O(4)—N(2)	1.182 (6)	1.185 (5)
N(1)—C(1)	1.465 (4)	1.469 (4)
N(2)—C(3)	1.476 (6)	1.471 (4)
N(3)—N(4)	1.373 (5)	1.376 (3)
N(3)—C(6)	1.408 (4)	1.416 (3)
N(3)—C(7)	1.363 (4)	1.362 (4)
N(4)—C(10)	1.334 (5)	1.332 (4)
C(7)—C(8)	1.483 (4)	1.480 (6)
C(7)—C(9)	1.356 (6)	1.358 (5)
C(9)—C(10)	1.394 (4)	1.395 (6)
C(10)—C(11)	1.494 (5)	1.495 (5)
O(1)—N(1)—O(2)	123.9 (3)	124.1 (3)
O(2)—N(1)—C(1)	117.1 (3)	117.6 (3)
O(1)—N(1)—C(1)	119.0 (3)	118.3 (3)
O(3)—N(2)—O(4)	122.7 (5)	123.3 (4)
O(4)—N(2)—C(3)	118.3 (4)	119.0 (4)
O(3)—N(2)—C(3)	118.7 (4)	117.7 (4)
C(6)—N(3)—C(7)	128.4 (3)	128.0 (3)
N(4)—N(3)—C(7)	112.5 (3)	113.0 (2)
N(4)—N(3)—C(6)	119.0 (2)	118.9 (2)
N(3)—N(4)—C(10)	103.8 (3)	103.4 (3)
N(1)—C(1)—C(6)	121.9 (3)	122.2 (3)
N(1)—C(1)—C(2)	116.5 (3)	116.3 (3)
N(2)—C(3)—C(2)	117.9 (4)	118.0 (3)
N(2)—C(3)—C(4)	119.8 (3)	119.1 (3)
N(3)—C(6)—C(5)	119.5 (3)	119.3 (3)
N(3)—C(6)—C(1)	122.8 (3)	122.2 (3)
N(3)—C(7)—C(9)	105.5 (3)	105.0 (3)
N(3)—C(7)—C(8)	122.8 (3)	123.1 (3)
C(8)—C(7)—C(9)	131.6 (3)	131.8 (3)
C(7)—C(9)—C(10)	107.1 (4)	107.3 (3)
N(4)—C(10)—C(9)	111.1 (4)	111.2 (3)
C(9)—C(10)—C(11)	128.2 (3)	128.2 (3)
N(4)—C(10)—C(11)	120.6 (3)	120.5 (3)

The structure of the title compound was solved by direct methods using SHELXS86 (Sheldrick, 1985) and refined by full-matrix least squares using SHELX76 (Sheldrick, 1976). The H-atom positions were located from difference Fourier maps. The positional parameters of the non-H atoms were refined anisotropically, whereas the positional and isotropic displacement parameters, set equal to those of the corresponding attached C atoms, of the H atoms were included in the final cycles of refinement but were not refined. The geometrical calculations for the structure were carried out using PARST (Nardelli, 1983).

References

Fronczek, F. R., Parodi, F. J., Fischer, N. H., Hsieh, T. C.-Y. & Chang, B.-Y. (1989). Acta Cryst. C45, 2027–2028.
Galigne, J. L. & Falgueirettes, J. (1969). Acta Cryst. B25, 1637–1643.
Galigne, J. L. & Falgueirettes, J. (1970). Acta Cryst. B26, 380–386.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). Comput. Chem. 7, 95–98.
Potts, K. T. (1986). In Comprehensive Heterocyclic Chemistry, Vol. 5, part 4A. Oxford: Pergamon Press.
Sheldrick, G. M. (1976). SHELX76. Program for Crystal Structure Determination. University of Cambridge, England.
Sheldrick, G. M. (1985). SHELXS86. Program for the Solution of Crystal Structures. University of Göttingen, Germany.

3-Hydroxy-6-methyl-2-pyridylmethyl Isopropylphosphonate Sesquihydrate

S. Mani Naidu,[a] M. Krishnaiah[a]* and K. Sivakumar[b]

[a]Department of Physics, College of Engineering, S. V. University, Tirupati 517 502, India, and [b]Department of Physics, Anna University, Madras 600 025, India

Abstract

The title compound, $C_{10}H_{16}NO_4P.\frac{3}{2}H_2O$, contains a zwitterion with a negative charge on the unsubstituted phosphonate O atoms and a positive charge on the N atom of the pyridine ring. The distances between the P and the two unsubstituted phosphonate O atoms [1.503 (2) and 1.483 (2) Å] lie between P—O single- and double-bond distances. The bond angle at the P atom between these O atoms [116.4 (1)°] is larger than the other O—P—O angles. Hydrogen bonds link the unsubstituted phosphonate O atoms through water molecules to the pyridyl N atoms of neighbouring molecules. The presence of the H atom on the N atom of the pyridine ring is associated with a large C—N—C bond angle [124.6 (2)°].

Comment

Organic phosphates are the components of many biologically important molecules, such as nucleic acids, enzymes and vitamins, performing important biochemical functions, such as participation in genetic processes and catalyzed metabolic reactions. This has prompted numerous structural studies of which the present study of 3-hydroxy-6-methyl-2-pyridylmethyl isopropylphosphonate sesquihydrate, (I), is one.

(I)
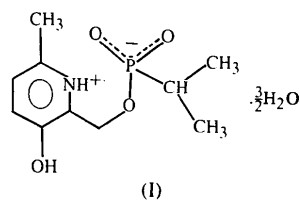
We find that the P—O(1) bond [1.601 (2) Å] is longer than the P—O(2) and P—O(3) bonds [1.503 (2) and 1.483 (2) Å, respectively], which is in agreement with the proposals of Cruickshank (1961) for monoionic phosphates, i.e. P—OC > P—OH > P—O$^{\frac{1}{2}-}$, and is also seen in other phosphate structures (Reddy & Viswamitra, 1975; Emerson & Sundaralingam, 1980).

The presence of an H atom on the pyridine N atom was indicated by difference Fourier synthesis and the

large value of the C(2)—N—C(6) angle [124.6(2)°] supports this assignment. Singh (1965) has shown that the presence of the extra annular H atom on the N atom in a six-membered ring is always associated with an endocyclic bond angle in the range 125±3° at the N atom.
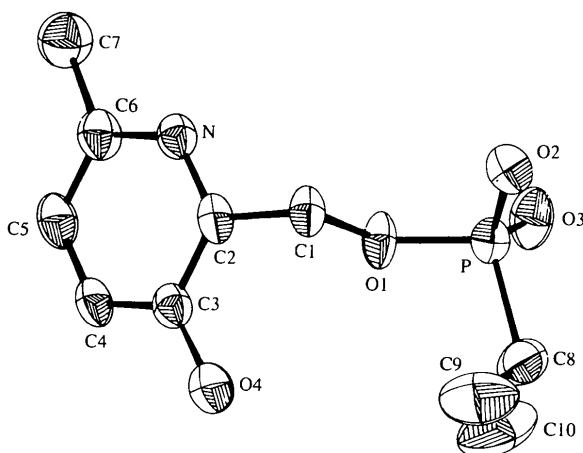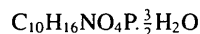

Fig. 1. An *ORTEP*II view (Johnson, 1976) of the zwitterion showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title compound was synthesized by Dr C. D. Reddy, Department of Chemistry, College of Engineering, S. V. University, Tirupati. To a stirred solution of 3-hydroxy-6-methyl-2-pyridinemethanol and triethylamine in a mixture of dry benzene and pyridine at room temperature, was added dropwise a solution of isopropylphosphonic acid dichloride in dry benzene. The temperature was gradually raised to 323–333 K with stirring until the reaction was complete. The triethylamine hydrochloride salt was removed by filtration and the solvent was evaporated under reduced pressure. The resulting product was washed with water and recrystallized from methanol. This was expected to be 2-isopropyl-6-methyl-4*H*-1,3,2-dioxaphosphorino[5,4-*b*]pyridine 2-oxide but the X-ray crystallographic analysis showed it to be the title compound, (I). The density D_m was measured by flotation in KI solution.

Crystal data

$C_{10}H_{16}NO_4P.\frac{3}{2}H_2O$
$M_r = 272.24$
Monoclinic
$C2/c$
$a = 22.516(5)$ Å
$b = 6.937(1)$ Å
$c = 17.469(4)$ Å
$\beta = 101.51(2)°$
$V = 2673.7(9)$ Å^3
$Z = 8$
$D_x = 1.351$ Mg m^{-3}
$D_m = 1.36$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 22.5–27.5°$
$\mu = 1.98$ mm^{-1}
$T = 298$ K
Needle
$0.5 \times 0.4 \times 0.3$ mm
Colourless, transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2516 measured reflections
2516 independent reflections
2351 observed reflections
[$I > 3\sigma(I)$]

$\theta_{max} = 70°$
$h = -27 \rightarrow 27$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 21$
1 standard reflection monitored every 100 reflections
intensity decay: <3%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.068$
$S = 1.87$
2351 reflections
162 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.034F_o^2]$

$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrich, 1976) and *SHELXS*86 (Sheldrick, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
P	0.3829	0.1662(1)	0.2184	2.66(2)
O(1)	0.4209(1)	0.1751(2)	0.1502(1)	3.35(3)
O(2)	0.4010(1)	0.3339(2)	0.2725(1)	3.27(3)
O(3)	0.3944(1)	-0.0286(2)	0.2532(1)	4.31(4)
O(4)	0.3907(1)	0.3130(2)	-0.0311(1)	3.73(4)
N	0.5393(1)	0.2703(2)	0.0846(1)	2.76(3)
C(1)	0.4462(1)	0.3516(2)	0.1289(1)	2.92(4)
C(2)	0.4795(1)	0.3023(2)	0.0651(1)	2.69(4)
C(3)	0.4500(1)	0.2803(2)	-0.0124(1)	2.81(4)
C(4)	0.4849(1)	0.2253(2)	-0.0664(1)	3.23(5)
C(5)	0.5457(1)	0.1960(2)	-0.0440(1)	3.18(4)
C(6)	0.5742(1)	0.2192(2)	0.0342(1)	3.09(4)
C(7)	0.6402(1)	0.1910(3)	0.0636(1)	4.37(6)
C(8)	0.3044(1)	0.1869(3)	0.1713(1)	4.26(5)
C(9)	0.2894(1)	0.3828(5)	0.1332(2)	7.01(9)
C(10)	0.2854(1)	0.0304(6)	0.1119(2)	8.54(12)
O(W1)	0.3527(1)	-0.3326(2)	0.3200(1)	3.65(4)
O(W2)	1/2	3/4	1/4	4.55(6)

Table 2. *Selected geometric parameters (Å, °)*

P—O(1)	1.601(2)	P—O(2)	1.503(2)
P—O(3)	1.483(2)	P—C(8)	1.800(2)
O(1)—C(1)	1.431(2)	O(4)—C(3)	1.329(3)
N—C(2)	1.340(3)	N—C(6)	1.340(3)
C(1)—C(2)	1.502(3)	C(2)—C(3)	1.392(2)
C(3)—C(4)	1.396(3)	C(4)—C(5)	1.362(3)
C(5)—C(6)	1.398(2)	C(6)—C(7)	1.485(3)
C(8)—C(10)	1.504(4)	C(8)—C(9)	1.521(4)
O(3)—P—C(8)	109.6(1)	O(2)—P—C(8)	110.1(1)
O(2)—P—O(3)	116.4(1)	O(1)—P—C(8)	106.2(1)
O(1)—P—O(3)	105.4(1)	O(1)—P—O(2)	108.7(1)
P—O(1)—C(1)	121.8(1)	P—C(8)—C(9)	112.5(2)
C(2)—N—C(6)	124.6(2)	O(1)—C(1)—C(2)	106.4(1)
N—C(2)—C(1)	118.3(2)	N—C(6)—C(7)	119.0(2)
C(1)—C(2)—C(3)	122.3(2)	N—C(2)—C(3)	119.3(2)
O(4)—C(3)—C(2)	118.8(2)	C(2)—C(3)—C(4)	117.6(2)

$C_{10}H_{16}NO_4P.\frac{3}{2}H_2O$

O(4)—C(3)—C(4)	123.6 (2)	P—C(8)—C(10)	112.1 (2)
C(3)—C(4)—C(5)	121.1 (2)	C(4)—C(5)—C(6)	120.2 (2)
N—C(6)—C(5)	117.2 (2)	C(9)—C(8)—C(10)	109.6 (2)
C(5)—C(6)—C(7)	123.7 (2)		

Hydrogen-bond distances

D—H···A	D···A	D—H···A	D···A
O(W1)···O(3)	2.670 (2)	N···O(2$^{\mathrm{iii}}$)	2.626 (2)
O(4)···O(W1$^{\mathrm{i}}$)	2.575 (2)	O(W1)···O(2$^{\mathrm{iv}}$)	2.754 (2)
O(W2)···O(3$^{\mathrm{ii}}$)	2.840 (2)	O(W2)···O(3$^{\mathrm{v}}$)	2.840 (2)

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

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). The positions of the H atoms were found from a difference Fourier map and their isotropic displacement parameters were set equal to those of their corresponding attached C atoms. All geometrical calculations were carried out using *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data, torsion angles and intermolecular contact distances less than 3.75 Å, together with a unit-cell packing diagram, have been deposited with the IUCr (Reference: HA1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cruickshank, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
Emerson, J. & Sundaralingam, M. (1980). *Acta Cryst.* B36, 1510–1513.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.
Reddy, B. S. & Viswamitra, M. A. (1975). *Acta Cryst.* B31, 19–26.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination.* University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Singh, C. (1965). *Acta Cryst.* 19, 861–864.