Acta Crystallographica Section C Crystal Structure Communications

ISSN 0108-2701

Anilinium dihydrogen phosphate

Ondřej Kaman,^{a,b} Ľubomír Smrčok,^c* Róbert Gyepes^d‡ and David Havlíček^d

^aDepartment of Cell Biology, Faculty of Science, Charles University, Viniční 7, 128 40 Prague 2, Czech Republic, ^bInstitute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10/112, 162 00 Prague 6, Czech Republic, ^cInstitute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic, and ^dDepartment of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 40 Prague 2, Czech Republic Correspondence e-mail: uachsmrk@savba.sk

Received 14 November 2011 Accepted 20 December 2011 Online 6 January 2012

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 $-H \cdot \cdot \cdot O$ 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 $-H \cdot \cdot \cdot O$ 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 protonconducting 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 H₂PO₄ tetrahedra with two narrow groups of O-P-O angles (median values ~105 and ~111°) 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.

[‡] Current address: Faculty of Education, J. Selye University, Bratislavská cesta 3322, 945 01 Komárno, Slovak Republic.



Figure 2

The unit-cell packing in (I), viewed along the c axis. All H atoms have been omitted for clarity.

are, as expected, longer than the other presumably P=0 bonds (Blessing, 1986; Mahmoudkhani & Langer, 2002; Demir *et al.*, 2003; Smrčok *et al.*, 2009; Balamurugan *et al.*, 2010; Kaman *et al.*, 2011; Marouani *et al.*, 2011). Examination of the geometry of the anilinium cations forming the organic layers shows that the values of the bond distances, bond angles and torsion angles have expected values (Elmokhtar *et al.*, 1995).

The dihydrogen phosphate anions of (I) are assembled into infinite 'ladders' by short and hence strong hydrogen bonds (Fig. 3 and Table 2). The hydrogen bonds with atoms O6 and



Figure 3

A view of part of the crystal structure of (I), showing the spatial arrangement of the dihydrogen phosphate anions. Symmetry codes are defined in Table 2.

O10 acting as donors have the shortest $O \cdots O$ separations and, according to the standard classification, they fall within the range for very strong hydrogen bonds, while the other O- $H \cdots O$ hydrogen bonds are ranked as moderately strong hydrogen bonds (Jeffrey, 1997). Considering the flexibility of this arrangement, it is suggested that proton mobility would not be enabled just by simple proton transfer along the O- $H \cdots O$ hydrogen bonds, but also by some reorientational movements of the H₂PO₄ tetrahedra.

The bond lengths and angles in the anilinium cations of (I) are all normal for this moiety. The anilinium cations act as triple donors of $N-H\cdots O$ hydrogen bonds, crosslinking the dihydrogen phosphate chains of adjacent ladders (Fig. 4). Two H atoms of each $-NH_3$ group form one normal and one bifurcated $N-H\cdots O$ hydrogen bond to the double-bonded O atoms of two tetrahedra of a chain, while the third H atom bonds to the nearest O atom of an adjacent chain. The bifurcated $N-H\cdots O$ hydrogen bonds have recognizable major and minor parts and, in addition to their different lengths, also have very different $N-H\cdots O$ hydrogen-bond angles (Table 2).

In line with the individual $N \cdots O$ separations, these hydrogen bonds formally belong to three groups: firstly, three rather short and thus strong hydrogen bonds with N···O separations in the range 2.743(3)–2.791(2) Å, secondly, five medium-strong hydrogen bonds lying in the range 2.818 (2)-2.924 (2) Å, and finally, four weaker hydrogen bonds with the largest N···O separations, viz. 2.965 (2)-3.296 (2) Å. Considering the unimodal distribution of well defined $N \cdots O$ contact distances (Kumara Swamy et al., 2001), the N···O distances of the first and third groups are among those found less frequently, being either significantly shorter or longer than the mean value. The values in the second group agree well with those most frequently reported. Due to the various bonding opportunities, the range of $N \cdots O$ contact distances is noticeably broader in (I) than in chemically related structures, e.g. bis(4-hydroxyanilinium) dihydrogen diphosphate monohydrate (Soumhi & Jouini, 1995), 2-aminopyrimidinium dihydrogen phosphate monohydrate (Marouani et al., 2011),



Figure 4 Detail of the $N-H\cdots O$ hydrogen bonds in (I). Symmetry codes and hydrogen-bond labels are defined in Table 2.

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

Considering the strength of the $N-H\cdots O$ hydrogen bonds in (I), it can be assumed that their dynamics have an impact on proton mobility along the strong $O-H \cdots O$ hydrogen bonds and *vice versa*. The strength of both $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds is also documented by the absence of standard $\nu(OH)$ and $\nu(NH)$ 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 alkalized by the addition of NaHCO₃, and the mixture was extracted with chloroform four times. The organic phases were collected, washed once with water and dried using anhydrous Na₂SO₄. After filtration, the solution was evaporated in vacuo, providing purified aniline. This was mixed with $\sim 0.03 M H_3 PO_4$ (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

$C_6H_8N^+ H_2PO_4^-$	$\gamma = 83.016 \ (2)^{\circ}$
$M_r = 191.12$	V = 1243.71 (8) Å ³
Triclinic, $P\overline{1}$	Z = 6
a = 8.8040 (3) Å	Mo $K\alpha$ radiation
b = 10.4220 (4) Å	$\mu = 0.31 \text{ mm}^{-1}$
c = 14.0890 (6) Å	T = 150 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	23949 measured reflections
diffractometer	6720 independent reflection
Absorption correction: multi scan	3848 reflections with $I > 2$

(SORTAV; Blessing, 1995) $T_{\rm min}=0.919,\;T_{\rm max}=0.987$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.051$ $wR(F^2) = 0.144$ S = 1.006720 reflections

ns 48 reflections with I > $2\sigma(I)$ $R_{\rm int} = 0.067$

334 parameters H-atom parameters constrained $\Delta \rho_{\rm max} = 0.35 \text{ e} \text{ Å}^{-3}$ $\Delta \rho_{\min} = -0.57 \text{ e} \text{ Å}^{-3}$

Aromatic H atoms were constrained to an ideal geometry and refined using a riding model, with C-H = 0.95 Å and $U_{iso}(H) =$ $1.2U_{eq}(C)$. For the NH₃ groups, C-N-H angles (109.5°) 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 $(Å,^{\circ})$.

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

$D - H \cdots A$	$D-{\rm H}$	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$	Label
$O1 - H1 \cdots O11^{iii}$	0.84	1.76	2.563 (2)	158	
$O2-H2\cdots O8^{iv}$	0.84	1.81	2.627(2)	165	
O5−H5···O4 ⁱⁱ	0.84	1.77	2.592 (2)	164	
$O6-H6\cdots O3^{i}$	0.84	1.75	2.545 (2)	157	
$O9-H9\cdots O12^{v}$	0.84	1.81	2.636 (2)	166	
O10−H10···O7	0.84	1.78	2.541 (2)	150	
N11 H114 Ω^{pl}	0.01	1.02	2 820 (2)	174	
$N11 - H11A \cdots 08$	0.91	1.95	2.839 (3)	1/4	a L
NII-HIIC···O3	0.91	2.39	2.917 (2)	11/	D
$N11 - H11C \cdots O4$	0.91	2.40	3.296 (3)	169	c
$N11-H11B\cdots O7$	0.91	1.83	2.743 (3)	179	d
$N21 - H21A \cdots O8$	0.91	2.01	2,924 (2)	177	е
$N21 - H21B \cdots O12$	0.91	1.88	2.791(2)	177	f
$N21 - H21C \cdots O3$	0.91	1.91	2.819 (2)	176	ø
$N21 - H21A \cdots O7$	0.91	2.59	3.075 (2)	114	ĥ
$N31 - H31B \cdots O11$	0.91	2.49	2.965 (2)	113	i
$N31 - H31A \cdot \cdot \cdot O11^{iii}$	0.91	1.85	2.757 (2)	174	j
$N31 - H31B \cdots O12$	0.91	2.15	3.051(2)	174	k
$N31 - H31C \cdots O4^{iii}$	0.91	1.94	2.849 (3)	172	1

Symmetry codes: (i) -x + 1, -y + 1, -z; (ii) x + 1, y, z; (iii) -x, -y + 1, -z + 1; (iv) x - 1, y, z; (y) - 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 $U_{iso}(H) = 1.2U_{eq}(N)$ 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 $U_{\rm iso}({\rm H}) = 1.2 U_{\rm eq}({\rm O}).$

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).

Financial support from Charles University, Prague, through project No. GAUK 13350, is acknowledged. This work was also partially supported by the Slovak Grant Agency VEGA under contract No. 2/0150/09.

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.

References

- Anderson, K. M., Goeta, A. E., Hancock, K. S. B. & Steed, J. W. (2006). Chem. Commun. pp. 2138-2140.
- Balamurugan, P., Jagan, R. & Sivakumar, K. (2010). Acta Cryst. C66, o109o113.
- Bhadra, S., Kim, N. H. & Lee, J. H. (2010). J. Membr. Sci. 349, 304-311.
- Blessing, R. H. (1986). Acta Cryst. B42, 613-621.
- Blessing, R. H. (1995). Acta Cryst. A51, 33-38.
- Brandenburg, K. (2000). DIAMOND. Crystal Impact GbR, Bonn, Germany.
- Demir, S., Yilmaz, V. T. & Harrison, W. T. A. (2003). Acta Cryst. C59, 0378o380.
- Elmokhtar, O. S. M., Abid, S., Rzaigui, M. & Durif, A. (1995). Mater. Chem. Phys. 42, 225-230.
- Fábry, J., Krupková, R., Vaněk, P. & Dušek, M. (2006). Acta Cryst. C62, 073-075.
- Jeffrey, G. A. (1997). In An Introduction to Hydrogen Bonding. New York: Oxford University Press Inc.

- Kaman, O., Smrčok, Ľ., Císařová, I. & Havlíček, D. (2011). J. Chem. Crystallogr. 41, 1539-1546.
- Kroupa, J. & Fuith, A. (1993). Phys. Rev. B, 48, 4119-4121.
- Kumara Swamy, K. C., Kumaraswamy, S. & Kommana, P. (2001). J. Am. Chem. Soc. 123, 12642-12649.
- Mahmoudkhani, A. H. & Langer, V. (2002). J. Mol. Struct. 609, 97-108.
- Marouani, H., Al-Deyab, S. S. & Rzaigui, M. (2011). Acta Cryst. E67, 0970-0971. Nonius (1998). COLLECT. Nonius BV, Delft, the Netherlands.
- Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307-326. New York: Academic Press.
- Pringle, J. M., Howlett, P. C., MacFarlane, D. R. & Forsyth, M. (2010). J. Mater. Chem. 20, 2056-2062.
- Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
- Smrčok, Ľ., Havlíček, D., Kaman, O. & Rundlöf, H. (2009). Z. Kristallogr. 224, 174-178
- Soumhi, E. H. & Jouini, T. (1995). Acta Cryst. C51, 1213-1215.
- Spek, A. L. (2009). Acta Cryst. D65, 148-155.