Two new phosphinic amides: synthesis, crystal structure and theoretical study of hydrogen bonding

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Abstract

Two novel phosphinic amides, $(C_6H_5)_2P(O)(NH-cyclo-C_7H_{13})$ (I) and $(C_6H_5)_2P(O)(NH-cyclo-C_6H_{11})$ (II) were synthesized and characterized by spectroscopic methods and X-ray crystallography. Both compounds crystallize in the orthorhombic chiral space group $P2_12_12_1$ and in both structures, the N—H···O hydrogen bonds lead to one-dimensional arrangements along the *a* axis. The molecular geometries and vibrational frequencies of I and II were investigated with quantum chemical calculations at the B3LYP/6-311G** level of theory. Furthermore, the hydrogen bonds were studied by means of the Bader theory of atoms in molecules (AIM) and natural bond orbital (NBO) analysis.

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Keywords

Phosphinic amide; X-ray crystallography; hydrogen bond; AIM; NBO

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Introduction

The amounts of data reported on phosphorus-nitrogen compounds have increased in recent years, due to their numerous applications in biochemistry,¹ medicine,^{2–5} pharmacology,^{6–9} agriculture^{10–12} and coordination chemistry.^{13–15} Additionally, *ab initio* studies have been carried out on different aspects of these compounds, such as structural features, conformational states and spectroscopic assignments.^{16–23}

In continuation of our previous studies on design, synthesis, X-ray crystallography and analysis of hydrogen bond strength^{24–27} as well as theoretical studies on the IR spectra and evaluation of the strength of hydrogen bonding in phosphoramides,^{28,29} here we report the synthesis, crystal structure and spectroscopic characterization of two new derivatives, belonging to another family of phosphorus-nitrogen compounds, called phosphinic amides. The new compounds are $(C_6H_5)_2P(O)(NH$ -cyclo- $C_7H_{13})$ (I) and $(C_6H_5)_2P(O)(NH$ -cyclo- $C_6H_{11})$ (II) as shown in Figures 1 and 2. Furthermore, the molecular geometries, vibrational frequencies and hydrogen bond energies were studied by quantum chemical calculations.

Results and discussion

Crystal Structure Analysis and Optimized Geometry

The crystallographic data and the details of the X-ray diffraction study of **I** and **II** are represented in Table 1. For both structures the asymmetric unit contains one complete molecule (Figures 3 and 4). The P=O bond lengths of **I** and **II** (1.485(5) Å and 1.490(4) Å) are slightly longer than the phosphorus-oxygen double bond length (1.45 Å).³⁰ The P–N bond lengths (1.646(6) Å for **I**

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and 1.641(5) Å for **II**) are shorter than the standard P–N single bond length (1.77 Å).³⁰ The phosphorus atoms have a distorted tetrahedral configuration with bond angles at the phosphorus atoms in the range of 104.0(3)° (N1-P1-C7) to 119.5(3)° (O1-P1-N1) for **I** and 102.4(3)° (N1-P1-C13) to 119.5(3)° (O1-P1-N1) for **II**. In both compounds, the nitrogen atom shows a non-planar geometry with the bond-angle sum of 342.2(4)° for **I** and 348(4)° for **II**. The hydrogen bond patterns of both structures are very similar to each other, in which the molecules are aggregated through N1-H1…O1-P1 hydrogen bonds (with d(N1…O1) = 2.905(7) Å for **I** and 2.842(7) Å for **II**) in a one-dimensional chain along the *a* axis for both structures, Figures 5 and 6.

In the computational study the structures of monomers and dimers of both compounds were fully optimized without symmetry restrictions at the B3LYP/6-311G** level of theory. Optimized selected geometry parameters and X-ray diffraction results of both compounds are summarized in Tables 2 and 3. The agreement between the geometrical parameters calculated on the basis of theoretical study and the experimental data is satisfactory except for dihedral angles which are different. Comparing structures of monomer and dimer of both compounds shows that P1-O1 bond lengths of both dimers are longer than their monomers (0.007 Å in I and 0.008 Å in II). Also the mean values of N-H bond lengths for the dimers of both structures are predicted as 0.011 Å longer than from the corresponding monomer values. These differences in the geometry parameters show the existence of hydrogen bonds in the dimer structures.

We quantitatively evaluated the binding energies of the dimer structures of I and II, which are -65829.667 eV and -63691.070 eV, respectively, by subtracting the two

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monomer energies (-32914.680 eV for **I** and -31845.372 eV for **II** from the dimer energies of -0.307 eV and -0.326 eV, respectively).

Vibrational Frequencies

Fundamental infrared band frequencies for **I** and **II** in the solid phase with the calculated frequencies and their assignments are given in Table 4. The assignments reported in this table are based on the calculated intensity of the bands. For the high frequencies, the assignments are straightforward. For the low frequency motions, however, the assignments are less clear cut. Table 4 includes an approximate description based on the normal modes in terms of the stretching (υ) and bending (δ) of the bonds at the B3LYP method with 6-311G** basis set. The calculated vibrational frequencies for both compounds were compared with the experimental values, using the root mean square (RMS) error analysis. The calculated frequencies are slightly higher than the observed values for the majority of the normal modes. Two factors may be responsible for the discrepancies between the experimental and computed spectra of these compounds. The first factor is caused by the environment. The second factor for these discrepancies is the fact that the experimental value is an inharmonic frequency while the calculated value is a harmonic frequency.

In this part just the vibrational bands of **I** were analyzed and the ones of **II** are similar to **I**. By analyzing IR bands of **I**, the highest frequency at 3535 cm⁻¹ is assigned to the stretching of the N1-H1 bond. The two vibrational frequencies at 1449 and 605 cm⁻¹ are assigned to the in plane and out of plane bending motions of the N1-H1 bond, respectively. We have experimentally assigned these modes to the bending of N1-H1 at 1447 and 696 cm⁻¹ with medium broad and

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weak intensities. The IR band at 1194 cm⁻¹ with stronger intensity, which has been assigned to the stretching of the P1-O1 bond, is calculated at 1211 cm⁻¹. The largest difference between calculated frequencies and experimental data in compounds I and II are for the frequencies at about 396 and 410 cm⁻¹, respectively. These modes involve symmetric stretching of the N–H bonds, having a larger effect on the dipole moment. Since in real systems N–H bonds are engaged in interactions (e.g. hydrogen bonding) that are ignored in the "gas-phase model" calculations, the vibrational frequencies seem to have increased. The other source of error may be due to the fact that the absorption band is relatively broad. However, the intensity of the peaks implies that they are correctly assigned.

Comparing selected vibrational modes of the monomers with those of the corresponding dimers, in both structure **I** and **II** the frequencies for the symmetrical stretching of the N-H bands have red shifted in the dimers from 3535 and 3536 to 3412 cm^{-1} and also the stretching modes of the P=O bonds have red shifted from 1211 and 1212 to 1188 and 1186 cm⁻¹, respectively. The results demonstrate that the N-H and P=O bonds are weakened owing the existence the hydrogen bond interaction in these structures.

Hydrogen Bonding

AIM Analysis

Atoms in molecules (AIM) is a very popular and useful method to analyze weak interactions.³¹ To better describe the nature of intermolecular interactions in the dimers of **I** and **II**, AIM analysis was carried out for structures **I** and **II** and their dimer structures (see Table 5) and the resultant graphs are shown in Figures 7, 8 and 9. According to AIM theory,³² presence of a

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hydrogen bond like any chemical bond must correspond to the existence of a bond path between hydrogen atom and acceptor containing the bond critical point (BCP), in topological analysis of electron density distribution. The most often used criteria to determine the existence of hydrogen bonding interactions is the electron density, $\rho(\mathbf{r})$, and the Laplacian of the electron density, ∇ (r), at the BCPs. Laplacian of $\rho(\mathbf{r})$ is related to bond interaction energy by a local expression of the viral theorem.³³

In structure **I**, it can be seen that P=O···H–N and P=O···H–C interactions have respective bond critical points (BCPs) and the values for the charge densities for these paths are 0.022 and 0.010 a.u., respective. The presence of the BCP corresponding to P=O···H–N further justifies the existence of this hydrogen bond. It was shown by Espinosa that the relationship between hydrogen bond energy (E) and potential energy density at the corresponding BCP (V_{BCP}) can be approximately described as $E = V_{BCP}/2.^{34}$ This enables us to evaluate the strength of the P=O···H–N and P=O···H–C hydrogen bonds separately. The V_{BCP} for the former and the latter are 0.0161 and 0.006 a.u., corresponding to hydrogen bonding energy of 0.219 eV and 0.075 eV, respectively; the sum of them is 0.294 eV (5.27 kcal.mol⁻¹). From a comparison it is clear that the P=O···H–N interaction has a major contribution to the intermolecular interaction between two molecules in **I** as well as in **II**, while the contribution from P=O···H–C is much smaller, though not completely negligible.

For the further investigation of the hydrogen bonding in these compounds the surfaces of the total electron densities of the two dimers are displayed in Figure 10. On the basis of the

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monomer analysis there is a strong interaction between the two monomers in each dimer but the interaction in the dimer of **II** is stronger as shown on the right side of Figure 10.

NBO Analysis

In the NBO analysis the electronic wave functions are interpreted in terms of a set of occupied Lewis and a set of non-Lewis localized orbital's.³⁵ Delocalization effects can be identified from the presence of off diagonal elements of the Fock matrix in the NBO basis. The strengths of these delocalization interactions are estimated by second order perturbation theory. In Tables 6 and 7, the NBO occupation numbers for the $\sigma^*(N1-H1)$ antibonding MO, the oxygen lone pairs, LP(O1), and their respective orbital energies, E, are reported. Furthermore, some significant donor–acceptor interactions and their second order perturbation stabilization energies $E^{(2)}$, which were calculated at the B3LYP/6-311G** level of theory, for the dimers of I and II are given in these tables. As is common, the orbital energies E are reported in atomic unit (a.u.), while the second order perturbation energies $E^{(2)}$ are reported in kcal.mol⁻¹.

It seems that in NBO analysis of hydrogen bonded systems, the charge transfer between the lone pairs of proton acceptor and antibonding molecular orbital of proton donor is most significant. The occupation number of $\sigma^*(N1-H1)$ antibonding MO in the dimer structures of both compounds are fairly high as compared to the monomer structures (for I the occupation number is 0.01583 e⁻ in monomer which increased to 0.02802 e⁻ in its dimer and for II the corresponding values are 0.01586 e⁻ and 0.02844 e⁻, respectively). The occupation number of antibonding MO increases from I to II and the corresponding orbital energy also increases in the same manner. It is important to note that the oxygen lone pair's occupation numbers differ from

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the ideal occupation significantly. These results can be rationalized in terms of the charge transfer interaction between the orbitals. As revealed at the bottom of Tables 6 and 7, the results of NBO analysis show that three lone pairs of the oxygen atom (O1 in I and II) participate as donor relative to the $\sigma^*(N1-H1)$ antibonding MO as acceptor in the relatively strong intermolecular charge transfer interactions, with stabilization energy values of 6.39, 0.70 and 0.27 kcal \cdot mol⁻¹ for I and 10.52, 5.14 and 0.39 kcal \cdot mol⁻¹ for II, respectively.

The contour diagrams of LPOs orbitals, BD*N–H orbitals and all hydrogen bond interactions (HB1, HB2 and HB3) of compounds **I** and **II** are shown in Figures 11 and 12. As becomes evident from these figures, the interaction between the lone pair orbitals of the oxygen atom and the antibonding molecular orbital of the N–H bond causes the formation of the hydrogen bonds in these structures. For the formation of HB1 the interaction between the orbitals is positive, but for HB2 and HB3 the interactions are about zero. Therefore HB1 interactions in both structures lead to more stabilization than HB2 and HB3 ones.

Conclusion

The synthesis and spectroscopic characterization of the two new phosphinic amides, $(C_6H_5)_2P(O)(NH-cyclo-C_7H_{13})$ (I) and $(C_6H_5)_2P(O)(NH-cyclo-C_6H_{11})$ (II), are reported and the crystal structures of them have been determined by single crystal X-ray diffraction. The hydrogen bonds for both compounds have been theoretically investigated applying B3LYP/6-311G** level of theory. The results obtained from the DFT optimization calculations, NBO analysis and the topological parameters derived from the Bader theory suggest that the hydrogen bond existing in the compound II is more stronger than compound I. There is good agreement

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between the energy of the hydrogen bond (HB) calculated from the topological parameters and from the optimization energy.

Experimental

Instrumentation

IR spectra were obtained using KBr pellets with a Buck 500 scientific spectrometer. A Varian Star 3400 CX mass spectrometer was used for mass spectrometry investigations. ¹H, ¹³C and ³¹P NMR spectra were obtained with a FT NMR Bruker Avance 300 spectrometer. Chemical shifts are given for ¹H and ¹³C relative to TMS and for ³¹P relative to 85 % H₃PO₄ as external standards. All calculations were carried out at density functional theory (DFT) level, using Gaussian 09 program.³⁶ The B3LYP/6-311G** level of theory were used to optimize the geometry of the molecules. Additionally the AIM theory of Bader³³ was used to localize bond critical points and to calculate their electron densities at bond critical points: pBCPs. The Laplacians of these densities were also calculated (Laplacians of electronic densities at bond critical points: ∇ BCPs and Laplacians of electronic densities at ring critical points: ∇ RCPs). All AIM calculations were performed using AIM2000 program.³¹ The NBO analysis was carried out using version 3.1 of NBO package³⁷ included in Gaussian 09 program at B3LYP/6-311G** level of theory. Harmonic vibrational frequency calculations at B3LYP/6-311G** level confirmed the structures as minima and enabled the evaluation of zero-point vibrational energies (ZPVE). The crystal structures of both compounds were measured using a Bruker D8 Venture diffractometer with multilayer monochromated Mo- $K\alpha$ radiation. In both compounds the hydrogen atoms attached to carbon atoms were kept in ideal positions with C-H = 0.95 - 1.00 Å

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and U_{iso} (H) set to $1.2U_{eq}$ (C) according to common practice. The non-hydrogen atoms were refined using harmonic refinement. The hydrogen atom bonded to the nitrogen atom was refined without any constrains and data were processed with the program Bruker Apex2. Both structures were solved with direct methods and refined using SHELX software.³⁸

Synthesis

Synthesis of (C₆H₅)₂P(O)(NH-cyclo-C₇H₁₃) (I)

A solution of cycloheptylamine (0.589 g, 5.2 mmol) in dry chloroform (10 mL) was added to a solution of diphenylphosphinic chloride (0.615 g, 2.6 mmol) in the same solvent at 273 K. After stirring for 3 h the solvent was removed in vacuum and the product was washed with deionized water. Single crystals of **I** were obtained from a solution of the product in methanol / heptane (4 : 1 ν/ν) after slow evaporation at room temperature. - IR (KBr, cm⁻¹): 3139, 2927, 2860, 1447, 1194, 1116, 1071, 948, 885, 749, 722, 696. MS (70 eV, EI): 312 (5) [M – 1]⁺, 310 (95) [C₁₉H₂₁NOP]⁺, 267 (29) [M – H₂ – C₃H₈]⁺, 253 (95) [M – H₂ – C₄H₁₀]⁺, 216 (78) [M – C₇H₁₃]⁺, 199 (100) [C₁₂H₈OP]⁺, 82 (38) [C₆H₁₀]⁺, 77 (93) [C₆H₅]⁺, 56 (52) [C₄H₈]⁺, 43 (44) [C₃H₇]⁺, 29 (95) [C₂H₅]⁺. ³¹P NMR (DMSO-d₆, 121.78 MHz): $\delta = 21.9$ (s). ¹H NMR: (DMSO-d₆, 300.85 MHz): $\delta = 1.28 - 2.12$ (m, 12H, CH₂ of C₇H₁₃), 2.93 (m, 1H, CH of C₇H₁₃), 3.24 (s, 1H, NH), 7.29 – 7.51 (m, 6H, Ar-H), 7.92 (m, 4H, Ar-H). ¹³C NMR (DMSO-d₆, 75.65 MHz): $\delta = 23.7$ (s), 28.1 (s), 38.4 (d, ³J_{CP} = 5.3 Hz), 52.7 (d, ²J_{CP} = 2.3 Hz), 128.5 (d, J_{CP} = 12.1 Hz), 131.7 (d, J_{CP} = 2.3 Hz), 132.1 (d, J_{CP} = 9.1 Hz), 133.2 (d, ¹J_{CP} = 129.4 Hz).

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Synthesis of (C₆H₅)₂P(O)(NH-cyclo-C₆H₁₁) (II)

Compound **II** was synthesized by a similar method as described for **I**, however using a solution of cyclohexylamine (0.595 g, 6.0 mmol) instead of cycloheptylamine [diphenylphosphinic chloride (0.710 g, 3.0 mmol)]. Single crystals of **II** were obtained from a solution of the product in ethanol / heptane (3 : 1 ν/ν) after slow evaporation at room temperature. - IR (KBr, cm⁻¹): 3126, 2927, 2858, 1745, 1442, 1375, 1308, 1197, 1101, 995, 918, 885, 726, 692. MS (70 eV, EI): 299 (15) [M]⁺, 297 (81) [M – H₂]⁺, 268 (11) [M – H – C₂H₆]⁺, 254 (81) [M – H – C₃H₈]⁺, 215 (80) [M – C₆H₁₂]⁺, 200 (92) [C₁₂H₉OP]⁺, 182 (31) [C₁₂H₇P]⁺, 98 (100) [C₆H₁₂N]⁺, 77 (80) [C₆H₅]⁺, 56 (81) [C₄H₈]⁺, 28 (79) [C₂H₄]⁺. ³¹P NMR (DMSO-d₆, 121.49 MHz): δ = 19.9 (s). ¹H NMR: (DMSO-d₆, 300.13 MHz): δ = 0.93 – 1.87 (m, 10H, CH₂ of C₆H₁₁), 2.69 (m, 1H, CH of C₆H₁₁), 5.22 (t, *J* = 9.6 Hz, 1H, NH), 7.47 (m, 6H, Ar-H), 7.78 (m, 4H, Ar-H). ¹³C NMR (DMSO-d₆, 75.47 MHz): δ = 24.97 (s), 25.02 (s), 35.6 (d, ³J_{CP} = 5.2 Hz), 4.99 (s), 128.3 (d, J_{CP} = 12.1 Hz), 131.2 (d, J_{CP} = 2.3 Hz), 131.6 (d, J_{CP} = 9.2 Hz), 134.5 (d, ¹J_{CP} = 126.3 Hz).

Supplementary material

Crystallographic data for the structures of compounds **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre CCDC, Nos. 1494129 for **I** and 1494129 for **II**. Copies of the information may 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 www: http://www.ccdc.cam.ac.uk).

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 Table 1 Crystal data and structure refinement

	Ι	II
Empirical formula	C ₁₉ H ₂₄ NOP	C ₁₈ H ₂₂ NOP
Formula weight	313.36	299.33
<i>T</i> (K)	100.0	100.0
Wave length (Å)	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P212121
<i>a</i> (Å)	8.1412(4)	8.1279(2)
<i>b</i> (Å)	12.0198(6)	11.6810(4)
<i>c</i> (Å)	16.9183(8)	16.7596(5)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
$V(\text{\AA}^3)$	1655.55(14)	1591.19(8)
Ζ	4	4
Calculated density (g/cm ³)	1.257	1.250
Absorption coefficient (µ)	0.168	0.172
F (000)	672	640
Crystal size	$0.12 \times 0.12 \times 0.1$	$0.12 \times 0.12 \times 0.11$
θ range for data collection (°)	2.078 to 25.160	2.430 to 25.024
Index ranges	$-11 \le h \le 11$	$-9 \le h \le 9$
	$-17 \le k \le 16$	$-13 \le k \le 13$
	$-23 \le l \le 24$	$-19 \le l \le 19$

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Completeness to theta	25.160°, 98.6%	25.024°, 99.8%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max and min transmission	0.8012 and 0.7039	0.7455 and 0.6593
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraint / parameter	2932 / 0 / 202	2803 / 0 / 193
Goodness of fit on F^2	1.114	1.195
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0724, wR_2 = 0.1908$	$R_1 = 0.0682, wR_2 = 0.1766$
R indices (all data)	$R_1 = 0.0784, wR_2 = 0.1947$	$R_1 = 0.0683, wR_2 = 0.1766$
Largest diff. peak and hole (e $Å^{-3}$)	1.349 and -0.520	1.141 and -0.487

Table 2 Selected geometry parameters (Å, °) of compound I

Parameters	Experimental	Theoretical		
		Monomer	Dimer	
Bonds				
P1-01	1.485(5)	1.498	1.505 1.504	
P1-C14	1.817(6)	1.829	1.830 1.830	
Р1-С8	1.817(7)	1.830	1.825 1.833	
P1-N1	1.646(6)	1.690	1.683 1.677	
N1-H1*	0.96(8)	1.015	1.014 1.026	
N1C1	1.482(8)	1.483	1.481 1.482	
C1–H1A	1.0000	1.096	1.095 1.096	
H101 ⁱ *	1.99(8)		1.971	
N101 ⁱ *	2.905(7)		2.986	
Angles				
O1-P1-C14	111.5(3)	111.724	110.842 111.119	
O1-P1-C8	109.9(3)	110.576	111.094 110.035	
01-P1-N1	119.9(3)	120.032	119.935 120.391	
P1-N1-H1	118(4)	112.438	113.063 112.394	
C1-N1-P1	121.2(5)	120.992	123.495 121.481	
C1-N1-H1	103(4)	112.275	112.780 112.241	
N1-C1-H1A	107.5	106.052	106.347 106.517	
N1-H101 ⁱ *	160(6)		169.94	
Torsion angles				
O1-P1-N1-H1	63.8(5)	81.907	77.608 67.303	

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C14-P1-N1-H1	-60.1(5)	-41.675	-44.352 -57.206
C8–P1–N1–H1	-172.4(5)	-154.364	-157.822 -168.500
H1-N1-C1-H1A	-177.69	-172.672	-168.624 -177.662

*Hydrogen bonding parameters (symmetry code (i) for I: x + 1/2, -y + 3/2, -z + 1).

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Parameters	Experimental	Theoretical		
i ulunotorio	Experimental	Monomer	Dimer	
Bonds				
P101	1.490(4)	1.498	1.506 1.504	
P1-C13	1.821(6)	1.829	1.830 1.830	
P1-C7	1.819(6)	1.829	1.823 1.833	
N1-P1	1.641(5)	1.691	1.685 1.677	
N1-H1A*	0.96(7)	1.015	1.026 1.014	
C1-N1	1.487(7)	1.477	1.476 1.477	
С1-Н1	1.000	1.096	1.096 1.096	
H1O1 ⁱ *	1.89(7)		1.976	
N101 ⁱ *	2.842(7)		2.989	
Angles				
O1-P1-C13	111.8(3)	111.81	111.25 111.20	
O1-P1-C7	110.1(3)	110.67	111.41 110.28	
O1-P1-N1	119.5(3)	119.98	119.33 120.48	
P1-N1-H1A	110(4)	112.57	112.95 112.69	
C1-N1-P1	121.0(4)	120.82	122.92 121.89	
H1A-N1-C1	117(4)	112.29	112.76 111.54	
N1C1H1	107.6	106.47	106.69 107.11	
N1-H1A01 ⁱ *	168(6)		168.61	
Torsion angles				
01-P1-N1-H1	76.23(4)	82.51	83.80 67.04	

Table 3 Selected geometry parameters (Å, °) of compound II

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C13–P1–N1–H1A	-47.94(4)	-41.13	-38.26 -57.22
C7-P1-N1-H1	-160.64(4)	-153.77	-151.22 -168.72
H1-N1-C1-H1A	-177.12	-174.40	-173.55 179.96

*Hydrogen bonding parameters (symmetry code (i) for **II**: x + 1/2, -y + 3/2, -z + 1).

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Table 4 Selected experimental and computed vibrational frequencies (cm^{-1}) for compounds I

Compound I		Com	Assignment	
Experimental	Theoretical (cm ⁻¹)	Experimental	Theoretical (cm ⁻¹)	Assignment
3139	3535 ^a (3412 ^b)	3126	3536 (3412)	υN1-H1
1447	1449 (1461)	1442	1450 (1471)	δN1-H1
1194	1211 (1188)	1197	1207 (1186)	vP1-O1
696	605 (667)	692	606 (671)	ρN1-H1

and II, using the B3LYP/6-311++G(d, p) level of the theory

a: Vibrational frequencies of monomer, b: Vibrational frequencies of dimer

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AIM analysis	Mono	omer		Dimer	
	Bonds	ρ(a.u.)	∇ (a.u.)	ρ(a.u.)	∇ (a.u.)
Compound I					
	P1-O1	0.201	-0.255	0.207 0.221	-0.194 -0.322
	N1-H1	0.316	0.288	0.308 0.333	0.384 0.370
	P1-N1	0.153	-0.068	0.004 0.175	-0.003 -0.094
	P1-C14	0.146	0.051	0.168 0.169	0.049 0.051
	P1-C8	0.146	0.052	0.013 0.171	-0.012 0.055
	P1O1H1N1			0.022	-0.022
	P1O1H1C1			0.010	-0.007
Compound II					
	P1-O1	0.224	-0.332	0.157 0.159	-0.126 -0.117
	N1-H1	0.333	0.369	0.301 0.315	0.346 0.351
	P1-N1	0.174	-0.088	0.136 0.140	-0.056 -0.054
	P1-C13	0.169	0.050	0.140 0.139	0.045 0.042
	P1-C7	0.169	0.051	0.141 0.139	0.050 0.043
	P1O1H1AN1			0.031	-0.028
	Р101Н1С1			0.005	-0.005

Table 5 AIM analysis of compounds I and II and their dimer structures

 Table 6
 NBO analysis of compound I and its dimer structure

MOs	Monor	mer	Dime	er	
	Occupancy	E (a.u.)	Occupancy	E (a.u.)	
LP1(O1)	1.98022	_ 0.70337	1.96826	-0.70606	
LP2(O1)	1.83024	- 0.24169	1.84468	-0.25547	
LP3(O1)	1.79705	- 0.24084	1.8128	-0.25461	
σ*(N1-H1)	0.01583	- 0.41766	0.02802	0.47162	
Donor MOs in dimer		Acceptor MOs in dimer	$E^{(2)}$ (kcal.mol ⁻¹)		
LP1(O1)		σ*(N1-H1)	6.39		
LP2(O1)		σ*(N1-H1)	0.70		
LP3(O1)			σ*(N1-H1)	0.27	

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MOs	Monomer		Dimer	
1.200	Occupancy	E (a.u.)	Occupancy	E (a.u.)
LP1(O1)	1.98028	-0.70380	1.96870	-0.70875
LP2(O1)	1.83002	-0.24182	1.84420	-0.25706
LP3(O1)	1.79706	-0.24090	1.81413	-0.25584
σ*(N1-H1)	0.01586	0.41689	0.02844	0.47006
Donor MOs in dimer		Acceptor MOs in dimer	$E^{(2)}$ (kcal.mol ⁻¹)	
LP1(O1)			σ*(N1-H1)	10.52
LP2(O1)		σ*(N1-H1)	5.14	
LP3(O1)			σ*(N1-H1)	0.39

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Figure 1 Chemical structure of compound ${\bf I}$

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Figure 2 Chemical structure of compound II

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Figure 3 Displacement ellipsoid plot (50 % probability) and atom numbering scheme for **I**. H atoms are drawn as spheres of arbitrary radii.

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Figure 4 Displacement ellipsoid plot (50 % probability) and atom numbering scheme for **II**. H atoms are drawn as spheres of arbitrary radii.

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Figure 5 A partial view of the crystal packing of **I**, showing the linear arrangement built from $N-H\cdots O=P$ hydrogen bonds. The hydrogen bonds are shown as dotted lines.

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Figure 6 A partial view of the crystal packing of **II**, showing the linear arrangement built from N–H···O=P hydrogen bonds. The hydrogen bonds are shown as dotted lines.

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Figure 7 Bond critical point of **a**: **I** and **b**: **II**. Orange spheres correspond to (3,–1) types of critical points (CPs), brown lines denote bond paths

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Figure 8 Selected bond critical points of the dimer of I

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Figure 9 Selected bond critical points of the dimer of II

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Figure 10 Contour diagram of the total electron density of **a**: dimer of **I** and **b**: dimer of **II**

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Figure 11 Contour diagram of the BD* orbital of N–H, LPs orbitals of oxygen atom and the all hydrogen bonds in compound **I**

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Figure 12 Contour diagram of the BD* orbital of N–H, LPs orbitals of oxygen atom and the all hydrogen bonds in compound **II**

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