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Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
R factor = 0.029
wR factor = 0.059
Data-to-parameter ratio = 17.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

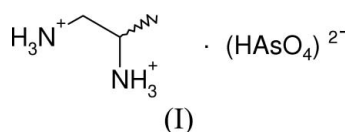
Propane-1,2-diaminium hydrogenarsenate

The title compound, $(\text{C}_3\text{H}_{12}\text{N}_2)[\text{AsHO}_4]$, is a molecular salt containing a network of propane-1,2-diaminium cations and hydrogenarsenate anions [mean As—O 1.686 (2) Å]. The crystal packing involves cation-to-anion N—H...O and anion-to-anion O—H...O hydrogen bonds, the latter resulting in dimeric associations of two adjacent hydrogenarsenate anions.

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Comment

The title compound, (I) (Fig. 1), was prepared as part of our ongoing structural studies of hydrogen-bonding interactions in protonated-amine (di)hydrogenarsenates (Todd & Harrison, 2005).



The $[\text{HAsO}_4]^{2-}$ hydrogenarsenate group in (I) shows its normal tetrahedral geometry [mean As—O 1.686 (2) Å], with the protonated As1—O4 vertex showing its usual lengthening relative to the unprotonated As—O bonds (Table 1). The propane-1,2-diaminium cation is disordered over two overlapped positions (Fig. 1). This positional disorder manifests itself as a terminal methyl group (atoms C3 or C4) being attached to either C1 or C2, with 50% occupancy in each case. The N atoms and atoms C1 and C2 of the two orientations of the cation are not resolved. Allowing for the disorder, this ion is chiral, but crystal symmetry generates a 50:50 mix of enantiomers, which is consistent with the racemic starting material. Atoms N1 and N2 are close to being *trans* with respect to the C1—C2 backbone of the molecule (Table 1).

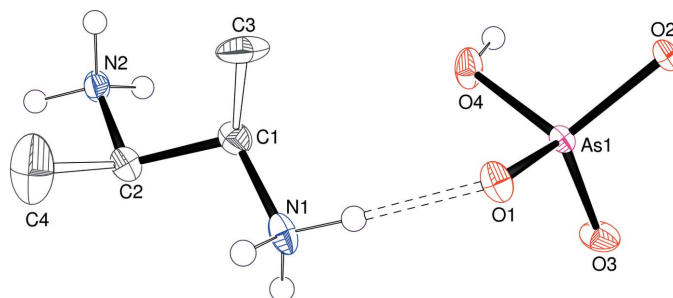


Figure 1
A view of (I), showing 50% probability displacement ellipsoids, with H atoms drawn as spheres of arbitrary radius. C-bound H atoms have been omitted for clarity and the hydrogen bond is indicated by a dashed line. Bonds to the disordered atoms C3 and C4 (see text) are shown as open lines.

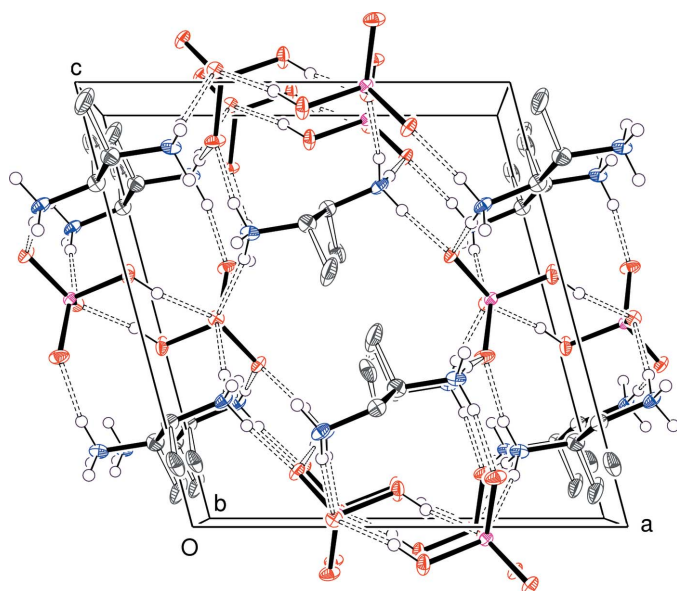


Figure 2
The packing for (I), with all C-bound H atoms omitted for clarity. Hydrogen bonds are indicated by dashed lines.

As well as electrostatic attractions, the component species in (I) interact by means of a network of O—H···O and N—H···O hydrogen bonds (Table 2). The (HAsO₄)²⁻ units are linked into inversion-generated dimeric pairs by way of the O4—H1···O2ⁱⁱ bond (see Table 2 for symmetry code), with a resulting As1···As1ⁱ separation of 4.3963 (4) Å. This situation is distinct from that observed in related materials, where chains (Lee & Harrison, 2003) and sheets (Wilkinson & Harrison, 2005) of (di)hydrogenarsenate ions linked by O—H···O bonds are seen.

In (I), the organic species interacts with the hydrogenarsenate dimers by way of six N—H···O hydrogen bonds [mean H···O 1.85 Å, mean N—H···O 170° and mean N···O 2.744 (3) Å]. Atoms O1, O2 and O3 accept two N—H···O bonds each. This hydrogen-bonding scheme results in a three-dimensional network (Fig. 2).

Experimental

Aqueous propane-1,2-diamine solution (0.5 M, 10 ml) was added to aqueous H₃AsO₄ solution (0.5 M, 10 ml) to result in a clear mixture. Aqueous ammonia was added to this solution to raise the pH to about 12, which is beyond the second end-point for H₃AsO₄ (*i.e.* the predominant solution species is HAsO₄²⁻). Crystals of (I) grew as the water evaporated over the course of a few days.

Crystal data

(C₃H₁₂N₂)[AsHO₄]
M_r = 216.07
Monoclinic, P2₁/n
a = 10.9568 (4) Å
b = 6.4297 (3) Å
c = 11.5999 (5) Å
β = 104.816 (2)°
V = 790.03 (6) Å³
Z = 4
D_x = 1.817 Mg m⁻³

Mo Kα radiation
Cell parameters from 1952 reflections
θ = 2.9–27.5°
μ = 4.27 mm⁻¹
T = 120 (2) K
Shard (broken from plate), colourless
0.08 × 0.06 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 1999)
T_{min} = 0.726, T_{max} = 0.883
10517 measured reflections

1816 independent reflections
1533 reflections with I > 2σ(I)
R_{int} = 0.051
θ_{max} = 27.5°
h = -14 → 14
k = -8 → 8
l = -15 → 15

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.029
wR(F²) = 0.059
S = 1.11
1816 reflections
103 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0164P)² + 0.583P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.51 e Å⁻³
Δρ_{min} = -0.41 e Å⁻³
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.0047 (7)

Table 1

Selected geometric parameters (Å, °).

As1—O1	1.6642 (17)	As1—O2	1.6817 (18)
As1—O3	1.6659 (18)	As1—O4	1.7336 (18)
N1—C1—C2—N2			
		-164.9 (2)	

Table 2

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H1···O2 ⁱ	0.93	1.76	2.679 (2)	170
N1—H2···O2 ⁱⁱ	0.91	1.87	2.765 (3)	168
N1—H3···O1 ⁱⁱⁱ	0.91	1.83	2.738 (3)	175
N1—H4···O1	0.91	1.81	2.716 (3)	177
N2—H5···O3 ^{iv}	0.91	1.82	2.713 (3)	168
N2—H6···O2 ^v	0.91	1.95	2.829 (3)	162
N2—H7···O3 ^{vi}	0.91	1.80	2.702 (3)	169

Symmetry codes: (i) -x + 1, -y, -z; (ii) x, y + 1, z; (iii) -x + ½, y + ½, -z + ½; (iv) -x + 1, -y + 1, -z; (v) x + ½, -y + ½, z + ½; (vi) x + ½, -y + ½, z + ½.

The organic cation is orientationally disordered, such that the two positions of atoms N1, N2, C1, and C2 overlap and cannot be resolved. The site-occupation factors of atoms C3 and C4 refined to 50% within experimental error and were both fixed at 0.50 for the final cycles of refinement. The O-bound H atom was found in a difference map and refined as riding in its as-found relative position. The H atoms bonded to C and N were located in idealized positions, with N—H = 0.91 Å and C—H = 0.98–0.99 Å, and refined as riding, allowing for free rotation of the -NH₃ groups. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) or U_{iso}(H) = 1.5U_{eq}(methyl carrier) was applied.

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor 1997), SCALEPACK and SORTAV (Blessing 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

We thank the EPSRC National Crystallography Service (University of Southampton) for the data collection.

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supporting information

Acta Cryst. (2005). E61, m2026–m2028 [doi:10.1107/S1600536805028722]

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S1. Comment

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The (HAsO₄)²⁻ hydrogenarsenate group in (I) shows its normal tetrahedral geometry [mean As—O 1.686 (2) Å], with the protonated As1—O4 vertex showing its usual lengthening relative to the unprotonated As—O bonds (Table 1). The propane 1,2-diaminium cation is disordered over two overlapped positions (Fig. 1). This positional disorder manifests itself as a terminal methyl group (atoms C3 or C4) being attached to either C1 or C2, with 50% occupancy in each case. The N atoms and atoms C1 and C2 of the two orientations of the molecule are not resolved. Allowing for the disorder, this molecular ion is chiral, but crystal symmetry generates a 50:50 mix of enantiomers, which is consistent with the racemic starting material. Atoms N1 and N2 are close to being *trans* with respect to the C1—C2 backbone of the molecule (Table 1).

As well as electrostatic attractions, the component species in (I) interact by means of a network of O—H···O and N—H···O hydrogen bonds (Table 2). The (HAsO₄)²⁻ units are linked into inversion-symmetry generated dimeric pairs by way of the O4—H1···O2ⁱ bond (see Table 2 for symmetry code), with a resulting As1···As1ⁱ separation of 4.3963 (4) Å. This situation is distinct from that observed in related materials, where chains (Lee & Harrison, 2003) and sheets (Wilkinson & Harrison, 2005) of (di)hydrogenarsenate moieties linked by O—H···O bonds are seen.

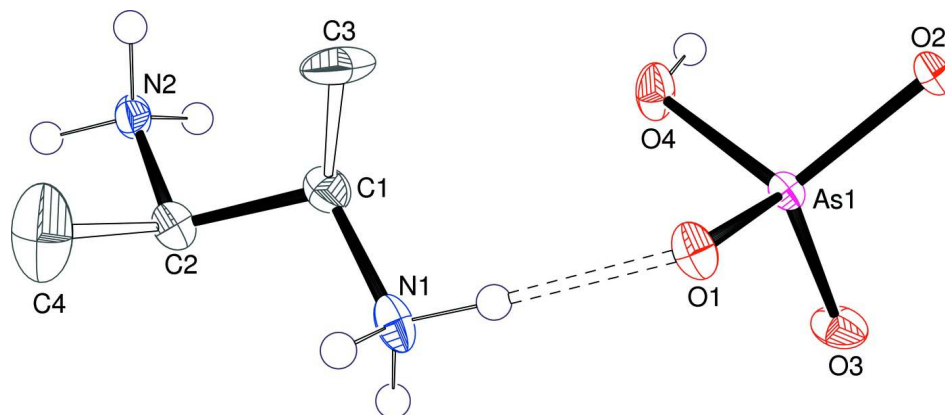
In (I), the organic species interacts with the hydrogenarsenate dimers by way of six N—H···O hydrogen bonds [mean H···O 1.85 Å, mean N—H···O 170° and mean N···O 2.744 (3) Å]. Atoms O1, O2 and O3 accept two N—H···O bonds each. This hydrogen-bonding scheme results in a three-dimensional network (Fig. 2).

S2. Experimental

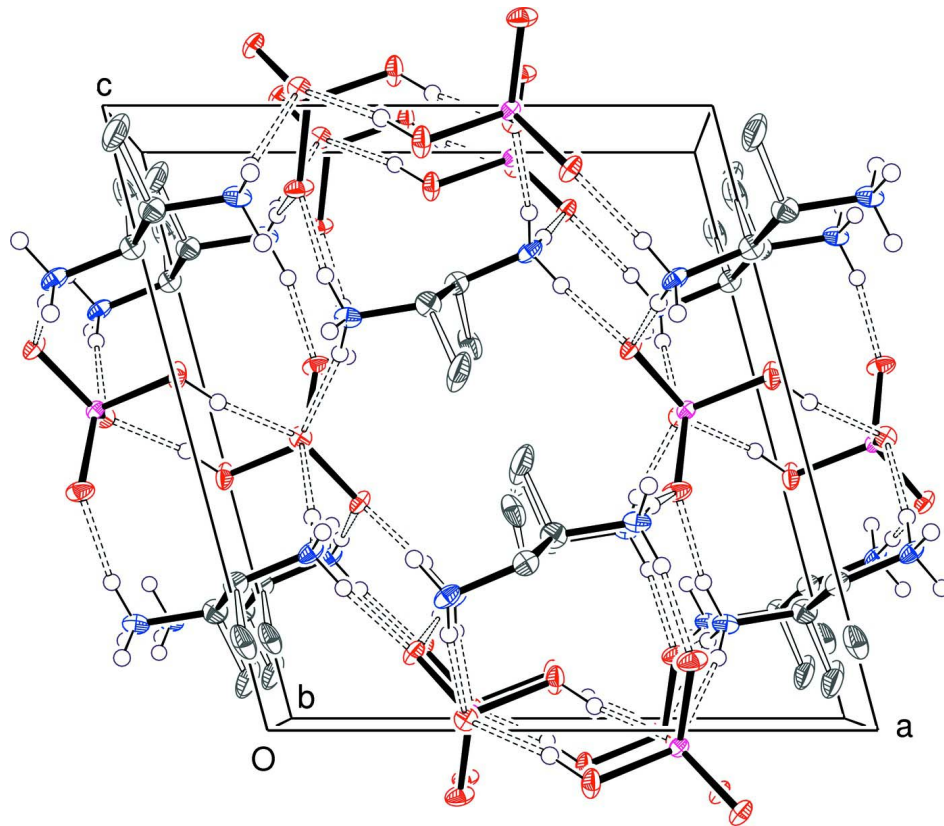
Aqueous propane 1,2-diamine solution (0.5 M, 10 ml) was added to aqueous H₃AsO₄ solution (0.5 M, 10 ml) to result in a clear mixture. Aqueous ammonia was added to this solution to raise the pH to about 12, which is beyond the second end-point for H₃AsO₄ (*i.e.* the predominant solution species is HAsO₄²⁻). Plate-like [Shard below?] crystals of (I) grew as the water evaporated over the course of a few days.

S3. Refinement

The organic cation is orientationally disordered, such that the two positions of atoms N1, N2, C1, and C2 overlap and cannot be resolved. The site-occupation factors of atoms C3 and C4 refined to 50% within experimental error and were both fixed at 0.50 for the final cycles of refinement. The O-bound H atom was found in a difference map and refined as riding in its as-found relative position. The H atoms bonded to C and N were located in idealized positions, with N—H = 0.91 Å and C—H = 0.98–0.99 Å, and refined as riding, allowing for free rotation of the —NH₃ groups. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl carrier})$ was applied.

**Figure 1**

A view of (I), showing 50% probability displacement ellipsoids, with H atoms drawn as spheres of arbitrary radius. C-bound H atoms have been omitted for clarity and the hydrogen bond is indicated by a dashed line. Bonds to the disordered atoms C3 and C4 (see text) are shown as open lines.

**Figure 2**

The unit-cell packing for (I), with all C-bound H atoms omitted for clarity. Hydrogen bonds are indicated by dashed lines.

Propane 1,2-diaminium hydrogenarsenate

Crystal data

 $C_3H_{12}N_2^{2+} \cdot AsHO_4^{2-}$ $M_r = 216.07$ Monoclinic, $P2_1/n$ Hall symbol: $-P\ 2_1n$ $a = 10.9568\ (4)\ \text{\AA}$ $b = 6.4297\ (3)\ \text{\AA}$ $c = 11.5999\ (5)\ \text{\AA}$ $\beta = 104.816\ (2)^\circ$ $V = 790.03\ (6)\ \text{\AA}^3$ $Z = 4$ $F(000) = 440$ $D_x = 1.817\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1952 reflections

 $\theta = 2.9\text{--}27.5^\circ$ $\mu = 4.27\ \text{mm}^{-1}$ $T = 120\ \text{K}$

Shard, colourless

 $0.08 \times 0.06 \times 0.03\ \text{mm}$

Data collection

Nonius KappaCCD area-detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω and φ scans

Absorption correction: multi-scan

(SADABS; Bruker, 1999)

 $T_{\min} = 0.726$, $T_{\max} = 0.883$

10517 measured reflections

1816 independent reflections

1533 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.051$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.6^\circ$ $h = -14 \rightarrow 14$ $k = -8 \rightarrow 8$ $l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.029$ $wR(F^2) = 0.059$ $S = 1.11$

1816 reflections

103 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: difmap (O-H) and geom (others)

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0164P)^2 + 0.583P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.51\ \text{e \AA}^{-3}$ $\Delta\rho_{\min} = -0.41\ \text{e \AA}^{-3}$ Extinction correction: *SHELXL97* (Sheldrick, 1997), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0047 (7)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
As1	0.33664 (2)	0.17853 (4)	0.02271 (2)	0.01169 (11)	
O1	0.26787 (18)	0.2809 (3)	0.12195 (16)	0.0177 (4)	
O2	0.33133 (16)	-0.0828 (3)	0.01944 (15)	0.0151 (4)	

O3	0.28115 (19)	0.2764 (3)	-0.11362 (16)	0.0219 (5)	
O4	0.49363 (17)	0.2485 (3)	0.07736 (17)	0.0216 (5)	
H1	0.5479	0.1924	0.0355	0.026*	
N1	0.3572 (2)	0.6561 (3)	0.2137 (2)	0.0177 (5)	
H2	0.3424	0.7540	0.1551	0.021*	
H3	0.3197	0.6952	0.2718	0.021*	
H4	0.3248	0.5319	0.1825	0.021*	
N2	0.6919 (2)	0.8345 (3)	0.3314 (2)	0.0175 (5)	
H5	0.7120	0.8045	0.2618	0.021*	
H6	0.7234	0.7338	0.3861	0.021*	
H7	0.7258	0.9596	0.3593	0.021*	
C1	0.4949 (3)	0.6349 (4)	0.2652 (3)	0.0188 (6)	
H8	0.5349	0.5819	0.2035	0.023*	
H9	0.5110	0.5335	0.3315	0.023*	0.50
C2	0.5524 (3)	0.8435 (4)	0.3103 (3)	0.0211 (6)	
H10	0.5176	0.9533	0.2512	0.025*	
H11	0.5308	0.8785	0.3858	0.025*	0.50
C3	0.4994 (6)	0.4684 (10)	0.3584 (6)	0.0290 (15)	0.50
H12	0.4607	0.3406	0.3195	0.043*	0.50
H13	0.4530	0.5159	0.4153	0.043*	0.50
H14	0.5875	0.4408	0.4007	0.043*	0.50
C4	0.5312 (6)	0.9222 (13)	0.4236 (6)	0.046 (2)	0.50
H15	0.5721	1.0580	0.4422	0.069*	0.50
H16	0.5672	0.8242	0.4880	0.069*	0.50
H17	0.4404	0.9363	0.4156	0.069*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.01350 (16)	0.00989 (16)	0.01258 (16)	0.00009 (11)	0.00497 (11)	-0.00047 (11)
O1	0.0206 (10)	0.0162 (10)	0.0206 (10)	-0.0026 (8)	0.0131 (9)	-0.0039 (8)
O2	0.0184 (10)	0.0087 (10)	0.0181 (10)	-0.0007 (8)	0.0044 (8)	-0.0016 (8)
O3	0.0314 (12)	0.0209 (11)	0.0141 (10)	0.0082 (9)	0.0072 (9)	0.0053 (8)
O4	0.0130 (10)	0.0235 (11)	0.0298 (11)	-0.0049 (9)	0.0084 (9)	-0.0116 (9)
N1	0.0263 (14)	0.0128 (12)	0.0179 (12)	-0.0042 (10)	0.0127 (11)	-0.0034 (10)
N2	0.0247 (13)	0.0122 (12)	0.0141 (12)	-0.0017 (10)	0.0021 (10)	-0.0009 (9)
C1	0.0220 (15)	0.0154 (15)	0.0197 (15)	0.0007 (12)	0.0065 (13)	0.0010 (12)
C2	0.0236 (16)	0.0177 (15)	0.0218 (15)	0.0019 (13)	0.0052 (13)	-0.0035 (12)
C3	0.017 (3)	0.025 (3)	0.040 (4)	0.001 (3)	-0.002 (3)	0.019 (3)
C4	0.029 (4)	0.067 (6)	0.051 (5)	-0.016 (4)	0.027 (4)	-0.030 (4)

Geometric parameters (Å, °)

As1—O1	1.6642 (17)	C1—C3	1.514 (6)
As1—O3	1.6659 (18)	C1—C2	1.517 (4)
As1—O2	1.6817 (18)	C1—H8	0.9900
As1—O4	1.7336 (18)	C1—H9	0.9900
O4—H1	0.9304	C2—C4	1.481 (7)

N1—C1	1.480 (4)	C2—H10	0.9900
N1—H2	0.9100	C2—H11	0.9900
N1—H3	0.9100	C3—H12	0.9800
N1—H4	0.9100	C3—H13	0.9800
N2—C2	1.486 (4)	C3—H14	0.9800
N2—H5	0.9100	C4—H15	0.9800
N2—H6	0.9100	C4—H16	0.9800
N2—H7	0.9100	C4—H17	0.9800
O1—As1—O3	112.79 (9)	C4—C2—N2	104.8 (3)
O1—As1—O2	113.06 (8)	C4—C2—C1	117.5 (4)
O3—As1—O2	110.74 (9)	N2—C2—C1	110.0 (2)
O1—As1—O4	103.11 (9)	C4—C2—H10	104.5
O3—As1—O4	109.65 (10)	N2—C2—H10	109.9
O2—As1—O4	107.04 (9)	C1—C2—H10	109.9
As1—O4—H1	114.5	N2—C2—H11	109.3
C1—N1—H2	109.5	C1—C2—H11	109.5
C1—N1—H3	109.5	H10—C2—H11	108.2
H2—N1—H3	109.5	C1—C3—H12	109.5
C1—N1—H4	109.5	H9—C3—H12	120.5
H2—N1—H4	109.5	C1—C3—H13	109.5
H3—N1—H4	109.5	H9—C3—H13	112.0
C2—N2—H5	109.5	H12—C3—H13	109.5
C2—N2—H6	109.5	C1—C3—H14	109.5
H5—N2—H6	109.5	H9—C3—H14	94.6
C2—N2—H7	109.5	H12—C3—H14	109.5
H5—N2—H7	109.5	H13—C3—H14	109.5
H6—N2—H7	109.5	C2—C4—H15	109.5
N1—C1—C3	101.4 (3)	H11—C4—H15	124.9
N1—C1—C2	110.4 (2)	C2—C4—H16	109.5
C3—C1—C2	116.4 (3)	H11—C4—H16	102.2
N1—C1—H8	109.5	H15—C4—H16	109.5
C3—C1—H8	109.5	C2—C4—H17	109.5
C2—C1—H8	109.4	H11—C4—H17	100.4
N1—C1—H9	109.5	H15—C4—H17	109.5
C2—C1—H9	109.8	H16—C4—H17	109.5
H8—C1—H9	108.2		
N1—C1—C2—C4	75.4 (5)	N1—C1—C2—N2	-164.9 (2)
C3—C1—C2—C4	-39.4 (5)	C3—C1—C2—N2	80.3 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H1 \cdots O2 ⁱ	0.93	1.76	2.679 (2)	170
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N1—H3 \cdots O1 ⁱⁱⁱ	0.91	1.83	2.738 (3)	175
N1—H4 \cdots O1	0.91	1.81	2.716 (3)	177

N2—H5···O3 ^{iv}	0.91	1.82	2.713 (3)	168
N2—H6···O2 ^v	0.91	1.95	2.829 (3)	162
N2—H7···O3 ^{vi}	0.91	1.80	2.702 (3)	169

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