

# The betainic form of (imidazol-2-yl)-phenylphosphinic acid hydrate

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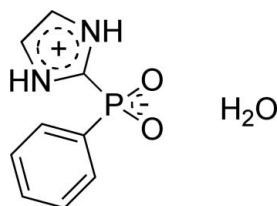
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Key indicators: single-crystal X-ray study;  $T = 223$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.092; data-to-parameter ratio = 14.0.

Single crystals of the title compound, (imidazolium-2-yl)-phenylphosphinate monohydrate,  $\text{C}_9\text{H}_9\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}$ , were obtained from methanol/water after deprotection and oxidation of bis(1-diethoxymethylimidazol-2-yl)phenylphosphane. In the structure, several  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{P}-\text{O} \cdots \text{H}-\text{O}$  hydrogen bonds are found.  $\pi-\pi$  interactions between the protonated imidazolyl rings [centroid-centroid distance =  $3.977(2)$  Å] help to establish the crystal packing. The hydrate water molecule builds hydrogen bridges to three molecules of the phosphinic acid by the O and both H atoms.

## Related literature

For structures of related imidazolyl phosphinic acids, see: Ball *et al.* (1984); Britten *et al.* (1993). For the chemistry of imidazolyl phosphanes, see: Enders *et al.* (2004); Kimblin *et al.* (1996a,b, 2000a,b); Kunz *et al.* (2003).



## Experimental

### Crystal data

$\text{C}_9\text{H}_9\text{N}_2\text{O}_2 \cdot \text{P} \cdot \text{H}_2\text{O}$   
 $M_r = 226.17$

Monoclinic,  $P2_1/n$   
 $a = 8.5890(6)$  Å

$b = 12.1091(7)$  Å  
 $c = 10.9534(7)$  Å  
 $\beta = 111.766(7)^\circ$   
 $V = 1057.99(12)$  Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>  
 $T = 223$  K  
 $0.2 \times 0.2 \times 0.2$  mm

### Data collection

Stoe IPDS diffractometer  
14882 measured reflections  
2069 independent reflections

1606 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.052$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.092$   
 $S = 0.93$   
2069 reflections  
148 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.16$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1} \cdots \text{O1}^{\text{i}}$	0.87	1.80	2.6302 (19)	160
$\text{N2}-\text{H2} \cdots \text{O3}^{\text{ii}}$	0.91 (2)	1.78 (2)	2.684 (2)	168 (2)
$\text{O3}-\text{H3} \cdots \text{O2}$	0.83 (3)	1.94 (3)	2.773 (2)	177 (3)
$\text{O3}-\text{H4} \cdots \text{O2}^{\text{iii}}$	0.79 (3)	2.00 (3)	2.777 (2)	164 (3)

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

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

We thank Ms E. Hammes and Dr M. Schilling for technical assistance.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2181).

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**supplementary materials**

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## The betainic form of (imidazol-2-yl)phenylphosphinic acid hydrate

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### Comment

Imidazolphosphanes of the type  $\text{PPh}_{3-n}(\text{im})_n$  (im = imidazol-2-yl) can resemble the chemistry of pyridylphosphanes  $\text{PPh}_{3-n}(2\text{-py})_n$  (pyridin-2-yl). In addition, imidazolylphosphanes can not only act as neutral polydentate ligands but due to their N—H functionalities act as (poly)anionic ligands, e.g. a tris(lithium) salt of tris(imidazol-2-yl)phosphane has been described (Enders *et al.*, 2004). Also, tris(imidazolyl)phosphanes and their oxides were used to mimic the tris(histidine) motif found in many metalloenzymes (Kimblin *et al.* 1996a,b, 2000a,b). The use of imidazol-2-ylphosphanes is limited due to degradation, e.g. oxidative hydrolysis. Britten reported upon the attempted synthesis of tris(imidazol-2-yl)-phosphane. They yielded unexpectedly the bis(imidazol-2-yl)-phosphinic acid, presumably due to oxidation of the phosphane and subsequent hydrolysis (Britten *et al.*, 1993). Brown reported that the catalytic activity of a catalyst formed by zinc chloride and bis(4,5-diisopropylimidazol-2-yl)imidazol-2-ylphosphane decreased due to formation of a zinc complex of bis(4,5-diisopropylimidazol-2-yl)phosphinic acid as degradation product (Ball *et al.*, 1984). Here we report that the oxidation of bis(imidazol-2-yl)phosphane using  $\text{H}_2\text{O}_2$  in methanol did not yield the corresponding phosphane oxide, too. Upon oxidation in the presence of water, hydrolysis occurred to imidazol-2-yl phenylphosphinic acid.

The molecular structure of the title compound is shown in Figure 1. In the crystal structure of the title compound the molecules are connected into chains via N—H $\cdots$ O—P hydrogen bonding between the N—H H atom of the protonated imidazolyl ring and the O atom of the  $\text{PO}_2$  group (Figure 2 and Table 1). These chains are further connected by N—H $\cdots$ O and O—H $\cdots$ O hydrogen bonding to the water molecules. Each two water molecules and two symmetry related molecules of the title compounds forms 8-membered hydrogen bonded rings that are located on centres of inversion. Additionally to the hydrogen bonding network, in the solid state packing a pairwise  $\pi$ - $\pi$  stacking of imidazolyl rings with a centroid distance of 3.977 Å is observed (Figure 3).

### Experimental

To a solution of 1-diethoxy-2-isopropylimidazole (Kunz *et al.*, 2003) in diethyl ether a solution of *tert.*-BuLi in hexane (1.5 M, 1.1 equivalents) is added dropwise at  $-78^\circ\text{C}$ . After the solution was stirred for 30 min at  $-78^\circ\text{C}$  and 30 min at room temperature the temperature is lowered again to  $-78^\circ\text{C}$  and half an equivalent of dichlorophenylphosphane in diethyl ether (20 ml) is added drop-wise. After the mixture was stirred over night conc. ammonia was added, the phases were separated and the organic layer washed with bidest. water (3 x 100 ml). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removal of the volatiles in vacuo the protected (imidazolyl)phosphane was obtained. After deprotection in an acetone-water mixture (10:1) perhydrol was added. The product precipitated as white solid which was collected by filtration, washed with acetone and diethyl ether and dried in vacuo. Single crystals were grown from a methanol / water solution.  $^1\text{H}$  NMR (200 MHz,  $[\text{D}_4]$ methanol/ $\text{D}_2\text{O}$ ):  $\delta = 7.37$  (d, 2H,  $J_{\text{PH}} = 1.5$  Hz,  $\text{H}_{\text{im}}$ ), 7.4 – 7.6 (m, 3 H, Ph), 7.85 – 8.0 (m, 2H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $[\text{D}_4]$ methanol/ $\text{D}_2\text{O}$ ):  $\delta = 3$  ppm.  $\text{C}_9\text{H}_9\text{N}_2\text{O}_2\text{P}\cdot\text{H}_2\text{O}$  (214.16): calc. C 47.8 H 4.9 N 12.4, found C 47.2 H 4.9 N 12.1.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker DRX 200 spectrometer. The  $^1\text{H}$  NMR

## supplementary materials

spectra were calibrated against the residual proton signals of the solvents as internal references ([D<sub>4</sub>]methanol:  $\delta = 5.84$  ppm) while the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were referenced to external 85 % H<sub>3</sub>PO<sub>4</sub>.

### Refinement

Appropriate positions of all H atoms were found in difference map. The C—H atoms and the H atom of N1 were positioned with idealized geometry and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$ . For the O—H H atoms and the H atom at N2 positional and isotropic displacement parameters were refined.

### Figures

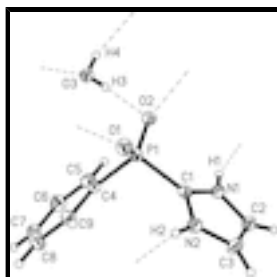


Fig. 1. The components of the title compound with their hydrogen bond environment. Hydrogen atoms are drawn with an arbitrary radius and displacement ellipsoids at the 30% probability level. Dashed lines indicate hydrogen bonding establishing a three dimensional network.

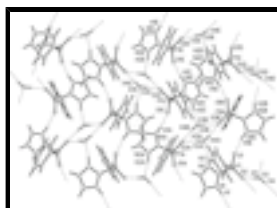


Fig. 2. Diagram showing the supramolecular association of the betainic acid and water molecules of **I** in layers perpendicular to  $[-1\ 0\ 1]$ ; symmetry codes: (A)  $x + 1/2, y - 1/2, z - 3/2$ ; (B)  $x + 1/2, -y + 3/2, z + 1/2$  (C)  $-x + 1, -y + 1, -z + 2$ ; (D)  $x + 1, y, z + 1$ ; (E)  $-x + 3/2, y - 1/2, -z + 5/2$ ; the atoms of the unlabeled left part of the figure are generated by translation along  $[0\ 0\ -1]$ .

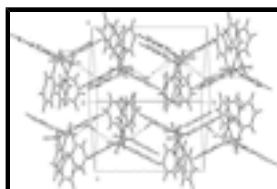


Fig. 3. Packing diagram, view along  $[1\ 0\ -1]$ , showing the arrangement of layers perpendicular to  $[-1\ 0\ 1]$

### (imidazolium-2-yl)phenylphosphinate monohydrate

#### Crystal data

$\text{C}_9\text{H}_9\text{N}_2\text{O}_2\text{P}\cdot\text{H}_2\text{O}$

$M_r = 226.17$

Monoclinic,  $P2_1/n$

$a = 8.5890$  (6) Å

$b = 12.1091$  (7) Å

$c = 10.9534$  (7) Å

$\beta = 111.766$  (7)°

$V = 1057.99$  (12) Å<sup>3</sup>

$Z = 4$

$F(000) = 472$

$D_x = 1.420$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8000 reflections

$\theta = 2.6\text{--}26.1^\circ$

$\mu = 0.25$  mm<sup>-1</sup>

$T = 223$  K

Isometric, colourless

$0.2 \times 0.2 \times 0.2$  mm

*Data collection*

Stoe IPDS diffractometer	1606 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube graphite	$R_{\text{int}} = 0.052$
Detector resolution: 6.67 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 26.1^\circ$ , $\theta_{\text{min}} = 2.6^\circ$
$\varphi$ -scans	$h = -10 \rightarrow 10$
14882 measured reflections	$k = -14 \rightarrow 14$
2069 independent reflections	$l = -13 \rightarrow 13$

*Refinement*

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.092$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.93$	$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2]$
2069 reflections	where $P = (F_o^2 + 2F_c^2)/3$
148 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.21068 (5)	0.75986 (4)	0.66209 (4)	0.02580 (15)
O1	0.38922 (15)	0.77558 (11)	0.74699 (13)	0.0357 (3)
O2	0.11462 (16)	0.84520 (10)	0.56559 (13)	0.0348 (3)
O3	-0.03925 (18)	1.01453 (13)	0.64926 (14)	0.0353 (3)
H3	0.007 (3)	0.965 (2)	0.622 (3)	0.054 (7)*
H4	-0.068 (3)	1.063 (3)	0.596 (3)	0.061 (8)*
N1	0.11416 (18)	0.61686 (12)	0.44158 (15)	0.0296 (3)

## supplementary materials

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H1	0.0343	0.6596	0.3921	0.044*
N2	0.3181 (2)	0.55296 (12)	0.60673 (16)	0.0329 (4)
H2	0.399 (3)	0.5492 (17)	0.689 (2)	0.037 (6)*
C1	0.2123 (2)	0.63787 (14)	0.56488 (18)	0.0269 (4)
C2	0.1578 (3)	0.51769 (16)	0.4043 (2)	0.0383 (5)
H10	0.1080	0.4839	0.3216	0.057*
C3	0.2853 (3)	0.47751 (16)	0.5081 (2)	0.0403 (5)
H11	0.3412	0.4101	0.5119	0.060*
C4	0.0927 (2)	0.71894 (14)	0.76010 (18)	0.0276 (4)
C5	-0.0757 (2)	0.74606 (15)	0.7218 (2)	0.0346 (4)
H5	-0.1292	0.7856	0.6435	0.052*
C6	-0.1654 (2)	0.71519 (18)	0.7985 (2)	0.0430 (5)
H6	-0.2793	0.7341	0.7726	0.064*
C7	-0.0874 (3)	0.65688 (18)	0.9125 (2)	0.0436 (5)
H7	-0.1482	0.6361	0.9646	0.065*
C8	0.0794 (3)	0.62866 (18)	0.9510 (2)	0.0428 (5)
H8	0.1316	0.5883	1.0289	0.064*
C9	0.1702 (2)	0.65964 (17)	0.87531 (19)	0.0356 (4)
H9	0.2841	0.6406	0.9018	0.053*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
P1	0.0274 (2)	0.0255 (2)	0.0236 (3)	-0.00120 (16)	0.00835 (18)	-0.00096 (18)
O1	0.0315 (7)	0.0423 (7)	0.0312 (8)	-0.0076 (5)	0.0094 (6)	-0.0054 (6)
O2	0.0456 (7)	0.0294 (6)	0.0305 (8)	0.0057 (5)	0.0154 (6)	0.0035 (5)
O3	0.0428 (8)	0.0301 (7)	0.0295 (8)	0.0019 (6)	0.0092 (6)	-0.0007 (6)
N1	0.0308 (8)	0.0275 (7)	0.0265 (8)	0.0012 (6)	0.0060 (6)	0.0000 (6)
N2	0.0359 (8)	0.0303 (8)	0.0280 (9)	0.0054 (6)	0.0067 (7)	0.0014 (7)
C1	0.0259 (8)	0.0270 (9)	0.0263 (10)	0.0004 (6)	0.0080 (7)	0.0029 (7)
C2	0.0490 (11)	0.0325 (9)	0.0296 (10)	-0.0005 (8)	0.0104 (9)	-0.0088 (8)
C3	0.0495 (11)	0.0293 (10)	0.0380 (12)	0.0088 (8)	0.0116 (9)	-0.0036 (8)
C4	0.0310 (9)	0.0259 (8)	0.0260 (10)	-0.0017 (6)	0.0108 (7)	-0.0034 (7)
C5	0.0321 (9)	0.0321 (9)	0.0387 (11)	0.0035 (7)	0.0122 (8)	0.0000 (8)
C6	0.0351 (10)	0.0423 (11)	0.0571 (14)	-0.0004 (8)	0.0236 (10)	-0.0070 (10)
C7	0.0476 (11)	0.0486 (12)	0.0450 (13)	-0.0119 (9)	0.0291 (10)	-0.0092 (10)
C8	0.0453 (11)	0.0516 (12)	0.0316 (11)	-0.0100 (9)	0.0145 (9)	0.0042 (9)
C9	0.0317 (9)	0.0416 (10)	0.0316 (11)	-0.0012 (7)	0.0095 (8)	0.0045 (8)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

P1—O1	1.4815 (13)	C2—H10	0.9400
P1—O2	1.4897 (13)	C3—H11	0.9400
P1—C4	1.7974 (18)	C4—C5	1.388 (3)
P1—C1	1.8240 (18)	C4—C9	1.389 (3)
O3—H3	0.83 (3)	C5—C6	1.385 (3)
O3—H4	0.79 (3)	C5—H5	0.9400
N1—C1	1.325 (2)	C6—C7	1.373 (3)
N1—C2	1.365 (2)	C6—H6	0.9400

N1—H1	0.8700	C7—C8	1.377 (3)
N2—C1	1.335 (2)	C7—H7	0.9400
N2—C3	1.362 (2)	C8—C9	1.385 (3)
N2—H2	0.91 (2)	C8—H8	0.9400
C2—C3	1.344 (3)	C9—H9	0.9400
O1—P1—O2	121.89 (8)	C2—C3—H11	126.5
O1—P1—C4	110.00 (8)	N2—C3—H11	126.5
O2—P1—C4	109.18 (8)	C5—C4—C9	119.45 (17)
O1—P1—C1	103.90 (8)	C5—C4—P1	120.62 (14)
O2—P1—C1	105.65 (8)	C9—C4—P1	119.93 (13)
C4—P1—C1	104.68 (8)	C6—C5—C4	120.30 (19)
H3—O3—H4	109 (3)	C6—C5—H5	119.8
C1—N1—C2	109.43 (15)	C4—C5—H5	119.8
C1—N1—H1	125.3	C7—C6—C5	119.77 (18)
C2—N1—H1	125.3	C7—C6—H6	120.1
C1—N2—C3	109.27 (16)	C5—C6—H6	120.1
C1—N2—H2	123.3 (14)	C6—C7—C8	120.50 (19)
C3—N2—H2	127.4 (14)	C6—C7—H7	119.7
N1—C1—N2	107.26 (16)	C8—C7—H7	119.7
N1—C1—P1	127.65 (13)	C7—C8—C9	120.1 (2)
N2—C1—P1	125.07 (14)	C7—C8—H8	119.9
C3—C2—N1	107.04 (17)	C9—C8—H8	119.9
C3—C2—H10	126.5	C8—C9—C4	119.84 (18)
N1—C2—H10	126.5	C8—C9—H9	120.1
C2—C3—N2	106.99 (17)	C4—C9—H9	120.1
C2—N1—C1—N2	-0.1 (2)	O2—P1—C4—C5	14.52 (17)
C2—N1—C1—P1	178.80 (14)	C1—P1—C4—C5	-98.21 (15)
C3—N2—C1—N1	-0.1 (2)	O1—P1—C4—C9	-29.28 (17)
C3—N2—C1—P1	-179.06 (14)	O2—P1—C4—C9	-165.48 (14)
O1—P1—C1—N1	-145.99 (16)	C1—P1—C4—C9	81.80 (16)
O2—P1—C1—N1	-16.61 (18)	C9—C4—C5—C6	0.6 (3)
C4—P1—C1—N1	98.60 (17)	P1—C4—C5—C6	-179.36 (15)
O1—P1—C1—N2	32.72 (18)	C4—C5—C6—C7	-0.4 (3)
O2—P1—C1—N2	162.09 (15)	C5—C6—C7—C8	-0.1 (3)
C4—P1—C1—N2	-82.69 (17)	C6—C7—C8—C9	0.4 (3)
C1—N1—C2—C3	0.3 (2)	C7—C8—C9—C4	-0.2 (3)
N1—C2—C3—N2	-0.3 (2)	C5—C4—C9—C8	-0.3 (3)
C1—N2—C3—C2	0.3 (2)	P1—C4—C9—C8	179.68 (16)
O1—P1—C4—C5	150.71 (14)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O1 <sup>i</sup>	0.87	1.80	2.6302 (19)	160
N2—H2 $\cdots$ O3 <sup>ii</sup>	0.91 (2)	1.78 (2)	2.684 (2)	168 (2)
O3—H3 $\cdots$ O2	0.83 (3)	1.94 (3)	2.773 (2)	177 (3)
O3—H4 $\cdots$ O2 <sup>iii</sup>	0.79 (3)	2.00 (3)	2.777 (2)	164 (3)

Symmetry codes: (i)  $x-1/2, -y+3/2, z-1/2$ ; (ii)  $-x+1/2, y-1/2, -z+3/2$ ; (iii)  $-x, -y+2, -z+1$ .

Fig. 1

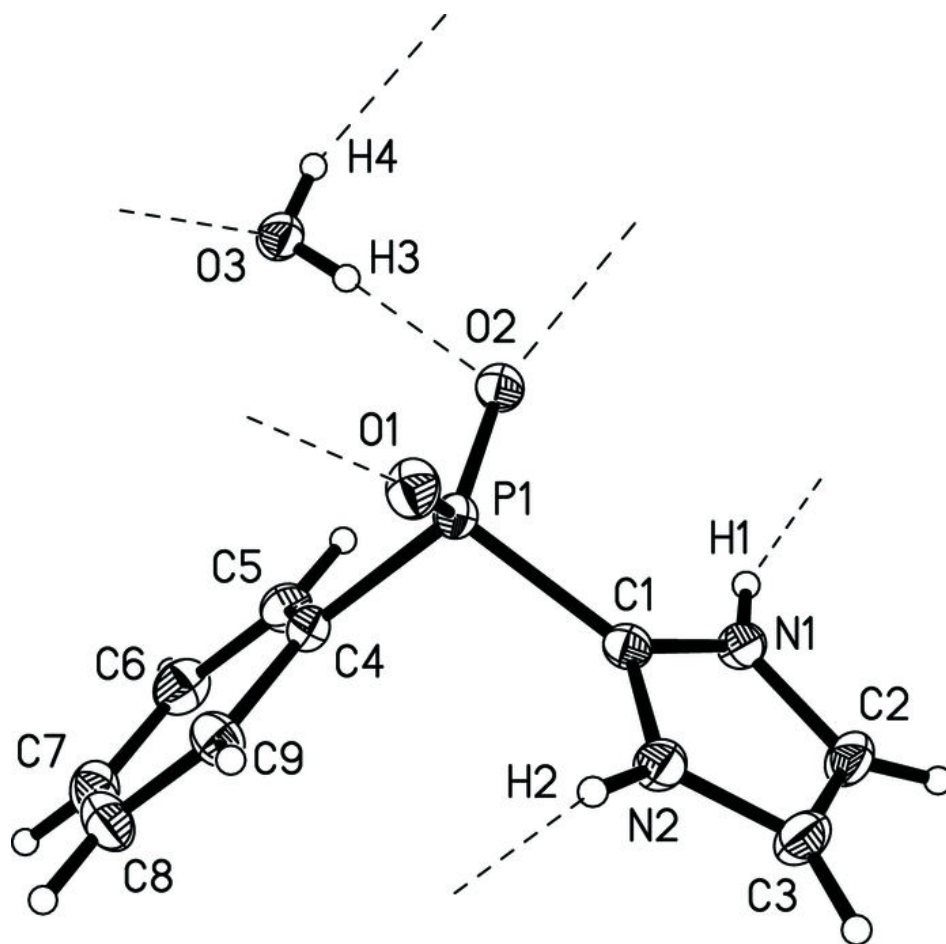




Fig. 2

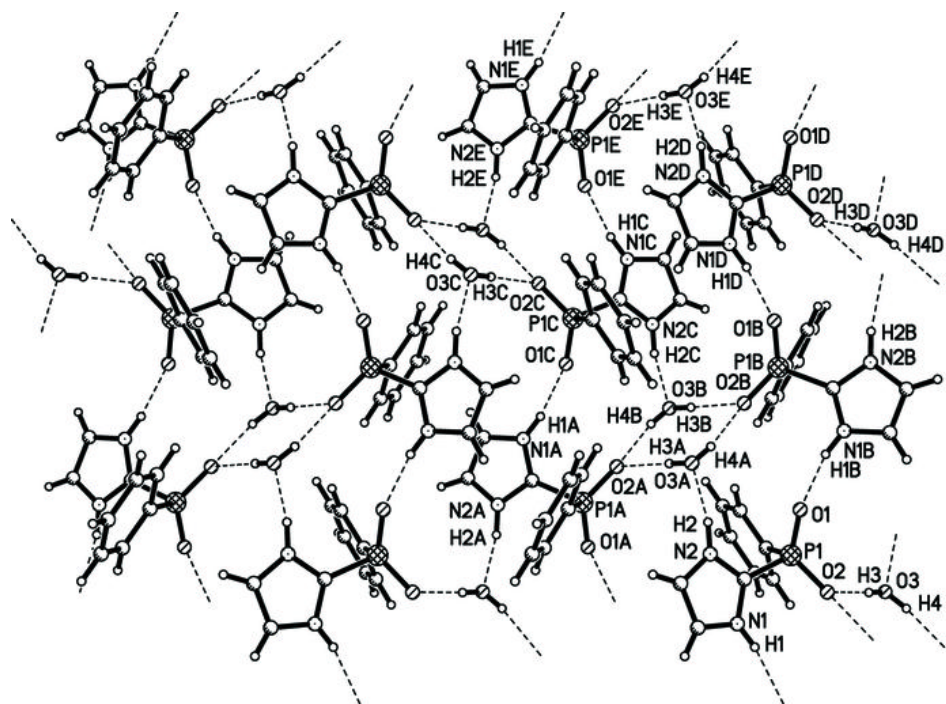


Fig. 3

