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2,3-Diaminopyridinium hydrogen malonate

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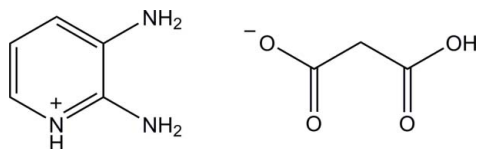
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.094; data-to-parameter ratio = 11.1.

In the title molecular salt, $\text{C}_5\text{H}_8\text{N}_3^+ \cdot \text{C}_3\text{H}_3\text{O}_4^-$, the cation is essentially planar, with a maximum deviation of 0.005 (1) Å for all non-H atoms. In the anion, an intramolecular O—H...O hydrogen bond generates an $S(6)$ ring. In the crystal, the cations and anions are connected *via* N—H...O hydrogen bonds and a weak C—H...O interaction, forming layers parallel to the *ab* plane.

Related literature

For background to the chemistry of substituted pyridines, see: Amr *et al.* (2006); Bart *et al.* (2001); Shinkai *et al.* (2000). For related structures, see: Betz *et al.* (2011); Hemamalini *et al.* (2011); Balasubramani & Fun (2009); Fun & Balasubramani (2009). For the conformation of the malonate ion, see: Djinović *et al.* (1990). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

 $\text{C}_5\text{H}_8\text{N}_3^+ \cdot \text{C}_3\text{H}_3\text{O}_4^-$ $M_r = 213.20$ Monoclinic, $P2_1$ $a = 5.0843$ (1) Å $b = 8.0771$ (1) Å $c = 11.1928$ (2) Å $\beta = 91.214$ (1)° $V = 459.55$ (1) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 0.13$ mm⁻¹ $T = 100$ K $0.28 \times 0.25 \times 0.14$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)
 $T_{\min} = 0.966$, $T_{\max} = 0.983$

6631 measured reflections
1778 independent reflections
1695 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.094$ $S = 1.07$

1778 reflections

160 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.35$ e Å⁻³ $\Delta\rho_{\min} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H1O3}\cdots\text{O1}$	0.93 (4)	1.63 (3)	2.5208 (16)	159 (3)
$\text{N3}-\text{H2N3}\cdots\text{O4}^{\text{i}}$	0.88 (3)	2.16 (3)	2.9133 (19)	143 (2)
$\text{N2}-\text{H2N2}\cdots\text{O2}^{\text{ii}}$	0.87 (3)	2.15 (3)	3.0066 (18)	168 (2)
$\text{N1}-\text{H1N1}\cdots\text{O1}^{\text{iii}}$	0.92 (3)	1.87 (3)	2.7782 (16)	168 (3)
$\text{N2}-\text{H1N2}\cdots\text{O2}^{\text{iii}}$	0.88 (3)	2.12 (3)	2.9470 (18)	157 (3)
$\text{N3}-\text{H1N3}\cdots\text{O2}^{\text{ii}}$	0.87 (2)	2.18 (2)	3.0574 (19)	178 (3)
$\text{C7}-\text{H7B}\cdots\text{O2}^{\text{iv}}$	0.99	2.46	3.3532 (19)	149

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

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5228).

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supporting information

Acta Cryst. (2013). E69, o92–o93 [https://doi.org/10.1107/S1600536812050386]

2,3-Diaminopyridinium hydrogen malonate

Kaliyaperumal Thanigaimani, Nuridayanti Che Khalib, Suhana Arshad and Ibrahim Abdul Razak

S1. Comment

Pyridine and its derivatives continue to attract great interest due to the wide variety of interesting biological activities observed for these compounds, such as anticancer, analgesic, antimicrobial and antidepressant activities (Amr *et al.*, 2006; Bart *et al.*, 2001; Shinkai *et al.*, 2000). They are also often involved in hydrogen-bond interactions. The related crystal structures of 2,3-diaminopyridinium 2-hydroxybenzoate (Hemamalini *et al.*, 2011), 2,3-diaminopyrimidinium benzoate (Balasubramani & Fun, 2009) and 2,3-diaminopyridinium 4-hydroxybenzoate (Fun & Balasubramani, 2009) have been recently reported. In order to study potential hydrogen bonding interactions, the crystal structure determination of the title compound (I) was carried out.

The asymmetric unit (Fig. 1) contains one 2,3-Diaminopyridinium cation and one hydrogen malonate anion. The proton transfers from one of the carboxyl group oxygen atom (O1) to atom N1 of 2,3-diaminopyridine resulted in widening of C1—N1—C5 angle of the pyridinium ring to 123.69 (13)°, compared to the corresponding angle of 118.97 (15)° in neutral 2,3-diaminopyridine (Betz *et al.*, 2011). The 2,4-diaminopyridinium cation is planar, with a maximum deviation of 0.005 (1) Å for atom N1. The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing (Fig. 2), the protonated N1 atom and the 2-amino group (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) *via* a pair of intermolecular N1—H1N1ⁱⁱⁱ⋯O1ⁱⁱⁱ and N2—H1N2ⁱⁱⁱ⋯O2ⁱⁱⁱ hydrogen bonds (symmetry code in Table 1), forming a ring motif $R_2^2(8)$ (Bernstein *et al.*, 1995). Atom O3 of the carboxyl group of the hydrogen malonate anion forms an intramolecular O3—H1O3ⁱⁱⁱ⋯O1 hydrogen bond with the O atom of the carboxylate group (O1) [with graph-set notation S(6)], leading to a folded conformation. A similar intramolecular hydrogen bond has been observed in the crystal structures of benzylammonium hydrogen malonate and 4-picolinium hydrogen malonate (Djinović *et al.*, 1990). The 2-amino groups (N2 and N3) are involved in the intermolecular N—Hⁱⁱⁱ⋯O hydrogen bonds with hydrogen malonate oxygen atom (O2), forming an $R_2^1(7)$ ring motif. The crystal structure is further stabilized by a weak C7—H7B^{iv}⋯O2^{iv} interaction (symmetry code in Table 1), forming a layer lying parallel to the *ab* plane.

S2. Experimental

Hot methanol solutions (20 ml) of 2,3-diaminopyrimidine (27 mg, Aldrich) and malonic acid (26 mg, Merck) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound (I) appeared after a few days.

S3. Refinement

O- and N-bound H atoms were located in a difference Fourier map and allowed to be refined freely [O—H = 0.93 (4) Å and N—H = 0.87 (3)–0.92 (3) Å]. The remaining hydrogen atoms were positioned geometrically (C—H = 0.95 or 0.99 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. In the final refinement, 1237 Friedel pairs were merged.

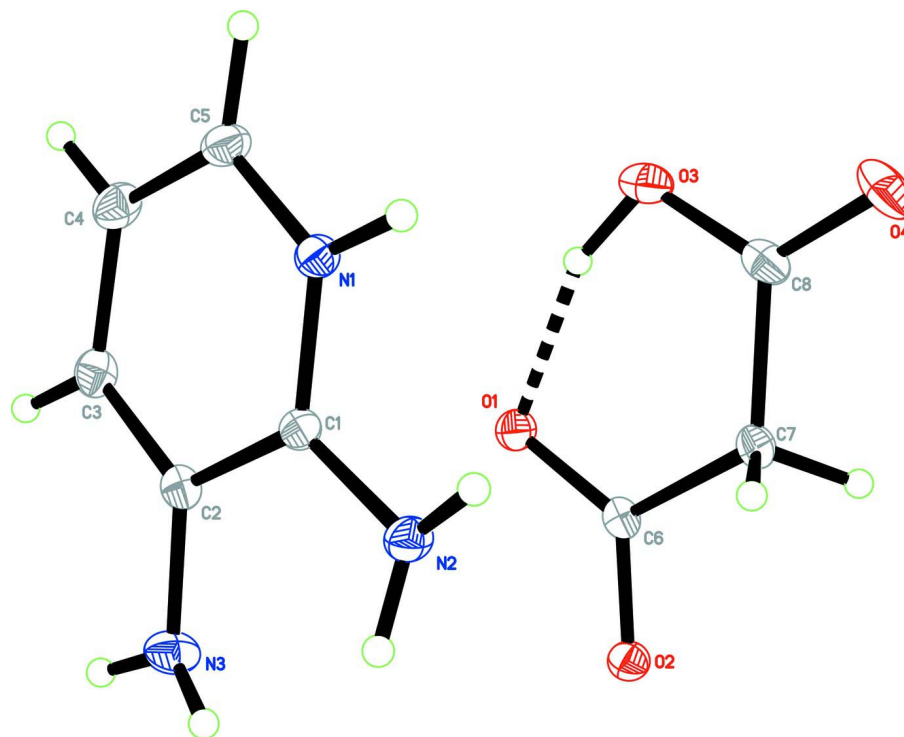


Figure 1

The molecular structure of the title compound with atom labels with 50% probability displacement ellipsoids.

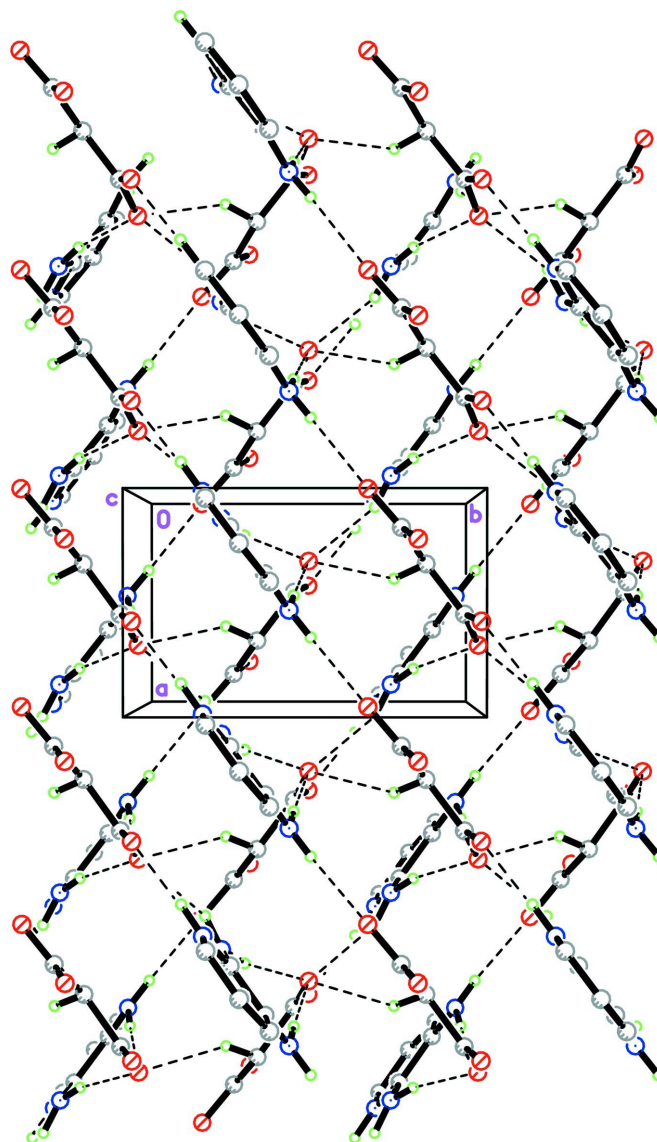


Figure 2

The crystal packing of the title compound. The H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

2,3-Diaminopyridinium hydrogen malonate

Crystal data

$C_5H_8N_3^+ \cdot C_3H_3O_4^-$

$M_r = 213.20$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 5.0843 (1) \text{ \AA}$

$b = 8.0771 (1) \text{ \AA}$

$c = 11.1928 (2) \text{ \AA}$

$\beta = 91.214 (1)^\circ$

$V = 459.55 (1) \text{ \AA}^3$

$Z = 2$

$F(000) = 224$

$D_x = 1.541 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3153 reflections

$\theta = 3.1\text{--}32.6^\circ$

$\mu = 0.13 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, brown

$0.28 \times 0.25 \times 0.14 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.966$, $T_{\max} = 0.983$

6631 measured reflections

1778 independent reflections

1695 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 32.7^\circ$, $\theta_{\min} = 1.8^\circ$

$h = -7 \rightarrow 7$

$k = -10 \rightarrow 12$

$l = -17 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.094$

$S = 1.07$

1778 reflections

160 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.057P]$

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

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

$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

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 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.4162 (2)	0.50089 (15)	0.24888 (10)	0.0139 (2)
O2	0.3017 (2)	0.50412 (15)	0.44060 (10)	0.0139 (2)
O3	0.7878 (2)	0.31758 (17)	0.18357 (11)	0.0209 (3)
O4	1.0228 (2)	0.17757 (17)	0.31863 (13)	0.0222 (3)
N1	0.9986 (2)	0.70786 (17)	0.18711 (12)	0.0123 (2)
N2	0.8913 (3)	0.75149 (17)	0.38452 (12)	0.0136 (3)
N3	0.4668 (3)	0.95043 (19)	0.30805 (14)	0.0163 (3)
C1	0.8441 (3)	0.78141 (18)	0.26789 (13)	0.0107 (3)
C2	0.6311 (3)	0.88272 (18)	0.22541 (14)	0.0119 (3)
C3	0.5946 (3)	0.8991 (2)	0.10331 (14)	0.0142 (3)
H3A	0.4551	0.9663	0.0730	0.017*
C4	0.7607 (3)	0.8179 (2)	0.02293 (14)	0.0161 (3)
H4A	0.7326	0.8294	-0.0608	0.019*
C5	0.9617 (3)	0.7228 (2)	0.06655 (14)	0.0153 (3)

H5A	1.0754	0.6673	0.0135	0.018*
C6	0.4477 (3)	0.45888 (19)	0.35774 (14)	0.0112 (3)
C7	0.6803 (3)	0.34858 (19)	0.39221 (14)	0.0129 (3)
H7A	0.7997	0.4142	0.4448	0.016*
H7B	0.6122	0.2564	0.4410	0.016*
C8	0.8449 (3)	0.27351 (19)	0.29470 (15)	0.0148 (3)
H2N3	0.343 (5)	1.013 (4)	0.276 (2)	0.023 (6)*
H2N2	0.814 (5)	0.817 (4)	0.434 (2)	0.026 (6)*
H1N1	1.136 (6)	0.645 (4)	0.218 (3)	0.044 (8)*
H1N2	1.043 (5)	0.703 (4)	0.401 (2)	0.029 (6)*
H1N3	0.534 (5)	0.963 (3)	0.380 (2)	0.018 (5)*
H1O3	0.654 (6)	0.395 (5)	0.190 (3)	0.048 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0137 (4)	0.0153 (5)	0.0126 (5)	0.0024 (4)	-0.0005 (4)	0.0011 (4)
O2	0.0129 (4)	0.0152 (5)	0.0136 (5)	0.0025 (4)	0.0018 (3)	0.0004 (4)
O3	0.0217 (5)	0.0231 (6)	0.0183 (6)	0.0068 (5)	0.0060 (4)	-0.0012 (5)
O4	0.0143 (5)	0.0164 (6)	0.0360 (8)	0.0056 (4)	0.0016 (4)	-0.0008 (5)
N1	0.0115 (5)	0.0135 (6)	0.0119 (6)	0.0010 (4)	0.0004 (4)	0.0006 (5)
N2	0.0134 (5)	0.0160 (6)	0.0114 (6)	0.0024 (4)	-0.0001 (4)	0.0004 (5)
N3	0.0115 (5)	0.0211 (6)	0.0162 (6)	0.0053 (5)	0.0001 (4)	-0.0023 (5)
C1	0.0096 (5)	0.0114 (6)	0.0112 (6)	-0.0005 (4)	0.0006 (4)	0.0001 (5)
C2	0.0099 (5)	0.0112 (6)	0.0147 (7)	-0.0001 (5)	-0.0005 (4)	0.0005 (5)
C3	0.0124 (5)	0.0154 (6)	0.0148 (7)	0.0012 (5)	-0.0022 (5)	0.0026 (6)
C4	0.0168 (6)	0.0201 (7)	0.0114 (7)	0.0012 (5)	-0.0011 (5)	0.0021 (6)
C5	0.0165 (6)	0.0184 (7)	0.0111 (6)	0.0015 (6)	0.0022 (5)	0.0002 (6)
C6	0.0089 (5)	0.0101 (6)	0.0145 (6)	-0.0006 (5)	-0.0007 (4)	0.0002 (5)
C7	0.0118 (5)	0.0130 (6)	0.0140 (6)	0.0028 (5)	-0.0007 (4)	0.0012 (5)
C8	0.0113 (6)	0.0114 (6)	0.0219 (8)	-0.0008 (5)	0.0032 (5)	-0.0019 (6)

Geometric parameters (Å, °)

O1—C6	1.2716 (19)	N3—H1N3	0.87 (2)
O2—C6	1.2542 (17)	C1—C2	1.4305 (19)
O3—C8	1.320 (2)	C2—C3	1.382 (2)
O3—H1O3	0.93 (4)	C3—C4	1.409 (2)
O4—C8	1.2168 (19)	C3—H3A	0.9500
N1—C1	1.3482 (18)	C4—C5	1.361 (2)
N1—C5	1.3638 (19)	C4—H4A	0.9500
N1—H1N1	0.92 (3)	C5—H5A	0.9500
N2—C1	1.344 (2)	C6—C7	1.524 (2)
N2—H2N2	0.87 (3)	C7—C8	1.516 (2)
N2—H1N2	0.88 (3)	C7—H7A	0.9900
N3—C2	1.3731 (19)	C7—H7B	0.9900
N3—H2N3	0.88 (3)		

C8—O3—H1O3	104.9 (19)	C5—C4—C3	119.31 (14)
C1—N1—C5	123.70 (13)	C5—C4—H4A	120.3
C1—N1—H1N1	116.0 (18)	C3—C4—H4A	120.3
C5—N1—H1N1	120.3 (18)	C4—C5—N1	119.42 (14)
C1—N2—H2N2	115.8 (16)	C4—C5—H5A	120.3
C1—N2—H1N2	114.6 (16)	N1—C5—H5A	120.3
H2N2—N2—H1N2	123 (2)	O2—C6—O1	124.51 (13)
C2—N3—H2N3	113.0 (16)	O2—C6—C7	116.82 (13)
C2—N3—H1N3	115.7 (15)	O1—C6—C7	118.66 (12)
H2N3—N3—H1N3	125 (2)	C8—C7—C6	119.27 (13)
N2—C1—N1	118.52 (13)	C8—C7—H7A	107.5
N2—C1—C2	122.95 (13)	C6—C7—H7A	107.5
N1—C1—C2	118.48 (13)	C8—C7—H7B	107.5
N3—C2—C3	123.85 (13)	C6—C7—H7B	107.5
N3—C2—C1	118.10 (13)	H7A—C7—H7B	107.0
C3—C2—C1	117.95 (12)	O4—C8—O3	121.78 (15)
C2—C3—C4	121.14 (13)	O4—C8—C7	121.03 (16)
C2—C3—H3A	119.4	O3—C8—C7	117.19 (13)
C4—C3—H3A	119.4		
C5—N1—C1—N2	176.82 (14)	C2—C3—C4—C5	-0.5 (2)
C5—N1—C1—C2	-0.8 (2)	C3—C4—C5—N1	0.0 (2)
N2—C1—C2—N3	-0.7 (2)	C1—N1—C5—C4	0.7 (2)
N1—C1—C2—N3	176.80 (14)	O2—C6—C7—C8	172.90 (13)
N2—C1—C2—C3	-177.26 (15)	O1—C6—C7—C8	-8.2 (2)
N1—C1—C2—C3	0.3 (2)	C6—C7—C8—O4	-175.86 (14)
N3—C2—C3—C4	-175.92 (16)	C6—C7—C8—O3	4.6 (2)
C1—C2—C3—C4	0.4 (2)		

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>
O3—H1O3...O1	0.93 (4)	1.63 (3)	2.5208 (16)	159 (3)
N3—H2N3...O4 ⁱ	0.88 (3)	2.16 (3)	2.9133 (19)	143 (2)
N2—H2N2...O2 ⁱⁱ	0.87 (3)	2.15 (3)	3.0066 (18)	168 (2)
N1—H1N1...O1 ⁱⁱⁱ	0.92 (3)	1.87 (3)	2.7782 (16)	168 (3)
N2—H1N2...O2 ⁱⁱⁱ	0.88 (3)	2.12 (3)	2.9470 (18)	157 (3)
N3—H1N3...O2 ⁱⁱ	0.87 (2)	2.18 (2)	3.0574 (19)	178 (3)
C7—H7B...O2 ^{iv}	0.99	2.46	3.3532 (19)	149

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