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2,4-Dimethylanilinium dihydrogenphosphate

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Key indicators

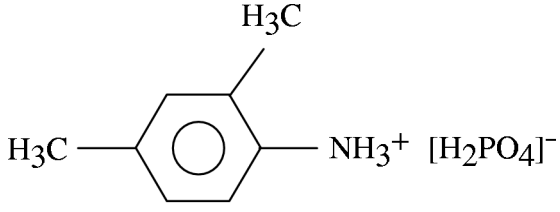
Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.041
Data-to-parameter ratio = 11.1

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

2,4–Dimethylanilinium dihydrogenphosphate, $C_8H_{12}N^+.H_2PO_4^-$, (I), is monoclinic ($P2_1/c$). The ions are held together by O—H···O and N—H···O hydrogen bonds. In addition there is one C_{methyl}—H···O hydrogen bond. The dihydrogenphosphates and the —NH_3 groups are arranged in sheets which are parallel to the (010) plane. In each sheet there are centrosymmetric pairs of dihydrogenphosphates held by O—H···O bonds. These pairs of dihydrogenphosphates are arranged in columns that are parallel to the unit-cell b axis. These columns are held together *via* —NH_3 groups through N—H···O bonds. Each hydrogen from an —NH_3 group is donated to a different dihydrogenphosphate ion. The differential scanning calorimetry experiment showed anomaly during heating at ∼442 K.

Comment

The main purpose of this structural study was a determination of the arrangement of arylammonium and dihydrogenphosphate ions which are held together by hydrogen bonds. R—NH_3^+ cations (R = aryl, alkyl or H) can bind in various ways to $[H_2PO_4]^-$ anions. Some of these structures show interesting phase transitions and physical properties which are influenced by hydrogen bonding. Examples include $[NH_4]^+[H_2PO_4]^-$ (*e.g.* Baur, 1973) or *n*-alkylammonium dihydrogenphosphates (Kroupa & Fuith, 1993, 1994; Fábry *et al.* 2000).



(I)

A search of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) yielded the structure SOMHUX (2-methyl-4-nitroanilinium dihydrogenmonophosphate) determined by Masse & Levy (1991). The latter structure is orthorhombic (*Pbca*) and contains layers of dihydrogenphosphates. Symmetry and structural similarity to the room-temperature phases of *n*-alkylammonium dihydrogenphosphates, which also contain layers of dihydrogenphosphates and which are closely related to the prototypic orthorhombic phase (*Pbna*), made us think about the possibility of phase transitions in other related compounds. Therefore similarly substituted anilines were chosen for investigation, among them 2,4-dimethylaniline.

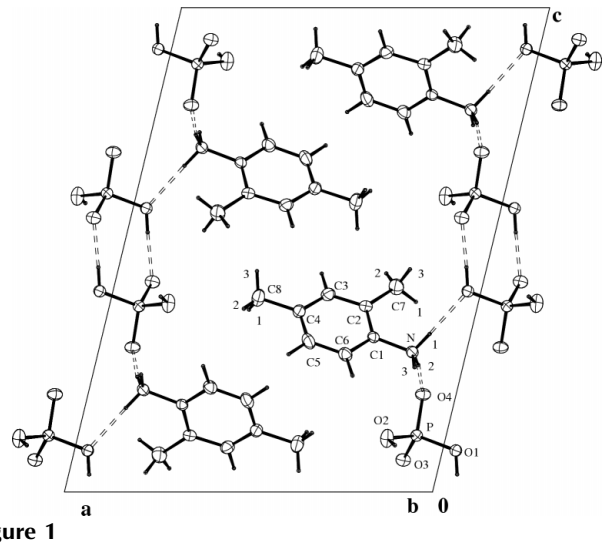


Figure 1
View of the unit cell of 2,4-dimethylanilinium dihydrogenphosphate along the unit-cell *b* axis with 30% probability displacement ellipsoids (*ORTEP*III; Burnett & Johnson, 1996). For clarity the hydrogen bonds from H3n and H2o are not depicted.

It was found that in this compound there are also sheets of dihydrogenphosphates. These sheets are interconnected by ammonium groups (Fig. 1). Each hydrogen from the ammonium group is donated to a different dihydrogenphosphate ion. In all the compounds, the H atoms are ordered at room temperature. The N—H···O contacts are in the range 2.71 (CSD refcode SOMHUX) to 3.04 Å (*e.g.* WINKUZ01; Fábry *et al.*, 1997), while the pertinent angles fall in the interval 153 (FUQNAG; Fábry, Petříček *et al.*, 2000) to 177° (SOMHUX). The O—H···O bond lengths are shorter, being in the range 2.49 (WOBZES; Fábry, Císařová *et al.*, 2000) to 2.63 Å (SOMHUX), while the angles fall into the interval 157 (SOMHUX) to 177° (*e.g.* FUQMOT; Fábry, Petříček *et al.*, 2000).

Despite these similarities, the aforementioned compounds differ in how the sheets composed of dihydrogenphosphates and ammonium groups are linked by hydrogen bonds. In the title compound there are columns of aggregated dihydrogenphosphates parallel to (100) and directed along [010] (Fig. 1). These columns are held together by N—H···O hydrogen bonds while in *n*-alkylammoniumdihydrogenphosphates as well as in SOMHUX, the O—H···O hydrogen-bond network itself makes sheets of $H_2PO_4^-$. (In the latter compounds, these sheets are also different.)

It is interesting that there is one C—H···O contact that should be considered as a hydrogen bond according to the criteria given by Desiraju & Steiner (1999). The angle between the planes C2—C7—H1C7 and C2—C7—O1^{i} is only 15 (1)°, indicating attraction of the hydrogen H1C7 to the atom O1 [symmetry code: (i) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. [The distance C7···O1^{i} is 3.586 (3) Å; the distance H1C7···O1^{i} is 3.48 (2) Å, pointing to a possible electrostatic interaction.] The interatomic distances and angles are otherwise normal.

The differential scanning calorimetry experiments [Perkin–Elmer DSC 7 using *PYRIS* software (Perkin–Elmer,1997)] showed interesting behaviour. During heating an anomaly ocurred between 441 and 443 K (aluminium pans, m = 9.35 mg, scanning rate 10 K/min, ΔH = 21 J/g). Interestingly, cooling caused no corresponding anomaly. An immediate heating of the sample after it had been cooled down to room temperature did not bring about the anomaly at ∼442 K.

Nevertheless, after several hours since the last cooling, repeated heating caused partial or full restoration of the anomaly at ∼442 K. The degree of restoration depended on the time that had elapsed since the last cooling. Both phenomena (*i.e.* no anomaly during cooling as well as relaxation necessary for restoration of the anomaly at ∼442 K) indicate a structural change with much faster kinetics on heating than on cooling.

Experimental

Precipitation of 2,4-dimethylaniline and H_3PO_4. The precipitate was filtered off, dried and dissolved in 96% ethanol from which the single crystals were grown by slow evaporation at room temperature.

Crystal data

$(C_8H_9NH_3)(H_2PO_4)$	D_x = 1.394 Mg m^{-3}
M_r = 219.2	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 68 reflections
a = 13.009 (3) Å	θ = 6.1–18.1°
b = 4.688 (1) Å	μ = 0.25 mm^{-1}
c = 17.607 (4) Å	T = 290 (1) K
β = 103.60 (2)°	Prism, colourless
V = 1043.7 (4) Å^3	0.24 × 0.19 × 0.14 mm
Z = 4	

Data collection

Kuma KM-4 diffractometer	R_{int} = 0.055
ω–2θ scans	θ_{max} = 26.0°
Absorption correction: Gaussian ntegration (Coppens *et al.*, 1965)	$h = -16 \rightarrow 15$
T_{min} = 0.942, T_{max} = 0.967	$k = -5 \rightarrow 5$
3969 measured reflections	$l = 0 \rightarrow 21$
2050 independent reflections	3 standard reflections every 200 reflections
1258 reflections with $I > 3\sigma(I)$	intensity decay: 2.1%

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0001F^2]$
R = 0.034	$(\Delta/\sigma)_{max} < 0.001$
wR = 0.041	$\Delta\rho_{max}$ = 0.57 e Å^{-3}
S = 1.75	$\Delta\rho_{min}$ = −0.92 e Å^{-3}
2050 reflections	Extinction correction: Becker & Coppens (1974) type 2
184 parameters	Extinction coefficient: 0.00063 (3)
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

P—O1	1.583 (2)	C2—C3	1.395 (3)
P—O2	1.562 (2)	C2—C7	1.508 (4)
P—O3	1.515 (2)	C3—C4	1.385 (3)
P—O4	1.510 (2)	C4—C5	1.384 (3)
C1—N	1.470 (2)	C4—C8	1.525 (3)
C1—C2	1.396 (2)	C5—C6	1.388 (3)
C1—C6	1.383 (3)		
O1—P—O2	107.77 (9)	O2—P—O3	108.5 (1)
O1—P—O3	110.36 (9)	O2—P—O4	109.2 (1)
O1—P—O4	105.7 (1)	O3—P—O4	115.14 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1o···O3^{i}	0.85 (2)	1.76 (2)	2.605 (2)	175 (2)
O2—H2o···O3^{ii}	0.85 (3)	1.72 (2)	2.563 (2)	170 (3)
N—H1n···O1^{iii}	0.90 (2)	2.14 (2)	3.030 (2)	169 (2)
N—H2n···O4	0.92 (2)	1.94 (2)	2.848 (2)	172 (2)
N—H3n···O4^{ii}	0.95 (2)	1.82 (2)	2.766 (2)	175 (2)
C7—H1c7···O1^{iv}	0.95 (2)	2.60 (2)	3.315 (3)	132 (2)

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

The O—H, N—H, Csp^2—H and Csp^3 bond lengths were restrained to 0.85 (2), 0.90 (3), 0.97 (1) and 0.95 (1) Å, respectively. The H—C—H angles of the methyl groups were restrained to the value 109.5 (1)°.

Cell refinement: *KM4B*8 (Gałdecki *et al*., 1997); data reduction: *JANA*2000 (Petříček & Dušek, 2000); program(s) used to solve structure: *JANA*2000; program(s) used to refine structure: *JANA*2000; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

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