

N—H···O and O—H···O hydrogen-bonded supramolecular networks in 4-chloroanilinium, 2-hydroxyanilinium and 3-hydroxyanilinium hydrogen phthalates

R. Jagan and K. Sivakumar*

Department of Physics, Anna University, Chennai 600 025, India

Correspondence e-mail: ksivakumar@annauniv.edu

Received 19 June 2009

Accepted 2 July 2009

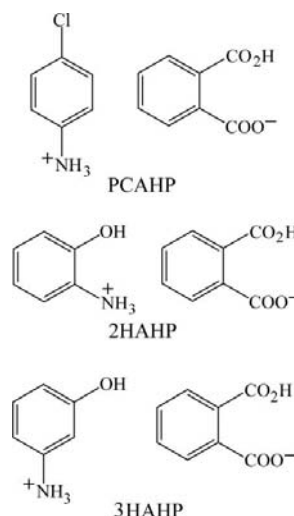
Online 18 July 2009

The title salts, 4-chloroanilinium hydrogen phthalate (PCAHP), $C_6H_7ClN^+ \cdot C_8H_5O_4^-$, 2-hydroxyanilinium hydrogen phthalate (2HAHP), $C_6H_8NO^+ \cdot C_8H_5O_4^-$, and 3-hydroxyanilinium hydrogen phthalate (3HAHP), $C_6H_8NO^+ \cdot C_8H_5O_4^-$, all crystallize in the space group $P2_1/c$. The asymmetric unit of 2HAHP contains two independent ion pairs. The hydrogen phthalate ions of 2HAHP and 3HAHP show a short intramolecular O—H···O hydrogen bond, with O···O distances ranging from 2.3832 (15) to 2.3860 (14) Å. N—H···O and O—H···O hydrogen bonds, together with short C—H···O contacts in PCAHP and 3HAHP, generate extended hydrogen-bond networks. PCAHP forms a two-dimensional supramolecular sheet extending in the (100) plane, whereas 2HAHP has a supramolecular chain running parallel to the [100] direction and 3HAHP has a two-dimensional network extending parallel to the (001) plane.

Comment

Phthalic acid forms hydrogen phthalate salts with various organic and other compounds. Reported hydrogen phthalates include calcium phthalate monohydrate (Schuckmann *et al.*, 1978), lithium hydrogen phthalate monohydrate (Küppers *et al.*, 1985), tetramethylammonium hydrogen phthalate (Jessen, 1990), 2,4,6-triamino-1,3,5-triazinium hydrogen phthalate (Janczak & Perpétuo, 2001) and *N,N'*-diphenylguanidinium dihydrogen phthalate (Pereira Silva *et al.*, 2006). Analysis of the structures archived in the Cambridge Structural Database (Version 5.28; Allen, 2002) shows that the hydrogen phthalate ions of phthalate salts occur in two different forms: (i) nonplanar, where both the carboxyl (COOH) and the carboxylate (COO[−]) groups are twisted out of the plane of the benzene ring (Jessen, 1990; Janczak & Perpétuo, 2001; Jin *et al.*, 2003), and (ii) planar, in which both the COOH and the COO[−] groups are coplanar with the benzene plane (Küppers,

1978). The planarity is achieved through an extraordinarily short intramolecular hydrogen bond linking the carboxyl and carboxylate groups (O···O \simeq 2.4 Å; Küppers *et al.*, 1985; Steiner & Saenger, 1994). This intramolecular hydrogen bond with an *S*(7) graph set motif is a common occurrence in 1,2-substituted dicarboxylic acids (Leiserowitz, 1976). Hydrogen phthalates also form supramolecular assemblies, such as extended chains, ribbons and three-dimensional networks (Dale *et al.*, 2004; Ballabh *et al.*, 2005). In order to understand the nature of the intramolecular hydrogen bond and the N—H···O and O—H···O hydrogen-bond-assisted supramolecular motifs and networks, the crystal structures of three hydrogen phthalate salts were determined.



The asymmetric unit of PCAHP (Fig. 1) contains a 4-chloroanilinium cation and a hydrogen phthalate anion. The hydrogen phthalate anion is almost planar except for the two carboxyl groups. The plane defined by the atoms of the COO[−] group and the least-squares plane of the benzene ring are almost perpendicular, with an angle of 77.1 (1)°, while the plane defined by the COOH group is inclined at an angle of 17.5 (2)°. Similar out-of-plane and near-in-plane twisting is also found in the structures of ammonium hydrogen phthalate (Smith, 1975) and tetramethylammonium hydrogen phthalate (Jessen, 1990). Within the benzene ring, the endocyclic angles at C1 and C2 are significantly smaller than 120° [119.0 (2) and 118.7 (2)°, respectively], compensating for the substitutional effects of the COO[−] and COOH groups. The C—C bond length joining the COO[−] group [C1—C7 = 1.508 (3) Å] is

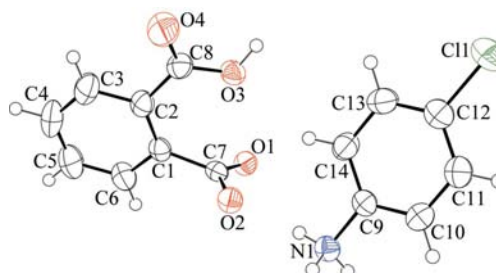


Figure 1
The independent components in PCAHP, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level.

slightly longer than that of the COOH group [C2—C8 = 1.488 (3) Å] as a result of the dissociation of the H atom from the carboxyl group substituted at C1 to the neighboring 4-chloroaniline, forming an acid–base salt (Janczak & Perpétuo, 2001). The 4-chloroanilinium cation shows characteristic bond-length and angle values, which are consistent with those of other reported structures (Glidewell *et al.*, 2005). The C—N distance of the 4-chloroanilinium cation [C9—N1 = 1.457 (3) Å] is longer than the C—N distance [C—N = 1.386 (4) Å; Ploug-Sørensen & Andersen, 1985] of neutral 4-chloroaniline. This lengthening is observed when the amine N atom of 4-chloroaniline accepts an H atom from the carboxyl group of phthalic acid (Markworth *et al.*, 1987; Glidewell *et al.*, 2005).

Both 2HAHP and 3HAHP crystallize in the space group $P2_1/c$ (Figs. 2 and 3). The asymmetric unit of 2HAHP comprises two sets of hydrogen phthalate anions and 2-hydroxyanilinium cations, whereas 3HAHP contains only one hydrogen phthalate anion and one 3-hydroxyanilinium cation. The hydrogen phthalate anions of 2HAHP and 3HAHP are almost planar, with distinctly asymmetric intramolecular hydrogen bonds (Jin *et al.*, 2000). The noncentered H atoms H2AA, H2BA and H2A are found at distances of 1.05 (2), 1.11 (2) and 1.10 (2) Å, respectively, from O2A, O2B and O2, and 1.34 (3), 1.28 (2) and 1.29 (2) Å, respectively, from O3A, O3B and O3 of 2HAHP and 3HAHP in the short intramolecular hydrogen bonds O2A—H2AA...O3A, O2B—H2BA...O3B and O2—H2A...O3 (Tables 2 and 3), with similar values to those reported in related structures (Jessen & Küppers, 1991; Barrett *et al.*, 1995). The formation of this intramolecular hydrogen bond is responsible for the lengthening of the C1—C2 bond [C1A—C2A = 1.412 (2) Å and C1B—C2B = 1.411 (2) Å in 2HAHP, and C1—C2 = 1.412 (2) Å in 3HAHP], where both carboxy groups are substituted (Langkilde *et al.*, 2004). The considerable strain produced by the presence of the intramolecular hydrogen bond within the molecule causes some displacement of the inner O atoms O2A, O3A, O2B and O3B (2HAHP), and O2 and O3 (3HAHP) (Adiwidjaja & Küppers, 1978). The dihedral angles between the least-squares planes of the benzene rings and the carboxyl–carboxylate groups are 3.2 (2) (O1A/C7A/O2A), 2.0 (1) (O3A/C8A/O4A), 11.8 (1) (O1B/C7B/O2B), 13.5 (1) (O3B/C8B/O4B), 14.3 (1) (O1/C7/O2) and 5.5 (1)° (O3/C8/O4). The cations of both phthalate salts show normal aromatic C—C bond-length values, except for the C10—C11 [1.388 (2) Å] and C11—C12 [1.389 (2) Å] bond lengths of the 3-hydroxyanilinium cation, which are slightly greater than the other C—C bond lengths. This lengthening is due to the OH group substituted at C11, which is involved in a strong intermolecular interaction with the nearby cations and anions. The C—N bond lengths of the 2-hydroxyanilinium [C9A—N1A = 1.455 (2) Å and C9B—N1B = 1.452 (2) Å] and 3-hydroxyanilinium [C9—N1 = 1.468 (2) Å] cations are longer than the C—N bond distances of neutral 2-hydroxyaniline and 3-hydroxyaniline [1.413 (2) and 1.424 (3) Å, respectively; Allen *et al.*, 1997] as a result of proton transfer from the acid to the amine group of the base.

The hydrogen-bonded supramolecular motifs and networks of PCAHP, 2HAHP and 3HAHP are determined primarily by a combination of N—H...O and O—H...O hydrogen bonds (Tables 1–3). In PCAHP, the hydrogen phthalate anions alone form chains through O3—H3A...O1ⁱⁱⁱ [symmetry code: (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$] hydrogen bonds running parallel to the [010] direction, forming a $C(7)$ motif (Bernstein *et al.*, 1995) generated by a 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$. In addition, along with the $C(7)$ chain, N1—H1C...O1ⁱⁱ [symmetry code: (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$] and N1—H1A...O2 hydrogen bonds form an extended chain of edge-fused $R_3^3(13)$ rings parallel to the [010] direction. A third hydrogen bond, *viz.* N1—H1B...O2ⁱ [symmetry code: (i) $-x + 1, -y, -z + 1$], links these parallel chains with a hydrogen-bond motif of $R_4^2(8)$, which leads to a two-dimensional supramolecular sheet extending in the (100) plane, as shown in Fig. 4. These supramolecular sheets are further strengthened by C13—H13...O1ⁱⁱⁱ and C14—H14...O3 interactions. Overall, the N—H...O and O—H...O hydrogen bonds along with the C—H...O interactions link adjacent anions and cations to one another to form a network measuring one-unit-cell in thickness and extending parallel to the [001] and [010] directions, with the sheets arranged in the form of a sandwich. Adjacent layers of the molecular network are linked through Cl...Cl interactions, with Cl...Cl = 3.376 (1) Å between the inversely related 4-chloroanilinium cations.

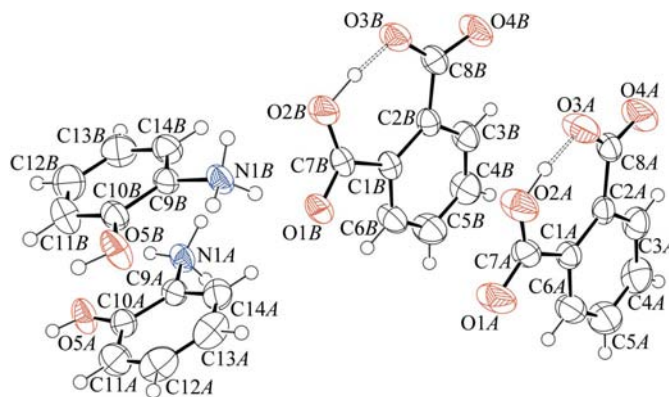


Figure 2
The independent components in 2HAHP, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. Dashed lines indicate the intramolecular hydrogen bonds.

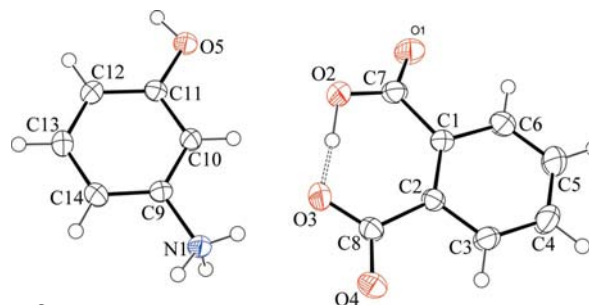


Figure 3
The independent components in 3HAHP, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond.

In 2HAHP, the *A* and *B* hydrogen phthalate anions are coplanar, facing opposite to each other, while their corresponding 2-hydroxyanilinium cations are linked to the anions through $\text{N1A} - \text{H1AB} \cdots \text{O1A}^{\text{iv}}$, $\text{N1A} - \text{H1AC} \cdots \text{O3B}^{\text{iii}}$, $\text{N1B} - \text{H1BA} \cdots \text{O1B}$ and $\text{N1B} - \text{H1BC} \cdots \text{O3A}^{\text{i}}$ [symmetry codes: (i) $-x + 1, -y, -z + 1$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$] hydrogen bonds, with the phenyl planes of the *A* and *B* cations lying almost perpendicular to the planar *A* and *B* hydrogen phthalate ions. These $\text{N} - \text{H} \cdots \text{O}$ hydrogen bonds result in a supramolecular $R_4^4(16)$ motif, which forms the asymmetric unit of *A* and *B* anion–cation pairs. Such units are joined together through two $\text{O} - \text{H} \cdots \text{O}$ hydrogen bonds, viz. $\text{O5A} - \text{H5AA} \cdots \text{O4A}^{\text{v}}$ and $\text{O5B} - \text{H5BA} \cdots \text{O4B}^{\text{vii}}$ [symmetry codes: (v) $x + 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (vii) $x + 1, y, z$], to generate a supramolecular $R_4^4(18)$ motif, which creates a chain of alternately fused $R_4^4(16)$ and $R_4^4(18)$ motifs extending parallel to the [100] direction, as shown in Fig. 5. The inversion-related antiparallel supramolecular chains are interlinked by $\text{N1A} - \text{H1AA} \cdots \text{O1B}^{\text{iv}}$ and $\text{N1B} - \text{H1BB} \cdots \text{O5B}^{\text{vi}}$ [symmetry code: (vi) $-x + 2, -y, -z + 1$] hydrogen bonds, forming an infinite supramolecular chain extending along the [100] direction, illustrated in Fig. 6. In this supramolecular network, inversion-related *B* cations are connected to each other through $\text{N1B} - \text{H1BB} \cdots \text{O5B}^{\text{vi}}$ hydrogen bonds to form an $R_2^2(10)$ dimer lying on the inversion center of the $P2_1/c$ space-group symmetry. The infinitely extending networks parallel to the [100] direction formed through all possible $\text{N} - \text{H} \cdots \text{O}$ and $\text{O} - \text{H} \cdots \text{O}$ hydrogen bonds along with $\text{C} - \text{H} \cdots \text{O}$ interactions are interconnected through $\text{C14A} - \text{H14A} \cdots \text{O1B}$ and $\text{C13A} - \text{H13A} \cdots \text{O5A}^{\text{xi}}$ interactions [symmetry code: (xi) $x, -y + \frac{1}{2}$,

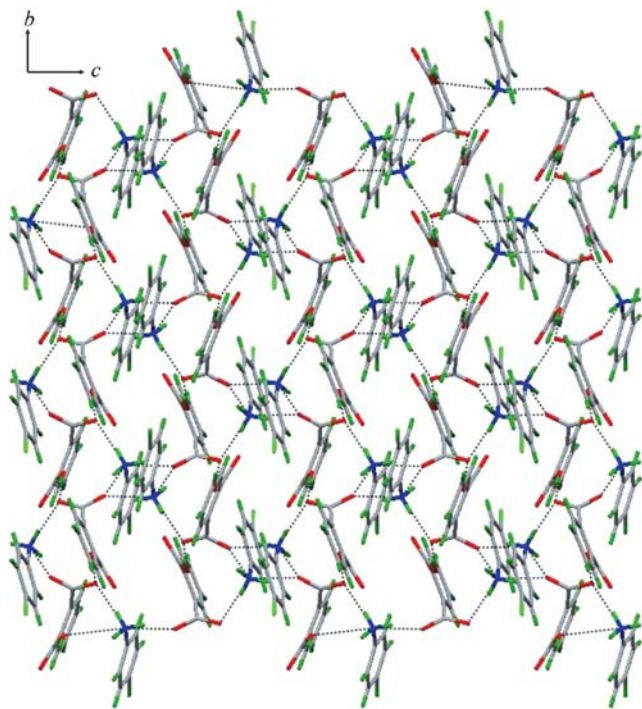


Figure 4

The two-dimensional sheet of anions and cations in PCAHP, interlinked through $\text{N} - \text{H} \cdots \text{O}$ and $\text{O} - \text{H} \cdots \text{O}$ hydrogen bonds, extending parallel to the (100) crystallographic plane.

$z + \frac{1}{2}$]. The centroid–centroid separation distance between the *A* and *B* 2-hydroxyanilinium cations is approximately 3.67 Å.

The hydrogen phthalate anions and 3-hydroxyanilinium cations of 3HAHP are linked through $\text{N1} - \text{H1A} \cdots \text{O4}^{\text{viii}}$ [symmetry code: (viii) $-x + 3, -y + 2, -z + 1$] and $\text{N1} -$

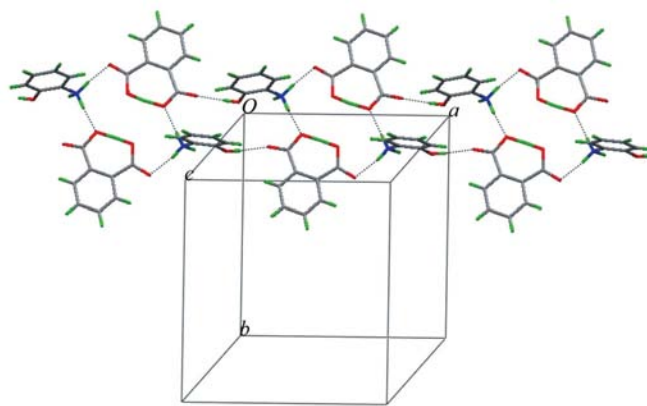


Figure 5

Part of the crystal structure of 2HAHP, showing the formation of a supramolecular chain of alternately fused hydrogen-bonded $R_4^4(16)$ and $R_4^4(18)$ motifs extending parallel to the [100] direction.

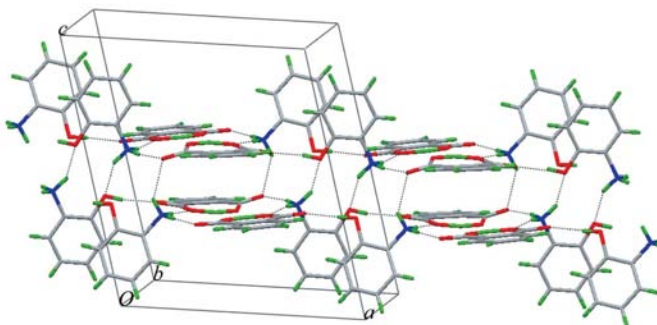


Figure 6

The extended supramolecular hydrogen-bonded network approximately along the [100] direction in 2HAHP, showing the $R_2^2(10)$ dimer.

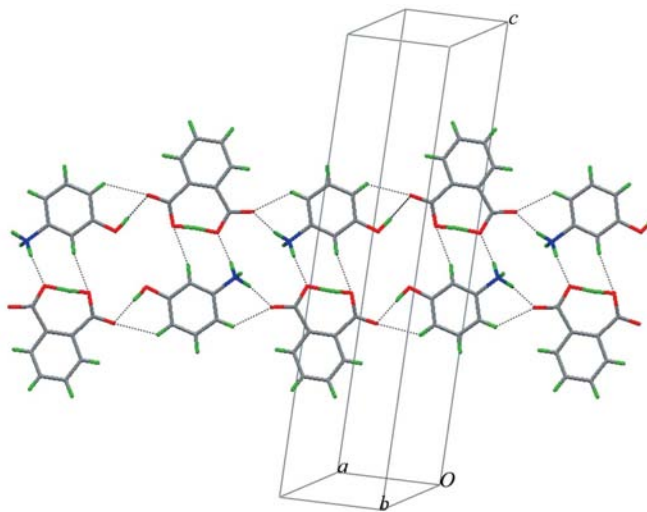


Figure 7

The hydrogen-bonded supramolecular chain in 3HAHP, showing the formation of $R_4^4(12)$, $R_4^4(16)$, $R_2^1(6)$ and $R_2^2(8)$ motifs.

H1B...O3 hydrogen bonds to form a supramolecular motif of type $R_4^4(12)$ (Fig. 7). An O5—H5A...O1^x [symmetry code: (x) $-x + 1, -y + 1, -z + 1$] hydrogen bond links these ionic pairs, resulting in an extended supramolecular chain. All molecules link into a two-dimensional network parallel to the (001) plane. Apart from these N—H...O and O—H...O hydrogen bonds, two C—H...O hydrogen bonds, *viz.* C12—H12...O1^x and C10—H10...O2, further strengthen the chain. The C10—H10...O2 and O5—H5A...O1^x hydrogen bonds form a supramolecular $R_4^4(16)$ motif in addition to other supramolecular $R_2^1(6)$ and $R_2^2(8)$ motifs through N1—H1A...O4^{viii} and C12—H12...O1^x, and C10—H10...O2 and N1—H1B...O3 hydrogen bonds, respectively. The formation of $R_4^4(12)$, $R_4^4(16)$, $R_2^1(6)$ and $R_2^2(8)$ motifs constituting the supramolecular chain is shown in Fig. 7. Parallel arrays of these chains are linked through N1—H1C...O5^{ix} hydrogen bonding [symmetry code: (ix) $x + 1, y, z$], thus building up an extended two-dimensional network parallel to the (001) plane.

Experimental

All three title salts were prepared by taking equimolar amounts of phthalic acid with 4-chloroaniline, 2-hydroxyaniline and 3-hydroxyaniline separately in methanol as solvent. Each solution was stirred well before being left to stand for crystallization. Good diffraction quality crystals were obtained after a few days of slow evaporation.

PCAHP

Crystal data

$C_6H_7ClN^+ \cdot C_8H_5O_4^-$	$V = 1400.8 (2) \text{ \AA}^3$
$M_r = 293.70$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.3610 (16) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$b = 8.0094 (7) \text{ \AA}$	$T = 292 \text{ K}$
$c = 13.0715 (14) \text{ \AA}$	$0.30 \times 0.25 \times 0.15 \text{ mm}$
$\beta = 111.301 (2)^\circ$	

Data collection

Bruker Kappa-APEXII CCD diffractometer	12823 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	2471 independent reflections
$T_{\min} = 0.831, T_{\max} = 0.959$	1959 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.133$	$\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
$S = 1.10$	$\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$
2471 reflections	
185 parameters	

2HAHP

Crystal data

$C_6H_8NO^+ \cdot C_8H_5O_4^-$	$V = 2538.65 (14) \text{ \AA}^3$
$M_r = 275.25$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.7082 (4) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 14.4422 (5) \text{ \AA}$	$T = 292 \text{ K}$
$c = 14.3394 (4) \text{ \AA}$	$0.30 \times 0.25 \times 0.25 \text{ mm}$
$\beta = 105.287 (2)^\circ$	

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for PCAHP.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1B...O2 ⁱ	0.89	1.85	2.716 (2)	163
N1—H1C...O1 ⁱⁱ	0.89	1.97	2.836 (2)	165
O3—H3A...O1 ⁱⁱⁱ	0.94 (3)	1.68 (3)	2.608 (2)	169 (2)
N1—H1A...O2	0.89	1.92	2.779 (2)	163
C13—H13...O1 ⁱⁱⁱ	0.93	2.52	3.369 (3)	151
C14—H14...O3	0.93	2.60	3.455 (3)	154

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

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for 2HAHP.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1A—H1AA...O1B ^{iv}	0.88 (2)	2.169 (19)	2.8824 (19)	137.4 (17)
N1A—H1AB...O1A ^{iv}	1.00 (2)	1.73 (2)	2.7326 (19)	175 (2)
N1A—H1AC...O3B ⁱⁱⁱ	0.99 (2)	1.79 (2)	2.7727 (18)	176.6 (17)
O5A—H5AA...O4A ^v	0.87 (2)	1.81 (2)	2.6728 (17)	174 (2)
N1B—H1BB...O5B ^{vi}	0.94 (2)	2.25 (2)	3.0395 (19)	140.5 (18)
N1B—H1BC...O3A ⁱ	0.93 (2)	1.84 (2)	2.7534 (19)	166.7 (17)
O5B—H5BA...O4B ^{vii}	0.88 (2)	1.77 (2)	2.6402 (16)	169 (2)
N1B—H1BA...O1B	0.94 (2)	1.84 (2)	2.7760 (17)	170.9 (17)
O2A—H2AA...O3A	1.05 (2)	1.34 (3)	2.3838 (17)	173 (2)
O2B—H2BA...O3B	1.11 (2)	1.28 (2)	2.3832 (15)	171 (2)

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

Data collection

Bruker Kappa-APEXII CCD diffractometer	30515 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	6404 independent reflections
$T_{\min} = 0.879, T_{\max} = 0.973$	4195 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.132$	$\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
$S = 1.01$	$\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$
6404 reflections	
401 parameters	

3HAHP

Crystal data

$C_6H_8NO^+ \cdot C_8H_5O_4^-$	$V = 1224.63 (11) \text{ \AA}^3$
$M_r = 275.25$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.8924 (3) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 8.1467 (4) \text{ \AA}$	$T = 292 \text{ K}$
$c = 25.6509 (15) \text{ \AA}$	$0.25 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 95.984 (2)^\circ$	

Data collection

Bruker Kappa-APEXII CCD diffractometer	16385 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	3812 independent reflections
$T_{\min} = 0.890, T_{\max} = 0.977$	3009 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.117$	$\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$
3812 reflections	
201 parameters	

Table 3

Hydrogen-bond geometry (Å, °) for 3HAHP.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots O4^{viii}$	0.937 (19)	1.795 (19)	2.7187 (13)	168.1 (16)
$N1-H1C\cdots O5^{ix}$	0.947 (18)	2.323 (17)	3.0118 (15)	129.2 (13)
$O5-H5A\cdots O1^x$	0.93 (2)	1.74 (2)	2.6691 (13)	175.7 (18)
$N1-H1B\cdots O3$	0.910 (19)	1.924 (19)	2.8241 (15)	169.5 (16)
$O2-H2A\cdots O3$	1.10 (2)	1.29 (2)	2.3860 (14)	174 (2)
$C12-H12\cdots O1^x$	0.93	2.53	3.2041 (15)	129
$C10-H10\cdots O2$	0.93	2.55	3.3932 (15)	150

Symmetry codes: (viii) $-x+3, -y+2, -z+1$; (ix) $x+1, y, z$; (x) $-x+1, -y+1, -z+1$.

For all the three salts, H atoms bound to O and N atoms were located from difference electron-density maps. While the H atoms associated with O and N atoms in 2HAHP and 3HAHP were refined freely, those for the N atom of PCAHP were constrained to ride on their parent atom, with $N-H = 0.89$ Å and $U_{iso}(H) = 1.5U_{eq}(N)$. H atoms bound to C atoms of all the salts were constrained as riding [$C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The positions of the three H atoms on N1 were identified from a difference electron-density peak and were fixed geometrically during refinement.

For all three salts, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT-Plus* (Bruker, 2004); data reduction: *XPREF* in *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009).

The authors thank Dr Babu Varghese, Senior Scientific Officer, SAIF, at IITM for helping with the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3331). Services for accessing these data are described at the back of the journal.

References

- Adiwidjaja, G. & Küppers, H. (1978). *Acta Cryst.* **B34**, 2003–2005.
 Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Allen, F. H., Hoy, V. J., Howard, J. A. K., Thalladi, V. R., Desiraju, G. R., Wilson, C. C. & McIntyre, G. J. J. (1997). *J. Am. Chem. Soc.* **119**, 3477–3480.
 Ballabh, A., Trivedi, D. R. & Dastidar, P. (2005). *Cryst. Growth. Des.* **5**, 1548–1553.
 Barrett, D. M. Y., Kahwa, I. A., Mague, J. T. & McPherson, G. L. (1995). *J. Org. Chem.* **60**, 5946–5953.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (1999). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2004). *APEX2* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Dale, S. H., Elsegood, M. R. J., Hemmings, M. & Wilkinson, A. L. (2004). *CrystEngComm*, **6**, 207–214.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* **C61**, o276–o280.
 Janczak, J. & Perpétuo, G. J. (2001). *Acta Cryst.* **C57**, 123–125.
 Jessen, S. M. (1990). *Acta Cryst.* **C46**, 1513–1515.
 Jessen, S. M. & Küppers, H. (1991). *J. Mol. Struct.* **263**, 247–265.
 Jin, Z. M., Pan, Y. J., He, L., Li, Z. G. & Yu, K. B. (2003). *Anal. Sci.* **19**, 333–334.
 Jin, M. N., Pan, Y. J., Xu, D. J. & Xu, Y. Z. (2000). *J. Chem. Crystallogr.* **30**, 119–122.
 Küppers, H. (1978). *Acta Cryst.* **B34**, 3763–3765.
 Küppers, H., Takusagawa, F. & Koetzle, T. F. (1985). *J. Chem. Phys.* **82**, 5636–5647.
 Langkilde, A., Madsen, D. & Larsen, S. (2004). *Acta Cryst.* **B60**, 502–511.
 Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
 Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
 Markworth, A., Weiden, N. & Weiss, A. (1987). *Ber. Bunsen Ges. Phys. Chem.* **91**, 1158–1166.
 Pereira Silva, P. S., Ramos Silva, M., Matos Beja, A. & Paixão, J. A. (2006). *Acta Cryst.* **E62**, o1067–o1069.
 Ploug-Sørensen, G. & Andersen, E. K. (1985). *Acta Cryst.* **C41**, 613–615.
 Schuckmann, W., Fuess, H. & Bats, J. W. (1978). *Acta Cryst.* **B34**, 3754–3756.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Smith, R. A. (1975). *Acta Cryst.* **B31**, 2508–2509.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Steiner, T. & Saenger, W. (1994). *Acta Cryst.* **B50**, 348–357.