to 173° and average 162°; only one angle deviates by more than 25°

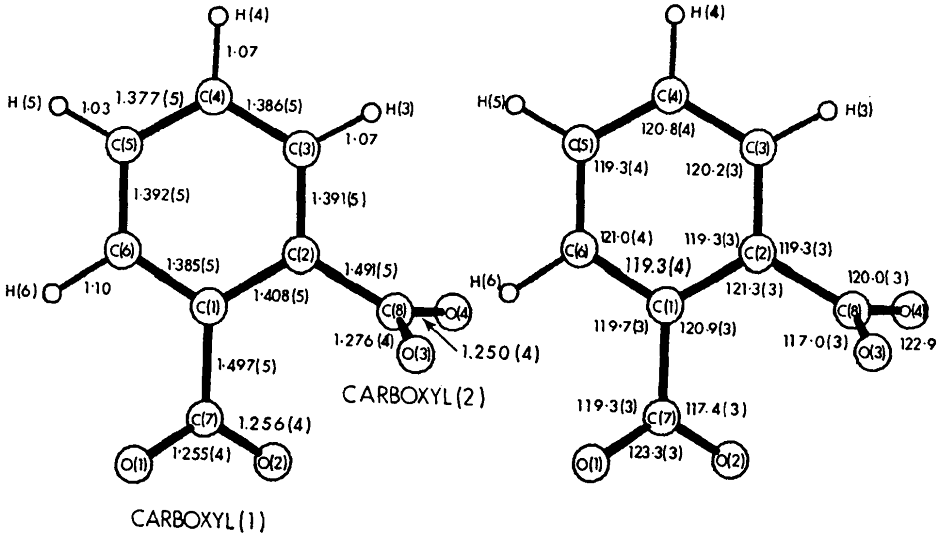

Fig. 1. Bond angles and distances in the phthalate ion, from diammonium salt. The planes of carboxyl groups (1) and (2) make angles of 32° and 71° respectively with that of the aromatic ring.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30930 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic coordinates and their standard deviations*

	x	y	z
N(1)	0·8709 (4)	0·3360 (2)	0·5733 (1)
N(2)	0·2982 (4)	0·3993 (2)	0·4656 (1)
O(1)	0·8472 (4)	0·3080 (2)	0·4469 (1)
O(2)	0·9131 (3)	0·4729 (2)	0·4365 (1)
O(3)	0·5020 (3)	0·5677 (2)	0·4210 (1)
O(4)	0·7139 (4)	0·6551 (2)	0·3651 (1)
C(7)	0·8373 (5)	0·3908 (3)	0·4182 (2)
C(8)	0·6221 (5)	0·5747 (3)	0·3770 (2)
C(1)	0·7356 (4)	0·3929 (3)	0·3583 (2)
C(2)	0·6433 (4)	0·4828 (3)	0·3374 (2)
C(3)	0·5598 (5)	0·4837 (3)	0·2801 (2)
C(4)	0·5684 (5)	0·3971 (4)	0·2438 (2)
C(5)	0·6602 (5)	0·3094 (3)	0·2636 (2)
C(6)	0·7418 (5)	0·3074 (3)	0·3212 (2)

Unrefined hydrogen atom positional parameters

	x	y	z
H(3)	0·5058	0·5551	0·2631
H(4)	0·4953	0·4003	0·2009
H(5)	0·6635	0·2443	0·2372
H(6)	0·8028	0·2363	0·3407
H1(N1)	0·8724	0·3253	0·5328
H2(N1)	0·9779	0·3760	0·5868
H3(N1)	0·8691	0·2695	0·5930
H4(N1)	0·7519	0·3779	0·5794
H1(N2)	0·3133	0·3221	0·4488
H2(N2)	0·3800	0·4502	0·4392
H3(N2)	0·3606	0·4013	0·5023
H4(N2)	0·1685	0·4267	0·4591

Thermal parameters in the form $\exp\,[-2\pi^2(U_{11}h^2{}^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*\times 10^{-3})]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	39 (2)	32 (2)	50 (2)	−4 (2)	−1 (2)	−1 (2)
N(2)	35 (2)	33 (2)	48 (2)	0 (2)	−6 (2)	0 (2)
O(1)	77 (1)	33 (2)	51 (2)	−4 (2)	−17 (2)	10 (2)
O(2)	48 (2)	33 (2)	57 (2)	−2 (2)	−18 (2)	−6 (2)
O(3)	35 (2)	41 (2)	43 (2)	1 (2)	10 (2)	−3 (2)
O(4)	65 (2)	30 (2)	59 (2)	−7 (2)	20 (2)	−4 (2)
C(7)	29 (2)	32 (3)	42 (3)	5 (2)	2 (2)	−4 (2)
C(8)	27 (2)	29 (2)	43 (2)	2 (2)	−3 (2)	3 (2)
C(1)	27 (2)	29 (2)	39 (2)	−4 (2)	3 (2)	−5 (2)
C(2)	24 (2)	30 (2)	41 (2)	−2 (2)	2 (2)	−4 (2)
C(3)	40 (2)	46 (3)	44 (3)	5 (2)	−7 (2)	−5 (2)
C(4)	44 (2)	66 (3)	46 (3)	−2 (2)	−8 (2)	−11 (3)
C(5)	46 (2)	48 (3)	53 (3)	−5 (2)	−1 (2)	−20 (2)
C(6)	37 (2)	38 (3)	53 (3)	−2 (2)	1 (2)	−7 (2)

All H's $U=0·05066$ constrained to isotropic temperature factors.

from a straight line and it is this bond for which the N–H···O distance is large. Fig. 2 is a packing diagram viewed down **a**.

Table 3. *Hydrogen bonding in diammonium phthalate*

Bond No.	N H O	N···O	∠N–H···O
1	N(1)–H1(N1)···O(1)$[x,y,z]$	2·824 (5) Å	174°
2	N(1)–H2(N1)···O(4)$[2-x,1-y,1-z)$	3·152 (5)	137
3	N(1)–H3(N1)···O(4)$[\frac{3}{2}-x,y-\frac{1}{2},1-z]$	2·786 (4)	162
4	N(1)–H4(N1)···O(3)$[1-x,1-y,1-z]$	2·846 (5)	166
5	N(2)–H1(N2)···O(1)$[x-\frac{1}{2},\frac{1}{2}-y,z]$	2·754 (4)	161
6	N(2)–H2(N2)···O(3)$[x,y,z]$	2·782 (4)	157
7	N(2)–H3(N2)···O(3)$[1-x,1-y,1-z]$	2·889 (5)	170
8	N(2)–H4(N2)···O(2)$[x-1,y,z]$	2·876 (5)	173

Miller, Curtin & Paul (1974) have reported the reactions of a series of aromatic acids and ammonia gas which, with phthalic acid, leads to the diammonium salt with shattering of the crystal. Monocarboxylic acids do not shatter under these conditions. A comparison of the packing diagrams for diammonium phthalate, Fig. 2, ammonium acid phthalate (Okaya & Pepinsky, 1957) and phthalic acid (Miller, Curtin & Paul, 1974) shows that substantial rearrangement occurs in going from phthalic acid to ammonium acid phthalate and by comparison the additional rearrangement caused in the step from the acid salt to diammonium phthalate is minor.

The mean molecular planes of the carboxyl groups make angles of 32° and 71° with that of the benzene ring. These values may be compared with those reported for several monoprotonated acids containing adjacent carboxyl groups where the ionized group makes an angle of around 70° and the un-ionized group around 30° to the mean molecular plane (Okaya, 1965, and references therein). In phthalic acid both groups make angles of 33° with the aromatic ring (Nowacki & Jaggi, 1957). This change in shape of phthalic acid, upon ionization, may be responsible for the shattering of phthalic acid crystals exposed to ammonia gas.

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