

# The Crystal Structure of Ammonium Acid Phthalate\*

BY YOSHIHARU OKAYA AND RAY PEPINSKY

*X-Ray and Crystal Structure Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pa., U.S.A.*

(Received 30 October 1956 and in revised form 12 December 1956)

Ammonium acid phthalate crystallizes in the orthorhombic system with  $a = 6.397$ ,  $b = 10.231$ ,  $c = 26.141$  Å. The space group is  $Pcab$ , and there are 8 molecules in the cell. The structure was analyzed via two-dimensional electron-density projections and a bounded projection  $\int_{-1/4}^{1/4} \rho(x, y, z) dy$ .

The benzene ring (which is slightly distorted from a regular hexagon) and the two carbon atoms of the carboxyl groups lie in a plane, but the planes of the two carboxyl groups are inclined to the benzene ring by angles of  $21^\circ$  and  $65^\circ$ . The benzene ring is slightly distorted from a regular hexagon, with C-C distances ranging from 1.35 to 1.40 Å. The distance of 3.08 Å between two oxygen atoms belonging to different carboxyl groups of the same phthalate ion suggests a weak hydrogen bond, but a neutron study would be required to confirm this. General features of other alkali acid phthalates are discussed.

## Introduction

The morphology of the acid phthalates of ammonium and several alkali metals was examined by Muthmann & Ramsay (1890) and Zirngiebl (1902), and parameters are given in Groth's *Chemische Krystallographie* (1917). These data suggest isomorphism of the Na, K, NH<sub>4</sub>, Rb and Cs acid salts, with rhombic bipyramidal symmetry and perfect or nearly perfect cleavage parallel to (001).

Crystals were grown by simple evaporation of aqueous solution. The K salt grows with particular ease in very large crystals. X-ray data for several related salts are given in Table 1. The appearance of

Table 1. Cell constants, space groups and observed densities for several acid phthalates:

$M^+$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$Z$	$\rho$ (g.cm. <sup>-3</sup> )	Space group
Na <sup>+</sup>	6.76	9.31	26.42	8	1.504	$C_{2v}^{17}-B2ab$
NH <sub>4</sub> <sup>+</sup>	6.40	10.23	26.14	8	1.415	$D_{2h}^{15}-Pcab$
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	7.22	11.01	24.46	8	1.349 <sub>0</sub>	$D_{2h}^{15}-Pcab$
K <sup>+</sup>	6.47	9.61	13.26	4	1.636	$D_2^3-P2_12_12$
Rb <sup>+</sup>	6.55	10.02	12.99	4	1.933	$D_2^3-P2_12_12$
Tl <sup>+</sup>	6.63	10.54	12.95	4	2.29	$D_2^3-P2_12_12$
Cs <sup>+</sup>	6.58	10.81	12.84	4	2.178	$D_2^3-P2_12_12$

three different space groups is intriguing. The present report chiefly concerns the NH<sub>4</sub> salt; but X-ray data from the Rb salt were very helpful in solving the NH<sub>4</sub> salt structure.

\* Research supported by Grant A-228 from the National Institutes of Health. X-RAC and S-FAC computations supported by Contract N6onr-26916, T. O. 16, with the Office of Naval Research.

## Experimental

Cu  $K\alpha$  X-ray intensity data for the NH<sub>4</sub> and Rb salts were obtained from Weissenberg photographs about the  $a$  and  $b$  axes. The multiple-film technique was used, with 7-12 sheets of Dupont Type 608 film (transmission factor 0.57). Almost all reflections within the Cu  $K\alpha$  sphere were observed. Owing to the small size of the crystals utilized and the low absorption coefficient of the NH<sub>4</sub> salt, no absorption correction was made. A comparison of  $F_o$  and  $F_c$  values at the end of the analysis showed that extinction effects were negligible.

### Unit cell and space group of NH<sub>4</sub> salt

The unit cell constants of the NH<sub>4</sub> salt are given in Table 1. These were obtained from Weissenberg photographs with crystals mounted on pure aluminum rods, the latter being used for calibration. Zirngiebl's (1902) density value leads to  $7.96 \approx 8$  molecules per cell;  $\rho_o = 1.416$  g.cm.<sup>-3</sup>;  $\rho_c = 1.423$  g.cm.<sup>-3</sup>. Space group  $D_{2h}^{15}-Pcab$  is deduced from the following systematic absences: ( $h0l$ ) for  $h \neq 2h$ ; ( $0kl$ ) for  $l \neq 2h$ ; ( $hk0$ ) for  $k \neq 2n$ . Eightfold general positions are

$$\pm(x, y, z); \pm(x, \frac{1}{2}-y, z); \pm(\frac{1}{2}-x, y, \frac{1}{2}+z); x, \frac{1}{2}+y, \frac{1}{2}-z).$$

Every atom must be in a general position.

### Electron-density projections on (100)

As a first step in the structure determination, the electron-density projection of the rubidium salt on (100) was studied, since the asymmetric unit of the rubidium salt projected on this plane was expected to have a structure similar to the corresponding projection of the ammonium salt. This was concluded by

comparison of the three space groups, as shown in Fig. 1. The position of the rubidium atom was easily

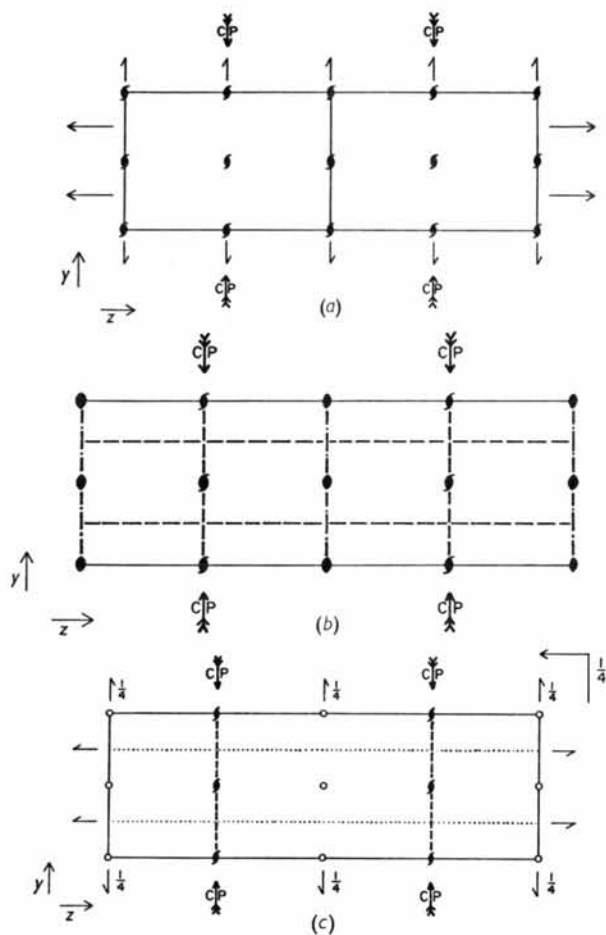


Fig. 1. Comparison of three space groups of alkali acid phthalates. Contacts of benzene rings are made through twofold screw axes. Cleavage planes are indicated by symbol CP. (a)  $D_{2h}^3-P2_12_12$  (two unit cells), origin half way between 2 in plane of  $2_12_1$ . (b)  $C_{2h}^2-B2ab$  (one unit cell), origin on 2. (c)  $D_{2h}^1-Pcab$  (one unit cell), origin at  $\bar{1}$ .

fixed by the Patterson projection on (100). The first approximate electron-density projections, using signs as determined by rubidium contribution only, were difficult to interpret. This was due to the fact that the rubidium contribution was not predominant for many structure factor signs. The position of the phthalate ion was assigned only after structure-factor calculations based on several trial structures. Successive refinements of the structure projection on (100) were done as usual, using X-RAC. Once a reasonable approximate structure was attained for the rubidium salt, the projections were of much help in the structure determination of the ammonium salt.

Starting from an approximate structure deduced from that of the rubidium salt, successive electron-density projections of the ammonium salt on (100) led to the final projection, as shown in Fig. 2.

It is interesting that hydrogen atoms attached to the benzene ring are discernible, even in this projection (Fig. 2), in the deformation of the lowest contour

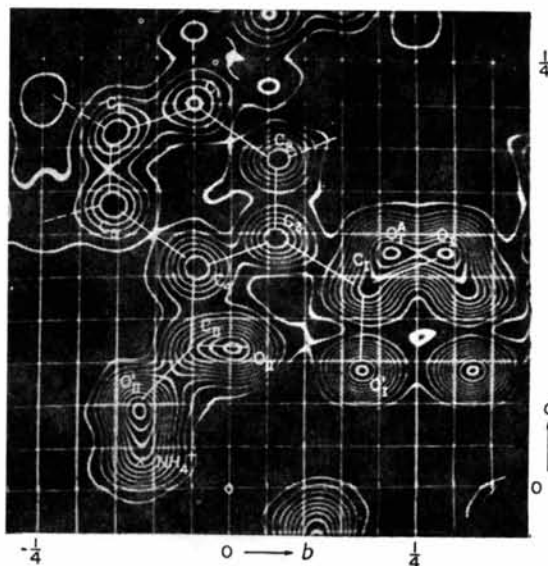


Fig. 2. Electron-density projection of  $NH_4$  acid phthalate on (100). Equi-interval contours on an arbitrary scale; atom denumerations as used throughout this paper;  $O_1^I$  used as in Fig. 4.

(approximately  $1.5 \text{ e. \AA}^{-2}$ ). Atoms  $C_{II}$ ,  $O'_{II}$ ,  $O_{II}$  and the ammonium ion are not well resolved, and their  $y$  coordinates were adjusted by choosing positions which give the best possible agreement between  $F_o$  and  $F_c$ .

#### Electron-density projection on (010), and bounded projection $\int_{-1/4}^{1/4} \rho(x, y, z) dy$

The electron-density projection on (010) was next considered, using  $z$  coordinates hitherto obtained and trial  $x$  coordinates deduced from packing considerations. Refinement of this projection resulted in the (010) projection shown in Fig. 3. In order to resolve all the atoms, especially the overlapping  $O_I$ ,  $C_3$  and  $C_1$ ,

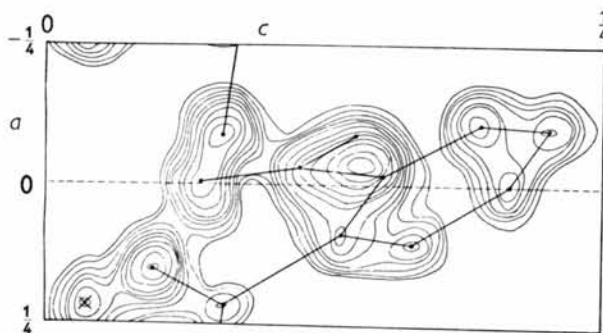


Fig. 3. Electron-density projection of  $NH_4$  acid phthalate on (010). Equi-interval contours on an arbitrary scale.

use was made of a bounded projection  $\int_{-\frac{1}{4}}^{\frac{1}{4}} \rho(x, y, z) dy$ , calculated from

$$\sum_l \left[ \sum_{\substack{h \\ \text{even}}} F_{h0l} + 2 \sum_{\substack{h \\ \text{odd}}} \left\{ \sum_{\substack{k \\ \text{odd}}}^{\infty} \frac{(-1)^{\frac{1}{2}(k-1)}}{\pi k} F_{hkl} \right\} \right] \cos 2\pi(hx + lz).$$

These limits were chosen because the  $y$  coordinate of  $O_I$  is greater than  $\frac{1}{4}$ . This bounded projection is shown in Fig. 4. The projection on (010) and the bounded

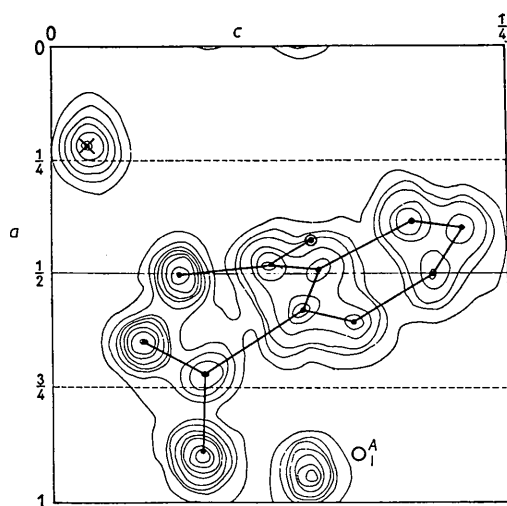


Fig. 4. Bounded projections  $\int_{-\frac{1}{4}}^{\frac{1}{4}} \rho(x, y, z) dy$ . Contours at intervals of  $1 \text{ e.}\text{\AA}^{-2}$ , lowest contour at  $2 \text{ e.}\text{\AA}^{-2}$ . Atom  $O_I^A$  corresponds to  $O_I$ , but in phthalate ion related by glide plane at  $y = \frac{1}{4}$ .

projection were calculated manually at  $\frac{1}{60}$  and  $\frac{1}{120}$  intervals along the  $a$  and  $c$  axes respectively.

The  $x$  and  $z$  coordinates were determined from the bounded projection, and are listed in Table 2 together with the  $y$  coordinates obtained earlier. Only slight

Table 2. Atomic coordinates for ammonium acid phthalate

Atom	$x$	$y$	$z$
$\text{NH}_4$	0.219	-0.120	0.0175
$C_1$	0.389	-0.050	0.2250
$C_2$	0.380	0.061	0.1935
$C_3$	0.486	0.062	0.1475
$C_4$	0.586	-0.050	0.1298
$C_5$	0.593	-0.158	0.1620
$C_6$	0.505	-0.152	0.2090
$C_I$	0.479	0.192	0.1170
$C_{II}$	0.724	-0.050	0.0821
$O_I$	0.443	0.290	0.1385
$O_I'$	0.506	0.177	0.0703
$O_{II}$	0.899	0.005	0.0820
$O_{II}'$	0.652	-0.120	0.0475

corrections were required for series-termination effects; and these have been made. In Table 3, structure factors are listed for  $(0kl)$  and  $(h0l)$ ; the disagreement factors  $\sum ||F_o| - |F_c|| \div \sum |F_o|$  are 0.159 and 0.148 respectively for these projections. Temperature factors of  $4.0 \times 10^{-16} \text{ cm.}^2$  for carbon and nitrogen atoms, and  $3.1 \times 10^{-16} \text{ cm.}^2$  for oxygen atoms, were applied to the atomic scattering factor given by McWeeny (1951).

### Description of the $\text{NH}_4$ -salt structure

The ammonium acid phthalate crystal is essentially ionic, containing the ammonium ion and the monobasic acid phthalate ion. Each ammonium ion is surrounded by six oxygen atoms: five from carboxyl group II with distances 2.81, 2.87, 2.92, 2.97 and 3.10 Å; and one from group I with distance 2.95 Å. These oxygens form a distorted octahedron around the ammonium ion. The distances are comparable to those in ammonium trioxalatochromate(III) (van Niekerk & Schoening, 1952), which has distances down to 2.70 Å; in the case of ammonium trinitrate (Duke & Llewellyn, 1950) all  $\text{NH}_4\text{-O}$  distances are longer than 3.01 Å.

All the polar parts of the structure lie near the planes  $z = 0$  and  $z = \frac{1}{2}$ , and are clearly distinguished from the non-polar parts which are formed by contact between benzene rings around the twofold screw axes at  $z = \frac{1}{4}$  and  $\frac{3}{4}$ . The perfect cleavage parallel to the

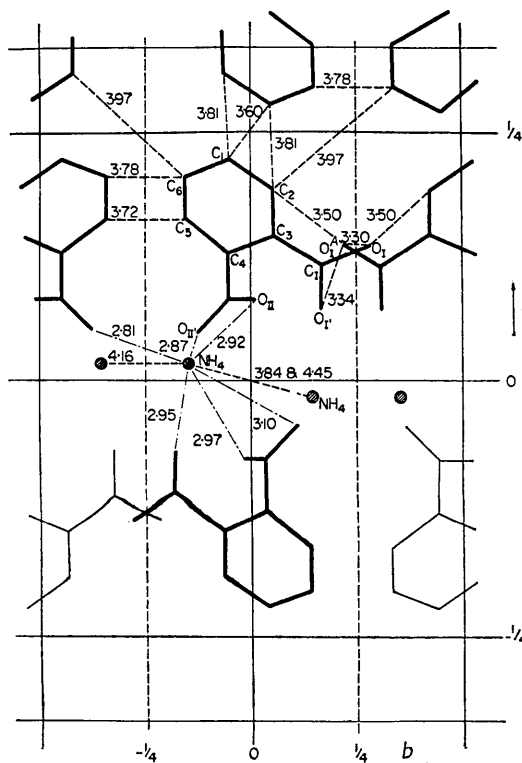


Fig. 5. Schematic projection of  $\text{NH}_4$  acid phthalate on (100).

Table 3. Observed and calculated structure factors for ammonium acid phthalate

0 k l	F <sub>obs.</sub>	F <sub>calc.</sub>	ΔF	0 k l	F <sub>obs.</sub>	F <sub>calc.</sub>	ΔF	h 0 l	F <sub>obs.</sub>	F <sub>calc.</sub>	ΔF
0 0 0	—	758.0	—	0 12 2	3.3	-1.2	2.1	2 0 0	156.9	145.4	11.5
0 2 0	77.0	77.3	.3	0 12 4	0.0	-2.7	(2.7)	4 0 0	3.2	5.7	2.5
0 4 0	48.2	-35.2	13.0	0 12 6	3.0	-3.8	.8	6 0 0	0.0	-1.6	(1.6)
0 6 0	45.0	43.4	1.6	0 12 8	8.9	-8.1	.8	8 0 0	18.5	19.2	.7
0 8 0	37.9	-29.5	8.4	0 12 10	6.3	6.8	.5	2 0 2	85.7	-83.7	2.0
0 10 0	16.8	-14.8	2.0	0 12 12	8.9	8.9	.0	2 0 4	121.4	-129.6	8.2
0 12 0	8.0	-6.0	2.0	0 1 2	55.0	-55.9	.3	2 0 6	6	13.4	-7.3
0 0 2	28.1	25.2	2.9	0 1 4	16.6	-21.6	5.0	2 0 8	18.5	15.6	2.9
0 0 4	124.6	-127.8	3.2	0 1 6	137.6	126.1	11.5	2 0 12	29.3	-33.3	.9
0 0 6	30.5	-34.3	3.8	0 1 8	31.3	23.8	7.5	2 0 16	70.2	65.3	4.9
0 0 8	34.3	-37.0	2.7	0 1 10	30.1	23.9	6.2	2 0 18	18.9	15.3	3.6
0 0 10	52.9	-43.5	9.4	0 1 12	37.9	45.3	7.4	2 0 20	3.2	-1.8	6.4
0 0 12	22.2	-19.3	2.9	0 1 14	39.3	-38.2	1.1	2 0 22	3.2	-1.4	1.8
0 0 14	101.3	102.4	1.1	0 1 16	40.9	-38.2	2.7	2 0 24	16.4	-12.8	3.6
0 0 16	19.2	8.6	10.6	0 1 18	27.3	-30.2	2.5	2 0 26	13.3	3.2	10.1
0 0 18	40.8	-38.2	2.6	0 1 20	10.1	19.5	9.4	2 0 28	10.3	4.6	5.7
0 0 20	16.0	-27.2	11.2	0 1 22	15.4	-10.9	4.5	2 0 28	24.5	25.6	1.1
0 0 22	0.0	4.7	(4.7)	0 1 24	21.9	17.4	4.5	4 0 2	19.2	19.0	.2
0 0 24	0.0	13.4	(13.4)	0 1 26	22.5	30.1	7.6	4 0 4	11.0	-11.0	.0
0 0 26	10.9	10.4	.5	0 1 28	3.0	3.0	.0	4 0 6	2.7	-0.3	2.4
0 0 28	3.8	-3.5	.3	0 1 30	9.2	-6.8	3.4	4 0 8	23.3	16.9	6.4
0 0 30	8.9	-11.2	3.3	0 1 32	0.0	-5.6	(5.6)	4 0 10	8.9	7.3	1.6
0 0 32	12.1	-20.1	8.0	0 3 2	91.2	93.5	2.3	4 0 12	0.0	4.5	(4.5)
0 2 2	0.0	-4.1	(4.1)	0 3 4	85.5	85.9	.4	4 0 14	17.4	27.2	9.8
0 2 4	23.4	17.8	5.6	0 3 6	17.8	23.5	5.7	4 0 16	6.8	5.5	1.3
0 2 6	65.8	-66.0	.2	0 3 8	25.5	14.7	10.8	4 0 18	0.0	-7.3	(7.3)
0 2 8	27.8	-35.2	7.4	0 3 10	59.5	60.2	.7	4 0 20	0.0	-7.3	(7.3)
0 2 10	40.0	41.5	1.5	0 3 12	29.0	-31.2	2.2	4 0 22	28.1	-32.2	4.1
0 2 12	32.3	37.1	4.8	0 3 14	8.5	-4.6	3.9	4 0 24	10.7	-10.1	.6
0 2 14	5.0	7.9	2.9	0 3 16	0.0	0.0	(0.0)	4 0 26	0.0	-4.3	(4.3)
0 2 16	24.8	-22.8	2.0	0 3 18	13.1	13.7	.6	4 0 28	17.1	20.1	3.0
0 2 18	34.6	-24.7	9.9	0 3 20	9.8	2.2	7.6	6 0 2	3.2	3.6	.4
0 2 20	8.6	-10.6	3.0	0 3 22	17.4	-22.1	5.7	6 0 4	5.2	7.5	4.3
0 2 22	29.0	20.2	8.8	0 3 24	22.2	19.9	2.3	6 0 6	0.0	-5.7	(5.7)
0 2 24	8.8	8.6	.2	0 3 26	3.0	10.0	(10.0)	6 0 8	3.9	-9.8	5.9
0 2 26	11.0	18.2	7.2	0 3 28	3.6	1.6	2.0	6 0 10	9.1	-3.9	5.2
0 2 28	16.0	-14.8	1.2	0 5 2	12.4	-13.2	.8	6 0 12	14.8	-12.8	2.0
0 4 2	50.6	-47.0	3.6	0 5 4	57.9	65.0	7.1	6 0 14	0.0	1.1	(1.1)
0 4 4	81.6	-85.4	3.8	0 5 6	44.4	-30.0	16.4	6 0 16	5.9	3.0	2.9
0 4 6	49.1	-51.5	2.4	0 5 8	64.4	-64.5	.1	6 0 18	17.8	10.2	7.4
0 4 8	34.3	31.7	2.6	0 5 10	11.2	-10.4	.8	6 0 20	13.3	12.2	1.1
0 4 10	14.2	18.9	4.7	0 5 12	12.7	-22.3	9.6	6 0 22	8.5	-8.7	.2
0 4 12	41.1	32.6	8.5	0 5 14	0.0	5.6	(5.6)	2 0 1	48.9	47.1	1.8
0 4 14	30.7	30.3	.4	0 5 16	10.7	-2.9	7.8	2 0 3	51.0	-42.1	8.9
0 4 16	0.0	0.4	(.4)	0 5 18	36.1	40.8	4.7	2 0 5	10.5	-10.3	.2
0 4 18	36.1	-36.6	.5	0 5 20	12.4	-5.3	7.1	2 0 7	62.2	-62.8	.6
0 4 20	10.1	-17.3	7.2	0 5 22	20.4	-26.8	6.4	2 0 9	66.9	-59.2	7.7
0 4 22	19.9	19.3	.6	0 5 24	3.0	-6.8	3.8	2 0 11	16.5	5.9	10.6
0 4 24	0.0	-0.4	(.4)	0 5 26	5.9	-9.8	3.9	2 0 13	1.6	1.8	.2
0 4 26	9.7	10.1	.4	0 5 28	2.3	2.2	.1	2 0 15	37.8	42.3	4.5
0 4 28	3.6	5.1	1.5	0 7 2	29.6	-25.7	3.9	2 0 17	31.6	32.6	1.0
0 6 2	14.2	19.2	5.0	0 7 4	48.3	-48.3	.0	2 0 19	12.8	-19.4	6.6
0 6 4	29.0	-22.5	6.5	0 7 6	24.8	-17.2	7.6	2 0 21	11.7	-17.6	5.9
0 6 6	44.4	-43.4	1.0	0 7 8	20.1	-25.5	5.4	2 0 23	3.2	-13.7	10.5
0 6 8	29.6	-29.6	.0	0 7 10	0.0	0.0	.0	2 0 25	34.7	-34.0	.7
0 6 10	18.4	14.1	4.3	0 7 12	7.1	-7.1	.0	2 0 27	5.9	2.5	3.4
0 6 12	23.4	25.4	2.0	0 7 14	13.6	21.2	8.6	2 0 29	3.7	2.7	1.0
0 6 14	15.1	14.2	.9	0 7 16	0.0	-2.6	(2.6)	4 0 1	40.2	29.7	10.5
0 6 16	9.2	-0.6	8.6	0 7 18	8.3	-7.1	1.2	4 0 3	43.8	-40.9	2.9
0 6 18	17.1	8.6	8.5	0 7 20	15.3	-8.6	6.7	4 0 5	17.4	20.1	2.7
0 6 20	16.9	-19.6	2.7	0 7 22	10.1	-15.4	5.3	4 0 7	0.0	0.0	.0
0 6 22	18.1	-18.9	.8	0 7 24	13.3	5.9	7.4	4 0 9	12.8	12.8	.0
0 6 24	11.2	18.6	7.4	0 7 26	8.3	3.4	4.9	4 0 11	4.3	3.2	11.1
0 6 26	0.0	2.9	(2.9)	0 7 28	6.5	-6.5	.0	4 0 13	3.0	-6.1	3.1
0 6 28	4.1	4.1	.0	0 9 2	34.3	35.6	1.3	4 0 15	16.9	20.1	3.2
0 8 2	32.6	34.2	1.6	0 9 4	4.1	3.0	1.1	4 0 17	0.0	14.8	(14.8)
0 8 4	38.8	36.2	2.4	0 9 6	3.0	5.0	2.0	4 0 19	11.2	-13.7	2.5
0 8 6	0.0	1.5	(1.5)	0 9 8	9.5	4.2	5.1	4 0 21	0.0	-5.7	(5.7)
0 8 8	12.4	-13.0	.6	0 9 10	11.3	8.9	2.5	4 0 23	11.0	16.0	5.0
0 8 10	0.0	3.5	(3.5)	0 9 12	11.5	-11.3	.2	4 0 25	2.7	-3.7	.0
0 8 12	0.0	7.4	(7.4)	0 9 14	4.2	-5.6	1.4	4 0 27	7.3	7.5	.2
0 8 14	20.4	-20.0	.4	0 9 16	0.0	7.5	(7.5)	6 0 1	0.0	-5.5	(5.5)
0 8 16	8.9	-17.8	8.9	0 9 18	0.0	1.7	(1.7)	6 0 3	8.0	8.2	.2
0 8 18	9.1	4.5	4.6	0 9 20	3.2	2.2	1.0	6 0 5	35.2	-32.0	3.2
0 8 20	0.0	9.0	(9.0)	0 9 22	3.0	-3.5	.5	6 0 7	5.0	-0.9	2.5
0 8 22	3.6	5.0	1.4	0 11 2	8.0	-5.1	2.9	6 0 9	31.1	34.2	3.1
0 8 24	7.1	12.3	5.2	0 11 4	8.8	11.9	3.1	6 0 11	8.6	-5.5	3.1
0 8 26	8.6	-9.2	.6	0 11 6	9.8	14.2	4.4	6 0 13	13.3	-14.4	1.1
0 10 2	20.1	22.1	2.0	0 11 8	9.5	5.8	3.7	6 0 15	15.6	-16.7	1.1
0 10 4	0.0	-4.3	(4.3)	0 11 10	4.1	-3.7	.4	6 0 17	13.5	-13.0	.5
0 10 6	4.1	-7.3	3.2	0 11 12	8.0	4.7	3.3	6 0 19	0.0	-7.3	(7.3)
0 10 8	4.2	3.8	.4	0 11 14	6.2	-1.8	4.4	6 0 21	6.4	5.7	.7
0 10 10	0.0	-2.9	2.9	0 11 16	2.9	2.5	.4	6 0 23	2.7	2.9	.2
0 10 12	0.0	3.3	3.3	0 13 2	2.4	-0.9	1.5				
0 10 14	8.3	-2.9	5.4	0 13 4	8.0	-8.3	.3				
0 10 16	2.4	3.3	.9								
0 10 18	3.3	-6.2	2.9								
0 10 20	3.6	1.5	2.1								

(001) plane is accounted for by these non-polar regions. This structural principle is characteristic of the crystal structure of salts of aromatic acids such as potassium hydrogen bisphenylacetate (Speakman, 1949), zinc and magnesium benzene sulphonates (Broomhead & Nicol, 1948), and sodium, potassium and rubidium benzylpenicillin (Crowfoot, Bunn, Rogers-Low & Turner-Jones, 1949). It is interesting to note that in every one of these crystals, just as in the series of alkali acid

phthalates discussed here, the contact between benzene rings always involves twofold screw axes.

No hydrogen bond is found between the phthalate ions; but the approach of 3.08 Å between O<sub>I</sub> and O<sub>II</sub> of the same ion might be due to a weak hydrogen bond, since the 128° angle of C<sub>I</sub>-O<sub>I</sub>-O<sub>II</sub> is somewhat favorable. This is in contrast to free phthalic acid, where no such intramolecular hydrogen bond is formed (van Schalkwyk, 1954). This point in the alkali acid

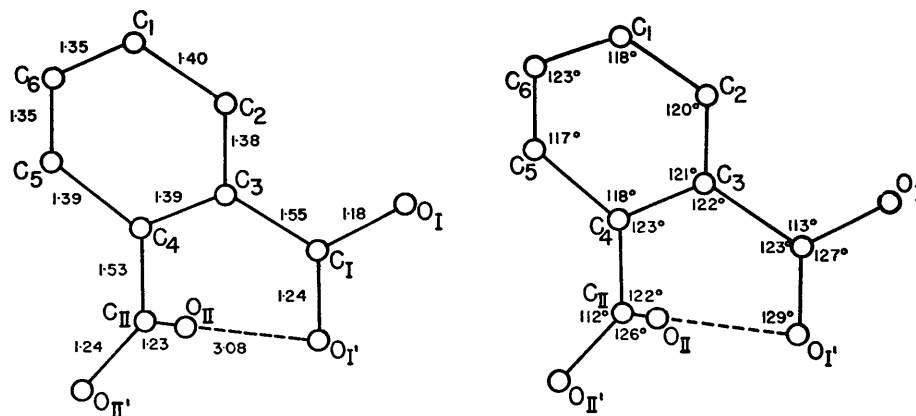


Fig. 6. Bond distances and bond angles in phthalate ion, from  $\text{NH}_4$  acid salt.

phthalate structures cannot be properly clarified without a neutron diffraction analysis.

A projection of the structure, illustrating packing and coordination around the ammonium ion, is shown in Fig. 5. All van der Waals' distances between aromatic carbons are normal.

That the benzene ring and  $\text{C}_I$  and  $\text{C}_{II}$  lie in a single plane was established by obtaining the equation of the plane through these eight carbon atoms. The equation, evaluated by least squares, is

$$x + 0.647_5y + 2.099_0z = 0.832_9,$$

$x$ ,  $y$  and  $z$  being measured in fractions of cell edges. The displacement of all eight atoms from this plane is less than 0.05 Å. The benzene ring is a slightly distorted regular hexagon, with somewhat short distances of 1.35 Å for the bonds  $\text{C}_6-\text{C}_1$  and  $\text{C}_5-\text{C}_6$ . All carboxyl groups are planar within the limits of error. Carboxyl group I has two non-equivalent bonds, with  $\text{C}-\text{O}_I$  probably a double bond and  $\text{C}-\text{O}'_I$  a single bond. The non-equivalency of  $\text{C}-\text{O}$  bond lengths in a carboxyl group is of course found in other crystals: 1.184 and 1.338 Å in nicotinic acid (Wright & King, 1953); 1.16 and 1.26 Å in furoic acid (Goodwin & Thomson, 1954); and 1.187 and 1.285 Å in oxalic acid dihydrate (Ahmed & Cruickshank, 1953).

Bond lengths and angles are shown in Fig. 6.

Owing to steric hindrance, the carboxyl groups are not in the plane of the benzene ring. The angle be-

tween the plane of the benzene ring and that of the carboxyl group is  $21^\circ$  for group I and  $65^\circ$  for group II.

Coordinate accuracy was assessed by the method of Cruickshank (1949). The standard deviation of bond lengths is calculated as 0.03 Å, and that of bond angles as  $5^\circ$ .

#### References

- AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.  
 BROOMHEAD, J. M. & NICOL, A. D. I. (1948). *Acta Cryst.* **1**, 88.  
 CROWFOOT, D., BUNN, C. W., ROGERS-LOW, B. W. & TURNER-JONES, A. (1949). *The Chemistry of Penicillin*, p. 310. Princeton: University Press.  
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.  
 DUKE, J. R. C. & LLEWELLYN, F. J. (1950). *Acta Cryst.* **3**, 305.  
 GOODWIN, T. H. & THOMSON, C. M. (1954). *Acta Cryst.* **7**, 166.  
 GROTH, P. (1917). *Chemische Kristallographie*, vol. 4, pp. 724-6. Leipzig: Engelmann.  
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.  
 MUTHMANN, W. & RAMSAY, W. (1890). *Z. Kristallogr.* **17**, 83.  
 NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1952). *Acta Cryst.* **5**, 499.  
 SCHALKWYK, T. G. D. VAN (1954). *Acta Cryst.* **7**, 775.  
 SPEAKMAN, J. C. (1949). *J. Chem. Soc.* p. 3357.  
 WRIGHT, W. B. & KING, G. S. D. (1953). *Acta Cryst.* **6**, 305.  
 ZIRNGIEBL, H. (1902). *Z. Kristallogr.* **36**, 118.