Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Creatininium dihydrogenarsenate

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 17 May 2005
Accepted 20 May 2005
Online 28 May 2005

Key indicators

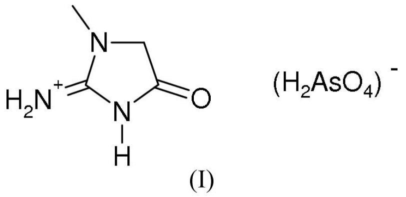
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.069
Data-to-parameter ratio = 26.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_4H_8N_3O)[H_2AsO_4]$, contains a network of creatininium cations and dihydrogenarsenate anions [mean As—O = 1.681 (2) Å]. The crystal packing involves anion-to-anion O—H$\cdots$O, cation-to-anion N—H$\cdots$O and cation-to-cation N—H$\cdots$O hydrogen bonds, resulting in a chain structure.

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 arsenate molecular salts (Wilkinson & Harrison, 2004; Todd & Harrison, 2005). The $[H_2AsO_4]^-$ dihydrogenarsenate group in (I) shows a normal tetrahedral geometry [mean As—O = 1.681 (2) Å], with the protonated As1—O3 and As1—O4 vertices showing their usual lengthening relative to the unprotonated As1—O1 and As1—O2 bonds, which have formal partial double-bond character (Table 1).



(I)

The creatininium cation is approximately planar [r.m.s. deviation for the non-H atoms = 0.031 Å; maximum deviation from the mean plane = 0.0597 (16) Å for N2]. The three C1—N bond distances (Table 1) are distinctly different, with C1—N1 much longer than the other two. This configuration perhaps indicates that the canonical form of the molecule, with a formal double bond in the C1—N1 position and a formal positive charge on N1, is of less importance than the forms that place the double bond in the C1—N2 and C1—N3 positions and the positive charge on the respective N atoms. However, the rather short C2—N1 bond length suggests that some conjugation involving the C2═O5 group may also be significant. In the structure of creatininium dipicolinate monohydrate (Moghimi *et al.*, 2004), the creatininium cation is constrained to be planar by mirror symmetry and an almost identical pattern of C—N bond lengths is observed.

As well as electrostatic attractions, the component species in (I) interact by means of a network of cation-to-anion N—H$\cdots$O, anion-to-anion O—H$\cdots$O and cation-to-cation N—H$\cdots$O hydrogen bonds (Table 2). The $[H_2AsO_4]^-$ units are linked into polymeric chains (Fig. 2) propagating along [100] by way of inversion-generated pairs of O3—H1$\cdots$O2^{i} and

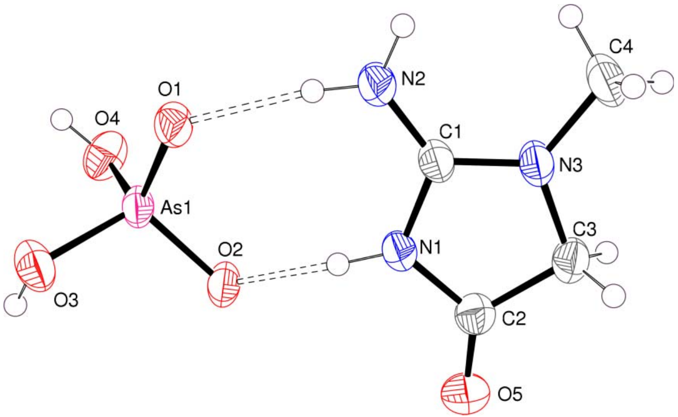


Figure 1
View of the asymmetric unit of (I), showing 50% probability displacement ellipsoids, with hydrogen bonds indicated by dashed lines.

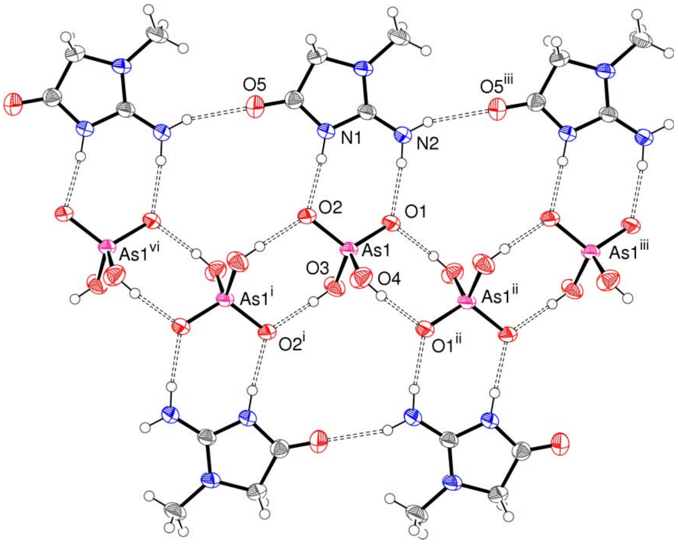


Figure 2
Detail of a hydrogen-bonded chain in (I). Hydrogen bonds are indicated by dashed lines. [Symmetry codes as in Table 2; additionally, (vi) $x - 1$, y, z.]

O4—H2···O1^{ii} bonds (see Table 2 for symmetry codes). In graph-set notation (Bernstein *et al.*, 1995), each inter-tetrahedral linking motif corresponds to an $R_2^2(8)$ loop. The As1···As1^{i} and As1···As1^{ii} separations are 4.0608 (3) and 3.9286 (3) Å, respectively.

The organic species interacts with the dihydrogenarsenate chains by way of two N—H···O hydrogen bonds (Fig. 1), such that both sides of each [100] chain are decorated by the creatininium cations. The third creatininium N—H group is involved in a cation-to-cation N—H···O bond (Fig. 2) that appears to reinforce the chains. Overall, a chain structure along the *a* axis arises for (I), as shown in Fig. 3. Atoms O1 and O2 accept two hydrogen bonds each (bond angle sums about these atoms are 358.3 and 359.3°, respectively). A *PLATON* (Spek, 2003) analysis of (I) flagged the possible presence of two short C—H···O interactions (Table 2), although their structural significance is not clear.

PLATON also flagged a short C2···C2^{v} [symmetry code: (v) $-x$, $1 - y$, $-z$] intermolecular contact of 3.158 (3) Å, compared with a van der Waals radius sum of 3.40 Å (Bondi, 1964). This close contact might arise as part of a carbonyl–carbonyl interaction, as described by Allen *et al.* (1998). In the notation of these workers, the situation in (I) corresponds to a 'sheared antiparallel' or motif II interaction (Fig. 4), generated by a centre of symmetry. Here, the O5═C2···O5^{v} and C2═O5···C2^{v} interaction angles are 100.50 (14) and 79.50 (13)°, respectively, compared with the nominal values of 2 × 90° for a perfect rectangle of the four constituent atoms. This is slightly more distorted than the mean O═C···O and C═O···C angles of 96.5 (4) and 83.5 (4)° based on 553 contributors, as cited by Allen *et al.* (1998). The C2···O5^{v} separation of 3.147 (3) Å in (I) is slightly less than the C···O van der Waals separation of 3.22 Å.

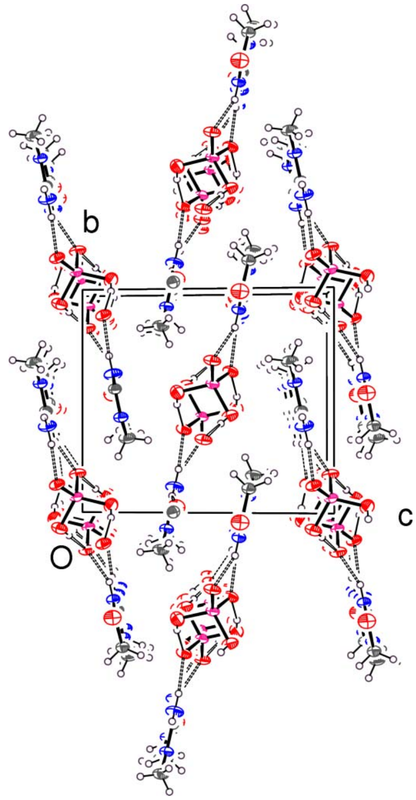


Figure 3
Projection of the packing of (I) along the *a* axis. Hydrogen bonds are indicated by dashed lines.

The dihydrogenarsenate chain motif in (I) replicates that seen in *t*-butylammonium dihydrogenarsenate (Wilkinson & Harrison, 2004). However, a different cation-to-anion hydrogen-bonding scheme leads to a layered structure in this phase. The intrachain As···As separations of 4.2662 (3) and 4.3002 (4) Å in the *t*-butylammonium compound are significantly larger than those seen in (I).

Experimental

A 0.5 *M* aqueous creatine solution (10 ml) was added to a 0.5 *M* aqueous H_3AsO_4 solution (20 ml) to result in a clear solution. A mass of block-like crystals of (I) grew as the water evaporated over the course of a few days. The creatine transformed to creatinine under the low-pH conditions of the reaction.

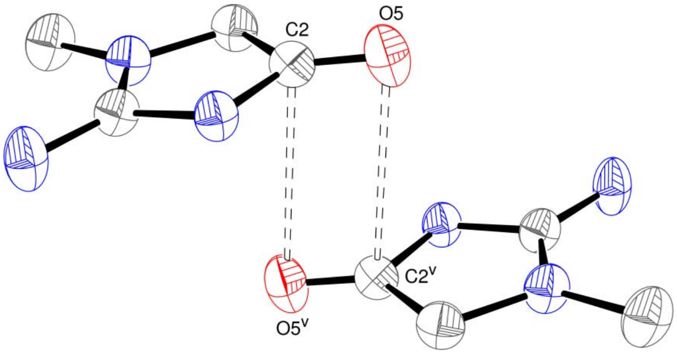


Figure 4

Detail of (I), showing the possible carbonyl–carbonyl interaction, with H atoms omitted for clarity. Hydrogen bonds are indicated by dashed lines. [Symmetry code: (v) $-x, 1-y, -z$.]

Crystal data

$(C_4H_8N_3O)[H_2AsO_4]$
$M_r = 255.07$
Monoclinic, $P2_1/n$
$a = 7.3576$ (3) Å
$b = 10.4263$ (5) Å
$c = 11.9471$ (5) Å
$\beta = 102.908$ (1)°
$V = 893.33$ (7) Å^3
$Z = 4$

$D_x = 1.897$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5020 reflections
$\theta = 2.6$–32.2°
$\mu = 3.80$ mm^{-1}
$T = 293$ (2) K
Chunk, colourless
$0.49 \times 0.33 \times 0.24$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.223$, $T_{max} = 0.401$
11192 measured reflections

3202 independent reflections
2403 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 32.5$°
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.069$
$S = 1.00$
3202 reflections
119 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

Table 1

Selected interatomic distances (Å).

As1—O1	1.6512 (13)	C1—N2	1.305 (2)
As1—O2	1.6563 (12)	C1—N3	1.321 (2)
As1—O4	1.7013 (15)	C1—N1	1.374 (2)
As1—O3	1.7134 (13)	C2—N1	1.367 (2)

Table 2

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O2^{i}	0.85	1.77	2.618 (2)	177
O4—H2···O1^{ii}	0.82	1.79	2.598 (2)	169
N1—H3···O2	0.86	1.89	2.703 (2)	158
N2—H4···O5^{iii}	0.86	2.16	2.983 (2)	161
N2—H5···O1	0.86	1.89	2.747 (2)	172
C3—H6···O1^{iv}	0.97	2.46	3.334 (2)	149
C3—H7···O2^{v}	0.97	2.46	3.384 (2)	159

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

The hydroxy H atoms were found in difference maps and refined as riding on their carrier O atoms in their as-found relative positions. The H atoms bonded to C and N atoms were placed in idealized positions (C—H = 0.96–0.97 Å and N—H = 0.86 Å) and refined as riding, allowing for free rotation of the –CH_3 group. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier) was applied.

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.

References

Allen, F. H., Baalham, C. A., Lommerse, J. P. M. & Raithby, P. R. (1998). *Acta Cryst.* B**54**, 320–329.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
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.
Moghimi, A., Sharif, M. A. & Aghabozorg, H. (2004). *Acta Cryst.* E**60**, o1790–o1792.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Todd, M. J. & Harrison, W. T. A. (2005). *Acta Cryst.* E**61**, m1024–m1026.
Wilkinson, H. S. & Harrison, W. T. A. (2004). *Acta Cryst.* E**60**, m1359–m1361.