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Design and Synthesis of A Novel N-Substituted Aminoalcohol Derivative with Hexachlorocyclotriphosphazene

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Abstract

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, are cyclical and give substitution reactions with amines, alcohols, etc., nucleophiles. Nucleophilic substitution reactions of cyclotriphosphazene with bifunctional nucleophiles such as diols, diamines and aminoalcohols have been a subject of intense study over decades. Due to the stable P=N bond in phosphazenes, phosphazene derivatives can have properties such as resistance to heat, radiation, combustion, reducing and oxidizing substances. Cyclophosphazene derivatives usually have biological compatibility and degrade into non-toxic small molecules, thus are advantageous to biological activities and DNA interactions. For this reason, the properties of cyclic phosphazene compounds, anticarcinogenic, antibacterial and DNA interactions are currently studied topics. Also, Raman spectroscopy is widely used to obtain chemical information about the interaction of intramolecular bonds of newly synthesized compounds and drugs, the effects of these compounds on the cell, and understanding their mechanisms. In this study, the changes in molecular interactions of cyclophosphazene derivatives were investigated by Raman spectroscopy.

The condensation reactions of N/O donor type bifunctional N-substituted aminoalcohols with hexachlorocyclotriphosphazene were investigated and the spiro-cyclic tetrachlorocyclotriphosphazene derivatives were prepared. Elemental analyses, ESI-MS, FT-Raman, FTIR and NMR spectroscopy techniques were employed to characterize all of the compounds.

Key Words

"Cyclophosphazenes, Spiro-phosphazenes, N-substituted aminoalcohols."

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1. Introduction

Cyclophosphazenes containing a ($N=PX_2$) repeated unit are known as inorganic heterocyclic rings. The first two heterocyclic compounds of this composition, $N_3P_3Cl_6$ and $N_4P_4Cl_8$, were isolated by reaction of PCl_5 with NH_4Cl (Gladstone & Holmes, 1864; Rose, 1834). Interest in the chemistry of these compounds has continued for many years, as there are a variety of applications. Cyclophosphazene derivatives generally have beneficial effects on biological processes and DNA interactions (Asmafiliz et al., 2009; Işıklan et al., 2010) because they decompose into non-toxic small molecules. In terms of ionic liquids (Omotowa et al., 2004),, liquid crystals (Jiménez et al., 2011), flame retardants (Shin et al., 2010), and especially spirocyclic triphosphazene derivatives, that can form inclusion bonds with both organic and inorganic molecules (Allcock et al., 1981; Reynes et al., 2011), cyclophosphazene derivatives are also of great interest.

Nucleophilic substitution reactions of cyclotriphosphazene with bifunctional nucleophiles such as diols, diamines and aminoalcohols have been the subject of intense investigation for decades (Okumuş et al., 2017; Tümer et al., 2015). It has been observed that $N_3P_3Cl_6$ and bifunctional reagents give spiro-, ansa-, bino- and open-chain (vibrational) products in the reactions. There is limited research on the reactions between $N_3P_3Cl_6$ and N-substituted amino alcohols (Begeç, 2022; Beşli et al., 2007; Chandrasekhar et al., 1984; Coles et al., 2004; Eçik et al., 2012; Işıklan, Sayın, et al., 2016; Işıklan et al., 2013a, 2013b; Işıklan, Yıldırım, et al., 2016). Microwave-assisted synthesis is a new concept in the synthetic chemistry. Several organic reactions have been successfully carried out using this technique. In contrast to conventional methot, microwave-assisted synthesis has been shown to drastically reduce reaction times and increase overall yields. Our previous work was the first to report a study comparing conventional and microwave irradiation methods for nucleophilic substitution reactions of cyclotriphosphazene derivatives (Işıklan et al., 2010). In this work, it was demonstrated that the microwave irradiation method for the synthesis of fully substituted cyclotriphosphazenes is a more powerful technique for improving the yields and shortening reaction times than conventional methods.

Raman spectroscopy is one of the most important techniques for determining the structures of compounds in a wide range of samples, from crystals to biological tissues, from aqueous solutions to protein structures. Infrared spectroscopy (IR) and Raman spectroscopy are similar analytical techniques. Raman, on the other hand, monitors the vibrational change of bonds in a group while IR monitors the atoms of a functional group in both stretching and vibrational modes. For a given specific chemical or functional group, the IR peak frequency and Raman frequency shift are identical. The Raman expression depends on the polarizability of a group. This is the speed at which a group moves in an electric field. The most important determinant of this variable is the ease with which electrons move in the bond creating a temporary dipole. The polarizability is also high when there is a high electron concentration in a bond and a dense group or molecule. Therefore, Raman is generally more sensitive to the molecular framework of a stain rather than a specific functional group as at IR. Raman spectroscopy allows us to obtain information about inorganic and organic compounds. Raman is also very useful in identifying functional groups and fingerprints of organic molecules. Raman vibrations are very important for the determination of functional groups, because the vibrations occur in molecules as a whole rather than, not in isolated molecules.

In the present work, we report new spiro-tetrachlorocyclotriphosphazene derivatives (1-4) (Figure 1) synthesized by the reaction of hexachlorocyclotriphosphazene with N-substituted amino alcohols in THF at 25^{o}C. The new spiro-tetrachlorocyclotriphosphazene derivatives were fully characterized by FT-Raman, GC-MS, FTIR and NMR spectroscopy techniques.

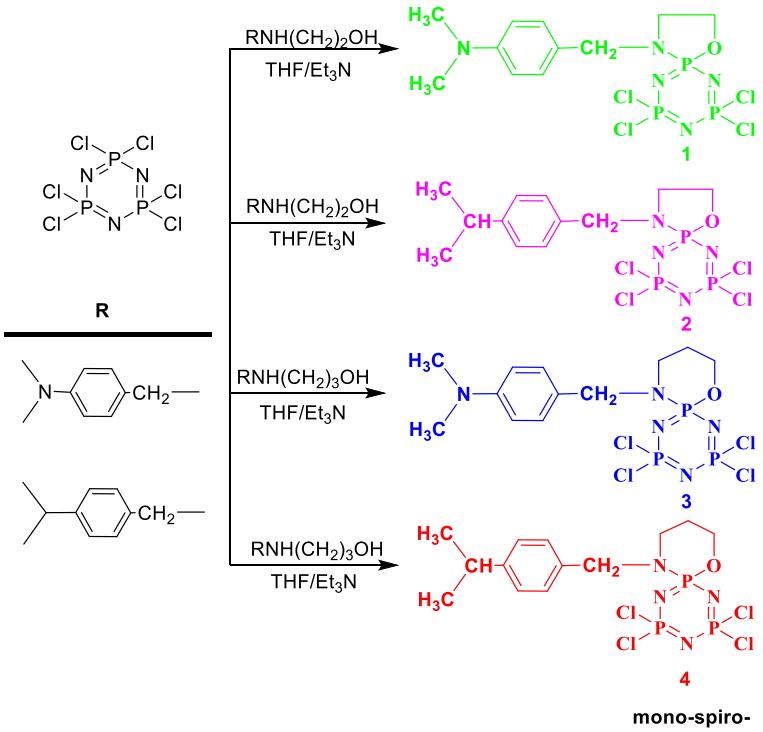

Figure 1. Reactions of Nucleophiles with the $N_3P_3Cl_6$.

2. Method

2.1. Materials

$N_3P_3Cl_6$ (Aldrich), was purified with n-hexane. Ethanolamine, 4-dimethylaminobenzaldehyde and 4-isopropylbenzaldehyde (Sigma-Aldrich) were used commercially. Standard techniques were used to dry and purify the reaction solvents (Perrin et al., 1966). All reactions were chromatographed with silica gel and TLC in different solvents. TLC was used in different solvents to follow all of the reactions. NMR spectra were recorded using a Bruker DPX FT-NMR (500 MHz) spectrometer and IR spectra were recorded using a VERTEX70V FTIR spectrometer equipped with a diamond ATR device. Elemental analyses were performed using the Elementar Microcube instrument. The BRUKER Senterra spectrometer at 732 nm was used to record the RAMAN spectra.

2.2. Preparation of the compounds.

N-substituted amino alcohols were prepared by adapting the method specified in the literature. (Dagan & Lowden, 2003).

2.3. Synthesis of compound 1

Hexachlorocyclotriphosphazene (2.00 g) in THF (125 mL) was dissolved in a 250 mL bottom flask. Then, N-benzyl-4-dimethylylaminoethanol (1.104 g) and triethylamine (5.00 mL) added to medium using a dropping funnel. It was allowed to react for 24 hours at 25oC and in an inert atmosphere. The reaction medium was terminated in a controlled manner by TLC. The precipitated part in the reaction medium was filtered. Solvent of the filtrate was removed with the help of rotary evaporator. The remainder was purified by medium pressure liquid chromatography. The product was then crystallized with n-hexane. The yield, based on hexachlorocyclotriphosphazene,, was 1.28 g (47 %). R_f = 0.75 (Toluene:THF 5:1) and mp: 130.2 °C. MS ESCI+: m/z: calcd 468,93; found 469.86 (M+H+). Anal. Calcd. for $C_{11}H_{16}N_5P_3OCl_4$; C, 28.17; H, 3.44; N, 14.93. Found; C, 28.03; H, 3.474; N, 14.64. FTIR (cm^{-1}): ν 2971(C-H arom.), 2904(C-H aliph.), 1228; 1165 (P=N),1021 (C-O), 920; 965 (P-O), 566; 505(P-Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.37 (s, 6H, NCH_3), 3.28 (m, 2H, NCH_2), 4.08 (d, 2H, $^3J_{PH}$ = 9.5 Hz, $ArCH_2$), 4.36 (m, 2H, OCH_2), 7.26 (d, 2H, Ar-H), 7.20 (d, 2H, Ar-H). ^{13}C NMR: 21.28, 26.04 45.59, 51.05, 129.77,130.06, 133.95, 138.36.

2.4. Synthesis of compound 2

Hexachlorocyclotriphosphazene (2.00 g) in THF (125 mL) was dissolved in a 250 mL bottom flask. Then, N-benzyl-4-isopropylaminoethanol (1.098 g) and triethylamine (5.00 mL) added to medium using a dropping funnel. It was allowed to react for 24 hours at 25oC and in an inert atmosphere. The reaction medium was terminated in a controlled manner by TLC. The precipitated part in the reaction medium was filtered. Solvent of the filtrate was removed with the help of rotary evaporator. The remainder was purified by medium pressure liquid chromatography. The product was then crystallized with n-hexane. The yield, based on hexachlorocyclotriphosphazene, The product was then crystallized with n-hexane. The yield, in terms of hexachlorocyclotriphosphazene, was 1.21 g (45 %). R_f = 0.70 (Toluene:THF 5:1) and mp: 124 °C. MS ESCI+: m/z: calcd 467,93; found 468.86 (M+H+). Anal. Calcd. for $C_{12}H_{17}N_4P_3OCl_4$; C, 30.80; H, 3.66; N, 11.97. Found; C, 30.49; H, 3.47; N, 11.34. FTIR (cm^{-1}): ν 2958 (C-H arom.), 2930(C-H aliph.), 1221; 1172 (P=N),1023 (C-O), 926; 970 (P-O), 570; 514(P-Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.27 (s, 6H, $CHCH_3$), 2.92 (m, 1H, $CHCH_3$), 3.27 (m, 2H, NCH_2), 4.07 (d, 2H, $^3J_{PH}$ = 9.5 Hz, $ArCH_2$), 4.37 (m, 2H, OCH_2), 7.24 (d, 2H, Ar-H), 7.33 (d, 2H, Ar-H). ^{13}C NMR: δ 23.99, 33.83 45.92,47.76, 65.57, 126.80,128.23, 133.43, 148.69.

2.5. Synthesis of compound 3

Hexachlorocyclotriphosphazene (2.00 g) in THF (125 mL) was dissolved in a 250 mL bottom flask. Then, N-benzyl-4-dimetyhlaminopropane (1.196 g) and triethylamine (5.00 mL) added to medium using a dropping funnel. It was allowed to react for 24 hours at 25oC and in an inert atmosphere. The reaction medium was terminated in a controlled manner by TLC. The precipitated part in the reaction medium was filtered. Solvent of the filtrate was removed with the help of rotary evaporator. The remainder was purified by medium pressure liquid chromatography. The product was then crystallized with n-hexane. The yield, based on hexachlorocyclotriphosphazene,, was 1.21 g (45 %). R_f = 0.68 (Toluene:THF 5:1) and mp: 132 °C. MS ESCI$^+$: m/z: calcd 482.94; found 484.12 ($M+H^+$). Anal. Calcd. for $C_{12}H_{18}N_5P_3OCl_4$; C, 29.84; H, 3.76; N, 14.50. Found; C, 29.63; H, 3.74; N, 14.64. FTIR (KBr, cm^{-1}): ν 2958(C-H arom.), 2900(C-H aliph.), 1237; 1176 (P=N),1021 (C-O), 927; 947 (P-O), 583; 516 (P-Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.26 (s, 2H, $ArCH_2$), 3.33 (s, 6H, NCH_3), 3.39 (m, 2H), 4.25 (d, 2H, NCH_2), 4.74 (m, 2H), 7.20 (d, 2H, Ar-H), 7.63 (d, 2H, Ar-H).

2.5. Synthesis of compound 4

Hexachlorocyclotriphosphazene (2.00 g) in THF (125 mL) was dissolved in a 250 mL bottom flask. Then, N-benzyl-4-isopropylaminopropane (1.190 g) and triethylamine (5.00 mL) added to medium using a dropping funnel. It was allowed to react for 24 hours at 25oC and in an inert atmosphere. The reaction medium was terminated in a controlled manner by TLC. The precipitated part in the reaction medium was filtered. Solvent of the filtrate was removed with the help of rotary evaporator. The remainder was purified by medium pressure liquid chromatography. The product was then crystallized with n-hexane. The yield, based on hexachlorocyclotriphosphazene, was 1.21 g (45 %). Rf = 0.65 (Toluene:THF 5:1) and mp: 128 °C. MS ESCI$^+$: m/z: calcd 481,95; found 483.12 ($M+H^+$). Anal. Calcd. for $C_{13}H_{19}N_4P_3OCl_4$; C, 32.39; H, 3.97; N, 11.62. Found; C, 32.03; H, 3.96; N, 11.56. FTIR (KBr, cm^{-1}): ν 2959(C-H arom.), 2900(C-H aliph.), 1223; 1165 (P=N),1041 (C-O), 927; 946 (P-O), 580; 515(P-Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.14 (s, 6H), 1.81 (m, 2H), 2.80 (m, 1H), 2.95 (m, 2H), 3.84 (d, 2H), 4.28 (m, 2H), 7.09 (d, 2H, Ar-H), 7.18 (d, 2H, Ar-H).

3. Results and Discussion

The monospirocyclic cyclotriphosphazene derivatives (**1-4**) were synthesized by conventional methods at room temperature, by reacting N-substituted aminoalcohols and $N_3P_3Cl_6$ in THF. All studies, including NMR, FTIR, FT-RAMAN, and MS data, are in agreement with the proposed calculations for the structures of the compounds.

3.1. FTIR, FT-RAMAN and NMR spectroscopy

In the FTIR spectra of all phosphazenes, stretching bands between 1228 and 1165 cm^{-1} were visible, which were caused by the vP=N bonds in the phosphazene ring. For the partially substituted phosphazenes (**1-4**) asymmetric and symmetric stretching P-Cl absorption peaks occured at 566-505 cm^{-1} and 570-514 cm^{-1}, respectively. While the aliphatic C-H protons exhibited stretching absorption peaks in the range of 2930 cm^{-1}, the Ar-H protons were seen in the range of 2958 cm^{-1}. In addition P-O absorption bands were observed between 970 and 926 cm^{-1}. The FT-IR spectra are shown in Figure 2.

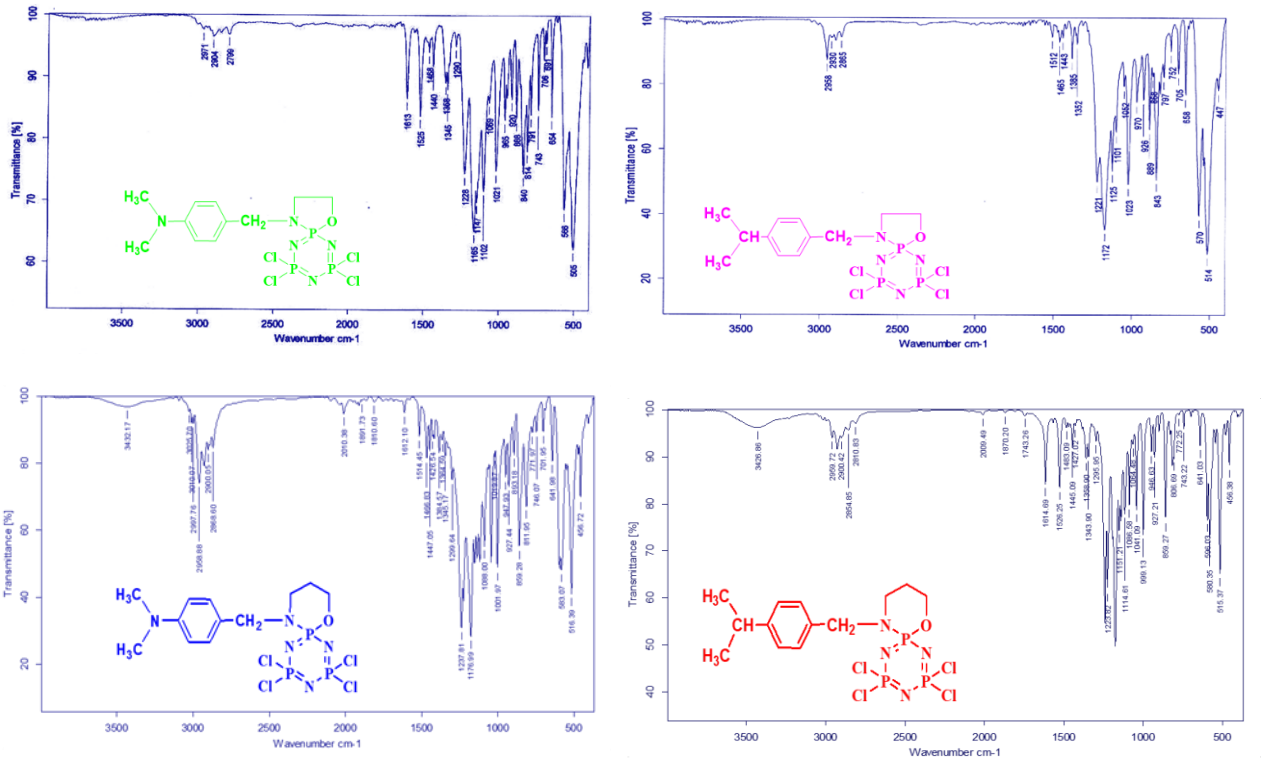

Figure 2. FT-IR spectra of compounds (**1-4**).

In the FT-RAMAN spectra of all phosphazenes, stretching bands between 1215 and 1191 cm^{-1} were caused by the vP=N bonds in the phosphazene ring. For the partially substituted phosphazenes (**1-4**) asymmetric and symmetric stretching P-Cl absorption peaks occurred at 346 cm^{-1} and 688 cm^{-1} respectively. While the aliphatic C-H protons exhibited stretching absorption peaks at a range of 2870-2962 cm^{-1}, the Ar-H protons were seen at a range of 2999-3063 cm^{-1}. In addition, the P-O-C absorption bands were observed between 1613 and 1615 cm^{-1}. The FT-RAMAN spectra are shown in Figure 3.

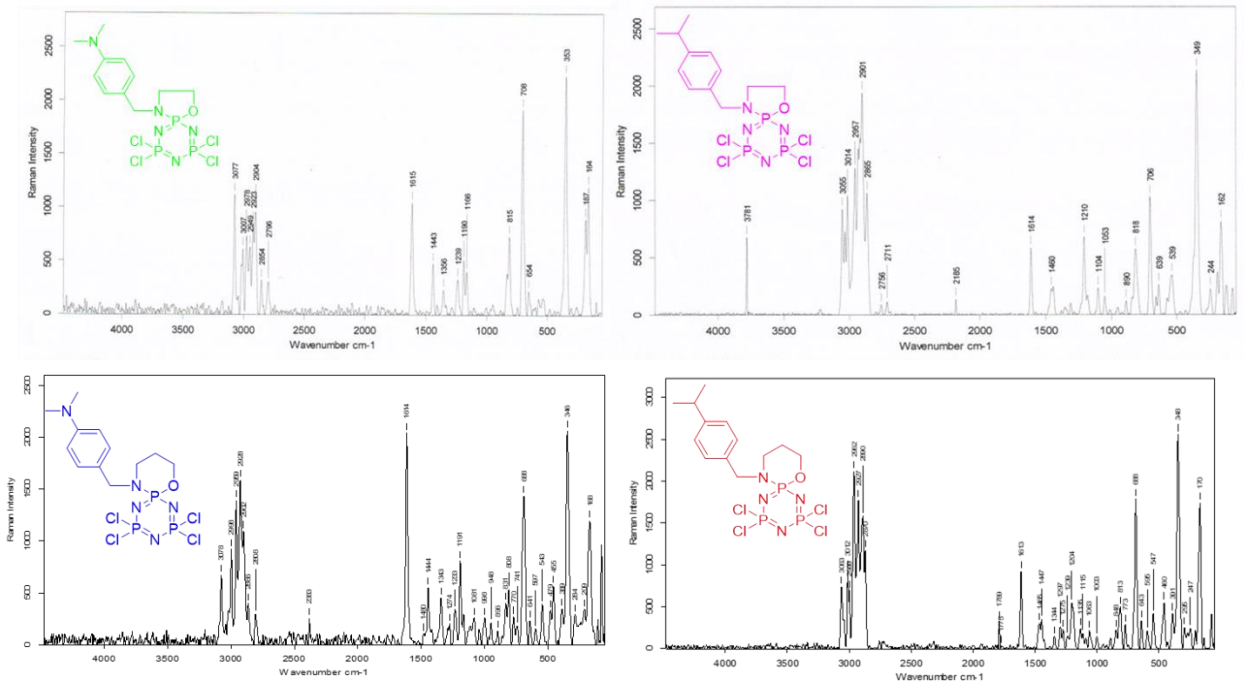

Figure 3. FT-RAMAN spectra of compounds (**1-4**).

Table **1** contains ^{31}P NMR data of phosphazenes. The data show that all phosphazenes have a spiro structure. Compounds **1–4** exhibit typical five-line resonance patterns due to the triplet P atom (spiro) and two additional P atoms of the doublet. In Figure **4** the spin system is referred to as AX_2.

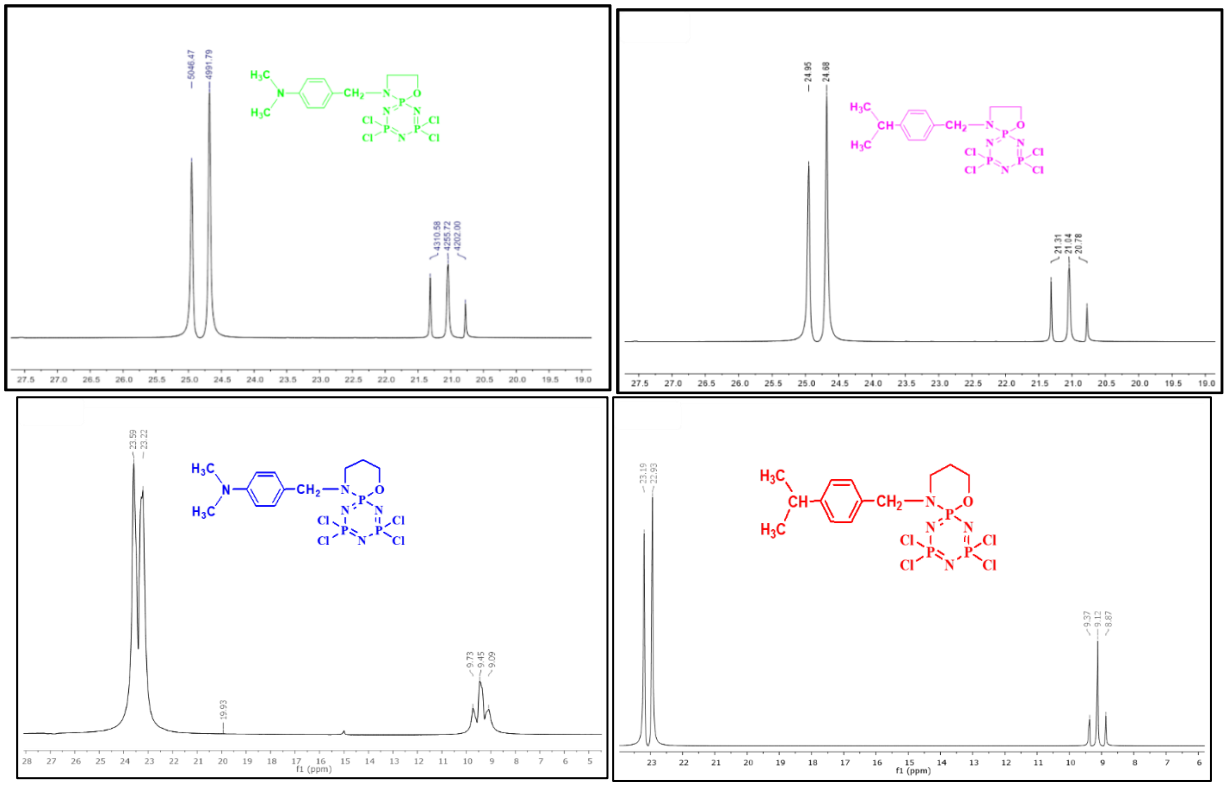

Figure 4. ^{31}P NMR spectra of compound **1-4.** Signals showing AX_2 spin system.

Table 1. ^{31}P NMR parameters

^{31}P NMR chemical shifts (ppm)					
Comp.	Spin System	>PA	>PX_2	X	$^{2}J_{PNP}$ coupling constants(Hz)
1	AX_2	21.27	25.10	Cl	52.4
2	AX_2	21.04	24.95	Cl	55.7
3	AX_2	9.45	23.59	Cl	55.7
4	AX_2	9.12	22.95	Cl	55.7

Information from NMR spectra of phosphazene derivatives was used to determine NMR signals based on chemical shifts, multiplications and binding constants. Protons of Ar-CH_2 protons in benzyl groups were observed in pairs at positions **1-4,** respectively. The structures of the compounds were found to be compatible with the NMR spectra.

Conclusion

The results reported here, in conjunction with previous studies of similar systems, indicate that the reactions of N-substituted aminoalcohols with $N_3P_3Cl_6$ lead to spirocyclotriphosphazenes (**1-4**). Elemental analysis, ESI-MS, FT-Raman, FTIR, and NMR spectroscopic techniques have been used to describe all of these new spirocyclophosphazene derivatives **(1-4).**

Raman spectroscopy is widely used to obtain chemical information about the interaction of intramolecular bonds of newly synthesized compounds and drugs, the effects of these compounds on the cell, and understanding their mechanisms. In this study, the changes in molecular interactions of cyclophosphazene derivatives were investigated by Raman spectroscopy. In addition, the anticarcinogenic, antibacterial and DNA interactions of these compounds are other topics that can be studied. Thus, these properties of compounds the produced can be studied.

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Conflicts of interest

The authors declare no conflicts of interest.

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