

## Anilinium dihydrogen phosphate

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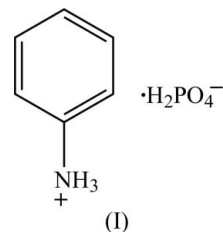
The triclinic structure of the title compound,  $C_6H_8N^+ \cdot H_2PO_4^-$ , with three symmetry-independent structural units ( $Z' = 3$ ), is formed of separate organic and inorganic layers alternating along the  $b$  axis. The building blocks of the inorganic layer are deformed  $H_2PO_4$  tetrahedra assembled into infinite ladders by short and hence strong hydrogen bonds. The anilinium cations forming the organic layer are not hydrogen bonded to one another, but they are anchored by four  $N-H \cdots O$  crosslinks between the dihydrogen phosphate chains of adjacent ladders. Two H atoms of each  $-NH_3$  group then form one normal and one bifurcated  $N-H \cdots O$  hydrogen bond to the  $P=O$  oxygens of two tetrahedra of one chain, while the third H atom is hydrogen bonded to the nearest O atom of an adjacent chain belonging to another dihydrogen phosphate ladder.

## Comment

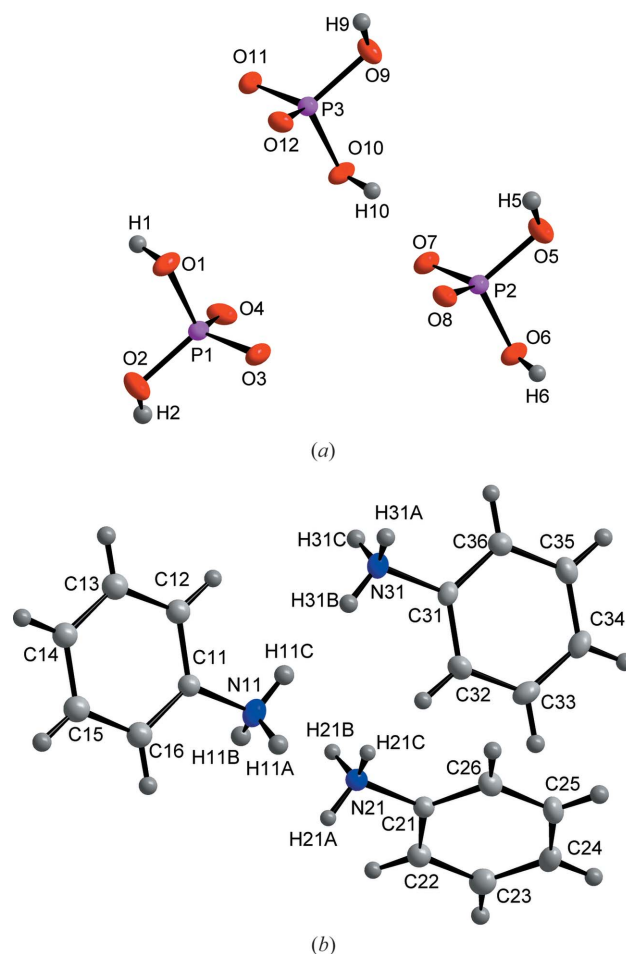
Anilinium dihydrogen phosphate, (I), belongs to the class of substances that are studied as promising proton conductors, and of which the several important physical properties have their roots in the presence of specific spatially arranged hydrogen bonds of suitable energies. Salt (I) provides a convenient model for proton-conducting materials based on dihydrogen phosphates of organic cations that can form organic ionic plastic crystals (Pringle *et al.*, 2010), and for proton-conducting membranes involving similar building blocks, like the membranes employing poly(benzimidazole-co-aniline) (Bhadra *et al.*, 2010).

As the presence of water in the structures of proton-conducting salts usually undesirably decreases their chemical stability and makes them unsuitable for applications at elevated temperatures (Kroupa & Fuith, 1993), where various superprotonic and plastic phases are expected to exist, we

have attempted to prepare a compound chemically related to anilinium dihydrogen phosphate monohydrate (Anderson *et al.*, 2006) but crystallizing without water. This work was undertaken in order to determine the geometry of the hydrogen bonds, which can prove crucial for understanding the mechanism of proton transfer.



The atom-numbering scheme of the anilinium cations and dihydrogen phosphate anions of (I) is shown in Fig. 1. The triclinic ( $Z' = 3$ ) structure is composed of separate organic and inorganic layers alternating along the  $b$  axis (Fig. 2). The building blocks of the inorganic layer are deformed  $H_2PO_4$  tetrahedra with two narrow groups of  $O-P-O$  angles (median values  $\sim 105$  and  $\sim 111^\circ$ ) and with the  $P-O$  bond lengths falling into two groups (Table 1); the  $P-O(H)$  bonds



**Figure 1**  
The atom-numbering scheme for (a) the dihydrogen phosphate anions of (I) and (b) the anilinium cations of (I). Displacement ellipsoids are drawn at the 50% probability level.

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*p*-phenylazobenzilium phenylphosphonate (Mahmoudkhani & Langer, 2002) or tris(methylammonium) hydrogen phosphate dihydrogen phosphate (Fábry *et al.*, 2006).

Considering the strength of the N—H···O hydrogen bonds in (I), it can be assumed that their dynamics have an impact on proton mobility along the strong O—H···O hydrogen bonds and *vice versa*. The strength of both O—H···O and N—H···O hydrogen bonds is also documented by the absence of standard  $\nu(\text{OH})$  and  $\nu(\text{NH})$  bands in the IR spectrum of (I) and their replacement with a diffuse asymmetric band rising slowly from  $\sim 2000\text{ cm}^{-1}$  and ending sharply at  $\sim 3600\text{ cm}^{-1}$ .

Despite favorable centroid–centroid distances between the phenyl rings, their mutual orientations effectively prevent the formation of  $\pi$ – $\pi$  interactions.

## Experimental

Aniline (99.8%, Acros) was purified *via* the preparation of anilinium chloride as follows. Raw aniline was mixed with 2 M HCl with cooling and the solution filtered through active carbon. The filtrate was concentrated *in vacuo* and crystallization of anilinium chloride was carried out in a refrigerator. The crystals were filtered off and washed with a small amount of cold water. The wet product was dissolved in water subsequently alkalinized by the addition of  $\text{NaHCO}_3$ , and the mixture was extracted with chloroform four times. The organic phases were collected, washed once with water and dried using anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration, the solution was evaporated *in vacuo*, providing purified aniline. This was mixed with  $\sim 0.03\text{ M H}_3\text{PO}_4$  (Lachema, pure 85%), the concentration of which was determined by titration on methyl orange, in a 1:1.5 molar ratio. The resulting mixture was stirred with heating at 313 K and further diluted in order to dissolve the small amount of salts formed immediately upon mixing. Finally, the solution was filtered and the filtrate was left to crystallize very slowly in air at room temperature.

### Crystal data

$\text{C}_6\text{H}_8\text{N}^+\cdot\text{H}_2\text{PO}_4^-$	$\gamma = 83.016 (2)^\circ$
$M_r = 191.12$	$V = 1243.71 (8)\text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 6$
$a = 8.8040 (3)\text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.4220 (4)\text{ \AA}$	$\mu = 0.31\text{ mm}^{-1}$
$c = 14.0890 (6)\text{ \AA}$	$T = 150\text{ K}$
$\alpha = 86.418 (2)^\circ$	$0.18 \times 0.18 \times 0.05\text{ mm}$
$\beta = 75.8890 (19)^\circ$	

### Data collection

Nonius KappaCCD area-detector diffractometer	23949 measured reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	6720 independent reflections
$T_{\min} = 0.919$ , $T_{\max} = 0.987$	3848 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.067$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	334 parameters
$wR(F^2) = 0.144$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.35\text{ e \AA}^{-3}$
6720 reflections	$\Delta\rho_{\text{min}} = -0.57\text{ e \AA}^{-3}$

Aromatic H atoms were constrained to an ideal geometry and refined using a riding model, with C—H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . For the  $\text{NH}_3$  groups, C—N—H angles ( $109.5^\circ$ ) were kept

**Table 1**

Selected bond lengths (Å).

P1—O1	1.5588 (16)	P2—O7	1.5007 (16)
P1—O2	1.5631 (16)	P2—O8	1.5211 (15)
P1—O3	1.4972 (16)	P3—O9	1.5632 (15)
P1—O4	1.5133 (16)	P3—O10	1.5607 (16)
P2—O5	1.5574 (15)	P3—O11	1.5034 (16)
P2—O6	1.5623 (16)	P3—O12	1.5169 (15)

**Table 2**

Hydrogen-bond geometry (Å, °).

The letters in the rightmost column are the bond labels used in Fig. 4.

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$	Label
O1—H1···O11 <sup>iii</sup>	0.84	1.76	2.563 (2)	158	
O2—H2···O8 <sup>iv</sup>	0.84	1.81	2.627 (2)	165	
O5—H5···O4 <sup>ii</sup>	0.84	1.77	2.592 (2)	164	
O6—H6···O3 <sup>i</sup>	0.84	1.75	2.545 (2)	157	
O9—H9···O12 <sup>v</sup>	0.84	1.81	2.636 (2)	166	
O10—H10···O7	0.84	1.78	2.541 (2)	150	
N11—H11A···O8 <sup>i</sup>	0.91	1.93	2.839 (3)	174	<b>a</b>
N11—H11C···O3	0.91	2.39	2.917 (2)	117	<b>b</b>
N11—H11C···O4	0.91	2.40	3.296 (3)	169	<b>c</b>
N11—H11B···O7	0.91	1.83	2.743 (3)	179	<b>d</b>
N21—H21A···O8	0.91	2.01	2.924 (2)	177	<b>e</b>
N21—H21B···O12	0.91	1.88	2.791 (2)	177	<b>f</b>
N21—H21C···O3	0.91	1.91	2.819 (2)	176	<b>g</b>
N21—H21A···O7	0.91	2.59	3.075 (2)	114	<b>h</b>
N31—H31B···O11	0.91	2.49	2.965 (2)	113	<b>i</b>
N31—H31A···O11 <sup>iii</sup>	0.91	1.85	2.757 (2)	174	<b>j</b>
N31—H31B···O12	0.91	2.15	3.051 (2)	174	<b>k</b>
N31—H31C···O4 <sup>iii</sup>	0.91	1.94	2.849 (3)	172	<b>l</b>

Symmetry codes: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x, -y + 1, -z + 1$ ; (iv)  $x - 1, y, z$ ; (v)  $-x + 1, -y + 1, -z + 1$ .

fixed, while the torsion angles were allowed to refine with starting positions based on the circular Fourier synthesis averaged using the local threefold axis, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  and a constrained N—H distance of 0.98 Å. The positions of the H atoms of the dihydrogen phosphate anions were constrained to an ideal geometry, keeping the O—H bond length fixed at 0.84 Å, while the O—H vectors were allowed to rotate about the P—O bonds, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ .

Data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3072). Services for accessing these data are described at the back of the journal.

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