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# Revision of Ferroelastic Structures of *n*-Heptyl- and *n*-Octylammonium Dihydrogen Phosphate Crystals

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## Abstract

This study deals with the structure determination of $C_7H_{15}NH_3^+.H_2PO_4^-$ (C7ADP) and $C_8H_{17}NH_3^+.H_2PO_4^-$ (C8ADP). The samples used in this study were not subjected to a phase transition after they had been crystallized. Unlike a previous structure determination, weak reflections, now with indices $h = 2n + 1$, were included. This means that both structures are described in unit cells with the lattice parameters *a* twice as long as given previously. Both structures are quite similar; two double layers of dihydrogen phosphates, which are interconnected by hydrogen bonds (2.52–2.62 Å), pass through each unit cell. Alkylammonium groups interact with these dihydrogen phosphates *via* longer hydrogen bonds (>2.75 Å), while the rest of the aliphatic chains interact *via* van der Waals contacts. All H atoms were localized and no disorder of the H atoms was detected. Both structures described in the space group $P12_1/n1$ exhibit a reproducible ferroelastic switching. The hypothetical prototypic phase is orthorhombic with the space group number 60 $P2/b2_1/n2_1/a$. All atoms except two hydrogen species exist in pairs linked by the lost symmetry operations derived from the prototypic space group and are brought close to each other – up to 0.25 Å – under the action of them. Each of these two different hydrogens is involved in an asymmetric hydrogen bond between an oxygen pair. Under the action of a lost symmetry operation each of these hydrogens is displaced from one oxygen towards the other. Therefore, it is asssumed that during the ferroelastic switching the jumps of these two hydrogen species take place between the pertinent hydrogen-bond acceptor and donor oxygens. Hence, these oxygens reverse their role as hydrogen-bond donors and acceptors during the ferroelastic switching.

## 1. Introduction

In the course of the further investigation of the ferroelastic species $C_7H_{15}NH_3^+.H_2PO_4^-$ (C7ADP) and $C_8H_{17}NH_3^+.H_2PO_4^-$ (C8ADP) it was found that the lattice parameters *a* are in fact twice as long as reported in the previous study (Waśkowska & Kroupa, 1995). Thus, their communication reports only the superimposed structure from the regions $x \in <0,0.5)$ and $x \in <0.5,1)$ in the space group $P12_1/c1$.

Both compounds are representatives of a group of $C_nH_{2n+1}NH_3.H_2PO_4^-$ ($n$ = 1–9; $n$ = 12) and $C_nH_{2n+1}NH_3.H_2AsO_4^-$ ($n$ = 6–8) compounds. These species exhibit phase transitions and some of the phases are ferroelastic (Kroupa & Fuith, 1993, 1994). In these articles the authors pointed out the importance of a hydrogen-bond pattern for the occurrence of ferroelasticity and phase transitions in these compounds. Notably, in the deuterated C7ADP no ferroelastic domains were observed (Kroupa & Fuith, 1993).

Phase transitions both in C7ADP and C8ADP are summarized in Table 1. It follows from this table that the occurrence of some phase transitions depends on whether a sample had been heated previously. Further, the thermal dilatation in virgin and previously heated samples is different.

Table 1. *Overview of temperatures (K) of phase transitions in C7ADP and C8ADP during heating and cooling (Kroupa & Fuith, 1993, 1994)*

+ and − indicate the existence and non-existence of the pertinent phase transition when a sample is heated for the first time.

| C7ADP | | C8ADP | |
|---|---|---|---|
| Heating | Cooling | Heating | Cooling |
| 345 (1) | 333 (1) | 358 (1) | 350 (1) |
| 362 (1) + | | | |
| 368 (1) | 367 (1) | 368 (1) − | 367 (1) |

## 2. Experimental

The preparation of the title compounds is described elsewhere (Waśkowska & Kroupa, 1995, Table 2). 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

Table 2. *Experimental details*

| | C7ADP | C8ADP |
|---|---|---|
| Crystal data | | |
| Chemical formula | $C_7H_{15}NH_3^+.H_2PO_4^-$ | $C_8H_{17}NH_3^+.H_2PO_4^-$ |
| Chemical formula weight | 213.21 | 227.24 |
| Cell setting | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 9.155 (2) | 9.163 (1) |
| $b$ (Å) | 32.074 (3) | 34.677 (4) |
| $c$ (Å) | 7.350 (1) | 7.361 (7) |
| $\beta$ (°) | 90.90 (1) | 90.81 (1) |
| $V$ (Å$^3$) | 2158.1 (5) | 2338.7 (5) |
| $Z$ | 8 | 8 |
| $F(000)$ | 928 | 992 |
| $D_x$ (Mg m$^{-3}$) | 1.312 | 1.290 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| Wavelength (Å) | 0.71073 | 0.71073 |
| No. of reflections for cell parameters | 25 | 25 |
| $\theta$ range (°) | 7–19 | 6.5–26 |
| $\mu$ (mm$^{-1}$) | 0.234 | 0.220 |
| Temperature (K) | 290 (2) | 290 (2) |
| Crystal form | Plate | Elongated plate |
| Crystal size (mm) | 0.56 × 0.42 × 0.15 | 0.36 × 0.23 × 0.14 |
| Crystal colour | Colourless | Colourless |
| Data collection | | |
| Diffractometer | Enraf–Nonius CAD-4-MACHIII–PC | Enraf–Nonius CAD-4-MACHIII–PC |
| Data collection method | $\omega$ scans | $\omega$–$2\theta$ scans |
| Absorption correction | None | None |
| No. of measured reflections | 3879 | 4519 |
| No. of independent reflections | 3785 | 4099 |
| No. of observed reflections | 2877 | 2739 |
| Criterion for observed reflections | $F > 3\sigma(F)$ | $F > 3\sigma(F)$ |
| $R_{\rm int}$ | – | 0.0158 |
| $\theta_{\rm max}$ (°) | 25 | 25 |
| Range of $h, k, l$ | $0 \rightarrow h \rightarrow 10$ | $-10 \rightarrow h \rightarrow 10$ |
| | $-38 \rightarrow k \rightarrow 0$ | $0 \rightarrow k \rightarrow 41$ |
| | $-8 \rightarrow l \rightarrow 8$ | $0 \rightarrow l \rightarrow 8$ |
| No. of standard reflections | 5 | 6 |
| Frequency of standard reflections (min) | 3600 | 7200 |
| Intensity decay (%) | 2 | 3 |
| Refinement | | |
| Refinement on | $F$ | $F$ |
| $R$ | 0.0390 | 0.0333 |
| $wR$ | 0.0594 | 0.0478 |
| $S$ | 1.66 | 1.23 |
| No. of reflections used in refinement | 3785 | 4099 |
| No. of parameters used | 396 | 430 |
| H-atom treatment | All H-atom parameters refined | All H-atom parameters refined |
| Weighting scheme | $w = [\sigma^2(F_o) + 0.0009(F_o)^2]^{-1}$ | $w = [\sigma^2(F_o) + 0.0009(F_o)^2]^{-1}$ |
| $(\Delta/\sigma)_{\rm max}$ | 0.01 | 0.01 |
| $\Delta\rho_{\rm max}$ (e Å$^{-3}$) | 0.44 | 0.37 |
| $\Delta\rho_{\rm min}$ (e Å$^{-3}$) | −0.41 | −0.36 |
| Extinction method | Lorentzian isotropic (Becker & Coppens, 1974) | Lorentzian isotropic (Becker & Coppens, 1974) |
| Extinction coefficient | $1.7\,(2) \times 10^{-4}$ | $1.0\,(1) \times 10^{-4}$ |
| Source of atomic scattering factors | *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A and 2.3.1) | *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A and 2.3.1) |
| Computer programs | | |
| Data collection | *CAD*-4 *Software* (Enraf–Nonius, 1989) | *CAD*-4 *Software* (Enraf–Nonius, 1989) |
| Cell refinement | *CAD*-4 *Software* (Enraf–Nonius, 1989) | *CAD*-4 *Software* (Enraf–Nonius, 1989) |
| Data reduction | *ZPRAC* (Fábry, 1993) | *ZPRAC* (Fábry, 1993) |
| Structure solution | *SDS* (Petříček, 1995) | *SDS* (Petříček, 1995) |
| Structure refinement | *SDS* (Petříček, 1995) | *SDS* (Petříček, 1995) |
| Molecular graphics | *PICTUR* (Dušek, 1993) | *PICTUR* (Dušek, 1993) |

underwent reproducible ferroelastic switching could be observed under the polarization microscope. 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 the pressure exceeded some limits, then either cracks appeared along the **a** direction or the crystal disintegrated. Cracks either perpendicular or parallel to the **a** direction can also be developed by heating above 370 K and subsequent cooling. Such a thermal treatment also caused the development of domain walls, which were much denser compared with those of virgin (unheated) samples.

Several different crystals of C7ADP with developed domains were mounted on a Weissenberg camera. The **a**-axis oscillation photographs showed the presence of faint reflections in the odd layers. These reflections had been overlooked in the previous study (Waśkowska & Kroupa, 1995). They faded out for angles of $\theta$ larger than ~40° (Cu $K\alpha$), while the reflections from the even layers were observable in the whole range of $\theta$. The Weissenberg photographs $0kl$ revealed slight splitting of the **c** axis. The oscillation and Weissenberg photographs $hkl$, $h \in \langle 0,3 \rangle$, confirmed the monoclinic symmetry and the systematic absences conformed to the space group $P12_1/n1$. Some of the Weissenberg photographs of the level $1kl$ taken on a relatively large crystal revealed a diffuse festoon-shaped background below reflections.

An **a**-axis oscillation photograph of a crystal of C8ADP (and also C9ADP) also revealed the presence of weak odd layers. The appearance of a $0kl$ Weissenberg photograph of C8ADP resembled closely the corresponding one for C7ADP.

Another crystal of C7ADP with clearly developed ferroelastic domains was mounted on a diffractometer. Well distinguished pairs of reflections of the $00l$ type (angular difference $\simeq$ 1.6°) were detected, while no splitting of the reflections of the $h00$ type was observed. Similar reflection pairs were also observed for several $h0l$ reflections. Integrated intensities of a few of these reflections were measured before and after a uniaxial stress had been exerted in order to change the domain fractions. Notably, the intensities of the $h00$ reflections remained the same, while the intensities of the pertinent paired $00l$ reflections increased and decreased, respectively.

Luckily, and with care, it was possible to cut out apparently single domain crystals from the virgin (unheated) samples of both C7ADP and C8ADP. Such single-domain crystals were employed in the data collection experiments (Table 2). These samples were stressed since a slight force exerted in the <001> direction caused revelation of the domain walls, which disappeared immediately after the pressure had been relieved.

The structure of both crystals was determined in the following way: At the first stage only the reflections $hkl$ with $h = 2n$ were used and the superimposed structure was calculated *in the small unit cell with* $\mathbf{a}' = \mathbf{a}/2$. [The contents of halves of the unit cell with $x \in \langle 0,0.5)$ and $x \in \langle 0.5,1)$ are superimposed.] The Patterson synthesis revealed the P atoms, and subsequent Fourier syntheses and refinements resulted in a localization of all non-H and H atoms connected to the alkane chains. The respective superimposed structures of C7ADP and C8ADP corresponded well to those determined by Waśkowska & Kroupa (1995). In these superimposed structures the dihydrogen phosphates were disordered.

In the second step an idealized structure was calculated by copying the structure into the large unit cell; in the idealized structure there are pairs of atoms related by the translation ($\frac{1}{2}$, 0, 0). It was then assumed that the pairs of crystallographically independent molecules (*i.e.* dihydrogen phosphates as well as $n$-alkylammoniums) are of the same geometry and the positions of these molecules as well as their average geometry were refined at the beginning. It was also checked whether or not the disorder of the dihydrogen phosphates had been removed completely by the copying of the atoms into the double unit cell. Therefore, a constrained refinement regarding the occupation of the disordered dihydrogen phosphates in both positions was applied. [Let us suppose that a dihydrogen phosphate is disordered in a particular position; $m$ and $n$ are the fractions and $m + n = 1$. Then the occupation factors of the molecules related by the translation ($\frac{1}{2}$,0,0) will be $1 - m$, $1 - n$, respectively, *i.e.* $n$ and $m$.] No such disorder was detected. This means that the disorder of the dihydrogen phosphates observed in Waśkowska & Kroupa (1995) was caused by the omission of the reflections with $h = 2n + 1$.

After the refinement had converged the atoms were refined individually and the H atoms found in the Fourier maps were also included in the refinement. Especially the H atoms belonging to the methylene groups were clearly recognizable, while the H atoms belonging to the phosphate oxygens were the most difficult to be found. At the final stage of the refinement an extinction correction (Becker & Coppens, 1974) was introduced into the refinement.

Information regarding crystal data, data collection and refinement for C7ADP and C8ADP is summarized in Table 2.

## 3. Discussion

Figs. 1–4 depict C7ADP and C8ADP. The atomic coordinates of C7ADP and C8ADP, as well as $U_{\rm iso}/U^*_{\rm eq}$, are given in Tables 3 and 4, respectively. The relevant atomic distances and angles are listed in Tables 5 and 6.† The geometric features of the dihydrogen phosphates compared with the structures with $R \leq 0.05$ found in the ICSD (ICSD, 1990; Bergerhoff, Hundt, Sievers & Brown, 1983) and the CSD (Cambridge Structural Database, 1995; Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Mitchell, Smith & Watson, 1991) are normal. The corresponding interatomic distances of the crystallographically independent molecules are in accordance with C7ADP as well as in C8ADP (see also Tables 5 and 6).

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† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: SH0085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Although the hydrogen-bond pattern within each dihydrogen phosphate layer and the localization of the alkylammonium chains in the respective unit cells are quite similar in C7ADP and C8ADP, there is a clear difference in packing of these chains in C7ADP and C8ADP, as viewed along the **c** axis (Figs. 2 and 4). Nevertheless, in C7ADP as well as in C8ADP the closest non-bonding distances of methylene and the methyl groups are ~4 Å. These distances correspond well to the values of van der Waals contacts between these groups (Weast & Astle, 1980).

The localization of the H atoms belonging to the $H_2PO_4^-$ groups is in accordance with the distribution of the P—O distances in C7ADP and C8ADP. The longer axes of oxygens thermal ellipsoids are rather perpendicular to the P—O axes. This also supports the conclusion that most of the hydrogens are ordered in the room-temperature phases of C7ADP and C8ADP, otherwise the longer axes of the ellipsoids of thermal vibrations would be oriented along the P—O bonds.

Hydrogen bonds connect mutually the $H_2PO_4^-$ groups and the $H_2PO_4^-$ groups with alkylammonium groups in each double layer of dihydrogen phosphates (Fig. 5). The hydrogen bonds between the oxygens of the $H_2PO_4^-$ groups are shorter than those between alkylammoniums and $H_2PO_4^-$ groups (Tables 5 and 6). The shorter the hydrogen bonds, the angles contained by the contacts between the hydrogen and the respective donor and acceptor atoms tend to be closer to 180° (Jeffrey, 1995). The O—H···O bridges are straighter than N—H···O both in C7ADP and C8ADP. This is in accordance with Jeffrey's (1995) overview. It is worthwhile pointing out that the O···O hydrogen bond lengths are distributed between two distances *ca* 2.53 and 2.61 Å long. In these shorter O···O hydrogen bonds the hydrogens which jump from the donor to the acceptor oxygens during ferroelastic switching are involved (see below).

Each alkylammonium is connected *via* hydrogen bonds to three different dihydrogen phosphates. Two out of three alkylammonium H atoms are directed towards

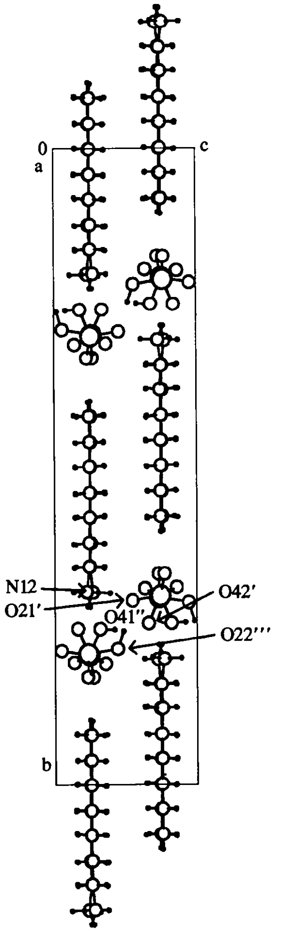

Fig. 1. View of the unit cell of C7ADP along the **a** axis. The primed, double- and triple-primed atoms are derived from those given in Table 2 by the operations: $1-x, 1-y, 1-z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$, respectively.

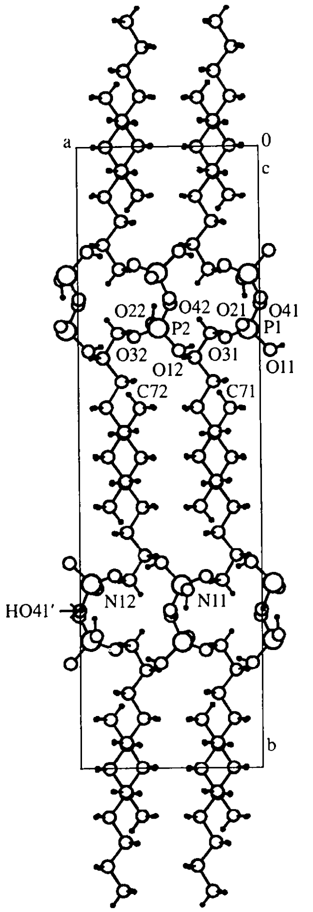

Fig. 2. View of the unit cell of C7ADP along the **c** axis. The primed HO41 is derived from the position given in Table 2 by the operation $1-x, 1-y, 1-z$.

the oxo groups of a $H_2PO_4^-$ group, while the third points to an OH group of the $H_2PO_4^-$. Fig. 5 depicts the hydrogen-bonding pattern in C8ADP within the double layer of dihydrogen phosphate with fractional coordinates $0 < y < 0.5$. The corresponding picture regarding C7ADP is quite similar and is therefore not given in this article.

The most intriguing point of the present structural study is the elucidation of the ferroelastic switching, described in the *Experimental*.

A closer inspection of both structures showed that they may be considered as distorted orthorhombic structures described in $P2/b2_1/n\ 2_1/a$ (space group number 60). The crystallographically independent atoms, whose coordinates are given in Tables 4 and 5, respectively, are brought very close together by the operation $-\frac{1}{2} + x, y, \frac{1}{2} - z$, with the exception of the atoms HO41 and HO22. (HO41 and HO22 are connected to just one crystallographically independent dihydrogen phosphate.) Table 7 lists the corresponding atomic displacement vectors for both compounds (Abrahams & Keve, 1971). Of course, these atomic displacement vectors can be related to any of the operations of the space group $P2/b2_1/n2_1/a$ which are not present in its subgroup $P12_1/n1$. If we take a lost twofold axis perpendicular to the **bc** plane of the unit cell (or almost parallel to the **a** axis), which passes *e.g.* through $y = 3/4$ and $z = 1/2$ between the atoms O41″ and O42′ in Fig. 1, then it is clear from Figs. 1 and 3, respectively, that all the atoms except HO41 and HO22 (which are close to this axis) are almost brought into coincidence with their counterparts related by this lost symmetry operation.

The hydrogens HO41 and HO22 are transformed as any other atoms into the other domain by the lost symmetry operations, but in contrast, no counterpart atom can be found for them in the vicinity of an image atom generated by a lost symmetry operation. This would imply (assuming that the structure in each

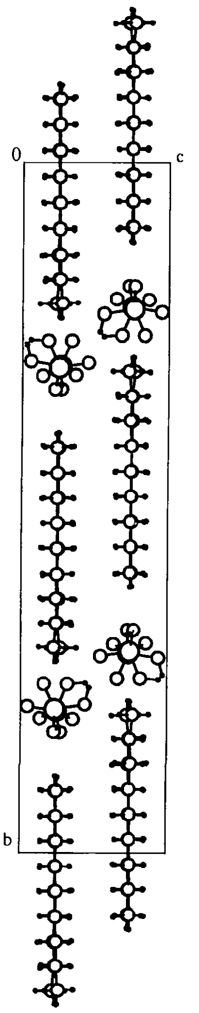

Fig. 3. View of the unit cell of C8ADP along the **a** axis. The denomination of atoms is analogous, as in C7ADP (Fig. 1).

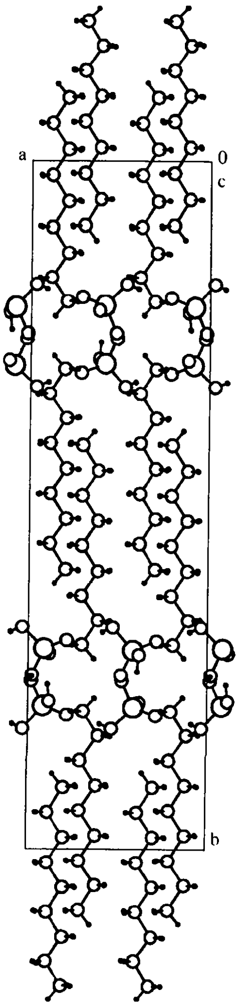

Fig. 4. View of the unit cell of C8ADP along the **c** axis. The denomination of atoms is analogous, as in C7ADP (Fig. 2).

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for C7ADP*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| P1 | 0.06345 (5) | 0.29667 (1) | 0.25522 (6) | 0.0186 (2) |
| O11 | −0.0570 (2) | 0.33073 (5) | 0.2280 (2) | 0.0333 (5) |
| O21 | 0.0935 (2) | 0.28917 (4) | 0.4536 (2) | 0.0314 (5) |
| O31 | 0.1915 (1) | 0.30973 (4) | 0.1430 (2) | 0.0275 (4) |
| O41 | −0.0017 (2) | 0.25452 (4) | 0.1803 (2) | 0.0287 (5) |
| P2 | 0.55942 (5) | 0.29390 (1) | 0.26447 (6) | 0.0189 (2) |
| O12 | 0.4474 (2) | 0.33045 (5) | 0.2688 (2) | 0.0328 (5) |
| O22 | 0.5911 (2) | 0.28638 (5) | 0.0578 (2) | 0.0343 (5) |
| O32 | 0.6938 (2) | 0.30783 (5) | 0.3647 (2) | 0.0322 (5) |
| O42 | 0.4939 (2) | 0.25420 (4) | 0.3389 (2) | 0.0271 (4) |
| N11 | 0.2186 (2) | 0.69794 (6) | 0.2694 (3) | 0.0270 (6) |
| C11 | 0.1374 (2) | 0.65802 (6) | 0.2487 (3) | 0.0270 (7) |
| C21 | 0.2380 (3) | 0.62074 (7) | 0.2559 (3) | 0.0303 (7) |
| C31 | 0.1531 (3) | 0.58017 (7) | 0.2496 (3) | 0.0324 (7) |
| C41 | 0.2487 (3) | 0.54140 (6) | 0.2526 (3) | 0.0304 (7) |
| C51 | 0.1609 (3) | 0.50097 (6) | 0.2513 (3) | 0.0316 (7) |
| C61 | 0.2543 (3) | 0.46195 (7) | 0.2533 (3) | 0.0358 (8) |
| C71 | 0.1668 (4) | 0.42185 (8) | 0.2547 (4) | 0.050 (1) |
| N12 | 0.7278 (2) | 0.69724 (6) | 0.2262 (3) | 0.0253 (6) |
| C12 | 0.6428 (2) | 0.65833 (6) | 0.2440 (3) | 0.0263 (7) |
| C22 | 0.7409 (3) | 0.62029 (6) | 0.2426 (3) | 0.0298 (7) |
| C32 | 0.6538 (3) | 0.58000 (7) | 0.2476 (3) | 0.0313 (7) |
| C42 | 0.7485 (3) | 0.54100 (6) | 0.2475 (3) | 0.0303 (7) |
| C52 | 0.6601 (3) | 0.50075 (6) | 0.2465 (3) | 0.0315 (7) |
| C62 | 0.7533 (3) | 0.46165 (7) | 0.2464 (3) | 0.0359 (8) |
| C72 | 0.6652 (4) | 0.42165 (8) | 0.2437 (4) | 0.049 (1) |
| HO11 | −0.126 (4) | 0.324 (1) | 0.274 (4) | 0.06 (1) |
| HO41 | 0.006 (4) | 0.256 (1) | 0.081 (5) | 0.09 (1) |
| HO12 | 0.374 (3) | 0.3237 (8) | 0.240 (3) | 0.034 (8) |
| HO22 | 0.581 (4) | 0.258 (1) | 0.018 (5) | 0.09 (1) |

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for C8ADP*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| P1 | 0.08744 (6) | 0.29317 (2) | 0.25535 (7) | 0.0203 (2) |
| O11 | −0.0335 (2) | 0.32453 (5) | 0.2284 (2) | 0.0343 (6) |
| O21 | 0.1178 (2) | 0.28620 (4) | 0.4535 (2) | 0.0317 (5) |
| O31 | 0.2148 (2) | 0.30518 (5) | 0.1427 (2) | 0.0287 (5) |
| O41 | 0.0224 (2) | 0.25405 (4) | 0.1804 (2) | 0.0290 (5) |
| P2 | 0.5832 (6) | 0.29056 (2) | 0.2653 (7) | 0.0205 (2) |
| O12 | 0.4711 (2) | 0.32433 (5) | 0.2697 (3) | 0.0349 (6) |
| O22 | 0.6167 (2) | 0.28371 (5) | 0.0591 (2) | 0.0360 (6) |
| O32 | 0.7170 (2) | 0.30381 (5) | 0.3659 (2) | 0.0315 (5) |
| O42 | 0.5176 (2) | 0.25381 (4) | 0.3394 (2) | 0.0284 (5) |
| N11 | 0.1931 (2) | 0.70162 (6) | 0.2680 (3) | 0.0268 (6) |
| C11 | 0.1087 (3) | 0.66539 (7) | 0.2489 (4) | 0.0286 (7) |
| C21 | 0.2048 (3) | 0.63000 (7) | 0.2556 (4) | 0.0309 (8) |
| C31 | 0.1150 (3) | 0.59309 (7) | 0.2494 (4) | 0.0343 (8) |
| C41 | 0.2066 (3) | 0.55655 (6) | 0.2523 (4) | 0.0326 (8) |
| C51 | 0.1168 (3) | 0.51978 (7) | 0.2506 (4) | 0.0350 (8) |
| C61 | 0.2060 (3) | 0.48293 (7) | 0.2536 (4) | 0.0350 (8) |
| C71 | 0.1155 (3) | 0.44657 (8) | 0.2523 (4) | 0.0431 (9) |
| C81 | 0.2045 (5) | 0.40960 (8) | 0.2546 (5) | 0.0545 (1) |
| N12 | 0.7027 (2) | 0.70110 (6) | 0.2260 (3) | 0.0268 (6) |
| C12 | 0.6140 (2) | 0.66548 (6) | 0.2428 (3) | 0.0279 (7) |
| C22 | 0.7071 (3) | 0.62980 (6) | 0.2422 (4) | 0.0305 (8) |
| C32 | 0.6163 (3) | 0.59327 (7) | 0.2465 (4) | 0.0337 (8) |
| C42 | 0.7062 (3) | 0.55642 (6) | 0.2463 (4) | 0.0327 (8) |
| C52 | 0.6158 (3) | 0.51967 (7) | 0.2484 (4) | 0.0347 (8) |
| C62 | 0.7056 (3) | 0.48291 (6) | 0.2468 (4) | 0.0340 (8) |
| C72 | 0.6152 (3) | 0.4462 (7) | 0.2483 (4) | 0.0421 (9) |
| C82 | 0.7042 (5) | 0.40955 (8) | 0.2467 (5) | 0.054 (1) |
| HO11 | −0.099 (3) | 0.3174 (9) | 0.272 (4) | 0.06 (1) |
| HO41 | 0.019 (4) | 0.2524 (8) | 0.057 (4) | 0.07 (1) |
| HO12 | 0.413 (3) | 0.3173 (9) | 0.237 (4) | 0.04 (1) |
| HO22 | 0.608 (5) | 0.259 (1) | 0.031 (6) | 0.12 (2) |

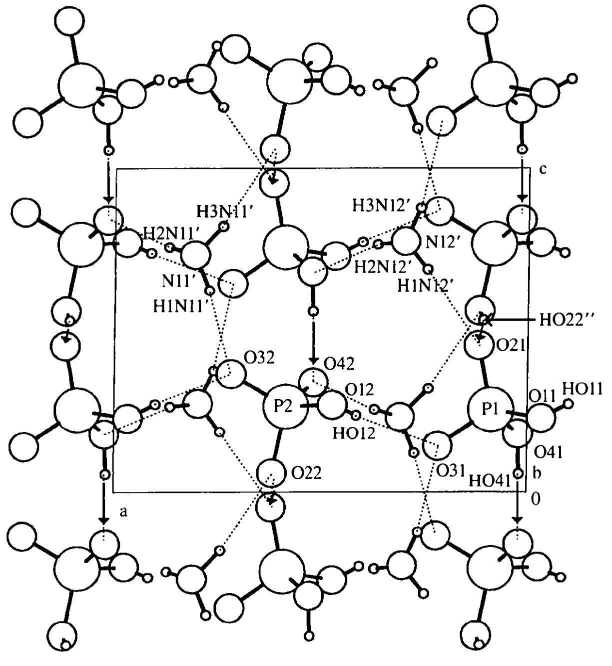

Fig. 5. The hydrogen-bonding pattern interconnecting a double layer of dihydrogen phosphates and the $NH_3$ groups in C8ADP. (The view of C7ADP is virtually the same.) The primed and double-primed atoms are linked to the corresponding atoms given in Table 8 by the operations $1 - x$, $1 - y$, $1 - z$ and $x - \frac{1}{2}$, $\frac{1}{2} - y$, $\frac{1}{2} + z$, respectively. The hydrogen jumps which occur during the ferroelastic switching are indicated by arrows.

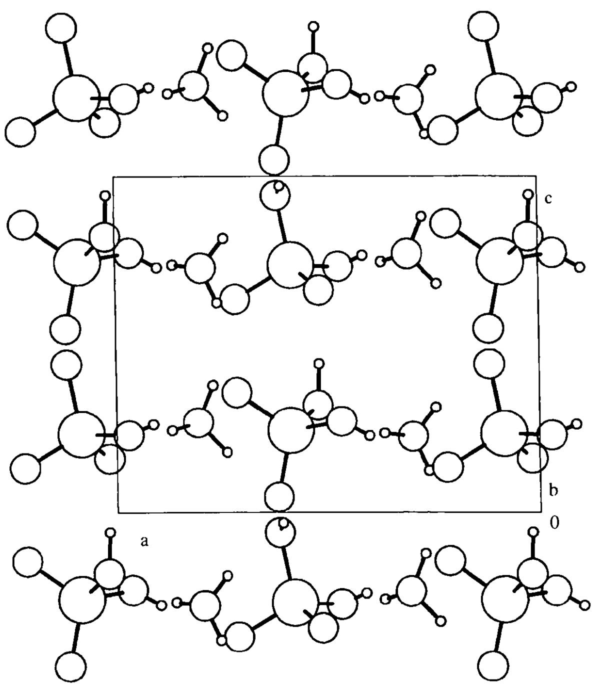

Fig. 6. Projection of a doubled layer of dihydrogen phosphates and the $NH_3$ groups in C8ADP after the ferroelastic switching. The positions of the atoms here are related to those in Fig. 5 by the operation $\frac{1}{2} + x$, $y$, $\frac{1}{2} - z$ and the monoclinic angle $\beta'$ here equals 89.18°.

Table 5. *Selected geometric parameters (Å, °) for C7ADP*

| | | | |
|---|---|---|---|
| P1—O11 | 1.563 (2) | O31—N12$^{\mathrm{v}}$ | 2.834 (3) |
| P1—O21 | 1.500 (1) | O41—N12$^{\mathrm{vi}}$ | 2.860 (3) |
| P1—O31 | 1.504 (1) | P2—O12 | 1.558 (2) |
| P1—O41 | 1.574 (2) | P2—O22 | 1.571 (1) |
| O11—HO11 | 0.76 (3) | P2—O32 | 1.493 (2) |
| O41—HO41 | 0.74 (4) | P2—O42 | 1.513 (1) |
| N11—C11 | 1.487 (3) | O12—HO12 | 0.74 (3) |
| C11—C21 | 1.510 (3) | O22—HO22 | 0.97 (3) |
| C21—C31 | 1.516 (3) | N12—C12 | 1.478 (3) |
| C31—C41 | 1.521 (3) | C12—C22 | 1.515 (3) |
| C41—C51 | 1.526 (3) | C22—C32 | 1.519 (3) |
| C51—C61 | 1.516 (3) | C32—C42 | 1.521 (3) |
| C61—C71 | 1.515 (4) | C42—C52 | 1.524 (3) |
| N11—H1N11 | 0.94 (2) | C52—C62 | 1.517 (3) |
| N11—H2N11 | 0.93 (3) | C62—C72 | 1.516 (4) |
| N11—H3N11 | 0.85 (3) | N12—H1N12 | 0.77 (2) |
| C11—H1C11 | 0.99 (3) | N12—H2N12 | 0.93 (3) |
| C11—H2C11 | 0.92 (2) | N12—H3N12 | 0.81 (3) |
| C21—H1C21 | 1.02 (3) | C12—H1C12 | 0.88 (3) |
| C21—H2C21 | 0.89 (3) | C12—H2C12 | 0.90 (2) |
| C31—H1C31 | 1.03 (3) | C22—H1C22 | 0.98 (2) |
| C31—H2C31 | 0.96 (3) | C22—H2C22 | 0.99 (3) |
| C41—H1C41 | 1.01 (2) | C32—H1C32 | 0.97 (3) |
| C41—H2C41 | 0.98 (2) | C32—H2C32 | 0.93 (3) |
| C51—H1C51 | 0.99 (2) | C42—H1C42 | 1.00 (2) |
| C51—H2C51 | 0.93 (3) | C42—H2C42 | 1.01 (3) |
| C61—H1C61 | 1.01 (3) | C52—H1C52 | 0.98 (2) |
| C61—H2C61 | 0.89 (3) | C52—H2C52 | 0.99 (3) |
| C71—H1C71 | 0.90 (3) | C62—H1C62 | 0.97 (3) |
| C71—H2C71 | 0.94 (4) | C62—H2C62 | 0.93 (2) |
| C71—H3C71 | 0.98 (3) | C72—H1C72 | 1.02 (3) |
| O11—O32$^{\mathrm{i}}$ | 2.613 (2) | C72—H2C72 | 0.90 (3) |
| O21—O22$^{\mathrm{ii}}$ | 2.541 (2) | C72—H3C72 | 1.07 (3) |
| O31—O12 | 2.593 (2) | O22—N11$^{\mathrm{v}}$ | 3.035 (3) |
| O41—O42$^{\mathrm{iii}}$ | 2.526 (2) | O32—N11$^{\mathrm{iv}}$ | 2.802 (2) |
| O21—N12$^{\mathrm{iv}}$ | 2.879 (3) | O42—N11$^{\mathrm{vi}}$ | 2.762 (2) |
| O11—P1—O21 | 110.79 (9) | O12—P2—O22 | 105.48 (9) |
| O11—P1—O31 | 106.82 (8) | O12—P2—O32 | 107.56 (9) |
| O11—P1—O41 | 107.01 (8) | O12—P2—O42 | 111.17 (8) |
| O21—P1—O31 | 116.52 (8) | O22—P2—O32 | 111.16 (9) |
| O21—P1—O41 | 105.39 (8) | O22—P2—O42 | 107.52 (8) |
| O31—P1—O41 | 109.97 (8) | O32—P2—O42 | 113.66 (8) |

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

Table 6. *Selected geometric parameters (Å, °) for C8ADP*

| | | | |
|---|---|---|---|
| P1—O11 | 1.563 (2) | O31—N12$^{\mathrm{v}}$ | 2.836 (3) |
| P1—O21 | 1.501 (2) | O41—N12$^{\mathrm{vi}}$ | 2.853 (3) |
| P1—O31 | 1.500 (2) | P2—O12 | 1.558 (2) |
| P1—O41 | 1.578 (2) | P2—O22 | 1.571 (2) |
| O11—HO11 | 0.73 (3) | P2—O32 | 1.496 (2) |
| O41—HO41 | 0.91 (3) | P2—O42 | 1.514 (2) |
| N11—C11 | 1.482 (3) | O12—HO12 | 0.63 (3) |
| C11—C21 | 1.511 (3) | O22—HO22 | 0.88 (4) |
| C21—C31 | 1.522 (3) | N12—C12 | 1.485 (3) |
| C31—C41 | 1.520 (3) | C12—C22 | 1.503 (3) |
| C41—C51 | 1.518 (3) | C22—C32 | 1.517 (3) |
| C51—C61 | 1.517 (4) | C32—C42 | 1.521 (3) |
| C61—C71 | 1.510 (4) | C42—C52 | 1.520 (3) |
| C71—C81 | 1.520 (4) | C52—C62 | 1.517 (3) |
| N11—H1N11 | 0.87 (3) | C62—C72 | 1.518 (4) |
| N11—H2N11 | 0.89 (3) | C72—C82 | 1.512 (4) |
| N11—H3N11 | 0.91 (3) | N12—H1N12 | 0.81 (3) |
| C11—H1C11 | 0.93 (3) | N12—H2N12 | 0.95 (3) |
| C11—H2C11 | 0.88 (3) | N12—H3N12 | 0.83 (3) |
| C21—H1C21 | 0.98 (3) | C12—H1C12 | 0.88 (3) |
| C21—H2C21 | 0.98 (3) | C12—H2C12 | 0.97 (3) |
| C31—H1C31 | 0.95 (3) | C22—H1C22 | 0.98 (3) |
| C31—H2C31 | 0.90 (3) | C22—H2C22 | 0.97 (3) |
| C41—H1C41 | 0.95 (3) | C32—H1C32 | 0.94 (3) |
| C41—H2C41 | 0.99 (3) | C32—H2C32 | 0.94 (3) |
| C51—H1C51 | 0.91 (3) | C42—H1C42 | 0.97 (3) |
| C51—H2C51 | 0.98 (3) | C42—H2C42 | 1.00 (3) |
| C61—H1C61 | 0.93 (3) | C52—H1C52 | 0.90 (3) |
| C61—H2C61 | 0.96 (3) | C52—H2C52 | 0.96 (3) |
| C71—H1C71 | 0.88 (3) | C62—H1C62 | 0.95 (3) |
| C71—H2C71 | 0.92 (3) | C62—H2C62 | 1.01 (3) |
| C81—H1C81 | 0.96 (4) | C72—H1C72 | 0.96 (3) |
| C81—H2C81 | 0.93 (4) | C72—H2C72 | 0.94 (3) |
| C81—H3C81 | 0.93 (4) | C82—H1C82 | 0.94 (4) |
| O11—O32$^{\mathrm{i}}$ | 2.615 (2) | C82—H2C82 | 0.89 (4) |
| O21—O22$^{\mathrm{ii}}$ | 2.546 (2) | C82—H3C82 | 0.95 (4) |
| O31—O12 | 2.602 (2) | O22—N11$^{\mathrm{v}}$ | 3.035 (3) |
| O41—O42$^{\mathrm{iii}}$ | 2.525 (2) | O32—N11$^{\mathrm{iv}}$ | 2.813 (3) |
| O21—N12$^{\mathrm{iv}}$ | 2.890 (3) | O42—N11$^{\mathrm{vi}}$ | 2.754 (3) |
| O11—P1—O21 | 110.92 (9) | O12—P2—O22 | 105.76 (10) |
| O11—P1—O41 | 106.87 (9) | O12—P2—O42 | 111.13 (9) |
| O11—P1—O31 | 106.98 (9) | O12—P2—O32 | 107.12 (10) |
| O21—P1—O41 | 105.38 (9) | O22—P2—O42 | 107.76 (9) |
| O21—P1—O31 | 116.54 (9) | O22—P2—O32 | 110.77 (9) |
| O31—P1—O41 | 109.77 (9) | O32—P2—O42 | 114.01 (9) |

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

domain is identical) that the hydrogens HO41 and HO22 interchange their positions between the oxygen pairs which are bridged by them. The sites which are occupied by these hydrogens are generated by a lost symmetry operation.

This would mean that during the ferroelastic switching the hydrogens HO41 and HO22 jump from one site to the other. Thus, the pertinent oxygens, involved in these hydrogen bonds, reverse their role as donor and acceptor atoms. This must occur as a collective phenomenon at distances as large as a domain size. The hydrogen jumps are accompanied by slight shifts and rotations of dihydrogen phosphates and alkylammoniums.

Figs. 5 and 6 depict projections of a double layer of dihydrogen phosphates and $NH_3$ groups of C8ADP before and after ferroelastic switching, respectively: Fig. 5 shows the double layer related to the atomic coordinates given in Table 4 in the unit cell with $\beta = 90.81°$, while in Fig. 6 the atomic coordinates are transformed by the operation $\frac{1}{2}+x, y, \frac{1}{2}-z$ into the unit cell whose angle $\beta' = 180° - \beta$. (The analogous pictures of C7ADP are almost identical to Figs. 5 and 6 and, therefore, are not given here.) The arrows in Fig. 5 indicate the hydrogen jumps during ferroelastic switching.

The change of angle $\beta$ into $\beta'$ corresponds to the unit-cell transformation

$$[\mathbf{a}'\ \mathbf{b}'\ \mathbf{c}'] = [\mathbf{a}\ \mathbf{b}\ \mathbf{c}]\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

Such a unit-cell transformation with simultaneous transformation of coordinates $\frac{1}{2}+x, y, \frac{1}{2}-z$ preserves the structure intact and is suitable for the description of the mutual orientation of both domains.

The development of cracks as well as new domains, which is caused by heating above 370 K and subsequent cooling to room temperature, may be explained by a disorder of the pertinent hydrogens HO41 and HO22 above 370 K. Subsequent cooling might call forth a

Table 7. *Absolute values of atomic displacement vectors /Δ/ (Å) in C7ADP and C8ADP*

All but HO41 and HO22 atoms (marked with '*') are brought close to each other by the operation $\frac{1}{2}+x, y, \frac{1}{2}-z$. The HO41 and HO22 atoms are brought to each other by the operation $x, \frac{1}{2}-y, -z$.

| | C7ADP \|Δ\| | C8ADP \|Δ\| |
|---|---|---|
| P1—P2 | 0.1735 (6) | 0.1809 (7) |
| O11—O12 | 0.048 (2) | 0.045 (3) |
| O21—O22 | 0.124 (2) | 0.127 (2) |
| O31—O32 | 0.086 (2) | 0.082 (2) |
| O41—O42 | 0.146 (2) | 0.152 (2) |
| N11—N12 | 0.092 (3) | 0.099 (3) |
| C11—C12 | 0.073 (3) | 0.078 (4) |
| C21—C22 | 0.032 (3) | 0.028 (3) |
| C31—C32 | 0.022 (3) | 0.033 (4) |
| C41—C42 | 0.013 (3) | 0.012 (4) |
| C51—C52 | 0.020 (3) | 0.013 (4) |
| C61—C62 | 0.013 (4) | 0.006 (4) |
| C71—C72 | 0.020 (5) | 0.012 (4) |
| C81—C82 | — | 0.010 (5) |
| H1N11—H3N12 | 0.21 (4) | 0.12 (4) |
| H2N11—H2N12 | 0.15 (3) | 0.15 (4) |
| H3N11—H1N12 | 0.09 (3) | 0.07 (4) |
| H1C11—H2C12 | 0.11 (4) | 0.17 (4) |
| H2C11—H1C12 | 0.12 (4) | 0.14 (4) |
| H1C21—H2C22 | 0.04 (4) | 0.04 (4) |
| H2C21—H1C22 | 0.11 (4) | 0.09 (4) |
| H1C31—H2C32 | 0.07 (4) | 0.07 (4) |
| H2C31—H1C32 | 0.10 (4) | 0.07 (4) |
| H1C41—H2C42 | 0.11 (3) | 0.07 (4) |
| H2C41—H1C42 | 0.03 (4) | 0.06 (4) |
| H1C51—H2C52 | 0.07 (3) | 0.07 (4) |
| H2C51—H1C52 | 0.11 (3) | 0.06 (4) |
| H1C61—H2C62 | 0.09 (4) | 0.10 (4) |
| H2C61—H1C62 | 0.08 (4) | 0.04 (4) |
| H1C71—H3C72 | 0.21 (5) | 0.05 (4) |
| H2C71—H2C72 | 0.09 (5) | 0.08 (5) |
| H3C71—H1C72 | 0.10 (4) | — |
| H1C81—H3C82 | — | 0.06 (5) |
| H2C81—H2C82 | — | 0.05 (5) |
| H3C81—H1C82 | — | 0.03 (5) |
| HO11—HO12 | 0.10 (4) | 0.13 (4) |
| *HO41—HO41 | 1.24 (5) | 0.86 (5) |
| *HO22—HO22 | 0.56 (5) | 0.77 (6) |

rearrangement of these hydrogens into an ordered state with concomitant development of new domains.

Similar hydrogen jumps were described for $H_3BO_3$ by Wadhawan (1978). The neutron diffraction determination of $D_3BO_3$ (Craven & Sabine, 1966) revealed the O···O distances bridged by the hydrogen bonds, which are 2.68 (2)–2.72 (2) Å long. An even more complicated example of urea inclusion compounds, where hydrogen bonds break and reestablish during ferroelastic switching, has recently been described by Brown & Hollingsworth (1995).

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