metal-organic compounds

Phase transitions in *n*-alkylammonium dihydrogenphosphates and -arsenates and ferroelastic *n*-hexyl- and *n*-octyl-ammonium dihydrogenarsenate

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n-Hexylammonium dihydrogenarsenate, $(C_6H_{16}N)[AsO_2(OH)_2]$, and *n*-octylammonium dihydrogenarsenate, $(C_8H_{20}N)[AsO_2(OH)_2]$, are both ferroelastic at room temperature. The samples used in this study were not subjected to a phase transition after they had been crystallized. The structures are monoclinic ($P2_1/n$) and isostructural with the corresponding dihydrogenphosphates. Each sample contained two domains and each structure was refined as a twin. There are strong hydrogen bonds between dihydrogenarsenates and moderate hydrogen bonds between dihydrogenarsenates and *n*-alkylammonium groups. The hydrogen-bond distances correspond well to those observed in the dihydrogenphosphates. All the atoms except two H atoms exist in pairs linked by the lost symmetry operations derived from the prototypic space group $P2/b2_1/n2_1/a$. Each of these two different H atoms is involved in an asymmetric hydrogen bond between an oxygen pair. These oxygens are supposed to change their roles as hydrogen-bond donors and acceptors during the ferroelastic switching. The phase-transition sequences are affected by interactions between the neighbouring organic chains in the structure.

Comment

Ferroelasticity and complicated phase-transition sequences were discovered in the series of related dihydrogenphosphates C1ADP–C12ADP by Kroupa & Fuith (1993, 1994). The phase transition in C3ADP (ADP is ammonium dihydrogenphosphate) was also investigated by Iwata *et al.* (1996). Regarding the phase transitions, the compounds C*n*ADP can be divided into three groups: (*a*) C1ADP–C4ADP, (*b*) compounds with *n* > 5 and *n* even, and (*c*) compounds with *n* ≥ 5 and *n* odd.

Each compound of group (*a*) undergoes a continuous ferroelastic phase transition. In contrast to group (*a*), each of the compounds in groups (*b*) and (*c*) undergoes a discontinuous ferroelastic phase transition. In addition, the compounds of the latter two groups, (*b*) and (*c*), undergo other phase transitions when they are heated from the room-temperature phase up to the ferroelastic phase transition. The hysteresis effects are common. [In the case of C9ADP, the original room-temperature phase does not even recover after cooling (Kroupa & Fuith, 1993).] The compounds in group (*c*) undergo more complicated phase transitions. The differences between the phase-transition sequences of the first-time and at least once heated crystals are more prominent in group (*c*) than in group (*b*).

The ferroelastic phase transitions in the dihydrogenarsenates occur at considerably higher temperatures (by tens of K) than in the corresponding dihydrogenphosphates. C6ADA (ADA is ammonium dihydrogenarsenate) undergoes a ferroelastic phase transition at ∼378 K, C7ADA at ∼364 K and C8ADA melts at ∼380 K before a phase transition takes place (Kroupa & Fuith, 1994)

Until now, the structural studies were performed only with regard to the series of dihydrogenphosphates C2ADP–C10ADP (Cambridge Structural Database, April 2000 release; Allen & Kennard, 1993). 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, Petříček *et al.* (2000), C7ADP and C8ADP by Fábry *et al.* (1997), and C10ADP by Oliver *et al.* (1998). The reasons for the different packing of *n*-alkylammonium chains were explained by Fábry, Petříček *et al.* (2000) by dominancy of the hydrogen bonding of the ammonium groups to the double layers of the dihydrogenphosphates. Until now, however, no structure determination of any of the dihydrogenarsenates has been performed.
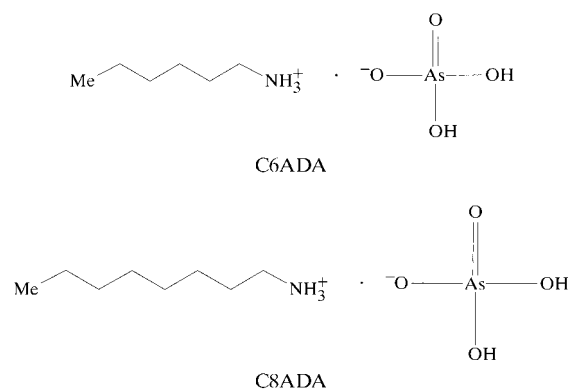
The aim of this study was a structure determination of C6ADA and C8ADA in order to determine structural differences between these compounds and the corresponding dihydrogenphosphates, and to find out the reason for differences in the phase transitions.

The twinning matrix which relates the diffractions $h_1k_1l_1$ and $h_2k_2l_2$ from the dominant and minor domains, respectively, is analogous to that in the dihydrogenphosphates. The diffractions $h_1k_1l_1$ and $h_2k_2l_2$ are expressed in the reciprocal space basis of the first domain, and a, c and β mean the lattice parameters.

$$\left(h_2 k_2 l_2\right) = \left(h_1 k_1 l_1\right) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 2(a/c)\cos\beta & 0 & 1 \end{pmatrix}$$

The structures are similar to C6ADP and C8ADP which are depicted elsewhere. Figs. 1 and 2 depict the closest C···C intermolecular contacts in C6ADA. The refined values of the minor domain proportion are in good accordance with the values calculated from the intensities of well separated pertinent diffractions from the minor and the prevailing domains. The differences are due to imprecision in the reading of the crystal shape, and consequently in absorption correction, as well as in shielding of the domains which may be unevenly distributed within the specimen. The interatomic distances are normal (Cambridge Structural Database, 2000; Allen & Kennard, 1993). The hydrogen-bond distances and angles regarding the double layers of dihydrogenarsenates are comparable to those in the dihydrogenphosphates C6ADP and C8ADP (Table 3). The N···O hydrogen bonds are shorter by ∼0.033 Å in the dihydrogenarsenates than in the dihydrogenphosphates. The N···O distances are more evenly distributed in C6ADA and C8ADA than in the corresponding dihydrogenphosphates. The absolute values of the atomic displacement vectors – a measure of the distortion of a structure from a prototypic phase (Abrahams & Keve, 1971) – for the non-H atoms are in the range 0.01–0.14 Å.

The differences in the phase-transition sequences between the members of the CnADP family with $n \leq 4$ and $n \geq 5$ (which depend also on the parity of n) and in CnADA are
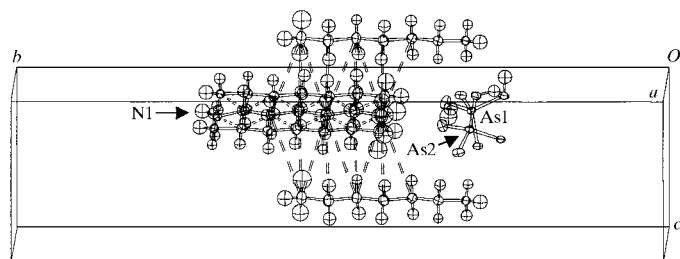

Figure 1
View of the fragment of C6ADA along the a axis with C—C and C—N intermolecular contacts up to 4.2 Å and 50% probability displacement ellipsoids (*ORTEP*III; Burnett & Johnson, 1996).
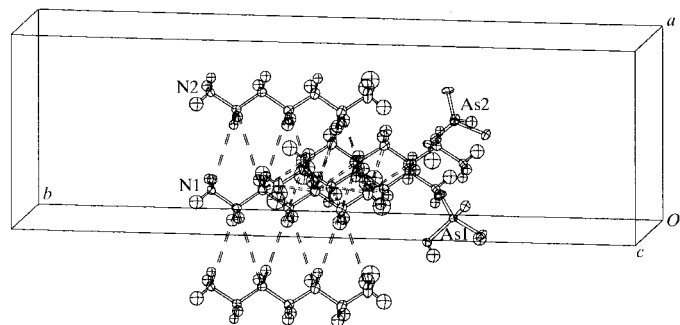

Figure 2
View of the fragment of C6ADA along the c axis with C—C and C—N intermolecular contacts up to 4.2 Å and 50% probability displacement ellipsoids (*ORTEP*III; Burnett & Johnson, 1996).

affected by the number of C···C and C···N contacts and their distances. As already pointed out by Fábry *et al.* (1997), the closest C···C distances correspond well to van der Waals contacts (Weast & Astle, 1980). However, in C5ADP, C7ADP and C9ADP, the closest C···C distances are as short as 3.7 Å, in contrast to those in the dihydrogenphosphates with n even, which are about 3.8 Å long (in C4ADP, 3.9 Å). It should be noted that C5ADP, C7ADP and C9ADP are the compounds where hysteresis effects are the most prominent. On the other hand, in CnADP with $n \leq 4$, the chains are so short that a sufficient number of C atoms can not interact.

The larger dihydrogenarsenates would cause the n-alkylammonium chains in the dihydrogenarsenates to be more distant from each other than in the pertinent dihydrogenphosphates (Table 4). The average differences between the corresponding C···C distances in C6ADA–C6ADP and C8ADA–C8ADP are 0.065 and 0.062 Å, respectively.

The phase-transition phenomena observed in these compounds can be explained at least qualitatively by the distances between the atoms in the neighbouring chains as well as by the number of these contacts. The closer the n-alkylammonium chains, the more complicated the phase transitions observed. Not surprisingly, the phase transitions in the dihydrogenarsenates take place at higher temperatures than in the analogous dihydrogenphosphates. This is because the molecules in the dihydrogenarsenates have more space, and thermal agitation must be more intensive to bring these molecules to interact and provoke a phase transition.

From this point of view on the phase transitions, it may also be predicted that not only in C9ADP (Kroupa & Fuith, 1993), but also in other CnADP with n odd and $n \geq 11$, the room-temperature phase would not recover after the crystals were heated and cooled. This is because the longer chains would be less able to restore the original low-temperature arrangement.

As in the dihydrogenphosphates, the ferroelastic switching in C6ADA and C8ADA is concomitant to hopping of the H atoms HO41 and HO22 from the donor (O41, O22, respectively) to the acceptor oxygens (O42, O21, respectively) (Table 3).

Experimental

Crystallization of the n-alkylamine and H_3AsO_4 was carried out in methanol solutions (Kroupa & Fuith, 1994). Crystals which appeared single domained under a polarization microscope were selected for analysis.

Compound C6ADA

Crystal data

$(C_6H_{16}N)[AsO_2(OH)_2]$	$D_x = 1.555$ Mg m^{-3}
$M_r = 243.13$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 9.3105$ (7) Å	reflections
$b = 29.929$ (2) Å	$\theta = 12.6$–$13.9°$
$c = 7.453$ (6) Å	$\mu = 3.255$ mm^{-1}
$\beta = 90.64$ (7)$°$	$T = 292$ (1) K
$V = 2077$ (2) Å^3	Plate, colourless
$Z = 8$	$0.43 \times 0.20 \times 0.09$ mm

Table 1
Selected bond lengths (Å) for C6ADA.

As1—O11	1.700 (3)	As2—O22	1.706 (2)
As1—O21	1.653 (2)	As2—O32	1.645 (2)
As1—O31	1.645 (2)	As2—O42	1.658 (2)
As1—O41	1.703 (2)	N1—C11	1.484 (5)
As2—O12	1.695 (3)	N2—C12	1.488 (5)

Table 2
Selected bond lengths (Å) for C8ADA.

As1—O11	1.703 (2)	As2—O22	1.707 (2)
As1—O21	1.652 (2)	As2—O32	1.634 (2)
As1—O31	1.648 (2)	As2—O42	1.666 (2)
As1—O41	1.709 (2)	N1—C11	1.480 (4)
As2—O12	1.699 (2)	N2—C12	1.490 (4)

Table 3
Relevant distances and angles (Å, °) of the hydrogen-bond pattern in C6ADA, C8ADA, C6ADP and C8ADP.

D—H$\cdots A$	D—H	$D\cdots A$	D—H$\cdots A$
C6ADA			
O11—HO11$\cdots$O32^{i}	0.84 (2)	2.610 (3)	167 (3)
O41—HO41$\cdots$O42^{ii}	0.85 (1)	2.511 (3)	174 (3)
O12—HO12$\cdots$O31	0.85 (2)	2.580 (3)	172 (3)
O22—HO22$\cdots$O21^{iii}	0.85 (1)	2.551 (3)	168 (3)
N1—H3N1$\cdots$O22^{iv}	0.79 (3)	3.014 (3)	155 (3)
N1^{v}—H1N1$\cdots$O32^{vi}	0.92 (3)	2.796 (3)	167 (3)
N1—H2N1$\cdots$O42^{vii}	0.88 (3)	2.746 (3)	163 (3)
N2^{v}—H1N2$\cdots$O21^{vi}	0.78 (3)	2.870 (3)	159 (3)
N2—H3N2$\cdots$O31^{iv}	0.95 (4)	2.813 (3)	168 (3)
N2—H2N2$\cdots$O41^{vii}	0.93 (3)	2.850 (3)	158 (2)
C8ADA			
O11—HO11$\cdots$O32^{i}	0.75 (3)	2.613 (2)	173 (3)
O41—HO41$\cdots$O42^{ii}	0.90 (3)	2.525 (2)	176 (3)
O12—HO12$\cdots$O31	0.62 (3)	2.603 (2)	169 (3)
O22—HO22$\cdots$O21^{iii}	0.89 (4)	2.546 (2)	170 (4)
N1—H3N1$\cdots$O22^{iv}	0.91 (3)	3.036 (3)	162 (2)
N1—H1N1$\cdots$O32^{vi}	0.87 (3)	2.813 (3)	170 (2)
N1—H2N1$\cdots$O42^{vii}	0.90 (3)	2.754 (2)	168 (2)
N2—H1N2$\cdots$O21^{vi}	0.81 (3)	2.889 (3)	170 (2)
N2—H3N2$\cdots$O31^{iv}	0.83 (3)	2.837 (3)	168 (2)
N2—H2N2$\cdots$O41^{vii}	0.94 (3)	2.853 (3)	163 (2)
C6ADP			
O11—HO11$\cdots$O32^{i}	0.83 (3)	2.588 (3)	174 (4)
O41—HO41$\cdots$O42^{ii}	0.87 (2)	2.504 (3)	178 (4)
O12—HO12$\cdots$O31	0.83 (3)	2.579 (3)	176 (4)
O22—HO22$\cdots$O21^{iii}	0.86 (2)	2.543 (3)	175 (3)
N1—H3N1$\cdots$O22^{iv}	0.89 (2)	2.960 (4)	160 (2)
N1—H1N1$\cdots$O32^{vi}	0.90 (2)	2.771 (3)	160 (2)
N1—H2N1$\cdots$O42^{vii}	0.90 (3)	2.747 (4)	167 (2)
N2—H1N2$\cdots$O21^{vi}	0.87 (2)	2.841 (3)	170 (2)
N2—H3N2$\cdots$O31^{iv}	0.89 (2)	2.785 (3)	159 (2)
N2—H2N2$\cdots$O41^{vii}	0.90 (3)	2.814 (4)	161 (2)
C8ADP			
O11—HO11$\cdots$O32^{i}	0.84 (3)	2.588 (3)	174 (5)
O41—HO41$\cdots$O42^{ii}	0.87 (2)	2.513 (3)	165 (3)
O12—HO12$\cdots$O31	0.83 (2)	2.571 (3)	168 (3)
O22—HO22$\cdots$O21^{iii}	0.84 (2)	2.552 (3)	163 (3)
N1—H3N1$\cdots$O22^{iv}	0.89 (2)	2.975 (4)	165 (2)
N1—H1N1$\cdots$O32^{vi}	0.90 (2)	2.785 (3)	164 (2)
N1—H2N1$\cdots$O42^{vii}	0.90 (3)	2.735 (3)	162 (2)
N2—H1N2$\cdots$O21^{vi}	0.89 (2)	2.843 (3)	166 (3)
N2—H3N2$\cdots$O31^{iv}	0.89 (2)	2.803 (3)	153 (2)
N2—H2N2$\cdots$O41^{vii}	0.89 (3)	2.809 (4)	163 (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) $1 - x, 1 - y, -z$; (v) $x, y, 1 + z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Data collection

Enraf–Nonius CAD-4 MACHIII– PC diffractometer	$R_{int} = 0.038$
ω–2θ scans	$\theta_{max} = 26.52°$
Absorption correction: Gaussian (Templeton & Templeton, 1978)	$h = -11 \rightarrow 11$
	$k = 0 \rightarrow 37$
$T_{min} = 0.482$, $T_{max} = 0.749$	$l = 0 \rightarrow 9$
4613 measured reflections	3 standard reflections frequency: 3600 min intensity decay: 7.0%
4290 independent reflections	
2505 reflections with $I > 3\sigma(I)$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R = 0.036$	$\Delta\rho_{max} = 1.86$ e Å^{-3}
$wR = 0.047$	$\Delta\rho_{min} = -2.43$ e Å^{-3}
$S = 1.89$	Extinction correction: type I, Lorentzian isotropic (Becker & Coppens, 1974)
4290 reflections	
362 parameters	
H-atom refinement: see below	Extinction coefficient: 2.9 (2) × 10^{-5}
$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$	

Compound C8ADA

Crystal data

$(C_8H_{20}N)[AsO_2(OH)_2]$	$D_x = 1.479$ Mg m^{-3}
$M_r = 271.19$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 9.307 (1)$ Å	$\theta = 11$–14°
$b = 34.936 (4)$ Å	$\mu = 2.785$ mm^{-1}
$c = 7.488 (1)$ Å	$T = 292 (1)$ K
$\beta = 90.58 (1)°$	Plate, colourless
$V = 2434.6 (5)$ Å^3	$0.41 \times 0.26 \times 0.12$ mm
$Z = 8$	

Data collection

Enraf–Nonius CAD-4 MACHIII– PC diffractometer	$R_{int} = 0.015$
ω–2θ scans	$\theta_{max} = 26°$
Absorption correction: Gaussian (Templeton & Templeton, 1978)	$h = -11 \rightarrow 11$
	$k = 0 \rightarrow 42$
$T_{min} = 0.348$, $T_{max} = 0.717$	$l = 0 \rightarrow 9$
5743 measured reflections	3 standard reflections frequency: 3600 min intensity decay: 5.0%
4771 independent reflections	
3125 reflections with $I > 3\sigma(I)$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.043$	$\Delta\rho_{max} = 1.36$ e Å^{-3}
$wR = 0.070$	$\Delta\rho_{min} = -1.07$ e Å^{-3}
$S = 3.19$	Extinction correction: type I, Lorentzian isotropic (Becker & Coppens, 1974)
4771 reflections	
431 parameters	
H-atom refinement: see below	Extinction coefficient: 6.9 (3) × 10^{-5}
$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$	

Table 4
Number of intermolecular C—C and C—N distances up to 4.2 Å between the n-alkylammonium chains in CnADP for the given atoms.

	C3ADP	C4ADP	C5ADP	C6ADP	C7ADP	C8ADP	C9ADP	C6ADA	C8ADA
N1	1	1	1	1	1	1	1	1	1
C1	2	2	2	2	2	2	2	2	2
C2	4	4	4	4	4	4	4	4	4
C3	5	4	6	4	6	4	6	4	4
C4		6	8	8	8	8	8	8	8
C5			7	4	8	4	8	4	4
C6				7	8	8	8	7	8
C7					7	4	8		4
C8						7	8		7
C9							7		

The structures are superstructures as well as ferroelastic structures. They can be related to the prototypic space group $P2/b2_1/n2_1/a$. Therefore, the crystals were expected to be twinned although samples were chosen which seemed to be single domained when viewed under a polarization microscope. The domain proportion f was a refined parameter which converged to values of -0.006 (4) and 0.026 (4) for C6ADA and C8ADA, respectively. (Therefore, in the case of C6ADA, the domain proportion was set to 0.0 and this parameter was not refined.) The domain proportion was also determined from well separated diffractions. In the case of C6ADA, 19 pairs of the diffraction 004 were measured at various azimuthal angles. The determined value of the domain proportion was 0.007 (3). In the case of C8ADA, 31 pairs of different diffractions were used, among them also the reflections of type 004. The value of the domain proportion determined in this way resulted in 0.009 (3). All H atoms could be found in the difference Fourier maps. Most were refined to tolerable positions, nevertheless, they were all restrained during refinement in order to prevent the H atoms being misplaced. The bond distances and angles in which the H atoms were involved were restrained. The O—H, N—H and C—H bond lengths were restrained to 0.85, 0.90 and 0.95 Å, respectively. The maximum and minimum electron densities are 1.13 Å from O32 and 0.27 Å from As2 in C6ADA, and 1.39 Å from O31 and 0.79 Å from As2 in C8ADA.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *JANA*2000 (Petříček & Dušek, 2000); program(s) used to solve structure: *JANA*2000; program(s) used to refine structure: *JANA*2000; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *JANA*98 (Petříček & Dušek, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1051). Services for accessing these data are described at the back of the journal.

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