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1-(2-Azaniumylethyl)piperazine-1,4-diium trinitrate

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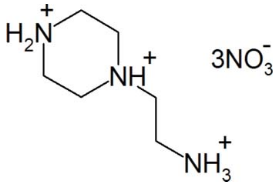
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.042; wR factor = 0.129; data-to-parameter ratio = 22.5.

In the title salt, $C_6H_{18}N_3^{3+}\cdot 3NO_3^-$, the piperazine ring adopts a chair conformation and the ethylammonium group is equatorial relative to the piperazine ring, and in an all-*trans* conformation. In the crystal, strong charge-assisted N—H⋯O hydrogen bonds link the piperazinediium trications and the nitrate anions into a three-dimensional network

Related literature

The structure of a related salt, bis(1-(2-ammoniumethyl)-piperazinium) cyclohexaphosphate hexahydrate, has been reported (Charfi & Jouini, 1996).



Experimental

Crystal data

$C_6H_{18}N_3^{3+}\cdot 3NO_3^-$
M_r = 318.26
Monoclinic, $P2_1/c$
a = 7.7946 (6) Å
b = 8.9320 (6) Å
c = 19.6910 (13) Å
β = 96.635 (6)°
V = 1361.73 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 293 K
0.35 × 0.30 × 0.20 mm

Data collection

Oxford Xcalibur2 diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.966, T_{max} = 1.043
13603 measured reflections
4319 independent reflections
2517 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.129
S = 1.01
4319 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N5—H5⋯O1^{i}	0.91	2.00	2.8074 (16)	146
N5—H5⋯O2^{i}	0.91	2.34	3.1755 (17)	152
N4—H4A⋯O9	0.90	2.05	2.9008 (15)	158
N4—H4A⋯O7	0.90	2.29	2.9947 (15)	135
N4—H4B⋯O5^{ii}	0.90	1.93	2.8065 (16)	165
N4—H4B⋯O6^{ii}	0.90	2.43	3.0387 (15)	125
N6—H7A⋯O1^{iii}	0.89	2.16	2.9224 (15)	144
N6—H7A⋯O3^{iii}	0.89	2.47	3.322 (2)	161
N6—H7B⋯O9^{iv}	0.89	2.15	3.0360 (15)	173
N6—H7B⋯O8^{iv}	0.89	2.45	3.1171 (16)	132
N6—H7C⋯O4^{v}	0.89	1.99	2.8033 (14)	152

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009) and *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5713).

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supporting information

Acta Cryst. (2011). E**67**, o3301 [https://doi.org/10.1107/S1600536811047507]

1-(2-Azaniumylethyl)piperazine-1,4-diium trinitrate

M. Rademeyer

S1. Comment

In the field of crystal engineering, an understanding of the role of the anion geometry on the molecular packing and non-covalent interactions in salt crystal structures is central to the area of molecular recognition. The current structure was determined as part of a wider study that considers this role of anion geometry on a crystal structure.

The molecular geometry and labelling scheme of 1-(2-ammoniumethyl)piperazinium) trinitrate, I, is illustrated in Fig. 1. In this structure, the asymmetric unit consists of one 1-(2-ammoniumethyl)piperazinium cation and three isolated, trigonal planar nitrate anions, with four asymmetric units in the unit cell. In the cation the piperazine ring adopts the chair conformation, and the ethylammonium group is equatorial relative to the piperazine ring, and in the all-*trans* conformation.

Fig. 2 shows the molecular packing of I, viewed down the *a*-axis, with double rows of cations alternating in orientation along the *c*-axis. Each cation is hydrogen bonded to six different surrounding nitrate anions, and strong $N—H^{+}\cdots{}^{-}O—N$ hydrogen bonds link the cations and the anions. The ammonium group on the cation froms one conventional and two bifurcated hydrogen bonds to three different nitrate anions, while the $–NH_2^{+}$ group is involved in two bifurcated hydrogen bonds to two nitrate anions, and the $–NH^{+}$ group forms one bifurcated hydrogen bond to one nitrate anion. Hydrogen bonding interactions are listed in Table 1, and the resulting, complex, three-dimensional hydrogen bonding network is shown in Fig. 3.

S2. Experimental

1-(2-Ammoniumethyl)piperazinium trinitrate was prepared by the dropwise addition of excess concentrated nitric acid (3.0 ml, 0.047 mol, 70%, Saarchem) to a solution of 1-(2-aminoethyl)piperazine (1.5 ml, 0.011 mol 99%, Aldrich) in 40 ml chloroform (99%, Saarchem). The resulting precipitate was filtered, dried in air and re-crystallized from distilled water. Colourless crystals formed on evaporation, open to the air, at room temperature.

S3. Refinement

All H atoms were refined using a riding model, with C—H distances of 0.97 Å and N—H distances of 0.89 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ or $1.2U_{eq}(C)$ or $1.2U_{eq}(N)$. The highest residual peak (0.24eÅ^{-3}) is 0.83 Å from atom O1.

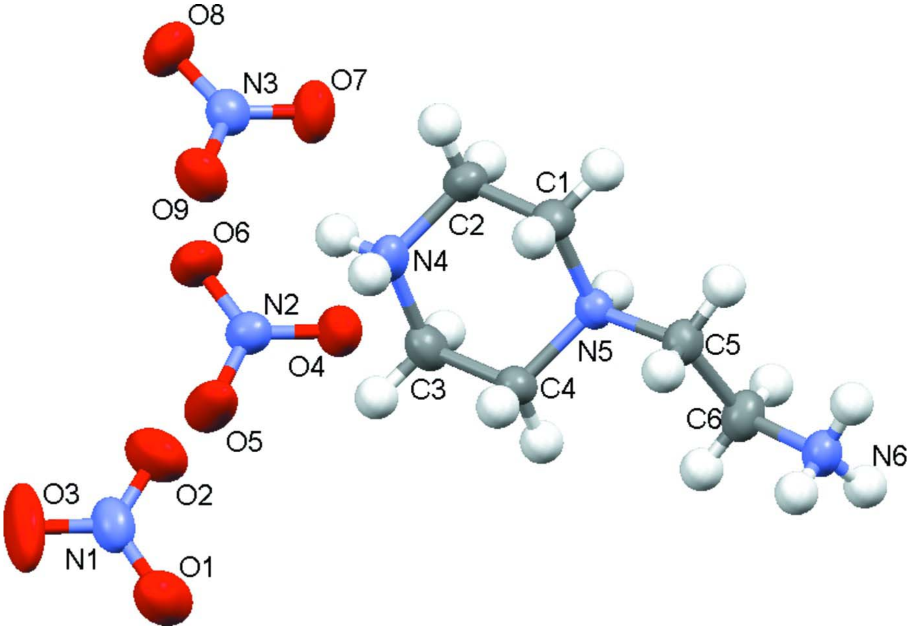

Figure 1

The asymmetric unit of I, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

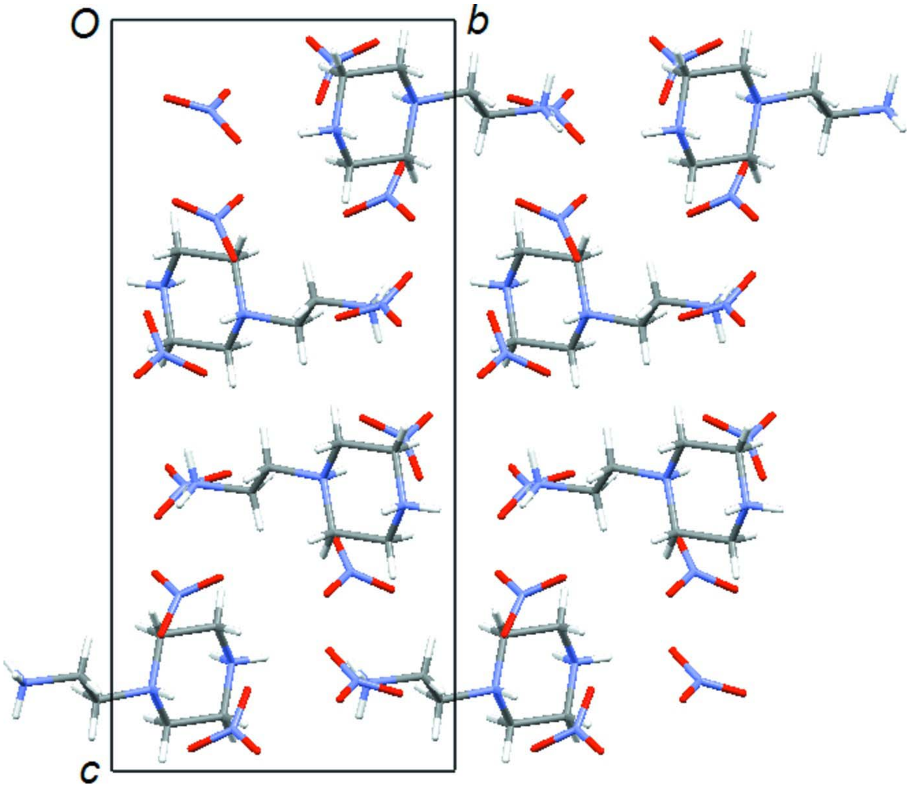

Figure 2

Packing diagram of I viewed down the *a*-axis.

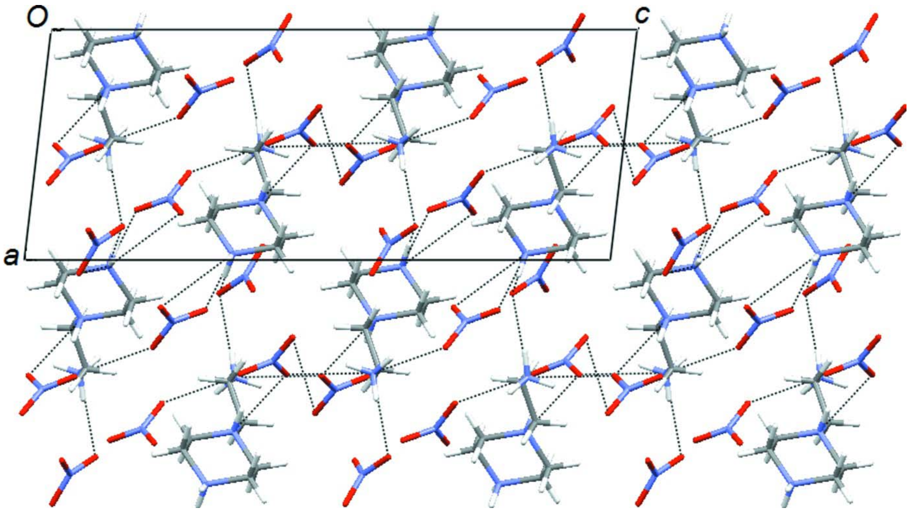

Figure 3

Hydrogen bonding network in I.

1-(2-Azaniumylethyl)piperazine-1,4-diium trinitrate

Crystal data

$C_6H_{18}N_3^{3+}\cdot 3NO_3^-$
$M_r = 318.26$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.7946$ (6) Å
$b = 8.9320$ (6) Å
$c = 19.6910$ (13) Å
$\beta = 96.635$ (6)°
$V = 1361.73$ (17) Å^3
$Z = 4$

$F(000) = 672$
$D_x = 1.552$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5277 reflections
$\theta = 3.7$–32.0°
$\mu = 0.14$ mm^{-1}
$T = 293$ K
Block, colourless
0.35 × 0.30 × 0.20 mm

Data collection

Oxford Xcalibur2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–2θ scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min} = 0.966$, $T_{\max} = 1.043$

13603 measured reflections
4319 independent reflections
2517 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 32.0°$, $\theta_{\min} = 3.7°$
$h = -11 \rightarrow 6$
$k = -12 \rightarrow 12$
$l = -28 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.129$
$S = 1.01$
4319 reflections
192 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.074P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.033 (3)

Special details

Experimental. CrysAlis RED (Oxford Diffraction, 2006) Version 1.171.29.9 Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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}
O8	−0.12932 (14)	0.16141 (11)	0.10385 (6)	0.0633 (3)
O9	−0.14426 (14)	0.36595 (11)	0.16044 (5)	0.0567 (3)
N5	0.25593 (12)	0.88408 (10)	0.10913 (5)	0.0323 (2)
H5	0.3465	0.8265	0.0997	0.039*
N4	0.02701 (14)	0.65031 (12)	0.14525 (6)	0.0448 (3)
H4A	0.0034	0.5530	0.1515	0.054*
H4B	−0.0651	0.7043	0.1544	0.054*
N6	0.49105 (14)	1.25521 (12)	0.11758 (5)	0.0432 (3)
H7A	0.4563	1.2789	0.0743	0.065*
H7B	0.6012	1.2814	0.1278	0.065*
H7C	0.4265	1.3035	0.1449	0.065*
C4	0.22499 (17)	0.85655 (14)	0.18187 (6)	0.0387 (3)
H4C	0.1312	0.9198	0.1932	0.046*
H4D	0.3278	0.8830	0.2120	0.046*
C1	0.09846 (17)	0.83708 (15)	0.06264 (6)	0.0428 (3)
H1A	0.0008	0.8981	0.0718	0.051*
H1B	0.1182	0.8531	0.0154	0.051*
C5	0.29617 (16)	1.04353 (13)	0.09492 (6)	0.0398 (3)
H5A	0.2098	1.1071	0.1120	0.048*
H5B	0.2890	1.0580	0.0458	0.048*
C3	0.18042 (18)	0.69465 (15)	0.19308 (7)	0.0445 (3)
H3A	0.2779	0.6317	0.1856	0.053*
H3B	0.1561	0.6806	0.2399	0.053*
C2	0.05773 (17)	0.67486 (15)	0.07315 (6)	0.0445 (3)
H2A	−0.0442	0.6465	0.0429	0.053*
H2B	0.1533	0.6131	0.0624	0.053*
C6	0.47308 (16)	1.09143 (14)	0.12711 (7)	0.0442 (3)
H6A	0.4868	1.0674	0.1755	0.053*
H6B	0.5616	1.0388	0.1058	0.053*
O7	0.05818 (13)	0.33529 (11)	0.09607 (6)	0.0573 (3)
N3	−0.07066 (14)	0.28710 (12)	0.12031 (5)	0.0409 (3)

N2	0.26751 (13)	0.30391 (12)	0.26544 (5)	0.0410 (3)
O4	0.37816 (13)	0.37345 (12)	0.23659 (5)	0.0573 (3)
O5	0.21779 (16)	0.35660 (13)	0.31806 (7)	0.0743 (4)
O6	0.20595 (15)	0.18569 (12)	0.24225 (5)	0.0625 (3)
N1	0.43842 (14)	0.14691 (14)	0.44408 (6)	0.0486 (3)
O1	0.49718 (18)	0.26837 (13)	0.46985 (6)	0.0719 (3)
O2	0.49348 (16)	0.10390 (15)	0.39153 (6)	0.0766 (4)
O3	0.33557 (14)	0.07557 (17)	0.47326 (8)	0.0917 (5)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O8	0.0685 (7)	0.0463 (6)	0.0767 (7)	−0.0175 (5)	0.0153 (6)	−0.0120 (5)
O9	0.0719 (7)	0.0479 (6)	0.0544 (6)	0.0080 (5)	0.0245 (5)	−0.0032 (4)
N5	0.0334 (5)	0.0314 (5)	0.0327 (5)	0.0000 (4)	0.0066 (4)	0.0000 (4)
N4	0.0540 (6)	0.0339 (5)	0.0495 (6)	−0.0102 (5)	0.0187 (5)	−0.0043 (4)
N6	0.0467 (6)	0.0392 (6)	0.0450 (6)	−0.0089 (4)	0.0112 (5)	−0.0005 (4)
C4	0.0464 (7)	0.0388 (6)	0.0310 (6)	−0.0053 (5)	0.0050 (5)	−0.0014 (4)
C1	0.0463 (7)	0.0442 (7)	0.0363 (6)	−0.0068 (5)	−0.0017 (5)	0.0017 (5)
C5	0.0439 (6)	0.0331 (6)	0.0420 (7)	−0.0028 (5)	0.0035 (5)	0.0057 (5)
C3	0.0580 (8)	0.0391 (7)	0.0377 (7)	0.0003 (6)	0.0109 (6)	0.0048 (5)
C2	0.0487 (7)	0.0451 (7)	0.0401 (7)	−0.0117 (6)	0.0066 (6)	−0.0092 (5)
C6	0.0389 (6)	0.0374 (7)	0.0565 (8)	−0.0016 (5)	0.0059 (6)	0.0043 (6)
O7	0.0538 (6)	0.0439 (5)	0.0785 (7)	−0.0018 (4)	0.0255 (5)	0.0070 (5)
N3	0.0442 (6)	0.0383 (6)	0.0402 (6)	0.0027 (5)	0.0050 (4)	0.0053 (4)
N2	0.0399 (5)	0.0419 (6)	0.0414 (6)	−0.0011 (4)	0.0059 (5)	−0.0061 (4)
O4	0.0572 (6)	0.0620 (7)	0.0559 (6)	−0.0157 (5)	0.0205 (5)	−0.0081 (5)
O5	0.0777 (7)	0.0731 (8)	0.0802 (8)	−0.0278 (6)	0.0434 (6)	−0.0406 (6)
O6	0.0849 (8)	0.0474 (6)	0.0571 (6)	−0.0186 (5)	0.0162 (6)	−0.0165 (5)
N1	0.0379 (5)	0.0574 (7)	0.0515 (7)	0.0028 (5)	0.0087 (5)	0.0133 (5)
O1	0.1058 (9)	0.0543 (7)	0.0572 (7)	−0.0008 (6)	0.0166 (6)	−0.0007 (5)
O2	0.0825 (8)	0.0947 (10)	0.0554 (7)	−0.0013 (7)	0.0206 (6)	−0.0126 (6)
O3	0.0447 (6)	0.1131 (11)	0.1208 (11)	−0.0054 (6)	0.0251 (7)	0.0587 (9)

Geometric parameters (Å, º)

O8—N3	1.2411 (14)	C1—H1A	0.9700
O9—N3	1.2468 (14)	C1—H1B	0.9700
N5—C5	1.4918 (15)	C5—C6	1.5114 (18)
N5—C4	1.5000 (15)	C5—H5A	0.9700
N5—C1	1.5037 (15)	C5—H5B	0.9700
N5—H5	0.9100	C3—H3A	0.9700
N4—C2	1.4831 (16)	C3—H3B	0.9700
N4—C3	1.4878 (17)	C2—H2A	0.9700
N4—H4A	0.9000	C2—H2B	0.9700
N4—H4B	0.9000	C6—H6A	0.9700
N6—C6	1.4836 (16)	C6—H6B	0.9700
N6—H7A	0.8900	O7—N3	1.2379 (14)

N6—H7B	0.8900	N2—O6	1.2261 (14)
N6—H7C	0.8900	N2—O5	1.2402 (14)
C4—C3	1.5094 (17)	N2—O4	1.2512 (14)
C4—H4C	0.9700	N1—O3	1.2187 (15)
C4—H4D	0.9700	N1—O2	1.2269 (16)
C1—C2	1.5028 (19)	N1—O1	1.2611 (16)

C5—N5—C4	113.34 (9)	C6—C5—H5A	109.0
C5—N5—C1	109.08 (9)	N5—C5—H5B	109.0
C4—N5—C1	109.00 (9)	C6—C5—H5B	109.0
C5—N5—H5	108.4	H5A—C5—H5B	107.8
C4—N5—H5	108.4	N4—C3—C4	110.13 (10)
C1—N5—H5	108.4	N4—C3—H3A	109.6
C2—N4—C3	111.09 (9)	C4—C3—H3A	109.6
C2—N4—H4A	109.4	N4—C3—H3B	109.6
C3—N4—H4A	109.4	C4—C3—H3B	109.6
C2—N4—H4B	109.4	H3A—C3—H3B	108.1
C3—N4—H4B	109.4	N4—C2—C1	109.54 (10)
H4A—N4—H4B	108.0	N4—C2—H2A	109.8
C6—N6—H7A	109.5	C1—C2—H2A	109.8
C6—N6—H7B	109.5	N4—C2—H2B	109.8
H7A—N6—H7B	109.5	C1—C2—H2B	109.8
C6—N6—H7C	109.5	H2A—C2—H2B	108.2
H7A—N6—H7C	109.5	N6—C6—C5	108.72 (10)
H7B—N6—H7C	109.5	N6—C6—H6A	109.9
N5—C4—C3	111.21 (10)	C5—C6—H6A	109.9
N5—C4—H4C	109.4	N6—C6—H6B	109.9
C3—C4—H4C	109.4	C5—C6—H6B	109.9
N5—C4—H4D	109.4	H6A—C6—H6B	108.3
C3—C4—H4D	109.4	O7—N3—O8	120.31 (11)
H4C—C4—H4D	108.0	O7—N3—O9	120.08 (11)
C2—C1—N5	110.85 (10)	O8—N3—O9	119.59 (11)
C2—C1—H1A	109.5	O6—N2—O5	119.43 (11)
N5—C1—H1A	109.5	O6—N2—O4	121.27 (11)
C2—C1—H1B	109.5	O5—N2—O4	119.29 (11)
N5—C1—H1B	109.5	O3—N1—O2	123.17 (15)
H1A—C1—H1B	108.1	O3—N1—O1	119.22 (14)
N5—C5—C6	113.14 (10)	O2—N1—O1	117.55 (12)
N5—C5—H5A	109.0		

C5—N5—C4—C3	178.55 (10)	C2—N4—C3—C4	57.49 (14)
C1—N5—C4—C3	56.88 (13)	N5—C4—C3—N4	−56.80 (14)
C5—N5—C1—C2	177.55 (10)	C3—N4—C2—C1	−58.69 (14)
C4—N5—C1—C2	−58.23 (13)	N5—C1—C2—N4	59.29 (14)
C4—N5—C5—C6	71.34 (13)	N5—C5—C6—N6	−172.78 (10)
C1—N5—C5—C6	−167.04 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···O1^{i}	0.91	2.00	2.8074 (16)	146
N5—H5···O2^{i}	0.91	2.34	3.1755 (17)	152
N4—H4*A*···O9	0.90	2.05	2.9008 (15)	158
N4—H4*A*···O7	0.90	2.29	2.9947 (15)	135
N4—H4*B*···O5^{ii}	0.90	1.93	2.8065 (16)	165
N4—H4*B*···O6^{ii}	0.90	2.43	3.0387 (15)	125
N6—H7*A*···O1^{iii}	0.89	2.16	2.9224 (15)	144
N6—H7*A*···O3^{iii}	0.89	2.47	3.322 (2)	161
N6—H7*B*···O9^{iv}	0.89	2.15	3.0360 (15)	173
N6—H7*B*···O8^{iv}	0.89	2.45	3.1171 (16)	132
N6—H7*C*···O4^{v}	0.89	1.99	2.8033 (14)	152

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