Crystal structure and Hirshfeld surface analysis of the hydrated 2:1 adduct of piperazine-1,4-diium 3,5-dinitro-2-oxidobenzoate and piperazine

Veerappan Subha, a Thangaraj Seethalakshmi,a* Thangavelu Balakrishnan, b M Judith Percinoc and Perumal Venkatesan d*

a PG and Research Department of Physics, Government Arts College (Autonomous and affiliated to Bharathidasan University, Tiruchirappalli), Thanthonimalai, Karur-639 005, Tamil Nadu, India, b Crystal Growth Laboratory, PG and Research Department of Physics, Periyar EVR Government College (Autonomous and affiliated to Bharathidasan University, Tiruchirappalli), Tiruchirappalli-620 023, Tamil Nadu, India, c Unidad de Polímeros y Electrónica Orgánica, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Val3-Ecocampus Valsequillo, Independencia O2 Sur 50, San Pedro Zacachimalpa, 72960, Puebla, Mexico, and d Department of Chemistry, Srimad Andavan Arts and Science College (Autonomous), Tiruchirappalli-620 005, Tamil Nadu, India. *Correspondence e-mail: seethabala@gmail.com, venkat@andavancollege.ac.in

The crystal structure of the adduct piperazine-1,4-diium 3,5-dinitro-2-oxidobenzoate–piperazine–water (2/1/2) shows the existence of a 3,5-dinitrosalicylate dianion (DNSA2−) and a protonated piperazine-1,4-diium cation (PIP2+) along with a piperazine molecule. The formula of the title adduct in the asymmetric unit is 2C4H12N22+/C12C7H2N2O72−/C0 /C1C4H10N2/C12H2O with Z = 1. The piperazine ring in the piperazine-1,4-diium cation and in the neutral piperazine molecule adopt chair conformations. All O atoms in the DNSA2− moiety and the water molecule act as hydrogen-bonding acceptors for various intermolecular O–H⋯O, N–H⋯O and C–H⋯O interactions, which stabilize the crystal structure. Various supramolecular architectures formed by the different intermolecular interactions are discussed. The relative contribution of various intermolecular contacts is analysed with the aid of two-dimensional (full and decomposed) fingerprint plots, indicating that H⋯O/O⋯H (50.2%) and H⋯H (36.2%) contacts are the major contributors to the stabilization of the crystal structure.

1. Chemical context

3,5-Dinitrosalicylic acid (DNSA) is one of the most prevalent proton-donor molecules for forming organic salts with different Lewis bases. There are more than 150 examples found in the Cambridge Structural Database (CSD, Version 5.41, update of August 2020; Groom et al., 2016) containing the DNSA moiety. Among them, there are 20 structures containing the neutral DNSA molecule with the rest being proton-transfer salts of the monoanion DNSA− and the dianion DNSA2−. The loss of both acidic protons from the carboxylic acid (−COOH) and phenolic (−OH) groups in the DNSA molecule forms the DNSA2− dianion. In general, the removal of the acidic proton from the −COOH group in DNSA [pKₐ(COOH) = 2.2] would be expected to occur more readily than the removal of the proton from the phenolic −OH group [pKₐ(OH) = 6.8]. Consequently, the DNSA molecule easily forms 1:1 proton-transfer salts with aliphatic amines (Smith et al., 2002), monocyclic, polycyclic aromatic and heteroaromatic amines (Smith et al., 2003, 2007), substituted primary and secondary amines and phenylenediamines (Issa...
et al., 1980, 1981; Hindawy et al., 1980). However, 1:2 proton-transfer salts of DNSA containing the DNSA$^{2–}$ dianion are much fewer in number. Briefly, the structurally characterized 1:2 proton-transfer salts were formed with ethylenediamine (EGUVAD; Smith et al., 2002), cyclohexylamine (ROFLIJ; Gao et al., 2014), piperidine (XEBFAM; Smith et al., 2006) and diethylenetriamine (ZONBIP; Chen et al., 2014). Among the four DNSA$^{2–}$ salts, the asymmetric unit of ROFLIJ consists of two cyclohexylaminium cations and a DNSA$^{2–}$ moiety while one dication (diethylenetriaminium dication in ZONBIP or ethylenediaminum dication in EGUVAD), DNSA$^{2–}$ and one water molecule are found in the asymmetric unit of ZONBIP or EGUVAD. The dianions (DNSA$^{2–}$), mono anions (DNSA$^{1–}$), and partially substituted mono picate anion along with three piperidinium cations and a water molecule are found in the asymmetric unit of XEBFAM. The crystal structures (EGUVAD, ROFLIJ, ZONBIP, and XEBFAM) of these DNSA$^{2–}$ salts are mainly stabilized by N—H···O, C—H···π and π—π interactions. On the other hand, co-crystals of DNSA were reported with phenazine (Senthil Kumar et al., 2002), urea or substituted ureas (Smith et al., 1997, 2000; Bott et al., 2000) and trans-1,4-dithiane-1,4-dioxide (Senthil Kumar et al., 2002b). In this study, the crystal structure, Hirshfeld surface (HS) analysis, structural features, and various intermolecular interactions that exist in the monohydrated 1:1 adduct of bis(piperazine-1,4-diium) 3,5-dinitro-2-oxido-benzoate and piperazine (I) are reported. The various intermolecular interactions and the relative contribution of various intermolecular contacts are compared with a similar structure (XEBFAM).

2. Structural commentary

The title compound crystallizes in the triclinic space group $P\overline{1}$ with $Z = 1$ with the asymmetric unit comprising two DNSA$^{2–}$ ions, two protonated piperazine-1,4-diium cations, and a neutral piperazine molecule along with two water molecules and having the formula $C_2H_8N_2^{2+}-2C_4H_7N_2O_7^{2–}$ or $C_4H_8N_2·2H_2O$. The atom-numbering scheme and molecular structure of (I) are shown in Fig. 1. The distance between the phenolate oxygen atom, $O^7$, and the carboxylate oxygen atom, $O^6$, in the anion is 2.770 (2) Å and is comparable to that found earlier reported dianionic salts (2.735–2.912 Å). This, together with the absence of a locateable H atom between these oxygen atoms ($O^6$ and $O^7$) is good evidence for the existence of the dianion in this adduct. One of the nitro groups (N1, O1, and O2) and the phenolate oxygen atom, $O^7$ are coplanar with the mean plane of the phenyl ring, while the second nitro group (N2, O3, and O4) and the carboxylate group (C7, O5, and O6) are slightly twisted from the above plane. These twists are measured by the dihedral angles between the mean plane of the phenyl ring and those of the second nitro and carboxylate groups of 19.4 (3) and 24.4 (3)$^\circ$, respectively, and by the $C_2$—$C_3$—$N_2$—$O_4$ and $C_6$—$C_5$—$C_7$—$O_6$ torsion angles of 161.1 (2)$^\circ$ and 156.6 (2)$^\circ$, respectively. These slight twists of the nitro and carboxylate groups are due to the differences in the intermolecular hydrogen-bonding patterns in which the $N_2/O_3/O_4$ and $C_7/O_6/O_7$ groups participate as compared to the N1/O1/O2 group.

The piperazine rings in the piperazine-1,4-diium cations and the neutral piperazine molecule in (I) adopt chair conformatio with puckering parameters (Cremer & Pope, 1975), $Q = 0.563$ (3) Å, $\theta = 180.0$ (3)$^\circ$, $\varphi = 0^\circ$ for the the N3 ring, $Q = 0.571$ (3) Å, $\theta = 1.87$ (1)$^\circ$, $\varphi = 0^\circ$ for the N5 ring and $Q = 0.517$ (3) Å, $\theta = 180.0$ (3)$^\circ$, $\varphi = 0^\circ$ for the N4 ring in the neutral PIP molecule.

Additionally, we carried out a structural overlay study of the DNSA$^{2–}$ units in the di-anionic salts found in (I), EGUVAD (Smith et al., 2002), ROFLIJ (Gao et al., 2014), ZONBIP (Chen et al., 2014) and XEBFAM (Smith et al., 2006) using the six carbon atoms in the phenyl ring in DNSA$^{2–}$ as the basis. The DNSA$^{2–}$ units in all five structures overlay quite well with one another. The maximum r.m.s.d. observed between any molecular pair is 0.0095 Å (for ROFLIJ and ZONBIP). However, the slight rotation of the nitro and carboxylate groups in the DNSA$^{2–}$ unit (Fig. 2) may well be due to the oxygen atoms in these functional groups participating in different intermolecular interactions in their crystal structures as noted above.

In the unit cell, two piperazine-1,4-diium cations and one DNSA$^{2–}$ anion are linked via N3—H3B···O7, N3—H3B···O4 and N5—H5B···O5 hydrogen bonds (Table 1). Furthermore, the second piperazine-1,4-diium cation is linked...
to a piperazine molecule through a water molecule via N5—H5A···O8 and O8—H8C···N4 hydrogen bonds.

### 3. Supramolecular features

The O1—O4 oxygen atoms in both nitro groups and the oxygen atoms in the carboxylate (O6 and O7) and the phenolate groups (O8) in the DNSA\textsuperscript{2−} ion act as acceptors for various intermolecular N—H···O and C—H···O interactions (Table 1). The atoms O1 and O2 in one nitro group form C8—H8A···O1 and C9—H9B···O2 hydrogen bonds, which link neighbouring DNSA\textsuperscript{2−} and PIP\textsuperscript{2+} ions with \( R_2^2(8) \) motifs. The O6 and O7 atoms (from phenolate and carboxylate groups) form a cyclic bidentate hydrogen bond with the H3A···N3 unit N3—H3A···O6 and N3—H3A···O7 with an \( R_2^2(6) \) motif. This \( R_2^2(6) \) motif is a common one in proton-transfer compounds of DNSA and it helps to extend their secondary structures (Smith et al., 2007). These two ring motifs \( [R_2^2(8)] \) and \( R_2^2(6) \) link a DNSA\textsuperscript{2−} anion and one of the PIP\textsuperscript{2+} cations into a molecular chain, which propagates parallel to the c axis (Fig. 3a). Furthermore, N3—H3A···O6, N3—H3A···O7, N3—H3B···O4 and N3—H3B···O7 interactions link two neighbouring molecular chains through the PIP\textsuperscript{2+} cations into a sheet-like architecture containing two \( R_2^2(6) \) motifs. Also involved is a weak C9—H9B···O2 interaction (Fig. 3b) which, although quite long, has precedent in recent work (Sosa-Rivadeneyra et al., 2020). The water molecule links the second piperazine-1,4-diium cation and a piperazine molecule, PIP through O8—H8C···N4 and N5—H5A···O8 hydrogen bonds to form a molecular chain (Fig. 4). Additional O···H···O, N···H···O and C···H···O hydrogen bonds produce a three-dimensional framework (Fig. 5).

### 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) of the title adduct and generate two-dimensional fingerprint plots (full and decomposed, 2D-FP; Spackman & McKinnon, 2002; Spackman & Jayatilaka, 2009). The HS and 2D-FP were used to provide additional information and to quantify the intermolecular interactions using distinct colours and intensities to indicate short and long contacts, as well as the relative contribution of the different interactions in the solid-state (Venkatesan et al., 2015, 2016). The HS is plotted over \( d_{norm} \) in the range \(-0.7438\) to \(1.3459\) a.u. and two views (front and back) of the HS are shown in Fig. 6. Bright-red spots on the HS confirm the existence of hydrogen-bonding contacts in the

Table 1

| D—H ···A | D—H | H···A | D···A | D—H ···A |
|-----------|------|-------|-------|----------|
| O8—H82···O6\textsuperscript{ii} | 0.84 (4) | 1.98 (4) | 2.807 (3) | 173 (4) |
| N3—H3A···O6\textsuperscript{ii} | 0.90 (2) | 1.92 (2) | 2.752 (3) | 153 (3) |
| N3—H3A···O7\textsuperscript{ii} | 0.90 (2) | 2.33 (3) | 2.940 (3) | 125 (2) |
| N3—H3B···O4\textsuperscript{iv} | 0.90 (2) | 2.50 (2) | 3.142 (3) | 129 (2) |
| N3—H3B···O7\textsuperscript{iv} | 0.90 (2) | 1.84 (2) | 2.696 (3) | 157 (3) |
| N4—H4···O3 | 0.860 (17) | 2.59 (2) | 3.304 (3) | 141 (2) |
| N5—H5A···O8 | 0.900 (17) | 1.83 (2) | 2.712 (3) | 166 (3) |
| N5—H5B···O5\textsuperscript{v} | 0.918 (17) | 1.74 (2) | 2.637 (3) | 165 (3) |
| O8—H8C···N4 | 0.84 (4) | 1.88 (4) | 2.717 (3) | 169 (3) |
| C8—H8A···O1 | 0.97 | 2.49 | 3.169 (3) | 151 |
| C9—H9B···O2 | 0.97 | 2.67 | 3.482 (3) | 141 |
| C12—H12A···O2\textsuperscript{v} | 0.97 | 2.58 | 3.455 (4) | 151 |
| C12—H12B···O5\textsuperscript{v} | 0.97 | 2.59 | 3.353 (4) | 136 |

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

Figure 2

Superimposition of DNSA\textsuperscript{2−} units in (I) and its analogs [colour codes: EGUVAD (green), ROFLJJ (blue), ZONBP (red) and XEBFAM (magenta)].

Figure 3

(a) Part of the crystal structure of (I) showing the \( R_2^2(8) \) and \( R_2^2(6) \) motifs formed by intermolecular N—H···O and C—H···O hydrogen bonds (see Table 1), which link the neighbouring anionic unit (DNSA\textsuperscript{2−}) and cationic moiety (PIP\textsuperscript{2+}) into a molecular chain, which propagates parallel to the c axis. (b) Part of the crystal structure of (I) showing the sheet-like architecture.
crystal structure. The 2D FP plots show that the relative contributions of the various non-covalent contacts (Fig. 7). O···H contacts contribute most (50.2%) to the crystal packing while the second significant contact is H···H, which contributes 36.2%. The relative contributions of C···O, C···H, N···H, C···N and C···C contacts are 4.6%, 2.9%, 2.7%, 1.7% and 1.0%, respectively. In the XEBFAM structure, the relative contributions of O···H, H···H, C···O, C···H, N···H, C···N and C···C contacts are 49.7%, 37.6%, 3.6%, 2.7%, 1.3%, 0.7%, and 2.1%, respectively. The relative contribution of various interatomic contacts in XEBFAM and the title adduct (I) are similar, even though the compounds have different compositions as discussed earlier.

5. Database survey
A search of the Cambridge Structural Database (CSD, Version 5.41, update of August 2020; Groom et al., 2016) using Conquest (Bruno et al., 2002) for the neutral DNSA molecule found 20 structures of co-crystals, including those with urea (NUHYAQQ; Smith et al., 1997), trans-1,4-dithiane-1,4-dioxide (OGAHEJ; Senthil Kumar et al., 2002a), 4-(dimethylamino)benzaldehyde (SUYYYW; Jin et al., 2016) and dioxane (GORXAM, GORXAM01, GORXEQ, GORXEO01; Senthil Kumar et al., 1999). For monoanions of DNSA, a total of 62 structures containing the carboxylate (COO···O) moiety and 70 containing the phenolate anion (O···O) were found. As mentioned earlier, the removal of the carboxylic acid proton is expected to be easier than the removal of the proton from the phenolic –OH group in DNSA so it is somewhat surprising that the number of crystal structures containing phenolate ions is larger than those containing carboxylate ions. These seemingly conflicting results may suggest that the formation and stability of the salts with phenolate ions of the DNSA moiety is governed by intermolecular interactions in the crystal. However, it has been pointed out (Fábry, 2018), that since the monoanions generally contain a hydrogen atom bridging between the the carboxylate and phenolate oxygen atoms, how one formulates the anion (carboxylate or phenolate) depends critically on how this hydrogen atom is treated in the refinement so that some of the reported phenolate structures may actually be carboxylates.

As mentioned earlier, there are four structures of the dianionic salt of DNSA, which are formed with ethylenediamine (EGUVAD; Smith et al., 2002), cyclohexylamine (ROFLIJ; Gao et al., 2014), piperidine (XEBFAM; Smith et al., 2006) and diethylenetriamine (ZONBIP; Chen et al., 2014). The cation (ethylenediammonium or 2,2'-iminodiethanaminium) and dianion (DNSA·2-) along with a water molecule are connected via intermolecular O···H, N···H and C···O interactions in the asymmetric unit of EGUVAD and ZONBIP. An N···H···O hydrogen bond connects the cyclohexylaminonium moiety and the dianion in ROFLIJ, while the piperazine-1,4-diium cations form a mixed salt with the dianion and monoanion of 3,5-dinitrosalicylate along with a picrate anion in XEBFAM. The cation and anions are linked via O···H, N···H···O and C···H···O interactions in XEBFAM.

6. Synthesis and crystallization
The title adduct was synthesized from 3,5-dinitrosalicylic acid (1 mmol, 228 mg) and piperazine (5 mmol, 426 mg, 0.5 mL)
dissolved in 50 mL of methanol and stirred well for 6 h. The homogeneous solution was filtered and the solution was allowed to evaporate slowly at room temperature. Red block-like crystals suitable for single X-ray diffraction were harvested after a growth period of 10 days.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The amino H atoms and O-bound H atoms were refined with DFIX instructions. The C-bound H atoms were included in calculated positions and treated as riding atoms: C–H = 0.93–0.98 Å, O–H = 0.82 Å with \( U_{iso}(H) = 1.2U_{eq}(C) \) and \( U_{iso}(H) = 1.5U_{eq}(O) \).

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Computer programs: APEX2, SAINT and XPREP (Bruker, 2012), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and PLATON (Spek, 2020).

Table 2

| Experimental details |
|----------------------|
| Crystal data Chemical formula | \( \text{C}_4\text{H}_7\text{N}_2^+\cdot\text{C}_3\text{H}_7\text{N}_2\text{O}_7^2^- \cdot 0.5\text{C}_6\text{H}_{10}\text{N}_2\text{H}_2\text{O} \) |
| Mass | 375.35 |
| Crystal system, space group | Triclinic, \( P \text{T} \) |
| Temperature (K) | 296 |
| No. of measured, independent and observed \([ I > 2\sigma(I)] \) reflections | 15411, 3265, 1835 |
| \( R_{max}, I_{max} \) | 0.049, 0.133, 1.02 |
| No. of reflections | 3265 |
| No. of parameters | 264 |
| No. of restraints | 7 |
| H-atom treatment | H atoms treated by a mixture of riding atoms: C—H = 0.93–0.98 Å, O—H = 0.82 Å with \( U_{iso}(H) = 1.2U_{eq}(C) \) and \( U_{iso}(H) = 1.5U_{eq}(O) \). |
| \( \Delta \rho_{max}, \Delta \rho_{min} \) (e Å\(^{-3}\)) | 0.24, –0.21 |

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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: Mercury (Macrae et al., 2020); software used to prepare material for publication: PLATON (Spek, 2020).

Bis(piperazine-1,4-diium)-3,5-dinitro-2-oxidobenzoate–piperazine (1/1)

Crystal data

C$_{4}$H$_{12}$N$_{2+}$·C$_{7}$H$_{2}$N$_{2}$O$_{7}$·0.5C$_{4}$H$_{10}$N$_{2}$·H$_{2}$O  
Mr = 375.35  
Triclinic, $P\bar{1}$  
$\alpha$ = 6.6211 (16) Å  
$\beta$ = 11.891 (3) Å  
$\gamma$ = 12.389 (3) Å  
$\alpha$ = 116.320 (5)$^\circ$  
$\beta$ = 98.878 (5)$^\circ$  
$\gamma$ = 98.390 (5)$^\circ$  
$V$ = 838.1 (3) Å$^3$  
$Z$ = 2  
$F(000)$ = 396  
$D_\text{x}$ = 1.487 Mg m$^{-3}$  
Cell parameters from 2314 reflections  
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å  
Cell parameters from 2314 reflections

Data collection

Bruker Kappa APEXII diffractometer  
Radiation source: fine-focus sealed tube  
$\omega$ and $\varphi$ scan  
Absorption correction: multi-scan  
(SADABS; Bruker, 2012)  
$T$ = 296 K  
$T$ = 296 K  
$R_{\text{min}}$ = 0.834, $T_{\text{max}}$ = 0.942  
3265 independent reflections  
15411 measured reflections

Refinement

Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)]$ = 0.049  
w$R(F^2)$ = 0.133  
$S$ = 1.02  
3265 reflections  
264 parameters  
7 restraints

Primary atom site location: dual  
Secondary atom site location: difference Fourier map  
Hydrogen site location: mixed  
H atoms treated by a mixture of independent and constrained refinement

$w = 1/\sigma^2(F_c^2) + (0.0514P)^2 + 0.1429P$  
where $P = (F_c^2 + 2F_s^2)/3$
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.24 e Å⁻³
Δρ_{min} = −0.21 e Å⁻³

Extinction correction: SHELXL2018/3 (Sheldrick 2015b),
Fκ = kF0[1+0.001xFκ²λ³/sin(2θ)]⁻¹/₄
Extinction coefficient: 0.022 (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 |
|---|-------|-------|-------|-----------|
| C1 | 0.2400 (4) | 0.4979 (2) | 0.4846 (2) | 0.0331 (6) |
| C2 | 0.1716 (4) | 0.5004 (2) | 0.3755 (2) | 0.0376 (6) |
| H2 | 0.09702 | 0.424987 | 0.303896 | 0.045* |
| C3 | 0.2150 (4) | 0.6162 (3) | 0.3737 (2) | 0.0353 (6) |
| C4 | 0.3382 (4) | 0.7355 (2) | 0.4796 (2) | 0.0335 (6) |
| C5 | 0.4064 (4) | 0.7254 (2) | 0.5918 (2) | 0.0303 (6) |
| C6 | 0.3534 (4) | 0.6100 (2) | 0.5917 (2) | 0.0325 (6) |
| H6 | 0.394113 | 0.606279 | 0.665144 | 0.039* |
| C7 | 0.5309 (4) | 0.8402 (2) | 0.7123 (2) | 0.0362 (6) |
| C8 | 0.1947 (4) | 0.0896 (2) | 0.5817 (2) | 0.0388 (7) |
| H8A | 0.166572 | 0.172139 | 0.595530 | 0.047* |
| H8B | 0.336846 | 0.105846 | 0.628741 | 0.047* |
| C9 | −0.0406 (4) | −0.0246 (3) | 0.3735 (2) | 0.0379 (7) |
| H9A | −0.048896 | −0.081723 | 0.286864 | 0.046* |
| H9B | −0.077271 | 0.053723 | 0.379768 | 0.046* |
| C10 | 0.4553 (5) | 0.5527 (3) | −0.0810 (3) | 0.0530 (8) |
| H10A | 0.593339 | 0.595334 | −0.079123 | 0.064* |
| H10B | 0.351574 | 0.562706 | −0.138468 | 0.064* |
| C11 | 0.5558 (5) | 0.5896 (3) | 0.1283 (3) | 0.0519 (8) |
| H11A | 0.517856 | 0.623969 | 0.207334 | 0.062* |
| H11B | 0.699858 | 0.634402 | 0.142542 | 0.062* |
| C12 | 0.9027 (5) | 1.0964 (3) | 0.0763 (3) | 0.0663 (9) |
| H12A | 0.991252 | 1.127416 | 0.158769 | 0.080* |
| H12B | 0.793302 | 1.143558 | 0.084060 | 0.080* |
| C13 | 0.9676 (5) | 0.8797 (3) | 0.0037 (3) | 0.0660 (9) |
| H13A | 0.899018 | 0.788492 | −0.035061 | 0.079* |
| H13B | 1.058073 | 0.903815 | 0.083872 | 0.079* |
| N1 | 0.1911 (3) | 0.3784 (2) | 0.4897 (3) | 0.0448 (6) |
| N2 | 0.1279 (4) | 0.6133 (3) | 0.2575 (2) | 0.0498 (6) |
| N3 | 0.1777 (3) | 0.0079 (2) | 0.4483 (2) | 0.0366 (6) |
| N4 | 0.4177 (4) | 0.6159 (2) | 0.0429 (2) | 0.0492 (6) |
| N5 | 0.8059 (4) | 0.9568 (3) | 0.0213 (2) | 0.0594 (8) |
| O1 | 0.2522 (3) | 0.37951 (19) | 0.5894 (2) | 0.0588 (6) |
| O2 | 0.0900 (3) | 0.28024 (19) | 0.3949 (2) | 0.0618 (6) |
| O3 | 0.0716 (3) | 0.5083 (2) | 0.16184 (19) | 0.0659 (6) |
|    | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|----|-----|-----|-----|-----|-----|-----|
| C1 | 0.0281 (14) | 0.0283 (14) | 0.0472 (17) | 0.0077 (11) | 0.0161 (12) | 0.0193 (13) |
| C2 | 0.0297 (14) | 0.0347 (15) | 0.0386 (16) | 0.0071 (12) | 0.0120 (12) | 0.0082 (13) |
| C3 | 0.0316 (14) | 0.0434 (17) | 0.0343 (15) | 0.0110 (12) | 0.0105 (12) | 0.0202 (14) |
| C4 | 0.0272 (14) | 0.0344 (15) | 0.0453 (16) | 0.0096 (12) | 0.0129 (12) | 0.0227 (14) |
| C5 | 0.0288 (14) | 0.0316 (14) | 0.0349 (15) | 0.0091 (11) | 0.0129 (11) | 0.0174 (13) |
| C6 | 0.0284 (13) | 0.0352 (15) | 0.0404 (16) | 0.0104 (12) | 0.0143 (12) | 0.0209 (14) |
| C7 | 0.0346 (15) | 0.0327 (15) | 0.0416 (17) | 0.0087 (12) | 0.0139 (13) | 0.0164 (14) |
| C8 | 0.0344 (15) | 0.0385 (16) | 0.0378 (17) | 0.0012 (12) | 0.0044 (12) | 0.0170 (14) |
| C9 | 0.0399 (16) | 0.0409 (16) | 0.0346 (15) | 0.0057 (12) | 0.0073 (12) | 0.0212 (14) |
| C10| 0.057 (2) | 0.0492 (19) | 0.057 (2) | 0.0128 (15) | 0.0165 (16) | 0.0281 (17) |
| C11| 0.0501 (18) | 0.0477 (19) | 0.0454 (18) | 0.0058 (15) | 0.0065 (15) | 0.0150 (16) |
| C12| 0.054 (2) | 0.068 (2) | 0.052 (2) | 0.006 (17) | 0.0126 (17) | 0.0117 (18) |
| C13| 0.053 (2) | 0.071 (2) | 0.067 (2) | −0.003 (18) | 0.0156 (18) | 0.032 (2) |
| N1 | 0.0357 (14) | 0.0330 (15) | 0.0707 (19) | 0.0119 (11) | 0.0243 (13) | 0.0244 (15) |
| N2 | 0.0439 (15) | 0.0615 (18) | 0.0459 (17) | 0.0146 (13) | 0.0126 (12) | 0.0261 (16) |
| N3 | 0.0358 (13) | 0.0362 (14) | 0.0446 (15) | 0.0078 (11) | 0.0133 (11) | 0.0241 (12) |
| N4 | 0.0466 (16) | 0.0431 (15) | 0.0527 (16) | 0.0098 (13) | 0.0149 (13) | 0.0180 (13) |
| N5 | 0.0428 (16) | 0.081 (2) | 0.0382 (16) | −0.0074 (15) | 0.0115 (14) | 0.0208 (16) |
| O1 | 0.0646 (14) | 0.0533 (14) | 0.0814 (16) | 0.0181 (11) | 0.0241 (12) | 0.0485 (13) |
| O2 | 0.0579 (14) | 0.0295 (12) | 0.0816 (16) | 0.0017 (10) | 0.0193 (12) | 0.0146 (12) |
| O3 | 0.0694 (15) | 0.0694 (16) | 0.0389 (13) | 0.0079 (12) | 0.0052 (11) | 0.0141 (12) |
| O4 | 0.0837 (17) | 0.0753 (17) | 0.0615 (16) | 0.0283 (13) | 0.0092 (12) | 0.0435 (14) |
| O5 | 0.0679 (14) | 0.0570 (13) | 0.0370 (12) | −0.0114 (10) | 0.0063 (10) | 0.0226 (11) |
| O6 | 0.0558 (12) | 0.0350 (11) | 0.0451 (12) | −0.0015 (9) | 0.0207 (9) | 0.0130 (9) |
| O7 | 0.0409 (11) | 0.0458 (12) | 0.0705 (14) | 0.0011 (9) | 0.0020 (10) | 0.0408 (11) |
| O8 | 0.0809 (18) | 0.0400 (15) | 0.0751 (18) | 0.0151 (14) | 0.0457 (14) | 0.0240 (14) |

**Geometric parameters (Å, °)**

|    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|
| C1—C2 | 1.373 (3) | C10—H10A | 0.9700 |
| C1—C6 | 1.390 (3) | C10—H10B | 0.9700 |
| C1—N1 | 1.442 (3) | C11—N4 | 1.460 (3) |
C2—C3 1.376 (3)  C11—H11A 0.9700
C2—H2 0.9300  C11—H11B 0.9700
C3—C4 1.443 (3)  C12—N5 1.478 (4)
C3—N2 1.448 (3)  C12—C13\textsuperscript{iii} 1.497 (4)
C4—O7 1.257 (3)  C12—H12A 0.9700
C4—C5 1.455 (3)  C12—H12B 0.9700
C5—C6 1.366 (3)  C13—N5 1.488 (4)
C5—C7 1.503 (3)  C13—H13A 0.9700
C6—H6 0.9300  C13—H13B 0.9700
C7—O6 1.251 (3)  N1—O2 1.227 (3)
C7—O5 1.251 (3)  N1—O1 1.232 (3)
C8—N3 1.475 (3)  N2—O3 1.232 (3)
C8—C9\textsuperscript{i} 1.507 (3)  N2—O4 1.233 (3)
C8—H8A 0.9700  N3—H3A 0.903 (16)
C8—H8B 0.9700  N3—H3B 0.900 (16)
C9—N3 1.484 (3)  N4—H4 0.860 (17)
C9—H9A 0.9700  N5—H5A 0.900 (17)
C9—H9B 0.9700  N5—H5B 0.918 (17)
C10—N4 1.461 (3)  O8—H8C 0.84 (4)
C10—C11\textsuperscript{ii} 1.510 (4)  O8—H8D 0.84 (4)

C2—C1—C6 120.9 (2)  N4—C11—H11A 108.9
C2—C1—N1 120.0 (2)  C10\textsuperscript{ii}—C11—H11A 108.9
C6—C1—N1 119.1 (2)  N4—C11—H11B 108.9
C1—C2—C3 119.0 (2)  C10\textsuperscript{ii}—C11—H11B 108.9
C1—C2—H2 120.5  H11A—C11—H11B 107.7
C3—C2—H2 120.5  N5—C12—C13\textsuperscript{iii} 110.2 (3)
C2—C3—C4 123.4 (2)  N5—C12—H12A 109.6
C2—C3—N2 116.1 (2)  C13\textsuperscript{iii}—C12—H12A 109.6
C4—C3—N2 120.5 (2)  N5—C12—H12B 109.6
O7—C4—C3 123.7 (2)  C13\textsuperscript{iii}—C12—H12B 109.6
O7—C4—C5 121.7 (2)  H12A—C12—H12B 108.1
C3—C4—C5 114.5 (2)  N5—C13—C12\textsuperscript{iii} 110.0 (3)
C6—C5—C4 120.6 (2)  N5—C13—H13A 109.7
C6—C5—C7 117.2 (2)  C12\textsuperscript{iii}—C13—H13A 109.7
C4—C5—C7 122.2 (2)  N5—C13—H13B 109.7
C5—C6—C1 121.6 (2)  C12\textsuperscript{iii}—C13—H13B 109.7
C5—C6—H6 119.2  H13A—C13—H13B 108.2
C1—C6—H6 119.2  O2—N1—O1 122.8 (2)
O6—C7—O5 123.4 (2)  O2—N1—C1 118.6 (3)
O6—C7—C5 120.5 (2)  O1—N1—C1 118.5 (2)
O5—C7—C5 116.1 (2)  O3—N2—O4 121.8 (2)
N3—C8—C9\textsuperscript{i} 110.7 (2)  O3—N2—C3 118.6 (2)
N3—C8—H8A 109.5  O4—N2—C3 119.7 (3)
C9\textsuperscript{i}—C8—H8A 109.5  C8—N3—C9 111.2 (2)
N3—C8—H8B 109.5  C8—N3—H3A 113.0 (19)
C9\textsuperscript{i}—C8—H8B 109.5  C9—N3—H3A 109.0 (18)
H8A—C8—H8B 108.1  C8—N3—H3B 108.8 (17)
### Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H  | H···A  | D···A  | D—H···A |
|---------------|------|--------|--------|---------|
| O8—H8D···O6iv | 0.84 (4) | 1.98 (4) | 2.807 (3) | 173 (4) |
| N3—H3A···O6v  | 0.90 (2) | 1.92 (2) | 2.752 (3) | 153 (3) |
| N3—H3A···O7v  | 0.90 (2) | 2.33 (3) | 2.940 (3) | 125 (2) |
| N3—H3B···O4vi | 0.90 (2) | 2.50 (2) | 3.142 (3) | 129 (2) |
| N3—H3B···O7vi | 0.90 (2) | 1.84 (2) | 2.696 (3) | 157 (3) |
| N4—H4···O3    | 0.860 (17) | 2.59 (2) | 3.304 (3) | 141 (2) |
| N5—H5A···O8   | 0.900 (17) | 1.83 (2) | 2.712 (3) | 166 (3) |
| N5—H5B···O5vi | 0.918 (17) | 1.74 (2) | 2.637 (3) | 165 (3) |
| O8—H8C···N4   | 0.84 (4) | 1.88 (4) | 2.717 (3) | 169 (3) |
| C8—H8A···O1   | 0.97 | 2.49 | 3.369 (3) | 151 |
| C9—H9B···O2   | 0.97 | 2.67 | 3.482 (3) | 141 |

Symmetry codes: (i) −x, −y, −z+1; (ii) −x+1, −y+1, −z; (iii) −x+2, −y+2, −z.
|                  |     |     |       |     |
|------------------|-----|-----|-------|-----|
| C12—H12····O2^viii | 0.97| 2.58| 3.455 (4) | 151 |
| C12—H12B···O5^iv  | 0.97| 2.59| 3.353 (4) | 136 |

Symmetry codes: (iv) −x+1, −y+2, −z+1; (v) −x+1, −y+1, −z+1; (vi) x, y−1, z; (vii) x, y, z−1; (viii) x+1, y+1, z.