

## 4-Chloro-2-methylanilinium dihydrogenphosphate

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## Key indicators

Single-crystal X-ray study

T = 290 K

Mean  $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$ 

R factor = 0.045

wR factor = 0.170

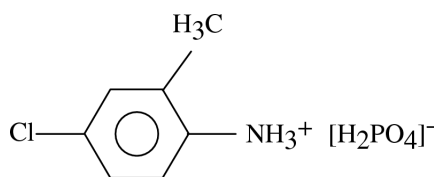
Data-to-parameter ratio = 16.3

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title salt,  $\text{C}_7\text{H}_9\text{ClN}^+\cdot\text{H}_2\text{PO}_4^-$ , is monoclinic ( $P2_1/c$ ). The ions are held together by  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds. The  $\text{O}-\text{H}\cdots\text{O}$  bonds interconnect the dihydrogenphosphates into sheets which are parallel to the (100) plane. In each sheet, there are centrosymmetric pairs of dihydrogenphosphates held together by  $\text{O}-\text{H}\cdots\text{O}$  bonds. In addition, the dihydrogenphosphates are interconnected by  $-\text{NH}_3$  groups. Each H atom from an  $-\text{NH}_3$  group is donated to a different dihydrogenphosphate ion. A differential scanning calorimetry experiment showed no anomaly between 98 and 420 K.

## Comment

The main purpose of this structural study was a determination of the arrangement of arylammoniums and dihydrogenphosphates which are held together by hydrogen bonds.  $R-\text{NH}_3^+$  cations ( $R = \text{aryl, alkyl or H}$ ) can bind in various ways to  $[\text{H}_2\text{PO}_4]^-$  anions. Some of these structures show interesting phase transitions and physical properties which are influenced by hydrogen bonding. Among examples can be named the simplest representative of the series:  $[\text{NH}_4]^+[\text{H}_2\text{PO}_4]^-$  (e.g. Baur, 1973). Recently, we have determined a similar structure for 2,4-dimethylanilinium dihydrogenphosphate (Fábry *et al.*, 2001) and observed a phase transition in this compound at about 442 K. The latter and the title compound differ only by a substituent at C4. The aim of this study is a comparison of this compound with 2,4-dimethylanilinium dihydrogenphosphate.



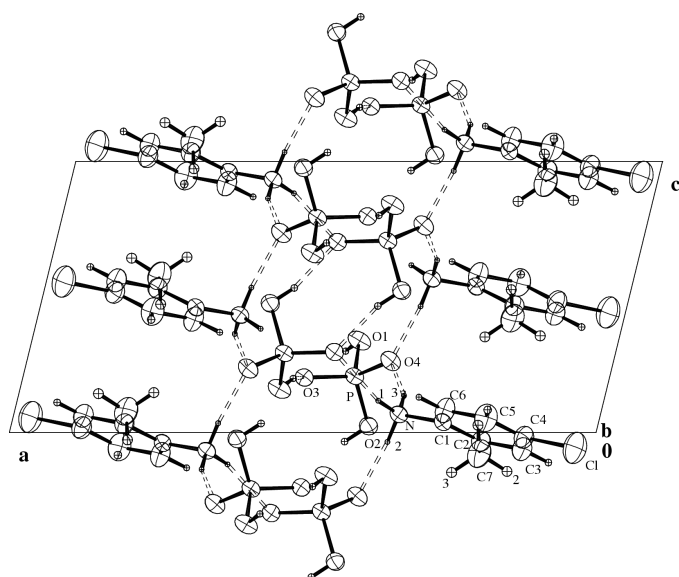
(I)

The title structure, (I), contains dihydrogenphosphates interconnected by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. The dihydrogenphosphates form a double layer that is parallel to (100) (Fig. 1). This is the principal difference from 2,4-dimethylanilinium dihydrogenphosphate where the  $\text{O}-\text{H}\cdots\text{O}$  bind the dihydrogenphosphates into isolated double columns. In both structures the substructures of the dihydrogenphosphates contain centrosymmetric pairs of dihydrogenphosphates, where each dihydrogenphosphate is simultaneously donor and acceptor of a hydrogen bond. In

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**Figure 1**

View of the unit cell of 4-chloro-2-methylanilinium dihydrogenphosphate along the unit-cell *b* axis. Probability displacement ellipsoids are shown at the 30% level (ORTEP III; Burnett & Johnson, 1996).

In addition, the dihydrogenphosphates are interconnected by arylammonium groups in both structures, each arylammonium hydrogen being donated to a different dihydrogenphosphate. In the title compound, all the donated H atoms are accepted by the O atoms that are not part of an OH group. The title structure differs in this aspect from 2,4-dimethylanilinium dihydrogenphosphate where one hydroxyl oxygen accepts one hydrogen donated by the arylammonium. In addition, there is no C—H...O hydrogen bond between the methyl and dihydrogenphosphate as there is in 2,4-dimethylanilinium dihydrogenphosphate.

It should be noted that the non-standard setting  $C112_1/b$  can be chosen. The lattice parameters then correspond to orthorhombic metric symmetry within one standard uncertainty: 7.894 (5), 32.215 (16), 8.330 (4) Å,  $\gamma = 90.01$  (4)°. The transformation is  $(a_o, b_o, c_o) = (a_m, b_m, c_m)(020/00\bar{1}/\bar{1}10)$ , where the subscripts 'o' and 'm' refer to the settings for  $C112_1/b$  and  $P12_1/c1$ , respectively). An experiment on a Nonius Kappa-CCD diffractometer did not detect any additional diffraction (Otwinowski & Minor, 1997) which would conflict with the suggested lattice.

The  $h00$  and  $00l$  reflections (and their combinations) were proved on several samples of the title crystal to be split by 0.6° in  $\omega$  in contrast to the  $0k0$  diffractions. The latter  $hkl$  indices refer to the choice of the  $P12_1/c1$  unit cell. No domains were observed in the microscope under polarized light. Because of this splitting we decided to refine the lattice parameters from powder data, though we did not find the reason for this splitting though twinning ( $\bar{1}00/010/001$ ) in  $C112_1/b$  was assumed. The domain fraction converged to the value 0.002 (1). Neither refinement in  $P12_1/c1$  nor in  $P1c1$  with assumed twinning ( $\bar{1}00/0\bar{1}0/00\bar{1}$ ) yielded reasonable results.

The differential scanning calorimetry measurements [Perkin-Elmer DSC 7 using Pyris software (Perkin-Elmer,

1997),  $m = 10.39$  mg, scanning rate 10 K/min] did not show any reproducible anomalies indicating structural phase transitions in the solid state between 98 K (cooling accessory limit) and 420 K where decomposition clearly started.

## Experimental

Reaction of 4-chloro-2-methylaniline and  $H_3PO_4$  produced a precipitate. This was filtered off, dried and dissolved in 96% ethanol from which the single crystals were grown by slow evaporation at room temperature.

### Crystal data

$C_7H_9ClN^+ \cdot H_2PO_4^-$   
 $M_r = 239.59$   
 Monoclinic,  $P2_1/c$   
 $a = 16.603$  (4) Å  
 $b = 8.339$  (3) Å  
 $c = 7.903$  (4) Å  
 $\beta = 103.76$  (6)°  
 $V = 1062.8$  (7) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.497$  Mg m<sup>-3</sup>

Cell parameters determined with Cu K $\alpha$ 1 radiation (powder diffraction); intensity data measured with Mo K $\alpha$  radiation  
 Cell parameters from 18 reflections  
 $\theta = 2.7$ – $15.8$ °  
 $\mu = 0.50$  mm<sup>-1</sup>  
 $T = 290$  (1) K  
 Plate, colourless  
 $0.30 \times 0.14 \times 0.06$  mm

### Data collection

Kuma KM-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: by Gaussian integration (Coppens *et al.*, 1965)  
 $T_{\min} = 0.919$ ,  $T_{\max} = 0.977$   
 4283 measured reflections  
 2151 independent reflections  
 911 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.141$   
 $\theta_{\text{max}} = 26.3$ °  
 $h = -20 \rightarrow 20$   
 $k = -10 \rightarrow 0$   
 $l = -9 \rightarrow 9$   
 3 standard reflections every 200 reflections  
 intensity decay: 9.8%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.170$   
 $S = 0.82$   
 2151 reflections  
 132 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.014 (3)

**Table 1**

Selected geometric parameters (Å, °).

P1—O4	1.493 (4)	P1—O1	1.564 (3)
P1—O3	1.504 (3)	Cl—C4	1.732 (6)
P1—O2	1.560 (4)		
O4—P1—O3	115.8 (2)	O4—P1—O1	105.2 (2)
O4—P1—O2	108.4 (2)	O3—P1—O1	110.2 (2)
O3—P1—O2	109.2 (2)	O2—P1—O1	107.7 (2)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O3 <sup>i</sup>	0.82	1.86	2.611 (4)	151
O2—H2...O3 <sup>ii</sup>	0.82	1.84	2.644 (5)	166
N—H1N...O3 <sup>iii</sup>	0.89	2.04	2.900 (5)	162
N—H2N...O4 <sup>iv</sup>	0.89	1.82	2.704 (5)	173
N—H3N...O4	0.89	1.88	2.722 (5)	158

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

Data collection: *KM4B8* (Galdecki *et al.*, 1997); cell refinement: *LATCO* (Allmann, 1988); data reduction: *JANA2000* (Petříček & Dušek, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).

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