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Benzyltrimethylammonium dihydrogen orthophosphate monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.051
wR factor = 0.143
Data-to-parameter ratio = 11.3

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

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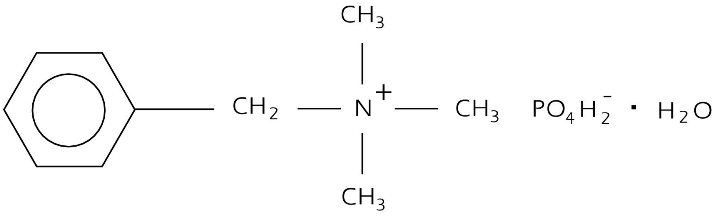
The title compound, $C_{10}H_{16}N^+\cdot H_2PO_4^-\cdot H_2O$, crystallizes in the centrosymmetric space group $P2_1/c$ with two independent molecules in the asymmetric unit. Therefore, nonlinear optical properties are absent. The crystal packing is governed by hydrogen bonds, so that the phosphate anions are linked head-to-tail, forming chains running parallel to the *a* direction. These chains in turn are interconnected by hydrogen bonds to water molecules, forming hydrogen-bonded molecular layers stacked parallel to the *ab* plane.

Comment

Inorganic salts of phosphoric acids form compounds that exhibit many interesting structural properties, such as phase transitions, physical properties like ferroelectricity, and optical nonlinear phenomena like second harmonic generation, as is the case for potassium dihydrogen orthophosphate (KDP; Rashkovich, 1991). As for organic salts, a general synthetic route to obtain organo dihydrogen phosphate crystals has been detailed in the literature (Masse & Zyss, 1991). In all these compounds, there is an inorganic hydrogen-bond sub-network formed by the dihydrogen orthophosphate anions. The organic cation benzyltrimethylammonium (hereafter BTA) is known to form with selenious acid a compound, benzyltrimethylammonium trihydrogen selenite, which exhibits structural phase transitions (de Matos Gomes *et al.*, 1995). No other crystal structures of BTA salts with other acid oxoanions have been reported in the literature. On the other hand, the structures of the related tetramethylammonium (Ohama *et al.*, 1987) and *N*-benzylmethylammonium (Elaoud *et al.*, 1998) dihydrogen orthophosphates have been reported.



(I)

In the search for new compounds with structural instabilities and ferroelectricity, the title compound, (I) (Fig. 1), was synthesized. The space group is centrosymmetric, with two formula units in the asymmetric unit, and therefore nonlinear optical properties are absent in this compound. Differential scanning calorimetry measurements performed from 93 to 673 K did not show the existence of any phase transition. At about 353 K there is loss of water, and melting occurs at about 513 K, followed by decomposition.

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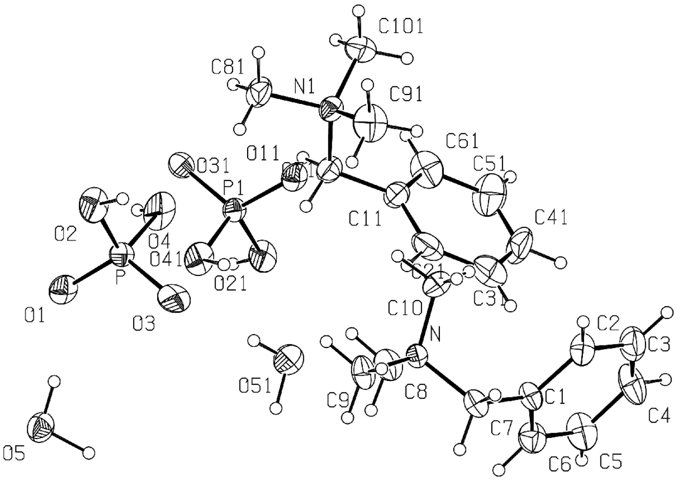

Figure 1
An *ORTEPII* plot (Johnson, 1976) of (I), showing 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

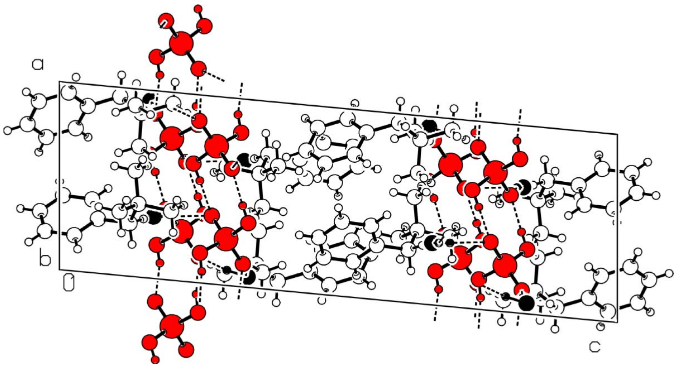

Figure 2
Molecular packing of (I), viewed along the *b* direction, showing the hydrogen bonds (dashed lines) between phosphate ions.

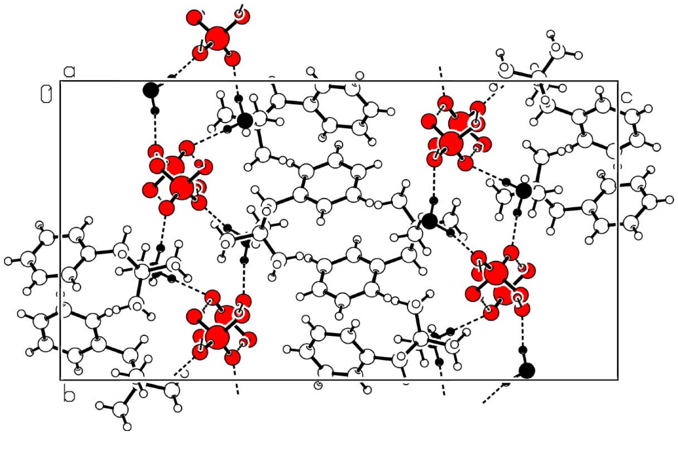

Figure 3
Molecular packing of (I), viewed along the *a* direction, showing the hydrogen bonds (dashed lines) involving water molecules.

As may be expected, the two P—O distances for the OH groups are significantly longer than the other two P—O distances. The bond lengths in both symmetry-independent BTA cations are very similar and also agree with previous work (de Matos Gomes *et al.*, 1995), whereas the bond angles show a larger range as a result of the intermolecular crystal packing forces. The most interesting crystallographic feature in these organic salts is the hydrogen-bond packing network. As in the case of 1,1,3,3-tetramethylguanidinium dihydrogen orthophosphate (Criado *et al.*, 2000), the phosphate anions are arranged in linear chains (Fig. 2). These chains parallel to the *a* direction are formed by the two phosphate ions in the asymmetric unit and all the translationally equivalent ions along the *a* direction. Each ion is connected by two hydrogen bonds to each neighbouring phosphate ion in the chain, so that alternate ions in the chain are related by a lattice translation *a* and adjacent ions are symmetrically-independent. In addition to this, linear chains related to each other by a screw axis are interconnected by two water molecules, forming four hydrogen bonds (Fig. 3), resulting in a crystal packing of hydrogen-bonded layers stacked parallel to the *ab* plane so that adjacent layers are related by an inversion centre and alternate layers are separated by a lattice period *c*.

Five C—H···O short contacts not depicted in the Figures have been found.

Experimental

The present compound was synthesized by mixing equimolar amounts of benzyltrimethylammonium hydroxide and phosphoric acid in a mixed solvent of water and methanol. The crystals were grown by slow evaporation and were of prismatic habit, colourless and transparent.

Crystal data

$C_{10}H_{16}N^+\cdot H_2PO_4^-\cdot H_2O$
$M_r = 265.24$
Monoclinic, $P2_1/c$
$a = 8.295$ (2) Å
$b = 13.178$ (7) Å
$c = 24.714$ (4) Å
$\beta = 95.412$ (1)°
$V = 2689.5$ (16) Å^3
$Z = 8$
$D_x = 1.310$ Mg m^{-3}
$D_m = 1.30$ Mg m^{-3}
D_m measured by flotation in bromobenzene and acetone
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7$–12°
$\mu = 0.21$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.48 × 0.40 × 0.28 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
4723 measured reflections
4723 independent reflections
3482 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 29$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.143$
$S = 1.01$
4723 reflections
419 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1215P)^2 + 0.1493P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.010$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P—O1	1.492 (2)	P1—O31	1.494 (2)
P—O3	1.492 (2)	P1—O11	1.494 (2)
P—O2	1.556 (2)	P1—O41	1.569 (2)
P—O4	1.560 (2)	P1—O21	1.571 (2)
N—C10	1.488 (4)	N1—C91	1.487 (4)
N—C8	1.490 (4)	N1—C81	1.504 (4)
N—C9	1.497 (4)	N1—C71	1.522 (4)
N—C7	1.524 (4)		
O1—P—O3	116.4 (1)	O31—P1—O11	117.9 (1)
O1—P—O2	108.2 (1)	O31—P1—O41	107.8 (1)
O3—P—O2	108.6 (1)	O11—P1—O41	109.7 (1)
O1—P—O4	109.6 (1)	O31—P1—O21	108.2 (1)
O3—P—O4	106.0 (2)	O11—P1—O21	106.5 (1)
O2—P—O4	107.7 (2)	O41—P1—O21	106.0 (2)
C10—N—C8	109.6 (3)	C101—N1—C91	109.3 (3)
C10—N—C9	108.1 (3)	C101—N1—C81	108.2 (3)
C8—N—C9	108.2 (3)	C91—N1—C81	108.8 (3)
C10—N—C7	111.7 (3)	C101—N1—C71	110.5 (3)
C8—N—C7	110.7 (2)	C91—N1—C71	112.2 (3)
C9—N—C7	108.4 (2)	C81—N1—C71	107.7 (2)
C1—C7—N	113.8 (2)	C11—C71—N1	115.6 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O1	0.80 (5)	2.02 (5)	2.807 (3)	168 (5)
O5—H5*B*···O11^{i}	0.86 (5)	2.03 (5)	2.870 (3)	170 (4)
O51—H51*A*···O31	0.79 (5)	2.05 (5)	2.826 (4)	177 (5)
O51—H51*B*···O3^{ii}	0.79 (5)	2.08 (5)	2.860 (4)	171 (5)
O2—H2···O31	0.82	1.82	2.629 (3)	168
O4—H4···O11^{iii}	0.83	1.86	2.566 (3)	143
O21—H21···O3	0.82	1.77	2.582 (3)	170
O41—H41···O1^{iv}	0.82	1.79	2.579 (3)	159
C8—H8*B*···O21^{iii}	0.90 (4)	2.43 (5)	3.311 (5)	168 (4)
C4—H4*A*···O31^{v}	0.99 (4)	2.41 (5)	3.388 (4)	173 (4)
C8—H8*C*···O2^{vi}	0.95 (5)	2.53 (5)	3.467 (5)	169 (4)
C81—H81*B*···O3^{ii}	0.95 (5)	2.43 (4)	3.372 (5)	174 (4)
C71—H71*B*···O5^{vii}	0.96 (4)	2.43 (3)	3.359 (4)	162 (3)

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

C-bound H atoms were refined freely [C—H = 0.79 (5)–1.06 (5) Å]. Water H atoms were also refined freely. H-atom bond lengths and angles in the phosphate ion were constrained in the refinement [O—H distances given in Table 2; $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)] so that only the torsion angles of the OH groups have been allowed to refine.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duissenberg, 1984) and *CELDIM* (Retting, 1989); data reduction: *XRAY76 System* (Stewart *et al.*, 1976); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *PARSTCIF* (Nardelli, 1991).

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