Different packing motifs in the crystal structures of three molecular salts containing the 2-amino-5-carboxyanilinium cation: $C_7H_9N_2O_2^+\cdot Cl^-$, $C_7H_9N_2O_2^+\cdot Br^-$ and $C_7H_9N_2O_2^+\cdot NO_3^-\cdot H_2O$

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The syntheses and crystal structures of three molecular salts of protonated 3,4-diaminobenzoic acid, *viz.* 2-amino-5-carboxyanilinium chloride, $C_7H_9N_2O_2^+\cdot Cl^-$, (I), 2-amino-5-carboxyanilinium bromide, $C_7H_9N_2O_2^+\cdot Br^-$, (II), and 2-amino-5-carboxyanilinium nitrate monohydrate, $C_7H_9N_2O_2^+\cdot NO_3^-\cdot H_2O$, (III), are described. The cation is protonated at the *meta*-N atom (with respect to the carboxy group) in each case. In the crystal of (I), carboxylic acid inversion dimers linked by pairwise O—H···O hydrogen bonds are seen and each N—H group forms a hydrogen bond to a chloride ion to result in (100) undulating layers of chloride ions bridged by the inversion dimers into a three-dimensional network. The extended structure of (II) features O—H···Br, N—H···Br and N—H···O hydrogen bonds: the last of these generates $C(7)$ chains of cations. Overall, the packing in (II) features undulating (100) sheets of bromide ions alternating with the organic cations. Intermolecular interactions in the crystal of (III) include O—H···O, O—H···(O,O), N—H···O, N—H···N and O—H···N links. The cations are linked into (001) sheets, and the nitrate ions and water molecules form undulating chains. Taken together, alternating (001) slabs of organic cations plus anions/water molecules result. Hirshfeld surfaces and fingerprint plots were generated to give further insight into the intermolecular interactions in these structures. The crystal used for the data collection of (II) was twinned by rotation about [100] in reciprocal space in a 0.4896 (15):0.5104 (15) ratio.
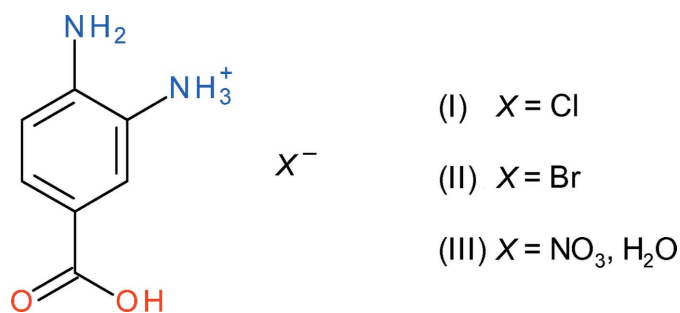
1. Chemical context

The benzoate anion, $C_7H_5O_2^-$ is a classic ligand in coordination chemistry, with over 1500 crystal structures reported in the Cambridge Structural Database (version 5.40, updated to February 2020; Groom *et al.*, 2016) for benzoate complexes of first-row transition metals alone. Functionalized benzoic acid derivatives add further structural variety: for example, –NH2 substituents at the *ortho*, *meta* and/or *para* positions of the benzene ring can form or accept hydrogen bonds with respect to nearby acceptor or donor groups and/or bond as Lewis bases to another metal ion (*i.e.* as a μ^2-*N,O* or μ^3-*N,O,O* bridging ligand). It should be noted that the presence of amine groups allows for protonation and the possible formation of molecular salts with the aminobenzoic acid acting as the cation.

As part of our ongoing studies in this area (Khosa *et al.*, 2015), we now describe the syntheses and structures of three molecular salts of protonated 3,4-diaminobenzoic acid, *viz.* $C_7H_9N_2O_2\cdot Cl$ (I), $C_7H_9N_2O_2\cdot Br$ (II) and $C_7H_9N_2O_2\cdot NO_3\cdot H_2O$
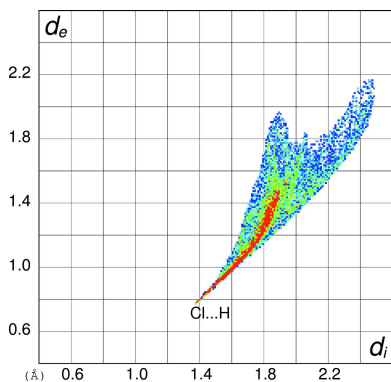
(III). Hirshfeld surface analyses have been performed to gain further insight into the intermolecular interactions.

Figure 2
The molecular structure of (II) showing 50% displacement ellipsoids. The N—H···Br hydrogen bond is indicated by a double-dashed line.

2. Structural commentary

The contents of the asymmetric units of (I) (Fig. 1), (II) (Fig. 2) and (III) (Fig. 3) confirm them to be molecular salts of 3,4-diaminobenzoic acid (*i.e.* the $C_7H_9N_2O_2^+$ 2-amino-5-carboxy-anilinium cation has been formed) and the appropriate strong acid (hydrochloric acid, hydrobromic acid and nitric acid, respectively); compound (III) also includes a water molecule of crystallization. The neutral organic molecule ($C_7H_8N_2O_2$) is known to crystallize as a zwitterion (Rzaczyńska *et al.*, 2000) with nominal intramolecular proton transfer from the carboxylic acid to the *meta*-N atom and presumably exists in the same form in solution, thus the formal acid–base reaction to form the title salts involves proton transfer from the strong acid to the $-CO_2^-$ carboxylate group of zwitterionic $C_7H_8N_2O_2$ to form a $-CO_2H$ carboxylic acid group; atom N1 remains protonated, to result in the $C_7H_9N_2O_2^+$ cation.

The preference for the *meta* $-NH_2$ group to be protonated in these salts compared to the *para* $-NH_2$ group can be rationalized in terms of the potential loss of conjugation of the *para*-N-atom lone pair of electrons with the carboxylic acid grouping *via* the benzene ring, *i.e.*, a small contribution of a quinoid (C=N$^+$ containing) resonance form to the structure (Lai & Marsh, 1967): the mean bond lengths for C1—C2, C3—C4, C4—C5 and C1—C6 (single bonds in the quinoid struc-
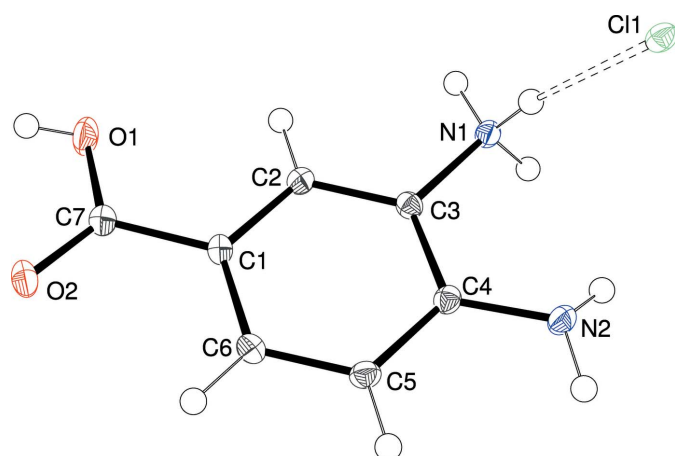
ture) and C2—C3 and C5—C6 (double bonds) are 1.401/1.380, 1.400/1.381 and 1.403/1.373 Å for (I), (II) and (III), respectively (global averages = 1.401/1.378 Å). These data compare very well to the equivalent values of 1.399/1.375 Å established over 50 years ago from Weissenberg data for *p*-aminobenzoic acid (Lai & Marsh, 1967).

This electronic effect is also no doubt reflected in the fact that the C4—N2 (*para*) bond in the title compounds is notably shorter than the C3—N1 (*meta*) bond [distances in (I) = 1.378 (2) and 1.4640 (19), respectively; (II) = 1.387 (6) and 1.468 (6); (III) = 1.386 (5) and 1.457 (5) Å]. Even so, it may be noted that the bond-angle sums about N2 are 348.0, 340.4, and 339.2° for (I), (II) and (III), respectively, suggesting a tendency towards sp^3 hybridization (and presumably lone-pair localization) for the nitrogen atom in each case: it also correlates with the fact that N2 accepts a hydrogen bond in the crystal of (III) (*vide infra*).

For each structure, the carboxylic acid group shows the expected clear distinction between the C7—O1H [(I) = 1.296 (2), (II) = 1.326 (5), (III) = 1.323 (6)Å] and C7=O2 [(I) = 1.252 (2), (II) = 1.216 (5), (III) = 1.232 (5) Å] bond lengths. The degree of twist of the $-CO_2H$ group with respect to the

Figure 1
The molecular structure of (I) showing 50% displacement ellipsoids. The N—H···Cl hydrogen bond is indicated by a double-dashed line.
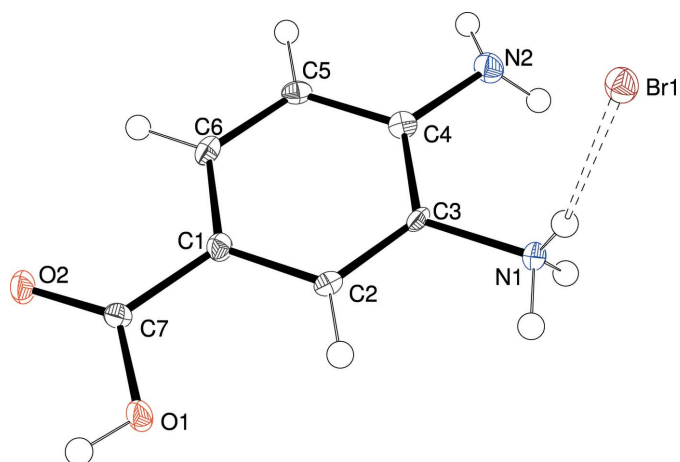

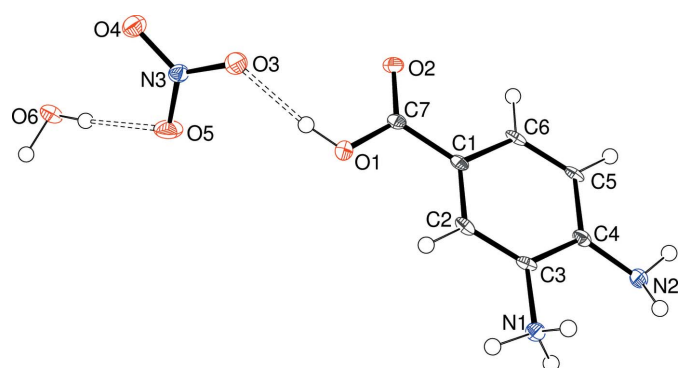**Figure 3**
The molecular structure of (III) showing 50% displacement ellipsoids. The O—H···O hydrogen bonds are indicated by double-dashed lines.
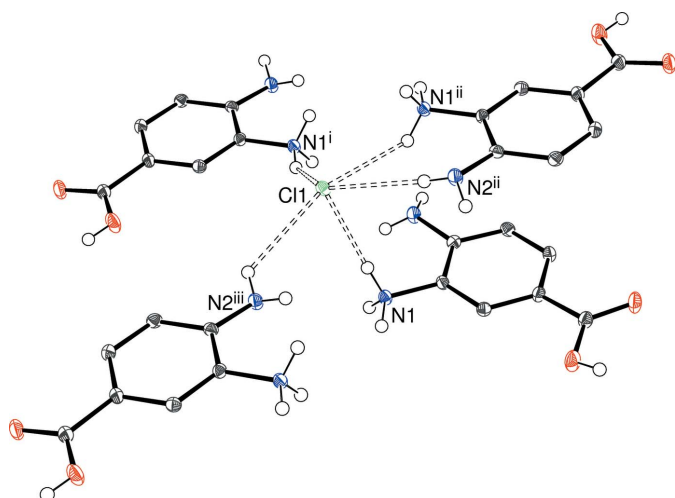
Figure 4
Environment of the chloride ion in the structure of (I) with N—H···Cl hydrogen bonds indicated by double-dashed lines. Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

benzene ring is similar in the three salts [the angles between the mean planes passing through atoms C1–C6 and O1/O2/C7 are (I) = 6.39 (16), (II) = 0.5 (4), (III) = 3.8 (5)°].

3. Supramolecular features

In the crystal of (I), the cations are connected into carboxylic acid inversion dimers *via* pairwise O—H···O hydrogen bonds (Table 1), thereby generating classical $R_2^2(8)$ loops. All five N—H groups link to a nearby chloride ion: the H···Cl contacts from the protonated –N1H$_3^+$ moiety (mean = 2.35 Å) are substantially shorter than those arising from the unprotonated –N2H$_2$ group (mean = 2.70 Å). As a result, the chloride ion accepts five N—H···Cl bonds from four cations (one cation bonds from both N1 and N2) in an irregular geometry (Fig. 4). The overall packing for (I) results in
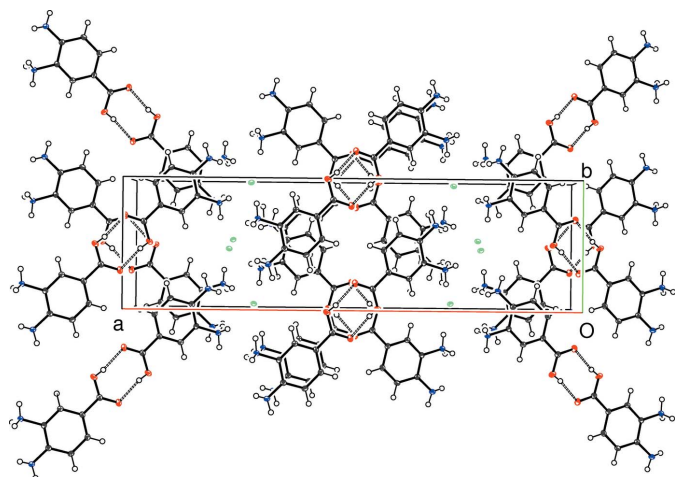

Figure 6
Environment of the bromide ion in the structure of (II) with N—H···Br and O—H···Br hydrogen bonds indicated by double-dashed lines. Symmetry codes: (i) $x, y, z - 1$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 - x, 1 - y, -z$.

corrugated (100) sheets of chloride ions bridged by the carboxylic acid dimers into a three-dimensional supramolecular network (Fig. 5).

Rather than carboxylic acid inversion dimers, the packing for (II) features O—H···Br hydrogen bonds as well as N—H···Br and N—H···O contacts (Table 2). The bromide ion (Fig. 6) is five-coordinated in an irregular geometry by four N—H···Br and one O—H···Br link arising from five different cations. The N1—H2*N*···O2 interaction from the protonated –NH$_3^+$ group to the C=O bond of the carboxylic acid generates [010] $C(7)$ chains of cations, with adjacent ions in the chain related by the 2_1 screw axis. When all the hydrogen bonds are considered together, the packing for (II) can be described as a three-dimensional supramolecular network of undulating (100) sheets of bromide ions alternating with the organic cations (Fig. 7). A notably short C—H···O interaction (H···O = 2.23 Å), which reinforces the $C(7)$ chain of cations, is also observed.

The directional intermolecular interactions in (III) (Table 3) include O$_c$—H···O$_n$, O$_w$—H···(O$_n$,O$_n$), N—H···O$_c$, N—H···N and N—H···O$_n$ (c = carboxylic acid, n = nitrate, w = water) hydrogen bonds. The O atoms of the nitrate ion collectively accept four simple and one bifurcated hydrogen

Figure 5
The packing for (I) viewed down [001]. The hydrogen bonds linking the carboxylic-acid inversion dimers are shown as double-dashed lines.
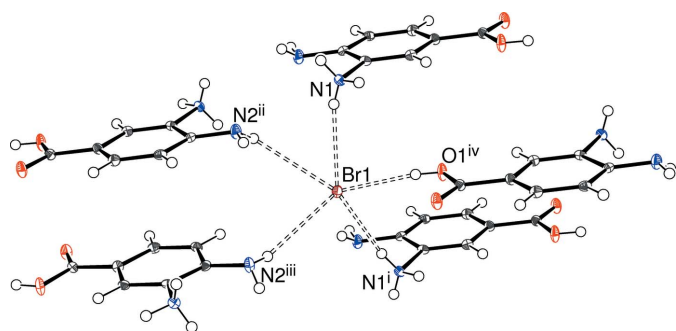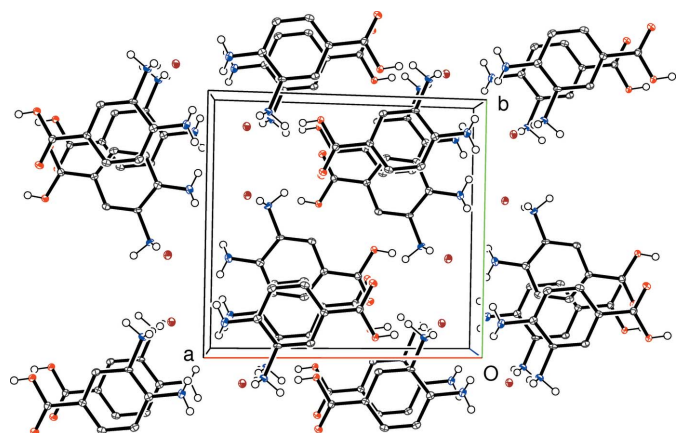

Figure 7
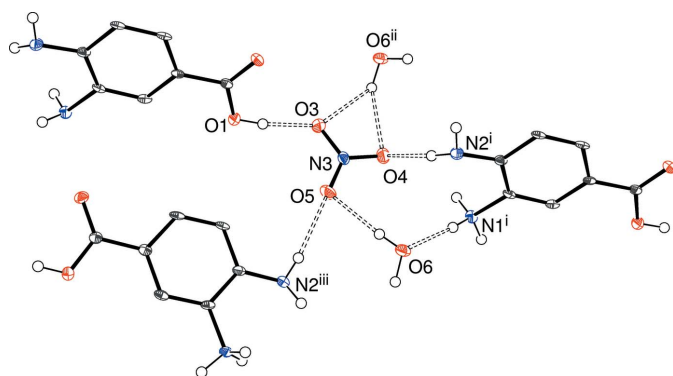The packing for (II) viewed down [001].

Figure 8
Environment of the nitrate ion in the structure of (III) with N—H···O and O—H···O hydrogen bonds indicated by double-dashed lines. Symmetry codes: (i) $1 + x, y, 1 + z$; (ii) $2 - x, \frac{1}{2} + y, 2 - z$; (iii) $-x, y - \frac{1}{2}; 1 - z$.

bond (Fig. 8) from three cations and two water molecules. As in (II), an N1—H2N···O2 hydrogen bond in (III) generates $C(7)$ chains of cations propagating in [010] with adjacent ions related by the screw axis but an N1—H3N···N2 interaction also occurs; by itself it leads to [100] $C(5)$ chains with adjacent ions related by translation; together, (001) hydrogen-bonded sheets of cations arise. When the nitrate ion and water molecules are taken together, undulating hydrogen-bonded chains propagating in the [010] direction arise. Collectively, the packing in (III) (Fig. 9) can be described as alternating (001) slabs of nitrate anions + water molecules and organic cations arising from a three-dimensional supramolecular network of hydrogen bonds.

The three structures feature weak aromatic π–π stacking (Table 4). In each case, infinite stacks of molecules, with considerable slippage between adjacent benzene rings, arise: these stacks propagate in the [001], [001] and [100] directions for (I), (II) and (III), respectively. A crystallographic c-glide generates the stacks in (I) and (II), whereas in (III) adjacent molecules are related by simple translation.
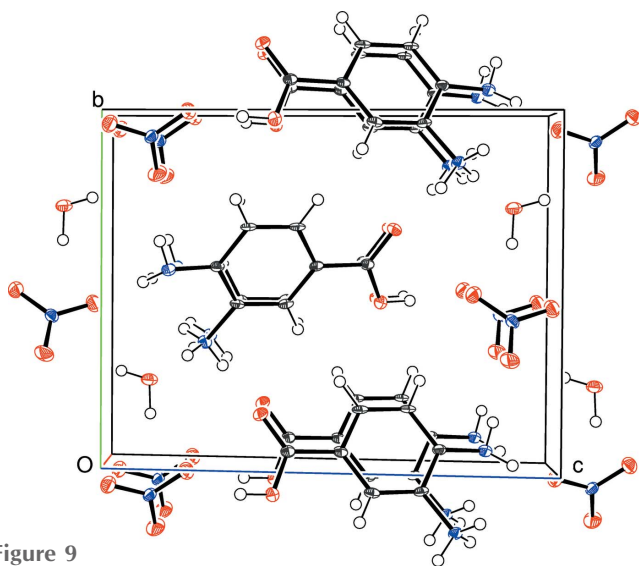

Figure 9
The packing for (III) viewed down [100].

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O2^i	0.74 (3)	1.88 (3)	2.6169 (18)	170 (3)
N1—H1N···Cl1^{ii}	0.90 (2)	2.32 (2)	3.1578 (14)	153.4 (17)
N1—H2N···Cl1	0.91 (2)	2.25 (2)	3.1576 (15)	172.1 (18)
N1—H3N···Cl1^{iii}	0.90 (2)	2.49 (2)	3.1722 (14)	132.9 (16)
N2—H4N···Cl1^{iv}	0.86 (2)	2.72 (2)	3.2382 (15)	120.3 (17)
N2—H5N···Cl1^{iii}	0.81 (2)	2.68 (2)	3.4852 (15)	176 (2)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···Br1^i	0.79 (7)	2.42 (7)	3.199 (3)	169 (6)
N1—H1N···Br1	0.73 (6)	2.70 (7)	3.404 (5)	163 (6)
N1—H2N···O2^{ii}	0.90 (6)	1.90 (6)	2.787 (5)	168 (5)
N1—H3N···Br1^{iii}	0.85 (6)	2.49 (6)	3.333 (5)	171 (5)
N2—H4N···Br1^{iv}	0.81 (7)	2.98 (6)	3.705 (5)	150 (5)
N2—H5N···Br1^v	0.82 (6)	2.98 (6)	3.513 (4)	125 (5)
C2—H2···O2^{ii}	0.95	2.23	3.024 (5)	140

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O6^i	0.91	1.87	2.764 (5)	165
N1—H2N···O2^{ii}	0.91	1.91	2.808 (5)	168
N1—H3N···N2^{iii}	0.91	2.32	3.094 (6)	143
N1—H3N···O6^{iv}	0.91	2.33	2.862 (5)	118
N2—H4N···O4^i	0.91 (6)	2.07 (6)	2.972 (5)	169 (5)
N2—H5N···O5^v	0.83 (6)	2.34 (7)	3.129 (5)	159 (5)
O1—H1O···O3	0.88 (6)	1.79 (6)	2.662 (5)	170 (6)
O6—H2O···O5	0.86	2.02	2.884 (5)	176
O6—H3O···O3^{vi}	0.96	2.26	2.920 (5)	125
O6—H3O···O4^{vi}	0.96	2.33	3.068 (5)	133
C2—H2···O2^{ii}	0.95	2.54	3.285 (5)	135

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

Table 4
Aromatic π–π stacking interactions in the title compounds.

All interactions involve the C1–C6 benzene rings. Cg···Cg is the centroid–centroid separation, α is the dihedral angle between the ring planes.

Compound	Cg···Cg (Å)	α (°)	slippage (Å)	symmetry
(I)	3.8895 (9)	1.79 (7)	1.902	$x, 1 - y, z - \frac{1}{2}$
(I)	3.8895 (9)	1.79 (7)	1.822	$x, 1 - y, z + \frac{1}{2}$
(II)	3.736 (3)	1.5 (2)	2.035	$x, \frac{1}{2} - y, z - \frac{1}{2}$
(II)	3.736 (3)	1.5 (2)	1.954	$x, \frac{1}{2} - y, z + \frac{1}{2}$
(III)	3.890 (2)	0.0 (2)	2.105	$x - 1, y, z$
(III)	3.890 (2)	0.0 (2)	2.105	$x + 1, y, z$

4. Hirshfeld surface analyses

In order to gain further insight into the intermolecular interactions in (I), (II) and (III), their Hirshfeld surfaces and two-dimensional fingerprint plots were calculated using *Crystal-Explorer* (Turner *et al.*, 2017) following the approach recently

Table 5
Hirshfeld fingerprint contact percentages for different intermolecular interactions in the title compounds.

Interaction	(I)	(II)	(III)
H⋯H	30.3	30.7	23.3
H⋯X^a	14.5	15.2	–
H⋯O (donor)	10.6	10.0	32.2
H⋯C	6.8	6.7	5.8
H⋯N	1.9	2.2	2.3
C⋯C	6.7	6.8	6.4
C⋯H	8.6	8.6	9.0
C⋯O	2.2	2.4	2.9
N⋯H	2.1	2.7	2.1
O⋯H (acceptor)	13.3	11.6	12.6
X^a⋯H	99.8	98.7	–

Note: (a) For (I), X = Cl; for (II) X = Br.

described by Tan *et al.* (2019). The Hirshfeld surfaces of the cations in (I), (II) and (III) (see supplementary materials) show the expected red spots of varying intensity corresponding to close contacts resulting from the hydrogen bonds described above. The percentage contributions of the different type of contacts to the surfaces (Table 5) call for some comment. Despite their different packing motifs, especially the presence of pairwise O—H⋯O hydrogen bonds in (I) and O—H⋯Br and N—H⋯O interactions in (II), the contact percentages for the $C_7H_9N_2O_2^+$ cations in (I) and (II) are strikingly similar, being mostly within 1% of each other. It may be seen that H⋯H (van der Waals) contacts dominate, followed by H⋯X (X = Cl, Br), H⋯O (donor) and then O⋯H (acceptor), with other contacts playing a minor role. The contact percentage data for (III) are decidedly different with H⋯O (donor) (32.2%) dominating and H⋯H (23.3%) relegated to second place, followed by O⋯H (acceptor) (12.6%). Despite the N—H⋯N hydrogen bond in (III), the H⋯N contact percentages barely differ for the three compounds. The contact percentages for the anions in (I) and (II) (Table 5) show them to be essentially 'saturated' by their hydrogen bonds, despite the irregular coordination geometries.

Figure 11
Hirshfeld fingerprint plot for the $C_7H_9N_2O_2^+$ cation in (II).

The fingerprint plot for the cation in (I) (Fig. 10) of outward (*i.e.* non-reciprocal) contacts shows three prominent features: the spike ending at (d_i, d_e) = (∼0.76, ∼1.36 Å) and extending backwards corresponds to the short intermolecular H⋯Cl contacts associated with the N—H⋯Cl hydrogen bonds. The pronounced (0.65, 1.00 Å) feature equates with the H⋯O (donor) contact of the O—H⋯O hydrogen bond and that at (1.00, 0.65 Å) is associated with the H⋯O (acceptor) contact. The fingerprint plot for the cation in (II) (Fig. 11) shows the equivalent three spikes ending at (0.76, 1.45), (0.72, 1.08) and (1.06, 0.72 Å): the greater value of d_e for the first of these presumably reflects the larger size of the bromide ion in (II) compared to the chloride ion in (I). The fingerprint plot for the cation in (III) (Fig. 12) naturally lacks the H⋯X (X = Cl, Br) features and has a more symmetric appearance, with the spike at (0.68, 1.02) equating to H⋯O (donor) and that at (1.08, 0.74 Å) equating to the O⋯H (acceptor) contact. The H⋯N (donor) contact is just perceptible as a shoulder-like feature terminating at (0.94, 1.30 Å) but mostly superimposed on the tail of the H⋯O spike. The 'wing' like fingerprint plot for the

Figure 10
Hirshfeld fingerprint plot for the $C_7H_9N_2O_2^+$ cation in (I).
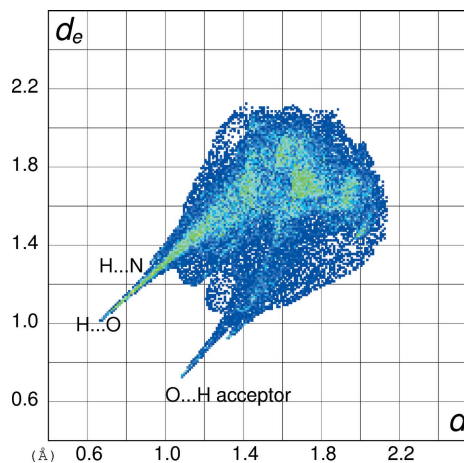

Figure 12
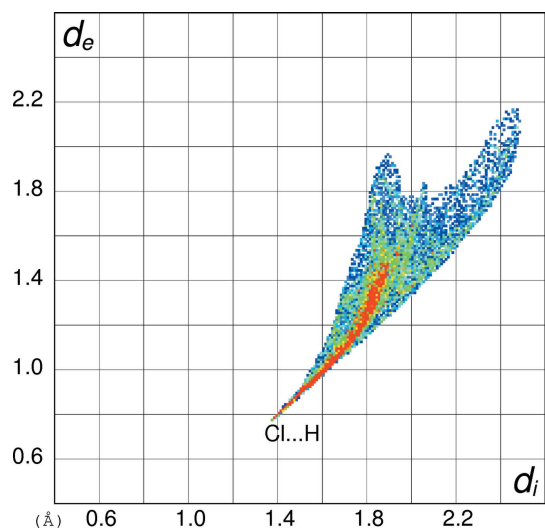Hirshfeld fingerprint plot for the $C_7H_9N_2O_2^+$ cation in (III).

Figure 13
Hirshfeld fingerprint plot for the chloride anion in (I).

chloride ion in (I) (Fig. 13) looks radically different to that of the cation (Fig. 10) although the end-point at (1.38, 0.77 Å) of the sweeping feature corresponds well with the H···Cl contact for the cation. The fingerprint plot for the bromide ion in (II) (Fig. 14) with its sweeping feature terminating at (1.45, 0.77 Å) shows similar correspondence with the H···Br spike for the cation in (II) (Fig. 11).

5. Database survey

So far as we are aware, no molecular salts containing the $C_7H_9N_2O_2^+$ cation have been structurally characterized up to this point. A search of the Cambridge Structural Database (Version 5.40, updated to February 2020; Groom *et al.*, 2016) yielded five complexes of the 3,4-diaminobenzoate *anion* (*i.e.* $C_7H_7N_2O_2^-$) with sodium (CCDC refcode BEHJEE; Rzac-
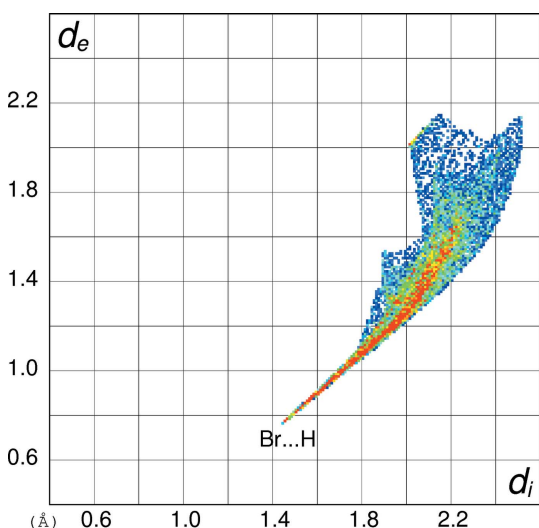
Figure 14
Hirshfeld fingerprint plot for the bromide anion in (II).

zyńska *et al.*, 2003), zinc (MIWSES; Fernández-Palacio *et al.*, 2014), tin (XUPRUV and XUPSAC; Pruchnik *et al.*, 2002) and neodymium (YENKOR; Rzaczyńska *et al.*, 1994). As noted above, the structure of the zwitterionic free molecule of $C_7H_8N_2O_2$ is known (VODWIU; Rzaczyńska *et al.*, 2000). Interestingly, the neutral, non-zwitterionic form of $C_7H_8N_2O_2$ has been co-crystallized with an organo-rhenium compound and other species (DONDUH; Davies *et al.*, 2014). In VODWIU, the $-CO_2^-$ group accepts several N—H···O hydrogen bonds while in DONDUH pairwise carboxylic-acid inversion dimers are formed. The different possible structures of the organic species are shown in Fig. 15.

6. Synthesis and crystallization

Equimolar mixtures of 3,4-diaminobenzoic acid and hydrochloric acid (I), hydrobromic acid (II) and nitric acid (III) dissolved in water were decanted into petri dishes at room temperature and brown plates of (I), pale-brown laths of (II) and colourless slabs of (III) formed as the water evaporated over the course of a few days. The IR spectra for 3,4-diaminobenzoic acid, (I), (II) and (III) are available as supporting information.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. For each structure, the N-bound H atoms were located in difference maps and their positions were freely refined. The C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding atoms. The water

Figure 15
Different structures based on 3,4-diaminobenzoic acid: (*a*) neutral $C_7H_8N_2O_2$ molecule as found in DONDUH; (*b*) zwitterion in VODWIU; (*c*) quinoid resonance form of the $C_7H_9N_2O_2^+$ cation in the title compounds (see text and compare scheme 1); (*d*) $C_7H_7N_2O_2^-$ anion as found in the metal complexes noted in the text.

Table 6
Experimental details.

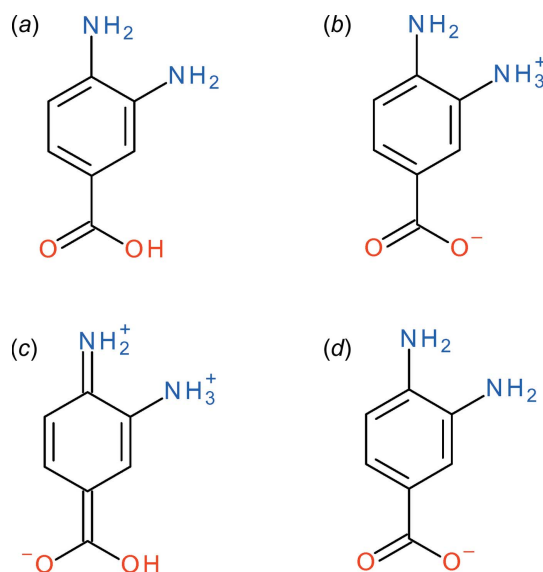|	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_7H_9N_2O_2{}^+\cdot Cl^-$	$C_7H_9N_2O_2{}^+\cdot Br^-$	$C_7H_9N_2O_2{}^+\cdot NO_3{}^-\cdot H_2O$
M_r	188.61	233.07	233.19
Crystal system, space group	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1$
Temperature (K)	100	100	100
a, b, c (Å)	28.0521 (6), 8.0469 (2), 7.2511 (2)	12.1190 (7), 11.0708 (5), 6.3795 (3)	3.8899 (3), 9.8238 (6), 12.5799 (9)
β (°)	91.309 (2)	103.047 (6)	98.673 (7)
V (Å^3)	1636.38 (7)	833.82 (8)	475.22 (6)
Z	8	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.43	4.89	0.14
Crystal size (mm)	$0.41 \times 0.26 \times 0.04$	$0.25 \times 0.12 \times 0.04$	$0.20 \times 0.10 \times 0.05$
Data collection			
Diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD	Rigaku Mercury CCD
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku, 2017)	Multi-scan (*CrysAlis PRO*; Rigaku, 2017)	Multi-scan (*CrysAlis PRO*; Rigaku, 2017)
T_{min}, T_{max}	0.624, 1.000	0.538, 1.000	0.861, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13456, 1865, 1765	3343, 3343, 3031	10770, 2157, 2100
R_{int}	0.035	?	0.067
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.649	0.649
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.093, 1.13	0.036, 0.100, 1.14	0.058, 0.149, 1.15
No. of reflections	1865	3343	2157
No. of parameters	127	128	155
No. of restraints	0	0	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.45, −0.27	1.01, −0.70	0.48, −0.37

Computer programs: *CrysAlis PRO* (Rigaku, 2017), *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

H atoms in (III) were located in difference maps and refined as riding atoms in their as-found relative locations. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases. The crystal used for the data collection of (II) was twinned by rotation about [100] in reciprocal space in a 0.4896 (15):0.5104 (15) ratio and data merging was not performed (*i.e.* HKLF 5 refinement). The absolute structure of (III) could not be determined based on the refinement reported here.

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supporting information

Different packing motifs in the crystal structures of three molecular salts containing the 2-amino-5-carboxyanilinium cation: $C_7H_9N_2O_2^+ \cdot Cl^-$, $C_7H_9N_2O_2^+ \cdot Br^-$ and $C_7H_9N_2O_2^+ \cdot NO_3^- \cdot H_2O$

Edson T. Mukombiwa and William T A Harrison

Computing details

For all structures, data collection: *CrysAlis PRO* (Rigaku, 2017); cell refinement: *CrysAlis PRO* (Rigaku, 2017); data reduction: *CrysAlis PRO* (Rigaku, 2017); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

2-Amino-5-carboxyanilinium chloride (I)

Crystal data

$C_7H_9N_2O_2^+ \cdot Cl^-$	$F(000) = 784$
$M_r = 188.61$	$D_x = 1.531$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 28.0521$ (6) Å	Cell parameters from 8736 reflections
$b = 8.0469$ (2) Å	$\theta = 2.9$–30.1°
$c = 7.2511$ (2) Å	$\mu = 0.43$ mm^{-1}
$\beta = 91.309$ (2)°	$T = 100$ K
$V = 1636.38$ (7) Å^3	Plate, brown
$Z = 8$	$0.41 \times 0.26 \times 0.04$ mm

Data collection

Rigaku Mercury CCD diffractometer	1865 independent reflections
ω scans	1765 reflections with $I > 2\sigma(I)$
Absorption correction: gaussian (CrysAlisPRO; Rigaku, 2017)	$R_{int} = 0.035$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$
$T_{min} = 0.624$, $T_{max} = 1.000$	$h = -36 \rightarrow 36$
13456 measured reflections	$k = -10 \rightarrow 10$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: mixed
$wR(F^2) = 0.093$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.13$	
1865 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 2.8134P]$
127 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.45$ e Å^{-3} $\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.42198 (5)	0.7087 (2)	0.6424 (2)	0.0132 (3)
C2	0.37721 (5)	0.7561 (2)	0.7037 (2)	0.0124 (3)
H2	0.3696	0.8704	0.7173	0.015*
C3	0.34405 (5)	0.6353 (2)	0.7443 (2)	0.0115 (3)
C4	0.35376 (5)	0.46541 (19)	0.7258 (2)	0.0118 (3)
C5	0.39962 (5)	0.4200 (2)	0.6688 (2)	0.0132 (3)
H5	0.4077	0.3058	0.6586	0.016*
C6	0.43292 (6)	0.5395 (2)	0.6276 (2)	0.0139 (3)
H6	0.4636	0.5067	0.5887	0.017*
C7	0.45674 (6)	0.8354 (2)	0.5858 (2)	0.0150 (3)
N1	0.29675 (5)	0.68573 (18)	0.8047 (2)	0.0126 (3)
H1N	0.2945 (7)	0.797 (3)	0.818 (3)	0.015*
H2N	0.2748 (7)	0.653 (3)	0.717 (3)	0.015*
H3N	0.2895 (7)	0.641 (3)	0.914 (3)	0.015*
N2	0.31909 (5)	0.34702 (18)	0.7525 (2)	0.0158 (3)
H4N	0.3282 (7)	0.246 (3)	0.768 (3)	0.019*
H5N	0.2970 (8)	0.371 (3)	0.817 (3)	0.019*
O1	0.44480 (5)	0.98914 (17)	0.6117 (2)	0.0226 (3)
H1O	0.4634 (9)	1.042 (3)	0.570 (3)	0.027*
O2	0.49517 (4)	0.79238 (15)	0.51547 (18)	0.0203 (3)
Cl1	0.22232 (2)	0.53660 (4)	0.51641 (5)	0.01266 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0110 (7)	0.0134 (8)	0.0153 (7)	−0.0017 (6)	0.0015 (5)	0.0010 (6)
C2	0.0130 (7)	0.0109 (7)	0.0132 (7)	−0.0002 (6)	0.0004 (5)	0.0004 (6)
C3	0.0107 (7)	0.0131 (7)	0.0108 (7)	0.0007 (6)	0.0011 (5)	−0.0002 (6)
C4	0.0128 (7)	0.0123 (8)	0.0104 (7)	−0.0010 (5)	−0.0002 (5)	0.0013 (5)
C5	0.0144 (7)	0.0107 (7)	0.0145 (7)	0.0019 (6)	0.0011 (5)	0.0001 (6)
C6	0.0111 (7)	0.0150 (8)	0.0157 (8)	0.0012 (6)	0.0019 (6)	0.0003 (6)
C7	0.0129 (7)	0.0141 (8)	0.0180 (8)	−0.0013 (6)	0.0015 (6)	0.0014 (6)
N1	0.0124 (6)	0.0106 (7)	0.0149 (7)	0.0001 (5)	0.0032 (5)	0.0008 (5)
N2	0.0144 (7)	0.0094 (7)	0.0236 (7)	0.0003 (5)	0.0050 (5)	0.0014 (6)
O1	0.0181 (6)	0.0132 (6)	0.0370 (8)	−0.0040 (5)	0.0096 (5)	0.0020 (5)
O2	0.0130 (5)	0.0189 (6)	0.0294 (7)	−0.0015 (5)	0.0074 (5)	0.0026 (5)
Cl1	0.0148 (2)	0.0094 (2)	0.0138 (2)	0.00125 (12)	0.00239 (14)	0.00038 (12)

Geometric parameters (Å, º)

C1—C2	1.395 (2)	C5—H5	0.9500
C1—C6	1.401 (2)	C6—H6	0.9500
C1—C7	1.475 (2)	C7—O2	1.252 (2)
C2—C3	1.382 (2)	C7—O1	1.296 (2)
C2—H2	0.9500	N1—H1N	0.90 (2)
C3—C4	1.401 (2)	N1—H2N	0.91 (2)
C3—N1	1.4640 (19)	N1—H3N	0.90 (2)
C4—N2	1.378 (2)	N2—H4N	0.86 (2)
C4—C5	1.408 (2)	N2—H5N	0.81 (2)
C5—C6	1.378 (2)	O1—H1O	0.74 (3)
C2—C1—C6	119.38 (14)	C5—C6—H6	119.6
C2—C1—C7	120.35 (15)	C1—C6—H6	119.6
C6—C1—C7	120.22 (14)	O2—C7—O1	123.41 (15)
C3—C2—C1	119.42 (15)	O2—C7—C1	120.19 (15)
C3—C2—H2	120.3	O1—C7—C1	116.40 (14)
C1—C2—H2	120.3	C3—N1—H1N	111.9 (13)
C2—C3—C4	122.18 (14)	C3—N1—H2N	108.2 (12)
C2—C3—N1	119.22 (14)	H1N—N1—H2N	108.3 (18)
C4—C3—N1	118.59 (14)	C3—N1—H3N	112.1 (13)
N2—C4—C3	121.45 (14)	H1N—N1—H3N	106.6 (19)
N2—C4—C5	120.93 (15)	H2N—N1—H3N	109.6 (18)
C3—C4—C5	117.53 (14)	C4—N2—H4N	117.6 (14)
C6—C5—C4	120.72 (15)	C4—N2—H5N	118.0 (16)
C6—C5—H5	119.6	H4N—N2—H5N	112 (2)
C4—C5—H5	119.6	C7—O1—H1O	107.7 (19)
C5—C6—C1	120.73 (14)		
C6—C1—C2—C3	−1.6 (2)	C3—C4—C5—C6	−2.0 (2)
C7—C1—C2—C3	175.73 (14)	C4—C5—C6—C1	0.3 (2)
C1—C2—C3—C4	−0.1 (2)	C2—C1—C6—C5	1.5 (2)
C1—C2—C3—N1	−178.67 (14)	C7—C1—C6—C5	−175.82 (15)
C2—C3—C4—N2	−174.64 (15)	C2—C1—C7—O2	−173.60 (15)
N1—C3—C4—N2	3.9 (2)	C6—C1—C7—O2	3.7 (2)
C2—C3—C4—C5	1.9 (2)	C2—C1—C7—O1	5.8 (2)
N1—C3—C4—C5	−179.57 (13)	C6—C1—C7—O1	−176.96 (16)
N2—C4—C5—C6	174.58 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O2[i]	0.74 (3)	1.88 (3)	2.6169 (18)	170 (3)
N1—H1*N*···Cl1[ii]	0.90 (2)	2.32 (2)	3.1578 (14)	153.4 (17)
N1—H2*N*···Cl1	0.91 (2)	2.25 (2)	3.1576 (15)	172.1 (18)
N1—H3*N*···Cl1[iii]	0.90 (2)	2.49 (2)	3.1722 (14)	132.9 (16)

N2—H4N···Cl1^{iv}	0.86 (2)	2.72 (2)	3.2382 (15)	120.3 (17)
N2—H5N···Cl1^{iii}	0.81 (2)	2.68 (2)	3.4852 (15)	176 (2)

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

2-Amino-5-carboxyanilinium bromide (II)

Crystal data

$C_7H_9N_2O_2{}^+ \cdot Br^-$
$M_r = 233.07$
Monoclinic, $P2_1/c$
$a = 12.1190\ (7)$ Å
$b = 11.0708\ (5)$ Å
$c = 6.3795\ (3)$ Å
$\beta = 103.047\ (6)°$
$V = 833.82\ (8)$ Å^3
$Z = 4$

$F(000) = 464$
$D_x = 1.857$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8521 reflections
$\theta = 3.4$–30.1°
$\mu = 4.89$ mm^{-1}
$T = 100$ K
Lath, pale brown
$0.25 \times 0.12 \times 0.04$ mm

Data collection

Rigaku Mercury CCD
   diffractometer
ω scans
Absorption correction: multi-scan
   (CrysAlisPRO; Rigaku, 2017)
$T_{min} = 0.538$, $T_{max} = 1.000$
3343 measured reflections

3343 independent reflections
3031 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.5°$
$h = -15 \rightarrow 15$
$k = -14 \rightarrow 14$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.100$
$S = 1.14$
3343 reflections
128 parameters
0 restraints

Primary atom site location: structure-invariant
   direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent
   and constrained refinement
$w = 1/[\sigma^2(F_o{}^2) + (0.0423P)^2 + 2.9863P]$
   where $P = (F_o{}^2 + 2F_c{}^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a two-component twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.5791 (4)	0.3232 (4)	0.3020 (7)	0.0114 (9)
C2	0.6253 (4)	0.4394 (4)	0.3348 (7)	0.0105 (8)
H2	0.5781	0.5085	0.3035	0.013*
C3	0.7405 (4)	0.4520 (4)	0.4131 (7)	0.0093 (8)
C4	0.8130 (4)	0.3529 (4)	0.4643 (7)	0.0110 (9)

C5	0.7646 (4)	0.2369 (4)	0.4251 (7)	0.0113 (9)
H5	0.8119	0.1677	0.4535	0.014*
C6	0.6494 (4)	0.2226 (4)	0.3460 (7)	0.0122 (9)
H6	0.6181	0.1438	0.3216	0.015*
C7	0.4558 (4)	0.3082 (4)	0.2165 (7)	0.0107 (9)
N1	0.7876 (4)	0.5748 (3)	0.4373 (8)	0.0110 (8)
H1N	0.816 (5)	0.593 (5)	0.352 (10)	0.013*
H2N	0.729 (5)	0.627 (5)	0.409 (9)	0.013*
H3N	0.815 (5)	0.590 (5)	0.569 (10)	0.013*
N2	0.9285 (4)	0.3686 (4)	0.5425 (7)	0.0155 (9)
H4N	0.959 (5)	0.304 (6)	0.578 (9)	0.019*
H5N	0.951 (5)	0.420 (6)	0.635 (10)	0.019*
O1	0.3992 (3)	0.4115 (3)	0.1817 (6)	0.0167 (7)
H1O	0.334 (6)	0.400 (5)	0.130 (10)	0.020*
O2	0.4107 (3)	0.2098 (3)	0.1823 (6)	0.0161 (7)
Br1	0.86980 (4)	0.61815 (4)	−0.03325 (7)	0.01281 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.011 (2)	0.009 (2)	0.013 (2)	−0.0010 (16)	0.0028 (17)	0.0006 (16)
C2	0.013 (2)	0.009 (2)	0.010 (2)	0.0014 (16)	0.0034 (16)	−0.0008 (16)
C3	0.014 (2)	0.005 (2)	0.010 (2)	−0.0009 (16)	0.0047 (17)	−0.0012 (16)
C4	0.013 (2)	0.012 (2)	0.008 (2)	0.0008 (17)	0.0021 (16)	0.0011 (16)
C5	0.014 (2)	0.011 (2)	0.010 (2)	0.0028 (17)	0.0048 (17)	0.0011 (17)
C6	0.016 (2)	0.009 (2)	0.012 (2)	−0.0017 (16)	0.0033 (18)	−0.0015 (17)
C7	0.010 (2)	0.011 (2)	0.012 (2)	0.0009 (16)	0.0032 (17)	0.0000 (17)
N1	0.0112 (19)	0.0086 (18)	0.013 (2)	−0.0019 (15)	0.0034 (16)	−0.0003 (16)
N2	0.010 (2)	0.015 (2)	0.020 (2)	0.0019 (17)	0.0002 (16)	0.0013 (17)
O1	0.0083 (16)	0.0094 (15)	0.029 (2)	0.0007 (12)	−0.0025 (14)	0.0008 (13)
O2	0.0118 (15)	0.0097 (15)	0.0247 (19)	−0.0020 (13)	−0.0001 (14)	−0.0012 (13)
Br1	0.0108 (2)	0.0136 (2)	0.0130 (2)	−0.00047 (18)	0.00053 (16)	−0.00011 (17)

Geometric parameters (Å, º)

C1—C6	1.391 (6)	C5—H5	0.9500
C1—C2	1.400 (6)	C6—H6	0.9500
C1—C7	1.479 (6)	C7—O2	1.216 (5)
C2—C3	1.379 (6)	C7—O1	1.326 (5)
C2—H2	0.9500	N1—H1N	0.73 (6)
C3—C4	1.398 (6)	N1—H2N	0.90 (6)
C3—N1	1.468 (5)	N1—H3N	0.85 (6)
C4—N2	1.387 (6)	N2—H4N	0.81 (7)
C4—C5	1.410 (6)	N2—H5N	0.82 (6)
C5—C6	1.383 (6)	O1—H1O	0.79 (7)
C6—C1—C2	119.9 (4)	C5—C6—H6	119.9
C6—C1—C7	120.4 (4)	C1—C6—H6	119.9

C2—C1—C7	119.7 (4)	O2—C7—O1	123.2 (4)
C3—C2—C1	119.1 (4)	O2—C7—C1	122.8 (4)
C3—C2—H2	120.5	O1—C7—C1	114.0 (4)
C1—C2—H2	120.5	C3—N1—H1N	114 (5)
C2—C3—C4	122.4 (4)	C3—N1—H2N	107 (4)
C2—C3—N1	118.1 (4)	H1N—N1—H2N	99 (6)
C4—C3—N1	119.5 (4)	C3—N1—H3N	111 (4)
N2—C4—C3	121.1 (4)	H1N—N1—H3N	122 (6)
N2—C4—C5	121.6 (4)	H2N—N1—H3N	101 (5)
C3—C4—C5	117.3 (4)	C4—N2—H4N	110 (4)
C6—C5—C4	120.9 (4)	C4—N2—H5N	119 (5)
C6—C5—H5	119.5	H4N—N2—H5N	111 (6)
C4—C5—H5	119.5	C7—O1—H1O	111 (4)
C5—C6—C1	120.3 (4)		
C6—C1—C2—C3	−0.7 (6)	C3—C4—C5—C6	−2.1 (7)
C7—C1—C2—C3	−179.5 (4)	C4—C5—C6—C1	0.5 (7)
C1—C2—C3—C4	−1.0 (7)	C2—C1—C6—C5	1.0 (7)
C1—C2—C3—N1	177.4 (4)	C7—C1—C6—C5	179.8 (4)
C2—C3—C4—N2	179.9 (4)	C6—C1—C7—O2	0.4 (7)
N1—C3—C4—N2	1.5 (7)	C2—C1—C7—O2	179.2 (4)
C2—C3—C4—C5	2.4 (7)	C6—C1—C7—O1	−179.9 (4)
N1—C3—C4—C5	−176.0 (4)	C2—C1—C7—O1	−1.1 (6)
N2—C4—C5—C6	−179.6 (5)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···Br1[i]	0.79 (7)	2.42 (7)	3.199 (3)	169 (6)
N1—H1N···Br1	0.73 (6)	2.70 (7)	3.404 (5)	163 (6)
N1—H2N···O2[ii]	0.90 (6)	1.90 (6)	2.787 (5)	168 (5)
N1—H3N···Br1[iii]	0.85 (6)	2.49 (6)	3.333 (5)	171 (5)
N2—H4N···Br1[iv]	0.81 (7)	2.98 (7)	3.705 (5)	150 (5)
N2—H5N···Br1[v]	0.82 (6)	2.98 (6)	3.513 (4)	125 (5)
C2—H2···O2[ii]	0.95	2.23	3.024 (5)	140

Symmetry codes: (i) −x+1, −y+1, −z; (ii) −x+1, y+1/2, −z+1/2; (iii) x, y, z+1; (iv) −x+2, y−1/2, −z+1/2; (v) −x+2, −y+1, −z+1.

2-Amino-5-carboxyanilinium nitrate monohydrate (III)

Crystal data

$C_7H_9N_2O_2{}^+ \cdot NO_3{}^- \cdot H_2O$	$F(000) = 244$
$M_r = 233.19$	$D_x = 1.630$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 3.8899$ (3) Å	Cell parameters from 3653 reflections
$b = 9.8238$ (6) Å	$\theta = 2.7–30.8°$
$c = 12.5799$ (9) Å	$\mu = 0.14$ mm^{-1}
$\beta = 98.673$ (7)°	$T = 100$ K
$V = 475.22$ (6) Å^3	Slab, colourless
$Z = 2$	$0.20 \times 0.10 \times 0.05$ mm

Data collection

Rigaku Mercury CCD diffractometer	2157 independent reflections
ω scans	2100 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (CrysAlisPRO; Rigaku, 2017)	$R_{int} = 0.067$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$
$T_{min} = 0.861$, $T_{max} = 1.000$	$h = -5 \rightarrow 5$
10770 measured reflections	$k = -12 \rightarrow 12$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.058$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.149$	
$S = 1.15$	$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.3934P]$
2157 reflections	where $P = (F_o^2 + 2F_c^2)/3$
155 parameters	$(\Delta/\sigma)_{max} = 0.005$
1 restraint	$\Delta\rho_{max} = 0.48$ e Å^{-3}
	$\Delta\rho_{min} = -0.37$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.2205 (11)	0.5688 (5)	0.4736 (3)	0.0120 (8)
C2	0.2777 (10)	0.4617 (5)	0.4062 (3)	0.0121 (8)
H2	0.4231	0.3880	0.4334	0.014*
C3	0.1240 (10)	0.4617 (4)	0.2997 (3)	0.0120 (8)
C4	−0.0999 (11)	0.5677 (4)	0.2573 (3)	0.0124 (8)
C5	−0.1462 (11)	0.6769 (4)	0.3255 (3)	0.0128 (8)
H5	−0.2878	0.7516	0.2982	0.015*
C6	0.0082 (11)	0.6778 (4)	0.4303 (3)	0.0121 (8)
H6	−0.0277	0.7530	0.4748	0.014*
C7	0.3867 (11)	0.5736 (4)	0.5864 (3)	0.0127 (8)
N1	0.1979 (10)	0.3534 (4)	0.2274 (3)	0.0137 (8)
H1N	−0.0055	0.3198	0.1919	0.016*
H2N	0.3174	0.2856	0.2661	0.016*
H3N	0.3279	0.3871	0.1790	0.016*
N2	−0.2843 (11)	0.5597 (4)	0.1542 (3)	0.0167 (8)
H4N	−0.198 (16)	0.524 (6)	0.097 (5)	0.020*
H5N	−0.358 (16)	0.637 (6)	0.136 (4)	0.020*
O1	0.5752 (9)	0.4650 (3)	0.6185 (2)	0.0182 (7)
H1O	0.685 (15)	0.469 (7)	0.685 (5)	0.022*
O2	0.3588 (8)	0.6720 (3)	0.6453 (2)	0.0156 (7)
N3	0.9275 (9)	0.4263 (4)	0.8918 (3)	0.0147 (8)

O3	0.9624 (10)	0.4968 (4)	0.8102 (3)	0.0234 (8)
O4	1.0903 (8)	0.4593 (4)	0.9805 (2)	0.0210 (7)
O5	0.7311 (10)	0.3252 (4)	0.8821 (3)	0.0263 (8)
O6	0.6514 (8)	0.2329 (3)	1.0947 (3)	0.0181 (7)
H2O	0.6684	0.2566	1.0297	0.022*
H3O	0.6328	0.1351	1.0976	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0129 (19)	0.0080 (18)	0.0155 (19)	−0.0052 (15)	0.0033 (14)	0.0015 (16)
C2	0.0105 (17)	0.0076 (18)	0.019 (2)	0.0003 (16)	0.0059 (14)	0.0019 (16)
C3	0.0133 (19)	0.0064 (18)	0.0172 (19)	−0.0016 (17)	0.0055 (14)	−0.0018 (16)
C4	0.015 (2)	0.0084 (19)	0.015 (2)	0.0014 (16)	0.0058 (15)	0.0003 (17)
C5	0.015 (2)	0.0044 (18)	0.020 (2)	0.0005 (16)	0.0043 (15)	0.0006 (17)
C6	0.0125 (19)	0.0046 (17)	0.021 (2)	−0.0010 (15)	0.0076 (15)	0.0000 (16)
C7	0.013 (2)	0.0098 (19)	0.015 (2)	−0.0043 (16)	0.0020 (15)	0.0000 (17)
N1	0.0137 (17)	0.0123 (18)	0.0148 (17)	0.0055 (14)	0.0014 (13)	−0.0014 (14)
N2	0.023 (2)	0.0115 (18)	0.0151 (18)	0.0049 (15)	0.0003 (14)	0.0008 (15)
O1	0.0250 (17)	0.0146 (16)	0.0134 (14)	0.0011 (14)	−0.0017 (12)	0.0004 (13)
O2	0.0183 (16)	0.0123 (15)	0.0159 (14)	−0.0029 (12)	0.0017 (11)	−0.0030 (13)
N3	0.0165 (17)	0.0137 (18)	0.0137 (17)	0.0016 (14)	0.0021 (13)	−0.0029 (14)
O3	0.0313 (19)	0.0206 (17)	0.0176 (16)	−0.0073 (14)	0.0010 (13)	0.0017 (14)
O4	0.0226 (16)	0.0222 (18)	0.0176 (15)	−0.0014 (14)	0.0012 (12)	−0.0029 (13)
O5	0.032 (2)	0.0202 (18)	0.0268 (19)	−0.0136 (16)	0.0056 (15)	−0.0046 (15)
O6	0.0214 (16)	0.0113 (14)	0.0223 (16)	0.0000 (13)	0.0061 (13)	−0.0008 (12)

Geometric parameters (Å, º)

C1—C2	1.391 (6)	C7—O1	1.323 (6)
C1—C6	1.410 (6)	N1—H1N	0.9100
C1—C7	1.469 (5)	N1—H2N	0.9100
C2—C3	1.382 (5)	N1—H3N	0.9100
C2—H2	0.9500	N2—H4N	0.91 (6)
C3—C4	1.409 (6)	N2—H5N	0.83 (6)
C3—N1	1.457 (5)	O1—H1O	0.88 (6)
C4—N2	1.386 (5)	N3—O4	1.240 (5)
C4—C5	1.402 (6)	N3—O5	1.247 (5)
C5—C6	1.363 (6)	N3—O3	1.262 (5)
C5—H5	0.9500	O6—H2O	0.8625
C6—H6	0.9500	O6—H3O	0.9644
C7—O2	1.232 (5)		
C2—C1—C6	118.5 (4)	O2—C7—O1	123.0 (4)
C2—C1—C7	121.7 (4)	O2—C7—C1	122.7 (4)
C6—C1—C7	119.7 (4)	O1—C7—C1	114.3 (4)
C3—C2—C1	120.3 (4)	C3—N1—H1N	109.5
C3—C2—H2	119.8	C3—N1—H2N	109.5

C1—C2—H2	119.8	H1N—N1—H2N	109.5
C2—C3—C4	121.3 (4)	C3—N1—H3N	109.5
C2—C3—N1	120.5 (4)	H1N—N1—H3N	109.5
C4—C3—N1	118.2 (4)	H2N—N1—H3N	109.5
N2—C4—C5	121.3 (4)	C4—N2—H4N	124 (4)
N2—C4—C3	121.0 (4)	C4—N2—H5N	108 (4)
C5—C4—C3	117.6 (4)	H4N—N2—H5N	107 (5)
C6—C5—C4	121.2 (4)	C7—O1—H1O	115 (4)
C6—C5—H5	119.4	O4—N3—O5	121.2 (4)
C4—C5—H5	119.4	O4—N3—O3	119.0 (4)
C5—C6—C1	121.0 (4)	O5—N3—O3	119.8 (4)
C5—C6—H6	119.5	H2O—O6—H3O	108.8
C1—C6—H6	119.5		
C6—C1—C2—C3	−1.1 (6)	C3—C4—C5—C6	−2.7 (6)
C7—C1—C2—C3	−178.4 (4)	C4—C5—C6—C1	0.1 (6)
C1—C2—C3—C4	−1.6 (6)	C2—C1—C6—C5	1.8 (6)
C1—C2—C3—N1	176.7 (4)	C7—C1—C6—C5	179.2 (4)
C2—C3—C4—N2	−172.5 (4)	C2—C1—C7—O2	174.8 (4)
N1—C3—C4—N2	9.2 (6)	C6—C1—C7—O2	−2.5 (6)
C2—C3—C4—C5	3.4 (6)	C2—C1—C7—O1	−3.7 (6)
N1—C3—C4—C5	−174.9 (4)	C6—C1—C7—O1	179.0 (4)
N2—C4—C5—C6	173.3 (4)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O6[i]	0.91	1.87	2.764 (5)	165
N1—H2*N*···O2[ii]	0.91	1.91	2.808 (5)	168
N1—H3*N*···N2[iii]	0.91	2.32	3.094 (6)	143
N1—H3*N*···O6[iv]	0.91	2.33	2.862 (5)	118
N2—H4*N*···O4[i]	0.91 (6)	2.07 (6)	2.972 (5)	169 (5)
N2—H5*N*···O5[v]	0.83 (6)	2.34 (7)	3.129 (5)	159 (6)
O1—H1*O*···O3	0.88 (6)	1.79 (6)	2.662 (5)	170 (6)
O6—H2*O*···O5	0.86	2.02	2.884 (5)	176
O6—H3*O*···O3[vi]	0.96	2.26	2.920 (5)	125
O6—H3*O*···O4[vi]	0.96	2.33	3.068 (5)	133
C2—H2···O2[ii]	0.95	2.54	3.285 (5)	135

Symmetry codes: (i) *x*−1, *y*, *z*−1; (ii) −*x*+1, *y*−1/2, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) *x*, *y*, *z*−1; (v) −*x*, *y*+1/2, −*z*+1; (vi) −*x*+2, *y*−1/2, −*z*+2.