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# Ferroelastic *n*-propylammonium dihydrogenphosphate

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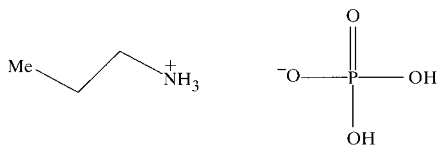
*n*-Propylammonium dihydrogenphosphate, $C_3H_7NH_3^+\cdot H_2PO_4^-$, crystals are ferroelastic at room temperature. The phase transition into the prototypic phase takes place at approximately 378 K. All atoms except two H atoms are linked by the lost symmetry operations derived from the prototypic 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. Ferroelastic switching is concomitant with jumps of these H atoms from the donor to the acceptor O atoms. The compound belongs to the structural family of *n*-alkylammonium dihydrogenphosphate and in particular to the structure type of pentylammonium dihydrogenphosphate, which differs by localization of alternating layers from the rest of the known alkylammonium dihydrogenphosphates. The crystal was slightly twinned; the proportion of the minor domain was approximately 3.5%.

## Comment

The title compound, (I), belongs to the series of *n*-alkylammonium dihydrogenphosphates which show ferroelasticity, as well as a number of interesting phase transitions. (Hereafter the denomination C*n*ADP will be applied for *n*-alkylammonium dihydrogenphosphates.) Among other factors, these phase transitions depend on parity of the C atoms in an alkylammonium chain and some of them show hysteresis effects (Kroupa & Fuith, 1993, 1994). Up to now, several structures have been determined: C2ADP and C3ADP (Kasatani *et al.*, 1998), C4ADP (Kasatani *et al.*, 1998; Fábry, Císařová & Kroupa, 2000), C5ADP and C6ADP (Kasatani *et al.*, 1999; Fábry, Petříček *et al.*, 2000), C7ADP and C8ADP (Fábry *et al.*, 1997), C9ADP (Fábry, Petříček *et al.*, 2000) and C10ADP (Oliver *et al.*, 1998). All these compounds crystallize in the space group $P2_1/n$. The prototypic space group of all these compounds is $P2/b2_1/n2_1/a$. In all the compounds, there exists a couple of H atoms which are involved in asymmetric O$\cdots$O hydrogen bonds. The ferroelastic switching is accompanied by hopping of these H atoms from donor to acceptor O atoms.

The structures which have been determined so far are similar. Each unit cell contains two double layers of dihydrogenphosphates which are mutually bonded by hydrogen bonds, among them being those with hopping H atoms. In addition, the double layers of dihydrogenphosphates are bonded by hydrogen bonds to *n*-alkylammonium groups *via* $NH_3$ groups. The *n*-alkyl chains are separated from each other by van der Waals distances (Weast & Astle, 1980) and are oriented with their methyl group on the outside of the double layers.



(I)

It was also found that the packing of *n*-alkylammonium chains depends on the parity of C atoms.

Despite their similarity the structures of C3ADP and C5ADP belong to a different structure type in contrast to the rest of the compounds. This difference concerns the mutual position of the alternating double layers of dihydrogenphosphates which are situated among the *n*-alkylammonium chains.

In C7ADP and C9ADP, there were observed stacking faults which halve the *a* axis. These stacking faults can be viewed as a disorder of dihydrogenphosphates or as a co-existence of both structure types: that of C5ADP and of C7ADP. The aim of the present study was to redetermine the structure of C3ADP as well as to find out whether the dihydrogenphosphates are disordered as was observed in C7ADP and C9ADP.

All important structural features of C3ADP (twinning, hydrogen bonding, hopping of H atoms, packing of *n*-alkylammonium chains *etc.*) are analogous to the structures which are referenced above.

No disorder of dihydrogenphosphates which can be interpreted as stacking faults halving the periodicity along the *a* axis was observed.

## Experimental

The title compound was obtained by crystallization of *n*-propylamine and $H_3PO_4$ from methanol. A crystal which appeared single domained under the polarization microscope was selected for a diffractometer measurement.

*Crystal data*

$C_3H_{10}N^+\cdot H_2PO_4^-$
$M_r = 157.1$
Monoclinic, $P2_1/n$
$a = 9.131$ (2) Å
$b = 22.090$ (5) Å
$c = 7.175$ (3) Å
$\beta = 90.67$ (3)°
$V = 1447.1$ (8) Å$^3$
$Z = 8$

$D_x = 1.442$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9$–18°
$\mu = 0.333$ mm$^{-1}$
$T = 150$ (2) K
Plate, colourless
0.56 × 0.32 × 0.15 mm

*Data collection*

Enraf–Nonius CAD-4 MACHIII-PC diffractometer
$\omega$–$2\theta$ scans
2750 measured reflections
2544 independent reflections
1602 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 25°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity decay: 5.2%

*Refinement*

Refinement on $F$
$R = 0.034$
$wR = 0.039$
$S = 1.39$
2544 reflections
261 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.64$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.59$ e Å$^{-3}$
Extinction correction: type I, Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.00014 (2)

**Table 1**
Selected geometric parameters (Å).

| | | | |
|---|---|---|---|
| P1—O11 | 1.564 (2) | P2—O42 | 1.516 (2) |
| P1—O21 | 1.505 (2) | N1—C11 | 1.486 (3) |
| P1—O31 | 1.507 (2) | C11—C21 | 1.505 (3) |
| P1—O41 | 1.569 (2) | C21—C31 | 1.510 (4) |
| P2—O12 | 1.553 (2) | N2—C12 | 1.492 (3) |
| P2—O22 | 1.568 (2) | C12—C22 | 1.508 (3) |
| P2—O32 | 1.498 (2) | C22—C32 | 1.517 (4) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H3*n*1···O22$^{\rm i}$ | 0.87 (2) | | 2.963 (2) | 165 (2) |
| N1—H1*n*1···O32$^{\rm ii}$ | 0.92 (2) | | 2.770 (2) | 169 (2) |
| N1—H2*n*1···O42$^{\rm iii}$ | 0.89 (2) | | 2.756 (2) | 164 (2) |
| N2—H1*n*2···O21$^{\rm iv}$ | 0.90 (2) | | 2.829 (2) | 169 (2) |
| N2—H3*n*2···O31$^{\rm v}$ | 0.90 (2) | | 2.775 (2) | 163 (2) |
| N2—H2*n*2···O41$^{\rm vi}$ | 0.90 (2) | | 2.844 (2) | 164 (2) |
| O11—H*o*11···O32$^{\rm vii}$ | 0.80 (2) | | 2.583 (2) | 173 (2) |
| O41—Ho41···O42$^{\rm viii}$ | 0.86 (2) | | 2.491 (2) | 173 (3) |
| O12—H*o*12···O31 | 0.86 (2) | | 2.568 (2) | 177 (3) |
| O22—H*o*22···O21$^{\rm ix}$ | 0.82 (2) | | 2.543 (2) | 175 (3) |

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

The structure is a superstucture, as well as a ferroelastic structure, which can be related to the prototypic space group $P2/b2_1/n2_1/a$. Therefore, the crystal was expected to be twinned though a sample was chosen which seemed to be single domained when viewed under the polarization microscope. The domain proportion $f$ was a refined parameter which converged to a value of 0.037 (5). All the H atoms were refined with angles and/or distances restrained; N—H 0.87 (2)–0.92 (2), C—H 0.94 (2)–0.98 (2) and O—H 0.80 (2)–0.86 (2) Å.

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: *SHELX*86 (Sheldrick, 1985); program(s) used to refine structure: *JANA*2000; software used to prepare material for publication: *JANA*2000.

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