

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
 $T = 293$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.022
 wR factor = 0.057
 Data-to-parameter ratio = 31.9

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

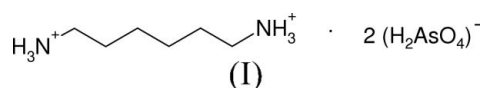
Hexane-1,6-diammonium bis(dihydrogenarsenate): infinite anionic layers containing $R_6^6(24)$ loops

 Received 13 February 2007
 Accepted 14 February 2007

The title compound, $\text{C}_6\text{H}_{18}\text{N}_2^{2+} \cdot 2\text{H}_2\text{AsO}_4^-$, contains a network of doubly protonated centrosymmetric hexane-1,6-diammonium cations and dihydrogenarsenate anions. These species interact by way of cation-to-anion $\text{N}-\text{H} \cdots \text{O}$ and anion-to-anion $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, the latter leading to infinite sheets of the H_2AsO_4^- anions.

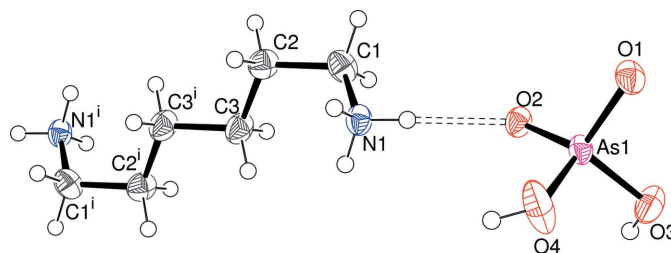
Comment

The title compound, (I) (Fig. 1), was prepared as part of our ongoing studies of hydrogen-bonding interactions in the molecular salts of oxo-anions (Wilkinson & Harrison, 2005).



The tetrahedral H_2AsO_4^- anion in (I) [mean $\text{As}-\text{O} = 1.683$ (2) Å] shows the usual distinction (Table 1) between the protonated and unprotonated $\text{As}-\text{O}$ bond lengths. The complete hexane-1,6-diammonium dication has a centre of symmetry at the mid-point of the $\text{C}3-\text{C}3^i$ bond [symmetry code: (i) $-x, -y, -z$]. The $\text{N}1-\text{C}1-\text{C}2-\text{C}3$ torsion angle of -72.87 (18) $^\circ$ indicates a *gauche* conformation for these four atoms within the dication, whereas $\text{C}1-\text{C}2-\text{C}3-\text{C}3^i$ are *anti* [torsion angle = 179.17 (19) $^\circ$]

As well as Coulombic forces, the component species in (I) interact by way of a network of $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2). The H_2AsO_4^- units are linked into infinite sheets (Fig. 2) by way of the $\text{O}-\text{H} \cdots \text{O}$ bonds. The $\text{O}3-\text{H}1 \cdots \text{O}2^{\text{ii}}$ bond (see Table 2 for symmetry code) results in inversion-generated dimeric pairs of H_2AsO_4^- tetrahedra linked by a double (*i.e.* $\text{O}-\text{H} \cdots \text{O} + \text{O} \cdots \text{H}-\text{O}$) hydrogen bond. The $\text{O}4-\text{H}2 \cdots \text{O}1^{\text{iii}}$ bond links the dimers into an infinite sheet (Fig. 3) propagating in (100). The $\text{As} \cdots \text{As}^{\text{ii}}$ and


Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius. The hydrogen bond is indicated by a double-dashed line. [Symmetry code: (i) $-x, -y, -z$.]

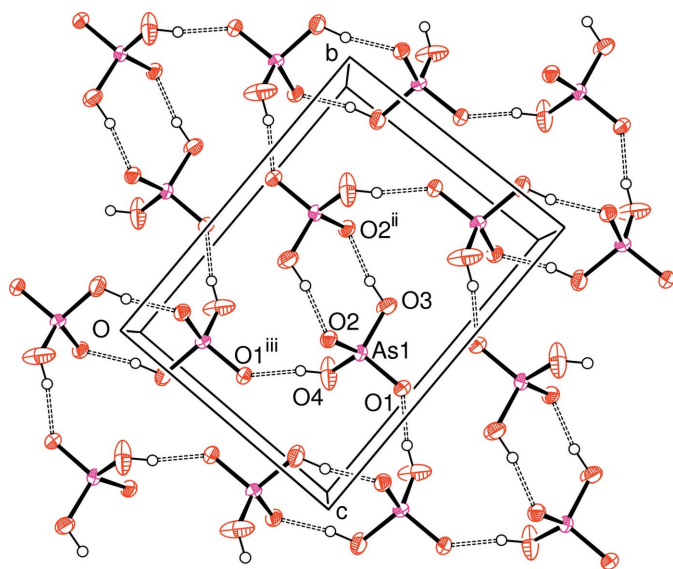


Figure 2
Detail of a part of a (100) hydrogen-bonded sheet of H_2AsO_4^- groups in (I), with hydrogen bonds indicated by double-dashed lines. Symmetry codes as in Table 2

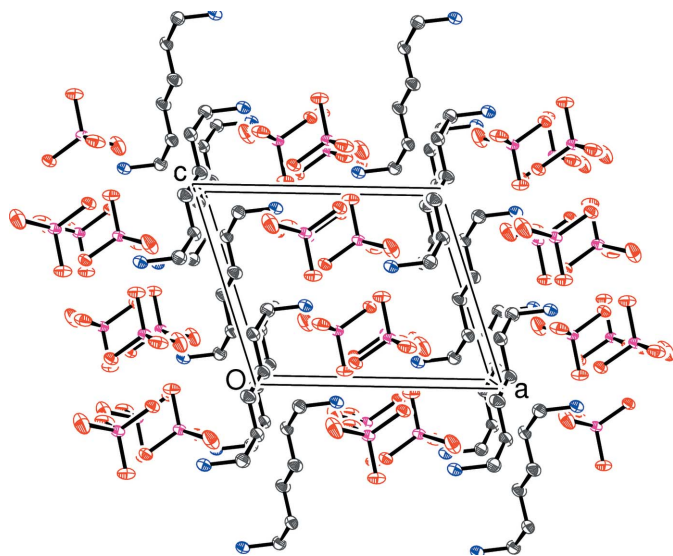


Figure 3
The packing in (I), viewed down [010], showing the (100) dihydrogen-arsenate layers mediated by the organic cations. H atoms have been omitted for clarity.

$\text{As}\cdots\text{As}^{\text{iii}}$ separations are 4.3922 (3) and 4.8900 (3) Å, respectively. A supramolecular $R_6^6(24)$ loop (Bernstein *et al.*, 1995) arises for each circuit of six tetrahedra within the sheet.

The anionic sheets are bridged by the organic cations, each of which participates in three nearly linear $\text{N}-\text{H}\cdots\text{O}$ interactions from its $-\text{NH}_3^+$ group (Table 2), resulting in a layered crystal structure (Fig. 3).

Guanidinium dihydrogenarsenate, $\text{CH}_6\text{N}_3\cdot\text{H}_2\text{AsO}_4$ (Wilkinson & Harrison, 2005), contains a hydrogen-bonded tetrahedral sheet topology similar to that in the title compound, despite the different cation–anion ratio in $\text{CH}_6\text{N}_3\cdot\text{H}_2\text{AsO}_4$.

Experimental

An aqueous 1,6-diaminohexane solution (0.5 M, 10 ml) was added to an aqueous H_3AsO_4 solution (0.5 M, 10 ml), resulting in 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

$\text{C}_6\text{H}_{18}\text{N}_2^{2+}\cdot 2\text{AsH}_2\text{O}_4^-$	$V = 737.27$ (6) Å ³
$M_r = 400.10$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.5237$ (5) Å	$\mu = 4.56$ mm ⁻¹
$b = 10.1029$ (5) Å	$T = 293$ (2) K
$c = 8.0747$ (4) Å	$0.33 \times 0.31 \times 0.13$ mm
$\beta = 108.385$ (1)°	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	7129 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	2649 independent reflections
$T_{\text{min}} = 0.314$, $T_{\text{max}} = 0.589$	2187 reflections with $I > 2\sigma(I)$
(expected range = 0.295–0.553)	$R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	83 parameters
$wR(F^2) = 0.057$	H-atom parameters constrained
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.52$ e Å ⁻³
2649 reflections	$\Delta\rho_{\text{min}} = -0.53$ e Å ⁻³

Table 1

Selected bond lengths (Å).

As1—O1	1.6501 (11)	As1—O4	1.6998 (13)
As1—O2	1.6656 (11)	As1—O3	1.7169 (11)

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H1}\cdots\text{O2}^{\text{ii}}$	0.92	1.70	2.6103 (15)	169
$\text{O4}-\text{H2}\cdots\text{O1}^{\text{iii}}$	0.86	1.71	2.5613 (16)	170
$\text{N1}-\text{H3}\cdots\text{O2}$	0.89	2.01	2.8938 (17)	172
$\text{N1}-\text{H4}\cdots\text{O2}^{\text{iii}}$	0.89	2.12	2.9681 (19)	159
$\text{N1}-\text{H5}\cdots\text{O1}^{\text{iv}}$	0.89	1.89	2.7714 (16)	169

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

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. The other H atoms were positioned geometrically, with $\text{C}-\text{H} = 0.97$ Å and $\text{N}-\text{H} = 0.89$ Å, and refined as riding atoms. $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ for all H atoms.

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.

HSW thanks the Carnegie Trust for the Universities of Scotland for an undergraduate vacation studentship.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (1999). *SMART* (Version 5.624), *SAINTE* (Version 6.02a) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Wilkinson, H. S. & Harrison, W. T. A. (2005). *Acta Cryst.* **E61**, m2023–m2025.

supporting information

Acta Cryst. (2007). E63, m902–m904 [https://doi.org/10.1107/S1600536807007672]

Hexane-1,6-diammonium bis(dihydrogenarsenate): infinite anionic layers containing $R_6^6(24)$ loops

Hazel S. Wilkinson and William T. A. Harrison

Hexane-1,6-diammonium bis(dihydrogenarsenate)

Crystal data

$C_6H_{18}N_2^{2+} \cdot 2AsH_2O_4^-$

$M_r = 400.10$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.5237$ (5) Å

$b = 10.1029$ (5) Å

$c = 8.0747$ (4) Å

$\beta = 108.385$ (1)°

$V = 737.27$ (6) Å³

$Z = 2$

$F(000) = 404$

$D_x = 1.802$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4034 reflections

$\theta = 2.3$ – 32.5 °

$\mu = 4.56$ mm⁻¹

$T = 293$ K

Block, colourless

$0.33 \times 0.31 \times 0.13$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 1999)

$T_{\min} = 0.314$, $T_{\max} = 0.589$

7129 measured reflections

2649 independent reflections

2187 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 32.5$ °, $\theta_{\min} = 2.3$ °

$h = -14 \rightarrow 11$

$k = -15 \rightarrow 10$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.057$

$S = 0.99$

2649 reflections

83 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difmap and geom

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2]$

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

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

$\Delta\rho_{\max} = 0.52$ e Å⁻³

$\Delta\rho_{\min} = -0.53$ e Å⁻³

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	0.606026 (16)	0.386539 (14)	0.738786 (17)	0.02384 (5)
O1	0.62562 (15)	0.38557 (10)	0.94925 (14)	0.0325 (2)
O2	0.43378 (12)	0.35753 (10)	0.61094 (14)	0.0277 (2)
O3	0.66259 (15)	0.54220 (12)	0.70262 (14)	0.0411 (3)
H1	0.6218	0.5675	0.5883	0.049*
O4	0.72953 (15)	0.28059 (16)	0.69736 (19)	0.0584 (4)
H2	0.6928	0.2329	0.6059	0.070*
N1	0.30110 (15)	0.13220 (12)	0.39759 (17)	0.0276 (3)
H3	0.3475	0.1963	0.4699	0.033*
H4	0.3171	0.1418	0.2954	0.033*
H5	0.3354	0.0539	0.4432	0.033*
C1	0.13969 (19)	0.13983 (17)	0.3713 (2)	0.0341 (3)
H1A	0.1030	0.2257	0.3230	0.041*
H1B	0.1230	0.1316	0.4833	0.041*
C2	0.05421 (18)	0.03200 (17)	0.2497 (2)	0.0330 (3)
H2A	0.1027	-0.0523	0.2869	0.040*
H2B	-0.0445	0.0266	0.2596	0.040*
C3	0.04181 (19)	0.05463 (17)	0.0598 (2)	0.0349 (3)
H3A	-0.0081	0.1382	0.0217	0.042*
H3B	0.1404	0.0612	0.0498	0.042*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.02682 (8)	0.02320 (8)	0.01871 (7)	-0.00187 (5)	0.00318 (5)	-0.00245 (5)
O1	0.0462 (7)	0.0285 (5)	0.0195 (5)	-0.0035 (5)	0.0055 (5)	0.0019 (4)
O2	0.0270 (5)	0.0288 (5)	0.0230 (5)	-0.0047 (4)	0.0019 (4)	0.0001 (4)
O3	0.0503 (8)	0.0394 (7)	0.0247 (5)	-0.0200 (6)	-0.0007 (5)	0.0064 (5)
O4	0.0353 (7)	0.0683 (10)	0.0603 (9)	0.0106 (6)	-0.0012 (6)	-0.0400 (8)
N1	0.0296 (6)	0.0261 (6)	0.0238 (6)	-0.0021 (5)	0.0035 (5)	-0.0016 (4)
C1	0.0320 (8)	0.0372 (9)	0.0314 (8)	0.0057 (6)	0.0077 (6)	-0.0043 (6)
C2	0.0256 (7)	0.0395 (9)	0.0310 (8)	-0.0040 (6)	0.0049 (6)	0.0003 (6)
C3	0.0334 (8)	0.0365 (9)	0.0303 (8)	-0.0104 (7)	0.0037 (6)	-0.0006 (6)

Geometric parameters (Å, °)

As1—O1	1.6501 (11)	C1—C2	1.520 (2)
As1—O2	1.6656 (11)	C1—H1A	0.9700
As1—O4	1.6998 (13)	C1—H1B	0.9700
As1—O3	1.7169 (11)	C2—C3	1.518 (2)
O3—H1	0.9179	C2—H2A	0.9700
O4—H2	0.8586	C2—H2B	0.9700
N1—C1	1.486 (2)	C3—C3 ⁱ	1.516 (3)
N1—H3	0.8900	C3—H3A	0.9700
N1—H4	0.8900	C3—H3B	0.9700
N1—H5	0.8900		
O1—As1—O2	113.99 (6)	C2—C1—H1A	109.2
O1—As1—O4	109.78 (7)	N1—C1—H1B	109.2
O2—As1—O4	112.00 (6)	C2—C1—H1B	109.2
O1—As1—O3	103.94 (5)	H1A—C1—H1B	107.9
O2—As1—O3	110.87 (5)	C3—C2—C1	113.58 (14)
O4—As1—O3	105.64 (8)	C3—C2—H2A	108.8
As1—O3—H1	111.7	C1—C2—H2A	108.8
As1—O4—H2	113.8	C3—C2—H2B	108.8
C1—N1—H3	109.5	C1—C2—H2B	108.8
C1—N1—H4	109.5	H2A—C2—H2B	107.7
H3—N1—H4	109.5	C3 ⁱ —C3—C2	113.04 (17)
C1—N1—H5	109.5	C3 ⁱ —C3—H3A	109.0
H3—N1—H5	109.5	C2—C3—H3A	109.0
H4—N1—H5	109.5	C3 ⁱ —C3—H3B	109.0
N1—C1—C2	111.98 (13)	C2—C3—H3B	109.0
N1—C1—H1A	109.2	H3A—C3—H3B	107.8
N1—C1—C2—C3	-72.87 (18)	C1—C2—C3—C3 ⁱ	179.17 (19)

Symmetry code: (i) $-x, -y, -z$.

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—H1...O2 ⁱⁱ	0.92	1.70	2.6103 (15)	169
O4—H2...O1 ⁱⁱⁱ	0.86	1.71	2.5613 (16)	170
N1—H3...O2	0.89	2.01	2.8938 (17)	172
N1—H4...O2 ⁱⁱⁱ	0.89	2.12	2.9681 (19)	159
N1—H5...O1 ^{iv}	0.89	1.89	2.7714 (16)	169

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