

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2,3-Diaminopyridinium 2-hydroxybenzoate

 Madhukar Hemamalini, Jia Hao Goh[‡] and Hoong-Kun Fun*[§]

X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: hkfun@usm.my

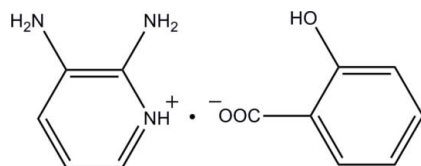
Received 19 October 2011; accepted 25 October 2011

 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.050; wR factor = 0.144; data-to-parameter ratio = 15.7.

In the title molecular salt, $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_7\text{H}_5\text{O}_3^-$, the 2,3-diaminopyridinium cation is essentially planar, with a maximum deviation of 0.006 (2) Å. In the crystal, adjacent cations and anions are linked by pairs of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, generating $R_2^2(8)$ loops. These dimers are linked by further $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and $\text{C}-\text{H}\cdots\text{O}$ interactions to form sheets lying parallel to (001). A typical intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond is also observed in the salicylate (2-hydroxybenzoate) anion, which generates an $S(6)$ ring. The crystal structure also features $\pi-\pi$ stacking interactions between the pyridinium rings of the cations, with a centroid-centroid distance of 3.5896 (15) Å.

Related literature

For details of 2-aminopyridine and its derivatives, see: Banerjee & Murugavel (2004); Bis & Zaworotko (2005); Bis *et al.* (2006). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

 $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_7\text{H}_5\text{O}_3^-$
 $M_r = 247.25$

 Orthorhombic, Pbc_2
 $a = 10.484$ (3) Å

 $b = 11.260$ (3) Å
 $c = 20.033$ (6) Å
 $V = 2364.9$ (12) Å³
 $Z = 8$

 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 100$ K
 $0.54 \times 0.47 \times 0.10$ mm

Data collection

 Bruker APEXII DUO CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.947$, $T_{\max} = 0.990$

 12688 measured reflections
 3388 independent reflections
 1989 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.144$
 $S = 1.03$
 3388 reflections

 216 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1O1}\cdots\text{O3}$	0.96 (2)	1.69 (2)	2.573 (2)	151.2 (18)
$\text{N1}-\text{H1N1}\cdots\text{O2}$	0.94 (2)	1.80 (2)	2.736 (2)	171.1 (19)
$\text{N2}-\text{H1N2}\cdots\text{O3}$	0.900 (19)	2.019 (19)	2.905 (2)	167.7 (18)
$\text{N2}-\text{H2N2}\cdots\text{O2}^i$	0.91 (2)	2.04 (2)	2.942 (2)	169.6 (18)
$\text{N3}-\text{H1N3}\cdots\text{O2}^i$	0.92 (2)	1.99 (2)	2.907 (2)	174.3 (19)
$\text{N3}-\text{H2N3}\cdots\text{O3}^{ii}$	0.88 (2)	2.14 (2)	2.994 (2)	163.9 (19)
$\text{C7}-\text{H7}\cdots\text{O3}^{iii}$	0.99 (2)	2.56 (2)	3.376 (3)	139.8 (17)

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

MH, JHG and HKF thank the Malaysian Government and Universiti Sains Malaysia for the Research University Grant No. 1001/PFIZIK/811160. MH also thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6455).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Banerjee, S. & Murugavel, R. (2004). *Cryst. Growth Des.* **4**, 545–552.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bis, J. A., McLaughlin, O. L., Vishweshwar, P. & Zaworotko, M. J. (2006). *Cryst. Growth Des.* **6**, 2648–2650.
- Bis, J. A. & Zaworotko, M. A. (2005). *Cryst. Growth Des.* **5**, 1169–1179.
- Bruker (2009). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

[‡] Thomson Reuters ResearcherID: C-7576-2009.

[§] Thomson Reuters ResearcherID: A-3561-2009

supporting information

Acta Cryst. (2011). E67, o3121 [doi:10.1107/S1600536811044461]

2,3-Diaminopyridinium 2-hydroxybenzoate

Madhukar Hemamalini, Jia Hao Goh and Hoong-Kun Fun

S1. Comment

2-Aminopyridine and its derivatives are some of the most frequently used synthons in supramolecular chemistry based on hydrogen bonds (Banerjee & Murugavel, 2004; Bis & Zaworotko, 2005; Bis *et al.*, 2006). In this paper, we report the crystal structure of the title compound, (I), which belongs to this class of compounds.

The asymmetric unit, (Fig 1), contains a protonated 2,3-diaminopyridinium cation and a benzoate anion. The 2,3-diaminopyridinium cation is planar, with a maximum deviation of 0.006 (2) Å for atom C1. The dihedral angle between the pyridine (N1/C1–C5) and the benzene (C6–C11) rings is 3.35 (9)°. The bond lengths (Allen *et al.*, 1987) and angles are normal. A typical intramolecular O—H···O hydrogen bond is also observed in the salicylate anion, which generates an *S*(6) ring.

In the crystal packing, the protonated N1 atom and the 2-amino group (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O2 and O3) *via* a pair of N—H···O hydrogen bonds forming an *R*²₂(8) ring motif (Bernstein *et al.*, 1995). The cationic and anionic units are linked through N—H···O and C—H···O hydrogen bonds (Table 1 and Fig 2) to form a two-dimensional network parallel to the (0 0 1) plane. The crystal structure is further stabilized by π – π stacking interactions between the pyridinium (Cg1 = N1/C1–C5) rings (Cg1···Cg1 = 3.5896 (15) Å; 1-x, 1-y, 1-z) of the cations.

S2. Experimental

Hot methanol solutions (20 ml) of 2,3-diaminopyridine (27 mg, Aldrich) and salicylic acid (34 mg, Merck) were mixed and warmed over a heating magnetic stirrer for 5 minutes. The resulting solution was allowed to cool slowly at room temperature. Brown plates of the title compound appeared from the mother liquor after a few days.

S3. Refinement

All hydrogen atoms were located from a difference Fourier maps and refined freely [N–H = 0.88 (2)–0.94 (2) Å; O–H = 0.96 (2) Å and C–H = 0.93 (2)–1.01 (2) Å].

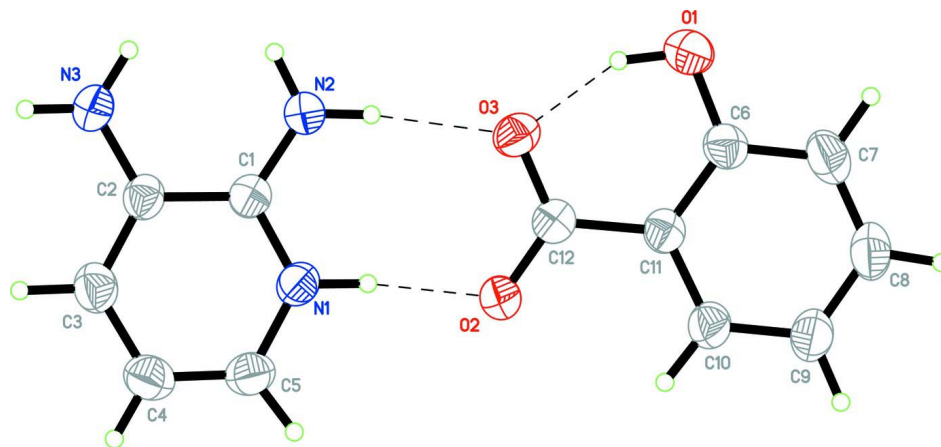


Figure 1

The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids. Hydrogen bonds are indicated by dashed lines.

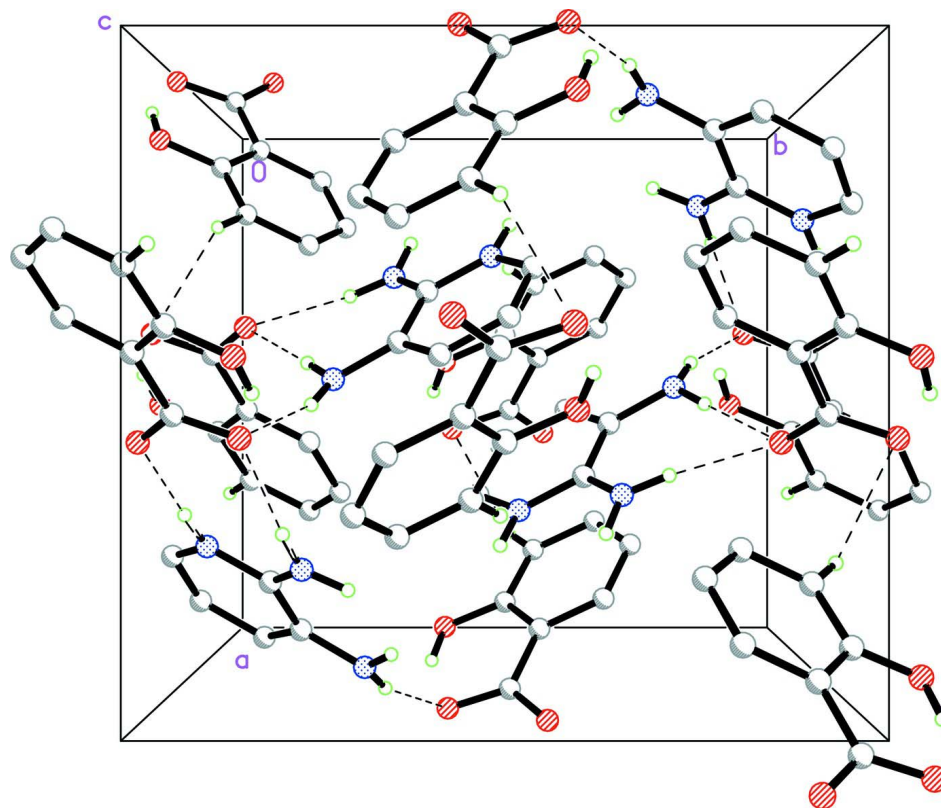


Figure 2

The crystal packing of title compound (I).

2,3-Diaminopyridinium 2-hydroxybenzoate

Crystal data

$C_5H_8N_3^+ \cdot C_7H_5O_3^-$
 $M_r = 247.25$

Orthorhombic, *Pbca*
 Hall symbol: -P 2ac 2ab

$a = 10.484 (3) \text{ \AA}$
 $b = 11.260 (3) \text{ \AA}$
 $c = 20.033 (6) \text{ \AA}$
 $V = 2364.9 (12) \text{ \AA}^3$
 $Z = 8$
 $F(000) = 1040$
 $D_x = 1.389 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 2044 reflections
 $\theta = 2.8\text{--}27.3^\circ$
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Plate, brown
 $0.54 \times 0.47 \times 0.10 \text{ mm}$

Data collection

Bruker APEXII DUO CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2009)
 $T_{\min} = 0.947$, $T_{\max} = 0.990$

12688 measured reflections
 3388 independent reflections
 1989 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 2.8^\circ$
 $h = -14 \rightarrow 14$
 $k = -8 \rightarrow 15$
 $l = -27 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.144$
 $S = 1.03$
 3388 reflections
 216 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
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.2876P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXTL* (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0084 (15)

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.28118 (14)	0.47769 (11)	0.49919 (8)	0.0372 (3)
N2	0.31269 (15)	0.31738 (13)	0.42951 (8)	0.0399 (4)
N3	0.49319 (18)	0.22674 (14)	0.52153 (10)	0.0515 (4)
C1	0.34064 (15)	0.37422 (13)	0.48633 (8)	0.0329 (4)
C2	0.43007 (15)	0.33158 (13)	0.53385 (9)	0.0356 (4)
C3	0.45227 (17)	0.39879 (16)	0.58971 (10)	0.0427 (4)

C4	0.38911 (19)	0.50631 (16)	0.60051 (11)	0.0462 (5)
C5	0.30414 (18)	0.54408 (15)	0.55483 (10)	0.0441 (4)
O1	-0.04088 (13)	0.39481 (11)	0.24975 (8)	0.0517 (4)
O2	0.09892 (12)	0.57050 (10)	0.41657 (6)	0.0432 (3)
O3	0.08969 (11)	0.40353 (9)	0.35839 (6)	0.0392 (3)
C6	-0.09061 (16)	0.50000 (14)	0.26928 (9)	0.0377 (4)
C7	-0.18426 (18)	0.54995 (18)	0.22901 (11)	0.0494 (5)
C8	-0.23979 (19)	0.65666 (18)	0.24675 (11)	0.0502 (5)
C9	-0.20179 (18)	0.71566 (17)	0.30334 (11)	0.0475 (5)
C10	-0.10732 (17)	0.66749 (14)	0.34298 (10)	0.0418 (4)
C11	-0.04980 (14)	0.55892 (13)	0.32692 (9)	0.0331 (4)
C12	0.05192 (15)	0.50816 (13)	0.37001 (8)	0.0331 (4)
H3	0.5167 (19)	0.3712 (17)	0.6237 (10)	0.056 (6)*
H4	0.4035 (18)	0.5488 (16)	0.6398 (10)	0.049 (5)*
H5	0.2538 (19)	0.6171 (18)	0.5580 (10)	0.054 (5)*
H7	-0.212 (2)	0.5068 (18)	0.1886 (12)	0.066 (6)*
H8	-0.304 (2)	0.6964 (16)	0.2196 (10)	0.050 (5)*
H9	-0.2398 (17)	0.7915 (16)	0.3162 (9)	0.042 (5)*
H10	-0.0825 (19)	0.7010 (16)	0.3859 (11)	0.048 (5)*
H1O1	0.016 (2)	0.3733 (17)	0.2853 (11)	0.059 (6)*
H1N1	0.224 (2)	0.5073 (16)	0.4672 (10)	0.048 (5)*
H1N2	0.2509 (18)	0.3436 (15)	0.4020 (10)	0.038 (5)*
H2N2	0.3459 (18)	0.2443 (19)	0.4211 (10)	0.054 (6)*
H1N3	0.465 (2)	0.1816 (17)	0.4864 (11)	0.056 (6)*
H2N3	0.536 (2)	0.1958 (16)	0.5553 (11)	0.052 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0357 (8)	0.0335 (7)	0.0423 (9)	0.0034 (6)	-0.0022 (7)	-0.0001 (6)
N2	0.0419 (8)	0.0376 (7)	0.0401 (9)	0.0062 (7)	-0.0096 (7)	-0.0050 (6)
N3	0.0599 (11)	0.0414 (8)	0.0531 (11)	0.0154 (8)	-0.0212 (9)	-0.0047 (8)
C1	0.0295 (8)	0.0312 (7)	0.0380 (9)	-0.0034 (6)	-0.0004 (7)	0.0020 (6)
C2	0.0347 (8)	0.0330 (7)	0.0391 (10)	-0.0017 (7)	-0.0035 (7)	0.0037 (7)
C3	0.0405 (10)	0.0447 (9)	0.0429 (11)	-0.0018 (8)	-0.0079 (8)	0.0017 (8)
C4	0.0495 (11)	0.0454 (9)	0.0436 (11)	-0.0020 (9)	-0.0021 (9)	-0.0086 (8)
C5	0.0453 (10)	0.0373 (8)	0.0496 (12)	0.0035 (8)	-0.0010 (9)	-0.0071 (8)
O1	0.0476 (8)	0.0510 (8)	0.0565 (9)	0.0040 (6)	-0.0077 (7)	-0.0173 (6)
O2	0.0458 (7)	0.0389 (6)	0.0449 (8)	0.0057 (5)	-0.0135 (6)	-0.0061 (5)
O3	0.0405 (6)	0.0319 (6)	0.0453 (7)	0.0023 (5)	0.0005 (5)	-0.0002 (5)
C6	0.0315 (8)	0.0394 (8)	0.0423 (10)	-0.0046 (7)	0.0007 (7)	-0.0031 (7)
C7	0.0397 (10)	0.0614 (12)	0.0471 (12)	-0.0056 (9)	-0.0103 (9)	-0.0050 (9)
C8	0.0377 (10)	0.0561 (11)	0.0568 (13)	0.0006 (9)	-0.0133 (9)	0.0056 (9)
C9	0.0405 (10)	0.0403 (9)	0.0617 (13)	0.0022 (8)	-0.0126 (9)	0.0024 (9)
C10	0.0380 (9)	0.0362 (8)	0.0513 (12)	0.0001 (7)	-0.0092 (8)	-0.0021 (8)
C11	0.0276 (8)	0.0321 (7)	0.0395 (10)	-0.0052 (6)	-0.0004 (7)	0.0019 (6)
C12	0.0304 (8)	0.0324 (7)	0.0366 (9)	-0.0028 (6)	0.0031 (7)	0.0032 (7)

Geometric parameters (Å, °)

N1—C1	1.346 (2)	O1—C6	1.352 (2)
N1—C5	1.364 (2)	O1—H1O1	0.96 (2)
N1—H1N1	0.94 (2)	O2—C12	1.267 (2)
N2—C1	1.338 (2)	O3—C12	1.2646 (19)
N2—H1N2	0.90 (2)	C6—C7	1.390 (3)
N2—H2N2	0.91 (2)	C6—C11	1.399 (2)
N3—C2	1.376 (2)	C7—C8	1.382 (3)
N3—H1N3	0.92 (2)	C7—H7	0.99 (2)
N3—H2N3	0.88 (2)	C8—C9	1.373 (3)
C1—C2	1.420 (2)	C8—H8	0.97 (2)
C2—C3	1.371 (3)	C9—C10	1.380 (3)
C3—C4	1.397 (3)	C9—H9	0.977 (18)
C3—H3	1.01 (2)	C10—C11	1.401 (2)
C4—C5	1.346 (3)	C10—H10	0.97 (2)
C4—H4	0.93 (2)	C11—C12	1.486 (2)
C5—H5	0.98 (2)		
C1—N1—C5	123.31 (15)	N1—C5—H5	114.7 (12)
C1—N1—H1N1	118.2 (12)	C6—O1—H1O1	104.2 (12)
C5—N1—H1N1	118.4 (12)	O1—C6—C7	117.32 (16)
C1—N2—H1N2	121.4 (12)	O1—C6—C11	122.45 (16)
C1—N2—H2N2	120.4 (13)	C7—C6—C11	120.22 (16)
H1N2—N2—H2N2	117.3 (17)	C8—C7—C6	120.02 (18)
C2—N3—H1N3	117.2 (13)	C8—C7—H7	120.9 (12)
C2—N3—H2N3	116.5 (13)	C6—C7—H7	119.1 (12)
H1N3—N3—H2N3	122.2 (18)	C9—C8—C7	120.72 (19)
N2—C1—N1	118.37 (15)	C9—C8—H8	116.0 (11)
N2—C1—C2	123.58 (15)	C7—C8—H8	123.2 (11)
N1—C1—C2	118.05 (15)	C8—C9—C10	119.54 (18)
C3—C2—N3	122.58 (16)	C8—C9—H9	121.5 (11)
C3—C2—C1	118.21 (15)	C10—C9—H9	118.9 (11)
N3—C2—C1	119.18 (16)	C9—C10—C11	121.31 (17)
C2—C3—C4	121.63 (17)	C9—C10—H10	123.2 (11)
C2—C3—H3	119.6 (11)	C11—C10—H10	115.2 (11)
C4—C3—H3	118.7 (11)	C6—C11—C10	118.16 (15)
C5—C4—C3	118.84 (18)	C6—C11—C12	121.10 (14)
C5—C4—H4	121.2 (12)	C10—C11—C12	120.74 (15)
C3—C4—H4	119.9 (12)	O3—C12—O2	122.00 (15)
C4—C5—N1	119.95 (17)	O3—C12—C11	118.43 (14)
C4—C5—H5	125.3 (12)	O2—C12—C11	119.57 (14)
C5—N1—C1—N2	-178.69 (16)	C6—C7—C8—C9	1.3 (3)
C5—N1—C1—C2	1.1 (2)	C7—C8—C9—C10	-0.2 (3)
N2—C1—C2—C3	178.90 (16)	C8—C9—C10—C11	-0.5 (3)
N1—C1—C2—C3	-0.9 (2)	O1—C6—C11—C10	-179.94 (16)
N2—C1—C2—N3	0.5 (3)	C7—C6—C11—C10	1.0 (2)

N1—C1—C2—N3	-179.27 (15)	O1—C6—C11—C12	0.2 (2)
N3—C2—C3—C4	178.57 (18)	C7—C6—C11—C12	-178.86 (16)
C1—C2—C3—C4	0.2 (3)	C9—C10—C11—C6	0.0 (3)
C2—C3—C4—C5	0.2 (3)	C9—C10—C11—C12	179.93 (16)
C3—C4—C5—N1	-0.1 (3)	C6—C11—C12—O3	-8.9 (2)
C1—N1—C5—C4	-0.6 (3)	C10—C11—C12—O3	171.22 (15)
O1—C6—C7—C8	179.24 (17)	C6—C11—C12—O2	170.49 (15)
C11—C6—C7—C8	-1.7 (3)	C10—C11—C12—O2	-9.4 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O1 \cdots O3	0.96 (2)	1.69 (2)	2.573 (2)	151.2 (18)
N1—H1N1 \cdots O2	0.94 (2)	1.80 (2)	2.736 (2)	171.1 (19)
N2—H1N2 \cdots O3	0.900 (19)	2.019 (19)	2.905 (2)	167.7 (18)
N2—H2N2 \cdots O2 ⁱ	0.91 (2)	2.04 (2)	2.942 (2)	169.6 (18)
N3—H1N3 \cdots O2 ⁱ	0.92 (2)	1.99 (2)	2.907 (2)	174.3 (19)
N3—H2N3 \cdots O3 ⁱⁱ	0.88 (2)	2.14 (2)	2.994 (2)	163.9 (19)
C7—H7 \cdots O3 ⁱⁱⁱ	0.99 (2)	2.56 (2)	3.376 (3)	139.8 (17)

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