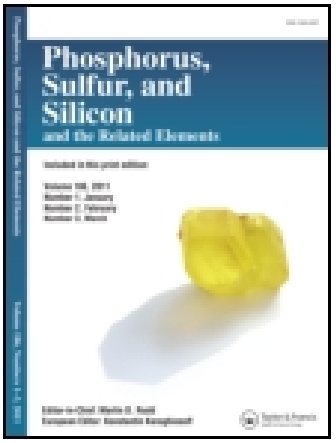

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The Spectroscopy and Structure of New 1,3,2-Diazaphospholes and 1,3,2-Diazaphosphorinanes

N. Oroujzadeh [a] , K. Gholivand [a] & Z. Shariatinia [b]
[a] Department of Chemistry , Tarbiat Modares University , Tehran , Iran
[b] Department of Chemistry , Amirkabir University of Technology , Tehran , Iran
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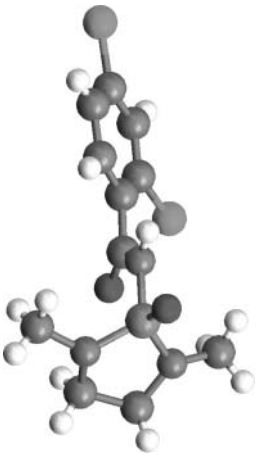
THE SPECTROSCOPY AND STRUCTURE OF NEW 1,3,2-DIAZAPHOSPHOLES AND 1,3,2-DIAZAPHOSPHORINANES

N. Oroujzadeh,[1] K. Gholivand,[1] and Z. Shariatinia[2]
[1]*Department of Chemistry, Tarbiat Modares University, Tehran, Iran*
[2]*Department of Chemistry, Amirkabir University of Technology, Tehran, Iran*

GRAPHICAL ABSTRACT



Abstract *New 1,3,2-diazaphospholes and 1,3,2-diazaphosphorinanes with formula 2,4-Cl_2-C_6H_3-C(O)NHP(O)X where X = $\overline{NH(CH_2)_2NH}$ (**1**), $CH_3\overline{N(CH_2)_2NCH_3}$ (**2**), $\overline{NH(CH_2)_3NH}$ (**3**), and $\overline{NHCH_2C(CH_3)_2CH_2NH}$ (**4**) were synthesized and characterized by ^1H, ^{13}C, ^{31}P NMR, IR spectroscopy, and elemental analysis. The ^{31}P NMR spectra revealed that the phosphorus atoms are more deshielded in the diazaphospholes than in the diazaphosphorinanes. The ^{13}C NMR spectrum of **2** indicated that $^2J_{PC(aliphatic)} = 14.2$ Hz for the endocyclic carbon atom is larger than that for the exocyclic CH_3 carbon atom (5.2 Hz). Furthermore, for diazaphosphorinanes, $^3J_{PC(aliphatic)} \approx 2 \times {}^2J_{PC(aliphatic)}$. The molecular structure of compound **2** was determined by X-ray crystallography. In this structure, a centrosymmetric dimer is formed via connection of two molecules by strong intermolecular N–H···O hydrogen bonds. The presence of weak intermolecular C–H···O and C–H···Cl hydrogen bonds creates a three dimensional polymeric chain in the crystal lattice.*

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Address correspondence to K. Gholivand, Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran. E-mail: gholi_kh@modares.ac.ir

Keywords 1,3,2-Diazaphosphole; 1,3,2-diazaphosphorinane; NMR; X-ray crystallography; hydrogen bonds

INTRODUCTION

Recently, there has been great interest in the chemistry of heterocyclic diazaphosphorinanes and diazaphospholes due to their significant pharmacological properties.[1,2] Cyclophosphamide and ifosphamide are well-known diazaphosphorinanes that exhibit anticancer activities.[3–6] The synthesis and structural properties of some diazaphospholes was reported by Spilling et al.[7] Diazaphosphole derivatives have been used in organic[8] and asymmetric[9] synthesis as well as in coordination chemistry.[10] The preparation and crystal structures of several tungsten complexes bearing diazaphospholes has been investigated.[11] In this area, conformational studies, X-ray structure determinations, and complexation of semirigid macrocyclic phosphonamides have also been reported.[12] The two polymorphs of a diazaphosphole oxide were determined by Norman et al.[13] Furthermore, the synthesis and structure of mono- and diphosphorus containing diazaphospholes were reported.[14]

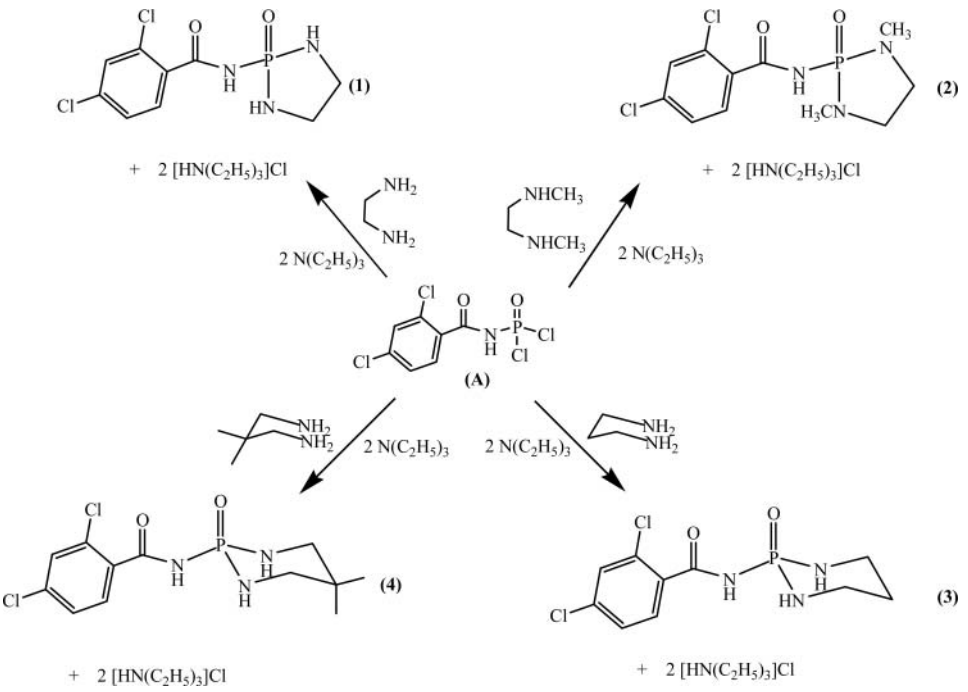
In this work, following on our previous results about diazaphospholes and diazaphosphorinanes,[15–19] new derivatives of this family were synthesized and characterized by multinuclear (^{1}H, ^{13}C and ^{31}P) NMR, IR spectroscopy, and elemental analysis. Also, the molecular structure of compound **2** was determined by single crystal X-ray diffraction. The effects of the substituents on the spectroscopic results were interpreted and are discussed.

RESULTS AND DISCUSSION

Spectroscopic Study

In this study, new phosphoramides **1**–**4** were synthesized from the reaction of $POCl_3$/$RPOCl_2$ with different amines (Scheme 1) and fully characterized by NMR and IR spectroscopy. A summary of the spectroscopic data of these compounds is given in Table 1. The $^{31}P\{^1H\}$ NMR spectra indicate a phosphorus chemical shift, $\delta^{31}P$, in the range of 21.0 ppm (in **1**) to 1.1 ppm (in **4**) displaying very different electron donation power of the substituents at the phosphorus atoms. A comparison of the $\delta^{31}P$ values indicates that the shielding of the phosphorus atom changes in the order **1** < **2** < **3** < **4**. Moreover, the phosphorus atoms in the diazaphospholes **1** and **2** are more deshielded than in the diazaphosphorinanes **3** and **4**. Comparing the $\delta^{31}P$ values of compounds **1** and **2** and also those of compounds **3** and **4** demonstrates that the derivatives containing endocylic N-methyl groups have more shielded phosphorus atoms than those including endocyclic NH moieties. This is due to the increased electron donation to the phosphorus atoms by methyl groups.

The ^{1}H NMR spectrum of **4** shows geminal $^2J_{HH}$ coupling constant of 11.9 Hz as well as vicinal coupling constant $^3J_{PNCH} = 26.7$ Hz. Such couplings were also observed in our previously reported similar phosphorus compounds.[20–23] The ^{13}C NMR spectra of compounds **1**–**4** display $^{2,3}J_{PC(aliphatic)}$ coupling constants; the value of $^2J_{PC(aliphatic)}$ for the endocyclic carbon atom of **2** (14.2 Hz) is larger that for the exocyclic CH_3 carbon atom (5.2 Hz). Furthermore, it becomes evident that for diazaphosphorinanes **3** and **4** $^3J_{PC(aliphatic)} \approx 2 \times {}^2J_{PC(aliphatic)}$. The values of $^3J_{PC(aromatic)}$ in these molecules are about 8.0 Hz.



Scheme 1

The analysis of the IR spectra indicates that the P=O and C=O bonds in the diazaphospholes **1** and **2** are stronger than those in the diazaphosphorinanes **3** and **4**. Also, the stretching frequencies ν(P–N_{amine}) and ν(P–N_{amide}) are observed at about 1011–1097 and 886–956 cm^{-1}, respectively, indicating that the P–N_{amine} bonds are stronger than the P–N_{amide} bonds. This matter has been confirmed by the results of X-ray crystallography of compound **2** as well as our earlier investigated structures.[21–23]

X-Ray Crystallography

To gain more insight into the structural properties of the diazaphospholes, the structure of compound **2** has been determined by single crystal X-ray diffraction. Single crystals of the compound were obtained from a solution of CH_3CN/n-hexane at room temperature. The crystallographic data and the details of the X-ray analysis are presented in Table 2, selected bond lengths and angles are given in Table 3. The ORTEP view of the molecular structure and of the unit cell packing is shown in Figures 1 and 2, respectively.

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

Compound	δ^{31} P (ppm)	$^2J_{PC(aliphatic)}$ (Hz)	$^3J_{PC(aliphatic)}$ (Hz)	$^3J_{PC(aromatic)}$ (Hz)	ν(P=O) (cm^{-1})	ν(C=O) (cm^{-1})	ν(P–N_{amine}) (cm^{-1})	ν(P–N_{amide}) (cm^{-1})
1	21.0	—	—	8.7	1202	1678	1045	917
2	17.3	5.2 (CH_3), 14.2 (CH_2)	—	8.7	1209	1679	1032	941
3	3.3	3.03	6.2	8.1	1165	1671	1011	886
4	1.1	1.8	4.7	8.0	1185	1669	1097	956

Table 2 Crystallographic data for compound **2**

Chemical formula	$C_{11}H_{14}Cl_2N_3O_2P$
Formula weight	322.12
Crystal system, space group	Triclinic, P-1
Temperature (K)	120(2)
a, b, c (Å)	7.5550(8), 9.9104(10), 10.0411(10)
α, β, γ (°)	109.777(1), 90.778(2), 94.626(2)
Volume (Å^3)	704.49(12)
Z	2
Density (calculated, g/cm^3)	1.519
Absorption coefficient (mm^{-1})	0.575
Crystal size (mm^3)	0.24 × 0.18 × 0.14
Theta range for data collection (°)	2.16 to 28.00
Index ranges	$-9 \le h \le 9$, $-13 \le k \le 13$, $-13 \le l \le 13$
Reflections collected	7280
Independent reflections	3385 [$R_{int} = 0.0223$]
Completeness to theta = 28.00°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.927 and 0.873
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3385/0/174
Goodness-of-fit on F^2	1.011
Final R indices for 3613 refl. with [I > 2sigma(I)]	R1 = 0.0437, wR2 = 0.1038
R indices (all data)	R1 = 0.0504, wR2 = 0.1085
Largest diff. peak and hole	0.539 and –0.518 e.Å^{-3}

The five-membered aliphatic ring adopts a puckered shape. The P=O bond length in the molecule is 1.483(2) Å, which is slightly longer than the normal P=O bond length (1.45 Å).[24] The phosphorus atom adopts a slightly distorted tetrahedral configuration; the surrounding angles around the P atom are in the range of 95.40(9)°–120.06(9)°. All P–N bonds (1.631(2), 1.640(2), and 1.689(2) Å) are shorter than the typical P–N single bonds (1.77 Å)[24] revealing partial multiple bond character. The P–N_{amide} bond lengths are longer than the P–N_{amine} bond lengths because of the resonance interaction of the N_{amide} with the C=O π system, which causes a partial multiple bond character of the C–N_{amide} bond (the C–N_{amide} bond lengths are shorter than the C–N_{amine} bond lengths, that is, N(3)–C(5) = 1.374(3) Å while N(1)–C(1) = 1.469(3) Å, N(1)–C(3) = 1.451(3) Å). The O(2)–C(5) and

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

P(1)–O(1)	1.483(2)	O(1)–P(1)–N(1)	120.0(1)
P(1)–N(1)	1.631(2)	O(1)–P(1)–N(2)	115.3(1)
P(1)–N(2)	1.640(2)	N(1)–P(1)–N(2)	95.4(1)
P(1)–N(3)	1.689(2)	O(1)–P(1)–N(3)	103.7(1)
Cl(1)–C(7)	1.737(2)	N(1)–P(1)–N(3)	109.7(1)
Cl(2)–C(9)	1.741(2)	N(2)–P(1)–N(3)	113.0(1)
O(2)–C(5)	1.223(2)	C(3)–N(1)–C(1)	118.0(2)
N(1)–C(3)	1.451(3)	C(3)–N(1)–P(1)	124.6(2)
N(1)–C(1)	1.469(3)	C(1)–N(1)–P(1)	113.6(1)
N(2)–C(4)	1.454(3)	C(4)–N(2)–C(2)	118.6(2)
N(2)–C(2)	1.463(3)	C(4)–N(2)–P(1)	122.7(2)
N(3)–C(5)	1.374(3)	C(2)–N(2)–P(1)	112.9(1)

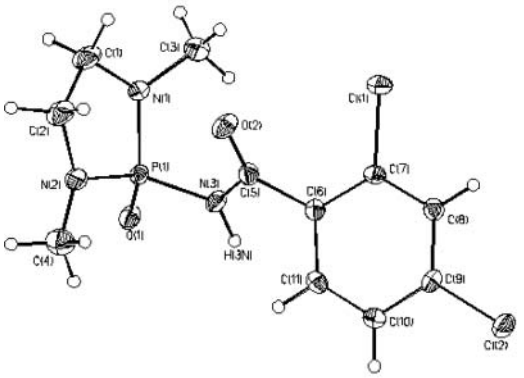


Figure 1 ORTEP view of the molecular structure of compound **2** in the crystal.

Cl(1)–C(7), Cl(2)–C(9) bond lengths are 1.223(2) Å and 1.737(2), 1.741(2) Å, respectively. In the five-membered ring the endocyclic C–N bonds are longer than the exocyclic ones. For example, N(2)–C(2) = 1.463(3) Å but N(2)–C(2) = 1.454(3) Å.

In compound **2**, the angles P(1)–N(1)–C(1), P(1)–N(1)–C(3), and C(1)–N(1)–C(3) are 113.6(1)°, 124.6(2)°, and 118.0(2)°, respectively, with average of 118.71°. The sum of the angles around N(2) and N(3) are 354.20° and 359.72°. The angles OPN_{amide} (N_{amide} is the nitrogen atom of the P(O)N(H)C(O) moiety) are smaller than the angles OPN_{amine} (N_{amine} is the nitrogen atom of P(O)NR moiety). This was also observed in our previously reported compounds.[21–23]

In the structure of compound **2**, a centrosymmetric dimer is formed through connection of two molecules by strong intermolecular N(3)–H(3N)···O (1) hydrogen bonds (D−H = 0.95 Å, H···A = 1.90 Å, D···A = 2.844(2) Å, ∠D−H···A = 177.0°, symmetry codes = −x + 1,−y + 2,−z + 1). Considering weak intermolecular C(8)–H(8A)···O(1),

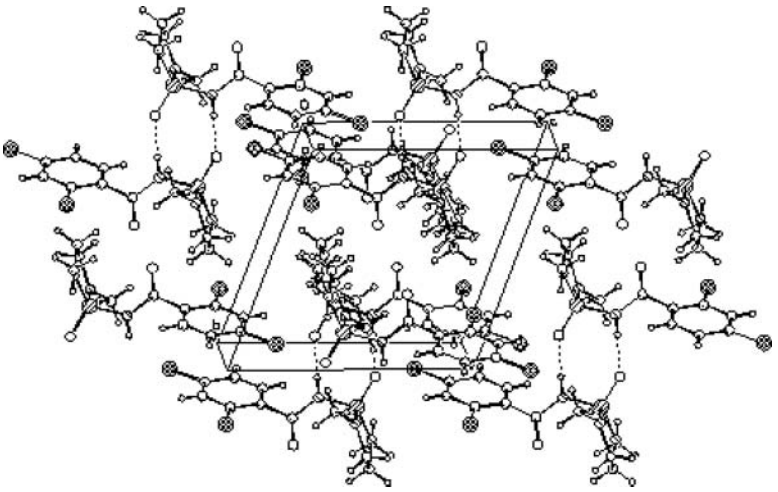


Figure 2 The unit cell packing of compound **2**.

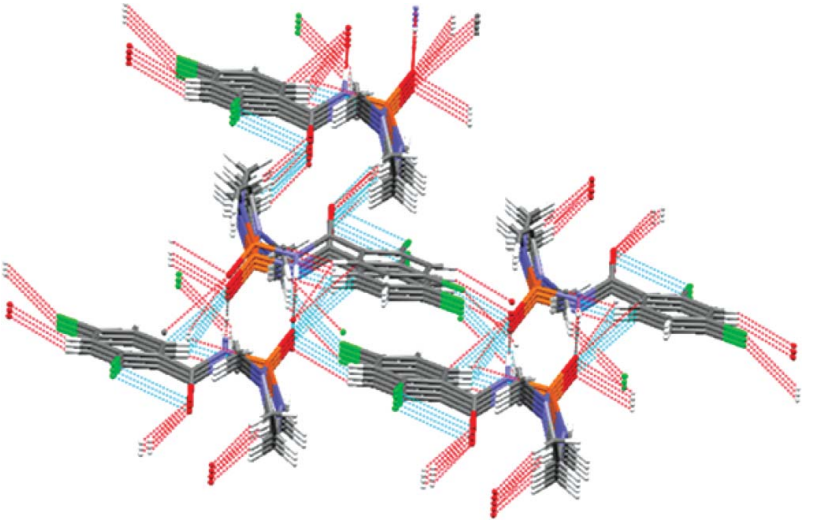


Figure 3 The three-dimensional polymeric chain formed by strong and weak hydrogen bonds in compound **2** (Color figure available online).

C(1)–H(1B)···O(2), and C(3)–H(3B)···Cl(2) interactions a three dimensional polymeric chain is produced in the crystalline network (Figure 3).

EXPERIMENTAL

X-Ray Measurements

X-ray data of compound **2** were collected with a Bruker SMART 1000 CCD area detector[25] with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were refined with SHELXL-97[26] by full matrix least squares on F^2. The positions of the hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program.[27]

Spectroscopic Measurements

^{1}H, ^{13}C, and ^{31}P NMR 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% H_3PO_4 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.

Synthesis of compounds 1–4: General Procedure

To a solution of 10 mmol 2,4-dichloro-N-benzoyl phosphoramidic dichloride[28] in dry acetonitrile, 10 mmol of the corresponding diamine, and 20 mmol of $N(C_2H_5)_3$ were added

dropwise at 0°C and the mixture was stirred for 10 h. Then, the solvent was evaporated and the residue was washed with distilled water and dried.

2-(2,4-Dichloro-N-benzoyl)-1,3,2-diazaphosphole-2-oxide (1). Yield: 74%; mp = 200.3°C. Elemental analysis: Calcd: C, 36.73; H, 3.40; N, 14.28. Found: C, 36.71; H, 3.42; N, 14.25%. IR (KBr, cm^{-1}): 3360 (m, NH), 3085 (m), 2960 (m), 1660 (s, C=O), 1578 (m), 1469 (m), 1436 (vs), 1369 (w), 1262 (s), 1202 (s, P=O), 1131 (w), 1094 (m), 1070 (m), 1045 (m, P–N_{amine}), 917 (m, P–N_{amide}), 893 (m), 866 (m), 835 (m), 807 (m), 769 (m), 744 (m), 699 (w), 581 (m), 483 (m), 432 (m). ^{1}H NMR (500.13 MHz, D_6-DMSO, 25°C, TMS): δ = 3.18 (m, 2H, CH_2), 3.34 (m, 2H, CH_2), 4.73 (d, $^2J_{PNH}$ = 12.8 Hz, 2H, NH_{amine}), 7.45 (m, 2H, arom-H), 7.64 (s, 1H, arom-H), 9.35 (d, $^2J_{PNH}$ = 5.5 Hz, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, D_6-DMSO, 25°C, TMS): δ = 40.9 (s, CH_2), 41.0 (s, CH_2), 127.0 (s), 129.0 (s), 130.2 (s), 131.0 (s), 134.5 (s), 135.5 (d, $^3J_{PC}$ = 8.7 Hz, C_{ipso}), 167.1 (s, C=O). ^{31}P NMR (202.46 MHz, D_6-DMSO, 25°C, H_3PO_4 external): δ = 21.0.

1,3-Dimethyl-2-(2,4-dichloro-N-benzoyl)-1,3,2-diazaphosphole-2-oxide (2). Yield: 95%; mp = 219.2°C. Elemental analysis: Calcd.: C, 40.99; H, 4.35; N, 13.04. Found: C, 40.98; H, 4.37; N, 13.03. IR (KBr, cm^{-1}): 3090 (s), 2860 (s), 1679 (s, C=O), 1576 (ms), 1468 (s), 1437 (vs), 1378 (mw), 1279 (s), 1249 (s), 1209 (vs, P=O), 1160 (vs), 1122 (s), 1099 (s), 1032 (s, P–N_{amine}), 941 (s, P–N_{amide}), 872 (s), 814 (m), 772 (ms), 750 (s), 693 (m), 659 (mw), 567 (w), 499 (ms), 434 (ms). ^{1}H NMR (500.13 MHz, D_6-DMSO, 25°C, TMS): δ = 2.51 (s, 6H, CH_3), 3.16 (m, 2H, CH_2), 3.30 (m, 2H, CH_2), 7.45 (m, 2H, arom-H), 7.66 (s, 1H, arom-H), 9.50 (d, $^2J_{PNH}$ = 6.0 Hz, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, D_6-DMSO, 25°C, TMS): δ = 30.6 (d, $^2J_{PC}$ = 5.2 Hz, CH_3), 46.3 (d, $^2J_{PC}$ = 14.2 Hz), 127.2 (s), 129.0 (s), 130.1 (s), 130.7 (s), 134.7 (s), 135.3 (d, $^3J_{PC}$ = 8.7 Hz, C_{ipso}), 167.5 (s, C=O). ^{31}P NMR (202.46 MHz, D_6-DMSO, 25°C, H_3PO_4 external): δ = 17.3.

2-(2,4-Dichloro-N-benzoyl)-1,3,2-diazaphosphorinane-2-oxide (3). Yield: 75%; mp = 177.9°C. Elemental analysis: Calcd: C, 31.58; H, 3.16; N, 11.05. Found: C, 31.56; H, 3.17; N, 11.03. IR (KBr, cm^{-1}): 3335 (m, NH), 3230 (m, NH), 2915 (m), 1671 (s, C=O), 1578 (m), 1465 (m), 1434 (s), 1378 (w), 1340 (w), 1280 (m), 1239 (w), 1216 (w), 1165 (s, P=O), 1118 (w), 1092 (s), 1044 (m), 1011 (m, P–N_{amine}), 956 (w), 886 (m, P–N_{amide}), 855 (m), 776 (m), 736 (w), 701 (w), 663 (w), 629(w), 570 (m), 496 (m), 437 (m), 407 (m). ^{1}H NMR (500.13 MHz, D_6-DMSO, 25°C, TMS): 1.59 (m, 2H, CH_2), 3.11 (m, 4H, CH_2), 4.62 (s, 2H, NH_{amine}), 7.49 (m, 2H, arom-H), 7.69 (s, 1H, arom-H), 9.43 (b, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, D_6-DMSO, 25°C, TMS): δ = 26.1 (d, $^3J_{PC}$ = 6.1 Hz, CH_2), 41.6 (d, $^2J_{PC}$ = 3.0 Hz, CH_2), 127.2 (s), 129.0 (s), 130.0 (s), 130.2 (s), 134.6 (s), 135.5 (d, $^3J_{PC}$ = 8.1 Hz, C_{ipso}), 167.7 (s, C=O). ^{31}P NMR (202.46 MHz, D_6-DMSO, 25°C, H_3PO_4 external): δ = 3.3.

5,5-Dimethyl-2-(2,4-dichloro-N-benzoyl)-1,3,2-diazaphosphorinane-2-oxide (4). Yield: 83%; mp = 179.1°C. Elemental analysis: Calcd: C, 43.90; H, 4.88; N, 12.80. Found: C, 43.89; H, 4.89; N, 12.82%. IR (KBr, cm^{-1}): 3455 (m, NH), 3345 (s, NH), 3225 (s), 3095 (w), 2955 (m), 1669 (s, C=O), 1590 (m), 1473 (s), 1433 (s), 1379 (m), 1344 (m), 1307 (w), 1280 (m), 1247 (w), 1185 (s, P=O), 1136 (m), 1097 (s, P–N_{amine}), 1048 (w), 956 (m, P–N_{amide}), 878 (m), 844 (m), 821 (m), 774 (m), 701 (m), 669 (w), 577 (m), 523 (w), 490 (m), 435 (m). ^{1}H NMR (500.13 MHz, D_6-DMSO, 25°C, TMS): 0.76 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 2.57 (ddd, $^3J_{HH}$ = 5.6 Hz, $^2J_{HH}$ = 11.9 Hz, $^3J_{PNCH}$ = 26.7 Hz, 2H, CH_2), 2.98 (d, $^2J_{HH}$ = 12.3 Hz, 2H, CH_2), 4.62 (s, 2H, NH_{amine}), 7.47 (m, 2H, arom-H), 7.66 (s, 1H, arom-H), 9.42 (b, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, D_6-DMSO, 25°C, TMS): δ = 22.9 (s, CH_3), 24.8 (s, CH_3), 30.1 (d, $^3J_{PC}$ = 4.7 Hz, CH_2), 52.9 (d, $^2J_{PC}$ = 1.8 Hz, CH_2), 127.2 (s), 129.0 (s), 130.2 (s), 130.8 (s), 134.6 (s), 135.5 (d,

$^3J_{PC}$ = 8.0 Hz, C_{ipso}), 167.7 (s, C=O). ^{31}P NMR (202.46 MHz, D_6-DMSO, 25°C, H_3PO_4 external): δ = 1.1.

CONCLUSION

The synthesis, spectroscopic, and structural characterization of new diazaphospholes and diazaphosphorinanes has been performed. The structure of compound **2** showed a three dimensional polymeric chain in the crystalline lattice by intermolecular strong N–H···O and weak C–H···O and C–H···Cl hydrogen bonds. The phosphorus atoms are more deshielded in diazaphospholes than in diazaphosphorinanes. The ^{13}C NMR spectrum of **2** reveals a larger $^2J_{PC(aliphatic)}$ value for endocyclic carbon atom (14.2 Hz) than for the exocyclic CH_3 carbon atom (5.2 Hz). Furthermore, for diazaphosphorinanes $^3J_{PC(aliphatic)} \approx 2 \times {}^2J_{PC(aliphatic)}$.

SUPPLEMENTARY INFORMATION

Crystallographic data for the structure of compound **2** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 709121. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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