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Hydrogen-bonding motifs in 3-carboxyanilinium bromide and iodide

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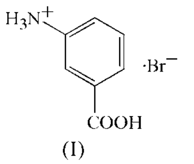
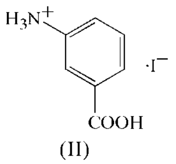
In the title compounds, $C_7H_8NO_2^+\cdot Br^-$, (I), and $C_7H_8NO_2^+\cdot I^-$, (II), the asymmetric unit contains a discrete 3-carboxyanilinium cation, with a protonated amine group, and a halide anion. The compounds are not isostructural, and the crystal structures of (I) and (II) are characterized by different two-dimensional hydrogen-bonded networks. The ions in (I) are connected into ladder-like ribbons *via* N—H···Br hydrogen bonds, while classic cyclic O—H···O hydrogen bonds between adjacent carboxylic acid functions link adjacent ribbons to give three characteristic graph-set motifs, *viz.* $C_2^1(4)$, $R_4^2(8)$ and $R_2^2(8)$. The ions in (II) are connected *via* N—H···I, N—H···O and O—H···I hydrogen bonds, also with three characteristic graph-set motifs, *viz.* $C(7)$, $C_2^1(4)$ and $R_4^2(18)$, but an O—H···O interaction is not present.

Comment

Predictable and reliable noncovalent interactions play a major role in the formation of supramolecular systems. In the area of supramolecular research and crystal engineering, most common supramolecular synthons are based on hydrogen bonds, π–π interactions, van der Waals forces and, most recently, halogen bonds (Desiraju, 1989; Metrangolo & Resnati, 2001; Cinčić *et al.*, 2008). The present paper reports a part of our research on intermolecular interactions in hydrogen-bonded ionic crystals of acid salts (Cinčić & Kaitner, 2007*a*,*b*). The title compounds were originally investigated during salt screening of hydroxy- and carboxyanilines. 3-Aminobenzoic acid is a less studied isomer than the 2-amino and 4-amino analogues. 2-Aminobenzoic (anthranilic) acid is known as vitamin L, and as trimorphic material it has been widely studied (Boone *et al.*, 1977; Brown & Ehrenberg, 1985; Takazawa *et al.*, 1986). 4-Aminobenzoic acid is widely known as bacterial vitamin H and as one of the components of vitamin B complex.



(I)



(II)

In the structures of the title bromide, (I), and iodide, (II), salts, the bond lengths and angles correspond to those expected for the atom types and the type of hybridization (Allen *et al.*, 1987). The asymmetric unit in both (I) and (II) contains a discrete 3-carboxyanilinium cation, with a protonated amine group, and a halide anion (Figs. 1 and 2). Compound (I) is isostructural with the analogous chloride salt (Arora *et al.*, 1973), although the earlier work assigned the unit-cell dimensions in a different sequence (*c*, *b* and *a* relative to the currently used unit cell). Because of the difference in anionic radii, the volume of the unit cell in (I) is about 15.6 Å^3 larger than that of the chloride salt. Compound (II) is not isostructural with the chloride and bromide salts. This may be

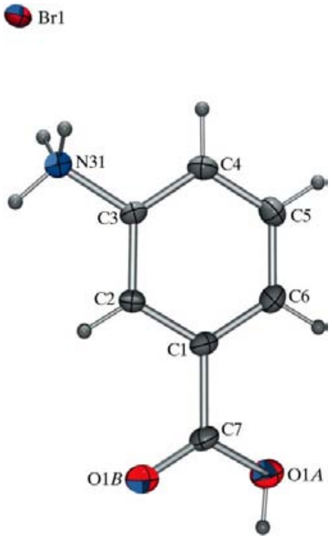


Figure 1
The asymmetric unit of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The minor disordered H atom of the carboxylic acid group has been omitted.

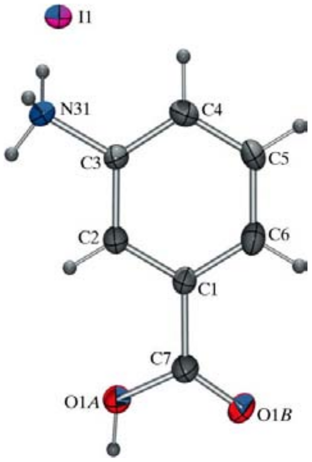


Figure 2
The asymmetric unit of (II), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

a consequence of the packing inefficiency caused by the large iodide ion and results in a different crystal packing and hydrogen-bonding arrangement, as described below.

In (I), the ions are connected into a two-dimensional hydrogen-bonded network parallel to the (100) plane *via* O—H···O and N—H···Br hydrogen bonds (Table 1). All ammonium H atoms are involved in hydrogen bonds with three different Br^- ions, and each anion accepts hydrogen bonds from three different cations. Two of these interactions link the anions and cations in an alternating fashion into extended chains along the [010] direction, which can be described by the graph-set motif $C_2^1(4)$ (Bernstein *et al.*, 1995). The third interaction is a crosslink from an adjacent chain, which serves to complete a ladder-like ribbon composed of two chains as the ladder uprights, while each rung is formed by an ammonium group and a Br^- ion, with the directionality of the rung alternating along the ladder (Fig. 3). The remainder of each cation extends out from the rung on each side of the ladder. The centrosymmetric hydrogen-bonded rings formed by adjacent rungs of the ladder can be described by the graph-set motif $R_4^2(8)$. There are actually two different symmetry-independent eight-membered rings of this type in the ladder, because adjacent rings are not related by a single unit-cell translation. At the same time, the carboxylic acid group at the opposite end of the carboxyanilinium cation forms a centrosymmetric hydrogen-bonded dimer with its counterpart in a cation from an adjacent ribbon (Fig. 3). These interactions lead to the graph-set motif $R_2^2(8)$, which is a characteristic feature found in most salts of 3- and 4-aminobenzoic acid (Cambridge Structural Database; Allen, 2002). The very similar covalent bond distances found between the carboxylic acid O atoms and the C atom indicate that the acidic H atom is disordered across both O atoms, so that the hydrogen-bonded dimer is disordered. The disordered H atom occupies the sites on atoms O1*A* and O1*B* almost equally. The crosslinking of the ribbons by the carboxylic acid interactions results in a two-dimensional hydrogen-bonded sheet-like structure overall (Fig. 3). Adjacent sheets are stacked in the [100] direction to give a three-dimensional framework, where the interplanar distance between the aromatic rings of each sheet is *ca* 3.36 Å and a weak interlayer C—H···Br [C4···Br1($-x$, $-y + 2$, $-z + 2$) = 3.664 (4) Å] interaction is present. The interplanar distance between aromatic rings of each sheet in the isostructural chloride salt is, as expected, smaller at *ca* 3.04 Å.

The supramolecular structure of (II) differs markedly from that of (I). The ions are connected into a two-dimensional hydrogen-bonded network, this time parallel to the (010) plane, *via* O—H···I, N—H···I and N—H···O hydrogen bonds. Unexpectedly, there are no centrosymmetric hydrogen-bonded dimers between the carboxylic acid groups of adjacent 3-carboxyanilinium cations. The carbonyl O atom participates in hydrogen bonding with another neighbouring cation through an N—H···O hydrogen bond. This interaction links the glide-plane-related cations into zigzag chains, which run

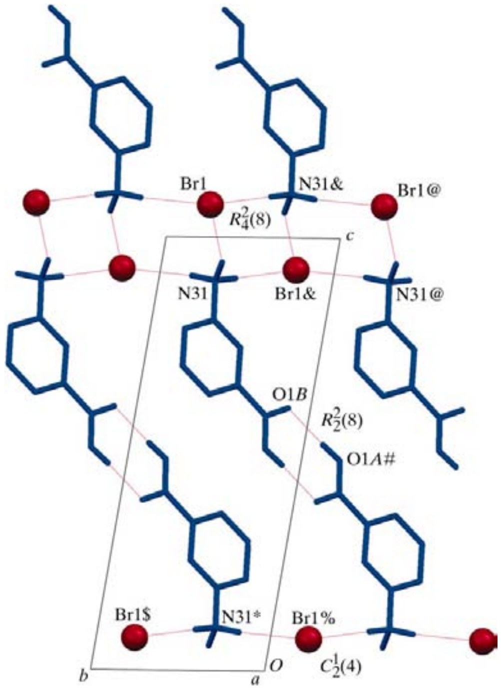


Figure 3
A view of the two-dimensional hydrogen-bonded network parallel to the (100) plane of (I), showing the aggregation of three hydrogen-bonding motifs, $C_2^1(4)$, $R_2^2(8)$ and $R_4^2(8)$. Hydrogen bonds are drawn as dotted lines and C-bound H atoms have been omitted. Atoms marked with an ampersand (&), an 'at' sign (@), a hash (#), a dollar sign ($), an asterisk (*) and a percent sign (%) are at the symmetry positions ($-x + 1$, $-y + 1$, $-z + 2$), (x, $y - 1$, z), ($-x + 1$, $-y$, $-z + 1$), (x, y, $z - 1$), ($-x + 1$, $-y + 1$, $-z + 1$) and (x, $y - 1$, $z - 1$), respectively.

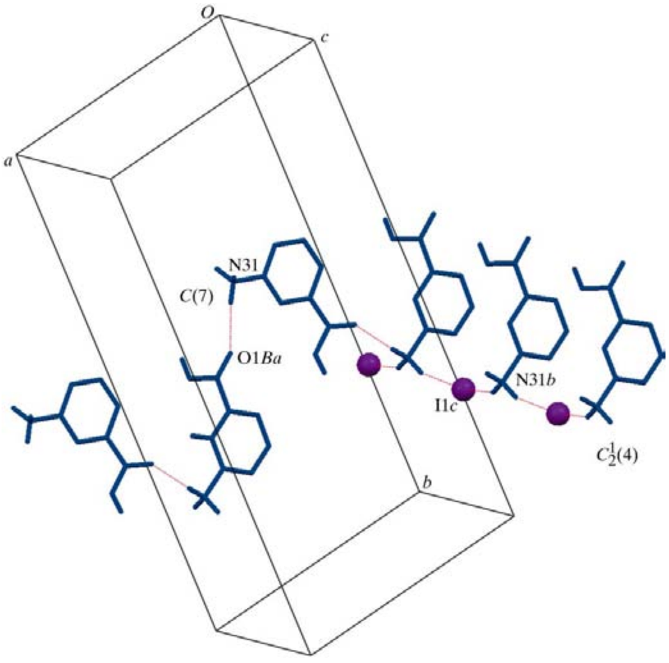


Figure 4
A view of part of the crystal structure of (II), showing the formation of two chain motifs spreading parallel to [100] and [001]. Hydrogen bonds are drawn as dotted lines and C-bound H atoms have been omitted. Atoms marked with the suffixes *a*, *b* and *c* are at the symmetry positions ($x + \frac{1}{2}$, $-y + 1$, $-z + \frac{3}{2}$), ($x - \frac{1}{2}$, $-y + 1$, $-z + \frac{5}{2}$) and ($-x + \frac{1}{2}$, y, $z + \frac{1}{2}$), respectively.

parallel to the [100] direction and which can be described by the graph-set motif $C(7)$ (Fig. 4). The carboxylic acid H atom participates in hydrogen bonding with a neighbouring anion through an O—H···I hydrogen bond. As in (I), all ammonium H atoms are involved in hydrogen bonds, but this time with two different I^- ions and with the carbonyl O atom of a neighbouring cation, while each anion accepts three hydrogen bonds. The two ammonium–anion interactions link the anions and cations in an alternating fashion into extended chains along the [001] direction, which, as in (I), can be described by a graph-set motif of $C_2^1(4)$. However, the crosslinking of adjacent chains into a ladder-like ribbon involving just the ammonium groups and anions is not present. Instead, the O—H···I interaction forms the link between adjacent chains to give a different type of ladder with much longer rungs than in (I) and the cations do not protrude outside the ladder uprights (Fig. 5); instead, the cation itself forms the rung. The centrosymmetric hydrogen-bonded rings formed by adjacent rungs of the ladder can be described by the graph-set motif $R_4^2(18)$ and, again, there are two symmetry-independent adjacent 18-membered rings of this type in the ladder. The aggregation of ring and chain motifs in (II) also leads to a two-dimensional hydrogen-bonded sheet-like structure. The distance between planes calculated through the I^- anions of each sheet is *ca* 2.75 Å.

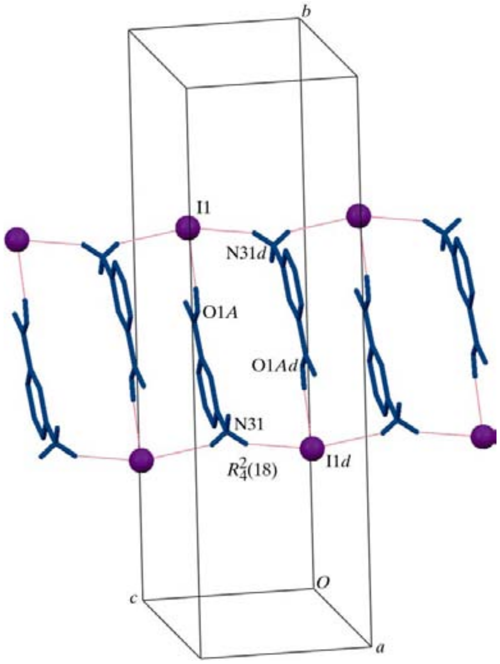


Figure 5
A view of the one-dimensional hydrogen-bonded ladder parallel to [001] in (II), showing the aggregation of $R_4^2(18)$ hydrogen-bonding motifs. Hydrogen bonds are drawn as dotted lines and C-bound H atoms have been omitted. Atoms marked with the suffix *d* are at the symmetry position $(-x + 1, -y + 1, -z + 1)$.

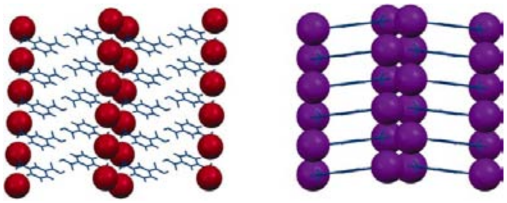


Figure 6
Packing diagrams of (I) (left) and (II) (right), viewed along the *b* and *a* axes, respectively. The anions are shown as spheres.

Fig. 6 clearly compares the packing arrangement of both compounds in which layers of 3-carboxyanilinium cations are embedded between ionic layers of anions, forming an alternating hydrocarbon–ionic layer structure. No intermolecular π–π interactions are evident in the hydrocarbon layer in either crystal structure. The shortest centroid-to-centroid distances in (I) and (II) are *ca* 4.55 and 4.24 Å, respectively.

Experimental

For the preparation of (I), 3-aminobenzoic acid (100 mg, 0,73 mmol) was dissolved in hot ethanol (2 ml). The clear solution was added to hydrobromic acid (1 ml, 2 *M*) and cooled to room temperature. Colourless crystals of (I) were grown by slow evaporation. For the preparation of (II), 3-aminobenzoic acid (100 mg, 0,73 mmol) was dissolved in hot acetone (2 ml). The clear solution was added to hydroiodic acid (2 ml, 2 *M*) and cooled to room temperature. Colourless crystals of (II) were grown by slow evaporation. The crystals of (I) and (II) were collected by vacuum filtration, washed with cold acetone and dried in air. In a nitrogen atmosphere, (I) and (II) melt at 558 and 544 K, respectively.

Compound (I)

Crystal data

$C_7H_8NO_2^+\cdot Br^-$
$M_r = 218.05$
Triclinic, $P\overline{1}$
$a = 4.5536$ (4) Å
$b = 6.0010$ (7) Å
$c = 15.011$ (2) Å
$\alpha = 99.025$ (11)°
$\beta = 90.581$ (11)°
$\gamma = 98.832$ (11)°
$V = 400.05$ (8) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 5.08$ mm^{-1}
$T = 295$ K
0.46 × 0.17 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.276$, $T_{\max} = 0.760$
5296 measured reflections
1735 independent reflections
1503 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 1.20$
1735 reflections
104 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.49$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N31—H31*B*···Br1	0.92	2.49	3.342 (3)	154
N31—H31*A*···Br1$^{\rm i}$	0.91	2.43	3.334 (4)	169
N31—H31*C*···Br1$^{\rm ii}$	0.92	2.44	3.332 (3)	163
O1*A*—H1*A*···O1*B*$^{\rm iii}$	0.85	1.80	2.650 (4)	174
O1*B*—H1*B*···O1*A*$^{\rm iii}$	0.84	1.83	2.650 (4)	165

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

Compound (II)

Crystal data

$C_7H_8NO_2^+\cdot I^-$
$M_r = 265.04$
Orthorhombic, *Pccn*
$a = 11.1815$ (6) Å
$b = 23.1582$ (8) Å
$c = 6.9066$ (4) Å
$V = 1788.42$ (15) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 3.53$ mm^{-1}
$T = 295$ K
0.53 × 0.11 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.387$, $T_{\max} = 0.923$
17853 measured reflections
1944 independent reflections
1544 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.078$
$S = 1.25$
1944 reflections
114 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 1.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1A···I1	0.90	2.46	3.359 (3)	176
N31—H31A···I1$^{\rm i}$	0.82 (7)	2.87 (7)	3.587 (4)	147 (6)
N31—H31B···O1$B^{\rm ii}$	0.86 (6)	2.10 (6)	2.957 (5)	173 (5)
N31—H31C···I1$^{\rm iii}$	0.93 (7)	2.73 (7)	3.575 (4)	151 (6)

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

For both compounds, all N- and O-bound H atoms were located in difference Fourier maps, and for (I) their positions were then held fixed. For (II), the positions of the N-bound H atoms were refined, but the O-bound H atom was fixed in its as-found position. The isotropic displacement parameters were refined for these atoms. Aromatic H atoms were placed in calculated positions and treated as riding on their parent C atoms [C—H = 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C)]. For (II), the largest peak of residual electron density is 1.10 Å from atom H5.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST97* (Nardelli, 1995), *Mercury* (Macrae *et al.*, 2006) and *POVRay* (Persistence of Vision Pty, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3083). Services for accessing these data are described at the back of the journal.

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