Syntheses and characterizations of cyclotriphosphazenes containing a 4-oxy-1-naphthaldehyde group

Hanife İBİŞOĞLU[*], **Esra TANRIVERDİ EÇİK**, **Gönül YENİLMEZ ÇİFTÇİ**[iD]
Department of Chemistry, Faculty of Science, Gebze Technical University, Gebze, Kocaeli, Turkey

Abstract: The nucleophilic substitution reaction of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$, trimer) (**1**) with 4-hydroxy-1-naphthaldehyde (**2**) has been investigated for the first time. $4'$-Oxy-$1'$-naphthaldehyde substituted mono- (**3**), bis- (**4**), and tris- (**5**) cyclotriphosphazenes were obtained from the nucleophilic substitution of compound **1** with **2** in a 1:2 molar ratio in the presence of Cs_2CO_3 in acetone at reflux. The pentakis-(**6**) and hexakis-substituted (**7**) cyclotriphosphazenes were prepared from the reaction of **1** with **2** in a 1:7 molar ratio using K_2CO_3 as a proton abstractor in tetrahydrofuran at room temperature. The structures of the new compounds (**3**–**7**) were determined by elemental analysis, FT-IR, and mass and nuclear magnetic resonance (^{1}H and ^{31}P) spectroscopies.

Key words: Cyclotriphosphazene, 4-hydroxy-1-naphthaldehyde, nuclear magnetic resonance

1. Introduction

$N_3P_3Cl_6$, which is an inorganic heterocyclic ring, has six active P-Cl bonds.[1,2] These chlorine atoms can be easily functionalized by different nucleophile groups, such as organic, inorganic, or organometallic groups. Thus, new cyclotriphosphazene derivatives are synthesized.[3,4] The chemical and physical properties of these compounds can be changed depending on the type and number of the substituted side groups on the phosphorus atoms.[5−7] Therefore, cyclotriphosphazenes have found numerous applications from industrial to medical areas, such as liquid crystallines,[7] fluorescent probes,[3,5] ionic liquids,[8] flame-retardant agents,[9] and anticancer and antimicrobial agents.[1,10]

Several naphthalene derivatives have been reported that possess significant and satisfactory antimicrobial agent properties.[11,12] Moreover, these compounds exhibited antioxidant and cytotoxic activities.[12,13] Furthermore, naphthaldehyde derivatives are often used as a fluorescent chemosensors.[13−15] 4-Hydroxy-1-naphthaldehyde is utilized for preparing antimicrobial 4- and 5-substituted 1-phenylnaphthalenes.[16] In addition, it is also used for the synthesis of Schiff bases, which have interesting keto–enol equilibria.[17,18]

Although nucleophilic substitution reactions of the trimer with $p-$hydroxybenzaldehyde have been investigated in detail,[19−26] to the best of our knowledge there is no report so far about $4'$-oxy-$1'$-naphthaldehyde-substituted phosphazenes.

In the present work, we have reported on the synthesis and characterization of five novel $4'$-oxy-$1'$-naphthaldehyde-substituted cyclotriphosphazenes (**3**–**7**) (Scheme). Furthermore, the reactions of the trimer with

[*]Correspondence: ibisoglu@gtu.edu.tr

4-hydroxy-1-naphthaldehyde were observed to compare the results with those for the reactions of $p-$hydroxybenzaldehyde with **1** studied previously.[19−26]
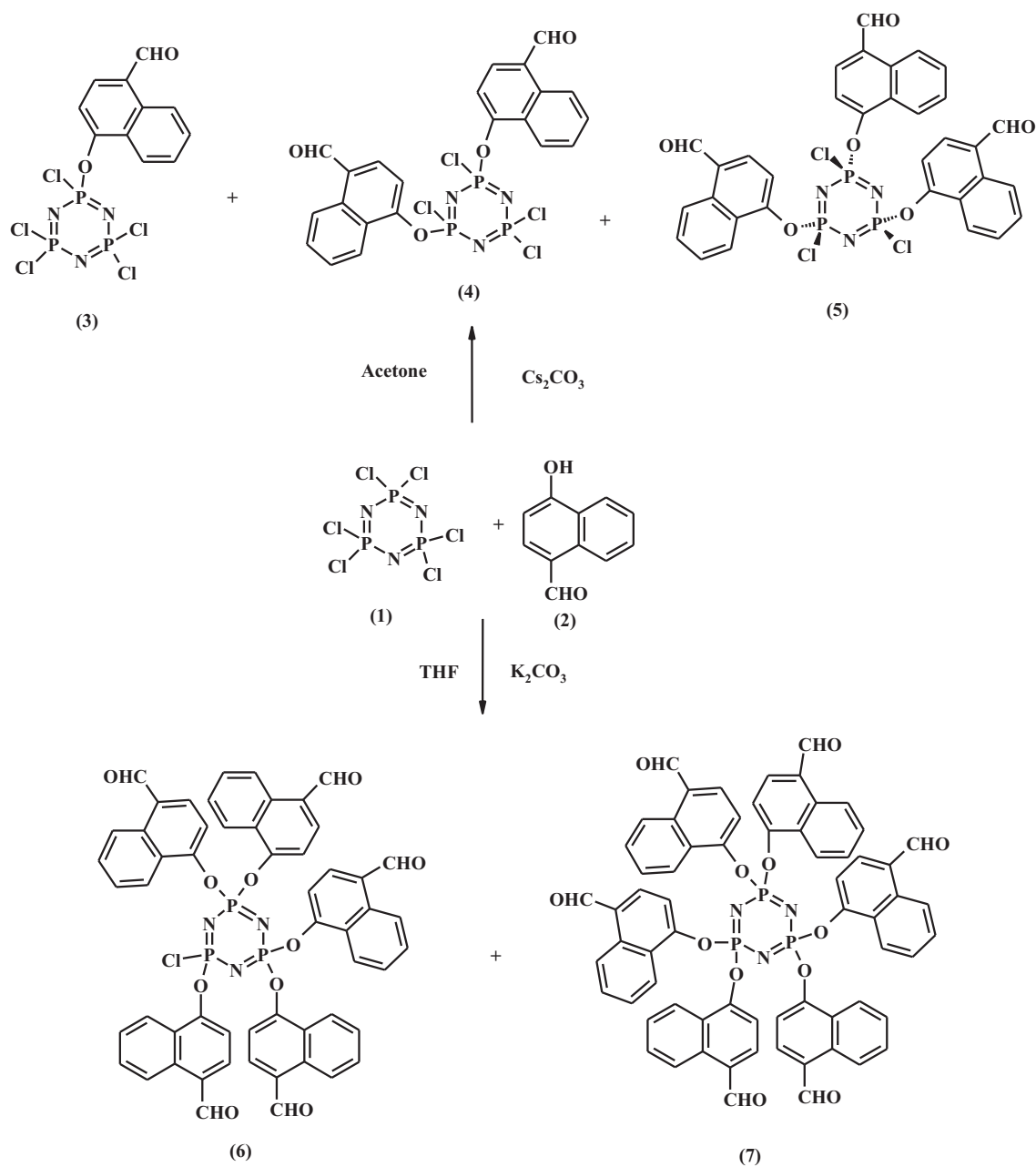
Scheme. The synthetic pathway of compounds **3**–**7**.

2. Results and discussion

2.1. Syntheses of cyclotriphosphazenes (3–7)

There are a large number of studies about the nucleophilic substitution reactions of alcohols and their anions with the trimer.[2,19−27] Generally, these reactions follow the S_{N^2} reaction mechanism and yield nongemi-

nal isomeric derivatives. The product variety of alkoxyphosphazenes depends on reaction conditions such as reaction time, solvent, temperature, and base.[2] In previous work, the reaction of monofunctional reagent $p-$hydroxybenzaldehyde with the trimer yielded the mono-($p-$oxybenzaldehyde)-pentachloro-cyclotriphosphazene, using triethylamine in tetrahydrofuran (THF) at room temperature.[26] Furthermore, the pentakis-($p-$oxy-benzaldehyde)-mono-chlorocyclotriphosphazene was synthesized using K_2CO_3 in the same solvent at room temperature.[24] The reactions of the trimer with the same reagent in the presence of the basic carbonate (Cs_2CO_3 or K_2CO_3) in refluxing acetone gave hexakis (p-oxybenzaldehyde)cyclotriphosphazene.[19,20] The use of Cs_2CO_3 in place of K_2CO_3 was much more efficient and reactions were much faster with this reagent.[19,20,28,29] In addition, the reaction in acetone was formed by unwanted side reactions, presumably owing to a condensation between the CHO and the acetone in the presence of the basic carbonate.[19,20] To avoid these effects, as previously reported,[19,20,23,25] a hexakis derivative was prepared from the same reagents using K_2CO_3 in THF at room temperature.

For comparison with $p-$hydroxybenzaldehyde, we reacted the trimer with **2** using Cs_2CO_3 in refluxing acetone at an approximately 1:2 molar ratio, and partial substituted cyclotriphosphazenes (**3**, **4**, and **5**) were isolated from this reaction. The reaction of **1** with **2** using K_2CO_3 in THF at room temperature at an approximately 1:7 molar ratio also yielded products **6** and **7** (Scheme).

In both cases, and consistent with previous knowledge,[19−26,28,29] the reaction of **1** with **2** in THF at room temperature with K_2CO_3 was slow, whereas it was fast in boiling acetone solution with Cs_2CO_3 as a proton abstractor. By contrast, using Cs_2CO_3 with the p-hydroxybenzaldehyde yielded only hexa(oxybenzaldehyde),[19−23] while 4-hydroxy-1-naphthaldehyde yielded three new compounds (**3**, **4**, and **5**) in this work.

All new compounds (**3–7**) were isolated by column chromatography. In general, all products were obtained in low yields after purification using a silica gel column. The low yield is attributed to the reactivity of the P-Cl bonds in trimer and the tautomeric nature of compound **2**.[30]

2.2. Characterizations of compounds 3–7

Each of the compounds (**3–7**) was characterized by elemental analysis, FT-IR, mass, and nuclear magnetic resonance (NMR) (^{1}H and ^{31}P) spectroscopies. The elemental, mass, and ^{1}H NMR results for each new isolated compound are provided in the synthesis section as a part of the analytical data. All spectroscopic results were in good agreement with the proposed structures, as shown in the Scheme. ^{31}P NMR parameters of synthesized compounds **3–7** are summarized in the Table.

Table. ^{31}P NMR parameters of 4′-oxy-1′-naphthaldehyde-substituted cyclotriphosphazenes (**3–7**).

Compound	Spin system	δ (^{31}P-NMR) [ppm]			$^2J_{(PNP)}$ [Hz]		
		PCl_2 (1)	$PCl(O_2C_{11}H_7)$ (2)	$P(O_2C_{11}H_7)_2$ (3)	1, 2	1, 3	2, 3
3[a]	A_2X	22.4	11.8	-	62.4	-	-
4[a,b]	AX_2; $A'X'_2$	24.9; 24.6	14.8; 15.2	-	66.2; 67.8	-	-
5[a]	A_3	-	17.9	-	-	-	-
6[a]	AX_2	-	20.7	5.5			86.6
7[a]	A_3	-	-	7.33	-	-	-

[a] 202.38 MHz ^{31}P NMR chemical shifts (ppm) in $CDCl_3$ with respect to external 85% H_3PO_4.

[b] *cis*- and *trans*-isomers.

The mass and elemental analysis data of compound **3** indicate that only one chlorine atom on the cyclotriphosphazene ring was replaced with 4′-oxy-1′-naphthaldehyde. The proton-decoupled ^{31}P NMR spectrum of **3** showed an A_2X spin system due to two different phosphorus environments within the molecule (Figure 1a). A doublet for two equivalent PCl_2 groups at approximately $\delta = 22.4$ ppm and a triplet for the $PCl(O_2C_{11}H_7)$ group at approximately $\delta = 11.8$ ppm were observed with $^2J_{PNP}$ of 62.4 Hz.
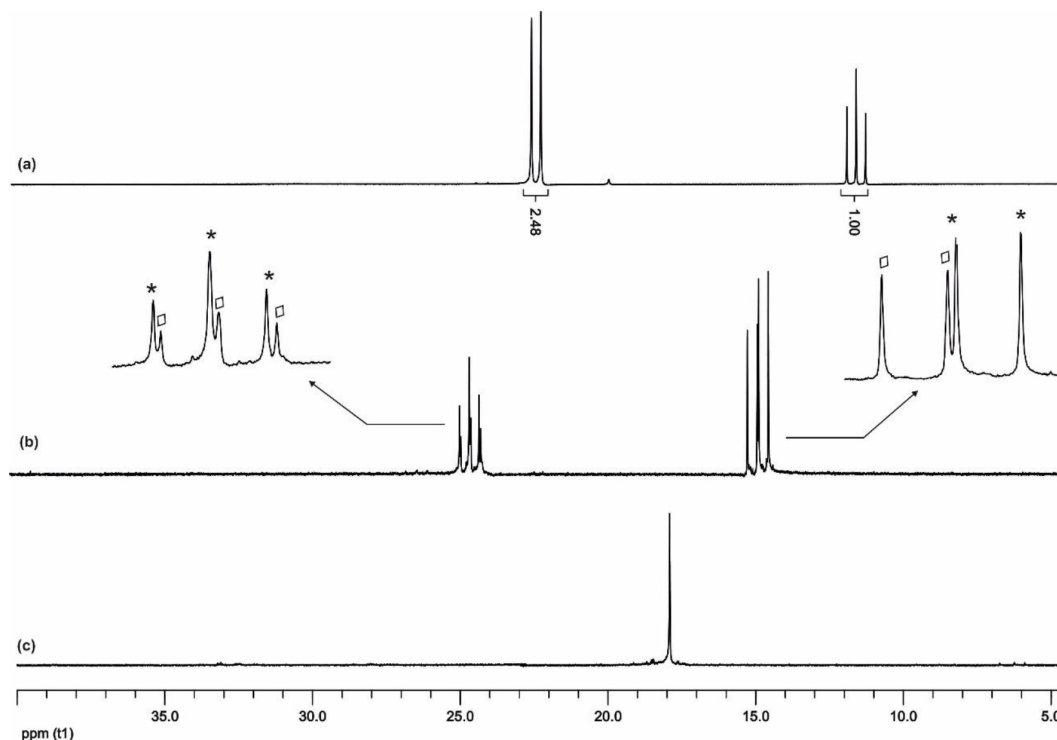

Figure 1. The proton-decoupled ^{31}P NMR spectrum of (a) **3**, (b) **4**, and (c) **5**.

The mass and elemental analyses of compound **4** reveal that two of the chlorine atoms in the trimer were replaced by a 4′-oxy-1′-naphthaldehyde group. The proton-decoupled ^{31}P NMR spectrum (Figure 1b) of the bis-derivative (**4**) showed two unique spin systems (AX_2 and $A'X_2'$ type) having similar chemical shifts ($\delta = 24.9$ and 24.6 ppm for PCl_2 groups; 14.8 and 15.2 ppm for $PCl(O_2C_{11}H_7)$ groups) and similar coupling constants ($^2J_{PNP} = 66.2$ and 67.8 Hz) (Table). It is expected that the bis-substituted nongeminal derivatives correspond to geometrical isomers in which the new substituent is in either a *cis* or a *trans* configuration.[31] Although the formation of *cis* and *trans* isomers was observed in the ^{31}P NMR spectrum, we could not obtain pure isomers by column chromatography. Usually, the coupling constant value of a *trans* isomer is higher than that of a *cis* isomer.[31,32] Using this criterion, an isomer having $^2J_{PNP} = 67.8$ Hz may be assigned to the *trans* isomer. The relative proportion of the isomers (having $^2J_{PNP} = 66.2$ Hz : $^2J_{PNP} = 67.8$ Hz, respectively) was determined as 61:39 from the proton decoupled ^{31}P NMR spectrum of **4**.

The mass and elemental analysis results of compound **5** confirmed that three chlorine atoms on the trimer were substituted by 4′-oxy-1′-naphthaldehyde groups. The ^{31}P NMR spectrum (A_3 spin system) of **5** in Figure 1c shows a sharp singlet at 17.9 ppm and the singlet resonance indicated that **5** was the tris-nongeminal *cis* isomer, as expected.[33]

The mass and elemental analysis data show that penta and hexa chlorine atoms on the cyclotriphosphazene ring were replaced with $4'$-oxy-$1'$-naphthaldehyde for compounds **6** and **7**, respectively. The matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) spectrum of **7** is depicted as an example in Figure 2. The proton-decoupled ^{31}P NMR spectrum of compound **6** exhibited an AX_2 nuclear spin system due to two different phosphorus environments within the molecule (Figure 3a). The doublet for two equivalent $P(O_2C_{11}H_7)_2$ groups at approximately $\delta = 5.5$ ppm and the triplet for the $PCl(O_2C_{11}H_7)$ group at approximately $\delta = 20.7$ ppm were observed with $^2J_{PNP}$ of 86.6 Hz (Table 1), as expected.[8] The proton-decoupled ^{31}P NMR spectrum (A_3 nuclear spin system) of **7** showed a singlet peak (at approximately $\delta = 7.3$ ppm) because of the chemical environment equivalence of all the phosphorus nuclei (Figure 3b).
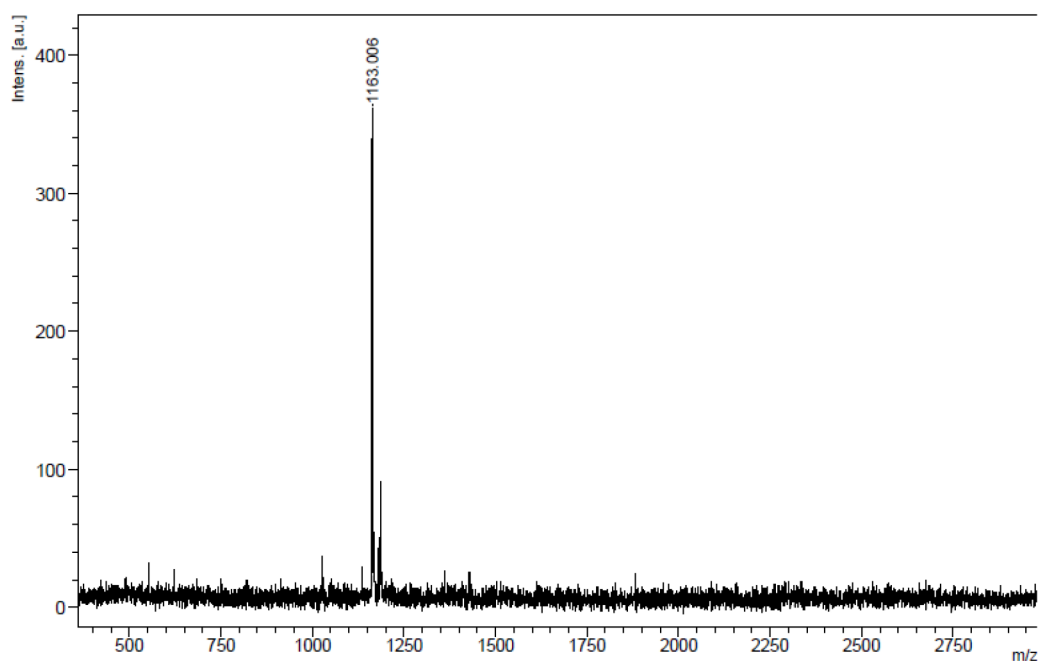

Figure 2. The MALDI-TOF spectrum of compound **7**.

The ^{1}H NMR spectra of all the new compounds (**3**–**7**) showed similarity. The ^{1}H NMR spectrum of **3** is depicted as an example in Figure 4. The aromatic protons were observed between $\delta = 7.3$ and 8.4 ppm. The aldehyde protons for **3**–**7** appeared between $\delta = 10.3$ and 10.4 ppm.

Fourier transform infrared (FT-IR) frequencies of various diagnostic bands for **3**–**7** are also given in experimental section. The P=N stretching vibrations, which were observed between 1141 and 1210 cm^{-1}, are characteristic of cyclophosphazenes. The stretching frequencies of the aldehyde carbonyl groups of **3**–**7** were observed at 1688–1703 cm^{-1}. The stretching vibrations of the aromatic C-H groups were seen at 3037–3060 cm^{-1}.

2.3. Conclusion

Novel $4'$-oxy-$1'$-naphthaldehyde-substituted cyclotriphosphazene derivatives (**3**–**7**) were synthesized from the reactions of trimer with 4-hydroxy-1-naphthaldehyde in the presence of Cs_2CO_3 or K_2CO_3 as a proton abstractor in acetone or THF as solvent in two stoichiometries (1:2 and 1:7) in this work. The identities of
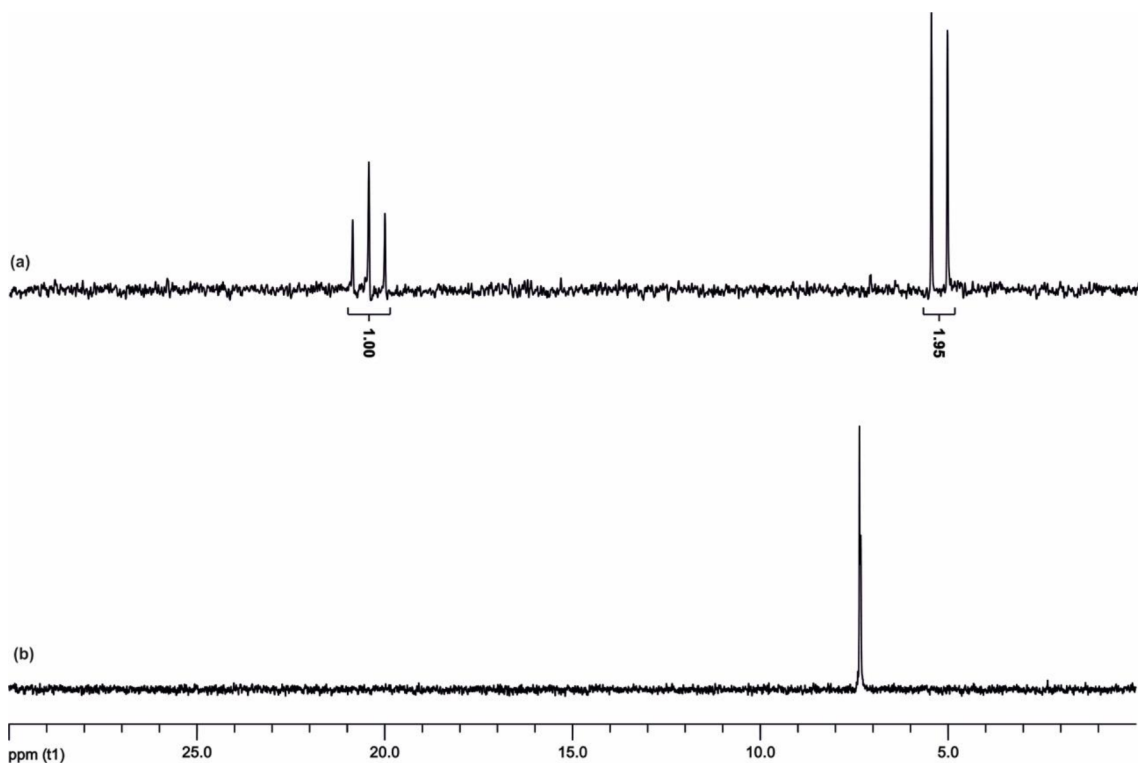
Figure 3. The proton-decoupled ^{31}P NMR spectrum of (a) **6** and (b) **7**.

the newly synthesized compounds were confirmed using elemental analysis, mass, FT-IR, and NMR (^{1}H and ^{31}P) spectroscopies. Compounds **3**–**7** were reported as the first examples of cyclotriphosphazenes containing 4′-oxy-1′-naphthaldehyde groups in the literature. These compounds could be useful as starting compounds or intermediates in the synthesis of mixed substituted derivatives since chiral systems and biological materials show antimicrobial agent behaviors.

3. Experimental

3.1. Materials and methods

$N_3P_3Cl_6$ (Aldrich, St. Louis, MO, USA) was purified by fractional crystallization from n-hexane. The following chemicals were obtained from Merck (Kenilworth, NJ, USA): THF, 4-hydroxy-1-naphthaldehyde, cesium carbonate (Cs_2CO_3), potassium carbonate (K_2CO_3), acetone, n-hexane, and ethyl acetate. Acetone was dried over 3Å molecular sieves. THF was distilled over a sodium-potassium alloy under an argon atmosphere. The solvent ($CDCl_3$) for NMR spectroscopy was also obtained from Merck. All solvents used in this work were purified by conventional methods. The reaction was carried out under an atmosphere of dry argon.

Thin-layer chromatography (TLC) was performed on Merck silica gel plates (Merck 60, 0.25 mm thickness) with an F254 indicator. Column chromatography was performed on silica gel (Merck 60, 0.063–0.200 mm; for 3 g of crude mixture, 120 g of silica gel was used in a column of 3 cm in diameter and 110 cm in length). The melting point was measured with a Gallenkamp apparatus using a capillary tube. Elemental analyses were obtained using a Thermo Finnigan Flash 1112 instrument (Waltham, MA, USA). Infrared spectra were recorded on a PerkinElmer Spectrum 100 Optica FT-IR spectrometer (Waltham, MA, USA). The mass spectra
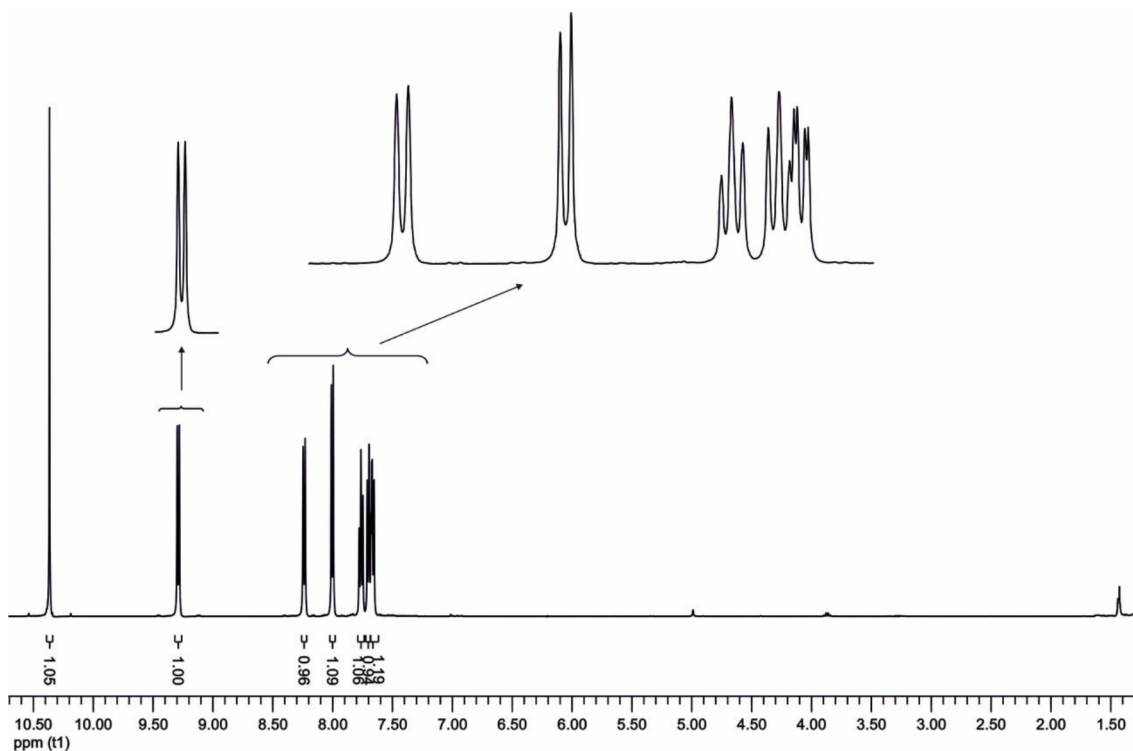
Figure 4. The ^{1}H NMR spectrum of compound **3**.

were recorded on a Bruker MALDI-TOF spectrometer (Rheinstetten, Germany) using DHB (for **3**–**5**) or DIT (for **6** and **7**) as a matrix. The ^{1}H and ^{31}P NMR spectra of compounds 3–**7** in CDCl$_3$ solutions were recorded on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^{1}H NMR and 85% H$_3$PO$_4$ as an external reference for ^{31}P NMR measurements (Palo Alto, CA, USA).

3.2. Syntheses

3.2.1. 2-Mono (4′-oxy-1′-naphthaldehyde)-2,4,4,6,6-pentachlorocyclotriphosphazene (3), 2,2-bis-(4′-oxy-1′-naphthaldehyde)-4,4,6,6-tetrachlorocyclotriphosphazene (4), and 2,2,4-tris-*cis*-(4′-oxy-1′-naphthaldehyde)-4,6,6-trichlorocyclotriphosphazene (5)

A solution of Cs$_2$CO$_3$ (1.875 g, 5.754 mmol) in dry acetone (10 mL) was added dropwise to a stirred solution of trimer (1 g, 2.87 mmol) in dry acetone (20 mL) under an argon atmosphere in a 100-mL three-necked round-bottomed flask. Then 4-hydroxyl-1-naphthaldehyde (**2**) (0.99 g, 5.754 mmol) in dry acetone (10 mL) was added to the stirred solution. The reaction mixture was refluxed in an oil bath, stirring with a magnetic stirrer for 24 h. The reaction was followed on TLC silica gel plates using *n*-hexane:ethyl acetate (4:1) as the eluent. The absence of starting material and the formation of three products was observed. The reaction mixture was allowed to cool to room temperature. Cesium chloride and any other insoluble materials were filtered off and the solvent was removed under reduced pressure at 30 °C. The crude product was isolated by column chromatography with *n*-hexane:ethyl acetate (4:1) as the mobile phase. The first product was 2-mono (4′-oxy-1′-naphthaldehyde)-2,4,4,6,6-pentachlorocyclotriphosphazene (**3**) (0.1 g, 7%), isolated as an oil. Anal. Calc. for N$_3$P$_3$Cl$_5$C$_{11}$H$_7$O$_2$: C, 27.33; H, 1.46; N, 8.69. Found: C, 27.31; H, 1.45; N, 8.65%. FT-IR (ν_{max}

cm^{-1}): 3037, 2980 (ArC-H), 1608, 1578 (ArC=C), 1465 (ArC-C), 1700 (C=O), 1243, 1183 (P=N), 1018 (P-O-C). MALDI-TOF-MS (m/z): [M + H]$^+$, 484.58 (calcd. 483.38). ^{1}H NMR (CDCl$_3$, TMS, 298 K, δ, ppm): 10.23 (s, 1 H, CHO), 9.29 (d, 1H, CH, ^{3}J$_{HH}$ = 8.52 Hz), 8.24 (d, 1 H, CH, ^{3}J$_{HH}$ = 8.40 Hz), 8.00 (d, 1 H, CH, ^{3}J$_{HH}$ = 7.87 Hz), 7.76 (t, 1 H, CH, ^{3}J$_{HH}$ = 7.69 Hz), 7.70 (d, 1 H, CH, ^{3}J$_{HH}$ = 7.59 Hz), 7.66 (1 H, CH, ^{3}J$_{HH}$ = 7.87 Hz).

The 2,2-bis-(4′-oxy-1′-naphthaldehyde)-4,4,6,6-tetrachlorocyclotriphosphazene (**4**) (0.2 g, 11%, oil) was eluted second from the column. Anal. Calc. for N$_3$P$_3$Cl$_4$C$_{22}$H$_{14}$O$_4$: C, 42.68; H, 2.28; N, 6.79. Found: C, 42.66; H, 2.26; N, 6.75%. MALDI-TOF-MS (m/z): [M + H]$^+$, 620.52 (calcd. 619.11). FT-IR (ν_{max} cm^{-1}): 3042, 2980 (ArC-H), 1622, 1575 (ArC=C), 1433 (ArC-C), 1704 (C=O), 1202, 1161 (P=N), 958 (P-O-C). ^{1}H NMR (CDCl$_3$, TMS, 298 K, δ, ppm): 10.40 (s, 2 H, CHO), 9.35–7.65 (m, 12H, Ar-CH).

The third product was 2,2,4-tris-*cis*-(4′-oxy-1′-naphthaldehyde)-4,6,6-trichlorocyclotriphosphazene (**5**) (oil, 0.1 g, 5%). Anal. Calc. for N$_3$P$_3$Cl$_3$C$_{33}$H$_{21}$O$_6$: C, 52.51; H, 2.80; N, 5.57. Found: C, 52.49; H, 2.75; N, 5.53%. MALDI-TOF-MS (m/z): [M + H]$^+$, 755.41 (calcd. 754.83). FT-IR (ν_{max} cm^{-1}): 3060, 2889 (ArC-H), 1622, 1570 (ArC=C), 1455 (ArC-C), 1700 (C=O), 1200, 1168 (P=N), 960 (P-O-C). ^{1}H NMR (CDCl$_3$, TMS, 298 K, δ, ppm): 10.38 (s, 3H, CHO), 9.31–7.35 (m, 18H, Ar-CH).

3.2.2. 2,2,4,4,6-Pentakis (4′-oxy-1′-naphthaldehyde)-6-monochlorocyclotriphosphazene (6) and 2,2,4,4,6,6-hexakis (4′-oxy-1′-naphthaldehyde)cyclotriphosphazene (7)

A solution of K$_2$CO$_3$ (2.33 g, 16.9 mmol) in dry THF (10 mL) was added dropwise to a stirred solution of trimer (0.815 g, 2.35 mmol) in dry THF (20 mL) under an argon atmosphere in a 100-mL three-necked round-bottomed flask. Then 4-hydroxyl-1-naphthaldehyde (2.911, 16.9 mmol) in dry THF (10 mL) was added to the stirred solution. The reaction mixture was stirred at room temperature for 24 h. The reaction was followed on TLC silica gel plates using *n*-hexane:THF (2:1) as the eluent. The absence of starting material and the formation of the two products was observed. Potassium chloride and any other insoluble materials were filtered off and the solvent was removed under reduced pressure at 30 °C. The crude product was isolated by column chromatography with *n*-hexane:THF (2: 1) as the mobile phase. The first product was 2,2,4,4,6-pentakis (4′-oxy-1′-naphthaldehyde)-6-monochlorocyclotriphosphazene (**6**) (oil, 0.1 g, 4%). Anal. Calc. for N$_3$P$_3$ClC$_{55}$H$_{35}$O$_{10}$: C, 64.37; H, 3.44; N, 4.09. Found: C, 64.31; H, 3.35; N, 4.01%. FT-IR (ν_{max} cm^{-1}): 3050, 2851 (ArC-H), 1622, 1572 (ArC=C), 1464 (ArC-C), 1688 (C=O), 1202, 1141 (P=N), 1018 (P-O-C). MALDI-TOF-MS (m/z): [M + 2H]$^+$, 1028.73 (calcd. 1026.28). ^{1}H NMR (CDCl$_3$, TMS, 298 K, δ, ppm): 10.26 (s, 5 H, CHO), 9.43–7.42 (m, 30H, Ar-CH).

The 2,2,4,4,6,6-hexakis (4′-oxy-1′-naphthaldehyde)cyclotriphosphazene (**7**) was the second product (solid, mp >200 °C, 0.3 g, 9%). Anal. Calc. for N$_3$P$_3$C$_{66}$H$_{42}$O$_{12}$: C, 68.22; H, 3.64; N, 3.62. Found: C, 68.17; H, 3.59; N, 3.56%. MALDI-TOF-MS (m/z): [M + H]$^+$, 1163.00 (calcd. 1162.00). FT-IR (ν_{max} cm^{-1}): 3041, 2983 (ArC-H), 1620, 1571 (ArC=C), 1464 (ArC-C), 1703 (C=O), 1210, 1161 (P=N), 1049 (P-O-C). ^{1}H NMR (CDCl$_3$, TMS, 298 K, δ, ppm): 10.13 (s, 6H, CHO), 9.17 (d, 6 H, CH, ^{3}J$_{HH}$ = 8.52 Hz), 7.90 (d, 6 H, CH, ^{3}J$_{HH}$ = 8.30 Hz), 7.66 (t, 6H, CH, ^{3}J$_{HH}$ = 7.48 Hz), 7.39 (d, 6 H, CH, ^{3}J$_{HH}$ = 7.64 Hz), 7.36 (d, 6 H, CH, ^{3}J$_{HH}$ = 8.09 Hz), 7.30 (m, 6H, CH).

Acknowledgment

References

1. Akbaş, H.; Karadağ, A.; Aydın, A.; Destegül, A.; Kılıç, Z. *J. Mol. Liq.* **2017**, *230*, 482-495.

2. Allen, C. W. *Chem. Rev.* **1991**, *91*, 119-135.

3. Şenkuytu, E. *Inorg. Chim Acta* **2018**, *479*, 58-65.

4. Uslu, A.; Özcan, E.; Dural, S.; Yuksel, F. *Polyhedron* **2016**, *117*, 394-403.

5. Tümay, S. O.; Sarıkaya, S. Y.; Yeşilot, S. *J. Lumin.* **2018**, *196*, 126-135.

6. Eçik, E. T.; Şenkuytu, E.; Cebesoy, Z.; Çiftçi, G. Y. *RSC Adv.* **2016**, *6*, 47600-47606.

7. Jimeénez, J.; Callizo, L.; Serrano, J. L.; Barberaé, J.; Oriol, L. *Inorg. Chem.* **2017**, *56*, 7907-7921.

8. Choi, J. A.; Kang, Y.; Kim, D. W. *Electrochim. Acta* **2013**, *89*, 359-364.

9. Dutkiewicz, M.; Przybylak, M.; Januszewski, R.; Maciejewski, H. *Polym. Degrad. Stab.* **2018**, *148*, 10-18.

10. Akbaş, H.; Okumuş, A.; Karadağ, A.; Kılıç, Z.; Hökelek, T.; Koç, L. Y.; Açık, L.; Aydın, B.; Türk, M. *J. Therm. Anal. Calorim.* **2016**, *123*, 1627-1641.

11. Rokade, Y. B.; Sayyed, R. Z. *Rasayan J. Chem.* **2009**, *2*, 972-980.

12. El-Zahara, M. I.; El-Karima, S. S. A.; Anwara, M. M.; Danial, E. M. *Der Pharma Chemica* **2010**, *2*, 118-134.

13. Matsushita, Y.; Jang, I. C.; Takanori, I.; Fukushima, K.; Lee, J. M.; Park, H. R.; Lee, S. C. *J. Wood Sci.* **2011**, *57*, 161-165.

14. Das, A. K.; Goswami S. *Sens. Actuators B* **2017**, *245*, 1062-1125.

15. Vela, M. A.; Fronczek, F. R.; Horn, G. W.; McLaughlin, M. L. *J. Org. Chem.* **1990**, *55*, 2913-2918.

16. Kelley, C.; Lu, S.; Parhi, A.; Kaul, M.; Pilch, D. S.; LaVoie, E. J. *Eur. J. Med. Chem.* **2013**, *60*, 395-409.

17. Deneva, V.; Manolova, Y.; Lubenov, L.; Kuteva, V.; Kamounah, F. S.; Nikolova, R.; Shivachev, B.; Antonov, L. *J. Mol. Struct.* **2013**, *1036*, 267-273.

18. Fabian, W. M. F.; Antonov, L.; Nedeltcheva, D.; Kamounah, F. S.; Taylor, P. J. *J. Phys. Chem. A* **2004**, *108*, 7603-7612.

19. Carriedo, G. A.; Alonso, F. J. G.; Gonzdlez, P. A. *Macromol. Rapid Commun.* **1997**, *18*, 371-377.

20. Carriedo, C. A.; Fernandez-Catuxo, L.; Alonso, F. J. G.; Elipe, P. G.; Gonzalez, P. A.; Sanchez, C. *J. Polym. Sci.* **1996**, *59*, 1879-1885.

21. Albayrak, Ç.; Koşar, B.; Odabaşoğlu, M.; Büyükgüngör, O. *Crystallography Reports* **2010**, *55*, 1203-1206.

22. Launay, N.; Caminade, A. M.; Majoral, J. P. *J. Organomet. Chem.* **1997**, *529*, 51-58.

23. Muhammad, R.; Rekha, P.; Mohanty, P. *RSC Adv.* **2016**, *6*, 17100-17105.

24. Ju, Z.; Ye, Y.; Wang, L.; Liao, X.; Zhao, Y. *Phosphorus Sulfur* **2009**, *184*, 2103-2108.

25. Zhou, L.; Zhang, G.; Li, J.; Feng, Y. *Phosphorus Sulfur* **2016**, *191*, 1194-1198.

26. Chandrasekhar, V.; Athimoolam, A.; Srivatsan, S. G.; Sundaram, P. S.; Verma, S.; Steiner, A.; Zacchini, S.; Butcher, R. *Inorg. Chem.* **2002**, *241*, 5162-5173.

27. Eçik, E. T.; Beşli, S.; Çiftçi, G. Y.; Davies, D. B.; Kılıç, A.; Yuksel, F. *Dalton Trans.* **2012**, *41*, 6715-6725.

28. Carriedo, G. A.; Martínez, J. I. F.; Alonso, F. J. G.; González, E. R.; Soto, A. P. *Eur. J. Inorg. Chem.* **2002**, *2002*, 1502-1510.

29. İbişoğlu, H.; Güzel, A. M. *Polyhedron* **2015**, *100*, 139-145.

30. Manolova, Y.; Kurteva, V.; Antonov, L.; Marciniak, H.; Lochbrunner, S.; Crochet, A.; Fromm, K. M.; Kamounahd F. S.; Hansend P. E. *Phys. Chem. Chem. Phys.* **2015**, *17*, 10238-10249.

31. Beşli, S.; Coles, S. J.; Davies, D. B.; Kılıç, A.; Okutan E.; Shaw, R. A.; Eçik, E. T.; Çiftçi, G. Y. *Dalton Trans.* **2011**, *40*, 4959-4969.

32. Coles, S. J.; Davies, D. B.; Eaton, R. J.; Hursthone, M. B.; Kılıç, A.; Shaw, R. A.; Şahin, Ş.; Uslu, A.; Yeşilot, S. *Inorg. Chem. Comm.* **2004,** *7*, 657-661.

33. Uslu, A.; Kılıç, A.; Güvenaltın, Ş. *Inorg. Chim. Acta* **2010**, *363*, 3721-3726.