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# The crystal structures of benzylammonium phenylacetate and its hydrate

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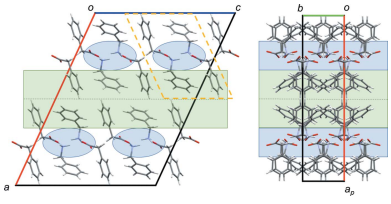
The title compounds benzylammonium phenylacetate, $C_7H_{10}N^+\cdot C_8H_7O_2^-$ (**1**), and its monohydrate, $C_7H_{10}N^+\cdot C_8H_7O_2^-\cdot H_2O$ (**2**), can be obtained by evaporating methanolic solutions containing equimolar amounts of benzylamine and phenylacetic acid in the absence and presence of water, respectively. N—H···O hydrogen bonds in the crystal structure of **1** lead to the formation of hydrophilic channels running along the *b*-axis direction. The hydrogen-bonding system is best described by fused $R_4^3(10)$ ring patterns, often observed in ammonium carboxylate salts. In **2**, the presence of the crystal water leads to the formation of a two-dimensional hydrogen-bonding network. The benzyl moieties in **1** and **2** form hydrophobic layers in the crystal structures with the aromatic rings adopting edge-to-face arrangements.

## 1. Chemical context

Many proteins can self-assemble into insoluble aggregates, so-called amyloids, with a high content of $\beta$-strands. Amyloid fibrils are qualitatively similar for different proteins, with filaments of a few nanometers in diameter that can grow up to several micrometers in length (McManus *et al.*, 2016). The amyloid state of proteins is linked to various human diseases, *e.g.* Alzheimer's disease (Eisenberg & Jucker, 2012). Besides proteins, oligopeptides (Ozbas *et al.*, 2004) down to simple dipeptides (Reches & Gazit, 2003) and even the amino acid phenylalanine (Mossou *et al.*, 2014; Do *et al.*, 2015) can also self-assemble into stable nanofilaments in aqueous solution. Apart from the obvious link to amyloid diseases, such structures are also interesting for technical applications (Gazit, 2007; Manna *et al.*, 2015). Hydrogen bonds between ammonium and carboxylate groups, as well as the presence of hydrophobic residues (*e.g.* aromatic residues) play an important role in the formation of self-assembled structures of (di)peptides or amino acids (Görbitz, 2010; Mossou *et al.*, 2014; Reches & Gazit, 2003). Similarly, the packing motifs of ammonium carboxylate salts are governed by the formation of hydrogen-bonded networks between the ammonium and carboxylate groups, as well as the nature of the residues of the ammonium and carboxylate residues (Kinbara *et al.*, 1996; Odendal *et al.*, 2010).



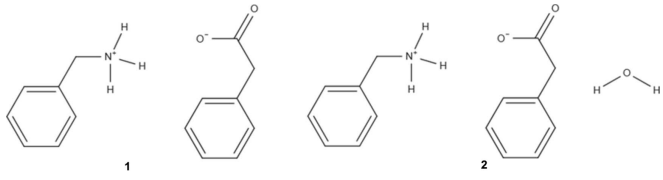


**Table 1**
Contributions of close intermolecular contacts to the Hirshfeld surface areas of the molecules in **1** and **2**.

| Compound | molecule | O···H | H···O | C···H | H···C | C···O | O···C | H···H |
|---|---|---|---|---|---|---|---|---|
| 1 | benzylammonium | 0.0 | 15.8 | 13.6 | 13.8 | 1.3 | 0.0 | 55.5 |
| | phenylacetate | 21.5 | 4.1 | 16.9 | 6.6 | 0.0 | 0.7 | 50.2 |
| 2 | benzylammonium | 0.0 | 13.2 | 15.6 | 11.4 | 0.0 | 0.0 | 59.7 |
| | phenylacetate | 21.6 | 5.2 | 15.7 | 11.3 | 0.3 | 0.2 | 45.7 |
| | water | 30.5 | 22.4 | 0.0 | 1.8 | 0.0 | 0.0 | 44.9 |

Herein, we report the crystal structures of benzylammonium phenylacetate and its hydrate. Both show a similar crystal packing to the zwitterionic form of L-phenylalanine reported by Mossou *et al.* (2014). This resemblance raises the question of whether a system such as benzylammonium phenylacetate is also capable of forming nanofilaments.

## 2. Structural commentary

Benzylammonium phenylacetate (**1**) crystallizes in the monoclinic space group $C2/c$ and its hydrate (**2**) in the monoclinic space group $P2_1/n$. The asymmetric units of **1** and its hydrate **2** are shown in Fig. 1. In compound **1**, the ammonium group of the benzylammonium is orientated almost perpendicular to the phenyl ring [90.2 (2)°], while the carboxylate group of the phenylacetate adopts a torsion angle of −70.2 (4)°, while in the hydrate **2** the torsion angles between the phenyl rings and the functional groups are 72.4 (4) and 54.4 (4)° for the phenylacetate and benzylammonium, respectively.

## 3. Supramolecular features

### 3.1. Crystal packing

The crystal packing of benzylammonium phenylacetate (**1**) consists of columns arranged around the twofold screw axis along $b$ (Fig. 2). These columns are composed of hydrophilic channels, formed by the ammonium and carboxylate groups, surrounded by a shell made up by the phenyl moieties. The crystal packing of the hydrate (**2**) consists of hydrophilic and hydrophobic layers alternating along the $c$-axis direction, as shown in Fig. 3. The hydrophilic layer is composed of the water molecules, the ammonium and the carboxylate groups.

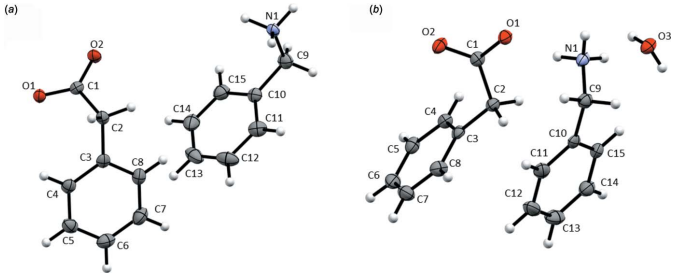



**Figure 1**
*ORTEP* representation of the asymmetric unit in (*a*) **1** and (*b*) **2** (50% probability ellipsoids).

### 3.2. Intermolecular contacts and Hirshfeld analysis

We used *CrystalExplorer17* to analyse the Hirshfeld surfaces of the molecules in the crystal structures of **1** and **2** and to quantify intermolecular contacts between them (Turner *et al.*, 2017; McKinnon *et al.*, 2007). Table 1 summarizes the relative contributions to the Hirshfeld surface areas for the intermolecular contacts found in the molecules of **1** and **2**.

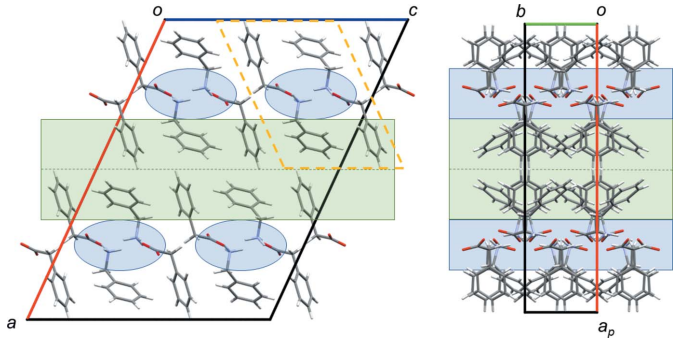



**Figure 2**
Crystal packing of **1** with views along the $b$ axis (left) and along the $c$ axis (right). Yellow dotted lines mark a column arranged around a twofold screw axis. Hydrophilic areas are highlighted in blue, hydrophobic areas in green.

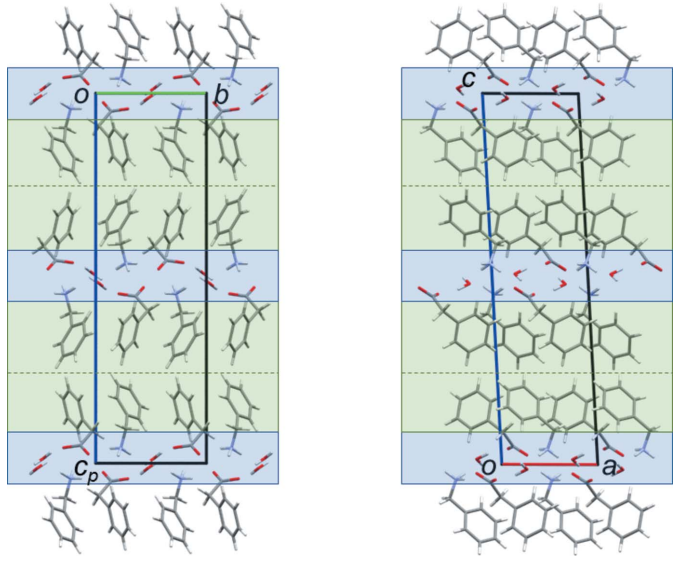



**Figure 3**
Crystal packing of **2** with views along the $a$ axis (left) and along the $b$ axis (right). Hydrophilic areas are highlighted in blue, hydrophobic areas in green.

There are three main groups of (inner···outer) intermolecular contacts that can be found on the Hirshfeld surfaces, namely O···H/H···O, C···H/H···C and H···H intermolecular contacts. Fig. 4 shows the fingerprint plots of the benzylammonium and phenylacetate molecules in **1** and **2**, highlighting the O···H/H···O and C···H/H···C contacts.

Mapping the Hirshfeld surfaces with different functions is a helpful tool for visualizing the nature of those intermolecular contacts. For example, the normalized contact distance $d_{norm}$ mapped on the Hirshfeld surface using a red–white–blue colour scheme indicates distances shorter, around or greater than the van der Waals separation distances, respectively. The normalized contact distance is defined by the following equation

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}},$$

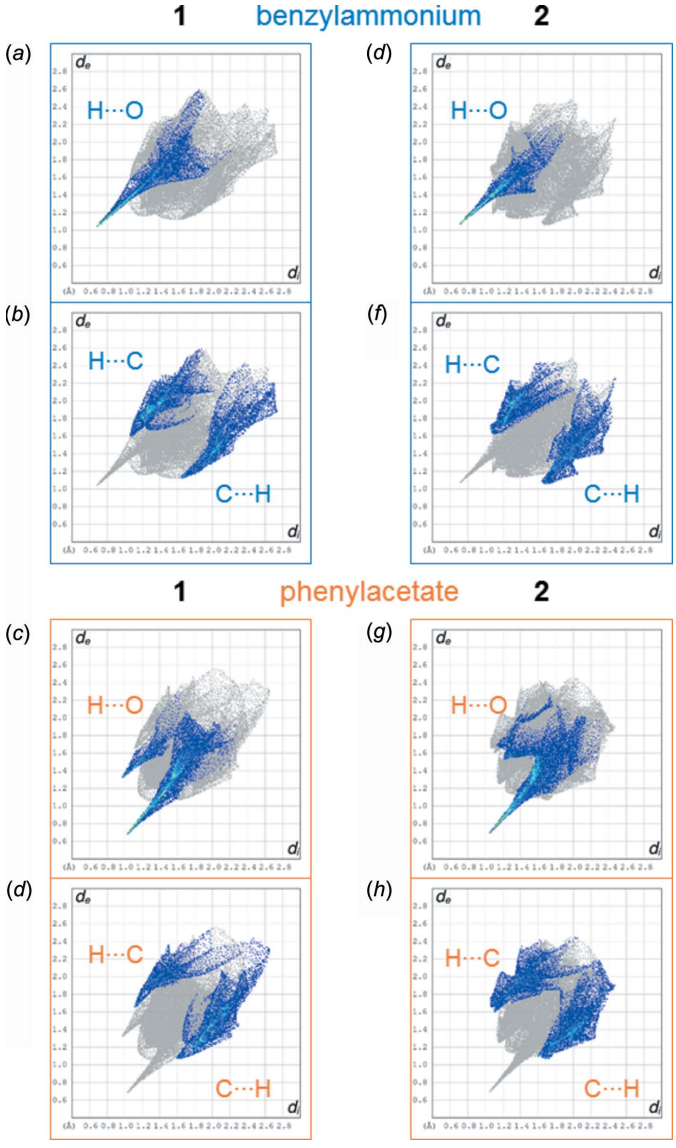



**Figure 4**
Comparison of the fingerprint plots of the benzylammonium and phenylacetate molecules in **1** and **2**, highlighting O···H/H···O and C···H/H···C contacts. $d_i$ and $d_e$ are plotted in Å on the *x*- and *y*-axis, respectively.

where $d_i$ and $d_e$ are the distances to the nearest atoms inside and outside the surface and $r^{vdw}$ is the van der Waals radius of the appropriate atom internal or external to the surface (McKinnon *et al.*, 2007). Fig. 5 shows the benzylammonium and phenylacetate molecules in **1** with $d_{\rm norm}$ mapped. A number of contacts with distances below the sum of the van der Waals radius can directly be identified by red spots. The most intense ones (*A*/*A*′, *B*/*B*′, *C*/*C*′ in Fig. 5) can be attributed to N—H···O hydrogen bonds between the benzylammonium and phenylacetate molecules. The remaining spots are due to non-classical C—H···O hydrogen bonds among the phenylacetate molecules (*D*/*D*′, *E*/*E*′ in Fig. 5) and an aliphatic C—H···$\pi$ interaction between benzylammonium and phenylacetate (*F*/*F*′ in Fig. 5). Fig. 6 shows the normalized contact distance $d_{\rm norm}$ mapped on the Hirshfeld surface of the molecules in **2**, highlighting the N—H···O (*C*/*C*′, *D*/*D*′ and *E*/*E*′) and O—H···O (*A*/*A*′, *B*/*B*′) hydrogen bonds as the primary intermolecular interactions, followed by the non-classical C—H···O hydrogen bonds (*F*/*F*′ and *G*/*G*′). Two further close contacts of the type C—H···C (*H*/*H*′ and *I*/*I*′) can be identified.

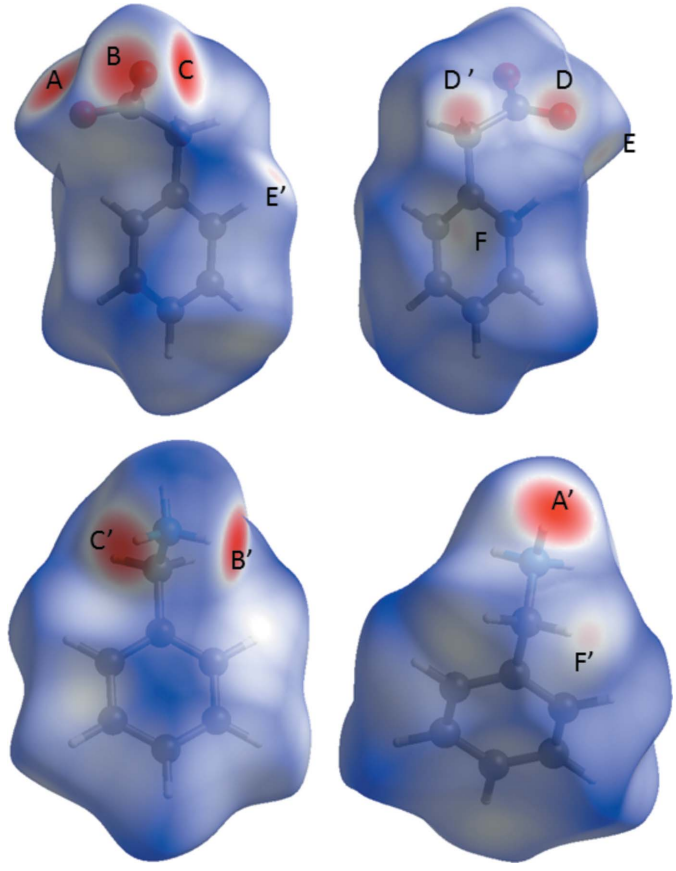



**Figure 5**
Hirshfeld surfaces of benzylammonium (bottom) and phenylacetate (top) molecules in **1** mapped with $d_{\rm norm}$. Red spots indicate contact areas shorter than the van der Waals separation. Those contacts can be attributed to the following intermolecular interactions: N1—H11···O1 (*A*/*A*′), N—H13···O2 (*B*/*B*′), N—H12···O2 (*C*/*C*′), C2—H2*B*···O1 (*D*/*D*′), C8—H8···O1 (*E*/*E*′), and C9—H9*B*···$\pi$ (*F*/*F*′). The map ranges from −0.6825 to 1.3335 a.u. for phenylacetate and −0.6822 to 1.4269 a.u. for benzylammonium.

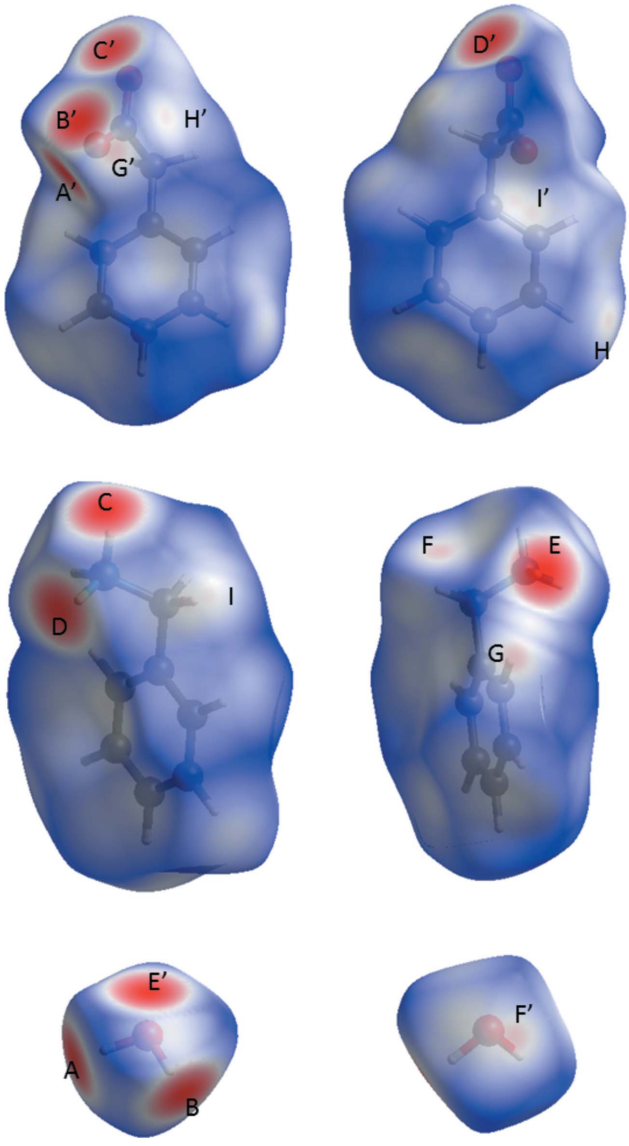



**Figure 6**
Hirshfeld surfaces of phenylacetate (top), benzylammonium (middle) and water (bottom) molecules in **2** mapped with $d_{norm}$. Red spots indicate contact areas shorter than the van der Waals separation. Contacts can be attributed to the following intermolecular interactions: O3—H32···O2 (*A*/*A*′), O3—H31···O2 (*B*/*B*′), N—H12···O1 (*C*/*C*′), N—H11···O1 (*D*/*D*′), N—H13···O3 (*E*/*E*′), C9—H9*B*···O3 (*F*/*F*′), C15—H15···O2 (*G*/*G*′), C5—H5···C1 (*H*/*H*′) and C9—H9*A*···C4 (*I*/*I*′). The map ranges from −0.6666 to 1.2024 a.u. for phenylacetate, −0.6268 to 1.1600 a.u. for benzylammonium and −0.6680 to 1.0780 a.u. for water.

Fig. 4 shows the fingerprint plots of the benzylammonium and phenylacetate molecules in **1** and **2**. O···H/H···O contacts can be attributed mainly to classical and non-classical, *i.e.* C—H···O, hydrogen bonds. Naturally no O···H contacts, but only H···O contacts are found on the Hirshfeld surface of the benzylammonium molecules, resulting in a single spike (*i.e.* N—H···O hydrogen bonds) highlighted in the fingerprint plots (*a*) and (*e*) in Fig. 4. The phenylacetate molecules can act as hydrogen-bond acceptors *via* their oxygen atoms (*i.e.* O···H contacts), visible through the intense spike in the fingerprint plots (*c*) and (*d*) in Fig. 4. In addition, H···O contacts are observed for the phenylacetate molecules in **1** and **2**. Such contacts can come from non-classical C—H···O hydrogen bonds, where the phenylacetate acts as a donor. However, a spike in the fingerprint plots indicating short hydrogen–oxygen distances is only observed for phenylacetate in compound **1** (Fig. 4*c*) and not in compound **2** (Fig. 4*g*), implying that C—H···O hydrogen bonds may be more important in **1** than in the hydrate **2**. C···H/H···C intermolecular contacts can arise from close ring contacts of the phenyl rings in the hydrophobic layers, but also from aliphatic C—H···$\pi$ interactions. An examination of the crystal packings in Figs. 2 and 3 reveals that the phenyl rings are not stacked in a planar, parallel fashion. This is consistent with the absence of C···C intermolecular contacts, which would be expected in such a case (Turner *et al.*, 2017). O···H/H···O and C···H/H···C contacts will be discussed in more detail below.

**Table 2**
Hydrogen-bond geometry (Å, °) for **1**.

*Cg*1 is the centroid of the C3–C8 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H11···O1$^{i}$ | 0.97 (2) | 1.77 (2) | 2.7177 (19) | 165 (2) |
| N1—H12···O2$^{ii}$ | 1.01 (2) | 1.73 (2) | 2.7306 (19) | 170.1 (18) |
| N1—H13···O2$^{iii}$ | 0.95 (3) | 1.85 (3) | 2.7938 (19) | 174 (2) |
| C2—H2*B*···O1$^{iv}$ | 0.99 | 2.40 | 3.375 (2) | 169 |
| C8—H8···O1$^{iii}$ | 0.95 | 2.63 | 3.539 (2) | 161 |
| C9—H9···*Cg*1$^{v}$ | 0.95 | 2.92 | 3.877 (2) | 163 |

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

**Table 3**
Hydrogen-bond geometry (Å, °) for **2**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H32···O2$^{i}$ | 0.83 (4) | 1.90 (4) | 2.728 (4) | 175 (4) |
| O3—H31···O2$^{ii}$ | 0.97 (4) | 1.81 (4) | 2.771 (4) | 169 (3) |
| N1—H11···O1 | 0.89 (4) | 1.92 (4) | 2.791 (4) | 168 (4) |
| N1—H12···O1$^{iii}$ | 0.90 (4) | 1.96 (4) | 2.805 (4) | 157 (4) |
| N1—H13···O3 | 0.94 (4) | 1.87 (4) | 2.809 (4) | 170 (3) |
| C9—H9*B*···O3$^{iv}$ | 0.99 | 2.51 | 3.196 (4) | 126 |
| C15—H15···O2$^{i}$ | 0.95 | 2.57 | 3.412 (4) | 147 |

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

**3.2.1. O···H/H···O intermolecular contacts.** As mentioned above, O···H/H···O contacts can be attributed mainly to classical and non-classical hydrogen bonds. In compound **1**, intermolecular oxygen–hydrogen contacts amount to about 16 and 26% of the Hirshfeld surface area for the benzylammonium and phenylacetate molecules, respectively. In the hydrate **2**, the values are about 13 and 27%, respectively. The hydrogen-bond parameters for **1** and **2** are summarized in Tables 2 and 3, respectively. In **1**, the classical hydrogen-bonding system involves the benzylammonium molecule as a donor and the phenylacetate molecule as an acceptor for N—H···O hydrogen bonds. In **2**, this system is extended by the presence of the water molecule of crystallization acting as a hydrogen-bond donor and acceptor at the same time. The hydrogen-bonding system in **1** can be described by chain patterns corresponding to a second level graph set

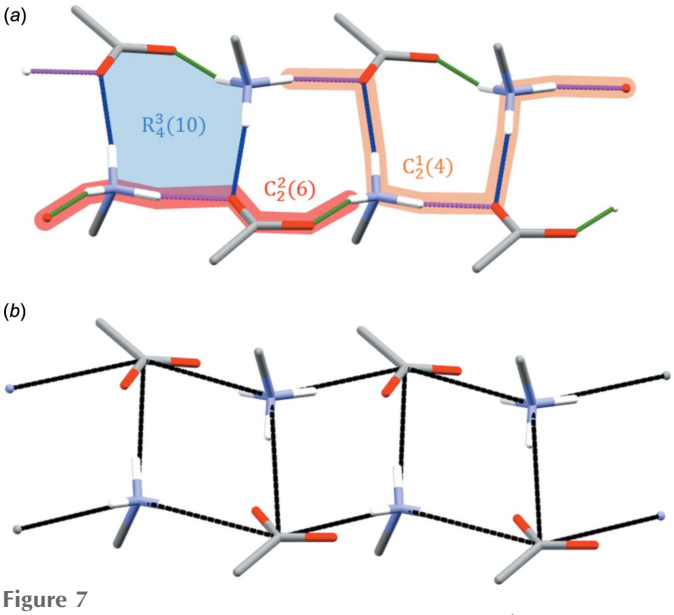



**Figure 7**
(*a*) Hydrogen-bonding patterns in **1**. A section of the $C_2^1(4)$ chain pattern is highlighted in orange, and a section of one of the two possible $C_2^2(6)$ chain patterns is highlighted in red. The $R_4^3(10)$ ring pattern is highlighted in blue. Colour code for the hydrogen bonds: N1—H11···O1 green, N1—H12···O2 magenta, N1—H13···O2 blue. (*b*) Cation–anion ladder motif in **1** formed by the repetition of benzylammonium–phenylacetate pairs. Phenyl rings and $CH_2$ H atoms are omitted for clarity.

$C_2^2(6)C_2^2(6)C_2^1(4)$ (Bernstein *et al.*, 1995). However, a more obvious feature is the ring structure denoted by a third level pattern $R_4^3(10)$ (Fig. 7*a*).

The $R_4^3(10)$ ring pattern is a common feature of ammonium carboxylate salts and has been described earlier (Kinbara *et al.*, 1996). Related to this particular ring pattern is an electrostatic ladder motif. Two benzylammonium–phenylacetate (cation–anion) pairs form a dimeric ring, which associates with further cation–anion pairs to form a ladder running along the twofold screw axis of the crystal (Fig. 7*b*). Such a motif is common in ammonium carboxylate salts (Odendal *et al.*, 2010). Evidently, the presence of crystal water in **2** leads to a change in the hydrogen-bonding system compared to **1**. Going from **1** to **2**, water replaces one of the N—H···O bonds between benzylammonium and phenylacetate. Consequently, the fused $R_4^3(10)$ pattern in **1** is disrupted and two alternating $R_4^2(8)$ patterns bridged by a carboxylate group are formed (Fig. 8*a*). Those rows are then connected among each other *via* the freed N—H donor group of the benzylammonium molecules and water molecules as acceptors to form a two-dimensional hydrogen-bonding network network (Fig. 8*b*). Non-classical hydrogen bonds in **1** are formed exclusively between the phenylacetate molecules, forming fused $R_2^2(8)$ and $R_2^2(10)$ ring patterns alternating along the columns around the twofold screw axis along *b*. The hydrogen-bonding system is shown in Fig. 9*a*. In **2**, the benzylammonium molecule acts as a donor for two discrete non-classical C—H···O hydrogen bonds (Fig. 9*b*), one with the water molecule of crystallization as acceptor (C9—H9*B*···O3) and a second one with an oxygen atom of the carboxylate group of phenylacetate (C15—H15···O2).

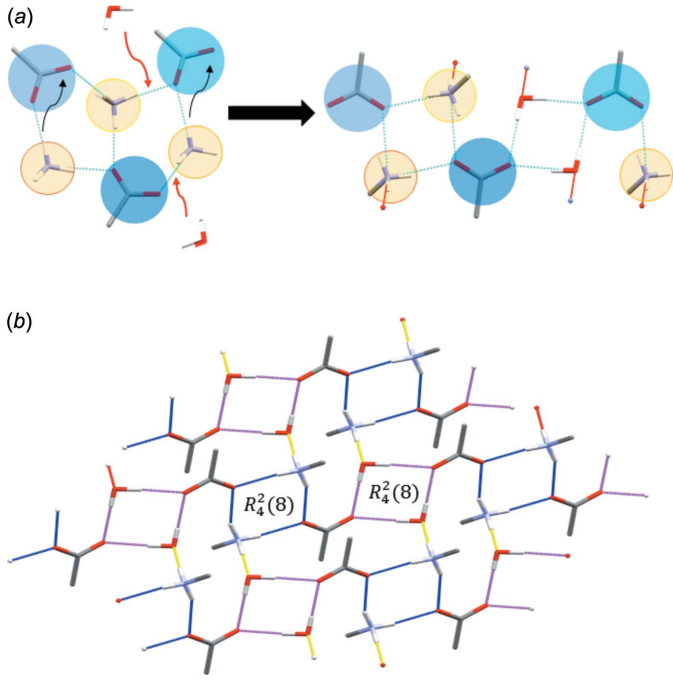



**Figure 8**
(*a*) Transformation of the hydrogen-bonding network in **1** to the network found in **2** by incorporation of crystal water. (*b*) The two-dimensional hydrogen-bonding network in **2**. Rows of alternating $R_4^2(8)$ motifs (hydrogen bonds highlighted in blue and magenta, respectively) are connected *via* discrete N—H···O hydrogen bonds (highlighted in yellow). Phenyl rings and $CH_2$ H atoms are omitted for clarity.

**3.2.2. C···H/H···C intermolecular contacts.** Carbon–hydrogen intermolecular contacts contribute to around one quarter of the Hirshfeld surface areas of the benzylammonium and phenylacetate molecules in both **1** and **2**. As explained above, those contacts are mainly due to close contacts between the phenyl rings in the hydrophobic layers of the crystal packing, but also to (aliphatic) C—H···$\pi$ interactions. An automated search using *PLATON* (Spek, 2009) revealed four short ring interactions and one aliphatic C—H···$\pi$ interaction in **1** (Fig. 10) and six short ring interactions and one aliphatic C—H···$\pi$ interaction in **2** (Fig. 11). The phenyl rings adopt 'Y'- and 'T'-shaped edge-to-face arrangements (Martinez & Iverson, 2012) with centroid–centroid distances of 5.019 (1)–5.738 (1) Å in **1** and 5.177 (2)–5.961 (2) Å in **2**. Those

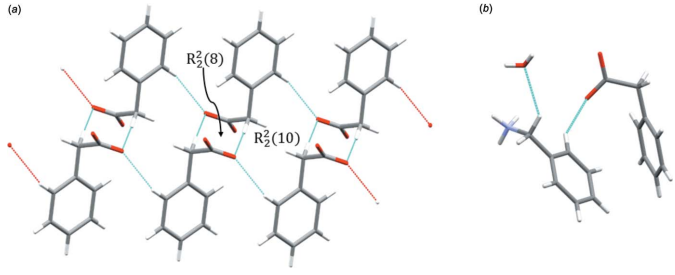



**Figure 9**
(*a*) The C—H···O hydrogen-bonding pattern among the phenylacetate molecules in **1** consisting of alternating, fused $R_2^2(8)$ and $R_2^2(10)$rings. (*b*) Discrete C—H···O hydrogen bonds in **2**.

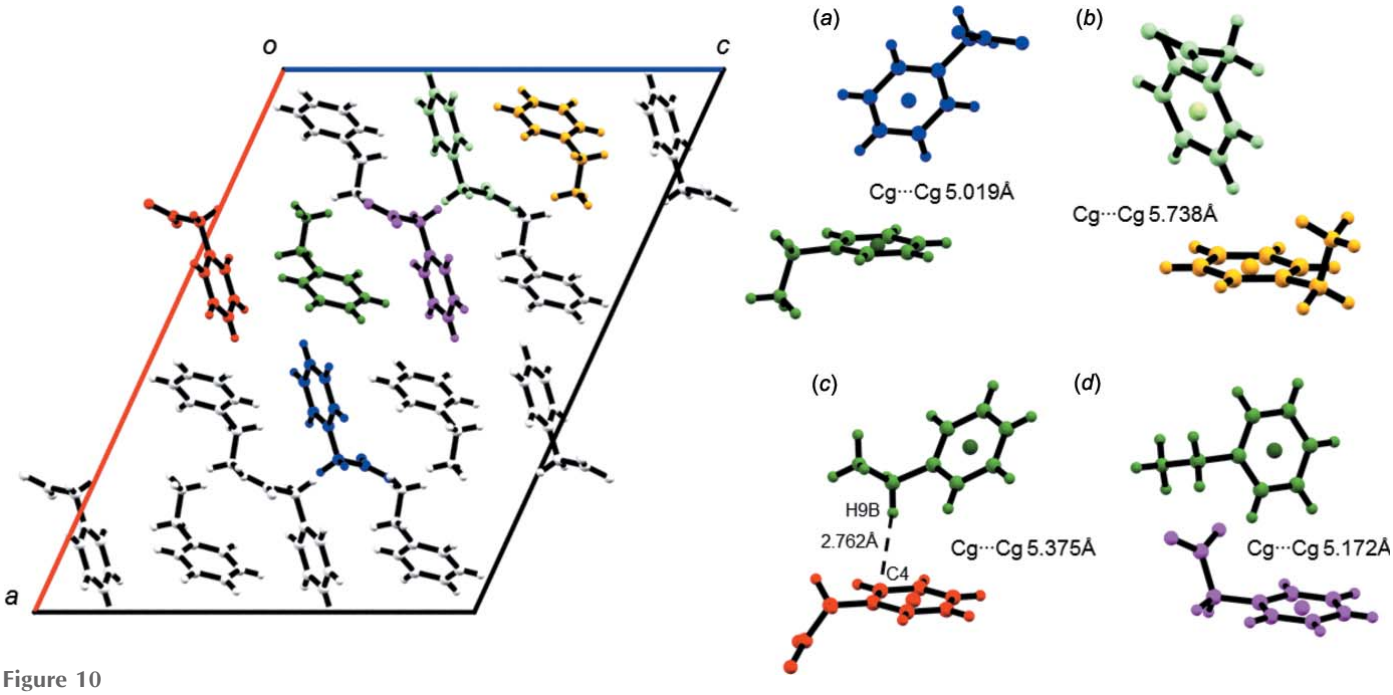



**Figure 10**
Short ring and aliphatic C—H···$\pi$ interactions in **1**.

distances are in the same range as the centroid–centroid distance observed in crystalline benzene (Klebe & Diederich, 1993). Close H···C contacts, *i.e.* smaller than the sum of the van der Waals radii (Bondi, 1964; Hu *et al.*, 2014) of the two elements, are found as part of the aliphatic C—H···$\pi$ interactions. In **1**, the aliphatic C—H···$\pi$ interaction is observed between benzylammonium (donor) and phenylacetate (acceptor), with the shortest distance being 2.762 Å between

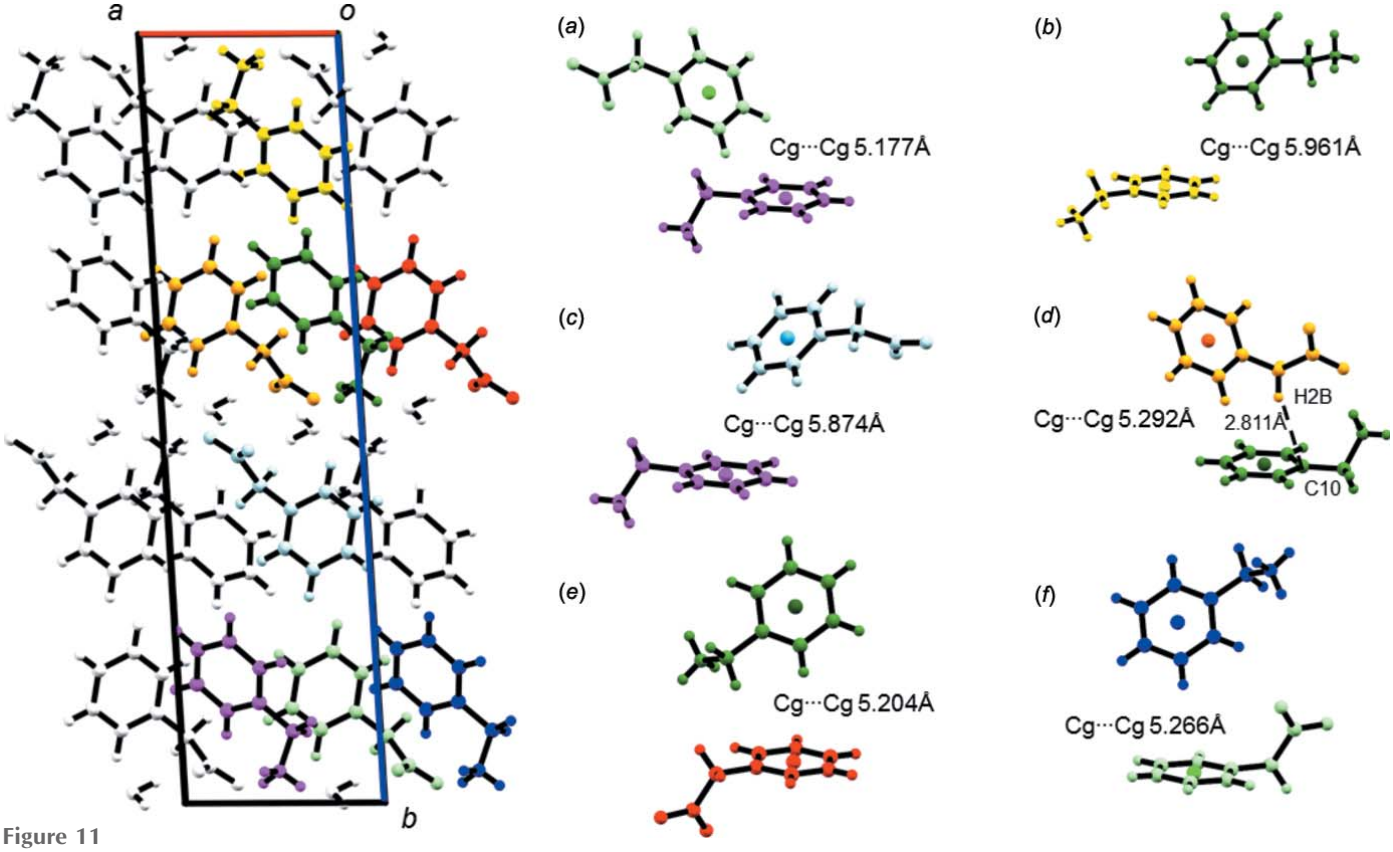



**Figure 11**
Short ring and aliphatic C—H···$\pi$ interactions in **2**.

**Table 4**
Experimental details.

| | **1** | **2** |
|---|---|---|
| Crystal data | | |
| Chemical formula | $C_7H_{10}N^+\cdot C_8H_7O_2^-$ | $C_7H_{10}N^+\cdot C_8H_7O_2^-\cdot H_2O$ |
| $M_r$ | 243.29 | 261.31 |
| Crystal system, space group | Monoclinic, *C*2/*c* | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 | 100 |
| *a*, *b*, *c* (Å) | 25.913 (2), 5.9021 (5), 19.0842 (16) | 6.8235 (7), 7.8766 (7), 26.364 (2) |
| $\beta$ (°) | 114.692 (3) | 93.218 (3) |
| *V* (Å$^3$) | 2651.9 (4) | 1414.7 (2) |
| *Z* | 8 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.08 | 0.09 |
| Crystal size (mm) | 0.10 × 0.04 × 0.02 | 0.10 × 0.06 × 0.04 |
| Data collection | | |
| Diffractometer | Bruker D8 Venture TXS | Bruker D8 Venture TXS |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2016) | Multi-scan (*SADABS*; Bruker, 2016) |
| $T_{min}$, $T_{max}$ | 0.651, 0.971 | 0.814, 0.971 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 14421, 2398, 1800 | 7319, 2461, 2090 |
| $R_{int}$ | 0.092 | 0.043 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.602 | 0.595 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.043, 0.103, 1.03 | 0.075, 0.170, 1.25 |
| No. of reflections | 2398 | 2461 |
| No. of parameters | 175 | 187 |
| 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 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.17, −0.23 | 0.30, −0.27 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006), *CrystalExplorer17* (Turner *et al.*, 2017), *PLATON* (Spek, 2009) and *RPLUTO* (CCDC, 2018).

C9—H9*B*···C4 (Fig. 10*c*). In **2**, phenylacetate acts as a donor and benzlyammonium as an acceptor for the aliphatic C—H···$\pi$ interaction. The closest distance of 2.811 Å is found between C2—H2*B*···C10 (Fig. 11*d*). Two more close contacts of the type (C—)H···C can be identified in **2** *via* the $d_{norm}$-mapped Hirshfeld surfaces (see *H*/*H*′ and *I*/*I*′ in Fig. 6). In the first case, the carbon hydrogen distance C5—H5···C1 (2.812 Å) between two phenylacetate molecules is just below the sum of the van der Waals distances. In the second case, the carbon hydrogen distance C9—H9*A*···C4 between benzylammonium and phenylacetate is 2.798 Å.

## 4. Database survey

A structure search on WebCSD (30.11.2018) resulted in 196 hits for structures including benzylammonium and 22 hits for structures including phenylacetate. Structures with packings closely related to those of **1** and **2** containing molecules similar to benzylammonium and phenylacetate can be found in Trivedi & Dastidar (2006; CEKJEI, CEKJIM, CEKJOS), Olmstead *et al.* (2008; HOLDOC), Cai *et al.*. (2009; BUDQEX), Das *et al.* (2009; HUKJIH), Mahieux *et al.* (2012; FAHGIG), Tiritiris & Kantlehner (2011; HOLDOC01) and Mossou *et al.* (2014; QQQAUJ03). For a more general view on ammonium carboxylate salts, see Odendal *et al.* (2010) who described the packing motifs in the crystal structures of such salts, and Kinbara *et al.* (1996) who described the role of hydrogen-bonded networks in the crystal structures of salts of chiral primary amines with achiral carboxylic acids.

## 5. Synthesis and crystallization

Benzylamine (185701), phenylacetic acid (P16621) and methanol (32213) were obtained from Sigma–Aldrich.

Benzylammonium phenylacetate (**1**) was obtained as follows. 40 mg of phenylacetic acid (0.29 mmol) were dissolved in 1 ml of methanol and 32 µl of benzylamine (0.29 mmol) were added under gentle stirring. The solvent was then evaporated slowly under ambient conditions to yield colourless crystals of compound **1**.

Benzylammonium phenylacetate hydrate (**2**) was obtained by dissolving 40 mg of phenylacetic acid (0.29 mmol) in 200 µl of methanol and 32 µl of benzylamine (0.29 mmol) were added under gentle stirring. The solution was diluted with 1.8 ml of ultra-pure water and evaporated slowly at ambient conditions to yield colourless crystals of compound **2**.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. In **1** and **2**, the C-bound hydrogen atoms were positioned with idealized coordinates (C—H =

0.95–0.99 Å) and refined as riding on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(N/O)$. The N-bound hydrogen atoms in **1** were refined freely. In **2**, the coordinates of the N- and O-bound hydrogen atoms were freely refined while the isotropic displacement parameters of the hydrogen atoms were calculated as $U_{iso}(H) = 1.2U_{eq}(N/O)$.

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# supporting information

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## The crystal structures of benzylammonium phenylacetate and its hydrate

**David Hess and Peter Mayer**

### Computing details

For both structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006), *CrystalExplorer17* (Turner *et al.*, 2017); software used to prepare material for publication: *PLATON* (Spek, 2009), *RPLUTO* (CCDC, 2018).

### Benzylammonium phenylacetate (1)

*Crystal data*

$C_7H_{10}N^+\cdot C_8H_7O_2^-$
$M_r$ = 243.29
Monoclinic, $C2/c$
$a$ = 25.913 (2) Å
$b$ = 5.9021 (5) Å
$c$ = 19.0842 (16) Å
$\beta$ = 114.692 (3)°
$V$ = 2651.9 (4) Å$^3$
$Z$ = 8
$F(000)$ = 1040
$D_x$ = 1.219 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4302 reflections
$\theta$ = 3.5–25.4°
$\mu$ = 0.08 mm$^{-1}$
$T$ = 100 K
Block, colourless
0.10 × 0.04 × 0.02 mm

*Data collection*

Bruker D8 Venture TXS diffractometer
Radiation source: rotating anode (TXS), Bruker TXS
Focusing mirrors monochromator
Detector resolution: 7.4074 pixels mm$^{-1}$
mix of phi and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.651, $T_{max}$ = 0.971
14421 measured reflections
2398 independent reflections
1800 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.092
$\theta_{max}$ = 25.4°, $\theta_{min}$ = 3.3°
$h = -30 \rightarrow 30$
$k = -7 \rightarrow 7$
$l = -22 \rightarrow 22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.103
$S$ = 1.03
2398 reflections
175 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 1.6577P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.22 e Å$^{-3}$

*Special details*

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

**Refinement**. C-H: constr N-H: refall
Reflections affected by the beamstop or those of higher order and significant higher $Fo^2$ than $Fc^2$ (caused by X-ray mirror) have been omitted in the refinement.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.28279 (5) | −0.35459 (19) | 0.41706 (7) | 0.0205 (3) |
| O2 | 0.24772 (5) | −0.07061 (19) | 0.33362 (7) | 0.0214 (3) |
| N1 | 0.27388 (7) | 0.8748 (3) | 0.20667 (9) | 0.0204 (4) |
| H11 | 0.2496 (9) | 0.977 (4) | 0.1667 (13) | 0.040 (6)* |
| H12 | 0.2666 (8) | 0.714 (4) | 0.1867 (12) | 0.035 (6)* |
| H13 | 0.2661 (10) | 0.883 (4) | 0.2511 (14) | 0.048 (7)* |
| C1 | 0.27013 (7) | −0.1506 (3) | 0.40169 (10) | 0.0169 (4) |
| C2 | 0.28113 (7) | 0.0118 (3) | 0.46855 (10) | 0.0190 (4) |
| H2A | 0.2687 | 0.1656 | 0.4476 | 0.023* |
| H2B | 0.2577 | −0.0353 | 0.4958 | 0.023* |
| C3 | 0.34259 (7) | 0.0220 (3) | 0.52591 (10) | 0.0186 (4) |
| C4 | 0.36866 (8) | −0.1595 (3) | 0.57485 (10) | 0.0223 (4) |
| H4 | 0.3476 | −0.2937 | 0.5719 | 0.027* |
| C5 | 0.42493 (8) | −0.1460 (3) | 0.62768 (11) | 0.0266 (4) |
| H5 | 0.4421 | −0.2705 | 0.6608 | 0.032* |
| C6 | 0.45623 (8) | 0.0480 (3) | 0.63248 (11) | 0.0307 (5) |
| H6 | 0.4948 | 0.0573 | 0.6688 | 0.037* |
| C7 | 0.43098 (8) | 0.2279 (3) | 0.58411 (12) | 0.0321 (5) |
| H7 | 0.4523 | 0.3611 | 0.5869 | 0.038* |
| C8 | 0.37457 (8) | 0.2153 (3) | 0.53139 (11) | 0.0255 (4) |
| H8 | 0.3576 | 0.3407 | 0.4986 | 0.031* |
| C9 | 0.33454 (8) | 0.9379 (3) | 0.22888 (11) | 0.0273 (5) |
| H9A | 0.3411 | 1.0948 | 0.2491 | 0.033* |
| H9B | 0.3428 | 0.9326 | 0.1828 | 0.033* |
| C10 | 0.37371 (7) | 0.7794 (3) | 0.28918 (10) | 0.0220 (4) |
| C11 | 0.38860 (8) | 0.8179 (3) | 0.36684 (11) | 0.0281 (5) |
| H11A | 0.3763 | 0.9525 | 0.3826 | 0.034* |
| C12 | 0.42124 (8) | 0.6622 (4) | 0.42177 (11) | 0.0354 (5) |
| H12A | 0.4310 | 0.6898 | 0.4748 | 0.042* |
| C13 | 0.43957 (9) | 0.4672 (4) | 0.39950 (13) | 0.0375 (5) |
| H13A | 0.4614 | 0.3592 | 0.4371 | 0.045* |
| C14 | 0.42609 (8) | 0.4292 (3) | 0.32244 (13) | 0.0357 (5) |
| H14 | 0.4394 | 0.2962 | 0.3072 | 0.043* |
| C15 | 0.39330 (8) | 0.5841 (3) | 0.26732 (12) | 0.0296 (5) |
| H15 | 0.3841 | 0.5570 | 0.2144 | 0.035* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0266 (7) | 0.0168 (7) | 0.0177 (6) | 0.0002 (5) | 0.0089 (5) | 0.0000 (5) |
| O2 | 0.0305 (7) | 0.0202 (7) | 0.0134 (6) | 0.0023 (5) | 0.0091 (5) | 0.0006 (5) |
| N1 | 0.0279 (9) | 0.0181 (9) | 0.0150 (8) | 0.0000 (7) | 0.0089 (7) | 0.0013 (7) |
| C1 | 0.0161 (9) | 0.0203 (10) | 0.0168 (9) | −0.0024 (7) | 0.0093 (7) | −0.0017 (7) |
| C2 | 0.0233 (10) | 0.0179 (9) | 0.0177 (9) | 0.0015 (7) | 0.0104 (8) | 0.0006 (7) |
| C3 | 0.0246 (10) | 0.0200 (9) | 0.0152 (9) | 0.0000 (7) | 0.0122 (8) | −0.0030 (7) |
| C4 | 0.0282 (10) | 0.0225 (10) | 0.0185 (9) | −0.0023 (8) | 0.0119 (8) | −0.0019 (7) |
| C5 | 0.0301 (11) | 0.0271 (10) | 0.0219 (10) | 0.0060 (8) | 0.0102 (8) | 0.0001 (8) |
| C6 | 0.0220 (10) | 0.0371 (12) | 0.0287 (11) | −0.0007 (9) | 0.0064 (9) | −0.0081 (9) |
| C7 | 0.0290 (11) | 0.0275 (11) | 0.0393 (12) | −0.0081 (9) | 0.0140 (10) | −0.0062 (9) |
| C8 | 0.0301 (11) | 0.0197 (10) | 0.0283 (11) | −0.0014 (8) | 0.0138 (9) | −0.0005 (8) |
| C9 | 0.0283 (11) | 0.0274 (11) | 0.0263 (10) | −0.0026 (8) | 0.0116 (9) | 0.0046 (8) |
| C10 | 0.0200 (10) | 0.0245 (10) | 0.0232 (10) | −0.0038 (7) | 0.0105 (8) | 0.0019 (8) |
| C11 | 0.0233 (10) | 0.0377 (12) | 0.0260 (11) | −0.0018 (8) | 0.0128 (9) | −0.0017 (9) |
| C12 | 0.0253 (11) | 0.0591 (15) | 0.0216 (10) | −0.0011 (10) | 0.0097 (9) | 0.0073 (10) |
| C13 | 0.0219 (11) | 0.0422 (13) | 0.0402 (13) | 0.0006 (9) | 0.0051 (10) | 0.0176 (10) |
| C14 | 0.0222 (11) | 0.0292 (11) | 0.0481 (14) | 0.0001 (8) | 0.0073 (10) | −0.0029 (10) |
| C15 | 0.0246 (11) | 0.0318 (11) | 0.0299 (11) | −0.0029 (8) | 0.0090 (9) | −0.0037 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.250 (2) | C7—C8 | 1.388 (3) |
| O2—C1 | 1.272 (2) | C7—H7 | 0.9500 |
| N1—C9 | 1.494 (2) | C8—H8 | 0.9500 |
| N1—H11 | 0.97 (2) | C9—C10 | 1.501 (3) |
| N1—H12 | 1.01 (2) | C9—H9A | 0.9900 |
| N1—H13 | 0.95 (3) | C9—H9B | 0.9900 |
| C1—C2 | 1.525 (2) | C10—C11 | 1.385 (3) |
| C2—C3 | 1.511 (2) | C10—C15 | 1.392 (3) |
| C2—H2A | 0.9900 | C11—C12 | 1.385 (3) |
| C2—H2B | 0.9900 | C11—H11A | 0.9500 |
| C3—C8 | 1.388 (3) | C12—C13 | 1.378 (3) |
| C3—C4 | 1.396 (2) | C12—H12A | 0.9500 |
| C4—C5 | 1.386 (3) | C13—C14 | 1.381 (3) |
| C4—H4 | 0.9500 | C13—H13A | 0.9500 |
| C5—C6 | 1.384 (3) | C14—C15 | 1.385 (3) |
| C5—H5 | 0.9500 | C14—H14 | 0.9500 |
| C6—C7 | 1.379 (3) | C15—H15 | 0.9500 |
| C6—H6 | 0.9500 | | |
| | | | |
| C9—N1—H11 | 109.1 (13) | C8—C7—H7 | 119.8 |
| C9—N1—H12 | 110.4 (11) | C7—C8—C3 | 120.88 (18) |
| H11—N1—H12 | 109.2 (17) | C7—C8—H8 | 119.6 |
| C9—N1—H13 | 109.0 (14) | C3—C8—H8 | 119.6 |
| H11—N1—H13 | 111.2 (19) | N1—C9—C10 | 110.87 (15) |

| | | | |
|---|---|---|---|
| H12—N1—H13 | 107.9 (17) | N1—C9—H9A | 109.5 |
| O1—C1—O2 | 124.09 (15) | C10—C9—H9A | 109.5 |
| O1—C1—C2 | 118.04 (15) | N1—C9—H9B | 109.5 |
| O2—C1—C2 | 117.86 (15) | C10—C9—H9B | 109.5 |
| C3—C2—C1 | 113.80 (14) | H9A—C9—H9B | 108.1 |
| C3—C2—H2A | 108.8 | C11—C10—C15 | 118.89 (17) |
| C1—C2—H2A | 108.8 | C11—C10—C9 | 120.98 (17) |
| C3—C2—H2B | 108.8 | C15—C10—C9 | 120.05 (17) |
| C1—C2—H2B | 108.8 | C12—C11—C10 | 120.66 (19) |
| H2A—C2—H2B | 107.7 | C12—C11—H11A | 119.7 |
| C8—C3—C4 | 118.27 (17) | C10—C11—H11A | 119.7 |
| C8—C3—C2 | 120.20 (16) | C13—C12—C11 | 120.06 (19) |
| C4—C3—C2 | 121.53 (16) | C13—C12—H12A | 120.0 |
| C5—C4—C3 | 120.69 (17) | C11—C12—H12A | 120.0 |
| C5—C4—H4 | 119.7 | C12—C13—C14 | 119.87 (19) |
| C3—C4—H4 | 119.7 | C12—C13—H13A | 120.1 |
| C6—C5—C4 | 120.34 (18) | C14—C13—H13A | 120.1 |
| C6—C5—H5 | 119.8 | C13—C14—C15 | 120.2 (2) |
| C4—C5—H5 | 119.8 | C13—C14—H14 | 119.9 |
| C7—C6—C5 | 119.42 (18) | C15—C14—H14 | 119.9 |
| C7—C6—H6 | 120.3 | C14—C15—C10 | 120.26 (19) |
| C5—C6—H6 | 120.3 | C14—C15—H15 | 119.9 |
| C6—C7—C8 | 120.39 (18) | C10—C15—H15 | 119.9 |
| C6—C7—H7 | 119.8 | | |

| | | | |
|---|---|---|---|
| O1—C1—C2—C3 | 59.1 (2) | C2—C3—C8—C7 | 179.60 (17) |
| O2—C1—C2—C3 | −122.12 (17) | N1—C9—C10—C11 | −86.5 (2) |
| C1—C2—C3—C8 | 110.26 (18) | N1—C9—C10—C15 | 90.2 (2) |
| C1—C2—C3—C4 | −70.2 (2) | C15—C10—C11—C12 | −1.6 (3) |
| C8—C3—C4—C5 | 0.3 (2) | C9—C10—C11—C12 | 175.07 (17) |
| C2—C3—C4—C5 | −179.29 (16) | C10—C11—C12—C13 | 0.4 (3) |
| C3—C4—C5—C6 | −0.3 (3) | C11—C12—C13—C14 | 1.0 (3) |
| C4—C5—C6—C7 | −0.1 (3) | C12—C13—C14—C15 | −1.3 (3) |
| C5—C6—C7—C8 | 0.4 (3) | C13—C14—C15—C10 | 0.0 (3) |
| C6—C7—C8—C3 | −0.4 (3) | C11—C10—C15—C14 | 1.4 (3) |
| C4—C3—C8—C7 | 0.0 (3) | C9—C10—C15—C14 | −175.34 (18) |

*Hydrogen-bond geometry (Å, º)*

*Cg*1 is the centroid of the C3–C8 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H11···O1$^{i}$ | 0.97 (2) | 1.77 (2) | 2.7177 (19) | 165 (2) |
| N1—H12···O2$^{ii}$ | 1.01 (2) | 1.73 (2) | 2.7306 (19) | 170.1 (18) |
| N1—H13···O2$^{iii}$ | 0.95 (3) | 1.85 (3) | 2.7938 (19) | 174 (2) |
| C2—H2*B*···O1$^{iv}$ | 0.99 | 2.40 | 3.375 (2) | 169 |

| | | | | |
|---|---|---|---|---|
| C8—H8···O1$^{iii}$ | 0.95 | 2.63 | 3.539 (2) | 161 |
| C9—H9···*Cg*1$^{v}$ | 0.95 | 2.92 | 3.877 (2) | 163 |

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

### Benzylammonium phenylacetate (2)

*Crystal data*

$C_7H_{10}N^+\cdot C_8H_7O_2^-\cdot H_2O$
$M_r$ = 261.31
Monoclinic, $P2_1/n$
$a$ = 6.8235 (7) Å
$b$ = 7.8766 (7) Å
$c$ = 26.364 (2) Å
$\beta$ = 93.218 (3)°
$V$ = 1414.7 (2) Å$^3$
$Z$ = 4
$F(000)$ = 560
$D_x$ = 1.227 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4619 reflections
$\theta$ = 2.7–25.0°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 100 K
Block, colourless
0.10 × 0.06 × 0.04 mm

*Data collection*

Bruker D8 Venture TXS diffractometer
Radiation source: rotating anode (TXS), Bruker TXS
Focusing mirrors monochromator
Detector resolution: 7.4074 pixels mm$^{-1}$
mix of phi and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.814, $T_{max}$ = 0.971
7319 measured reflections
2461 independent reflections
2090 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 3.5°
$h = -7\rightarrow7$
$k = -9\rightarrow8$
$l = -31\rightarrow27$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.075
$wR(F^2)$ = 0.170
$S$ = 1.25
2461 reflections
187 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 3.8665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.27 e Å$^{-3}$

*Special details*

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

**Refinement**. C-H constr N-H and O-H: refxyz

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.2350 (3) | 0.5687 (3) | 0.47484 (9) | 0.0213 (6) |
| O2 | 0.4238 (4) | 0.7897 (3) | 0.45801 (10) | 0.0245 (6) |
| O3 | 0.2403 (4) | 0.0283 (3) | 0.51346 (10) | 0.0230 (6) |
| H32 | 0.296 (6) | −0.048 (6) | 0.4981 (15) | 0.028* |
| H31 | 0.355 (6) | 0.089 (5) | 0.5279 (15) | 0.028* |

| | | | | |
|---|---|---|---|---|
| N1 | 0.0153 (5) | 0.2727 (4) | 0.45885 (12) | 0.0205 (7) |
| H11 | 0.091 (6) | 0.364 (5) | 0.4595 (14) | 0.025* |
| H12 | −0.084 (6) | 0.296 (5) | 0.4786 (15) | 0.025* |
| H13 | 0.101 (6) | 0.191 (5) | 0.4742 (14) | 0.025* |
| C1 | 0.3709 (5) | 0.6394 (4) | 0.45153 (13) | 0.0174 (7) |
| C2 | 0.4705 (5) | 0.5289 (5) | 0.41280 (13) | 0.0213 (8) |
| H2A | 0.5366 | 0.4332 | 0.4311 | 0.026* |
| H2B | 0.3676 | 0.4802 | 0.3892 | 0.026* |
| C3 | 0.6199 (5) | 0.6182 (4) | 0.38174 (13) | 0.0190 (8) |
| C4 | 0.8017 (5) | 0.6658 (4) | 0.40418 (14) | 0.0210 (8) |
| H4 | 0.8333 | 0.6385 | 0.4388 | 0.025* |
| C5 | 0.9377 (5) | 0.7532 (5) | 0.37627 (14) | 0.0236 (8) |
| H5 | 1.0604 | 0.7860 | 0.3921 | 0.028* |
| C6 | 0.8942 (6) | 0.7920 (5) | 0.32577 (14) | 0.0272 (9) |
| H6 | 0.9862 | 0.8522 | 0.3069 | 0.033* |
| C7 | 0.7154 (6) | 0.7424 (5) | 0.30294 (14) | 0.0280 (9) |
| H7 | 0.6851 | 0.7674 | 0.2681 | 0.034* |
| C8 | 0.5802 (5) | 0.6560 (5) | 0.33093 (14) | 0.0239 (8) |
| H8 | 0.4583 | 0.6223 | 0.3149 | 0.029* |
| C9 | −0.0635 (5) | 0.2271 (5) | 0.40676 (13) | 0.0226 (8) |
| H9A | −0.1605 | 0.3136 | 0.3947 | 0.027* |
| H9B | −0.1320 | 0.1165 | 0.4080 | 0.027* |
| C10 | 0.0974 (5) | 0.2156 (4) | 0.36952 (13) | 0.0198 (8) |
| C11 | 0.0829 (6) | 0.3063 (5) | 0.32460 (14) | 0.0253 (8) |
| H11A | −0.0272 | 0.3778 | 0.3174 | 0.030* |
| C12 | 0.2285 (6) | 0.2938 (5) | 0.28976 (14) | 0.0330 (10) |
| H12A | 0.2175 | 0.3567 | 0.2590 | 0.040* |
| C13 | 0.3896 (6) | 0.1892 (5) | 0.30013 (15) | 0.0315 (10) |
| H13A | 0.4887 | 0.1800 | 0.2764 | 0.038* |
| C14 | 0.4056 (6) | 0.0986 (5) | 0.34496 (14) | 0.0273 (9) |
| H14 | 0.5164 | 0.0278 | 0.3521 | 0.033* |
| C15 | 0.2608 (5) | 0.1105 (4) | 0.37956 (14) | 0.0222 (8) |
| H15 | 0.2722 | 0.0472 | 0.4102 | 0.027* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0211 (13) | 0.0190 (13) | 0.0243 (13) | −0.0042 (10) | 0.0064 (10) | −0.0027 (11) |
| O2 | 0.0237 (14) | 0.0181 (13) | 0.0321 (15) | −0.0035 (11) | 0.0068 (10) | −0.0066 (12) |
| O3 | 0.0200 (14) | 0.0212 (14) | 0.0279 (15) | −0.0001 (11) | 0.0032 (10) | −0.0061 (12) |
| N1 | 0.0205 (16) | 0.0160 (16) | 0.0254 (17) | −0.0024 (13) | 0.0050 (13) | −0.0044 (14) |
| C1 | 0.0122 (17) | 0.0197 (18) | 0.0201 (18) | −0.0014 (14) | −0.0011 (13) | −0.0014 (15) |
| C2 | 0.0248 (19) | 0.0182 (18) | 0.0213 (19) | −0.0018 (15) | 0.0051 (14) | −0.0035 (15) |
| C3 | 0.0200 (18) | 0.0145 (17) | 0.0229 (19) | 0.0030 (14) | 0.0052 (14) | −0.0045 (15) |
| C4 | 0.0241 (19) | 0.0192 (18) | 0.0197 (18) | −0.0003 (15) | 0.0020 (14) | −0.0012 (15) |
| C5 | 0.0208 (18) | 0.0188 (19) | 0.031 (2) | 0.0001 (15) | 0.0034 (15) | −0.0036 (16) |
| C6 | 0.029 (2) | 0.025 (2) | 0.029 (2) | −0.0042 (17) | 0.0114 (16) | −0.0020 (17) |
| C7 | 0.032 (2) | 0.031 (2) | 0.0213 (19) | 0.0023 (18) | 0.0045 (15) | 0.0034 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C8 | 0.0175 (18) | 0.030 (2) | 0.024 (2) | −0.0029 (16) | 0.0018 (14) | −0.0048 (17) |
| C9 | 0.0228 (19) | 0.0222 (19) | 0.0229 (19) | −0.0023 (15) | 0.0019 (14) | −0.0030 (16) |
| C10 | 0.0242 (19) | 0.0157 (17) | 0.0195 (18) | −0.0086 (15) | 0.0026 (14) | −0.0055 (15) |
| C11 | 0.030 (2) | 0.025 (2) | 0.0211 (19) | −0.0030 (16) | −0.0035 (15) | −0.0024 (16) |
| C12 | 0.046 (3) | 0.035 (2) | 0.0176 (19) | −0.011 (2) | 0.0033 (17) | 0.0000 (18) |
| C13 | 0.029 (2) | 0.039 (2) | 0.028 (2) | −0.0050 (18) | 0.0110 (16) | −0.0072 (19) |
| C14 | 0.028 (2) | 0.025 (2) | 0.029 (2) | −0.0025 (16) | 0.0054 (16) | −0.0052 (17) |
| C15 | 0.029 (2) | 0.0142 (17) | 0.0236 (19) | −0.0006 (15) | 0.0046 (15) | −0.0017 (15) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.270 (4) | C6—H6 | 0.9500 |
| O2—C1 | 1.247 (4) | C7—C8 | 1.391 (5) |
| O3—H32 | 0.83 (4) | C7—H7 | 0.9500 |
| O3—H31 | 0.97 (4) | C8—H8 | 0.9500 |
| N1—C9 | 1.490 (4) | C9—C10 | 1.516 (5) |
| N1—H11 | 0.89 (4) | C9—H9A | 0.9900 |
| N1—H12 | 0.90 (4) | C9—H9B | 0.9900 |
| N1—H13 | 0.94 (4) | C10—C11 | 1.382 (5) |
| C1—C2 | 1.529 (5) | C10—C15 | 1.402 (5) |
| C2—C3 | 1.516 (5) | C11—C12 | 1.394 (5) |
| C2—H2A | 0.9900 | C11—H11A | 0.9500 |
| C2—H2B | 0.9900 | C12—C13 | 1.389 (6) |
| C3—C8 | 1.384 (5) | C12—H12A | 0.9500 |
| C3—C4 | 1.395 (5) | C13—C14 | 1.380 (6) |
| C4—C5 | 1.398 (5) | C13—H13A | 0.9500 |
| C4—H4 | 0.9500 | C14—C15 | 1.385 (5) |
| C5—C6 | 1.382 (5) | C14—H14 | 0.9500 |
| C5—H5 | 0.9500 | C15—H15 | 0.9500 |
| C6—C7 | 1.386 (5) | | |
| | | | |
| H32—O3—H31 | 100 (4) | C6—C7—H7 | 120.0 |
| C9—N1—H11 | 113 (3) | C8—C7—H7 | 120.0 |
| C9—N1—H12 | 110 (2) | C3—C8—C7 | 121.3 (3) |
| H11—N1—H12 | 106 (4) | C3—C8—H8 | 119.4 |
| C9—N1—H13 | 114 (2) | C7—C8—H8 | 119.4 |
| H11—N1—H13 | 102 (3) | N1—C9—C10 | 112.0 (3) |
| H12—N1—H13 | 111 (3) | N1—C9—H9A | 109.2 |
| O2—C1—O1 | 124.3 (3) | C10—C9—H9A | 109.2 |
| O2—C1—C2 | 119.7 (3) | N1—C9—H9B | 109.2 |
| O1—C1—C2 | 116.0 (3) | C10—C9—H9B | 109.2 |
| C3—C2—C1 | 115.7 (3) | H9A—C9—H9B | 107.9 |
| C3—C2—H2A | 108.3 | C11—C10—C15 | 119.0 (3) |
| C1—C2—H2A | 108.3 | C11—C10—C9 | 120.3 (3) |
| C3—C2—H2B | 108.3 | C15—C10—C9 | 120.7 (3) |
| C1—C2—H2B | 108.3 | C10—C11—C12 | 120.6 (4) |
| H2A—C2—H2B | 107.4 | C10—C11—H11A | 119.7 |
| C8—C3—C4 | 118.3 (3) | C12—C11—H11A | 119.7 |

| | | | |
|---|---|---|---|
| C8—C3—C2 | 121.5 (3) | C13—C12—C11 | 119.9 (4) |
| C4—C3—C2 | 120.3 (3) | C13—C12—H12A | 120.1 |
| C3—C4—C5 | 120.7 (3) | C11—C12—H12A | 120.1 |
| C3—C4—H4 | 119.7 | C14—C13—C12 | 119.9 (4) |
| C5—C4—H4 | 119.7 | C14—C13—H13A | 120.0 |
| C6—C5—C4 | 120.2 (3) | C12—C13—H13A | 120.0 |
| C6—C5—H5 | 119.9 | C13—C14—C15 | 120.3 (4) |
| C4—C5—H5 | 119.9 | C13—C14—H14 | 119.9 |
| C5—C6—C7 | 119.5 (3) | C15—C14—H14 | 119.9 |
| C5—C6—H6 | 120.3 | C14—C15—C10 | 120.3 (3) |
| C7—C6—H6 | 120.3 | C14—C15—H15 | 119.8 |
| C6—C7—C8 | 120.1 (3) | C10—C15—H15 | 119.8 |

| | | | |
|---|---|---|---|
| O2—C1—C2—C3 | −4.5 (5) | C6—C7—C8—C3 | 0.2 (6) |
| O1—C1—C2—C3 | 174.7 (3) | N1—C9—C10—C11 | −126.9 (4) |
| C1—C2—C3—C8 | −107.2 (4) | N1—C9—C10—C15 | 54.4 (4) |
| C1—C2—C3—C4 | 72.2 (4) | C15—C10—C11—C12 | 0.0 (5) |
| C8—C3—C4—C5 | 1.6 (5) | C9—C10—C11—C12 | −178.8 (3) |
| C2—C3—C4—C5 | −177.8 (3) | C10—C11—C12—C13 | 0.1 (6) |
| C3—C4—C5—C6 | −0.7 (5) | C11—C12—C13—C14 | −0.3 (6) |
| C4—C5—C6—C7 | −0.5 (6) | C12—C13—C14—C15 | 0.5 (6) |
| C5—C6—C7—C8 | 0.8 (6) | C13—C14—C15—C10 | −0.5 (6) |
| C4—C3—C8—C7 | −1.4 (5) | C11—C10—C15—C14 | 0.2 (5) |
| C2—C3—C8—C7 | 178.1 (3) | C9—C10—C15—C14 | 178.9 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H32···O2$^{i}$ | 0.83 (4) | 1.90 (4) | 2.728 (4) | 175 (4) |
| O3—H31···O2$^{ii}$ | 0.97 (4) | 1.81 (4) | 2.771 (4) | 169 (3) |
| N1—H11···O1 | 0.89 (4) | 1.92 (4) | 2.791 (4) | 168 (4) |
| N1—H12···O1$^{iii}$ | 0.90 (4) | 1.96 (4) | 2.805 (4) | 157 (4) |
| N1—H13···O3 | 0.94 (4) | 1.87 (4) | 2.809 (4) | 170 (3) |
| C9—H9*B*···O3$^{iv}$ | 0.99 | 2.51 | 3.196 (4) | 126 |
| C15—H15···O2$^{i}$ | 0.95 | 2.57 | 3.412 (4) | 147 |

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