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Structures of three salts of phthalic acid; variation in crystal packing and geometry of the hydrogen phthalate ion

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The hydrogen-bond patterns in hydrogen phthalates (HP) have been elucidated by the determination of the crystal structures of hydrogen phthalate salts of $[\text{Mg}(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})_2]^{2+}$, 2-(2'-pyridylamine)pyridinium and diethylammonium. The stoichiometry of the latter salt corresponds to a hydrogen phthalate salt; however, it contains the phthalic acid in its three possible acid–base forms. The hydrogen phthalate ions in the three salts display the two common hydrogen-bonding motifs. One has a very short intramolecular O–H–O hydrogen bond (Intra-H), as seen in the magnesium salt $[\text{O}\cdots\text{O} 2.397(2) \text{ \AA}]$. In the other two salts the hydrogen phthalate ions are connected by hydrogen bonds into infinite chains (Chain-H) with O \cdots O distances of 2.460(1) Å in the diethylamine salt and 2.610(1) Å in the 2,2'-dipyridylamine salt. This difference in hydrogen-bond pattern was further elucidated by a search in the Cambridge Structural Database for other hydrogen phthalate salts. Intra-H possesses the shortest O \cdots O distances and an almost planar hydrogen phthalate ion, whereas the hydrogen phthalate ions show significantly more variation in the Chain-H salts. The two hydrogen-bonding motifs are reflected in the molecular geometry of the hydrogen phthalate ion.

1. Introduction

Acid salts of dicarboxylic acids are characterized by their ability to form salts where the two carboxy groups are linked by very short O–H \cdots O hydrogen bonds. Maleic and phthalic acid appear to be closely related dicarboxylic acids differing only in the bond character of the C–C bond that connects the two carboxylic acid groups, the C–C bond in hydrogen phthalates (HP) being 0.1 Å longer. Considering this small difference, it is noteworthy that their acid salts show differences in their hydrogen-bond pattern. A characteristic feature of the hydrogen maleates is the very short intramolecular (or intraionic) hydrogen bond that connects the carboxylate and carboxylic acid groups with very short O \cdots O distances around 2.4 Å. The short intramolecular hydrogen bond is symmetric and in many of the salts a result of crystallographic symmetry (mirror plane or twofold axis) (Olovsson *et al.*, 1984). A similar short intramolecular hydrogen bond (Intra-H) is also observed in hydrogen phthalates, but in these systems the hydrogen bond is usually not symmetrical and not constrained by crystallographic symmetry. Despite this HP salts display some of the shortest O \cdots O distances (Steiner & Saenger, 1994). In addition to the Intra-H the hydrogen phthalates show another equally frequent hydrogen-bonding pattern: the carboxy groups from HP ions related by crystallographic symmetry are connected by longer O–H \cdots O hydrogen bonds

with O...O distances in the range 2.45–2.65 Å forming infinite chains (Chain-H). Schematic drawings of the two different hydrogen bond patterns are shown in Fig. 1. Which of the two possible hydrogen-bonding modes that is adopted in a hydrogen phthalate salt depends obviously on the nature of the cation and the conditions for the preparation of the HP salt. A study by Gonschorek & Küppers (1975) concluded that Intra-H hydrogen bonds appear to be favoured in salts of cations with a small coordination number. The variation in hydrogen-bond patterns was later reinvestigated by Jessen & Küppers (1991), in terms of cation size and Coulombic attraction. Assuming that the HP ion with the Intra-H bond is energetically favoured, they concluded that the smaller Coulombic force exerted by the larger cations could explain the decreasing trend to twist the carboxy groups out of the plane of the phenyl group, as required for the formation of the Chain-H hydrogen pattern. This was illustrated by the Chain-H hydrogen-bond patterns seen in the HP salts of NH_4^+ and $(\text{CH}_3)_4\text{N}^+$, and the Intra-H hydrogen bonds in the HP salts of $(\text{C}_2\text{H}_5)_4\text{N}^+$ and $(\text{C}_4\text{H}_9)_4\text{N}^+$.

In order to further investigate these earlier findings we undertook structure determinations of the salts of phthalic acid with a small inorganic ion, magnesium, a relatively small organic amine, diethylamine $[(\text{C}_2\text{H}_5)_2\text{NH}]$, and a larger aromatic amine, 2,2'-dipyridylamine $[(\text{C}_5\text{NH}_4)_2\text{NH}]$. Additionally the increasing number of structures in the Cambridge Structural Database presented the opportunity to investigate the distribution among the two different hydrogen-bond patterns (Intra-H and Chain-H).

We present here the three new structures, along with the results of an analysis of the influence of the hydrogen-bonding

modes (Intra-H and Chain-H) on the molecular geometry of the hydrogen phthalate ions.

2. Experimental

The three salts of phthalic acid were obtained by the reaction of stoichiometric amounts of the acid with MgO, diethylamine (dea) and 2,2'-dipyridylamine (dpa). The crystalline materials obtained in the processes are referred to as MgHP, deaHP and dpaHP hereinafter.

2.1. Preparation of diffraction-quality crystals

2.1.1. MgHP. The precipitate obtained from a solution containing stoichiometric amounts of phthalic acid and MgO in water (mole ratio 2:1) was recrystallized from methanol to obtain single crystals suitable for diffraction.

2.1.2. deaHP. The compound was prepared by dissolving phthalic acid in water followed by the slow addition of an equimolar amount of diethylamine $(\text{C}_2\text{H}_5)_2\text{NH}$. Colourless crystals appeared several weeks after the evaporation of the solvent.

2.1.3. dpaHP. The crystals were obtained by dissolving phthalic acid in boiling 96% ethanol and adding an equimolar amount of 2,2'-dipyridylamine $(\text{C}_5\text{H}_4\text{N})_2\text{NH}$. Slow evaporation of the solvent resulted in colourless crystals.

2.2. X-ray crystallography

2.2.1. MgHP. Low-temperature data (122 K) were collected on a Nonius Kappa CCD diffractometer. Cell parameters were determined using φ/χ scans (Duisenberg *et al.*, 2000) with *DIRAX* (Duisenberg, 1992). The data were integrated using *EvalCCD* (Duisenberg *et al.*, 2003) and reduced in *maxUs* (Mackay *et al.*, 1998). The structure was solved using *SIR92* (Altomare *et al.*, 1994) and refined with *SHELXL97* (Sheldrick, 1997). The methyl group of the coordinated CH_3OH molecule is disordered and attempts to model the disorder did not yield satisfying results. In the final model an isotropic temperature factor was used for the methyl C atom and H atoms were introduced in idealized positions. All other H atoms were located in the difference-density map and refined with displacement parameters constrained to be $1.2U_{\text{eq}}$ of the bonded non-H atom.

2.2.2. deaHP and dpaHP. Low-temperature data (122 K) were collected on a CAD-4 diffractometer. Data reductions were performed using the *DREADD* program package (Blessing, 1987); the structures were solved using *SHELXS* (Sheldrick, 1990) and subsequently refined with *SHELXL97* (Sheldrick, 1997). The data of deaHP were corrected for extinction by the introduction of an isotropic extinction parameter in the *SHELXL* refinement. The positional parameters and isotropic displacement parameters of all H atoms were included in the refinement. In the dpaHP structure the 2-(2'-pyridylamine)pyridinium ion is disordered and a refinement of the site occupancy factors for the two different orientations gave 0.843 (2) and 0.157 (2). H atoms of the disordered cation were introduced in idealized positions,

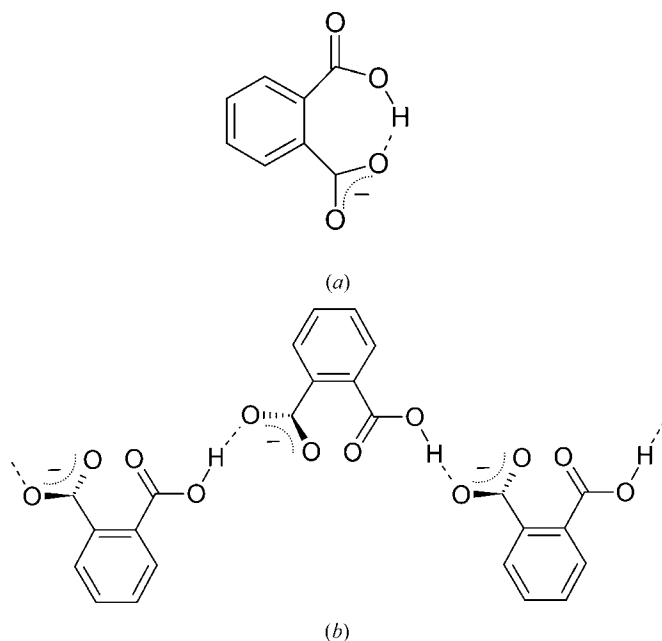


Figure 1

Schematic drawing of the two hydrogen-bonding modes of the hydrogen phthalate ion. (a) Intra-H; (b) Chain-H.

Table 1
Experimental details.

	MgHP	deaHP	dpaHP
Crystal data			
Chemical formula	C ₂ H ₁₆ MgO ₆ ·2C ₈ H ₅ O ₄	C ₈ H ₅ O ₄ ·C ₄ H ₁₂ N	C ₁₀ H ₁₀ N ₃ ·C ₈ H ₅ O ₄
<i>M_r</i>	490.70	239.27	337.33
Cell setting, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.082 (1), 7.8470 (7), 15.1970 (8)	23.289 (5), 10.279 (3), 15.298 (2)	7.179 (3), 9.0034 (17), 24.610 (4)
β (°)	96.842 (5)	93.80 (2)	98.76 (2)
<i>V</i> (Å ³)	1075.32 (16)	3654.0 (15)	1572.2 (7)
<i>Z</i>	2	12	4
<i>D_x</i> (Mg m ⁻³)	1.515	1.305	1.425
Radiation type	Mo <i>K</i> α	Cu <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	1.5418	0.71073
No. of reflections for cell parameters	537	20	25
θ range (°)	0.8–20.4	38.5–45.0	20.2–22.0
μ (mm ⁻¹)	0.16	0.81	0.10
Temperature (K)	122.4 (5)	122.4 (5)	122.4 (5)
Crystal size (mm)	0.45 × 0.21 × 0.18	0.52 × 0.26 × 0.24	0.52 × 0.32 × 0.14
Crystal form, colour	Prismatic, colourless	Prismatic, colourless	Prismatic, colourless
Data collection			
Diffractometer	Nonius KappaCCD	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Data collection method	–	ω – 2θ scans	ω – 2θ scans
Absorption correction	None	None	None
No. of measured, independent and observed reflections	11 508, 2464, 1897	13 837, 7504, 5934	20 676, 12 908, 10 136
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.050	0.014	0.017
θ _{max} (°)	27.5	74.9	45.0
Range of <i>h</i> , <i>k</i> , <i>l</i>	–11 ⇒ <i>h</i> ⇒ 11 –10 ⇒ <i>k</i> ⇒ 10 –19 ⇒ <i>l</i> ⇒ 19	–29 ⇒ <i>h</i> ⇒ 15 –5 ⇒ <i>k</i> ⇒ 12 –19 ⇒ <i>l</i> ⇒ 19	–14 ⇒ <i>h</i> ⇒ 14 0 ⇒ <i>k</i> ⇒ 17 0 ⇒ <i>l</i> ⇒ 48
No. and frequency of standard reflections	–	5 every 167 min	5 every 167 min
Intensity decay (%)	–	0	3
Refinement			
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
R[<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 148, 1.23	0.034, 0.094, 1.03	0.054, 0.149, 1.18
No. of reflections used	2464	7504	12 908
No. of parameters	190	665	362
H-atom treatment	Mixture of independent and constrained refinement	Refined independently	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0756P)^2 + 0.4222P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.8572P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.4582P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.001	0.001	0.022
$\Delta\rho$ _{max} (e Å ⁻³)	0.46	0.29	0.69
$\Delta\rho$ _{min} (e Å ⁻³)	–0.52	–0.21	–0.33
Extinction method	–	SHELXL	–
Extinction coefficient	–	0.00119 (7)	–

Computer programs used: *KappaCCD*, *Enraf–Nonius Express* (Enraf–Nonius, 1994), *COLLECT* (Nonius BV, 1999), *DIRAX* (Duisenberg, 1992), *EvalCCD* (Duisenberg *et al.*, 2003), *DREADD* (Blessing, 1987), *SHELXS97* (Sheldrick, 1990), *SHELXL97* (Sheldrick, 1997), *ORTEPII* (Johnson, 1976).

while the H atoms of the HP ion were located in the difference density map and refined with displacement parameters constrained to be 1.2*U*_{eq} of the bonded non-H atom. The H atom of the secondary amine N1 (major orientation) was refined as were those of the HP ion. One H atom was not located because of the nature of the cation and the disorder. Details of the three data collections, reductions and refinements are summarized in Table 1.¹

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: NS5001). Services for accessing these data are described at the back of the journal.

3. Results

3.1. Structure of MgHP

The asymmetric unit contains half of a hexa-coordinated Mg ion [Mg(H₂O)₄(CH₃OH)₂]²⁺ located on a crystallographic inversion centre and one hydrogen phthalate ion. An *ORTEPII* (Johnson, 1976) drawing of the two entities is shown in Fig. 2. The structures of four other magnesium hydrogen phthalate salts have previously been determined (Kariuki & Jones, 1989, 1992). These comprise the structure of [Mg(H₂O)₂](HP)₂, two crystal forms of [Mg(H₂O)₆](HP)₂ and the structure of [Mg(H₂O)₆](HP)₂·2H₂O. In three of these structures the Mg²⁺ ion is also located on a crystallographic

Table 2
Selected bond distances in the MgHP structure (Å).

C7—O1	1.227 (3)	Mg—O11	2.069 (2)
C7—O2	1.296 (3)	Mg—O12	2.011 (2)
C8—O3	1.286 (3)	Mg—O13	2.104 (2)
C8—O4	1.233 (3)		

inversion centre. The Mg^{2+} ion of MgHP is octahedrally coordinated to the O atoms from four H_2O molecules and two CH_3OH molecules. The Mg—O distances (listed in Table 2) correspond well to the range observed in the previous Mg hydrogen phthalate structures (1.977–2.163 Å), where the Mg^{2+} ion is coordinated to water molecules and in one case also to O atoms of the hydrogen phthalate ion.

The hydrogen phthalate ion is almost planar with a distinctly asymmetric intramolecular hydrogen bond (Table 3). Based on the C—O distances (Table 2) the negative charge appears to be concentrated on O3 as both C7—O1 and C8—O4 distances resemble those of normal double bonds. The intramolecular hydrogen bond exerts a significant effect on the geometry of the hydrogen phthalate ion. The two COO groups are twisted slightly out of the plane of the benzene ring, thus locating the 'inner' O atoms on the same side of the plane. The angle between the least-squares plane of the benzene ring and COO of the carboxylic group is $2.7(2)^\circ$, while the corresponding angle between the benzene ring and the carboxylate group is $9.9(2)^\circ$. The intramolecular hydrogen bond causes a lengthening of the C1—C2 bond, $d(\text{C1—C2}) = 1.422(3)$ Å. Viewed along the crystallographic *b* axis the packing can be described as alternating ribbons of HP ions and hexa-coordinated Mg^{2+} ions, as shown in Fig. 3. The HP ions are stacked along the *c* axis, the benzene rings almost overlap with the carboxy groups pointing in opposite directions and with a distance of approximately 7.5 Å between the benzene rings. All possible donor atoms are involved in hydrogen bonds, as illustrated in Table 3.

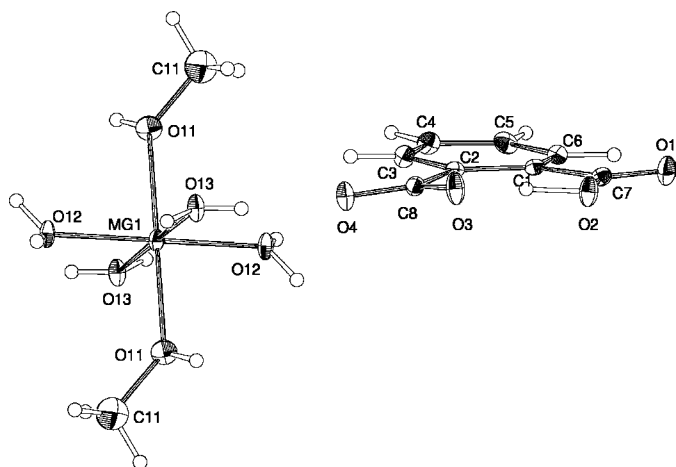


Figure 2
ORTEPII (Johnson, 1976) drawings of the ions of MgHP. The asymmetric unit contains one HP ion and $1/2[\text{Mg}(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})_2]^{2+}$. Thermal ellipsoids are drawn at the 50% probability level.

Table 3
Hydrogen bonds in MgHP (Å, °).

<i>D</i> —H	<i>A</i>	<i>d</i> (<i>D</i> — <i>A</i>)	<i>d</i> (<i>D</i> —H)	<i>d</i> (H— <i>A</i>)	\angle <i>D</i> —H— <i>A</i>
O2—H2	O3	2.378 (2)	1.08 (3)	1.30 (3)	178 (3)
O11—H11	O1 ⁱ	2.690 (2)	0.76 (3)	1.94 (3)	175 (3)
O12—H12A	O3 ⁱⁱ	2.686 (2)	0.71 (3)	1.99 (3)	173 (3)
O12—H12B	O2 ⁱⁱⁱ	2.786 (2)	0.85 (3)	1.95 (3)	170 (3)
O13—H13A	O4	2.914 (2)	0.81 (3)	2.14 (3)	160 (3)
O13—H13B	O4 ^{iv}	2.831 (2)	0.83 (3)	2.01 (3)	169 (3)

Symmetry codes: (i) $x-1, y-1, z$; (ii) $x, y-1, z$; (iii) $-x+2, -y+2, -z+1$; (iv) $-x+1, -y+2, -z+1$.

3.2. Structure of deaHP

This crystal structure is remarkable because it contains 'phthalic acid' in its three possible protonation states. The ORTEPII (Johnson, 1976) drawings of the entities of this structure are shown in Fig. 4, while the crystal packings are depicted in Fig. 6. The different protonation states are clearly reflected in the variation of the C—O bond lengths of the six carboxy groups (1.274–1.325 Å, Table 4). The entity labeled *A* is a phthalate dianion, entity *B* is a hydrogen phthalate anion and entity *C* the neutral phthalic acid. In all three moieties the carboxy groups are twisted out of the plane of the benzene ring. Least-squares planes were calculated for the benzene rings and the planes of the respective COO fragments. The degree of protonation does not affect the angle between the two COO fragments: *A* $58.0(1)$, *B* $59.1(1)$ and *C* $58.5(1)^\circ$. The angles between the benzene rings and their respective COO fragments do, however, show a large variation: in *A* $57.66(5)$ and $49.28(6)^\circ$, in *B* $43.51(7)$ and $46.00(7)^\circ$, and in *C* $46.92(7)$ and $37.96(8)^\circ$, respectively. It is noteworthy that the

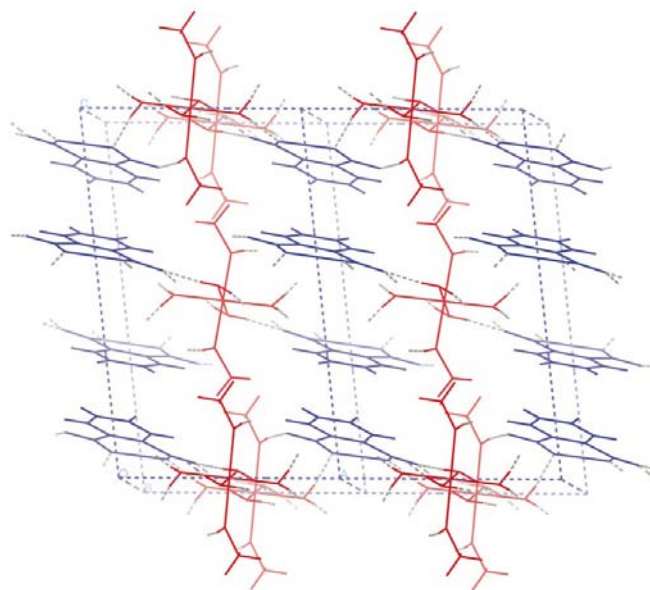


Figure 3
Crystal packing of MgHP viewed along the *b* axis. HP ions are blue while the hexa-coordinated Mg ions are red.

Table 4
C—O distances (Å) and selected torsion angles (°) in the deaHP structure.

'C—O'		'C=O'			
C7A—O1A	1.280 (2)	C7A—O2A	1.239 (2)	C13—N1—C12—C14	−69.78 (2)
C8A—O3A	1.274 (2)	C8A—O4A	1.239 (2)	C12—N1—C13—C11	−176.1 (1)
C7B—O2B(H)	1.290 (2)	C7B—O1B	1.231 (2)	C23—N2—C22—C21	−88.6 (2)
C8B—O4B	1.283 (2)	C8B—O3B	1.238 (2)	C22—N2—C23—C24	176.9 (1)
C7C—O1C(H)	1.325 (2)	C7C—O2C	1.211 (2)	C33—N3—C32—C31	170.6 (1)
C8C—O3C(H)	1.296 (2)	C8C—O4C	1.231 (2)	C32—N3—C33—C34	178.4 (1)

largest difference is observed for the angles of the *A* and *C* entities, in which the two COO fragments are chemically identical.

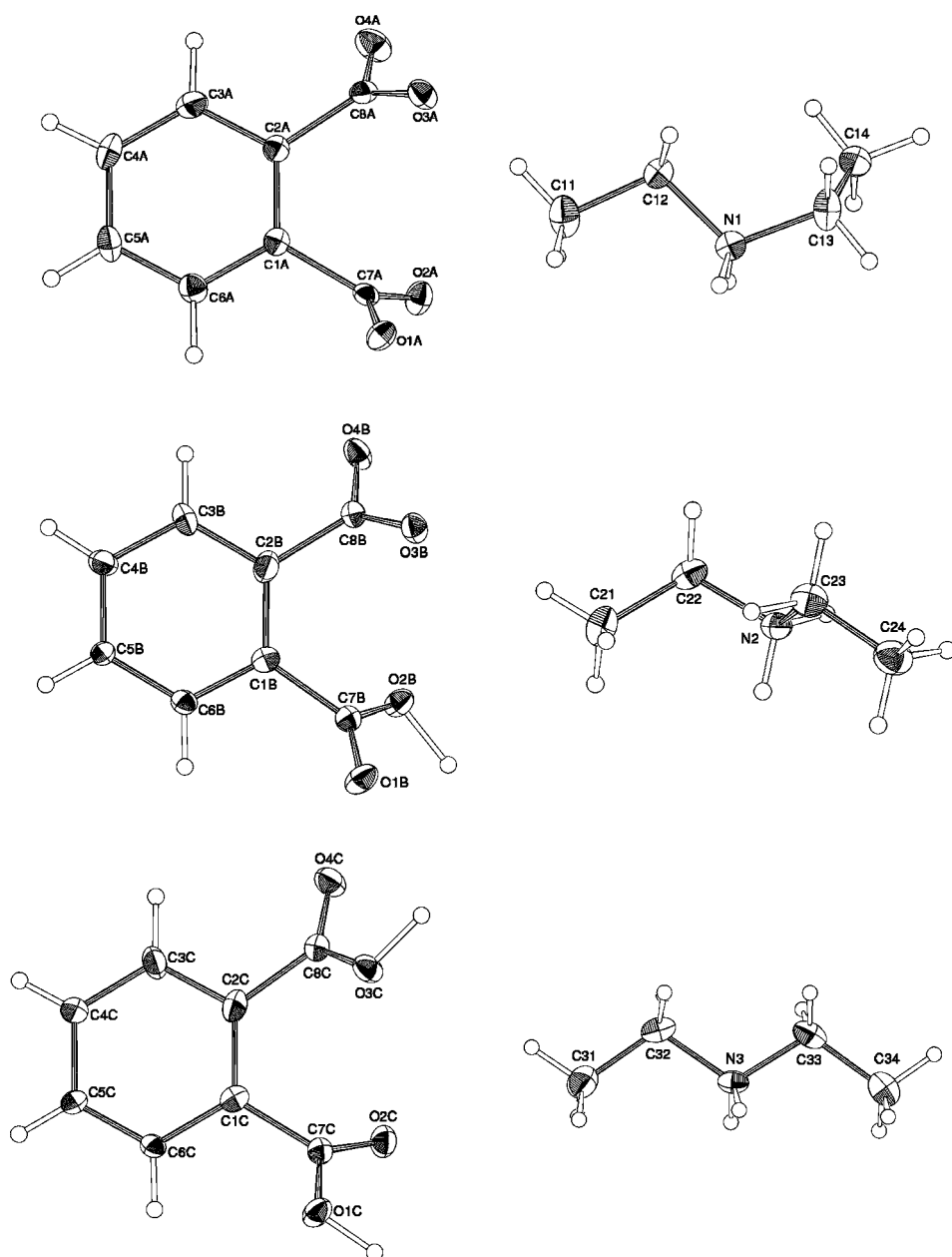


Figure 4
ORTEPII (Johnson, 1976) drawings of the entities in deaHP. Thermal ellipsoids are drawn at the 50% probability level.

The hydrogen bonds listed in Table 5 show that all the possible donor atoms participate in hydrogen bonds. The phthalate dianion (*A*) is hydrogen bonded to all three cations, the hydrogen phthalate anion (*B*) is hydrogen bonded to cations 1 and 3, and phthalic acid (*C*) is hydrogen bonded to cation 3 only. The carboxy groups are connected *via* short O—H···O hydrogen bonds in such a way that entities *A* and *C* are linked to each other *via* two hydrogen bonds. The hydrogen phthalate ions (*B*) are connected by the symmetry of the twofold screw axis into a Chain-H arrangement with short intermolecular O—H···O hydrogen bonds.

The three independent diethyl ammonium ions differ in their conformation, as illustrated in Fig. 4, and in the torsion angles listed in Table 4. This variation shows that the diethyl ammonium ion is rather flexible and able to change its conformation, which would optimize the interactions with the carboxy groups without changes of the bond lengths and angles.

3.3. Structure of dpaHP

The asymmetric unit of dpaHP contains one hydrogen phthalate ion and a disordered 2-(2'-pyridylamine)pyridinium ion, illustrated in the ORTEPII (Johnson, 1976) drawings of Fig. 5. In this structure the hydrogen phthalate ion forms a Chain-H arrangement (Table 6). The anions in the chain are directly related through translational symmetry with period of 7.179 (3) Å. Only one of the O atoms in the carboxylate group is involved in hydrogen bonding. This is reflected in the C—O distances of the carboxylate group (C7) that are close to the values of C—O single and double bonds (Table 7).

Table 5
 Hydrogen bonds in deaHP (units are Å and °).

<i>D</i> — <i>H</i>	<i>A</i>	<i>d</i> (<i>D</i> — <i>A</i>)	<i>d</i> (<i>D</i> — <i>H</i>)	<i>d</i> (<i>H</i> — <i>A</i>)	\angle <i>D</i> — <i>H</i> — <i>A</i>
O2 <i>B</i> —H <i>B</i> <i>B</i>	O4 <i>B</i> ⁱ	2.460 (1)	1.21 (2)	1.25 (2)	176 (2)
O3 <i>C</i> —H <i>C</i> <i>A</i>	O1 <i>A</i>	2.473 (1)	1.14 (2)	1.33 (2)	175 (2)
O1 <i>C</i> —H <i>A</i> <i>C</i>	O3 <i>A</i> ⁱⁱ	2.586 (1)	1.00 (2)	1.59 (2)	171 (2)
N1—H1 <i>N</i> <i>A</i>	O3 <i>B</i> ⁱ	2.769 (1)	0.94 (2)	1.85 (2)	167 (2)
N1—H2 <i>N</i> <i>B</i>	O4 <i>A</i>	2.724 (2)	0.93 (2)	1.83 (2)	159 (2)
N2—H2 <i>N</i> <i>A</i>	O4 <i>C</i>	2.848 (2)	0.93 (2)	1.96 (2)	161 (2)
N2—H2 <i>N</i> <i>B</i>	O3 <i>A</i>	2.791 (2)	0.90 (2)	1.89 (2)	179 (2)
N3—H3 <i>N</i> <i>A</i>	O1 <i>B</i> ⁱⁱⁱ	2.796 (2)	0.92 (2)	1.95 (2)	153 (2)
N3—H3 <i>N</i> <i>B</i>	O2 <i>A</i>	2.808 (1)	0.95 (2)	1.87 (2)	172 (2)

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

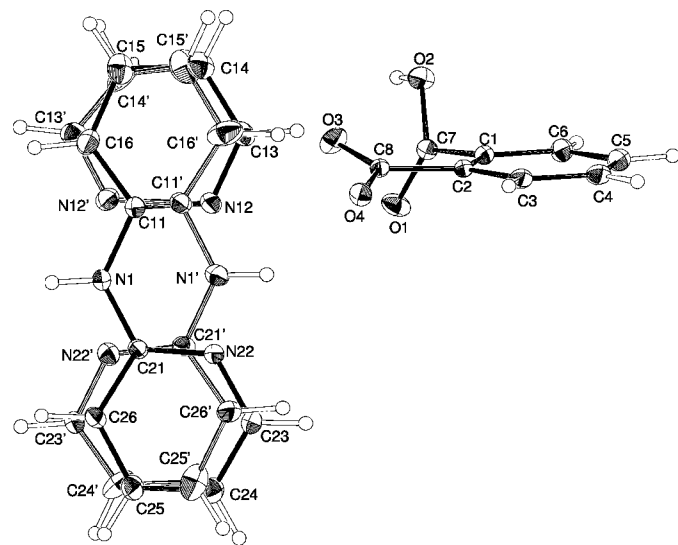
Table 6
 Hydrogen bonds (Å, °) in dpaHP.

<i>D</i> — <i>H</i>	<i>A</i>	<i>d</i> (<i>D</i> — <i>A</i>)	<i>d</i> (<i>D</i> — <i>H</i>)	<i>d</i> (<i>H</i> — <i>A</i>)	\angle <i>D</i> — <i>H</i> — <i>A</i>
O2—H0	O4 ⁱ	2.610 (1)	0.87 (1)	1.75 (1)	169 (2)
N1—H1	O4 ⁱⁱ	2.757 (1)	0.88 (2)	1.88 (2)	177 (2)
N1—H1	O3 ⁱⁱⁱ	3.124 (1)	0.88 (2)	2.58 (2)	121 (1)
N1'—H1'	O3 ⁱⁱⁱ	2.604 (4)	0.88	1.82	147

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z$; (iii) $x - 1, y, z$.

Table 7
 C—O distances (Å) and selected torsion angles (°) in the dpaHP structure.

C7—O1	1.2141 (9)	C21—N1—C11—N12	0.20 (13)
C7—O2	1.3258 (9)	C11—N1—C21—N22	1.17 (13)
C8—O3	1.2412 (8)	C21'—N1'—C11'—N12'	−2.2 (8)
C8—O4	1.2772 (9)	C11'—N1'—C21'—N22'	−1.9 (8)


Figure 5
 ORTEP (Johnson, 1976) drawings of dpaHP. Both positions of the disordered cation are shown, but protonation of the pyridyl group is not shown as the H is most likely distributed over four positions (connected to N12, N22, N12' and N22', respectively). Thermal ellipsoids are drawn at the 50% probability level.

The twist of the COO groups relative to the plane of the benzene rings is illustrated by the angles between least-squares planes. The carboxylate group and benzene ring form an angle of 15.5 (1)°, while the angle between the carboxylic group and the benzene ring is 74.80 (5)°. The 2-(2'-pyridylamine)pyridinium ion is almost planar, as shown by the torsion angles around the central N (Table 7). The cation is disordered over two positions so the pyridine rings of the two components almost coincide, whereas the central N adopts different positions (see Fig. 5). The protonation occurs at the N atoms of the pyridine with the possibility of an intramolecular N—H...N

hydrogen bond, as described in a study of pK_a values and dipole moments (Sobczyk & Koll, 1964). This protonation has been observed in several other salts of 2,2'-dipyridylamine, some (*e.g.* Ng, 1999) with disorder of the cation similar to that observed in the dpaHP structure. With two equivalent pyridine N atoms and disorder the H atom of the protonated pyridyl group can be distributed between four different positions, which explains why it could not be located in the difference density. The position of the H atom bound to the central N atom was refined, resulting in a position in the molecular plane [0.07 (2) Å from the least-squares plane of N1, C11 and C21], confirming the protonation at the pyridine moiety. The crystal packing can be described as alternating stacks of cations and chains of anions as illustrated in Fig. 6.

3.4. The HP ions in the salts

The two hydrogen-bonding modes observed in the three structures are reflected in different conformations of the hydrogen phthalate ions, where the Chain-H mode provides most conformational flexibility. The flexibility of the HP ion leads to quite different conformations evident from the twist of the carboxy groups in the ORTEP (Johnson, 1976) drawings in Figs. 2, 4 and 5. The angles between the carboxy groups and the benzene rings in the three structures vary from 2.7 (2)° for the carboxylic group of MgHP to 74.80 (5)° for the carboxylate group of the HP ion in dpaHP. The variation in C—O distances of the HP ions reflects the number and strength of the hydrogen bonds in which the O atoms are involved. Longer distances correspond to more and stronger interactions. This can be exemplified by the O2C of the deaHP structure, which is the only double-bonded O atom in this structure not to be an acceptor of a hydrogen bond. Therefore, this double-bonded O atom has a significantly shorter bond length (Table 4). The structural analysis has shown that the geometries of the carboxy groups of the HP ions are severely affected by the crystal packing with respect to the relative orientation and conformation, whereas the benzene ring appears to be relatively unperturbed by the orientation and protonization of its two carboxy groups.

3.5. Cambridge Structural Database

The three structures presented in this study show a large variation in the packing and molecular geometry of the hydrogen phthalate ion. We wanted to make a further investigation in this feature and conducted a search of the Cambridge Structural Database (Cambridge Structural Database, 2002) for hydrogen phthalate ions. In the search, structures with an *R*-factor larger than 0.075 were eliminated, resulting in 43 structures with HP ions. The structures were classified into types depending on the hydrogen-bond pattern of the HP ions: Intra-H (18 structures/23 HP ions) with intramolecular hydrogen bonds in the hydrogen phthalate ions and Chain-H (19 structures/21 HP ions) with intermolecular hydrogen bonds between the HP ions. Five structures did not conform to these motifs, they represent salts of very large cations and/or cases where the HP ions serve as ligands. In four of these compounds the HP ions are hydrogen bonded to water molecules and in the salt of a large molybdenum cluster (Wu *et al.*, 1998) the intermolecular hydrogen bonds connect two HP ions into a dimer. Additionally one structure was omitted because of an obviously wrong geometry of the HP ion. The salts belonging to the two general types (Intra-H and

Chain-H) are listed in Tables 8 and 9, respectively. After this classification the average molecular geometry was calculated and is listed in Table 10.

3.6. Intra-H-type hydrogen phthalates

The hydrogen phthalates with the Intra-H motif include salts of the small lithium ion, larger organic bases and a few transition metal complex cations. The intramolecular hydrogen bonds appear asymmetrical in all the structures in Table 8. The two carboxy groups have very similar geometry and the bridging H atom is not well defined in any of the structures. The crystal packing of the salts belonging to this group differs, but the molecular geometry of the hydrogen phthalate ion is well defined and similar in all the salts. The O...O distances fall in the narrow range 2.36–2.46 Å, which reflects the strength and covalent character of the hydrogen bond. The intramolecular hydrogen bond makes the anion almost planar with the carboxylate and carboxylic groups twisted out of the plane of the phenyl group, keeping the 'inner' O atoms on the same side. The scattergram in Fig. 7 shows the variation in the angles between the least-squares planes of the COO groups and phenyl groups. The angle between the phenyl group and the carboxy group can be as large as 32° and the two groups show an almost identical twist relative to the phenyl group. Different stacking can occur for the almost planar HP ion, in bis(*p*-phthalimidoethyl)ammonium hydrogen phthalate (Barrett *et al.*, 1995) where the angles between the phenyl group of HP and one of the aromatic rings of the cation is 5.3 (2)°. Another stacking pattern is seen in the salt of the tris-thioureacopper cation (Cingi *et al.*, 1977) where the anions and cations form separate stacks.

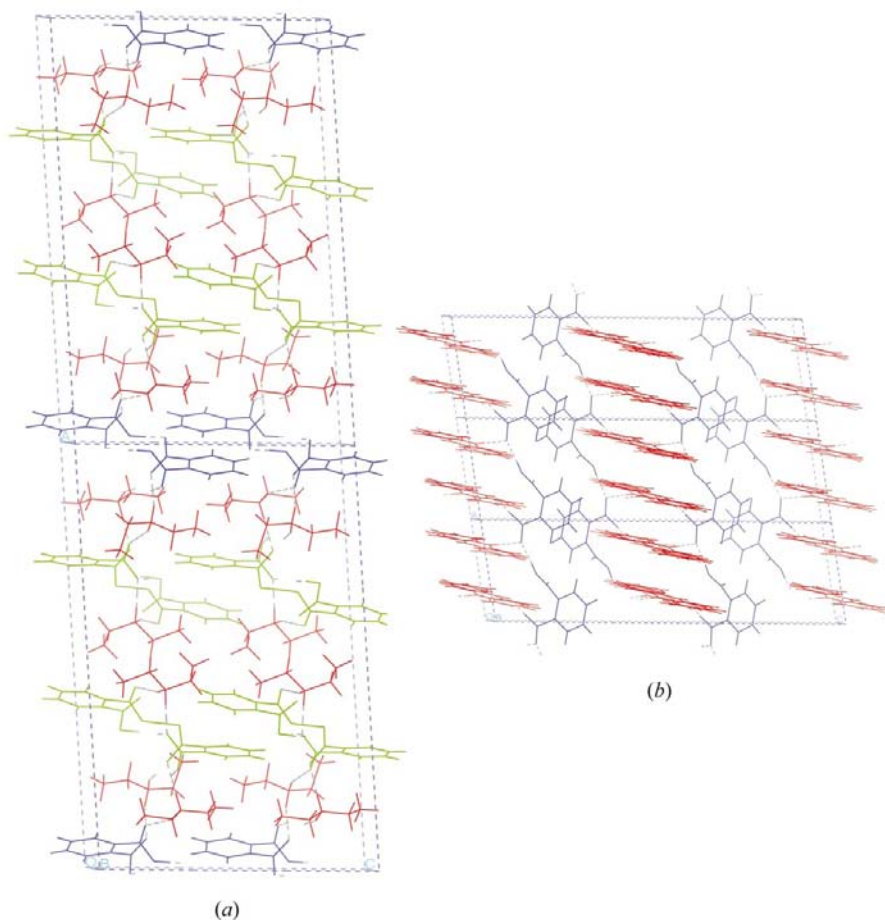


Figure 6

Crystal packing of the two organic salts. Left: deaHP, right: dpaHP. HP anions are blue, cations are red and in green are the phthalic acid molecules and phthalate dianions. Both are views along the *b* axis.

3.7. Chain-H type hydrogen phthalates

Some of the salts of this type display the same packing features and isomorphism between the Na⁺, K⁺, NH₄⁺ and Rb⁺ salts of hydrogen phthalate was suggested early on by Okaya & Pepinsky (1957). Many of the

Table 8

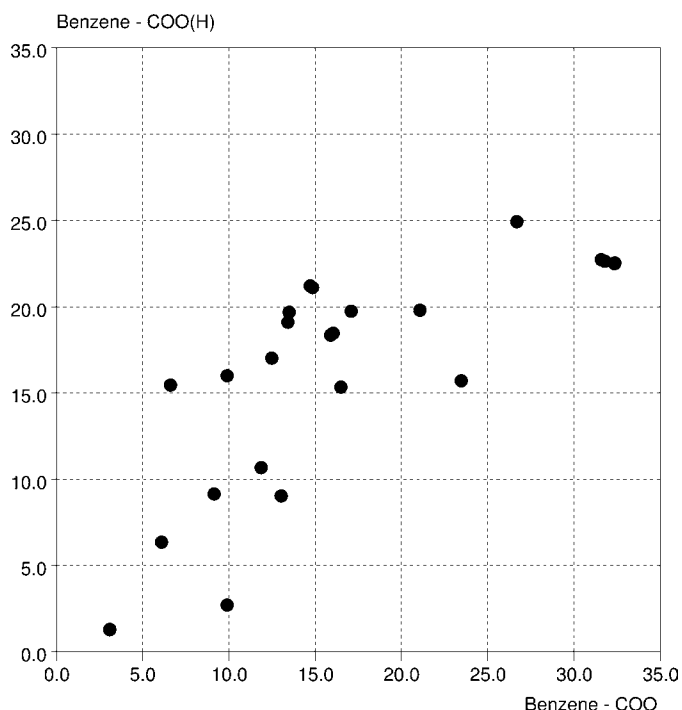
Structures of Intra-H type with the O...O distances of the intramolecular hydrogen bonds in the HP ions.

HP: hydrogen phthalate, C₈H₅O₄⁻.

Compound	O...O (Å)	CSD Refcode
MgHP	2.379 (2)	This study
LiHP...H ₂ O	2.400 (2)	LIHPAL
	2.390 (2)	
LiHP-H ₂ O	2.400†	LIHPAL01
	2.390†	
LiHP-H ₂ O	2.401†	LIHPAL02
	2.390†	
LiHP-H ₂ O	2.404†	LIHPAL03
	2.394†	
LiHP-CH ₃ OH	2.386 (3)	LIHPHM10
	2.382 (3)	
[N(C ₂ H ₅) ₄]HP	2.373	WEWGEK
[N(C ₄ H ₉) ₄]HP	2.384	WEWGIO
(C ₇ H ₁₀ N)HP	2.398 (2)	GUHREG
[Cu(H ₂ O) ₂ (HP) ₂]	2.390 (2)	CUHOPT03
[Cu(H ₂ O) ₂ (HP) ₂]	2.391 (2)	CUHOPT04
[Sb(C ₆ H ₅) ₄]HP	2.407	RAFAC
Cu[SC(NH ₂) ₂] ₃ HP	2.351 (9)	TUCHPL
C ₆ H ₅ CH(NH ₂)CH ₃ HP	2.379 (5)	LIJNAT
[(η^6 -(C ₆ H ₅) ₂ Cr]HP(C ₈ H ₆ O ₄)	2.356 (2)	HOQFOI
(Mn(C ₁₉ H ₂₀ N ₂ O ₄)HP) _n	2.373	COXQOV
(C ₂₀ H ₁₈ N ₃ O ₄)HP	2.384	REVZAT
(C ₂₀ H ₁₈ N ₃ O ₄)HP·1.75H ₂ O	2.385	HONXUD
(C ₂₃ H ₂₅ N ₂)HP(C ₈ H ₆ O ₄)	2.456	NACWOD

† E.s.d.'s are 0.001–0.002 Å.

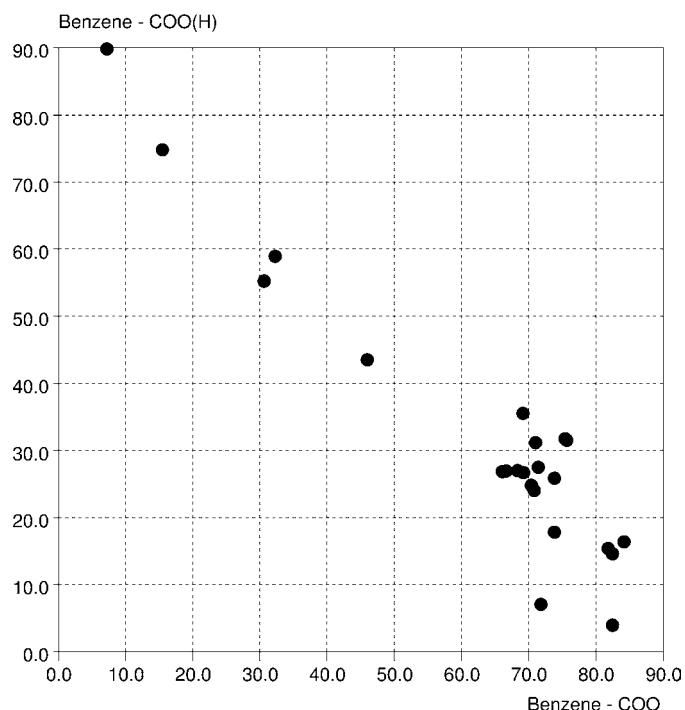
structures contain double layers of HP ions between sheets of cations (and solvent molecules) and infinite chains of anions connected by relatively short intermolecular hydrogen bonds.

**Figure 7**

Angles between the least-squares planes of the carboxy groups and the benzene ring in the Intra-H type HP ions.

This type of packing in these hydrogen phthalate salts was referred to as 'sandwich packing' [anion-cation(+solvent)-anion] by Kariuki & Jones (1992). In nearly all of the structures the HP ions are connected by glide planes to form the infinite chains with O...O distances in the range 2.46–2.66 Å. There is, however, some variation in the relative orientation of the HP ions which is reflected in the different translational periods, while the isomorphism mentioned above results in a common translational period. The COO groups are twisted relative to the phenyl group. In general, angles between the phenyl plane and the carboxylic group are in the range 5–40°, while the angles between the carboxylate group and the phenyl group range from 65 to 85°. The exceptions are the structures from this study and a few structures with highly coordinated HP ions. The angles are listed in Table 9 and the variation is illustrated by the scattergram in Fig. 8. The almost linear dependence of the two angles reveals a sum of the twist angles close to 90°.

3.7.1. Molecular geometry of the HP anions. The molecular geometries of the hydrogen phthalate ions of the two groups (Table 10) differ significantly. When the intramolecular hydrogen bond is present a significant lengthening is observed for the C–C bond between the substituted C atoms in the ring and the two formal single C–C bonds. The angles of the seven-membered ring formed by the strong O–H–O bond increase considerably. The angles C2–C1–C7 and C1–C2–C8 are approximately 3° smaller than the corresponding angles in hydrogen maleates. The twist observed for the carboxylate groups appears to compensate for the more rigid structure of the hydrogen phthalate. The fact that the Intra-H

**Figure 8**

Angles between the least-squares planes of the carboxy groups and the benzene ring in the Chain-H type HP ions.

Table 9

Structures of Chain-H-type with the O...O distances of the intermolecular hydrogen bonds in the HP ions.

The symmetries relating the connected HP ions and the translation periods are given as well as the angles between the least-squares planes of the carboxy groups and benzene rings. HP: hydrogen phthalate, C₈H₅O₄⁻.

Compound	O...O (Å)	Symmetry	Trans. period (Å)	COO(H) ∠ benz (°)	COO(-) ∠ benz (°)	CSD Refcode
deaHP	2.460 (1)	2 ₁	10.279 (3)	43.51 (7)	46.00 (7)	This study
dpaHP	2.610 (1)	Transl.	7.179 (3)	74.80 (5)	15.5 (1)	This study
NaHP·½H ₂ O	2.495	<i>a</i> glide	6.75(1)	26.8	66.1	NAHPHT
NaHP·½H ₂ O	2.511	<i>a</i> glide	6.77	27.0	66.7	NAHPHT02
KHP	2.546	<i>a</i> glide	6.46(1)	31.7	75.4	KHPHAL
KHP	2.552	<i>a</i> glide	6.48	31.5	75.7	KHPHAL01
KHP·½H ₂ O ₂	2.538	<i>b</i> glide	7.463 (1)	17.8	73.8	YUHTAW
RbHP	2.562	<i>a</i> glide	6.561 (1)	31.1	71.0	RBHPHT
Sr(HP) ₂ ·2H ₂ O	2.554 (3)	<i>c</i> glide	6.961 (1)	27.5	71.4	HPHTSR
[NH ₄]HP	2.61 (1)	<i>a</i> glide	6.430 (3)	25.9	73.8	AHPHAL01
[Ni(H ₂ O) ₄ (HP) ₂]·2H ₂ O	2.581 (36)	<i>c</i> glide	12.500 (2)	3.9	82.5	TAHPNI
[Cu(H ₂ O) ₂ (HP) ₂] _n	2.614 (2)	<i>c</i> glide	12.972 (2)	89.8	7.2	DICWER
[Co(H ₂ O) ₆](HP) ₂	2.550	Transl.†	6.560 (1)	26.7	69.3	COHDPH
	2.571	(pseudo <i>a</i>)		15.4	81.8	
[Co(H ₂ O) ₆](HP) ₂	2.586	<i>a</i> glide	12.760 (6)	7.0	71.8	COHDPH02
[Mg(H ₂ O) ₆](HP) ₂	2.526 (11)	Transl.†	6.565 (1)	14.6	82.5	JAPFOV
	2.536			27.6	67.6	
[N(CH ₃) ₄]HP	2.555 (4)	<i>c</i> glide	11.384 (2)	35.5	69.1	KEPNOI
K ₂ [Ni(H ₂ O) ₆](HP) ₄ ·4H ₂ O	2.534	<i>b</i> glide	6.864 (4)	24.0	70.8	CEJMEJ
K ₂ [Co(H ₂ O) ₆](HP) ₄ ·4H ₂ O	2.538	Transl.†	6.86	27.0	68.4	QEQTAH
	2.559	(pseudo <i>b</i>)		24.8	70.4	
(C ₃ H ₇ N ₆)(HP)	2.533 (3)	<i>c</i> glide	7.067 (1)	16.4	84.2	WOVZOW
[Cu(C ₅ H ₅ N) ₂ (HP) ₂]	2.610	<i>c</i> glide	11.853 (2)	58.9	32.3	LITMEG
[Cu(C ₆ H ₈ N) ₂ (HP) ₂]	2.657	<i>c</i> glide	12.107 (2)	55.2	30.6	LITMIK

† Two HP ions in the asymmetric unit which are connected by an intermolecular HB and form the base of the infinite chains.

Table 10

Average molecular geometry of the two types of HP ions (units are Å and °) with sample standard deviation in parentheses.

	Intra-H	Chain-H		Intra-H	Chain-H
C1—C2	1.415 (6)	1.398 (11)	C6—C1—C2	118.3 (5)	119.7 (8)
C2—C3	1.396 (5)	1.391 (7)	C1—C2—C3	118.2 (7)	118.9 (6)
C3—C4	1.378 (10)	1.382 (12)	C2—C3—C4	122.2 (7)	120.8 (6)
C4—C5	1.378 (10)	1.379 (10)	C3—C4—C5	119.4 (4)	120.3 (8)
C5—C6	1.379 (11)	1.381 (14)	C4—C5—C6	119.7 (4)	119.7 (8)
C6—C1	1.397 (7)	1.393 (8)	C5—C6—C1	122.0 (6)	120.6 (8)
C1—C7	1.515 (9)	1.491 (16)	C6—C1—C7	113.8 (7)	119.4 (16)
C2—C8	1.513 (12)	1.505 (14)	C2—C1—C7	127.9 (10)	120.9 (16)
C7—O1	1.226 (9)	1.215 (12)	C1—C2—C8	127.4 (9)	123.6 (13)
C7—O2	1.288 (11)	1.314 (14)	C3—C2—C8	114.3 (6)	117.7 (12)
C8—O3	1.275 (14)	1.243 (12)	C1—C7—O1	119.5 (6)	122.7 (16)
C8—O4	1.236 (16)	1.265 (12)	C1—C7—O2	120.0 (5)	113.6 (12)
			O1—C7—O2	120.4 (7)	123.7 (10)
			C2—C8—O3	118.7 (11)	118.8 (14)
			C2—C8—O4	119.9 (10)	117.5 (10)
			O3—C8—O4	121.3 (15)	123.6 (17)

type hydrogen phthalate ions are not completely planar is a result of the strain exerted on the ring by the formation of the intramolecular hydrogen bond. In the Chain-H motif the C—O bond lengths correspond to well defined carboxylic acid and carboxylate groups. In Intra-H types the C—O bond lengths are more symmetrical with respect to the intramolecular hydrogen bond, an indication of a more delocalized charge resulting from the higher conjugated system with the phenyl group and carboxy groups almost coplanar. The largest differences between the molecular geometry of the two groups are observed in the torsion angles involving the O atoms. The mean angles between the plane of the phenyl ring and COO of the carboxylate/carboxylic group in Intra-H type are 16.3 (6.5)

and 16.8 (8.7)°. The corresponding angles in the Chain-H type salts vary so much that it is not justified to present the average angles (Table 9).

4. Conclusions

The HP ion of MgHP belong to the Intra-H type and the changes in bond lengths and angles observed in this structure are consistent with the previous descriptions of other HP ions in the Intra-H motif. The deaHP structure contains HP ions of Chain-H type. This structure includes the shortest O—H...O hydrogen bond within the Chain-H type and the HP ions are connected by a 2₁ axis. The twist of the COO groups relative to

the phenyl group is atypical. The HP of the dpaHP is also of Chain-H-type, but the hydrogen phthalate ions are connected through direct translation giving rise to an O...O distance which is relatively long compared with the other Chain-H type hydrogen bonds. The conformation of the hydrogen phthalate ion resembles the conformations found in the other salts, but with an opposite twist of the carboxylic and carboxylate groups. The number of structures of each type and the similarity of the hydrogen phthalates within the two modes suggest that the two conformations have almost equal energy. The Intra-H mode gives rise to the strongest hydrogen bond, while the Chain-H mode appears to have the tightest packing. The hydrogen phthalates of hexaaquamagnesium (Kariuki & Jones, 1989, 1992) and the hexaaquacobalt(II) (Adiwidjaja *et al.*, 1978; Küppers, 1990; Kariuki & Jones, 1993) ion form two different crystal forms, one with the Intra-H motif and one with the Chain-H motif. This observation that the same cation can give HP salts with both hydrogen-bonding motifs emphasizes the small difference in their free energies.

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