Acta Cryst. (1999). C**55**, 1929–1930

4-(1*H*,3*H*$^+$-1,3-Benzimidazol-2-ylio)pyridine *N*-oxide dihydrogenphosphate monohydrate

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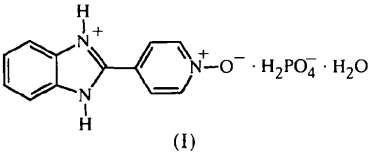
(*Received 14 May 1999; accepted 26 July 1999*)

Abstract

The title structure, $C_{12}H_{10}N_3O^+\cdot H_2PO_4^-\cdot H_2O$, is composed of alternate layers of organic cations and layers containing dimeric hydrogen-bonded anions and water molecules. There is an extensive network of hydrogen bonding within the anion–water layer extending to the electronegative atoms of the organic cations.

Comment

There is considerable interest in novel and efficient non-linear optical materials because of their potential use in devices used in the telecommunications, optical computing, optical storage and optical information processing industries (Williams, 1984; Chemla & Zyss, 1987; Long, 1995; Tian *et al.*, 1997). As part of our research in this area (Niu *et al.*, 1996; Liu *et al.*, 1999), we report here the structure of 4-(1*H*,3*H*$^+$-1,3-benzimidazol-2-ylio)pyridine *N*-oxide dihydrogenphosphate monohydrate, (I).



(I)

The crystal structure of (I) (Fig. 1) is composed of alternate layers of organic cations and layers containing anions and water molecules oriented parallel to (001) (Fig. 2). The organic cations are virtually planar, with the largest and mean deviations from the best plane being *ca* 0.10 and 0.05 Å, respectively. It has been suggested that extensive planar organic cations are more likely to show large hyperpolarizability (Chemla & Zyss, 1987).

There is an extensive network of hydrogen bonding within the anion–water layer extending to the electronegative atoms of the organic cations (Fig. 2 and Table 2). The dihydrogenphosphate anions are

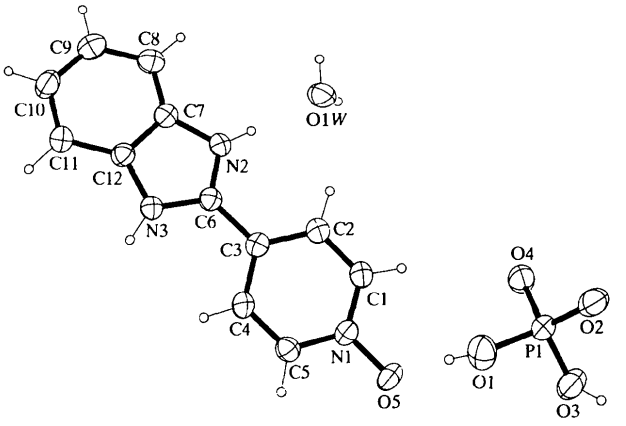


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

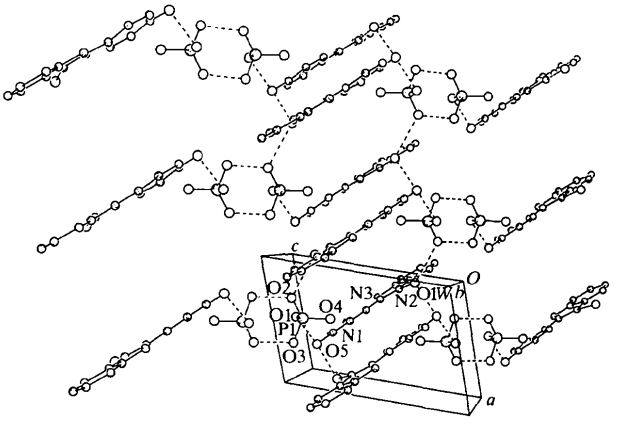


Fig. 2. The hydrogen-bonding scheme showing the layered structure. H atoms have been omitting for clarity.

hydrogen-bonded centrosymmetric dimers centred on $\bar{1}10$. This centrosymmetric motif induces a centrosymmetric arrangement of hydrogen-bonded cations and water molecules around it, thus possibly leading to crystallization in a centrosymmetric space group and the lack of an SHG (second harmonic generation) response from the crystal.

Experimental

The title salt was prepared by a similar method to that reported by Alcalde *et al.* (1991, 1992). In a dry N_2-filled three-necked flask fitted with stirrer, 1,2-diaminobenzene (5 mmol) and 4-pyridinecarboxylic acid (5 mmol) were suspended in polyphosphoric acid (PPA) (20 ml), and this suspension was heated in a bath at 453 K for 2 h. The cooled mixture was poured into ice water (50 ml) and the resulting solution was then neutralized to pH 9 with 25% NH_4OH. The precipitated product was filtered and washed with water. Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a 2 mol dm^{-3} phosphoric acid/water solution in air.

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Crystal data

$C_{12}H_{10}N_3O^+\cdot H_2PO_4^-\cdot H_2O$
M_r = 327.23
Triclinic
$P\overline{1}$
a = 7.503 (8) Å
b = 9.702 (5) Å
c = 10.501 (3) Å
α = 93.93 (4)°
β = 103.99 (3)°
γ = 107.26 (7)°
V = 700.1 (8) Å^3
Z = 2
D_x = 1.552 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 41 reflections
θ = 4.90–12.74°
μ = 0.232 mm^{-1}
T = 293 (2) K
Block
0.40 × 0.30 × 0.30 mm
Colourless

Data collection

Siemens $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3084 measured reflections
2467 independent reflections
2177 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

θ_{max} = 25°
$h = -1 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections
every 97 reflections
intensity decay: 5.17%

Refinement

Refinement on F^2
$R(F)$ = 0.033
$wR(F^2)$ = 0.089
S = 1.086
2467 reflections
256 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.2386P]$ where $P = F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.076 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

P1—O2	1.497 (2)	N1—C5	1.351 (2)
P1—O4	1.5318 (14)	N2—C6	1.344 (2)
P1—O1	1.551 (2)	N2—C7	1.381 (2)
P1—O3	1.552 (2)	N3—C6	1.337 (2)
O5—N1	1.332 (2)	N3—C12	1.381 (2)
N1—C1	1.344 (2)		
O2—P1—O4	114.30 (9)	O5—N1—C1	119.9 (2)
O2—P1—O1	108.69 (10)	O5—N1—C5	118.9 (2)
O4—P1—O1	107.70 (9)	C1—N1—C5	121.2 (2)
O2—P1—O3	111.32 (10)	N1—C1—C2	120.4 (2)
O4—P1—O3	106.16 (10)	C1—C2—C3	120.1 (2)
O1—P1—O3	108.46 (10)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O5	0.89 (4)	1.67 (4)	2.563 (3)	176 (3)
N2—H2N···O1W	0.83 (2)	1.89 (3)	2.717 (3)	173 (2)
O3—H3O···O2^{i}	0.77 (3)	1.80 (3)	2.565 (2)	173 (3)
O1W—H1WA···O5^{ii}	0.83 (3)	1.97 (3)	2.800 (2)	174 (3)
O1W—H1WB···O2^{iii}	0.83 (3)	1.91 (3)	2.742 (3)	175 (4)
N3—H4O···O4^{iv}	0.87 (3)	1.69 (3)	2.555 (2)	168 (3)

Symmetry codes: (i) $1-x, 2-y, 2-z$; (ii) $1-x, 1-y, 1-z$; (iii) $-x, 1-y, 1-z$; (iv) $x, y-1, z$.

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Refined C—H distances are in the range 0.90 (2)–0.98 (2) Å.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1261). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1930–1932

Acetonyldichloro[(*Z*)-2-chloro-1-methyl-2-phenylethenyl]tellurium(IV)

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(*Received 11 June 1999; accepted 6 July 1999*)

Abstract

The primary geometry about the Te^{IV} atom in the title compound, $C_{12}H_{13}Cl_3OTe$ or $[TeCl_2(C_9H_8Cl)(C_3H_5O)]$, is a pseudo-trigonal-bipyramidal arrangement with the