

Two-component molecular crystals composed of chloronitrobenzoic acids and 4-aminopyridine

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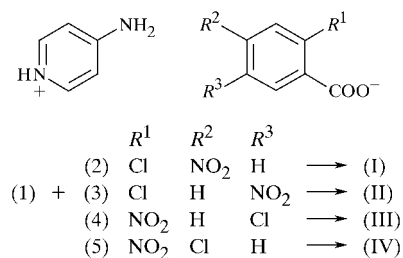
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The crystal structures of the four isomeric organic salts 4-aminopyridinium 2-chloro-4-nitrobenzoate, (I), 4-aminopyridinium 2-chloro-5-nitrobenzoate, (II), 4-aminopyridinium 5-chloro-2-nitrobenzoate, (III), and 4-aminopyridinium 4-chloro-2-nitrobenzoate, (IV), all $C_5H_7N_2^+ \cdot C_7H_3ClNO_4^-$, are presented. Compound (I) has one intramolecular hydrogen bond, one intermolecular $C-H \cdots O$ hydrogen bond and π - π -stacking interactions. Compound (II) has $N-H \cdots O$, $C-H \cdots O$ and $C-H \cdots Cl$ hydrogen bonds, and $Cl \cdots O-C$ electrostatic interactions. Compound (III) has $N-H \cdots O$ and $C-H \cdots O$ hydrogen bonds. Compound (IV) has a π - π -stacking interaction, but no $C-H \cdots O$ hydrogen bonds.

Comment

We have been interested in the preparation and uses of two-component molecular crystals (Koshima, Ding *et al.*, 1996; Koshima, Wang *et al.*, 1996). In order to predict packing modes in such systems and to design specific crystal structures, we have studied how the weaker intermolecular interactions, such as aromatic π - π -stacking interactions and $C-H \cdots O$ hydrogen bonding, affect packing modes in molecular crystals



(Sugiyama, Meng, Wen *et al.*, 2002). In this paper, we describe the syntheses and structures of four different two-component molecular crystals, (I)–(IV), comprising 4-aminopyridine, (1), with four isomers of chloronitrobenzoic acid, (2)–(5), and we report their packing modes, which exhibit many of the intermolecular interactions described above.

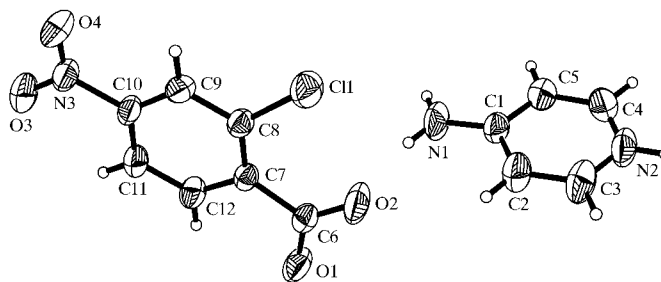


Figure 1

A view of the molecule of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

X-ray analysis of the four single crystals confirmed that the ratio of acid to base is 1:1, and the molecular pairs are connected through $COO^- \cdots HN^+$ hydrogen bonds, with the transfer of an H atom, to form the salt in all cases. We were interested in seeing whether any of the products crystallized in chiral space groups, since (1) itself is known to crystallize in space group $P2_12_12_1$ (Sugiyama, Meng & Matsuura, 2002). However, all four salts were found to crystallize in achiral space groups.

For (I) (space group $Pbca$), there is an intramolecular hydrogen bond (Fig. 1 and Table 1), which occurs only in (I). An intermolecular $C-H \cdots O$ hydrogen bond links the two-

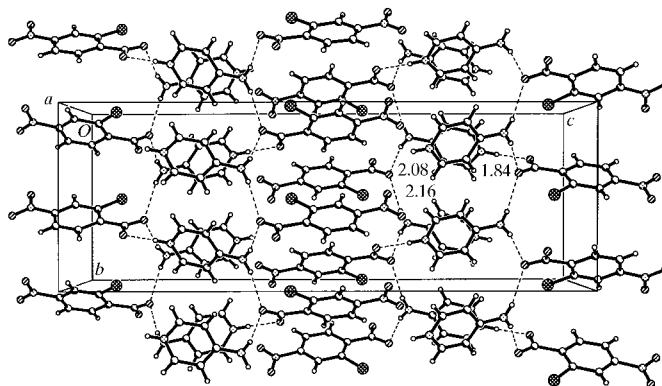


Figure 2

The crystal structure of (I) viewed along the a axis. Hydrogen bonds are indicated by broken lines and distances are in Å.

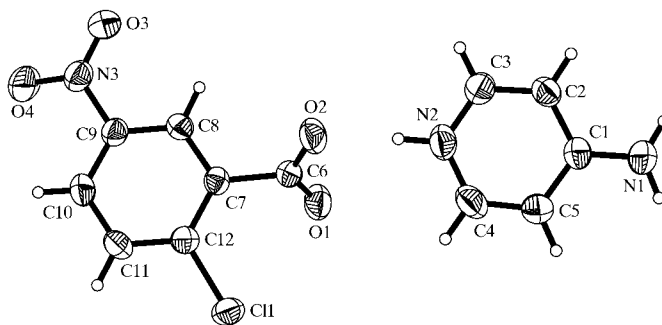


Figure 3

A view of the molecule of (II) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

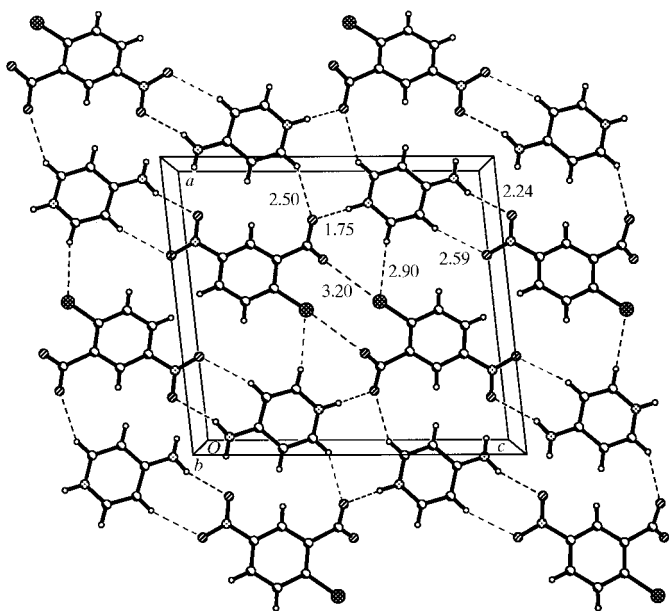


Figure 4

The planar structure of (II) viewed along the *b* axis. Hydrogen bonds and electrostatic interactions are indicated by broken lines, and distances are in Å.

dimensional (001) sheets formed by hard hydrogen bonds. Furthermore, (I) exhibits π - π -stacking interactions, in which neighbouring benzoate aromatic rings are stacked with an interplanar separation of 3.39 Å (Fig. 2).

Compound (II), which crystallizes in space group $P2_1/n$ (Fig. 3), forms a planar network through a variety of hydrogen bonds (Table 2). In this network, there are, in addition to N—H \cdots O hydrogen bonds, two kinds of C—H \cdots O hydrogen bonds and a single C—H \cdots Cl hydrogen bond, although this last type is not as common as the C—H \cdots O type (Fig. 4). Besides these hydrogen bonds, an additional feature of (II) is the presence of a Cl1 \cdots O1—C6 electrostatic interaction (Cl \cdots O 3.20 Å), forming a centrosymmetric ring. Each (010) sheet is connected to a neighbouring sheet along [010] through

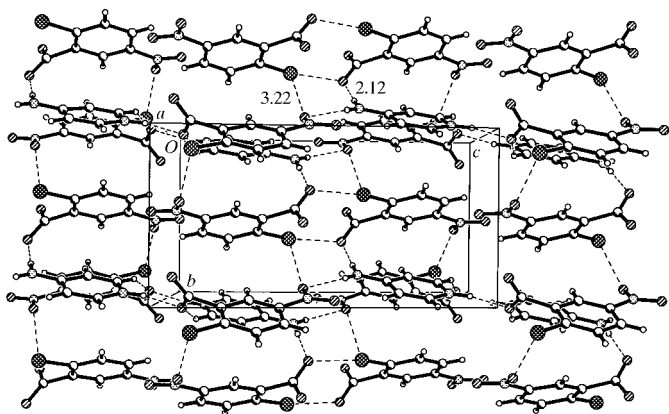


Figure 5

The crystal structure of (II) viewed along the *a* axis. Hydrogen bonds and electrostatic interactions are indicated by broken lines, and distances are in Å.

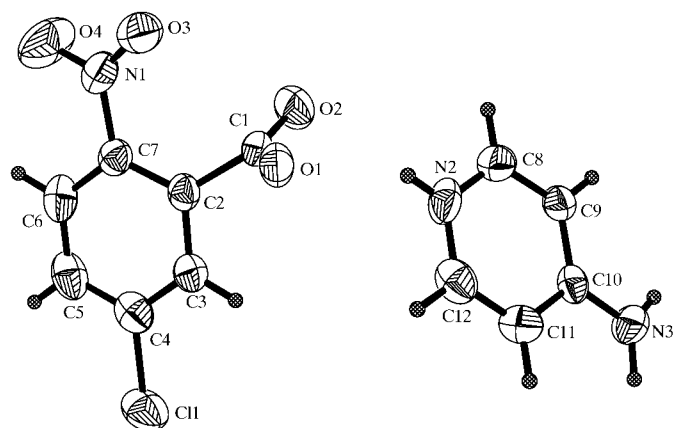


Figure 6

A view of the molecule of (III) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small hatched spheres of arbitrary radii.

a Cl1 \cdots O3 electrostatic interaction (Cl \cdots O 3.22 Å) (Fig. 5).

The molecular structure of (III), which crystallizes in space group $P2_1/c$, is shown in Fig. 6. Compound (III) forms (100) sheets, in which the components are linked by both hard and soft hydrogen bonds (Table 3); the soft hydrogen bonds alone generate a chain along [001] (Fig. 7).

In the crystal structure of (IV) ($C2/c$; Fig. 8 and Table 4), there are no C—H \cdots O hydrogen bonds, but the (100)

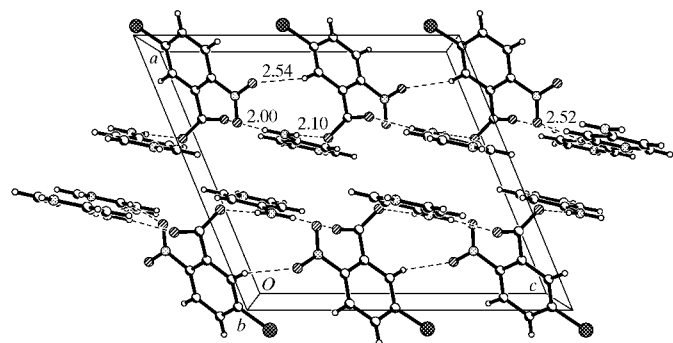


Figure 7

The crystal structure of (III) viewed along the *b* axis. Hydrogen bonds are indicated by broken lines and distances are in Å.

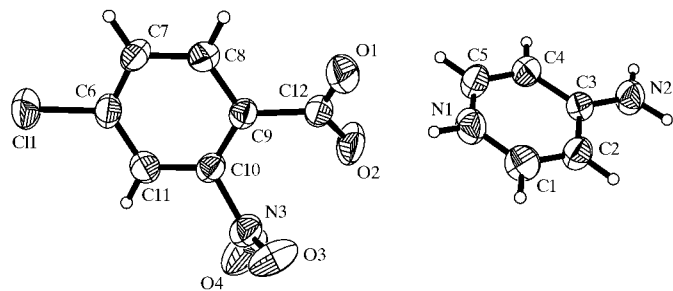


Figure 8

A view of the molecule of (IV) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

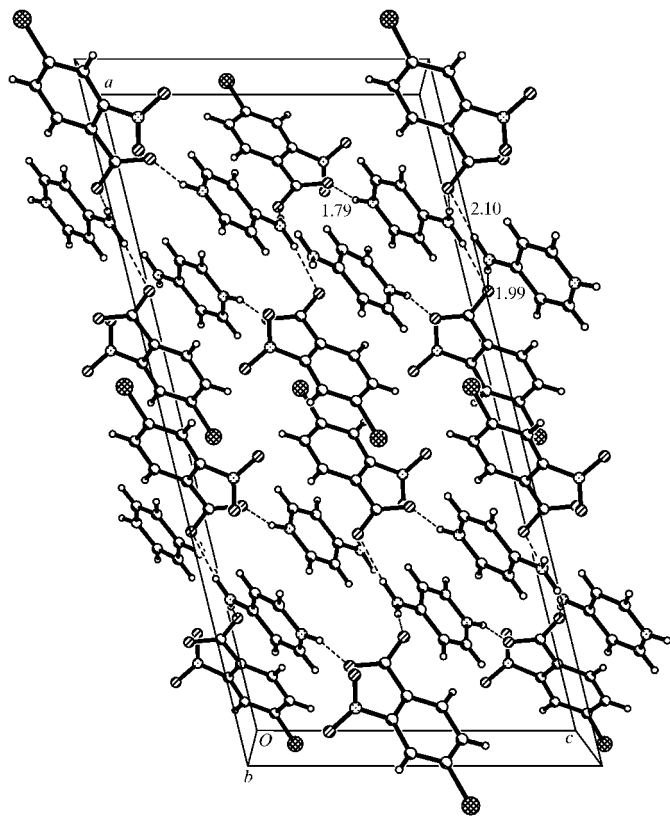


Figure 9
The crystal structure of (IV) viewed along the *b* axis. Hydrogen bonds are indicated by broken lines and distances are in Å.

hydrogen-bonded sheets are linked by a π - π -stacking interaction in which two benzoate aromatic rings have an interplanar separation of 3.41 Å (Fig. 9).

We have found that many of the two-component molecular crystals formed by chloronitrobenzoic acids with organic bases crystallize to give good single crystals suitable for X-ray crystallographic analysis more easily than the corresponding series of two-component molecular crystals formed by the non-chlorinated nitrobenzoic acids with organic bases (Sugiyama, Meng *et al.*, 2002). Thus, the Cl atoms may play a space-filling role in the crystallization process.

We also found that the C—H...O hydrogen bonds involving the O atom of the nitro group, with a large β value (Kamlet *et al.*, 1983), played a significant role in determining the packing modes in this study, although it has been reported that nitro groups are not used as hydrogen-bond acceptors (Etter & Panunto, 1988).

Experimental

The title salts, (I)–(IV), were prepared by spontaneous crystallization from solutions of the respective individual components in methanol–acetonitrile (1:1) for (I), acetonitrile for (II) and (IV), and methanol for (III). In spite of many attempts, we only obtained separate crystals of the acid and base components when trying to prepare the salt of

4-aminopyridine and 4-chloro-3-nitrobenzoic acid. Solid-state IR spectra were recorded as KBr discs on a PYE UNICAM SP-300 IR spectrophotometer. Elemental analyses were carried out with a Yanako CHN Corder MT-3. Melting points were determined using differential scanning calorimetry (DSC) on a NETZSCH DSC 204. All non-covalent bonds were calculated using *PLATON* (Spek, 1990).

Analysis for (I): m.p. 424 K; IR (KBr, cm^{-1}): 3333 (*br*), 3164, 3099, 2551 (*br*), 2001 (*br*), 1661, 1608, 1577, 1534, 1381, 1352, 1196, 1121, 1047, 895, 817, 754; analysis calculated for $\text{C}_{12}\text{H}_{10}\text{ClN}_3\text{O}_4$: C 48.8, H 3.4, N 14.2%; found: C 48.6, H 3.3, N 14.0%.

Analysis for (II): m.p. 437 K; IR (KBr, cm^{-1}): 3411, 3168, 2500 (*br*), 2072 (*br*), 1657, 1643, 1588, 1525, 1403, 1357, 1196, 1159, 1045, 912, 837, 740; analysis calculated for $\text{C}_{12}\text{H}_{10}\text{ClN}_3\text{O}_4$: C 48.8, H 3.4, N 14.2%; found: C 48.6, H 3.6, N 14.2%.

Analysis for (III): m.p. 431 K; IR (KBr, cm^{-1}): 3319 (*br*), 3198, 3097, 2667, 2362 (*br*), 1662, 1626, 1563, 1530, 1385, 1361, 1337, 1196, 1147, 1055, 898, 832, 791, 761; analysis calculated for $\text{C}_{12}\text{H}_{10}\text{ClN}_3\text{O}_4$: C 48.8, H 3.4, N 14.2%; found: C 48.6, H 3.4, N 14.1%.

Analysis for (IV): m.p. 417 K; IR (KBr, cm^{-1}): 3320 (*br*), 3104 (*br*), 2651 (*br*), 2041 (*br*), 1961 (*br*), 1659, 1590, 1563, 1530, 1372, 1278, 1195, 1143, 1102, 1045, 889, 874, 821; analysis calculated for $\text{C}_{12}\text{H}_{10}\text{ClN}_3\text{O}_4$: C 48.8, H 3.4, N 14.2%; found: C 48.8, H 3.4, N 14.3%.

Compound (I)

Crystal data

$\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_7\text{H}_3\text{ClNO}_4^-$
 $M_r = 295.68$
 Orthorhombic, *Pbc1*
 $a = 9.923$ (3) Å
 $b = 9.527$ (3) Å
 $c = 27.337$ (7) Å
 $V = 2584.5$ (12) Å³
 $Z = 8$

$D_x = 1.520$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 90 reflections
 $\theta = 2.3$ – 24.5°
 $\mu = 0.31$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.912$, $T_{\max} = 0.940$
 10 028 measured reflections

2288 independent reflections
 1249 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$
 $\theta_{\text{max}} = 25^\circ$
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 9$
 $l = -27 \rightarrow 32$

Refinement

Refinement on F^2
 $R(F) = 0.040$
 $wR(F^2) = 0.137$
 $S = 0.96$
 2288 reflections
 181 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °) for (I).

<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—H1B...O2	0.86	2.08	2.915 (4)	165
N1—H1A...O2 ⁱ	0.86	2.16	2.961 (4)	155
N2—H2B...O1 ⁱⁱ	0.86	1.84	2.699 (3)	178
C3—H3A...O4 ⁱⁱⁱ	0.93	2.64	3.434 (5)	144
Cl2—H12A...O1	0.93	2.39	2.729 (4)	101

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

Compound (II)

Crystal data

$C_5H_7N_2^+ \cdot C_7H_3ClNO_4^-$
 $M_r = 295.68$
 Monoclinic, $P2_1/n$
 $a = 12.624$ (4) Å
 $b = 7.270$ (2) Å
 $c = 14.023$ (5) Å
 $\beta = 96.329$ (5)°
 $V = 1279.1$ (7) Å³
 $Z = 4$

Data collection

Bruker CCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.897$, $T_{max} = 0.925$
 5062 measured reflections

Refinement

Refinement on F^2
 $R(F) = 0.034$
 $wR(F^2) = 0.093$
 $S = 1.02$
 2256 reflections
 193 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$D_x = 1.535$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 74 reflections
 $\theta = 2.6$ – 27.5°
 $\mu = 0.32$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.35 \times 0.30 \times 0.25$ mm

2256 independent reflections
 1660 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.023$
 $\theta_{max} = 25^\circ$
 $h = -14 \rightarrow 15$
 $k = -8 \rightarrow 4$
 $l = -16 \rightarrow 16$

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.08P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.026$
 $\Delta\rho_{max} = 0.15$ e Å⁻³
 $\Delta\rho_{min} = -0.23$ e Å⁻³

Table 2

Hydrogen-bonding geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O1^i$	0.892 (10)	2.115 (10)	3.006 (3)	177 (2)
$N1-H2 \cdots O3^{ii}$	0.894 (10)	2.241 (12)	3.113 (2)	165 (2)
$N2-H3 \cdots O2$	0.920 (10)	1.751 (11)	2.665 (2)	172 (2)
$C5-H5A \cdots O4^{ii}$	0.93	2.59	3.491 (3)	163
$C3-H3A \cdots O2^{iii}$	0.93	2.50	3.271 (3)	141
$C4-H4A \cdots Cl^{iv}$	0.93	2.90	3.651 (2)	139

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

Compound (III)

Crystal data

$C_5H_7N_2^+ \cdot C_7H_3ClNO_4^-$
 $M_r = 295.68$
 Monoclinic, $P2_1/c$
 $a = 12.219$ (6) Å
 $b = 8.488$ (4) Å
 $c = 13.368$ (6) Å
 $\beta = 112.467$ (9)°
 $V = 1281.1$ (10) Å³
 $Z = 4$

Data collection

Bruker CCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.911$, $T_{max} = 0.940$
 5126 measured reflections

$D_x = 1.533$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1254
 reflections
 $\theta = 3.0$ – 30.0°
 $\mu = 0.32$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.30 \times 0.25 \times 0.20$ mm

2255 independent reflections
 1174 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.069$
 $\theta_{max} = 25^\circ$
 $h = -14 \rightarrow 10$
 $k = -10 \rightarrow 9$
 $l = -10 \rightarrow 15$

Table 3

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H2 \cdots O1^i$	0.82 (4)	2.10 (4)	2.925 (5)	178 (4)
$N2-H1 \cdots O1$	0.76 (4)	2.10 (4)	2.781 (5)	150 (4)
$N3-H3 \cdots O2^{ii}$	0.94 (4)	2.00 (4)	2.928 (5)	171 (4)
$C3-H3A \cdots O4^{iii}$	0.93	2.54	3.414 (5)	156
$Cl2-H12A \cdots O3^{iii}$	0.93	2.52	3.424 (5)	163

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

Refinement

Refinement on F^2
 $R(F) = 0.049$
 $wR(F^2) = 0.146$
 $S = 0.98$
 2255 reflections
 193 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.24$ e Å⁻³
 $\Delta\rho_{min} = -0.30$ e Å⁻³

Compound (IV)

Crystal data

$C_5H_7N_2^+ \cdot C_7H_3ClNO_4^-$
 $M_r = 295.68$
 Monoclinic, $C2/c$
 $a = 25.608$ (19) Å
 $b = 8.475$ (6) Å
 $c = 12.433$ (10) Å
 $\beta = 103.749$ (14)°
 $V = 2621$ (3) Å³
 $Z = 8$

$D_x = 1.499$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 80 reflections
 $\theta = 2.5$ – 23.5°
 $\mu = 0.31$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker CCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.913$, $T_{max} = 0.941$
 5262 measured reflections

2308 independent reflections
 1579 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.028$
 $\theta_{max} = 25^\circ$
 $h = -30 \rightarrow 26$
 $k = -10 \rightarrow 9$
 $l = -14 \rightarrow 12$

Refinement

Refinement on F^2
 $R(F) = 0.037$
 $wR(F^2) = 0.120$
 $S = 1.04$
 2308 reflections
 194 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 1.1026P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.23$ e Å⁻³
 $\Delta\rho_{min} = -0.25$ e Å⁻³
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0061 (7)

All H atoms in (I) were constrained. In (II)–(IV), H atoms on N were refined freely. In all four compounds, H atoms which were not

Table 4

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O2$	0.93 (3)	1.79 (3)	2.694 (3)	164 (3)
$N2-H2 \cdots O1^i$	0.80 (3)	2.10 (3)	2.891 (4)	172 (3)
$N2-H21 \cdots O1^{ii}$	0.95 (3)	1.99 (3)	2.931 (4)	169 (3)

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

refined were treated as riding atoms, with C—H = 0.93 Å and N—H = 0.86 Å.

For all compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1189). Services for accessing these data are described at the back of the journal.

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