

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

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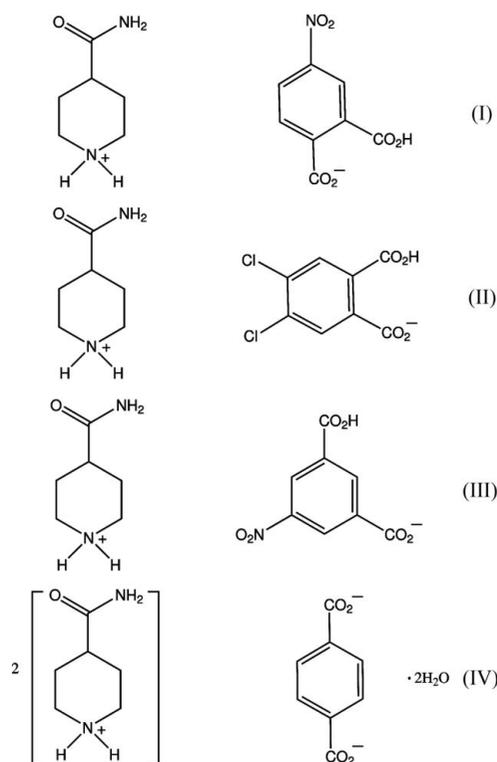
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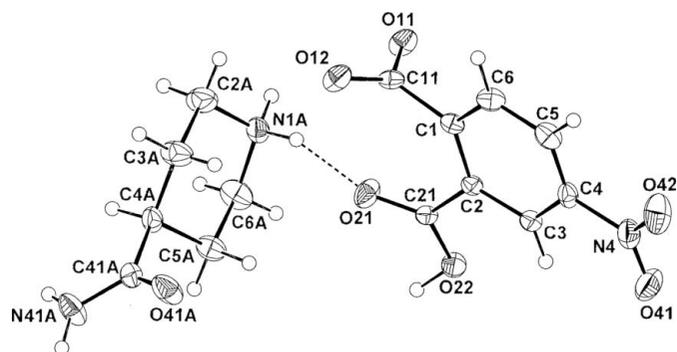
The structures of the 1:1 proton-transfer compounds of isonipecotamide (piperidine-4-carboxamide) with 4-nitrophthalic acid [4-carbamoylpiperidinium 2-carboxy-4-nitrobenzoate,  $C_6H_{13}N_2O_8^+ \cdot C_8H_4O_6^-$ , (I)], 4,5-dichlorophthalic acid [4-carbamoylpiperidinium 2-carboxy-4,5-dichlorobenzoate,  $C_6H_{13}N_2O_8^+ \cdot C_8H_3Cl_2O_4^-$ , (II)] and 5-nitroisophthalic acid [4-carbamoylpiperidinium 3-carboxy-5-nitrobenzoate,  $C_6H_{13}N_2O_8^+ \cdot C_8H_4O_6^-$ , (III)], as well as the 2:1 compound with terephthalic acid [bis(4-carbamoylpiperidinium) benzene-1,2-dicarboxylate dihydrate,  $2C_6H_{13}N_2O_8^+ \cdot C_8H_4O_4^{2-} \cdot 2H_2O$ , (IV)], have been determined at 200 K. All salts form hydrogen-bonded structures, *viz.* 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  $R_4^2(8)$ ,  $R_4^3(10)$ ,  $R_4^4(12)$ ,  $R_3^3(18)$  and  $R_6^4(22)$ ]. The one-dimensional structure of (I) features the common ‘planar’ hydrogen 4,5-dichlorophthalate anion, together with enlarged cyclic  $R_3^3(13)$  and  $R_4^3(17)$  associations. In 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–carboxylate  $N-H \cdots O$  and water–carboxylate  $O-H \cdots O$  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–carboxylate  $N-H \cdots O, O'$  interaction in the first-reported structure of a 2:1 isonipecotamide–carboxylate salt.

## Comment

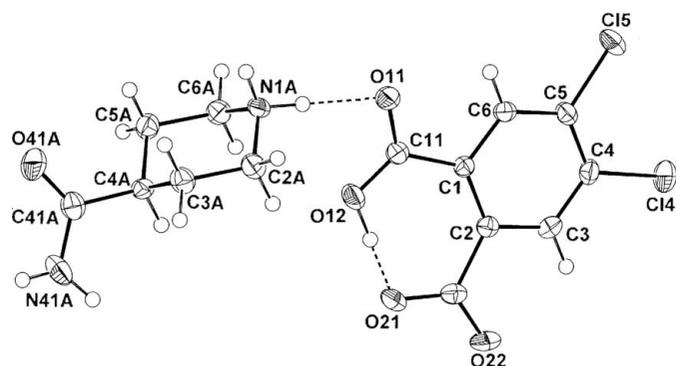
Our project investigating the hydrogen-bonding modes in salts of the Lewis base piperidine-4-carboxamide (isonipecotamide; INIPA) with carboxylic acids has provided a considerable number of structures, the majority being anhydrous 1:1 salts with aromatic acids (Smith & Wermuth, 2010*d,f*, 2011*a*). Solvated 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 formed (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). In the light of the unusual formation of a 1:1:1 cation–anion–phthalic acid adduct from a 1:1 stoichiometric reaction (Smith & Wermuth, 2011*b*), our further aim was to investigate the nature of the products formed from 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 4-carbamoylpiperidinium 2-carboxy-4-nitrobenzoate, (I), 4-carbamoylpiperidinium 2-carboxy-4,5-dichlorobenzoate, (II), and 4-carbamoylpiperidinium 3-carboxy-5-nitrobenzoate, (III), were obtained, and the 2:1 hydrated salt of the terephthalate, bis(4-carbamoylpiperidinium) benzene-1,2-dicarboxylate dihydrate, (IV), was also identified. The structures of (I)–(IV) are described here.



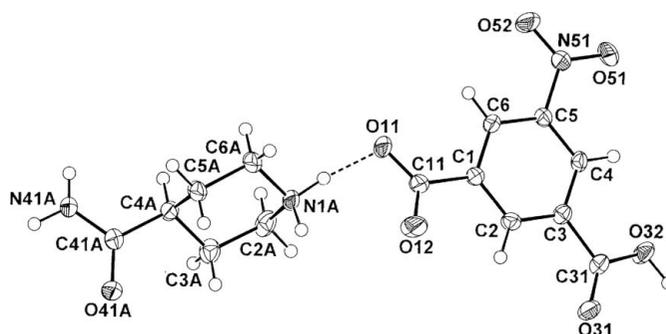
**Figure 1**  
The molecular conformation and atom-numbering scheme for the INIPA cation and NPHA monoanion in (I). Displacement ellipsoids are drawn at the 40% probability level and the inter-species hydrogen bond is shown as a dashed line.



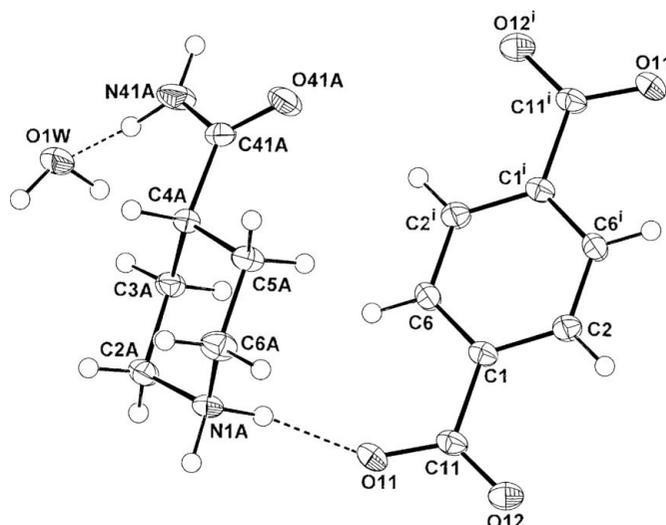
**Figure 2**  
The molecular configuration and atom-numbering scheme for the INIPA cation and DCPA monoanion in (II). Displacement ellipsoids are drawn at the 40% probability level and the inter-species hydrogen bond is shown as a dashed line.

With the 1:1 salts, (I)–(III) (Figs. 1–4), proton transfer has occurred to the hetero N atom of the piperidine ring, while with the terephthalate salt, (IV), a two-proton transfer is involved, with the formation of a dianion. The resulting piperidinium group of the anion in each salt, together with the hydrogen donor and acceptor *p*-related substituent amide group, are subsequently involved in hydrogen-bonding interactions. These result in supramolecular structures, which are three-dimensional in (I), (III) and (IV), 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···O hydrogen-bonded amide–amide motif (Allen *et al.*, 1998), with 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.

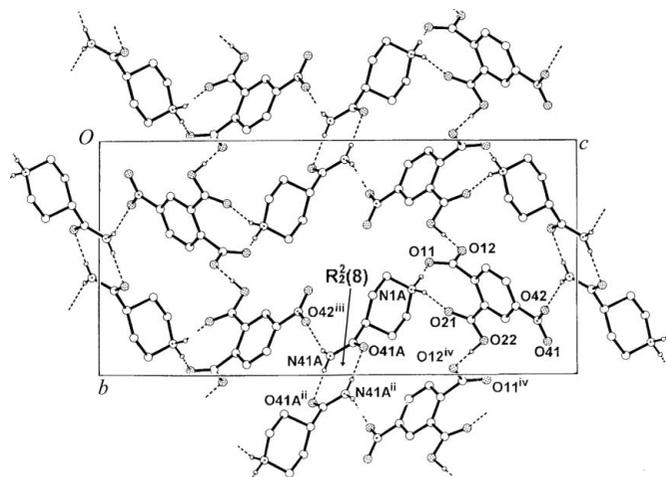
In the structure of the 1:1 INIPA salt with 4-nitrophthalic acid, (I), the 1-carboxy rather than the 2-carboxy group is deprotonated (Fig. 1), giving a primary piperidinium–carboxylate N–H···O ion-pair interaction. The hydrogen phthalate anions form head-to-tail hydrogen-bonded chain substructures featuring short carboxy–carboxylate O–H···O hydrogen bonds [graph set  $C(7)$ ; Fig. 5]. These substructures



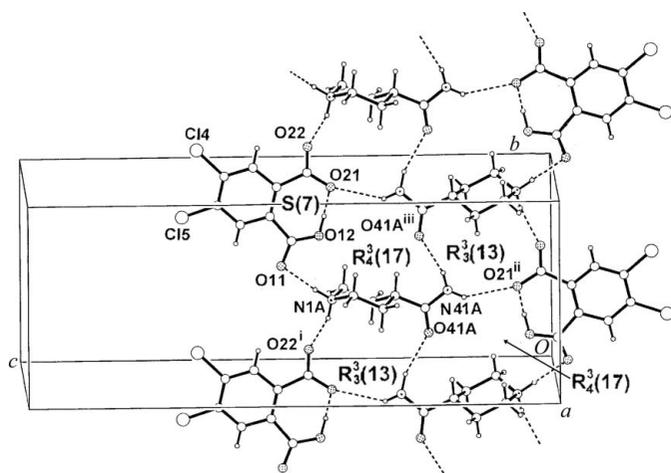
**Figure 3**  
The molecular conformation and atom-numbering scheme for the INIPA cation and NIPA monoanion in (III). Displacement ellipsoids are drawn at the 40% probability level. The inter-species hydrogen bond is shown as a dashed line.



**Figure 4**  
The molecular conformation and atom-numbering scheme for the INIPA cation, the TPA dianion and the solvent water molecule in the asymmetric unit of (IV). The dianion has inversion symmetry [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**  
The two-dimensional hydrogen-bonded network structure of (I), extending across the *bc* plane of the unit cell, showing hydrogen-bonding associations as dashed lines. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. (For symmetry codes, see Table 1.)

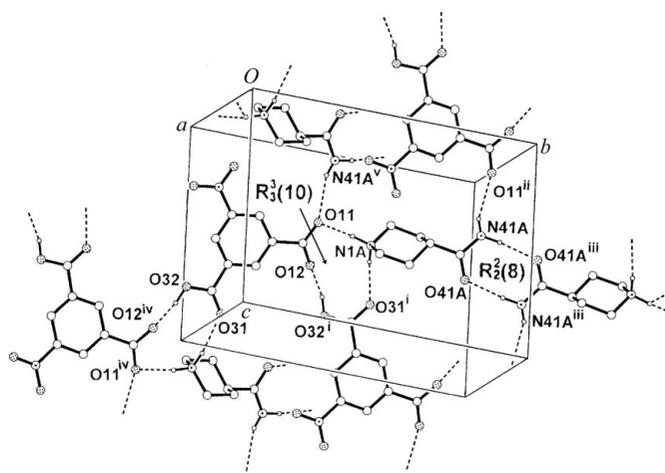


**Figure 6**

The one-dimensional hydrogen-bonded ribbon structure of (II), extending along the *b* cell direction, showing hydrogen-bonding associations as dashed lines. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. (For symmetry codes, see Table 2.)

are common among hydrogen phthalate salt structures (Glidewell *et al.*, 2005; Smith & Wermuth, 2010*b*). The peripherally bound INIPA anions give structure extension across (011) through classic centrosymmetric  $R_2^2(8)$  amide–amide  $N-H\cdots O$  hydrogen-bonded dimer associations. In addition, amide–nitro  $N-H\cdots O$  and piperidinium–carboxylate  $N-H\cdots O$  associations (Table 1) result in a three-dimensional structure. In the nitrophthalate anion, the carboxylate group is rotated significantly 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  $C3-C4-N4-O42 = -174.03(18)^\circ$ ].

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 [ $N1A\cdots O12 = 3.042(4) \text{ \AA}$  and  $N1A-H11A\cdots O12 = 117(3)^\circ$ ], which is probably an artefact of the overall cyclic hydrogen-bonding motif. This association [graph set  $R_4^3(17)$ ] involves piperidinium–carboxylate  $N-H\cdots O$ , amide–carboxylate  $N-H\cdots O$  and amide–amide  $N-H\cdots O$  hydrogen bonds from two INIPA cations and one DCPA anion, and is closed by the intramolecular carboxy–carboxylate  $O-H\cdots O$  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 DCPA anions peripherally into head-to-head  $N-H\cdots O$  amide-linked cation chain substructures. This results in one-dimensional ribbon structures which extend along the *b* cell direction. In the crystal structures of 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 carboxy–carboxylate  $O-H\cdots O$  hydrogen-bonding association [graph set  $S(7)$ ; Smith & Wermuth, 2010*a*]. The



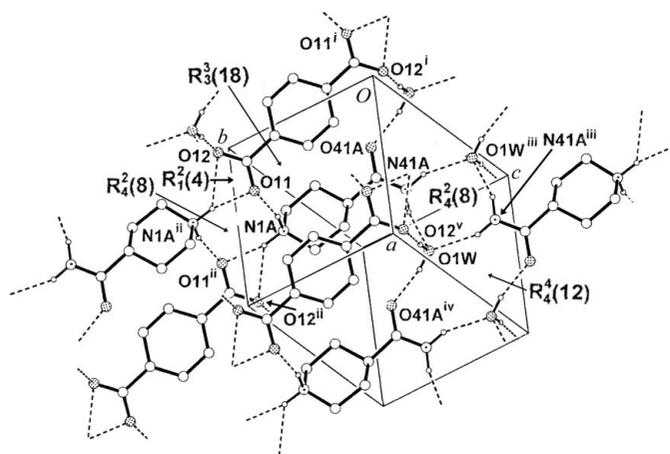
**Figure 7**

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. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. [Symmetry code: (v)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; for other codes, see Table 3.]

short hydrogen bond [2.393(3) Å] in the ‘planar’ DCPA anion in (II) results in a  $C2-C1-C11-O11$  torsion angle of  $174.1(3)^\circ$ , while another feature of this conformation is elongation of the  $C1-C11$  and  $C2-C21$  bonds [1.522(4) and 1.533(4) Å, respectively] and distortion of the external bond angles at C1 and C2 [ $128.1(2)$  and  $128.8(2)^\circ$ , respectively; Smith & Wermuth, 2010*a*].

In the structure of the hydrogen 5-nitroisphthalate salt, (III) (Fig. 3), the primary cation–anion interaction has a second longer  $N-H\cdots O_{\text{carboxylate}}$  contact [ $N1A\cdots O12 = 3.0366(19) \text{ \AA}$  and  $N1A-H12A\cdots O12 = 118.1(17)^\circ$ ], similar to that in (II). The cation–anion associations are also similar in some respects to those of (I). The hydrogen isophthalate anions give zigzag head-to-tail hydrogen-bonded chain substructures through carboxy–carboxylate  $O-H\cdots O$  hydrogen bonds (Table 3) but these are classified as graph set  $C(8)$ , rather than  $C(7)$  as in (I). In addition, the centrosymmetric  $R_2^2(8)$  hydrogen-bonded INIPA amide–amide dimers give peripheral structure extension through piperidinium–carboxylate  $N-H\cdots O$  hydrogen bonds which involve two anions, enclosing cyclic  $R_3^3(10)$  rings (Fig. 7). The three-dimensional framework structure is generated through amide–carboxylate  $N-H\cdots O$  hydrogen-bonding associations. The nitro O atoms are unassociated, except for weak intermolecular cation  $C-H\cdots O$  associations [ $C2A\cdots O52^{ii} = 3.308(2) \text{ \AA}$  and  $C2A-H22A\cdots O52^{ii} = 151^\circ$ ] (see Table 3 for symmetry code). The anion in (III) is essentially planar, but with the carboxylate group rotated slightly out of the plane of the benzene ring [torsion angle  $C2-C1-C11-O11 = -161.47(16)^\circ$ , *cf.*  $C2-C3-C31-O32 = 172.04(15)^\circ$  (the carboxylic acid group) and  $C4-C5-N51-O52 = 175.06(17)^\circ$  (the nitro group)].

With the terephthalate salt, (IV), one of the piperidinium–carboxylate  $N-H\cdots O$  hydrogen bonds seen in Fig. 4


**Figure 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. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. [For symmetry code (i), see Fig. 1; for other codes, see Table 4.]

is accompanied by an asymmetric three-centre piperidinium-carboxylate  $N-H \cdots O, O'$  interaction [graph set  $R_2^2(4)$ ] 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  $R_4^4(12)$ ]. The water molecules also act as acceptors in bridging these chains laterally through amide  $N-H \cdots O$  hydrogen bonds (Table 4), forming centrosymmetric cyclic  $R_4^4(8)$  associations. The lateral piperidinium-carboxylate  $N-H \cdots O$  hydrogen bonds shown in Fig. 4, together with the water-carboxylate  $O-H \cdots O$  associations [graph sets  $R_3^3(10)$ ,  $R_3^3(18)$  and  $R_6^6(22)$ ], complete a three-dimensional framework structure. The centrosymmetric terephthalate dianion deviates slightly from planarity [torsion angle  $C2-C1-C11-O11 = 169.25(12)^\circ$ ].

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-carboxylate  $N-H \cdots O, O'$  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 piperidine-4-carboxamide (isonipecotamide, 1 mmol) with either 4-nitrophthalic acid (1 mmol) for (I), 4,5-dichlorophthalic acid (1 mmol) for (II), 5-nitroisophthalic acid (1 mmol) for (III) or terephthalic acid (1 mmol) for (IV), in either methanol (50 ml) for (III), methanol-water (80%, 50 ml) for (I) and (IV), or ethanol-water (50%, 50 ml) for (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).

**Table 1**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H11A \cdots O11^i$	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)  $x-\frac{3}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$ ; (iv)  $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$ .

## Compound (I)

### Crystal data

 $C_6H_{13}N_2O^+ \cdot C_8H_4NO_6^-$ 
 $M_r = 339.31$ 

 Monoclinic,  $P2_1/n$ 
 $a = 5.8637(5) \text{ \AA}$ 
 $b = 11.2707(8) \text{ \AA}$ 
 $c = 23.0268(19) \text{ \AA}$ 
 $\beta = 93.082(8)^\circ$ 
 $V = 1519.6(2) \text{ \AA}^3$ 
 $Z = 4$ 

 Mo  $K\alpha$  radiation

 $\mu = 0.12 \text{ mm}^{-1}$ 
 $T = 200 \text{ K}$ 
 $0.40 \times 0.40 \times 0.12 \text{ mm}$ 

### Data collection

Oxford Gemini-S CCD area-detector diffractometer

Absorption correction: multi-scan

 (*CrysAlis PRO*; Oxford

Diffraction, 2009)

 $T_{\min} = 0.915, T_{\max} = 0.980$ 

10364 measured reflections

2989 independent reflections

 2375 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.023$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$ 
 $wR(F^2) = 0.114$ 
 $S = 1.05$ 

2989 reflections

233 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$ 
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$ 

## Compound (II)

### Crystal data

 $C_6H_{13}N_2O^+ \cdot C_8H_5Cl_2O_4^-$ 
 $M_r = 363.19$ 

 Monoclinic,  $P2_1/n$ 
 $a = 6.6897(4) \text{ \AA}$ 
 $b = 9.7392(5) \text{ \AA}$ 
 $c = 24.1222(13) \text{ \AA}$ 
 $\beta = 92.479(4)^\circ$ 
 $V = 1570.15(15) \text{ \AA}^3$ 
 $Z = 4$ 

 Mo  $K\alpha$  radiation

 $\mu = 0.44 \text{ mm}^{-1}$ 
 $T = 200 \text{ K}$ 
 $0.30 \times 0.25 \times 0.20 \text{ mm}$ 

### Data collection

Oxford Gemini S CCD area-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  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.028$ 
**Table 2**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H11A \cdots O11$	0.92 (4)	1.90 (4)	2.810 (3)	170 (3)
$N1A-H12A \cdots O21^i$	0.87 (4)	1.96 (4)	2.753 (3)	152 (3)
$N41A-H41A \cdots O21^{ii}$	0.82 (4)	2.48 (4)	3.158 (3)	142 (4)
$N41A-H42A \cdots O41A^{iii}$	0.93 (4)	2.19 (4)	3.086 (4)	163 (3)
$O12-H12 \cdots O21$	1.00	1.40	2.393 (3)	180

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

**Table 3**

Hydrogen-bond geometry (Å, °) for (III).

<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>
N1A—H11A...O31 <sup>i</sup>	0.93 (2)	2.06 (2)	2.9236 (18)	153.6 (17)
N1A—H12A...O11	0.98 (2)	1.87 (2)	2.8229 (16)	164 (2)
N1A—H12A...O12	0.98 (2)	2.45 (2)	3.0366 (19)	118.1 (17)
N41A—H41A...O11 <sup>ii</sup>	0.822 (19)	2.298 (19)	3.0669 (19)	155.9 (17)
N41A—H42A...O41A <sup>iii</sup>	0.940 (19)	1.996 (19)	2.9321 (18)	174.1 (16)
O32—H32...O12 <sup>iv</sup>	0.93 (2)	1.63 (2)	2.5336 (17)	164 (3)

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

**Refinement**

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

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

**Compound (III)****Crystal data**

$\text{C}_6\text{H}_{13}\text{N}_2\text{O}^+ \cdot \text{C}_8\text{H}_4\text{NO}_6^-$   $V = 1502.27 (11) \text{ Å}^3$   
 $M_r = 339.31$   $Z = 4$   
 Monoclinic,  $P2_1/c$  Mo  $K\alpha$  radiation  
 $a = 9.4117 (4) \text{ Å}$   $\mu = 0.12 \text{ mm}^{-1}$   
 $b = 14.3552 (5) \text{ Å}$   $T = 200 \text{ K}$   
 $c = 11.4490 (5) \text{ Å}$   $0.45 \times 0.40 \times 0.18 \text{ mm}$   
 $\beta = 103.787 (4)^\circ$

**Data collection**

Oxford Gemini-S CCD area-detector diffractometer 9866 measured reflections  
 Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009) 2940 independent reflections  
 $T_{\min} = 0.980, T_{\max} = 0.990$  2284 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.106$   
 $S = 1.01$   
 2940 reflections  
 237 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$

**Compound (IV)****Crystal data**

$2\text{C}_6\text{H}_{13}\text{N}_2\text{O}_8^+ \cdot \text{C}_8\text{H}_4\text{O}_4^{2-} \cdot 2\text{H}_2\text{O}$   $\gamma = 80.885 (7)^\circ$   
 $M_r = 458.51$   $V = 556.89 (9) \text{ Å}^3$   
 Triclinic,  $P\bar{1}$   $Z = 1$   
 $a = 6.5099 (5) \text{ Å}$  Mo  $K\alpha$  radiation  
 $b = 7.7777 (6) \text{ Å}$   $\mu = 0.11 \text{ mm}^{-1}$   
 $c = 11.6865 (12) \text{ Å}$   $T = 200 \text{ K}$   
 $\alpha = 76.429 (8)^\circ$   $0.50 \times 0.15 \times 0.08 \text{ mm}$   
 $\beta = 76.968 (7)^\circ$

**Data collection**

Oxford Gemini-S CCD area-detector diffractometer 6562 measured reflections  
 Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009) 2177 independent reflections  
 $T_{\min} = 0.965, T_{\max} = 0.990$  1746 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$

**Table 4**

Hydrogen-bond geometry (Å, °) for (IV).

<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>
N1A—H11A...O11	0.966 (17)	1.856 (18)	2.7937 (16)	162.9 (14)
N1A—H12A...O11 <sup>i</sup>	0.979 (17)	1.847 (17)	2.8030 (15)	164.7 (17)
N1A—H12A...O12 <sup>i</sup>	0.979 (17)	2.367 (19)	3.1200 (16)	133.3 (14)
N41A—H41A...O1W <sup>ii</sup>	0.927 (17)	2.045 (17)	2.9181 (16)	156.5 (17)
N41A—H42A...O1W	0.95 (2)	2.111 (19)	2.9870 (17)	153.2 (14)
O1W—H11W...O41A <sup>iii</sup>	0.861 (18)	1.892 (18)	2.7410 (15)	168.7 (17)
O1W—H12W...O12 <sup>iv</sup>	0.932 (19)	1.833 (19)	2.7632 (15)	175.6 (19)

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

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.093$   
 $S = 1.05$   
 2177 reflections  
 169 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{Å}^{-3}$

H atoms involved in hydrogen-bonding interactions were located by difference methods and, with the exception of the carboxylic acid H atoms in (I) and (II), which were set to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$  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 (aliphatic C—H = 0.97 or 0.98 Å, and aromatic C—H = 0.93 Å) using a riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

For all four compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I), (II) and (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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3064). Services for accessing these data are described at the back of the journal.

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