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# Syntheses, crystal structures and Hirshfeld surface analysis of three salts of 1-(4-nitrophenyl)piperazine

Sreeramapura D. Archana,[a] Sabine Foro,[b] Hemmige S. Yathirajan,[a]* Haruvegowda Kiran Kumar,[a] Rishik Balerao[c] and Ray J. Butcher[d]

[a]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore-570 006, India, [b]Institute of Materials Science, Darmstadt University of Technology, Alarich-Weiss-Strasse 2, D-64287 Darmstadt, Germany, [c]Thomas Jefferson High School for Science and Technology, 6560 Braddock Rd, Alexandria VA 22312, USA, and [d]Department of Chemistry, Howard University, 525 College Street NW, Washington DC 20059, USA. *Correspondence e-mail: yathirajan@hotmail.com

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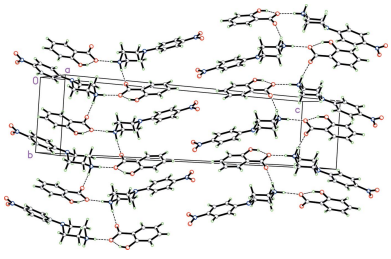
The structures and Hirshfeld surface analysis of three salts of 1-(4-nitrophenyl)-piperazine are discussed. In 4-(4-nitrophenyl)piperazin-1-ium salicylate ($C_{10}H_{14}N_3O_2^+\cdot C_7H_5O_3^-$), there are strong hydrogen bonds between cation and anion and the 4-nitrophenyl substituent occupies an equatorial position in the piperazinium ring. The cation and anion are linked together by supramolecular interactions [graph-set notation of hydrogen bonding $C_2^2(6)$ propagating in the *a*-axis direction]. Additionally, there is $\pi$–$\pi$ stacking involving the salicylate anion and the piperazinium cation in adjacent asymmetric units as well as a C—H$\cdots\pi$ interaction between a hydrogen atom on the piperazine ring and the phenyl ring within the salicyclate anion. In bis[4-(4-nitrophenyl)piperazin-1-ium] bis(4-fluorobenzoate) trihydrate ($2C_{10}H_{14}N_3O_2^+\cdot 2C_7H_4FO_2^-\cdot 3H_2O$), there are two cations, two anions, and three water molecules of solvation in the asymmetric unit, all linked by hydrogen bonds [graph-set notation of hydrogen bonding $R_2^2(20)$ between adjacent cations and $R_3^3(9)$ between a cation and its adjacent anion]. In the anion, the 4-nitrophenyl ring occupies an axial substitution position in the piperazinium ring, which is relatively rare. Within the asymmetric unit, the phenyl groups in the cations show an offset $\pi$–$\pi$ interaction. Additionally, there is a C—H$\cdots\pi$ interaction between a hydrogen atom on the phenyl ring within a cation and the phenyl ring within an anion. In 4-(4-nitrophenyl)piperazin-1-ium 3,5-dinitrobenzoate ($C_{10}H_{14}N_3O_2^+\cdot C_7H_4N_2O_6^-$), there is a strong N—H$\cdots$O hydrogen bond linking the cation and anion and the 4-nitrophenyl ring occupies an axial substitution position in the piperazinium ring, as seen in the previous structure. In the crystal, the cation and the anion form a complex three-dimensional hydrogen-bonded array involving $R_2^2(8)$, $R_4^4(12)$ and $R_4^4(20)$ rings propogating in the *a*-axis direction. The nitrophenyl group is disordered with occupancies of 0.806 (10) and 0.194 (10).



## 1. Chemical context

Piperazines and substituted piperazines are important pharmacophores that can be found in many biologically active compounds across a number of different therapeutic areas (Berkheij, 2005), being used as antifungal (Upadhayaya *et al.*, 2004), anti-bacterial, anti-malarial and anti-psychotic agents (Chaudhary *et al.*, 2006). An insight into advances on the antimicrobial activity of piperazine derivatives has been reported (Kharb *et al.*, 2012).

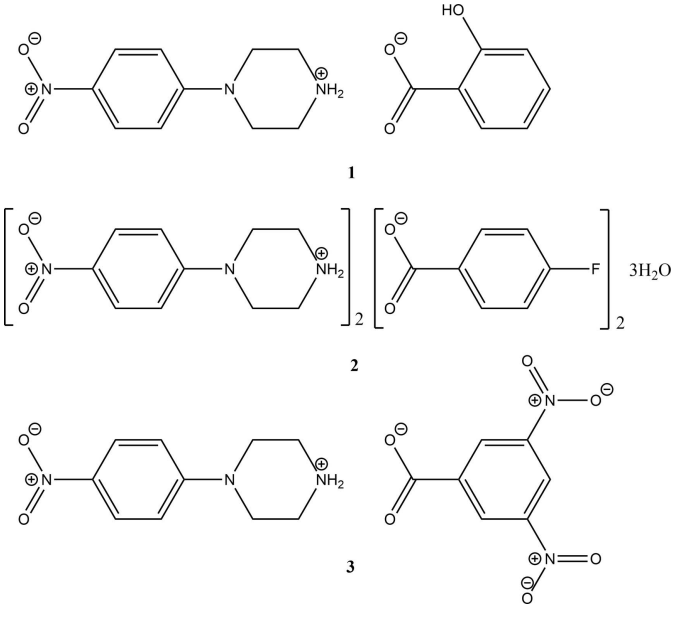
Piperazines are among the most important building blocks in today's drug discovery and are found in biologically active compounds across a number of different therapeutic areas

(Brockunier *et al.*, 2004; Bogatcheva *et al.*, 2006). A review of pharmacological and toxicological information for piperazine derivatives is given by Elliott (2011).

4-Nitrophenylpiperazinium chloride monohydrate has been used as an intermediate in the synthesis of anticancer drugs, transcriptase inhibitors and antifungal reagents and is also an important reagent for potassium channel openers, which show considerable biomolecular current-voltage rectification characteristics (Lu, 2007).

The inclusion behaviour of 4-sulfonatocalix[*n*]arenes (SCXn) (*n* = 4, 6, 8) with 1-(4-nitrophenyl)piperazine (NPP) has been investigated by UV spectroscopy and fluorescence spectroscopy at different pH values (Zhang *et al.*, 2014). The design, synthesis and biological profiling of aryl piperazine-based scaffolds for the management of androgen-sensitive prostatic disorders has been published (Gupta *et al.*, 2016). 4-Nitrophenylpiperazine was the starting material in the synthesis and biological evaluation of novel piperazine-containing hydrazone derivatives (Kaya *et al.*, 2016). Several previous investigations in this area are outlined in the *Database Survey* section.

In view of the importance of piperazines in general, and the use of 4-nitrophenylpiperazine in particular, the present paper reports the crystal structure studies of three salts of 4-nitrophenylpiperazine, *viz*., 4-nitrophenylpiperazinium salicylate (**1**), 4-nitrophenylpiperazinium 4-fluorobenzoate trihydrate (**2**) and 4-nitrophenylpiperazinium 3,5-dinitrobenzoate (**3**).



## 2. Structural commentary

Compound **1**, (4-nitrophenylpiperazinium salicylate; $C_{10}H_{14}N_3O_2{\cdot}C_7H_5O_3$), crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Fig. 1). The structure contains a 4-phenylpiperazinium cation linked to a salicylate anion by an N—H···O hydrogen bond [H···O = 1.792 (15) Å; N···O = 2.6957 (18) Å; N—H···O = 174.0 (18)°, Table 1]. In the salicylate anion, there is an intramolecular hydrogen bond involving the phenol hydrogen and the carboxylate group [$S_1^1(6)$ in graph-set notation (Etter *et al.*, 1990): H···O = 1.733 (17) Å; O···O = 2.5221 (17) Å; O—H···O = 152 (2)°]. In the conformation of the cation and anion, the dihedral angles between the piperazine ring and the phenyl ring, the piperazine ring with the salicylate ring, the phenyl ring with the salicylate ring, the nitro group and the phenyl ring, and the salicylate ring and its carboxylate group are 36.83 (6), 28.65 (6), 55.01 (5), 1.8 (3) and 7.0 (2)°, respectively. The first dihedral angle of 36.83 (6)° is indicative of the fact that the 4-nitrophenyl ring occupies an equatorial position in the phenyl ring, with the nitrogen lone pair occupying an axial position (see Fig. 1).

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C8—H8*A*···O5$^{i}$ | 0.97 | 2.53 | 3.430 (2) | 155 |
| C9—H9*A*···O5$^{ii}$ | 0.97 | 2.47 | 3.407 (2) | 164 |
| N2—H21···O3$^{iii}$ | 0.92 (2) | 1.88 (2) | 2.784 (2) | 170 (2) |
| N2—H22···O4 | 0.91 (2) | 1.79 (2) | 2.6957 (18) | 174 (2) |
| O5—H5*O*···O4 | 0.86 (2) | 1.73 (2) | 2.5221 (17) | 152 (2) |

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

Compound **2**, (4-nitrophenylpiperazinium 4-fluorobenzoate; $2C_{10}H_{14}N_3O_2{\cdot}2C_7H_4FO_2{\cdot}3H_2O$, crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. The structure consists of two 4-nitrophenylpiperazinium cations, two 4-fluorobenzoate anions and three water solvate molecules (see Fig. 2). Each cation is linked to a corresponding anion by a strong N—H···O hydrogen bond (Table 2). The water molecules are also involved in hydrogen bonding, which will be discussed in further detail in section 3. As shown by Fig. 2, the structure has been divided into four rings, with rings *A* and *D* representing the two 4-fluoro-

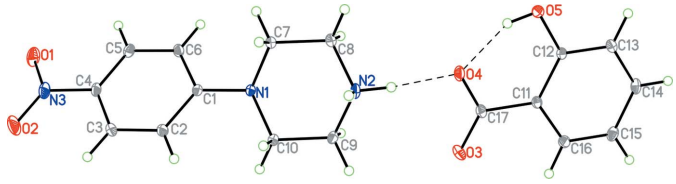


**Figure 1**
Diagram showing atom labelling and the arrangement of cation and anion in **1**. Hydrogen bonds are shown by dashed lines. Atomic displacement parameters are at the 30% probability level.

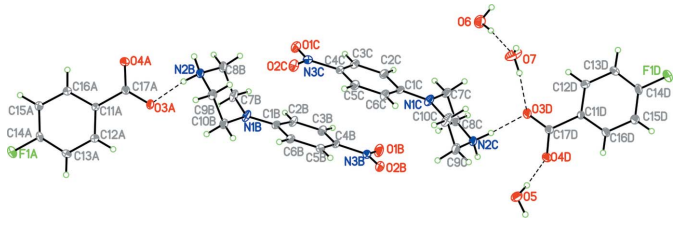


**Figure 2**
Diagram showing atom labelling indicating four rings *A*–*D*, the arrangement of cation and anion and the three water molecules of solvation in **2**. Hydrogen bonds are shown by dashed lines. Atomic displacement parameters are at the 30% probability level.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2*C*—H2*CA*···O3*D* | 0.90 (2) | 1.84 (2) | 2.733 (5) | 176 (4) |
| N2*C*—H2*CB*···O4*A*$^{i}$ | 0.87 (2) | 1.87 (2) | 2.726 (5) | 166 (4) |
| C3*C*—H3*C*···O1*C*$^{ii}$ | 0.93 | 2.62 | 3.261 (7) | 126 |
| C9*C*—H9*CA*···O5 | 0.97 | 2.51 | 3.332 (6) | 142 |
| C9*C*—H9*CB*···O2*B* | 0.97 | 2.53 | 3.401 (6) | 149 |
| C15*D*—H15*D*···F1*A*$^{iii}$ | 0.93 | 2.52 | 3.369 (5) | 152 |
| N2*B*—H2*BA*···O4*D*$^{iv}$ | 0.88 (2) | 1.92 (2) | 2.764 (5) | 163 (4) |
| N2*B*—H2*BB*···O3*A* | 0.89 (2) | 1.86 (2) | 2.739 (5) | 169 (4) |
| C3*B*—H3*B*···F1*D*$^{v}$ | 0.93 | 2.63 | 3.436 (6) | 145 |
| C8*B*—H8*BA*···O1*C* | 0.97 | 2.53 | 3.437 (6) | 155 |
| C8*B*—H8*BB*···O6$^{ii}$ | 0.97 | 2.49 | 3.182 (6) | 129 |
| C15*A*—H15*A*···F1*D*$^{vi}$ | 0.93 | 2.48 | 3.310 (5) | 149 |
| O5—H5*A*···O3*A*$^{vii}$ | 0.84 (2) | 1.96 (2) | 2.794 (4) | 172 (5) |
| O5—H5*D*···O4*D* | 0.83 (2) | 1.95 (2) | 2.778 (5) | 175 (5) |
| O6—H6*A*···O4*A*$^{ii}$ | 0.84 (2) | 2.04 (4) | 2.795 (6) | 149 (7) |
| O6—H6*D*···O7 | 0.84 (2) | 1.91 (2) | 2.744 (7) | 174 (8) |
| O7—H7*A*···O3*D* | 0.83 (2) | 1.99 (3) | 2.794 (5) | 163 (7) |
| O7—H7*B*···O5$^{viii}$ | 0.83 (2) | 1.93 (2) | 2.759 (6) | 172 (7) |

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

benzoate anions and rings *C* and *D* representing the two nitrophenylpiperazinium cations. Rings *A* and *B* are linked by a strong N—H···O hydrogen bond [H···O = 1.86 (2) Å; N···O = 2.739 (5) Å; N—H···O = 169 (4)°], as are rings *C* and *D* [H···O = 1.84 (2) Å; N···O = 2.733 (5)Å; N—H···O = 176 (4)°]. Additionally, ring *B*′s piperazine substituent forms a weak C—H···O interaction with an oxygen atom in ring *C*′s terminal nitro group [H···O = 2.53 Å; C···O = 3.437 (6) Å; C—H···O = 155°]. Ring *C*′s piperazine substituent forms a similar interaction with ring *B*′s terminal nitro group [H···O = 2.53 Å; C···O = 3.401 (6) Å; C—H···O = 149°]. In the conformation of rings *A*–*D*, the dihedral angles between the 4-nitrophenyl rings in rings *B* and *C*, the 4-nitrophenyl ring and nitro group in ring *B*, the 4-nitrophenyl ring and nitro group in ring *C*, the piperazine ring and the 4-nitrophenyl ring in ring *B*, the piperazine ring and 4-nitrophenyl ring in ring *C*, the fluorobenzene ring in ring *D* and the phenyl ring in ring *C*, and the fluorobenzene ring in *A* and the phenyl ring in *C* are 11.4 (4), 1.1 (2), 0.2 (2), 141.72 (16), 145.17 (17), 101.47 (17) and 103.32 (17)°, respectively. The third and fourth angles listed indicate that the 4-nitrophenyl ring occupies an axial position in both cations, which is relatively rare. In a previous

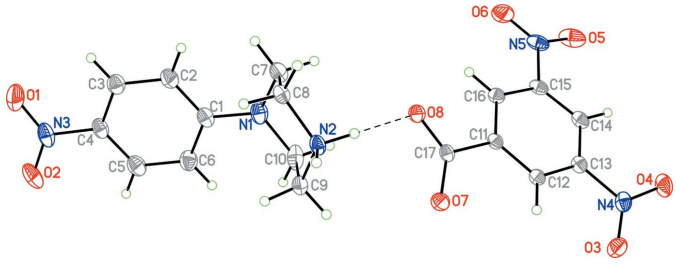



**Figure 3**
Diagram showing atom labelling and the arrangement of cation and anion in **3** (only major component shown). Hydrogen bonds are shown by dashed lines. Atomic displacement parameters are at the 30% probability level.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H21···O8 | 0.95 (2) | 1.77 (2) | 2.705 (3) | 170.7 (17) |
| N2—H22···O7$^{i}$ | 0.92 (2) | 1.81 (2) | 2.715 (3) | 166.4 (18) |
| C8—H8*A*···O4$^{ii}$ | 0.97 | 2.54 | 3.245 (3) | 130 |
| C8—H8*B*···O2$^{iii}$ | 0.97 | 2.40 | 3.354 (4) | 168 |
| C8—H8*B*···O2*A*$^{iii}$ | 0.97 | 2.39 | 3.353 (16) | 172 |
| C9—H9*A*···O1$^{iii}$ | 0.97 | 2.54 | 3.497 (5) | 171 |
| C9—H9*A*···O1*A*$^{iii}$ | 0.97 | 2.47 | 3.378 (14) | 155 |
| C10—H10*B*···O4$^{iv}$ | 0.97 | 2.60 | 3.425 (3) | 143 |
| C12—H12···O2$^{v}$ | 0.93 | 2.53 | 3.231 (4) | 133 |

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

paper containing eleven analogous structures, only one had this substitution pattern (Archana *et al.*, 2022).

Compound **3**, (4-nitrophenylpiperazinium 3,5-dinitrobenzoate; $C_{10}H_{14}N_3O_2{\cdot}C_7H_4N_2O_6$), crystallizes in the monoclinic space group *C*2/*c* with eight formula units in the unit cell. The structure consists of a 4-nitrophenylpiperazinium cation and a 3,5-dinitrobenzoate anion linked by a strong N—H···O hydrogen bond [H···O = 1.77 (2) Å; N···O = 2.705 (3) Å; N—H···O = 170.7 (17)°, Table 3] as shown in Fig. 3. The nitrophenyl ring is disordered with occupancies of 0.806 (10)/0.194 (10). In the cation, the dihedral angles between the piperazine ring and the major component of the 4-nitrophenyl ring, and the phenyl ring and its attached nitro group are 62.4 (1) and 10.1 (7)°, respectively. The former angle is indicative of the fact that the 4-nitrophenyl ring occupies an axial position, as it also did in **2**. In the anion, the dihedral angle between the 3,5-dinitrobenzoate phenyl ring and its carboxylate substituent is 18.7 (1)°.

## 3. Supramolecular features

In discussing the supramolecular features of the three structures, the direct hydrogen bonding involving the linking of the 4-nitrophenylpiperazinium cations and organic acid anions is omitted since it has already been discussed in the previous section. For **1**, there is a zigzag chain of hydrogen bonds

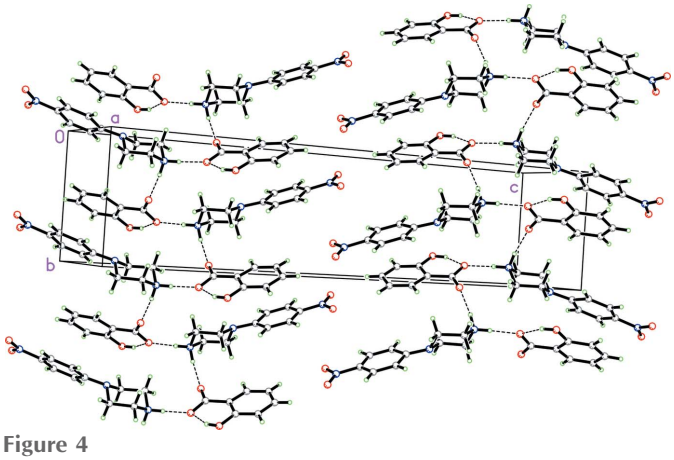



**Figure 4**
Packing diagram for **1** showing the zigzag chain of hydrogen bonds [graph-set notation $C_2^2(6)$] propagating in the *a*-axis direction.

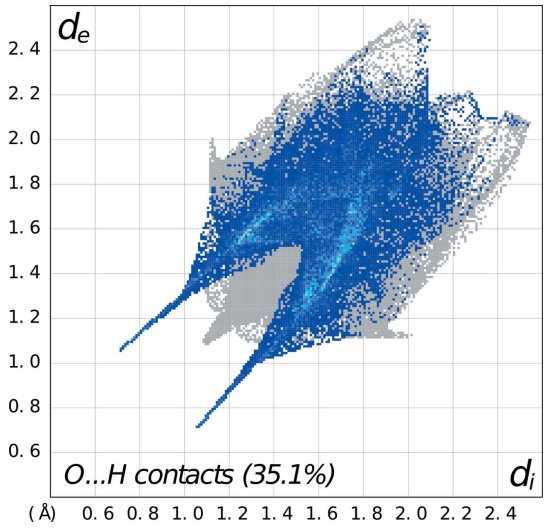



**Figure 5**
Fingerprint plot for **1** delineated into O···H/H···O contacts showing the prominent spikes indicating N—H···O hydrogen bonds.

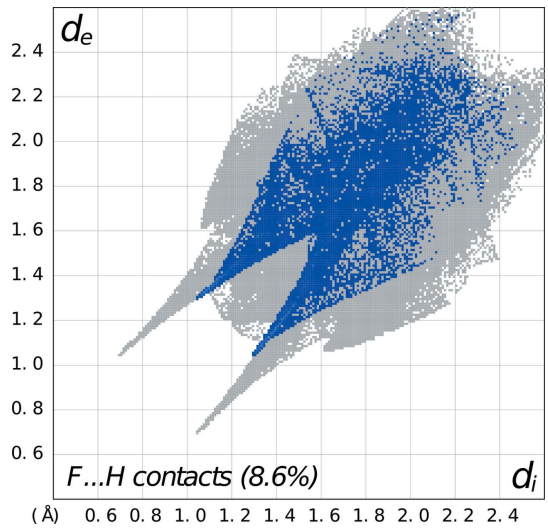



**Figure 7**
Fingerprint plot for **2** delineated into F···H/H···F contacts showing the prominent spikes as C—H···F interactions.

[graph-set notation $C_2^2(6)$ (Etter *et al.*, 1990)], propagating in the *b*-axis direction involving the piperazinium cations and salicylate anions, as shown in Fig. 4. These are also illustrated in the Hirshfeld fingerprint plot (Spackman *et al.*, 2021), which shows the prominent spikes involving both types of N—H···O hydrogen bonding (see Fig. 5). In the packing of the piperazinium cation and the salicylate anion, the salicylate anion forms a $\pi$–$\pi$ interaction with the phenyl ring of a piperazinium cation [$Cg2\cdots Cg3^{i}$ distance = 3.9296 (2) Å; symmetry code: (i) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; slippage:1.505 Å; *Cg*2 and *Cg*3 are the centroids of the C1–C6 and C11–C16 rings, respectively]. Additionally, there is a C—H···$\pi$ interaction between a hydrogen atom in the piperazine ring and the phenyl ring within the salicyclate anion (H···$Cg^{ii}$ distance, 2.76 Å; C8—H8*B*···$Cg2^{ii}$ angle of 156°, symmetry code: (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$).

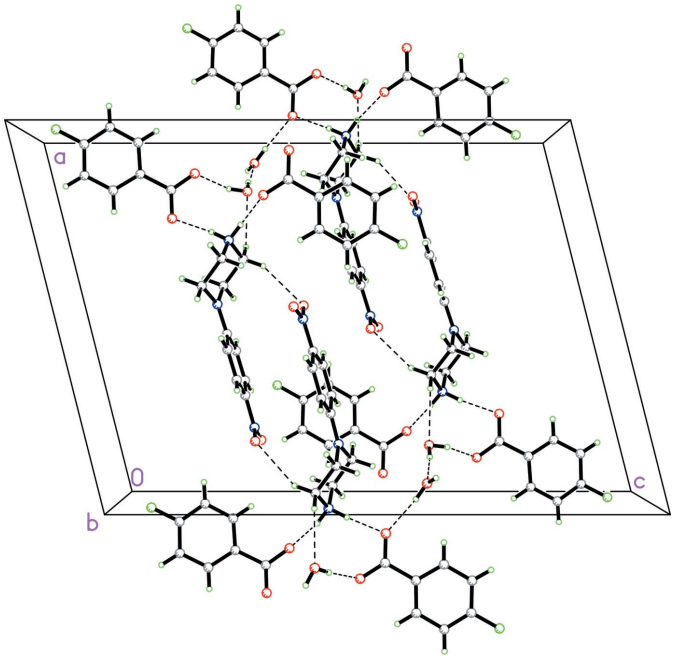



**Figure 6**
Packing diagram for **2** showing the complex three-dimensional array of hydrogen bonding involving both $R_2^2(20)$ motifs between rings *B* and *C* (middle left in diagram with ring *B* on right and ring *C* on left) and $R_3^3(9)$ motifs between rings *C* and *D* (ring *D* on upper left of diagram) as well as one water molecule.

For **2**, there are two anions and two cations as well as three water molecules of solvation in the asymmetric unit. This leads to a complex three-dimensional array of hydrogen bonding involving both $R_2^2(20)$ motifs between rings *B* and *C*, and $R_3^3(9)$ motifs between rings *C* and *D* as well as one water molecule, as seen in Fig. 6. There are also C—H···F interactions between adjacent fluorobenzoate anions linking them into centrosymmetric dimers (symmetry code: $\frac{3}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; see Table 2

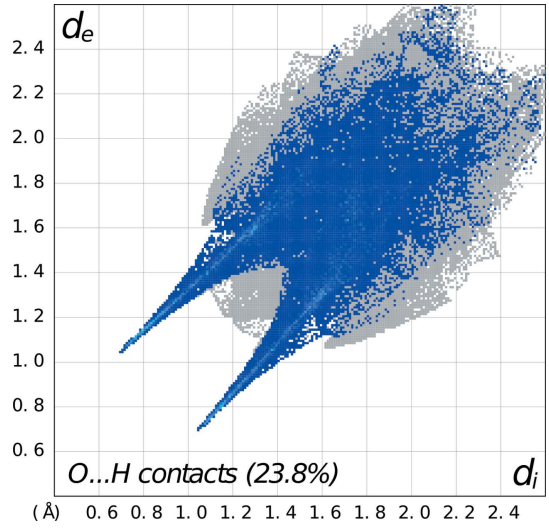



**Figure 8**
Fingerprint plot for **2** delineated into O···H/H···O contacts showing the prominent spikes as N—H···O interactions.

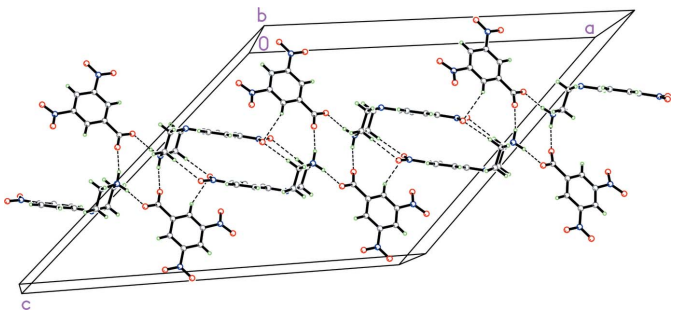



**Figure 9**
Packing diagram for **3** (only major component shown) showing the complex three-dimensional array of hydrogen bonding involving $R_2^2(8)$, $R_4^4(12)$ and $R_4^4(20)$ rings propagating in the *a*-axis direction between the the 4-nitrophenyl group of one cation with the piperazinium ring of an adjacent cation (symmetry code: $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$, involving O1$^{iii}$ and O2$^{iii}$; Table 4), two cations and two anions in adjacent asymmetric units ($-x, -y, 1-z$, involving O7$^{i}$), and two cations and two anions in adjacent asymmetric units (symmetry code: $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$, involving O4$^{iv}$) .

for numerical details). These interactions are shown clearly as spikes in the fingerprint plots delineated into C—H···F and N—H···O interactions (Figs. 7 and 8, respectively). In the crystal, the phenyl ring in *B* forms an offset $\pi$–$\pi$ interaction with the phenyl ring in *C* [*Cg*2···*Cg*4 distance, 3.8568 (7) Å; slippage of 1.835 Å; perpendicular distance of 3.454 (2) Å; *Cg*2 and *Cg*4 are the centroids of the C1*B*–C6*B* and C1*C*–C6*C* rings, respectively]. Additionally, there is a C–H···$\pi$ interaction between a hydrogen atom on the phenyl ring in *C* and the phenyl ring in *D* [H6*C*···*Cg*6$^{i}$, 2.91; C6—H6*C*···*Cg*6$^{i}$ angle of 161°, symmetry code: (i) $1-x, 1-y, -z$; *Cg*6 is the centroid of the C11*D*–C16*D* ring].

For **3**, the cation and the anion form a complex three-dimensional array of hydrogen bonding involving $R_2^2(8)$, $R_4^4(12)$ and $R_4^4(20)$ rings propogating in the *a*-axis direction between the 4-nitrophenyl group of one cation with the piperazinium ring of an adjacent cation (symmetry code: $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$), two cations and two anions in adjacent asymmetric units ($-x, -y, 1-z$), two cations and two anions in adjacent asymmetric units (symmetry code: $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$), respectively, as seen in Fig. 9 (Table 3). These show as sharp spikes in the fingerprint plot showing the N—H···O interactions (Fig. 10). Additionally, the nitrobenzene group within the piperazinium cation forms a $\pi$–$\pi$ interaction with the phenyl group of another piperazinium cation in an adjacent asymmetric unit [*Cg*2···*Cg*2$^{i}$ distance, 4.4132 (9) Å; perpendicular distance: 3.5596 (9) Å; slippage of 2.609 Å, symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; *Cg*2 is the centroid of the C1–C6*D* ring].

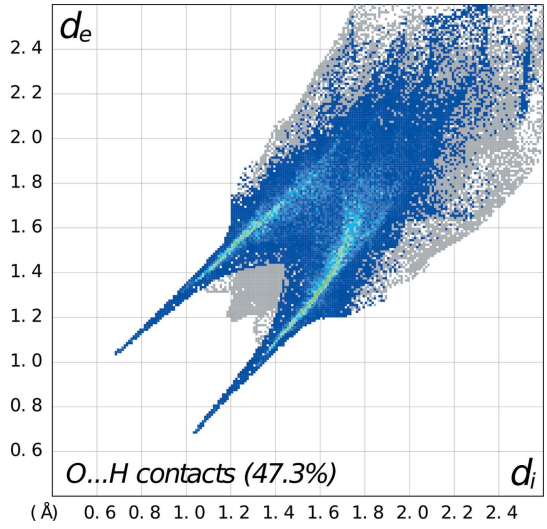



**Figure 10**
Fingerprint plot for **3** delineated into O···H/H···O contacts showing the prominent spikes as N—H···O interactions.

## 4. Database survey

Related structures containing 1-phenylpiperazine or the 1-phenylpiperazinium cation include racemic perhydrotriphenylene (PHTP), which has been shown to form a polar inclusion compound with 1-(4-nitrophenyl)piperazine (NPP) as a guest molecule (CSD refcode NOVWOK; König *et al.*, 1997). The crystal structure of the simple salt 4-nitrophenylpiperazinium chloride monohydrate has been reported (LIJNAU; Lu, 2007). The crystal structure of 4,6-dimethoxypyrimidin-2-amine-1-(4-nitrophenyl)piperazine (1:1) has been published (LUDMUU; Wang *et al.*, 2014) as well as the synthesis and crystal structure of a Schiff base, 5-methyl-2-{[4-(4-nitrophenyl)piperazin-1-yl]methyl}phenol (WUWBIC; Ayeni *et al.*, 2019).

NMR-based investigations of acyl-functionalized piperazines concerning their conformational behavior in solution has been studied and crystal structures of 1-(4-fluorobenzoyl)-4-(4-nitrophenyl)piperazine (BIQYIM), 1-(4-bromobenzoyl)-4-(4-nitrophenyl)piperazine (BIRHES), 1-(3-bromobenzoyl)-4-(4-nitrophenyl)piperazine (BIRHIW) and (piperazine-1,4-diyl)bis[(4-fluorophenyl)methanone] (BIRGOB) have been reported (Wodtke *et al.*, 2018). We have recently reported the crystal structures of some salts of 4-methoxyphenylpiperazine (Kiran Kumar *et al.*, 2019) and also 2-methoxyphenylpiperazine (Harish Chinthal *et al.*, 2020). We have recently reported the crystal structures of some salts of piperazine derivatives (Archana *et al.*, 2021). Very recently, we have reported the crystal structures of six salts of 4-nitrophenylpiperazine (NEBVOJ; NEBVUP; NEBWAW; NEBWEA; NEBWIE; NEBWOK) and four salts of 1-phenylpiperazine (Mahesha *et al.*, 2022*a*, 2022*b*). The syntheses and crystal structures of 4-(4-nitrophenyl)piperazin-1-ium benzoate monohydrate (BEFGIG) and 4-(4-nitrophenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate (BEFGOM) have been reported (Shankara Prasad *et al.*, 2022).

## 5. Synthesis and crystallization

For the synthesis of salts **1**–**3**, a solution of commercially available (from Sigma-Aldrich) 4-nitrophenylpiperazine (100 mg, 0.483 mol) in methanol (10 ml) was mixed with equimolar solutions of the appropriate acids in methanol (10 ml) and ethyl acetate (10 ml) *viz*., salicylic acid (67 mg) for

Table 4
Experimental details.

| | 1 | 2 | 3 |
|---|---|---|---|
| Crystal data | | | |
| Chemical formula | $C_{10}H_{14}N_3O_2^+\cdot C_7H_5O_3^-$ | $2C_{10}H_{14}N_3O_2^+\cdot 2C_7H_4FO_2^-\cdot 3H_2O$ | $C_{10}H_{14}N_3O_2^+\cdot C_7H_3N_2O_6^-$ |
| $M_r$ | 345.35 | 748.73 | 419.35 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/n$ | Monoclinic, $C2/c$ |
| Temperature (K) | 293 | 293 | 293 |
| $a, b, c$ (Å) | 7.0018 (3), 7.3938 (3), 31.531 (1) | 16.882 (2), 9.719 (1), 23.445 (4) | 27.953 (6), 8.1422 (6), 24.657 (5) |
| $\beta$ (°) | 90.132 (4) | 104.17 (1) | 136.55 (4) |
| $V$ (Å$^3$) | 1632.35 (11) | 3729.7 (9) | 3859 (2) |
| $Z$ | 4 | 4 | 8 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.11 | 0.11 | 0.12 |
| Crystal size (mm) | 0.48 × 0.40 × 0.40 | 0.32 × 0.16 × 0.14 | 0.48 × 0.48 × 0.40 |
| Data collection | | | |
| Diffractometer | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD |
| Absorption correction | Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009) | Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009) | Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009) |
| $T_{min}$, $T_{max}$ | 0.886, 1.000 | 0.887, 1.000 | 0.621, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 6955, 3506, 2606 | 14552, 6755, 2429 | 8107, 4119, 2838 |
| $R_{int}$ | 0.016 | 0.063 | 0.015 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.655 | 0.602 | 0.655 |
| Refinement | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.049, 0.119, 1.04 | 0.089, 0.154, 1.06 | 0.044, 0.119, 1.03 |
| No. of reflections | 3506 | 6755 | 4119 |
| No. of parameters | 235 | 508 | 337 |
| No. of restraints | 3 | 10 | 262 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.22, −0.21 | 0.19, −0.18 | 0.24, −0.24 |

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

**1**, 4-fluorobenzoic acid (68 mg) for **2** and 3,5-dinitrobenzoic acid (102 mg) for **3** (see Fig. 11 for reaction scheme). The corresponding solutions were stirred for 15 minutes at room temperature and allowed to stand at the same temperature. X-ray quality crystals were formed on slow evaporation (for **1** and **2**) for a week. For **3**, DMF (3 ml) was used for crystallization. The corresponding melting points were 453–458 K (**1**), 373–378 K (**2**) and 445–447 K (**3**).

## 6. Refinement

Crystal data, data collection and structure refinement details for the three structures are summarized in Table 4. In all structures, a riding model was used for the H atoms attached to C with $U_{iso}(H) = 1.2U_{eq}(C)$ while the N–H and water O–H hydrogen atoms were refined isotropically. In **3** the nitrophenyl group is disordered with occupancies of 0.806 (10)/0.194 (10) and constrained to have similar metrical parameters.

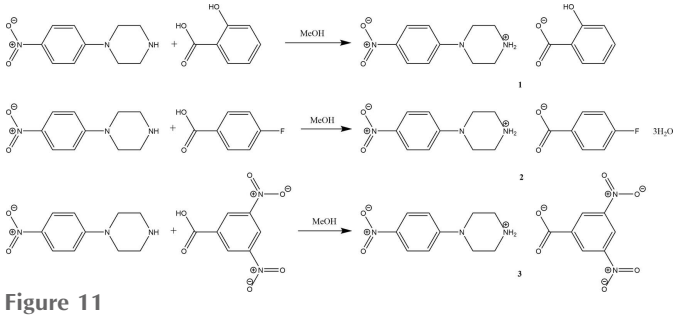



**Figure 11**
Reaction scheme for the synthesis of **1**, **2** and **3**.

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# supporting information

*Acta Cryst.* (2023). E**79**, 373-379 [https://doi.org/10.1107/S2056989023002517]

## Syntheses, crystal structures and Hirshfeld surface analysis of three salts of 1-(4-nitrophenyl)piperazine

**Sreeramapura D. Archana, Sabine Foro, Hemmige S. Yathirajan, Haruvegowda Kiran Kumar, Rishik Balerao and Ray J. Butcher**

### Computing details

For all structures, data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

### 4-(4-Nitrophenyl)piperazin-1-ium 2-hydroxybenzoate (1)

*Crystal data*

$C_{10}H_{14}N_3O_2^+ \cdot C_7H_5O_3^-$
$M_r$ = 345.35
Monoclinic, $P2_1/n$
$a$ = 7.0018 (3) Å
$b$ = 7.3938 (3) Å
$c$ = 31.531 (1) Å
$\beta$ = 90.132 (4)°
$V$ = 1632.35 (11) Å$^3$
$Z$ = 4
$F(000)$ = 728
$D_x$ = 1.405 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 3505 reflections
$\theta$ = 2.6–27.7°
$\mu$ = 0.11 mm$^{-1}$
$T$ = 293 K
Prism, yellow
0.48 × 0.40 × 0.40 mm

*Data collection*

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Rotation method data acquisition using $\omega$ scans.
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
$T_{min}$ = 0.886, $T_{max}$ = 1.000
6955 measured reflections
3506 independent reflections
2606 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016
$\theta_{max}$ = 27.8°, $\theta_{min}$ = 2.6°
$h$ = −8→7
$k$ = −5→9
$l$ = −30→41

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.119
$S$ = 1.04
3506 reflections
235 parameters
3 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.6706P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å$^{-3}$
$\Delta\rho_{min} = -0.21$ e Å$^{-3}$

*Special details*

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

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.9480 (2) | 0.4305 (2) | 0.40335 (5) | 0.0322 (4) |
| C2 | 1.1448 (3) | 0.4516 (3) | 0.40783 (6) | 0.0420 (4) |
| H2 | 1.214403 | 0.506875 | 0.386354 | 0.050* |
| C3 | 1.2372 (3) | 0.3912 (3) | 0.44378 (6) | 0.0481 (5) |
| H3 | 1.368446 | 0.406601 | 0.446657 | 0.058* |
| C4 | 1.1344 (3) | 0.3082 (3) | 0.47539 (5) | 0.0410 (4) |
| C5 | 0.9401 (3) | 0.2866 (3) | 0.47224 (6) | 0.0435 (4) |
| H5 | 0.871988 | 0.231148 | 0.493930 | 0.052* |
| C6 | 0.8476 (3) | 0.3485 (3) | 0.43645 (6) | 0.0416 (4) |
| H6 | 0.715817 | 0.335531 | 0.434273 | 0.050* |
| C7 | 0.6915 (2) | 0.6105 (3) | 0.37246 (5) | 0.0376 (4) |
| H7A | 0.742612 | 0.729932 | 0.378242 | 0.045* |
| H7B | 0.616032 | 0.573640 | 0.396727 | 0.045* |
| C8 | 0.5651 (2) | 0.6186 (3) | 0.33363 (5) | 0.0380 (4) |
| H8A | 0.499976 | 0.503859 | 0.330013 | 0.046* |
| H8B | 0.469135 | 0.711902 | 0.337361 | 0.046* |
| C9 | 0.8353 (3) | 0.5226 (3) | 0.29013 (5) | 0.0423 (4) |
| H9A | 0.909732 | 0.550803 | 0.265077 | 0.051* |
| H9B | 0.780236 | 0.403244 | 0.286470 | 0.051* |
| C10 | 0.9632 (2) | 0.5244 (3) | 0.32892 (5) | 0.0371 (4) |
| H10A | 1.064043 | 0.435557 | 0.325689 | 0.045* |
| H10B | 1.021744 | 0.642570 | 0.332035 | 0.045* |
| C11 | 0.3106 (2) | 0.5498 (2) | 0.16617 (5) | 0.0327 (4) |
| C12 | 0.1281 (2) | 0.6228 (2) | 0.17173 (5) | 0.0322 (4) |
| C13 | −0.0084 (3) | 0.6071 (3) | 0.13974 (6) | 0.0407 (4) |
| H13 | −0.130219 | 0.654106 | 0.143688 | 0.049* |
| C14 | 0.0370 (3) | 0.5219 (3) | 0.10231 (6) | 0.0462 (5) |
| H14 | −0.055100 | 0.510333 | 0.081179 | 0.055* |
| C15 | 0.2181 (3) | 0.4534 (3) | 0.09584 (6) | 0.0500 (5) |
| H15 | 0.248883 | 0.397864 | 0.070291 | 0.060* |
| C16 | 0.3527 (3) | 0.4681 (3) | 0.12755 (6) | 0.0434 (5) |
| H16 | 0.474660 | 0.422323 | 0.123046 | 0.052* |
| C17 | 0.4577 (2) | 0.5577 (2) | 0.20097 (6) | 0.0383 (4) |
| N1 | 0.84988 (19) | 0.4826 (2) | 0.36656 (4) | 0.0346 (3) |
| N2 | 0.6802 (2) | 0.6586 (2) | 0.29534 (5) | 0.0402 (4) |
| H21 | 0.735 (3) | 0.771 (2) | 0.2977 (6) | 0.048* |

| | | | | |
|---|---|---|---|---|
| H22 | 0.597 (2) | 0.659 (3) | 0.2733 (5) | 0.048* |
| N3 | 1.2348 (3) | 0.2403 (3) | 0.51271 (6) | 0.0578 (5) |
| O1 | 1.1425 (3) | 0.1642 (3) | 0.54024 (5) | 0.0781 (5) |
| O2 | 1.4076 (3) | 0.2658 (3) | 0.51533 (6) | 0.0970 (7) |
| O3 | 0.61169 (19) | 0.4778 (2) | 0.19676 (5) | 0.0570 (4) |
| O4 | 0.41348 (19) | 0.6511 (2) | 0.23358 (4) | 0.0500 (4) |
| O5 | 0.07825 (18) | 0.7116 (2) | 0.20780 (4) | 0.0468 (3) |
| H5O | 0.178 (2) | 0.710 (3) | 0.2234 (6) | 0.056* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0357 (9) | 0.0313 (9) | 0.0295 (8) | 0.0005 (7) | −0.0032 (7) | −0.0013 (7) |
| C2 | 0.0369 (9) | 0.0525 (11) | 0.0367 (9) | 0.0005 (8) | −0.0012 (7) | 0.0080 (8) |
| C3 | 0.0357 (9) | 0.0647 (13) | 0.0439 (11) | 0.0055 (9) | −0.0085 (8) | 0.0037 (10) |
| C4 | 0.0503 (11) | 0.0412 (10) | 0.0315 (9) | 0.0072 (9) | −0.0107 (8) | 0.0010 (8) |
| C5 | 0.0532 (11) | 0.0445 (11) | 0.0329 (9) | −0.0067 (9) | −0.0016 (8) | 0.0052 (8) |
| C6 | 0.0366 (9) | 0.0507 (11) | 0.0374 (9) | −0.0081 (8) | −0.0053 (7) | 0.0048 (8) |
| C7 | 0.0338 (9) | 0.0470 (11) | 0.0320 (9) | 0.0031 (8) | −0.0028 (7) | −0.0005 (8) |
| C8 | 0.0354 (9) | 0.0405 (10) | 0.0382 (9) | −0.0016 (8) | −0.0072 (7) | 0.0009 (8) |
| C9 | 0.0453 (10) | 0.0538 (12) | 0.0279 (9) | −0.0024 (9) | −0.0022 (7) | −0.0002 (8) |
| C10 | 0.0359 (9) | 0.0453 (10) | 0.0301 (9) | 0.0003 (8) | −0.0014 (7) | 0.0010 (8) |
| C11 | 0.0349 (9) | 0.0287 (8) | 0.0344 (9) | 0.0014 (7) | −0.0043 (7) | 0.0036 (7) |
| C12 | 0.0341 (8) | 0.0309 (9) | 0.0317 (8) | −0.0008 (7) | −0.0033 (7) | 0.0027 (7) |
| C13 | 0.0348 (9) | 0.0412 (10) | 0.0462 (10) | 0.0003 (8) | −0.0078 (8) | 0.0045 (8) |
| C14 | 0.0573 (12) | 0.0411 (11) | 0.0400 (10) | −0.0038 (9) | −0.0191 (9) | 0.0009 (8) |
| C15 | 0.0727 (14) | 0.0436 (11) | 0.0337 (10) | 0.0077 (10) | −0.0050 (9) | −0.0050 (8) |
| C16 | 0.0475 (11) | 0.0419 (10) | 0.0409 (10) | 0.0124 (9) | 0.0005 (8) | 0.0005 (8) |
| C17 | 0.0369 (9) | 0.0351 (9) | 0.0429 (10) | −0.0007 (8) | −0.0076 (8) | 0.0074 (8) |
| N1 | 0.0338 (7) | 0.0434 (8) | 0.0267 (7) | 0.0016 (6) | −0.0025 (6) | 0.0036 (6) |
| N2 | 0.0442 (9) | 0.0431 (9) | 0.0333 (8) | −0.0078 (7) | −0.0150 (6) | 0.0049 (7) |
| N3 | 0.0719 (13) | 0.0590 (11) | 0.0423 (10) | 0.0081 (10) | −0.0188 (9) | 0.0060 (9) |
| O1 | 0.0997 (13) | 0.0862 (13) | 0.0481 (9) | −0.0073 (11) | −0.0204 (9) | 0.0270 (9) |
| O2 | 0.0658 (11) | 0.1458 (19) | 0.0794 (13) | 0.0075 (12) | −0.0338 (9) | 0.0346 (12) |
| O3 | 0.0401 (8) | 0.0599 (9) | 0.0710 (10) | 0.0141 (7) | −0.0141 (7) | 0.0035 (8) |
| O4 | 0.0517 (8) | 0.0608 (9) | 0.0375 (7) | 0.0066 (7) | −0.0175 (6) | −0.0052 (7) |
| O5 | 0.0427 (7) | 0.0608 (9) | 0.0368 (7) | 0.0106 (7) | −0.0033 (5) | −0.0085 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.394 (2) | C10—N1 | 1.462 (2) |
| C1—C6 | 1.398 (2) | C10—H10A | 0.9700 |
| C1—N1 | 1.401 (2) | C10—H10B | 0.9700 |
| C2—C3 | 1.378 (2) | C11—C16 | 1.391 (2) |
| C2—H2 | 0.9300 | C11—C12 | 1.399 (2) |
| C3—C4 | 1.375 (3) | C11—C17 | 1.504 (2) |
| C3—H3 | 0.9300 | C12—O5 | 1.359 (2) |
| C4—C5 | 1.373 (3) | C12—C13 | 1.393 (2) |

| | | | |
|---|---|---|---|
| C4—N3 | 1.458 (2) | C13—C14 | 1.375 (3) |
| C5—C6 | 1.378 (2) | C13—H13 | 0.9300 |
| C5—H5 | 0.9300 | C14—C15 | 1.381 (3) |
| C6—H6 | 0.9300 | C14—H14 | 0.9300 |
| C7—N1 | 1.470 (2) | C15—C16 | 1.376 (3) |
| C7—C8 | 1.510 (2) | C15—H15 | 0.9300 |
| C7—H7A | 0.9700 | C16—H16 | 0.9300 |
| C7—H7B | 0.9700 | C17—O3 | 1.237 (2) |
| C8—N2 | 1.483 (2) | C17—O4 | 1.277 (2) |
| C8—H8A | 0.9700 | N2—H21 | 0.918 (15) |
| C8—H8B | 0.9700 | N2—H22 | 0.907 (15) |
| C9—N2 | 1.489 (2) | N3—O1 | 1.221 (2) |
| C9—C10 | 1.514 (2) | N3—O2 | 1.227 (3) |
| C9—H9A | 0.9700 | O5—H5O | 0.855 (15) |
| C9—H9B | 0.9700 | | |

| | | | |
|---|---|---|---|
| C2—C1—C6 | 118.13 (15) | C9—C10—H10A | 109.8 |
| C2—C1—N1 | 122.42 (15) | N1—C10—H10B | 109.8 |
| C6—C1—N1 | 119.41 (15) | C9—C10—H10B | 109.8 |
| C3—C2—C1 | 120.64 (17) | H10A—C10—H10B | 108.2 |
| C3—C2—H2 | 119.7 | C16—C11—C12 | 118.20 (15) |
| C1—C2—H2 | 119.7 | C16—C11—C17 | 120.64 (16) |
| C4—C3—C2 | 119.66 (17) | C12—C11—C17 | 121.15 (15) |
| C4—C3—H3 | 120.2 | O5—C12—C13 | 117.97 (15) |
| C2—C3—H3 | 120.2 | O5—C12—C11 | 121.87 (14) |
| C5—C4—C3 | 121.31 (16) | C13—C12—C11 | 120.15 (16) |
| C5—C4—N3 | 119.60 (18) | C14—C13—C12 | 120.03 (17) |
| C3—C4—N3 | 119.09 (18) | C14—C13—H13 | 120.0 |
| C4—C5—C6 | 118.97 (18) | C12—C13—H13 | 120.0 |
| C4—C5—H5 | 120.5 | C13—C14—C15 | 120.56 (17) |
| C6—C5—H5 | 120.5 | C13—C14—H14 | 119.7 |
| C5—C6—C1 | 121.28 (17) | C15—C14—H14 | 119.7 |
| C5—C6—H6 | 119.4 | C16—C15—C14 | 119.40 (18) |
| C1—C6—H6 | 119.4 | C16—C15—H15 | 120.3 |
| N1—C7—C8 | 111.35 (14) | C14—C15—H15 | 120.3 |
| N1—C7—H7A | 109.4 | C15—C16—C11 | 121.61 (17) |
| C8—C7—H7A | 109.4 | C15—C16—H16 | 119.2 |
| N1—C7—H7B | 109.4 | C11—C16—H16 | 119.2 |
| C8—C7—H7B | 109.4 | O3—C17—O4 | 123.89 (16) |
| H7A—C7—H7B | 108.0 | O3—C17—C11 | 119.89 (17) |
| N2—C8—C7 | 110.44 (14) | O4—C17—C11 | 116.22 (15) |
| N2—C8—H8A | 109.6 | C1—N1—C10 | 117.67 (13) |
| C7—C8—H8A | 109.6 | C1—N1—C7 | 116.15 (13) |
| N2—C8—H8B | 109.6 | C10—N1—C7 | 112.18 (13) |
| C7—C8—H8B | 109.6 | C8—N2—C9 | 110.67 (14) |
| H8A—C8—H8B | 108.1 | C8—N2—H21 | 109.9 (13) |
| N2—C9—C10 | 109.57 (14) | C9—N2—H21 | 108.5 (12) |
| N2—C9—H9A | 109.8 | C8—N2—H22 | 105.9 (12) |

| | | | |
|---|---|---|---|
| C10—C9—H9A | 109.8 | C9—N2—H22 | 112.8 (13) |
| N2—C9—H9B | 109.8 | H21—N2—H22 | 109.1 (18) |
| C10—C9—H9B | 109.8 | O1—N3—O2 | 123.11 (18) |
| H9A—C9—H9B | 108.2 | O1—N3—C4 | 118.53 (19) |
| N1—C10—C9 | 109.44 (14) | O2—N3—C4 | 118.3 (2) |
| N1—C10—H10A | 109.8 | C12—O5—H5O | 105.3 (15) |

| | | | |
|---|---|---|---|
| C6—C1—C2—C3 | 0.7 (3) | C12—C11—C16—C15 | −2.0 (3) |
| N1—C1—C2—C3 | −177.07 (17) | C17—C11—C16—C15 | 177.55 (18) |
| C1—C2—C3—C4 | 0.5 (3) | C16—C11—C17—O3 | −6.2 (3) |
| C2—C3—C4—C5 | −1.1 (3) | C12—C11—C17—O3 | 173.34 (17) |
| C2—C3—C4—N3 | 178.25 (18) | C16—C11—C17—O4 | 173.08 (17) |
| C3—C4—C5—C6 | 0.5 (3) | C12—C11—C17—O4 | −7.4 (2) |
| N3—C4—C5—C6 | −178.85 (17) | C2—C1—N1—C10 | 12.9 (2) |
| C4—C5—C6—C1 | 0.7 (3) | C6—C1—N1—C10 | −164.78 (16) |
| C2—C1—C6—C5 | −1.3 (3) | C2—C1—N1—C7 | −124.13 (18) |
| N1—C1—C6—C5 | 176.53 (17) | C6—C1—N1—C7 | 58.1 (2) |
| N1—C7—C8—N2 | −54.0 (2) | C9—C10—N1—C1 | 163.32 (15) |
| N2—C9—C10—N1 | 59.2 (2) | C9—C10—N1—C7 | −58.00 (19) |
| C16—C11—C12—O5 | −177.19 (16) | C8—C7—N1—C1 | −164.92 (15) |
| C17—C11—C12—O5 | 3.3 (3) | C8—C7—N1—C10 | 55.73 (19) |
| C16—C11—C12—C13 | 2.3 (3) | C7—C8—N2—C9 | 56.27 (19) |
| C17—C11—C12—C13 | −177.21 (16) | C10—C9—N2—C8 | −59.12 (19) |
| O5—C12—C13—C14 | 178.56 (17) | C5—C4—N3—O1 | 0.6 (3) |
| C11—C12—C13—C14 | −1.0 (3) | C3—C4—N3—O1 | −178.8 (2) |
| C12—C13—C14—C15 | −0.8 (3) | C5—C4—N3—O2 | −177.9 (2) |
| C13—C14—C15—C16 | 1.2 (3) | C3—C4—N3—O2 | 2.7 (3) |
| C14—C15—C16—C11 | 0.3 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C8—H8*A*···O5$^{i}$ | 0.97 | 2.53 | 3.430 (2) | 155 |
| C9—H9*A*···O5$^{ii}$ | 0.97 | 2.47 | 3.407 (2) | 164 |
| N2—H21···O3$^{iii}$ | 0.92 (2) | 1.88 (2) | 2.784 (2) | 170 (2) |
| N2—H22···O4 | 0.91 (2) | 1.79 (2) | 2.6957 (18) | 174 (2) |
| O5—H5*O*···O4 | 0.86 (2) | 1.73 (2) | 2.5221 (17) | 152 (2) |

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

**Bis[4-(4-nitrophenyl)piperazin-1-ium] bis(4-fluorobenzoate) trihydrate (2)**

*Crystal data*

$2C_{10}H_{14}N_3O_2^+·2C_7H_4FO_2^-·3H_2O$
$M_r$ = 748.73
Monoclinic, $P2_1/n$
*a* = 16.882 (2) Å
*b* = 9.719 (1) Å
*c* = 23.445 (4) Å
*β* = 104.17 (1)°
*V* = 3729.7 (9) Å$^3$
*Z* = 4
*F*(000) = 1576
$D_x$ = 1.333 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3000 reflections
*θ* = 2.7–27.9°

$\mu$ = 0.11 mm$^{-1}$
$T$ = 293 K

Prism, yellow
0.32 × 0.16 × 0.14 mm

*Data collection*

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Rotation method data acquisition using $\omega$ scans.
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
$T_{min}$ = 0.887, $T_{max}$ = 1.000

14552 measured reflections
6755 independent reflections
2429 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.063
$\theta_{max}$ = 25.4°, $\theta_{min}$ = 2.7°
$h$ = −18→20
$k$ = −10→11
$l$ = −27→28

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.089
$wR(F^2)$ = 0.154
$S$ = 1.06
6755 reflections
508 parameters
10 restraints
Primary atom site location: dual

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 1.3296P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$

*Special details*

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

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1C | −0.0312 (2) | 0.0993 (6) | 0.05767 (19) | 0.1313 (19) |
| O2C | −0.0276 (2) | 0.3166 (5) | 0.07469 (19) | 0.1200 (17) |
| N1C | 0.3330 (2) | 0.2257 (4) | 0.05682 (18) | 0.0771 (13) |
| N2C | 0.5029 (2) | 0.2032 (6) | 0.10503 (19) | 0.0755 (13) |
| H2CA | 0.525 (3) | 0.228 (5) | 0.0755 (15) | 0.091* |
| H2CB | 0.5443 (19) | 0.181 (4) | 0.1336 (15) | 0.091* |
| N3C | 0.0042 (3) | 0.2079 (7) | 0.0642 (2) | 0.0969 (18) |
| C1C | 0.2521 (3) | 0.2222 (5) | 0.05718 (18) | 0.0548 (12) |
| C2C | 0.2079 (3) | 0.1001 (5) | 0.0481 (2) | 0.0711 (15) |
| H2C | 0.233224 | 0.019457 | 0.040707 | 0.085* |
| C3C | 0.1267 (3) | 0.0971 (6) | 0.0501 (2) | 0.0772 (16) |
| H3C | 0.097724 | 0.014854 | 0.044109 | 0.093* |
| C4C | 0.0892 (3) | 0.2159 (7) | 0.0607 (2) | 0.0682 (15) |
| C5C | 0.1305 (3) | 0.3366 (6) | 0.0683 (2) | 0.0733 (15) |
| H5C | 0.104210 | 0.417170 | 0.074714 | 0.088* |
| C6C | 0.2101 (3) | 0.3398 (5) | 0.0666 (2) | 0.0683 (14) |
| H6C | 0.237594 | 0.423523 | 0.071920 | 0.082* |
| C7C | 0.3781 (3) | 0.1119 (5) | 0.0402 (2) | 0.0780 (16) |

| | | | | |
|---|---|---|---|---|
| H7CA | 0.395409 | 0.135654 | 0.004936 | 0.094* |
| H7CB | 0.343097 | 0.031626 | 0.031706 | 0.094* |
| C8C | 0.4513 (3) | 0.0795 (5) | 0.0889 (2) | 0.0778 (15) |
| H8CA | 0.433740 | 0.046830 | 0.122885 | 0.093* |
| H8CB | 0.482818 | 0.007113 | 0.076378 | 0.093* |
| C9C | 0.4560 (3) | 0.3197 (6) | 0.1201 (2) | 0.0896 (18) |
| H9CA | 0.490449 | 0.400734 | 0.127955 | 0.107* |
| H9CB | 0.438091 | 0.298123 | 0.155397 | 0.107* |
| C10C | 0.3834 (3) | 0.3483 (5) | 0.0706 (3) | 0.0967 (19) |
| H10A | 0.351600 | 0.422484 | 0.081479 | 0.116* |
| H10B | 0.401437 | 0.376935 | 0.036203 | 0.116* |
| F1D | 0.80958 (18) | 0.2961 (4) | −0.15139 (13) | 0.1174 (11) |
| O3D | 0.56389 (18) | 0.2765 (4) | 0.01163 (13) | 0.0890 (12) |
| O4D | 0.68138 (17) | 0.2812 (3) | 0.07894 (14) | 0.0732 (9) |
| C11D | 0.6858 (2) | 0.2799 (4) | −0.02171 (19) | 0.0491 (11) |
| C12D | 0.6447 (3) | 0.2743 (5) | −0.0801 (2) | 0.0695 (14) |
| H12D | 0.588034 | 0.266742 | −0.090222 | 0.083* |
| C13D | 0.6866 (3) | 0.2796 (5) | −0.1238 (2) | 0.0842 (17) |
| H13D | 0.658864 | 0.276926 | −0.163259 | 0.101* |
| C14D | 0.7692 (3) | 0.2888 (5) | −0.1075 (2) | 0.0737 (15) |
| C15D | 0.8119 (3) | 0.2932 (5) | −0.0508 (2) | 0.0707 (14) |
| H15D | 0.868565 | 0.299146 | −0.041181 | 0.085* |
| C16D | 0.7698 (3) | 0.2886 (5) | −0.0074 (2) | 0.0629 (13) |
| H16D | 0.798341 | 0.291399 | 0.031866 | 0.075* |
| C17D | 0.6400 (3) | 0.2786 (5) | 0.0263 (2) | 0.0595 (13) |
| O2B | 0.3231 (2) | 0.2769 (5) | 0.20682 (17) | 0.1045 (14) |
| O1B | 0.3290 (2) | 0.0563 (5) | 0.20074 (18) | 0.1105 (15) |
| N1B | −0.0349 (2) | 0.1235 (4) | 0.21687 (19) | 0.0790 (13) |
| N2B | −0.2044 (2) | 0.1456 (5) | 0.16528 (17) | 0.0588 (11) |
| H2BA | −0.2443 (18) | 0.172 (4) | 0.1358 (13) | 0.071* |
| H2BB | −0.227 (2) | 0.120 (4) | 0.1942 (13) | 0.071* |
| N3B | 0.2917 (3) | 0.1638 (6) | 0.20481 (18) | 0.0761 (14) |
| C1B | 0.0441 (3) | 0.1348 (5) | 0.21270 (19) | 0.0566 (13) |
| C2B | 0.0898 (3) | 0.0181 (5) | 0.2067 (2) | 0.0733 (15) |
| H2B | 0.065666 | −0.068307 | 0.204790 | 0.088* |
| C3B | 0.1698 (3) | 0.0287 (6) | 0.2037 (2) | 0.0735 (15) |
| H3B | 0.199054 | −0.050062 | 0.199530 | 0.088* |
| C4B | 0.2063 (3) | 0.1544 (7) | 0.20692 (19) | 0.0605 (14) |
| C5B | 0.1634 (3) | 0.2711 (5) | 0.21249 (18) | 0.0651 (14) |
| H5B | 0.188542 | 0.356672 | 0.214251 | 0.078* |
| C6B | 0.0836 (3) | 0.2623 (5) | 0.21548 (18) | 0.0640 (14) |
| H6B | 0.055117 | 0.342280 | 0.219424 | 0.077* |
| C7B | −0.0848 (3) | −0.0001 (5) | 0.2001 (2) | 0.0835 (16) |
| H7BA | −0.104035 | −0.032659 | 0.233468 | 0.100* |
| H7BB | −0.051975 | −0.072114 | 0.188784 | 0.100* |
| C8B | −0.1567 (3) | 0.0313 (5) | 0.1496 (2) | 0.0746 (15) |
| H8BA | −0.137606 | 0.055819 | 0.115176 | 0.090* |
| H8BB | −0.191039 | −0.049624 | 0.140231 | 0.090* |

| | | | | |
|---|---|---|---|---|
| C9B | −0.1539 (3) | 0.2701 (5) | 0.1840 (2) | 0.0664 (14) |
| H9BA | −0.186574 | 0.340691 | 0.196546 | 0.080* |
| H9BB | −0.134516 | 0.305835 | 0.151264 | 0.080* |
| C10B | −0.0822 (3) | 0.2335 (5) | 0.2341 (2) | 0.0730 (15) |
| H10C | −0.047802 | 0.313746 | 0.245332 | 0.088* |
| H10D | −0.101734 | 0.204666 | 0.267845 | 0.088* |
| F1A | −0.49683 (18) | 0.1699 (4) | 0.43216 (14) | 0.1397 (14) |
| O4A | −0.38370 (18) | 0.0984 (4) | 0.19821 (14) | 0.0888 (11) |
| O3A | −0.26382 (17) | 0.0937 (3) | 0.26186 (12) | 0.0729 (10) |
| C11A | −0.3810 (2) | 0.1255 (4) | 0.29882 (19) | 0.0477 (11) |
| C16A | −0.4654 (3) | 0.1210 (4) | 0.2880 (2) | 0.0600 (13) |
| H16A | −0.496139 | 0.108480 | 0.249617 | 0.072* |
| C15A | −0.5051 (3) | 0.1346 (5) | 0.3326 (2) | 0.0745 (15) |
| H15A | −0.561728 | 0.129803 | 0.325026 | 0.089* |
| C14A | −0.4589 (3) | 0.1549 (6) | 0.3875 (2) | 0.0849 (17) |
| C13A | −0.3756 (3) | 0.1629 (6) | 0.4012 (2) | 0.0885 (18) |
| H13A | −0.345964 | 0.178267 | 0.439690 | 0.106* |
| C12A | −0.3368 (3) | 0.1473 (5) | 0.3559 (2) | 0.0666 (14) |
| H12A | −0.280128 | 0.151696 | 0.364060 | 0.080* |
| C17A | −0.3395 (3) | 0.1061 (5) | 0.2497 (2) | 0.0585 (13) |
| O5 | 0.6374 (2) | 0.4752 (4) | 0.15259 (17) | 0.0930 (12) |
| H5A | 0.678 (2) | 0.513 (5) | 0.1756 (19) | 0.112* |
| H5D | 0.653 (3) | 0.419 (4) | 0.131 (2) | 0.112* |
| O6 | 0.3427 (3) | 0.0628 (6) | −0.1109 (2) | 0.1407 (17) |
| H6A | 0.349 (4) | 0.042 (7) | −0.1444 (15) | 0.169* |
| H6D | 0.371 (4) | 0.135 (4) | −0.106 (3) | 0.169* |
| O7 | 0.4318 (3) | 0.3010 (5) | −0.0864 (3) | 0.1502 (18) |
| H7A | 0.473 (3) | 0.311 (7) | −0.059 (2) | 0.180* |
| H7B | 0.414 (4) | 0.373 (4) | −0.104 (3) | 0.180* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1C | 0.077 (3) | 0.203 (5) | 0.119 (4) | −0.059 (3) | 0.032 (2) | −0.048 (4) |
| O2C | 0.064 (3) | 0.187 (5) | 0.111 (4) | 0.008 (3) | 0.025 (2) | −0.019 (4) |
| N1C | 0.045 (3) | 0.063 (3) | 0.120 (4) | 0.003 (2) | 0.014 (2) | −0.015 (3) |
| N2C | 0.043 (3) | 0.123 (4) | 0.060 (3) | 0.001 (3) | 0.012 (2) | 0.013 (3) |
| N3C | 0.062 (4) | 0.165 (6) | 0.060 (3) | −0.010 (4) | 0.010 (3) | −0.029 (4) |
| C1C | 0.041 (3) | 0.065 (3) | 0.052 (3) | −0.002 (3) | 0.000 (2) | 0.002 (3) |
| C2C | 0.055 (3) | 0.075 (4) | 0.080 (4) | −0.008 (3) | 0.012 (3) | −0.012 (3) |
| C3C | 0.059 (4) | 0.091 (5) | 0.078 (4) | −0.026 (3) | 0.011 (3) | −0.013 (3) |
| C4C | 0.040 (3) | 0.111 (5) | 0.051 (3) | −0.003 (4) | 0.007 (2) | −0.009 (4) |
| C5C | 0.053 (3) | 0.091 (5) | 0.073 (4) | 0.010 (3) | 0.010 (3) | −0.003 (3) |
| C6C | 0.049 (3) | 0.065 (4) | 0.088 (4) | 0.003 (3) | 0.013 (3) | 0.000 (3) |
| C7C | 0.052 (3) | 0.088 (4) | 0.090 (4) | 0.003 (3) | 0.011 (3) | −0.019 (3) |
| C8C | 0.058 (3) | 0.089 (4) | 0.089 (4) | 0.009 (3) | 0.022 (3) | 0.007 (3) |
| C9C | 0.063 (4) | 0.103 (5) | 0.110 (5) | −0.023 (3) | 0.035 (3) | −0.025 (4) |
| C10C | 0.054 (3) | 0.069 (4) | 0.162 (6) | −0.001 (3) | 0.017 (3) | 0.004 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| F1D | 0.107 (2) | 0.179 (3) | 0.084 (2) | −0.010 (2) | 0.0579 (19) | −0.012 (2) |
| O3D | 0.048 (2) | 0.157 (3) | 0.063 (2) | 0.004 (2) | 0.0152 (17) | 0.019 (2) |
| O4D | 0.065 (2) | 0.100 (3) | 0.054 (2) | 0.0097 (18) | 0.0136 (17) | 0.009 (2) |
| C11D | 0.045 (3) | 0.053 (3) | 0.050 (3) | 0.000 (2) | 0.014 (2) | 0.005 (3) |
| C12D | 0.056 (3) | 0.090 (4) | 0.059 (4) | −0.005 (3) | 0.009 (3) | −0.008 (3) |
| C13D | 0.084 (4) | 0.124 (5) | 0.048 (3) | −0.010 (4) | 0.024 (3) | −0.017 (3) |
| C14D | 0.073 (4) | 0.090 (4) | 0.074 (4) | −0.006 (3) | 0.048 (3) | −0.008 (4) |
| C15D | 0.058 (3) | 0.085 (4) | 0.069 (4) | 0.003 (3) | 0.016 (3) | 0.002 (4) |
| C16D | 0.058 (3) | 0.080 (4) | 0.054 (3) | 0.004 (3) | 0.019 (3) | 0.011 (3) |
| C17D | 0.056 (3) | 0.072 (4) | 0.050 (3) | 0.004 (3) | 0.012 (3) | 0.008 (3) |
| O2B | 0.073 (3) | 0.147 (4) | 0.101 (3) | −0.043 (3) | 0.036 (2) | −0.035 (3) |
| O1B | 0.055 (2) | 0.145 (4) | 0.134 (4) | 0.022 (2) | 0.028 (2) | 0.016 (3) |
| N1B | 0.041 (2) | 0.065 (3) | 0.131 (4) | −0.004 (2) | 0.020 (2) | −0.014 (3) |
| N2B | 0.047 (3) | 0.074 (3) | 0.056 (3) | 0.008 (3) | 0.0141 (19) | 0.009 (3) |
| N3B | 0.051 (3) | 0.123 (5) | 0.054 (3) | −0.006 (3) | 0.012 (2) | 0.001 (3) |
| C1B | 0.039 (3) | 0.065 (4) | 0.059 (3) | 0.007 (3) | −0.001 (2) | 0.002 (3) |
| C2B | 0.044 (3) | 0.069 (4) | 0.103 (4) | 0.002 (3) | 0.010 (3) | 0.009 (3) |
| C3B | 0.052 (3) | 0.080 (4) | 0.085 (4) | 0.011 (3) | 0.010 (3) | 0.006 (3) |
| C4B | 0.038 (3) | 0.091 (4) | 0.050 (3) | −0.008 (3) | 0.005 (2) | 0.002 (3) |
| C5B | 0.060 (3) | 0.078 (4) | 0.054 (3) | −0.010 (3) | 0.009 (2) | −0.005 (3) |
| C6B | 0.053 (3) | 0.069 (4) | 0.068 (4) | −0.002 (3) | 0.010 (2) | −0.010 (3) |
| C7B | 0.049 (3) | 0.066 (4) | 0.137 (5) | 0.002 (3) | 0.025 (3) | 0.003 (4) |
| C8B | 0.057 (3) | 0.074 (4) | 0.100 (4) | −0.004 (3) | 0.033 (3) | −0.017 (3) |
| C9B | 0.060 (3) | 0.060 (3) | 0.081 (4) | 0.004 (3) | 0.021 (3) | 0.001 (3) |
| C10B | 0.052 (3) | 0.082 (4) | 0.086 (4) | 0.004 (3) | 0.018 (3) | −0.014 (3) |
| F1A | 0.100 (2) | 0.246 (4) | 0.090 (2) | −0.018 (2) | 0.055 (2) | −0.043 (3) |
| O4A | 0.067 (2) | 0.145 (3) | 0.051 (2) | 0.020 (2) | 0.0076 (18) | −0.003 (2) |
| O3A | 0.0438 (19) | 0.116 (3) | 0.061 (2) | 0.0097 (18) | 0.0175 (16) | 0.012 (2) |
| C11A | 0.042 (3) | 0.052 (3) | 0.048 (3) | 0.001 (2) | 0.010 (2) | 0.000 (3) |
| C16A | 0.055 (3) | 0.070 (3) | 0.054 (3) | −0.001 (3) | 0.010 (2) | −0.005 (3) |
| C15A | 0.055 (3) | 0.102 (4) | 0.070 (4) | −0.013 (3) | 0.021 (3) | −0.018 (4) |
| C14A | 0.068 (4) | 0.131 (5) | 0.069 (4) | −0.011 (4) | 0.043 (3) | −0.023 (4) |
| C13A | 0.075 (4) | 0.141 (5) | 0.050 (3) | −0.012 (4) | 0.017 (3) | −0.024 (4) |
| C12A | 0.055 (3) | 0.090 (4) | 0.053 (3) | −0.005 (3) | 0.010 (3) | −0.009 (3) |
| C17A | 0.055 (3) | 0.072 (4) | 0.050 (3) | 0.007 (3) | 0.016 (3) | 0.007 (3) |
| O5 | 0.061 (2) | 0.112 (3) | 0.100 (3) | −0.002 (2) | 0.008 (2) | −0.036 (3) |
| O6 | 0.115 (3) | 0.170 (5) | 0.149 (4) | −0.041 (3) | 0.056 (3) | −0.068 (4) |
| O7 | 0.122 (4) | 0.128 (4) | 0.156 (5) | −0.024 (3) | −0.050 (3) | 0.019 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1C—N3C | 1.203 (6) | N1B—C10B | 1.449 (5) |
| O2C—N3C | 1.237 (6) | N1B—C7B | 1.464 (5) |
| N1C—C1C | 1.368 (5) | N2B—C8B | 1.470 (5) |
| N1C—C7C | 1.449 (5) | N2B—C9B | 1.483 (5) |
| N1C—C10C | 1.454 (5) | N2B—H2BA | 0.875 (18) |
| N2C—C9C | 1.474 (6) | N2B—H2BB | 0.892 (18) |
| N2C—C8C | 1.478 (6) | N3B—C4B | 1.456 (6) |

| | | | |
|---|---|---|---|
| N2C—H2CA | 0.897 (19) | C1B—C2B | 1.398 (6) |
| N2C—H2CB | 0.869 (19) | C1B—C6B | 1.402 (5) |
| N3C—C4C | 1.460 (6) | C2B—C3B | 1.372 (5) |
| C1C—C2C | 1.391 (5) | C2B—H2B | 0.9300 |
| C1C—C6C | 1.391 (5) | C3B—C4B | 1.363 (6) |
| C2C—C3C | 1.382 (6) | C3B—H3B | 0.9300 |
| C2C—H2C | 0.9300 | C4B—C5B | 1.369 (6) |
| C3C—C4C | 1.368 (6) | C5B—C6B | 1.369 (5) |
| C3C—H3C | 0.9300 | C5B—H5B | 0.9300 |
| C4C—C5C | 1.354 (6) | C6B—H6B | 0.9300 |
| C5C—C6C | 1.355 (5) | C7B—C8B | 1.505 (5) |
| C5C—H5C | 0.9300 | C7B—H7BA | 0.9700 |
| C6C—H6C | 0.9300 | C7B—H7BB | 0.9700 |
| C7C—C8C | 1.495 (5) | C8B—H8BA | 0.9700 |
| C7C—H7CA | 0.9700 | C8B—H8BB | 0.9700 |
| C7C—H7CB | 0.9700 | C9B—C10B | 1.508 (5) |
| C8C—H8CA | 0.9700 | C9B—H9BA | 0.9700 |
| C8C—H8CB | 0.9700 | C9B—H9BB | 0.9700 |
| C9C—C10C | 1.493 (6) | C10B—H10C | 0.9700 |
| C9C—H9CA | 0.9700 | C10B—H10D | 0.9700 |
| C9C—H9CB | 0.9700 | F1A—C14A | 1.363 (5) |
| C10C—H10A | 0.9700 | O4A—C17A | 1.257 (5) |
| C10C—H10B | 0.9700 | O3A—C17A | 1.245 (4) |
| F1D—C14D | 1.368 (5) | C11A—C12A | 1.379 (5) |
| O3D—C17D | 1.247 (4) | C11A—C16A | 1.386 (5) |
| O4D—C17D | 1.260 (5) | C11A—C17A | 1.499 (6) |
| C11D—C12D | 1.376 (5) | C16A—C15A | 1.380 (6) |
| C11D—C16D | 1.377 (5) | C16A—H16A | 0.9300 |
| C11D—C17D | 1.514 (6) | C15A—C14A | 1.346 (6) |
| C12D—C13D | 1.381 (6) | C15A—H15A | 0.9300 |
| C12D—H12D | 0.9300 | C14A—C13A | 1.365 (6) |
| C13D—C14D | 1.356 (6) | C13A—C12A | 1.387 (6) |
| C13D—H13D | 0.9300 | C13A—H13A | 0.9300 |
| C14D—C15D | 1.350 (6) | C12A—H12A | 0.9300 |
| C15D—C16D | 1.375 (6) | O5—H5A | 0.843 (19) |
| C15D—H15D | 0.9300 | O5—H5D | 0.833 (19) |
| C16D—H16D | 0.9300 | O6—H6A | 0.84 (2) |
| O2B—N3B | 1.216 (5) | O6—H6D | 0.84 (2) |
| O1B—N3B | 1.236 (5) | O7—H7A | 0.83 (2) |
| N1B—C1B | 1.365 (5) | O7—H7B | 0.83 (2) |

| | | | |
|---|---|---|---|
| C1C—N1C—C7C | 125.0 (4) | C10B—N1B—C7B | 111.1 (4) |
| C1C—N1C—C10C | 123.3 (4) | C8B—N2B—C9B | 112.3 (3) |
| C7C—N1C—C10C | 111.6 (4) | C8B—N2B—H2BA | 113 (3) |
| C9C—N2C—C8C | 111.6 (4) | C9B—N2B—H2BA | 106 (3) |
| C9C—N2C—H2CA | 109 (3) | C8B—N2B—H2BB | 110 (3) |
| C8C—N2C—H2CA | 111 (3) | C9B—N2B—H2BB | 109 (3) |
| C9C—N2C—H2CB | 113 (3) | H2BA—N2B—H2BB | 107 (4) |

| | | | |
|---|---|---|---|
| C8C—N2C—H2CB | 108 (3) | O2B—N3B—O1B | 122.8 (5) |
| H2CA—N2C—H2CB | 105 (4) | O2B—N3B—C4B | 118.7 (5) |
| O1C—N3C—O2C | 123.3 (6) | O1B—N3B—C4B | 118.5 (5) |
| O1C—N3C—C4C | 120.2 (6) | N1B—C1B—C2B | 121.0 (5) |
| O2C—N3C—C4C | 116.5 (6) | N1B—C1B—C6B | 122.0 (5) |
| N1C—C1C—C2C | 121.3 (5) | C2B—C1B—C6B | 117.0 (4) |
| N1C—C1C—C6C | 122.0 (5) | C3B—C2B—C1B | 121.2 (5) |
| C2C—C1C—C6C | 116.7 (4) | C3B—C2B—H2B | 119.4 |
| C3C—C2C—C1C | 120.9 (5) | C1B—C2B—H2B | 119.4 |
| C3C—C2C—H2C | 119.6 | C4B—C3B—C2B | 120.2 (5) |
| C1C—C2C—H2C | 119.6 | C4B—C3B—H3B | 119.9 |
| C4C—C3C—C2C | 119.6 (5) | C2B—C3B—H3B | 119.9 |
| C4C—C3C—H3C | 120.2 | C3B—C4B—C5B | 120.3 (4) |
| C2C—C3C—H3C | 120.2 | C3B—C4B—N3B | 119.5 (6) |
| C5C—C4C—C3C | 120.6 (5) | C5B—C4B—N3B | 120.2 (5) |
| C5C—C4C—N3C | 121.3 (6) | C6B—C5B—C4B | 120.3 (5) |
| C3C—C4C—N3C | 118.1 (6) | C6B—C5B—H5B | 119.9 |
| C4C—C5C—C6C | 119.9 (5) | C4B—C5B—H5B | 119.9 |
| C4C—C5C—H5C | 120.1 | C5B—C6B—C1B | 121.1 (5) |
| C6C—C5C—H5C | 120.1 | C5B—C6B—H6B | 119.5 |
| C5C—C6C—C1C | 122.3 (5) | C1B—C6B—H6B | 119.5 |
| C5C—C6C—H6C | 118.9 | N1B—C7B—C8B | 110.2 (4) |
| C1C—C6C—H6C | 118.9 | N1B—C7B—H7BA | 109.6 |
| N1C—C7C—C8C | 110.3 (4) | C8B—C7B—H7BA | 109.6 |
| N1C—C7C—H7CA | 109.6 | N1B—C7B—H7BB | 109.6 |
| C8C—C7C—H7CA | 109.6 | C8B—C7B—H7BB | 109.6 |
| N1C—C7C—H7CB | 109.6 | H7BA—C7B—H7BB | 108.1 |
| C8C—C7C—H7CB | 109.6 | N2B—C8B—C7B | 110.0 (4) |
| H7CA—C7C—H7CB | 108.1 | N2B—C8B—H8BA | 109.7 |
| N2C—C8C—C7C | 110.4 (4) | C7B—C8B—H8BA | 109.7 |
| N2C—C8C—H8CA | 109.6 | N2B—C8B—H8BB | 109.7 |
| C7C—C8C—H8CA | 109.6 | C7B—C8B—H8BB | 109.7 |
| N2C—C8C—H8CB | 109.6 | H8BA—C8B—H8BB | 108.2 |
| C7C—C8C—H8CB | 109.6 | N2B—C9B—C10B | 109.4 (4) |
| H8CA—C8C—H8CB | 108.1 | N2B—C9B—H9BA | 109.8 |
| N2C—C9C—C10C | 110.1 (4) | C10B—C9B—H9BA | 109.8 |
| N2C—C9C—H9CA | 109.6 | N2B—C9B—H9BB | 109.8 |
| C10C—C9C—H9CA | 109.6 | C10B—C9B—H9BB | 109.8 |
| N2C—C9C—H9CB | 109.6 | H9BA—C9B—H9BB | 108.2 |
| C10C—C9C—H9CB | 109.6 | N1B—C10B—C9B | 110.4 (4) |
| H9CA—C9C—H9CB | 108.2 | N1B—C10B—H10C | 109.6 |
| N1C—C10C—C9C | 110.2 (4) | C9B—C10B—H10C | 109.6 |
| N1C—C10C—H10A | 109.6 | N1B—C10B—H10D | 109.6 |
| C9C—C10C—H10A | 109.6 | C9B—C10B—H10D | 109.6 |
| N1C—C10C—H10B | 109.6 | H10C—C10B—H10D | 108.1 |
| C9C—C10C—H10B | 109.6 | C12A—C11A—C16A | 118.0 (4) |
| H10A—C10C—H10B | 108.1 | C12A—C11A—C17A | 121.4 (4) |
| C12D—C11D—C16D | 118.9 (4) | C16A—C11A—C17A | 120.5 (4) |

| | | | |
|---|---|---|---|
| C12D—C11D—C17D | 120.9 (4) | C15A—C16A—C11A | 121.8 (4) |
| C16D—C11D—C17D | 120.2 (4) | C15A—C16A—H16A | 119.1 |
| C11D—C12D—C13D | 120.7 (4) | C11A—C16A—H16A | 119.1 |
| C11D—C12D—H12D | 119.7 | C14A—C15A—C16A | 117.6 (5) |
| C13D—C12D—H12D | 119.7 | C14A—C15A—H15A | 121.2 |
| C14D—C13D—C12D | 118.2 (5) | C16A—C15A—H15A | 121.2 |
| C14D—C13D—H13D | 120.9 | C15A—C14A—F1A | 118.7 (5) |
| C12D—C13D—H13D | 120.9 | C15A—C14A—C13A | 123.8 (5) |
| C15D—C14D—C13D | 122.9 (5) | F1A—C14A—C13A | 117.6 (5) |
| C15D—C14D—F1D | 119.7 (5) | C14A—C13A—C12A | 117.7 (5) |
| C13D—C14D—F1D | 117.4 (5) | C14A—C13A—H13A | 121.1 |
| C14D—C15D—C16D | 118.7 (5) | C12A—C13A—H13A | 121.1 |
| C14D—C15D—H15D | 120.7 | C11A—C12A—C13A | 121.1 (4) |
| C16D—C15D—H15D | 120.7 | C11A—C12A—H12A | 119.5 |
| C15D—C16D—C11D | 120.6 (4) | C13A—C12A—H12A | 119.5 |
| C15D—C16D—H16D | 119.7 | O3A—C17A—O4A | 123.3 (4) |
| C11D—C16D—H16D | 119.7 | O3A—C17A—C11A | 118.9 (4) |
| O3D—C17D—O4D | 123.9 (4) | O4A—C17A—C11A | 117.8 (4) |
| O3D—C17D—C11D | 118.3 (4) | H5A—O5—H5D | 110 (5) |
| O4D—C17D—C11D | 117.8 (4) | H6A—O6—H6D | 98 (7) |
| C1B—N1B—C10B | 125.1 (4) | H7A—O7—H7B | 115 (7) |
| C1B—N1B—C7B | 123.7 (4) | | |

| | | | |
|---|---|---|---|
| C7C—N1C—C1C—C2C | 8.1 (7) | C10B—N1B—C1B—C2B | 167.7 (4) |
| C10C—N1C—C1C—C2C | −175.0 (5) | C7B—N1B—C1B—C2B | −17.0 (7) |
| C7C—N1C—C1C—C6C | −172.0 (4) | C10B—N1B—C1B—C6B | −10.8 (7) |
| C10C—N1C—C1C—C6C | 4.9 (7) | C7B—N1B—C1B—C6B | 164.5 (5) |
| N1C—C1C—C2C—C3C | 178.4 (4) | N1B—C1B—C2B—C3B | −178.7 (4) |
| C6C—C1C—C2C—C3C | −1.6 (7) | C6B—C1B—C2B—C3B | −0.1 (7) |
| C1C—C2C—C3C—C4C | 0.3 (7) | C1B—C2B—C3B—C4B | 0.4 (7) |
| C2C—C3C—C4C—C5C | 1.3 (8) | C2B—C3B—C4B—C5B | −0.7 (7) |
| C2C—C3C—C4C—N3C | −178.2 (4) | C2B—C3B—C4B—N3B | 178.8 (4) |
| O1C—N3C—C4C—C5C | −179.5 (5) | O2B—N3B—C4B—C3B | 178.9 (5) |
| O2C—N3C—C4C—C5C | −0.4 (7) | O1B—N3B—C4B—C3B | −0.7 (7) |
| O1C—N3C—C4C—C3C | −0.1 (7) | O2B—N3B—C4B—C5B | −1.6 (7) |
| O2C—N3C—C4C—C3C | 179.0 (5) | O1B—N3B—C4B—C5B | 178.8 (5) |
| C3C—C4C—C5C—C6C | −1.4 (7) | C3B—C4B—C5B—C6B | 0.6 (7) |
| N3C—C4C—C5C—C6C | 178.0 (4) | N3B—C4B—C5B—C6B | −178.9 (4) |
| C4C—C5C—C6C—C1C | 0.0 (7) | C4B—C5B—C6B—C1B | −0.3 (7) |
| N1C—C1C—C6C—C5C | −178.5 (4) | N1B—C1B—C6B—C5B | 178.6 (4) |
| C2C—C1C—C6C—C5C | 1.4 (7) | C2B—C1B—C6B—C5B | 0.0 (6) |
| C1C—N1C—C7C—C8C | −124.1 (5) | C1B—N1B—C7B—C8B | −116.6 (5) |
| C10C—N1C—C7C—C8C | 58.7 (5) | C10B—N1B—C7B—C8B | 59.3 (5) |
| C9C—N2C—C8C—C7C | 55.0 (5) | C9B—N2B—C8B—C7B | 55.5 (5) |
| N1C—C7C—C8C—N2C | −55.7 (5) | N1B—C7B—C8B—N2B | −56.2 (5) |
| C8C—N2C—C9C—C10C | −55.5 (5) | C8B—N2B—C9B—C10B | −55.5 (5) |
| C1C—N1C—C10C—C9C | 123.4 (5) | C1B—N1B—C10B—C9B | 116.0 (5) |
| C7C—N1C—C10C—C9C | −59.4 (6) | C7B—N1B—C10B—C9B | −59.8 (5) |

| | | | |
|---|---|---|---|
| N2C—C9C—C10C—N1C | 56.9 (6) | N2B—C9B—C10B—N1B | 56.8 (5) |
| C16D—C11D—C12D—C13D | −1.1 (8) | C12A—C11A—C16A—C15A | −1.5 (7) |
| C17D—C11D—C12D—C13D | 178.1 (5) | C17A—C11A—C16A—C15A | 178.1 (5) |
| C11D—C12D—C13D—C14D | 0.8 (8) | C11A—C16A—C15A—C14A | 1.1 (8) |
| C12D—C13D—C14D—C15D | −0.1 (9) | C16A—C15A—C14A—F1A | 179.4 (5) |
| C12D—C13D—C14D—F1D | −179.0 (5) | C16A—C15A—C14A—C13A | 0.1 (9) |
| C13D—C14D—C15D—C16D | −0.3 (9) | C15A—C14A—C13A—C12A | −0.8 (9) |
| F1D—C14D—C15D—C16D | 178.6 (4) | F1A—C14A—C13A—C12A | 179.8 (5) |
| C14D—C15D—C16D—C11D | −0.1 (8) | C16A—C11A—C12A—C13A | 0.6 (7) |
| C12D—C11D—C16D—C15D | 0.8 (7) | C17A—C11A—C12A—C13A | −178.9 (5) |
| C17D—C11D—C16D—C15D | −178.5 (5) | C14A—C13A—C12A—C11A | 0.4 (8) |
| C12D—C11D—C17D—O3D | −2.2 (7) | C12A—C11A—C17A—O3A | 8.3 (7) |
| C16D—C11D—C17D—O3D | 177.0 (4) | C16A—C11A—C17A—O3A | −171.2 (4) |
| C12D—C11D—C17D—O4D | 178.6 (4) | C12A—C11A—C17A—O4A | −174.1 (4) |
| C16D—C11D—C17D—O4D | −2.2 (7) | C16A—C11A—C17A—O4A | 6.4 (7) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2*C*—H2*CA*···O3*D* | 0.90 (2) | 1.84 (2) | 2.733 (5) | 176 (4) |
| N2*C*—H2*CB*···O4*A*$^{i}$ | 0.87 (2) | 1.87 (2) | 2.726 (5) | 166 (4) |
| C3*C*—H3*C*···O1*C*$^{ii}$ | 0.93 | 2.62 | 3.261 (7) | 126 |
| C9*C*—H9*CA*···O5 | 0.97 | 2.51 | 3.332 (6) | 142 |
| C9*C*—H9*CB*···O2*B* | 0.97 | 2.53 | 3.401 (6) | 149 |
| C15*D*—H15*D*···F1*A*$^{iii}$ | 0.93 | 2.52 | 3.369 (5) | 152 |
| N2*B*—H2*BA*···O4*D*$^{iv}$ | 0.88 (2) | 1.92 (2) | 2.764 (5) | 163 (4) |
| N2*B*—H2*BB*···O3*A* | 0.89 (2) | 1.86 (2) | 2.739 (5) | 169 (4) |
| C3*B*—H3*B*···F1*D*$^{v}$ | 0.93 | 2.63 | 3.436 (6) | 145 |
| C8*B*—H8*BA*···O1*C* | 0.97 | 2.53 | 3.437 (6) | 155 |
| C8*B*—H8*BB*···O6$^{ii}$ | 0.97 | 2.49 | 3.182 (6) | 129 |
| C15*A*—H15*A*···F1*D*$^{vi}$ | 0.93 | 2.48 | 3.310 (5) | 149 |
| O5—H5*A*···O3*A*$^{vii}$ | 0.84 (2) | 1.96 (2) | 2.794 (4) | 172 (5) |
| O5—H5*D*···O4*D* | 0.83 (2) | 1.95 (2) | 2.778 (5) | 175 (5) |
| O6—H6*A*···O4*A*$^{ii}$ | 0.84 (2) | 2.04 (4) | 2.795 (6) | 149 (7) |
| O6—H6*D*···O7 | 0.84 (2) | 1.91 (2) | 2.744 (7) | 174 (8) |
| O7—H7*A*···O3*D* | 0.83 (2) | 1.99 (3) | 2.794 (5) | 163 (7) |
| O7—H7*B*···O5$^{viii}$ | 0.83 (2) | 1.93 (2) | 2.759 (6) | 172 (7) |

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

### 4-(4-Nitrophenyl)piperazin-1-ium 3,5-dinitrobenzoate (3)

*Crystal data*

$C_{10}H_{14}N_3O_2^+·C_7H_3N_2O_6^-$
$M_r$ = 419.35
Monoclinic, *C*2/*c*
*a* = 27.953 (6) Å
*b* = 8.1422 (6) Å
*c* = 24.657 (5) Å
*β* = 136.55 (4)°
*V* = 3859 (2) Å$^3$
*Z* = 8
*F*(000) = 1744
$D_x$ = 1.443 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å

Cell parameters from 4154 reflections
$\theta$ = 2.6–27.7°
$\mu$ = 0.12 mm$^{-1}$
$T$ = 293 K
Prism, orange
0.48 × 0.48 × 0.40 mm

*Data collection*

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Rotation method data acquisition using $\omega$ scans.
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
$T_{min}$ = 0.621, $T_{max}$ = 1.000
8107 measured reflections
4119 independent reflections
2838 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.015
$\theta_{max}$ = 27.7°, $\theta_{min}$ = 2.6°
$h$ = −35→23
$k$ = −10→10
$l$ = −31→30

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.119
$S$ = 1.03
4119 reflections
337 parameters
262 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 1.7099P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

*Special details*

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

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| N1 | 0.02612 (8) | 0.1284 (2) | 0.33993 (9) | 0.0580 (4) | |
| N2 | 0.02315 (7) | −0.0150 (2) | 0.44281 (9) | 0.0452 (4) | |
| H21 | −0.0246 (11) | −0.041 (2) | 0.4078 (11) | 0.054 (5)* | |
| H22 | 0.0488 (10) | −0.044 (2) | 0.4941 (13) | 0.060 (6)* | |
| O1 | 0.29131 (19) | 0.2691 (7) | 0.4152 (3) | 0.0936 (12) | 0.806 (10) |
| O2 | 0.28193 (17) | 0.5004 (6) | 0.4502 (2) | 0.0809 (12) | 0.806 (10) |
| N3 | 0.26170 (14) | 0.3612 (7) | 0.42375 (18) | 0.0631 (11) | 0.806 (10) |
| C1 | 0.08449 (14) | 0.1834 (4) | 0.3603 (2) | 0.0484 (8) | 0.806 (10) |
| C2 | 0.12478 (14) | 0.0767 (5) | 0.36260 (19) | 0.0547 (7) | 0.806 (10) |
| H2A | 0.112973 | −0.033824 | 0.350722 | 0.066* | 0.806 (10) |
| C3 | 0.18272 (12) | 0.1354 (5) | 0.38267 (16) | 0.0554 (8) | 0.806 (10) |
| H3A | 0.209682 | 0.064018 | 0.384227 | 0.067* | 0.806 (10) |
| C4 | 0.20037 (11) | 0.3006 (5) | 0.40042 (16) | 0.0508 (8) | 0.806 (10) |
| C5 | 0.16008 (13) | 0.4073 (4) | 0.3981 (2) | 0.0621 (8) | 0.806 (10) |
| H5A | 0.171890 | 0.517846 | 0.409976 | 0.075* | 0.806 (10) |
| C6 | 0.10214 (14) | 0.3487 (4) | 0.3780 (2) | 0.0613 (8) | 0.806 (10) |
| H6A | 0.075181 | 0.420007 | 0.376471 | 0.074* | 0.806 (10) |

| | | | | | |
|---|---|---|---|---|---|
| O1A | 0.2969 (7) | 0.342 (2) | 0.4346 (10) | 0.082 (3) | 0.194 (10) |
| O2A | 0.2788 (8) | 0.575 (2) | 0.4647 (10) | 0.092 (4) | 0.194 (10) |
| N3A | 0.2640 (8) | 0.436 (2) | 0.4386 (12) | 0.067 (2) | 0.194 (10) |
| C1A | 0.0900 (6) | 0.2138 (18) | 0.3708 (9) | 0.0517 (19) | 0.194 (10) |
| C2A | 0.1283 (6) | 0.1262 (16) | 0.3643 (9) | 0.0519 (18) | 0.194 (10) |
| H2AA | 0.116265 | 0.018417 | 0.346160 | 0.062* | 0.194 (10) |
| C3A | 0.1845 (6) | 0.1997 (19) | 0.3848 (7) | 0.0519 (17) | 0.194 (10) |
| H3AA | 0.210172 | 0.141125 | 0.380427 | 0.062* | 0.194 (10) |
| C4A | 0.2025 (5) | 0.3609 (18) | 0.4119 (7) | 0.0608 (19) | 0.194 (10) |
| C5A | 0.1642 (6) | 0.4485 (14) | 0.4184 (8) | 0.064 (2) | 0.194 (10) |
| H5AA | 0.176195 | 0.556282 | 0.436505 | 0.077* | 0.194 (10) |
| C6A | 0.1079 (6) | 0.3750 (17) | 0.3979 (9) | 0.062 (2) | 0.194 (10) |
| H6AA | 0.082288 | 0.433576 | 0.402238 | 0.075* | 0.194 (10) |
| C7 | 0.01491 (10) | −0.0473 (3) | 0.33759 (11) | 0.0549 (5) | |
| H7A | 0.033495 | −0.105603 | 0.321795 | 0.066* | |
| H7B | −0.034605 | −0.069484 | 0.298825 | 0.066* | |
| C8 | 0.04986 (8) | −0.1082 (2) | 0.41735 (9) | 0.0453 (4) | |
| H8A | 0.040452 | −0.224338 | 0.414378 | 0.054* | |
| H8B | 0.099796 | −0.093615 | 0.455510 | 0.054* | |
| C9 | 0.02899 (9) | 0.1652 (3) | 0.44076 (12) | 0.0566 (5) | |
| H9A | 0.077636 | 0.196839 | 0.480671 | 0.068* | |
| H9B | 0.006349 | 0.220270 | 0.452198 | 0.068* | |
| C10 | −0.00458 (10) | 0.2165 (3) | 0.36060 (13) | 0.0665 (6) | |
| H10A | −0.054078 | 0.193843 | 0.321442 | 0.080* | |
| H10B | 0.001467 | 0.333748 | 0.360480 | 0.080* | |
| O3 | −0.34048 (7) | 0.22513 (19) | 0.30638 (8) | 0.0637 (4) | |
| O4 | −0.43333 (6) | 0.11002 (19) | 0.19876 (9) | 0.0728 (4) | |
| O5 | −0.43221 (7) | −0.0409 (2) | 0.00913 (7) | 0.0831 (5) | |
| O6 | −0.33493 (8) | −0.1049 (2) | 0.05113 (8) | 0.0724 (4) | |
| O7 | −0.11517 (5) | 0.10834 (17) | 0.40386 (6) | 0.0513 (3) | |
| O8 | −0.11592 (5) | −0.06375 (17) | 0.33293 (7) | 0.0543 (3) | |
| N4 | −0.37128 (7) | 0.14524 (19) | 0.24700 (10) | 0.0500 (4) | |
| N5 | −0.36882 (8) | −0.05526 (19) | 0.06164 (8) | 0.0563 (4) | |
| C11 | −0.22389 (7) | 0.03229 (19) | 0.27718 (9) | 0.0358 (4) | |
| C12 | −0.26050 (8) | 0.0878 (2) | 0.29183 (9) | 0.0379 (4) | |
| H12 | −0.237068 | 0.124431 | 0.341817 | 0.046* | |
| C13 | −0.33255 (8) | 0.0880 (2) | 0.23089 (10) | 0.0411 (4) | |
| C14 | −0.36957 (8) | 0.0396 (2) | 0.15541 (10) | 0.0457 (4) | |
| H14 | −0.417939 | 0.040358 | 0.115159 | 0.055* | |
| C15 | −0.33151 (8) | −0.0098 (2) | 0.14243 (9) | 0.0432 (4) | |
| C16 | −0.25940 (8) | −0.0165 (2) | 0.20176 (9) | 0.0398 (4) | |
| H16 | −0.235352 | −0.053046 | 0.191140 | 0.048* | |
| C17 | −0.14489 (7) | 0.0247 (2) | 0.34377 (9) | 0.0376 (4) | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0508 (8) | 0.0655 (11) | 0.0574 (9) | −0.0030 (8) | 0.0391 (8) | 0.0125 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N2 | 0.0288 (7) | 0.0606 (10) | 0.0318 (7) | −0.0051 (7) | 0.0173 (6) | 0.0001 (7) |
| O1 | 0.0676 (16) | 0.116 (3) | 0.112 (2) | −0.0083 (18) | 0.0703 (18) | −0.002 (2) |
| O2 | 0.0652 (15) | 0.090 (3) | 0.0628 (17) | −0.0371 (19) | 0.0384 (14) | −0.006 (2) |
| N3 | 0.0402 (13) | 0.088 (3) | 0.0429 (14) | −0.0095 (16) | 0.0242 (12) | 0.0118 (16) |
| C1 | 0.0460 (11) | 0.0555 (16) | 0.0392 (12) | −0.0086 (10) | 0.0294 (10) | 0.0044 (11) |
| C2 | 0.0532 (11) | 0.0565 (18) | 0.0525 (11) | −0.0103 (12) | 0.0378 (10) | −0.0025 (13) |
| C3 | 0.0523 (11) | 0.0624 (19) | 0.0520 (11) | −0.0039 (13) | 0.0380 (10) | 0.0016 (13) |
| C4 | 0.0438 (10) | 0.061 (2) | 0.0415 (11) | −0.0109 (11) | 0.0291 (9) | 0.0037 (12) |
| C5 | 0.0620 (12) | 0.0578 (17) | 0.0624 (15) | −0.0131 (12) | 0.0438 (12) | −0.0005 (13) |
| C6 | 0.0606 (12) | 0.0606 (17) | 0.0696 (18) | −0.0051 (12) | 0.0495 (13) | 0.0016 (14) |
| O1A | 0.045 (4) | 0.091 (8) | 0.075 (6) | −0.005 (5) | 0.032 (4) | 0.013 (6) |
| O2A | 0.061 (5) | 0.068 (6) | 0.074 (7) | −0.026 (5) | 0.025 (4) | 0.004 (5) |
| N3A | 0.049 (3) | 0.065 (4) | 0.053 (3) | −0.013 (3) | 0.026 (3) | 0.008 (3) |
| C1A | 0.054 (2) | 0.060 (3) | 0.050 (2) | −0.007 (2) | 0.0401 (18) | 0.000 (2) |
| C2A | 0.049 (2) | 0.058 (3) | 0.051 (2) | −0.013 (2) | 0.0370 (17) | 0.001 (2) |
| C3A | 0.0483 (18) | 0.060 (3) | 0.053 (2) | −0.010 (2) | 0.0386 (16) | 0.006 (2) |
| C4A | 0.0518 (19) | 0.060 (3) | 0.052 (2) | −0.012 (2) | 0.0315 (17) | 0.006 (2) |
| C5A | 0.060 (2) | 0.062 (3) | 0.054 (2) | −0.014 (2) | 0.0357 (19) | 0.000 (2) |
| C6A | 0.060 (2) | 0.058 (3) | 0.056 (3) | −0.014 (2) | 0.0379 (19) | 0.000 (2) |
| C7 | 0.0513 (10) | 0.0639 (13) | 0.0459 (10) | −0.0144 (9) | 0.0341 (9) | −0.0059 (9) |
| C8 | 0.0346 (8) | 0.0487 (10) | 0.0395 (9) | −0.0048 (7) | 0.0227 (7) | −0.0014 (8) |
| C9 | 0.0436 (9) | 0.0572 (12) | 0.0699 (13) | −0.0088 (9) | 0.0415 (10) | −0.0121 (10) |
| C10 | 0.0492 (10) | 0.0591 (13) | 0.0887 (15) | 0.0088 (10) | 0.0493 (11) | 0.0230 (11) |
| O3 | 0.0575 (8) | 0.0796 (10) | 0.0590 (8) | 0.0076 (7) | 0.0439 (7) | −0.0009 (8) |
| O4 | 0.0396 (7) | 0.0735 (10) | 0.0930 (11) | 0.0004 (7) | 0.0441 (8) | −0.0027 (8) |
| O5 | 0.0490 (8) | 0.0826 (11) | 0.0350 (7) | 0.0164 (7) | 0.0035 (6) | −0.0085 (7) |
| O6 | 0.0707 (9) | 0.0865 (11) | 0.0444 (8) | −0.0093 (8) | 0.0367 (7) | −0.0170 (7) |
| O7 | 0.0331 (6) | 0.0708 (9) | 0.0299 (6) | −0.0012 (6) | 0.0163 (5) | −0.0073 (6) |
| O8 | 0.0301 (6) | 0.0648 (8) | 0.0530 (7) | −0.0033 (6) | 0.0253 (6) | −0.0166 (6) |
| N4 | 0.0391 (8) | 0.0462 (9) | 0.0597 (10) | 0.0086 (7) | 0.0341 (8) | 0.0102 (8) |
| N5 | 0.0507 (9) | 0.0451 (9) | 0.0328 (8) | 0.0016 (7) | 0.0172 (7) | −0.0044 (7) |
| C11 | 0.0291 (7) | 0.0349 (9) | 0.0316 (8) | 0.0000 (6) | 0.0182 (6) | 0.0014 (7) |
| C12 | 0.0327 (7) | 0.0384 (9) | 0.0313 (8) | 0.0006 (7) | 0.0195 (7) | 0.0015 (7) |
| C13 | 0.0327 (8) | 0.0366 (9) | 0.0433 (9) | 0.0042 (7) | 0.0241 (7) | 0.0044 (7) |
| C14 | 0.0273 (7) | 0.0395 (9) | 0.0396 (9) | 0.0024 (7) | 0.0143 (7) | 0.0008 (7) |
| C15 | 0.0360 (8) | 0.0366 (9) | 0.0284 (8) | 0.0008 (7) | 0.0140 (7) | −0.0017 (7) |
| C16 | 0.0351 (8) | 0.0393 (9) | 0.0332 (8) | 0.0012 (7) | 0.0209 (7) | −0.0004 (7) |
| C17 | 0.0291 (7) | 0.0422 (9) | 0.0319 (8) | −0.0022 (7) | 0.0190 (7) | 0.0014 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C1 | 1.388 (3) | C5A—C6A | 1.3900 |
| N1—C7 | 1.457 (3) | C5A—H5AA | 0.9300 |
| N1—C10 | 1.465 (3) | C6A—H6AA | 0.9300 |
| N1—C1A | 1.508 (9) | C7—C8 | 1.509 (3) |
| N2—C9 | 1.481 (3) | C7—H7A | 0.9700 |
| N2—C8 | 1.486 (2) | C7—H7B | 0.9700 |
| N2—H21 | 0.95 (2) | C8—H8A | 0.9700 |

| | | | |
|---|---|---|---|
| N2—H22 | 0.92 (2) | C8—H8B | 0.9700 |
| O1—N3 | 1.243 (4) | C9—C10 | 1.506 (3) |
| O2—N3 | 1.222 (4) | C9—H9A | 0.9700 |
| N3—C4 | 1.443 (3) | C9—H9B | 0.9700 |
| C1—C2 | 1.3900 | C10—H10A | 0.9700 |
| C1—C6 | 1.3900 | C10—H10B | 0.9700 |
| C2—C3 | 1.3900 | O3—N4 | 1.216 (2) |
| C2—H2A | 0.9300 | O4—N4 | 1.229 (2) |
| C3—C4 | 1.3900 | O5—N5 | 1.224 (2) |
| C3—H3A | 0.9300 | O6—N5 | 1.219 (2) |
| C4—C5 | 1.3900 | O7—C17 | 1.250 (2) |
| C5—C6 | 1.3900 | O8—C17 | 1.2491 (19) |
| C5—H5A | 0.9300 | N4—C13 | 1.473 (2) |
| C6—H6A | 0.9300 | N5—C15 | 1.475 (2) |
| O1A—N3A | 1.251 (16) | C11—C12 | 1.385 (2) |
| O2A—N3A | 1.217 (15) | C11—C16 | 1.386 (2) |
| N3A—C4A | 1.455 (12) | C11—C17 | 1.520 (2) |
| C1A—C2A | 1.3900 | C12—C13 | 1.386 (2) |
| C1A—C6A | 1.3900 | C12—H12 | 0.9300 |
| C2A—C3A | 1.3900 | C13—C14 | 1.376 (2) |
| C2A—H2AA | 0.9300 | C14—C15 | 1.375 (3) |
| C3A—C4A | 1.3900 | C14—H14 | 0.9300 |
| C3A—H3AA | 0.9300 | C15—C16 | 1.387 (2) |
| C4A—C5A | 1.3900 | C16—H16 | 0.9300 |

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| C1—N1—C7 | 119.6 (2) | C1A—C6A—H6AA | 120.0 |
| C1—N1—C10 | 123.3 (2) | N1—C7—C8 | 110.72 (15) |
| C7—N1—C10 | 109.32 (15) | N1—C7—H7A | 109.5 |
| C7—N1—C1A | 127.9 (6) | C8—C7—H7A | 109.5 |
| C10—N1—C1A | 112.1 (6) | N1—C7—H7B | 109.5 |
| C9—N2—C8 | 112.95 (14) | C8—C7—H7B | 109.5 |
| C9—N2—H21 | 108.0 (12) | H7A—C7—H7B | 108.1 |
| C8—N2—H21 | 107.8 (11) | N2—C8—C7 | 109.52 (15) |
| C9—N2—H22 | 108.0 (12) | N2—C8—H8A | 109.8 |
| C8—N2—H22 | 108.5 (12) | C7—C8—H8A | 109.8 |
| H21—N2—H22 | 111.6 (17) | N2—C8—H8B | 109.8 |
| O2—N3—O1 | 122.9 (3) | C7—C8—H8B | 109.8 |
| O2—N3—C4 | 119.0 (3) | H8A—C8—H8B | 108.2 |
| O1—N3—C4 | 118.1 (3) | N2—C9—C10 | 109.91 (17) |
| N1—C1—C2 | 121.22 (19) | N2—C9—H9A | 109.7 |
| N1—C1—C6 | 118.78 (19) | C10—C9—H9A | 109.7 |
| C2—C1—C6 | 120.0 | N2—C9—H9B | 109.7 |
| C3—C2—C1 | 120.0 | C10—C9—H9B | 109.7 |
| C3—C2—H2A | 120.0 | H9A—C9—H9B | 108.2 |
| C1—C2—H2A | 120.0 | N1—C10—C9 | 110.88 (16) |
| C2—C3—C4 | 120.0 | N1—C10—H10A | 109.5 |
| C2—C3—H3A | 120.0 | C9—C10—H10A | 109.5 |
| C4—C3—H3A | 120.0 | N1—C10—H10B | 109.5 |

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| C5—C4—C3 | 120.0 | C9—C10—H10B | 109.5 |
| C5—C4—N3 | 119.7 (2) | H10A—C10—H10B | 108.1 |
| C3—C4—N3 | 120.3 (2) | O3—N4—O4 | 123.95 (17) |
| C4—C5—C6 | 120.0 | O3—N4—C13 | 118.51 (14) |
| C4—C5—H5A | 120.0 | O4—N4—C13 | 117.53 (17) |
| C6—C5—H5A | 120.0 | O6—N5—O5 | 123.96 (17) |
| C5—C6—C1 | 120.0 | O6—N5—C15 | 118.28 (15) |
| C5—C6—H6A | 120.0 | O5—N5—C15 | 117.76 (19) |
| C1—C6—H6A | 120.0 | C12—C11—C16 | 119.88 (14) |
| O2A—N3A—O1A | 128.2 (14) | C12—C11—C17 | 120.03 (14) |
| O2A—N3A—C4A | 117.8 (13) | C16—C11—C17 | 120.08 (15) |
| O1A—N3A—C4A | 114.0 (13) | C11—C12—C13 | 119.02 (15) |
| C2A—C1A—C6A | 120.0 | C11—C12—H12 | 120.5 |
| C2A—C1A—N1 | 115.7 (8) | C13—C12—H12 | 120.5 |
| C6A—C1A—N1 | 124.0 (8) | C14—C13—C12 | 122.68 (17) |
| C1A—C2A—C3A | 120.0 | C14—C13—N4 | 118.49 (15) |
| C1A—C2A—H2AA | 120.0 | C12—C13—N4 | 118.82 (16) |
| C3A—C2A—H2AA | 120.0 | C15—C14—C13 | 116.72 (15) |
| C4A—C3A—C2A | 120.0 | C15—C14—H14 | 121.6 |
| C4A—C3A—H3AA | 120.0 | C13—C14—H14 | 121.6 |
| C2A—C3A—H3AA | 120.0 | C14—C15—C16 | 122.91 (16) |
| C3A—C4A—C5A | 120.0 | C14—C15—N5 | 118.67 (15) |
| C3A—C4A—N3A | 120.6 (8) | C16—C15—N5 | 118.41 (17) |
| C5A—C4A—N3A | 119.3 (8) | C11—C16—C15 | 118.74 (16) |
| C6A—C5A—C4A | 120.0 | C11—C16—H16 | 120.6 |
| C6A—C5A—H5AA | 120.0 | C15—C16—H16 | 120.6 |
| C4A—C5A—H5AA | 120.0 | O8—C17—O7 | 126.27 (14) |
| C5A—C6A—C1A | 120.0 | O8—C17—C11 | 116.84 (14) |
| C5A—C6A—H6AA | 120.0 | O7—C17—C11 | 116.90 (15) |

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| C7—N1—C1—C2 | 13.5 (3) | N1—C1A—C6A—C5A | −174.0 (12) |
| C10—N1—C1—C2 | 159.33 (19) | C1—N1—C7—C8 | 88.7 (2) |
| C7—N1—C1—C6 | −166.94 (18) | C10—N1—C7—C8 | −61.5 (2) |
| C10—N1—C1—C6 | −21.1 (3) | C1A—N1—C7—C8 | 79.6 (8) |
| N1—C1—C2—C3 | 179.6 (3) | C9—N2—C8—C7 | −53.44 (19) |
| C6—C1—C2—C3 | 0.0 | N1—C7—C8—N2 | 57.24 (19) |
| C1—C2—C3—C4 | 0.0 | C8—N2—C9—C10 | 53.10 (19) |
| C2—C3—C4—C5 | 0.0 | C1—N1—C10—C9 | −87.8 (3) |
| C2—C3—C4—N3 | 178.0 (2) | C7—N1—C10—C9 | 61.0 (2) |
| O2—N3—C4—C5 | 8.8 (4) | C1A—N1—C10—C9 | −86.7 (7) |
| O1—N3—C4—C5 | −170.6 (3) | N2—C9—C10—N1 | −56.3 (2) |
| O2—N3—C4—C3 | −169.2 (3) | C16—C11—C12—C13 | 2.3 (2) |
| O1—N3—C4—C3 | 11.4 (4) | C17—C11—C12—C13 | −177.66 (15) |
| C3—C4—C5—C6 | 0.0 | C11—C12—C13—C14 | −2.0 (3) |
| N3—C4—C5—C6 | −178.0 (2) | C11—C12—C13—N4 | 179.25 (15) |
| C4—C5—C6—C1 | 0.0 | O3—N4—C13—C14 | −161.90 (16) |
| N1—C1—C6—C5 | −179.6 (3) | O4—N4—C13—C14 | 17.5 (2) |
| C2—C1—C6—C5 | 0.0 | O3—N4—C13—C12 | 16.9 (2) |

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| C7—N1—C1A—C2A | 30.4 (11) | O4—N4—C13—C12 | −163.67 (16) |
| C10—N1—C1A—C2A | 170.6 (5) | C12—C13—C14—C15 | −0.1 (3) |
| C7—N1—C1A—C6A | −155.4 (6) | N4—C13—C14—C15 | 178.72 (15) |
| C10—N1—C1A—C6A | −15.1 (10) | C13—C14—C15—C16 | 1.9 (3) |
| C6A—C1A—C2A—C3A | 0.0 | C13—C14—C15—N5 | −177.15 (15) |
| N1—C1A—C2A—C3A | 174.5 (11) | O6—N5—C15—C14 | −177.23 (17) |
| C1A—C2A—C3A—C4A | 0.0 | O5—N5—C15—C14 | 2.7 (3) |
| C2A—C3A—C4A—C5A | 0.0 | O6—N5—C15—C16 | 3.7 (3) |
| C2A—C3A—C4A—N3A | 175.8 (13) | O5—N5—C15—C16 | −176.40 (17) |
| O2A—N3A—C4A—C3A | −177.1 (15) | C12—C11—C16—C15 | −0.6 (2) |
| O1A—N3A—C4A—C3A | 0 (2) | C17—C11—C16—C15 | 179.33 (15) |
| O2A—N3A—C4A—C5A | −1 (2) | C14—C15—C16—C11 | −1.5 (3) |
| O1A—N3A—C4A—C5A | 175.8 (13) | N5—C15—C16—C11 | 177.46 (15) |
| C3A—C4A—C5A—C6A | 0.0 | C12—C11—C17—O8 | 161.97 (15) |
| N3A—C4A—C5A—C6A | −175.9 (13) | C16—C11—C17—O8 | −18.0 (2) |
| C4A—C5A—C6A—C1A | 0.0 | C12—C11—C17—O7 | −18.5 (2) |
| C2A—C1A—C6A—C5A | 0.0 | C16—C11—C17—O7 | 161.58 (15) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H21···O8 | 0.95 (2) | 1.77 (2) | 2.705 (3) | 170.7 (17) |
| N2—H22···O7$^{i}$ | 0.92 (2) | 1.81 (2) | 2.715 (3) | 166.4 (18) |
| C8—H8*A*···O4$^{ii}$ | 0.97 | 2.54 | 3.245 (3) | 130 |
| C8—H8*B*···O2$^{iii}$ | 0.97 | 2.40 | 3.354 (4) | 168 |
| C8—H8*B*···O2*A*$^{iii}$ | 0.97 | 2.39 | 3.353 (16) | 172 |
| C9—H9*A*···O1$^{iii}$ | 0.97 | 2.54 | 3.497 (5) | 171 |
| C9—H9*A*···O1*A*$^{iii}$ | 0.97 | 2.47 | 3.378 (14) | 155 |
| C10—H10*B*···O4$^{iv}$ | 0.97 | 2.60 | 3.425 (3) | 143 |
| C12—H12···O2$^{v}$ | 0.93 | 2.53 | 3.231 (4) | 133 |

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