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Key indicators

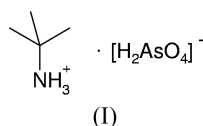
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.024
 wR factor = 0.064
Data-to-parameter ratio = 33.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*tert*-Butylammonium dihydrogenarsenate

The title compound, $(\text{C}_4\text{H}_{12}\text{N})[\text{H}_2\text{AsO}_4]$, contains a network of *tert*-butylammonium cations and dihydrogenarsenate anions [$d_{\text{av}}(\text{As}-\text{O}) = 1.682(2)$ Å]. The crystal packing involves $\text{N}-\text{H}\cdots\text{O}$ [$d_{\text{av}}(\text{H}\cdots\text{O}) = 1.96$ Å, $\theta_{\text{av}}(\text{N}-\text{H}\cdots\text{O}) = 169^\circ$ and $d_{\text{av}}(\text{N}\cdots\text{O}) = 2.837(3)$ Å] and $\text{O}-\text{H}\cdots\text{O}$ [$d_{\text{av}}(\text{H}\cdots\text{O}) = 1.68$ Å, $\theta_{\text{av}}(\text{O}-\text{H}\cdots\text{O}) = 169^\circ$ and $d_{\text{av}}(\text{O}\cdots\text{O})$ 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 structural studies of hydrogen-bonding interactions in protonated amine (di)hydrogen arsenates (Lee & Harrison, 2003*a,b,c*).



The $[\text{H}_2\text{AsO}_4]^-$ dihydrogenarsenate group in (I) shows its normal tetrahedral geometry [$d_{\text{av}}(\text{As}-\text{O}) = 1.682(2)$ Å], with the protonated As1—O3 and As1—O4 vertices showing their expected lengthening relative to the unprotonated As—O bonds, which have formal partial double-bond character (Table 1). The *tert*-butylammonium cation shows no unusual geometrical features.

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 chains propagating along [010] by way of inversion-generated pairs of $\text{O}-\text{H}\cdots\text{O}$ bonds, alternately involving O3—H1 \cdots O1

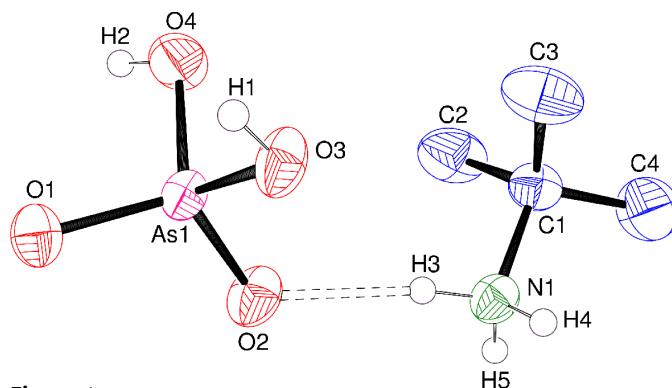
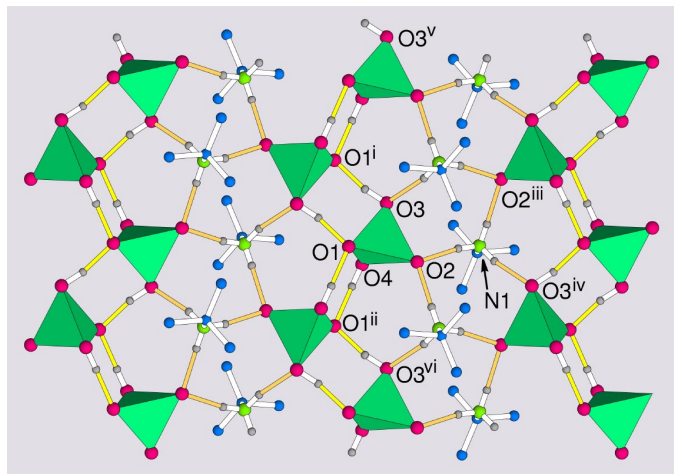


Figure 1

The asymmetric unit of (I) (50% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius and the hydrogen bond is indicated by a dashed line. C—H H atoms have been omitted for clarity.


Figure 2

Detail of a hydrogen-bonded dihydrogenarsenate/*tert*-butylammonium sheet in (I). Colour key: $[\text{H}_2\text{AsO}_4]^-$ tetrahedra green, O atoms red, H atoms grey, C atoms blue, N atoms green (all radii arbitrary). The $\text{H}\cdots\text{O}$ portions of the $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are highlighted in yellow and orange, respectively. Symmetry codes as in Table 2; additionally, (v) $x, y - 1, z$; (vi) $x, 1 + y, z$.

and $\text{O}4-\text{H}2\cdots\text{O}1$ links (Fig. 2). This results in every $[\text{H}_2\text{AsO}_4]^-$ tetrahedron in the chain making one hydrogen bond to each of its neighbours and accepting one hydrogen bond from each neighbour. The $\text{As}\cdots\text{As}^i$ (via $\text{O}3-\text{H}1\cdots\text{O}1^i$) and $\text{As}\cdots\text{As}^{ii}$ (via $\text{O}4-\text{H}2\cdots\text{O}1^{ii}$) separations are 4.3002 (4) and 4.2662 (3) Å, respectively (see Table 2 for symmetry codes). Similar hydrogen-bonded chains of $[\text{H}_2\text{AsO}_4]^-$ anions have been seen in piperidinium dihydrogenarsenate, $(\text{C}_5\text{H}_{12}\text{N})[\text{H}_2\text{AsO}_4]$ (Lee & Harrison, 2003*b*), although in this case they are generated by a 2_1 screw axis.

As shown in Table 2, the organic species interacts with the dihydrogenarsenate chains by way of three $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds [$d_{\text{av}}(\text{H}\cdots\text{O}) = 1.96$ Å, $\theta_{\text{av}}(\text{N}-\text{H}\cdots\text{O}) = 169^\circ$ and $d_{\text{av}}(\text{N}\cdots\text{O}) = 2.837$ (3) Å], such that each *tert*-butylammonium cation cross-links a dihydrogenarsenate chain to its neighbour by forming two hydrogen bonds to one chain, and one to the other. This results in neutral (101) layers (Fig. 3) of stoichiometry $(\text{C}_4\text{H}_{12}\text{N})[\text{H}_2\text{AsO}_4]$, which interact with each other by van der Waals forces.

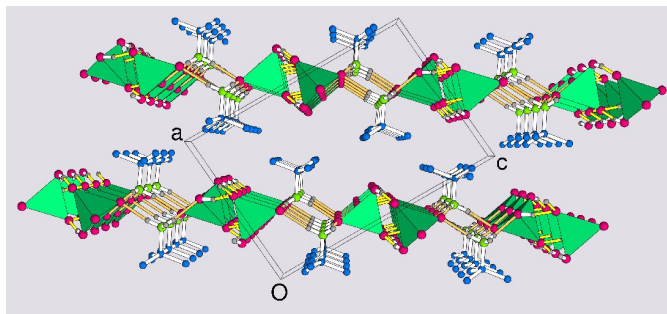
Experimental

An aqueous *tert*-butylamine solution (10 ml of 0.5 *M*) was added to a H_3AsO_4 solution (10 ml of 0.5 *M*), resulting in a clear solution. A mass of plate-shaped and rod-like crystals of (I) grew as the water evaporated over the course of a few days.

Crystal data

$(\text{C}_4\text{H}_{12}\text{N})[\text{H}_2\text{AsO}_4]$
 $M_r = 215.08$
 Monoclinic, $P2_1/n$
 $a = 9.7364$ (5) Å
 $b = 6.3254$ (3) Å
 $c = 14.2606$ (8) Å
 $\beta = 94.864$ (1)°
 $V = 875.10$ (8) Å³
 $Z = 4$

$D_x = 1.633$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3025 reflections
 $\theta = 2.4-32.4^\circ$
 $\mu = 3.85$ mm⁻¹
 $T = 293$ (2) K
 Bar, colourless
 $0.55 \times 0.15 \times 0.05$ mm


Figure 3

Projection of (I) onto (010). The colour key is as in Fig. 2.

Data collection

Bruker SMART1000 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\text{min}} = 0.226$, $T_{\text{max}} = 0.831$
 8742 measured reflections

3165 independent reflections
 1807 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 32.5^\circ$
 $h = -10 \rightarrow 14$
 $k = -7 \rightarrow 9$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.064$
 $S = 0.88$
 3165 reflections
 95 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0332P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Table 1

Selected bond distances (Å).

As1—O2	1.6412 (13)	As1—O3	1.7061 (13)
As1—O1	1.6687 (13)	As1—O4	1.7101 (14)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}3-\text{H}1\cdots\text{O}1^i$	0.97	1.62	2.5752 (19)	166
$\text{O}4-\text{H}2\cdots\text{O}1^{ii}$	0.94	1.74	2.6763 (19)	172
$\text{N}1-\text{H}3\cdots\text{O}2$	0.89	1.92	2.801 (2)	168
$\text{N}1-\text{H}4\cdots\text{O}2^{iii}$	0.89	1.88	2.765 (2)	173
$\text{N}1-\text{H}5\cdots\text{O}3^{iv}$	0.89	2.07	2.944 (2)	166

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

The $\text{O}-\text{H}$ H atoms were found in difference maps and refined by riding on their carrier O atoms in their as-found relative positions. H atoms bonded to C and N atoms were placed in calculated positions [$d(\text{C}-\text{H}) = 0.96$ Å and $d(\text{N}-\text{H}) = 0.89$ Å] and refined as riding, with the rigid NH_3 or CH_3 groups allowed to freely rotate about the bond joining the atoms in question to atom C1. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O or N parent atom})$ or $1.5U_{\text{eq}}(\text{methyl C parent atom})$ was applied as appropriate.

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

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supporting information

Acta Cryst. (2004). E60, m1359–m1361 [https://doi.org/10.1107/S1600536804020963]

***tert*-Butylammonium dihydrogenarsenate**

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tert*-Butylammonium dihydrogenarsenateCrystal data*

(C₄H₁₂N)[H₂AsO₄]

M_r = 215.08

Monoclinic, *P*2₁/*n*

Hall symbol: -*P* 2₁*y**n*

a = 9.7364 (5) Å

b = 6.3254 (3) Å

c = 14.2606 (8) Å

β = 94.864 (1)°

V = 875.10 (8) Å³

Z = 4

F(000) = 440

D_x = 1.633 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3025 reflections

θ = 2.4–32.4°

μ = 3.85 mm⁻¹

T = 293 K

Bar, colourless

0.55 × 0.15 × 0.05 mm

Data collection

Bruker SMART1000 CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 1999)

T_{min} = 0.226, *T_{max}* = 0.831

8742 measured reflections

3165 independent reflections

1807 reflections with *I* > 2σ(*I*)

R_{int} = 0.023

θ_{\max} = 32.5°, θ_{\min} = 2.4°

h = -10→14

k = -7→9

l = -21→21

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.024

wR(*F*²) = 0.064

S = 0.88

3165 reflections

95 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difmap (O-H) and geom
(C-H and N-H)

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0332*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.47 e Å⁻³

Δρ_{min} = -0.51 e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	0.096480 (18)	0.25182 (3)	0.428460 (11)	0.02877 (6)
O1	-0.07070 (14)	0.2606 (2)	0.44605 (10)	0.0360 (3)
O2	0.13620 (15)	0.3528 (2)	0.32825 (9)	0.0424 (4)
O3	0.15368 (15)	-0.0032 (2)	0.43072 (9)	0.0402 (3)
H1	0.1102	-0.0863	0.4773	0.048*
O4	0.18923 (15)	0.3676 (3)	0.52194 (10)	0.0482 (4)
H2	0.1545	0.5006	0.5378	0.058*
N1	0.38027 (16)	0.2563 (2)	0.24651 (10)	0.0334 (3)
H3	0.3062	0.2725	0.2783	0.040*
H4	0.3824	0.1249	0.2243	0.040*
H5	0.3766	0.3474	0.1988	0.040*
C1	0.5091 (2)	0.2971 (3)	0.31140 (15)	0.0380 (5)
C2	0.4956 (3)	0.5164 (4)	0.35241 (18)	0.0608 (7)
H6	0.4147	0.5224	0.3865	0.091*
H7	0.4880	0.6185	0.3024	0.091*
H8	0.5755	0.5471	0.3943	0.091*
C3	0.5148 (3)	0.1313 (4)	0.38747 (18)	0.0643 (7)
H9	0.5211	-0.0062	0.3597	0.097*
H10	0.4328	0.1392	0.4203	0.097*
H11	0.5940	0.1553	0.4309	0.097*
C4	0.6306 (3)	0.2805 (4)	0.2525 (2)	0.0677 (8)
H12	0.6329	0.1418	0.2254	0.102*
H13	0.7143	0.3051	0.2916	0.102*
H14	0.6217	0.3842	0.2032	0.102*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.03246 (9)	0.02705 (9)	0.02761 (8)	0.00106 (11)	0.00722 (6)	-0.00055 (9)
O1	0.0324 (6)	0.0318 (7)	0.0448 (7)	0.0000 (7)	0.0090 (5)	0.0018 (7)
O2	0.0539 (10)	0.0385 (9)	0.0368 (8)	0.0031 (7)	0.0162 (7)	0.0104 (6)
O3	0.0507 (9)	0.0294 (7)	0.0433 (8)	0.0085 (7)	0.0196 (6)	0.0027 (6)
O4	0.0452 (9)	0.0500 (10)	0.0474 (9)	0.0071 (8)	-0.0072 (7)	-0.0177 (7)
N1	0.0389 (8)	0.0304 (7)	0.0312 (7)	0.0000 (9)	0.0053 (6)	0.0001 (8)
C1	0.0392 (11)	0.0367 (12)	0.0371 (10)	-0.0018 (8)	-0.0017 (8)	0.0006 (7)
C2	0.0685 (18)	0.0454 (14)	0.0640 (16)	-0.0033 (13)	-0.0198 (13)	-0.0125 (12)
C3	0.0716 (19)	0.0592 (17)	0.0592 (16)	-0.0032 (15)	-0.0123 (13)	0.0228 (14)
C4	0.0391 (12)	0.099 (2)	0.0653 (16)	-0.0058 (14)	0.0064 (11)	-0.0033 (15)

Geometric parameters (\AA , $^\circ$)

As1—O2	1.6412 (13)	C1—C4	1.511 (3)
As1—O1	1.6687 (13)	C1—C2	1.515 (3)
As1—O3	1.7061 (13)	C2—H6	0.9600
As1—O4	1.7101 (14)	C2—H7	0.9600
O3—H1	0.9710	C2—H8	0.9600
O4—H2	0.9415	C3—H9	0.9600
N1—C1	1.516 (3)	C3—H10	0.9600
N1—H3	0.8900	C3—H11	0.9600
N1—H4	0.8900	C4—H12	0.9600
N1—H5	0.8900	C4—H13	0.9600
C1—C3	1.506 (3)	C4—H14	0.9600
O2—As1—O1	115.01 (7)	C2—C1—N1	107.28 (18)
O2—As1—O3	106.49 (7)	C1—C2—H6	109.5
O1—As1—O3	110.46 (7)	C1—C2—H7	109.5
O2—As1—O4	111.36 (8)	H6—C2—H7	109.5
O1—As1—O4	109.03 (7)	C1—C2—H8	109.5
O3—As1—O4	103.90 (7)	H6—C2—H8	109.5
As1—O3—H1	111.3	H7—C2—H8	109.5
As1—O4—H2	113.1	C1—C3—H9	109.5
C1—N1—H3	109.5	C1—C3—H10	109.5
C1—N1—H4	109.5	H9—C3—H10	109.5
H3—N1—H4	109.5	C1—C3—H11	109.5
C1—N1—H5	109.5	H9—C3—H11	109.5
H3—N1—H5	109.5	H10—C3—H11	109.5
H4—N1—H5	109.5	C1—C4—H12	109.5
C3—C1—C4	111.7 (2)	C1—C4—H13	109.5
C3—C1—C2	111.0 (2)	H12—C4—H13	109.5
C4—C1—C2	112.1 (2)	C1—C4—H14	109.5
C3—C1—N1	107.39 (18)	H12—C4—H14	109.5
C4—C1—N1	107.17 (18)	H13—C4—H14	109.5

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1 \cdots O1 ⁱ	0.97	1.62	2.5752 (19)	166
O4—H2 \cdots O1 ⁱⁱ	0.94	1.74	2.6763 (19)	172
N1—H3 \cdots O2	0.89	1.92	2.801 (2)	168
N1—H4 \cdots O2 ⁱⁱⁱ	0.89	1.88	2.765 (2)	173
N1—H5 \cdots O3 ^{iv}	0.89	2.07	2.944 (2)	166

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