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Homopiperazinium bis(dihydrogenarsenate)

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The crystal packing in the title compound, $C_5H_{14}N_2^{2+}\cdot$-$2H_2AsO_4^-$, involves anion-to-anion O—H···O hydrogen bonds, resulting in double chains of dihydrogenarsenate tetrahedra. The double chains are crosslinked by further O—H···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 N—H···O bonds.

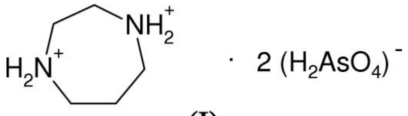
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–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.

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 N—H···O and O—H···O hydrogen bonds.



(I)

Both the $(H_2AsO_4)^-$ dihydrogenarsenate groups in (I) show their normal tetrahedral geometry [mean As—O = 1.677 (2) Å], with the protonated As—OH vertices showing their expected lengthening relative to the unprotonated As—

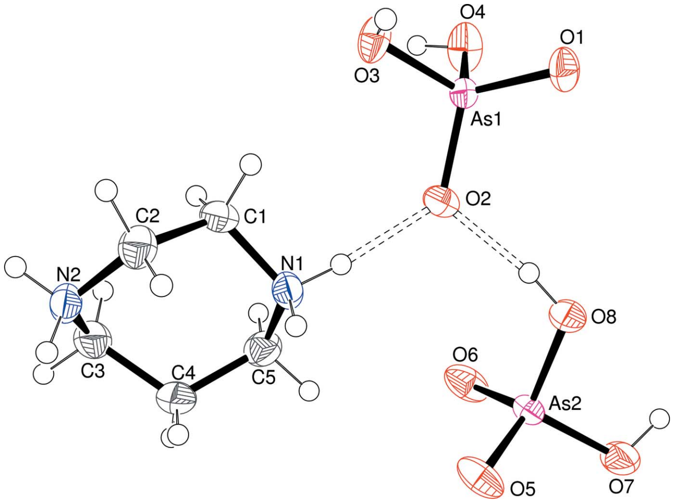


Figure 1
The asymmetric unit of (I), showing 50% displacement ellipsoids (arbitrary spheres for H atoms). Hydrogen bonds are indicated by dashed lines.

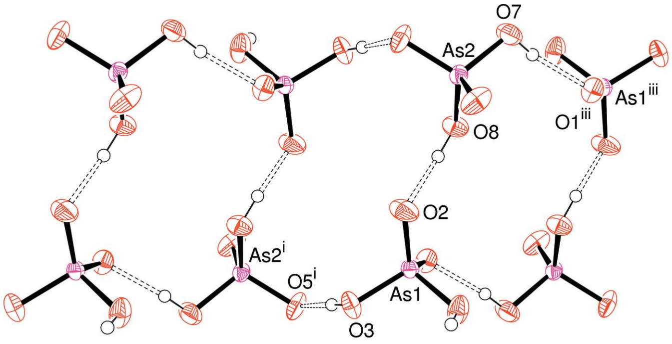


Figure 2
Detail of a hydrogen-bonded (dashed lines) dihydrogenarsenate double chain in (I). Symmetry codes are as in Table 2.

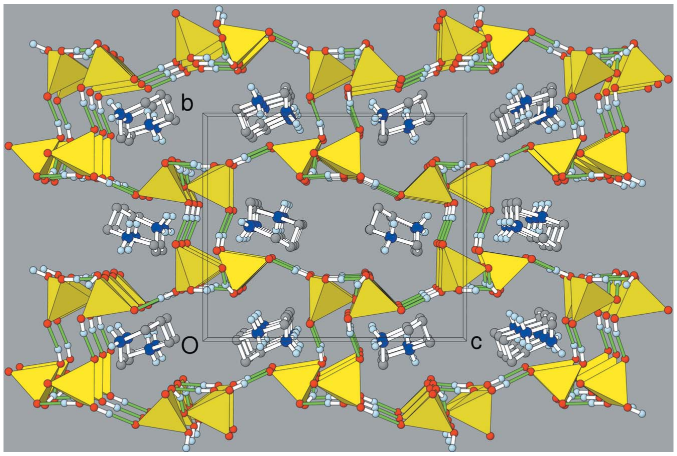


Figure 3
The packing in (I), viewed down [100], with the dihydrogenarsenate groups represented by polyhedra. Colour key: $H_2AsO_4^-$ groups yellow, O atoms red, N dark blue, C grey, H pale blue, H···O portions of the O—H···O hydrogen bonds green.

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 N—H···O and anion-to-anion O—H···O hydrogen bonds (Table 2). The $(H_2AsO_4)^-$ 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 O3—H1···O5^{i} and O7—H3···O1^{iii} providing the hydrogen-bond links (see Table 2 for symmetry codes). The two strands are then crosslinked by the O8—H4···O2 interaction. The graph-set notation (Bernstein *et al.*, 1995) for this hydrogen-bonding pattern within the double chain is an $R_4^4(16)$ loop. The As1···As2^{i} and As1···As2^{iii} intra-strand separations are 4.7032 (3) and 4.7531 (3) Å, respectively, and the As1···As2 inter-strand separation is 5.0014 (3) Å. Finally, the [100] double chains are crosslinked in [001] by the O4—H2···O6^{ii} bonds [with As1···As2^{ii} = 4.5461 (3) Å], to result in 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 N—H···O bonds. It should be noted that the mean H···O contact distance for the O—H···O bonds (1.71 Å) is significantly smaller than the mean H···O distance (1.84 Å) for the N—H···O bonds. The graph-set notation for the eight-membered ring loop is $R_8^8(32)$.

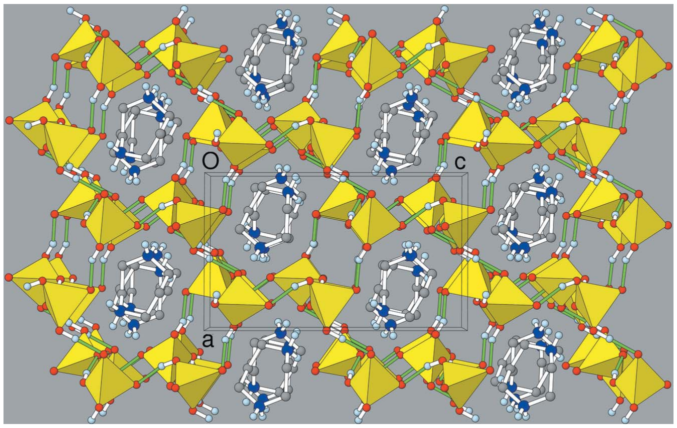


Figure 4
The packing in (I), viewed down [010]. Drawing conventions as in Fig. 3.

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 α-$C_5H_7N_2\cdot H_2PO_4$ ($C_5H_7N_2$ is the 2-aminopyridinium cation; Czapla *et al.*, 2003). In the phosphate, symmetrical O···H···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

$C_5H_{14}N_2^{2+}\cdot 2AsH_2O_4^-$
M_r = 384.05
Monoclinic, $P2_1/n$
a = 8.1495 (3) Å
b = 11.7163 (4) Å
c = 13.5730 (5) Å
β = 90.234 (1)°
V = 1295.97 (8) Å^3
Z = 4
D_x = 1.968 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 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_{int} = 0.025
θ_{max} = 32.5°

Refinement

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

Table 1
Selected geometric parameters (Å, °).

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 (Å, °).

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—H2$A\cdots$O6^{iv}	0.90	1.80	2.698 (2)	174
N2—H2$B\cdots$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 $\beta \simeq 90°$ 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 ($\overline{1}$ 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 Å and N—H = 0.90 Å) and refined as riding. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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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