Homopiperazinium bis(dihydrogenarsenate)

Hazel S. Wilkinson and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

The crystal packing in the title compound, $C_5H_{14}N_2^{2+} \cdot 2H_2AsO_4^-$, involves anion-to-anion O—H$\cdots$O hydrogen bonds, resulting in double chains of dihydrogenarsenate tetrahedra. The double chains are crosslinked by further O—H$\cdots$O bonds to result in a three-dimensional framework that accommodates the organic cations in large cavities. The cations interact with the framework by way of N—H$\cdots$O bonds.

Comment

The title compound, (I) (Fig. 1), was prepared as part of our ongoing structural studies of hydrogen-bonding interactions in protonated-amine (di)hydrogen arsenates (Wilkinson & Harrison, 2005a,b; Todd & Harrison, 2005). These simple organic salts show interesting packing motifs, strongly influenced by the interplay of N—H$\cdots$O and O—H$\cdots$O hydrogen bonds.
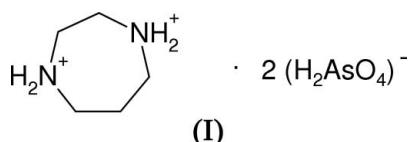
Both the $(H_2AsO_4)^-$ dihydrogenarsenate groups in (I) show their normal tetrahedral geometry [mean As—O = 1.677 (2) Å], with the protonated As—OH vertices showing their expected lengthening relative to the unprotonated As—
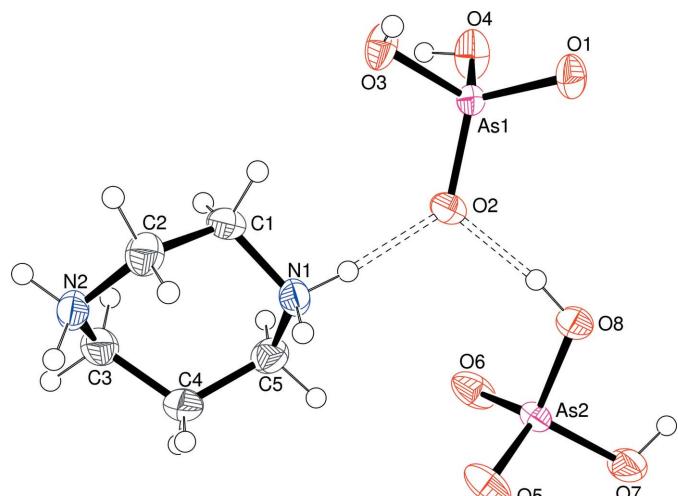
Figure 1
The asymmetric unit of (I), showing 50% displacement ellipsoids (arbitrary spheres for H atoms). Hydrogen bonds are indicated by dashed lines.
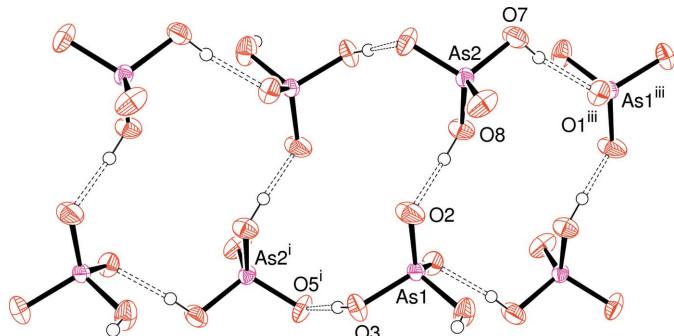
Figure 2
Detail of a hydrogen-bonded (dashed lines) dihydrogenarsenate double chain in (I). Symmetry codes are as in Table 2.
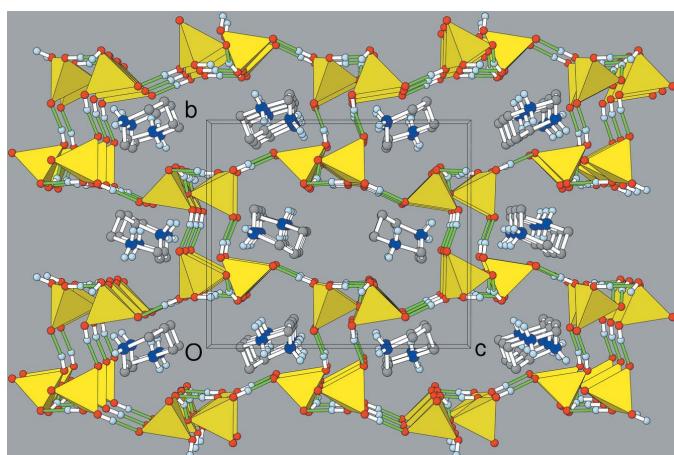

Figure 3
The packing in (I), viewed down [100], with the dihydrogenarsenate groups represented by polyhedra. Colour key: $H_2AsO_4{}^-$ groups yellow, O atoms red, N dark blue, C grey, H pale blue, H···O portions of the O—H···O hydrogen bonds green.

O bonds, which have formal partial double-bond character (Table 1). The homopiperazinium cation adopts a chair conformation, with atoms N1, C1, C3 and C4 almost coplanar (r.m.s. deviation from the mean plane = 0.029 Å) and atoms C5, C2 and N2 displaced from the plane by 0.667 (3), −1.186 (3) and −1.045 (3) Å, respectively.

As well as electrostatic attractions, the component species in (I) interact by means of a network of cation-to-anion N—H···O and anion-to-anion O—H···O hydrogen bonds (Table 2). The $(H_2AsO_4)^-$ units are linked into polymeric double chains (Fig. 2) propagating along [100]. Each strand of the chain consists of alternating As1- and As2-centred groups, with O3—H1···O5^i and O7—H3···O1^{iii} providing the hydrogen-bond links (see Table 2 for symmetry codes). The two strands are then crosslinked by the O8—H4···O2 interaction. The graph-set notation (Bernstein *et al.*, 1995) for this hydrogen-bonding pattern within the double chain is an $R_4^4(16)$ loop. The As1···As2^i and As1···As2^{iii} intra-strand separations are 4.7032 (3) and 4.7531 (3) Å, respectively, and the As1···As2 inter-strand separation is 5.0014 (3) Å. Finally, the [100] double chains are crosslinked in [001] by the O4—H2···O6^{ii} bonds [with As1···As2^{ii} = 4.5461 (3) Å], to result in
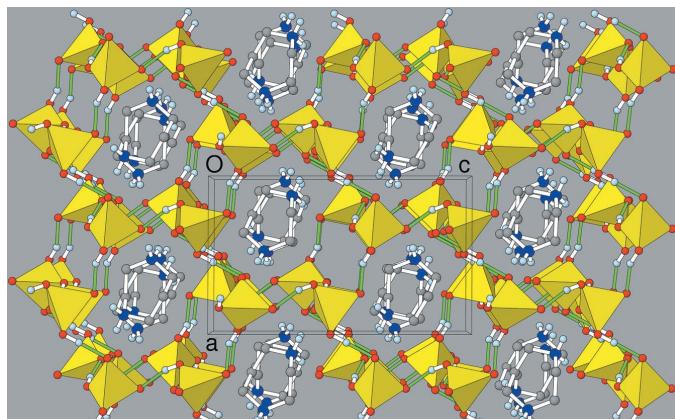
Figure 4
The packing in (I), viewed down [010]. Drawing conventions as in Fig. 3.

a very open three-dimensional network of dihydrogenarsenate groups, delimiting intersecting channels that propagate in [100] and [010] (Figs. 3 and 4). The organic cations occupy the large eight-membered ring (*i.e.* eight H_2AsO_4 tetrahedra) [100] channels in the framework and interact with them by way of the four N—H···O bonds. It should be noted that the mean H···O contact distance for the O—H···O bonds (1.71 Å) is significantly smaller than the mean H···O distance (1.84 Å) for the N—H···O bonds. The graph-set notation for the eight-membered ring loop is $R_8^8(32)$.

The situation in (I) of a hydrogen-bonded array of tetrahedral anions encompassing a network of channels occupied by organic cations is similar to that of α-$C_5H_7N_2$·H_2PO_4 ($C_5H_7N_2$ is the 2-aminopyridinium cation; Czapla *et al.*, 2003). In the phosphate, symmetrical O···H···O hydrogen bonds appear to be present at room temperature, and a paraelectric-to-ferroelectric phase transition occurs on cooling below 104 K.

Experimental

An aqueous homopiperazine solution (10 ml, 0.5 *M*) was added to an aqueous H_3AsO_4 solution (10 ml, 0.5 *M*), giving a clear solution. A mass of plate- and slab-like crystals of (I) grew as the water evaporated over the course of a few days.

Crystal data

$C_5H_{14}N_2{}^{2+}$·$2AsH_2O_4{}^-$	$Z = 4$
$M_r = 384.05$	$D_x = 1.968$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.1495$ (3) Å	$\mu = 5.19$ mm^{-1}
$b = 11.7163$ (4) Å	$T = 293$ (2) K
$c = 13.5730$ (5) Å	Block cut from slab, colourless
$\beta = 90.234$ (1)°	$0.32 \times 0.19 \times 0.16$ mm
$V = 1295.97$ (8) Å^3	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	14796 measured reflections
	4639 independent reflections
ω scans	3760 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$R_{int} = 0.025$
	$\theta_{max} = 32.5°$
$T_{min} = 0.288$, $T_{max} = 0.491$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.95$	$\Delta\rho_{max} = 0.40$ e Å^{-3}
4639 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}
156 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.0013 (3)

Table 1
Selected geometric parameters (Å, °).

As1—O1	1.6530 (14)	As2—O5	1.6492 (14)
As1—O2	1.6543 (15)	As2—O6	1.6516 (15)
As1—O4	1.7001 (15)	As2—O7	1.6973 (16)
As1—O3	1.7053 (14)	As2—O8	1.7072 (13)
N1—C1—C2—N2	−77.8 (2)	C3—C4—C5—N1	65.9 (3)
C1—C2—N2—C3	15.0 (3)	C4—C5—N1—C1	−59.7 (2)
C2—N2—C3—C4	55.6 (3)	C5—N1—C1—C2	83.3 (2)
N2—C3—C4—C5	−85.6 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O5^i	0.90	1.65	2.555 (2)	178
O4—H2···O6^{ii}	0.86	1.73	2.579 (2)	165
O7—H3···O1^{iii}	0.89	1.76	2.600 (2)	156
O8—H4···O2	0.88	1.70	2.567 (2)	169
N1—H5···O2	0.90	1.82	2.716 (2)	174
N1—H6···O1^i	0.90	1.91	2.802 (2)	171
N2—H2A···O6^{iv}	0.90	1.80	2.698 (2)	174
N2—H2B···O5^v	0.90	1.83	2.721 (2)	173

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

The initial refinement stalled with $R(F) \simeq 0.20$. The pseudo-orthorhombic unit cell with $\beta \simeq 90°$ suggested the possibility of twinning. Inserting a mirror plane perpendicular to the *a* axis as a twinning operation with the aid of the twin matrix ($\bar{1}$ 0 0, 0 1 0, 0 0 1) led to a straightforward convergence to the final answer, with volume fractions of 0.875 (6):0.125 (6) for the two components. For a similar case, see Pompetzki *et al.* (2003).

The O-bound H atoms were found in difference maps and refined as riding in their as-found relative positions. The C– and N-bound H atoms were placed in idealized positions (C—H = 0.97 Å and N—H = 0.90 Å) and refined as riding. The constraint $U_{iso}(H) = 1.2U_{eq}(carrier)$ was applied in all cases.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

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Crystal data
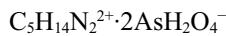
$C_5H_{14}N_2^{2+} \cdot 2AsH_2O_4^-$	$F(000) = 768$
$M_r = 384.05$	$D_x = 1.968$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 6614 reflections
$a = 8.1495$ (3) Å	$\theta = 2.3$–32.5°
$b = 11.7163$ (4) Å	$\mu = 5.19$ mm^{-1}
$c = 13.5730$ (5) Å	$T = 293$ K
$\beta = 90.234$ (1)°	Block, colourless
$V = 1295.97$ (8) Å^3	$0.32 \times 0.19 \times 0.16$ mm
$Z = 4$	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	14796 measured reflections
Radiation source: fine-focus sealed tube	4639 independent reflections
Graphite monochromator	3760 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$\theta_{max} = 32.5°$, $\theta_{min} = 2.3°$
	$h = -12 \rightarrow 10$
	$k = -17 \rightarrow 16$
$T_{min} = 0.288$, $T_{max} = 0.491$	$l = -19 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: difmap (O-H) and geom (others)
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$
$wR(F^2) = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{max} = 0.001$
4639 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
156 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
0 restraints	Extinction correction: SHELXL97 (Sheldrick, 1997), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0013 (3)
Secondary atom site location: difference Fourier map	

Special details

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}
As1	0.68569 (2)	0.303928 (15)	0.034816 (14)	0.02193 (5)
O1	0.76061 (19)	0.32062 (13)	−0.07725 (10)	0.0314 (3)
O2	0.6564 (2)	0.42518 (14)	0.09465 (14)	0.0511 (5)
O3	0.50652 (19)	0.22875 (14)	0.03389 (11)	0.0341 (3)
H1	0.4560	0.2282	−0.0254	0.041*
O4	0.8174 (2)	0.21845 (14)	0.09834 (12)	0.0399 (4)
H2	0.7830	0.1909	0.1536	0.048*
As2	0.81196 (2)	0.702982 (15)	0.141776 (14)	0.02319 (5)
O5	0.64072 (19)	0.77730 (14)	0.13254 (12)	0.0383 (4)
O6	0.8354 (2)	0.64027 (14)	0.24990 (10)	0.0415 (4)
O7	0.9719 (2)	0.79097 (13)	0.11673 (15)	0.0475 (5)
H3	1.0517	0.7524	0.0866	0.057*
O8	0.8236 (2)	0.60340 (12)	0.05025 (10)	0.0334 (3)
H4	0.7680	0.5397	0.0579	0.040*
C1	0.2683 (3)	0.39324 (17)	0.18419 (15)	0.0293 (4)
H1A	0.2968	0.3474	0.2412	0.035*
H1B	0.2899	0.3479	0.1259	0.035*
C2	0.0894 (3)	0.4205 (2)	0.18770 (17)	0.0360 (5)
H2C	0.0288	0.3538	0.1658	0.043*
H2D	0.0674	0.4813	0.1411	0.043*
N1	0.3756 (2)	0.49654 (14)	0.18250 (13)	0.0293 (4)
H5	0.4714	0.4778	0.1541	0.035*
H6	0.3274	0.5499	0.1445	0.035*
C3	0.1419 (3)	0.48886 (19)	0.36471 (16)	0.0387 (5)
H3A	0.2062	0.4225	0.3832	0.046*
H3B	0.0810	0.5132	0.4223	0.046*
C4	0.2583 (3)	0.58472 (19)	0.33405 (17)	0.0375 (5)
H4A	0.1984	0.6375	0.2922	0.045*
H4B	0.2915	0.6262	0.3927	0.045*
C5	0.4107 (3)	0.54720 (19)	0.28025 (17)	0.0345 (5)
H5A	0.4823	0.6125	0.2718	0.041*
H5B	0.4686	0.4916	0.3203	0.041*
N2	0.0242 (2)	0.45573 (15)	0.28616 (15)	0.0351 (4)
H2A	−0.0442	0.5150	0.2763	0.042*
H2B	−0.0368	0.3977	0.3094	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.02024 (9)	0.02205 (9)	0.02354 (9)	−0.00063 (7)	0.00305 (7)	0.00010 (7)
O1	0.0299 (7)	0.0391 (8)	0.0253 (7)	0.0027 (6)	0.0061 (6)	0.0103 (6)
O2	0.0463 (10)	0.0324 (8)	0.0749 (13)	−0.0089 (7)	0.0309 (9)	−0.0224 (8)
O3	0.0252 (7)	0.0476 (9)	0.0295 (7)	−0.0123 (7)	−0.0023 (6)	0.0063 (7)
O4	0.0291 (8)	0.0560 (10)	0.0346 (8)	0.0050 (7)	−0.0018 (7)	0.0176 (7)
As2	0.02066 (9)	0.02539 (9)	0.02351 (9)	0.00275 (7)	−0.00057 (7)	−0.00614 (7)
O5	0.0277 (8)	0.0512 (9)	0.0360 (8)	0.0179 (7)	−0.0075 (6)	−0.0145 (7)
O6	0.0559 (11)	0.0449 (9)	0.0237 (7)	0.0201 (8)	−0.0018 (7)	−0.0036 (6)
O7	0.0350 (9)	0.0323 (9)	0.0754 (14)	−0.0087 (7)	0.0180 (9)	−0.0190 (8)
O8	0.0436 (9)	0.0294 (7)	0.0271 (7)	−0.0041 (7)	0.0047 (7)	−0.0092 (6)
C1	0.0353 (11)	0.0238 (9)	0.0287 (9)	0.0041 (8)	0.0010 (8)	−0.0031 (8)
C2	0.0287 (11)	0.0394 (12)	0.0400 (12)	−0.0041 (9)	−0.0013 (9)	−0.0004 (9)
N1	0.0259 (8)	0.0301 (9)	0.0322 (9)	0.0045 (7)	0.0074 (7)	0.0058 (7)
C3	0.0494 (14)	0.0342 (11)	0.0326 (11)	0.0016 (10)	0.0135 (10)	0.0013 (9)
C4	0.0451 (13)	0.0277 (10)	0.0396 (12)	−0.0009 (9)	0.0066 (10)	−0.0077 (9)
C5	0.0298 (11)	0.0296 (11)	0.0441 (12)	−0.0033 (8)	−0.0020 (9)	−0.0014 (9)
N2	0.0273 (9)	0.0292 (9)	0.0488 (11)	0.0024 (7)	0.0115 (8)	0.0103 (8)

Geometric parameters (Å, °)

As1—O1	1.6530 (14)	C2—H2C	0.9700
As1—O2	1.6543 (15)	C2—H2D	0.9700
As1—O4	1.7001 (15)	N1—C5	1.480 (3)
As1—O3	1.7053 (14)	N1—H5	0.9000
O3—H1	0.9028	N1—H6	0.9000
O4—H2	0.8642	C3—N2	1.483 (3)
As2—O5	1.6492 (14)	C3—C4	1.529 (3)
As2—O6	1.6516 (15)	C3—H3A	0.9700
As2—O7	1.6973 (16)	C3—H3B	0.9700
As2—O8	1.7072 (13)	C4—C5	1.509 (3)
O7—H3	0.8921	C4—H4A	0.9700
O8—H4	0.8799	C4—H4B	0.9700
C1—N1	1.493 (3)	C5—H5A	0.9700
C1—C2	1.494 (3)	C5—H5B	0.9700
C1—H1A	0.9700	N2—H2A	0.9000
C1—H1B	0.9700	N2—H2B	0.9000
C2—N2	1.498 (3)		
O1—As1—O2	113.88 (8)	C5—N1—H5	108.5
O1—As1—O4	107.56 (8)	C1—N1—H5	108.5
O2—As1—O4	110.43 (9)	C5—N1—H6	108.5
O1—As1—O3	111.95 (8)	C1—N1—H6	108.5
O2—As1—O3	108.77 (8)	H5—N1—H6	107.5
O4—As1—O3	103.78 (8)	N2—C3—C4	113.39 (18)
As1—O3—H1	113.4	N2—C3—H3A	108.9

As1—O4—H2	117.0	C4—C3—H3A	108.9
O5—As2—O6	113.40 (8)	N2—C3—H3B	108.9
O5—As2—O7	108.32 (9)	C4—C3—H3B	108.9
O6—As2—O7	111.23 (10)	H3A—C3—H3B	107.7
O5—As2—O8	110.81 (8)	C5—C4—C3	115.50 (18)
O6—As2—O8	109.63 (7)	C5—C4—H4A	108.4
O7—As2—O8	102.95 (8)	C3—C4—H4A	108.4
As2—O7—H3	110.2	C5—C4—H4B	108.4
As2—O8—H4	117.6	C3—C4—H4B	108.4
N1—C1—C2	113.53 (17)	H4A—C4—H4B	107.5
N1—C1—H1A	108.9	N1—C5—C4	113.23 (18)
C2—C1—H1A	108.9	N1—C5—H5A	108.9
N1—C1—H1B	108.9	C4—C5—H5A	108.9
C2—C1—H1B	108.9	N1—C5—H5B	108.9
H1A—C1—H1B	107.7	C4—C5—H5B	108.9
C1—C2—N2	115.93 (19)	H5A—C5—H5B	107.7
C1—C2—H2C	108.3	C3—N2—C2	118.85 (17)
N2—C2—H2C	108.3	C3—N2—H2A	107.6
C1—C2—H2D	108.3	C2—N2—H2A	107.6
N2—C2—H2D	108.3	C3—N2—H2B	107.6
H2C—C2—H2D	107.4	C2—N2—H2B	107.6
C5—N1—C1	114.97 (16)	H2A—N2—H2B	107.0
N1—C1—C2—N2	−77.8 (2)	C3—C4—C5—N1	65.9 (3)
C1—C2—N2—C3	15.0 (3)	C4—C5—N1—C1	−59.7 (2)
C2—N2—C3—C4	55.6 (3)	C5—N1—C1—C2	83.3 (2)
N2—C3—C4—C5	−85.6 (2)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H1⋯O5[i]	0.90	1.65	2.555 (2)	178
O4—H2⋯O6[ii]	0.86	1.73	2.579 (2)	165
O7—H3⋯O1[iii]	0.89	1.76	2.600 (2)	156
O8—H4⋯O2	0.88	1.70	2.567 (2)	169
N1—H5⋯O2	0.90	1.82	2.716 (2)	174
N1—H6⋯O1[i]	0.90	1.91	2.802 (2)	171
N2—H2*A*⋯O6[iv]	0.90	1.80	2.698 (2)	174
N2—H2*B*⋯O5[v]	0.90	1.83	2.721 (2)	173

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