Journal of Structural Chemistry. Vol. 52, No. 2, pp. 287-294, 2011
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SPECTROSCOPIC CHARACTERIZATION AND *AB INITIO* CALCULATIONS OF NEW DIAZAPHOSPHOLE AND DIAZAPHOSPHORINANE

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UDC 541.6:538.11:547.24

Phosphoryl chloride is used as a starting material to synthesize new diazaphosphole, $4{-}OCH_3{-}C_6H_4NH\overline{P(O)[4{-}CH_3{-}NH{-}C_6H_3{-}NH}]$ (**1**) and diazaphosphorinane, $4{-}OCH_3{-}C_6H_4NH\overline{P(O)[NH{-}C_{10}H_6{-}NH}]$ (**2**). The products are characterized by ^1H, ^{13}C, ^{31}P NMR, and IR spectroscopy. A high value $^2J(PNH) = 17.0$ Hz, 17.2 Hz is measured for two non-equivalent NH protons of endocyclic nitrogen atoms in compound **1,** while it greatly decreases to 4.5 Hz in **2**. Also, great amounts are obtained for two $^2J(P,C)$ as well as two $^3J(P,C)$ in the ^{13}C NMR spectrum of **1**, but they are zero in **2**. Here, the effect of ring strain and ring size on the structural and spectroscopic parameters is observed. The ^{31}P NMR spectra reveal that $\delta(^{31}P)$ of compound **1** is far much more downfield (12.63 ppm) relative to that of compound **2** (–10.39 ppm). Furthermore, *ab initio* quantum chemical calculations are performed to optimize the structures of these molecules by density functional theory (B3LYP) and Hartree-Fock (HF) methods, using the standard 6-31+G** basis set. The stabilization energies are calculated by the equation $\Delta E_{\text{stabilization}} = E_{\text{molecule}} - \sum E_i$, where i = atom. To obtain the atomic hybridizations, NBO computations are made at the B3LYP/6-31+G** level. Also, by NMR calculations the ^1H, ^{13}C, ^{31}P chemical shifts are obtained and compared with the experimental ones.

Keywords: diazaphosphole, diazaphosphorinane, ^1H, ^{13}C, ^{31}P NMR, *ab initio* calculations.

INTRODUCTION

Diazaphospholes and diazaphosphorinanes are considered to be important compounds due to their great application in chemistry and medicine [1, 2]. So far, the structures [3-5] and coupling constant assignments of these compounds have been reported [3]. The stereochemistry and P–C coupling constants of 2-oxo-, 2-thio-diazaphosphorinanes [6], and 1,3,2-benzodiazaphospholes were already discussed [7]. Also, phosphorus-hydrogen coupling constants in some diazaphospholes with three coordinated phosphorus atoms were studied [8]. Near-range phosphorus-hydrogen and phosphorus-carbon coupling constants have been measured and applied for assignments and descriptions of the structural and chemical properties [9, 10]. The $^{2,3}J(P{-}X)$ [X = H, C] coupling constant dependence on the ring size, hybridization and substituents in some diazaphospholes and diazaphosphorinanes have been reported [5]. The chemistry of 1,3,2-diazaphosphorinanes including synthesis, [11, 12] stereochemistry, [13] coordination chemistry, [14, 15] and X-ray crystal structures [3-5, 16] have recently

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been studied. In this work, new 1,3,2-diazaphosphorinane and 1,3,2-diazaphosphole were synthesized and characterized by NMR and IR spectroscopic methods. Moreover, *ab initio* quantum chemical calculations were conducted at the B3LYP and HF levels of theory with the standard 6-31+G** basis set, and the stabilization energies were calculated from the equation $\Delta E_{\text{stabilization}} = E_{\text{molecule}} - \sum E_i$, where i = atom. In addition, NBO computations were made at the B3LYP/6-31+G** level to obtain atomic hybridizations as well as to discuss their different structural properties. Also, the NMR calculations yielded the ^{1}H, ^{13}C, ^{31}P chemical shifts that were compared with the experimental results.

EXPERIMENTAL.
SPECTROSCOPIC MEASUREMENTS

All reagents and solvents for synthesis were obtained from a commercial source (Merck). All reactions were performed under the argon atmosphere and in dry solvents. Melting points were determined using the Electrothermal instrument. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to internal TMS and ^{31}P chemical shifts relative to 85% H_3PO_4 as the external standard. Infrared (IR) spectra were recorded on a Shimadzu IR-60 spectrometer.

SYNTHESES.
GENERAL PROCEDURE

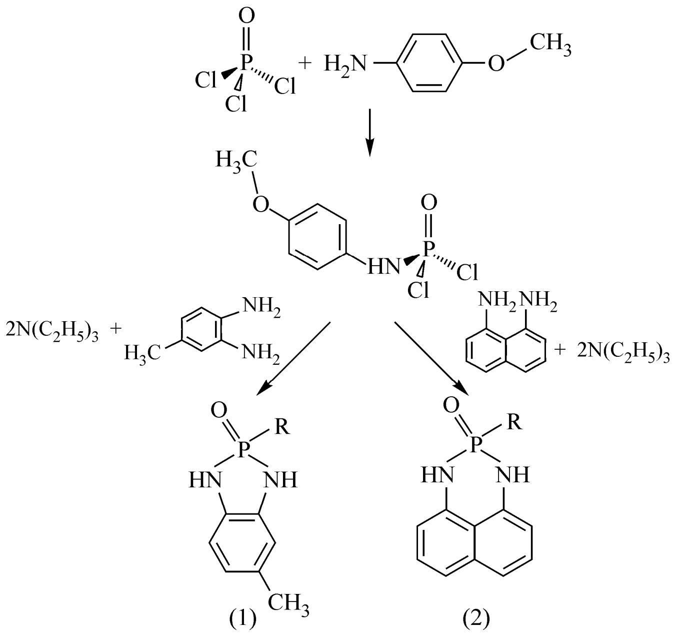
N-4-Methoxyphenyl phosphoramidic dichloride, $4\text{-}CH_3O\text{–}C_6H_4NHP(O)Cl_2$ was prepared by the reaction of phosphorylchloride with *p*-anisidine (4-methoxyaniline) in acetonitrile at –5°C according to the literature method [17]. The synthesis of compounds **1** and **2** was carried out by the reaction of N-4-methoxyphenyl phosphoramidic dichloride with 4-methyl-1,2-phenylenediamine (for **1**) and 1,8-naphthalenediamine (for **2**) in the presence of an HCl scavenger, i.e. triethylamine (Scheme 1).

7-Methyl-2-(4-methoxyanilino)-1,3,2-diazaphosphol-2-oxide (1). Yield: 72%. M.p. 245°C. ^{1}H NMR (500.13 MHz, d_6-DMSO): $\delta = 2.19$ (s, 3H, CH_3), 3.58 (s, 3H, OCH_3), 6.49 (m, 3H, Ar–H), 6.59 (d, ^2J(H,H) = 9.9 Hz, 2H, Ar–H), 6.63 (d, ^2J(H,H) = 8.9 Hz, 2H, Ar–H), 7.68 (d, ^2J(PNH) = 8.6 Hz, 1H, $NH_{\text{exocyclic}}$), 8.25 (d, ^2J(PNH) = 17.0 Hz, 1H, $NH_{\text{endocyclic}}$), 8.33 (d, ^2J(PNH) = 17.2 Hz, 1H, $NH_{\text{endocyclic}}$). ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 153.34$ (s), 135.37 (s), 132.09 (d, ^2J(P,C) = 13.5 Hz), 129.64 (d, ^2J(P,C) = 13.5 Hz), 127.44 (s), 119.00 (s), 118.26 (d, ^3J(P,C) = 7.5 Hz), 114.14 (s), 110.29 (d, ^3J(P,C) = 12.2 Hz), 109.20 (d, ^3J(P,C) = 12.2 Hz), 55.13 (s), 20.93 (s). ^{31}P NMR (202.46 MHz, d_6-DMSO): $\delta = 12.63$ (dt, ^2J(PNH) = 17.0 Hz, ^2J(PNH) = 8.6 Hz). IR (KBr): $\bar{\nu} = 3320$ (NH), 3100 cm^{-1} (NH), 2915 cm^{-1}, 1545 cm^{-1}, 1504 cm^{-1}, 1460 cm^{-1}, 1285 cm^{-1}, 1175 cm^{-1} (P=O), 1097 cm^{-1}, 956 cm^{-1}, 840 cm^{-1}, 450 cm^{-1}.

2-(4-Methoxyanilino)-1,3,2-naphtho diazaphosphorinane-2-oxide (2). Yield: 70%. M.p. 293°C. ^{1}H NMR (500.13 MHz, d_6-DMSO): $\delta = 3.75$ (s, 3 H, OCH_3), 6.56 (d, ^3J(H,H) = 3.7 Hz, 2H, Ar–H), 6.67 (d, ^3J(H,H) = 8.9 Hz , 2H, Ar–H), 6.91 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar–H), 7.10 (d, ^3J(H,H) = 8.2 Hz, 2H, Ar–H), 7.16 (t, ^3J(H,H) = 7.8Hz, 2H, Ar–H), 7.67 (d, ^2J(PNH) = 8.9 Hz, 1H, $NH_{\text{exocyclic}}$), 8.57 (d, ^2J(PNH) = 4.5 Hz, 2H, $NH_{\text{endocyclic}}$). ^{13}C NMR (125.77 MHz, d_6-DMSO): $\delta = 153.37$ (s), 139.89 (s), 135.15 (s), 127.31 (s), 118.55 (s), 118.52 (s), 117.75 (s), 114.12 (s) 107.58 (s), 107.52 (s), 55.11 (s). ^{31}P NMR (202.46 MHz, d_6-DMSO) $\delta = -10.39$ (td, ^2J(PNH) = 8.9 Hz, ^2J(PNH) = 4.5 Hz). IR (KBr): $\bar{\nu} = 3220$ cm^{-1} (NH), 2935 cm^{-1} (NH), 2595 cm^{-1}, 2480 cm^{-1}, 1585 cm^{-1}, 1503 cm^{-1}, 1465 cm^{-1}, 1364 cm^{-1}, 1234 cm^{-1}, 1100 cm^{-1} (P=O), 1059 cm^{-1}, 1027 cm^{-1}, 957 cm^{-1}, 819 cm^{-1}, 752 cm^{-1}.

COMPUTATIONAL DETAILS

The optimized structures of molecules **1** and **2** were obtained by *ab initio* quantum chemical calculations using the Gaussian-98 software [18] with density functional theory (B3LYP) and Hartree–Fock (HF) methods and the standard



Scheme 1. Preparation pathway of compounds **1** and **2**.

TABLE 1. Some NMR Spectroscopic Data for Compounds **1** and **2**

Molecule	$^2J(PNH_{endocyclic})$, Hz	$^2J(PNH_{exocyclic})$, Hz	$\delta(^{31}P)$, ppm	$\overline{\nu}$ (P=O), cm^{-1}
1	17.0, 17.2	8.6	12.63	1175
2	4.5	8.9	–10.39	1100

6-31+G** basis set without symmetry constrains. The optimizations were followed by computations of harmonic and vibrational frequencies so that no imaginary frequency was obtained. The NBO computations were made at the B3LYP/6-31+G** level of theory to obtain atomic hybridizations. Moreover, the ^1H, ^{13}C, ^{31}P NMR chemical shifts were calculated by both HF and B3LYP methods to compare the results with the experimental ones.

RESULTS AND DISCUSSION

Spectroscopic study. In this research, two new phosphorus compounds, diazaphosphole (**1**) and diazaphosphorinane (**2**), were prepared from the reaction of N-4-methoxyphenyl phosphoramidic dichloride with corresponding diamines (Scheme 1). A summary of the spectroscopic data of these molecules is presented in Table 1.

The ^1H NMR spectrum of compound **1** shows two doublet signals with a high value of $^2J(PNH_{endocyclic})$ coupling constants (17.0 Hz, 17.2 Hz) for two non-equivalent NH protons of endocyclic nitrogen atoms. It seems that these high values are related to the strain of the ring. This phenomenon has recently been reported for the other similar compounds [5]. To confirm the effect of the ring strain and ring size, compound **2** was considered, which exhibits a drastic reduction for the $^2J(PNH_{endocyclic})$ coupling constant (4.5 Hz) with increasing ring members from five to six. On the other hand, the $^2J(PNH_{exocyclic})$ values for both **1** and **2** molecules are nearly the same (about 9.0 Hz). Moreover, the ^{13}C NMR spectrum of **1** reveals high values for two $^2J(P,C) = 13.5$ Hz as well as for two $^2J(P,C) = 12.2$ Hz, while these constants are zero in **2**. Surprisingly, the ^{31}P NMR spectra display that $\delta(^{31}P)$ of compound **1** is far much more downfield (12.63 ppm) relative to that of compound **2** (–10.39 ppm). This result shows that the electron donation of the aromatic naphthalene group is much more than that of 4-methyl-1,2-phenylenediamine. The IR spectra demonstrate that the $\overline{\nu}$ (P=O) values for compounds **1** and **2** are 1175 cm^{-1} and 1100 cm^{-1}, respectively, indicating a stronger P=O bond for **1** molecule.

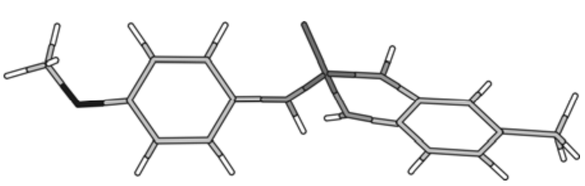


Fig. 1. Optimized structure of compound **1** obtained from HF/6-31+G** and B3LYP/6-31+G** calculations.

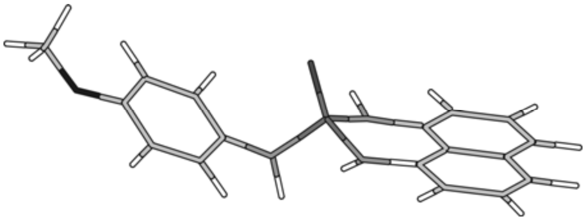
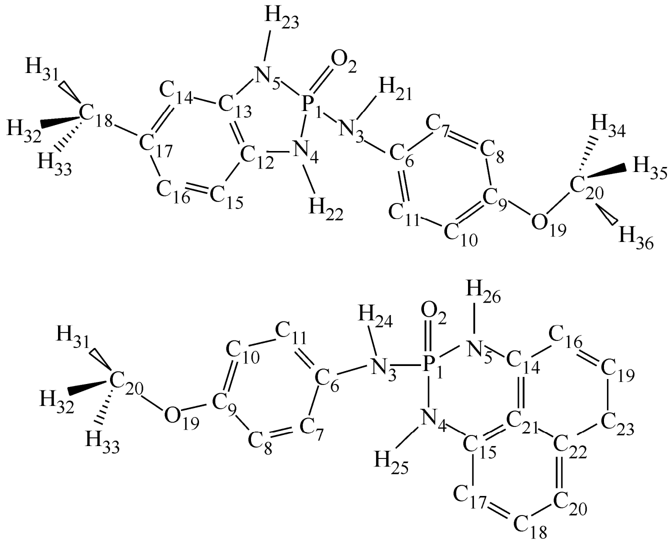


Fig. 2. Optimized structure of compound **2** obtained from HF/6-31+G** and B3LYP/6-31+G** calculations.



Scheme 2. Expanded structures of compounds **1** and **2** with atom numbering obtained from HF/6-31+G** and B3LYP/6-31+G** calculations (some hydrogen atoms are omitted for clarity).

TABLE 2. Calculated Stabilization Energies (kcal·mol^{-1}) and Dipole Moments (Debye) for Compounds **1** and **2**

Molecule	*$\Delta E_{\text{stabilization}}$		Dipole moment	
	HF/6-31+G**	B3LYP/6-31+G**	HF/6-31+G**	B3LYP/6-31+G**
1	–3556.4	–3902.7	2.2	1.9
2	–4082.5	–4391.7	2.1	1.8

*$\Delta E_{\text{stabilization}} = E_{\text{molecule}} - \sum E_i$, where i = atom.

Computational study. In order to further investigate the structures of compounds **1** and **2**, *ab initio* calculations were performed using the Gaussian 98 program [18] to obtain the optimized geometry of these molecules. The optimizations were made using the HF and B3LYP methods with the 6-31+G** standard basis set that reveals nearly planar planes for the five- and six-membered rings of **1** and **2** molecules (Figs. 1 and 2). The expanded structures with atom numbering scheme are shown in Scheme 2. The calculated stabilization energies (kcal·mol^{-1}) and dipole moments (Debye) are presented in Table 2. Selected calculated bond lengths, bond angles, and torsion angles of **1** and **2** molecules are listed in Tables 3 and 4 respectively.

The stabilization energies for both **1** and **2** molecules were calculated from the equation $\Delta E_{\text{stabilization}} = E_{\text{molecule}} - \sum E_i$, where i = atom. It is observed from Table 2 that the B3LYP method yields lower stabilization energies than the HF method for both compounds **1** and **2**. A comparison of the dipole moments indicates that compound **1**

TABLE 3. Selected Calculated Bond Lengths (Å), Angles (deg) and Torsion Angles (deg) of Compound **1**

HF/6-31+G**					
P(1)–O(2)	1.459	O(2)–P(1)–N(3)	111.2	O(2)–P(1)–N(3)–C(6)	–38.9
P(1)–N(3)	1.657	O(2)–P(1)–N(4)	115.6	O(2)–P(1)–N(4)–C(12)	–115.8
P(1)–N(4)	1.684	O(2)–P(1)–N(5)	121.5	O(2)–P(1)–N(5)–C(13)	110.7
P(1)–N(5)	1.672	N(3)–P(1)–N(4)	112.0	N(3)–P(1)–N(4)–C(12)	115.4
N(3)–C(6)	1.425	N(3)–P(1)–N(5)	103.1	N(3)–P(1)–N(5)–C(13)	–124.0
N(4)–C(12)	1.408	N(4)–P(1)–N(5)	91.6	N(4)–P(1)–N(3)–C(6)	92.2
N(5)–C(13)	1.402	C(6)–N(3)–P(1)	125.5	N(5)–P(1)–N(3)–C(6)	–170.6
C(9)–O(19)	1.351	C(12)–N(4)–P(1)	112.0		
C(20)–O(19)	1.400	C(13)–N(5)–P(1)	112.9		
		C(9)–O(19)–C(20)	119.8		
B3LYP/6-31+G**					
P(1)–O(2)	1.489	O(2)–P(1)–N(3)	111.4	O(2)–P(1)–N(3)–C(6)	–32.3
P(1)–N(3)	1.680	O(2)–P(1)–N(4)	116.3	O(2)–P(1)–N(4)–C(12)	–115.2
P(1)–N(4)	1.709	O(2)–P(1)–N(5)	122.5	O(2)–P(1)–N(5)–C(13)	109.8
P(1)–N(5)	1.697	N(3)–P(1)–N(4)	111.6	N(3)–P(1)–N(4)–C(12)	115.5
N(3)–C(6)	1.426	N(3)–P(1)–N(5)	102.4	N(3)–P(1)–N(5)–C(13)	–124.5
N(4)–C(12)	1.409	N(4)–P(1)–N(5)	90.4	N(4)–P(1)–N(3)–C(6)	99.6
N(5)–C(13)	1.408	C(6)–N(3)–P(1)	129.0	N(5)–P(1)–N(3)–C(6)	–165.0
C(9)–O(19)	1.371	C(12)–N(4)–P(1)	112.6		
C(20)–O(19)	1.421	C(13)–N(5)–P(1)	113.3		
		C(9)–O(19)–C(20)	118.3		

TABLE 4. Selected Calculated Bond Lengths (Å), Angles (deg) and Torsion Angles (deg) of Compound **2**

HF/6-31+G**					
P(1)–O(2)	1.459	O(2)–P(1)–N(3)	111.4	O(2)–P(1)–N(3)–C(6)	–35.6
P(1)–N(3)	1.659	O(2)–P(1)–N(4)	115.0	O(2)–P(1)–N(4)–C(14)	–99.2
P(1)–N(4)	1.672	O(2)–P(1)–N(5)	119.7	O(2)–P(1)–N(5)–C(15)	94.3
P(1)–N(5)	1.661	N(3)–P(1)–N(4)	109.1	N(3)–P(1)–N(4)–C(14)	134.9
N(3)–C(6)	1.425	N(3)–P(1)–N(5)	101.4	N(3)–P(1)–N(5)–C(15)	–142.9
N(4)–C(14)	1.401	N(4)–P(1)–N(5)	98.8	N(4)–P(1)–N(3)–C(6)	92.4
N(5)–C(15)	1.402	C(6)–N(3)–P(1)	125.6	N(5)–P(1)–N(3)–C(6)	–164.0
C(9)–O(12)	1.351	C(14)–N(4)–P(1)	125.6		
C(13)–O(12)	1.400	C(15)–N(5)–P(1)	125.8		
		C(9)–O(12)–C(13)	119.8		
B3LYP/6-31+G**					
P(1)–O(2)	1.489	O(2)–P(1)–N(3)	111.8	O(2)–P(1)–N(3)–C(6)	–28.8
P(1)–N(3)	1.680	O(2)–P(1)–N(4)	115.7	O(2)–P(1)–N(4)–C(14)	–99.5
P(1)–N(4)	1.695	O(2)–P(1)–N(5)	120.12	O(2)–P(1)–N(5)–C(15)	94.8
P(1)–N(5)	1.684	N(3)–P(1)–N(4)	108.4	N(3)–P(1)–N(4)–C(14)	134.0
N(3)–C(6)	1.427	N(3)–P(1)–N(5)	101.1	N(3)–P(1)–N(5)–C(15)	–141.7
N(4)–C(15)	1.409	N(4)–P(1)–N(5)	97.8	N(4)–P(1)–N(3)–C(6)	100.0
N(5)–C(14)	1.410	C(6)–N(3)–P(1)	128.7	N(5)–P(1)–N(3)–C(6)	–157.8
C(9)–O(12)	1.371	C(14)–N(4)–P(1)	125.9		
C(13)–O(12)	1.421	C(15)–N(5)–P(1)	126.0		
		C(9)–O(12)–C(13)	118.3		

TABLE 5. Selected Calculated IR Frequencies (cm^{-1}) and Intensities as Well as Raman Activities for **1** and **2**

Compound **1**			Compound **2**		
IR frequency	IR intensity	Raman active	IR frequency	IR intensity	Raman active
561.5	62.8	5.1	609.9	30.8	20.0
570.1	129.2	0.3	658.5	76.8	11.9
649.6	68.3	1.4	743.3	46.4	7.5
717.8	57.0	1.4	819.7	43.2	1.0
819.9	35.0	2.5	828.1	44.2	1.5
877.9	5.4	51.1	899.5	140.2	8.5
912.0	61.1	1.9	936.1	49.5	7.4
931.5	64.4	5.9	945.8	74.3	3.2
951.7	113.5	0.6	998.4	66.2	0.9
1012.2	411.3	3.1	1007.2	373.7	4.9
1027.6	71.7	11.5	1097.9	71.8	4.9
1176.7	91.7	4.4	1156.2	292.8	28.5
1193.7	20.1	2.0	1176.4	75.6	5.7
1207.9	49.6	1.2	1194.1	20.5	2.2
1301.5	214.2	5.9	1254.1	9.2	0.9
1336.0	91.1	4.5	1256.4	14.0	0.4
1353.4	229.9	13.2	1351.8	180.0	21.5
1400.6	56.6	23.9	1354.3	335.0	7.6
1424.7	223.2	37.5	1390.2	53.8	65.4
1444.3	36.9	10.0	1425.0	234.0	42.0
1517.7	126.1	34.4	1444.2	52.1	6.7
1527.8	546.0	9.0	1469.0	0.7	318.6
1599.0	98.6	10.3	1519.7	725.8	2.3
1608.7	82.8	8.6	1636.6	244.5	63.3
1670.9	203.0	6.9	1684.6	404.2	0.8
1685.0	301.7	2.9	1782.4	450.0	294.4
1815.8	5.2	111.6	1790.7	95.8	2.8
3180.4	64.2	178.8	1816.1	17.2	111.9
3180.7	50.0	176.8	3181.2	60.4	132.4
3232.6	26.4	90.1	3305.0	42.8	153.9
3304.1	42.9	150.4	3355.9	9.4	177.5
3363.1	16.2	156.5	3373.5	22.3	399.6
3377.1	7.2	120.3	3377.4	6.8	124.1

has a slightly higher value, which probably owes to its less symmetric structure than that of **2** (Table 2). The P=O bond lengths in **1** and **2** molecules are 1.459 Å, 1.459 Å and 1.489 Å, 1.489 Å in HF and B3LYP methods respectively, which are slightly longer than the PO double bond length (1.45 Å) [19]. The P–N bond lengths are shorter than the P–N single bond (1.77 Å) [19]. The observation suggests the existence of a partial multiple bond character between the phosphorus and nitrogen atoms, which has always been confirmed by the crystallographic data of our previous similar compounds [3-5]. The exocyclic N(3) atom of the 4-methoxyaniline group as well as endocyclic N(4) and N(5) atoms in compound **1** much deviate from planarity. That is, the sum of the surrounding angles around N(3), N(4) and N(5) atoms at HF/6-31+G** are 353.7°, 348.6°, and 355.7°; they have the averages of 117.9°, 116.2°, and 118.6° respectively. It is clear that the N(4) atom has a very distorted configuration that is not planar. Similarly, the exocyclic N(3) and also endocyclic N(4) and N(5) atoms of compound **2** deviate from planarity with the summations of 353.5°, 355.3°, and 353.1° and the averages of 117.8°, 118.6°, and 117.7° respectively. Similar results were obtained by the B3LYP/6-31+G** method for **1** and **2**. The C(9)–O(19)–C(20) and C(9)–O(12)–C(13) angles are near 120.0°, and with this value one may expect the *sp*^{2} hybridization for the oxygen

TABLE 6. Selected Calculated Hybridizations of Atoms in Compound **1** at B3LYP/6-31+G**

Bond	P(1)	O(2)	N(3)	N(4)	N(5)	O(19)
P(1)–O(2)	$sp^{2.08}$	$sp^{7.95}$	—	—	—	—
P(1)–N(3)	$sp^{3.13}$	—	$sp^{2.33}$	—	—	—
P(1)–N(4)	$sp^{3.65}$	—	—	$sp^{2.67}$	—	—
P(1)–N(5)	$sp^{3.57}$	—	—	—	$sp^{2.51}$	—
N(3)–C(6)	—	—	$sp^{1.93}$	—	—	—
N(3)–H(21)	—	—	$sp^{2.37}$	—	—	—
N(4)–C(12)	—	—	—	$sp^{2.09}$	—	—
N(4)–H(22)	—	—	—	$sp^{2.17}$	—	—
N(5)–C(13)	—	—	—	—	$sp^{2.01}$	—
N(5)–H(23)	—	—	—	—	$sp^{2.06}$	—
C(9)–O(19)	—	—	—	—	—	$sp^{4.43}$
C(20)–O(19)	—	—	—	—	—	$sp^{2.52}$

TABLE 7. Selected Calculated Hybridizations of Atoms in Compound **2** at B3LYP/6-31+G**

Bond	P(1)	O(2)	N(3)	N(4)	N(5)	O(19)
P(1)–O(2)	$sp^{2.11}$	$sp^{7.90}$	—	—	—	—
P(1)–N(3)	$sp^{3.19}$	—	$sp^{2.36}$	—	—	—
P(1)–N(4)	$sp^{3.49}$	—	—	$sp^{2.41}$	—	—
P(1)–N(5)	$sp^{3.61}$	—	—	—	$sp^{2.42}$	—
N(3)–C(6)	—	—	$sp^{1.96}$	—	—	—
N(3)–H(24)	—	—	$sp^{2.38}$	—	—	—
N(4)–C(14)	—	—	—	$sp^{1.94}$	—	—
N(4)–H(25)	—	—	—	$sp^{2.34}$	—	—
N(5)–C(14)	—	—	—	—	$sp^{1.93}$	—
N(5)–H(26)	—	—	—	—	$sp^{2.39}$	—
C(9)–O(19)	—	—	—	—	—	$sp^{3.91}$
C(20)–O(19)	—	—	—	—	—	$sp^{4.41}$

atoms. The O(2)–P(1)–N(3)–C(6) torsion angles for compounds **1** and **2** are about –35° and –32° respectively, indicating that the P=O bonds and the phenyl rings are not in the same plane (Tables 4 and 5).

The IR and Raman spectral data of heterophosphorinanes **1** and **2** calculated at the HF/6-31+G** level of theory are presented in Table 5. It is observed from the spectra that there are a number of IR and Raman bands at identical wave numbers indicating no symmetry center for both compounds **1** and **2**. Table 6 lists the selected intense bands of IR and Raman spectra. The obtained P=O bond frequencies are 1176 and 1156 cm^{-1} for **1** and **2** molecules respectively. The NH frequencies calculated for **1** and **2** are about 3180 and 3300 cm^{-1}.

To further consider atomic hybridizations, NBO computations were made at the B3LYP/6-31+G** level, and atomic hybrids are presented in Tables 6 and 7. The results exhibit that in both compounds **1** and **2**, the P(1) atom hybridization in P=O and P–N bonds is nearly sp^3, while N(3), N(4), and N(5) atoms have sp^2 hybridization. It is worth noting that the O(19) atom indicates sp^3 hybridization, but the bond angles around it was about 120.0°.

The ^{1}H, ^{13}C, ^{31}P NMR chemical shifts for compounds **1** and **2** were computed and compared with the experimental data. As Table 8 indicates, the $\delta(^{1}H)$ values for all protons, except amino NH protons, are in relatively good agreement with the experimental results. Also, the ^{13}C chemical shifts approximately correspond to the obtained values. There are no compatible relations between the calculated and observed $\delta(^{31}P)$ values. Therefore, it could be concluded that to compute the NMR chemical shifts, only the ^{1}H, ^{13}C shifts present almost reliable data.

TABLE 8. Experimental and Calculated ^{31}P, ^{1}H, ^{13}C NMR Chemical Shifts (ppm) for Compounds **1** and **2**

Spectrum	Compound **1**			Compound **2**		
	Experimental value	HF/6-31+G**	B3LYP/6-31+G**	Experimental value	HF/6-31+G**	B3LYP/6-31+G**
^{31}P NMR	12.63	38.31	30.94	–10.39	15.89	17.12
^{1}H NMR	2.19	1.41	1.39	3.75	2.62	2.76
	3.58	2.61	2.80	6.56	4.80	4.89
	6.49	5.06	4.81	6.67	5.33	5.23
	6.59	5.31	5.06	6.91	5.83	6.52
	6.63	5.82	5.52	7.10	5.57	5.55
	7.68	1.77	2.34	7.16	5.78	5.60
	8.25	2.31	2.98	7.67	1.94	2.75
	8.33	2.72	3.16	8.57	2.74	3.55
^{13}C NMR	153.34	159.09	156.61	153.37	159.11	156.84
	135.37	139.94	136.84	139.89	147.57	145.49
	132.09	136.25	134.94	135.15	145.40	140.53
	129.64	136.18	133.74	127.31	135.39	137.37
	127.44	135.03	132.05	118.55	134.74	129.11
	119.00	133.84	123.05	118.52	130.92	123.46
	118.26	125.24	120.52	117.75	121.88	119.04
	114.14	118.90	116.14	114.12	119.61	117.49
	110.29	117.66	112.23	107.52	119.10	116.41
	109.20	115.79	111.79	107.50	109.69	112.13
	55.13	52.29	56.87	55.11	52.33	55.84
	20.93	23.10	24.48			

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