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Hydrogen bonding in 4-carboxyanilinium dihydrogenphosphate

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.043
 wR factor = 0.120
Data-to-parameter ratio = 20.5

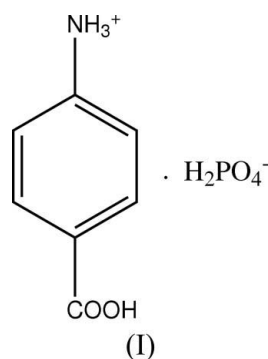
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

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The crystal structure analysis of the title compound, $\text{C}_7\text{H}_8\text{NO}_2^+\cdot\text{H}_2\text{PO}_4^-$, has revealed a three-dimensional hydrogen-bonded network structure, involving the dihydrogenphosphate anions, the carboxyl groups and the ammonium groups. The anions are held together *via* strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. In addition to the $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ interactions, involving all the H atoms covalently bonded to the anion, the nitrogen and the carboxyl group, the crystal structure is also stabilized by $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ short contacts.

Comment

Hydrogen bonding in hybrid materials is of intense interest because of their widespread occurrence in biological systems. Their potential importance in the structure and function of biomolecules is well established (Jeffrey & Saenger, 1991). In particular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are predominant in determining the formation of secondary structure elements in proteins, and base-pairing in nucleic acids and their biomolecular interactions.



The title compound, (I), was investigated as part of a study on $\text{D}-\text{H}\cdots\text{A}$ hydrogen bonding in systems of hybrid materials including organic bases or amino acids and phosphoric acids in their crystalline forms, such as *p*-carboxyphenylammonium dihydrogenmonophosphate monohydrate, (II) [Cambridge Structural Database (Version 5.23; Allen, 2002) refcode MIFVEC (Benali-Cherif *et al.*, 2002)], *L*-valinium hydrogenphosphite (Bendheif *et al.*, 2003), and *m*-carboxyphenylammonium monohydrogenphosphite (Bendeif *et al.*, 2005).

In order to examine the influence of the solvent (water) on the hydrogen-bonding properties of (II) we prepared the anhydrous form, (I). The molecular structure of complex (I) is illustrated in Fig. 1, and selected geometric parameters are given in Table 1. The H_2PO_4^- anions contain two types of P—O bonds. The mean length of the terminal bonds is

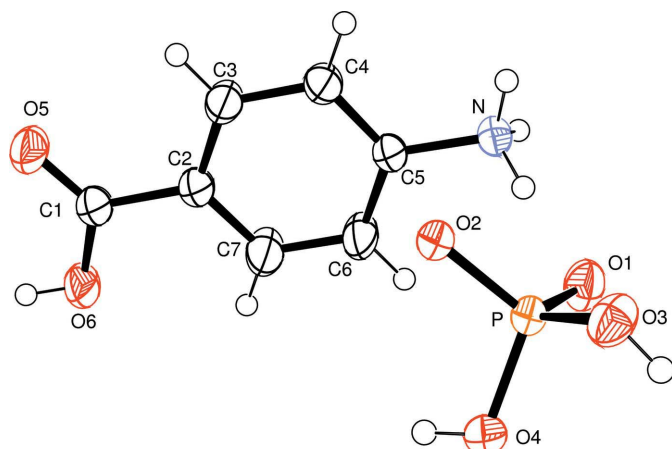


Figure 1
The asymmetric unit of (I) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

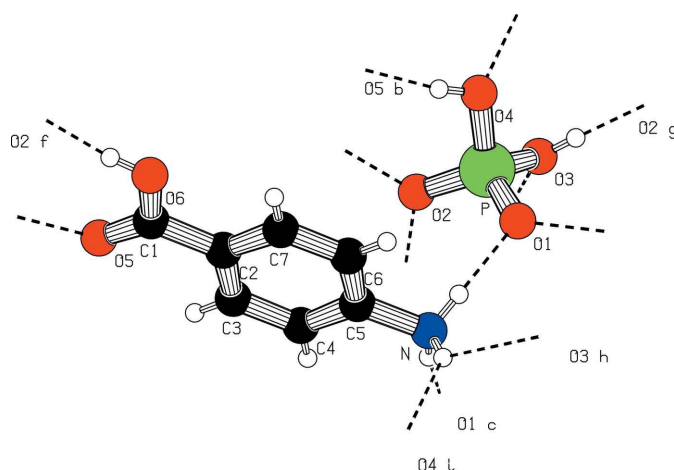


Figure 2
PLATON (Spek, 2003) view of the hydrogen-bonding network (dashed lines) in compound (I).

1.5005 (9) Å, which is significantly shorter than the mean length of the P—OH bonds [1.5675 (9) Å]. Bond lengths of the phosphate anions are in accordance with those observed in (II), and in other ionic compounds (Fábry *et al.*, 1997; Trojette *et al.*, 1998). There is considerable expansion and reduction in bond angles O4—P—O2 [109.17 (7)° in (I) compared with 105.9° in (II)] and O4—P—O3 [103.44 (7)° in (I) compared with 106.8° in (II)], respectively. This may be due to the absence of hydrogen bonds between the H₂PO₄[−] anions and the water molecules, which are present in (II).

The carboxyl group is not deprotonated and atom C1 has a slightly distorted *sp*² environment. The environment around the N atom is tetrahedrally distorted. Moreover, the C—NH₃⁺ bond is longer [1.4565 (19) Å] than the corresponding C—NH₂ bond (1.380–1.422 Å) reported in the literature (Lai & Marsh, 1967; Alleaume *et al.*, 1966), and the endocyclic angle to the *para* substituent, C4—C5—C6, is slightly larger than 120° [121.04 (15)°], as predicted by charge considerations. This reveals a decrease of the π bond character in the C—NH₃⁺ bond due to the protonation of the amino group occurring in the reaction with phosphoric acid.

The geometrical features of the *p*-carboxyphenyl-ammonium cations are consistent with the data reported in the literature: *p*-aminobenzoic acid hydrochloride (Colapietro *et al.*, 1980), bis(4-carboxybenzeneammonium) hexafluoro-silicate tetrahydrate (Gelmboldt *et al.*, 2004), 3-carboxy-4-hydroxybenzenesulfonate 4-carboxyanilinium (Smith *et al.*, 2005) and in (II). In (I) each *p*-carboxyanilinium cation is connected to five dihydrogenmonophosphate anions *via* hydrogen bonds, as shown in Fig. 2. As expected, the O atoms of H₂PO₄[−] act as proton acceptors or as proton donors, giving rise to a three-dimensional network.

The H₂PO₄[−] tetrahedra are linked together in pairs by strong O—H...O hydrogen bonds [O3...O2 = 2.550 (1) Å] which are shorter than in the dimers observed in (II), and give rise to the formation of C(4) chains (Bernstein *et al.*, 1995). Details of the hydrogen bonding are given in Table 2. Both O atoms, O2 and O1, of the phosphate anions are bifurcated acceptors of hydrogen bonds, while atoms O3 and O4 act as hydrogen-bond donors and acceptors. The three H atoms of the anilinium group are involved in strong N—H...O hydrogen-bonding interactions with hydroxyl O atoms of two different anions, and the terminal O atoms of two other, but different, H₂PO₄[−] tetrahedra. In addition, there are other interactions involving the carboxylic acid group of 4-aminobenzoic acid and the hydroxyl and terminal O atoms of the dihydrogenmonophosphate anions, which generate R₂²(8) rings. These O—H...O hydrogen bonds appear to be shorter than those observed between the ammonium group and the H₂PO₄[−] anions, and compare well with those present between both anions (Table 2). This shortness of the anion–anion (Philippot & Lindqvist, 1971; Calleri & Speakman, 1964) and anion–cation interactions (Blessing & McGandy, 1972) is probably due to the strong interactions between neighbouring anions and cations. The coplanarity of the carboxyl group and the benzene ring [torsion angle C7—C2—C1—O6 = 0.5 (3)°] is assured by an unusually weak intramolecular C—H...O (Desiraju, 2002; 2005) interaction and a close short contact between the phenyl rings.

Experimental

Single crystals of compound (I) were prepared by slow evaporation at room temperature of an aqueous solution of 4-aminobenzoic acid and orthophosphoric acid (H₃PO₄) in the stoichiometric ratio 1:1.

Crystal data

C₇H₈O₂N⁺·H₂PO₄[−]
M_r = 235.13
Monoclinic, P2₁/n
a = 6.3368 (2) Å
b = 22.8812 (7) Å
c = 7.3843 (2) Å
β = 111.101 (2)°

V = 998.88 (5) Å³
Z = 4
Mo Kα radiation
μ = 0.28 mm^{−1}
T = 293 (2) K
0.20 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
13869 measured reflections

2865 independent reflections
2428 reflections with I > 2σ(I)
R_{int} = 0.080

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	140 parameters
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 0.33 \text{ e } \text{Å}^{-3}$
2865 reflections	$\Delta\rho_{\min} = -0.49 \text{ e } \text{Å}^{-3}$

Table 1
Selected geometric parameters (Å, °).

P—O1	1.4908 (13)	O5—C1	1.217 (2)
P—O2	1.5100 (13)	O6—C1	1.308 (2)
P—O3	1.5605 (13)	N—C5	1.4571 (19)
P—O4	1.5747 (12)		
O2—P—O3	107.23 (7)	O6—C1—C2	113.66 (17)
O2—P—O4	109.17 (7)	O5—C1—O6	124.07 (16)
O3—P—O4	103.44 (7)	O5—C1—C2	122.27 (17)
O1—P—O2	114.00 (7)	N—C5—C4	120.56 (14)
O1—P—O3	111.36 (7)	N—C5—C6	118.36 (16)
O1—P—O4	111.05 (7)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H1 \cdots O2 ⁱ	0.82	1.75	2.5586 (18)	170
O3—H03 \cdots O2 ⁱⁱ	0.82	1.75	2.5497 (17)	164
N—H1N \cdots O4 ⁱⁱⁱ	0.89	2.27	3.0160 (18)	141
N—H1N \cdots O3 ^{iv}	0.89	2.41	2.9633 (19)	121
O4—H04 \cdots O5 ⁱ	0.82	1.82	2.6265 (18)	170
N—H2N \cdots O1	0.89	1.85	2.7273 (17)	169
N—H3N \cdots O1 ^v	0.89	1.83	2.7150 (18)	170
C7—H7 \cdots O6	0.93	2.38	2.707 (3)	101

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

The OH and NH₃ H atoms were located in difference Fourier syntheses and refined as riding atoms with distances constraints of N—H = 0.89 Å and O—H = 0.82 Å [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N}, \text{O})$]. Aromatic H atoms were positioned geometrically and were allowed to ride on their parent C atoms with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used

to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

- Alleaume, M., Salas-Cimingo, G. & Decap, J. (1966). *C. R. Acad. Sci. Ser. C*, **262**, 416–417.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Benali-Cherif, N., Abouimrane, A., Sbai, K., Merazig, H., Cherouana, A. & Bendjeddou, L. (2002). *Acta Cryst.* **E58**, o160–o161.
- Bendeif, E.-E., Dahaoui, S., François, M., Benali-Cherif, N. & Lecomte, C. (2005). *Acta Cryst.* **B61**, 700–709.
- Bendheif, L., Benali-Cherif, N., Benguedouar, L., Bouchouit, K. & Merazig, H. (2003). *Acta Cryst.* **E59**, o141–o142.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blessing, R. H. & McGandy, E. L. (1972). *J. Am. Chem. Soc.* **94**, 4034–4035.
- Burla, M. C., Calandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Calleri, M. & Speakman, J. C. (1964). *Acta Cryst.* **17**, 1097–1103.
- Colapietro, M., Domenicano, A. & Portalone, G. (1980). *Acta Cryst.* **B36**, 354–358.
- Desiraju, G. R. (2002). *Acc. Chem. Res.* **35**, 565–573.
- Desiraju, G. R. (2005). *Chem. Commun.* pp. 2995–3001.
- Fábry, J., Petríček, V., Císarová, I. & Kroupa, J. (1997). *Acta Cryst.* **B53**, 272–279.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gelmboldt, V. O., Ennan, A. A., Ganin, Ed. V., Simonov, Yu. A., Fonari, M. S. & Botoshansky, M. M. (2004). *J. Fluorine Chem.* **125**, 1951–1957.
- Jeffrey, G. A. & Saenger, W. (1991). *An Introduction to Hydrogen Bonding*, pp. 245–250. Berlin: Springer Verlag.
- Lai, T. F. & Marsh, R. E. (1967). *Acta Cryst.* **22**, 885–893.
- Nonius (1998). *KappaCCD Server Software*. 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.
- Philippot, E. & Lindqvist, O. (1971). *Acta Chem. Scand.* **25**, 512–524.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Smith, G., Wermuth, U. D. & White, J. M. (2005). *Acta Cryst.* **E61**, o313–o316.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Trojette, B., Hajem, A. A., Driss, A. & Jouini, T. (1998). *Acta Cryst.* **C54**, 1867–1869.