

**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  $\sigma(C-C)$  = 0.002 Å  
 R factor = 0.018  
 wR factor = 0.050  
 Data-to-parameter ratio = 28.1

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

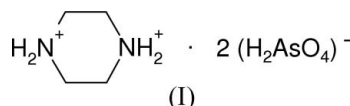
**Piperazinium bis(dihydrogenarsenate)**

The title compound,  $C_4H_{12}N_2^{2+} \cdot 2H_2AsO_4^-$ , contains a network of doubly protonated piperazinium cations (lying on centres of inversion) and dihydrogenarsenate anions. The component species interact by way of cation-to-anion  $N-H \cdots O$  and anion-to-anion  $O-H \cdots O$  hydrogen bonds, the latter leading to infinite sheets of  $(H_2AsO_4)^-$  anions.

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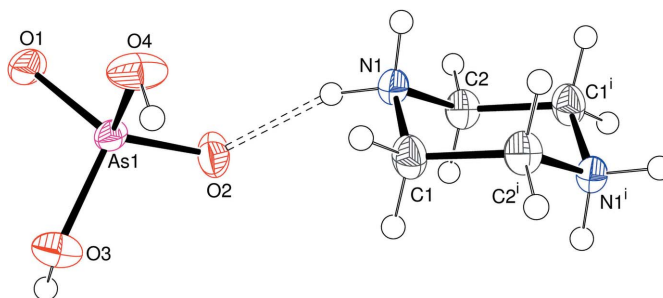
**Comment**

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, 2004). Such materials show interesting crystal structures arising from the interplay of cation-to-anion  $N-H \cdots O$  and anion-to-anion  $O-H \cdots O$  hydrogen bonds (Lee & Harrison, 2003).

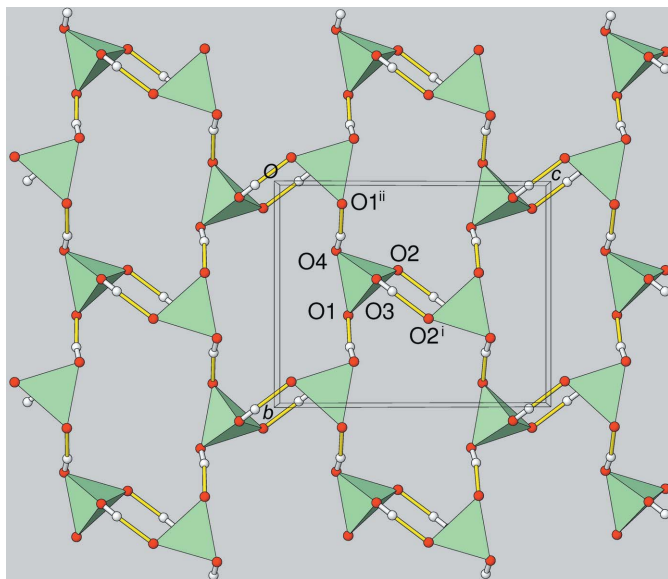


The  $(H_2AsO_4)^-$  anion in (I) shows its normal tetrahedral geometry about As, with the usual distinction (Table 1) between protonated and unprotonated As–O bond lengths (Wilkinson & Harrison, 2004). The piperazinium dication lies on a centre of inversion and adopts a typical chair conformation.

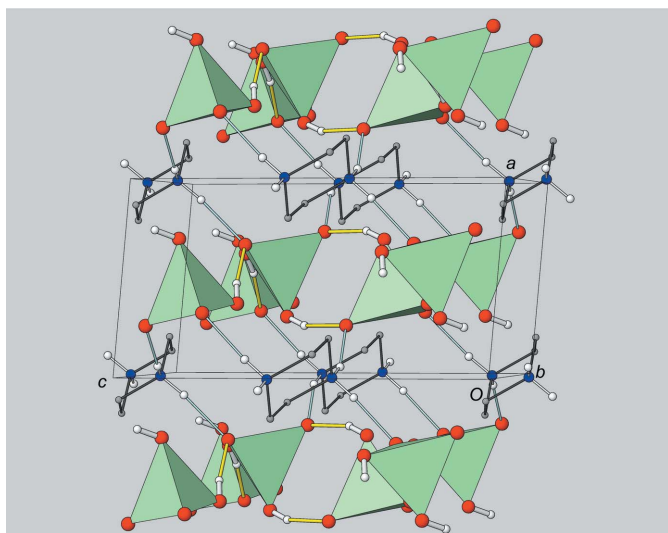
As well as coulombic forces, the component species in (I) interact by way of a network of  $N-H \cdots O$  and  $O-H \cdots O$  hydrogen bonds (Table 2). The  $(H_2AsO_4)^-$  units are linked into infinite sheets (Fig. 2) by the  $O-H \cdots O$  hydrogen bonds. The  $O3-H1 \cdots O2^i$  interaction (see Table 2 for symmetry codes) results in centrosymmetric dimeric pairs of  $(H_2AsO_4)^-$  tetrahedra linked by pairs of  $O-H \cdots O$  hydrogen bonds. The  $O4-H2 \cdots O1^{ii}$  hydrogen bond links these dimers into an



**Figure 1**  
 The molecular structure of (I) (50% displacement ellipsoids and H atoms are drawn as spheres of arbitrary radius). The hydrogen bond is indicated by a dashed line. [Symmetry code: (i)  $-x, -y, 1 - z$ .]



**Figure 2**  
Detail of a part of a (100) hydrogen-bonded sheet of  $(\text{H}_2\text{AsO}_4)^-$  groups in (I) in polyhedral representation, with the  $\text{H}\cdots\text{O}$  parts of the hydrogen bonds coloured yellow. [Symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ .]



**Figure 3**  
The packing in (I), showing the (100) dihydrogenarsenate layers mediated by the organic cations. The  $\text{H}\cdots\text{O}$  parts of the  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds are coloured blue and yellow, respectively. H atoms bound to C atoms are omitted for clarity.

infinite sheet (Fig. 3) lying parallel to (100). The  $\text{As}\cdots\text{As}^{\text{i}}$  and  $\text{As}\cdots\text{As}^{\text{ii}}$  separations are 4.0148 (3) and 5.0190 (3) Å, respectively. The topological connectivity of the As atoms defines a  $6^3$  sheet (O'Keeffe & Hyde, 1996), *i.e.* every As node participates in three polyhedral six-ring loops.

The anionic sheets are bridged by piperazinium cations, each of which participates in two  $\text{N}-\text{H}\cdots\text{O}$  interactions from each of its  $\text{NH}_2$  groups to nearby dihydrogenarsenate tetrahedra. This results (Fig. 3) in organic and inorganic layers that alternate along the  $a$  axis. A similar layered structure has been

reported for guanidinium dihydrogenarsenate,  $\text{CH}_6\text{N}_3^+\text{H}_2\text{AsO}_4^-$  (Wilkinson & Harrison, 2005), despite the different cation:anion ratios in the two compounds. Other ammonium hydrogenarsenate salts contain isolated pairs of tetrahedra (Todd & Harrison, 2005) or polymeric chains of anions (Wilkinson & Harrison, 2004).

## Experimental

A 0.5 M aqueous piperazine solution (10 ml) was added to a 0.5 M aqueous  $\text{H}_3\text{AsO}_4$  solution (10 ml) to give a clear solution. Crystals of (I) were obtained as the water evaporated over the course of a few days.

### Crystal data

$\text{C}_4\text{H}_{12}\text{N}_2^{2+}\cdot 2\text{H}_2\text{AsO}_4^-$   
 $M_r = 370.02$   
 Monoclinic,  $P2_1/c$   
 $a = 5.8208$  (3) Å  
 $b = 8.9966$  (4) Å  
 $c = 11.0369$  (5) Å  
 $\beta = 95.126$  (1)°  
 $V = 575.66$  (5) Å<sup>3</sup>

$Z = 2$   
 $D_x = 2.135$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 5.84$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, colourless  
 $0.44 \times 0.41 \times 0.22$  mm

### Data collection

Bruker SMART1000 CCD  
 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 1999)  
 $T_{\min} = 0.141$ ,  $T_{\max} = 0.277$

5723 measured reflections  
 2081 independent reflections  
 1843 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$   
 $\theta_{\max} = 32.5^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.050$   
 $S = 1.05$   
 2081 reflections  
 74 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 0.0622P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.54$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.50$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.061 (2)

**Table 1**

Selected geometric parameters (Å, °).

As1—O1	1.6633 (11)	As1—O3	1.7214 (11)
As1—O2	1.6577 (11)	As1—O4	1.7095 (11)
O1—As1—O2	115.12 (6)	O2—As1—O3	111.08 (6)
O1—As1—O3	110.51 (5)	O2—As1—O4	110.53 (6)
O1—As1—O4	106.14 (6)	O3—As1—O4	102.62 (5)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O3—H1 <sup>i</sup> ⋯O2 <sup>i</sup>	0.83	1.82	2.6211 (16)	161
O4—H2 <sup>i</sup> ⋯O1 <sup>ii</sup>	0.84	1.72	2.5533 (16)	170
N1—H3 <sup>i</sup> ⋯O2	0.90	1.86	2.7163 (16)	158
N1—H4 <sup>i</sup> ⋯O1 <sup>iii</sup>	0.90	1.87	2.7617 (16)	173

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

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 2004); software used to prepare material for publication: *SHELXL97*.

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