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Hydrogen Bonds in 2-(Diorganylphosphorylhydroxymethyl)-1-organylimidazoles

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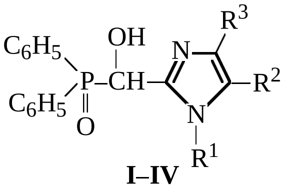
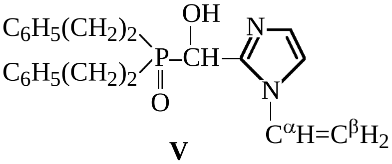
Abstract—Structures of 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles were studied by IR and ^1H and ^{31}P NMR spectroscopy, and also by *ab initio* calculations (HF/6-31G*). Formation of intramolecular O–H···O=P hydrogen bonds in solutions of these compounds in CCl_4 and $CHCl_3$ was established.

2-(Diorganylphosphorylhydroxymethyl)-1-organylimidazoles are new promising polydentate ligand systems of the azole series. Their facile synthesis was developed by us previously [1]. The presence of phosphine oxide and hydroxy groups, and also of the pyridine-like N^3 atom in such compounds suggests the possibility of formation of intra- and intermolecular hydrogen bonds involving heteroatoms of the ring and substituents. The electron-donor powers of the P=O group and N^3 atom of the ring depend on the mutual effect of functional groups in these molecules and may be both similar and significantly different. For example, the IR data show that the relative basicities evaluated from the interaction with phenol ($\Delta\nu_{OH}$) are 510 and 430 cm^{-1}, respectively, for triethyl- and triphenylphosphine oxides [2] and 330–530 cm^{-1} [3] for 1-vinyl- and 1-ethyl-substituted azoles. Formation of hydrogen bonds can also be largely affected by the steric factors.

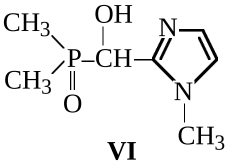
In the present work, with the aim to elucidate the type of hydrogen bonds in 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles **I**–**V**, we studied their IR spectra in the solid phase and in solutions and also calculated *ab initio* the heats of formation and vibrational frequencies for certain model compounds: 2-(dimethylphosphorylhydroxymethyl)-1-methylimidazole **VI**, 1-organyl-2-hydroxymethylimidazoles **VII**–**XI**, and phosphine oxides **XII**–**XVI**, which are the fragments of phosphoryl imidazoles **I**–**V** [1].



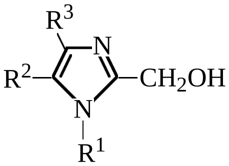
I–IV



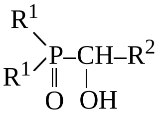
V



VI



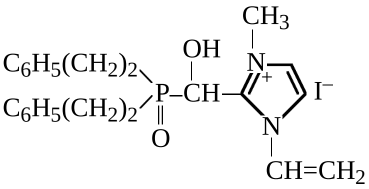
VI–XI



XII–XV

$[C_6H_5(CH_2)_2]_3P{=}O$

XVI



XVII

I–IV, VII–XI, $R^1 = CH_3$, $R^2 = R^3 = H$ (**I, VII**); $R^1 = CH{=}CH_2$, $R^2 = R^3 = H$ (**II, IX**), $R^2 + R^3 = (CH)_4$ (**IV, XI**); $R^1 = C_2H_5$, $R^2 + R^3 = (CH)_4$ (**III, X**), $R^2 = R^3 = H$ (**VIII**). **XII–XV**, $R^1 = CH_3$, $R^2 = H$ (**XII**); $R^1 = C_6H_5$, $R^2 = H$ (**XIII**); $R^1 = C_6H_5(CH_2)$, $R^2 = H$ (**XIV**), C_6H_5 (**XV**).

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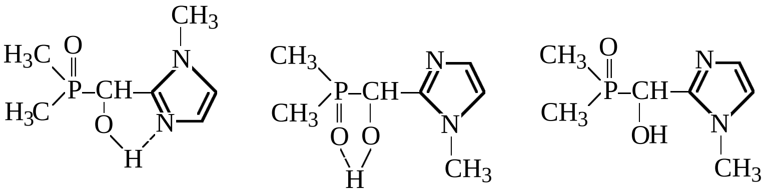
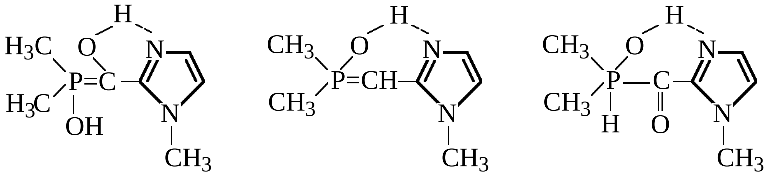
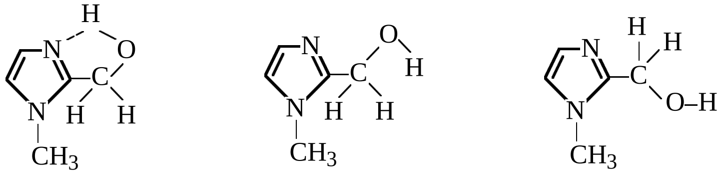
The HF/6-31G* calculations were performed for 2-(dimethylphosphorylhydroxymethyl)-1-methylimidazole **VI**, 1-methyl-2-hydroxymethylimidazole **VII**, and hydroxymethyldimethylphosphine oxide **XII**, existing in the forms with an intramolecular hydrogen bond or free OH group (see scheme).



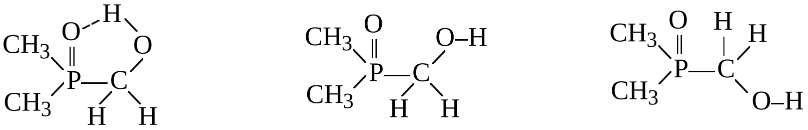
	VIa	**VIb**	**VIc**
μ, D	1.09	4.99	2.11
Δ*E*, kJ mol^{-1}	0	21.4	19.3
ν_{OH}, cm^{-1}	4007	4006	4083



	VId	**VIe**	**VIf**
Δ*E*, kJ mol^{-1}	225		226



	VIIa	**VIIb**, *sp*	**VIIc**, *ap*
Δ*E*, kJ mol^{-1}	1.5	8.3	0



	XIIa	**XIIb**, *sp*	**XIIc**, *ap*
Δ*E*, kJ mol^{-1}	0	14.3	0.8

For **VI**, the most energetically favorable is form **VIa** with intramolecular O–H···N bond (see scheme). The difference between the heats of formation of forms **VIa** and **VIc** (with the free OH group) is equal to the energy of formation of this bond Δ*E* (accurate to the difference in the energies of conformational transition), being as high as 19.3 kJ mol^{-1}. Together with the the considered forms of phosphine oxide **VIa**–**VIc**, structures **VId**–**VIf** yielded by prototropic rearrangements are also possible. However, forms **VId** and **VIf** are less energetically favorable than **VIa**–**VIc**. Form **VIe** has no local minimum and in the course of calculations transforms into **VIf**. In the case of 1-methyl-2-hydroxymethylimidazole **VII**, two forms are close in energy (Δ*E* = 1.5 kJ mol^{-1}). One of them, **VIIa**, has an intramolecular hydrogen bond. Another conformer, **VIIc**, has no hydrogen bond, and it is *anti*-periplanar (*ap*) in relation to O and N^3 atoms. The energy gain due to the formation of the O–H···N bond in **VIIa** as compared to *syn*-periplanar (*sp*) conformer **VIIb** is 6.8 kJ mol^{-1}. This means that the energy of formation of H-bond in the molecule of **VII**

Frequences ν_{OH} and $\nu_{P=O}$ in the IR spectra of 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles **I**–**V**, 2-hydroxymethylimidazoles **VIII**–**XI**, hydroxymethyldiphenylphosphine oxide **XIII**, and hydroxymethyldi(ethylphenyl)-phosphine oxide **XIV** in KBr pellets and CCl_4 and $CHCl_3$ solutions; ^1H and ^{31}P NMR data for **V** and **XIV**–**XVII**

Comp. no.	IR spectrum, ν_{OH}, cm^{-1}		^1H NMR spectrum, δ_{OH}, ppm		^{31}P NMR spectrum, δ_P, ppm	
	KBr	*c* 0.01–0.0006 M	$CDCl_3$	DMSO-d_6	$CDCl_3$	DMSO-d_6
I	3180	3414				
II	3000	3414				
III	3000	3403				
IV	3100	3428				
V	3100[a]	3422	5.75	6.58	52.15	47.92
VIII	3170	3491, 3611				
IX	3130	3501, 3612				
X	3180	3489, 3611				
XI	3130	3498, 3611				
XIII[b]	3225	3420, 3590 3570				
XIV[c]	3170	3613	4.85	5.41	51.32	46.30
XV[c]	3165	3540, 3585	5.05	–	49.28	47.15
XVI			–	–	46.26	–
XVII	3100		5.00	6.62	52.02	48.08

[a] Liquid film. [b] Data of [4]. [c] $CHCl_3$ solution.

is close to the energy of its conformational transition *ap*→*sp* (ΔE = 8.3 kJ mol^{-1}). Similar result was obtained for phosphine oxide **XII** in which the energy of the O–H···O=P bond (ΔE = 14.3 kJ mol^{-1}) in **XIIa** relative to **XIIb** is close to the energy of the *ap*→*sp* transition (ΔE = 13.5 kJ mol^{-1}). Thus, the character of formation of intramolecular hydrogen bonds in **VI** and its fragments differs essentially. Theoretically, for imidazole phosphine oxide **VI** in the gas phase, the structure with intramolecular O–H···N bond is preferred, and for imidazole **VII** and phosphine oxide **XII** chelate structures **VIIa** and **XIIa** are similar in energy to the *ap* forms **VIIc** and **XIIc** with free OH group.

The IR spectra of solid compounds **I**–**V** (KBr pellets or mulls in mineral oil) have a broad intense absorption band ν_{OH} at 3000–3200 cm^{-1} (see table), also observed in CCl_4 solutions at concentrations C > 0.1 M. Dilution of the solutions leads to a decrease in its intensity, and at C < 0.01 M it disappears completely, with the appearance of a band at 3400–3430 cm^{-1} (see table; Fig. 1a), whose intensity does not change at further dilution to C ~0.0006 M. The location of these bands and their behavior with variation of the solution concentration prove their assignment to OH groups taking part in intermolecular (3000–3200 cm^{-1}) and intramolecular (3400–3430 cm^{-1}) hydrogen bonds. The free OH group in the molecules is characterized by the high-frequency band at ~3610 cm^{-1}.

To assign the observed bands to definite types of hydrogen bonds (OH···N, OH···O=P) in **I**–**V**, we have considered the IR data for the compounds simulating their fragments, i.e., hydroxy derivatives of alkyl-, phenylphosphine oxides, and 1-ethyl(vinyl)-2-hydroxymethylimidazoles **VIII**–**XI**. It is known [5–7] that the band of stretching vibrations ν_{OH} of hydroxy derivatives of alkyl- and phenylphosphine oxides, forming self-associates by intermolecular hydrogen bonds O–H···O=P in the condensed and crystalline states, is located at 3100–3300 cm^{-1}. The frequency of ν_{OH} stretching vibrations in solid phosphine oxides **XIII**–**XV** is 3160–3230 cm^{-1} and belongs to intermolecular O–H···O=P hydrogen bonds. The spectra of dilute solutions of hydroxymethyldiphenylphosphine oxide **XIII** contain the bands of the free OH group (3590 cm^{-1}) and that taking part in the formation of a five-membered hydogen-bonded ring (3570 cm^{-1}) [5]. The band at 3420 cm^{-1} in the spectrum of the dilute solution is assigned to the cyclic dimer. Its existence in the crystalline state was proved by X-ray diffraction data [5]. The spectra of phosphine oxides **XIV** and **XV** under similar conditions contain also the bands ν_{OH} of a free OH group (3613, 3585 cm^{-1}) and that involved in intramolecular O–H···O=P bond (3570, 3540 cm^{-1}) (see table; Fig. 1b).

In the spectra of crystalline 1-ethyl- and 1-vinyl-2-

hydroxymethylimidazoles **VIII** and **IX** and benzimidazoles **X** and **XI** studied by us for comparison, and also in the spectra of their concentrated solutions in CCl_4, the band of stretching vibrations of associated OH groups taking part in intermolecular O–H···N bonds is located at 3130–3180 cm^{-1} (see table). As the solutions are diluted to a concentration of about 0.01 M, this band disappears, and two new bands appear. The first of these bands is narrow and is located at 3610 cm^{-1}, while the other band is broad and weak and is observed at 3490–35100 cm^{-1} (see table; Fig. 1c). Further dilution of solutions does not alter their intensity. The shape and location of the highest-frequency band allows its assignment to the vibrations ν_{OH} of the free hydroxy groups of azoles **VIII**–**XI**. The band at 3490–3500 cm^{-1}, judging from its shape, may be assigned to vibrations of OH groups taking part in the formation of intramolecular O–H···N bonds.

This, the ranges of ν(OH) frequencies characterizing intermolecular and intramolecular hydrogen bonds O–H···N and O–H···O=P in **VIII**–**XV** are close to each other. The frequency of the stretching vibrations of the OH group in the calculated vibrational spectra of the two forms of **VI** (**VIa**, **VIb**) with the O–H···N and O–H···O=P bonds is also practically the same (4006, 4007 cm^{-1}).

The type of intramolecular hydrogen bond (O–H···N or O–H···O=P) in **V** was additionally studied by ^1H and ^{31}P NMR spectroscopy. As type of intramolecular hydrogen bond in this compound cannot be determined by NMR spectroscopy directly, we used the method of analogies, namely, comparison with diorganylphosphine oxides **XIV** and **XV** in which only one (O–H···O=P) type of inter- and intramolecular binds is possible.

The parameters of the NMR spectra of the diorganylphosphine oxides under study are given in the table. In the ^1H NMR spectra of the compounds in an inert solvent ($CDCl_3$), the OH proton signals are strongly broadened, suggesting intense intermolecular exchange between two forms with intra- and intermolecular hydrogen bonds. Dissolution of the above compounds in a protophilic solvent (DMSO-d_6) shifts the equilibrium toward formation of a complex with the solvent. Under these conditions, the OH signals in the spectra of **V** and **XIV** become narrow and are shifted downfield. The OH signal in the spectrum of **XV** overlaps with the signals of aromatic ring protons. The chemical shift of the OH proton in **XVII**, where intramolecular O–H···N bond cannot be formed, is in the same range as in compound **XV** with intramolecular O–H···O=P bond. This means that the location of OH signals in diorganylphosphine oxides, including the azole derivative **V**, is predictable and similar. It indirectly suggests the existence of an intramolecular O–H···O=P bond in **V**. This is also confirmed by variations in the ^{31}P chemical shifts in going from an inert to a strongly basic solvent. In formation of a stable complex with DMSO-d_6, the ^{31}P chemical shift in the spectrum of **V** shifts upfield and becomes close to the ^{31}P shift in **XVI**.

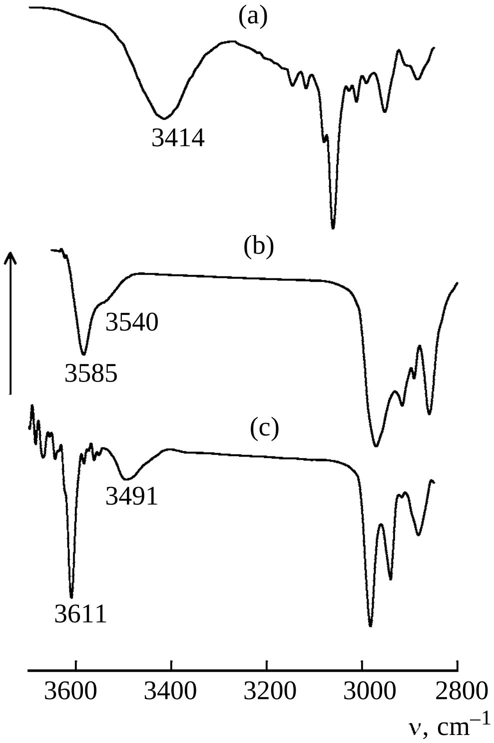


Fig. 1.IR spectra of solutions of (a) 2-(diphenylphosphorylhydroxymethyl)-1-methylimidazole **I** (CCl_4, 0.0006 M), (b) bis(2-phenylethyl)(1,1'-hydroxyphenylmethyl)phosphine oxide **XV** ($CHCl_3$, 0.01 M), and (c) 1-ethyl-2-hydroxymethylimidazole **VIII** (CCl_4, 0.01 M).

Additional, though also indirect, data proving the existence of **V** mainly as a conformer with the O–H···O=P bond were obtained in a 2D NOESY expeiment. The hydrogen atom of the methine group –CH(OH) in phosphine oxide **V** has no cross peak with H^{α} of the vinyl fragment, while in the NOESY spectrum of imidazole **IX** the cross peak of these atoms is observed.

Hence, the NMR data suggest that, for 2-(diphenylethylphosphorylhydroxymethyl)-1-vinylimidazole **V**, the conformation with the intramolecular O–H···O=P bond is preferred.

This conclusion is confirmed by the IR data on the frequences of P=O stretching vibrations in phosphine oxides. The ν(P=O) band in the spectra of solutions in $CHCl_3$ and DMSO is located, respectively, at 1154 and 1169 cm^{-1} (**V**), 1150 and 1163 cm^{-1} (**XIV**), and 1156 and 1162 cm^{-1} (**XVI**). The frequency shift under the action of such a protophilic solvent as DMSO is 6 cm^{-1} in the case of compound **XVI** with a free P=O group, whereas for compounds **V** and **XIV** with the similar O–H···O=P bond it is 15 and 13 cm^{-1}, respectively. The contradiction between the data obtained and the results of quantum-chemical calculations may be due to stabilization in solutions of conformers **VIb** with the O–H···O=P bond, which are considerably more polar than conformers **VIa** with the O–H···N bond (see scheme). As shown by the IR spectrum of solid iodomethylate **XVII**, addition of methyl iodide to the pyridine nitrogen atom causes a high-frequency shift of the bands of stretching vibrations of the imidazole ring from 1520 to 1580 cm^{-1}. The ν(P=O) band with the frequency of 1157 cm^{-1} belongs to the P=O group involved in the O–H···O=P bond. Hence, the ν(P=O) band with the similar frequency of 1157 cm^{-1} in the spectrum of solid phosphine oxide **V** suggests its association also via the O–H···O=P bond.

EXPERIMENTAL

Syntheses and characteristics of **I**–**V** and **XII**–**XVI** were described in [1], and those of **VII**–**XI**, in [8]. The IR spectra of solid samples and solutions were measured on a Bruker IFS-25 spectrometer. The ^1H and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ and DMSO-d_6 solutions against internal HMDS and external H_3PO_4. Quantum-chemical calculations of the molecules were carried out with complete optimization of the geometry using the GAUSSIAN 98 program package [9].

2-[Bis(phenylethyl)phosphorylhydroxymethyl]-1-vinyl-3-methylimidazolium iodide XV. A mixture of 0.2 g of imidazole **V** and 0.36 g of CH_3I was stirred in 3 ml of absolute methanol at 40°C for 5 h. The product (**XV**) was precipitated with ether, filtered off, and dried in a vacuum. Yield 0.25 g (92%). Found, %: C 53.09; H 5.06; N 5.58; P 5.77. $C_{23}H_{28}\cdot IN_2O_2P$. Calculated, %: C 52.89; H 5.36; N 5.36; P 5.94.

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