

Supramolecular structures of four isomorphous anilinium 2-carboxy-4-nitrobenzoate salts: 4-*X*-C₆H₄NH₃⁺·C₈H₄NO₆⁻ (*X* = H, Cl, Br and I)

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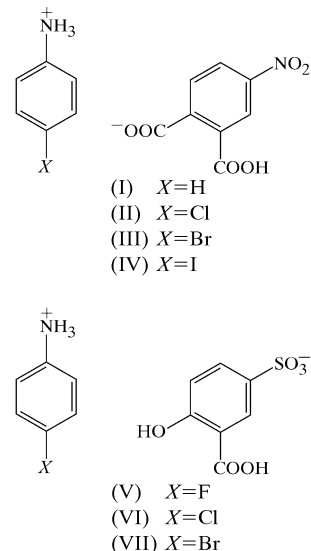
Anilinium 2-carboxy-4-nitrobenzoate, C₆H₈N⁺·C₈H₄NO₆⁻, (I), 4-chloroanilinium 2-carboxy-4-nitrobenzoate, C₆H₇ClN⁺·C₈H₄NO₆⁻, (II), 4-bromoanilinium 2-carboxy-4-nitrobenzoate, C₆H₇BrN⁺·C₈H₄NO₆⁻, (III), and 4-iodoanilinium 2-carboxy-4-nitrobenzoate, C₆H₇I⁺·C₈H₄NO₆⁻, (IV), are approximately isostructural. In each compound, the ions are linked into complex sheets by a combination of O—H···O and N—H···O hydrogen bonds. Within the sheets, two distinct one-dimensional substructures can be identified, *viz.* a chain of edge-fused *R*₃²(13) rings and a double helix of simple *C*₂²(9) chains. In (I) and (IV), the sheets are linked by a C—H···O_{nitro} hydrogen bond and a two-centre C—I···O_{nitro} interaction, respectively, but the corresponding C—Cl···O and C—Br···O contact distances in (II) and (III) are not significantly shorter than the sum of the van der Waals radii.

Comment

We have recently reported the supramolecular structure of 4-iodoanilinium 2-carboxy-6-nitrobenzoate (Glidewell *et al.*, 2003). We report here the structures of four closely related anilinium 2-carboxy-4-nitrobenzoate salts, 4-*X*-C₆H₄NH₃⁺·C₈H₄NO₆⁻ [(I) *X* = H, (II) *X* = Cl, (III) *X* = Br, and (IV) *X* = I], where (IV) differs from the previously reported compound in the location of the nitro group in the anion.

Compounds (I)–(IV) all crystallize in space group *C2/c*, with unit cells of very similar size and shape; the only major differences between the unit-cell dimensions of (I)–(IV) occur in the *c* dimension, which increases monotonically as the 4-substituent *X* changes from H, *via* Cl and Br, to I, with an overall change of nearly 7.4%. By contrast, the *a* and *b*

dimensions show much smaller changes, and these are not monotonic in the same order as for *c*; thus, *a* shows its smallest value and *b* its largest value when *X* = Cl, *i.e.* compound (II). The β angle decreases monotonically from (I) to (IV), and the unit-cell volumes increase likewise, with an overall increase from (I) to (IV) of nearly 9%.



The title compounds (Figs. 1–4) are all salts, in which one carboxyl group of the anion is fully ionized; the remaining carboxyl H atom is fully ordered, as shown by the difference maps, and the C—O distances in the carboxyl and carboxylate units (Table 1) are fully consistent with the H-atom locations deduced from the difference maps. While the nitro group and the un-ionized carboxyl group show only modest displacements from the plane of the C1–C6 aryl ring, as shown by the relevant torsion angles (Table 5), the carboxylate group is almost orthogonal to the adjacent aryl ring, presumably for steric reasons. Consequently, there is no quinonoid-type bond fixation involving the nitro and carboxylate substituents.

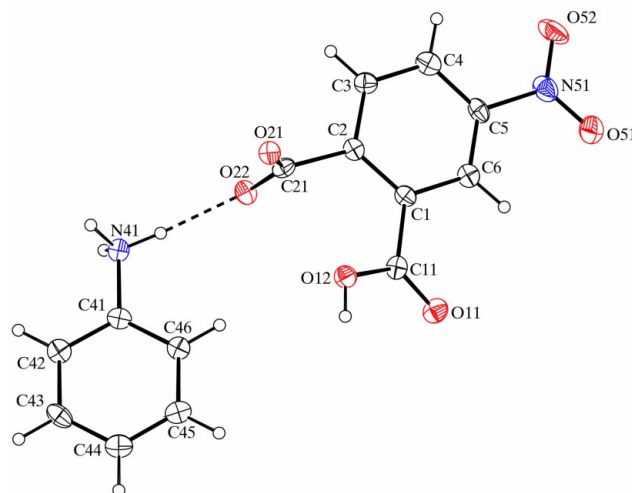


Figure 1
The independent components in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The hydrogen-bonded supramolecular structures of (I)–(IV), which are determined primarily by a combination of O–H···O and N–H···O hydrogen bonds, reinforced by aromatic π – π stacking interactions, are all extremely similar and hence need be discussed in detail only for (I). The molecular constitutions differ, of course, in respect of the nature of the 4-*X* substituent, but even here the supramolecular interactions are strikingly similar, with a C–H···O_{nitro} hydrogen bond in (I) closely echoed by two-centre X···O_{nitro} contacts in (II)–(IV) (Table 2).

The two independent components in (I) are linked into a single three-dimensional framework by a combination of O–H···O, N–H···O and C–H···O hydrogen bonds (Tables 2 and 3), reinforced by aromatic π – π stacking interactions. The formation of this framework is readily analysed in terms of its component one-dimensional substructures. The anions alone form chains running parallel to the [010] direction; carboxyl

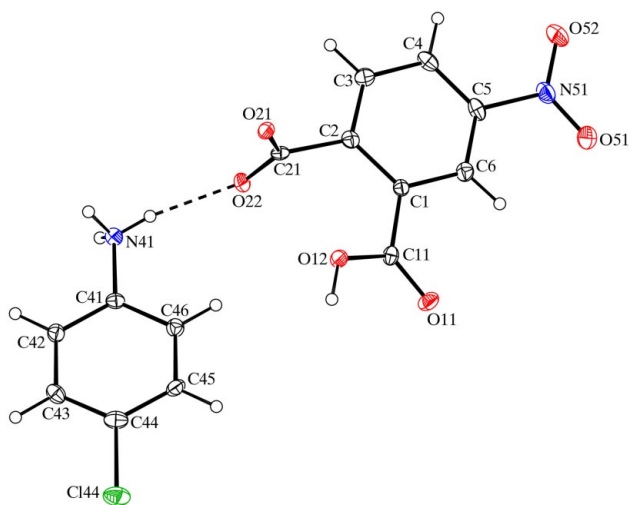


Figure 2
The independent components in (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

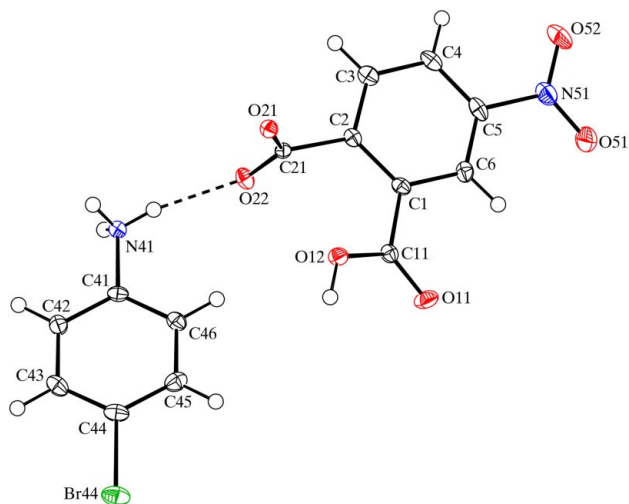


Figure 3
The independent components in (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

atom O12 in the anion at (x, y, z) acts as a hydrogen-bond donor to carboxylate atom O21 in the anion at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, so forming a $C(7)$ chain (Bernstein *et al.*, 1995) generated by the 2_1 screw axis along $(\frac{3}{4}, y, \frac{1}{4})$ (Fig. 5). In addition, atom N41 in the cation at (x, y, z) acts as a hydrogen-bond donor, *via* H41A and H41B, to carboxylate atoms O22 at (x, y, z) and O21 at $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively, so enhancing the simple $C(7)$ anion chain to form a chain of edge-fused $R_3^2(13)$ rings (Fig. 6).

The third, and final, N–H···O hydrogen bond generates a second [010] motif; atom N41 at (x, y, z) acts as a hydrogen-bond donor, *via* H41C, to carboxyl atom O11 in the anion at $(1 - x, -1 + y, \frac{1}{2} - z)$, and atom N41 at $(1 - x, -1 + y, \frac{1}{2} - z)$ in turn acts as a donor to atom O11 at $(x, -2 + y, z)$, so forming a $C_2^2(9)$ chain running parallel to the [010] direction. Since the repeat period of this chain encompasses two unit cells, there must be two such chains to complete the structure; these two chains are related by the twofold rotation axis along $(\frac{1}{2}, y, \frac{1}{4})$, so forming a double helix of $C_2^2(9)$ chains generated by the

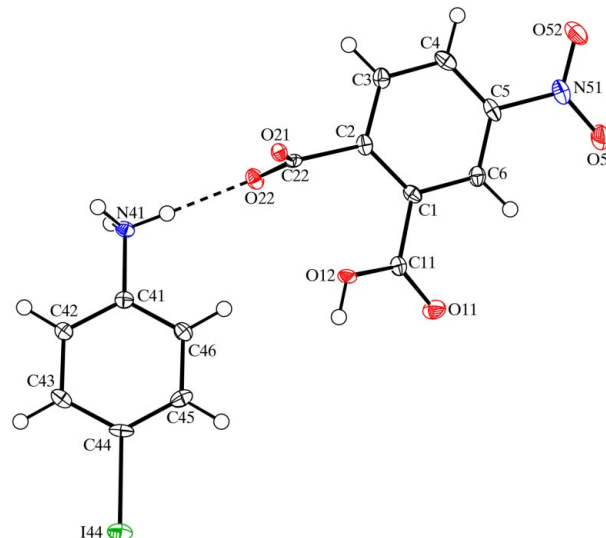


Figure 4
The independent components in (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

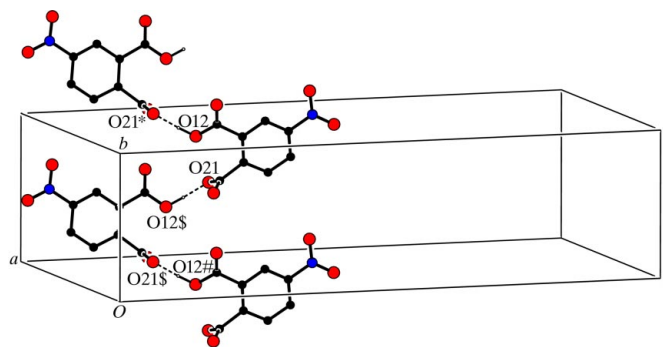


Figure 5
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C(7)$ chain of anions along [010]. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign (\$) are at the symmetry positions $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, $(x, -1 + y, z)$ and $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

twofold rotation axis along $(\frac{1}{2}, y, \frac{1}{4})$ (Fig. 7). The combination of the two [010] motifs generated by the axes along $(\frac{3}{4}, y, \frac{1}{4})$ and $(\frac{1}{2}, y, \frac{1}{4})$, respectively, then generates a (001) sheet of some complexity. This sheet is reinforced by two independent π - π stacking interactions. The first of these interactions lies within the chain of $R_3^3(13)$ rings. The aryl rings of the cation at (x, y, z) and the anion at $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ are nearly parallel, with a dihedral angle of only $3.4(2)^\circ$ between their planes; the interplanar spacing is *ca* 3.46 Å and the ring-centroid separation is 3.705(2) Å, corresponding to a ring offset of *ca* 1.33 Å. The second of these interactions lies within the double helix and involves the corresponding rings at (x, y, z) and $(1 - x, y, \frac{1}{2} - z)$, with again a dihedral angle of only $3.4(2)^\circ$ between their planes; here the interplanar spacing is *ca* 3.45 Å and the centroid separation is 3.752(2) Å, giving a ring offset of *ca* 1.47 Å.

In each of (II)–(IV), the formation of the hydrogen-bonded sheet and its two substructures is identical to that in (I) (Tables 4–6). Two sheets of this type pass through each unit cell, in the domains $0 < z < 0.50$ and $0.50 < z < 1$; however, the interactions between adjacent sheets are not the same in the four structures (Table 2). In (I), atom C44 in the cation at (x, y, z) acts as a hydrogen-bond donor to nitro atom O51 in the anion at $(x, 2 - y, -\frac{1}{2} + z)$, so producing a $C_2^2(15)$ chain

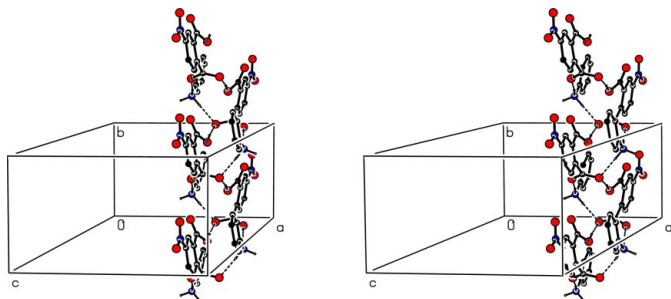


Figure 6
A stereoview of part of the crystal structure of (I), showing the formation of a [010] chain of $R_3^3(13)$ rings. For clarity, H atoms bonded to C atoms have been omitted.

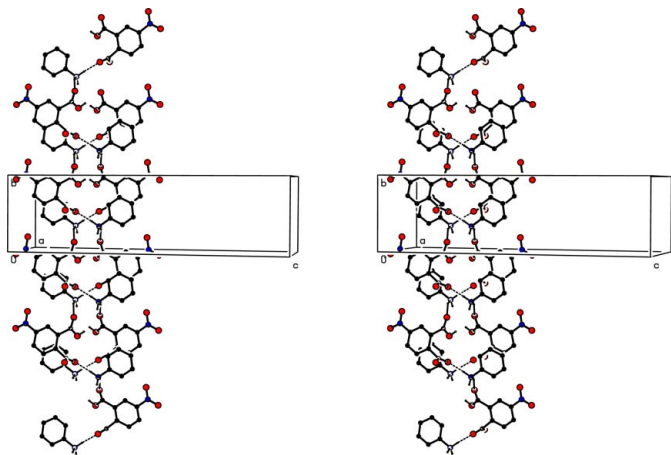


Figure 7
A stereoview of part of the crystal structure of (I), showing the formation of a double helix of $C_2^2(9)$ chains along [010]. For clarity, H atoms bonded to C atoms have been omitted.

running parallel to the [001] direction, generated by the *c*-glide plane at $y = 1.0$ (Fig. 8), and linking the (001) sheets into a single framework. In a similar manner, in each of compounds (II)–(IV), the halogen atoms $X44$ ($X = \text{Cl}, \text{Br}$ and I) in the cation at (x, y, z) form a two-centre $X \cdots \text{O}$ contact with nitro atom O51 at $(x, 2 - y, -\frac{1}{2} + z)$. The $\text{C}-\text{X} \cdots \text{O}$ units are all nearly linear (Table 2) and the $\text{I} \cdots \text{O}$ distance in (IV) is significantly shorter than the sum of the van der Waals radii (3.30 Å), taking into account the polar flattening of the I atom (Nyburg & Faerman, 1985). This iodo–nitro interaction then generates a $C_2^2(15)$ chain (Starbuck *et al.*, 1999) along [001] (Fig. 9). By contrast, the $\text{Cl} \cdots \text{O}$ and $\text{Br} \cdots \text{O}$ contact distances in (II) and (III) are not significantly shorter than the sum of the van der Waals radii (3.12 and 3.08 Å, respectively; Nyburg & Faerman, 1985), and so no structurally significant attractive interactions can be associated with these $\text{X} \cdots \text{O}$ contacts in (II) and (III).

It is of interest briefly to compare the structurally very similar series of salts (I)–(IV) with the substituted anilinium salts (V)–(VII) formed by 5-sulfosalicylic acid. These salts crystallize from aqueous ethanol as mono-, hemi- and mono-

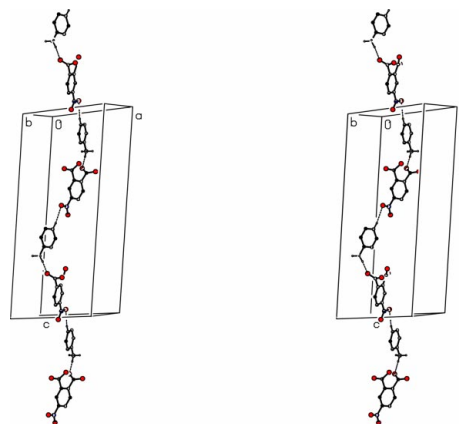


Figure 8
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C_2^2(15)$ chain along [001]. For clarity, H atoms bonded to O or C atoms and not taking part in the motif shown have been omitted.

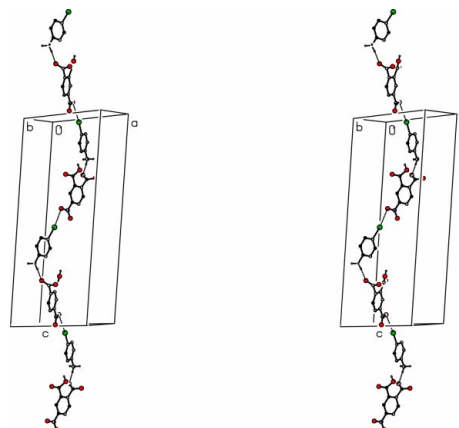


Figure 9
A stereoview of part of the crystal structure of (IV), showing the formation of a $C_2^2(15)$ chain along [001] generated by the iodo–nitro interaction. For clarity, H atoms bonded to C atoms have been omitted.

hydrates, respectively, in space groups $P2_1$ ($Z = 2$ and $Z' = 1$), $P2_1/c$ ($Z = 8$ and $Z' = 2$) and $Pbca$ ($Z = 8$ and $Z' = 1$) (Smith *et al.*, 2005). All three salts (V)–(VII) form three-dimensional hydrogen-bonded structures in which the water molecules play a key role. In (V), the anions form chains generated by translation, whereas each of (VI) and (VII) contains the $R_2^2(8)$ dimer motif characteristic of simple carboxylic acids although absent from the structures of (I)–(IV).

Experimental

A solution of 4-nitrophthalic acid (0.42 g, 2 mmol) in hot ethanol (20 ml) was added to a solution of the appropriate aniline (2 mmol), also in ethanol (10 ml). The mixture was heated under reflux for 30 min and then allowed to cool to room temperature. The products, which precipitated after 24–48 h, were collected by filtration and recrystallized from methanol. Each product exhibited strong broad absorptions in the IR region 3000–2500 cm^{-1} . Strong absorptions in the 1720–1490 cm^{-1} range were at 1716, 1610, 1529 and 1496 cm^{-1} for (I); 1716, 1612, 1536 and 1495 cm^{-1} for (II); 1698, 1610, 1529 and 1488 cm^{-1} for (III); and 1704, 1610, 1529 and 1489 cm^{-1} for (IV).

Compound (I)

Crystal data

$\text{C}_6\text{H}_8\text{N}^+\cdot\text{C}_8\text{H}_4\text{NO}_6^-$
 $M_r = 304.26$
 Monoclinic, $C2/c$
 $a = 12.8131$ (10) Å
 $b = 7.5521$ (6) Å
 $c = 28.114$ (2) Å
 $\beta = 98.13$ (3)°
 $V = 2693.1$ (4) Å³
 $Z = 8$

$D_x = 1.501$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2656
 $\theta = 3.1$ – 26.1 °
 $\mu = 0.12$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.14 \times 0.10 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.980$, $T_{\max} = 0.998$
 13 132 measured reflections
 2656 independent reflections

1474 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.097$
 $\theta_{\max} = 26.1$ °
 $h = -15 \rightarrow 15$
 $k = -9 \rightarrow 9$
 $l = -33 \rightarrow 34$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.077$
 $wR(F^2) = 0.210$
 $S = 1.03$
 2656 reflections
 200 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 5.7738P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43$ e Å⁻³
 $\Delta\rho_{\min} = -0.30$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for compounds (I)–(IV).

	(I)	(II)	(III)	(IV)
C11–O11	1.211 (5)	1.210 (5)	1.220 (4)	1.277 (6)
C11–O12	1.308 (5)	1.306 (5)	1.310 (3)	1.302 (6)
C21–O21	1.283 (4)	1.280 (5)	1.286 (3)	1.289 (6)
C21–O22	1.277 (5)	1.231 (5)	1.236 (3)	1.235 (6)
C2–C1–C11–O11	163.1 (4)	162.1 (5)	162.4 (3)	161.0 (5)
C1–C2–C21–O21	101.1 (4)	99.4 (5)	100.2 (3)	100.0 (5)
C4–C5–N51–O51	173.5 (4)	–176.4 (5)	–175.1 (3)	–172.9 (5)

Compound (II)

Crystal data

$\text{C}_6\text{H}_7\text{ClN}^+\cdot\text{C}_8\text{H}_4\text{NO}_6^-$
 $M_r = 338.70$
 Monoclinic, $C2/c$
 $a = 12.7725$ (16) Å
 $b = 7.5825$ (7) Å
 $c = 29.595$ (3) Å
 $\beta = 97.202$ (5)°
 $V = 2843.6$ (5) Å³
 $Z = 8$

$D_x = 1.582$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2342
 reflections
 $\theta = 3.1$ – 25.0 °
 $\mu = 0.30$ mm⁻¹
 $T = 120$ (2) K
 Needle, colourless
 $0.36 \times 0.09 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.910$, $T_{\max} = 0.994$
 7613 measured reflections
 2342 independent reflections

1887 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$
 $\theta_{\max} = 25.0$ °
 $h = -14 \rightarrow 14$
 $k = -8 \rightarrow 8$
 $l = -34 \rightarrow 35$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.190$
 $S = 1.13$
 2342 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 21.7547P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.75$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

Table 2

Short intermolecular C44–X44···O51^{iv} contacts (Å, °) for compounds (I)–(IV).

Compound	C–X	X···O ^{iv}	C···O ^{iv}	C–X···O ^{iv}	X···O ^{iv} –N ^{iv}
(I) (X = H)	0.95	2.55	3.477 (6)	167	103
(II) (X = Cl)	1.751 (5)	3.109 (4)	4.849 (6)	171.8 (2)	111.0 (3)
(III) (X = Br)	1.904 (3)	3.108 (3)	5.001 (4)	172.0 (2)	111.2 (2)
(IV) (X = I)	2.115 (5)	3.168 (4)	5.270 (4)	171.8 (2)	110.9 (3)

Symmetry code: (iv) $x, 2 - y, -\frac{1}{2} + z$.

Compound (III)

Crystal data

$\text{C}_6\text{H}_7\text{BrN}^+\cdot\text{C}_8\text{H}_4\text{NO}_6^-$
 $M_r = 383.16$
 Monoclinic, $C2/c$
 $a = 12.8292$ (6) Å
 $b = 7.5750$ (3) Å
 $c = 29.8202$ (13) Å
 $\beta = 97.0270$ (11)°
 $V = 2876.2$ (2) Å³
 $Z = 8$

$D_x = 1.770$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3305
 reflections
 $\theta = 3.1$ – 27.6 °
 $\mu = 2.89$ mm⁻¹
 $T = 120$ (2) K
 Plate, yellow
 $0.26 \times 0.04 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.520$, $T_{\max} = 0.944$
 16 011 measured reflections
 3305 independent reflections

2941 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\max} = 27.6$ °
 $h = -16 \rightarrow 16$
 $k = -9 \rightarrow 9$
 $l = -38 \rightarrow 38$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.114$
 $S = 1.08$
 3304 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 13.8988P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.36$ e Å⁻³
 $\Delta\rho_{\min} = -0.76$ e Å⁻³

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

D—H...A	D—H	H...A	D...A	D—H...A
O12—H12...O21 ⁱ	1.00	1.48	2.476 (4)	176
N41—H41A...O22	0.91	1.89	2.799 (4)	173
N41—H41B...O21 ⁱⁱ	0.91	1.92	2.828 (4)	172
N41—H41C...O11 ⁱⁱⁱ	0.91	2.02	2.884 (4)	158

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

Compound (IV)

Crystal data

C₆H₇IN⁺·C₈H₄NO₆⁻ $D_x = 1.949 \text{ Mg m}^{-3}$
M_r = 430.15 Mo *K*α radiation
 Monoclinic, *C*2/*c* Cell parameters from 3354 reflections
a = 12.9459 (3) Å $\theta = 3.1\text{--}27.5^\circ$
b = 7.5576 (1) Å $\mu = 2.22 \text{ mm}^{-1}$
c = 30.1790 (6) Å *T* = 120 (2) K
 $\beta = 96.784 (1)^\circ$ Plate, colourless
V = 2932.04 (10) Å³ $0.40 \times 0.10 \times 0.02 \text{ mm}$
Z = 8

Data collection

Nonius KappaCCD diffractometer 2941 reflections with *I* > 2σ(*I*)
 φ and ω scans *R*_{int} = 0.051
 Absorption correction: multi-scan $\theta_{\text{max}} = 27.5^\circ$
 (SADABS; Sheldrick, 2003) *h* = -16 → 16
*T*_{min} = 0.471, *T*_{max} = 0.957 *k* = -9 → 9
 16 634 measured reflections *l* = -39 → 39
 3354 independent reflections

Refinement

Refinement on *F*² $w = 1/[\sigma^2(F_o^2) + (0.104P)^2 + 15.6247P]$
 $R[F^2 > 2\sigma(F^2)] = 0.039$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.160$ $(\Delta/\sigma)_{\text{max}} < 0.001$
S = 1.13 $\Delta\rho_{\text{max}} = 2.65 \text{ e \AA}^{-3}$
 3354 reflections $\Delta\rho_{\text{min}} = -1.79 \text{ e \AA}^{-3}$
 210 parameters
 H-atom parameters constrained

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
O12—H12...O21 ⁱ	0.92	1.58	2.484 (4)	169
N41—H41A...O22	0.83	1.99	2.806 (4)	166
N41—H41B...O21 ⁱⁱ	0.84	1.97	2.804 (5)	173
N41—H41C...O11 ⁱⁱⁱ	0.84	2.07	2.888 (5)	166

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

Table 5
Hydrogen-bond geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
O12—H12...O21 ⁱ	0.92	1.57	2.481 (3)	169
N41—H41A...O22	0.84	1.98	2.806 (3)	166
N41—H41B...O21 ⁱⁱ	0.84	1.97	2.811 (3)	173
N41—H41C...O11 ⁱⁱⁱ	0.84	2.06	2.888 (3)	167

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

Table 6
Hydrogen-bond geometry (Å, °) for (IV).

D—H...A	D—H	H...A	D...A	D—H...A
O12—H12...O21 ⁱ	0.84	1.69	2.479 (5)	156
N41—H41A...O22	0.91	1.91	2.812 (5)	173
N41—H41B...O21 ⁱⁱ	0.91	1.92	2.826 (5)	174
N41—H41C...O11 ⁱⁱⁱ	0.91	2.03	2.896 (5)	159

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

For each of (I)–(IV), the systematic absences permitted *C*2/*c* and *Cc* as possible space groups; *C*2/*c* was selected in each case and confirmed by the subsequent analyses. All H atoms were located from difference maps. H atoms bonded to C atoms were then treated as riding atoms, with C—H distances of 0.95 Å and *U*_{iso}(H) values of 1.2*U*_{eq}(C). H atoms bonded to N or O atoms were allowed to ride at the distances deduced from the difference maps and with *U*_{iso}(H) = 1.2*U*_{eq}(N) or 1.5*U*_{eq}(O); the resulting N—H distances were 0.83–0.91 Å and the O—H distances were 0.84–0.92 Å. For (III), the highest difference peak was located 0.88 Å from atom Br44, while the deepest hole was located 0.64 Å from Br44.

For all compounds, data collection: COLLECT (Hooft, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; structure solution: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); structure refinement: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1823). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
 Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2003). *Acta Cryst. C* **59**, o509–o511.
 Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
 McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
 Nyburg, S. C. & Faerman, C. H. (1985). *Acta Cryst. B* **41**, 274–279.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
 Smith, G., Wermuth, U. D. & White, J. M. (2005). *Acta Cryst. C* **61**, o105–o109.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Starbuck, J., Norman, N. C. & Orpen, A. G. (1999). *New J. Chem.* **23**, 969–972.