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## Key indicators

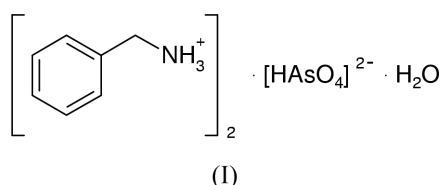
Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å  
Disorder in main residue  
 $R$  factor = 0.045  
 $wR$  factor = 0.112  
Data-to-parameter ratio = 24.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis(benzylammonium) hydrogenarsenate  
monohydrate

The title compound,  $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2[\text{HAsO}_4]\cdot\text{H}_2\text{O}$ , contains a network of benzylammonium cations, hydrogenarsenate anions [ $d_{\text{av}}(\text{As}-\text{O}) = 1.689$  (2) Å] and water molecules. The crystal packing involves  $\text{N}-\text{H}\cdots\text{O}$  [ $d_{\text{av}}(\text{H}\cdots\text{O}) = 1.91$  Å,  $\theta_{\text{av}}(\text{N}-\text{H}\cdots\text{O}) = 167^\circ$  and  $d_{\text{av}}(\text{N}\cdots\text{O}) = 2.794$  (3) Å] and  $\text{O}-\text{H}\cdots\text{O}$  [ $d_{\text{av}}(\text{H}\cdots\text{O}) = 1.83$  Å,  $\theta_{\text{av}}(\text{O}-\text{H}\cdots\text{O}) = 173^\circ$  and  $d_{\text{av}}(\text{O}\cdots\text{O}) = 2.729$  (3) Å] hydrogen bonds, resulting in a layered structure.

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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 crystal structures of (protonated) amine phosphates (Demir *et al.*, 2003), phosphites (Harrison, 2003), selenites (Ritchie & Harrison, 2003) and arsenates (Lee & Harrison, 2003).



The crystal structure of (I) contains two unique  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+$  benzylammonium cations, one unique  $[\text{HAsO}_4]^{2-}$  hydrogenarsenate anion and one unique water molecule. The phenyl ring of the N2 benzylammonium species is disordered over two orientations twisted approximately about the  $\text{C}8-\text{C}9a/b\cdots\text{C}12a/b$  axis [dihedral angle between the ring planes =  $29.6^\circ$ ; relative populations = 0.597 (7):0.403 (7) for the  $\text{C}9-\text{C}14$  atoms with suffixes *a* and *b*, respectively]. Otherwise, the geometrical parameters for the organic species are not significantly different from those of the same cation in the non-linear optical material benzyl-

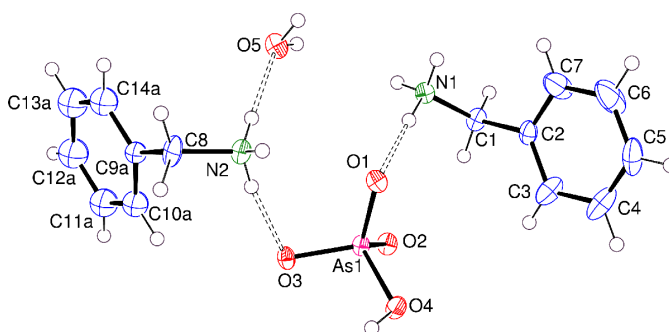
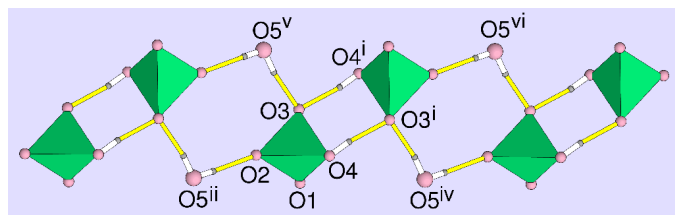
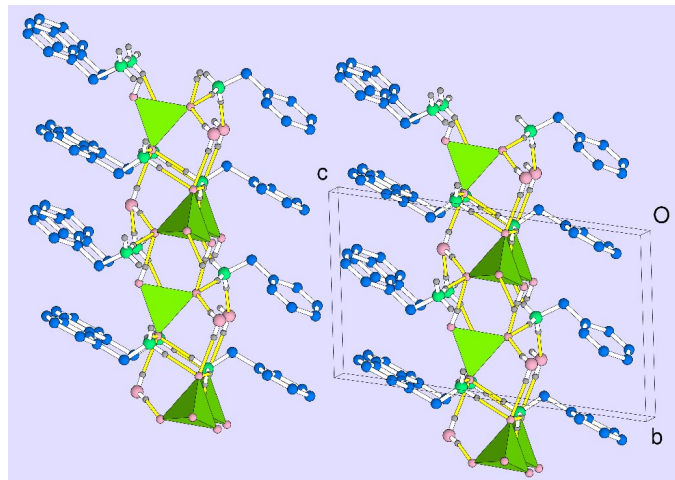


Figure 1

The asymmetric unit of (I) (50% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radii and hydrogen bonds are indicated by dashed lines. Only one orientation of the disordered phenyl ring of the N2-cation is shown.



**Figure 2**  
Detail of a hydrogen-bonded hydrogenarsenate/water chain in (I). Colour key:  $[\text{HAsO}_4]^{2-}$  tetrahedra green, O atoms rose and H atoms grey. The  $\text{H}\cdots\text{O}$  portions of the hydrogen bonds are highlighted in yellow. Symmetry labels as in Table 2; additionally, (v)  $1+x, y, z$ ; (vi)  $1+x, 1+y, z$ .



**Figure 3**  
[100] projection of (I). Colour key as in Fig. 2; additionally, C atoms blue and N atoms green. C—H atoms have been omitted for clarity. The  $\text{H}\cdots\text{O}$  portions of the hydrogen bonds are highlighted in yellow.

ammonium dihydrogenphosphate,  $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)[\text{H}_2\text{PO}_4]$  (Aakeroy *et al.*, 1989).

The  $[\text{HAsO}_4]^{2-}$  hydrogenarsenate group in (I) shows its standard (Lee & Harrison, 2003) tetrahedral geometry [ $d_{\text{av}}(\text{As—O}) = 1.689(2) \text{ \AA}$  and  $\theta_{\text{av}}(\text{O—As—O}) = 109.4(1)^\circ$ ], with the protonated As—O4 vertex showing its expected lengthening relative to the other As—O bonds.

As well as electrostatic attractions, the component species in (I) interact by means of a network of  $\text{N—H}\cdots\text{O}$  and  $\text{O—H}\cdots\text{O}$  links (Table 2). The  $[\text{HAsO}_4]^{2-}$  units and the water molecule (atom O5) are linked into a polymeric chain in the [010] direction by hydrogen bonds (Fig. 2). Inversion symmetry generates linked pairs of  $[\text{HAsO}_4]^{2-}$  units (by way of two  $\text{O4—H1}\cdots\text{O3}$  bonds) which, in turn, are bridged by pairs of water molecules. The hydrogen-bonding scheme in propane-1,2-diammonium hydrogenarsenate monohydrate (Lee & Harrison, 2003) led to a quite different arrangement of  $[\text{HAsO}_4]^{2-}$  and  $\text{H}_2\text{O}$  units. In 4-carboxyanilinium dihydrogenarsenate monohydrate (Tordjman *et al.*, 1988), hydrogen bonding between the  $[\text{H}_2\text{AsO}_4]^-$  and  $\text{H}_2\text{O}$  species results in a sheet structure, but otherwise structural data are lacking for these systems.

The organic species interact with the hydrogenarsenate/water chains by way of  $\text{N—H}\cdots\text{O—As}$  hydrogen bonds (Table 2). All six of the  $\text{NH}_3^+$  H atoms are involved in these

links [ $d_{\text{av}}(\text{H}\cdots\text{O}) = 1.91 \text{ \AA}$ ,  $\theta_{\text{av}}(\text{N—H}\cdots\text{O}) = 167^\circ$  and  $d_{\text{av}}(\text{N}\cdots\text{O}) = 2.794(3) \text{ \AA}$ ]. This results in (001) hydrogenarsenate/water/ammonium layers sandwiched between the benzyl moieties (Fig. 3) which, in turn, interact by way of van der Waals forces. A *PLATON* (Spek, 2003) analysis of (I) indicated that the minimum separation between phenyl ring centroids is  $4.06 \text{ \AA}$ ; therefore, any  $\pi$ – $\pi$  stacking interactions in (I) are extremely weak.

## Experimental

4 ml of a 1 M benzylamine aqueous solution was added to 8 ml of a 0.5 M  $\text{H}_3\text{AsO}_4$  aqueous solution, resulting in a brown solution. A mass of plate-shaped slightly translucent crystals of (I) grew as the water evaporated over the course of a few days.

### Crystal data

|   |   |
|---|---|
| $(\text{C}_7\text{H}_{10}\text{N})_2[\text{HAsO}_4]\cdot\text{H}_2\text{O}$ | $Z = 2$                                   |
| $M_r = 374.26$  | $D_x = 1.483 \text{ Mg m}^{-3}$           |
| Triclinic, $P\bar{1}$   | Mo $K\alpha$ radiation                    |
| $a = 6.4400(2) \text{ \AA}$   | Cell parameters from 24 435 reflections   |
| $b = 8.9128(3) \text{ \AA}$   | $\theta = 2.9\text{--}27.5^\circ$         |
| $c = 14.9957(5) \text{ \AA}$  | $\mu = 2.05 \text{ mm}^{-1}$              |
| $\alpha = 99.7048(11)^\circ$  | $T = 120(2) \text{ K}$                    |
| $\beta = 93.1574(12)^\circ$   | Plate, colourless                         |
| $\gamma = 97.7776(18)^\circ$  | $0.35 \times 0.12 \times 0.03 \text{ mm}$ |
| $V = 837.93(5) \text{ \AA}^3$   |   |

### Data collection

|  |  |
|--|--|
| Enraf–Nonius KappaCCD diffractometer                       | 3846 independent reflections           |
| $\omega$ and $\varphi$ scans                               | 3538 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SORTAV; Blessing, 1995) | $R_{\text{int}} = 0.122$               |
| $T_{\text{min}} = 0.534$ , $T_{\text{max}} = 0.941$        | $\theta_{\text{max}} = 27.5^\circ$     |
| 18 359 measured reflections                                | $h = -8 \rightarrow 8$                 |
|  | $k = -11 \rightarrow 11$               |
|  | $l = -19 \rightarrow 19$               |

### Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 2.1999P]$    |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $wR(F^2) = 0.112$               | $(\Delta/\sigma)_{\text{max}} = 0.001$               |
| $S = 1.02$                      | $\Delta\rho_{\text{max}} = 1.39 \text{ e \AA}^{-3}$  |
| 3846 reflections                | $\Delta\rho_{\text{min}} = -0.69 \text{ e \AA}^{-3}$ |
| 158 parameters                  | Extinction correction: <i>SHELXL97</i>               |
| H-atom parameters constrained   | Extinction coefficient: 0.021(2)                     |

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ).

|        |          |        |          |
|--------|----------|--------|----------|
| As1—O1 | 1.666(2) | As1—O3 | 1.681(2) |
| As1—O2 | 1.675(2) | As1—O4 | 1.732(2) |

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

| $D\text{—H}\cdots A$             | $D\text{—H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D\text{—H}\cdots A$ |
|----------------------------------|--------------|--------------------|-------------|----------------------|
| O4—H1 $\cdots$ O3 <sup>i</sup>   | 0.89         | 1.74               | 2.632(3)    | 173                  |
| N1—H4 $\cdots$ O2 <sup>ii</sup>  | 0.91         | 1.94               | 2.830(3)    | 166                  |
| N1—H5 $\cdots$ O2 <sup>iii</sup> | 0.91         | 1.99               | 2.843(3)    | 155                  |
| N1—H6 $\cdots$ O1                | 0.91         | 1.80               | 2.704(3)    | 174                  |
| N2—H7 $\cdots$ O1 <sup>iv</sup>  | 0.91         | 1.86               | 2.731(3)    | 161                  |
| N2—H8 $\cdots$ O5                | 0.91         | 1.92               | 2.823(3)    | 174                  |
| N2—H9 $\cdots$ O3                | 0.91         | 1.94               | 2.835(3)    | 169                  |
| O5—H2 $\cdots$ O3 <sup>iii</sup> | 0.96         | 1.78               | 2.731(3)    | 171                  |
| O5—H3 $\cdots$ O2 <sup>ii</sup>  | 0.85         | 1.98               | 2.825(2)    | 176                  |

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

The C atoms forming the two orientations of the disordered phenyl group (atoms C9a–C14a and C9b–C14b) were constrained to lie at the vertices of regular hexagons, with  $d(\text{C}–\text{C}) = 1.39 \text{ \AA}$ , and were refined isotropically. The O–H H atoms were found in difference maps and refined as riding, starting from these positions. The H atoms bonded to C and N atoms were placed in calculated positions [ $d(\text{C}–\text{H}) = 0.95–0.99 \text{ \AA}$  and  $d(\text{N}–\text{H}) = 0.91 \text{ \AA}$ ] and refined as riding, allowing free rotation of the rigid  $R–\text{NH}_3$  groups about the  $R–\text{N}$  bonds. The constraint  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$  was applied in all cases. The highest difference peak is  $0.54 \text{ \AA}$  from C12b and the deepest difference hole is  $0.79 \text{ \AA}$  from As1.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*, and *SORTAV* (Blessing, 1995); 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, 1999); software used to prepare material for publication: *SHELXL97*.

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## References

- Aakeroy, C. B., Hitchcock, P. B., Moyle, B. D., Seddon, K. R. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1856–1859.
- Blessing, R. H. (1995). *Acta Cryst.* **E51**, 33–38.
- Demir, S., Yilmaz, V. T. & Harrison, W. T. A. (2003). *Acta Cryst.* **E59**, o907–o909.
- Enraf–Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Harrison, W. T. A. (2003). *Acta Cryst.* **E59**, o1267–o1269.
- Lee, C. & Harrison, W. T. A. (2003). *Acta Cryst.* **E59**, m739–m741.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Ritchie, L. K. & Harrison, W. T. A. (2003). *Acta Cryst.* **E59**, o1296–o1298.
- Shape Software (1999). *ATOMS*. Shape Software, 525 Hidden Valley Road, Kingsport, Tennessee, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Tordjman, I., Masse, R. & Guitel, J. C. (1988). *Acta Cryst.* **C44**, 2057–2059.