organic compounds

Hydrogen bonding in 2-carboxyanilinium dihydrogen phosphite at 100 K

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The title compound, $C_7H_8NO_2^+ \cdot H_2PO_3^-$, is formed from alternating layers of organic cations and inorganic anions stacked along the a-axis direction. They are associated via O—H···O, N—H···O and C—H···O hydrogen bonding, giving rise to two different $R_2^2(8)$ graph-set motifs and generating a three-dimensional network.

Related literature

For applications of hybrid compounds, see: Kagan *et al.* (1999); Mazeaud *et al.* (2000); Benali-Cherif, Direm *et al.* (2007). For applications of anthranilic acid derivatives, see: He *et al.* (2003); Per Wiklund *et al.* (2004); Congiu *et al.* (2005); Nittoli *et al.* (2005). For related structured, see: Bendeif *et al.* (2003, 2009); Benali-Cherif, Allouche *et al.* (2007). For graph-set theory, see: Bernstein *et al.* (1995).
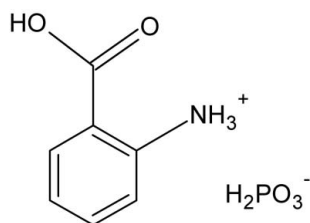
Experimental

Crystal data

$C_7H_8NO_2^+ \cdot H_2PO_3^-$
$M_r = 219.13$
Triclinic, $P\bar{1}$
$a = 4.8757$ (6) Å
$b = 9.4597$ (6) Å
$c = 10.0801$ (5) Å
$\alpha = 78.929$ (3)°
$\beta = 76.058$ (4)°

$\gamma = 86.814$ (2)°
$V = 442.81$ (7) Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.31$ mm^{-1}
$T = 100$ K
$0.25 \times 0.18 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur Saphire2 diffractometer
Absorption correction: integration (*ABSORB*; DeTitta, 1985)
$T_{min} = 0.972$, $T_{max} = 0.985$

11058 measured reflections
2581 independent reflections
2559 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.093$
$S = 1.07$
2581 reflections

127 parameters
H-atom parameters not refined
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^i	0.84	1.77	2.6085 (13)	178
N1—H1A···O4	0.91	1.96	2.8589 (14)	169
N1—H1B···O4^{ii}	0.91	2.02	2.9160 (13)	169
N1—H1C···O4^{iii}	0.91	1.97	2.8740 (14)	173
O5—H5O···O3^{iv}	0.84	1.78	2.6059 (13)	167
C6—H6···O5^v	0.95	2.55	3.2542 (15)	132

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

Data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2238).

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supplementary materials

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Comment

The crystal structures of organic-inorganic hybrid materials have been extensively investigated due to their interest in the field of new materials, and the number of reported structures is rapidly growing owing to their applications in medicine, material science and to their electrical, magnetic and optical properties (Kagan *et al.*, 1999; Mazeaud *et al.*, 2000) and the hydrogen bonding richness of these structures. This kind of hydrogen bonding appears in the active sites of several biological systems and is observed in similar previously studied hybrid compounds (Benali-Cherif, Direm *et al.*, 2007).

As well as being a biochemical precursor of the amino acids tryptophan, phenylalanine and tyrosine, anthranilic acid is used as a useful derivating agent for carbohydrate analysis (He *et al.*, 2003). 2-Aminobenzoic acid is present as a part of the core structure of certain alkaloids, synthetic drugs (Per Wiklund *et al.*, 2004), antiinflammatory, anticancer agents (Congiu *et al.*, 2005) and as inhibitor of Hepatitis C NS5B polymerase (Nittoli *et al.*, 2005).

The title compound structure (I) is composed of cationic HOO-C_6H_4—NH_3^+ and anionic ($H_2PO_3^-$) groups (Fig.1). All bond lengths and angles of the ($H_2PO_3^-$) tetrahedra and the *o*-carboxyanilinium cations are within normal ranges, in a good agreement with those observed in the litterature (Bendeif *et al.* 2003, Bendeif *et al.* 2009) and (Benali-Cherif, Allouche *et al.*, 2007), respectively.

The three H atoms of the anilinium group are subsequently involved in extensive N—H···O hydrogen-bonding (Table 1) interactions with O4 being a multiple acceptor of three different phosphite anions, while O3 behaves as double acceptor of hydrogen bonds from one cation, *via* O1 in the carboxylic group, and one anion, *via* O5 in the phosphite anion. These interactions give raise to two different $R_2^2(8)$ graph set motifs (Bernstein *et al.* 1995), shown in Fig. 2. In addition, there are intramolecular interactions involving the benzene ring and the carboxylic group ensuring cohesion and stability of the crystal structiure.

Experimental

Crystals of anthranilicium phosphite are prepared by slow evaporation at room temperature of an aqueous solution of 2-aminobenzoic acid and H_3PO_3 in a 1:1 stochimetric ratio.

Refinement

The title compound crystallizes in the centrosymmetric space group P-1. A l l non-H atoms were refined with anisotropic atomic displacement parameters. All H-atoms were located in difference Fourier syntheses and refined as riding model with C—H, N—H, O—H bond lengths constrained to 0.950 Å, 0.910 Å, 0.840Å respectively.
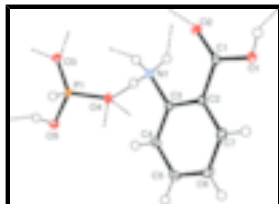
supplementary materials

Figures

Fig. 1. View of the asymmetric unit of $C_7H_8NO_2^+ \cdot H_2PO_3^-$ showing atom labels and suggesting the hydrogen bondings richness. Displacement factors drawn at a 50% level.
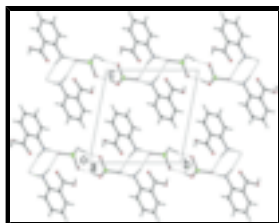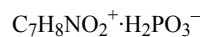

Fig. 2. Unit cell projection down a, showing the two different $R_2^2(8)$ graph motifs in the structure.

2-carboxyanilinium dihydrogen phosphite

Crystal data

$C_7H_8NO_2^+ \cdot H_2PO_3^-$	$Z = 2$
$M_r = 219.13$	$F_{000} = 228$
Triclinic, $P\overline{1}$	$D_x = 1.643$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 4.8757$ (6) Å	Cell parameters from 11058 reflections
$b = 9.4597$ (6) Å	$\theta = 2.8–32.7°$
$c = 10.0801$ (5) Å	$\mu = 0.31$ mm^{-1}
$\alpha = 78.929$ (3)°	$T = 100$ K
$\beta = 76.058$ (4)°	Prism, colourless
$\gamma = 86.814$ (2)°	$0.25 \times 0.18 \times 0.05$ mm
$V = 442.81$ (7) Å^3	

Data collection

Oxford Diffraction Xcalibur Saphire2 diffractometer	2581 independent reflections
Radiation source: fine-focus sealed tube	2559 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.035$
Detector resolution: 8.4221 pixels mm^{-1}	$\theta_{max} = 30.0°$
$T = 100$ K	$\theta_{min} = 2.8°$
ω and θ scans	$h = -6 \rightarrow 6$
Absorption correction: integration (ABSORB; DeTitta, 1985)	$k = -12 \rightarrow 13$
$T_{min} = 0.972$, $T_{max} = 0.985$	$l = 0 \rightarrow 14$
11058 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters not refined
$wR(F^2) = 0.093$	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.2002P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2581 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	1.22190 (19)	0.11913 (10)	0.23669 (10)	0.01503 (19)
H1	1.3765	0.1163	0.1783	0.023*
O2	1.18445 (19)	0.33344 (10)	0.10200 (9)	0.01319 (18)
N1	0.6956 (2)	0.48161 (11)	0.14593 (10)	0.0107 (2)
H1A	0.5423	0.5400	0.1407	0.013*
H1B	0.7309	0.4308	0.0754	0.013*
H1C	0.8484	0.5361	0.1386	0.013*
C1	1.0902 (2)	0.24260 (13)	0.20403 (12)	0.0109 (2)
C2	0.8201 (2)	0.26393 (13)	0.30600 (12)	0.0106 (2)
C3	0.6396 (3)	0.38167 (13)	0.27952 (12)	0.0104 (2)
C4	0.3987 (3)	0.40572 (13)	0.37899 (13)	0.0131 (2)
H4	0.2794	0.4862	0.3601	0.016*
C5	0.3322 (3)	0.31144 (14)	0.50686 (13)	0.0150 (2)
H5	0.1688	0.3284	0.5755	0.018*
C6	0.5051 (3)	0.19272 (15)	0.53363 (13)	0.0157 (2)
H6	0.4584	0.1276	0.6199	0.019*
C7	0.7466 (3)	0.16969 (14)	0.43364 (13)	0.0141 (2)
H7	0.8639	0.0883	0.4525	0.017*
P1	0.19035 (6)	0.80587 (3)	0.08601 (3)	0.01016 (10)

O3	0.29056 (19)	0.88933 (10)	−0.06075 (9)	0.01379 (18)
O4	0.20062 (18)	0.64347 (9)	0.10464 (9)	0.01255 (18)
O5	−0.1212 (2)	0.85119 (10)	0.14917 (10)	0.0166 (2)
H5O	−0.1511	0.9363	0.1122	0.025*
H	0.3396	0.8447	0.1629	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0120 (4)	0.0112 (4)	0.0180 (4)	0.0041 (3)	−0.0003 (3)	0.0013 (3)
O2	0.0124 (4)	0.0120 (4)	0.0132 (4)	0.0011 (3)	−0.0016 (3)	0.0003 (3)
N1	0.0102 (5)	0.0093 (4)	0.0118 (5)	0.0016 (3)	−0.0022 (3)	−0.0011 (3)
C1	0.0102 (5)	0.0099 (5)	0.0131 (5)	0.0011 (4)	−0.0039 (4)	−0.0025 (4)
C2	0.0097 (5)	0.0101 (5)	0.0118 (5)	0.0003 (4)	−0.0030 (4)	−0.0013 (4)
C3	0.0117 (5)	0.0093 (5)	0.0101 (5)	−0.0004 (4)	−0.0031 (4)	−0.0013 (4)
C4	0.0122 (5)	0.0128 (5)	0.0141 (5)	0.0013 (4)	−0.0020 (4)	−0.0036 (4)
C5	0.0134 (5)	0.0180 (6)	0.0128 (5)	−0.0004 (4)	−0.0006 (4)	−0.0042 (4)
C6	0.0172 (6)	0.0175 (6)	0.0103 (5)	−0.0013 (5)	−0.0016 (4)	0.0014 (4)
C7	0.0137 (5)	0.0130 (6)	0.0142 (5)	0.0016 (4)	−0.0036 (4)	0.0008 (4)
P1	0.01028 (15)	0.00778 (15)	0.01211 (15)	0.00126 (10)	−0.00279 (11)	−0.00126 (10)
O3	0.0124 (4)	0.0106 (4)	0.0148 (4)	0.0029 (3)	0.0006 (3)	0.0007 (3)
O4	0.0124 (4)	0.0082 (4)	0.0166 (4)	0.0013 (3)	−0.0040 (3)	−0.0009 (3)
O5	0.0149 (4)	0.0110 (4)	0.0181 (4)	0.0053 (3)	0.0026 (3)	0.0018 (3)

Geometric parameters (Å, °)

O1—C1	1.3250 (14)	C4—H4	0.9500
O1—H1	0.8399	C5—C6	1.3902 (18)
O2—C1	1.2182 (15)	C5—H5	0.9500
N1—C3	1.4643 (15)	C6—C7	1.3908 (17)
N1—H1A	0.9100	C6—H6	0.9500
N1—H1B	0.9100	C7—H7	0.9500
N1—H1C	0.9101	P1—O4	1.5110 (9)
C1—C2	1.4930 (16)	P1—O3	1.5154 (9)
C2—C7	1.3970 (16)	P1—O5	1.5695 (9)
C2—C3	1.4060 (16)	P1—H	1.2947
C3—C4	1.3880 (16)	O5—H5O	0.8400
C4—C5	1.3969 (17)		
C1—O1—H1	109.5	C5—C4—H4	120.1
C3—N1—H1A	109.5	C6—C5—C4	120.00 (11)
C3—N1—H1B	109.5	C6—C5—H5	120.0
H1A—N1—H1B	109.5	C4—C5—H5	120.0
C3—N1—H1C	109.5	C5—C6—C7	119.76 (12)
H1A—N1—H1C	109.5	C5—C6—H6	120.1
H1B—N1—H1C	109.5	C7—C6—H6	120.1
O2—C1—O1	123.21 (11)	C6—C7—C2	121.25 (12)
O2—C1—C2	122.48 (11)	C6—C7—H7	119.4
O1—C1—C2	114.27 (10)	C2—C7—H7	119.4

C7—C2—C3	118.21 (11)	O4—P1—O3	116.92 (5)
C7—C2—C1	120.31 (11)	O4—P1—O5	107.62 (5)
C3—C2—C1	121.42 (11)	O3—P1—O5	109.90 (5)
C4—C3—C2	120.87 (11)	O4—P1—H	108.37
C4—C3—N1	117.68 (10)	O3—P1—H	108.24
C2—C3—N1	121.44 (10)	O5—P1—H	105.16
C3—C4—C5	119.89 (11)	P1—O5—H5O	109.5
C3—C4—H4	120.1		
O2—C1—C2—C7	−168.18 (12)	C2—C3—C4—C5	−0.57 (19)
O1—C1—C2—C7	9.66 (16)	N1—C3—C4—C5	178.45 (11)
O2—C1—C2—C3	9.07 (18)	C3—C4—C5—C6	−0.83 (19)
O1—C1—C2—C3	−173.09 (11)	C4—C5—C6—C7	1.1 (2)
C7—C2—C3—C4	1.67 (18)	C5—C6—C7—C2	0.1 (2)
C1—C2—C3—C4	−175.63 (11)	C3—C2—C7—C6	−1.42 (18)
C7—C2—C3—N1	−177.31 (11)	C1—C2—C7—C6	175.92 (12)
C1—C2—C3—N1	5.39 (17)		

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O3[i]	0.84	1.77	2.6085 (13)	178
N1—H1A$\cdots$O4	0.91	1.96	2.8589 (14)	169
N1—H1B$\cdots$O4[ii]	0.91	2.02	2.9160 (13)	169
N1—H1C$\cdots$O4[iii]	0.91	1.97	2.8740 (14)	173
O5—H5O$\cdots$O3[iv]	0.84	1.78	2.6059 (13)	167
C6—H6$\cdots$O5[v]	0.95	2.55	3.2542 (15)	132
C7—H7$\cdots$O1	0.95	2.42	2.7503 (16)	101

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*; (ii) −*x*+1, −*y*+1, −*z*; (iii) *x*+1, *y*, *z*; (iv) −*x*, −*y*+2, −*z*; (v) −*x*, −*y*+1, −*z*+1.

Fig. 1

Fig. 2