Crystal structure of 4-(2-methoxyphenyl)piperazin-1-ium 3,5-dintrosalicylate

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The title salt [systematic name: 4-(2-methoxyphenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate], C_{11}H_{17}N_{2}O^{+}·C_{7}H_{3}N_{2}O_{7}, exhibits secondary nitrogen atoms (N—H) in the 2-methoxyphenylpiperazine (2MeOPP) cation, which is protonated with a phenolic hydrogen atom of 3,5-dinitrosalicylic acid (DNSA). One of the oxygen atoms of the nitro group in the 3,5-dinitrosalicylate anion is disordered over two orientations with occupancy factors of 0.65 (7) and 0.35 (7). The 2-methoxyphenylpiperazinium cation and 3,5-dinitrosalicylate anion are linked in the asymmetric unit by a bifurcated N—H/C1/C1/N hydrogen bond, which formed is between the H atom in the protonated piperazinium unit of the cation and the carboxylic acid group in the anion. The piperazine ring adopts a chair conformation. The crystal structure features N—H/C1/C1/N hydrogen bonds interactions, which lead to the formation of a sandwich-like arrangement. Hirshfeld surface analysis was used to determine the relative contributions of various intermolecular interactions, indicating that that H···O/O···H (38.3%) and H···H (31.8%) contacts are the major contributors.

1. Chemical context

1-(2-Methoxyphenyl)piperazine is a substituted cyclo aliphatic amine with two nitrogen atoms at opposite positions of the six-membered ring. A substituent 2-methoxyphenyl group is attached to one of the nitrogen atoms while the other has one attached hydrogen atom (i.e. the secondary nitrogen atom, N−H). Piperazine and substituted piperazine derivatives are often used as intermediates for a wide range of pharmaceuticals, polymers, dyes, corrosion inhibitors and surfactants. In particular, (2-methoxyphenyl)piperazine derivatives are used as 5-HT_{1A} receptor ligands with reduced α1-adrenergic activity (Raghupathi et al., 1991; Orjales et al., 1995; Zhuang et al., 1998). 1-(2-Methoxyphenyl)piperazine-impregnated filters have been used for the detection of isocyanates in air (Sennbro et al., 2004). 1-Cinnamyl-4-(2-methoxyphenyl)piperazine derivatives are used as ligands for D_{2} and D_{3} dopamine and serotonin 5-HT_{3R} receptors (Penjišević et al., 2007). The crystal structure of eleven protonated 4-(2-methoxyphenyl)piperazin-1-ium salts with eleven different substituted benzoic acids (namely, 4/2-chlorobenzoic acid, 4/2-bromobenzoic acid, 4/2-iodobenzoic acid, 4/2-fluorobenzoic acid, 4/2-methylbenzoic acid, 4/2-ethylenbenzoic acid, 4/2-phenoxynbenzoic acid, 4/2-naphthoic acid, 4/2-aminobenzoic acid, 4/2-picolinic acid, 4/2-carboxylic acid) was determined and analyzed.
acid, 4-amino/4-nitro-benzoic acid, 3,5-dinitrobenzoic acid and picric acid) and three aliphatic dicarboxylic acid [maleic acid, fumaric acid and (2R,3R)-tartaric acid] salts and their supramolecular features have been reported (Harish Chinthal et al., 2020).

As a continuation of our earlier study on the crystal structure and supramolecular analysis of a monohydrated 1:1 adduct of bis(piperazine-1,4-diium), 3,5-dinitro-2-oxido-benzoate and piperazine, we have now investigated the crystal structure of 1-(2-methoxyphenyl) piperazinium 3,5-dinitro-salicylate (I). In this study, the crystal structure, Hirshfeld surface (HS) analysis, structural features and various intermolecular interactions that exist in the title protonated salt are reported.

2. Structural commentary

The title salt crystallizes in the triclinic space group Pı with the asymmetric unit comprising one 2-methoxyphenyl-piperazinium (2MeOPP)1+ cation and one 3,5-dinitrosalicylate (DNSA)1− anion (Fig. 1). The piperazine ring in the cation adopts a chair conformation with puckering parameters \( Q = 0.582 (3) \) Å, \( \theta = 176.3 (3) ^\circ \), \( \varphi = 338 (4) ^\circ \). One of the oxygen atoms of the nitro group (atom O4) in the 3,5-dinitrosalicylate anion is disordered over two orientations with occupancy factors of 0.65 (7) and 0.35 (7). Both nitro groups, the phenoxylate oxygen atom and a carboxylic acid group in the anion are coplanar with an r.m.s. deviation of 0.0074 Å. A bifurcated intermolecular N—H···O hydrogen bond [N3—H3A···O5 = 2.936 (3) Å and N3—H3A···O6 = 3.153 (3) Å] links the cation and anion in the asymmetric unit.

Figure 1
The molecular structure of the title molecular salt, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

In the DNSA molecule, deprotonation of the –COOH group (\( pK_a \) COOH = 2.2) is easier than that of the phenolic –OH group (\( pK_a \) OH = 6.8). 62 carboxylate moiety structures (COO−) and 70 phenolate anion structures (O−) were found in a search of the Cambridge Structural Database (CSD, Version 5.43, update of March 2020; Groom et al., 2016), which is perhaps unexpected because the number of crystal structures containing phenolate anions is larger than those containing carboxylate anions. These conflicting results may suggest that the formation of protonated salts of the DNSA molecule with phenolate ions is favoured by the thermodynamic stability and the intermolecular interactions between the phenolate anion and counter-ions in the respective crystal structures. The crystal structure of (I) suggests that the title salt was formed by deprotonation of the phenolic group in the DNSA molecule. In order to better understand the deprotonation of the phenolic group in DNSA molecule, the H-atom electron density in the difference-Fourier electron-density maps was calculated as they can yield additional insight into the proton-transfer behaviour. From Fig. 2, the electron density associated with atom H6 is shown to be smeared out between the O6 and O7 atoms, with the maximum lying closer to O6 atom than O7. It suggests that the H6A atom is attached to the carboxylic acid group and that deprotonation occurs through the phenolic group. As a result, the strong intra-molecular O6—H6A···O7 hydrogen bond formed. The interatomic distance between the phenolate oxygen atom, O7, and the O6 atom in the carboxylic acid group is 2.448 (2) Å, which also indicates that the strong intramolecular hydrogen bond between the O6 and O7 atoms. Similar types of intramolecular hydrogen bonds were observed in salicylic acid with a distance of 2.62 Å (Woiniska et al., 2016; Montis & Hursthouse et al., 2012) and in other proton-transfer salts of DNSA in the range 2.409–2.540 Å (Smith et al., 1995, 1996, 1997, 2000, 2001a,b,c,d,e, 2002, 2006). The proton in the carboxylc acid group is located between the carboxyl-O atom [O6 at

Figure 2
Difference-Fourier electron-density map showing the electron density associated with the H atom involved in the O6—H6···O7 hydrogen bond.
1.14 (3) Å] and the phenolate oxygen atom, [O7 at 1.37 (3) Å]. A similar trend was found in the various proton-transfer salts of DNSA (Smith et al., 2002).

3. Supramolecular features

The oxygen atoms in both nitro groups (O1–O4), the carboxylic acid group (O5 and O6) and a phenolate moiety (O7) in the DNSA anion all act as acceptors for various intermolecular N—H/C1/C1/C1 and C—H/C1/C1/C1 interactions, except for atom O4 (Table 1). In the cation, the O8 atom of the methoxy group is not involved in intermolecular interactions. The oxygen atoms of the carboxylic acid group (O5 and O6) act as acceptors for a bifurcated N3—H3A/C1/C1/C1(O5,O6) interaction, which links two neighbouring cations and anions into a centrosymmetric tetrameric architecture, which is further stabilized by the C14—H14/C1/C1/C1O5v interaction [3.481 (3) Å] and yields a macrocyclic ring structure with an \( R_2^2(20) \) motif (Fig. 3). Atom O1 of the nitro group is involved in the centrosymmetric C2—H2/C1/C1/C1O1ii interaction [3.581 (3) Å], which links two neighbouring (DNSA)\(^+\)/C0 units with an \( R_2^2(10) \) motif (Fig. 4). Neighbouring dimeric DNSA\(^+\)/C0 units are further linked through the previously mentioned bifurcated N3—H3A/C1/C1/C1(O5,O6) interaction and the N3—H3B/C1/C1/C1O7i [2.787 (3) Å], C10—H10/C1/C1/C1O4A [3.118 (10) Å] interactions.

![Figure 3](image3.png)
**Figure 3**
The bifurcated intermolecular N3—H3A···(O5,O6) hydrogen bond and the C14—H14···O5 interaction linking the 2MeOPP\(^+\) cation and (DNSA)^- anion into a centrosymmetric tetrameric architecture with an \( R_2^2(20) \) motif.

![Figure 4](image4.png)
**Figure 4**
Part of the crystal structure of (I) showing the centrosymmetric dimer motif with the \( R_2^2(10) \) motif formed by the C2—H2···O1 interaction.

![Figure 5](image5.png)
**Figure 5**
Part of the crystal structure of (I) showing the layered molecular architecture formed by the N3—H3A···(O5,O6), N3—H3B···O7 and C10—H10···O4A interactions, which propagates parallel to the b axis.

![Table 1](image6.png)
**Table 1**
Hydrogen-bond geometry (Å, °).

| D—H—A | D—H   | H—A   | D···A | D—H—A |
|--------|--------|--------|-------|--------|
| O6—H6A···O7 | 1.14 (3) | 1.37 (3) | 2.448 (2) | 154 (3) |
| N3—H3A···O5 | 0.94 (4) | 2.02 (4) | 2.936 (3) | 165 (3) |
| N3—H3A···O6 | 0.94 (4) | 2.44 (3) | 3.153 (3) | 133 (2) |
| N3—H3B···O7i | 0.97 (3) | 1.83 (3) | 2.787 (3) | 166 (3) |
| C2—H2···O1v | 0.93 | 2.66 | 3.581 (3) | 174 |
| C9—H9C···O3ii | 0.97 | 2.44 | 3.254 (4) | 152 |
| C10—H10A···O4A | 0.97 | 2.43 | 3.319 (3) | 152 |
| C14—H14···O5v | 0.93 | 2.74 | 3.481 (3) | 137 |
| C18—H18C···N4vi | 0.96 | 2.74 | 3.552 (4) | 143 |

Symmetry codes: (i) \(-x + 2, -y + 1, -z\); (ii) \(-x, -y, -z\); (iii) \(-x + 1, -y + 1, -z\); (iv) \(x + 1, y, z\); (v) \(-x + 1, -y + 1, -z + 1\); (vi) \(-x + 2, -y + 2, -z + 1\).
into a layered structure propagating parallel to the \( b \) axis (Fig. 5). Of the above three \( N{-}H\cdots O \) interactions [\( N3{-}H3A\cdots (O5,O6) \), and \( N3{-}H3B\cdots O7 \)], the \( N3{-}H3B\cdots O7 \) interaction is stronger \([D\cdots A = 2.787 (3) \AA]\) than the other two, which is due to the fact that two charged components are involved in this interaction, \( i.e. \) the phenolate \( O7 \) atom in DNSA\(^{-1}\) and the protonated \( N3{-}H3B \) unit in 2MeOPP\(^{+1}\). All of the above interactions facilitate the arrangement of the DNSA\(^{-1}\) ions in a layered molecular structure. The top and bottom sides of the DNSA\(^{-1}\) layers are stabilized by the two adjacent cationic layers. As a result, a sandwich-like arrangement is observed. An overall packing diagram is shown Fig. 6.

4. Hirshfeld surface analysis

*Crystal Explorer 17.5* (Turner et al., 2017) was used to calculate the Hirshfeld surfaces (HS; McKinnon et al., 1998, 2004; Spackman & Jayatilaka, 2009) of the title protonated salt and generate two-dimensional fingerprint plots (full and decomposed, 2D-FP; Spackman & McKinnon, 2002) in order to investigate and quantify the different intermolecular interactions. Distinct colours and intensities indicate short and long contacts, as well as the relative contribution of the different interactions in the solid state (Venkatesan et al., 2015, 2016). Two views of the HS mapped with \( d_{\text{norm}} \) in the range \([-0.6295 \text{ to } 1.3240 \text{ a.u.}] \) (front and back) are shown in Fig. 7. Bright red spots on the surface near \( O2, O3, O4A, O7, O6, H10B \) and \( H3B \) suggest that these atoms participate in hydrogen-bonding interactions (see Table 1). No significant pattern of convex blue and concave red triangles are observed in the shape-index (SI) diagram, indicating the absence of \( \pi \)-stacking interactions in the title salt. The 2D-FP plots show the relative contributions of the various non-covalent contacts (Fig. 8), indicating that intermolecular \( O\cdots H \) contacts [sharp symmetrical spikes are observed in the FP plot at \( d_e + d_i = 1.8 \AA \)] make the most significant contribution (38.3%), followed by \( H\cdots H \) contacts [symmetrical blunt spikes at \( d_e + d_i = 2.4 \AA \)], which contribute 31.8%, while \( C\cdots H, N\cdots H, C\cdots O, O\cdots N, C\cdots N \) and \( C\cdots C \) contacts contribute 11.6%, 1.7%, 6.7%, 2.7%, 1.9%, 0.5% and 2.8%, respectively. Other significant peaks for various non-covalent contacts are indicated in the FP plot (Fig. 8).

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, update of March 2020; Groom et al., 2016) using *Conquest* (Bruno et al., 2002) for 1-(2-methoxyphenyl)piperazine gave 111 hits, of which seven hits were for the protonated piperazinium unit. In particular, the crystal structure of 1-(2-methoxyphenyl)piperazin-4-ium picrate, which like the title compound has a phenolate anion, has been reported (CSD refcode NEBGIK; Verdonk et al., 1997). In the case of the DNSA molecule, 21 hits were observed for neutral DNSA molecules and 65 and 71 hits for DNSA carboxylate and DNSA phenolate, respectively.

6. Synthesis and crystallization

The title protonated salt was synthesized using 1-(2-methoxyphenyl)piperazine (Sigma Aldrich, 99%) and 3,5-dinitrosalicylic acid (Merck India, 99.5%) in an equimolar ratio. The stoichiometrically (1 mmol) weighed starting materials were completely dissolved in 50 mL of methanol at room temperature and stirred continuously for 3 h. The homogeneous solution was filtered using Whatmann filter paper and placed in a dust-free atmosphere, and allowed to evaporate.
slowly at room temperature. A suitable single crystal was harvested after a growth period of 25 days.

7. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2. The amine H atoms and O-bound H atoms were located in a difference-Fourier map and refined freely along with their isotropic displacement parameters. C-bound H atoms were included in calculated positions and treated as riding atoms [C—H = 0.93–0.98 Å, with Uiso(H) = 1.2Ueq(C)].

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Crystal structure of 4-(2-methoxyphenyl)piperazin-1-ium 3,5-dinitrosalicylate

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Computing details
Data collection: APEX2 (Bruker, 2012); cell refinement: APEX2 and SAINT (Bruker, 2012); data reduction: SAINT and XPREP (Bruker, 2012); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae et al., 2020); software used to prepare material for publication: PLATON (Spek, 2020).

4-(2-Methoxyphenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate

Crystal data
C_{11}H_{17}N_{2}O^{+}·C_{7}H_{3}N_{2}O_{7}^{−}
Mr = 420.38
Triclinic, P1
a = 7.3729 (6) Å
b = 8.4842 (7) Å
c = 15.5411 (13) Å
α = 88.954 (4)°
β = 81.333 (4)°
g = 89.352 (3)°
V = 960.85 (14) Å³
Z = 2
F(000) = 440
D_x = 1.453 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 3479 reflections
θ = 2.7–21.4°
µ = 0.12 mm⁻¹
T = 296 K
BLOCK, yellow
0.18 × 0.15 × 0.10 mm

Data collection
Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and ϕ scan
Absorption correction: multi-scan (SADABS; Bruker, 2012)
T_{min} = 0.608, T_{max} = 0.745
24028 measured reflections
3513 independent reflections
2035 reflections with I > 2σ(I)
R_{int} = 0.084
θ_{max} = 25.4°, θ_{min} = 2.4°
h = −8→8
k = −10→10
l = −18→18

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.048
wR(F²) = 0.140
S = 1.02
3513 reflections
294 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(F²) + (0.0588P)² + 0.1844P]
where P = (F² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.23 e Å⁻³
Δρ_{min} = −0.21 e Å⁻³

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Extinction correction: SHELXL-2018/3 (Sheldrick 2015b),
$F_c^\text{c} = kF_c[1+0.001xF_c^2/\lambda^2\sin(2\theta)]^{1/4}$
Extinction coefficient: 0.050 (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 ($\AA^2$)**

|    | $x$      | $y$      | $z$      | $U_{	ext{iso}}^\text{*}$ or $U_{	ext{eq}}$ | Occ. (<1) |
|----|----------|----------|----------|-------------------------------------------|-----------|
| C1 | 0.2780   | 0.2159   | 0.07284  | 0.0394 (6)                                | 0.0394 (6) |
| C2 | 0.3262   | 0.1599   | −0.00995 | 0.0403 (6)                                | 0.0403 (6) |
| H2 | 0.2459   | 0.096812 | −0.03449 | 0.048*                                    | 0.048*    |
| C3 | 0.4942   | 0.1982   | −0.05608 | 0.0381 (6)                                | 0.0381 (6) |
| C4 | 0.6246   | 0.2917   | −0.02095 | 0.0386 (6)                                | 0.0386 (6) |
| C5 | 0.5670   | 0.3451   | 0.06598  | 0.0357 (6)                                | 0.0357 (6) |
| C6 | 0.3973   | 0.3079   | 0.11107  | 0.0402 (6)                                | 0.0402 (6) |
| H6 | 0.36270  | 0.344693 | 0.166821 | 0.048*                                    | 0.048*    |
| C7 | 0.6924   | 0.4410   | 0.10897  | 0.0437 (6)                                | 0.0437 (6) |
| C8 | 0.7613   | 0.7961   | 0.32628  | 0.0453 (7)                                | 0.0453 (7) |
| H8A| 0.714529 | 0.899464 | 0.344577 | 0.054*                                    | 0.054*    |
| H8B| 0.659791 | 0.734255 | 0.312652 | 0.054*                                    | 0.054*    |
| C9 | 0.9053   | 0.8122   | 0.24697  | 0.0547 (8)                                | 0.0547 (8) |
| H9A| 0.851985 | 0.862088 | 0.199882 | 0.066*                                    | 0.066*    |
| H9B| 1.003753 | 0.878425 | 0.260013 | 0.066*                                    | 0.066*    |
| C10| 1.0516   | 0.5698   | 0.29246  | 0.0528 (7)                                | 0.0528 (7) |
| C11| 1.157647 | 0.624708 | 0.306580 | 0.063*                                    | 0.063*    |
| H10A| 1.090079 | 0.464033 | 0.274758 | 0.063*                                    | 0.063*    |
| C12| 0.9068   | 0.5609   | 0.37158  | 0.0449 (7)                                | 0.0449 (7) |
| H11A| 0.804693 | 0.498591 | 0.359076 | 0.054*                                    | 0.054*    |
| H11B| 0.957081 | 0.510002 | 0.419258 | 0.054*                                    | 0.054*    |
| C13| 0.7467   | 0.7377   | 0.48169  | 0.0349 (6)                                | 0.0349 (6) |
| H13| 0.6760   | 0.6130   | 0.53447  | 0.0438 (6)                                | 0.0438 (6) |
| C14| 0.5896   | 0.6383   | 0.61938  | 0.0586 (8)                                | 0.0586 (8) |
| C15| 0.542766 | 0.553503 | 0.654172 | 0.070*                                    | 0.070*    |
| C16| 0.5738   | 0.7860   | 0.65120  | 0.0644 (9)                                | 0.0644 (9) |
| H15| 0.514640 | 0.802436 | 0.707561 | 0.077*                                    | 0.077*    |
| C17| 0.6448   | 0.9121   | 0.60065  | 0.0572 (8)                                | 0.0572 (8) |
| H16| 0.634257 | 1.013138 | 0.623208 | 0.069*                                    | 0.069*    |
| C18| 0.7317   | 0.8895   | 0.51661  | 0.0418 (6)                                | 0.0418 (6) |
| H18A| 0.667923 | 1.193863 | 0.505074 | 0.117*                                    | 0.117*    |
| H18B| 0.855921 | 1.233884 | 0.447752 | 0.117*                                    | 0.117*    |
| H18C| 0.851231 | 1.172510 | 0.543815 | 0.117*                                    | 0.117*    |
### Atomic displacement parameters (Å²)

|   | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| C1 | 0.0373 (14) | 0.0422 (15) | 0.0384 (14) | −0.0082 (11) | −0.0043 (11) | 0.0015 (11) |
| C2 | 0.0411 (15) | 0.0404 (15) | 0.0405 (14) | −0.0013 (12) | −0.0097 (12) | −0.0042 (11) |
| C3 | 0.0407 (15) | 0.0418 (15) | 0.0325 (13) | 0.0016 (11)  | −0.0071 (11) | −0.0069 (11) |
| C4 | 0.0351 (14) | 0.0442 (15) | 0.0359 (14) | −0.0003 (12) | −0.0030 (11) | −0.0010 (11) |
| C5 | 0.0371 (15) | 0.0383 (14) | 0.0317 (13) | −0.0034 (11) | −0.0044 (11) | −0.0012 (10) |
| C6 | 0.0443 (16) | 0.0433 (15) | 0.0323 (13) | −0.0018 (12) | −0.0035 (11) | −0.0019 (11) |
| C7 | 0.0445 (16) | 0.0525 (17) | 0.0342 (14) | −0.0060 (13) | −0.0057 (12) | −0.0039 (12) |
| C8 | 0.0415 (15) | 0.0600 (17) | 0.0341 (14) | 0.0018 (13)  | −0.0045 (12) | 0.0008 (12)  |
| C9 | 0.0509 (18) | 0.075 (2)   | 0.0384 (15) | −0.0005 (15) | −0.0074 (13) | 0.0067 (13)  |
| C10| 0.0530 (18) | 0.0567 (18) | 0.0472 (16) | 0.0080 (14)  | −0.0015 (13) | −0.0198 (13) |
| C11| 0.0485 (16) | 0.0438 (16) | 0.0425 (14) | −0.0002 (12) | −0.0063 (12) | −0.0082 (12) |
| C12| 0.0317 (13) | 0.0407 (14) | 0.0329 (13) | 0.0011 (11)  | −0.0064 (10) | −0.0044 (11) |
| C13| 0.0420 (15) | 0.0453 (16) | 0.0435 (15) | −0.0025 (12) | −0.0048 (12) | 0.0021 (12)  |
| C14| 0.0474 (17) | 0.082 (2)   | 0.0441 (17) | −0.0007 (15) | −0.0009 (13) | 0.0173 (16)  |
| C15| 0.059 (2)   | 0.097 (3)   | 0.0361 (16) | 0.0148 (18)  | −0.0058 (14) | −0.0090 (17) |
| C16| 0.0563 (19) | 0.063 (2)   | 0.0547 (18) | 0.0131 (15)  | −0.0133 (15) | −0.0260 (15) |
| C17| 0.0377 (15) | 0.0451 (16) | 0.0441 (15) | 0.0018 (12)  | −0.0097 (12) | −0.0086 (12) |
| C18| 0.069 (2)   | 0.0371 (18) | 0.135 (3)   | 0.0035 (15)  | −0.034 (2)   | −0.0234 (18) |
| N1 | 0.0508 (15) | 0.0625 (16) | 0.0497 (14) | −0.0172 (12) | 0.0025 (12)  | −0.0061 (12) |
| O4A| 0.062 (5)   | 0.135 (8)   | 0.039 (2)   | −0.029 (4)   | 0.005 (3)    | −0.027 (4)   |
| N3 | 0.0492 (15) | 0.0839 (19) | 0.0336 (13) | −0.0120 (14) | −0.0018 (12) | −0.0168 (12) |
| N4 | 0.0427 (12) | 0.0379 (12) | 0.0291 (10) | 0.0057 (9)   | −0.0038 (9)  | −0.0034 (8)  |
| O1 | 0.0652 (14) | 0.1054 (18) | 0.0711 (14) | −0.0428 (13) | −0.0005 (11) | −0.0193 (12) |
| O2 | 0.0637 (14) | 0.1058 (18) | 0.0572 (13) | −0.0293 (12) | 0.0162 (11)  | −0.0244 (12) |
| O3 | 0.0679 (14) | 0.0792 (15) | 0.0646 (13) | −0.0108 (12) | −0.0125 (11) | −0.0313 (11) |
| O5 | 0.0585 (12) | 0.0813 (14) | 0.0388 (10) | −0.0220 (10) | −0.0024 (9)  | −0.0154 (9)  |
| O6 | 0.0467 (12) | 0.0858 (15) | 0.0409 (11) | −0.0250 (10) | 0.0027 (9)   | −0.0117 (10) |
| O7 | 0.0413 (11) | 0.0782 (14) | 0.0374 (10) | −0.0139 (9)  | 0.0025 (8)   | −0.0111 (9)  |
Geometric parameters (Å, °)

|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| O8 | 0.0570 (12) | 0.0373 (11) | 0.0730 (13) | −0.0040 (9) | −0.0105 (10) | −0.0069 (9) |
| N2 | 0.0423 (14) | 0.0683 (17) | 0.0439 (14) | 0.0018 (12) | −0.0067 (12) | −0.0136 (12) |
| O4B | 0.048 (7) | 0.138 (16) | 0.078 (12) | −0.028 (8) | 0.023 (7) | −0.052 (9) |

Geometric parameters (Å, °)

|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| C1—C2 | 1.374 (3) | C11—H11B | 0.9700 |
| C1—C6 | 1.385 (3) | C12—C13 | 1.384 (3) |
| C1—N1 | 1.453 (3) | C12—C17 | 1.403 (3) |
| C2—C3 | 1.374 (3) | C12—N4 | 1.416 (3) |
| C2—H2 | 0.9300 | C13—C14 | 1.395 (3) |
| C3—C4 | 1.429 (3) | C13—H13 | 0.9300 |
| C3—N2 | 1.460 (3) | C14—C15 | 1.353 (4) |
| C4—O7 | 1.283 (3) | C14—H14 | 0.9300 |
| C4—C5 | 1.434 (3) | C15—C16 | 1.376 (4) |
| C5—C6 | 1.373 (3) | C15—H15 | 0.9300 |
| C5—C7 | 1.479 (3) | C16—C17 | 1.381 (3) |
| C6—H6 | 0.9300 | C16—H16 | 0.9300 |
| C7—O5 | 1.225 (3) | C17—O8 | 1.367 (3) |
| C7—O6 | 1.309 (3) | C18—O8 | 1.422 (3) |
| C8—N4 | 1.465 (3) | C18—H18A | 0.9600 |
| C8—C9 | 1.506 (3) | C18—H18B | 0.9600 |
| C8—H8A | 0.9700 | C18—H18C | 0.9600 |
| C8—H8B | 0.9700 | N1—O1 | 1.217 (3) |
| C9—N3 | 1.492 (4) | N1—O2 | 1.225 (3) |
| C9—H9A | 0.9700 | O4A—N2 | 1.225 (8) |
| C9—H9B | 0.9700 | N3—H3A | 0.94 (4) |
| C10—N3 | 1.487 (3) | N3—H3B | 0.97 (3) |
| C10—C11 | 1.503 (3) | O3—N2 | 1.215 (3) |
| C10—H10A | 0.9700 | O6—H6A | 1.13 (4) |
| C10—H10B | 0.9700 | O7—H6A | 1.38 (4) |
| C11—N4 | 1.452 (3) | N2—O4B | 1.228 (13) |
| C11—H11A | 0.9700 |   |   |

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| Bond                  | Angle (°)  | Bond                  | Angle (°)  |
|----------------------|-----------|----------------------|-----------|
| C4—C5—C7            | 119.7 (2) | C17—C16—H16          | 119.8     |
| C5—C6—C1            | 120.5 (2) | O8—C17—C16           | 124.5 (2) |
| C5—C6—H6            | 119.8     | O8—C17—C12           | 115.3 (2) |
| C1—C6—H6            | 119.8     | C16—C17—C12          | 120.2 (2) |
| O5—C7—O6            | 120.0 (2) | O8—C18—H18A          | 109.5     |
| O5—C7—C5            | 123.1 (2) | O8—C18—H18B          | 109.5     |
| O6—C7—C5            | 116.8 (2) | H18A—C18—H18B        | 109.5     |
| N4—C8—C9            | 109.1 (2) | O8—C18—H18C          | 109.5     |
| N4—C8—H8A           | 109.9     | H18A—C18—H18C        | 109.5     |
| N4—C8—H8B           | 109.9     | O1—N1—O2             | 122.7 (2) |
| C9—C8—H8B           | 109.9     | O1—N1—C1             | 118.9 (2) |
| H8A—C8—H8B          | 108.3     | O2—N1—C1             | 118.4 (2) |
| N3—C9—C8            | 110.1 (2) | C10—N3—C9            | 110.9 (2) |
| N3—C9—H9A           | 109.6     | C10—N3—H3A           | 107.2     |
| C8—C9—H9A           | 109.6     | C9—N3—H3A            | 112.2     |
| N3—C9—H9B           | 109.6     | C10—N3—H3B           | 115.4 (18)|
| C8—C9—H9B           | 109.6     | C9—N3—H3B            | 104.9 (17)|
| H9A—C9—H9B          | 108.1     | H3A—N3—H3B           | 107.3     |
| N3—C10—C11          | 110.8 (2) | C12—N4—C11           | 117.54 (18)|
| N3—C10—H10A         | 109.5     | C12—N4—C8            | 115.96 (18)|
| C11—C10—H10A        | 109.5     | C11—N4—C8            | 110.66 (19)|
| N3—C10—H10B         | 109.5     | C7—O6—H6A            | 106.5 (19)|
| C11—C10—H10B        | 109.5     | C4—O7—H6A            | 102.6 (15)|
| H10A—C10—H10B       | 108.1     | C17—O8—C18           | 118.5 (2) |
| N4—C11—C10          | 109.9 (2) | O3—N2—O4A            | 122.2 (7) |
| N4—C11—H11A         | 109.7     | O3—N2—O4B            | 118.7 (15)|
| C10—C11—H11A        | 109.7     | O3—N2—C3             | 118.5 (2) |
| N4—C11—H11B         | 109.7     | O4A—N2—C3            | 118.2 (8) |
| C10—C11—H11B        | 109.7     | O4B—N2—C3            | 119.7 (14)|
| H11A—C11—H11B       | 108.2     |                     |           |

| Bond                  | Angle (°)  | Bond                  | Angle (°)  |
|----------------------|-----------|----------------------|-----------|
| C6—C1—C2—C3         | −1.0 (4)  | C15—C16—C17—C12     | 0.6 (4)   |
| N1—C1—C2—C3         | 179.6 (2) | C13—C12—C17—O8      | 177.5 (2) |
| C1—C2—C3—C4         | 1.4 (4)   | N4—C12—C17—O8       | 1.3 (3)   |
| C1—C2—C3—N2         | −179.4 (2)| C13—C12—C17—C16     | −1.4 (4)  |
| C2—C3—C4—O7         | 179.3 (2) | N4—C12—C17—C16      | −177.7 (2)|
| N2—C3—C4—O7         | 0.2 (4)   | C2—C1—N1—O1         | −0.8 (4)  |
| C2—C3—C4—C5         | −0.8 (4)  | C6—C1—N1—O1         | 179.8 (3) |
| N2—C3—C4—C5         | −179.9 (2)| C2—C1—N1—O2         | 178.7 (2) |
| O7—C4—C5—C6         | 179.6 (2) | C6—C1—N1—O2         | −0.7 (4)  |
| C3—C4—C5—C6         | −0.3 (3)  | C11—C10—N3—C9       | 54.4 (3)  |
| O7—C4—C5—C7         | −0.9 (4)  | C8—C9—N3—C10        | −55.3 (3) |
| C3—C4—C5—C7         | 179.2 (2) | C13—C12—N4—C11      | −14.9 (3) |
| C4—C5—C6—C1         | 0.7 (4)   | C17—C12—N4—C11      | 161.1 (2) |
| C7—C5—C6—C1         | −178.8 (2)| C13—C12—N4—C8       | 119.2 (3) |
| C2—C1—C6—C5         | 0.0 (4)   | C17—C12—N4—C8       | −64.7 (3) |
| N1—C1—C6—C5         | 179.3 (2) | C10—C11—N4—C12      | −162.6 (2)|
C6—C5—C7—O5  −1.3 (4)  C10—C11—N4—C8  61.0 (3)
C4—C5—C7—O5  179.1 (2)  C9—C8—N4—C12  161.0 (2)
C6—C5—C7—O6  178.9 (2)  C9—C8—N4—C11  −61.9 (3)
C4—C5—C7—O6  −0.6 (4)  C16—C17—O8—C18  −3.3 (4)
N4—C8—C9—N3  58.4 (3)  C12—C17—O8—C18  177.8 (2)
N3—C10—C11—N4  −56.8 (3)  C2—C3—N2—O3  −13.1 (3)
C17—C12—C13—C14  1.1 (4)  C4—C3—N2—O3  166.1 (2)
N4—C12—C13—C14  177.1 (2)  C2—C3—N2—O4A  155.4 (6)
C12—C13—C14—C15  0.1 (4)  C4—C3—N2—O4A  −25.4 (7)
C13—C14—C15—C16  −0.9 (4)  C2—C3—N2—O4B  −172.7 (12)
C14—C15—C16—C17  0.5 (4)  C4—C3—N2—O4B  6.4 (13)
C15—C16—C17—O8  −178.2 (2)

Hydrogen-bond geometry (Å, °)

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|----------|-------|--------|--------|---------|
| O6—H6A···O7 | 1.14 (3) | 1.37 (3) | 2.448 (2) | 154 (3) |
| N3—H3A···O5 | 0.94 (4) | 2.02 (4) | 2.936 (3) | 165 (3) |
| N3—H3A···O6 | 0.94 (4) | 2.44 (3) | 3.153 (3) | 133 (2) |
| N3—H3A···O7i | 0.97 (3) | 1.83 (3) | 2.787 (3) | 166 (3) |
| C2—H2···O1i  | 0.93 | 2.66 | 3.581 (3) | 174 |
| C9—H9A···O3ii | 0.97 | 2.44 | 3.254 (4) | 141 |
| C10—H10B···O2iv | 0.97 | 2.43 | 3.319 (3) | 152 |
| C10—H10A···O4Aiv | 0.97 | 2.50 | 3.118 (10) | 122 |
| C14—H14···O5v | 0.93 | 2.74 | 3.481 (3) | 137 |
| C18—H18C···N4vi | 0.96 | 2.74 | 3.552 (4) | 143 |

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