Propane-1,3-diaminium bis(dihydrogenarsenate)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.094
Data-to-parameter ratio = 26.7

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

The title compound, $(C_3H_{12}N_2)[H_2AsO_4]_2$, contains a network of propane-1,3-diaminium cations and dihydrogenarsenate anions [mean As—O = 1.682 (2) Å]. The crystal packing involves anion-to-anion O—H$\cdots$O hydrogen bonds, resulting in double chains of dihydrogenarsenate tetrahedra. Cation-to-anion N—H$\cdots$O hydrogen bonds generate a three-dimensional overall structure. One C atom occupies a special position with twofold symmetry.
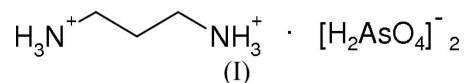
Comment

The title compound, $C_3H_{12}N_2{}^{2+}\cdot2[H_2AsO_4)]^-$, (I), (Fig. 1), was prepared as part of our ongoing structural studies of hydrogen-bonding interactions in protonated-amine (di)hydrogen arsenates (Lee & Harrison, 2003*a*,*b*,*c*; Wilkinson & Harrison, 2004; Todd & Harrison, 2005*a*).

$$H_3N^+ \diagdown\diagup\diagdown NH_3^+ \cdot [H_2AsO_4]^-{}_2$$

(I)

The $[H_2AsO_4]^-$ dihydrogenarsenate group in (I) has normal tetrahedral geometry [mean As—O = 1.682 (2) Å], with the protonated As1—O1 and As1—O2 vertices showing their expected lengthening relative to the unprotonated As1—O3 and As1—O4 bonds, which have formal partial double-bond character (Table 1). The propane-1,3-diaminium cation, which is generated by twofold symmetry from the atoms of the asymmetric unit (C2 occupies a special position with site symmetry 2), shows no unusual geometrical features.

As well as electrostatic attractions, the component species in (I) interact by means of a network of cation-to-anion N—H$\cdots$O and anion-to-anion O—H$\cdots$O hydrogen bonds (Table 2). The $[H_2AsO_4]^-$ units are linked into polymeric
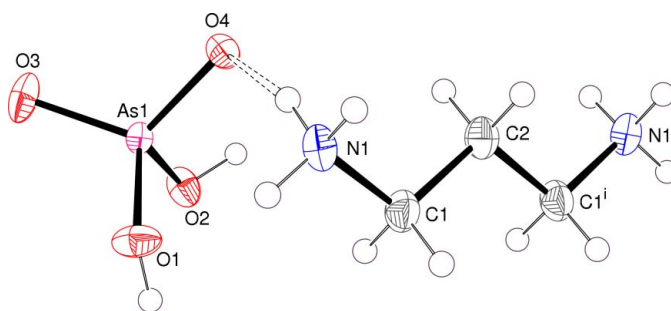

Figure 1
View of (I), showing 50% probability displacement ellipsoids (H atoms are drawn as spheres of arbitrary radii and the hydrogen bond is indicated by dashed lines). Symmetry code as in Table 1.
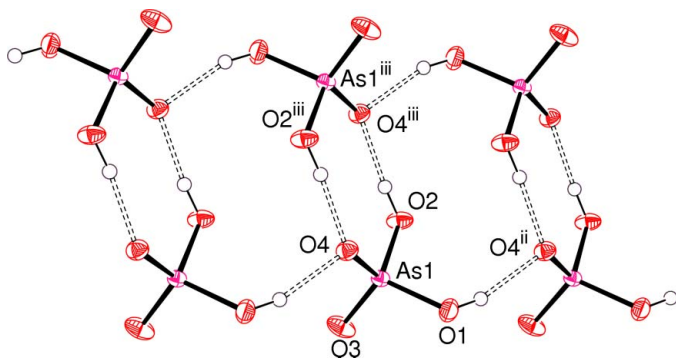
Figure 2
Detail of a hydrogen-bonded (dashed lines) dihydrogenarsenate double chain in (I). Symmetry codes as in Table 2.
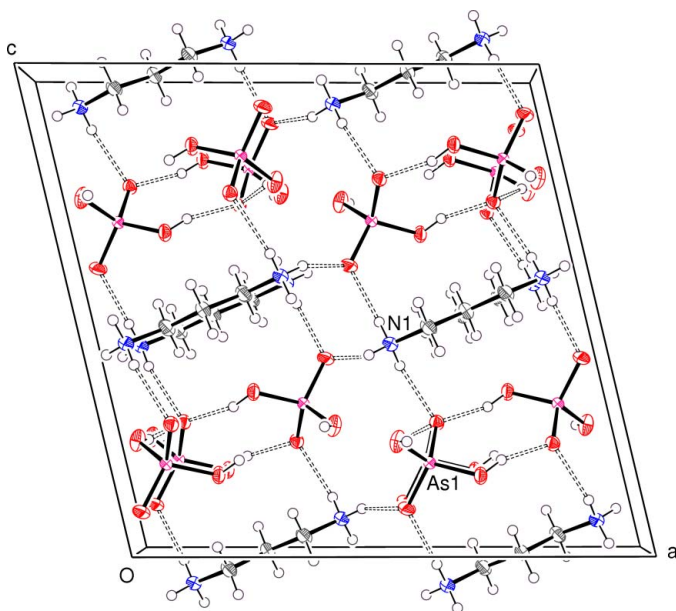

Figure 3
Projection of the unit cell contents of (I) on to (010). Dashed lines indicate hydrogen bonds.

double chains (Fig. 2) propagating along [010] by way of inversion-symmetry-generated pairs of O2—H2···O4^{iii} and O1—H1···O4^{ii} bonds (see Table 2 for symmetry codes). The first of these bonds results in 'dimers' of dihydrogenarsenate tetrahedra, which in turn are linked into double chains by the second hydrogen bond. In graph-set notation (Bernstein *et al.*, 1995), these bonding patterns correspond to $R_2^2(8)$ and $R_4^4(12)$ loops, respectively. This scheme results in every [H$_2$AsO$_4$]$^-$ group in the chain forming two hydrogen bonds to its neighbours and accepting two hydrogen bonds from its neighbours. The As···As^{iii} (*via* O2—H2···O4^{iii}) and As···As^{ii} (*via* O1—H1···O4^{ii}) separations are 4.5325 (4) and 4.6549 (4) Å, respectively (symmetry codes as in Table 2).

The organic species interacts with the dihydrogenarsenate anions by way of three N—H···O hydrogen bonds [mean H···O = 2.00 Å, mean N—H···O = 158° and mean N···O = 2.892 (3) Å], such that the [010] dihydrogenarsenate double chains are crosslinked in the *a* and *c* directions to result in a

three-dimensional network (Fig. 3). A *PLATON* (Spek, 2003) analysis of (I) indicated the presence of two short C—H···O contacts (Table 2) although their structural significance is not clear.

The hydrogen-bonded tetrahedral double chains in (I) are different from the motifs seen in related structures. In bis-(cycloheptylaminium) hydrogenarsenate monohydrate (Todd & Harrison, 2005a) and bis(benzylammonium) hydrogen-arsenate monohydrate (Lee & Harrison, 2003c), hydrogen-bonded dimers of [HAsO$_4$]$^{2-}$ units occur, with the dimers bridged into double chains by intervening water molecules. In piperidinum dihydrogenarsenate (Lee & Harrison, 2003b) and *t*-butylammonium dihydrogenarsenate (Wilkinson & Harrison, 2004), single chains of [H$_2$AsO$_4$]$^-$ anions occur with each adjacent dihydrogenarsenate pair linked by a pair of hydrogen bonds. In propane-1,3-diaminium hydrogenarsenate monohydate (Todd & Harrison, 2005b), containing the same cation as (I) but prepared at higher pH, yet another hydrogen-bonded chain motif occurs.

Experimental

0.5 *M* aqueous propane-1,3-diamine solution (10 ml) was added to 0.5 *M* aqueous H$_3$AsO$_4$ solution (10 ml) to result in 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$_3$H$_{12}$N$_2$)[AsH$_2$O$_4$]$_2$	D_x = 2.244 Mg m^{-3}
M_r = 358.02	Mo $K\alpha$ radiation
Monoclinic, $I2/a$	Cell parameters from 3458
a = 15.5563 (8) Å	reflections
b = 4.6549 (2) Å	θ = 2.7–32.5°
c = 15.0454 (7) Å	μ = 6.33 mm^{-1}
β = 103.399 (1)°	T = 293 (2) K
V = 1059.83 (9) Å^3	Plate, colourless
Z = 4	0.50 × 0.19 × 0.03 mm

Data collection

Bruker SMART 1000 CCD	1899 independent reflections
diffractometer	1667 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.044
Absorption correction: multi-scan	θ_{max} = 32.5°
(*SADABS*; Bruker, 1999)	h = −23 → 23
T_{min} = 0.144, T_{max} = 0.833	k = −7 → 5
5128 measured reflections	l = −22 → 17

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.037	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.094	$(\Delta/\sigma)_{max}$ = 0.002
S = 1.02	$\Delta\rho_{max}$ = 1.07 e Å^{-3}
1899 reflections	$\Delta\rho_{min}$ = −1.49 e Å^{-3}
71 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	Extinction coefficient: 0.0037 (6)

Table 1
Selected geometric parameters (Å, °).

As1—O3	1.6375 (17)	As1—O1	1.7071 (17)
As1—O4	1.6669 (16)	As1—O2	1.7180 (18)
N1—C1—C2—C1^i	179.5 (3)		

Symmetry code: (i) $-x + \frac{3}{2}, y, -z + 1$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$\cdots$O4^{ii}	0.83	1.82	2.608 (3)	159
O2—H2$\cdots$O4^{iii}	0.90	1.74	2.603 (3)	161
N1—H3$\cdots$O3^{iv}	0.89	1.89	2.740 (3)	160
N1—H4$\cdots$O4	0.89	2.13	2.967 (3)	156
N1—H5$\cdots$O3^{v}	0.89	1.97	2.818 (3)	158
C1—H7$\cdots$O2^{vi}	0.97	2.48	3.389 (3)	156
C2—H8$\cdots$O2^{v}	0.97	2.52	3.482 (3)	174

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

The I-centred unit cell was chosen in preference to the C-centred setting (space group $C2/c$) to avoid a very obtuse β angle of 127° (Mighell, 2003). The O-bound H atoms were found in difference maps and refined as riding on their carrier O atoms in their as-found relative positions. H atoms bonded to C and N atoms were placed in idealized positions (C—H = 0.97 Å and N—H = 0.89 Å) and refined as riding, allowing for free rotation of the –NH$_3$ group. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases. The highest difference peak is 0.95 Å from O3 and the deepest difference hole is 1.20 Å from As1.

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: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

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$M_r = 358.02$	$D_x = 2.244$ Mg m^{-3}
Monoclinic, $I2/a$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -I 2ya	Cell parameters from 3458 reflections
$a = 15.5563\ (8)$ Å	$\theta = 2.7–32.5°$
$b = 4.6549\ (2)$ Å	$\mu = 6.33$ mm^{-1}
$c = 15.0454\ (7)$ Å	$T = 293$ K
$\beta = 103.399\ (1)°$	Plate, colourless
$V = 1059.83\ (9)$ Å^3	$0.50 \times 0.19 \times 0.03$ mm
$Z = 4$	

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Radiation source: fine-focus sealed tube	1899 independent reflections
Graphite monochromator	1667 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.044$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$\theta_{max} = 32.5°$, $\theta_{min} = 2.7°$
$T_{min} = 0.144$, $T_{max} = 0.833$	$h = -23 \rightarrow 23$
	$k = -7 \rightarrow 5$
	$l = -22 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: difmap (O-H) and geom (others)
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.002$
1899 reflections	$\Delta\rho_{max} = 1.07$ e Å^{-3}
71 parameters	$\Delta\rho_{min} = -1.49$ e Å^{-3}
0 restraints	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0037 (6)
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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
As1	0.610145 (14)	0.09809 (4)	0.190204 (14)	0.01589 (11)
O1	0.55861 (13)	−0.1697 (4)	0.23548 (14)	0.0284 (4)
H1	0.5753	−0.3385	0.2364	0.034*
O2	0.70063 (13)	−0.0671 (4)	0.16560 (14)	0.0250 (4)
H2	0.7484	0.0281	0.1966	0.030*
O3	0.54520 (12)	0.2119 (5)	0.09502 (11)	0.0304 (4)
O4	0.64362 (12)	0.3454 (3)	0.27093 (12)	0.0212 (3)
N1	0.58882 (16)	0.1073 (4)	0.43221 (15)	0.0242 (4)
H3	0.5430	−0.0066	0.4097	0.029*
H4	0.5975	0.2257	0.3887	0.029*
H5	0.5778	0.2094	0.4783	0.029*
C1	0.66881 (18)	−0.0695 (5)	0.46541 (19)	0.0262 (5)
H6	0.6782	−0.1908	0.4161	0.031*
H7	0.6599	−0.1934	0.5143	0.031*
C2	0.7500	0.1146 (7)	0.5000	0.0252 (7)
H8	0.7405	0.2370	0.5490	0.030*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.01398 (14)	0.01850 (15)	0.01456 (14)	0.00068 (6)	0.00202 (9)	0.00031 (6)
O1	0.0256 (9)	0.0181 (7)	0.0455 (11)	0.0000 (7)	0.0163 (8)	0.0041 (7)
O2	0.0154 (8)	0.0319 (9)	0.0282 (9)	0.0004 (6)	0.0061 (7)	−0.0091 (6)
O3	0.0263 (9)	0.0458 (10)	0.0166 (7)	0.0110 (8)	−0.0004 (6)	0.0049 (7)
O4	0.0193 (7)	0.0216 (7)	0.0223 (8)	−0.0016 (6)	0.0039 (6)	−0.0038 (6)
N1	0.0206 (10)	0.0326 (11)	0.0184 (9)	−0.0023 (7)	0.0025 (8)	−0.0023 (6)
C1	0.0214 (11)	0.0290 (11)	0.0253 (12)	−0.0015 (9)	−0.0007 (9)	0.0031 (9)
C2	0.0181 (15)	0.0301 (16)	0.0251 (16)	0.000	0.0004 (12)	0.000

Geometric parameters (Å, º)

As1—O3	1.6375 (17)	N1—H4	0.8900
As1—O4	1.6669 (16)	N1—H5	0.8900
As1—O1	1.7071 (17)	C1—C2	1.515 (3)
As1—O2	1.7180 (18)	C1—H6	0.9700
O1—H1	0.8265	C1—H7	0.9700

O2—H2	0.8979	C2—C1^i	1.515 (3)
N1—C1	1.479 (3)	C2—H8	0.9700
N1—H3	0.8900		
O3—As1—O4	116.04 (9)	H3—N1—H5	109.5
O3—As1—O1	109.49 (10)	H4—N1—H5	109.5
O4—As1—O1	108.06 (9)	N1—C1—C2	111.72 (19)
O3—As1—O2	109.06 (9)	N1—C1—H6	109.3
O4—As1—O2	109.45 (9)	C2—C1—H6	109.3
O1—As1—O2	104.07 (8)	N1—C1—H7	109.3
As1—O1—H1	121.7	C2—C1—H7	109.3
As1—O2—H2	106.8	H6—C1—H7	107.9
C1—N1—H3	109.5	C1—C2—C1^i	111.1 (3)
C1—N1—H4	109.5	C1—C2—H8	109.4
H3—N1—H4	109.5	C1^i—C2—H8	109.4
C1—N1—H5	109.5		
N1—C1—C2—C1^i	179.5 (3)		

Symmetry code: (i) $-x+3/2, y, -z+1$.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{ii}	0.83	1.82	2.608 (3)	159
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