organic compounds

1,1,3,3-Tetramethylguanidinium dihydrogenorthophosphate

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In the title compound, $C_5H_{14}N_3^+ \cdot H_2PO_4^-$, the cation has a central guanidinium fragment with a planar geometry, as expected for a central Csp^2 atom with a small charge delocalization along the three C—N bonds. The crystal packing is governed by hydrogen bonds so that the phosphate anions are linked head to tail, forming chains running parallel to the c direction. These chains in turn are interconnected by hydrogen bonds to intermediate tetramethylguanidinium cations forming hydrogen-bonded molecular layers stacked parallel to the bc crystal planes.

Comment

Inorganic salts of phosphoric acids form compounds that exhibit a wealth of interesting physical properties such as ferroelectricity and non-linear optical phenomena like second harmonic generation; a classical example is potassium dihydrogen orthophosphate (KDP) (Rafhkovich, 1991). A general synthetic route to obtain organo-dihydrogen orthophosphate crystals has been detailed (Masse & Zyss, 1991). In all these compounds, there is an inorganic subnetwork formed by the dihydrogen orthophosphate anions $(H_2PO_4)_n$. When the organic species are strongly dipolar, the anion sublattice is

(I)
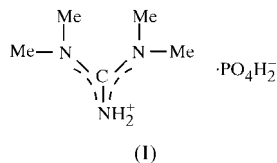
organized in a polar structure; examples are L-argininium dihydrogen orthophosphate monohydrate (Aoki et al., 1971), 2-amino-5-nitropyridinium dihydrogen orthophosphate (Kotler et al., 1992) and sarcosine dihydrogen orthophosphate (Averbuch-Pouchot et al., 1988). In the case of a weakly dipolar organic species such as glycine, the anion sublattice will organize in a nonpolar structure (Averbuch-Pouchot et al., 1988). As part of a project to study new compounds with potentially interesting optical and dielectric properties, we

have synthesized the title compound, (I). Similar to aminoguanidinium dihydrogen orthophosphate (Adams, 1977), we report here its crystal structure, as determined by single-crystal X-ray diffraction.

The compound crystallizes in a centrosymmetric space group; consequently, no non-linear optical effects are observed. Differential scanning calorimetry measurements performed from 93 to 673 K did not show any phase transition. The melting point occurs at about 493 K, followed by decomposition.

The geometry of the guanidinium group in (I) is planar, as expected for sp^2 hybridization of the central C atom (Fig. 1). The π delocalization along the three C—N bonds gives rise to C1—N2 [1.344 (1) Å] and C1—N3 [1.346 (1) Å] bond lengths larger than the value expected for a Csp^2══N bond (1.295 Å) and close to the expected value for a delocalized C══N double bond [1.339 (5) Å]. The C1—N1 bond length [1.320 (1) Å] is somewhat shorter and compares well with the average value for the guanidinium cation (1.321 Å) (Allen et al., 1987). The larger value for the C1—N2 and C1—N3 bond lengths must be ascribed to the methyl substitution which makes the three bonds non-equivalent. Indeed, simple molecular-orbital semiempirical calculations (extended Hückel) give different atomic charges on N1 (-0.376 e) and N2 and N3 (-0.590 e). As may be expected, the two P—O distances for the OH groups are significantly longer than the other two P—O distances.

The basis of the molecular engineering interest in these salts is the obtention of structures with potential physical properties as a result of the hydrogen-bond crystal network, which tends to reinforce the properties exhibited by the isolated molecule by arranging them as linear or layered molecular patterns.

In our case the hydrogen bonds also give rise to an interesting arrangement, which is best understood with the aid of the diagram corresponding to the crystal structure viewed perpendicular to the ab plane (Fig. 2). On one hand, each phosphate ion is connected by two hydrogen bonds to each phosphate ion related to it by a c glide plane with both positive and negative fractional c translations. Given that the central P atoms lie at a very close distance to the glide planes (0.32 Å), it results in approximately linear phosphate chains parallel to the c direction. On the other hand, each tetramethylguanidinium ion is hydrogen-bonded to two phosphate ions related to each other by an inversion centre and belonging to different chains, giving rise to a framework of molecules
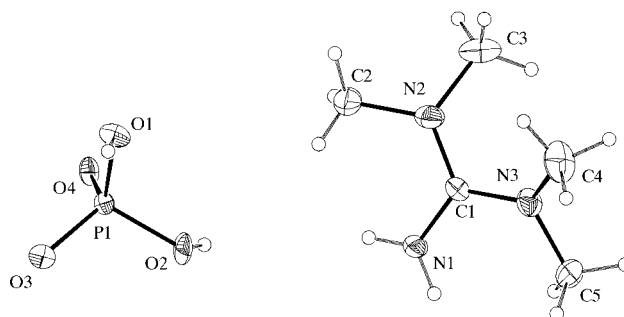
Figure 1
Structure of (I) showing 30% probability displacement ellipsoids.

connected by hydrogen bonds in the form of layers parallel to the *bc* crystal planes and stacked according to the *a* lattice translation period. Besides the above, two C—H···O contacts interrelating molecules within the same layer and not depicted in the diagram have been detected.
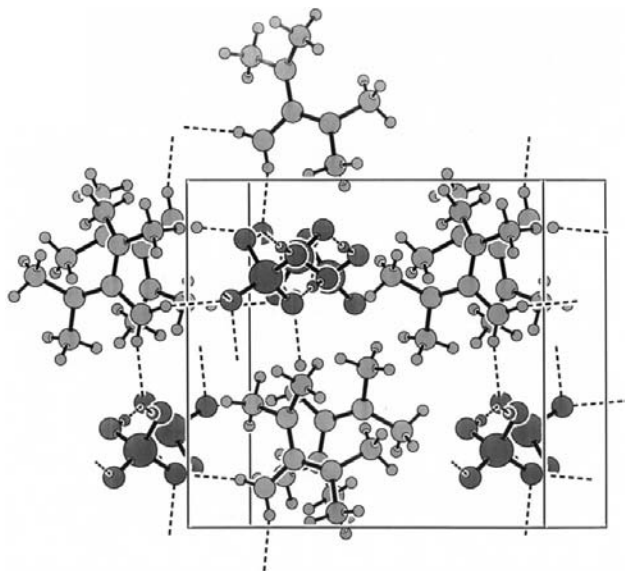
Figure 2
The molecular packing viewed along an axis perpendicular to the *ab* plane showing the hydrogen bonding.

Experimental

The title compound was prepared by mixing equimolar portions of two reagents: 1,1,3,3-tetramethylguanidine (99%) and phosphoric acid (85%) in a 1:1 solution of ethanol and water at room temperature. Good quality, colourless single crystals of prism habit were grown from the solution by slow evaporation, one of which was selected and used for the X-ray analysis.

Crystal data

$C_5H_{14}N_3^+·H_2PO_4^-$
$M_r = 213.18$
Monoclinic, $P2_1/c$
$a = 11.225$ (3) Å
$b = 10.951$ (1) Å
$c = 8.430$ (2) Å
$\beta = 103.50$ (1)°
$V = 1007.6$ (4) Å^3
$Z = 4$
$D_x = 1.405$ Mg m^{-3}
$D_m = 1.40$ Mg m^{-3}

D_m measured by flotation in bromobenzene and acetone
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7–12°$
$\mu = 0.264$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
$0.80 \times 0.50 \times 0.40$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
3777 measured reflections
3777 independent reflections
3257 reflections with $I > 2\sigma(I)$
$\theta_{max} = 32.96°$

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 16$
$l = -12 \rightarrow 12$
3 standard reflections
  frequency: 60 min
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.105$
$S = 1.080$
3777 reflections
124 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.1114P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—O4	1.4968 (7)	N3—C5	1.461 (2)
P1—O3	1.5148 (7)	N3—C4	1.458 (2)
P1—O1	1.5629 (8)	N2—C1	1.3447 (15)
P1—O2	1.5800 (8)	N2—C3	1.466 (2)
N1—C1	1.3198 (13)	N2—C2	1.455 (2)
N3—C1	1.3451 (14)		
O4—P1—O3	114.78 (5)	C5—N3—C4	114.50 (12)
O4—P1—O1	108.64 (5)	C1—N2—C3	121.02 (12)
O3—P1—O1	109.11 (4)	C1—N2—C2	121.27 (11)
O4—P1—O2	110.24 (4)	C3—N2—C2	115.34 (12)
O3—P1—O2	108.20 (5)	N1—C1—N2	120.78 (11)
O1—P1—O2	105.47 (5)	N1—C1—N3	120.22 (10)
C1—N3—C5	120.91 (10)	N2—C1—N3	119.01 (10)
C1—N3—C4	121.53 (12)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3	0.88	2.08	2.924 (1)	161
O2—H2···O3^i	0.84	1.79	2.616 (1)	167
O1—H1···O4^{ii}	0.84	1.71	2.541 (1)	169
N1—H1B···O3^{iii}	0.88	2.07	2.894 (1)	155
C5—H5B···O2^{iii}	0.98	2.56	3.521 (2)	167
C5—H5A···O2^{iv}	0.98	2.67	3.607 (2)	159

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

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *XRAY*76 (Stewart *et al.*, 1976); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1994); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *PARSTCIF* (Nardelli, 1991).

References

Adams, J. M. (1977). *Acta Cryst.* B**33**, 1513–1515.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Aoki, K., Nagano, K. & Iitaka, Y. (1971). *Acta Cryst.* B**27**, 11–23.
Averbuch-Pouchot, A. T., Durif, A. & Guitel, J. C. (1988). *Acta Cryst.* C**44**, 99–102.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Kotler, Z., Hierle, R., Josse, D., Zyss, J. & Masse, R. (1992). *J. Opt. Soc. Am.* B**9**, 534–547.
Masse, R. & Zyss, J. (1991). *Mol. Eng.* **1**, 141–152.
Nardelli, M. (1991). *PARSTCIF*. University of Parma, Italy.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Rafhkovich, L. N. (1991). *KDP-Family Single Crystals*. Bristol: IOP Publishing.
Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.
Spek, A. L. (1994). *PLATON*. University of Utrecht, The Netherlands.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY*76 *System*. Technical Report TR-446. Computer Science Center, University of Maryland, USA.