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New Phosphoramidates: Spectroscopic Study and Ab Initio Computations

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NEW PHOSPHORAMIDATES: SPECTROSCOPIC STUDY AND AB INITIO COMPUTATIONS

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GRAPHICAL ABSTRACT



Abstract New phosphoramidates with formula $P(O)(X)[NH-N = C(C_6H_5)_2]_2$, X = Cl (1), $C_6H_5C(O)NH(2)$, $CCl_3C(O)NH(3)$, $C_6H_5C(O)NHP(O)[NHCH(CH_3)_2]_2$ (4), and $P(O)(Cl)[2-NH-C_6H_4-C(O)OC_2H_5]_2$ (5) were synthesized and characterized by ¹H, ¹³C, ³¹P NMR, IR spectroscopy, and elemental analysis. The ¹H and ¹³C NMR spectra of 4 display two sets of signals for the two unequivalent CH₃ groups of the isopropyl substituents due to the presence of prochiral CH units. Interestingly, the ¹³C NMR spectrum of 5 indicates long-range ⁴J(P,C_{meta}) = 0.9 Hz. Such a coupling was not observed in previous studies for similar phosphoramidates. The geometries of phosphoramidates 1–5 were optimized by Gaussian 98 software at HF and B3LYP levels of theory with standard 6-31G^{*} and 6-31+G^{**} basis sets. The stabilization energies were calculated from the equation $\Delta E = E(molecule) - \Sigma_i E(i)$, i = atom. For all compounds, the B3LYP/6-31G^{*} basis set provided the highest negative stabilization energies. The nuclear quadrupole coupling constants (χ) for ¹⁴N, ²H, and ³⁵Cl nuclei were computed to be 4–6 MHz, 180–190 KHz, and 50, 80 MHz, respectively. The χ values for the ¹⁷O atoms of phosphoryl moieties (5.0 MHz) are almost half than those of C=O bonds (10.0 MHz). Moreover, the χ values of amidic N atoms are smaller than those of amino N atoms.

Keywords Ab initio computation; DFT; NMR; NQR; phosphoramidate

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INTRODUCTION

Nowadays, the phosphoramidate chemistry is of great interest due to the wide application of phosphoramidates in various areas of science such as medicine, ¹⁻³ agriculture, ⁴⁻⁶ coordination chemistry,⁷⁻¹⁰ theoretical chemistry,^{11,12} and structural¹³⁻¹⁵ investigations. There have been many efforts for the synthesis, characterization, and structural studies on these compounds,^{16–18} Ab initio quantum chemical computations were conducted on phosphoramidates to predict their structural parameters and to compare the calculated results with the experimental ones.^{19,20} Nuclear quadrupole coupling constants are very helpful to estimate the structural properties.^{21,22} Previous studies have reported the χ values for the ¹⁴N, ¹⁷O, and ²H atoms to be 5.0, 10.0 MHz and 300.0 kHz, respectively.^{21,22} The χ values for the ³⁵Cl atoms were measured from 35-40 MHz²³ to 50-70 MHz.²⁴ In this article, we report on new phosphoramidates with the formula $P(O)(X)[NH-N = C(C_6H5)_2]_2$, X = Cl (1), C₆H₅C(O)NH (2), CCl₃C(O)NH (3), C₆H₅C(O)NHP(O)[NHCH(CH₃)₂]₂ (4), and $P(O)(C1)[2-NH-C_6H_4-C(O)OC_2H_5]_2$ (5), which were synthesized and characterized by ¹H, ¹³C, ³¹P NMR, IR spectroscopy and elemental analysis. To further study the structural properties of these compounds, their geometries were initially optimized with Hyperchem 7.0 software and then by the Gaussian 98 program²⁵ at the HF and B3LYP levels of theory using standard 6-31G* and 6-31+G** basis sets. The stabilization energies were computed from the equation $\Delta E = E(\text{molecule}) - \Sigma_i E(i)$, i = atom. Nuclear quadrupole couplingconstants (χ) were calculated for the quadrupole ¹⁴N, ²H, ¹⁷O, and ³⁵Cl atoms. Finally, these results were compared with previously reported data and found to be in good agreement with them.

RESULTS AND DISCUSSION

Spectroscopic Study

In the present study, novel phosphoramidates 1–5 were synthesized from the reaction of POCl₃ and some phosphoramidic dichlorides with benzophenonehydrazone, isopropylamine, and ethyl 2-aminobenzoate (Scheme 1). A summary of the NMR and IR parameters of these compounds are given in Table 1. The ³¹P{¹H} NMR spectrum of compound 1 shows the ³¹P NMR signal at 3.78 ppm, which is shifted upfield in the spectra of compounds 2 and **3**. This upfield shift shows stronger electron donation of benzoyl and acetyl substituents relative to the Cl atom. A comparison of the analogous molecules 2 and 4 reveals that δ^{31} P is at higher field in compound **2**, indicating stronger electron donation of benzophenone hydrazone moiety as compared to isopropyl groups at the phosphorus atom. Also, comparing the analogous compounds **1** and **5**, containing one Cl substituent, δ^{31} P of **1** appears at lower field, which indicates lower electron donation of benzophenone hydrazone group with respect to the 2-ethylbenzoate moiety.

The ¹H and ¹³C NMR spectra of compound **1** exhibit two sets of signals for the two phenyl groups of the benzophenonehydrazone substituent, confirming that the two phenyl moieties are not equivalent. Interestingly, the ¹H and ¹³C NMR spectra of compound **4** display two sets of signals for the two diastereotopic CH₃ groups of the isopropyl substituents, due to the presence of prochiral CH units. Two ³*J*_{HH} (6.5, 6.5 Hz) and two ³*J*_{PC} (5.0, 7.0 Hz) coupling constants were observed. When comparing compound **1** with its analogues **6** and **7** (Table 1), it can be noted that the isopropyl groups in these compounds show similar effect. That is, there are two distinct signals for the two methyl moieties of an isopropyl group, confirming that the CH₃ groups are diastereotopic.



Scheme 1 Syntheses of phosphoramidates 1-5.

Long-range coupling constant ${}^{4}J(P,C_{meta}) = 0.9$ Hz was observed in the ${}^{13}C$ NMR spectrum of **5** (Figure 1). Such a coupling has not been observed in our previous studies for other similar phosphoramidates. ${}^{16-20} {}^{7}J_{PH}$, ${}^{26} {}^{6}J_{PH}$, and ${}^{4}J_{HH} {}^{27}$ coupling constants have been reported earlier, but there is no statement about the presence of ${}^{4}J_{PC}$ in phosphoramidates. Moreover, two different values of ${}^{3}J_{PC} = 3.7, 8.7$ Hz were observed for the coupling of the *ortho* carbon atoms with the phosphorus atom in compound **5**.

| Table | 1 | Selected | spectroscopic | NMR and | IR data | of compounds | 1-5 |
|-------|---|----------|---------------|---------|---------|--------------|-----|
|-------|---|----------|---------------|---------|---------|--------------|-----|

| No. | Compound* | δ^{31} P (ppm) | ² J(PNH) _{amine} (Hz) | ³ J(P,C) _{aliphatic} (Hz) | ³ J(P,C) _{aromatic} (Hz) | $\nu(P=O)$ (cm ⁻¹) | ν (C=O) (cm ⁻¹) | Ref. |
|-----|--|--------------------------|--|--|---|-----------------------------------|------------------------------------|------|
| 1 | (Cl)P(O)R ¹ ₂ | 3.8 | _ | _ | _ | 1176 | _ | ** |
| 2 | (C ₆ H ₅ C(O)NH)P(O)R ¹ ₂ | 0.4 | _ | _ | _ | 1197 | 1658 | ** |
| 3 | (CCl ₃ C(O)NH)P(O)R ¹ ₂ | -1.1 | _ | _ | 2.8 | 1176 | 1686 | ** |
| 4 | (C ₆ H ₅ C(O)NH)P(O)R ² ₂ | 7.3 | 12.1 | 5.0, 7.0 (CH ₃) | 8.1 | 1207 | 1650 | ** |
| 5 | $(Cl)P(O)R_2^3$ | -5.6 | 11.1 | | 3.7, 8.7 | 1166 | 1687 | ** |
| 6 | [(CH ₃) ₂ N](<i>p</i> -CH ₃ -C ₆ H ₄ - O)P(O)R ² ₂ | 13.7 | _ | 5.9, 5.3 (CH ₃) | 4.8 | 1227 | — | 35 |
| 7 | $R_2P(O)(NHC_6H_4C(O)$ NH)P(O)R ₂ | 9.2 | — | 4.7, 5.4, | 7.0, 8.0 | 1225, | 1602 | 36 |
| | 2 | 9.3 | | 3.4, 2.1 | | 1169 | | |

 $*R^1 = NH-N = C(C_6H_5)_2, R^2 = NH-CH(CH_3)_2, R^3 = 2-NH-C_6H_4-C(O)OC_2H_5.$

^{**}This work.



Figure 1 Selected region of the ${}^{13}C{}^{1}H$ NMR spectrum of 5 showing long-range ${}^{4}J(P,C_{meta}) = 0.9$ Hz.

A comparison of the IR spectra of the two analogue compounds 2 and 3 (and also of compounds 2 and 4) shows that as the $\delta^{31}P$ shifts to upfield, the $\nu(P=O)$ value decreases, a behavior which is just the opposite to that of $\nu(C=O)$. The IR spectra reveal that $\nu(P=O)$ has the greatest value in compound 4 while it has the smallest value in compound 5. The frequency $\nu(C=O)$ shows the opposite trend: it has the largest value in compound 5 and the smallest value in compound 4. This phenomenon can be attributed to the resonance interaction between P=O and C=O bonds (Scheme 2) in compound 5, and the C=O bonds are free and strong. The tautomerism effect has been extensively described in other similar phosphoramidates.²⁸ For example, it was proposed that the acidic cleavage of P-N or P-S bonds takes place via an amide-imidoyl tautomerism.²⁹



Scheme 2 Tautomerism involving the carbonyl and phosphoryl moiety.

Computational Details

The structures of compounds **1–5** were optimized with the Hyperchem 7.0 program suite. Also, log P values were computed with Hyperchem in order to evaluate the lipophilicity of these molecules. Ab initio quantum chemical calculations were performed to fully optimize the geometry of the structures using the Gaussian 98 program²⁵ at the HF and B3LYP levels of theory and standard 6-31G^{*}, 6-31+G^{**} basis sets. The optimizations were followed by computations of the harmonic and vibrational frequencies, so that no imaginary frequencies were obtained in these computations. Nuclear quadrupole coupling constants (χ) were calculated from the equation $\chi = e^2 q_{zz} Q/h$,³⁰ assuming that the electric quadrupole moments (Q) of ²H, ¹⁷O, ³⁵Cl, and ¹⁴N nuclei are 2.860, -25.58, -81.65, and 20.44 mb, respectively.³¹ The principal components of the EFG tensor, q_{ii}, are computed in atomic units (1 au = 9.717365 × 10²¹ V m⁻²), with $|q_{zz}| \ge |q_{yy}| \ge |q_{xx}|$ and $q_{xx} + q_{yy} + q_{zz} = 0$. These diagonal elements relate to each other by the asymmetry parameter: $\eta_Q = |q_{yy} - q_{xx}|/|q_{zz}|$, $0 \le \eta_Q \le 1$, which measures the EFG tensor deviation from axial symmetry. The computed q_{zz} component of the EFG tensor is used to obtain the nuclear quadrupole coupling coupling constants (χ).

Ab Initio Calculations

To further study the structural properties of phosphoramidates 1–5, their geometries were optimized using Gaussian 98 software at the HF and B3LYP levels of theory with standard 6-31G* and 6-31+G** basis sets (Scheme 3). Stabilization energies were calculated from the equation $\Delta E = E(\text{molecule}) - \Sigma_i E(i)$, i = atom (Table 2). For all compounds, the B3LYP/6-31G* basis set provides the highest negative stabilization energies. Among compounds 1–5, molecule 2 has the greatest stabilization energy. The stabilization energy decreases in the order 2 >> 3 >> 1 >> 4 > 5. Although molecules 4 and 5 do not have similar structures, their ΔE values are very close to each other. The results show that the ΔE values do not increase by increasing the level of the basis set from 6-31G* to 6-31+G**.

Calculated dipole moments (μ , Debye) for compounds **1–5** are given in Table 3. The data show higher values at the HF as compared to the B3LYP level of theory. Among these compounds, **5** indicates the largest μ value at the HF/6-31G* level of theory. Compounds **2** and **3** with similar structures reveal nearly the same dipole moments. Structure-activity relationship (SAR) investigations are based on the idea that physicochemical changes affecting the biological activities have electronic, steric, and hydrophobic origins, while other factors such as hydrogen bonding, polarizability, and dipole moment appear to be

Table 2 Calculated stabilization energies (kcal/mol) for compounds 1-5*

| Compound | E(HF/6-31G*) | E(HF/6-31+G**) | E(B3LYP/6-31G*) | E(B3LYP/6-31+G**) |
|----------|--------------|----------------|-----------------|-------------------|
| 1 | -5759.808 | -5754.394 | -7620.470 | -7588.150 |
| 2 | -7306.097 | -7299.737 | -9658.732 | -9619.991 |
| 3 | -6489.488 | -6482.225 | -8616.063 | -8580.914 |
| 4 | -4579.041 | -4584.786 | -5797.174 | -5795.914 |
| 5 | -4269.931 | -4265.272 | -5774.118 | -5759.036 |

 $^{*}\Delta E = E(molecule) - \Sigma_{i} E(i), i = atom.$



Scheme 3 Selected numbering of the atoms for the optimized structures of phosphoramidates 1-5.

less important.³² It has been indicated that lipophilicity is an important parameter for biochemical, pharmacological, and environmental processes in quantitative structure-activity relationship (QSAR) studies.³³ Here, the lipophilicities of compounds **1**–5 were computed using Hyperchem software to predict their toxicities (Table 3). The log P values, which correspond to log (1/IC₅₀), reveal an order of toxicity $\mathbf{2} \approx \mathbf{3} > \mathbf{1} \approx \mathbf{5} > \mathbf{4}$. It can be seen that the size of a molecule is the most important parameter (steric effect) affecting log P,

| Compound | $\mu(\text{HF/6-31G}^*)$ | μ (HF/6-31+G**) | μ (B3LYP/6-31G*) | μ (B3LYP/6-31+G**) | log P |
|----------|--------------------------|---------------------|----------------------|------------------------|-------|
| 1 | 7.036 | 6.960 | 6.503 | 6.560 | 9.14 |
| 2 | 5.714 | 5.722 | 4.835 | 5.372 | 11.71 |
| 3 | 5.572 | 5.392 | 4.758 | 4.737 | 11.67 |
| 4 | 3.768 | 3.948 | 3.582 | 3.856 | 6.38 |
| 5 | 7.577 | 7.489 | 6.692 | 6.639 | 9.16 |

Table 3 Calculated dipole moments (μ , Debye) and log P for compounds 1–5

i.e., with decreasing size of a molecule, log P decreases. Thus the analogous compounds 2 and 3 and also compounds 1 and 5 with nearly the same size indicate similar toxicities. It is interesting that the lipophilicity of compound 2 is the greatest, while that of 4 is the smallest, although they have similar structures (both of them have a benzoyl substituent).

Selected computed bond lengths, angles, and torsion angles are presented in Table 4. These data are compared with those of previously reported similar compounds, $^{10-12,16-20,26,27,35,36}$ and are in good agreement with the published data. It becomes evident that the B3LYP method yields a better agreement with the experimental values as compared to the HF method. In compounds **2–4**, 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 π system. All P-N bonds are shorter than the typical P-N single bond (1.77 Å),³⁴ and the P=O bond lengths are larger than the normal P=O bond length (1.45 Å).³⁴

In molecules 1–5, the nitrogen environment is practically planar. In compound 1, the angles P(1)-N(2)-N(5), P(1)-N(2)-H(8), and N(5)-N(2)-H(8) are 118.73°, 118.48°, and 119.13°, respectively, with an average value of 118.78°. The sum of angles around the N(4) atom is 348.43°, with an average of 116.14°, indicating deviation from planarity. The N(5) and N(6) atoms have a planar surroundings, with N-N-C angles equal to 119.97° and 120.17°, respectively. Similar results were obtained for the nitrogen atoms of structures 2–5. This observation suggests the existence of partial multiple bond character between phosphorus and nitrogen atoms, which has been confirmed by the crystallographic data of similar compounds previously studied by us.^{10–12,16–20,26,27,35,36}

The P=O and C=O bonds in compounds 2–4 have *anti* configuration relative to each other with P=O…C=O pseudo-torsion angle of 54.63° (in 2), 98.55° (in 3) and 75.50° (in 4) at the B3LYP/6-31G* level of theory. In these molecules, the phosphorus atoms display distorted tetrahedral configuration; for example, the angles around it vary from 97.75° to 121.39° in 1 at the HF/6-31G* level of theory. Similar results were observed for other compounds and at other levels of theory.

Selected calculated nuclear quadrupole coupling constants (χ) for the quadrupole ¹⁴N, ²H, ¹⁷O, and ³⁵Cl nuclei of compounds **1–5** are presented in Table 5. The B3LYP method yields higher χ values than HF method. In molecules **1–3**, the nitrogen atoms connected to the phosphorus atom have smaller χ values than the N atoms of the N=C groups. Also, in compounds **2–4**, the smaller χ values for the amidic N atoms as compared with those of the amino N nuclei are perhaps due to the electron withdrawing amidic moiety, which leads to a shielding of the amidic N atom. In compounds **2–5**, the oxygen atoms of P=O and C=O units have χ values about 5.0 and 10.0 MHz, respectively. The reason for the fact that the χ values of the oxygen atoms in phosphoryl moieties are almost half of the corresponding values of the oxygen atoms in the carbonyl groups might be the more positive carbonyl oxygen atoms, as well as resonance interactions. The χ values for ¹⁴N and ²H were obtained to be 4–6 MHz and 180–190 KHz, respectively. The ³⁵Cl nuclei in compounds **1** and **5** show χ values of about 50 MHz, while the ³⁵Cl atoms of compound **3** display $\chi \approx 80$ MHz.

To find which resonance structures of compounds 2 and 3 are in agreement with above results, the two tautomeric structures A and B for each molecule were optimized at the HF and B3LYP levels of theory using the 6-31G* basis set (Scheme 4). Results indicate that the RC(OH) = N-P(O) form (2B, 3B) is the preferred form, as compared to RC(O)N = P(OH) (2A, 3A). Although the stabilization energies of the two resonance forms A and B are close to each other (Table 6), the χ values of 2A and 3A are very consistent with those of compounds 2 and 3 (Table 7). The dipole moments of 2B and 3B are smaller than those

NEW PHOSPHORAMIDATES: SPECTROSCOPIC STUDY



Scheme 4 Tautomeric structures 2A, 2B and 3A, 3B for compounds 2 and 3.

of 2A and 3A, respectively. The log P values show the order of 2A < 2B < 2 and also 3A < 3B < 3, indicating that the lipophilicity of form B is closer to the main structure than that of form A.

EXPERIMENTAL

 1 H, 13 C, and 31 P spectra were recorded with a Bruker Avance DRS 500 spectrometer. 1 H and 13 C chemical shifts are given relative to internal TMS, 31 P chemical shifts relative to 85% H₃PO₄ as external standard. Infrared (IR) spectra were recorded with 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.

N,N'-Bis(benzophenone hydrazinyl) Phosphoramidic Chloride (1)

To a solution of phosphorylchloride (1.54 g, 10 mmol) in dry acetonitrile, benzophenonehydrazone (3.92 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were added dropwise at 0°C, and the mixture was stirred for 12 h. Then the white precipitate was filtered, washed with distilled water, and dried. Yield: 59%; Anal. Calcd. For C₂₆H₂₂ClN₄OP: C, 66.03; H, 4.96; N, 11.85%. Found: C, 66.00; H, 4.95; N, 11.86%. ³¹P{¹H} NMR (CDCl₃): δ = 7.26–7.51 (m, 11H, arom-H). ¹³C NMR (CDCl₃): δ = 127.9,

| | 14010 |
|---|-------------------------|
| | Compound |
| | 1 |
| | P=O |
| | P-N P-Cl |
| | N-N |
| | C=N |
| | O=P-N |
| | O=P-Cl |
| 4 | P-N-N O=P-N-N |
| 201 | P-N-N=C |
| er | 2 |
| nbe | P=O |
| ven | P-N _{amide} |
| 0 Z | P-N _{amine} |
| 21 1 | N-N |
| 2 | C=N |
| 4:1 | O=P-Nomi |
| t Ó | O=P-N _{ami} |
| Ja | P-N-N |
| bia | O=P-N-N |
| Line in the second s | P-N-N=C |
| Jol | 3 |
| hO | P=O P N |
| tis | P-Namina |
| Bri | N-N |
| of | C=N |
| ty | O=P-N _{ami} |
| ersi | O=P-N _{ami} |
| iive | O = P - N - N |
| U | P-N-N=C |
| he | 4 |
| E | P=O |
| by | P-N _{amide} |
| eq | P-N _{amine} |
| pad | C=0 C-N |
| nlc | O=P-N |
| MO | O=P-N _{ami} |
| Ā | P-N _{amide} -C |

 $\label{eq:table 4} \mbox{Table 4} \mbox{Selected calculated bond lengths (Å), angles (°), and torsion angles (°) for compounds 1-5$

B3LYP/6-31G*

B3LYP/6-31+G**

HF/6-31+G**

HF/6-31G*

| 1 | | | | |
|---------------------------|---------|---------|---------|---------|
| P=O | 1.446 | 1.447 | 1.476 | 1.477 |
| P-N | 1.647 | 1.646 | 1.672 | 1.673 |
| P-Cl | 2.042 | 2.045 | 2.089 | 2.089 |
| N-N | 1.364 | 1.363 | 1.367 | 1.368 |
| C=N | 1.260 | 1.261 | 1.292 | 1.292 |
| O=P-N | 121 39 | 116 19 | 116 31 | 116 11 |
| $O = P - C^{1}$ | 111.03 | 110.93 | 111.67 | 111.62 |
| P-N-N | 118.72 | 118.62 | 119.04 | 119.16 |
| $\Omega = P_N N$ | 10.72 | 40.046 | 37 684 | 37 860 |
| $P_N = C$ | 171 /1 | 170.80 | 170.48 | 170.72 |
| 1-10-10-0 | -1/1.41 | -170.00 | -170.46 | -170.72 |
| 2 | 1 457 | 1.460 | 1 404 | 1 400 |
| P=0 | 1.457 | 1.460 | 1.484 | 1.488 |
| P-N _{amide} | 1.672 | 1.671 | 1.693 | 1.691 |
| P-N _{amine} | 1.665 | 1.662 | 1.692 | 1.686 |
| N-N | 1.358 | 1.359 | 1.361 | 1.364 |
| C=N | 1.261 | 1.262 | 1.293 | 1.294 |
| C=O | 1.195 | 1.197 | 1.221 | 1.224 |
| O=P-N _{amide} | 120.52 | 120.19 | 121.51 | 121.63 |
| O=P-N _{amine} | 108.45 | 108.27 | 108.45 | 107.70 |
| P-N-N | 121.46 | 121.35 | 120.77 | 121.30 |
| O=P-N-N | -178.65 | -178.59 | -178.89 | -179.90 |
| P-N-N=C | -175.99 | -174.52 | 179.18 | -176.12 |
| 3 | | | | |
| Р=О | 1 453 | 1 455 | 1 481 | 1 484 |
| I -O | 1.455 | 1.455 | 1.401 | 1.484 |
| r-N _{amide} | 1.707 | 1.703 | 1.734 | 1./34 |
| P-N _{amine} | 1.009 | 1.004 | 1.081 | 1.081 |
| N-N | 1.369 | 1.30/ | 1.376 | 1.373 |
| C=N | 1.261 | 1.261 | 1.293 | 1.293 |
| O=P-N _{amide} | 115.80 | 115.53 | 115.86 | 115.61 |
| O=P-N _{amine} | 110.40 | 110.05 | 110.54 | 109.72 |
| P-N-N | 119.94 | 120.00 | 119.86 | 120.74 |
| O=P-N-N | 166.64 | 175.29 | 179.07 | 177.67 |
| P-N-N=C | -152.86 | -157.60 | -154.52 | -162.07 |
| 4 | | | | |
| P=O | 1.462 | 1.463 | 1.492 | 1.493 |
| P-N _{amide} | 1.703 | 1.701 | 1.731 | 1.730 |
| P-N _{amine} | 1.657 | 1.653 | 1.681 | 1.677 |
| C=O | 1.198 | 1.200 | 1.225 | 1.228 |
| C-N _{amide} | 1.382 | 1.382 | 1.397 | 1.397 |
| O=P-N _{amide} | 114.69 | 114.66 | 114.52 | 114.69 |
| O=P-N _{amine} | 118.38 | 117.80 | 120.02 | 119.26 |
| P-Namide-C | 135.83 | 135.98 | 135.88 | 136.21 |
| O=P-Namide-C | 73.98 | 70.360 | 77.650 | 70.684 |
| O=P-N _{amine} -C | 43.76 | 41.416 | 44.524 | 40.982 |
| 5 | | | | |
| P=0 | 1 451 | 1 452 | 1 480 | 1 482 |
| P-N | 1.653 | 1.651 | 1 675 | 1.674 |
| P-C1 | 2 027 | 2 030 | 2 073 | 2 072 |
| C=0 | 1 201 | 1 202 | 1 220 | 1 220 |
| C=0 | 1.201 | 1.202 | 1.2.50 | 1.232 |
| O-PN | 1.310 | 1.317 | 1.345 | 1.343 |
| O = P - N | 117.94 | 117.01 | 117.09 | 118.00 |
| U-P-CI | 115.29 | 115.02 | 114.41 | 114.00 |
| P-N-C | 133.47 | 133.45 | 132.85 | 132.99 |
| U=P-N-C | 179.85 | -178.61 | 178.38 | 179.09 |
| N-P-N-C | -49.710 | -48.198 | -51.199 | -50.593 |

| | compounds 1–5 | |
|-------------|---------------|-----------|
| | Compound | HF/6-31G* |
| | 1 | |
| | 01 | 4.9178 |
| | N2 | 5.5122 |
| | C13 | 49.092 |
| | N4 | 5.4919 |
| | N5 | 5.9770 |
| | N6 | 5.8462 |
| | H7 | 278.9 |
|)17 | H8 | 274.8 |
| 5(| 2 | |
| er | 01 | 5.0526 |
| nb | N2 | 5.6141 |
| /eI | N3 | 5.6226 |
| 6 | N4 | 4.2568 |
| Z | N5 | 5.9437 |
| 21 | N6 | 5.9031 |
| 2 | 07 | 10.530 |
| | H8 | 280.0 |
| Õ | H9 | 281.3 |
| at | H10 | 279.7 |
| ia] | 3 | |
| hb | 01 | 4,7398 |
| In | N2 | 5 4930 |
| 0 | N3 | 5 5159 |
| | N4 | 4,4101 |
| isl | N5 | 5.8154 |
| Li | N6 | 5.7730 |
| Е Н | 07 | 10.024 |
| б | C18 | 83.951 |
| ity | C19 | 80.576 |
| SIS | C110 | 79.530 |
| IVE | H11 | 284.1 |
| in | H12 | 277.1 |
| | H13 | 268.8 |
| The | 4 | |
| y [| 01 | 4.8597 |
| Â. | N2 | 5.0674 |
| led | N3 | 5.2362 |
| ad | N4 | 4.2818 |
| olı | 05 | 10.408 |
| WI | H6 | 285.5 |
| OC | H7 | 289.9 |
| Ι | H8 | 294.9 |
| | H9 | 201.3 |
| | H10 | 202.8 |
| | 5 | |
| | 01 | 5.0775 |

Table 5 Calculated nuclear quadrupole coupling constants (χ) for ²H (KHz) and ¹⁷O, ¹⁴N, ³⁵Cl (MHz) atoms of compounds **1–5**

B3LYP/6-31G*

HF/6-31+G**

| 1 | | | | |
|----------|---------|--------|---------|--------------------------------------|
| 01 | 4.9178 | 4.9169 | 5.2541 | 5.3367 |
| N2 | 5.5122 | 5.5033 | 4.9086 | 4.8960 |
| Cl3 | 49.092 | 49.740 | 50.5535 | 51.511 |
| N4 | 5.4919 | 5.4757 | 4.9465 | 4.9411 |
| N5 | 5.9770 | 5.9705 | 5.1154 | 5.1043 |
| N6 | 5.8462 | 5.8298 | 5.0117 | 5.0099 |
| H7 | 278.9 | 282.7 | 236.2 | 239.9 |
| H8 | 274.8 | 278.9 | 234.3 | 238.2 |
| 2 | | | | |
| 01 | 5 0526 | 5 0990 | 5 3759 | 5 4908 |
| N2 | 5 6141 | 5 5969 | 5 0498 | 5.0027 |
| N3 | 5 6226 | 5 6680 | 5 1206 | 5 1083 |
| NJ NJ | 4 2568 | J.0000 | 2 8157 | 3,8055 |
| N5 | 4.2308 | 4.2447 | 5.0614 | 5.0346 |
| N6 | 5.9437 | 5.9102 | 4.0424 | 4 0244 |
| 07 | 10 520 | 10.420 | 4.9424 | 4.9244 |
| U/ | 280.0 | 10.420 | 9.7292 | 9.0459 |
| 118 | 280.0 | 202.0 | 235.0 | 230.1 |
| H9 | 281.3 | 285.1 | 240.0 | 243.1 |
| HIU | 279.7 | 284.4 | 239.2 | 242.6 |
| 3 | | | | |
| 01 | 4.7398 | 4.7745 | 5.0127 | 5.1280 |
| N2 | 5.4930 | 5.4751 | 4.9407 | 4.9493 |
| N3 | 5.5159 | 5.4994 | 4.9183 | 4.8989 |
| N4 | 4.4101 | 4.3721 | 3.8846 | 3.8031 |
| N5 | 5.8154 | 5.8192 | 4.9678 | 4.9887 |
| N6 | 5.7730 | 5.7907 | 4.9535 | 4.9928 |
| 07 | 10.024 | 10.045 | 8.9863 | 9.0141 |
| C18 | 83.951 | 84.004 | 81.780 | 81.898 |
| C19 | 80.576 | 80.761 | 79.176 | 79.573 |
| Cl10 | 79.530 | 79.576 | 77.065 | 77.080 |
| H11 | 284.1 | 288.0 | 246.7 | 249.0 |
| H12 | 277.1 | 281.4 | 235.8 | 240.6 |
| H13 | 268.8 | 271.9 | 224.8 | 227.1 |
| 4 | | | | |
| 01 | 4.8597 | 4.9202 | 5.1356 | 5.2366 |
| N2 | 5.0674 | 5.0511 | 4.7272 | 4.7410 |
| N3 | 5.2362 | 5.2072 | 5.0690 | 5.0210 |
| N4 | 4.2818 | 4.2122 | 3.9783 | 3.8751 |
| 05 | 10.408 | 10.336 | 9.5765 | 9.4903 |
| H6 | 285.5 | 288.3 | 249.3 | 251.5 |
| H7 | 289.9 | 297.3 | 249.0 | 257.8 |
| H8 | 294.9 | 300.2 | 257.8 | 263.1 |
| H9 | 201.3 | 200.5 | 181.1 | 181.4 |
| H10 | 202.8 | 202.2 | 183.2 | 183.9 |
| 5 | | | | |
| 01 | 5.0775 | 5,1108 | 5.3788 | 5.4407 |
| N2 | 4 2856 | 4 2604 | 3 8184 | 3 7737 |
| Cl3 | 51 1882 | 52.090 | 51,9943 | 53 086 |
| N4 | 4 6857 | 4 6280 | 4 1799 | 4 1005 |
| 05 | 9.4310 | 9,4262 | 8 5300 | \$ 5350 |
| 06 | 10 119 | 10.022 | 9 2551 | 9 1844 |
| 07 | 0.119 | 9 175 | 8 50381 | 9.10 11 8 5 710 |
| 08 | 10 133 | 10.028 | 0.2655 | 0.5710 |
| H0 | 251.8 | 254.0 | 202055 | 205.8 |
| H10 | 251.0 | 254.0 | 207.1 | 203.0 |
| 1110 | 201.4 | 203.4 | 212.3 | 212.1 |

B3LYP/6-31+G**

| | | E | μ | | | |
|----------|-----------|--------------|-----------|--------------|-------|--|
| Compound | HF/6-31G* | B3LYP/6-31G* | HF/6-31G* | B3LYP/6-31G* | log P | |
| 2A | -7293.777 | -9650.645 | 5.8360 | 5.8473 | 9.99 | |
| 2B | -7291.702 | -9645.995 | 2.4895 | 2.7128 | 10.34 | |
| 3A | -6479.449 | -8604.162 | 7.620 | 6.709 | 9.94 | |
| 3B | -6468.789 | -8597.365 | 4.534 | 4.036 | 10.29 | |

Table 6 Calculated stabilization energies, dipole moments, and log P values for compounds 2A, 2B, 3A, and 3B

128.0, 128.6, 128.7, 129.3, 129.6, 135.6, 138.2, 158.9. IR (KBr, cm⁻¹): 3421 (NH), 3098 (CH), 3023 (CH), 1176 (P=O).

N-Benzoyl-*N*,*N*'-bis(benzophenone hydrazinyl) Phosphoric Triamide (2)

To a solution of *N*-benzoyl phosphoramidic dichloride³⁷ (2.38 g, 10 mmol) in dry acetonitrile, benzophenonehydrazone (3.92 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were added dropwise at 0° C, and the mixture was stirred for 10 h. Then the white precipitate was filtered, washed with distilled water, and dried. Yield: 66%; Mp 158°C.

| compounds 2A, 2D, 5A, and 5D | | | | | | | |
|------------------------------|-----------|--------------|----------|-----------|--------------|--|--|
| Compound | HF/6-31G* | B3LYP/6-31G* | Compound | HF/6-31G* | B3LYP/6-31G* | | |
| 2A | | | 2B | | | | |
| O1 | 7.6854 | 6.4642 | 01 | 5.1208 | 5.4109 | | |
| N2 | 5.5484 | 5.0602 | N2 | 5.5791 | 4.9702 | | |
| N3 | 5.5083 | 4.9340 | N3 | 5.6864 | 4.9220 | | |
| N4 | 3.4494 | 3.0889 | N4 | 3.5012 | 3.2139 | | |
| N5 | 5.8710 | 5.0952 | N5 | 6.1970 | 5.2405 | | |
| N6 | 6.0502 | 5.0116 | N6 | 6.0981 | 5.1347 | | |
| 07 | 8.8216 | 7.1600 | O7 | 9.7340 | 8.8892 | | |
| H8 | 270.4 | 276.0 | H8 | 328.9 | 270.3 | | |
| H9 | 274.7 | 236.3 | H9 | 280.2 | 237.0 | | |
| H10 | 275.5 | 238.4 | H10 | 279.3 | 238.7 | | |
| 3A | | | 3B | | | | |
| 01 | 9.0279 | 8.4819 | 01 | 4.8785 | 5.1193 | | |
| N2 | 5.7301 | 5.2347 | N2 | 5.7086 | 5.1280 | | |
| N3 | 5.3410 | 4.6924 | N3 | 5.5176 | 4.8626 | | |
| N4 | 3.6621 | 3.3551 | N4 | 4.2957 | 3.7473 | | |
| N5 | 5.7756 | 4.9479 | N5 | 5.9941 | 5.0896 | | |
| N6 | 5.7764 | 4.9684 | N6 | 5.8896 | 5.0425 | | |
| 07 | 9.7405 | 8.8214 | 07 | 10.082 | 9.1661 | | |
| C18 | 80.444 | 79.356 | C18 | 79.515 | 77.968 | | |
| C19 | 78.688 | 77.235 | C19 | 79.096 | 77.127 | | |
| C110 | 79.519 | 78.108 | C110 | 85.609 | 83.561 | | |
| H11 | 337.6 | 284.2 | H11 | 333.6 | 274.7 | | |
| H12 | 280.0 | 239.8 | H12 | 280.9 | 239.2 | | |

H13

275.6

212.3

233.6

Table 7 Calculated nuclear quadrupole coupling constants (χ) for ²H (KHz) and ¹⁷O, ¹⁴N, ³⁵Cl (MHz) atoms of compounds **2A**, **2B**, **3A**, and **3B**

H13

261.8

Anal. Calcd. For $C_{33}H_{28}N_5O_2P$: C, 71.08; H, 5.06; N, 12.56%. Found: C, 71.06; H, 5.05; N, 12.55%. ³¹P{¹H} NMR (CDCl₃): $\delta = 0.4$ (s). ¹H NMR (CDCl₃): $\delta = 7.25-7.57$ (m, 28H, arom-H). ¹³C NMR (CDCl₃): $\delta = 127.3$, 127.9, 128.0, 128.1, 128.6, 128.7, 128.8, 129.3, 129.6, 158.9 (C=O). IR (KBr, cm⁻¹): 3368 (NH), 3169 (CH), 3056 (CH), 1658 (C=O), 1197 (P=O).

N-Trichloroacetyl-N',N'-bis(benzophenone hydrazinyl) Phosphoric Triamide (3)

To a solution of *N*-trichloroacetyl phosphoramidic dichloride³⁸ (2.80 g, 10 mmol) in dry acetonitrile, benzophenonehydrazone (3.92 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were added dropwise at 0°C, and the mixture was stirred for 13 h. Then the white precipitate was filtered, washed with distilled water, and dried. Yield: 56%; Anal. Calcd. For C₂₈H₂₃Cl₃N₅O₂P: C, 56.16; H, 3.87; N, 11.69%. Found: C, 56.15; H, 3.86; N, 11.68%. ³¹P{¹H} NMR (d₆-DMSO): $\delta = -1.1$ (s). ¹H NMR (d₆-DMSO): $\delta = 7.27$ (d, ³*J*_{HH} = 7.0 Hz, 4H, arom-H), 7.33–7.46 (m, 19H, arom-H). ¹³C NMR (d₆-DMSO): $\delta = 91.3$ (CCl₃), 128.0 (d, ³*J*_{PC} = 2.8 Hz), 128.2, 128.7, 135.1, 137.4, 168.8 (C=O). IR (KBr, cm⁻¹): 3241 (CH), 3022 (CH), 1686 (C=O), 1176 (P=O).

N-Benzoyl-N,N'-diisopropyl Phosphoric Triamide (4)

To a solution of *N*-benzoyl phosphoramidic dichloride³⁷ (2.38 g, 10 mmol) in dry acetonitrile, isopropylamine (1.18 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were added dropwise at 0°C, and the mixture was stirred for 15 h. Then the white precipitate was filtered, washed with distilled water, and dried. Yield: 73%; Mp 164°C. Anal. Calcd. For C₁₃H₂₀N₃O₂P: C, 55.51; H, 7.17; N, 14.94%. Found: C, 55.50; H, 7.18; N, 14.93%. ³¹P{¹H} NMR (CDCl₃): δ = 7.3 (s). ¹H NMR (CDCl₃): δ = 1.12 (d, ³*J*_{HH} = 6.5 Hz, 6H, CH₃), 1.19 (d, ³*J*_{HH} = 6.5 Hz, 6H, CH₃), 3.07 (dd, ³*J*_{HH} = 8.9 Hz, ²*J*_{PH} = 12.1 Hz, 2H, NH_{amine}), 3.54 (m, 2H, CH), 7.44 (t, ³*J*_{HH} = 7.7 Hz, 2H, arom-H), 7.64 (t, ³*J*_{HH} = 7.7 Hz, 1H, arom-H), 8.04 (d, ³*J*_{PC} = 5.0 Hz, CH₃), 25.7 (d, ³*J*_{PC} = 7.0 Hz, CH₃), 43.4 (CH), 128.0, 128.6, 132.4, 133.4 (d, ³*J*_{PC} = 8.1 Hz, C_{ipso}), 169.1 (s, C=O). IR (KBr, cm⁻¹): 3261 (CH), 2957 (CH), 1650 (C=O), 1207 (P=O).

N,N-Bis(ethyl 2-benzoate) Phosphoramidic Chloride (5)

To a solution of phosphorylchloride (1.54 g, 10 mmol) in dry acetonitrile, ethyl 2aminobenzoate (3.30 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were added dropwise at 0°C, and the mixture was stirred for 15 h. Then the white precipitate was filtered, washed with distilled water, and dried. Yield: 51%; Mp 128°C. Anal. Calcd. For C₁₈H₂₀ClN₂O₅P: C, 52.63; H, 4.91; N, 6.82%. Found: C, 52.61; H, 4.90; N, 6.81%. ³¹P{¹H} NMR (CDCl₃): $\delta = -5.6$ (s). ¹H NMR (CDCl₃): $\delta = 1.36$ (t, ³*J*_{HH} = 7.2 Hz, 6H, CH₃), 4.31 (q, ³*J*_{HH} = 7.2 Hz, 4H, CH₂), 6.93 (t, ³*J*_{HH} = 8.3 Hz, 2H, arom-H), 7.42 (t, ³*J*_{HH} = 8.3 Hz, 2H, arom-H), 7.80 (t, ³*J*_{HH} = 8.3 Hz, 2H, arom-H), 7.99 (d, ³*J*_{HH} = 8.3 Hz, 2H, arom-H), 9.63 (d, ²*J*_{PH} = 11.1 Hz, 1H, NH). ¹³C NMR (CDCl₃): $\delta = 14.2$ (CH₃), 61.1 (CH₂), 114.7 (d, ³*J*_{PC} = 8.7 Hz), 118.6 (d, ³*J*_{PC} = 3.7 Hz), 120.4, 131.2, 134.5, 144.2 (d, ⁴*J*_{PC} = 0.9 Hz), 168.3 (C=O). IR (KBr, cm⁻¹): 3224 (CH), 2980 (CH), 1687 (C=O), 1166 (P=O).

Z. SHARIATINIA ET AL.

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