



# Synthesis, conformational and NQR analysis of phosphoric triamides containing the P(O)[N]<sub>3</sub> skeleton

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## ABSTRACT

New phosphoric triamides with general formula P(O)X<sub>3</sub> where X = N-4-methylpiperazinyl (**1**), N-4-phenylpiperazinyl (**2**), N-4-ethoxycarbonyl piperazinyl (**3**), N-2-tetrahydrofurfuryl (**4**) were synthesized and characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR, IR, Mass spectroscopy and elemental analysis. The molecular structure for compounds **1–4** were obtained by using quantum chemical calculations (HF and B3LYP methods with the 6-31+G\*\* basis set). Moreover, optimized structures for previously reported 4-FC<sub>6</sub>H<sub>4</sub>C(O)NHP(O)X<sub>2</sub> phosphoric triamides, X = pyrrolidin-1-yl (**5**), piperidin-1-yl (**6**) and hexamethyleneimin-1-yl (**7**) were obtained using the solid state structure (CIF files) as a starting point for the gas phase computation in which all independent molecules in structures **6** (seven structures) and **7** (two structures) were included. The computed results were in good agreement with the data obtained from the X-ray crystal structures reported earlier. The nuclear quadrupole coupling constants (NQCCs or  $\chi$ s) were calculated about 5.0 and 10.0 MHz for the <sup>17</sup>O atoms of P=O and C=O bonds. For nitrogen atoms bonded to the phosphorus the NQCCs were found in the range between 4.0 and 5.5 MHz, whereas for compounds **4–7**, the expected values for amidic hydrogen atoms are near 300 kHz.

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## 1. Introduction

Phosphoric triamides have attracted renewed attention since their feasibility for acting as ligands in coordination chemistry – especially with lanthanide metals – has been recently demonstrated [1,2]. Moreover, lithiated anions derived from phosphoric triamides have been early reported [3], which are recognized as homoenolate equivalent in the reaction with halogenated acetal and ketal giving regioselectively the  $\gamma$ -alkylation adducts [4]. Interesting features associated with distinctive crystal motif and conformational properties in the crystalline state have been also determined [5–7]. Thus, many efforts have been made for the synthesis, characterization and structural investigations on phosphoric triamides [8–10]. The presence of more than one conformer

on phosphoric triamides may be a result of non-rigidity of some parts of molecules resulting in different torsion angles [11–14]. Furthermore, several crystal structures with disordered atoms in the solid state owing to rapid inversions or rotations exist [11,14]. Ab initio quantum chemical computations were applied on them both to predict the structural parameters and for the sake of comparison with experimental results [15–17]. It is noteworthy that, as far as we know, the nuclear quadrupole coupling constants of these molecules have not been reported so far. Calculation of nuclear quadrupole coupling constants ( $\chi$ s) of nuclei with spin  $\geq 1$  is a powerful tool to estimate the structural properties of the molecules [18–22]. Previous studies have reported  $\chi$  values of about 5.0, 10.0 MHz, and 300.0 kHz, respectively, for the <sup>14</sup>N, <sup>17</sup>O and <sup>2</sup>H atoms [19].

In this work, four new phosphoric triamides (**1–4**) were synthesized and characterized by multinuclear (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P) NMR, IR, Mass spectroscopy and elemental analysis. Also, their molecular structures were computed and compared with previously reported phosphoric triamides for which X-ray crystallographic data are available [11]. Nuclear quadrupole coupling constants ( $\chi$ ) were calculated for the quadrupole <sup>14</sup>N, <sup>2</sup>H and <sup>17</sup>O atoms.

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## 2. Experimental

### 2.1. Spectroscopic measurements

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were determined relative to internal TMS,  $^{31}\text{P}$  chemical shifts relative to 85%  $\text{H}_3\text{PO}_4$  as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN–O–RAPID apparatus. Melting points were obtained with an Electrothermal instrument. The mass spectra were recorded on a 5973 Network Mass Selective Detector (Agilent Technology, HP) with 70 eV electron impact (EI).

### 2.2. Synthesis

#### 2.2.1. *N,N',N''-tris(4-methylpiperazinyl) phosphoric triamide (1)*

To a solution of phosphoryl chloride (10 mmol, 1.54 g) in dry acetonitrile, 1-amino-4-methylpiperazine (60 mmol, 2.33 g) was added dropwise at 0 °C. This mixture was stirred for 24 h and was filtered to remove the alkylamine hydrochloride by-products. Then the yellow solution was evaporated and the residue was washed with ethyl acetate and dissolved in diethyl ether. The resulting solution was evaporated again and the yellow precipitate was washed with  $\text{CCl}_4$ . Yield: 49%; Anal. Calc. For  $\text{C}_{15}\text{H}_{33}\text{N}_6\text{OP}$ : C, 52.31; H, 9.66; N, 24.40%. Found: C, 52.29; H, 9.65; N, 24.38%.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 18.50$  (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 2.30$  (s, 3 H, 4- $\text{CH}_3$ ), 2.34 (s, 4H,  $\text{CH}_2$ -ring), 3.11 (s, 4H,  $\text{CH}_2$ -ring).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 44.71$  (s, 4- $\text{CH}_3$ ), 46.20 (s,  $\text{CH}_2$ -ring), 55.42 (d,  $^3J(\text{P},\text{C}) = 5.6$  Hz,  $\text{CH}_2$ -ring). IR (KBr,  $\text{cm}^{-1}$ ): 2938 ( $\nu\text{CH}$ ), 2851 ( $\nu\text{CH}$ ), 2800 ( $\nu\text{CH}$ ), 1453, 1287, 1189 ( $\nu\text{P}=\text{O}$ ), 1000 ( $\nu\text{P}-\text{N}$ ), 782, 727. MS (70 eV, EI):  $m/z$  (%): 389  $[\text{M}]^+$  (2), 345  $[\text{P}(\text{O})((\text{NHN}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{CH}_3)_2)]^+$  (100), 274  $[\text{P}(\text{O})((\text{NHN}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{CH}_3)_2)]^+$

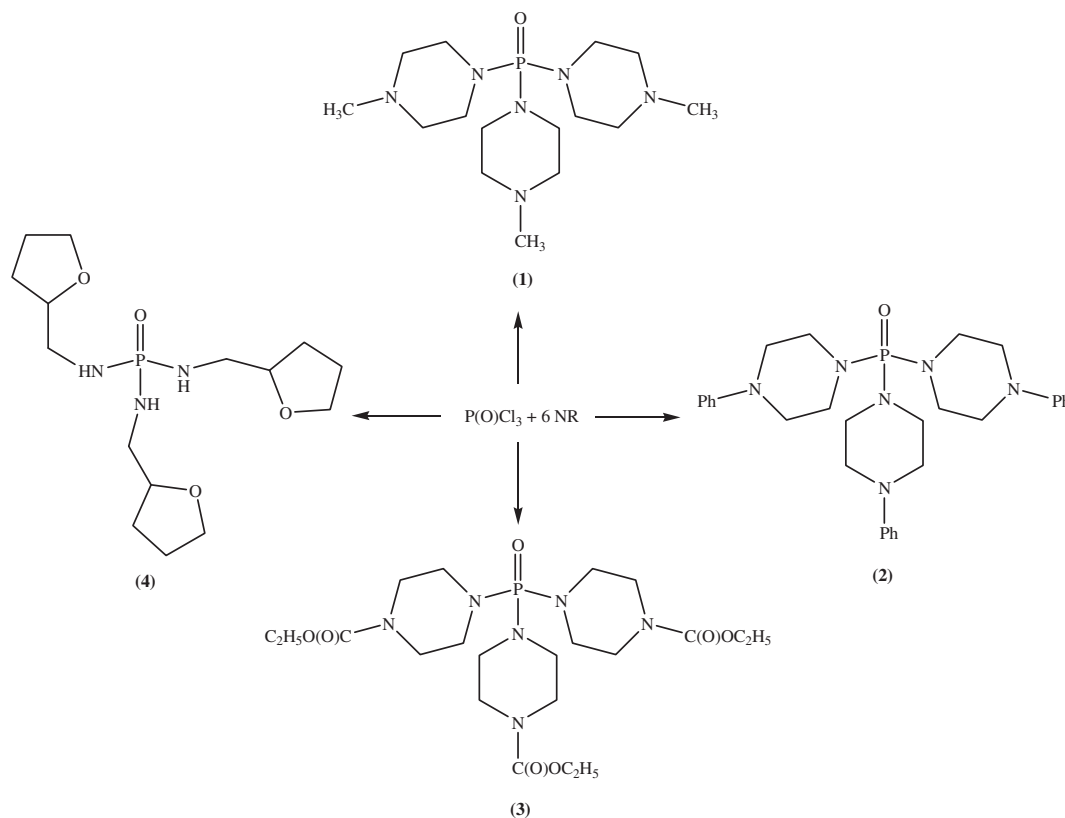
(7), 247  $[\text{P}(\text{O})((\text{NHN}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2)_2)]^+$  (27), 99  $[\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2]^+$  (13), 56  $[\text{N}(\text{CH}_2)_2\text{N}]$  (8).

#### 2.2.2. *N,N',N''-tris(4-phenylpiperazinyl) phosphoric triamide (2)*

To a solution of phosphoryl chloride (10 mmol, 1.54 g) in dry acetonitrile, N-4-phenylpiperazine (60 mmol, 3.18 g) was added dropwise at 0 °C and the mixture stirred for 20 h. Then the precipitate (by-product) was filtered and the solution was evaporated. The resulting solid was washed with *n*-hexane and diethyl ether. Yield: 62%; Anal. Calc. For  $\text{C}_{30}\text{H}_{39}\text{N}_6\text{OP}$ : C, 67.90; H, 7.41; N, 15.84%. Found: C, 67.88; H, 7.40; N, 15.85%.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 17.99$  (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.17$  (m, 4 H,  $\text{CH}_2$ -ring), 3.38 (m, 4 H,  $\text{CH}_2$ -ring), 6.91 (t,  $^3J(\text{H},\text{H}) = 7.3$  Hz, 2 H, Ar-H), 6.94 (d,  $^3J(\text{H},\text{H}) = 7.3$  Hz, 2 H, Ar-H), 7.29 (t,  $^3J(\text{H},\text{H}) = 7.3$  Hz, 1 H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 45.06$  (s,  $\text{CH}_2$ -ring), 50.16 (d,  $^3J(\text{P},\text{C}) = 5.9$  Hz,  $\text{CH}_2$ -ring), 116.51 (s), 120.36 (s), 129.16 (s), 151.34 (s). IR (KBr,  $\text{cm}^{-1}$ ): 2832 ( $\nu\text{CH}$ ), 1596, 1497, 1235 ( $\nu\text{P}=\text{O}$ ), 1127, 966 ( $\nu\text{P}-\text{N}$ ), 745, 684. MS (70 eV, EI):  $m/z$  (%): 530  $[\text{M}]^+$  (3), 513  $[\text{P}(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})_3]^+$  (3), 453  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})_2(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2)]^+$  (4), 369  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})_2]^+$  (5), 344  $[\text{P}(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2(\text{N}(\text{CH}_2)_2\text{N}))]^+$  (11), 287  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2)]^+$  (12), 274  $[\text{P}(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2)]^+$  (76), 245  $[\text{P}(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})(\text{N}(\text{CH}_2)_2\text{N})]^+$  (100), 174  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2)(\text{N}(\text{CH}_2)_2)]^+$  (24), 162  $[(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph})]^+$  (10), 147  $[(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{Ph}]^+$  (13), 120  $[\text{N}(\text{CH}_2)_2-\text{Ph}]^+$  (4), 99  $[\text{P}=\text{N}(\text{CH}_2)_2\text{NCH}_2]^+$  (63), 71  $[\text{N}(\text{CH}_2)_2\text{NCH}_2]^+$  (14), 56  $[(\text{N}(\text{CH}_2)_2\text{N})]^+$  (16), 42  $[(\text{N}(\text{CH}_2)_2)]^+$  (17).

#### 2.2.3. *N,N',N''-tris(4-ethoxy carbonylpiperazinyl) phosphoric triamide (3)*

To a solution of phosphoryl chloride (10 mmol, 1.54 g) in dry acetonitrile, N-4-ethoxy carbonylpiperazine (60 mmol, 3.11 g) was added dropwise at 0 °C and the mixture stirred for 48 h. Then



**Scheme 1.** The preparation pathway of compounds 1–4.

the precipitate (by-product) was filtered and the solution was evaporated. The resulting yellow solid was washed with  $\text{CCl}_4$  and diethyl ether. Yield: 62%; Anal. Calc. For  $\text{C}_{21}\text{H}_{39}\text{N}_6\text{O}_7\text{P}$ : C, 48.64; H, 7.58; N, 16.21%. Found: C, 48.62; H, 7.57; N, 16.20%.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 18.27$  (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.18$  (t,  $^3J(\text{H,H}) = 7.0$  Hz,  $\text{CH}_3$ ), 3.00 (m, 4H,  $\text{CH}_2$ -ring), 3.36 (m, 4H,  $\text{CH}_2$ -ring), 4.06 (q,  $^3J(\text{H,H}) = 7.0$  Hz,  $\text{OCH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 14.49$  (s,  $\text{CH}_3$ ), 44.28 (s,  $\text{CH}_2$ -ring), 48.26 (s,  $\text{CH}_2$ -ring), 61.48 (s,  $\text{OCH}_2$ ), 150.15 (s,  $\text{C}=\text{O}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 2982 ( $\nu\text{CH}$ ), 2906 ( $\nu\text{CH}$ ), 2849 ( $\nu\text{CH}$ ), 1687 ( $\nu\text{C}=\text{O}$ ), 1426, 1241 ( $\nu\text{P}=\text{O}$ ), 1130, 986 ( $\nu\text{P}-\text{N}$ ), 961, 766, 724. MS (70 eV, EI):  $m/z$  (%): 518  $[\text{M}]^+$  (2), 344  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{C}(\text{O})(\text{OC}_2\text{H}_5))(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{C}(\text{O})(\text{OCH}_2))]^+$  (9), 287  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{C}(\text{O})(\text{OC}_2\text{H}_5))(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2)]^+$  (8), 274  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{C}(\text{O})(\text{OC}_2\text{H}_5))(\text{N}(\text{CH}_2)_2\text{NCH}_2)]^+$  (55), 246  $[\text{P}(\text{O})(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{C}(\text{O})(\text{OC}_2\text{H}_5))(\text{N}(\text{CH}_2)_2)]^+$  (71), 174  $[\text{P}(\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{C}(\text{O})(\text{OCH}_3))]^+$  (22), 158  $[\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2-\text{C}(\text{O})(\text{OC}_2\text{H}_5)]^+$  (30), 101  $[\text{NCH}_2-\text{C}(\text{O})(\text{OC}_2\text{H}_5)]^+$  (24), 85  $[\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2]^+$  (16), 72  $[\text{OC}(\text{O})\text{NCH}_2]^+$  (17), 56  $[\text{CH}_3\text{CH}_2\text{C}]^+$  (88), 44  $[\text{OC}(\text{O})]^+$  (100).

#### 2.2.4. *N,N',N''-tris(2-tetrahydrofurfuryl) phosphoric triamide (4)*

To a solution of phosphorylchloride (10 mmol, 1.54 g) in dry acetonitrile, 2-tetrahydrofurfurylamine (60 mmol, 2.08 g) was added dropwise at  $0^\circ\text{C}$  and the mixture stirred for 24 h. Then the crude mixture was filtered and the yellow solution evaporated. The resulting solid was re-crystallized in acetone and the yellow solid was further washed with *n*-heptane and  $\text{CCl}_4$ . Yield: 62%; Anal. Calc. For  $\text{C}_{15}\text{H}_{30}\text{N}_3\text{O}_4\text{P}$ : C, 51.86; H, 8.70; N, 12.10%. Found: C, 51.84; H, 8.71; N, 12.09%.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 19.19$  (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.49$  (m, 6 H,  $\text{CH}_2$ ), 2.76 (m, 1 H, CH), 2.96 (m, 1 H, CH), 3.29 (m, 1 H, CH-ring), 3.76 (m, 1 H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 35.55$  (s), 35.59 (s), 42.83 (d,  $^3J(\text{P,C}) = 2.9$  Hz,  $\text{CH}_2$ ), 43.91 (s), 64.00 (d,  $^3J(\text{P,C}) = 7.7$  Hz, CH), 106.82 (s,  $\text{CH}_2\text{O}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3367 ( $\nu\text{NH}$ ), 2955 ( $\nu\text{CH}$ ), 2927 ( $\nu\text{CH}$ ), 2890 ( $\nu\text{CH}$ ), 1331, 1224, 1188 ( $\nu\text{P}=\text{O}$ ), 1147, 1042, 944 ( $\nu\text{P}-\text{N}$ ), 894, 725, 660. MS (70 eV, EI):  $m/z$  (%): 347  $[\text{M}]^+$  (2),  $[\text{P}(\text{NHCH}_2-\text{C}_4\text{H}_7\text{O})_3]^+$  (19), 142  $[\text{P}(\text{CH}_2)(\text{NCH}_2-\text{C}_4\text{H}_7\text{O})]^+$  (100), 99  $[\text{NCH}-\text{C}_4\text{H}_7\text{O}]^+$  (24), 87  $[\text{CH}_2-\text{C}_4\text{H}_7\text{O}]^+$  (24), 71  $[\text{C}_4\text{H}_7\text{O}]^+$  (4), 56  $[\text{NHCH}_2\text{CHCH}_2]^+$  (15), 42  $[\text{CH}_2\text{CH}_2\text{CH}_2]^+$  (18).

### 3. Computational details

The structures of compounds **1–4** and also those of phosphoric triamides with formula  $4\text{-F-C}_6\text{H}_4\text{C}(\text{O})\text{NHP}(\text{O})\text{X}_2$ ,  $\text{X} = \text{NC}_4\text{H}_8$  (**5**),  $\text{NC}_5\text{H}_{10}$  (**6**, **6A-1**, **6A-2**, **6B-1**, **6B-2**, **6C-1**, **6C-2**) and  $\text{NC}_6\text{H}_{12}$  (**7**, **7A**) were optimized using the Gaussian 98 program [23]. The optimizations were followed by computations of the harmonic vibrational frequencies at HF/6-31G\* method. No imaginary frequencies were obtained at these computations. Nuclear quadrupole coupling constants ( $\chi$ ) were calculated from the equation  $\chi = e^2 q_{zz} Q/h$  [24], supposing that the electric quadrupole moments ( $Q$ ) of  $^2\text{H}$ ,  $^{17}\text{O}$  and  $^{14}\text{N}$  nuclei are 2.860,  $-25.58$ , and  $20.44$  mb, respectively [25]. The principal components of the electron field gradient tensor (EFG),  $q_{ii}$ , are computed in atomic unit ( $1 \text{ au} = 9.717365 \times 10^{21} \text{ V m}^{-2}$ ), with  $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$  and  $q_{xx} + q_{yy} + q_{zz} = 0$ . These diagonal elements relate to each other by the asymmetry parameter:  $\eta_Q = |q_{yy} - q_{xx}|/|q_{zz}|$ ,  $0 \leq \eta_Q \leq 1$ , which measures the EFG tensor deviation from axial symmetry. The computed  $q_{zz}$  component of EFG tensor is used to obtain the nuclear quadrupole coupling constants ( $\chi$ ).

### 4. Results and discussion

#### 4.1. Spectroscopic study

In this study, new phosphoric triamides **1–4** were synthesized from the reaction of  $\text{POCl}_3$  with different amines (Scheme 1) and

**Table 1**  
Selected spectroscopic NMR and IR data of compounds **1–4**.

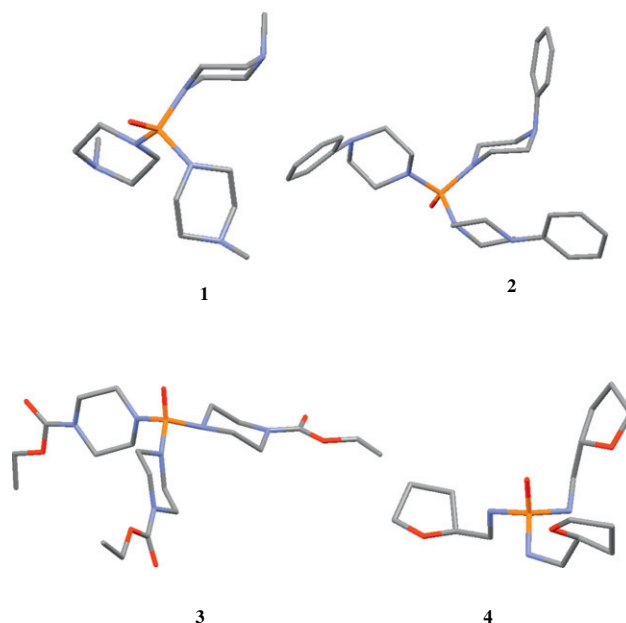
Compound	$\delta(^{31}\text{P})$ (ppm)	$^2J(\text{P,C})$ (Hz)	$^3J(\text{P,C})$ (Hz)	$\nu(\text{P}=\text{O})$ ( $\text{cm}^{-1}$ )	$\nu(\text{P}-\text{N})$ ( $\text{cm}^{-1}$ )
<b>1</b>	18.50	–	5.6	1189	1000
<b>2</b>	17.99	–	5.9	1235	966
<b>3</b>	18.27	–	–	1241	986
<b>4</b>	19.19	5.1	7.7	1188	944

**Table 2**  
The  $\text{P}=\text{O}$  stretching wavenumber and its square correlated with the sum of the Pauling electronegativities of the atoms and groups attached to the  $\text{P}=\text{O}$  group in OPXYZ compounds and with the vertical ionization potential.

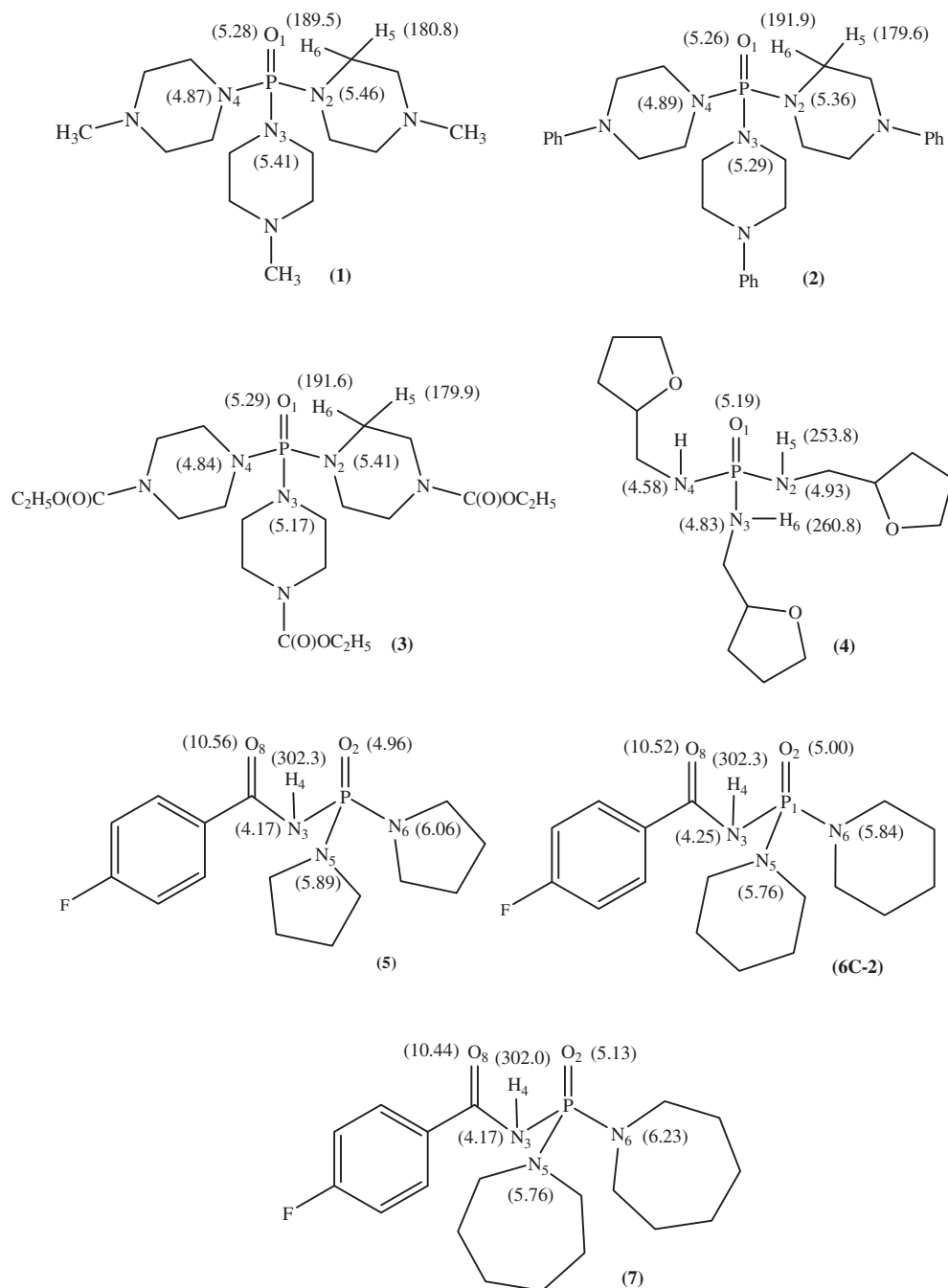
Compound	$\nu(\text{P}=\text{O})$ ( $\text{cm}^{-1}$ )	$(\nu(\text{P}=\text{O}))^2 \times 10^{-6}$ ( $\text{cm}^{-2}$ )	Sum of electronegativities of X, Y and Z	Vertical ionization potential (eV)
$\text{OPF}_3$	1415	2.002	11.94	13.52 [28] 12.62**
$\text{OPClF}_2$	1384	1.915	11.12	
$\text{OPBrF}_2$	1380	1.904	10.92	11.53**
$\text{OPCl}_2\text{F}$	1358	1.844	10.30	11.47**
$\text{OPBr}_2\text{F}$	1337	1.788	9.90	11.04**
$\text{OPCl}_3$	1290	1.664	9.48	11.91 [28] 11.16**
$\text{OPBrCl}_2$	1285	1.651	9.28	10.68**
$\text{OPBr}_2\text{Cl}$	1275	1.625	9.08	10.72**
$\text{OPBr}_3$	1261	1.590	8.88	11.07 [28] 10.76**
$\text{OP}[\text{N}(\text{CH}_3)_2]_3$	1160	1.346	8.52*	10.44 [28] 7.49**
Compound <b>3</b>	1241	1.540	8.52*	7.42**
Compound <b>2</b>	1235	1.525	8.52*	6.37**
Compound <b>1</b>	1189	1.414	8.52*	6.60**
Compound <b>4</b>	1188	1.411	8.28*	7.52**

\* Group electronegativity,  $E_g = [V_c^* E_c + \text{Sum of } N_i * E_i]/N$  where,  $V_c$  and  $E_c$  are the valence of the central atom and its atomic electronegativity value respectively.  $N_i$  and  $E_i$  are the number of the bond of atomic or group  $i$  connecting to the central atom and the atomic electronegativity of  $i$  atom.

\*\* Calculated at B3LYP/6-31+G\*\* level of theory.



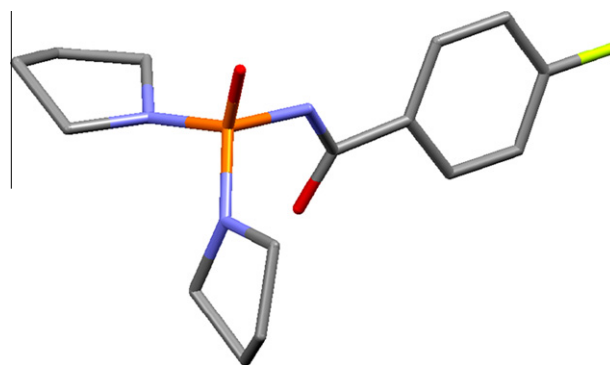
**Fig. 1.** Optimized structures obtained for compounds **1–4** at HF, B3LYP/6-31+G\*\* levels of theory.



**Scheme 2.** The structural formula along with the NQCCs in parentheses for compounds **1–4** (at B3LYP/6-31+G\*\* level) and **5, 6C-2, 7** (at HF/6-311++G\*\* level).

fully characterized by NMR and IR spectroscopy. A summary of the spectroscopic data of these compounds are given in Table 1. The comparative analysis of the NMR spectra reveals interesting features. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of compounds **1–4** indicate the phosphorus chemical shift,  $\delta(^{31}\text{P})$ , in the range of 17.99–19.19 ppm displaying nearly the same electron donation of amino substituents to the phosphorus atoms.

The  $^1\text{H}$  NMR spectra of molecules **1–3** exhibit two signals for the methylene protons of the six membered piperazinyl rings. The  $^{13}\text{C}$  NMR spectrum of this molecule indicates six separated peaks for the five carbon atoms that are due to the different orientations of the aliphatic five membered rings. The methylene carbon atom presents a  $^2J(\text{P},\text{C}) = 2.9$  Hz and the CH group shows the  $^3J(\text{P},\text{C}) = 7.7$  Hz. The signal related to the carbon atom of  $\text{CH}_2\text{—O}$  moiety appears at the most down field (106.82 ppm). The  $^{13}\text{C}$



**Fig. 2.** Optimized structures obtained for compound **5** at HF/6-311++G\*\* level of theory.

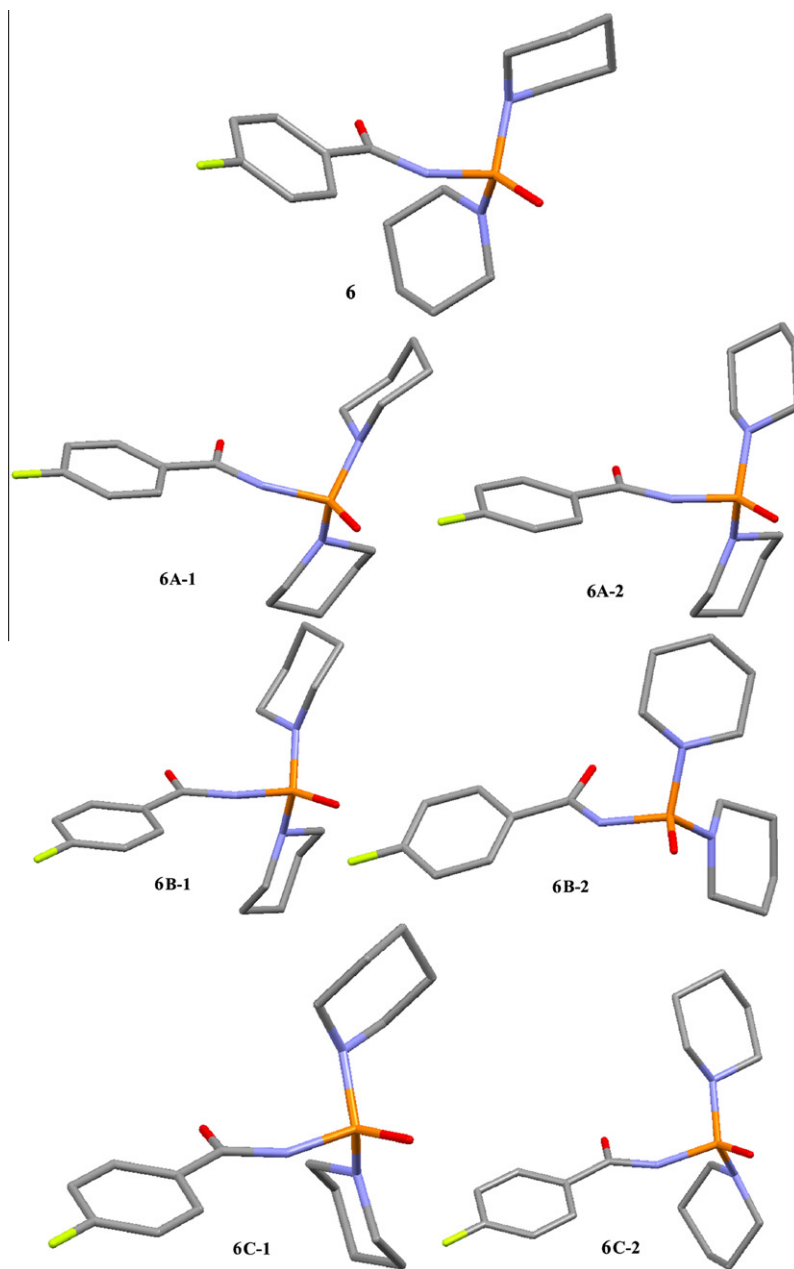


Fig. 3. Optimized structures obtained for compounds **6**, **6A-1**, **6A-2**, **6B-1**, **6B-2**, **6C-1** and **6C-2** at HF/6-311++G\*\* level of theory.

NMR spectra of compounds **1** and **2** also demonstrate  $^3J(\text{P},\text{C})$  equal to 5.6 and 5.9 Hz, respectively. In addition, the mass spectra confirm the formation of structures **1–4** by analyzing the fragmentation patterns and the corresponding base peaks.

The analysis of the IR spectra indicate that the fundamental  $\nu(\text{P}=\text{O})$  stretching modes for compounds **1** and **4** appear at lower frequencies than that of compounds **2–3**, while the  $\nu(\text{P}=\text{N})$  of **1** shows the greatest value among those of **1–4**. The trend of the  $\text{P}=\text{O}$  normal mode of vibration bears a resemblance to the behavior of the  $\text{C}=\text{O}$  stretching mode as earlier reported by the foundational work of Kagarise [26]. In the present case, the square of the  $\text{P}=\text{O}$  wavenumber correlates fairly well with the sum of the Pauling electronegativities of the atoms or groups attached to the  $\text{P}=\text{O}$  moiety. Table 2 serves to exemplify this behavior and lists data for relevant and simple selected exponents found in the literature [27]. Moreover, this correlation can be extended to the vertical ionization potentials. Thus, selected values [28] have been also in-

cluded for  $\text{OPF}_3$  (13.52 eV),  $\text{OPCl}_3$  (11.91 eV),  $\text{OPBr}_3$  (11.07 eV) and  $\text{OP}[\text{N}(\text{CH}_3)_2]_3$  (10.44 eV). As indicated in Table 2, the correlations between  $\nu(\text{P}=\text{O})^2$  and sum of substituents electronegativities attached to P atom, and vertical ionization potential for phosphoric triamides **1–4** are in qualitative agreement with the trend observed for simple phosphoryl halides. As expected for phosphoric triamide molecules, however, it is plausible that not only the electronegativity of the substituent, but also other phenomena – such as electron withdrawing/releasing nature, hyperconjugative effect – play a major role in determining the electronic properties of phosphoric triamide compounds.

#### 4.2. Computational study

##### 4.2.1. Compounds **1–4**

Herein, to more investigate on the above prepared phosphoric triamides (**1–4**), their molecular structures have been optimized



using Gaussian 98 software at HF and B3LYP method with 6-31+G\*\* standard basis set. Fig. 1 indicates the optimized structures of the compounds **1–4**. In the optimized structures of compounds **1** and **2**, the 4-Me and 4-Ph substituents place in pseudo-axial positions, but the 4-C(O)OEt moieties in **3** are in pseudo-equatorial positions (likely due to the planar carbon atom of C=O group). Also, the CH<sub>2</sub> groups in compound **4** connected to aliphatic five-membered rings are in pseudo-equatorial positions (Fig. 1). The selected calculated NQCCs ( $\chi$ s) for the quadrupole <sup>14</sup>N, <sup>2</sup>H and <sup>17</sup>O nuclei of compounds **1–4** at HF and B3LYP methods with 6-31+G\*\* basis set are represented in Table S3 and Scheme 2. The  $\chi$  values for the oxygen and nitrogen atoms are about 5.0 MHz, while for the <sup>2</sup>H atoms of CH and NH groups they are near 200 and 300 kHz, respectively.

#### 4.2.2. Compounds **5–7**

The structural properties of phosphoric triamides (**5–7**) that are similar to compounds (**1–4**) have also been optimized at HF/6-31G\* and HF/6-311++G\*\* levels of theory. In the Scheme 2, a drawing of the studied compounds is given and Figs. 2–4 show the optimized structures. The species **5–7** have been previously synthesized and the geometries of N-4-fluorobenzoyl phosphoric triamides including their conformers and disorders structures were studied by X-ray diffraction [11]. The aliphatic five- and seven-membered rings in compounds **5**, **7** and **7A** have puckered shapes while the six-membered rings of seven forms of **6** show chair conformation. For compounds **5–7**, the P=O bond presents an anti conformation with respect to the C=O double bonds. The pseudo-torsion angles O=P...C=O in compounds **5**, **6C-2** and **7** are 170.46°, 172.79° and 166.17°, respectively. This result confirms the earlier X-ray structures reported elsewhere [11]. In these molecules, the bond angles around the P atom indicate a distorted conformation varying from 103.95° to 119.67° in **5** at HF/6-31G\* method. Similar results were observed for other compounds at both HF/6-31G\* and HF/6-311++G\*\* levels of theory.

The computed bond lengths, angles and torsion angles at HF/6-31G\* and HF/6-311++G\*\* are compared with their related data obtained from the X-ray crystal structures of these molecules [11] that are in good agreement with each other, however it is seen that HF/6-31G\* has a better correspondence with the experimental values than HF/6-311++G\*\*. In compounds **5–7**, the P–N(amide) bonds are longer than the P–N(amine) bonds, because of the resonance interaction of the N(amide) with the C=O  $\pi$  system. In fact, all P–N bonds in compounds **1–7** are shorter than the typical P–N single bond (1.77 Å [29]) whereas the P=O bond lengths are larger than the reported P=O bond length (1.45 Å [29]). In molecules **1–7**, the nitrogen environment is practically planar. For example, in compound **5** the angles P(1)–N(3)–C(7), P(1)–N(3)–H(4) and C(7)–N(3)–H(4) are 130.00°, 111.07° and 118.09°, respectively with average 119.72°. The sum of surrounding angles around N(3), N(5) and N(6) atoms are 359.16°, 358.34° and 352.18°,

respectively. Similar results were obtained for the nitrogen atoms of other structures here presented.

Quantum chemical calculations also show that among seven plausible forms of compound **6**, compound **6C-2** is the most stable and between compounds **7** and **7A**, compound **7** is more stable than **7A**. The 4-fluorobenzoyl moieties in **7** and **7A** indicate cis and trans conformations relative to the P=O groups with O=P...F–C torsion angles equal to 176.26° and 147.84°, respectively.

The selected calculated NQCC ( $\chi$ ) for the quadrupole <sup>14</sup>N, <sup>2</sup>H and <sup>17</sup>O nuclei of compounds **5–7** at HF/6-311++G\*\* are represented in Scheme 2 and Table S4 (Supplementary material). The oxygen atoms of P=O and C=O bonds have  $\chi$  values about 5.0 and 10.0 MHz, respectively. The reason for the almost half  $\chi$  values of oxygen atoms in phosphoryl moieties with respect to carbonyl groups could be the more negative carbonyl oxygen atoms owing to the resonance interactions. For the amidic and endocyclic amino nitrogen atoms, the  $\chi$  values compute about 4.0 and 5.5 MHz, respectively, and for the H atoms they were near 300 kHz. The smaller  $\chi$  values for the amidic N atoms may be due to the electron withdrawing of 4-fluorobenzoyl moiety that leads to deshielding of amidic N compared with amino N atom.

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#### Appendix A. Supplementary material

The molecular formula of compounds **1–7** with atom numbering are shown in Scheme S1. The computed bond lengths, angles and torsion angles of compounds **1–4** (at B3LYP/6-31+G\*\* level) and **5–7** (at HF/6-311++G\*\* level) are presented in Tables S1 and S2, respectively. Selected calculated NQCCs ( $\chi$ s) for compounds **1–4** and **5–7** are given in Tables S3 and S4, respectively. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2012.03.045>.

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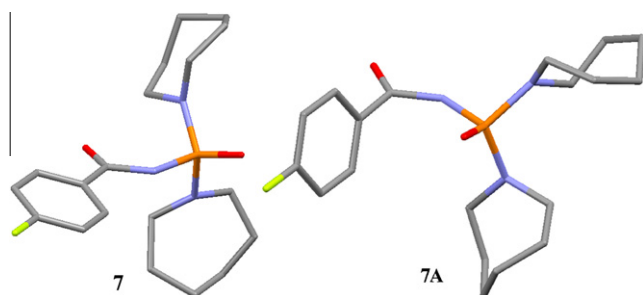


Fig. 4. Optimized structures obtained for compounds **7** and **7A** at HF/6-311++G\*\* level of theory.

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