

Tetraethylammonium dihydrogenarsenate bis(arsenic acid) and 1,4-diazoniabicyclo[2.2.2]octane bis(dihydrogenarsenate) arsenic acid: hydrogen-bonded networks containing dihydrogenarsenate anions and neutral arsenic acid molecules

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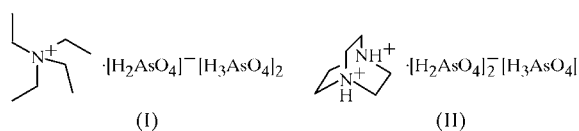
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The title compounds, $(C_8H_{20}N)[H_2AsO_4][H_3AsO_4]_2$, (I), and $(C_6H_{14}N_2)[H_2AsO_4]_2[H_3AsO_4]$, (II), are unusual salts containing organic cations, dihydrogenarsenate anions and neutral arsenic acid molecules. In (I), the dihydrogenarsenate anion lies across a twofold rotation axis in the space group $C2/c$, while the cation is disordered across a centre of inversion. The $[H_2AsO_4]^-$ and H_3AsO_4 species interact by way of $O-H \cdots O$ hydrogen bonds, leading to sheets and a three-dimensional network for (I) and (II), respectively.

Comment

Only a handful of crystal structures containing the neutral arsenic acid (H_3AsO_4) molecule have been determined, including *N,N,N*-trimethylglycine (betaine) arsenic acid (Schildkamp *et al.*, 1984), tetraphenylphosphonium chloride arsenic acid (Ruhlandt-Senge *et al.*, 1992), *L*-histidinium dihydrogenarsenate arsenic acid (Ratajczak *et al.*, 2000) and *DL*-threonine–arsenic acid (1/1) (Wilkinson & Harrison, 2005). We present here the syntheses and structures of the title compounds, $(C_8H_{20}N)[H_2AsO_4][H_3AsO_4]_2$, (I), and $(C_6H_{14}N_2)[H_2AsO_4]_2[H_3AsO_4]$, (II), which both contain organic cations, dihydrogenarsenate anions and neutral arsenic acid molecules.



The structure of (I) (Fig. 1) is built up from tetraethylammonium cations ($C_8H_{20}N^+$, TEA), dihydrogenarsenate anions ($[H_2AsO_4]^-$) and neutral arsenic acid molecules (H_3AsO_4) in a 1:1:2 ratio. The N atom of the cation occupies a

special position with site symmetry $\bar{1}$; thus, the ethyl arms of the TEA species are disordered, as is often seen for this cation (Majumdar *et al.*, 2006). The dihydrogenarsenate anion, containing As1, lies across a twofold rotation axis. The short and long As1–O bonds (Table 1) correspond to unprotonated As–O vertices with partial double-bond character and to protonated AsOH groups, respectively. The neutral arsenic acid molecule in (I), containing As2, with a mean As–O distance of 1.678 (2) Å, contains one short formal double bond (As2=O4) and three longer As–OH vertices, as seen in related structures (Wilkinson & Harrison, 2005).

As well as Coulombic and van der Waals forces, the component species in (I) interact by means of a network of $O-H \cdots O$ hydrogen bonds. All these bonds are short and nearly linear (Table 2). Pairs of arsenic acid molecules form inversion dimers *via* $O6-H4 \cdots O4^{iii} + O6^{iii}-H4^{iii} \cdots O4$ links (see Table 2 for symmetry codes). Similar dimers built up from $[H_2AsO_4]^-$ units have been seen in propane-1,2-diaminium hydrogenarsenate (Todd & Harrison, 2005). The As1-centred anion then serves to link the As2 dimers, by donating two O–

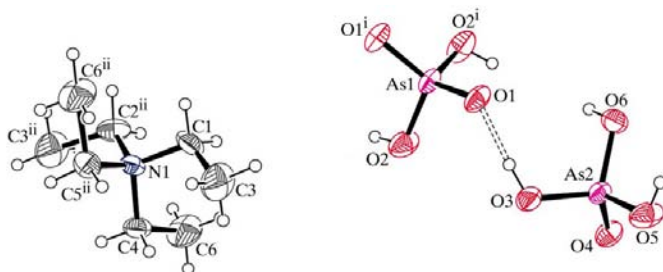


Figure 1
The molecular structure of (I) (50% probability displacement ellipsoids and H atoms drawn as spheres of arbitrary radii). The hydrogen bond is indicated by a double dashed line. Only one disorder component of the cation is shown. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.]

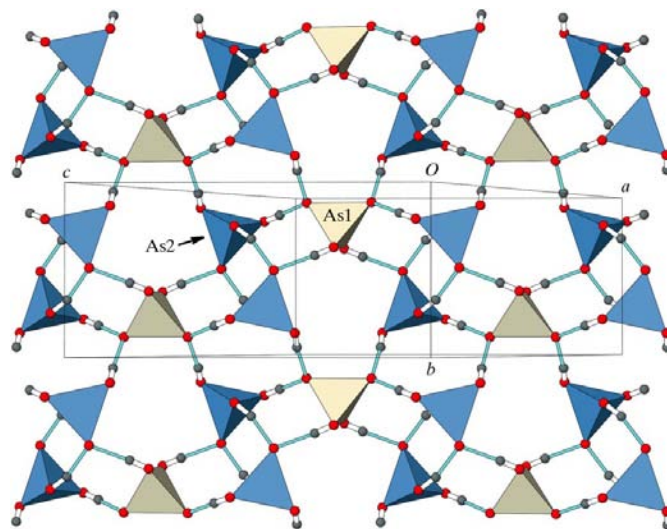


Figure 2
Part of a hydrogen-bonded sheet of tetrahedra in (I), shown in polyhedral representation, with the inter-tetrahedral hydrogen bonds shown as thin lines.

H···O hydrogen bonds and accepting two O—H···O bonds, into a sheet of tetrahedra propagating in (001) (Fig. 2). A number of unusual graph-set (Bernstein *et al.*, 1995) loops occur within these arsenate sheets, including $R_3^2(10)$, $R_4^2(12)$ and $R_4^1(16)$ circuits, as well as the more familiar $R_2^2(8)$ inversion dimer arising from the As2 units.

The arsenate sheets sandwich the disordered organic cations in (I) (Fig. 3), resulting in alternating inorganic and organic layers with respect to the *c* direction.

Compound (II) contains 1,4-diazoniabicyclo[2.2.2]octane dications ($C_2H_{14}N_2^{2+}$) accompanied by dihydrogenarsenate anions and arsenic acid molecules (Fig. 4), with all atoms occupying general crystallographic positions. Because the organic cation is divalent, a 1:2:1 ratio of $C_2H_{14}N_2^{2+}:H_2AsO_4^-:H_3AsO_4$ arises in (II). As in (I), the individual arsenate As—O bond lengths correlate with their protonation state (Table 3). The mean As—O distances for the As1, As2 and As3 (arsenic acid) tetrahedra are 1.679 (2), 1.681 (2) and 1.674 (2) Å, respectively

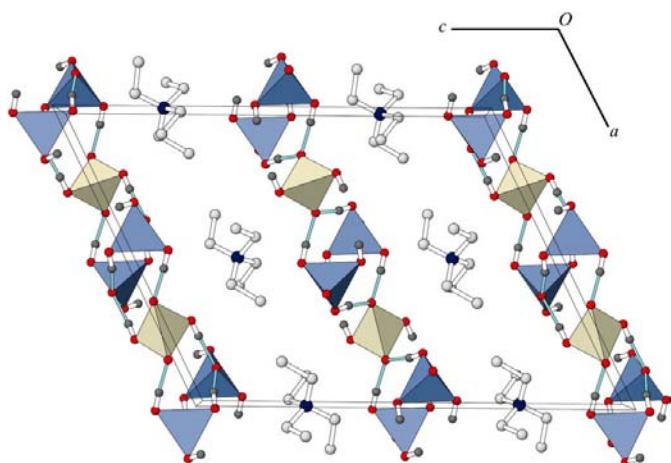


Figure 3
The packing in (I), viewed down [010], with the H atoms of the organic species omitted for clarity and hydrogen bonds indicated by thin bonds. Only one disorder component of each cation is shown.

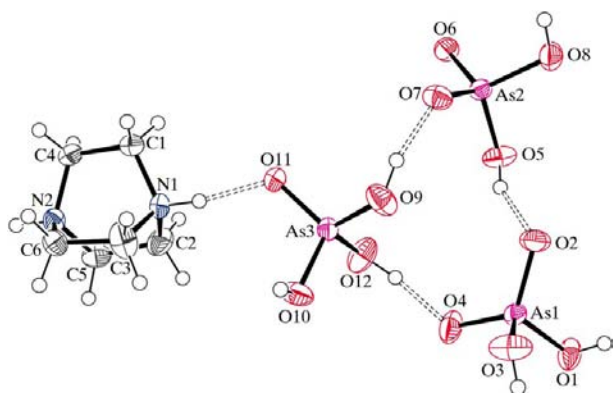


Figure 4
The molecular structure of (II) (50% probability displacement ellipsoids and H atoms drawn as spheres of arbitrary radii). Hydrogen bonds are indicated by dashed lines. Note the distinctive ‘three-ring’ of tetrahedra, leading to an $R_3^3(12)$ loop.

In (II), the As2-centred dihydrogenarsenate groups form inversion dimers *via* O—H···O hydrogen bonds, which contrasts with (I), where the arsenic acid molecules formed similar dimers. The dimers are fused by further O—H···O hydrogen bonds (Table 4) to form chains of alternating As1- and As3-centred units, resulting in slabs of tetrahedra propagating in [100] (Fig. 5). The graph-set loops found within the

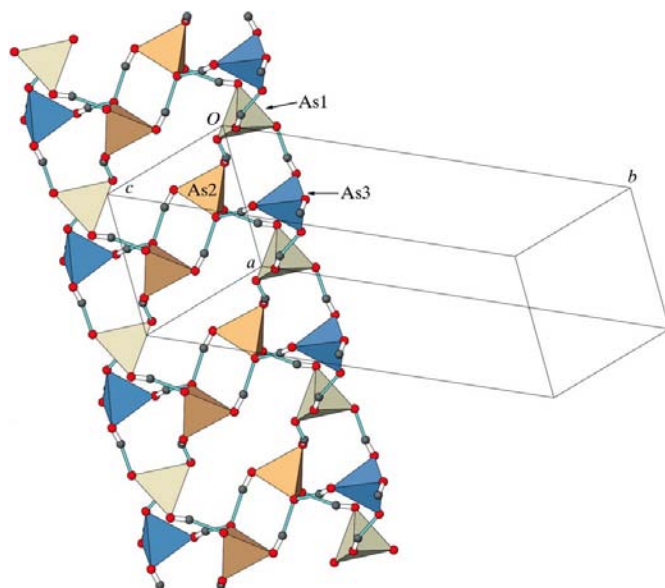


Figure 5
Part of a hydrogen-bonded [100] slab of tetrahedra in (II), shown in polyhedral representation, with the inter-tetrahedral O—H···O hydrogen bonds shown as thin bonds.

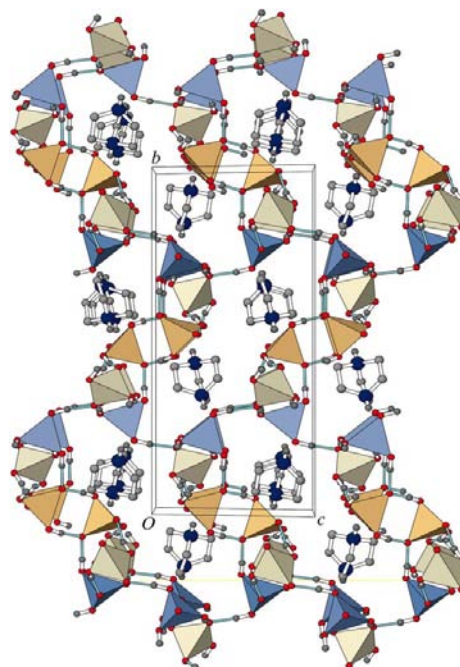


Figure 6
The packing in (I), viewed down [100], with the H atoms of the organic species omitted for clarity.

arsenate slabs in (II) include $R_2^2(8)$ inversion dimers, and $R_3^2(12)$, $R_3^3(12)$ and large $R_6^6(24)$ circuits.

The [100] slabs are crosslinked by the key O10—H10...O4ⁱⁱⁱ bond (Table 4), resulting in a three-dimensional hydrogen-bonded network encompassing [100] channels occupied by the organic cations (Fig. 6). These very large channels can accommodate two organic cations side-by-side and are characterized by an $R_{12}^8(40)$ graph-set motif. In turn, the cations interact with the tetrahedral framework by way of N—H...O hydrogen bonds (Table 4). A related supramolecular hydrogen-bonded tetrahedral framework encapsulating organic cations was seen in 2-aminopyridinium dihydrogenphosphate (Czapla *et al.*, 2003).

Experimental

For (I), 10 ml each of 0.5 mol dm⁻³ aqueous solutions of tetraethylammonium hydroxide (TEAOH) and arsenic acid were mixed in a Petri dish, resulting in a clear solution. Colourless rods and bars of (I) grew over a period of a few days as the water evaporated. For (II), a 0.5 mol dm⁻³ aqueous 1,4-diazabicyclo[2.2.2]octane solution (10 ml) replaced the TEAOH solution, and colourless blocks of (II) were formed using the same experimental procedure as for (I).

Compound (I)

Crystal data

(C₈H₂₀N)[H₂AsO₄][H₃AsO₄]₂
 $M_r = 555.08$
 Monoclinic, $C2/c$
 $a = 20.0518$ (13) Å
 $b = 7.3138$ (4) Å
 $c = 15.251$ (1) Å
 $\beta = 115.969$ (1)°

$V = 2010.7$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 5.01$ mm⁻¹
 $T = 293$ (2) K
 $0.25 \times 0.08 \times 0.06$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.360$, $T_{\max} = 0.739$

9940 measured reflections
 3610 independent reflections
 2301 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.066$
 $S = 0.86$
 3610 reflections

130 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.65$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.43$ e Å⁻³

Table 1

Selected bond lengths (Å) for (I).

As1—O1	1.6510 (15)	As2—O5	1.6797 (16)
As1—O2	1.6982 (17)	As2—O3	1.6895 (17)
As2—O4	1.6454 (15)	As2—O6	1.6985 (16)

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H1...O4 ⁱⁱⁱ	0.85	1.79	2.642 (2)	175
O3—H2...O1	0.90	1.65	2.547 (2)	176
O5—H3...O1 ^{iv}	0.88	1.70	2.564 (2)	168
O6—H4...O4 ^v	0.93	1.71	2.617 (2)	164

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

Compound (II)

Crystal data

(C₆H₁₄N₂)[H₂AsO₄]₂[H₃AsO₄]
 $M_r = 538.01$
 Monoclinic, $P2_1/n$
 $a = 8.1285$ (3) Å
 $b = 22.2104$ (9) Å
 $c = 10.0056$ (4) Å
 $\beta = 107.637$ (1)°

$V = 1721.47$ (12) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 5.85$ mm⁻¹
 $T = 293$ (2) K
 $0.24 \times 0.20 \times 0.14$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.297$, $T_{\max} = 0.441$

17889 measured reflections
 6212 independent reflections
 4321 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.056$
 $S = 0.89$
 6212 reflections

209 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.64$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³

Table 3

Selected bond lengths (Å) for (II).

As1—O2	1.6483 (15)	As2—O5	1.6896 (16)
As1—O4	1.6585 (16)	As2—O8	1.7163 (15)
As1—O3	1.7037 (17)	As3—O11	1.6365 (14)
As1—O1	1.7045 (15)	As3—O12	1.6793 (17)
As2—O6	1.6571 (14)	As3—O9	1.6871 (16)
As2—O7	1.6608 (16)	As3—O10	1.6928 (15)

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O6 ⁱ	0.89	1.70	2.557 (2)	163
O3—H3...O11 ⁱ	0.83	1.83	2.638 (2)	163
O5—H5...O2	0.91	1.64	2.487 (2)	154
O8—H8...O7 ⁱⁱ	0.90	1.77	2.666 (2)	170
O9—H9...O7	0.92	1.62	2.526 (2)	167
O10—H10...O4 ⁱⁱⁱ	0.96	1.63	2.578 (3)	171
O12—H12...O4	0.89	1.64	2.523 (2)	171
N1—H13...O11	0.91	1.72	2.610 (2)	167
N2—H14...O6 ^{iv}	0.91	1.81	2.655 (2)	154

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

The methylene groups of the organic molecule in (I) are disordered over two conformations, which are required to have equal occupancies by symmetry. Their H atoms were placed geometrically (C—H = 0.97 Å) and refined as riding. The H atoms of the terminal methyl groups were placed in two orientations (C—H = 0.92–0.98 Å), in order to achieve reasonable C—C—H angles for both disorder components of the bridging methylene groups, and refined as riding. For (II), the C- and N-bound H atoms were positioned geometrically (C—H = 0.97 Å and N—H = 0.91 Å) and refined as riding. For both (I) and (II), the O-bound H atoms were located in difference maps and refined as riding in the positions found from the difference maps, giving a range of O—H distances of 0.83–0.96 Å. For both (I) and (II), $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{carrier})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

For both compounds, 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) and *ATOMS* (Shape Software, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3110). Services for accessing these data are described at the back of the journal.

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