Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structures of the 1:1 salts of 2-amino-4-nitrobenzoate with each of (2-hydroxyethyl)dimethylazanium, *tert*-butyl(2-hydroxyethyl)azanium and 1,3-dihydroxy-2-(hydroxymethyl)propan-2-aminium

Received 2 November 2018
Accepted 2 November 2018

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

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Keywords: crystal structure; carboxylate; molecular salt; hydrogen-bonding.

CCDC references: 1876928; 1876927; 1876926

Supporting information: this article has supporting information at journals.iucr.org/e

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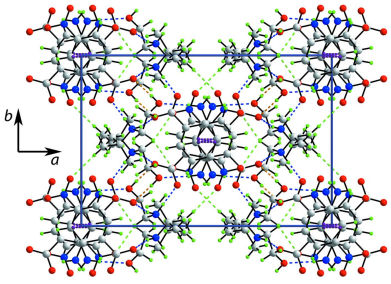
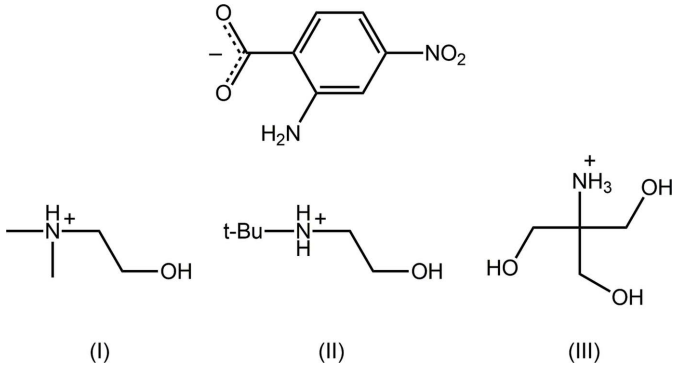
The crystal and molecular structures of the title molecular salts, $C_4H_{12}NO^+\cdot C_7H_5N_2O_4^-$, (I), $C_6H_{16}NO^+\cdot C_7H_5N_2O_4^-$, (II), and $C_4H_{12}NO_3^+\cdot C_7H_5N_2O_4^-$, (III), are described. The common feature of these salts is the presence of the 2-amino-4-nitrobenzoate anion, which exhibit non-chemically significant variations in the conformational relationships between the carboxylate and nitro groups, and between these and the benzene rings they are connected to. The number of ammonium-N—H H atoms in the cations increases from one to three in (I) to (III), respectively, and this variation significantly influences the supramolecular aggregation patterns in the respective crystals. Thus, a linear supramolecular chain along [100] sustained by charge-assisted tertiary-ammonium-N—H···O(carboxylate), hydroxy-O—H···O(carboxylate) and amino-N—H···O(carboxylate) hydrogen-bonds is apparent in the crystal of (I). Chains are connected into a three-dimensional architecture by methyl-C—H···O(hydroxy) and π–π interactions, the latter between benzene rings [inter-centroid separation = 3.5796 (10) Å]. In the crystal of (II), a supramolecular tube propagating along [901] arises as a result of charge-assisted secondary-ammonium-N—H···O(carboxylate) and hydroxy-O—H···O(carboxylate) hydrogen-bonding. These are connected by methylene- and methyl-C—H···O(nitro) and π–π stacking between benzene rings [inter-centroid separation = 3.5226 (10) Å]. Finally, double-layers parallel to (100) sustained by charge-assisted ammonium-N—H···O(carboxylate), ammonium-N—H···O(hydroxy) and hydroxy-O—H···O(carboxylate) hydrogen-bonds are apparent in the crystal of (III). These are connected in a three-dimensional architecture by amine-N—H···O(nitro) hydrogen-bonds.

1. Chemical context



Despite being tetramorphic (Wardell & Tiekink, 2011; Wardell & Wardell, 2016), readily forming co-crystals (Wardell & Tiekink, 2011) and providing systematic series of crystals of alkali metal, *e.g.* Na^+, K^+ (Smith, 2013), Rb^+ (Smith, 2014*a*) and Cs^+ (Smith & Wermuth, 2011), and ammonium salts, see below, studies of the relatively small benzoic acid derivative, 2-amino-4-nitrobenzoic acid, are still comparatively limited. Most crystallographic investigations of the acid have focused upon an evaluation of the hydrogen-bonding propensities occurring in derived ammonium salts of the 2-amino-4-nitrobenzoate anion. Thus, studies have been described with a range of salts, starting with the simplest, *i.e.* $N^{(+)}H_4$ (Smith, 2014*b*), $H_2NN^{(+)}H_3$ (Wardell *et al.*, 2017) and

$(H_2N)_2C{=}N^{(+)}H_2$ (Smith *et al.*, 2007) to $R_2N^{(+)}H_2$, *i.e.* R = Me, *n*-Bu (Wardell *et al.*, 2016), cyclohexyl (Smith *et al.*, 2004) and R_2 = $(CH_2CH_2)_2O$ (Smith & Lynch, 2016), and more complicated ammonium cations such as 4-(4-acetylphenyl)piperazin-1-ium (Jotani *et al.*, 2018) and the dication, $H_3N^{(+)}CH_2CH_2N^{(+)}H_3$ (Smith *et al.*, 2002). As a continuation of on-going interest in this area, the results of co-crystallization experiments between 2-amino-4-nitrobenzoic acid (*L*H) and amines substituted with hydroxy groups, *i.e.* each of $Me_2N(CH_2CH_2OH)$, (*t*-Bu)N(H)CH_2CH_2OH and $(HOCH_2)_3CNH_2$ are described whereupon the anhydrous 1:1 salts, *i.e.* $[Me_2N^{(+)}H(CH_2CH_2OH)]L$ (I), $[(t\text{-Bu})N^{(+)}H_2(CH_2CH_2OH)]L$ (II) and $[(HOCH_2)_3CN^{(+)}H_3]L$ (III), were isolated. Herein, a description of the crystal and molecular structures of (I)–(III) are presented.



(I) (II) (III)

2. Structural commentary

The molecular structures of the constituent ions in (I) are shown in Fig. 1 and selected geometric data for this and for (II) and (III), are collected in Table 1. That proton transfer occurred during co-crystallization is confirmed by the experimental equivalence of the C7···O1, O2 bond lengths of 1.270 (2) and 1.258 (2) Å, respectively, in the 2-amino-4-nitrobenzoate anion and in the pattern of hydrogen-bonding interactions, as described below in *Supramolecular features*. In the anion, the carboxylate group is tilted out of the plane of the benzene ring to which it is connected with the dihedral angle being 6.7 (3)°. Similarly, the nitro group lies out of the plane of the benzene ring, forming a dihedral angle of 6.6 (3)°. A dis-rotatory relationship between the carboxylate and nitro substituents is indicated by the dihedral angle between them of 11.5 (4)°. An intramolecular amine-N1—H···O1(carboxylate) hydrogen-bond is noted which closes an *S*(6) loop, Table 2. In the $Me_2N^{(+)}(H)CH_2CH_2OH$ cation, the N3—C8—C9—O5 torsion angle of −71.15 (19)° is indicative of a −syn-clinal conformation.

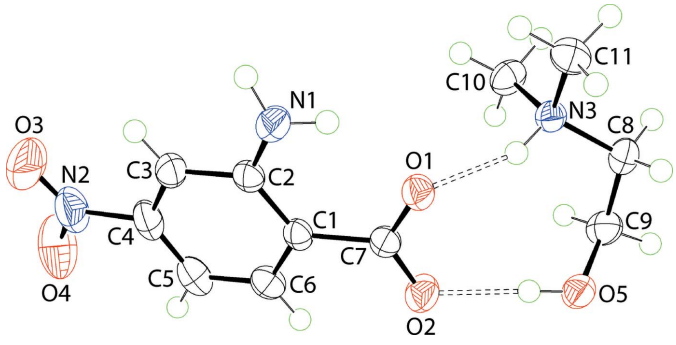


Figure 1
The molecular structures of the ions comprising the asymmetric unit of (I) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level. Dashed lines indicate a hydrogen bonds.

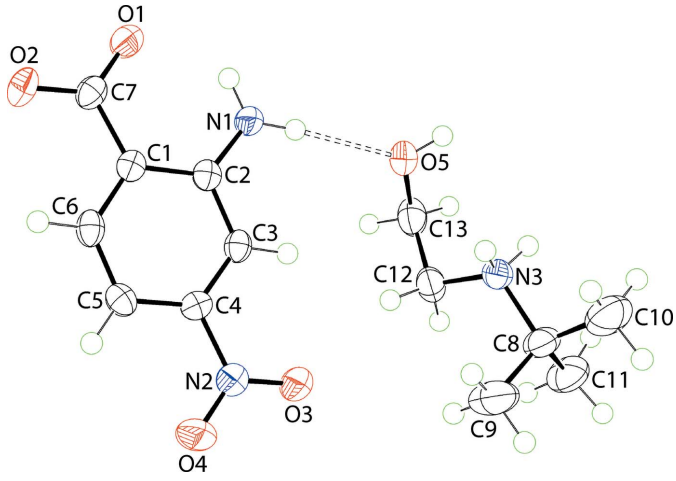


Figure 2
The molecular structures of the ions comprising the asymmetric unit of (II) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level. The dashed line indicates a hydrogen bond.

The anion in (II), Fig. 2, presents essentially the same features as just described for (I), Tables 1 and 3, with the exception of the con-rotatory relationship between the carboxylate and nitro substituents. The (*t*-Bu)$N^{(+)}H_2(CH_2CH_2OH)$ cation is relatively rare, being reported for the first time in its salt with sulfathiazolate only in 2012 (Arman *et al.*,

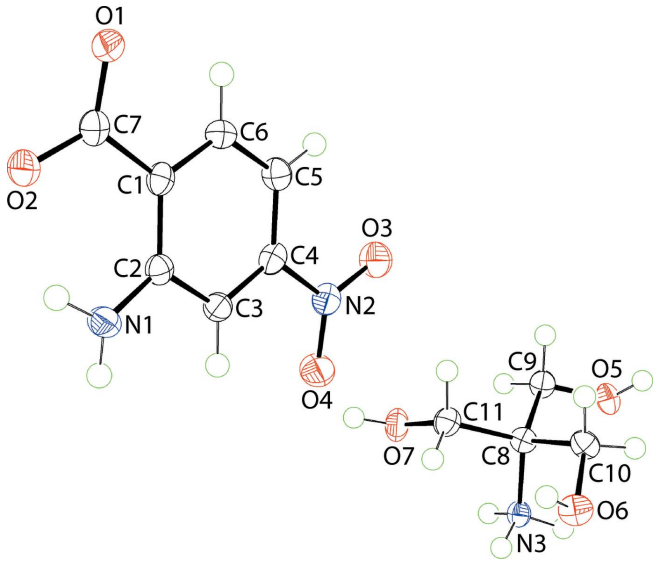


Figure 3
The molecular structures of the ions comprising the asymmetric unit of (III) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

Table 1
Selected geometric data (Å, °) for (I)–(III).

Parameter	(I)	(II)	(III)
C7···O1	1.270 (2)	1.259 (2)	1.270 (2)
C7···O2	1.258 (2)	1.2678 (19)	1.264 (2)
CO_2/C_6	6.7 (3)	6.21 (13)	14.80 (17)
NO_2/C_6	6.6 (3)	3.28 (13)	6.58 (18)
CO_2/NO_2	11.5 (4)	2.94 (17)	9.7 (3)

2012). As for the cation in (I), the N3—C12—C13—O5 torsion angle for the cation in (II) of −55.18 (18)° is indicative of a −syn-clinal conformation.

The anion in (III), Fig. 3, exhibits the greatest twist between the carboxylate and benzene groups among the series but, a con-rotatory relationship between the carboxylate and nitro substituents means the dihedral angle between them is not as great as in the anion of (I), Tables 1 and 4. The $(HOCH_2)_3CN^{(+)}H_3$ cation exhibits N3—C8—C9—O5, N3—C8—C10—O6 and N3—C8—C11—O7 torsion angles of −59.01 (18), −49.84 (19) and −58.12 (18)°, respectively, indicating −syn-clinal relationships.

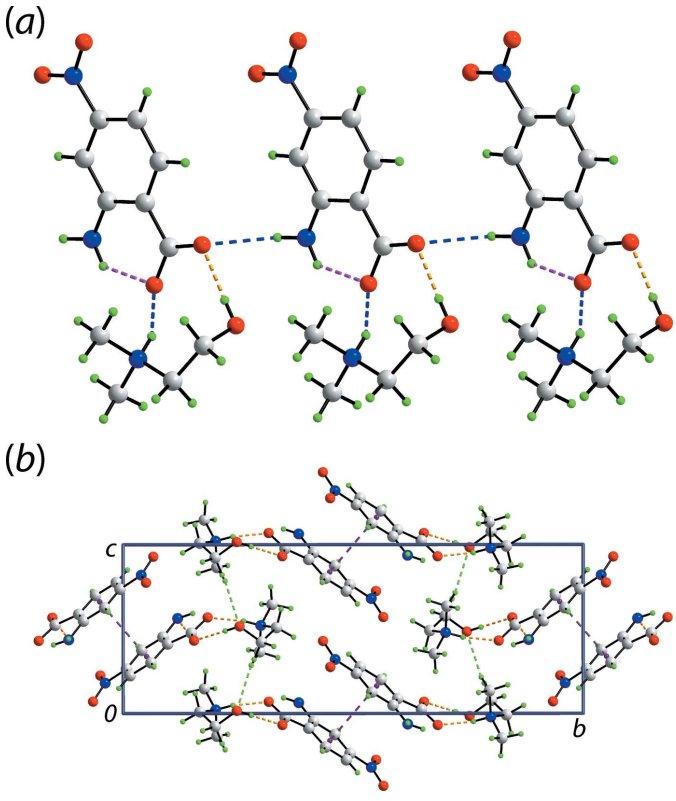


Figure 4
The molecular packing in (I): (*a*) linear, supramolecular chain along the *a* axis sustained by charge-assisted amine-N—H···O(carboxylate) and hydroxy-O—H···O(carboxylate) hydrogen-bonding interactions shown as blue and orange dashed lines, respectively; intramolecular amine-N—H···O(carboxylate) hydrogen bonds are represented by pink dashed lines, and (*b*) a view of the unit-cell contents in projection down the *a* axis. The methyl-C—H···O(hydroxy) and *π*–*π* interactions are shown as green and purple dashed lines, respectively.

3. Supramolecular features

As expected from the chemical compositions of (I)–(III), significant charge-assisted hydrogen-bonding is apparent in their respective crystals. Geometric data characterizing these and other identified interactions are collated in Tables 2–4, respectively.

As indicated in Fig. 1, the anion and cation in (I) are linked *via* charge-assisted ammonium-N3—H···O(carboxylate) and hydroxy-O—H···O(carboxylate) hydrogen-bonds to form a nine-membered {···OCO···HNC_2OH} heterosynthon. These are connected into a linear, supramolecular chain along the *a*-axis direction *via* amino-N—H···O(carboxylate) hydrogen-bonds, Fig. 4(*a*). The chains are linked along the *b* axis *via* *π*–*π* interactions between benzene rings [inter-centroid separation = 3.5796 (10) Å for symmetry operation: −*x*, −*y*, 1 − *z*], and

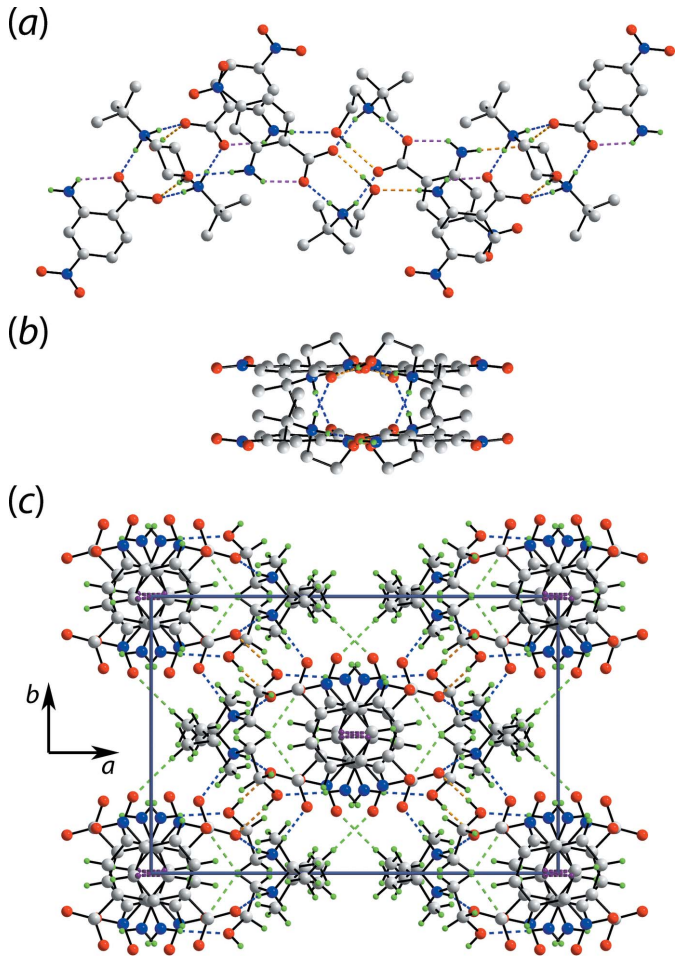


Figure 5
The molecular packing in (II): (*a*) linear, supramolecular tube along [901] sustained by charge-assisted amine-N—H···O(carboxylate) and hydroxy-O—H···O(carboxylate) hydrogen-bonding interactions shown as blue and orange dashed lines, respectively; intramolecular amine-N—H···O(carboxylate) hydrogen bonds are represented by pink dashed lines, (*b*) end-on view of the supramolecular tube and (*c*) a view of the unit-cell contents in projection down the *c* axis. The methylene-, methyl-C—H···O(nitro) and *π*–*π* interactions are shown as green and purple dashed lines, respectively. In each of (*a*) and (*b*), non-participating H atoms are omitted.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1	0.89 (2)	1.97 (2)	2.6698 (19)	135 (2)
N1—H2*N*···O2^{i}	0.88 (1)	2.24 (2)	3.010 (2)	146 (2)
N3—H3*N*···O1	0.90 (1)	1.82 (1)	2.6722 (18)	156 (2)
O5—H5*O*···O2	0.84 (2)	1.83 (2)	2.6731 (19)	179 (3)
C10—H10*B*···O5^{ii}	0.98	2.48	3.406 (2)	157

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1	0.87 (2)	2.00 (2)	2.665 (2)	132 (2)
N1—H2*N*···O5	0.89 (2)	2.17 (2)	3.058 (2)	176 (2)
N3—H3*N*···O1^{i}	0.90 (2)	1.73 (2)	2.637 (2)	178 (2)
N3—H4*N*···O2^{ii}	0.89 (2)	1.98 (2)	2.849 (2)	166 (2)
O5—H5*O*···O2^{i}	0.84 (2)	1.92 (2)	2.7546 (18)	173 (2)
C11—H11*A*···O4^{iii}	0.98	2.49	3.450 (3)	165
C12—H12*A*···O3	0.99	2.50	3.445 (2)	159

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

methyl-C—H···O(hydroxy) interactions link molecules along the *c*-axis to consolidate the three-dimensional packing, Fig. 4(*b*).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1	0.88 (2)	2.02 (2)	2.678 (2)	131 (2)
N1—H1*N*···O3^{i}	0.88 (2)	2.50 (2)	3.210 (2)	138 (1)
N1—H2*N*···O4^{ii}	0.88 (1)	2.56 (2)	3.094 (2)	120 (2)
N3—H3*N*···O6^{iii}	0.89 (2)	2.34 (2)	2.934 (2)	124 (1)
N3—H3*N*···O7^{iv}	0.89 (2)	2.44 (2)	3.065 (2)	128 (2)
N3—H4*N*···O5^{v}	0.89 (1)	2.08 (1)	2.945 (2)	165 (2)
N3—H5*N*···O2^{vi}	0.89 (2)	1.92 (2)	2.773 (2)	160 (2)
O5—H5*O*···O2^{vii}	0.85 (2)	1.90 (2)	2.7453 (18)	175 (2)
O6—H6*O*···O1^{viii}	0.84 (2)	1.88 (2)	2.6993 (19)	163 (2)
O7—H7*O*···O1^{ix}	0.84 (2)	2.07 (2)	2.8905 (18)	164 (2)

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

In the crystal of (II), the charge-assisted ammonium-N3—H···O(carboxylate) and hydroxy-O—H···O(carboxylate) hydrogen-bonds, that lead to the formation of a nine-membered {···OCO···HNC$_2$OH} heterosynthon, observed in (I) persist, Fig. 5(*a*). However, in (II), through the agency of having two ammonium-N—H H atoms, the second H atom bridges a neighbouring carboxylate-O2 atom leading to the formation of a supramolecular tube, as highlighted in Fig. 5(*b*). As seen from Fig. 5(*b*), the benzene rings are aligned to be

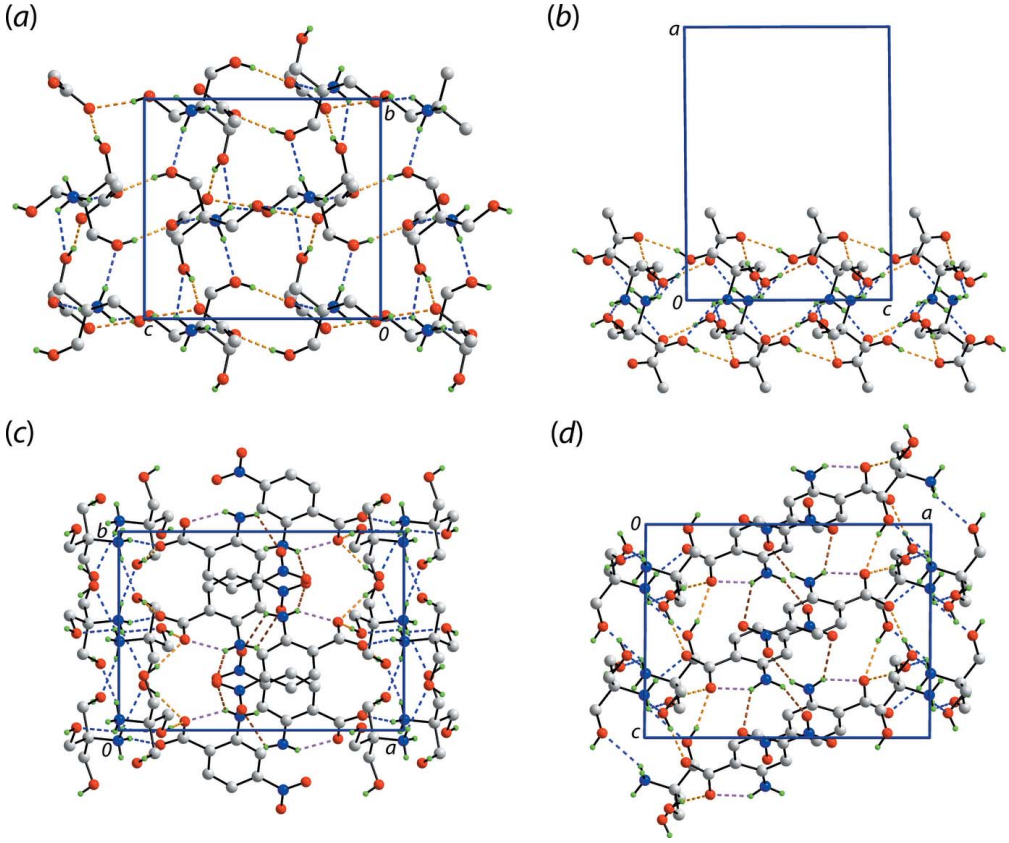


Figure 6
The molecular packing in (III): (*a*) plan and (*b*) views of the double-layer sustained by charge-assisted ammonium-N3—H···O(carboxylate), ammonium-N3—H···O(hydroxy) (blue dashed lines) and hydroxy-O—H···O(carboxylate) (orange dashed lines) hydrogen bonds, and views of the unit-cell contents in projection down the (*c*) *c* axis and (*d*) *b* axis. In (*c*) and (*d*), the intramolecular amine-N—H···O(carboxylate) and amine-N—H···O(nitro) interactions are represented by pink and brown dashed lines, respectively. In each of (*a*)–(*d*), non-participating H atoms are omitted.

Table 5
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_4H_{12}NO^+\cdot C_7H_5N_2O_4^-$	$C_6H_{16}NO^+\cdot C_7H_5N_2O_4^-$	$C_4H_{12}NO_3^+\cdot C_7H_5N_2O_4^-$
M_r	271.27	299.33	303.27
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
Temperature (K)	120	120	120
a, b, c (Å)	6.6816 (2), 22.8286 (8), 8.6570 (3)	21.1138 (5), 12.3635 (5), 13.1909 (4)	13.6269 (6), 9.4976 (3), 10.2042 (4)
β (°)	104.551 (2)	120.627 (2)	90.355 (2)
V (Å^3)	1278.11 (7)	2963.02 (17)	1320.63 (9)
Z	4	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.10	0.13
Crystal size (mm)	0.22 × 0.10 × 0.06	0.62 × 0.26 × 0.10	0.38 × 0.22 × 0.09
Data collection			
Diffractometer	Bruker–Nonius Roper CCD camera on κ-goniostat	Bruker–Nonius Roper CCD camera on κ-goniostat	Bruker–Nonius Roper CCD camera on κ-goniostat
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2007)	Multi-scan (*SADABS*; Sheldrick, 2007)	Multi-scan (*SADABS*; Sheldrick, 2007)
T_{min}, T_{max}	0.847, 1.000	0.652, 0.746	0.656, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9689, 2911, 2380	18353, 3406, 2349	16747, 3027, 2183
R_{int}	0.043	0.065	0.069
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.651	0.651
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.123, 1.07	0.050, 0.135, 1.02	0.048, 0.122, 1.04
No. of reflections	2911	3406	3027
No. of parameters	186	208	214
No. of restraints	4	5	8
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})	0.27, −0.32	0.24, −0.33	0.31, −0.26

Computer programs: *DENZO* (Otwinowski & Minor, 1997), *COLLECT* (Hooft, 1998), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

proximate and, indeed, they interact *via* π–π stacking with the inter-centroid separation being 3.4944 (9) Å (symmetry operation: $1-x, y, \frac{1}{2}-z$). The carboxylate-O2 atom forms two hydrogen-bonds. The connections between the tubes are of the type methylene- and methyl-C—H···O(nitro), involving both nitro-O atoms, as well as π–π stacking between benzene rings [inter-centroid separation = 3.5226 (10) Å for symmetry operation: $1-x, 1-y, -z$]. A view of the unit-cell contents is shown in Fig. 5(*c*), highlighting the intra- and inter-tube π–π stacking along the *c*-axis direction.

In the crystal of (III), supramolecular double-layers in the *bc*-plane are formed as a result of charge-assisted ammonium-N3—H···O(carboxylate), ammonium-N3—H···O(hydroxy) and hydroxy-O—H···O(carboxylate) hydrogen-bonds. The ammonium-N3—H3*N* atom is bifurcated, forming two weak ammonium-N3—H···O(hydroxy) hydrogen-bonds. A view normal to the plane of the double-layer and a side-on view are shown in Fig. 6(*a*) and (*b*), respectively. From the latter, the intra-layer region comprises the ammonium groups, each of which forms four N—H···O hydrogen-bonds to carboxylate and hydroxy groups on either side. Each hydroxy group of the cation forms a hydroxy-O—H···O(carboxylate) hydrogen-bond with a carboxylate-O atom derived from a different anion, and each accepts an ammonium-N—H atom derived from a different cation. Each carboxylate-O atom forms two hydrogen-bonds, the O1 accepts hydrogen-bonds from different hydroxy groups, and the O2 atom accept hydrogen-bonds from hydroxy and ammonium groups. Projecting to either side of the double-layer are the nitrobenzene groups, Fig. 6(*c*) and (*d*). These provide the links to construct the three-dimensional architecture, *i.e.* *via* amine-N—H···O(nitro) interactions, involving both nitro-O atoms.

The obvious trend from the present study is the increase in dimensionality of the supramolecular aggregation pattern, *i.e.* chain in (I), tube in (II) and double-layer in (III), as the number of acidic ammonium-N—H atoms increases.

4. Database survey

As indicated in the *Chemical context*, a number of ammonium salts of the anion derived from 2-amino-4-nitrobenzoic acid have now been described. The key conformational indicators for the anion are the dihedral angles formed between CO_2/C_6/NO_2. The smallest dihedral angles between the CO_2/C_6, C_6/NO_2 and CO_2/NO_2 pairs of least-squares planes of 3.44 (14), 0.69 (11) and 3.2 (2)° are found for the anion in the salt with $H_3N^{(+)}CH_2CH_2N^{(+)}H_3$ (Smith *et al.*, 2002). Conversely, the greatest CO_2/C_6, C_6/NO_2 and CO_2/NO_2 dihedral angles of

26.4 (3), 12.6 (3) and 26.73 (14)°, respectively, are found in the $N^{(+)}H_4$ (Smith, 2014*b*), *n*-$Bu_2N^{(+)}H_2$ (Wardell *et al.*, 2016) and $H_2NN^{(+)}H_3$ (Wardell *et al.*, 2017) salts, respectively. The respective dihedral angles in (I)–(III), described herein, fall within these ranges.

5. Synthesis and crystallization

Preparation of dimethyl(2-hydroxyethyl)ammonium 2-amino-4-nitrobenzoate (I). To a solution of 2-amino-4-nitrobenzoic acid (1 mmol) in methanol (10 ml) was added a solution of dimethyl(2-hydroxyethyl)amine (1 mmol) in methanol (10 ml). The reaction mixture was refluxed for 15 mins, and then maintained at room temperature. Crystals of (I) were collected after three days. M.p. 444–447 K. Anal. calcd.: C, 48.89; H, 5.97, N, 15.54. Found: C, 48.81; H, 5.89; N, 14.68%. IR (KBr, cm^{-1}): 3500–2700 (*br*, *s*; with maxima at 3439, 3324, 3219, 2978, 2826), 1632, 1537, 1433, 1381, 1346, 1329, 1279, 1263, 1209, 1140, 1099, 1072, 1022, 918, 858, 823, 785, 731, 692, 684, 577, 513, 486.

Preparation of *tert*-butyl(2-hydroxyethyl)ammonium 2-amino-4-nitrobenzoate (II). To a solution of 2-amino-4-nitrobenzoic acid (1 mmol) in methanol (10 ml) was added a solution of *tert*-butyl(2-hydroxyethyl)amine (1 mmol) in methanol (10 ml). The reaction mixture was refluxed for 15 mins, and then maintained at room temperature. Crystals of (II) were collected after 3 days. M.p. 429–431 K. Anal. calcd.: C, 52.34; H, 6.76, N, 14.09. Found: C, 52.27; H, 6.89; N, 13.99%. IR (KBr, cm^{-1}): 3550–2700 (*br*, *s*, with maxima at 3430, 3327, 3224, 2968, 2810), 1640, 1446, 1370, 1351, 1329, 1269, 1221 1137, 1085, 1034, 858, 8245, 739, 687, 587.

Preparation of tris(hydroxymethyl)methylammonium 2-amino-4-nitrobenzoate (III): To a solution of 2-amino-4-nitrobenzoic acid (1 mmol) in ethanol (10 ml) was added a solution of tris(hydroxymethyl)methylamine (1 mmol) in ethanol (10 ml). The reaction mixture was refluxed for 10 mins, and then maintained at room temperature. Crystals of (III) were collected after two days. M.p. 460–463 K. Anal. calcd.: C, 51.06; H, 5.71, N, 14.89. Found: C, 50.94; H, 5.80; N, 14.79% IR (KBr, cm^{-1}): 3700–2400 (*br*, *s*, with maxima at 3514, 3477, 3398, 3314, 3256, 3078, 2823 and 2538), 1647, 1431, 1350 1250, 1146, 1115, 1063, 1010, 872, 827, 736, 689, 596, 578 511, 484, 1549, 1356.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. Carbon-bound H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and were included in the refinement in the riding-model approximation, with U_{iso}(H) set to 1.2–1.5U_{eq}(C). The O- and N-bound H atoms were located from difference maps, but refined with O—H = 0.84±0.01 Å and U_{iso}(H) = 1.5U_{eq}(O), and with N—H = 0.86–0.88±0.01 Å and U_{iso}(H) = 1.2U_{eq}(N), respectively. In the refinement of (II), owing to poor agreement, a reflection, *i.e.* (0 2 0), was omitted from the final cycles of refinement.

Acknowledgements

The authors thank the National Crystallographic Service, based at the University of Southampton, for collecting the data.

Funding information

JLW thanks CNPq, Brazil, for a grant. The authors are also grateful to Sunway University (INT-RRO-2017-096) for support of this research.

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supporting information

Acta Cryst. (2018). E**74**, 1735-1740 [https://doi.org/10.1107/S2056989018015578]

Crystal structures of the 1:1 salts of 2-amino-4-nitrobenzoate with each of (2-hydroxyethyl)dimethylazanium, *tert*-butyl(2-hydroxyethyl)azanium and 1,3-dihydroxy-2-(hydroxymethyl)propan-2-aminium

James L. Wardell and Edward R. T. Tiekink

Computing details

For all structures, data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

2-Amino-4-nitrobenzoate (2-hydroxyethyl)dimethylazanium (I)

Crystal data

$C_4H_{12}NO^+·C_7H_5N_2O_4^-$
M_r = 271.27
Monoclinic, $P2_1/n$
a = 6.6816 (2) Å
b = 22.8286 (8) Å
c = 8.6570 (3) Å
β = 104.551 (2)°
V = 1278.11 (7) Å^3
Z = 4
$F(000)$ = 576
D_x = 1.410 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8678 reflections
θ = 2.9–27.5°
μ = 0.11 mm^{-1}
T = 120 K
Blade, yellow
0.22 × 0.10 × 0.06 mm

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer
Radiation source: Bruker–Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
T_{min} = 0.847, T_{max} = 1.000
9689 measured reflections
2911 independent reflections
2380 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −8→8
k = −29→29
l = −11→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.123
S = 1.07
2911 reflections
186 parameters
4 restraints
Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 1.1579P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.16272 (19)	0.18360 (5)	0.56894 (15)	0.0234 (3)
O2	0.3854 (2)	0.15398 (6)	0.43175 (16)	0.0276 (3)
O3	−0.4660 (3)	−0.04973 (8)	0.2249 (3)	0.0617 (6)
O4	−0.2616 (3)	−0.06559 (8)	0.0708 (2)	0.0553 (5)
N1	−0.1707 (2)	0.11839 (7)	0.5634 (2)	0.0270 (4)
H1N	−0.101 (3)	0.1513 (6)	0.593 (3)	0.032*
H2N	−0.3042 (16)	0.1187 (10)	0.558 (3)	0.032*
N2	−0.3090 (3)	−0.03927 (8)	0.1803 (2)	0.0385 (4)
C1	0.0836 (3)	0.09665 (7)	0.4120 (2)	0.0188 (3)
C2	−0.1058 (3)	0.08640 (7)	0.4521 (2)	0.0205 (4)
C3	−0.2321 (3)	0.04031 (8)	0.3743 (2)	0.0258 (4)
H3	−0.3606	0.0324	0.3984	0.031*
C4	−0.1684 (3)	0.00696 (8)	0.2634 (2)	0.0275 (4)
C5	0.0187 (3)	0.01502 (8)	0.2244 (2)	0.0283 (4)
H5	0.0602	−0.0094	0.1491	0.034*
C6	0.1419 (3)	0.06031 (8)	0.3006 (2)	0.0237 (4)
H6	0.2711	0.0670	0.2765	0.028*
C7	0.2213 (3)	0.14808 (7)	0.4763 (2)	0.0190 (3)
O5	0.59794 (19)	0.25309 (6)	0.51573 (16)	0.0249 (3)
H5O	0.529 (3)	0.2221 (7)	0.489 (3)	0.037*
N3	0.1711 (2)	0.29912 (6)	0.52114 (17)	0.0189 (3)
H3N	0.206 (3)	0.2616 (5)	0.548 (2)	0.023*
C8	0.3578 (3)	0.33333 (8)	0.5092 (2)	0.0250 (4)
H8A	0.4401	0.3433	0.6180	0.030*
H8B	0.3126	0.3705	0.4520	0.030*
C9	0.4932 (3)	0.30024 (8)	0.4229 (2)	0.0256 (4)
H9A	0.4067	0.2848	0.3209	0.031*
H9B	0.5960	0.3274	0.3976	0.031*
C10	0.0140 (3)	0.29638 (9)	0.3653 (2)	0.0252 (4)
H10A	−0.1042	0.2729	0.3768	0.038*
H10B	0.0753	0.2783	0.2853	0.038*
H10C	−0.0327	0.3361	0.3311	0.038*
C11	0.0766 (3)	0.32355 (8)	0.6464 (2)	0.0251 (4)
H11A	0.0397	0.3647	0.6223	0.038*

H11B	0.1760	0.3208	0.7508	0.038*
H11C	−0.0481	0.3012	0.6482	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0236 (6)	0.0214 (6)	0.0258 (7)	−0.0023 (5)	0.0074 (5)	−0.0044 (5)
O2	0.0251 (7)	0.0280 (7)	0.0326 (7)	−0.0051 (5)	0.0126 (6)	−0.0029 (6)
O3	0.0404 (10)	0.0457 (10)	0.0971 (16)	−0.0189 (8)	0.0135 (10)	−0.0275 (10)
O4	0.0809 (13)	0.0412 (9)	0.0422 (10)	−0.0246 (9)	0.0125 (9)	−0.0190 (8)
N1	0.0216 (8)	0.0259 (8)	0.0358 (9)	−0.0034 (6)	0.0115 (7)	−0.0050 (7)
N2	0.0422 (11)	0.0233 (8)	0.0432 (11)	−0.0063 (8)	−0.0018 (8)	−0.0034 (8)
C1	0.0206 (8)	0.0158 (8)	0.0182 (8)	0.0004 (6)	0.0015 (6)	0.0023 (6)
C2	0.0206 (8)	0.0171 (8)	0.0214 (8)	0.0016 (6)	0.0009 (6)	0.0034 (7)
C3	0.0214 (9)	0.0200 (8)	0.0328 (10)	−0.0014 (7)	0.0005 (7)	0.0039 (8)
C4	0.0332 (10)	0.0169 (8)	0.0266 (9)	−0.0031 (7)	−0.0028 (8)	−0.0002 (7)
C5	0.0388 (11)	0.0197 (9)	0.0253 (9)	0.0016 (8)	0.0061 (8)	−0.0015 (7)
C6	0.0269 (9)	0.0219 (9)	0.0217 (9)	0.0030 (7)	0.0052 (7)	0.0019 (7)
C7	0.0196 (8)	0.0177 (8)	0.0185 (8)	0.0005 (6)	0.0025 (6)	0.0046 (6)
O5	0.0202 (6)	0.0237 (6)	0.0296 (7)	−0.0017 (5)	0.0041 (5)	0.0036 (5)
N3	0.0183 (7)	0.0195 (7)	0.0186 (7)	−0.0002 (6)	0.0042 (5)	−0.0013 (6)
C8	0.0218 (9)	0.0229 (9)	0.0304 (10)	−0.0054 (7)	0.0067 (7)	−0.0026 (7)
C9	0.0225 (9)	0.0256 (9)	0.0307 (10)	−0.0007 (7)	0.0106 (7)	0.0070 (8)
C10	0.0208 (8)	0.0318 (10)	0.0209 (9)	−0.0013 (7)	0.0014 (7)	−0.0028 (7)
C11	0.0288 (9)	0.0273 (9)	0.0211 (9)	0.0027 (8)	0.0099 (7)	−0.0034 (7)

Geometric parameters (Å, º)

O1—C7	1.270 (2)	O5—C9	1.418 (2)
O2—C7	1.258 (2)	O5—H5O	0.843 (10)
O3—N2	1.229 (3)	N3—C10	1.488 (2)
O4—N2	1.229 (3)	N3—C11	1.493 (2)
N1—C2	1.363 (2)	N3—C8	1.498 (2)
N1—H1N	0.886 (10)	N3—H3N	0.902 (9)
N1—H2N	0.881 (9)	C8—C9	1.512 (3)
N2—C4	1.474 (2)	C8—H8A	0.9900
C1—C6	1.399 (2)	C8—H8B	0.9900
C1—C2	1.413 (2)	C9—H9A	0.9900
C1—C7	1.509 (2)	C9—H9B	0.9900
C2—C3	1.410 (2)	C10—H10A	0.9800
C3—C4	1.374 (3)	C10—H10B	0.9800
C3—H3	0.9500	C10—H10C	0.9800
C4—C5	1.387 (3)	C11—H11A	0.9800
C5—C6	1.382 (3)	C11—H11B	0.9800
C5—H5	0.9500	C11—H11C	0.9800
C6—H6	0.9500		
C2—N1—H1N	115.2 (14)	C10—N3—C8	111.68 (14)

C2—N1—H2N	117.5 (15)	C11—N3—C8	111.54 (14)
H1N—N1—H2N	117 (2)	C10—N3—H3N	105.8 (13)
O3—N2—O4	123.56 (18)	C11—N3—H3N	107.4 (13)
O3—N2—C4	118.39 (19)	C8—N3—H3N	110.1 (13)
O4—N2—C4	118.05 (19)	N3—C8—C9	112.70 (14)
C6—C1—C2	119.52 (16)	N3—C8—H8A	109.1
C6—C1—C7	117.77 (15)	C9—C8—H8A	109.1
C2—C1—C7	122.59 (15)	N3—C8—H8B	109.1
N1—C2—C3	118.61 (16)	C9—C8—H8B	109.1
N1—C2—C1	123.25 (15)	H8A—C8—H8B	107.8
C3—C2—C1	118.14 (16)	O5—C9—C8	111.72 (15)
C4—C3—C2	119.58 (17)	O5—C9—H9A	109.3
C4—C3—H3	120.2	C8—C9—H9A	109.3
C2—C3—H3	120.2	O5—C9—H9B	109.3
C3—C4—C5	123.60 (17)	C8—C9—H9B	109.3
C3—C4—N2	117.77 (18)	H9A—C9—H9B	107.9
C5—C4—N2	118.63 (18)	N3—C10—H10A	109.5
C6—C5—C4	116.63 (18)	N3—C10—H10B	109.5
C6—C5—H5	121.7	H10A—C10—H10B	109.5
C4—C5—H5	121.7	N3—C10—H10C	109.5
C5—C6—C1	122.49 (18)	H10A—C10—H10C	109.5
C5—C6—H6	118.8	H10B—C10—H10C	109.5
C1—C6—H6	118.8	N3—C11—H11A	109.5
O2—C7—O1	123.80 (16)	N3—C11—H11B	109.5
O2—C7—C1	117.90 (15)	H11A—C11—H11B	109.5
O1—C7—C1	118.28 (15)	N3—C11—H11C	109.5
C9—O5—H5O	108.9 (16)	H11A—C11—H11C	109.5
C10—N3—C11	110.07 (14)	H11B—C11—H11C	109.5

C6—C1—C2—N1	177.60 (16)	C3—C4—C5—C6	−1.6 (3)
C7—C1—C2—N1	−6.6 (3)	N2—C4—C5—C6	177.51 (17)
C6—C1—C2—C3	−1.6 (2)	C4—C5—C6—C1	0.1 (3)
C7—C1—C2—C3	174.24 (15)	C2—C1—C6—C5	1.5 (3)
N1—C2—C3—C4	−179.05 (17)	C7—C1—C6—C5	−174.52 (16)
C1—C2—C3—C4	0.2 (2)	C6—C1—C7—O2	−3.1 (2)
C2—C3—C4—C5	1.5 (3)	C2—C1—C7—O2	−178.95 (15)
C2—C3—C4—N2	−177.62 (16)	C6—C1—C7—O1	175.26 (15)
O3—N2—C4—C3	−7.2 (3)	C2—C1—C7—O1	−0.6 (2)
O4—N2—C4—C3	173.39 (19)	C10—N3—C8—C9	−73.87 (19)
O3—N2—C4—C5	173.7 (2)	C11—N3—C8—C9	162.49 (15)
O4—N2—C4—C5	−5.7 (3)	N3—C8—C9—O5	−71.15 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.89 (2)	1.97 (2)	2.6698 (19)	135 (2)
N1—H2*N*···O2^{i}	0.88 (1)	2.24 (2)	3.010 (2)	146 (2)
N3—H3*N*···O1	0.90 (1)	1.82 (1)	2.6722 (18)	156 (2)

O5—H5*O*···O2	0.84 (2)	1.83 (2)	2.6731 (19)	179 (3)
C10—H10*B*···O5^{ii}	0.98	2.48	3.406 (2)	157

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

2-Amino-4-nitrobenzoate *tert*-butyl(2-hydroxyethyl)azanium (II)

Crystal data

$C_6H_{16}NO^+·C_7H_5N_2O_4^-$
M_r = 299.33
Monoclinic, *C*2/*c*
a = 21.1138 (5) Å
b = 12.3635 (5) Å
c = 13.1909 (4) Å
β = 120.627 (2)°
V = 2963.02 (17) Å^3
Z = 8
F(000) = 1280
D_x = 1.342 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 8229 reflections
θ = 2.9–27.5°
μ = 0.10 mm^{-1}
T = 120 K
Slab, orange
0.62 × 0.26 × 0.10 mm

Data collection

Bruker–Nonius Roper CCD camera on *κ*-goniostat diffractometer
Radiation source: Bruker–Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & *ω* scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
T_{min} = 0.652, T_{max} = 0.746
18353 measured reflections
3406 independent reflections
2349 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 27.6°, θ_{min} = 3.0°
h = −27→27
k = −16→15
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.135
S = 1.02
3406 reflections
208 parameters
5 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 0.7685P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.38287 (6)	0.76025 (10)	0.01169 (10)	0.0301 (3)
O2	0.29310 (6)	0.63783 (10)	−0.04670 (10)	0.0263 (3)
O3	0.63480 (6)	0.33794 (10)	0.24135 (11)	0.0305 (3)

O4	0.54488 (7)	0.22405 (10)	0.17418 (13)	0.0400 (4)
N1	0.52324 (7)	0.69991 (12)	0.14202 (13)	0.0241 (3)
N2	0.56872 (7)	0.31665 (12)	0.18823 (12)	0.0241 (3)
C1	0.41726 (8)	0.57689 (13)	0.05554 (13)	0.0188 (4)
C2	0.49416 (8)	0.59915 (13)	0.12014 (12)	0.0187 (4)
C3	0.54245 (8)	0.51022 (13)	0.16275 (13)	0.0192 (4)
H3	0.5941	0.5221	0.2073	0.023*
C4	0.51565 (8)	0.40665 (13)	0.14053 (13)	0.0195 (4)
C5	0.44091 (8)	0.38249 (14)	0.07707 (13)	0.0215 (4)
H5	0.4235	0.3101	0.0624	0.026*
C6	0.39357 (8)	0.46956 (14)	0.03667 (13)	0.0214 (4)
H6	0.3421	0.4558	−0.0063	0.026*
C7	0.36039 (8)	0.66455 (14)	0.00382 (13)	0.0216 (4)
O5	0.69062 (6)	0.71809 (10)	0.29593 (11)	0.0303 (3)
N3	0.79731 (7)	0.56819 (12)	0.45647 (12)	0.0231 (3)
C8	0.84793 (9)	0.47891 (15)	0.53503 (16)	0.0292 (4)
C9	0.80464 (11)	0.37480 (16)	0.5120 (2)	0.0444 (5)
H9A	0.7623	0.3876	0.5219	0.067*
H9B	0.8363	0.3192	0.5678	0.067*
H9C	0.7873	0.3503	0.4313	0.067*
C10	0.87684 (12)	0.51860 (17)	0.66040 (17)	0.0448 (5)
H10A	0.8355	0.5298	0.6732	0.067*
H10B	0.9032	0.5870	0.6724	0.067*
H10C	0.9104	0.4646	0.7163	0.067*
C11	0.91074 (10)	0.46495 (17)	0.51089 (19)	0.0402 (5)
H11A	0.9478	0.4160	0.5696	0.060*
H11B	0.9333	0.5355	0.5155	0.060*
H11C	0.8916	0.4344	0.4320	0.060*
C12	0.75766 (9)	0.54960 (16)	0.32642 (15)	0.0310 (4)
H12A	0.7141	0.5033	0.3028	0.037*
H12B	0.7905	0.5118	0.3049	0.037*
C13	0.73361 (9)	0.65690 (16)	0.26214 (15)	0.0301 (4)
H13A	0.7777	0.6992	0.2789	0.036*
H13B	0.7046	0.6434	0.1762	0.036*
H1N	0.4925 (9)	0.7539 (12)	0.1137 (17)	0.036*
H2N	0.5715 (5)	0.7082 (16)	0.1885 (15)	0.036*
H5O	0.7197 (10)	0.7625 (14)	0.3464 (15)	0.045*
H3N	0.8263 (9)	0.6272 (11)	0.4739 (16)	0.036*
H4N	0.7637 (8)	0.5810 (16)	0.4767 (16)	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0220 (6)	0.0240 (7)	0.0377 (7)	0.0031 (5)	0.0104 (6)	0.0033 (5)
O2	0.0159 (6)	0.0339 (7)	0.0272 (6)	0.0023 (5)	0.0096 (5)	0.0055 (5)
O3	0.0197 (6)	0.0276 (7)	0.0389 (7)	0.0024 (5)	0.0112 (5)	−0.0006 (6)
O4	0.0337 (7)	0.0186 (7)	0.0580 (9)	−0.0016 (6)	0.0163 (7)	0.0032 (6)
N1	0.0169 (7)	0.0189 (8)	0.0318 (8)	−0.0002 (6)	0.0089 (6)	−0.0009 (6)

N2	0.0223 (7)	0.0237 (8)	0.0254 (7)	0.0007 (6)	0.0114 (6)	0.0000 (6)
C1	0.0181 (8)	0.0232 (9)	0.0162 (7)	0.0006 (7)	0.0096 (6)	0.0000 (6)
C2	0.0192 (8)	0.0221 (9)	0.0158 (7)	−0.0003 (7)	0.0097 (6)	−0.0004 (6)
C3	0.0160 (7)	0.0246 (9)	0.0177 (7)	−0.0009 (6)	0.0090 (6)	−0.0006 (6)
C4	0.0206 (8)	0.0194 (9)	0.0194 (7)	0.0028 (7)	0.0110 (6)	0.0018 (6)
C5	0.0222 (8)	0.0208 (9)	0.0229 (8)	−0.0042 (7)	0.0125 (7)	−0.0024 (7)
C6	0.0172 (7)	0.0294 (10)	0.0182 (7)	−0.0029 (7)	0.0095 (6)	−0.0022 (7)
C7	0.0200 (8)	0.0271 (10)	0.0174 (7)	0.0036 (7)	0.0093 (6)	0.0022 (7)
O5	0.0202 (6)	0.0296 (8)	0.0306 (7)	−0.0012 (5)	0.0053 (5)	−0.0053 (5)
N3	0.0181 (7)	0.0210 (8)	0.0295 (7)	−0.0011 (6)	0.0114 (6)	−0.0027 (6)
C8	0.0236 (8)	0.0234 (10)	0.0378 (10)	0.0060 (7)	0.0136 (8)	0.0037 (8)
C9	0.0352 (10)	0.0261 (11)	0.0740 (15)	0.0047 (9)	0.0295 (11)	0.0084 (10)
C10	0.0526 (12)	0.0396 (12)	0.0357 (11)	0.0156 (10)	0.0178 (10)	0.0129 (9)
C11	0.0247 (9)	0.0367 (12)	0.0578 (13)	0.0075 (8)	0.0200 (9)	0.0040 (10)
C12	0.0227 (8)	0.0326 (11)	0.0304 (9)	−0.0014 (7)	0.0083 (7)	−0.0104 (8)
C13	0.0250 (9)	0.0379 (11)	0.0232 (8)	−0.0032 (8)	0.0093 (7)	−0.0060 (8)

Geometric parameters (Å, º)

O1—C7	1.259 (2)	N3—C8	1.519 (2)
O2—C7	1.2678 (19)	N3—H3N	0.903 (9)
O3—N2	1.2292 (17)	N3—H4N	0.890 (9)
O4—N2	1.2262 (18)	C8—C9	1.517 (3)
N1—C2	1.353 (2)	C8—C11	1.523 (3)
N1—H1N	0.872 (9)	C8—C10	1.523 (3)
N1—H2N	0.887 (9)	C9—H9A	0.9800
N2—C4	1.473 (2)	C9—H9B	0.9800
C1—C6	1.395 (2)	C9—H9C	0.9800
C1—C2	1.424 (2)	C10—H10A	0.9800
C1—C7	1.499 (2)	C10—H10B	0.9800
C2—C3	1.407 (2)	C10—H10C	0.9800
C3—C4	1.370 (2)	C11—H11A	0.9800
C3—H3	0.9500	C11—H11B	0.9800
C4—C5	1.391 (2)	C11—H11C	0.9800
C5—C6	1.378 (2)	C12—C13	1.516 (3)
C5—H5	0.9500	C12—H12A	0.9900
C6—H6	0.9500	C12—H12B	0.9900
O5—C13	1.417 (2)	C13—H13A	0.9900
O5—H5O	0.841 (10)	C13—H13B	0.9900
N3—C12	1.494 (2)		

C2—N1—H1N	117.1 (13)	C9—C8—C11	111.21 (16)
C2—N1—H2N	119.3 (13)	N3—C8—C11	108.94 (15)
H1N—N1—H2N	123.4 (19)	C9—C8—C10	111.00 (17)
O4—N2—O3	123.05 (14)	N3—C8—C10	105.08 (14)
O4—N2—C4	118.44 (13)	C11—C8—C10	110.70 (16)
O3—N2—C4	118.50 (14)	C8—C9—H9A	109.5
C6—C1—C2	119.11 (14)	C8—C9—H9B	109.5

C6—C1—C7	118.37 (13)	H9A—C9—H9B	109.5
C2—C1—C7	122.50 (14)	C8—C9—H9C	109.5
N1—C2—C3	118.44 (13)	H9A—C9—H9C	109.5
N1—C2—C1	124.09 (14)	H9B—C9—H9C	109.5
C3—C2—C1	117.46 (14)	C8—C10—H10A	109.5
C4—C3—C2	120.56 (14)	C8—C10—H10B	109.5
C4—C3—H3	119.7	H10A—C10—H10B	109.5
C2—C3—H3	119.7	C8—C10—H10C	109.5
C3—C4—C5	123.22 (15)	H10A—C10—H10C	109.5
C3—C4—N2	118.23 (13)	H10B—C10—H10C	109.5
C5—C4—N2	118.54 (14)	C8—C11—H11A	109.5
C6—C5—C4	116.24 (15)	C8—C11—H11B	109.5
C6—C5—H5	121.9	H11A—C11—H11B	109.5
C4—C5—H5	121.9	C8—C11—H11C	109.5
C5—C6—C1	123.40 (14)	H11A—C11—H11C	109.5
C5—C6—H6	118.3	H11B—C11—H11C	109.5
C1—C6—H6	118.3	N3—C12—C13	109.85 (14)
O1—C7—O2	124.24 (15)	N3—C12—H12A	109.7
O1—C7—C1	117.45 (13)	C13—C12—H12A	109.7
O2—C7—C1	118.31 (15)	N3—C12—H12B	109.7
C13—O5—H5O	105.7 (15)	C13—C12—H12B	109.7
C12—N3—C8	117.35 (14)	H12A—C12—H12B	108.2
C12—N3—H3N	109.1 (12)	O5—C13—C12	112.15 (15)
C8—N3—H3N	105.3 (12)	O5—C13—H13A	109.2
C12—N3—H4N	107.8 (12)	C12—C13—H13A	109.2
C8—N3—H4N	108.4 (13)	O5—C13—H13B	109.2
H3N—N3—H4N	108.6 (18)	C12—C13—H13B	109.2
C9—C8—N3	109.71 (14)	H13A—C13—H13B	107.9

C6—C1—C2—N1	178.92 (14)	N2—C4—C5—C6	178.59 (13)
C7—C1—C2—N1	0.6 (2)	C4—C5—C6—C1	0.7 (2)
C6—C1—C2—C3	−0.6 (2)	C2—C1—C6—C5	−0.3 (2)
C7—C1—C2—C3	−178.87 (13)	C7—C1—C6—C5	178.09 (14)
N1—C2—C3—C4	−178.52 (14)	C6—C1—C7—O1	−173.13 (14)
C1—C2—C3—C4	1.0 (2)	C2—C1—C7—O1	5.2 (2)
C2—C3—C4—C5	−0.6 (2)	C6—C1—C7—O2	5.6 (2)
C2—C3—C4—N2	−179.45 (13)	C2—C1—C7—O2	−176.12 (14)
O4—N2—C4—C3	176.00 (14)	C12—N3—C8—C9	−58.0 (2)
O3—N2—C4—C3	−3.2 (2)	C12—N3—C8—C11	63.99 (19)
O4—N2—C4—C5	−2.9 (2)	C12—N3—C8—C10	−177.36 (15)
O3—N2—C4—C5	177.91 (14)	C8—N3—C12—C13	−159.11 (14)
C3—C4—C5—C6	−0.2 (2)	N3—C12—C13—O5	−55.18 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.87 (2)	2.00 (2)	2.665 (2)	132 (2)
N1—H2*N*···O5	0.89 (2)	2.17 (2)	3.058 (2)	176 (2)

N3—H3*N*···O1^{i}	0.90 (2)	1.73 (2)	2.637 (2)	178 (2)
N3—H4*N*···O2^{ii}	0.89 (2)	1.98 (2)	2.849 (2)	166 (2)
O5—H5*O*···O2^{i}	0.84 (2)	1.92 (2)	2.7546 (18)	173 (2)
C11—H11*A*···O4^{iii}	0.98	2.49	3.450 (3)	165
C12—H12*A*···O3	0.99	2.50	3.445 (2)	159

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

2-Amino-4-nitrobenzoate 1,3-dihydroxy-2-(hydroxymethyl)propan-2-aminium (III)

Crystal data

$C_4H_{12}NO_3^+·C_7H_5N_2O_4^-$
M_r = 303.27
Monoclinic, $P2_1/c$
a = 13.6269 (6) Å
b = 9.4976 (3) Å
c = 10.2042 (4) Å
β = 90.355 (2)°
V = 1320.63 (9) Å^3
Z = 4
$F(000)$ = 640
D_x = 1.525 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 10585 reflections
θ = 2.9–27.5°
μ = 0.13 mm^{-1}
T = 120 K
Slab, orange
0.38 × 0.22 × 0.09 mm

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer
Radiation source: Bruker–Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
T_{min} = 0.656, T_{max} = 0.746
16747 measured reflections
3027 independent reflections
2183 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 27.5°, θ_{min} = 2.9°
h = −17→17
k = −11→12
l = −11→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.122
S = 1.04
3027 reflections
214 parameters
8 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.4405P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.23149 (10)	1.04393 (14)	0.76677 (13)	0.0214 (3)

O2	0.14548 (9)	0.92617 (13)	0.61598 (12)	0.0175 (3)
O3	0.65621 (10)	0.73923 (15)	0.52281 (13)	0.0255 (3)
O4	0.56887 (10)	0.60326 (14)	0.39818 (13)	0.0226 (3)
N1	0.42471 (12)	1.07055 (17)	0.72756 (15)	0.0187 (4)
H1N	0.3741 (11)	1.100 (2)	0.7735 (18)	0.022*
H2N	0.4832 (9)	1.086 (2)	0.7608 (19)	0.022*
N2	0.57664 (12)	0.69917 (16)	0.47821 (14)	0.0179 (4)
C1	0.31934 (13)	0.89761 (19)	0.61872 (16)	0.0147 (4)
C2	0.41270 (14)	0.95131 (18)	0.65438 (16)	0.0144 (4)
C3	0.49671 (14)	0.88243 (19)	0.60661 (16)	0.0156 (4)
H3	0.5603	0.9150	0.6306	0.019*
C4	0.48646 (13)	0.76770 (19)	0.52504 (17)	0.0155 (4)
C5	0.39602 (14)	0.71363 (19)	0.48678 (17)	0.0167 (4)
H5	0.3910	0.6348	0.4298	0.020*
C6	0.31356 (14)	0.78010 (19)	0.53561 (17)	0.0160 (4)
H6	0.2507	0.7448	0.5120	0.019*
C7	0.22586 (14)	0.96075 (18)	0.66953 (16)	0.0151 (4)
O5	0.93618 (10)	0.33420 (13)	0.11526 (12)	0.0172 (3)
H5O	0.9100 (15)	0.357 (2)	0.0431 (13)	0.026*
O6	0.91226 (10)	0.77428 (13)	0.16735 (13)	0.0186 (3)
H6O	0.8659 (12)	0.820 (2)	0.201 (2)	0.028*
O7	0.85135 (10)	0.48735 (14)	0.47852 (12)	0.0212 (3)
H7O	0.8181 (15)	0.511 (2)	0.5444 (16)	0.032*
N3	0.99779 (11)	0.55298 (16)	0.30064 (15)	0.0137 (3)
H3N	1.0132 (15)	0.4938 (17)	0.3649 (15)	0.016*
H4N	1.0077 (15)	0.6377 (13)	0.3343 (18)	0.016*
H5N	1.0380 (12)	0.542 (2)	0.2325 (14)	0.016*
C8	0.89311 (13)	0.53736 (18)	0.25643 (16)	0.0144 (4)
C9	0.87415 (14)	0.38355 (18)	0.21779 (17)	0.0158 (4)
H9A	0.8839	0.3232	0.2959	0.019*
H9B	0.8049	0.3738	0.1894	0.019*
C10	0.87791 (14)	0.63603 (18)	0.13984 (17)	0.0163 (4)
H10A	0.9132	0.5982	0.0630	0.020*
H10B	0.8072	0.6399	0.1174	0.020*
C11	0.82764 (14)	0.5772 (2)	0.37062 (17)	0.0180 (4)
H11A	0.8386	0.6769	0.3951	0.022*
H11B	0.7578	0.5655	0.3457	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0188 (7)	0.0239 (7)	0.0215 (7)	0.0012 (6)	0.0027 (5)	−0.0081 (6)
O2	0.0149 (7)	0.0211 (7)	0.0165 (6)	0.0007 (5)	0.0004 (5)	−0.0007 (5)
O3	0.0150 (7)	0.0364 (8)	0.0250 (7)	0.0032 (6)	−0.0015 (6)	−0.0061 (6)
O4	0.0234 (8)	0.0204 (7)	0.0241 (7)	0.0033 (6)	0.0029 (6)	−0.0061 (6)
N1	0.0156 (9)	0.0203 (9)	0.0202 (8)	−0.0006 (7)	−0.0004 (7)	−0.0060 (7)
N2	0.0178 (9)	0.0195 (8)	0.0165 (8)	0.0016 (7)	0.0014 (6)	0.0008 (6)
C1	0.0164 (10)	0.0151 (9)	0.0125 (8)	0.0018 (7)	0.0014 (7)	0.0027 (7)

C2	0.0161 (10)	0.0145 (9)	0.0126 (8)	−0.0001 (7)	0.0004 (7)	0.0017 (7)
C3	0.0138 (9)	0.0193 (10)	0.0137 (8)	−0.0002 (7)	−0.0009 (7)	0.0011 (7)
C4	0.0142 (9)	0.0172 (9)	0.0150 (9)	0.0036 (7)	0.0018 (7)	0.0033 (7)
C5	0.0200 (10)	0.0136 (9)	0.0167 (9)	0.0010 (7)	0.0007 (7)	−0.0008 (7)
C6	0.0149 (9)	0.0162 (9)	0.0170 (9)	−0.0016 (7)	−0.0005 (7)	−0.0005 (7)
C7	0.0197 (10)	0.0121 (9)	0.0136 (8)	0.0008 (7)	0.0017 (7)	0.0031 (7)
O5	0.0225 (8)	0.0160 (7)	0.0132 (6)	0.0040 (5)	−0.0004 (5)	−0.0014 (5)
O6	0.0208 (8)	0.0108 (6)	0.0242 (7)	0.0015 (5)	0.0000 (6)	0.0002 (5)
O7	0.0264 (8)	0.0231 (7)	0.0143 (6)	−0.0016 (6)	0.0053 (6)	−0.0010 (5)
N3	0.0149 (8)	0.0133 (8)	0.0129 (7)	0.0010 (6)	0.0009 (6)	0.0006 (6)
C8	0.0143 (9)	0.0134 (9)	0.0156 (8)	0.0009 (7)	−0.0007 (7)	−0.0005 (7)
C9	0.0186 (10)	0.0131 (9)	0.0157 (8)	0.0004 (7)	0.0015 (7)	0.0000 (7)
C10	0.0193 (10)	0.0129 (9)	0.0167 (9)	0.0004 (7)	−0.0020 (7)	−0.0006 (7)
C11	0.0162 (10)	0.0197 (10)	0.0181 (9)	0.0005 (8)	0.0027 (7)	−0.0016 (7)

Geometric parameters (Å, º)

O1—C7	1.270 (2)	O5—H5O	0.844 (9)
O2—C7	1.264 (2)	O6—C10	1.421 (2)
O3—N2	1.233 (2)	O6—H6O	0.841 (10)
O4—N2	1.228 (2)	O7—C11	1.429 (2)
N1—C2	1.366 (2)	O7—H7O	0.844 (10)
N1—H1N	0.882 (9)	N3—C8	1.501 (2)
N1—H2N	0.877 (10)	N3—H3N	0.888 (9)
N2—C4	1.473 (2)	N3—H4N	0.885 (9)
C1—C6	1.404 (3)	N3—H5N	0.894 (9)
C1—C2	1.416 (3)	C8—C11	1.520 (2)
C1—C7	1.503 (3)	C8—C10	1.528 (2)
C2—C3	1.408 (3)	C8—C9	1.535 (2)
C3—C4	1.378 (3)	C9—H9A	0.9900
C3—H3	0.9500	C9—H9B	0.9900
C4—C5	1.389 (3)	C10—H10A	0.9900
C5—C6	1.384 (3)	C10—H10B	0.9900
C5—H5	0.9500	C11—H11A	0.9900
C6—H6	0.9500	C11—H11B	0.9900
O5—C9	1.428 (2)		

C2—N1—H1N	117.5 (14)	C8—N3—H3N	112.3 (13)
C2—N1—H2N	117.1 (15)	C8—N3—H4N	110.4 (13)
H1N—N1—H2N	117 (2)	H3N—N3—H4N	104.7 (18)
O4—N2—O3	123.12 (16)	C8—N3—H5N	109.9 (13)
O4—N2—C4	118.36 (15)	H3N—N3—H5N	111.1 (19)
O3—N2—C4	118.51 (15)	H4N—N3—H5N	108.2 (19)
C6—C1—C2	119.25 (17)	N3—C8—C11	107.84 (14)
C6—C1—C7	118.76 (16)	N3—C8—C10	107.31 (14)
C2—C1—C7	121.97 (16)	C11—C8—C10	111.52 (15)
N1—C2—C3	118.65 (17)	N3—C8—C9	109.24 (14)
N1—C2—C1	122.93 (17)	C11—C8—C9	109.60 (15)

C3—C2—C1	118.34 (16)	C10—C8—C9	111.22 (14)
C4—C3—C2	119.80 (17)	O5—C9—C8	113.65 (15)
C4—C3—H3	120.1	O5—C9—H9A	108.8
C2—C3—H3	120.1	C8—C9—H9A	108.8
C3—C4—C5	123.28 (17)	O5—C9—H9B	108.8
C3—C4—N2	117.63 (16)	C8—C9—H9B	108.8
C5—C4—N2	119.09 (16)	H9A—C9—H9B	107.7
C6—C5—C4	116.82 (17)	O6—C10—C8	111.71 (14)
C6—C5—H5	121.6	O6—C10—H10A	109.3
C4—C5—H5	121.6	C8—C10—H10A	109.3
C5—C6—C1	122.50 (17)	O6—C10—H10B	109.3
C5—C6—H6	118.7	C8—C10—H10B	109.3
C1—C6—H6	118.7	H10A—C10—H10B	107.9
O2—C7—O1	123.17 (17)	O7—C11—C8	108.12 (15)
O2—C7—C1	118.74 (16)	O7—C11—H11A	110.1
O1—C7—C1	118.06 (16)	C8—C11—H11A	110.1
C9—O5—H5O	107.9 (15)	O7—C11—H11B	110.1
C10—O6—H6O	108.1 (16)	C8—C11—H11B	110.1
C11—O7—H7O	109.4 (16)	H11A—C11—H11B	108.4

C6—C1—C2—N1	175.53 (16)	C2—C1—C6—C5	0.1 (3)
C7—C1—C2—N1	−5.8 (3)	C7—C1—C6—C5	−178.55 (16)
C6—C1—C2—C3	−1.2 (2)	C6—C1—C7—O2	−14.4 (2)
C7—C1—C2—C3	177.46 (15)	C2—C1—C7—O2	166.90 (16)
N1—C2—C3—C4	−175.49 (16)	C6—C1—C7—O1	163.83 (16)
C1—C2—C3—C4	1.4 (3)	C2—C1—C7—O1	−14.8 (2)
C2—C3—C4—C5	−0.5 (3)	N3—C8—C9—O5	−59.01 (18)
C2—C3—C4—N2	−179.78 (15)	C11—C8—C9—O5	−176.96 (14)
O4—N2—C4—C3	−174.88 (15)	C10—C8—C9—O5	59.3 (2)
O3—N2—C4—C3	6.3 (2)	N3—C8—C10—O6	−49.84 (19)
O4—N2—C4—C5	5.8 (2)	C11—C8—C10—O6	68.0 (2)
O3—N2—C4—C5	−173.00 (16)	C9—C8—C10—O6	−169.27 (15)
C3—C4—C5—C6	−0.5 (3)	N3—C8—C11—O7	−58.12 (18)
N2—C4—C5—C6	178.72 (15)	C10—C8—C11—O7	−175.70 (14)
C4—C5—C6—C1	0.7 (3)	C9—C8—C11—O7	60.70 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.88 (2)	2.02 (2)	2.678 (2)	131 (2)
N1—H1*N*···O3^{i}	0.88 (2)	2.50 (2)	3.210 (2)	138 (1)
N1—H2*N*···O4^{ii}	0.88 (1)	2.56 (2)	3.094 (2)	120 (2)
N3—H3*N*···O6^{iii}	0.89 (2)	2.34 (2)	2.934 (2)	124 (1)
N3—H3*N*···O7^{iv}	0.89 (2)	2.44 (2)	3.065 (2)	128 (2)
N3—H4*N*···O5^{v}	0.89 (1)	2.08 (1)	2.945 (2)	165 (2)
N3—H5*N*···O2^{vi}	0.89 (2)	1.92 (2)	2.773 (2)	160 (2)
O5—H5*O*···O2^{vii}	0.85 (2)	1.90 (2)	2.7453 (18)	175 (2)

O6—H6*O*···O1^{viii}	0.84 (2)	1.88 (2)	2.6993 (19)	163 (2)
O7—H7*O*···O1^{ix}	0.84 (2)	2.07 (2)	2.8905 (18)	164 (2)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+3/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*+2, *y*−1/2, −*z*+1/2; (iv) −*x*+2, −*y*+1, −*z*+1; (v) −*x*+2, *y*+1/2, −*z*+1/2; (vi) *x*+1, −*y*+1/2, *z*−3/2; (vii) −*x*+1, *y*−1/2, −*z*+1/2; (viii) −*x*+1, −*y*+2, −*z*+1; (ix) −*x*+1, *y*−1/2, −*z*+3/2.