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Proton-transfer compounds of isonipecotamide with the aromatic dicarboxylic acids 4-nitrophthalic, 4,5-dichlorophthalic, 5-nitroisophthalic and terephthalic acids

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The structures of the 1:1 proton-transfer compounds of isonipecotamide (4-piperidinecarboxamide) with 4-nitrophthalic acid, 4-carbamoylpiperidinium 2-carboxy-4-nitrobenzoate, $C_6H_{13}N_2O_8^+ C_8H_4O_6^-$ (I), 4,5-dichlorophthalic acid, 4-carbamoylpiperidinium 2-carboxy-4,5-dichlorobenzoate, $C_6H_{13}N_2O_8^+ C_8H_3Cl_2O_4^-$ (II) and 5-nitroisophthalic acid, 4-carbamoylpiperidinium 3-carboxy-5-nitrobenzoate, $C_6H_{13}N_2O_8^+ C_8H_4O_6^-$ (III) as well as the 2:1 compound with terephthalic acid, bis(4-carbamoylpiperidinium) benzene-1,2-dicarboxylate dihydrate, $2(C_6H_{13}N_2O_8^+) C_8H_4O_4^{2-} \cdot 2H_2O$ (IV) have been determined at 200 K. All salts form hydrogen-bonded structures, one-dimensional in (II) and three-dimensional in (I), (III) and (IV). In (I) and (III) the centrosymmetric $R^2_2(8)$ cyclic amide–amide association is found while in (IV) several different types of water-bridged cyclic associations are present [graph sets $R^2_4(8)$, $R^3_4(10)$, $R^4_4(12)$, $R^3_3(18)$ and $R^4_6(22)$]. The one-dimensional structure of (I), features the common 'planar' hydrogen 4,5-dichlorophthalate anion together with enlarged cyclic $R^3_3(13)$ and $R^3_4(17)$ associations. With the structures of (I) and (III) the presence of head-to-tail hydrogen phthalate chain substructures is found. In (IV) head-to-tail primary cation–anion associations are extended longitudinally into chains through the water-bridged cation associations and laterally by piperidinium $N-H \cdots O_{\text{carboxyl}}$ and water $O-H \cdots O_{\text{carboxyl}}$ hydrogen bonds. The structures reported here further demonstrate the utility of the isonipecotamide cation as a synthon for the generation of stable hydrogen-bonded structures. An additional example of cation–anion association with this cation is also shown in the asymmetric three-centre piperidinium $N-H \cdots O, O'_{\text{carboxyl}}$ interaction in the first-reported structure of a 2:1 isonipecotamide-carboxylate salt.

Comment

Our project of investigation of the hydrogen-bonding modes in the salts of the Lewis base 4-piperidinecarboxamide (isonipecotamide: INIPA) with carboxylic acids has provided a considerable number of structures, the majority being anhydrous 1:1 salts with aromatic acids (Smith & Wermuth, 2010*d*, 2011*a*); Smith *et al.*, 2010*b*). Solvated examples are the nicotinate (a partial hydrate) (Smith & Wermuth, 2011*c*), the acetate (a monohydrate) (Smith & Wermuth, 2010*e*) and the 6-carboxypyridine-2-carboxylate (a methanol monosolvate) (Smith & Wermuth, 2011*c*), while with *o*-phthalic acid, a 1:1 hydrogen phthalate-phthalic acid salt adduct is found (Smith & Wermuth, 2011*b*). Anhydrous picrates are also known (Smith & Wermuth, 2010*c*), together with a 2:1 salt with bipyridine-4,4'-disulfonate (Smith, *et al.*, 2010*a*). Considering the unusual formation of the a 1:1:1 cation:anion:phthalic acid adduct (Smith & Wermuth, 2011*b*), from a 1:1 stoichiometric reaction, our aim was to investigate the nature of the products formed from the similar reactions of INIPA with a series of aromatic dicarboxylic acids in various alcoholic and aqueous alcoholic solutions. Examples included 4-nitrophthalic acid

(NPHA), 4,5-dichlorophthalic acid (DCPA), 5-nitroisophthalic acid (NIPA) and terephthalic acid (TPA) which provided good crystalline products. The 1:1 anhydrous salts of $C_6H_{13}N_2O_8^+ C_8H_4O_6^-$ (I), 4-carbamoylpiperidinium 2-carboxy-4,5-dichlorobenzoate, $C_6H_{13}N_2O_8^+ C_8H_3Cl_2O_4^-$ (II) and 4-carbamoylpiperidinium 3-carboxy-5-nitrobenzoate, $C_6H_{13}N_2O_8^+ C_8H_4O_6^-$ (III) were obtained while the 2:1 hydrated salt of the terephthalate, bis(4-carbamoylpiperidinium) benzene-1,2-dicarboxylate dihydrate, $2(C_6H_{13}N_2O_8^+) C_8H_4O_4^{2-} \cdot 2H_2O$ (IV) was identified. The structures of (I)–(IV) are described here.

With the 1:1 salts (I)–(III) (Figs. 1–4), proton transfer has occurred to the hetero-N of the piperidine ring and with the terephthalate salt (IV), it involves a two-proton transfer with a dianion formation. The resulting piperidinium group of the anion in each, together with the hydrogen donor and acceptor *p*-related substituent amide group are subsequently involved in hydrogen-bonding interactions, resulting in supramolecular structures which in (I), (III) and (IV) are three-dimensional and one-dimensional in (II) (Figs. 5–8). A feature of the hydrogen-bonding in (I) and (III) is the presence of the centrosymmetric cyclic homomolecular N—H \cdots O hydrogen-bonded amide–amide motif (Allen *et al.*, 1998), having graph set $R^2_2(8)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995). This motif has now been found in 11 of the 24 known structures of INIPA proton-transfer salts, including the present examples.

In the structure of the 1:1 INIPA salt with 4-nitrophthalic acid (I), the 1-carboxy rather than the 2-carboxy group is deprotonated (Fig. 1) and gives a primary piperidinium N—H \cdots O_{carboxyl} ion-pair interaction. The hydrogen phthalate anions give head-to-tail hydrogen-bonded chain substructures featuring short carboxylic acid O—H \cdots O_{carboxyl} hydrogen bonds [graph set $C(7)$] (Fig. 5). These substructures are common among hydrogen phthalate salt structures (Glidewell *et al.*, 2005; Smith & Wermuth, 2010*b*). The peripherally bound INIPA anions give structure extension across (0 1 1) through the classic centrosymmetric $R^2_2(8)$ amide–amide N—H \cdots O hydrogen-bonded dimer associations. In addition amide N—H \cdots O_{nitro} and piperidinium N—H \cdots O_{carboxyl} associations (Table 1) result in a three-dimensional structure. In the nitrophthalate anion, the carboxylate group is significantly rotated out of the benzene plane [torsion angle C2–C1–C11–O12, $-76.7(2)^\circ$] while the carboxylic acid and nitro groups are essentially coplanar with the benzene plane [torsion angles C1–C2–C21–O22, $169.25(16)^\circ$ and C3–C4–N4–O42, $-174.03(18)^\circ$ respectively].

In the structure of the 1:1 INIPA salt with 4,5-dichlorophthalic acid (II), (Fig. 2) one of the two primary piperidinium cation–anion associations also involves a secondary longer three-centre interaction [N1A—H12A \cdots O12, $3.044(4) \text{ \AA}$, N—H \cdots O, $118(3)^\circ$] which is probably an artefact of the overall cyclic hydrogen-bonding motif. This association [graph set $R^3_4(17)$] involves piperidinium N—H \cdots O_{carboxy}, amide N—H \cdots O_{carboxy} and amide N—H \cdots O_{amide} hydrogen bonds from two INIPA cations and one DCPA anion and is closed by the intramolecular carboxylic acid O—H \cdots O_{carboxyl} hydrogen bond (Fig. 6). A second cyclic association [graph set $R^3_3(13)$] involves one piperidinium and two amide–carboxyl hydrogen bonds (Table 2) and the two motifs link the the DCPA anions peripherally into the head-to-head N—H \cdots O amide-linked cation chain substructures. This results in one-dimensional ribbon structures which extends along the *b* cell direction. In the crystal structures of the DCPA salts with Lewis bases, this low-dimensionality in the hydrogen-bonded structures is commonly associated with the 'planar' DCPA monoanion which features the cyclic intramolecular carboxylic acid O—H \cdots O_{carboxyl} hydrogen-bonding association [graph set $S(7)$] (Smith *et al.*, 2010*a*). The short hydrogen bond

[2.393 (3) Å] in the 'planar' DCPA anion in (II) results in a C2–C1–C11–O11 torsion angle of 174.1 (3) Å while another feature of this conformation is an elongation of the C1–C11 and C2–C21 bonds [1.522 (4), 1.534 (4) Å] and distortion of the external bond angles at C1 and C2 [128.8 (2), 128.1 (2)°] (Smith *et al.*, 2010a).

In the structure of the hydrogen 5-nitroisophthalate salt (III) (Fig. 3) the primary cation–anion interaction has a second longer N—H···O_{carboxyl} contact [N1A···O12, 3.0366 (17) Å; N—H···O, 118.1 (7)°], similar to that in (II). The cation-anion associations are also similar in some respects to those of (I). The hydrogen isophthalate anions give zig zag head-to-tail hydrogen-bonded chain substructures through carboxylic acid O—H···O_{carboxyl} hydrogen bonds (Table 3) but these are classified as graph set C(8) rather than C(7) as in (I). In addition, the centrosymmetric R²₂(8) hydrogen-bonded INPA amide–amide dimers give peripheral structure extension through piperidinium N—H···O_{carboxyl} hydrogen bonds which involve two anions, enclosing cyclic R³₃(10) rings (Fig. 7). The three-dimensional framework structure is generated through amide N—H···O_{carboxyl} hydrogen-bonding associations. The nitro-O atoms are unassociated except for weak intermolecular cation C—H···O associations [C2A···O52ⁱⁱ, 3.308 (2) Å; C—H···O, 151°] (for symmetry code (ii), see Table 3). The anion in (III) is essentially planar but with the carboxylate group rotated slightly out of the plane of the benzene ring [torsion angle C2–C1–C11–O11, -161.47 (16)° *cf.* 172.04 (15) for C2–C3–C31–O32 (the carboxylic acid group) and 175.06 (17)° for C4–C5–N51–O52 (the nitro group)].

With the terephthalate salt (IV) one of the piperidinium N—H···O_{carboxyl} hydrogen bonds seen in Fig 4 is accompanied by an asymmetric three-centre N—H···O,O'_{carboxyl} interaction [graph set R²₁(4) with the centrosymmetric terephthalate dianion (Fig. 8). This second association links two INIPA cations to the terephthalate dianion which is extended longitudinally in the approximate *b* cell direction through centrosymmetric cyclic water-bridged amide–amide associations [graph set R⁴₄(12)]. The water molecules also act as acceptors in bridging these chains laterally through amide N—H···O hydrogen bonds (Table 4) forming centrosymmetric cyclic R²₄(8) associations. The lateral piperidinium N—H···O_{carboxyl} hydrogen bonds shown in Fig. 4 together with water O—H···O_{carboxyl} associations [R³₄(10), R³₃(18) and R⁴₆(22)] complete a three-dimensional framework structure. The centrosymmetric terephthalate dianion deviates slightly from planarity [torsion angle C2–C1–C11–O11, 169.25 (12)°].

The structures reported here further demonstrate the utility of the isonipecotamide cation as a synthon for the generation of stable hydrogen-bonded structures. An additional example of INIPA cation–anion association is also shown in the asymmetric three-centre piperidinium N—H···O,O'_{carboxyl} interaction in the first-reported structure of a 2:1 isonipecotamide carboxylate salt.

Experimental

The title compounds were synthesized by heating together under reflux for 10 min, 1 mmol quantities of 4-piperidinecarboxamide (isonipecotamide) and 4-nitrophthalic acid [for (I)], 4,5-dichlorophthalic acid [for (II)], 5-nitroisophthalic acid [for (III)] or terephthalic acid [for (IV)] in 50 mL of either methanol (III), methanol-water (80%) [(I) and (IV)] or ethanol-water (50%) (II). After concentration to *ca.* 30 mL, partial room temperature evaporation of the hot-filtered solutions gave colourless plates of (I) and (III), blocks of (II) or prisms of (IV).

(I)

Crystal data

$C_6H_{13}N_2O \cdot C_8H_4NO_6$	$V = 1519.61 (18) \text{ \AA}^3$
$M_r = 339.31$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 5.8637 (5) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 11.2707 (8) \text{ \AA}$	$T = 200 \text{ K}$
$c = 23.0268 (19) \text{ \AA}$	$0.40 \times 0.40 \times 0.12 \text{ mm}$
$\beta = 93.082 (8)^\circ$	

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	2989 independent reflections
Absorption correction: Multi-scan CrysAlis PRO (Oxford Diffraction, 2009)	2375 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.915$, $T_{\max} = 0.980$	$R_{\text{int}} = 0.023$
10364 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	0 restraints
$wR(F^2) = 0.114$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
2989 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
233 parameters	

Table 1

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1A-H11A\cdots O11^i$	0.98 (3)	1.77 (3)	2.729 (2)	163 (2)
$N1A-H12A\cdots O21$	0.93 (3)	1.92 (3)	2.803 (2)	158 (2)
$N41A-H42A\cdots O41A^{ii}$	0.92 (3)	1.99 (3)	2.907 (3)	176 (2)
$N41A-H43A\cdots O42^{iii}$	0.83 (3)	2.40 (3)	3.200 (3)	161 (3)
$O22-H22\cdots O12^{iv}$	0.99	1.47	2.4562 (19)	179

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+2, -z+1$; (iii) $x-3/2, -y+3/2, z-1/2$; (iv) $-x+1/2, y+1/2, -z+3/2$.

(II)

Crystal data

$C_8H_5Cl_2O_4 \cdot C_6H_{13}N_2O$	$V = 1570.15 (15) \text{ \AA}^3$
$M_r = 363.19$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 6.6897 (4) \text{ \AA}$	$\mu = 0.44 \text{ mm}^{-1}$
$b = 9.7392 (5) \text{ \AA}$	$T = 200 \text{ K}$
$c = 24.1222 (13) \text{ \AA}$	$0.30 \times 0.25 \times 0.20 \text{ mm}$

$\beta = 92.479 (4)^\circ$

Data collection

Oxford Diffraction Gemini S CCD detector diffractometer
 Absorption correction: Multi-scan *CrysAlis PRO* (Oxford Diffraction, 2009)
 $T_{\min} = 0.908$, $T_{\max} = 0.980$
 19231 measured reflections

3084 independent reflections
 2777 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.113$
 $S = 1.30$
 3084 reflections
 224 parameters

0 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> — <i>H</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i> ⋯ <i>A</i>
N1 <i>A</i> —H11 <i>A</i> ⋯O11	0.92 (4)	1.90 (4)	2.810 (3)	170 (3)
N1 <i>A</i> —H12 <i>A</i> ⋯O22 ⁱ	0.87 (4)	1.96 (4)	2.753 (3)	152 (3)
N41 <i>A</i> —H41 <i>A</i> ⋯O21 ⁱⁱ	0.82 (4)	2.48 (4)	3.158 (3)	142 (4)
N41 <i>A</i> —H42 <i>A</i> ⋯O41 <i>A</i> ⁱⁱⁱ	0.93 (4)	2.19 (4)	3.086 (4)	163 (3)
O12—H12⋯O21	1.00	1.40	2.393 (3)	180

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+3/2, y-1/2, -z+1/2$; (iii) $-x+3/2, y+1/2, -z+1/2$.

(III)

Crystal data

$\text{C}_6\text{H}_{13}\text{N}_2\text{O}\cdot\text{C}_8\text{H}_4\text{NO}_6$
 $M_r = 339.31$
 Monoclinic, $P2_1/c$
 $a = 9.4117 (4) \text{ \AA}$
 $b = 14.3552 (5) \text{ \AA}$
 $c = 11.4490 (5) \text{ \AA}$
 $\beta = 103.787 (4)^\circ$

$V = 1502.27 (11) \text{ \AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 200 \text{ K}$
 $0.45 \times 0.40 \times 0.18 \text{ mm}$

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
 Absorption correction: Multi-scan *CrysAlis PRO* (Oxford Diffraction, 2009)
 $T_{\min} = 0.98$, $T_{\max} = 0.99$
 9866 measured reflections

2940 independent reflections
 2284 reflections with $I > 2s(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.106$

$S = 1.00$

2940 reflections

237 parameters

0 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Table 3Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1A-H11A\cdots O31^i$	0.93 (2)	2.06 (2)	2.9236 (18)	153.6 (17)
$N1A-H12A\cdots O11$	0.98 (2)	1.87 (2)	2.8229 (16)	164 (2)
$N1A-H12A\cdots O12$	0.98 (2)	2.45 (2)	3.0366 (19)	118.1 (17)
$N41A-H41A\cdots O11^{ii}$	0.822 (19)	2.298 (19)	3.0669 (19)	155.9 (17)
$N41A-H42A\cdots O41A^{iii}$	0.940 (19)	1.996 (19)	2.9321 (18)	174.1 (16)
$O32-H32\cdots O12^{iv}$	0.93 (2)	1.63 (2)	2.5336 (17)	164 (3)

Symmetry codes: (i) $-x+2, y+1/2, -z+3/2$; (ii) $-x+1, y+1/2, -z+1/2$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+2, y-1/2, -z+3/2$.**(IV)***Crystal data*

$M_r = 458.51$

Triclinic, $P\bar{1}$

$a = 6.5099 (5) \text{ \AA}$

$b = 7.7777 (6) \text{ \AA}$

$c = 11.6865 (12) \text{ \AA}$

$\alpha = 76.429 (8)^\circ$

$\beta = 76.968 (7)^\circ$

$\gamma = 80.885 (7)^\circ$

$V = 556.89 (9) \text{ \AA}^3$

$Z = 1$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

$\mu = 0.11 \text{ mm}^{-1}$

$T = 200 \text{ K}$

$0.50 \times 0.15 \times 0.08 \text{ mm}$

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

2177 independent reflections

Absorption correction: Multi-scan
CrysAlis PRO (Oxford Diffraction, 2009)1746 reflections with $I > 2\sigma(I)$

$T_{\min} = 0.965, T_{\max} = 0.990$

$R_{\text{int}} = 0.024$

6562 measured reflections

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.093$

$S = 1.05$

2177 reflections

169 parameters

0 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$

Table 4

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1 <i>A</i> —H11 <i>A</i> ...O11	0.966 (17)	1.856 (18)	2.7937 (16)	162.9 (14)
N1 <i>A</i> —H12 <i>A</i> ...O11 ⁱⁱ	0.979 (17)	1.847 (17)	2.8030 (15)	164.7 (17)
N1 <i>A</i> —H12 <i>A</i> ...O12 ⁱⁱ	0.979 (17)	2.367 (19)	3.1200 (16)	133.3 (14)
N41 <i>A</i> —H41 <i>A</i> ...O1 <i>W</i> ⁱⁱⁱ	0.927 (17)	2.045 (17)	2.9181 (16)	156.5 (17)
N41 <i>A</i> —H42 <i>A</i> ...O1 <i>W</i>	0.95 (2)	2.111 (19)	2.9870 (17)	153.2 (14)
O1 <i>W</i> —H11 <i>W</i> ...O41 <i>A</i> ^{iv}	0.861 (18)	1.892 (18)	2.7410 (15)	168.7 (17)
O1 <i>W</i> —H12 <i>W</i> ...O12 ^v	0.932 (19)	1.833 (19)	2.7632 (15)	175.6 (19)

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

Hydrogen atoms involved in hydrogen-bonding interactions were located by difference methods and with the exception of the carboxylic acid H atoms, which were set invariant in the final cycles of refinement, their positional and isotropic displacement parameters were refined. Other H-atoms were included in the refinements at calculated positions [C—H(aliphatic) = 0.97, 0.98 Å and C—H(aromatic) = 0.93 Å] using a riding model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: CrysAlisPro for (I); CrysAlis PRO for (II), (III); CrysAlis Pro for (IV). Cell refinement: CrysAlisPro for (I); CrysAlis PRO for (II), (III); CrysAlis Pro for (IV). Data reduction: CrysAlisPro for (I); CrysAlis PRO for (II), (III); CrysAlis Pro for (IV). Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994) for (I); SIR92 for (II); SIR 92 (Altomare, 1994) for (III); SHELXS97 (Sheldrick, 2008) for (IV). For all compounds, program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 1999); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

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Figure 1

Fig. 1. Molecular conformation and atom naming scheme for the INIPA cation and the NPHA monoanion in (I). Displacement ellipsoids are drawn at the 40% probability level and the inter-species hydrogen bond is shown as a dashed line.

Figure 2

Fig. 2. Molecular configuration and atom naming scheme for the INIPA cation and the DCPA monoanion anion in (II). Displacement ellipsoids are drawn at the 40% probability level and the inter-species hydrogen bond is shown as a dashed line.

Figure 3

Fig. 3. Molecular conformation and atom naming scheme for the INIPA cation and the NIPA monoanion in (III). Displacement ellipsoids are drawn at the 40% probability level. The inter-species hydrogen bonds is shown as a dashed line.

Figure 4

Fig. 4. Molecular conformation and atom naming scheme for the INIPA cation, the TPA dianion and the water molecule of solvation in the asymmetric unit of (IV). The dianion has inversion symmetry: [code (i) $-x, -y + 1, -z$]. Displacement ellipsoids are drawn at the 40% probability level and inter-species hydrogen bonds are shown as dashed lines.

Figure 5

Fig. 5. The two-dimensional hydrogen-bonded network structure of (I) extending across the bO_c plane of the unit cell, showing hydrogen-bonding associations as dashed lines. Non-interactive H atoms are omitted. For symmetry codes, see Table 1. In this figure and in Figs. 6–8, graph sets for cyclic hydrogen-bonding associations are also indicated.

Figure 6

Fig. 6. The one-dimensional hydrogen-bonded ribbon structure of (II) extending along the b cell direction, showing hydrogen-bonding associations as dashed lines. Non-interactive H atoms are omitted. For symmetry codes, see Table 2.

Figure 7

Fig. 7. A perspective view of the three-dimensional hydrogen-bonded framework structure of (III), showing the NIPA chain substructures and amide–amide dimer associations. Hydrogen-bonds are shown as dashed lines. Non-interactive H atoms are omitted. For symmetry code (v): $-x + 1, y - 1/2, -z + 1/2$. For other codes, see Table 3.

Figure 8

Fig. 8. The three-dimensional hydrogen-bonded framework structure of (IV) in a perspective view of the unit cell, showing hydrogen-bonding associations as dashed lines. Non-interactive H atoms are omitted. For symmetry code (i), see Fig. 1. For other codes, see Table 4.