research communications

Crystal structure of 2-(morpholino)ethylammonium picrate monohydrate

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The title compound, $C_6H_{15}N_2O^+ \cdot C_6H_2N_3O_7^- \cdot H_2O$, was synthesized *via* slow evaporation of an aqueous solution of picric acid with the substituted morpholine base and crystallized with one cation $(C_6H_{15}N_2O)^+$, one anion $(C_6H_2N_3O_7)^-$ and a water molecule in the asymmetric unit. The morpholine ring in the cation adopts a chair conformation. The structure is stabilized by C—H···O, O—H···O, O—H···N and N—H···O hydrogen-bonding interactions and π–π stacking. The intermolecular interactions of the synthesized compound were quantified by Hirshfeld surface analysis.

1. Chemical context

Morpholine complex materials are widely used in biomedical applications as this moiety serves as an important lysosome-targeting group. Its applications include use in the synthesis of lysosome-targetable fluorescent probes for hydrogen sulfide imaging in living cells. Morpholine can be used as a ligand in metal complexes. It is also a component of protective coatings on fresh fruits and is used as an emulsifier in the preparation of pharmaceuticals and cosmetic products (Kuchowicz & Rydzyński, 1998). Picric acid forms stable picrates with various organic molecules through bonding or ionic bonding. It is also a well-established material for non-linear optical (NLO) substances, which crystallize in the non-centrosymmetric space group $Pca2_1$ (Yamaguchi *et al.*, 1988). Compounds of the morpholine family such as 4-(2-chloroethyl)morpholinium picrate (Kant *et al.*, 2009), 4-(4-nitrophenyl)morpholine (Wang *et al.*, 2012), morpholinium picrate (Vembu & Fronczek, 2009) can be used in drug design. The phenolic group of the picrate anion might favour the formation of hydrogen-bonding interactions to increase the molecular hyperpolarizability and NLO effects (Takayanagi *et al.*, 1996). Organic molecules have attracted great attention because of their ability to combine low cost and ease of processing in the assembly of optical devices. In this context, the present investigation reports the synthesis, crystal structure, Hirshfeld surface, IR and NMR analyses of 2-(morpholinyl)ethylammonium picrate monohydrate.
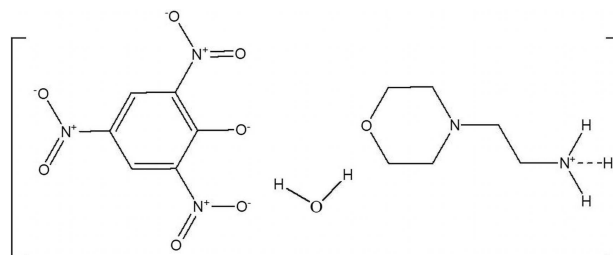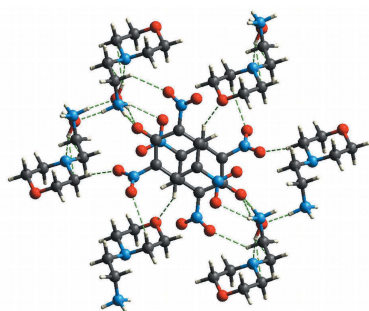
Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C7—H7$B\cdots$O7[i]	0.97	2.55	3.465 (2)	158
C10—H10$B\cdots$O6[ii]	0.97	2.63	3.503 (3)	150
C12—H12$A\cdots$O2[iii]	0.97	2.55	3.349 (3)	139
N5—H5$C\cdots$O9	0.89 (2)	1.86 (2)	2.741 (2)	172 (2)
N5—H5$A\cdots$O1[iii]	0.89 (2)	1.89 (2)	2.777 (2)	172 (2)
N5—H5$B\cdots$O5[iv]	0.85 (2)	2.35 (2)	3.054 (2)	142 (2)
N5—H5$B\cdots$O9[v]	0.85 (2)	2.48 (2)	3.048 (2)	126 (2)
O9—H9$D\cdots$N4[v]	0.84 (2)	1.98 (2)	2.7722 (19)	158 (2)
O9—H9$C\cdots$O1	0.82 (2)	1.94 (2)	2.7196 (19)	160 (2)

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

2. Structural commentary

The title compound crystallizes in the triclinic $P\bar{1}$ space group (Fig. 1) with two ion pairs and two solvating water molecules in the unit cell (Fig. 1). The asymmetric unit is shown in Fig. 2. In agreement with the pK_a constants for the parent 4-(2-ammonioethyl)morpholine (4.84, 9.45), the terminal NH$_2$ group of the base is protonated, forming the 2-(morpholino)ethylammonium anion. All three protons of the NH$_3^+$ group are involved in hydrogen bonding. The cation forms a strong charge-assisted hydrogen bond N5—H5$A\cdots$O1 [$1-x, -y, 1-z; D\cdots A = 2.777$ (2) Å] with the picrate anion, while H5C interacts with O9 from the solvating water molecule [$D\cdots A = 2.741$ (2) Å] and H5B is involved in a bifurcated hydrogen bond with O5 from a neighbouring picrate anion [$-1+x, -1+y, -1+z; D\cdots A = 3.054$ (2) Å] and O9 from other water molecule ($-x, -y, -z+1$), respectively. Additionally, the two protons of the water molecule interact with a picrate anion or the nitrogen atom of the morpholinyl
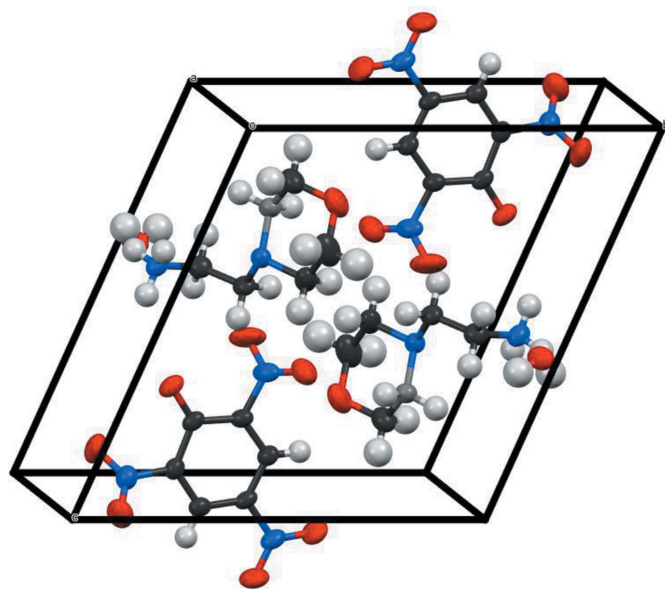
moiety [O9—H9$C\cdots$O1, $D\cdots A$ = 2.7196 (19) Å; O9—H9$D\cdots$N4, $-x, -y, -z+1$, $D\cdots A$ = 2.7722 (19) Å]. Further geometric details of these hydrogen bonds can be found in Table 1. In this scenario, the water molecule forms a bridge between the ammonium group and another picrate anion that cannot interact directly for steric reasons. Formation of these hydrogen bonds also lowers the energy of the crystal and thus increases the stability of the packing.

The refined geometry (Fig. 2) shows that the torsion angles N4—C7—C8—O8 and O8—C9—C10—N4 of the morpholine ring are -58.1 (2) and 59.4 (2)°, respectively, confirming the chair conformation. There are three nitro groups in the picrate anion. While the *para*-bound nitro group is nearly coplanar with the plane of the benzene ring [dihedral angle of -1.0 (2)°] and two *ortho*-oriented nitro groups are, probably as a result of repulsion with the phenolic oxygen atom, twisted from the ring plane by -51.9 (2) and 43.8 (2)°. It has been mentioned previously that the nitro groups of the picrate anion play an important role in stabilizing the crystal packing *via* weak coulombic interactions (George *et al.*, 2019; Anitha *et al.*, 2004).

3. Supramolecular features

Fig. 3 shows the three-dimensional molecular packing of the title compound viewed down the *a*-axis. Along with the six main hydrogen bonds described in the previous section, the cation interacts with neighboring picrate anions *via* C7—H7$B\cdots$O7($x-1, y, z$), C10—H10$B\cdots$O6($-x+1, -y+1, -z+1$) and C12—H12$A\cdots$O2($-x+1, -y, -z+1$) non-classical hydrogen bonds (Table 1). Several prominent supramolecular motifs are formed by these hydrogen bonds. Firstly, the interaction of the ammonium group with the water molecules creates a centrosymmetric motif described by an $R_4^2(8)$ graph set (Bernstein *et al.*, 1995; Motherwell *et al.*, 2000) (Fig. 4). Next, another centrosymmetric motif described by an $R_4^4(20)$ graph set is formed between two ammonium groups
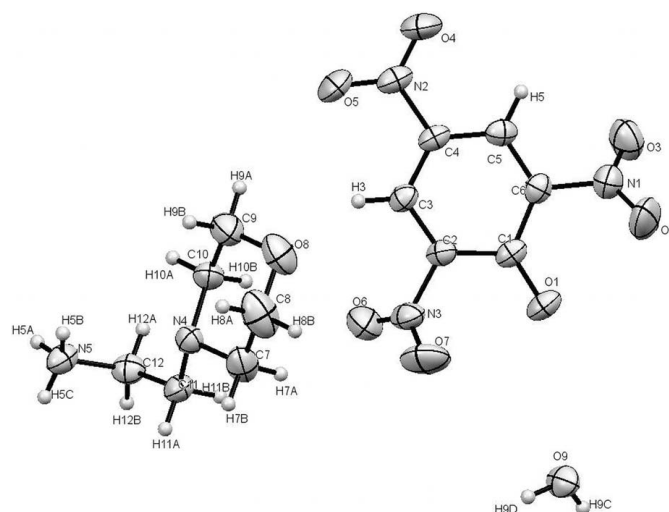
Figure 1
Molecular diagram of the title compound viewed down along *a** axis in the unit cell.

Figure 2
ORTEP diagram of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
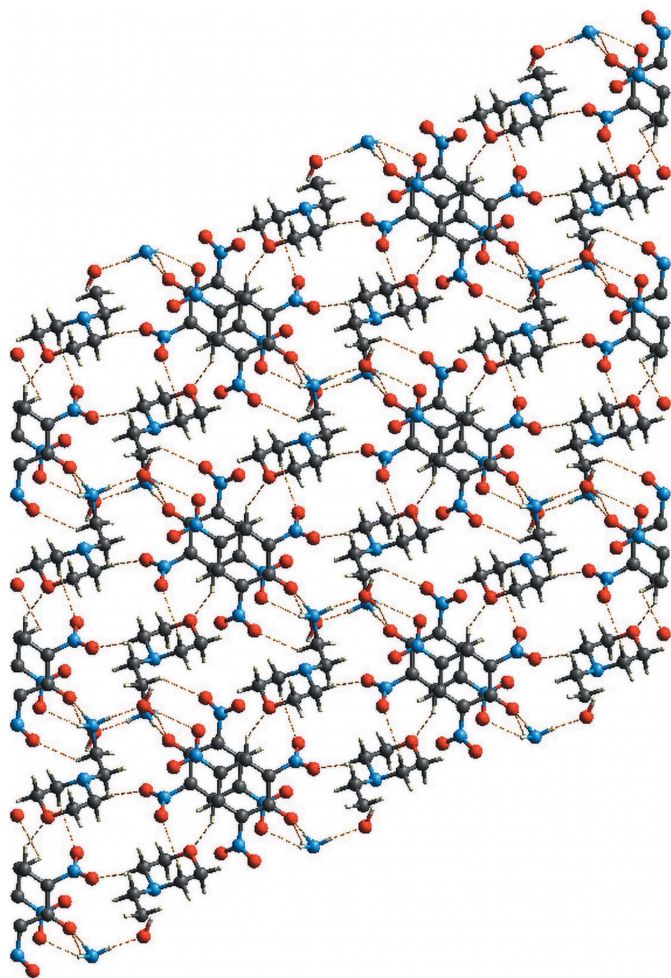
Figure 3
Three-dimensional supramolecular architecture of the title compound viewed down the *a* axis.

and two picrate anions and involves the phenolic oxygen anion and the *para* nitro group (Fig. 5). Furthermore, the picrate anions are coplanar, and are involved in two different π–π stacking interactions with perpendicular distances between the C1–C6 rings of 3.3532 (6) and 3.5533 (6) Å, slippage of 1.393 and 1.902 Å, and $Cg\cdots Cg$ distances of 3.6311 (18) and 4.0303 (19) Å, respectively, for the rings related by symmetry
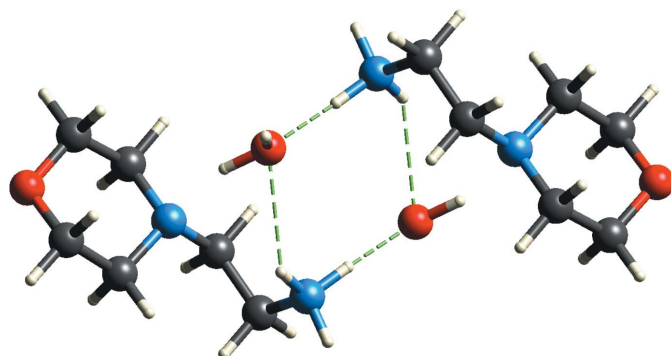

Figure 4
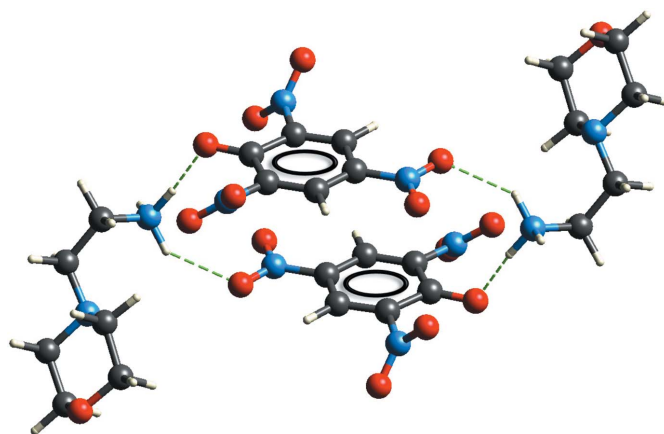$R_4^2(8)$ ring motif formed between ammonium group and water molecules.

Figure 5
$R_4^4(20)$ ring motif formed between two ammonium group and two picrate anions and π–π stacking interactions.

operations $1 - x, 1 - y, 2 - z$ and $2 - x, 1 - y, 2 - z$. Finally, a centrosymmetric twelve-membered ring [(picrate)O⁻···H—N—H···O—H]₂ with a third order graph set $R_6^4(12)$ involves two of each of the three different species present in the crystal (Fig. 6).

Analysis of the Hirshfeld surface and the associated two-dimensional fingerprint plot for 2-(morpholinyl)ethyl-ammonium picrate monohydrate was performed with *CrystalExplorer 21.5* (Spackman *et al.*, 2021). The normalized contact distance (d_{norm}) Hirshfeld surface of the title compound mapped over the limits −0.6471 to 1.3714 a.u. with close contacts to neighboring molecules is shown in Fig. 7. The contacts with distances equal to the sum of the van der Waals radii are indicated in white and the contacts with distances shorter than and longer than van der Waals radii are represented as red and blue, respectively (Venkatesan *et al.*, 2016).
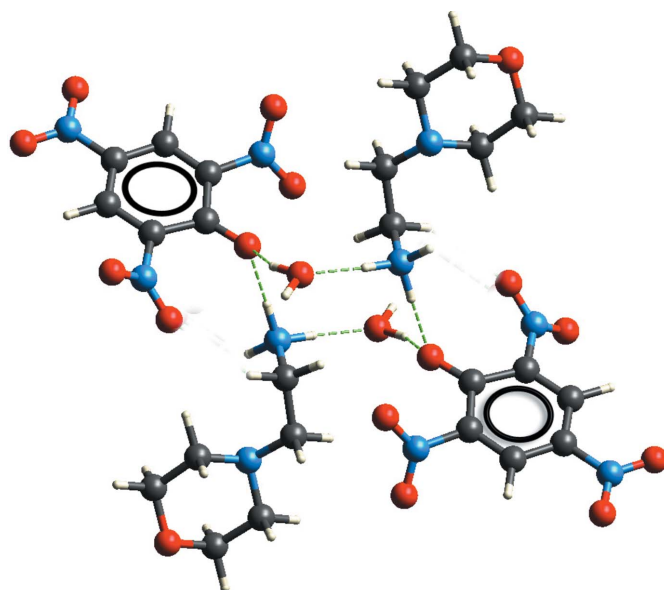

Figure 6
$R_6^4(12)$ ring motif formed through twelve-membered ring [(picrate)O⁻···H—N—H···O—H]₂ interactions.

atoms outside and inside the surface, respectively (McKinnon *et al.*, 2007; Seth, 2014; Nchioua *et al.*, 2022). The most significant contribution to the Hirshfeld surface is from the O···H/H···O (52.9%) interactions. In addition, the H···H (27.3%) and O···O (5.5%) interactions make significant contributions to the total Hirshfeld surface. Other interactions contributing less than 5.0% are C···C (3.9%), O···C/C···O (2.5%), N···H/H···N (2.2%), N···C/C···N (2.2%), H···C/C···H (1.8%) and O···N/N···O (1.8%).

4. Database survey

A search in the Cambridge Structural Database (CSD, version 5.40; Groom *et al.*, 2016) found eleven structures containing 4-(2-ammonioethyl)morpholinium including 4-(2-ammonioethyl)morpholinium tetrachlorocopper(II) (BOPWUY and BOPWUY01; Battaglia *et al.*, 1982), 4-(2-ammoniumethyl)morpholinium tetrachloromercury(II) (CUMGIA; Vezzosi *et al.*, 1984), 4-(2-ammonioethyl)morpholinium dichloride monohydrate (JAXBOC; Ghorab *et al.*, 2017), 4-(2-ammonioethyl)morpholinium tetrachloropalladium(II) (KETHOJ; Efimenko *et al.*, 2017), 4-(2-ammonioethyl)morpholinium sulfate methanol solvate (KUTZUV; Bi, 2010), *catena*-[4-(2-ammonioethyl)morpholinium] tetrakis[(μ_3-phosphito)trizinc(II)] hemihydrate (SEZPOE; Lin & Dehnen, 2009), 4-(2-ammonioethyl)morpholinium dichlorodiiodocadmium(II) chlorotriiodocadmium(II) (UVWEZ; Mahbouli Rhouma *et al.*, 2016), 4-(2-ammonioethyl)morpholinium tetrachlorozinc(II) (WUTGOI; Glaoui *et al.*, 2008 and WUTGOI01; Lamshöft *et al.*, 2011), *catena*-[bis[4-(2-ammonioethyl)morpholinium] tetrakis(μ-iodo)tetrakis(iodo)dilead(II)] and (NIXNEQ; Xiuli & Zhenhong, 2019). Unlike the title compound, all of these examples have both nitrogen atoms protonated. Another search in the CSD for the compound morpholinium picrate gave four hits, *viz.* 4-hydroxy-4-methylmorpholinium picrate (HIGYOM; Zukerman-Schpector *et al.*, 2007), morpholinium picrate (KOMTUC; Vembu & Fronczek, 2009), 4-(2-chloroethyl)morpholinium picrate (PUFFIG; Kant *et al.*, 2009) and 4,4-bis(2′-hydroxyethyl)morpholinium picrate (SEGGAM; Solov'ev *et al.*, 1988). It is noted that all of these structures are stabilized by hydrogen bonds and that in each one the morpholine ring has a chair conformation.

5. Synthesis and crystallization

2-(Morpholinyl)ethylammonium picrate monohydrate was synthesized by mixing one mole of 4-(2-ammonioethyl)morpholine and one mole of picric acid in double-distilled water at about 303 K. The solution was then allowed to evaporate at room temperature, which yielded yellow plate-like crystals of 2-(morpholinyl)ethylammonium picrate monohydrate. The reaction scheme is shown in Fig. 9. Melting point: 457–459 K; IR (KBr, cm^{-1}): 3384 (O—H), 2905 (NH$_3$), 3110 (C—H), 1382 (CH$_2$), 993 (C—O); ^{1}H NMR (500 MHz, D$_2$O, δ, ppm): 8.831 (*s*, 2H, picrate moiety), 3.63 (*t*, 4H, –CH$_2$–O–CH$_2$), 3.03 (*t*, 4H, –CH$_2$–N–CH$_2$), 2.58 (*t*, 2H, N–CH$_2$), 2.46
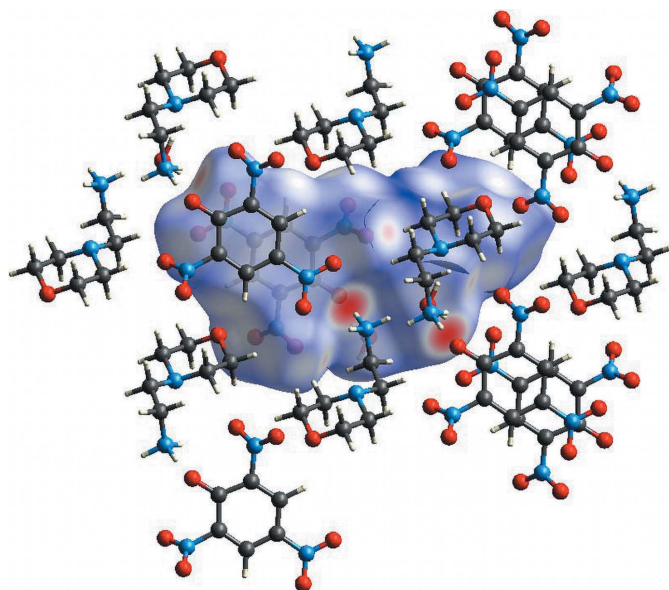

Figure 7
The Hirshfeld surface of the title compound mapped over d_{norm}, showing the closest molecules.

This analysis confirms that the most prominent intermolecular interactions present in the crystal are C—H···O, N—H···O, O—H···O and N—O···H contacts.

Two-dimensional fingerprint plots of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode are shown in Fig. 8. In the figure, d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest
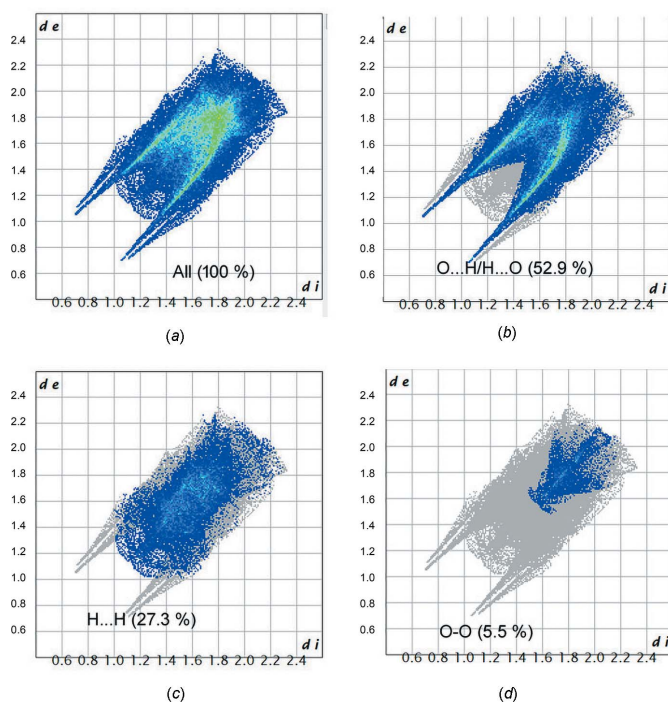

Figure 8
Two-dimensional fingerprint plots for the title compound showing (*a*) all interactions, (*b*) O···H/H···O interactions, (*c*) H···H interactions and (*d*) O···O interactions.
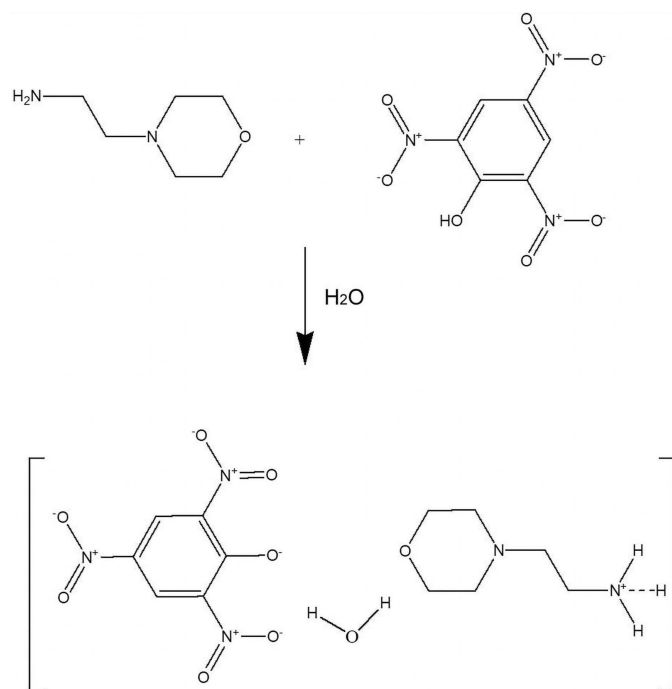
Figure 9
Reaction scheme for the title compound.

(t, 2H, $-CH_2-NH_3^+$). A suitable single crystal of 2-(morpholinyl)ethylammonium picrate monohydrate was selected for X-ray diffraction studies.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were positioned geometrically (C—H = 0.93 for anion and 0.97 Å for cation) and refined using an isotropic approximation, with $U_{iso}(H) = 1.2\, U_{eq}(C)$. The acidic protons were localized from the residual electron-density map and refined with distance restraints (0.82 Å for O—H and 0.86 Å for N—H) and $U_{iso}(H) = 1.2U_{eq}(N)$ and $1.5U_{eq}(O)$.

Acknowledgements

References

Anitha, K., Sridhar, B. & Rajaram, R. K. (2004). *Acta Cryst.* E**60**, o1530–o1532.
Battaglia, L. P., Bonamartini Corradi, A., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1982). *Inorg. Chem.* **21**, 3919–3922.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bi, Y. (2010). *Acta Cryst.* E**66**, o951.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_{15}N_2O^+ \cdot C_6H_2N_3O_7 \cdot H_2O$
M_r	377.32
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	297
a, b, c (Å)	6.938 (3), 11.583 (5), 12.077 (5)
α, β, γ (°)	114.362 (13), 94.261 (14), 103.841 (15)
V (Å^3)	841.8 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	$0.40 \times 0.38 \times 0.19$
Data collection	
Diffractometer	Bruker D8 Venture Diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker 2016)
T_{min}, T_{max}	0.504, 0.562
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19297, 3378, 2781
R_{int}	0.039
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.117, 1.04
No. of reflections	3378
No. of parameters	250
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.25, −0.21

Computer programs: *APEX3*, *SAINT* and *XPREP* (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020).

Bruker (2016). *APEX3*, *SAINT*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Efimenko, I. A., Churakov, A. V., Ivanova, N. A., Erofeeva, O. S. & Demina, L. I. (2017). *Russ. J. Inorg. Chem.* **62**, 1476–1485.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
George, J., George, M., Alex, J., Sajan, D., Shihab, N. K., Vinitha, G. & Chitra, R. (2019). *Opt. Laser Technol.* **119**, 105647, 1–9.
Ghorab, M., Alsaid, M. S. & Ghabbour, H. A. (2017). *Z. Kristallogr.* **232**, 501–502.
Glaoui, M. El, Smirani, W., Lefebvre, F., Rzaigui, M. & Nasr, C. B. (2008). *Can. J. Anal. Sci. Spectrosc.* **53**, 102–112.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Kant, R., Kohli, S., Sarmal, L., Narayana, B. & Samshuddin, S. (2009). *Acta Cryst.* E**65**, o2435.
Kuchowicz, E. & Rydzyński, K. (1998). *Appl. Occup. Environ. Hyg.* **13**, 113–121.
Lamshöft, M., Storp, V., Ivanova, B. & Spiteller, M. (2011). *Polyhedron*, **30**, 2564–2573.
Lin, Z. & Dehnen, S. (2009). *J. Solid State Chem.* **182**, 3143–3148.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Mahbouli Rhouma, N., Rayes, A., Mezzadri, F., Calestani, G. & Loukil, M. (2016). *Acta Cryst.* E**72**, 1404–1407.
McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* 3814–3816.
Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (2000). *Acta Cryst.* B**56**, 857–871.

Nchioua, I., Alsubari, A., Mague, J. T. & Ramli, Y. (2022). *Acta Cryst.* E**78**, 922–925.

Seth, S. K. (2014). *J. Mol. Struct.* **1064**, 70–75.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Solov'ev, V. N., Chekhlov, A. N., Gafurov, R. G., Chistyakov, V. G. & Martynov, I. V. (1988). *J. Struct. Chem.* **29**, 174–175.

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.

Takayanagi, H., Kai, T., Yamaguchi, S., Takeda, K. & Goto, M. (1996). *Chem. Pharm. Bull.* **44**, 2199–2204.

Vembu, N. & Fronczek, F. R. (2009). *Acta Cryst.* E**65**, o156–o157.

Venkatesan, P., Thamotharan, S., Ilangovan, A., Liang, H. & Sundius, T. (2016). *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **153**, 625–636.

Vezzosi, I. M., Benedetti, A., Albinati, A., Ganazzoli, F., Cariati, F. & Pellicciari, L. (1984). *Inorg. Chim. Acta*, **90**, 1–7.

Wang, L.-J., Li, W.-W., Yang, S.-Y. & Yang, L. (2012). *Acta Cryst.* E**68**, o1235.

Xiuli, Y. & Zhenhong, W. (2019). *Chin. J. Struct. Chem.* **38**, 284–292.

Yamaguchi, S., Goto, M., Takayanagi, H. & Ogura, H. (1988). *Bull. Chem. Soc. Jpn*, **61**, 1026–1028.

Zukerman-Schpector, J., Vega-Teijido, M., Carvalho, C. C., Isolani, P. C. & Caracelli, I. (2007). *Z. Kristallogr.* **222**, 427–431.

Crystal structure of 2-(morpholino)ethylammonium picrate monohydrate

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *APEX3*/*SAINT* (Bruker, 2016); data reduction: *SAINT*/*XPREP* (Bruker, 2016); program(s) used to solve structure: *SHELXT2018/2* (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: *SHELXL2018/2* (Sheldrick, 2015b).

2-(Morpholin-4-yl)ethan-1-aminium 2,4,6-trinitrobenzen-1-olate monohydrate

Crystal data

$C_6H_{15}N_2O^+ \cdot C_6H_2N_3O_7^- \cdot H_2O$	$Z = 2$
$M_r = 377.32$	$F(000) = 396$
Triclinic, $P\overline{1}$	$D_x = 1.489$ Mg m^{-3}
$a = 6.938$ (3) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.583$ (5) Å	Cell parameters from 7824 reflections
$c = 12.077$ (5) Å	$\theta = 3.2$–$26.2°$
$\alpha = 114.362$ (13)°	$\mu = 0.13$ mm^{-1}
$\beta = 94.261$ (14)°	$T = 297$ K
$\gamma = 103.841$ (15)°	Block, yellow
$V = 841.8$ (6) Å^3	$0.40 \times 0.38 \times 0.19$ mm

Data collection

Bruker D8 Venture Diffractometer	3378 independent reflections
Radiation source: fine focus sealed tube	2781 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.039$
Absorption correction: multi-scan (SADABS; Bruker 2016)	$\theta_{max} = 26.4°$, $\theta_{min} = 3.1°$
$T_{min} = 0.504$, $T_{max} = 0.562$	$h = -8 \rightarrow 8$
19297 measured reflections	$k = -14 \rightarrow 14$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.2721P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3378 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
250 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
5 restraints	

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*	U_{iso}*/U_{eq}
C1	0.6187 (2)	0.30558 (14)	0.82290 (13)	0.0335 (3)
C2	0.6867 (2)	0.43310 (15)	0.82356 (13)	0.0349 (3)
C3	0.7623 (2)	0.55224 (14)	0.92800 (13)	0.0355 (3)
H3	0.802400	0.631735	0.922088	0.043*
C4	0.7771 (2)	0.55051 (14)	1.04247 (13)	0.0336 (3)
C5	0.7107 (2)	0.43331 (15)	1.05278 (13)	0.0360 (3)
H5	0.716562	0.434004	1.130246	0.043*
C6	0.6359 (2)	0.31567 (14)	0.94612 (14)	0.0359 (3)
C7	0.0106 (3)	0.30407 (19)	0.38759 (18)	0.0542 (5)
H7A	0.121632	0.382644	0.406388	0.065*
H7B	−0.037972	0.314606	0.463429	0.065*
C8	−0.1579 (4)	0.2906 (3)	0.2924 (2)	0.0739 (6)
H8A	−0.272185	0.215447	0.277962	0.089*
H8B	−0.201836	0.369717	0.324210	0.089*
C9	−0.0362 (3)	0.1539 (2)	0.13116 (18)	0.0581 (5)
H9A	0.003134	0.139093	0.052136	0.070*
H9B	−0.150414	0.078921	0.117385	0.070*
C10	0.1378 (3)	0.16274 (16)	0.21970 (14)	0.0432 (4)
H10A	0.174467	0.080947	0.185378	0.052*
H10B	0.254271	0.234838	0.230153	0.052*
C11	0.2592 (3)	0.20986 (16)	0.43386 (14)	0.0425 (4)
H11A	0.214563	0.221718	0.511030	0.051*
H11B	0.358912	0.292112	0.449159	0.051*
C12	0.3601 (2)	0.10098 (17)	0.39727 (15)	0.0438 (4)
H12A	0.408246	0.090738	0.321368	0.053*
H12B	0.477074	0.128043	0.461345	0.053*
N1	0.5579 (2)	0.19374 (14)	0.95933 (14)	0.0490 (4)
N2	0.8605 (2)	0.67574 (14)	1.15356 (12)	0.0428 (3)
N3	0.6630 (2)	0.43738 (14)	0.70341 (12)	0.0476 (4)
N4	0.08400 (19)	0.18564 (12)	0.34122 (11)	0.0370 (3)
N5	0.2271 (2)	−0.02941 (14)	0.37799 (13)	0.0420 (3)
H5C	0.206 (3)	−0.0270 (19)	0.4503 (15)	0.050*
H5A	0.291 (3)	−0.0899 (17)	0.3458 (17)	0.050*
H5B	0.117 (2)	−0.0515 (19)	0.3291 (16)	0.050*
O1	0.54301 (17)	0.19894 (10)	0.72393 (10)	0.0447 (3)
O2	0.5959 (3)	0.09346 (14)	0.88953 (15)	0.0832 (5)
O3	0.4599 (2)	0.19858 (15)	1.03953 (15)	0.0684 (4)
O4	0.8730 (3)	0.67488 (14)	1.25430 (11)	0.0688 (4)
O5	0.9152 (2)	0.77882 (12)	1.14134 (12)	0.0644 (4)

O6	0.5699 (3)	0.50981 (15)	0.69044 (13)	0.0705 (4)
O7	0.7341 (3)	0.36689 (18)	0.62204 (13)	0.0786 (5)
O8	−0.0951 (2)	0.27241 (15)	0.17867 (14)	0.0665 (4)
O9	0.19445 (19)	−0.00465 (13)	0.61101 (11)	0.0519 (3)
H9D	0.137 (3)	−0.055 (2)	0.640 (2)	0.078*
H9C	0.293 (3)	0.055 (2)	0.661 (2)	0.078*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0244 (7)	0.0322 (7)	0.0346 (7)	0.0087 (5)	0.0061 (5)	0.0060 (6)
C2	0.0309 (7)	0.0369 (8)	0.0294 (7)	0.0056 (6)	0.0067 (5)	0.0100 (6)
C3	0.0317 (7)	0.0308 (7)	0.0358 (7)	0.0044 (6)	0.0063 (6)	0.0098 (6)
C4	0.0277 (7)	0.0330 (7)	0.0290 (7)	0.0096 (6)	0.0031 (5)	0.0036 (6)
C5	0.0344 (7)	0.0420 (8)	0.0321 (7)	0.0170 (6)	0.0075 (6)	0.0136 (6)
C6	0.0332 (7)	0.0331 (7)	0.0411 (8)	0.0128 (6)	0.0086 (6)	0.0144 (6)
C7	0.0680 (12)	0.0527 (10)	0.0598 (11)	0.0313 (9)	0.0337 (9)	0.0311 (9)
C8	0.0679 (13)	0.0920 (17)	0.1018 (18)	0.0464 (13)	0.0368 (13)	0.0651 (15)
C9	0.0679 (12)	0.0549 (11)	0.0506 (10)	0.0109 (9)	0.0020 (9)	0.0282 (9)
C10	0.0536 (10)	0.0408 (8)	0.0351 (8)	0.0137 (7)	0.0126 (7)	0.0163 (7)
C11	0.0480 (9)	0.0355 (8)	0.0338 (7)	0.0058 (7)	0.0037 (6)	0.0102 (6)
C12	0.0360 (8)	0.0482 (9)	0.0415 (8)	0.0089 (7)	0.0031 (6)	0.0174 (7)
N1	0.0560 (9)	0.0392 (8)	0.0507 (8)	0.0138 (6)	0.0090 (7)	0.0195 (6)
N2	0.0392 (7)	0.0411 (8)	0.0327 (7)	0.0122 (6)	0.0005 (5)	0.0028 (6)
N3	0.0478 (8)	0.0444 (8)	0.0316 (7)	−0.0044 (6)	0.0051 (6)	0.0092 (6)
N4	0.0404 (7)	0.0353 (7)	0.0366 (6)	0.0106 (5)	0.0110 (5)	0.0170 (5)
N5	0.0398 (7)	0.0380 (7)	0.0397 (7)	0.0140 (6)	0.0005 (6)	0.0091 (6)
O1	0.0401 (6)	0.0337 (6)	0.0401 (6)	0.0054 (5)	0.0035 (5)	0.0012 (5)
O2	0.1348 (15)	0.0412 (8)	0.0806 (11)	0.0375 (9)	0.0376 (10)	0.0248 (7)
O3	0.0757 (10)	0.0671 (9)	0.0775 (10)	0.0192 (7)	0.0320 (8)	0.0447 (8)
O4	0.0949 (11)	0.0606 (9)	0.0300 (6)	0.0171 (8)	−0.0013 (6)	0.0059 (6)
O5	0.0817 (10)	0.0347 (7)	0.0472 (7)	−0.0018 (6)	−0.0032 (6)	0.0034 (5)
O6	0.0939 (11)	0.0636 (9)	0.0541 (8)	0.0165 (8)	−0.0004 (7)	0.0324 (7)
O7	0.0844 (11)	0.0975 (12)	0.0404 (7)	0.0240 (9)	0.0276 (7)	0.0171 (7)
O8	0.0720 (9)	0.0768 (10)	0.0768 (9)	0.0316 (8)	0.0178 (7)	0.0532 (8)
O9	0.0455 (7)	0.0502 (7)	0.0456 (7)	−0.0059 (5)	0.0019 (5)	0.0199 (6)

Geometric parameters (Å, º)

C1—O1	1.2683 (18)	C9—H9B	0.9700
C1—C2	1.435 (2)	C10—N4	1.4736 (19)
C1—C6	1.437 (2)	C10—H10A	0.9700
C2—C3	1.375 (2)	C10—H10B	0.9700
C2—N3	1.471 (2)	C11—N4	1.477 (2)
C3—C4	1.387 (2)	C11—C12	1.511 (2)
C3—H3	0.9300	C11—H11A	0.9700
C4—C5	1.385 (2)	C11—H11B	0.9700
C4—N2	1.4547 (19)	C12—N5	1.482 (2)

C5—C6	1.378 (2)	C12—H12A	0.9700
C5—H5	0.9300	C12—H12B	0.9700
C6—N1	1.465 (2)	N1—O3	1.214 (2)
C7—N4	1.482 (2)	N1—O2	1.225 (2)
C7—C8	1.509 (3)	N2—O4	1.2175 (19)
C7—H7A	0.9700	N2—O5	1.236 (2)
C7—H7B	0.9700	N3—O7	1.216 (2)
C8—O8	1.420 (3)	N3—O6	1.224 (2)
C8—H8A	0.9700	N5—H5C	0.887 (15)
C8—H8B	0.9700	N5—H5A	0.889 (15)
C9—O8	1.426 (3)	N5—H5B	0.845 (15)
C9—C10	1.507 (3)	O9—H9D	0.836 (16)
C9—H9A	0.9700	O9—H9C	0.821 (17)
O1—C1—C2	122.65 (14)	N4—C10—H10A	109.4
O1—C1—C6	125.22 (14)	C9—C10—H10A	109.4
C2—C1—C6	112.03 (12)	N4—C10—H10B	109.4
C3—C2—C1	125.19 (14)	C9—C10—H10B	109.4
C3—C2—N3	117.32 (14)	H10A—C10—H10B	108.0
C1—C2—N3	117.40 (13)	N4—C11—C12	114.81 (13)
C2—C3—C4	118.10 (14)	N4—C11—H11A	108.6
C2—C3—H3	120.9	C12—C11—H11A	108.6
C4—C3—H3	120.9	N4—C11—H11B	108.6
C5—C4—C3	121.52 (13)	C12—C11—H11B	108.6
C5—C4—N2	119.86 (14)	H11A—C11—H11B	107.5
C3—C4—N2	118.61 (14)	N5—C12—C11	114.31 (14)
C6—C5—C4	118.77 (14)	N5—C12—H12A	108.7
C6—C5—H5	120.6	C11—C12—H12A	108.7
C4—C5—H5	120.6	N5—C12—H12B	108.7
C5—C6—C1	124.34 (14)	C11—C12—H12B	108.7
C5—C6—N1	117.80 (14)	H12A—C12—H12B	107.6
C1—C6—N1	117.76 (13)	O3—N1—O2	123.96 (16)
N4—C7—C8	110.78 (17)	O3—N1—C6	117.76 (14)
N4—C7—H7A	109.5	O2—N1—C6	118.28 (15)
C8—C7—H7A	109.5	O4—N2—O5	122.81 (14)
N4—C7—H7B	109.5	O4—N2—C4	118.89 (15)
C8—C7—H7B	109.5	O5—N2—C4	118.30 (14)
H7A—C7—H7B	108.1	O7—N3—O6	123.84 (16)
O8—C8—C7	111.62 (16)	O7—N3—C2	117.99 (17)
O8—C8—H8A	109.3	O6—N3—C2	118.16 (14)
C7—C8—H8A	109.3	C10—N4—C11	112.03 (13)
O8—C8—H8B	109.3	C10—N4—C7	108.96 (12)
C7—C8—H8B	109.3	C11—N4—C7	108.03 (13)
H8A—C8—H8B	108.0	C12—N5—H5C	109.9 (13)
O8—C9—C10	111.11 (16)	C12—N5—H5A	108.4 (13)
O8—C9—H9A	109.4	H5C—N5—H5A	106.8 (17)
C10—C9—H9A	109.4	C12—N5—H5B	111.1 (13)
O8—C9—H9B	109.4	H5C—N5—H5B	111.2 (18)

C10—C9—H9B	109.4	H5A—N5—H5B	109.2 (18)
H9A—C9—H9B	108.0	C8—O8—C9	108.77 (14)
N4—C10—C9	111.04 (14)	H9D—O9—H9C	112 (2)
O1—C1—C2—C3	177.25 (14)	C1—C6—N1—O3	−136.51 (16)
C6—C1—C2—C3	0.8 (2)	C5—C6—N1—O2	−139.62 (17)
O1—C1—C2—N3	0.9 (2)	C1—C6—N1—O2	43.8 (2)
C6—C1—C2—N3	−175.60 (12)	C5—C4—N2—O4	1.0 (2)
C1—C2—C3—C4	0.8 (2)	C3—C4—N2—O4	179.69 (15)
N3—C2—C3—C4	177.14 (13)	C5—C4—N2—O5	−178.77 (14)
C2—C3—C4—C5	−2.5 (2)	C3—C4—N2—O5	−0.1 (2)
C2—C3—C4—N2	178.84 (12)	C3—C2—N3—O7	129.37 (17)
C3—C4—C5—C6	2.6 (2)	C1—C2—N3—O7	−54.0 (2)
N2—C4—C5—C6	−178.78 (13)	C3—C2—N3—O6	−51.9 (2)
C4—C5—C6—C1	−0.9 (2)	C1—C2—N3—O6	124.75 (16)
C4—C5—C6—N1	−177.21 (13)	C9—C10—N4—C11	−173.52 (13)
O1—C1—C6—C5	−177.07 (14)	C9—C10—N4—C7	−54.04 (18)
C2—C1—C6—C5	−0.7 (2)	C12—C11—N4—C10	−56.71 (17)
O1—C1—C6—N1	−0.8 (2)	C12—C11—N4—C7	−176.74 (13)
C2—C1—C6—N1	175.61 (13)	C8—C7—N4—C10	53.41 (19)
N4—C7—C8—O8	−58.1 (2)	C8—C7—N4—C11	175.35 (14)
O8—C9—C10—N4	58.90 (19)	C7—C8—O8—C9	60.6 (2)
N4—C11—C12—N5	−61.64 (18)	C10—C9—O8—C8	−60.8 (2)
C5—C6—N1—O3	40.0 (2)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7*B*···O7[i]	0.97	2.55	3.465 (2)	158
C10—H10*B*···O6[ii]	0.97	2.63	3.503 (3)	150
C12—H12*A*···O2[iii]	0.97	2.55	3.349 (3)	139
N5—H5*C*···O9	0.89 (2)	1.86 (2)	2.741 (2)	172 (2)
N5—H5*A*···O1[iii]	0.89 (2)	1.89 (2)	2.777 (2)	172 (2)
N5—H5*B*···O5[iv]	0.85 (2)	2.35 (2)	3.054 (2)	142 (2)
N5—H5*B*···O9[v]	0.85 (2)	2.48 (2)	3.048 (2)	126 (2)
O9—H9*D*···N4[v]	0.84 (2)	1.98 (2)	2.7722 (19)	158 (2)
O9—H9*C*···O1	0.82 (2)	1.94 (2)	2.7196 (19)	160 (2)

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