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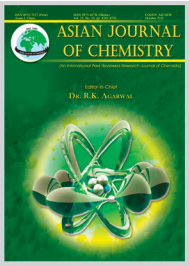

Synthesis and Spectroscopic Properties of Spiro, Ansa and Bino Phosphazenes

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The spiro (**1, 2**), ansa (**3**) and bino (**4**) phosphaza-lariat ethers have been synthesized. The structures of the compounds (**1**, **2**, **3** and **4**) are characterized by elemental analysis, mass spectrometry, IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.

Key Words: Spiro, Ansa, Bino, Phosphaza-lariat ethers, Phosphazene, Spectroscopy.

INTRODUCTION

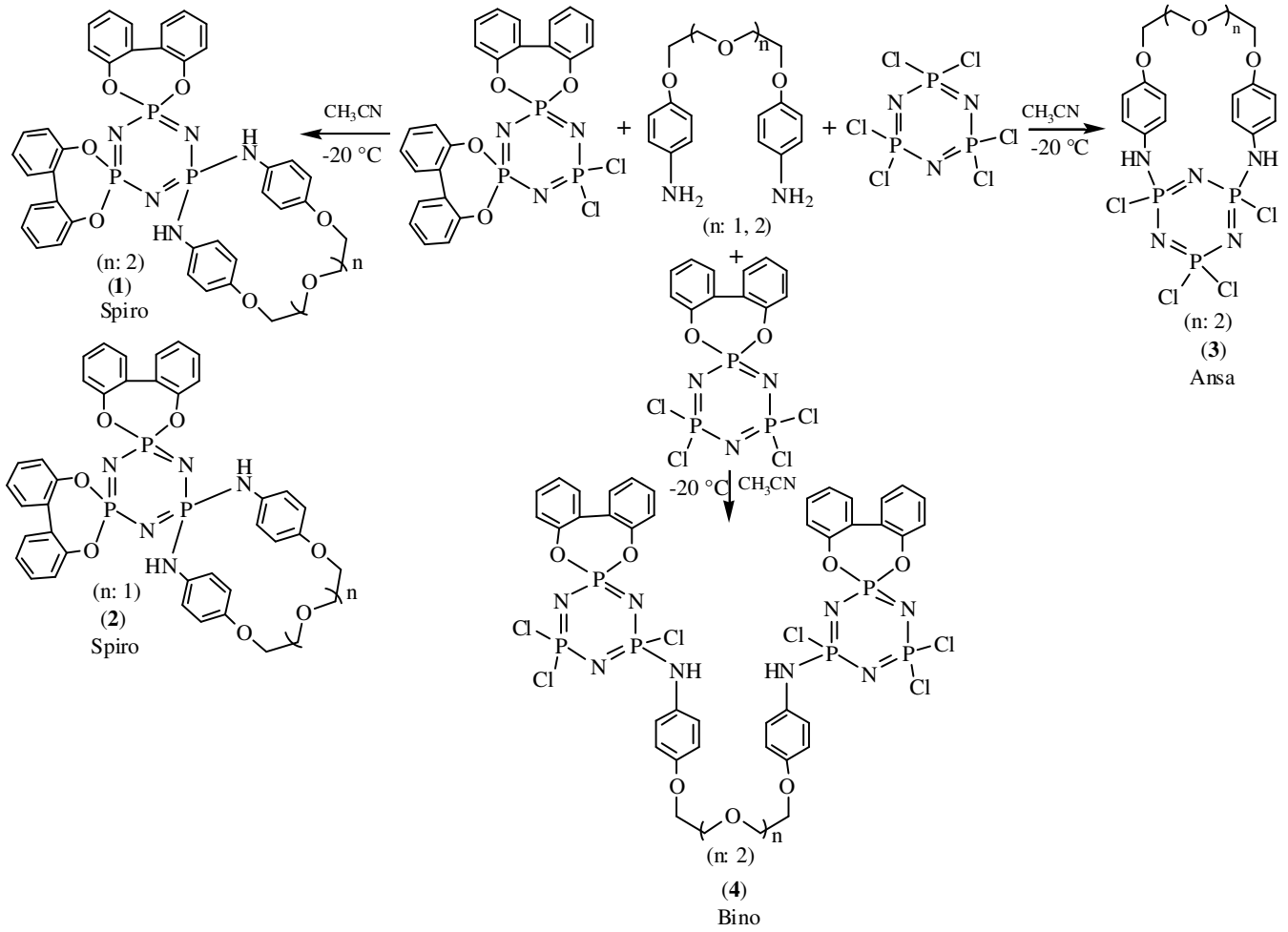
Phosphazenes are important compounds from which a large number of organophosphazenes can be derived by the reaction with amine and alcohol. A large variety of application areas of phosphazene compounds are reported by examining their features. Reaction of $N_3P_3Cl_6$ with difunctional reagents could, in principle, give rise to a number of different derivatives *i.e.*, *spiro*, *ansa*, *bino* and open chain[1-3]. There are four possible routes known for the reactions of $N_3P_3Cl_6$ with difunctional reagents; i) replacement of two *geminal* Cl-atoms to give a *spiro* architecture, ii) replacement of two non-*geminal* Cl-atoms to give an *ansa* architecture, iii) intermolecular reactions between Cl-atoms of phosphazene rings to yield a *bino* architecture, or intermolecular condensation reactions to yield cyclolinear or cyclomatrix polymers. There have been considerable work in the literature concerning the reactions of phosphazenes with amine and alcohol by mono- and difunctions[1,4-15]. Recently, phosphaza-lariat ethers, which are new types of compounds, have been obtained by reacting phosphazenes with aminopodand, cryptand and oligoethyleneglycol[16-26]. The design and synthesis of phosphaza-lariat ethers are significant; as ligating agents for alkali-, alkaline-earth and transition metal cations[27-29]. Despite the early studies on lariat ethers only a few phosphaza-lariat ethers have been reported[16-20, 25].

In this study, the reactions of aminopodand with hexachlorocyclotriphosphazene and mono- and di-*spiro* phenoxyphosphazene derivative are reported (**Scheme-I**). The structures of the compounds are characterized by elemental analysis, mass spectrometry, IR, ^{1}H, ^{13}C, ^{31}P NMR spectroscopy.

EXPERIMENTAL

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AVENCE-500 FT-NMR spectrometer operating at 500, 125, 7 and 202.4 MHz. Infrared absorption spectra were obtained from a Perkin Elmer BX II spectrometer in KBr discs and were reported in cm^{-1} units. Carbon, nitrogen and hydrogen analyses were performed on a LECO CHNS-932 analyzer. Melting points were determined on an electro thermal IA 9100 apparatus using a capillary tube. LC mass spectra were obtained on an AGILENT 6410 triple quad spectrometer using electro spray ionization (ESI) with an ion source temperature at 240 ºC. Hexachlorocyclotri-phosphazene was purchased from Aldrich. It was recrystallized from hexane and purified by fractional vacuum sublimation at 55 ºC before use. CH_3CN was purchased from Merck, distilled over sodium hydride and stored over molecular sieves. $CHCl_3$ (Merck), CH_2Cl_2 (Merck), *n*-hexane (Merck), THF (Merck), petroleum ether (50:70) (Merck), *tri*ethylamine (Merck), 4-nitrophenol (Merck), triethyleneglycoldichloride (Merck), diethyleneglycoldichloride (Merck), sodium hydride (Merck), Pd-C (10 %, Merck), hydrazine monohydrate (Merck), DMF (Merck), Na_2CO_3 (Merck), silica gel (Aldrich, 70-230 mesh, 60 Å) were used as received and all reactions were monitored by using Kieselgel 60 F 254 (silica gel) precoated TLC plates. All reactions and manipulations were carried out under an atmosphere of dry argon.

Synthesis of 2,2-[4,4'-(2,2'-(ethane-1,2-diyl*bis*(oxy))*bis*(ethane-2,1-diyl))*bis*(oxy)dianilino]-4,4,6,6-(2,2'-dioxy-1,1'-biphenyl)-cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene (*spiro*) (1): 4,4'-[2,2'-(Ethane-1,2-diyl*bis*(oxy))*bis*(ethane-2,1-diyl)]-



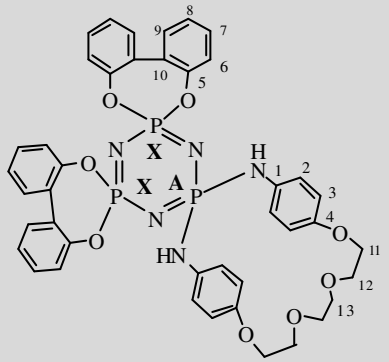
Scheme-I Synthesis route for the compounds **1-4**

bis(oxy)dianiline[18,30,31] (0.35 g; 1.05×10^{-3} mol) in CH_3CN (50 mL) was added drop wise to a stirred solution of di*spiro*-phenoxyphosphazene[32] (0.60 g; 1.04×10^{-3} mol) and triethylamine (0.21 g; 2.08×10^{-3} mol) in CH_3CN (150 mL) at -20 ºC for over 1 h, with argon being passed over the reaction mixture. After the mixture had been allowed to come to ambient temperature, it was boiled under reflux (12 h) using a condenser fitted with a $CaCl_2$ drying tube. The precipitated salt was filtered off and the solvent removed by rotary evaporation. The crude product was dried under *vacuo* and chromatographed (silica gel, 100 g, eluent; $CHCl_3$/THF, 3:1) to give the compound **1**. Then, it was recrystallized from CH_2Cl_2/petroleum ether (50:70) by the slow diffusion method yielding a white solid, m.p. 155 ºC, 0.14 g (15.9 %) yields. Found: C, 60.51; H, 4.59; N, 8.40 calc. for $C_{42}H_{38}N_5O_8P_3$: C, 60.50; H, 4.56; N, 8.40. IR (KBr, ν_{max}, cm^{-1}) ν(N-H) 3373 m, ν(Ar-H) 3063 m, ν(C-H, aliphatic) 2920-2871 s, ν(C=C) 1509 s, ν(C-O-C) 1265-1093 s, ν(P-O) 1230 s, ν(P=N) 1172 s. ^{31}P NMR-coupled ($CDCl_3$); δ ppm, 25.25 (d, $2P_X$, P(OArO'Ar'), $^2J_{PNP}$: 66.81 Hz), 22.74 (t, $1P_A$, P(NH-Ar-$OC_2H_4OC_2H_4OC_2H_4O$-Ar-NH), $^2J_{HNP}$: 10.12 Hz). MS (highest peak in multiplet, based on Cl^{35}; NaTFA solution used for ionization): m/z; 856 $(M+Na)^+$, 100 %), 834$(M+H)^+$, 24 %), 430 (M-2(OArO'Ar'), 76 %), 158.9 (M-(NH-Ar-$OC_2H_4OC_2H_4OC_2H_4O$-Ar-NH + Na), 56 %).

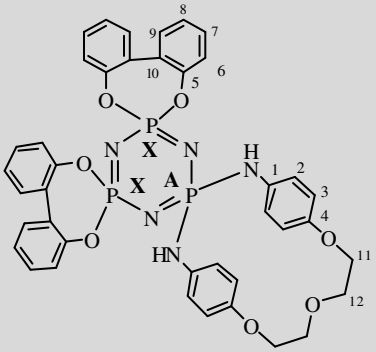
Synthesis of 2,2-[4,4'-(2,2'-oxy*bis*(ethane-2,1-diyl)*bis*(oxy))dianilino]-4,4,6,6-(2,2'-dioxy-1,1'-biphenyl)-cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene (*spiro*) (2): 4,4'-(2,2'-oxy*bis*(ethane-2,1-diyl)*bis*(oxy))dianiline[18,30,31] (0.41 g; 1.42 $\times 10^{-3}$ mol) in CH_3CN (50 mL) was added drop wise to a stirred solution of di*spiro*-phenoxyphosphazene[32] (0.82 g; 1.42 $\times 10^{-3}$ mol) and triethylamine (0.29 g; 2.87×10^{-3} mol) in CH_3CN (150 mL) at -20 ºC for over 1 h, with argon being passed over the reaction mixture. The compound **2** was isolated as the compound **1**. Compound **2**, white solid, m.p. 167 ºC, 0.24 g (21.4 %) yields. Found : C, 60.83; H, 4.30; N, 8.87 calc. for $C_{40}H_{34}N_5O_7P_3$: C, 60.83; H, 4.31; N, 8.87. IR (KBr, ν_{max}, cm^{-1}) ν(N-H) 3363 m, ν(Ar-H) 3063 w, ν(C-H, aliphatic) 2926-2871 m, ν(C=C) 1510 s, ν(C-O-C) 1270-1093 s, ν(P-O) 1229 s, ν(P=N) 1174 s. ^{31}P NMR-coupled ($CDCl_3$); δ ppm, 23.34 (d, $2P_X$, P(OArO'Ar'), $^2J_{PNP}$: 48.58 Hz), 22.68 (t, $1P_A$, P(NH-Ar-$OC_2H_4OC_2H_4O$-Ar-NH), $^2J_{PNP}$: 48.58 Hz, $^2J_{HNP}$: 14.11 Hz). MS (highest peak in multiplet, based on Cl^{35}; NaTFA solution used for ionization): m/z; 812 ($(M+Na)^+$, 100 %), 790 $(M+H)^+$, 46 %), 430 (M-2(OArO'Ar'), 67 %), 158.9 (M-(NH-Ar-$OC_2H_4OC_2H_4O$-Ar-NH + Na), 77 %).

Synthesis of 2,4-[4,4'-(2,2'-(ethane-1,2-diyl*bis*(oxy))*bis*(ethane-2,1-diyl))*bis*(oxy)dianilino]-2,4,6,6-tetrachloro-cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene (*ansa*) (3): 4,4'-(2,2'-(ethane-1,2-diyl*bis*(oxy))*bis*(ethane-2,1-diyl))*bis*(oxy)

TABLE-1
^{1}H NMR, ^{13}C NMR AND ^{31}P NMR SPECTRAL DATA IN $CDCl_3$. CHEMICAL SHIFTS (δ) ARE REPORTED IN PPM FOR THE COMPOUNDS **1**, **2**, **3** AND **4**



(**1**)



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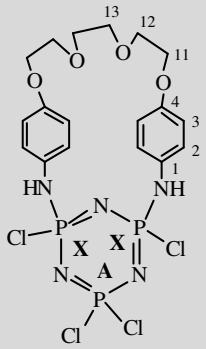
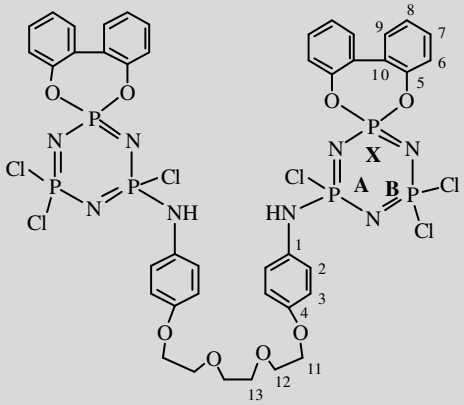


(**3**)



(**4**)

	Compound			
	1	**2**	**3**	**4**
Ar-H	7.35-6.56 (m, 24H)	7.65-6.02 (m, 24H)	7.32-6.66 (m, 8H)	7.64-6.60 (m, 24H)
ArOCH$_2$	4.09 (t, 4H)	4.13 (t, 4H)	4.15 (t, 4H)	4.38 (t, 4H)
ArOCH$_2$CH$_2$	3.85 (t, 4H)	3.92 (t, 4H)	3.87 (t, 4H)	3.80 (t, 4H)
OCH$_2$	3.72 (t, 4H)		3.75 (t, 4H)	3.68 (t, 4H)
N-H	10.30 (s, 2H)	10.45 (s, 2H)	5.15 (d, 2H)	4.95 (d, 2H)
C1	129.86 (s, 2C)	129.80 (s, 2C)	129.45 (s, 2C)	132.25 (s, 4C)
C2	121.95 (s, 4C)	121.86 (s, 4C)	124.93 (d, 4C, $^{3}J_{PNCC}$: 3.44 Hz)	122.14 (s, 4C)
C3	115.32 (s, 4C)	115.38 (s, 4C)	115.45 (s, 4C)	115.32 (s, 4C)
C4	148.03 (s, 2C)	147.97 (s, 2C)	156.57 (s, 2C)	148.02 (s, 2C)
C5	151.51 (s, 4C)	150.22 (s, 4C)		154.94 (s, 4C)
C6	121.94 (s, 4C)	121.86 (s, 4C)		121.94 (s, 4C)
C7	128.75 (s, 4C)	129.80 (s, 4C)		129.70 (s, 4C)
C8	124. 59 (s, 4C)	125.32 (s, 4C)		126.33 (s, 4C)
C9	129.74 (s, 4C)	129.61 (s, 4C)		129.76 (s, 4C)
C10	126.24 (s, 4C)	128.76 (s, 4C)		128.81 (s, 4C)
C11	70.87 (s, 2C)	69.91(s, 2C)	71.24 (s, 2C)	71.37 (s, 2C)
C12	69.83 (s, 2C)	67.81 (s, 2C)	69.78 (s, 2C)	69.74 (s, 2C)
C13	68.00 (s, 2C)		67.96 (s, 2C)	69.43 (s, 2C)
Spin system	AX_2	AX_2	AX_2	ABX
P_A	22.74 (t, 1P)	22.68 (t, 1P)	25.32 (t, 1P)	5.62 (q, 1P)
P_B				18.95 (q, 1P)
P_X	25.25 (d, 2P)	23.34 (d, 2P)	15.39 (d, 2P)	27.0 (q, 1P)

d: doublet, m: multiplet, q: quartet, s: singlet, t: triplet

dianiline[18,30,31] (1.00 g; 3.01 × 10^{-3} mol) in CH_3CN (50 mL) was added drop wise to a stirred solution of hexachlorocyclotriphosphazene (0.52 g; 1.49 × 10^{-3} mol) and triethylamine (0.91 g; 9.00 × 10^{-3} mol) in CH_3CN (150 mL) at -20 ºC for over 1 h, with argon being passed over the reaction mixture. The compound **3** was isolated as the compound **1**. Compound **3**, white solid, m.p. 223 ºC, 0.40 g (44 %) yields. Found : C, 35.60; H, 3.65; N, 11.54 calc. for $C_{18}H_{22}Cl_4N_5O_4P_3$: C, 35.61; H, 3.65; N, 11.54. IR (KBr, ν_{max}, cm^{-1}) ν(N-H) 3204 s, ν(Ar-H) 3075 w, ν(C-H, aliphatic) 2930-2871 s, ν(C=C) 1512 s,

ν(C-O-C) 1280-1172-1109 s, ν(P=N) 1195 s, ν(P-Cl) 584-519 s. ^{31}P NMR-decoupled ($CDCl_3$); δ ppm, 25.32 (t, 1P_A, PCl_2, $^2J_{PNP}$: 51.68 Hz), 15.39 (d, 2P_X, PCl(NH-Ar-$OC_2H_4OC_2H_4OC_2H_4$O-Ar-NH), $^2J_{PNP}$: 51.68 Hz). MS (highest peak in multiplet, based on Cl^{35}): m/z; 607 (M^+, 70 %), 258 (M- (NH-Ar-$OC_2H_4OC_2H_4$ OC_2H_4O-Ar-NH) + Cl, 45 %).

Synthesis of 2,2'-[4,4'-(2,2'-(ethane-1,2-diyl*bis*(oxy))*bis*(ethane-2,1-diyl))*bis*(oxy) dianilino]-4,4,4',4'-(2,2'-dioxy-1,1'-biphenyl)-2,2',6,6,6',6'-hexachlorocyclo-2λ^5,2'λ^5,4λ^5,4'λ^5,6λ^5,6'λ^5-triphosphazatriene (*bino*) (4): 4,4'-(2,2'-oxy*bis*(ethane-2,1-diyl)*bis*(oxy))dianiline[18,30,31] (0.19 g; 5.70 × 10^{-3} mol) in CH_3CN (50 mL) was added drop wise to a stirred solution of mono*spiro*-phenoxyphosphazene[32] (0.27 g; 5.86 × 10^{-3} mol) and triethylamine (1.15 g; 11.38 × 10^{-3} mol) in CH_3CN (150 mL) at -20 ºC for over 1 h, with argon being passed over the reaction mixture. Compound **4**, white solid, m.p. 138 ºC, 0.40 g (57.7 %) yields. Found : C, 42.69; H, 3.22; N, 9.48 calc. for $C_{42}H_{38}Cl_6N_8O_8P_6$: C, 42.68; H, 3.22; N, 9.48. IR (KBr, ν_{max}, cm^{-1}) ν(N-H) 3310 m, ν(Ar-H) 3069 w, ν(C-H, aliphatic) 2931-2884 m, ν(C=C) 1510 s, ν(C-O-C) 1189-1154-1094 s, ν(P-O) 1191 s, ν(P=N) 1171 s, ν(P-Cl) 586-518 s. ^{31}P NMR-decoupled ($CDCl_3$); δ ppm, 27.0 (q, 2P_X, (OArO'Ar'), $^2J_{PANPX}$: 65.07 Hz, $^2J_{PBNPX}$: 75.84 Hz), 18.95 (q, 2P_B, PCl_2, $^2J_{PANPB}$: 75.99.07 Hz, $^2J_{PXNPB}$: 75.84 Hz), 5.62 (q, 2P_A, PCl(NH-Ar-$OC_2H_4OC_2H_4OC_2H_4$O-Ar-NH), $^2J_{PXNPA}$: 65.07 Hz, $^2J_{PBNPA}$: 75.99 Hz). MS (highest peak in multiplet, based on Cl^{35}): m/z; 1181 (M^+, 33 %), 768 (M-2(OArO'Ar') + C_2H_4O) 60 %), 242 (M-2(OArO'Ar') + (NH-Ar-$OC_2H_4OC_2H_4OC_2H_4$O-Ar-NH + $N_3P_3Cl_3$) 35 %).

RESULTS AND DISCUSSION

The IR spectra of the compounds are given in synthetic procedures. The characteristic N-H, C-O-C and P=N bands are appeared respectively with the wave numbers (cm^{-1}) of 3373, 3363, 3204, 3310 δ(N-H), 1265-1093, 1270-1093, 1280-1172-1109, 1189-1154-1094 ν(C-O-C) and 1172, 1174, 1195, 1171 ν(P=N) were observed for compounds **1**, **2**, **3** and **4**, respectively. The P-Cl band is observed at 584-519 cm^{-1} and 586-518 cm^{-1} for compounds **3** and **4**, while it is not observed for compounds **1** and **2**. In addition, the asymmetric and symmetric vibrations of ν(P-O) arise at 1230, 1229 and 1191 cm^{-1} for **1**, **2** and **4**, respectively. The P=N vibration bands of **3** observed in a higher frequency such as 23, 21 and 24 cm^{-1} than the same band of **1**, **2** and **4**.

In the ^{1}H NMR spectra (Table-1), the N-H signal is singlet δ = 10.30 ppm singlet and δ = 10.45 ppm for compounds **1** and **2**, while it is doublet δ = 5.15 ppm ($^2J_{PNH}$: 7.52 Hz) and δ = 4.95 ppm ($^2J_{PNH}$: 9.76 Hz) for compounds **3** and **4**. The phenyl protons were observed multiplet at 7.35-6.56, 7.65-6.02, 7.32-6.66 and 7.64-6.60 ppm for compounds **1**, **2**, **3** and **4**, respectively. The protons of the etheric group at $ArOCH_2$ and $ArOCH_2CH_2$ in also gave a triplet at δ = 4.09, 4.13, 4.15, 4.38 ppm and δ = 3.85, 3.92, 3.87, 3.80 ppm ($^3J_{HCCH}$= 5.00, 5.12, 4.45 and 4.67 Hz), respectively, for **1**, **2**, **3** and **4**. The OCH_2 protons were singlet at δ = 3.72 ppm, 3.75 ppm and 3.68 ppm in **1**, **3** and **4**.

According to the proton de-coupled ^{13}C NMR spectra compounds **1**, **2**, **3** and **4** have 13, 12, 7 and 13 signals (Table- 1). The compounds (**1**, **2**, **3** and **4**) seem to have symmetric molecular structures in solution. The C2 is coupled with the P atom (δ = 124.93 ppm, d, 4C, $^3J_{PNCC}$: 3.44 Hz) in compound **3**, while it is not coupled with the P atom in compounds **1**, **2** and **4**.

The proton de-coupled ^{31}P NMR spectra of compounds were interpreted as a result of a simple AX_2, AX_2, AX_2 and ABX spin system for **1**, **2**, **3** and **4** (Table-1). According to the pattern of proton coupled ^{31}P NMR spectra of compounds (**1**, **2**, **3** and **4**), it was concluded that the only *spiro* (**1**, **2**), *ansa* (**3**) and *bino* (**4**) architectures were possible.

The MS spectrum of compounds (**1**, **2**, **3** and **4**) showed a well-defined parent ion at m/z 834, 790, 607 and 1181 ($(M+H)^+$, $(M+H)^+$, M^+ and M^+) with the expected isotope pattern. The peaks, at m/z values of 430 and 158.9 in **1** and **2**, 258 in **3** and 242 in **4** correspond to the loss of M-2(OArO'Ar') and M-(NH-Ar-$OC_2H_4OC_2H_4OC_2H_4$O-Ar-NH) + Na (**1**), M-2 (OArO'Ar') and M-(NH-Ar-$OC_2H_4OC_2H_4$O-Ar-NH) + Na (**2**), (M-(NH-Ar-$OC_2H_4OC_2H_4OC_2H_4$O-Ar-NH) + Cl (**3**) and M-2 (OArO'Ar') and M-(NH-Ar-$OC_2H_4OC_2H_4OC_2H_4$O-Ar-NH + $N_3P_3Cl_3$ (**4**). The fragmentation pattern of **1** and **2** was found as similar to that of **4**. N_3P_3 ring system in **1**, **2**, **3** and **4** was not stable (dominant ion was not observed: m/z 134) during the fragmentation that indicates the first loss of biphenol and aminopodand fragments.

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