Guanidinium 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

Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(s–O) = 0.001 Å
R factor = 0.021
wR factor = 0.058
Data-to-parameter ratio = 28.3

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

The title compound, $(CH_6N_3)[H_2AsO_4]$, contains a network of guanidinium cations and dihydrogenarsenate anions. The component species interact by way of cation-to-anion N—H···O and anion-to-anion O—H···O hydrogen bonds, the latter leading to infinite sheets of $[H_2AsO_4]^-$ anions.

Comment

The title compound, (I), was prepared as part of ongoing studies of hydrogen-bonding interactions in molecular salts (Wilkinson & Harrison, 2004).
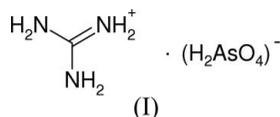
The $[H_2AsO_4]^-$ anion in (I) shows its normal tetrahedral geometry (Fig. 1) about As [mean As—O = 1.684 (2) Å], with the usual distinction between protonated and unprotonated As—O bond lengths (Wilkinson & Harrison, 2004); see Table 1. The three C—N bond lengths in the propeller-shaped $(CH_6N_3)^+$ cation are similar (Table 1), indicating that the usual model of electron delocalization in this species, leading to a C—N bond order of 1.33, is applicable here.

As well as Coulombic forces, 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, as detailed in Table 2. All the guanidinium atoms participate in hydrogen bonds (one of which, via H8, is bifurcated with notably longer H···O separations than the others), such that the $(CH_6N_3)^+$ cation makes N—H···O links to five adjacent $[H_2AsO_4]^-$ tetrahedra as shown in Fig. 2. For the simple N—H···O bonds, the mean H···O distance = 2.18 Å, mean N···O = 2.951 (3) Å, and the mean N—H···O angle is 150°.
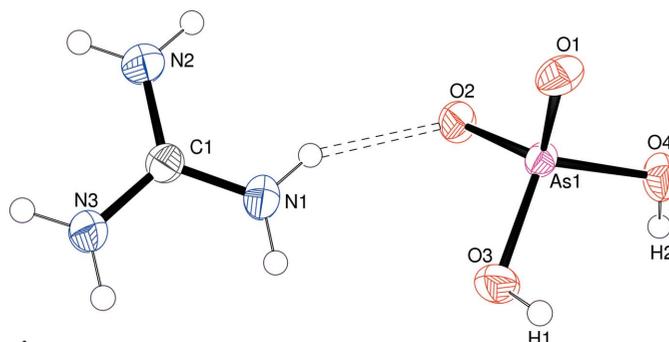
Figure 1
Asymmetric unit of (I) (50% displacement ellipsoids). The hydrogen bond is indicated by a dashed line.
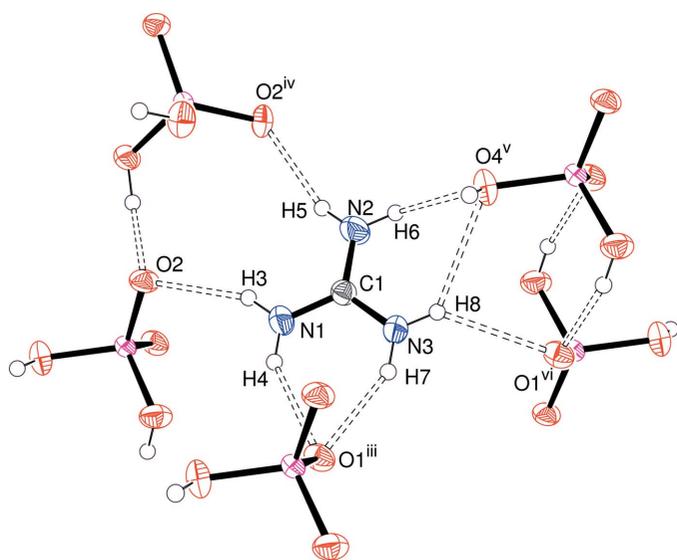
Figure 2
Detail of the cation-to-anion N—H···O links (dashed lines) in (I). Symmetry codes are as in Table 2.
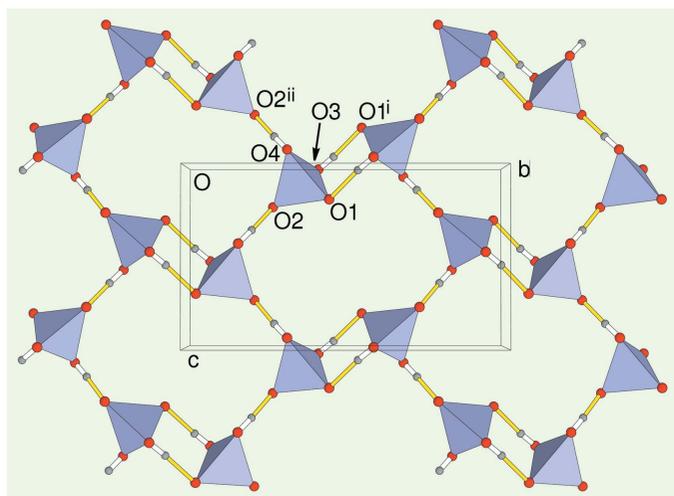
Figure 3
Detail of a part of a (100) hydrogen-bonded sheet of $[H_2AsO_4]^-$ groups in (I), in polyhedral representation. Symmetry codes are as in Table 2.

The $[H_2AsO_4]^-$ units are linked into infinite sheets (Fig. 3) by way of the O—H···O hydrogen bonds. The O3—H1···O1^i interaction (see Table 2 for symmetry codes) results in inversion-symmetry-generated dimeric pairs of $[H_2AsO_4]^-$ tetrahedra linked by a double (*i.e.* O—H···O + O···H—O) hydrogen bond. The O4—H2···O2^{ii} bond links the dimers into an infinite sheet (Fig. 3) propagating in (100). The As···As^i and As···As^{ii} separations are 4.0148 (3) and 5.0190 (3) Å, respectively. If the topological connectivity of the As atoms is considered, a 6^3 sheet (O'Keeffe & Hyde, 1996) arises, *i.e.* every As node participates in three polyhedral six-ring loops.

The packing for (I) (Fig. 4) results in alternating organic and inorganic layers with respect to the *a* axis direction. The structure of (I) is distinct from other ammonium hydrogenarsenate salts where isolated pairs of tetrahedra (Todd &
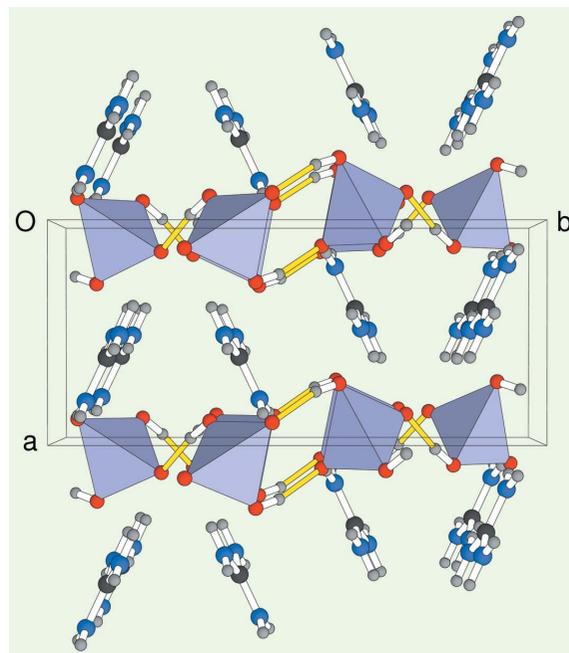
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The packing in (I), projected down [001], showing the (100) dihydrogenarsenate layers mediated by guanidinium cations. The N—H···O hydrogen bonds are not shown.

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Experimental

An aqueous guanidine solution (0.5 *M*, 10 ml) was added to an H_3AsO_4 solution (0.5 *M*, 10 ml) to give a clear solution. A mass of chunks and blocks of (I) grew as the water evaporated over the course of a few days.

Crystal data

$(CH_6N_3)[H_2AsO_4]$	$D_x = 2.050$ Mg m^{-3}
$M_r = 201.02$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4819
$a = 6.1571$ (3) Å	reflections
$b = 13.7052$ (6) Å	$\theta = 3.0$–$32.5°$
$c = 7.7208$ (3) Å	$\mu = 5.18$ mm^{-1}
$\beta = 91.715$ (1)°	$T = 295$ (2) K
$V = 651.22$ (5) Å^3	Block, colourless
$Z = 4$	$0.49 \times 0.29 \times 0.13$ mm

Data collection

Bruker SMART1000 CCD	2353 independent reflections
diffractometer	2068 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan	$\theta_{max} = 32.5°$
($SADABS$; Bruker, 1999)	$h = -9 \rightarrow 9$
$T_{min} = 0.172$, $T_{max} = 0.510$	$k = -18 \rightarrow 20$
7302 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.021$	$+ 0.0391P]$
$wR(F^2) = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2353 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
83 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
H-atom parameters constrained	Extinction correction: $SHELXL$
	Extinction coefficient: 0.0145 (12)

Table 1
Selected bond lengths (Å).

As1—O1	1.6532 (11)	C1—N1	1.314 (2)
As1—O2	1.6538 (10)	C1—N2	1.323 (2)
As1—O4	1.7135 (10)	C1—N3	1.324 (2)
As1—O3	1.7144 (11)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H1$\cdots$O1^{i}	0.85	1.83	2.6684 (16)	167
O4—H2$\cdots$O2^{ii}	0.92	1.65	2.5648 (16)	174
N1—H3$\cdots$O2	0.86	2.13	2.9185 (18)	153
N1—H4$\cdots$O1^{iii}	0.86	2.24	2.993 (2)	147
N2—H5$\cdots$O2^{iv}	0.86	2.15	2.955 (2)	157
N2—H6$\cdots$O4^{v}	0.86	2.28	2.994 (2)	140
N3—H7$\cdots$O1^{iii}	0.86	2.11	2.8962 (17)	152
N3—H8$\cdots$O1^{vi}	0.86	2.47	3.1582 (18)	138
N3—H8$\cdots$O4^{v}	0.86	2.55	3.1965 (18)	133

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

The O-bound H atoms were found in difference maps and allowed for as riding in their as-found relative positions with $U_{iso}(H) = 1.2U_{eq}(O)$. The N-bound H atoms were included in the riding model approximation, with N—H = 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) & *ATOMS* (Shape Software, 2004); software used to prepare material for publication: *SHELXL97*.

References

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supporting information

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S1. Comment

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S2. Experimental

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S3. Refinement

The O-bound H atoms were found in difference maps and fixed in these positions with $U_{iso}(H) = 1.2U_{eq}(O)$. The N-bound H atoms were included in the riding model approximation, with N—H = 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$.
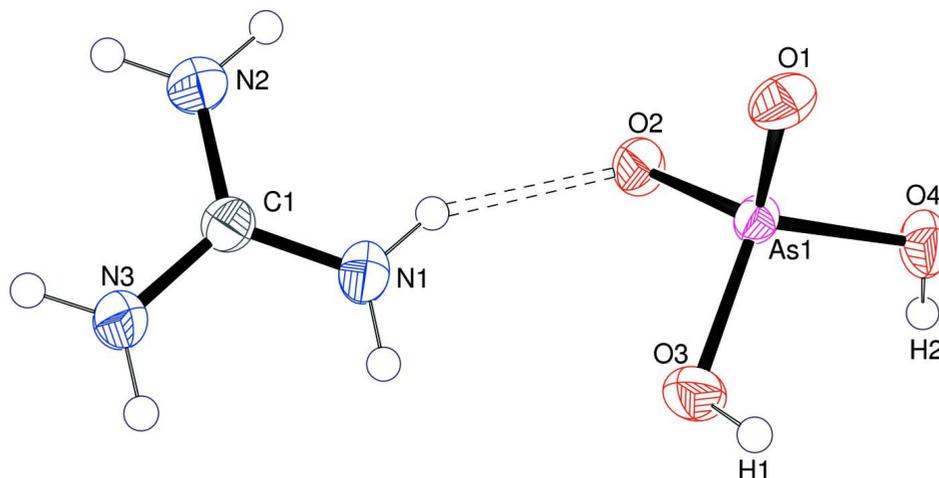
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Asymmetric unit of (I) (50% displacement ellipsoids). The hydrogen bond is indicated by a dashed line.
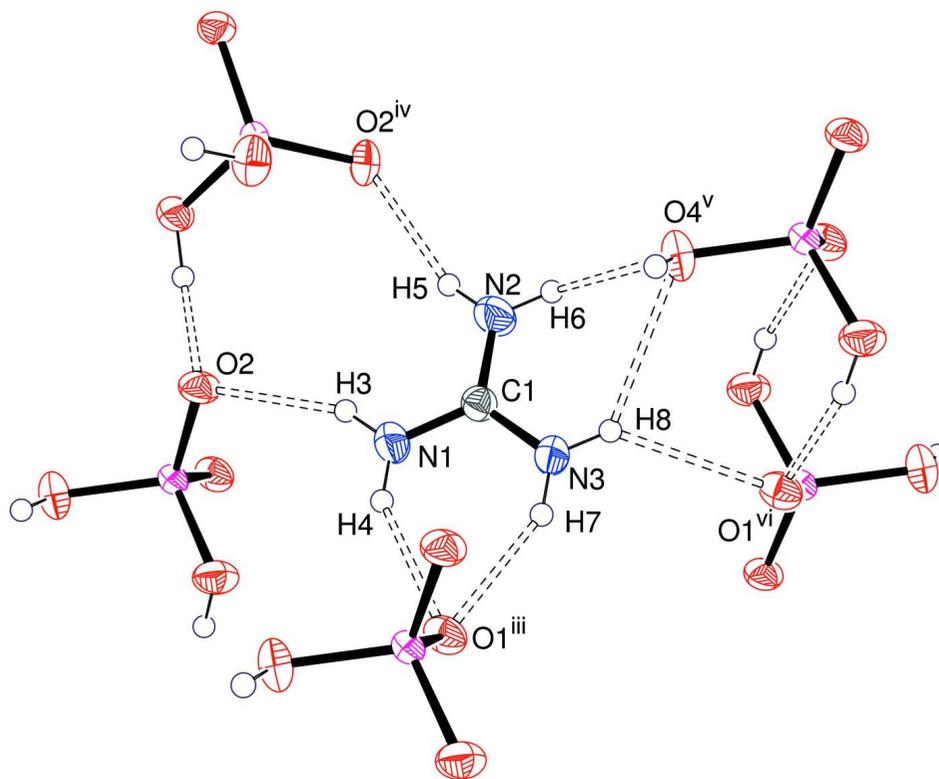
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Detail of the cation-to-anion N—H···O links (dashed lines) in (I). Symmetry codes are as in Table 2.
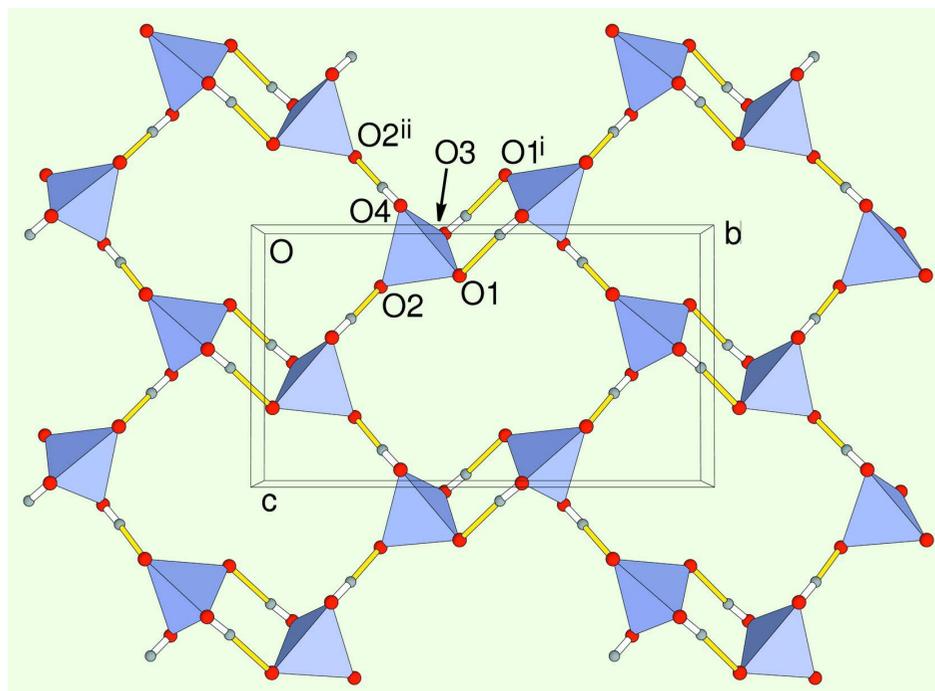
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Detail of a part of a (100) hydrogen-bonded sheet of $[H_2AsO_4]^-$ groups in (I), in polyhedral representation. Symmetry codes are as in Table 2.
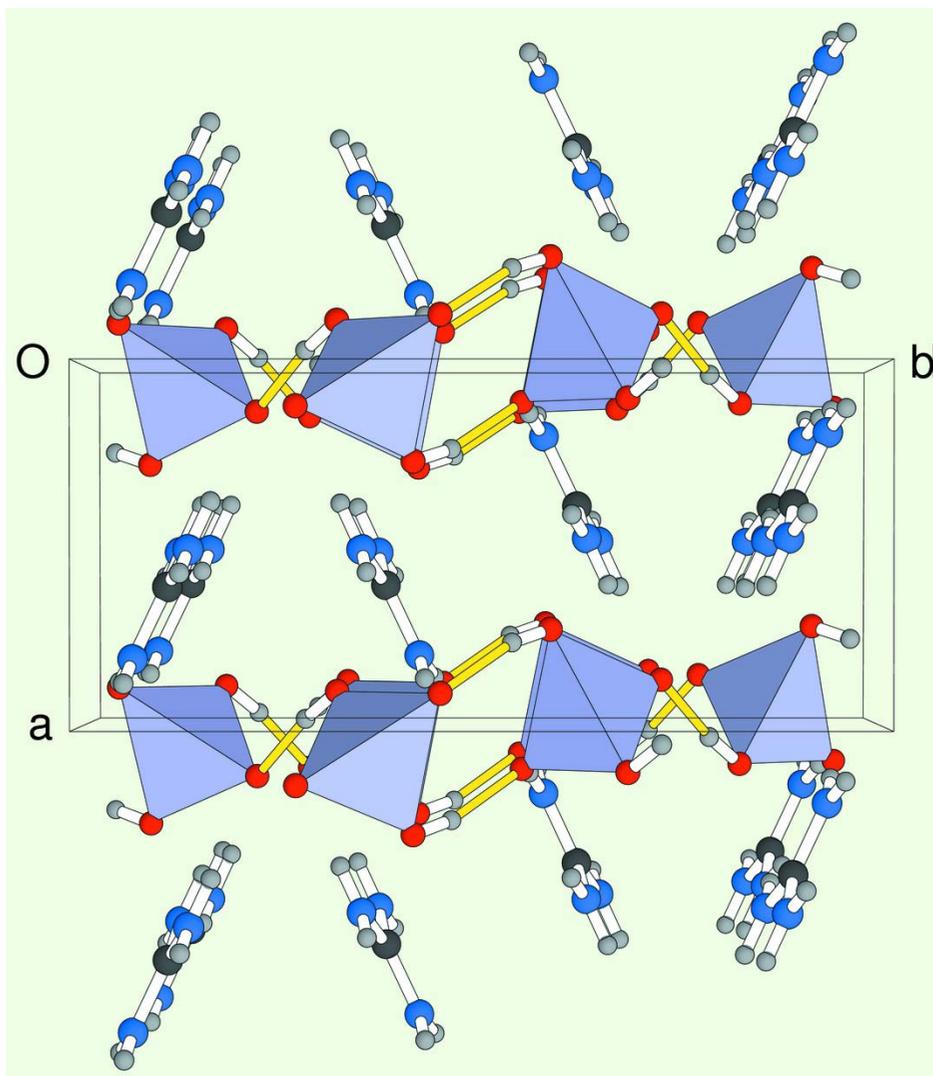
Figure 4
Unit-cell packing in (I), projected down [001], showing the (100) dihydrogenarsenate layers mediated by guanidinium cations. The N—H···O hydrogen bonds are not shown.

(I)

Crystal data

$(CH_6N_3)[H_2AsO_4]$	$F(000) = 400$
$M_r = 201.02$	$D_x = 2.050$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 4819 reflections
$a = 6.1571$ (3) Å	$\theta = 3.0–32.5°$
$b = 13.7052$ (6) Å	$\mu = 5.18$ mm^{-1}
$c = 7.7208$ (3) Å	$T = 295$ K
$\beta = 91.715$ (1)°	Block, colourless
$V = 651.22$ (5) Å^3	$0.49 \times 0.29 \times 0.13$ mm
$Z = 4$	

Data collection

Bruker SMART1000 CCD diffractometer	7302 measured reflections
Radiation source: fine-focus sealed tube	2353 independent reflections
Graphite monochromator	2068 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$\theta_{max} = 32.5°$, $\theta_{min} = 3.0°$
	$h = -9 \rightarrow 9$
	$k = -18 \rightarrow 20$
$T_{min} = 0.172$, $T_{max} = 0.510$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.021$	H-atom parameters constrained
$wR(F^2) = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.0391P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
2353 reflections	$(\Delta/\sigma)_{max} < 0.001$
83 parameters	$\Delta\rho_{max} = 0.48$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.62$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: *SHELXL*, Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0145 (12)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
As1	0.04340 (2)	0.367017 (10)	0.104376 (16)	0.02035 (6)
O1	−0.10944 (19)	0.45045 (8)	0.19597 (13)	0.0295 (2)
O2	0.13284 (18)	0.27840 (8)	0.23321 (14)	0.0304 (2)
O3	0.27494 (18)	0.41686 (9)	0.02378 (15)	0.0343 (3)
H1	0.2406	0.4633	−0.0444	0.041*
O4	−0.10648 (19)	0.32367 (9)	−0.06967 (14)	0.0324 (2)
H2	−0.0288	0.2840	−0.1419	0.039*
C1	0.6107 (3)	0.37973 (10)	0.5461 (2)	0.0256 (3)
N1	0.5194 (3)	0.36882 (10)	0.39137 (19)	0.0347 (3)
H3	0.3930	0.3424	0.3803	0.042*
H4	0.5860	0.3881	0.3012	0.042*
N2	0.5110 (3)	0.35063 (13)	0.6865 (2)	0.0418 (4)
H5	0.3846	0.3241	0.6772	0.050*
H6	0.5727	0.3582	0.7870	0.050*
N3	0.8045 (2)	0.42143 (11)	0.55908 (18)	0.0337 (3)

H7	0.8678	0.4407	0.4674	0.040*
H8	0.8670	0.4292	0.6592	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.02193 (8)	0.02172 (9)	0.01733 (8)	0.00041 (5)	−0.00081 (5)	0.00190 (4)
O1	0.0377 (6)	0.0279 (5)	0.0232 (5)	0.0053 (5)	0.0067 (4)	−0.0013 (4)
O2	0.0293 (5)	0.0311 (6)	0.0305 (5)	0.0011 (4)	−0.0031 (4)	0.0125 (4)
O3	0.0268 (5)	0.0405 (7)	0.0358 (6)	−0.0019 (5)	0.0041 (4)	0.0125 (5)
O4	0.0304 (5)	0.0377 (7)	0.0287 (5)	0.0057 (5)	−0.0080 (4)	−0.0100 (5)
C1	0.0269 (7)	0.0251 (7)	0.0247 (6)	0.0004 (5)	0.0002 (5)	0.0008 (5)
N1	0.0322 (7)	0.0448 (9)	0.0269 (7)	−0.0067 (6)	−0.0055 (5)	0.0017 (5)
N2	0.0361 (8)	0.0623 (10)	0.0272 (7)	−0.0125 (7)	0.0018 (6)	0.0078 (7)
N3	0.0327 (7)	0.0415 (8)	0.0266 (6)	−0.0126 (6)	−0.0011 (5)	−0.0010 (5)

Geometric parameters (Å, º)

As1—O1	1.6532 (11)	C1—N3	1.324 (2)
As1—O2	1.6538 (10)	N1—H3	0.8600
As1—O4	1.7135 (10)	N1—H4	0.8600
As1—O3	1.7144 (11)	N2—H5	0.8600
O3—H1	0.8491	N2—H6	0.8600
O4—H2	0.9226	N3—H7	0.8600
C1—N1	1.314 (2)	N3—H8	0.8600
C1—N2	1.323 (2)		
O1—As1—O2	115.74 (6)	N2—C1—N3	120.48 (16)
O1—As1—O4	105.97 (6)	C1—N1—H3	120.0
O2—As1—O4	112.26 (6)	C1—N1—H4	120.0
O1—As1—O3	111.71 (6)	H3—N1—H4	120.0
O2—As1—O3	104.21 (6)	C1—N2—H5	120.0
O4—As1—O3	106.72 (6)	C1—N2—H6	120.0
As1—O3—H1	109.2	H5—N2—H6	120.0
As1—O4—H2	113.7	C1—N3—H7	120.0
N1—C1—N2	120.96 (16)	C1—N3—H8	120.0
N1—C1—N3	118.57 (15)	H7—N3—H8	120.0

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
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N3—H8···O4[v]	0.86	2.55	3.1965 (18)	133

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