ORIGINAL RESEARCH

Different orientations of C=O versus P=O in P(O)NHC(O) skeleton: the first study on an aliphatic diazaphosphorinane with a *gauche* orientation

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Abstract Different orientations of P(O) versus C(O) in P(O)NHC(O) skeleton have been discussed in two new phosphorus(V)-nitrogen compounds with formula XP(O)Y and $XP(O)Z_2$ where $X = NHC(O)C_6H_4(4-F)$ and Y =NHCH₂C(CH₃)₂CH₂NH (1), $Z = NHC_6H_4(4-CH_3)$ (2). Compound 1 is the first example of an aliphatic diazaphosphorinane with a gauche orientation which has been studied by X-ray crystallography; the P=O bond is in the equatorial position of the ring. Both compounds show ^{*n*} J(F,C) and ^{*m*} J(F,H) coupling constants (n = 1, 2, 3 and 4; m = 3 and 4) and ${}^{3}J(P,C) > {}^{2}J(P,C)$. Quantum chemical calculations were performed with HF and Density Functional Theory (DFT) methods using 6-31+G(d,p) basis set. A tentative assignment of the observed vibrational bands for these molecules is discussed. Compound 1 shows a deshielded C atom of the carbonyl moiety (in ¹³C NMR spectrum) relative to that of 2, which is supported by IR spectroscopy in which the considerably lower C=O frequency is observed for 1. Comparing the X-ray crystallography and IR spectra of 1 and 2 shows that the acyclic

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A. L. Rheingold · J. A. Golen Department of Chemistry, University of California, San Diego, 9500 Gilman, Drive, La Jolla, CA 92093, USA compound **2**, containing P=O and C=O bonds in an *anti* position, are involving in a stronger N–H···O=P hydrogen bond in crystal network. This leads to a weaker P=O and $N_{C(O)NHP(O)}$ –H bonds and stronger N···O interaction. The N_{amide} –H is involved in an intramolecular N–H···O hydrogen bond.

Keywords Phosphoric triamides · NMR · X-ray crystallography · Hydrogen bonds · Chemical calculation

Introduction

The study on O atoms' orientation in P(O)NHC(O) moiety of N-carbonyl phosphoramidates is important because of the structural features, hydrogen bonding patterns, and binding manner to metal cations [1-5]. The *anti* orientation is preferred for the C=O versus P=O unit [6, 7]. Some researchers have employed the anionic form $[P(O)NC(O)]^{-}$ to obtain compounds with a non-anti orientation [8] and better donority properties [9]. Despite the numerous structures reported in this series [10–19], there are a few neutral structures with synclinal orientation [2, 5, 13–17, 19]. Here, we study on two new compounds with different orientations of C=O versus P=O. Moreover, the diazaphosphorinane reported in this work is the first example of a structurally investigated aliphatic diazaphosphorinane with a gauche orientation. The structural and spectroscopic features of new synthesized compounds (1 and 2) are studied. Moreover, their optimized geometric parameters and vibrational frequencies are calculated by theoretical methods (HF and DFT) and a tentative assignment of the observed vibrational bands is discussed.

Experimental

General methods and materials

¹H, ¹³C, ¹H–¹³C HSQC, ¹⁹F, ³¹P{¹H} NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ¹H and ¹³C chemical shifts were determined relative to TMS, and ³¹P and ¹⁹F chemical shifts, respectively, relative to 85% H₃PO₄ and CFCl₃ as external standards. Infrared (IR) spectra were recorded on a Buck 500 scientific spectrometer using KBr disc. 4-F-C₆H₄C(O)NHP(O)Cl₂ was prepared according to the literature method for 4-NO₂-C₆H₄C(O)NHP(O)Cl₂ by using 4-F-C₆H₄C(O)NH₂ instead of 4-NO₂-C₆H₄C(O)NH₂ [7].

X-ray measurements

A colorless crystal of compound 1 was mounted on a Mitegen Micromount with Bruker uv adhesive and was then automatically centered on a Bruker SMART X2S benchtop crystallographic instrument. Intensity measurements were performed using a monochromated (Doubly Curved Silicon Crystal) Mo K α radiation (0.71073 Å) from a sealed Micro Focus tube. Data were acquired under a stream of dry cold air at 200(2) K using three sets of omega scans at different phi settings with frame width of 0.5° and an exposure time of 30 s/frame. Apex 2 software was used for preliminary determination of the unit cell and determination of integral intensities and unit cell refinement were performed using SAINT. Data was corrected for absorption using SADABS and structure was solved by direct methods. A colorless crystal of sample 2 was mounted on a Cryoloop with Paratone-N oil. Data were collected on a Bruker APEX CCD X-ray system using Mo Ka radiation in a nitrogen gas stream at 100(2) K using phi and omega scans with frame width of 0.5° and exposure time of 10 s/frame. Data was integrated using the Bruker suite of software programs [20], corrected for absorption using SADABS and structure was solved by direct methods. For both structures all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^{2} (SHELXL-97) [21] and hydrogen atoms on atoms N1, N2, and N3 were found from a Fourier difference map and were allowed to refine. All other hydrogen atoms were placed in calculated positions with appropriate riding models.

Syntheses

5,5-Dimethyl-2-[*N*-(4-fluorobenzoyl)]-2-oxo-1,3, 2-diazaphosphorinane (1)

2,2-Dimethyl-1,3-propanediamine was added dropwise to a solution of 4-F-C₆H₄C(O)NHP(O)Cl₂ in chloroform

(2:1 mole ratio) and was stirred at -5 °C for 4 h. After the solvent was removed, the product was washed with distilled water and recrystallized from methanol/acetonitrile at room temperature. IR (KBr, cm^{-1}): v = 3327 (NH), 3199 (NH), 2941, 2230, 1636 (C=O), 1454, 1379, 1281 (P=O), 1209, 1088, 955 (P-Namide), 858, 785 (P-N_{C(O)NHP(O)}), 668. ¹H NMR (500.13 MHz, DMSO-*d*₆, 300.0 K, TMS): $\delta = 0.76$ (s, 3H, CH₃), 1.09 (s, 3H, CH₃), 2.59 (ddd, ${}^{3}J(H,H) = 5.3 \text{ Hz}, {}^{2}J(H,H) = 11.7 \text{ Hz}, {}^{3}J(P,H) = 26.3 \text{ Hz},$ 2H, CH_{equatorial}), 3.00 (d, ${}^{2}J(H,H) = 12.1$ Hz, 2H, CH_{axial}), 4.59 (s, 2H, NH_{amide}), 7.28 (t, ${}^{3}J[(H,H), (H,F)] = 8.8$ Hz, 2H, Ar–H), 8.04 (dd, ${}^{3}J(H,H) = 8.7$ Hz, ${}^{4}J(H,F) = 5.5$ Hz, 2H, Ar-H), 9.30 (s, 1H, NH_{C(O)NHP(O)}). ¹³C NMR (125.75 MHz, DMSO- d_6 , 300.0 K, TMS): $\delta = 23.05$ (s, 1C, CH₃), 24.83 (s, 1C, CH₃), 30.22 (d, ${}^{3}J(P,C) = 4.8$ Hz, 1C, CMe₂), 53.21 (d, ${}^{2}J(P,C) = 2.4$ Hz, 2C, CH₂), 115.16 (d, ${}^{2}J(F,C) = 21.9$ Hz, 2C), 130.35 (dd, ${}^{3}J(P,C) = 7.6$ Hz, ${}^{4}J(F,C) = 2.7$ Hz, 1C, C_{ipso}), 130.81 (d, ${}^{3}J(F,C) = 9.2$ Hz, 2C), 164.29 (d, ${}^{1}J(F,C) = 249.5$ Hz, 1C), 167.67 (s, 1C, C=O). ³¹P{¹H} NMR (202.45 MHz, DMSO-*d*₆, 300.0 K, H₃PO₄ external): $\delta = 2.15$ (s). ¹⁹F NMR (470.59 MHz, DMSO- d_6 , 300.0 K, CFCl₃): $\delta = -108.77$ (m).

N-(4-Fluorobenzoyl)-N',N''-bis (4-methyl-phenyl) phosphoric triamide (**2**)

To a solution of 4-F-C₆H₄C(O)NHP(O)Cl₂ in chloroform, a solution of *p*-toluidine and triethylamine (1:2:2 mole ratio) in chloroform were added at -5 °C. After 4 h stirring, the solvent was removed and product was washed with distilled water and recrystallized from methanol/n-heptane at room temperature. IR (KBr, cm^{-1}): v = 3270 (NH), 3091 (NH), 2920, 1656 (C=O), 1520, 1446, 1379, 1228 (P=O), 1101, 945, 824 (P-N_{amide}), 746 (P-N_{C(O)NHP(O)}). ¹H NMR $(500.13 \text{ MHz}, \text{DMSO-}d_6, 300.0 \text{ K}, \text{TMS}): \delta = 2.16 \text{ (s, 6H,}$ 2CH₃), 6.96 (d, ${}^{3}J(H,H) = 7.7$ Hz, 4H, Ar–H), 7.05 (d, ${}^{3}J(H,H) = 8.1$ Hz, 4H, Ar–H), 7.28 (t, 2H, Ar–H), 7.69 (d, ${}^{2}J(P,H) = 9.4$ Hz, 2H, NH), 7.99 (m, 2H, Ar–H), 9.88 (s, 1H, NH_{C(O)NHP(O)}). ¹³C NMR (125.75 MHz, DMSO-*d*₆, 300.0 K, TMS): $\delta = 20.17$ (s, 2C, CH₃), 115.29 (d, ${}^{2}J(F,C) = 21.9 \text{ Hz}, 2C), 117.84 \text{ (d, }{}^{3}J(P,C) = 7.2 \text{ Hz}, 4C),$ 129.15 (s, 4C), 129.20 (s, 2C), 129.85 (dd, 1C, C_{inso}), 130.95 (d, ${}^{3}J(F,C) = 9.3$ Hz, 2C), 138.61 (s, 2C), 164.48 $(d, {}^{1}J(F,C) = 250.1 \text{ Hz}, 1C), 166.85 (s, 1C, C=O). {}^{31}P{}^{1}H$ NMR (202.45 MHz, DMSO-d₆, 300.0 K, H₃PO₄ external): $\delta = -4.61$ (s).

Computational approaches

All calculations [Density functional (DF) and Hartree– Fock (HF)] were performed using the Gaussian 03W program package [22] and Gauss-View 3.07 molecular visualization program [23] and the X-ray data (cif files) were used as the initial structure. Among the variety of functionals, including nonlocal corrections, we used Becke's three-parameter hybrid functional using the Lee–Yang–Parr correlation functional (B3LYP) [24]. Geometry optimization and calculation of vibrational frequencies were investigated with the widely used 6-31+G(d,p) basis set for both HF and DFT methods. No scale factor was used in the calculated frequencies.

Results and discussion

Heterocyclic compound **1** (Scheme 1, right) was synthesized by the reaction of 4-F-C₆H₄C(O)NHP(O)Cl₂ and two times mole ratio of diamine (one half as nucleophile and others as HCl scavenger). Compound **2** (Scheme 1, left) was prepared in a similar manner but by using triethylamine as an organic base instead of the excess amount of amine. The phosphoramide functional group is NHP(O). Two different types of this functional group, NHP(O) and C(O)NHP(O) in compounds **1** and **2**, are introduced as N_{amide} and $N_{C(O)NHP(O)}$ for their related nitrogen atoms in the next sections of paper.

NMR studies

The related signals of H_{axial} and $H_{equatorial}$ in compound 1 can be differentiated by their different splitting patterns. Considering the Karplus equation [25] and the torsion



Scheme 1 The non-*anti* orientation of P(O) versus C=O (*right*, compound 1) and *anti* orientation (*left*, compound 2), the *values* in the scheme are the bond lengths (\mathring{A})

angles of about $\pm 70^{\circ}$ for P-N-C-H_{axial} and $\pm 170^{\circ}$ for P-N-C-H_{equatorial} obtained from X-ray crystallography, the value of 26.3 Hz is assigned to ${}^{3}J(\text{PNCH}_{\text{equatorial}})$. This is larger than the ${}^{3}J(PNCH)$ values for acyclic phosphoramidates, for example in compound CCl₃C(O)NHP(O) $[N(CH_3)(CH_2C_6H_5)]_2$ ³J(P,H) = 10.2 and 9.1 Hz for CH₃ and CH_2 units [10]. The phosphorus- H_{axial} coupling is not observed. Two doublet signals at 30.22 and 53.21 ppm in 13 C NMR spectrum of **1** are, respectively, assigned to the carbon atoms with three- and two-bond separations from phosphorus with ${}^{3}J(P,C) = 4.8 > {}^{2}J(P,C) = 2.4$ Hz. This is in agreement with the previously reported diazaphosphorinane compounds [26] and compounds with cyclic five- and six-membered ring amide groups linked to P atom, and in contrast with the reported acyclic amides such as N(CH₂CH₃)₂ and N(CH₂CH₃)(CH₂C₆H₅) which show ${}^{2}J(P,C) > {}^{3}J(P,C)$ [27] (NR¹R² is introduced as an amide moiety, where R^1 and/or R^2 are H, alkyl, or aryl). Moreover, in the 4-F-C₆H₄C(O)NHP(O) moiety, ${}^{3}J(P,C) =$ $7.6 > {}^{2}J(P,C) = 0.0$ Hz. A similar observation is found for compound 2: ${}^{3}J(P,C) > {}^{2}J(P,C)$ in both 4-F-C₆H₄C(O) NHP(O) and P(O)[NHC₆H₄-(4-CH₃)] moieties. In contrast to $NHCH_2C(CH_3)_2CH_2NH$ in compound 1, the NH proton of the 4-CH₃-C₆H₄NH moiety in 2 reveals as a doublet signal $({}^{2}J(P,H) = 9.4$ Hz). Compounds 1 and 2 show ^{*m*} J(F,H) and ^{*n*} J(F,C) coupling constants (m = 3 and 4; n = 1, 2, 3, and 4). For example, in compound 1: ${}^{3}J(H,F) = 8.8$ Hz, ${}^{4}J(H,F) = 5.5$ Hz (these fluorinehydrogen couplings lead to the multiplet peak in ¹⁹F NMR spectrum, Fig. S1 in Supplementary material), ${}^{1}J(F,C) =$ 249.5 Hz, ${}^{2}J(F,C) = 21.9$ Hz, ${}^{3}J(F,C) = 9.2$ Hz, ${}^{4}J(F,C) = 2.7$ Hz. To confirm this assignment, the ${}^{1}H^{-13}C$ HSQC (H-C correlation spectrum) spectrum was obtained for compound 1 (Fig. S2 in Supplementary material) which shows the signals at 7.28 and 8.04 ppm (showing the ${}^{3}J(H,F)$ and ${}^{4}J(H,F)$) in ${}^{1}H$ NMR spectrum are related, respectively, to the carbon atoms at 115.16 and 130.81 ppm (showing ${}^{2}J(F,C)$ and ${}^{3}J(F,C)$) in ${}^{13}C$ NMR spectrum. Compound 1 with a gauche orientation of C=O versus P=O shows a deshielded carbon atom of carbonyl moiety relative to that of 2 (167.67 ppm for 1 and 166.85 ppm for 2). This is supported by IR spectroscopy in which a lower C=O frequency is observed for 1 (1636 vs 1656 cm^{-1} for 2).

Structural description

Single crystals of compounds **1** and **2** were, respectively, obtained from CH_3OH/CH_3CN and $CH_3OH/n-C_7H_{16}$ at r.t. Crystallographic data and the details of X-ray analysis are presented in Table 1; selected experimental (X-ray) and calculated (at 6-31+G(d,p) basis set) geometrical parameters are given in Table 2. The molecular structures

 Table 1 Crystal data and structure refinement for compounds 1 and 2

	Compound 1	Compound 2	
Empirical formula	$C_{12}H_{17}FN_3O_2P$	$C_{21}H_{21}FN_3O_2P$	
Formula weight	285.26	397.38	
Temperature (K)	200(2)	100(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	Orthorhombic	Monoclinic	
Space group	<i>Pca2</i> (1)	C2/c	
Unit cell dimensions	a = 10.269(3) Å	a = 24.712(6) Å	
	b = 13.204(3) Å	b = 17.238(4) Å	
	c = 10.238(2) Å	c = 9.874(3) Å	
		$\beta = 110.052(4)^{\circ}$	
Volume (Å ³)	1388.1(6)	3951.1(17)	
Ζ	4	8	
Density (calculated) (Mg/m ³)	1.365	1.336	
Absorption coefficient (mm ⁻¹)	0.211	0.170	
F(000)	600	1664	
Crystal size (mm ³)	$0.50 \times 0.15 \times 0.15$	$0.45\times0.10\times0.10$	
Crystal color/habit	Colorless/block	Colorless/block	
Theta range for data collection (°)	2.51-28.11	1.47–27.91	
Index ranges	$-12 \le h \le 13$	$-32 \le h \le 32$	
	$-17 \le k \le 17$	$-22 \le k \le 22$	
	$-13 \le l \le 13$	$-12 \le l \le 12$	
Reflections collected	10,526	16,310	
Independent reflections	$3,169 \ [R(int) = 0.0528]$	$4,456 \ [R(int) = 0.0508]$	
Completeness to theta = 25.00°	99.90%	96.90%	
Absorption correction	Multi-scan/sadabs	Multi-scan/sadabs	
Max. and min. transmission	0.9690 and 0.9016	0.9832 and 0.9274	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	
Data/restraints/parameters	3169/1/186	4456/0/267	
Goodness-of-fit on F^2	1.011	1.036	
Final R indices $[I > 2 \text{sigma}(I)]$	$R_1 = 0.0460, wR_2 = 0.0915$	$R_1 = 0.0467, wR_2 = 0.1091$	
R indices (all data)	$R_1 = 0.0648, wR_2 = 0.0980$	$R_1 = 0.0757, wR_2 = 0.1235$	
Absolute structure parameter	-0.06(11)	_	
Largest diff. peak and hole $(e \cdot \text{\AA}^{-3})$	0.316 and -0.228	0.274 and -0.393	

of **1** and **2** are shown in Figs. 1 and 2, respectively. The phosphorus atoms have a distorted tetrahedral configuration with the bond angles in the range of $101.29(12)^{\circ}$ [N(2)–P(1)–N(3)] to $114.74(11)^{\circ}$ [O(1)–P(1)–N(1)] for **1** and $103.86(8)^{\circ}$ [N(3)–P(1)–N(1)] to $115.99(9)^{\circ}$ [O(1)– P(1)–N(3)] for **2**. The phosphoryl and carbonyl groups adopt an *anti* position in **2**, whereas they are in a *gauche* situation in **1**. Many phosphoric triamides of the type RC(O)NHP(O)[NR¹R²]₂ have been investigated structurally [1, 2, 5–7, 10, 11, 13–19, 27–55]; however, the non*anti* orientation has been observed for a few molecules [2, 5, 13–19]. In Tables S1 and S2 (Supplementary material), some structural parameters of selected molecules with different conformations are gathered. The O=P–N–C dihedral angles vary in the range of nearly $\pm 180^{\circ}$ to $\pm 150^{\circ}$ and $-62.3(3)^{\circ}$ to $-53.07(8)^{\circ}$ for molecules with *anti* and *gauche* conformations, Table S2 in Supplementary material. Moreover, the P–N_{C(O)NHP(O)}–C bond angles show a slight differences, Table S1 in Supplementary material; so that the P–N_{C(O)NHP(O)}–C angle (*h* in Table S1, Supplementary material) has a lower value in most cases of a *gauche* orientation, for example $h = 120.5(2)^{\circ}$ (for 1) and 123.40(13)° (for 2). Considering the present work, up to now, the structures of two diazaphosphorinanes with a C(O)NHP(O) skeleton have been studied (entries 2 and 23); so that the diazaphosphorinane 1 (entry 23) is the first example of a structurally investigated aliphatic diazaphosphorinane with a *gauche* orientation. The

 Table 2
 Selected bond distances (Å) and angles (°) for compounds 1 and 2

Parameter	Compound 1			Compound 2		
	X-ray	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)	X-ray	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
Length bonds						
P=O	1.4725(19)	1.456	1.485	1.4755(13)	1.458	1.486
P-N _{C(O)NHP(O)}	1.700(2)	1.712	1.741	1.6756(17)	1.700	1.729
P–N _{(1)amide}	1.631(2)	1.648	1.672	1.6450(17)	1.653	1.672
P-N _{(2)amide}	1.629(2)	1.657	1.680	1.6296(16)	1.656	1.680
C=O	1.232(3)	1.202	1.230	1.233(2)	1.207	1.235
C-N _{(1)amide}	1.474(3)	1.463	1.477	1.427(2)	1.419	1.421
C-N _{(2)amide}	1.468(3)	1.464	1.476	1.412(2)	1.420	1.423
C-N _{C(O)NHP(O)}	1.352(3)	1.368	1.380	1.369(2)	1.363	1.376
C–F	1.358(3)	1.329	1.356	1.357(2)	1.328	1.355
Angles						
O=P-N _{(1)amide}	114.74(11)	115.59	116.05	115.99(9)	117.54	118.80
O=P-N _{(2)amide}	113.91(12)	114.81	114.87	114.01(8)	114.42	114.53
O=P-N _{C(O)NHP(O)}	110.34(11)	113.67	113.61	107.85(8)	107.61	107.83
Namide-P-Namide	105.32(12)	104.25	104.57	104.60(8)	105.01	104.43
N _{(1)amide} -P-N _{C(O)NHP(O)}	110.32(11)	107.47	106.87	103.86(8)	103.21	102.17
N _{(2)amide} -P-N _{C(O)NHP(O)}	101.29(12)	99.42	99.11	110.01(8)	108.21	108.02
P-N _{(1)amide} -C	119.72(18)	119.88	119.17	124.69(14)	125.10	125.93
P-N _{(2)amide} -C	120.29(19)	119.72	119.38	128.70(13)	125.10	126.46
P-N _{C(O)NHP(O)} -C	120.5(2)	124.57	124.56	123.40(13)	125.99	125.88
N-C=O	120.9(2)	121.70	121.71	120.31(18)	120.78	120.64
Torsion angles						
O=P-N _{C(O)NHP(O)} -C	-57.2(2)	-75.65	-79.67	176.85(14)	178.36	-178.77
P-N _{C(O)NHP(O)} -C=O	-12.6(3)	-16.79	-15.13	8.7(2)	8.74	9.10
C-N _{C(O)NHP(O)} -P-N _{(1)amide}	70.6(2)	53.57	49.64	-59.54(16)	-56.69	-52.81
C-N _{C(O)NHP(O)} -P-N _{(2)amide}	-178.2(2)	161.86	157.99	51.94(17)	54.24	56.96

Fig. 1 Molecular structure and atom labeling scheme for compound 1 with displacement ellipsoids at the 50% probability level



C–N_{C(O)NHP(O)} bond length in **1** is shorter than that of **2** and the opposite is observed for the P–N_{C(O)NHP(O)} bond length, Scheme 1. The P=O bond lengths of 1.4725(19) Å (**1**) and 1.4755(13) Å (**2**) are standard for the phosphoric triamide compounds. The P–N_{C(O)NHP(O)} in **1** (1.700(2) Å) is slightly longer than that of **2** (1.6756(17) Å). The P–N_{amide} bond lengths of 1.629(2) and 1.631(2) Å in **1** and 1.6296(16) and 1.6450(17) Å in **2** are significantly shorter than the related P–N_{C(O)NHP(O)}. In both structures, the N atoms are almost planar and they do not form any HB as an acceptor, thus exhibiting low Lewis-base character. Deviation from planarity in nitrogen atoms of the diazaphosphorinane moiety in **1** is more than that of P(O)[NHC₆ H₄(4-CH₃)]₂ moiety in **2**. As expected, the C–N_{C(O)NHP(O)}



Fig. 2 Molecular structure and atom labeling scheme for compound 2 with displacement ellipsoids at the 50% probability level

bond lengths of 1.352(3) Å (1) and 1.369(2) Å (2) were found to be shorter than the other C-N bond lengths (1.474(3) and 1.468(3) Å in 1 and 1.412(2) and 1.427(2) Å in 2). In diazaphosphorinane ring, the P=O bond is placed in an equatorial position, attributed to the endo anomeric effect which was previously observed by Bentrude for 1,3,2-oxazaphosphorinane [56]. Moreover, this configuration has been found for another derivative of diazaphosphorinane family reported by Gholivand et al. [57]. This situation is observed for 1 probably via overlapping of the non-bonding orbital located on the endocyclic nitrogen atoms with the anti-bonding orbital of P-N(exocyclic) [56]. This *n* to σ^* overlap should stabilize the lying of $P-N_{NHC(O)C_6H_4-F}$ bond in axial position (Scheme 2). This overlap helps to decrease the pyramidality of the N atoms. The crystal packing adopted allows putting the benzoyl substituent in a position where it has the less steric effect. The HB interactions lead to a 2-D network parallel to the [010] plane. This arrangement is composed of cyclic tetramer motifs via two different types intermolecular N-H···O hydrogen bonds (N(3)-H(3C)···O(1) and N(2)- $H(2A)\cdots O(2)$ HBs, Table 3). This motif is a result of the gauche orientation of P=O versus C=O, due to the suitable arrangement of oxygen atoms which are gathered molecules in a cyclic arrangement through HBs, see the pinkcolored molecule in Fig. 3. Each molecule contains two H-acceptor centers (O atoms) which involve them with two



Scheme 2 The endo anomeric effect in 1,3,2-diazaphosphorinane 1; for related literature about endo anomeric effect in 1,3,2-oxazaphosphorinanes, see Ref. [56]

Table 3 Hydrogen bonds for compounds 1 and 2 (Å and °)

D–H···A	d(D-H)	$d(H \cdots A)$	$d(D \cdots A)$	∠(DHA)
Compound 1				
$N(3)-H(3C)\cdots O(1)^{\#1}$	0.82(3)	2.08(3)	2.885(3)	168(2)
$N(2)-H(2A)\cdots O(2)^{#2}$	0.79(3)	2.25(3)	3.019(3)	166(3)
N(1)-H(1C)···O(1) ^{#3}	0.81(3)	2.54(3)	3.183(3)	138(3)
N(1)-H(1C)···O(2)	0.81(3)	2.77(3)	3.184(3)	113(3)
Compound 2				
$N(1)-H(1B)\cdots O(1)^{\#1}$	0.79(2)	2.00(2)	2.792(2)	173(2)
$N(2)-H(2B)\cdots O(2)^{#2}$	0.83(2)	2.08(3)	2.897(2)	170(2)
$N(3)-H(3B)\cdots O(2)$	0.82(2)	2.39(2)	2.959(2)	128(2)

Symmetry transformations used to generate equivalent atoms for compound 1:#1 -x + 1/2, $y, z + \frac{1}{2}$; #2 x + 1/2, -y + 1, z; #3 x - 1/2, -y + 1, z; for compound 2: #1 -x + 1, y, $-z + \frac{1}{2}$; #2 -x + 1, y, $-z + \frac{3}{2}$

H-donor sites (N atoms) in the normal HB interactions; i.e., one of the N_{amide} -H units does not cooperate in the normal HB interaction (it cooperates in a weak HB). So, the four interacting molecules (within the tetramer motif) provide the following interacting sites: (a) two H-acceptor sites by the first molecule, (b) two H-donor sites by the second one, c and d) both two other molecules provide one H-acceptor and one H-donor in which one of them provides the C=O and the nitrogen atom of C(O)NHP(O) moiety and the other its P=O and the N_{amide}-H unit, Fig. 3. The other possible interacting sites, which are not involved within the mentioned tetramer, are responsible for the interaction of the tetramer with the neighboring tetramers. This causes to



Fig. 3 Cyclic tetramer motif in crystal structure of 1, the H-acceptor atoms in the tetramer are shown with *red balls* and the H-donor with *blue balls*; the *gauche* orientation of P=O versus C=O allows to arrange the molecule in a cyclic motif (Color figure online)

lay one tetramer between eight other tetramers. Moreover, if the weaker intramolecular $N(1)-H(1C)\cdots O(2)$ and intermolecular $N(1)-H(1C)\cdots O(1)$ hydrogen bonds have also been considered, the arrangement is still a 2-D array; i.e., these HBs have little influence on the architecture of the molecules in the network but they help in the stabilization of crystal packing. A fragment of crystal packing viewed along the *a* axis is shown in Fig. 4. Similar to HBs

Fig. 4 A fragment of crystal packing of 1

of compound 1 $[N(3)-H(3C)\cdots O(1)]$ and $N(2)-H(2A)\cdots O(2)$ HBs], compound 2 is also exhibited along with hydrogen bonding interactions involving the oxygen atoms (of P=O and C=O) and the H-donor sites, $H-N_{C(O)NHP(O)}$ and H-N_{amide}. The anti orientation is responsible to form the extended chain in the crystal network which is parallel to the c axis. Furthermore, both $P=O\cdots H-N_{C(O)NHP(O)}$ and C=O···H-N_{amide} hydrogen bonds are slightly stronger than the similar HBs in compound 1. These observations are supported by IR spectra in which the lower N-H and P=O frequencies are found for 2 that those of observed for 1. Moreover, an intramolecular HB exists between the N_{amide}-H and the carbonyl' O atom which is responsible to lowering N_{amide}-H frequency in 2 which will discuss later. A fragment of crystal packing viewed along the c axis is shown in Fig. 5.

Theoretical studies

Geometry optimization

The geometries of compounds **1** and **2** were optimized using the HF and DFT methods (the B3LYP functional) with 6-31+G(d,p) basis set. The optimized geometric parameters are shown in Table 2. By comparison, all bond lengths obtained by the DFT method are longer than those of HF, and, overall, better bond length prediction is achieved with DFT. For instance, C=O and C-F bond lengths in **1** and **2** are better predicted by DFT with a difference from experimental values about 0.002 Å for both. The HF method is slightly better than the DFT method for the bond angles





Fig. 5 A fragment of crystal packing of 2

(Table 2). In general, the optimized geometries of 1 and 2 are in good agreement with the experimental ones, and the general trends observed in the experimental data are well reproduced in the calculations.

Vibrational frequencies

The vibrational frequencies are computed for the optimized structures of molecules **1** and **2**, by the DFT (B3LYP) and HF methods using the 6-31+G(d,p) basis set. The most important experimental and calculated absorption bands are listed in Table 4. The observed bands are assigned by comparison of the calculated frequencies with experimental IR spectra of related molecules [58, 59]. The N–H bending modes occur in the 1600–1450 cm⁻¹ region. For example, the experimental value of 1446 cm⁻¹ for $\delta(N_{C(O)NHP(O)}-H)$ in **2** is supported by calculation (Table 4). The frequency

Table 4 Selected calculated and experimental vibrational data $(\rm cm^{-1})$ for compounds 1 and 2 using HF and DFT methods with $6{-}31{+}G(d,p)$ basis set

Experimental	Calculated		Tentative assignment
	HF	DFT	
Compound 1			
3199(s)	3883	3617	υ (N _{C(O)NHP(O)} –H)
3327(s)	3824	3594	υ (N _{amide} –H)
2941(s)	3158	2988	US CH ₂
1636(vs)	1922	1725	υ (C=O)
1454(s)	1597	1430	$\upsilon (\text{OC-N}_{\text{C(O)NHP(O)}}) + \delta (\text{N}_{\text{C(O)NHP(O)}}-\text{H})$
1281(m)	1374	1260	υ (P=O)
1088(s)	1175	1078	v_{as} (C–N _{amide}) + ρ CH ₃
955(m)	1038	956	v_{as} (P–N _{amide}) + ρ CH ₃ + τ CH ₂
858(s)	928	868	γ (C–H) ring
785(m)	895	796	$v (P-N_{C(O)NHP(O)}) + \Delta ring$
668(m)	692	644	$\gamma (N_{C(O)NHP(O)}-H) + \Delta ring$
Compound 2			
3091(s)	3875	3619	υ (N _{C(O)NHP(O)} –H)
3270(s)	3818	3525	υ (N _{amide} –H)
2920(s)	3180	3030	vs CH ₃
1656(vs)	1897	1706	υ (C=O)
1520(s)	1608	1507	$\delta ext{ CH}_3$
1446(s)	1552	1458	$\upsilon (\text{OC}-\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}) + \delta (\text{N}_{\text{C}(\text{O})\text{NHP}(\text{O})}-\text{H})$
1228(vs)	1347	1273	υ (P=O)
1101(w)	1114	1034	$\Delta \operatorname{ring} + \delta (C-H) \operatorname{ring}$
946(s)	1013	933	v_{as} (P–N _{amide}) + γ (C–H) ring
824(s)	925	826	γ (C–H) ring
746(s)	872	793	υ (P-N _{C(O)NHP(O)})

v Stretching, δ in plane bending, γ out of plane bending, τ twisting, ρ rocking, Δ in plane ring deformation

about the 1200 cm^{-1} wave number (for example, in 1, at 1281 cm⁻¹) is assigned to the stretching vibration of the phosphoryl group. The N_{C(O)NHP(O)}-P and N_{amide}-P stretching modes, the other characteristic fundamentals for this class of phosphoric triamide compounds, are observed in the 900–700 cm^{-1} region. These fundamental modes appear at 746 cm⁻¹ (calculated: 793 cm⁻¹) and 946 cm⁻¹ (calculated: 933 cm^{-1}) in IR spectrum of **2**, respectively. Moreover, two vibrational modes at 1088 and 668 cm^{-1} in **1** are, respectively, attributed to the C-Namide stretching and the N_{C(O)NHP(O)}-H out of plane bending modes. Also, in 2, the vibrational mode at 1101 cm^{-1} is assigned to the in plane ring deformation coupled with the bending mode of C-H (aromatic). The experimental $v(N_{C(O)NHP(O)}-H)$ frequency appears at lower frequency relative to the calculated one and then relative to experimental v(Namide-H) frequency. This is attributed to the presence of relatively strong HB between

the $N_{C(O)NHP(O)}$ -H acidic proton and the phosphoryl group of neighboring molecule in solid state. It had been found that [5] the coordination to the metal cation breaks this type of P=O…H-N intermolecular HB leading to the higher $v(N_{C(O)NHP(O)}-H)$ frequencies for complexes in the 3325-3345 cm⁻¹ range. Considering the experimental and calculated values of these stretching modes in the molecules only containing Namide and individually the molecules only having N_{C(O)NHP(O)}, with formula R¹P(O)[NHR]₂ [58] and RC(O)NHP(O)Cl₂ [59], confirm this assignment. In molecule $C_6H_5OP(O)(NHC_6H_{11})_2$, the experimental frequency for NH is 3230 cm⁻¹ (theoretical = 3578 and 3548 cm⁻¹) and in [N(CH₃)(C₆H₁₁)]P(O)(2-C₅H₄N-NH)₂ the frequencies 3390 and 3145 cm⁻¹ were found for v(NH) (theoreti $cal = 3575 and 3368 cm^{-1} [58]$). In ClF₂CC(O)NHP(O)Cl₂ having only $N_{C(O)NHP(O)}$ -H unit [59], the experimental frequency is 3064 cm^{-1} and the theoretical through two different methods are 3291 and 3251 cm^{-1} . It is well-known that the HB causes dramatic changes in the structural parameters of the molecules as observed in the infrared spectra [60, 61]. So, the lower N_{C(O)NHP(O)}-H and P=O frequencies in 2 relative to those similar in 1 (NH: 3091 and 3199 cm^{-1} and P=O: 1228 and 1281 cm⁻¹) are attributed to a stronger HB. This is supported by X-ray crystallography in which the $N_{C(O)NHP(O)}$ -H unit in 2 involves in a few stronger HB relative to HB in 1, Table 3. The Namide-H stretching mode of 2 (in 4-CH₃C₆H₄NH moiety) appears at lower frequency than the similar stretching mode of 1 (in NHCH₂C(CH₃)₂CH₂NH moiety) due to relatively strong intramolecular HB (N3–H3B···O2, N3···O2 = 2.959(2) Å). The calculated values are in good agreement with the experimental data.

Conclusions

The P(O)NHC(O) containing phosphoric triamides 1 and 2 with different orientations of P=O versus C=O have been studied by chemical calculation, spectroscopic data and X-ray crystallography. Compound 1 is the first example of aliphatic diazaphosphorinane with a rarely *gauche* position for the phosphoryl and carbonyl groups. The differences in the P–N–C bond angle, O–P–N–C dihedral angle, C=O frequency and the chemical shift of carbonyl carbon atom are discussed in two orientations. The tentative assignments of vibrational frequencies by comparison with theoretical wave numbers have been providing good comparisons.

Supplementary data

CCDC 777252 (1) and CCDC 777253 (2) contain the supplementary crystallographic data for this paper. These

data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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