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2-[(Pyridin-2-yl)amino]pyridinium
2,4,6-trinitrophenolateKateryna A. Ohui,^{a*} Irina A. Golenya^a and Nadezhda A. Bokach^b^aDepartment of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska 64/13, 01601 Kyiv, Ukraine, and ^bDepartment of Chemistry, Saint Petersburg State University, Universitetsky Pr. 26, 198504 Stary Peterhof, Russian Federation

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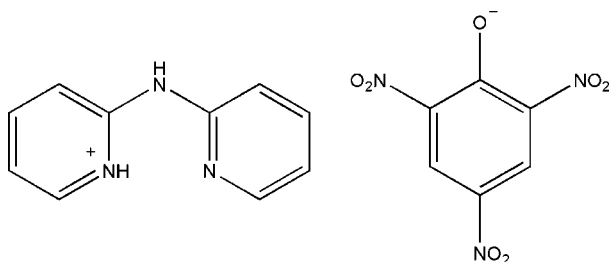
Received 23 May 2014; accepted 2 June 2014

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.043; wR factor = 0.102; data-to-parameter ratio = 12.0.

In the cation of the title salt, $\text{C}_{10}\text{H}_{10}\text{N}_3^+ \cdot \text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, the pyridine and pyridinium rings are linked by an intramolecular $\text{N}-\text{H} \cdots \text{N}$ hydrogen bond and are approximately coplanar, with a dihedral angle between their planes of 4.24 (6°). In the crystal, the cations and anions are linked through $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming supramolecular chains propagating along the c -axis direction. $\pi-\pi$ stacking is observed between neighbouring chains, the centroid-centroid distances being 3.7638 (11) (between pyridinium rings) and 3.5331 (11) Å (between benzene rings).

Related literature

For uses of picric acid and picrates, see: Shriner *et al.* (1980); In *et al.* (1997); Zaderenko *et al.* (1997). For related structures, see: Fritsky *et al.* (2006); Moroz *et al.* (2012); Penkova *et al.* (2009); Golenya *et al.* (2012).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_3^+ \cdot \text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$
 $M_r = 400.32$
 Monoclinic, $P2_1/c$
 $a = 9.1807$ (8) Å
 $b = 14.5892$ (12) Å

$c = 13.1649$ (10) Å
 $\beta = 108.925$ (2)°
 $V = 1668.0$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.13$ mm⁻¹
 $T = 100$ K

0.25 × 0.21 × 0.18 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.974$, $T_{\max} = 0.983$

10460 measured reflections
 3253 independent reflections
 2674 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.102$
 $S = 1.03$
 3253 reflections
 270 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.59$ e Å⁻³
 $\Delta\rho_{\min} = -0.55$ e Å⁻³

Table 1
 Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1N} \cdots \text{N3}$	0.92 (2)	1.86 (2)	2.618 (2)	139 (2)
$\text{N1}-\text{H1N} \cdots \text{O4}^{\text{ii}}$	0.92 (2)	2.45 (2)	3.056 (2)	123.8 (17)
$\text{N2}-\text{H2N} \cdots \text{O1}^{\text{ii}}$	0.87 (2)	1.97 (2)	2.756 (2)	149 (2)
$\text{N2}-\text{H2N} \cdots \text{O2}^{\text{ii}}$	0.87 (2)	2.42 (2)	3.114 (2)	136.6 (18)

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT (Bruker, 2007); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2009); software used to prepare material for publication: SHELXL97 (Sheldrick, 2008).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5794).

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supporting information

Acta Cryst. (2014). E70, o778 [doi:10.1107/S1600536814012835]

2-[(Pyridin-2-yl)amino]pyridinium 2,4,6-trinitrophenolate

Kateryna A. Ohui, Irina A. Golenya and Nadezhda A. Bokach

0.1. Synthesis and crystallization

The 2,2'-dipyridylamine (1.71 g, 0.01 mol) was added to picric acid (2.29 g, 0.01 mol) dissolved in ethanol (50ml). The obtained mixture was stirred for 24 hours, then this solution was left at room temperature for crystallization in the air. The crystals grown within 24 hours were separated, washed with ethanol and air-dried.

0.2. Refinement

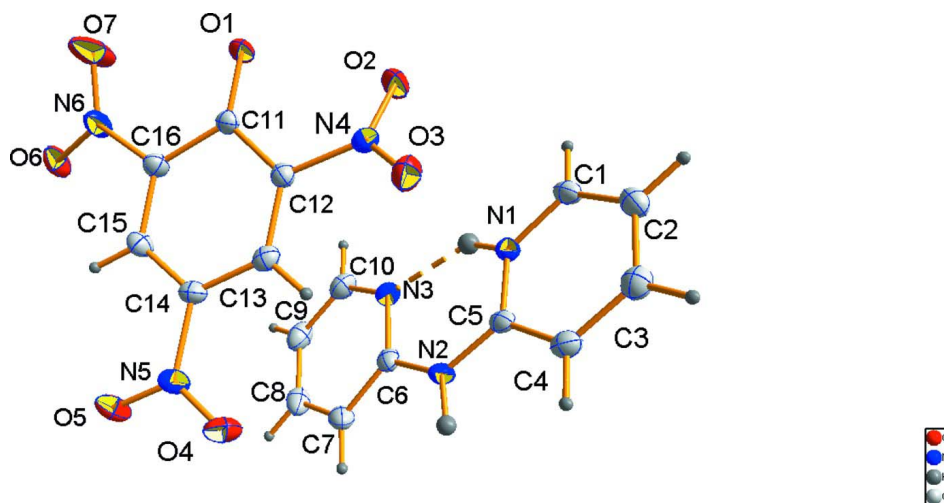
The NH hydrogen atoms were located from the difference Fourier map and refined isotropically. Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C—H = 0.95 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

1. Results and discussion

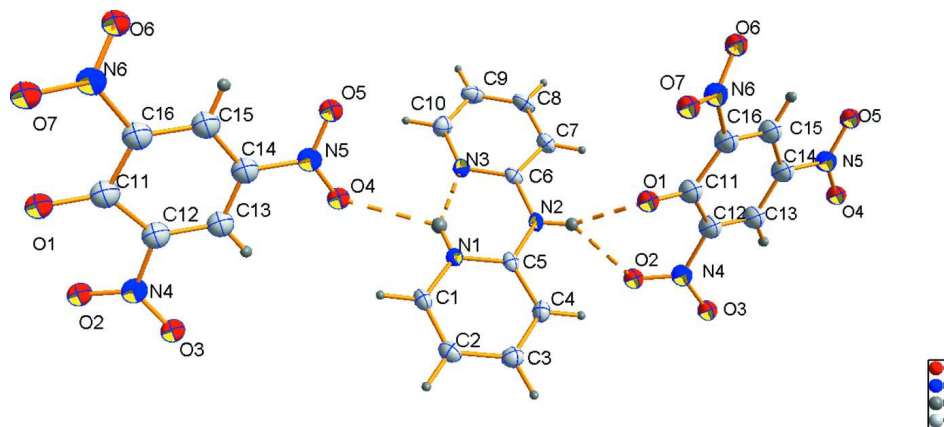
Picric acid is a common reagent widely used for isolation in crystalline state of various organic compounds, in particular, amines and alkaloids (Shriner *et al.*, 1980). In laboratorial practice it is also used in analysis of amines and polycyclic hydrocarbons (In *et al.*, 1997; Zaderenko *et al.*, 1997).

In the present communication we report the molecular structure of 2-(2-pyridylamino)pyridinium picrate. The crystal structure of the title compound $\text{C}_{10}\text{H}_{10}\text{N}_3^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$ is ionic and consists of the protonated cation $\text{C}_{10}\text{H}_{10}\text{N}_3^+$ and the deprotonated picrate anion $\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$. The cation is approximately planar. The dihedral angle between two heterocyclic rings is 4.24 (6)°. The picrate anion is not planar: the three nitro-groups [N4—O2—O3], [N5—O4—O5], [N6—O6—O7] are twisted with respect to the benzene ring, the dihedral angles between their square - least planes are 26.8 (2)°, 4.5 (1)°, 23.0 (3)°. The C—N and C—C bond lengths in the pyridine rings are normal for 2-substituted pyridine derivatives (Fritsky *et al.*, 2006; Moroz *et al.*, 2012; Penkova *et al.*, 2009; Golenya *et al.*, 2012).

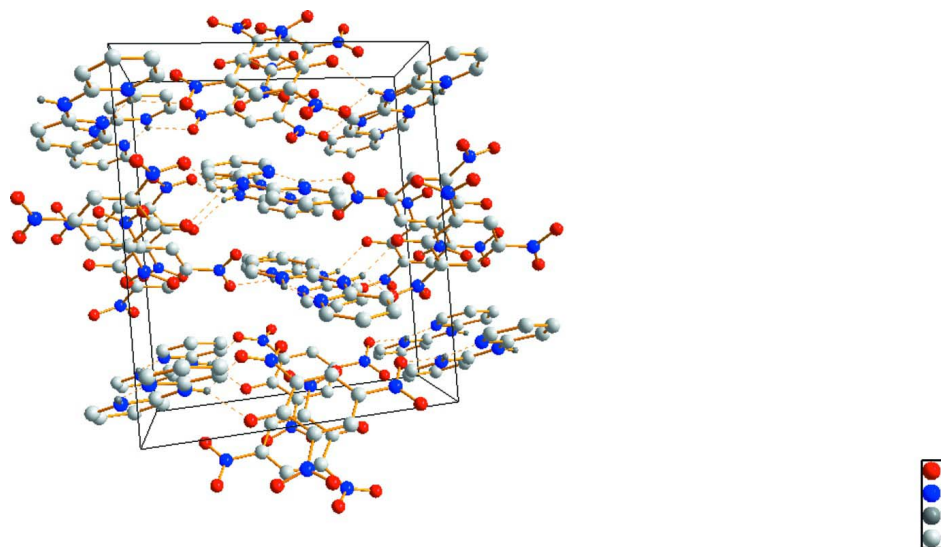
The 2-(2-pyridylamino)pyridinium cation and the picrate anion are connected to each other by the existence of N—H...O and N—H...N hydrogen-bonding interactions and form one-dimensional chains. The protonated NH pyridinium group of the 2-(2-pyridylamino)pyridinium cation is involved in a bifurcated intermolecular hydrogen bond with the oxygen atom of the nitro-group and the pyridyne nitrogen atom. The second of these H-bonds is an intramolecular. The amine oxygen atom of the 2-(2-pyridylamino)pyridinium cation also forms bifurcate N2—H2...O1 and N2—H2...O2 hydrogen bonds with the oxygen atom of the nitro-group and with the oxygen atom of the deprotonated hydroxo-group of the picrate anion.

**Figure 1**

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

A view of the one-dimensional chain formed via hydrogen bonds.

**Figure 3**

A packing diagram of the title compound. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

2-[(Pyridin-2-yl)amino]pyridinium 2,4,6-trinitrophenolate

Crystal data

$C_{10}H_{10}N_3^+ \cdot C_6H_2N_3O_7^-$

$M_r = 400.32$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 9.1807$ (8) Å

$b = 14.5892$ (12) Å

$c = 13.1649$ (10) Å

$\beta = 108.925$ (2)°

$V = 1668.0$ (2) Å³

$Z = 4$

$F(000) = 824$

$D_x = 1.594$ Mg m⁻³

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

Cell parameters from 3858 reflections

$\theta = 2.4$ – 29.9 °

$\mu = 0.13$ mm⁻¹

$T = 100$ K

Block, yellow

$0.25 \times 0.21 \times 0.18$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Horizontally mounted graphite crystal
monochromator

Detector resolution: 16 pixels mm⁻¹

φ scans and ω scans with κ offset

Absorption correction: multi-scan
(*SADABS*; Bruker, 2002)

$T_{\min} = 0.974$, $T_{\max} = 0.983$

10460 measured reflections

3253 independent reflections

2674 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.2$ °

$h = -11 \rightarrow 11$

$k = -17 \rightarrow 16$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.102$

$S = 1.03$

3253 reflections

270 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 1.2391P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$$\Delta\rho_{\max} = 0.59 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.55 \text{ e } \text{Å}^{-3}$$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.10222 (15)	0.54091 (9)	-0.17771 (10)	0.0236 (3)
O2	-0.06688 (18)	0.69273 (10)	-0.18938 (11)	0.0323 (4)
O3	-0.16715 (15)	0.69936 (9)	-0.06137 (11)	0.0259 (3)
O4	0.15975 (16)	0.63990 (10)	0.29479 (10)	0.0279 (3)
O5	0.35245 (15)	0.54601 (10)	0.32327 (10)	0.0282 (3)
O6	0.46259 (16)	0.40445 (10)	0.03187 (11)	0.0289 (3)
O7	0.2807 (2)	0.39426 (15)	-0.11952 (13)	0.0702 (7)
N1	-0.01574 (18)	0.88497 (10)	-0.04563 (12)	0.0176 (3)
H1N	0.079 (3)	0.8656 (16)	-0.0451 (18)	0.036 (6)*
N2	0.08719 (18)	0.86091 (11)	0.14029 (12)	0.0199 (3)
H2N	0.075 (2)	0.8730 (15)	0.2019 (18)	0.027 (6)*
N3	0.26368 (18)	0.82539 (11)	0.05248 (12)	0.0213 (4)
N4	-0.06696 (18)	0.67256 (11)	-0.09846 (12)	0.0212 (3)
N5	0.24186 (18)	0.58829 (11)	0.26247 (12)	0.0210 (4)
N6	0.3395 (2)	0.42975 (12)	-0.03160 (13)	0.0288 (4)
C1	-0.1325 (2)	0.90766 (13)	-0.13575 (14)	0.0206 (4)
H1	-0.1166	0.9064	-0.2035	0.025*
C2	-0.2720 (2)	0.93213 (13)	-0.12947 (15)	0.0232 (4)
H2	-0.3541	0.9481	-0.1923	0.028*
C3	-0.2925 (2)	0.93344 (13)	-0.02863 (15)	0.0238 (4)
H3	-0.3894	0.9507	-0.0230	0.029*
C4	-0.1746 (2)	0.91021 (13)	0.06177 (15)	0.0216 (4)
H4	-0.1889	0.9113	0.1300	0.026*
C5	-0.0325 (2)	0.88481 (12)	0.05260 (14)	0.0173 (4)
C6	0.2352 (2)	0.83475 (12)	0.14498 (15)	0.0192 (4)
C7	0.3446 (2)	0.81826 (13)	0.24528 (15)	0.0242 (4)
H7	0.3202	0.8258	0.3096	0.029*
C8	0.4886 (2)	0.79074 (14)	0.24768 (17)	0.0292 (5)
H8	0.5662	0.7791	0.3144	0.035*
C9	0.5205 (2)	0.77997 (14)	0.15200 (18)	0.0304 (5)
H9	0.6193	0.7604	0.1522	0.036*

C10	0.4057 (2)	0.79824 (14)	0.05736 (17)	0.0278 (5)
H10	0.4277	0.7914	-0.0079	0.033*
C11	0.1351 (2)	0.55224 (12)	-0.07926 (14)	0.0170 (4)
C12	0.0569 (2)	0.61648 (12)	-0.02980 (14)	0.0171 (4)
C13	0.0877 (2)	0.62673 (12)	0.07851 (14)	0.0176 (4)
H13	0.0282	0.6674	0.1055	0.021*
C14	0.2068 (2)	0.57704 (12)	0.14803 (14)	0.0180 (4)
C15	0.2908 (2)	0.51464 (13)	0.10980 (14)	0.0188 (4)
H15	0.3731	0.4814	0.1584	0.023*
C16	0.2538 (2)	0.50156 (12)	0.00165 (14)	0.0190 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0346 (8)	0.0227 (7)	0.0129 (6)	0.0057 (6)	0.0068 (6)	0.0021 (6)
O2	0.0471 (9)	0.0303 (8)	0.0171 (7)	0.0138 (7)	0.0070 (6)	0.0061 (6)
O3	0.0236 (7)	0.0218 (7)	0.0316 (8)	0.0031 (6)	0.0082 (6)	-0.0005 (6)
O4	0.0306 (8)	0.0354 (8)	0.0201 (7)	-0.0002 (6)	0.0116 (6)	-0.0062 (6)
O5	0.0250 (7)	0.0407 (9)	0.0158 (7)	0.0015 (6)	0.0021 (6)	0.0036 (6)
O6	0.0269 (8)	0.0336 (8)	0.0272 (7)	0.0120 (6)	0.0102 (6)	0.0095 (6)
O7	0.0931 (15)	0.0786 (14)	0.0221 (9)	0.0595 (12)	-0.0045 (9)	-0.0153 (9)
N1	0.0190 (8)	0.0170 (8)	0.0162 (8)	-0.0009 (6)	0.0052 (6)	-0.0003 (6)
N2	0.0224 (8)	0.0240 (8)	0.0132 (8)	0.0013 (7)	0.0056 (6)	-0.0013 (7)
N3	0.0222 (8)	0.0207 (8)	0.0215 (8)	-0.0001 (7)	0.0076 (7)	-0.0024 (7)
N4	0.0242 (8)	0.0166 (8)	0.0195 (8)	-0.0003 (7)	0.0026 (7)	-0.0029 (7)
N5	0.0212 (8)	0.0256 (8)	0.0161 (8)	-0.0062 (7)	0.0060 (7)	-0.0018 (7)
N6	0.0354 (10)	0.0328 (10)	0.0180 (8)	0.0142 (8)	0.0084 (7)	0.0023 (8)
C1	0.0252 (10)	0.0201 (9)	0.0147 (9)	-0.0021 (8)	0.0041 (7)	0.0006 (8)
C2	0.0225 (10)	0.0226 (10)	0.0213 (10)	0.0005 (8)	0.0025 (8)	0.0025 (8)
C3	0.0215 (10)	0.0228 (10)	0.0271 (10)	0.0009 (8)	0.0079 (8)	-0.0010 (8)
C4	0.0255 (10)	0.0215 (10)	0.0191 (9)	-0.0008 (8)	0.0092 (8)	-0.0023 (8)
C5	0.0228 (10)	0.0128 (8)	0.0155 (9)	-0.0028 (7)	0.0051 (7)	-0.0021 (7)
C6	0.0207 (9)	0.0141 (9)	0.0203 (9)	-0.0014 (7)	0.0034 (7)	-0.0025 (7)
C7	0.0271 (10)	0.0220 (10)	0.0197 (9)	-0.0001 (8)	0.0023 (8)	-0.0029 (8)
C8	0.0252 (11)	0.0229 (10)	0.0302 (11)	0.0018 (8)	-0.0036 (8)	-0.0031 (9)
C9	0.0208 (10)	0.0276 (11)	0.0399 (12)	0.0017 (8)	0.0059 (9)	-0.0076 (10)
C10	0.0273 (11)	0.0266 (11)	0.0316 (11)	0.0019 (9)	0.0124 (9)	-0.0043 (9)
C11	0.0199 (9)	0.0150 (9)	0.0154 (9)	-0.0033 (7)	0.0049 (7)	0.0012 (7)
C12	0.0171 (9)	0.0147 (9)	0.0178 (9)	-0.0023 (7)	0.0032 (7)	0.0002 (7)
C13	0.0182 (9)	0.0160 (9)	0.0196 (9)	-0.0043 (7)	0.0074 (7)	-0.0022 (7)
C14	0.0192 (9)	0.0209 (9)	0.0140 (9)	-0.0046 (7)	0.0057 (7)	-0.0019 (7)
C15	0.0156 (9)	0.0222 (9)	0.0172 (9)	-0.0014 (7)	0.0034 (7)	0.0022 (8)
C16	0.0200 (9)	0.0208 (9)	0.0173 (9)	0.0001 (8)	0.0074 (8)	0.0001 (8)

Geometric parameters (Å, °)

O1—C11	1.243 (2)	C2—H2	0.9500
O2—N4	1.233 (2)	C3—C4	1.367 (3)

O3—N4	1.237 (2)	C3—H3	0.9500
O4—N5	1.235 (2)	C4—C5	1.398 (3)
O5—N5	1.235 (2)	C4—H4	0.9500
O6—N6	1.224 (2)	C6—C7	1.396 (3)
O7—N6	1.222 (2)	C7—C8	1.371 (3)
N1—C5	1.351 (2)	C7—H7	0.9500
N1—C1	1.357 (2)	C8—C9	1.392 (3)
N1—H1N	0.92 (2)	C8—H8	0.9500
N2—C5	1.356 (2)	C9—C10	1.372 (3)
N2—C6	1.394 (2)	C9—H9	0.9500
N2—H2N	0.87 (2)	C10—H10	0.9500
N3—C6	1.333 (2)	C11—C16	1.455 (3)
N3—C10	1.345 (2)	C11—C12	1.456 (2)
N4—C12	1.454 (2)	C12—C13	1.369 (2)
N5—C14	1.444 (2)	C13—C14	1.382 (3)
N6—C16	1.460 (2)	C13—H13	0.9500
C1—C2	1.358 (3)	C14—C15	1.388 (3)
C1—H1	0.9500	C15—C16	1.366 (2)
C2—C3	1.400 (3)	C15—H15	0.9500
C5—N1—C1	122.30 (16)	N3—C6—C7	123.52 (17)
C5—N1—H1N	113.4 (14)	N2—C6—C7	118.76 (17)
C1—N1—H1N	124.3 (14)	C8—C7—C6	117.67 (18)
C5—N2—C6	128.13 (16)	C8—C7—H7	121.2
C5—N2—H2N	115.1 (14)	C6—C7—H7	121.2
C6—N2—H2N	115.7 (14)	C7—C8—C9	119.76 (19)
C6—N3—C10	117.47 (16)	C7—C8—H8	120.1
O2—N4—O3	122.87 (16)	C9—C8—H8	120.1
O2—N4—C12	119.43 (15)	C10—C9—C8	118.38 (19)
O3—N4—C12	117.69 (15)	C10—C9—H9	120.8
O4—N5—O5	123.15 (15)	C8—C9—H9	120.8
O4—N5—C14	118.32 (15)	N3—C10—C9	123.21 (19)
O5—N5—C14	118.53 (15)	N3—C10—H10	118.4
O7—N6—O6	123.04 (17)	C9—C10—H10	118.4
O7—N6—C16	118.18 (16)	O1—C11—C16	124.53 (16)
O6—N6—C16	118.66 (16)	O1—C11—C12	124.32 (16)
N1—C1—C2	120.28 (17)	C16—C11—C12	111.13 (15)
N1—C1—H1	119.9	C13—C12—N4	116.22 (16)
C2—C1—H1	119.9	C13—C12—C11	124.81 (16)
C1—C2—C3	118.75 (17)	N4—C12—C11	118.93 (15)
C1—C2—H2	120.6	C12—C13—C14	118.97 (17)
C3—C2—H2	120.6	C12—C13—H13	120.5
C4—C3—C2	120.68 (18)	C14—C13—H13	120.5
C4—C3—H3	119.7	C13—C14—C15	121.12 (16)
C2—C3—H3	119.7	C13—C14—N5	119.48 (16)
C3—C4—C5	119.23 (17)	C15—C14—N5	119.38 (16)
C3—C4—H4	120.4	C16—C15—C14	119.34 (17)
C5—C4—H4	120.4	C16—C15—H15	120.3

N1—C5—N2	120.20 (16)	C14—C15—H15	120.3
N1—C5—C4	118.76 (16)	C15—C16—C11	124.48 (16)
N2—C5—C4	121.04 (16)	C15—C16—N6	115.91 (16)
N3—C6—N2	117.71 (16)	C11—C16—N6	119.59 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots N3	0.92 (2)	1.86 (2)	2.618 (2)	139 (2)
N1—H1N \cdots O4 ⁱ	0.92 (2)	2.45 (2)	3.056 (2)	123.8 (17)
N2—H2N \cdots O1 ⁱⁱ	0.87 (2)	1.97 (2)	2.756 (2)	149 (2)
N2—H2N \cdots O2 ⁱⁱ	0.87 (2)	2.42 (2)	3.114 (2)	136.6 (18)

Symmetry codes: (i) $x, -y+3/2, z-1/2$; (ii) $x, -y+3/2, z+1/2$.