Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Amino-6-(quinoline-2-carboxamido)-pyridinium nitrate

Phillipus C. W. Van der Berg,* Hendrik G. Visser and Andreas Roodt

Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa
Correspondence e-mail: vanderbergpcw@ufs.ac.za

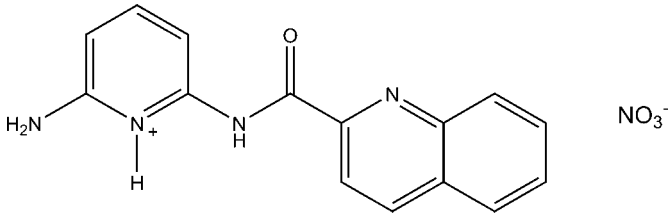
Received 31 July 2012; accepted 22 August 2012

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.100; data-to-parameter ratio = 15.3.

In the title salt, $C_{15}H_{13}N_4O^+\cdot NO_3^-$, an extensive network of N—H···N, N—H···O and C—H···O hydrogen-bond interactions are observed throughout the structure. Further stabilization is obtained by π–π stacking interactions between inversion-related quinoline systems and inversion-related pyridine rings, with respective centroid–centroid distances of 3.5866 (6) and 3.3980 (6) Å.

Related literature

For related radiopharmaceutical structures, see: Al-Dajani *et al.* (2010); Jain *et al.* (2004); Van der Berg *et al.* (2011).



Experimental

Crystal data

$C_{15}H_{13}N_4O^+\cdot NO_3^-$
M_r = 327.30
Monoclinic, $P2_1/c$
a = 8.183 (2) Å
b = 11.768 (3) Å
c = 14.979 (4) Å
β = 98.37 (1)°
V = 1427.1 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 100 K
0.49 × 0.41 × 0.31 mm

Data collection

Bruker X8 APEXII KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.990, T_{max} = 0.994
26710 measured reflections
3555 independent reflections
3180 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.1
S = 1.04
3555 reflections
233 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3	0.892 (18)	2.019 (19)	2.8721 (14)	159.7 (16)
N1—H1B···O4^{i}	0.836 (19)	2.204 (19)	3.0202 (14)	165.1 (16)
N2—H2A···O1	0.848 (19)	1.984 (18)	2.6458 (12)	134.1 (16)
N2—H2A···O3	0.848 (19)	2.496 (18)	3.2058 (12)	141.7 (15)
N3—H3A···O3^{ii}	0.857 (17)	2.153 (17)	2.9652 (12)	158.2 (15)
N3—H3A···N4	0.857 (17)	2.288 (16)	2.6879 (15)	108.7 (13)
C4—H4···O3^{ii}	0.93	2.44	3.1947 (14)	138
C11—H11···O4^{iii}	0.93	2.53	3.3460 (14)	147
C12—H12···O2^{iv}	0.93	2.5	3.2901 (14)	142
C14—H14···O2^{ii}	0.93	2.55	3.1840 (14)	126

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{5}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{5}{2}$; (iv) $-x+2, -y, -z+2$.

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors would like to thank the Department of Chemistry of the University of the Free State, the NRF, NTeMBI, THRIP and Sasol Ltd for funding.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2439).

References

Al-Dajani, M. T. M., Mohamed, N., Wahab, H. A., Yeap, C. S. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o2150.
Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2008). *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2011). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Jain, S. L., Bhattacharyya, P., Milton, H. L., Slawin, A. M. Z., Crayston, J. A. & Woollins, J. D. (2004). *Dalton Trans.* pp. 862–871.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Van der Berg, P. C. W., Visser, H. G. & Roodt, A. (2011). *Acta Cryst.* E**67**, o3130.

supporting information

Acta Cryst. (2012). E**68**, o2808 [doi:10.1107/S1600536812036562]

2-Amino-6-(quinoline-2-carboxamido)pyridinium nitrate

Phillipus C. W. Van der Berg, Hendrik G. Visser and Andreas Roodt

S1. Comment

The title compound was synthesized as a ligand for potential use in medical and radiopharmaceutical applications. The asymmetric unit in the title compound contains a $C_{15}H_{13}N_4O$ cation and a NO_3^- counter ion. A range of N—H···N, N—H···O and C—H···O hydrogen interactions are observed throughout the structure. Further stabilization of the crystal structure is obtained by π-π stacking interactions between inversion-related quinolines and inversion-related pyridines with respective centroid-to-centroid distances of 3.5866 (6) Å and 3.3980 (6) Å (see Fig. 2). For similar structures that form part of our radiopharmaceutical research see: Al-Dajani *et al.* (2010); Jain *et al.* (2004) and Van der Berg *et al.* (2011).

S2. Experimental

Under oxygen atmosphere: Quinaldic acid (0.8013 g, 4.627 mmol) was added as a solid in one portion to a suspension of 2,6-diaminopyridine (0.5000 g, 4.582 mmol) in pyridine (10 ml) and the mixture was stirred at 40 °C for 40 min. Triphenylphosphite (10 ml) was added dropwise over 10 minutes, after which the temperature was increased to 90–100 °C and stirred for a further 24 h. On cooling the precipitate was filtered, washed with H_2O (50 ml) and then MeOH (50 ml). The product was dissolved in diluted HNO_3 and left to stand at room temperature. Yellow crystals were obtained after five days.

S3. Refinement

The N-bound hydrogen atoms were located in a difference Fourier map and refined freely. The remaining H atoms were placed in geometrically idealized positions at C—H = 0.93 Å, respectively and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

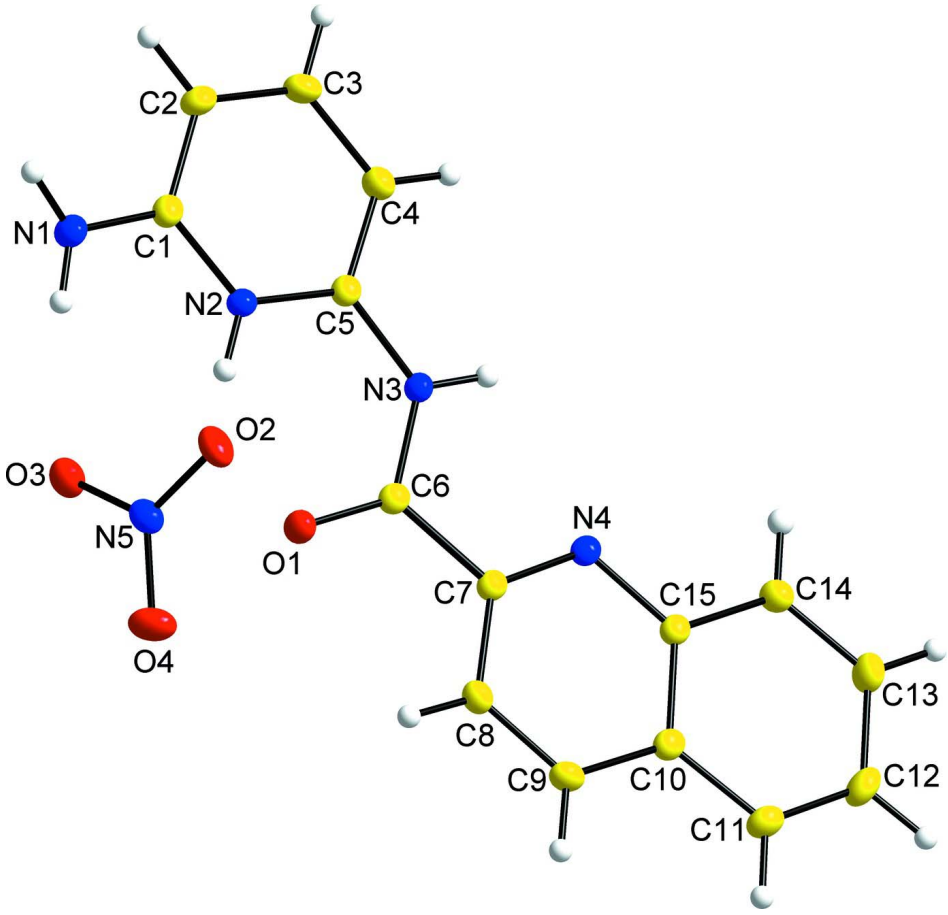


Figure 1

Representation of the title compound, showing displacement ellipsoids (50% probability).

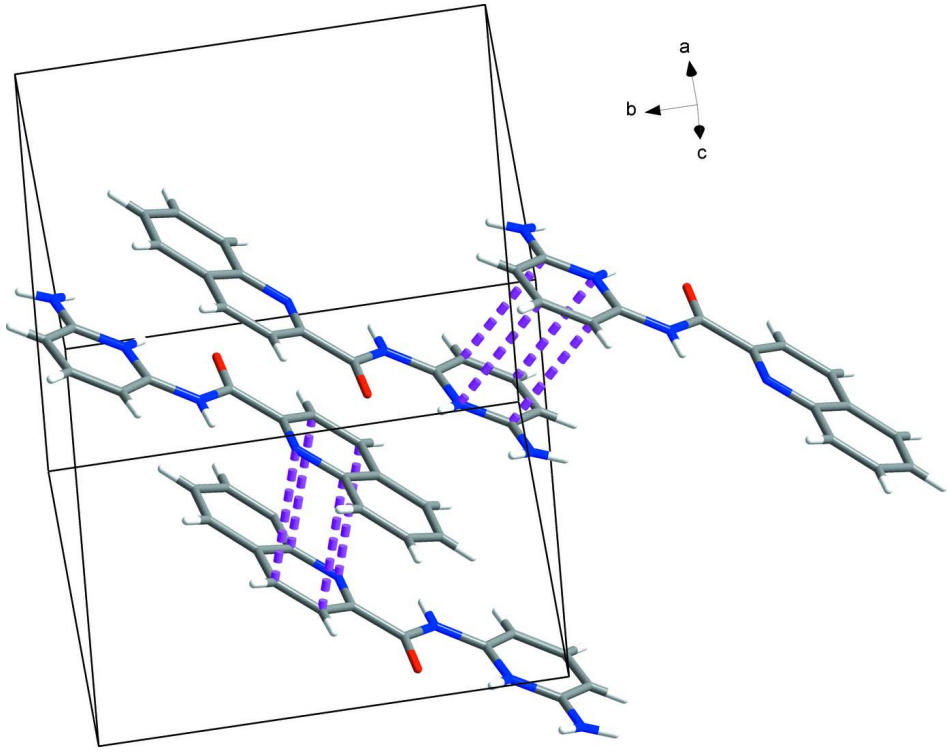


Figure 2

Packing and illustration of π-π stacking in the crystal.

2-Amino-6-(quinoline-2-carboxamido)pyridinium nitrate

Crystal data

$C_{15}H_{13}N_4O^+ \cdot NO_3^-$
$M_r = 327.30$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.183$ (2) Å
$b = 11.768$ (3) Å
$c = 14.979$ (4) Å
$\beta = 98.37$ (1)°
$V = 1427.1$ (6) Å^3
$Z = 4$
$F(000) = 680$
$D_x = 1.523$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9936 reflections
$\theta = 2.2$–$28.3°$
$\mu = 0.12$ mm^{-1}
$T = 100$ K
Cuboid, yellow
0.49 × 0.41 × 0.31 mm

Data collection

Bruker X8 APEXII KappaCCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.990$, $T_{max} = 0.994$
26710 measured reflections
3555 independent reflections
3180 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 28.4°$, $\theta_{min} = 2.2°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.1$
$S = 1.03$
3555 reflections
233 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
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.6672P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Experimental. The intensity data were collected on a Bruker X8 ApexII 4 K Kappa CCD diffractometer using an exposure time of 30 s/frame. A total of 1759 frames were collected with a frame width of 0.5° covering up to $\theta = 28.28°$ with 100.00% completeness accomplished.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C5	0.44014 (13)	0.29849 (9)	1.00107 (7)	0.0136 (2)
C4	0.36313 (14)	0.35271 (9)	0.92503 (7)	0.0165 (2)
H4	0.3674	0.323	0.8679	0.02*
C3	0.27835 (14)	0.45365 (10)	0.93606 (8)	0.0190 (2)
H3	0.2243	0.4909	0.8854	0.023*
C2	0.27319 (14)	0.49912 (10)	1.02018 (8)	0.0191 (2)
H2	0.2165	0.5665	1.0263	0.023*
C1	0.35435 (13)	0.44278 (9)	1.09694 (8)	0.0161 (2)
C6	0.61016 (12)	0.13855 (9)	1.06647 (7)	0.0130 (2)
C7	0.70961 (12)	0.03990 (9)	1.04078 (7)	0.0128 (2)
C8	0.80954 (13)	−0.01866 (9)	1.11085 (7)	0.0148 (2)
H8	0.812	0.0028	1.1708	0.018*
C9	0.90254 (13)	−0.10779 (9)	1.08810 (7)	0.0156 (2)
H9	0.9709	−0.1475	1.1325	0.019*
C10	0.89350 (13)	−0.13878 (9)	0.99620 (7)	0.0143 (2)
C11	0.98613 (14)	−0.23014 (10)	0.96740 (8)	0.0182 (2)
H11	1.0548	−0.2727	1.0098	0.022*
C12	0.97515 (14)	−0.25610 (10)	0.87763 (8)	0.0208 (2)
H12	1.0371	−0.3157	0.8593	0.025*
C13	0.86987 (14)	−0.19264 (10)	0.81263 (8)	0.0196 (2)
H13	0.8633	−0.2111	0.7518	0.024*

C14	0.77756 (14)	−0.10438 (9)	0.83805 (7)	0.0165 (2)
H14	0.7078	−0.064	0.7947	0.02*
C15	0.78850 (13)	−0.07462 (9)	0.93054 (7)	0.0133 (2)
N1	0.36061 (13)	0.48153 (9)	1.18100 (7)	0.0199 (2)
N2	0.43161 (11)	0.34266 (8)	1.08430 (6)	0.01391 (19)
N3	0.53164 (11)	0.20051 (8)	0.99536 (6)	0.01377 (19)
N4	0.69803 (11)	0.01543 (7)	0.95409 (6)	0.01317 (18)
N5	0.68666 (12)	0.29972 (8)	1.29263 (6)	0.01620 (19)
O1	0.60217 (10)	0.16082 (7)	1.14574 (5)	0.01639 (17)
O2	0.75498 (11)	0.36208 (7)	1.24246 (6)	0.0224 (2)
O3	0.53418 (10)	0.31398 (7)	1.29794 (5)	0.01974 (18)
O4	0.76463 (11)	0.22297 (7)	1.33845 (6)	0.0228 (2)
H1B	0.326 (2)	0.5477 (16)	1.1861 (12)	0.033 (4)*
H1A	0.423 (2)	0.4444 (15)	1.2254 (12)	0.031 (4)*
H2A	0.481 (2)	0.3072 (15)	1.1296 (12)	0.032 (4)*
H3A	0.5452 (19)	0.1790 (14)	0.9423 (11)	0.026 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C5	0.0144 (4)	0.0117 (5)	0.0151 (5)	−0.0008 (4)	0.0036 (4)	−0.0006 (4)
C4	0.0196 (5)	0.0159 (5)	0.0139 (5)	0.0001 (4)	0.0027 (4)	0.0000 (4)
C3	0.0215 (5)	0.0168 (5)	0.0182 (5)	0.0031 (4)	0.0017 (4)	0.0045 (4)
C2	0.0230 (5)	0.0134 (5)	0.0212 (6)	0.0051 (4)	0.0045 (4)	0.0017 (4)
C1	0.0182 (5)	0.0131 (5)	0.0178 (5)	0.0006 (4)	0.0060 (4)	−0.0002 (4)
C6	0.0127 (4)	0.0112 (5)	0.0152 (5)	−0.0015 (4)	0.0018 (4)	−0.0011 (4)
C7	0.0125 (5)	0.0111 (4)	0.0151 (5)	−0.0010 (3)	0.0027 (4)	−0.0007 (4)
C8	0.0152 (5)	0.0165 (5)	0.0129 (5)	−0.0006 (4)	0.0025 (4)	−0.0002 (4)
C9	0.0141 (5)	0.0165 (5)	0.0158 (5)	0.0010 (4)	0.0006 (4)	0.0031 (4)
C10	0.0125 (5)	0.0130 (5)	0.0177 (5)	−0.0005 (4)	0.0034 (4)	0.0004 (4)
C11	0.0164 (5)	0.0160 (5)	0.0219 (6)	0.0037 (4)	0.0018 (4)	0.0007 (4)
C12	0.0198 (5)	0.0165 (5)	0.0268 (6)	0.0041 (4)	0.0062 (4)	−0.0045 (4)
C13	0.0223 (5)	0.0198 (5)	0.0173 (5)	0.0010 (4)	0.0049 (4)	−0.0043 (4)
C14	0.0191 (5)	0.0153 (5)	0.0150 (5)	0.0006 (4)	0.0018 (4)	−0.0003 (4)
C15	0.0130 (4)	0.0115 (5)	0.0156 (5)	−0.0008 (3)	0.0035 (4)	−0.0001 (4)
N1	0.0288 (5)	0.0151 (5)	0.0166 (5)	0.0058 (4)	0.0059 (4)	−0.0011 (4)
N2	0.0171 (4)	0.0119 (4)	0.0129 (4)	0.0021 (3)	0.0027 (3)	0.0005 (3)
N3	0.0175 (4)	0.0120 (4)	0.0122 (4)	0.0018 (3)	0.0033 (3)	−0.0009 (3)
N4	0.0142 (4)	0.0111 (4)	0.0144 (4)	−0.0003 (3)	0.0026 (3)	−0.0008 (3)
N5	0.0221 (5)	0.0142 (4)	0.0121 (4)	−0.0034 (3)	0.0016 (3)	−0.0018 (3)
O1	0.0202 (4)	0.0155 (4)	0.0133 (4)	0.0019 (3)	0.0020 (3)	−0.0023 (3)
O2	0.0317 (5)	0.0184 (4)	0.0195 (4)	−0.0055 (3)	0.0111 (3)	0.0005 (3)
O3	0.0196 (4)	0.0234 (4)	0.0163 (4)	−0.0020 (3)	0.0031 (3)	−0.0002 (3)
O4	0.0269 (4)	0.0182 (4)	0.0206 (4)	−0.0006 (3)	−0.0052 (3)	0.0025 (3)

Geometric parameters (Å, º)

C5—N2	1.3618 (14)	C9—H9	0.93
C5—C4	1.3758 (15)	C10—C11	1.4183 (15)
C5—N3	1.3842 (13)	C10—C15	1.4246 (15)
C4—C3	1.3974 (15)	C11—C12	1.3690 (17)
C4—H4	0.93	C11—H11	0.93
C3—C2	1.3753 (16)	C12—C13	1.4156 (17)
C3—H3	0.93	C12—H12	0.93
C2—C1	1.4073 (16)	C13—C14	1.3704 (15)
C2—H2	0.93	C13—H13	0.93
C1—N1	1.3332 (15)	C14—C15	1.4191 (15)
C1—N2	1.3633 (14)	C14—H14	0.93
C6—O1	1.2270 (13)	C15—N4	1.3680 (13)
C6—N3	1.3711 (14)	N1—H1B	0.836 (19)
C6—C7	1.4997 (14)	N1—H1A	0.892 (18)
C7—N4	1.3200 (13)	N2—H2A	0.848 (19)
C7—C8	1.4125 (14)	N3—H3A	0.857 (17)
C8—C9	1.3679 (15)	N5—O2	1.2402 (12)
C8—H8	0.93	N5—O4	1.2516 (13)
C9—C10	1.4155 (15)	N5—O3	1.2729 (13)
N2—C5—C4	120.18 (10)	C11—C10—C15	119.15 (10)
N2—C5—N3	118.34 (9)	C12—C11—C10	120.42 (10)
C4—C5—N3	121.46 (10)	C12—C11—H11	119.8
C5—C4—C3	118.15 (10)	C10—C11—H11	119.8
C5—C4—H4	120.9	C11—C12—C13	120.28 (10)
C3—C4—H4	120.9	C11—C12—H12	119.9
C2—C3—C4	121.40 (10)	C13—C12—H12	119.9
C2—C3—H3	119.3	C14—C13—C12	120.90 (10)
C4—C3—H3	119.3	C14—C13—H13	119.5
C3—C2—C1	119.44 (10)	C12—C13—H13	119.5
C3—C2—H2	120.3	C13—C14—C15	119.95 (10)
C1—C2—H2	120.3	C13—C14—H14	120
N1—C1—N2	118.16 (10)	C15—C14—H14	120
N1—C1—C2	124.00 (10)	N4—C15—C14	118.90 (10)
N2—C1—C2	117.84 (10)	N4—C15—C10	121.82 (10)
O1—C6—N3	123.59 (10)	C14—C15—C10	119.28 (10)
O1—C6—C7	121.40 (9)	C1—N1—H1B	116.0 (12)
N3—C6—C7	115.01 (9)	C1—N1—H1A	118.4 (11)
N4—C7—C8	125.13 (10)	H1B—N1—H1A	123.6 (16)
N4—C7—C6	117.22 (9)	C5—N2—C1	122.93 (10)
C8—C7—C6	117.65 (9)	C5—N2—H2A	117.6 (12)
C9—C8—C7	118.16 (10)	C1—N2—H2A	119.4 (12)
C9—C8—H8	120.9	C6—N3—C5	126.27 (9)
C7—C8—H8	120.9	C6—N3—H3A	117.0 (11)
C8—C9—C10	119.18 (10)	C5—N3—H3A	116.6 (11)
C8—C9—H9	120.4	C7—N4—C15	117.29 (9)

C10—C9—H9	120.4	O2—N5—O4	121.37 (10)
C9—C10—C11	122.44 (10)	O2—N5—O3	119.49 (9)
C9—C10—C15	118.40 (9)	O4—N5—O3	119.14 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3	0.892 (18)	2.019 (19)	2.8721 (14)	159.7 (16)
N1—H1*B*···O4^{i}	0.836 (19)	2.204 (19)	3.0202 (14)	165.1 (16)
N2—H2*A*···O1	0.848 (19)	1.984 (18)	2.6458 (12)	134.1 (16)
N2—H2*A*···O3	0.848 (19)	2.496 (18)	3.2058 (12)	141.7 (15)
N3—H3*A*···O3^{ii}	0.857 (17)	2.153 (17)	2.9652 (12)	158.2 (15)
N3—H3*A*···N4	0.857 (17)	2.288 (16)	2.6879 (15)	108.7 (13)
C4—H4···O3^{ii}	0.93	2.44	3.1947 (14)	138
C11—H11···O4^{iii}	0.93	2.53	3.3460 (14)	147
C12—H12···O2^{iv}	0.93	2.5	3.2901 (14)	142
C14—H14···O2^{ii}	0.93	2.55	3.1840 (14)	126

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+5/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*+2, *y*−1/2, −*z*+5/2; (iv) −*x*+2, −*y*, −*z*+2.