

Ferroelastic *n*-heptylammonium
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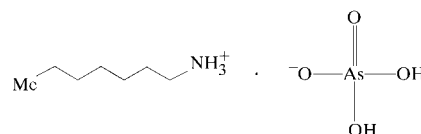
n-Heptylammonium dihydrogenarsenate, (C₇H₁₈N)[As(O)₂(OH)₂] (C7ADA), is ferroelastic at room temperature and isostructural with *n*-heptylammonium dihydrogenphosphate (C7ADP). In contrast to the other known *n*-alkylammonium dihydrogenphosphates (C_{*n*}ADP) and dihydrogenarsenates (C_{*n*}ADA), two independent anions in the present structure are substantially disordered (~88 and ~12%, respectively). There are strong hydrogen bonds between the dihydrogenarsenates themselves, and moderate hydrogen bonds between the dihydrogenarsenates and the *n*-alkylammonium groups. 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.

Comment

Ferroelasticity and a phase transition in the title compound at ~364 K were discovered by Kroupa & Fuith (1994). Until now, the structures of the dihydrogenphosphates C2ADP–C10ADP and of the dihydrogenarsenates C6ADA and C8ADA have been determined: C2ADP, C3ADP and C4ADP were studied by Kasatani *et al.* (1998), C3ADP by Fábry, Císařová & Kroupa (2000*a*), C4ADP by Fábry, Císařová & Kroupa (2000*b*), C5ADP and C6ADP by Kasatani *et al.* (1999), C5ADP, C6ADP and C9ADP by Fábry, Petříček *et al.* (2000), C7ADP and C8ADP by Fábry *et al.* (1997), and C10ADP by Oliver *et al.* (1998). C5ADA was determined by Fábry, Krupková & Císařová (2001), while C6ADA and C8ADA were determined by Fábry, Kroupa & Císařová (2001). All the structures are monoclinic (*P*₂₁/*n*). The prototypic phases are orthorhombic (*Pbna*).

The ferroelastic switching is concomitant with the 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 anions (dihydrogenphosphates or dihydrogenarsenates), as well as a pair of symmetry-independent *n*-alkylammonium cations. The latter ions are almost exactly displaced by [$\frac{1}{2}$,0,0].



C7ADA

It was found that two structure types exist in *n*-alkylammonium dihydrogenphosphates with *n* odd. The representatives of either structure type are C5ADP and C7ADP. All the respective molecules from each structure type can be superimposed with the exception of each second double layer of the dihydrogenphosphates which are mutually displaced by [$\frac{1}{2}$,0,0] (see Figs. 1 and 2). Thus, such a superposition of both structure types creates a disorder in every second anionic double layer. The symmetry operations of space group *P*₂₁/*n* spread this disorder into all the anionic double layers.

Such a disorder can result from alternative displacements by [$\frac{1}{2}$,0,0] of the anionic double layers at *y* ~ 0.25 and *y* ~ 0.75 (Figs. 1 and 2). Such a displacement of the anions is conceivable since NH₃ groups can accommodate the hydrogen-bonding pattern by rotation by about 20° and slight shifts of the anions as well as of the *n*-heptylammonium cations. The positions of the disordered As atoms need not coincide exactly. This explanation of the disorder is more probable than the stacking faults ($\frac{1}{2}$,0,0) *within* the anionic double layer. The hydrogen-bonding pattern between the anionic molecules would then be different.

This disorder of the anions can be viewed alternatively as a co-existence of both C5ADP and C7ADP structural types. The disorder can be formally expressed as stacking faults ($\frac{1}{2}$,0,0) and the structure can be refined using different scales for the reflections with *h* even and odd, respectively.

It is interesting that until now this type of disorder was observed in C7ADP and C9ADP only, *i.e.* in the compounds with odd *n* ≥ 7 and which belong to the structure type of C7ADP. In the case of C7ADP, this disorder was refined to occupancies of 0.990 (1) and 0.010 (1), while for C9ADP, the refinement resulted in occupancies of 0.956 (1) and 0.044 (1). In isostructural C5ADA and C5ADP, no disorder was observed.

The dihydrogenarsenate molecules are larger than the dihydrogenphosphates. Therefore, the *n*-alkylammonium chains in the dihydrogenarsenates would be more distant from each other than in the dihydrogenphosphates, *i.e.* these chains would be more loosely packed than in the corresponding dihydrogenphosphates. On the other hand, in C3ADP and C5ADP, there is a smaller number of intermolecular contacts between the *n*-alkylammonium chains because these chains are short. This would make these chains in C3ADP and C5ADP more loosely packed than in C7ADP and C9ADP. Therefore, it can be deduced that the C3ADP and C5ADP structure types may be preferred for C7ADA. However, by analogy with the isostructural pairs C6ADP and C6ADA, as

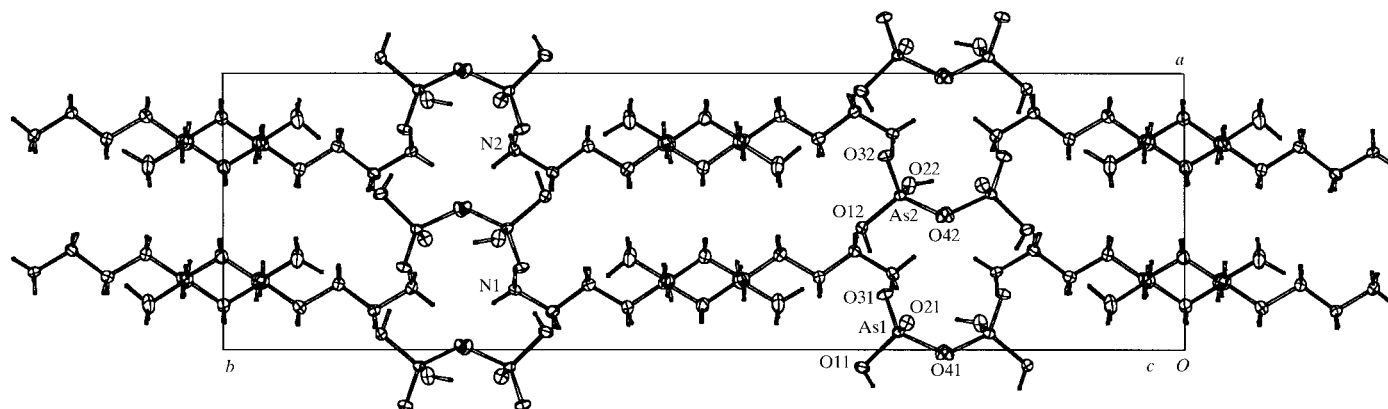


Figure 1
An ORTEP III (Burnett & Johnson, 1996) picture with 30% probability displacement ellipsoids of the unit cell of C7ADA along the *c* axis.

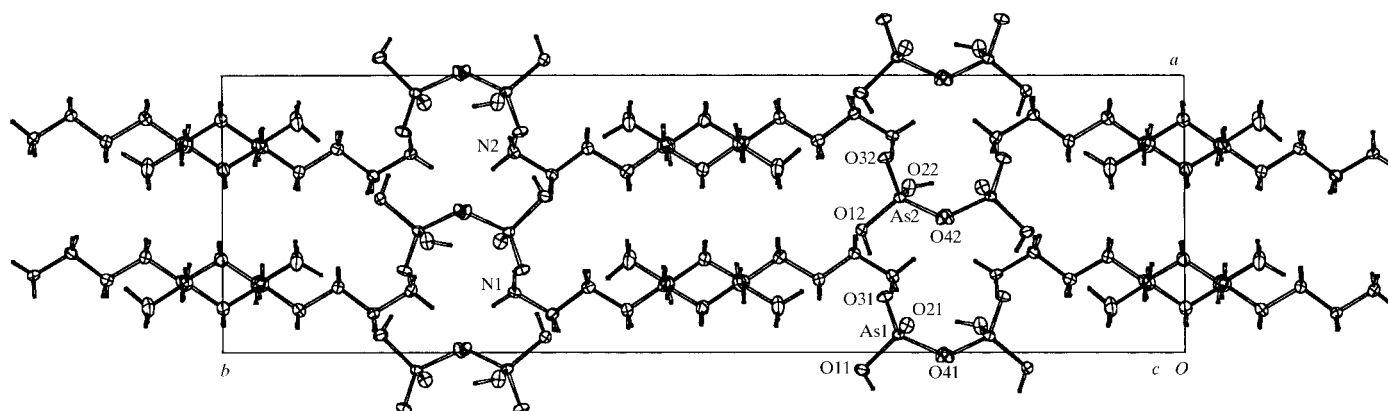


Figure 2
Modelling the stacking faults in C7ADA: the double layer of the dihydrogenarsenates at $y \sim 0.75$ is displaced with respect to that in Fig. 1 by $[\frac{1}{2}, 0, 0]$. The picture is otherwise made under the same conditions as in Fig. 1.

well as C8ADP and C8ADA, *n*-heptylammonium dihydrogenarsenate, C7ADA, and dihydrogenphosphate, C7ADP, should be isostructural. Therefore, it was of interest to determine the title structure because it is a boundary member of the structure series. The other point of interest was a confirmation of the possible disorder of the anions. For this reason, the title compound was chosen for a structure determination.

The most interesting feature of the present structure determination is the observed substantial disorder of the anionic molecules. The disorder (~ 85 and $\sim 15\%$) was also detected on a different sample placed on a four-circle diffractometer (Enraf–Nonius CAD-4 MACHIII-PC) with a point detector. However, the intensity of the standard reflections has decreased substantially (to $\sim 15\%$) by the completion of the data collection up to $\theta = 25^\circ$. Therefore, the other sample whose structure determination is given here was chosen and measured on a diffractometer with a CCD detector. Why the disorder has only been observed in the series of *n*-alkylammonium dihydrogenarsenates or dihydrogenphosphates with odd $n \geq 7$ remains unsolved.

Other structural features are analogous to the known structures of the series C_n ADP and C_n ADA. It is worthwhile

noting the As2–O bond lengths (Table 1). The As2–O12 bond length is 1.677 (3) Å while in C5ADA, C6ADA and C8ADA the corresponding distances are 1.696 (2), 1.695 (3) and 1.699 (2) Å, respectively. In all the known dihydrogenphosphates and dihydrogenarsenates, the bond lengths which correspond to As2–O32 are the shortest among the As–O or P–O bonds in these anions.

It was checked that the closest methylene and methyl H atoms are as close as 2.7 Å to the anion O atoms, while the pertinent C–O lengths are about 3.4–3.5 Å long. This would mean that van der Waals rather than C–H···O hydrogen bonds are pertinent. The shorter the H–O contacts, the closer the valence angles are to 180° (see, for example, Desiraju & Steiner, 1999).

Experimental

Precipitation of *n*-heptylamine and H_3AsO_4 . The precipitate was filtered off, dried and dissolved in 96% ethanol from which the single crystals were grown by slow evaporation at room temperature. The samples contained domains which could be reproducibly moved if stress was exerted. The crystals which appeared single-domained in the polarization microscope were selected for a diffractometer measurement.

Crystal data

(C₇H₁₈N)[As(O)₂(OH)₂]
M_r = 257.16
 Monoclinic, *P*2₁/*n*
a = 9.3261 (3) Å
b = 32.34003 (14) Å
c = 7.5005 (3) Å
 β = 90.595 (2)°
V = 2262.1 (1) Å³
Z = 8

D_x = 1.510 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 24 037 reflections
 θ = 1.02–27.52°
 μ = 2.993 mm⁻¹
T = 290 (1) K
 Prism, colourless
 0.22 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
 CCD scans
 Absorption correction: by Gaussian integration (Coppens *et al.*, 1965)
T_{min} = 0.614, *T_{max}* = 0.860
 13013 measured reflections
 4974 independent reflections

2700 reflections with *I* > 3σ(*I*)
R_{int} = 0.052
 θ_{max} = 27.52°
h = -12 → 12
k = -42 → 41
l = 0 → 9

Refinement

Refinement on *F*
R = 0.044
wR = 0.053
S = 1.46
 4972 reflections
 369 parameters

H-atom parameters restrained
w = 1/[σ²(*F_o*) + 0.0001(*F_o*)²]
 (Δ/σ)_{max} = 0.0012
 Δρ_{max} = 1.22 e Å⁻³
 Δρ_{min} = -1.07 e Å⁻³

Table 1
 Selected bond lengths (Å).

As1—O11	1.709 (3)	C12—C22	1.481 (6)
As1—O21	1.655 (2)	C22—C32	1.527 (7)
As1—O31	1.653 (2)	C32—C42	1.496 (7)
As1—O41	1.707 (3)	C42—C52	1.528 (7)
As2—O12	1.677 (3)	C52—C62	1.506 (7)
As2—O22	1.710 (3)	C62—C72	1.523 (7)
As2—O32	1.638 (2)	O11—O32 ⁱ	2.592 (4)
As2—O42	1.657 (2)	O21—O22 ⁱⁱ	2.541 (5)
N1—C11	1.475 (6)	O31—O12	2.591 (4)
C11—C21	1.514 (7)	O41—O42 ⁱⁱⁱ	2.513 (4)
C21—C31	1.506 (7)	N1—O22 ^{iv}	2.976 (5)
C31—C41	1.509 (7)	N1—O32 ^v	2.789 (4)
C41—C51	1.502 (7)	N1—O42 ^{vi}	2.756 (4)
C51—C61	1.502 (7)	N2—O21 ^v	2.850 (4)
C61—C71	1.512 (8)	N2—O31 ^{iv}	2.791 (4)
N2—C12	1.493 (6)	N2—O41 ^{vi}	2.824 (5)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) *x* - ½, ½ - *y*, ½ + *z*; (iii) *x* - ½, ½ - *y*, *z* - ½; (iv) 1 - *x*, 1 - *y*, -*z*; (v) 1 - *x*, 1 - *y*, 1 - *z*; (vi) ½ - *x*, ½ + *y*, ½ - *z*.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>
O11—HO11...O32 ⁱ	0.84 (3)	2.592 (4)	166 (3)
O41—HO41...O42 ⁱⁱ	0.88 (3)	2.513 (4)	159 (4)
O12—HO12...O31	0.84 (2)	2.591 (4)	164 (3)
O22—HO22...O21 ⁱⁱⁱ	0.88 (4)	2.541 (5)	155 (5)
N1—H3N1...O22 ^{iv}	0.88 (3)	2.976 (5)	152 (3)
N1—H1N1...O32 ^v	0.90 (2)	2.789 (4)	172 (3)
N1—H2N1...O42 ^{vi}	0.84 (3)	2.756 (4)	159 (3)
N2—H1N2...O21 ^v	0.86 (2)	2.850 (4)	161 (3)
N2—H3N2...O31 ^{iv}	0.90 (2)	2.791 (4)	148 (2)
N2—H2N2...O41 ^{vi}	0.91 (3)	2.824 (5)	164 (3)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) *x* - ½, ½ - *y*, *z* - ½; (iii) ½ + *x*, ½ - *y*, *z* - ½; (iv) 1 - *x*, 1 - *y*, -*z*; (v) 1 - *x*, 1 - *y*, 1 - *z*; (vi) ½ - *x*, ½ + *y*, ½ - *z*.

The structure is both a superstructure and a ferroelastic structure. It can be related to the prototypic space group *P*2/*b*2₁/*n*2₁/*a*. The twinning turned out to be insignificant in the sample, as did the

extinction correction (Becker & Coppens, 1974). The disorder was taken into account by the refinement on different scales (Sc) for the reflections with *h* even and odd, respectively. [Sc**F_c* = *F_o*; Sc_{odd} = 0.1574 (5), while Sc_{even} = 0.2059 (3)]. The disordered proportion *f* can be determined using the relation *f* = (Sc_{even} - Sc_{odd})/2Sc_{even}. The determined value of *f* equalled 0.118 (1). (This value was also confirmed from the refinement of another model with disordered anions. In this model, it was assumed that the As atoms of the disordered dihydrogenarsenates were exactly overlapped.) The bond distances and angles in which H atoms were involved were restrained. The O—H, N—H and C—H bond lengths were restrained to 0.85 (2) and 0.90 (2) Å for the former two distances, and to 0.90 (2) and 0.95 (1) Å for methylene and methyl groups, respectively. The H—C—H and H—N—H angles were restrained to 109 (1)°, while O11—HO11...O32 was restrained to 170 (2)°. The isotropic displacement parameters of the H atoms bonded to the corresponding C and N atoms from each respective independent *n*-alkylammonium were held equal. The structure was refined using the coordinates of C7ADP. All maxima of the disordered O atoms except one were clearly discernible. They were as high as 1.4 e Å⁻³. Not all H atoms could be distinguished on the difference Fourier maps.

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 refine structure: JANA2000 (Petříček & Dušek, 2000); molecular graphics: ORTEPIII (Burnett & Johnson, 1996); software used to prepare material for publication: JANA2000.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1066). Services for accessing these data are described at the back of the journal.

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