Crystal structures of six 4-(4-nitrophenyl)piperazinium-1-ium salts

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Six piperazinium salts, namely 4-(4-nitrophenyl)piperazinium-1-ium 4-bromobenzoate dihydrate, C10H14N3O2+·C7H4BrO2−·2H2O, (I), 4-(4-nitrophenyl)piperazinium-1-ium 4-iodobenzoate dihydrate, C10H14N3O2+·C7H4IO2−·2H2O, (II), 4-(4-nitrophenyl)piperazinium-1-ium 4-hydroxybenzoate monohydrate, C10H14N3O2+·C7H5O3−·H2O, (III), 4-(4-nitrophenyl)piperazinium-1-ium 4-methylbenzoate monohydrate, C10H14N3O2+·C8H7O2−·H2O, (IV), 4-(4-nitrophenyl)piperazinium-1-ium 4-methoxybenzoate hemihydrate, 2C10H14N3O2+·2C8H7O3−·H2O, (V), and 4-(4-nitrophenyl)piperazinium-1-ium 4-ethoxybenzoate, 2C10H14N3O2+·2C9H9O3−, (VI), have been synthesized and their crystal structures solved by single-crystal X-ray diffraction, revealing that all of them crystallize in the triclinic space group P1̅ except for (V), which crystallizes in the monoclinic space group P21/c and has a disordered nitro group. Compounds (I) and (II) are isostructural. The crystal packing of (I)–(V) is constructed from organic chains formed by a combination of hydrogen bonds of type N—H···O and/or O—H···O and other weak interactions of type C—H···O and/or C—H···π, forming sheets, whereas (VI) shows a cationic and anionic-based layer structure.

1. Chemical context

Piperazines and substituted piperazines are important pharmacophores that can be found in many biologically active compounds used to treat a number of different diseases (Berkheij, 2005) as antifungal (Upadhayaya et al., 2004), antibacterial, anti-malarial and anti-psychotic agents (Choudhary et al., 2006). A valuable insight into advances on the antimicrobial activity of piperazine derivatives was given by Kharb et al. (2012). Piperazines are among the most important building blocks in current drug discovery and are found in biologically active compounds across a number of different therapeutic areas (Brockunier et al., 2004; Bogatcheva et al., 2006). Pharmacological and toxicological information for piperazine derivatives is reviewed 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 behaviours of 4-sulfonato-calix[n]arenes (SCXn) (n = 4, 6, 8) with 1-(4-nitrophenyl)piperazine (NPP) were investigated by UV spectroscopy and fluorescence spectroscopy at different pH values (Zhang et al., 2014). The design, synthesis and biological profiling of arylpiperazine-based scaffolds for the manage-
ment of androgen-sensitive prostatic disorders was reported by 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). The crystal structure of 4-nitrophenyl piperazinium chloride monohydrate was reported by Lu (2007) and that of 4,6-dimethoxypyrimidin-2-amine-1-(4-nitrophenyl)piperazine (1:1) by Wang et al. (2014) while Ayeni et al. (2019) described the synthesis and crystal structure of a Schiff base, 5-methyl-2-[[4-(4-nitrophenyl)piperazin-1-yl)methyl]phenol is published. NMR-based investigations of acyl-functionalized piperazines concerning their conformational behaviour in solution has been studied and the crystal structures of 1-(4-fluorobenzoyl)-4-(4-nitrophenyl)piperazine, 1-(4-bromobenzoyl)-4-(4-nitrophenyl)piperazine and 1-(3-bromobenzoyl)-4-(4-nitrophenyl)piperazine 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), as well as some salts of piperazine derivatives (Archana et al., 2021).

In view of the importance of piperazines in general and the use of 4-nitrophenylpiperazine in particular, the present paper reports the crystal structures of some salts of 4-nitrophenylpiperazine with organic acids. The crystal structures of 4-(4-nitrophenyl)piperazin-1-ium 4-bromobenzoate dihydrate (I), 4-(4-nitrophenyl)piperazin-1-ium 4-iodobenzoate dihydrate (II), 4-(4-nitrophenyl)piperazin-1-ium 4-hydroxybenzoate monohydrate (III), 4-(4-nitrophenyl)piperazin-1-ium 4-bromobenzoate dihydrate (I), 4-(4-nitrophenyl)piperazin-1-ium 4-iodobenzoate dihydrate (II), 4-(4-nitrophenyl)piperazin-1-ium 4-hydroxybenzoate monohydrate (III), 4-(4-nitrophenyl)piperazin-1-ium 4-bromobenzoate dihy
4-methylbenzoate monohydrate (IV), 4-(4-nitrophenyl)piperazin-1-ium 4-methoxybenzoate hemihydrate (V) and 4-(4-nitrophenyl)piperazin-1-ium 4-ethoxybenzoate (VI) are reported herein.

2. Structural commentary

The asymmetric units of the title salts are shown in Figs. 1–6. They include 1:1 dihydrated salts [(I), (II)], 1:1 monohydrated salts [(III), (IV)], 2:2 monohydrated salt (V) and solvent-free 2:2 salt (VI). Compounds (I) and (II) are isostructural. In all salts, the cation is common and consists of a protonated chair-shaped piperazine ring (N1/N2/C7–C10), which makes dihedral angles of 10.91 (1), 12.13 (1), 14.82 (6), 3.11 (8), 5.73 (1) and 13.08 (9)°, respectively, for compounds (I)–(VI) with the nitrobenzene moiety (N3/O1/O2/C1–C6) and exhibits a maximum deviation from its mean plane at atom N2 of −0.253 (2), 0.254 (2), 0.288 (2), 0.278 (2), 0.241 (3) and 0.303 (3) Å in (I)–(VI), respectively. The piperazine rings of the additional cations (N4/N5/C25–C28) in compounds (V) and (VI) have the same conformation, making dihedral angles of 64.53 (1) and 21.70 (1)°, respectively, with the nitrobenzene moieties (N6/O6/O7/C19–C25). Within the cations, the benzene rings are almost planar, with maximum deviations from mean plane ranging from −0.016 (3) Å at atom C20 for (VI) to 0.003 (2) Å at atom C4 for (III). The p-nitro substituent groups deviate significantly from planes of the benzene rings in all compounds except the (C1–C6) ring of (VI). The anions of the title salts are formed from a benzoate anion with different p-substituents for each compound that deviate significantly from planarity, with maximum deviations of 0.045 (1) Å at Br1 for (I), 0.063 (1) Å at I1 for (II), −0.021 (2) Å at hydroxyl atom O3 for (III), −0.010 (1) Å at methyl atom C18 for (IV), −0.033 (1) and 0.034 (1) Å at methoxy atoms O5 and O10 for (V) and −0.025 (2) and −0.013 (2) Å at ethoxy atoms O5 and O10 for (VI).
3. Supramolecular features

In the crystal structures of the two isomorphous salts (I) and (II), the ions are arranged in chains perpendicular to the \( a \)-axis direction. The water molecules play an essential role in holding the chains together, forming complex sheets in the \( bc \) plane (Figs. 7 and 8, Tables 1 and 2). The cations and anions in

**Table 1**

| \( \text{D—H—A} \) | \( \text{D—H} \) | \( \text{H—A} \) | \( \text{D—A} \) | \( \text{D—H—A} \) |
|-----------------|-------------|-------------|-------------|-----------------|
| N2—H21···O5'    | 0.85 (2)    | 1.99 (2)    | 2.810 (3)   | 162 (3)         |
| N2—H22···O6''   | 0.83 (2)    | 1.91 (2)    | 2.707 (3)   | 160 (3)         |
| C3—H3···O1''    | 0.93        | 2.59        | 3.260 (4)   | 130             |
| C13—H13···O4''  | 0.93        | 2.57        | 3.483 (3)   | 166             |
| O5—H1W···O3''   | 0.80 (2)    | 2.00 (2)    | 2.772 (2)   | 161 (3)         |
| O6—H4W···O4     | 0.82 (2)    | 2.03 (2)    | 2.832 (3)   | 166 (3)         |
| O6—H3W···O4''   | 0.78 (2)    | 1.99 (2)    | 2.760 (3)   | 169 (3)         |

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

**Table 2**

| \( \text{D—H—A} \) | \( \text{D—H} \) | \( \text{H—A} \) | \( \text{D—A} \) | \( \text{D—H—A} \) |
|-----------------|-------------|-------------|-------------|-----------------|
| N2—H21···O5'    | 0.86 (2)    | 1.99 (2)    | 2.825 (4)   | 164 (4)         |
| N2—H22···O6''   | 0.85 (2)    | 1.88 (2)    | 2.702 (3)   | 163 (4)         |
| C3—H3···O1''    | 0.93        | 2.59        | 3.275 (4)   | 131             |
| C13—H13···O4''  | 0.93        | 2.62        | 3.526 (4)   | 166             |
| O5—H1W···O3''   | 0.81 (2)    | 1.96 (2)    | 2.756 (3)   | 170 (4)         |
| O6—H4W···O4     | 0.80 (2)    | 2.08 (2)    | 2.836 (3)   | 160 (4)         |
| O6—H3W···O4''   | 0.80 (2)    | 1.95 (2)    | 2.728 (3)   | 165 (4)         |

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

**Figure 7**

(a) A general view of the main intermolecular interactions (N—H···O and O—H···O) and (b) the molecular packing of (I) with hydrogen bonds shown as dashed lines.

**Figure 8**

(a) A general view of the main intermolecular interactions (N—H···O and O—H···O) in (II) and (b) the molecular packing of (II) with hydrogen bonds shown as dashed lines.
chains running along the [101] direction. Each chain is formed by linking the molecules through a combination of N—H⋯O, O—H⋯O and C—H⋯O interactions (Fig. 10a, Table 4); the resulting double chains are symmetrically related by an inversion center and are connected via N2—H21⋯O4 and C7—H7A⋯O4 interactions. These hydrated double chains are weakly linked into sheets lying in the bc plane by C—H⋯π (arene) interactions (Fig. 10b). The supramolecular assembly of compound (V), which has a disordered nitro group, is built up of N2—H22W⋯O11, O11—H11O⋯O4 and N5—H51⋯O9 hydrogen bonds linking the ions into organic chains running parallel to the [010] direction (Fig. 11a, Table 5). The chains are further connected cooperatively through other interactions of type N—H⋯O, generating a multilayer network along the b-axis direction (Fig. 11b). In compound (VI), a set of N—H⋯O, C—H⋯O and C—H⋯π interactions (Fig. 12a, Table 6) link the molecules into cationic and anionic layers running parallel to the b-axis direction and join these layer motifs, generating the complete molecular structure along the a axis (Fig. 12b).

(III) are linked through strong O—H⋯O and N—H⋯O hydrogen bonds, forming chains along the [011] direction (Fig. 9a, Table 3). These chains are further linked via the water molecules and C9—H9A⋯O3 interactions, generating a three-dimensional supramolecular architecture along the a axis (Fig. 9b). The structure of (IV) is constructed from double

**Table 3**

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

| D—H⋯A   | D—H   | H⋯A | D⋯A  | D—H⋯A  |
|----------|--------|-----|------|--------|
| N2—H21⋯O5 | 0.89 (2) | 1.93 (2) | 2.819 (2) | 177 (3) |
| N2—H22⋯O4* | 0.94 (2) | 1.65 (2) | 2.583 (2) | 177 (3) |
| O3—H17⋯O6 | 0.85 (2) | 1.82 (2) | 2.669 (2) | 177 (3) |
| O6—H1W⋯O5* | 0.83 (2) | 1.95 (2) | 2.768 (2) | 169 (3) |
| O6—H2W⋯O1* | 0.83 (2) | 2.11 (2) | 2.944 (2) | 178 (3) |

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

**Table 4**

Hydrogen-bond geometry (Å, °) for (IV).

| D—H⋯A   | D—H   | H⋯A | D⋯A  | D—H⋯A  |
|----------|--------|-----|------|--------|
| N2—H21⋯O4* | 0.89 (2) | 1.93 (2) | 2.811 (3) | 167 (4) |
| N2—H22⋯O3* | 0.91 (2) | 1.81 (2) | 2.717 (3) | 177 (4) |
| O3—H13⋯O1* | 0.93 | 2.54 | 3.427 (4) | 161 |
| C9—H9A⋯O5* | 0.97 | 2.31 | 3.113 (3) | 140 |
| O5—H1W⋯O4* | 0.84 (2) | 1.92 (2) | 2.756 (3) | 171 (4) |
| O5—H2W⋯O3 | 0.85 (2) | 1.94 (2) | 2.772 (3) | 164 (4) |
| C6—H6⋯Cg3* | 0.93 | 2.93 | 3.590 (3) | 129 |

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

Figure 9

(a) A general view of the main intermolecular interactions (N—H⋯O and O—H⋯O) in (III) and (b) the molecular packing of (III) with hydrogen bonds shown as dashed lines.

Figure 10

(a) A general view of the main intermolecular interactions (N—H⋯O and O—H⋯O) in (IV) and (b) the molecular packing of (IV) with hydrogen bonds shown as dashed lines.
Table 5
Hydrogen-bond geometry (Å, °) for (V).

| D—H · · · A | D—H | H···A | D···A | D—H · · · A |
|-------------|------|-------|-------|-------------|
| C7—H7B···O7i | 0.97 | 2.54  | 3.451 (5) | 157 |
| C9—H9B···O4a | 0.97 | 2.31  | 3.270 (5) | 169 |
| C20—H20···O9 | 0.93 | 2.53  | 3.461 (5) | 174 |
| C25—H25A···O2a | 0.97 | 2.5  | 3.206 (10) | 130 |
| C25—H25A···O2b | 0.97 | 2.49  | 3.212 (11) | 131 |
| C27—H27A···O7 | 0.97 | 2.58  | 3.548 (5) | 175 |
| C28—H28B···O9 | 0.97 | 2.55  | 3.489 (5) | 164 |
| C36—H36C···O1b | 0.96 | 2.49  | 3.395 (14) | 158 |

Symmetry codes: (i) x—1, y, z; (ii) x—1, y, z; (iii) x, y + 1, z; (iv) x, y + 1, z; (v) x, y + 1, z; (vi) x, y + 1, z; (vii) x, y + 1, z; (viii) x, y + 1, z.

Table 6
Hydrogen-bond geometry (Å, °) for (VI).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N2—H31N···O3f | 0.94 (2) | 1.68 (2) | 2.613 (3) | 172 (5) |
| N2—H31N···O4f | 0.94 (2) | 2.51 (4) | 3.157 (3) | 127 (4) |
| N2—H32N···O9f | 0.90 (2) | 1.96 (2) | 2.843 (3) | 171 (5) |
| N5—H61N···O8i | 0.91 (2) | 1.78 (2) | 2.686 (3) | 175 (5) |
| N5—H61N···O9i | 0.91 (2) | 2.59 (4) | 3.174 (3) | 124 (4) |
| N5—H62N···O4ii | 0.90 (2) | 1.83 (2) | 2.708 (3) | 165 (5) |
| C22—H22B···O2iv | 0.93 | 2.6 | 3.502 (5) | 165 |
| C27—H27B···O7i | 0.97 | 2.58 | 3.548 (5) | 175 |
| C28—H28B···O9i | 0.97 | 2.65 | 3.410 (4) | 135 |
| C36—H36B···O10i | 0.96 | 2.49 | 3.395 (14) | 158 |

Symmetry codes: (i) x, y + 1, z; (ii) x—1, y, z; (iv) x, y + 1, z; (iv) x, y + 1, z; (v) x, y + 1, z; (vi) x, y + 1, z; (vii) x, y + 1, z; (viii) x, y + 1, z.

Figure 11
(a) A general view of the main intermolecular interactions (N—H···O and O—H···O) in (V) and (b) the molecular packing of (V) with hydrogen bonds shown as dashed lines.

Figure 12
(a) A general view of the main intermolecular interactions (N—H···O, O—H···O and C—H···O) in (VI) and (b) the molecular packing of (VI) with hydrogen bonds shown as dashed lines.
Table 7
Experimental details.

| Crystal data | (I) | (II) | (III) |
|--------------|-----|------|-------|
| Chemical formula | C₁₀H₁₄N₃O₂·C₇H₅BrO₃·2H₂O | C₁₀H₁₄N₃O₂·C₇H₅I₂O₃·2H₂O | C₁₀H₁₄N₃O₂·C₇H₅O₂·H₂O |
| Mᵣ | 444.28 | 491.28 | 363.37 |
| Crystal system, space group | Triclinic, P₁ | Triclinic, P₁ | Triclinic, P₁ |
| Temperature (K) | 293 | 293 | 293 |
| a, b, c (Å) | 7.738 (1), 9.320 (1), 13.949 (2) | 7.7652 (4), 9.2852 (5), 13.930 (1) | 9.636 (1), 10.301 (1), 10.867 (1) |
| α, β, γ (°) | 94.46 (1), 95.04 (1), 104.71 (2) | 94.985 (5), 95.331 (5), 104.875 (6) | 103.90 (1), 108.32 (1), 112.96 (1) |
| V (Å³) | 964.0 (2) | 960.09 (10) | 857.80 (17) |
| Z | 2 | 2 | 2 |
| Radiation type | Mo Kα | Mo Kα | Mo Kα |
| μ (mm⁻¹) | 2.17 | 1.71 | 0.11 |
| Crystal size (mm) | 0.48 x 0.44 x 0.24 | 0.48 x 0.48 x 0.2 | 0.50 x 0.32 x 0.24 |

| Data collection | Diffractometer | Absorption correction | T_max, T_min, \(\theta(\lambda)\) max, min (Å⁻¹) |
|----------------|----------------|-----------------------|---------------------------------|
| (IV) | (V) | (VI) |
| Oxford Diffraction Xcalibur | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) |
| Oxford Diffraction Xcalibur | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) |
| 0.037, 0.104, 1.04 | 0.029, 0.069, 1.03 | 0.043, 0.106, 1.05 |
| 0.662 | 0.602 | 0.602 |

| Refinement | R[F² > 2σ(F²)], wR(F²), S |
|-------------|-------------------------|
| (IV) | (V) |
| Oxford Diffraction Xcalibur | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) |
| Oxford Diffraction Xcalibur | Multi-scan (CrysAlis RED; Oxford Diffraction, 2009) |
| 0.029, 0.069, 1.03 | 0.043, 0.106, 1.05 |
| 0.602 | 0.602 |

Computer programs: CrysAlis CCD (Oxford Diffraction, 2009), CrysAlis RED (Oxford Diffraction, 2009), SHELXT (Sheldrick, 2015a), Mercury (Macrae et al., 2020), SHELXL2014 (Sheldrick, 2015b), PLATON (Spek, 2020) and publICIF (Westrip, 2010).
4. Database survey
A search of the Cambridge Structural Database (Version 2020.3, last update February 2022; Groom et al., 2016) for the phenyl piperazinium cation and para substituent benzoate anion involved in the reported six salts gave the following hits: 4-(4-methoxyphenyl)piperazin-1-ium 4-fluorobenzoate monohydrate, 4-(4-methoxyphenyl)piperazin-1-ium 4-chlorobenzoate monohydrate and 4-(4-methoxyphenyl)piperazin-1-ium 4-bromobenzoate monohydrate (FOVPOY, FOVPUE and FOVQAL; Kiran Kumar et al., 2019) and 4-(4-methoxyphenyl)piperazin-1-ium 4-iodobenzoate monohydrate (KUJ-PUD; Kiran Kumar et al., 2020). They exhibit a methoxy group as a substituent in the phenyl piperazinium cation rather than a nitro group as in the title compounds (I)–(VI) and they also crystallize as monohydrates similar to compounds (III)–(V). Although the title compounds (I) and (II) have halogen-based anions and chain-based structures, they are not isostructurally with the above compounds, the crystal structures of which are based on differently sized chains of rings formed via a combination of hydrogen bonds of type N—H···O and O— H···O and other weak interactions of type C—H···O and C— H···π to form sheets. In 4-(4-methoxyphenyl)piperazin-1-ium 4-aminobenzoate monohydrate (IHIMEU; Kiran Kumar et al., 2020) the presence of an amino substituent on the anion, which acts as both a donor and an acceptor of hydrogen bonds, makes the supramolecular assembly of this compound more complex than for the compounds reported herein.

5. Synthesis and crystallization

Synthesis:
For the synthesis of salts (I)–(VI), 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, 4-bromobenzoic acid (97 mg, 0.483 mol) for (I), 4-iodobenzoic acid (120 mg, 0.483 mol) for (II), 4-hydroxybenzoic acid (67 mg, 0.483 mol) for (III), 4-methylbenzoic acid (66 mg, 0.483 mol) for (IV), 4-methoxybenzoic acid (73 mg, 0.483 mol) for (V) and 4-ethoxybenzoic acid (80 mg, 0.483 mol) for (VI). The corresponding solutions were stirred for 15 minutes at room temperature and allowed to stand at the same temperature. The products obtained were subjected to crystallization.

Crystallization: Crystallization was carried out using the slow evaporation technique. X-ray quality crystals were formed on slow evaporation in a week for all compounds, where ethanol:ethylacetate (1:1) was used for crystallization. The corresponding melting points were 430–432 K (I), 453–455 K (II), 446–448 K (III), 398–400 K (IV), 413–415 K (V) and 408–410 K (VI).

6. Refinement
Crystal data, data collection and refinement details are summarized in Table 7. C-bound H atoms were positioned with idealized geometry and refined using a riding model with C—H = 0.93 Å (aromatic), 0.96 Å (methyl) or 0.97 Å (methylenic). The H atoms on the N atom were located in a difference map and later restrained to N—H = 0.86 (2) Å. All H atoms were refined with isotropic displacement parameters set at 1.2 Ueq (C-aromatic, C-methylene, N) or 1.5 Ueq (C-methyl) times those of the parent atom. For the disordered nitro group in (V), the component atoms were restrained to have the same Ueq components and the occupancy ratio is 0.519 (6):0.481 (6).

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Crystal structures of six 4-(4-nitrophenyl)piperazin-1-ium salts

Ninganayaka Mahesha, Haruvegowda Kiran Kumar, Hemmige S. Yathirajan, Sabine Foro, Mohammed S. M. Abdelbaky and Santiago Garcia-Granda

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: SHELXL2014 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020). Software used to prepare material for publication: SHELXL2014 (Sheldrick, 2015b), PLATON (Spek, 2020) and publCIF (Westrip, 2010) for (I), (II), (III), (V), (VI); SHELXL2014 (Sheldrick, 2015b), PLATON (Spek, 2020) and publCIF (Westrip, 2010) for (IV).

4-(4-Nitrophenyl)piperazin-1-ium 4-bromobenzoate dihydrate (I)

Crystal data
\[\text{C}_{10}\text{H}_{14}\text{N}_{3}\text{O}_{2}^+\cdot\text{C}_{7}\text{H}_{4}\text{BrO}_{2}^-\cdot2\text{H}_{2}\text{O}\]

\[M_r = 444.28\]

Triclinic, \(\text{P} \bar{1}\)

Hall symbol: \(-\text{P} 1\)

\(a = 7.738 (1) \text{Å}\)

\(b = 9.320 (1) \text{Å}\)

\(c = 13.949 (2) \text{Å}\)

\(\alpha = 94.46 (1) ^\circ\)

\(\beta = 95.04 (1) ^\circ\)

\(\gamma = 104.71 (2) ^\circ\)

\(V = 964.0 (2) \text{Å}^3\)

\(Z = 2\)

\(F(000) = 456\)

\(D_x = 1.531 \text{ Mg m}^{-3}\)

Cell parameters from 6123 reflections

\(\theta = 3.0-25.3^\circ\)

\(\mu = 2.17 \text{ mm}^{-1}\)

\(T = 293 \text{ K}\)

Prism, yellow

\(0.48 \times 0.44 \times 0.24 \text{ mm}\)

Data collection

Oxford Diffraction Xcalibur diffractometer

\(\omega\) scans

Absorption correction: multi-scan

(CrysAlis RED; Oxford Diffraction, 2009)

\(T_{\min} = 0.367, T_{\max} = 0.422\)

6123 measured reflections

3536 independent reflections

2520 reflections with \(I > 2\sigma(I)\)

\(R_{int} = 0.019\)

\(\theta_{\max} = 25.3^\circ, \theta_{\min} = 3.0^\circ\)

\(h = -9 \rightarrow 8\)

\(k = -6 \rightarrow 11\)

\(l = -16 \rightarrow 16\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.037\)

\(wR(F^2) = 0.104\)

\(S = 1.04\)

3528 reflections

262 parameters

6 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: structure-invariant direct methods

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

\[ w = 1/[\sigma^2(F_o^2) + (0.0623P)^2] \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

\((\Delta/\sigma)_{\text{max}} < 0.001\)
\(\Delta\rho_{\text{max}} = 0.50\ \text{e}\ \text{Å}^{-3}\)
\(\Delta\rho_{\text{min}} = -0.51\ \text{e}\ \text{Å}^{-3}\)

Special details

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

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

|         | x            | y            | z            | Uiso* | Ueq  |
|---------|--------------|--------------|--------------|-------|------|
| O1      | 0.9273 (3)   | 0.7891 (3)   | 0.53814 (19) | 0.0873 (8) |
| O2      | 0.6916 (3)   | 0.6357 (3)   | 0.57409 (17) | 0.0767 (6) |
| N1      | 0.3360 (2)   | 1.0060 (2)   | 0.32960 (16) | 0.0542 (5) |
| N2      | 0.1306 (3)   | 1.1025 (2)   | 0.31398 (16) | 0.0433 (5) |
| N3      | 0.7641 (3)   | 0.7395 (3)   | 0.53118 (17) | 0.0537 (6) |
| C1      | 0.4412 (3)   | 0.9374 (2)   | 0.34950 (16) | 0.0353 (5)
| C2      | 0.3297 (3)   | 0.9791 (3)   | 0.35426 (19) | 0.0462 (6) |
| H2      | 0.685335  | 1.050743  | 0.316027 | 0.055*  |
| C3      | 0.7335 (3)   | 0.9160 (3)   | 0.4144 (2)   | 0.0479 (6) |
| H3      | 0.858174  | 0.947226  | 0.418128 | 0.057*  |
| C4      | 0.6524 (3)   | 0.8067 (3)   | 0.46921 (17) | 0.0401 (6) |
| C5      | 0.4678 (3)   | 0.7621 (3)   | 0.46618 (18) | 0.0460 (6) |
| H5      | 0.414057  | 0.688671  | 0.503722 | 0.055*  |
| C6      | 0.3636 (3)   | 0.8264 (3)   | 0.40761 (18) | 0.0430 (6) |
| H6      | 0.239197  | 0.796118  | 0.406198 | 0.052*  |
| C7      | 0.4258 (3)   | 1.1047 (3)   | 0.2239 (2)   | 0.0479 (6) |
| H7A     | 0.454966 | 1.044787  | 0.17075 | 0.058   |
| H7B     | 0.537417 | 1.169773  | 0.256358 | 0.058   |
| C8      | 0.3088 (3)   | 1.1978 (3)   | 0.1846 (2)   | 0.0493 (7) |
| H8A     | 0.29158 | 1.266385  | 0.236558 | 0.059   |
| H8B     | 0.368224 | 1.256083  | 0.136469 | 0.059   |
| C9      | 0.406 (3)    | 1.0114 (3)   | 0.2121 (2)   | 0.0495 (6) |
| H9A     | -0.074749 | 0.948618  | 0.20599 | 0.059   |
| H9B     | 0.01919 | 1.076165  | 0.265103 | 0.059   |
| C10     | 0.1561 (3)   | 0.9148 (3)   | 0.2506 (2)   | 0.0462 (6) |
| H10A    | 0.097528 | 0.858526  | 0.29974 | 0.055   |
| H10B    | 0.168666 | 0.844357  | 0.1984 | 0.055   |
| Br1     | 0.91659 (5)  | 0.45794 (4)  | 0.33416 (3)  | 0.08360 (18) |
| O3      | 0.4483 (2)   | 0.78822 (19) | 0.01696 (15) | 0.0543 (5) |
| O4      | 0.2197 (2)   | 0.63974 (18) | 0.07787 (14) | 0.0505 (5) |
| C11     | 0.5153 (3)   | 0.6356 (2)   | 0.13620 (18) | 0.0350 (5) |
| C12     | 0.6851 (3)   | 0.6376 (3)   | 0.10986 (19) | 0.0431 (6) |
| H12     | 0.71881 | 0.674975  | 0.052541 | 0.052*  |
| C13     | 0.8046 (3)   | 0.5846 (3)   | 0.1680 (2)   | 0.0499 (7) |
| H13     | 0.916747 | 0.583844  | 0.149142 | 0.06*   |
| Atom   | U11          | U22          | U33          | U12          | U13          | U23          |
|--------|--------------|--------------|--------------|--------------|--------------|--------------|
| C14    | 0.0490 (13)  | 0.0892 (16)  | 0.122 (2)    | 0.0142 (11)  | -0.0189 (13)| 0.0497 (15)  |
| C15    | 0.0701 (14)  | 0.0858 (15)  | 0.0809 (16)  | 0.0235 (12)  | -0.0004 (12)| 0.0500 (13)  |
| N1     | 0.0347 (10)  | 0.0406 (11)  | 0.0417 (11)  | 0.0091 (8)   | -0.0042 (9)  | 0.0124 (9)    |
| N2     | 0.0459 (12)  | 0.0431 (12)  | 0.0435 (13)  | 0.0189 (10)  | -0.0065 (10)| 0.0088 (10)  |
| N3     | 0.0542 (15)  | 0.0524 (13)  | 0.0551 (14)  | 0.0173 (11)  | -0.0090 (12)| 0.0161 (11)  |
| C1     | 0.0396 (13)  | 0.0344 (12)  | 0.0327 (13)  | 0.0132 (10)  | -0.0010 (10)| 0.0026 (10)  |
| C2     | 0.0378 (14)  | 0.0518 (15)  | 0.0515 (16)  | 0.0111 (11)  | 0.0047 (12)  | 0.0229 (12)  |
| C3     | 0.0361 (13)  | 0.0503 (15)  | 0.0583 (17)  | 0.0125 (11)  | -0.0001 (12)| 0.0145 (13)  |
| C4     | 0.0441 (14)  | 0.0411 (13)  | 0.0363 (13)  | 0.0156 (11)  | -0.0037 (11)| 0.0060 (11)  |
| C5     | 0.0489 (15)  | 0.0463 (14)  | 0.0429 (15)  | 0.0100 (11)  | 0.0016 (12)  | 0.0177 (11)  |
| C6     | 0.0339 (12)  | 0.0498 (14)  | 0.0455 (15)  | 0.0093 (11)  | 0.0025 (11)  | 0.0145 (12)  |
| C7     | 0.0416 (14)  | 0.0450 (14)  | 0.0524 (16)  | 0.0036 (11)  | -0.0082 (12)| 0.0166 (12)  |
| C8     | 0.0558 (16)  | 0.0385 (13)  | 0.0499 (16)  | 0.0096 (12)  | -0.0116 (13)| 0.0117 (11)  |
| C9     | 0.0392 (14)  | 0.0603 (16)  | 0.0517 (16)  | 0.0187 (12)  | -0.0040 (12)| 0.0138 (13)  |
| C10    | 0.0354 (13)  | 0.0487 (14)  | 0.0530 (16)  | 0.0077 (11)  | -0.0030 (12)| 0.0159 (12)  |
| Br1    | 0.0734 (3)   | 0.0942 (3)   | 0.0856 (3)   | 0.0319 (2)   | -0.02375 (19)| 0.0272 (2)   |
| O3     | 0.0418 (10)  | 0.0434 (10)  | 0.0808 (13)  | 0.0119 (8)   | 0.0005 (9)   | 0.0298 (9)   |
| O4     | 0.0291 (9)   | 0.0497 (10)  | 0.0727 (13)  | 0.0090 (7)   | 0.0003 (8)   | 0.0169 (9)   |
| C11    | 0.0330 (12)  | 0.0242 (11)  | 0.0468 (14)  | 0.0078 (9)   | -0.0007 (11)| 0.0021 (10)  |
| C12    | 0.0403 (14)  | 0.0432 (13)  | 0.0504 (16)  | 0.0160 (11)  | 0.0087 (12)  | 0.0125 (11)  |
| C13    | 0.0345 (13)  | 0.0548 (15)  | 0.0659 (19)  | 0.0194 (11)  | 0.0057 (13)  | 0.0145 (14)  |
| C14    | 0.0443 (15)  | 0.0381 (13)  | 0.0548 (17)  | 0.0096 (11)  | -0.0109 (13)| 0.0102 (12)  |
| C15    | 0.0500 (16)  | 0.0433 (14)  | 0.0403 (15)  | 0.0053 (11)  | -0.0007 (12)| 0.0082 (11)  |
| C16    | 0.0376 (13)  | 0.0378 (13)  | 0.0499 (16)  | 0.0068 (10)  | 0.0051 (12)  | 0.0034 (11)  |
| O5     | 0.0370 (10)  | 0.0413 (10)  | 0.0619 (12)  | 0.0103 (7)   | -0.0023 (9)  | 0.0133 (9)   |
| O6     | 0.0491 (12)  | 0.0429 (10)  | 0.0816 (15)  | 0.0141 (8)   | -0.0142 (10)| 0.0195 (10)  |
### Geometric parameters (Å, °)

| Bond/Distance | Value |
|---------------|-------|
| O1—N3         | 1.222 (3) |
| O2—N3         | 1.217 (3) |
| N1—C1         | 1.391 (3) |
| N1—C7         | 1.474 (3) |
| N1—C10        | 1.477 (3) |
| N2—C9         | 1.476 (4) |
| N2—C8         | 1.490 (3) |
| N2—H21        | 0.850 (17) |
| N2—H22        | 0.833 (18) |
| N3—C4         | 1.454 (3) |
| C1—C2         | 1.405 (3) |
| C1—C6         | 1.410 (3) |
| C2—C3         | 1.376 (3) |
| C2—H2         | 0.93 |
| C3—C4         | 1.377 (4) |
| C3—H3         | 0.93 |
| C4—C5         | 1.378 (4) |
| C5—C6         | 1.372 (3) |
| C5—H5         | 0.93 |
| C6—H6         | 0.93 |
| C7—C8         | 1.502 (3) |
| C7—H7A        | 0.97 |
| C7—H7B        | 0.97 |
| C8—H8A        | 0.97 |
| C1—N1—C7      | 117.46 (19) |
| C1—N1—C10     | 117.30 (18) |
| C7—N1—C10     | 112.08 (19) |
| C9—N2—C8      | 109.8 (2) |
| C9—N2—H21     | 113 (2) |
| C8—N2—H21     | 110 (2) |
| C9—N2—H22     | 115 (2) |
| C8—N2—H22     | 106 (2) |
| H21—N2—H22    | 102 (3) |
| O2—N3—O1      | 122.4 (2) |
| O2—N3—C4      | 118.8 (2) |
| O1—N3—C4      | 118.8 (2) |
| N1—C1—C2      | 121.5 (2) |
| N1—C1—C6      | 121.4 (2) |
| C2—C1—C6      | 117.1 (2) |
| C3—C2—C1      | 121.2 (2) |
| C3—C2—H2      | 119.4 |
| C1—C2—H2      | 119.4 |
| C2—C3—C4      | 119.9 (2) |
| C2—C3—H3      | 120 |
| C4—C3—H3      | 120 |

**Angles (°)**

| Angle         | Value |
|---------------|-------|
| C1—N1—C7      | 117.46 (19) |
| C1—N1—C10     | 117.30 (18) |
| C7—N1—C10     | 112.08 (19) |
| C9—N2—C8      | 109.8 (2) |
| C9—N2—H21     | 113 (2) |
| C8—N2—H21     | 110 (2) |
| C9—N2—H22     | 115 (2) |
| C8—N2—H22     | 106 (2) |
| H21—N2—H22    | 102 (3) |
| O2—N3—O1      | 122.4 (2) |
| O2—N3—C4      | 118.8 (2) |
| O1—N3—C4      | 118.8 (2) |
| N1—C1—C2      | 121.5 (2) |
| N1—C1—C6      | 121.4 (2) |
| C2—C1—C6      | 117.1 (2) |
| C3—C2—C1      | 121.2 (2) |
| C3—C2—H2      | 119.4 |
| C1—C2—H2      | 119.4 |
| C2—C3—C4      | 119.9 (2) |
| C2—C3—H3      | 120 |
| C4—C3—H3      | 120 |
C3—C4—C5 120.6 (2) C14—C13—C12 119.0 (2)
C3—C4—N3 119.2 (2) C14—C13—H13 120.5
C5—C4—N3 120.2 (2) C12—C13—H13 120.5
C6—C5—C4 119.8 (2) C13—C14—C15 121.4 (2)
C6—C5—H5 120.1 C13—C14—Br1 119.7 (2)
C4—C5—H5 120.1 C15—C14—Br1 118.9 (2)
C5—C6—C1 121.4 (2) C14—C15—C16 119.2 (2)
C5—C6—H6 119.3 C14—C15—H15 120.4
C1—C6—H6 119.3 C16—C15—H15 120.4
N1—C7—C8 111.5 (2) C15—C16—C11 120.9 (2)
N1—C7—H7A 109.3 C15—C16—C12 119.6
C8—C7—H7A 109.3 C11—C16—H16 119.6
N1—C7—H7B 109.3 O4—C17—O3 124.3 (2)
C8—C7—H7B 109.3 O4—C17—C11 117.8 (2)
H7A—C7—H7B 108 H3W—O6—H4W 109 (3)
N2—C8—H8A 109.4 H4W—O6—H3W 109 (3)
C7—C8—H8A 109.4
C7—N1—C1—C2 10.7 (3) C9—N2—C8—C7 58.1 (3)
C10—N1—C1—C2 148.9 (2) N1—C7—C8—N2 −55.1 (3)
C7—N1—C1—C6 −171.5 (2) C8—N2—C9—C10 −58.5 (3)
C10—N1—C1—C6 120.9 (2) C11—C10—C9—C8 −53.9 (3)
N1—C1—C2—C3 176.8 (2) C16—C11—C12—C13 1.3 (3)
C2—C1—C2—C3 −1.1 (4) C1—C10—C9—C8 165.8 (2)
C2—C1—C6—C5 −1.6 (4) N2—C9—C10—C11 56.8 (3)
C2—C1—C6—C5 179.9 (2) N2—C9—C10—C12 −1.7 (4)
O2—N3—C4—C3 −174.9 (3) C12—C13—C14—C15 0.4 (4)
O1—N3—C4—C3 5.0 (4) C12—C13—C14—Br1 179.36 (19)
O2—N3—C4—C5 5.7 (4) C13—C14—C15—C16 1.2 (4)
O1—N3—C4—C5 −174.4 (3) Br1—C14—C15—C16 −177.75 (18)
C3—C4—C5—C6 0.5 (4) C14—C15—C16—C11 −1.6 (3)
N3—C4—C5—C6 179.9 (2) C12—C11—C16—C15 0.4 (3)
C4—C5—C6—C1 0.3 (4) C17—C11—C16—C15 −178.9 (2)
N1—C1—C6—C5 −177.9 (2) C16—C11—C17—O4 −26.9 (3)
C2—C1—C6—C5 0.0 (4) C12—C11—C17—O4 153.8 (2)
C1—N1—C7—C8 −166.7 (2) C16—C11—C17—O3 −26.0 (3)
C10—N1—C7—C8 53.0 (3) C12—C11—C17—O3 153.3 (2)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|-------|-------|---------|
| N2—H21···O5i | 0.85 (2) | 1.99 (2) | 2.810 (3) | 162 (3) |
| N2—H22···O6ii | 0.83 (2) | 1.91 (2) | 2.707 (3) | 160 (3) |
| C3—H3···O1iii | 0.93 | 2.59 | 3.260 (4) | 130 |
| C13—H13···O4iv | 0.93 | 2.57 | 3.483 (3) | 166 |
| C15—H15···O2v | 0.93 | 2.47 | 3.269 (4) | 144 |
4-(4-Nitrophenyl)piperazin-1-ium 4-iodobenzoate dihydrate (II)

Crystal data

\[ C_{10}H_{14}N_3O_2^+ \cdot C_7H_4IO_2^- \cdot 2H_2O \]

Mr \( = 491.28 \)

Triclinic, \( P \bar{1} \)

Hall symbol: -\( P \bar{1} \)

\( a = 7.7652 (4) \) Å

\( b = 9.2852 (5) \) Å

\( c = 13.930 (1) \) Å

\( \alpha = 94.985 (5) ^\circ \)

\( \beta = 95.331 (5) ^\circ \)

\( \gamma = 104.875 (6) ^\circ \)

\( V = 960.09 (10) \) Å\(^3\)

Z = 2

\( F(000) = 492 \)

\( D_x = 1.699 \) Mg m\(^{-3}\)

Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \) Å

Cell parameters from 6331 reflections

\( \theta = 2.6–25.4 ^\circ \)

\( \mu = 1.71 \) mm\(^{-1}\)

\( T = 293 \) K

Prism, brown

0.48 × 0.48 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur diffractometer

\( \omega \) scans

Absorption correction: multi-scan

( \( \text{CrysAlis RED; Oxford Diffraction, 2009} \)

\( T_{\text{min}} = 0.458, T_{\text{max}} = 0.711 \)

6331 measured reflections

Refinement

Refinement on \( F^2 \)

\( R[F^2 > 2\sigma(F^2)] = 0.029 \)

\( wR(F^2) = 0.069 \)

\( S = 1.03 \)

3513 reflections

262 parameters

6 restraints

0 constraints

Hydrogen site location: mixed

\( H \) atoms treated by a mixture of independent and constrained refinement

\[ w = 1/\left[\sigma^2(F^2) + (0.0319P)^2 + 0.5892P\right] \]

where \( P = (\sigma^2(F^2) + 2F^2) / 3 \)

\( \Delta / \sigma \) max < 0.001

\( \Delta p_{\text{max}} = 0.54 \) e Å\(^{-3}\)

\( \Delta p_{\text{min}} = -0.66 \) 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     | \( U_{eq} \) |
|-----|-------|-------|-------|--------------|
| O1  | 0.9211 (3) | 0.7945 (3) | 0.5327 (2) | 0.0765 (8) |
| O2  | 0.6869 (3) | 0.6415 (3) | 0.5706 (2) | 0.0702 (7) |
| N1  | 0.3324 (3) | 1.0055 (2) | 0.29012 (17) | 0.0344 (5) |

Supporting information

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| Atom | x       | y       | z       | Temperature Anisotropic (Å²) |
|------|---------|---------|---------|-----------------------------|
| N2   | 0.1277 (3) | 1.1016 (3) | 0.13972 (19) | 0.0404 (6) |
| N3   | 0.7583 (4) | 0.7448 (3) | 0.52680 (19) | 0.0471 (6) |
| C1   | 0.4369 (3) | 0.9384 (3) | 0.34660 (19) | 0.0311 (6) |
| C2   | 0.6239 (4) | 0.9794 (3) | 0.3495 (2) | 0.0421 (7) |
| H2   | 0.678241 | 1.049839 | 0.310458 | 0.051* |
| C3   | 0.7273 (4) | 0.9175 (3) | 0.4087 (2) | 0.0434 (7) |
| C4   | 0.851637 | 0.947138 | 0.411003 | 0.052* |
| C5   | 0.6475 (4) | 0.8107 (3) | 0.4653 (2) | 0.0348 (6) |
| H5   | 0.411197 | 0.694461 | 0.502907 | 0.049* |
| C6   | 0.3609 (4) | 0.8297 (3) | 0.4063 (2) | 0.0390 (7) |
| C7   | 0.236893 | 0.800552 | 0.405831 | 0.047* |
| H7A  | 0.4203 (4) | 1.1048 (3) | 0.2222 (2) | 0.0412 (7) |
| H7B  | 0.448427 | 1.044706 | 0.168453 | 0.049* |
| C8   | 0.532139 | 1.170403 | 0.255077 | 0.049* |
| C9   | 0.3038 (4) | 1.1984 (3) | 0.1836 (2) | 0.0439 (7) |
| H9A  | 0.287569 | 1.267775 | 0.236 | 0.053* |
| H9B  | 0.361796 | 1.256375 | 0.135285 | 0.053* |
| C10  | 0.0381 (4) | 1.0095 (4) | 0.2115 (2) | 0.0456 (7) |
| C11  | 0.07676 | 0.945606 | 0.181239 | 0.055* |
| C12  | 0.016429 | 1.074515 | 0.264773 | 0.055* |
| C13  | 0.1531 (4) | 0.9144 (3) | 0.2497 (2) | 0.0413 (7) |
| C14  | 0.096206 | 0.859686 | 0.299686 | 0.05* |
| C15  | 0.163241 | 0.841846 | 0.19758 | 0.05* |
| C16  | 0.92211 (3) | 0.44728 (3) | 0.33815 (2) | 0.05798 (10) |
| O3   | 0.4459 (3) | 0.7894 (2) | 0.01595 (18) | 0.0503 (6) |
| O4   | 0.2183 (3) | 0.6411 (2) | 0.07685 (16) | 0.0463 (5) |
| C11  | 0.5106 (3) | 0.6368 (3) | 0.1340 (2) | 0.0321 (6) |
| C12  | 0.6798 (4) | 0.6390 (3) | 0.1072 (2) | 0.0387 (7) |
| C13  | 0.7975 (4) | 0.5851 (3) | 0.1648 (2) | 0.0411 (7) |
| C14  | 0.909115 | 0.584052 | 0.146196 | 0.049* |
| C15  | 0.7470 (4) | 0.5326 (3) | 0.2509 (2) | 0.0376 (7) |
| C15  | 0.5813 (4) | 0.5331 (3) | 0.2798 (2) | 0.0398 (7) |
| H15  | 0.550434 | 0.499714 | 0.338523 | 0.048* |
| C16  | 0.4631 (4) | 0.5834 (3) | 0.2208 (2) | 0.0378 (7) |
| H16  | 0.350345 | 0.581695 | 0.238875 | 0.045* |
| C17  | 0.3825 (4) | 0.6931 (3) | 0.0705 (2) | 0.0356 (6) |
| O5   | 0.7577 (3) | 0.0174 (2) | 0.02906 (17) | 0.0446 (5) |
| O6   | 0.0304 (3) | 0.3341 (3) | 0.06807 (19) | 0.0529 (6) |
| H21  | 0.144 (5) | 1.051 (4) | 0.0882 (19) | 0.063* |
| H22  | 0.076 (4) | 1.162 (3) | 0.116 (3) | 0.063* |
| H1W  | 0.671 (4) | −0.051 (3) | 0.032 (3) | 0.063* |
| H2W  | 0.711 (5) | 0.084 (3) | 0.022 (3) | 0.063* |
| H4W  | 0.100 (4) | 0.414 (3) | 0.080 (3) | 0.063* |
| H3W  | −0.052 (4) | 0.326 (4) | 0.027 (2) | 0.063* |
Atomic displacement parameters (Å²)

|    | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|----|-----|-----|-----|-----|-----|-----|
| O1 | 0.0437 (15) | 0.0752 (18) | 0.108 (2) | 0.0122 (13) | −0.0192 (14) | 0.0400 (16) |
| O2 | 0.0633 (16) | 0.0754 (18) | 0.0786 (18) | 0.0200 (13) | 0.0033 (13) | 0.0469 (15) |
| N1 | 0.0300 (12) | 0.0321 (13) | 0.0391 (13) | 0.0054 (10) | −0.0037 (10) | 0.0090 (10) |
| N2 | 0.0420 (14) | 0.0388 (15) | 0.0413 (15) | 0.0159 (11) | −0.0066 (12) | 0.0072 (11) |
| N3 | 0.0496 (17) | 0.0450 (16) | 0.0461 (15) | 0.0151 (13) | −0.0076 (13) | 0.0084 (13) |
| C1 | 0.0328 (14) | 0.0280 (14) | 0.0316 (14) | 0.0093 (11) | −0.0008 (11) | 0.0009 (11) |
| C2 | 0.0340 (15) | 0.0433 (17) | 0.0496 (18) | 0.0067 (13) | 0.0047 (13) | 0.0196 (14) |
| C3 | 0.0279 (15) | 0.0464 (18) | 0.0548 (19) | 0.0086 (13) | −0.0100 (13) | 0.0115 (15) |
| C4 | 0.0369 (15) | 0.0344 (15) | 0.0332 (15) | 0.0118 (12) | −0.0209 (12) | 0.0049 (12) |
| C5 | 0.0422 (17) | 0.0417 (17) | 0.0383 (16) | 0.0087 (13) | 0.0047 (13) | 0.0139 (13) |
| C6 | 0.0292 (14) | 0.0443 (17) | 0.0430 (17) | 0.0073 (12) | 0.0016 (12) | 0.0118 (13) |
| C7 | 0.0353 (15) | 0.0389 (17) | 0.0459 (17) | 0.0034 (13) | −0.0040 (13) | 0.0148 (14) |
| C8 | 0.0483 (18) | 0.0350 (16) | 0.0447 (17) | 0.0078 (14) | −0.0075 (14) | 0.0095 (13) |
| C9 | 0.0354 (16) | 0.055 (2) | 0.0479 (18) | 0.0160 (14) | −0.0023 (14) | 0.0103 (15) |
| C10 | 0.0297 (15) | 0.0401 (17) | 0.0524 (18) | 0.0071 (13) | −0.0035 (13) | 0.0110 (14) |
| I1 | 0.05063 (15) | 0.06217 (17) | 0.06139 (16) | 0.01852 (11) | −0.01269 (10) | 0.01870 (11) |
| O3 | 0.0370 (11) | 0.0400 (12) | 0.0758 (16) | 0.0088 (9) | 0.0016 (11) | 0.0276 (11) |
| O4 | 0.0283 (11) | 0.0460 (12) | 0.0629 (14) | 0.0073 (9) | −0.0016 (10) | 0.0134 (10) |
| C11 | 0.0290 (14) | 0.0241 (14) | 0.0415 (16) | 0.0059 (11) | −0.0004 (12) | 0.0023 (12) |
| C12 | 0.0376 (16) | 0.0394 (16) | 0.0431 (17) | 0.0138 (13) | 0.0088 (13) | 0.0119 (13) |
| C13 | 0.0315 (15) | 0.0436 (17) | 0.0516 (19) | 0.0157 (13) | 0.0044 (13) | 0.0082 (14) |
| C14 | 0.0336 (15) | 0.0306 (15) | 0.0458 (17) | 0.0078 (12) | −0.0064 (13) | 0.0047 (13) |
| C15 | 0.0421 (17) | 0.0365 (16) | 0.0373 (16) | 0.0043 (13) | 0.0025 (13) | 0.0068 (13) |
| C16 | 0.0288 (14) | 0.0356 (16) | 0.0471 (17) | 0.0062 (12) | 0.0048 (13) | 0.0018 (13) |
| C17 | 0.0328 (15) | 0.0241 (14) | 0.0475 (17) | 0.0073 (12) | −0.0011 (13) | −0.0012 (12) |
| O5 | 0.0345 (11) | 0.0374 (13) | 0.0610 (14) | 0.0094 (9) | −0.0027 (10) | 0.0111 (11) |
| O6 | 0.0442 (13) | 0.0383 (12) | 0.0735 (17) | 0.0097 (10) | −0.0123 (11) | 0.0164 (12) |

Geometric parameters (Å, °)

|    |     |     |     |     |     |     |
|----|-----|-----|-----|-----|-----|-----|
| O1—N3 | 1.222 (3) | C8—H8B | 0.97 |
| O2—N3 | 1.221 (3) | C9—C10 | 1.503 (4) |
| N1—C1 | 1.376 (3) | C9—H9A | 0.97 |
| N1—C10 | 1.462 (3) | C9—H9B | 0.97 |
| N1—C7 | 1.469 (4) | C10—H10A | 0.97 |
| N2—C8 | 1.473 (4) | C10—H10B | 0.97 |
| N2—C9 | 1.479 (4) | I1—C14 | 2.090 (3) |
| N2—H21 | 0.859 (18) | O3—C17 | 1.257 (3) |
| N2—H22 | 0.850 (18) | O4—C17 | 1.257 (3) |
| N3—C4 | 1.440 (4) | C11—C16 | 1.391 (4) |
| C1—C2 | 1.400 (4) | C11—C12 | 1.395 (4) |
| C1—C6 | 1.410 (4) | C11—C17 | 1.493 (4) |
| C2—C3 | 1.361 (4) | C12—C13 | 1.377 (4) |
| C2—H2 | 0.93 | C12—H12 | 0.93 |
| C3—C4 | 1.378 (4) | C13—C14 | 1.386 (4) |

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C3—H3 0.93 C13—H13 0.93
C4—C5 1.378 (4) C14—C15 1.385 (4)
C5—C6 1.357 (4) C15—C16 1.372 (4)
C5—H5 0.93 C15—H15 0.93
C6—C6 0.93 C16—H16 0.93
C7—C8 1.502 (4) O5—H1W 0.805 (18)
C7—H7A 0.97 O5—H2W 0.805 (18)
C7—H7B 0.97 O6—H4W 0.795 (18)
C8—H8A 0.97 O6—H3W 0.800 (18)

C1—N1—C10 117.2 (2) N2—C8—H8B 109.6
C1—N1—C7 117.8 (2) C7—C8—H8B 109.6
C10—N1—C7 112.8 (2) H8A—C8—H8B 108.1
C8—N2—C9 110.6 (2) N2—C9—C10 110.3 (2)
C8—N2—H21 108 (3) N2—C9—H9A 109.6
C9—N2—H21 115 (3) C10—C9—H9A 109.6
C8—N2—H22 104 (3) N2—C9—H9B 109.6
C9—N2—H22 118 (3) C10—C9—H9B 109.6
H21—N2—H22 101 (3) H9A—C9—H9B 108.1
O2—N3—O1 122.5 (3) N1—C10—C9 111.5 (2)
O2—N3—C4 119.1 (3) N1—C10—H10A 109.3
O1—N3—C4 118.4 (3) C9—C10—H10A 109.3
N1—C1—C2 121.1 (2) N1—C10—H10B 109.3
N1—C1—C6 121.5 (2) C9—C10—H10B 109.3
C2—C1—C6 117.4 (2) H10A—C10—H10B 108
C3—C2—C1 120.9 (3) C16—C11—C12 119.5 (3)
C3—C2—H2 119.6 C16—C11—C17 120.4 (2)
C1—C2—H2 119.6 C12—C11—C17 120.1 (2)
C2—C3—C4 119.9 (3) C13—C12—C11 120.4 (3)
C2—C3—H3 120.1 C13—C12—H12 119.8
C4—C3—H3 120.1 C11—C12—H12 119.8
C5—C4—C3 121.2 (3) C12—C13—C14 119.0 (3)
C5—C4—N3 119.5 (3) C12—C13—H13 120.5
C3—C4—N3 119.3 (3) C14—C13—H13 120.5
C6—C5—C4 118.9 (3) C15—C14—C13 121.4 (3)
C6—C5—H5 120.5 C15—C14—I1 119.1 (2)
C4—C5—H5 120.5 C13—C14—I1 119.6 (2)
C5—C6—C1 121.8 (3) C16—C15—C14 119.2 (3)
C5—C6—H6 119.1 C16—C15—H15 120.4
C1—C6—H6 119.1 C14—C15—H15 120.4
N1—C7—C8 111.9 (2) C15—C16—C11 120.5 (3)
N1—C7—H7A 109.2 C15—C16—H16 119.8
C8—C7—H7A 109.2 C11—C16—H16 119.8
N1—C7—H7B 109.2 O4—C17—O3 125.0 (3)
C8—C7—H7B 109.2 O4—C17—C11 116.9 (2)
H7A—C7—H7B 107.9 O3—C17—C11 118.1 (2)
N2—C8—C7 110.2 (2) H1W—O5—H2W 101 (4)
N2—C8—H8A 109.6 H4W—O6—H3W 117 (4)
C7—C8—H8A 109.6

C10—N1—C1—C2 148.6 (3) C9—N2—C8—C7 58.1 (3)
C7—N1—C1—C2 8.9 (4) N1—C7—C8—N2 −54.7 (3)
C10—N1—C1—C6 −33.7 (4) C1—C7—C8—N2 −173.4 (3)
N1—C1—C6—C5 −178.0 (3) C10—N1—C1—C6 −173.4 (3)
C6—C1—C2—C3 1.3 (5) C1—C10—C9—C10 165.8 (3)
C2—C3—C4—C5 −0.8 (4) C10—N1—C1—C6 165.8 (3)
N3—C4—C5—C6 0.1 (5) N1—C1—C6—C5 −178.0 (3)
C4—C5—C6—C1 0.4 (5) C2—C3—C4—C5 1.3 (5)
N3—C4—C5—C6 179.8 (3) C3—C4—C5—C6 179.8 (3)
C4—C5—C6—C1 0.4 (5) C16—C11—C12—C13 1.6 (4)
N1—C1—C2—C3 −178.0 (3) C12—C11—C16—C15 0.0 (4)
C1—C2—C3—C4 1.3 (5) C17—C11—C16—C15 −179.3 (3)
C2—C3—C4—C5 −178.0 (3) C13—C11—C16—C15 0.0 (4)
O2—N3—C4—C5 −173.9 (3) C14—C11—C16—C15 0.0 (4)
O1—N3—C4—C5 5.8 (4) C15—C11—C16—C15 −179.3 (3)
O2—N3—C4—C3 −173.9 (3) C12—C11—C16—C15 0.0 (4)
O1—N3—C4—C3 5.8 (4) C16—C11—C16—C15 0.0 (4)

Hydrogen-bond geometry (Å, °)

|                | D—H   | H···A  | D···A  | D—H···A |
|----------------|-------|--------|--------|---------|
| N2—H21···O5i   | 0.86 (2) | 1.99 (2) | 2.825 (4) | 164 (4) |
| N2—H22···O6ii  | 0.85 (2) | 1.88 (2) | 2.702 (3) | 163 (4) |
| C3—H3···O1iii  | 0.93   | 2.59   | 3.275 (4) | 131     |
| C13—H13···O4iv | 0.93   | 2.62   | 3.526 (4) | 144     |
| C15—H15···O2v  | 0.93   | 2.49   | 3.311 (4) | 177     |
| O5—H1W···O3vi  | 0.81 (2) | 1.96 (2) | 2.756 (3) | 170 (4) |
| O5—H2W···O3   | 0.81 (2) | 1.96 (2) | 2.753 (3) | 166 (4) |
| O6—H4W···O4    | 0.80 (2) | 2.08 (2) | 2.836 (3) | 160 (4) |
| O6—H3W···O4    | 0.80 (2) | 1.95 (2) | 2.728 (3) | 165 (4) |

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

4-(4-Nitrophenyl)piperazin-1-ium 4-hydroxybenzoate monohydrate (III)

Crystal data
C_{10}H_{14}N_{3}O_{2}^+·C_{7}H_{5}O_{3}^-·H_{2}O  
\( y = 112.96 (1)° \)
\( V = 857.80 (17) \text{ Å}^3 \)
Triclinic, \( P\overline{1} \)
\( Z = 2 \)
Hall symbol: -P 1
\( F(000) = 384 \)
\( D_\alpha = 1.407 \text{ Mg m}^{-3} \)
\( \lambda = 0.71073 \text{ Å} \)
\( \theta = 2.6–25.3° \)
\( \mu = 0.11 \text{ mm}^{-1} \)

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$T = 293$ K
Rod, yellow

**Data collection**

Oxford Diffraction Xcalibur

diffractometer

$\omega$ scans

Absorption correction: multi-scan

(CrysAlis RED; Oxford Diffraction, 2009)

$T_{\text{min}} = 0.959$, $T_{\text{max}} = 0.974$

5342 measured reflections

3140 independent reflections

2342 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\text{max}} = 25.3^\circ$, $\theta_{\text{min}} = 2.6^\circ$

$h = -11\rightarrow 11$

$k = -12 \rightarrow 11$

$l = -13 \rightarrow 12$

**Refinement**

Refinement on $F^2$

Least-squares matrix: full

$R(F^2 > 2\sigma(F^2)) = 0.043$

$wR(F^2) = 0.106$

$S = 1.05$

3135 reflections

251 parameters

5 restraints

0 constraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0386 P)^2 + 0.3231 P]$

where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{\text{max}} = 0.19$ e Å$^{-3}$

$\Delta\rho_{\text{min}} = -0.19$ e Å$^{-3}$

Extinction correction: SHELXL2018/3

(Sheldrick 2015b),

$F^2 = kF(000)+0.001xF^2/\sin(2\theta)]^{1/4}$

Extinction coefficient: 0.032 (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 ($\AA^2$)**

|         | $x$          | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|---------|--------------|--------------|--------------|----------------------------------|
| C1      | 0.3138 (2)   | 0.3700 (19)  | 0.65529 (18) | 0.0346 (4)                      |
| C2      | 0.1431 (2)   | 0.2527 (2)   | 0.57638 (19) | 0.0418 (4)                      |
| H2      | 0.068235     | 0.250847     | 0.613904     | 0.05*                           |
| C3      | 0.0843 (2)   | 0.1407 (2)   | 0.4450 (2)   | 0.0434 (5)                      |
| H3      | -0.029409    | 0.063818     | 0.39416      | 0.052*                          |
| C4      | 0.1942 (2)   | 0.1428 (2)   | 0.38907 (19) | 0.0411 (4)                      |
| C5      | 0.3624 (2)   | 0.2553 (2)   | 0.4636 (2)   | 0.0483 (5)                      |
| H5      | 0.436252     | 0.255393     | 0.42532      | 0.058*                          |
| C6      | 0.4208 (2)   | 0.3670 (2)   | 0.5942 (2)   | 0.0472 (5)                      |
| H6      | 0.53484      | 0.443048     | 0.64379      | 0.057*                          |
| C7      | 0.5230 (2)   | 0.6338 (2)   | 0.8284 (2)   | 0.0453 (5)                      |
| H7A     | 0.489341     | 0.67826      | 0.763471     | 0.054*                          |
| H7B     | 0.611237     | 0.616548     | 0.817407     | 0.054*                          |
| C8      | 0.5933 (2)   | 0.7472 (2)   | 0.9784 (2)   | 0.0493 (5)                      |
| H8A     | 0.643572     | 0.71093      | 1.044949     | 0.059*                          |
| H8B     | 0.681545     | 0.846719     | 0.99504      | 0.059*                          |
| C9      | 0.3302 (3)   | 0.6143 (2)   | 0.9836 (2)   | 0.0457 (5)                      |
| H9A     | 0.242868     | 0.625614     | 1.002896     | 0.055*                          |
### Supporting Information

#### Atomic coordinates (Å)

| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H9B  | 0.381743 | 0.579404 | 1.050389 | 0.055* |
| C10  | 0.2514 (2) | 0.4953 (2) | 0.83370 (19) | 0.0403 (4) |
| H10A | 0.176601 | 0.394834 | 0.82667 | 0.048* |
| H10B | 0.183115 | 0.521491 | 0.76885 | 0.048* |
| C11  | 0.1749 (2) | 0.5843 (2) | 0.29147 (19) | 0.0418 (5) |
| C12  | 0.2469 (3) | 0.7413 (2) | 0.3258 (2) | 0.0495 (5) |
| H12  | 0.262285 | 0.778209 | 0.258209 | 0.059* |
| C13  | 0.2959 (2) | 0.8431 (2) | 0.4597 (2) | 0.0438 (5) |
| H13  | 0.344454 | 0.94863 | 0.481898 | 0.053* |
| C14  | 0.2738 (2) | 0.7906 (2) | 0.56226 (18) | 0.0364 (4) |
| C15  | 0.2004 (2) | 0.6329 (2) | 0.52544 (19) | 0.0395 (4) |
| H15  | 0.18337 | 0.595519 | 0.592378 | 0.047* |
| C16  | 0.1520 (2) | 0.5299 (2) | 0.39188 (19) | 0.0410 (4) |
| H16  | 0.104259 | 0.424435 | 0.369591 | 0.049* |
| C17  | 0.3293 (2) | 0.9024 (2) | 0.7080 (2) | 0.0440 (5) |
| N1   | 0.37669 (18) | 0.48418 (16) | 0.78933 (15) | 0.0372 (4) |
| N2   | 0.4599 (2) | 0.76559 (19) | 1.00415 (18) | 0.0479 (4) |
| N3   | 0.1322 (2) | 0.02537 (19) | 0.25010 (18) | 0.0518 (4) |
| O1   | 0.2282 (2) | 0.04014 (19) | 0.19537 (17) | 0.0759 (5) |
| O2   | −0.0112 (2) | −0.08579 (18) | 0.19233 (16) | 0.0715 (5) |
| O3   | 0.1311 (2) | 0.48813 (18) | 0.15852 (15) | 0.0637 (4) |
| O4   | 0.3985 (2) | 1.04290 (17) | 0.73256 (16) | 0.0744 (5) |
| O5   | 0.30323 (18) | 0.85085 (16) | 0.79750 (14) | 0.0547 (4) |
| O6   | −0.0679 (3) | 0.1917 (2) | 0.09903 (19) | 0.0809 (6) |
| H21  | 0.412 (3) | 0.796 (3) | 0.941 (2) | 0.097* |
| H22  | 0.513 (3) | 0.838 (3) | 1.099 (2) | 0.097* |
| H1W  | −0.140 (3) | 0.168 (3) | 0.129 (3) | 0.097* |
| H2W  | −0.112 (3) | 0.128 (3) | 0.015 (2) | 0.097* |

#### Atomic displacement parameters (Å²)

| Atom | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|------|-----|-----|-----|-----|-----|-----|
| C1   | 0.0348 (10) | 0.0343 (9) | 0.0377 (10) | 0.0187 (8) | 0.0167 (8) | 0.0173 (8) |
| C2   | 0.0357 (10) | 0.0427 (10) | 0.0444 (11) | 0.0159 (8) | 0.0211 (8) | 0.0168 (9) |
| C3   | 0.0356 (10) | 0.0380 (10) | 0.0439 (11) | 0.0113 (8) | 0.0148 (8) | 0.0145 (9) |
| C4   | 0.0463 (11) | 0.0347 (9) | 0.0373 (10) | 0.0191 (8) | 0.0175 (8) | 0.0119 (8) |
| C5   | 0.0429 (11) | 0.0481 (11) | 0.0505 (12) | 0.0215 (9) | 0.0255 (9) | 0.0120 (10) |
| C6   | 0.0315 (10) | 0.0440 (11) | 0.0514 (12) | 0.0139 (8) | 0.0177 (9) | 0.0081 (9) |
| C7   | 0.0379 (10) | 0.0401 (10) | 0.0487 (11) | 0.0133 (8) | 0.0209 (9) | 0.0137 (9) |
| C8   | 0.0459 (11) | 0.0395 (11) | 0.0468 (11) | 0.0154 (9) | 0.0160 (9) | 0.0117 (9) |
| C9   | 0.0590 (12) | 0.0451 (11) | 0.0434 (11) | 0.0277 (10) | 0.0295 (10) | 0.0231 (9) |
| C10  | 0.0429 (10) | 0.0421 (10) | 0.0420 (10) | 0.0213 (9) | 0.0239 (9) | 0.0211 (9) |
| C11  | 0.0398 (10) | 0.0443 (11) | 0.0361 (10) | 0.0170 (9) | 0.0194 (8) | 0.0133 (9) |
| C12  | 0.0595 (13) | 0.0525 (12) | 0.0441 (11) | 0.0248 (10) | 0.0315 (10) | 0.0269 (10) |
| C13  | 0.0494 (11) | 0.0392 (10) | 0.0482 (11) | 0.0207 (9) | 0.0274 (9) | 0.0224 (9) |
| C14  | 0.0357 (9) | 0.0405 (10) | 0.0381 (10) | 0.0210 (8) | 0.0190 (8) | 0.0183 (8) |
| C15  | 0.0410 (10) | 0.0440 (10) | 0.0378 (10) | 0.0201 (8) | 0.0208 (8) | 0.0223 (9) |

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### Geometric parameters (Å, º)

| Bond/Angle | Length/Distance (Å) | Torsion/Angle (º) |
|------------|--------------------|-------------------|
| C1—N1      | 1.392 (2)          |                   |
| C1—C6      | 1.397 (2)          |                   |
| C1—C2      | 1.402 (2)          |                   |
| C2—C3      | 1.371 (3)          |                   |
| C2—H2      | 0.93               |                   |
| C3—C4      | 1.373 (3)          |                   |
| C3—H3      | 0.93               |                   |
| C4—C5      | 1.373 (3)          |                   |
| C4—N3      | 1.446 (2)          |                   |
| C5—C6      | 1.365 (3)          |                   |
| C5—H5      | 0.93               |                   |
| C6—H6      | 0.93               |                   |
| C7—N1      | 1.468 (2)          |                   |
| C7—C8      | 1.501 (3)          |                   |
| C7—H7A     | 0.97               |                   |
| C7—H7B     | 0.97               |                   |
| C8—N2      | 1.470 (3)          |                   |
| C8—H8A     | 0.97               |                   |
| C8—H8B     | 0.97               |                   |
| C9—N2      | 1.476 (2)          |                   |
| C9—C10     | 1.507 (3)          |                   |
| C9—H9A     | 0.97               |                   |
| C9—H9B     | 0.97               |                   |
| C10—N1     | 1.467 (2)          |                   |
| N1—C1—C6   | 120.65 (15)        |                   |
| N1—C1—C2   | 122.40 (15)        |                   |
| C6—C1—C2   | 116.95 (16)        |                   |
| C3—C2—C1   | 121.37 (17)        |                   |
| C3—C2—H2   | 119.3              |                   |
| C1—C2—H2   | 119.3              |                   |
| C2—C3—C4   | 119.60 (17)        |                   |
| C2—C3—H3   | 120.2              |                   |
| C4—C3—H3   | 120.2              |                   |

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C3—C4—C5 120.68 (17) C12—C13—C14 120.94 (17)
C3—C4—N3 119.73 (17) C12—C13—H13 119.5
C5—C4—N3 119.59 (17) C14—C13—H13 119.5
C6—C5—C4 119.67 (17) C15—C14—C13 118.02 (16)
C6—C5—H5 120.2 C15—C14—C17 121.42 (16)
C4—C5—H5 120.2 C13—C14—C17 120.55 (16)
C5—C6—C1 121.72 (17) C16—C15—C14 121.51 (17)
C5—C6—H6 119.1 C16—C15—H15 119.2
C1—C6—H6 119.1 C14—C15—H15 119.2
N1—C7—C8 113.07 (16) C15—C16—C11 119.60 (17)
N1—C7—H7A 109 C15—C16—H16 120.2
C8—C7—H7A 109 C11—C16—H16 120.2
N1—C7—C8 109 O4—C17—C14 116.82 (17)
H7A—C7—H7B 107.8 O5—C17—C14 119.04 (17)
N2—C8—C7 110.93 (16) C1—C10—C9 116.6 (15)
N2—C8—H8A 109.5 C1—C10—H10A 108.9
C7—C8—H8A 109.5 C2—C1—N1—C10 108.9
N2—C8—H8B 109.5 C9—C10—H10A 110.8 (17)
C7—C8—H8B 109.5 C11—O3—H17 110.2 (19)
H8A—C8—H8B 108 C16—C12—C13 119.62 (17)
N2—C9—C10 110.96 (15) C12—C11—C16—C15 0.4 (3)
N2—C9—H9A 109.4 C3—C4—N3—O2 179.46 (17)
N2—C9—H9B 109.4 C3—C4—N3—C10 119.30 (16)
H9A—C9—H9B 108 C3—C4—N3—H21 110.2 (19)
N1—C10—C9 113.15 (15) C1—C2—C3—C4 −179.46 (17)
N1—C10—H10A 108.9 C2—C3—C4—C5 −179.46 (17)
C9—C10—H10A 108.9 C2—C3—C4—N3 −179.46 (17)
C10—C9—H9A 109.4 C3—C4—N3—C10 119.30 (16)
N1—C1—C2—C3 −179.46 (17) C3—C4—N3—H21 110.2 (19)
C6—C1—C2—C3 −0.3 (3) C1—C2—C3—C4 179.46 (17)
C1—C2—C3—C4 0.0 (3) C2—C3—C4—C5 179.46 (17)
C2—C3—C4—C5 0.4 (3) C2—C3—C4—N3 179.46 (17)
C2—C3—C4—N3 −179.58 (17) C3—C4—C5—C6 −179.58 (17)
C3—C4—C5—C6 −0.5 (3) C3—C4—C5—C6 179.58 (17)
N3—C4—C5—C6 179.41 (18) C6—C1—C2—C3 179.41 (18)
C4—C5—C6—C1 0.3 (3) C2—C3—C4—C5 179.41 (18)
N1—C1—C2—C3 179.30 (18) C1—C2—C3—C4 179.30 (18)
N1—C1—C2—C3 −179.58 (17) C1—C2—C3—C4 −179.58 (17)
N1—C1—C2—C3 −179.46 (17) C1—C2—C3—C4 −179.46 (17)
N1—C1—C2—C3 −179.46 (17) C1—C2—C3—C4 −179.46 (17)
Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|--------|
| N2—H21···O5 | 0.89 (2) | 1.93 (2) | 2.819 (2) | 177 (3) |
| N2—H22···O4i | 0.94 (2) | 1.65 (2) | 2.583 (2) | 177 (3) |
| O3—H17···O6 | 0.85 (2) | 1.82 (2) | 2.669 (2) | 177 (3) |
| O6—H1W···O5ii | 0.83 (2) | 1.95 (2) | 2.768 (2) | 169 (3) |
| O6—H2W···O1iii | 0.83 (2) | 2.11 (2) | 2.944 (2) | 178 (3) |

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

4-(4-Nitrophenyl)piperazin-1-ium 4-methylbenzoate monohydrate (IV)

Crystal data

C_{10}H_{14}N_{3}O_{2}^+·C_{8}H_{7}O_{2}^-·H_{2}O

Mr = 361.39

Triclinic, P̅1

Hall symbol: -P 1

a = 6.1136 (5) Å

b = 7.6965 (7) Å

c = 19.708 (2) Å

α = 79.577 (8)°

β = 87.162 (8)°

γ = 86.699 (8)°

V = 909.79 (15) Å³

Z = 2

F(000) = 384

D_x = 1.319 Mg m⁻³

Mo Ka radiation, λ = 0.71073 Å

Cell parameters from 5980 reflections

θ = 3.1–25.4°

µ = 0.10 mm⁻¹

T = 293 K

Plate, yellow

0.48 × 0.26 × 0.02 mm

Data collection

Oxford Diffraction Xcalibur

diffractometer

ω scans

Absorption correction: multi-scan

(CrysAlis RED; Oxford Diffraction, 2009)

T_min = 0.970, T_max = 0.998

5980 measured reflections

Refinement

Refinement on F²

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

R[F² > 2σ(F²)] = 0.053

wR(F²) = 0.138

S = 1.01

3343 reflections

248 parameters

4 restraints

0 constraints

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**Special details**

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

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

| Atom | x     | y     | z       | Uiso* | Ueq  |
|------|-------|-------|---------|-------|------|
| O1   | 0.7597(5) | −0.1408(4) | 0.52918(12) | 0.1114(9) |
| O2   | 1.0599(5) | −0.2808(4) | 0.50875(13) | 0.1312(11) |
| N1   | 0.8270(3) | 0.0591(2) | 0.20408(9) | 0.0426(5) |
| N2   | 0.8376(3) | 0.2441(3) | 0.06365(10) | 0.0492(5) |
| N3   | 0.9029(6) | −0.1858(4) | 0.48992(13) | 0.0795(8) |
| C1   | 0.8503(4) | 0.0072(3) | 0.27523(12) | 0.0421(6) |
| C2   | 0.6848(5) | 0.0416(4) | 0.32264(13) | 0.0620(8) |
| H2   | 0.559385 | 0.107832 | 0.306884 | 0.074* |
| C3   | 0.7020(5) | −0.0200(4) | 0.39241(13) | 0.0660(8) |
| H3   | 0.58958 | 0.005008 | 0.423273 | 0.079* |
| C4   | 0.8844(5) | −0.1175(4) | 0.41582(13) | 0.0589(7) |
| C5   | 1.0511(5) | −0.1516(4) | 0.37142(15) | 0.0698(8) |
| H5   | 1.175889 | −0.217226 | 0.388096 | 0.084* |
| C6   | 1.0361(4) | −0.0894(4) | 0.30170(13) | 0.0606(8) |
| H6   | 1.152207 | −0.112351 | 0.271761 | 0.073* |
| C7   | 0.6682(4) | 0.2049(3) | 0.18122(12) | 0.0490(6) |
| H7A  | 0.721093 | 0.313511 | 0.191295 | 0.059* |
| H7B  | 0.530333 | 0.182601 | 0.207033 | 0.059* |
| C8   | 0.6287(4) | 0.2287(4) | 0.10502(12) | 0.0546(7) |
| H8A  | 0.553149 | 0.128385 | 0.095886 | 0.066* |
| H8B  | 0.535474 | 0.334375 | 0.091454 | 0.066* |
| C9   | 0.9774(4) | 0.0810(3) | 0.08466(12) | 0.0525(7) |
| H9A  | 1.113597 | 0.087916 | 0.057129 | 0.063* |
| H9B  | 0.902753 | −0.020822 | 0.076595 | 0.063* |
| C10  | 1.0256(4) | 0.0595(3) | 0.15971(12) | 0.0499(6) |
| H10A | 1.110342 | −0.050791 | 0.173238 | 0.06* |
| H10B | 1.11409 | 0.155146 | 0.166426 | 0.06* |
| O3   | 0.2656(3) | 0.7140(3) | 0.07107(9) | 0.0598(5) |
| O4   | 0.0053(3) | 0.5296(3) | 0.11199(9) | 0.0620(5) |
| C11  | 0.2728(4) | 0.5764(3) | 0.18855(12) | 0.0399(6) |
| C12  | 0.4646(4) | 0.6537(3) | 0.19936(13) | 0.0484(6) |
| H12  | 0.533917 | 0.726876 | 0.162881 | 0.058* |
| C13  | 0.5535(4) | 0.6230(3) | 0.26365(14) | 0.0575(7) |
| H13  | 0.68258 | 0.675862 | 0.269499 | 0.069* |
| C14  | 0.4567(5) | 0.5162(3) | 0.31955(14) | 0.0562(7) |
| C15  | 0.2645(4) | 0.4395(4) | 0.30874(14) | 0.0584(7) |
| H15  | 0.195058 | 0.366932 | 0.345395 | 0.07* |
| C16  | 0.1748(4) | 0.4689(3) | 0.24468(13) | 0.0496(6) |
| H16  | 0.045866 | 0.41565 | 0.238897 | 0.06* |

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|     |          |          |          |          |          |          |
|-----|----------|----------|----------|----------|----------|----------|
| C17 | 0.1749 (4)| 0.6080 (3)| 0.11893 (13)| 0.0437 (6)|          |
| C18 | 0.5550 (6)| 0.4855 (4)| 0.38973 (16)| 0.0863 (10)|        |
| H1A | 0.442848 | 0.502929 | 0.424033 | 0.129*    |
| H1B | 0.667715 | 0.567332 | 0.389742 | 0.129*    |
| H1C | 0.617002 | 0.366684 | 0.400046 | 0.129*    |
| O5  | 0.7006 (3)| 0.7136 (5)| 0.02422 (13)| 0.1211 (12)|        |
| H21 | 0.903 (6) | 0.338 (4) | 0.073 (2) | 0.145*    |
| H22 | 0.807 (6) | 0.256 (5) | 0.0183 (11)| 0.145*    |
| H1W | 0.792 (5) | 0.667 (5) | 0.0534 (17)| 0.145*    |
| H2W | 0.576 (4) | 0.720 (6) | 0.045 (2) | 0.145*    |

**Atomic displacement parameters (Å²)**

|     | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
| O1  | 0.145 (2) | 0.132 (2) | 0.0477 (14) | 0.0055 (18) | 0.0100 (15) | 0.0001 (14) |
| O2  | 0.153 (2) | 0.155 (3) | 0.0702 (17) | 0.044 (2) | −0.0390 (17) | 0.0148 (17) |
| N1  | 0.0427 (11) | 0.0478 (12) | 0.0358 (11) | 0.0059 (9) | −0.0018 (9) | 0.0064 (9) |
| N2  | 0.0540 (13) | 0.0562 (14) | 0.0357 (11) | 0.0002 (11) | −0.0042 (10) | 0.0041 (10) |
| N3  | 0.111 (2) | 0.078 (2) | 0.0469 (17) | −0.0053 (17) | 0.0089 (16) | 0.0005 (14) |
| C1  | 0.0675 (17) | 0.0685 (19) | 0.0442 (16) | 0.0202 (15) | 0.0004 (13) | 0.0008 (14) |
| C2  | 0.083 (2) | 0.072 (2) | 0.0394 (16) | 0.0130 (17) | 0.0050 (14) | 0.0057 (14) |
| C4  | 0.085 (2) | 0.0556 (17) | 0.0352 (15) | 0.0002 (16) | −0.0013 (14) | 0.0044 (13) |
| C5  | 0.0719 (19) | 0.083 (2) | 0.0515 (19) | 0.0176 (17) | −0.0020 (15) | 0.0060 (16) |
| C6  | 0.0564 (16) | 0.078 (2) | 0.0448 (16) | 0.0167 (15) | −0.0066 (13) | 0.0092 (14) |
| C7  | 0.0428 (14) | 0.0616 (17) | 0.0401 (14) | 0.0080 (12) | −0.0034 (11) | 0.0050 (12) |
| C8  | 0.0441 (14) | 0.0706 (18) | 0.0468 (16) | 0.0043 (13) | −0.0071 (12) | 0.0052 (13) |
| C9  | 0.0597 (16) | 0.0579 (17) | 0.0385 (15) | 0.0061 (13) | 0.0028 (12) | −0.0086 (12) |
| C10 | 0.0499 (15) | 0.0558 (16) | 0.0417 (15) | 0.0138 (12) | −0.0088 (12) | 0.0080 (12) |
| O3  | 0.0574 (11) | 0.0779 (13) | 0.0404 (10) | −0.0028 (10) | −0.0074 (8) | 0.0006 (9) |
| O4  | 0.0577 (11) | 0.0758 (13) | 0.0557 (12) | −0.0102 (10) | −0.0167 (9) | −0.0143 (10) |
| C11 | 0.0404 (13) | 0.0387 (13) | 0.0413 (14) | 0.0068 (11) | −0.0074 (11) | −0.0013 (11) |
| C12 | 0.0513 (15) | 0.0449 (15) | 0.0490 (16) | −0.0006 (12) | −0.0065 (12) | −0.0072 (12) |
| C13 | 0.0547 (16) | 0.0533 (17) | 0.0679 (19) | 0.0004 (13) | −0.0224 (14) | −0.0158 (15) |
| C14 | 0.0707 (18) | 0.0497 (16) | 0.0498 (17) | 0.0066 (14) | −0.0233 (14) | −0.0103 (13) |
| C15 | 0.0706 (18) | 0.0570 (17) | 0.0453 (16) | −0.0042 (14) | −0.0099 (13) | −0.0007 (13) |
| C16 | 0.0488 (15) | 0.0518 (16) | 0.0485 (16) | −0.0039 (13) | −0.0089 (12) | −0.0074 (13) |
| C17 | 0.0427 (14) | 0.0473 (15) | 0.0420 (15) | 0.0071 (12) | −0.0042 (12) | −0.0121 (12) |
| C18 | 0.114 (3) | 0.079 (2) | 0.068 (2) | −0.003 (2) | −0.0467 (19) | −0.0066 (17) |
| O5  | 0.0602 (14) | 0.210 (3) | 0.0697 (16) | −0.0101 (18) | −0.0093 (12) | 0.0407 (18) |

**Geometric parameters (Å, °)**

|     | O1—N3  | 1.216 (3) | C9—C10 | 1.500 (3) |
|-----|--------|-----------|--------|-----------|
| O2  | 1.204 (3) | C9—H9A  | 0.97   |
| N1  | 1.399 (3) | C9—H9B  | 0.97   |
| N1  | 1.460 (3) | C10—H10A| 0.97   |
| N1  | 1.463 (3) | C10—H10B| 0.97   |

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\begin{tabular}{lll}
N2—C8 & 1.480 (3) & O3—O3 & 0.000 (5) \\
N2—C9 & 1.483 (3) & O3—C17 & 1.259 (3) \\
N2—H21 & 0.892 (19) & O4—C17 & 1.254 (3) \\
N2—H22 & 0.908 (19) & C11—C12 & 1.387 (3) \\
N3—C4 & 1.468 (3) & C11—C16 & 1.389 (3) \\
C1—C2 & 1.390 (3) & C11—C17 & 1.498 (3) \\
C1—C6 & 1.391 (3) & C12—C13 & 1.379 (3) \\
C2—C3 & 1.378 (4) & C12—H12 & 0.93 \\
C2—H2 & 0.93 & C13—C14 & 1.380 (4) \\
C3—C4 & 1.360 (4) & C13—H13 & 0.93 \\
C3—H3 & 0.93 & C14—C15 & 1.387 (4) \\
C4—C5 & 1.356 (4) & C14—C18 & 1.509 (4) \\
C5—C6 & 1.377 (4) & C15—C16 & 1.377 (3) \\
C5—H5 & 0.93 & C15—H15 & 0.93 \\
C6—C1 & 1.390 (3) & C16—H16 & 0.93 \\
C7—C8 & 1.509 (3) & C18—H18A & 0.96 \\
C7—H7A & 0.97 & C18—H18B & 0.96 \\
C7—H7B & 0.97 & C18—H18C & 0.96 \\
C8—H8A & 0.97 & O5—H1W & 0.843 (19) \\
C8—H8B & 0.97 & O5—H2W & 0.854 (19) \\

& & & \\
C1—N1—C10 & 117.39 (18) & N2—C9—H9A & 109.6 \\
C1—N1—C7 & 117.37 (18) & C10—C9—H9A & 109.6 \\
C10—N1—C7 & 113.94 (18) & N2—C9—H9B & 109.6 \\
C8—N2—C9 & 108.7 (2) & C10—C9—H9B & 109.6 \\
C8—N2—H21 & 107 (3) & H9A—C9—H9B & 108.2 \\
C9—N2—H21 & 110 (3) & N1—C10—C9 & 112.7 (2) \\
C9—N2—H22 & 109 (3) & N1—C10—H10A & 109.1 \\
C9—N2—H22 & 110 (3) & C9—C10—H10A & 109.1 \\
H21—N2—H22 & 112 (4) & N1—C10—H10B & 109.1 \\
O2—N3—O1 & 123.5 (3) & C9—C10—H10B & 109.1 \\
O2—N3—C4 & 118.5 (3) & H10A—C10—H10B & 107.8 \\
O1—N3—C4 & 117.9 (3) & O3—O3—C17 & 0 (10) \\
C2—C1—C6 & 116.8 (2) & C12—C11—C16 & 117.5 (2) \\
C2—C1—N1 & 121.7 (2) & C12—C11—C17 & 121.2 (2) \\
C6—C1—N1 & 121.4 (2) & C16—C11—C17 & 121.2 (2) \\
C3—C2—C1 & 121.6 (3) & C13—C12—C11 & 120.7 (2) \\
C3—C2—H2 & 119.2 & C13—C12—H12 & 119.7 \\
C1—C2—H2 & 119.2 & C11—C12—H12 & 119.7 \\
C4—C3—C2 & 119.6 (3) & C12—C13—C14 & 122.0 (2) \\
C4—C3—H3 & 120.2 & C12—C13—H13 & 119 \\
C2—C3—H3 & 120.2 & C14—C13—H13 & 119 \\
C5—C4—C3 & 120.7 (2) & C13—C14—C15 & 117.3 (2) \\
C5—C4—N3 & 119.3 (3) & C13—C14—C18 & 121.3 (3) \\
C3—C4—N3 & 120.0 (3) & C15—C14—C18 & 121.4 (3) \\
C4—C5—C6 & 120.1 (3) & C16—C15—C14 & 121.2 (3) \\
C4—C5—H5 & 119.9 & C16—C15—H15 & 119.4 \\
C6—C5—H5 & 119.9 & C14—C15—H15 & 119.4 \\
\end{tabular}
C5—C6—C1 121.2 (2) C15—C16—C11 121.3 (2)
C5—C6—H6 119.4 C15—C16—H16 119.3
C1—C6—H6 119.4 C11—C16—H16 119.3
N1—C7—C8 112.6 (2) O4—C17—O3 123.8 (2)
N1—C7—H7A 109.1 O4—C17—O3 123.8 (2)
C8—C7—H7A 109.1 O3—C17—O3 0.0 (2)
N1—C7—H7B 109.1 O4—C17—C11 118.1 (2)
C8—C7—H7B 109.1 O3—C17—C11 118.0 (2)
H7A—C7—H7B 107.8 O3—C17—C11 118.0 (2)
N2—C8—C7 111.1 (2) C14—C18—H18A 109.5
N2—C8—H8A 109.4 C14—C18—H18B 109.5
C7—C8—H8A 109.4 H18A—C18—H18B 109.5
N2—C8—H8B 109.4 C14—C18—H18C 109.5
C7—C8—H8B 109.4 H18A—C18—H18C 109.5
H8A—C8—H8B 108 H18B—C18—H18C 109.5
N2—C9—C10 110.1 (2) C14—C18—H18A 109.5
C10—N1—C1—C2 164.4 (2) C1—N1—C10—C9 168.3 (2)
C7—N1—C1—C2 22.9 (3) C1—N1—C10—C9 168.3 (2)
C10—N1—C1—C6 −18.9 (3) C7—N1—C10—C9 −48.9 (3)
C7—N1—C1—C6 −160.4 (2) C10—N1—C10—C9 55.7 (3)
C6—C1—C2—C3 −1.2 (4) C1—C10—C9—C10 −168.3 (2)
N1—C1—C2—C3 175.6 (3) C1—C10—C9—C10 −168.3 (2)
C1—C2—C3—C4 −0.3 (5) C12—C13—C14—C15 0.1 (4)
C2—C3—C4—C5 1.3 (5) C12—C13—C14—C15 0.1 (4)
C2—C3—C4—N3 −179.1 (3) C12—C13—C14—C18 −179.4 (3)
O2—N3—C4—C5 −5.0 (4) C13—C14—C15—C16 0.1 (4)
O2—N3—C4—C3 175.5 (3) C13—C14—C15—C16 0.1 (4)
O1—N3—C4—C5 173.8 (3) C14—C15—C16—C15 0.1 (4)
O2—N3—C4—C3 175.5 (3) C14—C15—C16—C11 −0.1 (4)
O1—N3—C4—C5 173.8 (3) C12—C11—C16—C15 −0.1 (4)
O1—N3—C4—C3 175.5 (3) C12—C11—C16—C15 −0.1 (4)
C3—C4—C5—C6 −0.8 (5) C17—C11—C16—C15 179.9 (2)
N3—C4—C5—C6 179.6 (3) C17—C11—C16—C15 179.9 (2)
N3—C4—C5—C6 179.6 (3) O3—O3—C17—O4 0.0 (14)
C4—C5—C6—C1 −0.8 (5) O3—O3—C17—O4 0.0 (14)
C2—C1—C6—C5 1.8 (4) C12—C11—C16—C15 −0.1 (4)
N1—C1—C6—C5 −175.0 (3) C12—C11—C16—C15 −0.1 (4)
C1—N1—C7—C8 −170.1 (2) C12—C11—C17—O3 −3.5 (3)
C10—N1—C7—C8 47.0 (3) C12—C11—C17—O3 −3.5 (3)
C9—N2—C8—C7 59.5 (3) C12—C11—C17—O3 −3.5 (3)
N1—C7—C8—N2 −52.7 (3) C16—C11—C17—O3 176.4 (2)

Hydrogen-bond geometry (Å, °)
Cg3 is the centroids of the C11–C16 ring.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|------|---------|
| N2—H21···O4i | 0.89 (2) | 1.93 (2) | 2.811 (3) | 167 (4) |
| N2—H22···O3ii | 0.91 (2) | 1.81 (2) | 2.717 (3) | 177 (4) |
| C3—H3···O1iii | 0.93 | 2.54 | 3.427 (4) | 161 |
| C9—H9a···O5iv | 0.97 | 2.31 | 3.113 (3) | 140 |
sup-20

4-(4-Nitrophenyl)piperazin-1-ium 4-methoxybenzoate hemihydrate (V)

Crystal data

2C\textsubscript{10}H\textsubscript{14}N\textsubscript{3}O\textsubscript{2}\textsuperscript{+}·2C\textsubscript{8}H\textsubscript{7}O\textsubscript{3}\textsuperscript{−}·H\textsubscript{2}O

\( M_r = 736.77 \)

Monoclinic, \( P2_1/c \)

Hall symbol: -P 2ybc

\( a = 15.808 \) (1) Å

\( b = 7.5198 \) (7) Å

\( c = 31.020 \) (2) Å

\( \beta = 92.561 \) (7)°

\( V = 3683.8 \) (5) Å\(^3\)

\( Z = 4 \)

\( F(000) = 1560 \)

\( D_x = 1.328 \) Mg m\(^{-3}\)

\( \lambda = 0.71073 \) Å

Cell parameters from 2899 reflections

\( \theta = 2.6–25.3° \)

\( \mu = 0.1 \) mm\(^{-1}\)

\( T = 293 \) K

Prism, orange

Data collection

Oxford Diffraction Xcalibur diffractometer

ω scans

Absorption correction: multi-scan

(CrysAlis RED; Oxford Diffraction, 2009)

\( h = -19→18 \)

\( k = -9→8 \)

\( l = -37→33 \)

15326 measured reflections

6718 independent reflections

2602 reflections with \( I > 2\sigma(I) \)

\( R\text{int} = 0.066 \)

\( \theta\text{max} = 25.3° \)

\( \theta\text{min} = 2.6° \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.074 \)

\( wR(F^2) = 0.169 \)

\( S = 1.00 \)

6715 reflections

507 parameters

45 restraints

0 constraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

\( w = 1/\left[\sigma^2(F_0^2) + (0.0554P)^2 + 0.9198P\right] \)

where \( P = (F_0^2 + 2F_c^2)/3 \)

\( \Delta\sigma/\sigma < 0.001 \)

\( \Delta\rho_{\text{max}} = 0.27 \) e Å\(^{-3}\)

\( \Delta\rho_{\text{min}} = -0.18 \) e Å\(^{-3}\)

Extinction correction: SHELXL2018/3

(Sheldrick 2015b),

\( F_c^2 = kF_c[1+0.001xF_c^2/\sin(2\theta)]^{1/4} \)

Extinction coefficient: 0.0029 (4)

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\(^2\))

\[ \begin{array}{cccccc}
 & x & y & z & U_{eq} & \text{Occ. (<1)} \\
C1 & 0.2115 (2) & 0.2769 (5) & 0.15386 (13) & 0.0456 (11) \\
C2 & 0.2042 (3) & 0.2439 (6) & 0.19789 (14) & 0.0687 (14) \\
H2 & 0.151236 & 0.21805 & 0.208209 & 0.082* \\
\end{array} \]
| Atom | X      | Y      | Z      | U11 | U22 | U33 | U12 | U13 | U23 |
|------|--------|--------|--------|-----|-----|-----|-----|-----|-----|
| C3   | 0.2734 (3) | 0.2487 (7) | 0.22634 (14) | 0.0860 (16) |
| H3   | 0.26712 | 0.22698 | 0.255532 | 0.103* |
| C4   | 0.3512 (3) | 0.2855 (7) | 0.21153 (15) | 0.0702 (14) |
| C5   | 0.3613 (3) | 0.3157 (6) | 0.16906 (15) | 0.0722 (14) |
| H5   | 0.414916 | 0.339042 | 0.159279 | 0.087* |
| C6   | 0.2925 (3) | 0.3119 (6) | 0.14031 (13) | 0.0598 (12) |
| H6   | 0.300335 | 0.333225 | 0.111231 | 0.072* |
| C7   | 0.1555 (2) | 0.2450 (6) | 0.07998 (12) | 0.0599 (12) |
| H7A  | 0.166523 | 0.119002 | 0.076636 | 0.072* |
| H7B  | 0.205192 | 0.309359 | 0.07138 | 0.072* |
| C8   | 0.0813 (3) | 0.2965 (6) | 0.05086 (13) | 0.0690 (13) |
| H8A  | 0.075136 | 0.42483 | 0.050937 | 0.083* |
| H8B  | 0.09152 | 0.259489 | 0.021595 | 0.083* |
| C9   | -0.0117 (3) | 0.2610 (6) | 0.10976 (14) | 0.0669 (13) |
| H9A  | -0.062504 | 0.202151 | 0.118906 | 0.08* |
| H9B  | -0.020149 | 0.38837 | 0.112112 | 0.08* |
| C10  | 0.0624 (2) | 0.2059 (6) | 0.13852 (12) | 0.0631 (13) |
| H10A | 0.052793 | 0.242915 | 0.16785 | 0.076* |
| H10B | 0.066876 | 0.077208 | 0.138331 | 0.076* |
| C11  | 0.9721 (3) | 0.2971 (6) | 0.30361 (13) | 0.0510 (11) |
| C12  | 0.8980 (3) | 0.2023 (6) | 0.30443 (12) | 0.0563 (12) |
| H12  | 0.888658 | 0.13067 | 0.328178 | 0.068* |
| C13  | 0.8365 (3) | 0.2095 (6) | 0.27110 (14) | 0.0632 (13) |
| H13  | 0.78756 | 0.14142 | 0.272281 | 0.076* |
| C14  | 0.8487 (3) | 0.3182 (6) | 0.23643 (14) | 0.0628 (12) |
| C15  | 0.9229 (3) | 0.4129 (6) | 0.23467 (13) | 0.0649 (13) |
| H15  | 0.93208 | 0.484494 | 0.210883 | 0.078* |
| C16  | 0.9839 (3) | 0.4028 (6) | 0.26775 (14) | 0.0626 (13) |
| H16  | 1.033592 | 0.46798 | 0.26601 | 0.075* |
| C17  | 1.0355 (3) | 0.2887 (7) | 0.34129 (16) | 0.0608 (13) |
| C18  | 0.7146 (3) | 0.2457 (8) | 0.20218 (17) | 0.118 (2) |
| H18C | 0.681472 | 0.273815 | 0.176387 | 0.178* |
| H18B | 0.725759 | 0.120242 | 0.20308 | 0.178* |
| H18A | 0.684002 | 0.279268 | 0.226948 | 0.178* |
| C19  | 0.3816 (3) | 0.5044 (6) | -0.09170 (13) | 0.0503 (11) |
| C20  | 0.3778 (3) | 0.6432 (6) | -0.06180 (13) | 0.0582 (12) |
| H20  | 0.326082 | 0.697741 | -0.057457 | 0.07* |
| C21  | 0.4478 (3) | 0.6998 (6) | -0.03904 (13) | 0.0603 (12) |
| H21  | 0.443054 | 0.790435 | -0.018877 | 0.072* |
| C22  | 0.5251 (2) | 0.6260 (6) | -0.04523 (13) | 0.0499 (11) |
| C23  | 0.5330 (3) | 0.4942 (6) | -0.07542 (14) | 0.0610 (12) |
| H23  | 0.58581 | 0.445412 | -0.080183 | 0.073* |
| C24  | 0.4629 (3) | 0.4354 (6) | -0.09836 (13) | 0.0623 (13) |
| H24  | 0.468943 | 0.347143 | -0.119 | 0.075* |
| C25  | 0.3099 (3) | 0.2720 (7) | -0.13618 (14) | 0.0722 (14) |
| H25A | 0.36547 | 0.248859 | -0.147048 | 0.087* |
| H25B | 0.269401 | 0.27516 | -0.160582 | 0.087* |
| C26  | 0.2867 (3) | 0.1245 (6) | -0.10589 (14) | 0.0694 (13) |
|   | x    | y    | z    | Ueq  |
|---|------|------|------|------|
| H26A | 0.284623 | 0.011999 | -0.121195 | 0.083* |
| H26B | 0.329107 | 0.115475 | -0.082393 | 0.083* |
| C27  | 0.1998 (2) | 0.3414 (6) | -0.06853 (12) | 0.0579 (12) |
| H27A | 0.237409 | 0.345068 | -0.042968 | 0.07* |
| H27B | 0.142682 | 0.365292 | -0.059877 | 0.07* |
| C28  | 0.2258 (2) | 0.4799 (6) | -0.10009 (13) | 0.0583 (12) |
| H28A | 0.186099 | 0.480675 | -0.124849 | 0.07* |
| H28B | 0.224263 | 0.596261 | -0.086644 | 0.07* |
| C29  | 0.2315 (2) | 0.8165 (5) | 0.03520 (12) | 0.0442 (10) |
| C30  | 0.3063 (2) | 0.9094 (5) | 0.033221 (13) | 0.0517 (11) |
| H30  | 0.319956 | 0.957242 | 0.005761 | 0.062* |
| C31  | 0.3609 (2) | 0.9330 (6) | 0.06743 (15) | 0.0597 (12) |
| H31  | 0.411473 | 0.994162 | 0.064463 | 0.072* |
| C32  | 0.3412 (3) | 0.8662 (6) | 0.10717 (15) | 0.0570 (12) |
| C33  | 0.2661 (3) | 0.7752 (6) | 0.11108 (13) | 0.0590 (12) |
| H33  | 0.251489 | 0.731519 | 0.137782 | 0.071* |
| C34  | 0.2130 (2) | 0.7495 (5) | 0.07521 (13) | 0.0524 (11) |
| H34  | 0.163238 | 0.685277 | 0.07981 | 0.063* |
| C35  | 0.1734 (3) | 0.7879 (6) | -0.00372 (14) | 0.0459 (11) |
| C36  | 0.3801 (3) | 0.8360 (7) | 0.18157 (17) | 0.1098 (19) |
| H36C | 0.42611 | 0.863024 | 0.201777 | 0.165* |
| H36B | 0.329805 | 0.895356 | 0.190161 | 0.165* |
| H36A | 0.370656 | 0.709953 | 0.181018 | 0.165* |
| N1   | 0.14171 (19) | 0.2823 (4) | 0.12508 (10) | 0.0475 (9) |
| N2   | 0.0026 (2) | 0.2144 (5) | 0.06465 (13) | 0.0581 (10) |
| N3   | 0.4265 (6) | 0.2464 (13) | 0.2410 (3) | 0.075 (2) 0.519 (6) |
| N3'  | 0.4213 (6) | 0.3345 (15) | 0.2420 (3) | 0.075 (2) 0.481 (6) |
| N4   | 0.3106 (2) | 0.4437 (5) | -0.11425 (10) | 0.0583 (10) |
| N5   | 0.2034 (2) | 0.1639 (5) | -0.08869 (12) | 0.0612 (10) |
| N6   | 0.5983 (2) | 0.6796 (6) | -0.01867 (13) | 0.0650 (11) |
| O1   | 0.4960 (7) | 0.2571 (14) | 0.2266 (4) | 0.099 (2) 0.519 (6) |
| O1'  | 0.4904 (8) | 0.3633 (14) | 0.2283 (4) | 0.099 (2) 0.481 (6) |
| O2   | 0.4177 (6) | 0.2116 (13) | 0.2788 (3) | 0.097 (2) 0.519 (6) |
| O2'  | 0.4086 (6) | 0.3408 (15) | 0.2797 (3) | 0.097 (2) 0.481 (6) |
| O3   | 1.1003 (2) | 0.3818 (4) | 0.33942 (9) | 0.0826 (10) |
| O4   | 1.0196 (2) | 0.1889 (4) | 0.37194 (10) | 0.0789 (10) |
| O5   | 0.7922 (2) | 0.3398 (5) | 0.20234 (9) | 0.0895 (11) |
| O6   | 0.58881 (19) | 0.7838 (5) | 0.01114 (11) | 0.0827 (11) |
| O7   | 0.66853 (19) | 0.6203 (5) | -0.02668 (10) | 0.0881 (11) |
| O8   | 0.10807 (17) | 0.6951 (4) | 0.00037 (8) | 0.0590 (8) |
| O9   | 0.19207 (16) | 0.8596 (4) | -0.03853 (9) | 0.0593 (8) |
| O10  | 0.40056 (18) | 0.8950 (4) | 0.13979 (10) | 0.0790 (10) |
| O11  | 1.00751 (19) | 0.3517 (4) | 0.44766 (10) | 0.0649 (9) |
| H21N | -0.0388 (19) | 0.252 (5) | 0.0468 (11) | 0.078* |
| H22N | 0.007 (3) | 0.099 (3) | 0.0609 (12) | 0.078* |
| H51N | 0.190 (2) | 0.077 (4) | -0.0717 (11) | 0.078* |
| H52N | 0.164 (2) | 0.153 (6) | -0.1110 (9) | 0.078* |
| H11O | 1.010 (3) | 0.296 (5) | 0.4244 (9) | 0.078* |
### Atomic displacement parameters (Å²)

|    | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|----|-----|-----|-----|-----|-----|-----|
| C1 | 0.043 (3) | 0.040 (3) | 0.054 (3) | 0.002 (2) | 0.000 (2) | −0.002 (2) |
| C2 | 0.056 (3) | 0.100 (4) | 0.051 (3) | −0.008 (3) | 0.007 (3) | 0.001 (3) |
| C3 | 0.073 (3) | 0.145 (5) | 0.039 (3) | −0.011 (4) | −0.005 (3) | 0.004 (3) |
| C4 | 0.052 (3) | 0.108 (4) | 0.050 (3) | −0.009 (3) | −0.013 (2) | 0.001 (3) |
| C5 | 0.052 (3) | 0.107 (4) | 0.057 (3) | −0.017 (3) | −0.001 (3) | 0.005 (3) |
| C6 | 0.049 (3) | 0.082 (4) | 0.048 (3) | −0.005 (3) | −0.006 (2) | 0.009 (2) |
| C7 | 0.050 (3) | 0.082 (3) | 0.047 (3) | −0.009 (3) | −0.002 (2) | 0.002 (2) |
| C8 | 0.064 (3) | 0.077 (3) | 0.064 (3) | −0.023 (3) | −0.018 (2) | 0.017 (3) |
| C9 | 0.052 (3) | 0.076 (4) | 0.073 (4) | −0.003 (3) | −0.003 (2) | −0.015 (3) |
| C10 | 0.052 (3) | 0.089 (4) | 0.048 (3) | −0.013 (3) | 0.000 (2) | −0.003 (2) |
| C11 | 0.055 (3) | 0.049 (3) | 0.049 (3) | 0.004 (3) | 0.004 (2) | 0.002 (2) |
| C12 | 0.071 (3) | 0.059 (3) | 0.039 (3) | 0.007 (3) | 0.006 (2) | 0.008 (2) |
| C13 | 0.058 (3) | 0.074 (4) | 0.058 (3) | −0.010 (3) | 0.000 (2) | 0.010 (3) |
| C14 | 0.064 (3) | 0.071 (4) | 0.051 (3) | 0.007 (3) | −0.012 (3) | 0.004 (3) |
| C15 | 0.068 (3) | 0.070 (4) | 0.056 (3) | −0.009 (3) | −0.004 (3) | 0.018 (2) |
| C16 | 0.058 (3) | 0.064 (3) | 0.065 (3) | −0.009 (3) | 0.000 (3) | 0.009 (3) |
| C17 | 0.063 (3) | 0.057 (4) | 0.062 (3) | 0.014 (3) | −0.010 (3) | −0.011 (3) |
| C18 | 0.103 (5) | 0.148 (6) | 0.100 (4) | −0.040 (4) | −0.047 (3) | 0.023 (4) |
| C19 | 0.044 (3) | 0.065 (3) | 0.042 (3) | −0.002 (3) | 0.007 (2) | 0.009 (2) |
| C20 | 0.038 (3) | 0.071 (3) | 0.066 (3) | 0.003 (3) | 0.002 (2) | −0.004 (3) |
| C21 | 0.046 (3) | 0.071 (3) | 0.064 (3) | −0.002 (3) | 0.008 (2) | −0.009 (2) |
| C22 | 0.035 (3) | 0.064 (3) | 0.051 (3) | −0.007 (2) | 0.002 (2) | 0.009 (2) |
| C23 | 0.038 (3) | 0.068 (3) | 0.077 (3) | 0.004 (3) | 0.012 (2) | 0.005 (3) |
| C24 | 0.050 (3) | 0.067 (3) | 0.071 (3) | −0.003 (3) | 0.015 (3) | −0.011 (2) |
| C25 | 0.063 (3) | 0.100 (4) | 0.054 (3) | −0.009 (3) | 0.006 (2) | −0.023 (3) |
| C26 | 0.069 (3) | 0.068 (4) | 0.070 (3) | 0.003 (3) | −0.008 (3) | −0.015 (3) |
| C27 | 0.049 (3) | 0.070 (3) | 0.054 (3) | −0.004 (3) | −0.003 (2) | −0.012 (3) |
| C28 | 0.042 (3) | 0.063 (3) | 0.069 (3) | −0.006 (2) | −0.008 (2) | 0.001 (3) |
| C29 | 0.043 (2) | 0.045 (3) | 0.045 (3) | 0.005 (2) | 0.004 (2) | −0.003 (2) |
| C30 | 0.044 (3) | 0.063 (3) | 0.049 (3) | 0.006 (2) | 0.004 (2) | 0.007 (2) |
| C31 | 0.044 (3) | 0.071 (3) | 0.064 (3) | −0.005 (2) | −0.005 (2) | −0.001 (3) |
| C32 | 0.053 (3) | 0.064 (3) | 0.053 (3) | 0.012 (3) | −0.013 (3) | −0.008 (3) |
| C33 | 0.062 (3) | 0.067 (3) | 0.048 (3) | −0.001 (3) | −0.005 (2) | 0.005 (2) |
| C34 | 0.052 (3) | 0.055 (3) | 0.050 (3) | −0.004 (2) | −0.002 (2) | 0.006 (2) |
| C35 | 0.048 (3) | 0.040 (3) | 0.050 (3) | 0.009 (2) | −0.005 (2) | −0.002 (2) |
| C36 | 0.117 (5) | 0.125 (5) | 0.083 (4) | 0.008 (4) | −0.035 (3) | −0.004 (4) |
| N1 | 0.041 (2) | 0.055 (2) | 0.046 (2) | −0.0042 (18) | −0.0010 (17) | −0.0018 (17) |
| N2 | 0.055 (3) | 0.047 (2) | 0.070 (3) | −0.005 (2) | −0.0165 (19) | 0.004 (2) |
| N3 | 0.072 (3) | 0.081 (4) | 0.070 (3) | −0.002 (3) | −0.004 (2) | −0.001 (3) |
| N3′ | 0.072 (3) | 0.081 (4) | 0.070 (3) | −0.002 (3) | −0.004 (2) | −0.001 (3) |
| N4 | 0.051 (2) | 0.072 (3) | 0.052 (2) | −0.005 (2) | 0.0048 (19) | −0.002 (2) |
| N5 | 0.059 (3) | 0.063 (3) | 0.061 (3) | −0.012 (2) | −0.009 (2) | 0.010 (2) |
| N6 | 0.048 (3) | 0.084 (3) | 0.064 (3) | −0.012 (3) | 0.003 (2) | 0.021 (2) |
### Geometric parameters (Å, °)

| Bond or Angle | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| C1—N1         | 1.388 (4)  |           |
| C1—C6         | 1.391 (5)  |           |
| C1—C2         | 1.398 (5)  |           |
| C2—C3         | 1.375 (6)  |           |
| C2—H2         | 0.93       |           |
| C3—C4         | 1.359 (6)  |           |
| C3—H3         | 0.93       |           |
| C4—C5         | 1.354 (5)  |           |
| C4—N3’        | 1.471 (10) |           |
| C4—N3         | 1.499 (9)  |           |
| C5—C6         | 1.375 (5)  |           |
| C5—H5         | 0.93       |           |
| C6—H6         | 0.93       |           |
| C7—N1         | 1.453 (4)  |           |
| C7—C8         | 1.499 (5)  |           |
| C7—H7A        | 0.97       |           |
| C7—H7B        | 0.97       |           |
| C8—N2         | 1.469 (5)  |           |
| C8—H8A        | 0.97       |           |
| C8—H8B        | 0.97       |           |
| C9—N2         | 1.470 (5)  |           |
| C9—C10        | 1.499 (5)  |           |
| C9—H9A        | 0.97       |           |
| C9—H9B        | 0.97       |           |
| C10—N1        | 1.457 (4)  |           |
| C10—H10A      | 0.97       |           |
| C10—H10B      | 0.97       |           |
| C11—C12       | 1.372 (5)  |           |
| C11—C16       | 1.387 (5)  |           |
| C11—C17       | 1.506 (6)  |           |
| C12—C13       | 1.388 (5)  |           |
| C12—H12       | 0.93       |           |

**Supporting Information**

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| Bond                | Distance (Å) | Bond                | Distance (Å) |
|---------------------|--------------|---------------------|--------------|
| C13—C14             | 1.371 (5)    | C35—O9              | 1.254 (4)    |
| C13—H13             | 0.93         | C35—O8              | 1.258 (4)    |
| C14—O5              | 1.363 (5)    | C36—O10             | 1.421 (5)    |
| C14—C15             | 1.375 (5)    | C36—H36C            | 0.96         |
| C15—C16             | 1.378 (5)    | C36—H36B            | 0.96         |
| C15—H15             | 0.93         | C36—H36A            | 0.96         |
| C16—H16             | 0.93         | N2—H21N             | 0.884 (18)   |
| C17—O3              | 1.245 (5)    | N2—H22N             | 0.882 (18)   |
| C17—O4              | 1.246 (5)    | N3—O1               | 1.208 (9)    |
| C18—O5              | 1.416 (5)    | N3—O2               | 1.213 (9)    |
| C18—H18C            | 0.96         | N3’—O2’             | 1.196 (9)    |
| C18—H18B            | 0.96         | N3’—O1’             | 1.210 (10)   |
| C18—H18A            | 0.96         | N5—H51N             | 0.872 (18)   |
| C19—N4              | 1.374 (4)    | N5—H52N             | 0.910 (18)   |
| C19—C20             | 1.399 (5)    | N6—O6               | 1.228 (4)    |
| C19—C24             | 1.410 (5)    | N6—O7               | 1.232 (4)    |
| C20—C21             | 1.354 (5)    | O11—H11O            | 0.836 (18)   |
| C20—H20             | 0.93         | O11—H12O            | 0.838 (18)   |
| C21—C22             | 1.363 (5)    |                     |              |
|                     |              | N1—C1—C6            | 121.1 (4)    |
|                     |              | N1—C1—C2            | 122.4 (4)    |
|                     |              | C6—C1—C2            | 116.5 (4)    |
|                     |              | C3—C2—C1            | 121.6 (4)    |
|                     |              | C3—C2—H2            | 119.2        |
|                     |              | C1—C2—H2            | 119.2        |
|                     |              | C4—C3—C2            | 119.6 (4)    |
|                     |              | C4—C3—H3            | 120.2        |
|                     |              | C2—C3—H3            | 120.2        |
|                     |              | C5—C4—C3            | 120.7 (4)    |
|                     |              | C5—C4—N3’           | 117.8 (6)    |
|                     |              | C3—C4—N3’           | 120.0 (6)    |
|                     |              | C5—C4—N3            | 120.2 (6)    |
|                     |              | C3—C4—N3            | 117.3 (6)    |
|                     |              | C4—C5—C6            | 120.2 (4)    |
|                     |              | C4—C5—H5            | 119.9        |
|                     |              | C6—C5—H5            | 119.9        |
|                     |              | C5—C6—C1            | 121.3 (4)    |
|                     |              | C5—C6—H6            | 119.3        |
|                     |              | C1—C6—H6            | 119.3        |
|                     |              | N1—C7—C8            | 112.5 (3)    |
|                     |              | N1—C7—H7A           | 109.1        |
|                     |              | C8—C7—H7A           | 109.1        |
|                     |              | N1—C7—H7B           | 109.1        |
|                     |              | C8—C7—H7B           | 109.1        |
|                     |              | H7A—C7—H7B          | 107.8        |
|                     |              | N2—C8—C7            | 111.5 (3)    |
|                     |              | N2—C8—H8A           | 109.3        |
C7—C8—H8A 109.3  C30—C29—C34 117.5 (4)
N2—C8—H8B 109.3  C30—C29—C35 120.9 (4)
C7—C8—H8B 109.3  C34—C29—C35 121.6 (4)
H8A—C8—H8B 108  C31—C30—C29 121.5 (4)
N2—C9—C10 110.5 (3)  C31—C30—H30 119.3
N2—C9—H9A 109.5  C29—C30—H30 119.3
C10—C9—H9A 109.5  C30—C31—C32 120.3 (4)
N2—C9—H9B 109.5  C30—C31—H31 119.8
C10—C9—H9B 109.5  C32—C31—H31 119.8
H9A—C9—H9B 108.1  O10—C32—C31 115.4 (4)
N1—C10—C9 110.5 (3)  O10—C32—C33 125.3 (4)
N1—C10—H10A 109.1  C31—C32—C33 119.2 (4)
C9—C10—H10A 109.1  C30—C31—C32 119.6 (4)
N1—C10—H10B 109.1  C31—C30—C29 121.5 (4)
C9—C10—H10B 109.1  C32—C33—C34 121.8 (4)
H10A—C10—H10B 107.9  C33—C34—C29 120.9 (4)
C12—C11—C16 117.2 (4)  C34—C33—C35 119.1
C12—C11—C17 120.2 (4)  C33—C34—H34 119.1
C16—C11—C17 122.5 (4)  O9—C35—O8 123.4 (4)
C11—C12—C13 122.4 (4)  O9—C35—C29 118.2 (4)
C11—C12—H12 118.8  O8—C35—C29 118.3 (4)
C13—C12—H12 118.8  O10—C36—C33 119.5
C14—C13—C12 119.3 (4)  O10—C36—C31 119.5
C14—C13—H13 120.4  H36C—C36—H36B 109.5
C12—C13—H13 120.4  H36C—C36—H36A 109.5
O5—C14—C13 124.7 (4)  O2′—N3′—O1′ 122.0 (11)
O5—C14—C15 116.0 (4)  O2′—N3′—C4 119.0 (10)
C13—C14—C15 119.3 (4)  O1′—N3′—C4 119.0 (10)
C14—C15—C16 120.7 (4)  C1—N1—C7 117.7 (3)
C14—C15—C17 119.6  C1—N1—C10 118.2 (3)
C16—C15—C17 119.6  C7—N1—C10 111.6 (3)
C15—C16—C11 121.0 (4)  C8—N2—C9 110.2 (3)
C15—C16—H11 119.5  C8—N2—H21N 107 (3)
C11—C16—H11 119.5  C9—N2—H21N 112 (3)
O3—C17—O4 124.6 (4)  C8—N2—H22N 108 (3)
O3—C17—C11 117.5 (5)  C9—N2—H22N 112 (3)
O4—C17—C11 117.9 (5)  H21N—N2—H22N 107 (4)
O5—C18—H18C 109.5  O1—N3—O2 121.2 (11)
O5—C18—H18B 109.5  O1—N3—C4 118.2 (10)
H18C—C18—H18B 109.5  O2—N3—C4 120.6 (9)
O5—C18—H18A 109.5  O2′—N3′—O1′ 122.0 (11)
H18C—C18—H18A 109.5  O2′—N3′—C4 119.0 (9)
H18B—C18—H18A 109.5  O1′—N3′—C4 119.0 (10)
C10—N4—C28 121.8 (4)  C19—N4—C28 121.8 (3)
N4—C19—C20 122.2 (4)  C19—N4—C25 121.4 (4)
N4—C19—C24 116.0 (4)  C28—N4—C25 108.6 (3)
C20—C19—C24 121.5 (4)  C26—N5—C27 112.8 (3)
C21—C20—C19 119.3  C26—N5—H51N 108 (3)
C21—C20—H20 119.3  C27—N5—H51N 114 (3)
| Bond                  | Value | Bond                  | Value |
|-----------------------|-------|-----------------------|-------|
| C19—C20—H20          | 119.3 | C26—N5—H52N          | 107 (3) |
| C20—C21—C22          | 121.0 (4) | C27—N5—H52N          | 112 (3) |
| C20—C21—H21          | 119.5 | H51N—N5—H52N         | 103 (4) |
| C22—C21—H21          | 119.5 | O6—N6—O7             | 122.1 (4) |
| C21—C22—C23          | 120.0 (4) | O6—N6—C22            | 118.5 (4) |
| C21—C22—N6           | 120.4 (4) | O7—N6—C22            | 119.3 (4) |
| C23—C22—N6           | 119.6 (4) | C14—O5—C18           | 118.7 (4) |
| C24—C23—C22          | 119.6 (4) | C32—O10—C36          | 116.7 (4) |
| C24—C23—H23          | 120.2 | H11O—O11—H12O        | 108 (5) |
| N1—C1—C2—C3          | −176.3 (4) | O10—C32—C33—C34     | −177.5 (4) |
| C6—C1—C2—C3          | 1.0 (6) | C31—C32—C33—C34     | 1.3 (6) |
| C1—C2—C3—C4          | −0.3 (8) | C32—C33—C34—C29     | −1.7 (6) |
| C2—C3—C4—C5          | −0.7 (8) | C30—C29—C34—C33     | 0.7 (6) |
| C2—C3—C4—N3'         | 164.9 (6) | C35—C29—C34—C33     | 179.9 (4) |
| C2—C3—C4—N3          | −165.5 (6) | C30—C29—C35—O9      | −4.2 (5) |
| C3—C4—C5—C6          | 0.9 (8) | C34—C29—C35—O9      | 176.6 (3) |
| N3'—C4—C5—C6         | −165.0 (6) | C30—C29—C35—O8      | 176.7 (3) |
| N3—C4—C5—C6          | 165.4 (6) | C34—C29—C35—O8      | −2.5 (5) |
| C4—C5—C6—C1          | −0.2 (7) | C6—C1—N1—C7         | 27.3 (5) |
| N1—C1—C6—C5          | 176.6 (4) | C2—C1—N1—C7         | −155.5 (4) |
| C2—C1—C6—C5          | −0.7 (6) | C6—C1—N1—C10        | 166.2 (4) |
| N1—C7—C8—N2          | −54.0 (5) | C2—C1—N1—C10        | −16.6 (6) |
| N2—C9—C10—N1         | 56.1 (5) | C8—C7—N1—C1         | −166.4 (3) |
| C16—C11—C12—C13      | 0.2 (6) | C8—C7—N1—C10        | 52.2 (4) |
| C17—C11—C12—C13      | 178.1 (4) | C9—C10—N1—C1        | 165.3 (3) |
| C11—C12—C13—C14      | −1.6 (7) | C9—C10—N1—C7        | −53.4 (5) |
| C12—C13—C14—O5       | −178.3 (4) | C7—C8—N2—C9        | 55.9 (5) |
| C12—C13—C14—C15      | 2.3 (7) | C10—C9—N2—C8        | −56.8 (4) |
| O5—C14—C15—C16       | 179.0 (4) | C5—C4—N3—O1        | 5.9 (11) |
| C13—C14—C15—C16      | −1.6 (7) | C3—C4—N3—O1        | 170.9 (8) |
| C14—C15—C16—C11      | 0.1 (7) | C5—C4—N3—O2        | −176.8 (7) |
| C12—C11—C16—C15      | 0.6 (6) | C3—C4—N3—O2        | −11.8 (11) |
| C17—C11—C16—C15      | −177.3 (4) | C5—C4—N3—O2'       | 166.2 (8) |
| C12—C11—C17—O3       | −177.7 (4) | C3—C4—N3—O2'       | 0.2 (12) |
| C16—C11—C17—O3       | 0.1 (6) | C5—C4—N3—O1'       | −15.5 (12) |
| C12—C11—C17—O4       | 2.6 (6) | C3—C4—N3—O1'       | 178.5 (9) |
| C16—C11—C17—O4       | −179.5 (4) | C20—C19—N4—C28     | −18.5 (6) |
| N4—C19—C20—C21       | 178.6 (4) | C24—C19—N4—C28     | 163.8 (4) |
| C24—C19—C20—C21      | −3.6 (6) | C20—C19—N4—C25     | −163.3 (4) |
| C19—C20—C21—C22      | 1.6 (6) | C24—C19—N4—C25     | 19.0 (6) |
| C20—C21—C22—C23      | 1.1 (6) | C27—C28—N4—C19     | −86.8 (5) |
| C20—C21—C22—N6       | −175.8 (4) | C27—C28—N4—C25     | 61.9 (4) |
| C21—C22—C23—C24      | −1.4 (6) | C26—C25—N4—C19     | 86.9 (4) |
| N6—C22—C23—C24       | 175.5 (4) | C26—C25—N4—C28     | −61.9 (4) |
| C22—C23—C24—C19      | −0.8 (6) | C25—C26—N5—C27     | −54.1 (5) |
| N4—C19—C24—C23       | −179.0 (4) | C28—C27—N5—C26     | 54.7 (4) |
| C20—C19—C24—C23      | 3.2 (6) | C21—C22—N6—O6      | 4.5 (6) |

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N4—C25—C26—N5 57.6 (5) C23—C22—N6—O6 −172.4 (4)
N5—C27—C28—N4 −58.0 (4) C21—C22—N6—O7 −175.1 (4)
C34—C29—C30—C31 0.8 (6) C23—C22—N6—O7 8.0 (6)
C35—C29—C30—C31 −178.5 (4) C13—C14—O5—C18 0.5 (7)
C30—C31—C32—C33 0.2 (6) C31—C32—O10—C36 176.8 (4)
C30—C31—C32—O10 179.1 (4) C21—C22—N6—O7 −175.1 (4)

Hydrogen-bond geometry (Å, °)

D—H···A       D—H     H···A       D···A       D—H···A
C7—H7B···O7i    0.97     2.54     3.451 (5)    157
C9—H9B···O4ii   0.97     2.31     3.270 (5)    169
C20—H20···O9    0.93     2.53     3.461 (5)    174
C25—H25···O2aiii 0.97     2.50     3.206 (10)   130
C27—H27A···O7h  0.97     2.58     3.548 (5)    175
C28—H28B···O9   0.97     2.55     3.489 (5)    164
C36—H36C···O1bi 0.96     2.49     3.395 (14)   158
N2—H21···O8iv   0.88 (2)  1.83 (2)   2.697 (4)    166 (4)
N2—H21···O9iv   0.88 (2)  2.57 (3)   3.196 (4)    129 (3)
N2—H22···O11v   0.88 (2)  1.89 (2)   2.758 (5)    169 (4)
N5—H51···O9vi   0.87 (2)  1.93 (2)   2.778 (5)    164 (4)
N5—H52···O3vii  0.91 (2)  1.82 (2)   2.724 (5)    171 (4)
O11—H11O···O4   0.84 (2)  1.83 (2)   2.663 (4)    176 (4)
O11—H12O···O8v  0.84 (2)  1.92 (2)   2.754 (4)    173 (4)

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

4-(4-Nitrophenyl)piperazin-1-ium 4-ethoxybenzoate (VI)

Crystal data

C_{10}H_{14}N_{3}O_{2}+\cdotC_{9}H_{9}O_{3}^−

Z = 4

F(000) = 792

D_x = 1.324 Mg m^{-3}

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 4134 reflections

θ = 2.4–28.0°

µ = 0.10 mm^{-1}

T = 293 K

Plate, yellow

Plate, yellow

0.44 × 0.32 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur

diffractometer

13344 measured reflections

ω scans

6868 independent reflections

Absorption correction: multi-scan

(CrysAlis RED; Oxford Diffraction, 2009)

3803 reflections with I > 2σ(I)

R_{int} = 0.027

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$\theta_{\text{max}} = 25.4^\circ$, $\theta_{\text{min}} = 2.4^\circ$

$h = -9\rightarrow 5$

$\quad k = -11\rightarrow 10$

$l = -33\rightarrow 33$

**Refinement**

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.137$

$S = 1.05$

6858 reflections

501 parameters

16 restraints

0 constraints

**Hydrogen site location**: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.7484P]$

where $P = (F_o^2 + 2F_c^2)/3$

$\Delta/\sigma$ max < 0.001

$\Delta \rho_{\text{max}} = 0.23$ e Å$^{-3}$

$\Delta \rho_{\text{min}} = -0.22$ 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.

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

|          | $x$      | $y$      | $z$      | $U_{iso}/U_{eq}$ |
|----------|----------|----------|----------|------------------|
| O1       | -0.3466 (3) | 0.6545 (4) | 0.40786 (9) | 0.1126 (10) |
| O2       | -0.1630 (3) | 0.5811 (3) | 0.46683 (9) | 0.0901 (8)  |
| N3       | -0.1931 (4) | 0.6107 (3) | 0.42384 (10) | 0.0667 (7)  |
| N1       | 0.3914 (3)  | 0.5404 (2) | 0.29014 (7)  | 0.0412 (5)  |
| N2       | 0.6838 (3)  | 0.4199 (3) | 0.22275 (9)  | 0.0486 (6)  |
| C1       | 0.2485 (3)  | 0.5547 (3) | 0.32330 (9)  | 0.0364 (6)  |
| C2       | 0.0659 (4)  | 0.6276 (3) | 0.30870 (10) | 0.0452 (7)  |
| H2       | 0.041054    | 0.663561 | 0.276117    | 0.054*      |
| C3       | -0.0759 (4) | 0.6467 (3) | 0.34138 (10) | 0.0487 (7)  |
| H3       | -0.195824   | 0.69631 | 0.330993    | 0.058*      |
| C4       | -0.0417 (4) | 0.5927 (3) | 0.38966 (10) | 0.0470 (7)  |
| C5       | 0.1352 (4)  | 0.5197 (3) | 0.40558 (10) | 0.0460 (7)  |
| H5       | 0.157333    | 0.483265 | 0.438246    | 0.055*      |
| C6       | 0.2787 (4)  | 0.5009 (3) | 0.37309 (10) | 0.0430 (7)  |
| H6       | 0.397837    | 0.451799 | 0.384052    | 0.052*      |
| C7       | 0.5772 (3)  | 0.4477 (3) | 0.30663 (10) | 0.0473 (7)  |
| H7A      | 0.588757    | 0.338899 | 0.315234    | 0.057*      |
| H7B      | 0.597413    | 0.484321 | 0.33554     | 0.057*      |
| C8       | 0.7216 (4)  | 0.4565 (4) | 0.26954 (10) | 0.0539 (8)  |
| H8A      | 0.725864    | 0.561056 | 0.265102    | 0.065*      |
| H8B      | 0.839991    | 0.382613 | 0.280859    | 0.065*      |
| C9       | 0.5080 (4)  | 0.5395 (3) | 0.20545 (10) | 0.0528 (8)  |
| H9A      | 0.482935    | 0.520499 | 0.174084    | 0.063*      |
| H9B      | 0.516375    | 0.642512 | 0.201592    | 0.063*      |
| C10      | 0.3546 (4)  | 0.5366 (4) | 0.23985 (9)  | 0.0527 (8)  |
| H10A     | 0.245506    | 0.626087 | 0.229683    | 0.063*      |
| H10B     | 0.329888    | 0.442345 | 0.238274    | 0.063*      |
| Atom | x      | y      | z      | Ueq   |
|------|--------|--------|--------|-------|
| O3   | -0.0728 (3) | 0.4331 (2) | 0.15512 (7) | 0.0578 (5) |
| O4   | 0.1149 (2)  | 0.2978 (2)  | 0.21489 (7)  | 0.0532 (5) |
| O5   | 0.6778 (3)  | 0.3001 (3)  | 0.03965 (7)  | 0.0734 (7) |
| C11  | 0.2434 (4)  | 0.3357 (3)  | 0.13647 (9)  | 0.0400 (6) |
| C12  | 0.4193 (4)  | 0.2483 (3)  | 0.15096 (10) | 0.0518 (8) |
| H12  | 0.438717    | 0.198421    | 0.182667     | 0.062*    |
| C13  | 0.5679 (4)  | 0.2321 (4)  | 0.11995 (10) | 0.0572 (8) |
| H13  | 0.685415    | 0.171644    | 0.130663     | 0.069*    |
| C14  | 0.5409 (4)  | 0.3059 (3)  | 0.07314 (10) | 0.0524 (8) |
| C15  | 0.3656 (4)  | 0.3930 (4)  | 0.05764 (10) | 0.0609 (9) |
| H15  | 0.346406    | 0.442258    | 0.02587      | 0.073*    |
| C16  | 0.2192 (4)  | 0.4072 (3)  | 0.08898 (10) | 0.0520 (8) |
| H16  | 0.101521    | 0.466057    | 0.078056     | 0.062*    |
| C17  | 0.0851 (4)  | 0.3564 (3)  | 0.17148 (10) | 0.0424 (7) |
| C18  | 0.8615 (4)  | 0.2090 (4)  | 0.05351 (12) | 0.0820 (11) |
| H18A | 0.874909    | 0.100553    | 0.064059     | 0.098*    |
| H18B | 0.894362    | 0.249403    | 0.079923     | 0.098*    |
| C19  | 0.6924 (5)  | 0.2199 (5)  | 0.01002 (14) | 0.1126 (16) |
| H19A | 1.106148    | 0.152009    | 0.017216     | 0.169*    |
| H19B | 0.976652    | 0.32615     | 0.001769     | 0.169*    |
| H19C | 0.941525    | 0.188565    | -0.016723    | 0.169*    |
| O6   | 0.1516 (4)  | 0.7336 (4)  | 0.60499 (10) | 0.1157 (11) |
| O7   | 0.1799 (4)  | 0.9508 (4)  | 0.61439 (10) | 0.1162 (11) |
| N6   | 0.1845 (4)  | 0.8525 (5)  | 0.58929 (11) | 0.0830 (10) |
| N4   | 0.2839 (3)  | 0.9838 (3)  | 0.38867 (8)  | 0.0490 (6) |
| N5   | 0.2937 (3)  | 1.0699 (3)  | 0.28629 (8)  | 0.0462 (6) |
| C20  | 0.2721 (4)  | 0.9472 (3)  | 0.43812 (10) | 0.0459 (7) |
| C21  | 0.2534 (4)  | 0.8084 (4)  | 0.45928 (11) | 0.0653 (9) |
| H21  | 0.259467    | 0.733784    | 0.439839     | 0.078*    |
| C22  | 0.2260 (5)  | 0.7782 (4)  | 0.50814 (12) | 0.0747 (10) |
| H22  | 0.211482    | 0.684754    | 0.521174     | 0.09*     |
| C23  | 0.2199 (4)  | 0.8824 (5)  | 0.53759 (11) | 0.0636 (9) |
| C24  | 0.2430 (5)  | 1.0184 (5)  | 0.51872 (13) | 0.0783 (11) |
| H24  | 0.240692    | 1.089852    | 0.538938     | 0.094*    |
| C25  | 0.2700 (5)  | 1.0504 (4)  | 0.46951 (12) | 0.0711 (10) |
| H25  | 0.287119    | 1.143254    | 0.457048     | 0.085*    |
| C26  | 0.3867 (4)  | 1.0795 (3)  | 0.36697 (10) | 0.0563 (8) |
| H26A | 0.51213     | 1.012589    | 0.360971     | 0.068*    |
| H26B | 0.3881      | 1.149872    | 0.389107     | 0.068*    |
| C27  | 0.3030 (4)  | 1.1732 (3)  | 0.32039 (10) | 0.0539 (8) |
| H27A | 0.180752    | 1.245608    | 0.326783     | 0.065*    |
| H27B | 0.375328    | 1.234293    | 0.305927     | 0.065*    |
| C28  | 0.1907 (4)  | 0.9701 (3)  | 0.30890 (10) | 0.0498 (7) |
| H28A | 0.193308    | 0.897196    | 0.28723      | 0.06*     |
| H28B | 0.064102    | 1.035801    | 0.314055     | 0.06*     |
| C29  | 0.2714 (4)  | 0.8803 (3)  | 0.35626 (10) | 0.0529 (8) |
| H29A | 0.196135    | 0.822751    | 0.371369     | 0.064*    |
| H29B | 0.392544    | 0.804857    | 0.35057      | 0.064*    |
| Atomic displacement parameters ($\text{Å}^2$) |
|------------------------------------------|
| $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$  | $U_{13}$  | $U_{23}$  |
| O1        | 0.0514 (15) | 0.173 (3) | 0.0801 (19) | −0.0138 (17) | 0.0103 (14) | 0.0040 (18) |
| O2        | 0.0455 (17) | 0.129 (2) | 0.0317 (16) | −0.0086 (16) | 0.0107 (13) | −0.0023 (14) |
| N3        | 0.0550 (18) | 0.076 (2) | 0.0573 (19) | −0.0143 (15) | 0.0078 (15) | −0.0036 (15) |
| N1        | 0.0399 (13) | 0.0448 (14) | 0.0380 (13) | −0.0148 (11) | −0.0030 (10) | −0.0033 (11) |
| N2        | 0.0450 (14) | 0.0536 (16) | 0.0466 (15) | −0.0175 (13) | 0.0038 (11) | −0.0089 (13) |
| C1        | 0.0440 (16) | 0.0302 (15) | 0.0369 (16) | −0.0153 (13) | −0.0019 (13) | −0.0053 (12) |
| C2        | 0.0486 (17) | 0.0463 (17) | 0.0378 (16) | −0.0152 (14) | −0.0064 (14) | −0.0001 (13) |
| C3        | 0.0392 (16) | 0.0525 (19) | 0.0513 (19) | −0.0132 (14) | −0.0007 (14) | −0.0071 (15) |
| C4        | 0.0488 (18) | 0.0463 (18) | 0.0441 (18) | −0.0167 (15) | 0.0066 (14) | −0.0065 (14) |
| C5        | 0.0584 (19) | 0.0406 (17) | 0.0386 (16) | −0.0186 (15) | −0.0016 (14) | −0.0020 (13) |
| C6        | 0.0433 (16) | 0.0381 (16) | 0.0457 (17) | −0.0127 (13) | −0.0066 (14) | −0.0027 (13) |
| C7        | 0.0407 (16) | 0.0543 (18) | 0.0470 (18) | −0.0162 (14) | −0.0043 (13) | −0.0088 (14) |
| C8        | 0.0440 (17) | 0.066 (2) | 0.057 (2) | −0.0243 (15) | 0.0013 (15) | −0.0150 (16) |
| C9        | 0.0544 (18) | 0.0547 (19) | 0.0451 (18) | −0.0186 (16) | 0.0029 (14) | 0.0005 (14) |
| C10       | 0.0452 (17) | 0.068 (2) | 0.0392 (17) | −0.0168 (15) | −0.0010 (13) | −0.0005 (15) |
| O3        | 0.0458 (12) | 0.0732 (15) | 0.0477 (12) | −0.0181 (11) | 0.0023 (10) | 0.0009 (11) |
| O4        | 0.0585 (12) | 0.0634 (13) | 0.0375 (12) | −0.0259 (11) | 0.0003 (9) | 0.0022 (10) |
| O5        | 0.0505 (13) | 0.0959 (17) | 0.0504 (13) | −0.0107 (12) | 0.0086 (11) | 0.0129 (12) |
| C11       | 0.0480 (17) | 0.0392 (16) | 0.0352 (15) | −0.0199 (14) | 0.0001 (13) | −0.0026 (13) |
|     | C12  |     | O6  | C13  |     | O7  | C14  |     | O8  | C15  |     | O9  | C16  |     | O10 | C17  |     | O11 | C18  |     | O12 | C19  |     | O13 | C20  |     | O14 | C21  |     | O15 | C22  |     | O16 | C23  |     | O17 | C24  |     | O18 | C25  |     | O19 | C26  |     | O20 | C27  |     | O21 | C28  |     | O22 | C29  |     | O23 | C30  |     | O24 | C31  |     | O25 | C32  |     | O26 | C33  |     | O27 | C34  |     | O28 | C35  |     | O29 | C36  |     | O30 | C37  |     | O31 | C38  |     |  |
|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|-----|------|-----|--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| Bond        | Bond Length (Å) | Bond        | Bond Length (Å) |
|------------|-----------------|------------|-----------------|
| C1—C2      | 1.405 (3)       | C20—C21    | 1.384 (4)       |
| C1—C6      | 1.412 (3)       | C20—C25    | 1.391 (4)       |
| C2—C3      | 1.366 (4)       | C21—C22    | 1.370 (4)       |
| C2—H2      | 0.93            | C21—H21    | 0.93            |
| C3—C4      | 1.376 (4)       | C22—C23    | 1.349 (4)       |
| C3—H3      | 0.93            | C22—H22    | 0.93            |
| C4—C5      | 1.377 (4)       | C23—C24    | 1.359 (5)       |
| C5—C6      | 1.372 (3)       | C24—C25    | 1.381 (4)       |
| C5—H5      | 0.93            | C24—H24    | 0.93            |
| C6—H6      | 0.93            | C25—H25    | 0.93            |
| C7—C8      | 1.498 (3)       | C26—C27    | 1.497 (4)       |
| C7—H7A     | 0.97            | C26—H26A   | 0.97            |
| C7—H7B     | 0.97            | C26—H26B   | 0.97            |
| C8—H8A     | 0.97            | C27—H27A   | 0.97            |
| C8—H8B     | 0.97            | C27—H27B   | 0.97            |
| C9—C10     | 1.493 (3)       | C28—C29    | 1.498 (4)       |
| C9—H9A     | 0.97            | C28—H28A   | 0.97            |
| C9—H9B     | 0.97            | C28—H28B   | 0.97            |
| C10—H10A   | 0.97            | C29—H29A   | 0.97            |
| C10—H10B   | 0.97            | C29—H29B   | 0.97            |
| O3—C17     | 1.261 (3)       | O8—C36     | 1.264 (3)       |
| O4—C17     | 1.253 (3)       | O9—C36     | 1.252 (3)       |
| O5—C14     | 1.365 (3)       | O10—C33    | 1.363 (3)       |
| O5—C18     | 1.426 (3)       | O10—C37    | 1.431 (4)       |
| C11—C12    | 1.375 (4)       | C30—C35    | 1.372 (3)       |
| C11—C16    | 1.383 (3)       | C30—C31    | 1.387 (4)       |
| C11—C17    | 1.499 (4)       | C30—C36    | 1.500 (4)       |
| C12—C13    | 1.379 (4)       | C31—C32    | 1.376 (4)       |
| C12—H12    | 0.93            | C31—H31    | 0.93            |
| C13—C14    | 1.373 (4)       | C32—C33    | 1.383 (4)       |
| C13—H13    | 0.93            | C32—H32    | 0.93            |
| C14—C15    | 1.378 (4)       | C33—C34    | 1.381 (4)       |
| C15—C16    | 1.374 (4)       | C34—C35    | 1.378 (4)       |
| C15—H15    | 0.93            | C34—H34    | 0.93            |
| C16—H16    | 0.93            | C35—H35    | 0.93            |
| C18—C19    | 1.502 (4)       | C37—C38    | 1.496 (5)       |
| C18—H18A   | 0.97            | C37—H37A   | 0.97            |
| C18—H18B   | 0.97            | C37—H37B   | 0.97            |
| C19—H19A   | 0.96            | C38—H38A   | 0.96            |
| C19—H19B   | 0.96            | C38—H38B   | 0.96            |
| C19—H19C   | 0.96            | C38—H38C   | 0.96            |
| O2—N3—O1   | 122.7 (3)       | O7—N6—O6   | 123.5 (4)       |
| O2—N3—C4   | 119.3 (3)       | O7—N6—C23  | 118.2 (4)       |
| O1—N3—C4   | 118.0 (3)       | O6—N6—C23  | 118.2 (4)       |
| C1—N1—C7   | 118.1 (2)       | C20—N4—C26 | 121.3 (2)       |
| C1—N1—C10  | 117.0 (2)       | C20—N4—C29 | 121.3 (2)       |
| C7—N1—C10  | 116.3 (2)       | C26—N4—C29 | 111.9 (2)       |
C9—N2—C8 107.9 (2)  C27—N5—C28 110.0 (2)
C9—N2—H31N 110 (3)  C27—N5—H61N 112 (3)
C8—N2—H31N 108 (3)  C28—N5—H61N 110 (3)
C9—N2—H32N 111 (3)  C27—N5—H62N 108 (3)
C8—N2—H32N 106 (3)  C28—N5—H62N 110 (3)
H31N—N2—H32N 113 (4)  H61N—N5—H62N 107 (4)
N1—C1—C2  120.9 (2)  N4—C20—C21 121.8 (3)
N1—C1—C6  122.0 (2)  N4—C20—C25 122.0 (3)
C2—C1—C6  117.1 (2)  C21—C20—C25 116.2 (3)
C3—C2—C1  121.3 (3)  C22—C21—C20 121.6 (3)
C3—C2—H2  119.3  C22—C21—H21 119.2
C1—C2—H2  119.3  C20—C21—H21 119.2
C2—C3—C4  120.1 (3)  C23—C22—C21 120.9 (3)
C2—C3—H3  120  C23—C22—H22 119.6
C4—C3—H3  120  C21—C22—H22 119.6
C3—C4—C5  120.6 (3)  C22—C23—C24 119.7 (3)
C3—C4—N3  119.6 (3)  C22—C23—N6 120.8 (4)
C5—C4—N3  119.8 (3)  C24—C23—N6 119.5 (4)
C6—C5—C4  119.8 (3)  C23—C24—C25 119.9 (3)
C6—C5—H5  120.1  C23—C24—H24 120
C4—C5—H5  120.1  C25—C24—H24 120
C5—C6—C1  119.4  C24—C25—C20 119.6
C5—C6—H6  119.4  C24—C25—H25 119.2
C1—C6—H6  119.4  C20—C25—H25 119.2
N1—C7—C8  113.3 (2)  N4—C26—C27 110.5 (2)
N1—C7—H7A  108.9  N4—C26—H26A 109.5
C8—C7—H7A  108.9  C27—C26—H26A 109.5
N1—C7—H7B  108.9  N4—C26—H26B 109.5
C8—C7—H7B  108.9  C27—C26—H26B 109.5
H7A—C7—H7B  107.7  H26A—C26—H26B 108.1
N2—C8—C7  110.9 (2)  N5—C27—C26 111.0 (2)
N2—C8—H8A  109.5  N5—C27—H27A 109.4
C7—C8—H8A  109.5  C26—C27—H27A 109.4
N2—C8—H8B  109.5  N5—C27—H27B 109.4
C7—C8—H8B  109.5  C26—C27—H27B 109.4
H8A—C8—H8B  108  H27A—C27—H27B 108
N2—C9—C10  111.5 (2)  N5—C28—C29 111.1 (2)
N2—C9—H9A  109.3  N5—C28—H28A 109.4
C10—C9—H9A  109.3  C29—C28—H28A 109.4
N2—C9—H9B  109.3  N5—C28—H28B 109.4
C10—C9—H9B  109.3  C29—C28—H28B 109.4
H9A—C9—H9B  108  H28A—C28—H28B 108
N1—C10—C9  113.7 (2)  N4—C29—C28 111.5 (2)
N1—C10—H10A  108.8  N4—C29—H29A 109.3
C9—C10—H10A  108.8  C28—C29—H29A 109.3
N1—C10—H10B  108.8  N4—C29—H29B 109.3
C9—C10—H10B  108.8  C28—C29—H29B 109.3
H10A—C10—H10B  107.7  H29A—C29—H29B 108
| Bond/Angle/Distance | Value 1 | Value 2 | Value 3 | Value 4 |
|--------------------|---------|---------|---------|---------|
| C14—O5—C18        | 118.3 (2)|         |         | 118.5 (3)|
| C12—C11—C16       | 117.5 (2)|         |         | 117.1 (3)|
| C12—C11—C17       | 120.9 (2)|         |         | 120.9 (3)|
| C16—C11—C17       | 121.6 (3)|         |         | 122.0 (2)|
| C11—C12—C13       | 122.1 (3)|         |         | 121.5 (3)|
| C11—C12—H12       | 119      |         |         | 119.2    |
| C13—C12—H12       | 119      |         |         | 119.2    |
| C14—C13—C12       | 119.5 (3)|         |         | 120.0 (3)|
| C14—C13—H13       | 120.3    |         |         | 120      |
| C12—C13—H13       | 120.3    |         |         | 120      |
| O5—C14—C13        | 124.4 (3)|         |         | 124.5 (3)|
| O5—C14—C15        | 116.1 (3)|         |         | 116.1 (3)|
| C13—C14—C15       | 119.5 (3)|         |         | 119.4 (3)|
| C16—C15—C14       | 120.2 (3)|         |         | 119.2 (3)|
| C16—C15—H15       | 119.9    |         |         | 120.4    |
| C14—C15—H15       | 119.9    |         |         | 120.4    |
| C15—C16—C11       | 121.2 (3)|         |         | 122.7 (3)|
| C15—C16—H16       | 119.4    |         |         | 118.6    |
| C11—C16—H16       | 119.4    |         |         | 118.6    |
| O4—C17—O3         | 123.5 (2)|         |         | 124.0 (3)|
| O4—C17—C11        | 119.3 (3)|         |         | 118.3 (3)|
| O3—C17—C11        | 117.3 (2)|         |         | 117.7 (3)|
| O5—C18—C19        | 107.3 (3)|         |         | 107.4 (3)|
| O5—C18—H18A       | 110.3    |         |         | 110.2    |
| C19—C18—H18A      | 110.3    |         |         | 110.2    |
| O5—C18—H18B       | 110.3    |         |         | 110.2    |
| C19—C18—H18B      | 110.3    |         |         | 110.2    |
| H18A—C18—H18B     | 108.5    |         |         | 108.5    |
| C18—C19—H19A      | 109.5    |         |         | 109.5    |
| C18—C19—H19B      | 109.5    |         |         | 109.5    |
| H19A—C19—H19B     | 109.5    |         |         | 109.5    |
| C18—C19—H19C      | 109.5    |         |         | 109.5    |
| H19A—C19—H19C     | 109.5    |         |         | 109.5    |
| C7—N1—C1—C2       | −173.1 (2)|         |         | −149.7 (3)|
| C10—N1—C1—C2      | −26.5 (3)|         |         | 2.0 (4)  |
| C7—N1—C1—C6       | 8.5 (3)  |         |         | 33.3 (4) |
| C10—N1—C1—C6      | 155.0 (2)|         |         | −175.1 (3)|
| N1—C1—C2—C3       | −177.9 (2)|         |         | −174.3 (3)|
| C6—C1—C2—C3       | 0.6 (4)  |         |         | 2.8 (5)  |
| C1—C2—C3—C4       | −0.7 (4) |         |         | −1.3 (5) |
| C2—C3—C4—C5       | 0.3 (4)  |         |         | −0.7 (5) |
| C2—C3—C4—N3       | −178.7 (3)|         |         | 177.8 (3)|
| O2—N3—C4—C3       | −170.8 (3)|         |         | −179.8 (3)|
| O1—N3—C4—C3       | 9.6 (4)  |         |         | −3.4 (5) |
| O2—N3—C4—C5       | 10.2 (4) |         |         | −1.3 (5) |
| O1—N3—C4—C5       | −169.4 (3)|         |         | 175.1 (3)|
C3—C4—C5—C6  0.2 (4)  C22—C23—C24—C25  0.9 (5)
N3—C4—C5—C6  179.2 (3)  N6—C23—C24—C25  −177.6 (3)
C4—C5—C6—C1  −0.2 (4)  C23—C24—C25—C20  0.8 (5)
N1—C1—C6—C5  178.3 (2)  N4—C20—C25—C24  174.6 (3)
C2—C1—C6—C5  −0.2 (4)  C21—C20—C25—C24  −2.6 (5)
C1—N1—C7—C8  −173.0 (2)  C20—N4—C26—C27  −148.9 (3)
C9—N2—C8—C7  40.3 (3)  C29—N4—C26—C27  57.0 (3)
C2—C1—C6—C5  −0.2 (4)  C21—C20—C25—C24  −2.6 (5)
C1—N1—C10—C9  50.3 (3)  C26—N5—C27—C26  56.4 (3)
C7—N1—C10—C9  −39.5 (3)  C26—N5—C27—C26  56.4 (3)
N1—C7—C8—N2  −51.8 (3)  N4—C26—C27—N5  −57.5 (3)
C8—N2—C9—C10  −61.5 (3)  C27—N5—C28—C27  −54.8 (3)
C1—N1—C10—C9  173.4 (2)  C20—N4—C29—C28  150.1 (2)
C7—N1—C10—C9  −39.5 (3)  C26—N4—C29—C28  −55.8 (3)
N2—C9—C10—N1  50.3 (3)  C29—N4—C26—C27  174.6 (3)
C16—C11—C12—C13  0.5 (4)  C35—C30—C31—C32  −1.0 (4)
C17—C11—C12—C13  −177.6 (3)  C36—C30—C31—C32  177.1 (3)
C11—C12—C13—C14  0.4 (5)  C30—C31—C32—C33  1.6 (4)
C18—O5—C14—C13  1.3 (5)  C37—O10—C33—C34  0.7 (4)
C18—O5—C14—C15  −178.7 (3)  C37—O10—C33—C32  178.7 (3)
C12—C13—C14—O5  178.9 (3)  C31—C32—C33—O10  178.6 (3)
C12—C13—C14—C15  −1.0 (5)  C31—C32—C33—C34  −0.8 (4)
O5—C14—C15—C16  −179.2 (3)  C35—C30—C36—O10  15.2 (4)
C13—C14—C15—C16  0.7 (5)  C32—C33—C34—C35  −0.5 (4)
C14—C15—C16—C11  0.2 (5)  C31—C30—C35—C34  −0.3 (4)
C12—C11—C16—C15  −0.8 (4)  C36—C30—C35—C34  −178.5 (3)
C17—C11—C16—C15  177.3 (3)  C33—C34—C35—C30  1.1 (4)
C12—C11—C17—O4  2.7 (4)  C35—C30—C36—O9  15.2 (4)
C16—C11—C17—O4  −175.3 (2)  C31—C30—C36—O9  −162.9 (3)
C12—C11—C17—O3  −177.3 (3)  C35—C30—C36—O8  −166.4 (2)
C16—C11—C17—O3  4.6 (4)  C31—C30—C36—O8  15.5 (4)
C14—O5—C18—C19  178.7 (3)  C33—C34—C35—C30  176.2 (3)

Hydrogen-bond geometry (Å, °)

$Cg_2$ and $Cg_6$ are the centroids of the C1–C6 and C30–C35 rings, respectively.

|       | D—H···A   | D—H   | H···A   | D···A   | D—H···A   |
|-------|----------|-------|--------|---------|----------|
| N2—H31N···O3i | 0.94 (2)  | 1.68 (2) | 2.613 (3) | 172 (5) |
| N2—H31N···O4i | 0.94 (2)  | 2.51 (4) | 3.157 (3) | 127 (4) |
| N2—H32N···O9ii | 0.90 (2)  | 1.96 (2) | 2.843 (3) | 171 (5) |
| N5—H61N···O8i | 0.91 (2)  | 1.78 (2) | 2.686 (3) | 175 (5) |
| N5—H61N···O9i | 0.91 (2)  | 2.59 (4) | 3.174 (3) | 122 (4) |
| N5—H62N···O4iv | 0.90 (2)  | 1.83 (2) | 2.708 (3) | 165 (5) |
| C22—H22···O2vi | 0.93      | 2.6     | 3.502 (5) | 165    |
| C27—H27B···O9i | 0.97      | 2.59     | 3.215 (3) | 123    |
| C28—H28B···O7vi | 0.97      | 2.65     | 3.410 (4) | 135    |
| C29—H29B···O1i | 0.97      | 2.53     | 3.249 (4) | 131    |
| C35—H35···O4vii | 0.93       | 2.52     | 3.263 (3) | 137    |
|          |       |       |       |     |
|----------|-------|-------|-------|-----|
| C10—H10A···Cg6 | 0.97  | 2.82  | 3.746 (3) | 159 |
| C29—H29A···Cg2 | 0.97  | 2.76  | 3.556 (3) | 139 |

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