Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS
ISSN 2056-9890

Two dialkylammonium salts of 2-amino-4-nitrobenzoic acid: crystal structures and Hirshfeld surface analysis

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Received 22 October 2016
Accepted 26 October 2016

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

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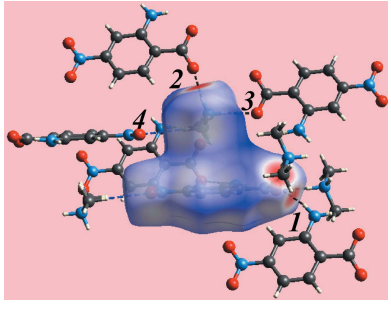
Keywords: crystal structure; carboxylate; salt; hydrogen bonding; Hirshfeld surface analysis.

CCDC references: 1511822; 1511821

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

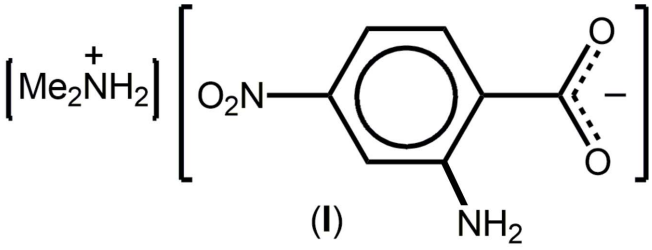
The crystal structures of two ammonium salts of 2-amino-4-nitrobenzoic acid are described, namely dimethylazanium 2-amino-4-nitrobenzoate, $C_2H_8N^+\cdot C_7H_5N_2O_4^-$, (I), and dibutylazanium 2-amino-4-nitrobenzoate, $C_8H_{20}N^+\cdot C_7H_5N_2O_4^-$, (II). The asymmetric unit of (I) comprises a single cation and a single anion. In the anion, small twists are noted for the carboxylate and nitro groups from the ring to which they are connected, as indicated by the dihedral angles of 11.45 (13) and 3.71 (15)°, respectively; the dihedral angle between the substituents is 7.9 (2)°. The asymmetric unit of (II) comprises two independent pairs of cations and anions. In the cations, different conformations are noted in the side chains in that three chains have an all-*trans* [(+)-antiperiplanar] conformation, while one has a distinctive kink resulting in a (+)-synclinal conformation. The anions, again, exhibit twists with the dihedral angles between the carboxylate and nitro groups and the ring being 12.73 (6) and 4.30 (10)°, respectively, for the first anion and 8.1 (4) and 12.6 (3)°, respectively, for the second. The difference between anions in (I) and (II) is that in the anions of (II), the terminal groups are conrotatory, forming dihedral angles of 17.02 (8) and 19.0 (5)°, respectively. In each independent anion of (I) and (II), an intramolecular amino-N—H···O(carboxylate) hydrogen bond is formed. In the crystal of (I), anions are linked into a jagged supramolecular chain by charge-assisted amine-N—H···O(carboxylate) hydrogen bonds and these are connected into layers *via* charge-assisted ammonium-N—H···O(carboxylate) hydrogen bonds. The resulting layers stack along the *a* axis, being connected by nitro-N—O···π(arene) and methyl-C—H···O(nitro) interactions. In the crystal of (II), the anions are connected into four-ion aggregates by charge-assisted amino-N—H···O(carboxylate) hydrogen bonding. The formation of ammonium-N—H···O(carboxylate) hydrogen bonds, involving all ammonium-N—H and carboxylate O atoms leads to a three-dimensional architecture; additional C—H···O(nitro) interactions contribute to the packing. The Hirshfeld surface analysis confirms the importance of the hydrogen bonding in both crystal structures. Indeed, O···H/H···O interactions contribute nearly 50% to the entire Hirshfeld surface in (I).



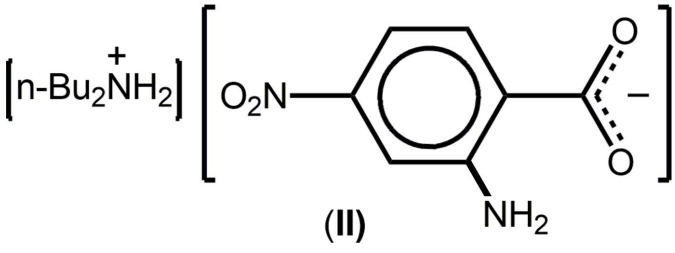
1. Chemical context

The simple carboxylic acid 2-amino-4-nitrobenzoic acid has been little studied from a crystallographic point of view: its molecular structure was only reported in 2011 (Wardell & Tiekink, 2011). Very recently, a number of polymorphs were described, *i.e.* with Z' = 1, 2 and 3 (Wardell & Wardell, 2016). The only other two structures described with 2-amino-4-nitrobenzoic acid are its 2:1 co-crystal with 2,2′-bipyridyl and

its 1:1 co-crystal with bis(pyridin-2-yl)methanone (Wardell & Tiekink, 2011). Besides the structure of a Pb^{II} coordination polymer (Chen & Huang, 2009), the remaining literature structures are salts featuring 2-amino-4-nitrobenzoic acid in its mono-anionic form, exclusively with a deprotonated carboxylate group. Thus, the structures of alkali metal salts, *i.e.* Na^+, K^+ (Smith, 2013), Rb^+ (Smith, 2014*a*) and Cs^+ (Smith & Wermuth, 2011) have been described along with a number of ammonium salts, *i.e.* with NH_4, as a hydrate (Smith, 2014*b*), dicyclohexylammonium (Smith *et al.*, 2004), guanidinium, as a hydrate (Smith *et al.*, 2007), morpholinium (Smith & Lynch, 2016) and ethylenediammonium, as a dihydrate (Smith *et al.*, 2002). As a continuation of our work in the area noted above (Wardell & Tiekink, 2011; Wardell & Wardell, 2016), we describe herein the crystal and molecular structures of two new anhydrous salts of 2-amino-4-nitrobenzoate, with the counter-cations $[Me_2NH_2]^+$ (I) and $[n\text{-}Bu_2NH_2]^+$ (II). Further insight into the self-assembly of the salts has been gained through a Hirshfeld surface analysis.



(I)



(II)

2. Structural commentary

The molecular structures of the constituents of (I) are shown in Fig. 1; the asymmetric unit comprises one cation and one anion. Confirmation of proton transfer during recrystallization of dimethylamine and 2-amino-4-nitrobenzoic acid is found in (i) the similarity of the C—O bond lengths [C7—O1, O2 = 1.2587 (17) and 1.2609 (16) Å, respectively] and (ii) the pattern of hydrogen bonding as discussed in *Supramolecular features*. The molecular structure of the cation is unremarkable with a C8—N3—C9 angle of 113.54 (11)°. The anion features an intramolecular amino-N—H···O(carboxylate) hydrogen bond (Table 1). Despite the presence of this interaction, there are small twists in the molecule as seen in the values of the C2—C1—C7—O2 and O3—N2—C4—C3 torsion angles of 169.51 (12) and 4.04 (19)°, respectively. In terms of dihedral angles, the angles between the central ring and the carboxylate and nitro groups are 11.45 (13) and 3.71 (15)°, respectively. The carboxylate and nitro substituents

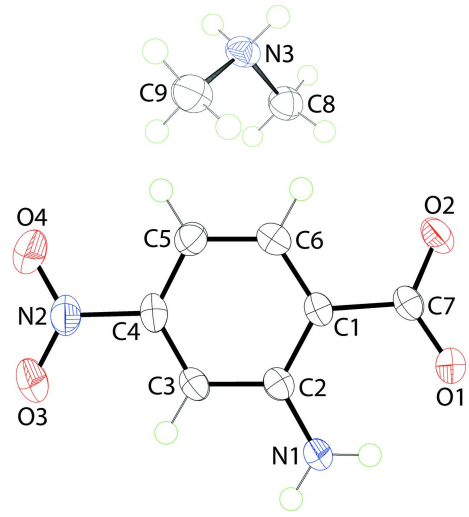


Figure 1
The molecular structure of the constituents of (I), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

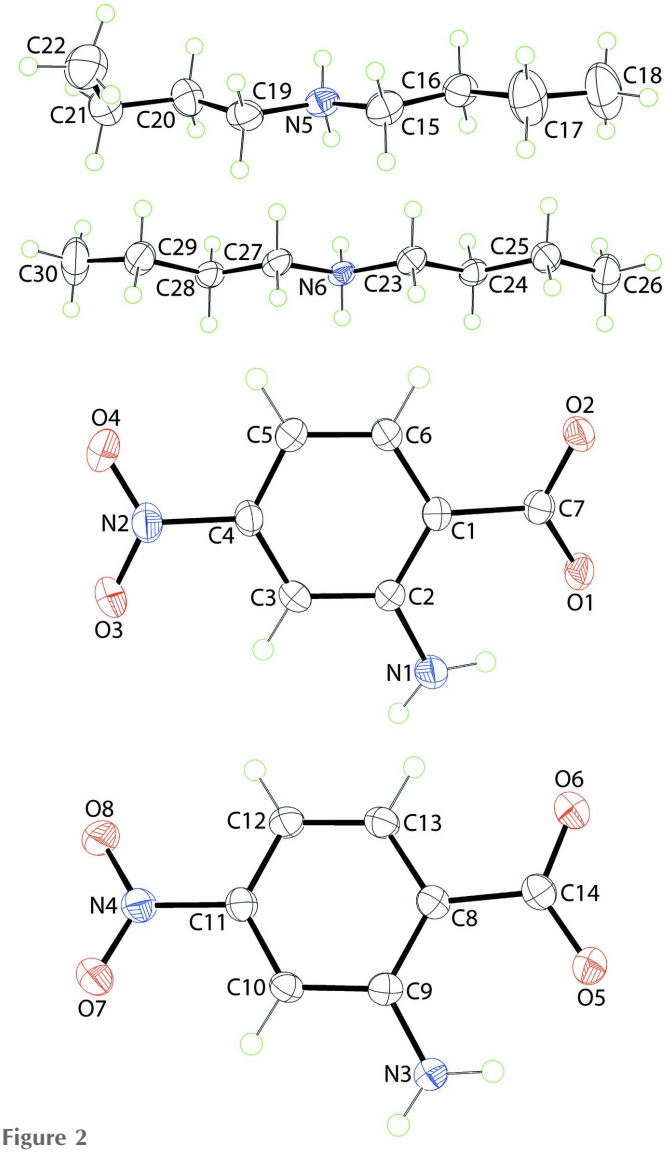


Figure 2
The molecular structure of the constituents of (II), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

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

*Cg*1 is the centroid of the (C1–C6) ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.869 (18)	2.012 (18)	2.6694 (17)	131.6 (15)
N1—H2*N*···O2^{i}	0.889 (18)	2.019 (18)	2.8900 (16)	166.2 (16)
N3—H3*N*···O1^{ii}	0.944 (17)	1.774 (17)	2.7141 (15)	173.4 (15)
N3—H4*N*···O2^{iii}	0.919 (16)	1.834 (15)	2.7385 (15)	167.6 (15)
C8—H8*C*···O4^{iv}	0.98	2.48	3.4589 (19)	174
N2—O4···*Cg*1^{v}	1.23 (1)	3.40 (1)	4.3668 (14)	136 (1)
C9—H9*C*···*Cg*1	0.98	2.64	3.5512 (16)	154

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.88 (1)	1.98 (2)	2.696 (2)	137 (2)
N1—H2*N*···O5^{i}	0.88 (2)	2.38 (2)	3.226 (3)	160 (2)
N3—H3*N*···O5	0.88 (2)	2.01 (2)	2.714 (3)	136 (2)
N3—H4*N*···O2^{ii}	0.88 (2)	2.19 (2)	3.052 (2)	168 (2)
N5—H5*N*···O5	0.88 (2)	1.89 (2)	2.757 (3)	166 (2)
N5—H6*N*···O6^{iii}	0.89 (2)	1.81 (2)	2.697 (3)	173 (2)
N6—H7*N*···O2	0.89 (2)	1.89 (2)	2.759 (2)	167 (2)
N6—H8*N*···O1^{iv}	0.89 (2)	1.85 (2)	2.712 (2)	163 (2)
C19—H19*A*···O7^{v}	0.99	2.56	3.343 (3)	136
C20—H20*B*···O6^{iii}	0.99	2.56	3.297 (3)	131
C27—H27*A*···O4^{vi}	0.99	2.57	3.550 (3)	169

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

are in the same relative orientation with the dihedral angle between them being 7.9 (2)°.

The asymmetric unit of (II) comprises two independent pairs of cations and anions. The molecular structures of these are shown Fig. 2. As for (I), the confirmation for proton transfer from acid to base is seen in the equivalence of the C—O [C7—O1, O2 = 1.262 (2) and 1.267 (3) Å, respectively and C14—O5, O6 = 1.269 (3) and 1.256 (3) Å, respectively] bond lengths and in the pattern of intermolecular interactions, see below. The C15—N5—C19 and C23—N6—C27 angles in the cations are 113.40 (19) and 112.99 (17)°, respectively, *i.e.* similar to the comparable angle in (I). The cations adopt different conformations as seen in the relative orientations of the terminal methyl groups. For the N5-cation, this is quantified in the values of the C15—C16—C17—C18 and C19—C20—C21—C22 torsion angles of 171.9 (3) and 49.5 (3)°, respectively, consistent with a (+)-antiperiplanar (+ap) and a (+)-synclinal (+sc) conformation, respectively. In the N6-cation, each chain is +ap, *i.e.* with torsion angles of 173.0 (2)° (C23-chain) and 176.0 (2)° (C27-chain). The anions present similar conformations as in (I) and each features an intramolecular amino-N—H···O(carboxylate) hydrogen bond, Table 2. However, there are some subtle differences between the anions in terms of the relationship between the central rings and terminal substituents. For the O1-anion, the angles between the central ring and the carboxylate and nitro groups are 12.73 (6) and 4.30 (10)°, respectively, and the comparable

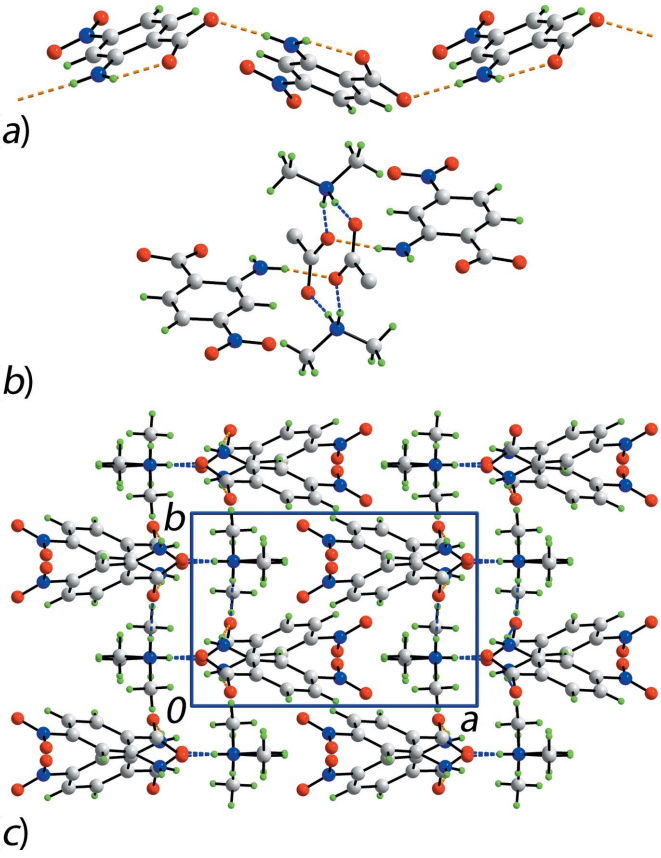


Figure 3
The molecular packing in (I), showing (*a*) supramolecular chain comprising anions only, orientated along the *c* axis and sustained by amino-N—H···O(carboxylate) interactions shown as orange dashed lines, (*b*) detail of the 12-membered {···HNH···OCO}$_2$ synthon with ammonium-N—H···O(carboxylate) hydrogen bonds shown as blue dashed lines and (*c*) a view of the unit-cell contents in projection down the *c* axis. In part (*b*), all but the CO$_2$ groups of the two central benzoate residues have been removed for clarity.

angles for the O5-cation are 8.1 (4) and 12.6 (3)°, respectively. The difference between (I) and (II) is that in the cations of (II), the terminal groups are con-rotatory, forming dihedral angles of 17.02 (8) and 19.0 (5)°, respectively.

3. Supramolecular features

As mentioned above, one H atom of the amino group forms an intramolecular hydrogen bond with the carboxylate-O1 atom. The second amino-H atom in (I) forms an intermolecular, charge-assisted amino-N—H···O2(carboxylate) hydrogen bond to link anions into a supramolecular chain, with a jagged topology, aligned along the *c* axis, Fig. 3*a*. Translationally-related chains stack along the *a* axis to define cavities in which reside the [Me$_2$NH$_2$]$^+$ cations. These serve to link the anionic chains into layers *via* charge-assisted ammonium-N—H···O(carboxylate) hydrogen bonds, involving both carboxylate-O atoms. This association leads to the formation of centrosymmetric, 12-membered {···HNH···OCO}$_2$ synthons, Fig. 3*b*. Layers stack along the *a* axis with the most notable interactions between the layers being nitro-N—

O···π(arene) and methyl-C—H···O(nitro) contacts. The nitro-O4 atom is crucial in the formation of these contacts, being the donor and acceptor, respectively, Table 1, Fig. 3*c*.

The crystal of (II) features extensive N—H···O hydrogen bonding, Table 2. The anions assemble into four-ion aggregates as a result of charge-assisted amino-N—H···O(carboxylate) hydrogen bonding. For the O1-anion, the carboxylate-O atom not participating in the intramolecular amino-N—H···O interaction forms an intermolecular amino-N—H···O interaction. However, for the O5-anion, the carboxylate-O atom participating in the intramolecular amino-N—H···O interaction also forms the intermolecular amino-N—H···O contact, as illustrated in Fig. 4*a*. The result of this self-assembly is a centrosymmetric, 20-membered {···HNH···OCO···HNH···O}$_2$ ring which encompasses two {···HNC$_3$O} loops formed by the intramolecular amino-N—H···O(carboxylate) hydrogen bonds. Each of the cations associates with two anions in a very similar fashion to that in (I), in that the H atoms of the N5-ammonium cation bridge two O1-anions over a centre of inversion to form a centrosymmetric, 12-membered {···HNH···OCO}$_2$ synthon, Fig. 4*b*. The N6-ammonium H atoms form similar bridges but with the O5-anion. The result is the formation of a three-dimensional architecture, Fig. 4*c*.

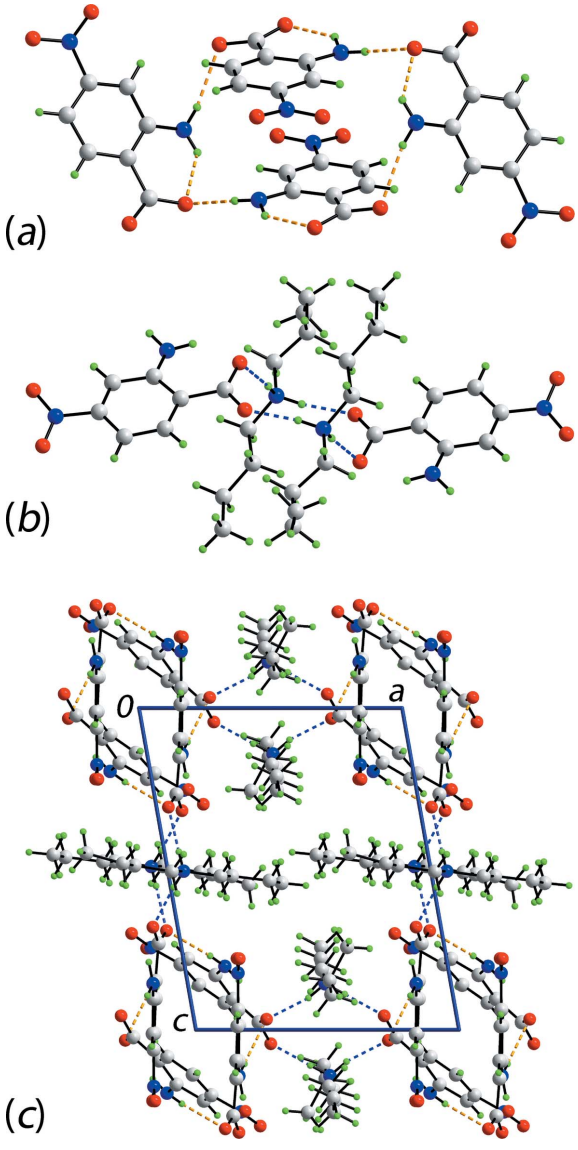


Figure 4
The molecular packing in (II), showing (*a*) four-anion aggregate sustained by amino-N—H···O(carboxylate) interactions shown as orange dashed lines, (*b*) detail of the 12-membered {···HNH···OCO}$_2$ synthon with ammonium-N—H···O(carboxylate) hydrogen bonds shown as blue dashed lines and (*c*) a view of the unit-cell contents in projection down the *b* axis.

4. Hirshfeld surface analysis

Hirshfeld surface analysis for (I) and (II) was carried out as described previously (Cardoso *et al.*, 2016). In the two views of

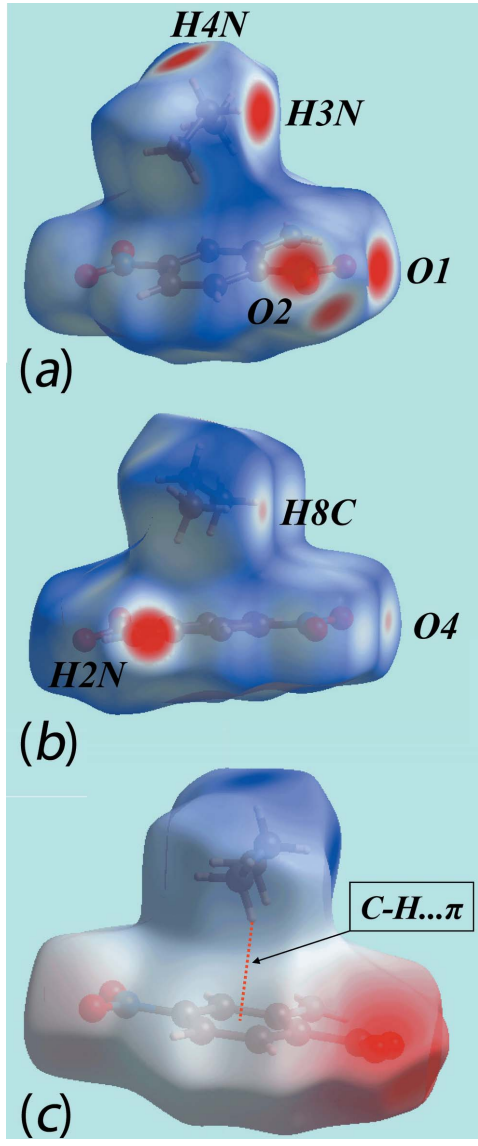


Figure 5
Views of Hirshfeld surfaces for (I) mapped over (*a*) and (*b*) d_{norm} and (*c*) the electrostatic potential (the red and blue regions represent negative and positive electrostatic potentials, respectively).

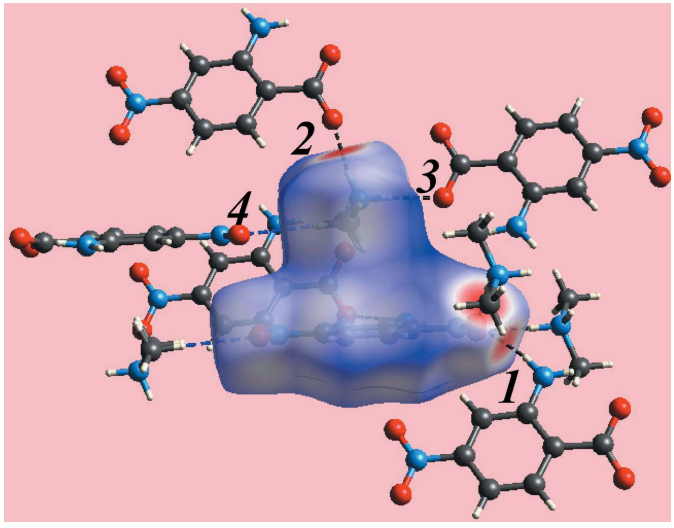


Figure 6
A view of Hirshfeld surface mapped over d_{norm} for (I), showing N—H···O hydrogen bonds about the reference molecule. The hydrogen bonds are indicated with black dashed lines and are labelled as 1, 2 and 3. The intermolecular C—H···O interaction is indicated with a blue dashed line and with label 4.

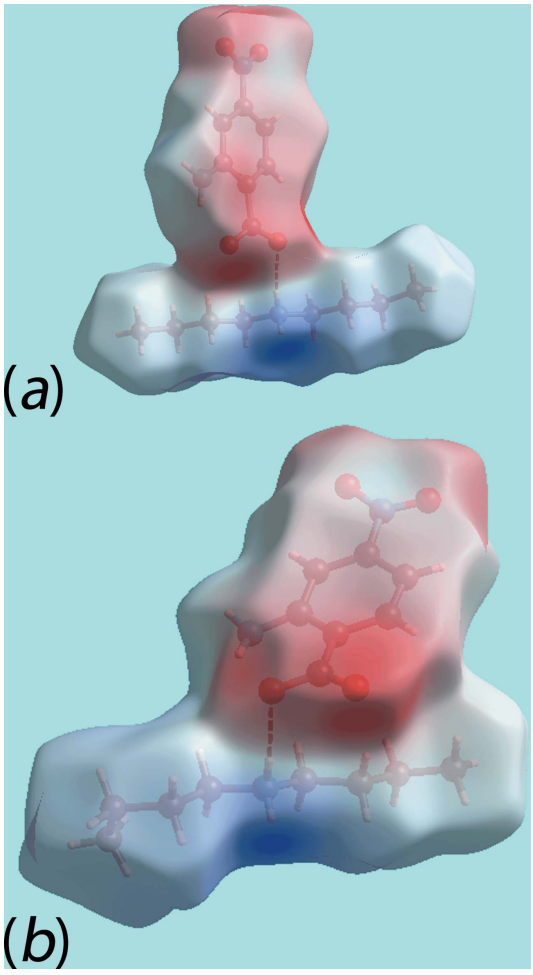


Figure 7
A view of Hirshfeld surface mapped over the electrostatic potential for (II) showing the N—H···O hydrogen bond leading to ion-pairs (*a*) 1 and (*b*) 2. The hydrogen bonds are indicated with black dashed lines.

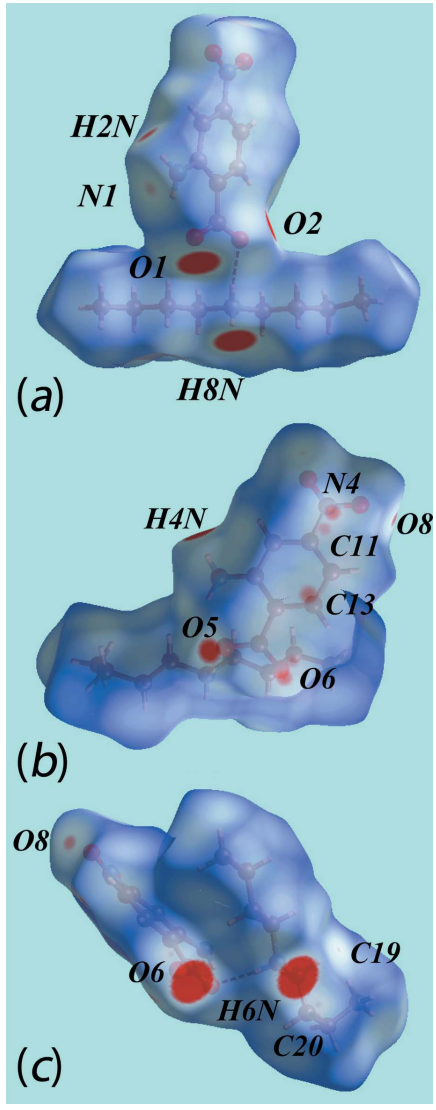


Figure 8
Views of Hirshfeld surfaces mapped over d_{norm} for (II), showing (*a*) ion-pair 1 in the range −0.2 to + 1.8 au, (*b*) ion-pair 2 in the range −0.2 to + 1.6 au and (*c*) ion-pair 2 in the range −0.1 to + 1.6 au.

the Hirshfeld surface for (I) mapped over d_{norm} in the range −0.3 to + 1.8 au shown in Fig. 5*a* and *b*, the bright-red spots appearing near the amino-H2*N*, ammonium-H3*N* and H4*N*, and carboxylate-O1 and O2 atoms represent donors and acceptors of the dominating hydrogen bonds; they are viewed as blue and red regions on Hirshfeld surfaces mapped over electrostatic potential in the range −0.24 to + 0.31 au in Fig. 5*c* and correspond to positive and negative potentials, respectively. The faint-red spots at the methyl-H8*C* and nitro-O4 atoms in Fig. 5*b* are due to the presence of comparatively weak C—H···O interactions. Also from Fig. 5*c*, it is evident that the electrostatic coulombic interaction between the dimethylammonium and 2-amino-4-nitrobenzoate species results in a cation–anion pair through a C—H···π contact between methyl-H9*C* and the benzene (C1–C6) ring, as highlighted by the dotted bond. The immediate environment about the ion-pair within the Hirshfeld surface mapped over d_{norm} mediated by the above interactions is illustrated in Fig. 6.

Table 3
Summary of short interatomic contacts (Å) in (I) and (II).

Contact	Distance	Symmetry operation
(I)		
O4···H9*B*	2.70	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
C3···H8*A*	2.89	*x*, *y*, *z*
(II)		
O8···H2*N*	2.70 (2)	$1+x, 1+y, z$
O6···N4	2.994 (2)	$2-x, 1-y, -z$
O6···C11	3.179 (3)	$2-x, 1-y, -z$
C13···C13	3.310 (3)	$2-x, 1-y, -z$
H19*A*·O7	2.56	$-1+x, y, z$
H20*B*···O6	2.56	$1-x, 1-y, -z$
H27*A*···O4	2.57	$x, y, 1+z$
H3···H3*N*	2.26	$1-x, 1-y, -z$
H5···H13	2.33	$1-x, 1-y, -z$
H18*B*···H22*B*	2.37	$x, 1+y, z$
O1···H28*A*	2.66	*x*, *y*, *z*
O5···H3	2.70	$1-x, -y, z$
O7···H25*A*	2.64	$1-x, 1-y, 1-z$
O8···H25*A*	2.66	$1-x, 1-y, 1-z$
C7···H4*N*	2.89 (2)	$-1+x, y, z$
C7···H7*N*	2.76 (2)	*x*, *y*, *z*
C7···H8*N*	2.78 (2)	$-x, -y, 1-z$
C10···H6	2.89	$1+x, y, z$
C14···H6*N*	2.78 (2)	$1-x, 1-y, -z$
C22···H27*B*	2.83	*x*, *y*, *z*
N2···H21*B*	2.72	$1-x, -y, -z$
C12···C14	3.391 (3)	$2-x, 1-y, -z$

In the crystal of the dibutylammonium salt, (II), each of the two independent pairs of cations and anions are connected by charge-assisted ammonium-N—H···O(carboxylate) hydrogen bonds. The Hirshfeld surfaces for each of the independent pairs, hereafter referred as ion-pair 1 (involving the N4-cation and O1-anion) and ion-pair 2 (involving the N3-cation and O5-anion), were generated as well that for the entire structure of (II). The Hirshfeld surfaces mapped over the electrostatic potential for the ion-pairs are shown in Fig. 7.

Views of Hirshfeld surfaces mapped over d_{norm}, in the ranges −0.2 to +1.8 au for ion-pair 1, Fig. 8*a*, −0.1 to +1.6 au for ion-pair 2, Fig. 8*b*, and in order to reveal more detail (red-spots) on the surface, −0.1 to +1.6, for ion-pair 2, Fig. 8*c*. The bright-red spots appearing near amino-H2*N* and H4*N*, ammonium-H6*N* and H8*N*, and carboxylate-O1, O2, O5 and O6 atoms indicate donors and acceptors of charge-assisted N—H···O hydrogen bonds between the respective ion-pairs. The short interatomic O···H contact between the amino-H2*N* and nitro-O8 atoms, Table 3, is evident from the faint-red spots at the N1, Fig. 8*a*, and nitro-O8 atoms, Fig. 8*c*. The faint-red spots present in Fig. 8*b* near atoms N4, C11, C13 and O6 of ion-pair 2 indicate their participation in short interatomic contacts in the crystal, Table 3. As the intermolecular C—H···O interactions involving the butyl-C19- and C20-H atoms of ion-pair 2 are very weak compared to the above, they only appear as very faint spots in Fig. 8*c*; the C27—H27*A*···O4 interaction is even weaker than these, showing no spots even at the lower d_{norm} range. The immediate environments about the ion-pairs within d_{norm} mapped Hirshfeld surface mediated by N—H···O hydrogen-bonding interactions are illustrated in Fig. 9.

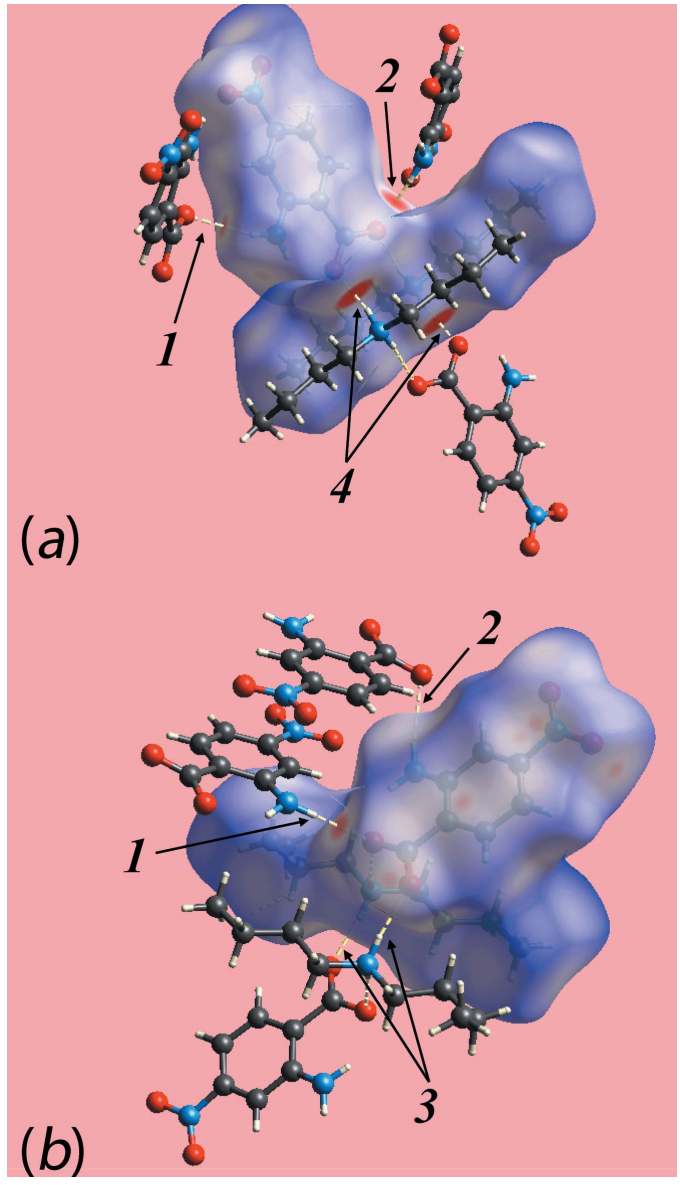


Figure 9
The immediate environment about reference ion-pairs within Hirshfeld surfaces mapped over d_{norm} showing N—H···O hydrogen bonding in (II), showing (*a*) ion-pair 1 and (*b*) ion-pair 2.

The overall two-dimensional fingerprint plots for (I), ion-pair 1 in (II), ion-pair 2 in (II) and (II), and those delineated into H···H, O···H/H···O, C···O/O···C, C···H/H···C, N···H/H···N and C···C contacts (McKinnon *et al.*, 2007) are shown in Fig. 10*a*–*g*, respectively. The relative contributions from different contacts to the Hirshfeld surfaces of (I) and (II) are summarized in Table 4.

The fingerprint plot delineated into O···H/H···O contacts for (I), Fig. 10*c*, shows that these contacts make the most significant contribution, *i.e.* almost half (49.4%), to the Hirshfeld surface. This may be due to salt formation through electrostatic interactions resulting in only a few hydrogen atoms being available on the surface to form interatomic H···H and other contacts. This is also reflected in a comparatively low contribution from H···H contacts to the

Table 4
Percentage contribution to interatomic contacts from the Hirshfeld surface for (I) and (II).

Contact	(I)	(II) - pair 1	(II) - pair 2	(II)
H···H	30.8	55.5	53.3	53.4
O···H/H···O	49.4	29.4	30.9	31.9
C···H/H···C	8.5	8.4	9.6	7.7
C···O/O···C	4.8	1.5	1.1	1.4
N···H/H···N	3.3	2.0	2.2	2.2
O···O	2.3	0.3	0.7	0.6
N···O/O···N	0.9	0.3	1.0	0.7
C··· C	0.0	1.4	1.2	1.4
C···N/N···C	0.0	0.7	0.0	0.4
N··· N	0.0	0.5	0.0	0.3

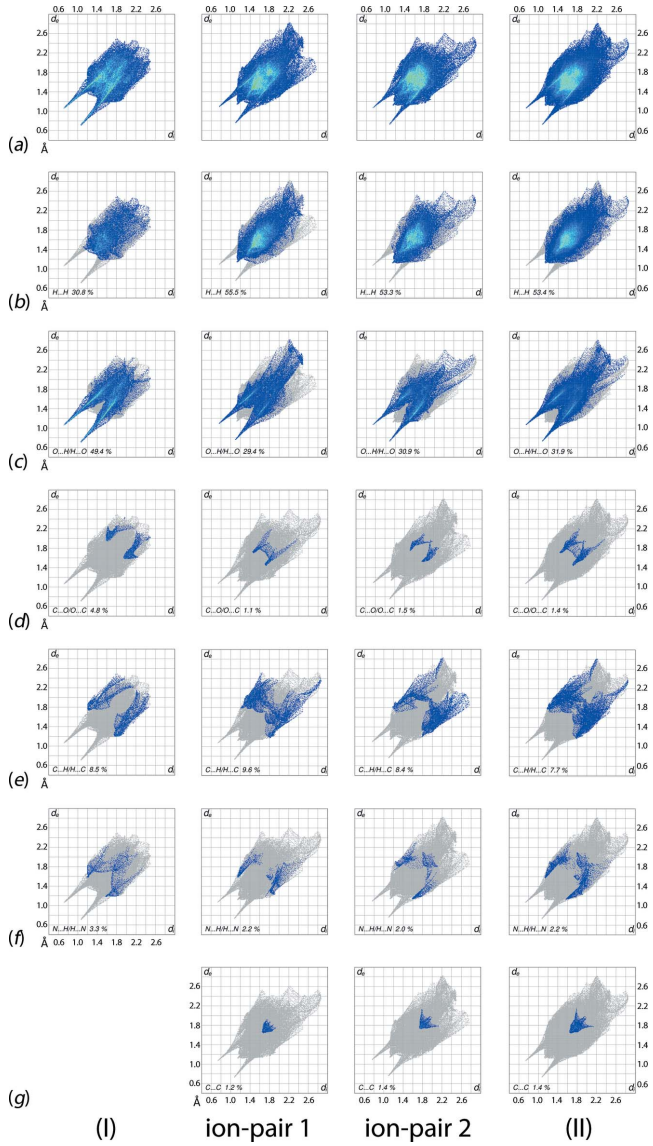


Figure 10
Comparison between (I), ion-pair 1 in (II), ion-pair 2 in (II) and (II) of the (*a*) full two-dimensional fingerprint plots, and the plots delineated into (*b*) H···H, (*c*) O···H/H···O, (*d*) C···O/O···C, (*e*) C···H/H···C, (*f*) N···H/H···N and (*g*) C···C contacts.

Hirshfeld surface, Fig. 10*b* and Table 4. A pair of long spikes with tips at $d_e + d_i$ ∼1.8 Å in Fig. 10*c* is the result of charge-assisted N—H···O hydrogen bonds, Table 1. The significant contributions from O···H/H···O to the Hirshfeld surfaces are also due to the presence of short interatomic O···H/H···O, C—H···O and N—H···O interactions, Tables 1 and 3. The fingerprint plot delineated into C···O/O···C contacts, Fig. 10*d*, having a fin-like distribution of points with tips at $d_e + d_i$ ∼3.5 Å and a 4.8% contribution to the surface, indicate the presence of influential N—O···π and C—H···O interactions in the crystal of (I), Tables 1 and 3. The 8.5% contribution from C···H/H·C contacts, Fig. 10*e*, is the result of a short interatomic contact, Table 3, and an intra-ion-pair methyl-C—H···π interaction within the cation–anion pair.

In the structure of (II), the most significant contribution to the Hirshfeld surface is from H···H contacts, an observation clearly related to the hydrogen-rich *n*-butyl side chains in the cations, *cf.* (I). This is also reflected through the appearance of green points in the fingerprint plot delineated into H···H contacts, Fig. 10*b*, and in the nearly same percentage contribution from these contacts in the plots for each ion-pair and overall Hirshfeld surface, Table 4. A pair of small peaks at $d_e + d_i$ ∼2.2 Å in Fig. 10*b* is the result of short interatomic H···H contacts in the crystal, Table 3.

A pair of long spikes with the tips at $d_e + d_i$ ∼1.8 Å in the fingerprint delineated into O···H/H···O contacts, Fig. 10*c*, are a result of the N—H···O hydrogen bonds. A pair of regions comprising aligned green points in the plot beginning at $d_e + d_i$ ∼2.7 Å are due to short interatomic O···H/H···O contacts present in the structure, Table 3. The distinct shapes in the fingerprint plots delineated into C···H/H···C contacts for ion-pairs 1 and 2, Fig. 10*e*, and their different percentage contributions to the respective Hirshfeld surfaces, Table 4, reflect the different conformations of the butyl chains in the cations; the small tips at $d_e + d_i$ ∼2.9 Å in the overall plot indicate short interatomic C···H/H···C contacts, Table 3.

Though the interatomic N···H/H···N, C···O/O···C and C···C contacts each makes a small percentage contribution to the Hirshfeld surface of (II), they reflect recognizable intermolecular interactions in the crystal. A short interatomic N···H/H···N contact between nitro-N2 and butyl-H21*B* is evident as a thin edge at $d_e + d_i$ ∼2.7 Å in the overall fingerprint plot which results from the superposition of the indivi-

Table 5
Geometric data (°) for ammonium salts of 2-amino-4-nitrobenzoate.

cation	Z'	C_6/CO_2	C_6/NO_2	CO_2/NO_2	Ref.
$[NH_4]^+$	1	26.4 (3)	2.9 (3)	24.1 (4)	Smith (2014*b*)
$[Cy_2NH_2]^+$	2	9.87 (10)	7.58 (15)	3.42 (19)	Smith *et al.* (2004)
		9.52 (9)	7.86 (11)	3.92 (2)	
$[(H_2N)_2C{=}NH_2]^+$	1	5.88 (11)	5.64 (12)		Smith *et al.* (2007)
$[O(CH_2CH_2)_2NH_2]^+$	1	17.92 (9)	1.28 (11)	19.19 (13)	Smith & Lynch (2016)
$[H_3NCH_2CH_2NH_3]^{2+}$	1	3.44 (14)	0.69 (11)	3.2 (2)	Smith *et al.* (2002)
$[Me_2NH_2]^+$	1	11.45 (13)	3.71 (15)	7.9 (2)	this work
$[n\text{-}Bu_2NH_2]^+$	2	12.73 (6)	4.30 (10)	17.02 (8)	this work
		8.1 (4)	12.6 (3)	19.0 (5)	

dual plots for ion-pairs 1 and 2, Fig. 10*f*. The overall 1.4% contribution from C···O/O···C contacts results from short interatomic C···O contacts, Table 3, and from C—H···O interactions involving butyl-C19, C20 and C27 and nitro-O4 and carboxylate-O6 and O7 atoms, Table 3. These intermolecular interactions are also viewed as a pair of short thick edges at $d_e + d_i$ ~3.2 Å in the overall fingerprint plot delineated into these contacts, Fig.10*d*.

The overall 1.4% contribution from C···C contacts to the Hirshfeld surfaces, Fig. 10*g*, is the result of π–π stacking between inversion-related benzene (C1–C6) rings [$Cg\cdots Cg$ = 3.9250 (13) Å; symmetry operation: $-x, -y, -z$] of ion-pair 1 and a 1.2% contribution from short C···C contacts in ion-pair 2, Table 3. In the fingerprint plot, the presence of π–π stacking interaction is viewed as a peak at $d_e + d_i$ ~3.4 Å, Fig. 10*g*.

5. Database survey

As indicated in the *Chemical context*, a good number of ammonium salts of anions derived from 2-amino-4-nitrobenzoic acid have been described in the crystallographic literature. Salient geometric data for these are collated in Table 5. The consistent feature of the 2-amino-4-nitrobenzoate anions is deprotonation of the original carboxylic acid. Most of the dianions are relatively close to being planar with the outlier structures being the salts with $[NH_4]^+$ (Smith, 2014*b*), with a dihedral angle of 26.4 (3)° between the C_6 ring and the carboxylate group, and (II) with a dihedral angle of 12.6 (3)° between the the nitro group and the C_6 ring. The greatest twist between the carboxylate and nitro substituents in any of the anions included in Table 3 is 24.1 (4)°, which also occurs in the aforementioned ammonium salt (Smith, 2014*b*).

Table 6
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_2H_8N^+\cdot C_7H_5N_2O_4^-$	$C_8H_{20}N^+\cdot C_7H_5N_2O_4^-$
M_r	227.22	311.38
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
Temperature (K)	120	120
a, b, c (Å)	11.2593 (5), 7.5563 (2), 13.0437 (6)	11.1615 (3), 12.5172 (4), 13.2399 (4)
α, β, γ (°)	90, 96.716 (2), 90	82.405 (1), 78.107 (2), 70.915 (2)
V (Å^3)	1102.13 (8)	1706.36 (9)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.09
Crystal size (mm)	0.35 × 0.25 × 0.16	0.20 × 0.14 × 0.12
Data collection		
Diffractometer	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)
T_{min}, T_{max}	0.649, 0.746	0.665, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15431, 2537, 1952	34976, 7811, 5022
R_{int}	0.051	0.074
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.125, 1.01	0.062, 0.180, 1.03
No. of reflections	2537	7811
No. of parameters	159	425
No. of restraints	0	8
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.24, −0.31	0.85, −0.40

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).

6. Synthesis and crystallization

The salts were isolated from the very similar reaction conditions. A solution of the respective R_2NH amine (0.1 mmol) in EtOH (5 ml) and 4-nitroanthranilic acid (0.1 mmol) in EtOH (10 ml) were mixed and left at room temperature. The yellow blocks of (I) and orange blocks of (II), which had formed after 4 days, were collected and used as such in the structure determinations. *R* = Me salt: M.p. 428–431 (*dec*.) K. IR (KBr, cm^{-1}) 3400–2500 (*br*), 1630, 1553, 1424, 1347, 1267, 1078, 822, 724, 692, 573 cm^{-1}. *R* = *n*-Bu salt: M.p. 415–417 (*dec*.) K. IR: 3400–2500 (*br*) 1626, 1535, 1535, 1348, 1323, 1261, 825, 735 cm^{-1}.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. 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 N-bound H atoms were located from difference maps but, refined with N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(N). In (II), owing to poor agreement, one reflection, *i.e.* ($\overline{1}11$), was omitted. Further, the maximum and minimum residual electron density peaks of 0.85 and 0.40 e $Å^{-3}$, respectively, were located 0.92 and 0.64 Å from the H21*A* and C22 atoms, respectively.

Acknowledgements

The authors thank the National Crystallographic Service, based at the University of Southampton, for collecting the data. JLW thanks CNPq, Brazil, for a grant. Sunway University is also thanked for support through Grant No. INT-FST-RCCM-2016-01.

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supporting information

Acta Cryst. (2016). E**72**, 1691-1699 [https://doi.org/10.1107/S2056989016017266]

Two dialkylammonium salts of 2-amino-4-nitrobenzoic acid: crystal structures and Hirshfeld surface analysis

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Computing details

For both compounds, 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).

(I) Dimethylazanium 2-amino-4-nitrobenzoate

Crystal data

$C_2H_8N^+·C_7H_5N_2O_4^-$
M_r = 227.22
Monoclinic, $P2_1/c$
a = 11.2593 (5) Å
b = 7.5563 (2) Å
c = 13.0437 (6) Å
β = 96.716 (2)°
V = 1102.13 (8) Å^3
Z = 4
$F(000)$ = 480
D_x = 1.369 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 11561 reflections
θ = 2.9–27.5°
μ = 0.11 mm^{-1}
T = 120 K
Block, yellow
0.35 × 0.25 × 0.16 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} = 0.649, T_{max} = 0.746
15431 measured reflections
2537 independent reflections
1952 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −14→14
k = −9→9
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.125
S = 1.01
2537 reflections
159 parameters
0 restraints
Hydrogen site location: mixed
$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2 + 0.2595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 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	0.03429 (9)	0.26005 (14)	0.33705 (8)	0.0267 (3)
O2	0.13527 (9)	0.07211 (13)	0.44549 (7)	0.0247 (3)
O3	0.51006 (10)	0.21618 (17)	0.03910 (9)	0.0389 (3)
O4	0.61013 (10)	0.06520 (18)	0.16030 (9)	0.0421 (3)
N1	0.11153 (11)	0.31535 (17)	0.15387 (10)	0.0251 (3)
H1N	0.0543 (16)	0.334 (2)	0.1919 (14)	0.030*
H2N	0.1060 (15)	0.355 (2)	0.0893 (14)	0.030*
N2	0.51972 (10)	0.14316 (17)	0.12332 (9)	0.0260 (3)
C1	0.22560 (12)	0.16283 (17)	0.29838 (10)	0.0179 (3)
C2	0.21430 (12)	0.23829 (17)	0.19798 (10)	0.0184 (3)
C3	0.31350 (12)	0.22848 (18)	0.14090 (10)	0.0197 (3)
H3	0.3084	0.2758	0.0730	0.024*
C4	0.41748 (12)	0.14978 (18)	0.18468 (11)	0.0210 (3)
C5	0.43157 (12)	0.07721 (18)	0.28298 (11)	0.0219 (3)
H5	0.5049	0.0248	0.3113	0.026*
C6	0.33365 (12)	0.08477 (18)	0.33791 (11)	0.0214 (3)
H6	0.3403	0.0348	0.4052	0.026*
C7	0.12404 (12)	0.16464 (17)	0.36448 (10)	0.0193 (3)
N3	0.14643 (10)	−0.25004 (16)	0.04241 (9)	0.0220 (3)
H3N	0.0796 (15)	−0.249 (2)	0.0799 (13)	0.026*
H4N	0.1435 (14)	−0.349 (2)	0.0013 (13)	0.026*
C8	0.14422 (13)	−0.0913 (2)	−0.02465 (12)	0.0270 (3)
H8A	0.1384	0.0153	0.0173	0.041*
H8B	0.0750	−0.0976	−0.0776	0.041*
H8C	0.2178	−0.0866	−0.0579	0.041*
C9	0.25270 (13)	−0.2585 (2)	0.12109 (12)	0.0281 (3)
H9A	0.3256	−0.2555	0.0867	0.042*
H9B	0.2506	−0.3686	0.1606	0.042*
H9C	0.2521	−0.1571	0.1679	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0227 (5)	0.0347 (6)	0.0244 (5)	0.0062 (4)	0.0091 (4)	0.0055 (4)
O2	0.0312 (6)	0.0269 (5)	0.0173 (5)	−0.0004 (4)	0.0084 (4)	0.0029 (4)
O3	0.0322 (6)	0.0597 (8)	0.0275 (6)	0.0024 (5)	0.0153 (5)	0.0093 (5)
O4	0.0229 (6)	0.0656 (8)	0.0395 (7)	0.0111 (5)	0.0106 (5)	0.0060 (6)
N1	0.0211 (6)	0.0369 (7)	0.0182 (6)	0.0052 (5)	0.0062 (5)	0.0073 (5)
N2	0.0206 (6)	0.0340 (7)	0.0245 (7)	−0.0022 (5)	0.0072 (5)	−0.0024 (5)

C1	0.0199 (7)	0.0183 (7)	0.0162 (7)	−0.0022 (5)	0.0049 (5)	−0.0016 (5)
C2	0.0201 (7)	0.0187 (6)	0.0165 (7)	−0.0029 (5)	0.0027 (5)	−0.0015 (5)
C3	0.0218 (7)	0.0228 (7)	0.0149 (6)	−0.0028 (5)	0.0042 (5)	0.0003 (5)
C4	0.0189 (7)	0.0244 (7)	0.0209 (7)	−0.0034 (5)	0.0075 (5)	−0.0041 (5)
C5	0.0192 (7)	0.0248 (7)	0.0216 (7)	0.0008 (5)	0.0016 (5)	−0.0005 (5)
C6	0.0245 (7)	0.0223 (7)	0.0174 (7)	−0.0010 (5)	0.0023 (5)	0.0014 (5)
C7	0.0219 (7)	0.0207 (7)	0.0157 (7)	−0.0035 (5)	0.0042 (5)	−0.0021 (5)
N3	0.0202 (6)	0.0245 (6)	0.0223 (6)	−0.0031 (5)	0.0067 (5)	−0.0031 (5)
C8	0.0256 (8)	0.0287 (8)	0.0275 (8)	−0.0006 (6)	0.0063 (6)	0.0024 (6)
C9	0.0242 (8)	0.0299 (8)	0.0301 (8)	−0.0026 (6)	0.0024 (6)	−0.0009 (6)

Geometric parameters (Å, º)

O1—C7	1.2587 (17)	C4—C5	1.387 (2)
O2—C7	1.2609 (16)	C5—C6	1.3845 (19)
O3—N2	1.2227 (16)	C5—H5	0.9500
O4—N2	1.2252 (16)	C6—H6	0.9500
N1—C2	1.3614 (18)	N3—C8	1.4833 (19)
N1—H1N	0.870 (18)	N3—C9	1.4838 (19)
N1—H2N	0.890 (18)	N3—H3N	0.944 (18)
N2—C4	1.4777 (17)	N3—H4N	0.917 (17)
C1—C6	1.3953 (19)	C8—H8A	0.9800
C1—C2	1.4203 (19)	C8—H8B	0.9800
C1—C7	1.5106 (18)	C8—H8C	0.9800
C2—C3	1.4148 (19)	C9—H9A	0.9800
C3—C4	1.376 (2)	C9—H9B	0.9800
C3—H3	0.9500	C9—H9C	0.9800
C2—N1—H1N	118.6 (12)	C1—C6—H6	118.7
C2—N1—H2N	120.5 (11)	O1—C7—O2	123.67 (12)
H1N—N1—H2N	120.6 (16)	O1—C7—C1	118.62 (12)
O3—N2—O4	123.59 (12)	O2—C7—C1	117.70 (12)
O3—N2—C4	118.57 (12)	C8—N3—C9	113.54 (11)
O4—N2—C4	117.84 (12)	C8—N3—H3N	109.9 (10)
C6—C1—C2	119.38 (12)	C9—N3—H3N	105.6 (10)
C6—C1—C7	118.58 (12)	C8—N3—H4N	108.4 (10)
C2—C1—C7	122.04 (12)	C9—N3—H4N	109.9 (10)
N1—C2—C3	118.96 (12)	H3N—N3—H4N	109.5 (14)
N1—C2—C1	122.78 (12)	N3—C8—H8A	109.5
C3—C2—C1	118.23 (12)	N3—C8—H8B	109.5
C4—C3—C2	119.33 (12)	H8A—C8—H8B	109.5
C4—C3—H3	120.3	N3—C8—H8C	109.5
C2—C3—H3	120.3	H8A—C8—H8C	109.5
C3—C4—C5	123.67 (12)	H8B—C8—H8C	109.5
C3—C4—N2	117.95 (12)	N3—C9—H9A	109.5
C5—C4—N2	118.38 (12)	N3—C9—H9B	109.5
C6—C5—C4	116.76 (13)	H9A—C9—H9B	109.5
C6—C5—H5	121.6	N3—C9—H9C	109.5

C4—C5—H5	121.6	H9A—C9—H9C	109.5
C5—C6—C1	122.61 (13)	H9B—C9—H9C	109.5
C5—C6—H6	118.7		
C6—C1—C2—N1	179.42 (13)	O4—N2—C4—C5	3.84 (19)
C7—C1—C2—N1	−0.8 (2)	C3—C4—C5—C6	0.7 (2)
C6—C1—C2—C3	1.04 (19)	N2—C4—C5—C6	−179.58 (12)
C7—C1—C2—C3	−179.14 (11)	C4—C5—C6—C1	−0.8 (2)
N1—C2—C3—C4	−179.59 (13)	C2—C1—C6—C5	−0.1 (2)
C1—C2—C3—C4	−1.14 (19)	C7—C1—C6—C5	−179.91 (12)
C2—C3—C4—C5	0.3 (2)	C6—C1—C7—O1	168.10 (13)
C2—C3—C4—N2	−179.47 (11)	C2—C1—C7—O1	−11.72 (19)
O3—N2—C4—C3	4.04 (19)	C6—C1—C7—O2	−10.67 (18)
O4—N2—C4—C3	−176.38 (13)	C2—C1—C7—O2	169.51 (12)
O3—N2—C4—C5	−175.73 (13)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the (C1–C6) ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.869 (18)	2.012 (18)	2.6694 (17)	131.6 (15)
N1—H2*N*···O2^{i}	0.889 (18)	2.019 (18)	2.8900 (16)	166.2 (16)
N3—H3*N*···O1^{ii}	0.944 (17)	1.774 (17)	2.7141 (15)	173.4 (15)
N3—H4*N*···O2^{iii}	0.919 (16)	1.834 (15)	2.7385 (15)	167.6 (15)
C8—H8*C*···O4^{iv}	0.98	2.48	3.4589 (19)	174
N2—O4···*Cg*1^{v}	1.23 (1)	3.40 (1)	4.3668 (14)	136 (1)
C9—H9*C*···*Cg*1	0.98	2.64	3.5512 (16)	154

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

(II) Dibutylazanium 2-amino-4-nitrobenzoate

Crystal data

$C_8H_{20}N^+·C_7H_5N_2O_4^-$
M_r = 311.38
Triclinic, $P\overline{1}$
a = 11.1615 (3) Å
b = 12.5172 (4) Å
c = 13.2399 (4) Å
α = 82.405 (1)°
β = 78.107 (2)°
γ = 70.915 (2)°
V = 1706.36 (9) Å^3
Z = 4
F(000) = 672
D_x = 1.212 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 14576 reflections
θ = 2.9–27.5°
μ = 0.09 mm^{-1}
T = 120 K
Block, orange
0.20 × 0.14 × 0.12 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} = 0.665, T_{max} = 0.746
34976 measured reflections
7811 independent reflections
5022 reflections with $I > 2\sigma(I)$

R_{int} = 0.074
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −14→14
k = −16→16
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.180
S = 1.03
7811 reflections
425 parameters
8 restraints
Hydrogen site location: mixed
$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2 + 0.4569P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 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	0.09438 (14)	−0.08417 (13)	0.31913 (11)	0.0291 (4)
O2	0.04512 (14)	0.10463 (12)	0.30797 (11)	0.0269 (3)
O3	0.20429 (17)	−0.04415 (15)	−0.22162 (12)	0.0406 (4)
O4	0.21251 (19)	0.12584 (15)	−0.22089 (13)	0.0457 (5)
N1	0.1320 (2)	−0.18640 (17)	0.14324 (15)	0.0346 (5)
H1N	0.133 (2)	−0.191 (2)	0.2101 (9)	0.042*
H2N	0.161 (2)	−0.2458 (15)	0.1058 (18)	0.042*
N2	0.19793 (18)	0.03761 (17)	−0.17638 (14)	0.0307 (4)
C1	0.12087 (19)	0.01094 (17)	0.15175 (15)	0.0223 (4)
C2	0.14160 (19)	−0.08524 (17)	0.09664 (16)	0.0231 (4)
C3	0.1667 (2)	−0.07341 (18)	−0.01259 (16)	0.0265 (5)
H3	0.1786	−0.1356	−0.0517	0.032*
C4	0.1740 (2)	0.02861 (18)	−0.06210 (15)	0.0250 (5)
C5	0.1602 (2)	0.12205 (18)	−0.01090 (16)	0.0275 (5)
H5	0.1692	0.1904	−0.0473	0.033*
C6	0.1326 (2)	0.11159 (18)	0.09631 (16)	0.0256 (5)
H6	0.1212	0.1750	0.1336	0.031*
C7	0.08429 (19)	0.00996 (18)	0.26807 (16)	0.0236 (4)
O5	0.72446 (14)	0.36339 (13)	0.03271 (12)	0.0295 (4)
O6	0.72498 (15)	0.53352 (13)	−0.04335 (12)	0.0317 (4)
O7	1.17970 (15)	0.40957 (13)	0.29913 (12)	0.0338 (4)
O8	1.13244 (16)	0.58920 (14)	0.25348 (13)	0.0364 (4)
N3	0.84740 (18)	0.28457 (16)	0.19704 (14)	0.0273 (4)
H3N	0.803 (2)	0.274 (2)	0.1533 (15)	0.033*
H4N	0.8967 (19)	0.2265 (14)	0.2297 (17)	0.033*
N4	1.11558 (18)	0.49651 (16)	0.25530 (14)	0.0276 (4)
C8	0.83927 (19)	0.46491 (17)	0.09567 (15)	0.0230 (4)
C9	0.88906 (19)	0.37761 (17)	0.17018 (16)	0.0228 (4)

C10	0.98276 (19)	0.39011 (17)	0.22045 (15)	0.0225 (4)
H10	1.0238	0.3304	0.2660	0.027*
C11	1.0146 (2)	0.48871 (18)	0.20342 (15)	0.0239 (4)
C12	0.9579 (2)	0.58021 (18)	0.13950 (17)	0.0273 (5)
H12	0.9762	0.6499	0.1339	0.033*
C13	0.8730 (2)	0.56440 (18)	0.08413 (17)	0.0271 (5)
H13	0.8362	0.6237	0.0364	0.033*
C14	0.75672 (19)	0.45293 (18)	0.02314 (16)	0.0250 (5)
N5	0.47820 (19)	0.39824 (17)	0.14284 (15)	0.0326 (5)
H5N	0.5508 (15)	0.393 (2)	0.0988 (16)	0.039*
H6N	0.4105 (17)	0.427 (2)	0.1109 (18)	0.039*
C15	0.4777 (2)	0.4736 (2)	0.22127 (19)	0.0390 (6)
H15A	0.5582	0.4420	0.2503	0.047*
H15B	0.4046	0.4754	0.2786	0.047*
C16	0.4667 (2)	0.5925 (2)	0.17610 (19)	0.0383 (6)
H16A	0.3855	0.6248	0.1482	0.046*
H16B	0.5391	0.5908	0.1181	0.046*
C17	0.4685 (4)	0.6673 (3)	0.2558 (3)	0.0668 (9)
H17A	0.3895	0.6770	0.3087	0.080*
H17B	0.5432	0.6287	0.2909	0.080*
C18	0.4764 (4)	0.7816 (3)	0.2122 (3)	0.0786 (11)
H18A	0.5545	0.7730	0.1599	0.118*
H18B	0.4791	0.8248	0.2678	0.118*
H18C	0.4007	0.8220	0.1802	0.118*
C19	0.4816 (2)	0.2812 (2)	0.1868 (2)	0.0381 (6)
H19A	0.4137	0.2859	0.2488	0.046*
H19B	0.5658	0.2421	0.2086	0.046*
C20	0.4617 (3)	0.2132 (2)	0.1099 (2)	0.0419 (6)
H20A	0.5314	0.2068	0.0490	0.050*
H20B	0.3791	0.2544	0.0861	0.050*
C21	0.4596 (3)	0.0938 (2)	0.1533 (2)	0.0498 (7)
H21A	0.4319	0.0589	0.1030	0.060*
H21B	0.5479	0.0467	0.1618	0.060*
C22	0.3696 (3)	0.0943 (3)	0.2571 (3)	0.0664 (9)
H22A	0.4065	0.1135	0.3107	0.100*
H22B	0.3589	0.0191	0.2752	0.100*
H22C	0.2856	0.1506	0.2521	0.100*
N6	0.05973 (18)	0.13511 (16)	0.50714 (14)	0.0260 (4)
H7N	0.055 (2)	0.1145 (19)	0.4468 (11)	0.031*
H8N	0.0105 (19)	0.1068 (19)	0.5573 (14)	0.031*
C23	0.0145 (2)	0.26079 (18)	0.50850 (17)	0.0303 (5)
H23A	0.0715	0.2928	0.4545	0.036*
H23B	0.0200	0.2821	0.5764	0.036*
C24	−0.1226 (2)	0.31081 (19)	0.48958 (17)	0.0330 (5)
H24A	−0.1804	0.2829	0.5463	0.040*
H24B	−0.1294	0.2849	0.4241	0.040*
C25	−0.1664 (3)	0.4403 (2)	0.48336 (19)	0.0413 (6)
H25A	−0.1697	0.4660	0.5517	0.050*

H25B	−0.1023	0.4677	0.4328	0.050*
C26	−0.2977 (3)	0.4922 (3)	0.4515 (3)	0.0643 (9)
H26A	−0.2953	0.4664	0.3841	0.096*
H26B	−0.3201	0.5750	0.4465	0.096*
H26C	−0.3624	0.4686	0.5033	0.096*
C27	0.1963 (2)	0.08328 (19)	0.52304 (17)	0.0305 (5)
H27A	0.2048	0.1045	0.5900	0.037*
H27B	0.2528	0.1141	0.4676	0.037*
C28	0.2400 (2)	−0.04449 (19)	0.52239 (17)	0.0294 (5)
H28A	0.2302	−0.0660	0.4559	0.035*
H28B	0.1847	−0.0757	0.5787	0.035*
C29	0.3800 (2)	−0.0954 (2)	0.53672 (19)	0.0369 (6)
H29A	0.4354	−0.0679	0.4778	0.044*
H29B	0.3906	−0.0690	0.6006	0.044*
C30	0.4242 (3)	−0.2240 (2)	0.5439 (2)	0.0482 (7)
H30A	0.3720	−0.2519	0.6038	0.072*
H30B	0.5149	−0.2525	0.5517	0.072*
H30C	0.4143	−0.2508	0.4807	0.072*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0392 (9)	0.0268 (9)	0.0183 (7)	−0.0083 (7)	−0.0038 (6)	0.0024 (6)
O2	0.0368 (8)	0.0238 (8)	0.0190 (7)	−0.0068 (7)	−0.0059 (6)	−0.0027 (6)
O3	0.0605 (11)	0.0468 (11)	0.0205 (8)	−0.0248 (9)	−0.0028 (7)	−0.0085 (7)
O4	0.0737 (13)	0.0404 (11)	0.0232 (9)	−0.0241 (10)	−0.0038 (8)	0.0056 (8)
N1	0.0565 (13)	0.0220 (10)	0.0253 (10)	−0.0134 (9)	−0.0050 (9)	−0.0015 (8)
N2	0.0352 (10)	0.0366 (12)	0.0204 (10)	−0.0123 (9)	−0.0034 (8)	−0.0017 (9)
C1	0.0219 (10)	0.0246 (11)	0.0194 (10)	−0.0061 (8)	−0.0038 (8)	−0.0010 (8)
C2	0.0253 (10)	0.0224 (11)	0.0218 (11)	−0.0082 (9)	−0.0032 (8)	−0.0007 (8)
C3	0.0321 (11)	0.0243 (11)	0.0241 (11)	−0.0094 (9)	−0.0025 (9)	−0.0071 (9)
C4	0.0294 (11)	0.0277 (12)	0.0176 (10)	−0.0079 (9)	−0.0054 (8)	−0.0012 (9)
C5	0.0361 (12)	0.0234 (11)	0.0229 (11)	−0.0099 (9)	−0.0064 (9)	0.0022 (9)
C6	0.0332 (11)	0.0225 (11)	0.0208 (11)	−0.0082 (9)	−0.0040 (9)	−0.0028 (8)
C7	0.0248 (10)	0.0251 (12)	0.0209 (11)	−0.0069 (9)	−0.0068 (8)	0.0009 (9)
O5	0.0340 (8)	0.0267 (9)	0.0317 (9)	−0.0113 (7)	−0.0112 (7)	−0.0024 (7)
O6	0.0343 (8)	0.0322 (9)	0.0307 (9)	−0.0104 (7)	−0.0138 (7)	0.0031 (7)
O7	0.0389 (9)	0.0316 (9)	0.0345 (9)	−0.0113 (7)	−0.0176 (7)	0.0043 (7)
O8	0.0516 (10)	0.0308 (9)	0.0384 (9)	−0.0237 (8)	−0.0189 (8)	0.0031 (7)
N3	0.0343 (10)	0.0233 (10)	0.0285 (10)	−0.0123 (8)	−0.0110 (8)	0.0014 (8)
N4	0.0350 (10)	0.0281 (11)	0.0230 (9)	−0.0127 (8)	−0.0083 (8)	−0.0005 (8)
C8	0.0249 (10)	0.0223 (11)	0.0204 (10)	−0.0050 (9)	−0.0034 (8)	−0.0034 (8)
C9	0.0247 (10)	0.0206 (11)	0.0216 (10)	−0.0056 (8)	−0.0018 (8)	−0.0034 (8)
C10	0.0276 (11)	0.0207 (11)	0.0185 (10)	−0.0064 (9)	−0.0053 (8)	0.0000 (8)
C11	0.0284 (11)	0.0252 (11)	0.0203 (10)	−0.0094 (9)	−0.0063 (8)	−0.0029 (8)
C12	0.0346 (12)	0.0192 (11)	0.0305 (12)	−0.0097 (9)	−0.0099 (9)	0.0005 (9)
C13	0.0333 (12)	0.0227 (11)	0.0261 (11)	−0.0085 (9)	−0.0095 (9)	0.0026 (9)
C14	0.0237 (10)	0.0254 (12)	0.0241 (11)	−0.0042 (9)	−0.0048 (8)	−0.0029 (9)

N5	0.0304 (10)	0.0398 (12)	0.0293 (11)	−0.0113 (9)	−0.0111 (8)	0.0018 (9)
C15	0.0408 (14)	0.0484 (16)	0.0320 (13)	−0.0154 (12)	−0.0119 (11)	−0.0047 (11)
C16	0.0372 (13)	0.0428 (15)	0.0375 (14)	−0.0105 (11)	−0.0105 (11)	−0.0100 (11)
C17	0.103 (3)	0.0514 (19)	0.0531 (19)	−0.0208 (18)	−0.0289 (18)	−0.0123 (15)
C18	0.114 (3)	0.045 (2)	0.085 (3)	−0.016 (2)	−0.042 (2)	−0.0154 (18)
C19	0.0331 (12)	0.0408 (15)	0.0379 (14)	−0.0100 (11)	−0.0120 (10)	0.0109 (11)
C20	0.0487 (15)	0.0346 (14)	0.0399 (15)	−0.0121 (12)	−0.0049 (12)	−0.0001 (11)
C21	0.0435 (15)	0.0359 (15)	0.0654 (19)	−0.0098 (12)	−0.0071 (13)	0.0027 (13)
C22	0.0600 (19)	0.063 (2)	0.076 (2)	−0.0274 (17)	−0.0110 (17)	0.0130 (18)
N6	0.0338 (10)	0.0256 (10)	0.0184 (9)	−0.0090 (8)	−0.0051 (8)	−0.0005 (7)
C23	0.0439 (13)	0.0235 (12)	0.0239 (11)	−0.0107 (10)	−0.0067 (10)	−0.0013 (9)
C24	0.0423 (13)	0.0289 (13)	0.0234 (12)	−0.0066 (10)	−0.0031 (10)	−0.0014 (9)
C25	0.0599 (16)	0.0298 (13)	0.0283 (13)	−0.0031 (12)	−0.0093 (11)	−0.0072 (10)
C26	0.071 (2)	0.0424 (17)	0.063 (2)	0.0158 (15)	−0.0266 (17)	−0.0103 (15)
C27	0.0350 (12)	0.0330 (13)	0.0258 (12)	−0.0112 (10)	−0.0103 (9)	−0.0001 (9)
C28	0.0332 (12)	0.0324 (13)	0.0228 (11)	−0.0087 (10)	−0.0076 (9)	−0.0013 (9)
C29	0.0332 (12)	0.0445 (15)	0.0298 (13)	−0.0059 (11)	−0.0078 (10)	−0.0037 (11)
C30	0.0473 (15)	0.0453 (16)	0.0444 (16)	0.0044 (13)	−0.0187 (13)	−0.0083 (13)

Geometric parameters (Å, º)

O1—C7	1.262 (2)	C17—C18	1.494 (5)
O2—C7	1.267 (3)	C17—H17A	0.9900
O3—N2	1.228 (2)	C17—H17B	0.9900
O4—N2	1.225 (2)	C18—H18A	0.9800
N1—C2	1.360 (3)	C18—H18B	0.9800
N1—H1N	0.882 (10)	C18—H18C	0.9800
N1—H2N	0.882 (10)	C19—C20	1.502 (4)
N2—C4	1.477 (3)	C19—H19A	0.9900
C1—C6	1.403 (3)	C19—H19B	0.9900
C1—C2	1.420 (3)	C20—C21	1.535 (3)
C1—C7	1.509 (3)	C20—H20A	0.9900
C2—C3	1.413 (3)	C20—H20B	0.9900
C3—C4	1.375 (3)	C21—C22	1.526 (4)
C3—H3	0.9500	C21—H21A	0.9900
C4—C5	1.379 (3)	C21—H21B	0.9900
C5—C6	1.387 (3)	C22—H22A	0.9800
C5—H5	0.9500	C22—H22B	0.9800
C6—H6	0.9500	C22—H22C	0.9800
O5—C14	1.269 (3)	N6—C23	1.488 (3)
O6—C14	1.256 (3)	N6—C27	1.496 (3)
O7—N4	1.236 (2)	N6—H7N	0.888 (10)
O8—N4	1.231 (2)	N6—H8N	0.884 (10)
N3—C9	1.370 (3)	C23—C24	1.512 (3)
N3—H3N	0.885 (10)	C23—H23A	0.9900
N3—H4N	0.878 (10)	C23—H23B	0.9900
N4—C11	1.470 (3)	C24—C25	1.529 (3)
C8—C13	1.396 (3)	C24—H24A	0.9900

C8—C9	1.421 (3)	C24—H24B	0.9900
C8—C14	1.512 (3)	C25—C26	1.519 (4)
C9—C10	1.408 (3)	C25—H25A	0.9900
C10—C11	1.371 (3)	C25—H25B	0.9900
C10—H10	0.9500	C26—H26A	0.9800
C11—C12	1.385 (3)	C26—H26B	0.9800
C12—C13	1.387 (3)	C26—H26C	0.9800
C12—H12	0.9500	C27—C28	1.512 (3)
C13—H13	0.9500	C27—H27A	0.9900
N5—C15	1.490 (3)	C27—H27B	0.9900
N5—C19	1.494 (3)	C28—C29	1.525 (3)
N5—H5N	0.884 (10)	C28—H28A	0.9900
N5—H6N	0.891 (10)	C28—H28B	0.9900
C15—C16	1.505 (4)	C29—C30	1.518 (4)
C15—H15A	0.9900	C29—H29A	0.9900
C15—H15B	0.9900	C29—H29B	0.9900
C16—C17	1.507 (4)	C30—H30A	0.9800
C16—H16A	0.9900	C30—H30B	0.9800
C16—H16B	0.9900	C30—H30C	0.9800

C2—N1—H1N	111.8 (17)	C17—C18—H18C	109.5
C2—N1—H2N	118.2 (18)	H18A—C18—H18C	109.5
H1N—N1—H2N	123 (2)	H18B—C18—H18C	109.5
O4—N2—O3	123.54 (18)	N5—C19—C20	111.95 (19)
O4—N2—C4	118.01 (18)	N5—C19—H19A	109.2
O3—N2—C4	118.44 (18)	C20—C19—H19A	109.2
C6—C1—C2	119.04 (18)	N5—C19—H19B	109.2
C6—C1—C7	118.41 (18)	C20—C19—H19B	109.2
C2—C1—C7	122.55 (18)	H19A—C19—H19B	107.9
N1—C2—C3	118.25 (19)	C19—C20—C21	113.6 (2)
N1—C2—C1	123.47 (19)	C19—C20—H20A	108.8
C3—C2—C1	118.19 (18)	C21—C20—H20A	108.8
C4—C3—C2	119.68 (19)	C19—C20—H20B	108.8
C4—C3—H3	120.2	C21—C20—H20B	108.8
C2—C3—H3	120.2	H20A—C20—H20B	107.7
C3—C4—C5	123.59 (19)	C22—C21—C20	112.5 (3)
C3—C4—N2	117.74 (19)	C22—C21—H21A	109.1
C5—C4—N2	118.67 (19)	C20—C21—H21A	109.1
C4—C5—C6	116.9 (2)	C22—C21—H21B	109.1
C4—C5—H5	121.6	C20—C21—H21B	109.1
C6—C5—H5	121.6	H21A—C21—H21B	107.8
C5—C6—C1	122.5 (2)	C21—C22—H22A	109.5
C5—C6—H6	118.7	C21—C22—H22B	109.5
C1—C6—H6	118.7	H22A—C22—H22B	109.5
O1—C7—O2	124.31 (19)	C21—C22—H22C	109.5
O1—C7—C1	118.35 (19)	H22A—C22—H22C	109.5
O2—C7—C1	117.34 (18)	H22B—C22—H22C	109.5
C9—N3—H3N	114.1 (16)	C23—N6—C27	112.99 (17)

C9—N3—H4N	116.8 (15)	C23—N6—H7N	110.4 (16)
H3N—N3—H4N	120 (2)	C27—N6—H7N	107.3 (15)
O8—N4—O7	122.87 (17)	C23—N6—H8N	108.9 (16)
O8—N4—C11	118.69 (17)	C27—N6—H8N	108.0 (15)
O7—N4—C11	118.45 (17)	H7N—N6—H8N	109 (2)
C13—C8—C9	119.18 (18)	N6—C23—C24	111.70 (18)
C13—C8—C14	117.69 (18)	N6—C23—H23A	109.3
C9—C8—C14	123.04 (18)	C24—C23—H23A	109.3
N3—C9—C10	119.05 (18)	N6—C23—H23B	109.3
N3—C9—C8	123.08 (18)	C24—C23—H23B	109.3
C10—C9—C8	117.84 (18)	H23A—C23—H23B	107.9
C11—C10—C9	119.77 (19)	C23—C24—C25	111.90 (19)
C11—C10—H10	120.1	C23—C24—H24A	109.2
C9—C10—H10	120.1	C25—C24—H24A	109.2
C10—C11—C12	123.66 (19)	C23—C24—H24B	109.2
C10—C11—N4	117.78 (18)	C25—C24—H24B	109.2
C12—C11—N4	118.56 (18)	H24A—C24—H24B	107.9
C11—C12—C13	116.31 (19)	C26—C25—C24	112.6 (2)
C11—C12—H12	121.8	C26—C25—H25A	109.1
C13—C12—H12	121.8	C24—C25—H25A	109.1
C12—C13—C8	122.68 (19)	C26—C25—H25B	109.1
C12—C13—H13	118.7	C24—C25—H25B	109.1
C8—C13—H13	118.7	H25A—C25—H25B	107.8
O6—C14—O5	124.39 (19)	C25—C26—H26A	109.5
O6—C14—C8	116.94 (18)	C25—C26—H26B	109.5
O5—C14—C8	118.67 (18)	H26A—C26—H26B	109.5
C15—N5—C19	113.40 (19)	C25—C26—H26C	109.5
C15—N5—H5N	104.6 (17)	H26A—C26—H26C	109.5
C19—N5—H5N	107.4 (17)	H26B—C26—H26C	109.5
C15—N5—H6N	111.7 (17)	N6—C27—C28	112.16 (17)
C19—N5—H6N	108.7 (16)	N6—C27—H27A	109.2
H5N—N5—H6N	111 (2)	C28—C27—H27A	109.2
N5—C15—C16	112.20 (19)	N6—C27—H27B	109.2
N5—C15—H15A	109.2	C28—C27—H27B	109.2
C16—C15—H15A	109.2	H27A—C27—H27B	107.9
N5—C15—H15B	109.2	C27—C28—C29	111.31 (18)
C16—C15—H15B	109.2	C27—C28—H28A	109.4
H15A—C15—H15B	107.9	C29—C28—H28A	109.4
C15—C16—C17	111.6 (2)	C27—C28—H28B	109.4
C15—C16—H16A	109.3	C29—C28—H28B	109.4
C17—C16—H16A	109.3	H28A—C28—H28B	108.0
C15—C16—H16B	109.3	C30—C29—C28	112.7 (2)
C17—C16—H16B	109.3	C30—C29—H29A	109.1
H16A—C16—H16B	108.0	C28—C29—H29A	109.1
C18—C17—C16	113.9 (3)	C30—C29—H29B	109.1
C18—C17—H17A	108.8	C28—C29—H29B	109.1
C16—C17—H17A	108.8	H29A—C29—H29B	107.8
C18—C17—H17B	108.8	C29—C30—H30A	109.5

C16—C17—H17B	108.8	C29—C30—H30B	109.5
H17A—C17—H17B	107.7	H30A—C30—H30B	109.5
C17—C18—H18A	109.5	C29—C30—H30C	109.5
C17—C18—H18B	109.5	H30A—C30—H30C	109.5
H18A—C18—H18B	109.5	H30B—C30—H30C	109.5
C6—C1—C2—N1	−179.7 (2)	C9—C10—C11—C12	1.0 (3)
C7—C1—C2—N1	−0.8 (3)	C9—C10—C11—N4	−178.27 (18)
C6—C1—C2—C3	−3.2 (3)	O8—N4—C11—C10	−169.46 (19)
C7—C1—C2—C3	175.69 (18)	O7—N4—C11—C10	10.3 (3)
N1—C2—C3—C4	178.5 (2)	O8—N4—C11—C12	11.2 (3)
C1—C2—C3—C4	1.8 (3)	O7—N4—C11—C12	−169.0 (2)
C2—C3—C4—C5	1.2 (3)	C10—C11—C12—C13	−5.7 (3)
C2—C3—C4—N2	−178.83 (18)	N4—C11—C12—C13	173.56 (19)
O4—N2—C4—C3	−175.5 (2)	C11—C12—C13—C8	3.7 (3)
O3—N2—C4—C3	3.3 (3)	C9—C8—C13—C12	2.8 (3)
O4—N2—C4—C5	4.5 (3)	C14—C8—C13—C12	−173.8 (2)
O3—N2—C4—C5	−176.7 (2)	C13—C8—C14—O6	0.6 (3)
C3—C4—C5—C6	−2.6 (3)	C9—C8—C14—O6	−175.88 (19)
N2—C4—C5—C6	177.44 (18)	C13—C8—C14—O5	−179.63 (19)
C4—C5—C6—C1	1.0 (3)	C9—C8—C14—O5	3.9 (3)
C2—C1—C6—C5	1.9 (3)	C19—N5—C15—C16	−176.79 (19)
C7—C1—C6—C5	−177.09 (19)	N5—C15—C16—C17	−179.1 (2)
C6—C1—C7—O1	−168.45 (18)	C15—C16—C17—C18	171.9 (3)
C2—C1—C7—O1	12.6 (3)	C15—N5—C19—C20	171.3 (2)
C6—C1—C7—O2	11.6 (3)	N5—C19—C20—C21	−177.9 (2)
C2—C1—C7—O2	−167.31 (18)	C19—C20—C21—C22	49.5 (3)
C13—C8—C9—N3	170.5 (2)	C27—N6—C23—C24	178.58 (17)
C14—C8—C9—N3	−13.1 (3)	N6—C23—C24—C25	−176.00 (18)
C13—C8—C9—C10	−7.5 (3)	C23—C24—C25—C26	173.0 (2)
C14—C8—C9—C10	168.91 (19)	C23—N6—C27—C28	179.47 (18)
N3—C9—C10—C11	−172.40 (19)	N6—C27—C28—C29	178.96 (18)
C8—C9—C10—C11	5.7 (3)	C27—C28—C29—C30	176.0 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.88 (1)	1.98 (2)	2.696 (2)	137 (2)
N1—H2*N*···O5^{i}	0.88 (2)	2.38 (2)	3.226 (3)	160 (2)
N3—H3*N*···O5	0.88 (2)	2.01 (2)	2.714 (3)	136 (2)
N3—H4*N*···O2^{ii}	0.88 (2)	2.19 (2)	3.052 (2)	168 (2)
N5—H5*N*···O5	0.88 (2)	1.89 (2)	2.757 (3)	166 (2)
N5—H6*N*···O6^{iii}	0.89 (2)	1.81 (2)	2.697 (3)	173 (2)
N6—H7*N*···O2	0.89 (2)	1.89 (2)	2.759 (2)	167 (2)
N6—H8*N*···O1^{iv}	0.89 (2)	1.85 (2)	2.712 (2)	163 (2)
C19—H19*A*···O7^{v}	0.99	2.56	3.343 (3)	136

C20—H20*B*···O6^{iii}	0.99	2.56	3.297 (3)	131
C27—H27*A*···O4^{vi}	0.99	2.57	3.550 (3)	169

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