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Syntheses and Spectroscopic Investigation of Some Cyclophosphazanes: Analysis of Pseudo-Triplet Splitting

Khodayar Gholivand, Zahra Shariatinia, Zahra Ahmadian Tabasi, and Azadeh Tadjarodi

Department of Chemistry, Faculty of Sciences, Tarbiat Modarres University, P.O. Box 14115-175, Tehran, Iran

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ABSTRACT: *Some new phosphoramidates,* **1–3**, *and the corresponding cyclophosphazanes,* **4–6**, *with formula* $Cl_2P(p\text{-}NHC_6H_4CH_3)$ **1**, $Cl_2P(O)(p\text{-}NHC_6H_4NO_2)$ **2**, $(CH_3)_2NP(O)Cl(p\text{-}NHC_6H_4CH_3)$**3**, $[ClP(p\text{-}NC_6H_4CH_3)]_2$ **4**, $[ClP(O)(p\text{-}NC_6H_4NO_2)]_2$ **5**, *and* $[(CH_3)_2NP(O)(p\text{-}NC_6H_4CH_3)]_2$ **6** *were synthesized and characterized by* ^1H, ^{13}C, ^{31}P *NMR, IR, mass spectroscopy, and elemental analysis. A pseudo-triplet signal was observed in the* ^1H *NMR spectrum of molecule* **6** *for the* $N(CH_3)_2$ *protons. The* $A_6A'_6X_2$ *spin system was suggested for the pseudo-triplet pattern of* $^3J_{PNCH}$ *coupling in this molecule. Ab initio calculations were performed at the HF and B3LYP levels of theory with 6-311G** standard basis set on the geometry of compound* **6**. *Also, the NMR chemical shift calculations were done to compare the computed results with the experimental ones. The calculated results are in good agreement with experimental data.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:337–343, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20229

INTRODUCTION

The chemistry of small inorganic heterocycles of the type $(P{-}N)_2$ are of great interest in recent researches [1–3], mainly because such molecules are good starting materials for polycyclic inorganic and organometallic compounds [4,5]. The wide range applications of cyclophosphazanes in nucleophilic substitution reactions on P—Cl bonds [6,7], coordination chemistry [8], and ring-opening polymerization reactions [9] causes a significant attraction to this area of chemistry. There are many articles reporting the synthesis and structure of phosphorus(III) [10–15] and phosphorus(V) cyclophosphazane compounds [16–21].

Johnson et al. [22] and others [23,24] reported the synthesis of $Cl_2P(O)(p\text{-}NHC_6H_4NO_2)$ and characterized it only by ^{31}P NMR spectroscopy and melting point, respectively. Vesterager et al. [25] prepared compound $[(CH_3)_2NP(O)(p\text{-}NC_6H_4CH_3)]_2$ from $P(O)[N(CH_3)_2]_3$ and *p*-toluidine and characterized this molecule only by elemental analysis. Davis et al. [26] obtained molecule $[ClP(p\text{-}NC_6H_4CH_3)]_2$ and identified it by IR, mass spectroscopy, and elemental analysis.

Ab initio NMR chemical shifts calculations are extended in all areas of chemistry to determine the configurations, conformations, and isomers [27–34] and also to find the NMR parameters [35,36].

In this paper, we prepared some new cyclophosphazanes and their corresponding phosphoramidates. The ^1H NMR spectrum of cyclophosphazane **6** indicated a pseudo-triplet pattern for ^{31}P–^1H splitting. Ab initio calculations showed a reasonable consistency with this splitting, and we

Correspondence to: Khodayar Gholivand; e-mail: gholi_kh@modares.ac.ir.

correlate this coupling with the steric effects in this compound.

RESULTS AND DISCUSSION

Synthetic and Spectroscopic Aspects

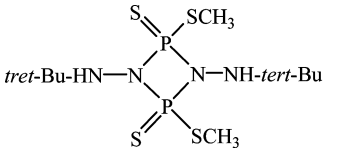
Syntheses of compounds **1–6** were performed by the reaction of phosphorus trichloride, phosphoryl chloride, and *N,N*-dimethyl phosphoramidic dichloride with *p*-toluidine (in excess or in the presence of an HCl scavenger such as triethylamine) and *p*-nitroaniline. The phosphorus chemical shifts and the J_{P-X} (X = H, C) coupling constants of compounds **1–6** are listed in Table 1. The general formula of these molecules is shown in Scheme 1. Phosphorus-31 NMR spectrum of molecule **1** indicates a signal at 150.68 ppm which towards down fields in the corresponding cyclophosphazane **4** (with a signal at 201.51 ppm). The spectra of compounds **2** and **3** show the ^{31}P signals at down fields relative to the signals of their corresponding cyclophosphazanes **5** and **6**, respectively. The shielding of phosphorus atoms in molecules **5** and **6** can be attributed to the increase of resonance interactions in these compounds compare with their related monomers **2** and **3**.

$^{2}J_{PNH}$ coupling constant in molecule (p-$CH_3C_6H_4NH)P(O)Cl_2$ is 11.6 Hz [37] that increases in compound **3** to 12.7 Hz. It seems that substitution of chlorine atom by $N(CH_3)_2$ group causes more interaction between phosphorus and nitrogen atoms and thus increasing this coupling constant.

The $^{3}J_{PNCH}$ coupling constant in compound $(CH_3)_2NP(O)Cl_2$ is 15.8 Hz [38,39] and it decreases to 14.0 and 5.4 Hz in molecules **3** and **6**, respectively. This phenomenon is described as the formation of partial multiple bonds between phosphorus and nitrogen atoms that cause decreasing of $^{3}J_{PNCH}$ coupling constant [37].

Usually, a doublet peak have seen for methyl protons in compounds with the $(CH_3)_2NP(O)XY$ skeleton and the $^{3}J_{PNCH}$ values depend on the X and Y substituents vary in the range of 9.89–15.8 Hz [37–39]. But the ^{1}H NMR spectrum of compound **6** shows a pseudo-triplet pattern of splitting for 12 protons of the dimethylamine groups with $^{3}J_{PNCH} = 5.4$ Hz (Fig. 1). Our low-temperature dynamic NMR experiments on the ^{1}H NMR spectrum of this compound were done only to 223 K and in this temperature the pseudo-triplet peak converts to a broad signal.

Meisel et al. already reported a similar phenomenon for compound **7** with fine splitting of an $A_3A'_3MM'XX'$spin system. The ^{1}H NMR spectrum of this compound shows a pseudo-triplet peak for the SCH_3 protons ($^{3}J_{PSCH} = 18.2$ Hz). Also, the ^{13}C NMR spectrum of this molecule indicated a pseudo-triplet for the SCH_3 carbon atoms. Hagele et al. obtained a calculated ^{1}H NMR spectrum for this compound by simplification of the $A_3A'_3MM'XX'$ spin system to an $A_3A'_3XX'$ system with the assumption that $^{2}J_{P-P} = 140.0$ Hz. The structure of pseudo-triplet they obtained consists of two sharp outer parts, and the central part is a quartet [40].

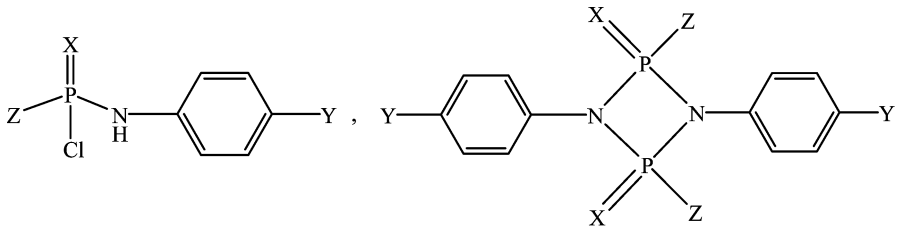


compound **7**

Because the $^{31}P\{^{1}H\}$ NMR spectrum of compound **6** shows only a singlet signal, the two phosphorus atoms are magnetically and chemically equivalent (X_2 spin system for two equal P atoms). In reviewing the literature, the observed geometry for four-membered ring crystalline cyclophosphazanes is the *cis* configuration of the two P=X moieties (X = S [10], Se [41], and lone pair [13–15]). Thus, we can conclude that perhaps only the *cis* isomer of cyclophosphazanes is present in the solution. Furthermore, we did not observe any $^{n}J_{P-H}$ ($n = 4–6$) for similar cyclophosphazanes [14,15,41]. This means that the $N(CH_3)_2$ protons could not couple with the phosphorus atom which is placed far from them ($^{5}J_{PNPNCH} = 0$ Hz). Therefore, the pseudo-triplet splitting pattern in the ^{1}H NMR spectrum must be due

TABLE 1 The δ_{31P} (ppm) and the J_{P-X} (X = H, C) Coupling Constants (Hz) for Compounds **1–6**

Compound	δ_{31P}	$^{2}J_{PNH}$	$^{3}J_{PNCH}$	$^{2}J_{P-C}$	$^{3}J_{P-Cortho}$	$^{4}J_{P-Cmeta}$	$^{5}J_{P-Cpara}$	$^{2}J_{P-Cipso}$
1	d, 150.68	7.1	–	s, 0	d, 5.4	s, 0	d, 2.1	d, 6.5
2	d, 6.34	10.6	–	s, 0	d, 9.0	s, 0	s, 0	s, 0
3	oct, 17.21	12.7	14.0	2.8	d, 2.8	s, 0	s, 0	s, 0
4	s, 201.51	s, 0	–	s, 0	t, 7.7	s, 0	s, 0	t, 8.5
5	s, 1.31	s, 0	–	s, 0	s, 0	s, 0	s, 0	s, 0
6	hept, −1.94	–	5.4	s, 0	t, 6.9	s, 0	s, 0	s, 0



1-3 **4-6**

1, **4**: X = Lone pair, Y = CH_3, Z = Cl
2, **5**: X = O, Y = NO_2, Z = Cl
3, **6**: X = O, Y = CH_3, Z = NMe_2

SCHEME 1 The formula of compounds **1–3** and corresponding cyclophosphazanes **4–6**.

to the presence of two unequivalent $N(CH_3)_2$ groups. In the solution, likely the low-rotational barrier along the P—N bonds cause the methyl groups in each $N(CH_3)_2$ moiety convert to each other and, thus, we observe only one singlet signal in the $^1H\{^{31}P\}$ NMR spectrum of this compound. An interesting point is that the ^{13}C NMR spectrum indicates a singlet peak for the four carbon atoms of two $N(CH_3)_2$ groups. One possibility for the formation of this pattern is probably that six equal protons of one $N(CH_3)_2$ group (A_6) split by its near phosphorus atom to give a doublet. Other six protons of another $N(CH_3)_2$ group

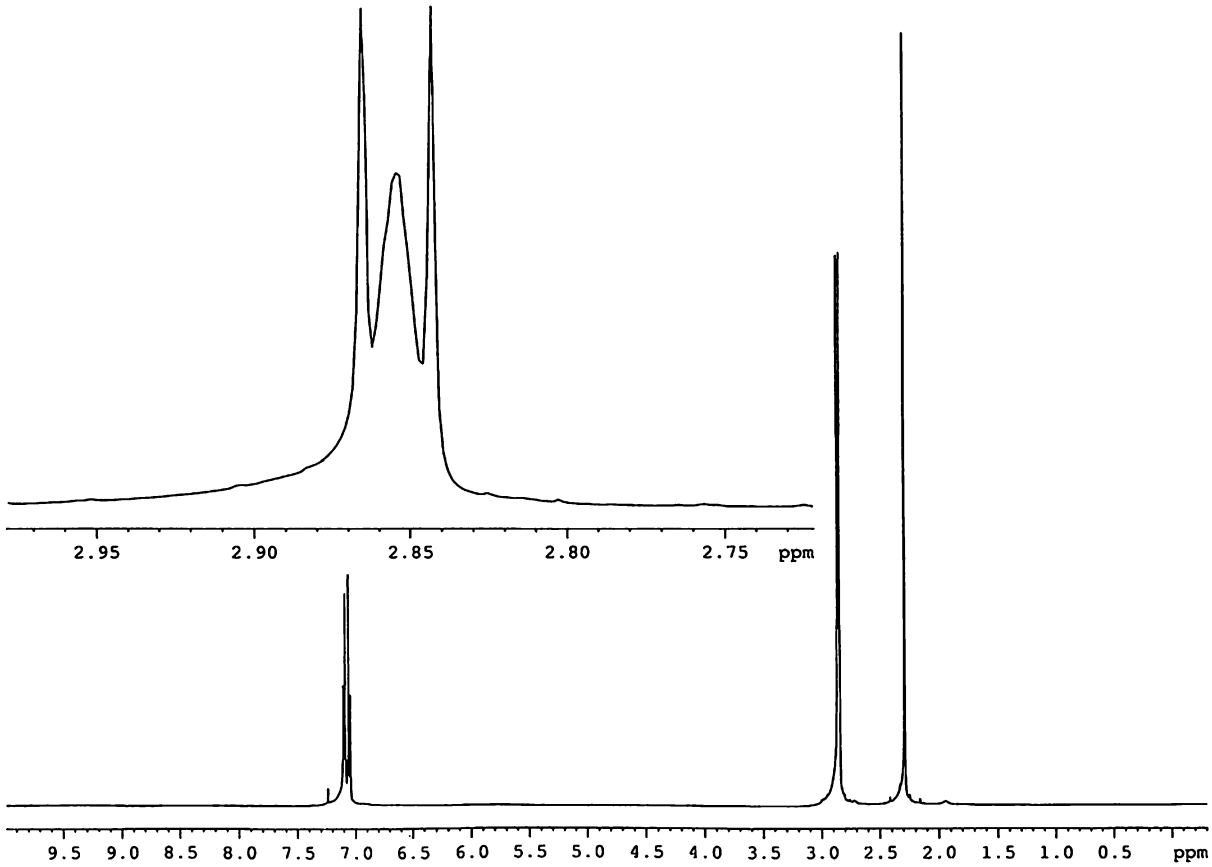


FIGURE 1 The pseudo-triplet splitting pattern in the ^1H NMR spectrum of compound **6**, $[(CH_3)_2NP(O)(p\text{-}NC_6H_4CH_3)]_2$.

(A'_6) couple with their P atom to produce a doublet. Combination of these two doublet peaks gives a pseudo-triplet signal. Based on these arguments, we can propose the $A_6A'_6X_2$ spin system for this splitting.

Carbon-13 NMR spectrum of compound **2** showed a doublet signal for $^3J_{P-Cortho}$ (9.0 Hz), but the spectrum of its corresponding dimmer **5** indicated a singlet. The spectra of cyclophosphazanes **4** and **6** show a triplet with $^3J_{P-Cortho} = 7.7$ and 6.9 Hz, respectively, but there is a singlet in compound **5**. The only triplet signal for ipso carbon with $^2J_{P-Cipso} = 8.5$ Hz was observed in compound **4**, while in compounds **5** and **6** it is a singlet peak. It should be mentioned that only in molecule **5** with *p*-nitroaniline substituent, all phosphorus–carbon couplings are vanished.

Computational Aspects

In order to further investigate on the structure of compound **6** and evaluation of our prediction on the geometry of this molecule, we performed ab initio calculations to obtain the optimized geometry of this molecule. The preferred geometry for similar compounds of these series is the *cis* configuration of two P=O moieties, therefore, full optimizations on the *cis* geometry of this compound were done using Hartree–Fock (HF) and B3LYP methods with 6-311G** standard basis set give two equal structures. The optimized structure is shown in Fig. 2 and Scheme 2 and indicates that the two $N(CH_3)_2$ groups have different spatial orientations. This means that the carbon atoms connected to N_7 have different spatial orientation relative to the two other carbon atoms linked to N_{11}. Therefore, our computations confirm the predicted structure for compound **6** and we can suggest the $A_6A'_6X_2$ spin system for pseudo-triplet splitting pattern in the ^{1}H NMR spectrum.

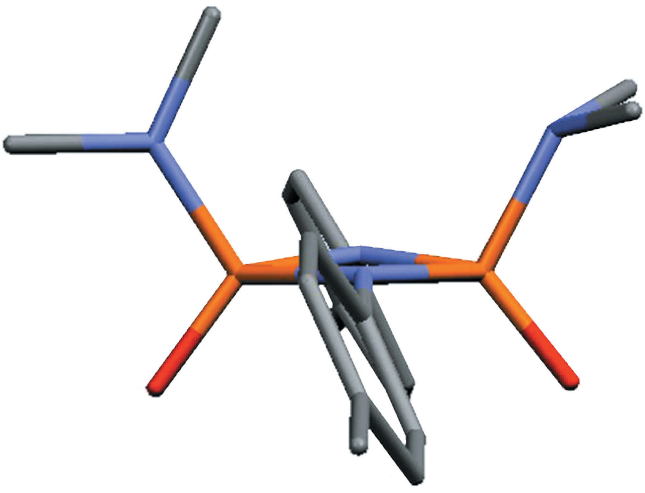
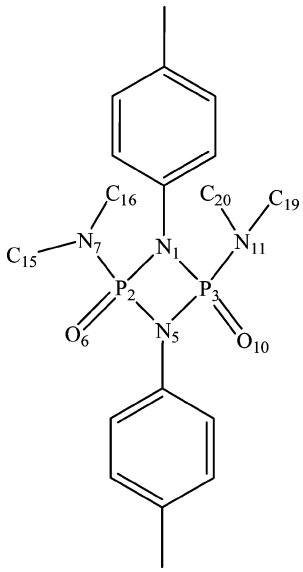


FIGURE 2 The optimized structure of molecule **6**, $[(CH_3)_2NP(O)(p\text{-}NC_6H_4CH_3)]_2$, obtained from the ab initio calculations at HF/6-311G** and B3LYP/6-311G** levels (H atoms are omitted for clarity).



SCHEME 2 The atom-labeling scheme for the optimized structure of compound **6** (H atoms are omitted for clarity).

The ^{1}H, ^{13}C, and ^{31}P NMR chemical shift calculations for this compound are done using HF and B3LYP methods and 6-311G**, 6-311+G**, and 6-311++G** basis sets, and results are summarized in Table 2. To calculate ^{1}H NMR chemical shifts, UHF/6-311++G** is rather suitable. Carbon-13 chemical shift calculations show that B3LYP/6-311++G** and B3LYP/6-311+G** give accurate results. The data show the best result for ^{31}P chemical shift by B3LYP/6-311G**.

EXPERIMENTAL

All reactions were carried out under argon atmosphere. Solvents and other chemical reagents were from Merck, Sigma, Aldrich, and Fluka. Solvents were dried by refluxing with the appropriate drying agent and distilled before use. Melting points were determined with a Gallenkamp apparatus. NMR spectra were run at room temperature (298 K) on a Bruker 500 (Avance DRS) spectrometer by dissolving 30 mg of sample in 0.5 mL of deuterated solvents at 500.13 MHz (^{1}H), 202.45 MHz (^{31}P), and 125.77 MHz (^{13}C) in different solvents. ^{1}H, ^{13}C, and ^{31}P chemical shifts were referenced to internal TMS and external 85% H_3PO_4 standards, respectively. The infrared spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed

TABLE 2 Experimental and Calculated ^{31}P, ^{1}H, and ^{13}C NMR Chemical Shifts (ppm) for Compound **6**

Exp. NMR	*UHF/ 6-311G***	*UHF/ 6-311+G***	*UHF/ 6-311++G***	*B3LYP/ 6-311G***	*B3LYP/ 6-311+G***	*B3LYP/ 6-311++G***
^{31}P, −1.95	8.98	61.30	59.33	3.78	59.21	59.33
^{1}H, 2.28	1.55	1.69	1.73	1.21	1.46	1.50
2.85	1.83	1.94	1.96	1.47	1.89	1.92
7.05	6.34	6.52	6.56	5.98	6.22	6.27
7.1	6.48	6.73	6.77	6.11	6.34	6.39
^{13}C, 20.83	20.61	20.25	20.27	9.07	21.1	21.19
36.57	33.67	33.52	33.54	22.13	35.99	36.13
118.27	130.46	131.74	131.76	118.95	128.39	128.43
130.28	131.74	132.41	132.43	120.19	130.75	130.78
133.25	135.48	136.39	136.43	123.92	135.99	136.05
133.47	141.08	142.57	142.62	129.56	140.5	140.59

using a Heraeus CHN-O-RAPID elemental analysis. Mass spectra were obtained on a 70 eV Finnigan mat (EI model) spectrometer. *N,N*-Dimethyl phosphoramidic dichloride was prepared according to the literature method [38].

N-(p-Methylphenylamino)dichlorophosphine, Cl_2 P(p-NHC_6H_4 CH_3) **1**

To a solution of 2.14 g (20 mmol) *p*-toluidine in diethyl ether (15 mL) under argon atmosphere and stirring, 1.37 g (10 mmol) phosphorus trichloride was added dropwise at −10°C. After 5 h stirring, CCl_4 (15 mL) was added to the filtered solution and diethyl ether was removed under vacuum to give compound **1**. Yield, 1.52 g (73%), mp 185–186°C; IR: 3490 (N—H), 2915, 1439, 1379, 1164, 814 (P—N), 710, 630, 471 cm^{-1}; ^{1}H NMR (CCl_4, $CDCl_3$): $\delta = 2.32$ (s, *p*-CH_3), 6.99 (d, $^{3}J_{H-H} = 8.0$ Hz), 7.16 (d, $^{3}J_{H-H} = 8.0$ Hz), 7.29 (d, $^{2}J_{PNH} = 7.1$ Hz); ^{13}C NMR (CCl_4, $CDCl_3$): $\delta = 135.10$ (d, $^{2}J_{P-Cipso} = 6.5$ Hz), 133.65 (d, $^{5}J_{P-Cpara} = 2.1$ Hz), 130.10 (s, C_{meta}), 121.7 (d, $^{3}J_{P-Cortho} = 5.4$ Hz), 20.82 (s, *p*-CH_3);^{31}P NMR (CCl_4, $CDCl_3$): $\delta = 150.68$ (d, $^{2}J_{PNH} = 7.1$ Hz); Anal. Calcd. for $C_7H_8Cl_2NP$ (208.03): C, 40.42; H, 3.88; N, 6.73. Found: C, 40.40; H, 3.85; N, 6.75%.

N-(p-Nitrophenyl)phosphoramidic Dichloride, $Cl_2P(O)(p\text{-}NHC_6H_4NO_2)$ **2**

A mixture of 4.60 g (30 mmol) phosphoryl chloride and 1.38 g (10 mmol) *p*-nitroaniline was heated for 2 h at 40°C. The product was washed with petroleum ether (20 mL) and was dried under vacuum. Yield, 2.12 g (83%), mp 149–151°C; IR: 3400 (N—H), 2925, 2605, 1590, 1512 (NO_2), 1336 (NO_2), 1282, 1249 (P═O), 1100, 1075, 942 (P—N), 845, 586, 557 cm^{-1}; $^{1}H\{^{31}P\}$ NMR ($CDCl_3$): $\delta = 7.3$ (d, $^{3}J_{H-H} = 9.0$ Hz), 7.58 (s, NH), 8.27 (d, $^{3}J_{H-H} = 9.0$ Hz). ^{1}H NMR ($CDCl_3$): $\delta = 7.30$ (d, $^{3}J_{H-H} = 9.0$ Hz), 7.58 (d, NH, $^{2}J_{PNH} = 10.6$ Hz), 8.27 (d, $^{3}J_{H-H} = 9.0$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 144.19$ (s, C_{para}), 142.54 (s, C_{ipso}), 125.70 (s, C_{meta}), 119.07 (d, $^{3}J_{P-Cortho} = 9.0$ Hz). ^{31}P NMR ($CDCl_3$): $\delta = 6.34$ (d, $^{2}J_{PNH} = 10.6$ Hz). Anal. Calcd. for $C_6H_5Cl_2N_2O_3P$ (254.99): C, 28.26; H, 1.98; N, 10.99. Found: C, 28.23; H, 1.96; N, 11.03%.

N,N-Dimethyl-N′-4-methylphenyl Phosphoramidic Chloride, $(CH_3)_2NP(O)Cl(p\text{-}NHC_6H_4CH_3$ **3**

1.62 g (10 mmol) of *N,N*-dimethyl phosphoramidic dichloride was dissolved in toluene (20 mL) and the solution flask was placed in an ice bath. Then, 2.14 g (20 mmol) of *p*-toluidine was added dropwise to the solution. After 3 h stirring, the mixture was kept at −10°C for 45 h. After filtration and removing the solvent, an oily compound was obtained which was purified by column chromatography method with ethyl acetate:*n*-hexane (1:1). Yield 1.98 g (85%); IR: 3135 (N–H), 3010, 1605, 1504, 1450, 1377, 1271, 1218 (P═O), 991 (P—N_{ar}), 948, 808, 745 (P—N_{al}), 577 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.25$ (s, *p*-CH_3), 2.76 (d, $^{3}J_{PNCH} = 14.0$ Hz, $2CH_3$), 6.35 (d, $^{2}J_{PNH} = 12.7$ Hz, NH), 7.01 (d, $^{3}J_{H-H} = 9.1$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 136.23$ (s, C_{para}), 132.37 (s, C_{ipso}), 129.82 (s, C_{meta}), 119.14 (d, $^{3}J_{P-Cortho} = 2.8$ Hz), 36.81 (d, $^{2}J_{PCH_3} = 2.8$ Hz), 20.68 (s, CH_3); ^{31}P NMR ($CDCl_3$): $\delta = 17.21$ (oct, $^{n}J_{P-H} = 13.6$ Hz). Anal. Calcd. for $C_9H_{14}ClN_2OP$ (232.65): C, 46.46; H, 6.07; N, 12.04. Found: C, 46.43; H, 6.06; N, 12.07%.

2,4-Dichloro-1,3-bis(4-methylphenyl)-1,3,2,4-diazadiphosphetidine, $[ClP(p\text{-}NC_6H_4CH_3)]_2$ **4**

A mixture of 1.07 g (10 mmol) *p*-toluidine and 1.01 g (10 mmol) triethylamine was dissolved in *n*-hexane (30 mL) and slowly added to a solution of

1.37 g (10 mmol) phosphorus trichloride in *n*-hexane (7 mL). A vigorous reaction occurred with the formation of a white mass (salt of triethylamine). After refluxing for 8 h, the mixture was cooled to room temperature and filtered under argon atmosphere. The filtrate was concentrated and kept at −10°C for 2 days to give the product. Yield, 2.69 g (78%), mp 180–181°C; IR: 2980, 2910, 1570, 1197, 1020, 806 (P—N), 482 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.33$ (s, 2*p*-CH_3), 6.94 (d, $^3J_{H-H} = 8.0$ Hz), 7.11 (d, $^3J_{H-H} = 8.0$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 134.97$ (t, $^2J_{P-Cipso} = 8.5$ Hz), 132.93 (s, C_{para}), 129.96 (s, C_{meta}), 117.21 (t, $^3J_{P-Cortho} = 7.6$ Hz), 20.66 (s, 2*p*-CH_3); ^{31}P NMR ($CDCl_3$): $\delta = 201.51$ (s); *m/z* (EI) (%): 342 (12) $[M]^+$, 307 ($[C_{14}H_{14}N_2ClP_2]^+$, 25), 276 ($[C_{14}H_{14}N_2ClP]^+$, 5), 241 ($[C_{14}H_{14}N_2P]^+$, 35), 171 ($[C_7H_7NClP]^+$, 20), 136 ($[C_7H_7NP]^+$, 74), 107 ($[C_7H_8N]^+$, 100); Anal. Calcd. for $C_{14}H_{14}Cl_2N_2P_2$ (343.13): C, 49.00; H, 4.11; N, 8.16. Found: C, 48.97; H, 4.09; N, 8.13%.

2,4-Dichloro-1,3-bis(4-nitrophenyl)-1,3,2,4-diazadiphosphetidine-2,4-dioxide, $[ClP(O)(p\text{-}NC_6H_4NO_2)]_2$ **5**

This compound was prepared in the same way as molecule **2**, but the mixture was heated for 4 h at 90°C. Yield 3.94 g (90%), mp 158–159°C; IR: 3335, 2835, 2625, 1586, 1512 (NO_2), 1466, 1344 (NO_2), 1295 (P═O), 1129, 983, 853, 733, 670 cm^{-1}; ^1H NMR (CD_3CN): $\delta = 6.89$ (d, $^3J_{H-H} = 9.0$ Hz), 8.08 (d, $^3J_{H-H} = 9.0$ Hz); ^{13}C NMR (CD_3CN): $\delta = 151.32$ (s, C_{para}), 139.64 (s, C_{ipso}), 126.01 (s, C_{meta}), 115.05 (s, C_{ortho}); ^{31}P NMR (CD_3CN): $\delta = 1.31$ (s); *m/z* (EI) (%): 300 ($[M\text{-}C_6H_5N_2O_2]^+$, 4), 138 ($[C_6H_4N_2O_2]^+$, 65), 122 ($[N_2O_2P_2]^+$, 3), 108 ($[NO_2P_2]^+$, 62), 92 ($[NOP_2]^+$, 28), 79 ($[HOP_2]^+$, 26), 63 ($[P_2]^+$, 100), 48 ($[HOP]^+$, 24); Anal. Calcd. for $C_{12}H_8Cl_2N_4O_6P_2$ (437.07): C, 32.98; H, 1.84; N, 12.82. Found: C, 32.96; H, 1.81; N, 12.79%.

2,4-Dimethylamino-1,3-bis(4-methylphenyl)-1,3,2,4-diazadiphosphetidine-2,4-dioxide, $[(CH_3)_2NP(O)(p\text{-}NC_6H_4CH_3)]_2$ **6**

This compound was prepared in the same way as compound **3**, but after filtration, the solution was concentrated and placed at room temperature for 1 month. Colorless and needle crystals were obtained. Yield 2.37 g (60%), mp 250–252°C, IR: 3025, 2923, 2850, 1600, 1503, 1472, 1442, 1296, 1257 (P═O), 1185, 986 (P—N), 947, 826, 638 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.29$ (s, 2*p*-CH_3), 2.85 (t, $^3J_{PNCH} = 5.4$ Hz, 2N(CH_3)$_2$), 7.04 (d, $^3J_{H-H} = 8.2$ Hz), 7.09 (d, $^3J_{H-H} = 8.2$ Hz). $^1H\{^{31}P\}$ NMR ($CDCl_3$): $\delta = 2.29$ (s, 2*p*-CH_3), 2.85 (s, 2N(CH_3)$_2$), 7.04 (d, $^3J_{H-H} = 8.2$ Hz), 7.09 (d, $^3J_{H-H} = 8.2$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 133.47$ (s, C_{para}), 133.25 (s, C_{ipso}), 130.28 (s, C_{meta}), 118.28 (t, $^3J_{P-Cortho} = 6.9$ Hz), 36.57 (s, 2N(CH_3)$_2$), 20.83 (s, 2*p*-CH_3). ^{31}P NMR ($CDCl_3$): $\delta = -1.94$ (hept, $^3J_{P-H} = 5.4$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -1.94$ (s); *m/z* (EI) (%): 392 (4) $[M]^+$, 243 (10) $[C_9H_{13}N_2O_2P_2]^+$, 196 (37) $[C_9H_{13}N_4O_2P_2]^+$, 153 (40) $[C_7H_8NOP]^+$, 136 (80) $[C_7H_7NP]^+$, 107 (26) $[C_7H_9N]^+$, 106 (36) $[C_7H_8N]^+$, 91 $(C_7H_7)^+$, 77 (20) $[C_6H_5]^+$, 49 (100) $[H_2PO]^+$; Anal. Calcd. for $C_{18}H_{26}N_4O_2P_2$ (392.38): C, 55.10; H, 6.68; N, 14.28. Found: C, 55.07; H, 6.65; N, 14.30%.

Computational Methodology

All quantum chemical calculations were performed with the GAUSSIAN-98 program suite [42]. The geometry of compound **6** is fully optimized using HF and DFT (B3LYP) levels of theory in the gas phase. The standard 6-311G** is applied in these calculations. The optimizations are followed by calculations of the harmonic and vibrational frequencies. No imaginary frequency is obtained in these calculations. NMR calculations are performed at the HF and DFT (B3LYP) levels of theory with 6-311G**, 6-311+G**, and 6-311++G** standard basis sets. Calibration of the calculated chemical shifts of compound **6** was performed by computing the ^1H and ^{13}C chemical shifts of TMS and ^{31}P chemical shift of H_3PO_4 as standards and then subtraction of these values from the calculated chemical shift values of compound **6**.

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