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ORIGINAL PAPER

NH···O and NH···N Hydrogen Bonded Networks in Imidazole-Based Phosphane Oxides: Structures of *Tris*(2-Isopropylimidazol-4(5)-yl)Phosphane Oxide, *Bis*(2-Isopropylimidazol-4(5)-yl)Phosphane Oxide and Diphenyl-2-Isopropylimidazol-4(5)-yl Phosphane Oxide

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Abstract The three title compounds show extensive hydrogen bonding networks in the solid state. The structure of diphenyl-2-isopropylimidazol-4(5)yl phosphane oxide (**3**) is dominated by N–H···OP hydrogen bonds, whereas in *bis*(2-isopropylimidazol-4(5)-yl)phenyl- (**2**) and *tris*(2-isopropylimidazol-4(5)yl)phosphane oxide (**1**) both, N–H···N and N–H···OP hydrogen bonds determine the solid-state structures. Compound **1** crystallises in the monoclinic space group *C*c with cell parameters $a = 19.5447(6)$ Å, $b = 10.45764(16)$ Å, $c = 10.8549(3)$ Å and $\beta = 121.418(4)°$; **2** in the orthorhombic space group $Pna2_1$, with $a = 11.5997(3)$ Å, $b = 9.5836(2)$ Å, $c = 16.1860(4)$ Å and **3** in the orthorhombic space group $Pca2_1$, with $a = 10.8430(2)$ Å, $b = 10.9277(2)$ Å and $c = 27.7088(6)$ Å.

Keywords *Tris*(imidazolyl)phosphane oxide · Imidazolyl phosphane oxide · Heterocyclic phosphane oxide

Introduction

Tris(azolyl)phosphanes show a plethora of interesting properties as ligands in coordination chemistry. Most notably, they can adopt different coordination modes as, e.g. *N,N,N*-, *N,P*- or *P*-ligands as well as bridging two or more metal atoms. *Tris*(imidazolyl)phosphane complexes, usually bearing imidazol-2-yl moieties, have been used to mimic the active site of carbonic anhydrase and as water soluble ligands for gold based anti-tumour drugs [1–8].

We are especially interested in the coordination chemistry of the not so common imidazolyl phosphane regioisomers where the phosphorous atom is bound to the heteroaromatic ring via the 4- or 5-position. Although a number of metal complexes of these ligands have already been reported, only a few structures of ligands or their oxidation products were determined so far [9–11].

Here, we report on the solid state structure of the series of imidazol-4(5)yl phosphane oxide which, due to their P=O and N–H functionalities, show distinct hydrogen bonding in the solid state.

Experimental

Crystallography

Crystallographic data were collected at 183(2) K on an Oxford Diffraction Xcalibur system with a Ruby detector using Mo Kα radiation ($\lambda = 0.7107$ Å) that was graphite-monochromated. Suitable crystals were covered with oil (Infineum V8512, formerly known as Paratone N), mounted on top of a glass fibre and immediately transferred to the diffractometer. The program suite CrysAlis$^{\text{Pro}}$ was used for data collection, semi-empirical absorption correction and data reduction [12]. Structures were solved with direct methods using SIR97 [13] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97 [14]. The structures were checked for higher symmetry with help of the program Platon [15].

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General Instrumentation

All preparations were carried out in Schlenk tubes under an atmosphere of dry nitrogen using anhydrous solvents purified according to standard procedures. All chemicals were used as purchased. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DRX 200 spectrometer. The ^{1}H and ^{13}C NMR spectra were calibrated against the residual proton signals and the carbon signals of the solvents as internal references ([D$_1$]chloroform: $\delta_H = 7.24$ ppm and $\delta_C = 77.0$ ppm; [D$_4$]methanol: $\delta_H = 5.84$ ppm and $\delta_C = 49.1$ ppm) while the ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4. Infrared spectra were recorded with a Bruker IFS 66 FT-IR spectrometer. Time-of-flight mass spectra were recorded on a Bruker Ultraflex TOF, ESI mass spectra on an ion-trap mass spectrometer Finnigan LCQ Deca and EI mass spectra on a GC/MS-system Thermo Finnigan Trace DSQ.

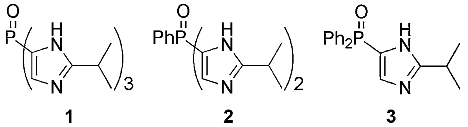

Fig. 1 Imidazoly-4(5)-yl phosphane oxides used in this study

Table 1 Selected bond lengths (Å) and angles (°) of **1**–**3**

Compound	**1**	**2**	**3**
d(P-O)	1.5014(10)	1.4957(10)	1.4956(13)
d(P-C)	1.7694(15)	1.7793(12)	1.7693(19)
	1.7706(13)	1.7792(13)	1.802(2)
	1.7765(13)	1.8001(12)	1.802(2)
<(C-P-C)	104.40(6)	106.34(6)	105.74(9)
	107.52(6)	109.63(6)	106.70(9)
	106.83(6)	103.81(6)	107.95(9)

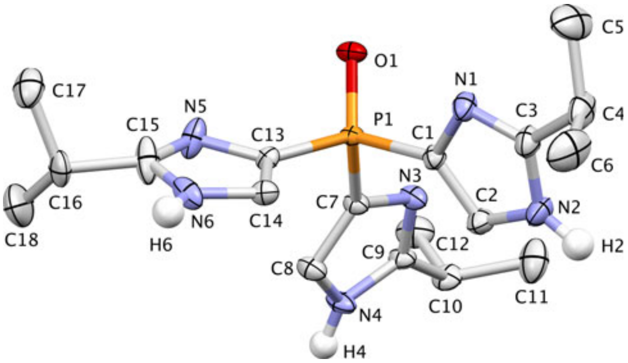

Fig. 2 View of the molecular structure of **1**, showing 50% probability ellipsoids (non acidic H-atoms are omitted for clarity). The isopropyl group consisting of C16, C17, C18 shows a twofold disorder, only one conformer is shown

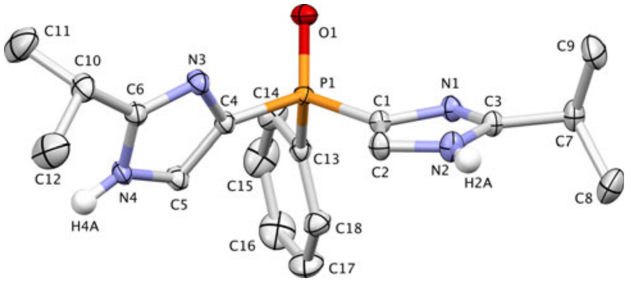

Fig. 3 View of the molecular structure of **2**, showing 50% probability ellipsoids (non acidic H-atoms are omitted for clarity)

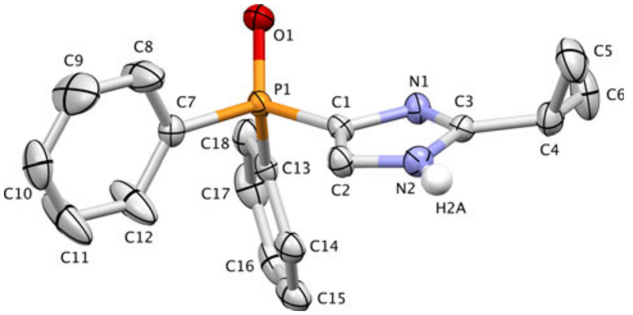

Fig. 4 View of the molecular structure of **3**, showing 50% probability ellipsoids (non acidic H-atoms and second molecule are omitted for clarity)

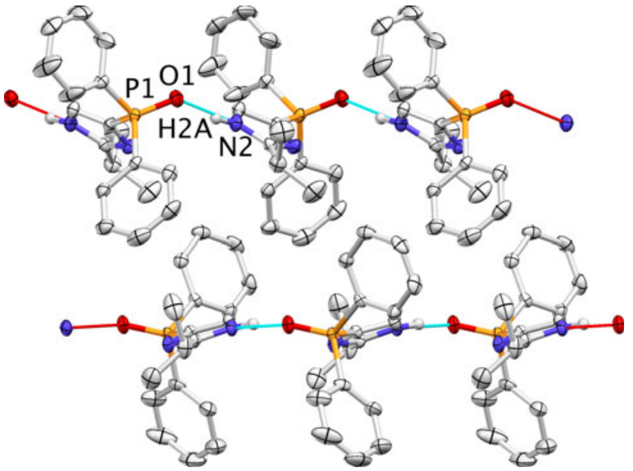

Fig. 5 Columnar arrangement in the hydrogen bonding network of **3** (view along the *b* axis)

Tris(2-Isopropylimidazol-4(5)-yl)Phosphane Oxide (**1**)

The compound **1** was prepared as previously described [1] and crystallised upon slow evaporation of a ethanolic solution to yield colourless needles.

Bis(2-Isopropylimidazol-4(5)-yl)Phenyl Phosphane Oxide (**2**)

To a solution of 1-diethoxymethyl-2-isopropylimidazole (10.6 g, 50.0 mmol) in 300 mL of diethyl ether 33 mL (53 mmol) of 1.6 M *n*-butyl lithium in hexane were added at −78 °C. The solution was stirred at −78 °C for 30 min and additionally for 30 min at room temperature. After cooling to −78 °C $PhPCl_2$ (3.39 mL, 25 mmol) in 10 mL diethyl ether was added. The white suspension was stirred over night at room temperature, 75 mL of conc. NH_4OH were added the organic layer separated, washed with water and dried over $MgSO_4$. After removal of the solvent the oily residue was re-dissolved in 100 mL of acetone/water 10:1 and heated to reflux for 12 h. The resulting white precipitated was collected and recrystallized from methanol/acetone. ^1H NMR (200MHz, $CDCl_3$): $\delta = 1{,}39$ (d, $^3J_{HH} = 7$ Hz, 12H), 3,12 (sept., $^3J_{HH} = 7$ Hz, 2H), 7,24 (m, 5H), 7,43 (d, $J_{PH} = 0{,}8$ Hz). $^{31}P\{^1H\}$-NMR (81 MHz, $CDCl_3$): $\delta = -63$ (s). EI MS (70 eV, 240 °C): *m/z* (%) = 326 (100) $[M]^+$, 249 (18) $[M\text{-}Ph]^+$, 217 (61) $[M\text{-}im^{iPr}]^+$. $C_{18}H_{23}N_4P$ (326.38): calc. C 66.2 H 7.1 N 17.2, found C 65.6 H 7.1 N 17.1. A solution of the phosphane in ethanol is treated with H_2O_2 and stirred over night at ambient temperature. The solvent is removed in vacuo and the residue crystallised from ethanol/water. ^1H NMR

Table 2 Crystal data and structure refinement for **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{18}H_{27}N_6OP$	$C_{18}H_{23}N_4OP$	$C_{18}H_{19}N_2OP$
Formula weight	374.43	342.37	310.32
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*C*c	*P*na2$_1$	*P*ca2$_1$
a (Å)	19.5447(6)	11.5997(3)	10.8430(2)
b (Å)	10.45764(16)	9.5836(2)	10.9277(2)
c (Å)	10.8549(3)	16.1860(4)	27.7088(6)
α (°)	90	90	90
β (°)	121.418(4)	90	90
γ (°)	90	90	90
Volume (Å^3)	1893.36(8)	1799.35(7)	3283.19(11)
Z	4	4	8
Density (calculated) (Mg m^{-3})	1.314	1.264	1.256
Absorption coefficient (mm^{-1})	0.166	0.165	0.171
F(000)	800	728	1312
Crystal size (mm^3)	0.53 × 0.25 × 0.21	0.44 × 0.24 × 0.18	0.30 × 0.20 × 0.10
Crystal description	Colourless plate	Colourless needle	Colourless plate
Theta range for data collection (°)	2.44–30.51	2.76–30.50	2.37–30.50
Index ranges	$-27 \le h \le 27$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-9 \le h \le 16$, $-12 \le k \le 13$, $-23 \le l \le 21$	$-15 \le h \le 14$, $-15 \le k \le 15$, $-29 \le l \le 39$
Reflections collected	14844	12583	25878
Independent reflections	5418 [R(int) = 0.0229]	5284 [R(int) = 0.0245]	9065 [R(int) = 0.0375]
Reflections observed	4983	4692	6701
Criterion for observation	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$
Completeness to Θ	100.0% to 30.51°	99.9% to 30.50°	100.0% to 30.50°
Max. and min. transmission	0.9660 and 0.9083	0.9709 and 0.9026	0.9831 and 0.8663
Data/restraints/parameters	5418/2/259	5284/1/221	9065/1/401
Goodness-of-fit on F^2	1.035	0.983	0.941
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0351$, $wR_2 = 0.0898$	$R_1 = 0.0336$, $wR_2 = 0.0782$	$R_1 = 0.0450$, $wR_2 = 0.0810$
R indices (all data)	$R_1 = 0.0386$, $wR_2 = 0.0913$	$R_1 = 0.0384$, $wR_2 = 0.0797$	$R_1 = 0.0689$, $wR_2 = 0.0859$
Absolute structure parameter	0.16(6)	−0.01(7)	0.00(6)
Largest diff. peak and hole (e Å^{-3})	0.472 and −0.204	0.310 and −0.175	0.370 and −0.292

(200 MHz, [D$_4$]methanol): $\delta = 1{,}37$ (d, $^3J_{HH} = 7$ Hz, 12H), 3,17 (sept., $^3J_{HH} = 7$ Hz, 1H), 7,37 (s, 2H), 7,74 (m, 5H). $^{31}P\{^1H\}$-NMR (81 MHz, [D$_4$]methanol): $\delta = 12$ (s). EI MS (70 eV, 290 °C): *m/z* (%) = 342 (100) [M]$^+$, 327 (99) [M-O]$^+$, 233 (49) [M-im^{iPr}]$^+$, 217 (72) [M-O-im^{iPr}]$^+$. $C_{18}H_{23}N_4OP \cdot 2H_2O$ (378.41): calc. C 57.1 H 7.2 N 14.8, found C 57.1 H 6.6 N 14.8.

Diphenyl-2-Isopropylimidazol-4(5)-yl Phosphane Oxide (**3**)

Diphenyl-2-isopropylimidazol-4(5)-yl phosphane (4-MIP^{iPr}) was prepared as previously reported [3]. For the oxidation of 4-MIP^{iPr} to 4-MIPO^{iPr} (**3**) diphenylimidazol-4(5)-yl phosphane was dissolved in ethanol and hydrogen peroxide was

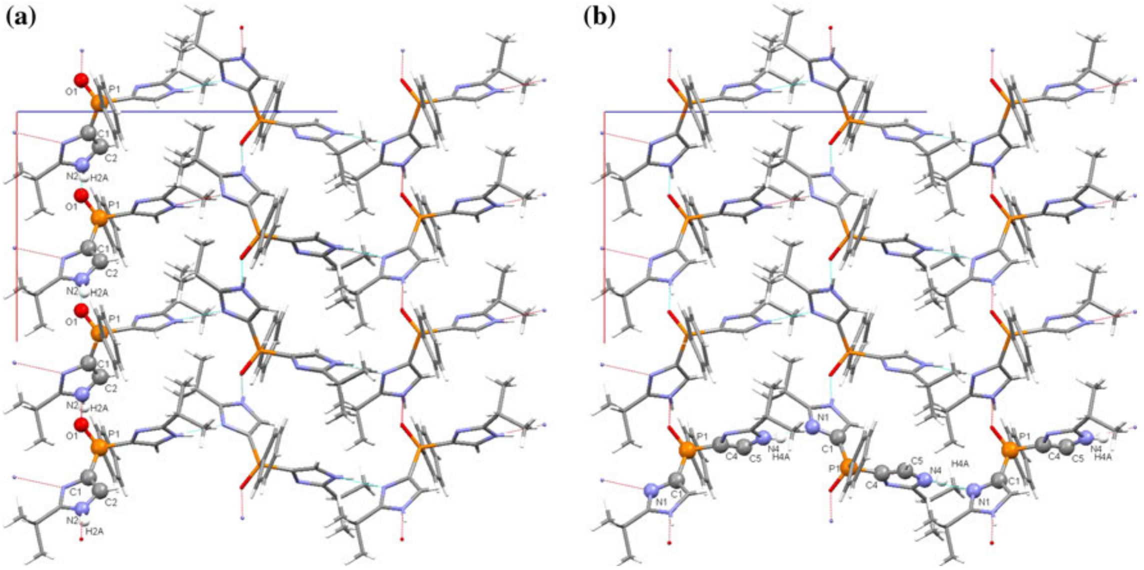

Fig. 6 Hydrogen bonding in the solid state of **2** (view along the *b* axis). **a** PO···HN chain along *a* axis and **b** NH···N chain along *c* axis

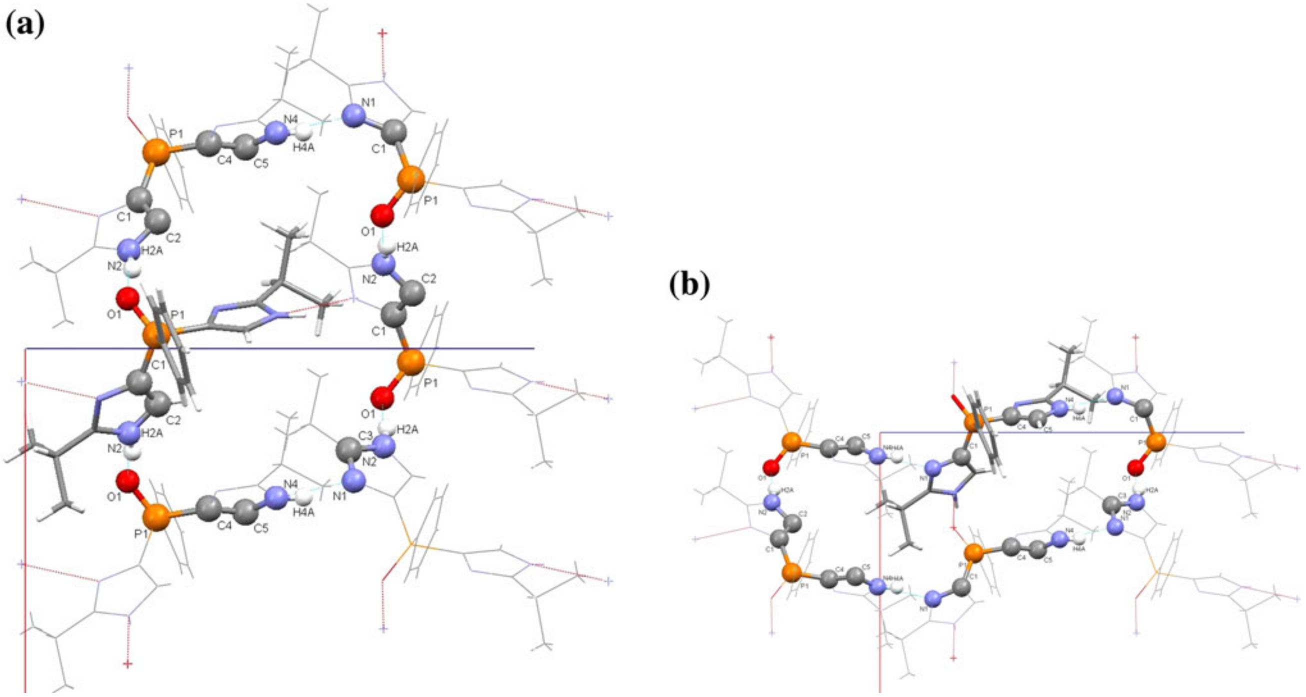

Fig. 7 Hydrogen bonding network in the solid state of **2**. The two independent networks $R^6_6(37)R^6_6(35)$ are shown

added until no more signal of the phosphane was observed in ^{31}P{^{1}H} NMR. The mixture was stirred over-night, the solvent removed in vacuo, the resulting solid washed with acetone and diethyl ether and dried in vacuo. The solid thus obtained was dissolved in a minimum amount of methanol and crystallized by slow diffusion of diethyl ether into this solution. ^{1}H NMR (200 MHz, [D$_4$]methanol): $\delta = 1.35$ (d, 6H, $J_{\mathrm{HH}} = 7$ Hz, CH(CH_3)$_2$), 3.16 (sept, 1H, $J_{\mathrm{HH}} = 7$ Hz, CH(CH$_3$)$_2$), 7.32 (s, br, 1H, H$_{\mathrm{im}}$), 7.5–7.9 (m, 10H, Ph). ^{31}P{^{1}H} NMR (81 MHz, [D$_4$]methanol): $\delta = 24$. EI MS (70 eV, 220 °C): *m/z* (%) = 310 (100) [M]$^+$, 295 (84) [M-Me]$^+$, 233 (17) [M-Ph]$^+$. $C_{18}H_{19}N_2OP$ (310.34): calc. C 69.7 H 6.2 N 9.0, found C 69.3 H 6.0 N 8.9.

Results and Discussion

The three phosphane oxides **1**–**3** (Fig. 1) are easily obtained by oxidising the corresponding phosphanes using hydrogen peroxide. Selected bond lengths and angles are summarised in Table 1.

The P=O bond lengths in compounds **1**–**3** is significantly longer than the P=O bond length found in triphenylphosphane oxide (1.479(2) Å) [16], even when taken in account, that the P=O bond is elongated when involved in hydrogen bonding [17, 18] (Figs. 2, 3, 4).

Compound **1** crystallises in the monoclinic space group *C*c whereas **2** and **3** crystallise in the orthorhombic space groups *P*na2$_1$ and *P*ca2$_1$, with one and two molecules in the asymmetric unit respectively. In all three compounds the aromatic substituents exhibit a comparable propeller arrangement as found for the phenyl substituents in PPh$_3$ [19, 20]. The conformation of the 2-isopropylimidazolyl substituent in **3** resembles the one found in the Au(I)chlorido complex of this ligand [3]. In non of these compounds interactions between the aryl substituents similar to the sextuple phenyl embrace (SPE) [21] commonly found in crystal structures containing PPh$_3$ are found, here hydrogen bonds are the more dominant intermolecular forces.

In the solid state structures of compounds **1**–**3** hydrogen bonding networks are found. Columns of **3** are orientated pair-wise parallel and anti-parallel to the *a* axis (Fig. 5). The graph set description [22] of NH···OP hydrogen bonding is *C*(6). The rungs of these zick-zack ladder-like columns are formed by the imidazolyl substituents and the stiles by the phenyl and isopropyl groups (Table 2).

The ladder motif is also found in **2** (Fig. 6). Additionally to the NH···OP hydrogen bonds the second imidazolyl substituents forms NH···N hydrogen bridges to the imine N atom of the imidazolyl ring involved in the NH···OP system. This leads to the formation of a set of hydrogen bonds in the solid-state best described by the graph set $R_6^6(37)R_6^6(35)$ (Fig. 7).

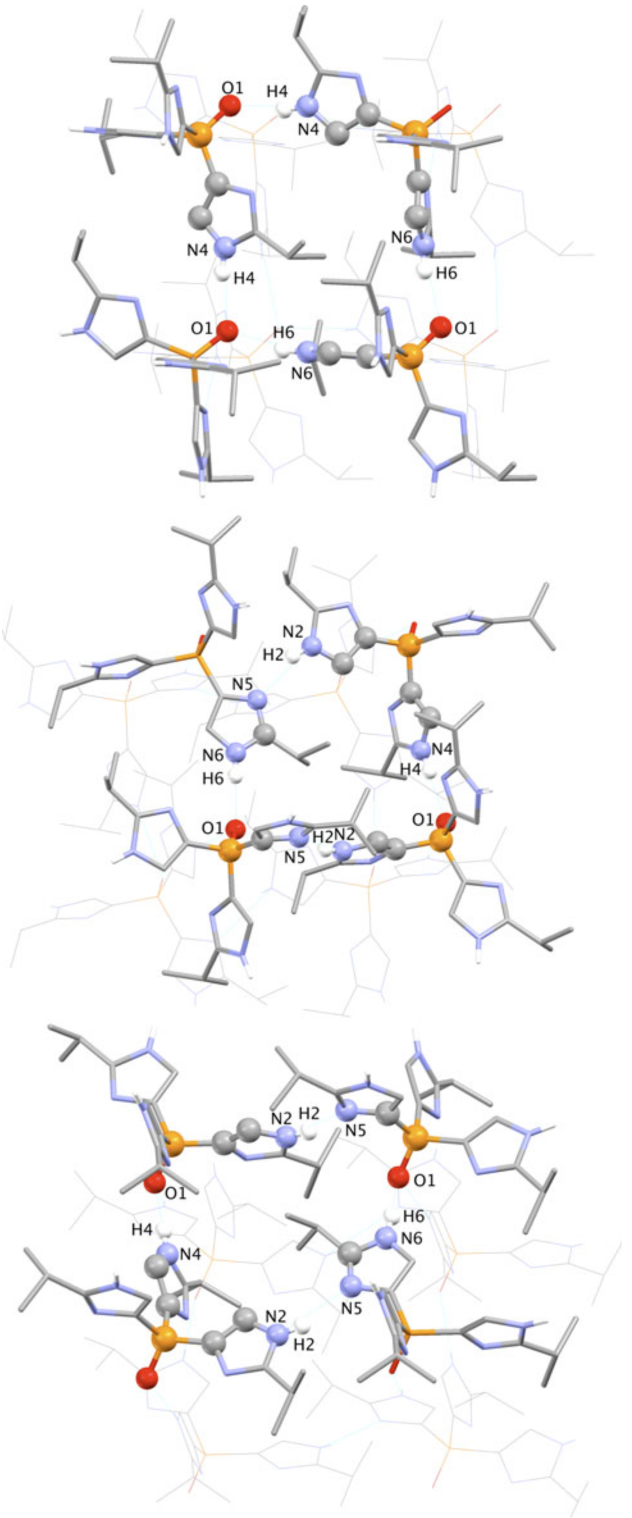

Fig. 8 Hydrogen bonding network in the solid state of **1**. The three independent networks $R_4^4(27)R_4^4(23)R_4^3(22)$ are shown

The situation in **1** is much more complicated due to the three imidazolyl substituents. Here a three-dimensional hydrogen bonded network is found in which one molecule is hydrogen bonded to five others. The PO group forms hydrogen bonds to the nitrogen atoms of two imidazolyl groups N2 and N4 of different molecules of **1**. The phosphorus atoms of four molecules can be placed on the corners of a distorted cube. Then, one each face a closed hydrogen-bonded pathway of four hydrogen bridges determines the network. The motif is described by the graph set $R_4^4(27)R_4^4(23)R_4^3(22)$ (Fig. 2). Interestingly, only hydrogen bridges between the atom pairs N4/O1, N6/O1 and N2/N5 describe these networks (Fig. 8).

In all three compounds only the imidazol-4-yl tautomer in the heteroaromatic substituents is found. Furthermore, the NH proton and the PO oxygen atom are located in a more or less transoid conformation, which contributes to the formation of the intermolecular NH···OP bonds in one direction.

Supplementary Material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 769495–769497 for compounds **1**–**3**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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