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Reinvestigations of the reactions of hexachlorocyclotriphosphazene with difunctional primary amines leading to novel dangler, ansa and bridged derivatives. Spectroscopic studies of the derived products

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ABSTRACT

In an extension of the research on the nucleophilic substitution reactions of hexachlorocyclotriphosphazene (**1**) with linear aliphatic primary diamines, NH_2-$(CH_2)_n$ $-NH_2$ (n = 3, 5, 6 and 8) are surveyed. In the presence of pyridine, NaH and in excess of the used amine as base, at 0 °C and room temperature, we subjected the reactions of **1,** to a systematic reinvestigation with aliphatic propane-1,3-, pentane-1,5-, hexane-1,6- and octane-1,8-diamines (**2**, **3**, 4 and **5** respectively) and we isolated a total of 18 compounds which include examples of all four structural types (open chain, spiro, ansa and the bino derivatives). The novel synthesized open chain (**6**), mono-ansa (**8a**), spiro-ansa (**10**), single-bridged (**12a**), double-bridged (**13a**) and tri-bridged (**14a**) cyclophosphazene derivatives are reported for the first time. The synthesized compounds are characterized by elemental analysis, MS, FT-IR, ^1H and ^{31}P NMR spectroscopy. Spectroscopic data, product types and the relative yields are compared with those of the previously reported cyclophosphazene derivatives derived from di-functional nucleophilic reagents.

1. Introduction

Due to having a variety of applications in science and technology, cylophosphazenes are an important family of inorganic cyclic systems [1]. Principally, they have active phosphorus-halogen bonds on the cyclic system (containing the $N{=}PX_2$ repeating unit), hence, cyclophosphazenes can form a wide variety of novel cyclophosphazene derivatives by giving nucleophilic substitution reactions with wide variety of nucleophilic reagents and the compounds formed according to the inorganic, organic or organometallic group bound may have also different properties [1,2]. The second reason why these compounds are interesting is; these compounds are used as starting materials for obtaining high molecular weight poly[(organo)phosphazenes] [3–6], which are the largest class of known inorganic polymers. The third property that emerged in recent years is that they form coordination compounds with transition metals [7–9]. Cyclophosphazenes can interact with the main group and with the transition metals in different ways. They can react with the donor atoms of the substituents attached to cyclophosphazene ring or the non-paired (endo) electrons of the nitrogen atoms on the cyclophosphazene ring. The application of the cyclophosphazenes derivatives also includes electrical conductivity [10], liquid crystals [6–16], chemosensors [17] and biologically active materials [18–30].

There is also a considerable amount of interest in the preparation of amino derivatives of cyclophosphazenes [18,31–41], because of their variety of applications as explained above. These can be studied not only exhibiting some interesting physical and chemical properties but also for the development of bioactive cyclophosphazenes in the search for new effective drug candidates for the therapy of various diseases, especially anticancer and antimicrobial.

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (1), with mono- and di-functional nucleophilic reagents have been explored extensively [42–56]. As mentioned, they have active phosphorus-halogen bonds that can be replaced by mono-, di-, tri- and poly-functional nucleophilic reagents, leading to the formation of different types of products, which may include examples of four structural types; spiro, ansa, open chain (dangling), and bridged

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(bino) derivatives.

The reactions of cyclotriphosphazene (1) with di-primary amines, $HN(CH_2)_nNH$ (n = 2–10) [42,45,51,55,64–68], and di-secondary amines, $HNR(CH_2)_nNRH$ (n = 2, 3) [56,57] have been studied extensively. Reactions with di-secondary amines, e.g. $HNMe(CH_2)_2NHMe$, gave rise to mono, $N_3P_3Cl_4[NMe(CH_2)_2NMe]$, bis-, $N_3P_3Cl_2[NMe(CH_2)_2NMe]_2$, and tris-spiro, $N_3P_3[NMe(CH_2)_2NMe]_3$ derivatives, which contained 5-membered spiro rings [56,57]. This contrasts with the analogous di-primary amine, $H_2N(CH_2)_2NH_2$, in which only the monospiro derivative, $N_3P_3Cl_4[NH(CH_2NH]$, could be isolated [58]. On the other hand, the reactions with 1,3-diaminopropane [59,60] and 1,4 diaminobutane [61–63] yielded mono-, $N_3P_3Cl_4[NH(CH_2)_3NH]$, and $N_3P_3Cl_4[NH(CH_2)_4NH]$; bis-, $N_3P_3Cl_2[NH(CH_2)_3NH]_2$, and $N_3P_3Cl_2[NH(CH_2)_4NH]_2$; and tri-, $N_3P_3[NH(CH_2)_3NH]_3$, spiro derivatives.

We concluded that when the number of methylene groups between the two amino functions is from two to four, spiro derivatives were the only products isolated. Whereas, when the number of methylene groups between the two amino functions are from five to ten, singly $N_3P_3Cl_5[NH(CH_2)_nNH]N_3P_3C1$ ($n = 5–10$) [64], doubly-, $N_3P_3Cl_4[NH(CH_2)_nNH]_2N_3P_3Cl_4$ (n = 6 and 8) [51,65], and tripyl-bridged, $N_3P_3Cl_3[NH(CH_2)_nNH]_3N_3P_3Cl_3$ ($n = 6$ or 8) derivatives [51,65] were isolated. Subsequently these studies were extended to mono-ansa, $N_3P_3Cl_4[NH(CH_2)_nNH]$ (n = 6 and 8) [51] derivatives as well.

We therefore wished to re-investigate and clarify the reactivity and the substitution patterns of hexachlorocyclotriphosphazene (1) with shorter and longer chain primary diamines, $H_2N(CH_2)_nNH_2$ (n = 3, 5, 6 and 8) under different reaction conditions.

Although we tried to carry out the reactions under different conditions, we could not obtain spiro derivatives with longer chain di-primary amines. We have also observed that reactions of compound 1 with hexane-1,6-diamine (4) and octane-1,8-diamine (5) give similar results comparing to preliminary reports [51,60–65].

This paper reports a series of novel cylophosphazene derivatives (**6**, **8a**, **10**, **12a**, **13a** and **14a**) derived from the reactions of compound **1** with 1,3-propane- (**2**) and pentane-1,5-diamines (**3**) (Fig. 1), and the characterizations of these compounds using MS, elemental analyses, FT-IR, ^1H, ^{13}C and ^{31}P NMR data.

2. Experimental

2.1. Materials

Reagent grade solvents were used throughout the work, benzene, light petroleum (b.p. 40–60 °C), anhydrous diethyl ether, acetonitrile, methanol, butanol, *n*-hexane (>96%), dichloromethane (>99.0%), chloroform, acetonitrile, THF, acetone (Sigma Aldrich). THF was distilled over a sodium-potassium alloy under an argon atmosphere. $CDCl_3$, deuterated solvent for NMR spectroscopy (Sigma Aldrich), silica gel (60, 0.063–0.200 mm Merck) was used for column chromatography, Kieselgel 60° 254 (silica gel) precoated TLC plates (Merck). The following materials were also obtained from Sigma Aldrich Chemicals: Phosphonitrilic trimer (purified by fractional crystallization from hexane), ninhydridine (0.5% w/v), 1,3-propane-, 1,5-pentane-, 1,6-hexane- and 1,8-octane-diamines; $NaBH_4$ and pyridine used as received, NaH (60% dispersion in mineral oil, which was removed by washing with dry *n*-heptane followed by decantation).

2.2. Methods

All reactions were monitored using Kieselgel 60° 254 (silica gel) precoated TLC plates and sprayed with ninhydridine (0.5% w/v) in butanol solution, and developed at approximately 130 °C. Required separations of mixtures were carried out by flash column chromatography using Kieselgel 60. (Merck 60, 0.063–0.200 mm; for 2 g crude mixture, 100 g silica gel was used in a column of 2.5 cm in diameter and 90 cm in length). Melting points were determined with a Reichart-Kofler micro heating stage and a Mettler FB 82 hot stage connected to a FP 800 central processor both fitted with a polarizing microscope. ^1H NMR spectra were recorded with a JEOL FX-200 spectrometer (operating at 199.5 MHz) and a Varian XL-400 spectrometer (operating at 399.5 MHz, at University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm NMR tubes. Measurements were carried out using a $CDCl_3$ lock, TMS as internal reference, and sample concentrations of 15–20 mg cm^{-3} ^{13}C NMR spectra were recorded using a Varian VXR 400 spectrometer (operating at 100.577 MHz -University College, London) TMS was used as an internal reference. ^{31}P NMR spectra were recorded using a Varian 400 spectrometer (operating at 162.0 MHz at University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm NMR tubes. Measurements were carried out using a $CDCl_3$ lock, 85% H_3PO_4 was used as an external reference and sample concentrations of 15–20 mg cm^{-3}. Experimental details together with product types and the relative yields are summarized in Tables 1 and 2 and the NMR data may be found in Tables 3 and 4.

2.3. The reactions of $N_3P_3Cl_6$ (1) with 1,3-propane-diamine (2)

2.3.1. One equivalent of compound 2, in THF solution at room temperature

Hexachlorocyclotriphosphazene (**1**) (4 g, 0.0115 mol) was dissolved in dry THF (80 mL) in a 1000 mL three-necked round-bottomed flask under an argon atmosphere and the reaction mixture was cooled to 0 °C in ice-bath. Anhydrous pyridine (1.82 g, 0.023 mol) in dry THF (10 mL) was added quickly to the stirred solution. After, 1,3-propane-diamine **(2)** (0.85 g, 0.0115 mol) was dissolved in dry THF (20 mL) and added dropwise into the stirred solution. Then the reaction mixture was kept stirring for about 46 h at room temperature. Reactions were also carried out in two and three equimolar ratios of compound **2,** in the presence of NaH; in acetonitrile, THF and in a mixture of *n*-hexane/dichloromethane (5:2) solutions; at room temperature and under reflux, as in the preliminary reported studies [44,54,59], we were only able to obtain spiro-cyclic derivatives (**7**, **9** and **11**). However, the solvent system affects the percentage yields of the derived products. Reaction details together with the previously reported studies are summarized in Tables 1 and 2

2.3.2. Two equivalents of compound (2), in THF (in dilute solution) at 0 °C

Synthesis of the novel open chain, $N_3P_3[NH(CH_2)_3NH_2]Cl_5$ (**6**) and single-bridged, $N_3P_3Cl_5[NH(CH_2)_3NH]N_3P_3Cl_5$ (**12a**) derivatives.

Hexachlorocyclotriphosphazene (**1**) (4 g, 0.0115 mol) was dissolved in dry THF (400 mL) in a 1000 mL three-necked round-bottomed flask under an argon atmosphere and the reaction mixture was cooled to 0 °C in ice-bath. 1,3-propane-diamine (**2**) (2.15 g, 0.029 mol, the amine was used excessively as a base) was dissolved in dry THF (200 mL) and added dropwise into the stirred solution under an argon atmosphere. Then the reaction mixture was kept stirring for about 3 h at 0 °C. After checking the reaction mixture on the TLC chromatogram, one major and one minor spots were observed. The reaction was stopped, quickly filtered off and the solvent was evaporated to the reduced point. The separation of the compounds was achieved by column chromatography using dichloromethane-diethylether (3:1) as the mobile phase. The major spot was the starting material, $N_3P_3Cl_6$, (**1**) (85%). The second

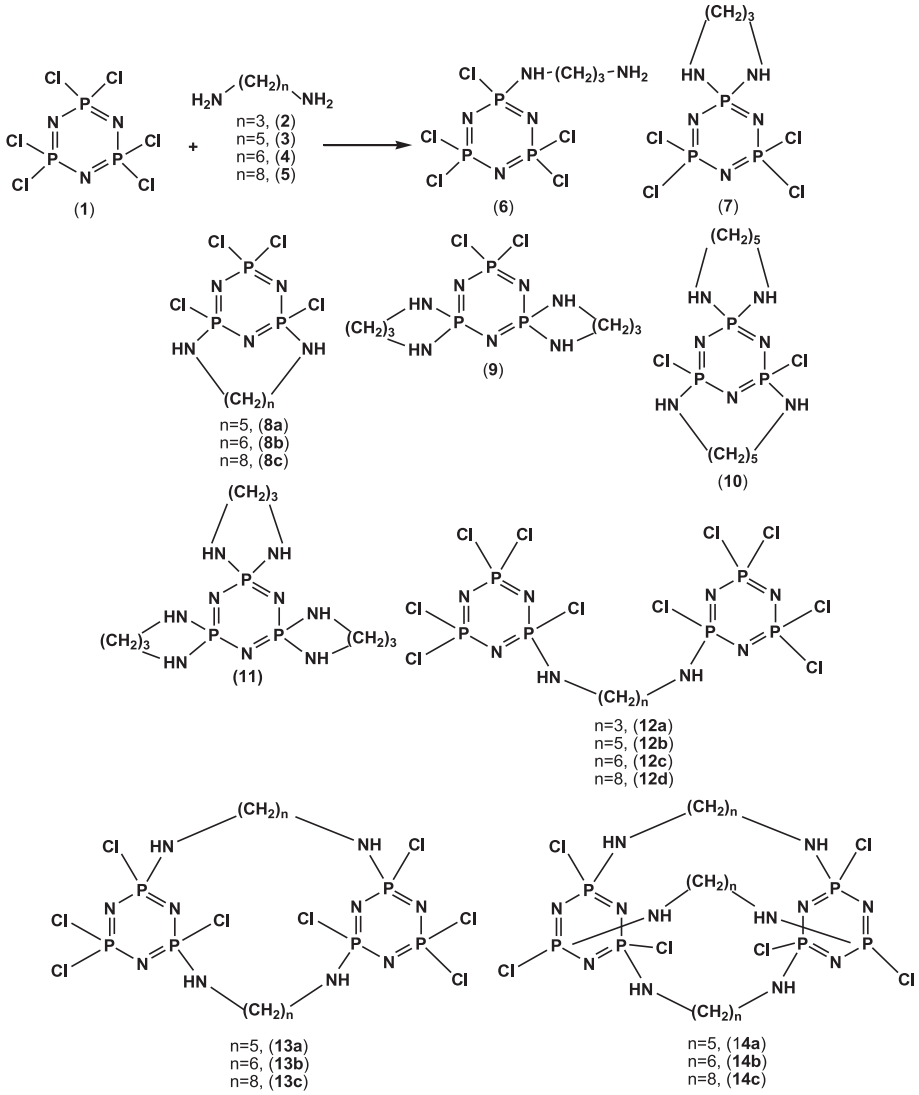

Fig. 1. Structures of cyclotriphosphazene (**1**) derivatives with aliphatic diamines (n = 3, 5, 6, 8). Compounds **7**, **9** and **11** were synthesized at r.t. or under refluxed conditions [45,55] and **6**, **8a**-**8c**, **10**, **12a**-**12d**, **13a**-**13c** and **14a**-**14c** were synthesized at 0 °C [45,51,62–65]. **6**, **8a**, **10**, **12a**, **13a** and **14a** are reported as the novel compounds.

Table 1
Analytical data (elemental analysis) and the percentage yields of cyclophosphazene derivatives (**6**–**14c**).

Compound	Classification (%)							
	Calculated				Found			
	C (%)	H (%)	N (%)	M^+	C (%)	H (%)	N (%)	$[M^+H]^+$
$C_3H_9Cl_5N_5P_3$ **6**	9.35	2.35	18.17	385.39	9.34	2.37	18.17	386.30
$C_3H_8Cl_4N_5P_3$ **7**	10.33	2.31	20.07	348.93	10.33	2.33	20.08	349.70
$C_5H_{12}Cl_4N_5P_3$ **8a**	15.93	3.21	18.58	376.98	15.94	3.23	18.58	377.91
$C_6H_{14}Cl_4N_5P_3$ **8b**	18.43	3.61	17.91	391.01	18.38	3.59	17.91	389.94
$C_8H_{18}Cl_4N_5P_3$ **8c**	22.93	4.33	16.71	419.06	22.90	4.31	16.70	420.02
$C_6H_{16}Cl_2N_7P_3$ **9**	19.90	7.80	27.06	362.24	19.91	4.64	27.05	363.09
$C_{10}H_{24}Cl_2N_7P_3$ **10**	29.57	5.95	24.13	406.25	29.61	5.99	24.13	407.10
$C_9H_{24}N_9P_3$ **11**	30.76	6.88	35.88	351.35	30.76	6.92	35.88	352.70
$C_3H_8Cl_{10}N_8P_6$ **12a**	5.17	1.16	16.08	696.65	5.19	1.17	16.09	697.52
$C_5H_{12}Cl_{10}N_8P_6$ **12b**	8.28	1.67	15.46	724.71	8.28	1.70	15.47	725.78
$C_6H_{14}Cl_{10}N_8P_6$ **12c**	9.75	1.91	15.16	738.73	9.77	1.95	15.17	739.67
$C_8H_{18}Cl_{10}N_8P_6$ **12d**	12.53	2.37	14.61	766.78	12.52	2.36	14.62	767.84
$C_{10}H_{24}Cl_8N_{10}P_6$ **13a**	15.93	3.20	18.58	753.97	15.93	3.23	18.58	754.98
$C_{12}H_{28}Cl_8N_{10}P_6$ **13b**	18.43	3.61	17.91	782.02	18.44	3.65	17.91	783.30
$C_{16}H_{36}Cl_8N_{10}P_6$ **13c**	22.93	4.33	16.71	838.13	22.91	4.31	16.70	839.42
$C_{15}H_{36}Cl_6N_{12}P_6$ **14a**	23.00	4.63	21.46	783.23	23.06	5.43	21.47	784.14
$C_{18}H_{42}Cl_6N_{12}P_6$ **14b**	26.20	5.12	20.36	825.31	26.21	5.15	20.36	825.16
$C_{24}H_{54}Cl_6N_{12}P_6$ **14c**	31.70	5.98	18.48	909.48	31.72	6.10	18.48	910.39

Table 2
Experimental details of the aliphatic primary diamines (**6**–**14c**), (H_2N-(CH_2)n-NH_2, n = 3, 5, 6 and 8).

Compound	Solvent	Base	Temperature	Molar ratio	Yield (%)	Reference
(6)	THF	[a]	0 °C	1:1	11	Present study
(7)	$(CH_3CH_2)_2O$	NEt_3	r.t.	1:2	85	[55]
	$(CH_3CH_2)_2O$	NEt_3	r.t.	1:3	40–60	[45,55,60]
	DCM/L. pet.(3:7)	C_5H_5N NEt_3	r.t.	1:4–6	45	[45,60,62]
(8a)	CH_3CN	[a]	0 °C	1:2	6	Present study
(8b)	CH_3CN	[a]	0 °C	1:3	5	[51]
(8c)	CH_3CN	[a]	0 °C	1:3	9	[51]
(9)	$CHCl_3$	NEt_3	r.t.	1:2	40	[45,55,62]
	DCM/L. pet.(3:7)	C_5H_5N NEt_3	reflux	1:4–6	40–45	[45,60]
	n-hexane/DCM (7:3)	NEt_3	reflux	1:4–6	60	[45,60,62]
(10)	*n*-hexane/DCM (5:2)	[a]	0 °C	1:2	5, trace	Present study
(11)	$CHCl_3$	C_5H_5N NEt_3	reflux	1:3	35	[55]
	n-hexane/DCM (7:3)	NEt_3	reflux	1:4–6	40	[45]
(12a)	THF	[a]	0 °C	1:1	7	Present study
(12b)	$(CH_3CH_2)_2O$	NEt_3	r.t.	1:3	42	[64]
	$(CH_3CH_2)_2O$	NEt_3	r.t.	1:3	40	[64]
	n-hexane/DCM (5:2)	[a]	0 °C	1:2	49	Present study
	THF/CH_3CN	Pyridine/NEt_3	r.t.	1:3	60	Present study
(12c)	$(CH_3CH_2)_2O$	NEt_3	r.t.	1:3	40	[64]
(12d)	$(CH_3CH_2)_2O$	NEt_3	r.t.	1:3	45	[64]
(13a)	CH_3CN	[a]		1:3	13	Present study
	THF	[a]		1:3	9	Present study
(13b)	CH_3CN	NEt_3,[a]	0 °C	1:3	12	[51,65]
(13c)	CH_3CN	NEt_3,[a]	0 °C	1:3	6	[51,65]
(14a)	CH_3CN	[a]	0 °C	1:3	24	Present study
(14b)	CH_3CN	NEt_3,[a]	0 °C	1:3	23	[51,65]
(14c)	CH_3CN	NEt_3,[a]	0 °C	1:3	18	[51,65]

[a] The amine was used excessively as a base.

Table 3
Selected ^{31}P NMR parameters of cyclophosphazene derivatives (6-14c)[a] with relative primary diamines.

Compound	$^{\delta}PCl_2$[b]	$^{\delta}P(HNR)_2$[b]	$\delta P(HNR)Cl$[b]	$^2J[P(HNR)_2\text{-}PCl_2]$[c]	$^2J[P(HNR)Cl\text{—}PCl_2]$[c]	Ref.
$N_3P_3Cl_6$ (1)	19.90					
6	25.50		17.70		48.17	
7	21.50	7.50		45.50		[45,55,60]
8a	25.01		17.22		49.33	
8b	25.04		17.72		48.61	[51]
8c	26.08		21.15		46.50	[51]
9	23.30	12.40		46.30		[45,55,60]
10		20.30	27.20		67.69[d]	
11		23.50				[45,55,62]
12a	24.10		20.60		49.61	
12b	22.69		19.94		47.29	[64]
12c	22.18		19.67		47.12	[64]
12d	22.18		19.66		47.17	[64]
13a	24.40		22.80		47.79	
13b	23.75		23.03		47.44	[51,64]
13c	24.91		24.23		47.21	[51,64]
14a			25.40			
14b			25.89			[51,64]
14c			27.30			[51,64]

[a] In $CDCl_3$ (with respect to 85% phosphoric acid external reference) at 162.00 MHz.
[b] In ppm.
[c] In Hz.
[d] $^2J[P(HNR)Cl\text{—}P(HNR)_2]$: 67.69.

separated spot was identified as the open chain (dangling), $N_3P_3Cl_5[NH(CH_2)_3NH_2]$ derivative (**6**), recrystallized from dichloromethane-hexane (1:1.5), yield 0.22 g (11%), m.p. 191 °C. Anal. Calc. for $C_3H_8Cl_5N_5P_3$: C, 9.35; H, 2.35; N, 18.17, M, 385.39. Found: C, 9.34; H, 2.37; N, 18.17, M^+, 386.30.

The above reaction was also carried out over a longer period of time (about 56 h) and one minor compound as the single-bridged, $N_3P_3Cl_5[NH(CH_2)_3NH]N_3P_3Cl_5$ (**12a**) derivative was separated by column chromatography using dichloromethane-diethylether (3:1) as the eluent. The derived compound was recrystallized from benzene-hexane (1:1), yield 0.26 g (7%), m.p. 156 °C. Anal. Calc. for $C_3H_8Cl_{10}N_8P_6$: C, 5.17; H, 1.16; N, 16.08, M, 696.65. Found: C, 5.19; H, 1.18; N, 16.09, M^+, 697.52.

2.4. The reactions of $N_3P_3Cl_6$ (1) with 1,5-pentane-diamine (3)

2.4.1. One equivalent of compound (3), in THF (in dilute solution), at 0 °C

Synthesis of the novel mono-ansa, $N_3P_3Cl_4[NH(CH_2)_5NH]$ (**8a**) derivative.

Hexachlorocyclotriphosphazene (**1**) (4 g, 0.0115 mol) was dissolved in dry THF (400 mL) in a 1000 mL three-necked round-

Table 4
Selected ^{1}H NMR parameters of cyclophosphazene derivatives (6-14c)[a] with relative primary diamines.

Comp.	δPNH[b]	δPNHCH$_2$[b]	δPNCCH$_2$[b]	δPCCCH$_2$[b]	δPCCCCH$_2$[b]	^{3}J(PH)[c]
(6)	2.94	3.39	1.61	3.58		9.60
(7)[d]	2.91	3.11	1.49			11.20 [44,54,59]
(8a)	3.27	3.10/3.20	1.63	1.50		
(8b)[f]	3.18	3.25/3.07	1.60−1.46			[50]
(8c)[f]	2.92	3.11	1.48−1.54	1.38−1.44	1.22−1.26	[50]
(9)[d]	2.97	3.10	1.50			11.71 [44,54,59]
(10)						
spiro	3.02	3.90	2.75		2.14	unresolved complex spec.
ansa	3.21	3.86	2.70		2.01	unresolved complex spec.
(11)[d]	3.21	3.16	1.51			11.79 [44,54,61]
(12a)	3.56	3.11	1.63			11.40
(12b)[e]	3.45	3.05	1.58	1.40		[62]
(12c)[e]	3.46	3.08	1.61	1.41		[62]
(12d)[e]	3.58	3.07	1.59	1.36		[62]
(13a)	3.34	3.93	2.80		2.02	
(13b)[f]	3.31	3.84−3.92	2.78−2.80		1.99−2.07	[50,62]
(13c)[f]	2.94	3.59	2.73−2.75		1.73	[50,62]
(14a)	1.76	3.81−3.96	2.70−2.75		1.73−2.04	
(14b)[f]	1.80	3.04			1.66−1.70	[50,62]
(14c)[f]	1.92	3.09	1.71−1.76			[50,62]

[a] In $CDCl_3$ (TMS internal reference), operating at 399.95 MHz (room temperature).
[b] In ppm.
[c] In Hz.

bottomed flask under an argon atmosphere and the reaction mixture was cooled to 0 °C in ice-bath. 1,5-pentane-diamine (**2**) (1.60 g, 0.0152 mol, the amine was used excessively as a base) was dissolved in dry THF (200 mL) and added dropwise into the stirred solution. The mixture was stirred (48 h) at 0 °C until TLC indicated the completion of the reaction. The reaction mixture was filtered to remove amine salts and any other insoluble materials. Then the reaction mixture was followed on TLC silica gel plates using hexane-dichloromethane (2:1) as the eluent. The solvent was removed under reduced pressure and the resulting brown oil was subjected to column chromatography, using hexane−dichloromethane (3:1) as eluent. Products were recrystallized from benzene:hexane (1:3) containing a few drops of light petroleum (b.p. 40−60 °C). Except one reported product, single-bridged derivative [62], one novel product was also synthesized and identified as the mono-ansa derivative, $N_3P_3Cl_4[NH(CH_2)_5NH]$ (**8a**), yield 0.17 g (12%), m.p. 254.5 °C. Anal. Calc. for $C_5H_{12}Cl_4N_5P_3$: C, 15.93; H, 3.21; N, 18.58, M, 376.98. Found: C, 15.94; H, 3.23; N, 18.58, M^+, 377.91.

2.4.2. Two equivalents of compound (3), in acetonitrile solution and at 0 °C

Synthesis of the novel double-bridged, $N_3P_3Cl_4[NH(CH_2)_5NH]_2N_3P_3Cl_4$ (**13a**) derivative.

Hexachlorocyclotriphosphazene (**1**) (4 g, 0.0115 mol) was dissolved in 150 mL of THF in a 1000 mL three-necked round-bottomed flask under an argon atmosphere and the reaction mixture was cooled to 0 °C in ice-bath. To this solution two equivalents of 1,5-pentane-diamine (**3**) (3.1 g, 0.030 mol, the amine was used excessively as a base) in 100 mL of THF was added dropwise with stirring. Then the reaction mixture was continued with stirring for 40 h at 0 °C. TLC analysis using hexane-dichloromethane (3:1) revealed essentially the formation of two products. The reaction mixture was filtered to remove the amine salts or some insoluble materials, the solvent was evaporated at reduced pressure and the resulting brown oil was subjected to column chromatography, using hexane-dichloromethane (3:1) as the eluent. (**i**) The first product was identified as the single-bridged derivative, $N_3P_3Cl_5[NH(CH_2)_5NH]_3N_3P_3Cl_5$ (12b) [64]. (**ii**) The second product was identified as the novel double-bridged derivative, $N_3P_3Cl_4[NH(CH_2)_5NH]_2N_3P_3Cl_4$ (**13a**), yield 0.33 g (13%), m.p. 242 °C. Anal. Calc. for $C_{10}H_{24}Cl_8N_{10}P_6$: C, 15.93; H, 3.20; N, 18.58, M, 753.97. Found: C, 15.93; H, 3.23; N, 18.58, M^+, 754.98.

2.4.3. Three equivalents of compound (3), in n-hexane/dichloromethane (5:2) solution and at 0 °C

Synthesis of the spiro-ansa, $N_3P_3Cl_2[NH(CH_2)_5NH]_2$ (**10**) and triple-bridged $N_3P_3Cl_3[NH(CH_2)_5NH]_3N_3P_3Cl_3$ (**14a**) derivatives.

The reaction procedure as for (b). Except single- (**12b**, 7%) and double-bridged (**13a**, 11%) derivatives, (**i**) the novel triply-bridged, $N_3P_3Cl_3[NH(CH_2)_5NH]_3N_3P_3Cl_3$ (**14a**) derivative was also synthesized. Yield 0.58 g (21%), m.p. > 300 °C. Anal. Calc. for $C_{15}H_{36}Cl_6N_{12}P_6$: C, 23.00; H, 4.63; N, 21.46, M, 783.23. Found: C, 23.06; H, 4.67; N, 21.47, M^+, 784.14. **(ii)** An another product was also synthesized and characterized as the spiro-ansa derivative, $N_3P_3Cl_2[NH(CH_2)_5NH]_2$ (**10**, 2%), which was in traceable amount and detected only by ^{31}P and ^{1}H NMR spectral data. All the other reaction details together with the preliminary reported studies are summarized in Tables 1 and 2

3. Results and discussion

The reactions of $N_3P_3Cl_6$ (**1**) with one, two and three equimolar ratios of linear aliphatic diamines, NH_2-$(CH_2)_n$-NH_2 (n = 3, 5, 6 and 8) were carried out in THF, acetonitrile, chloroform and in a mixtures of *n*-hexane/dichloromethane (5:2) solutions, at 0 °C, room temperature and heating under reflux and gave the following novel derived products: (**i**) Open chain, $N_3P_3[NH(CH_2)_3NH_2]Cl_5$ (**6**, 11%); (**ii**) single-bridged, $N_3P_3Cl_5[NH(CH_2)_3NH]N_3P_3Cl_5$ (**12a**, 7%); (**iii**) mono-ansa, $N_3P_3[NH(CH_2)_5NH]Cl_4$ (**8a**, 6%); (**iv**) spiro-ansa, $N_3P_3[NH(CH_2)_5NH]_2Cl_2$ (**10**, 5%); (**v**) double-bridged, $N_3P_3Cl_4[NH(CH_2)_5NH]_2N_3P_3Cl_4$ (**13a**, 13%); and (**vi**) tri-bridged, $N_3P_3Cl_3[NH(CH_2)_5NH]_3N_3P_3Cl_3$ (**14a**, 24%) derivatives. The reactions of $N_3P_3Cl_6$ (**1**) with 1,6-hexane-diamine (**4**) and 1,8-octane-diamine (**5**) as in previously reported studies [51,55,64,65], gave only ansa, single-, double- and tri-bridged derivatives. When compared to the other reported studies [51,55,64,65], where only small changes in yields of the derived products were observed.

This study covers not only newly (6, 8a, 10, 12a-14a) synthesized compounds but also the preliminary reports. The whole reaction details together with product types and the relative yields are

summarized in Tables 1 and 2

3.1. Characterization of the reaction products by ^{31}P and ^{1}H NMR spectroscopy

The diamino substituted cyclophosphazene derivatives **6**, **7**, **9**–**11**; **8a-c**, **12a-d**, **13a-c** and **14a-c** were synthesized from the reactions of $N_3P_3Cl_6$ (**1**) with primary aliphatic diamines, H_2N-$(CH_2)_n$-NH_2 (n = 3, 5, 6 and 8). The amine itself was also used as a base depending on the reaction stoichiometry (1:2.3–1:3.5 M ratios). Some of the soluble and solid parts of the reaction mixtures were previously monitored by {H}^{31}P NMR spectroscopy to examine the course of the reactions and which gave useful information about the number of products formed and the type of the formations.

The ^{31}P NMR chemical shifts and ^{2}J(PP) values of the novel derived compounds together with the previously reported ones are summarized in Table 3.

3.2. ^{31}P NMR spectra

Open chain **6** and single-bridged derivatives **12a**-**c** contain also ≡PCl_2 and ≡P(HNR)Cl groups and have A_2B type spectra with different chemical shift values but similar in appearance. The phosphorus-proton coupled NMR spectrum suggests that the A_2 parts of the spectra arise from the ≡PCl_2 groups, since these remain unaffected, whereas the B parts (at 17.81 and 21.17 ppm), which split into further lines. The doublet structures centred at 23.47 and 23.98 are attributed to the ≡PCl_2 moieties for compounds, $N_3P_3[NH(CH_2)_3NH_2]Cl_5$(**6**) and $N_3P_3Cl_5[NH(CH_2)_3NH]N_3P_3Cl_5$(**12a**) respectively. Whilst the triplet structures for ≡P(HNR)Cl entities centred at 17.81 ppm for compound **6** and at 21.17 ppm for compound **12a**. The ^{31}P NMR proton-decoupled (**6**, a) and proton-coupled (**12a**, b) spectra of these compounds are illustrated in Fig. 2 respectively.

Mono-ansa derivatives (**8a**-**c**) are expected to be of AX_2 type spin systems, with the X parts showing further splitting on proton coupling. The molecule is containing one ≡PCl_2 and two ≡P(HNR)Cl groups. The chemical shifts related to ≡PCl_2 group are a triplet at 25.01 ppm and a doublet at 17.81 ppm corresponds to the ansa part ≡P(HNR)Cl for the novel compound **8a**. Thus this compound can be assigned with confidence the mono-ansa structure. Similar observations were also made for the previously reported ansa derivatives **8b** and **8c** as well [51]. The spiro-ansa compound (**10**) has A_2X type spin system and ^{31}P NMR proton coupled spectrum allows identification of the lines due to the ≡P spiro (centred at 21.5 ppm) and P(HNR)Cl (centred at 30.54 ppm) groups, where each group split

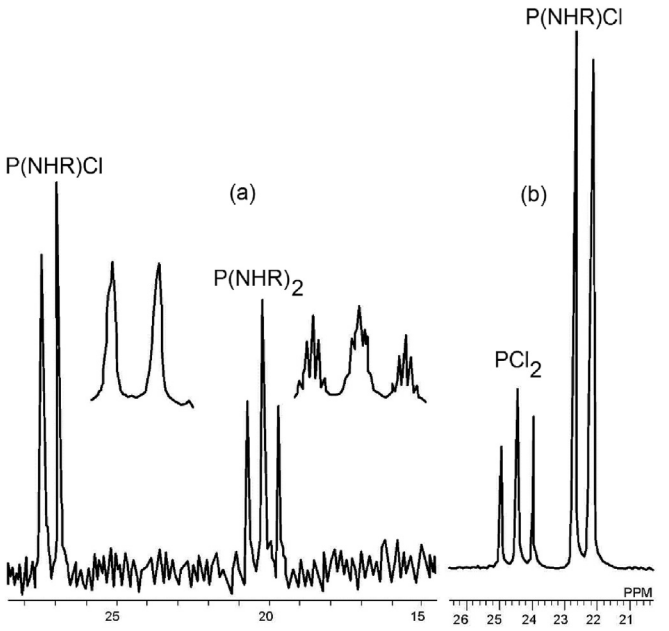

Fig. 3. (a) Proton decoupled and coupled ^{31}P NMR spectra of spiro-ansa (**10**) and (b) proton decoupled spectrum of double-bridged (**13a**) derivatives derived from the reactions of $N_3P_3Cl_6$ (**1**) with [H_2N–$(CH_2)_5$–NH_2] (**3**), in $CDCl_3$ at 162.00 MHz, room temperature, referenced to external 85% H_3PO_4.

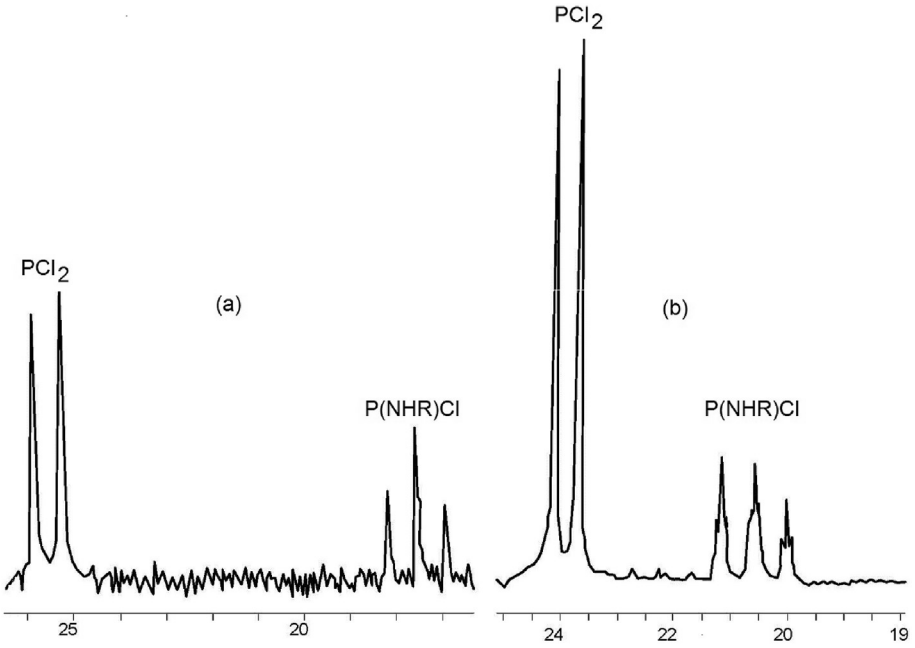

Fig. 2. (a) Proton decoupled ^{31}P NMR spectrum of open chain derivative (**6**) and (b) proton coupled ^{31}P NMR spectrum of single-bridged derivative (**12a**) derived from the reactions of $N_3P_3Cl_6$ (**1**) with [H_2N–$(CH_2)_3$–NH_2] (**2**), in $CDCl_3$ at 162.00 MHz, room temperature, referenced to external 85% H_3PO_4.

into further lines. Proton coupling experiments, MS spectrum as well as a complex ^{1}H NMR spectrum allows unambiguous assignment of the structure. The ^{31}P NMR proton-decoupled and −coupled spectra of compound **10** are shown in Fig. 3 (a).

The spectra of the tri-bridged derivatives **14a-c**, as expected, of the A_6 type, showing only a sharp single peak because of the chemical environment equivalence of all the phosphorus nuclei [≡P(NH)Cl], similar to the literature [45,51,55,62−65].

Double-bridged compounds (**13a-c**) contain ≡PCl_2 and ≡P(HNR)Cl moieties as well and they give rise to and AB_2 spin systems on proton decoupled ^{31}P NMR spectra with very close ≡PCl_2 and ≡P(HNR)Cl chemical shifts. Therefore, chemical shift values were observed at 22.98 ppm for the ≡PCl_2 groups and at 22.31 ppm for the ≡P(HNR)Cl groups for compound (**13a**). Its known that there are two configurationally isomers of double-bridged derivatives for diamino- and diol-substituted cyclophosphazenes [20,24,28]. It is expected that cyclotriphosphazene rings may exist in either *syn* or *anti*-configurations. Indicating that one has a center of symmetry and the other has plane of symmetry, which form with equal probability as diastereo isomers. In studies with diols, both syn and anti-configurational isomers of the double-bridged derivatives were synthesized and characterized separately [52].

It is known that optical activity refers to whether or not a compound has optical isomer. In our double-bridged compounds, there are two configuration isomers, in particular for diamino bridged cyclophosphazene derivatives (13a-c), i.e., there are two different meso forms, one having a center of symmetry and the other having a plane of symmetry with equal probability as diastereoisomer mixtures (this is called syn and anti diastereoisomers). Since diastereoisomers are existing in syn and anti-configuration, these molecules do not have symmetrical centers and can therefore be called chiral. In addition, since they do not have symmetrical centers, we can conclude that this molecule has optical isomers. If there is a plane of symmetry, then no optical isomers exist. On the other hand, if there is no plane of symmetry, the coordinate compound has optical isomers. Furthermore, if there is a plane of symmetry around the central atom, that molecule is called achiral, but if there is no plane of symmetry around the central molecule, that molecule then has a chiral center. However, the ^{31}P NMR spectra of the isolated product (**13a**) do not show two sets of closely-spaced signals of equal intensity. The configurations of these compounds can only be determined by the X-ray crystallographic measurements. The ^{31}P NMR proton-decoupled spectrum of compound **13a** is illustrated in Fig. 3 (b).

3.3. ^{1}H NMR data

The ^{1}H spectra of difunctional primary amine substituted cyclophosphazene derivatives reveal valuable information regarding the positional and geometric disposition of the substituents. The single- (**12a-d**), double- (**13a-c**) and tri-bridged (**14a-c**) derivatives show remarkable similarity in chemical shifts of HNC$\underline{H}_2$ and HNCC$\underline{H}_2$ protons. The shielding of PNH(C$\underline{H}_2$) protons for the single-bridged derivatives (**12a-d**) greater than for the corresponding spiro-ansa (**10**) and double-bridged (**13a-c**) derivatives.

The mono-ansa (**8a-c**), spiro (**7** and **9**), spiro-ansa (**10**) and open chain (**6**) cylophosphazene derivatives can be readily distinguished by the appearance in their ^{1}H NMR spectra of PNH(C$\underline{H}_2$-) and PNH(CC$\underline{H}_2$-) respectively. The N−H resonances for compounds (**6**) and (**12a-d**) appear as well resolved doublets and the coupling to phosphorus ^{2}J(P−H) can be measured. For mono ansa (**8a-c**), spiro-ansa (**10**), double- (**13a-c**) and tri-bridged (**14a-c**)

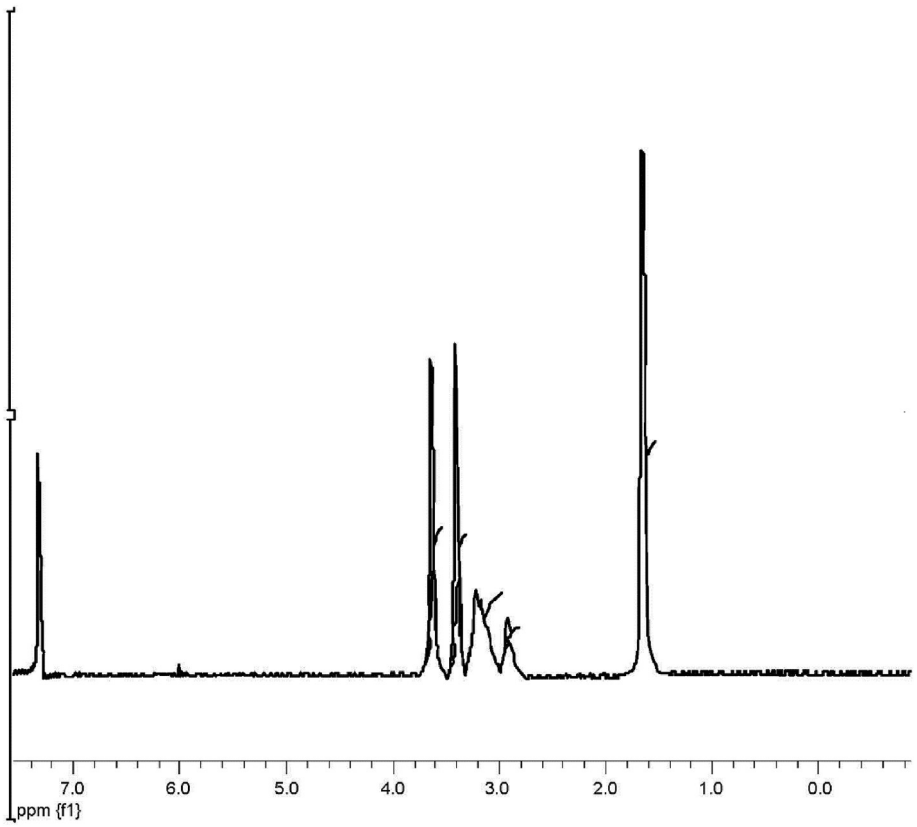

Fig. 4. ^{1}H NMR spectrum of compound (**6**), at room temperature, in $CDCl_3$ (TMS as internal reference) and at 399.95 MHz.

Table 5
Selected FT-IR vibrations of cylotriphosphazene derivatives; 6, 10, 12a, 13a and 14a (cm^{-1}).

Compound	ν(N–H)stretch	ν(C–H)aliph.	ν(N–H)bend	ν(CH_2)bend	ν(P–N)
6	3259 br	2925–2954 s	1567 m	1445 s	1196 vs
10	3233 br	2919-2852 vs	1565 m	1463 m	1189 s
12a	3245 br	2919-2850 vs	1568 m	1436 m	1191 s
13a	3259 br	2918-2853 vs	1565 m	1467 m	1190 m
14a	3249 br	2921-2849 vs	1561 m	1466 m	1192 m

Footnote: br, broad; s, strong; vs, very strong; m, medium.

aminocyclophosphazenes, the PHNC$\underline{H}_2$ and N–$\underline{H}$ resonances invariably appear as unresolved humps and the coupling to phosphorus nuclei cannot be measured. Intense virtual coupling is observed in the spectra of compounds (**9**) and (**11**) for PHNC$\underline{H}_2$ signals as anticipated from the closeness of the ^{31}P chemical shifts. As indicated in earlier works, alkane dioxyphosphazene derivatives can also show virtual coupling effect [66–69]. The bis and tri-spiro derivatives show multiplicities arising from virtual coupling to two, respectively three, phosphorus nuclei.

The mono-ansa (**8a-c**) and spiro-ansa (**10**) derivatives give rise to very complex ^1H NMR spectra. Especially for the spiro-ansa compound (**10**) a detailed consideration of the ^1H NMR spectrum was not possible due to the complexity of the PH(NC$\underline{H}_2$) and PNH(CC$\underline{H}_2$-) protons of the spiro and ansa groups. That may be attributed to the coalescence of large number of lines and because of the closeness of the chemical shifts [(in the spiro part of the spiro-ansa compound the *α-methylene* protons as well in the *β-methylene* protons are non-equivalent as the group above and below the phosphazene ring are in different chemical environment, those above the ring seeing the ansa group, those below the chlorine atoms. However, within each methylene group the two protons are equivalent. By contrast, in the ansa moiety and in the mono-ansa compounds (**8a-c**), the two α-methylene groups are equivalent. The same applies to the *β-methylene* groups, but all the methylene groups *α-*, *β-* and *γ-methylene* protons have non-equivalent protons (*but the two methylene protons within each methylene group are non-equivalent as one faces towards, the other away from, the N_3P_3 ring*). Therefore, it is difficult to make an assignment between the signals of the specific protons in the spiro and ansa rings. Selected chemical shift values and $^3J(PH)$ are presented in Table 4. ^1H NMR spectrum of open chain (**6**) derivative is shown in Fig. 4.

3.4. FT-IR spectral analysis

FT-IR spectra were recorded in PerkinElmer BX II FT model spectrometer with a number of scans at 4 cm^{-1} resolution in the range 4000-350 cm^{-1}. FT-IR spectra of cyclic and polyphosphazenes have two characteristic vibrations, P–N–P asymmetric vibration and P–N–P symmetric stress. These vibrations occur at 1200-1400 cm^{-1} and 700-950 cm^{-1} respectively. The region with the P–N–P symmetrical stress is 885 cm^{-1} for the trimer, 895 cm^{-1} for the tetramer and 750 cm^{-1} for the high polymers. Electronegativity of the ligand that is bound to cyclophosphazene affects the places of stress and bending vibrations. The characteristic P–N vibration frequency increases with the electronegativity of the ligands. The alkylamino groups have steric effect in the P–N strain. Amino and methyl amino substituents as expected give FT-IR peaks at low P–N frequencies (as they are electropositive). It is observed that long-chain primary amino substituents also cause a slight increase in vibration frequencies. In the spectra of the compounds we synthesized, the vibrations of the substituted groups were observed with the characteristic P=N and P–Cl vibrations. Shifts in these vibrations were evaluated according to the free trimer compound. P–Cl vibrations were not observed in the fully substituted product (**11**). P=N vibrations were observed at 1213 cm $^{-1}$ in free trimer compound. As the number of P=N groups in the ring increases, the vibrations shift to higher frequencies. This value is up to 1310 cm^{-1} in polymers. The P=N vibration peaks of the free trimer compound at 1214 cm^{-1} were not observed in the synthesized compounds (**6**–**14a-c**). These results show that the trimer is substituted with 1,3-propane-, 1,5-pentane-, 1,6-hexane- and 1,8-octane-diamines. From the derived compounds (**6**–**14c**), the peaks of P=N vibrations ranged from 1230 to 1275 (m) cm^{-1}. The characteristic P=N stress vibration of the obtained phosphazene compounds are decreased to about 30–55 cm^{-1} compared to the P=N frequencies of the free trimer (**1**). For compounds (**6**–**14c**), $^{\nu}$(N–H) vibrations are between 3169 and 3380 (m) cm^{-1}; $^{\nu}$(C=C), 1596–1610 (s) cm^{-1}; $^{\nu}$(C–N aliphat.) 1385–1420 (m) cm^{-1} respectively. The observed characteristic peaks of the IR spectra are listed in Table 5.

According to this schedule, the peaks of the functional groups confirm the proposed structures. The reason of the observed $=PCl_2$ symmetric and asymmetric stress vibrations in compounds **6, 10** and **12a-14a**, which was not observed at all in compound **11**, and partially observed in compounds **6, 10** and **12a-14a**, indicating the displacements of chlorine atoms in the structures.

4. Conclusion

In addition to those previously reported [51,60–65], a number of new cyclophosphazene derivatives (**6**, **8a**, **10**, **12a-14a**) have also been synthesized and all the derived compounds were fully identified by standard spectroscopic techniques. It can be concluded that the synthesized aminocyclophosphazene compounds (**13a-14c**) might be suitable for the preparation of new liquid crystalline materials and these findings (with better solubility in biological fluid and less toxicity) will also provide important preliminary data for the suitable drug pipeline for further pharmacological testing.

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Appendix A. Supplementary data

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