

Ferroelastic structures of *n*-pentyl-, *n*-hexyl- and *n*-nonylammonium dihydrogenphosphate crystalsJan Fábry,^{a*} Václav Petříček,^a
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This study reports the structure redeterminations of $C_5H_{11}NH_3^+ \cdot H_2PO_4^-$ (*n*-pentylammonium dihydrogenphosphate, C5ADP), $C_6H_{13}NH_3^+ \cdot H_2PO_4^-$ (*n*-hexylammonium dihydrogenphosphate, C6ADP) and $C_9H_{19}NH_3^+ \cdot H_2PO_4^-$ (*n*-nonylammonium dihydrogenphosphate, C9ADP). The structures are monoclinic ($P2_1/n$), belonging to the series of previously studied structures C2ADP–C8ADP and C10ADP. The structures exhibit reproducible ferroelastic switching. There are hydrogen bonds between the dihydrogenphosphates and the *n*-alkylammonium groups. Among them there are two hydrogen bonds with hydrogens which hop from the donor to the acceptor oxygens during the ferroelastic switching. C5ADP as well as C3ADP differ from the other members of the series by packing of the double layers of the dihydrogenphosphates. Moreover, the packing of *n*-alkylammonium molecules in all these structures depends on the parity of the number of atoms in the *n*-alkylammonium chains. All the samples contained two domains and their structures were refined as twins.

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1. Introduction

Ferroelasticity and complicated phase transition sequences in these compounds were discovered by Kroupa & Fuith (1993, 1994). Notably, the phase transition sequences differed in as-crystallized and once-heated samples. Minor differences in phase transition sequences exist between members of the family with even and odd numbers of C atoms in *n*-alkylammonium chains with $n \geq 7$.

The previously determined structures of C7ADP and C8ADP (Fábry *et al.*, 1997) revealed remarkable H atoms. These H atoms are involved in hydrogen bonds between O atoms. It is assumed that during the ferroelastic switching these H atoms jump within these bonds from the donor to the acceptor O atoms. Kasatani *et al.* (1998) published the structural studies about ferroelastic C2ADP, C3ADP and C4ADP, and Kasatani *et al.* (1999) about C5ADP and C6ADP. In the latter two structure determinations the H atoms were not localized. Independently of these studies we have performed the structure determination of C3ADP (Fábry *et al.*, 2000a) and C4ADP (Fábry *et al.*, 2000b). From the structural similarity of C10ADP (Oliver *et al.*, 1998) it may be deduced that C10ADP is also ferroelastic with the similar structural features.

Hydrogen jumps concomitant to ferroelastic switching were also observed in H_3BO_3 (Wadhawan, 1978), *cf.* neutron structure determination of H_3BO_3 (Craven & Sabine, 1966). In some urea inclusion compounds the hydrogen bonds break and reestablish during ferroelastic switching (Brown & Hollingsworth, 1995).

It was found that *n*-alkylammonium molecules are differently packed in the compounds so far determined with *n* odd and even. If *n* is odd the *n*-alkylammonium molecules are packed in a zigzag manner, while if *n* is even they are arranged in a parallel way when viewed along the *c* axis. In addition, it was found that C3ADP and C5ADP differ from the other compounds by localization of *n*-alkylammonium chains with regard to the double layers of the dihydrogenphosphates. The aim of the study was to determine the structures of some other members of the family (C5ADP, C6ADP and C9ADP), which were until now determined either poorly or not at all. The other reason was to determine the rule for the packing of *n*-alkylammoniums in these compounds.

2. Experimental

The preparation of the title compounds is described elsewhere (Wařkowska & Kroupa, 1995; Oliver *et al.*, 1998; Table 1). The crystals are colourless and transparent. Most of them are pinacoids {001}, {100} and {010}. The latter form is the basis of the crystals. The crystals are somewhat elongated in the *a* direction. The typical dimensions vary from 1 to 10 mm. The domain structure which underwent reproducible ferroelastic switching could be observed under the polarization microscope. The orientation of domain walls and creation of new domains by heating above 370 K and subsequent cooling was similar to that observed in C7ADP or C8ADP (Fábry *et al.*, 1997).

The domain walls are perpendicular to the *a* axis and in some cases there were single-domain regions as large as several tenths of a mm. If pressure exceeded some limits then either cracks appeared along the *a* direction or the crystal disintegrated. The cracks either perpendicular or parallel to the *a* direction can also develop by heating above 370 K and subsequent cooling. Such a thermal treatment also caused development of domain walls, which were much more dense compared with those of the unheated samples. Despite all efforts we failed in the preparation of single-domain crystals, although in the samples used in the diffractometer measurements no domains were visible in the polarization microscope.

The preliminary diffractometer measurements revealed that the reflections of the type 00*l* were split, while *h*00 was not. The angle between the respective reflections of the type 00*l*, which are pertinent to the prevailing and minor domains, is $\sim 1.6^\circ$. The twinning matrix is expressed as

$$(h_2k_2l_2) = (h_1k_1l_1) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ (2a/c) \cos \beta & 0 & 1 \end{pmatrix}. \quad (1)$$

In (1) *a*, *c* and β are lattice parameters and $h_1k_1l_1$ and $h_2k_2l_2$ are diffractions referring to the first and second domains, respectively, expressed in the reciprocal space basis of the first domain [the values $2(a/c)\cos \beta$ are equal to -0.0359 (4), -0.0376 (4) and -0.0380 (9) for C5ADP, C6ADP and C9ADP, respectively].

Well separated intensive reflections were used for the determination of domain fractions (Table 1), independent

from the refinement. The widths of the intensive reflections from the minor domains were comparable to their counterparts of the prevailing domain.

In all the crystals studied there were collected reflection intensities from the prevailing domains. In the case of C5ADP, which was measured on a CAD4 diffractometer (Table 1), the 'flat' mode for data collection was used. This mode was applied in order to prevent as much as possible the paired *hkl* reflections, $l \neq 0$, originating from the minor domain, to enter into the scan. The Hilger & Watts diffractometer does not enable the measurement of most reflections in a desired azimuthal angle and therefore the bisecting mode was applied for both C6ADP and C9ADP.

All atoms in the structure were found and the positions of H atoms as well as their isotropic displacement factors were refined. In C9ADP residual maxima on the difference Fourier map as high as $\sim 0.7\text{--}0.9 \text{ e \AA}^{-3}$ were found. The positions of these maxima indicated the possible disorder of the dihydrogenphosphate O atoms O21, O31 and O41, and their counterparts O22, O32 and O42.

There are two ways to describe the observed phenomenon. The first assumes the refinement of the reflections *hkl* with $h = 2n$ and $h = 2n + 1$, on separate scales. Such a refinement means that the stacking faults ($\frac{1}{2}, 0, 0$) are assumed. These stacking faults are conceivable since the alkylammonium chains are related by the translation $[\frac{1}{2}, 0, 0]$ almost exactly. This translation relates the dihydrogenphosphates as if they were disordered, see Fig. 1.

This disorder of each dihydrogenphosphate related by the $[\frac{1}{2}, 0, 0]$ displacement is a second explanation of the observed

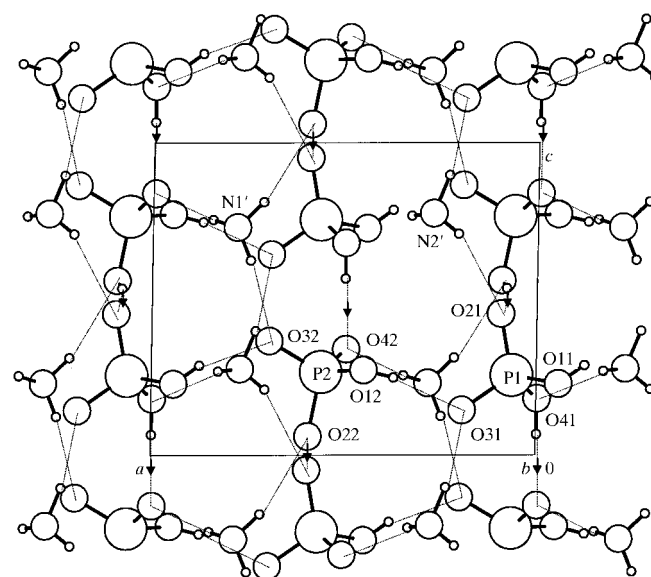


Figure 1 Projection of a double layer ($y \approx 0.25$) of dihydrogenphosphates and NH_3 groups in C9ADP. The primed atoms are linked to the corresponding atoms given in Table 4 by the operation $1 - x, 1 - y, 1 - z$. The layers at $y \approx 0.25$ and $y \approx 0.75$ of C5ADP are related to the depicted layer by the displacement of atoms by $x = 0.25$ and $x = 0.75$. Superposition of the layers of both structure types at e.g. $y \approx 0.25$ displaces the respective layers of C9ADP and C5ADP at $y \approx 0.75$ by $x = 0.50$.

Table 1
Experimental details.

	C5ADP	C6ADP	C9ADP
Crystal data			
Chemical formula	$C_5H_{14}N^+ \cdot H_2O_4P^-$	$C_6H_{16}N^+ \cdot H_2O_4P^-$	$C_9H_{22}N^+ \cdot H_2O_4P^-$
Chemical formula weight	185.16	199.19	241.27
Cell setting	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	9.149 (2)	9.143 (1)	9.138 (3)
b (Å)	27.081 (3)	29.637 (8)	36.984 (9)
c (Å)	7.290 (1)	7.299 (1)	7.383 (2)
β (°)	90.82 (1)	90.86 (1)	90.88 (2)
V (Å ³)	1806.2 (5)	1977.7 (7)	2495 (1)
Z	8	8	8
D_x (Mg m ⁻³)	1.361	1.338	1.284
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	50	50
θ range (°)	9–15	5.6–22.8	4.3–18.0
μ (mm ⁻¹)	0.278	0.259	0.217
Temperature (K)	290 (2)	290 (2)	290 (2)
Crystal form	Plate	Plate	Plate
Crystal size (mm)	0.56 × 0.32 × 0.15	0.33 × 0.20 × 0.10	0.33 × 0.21 × 0.10
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractionmeter	Enraf–Nonius CAD-4-MACHIII-PC	Hilger & Watts	Hilger & Watts
Data collection method	ω - 2θ scans	ω - 2θ scans	ω - 2θ scans
Absorption correction	None	None	Gaussian (Templeton & Templeton, 1978)
T_{\min}	–	–	0.942
T_{\max}	–	–	0.978
No. of measured reflections	3418	5446	13 662
No. of independent reflections	3167	3452	4906
No. of observed reflections	2417	2167	2948
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	0.0339	0.0601	0.0725
θ_{max} (°)	25	25	26
Range of h, k, l	–10 → h → 10 0 → k → 32 0 → l → 8	–10 → h → 10 –35 → k → 35 0 → l → 8	0 → h → 11 –45 → k → 45 –9 → l → 9
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 3600 min	Every 30 reflections	Every 30 reflections
Intensity decay (%)	2.2	6	7
Refinement			
Refinement on	F	F	F
R	0.0403	0.0499	0.0534
wR	0.0549	0.0556	0.0576
S	2.58	1.71	1.91
No. of reflections used in refinement	3167	3452	4906
No. of parameters used	329	363	466
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = [\sigma^2(F_o) + 0.0001(F_o)^2]^{-1}$	$w = [\sigma^2(F_o) + 0.0001(F_o)^2]^{-1}$	$w = [\sigma^2(F_o) + 0.0001(F_o)^2]^{-1}$
$(\Delta/\sigma)_{\text{max}}$	0.01	0.01	0.01
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.33	0.46	0.66
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	–0.34	–0.54	–0.59
Extinction method	Becker & Coppens (1974) type II	Becker & Coppens (1974) type II	Becker & Coppens (1974) type II
Extinction coefficient	0.00030 (4)	0.00017 (2)	0.00028 (3)
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2A and 2.3.1), see Cromer & Mann (1968)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2A and 2.3.1), see Cromer & Mann (1968)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2A and 2.3.1), see Cromer & Mann (1968)
Computer programs			
Data collection	Enraf–Nonius (1989)	HW (Petříček, 1996)	HW (Petříček, 1996)
Cell refinement	Enraf–Nonius (1989)	HW (Petříček, 1996)	HW (Petříček, 1996)
Data reduction	JANA98 (Petříček & Dušek, 1998)	JANA98 (Petříček & Dušek, 1998)	JANA98 (Petříček & Dušek, 1998)
Structure solution	SHELXS86 (Sheldrick, 1986)	SHELXS86 (Sheldrick, 1986)	JANA98 (Petříček & Dušek, 1998)
Structure refinement	JANA98 (Petříček & Dušek, 1998)	JANA98 (Petříček & Dušek, 1998)	JANA98 (Petříček & Dušek, 1998)
Preparation of material for publication	JANA98 (Petříček & Dušek, 1998)	JANA98 (Petříček & Dušek, 1998)	JANA98 (Petříček & Dušek, 1998)
Computer graphics	PICTUR (Dušek, 1993)	PICTUR (Dušek, 1993)	PICTUR (Dušek, 1993)

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of C5ADP.

$U_{\text{eq}} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$				
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
P1	0.31308 (4)	0.30565 (1)	0.25595 (5)	0.0222 (1)
O11	0.1925 (1)	0.34584 (4)	0.2291 (2)	0.0362 (4)
O21	0.3426 (1)	0.29679 (4)	0.4567 (1)	0.0337 (4)
O31	0.4408 (1)	0.32108 (4)	0.1431 (1)	0.0310 (3)
O41	0.2482 (1)	0.25574 (4)	0.1807 (1)	0.0314 (3)
P2	0.80901 (4)	0.30250 (1)	0.26376 (5)	0.0230 (1)
O12	0.6972 (1)	0.34574 (4)	0.2676 (2)	0.0365 (4)
O22	0.8409 (1)	0.29344 (4)	0.0554 (1)	0.0366 (4)
O32	0.9432 (1)	0.31934 (4)	0.3649 (1)	0.0335 (3)
O42	0.7432 (1)	0.25554 (4)	0.3394 (1)	0.0304 (3)
N1	0.9668 (2)	0.68778 (5)	0.2677 (2)	0.0302 (4)
C11	0.8861 (2)	0.64032 (6)	0.2487 (2)	0.0304 (5)
C21	0.9888 (2)	0.59645 (6)	0.2543 (2)	0.0350 (5)
C31	0.9045 (2)	0.54815 (6)	0.2472 (3)	0.0382 (6)
C41	1.0027 (2)	0.50263 (6)	0.2495 (3)	0.0415 (6)
C51	0.9156 (3)	0.45457 (8)	0.2453 (3)	0.0546 (8)
N2	0.4762 (2)	0.68722 (5)	0.2260 (2)	0.0290 (4)
C12	0.3915 (2)	0.64080 (6)	0.2442 (2)	0.0310 (5)
C22	0.4908 (2)	0.59622 (6)	0.2442 (2)	0.0348 (5)
C32	0.4042 (2)	0.54835 (6)	0.2504 (3)	0.0377 (6)
C42	0.5012 (2)	0.50265 (6)	0.2518 (3)	0.0405 (6)
C52	0.4125 (3)	0.45490 (8)	0.2531 (3)	0.0556 (8)
HO11	0.116 (2)	0.3398 (7)	0.271 (2)	0.047 (6)
HO41	0.245 (2)	0.2527 (7)	0.062 (3)	0.066 (7)
HO12	0.620 (2)	0.3399 (7)	0.239 (2)	0.044 (6)
HO22	0.838 (3)	0.2587 (8)	0.030 (3)	0.089 (8)

residual electron-density maxima. A rigid body constraint was applied for either dihydrogenphosphate. The occupations of the disordered dihydrogenphosphates were also constrained. The precise localization of the disordered dihydrogenphosphates is, however, biased since the assumed operations which describe the disorder bring the P atoms as well as the O1 atoms too close to each other.

The reflections hkl , $l \neq 0$, of C6ADP and C9ADP which were collected in a bisecting mode were checked for possible partial superposition by the *checkran* function of JANA98 (Petříček & Dušek, 1998). The indicators of refinement with a *checkran* option were not better than those given in Table 1. The positions of non-H atoms and H atoms in various refinements with varying parameters expressing the reflection superposition differed by not more than 2 and 3 standard uncertainties, respectively. Therefore, it can be assumed that the reflections hkl , $l \neq 0$, were well separated and the occasional imperfect overlapping of reflections influenced the results negligibly.

3. Discussion

Information regarding crystal data, data collection and calculations for all three crystals is given in Table 1.¹ The atomic coordinates and isotropic or equivalent isotropic displacement factors of non-H atoms and of the peculiar

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0106). Services for accessing these data are described at the back of the journal.

Table 3

Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for C6ADP.

$U_{\text{eq}} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$				
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
P1	0.08787 (7)	0.30071 (2)	0.25532 (9)	0.0232 (2)
O11	−0.0327 (2)	0.33731 (6)	0.2298 (3)	0.0368 (7)
O21	0.1194 (2)	0.29233 (6)	0.4548 (2)	0.0335 (6)
O31	0.2159 (2)	0.31489 (6)	0.1415 (2)	0.0324 (6)
O41	0.0230 (2)	0.25539 (6)	0.1804 (3)	0.0334 (6)
P2	0.58373 (7)	0.29784 (2)	0.26410 (9)	0.0236 (2)
O12	0.4712 (2)	0.33714 (6)	0.2666 (3)	0.0371 (7)
O22	0.6176 (2)	0.28995 (7)	0.0574 (2)	0.0379 (7)
O32	0.7172 (2)	0.31308 (7)	0.3665 (2)	0.0344 (6)
O42	0.5179 (2)	0.25485 (6)	0.3389 (2)	0.0302 (6)
N1	0.1904 (3)	0.69309 (9)	0.2676 (4)	0.0307 (8)
C11	0.1059 (3)	0.65055 (9)	0.2485 (4)	0.0315 (9)
C21	0.2023 (3)	0.60953 (9)	0.2565 (5)	0.035 (1)
C31	0.1128 (3)	0.5666 (1)	0.2502 (5)	0.038 (1)
C41	0.2032 (4)	0.5236 (1)	0.2529 (5)	0.038 (1)
C51	0.1132 (4)	0.4807 (1)	0.2502 (6)	0.048 (1)
C61	0.2029 (6)	0.4381 (1)	0.2539 (6)	0.058 (2)
N2	0.6999 (3)	0.69255 (8)	0.2263 (4)	0.0306 (8)
C12	0.6110 (3)	0.65082 (9)	0.2444 (4)	0.0316 (9)
C22	0.7048 (3)	0.60921 (9)	0.2425 (4)	0.0334 (9)
C32	0.6133 (3)	0.56635 (9)	0.2489 (5)	0.039 (1)
C42	0.7031 (4)	0.5236 (1)	0.2468 (5)	0.039 (1)
C52	0.6126 (4)	0.4806 (1)	0.2489 (6)	0.048 (1)
C62	0.7008 (6)	0.4380 (1)	0.2467 (6)	0.060 (2)
HO11	−0.117 (2)	0.329 (1)	0.257 (4)	0.05 (1)
HO41	0.017 (3)	0.253 (1)	0.065 (1)	0.06 (1)
HO12	0.391 (2)	0.327 (1)	0.224 (4)	0.05 (1)
HO22	0.606 (3)	0.2624 (4)	0.027 (4)	0.041 (9)

'jumping' H atoms, respectively, are given in Tables 2–4 for all three compounds.

The relevant interatomic distances and hydrogen bonds are given in Tables 5 and 6, respectively. The absolute values of the atomic displacement vectors (Abrahams & Keve, 1971) are given in Table 7. Figs. 2–7 depict the structures of the studied compounds.

The distances and angles compared with the data from the Inorganic Crystal Structure Database (ICSD, 1999; Bergerhoff *et al.*, 1983) and the Cambridge Crystallographic Database (CSD, 1999; Allen & Kennard, 1993) are normal, including the hydrogen bonds (Jeffrey, 1995). The hydrogen bonds which interconnect the dihydrogenphosphates are strong, while those between the *n*-alkylammonium molecules and the dihydrogenphosphates are of moderate strength. (It is of interest to note that the hydrogen bonds in the recently determined isostructural *n*-hexyl- and *n*-octylammonium dihydrogenarsenates are of about the same lengths; Fábry *et al.*, 2000c.)

From the structures of C2ADP–C10ADP determined so far a hypothesis on the packing of *n*-alkylammonium chains can be derived. In all these cases the *n*-alkylammonium chains are connected to the dihydrogenphosphates in a similar way. The localization of the N atoms makes the environment of the N atoms and the following two C atoms similar in the series C2ADP–C10ADP, independent of the parity of atoms in an *n*-alkylammonium chain, see Figs. 2–7 regarding the compounds of this study. It follows from this similarity that the localization

Table 4

Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for C9ADP.

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
P1	0.06381 (7)	0.29018 (2)	0.25460 (7)	0.0223 (2)
O11	-0.0570 (2)	0.31936 (5)	0.2272 (3)	0.0353 (6)
O21	0.0935 (2)	0.28355 (4)	0.4522 (2)	0.0334 (5)
O31	0.1915 (2)	0.30118 (4)	0.1433 (2)	0.0295 (5)
O41	-0.0019 (2)	0.25370 (4)	0.1801 (2)	0.0299 (5)
P2	0.55976 (7)	0.28770 (2)	0.26507 (7)	0.0222 (2)
O12	0.4483 (2)	0.31938 (4)	0.2715 (2)	0.0347 (6)
O22	0.5914 (2)	0.28178 (5)	0.0598 (2)	0.0384 (6)
O32	0.6946 (2)	0.29976 (4)	0.3648 (2)	0.0318 (5)
O42	0.4944 (2)	0.25338 (4)	0.3385 (2)	0.0304 (5)
N1	0.2188 (3)	0.70564 (6)	0.2699 (3)	0.0307 (7)
C11	0.1385 (3)	0.67063 (6)	0.2483 (3)	0.0293 (8)
C21	0.2380 (3)	0.63869 (6)	0.2569 (4)	0.0327 (8)
C31	0.1528 (3)	0.60349 (7)	0.2494 (4)	0.0354 (9)
C41	0.2475 (3)	0.56978 (6)	0.2528 (4)	0.0323 (8)
C51	0.1588 (3)	0.53509 (6)	0.2505 (4)	0.0341 (9)
C61	0.2521 (3)	0.50091 (6)	0.2521 (3)	0.0328 (8)
C71	0.1638 (3)	0.46631 (6)	0.2525 (4)	0.0346 (9)
C81	0.2563 (4)	0.43249 (7)	0.2546 (4)	0.0388 (9)
C91	0.1660 (5)	0.39808 (8)	0.2564 (5)	0.053 (1)
N2	0.7297 (3)	0.70470 (6)	0.2256 (3)	0.0291 (7)
C12	0.6438 (3)	0.67100 (6)	0.2436 (4)	0.0302 (8)
C22	0.7400 (3)	0.63820 (6)	0.2408 (4)	0.0311 (8)
C32	0.6536 (3)	0.60324 (7)	0.2478 (4)	0.0349 (9)
C42	0.7471 (3)	0.56961 (6)	0.2471 (4)	0.0326 (8)
C52	0.6589 (3)	0.53493 (7)	0.2467 (4)	0.0347 (9)
C62	0.7518 (3)	0.50082 (6)	0.2487 (4)	0.0328 (8)
C72	0.6638 (3)	0.46617 (7)	0.2461 (4)	0.0353 (9)
C82	0.7556 (4)	0.43219 (7)	0.2476 (4)	0.0396 (9)
C92	0.6655 (4)	0.39767 (8)	0.2429 (5)	0.052 (1)
HO11	-0.123 (5)	0.317 (1)	0.286 (5)	0.10 (2)
HO41	-0.003 (4)	0.2519 (9)	0.066 (4)	0.08 (1)
HO12	0.371 (2)	0.3133 (6)	0.247 (3)	0.011 (6)
HO22	0.581 (3)	0.2610 (8)	0.034 (3)	0.045 (8)

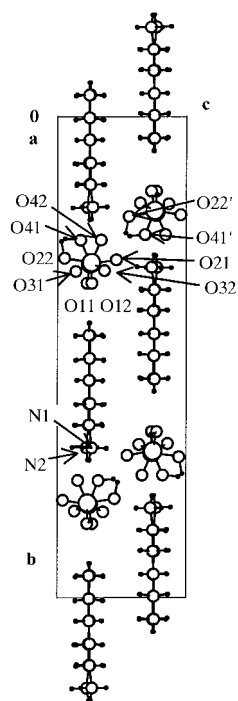


Figure 2

View of the unit cell of C5ADP along the *a* axis. The primed atoms are derived from those given in Table 2 by the operation $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

of the N atoms is governed by the hydrogen bonds between the alkylammonium groups and the dihydrogenphosphates, which are far stronger than the van der Waals contacts. The latter contacts determine the mutual positions of the *n*-alkylammonium molecules. In C5ADP, C7ADP and C9ADP the closest non-bonding C—C distances of the methylene and methyl groups are $\sim 3.7 \text{ \AA}$, in C3ADP $\sim 3.8 \text{ \AA}$, while in C4ADP, C6ADP, C8ADP and C10ADP $\sim 3.9 \text{ \AA}$. These distances correspond well to the values of the van der Waals contacts of the methylene groups (Weast & Astle, 1980).

It is the dominance of the binding of the N atoms which enables the different packing of the chains with even and uneven numbers of the chain C atoms to be explained: If an *n*-alkylammonium contains an odd number of C atoms, the chains are packed in a zigzag manner when viewed along the *c* axis (Figs. 3 and 7). This packing is in contrast to the anti-parallel packing in *e.g.* C6ADP (Fig. 5). The number of overlapping C atoms in *C_n*ADP projected onto the *b* axis equals *n* - 2. The centre of the 'overlapped' sections of the *n*-alkylammonium chains passes through *y* = 0. (In the case of C3ADP and C2ADP the C atoms do not 'overlap' in the projection along the *b* axis; Kasatani *et al.*, 1998.)

Besides the different packing of *n*-alkylammonium chains owing to the parity of the number of C atoms, the structures of C3ADP (Kasatani *et al.*, 1998; Fábry *et al.*, 2000*a*) and C5ADP (Kasatani *et al.*, 1999; this study) differ from the other known compounds *C_n*ADP. C3ADP and C5ADP thus belong to a different structure type. The independent atoms of C5ADP (Table 2) can be brought almost into coincidence with the independent atoms of *e.g.* C6ADP (Table 3) by the displace-

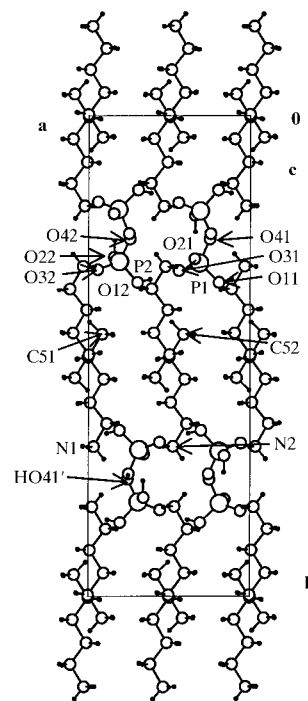


Figure 3

View of the unit cell of C5ADP along the *c* axis. The primed HO41 is derived from the position given in Table 2 by the operation $1 - x, 1 - y, 1 - z$.

ment $x = -0.25$. Both structure types differ by the localization of the molecules with respect to the symmetry elements. Nevertheless, the respective substructures which consist of the atoms which have a counterpart related by a translation $x \simeq 0.5$ (this holds well for all heavy atoms of *n*-alkylammonium chains, as well as for H atoms of the methylene groups, P1 and P2, and O11 and O12 atoms) are invariant to the displacements $x = -0.25$ or $x = 0.25$. This means that these substructures from either structure type of *C_nADP*, not only their independent atoms, can be brought into coincidence.

If the corresponding independent atoms from either structure type are put into coincidence the respective alternating double layers of dihydrogenphosphates are displaced by $x = 0.5$ (Fig. 1). This means that the disorder observed in *C9ADP* as well as in *C7ADP* can be viewed as the coexistence of both structure types.

The disordered O atoms can potentially take part in the hydrogen-bond networks with *n*-alkylammonium molecules as indicated by the N—O distances, which are similar both for the disordered and not disordered dihydrogenphosphates. The NH...O angles of the hydrogen bonds for molecules which are not disordered are in the interval 155 (2)–170 (2)° (Table 6), while for the disordered molecules ~140 (2)–160 (2)°. This means that if the disorder takes place the NH₃ groups should rotate slightly in order to accommodate for the more appropriate values of valence angles for the hydrogen bonding. Of course, concomitant small displacements of the atoms are probable.

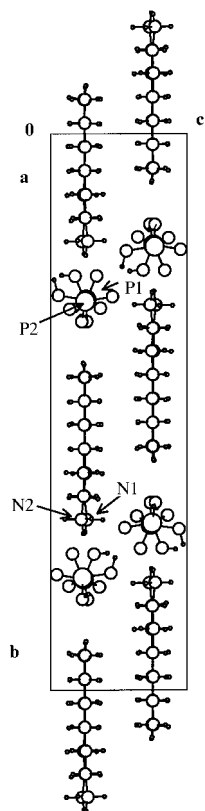


Figure 4
View of the unit cell of *C6ADP* along the *a* axis. The denomination of the O atoms is analogous to *C5ADP* (Fig. 2).

Table 5
Selected distances (Å) for *C5ADP*, *C6ADP* and *C9ADP*.

Compound denomination of atoms	<i>C5ADP</i> <i>d</i> (Å)	<i>C6ADP</i> <i>d</i> (Å)	<i>C9ADP</i> <i>d</i> (Å)
P1—O11	1.560 (1)	1.552 (3)	1.555 (2)
P1—O21	1.504 (1)	1.501 (3)	1.500 (1)
P1—O31	1.498 (1)	1.505 (3)	1.493 (2)
P1—O41	1.572 (1)	1.563 (3)	1.573 (2)
P2—O12	1.556 (1)	1.554 (2)	1.553 (2)
P2—O22	1.570 (1)	1.563 (2)	1.562 (2)
P2—O32	1.495 (1)	1.492 (2)	1.494 (2)
P2—O42	1.514 (1)	1.515 (2)	1.508 (2)
N1—C11	1.488 (2)	1.484 (4)	1.496 (3)
C11—C21	1.514 (2)	1.501 (4)	1.492 (3)
C21—C31	1.519 (2)	1.514 (5)	1.518 (4)
C31—C41	1.525 (3)	1.519 (5)	1.518 (4)
C41—C51	1.526 (3)	1.515 (5)	1.518 (4)
C51—C61		1.505 (6)	1.525 (4)
C61—C71			1.513 (4)
C71—C81			1.510 (4)
C81—C91			1.517 (4)
N2—C12	1.484 (2)	1.486 (4)	1.480 (3)
C12—C22	1.511 (2)	1.501 (4)	1.499 (3)
C22—C32	1.520 (2)	1.523 (4)	1.517 (4)
C32—C42	1.523 (3)	1.509 (5)	1.509 (4)
C42—C52	1.527 (3)	1.521 (5)	1.515 (4)
C52—C62		1.495 (6)	1.521 (4)
C62—C72			1.513 (4)
C72—C82			1.511 (4)
C82—C92			1.519 (5)

Since it was impossible to localize precisely the disordered dihydrogenphosphates the stacking-fault model was given preference for *C9ADP*. [If the disorder was assumed, the

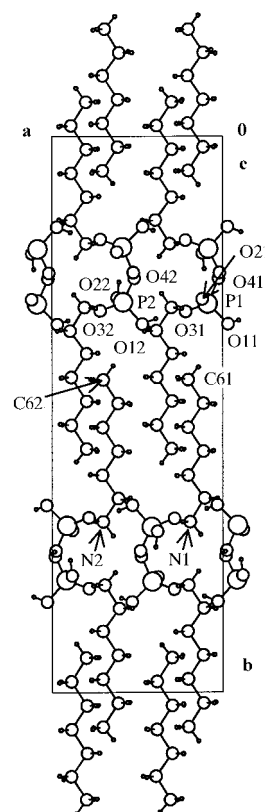


Figure 5
View of the unit cell of *C6ADP* along the *c* axis.

Table 6
Distances (Å) and angles (°) of the hydrogen-bond networks in C5ADP, C6ADP and C9ADP.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C5ADP				
O11—HO11...O32 ⁱ	0.78 (2)	1.82 (2)	2.600 (1)	174 (2)
O41—HO41...O42 ⁱⁱ	0.87 (2)	1.64 (2)	2.507 (1)	177 (2)
O12—HO12...O31	0.75 (2)	1.84 (2)	2.591 (1)	172 (2)
O22—HO22...O21 ⁱⁱⁱ	0.96 (2)	1.60 (2)	2.547 (2)	171 (2)
N1—H1N1...O32 ^{iv}	0.88 (2)	1.92 (2)	2.797 (2)	170 (2)
N1—H2N1...O42 ^v	0.91 (2)	1.87 (2)	2.761 (2)	166 (2)
N1—H3N1...O22 ^{vi}	0.82 (2)	2.24 (2)	3.003 (2)	156 (2)
N2—H1N2...O21 ^{vii}	0.85 (2)	2.04 (2)	2.859 (2)	162 (2)
N2—H2N2...O41 ^{viii}	0.87 (2)	2.02 (2)	2.857 (2)	162 (2)
N2—H3N2...O31 ^{ix}	0.91 (2)	1.94 (2)	2.815 (2)	161 (2)
C6ADP				
O11—HO11...O32 ⁱ	0.84 (2)	1.78 (2)	2.610 (3)	167 (3)
O41—HO41...O42 ⁱⁱ	0.85 (1)	1.67 (1)	2.511 (3)	174 (3)
O12—HO12...O31	0.85 (1)	1.72 (1)	2.551 (3)	168 (3)
O22—HO22...O21 ⁱⁱⁱ	0.85 (2)	1.74 (2)	2.580 (3)	172 (3)
N1—H1N1...O32 ^{iv}	0.92 (3)	1.89 (3)	2.796 (3)	167 (3)
N1—H2N1...O42 ^v	0.88 (3)	1.89 (3)	2.746 (3)	163 (3)
N1—H3N1...O22 ^{ix}	0.79 (3)	2.28 (3)	3.014 (3)	155 (3)
N2—H1N2...O21 ^{vii}	0.78 (3)	2.13 (3)	2.870 (3)	159 (3)
N2—H2N2...O41 ^{viii}	0.93 (3)	1.96 (3)	2.850 (3)	158 (2)
N2—H3N2...O31 ^{ix}	0.95 (3)	1.87 (3)	2.813 (3)	168 (3)
C9ADP				
O11—HO11...O32 ⁱ	0.75 (4)	1.89 (4)	2.604 (3)	160 (4)
O41—HO41...O42 ⁱⁱ	0.85 (3)	1.69 (3)	2.535 (2)	178 (4)
O12—HO12...O31	0.76 (2)	1.86 (2)	2.606 (2)	169 (2)
O22—HO22...O21 ⁱⁱⁱ	0.80 (3)	1.76 (3)	2.544 (2)	167 (3)
N1—H1N1...O32 ^{iv}	0.82 (3)	2.00 (3)	2.806 (3)	167 (3)
N1—H2N1...O42 ^v	0.97 (3)	1.79 (3)	2.739 (3)	164 (3)
N1—H3N1...O22 ^{ix}	0.85 (3)	2.22 (3)	3.047 (3)	163 (3)
N2—H1N2...O21 ^{vii}	0.89 (2)	2.06 (2)	2.888 (3)	153 (2)
N2—H2N2...O41 ^{viii}	0.79 (3)	2.10 (3)	2.854 (3)	161 (2)
N2—H3N2...O31 ^{ix}	0.94 (3)	1.91 (3)	2.837 (3)	167 (3)

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

respective occupancies of the dihydrogenphosphates were 0.956 (1) and 0.044 (1), and the R factors were the same as in Table 1.]

The R factors of the refinement of C9ADP when neither disorder nor stacking faults but twinning only was assumed converged to the values (*cf.* Table 1): $R_{\text{obs}} = 0.0589$, $wR_{\text{obs}} = 0.0619$, $R_{\text{all}} = 0.1216$, $wR_{\text{all}} = 0.0679$ for 465 parameters. The refined domain proportion then resulted in 0.090 (5), *i.e.* in a significantly higher value than observed directly (*cf.* Table 1). The differences between the respective fractional coordinates of both models of C9ADP did not exceed three standard uncertainties with the exception of O11 and O12 atoms (five standard uncertainties).

All other members of the series C3ADP–C9ADP were checked for the disorder. It was not detected except for the previously determined structure of C7ADP (Fábry *et al.*, 1997). Some maxima which were scattered among the other maxima in the difference Fourier synthesis (as high as $0.4 e \text{ \AA}^{-3}$) could be assigned to the O atoms which were disordered in a similar way as in C9ADP. The refinement with the disordered dihydrogenphosphates did not cause a signifi-

cant decrease in the R factors and the occupancies of the respective disordered dihydrogenphosphates were 0.990 (1) and 0.010 (1). Refinement for the reflections with $h = 2n$ and $h = 2n + 1$ refined on different scales, however, caused a significant decrease of the R factors: from $R_{\text{obs}} = 0.0390$, $wR_{\text{obs}} = 0.0594$, $R_{\text{all}} = 0.0567$, $wR_{\text{all}} = 0.0619$, $S = 1.48$, 396 parameters to $R_{\text{obs}} = 0.0358$, $wR_{\text{obs}} = 0.0572$, $R_{\text{all}} = 0.0535$, $wR_{\text{all}} = 0.0598$, $S = 1.44$, 397 parameters. $\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}$ were -0.37 and $0.34 e \text{ \AA}^{-3}$ for the model with lower R factors. Since the fractional coordinates of the P atoms as well as of the O11 and O12 atoms differed by five standard uncertainties, the new data (fractional coordinates of H atoms, anisotropic temperature parameters) are deposited.

It is interesting that the disorder/stacking faults were observed in the structures $C_n\text{ADP}$, with $n \geq 7$, n odd, and that C3ADP and C5ADP differ from the other compounds. However, more samples should be tested to determine whether the tendency to stacking faults depends on the parity of n in $C_n\text{ADP}$. No decisive geometrical differences in the bond-network were observed within the series C3ADP–C10ADP for which the atomic coordinates are available.

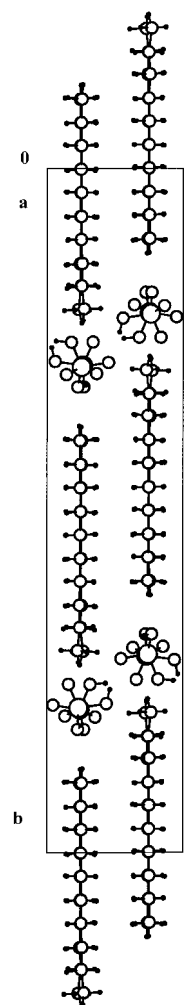


Figure 6
View of the unit cell of C9ADP along the a axis. The denomination of atoms is analogous to C5ADP (Fig. 2).

Table 7

Absolute values of atomic displacement vectors $|\Delta|$ (Å) in C5ADP, C6ADP and C9ADP, with the exception of alkylammonium H atoms.

The atoms on the right of the first, third and fifth column are brought to the pertinent left atoms by the following operations: if not otherwise indicated by the operation $-\frac{1}{2} + x, y, \frac{1}{2} - z$, (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $x, \frac{1}{2} - y, -z$.

C5ADP	$ \Delta $	C6ADP	$ \Delta $	C9ADP	$ \Delta $
P1–P2	0.1708 (7)	P1–P2	0.169 (1)	P1–P2	0.175 (1)
O11–O12	0.048 (3)	O11–O12	0.044 (3)	O11–O12	0.050 (3)
O21–O22	0.128 (2)	O21–O22	0.114 (3)	O21–O22	0.112 (2)
O31–O32	0.079 (2)	O31–O32	0.080 (3)	O31–O32	0.085 (2)
O41–O42	0.153 (2)	O41–O42	0.149 (3)	O41–O42	0.141 (2)
N1–N2 ⁱ	0.098 (3)	N1–N2	0.098 (4)	N1–N2	0.110 (4)
C11–C12 ⁱ	0.073 (4)	C11–C12	0.070 (4)	C11–C12	0.078 (4)
C21–C22 ⁱ	0.023 (4)	C21–C22	0.026 (4)	C21–C22	0.031 (4)
C31–C32 ⁱ	0.019 (4)	C31–C32	0.010 (5)	C31–C32	0.024 (4)
C41–C42 ⁱ	0.016 (4)	C41–C42	0.003 (5)	C41–C42	0.007 (4)
C51–C52 ⁱ	0.032 (6)	C51–C52	0.010 (5)	C51–C52	0.021 (4)
		C61–C62	0.019 (7)	C61–C62	0.007 (4)
				C71–C72	0.011 (4)
				C81–C82	0.020 (4)
				C91–C92	0.017 (5)
HO11–HO12	0.08 (4)	HO11–HO12	0.16 (4)	HO11–HO12	0.28 (4)
HO22–HO22 ⁱⁱ	0.65 (5)	HO22–HO22 ⁱⁱ	0.84 (2)	HO22–HO22 ⁱⁱ	0.96 (4)
HO41–HO41 ⁱⁱ	0.92 (4)	HO41–HO41 ⁱⁱ	0.97 (2)	HO41–HO41 ⁱⁱ	0.98 (5)

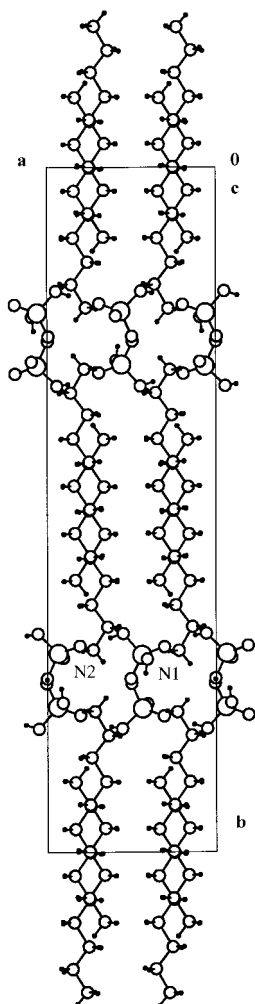


Figure 7

View of the unit cell of C9ADP along the *c* axis. The denomination of atoms is analogous to C6ADP (Fig. 5).

The twinning, despite its small fraction, turned out to be significant. In case of C5ADP the refinement if no twinning was assumed converged to $R_{\text{obs}} = 0.0407$, $wR_{\text{obs}} = 0.0561$, $R_{\text{all}} = 0.0568$, $wR_{\text{all}} = 0.0569$, 328 parameters, while in the case of C6ADP the refinement without the assumption of twinning converged to $R_{\text{obs}} = 0.0498$, $wR_{\text{obs}} = 0.0552$, $R_{\text{all}} = 0.1010$, $wR_{\text{all}} = 0.0622$, 362 parameters (*cf.* Table 1). The differences between the corresponding fractional coordinates were smaller than the 1.5 times the corresponding standard uncertainties.

The space group $P2_1/n$ of the studied compounds is a subgroup of $P2/b2_1/n2_1/a$ of the space groups of the prototypic phases. (Indeed the diffractions $0kl$, $k = 2n + 1$, and $hk0$, $h = 2n + 1$, are generally weak with a significant proportion being unobserved: $\sim 40\%$ in C5ADP and $\sim 60\%$ in C6ADP as well as C9ADP.) Similarly, as in C7ADP,

C8ADP and C10ADP the H atoms HO41 and HO22 are not related to a counterpart atom by a lost symmetry operation from the prototypic group in contrast to the other atoms in the structure (Table 7). (HO22 and HO41 correspond to the atoms H50 and H51, respectively, of the determination of C10ADP.) The symmetry reasons imposed by the assumption that the structures in both domains are the same, although differently oriented, suggest that the H atoms HO22 and HO41 should jump within a hydrogen bond from the donor to the acceptor O atoms. The situation is depicted in Fig. 1. In Fig. 2 the O atoms O22' and O41' are the hydrogen-bond donors, while O21 and O42 are the hydrogen-bond acceptors. All other atoms except HO22 and HO41 are linked by the lost twofold axis passing through $y = 1/4$ and $z = 1/2$. This lost symmetry element relates, however, the sites which can be occupied by the H atoms HO22 or HO41 after the ferroelastic switching.

Heating up to 373 K and subsequent cooling down calls forth the dense development of domains. This would mean that the H atoms HO22 and HO41 are either involved in the symmetric hydrogen bonds or disordered at the high-temperature phase: the H atoms HO22 and HO41 during phase transition from the high- to the low-temperature phases are forced to choose one of the two positions which is pertinent to either domain.

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