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Key indicators

 Single-crystal X-ray study
 $T = 293$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.024
 wR factor = 0.057
 Data-to-parameter ratio = 29.7

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

Homopiperazinium bis(dihydrogenarsenate)

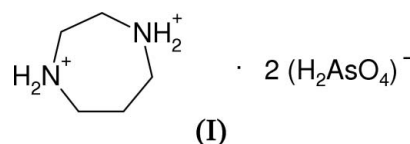
The crystal packing in the title compound, $\text{C}_5\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{H}_2\text{AsO}_4^-$, involves anion-to-anion $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, resulting in double chains of dihydrogenarsenate tetrahedra. The double chains are crosslinked by further $\text{O}-\text{H} \cdots \text{O}$ bonds to result in a three-dimensional framework that accommodates the organic cations in large cavities. The cations interact with the framework by way of $\text{N}-\text{H} \cdots \text{O}$ bonds.

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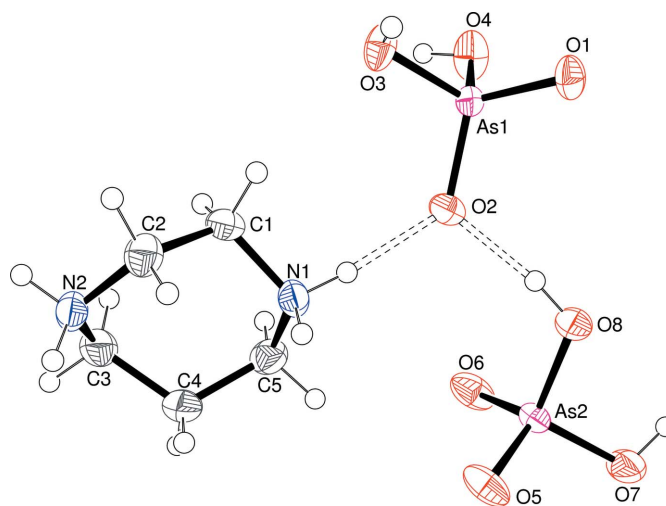
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Comment

The title compound, (I) (Fig. 1), was prepared as part of our ongoing structural studies of hydrogen-bonding interactions in protonated-amine (di)hydrogen arsenates (Wilkinson & Harrison, 2005*a,b*; Todd & Harrison, 2005). These simple organic salts show interesting packing motifs, strongly influenced by the interplay of $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.



Both the $(\text{H}_2\text{AsO}_4)^-$ dihydrogenarsenate groups in (I) show their normal tetrahedral geometry [mean $\text{As}-\text{O} = 1.677$ (2) Å], with the protonated $\text{As}-\text{OH}$ vertices showing their expected lengthening relative to the unprotonated $\text{As}-$


Figure 1

The asymmetric unit of (I), showing 50% displacement ellipsoids (arbitrary spheres for H atoms). Hydrogen bonds are indicated by dashed lines.

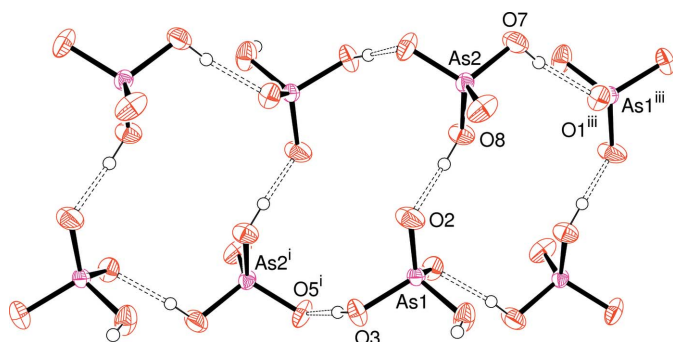


Figure 2
Detail of a hydrogen-bonded (dashed lines) dihydrogenarsenate double chain in (I). Symmetry codes are as in Table 2.

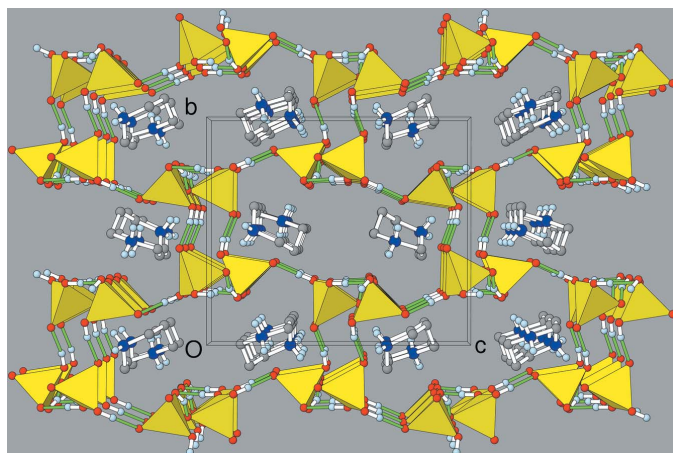


Figure 3
The packing in (I), viewed down [100], with the dihydrogenarsenate groups represented by polyhedra. Colour key: H_2AsO_4^- groups yellow, O atoms red, N dark blue, C grey, H pale blue, $\text{H}\cdots\text{O}$ portions of the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds green.

O bonds, which have formal partial double-bond character (Table 1). The homopiperazinium cation adopts a chair conformation, with atoms N1, C1, C3 and C4 almost coplanar (r.m.s. deviation from the mean plane = 0.029 Å) and atoms C5, C2 and N2 displaced from the plane by 0.667 (3), -1.186 (3) and -1.045 (3) Å, respectively.

As well as electrostatic attractions, the component species in (I) interact by means of a network of cation-to-anion $\text{N}-\text{H}\cdots\text{O}$ and anion-to-anion $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). The $(\text{H}_2\text{AsO}_4)^-$ units are linked into polymeric double chains (Fig. 2) propagating along [100]. Each strand of the chain consists of alternating As1- and As2-centred groups, with $\text{O}3-\text{H}1\cdots\text{O}5^i$ and $\text{O}7-\text{H}3\cdots\text{O}1^{iii}$ providing the hydrogen-bond links (see Table 2 for symmetry codes). The two strands are then crosslinked by the $\text{O}8-\text{H}4\cdots\text{O}2$ interaction. The graph-set notation (Bernstein *et al.*, 1995) for this hydrogen-bonding pattern within the double chain is an $R_4^1(16)$ loop. The $\text{As}1\cdots\text{As}2^i$ and $\text{As}1\cdots\text{As}2^{iii}$ intra-strand separations are 4.7032 (3) and 4.7531 (3) Å, respectively, and the $\text{As}1\cdots\text{As}2$ inter-strand separation is 5.0014 (3) Å. Finally, the [100] double chains are crosslinked in [001] by the $\text{O}4-\text{H}2\cdots\text{O}6^i$ bonds [with $\text{As}1\cdots\text{As}2^i = 4.5461$ (3) Å], to result in

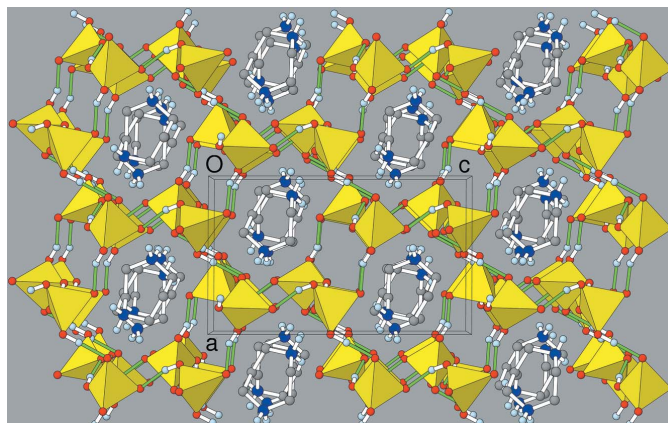


Figure 4
The packing in (I), viewed down [010]. Drawing conventions as in Fig. 3.

a very open three-dimensional network of dihydrogenarsenate groups, delimiting intersecting channels that propagate in [100] and [010] (Figs. 3 and 4). The organic cations occupy the large eight-membered ring (*i.e.* eight H_2AsO_4 tetrahedra) [100] channels in the framework and interact with them by way of the four $\text{N}-\text{H}\cdots\text{O}$ bonds. It should be noted that the mean $\text{H}\cdots\text{O}$ contact distance for the $\text{O}-\text{H}\cdots\text{O}$ bonds (1.71 Å) is significantly smaller than the mean $\text{H}\cdots\text{O}$ distance (1.84 Å) for the $\text{N}-\text{H}\cdots\text{O}$ bonds. The graph-set notation for the eight-membered ring loop is $R_8^8(32)$.

The situation in (I) of a hydrogen-bonded array of tetrahedral anions encompassing a network of channels occupied by organic cations is similar to that of $\alpha\text{-C}_5\text{H}_7\text{N}_2\cdot\text{H}_2\text{PO}_4$ ($\text{C}_5\text{H}_7\text{N}_2$ is the 2-aminopyridinium cation; Czaplá *et al.*, 2003). In the phosphate, symmetrical $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds appear to be present at room temperature, and a paraelectric-to-ferroelectric phase transition occurs on cooling below 104 K.

Experimental

An aqueous homopiperazine solution (10 ml, 0.5 M) was added to an aqueous H_3AsO_4 solution (10 ml, 0.5 M), giving 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

$\text{C}_5\text{H}_{14}\text{N}_2^{2+}\cdot 2\text{AsH}_2\text{O}_4^-$
 $M_r = 384.05$
Monoclinic, $P2_1/n$
 $a = 8.1495$ (3) Å
 $b = 11.7163$ (4) Å
 $c = 13.5730$ (5) Å
 $\beta = 90.234$ (1)°
 $V = 1295.97$ (8) Å³

$Z = 4$
 $D_x = 1.968$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 5.19$ mm⁻¹
 $T = 293$ (2) K
Block cut from slab, colourless
0.32 × 0.19 × 0.16 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.288$, $T_{\max} = 0.491$

14796 measured reflections
4639 independent reflections
3760 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 32.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 0.95$	$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
4639 reflections	$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
156 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.0013 (3)

Table 1
Selected geometric parameters (\AA , $^\circ$).

As1—O1	1.6530 (14)	As2—O5	1.6492 (14)
As1—O2	1.6543 (15)	As2—O6	1.6516 (15)
As1—O4	1.7001 (15)	As2—O7	1.6973 (16)
As1—O3	1.7053 (14)	As2—O8	1.7072 (13)
N1—C1—C2—N2	-77.8 (2)	C3—C4—C5—N1	65.9 (3)
C1—C2—N2—C3	15.0 (3)	C4—C5—N1—C1	-59.7 (2)
C2—N2—C3—C4	55.6 (3)	C5—N1—C1—C2	83.3 (2)
N2—C3—C4—C5	-85.6 (2)		

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1 \cdots O5 ⁱ	0.90	1.65	2.555 (2)	178
O4—H2 \cdots O6 ⁱⁱ	0.86	1.73	2.579 (2)	165
O7—H3 \cdots O1 ⁱⁱⁱ	0.89	1.76	2.600 (2)	156
O8—H4 \cdots O2	0.88	1.70	2.567 (2)	169
N1—H5 \cdots O2	0.90	1.82	2.716 (2)	174
N1—H6 \cdots O1 ⁱ	0.90	1.91	2.802 (2)	171
N2—H2A \cdots O6 ^{iv}	0.90	1.80	2.698 (2)	174
N2—H2B \cdots O5 ^v	0.90	1.83	2.721 (2)	173

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

The initial refinement stalled with $R(F) \simeq 0.20$. The pseudo-orthorhombic unit cell with $\beta \simeq 90^\circ$ suggested the possibility of twinning. Inserting a mirror plane perpendicular to the a axis as a twinning operation with the aid of the twin matrix $(\bar{1} 0 0, 0 1 0, 0 0 1)$ led to a straightforward convergence to the final answer, with volume fractions of 0.875 (6):0.125 (6) for the two components. For a similar case, see Pompetzki *et al.* (2003).

The O-bound H atoms were found in difference maps and refined as riding in their as-found relative positions. The C- and N-bound H atoms were placed in idealized positions (C—H = 0.97 \AA and N—H = 0.90 \AA) 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, 1990); 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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