Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

A 1:1 adduct of DL-threonine and arsenic acid

Hazel S. Wilkinson and William T. A. Harrison*

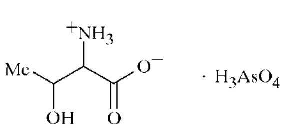
Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen
AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

Received 15 April 2005
Accepted 19 April 2005
Online 13 May 2005

The title compound, DL-threonine–arsenic acid (1/1), $C_4H_9NO_3\cdot H_3AsO_4$, is an unusual adduct containing zwitterionic threonine and neutral arsenic acid molecules. The component species interact by way of N—H···O and O—H···O hydrogen bonds, leading to parallel [001] chains of threonine and arsenic acid molecules which are crosslinked by further O—H···O and N—H···O bonds, resulting in a three-dimensional network.

Comment

Only a handful of crystal structures conaining the neutral arsenic acid (H_3AsO_4) moiety have been determined, including *N*,*N*,*N*-trimethylglycine (beatine) arsenic acid (Schildkamp *et al.*, 1984), tetraphenylphosphonium chloride arsenic acid (Ruhlandt-Senge *et al.*, 1992) and L-histininium dihydrogen arsenate arsenic acid (Ratajczak *et al.*, 2000). We present here the synthesis and structure of the title compound, $C_4H_9NO_3\cdot H_3AsO_4$, (I) (Fig. 1), an unusual 1:1 adduct of neutral DL-threonine (*threo*-α-amino-β-hydroxy-*n*-butyric acid) and arsenic acid moieties.



(I)

The H_3AsO_4 arsenic acid molecule in (I) shows its normal tetrahedral geometry about As [mean As—O = 1.680 (2) Å], with the unprotonated formal As1═O4 double bond showing its expected (Lee & Harrison, 2003*a*) shortening relative to the three As—OH vertices (Table 1).

Each threonine molecule is chiral (the arbitrarily chosen asymmetric unit molecule has an *S* conformation at C2 and an *R* conformation at C3), but space-group symmetry generates a 50:50 mix of enantiomers, which is consistent with the racemic starting material. The DL-threonine entity is zwitterionic (*i.e.* nominal H-atom transfer from O1 or O2 to N1) and the C1—O1 and C1—O2 bond lengths of the delocalized carboxyl group are almost identical (Table 1). It is perhaps surprising that the threonine is not protonated (overall positive charge) under the low pH reaction conditions.

For ease of comparison with other structures, we refer to atoms C2, C3 and C4 as Cα, Cβ and Cγ, respectively, and atom O3 as Oγ. In (I), with respect to N1 and the Cα—Cβ bond, both Cγ and Oγ are *gauche* [torsion angles = −61.4 (3) and 61.5 (3)°, respectively], as are the two H atoms attached to Cα and Cβ (H—Cα—Cβ—H = −62.4°). A similar so-called *gauche*-I/*gauche*-II molecular conformation was seen in DL-threoninium hydrogen phosphate (Ravikumar *et al.*, 2002), with equivalent torsion angles of N1—Cα—Cβ—Cγ = −64.1 (3)°, N1—Cα—Cβ—Oγ = 59.5 (2)° and H—Cα—Cβ—H = −64.4°. By way of contrast, L-threonine (Janczak *et al.*, 1997) has a quite different *trans*(Cγ)/*gauche*(Oγ) conformation about the Cα—Cβ bond, with equivalent angles of N1—Cα—Cβ—Cγ = −174.82 (9)°, N1—Cα—Cβ—Oγ = −54.6 (1)° and H—Cα—Cβ—H = −179.3°. The 'backbone' O2—C1—Cα—N1 (ψ^1) torsion angle in (I) is −12.3 (3)°, which compares well with the value of −7.8 (3)° seen in DL-threoninium hydrogen phosphate (Ravikumar *et al.*, 2002). In L-threonine itself, the carboxyl group is somewhat more twisted about the Cα—C1 bond, yielding (using our atom-numbering scheme) a O2—C1—Cα—N1 torsion angle of −25.3 (2)°. The *gauche*/*gauche* threonine geometry in (I) could be reinforced by the intramolecular N1—H1*B*···O3 and N1—H1*C*···O2 hydrogen bonds (Fig. 1 and Table 2).

As well as van der Waals forces, the component species in (I) interact by means of a network of N—H···O and O—H···O hydrogen bonds (Table 2). It is notable that atom H1*B* is involved in a bifurcated N—H···(O,O) hydrogen bond (angle sum about H1*B* = 360°) and atom H1*C* makes a trifurcated N—H···(O,O,O) link (average angle about H1*C* =

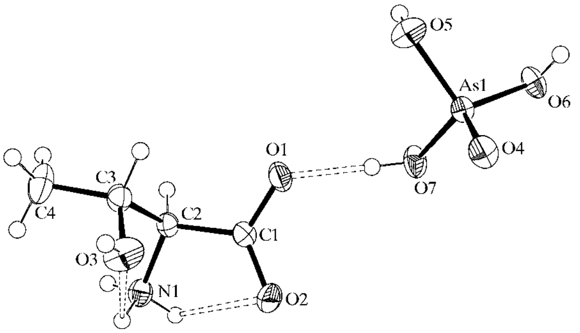


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

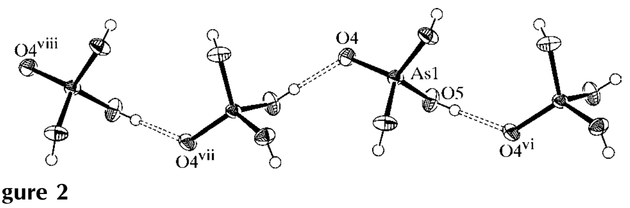


Figure 2
Detail of a hydrogen-bonded arsenic acid chain in (I). [Symmetry codes are as in Table 2, with the addition of (vii) $x, \frac{1}{2} - y, z + \frac{1}{2}$; (viii) $x, y, 1 + z$.]

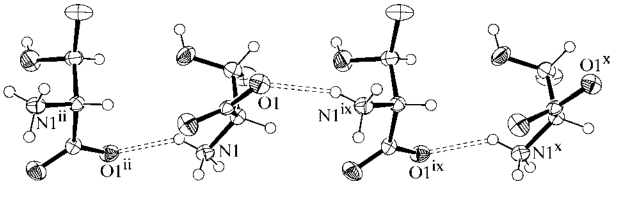


Figure 3
Detail of a hydrogen-bonded DL-threonine chain in (I). Methyl H atoms have been omitted for clarity. [Symmetry codes are as in Table 2, with the addition of (ix) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (x) $x, y, z - 1$.]

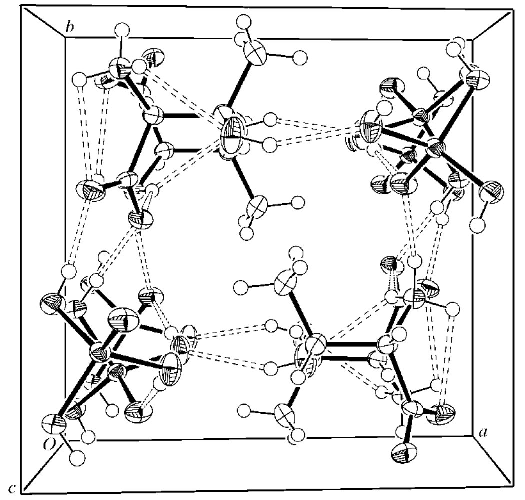


Figure 4
The unit-cell packing in (I) projected down [001], showing the cross-linked stacks of DL-threonine and arsenic acid moieties.

108°). The H_3AsO_4 units are linked into polymeric chains of single tetrahedra propagating along [001] (Fig. 2) by way of the O5—H5$\cdots$O4^{vi} bond (see Table 2 for symmetry code). Adjacent tetrahedra in the chain are thus related by *c*-glide symmetry. The As$\cdots$As^{vi} separation is 4.5516 (5) Å. The other two As—OH vertices (atoms O6 and O7) act as hydrogen-bond donors to carboxyl acceptor O atoms on nearby threonine molecules. The organic species of (I) also forms *c*-glide symmetry-generated chains, *via* N1—H1*B*$\cdots$O1^{ii} (Fig. 3). Adjacent threonine molecules in the [001] chain therefore have opposite chiralities. Finally, the other N—H moieties (N1—H1*B* and N1—H1*C*) and the O3—H3 hydroxyl group make hydrogen bonds to nearby arsenic acid molecules (Table 2), complementing the arsenic acid-to-threonine hydrogen bonds involving atoms H6 and H7 (Fig. 4). All of the O atoms in the structure accept at least one hydrogen bond.

The structure of (I) is quite distinct from those of salt-like ammonium hydrogenarsenates (Lee & Harrison, 2003*a*,*b*,*c*), where H-atom transfer from arsenic acid to amine occurs.

Experimental

Aqueous DL-threonine solution (0.5 *M*, 10 ml) was added to an aqueous H_3AsO_4 solution (0.5 *M*, 10 ml), giving a clear solution. A mass of needles of (I) grew as the water evaporated from the increasingly viscous liquor over the course of a few days.

Crystal data

$C_4H_9NO_3 \cdot H_3AsO_4$
$M_r = 261.07$
Monoclinic, $P2_1/c$
$a = 10.1195$ (6) Å
$b = 9.8062$ (6) Å
$c = 8.9643$ (6) Å
$\beta = 99.098$ (1)°
$V = 878.37$ (10) Å^3
$Z = 4$
$D_x = 1.974$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2540 reflections
$\theta = 2.9$–32.2°
$\mu = 3.88$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.45 × 0.03 × 0.01 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.274$, $T_{max} = 0.962$
7588 measured reflections
3122 independent reflections
2165 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 32.5°$
$h = -14 \rightarrow 15$
$k = -14 \rightarrow 14$
$l = -9 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.087$
$S = 0.94$
3122 reflections
120 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O2	1.263 (3)	As1—O6	1.6769 (19)
C1—O1	1.264 (3)	As1—O7	1.699 (2)
As1—O4	1.639 (2)	As1—O5	1.704 (2)
O2—C1—C2—N1	−12.3 (3)	C1—C2—C3—O3	−59.3 (3)
O1—C1—C2—N1	165.4 (2)	N1—C2—C3—C4	−61.4 (3)
O2—C1—C2—C3	109.0 (3)	C1—C2—C3—C4	177.7 (2)
O1—C1—C2—C3	−73.2 (3)	H2—C2—C3—H3*A*	−62.4
N1—C2—C3—O3	61.5 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N1—H1*A*$\cdots$O4^{i}	0.89	1.92	2.800 (3)	170
N1—H1*B*$\cdots$O1^{ii}	0.89	2.15	2.903 (3)	143
N1—H1*B*$\cdots$O3	0.89	2.38	2.810 (3)	110
N1—H1*C*$\cdots$O7^{iii}	0.89	2.30	3.069 (3)	145
N1—H1*C*$\cdots$O2	0.89	2.33	2.646 (3)	101
N1—H1*C*$\cdots$O6^{iv}	0.89	2.35	2.890 (3)	119
O3—H3$\cdots$O5^{v}	0.82	2.14	2.906 (3)	156
O5—H5$\cdots$O4^{vi}	0.79	1.79	2.580 (3)	179
O6—H6$\cdots$O2^{vi}	0.77	1.76	2.514 (3)	169
O7—H7$\cdots$O1	0.84	1.73	2.569 (3)	179

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

The hydroxy H atoms were found in difference maps and refined as riding on their parent O atoms in their as-found relative positions. H atoms bonded to C and N atoms were placed in idealized positions, with C—H = 0.96–0.98 Å and N—H = 0.89 Å, and refined as riding, with the rigid NH_3 or CH_3 groups allowed to rotate freely about the bond joining the atoms in question to C1. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier) was applied as appropriate.

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); software used to prepare material for publication: *SHELXL97*.

HSW thanks the Carnegie Trust for the Universities of Scotland for an undergraduate vacation studentship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1837). Services for accessing these data are described at the back of the journal.

References

Bruker (1999). *SMART* (Version 5.624), *SAINT* (Version 6.02a) and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Janczak, J., Zobel, D. & Luger, P. (1997). *Acta Cryst.* C**53**, 1901–1904.

Lee, C. & Harrison, W. T. A. (2003*a*). *Acta Cryst.* E**59**, m739–m741.

Lee, C. & Harrison, W. T. A. (2003*b*). *Acta Cryst.* E**59**, m959–m960.

Lee, C. & Harrison, W. T. A. (2003*c*). *Acta Cryst.* E**59**, m1151–m1153.

Ratajczak, H., Barycki, J., Pietraszko, A., Baran, J., Debrus, S., May, M. & Venturini, J. (2000). *J. Mol. Struct.* **526**, 269–278.

Ravikumar, B., Sridhar, B. & Rajaram, R. K. (2002). *Acta Cryst.* E**58**, o1185–o1187.

Ruhlandt-Senge, K., Bacher, A.-D. & Müller, U. (1992). *Z. Naturforsch. Teil B*, **47**, 1677–1680.

Schildkamp, W., Schafer, G. & Spilker, J. (1984). *Z. Kristallogr.* **168**, 187–195.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.