

## **Ferroelastic *n*-butylammonium dihydrogenphosphate**

**Jan Fábry *et al.***

---

### **Electronic paper**

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

Ferroelastic *n*-butylammonium  
dihydrogenphosphateJan Fábry,<sup>a\*</sup> Ivana Císařová<sup>b</sup> and Jan Kroupa<sup>a</sup><sup>a</sup>Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 180 40 Praha 8, Czech Republic, and <sup>b</sup>Faculty of Science, Hlavova 2030, Praha 2, Czech Republic

Correspondence e-mail: fabry@fzu.cz

Received 18 April 2000

Accepted 25 April 2000

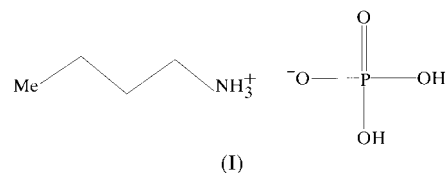
Data validation number: IUC0000130

Crystals of *n*-butylammonium dihydrogenphosphate,  $C_4H_9NH_3^+ \cdot H_2PO_4^-$ , reveal ferroelasticity at room temperature and a number of phase transitions when heated up to approximately 373 K. Some of these phase transitions show hysteresis effects. All atoms except two H atoms exist in pairs linked by the lost symmetry operations derived from the prototypic space group  $P2_1/b2_1/n2_1/a$ . 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 hydrogen species from donor to acceptor O atoms. The studied structure belongs to the structural family of *n*-hexyl- to *n*-decylammonium dihydrogenphosphates and differs by localization of alternating layers from *n*-propyl- and *n*-pentylammonium dihydrogenphosphates. The studied crystal was slightly twinned; the minor domain constituted approximately 2%.

## Comment

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

hopping of these H atoms from donor towards acceptor O atoms.



The structures determined so far are similar. Each unit cell contains two double layers of dihydrogenphosphates which are mutually bonded by hydrogen bonds, among them being these 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 by their methyl group outwards the double layers. 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 (Kasatani *et al.*, 1998; Fábry, Kroupa & Císařová, 2000) and C5ADP (Kasatani *et al.*, 1999; Fábry, Petříček, Císařová & Kroupa, 2000) belong to a different structural type in contrast to the compounds C4ADP (Kasatani *et al.*, 1998) and C6ADP–C9ADP (Fábry *et al.*, 1997) and C10ADP (Oliver *et al.*, 1998). This difference concerns the mutual position of the alternating double layers of dihydrogenphosphates which are merged among the *n*-alkylammonium chains. The aim of the present study was to redetermine the structure of C4ADP as well as to find out whether the dihydrogenphosphates are disordered as was observed in C7ADP and C9ADP.

It was found that C4ADP belongs to the structural type of C6ADP–C10ADP. All important structural features of C4ADP (twinning, hydrogen bonding, hopping of H atoms and packing of *n*-alkylammonium chains) are analogous to the structures which are referenced above. The minor domain fraction was refined to the value 0.022 (4) which is in accordance with the value 0.023 (1) determined from the comparison of the intensities of the reflection (00 $\bar{4}$ ) measured from each of the two domains at 33 different azimuthal angles.

No disorder of dihydrogenphosphates which can be interpreted as stacking faults halving the periodicity along the axis *a* was observed. Such a disorder may be viewed as a co-existence of both structural types in a crystal.

It is of interest that this disorder was observed in C7ADP and C9ADP but not in compounds with even number of C atoms in a *n*-alkylammonium chain.

## Experimental

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

Crystal data

$C_4H_9NH_3^+H_2PO_4^-$   
 $M_r = 171.13$   
 Monoclinic,  $P2_1/n$   
 $a = 9.1481$  (9) Å  
 $b = 24.877$  (2) Å  
 $c = 7.225$  (1) Å  
 $\beta = 90.82$  (1)°  
 $V = 1644.0$  (4) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.382$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 13$ – $14^\circ$   
 $\mu = 0.299$  mm<sup>-1</sup>  
 $T = 292$  (1) K  
 Plate, colourless  
 $0.45 \times 0.30 \times 0.12$  mm

Data collection

Enraf–Nonius CAD-4-MACHIII-PC diffractometer  
 $\omega$ - $2\theta$  scans  
 3844 measured reflections  
 3574 independent reflections  
 2828 reflections with  $I > 3\sigma(I)$   
 $R_{int} = 0.008$

$\theta_{max} = 27^\circ$   
 $h = -11 \rightarrow 11$   
 $k = 0 \rightarrow 31$   
 $l = 0 \rightarrow 9$   
 3 standard reflections  
 frequency: 3600 min  
 intensity decay: 2.0%

Refinement

Refinement on  $F$   
 $R = 0.031$   
 $wR = 0.042$   
 $S = 2.13$   
 3574 reflections  
 295 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$   
 $(\Delta/\sigma)_{max} = 0.01$   
 $\Delta\rho_{max} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.43$  e Å<sup>-3</sup>  
 Extinction correction: Becker & Coppens (1974) type I, Lorentz, iso.  
 Extinction coefficient:  $1.02(5) \times 10^{-4}$

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

P1—O11	1.5576 (8)	C32—C42	1.504 (2)
P1—O21	1.5052 (7)	O11—HO11	0.73 (1)
P1—O31	1.4996 (7)	O41—HO41	0.93 (2)
P1—O41	1.5710 (8)	O12—HO12	0.72 (1)
P2—O12	1.5546 (8)	O22—HO22	1.01 (2)
P2—O22	1.5687 (7)	O11...O32 <sup>i</sup>	2.598 (1)
P2—O32	1.4940 (7)	O21...O22 <sup>ii</sup>	2.542 (1)
P2—O42	1.5138 (7)	O31...O12	2.582 (1)
N1—C11	1.484 (1)	O41...O42 <sup>iii</sup>	2.491 (1)
C11—N1	1.484 (1)	O21...N2 <sup>iv</sup>	2.838 (1)
C11—C21	1.500 (2)	O31...N2 <sup>v</sup>	2.805 (1)
C21—C31	1.513 (2)	O41...N2 <sup>vi</sup>	2.850 (1)
C31—C41	1.503 (2)	O22...N1 <sup>v</sup>	2.980 (1)
N2—C12	1.482 (1)	O32...N1 <sup>iv</sup>	2.786 (1)
C12—C22	1.498 (2)	O42...N1 <sup>vi</sup>	2.760 (1)
C22—C32	1.516 (2)		

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)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

The structure is a superstructure, and a ferroelastic structure as well, which can be related to the prototypic space group  $P2_1/b2_1/n2_1/a$ .

Therefore, the crystal was expected to be twinned though a sample was chosen which seemed to be single domained when viewed in the polarizing microscope. The domain fraction  $f$  was a refined parameter which converged to the value 0.022 (4). This value corresponds well to that determined from 33 pairs of measured intensities of different azimuthal angle settings of the reflection (00 $\bar{4}$ ) which were well resolved from the two domains. The domain fraction determined this way was 0.023 (1).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *JANA98* (Petříček & Dušek, 1998); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *JANA2000* (Petříček & Dušek, 2000); molecular graphics: *PICTUR* (Dušek, 1993); software used to prepare material for publication: *JANA98*.

The support of this study by the grant 203/99/0067 of the Grant Agency of the Czech Republic is gratefully acknowledged.

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–141.  
 Dušek, M. (1993). *PICTUR*. Institute of Physics, Czech Academy of Sciences, Czech Republic.  
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.  
 Fábry, J., Kroupa, J. & Císařová, I. (2000). *Collect. Czech. Chem. Commun.* Submitted. [Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-137551.]  
 Fábry, J., Petříček, V., Císařová, I. & Kroupa, J. (1997). *Acta Cryst.* **B53**, 272–279.  
 Fábry, J., Petříček, V., Císařová, I. & Kroupa, J. (2000). *Acta Cryst.* **B56**. Submitted.  
 Kasatani, H., Iwata, M., Ishibashi, Y. & Terauchi, H. (1998). *J. Korean Phys. Soc.* **32**, S1807–1809.  
 Kasatani, H., Iwata, M., Terauchi, H. & Ishibashi, Y. (1999). *Ferroelectrics*, **229**, 255–260.  
 Kroupa, J. & Fuith, A. (1993). *Phys. Rev. B*, **48**, 4119–4121.  
 Kroupa, J. & Fuith, A. (1994). *Ferroelectrics*, **159**, 115–119.  
 Oliver, S. R. J., Lough, A. J. & Ozin, G. A. (1998). *Inorg. Chem.* **37**, 5021–5028.  
 Petříček, V. & Dušek, M. (1998). *JANA98*. Institute of Physics, Czech Academy of Sciences, Czech Republic.  
 Petříček, V. & Dušek, M. (2000). *JANA2000*. Institute of Physics, Czech Academy of Sciences, Czech Republic.  
 Sheldrick, G. M. (1985). *SHELXS86*. University of Göttingen, Germany.  
 Weast, R. C. & Astle, M. J. (1980). Editors. *CRC Handbook of Chemistry and Physics*, 60th ed. Boca Raton, Florida: CRC Press.