

Ferroelastic *n*-pentylammonium dihydrogenarsenate

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Key indicators

Single-crystal X-ray study

T = 290 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.036

wR factor = 0.045

Data-to-parameter ratio = 13.3

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

n-Pentylammonium dihydrogenarsenate, $\text{C}_5\text{H}_{14}\text{N}^+\cdot\text{H}_2\text{AsO}_4^-$ (C5ADA), is ferroelastic at room temperature. The structure is monoclinic ($P2_1/n$) and isostructural with *n*-pentylammonium dihydrogenphosphate (C5ADP). In contrast to C7ADA and C9ADA, as well as to C7ADP and C9ADP, two independent dihydrogenarsenates in the present structure are not disordered. Similarly, as in other known members of the series (C2ADP–C10ADP and C6ADA–C9ADA), there are strong hydrogen bonds between the anions, and moderate hydrogen bonds between the anions and the cations. The hydrogen-bond distances correspond well to those observed in the dihydrogenphosphates. There are two H atoms in the structure which are involved in asymmetric hydrogen bonds between respective oxygen pairs. These H atoms jump from the donor to the acceptor O atoms during ferroelastic switching. A phase transition was observed at about 380 and 371 K during heating and cooling, respectively.

Comment

Ferroelasticity and a phase transition in the *n*-alkylammonium dihydrogenphosphates (*C_n*ADP) and dihydrogenarsenates (*C_n*ADA) were discovered by Kroupa & Fuith (1993, 1994). Until now, however, the presence of phase transitions in C5ADA was not investigated. The related dihydrogenphosphate (C2ADP–C10ADP) and dihydrogenarsenate (C6ADA–C8ADA) structures have been studied previously. C2ADP, C3ADP and C4ADP were studied by Kasatani *et al.* (1998), C3ADP by Fábry *et al.* (2000*a*), C4ADP by Fábry *et al.* (2000*b*), C5ADP and C6ADP by Kasatani *et al.* (1999), C5ADP, C6ADP and C9ADP by Fábry *et al.* (2000), C7ADP and C8ADP by Fábry *et al.* (1997), and C10ADP by Oliver *et al.* (1998). C6ADA and C8ADA were determined by Fábry, Kroupa & Čísařová (2001), while C7ADA was determined by Fábry, Krupková & Čísařová (2001). All the structures are monoclinic ($P2_1/n$). The prototypic phases are orthorhombic ($P2/b2_1/n2_1/a$).

The ferroelastic switching is concomitant with the hydrogen jumps of two H atoms within the hydrogen bridges from the donor to the acceptor O atoms: O41–HO41···O42 and O22–HO22···O21.

Each structure contains a pair of symmetry independent anion molecules (dihydrogenphosphates or dihydrogenarsenates) and a pair of symmetry independent *n*-alkylammonium molecules. The latter are almost exactly displaced by $(\frac{1}{2}, 0, 0)$.

It was found that C3ADP and C5ADP belong to a different structure type than C7ADP and C9ADP (Kasatani *et al.*, 1999; Fábry *et al.*, 2000). The preference for the different structure type, either C3ADP or C5ADP, seems to be related to the

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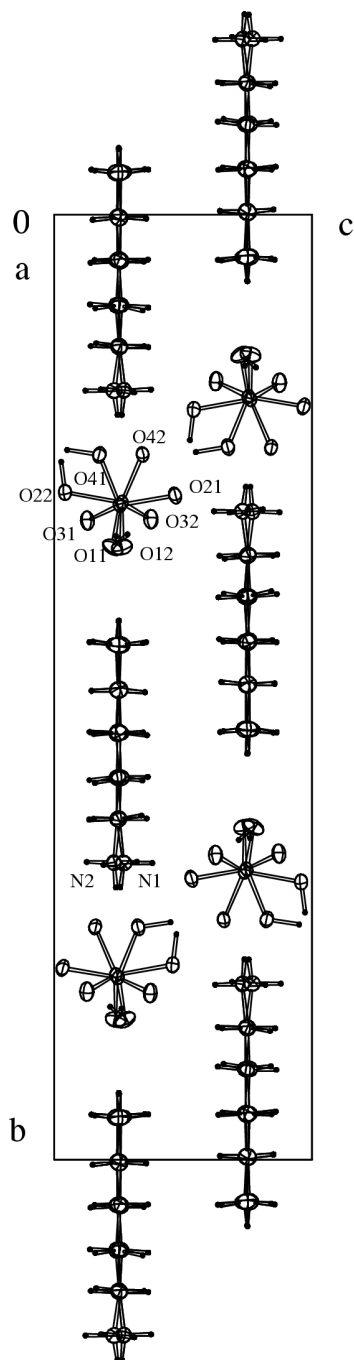
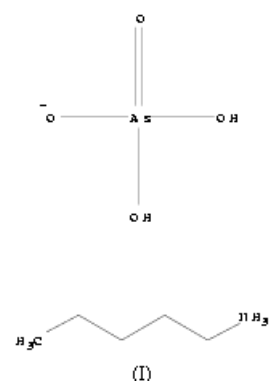


Figure 1
View of the unit cell of C5ADA along the *a* axis.

smaller number of intermolecular contacts between the *n*-alkylammonium chains in C3ADP and C5ADP (Fábry *et al.*, 2000) than in C7ADP and C9ADP. This means that these chains in C3ADP and C5ADP are more loosely packed than in C7ADP and C9ADP.

Disorder of the anionic molecules was first observed in C7ADP and C9ADP. Even more prominent disorder (the proportion was more than 10%) was observed in C7ADA. This means that until now the disorder was observed only in the compounds which belong to the structure type of C7ADP. This disorder can be envisaged as stacking faults ($\frac{1}{2}$, 0, 0) or,

alternatively, as the co-existence of both structure types, *i.e.* of C5ADP and of C7ADP. The greater prominence of the disorder in the dihydrogenarsenates is in accordance with its view as co-existence of both structure types of C5ADP and C7ADP since the structure type of C5ADP seems to be supported by a lesser number of contacts between *n*-alkylammonium chains. The lesser number of contacts between the *n*-alkylammonium chains in C3ADP and C5ADP implies more space between these molecules. On the other hand in the dihydrogenarsenates the larger size of the anions would cause the *n*-alkylammonium chains to be more separated, and therefore these chains would have more space around them. For these reasons, it may be expected that C5ADA, (I), would be isomorphous with C5ADP and no disorder would exist in it.



The non-existence of the disorder of the dihydrogenarsenate molecules was confirmed. Figs. 1 and 2 depict the studied structure (Burnett & Johnson, 1996). The structure is isostructural with C5ADP.

The presence of a phase transition in C5ADA was also investigated by DSC [Perkin–Elmer DSC 7, software *PYRIS* (1997); 10.7 mg of the powdered sample were put into an Al-capsule, rate 10 K min⁻¹, temperature range 298–423 K], as well as by observation of samples in the polarized light during heating and cooling. It was found by the DSC experiments that a phase transition occurs during heating at ~380 K and during cooling at ~371 K. Observation of the sample between crossed polarizers revealed that above 373 K the structure becomes gradually optically homogeneous though it does not turn into liquid. After repeated cooling, the domain pattern develops again. The domains partially recover if the temperature does not exceed 393 K. If the temperature reaches at least 393 K, then cooling results in a more dense domain pattern.

Experimental

Precipitation of *n*-pentylamine and H₃AsO₄. The precipitate was filtered off, dried and dissolved in 96% ethanol from which single crystals were grown by slow evaporation at room temperature. The crystal which appeared single-domained under the polarization

microscope was selected for a diffractometer measurement.

Crystal data

$C_5H_{11}NH_3^+ \cdot H_2AsO_4^-$	$D_x = 1.595 \text{ Mg m}^{-3}$
$M_r = 229.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 54194 reflections
$a = 9.3380(3) \text{ \AA}$	$\theta = 1.0\text{--}27.5^\circ$
$b = 27.3950(8) \text{ \AA}$	$\mu = 3.54 \text{ mm}^{-1}$
$c = 7.4570(8) \text{ \AA}$	$T = 290(1) \text{ K}$
$\beta = 90.568(1)^\circ$	Prism, colourless
$V = 1907.5(1) \text{ \AA}^3$	$0.32 \times 0.10 \times 0.04 \text{ mm}$
$Z = 8$	

Data collection

Nonius KappaCCD diffractometer	2740 reflections with $I > 3\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.053$
Absorption correction: by Gaussian integration (Coppens, 1970)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.461$, $T_{\text{max}} = 0.868$	$h = -12 \rightarrow 12$
27 031 measured reflections	$k = -35 \rightarrow 35$
4366 independent reflections	$l = 0 \rightarrow 9$

Refinement

Refinement on F	All H-atom parameters refined
$R = 0.036$	$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$
$wR = 0.045$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 2.02$	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
4365 reflections	$\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$
327 parameters	

Table 1

Selected bond lengths (\AA).

As1—O11	1.711 (2)	O22—HO22	0.90 (2)
As1—O21	1.6575 (19)	N1—C11	1.483 (4)
As1—O31	1.659 (2)	C11—C21	1.515 (5)
As1—O41	1.707 (2)	C21—C31	1.514 (5)
As2—O12	1.693 (2)	C31—C41	1.526 (5)
As2—O22	1.710 (2)	C41—C51	1.523 (6)
As2—O32	1.642 (2)	N2—C12	1.489 (4)
As2—O42	1.667 (2)	C12—C22	1.505 (5)
O11—HO11	0.96 (3)	C22—C32	1.519 (5)
O41—HO41	0.95 (2)	C32—C42	1.525 (5)
O12—HO12	0.90 (3)	C42—C52	1.523 (6)

Table 2

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

$D-H \cdots A$	$D-H$	$D \cdots A$	$D-H \cdots A$
O11—HO11 \cdots O32 ⁱ	0.96 (3)	2.591 (3)	172 (3)
O41—HO41 \cdots O42 ⁱⁱ	0.95 (2)	2.489 (3)	168 (4)
O12—HO12 \cdots O31	0.90 (3)	2.574 (3)	161 (3)
O22—HO22 \cdots O21 ⁱⁱⁱ	0.90 (3)	2.550 (3)	167 (5)
N1—H3N1 \cdots O22 ^{iv}	0.88 (2)	2.969 (4)	162 (2)
N1—H1N1 \cdots O32 ^v	0.90 (2)	2.774 (3)	168 (2)
N1—H2N1 \cdots O42 ^{vi}	0.88 (2)	2.759 (4)	160 (2)
N2—H1N2 \cdots O21 ^{vii}	0.90 (2)	2.833 (4)	162 (2)
N2—H3N2 \cdots O31 ^{viii}	0.89 (2)	2.785 (3)	161 (2)
N2—H2N2 \cdots O41 ^{ix}	0.87 (3)	2.835 (4)	157 (2)

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

The structure is ferroelastic. It can be related to the prototypic space group $P2_1/b2_1/n2_1/a$. Therefore, the sample was expected to be twinned but the twinning turned out to be insignificant. The disorder was taken into account by the refinement on separate scales for h even and odd, respectively, but it was found to be insignificant. The extinction correction was negligible and for the final refinement not

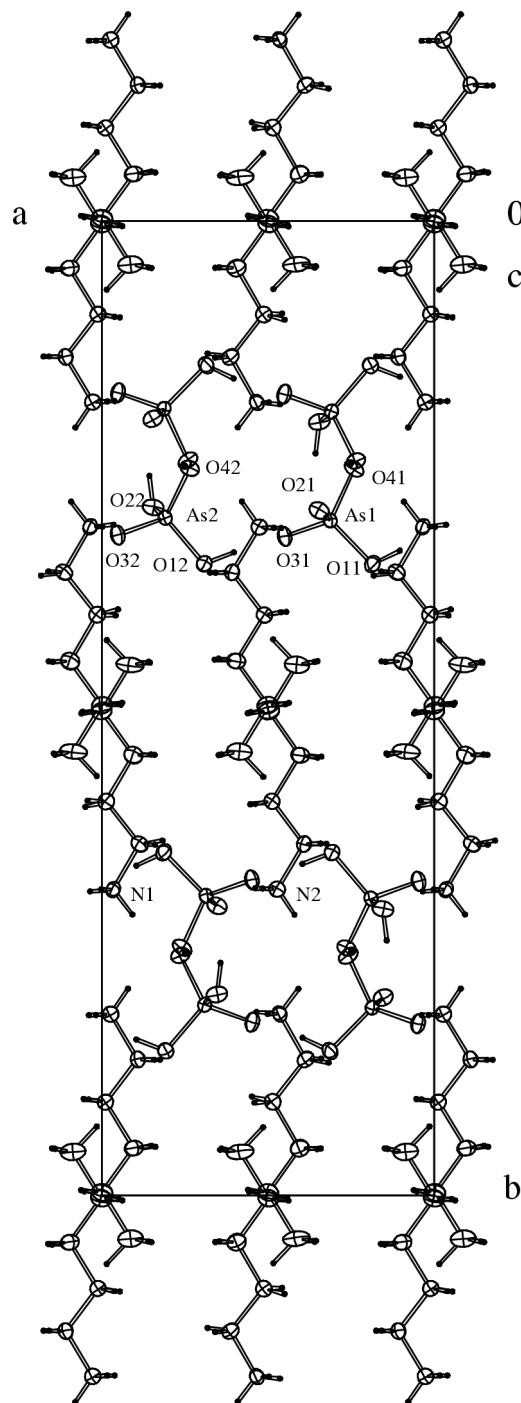


Figure 2

View of the unit cell of C5ADA along the c axis.

used. No maxima which would belong to the disordered dihydrogenarsenates were detected. All H atoms except those which are pertinent to the OH groups could be distinguished on the Fourier maps. The bond distances as well as the angles in which the H atoms were involved were restrained. The O—H, N—H and C—H bond lengths were restrained to 0.90 (3), 0.90 (2) and 0.95 (1) \AA , respectively. The H—C—H and H—N—H angles were restrained to 109 (1) $^\circ$.

Data collection: COLLECT (Nonius, 1997–2000); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction:

HKL DENZO and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *JANA2000* (Petříček & Dušek, 2000); program(s) used to refine structure: *JANA2000*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *JANA2000*.

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