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2-Amino-3-carboxypyridinium dihydrogenphosphate

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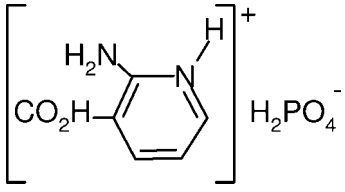
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.086; data-to-parameter ratio = 12.1.

The structure of a new monophosphate with an organic cation, $C_6H_7N_2O_2^+\cdot H_2PO_4^-$, is built up of organic (2-$NH_2C_5NH_4CO_2H^+$) and inorganic ($H_2PO_4^-$) entities located in planes parallel to $(10\bar{1})$. There are $(H_2PO_4^-)_n$ polyanions resulting from the aggregation of dihydrogenphosphate groups through strong hydrogen bonds, and these form infinite ribbons parallel to the b direction.

Related literature

For related literature, see: Adams (1977); Blessing (1986); Desiraju (1989, 1995); Hebert (1978); Masse & Durif (1990).



Experimental

Crystal data

$C_6H_7N_2O_2^+\cdot H_2PO_4^-$
M_r = 236.12
Monoclinic, $P2_1/n$
a = 12.877 (3) Å
b = 4.658 (3) Å
c = 15.978 (2) Å
β = 99.43 (3)°
V = 945.4 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 295 K
0.21 × 0.19 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
3295 measured reflections
1646 independent reflections
1317 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
2 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.086
S = 1.04
1646 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 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}	0.82	1.79	2.504 (3)	145
O2—H2···O4^{ii}	0.82	2.04	2.560 (3)	121
O6—H6···O3	0.82	1.78	2.579 (3)	165
N1—H1A···O4^{iii}	0.86	1.83	2.684 (3)	173
N2—H2A···O1^{iii}	0.86	2.03	2.873 (3)	169
N2—H2B···O5	0.86	2.09	2.712 (3)	129
N2—H2B···O5^{iv}	0.86	2.27	2.914 (3)	132
C3—H3···O6	0.93	2.36	2.694 (3)	101
C5—H5···O4^{v}	0.93	2.52	3.268 (3)	138

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, y-1, z$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); 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: GW2015).

References

Adams, J. M. (1977). *Acta Cryst.* B**33**, 1513–1515.
Blessing, R. H. (1986). *Acta Cryst.* B**42**, 613–621.
Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*, Vol 54. New York: Elsevier.
Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). J. Appl. Cryst. 30, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Hebert, H. (1978). *Acta Cryst.* B**34**, 611–615.
Masse, R. & Durif, A. (1990). *Z. Kristallogr.* **190**, 19–32.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

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supplementary materials

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2-Amino-3-carboxypyridinium dihydrogenphosphate

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Comment

Intermolecular and intramolecular H-bonds constitute an important factor to understand and interprate the properties of biological and pharmacological materials. For that purpose, organic phosphate could be used as interesting models. In the presence of organic cations, the formation of $(H_2PO_4–)_n$ polyanions is observed. These polymeric anions could provide interesting supramolecular networks with a variety of novel structural features (Blessing, (1986); Adams, (1977); Desiraju, (1989) and (1995)).

As part of our study of organic cation monophosphate, we have synthesized a new compound,2-amino-3-nicotinium acid dihydrogenmonophosphate (I). The formula unit (I) constitute the assymetric unit which is built of one $(H_2PO_4)_-$ anion and one $(C_5N_2H_6CO_2H)_+$ cation (Fig. 1).

The main geometrical features of anions and cations are reported in table 1. The monophosphate anions have slightly distorted tetrahedral geometry, with the P—O bond lengths ranging from 1.5049 (16)–1.5628 (14)Å and the O—P—O angles ranging from 106.46 (9)–115.27 (10)°. As expected, the geometric parameters of the H_2PO_{4-} anion agree with those previously observed for monophosphate polyanions with no internal symmetry (Hebert, (1978); Masse and Durif, (1990)).

The $H_2P\ O_{4-}$ tetrahedra are interconnected by strong hydrogen bonds in way to form infinite ribbons extending along the *b* axis. These ribbons, which are organized in planes parallel to (101), are interconnected by the organic molecules so to form thick layers of hybrid organic-inorganic entities parallel to the (10–1) plane (Fig. 2). These entities manifest multiple hydtogen bonds of types N—H···O, O—H···O and C—H···O to keep up the network cohesion.

Each H_2PO_4 group is linked to four adjacent phosphoric groups by two donors and two acceptors strong hydrogen bonds in which the corresponding O···O distances lie in the range 2.504 (3)–2.560 (3) Å on one side, and to two organic cations by three acceptors weak hydrogen bonds on the other side.

The hydrogen atoms belonging to NH_2 groups participate in addition in intramolecular interaction with N2—H2B···O5 = 2.086 Å distance to maintain the cohesion of organic cations.

Experimental

A solution of 2-amino nicotinic acid (0.036 mmol) in ethanol (5 ml) is added drop by drop under stirring to a dilute solution of H_3PO_4 (0.25 mmol) in water (20 ml). The obtained solution is slowly evaporated at the ambiant temperature. After some days, transparent thin single crystals of the title compound are formed in the reactionnel midle.

Figures

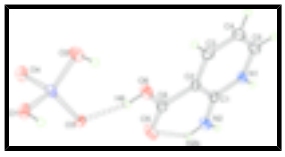

Fig. 1. view of (I) with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level

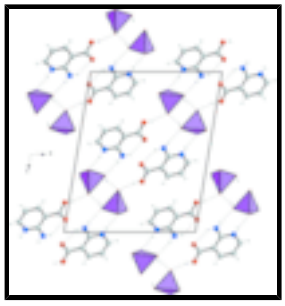

Fig. 2. Projection of (I) along *b* axis.

2-Amino-3-carboxypyridinium dihydrogenphosphate

Crystal data

$C_6H_7N_2O_2^+ \cdot H_2PO_4^-$	$F_{000} = 488$
$M_r = 236.12$	$D_x = 1.659$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 25 reflections
$a = 12.877$ (3) Å	$\theta = 10$–$13°$
$b = 4.658$ (3) Å	$\mu = 0.30$ mm^{-1}
$c = 15.978$ (2) Å	$T = 295$ K
$\beta = 99.43$ (3)°	Prism, colourless
$V = 945.4$ (7) Å^3	0.21 × 0.19 × 0.17 mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.013$
Radiation source: fine-focus sealed tube	$\theta_{max} = 30.0°$
Monochromator: graphite	$\theta_{min} = 3.2°$
$T = 295$ K	$h = -18 \rightarrow 17$
non–profiled ω scans	$k = -6 \rightarrow 6$
Absorption correction: none	$l = 0 \rightarrow 9$
3295 measured reflections	2 standard reflections
1646 independent reflections	every 120 min
1317 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H-atom parameters constrained
$wR(F^2) = 0.086$	$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.4272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.0001$
1646 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.32$ 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 $F^2 > 2$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}
P1	0.36597 (3)	0.04985 (10)	0.83326 (5)	0.0235 (3)
O1	0.25963 (9)	−0.0708 (3)	0.85358 (11)	0.0311 (5)
H1	0.2435	−0.2157	0.8253	0.047*
O2	0.45370 (9)	−0.1750 (3)	0.86498 (11)	0.0320 (5)
H2	0.4428	−0.3224	0.8368	0.048*
O3	0.36107 (10)	0.0954 (3)	0.73904 (14)	0.0301 (6)
O4	0.39050 (10)	0.3137 (3)	0.88724 (11)	0.0301 (5)
O5	0.50372 (11)	0.2632 (4)	0.57748 (13)	0.0443 (6)
N1	0.79601 (11)	0.0029 (4)	0.51515 (14)	0.0299 (6)
H1A	0.8213	0.0704	0.4726	0.036*
O6	0.53099 (11)	−0.0514 (4)	0.68426 (12)	0.0407 (6)
H6	0.4738	0.0078	0.6931	0.061*
C2	0.66074 (13)	−0.0149 (4)	0.59914 (17)	0.0245 (7)
N2	0.65346 (12)	0.2958 (4)	0.47661 (14)	0.0352 (6)
H2A	0.6827	0.3573	0.4354	0.042*
H2B	0.5931	0.3619	0.4837	0.042*
C1	0.70085 (13)	0.1010 (4)	0.52881 (16)	0.0257 (7)
C6	0.55708 (14)	0.0821 (4)	0.61901 (18)	0.0299 (8)

C5	0.85289 (14)	−0.1939 (5)	0.56455 (19)	0.0359 (8)
H5	0.9179	−0.2509	0.5521	0.043*
C3	0.71970 (14)	−0.2165 (5)	0.64914 (17)	0.0318 (7)
H3	0.6941	−0.2926	0.6956	0.038*
C4	0.81747 (15)	−0.3097 (5)	0.63169 (19)	0.0372 (8)
H4	0.8566	−0.4472	0.6654	0.045*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.02042 (19)	0.02154 (19)	0.0302 (9)	−0.00039 (15)	0.0089 (2)	0.0020 (2)
O1	0.0264 (6)	0.0365 (7)	0.0336 (17)	−0.0095 (5)	0.0141 (6)	−0.0093 (7)
O2	0.0266 (6)	0.0235 (6)	0.0452 (16)	0.0005 (5)	0.0037 (6)	0.0048 (7)
O3	0.0315 (6)	0.0500 (9)	0.0118 (18)	0.0117 (6)	0.0124 (7)	0.0124 (9)
O4	0.0345 (6)	0.0237 (6)	0.0354 (16)	−0.0055 (5)	0.0151 (7)	−0.0034 (7)
O5	0.0368 (7)	0.0500 (9)	0.0501 (18)	0.0181 (6)	0.0190 (8)	0.0159 (9)
N1	0.0252 (7)	0.0370 (9)	0.0306 (19)	0.0019 (6)	0.0136 (8)	0.0003 (9)
O6	0.0332 (7)	0.0656 (11)	0.0281 (19)	0.0147 (7)	0.0190 (8)	0.0142 (10)
C2	0.0244 (7)	0.0343 (9)	0.016 (2)	0.0023 (6)	0.0075 (8)	−0.0010 (9)
N2	0.0319 (8)	0.0428 (9)	0.034 (2)	0.0079 (7)	0.0154 (8)	0.0131 (10)
C1	0.0224 (7)	0.0310 (9)	0.024 (2)	0.0004 (6)	0.0063 (9)	−0.0020 (9)
C6	0.0247 (8)	0.0375 (10)	0.029 (3)	0.0024 (7)	0.0078 (9)	−0.0027 (11)
C5	0.0236 (8)	0.0451 (11)	0.039 (3)	0.0068 (7)	0.0065 (10)	0.0005 (12)
C3	0.0307 (8)	0.0442 (11)	0.022 (2)	0.0048 (8)	0.0078 (9)	0.0059 (11)
C4	0.0297 (9)	0.0507 (13)	0.031 (3)	0.0112 (9)	0.0041 (11)	0.0076 (13)

Geometric parameters (Å, °)

P1—O1	1.5627 (14)	C2—C3	1.377 (3)
P1—O2	1.5628 (14)	C2—C1	1.418 (3)
P1—O3	1.511 (2)	C2—C6	1.492 (3)
P1—O4	1.5049 (16)	N2—C1	1.313 (3)
O1—H1	0.8200	N2—H2A	0.8600
O2—H2	0.8200	N2—H2B	0.8600
O5—C6	1.214 (3)	C5—C4	1.346 (4)
N1—C5	1.346 (3)	C5—H5	0.9300
N1—C1	1.358 (2)	C3—C4	1.402 (3)
N1—H1A	0.8600	C3—H3	0.9300
O6—C6	1.304 (3)	C4—H4	0.9300
O6—H6	0.8200		
O4—P1—O3	115.27 (10)	H2A—N2—H2B	120.0
O4—P1—O1	106.46 (9)	N2—C1—N1	117.9 (2)
O3—P1—O1	111.25 (9)	N2—C1—C2	125.07 (17)
O4—P1—O2	106.78 (9)	N1—C1—C2	117.04 (18)
O3—P1—O2	109.09 (9)	O5—C6—O6	124.83 (19)
O1—P1—O2	107.64 (9)	O5—C6—C2	122.7 (2)
P1—O1—H1	109.5	O6—C6—C2	112.48 (18)
P1—O2—H2	109.5	C4—C5—N1	121.19 (19)

C5—N1—C1	123.6 (2)	C4—C5—H5	119.4
C5—N1—H1A	118.2	N1—C5—H5	119.4
C1—N1—H1A	118.2	C2—C3—C4	121.6 (2)
C6—O6—H6	109.5	C2—C3—H3	119.2
C3—C2—C1	118.77 (18)	C4—C3—H3	119.2
C3—C2—C6	120.7 (2)	C5—C4—C3	117.8 (2)
C1—C2—C6	120.53 (19)	C5—C4—H4	121.1
C1—N2—H2A	120.0	C3—C4—H4	121.1
C1—N2—H2B	120.0		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.82	1.79	2.504 (3)	145
O2—H2···O4^{ii}	0.82	2.04	2.560 (3)	121
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Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+3/2; (ii) *x*, *y*−1, *z*; (iii) *x*+1/2, −*y*+1/2, *z*−1/2; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+3/2, *y*−1/2, −*z*+3/2.

Fig. 1

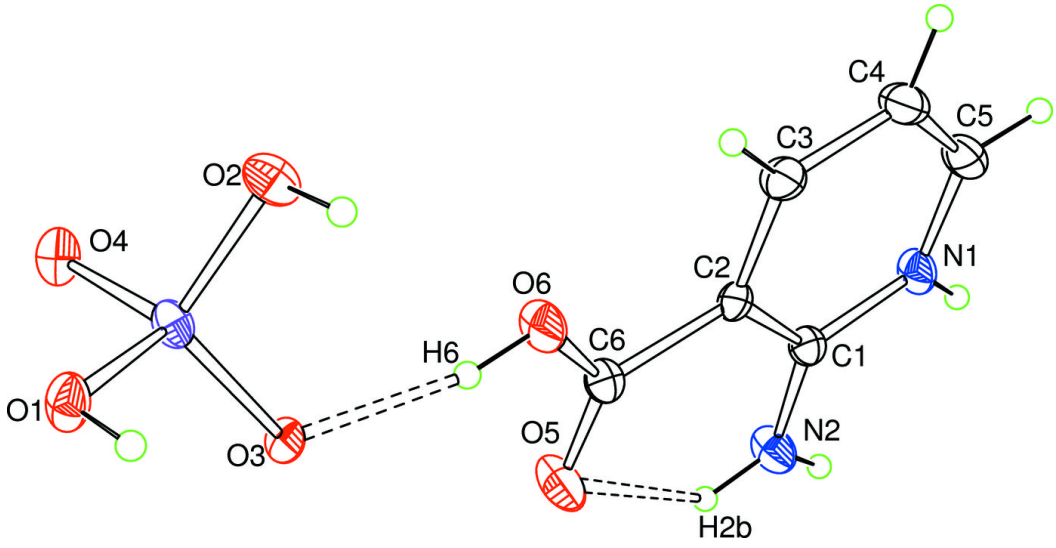

Fig. 2