



Received 3 September 2015

Accepted 11 September 2015

Edited by H. Stoeckli-Evans, University of  
Neuchâtel, Switzerland

**Keywords:** crystal structure; 3-methylpyridinium  
picrate; triclinic polymorph;  $\pi$ - $\pi$  stacking; anti-  
convulsant activity.

**CCDC reference:** 1417794

**Supporting information:** this article has  
supporting information at journals.iucr.org/e

# Crystal structure of 3-methylpyridinium picrate: a triclinic polymorph

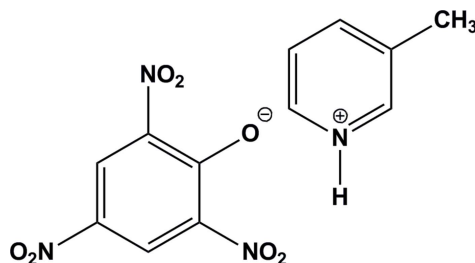
Jeganathan Gomathi and Doraisamyraja Kalaivani\*

PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli 620 002, Tamil Nadu, India. \*Correspondence e-mail: kalaivbalaj@yahoo.co.in

The title molecular salt,  $C_6H_8N^+ \cdot C_6H_2N_3O_7^-$  (systematic name: 3-methylpyridinium 2,4,6-trinitrophenolate), crystallizes in the triclinic space group  $P\bar{1}$ . The crystal structure of the monoclinic polymorph (space group  $P2_1/n$ ) has been reported [Stilinovic & Kaitner (2011). *Cryst. Growth Des.* **11**, 4110–4119]. In the crystal, the anion and cation are linked *via* bifurcated N—H $\cdots$ (O,O) hydrogen bonds, enclosing an  $R_1^2(6)$  graph-set motif. These units are linked *via* C—H $\cdots$ O hydrogen bonds, forming a three-dimensional framework. Within the framework there are  $\pi$ - $\pi$  interactions present, involving inversion-related picrate anions and inversion-related pyridinium cations, with inter-centroid distances of 3.7389 (14) and 3.560 (2) Å, respectively.

## 1. Chemical context

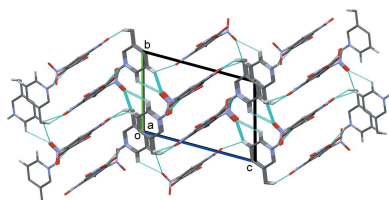
Stilinovic & Kaitner (2011) have synthesized a series of 20 crystalline picrates of pyridine derivatives and through single crystal X-ray diffraction studies revealed the presence of a common synthon. They reported the crystal structure of the monoclinic polymorph of the title molecular salt: space group  $P2_1/n$ .

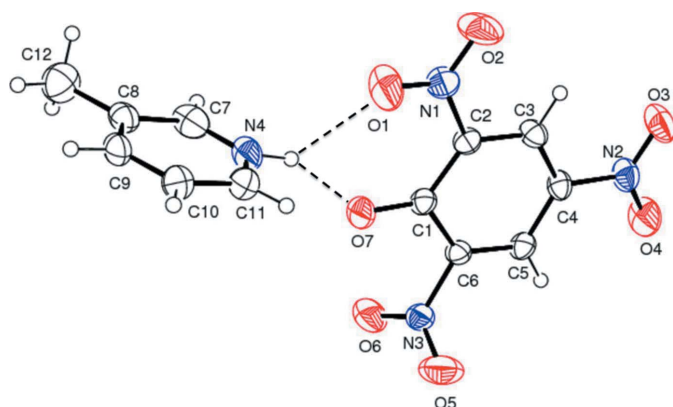


The observation that the presence of more than one heterocyclic component in a molecule enhances the biological response and thermal stability encouraged us to synthesize several new carbon-bonded anionic sigma complexes from chloronitro-aromatic compounds and pyrimidine derivatives in the presence of pyridine bases (Babykala *et al.*, 2014; Buvaneswari & Kalaivani, 2013; Mangaiyarkarasi & Kalaivani, 2013; Manickkum & Kalaivani, 2011, 2014; Sridevi & Kalaivani, 2012). Surprisingly, when we made an attempt to synthesize a similar type of complex from the electron-deficient chloronitroaromatic compound (picryl chloride), an imidazole derivative (hydantoin) and 3-methylpyridine, the title salt crystallized from the medium (ethanol) instead of the expected carbon-bonded anionic sigma complex.

## 2. Structural commentary

The molecular structure of the title molecular salt is shown in Fig. 1. The anion and cation are linked *via* bifurcated N—





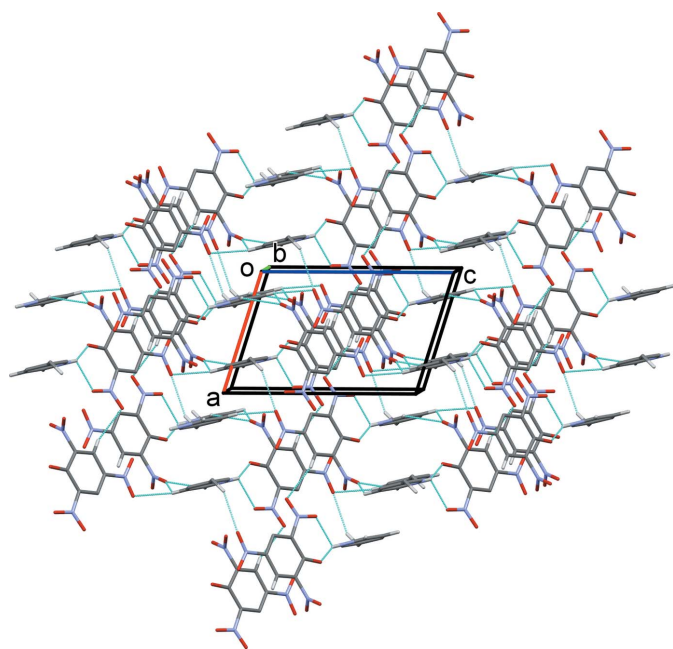
**Figure 1**

A view of the molecular structure of the title molecular salt, with atom labelling. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen bonds are shown as dashed lines (see Table 1).

$\text{H}\cdots(\text{O},\text{O})$  hydrogen bonds, enclosing an  $R_1^2(6)$  graph-set motif (Fig. 1 and Table 1). In the picrate anion, the two nitro groups flanking the  $\text{C}-\text{O}^-$  bond are oriented differently. Nitro group  $\text{O1/N1/O2}$ , involved in  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds as noted above, is inclined to the benzene ring by  $6.7(3)^\circ$ , while nitro group  $\text{O5/N3/O6}$  is inclined to the benzene ring by  $70.07(3)^\circ$ , probably to alleviate steric crowding. The third nitro group ( $\text{O3/N2/O4}$ ), *para* with respect to the  $\text{C}-\text{O}^-$  bond, deviates only slightly from the benzene ring, making a dihedral angle of  $6.6(3)^\circ$ .

### 3. Supramolecular features

In the crystal, the anionic and cationic hydrogen-bonded units are linked *via*  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, forming a three-



**Figure 2**

A view along the *b* axis of the crystal packing of the title molecular salt. Hydrogen bonds are shown as dashed lines (see Table 1), and H atoms not involved in these interactions have been omitted for clarity.

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N4}-\text{H4A}\cdots\text{O1}$	0.93 (4)	2.27 (4)	2.827 (4)	118 (4)
$\text{N4}-\text{H4A}\cdots\text{O7}$	0.93 (4)	1.79 (5)	2.638 (4)	152 (4)
$\text{C5}-\text{H5}\cdots\text{O2}^{\text{i}}$	0.93	2.51	3.406 (4)	162
$\text{C10}-\text{H10}\cdots\text{O3}^{\text{ii}}$	0.93	2.55	3.220 (4)	129
$\text{C12}-\text{H12B}\cdots\text{O3}^{\text{iii}}$	0.96	2.56	3.414 (5)	149

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

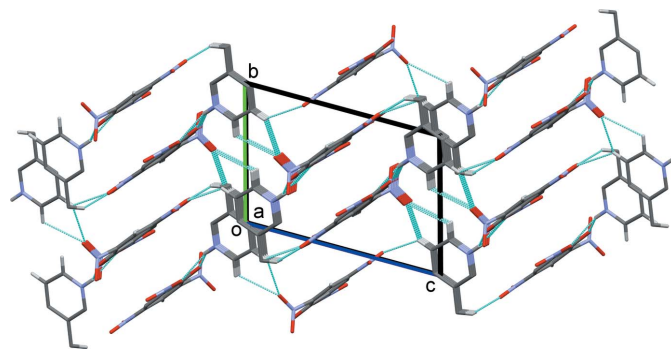
dimensional structure (Figs. 2 and 3, and Table 1). Within this framework there are slipped parallel  $\pi-\pi$  interactions present, involving inversion-related picrate anions [inter-centroid distance =  $3.7389(14)$   $\text{\AA}$ , inter-planar distance =  $3.5829(8)$   $\text{\AA}$ , slippage =  $1.069$   $\text{\AA}$ ] and inversion-related pyridinium cations [inter-centroid distance =  $3.560(2)$   $\text{\AA}$ , inter-planar distance =  $3.5548(14)$   $\text{\AA}$ , slippage =  $0.422$   $\text{\AA}$ ].

### 4. Anticonvulsant activity

The anticonvulsant activity of synthesized 3-methylpyridinium picrate has been measured by employing the maximal electro shock (MES) method (Bhattacharya & Chakrabarti, 1998; Misra *et al.*, 1973). Different stages of convulsion such as tonic flexion, tonic extensor, clonus convulsion, stupor and recovery/death have been examined. Though all phases are reduced, noticeable decrease is observed in the clonus phase and hence the title molecule may be a potent agent for controlling myoclonic type epilepsy in the future.

### 5. Database survey

A search of the Cambridge Structural Database (Version 5.36, last update May 2015; Groom & Allen, 2014) yielded 40 hits for *meta*- or *para*-substituted pyridinium picrate salts. In the picrate anions, the average dihedral angle of the nitro group *para* to the  $\text{C}-\text{O}^-$  bond with respect to the benzene ring is *ca*  $6^\circ$ , while for the two nitro groups on either side of the  $\text{C}-\text{O}^-$  bond the dihedral angles are both *ca*  $26-28^\circ$ . In the title



**Figure 3**

A view along the *a* axis of the crystal packing of the title molecular salt. Hydrogen bonds are shown as dashed lines (see Table 1), and H atoms not involved in these interactions have been omitted for clarity.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$C_6H_8N^+ \cdot C_6H_2N_3O_7^-$
$M_r$	322.24
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
$a, b, c$ (Å)	8.1224 (5), 8.7016 (5), 11.3161 (6)
$\alpha, \beta, \gamma$ (°)	98.239 (3), 100.318 (3), 117.635 (3)
$V$ (Å <sup>3</sup> )	673.17 (7)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.13
Crystal size (mm)	0.35 × 0.30 × 0.25
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2004)
$T_{\min}$ , $T_{\max}$	0.952, 0.969
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	13299, 2374, 1717
$R_{\text{int}}$	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.045, 0.131, 1.07
No. of reflections	2374
No. of parameters	212
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.24, -0.25

Computer programs: APEX2, SAINT and XPREP (Bruker, 2004), SIR92 (Altomare *et al.*, 1993), ORTEP-3 for Windows (Farrugia, 2012), Mercury (Macrae *et al.*, 2008), SHELXL2014 (Sheldrick, 2015) and PLATON (Spek, 2009).

compound, the latter two dihedral angles are quite different being 6.7 (3) and 70.07 (3)°. In the monoclinic polymorph (UBEFEO; Stilinovic & Kaitner, 2011), these three dihedral angle are *ca* 3.60, 6.92 and 13.83°, respectively, and the cation and anion are also linked *via* bifurcated N—H···(O,O) hydrogen bonds.

## 6. Synthesis and crystallization

Picryl chloride [2.56 g (0.01 mol)] was dissolved in 30 ml of rectified spirit and mixed with hydantoin [1.00 g (0.01 mol)] in 30 ml of rectified spirit. After mixing these solutions, 3 ml of 3-methylpyridine (0.03 mol) was added and the temperature of the mixture was raised to 313 K. At this temperature, the mixture was stirred for 5 to 6 h. The solution was then cooled

to room temperature, filtered and the filtrate kept at 298 K. After a period of 4 weeks, dark shiny maroon-red-coloured crystals formed from the solution. The crystals were filtered, powdered and dried. The dry solid was washed with 50 ml of dry ether (5 ml for each aliquot) and recrystallized from rectified spirit (yield: 60%; m.p. 483 K).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH H atom was located in a difference Fourier map and freely refined. The C-bound H atoms were included in calculated positions and refined as riding: C—H = 0.93–0.96 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Acknowledgements

The authors are thankful to the DST–SERB, New Delhi, for financial support and the SAIF, IIT Madras, Chennai, for the single crystal XRD data collection.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Babukala, R., Rajamani, K., Muthulakshmi, S. & Kalaivani, D. (2014). *J. Chem. Crystallogr.* **44**, 243–254.
- Bhattacharya, S. K. & Chakrabarti, A. (1998). *Ind. J. Exp. Biol.* **36**, 118–121.
- Bruker (2004). APEX2, SAINT, XPREP and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Buvaneswari, M. & Kalaivani, D. (2013). *J. Chem. Crystallogr.* **43**, 561–567.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Mangaiyarkarasi, G. & Kalaivani, D. (2013). *Crystallogr. Rep.* **58**, 1096–1102.
- Manickkum, V. & Kalaivani, D. (2011). *Acta Cryst.* **E67**, o3475.
- Manickkum, V. & Kalaivani, D. (2014). *Acta Cryst.* **E70**, 256–258.
- Misra, A. K., Dandiya, P. C. & Kulkarni, S. K. (1973). *Ind. J. Pharmacol.* **5**, 449–450.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Sridevi, G. & Kalaivani, D. (2012). *Acta Cryst.* **E68**, o1044.
- Stilinović, V. & Kaitner, B. (2011). *Cryst. Growth Des.* **11**, 4110–4119.

## supporting information

*Acta Cryst.* (2015). E71, 1196-1198 [doi:10.1107/S2056989015017090]

## Crystal structure of 3-methylpyridinium picrate: a triclinic polymorph

Jeganathan Gomathi and Doraisamyraja Kalaivani

### Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

### 3-Methylpyridinium 2,4,6-trinitrophenolate

#### Crystal data

$C_6H_8N^+ \cdot C_6H_2N_3O_7^-$

$M_r = 322.24$

Triclinic,  $P\bar{1}$

$a = 8.1224$  (5) Å

$b = 8.7016$  (5) Å

$c = 11.3161$  (6) Å

$\alpha = 98.239$  (3)°

$\beta = 100.318$  (3)°

$\gamma = 117.635$  (3)°

$V = 673.17$  (7) Å<sup>3</sup>

$Z = 2$

$F(000) = 332$

$D_x = 1.590$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5179 reflections

$\theta = 2.7$ – $26.9$ °

$\mu = 0.13$  mm<sup>-1</sup>

$T = 293$  K

Block, red

$0.35 \times 0.30 \times 0.25$  mm

#### Data collection

Bruker Kappa APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  and  $\phi$  scan

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2004)

$T_{\min} = 0.952$ ,  $T_{\max} = 0.969$

13299 measured reflections

2374 independent reflections

1717 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 25.0$ °,  $\theta_{\min} = 2.7$ °

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -13 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.131$

$S = 1.07$

2374 reflections

212 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.5934P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.25$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6227 (3)	0.5359 (3)	0.3281 (2)	0.0338 (5)
C2	0.8010 (3)	0.6555 (3)	0.4224 (2)	0.0342 (5)
C3	0.8216 (3)	0.7875 (3)	0.5161 (2)	0.0371 (6)
H3	0.9405	0.8616	0.5755	0.044*
C4	0.6675 (3)	0.8101 (3)	0.5224 (2)	0.0356 (6)
C5	0.4892 (3)	0.7045 (3)	0.4328 (2)	0.0352 (6)
H5	0.3854	0.7222	0.4356	0.042*
C6	0.4730 (3)	0.5752 (3)	0.3417 (2)	0.0320 (5)
C7	0.7112 (4)	0.0619 (4)	0.1648 (3)	0.0537 (7)
H7	0.6806	0.0272	0.2355	0.064*
C8	0.7330 (4)	-0.0490 (4)	0.0772 (2)	0.0441 (6)
C9	0.7774 (4)	0.0108 (4)	-0.0253 (2)	0.0460 (7)
H9	0.7911	-0.0610	-0.0875	0.055*
C10	0.8018 (4)	0.1739 (4)	-0.0378 (3)	0.0516 (7)
H10	0.8335	0.2132	-0.1071	0.062*
C11	0.7792 (4)	0.2771 (4)	0.0525 (3)	0.0530 (7)
H11	0.7960	0.3885	0.0460	0.064*
C12	0.7062 (5)	-0.2262 (4)	0.0915 (3)	0.0683 (9)
H12A	0.7274	-0.2835	0.0214	0.102*
H12B	0.7972	-0.2084	0.1665	0.102*
H12C	0.5769	-0.3007	0.0957	0.102*
N1	0.9729 (3)	0.6445 (3)	0.4219 (2)	0.0495 (6)
N2	0.6903 (3)	0.9444 (3)	0.6245 (2)	0.0461 (6)
N3	0.2906 (3)	0.4686 (3)	0.24334 (19)	0.0398 (5)
N4	0.7332 (3)	0.2180 (4)	0.1493 (2)	0.0549 (7)
O1	0.9718 (3)	0.5443 (3)	0.3360 (3)	0.0885 (9)
O2	1.1190 (3)	0.7419 (4)	0.5074 (2)	0.0792 (8)
O3	0.8528 (3)	1.0446 (3)	0.69676 (19)	0.0630 (6)
O4	0.5489 (3)	0.9540 (3)	0.6359 (2)	0.0670 (6)
O5	0.2505 (3)	0.5433 (3)	0.1711 (2)	0.0799 (7)
O6	0.1909 (3)	0.3122 (3)	0.2365 (2)	0.0673 (6)
O7	0.5902 (3)	0.4101 (3)	0.24116 (17)	0.0518 (5)
H4A	0.712 (6)	0.291 (5)	0.205 (4)	0.093 (12)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0374 (13)	0.0393 (13)	0.0313 (12)	0.0242 (11)	0.0115 (10)	0.0080 (10)
C2	0.0287 (12)	0.0393 (13)	0.0389 (13)	0.0200 (10)	0.0124 (10)	0.0079 (10)

C3	0.0301 (13)	0.0386 (13)	0.0358 (13)	0.0136 (10)	0.0085 (10)	0.0050 (10)
C4	0.0384 (14)	0.0339 (12)	0.0345 (12)	0.0186 (11)	0.0138 (11)	0.0031 (10)
C5	0.0361 (13)	0.0396 (13)	0.0381 (13)	0.0246 (11)	0.0141 (11)	0.0084 (11)
C6	0.0310 (12)	0.0372 (12)	0.0302 (12)	0.0203 (10)	0.0074 (10)	0.0063 (10)
C7	0.0408 (16)	0.072 (2)	0.0438 (15)	0.0268 (14)	0.0152 (12)	0.0057 (14)
C8	0.0328 (13)	0.0488 (15)	0.0427 (15)	0.0188 (12)	0.0067 (11)	0.0002 (12)
C9	0.0453 (15)	0.0493 (15)	0.0403 (14)	0.0272 (13)	0.0078 (12)	-0.0050 (12)
C10	0.0584 (18)	0.0547 (17)	0.0434 (15)	0.0330 (14)	0.0112 (13)	0.0048 (13)
C11	0.0496 (17)	0.0504 (16)	0.0557 (18)	0.0304 (14)	0.0038 (14)	-0.0005 (14)
C12	0.067 (2)	0.062 (2)	0.076 (2)	0.0307 (17)	0.0222 (18)	0.0207 (17)
N1	0.0350 (13)	0.0548 (14)	0.0596 (15)	0.0254 (11)	0.0136 (11)	0.0064 (12)
N2	0.0503 (14)	0.0424 (12)	0.0428 (12)	0.0233 (11)	0.0148 (11)	0.0009 (10)
N3	0.0386 (12)	0.0480 (13)	0.0360 (11)	0.0269 (11)	0.0076 (9)	0.0048 (10)
N4	0.0416 (13)	0.0639 (16)	0.0530 (15)	0.0316 (12)	0.0076 (11)	-0.0137 (13)
O1	0.0459 (13)	0.0855 (16)	0.114 (2)	0.0365 (12)	0.0156 (13)	-0.0352 (15)
O2	0.0415 (12)	0.116 (2)	0.0693 (15)	0.0458 (13)	-0.0011 (11)	-0.0092 (14)
O3	0.0572 (13)	0.0555 (12)	0.0524 (12)	0.0195 (10)	0.0083 (10)	-0.0134 (10)
O4	0.0646 (14)	0.0736 (14)	0.0663 (14)	0.0430 (12)	0.0233 (11)	-0.0078 (11)
O5	0.0700 (16)	0.0835 (16)	0.0718 (15)	0.0343 (13)	-0.0089 (12)	0.0310 (13)
O6	0.0546 (13)	0.0478 (13)	0.0684 (14)	0.0122 (10)	-0.0058 (10)	0.0049 (10)
O7	0.0504 (11)	0.0585 (12)	0.0472 (11)	0.0367 (10)	0.0068 (9)	-0.0093 (9)

*Geometric parameters (Å, °)*

C1—O7	1.251 (3)	C9—C10	1.371 (4)
C1—C2	1.432 (3)	C9—H9	0.9300
C1—C6	1.434 (3)	C10—C11	1.357 (4)
C2—C3	1.372 (3)	C10—H10	0.9300
C2—N1	1.444 (3)	C11—N4	1.318 (4)
C3—C4	1.366 (3)	C11—H11	0.9300
C3—H3	0.9300	C12—H12A	0.9600
C4—C5	1.394 (3)	C12—H12B	0.9600
C4—N2	1.439 (3)	C12—H12C	0.9600
C5—C6	1.351 (3)	N1—O1	1.205 (3)
C5—H5	0.9300	N1—O2	1.218 (3)
C6—N3	1.461 (3)	N2—O4	1.217 (3)
C7—N4	1.326 (4)	N2—O3	1.230 (3)
C7—C8	1.375 (4)	N3—O6	1.199 (3)
C7—H7	0.9300	N3—O5	1.205 (3)
C8—C9	1.377 (4)	N4—H4A	0.93 (4)
C8—C12	1.491 (4)		
O7—C1—C2	127.4 (2)	C8—C9—H9	119.3
O7—C1—C6	120.7 (2)	C11—C10—C9	119.0 (3)
C2—C1—C6	111.90 (19)	C11—C10—H10	120.5
C3—C2—C1	123.2 (2)	C9—C10—H10	120.5
C3—C2—N1	116.0 (2)	N4—C11—C10	119.4 (3)
C1—C2—N1	120.8 (2)	N4—C11—H11	120.3

C4—C3—C2	120.0 (2)	C10—C11—H11	120.3
C4—C3—H3	120.0	C8—C12—H12A	109.5
C2—C3—H3	120.0	C8—C12—H12B	109.5
C3—C4—C5	121.2 (2)	H12A—C12—H12B	109.5
C3—C4—N2	119.0 (2)	C8—C12—H12C	109.5
C5—C4—N2	119.7 (2)	H12A—C12—H12C	109.5
C6—C5—C4	117.4 (2)	H12B—C12—H12C	109.5
C6—C5—H5	121.3	O1—N1—O2	121.1 (2)
C4—C5—H5	121.3	O1—N1—C2	120.0 (2)
C5—C6—C1	126.1 (2)	O2—N1—C2	118.8 (2)
C5—C6—N3	118.5 (2)	O4—N2—O3	122.8 (2)
C1—C6—N3	115.36 (19)	O4—N2—C4	119.0 (2)
N4—C7—C8	120.7 (3)	O3—N2—C4	118.2 (2)
N4—C7—H7	119.6	O6—N3—O5	123.3 (2)
C8—C7—H7	119.6	O6—N3—C6	119.3 (2)
C7—C8—C9	116.5 (3)	O5—N3—C6	117.4 (2)
C7—C8—C12	121.8 (3)	C11—N4—C7	123.0 (2)
C9—C8—C12	121.8 (2)	C11—N4—H4A	115 (2)
C10—C9—C8	121.5 (2)	C7—N4—H4A	122 (2)
C10—C9—H9	119.3		
O7—C1—C2—C3	-178.4 (2)	C7—C8—C9—C10	1.2 (4)
C6—C1—C2—C3	1.9 (3)	C12—C8—C9—C10	-180.0 (3)
O7—C1—C2—N1	2.7 (4)	C8—C9—C10—C11	-0.8 (4)
C6—C1—C2—N1	-177.0 (2)	C9—C10—C11—N4	-0.4 (4)
C1—C2—C3—C4	-0.2 (4)	C3—C2—N1—O1	-172.7 (3)
N1—C2—C3—C4	178.7 (2)	C1—C2—N1—O1	6.3 (4)
C2—C3—C4—C5	-1.9 (4)	C3—C2—N1—O2	5.0 (4)
C2—C3—C4—N2	177.4 (2)	C1—C2—N1—O2	-176.0 (3)
C3—C4—C5—C6	2.0 (4)	C3—C4—N2—O4	-173.7 (2)
N2—C4—C5—C6	-177.3 (2)	C5—C4—N2—O4	5.6 (4)
C4—C5—C6—C1	0.0 (4)	C3—C4—N2—O3	6.1 (4)
C4—C5—C6—N3	-177.0 (2)	C5—C4—N2—O3	-174.6 (2)
O7—C1—C6—C5	178.5 (2)	C5—C6—N3—O6	-112.1 (3)
C2—C1—C6—C5	-1.8 (3)	C1—C6—N3—O6	70.5 (3)
O7—C1—C6—N3	-4.4 (3)	C5—C6—N3—O5	69.4 (3)
C2—C1—C6—N3	175.3 (2)	C1—C6—N3—O5	-108.0 (3)
N4—C7—C8—C9	-0.3 (4)	C10—C11—N4—C7	1.4 (4)
N4—C7—C8—C12	-179.1 (3)	C8—C7—N4—C11	-1.0 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4A...O1	0.93 (4)	2.27 (4)	2.827 (4)	118 (4)
N4—H4A...O7	0.93 (4)	1.79 (5)	2.638 (4)	152 (4)
C5—H5...O2 <sup>i</sup>	0.93	2.51	3.406 (4)	162

C10—H10 $\cdots$ O3 <sup>ii</sup>	0.93	2.55	3.220 (4)	129
C12—H12B $\cdots$ O3 <sup>iii</sup>	0.96	2.56	3.414 (5)	149

---

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