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2-Methylanilinium dihydrogen phosphate–phosphoric acid (1/1)

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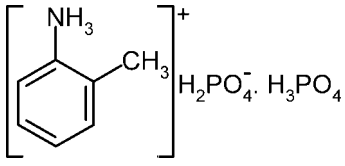
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.033; wR factor = 0.092; data-to-parameter ratio = 30.9.

In the title compound, $C_7H_{10}N^+\cdot H_2PO_4^-\cdot H_3PO_4$, there is a clear distinction between the P—O/P=O and P—OH bond lengths. In the crystal, the $H_2PO_4^-$ anions and H_3PO_4 molecules are linked by O—H···O hydrogen bonds, leading to layers propagating in the *bc* plane. The organic cations are located between these layers and interact with them by way of N—H···O hydrogen bonds.

Related literature

For related structures, see: Akriche & Rzaigui (2000); Zaccaro *et al.* (1996). For background, see: Desiraju (1995).



Experimental

Crystal data

$C_7H_{10}N^+\cdot H_2PO_4^-\cdot H_3PO_4$
M_r = 303.14
Monoclinic, $P2_1/c$
a = 10.8769 (10) Å
b = 7.938 (4) Å
c = 15.302 (3) Å
β = 91.57 (2)°
V = 1320.7 (7) Å^3
Z = 4
Ag $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 298 K
0.37 × 0.31 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
5416 measured reflections
5250 independent reflections
4134 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
2 standard reflections
frequency: 120 min
intensity decay: 18%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.092
S = 1.08
5250 reflections
170 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Selected bond lengths (Å).

P1—O3	1.4964 (9)	P2—O8	1.4942 (9)
P1—O4	1.5092 (10)	P2—O5	1.5422 (10)
P1—O2	1.5571 (9)	P2—O7	1.5445 (10)
P1—O1	1.5707 (9)	P2—O6	1.5493 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{i}	0.82	1.83	2.6483 (16)	178
O2—H2···O8^{i}	0.82	1.80	2.6132 (13)	170
O5—H5···O3	0.82	1.72	2.5351 (15)	176
O6—H6···O8^{ii}	0.82	1.81	2.6223 (16)	170
O7—H7···O4^{iii}	0.82	1.69	2.5109 (13)	177
N1—H1A···O1^{i}	0.89	2.08	2.9627 (16)	172
N1—H1B···O3	0.89	1.91	2.7808 (19)	164
N1—H1C···O7^{iv}	0.89	2.18	3.0086 (15)	154

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

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* Brandenburg (2005); 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: HB2955).

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supplementary materials

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2-Methylanilinium dihydrogen phosphate-phosphoric acid (1/1)

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Comment

Organic cation phosphates have been intensively studied due to their many uses in various fields such as biomolecular sciences, catalysts and nonlinear optics (e.g. Desiraju, 1995). Nevertheless, a bibliographical study on the organic monophosphates, and especially on the adduct monophosphate reveals that this kind of compounds are relatively very rare if compared with another types of phosphates (Zaccaro *et al.*, 1996).

In the atomic arrangement of the title compound (I), the asymmetric unit consists of three fundamentals entities, the H_2PO_4- anion, the H_3PO_4 molecule and the organic cation $C_7H_{10}N_+$ (Fig. 1). A view of the structure projected along the b direction (Fig. 2) shows that the inorganic entities are organized in layers developed around the *bc* plane. The organic cations are arranged in opposite direction along the *a* axis in the interlayer spacing to neutralize the negative charge of the inorganic layers. Inside each layer the H_2PO_4- anions form an inorganic chains parallel to b direction and situated at *Z* = 1/4 and *Z* = 3/4. The H_3PO_4 molecules are associated by strong hydrogen bonds to form a dimmer of formula $[H_6P_2O_8]$ centred at (0 1/2 0) and (0 0 1/2). The both entities are interconnected together *via* hydrogen bonds to form inorganic layer parallel to the *bc* plane (Fig. 2). In the two crystallographically independent phosphate groups, the P—O bonds are shorter than P—OH bonds (Table 1). The average values of P—O distances and O—P—O angles are 1,533 Å, 109,44° and 1,533 Å, 109,38°, respectively for $P(1)O_4$ and $P(2)O_4$ tetrahedra. These configurations are comparable to that observed elsewhere (Zaccaro *et al.*, 1996). The organic and inorganic species establish between them two types of hydrogen bonds. The first one is O—H···O, involving short contacts with H···O lengths ranging between 1,69 - 1,83 Å, connects the H_2PO_4- and H_3PO_4 entities to develop the inorganic layer parallel to *bc* plane. The second type is N—H···O, with H···O distances ranging from 1,91 Å to 2,18 Å, links the organic cations to the phosphoric layer. The pattern of hydrogen bonds participate with the electrostatic and van Der Waals interactions to the cohesion of the network. The atoms C1, C2, C3, C4, C5 and C6 of the anilinium ring of the title compound are coplanar and they form a conjugated plane with average deviation of 0.0013 Å. The C—C distances ranging from 1.374 (2) to 1.496 (3) Å agree with those observed in literature (Akriche & Rzaigui 2000).

Experimental

A solution of orthophosphoric acid (0.50 mmol in 30 ml of water) was added drop by drop to an ethanolic solution of 2-methylaniline (2.336 mmol in 5 ml). The so-obtained solution was slowly evaporated at room temperature, until colourless prisms of (I) formed.

Refinement

The H atoms were fixed geometrically and treated as riding with C—H = 0.93Å, N—H = 0.89 Å and O—H = 0.82 Å with U_{iso}(H) = 1.2 U_{eq}(carrier).

Figures

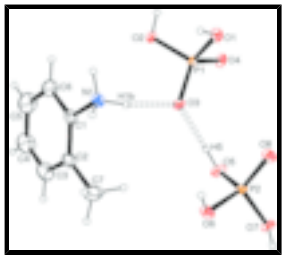

Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radius. Hydrogen bonds are represented as dashed lines.

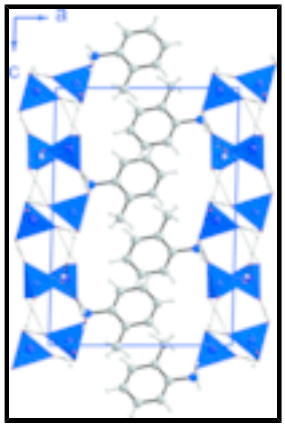

Fig. 2. *DIAMOND* (Brandenburg, 2005) Projection of (I) along the *b* axis.

2-Methylanilinium dihydrogen phosphate–phosphoric acid (1/1)

Crystal data

$C_7H_{10}N^+·H_2PO_4^-·H_3PO_4$	F_{000} = 632
M_r = 303.14	D_x = 1.525 Mg m^{-3}
Monoclinic, $P2_1/c$	Ag $K\alpha$ radiation λ = 0.56085 Å
Hall symbol: -P 2ybc	Cell parameters from 25 reflections
a = 10.8769 (10) Å	θ = 8–12º
b = 7.938 (4) Å	μ = 0.19 mm^{-1}
c = 15.302 (3) Å	T = 298 K
β = 91.57 (2)º	Prism, colorless
V = 1320.7 (7) Å^3	0.37 × 0.31 × 0.25 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{max} = 26.0º
Radiation source: fine-focus sealed tube	θ_{min} = 2.1º
T = 298 K	h = −16→16
Nonprofiled ω scans	k = 0→12
Absorption correction: none	l = 0→23
5416 measured reflections	2 standard reflections

5250 independent reflections
4134 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$

every 120 min
intensity decay: 18%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.092$
$S = 1.08$
5250 reflections
170 parameters
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.181P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
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}
P1	0.08064 (3)	0.43847 (3)	0.736601 (16)	0.02322 (6)
P2	0.10749 (3)	0.71819 (3)	0.986049 (17)	0.02487 (7)
O1	−0.06037 (8)	0.40074 (11)	0.74454 (6)	0.03314 (17)
H1	−0.0695	0.3079	0.7670	0.050*
O2	0.13778 (8)	0.28822 (10)	0.68641 (6)	0.03396 (18)
H2	0.0974	0.2708	0.6413	0.051*
O3	0.14542 (9)	0.44285 (11)	0.82411 (5)	0.03420 (18)
O4	0.08566 (9)	0.59919 (10)	0.68413 (6)	0.03335 (18)
O5	0.19612 (9)	0.70906 (12)	0.90923 (6)	0.0394 (2)
H5	0.1806	0.6250	0.8798	0.059*
O6	0.14555 (9)	0.58760 (11)	1.05701 (6)	0.0372 (2)
H6	0.1003	0.5052	1.0530	0.056*
O7	0.13831 (9)	0.89278 (10)	1.02544 (5)	0.03362 (18)
H7	0.1232	0.8928	1.0776	0.050*
O8	−0.02457 (8)	0.69700 (11)	0.95881 (6)	0.03445 (18)

N1	0.20745 (9)	0.11752 (14)	0.87628 (7)	0.0355 (2)
H1A	0.1698	0.0513	0.8370	0.053*
H1B	0.1808	0.2228	0.8695	0.053*
H1C	0.1910	0.0818	0.9298	0.053*
C1	0.34057 (12)	0.11198 (18)	0.86394 (10)	0.0400 (3)
C2	0.41777 (14)	0.1876 (2)	0.92552 (12)	0.0517 (4)
C3	0.54313 (16)	0.1826 (3)	0.90905 (19)	0.0797 (7)
H3C	0.5986	0.2305	0.9492	0.096*
C4	0.58628 (19)	0.1090 (4)	0.8354 (2)	0.0930 (8)
H4C	0.6702	0.1099	0.8252	0.112*
C5	0.5070 (2)	0.0340 (4)	0.7763 (2)	0.0930 (8)
H5C	0.5374	−0.0182	0.7269	0.112*
C6	0.38195 (18)	0.0357 (3)	0.78970 (14)	0.0643 (5)
H6C	0.3272	−0.0136	0.7496	0.077*
C7	0.3703 (2)	0.2703 (4)	1.00570 (16)	0.0795 (7)
H7A	0.3238	0.1902	1.0382	0.119*
H7B	0.3185	0.3634	0.9890	0.119*
H7C	0.4382	0.3104	1.0413	0.119*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.03254 (13)	0.01806 (11)	0.01906 (11)	0.00111 (9)	0.00062 (9)	−0.00078 (8)
P2	0.03360 (14)	0.02046 (11)	0.02043 (11)	−0.00449 (9)	−0.00143 (9)	0.00068 (9)
O1	0.0333 (4)	0.0282 (4)	0.0379 (4)	−0.0007 (3)	0.0019 (3)	0.0069 (3)
O2	0.0416 (5)	0.0282 (4)	0.0317 (4)	0.0095 (3)	−0.0053 (3)	−0.0105 (3)
O3	0.0498 (5)	0.0286 (4)	0.0238 (4)	−0.0003 (3)	−0.0071 (3)	−0.0040 (3)
O4	0.0491 (5)	0.0222 (3)	0.0292 (4)	0.0023 (3)	0.0101 (3)	0.0047 (3)
O5	0.0494 (5)	0.0385 (5)	0.0309 (4)	−0.0126 (4)	0.0104 (4)	−0.0106 (4)
O6	0.0437 (5)	0.0286 (4)	0.0387 (5)	−0.0069 (3)	−0.0126 (4)	0.0104 (3)
O7	0.0533 (5)	0.0225 (3)	0.0252 (4)	−0.0075 (3)	0.0034 (3)	−0.0037 (3)
O8	0.0366 (4)	0.0299 (4)	0.0363 (4)	−0.0056 (3)	−0.0082 (3)	0.0101 (3)
N1	0.0315 (5)	0.0339 (5)	0.0409 (5)	−0.0036 (4)	−0.0042 (4)	0.0062 (4)
C1	0.0318 (5)	0.0355 (6)	0.0526 (8)	0.0023 (5)	−0.0013 (5)	0.0065 (6)
C2	0.0360 (6)	0.0522 (9)	0.0662 (10)	0.0007 (6)	−0.0108 (6)	−0.0003 (8)
C3	0.0317 (7)	0.0912 (16)	0.1154 (19)	0.0004 (9)	−0.0107 (10)	−0.0069 (14)
C4	0.0366 (8)	0.123 (2)	0.120 (2)	0.0120 (11)	0.0082 (11)	−0.0074 (19)
C5	0.0630 (13)	0.113 (2)	0.105 (2)	0.0177 (13)	0.0272 (13)	−0.0215 (17)
C6	0.0528 (9)	0.0726 (12)	0.0677 (11)	0.0044 (9)	0.0066 (8)	−0.0128 (10)
C7	0.0610 (12)	0.1016 (18)	0.0752 (14)	−0.0020 (11)	−0.0123 (10)	−0.0313 (13)

Geometric parameters (Å, °)

P1—O3	1.4964 (9)	N1—H1C	0.8900
P1—O4	1.5092 (10)	C1—C6	1.374 (2)
P1—O2	1.5571 (9)	C1—C2	1.382 (2)
P1—O1	1.5707 (9)	C2—C3	1.394 (2)
P2—O8	1.4942 (9)	C2—C7	1.496 (3)
P2—O5	1.5422 (10)	C3—C4	1.365 (4)

P2—O7	1.5445 (10)	C3—H3C	0.9300
P2—O6	1.5493 (10)	C4—C5	1.368 (4)
O1—H1	0.8200	C4—H4C	0.9300
O2—H2	0.8200	C5—C6	1.381 (3)
O5—H5	0.8200	C5—H5C	0.9300
O6—H6	0.8200	C6—H6C	0.9300
O7—H7	0.8200	C7—H7A	0.9600
N1—C1	1.4659 (16)	C7—H7B	0.9600
N1—H1A	0.8900	C7—H7C	0.9600
N1—H1B	0.8900		
O3—P1—O4	115.69 (5)	C6—C1—N1	117.83 (14)
O3—P1—O2	105.94 (5)	C2—C1—N1	118.88 (14)
O4—P1—O2	111.37 (6)	C1—C2—C3	116.33 (18)
O3—P1—O1	111.84 (6)	C1—C2—C7	122.21 (15)
O4—P1—O1	104.60 (5)	C3—C2—C7	121.46 (18)
O2—P1—O1	107.21 (5)	C4—C3—C2	121.5 (2)
O8—P2—O5	113.47 (6)	C4—C3—H3C	119.3
O8—P2—O7	113.99 (6)	C2—C3—H3C	119.3
O5—P2—O7	101.89 (5)	C3—C4—C5	120.51 (19)
O8—P2—O6	110.89 (5)	C3—C4—H4C	119.7
O5—P2—O6	110.01 (6)	C5—C4—H4C	119.7
O7—P2—O6	106.02 (6)	C4—C5—C6	120.2 (2)
P1—O1—H1	109.5	C4—C5—H5C	119.9
P1—O2—H2	109.5	C6—C5—H5C	119.9
P2—O5—H5	109.5	C1—C6—C5	118.3 (2)
P2—O6—H6	109.5	C1—C6—H6C	120.9
P2—O7—H7	109.5	C5—C6—H6C	120.9
C1—N1—H1A	109.5	C2—C7—H7A	109.5
C1—N1—H1B	109.5	C2—C7—H7B	109.5
H1A—N1—H1B	109.5	H7A—C7—H7B	109.5
C1—N1—H1C	109.5	C2—C7—H7C	109.5
H1A—N1—H1C	109.5	H7A—C7—H7C	109.5
H1B—N1—H1C	109.5	H7B—C7—H7C	109.5
C6—C1—C2	123.26 (15)		
C6—C1—C2—C3	−0.3 (3)	C2—C3—C4—C5	−1.6 (5)
N1—C1—C2—C3	−178.19 (16)	C3—C4—C5—C6	1.6 (5)
C6—C1—C2—C7	179.8 (2)	C2—C1—C6—C5	0.3 (3)
N1—C1—C2—C7	1.9 (3)	N1—C1—C6—C5	178.2 (2)
C1—C2—C3—C4	0.9 (3)	C4—C5—C6—C1	−0.9 (4)
C7—C2—C3—C4	−179.1 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4^{i}	0.82	1.83	2.6483 (16)	178
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N1—H1A···O1^{i}	0.89	2.08	2.9627 (16)	172
N1—H1B···O3	0.89	1.91	2.7808 (19)	164
N1—H1C···O7^{iv}	0.89	2.18	3.0086 (15)	154

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+3/2; (ii) −*x*, −*y*+1, −*z*+2; (iii) *x*, −*y*+3/2, *z*+1/2; (iv) *x*, *y*−1, *z*.

Fig. 1

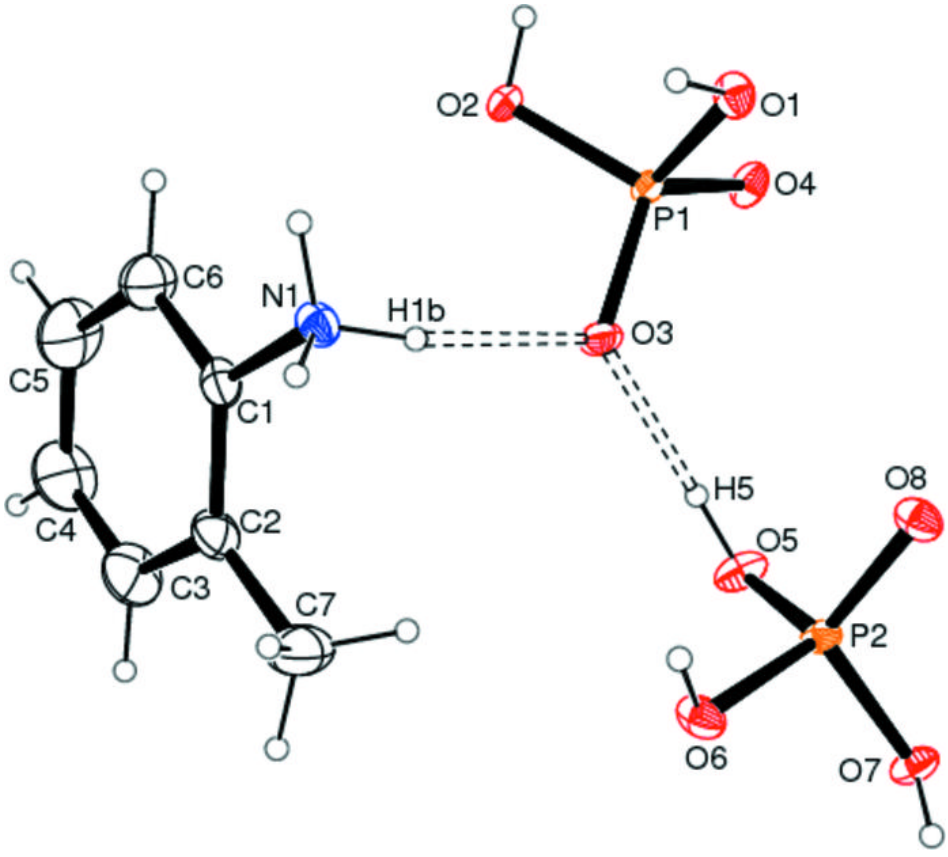

Fig. 2