Synthesis and Structure Determination of Novel Derivative of Cyclotriphosphazene with Phloroglusine Ligand with Two Protected Position

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ABSTRACT: *In this study we have been involved in the synthesis and characterization studies of a new cyclotriorganophosphazenes complex with protected phloroglusine ligand. Firstly, we synthesized hexachlorocyclotirphosphazene from ammonium chloride and phosphorus pentachloride reaction and then two hydroxyl groups of the phloroglusine ligand were protected with methyl iodide and tosyl chloride. Finally, the deprotonated and protected phloroglusine was reacted as an oxygen-containing ligand with hexachlorocyclotriphosphazene in the ratio of 6:1 in THF as a solvent, All of Cl atoms were substituted with hydroxyl groups of ligand to give a new product. This product identified by a series of spectroscopic techniques including FT-IR, 31P NMR, 13C NMR, 1H NMR and mass spectrometry.*

KEYWORDS: *Hexachlorotriphosphazene; Phloroglusine; Oxygen-containing ligand; Tosyl chloride; Phosphazene.*

INTRODUCTION

The chemistry of polyphosphazenes has played an integral role in the development of inorganic polymer science over the past four decades, due to the inherent tunability of the polymer‘s properties The carbon-free backbone of these inorganic polymers provides a versatile scaffold for widespread materials applications, in areas such as high performance elastomers, polymer electrolytes and biomedical membranes [1-3]. The advance of the phosphorus chemistry began with oxyphosphorus compounds which contain phosphorous- oxygen bonds and are usually called phosphates. Almost all natural phosphorous compounds have P-O bonds. The most

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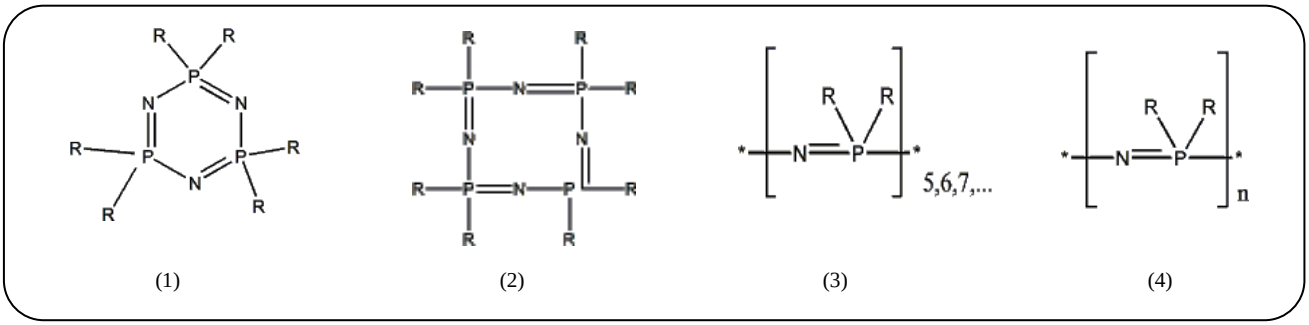

Fig. 1: typical structure of cyclic and polymeric phosphazenes.

important group of these compounds is called organo phosphate esters which contain P-O-C bond are biochemically important. Organic phosphorous compound with P-C bond as well as compounds with P-N bond (Aza phosphorous compounds) are also of great importance in the field of phosphorus compounds chemistry [1]. The analysis of the synthesis mechanism of cyclic and open-chain phosphazenes (phosphonitriles) has received considerable attention. Researches on polymeric and cyclic phosphazenes increased dramatically since 1950s, but works initially began in 19th century. *Lebing & Wehler* applied the reaction of ammonium chloride and phosphorous pentachloride to obtain HCTP in 1834 [2].

General structure of cyclic and polymeric phosphazenes is shown in Fig. 1. They are known as cyclic trimer (1), cyclic tetramer (2), cyclic oligomers with higher numbers (3), and polymers in which n may sometimes be up to 15000. The side group can be selected from halogens, pseudohalogens and organic amines such as alkyl, aryl, alkoxy, aryloxy, mercapto, alkyl amine, or aryl amine. Most trimers and tetramers have similar appearance. They are stable with crystalline solids with physical properties and solubility similar to organic compounds, however, their chemical properties are different depending on the nature of substituent groups, which leads to produce various materials from elastoplastics to thermoplastics [3-7].

In general synthesis methods of phosphazenes are: (1) the reaction of ammonium chloride and phosphorus pentachloride, (2) the reaction of ammonium halids with other halophosphors, (3) synthesis by azide inter mediates, (4) cyclization of linear phosphazenes, (5) dehydrohalogenation of aminochlorophosphorane and (6) chloroamination[8].

The first method is used more frequently. The reaction of ammonium chloride and phosphorus pentachloride occurs in a boiling solvent such as symmetric tetrachloroethane and a mixture of linear and cyclic phosphazenes and HCl (as by product) are produced

$$nNH_4Cl + nPCl_5 \rightarrow (NPCl_2)_n + 4nHCl$$

This reaction is often suitable for the synthesis of chlorophosphazenes, which are raw materials for the preparation of almost all organophosphazenes [9-10]. For lab scale production, approximately equal moles of above compounds must react in boiling tetrachloroethane for about 7.5 h. The solution must be filtered to remove the unreacted ammonium chloride. Cyclic phosphazenes are extracted by petroleum ether or n-heptane subsequently. They are separated by solvent extraction, fractional crystallization, fractional distillation, chromatography and so on. 60-70% of the products are cyclic chlorophosphazenes, which consist of 37% trimer, 28% tetramer and 35% mixture of larger cyclic chlorophosphazenrs. Trimer product, $(NPCl_2)_3$, is a crystalline white solid with melting point of 114°C, which is stable in atmospheric condition and can be sublimated under reduced pressure at 50°C. it is soluble in organic solvent and can be distilled with steam. Properties of the tetramer product with melting point of 124 °C are similar to those of the trimer product. However compared to trimer, its solubility in most solvents is lower. Moreover, the tetramer product is more sensitive to nucleophilic attacks and less resistant to hydrolysis [11-13].

EXPERIMENTAL SECTION

All chemicals were purchased in lab grade from Merck Company. For ^{1}HNMR and ^{13}CNMR spectroscopy samples were dissolved in $CDCl_3$ and TMS was used

Table 1: FTIR data of synthesized HCTP.

Absorbtion band (cm^{-1})	groups
517.20 and 600.29	Stretching PCl_2
874.35, 1184.54 and 1216.76	Absorbtion bands assigned to P=N vibration (ring stretching vibrations)

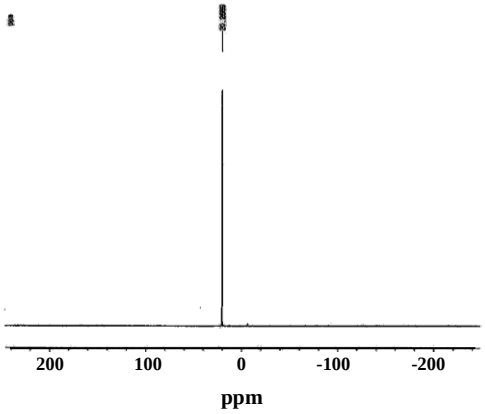

Fig. 2: ^{31}PNMR spectrum of synthesized HCTP.

as reference. For ^{31}PNMR samples were dissolved in $CDCl_3$ and H_3PO_4 (85%) was used as reference. All of these spectra were acquired with a Bruker Avance DPZ-500 spectrometer. The FTIR spectra of the samples were recorded on an IR-Shimadzo 470 in the range of 400-4000 cm^{-1} (sample was prepared by either KBr pellet technique or dissolving in a proper solvent).

Synthesis of HCTP

0.25 mole of PCl_5 and 0.25 mole of ammonium chloride (dry powder) were dissolved in chlorobenzene in a three-neck round bottom flask with a reflux condenser and the mixture was heated to 120 °C and stirred vigorously for 40 h. The HCl gas generated during the reaction was removed. The flask was then cooled and excess ammonium chloride was separated by filtration. The filtered solution was vacuum dried to remove the solvent and obtain a yellowish. Petroleum ether was added to the product and after mixing, the resulting mixture was decanted. The remaining dark portion of the mixture was mixed with petroleum ether again and the clear portion was separated. To the clear solution, concentrated sulfuric acid was added, leading to form two phases which were separated. The ether phase was mixed with sulfuric acid and separated again. Acid and ether phases contained trimer and tetramer, respectively. By evaporating the ether phase solvent white crystals of octachlorocyclotetra-phosphazene with melting point of 120 °C were formed. The acid phase was washed with distillated water and petroleum ether was then added to the washed product. After separating ether and aqueous phases, petroleum ether was added to the lower phases (aqueous) which were then discarded. In ether phase, white crystals were formed after the evaporation of the solvent. Crystals were mixed with absolute ethanol for more purification. The mixture was then filtered. Trimers, which are soluble in ethanol, pass through the filter. Ethanol was removed from the filtered mixture, and white crystals of HCTP with melting point of 112 °C were obtained.

Preparation of protected phloroglusine ligand

20 mL of dry acetone, 3.98×10^{-3} mole of phloroglusine, 3.77×10^{-3} mole of sodium carbonate and 1.98×10^{-3} mole of tosyl chloride were mixed in a round bottom flask and heated at 55 °C for 30 min at reflux. Then 1.98×10^{-3} mole tosyl chloride was added and the reflux was continued for 5 h. To this mixture, 1.5×10^{-2} mole sodium carbonate and 3.96×10^{-3} mole methyl iodide were added and the reflux was continued for 16 h at 55 °C. The solution allowed to be cooled and was subsequently filtered by evaporating the solvent using slow vaporization. A yellow solid was formed.

Addition of the ligand (protected phloroglusine) to HCTP

1.397×10^{-3} mole of the ligand was dissolved in dry THF solvent in a 3-neck round bottom flask. 1.396×10^{-3} mole of sodium carbonate was added to the flask and the solution was mixed at 60 °C for 12 h at reflux. Then 1.746×10^{-4} mole of HCTP was dissolved in dry THF. The resulting solution was added drop wise to the flask and the mixture was mixed at reflux for 2 days and filtered. The solution below the filter evaporated using slow vaporization to yield a reddish yellow solid which decompose to a red solid by heating at 110°C.

RESULTS AND DISCUSSION

FT-IR spectra of synthesized HCTP

Table 1 lists the important adsorption bands of HCTP extracted from FT-IR spectra.

Table 2: FT-IR data of final product.

Absorption band cm^{-1}	assignment
743.30	Phenyl C-H (out-plane vibration)
815.4	CH_3
880.32	Bending vibration of P-N
966.19	Stretching vibration of S-O
1193.21	Sys def. CH_3
1377.76	Stretching vibration of Ph-S
1418.22	Stretching vibration of S=O
1597.92	Stretching vibration of phenyl C=C
2876.41	Stretching vibration of phenyl C-H
2976.17	Stretching vibration of aliphatic C-H

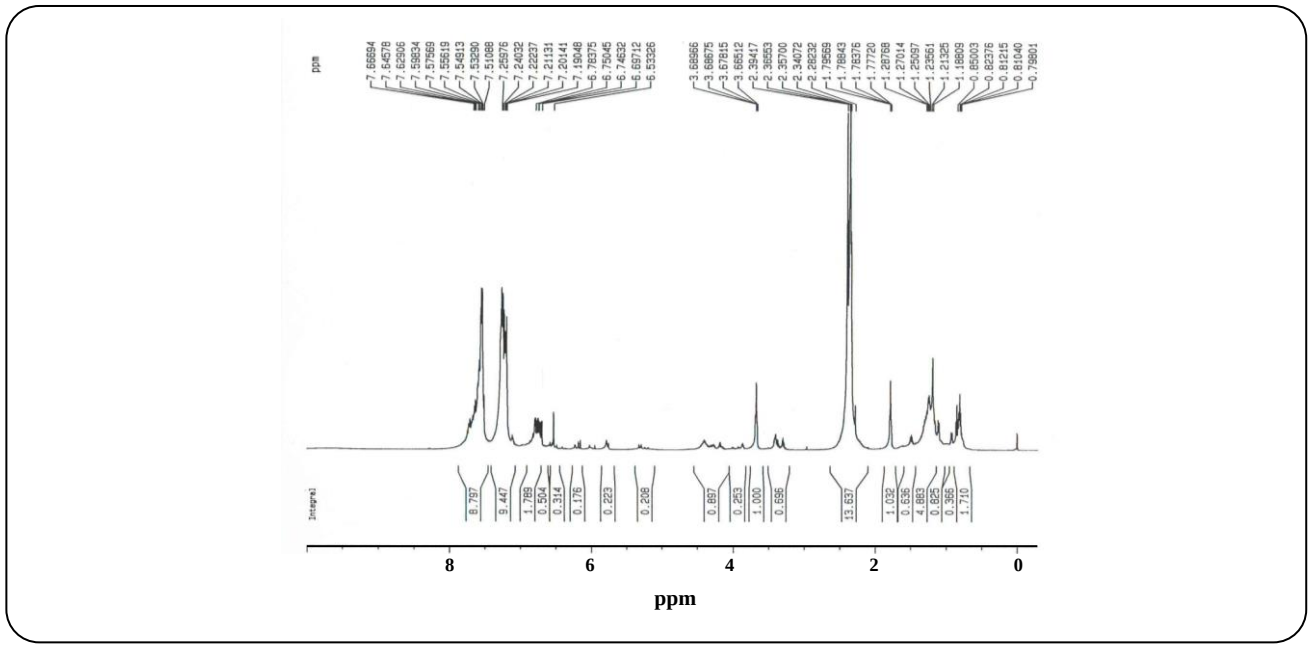

Fig. 3: ^{1}HNMR spectrum of final product.

^{31}PNMR spectrum of synthesized HCTP

A sharp single peak at 20.27 in ^{31}PNMR spectrum of HCTP indicates that all phosphorus atoms in the compound have identical position (Fig. 2). This peak is in accordance with the reference spectrum of HCTP.

Analysis of final product

FT-IR spectrum of final product

Important absorption bands are listed in Table 2. It is noticeable from final product FT-IR that there is no absorption band in the range of 3400-3600 cm^{-1}, indicating the absence of O-H band. Consequently the protection has been successfully accomplished and all ligands are attached to phosphazene ring. In addition, the absorption band assigned to the stretching vibration of the phosphazene ring can be clearly seen at 1179.64 cm^{-1}.

Analysis of ^{1}HNMR spectrum of final product

Peaks in the range of 7.51-7.66 ppm are assigned to hydrogen atoms in phloroglusine ring. These peaks shift towards lower fields because 3 oxygen atoms are attached to the ring. Peak in the range of 7.19-7.25 ppm

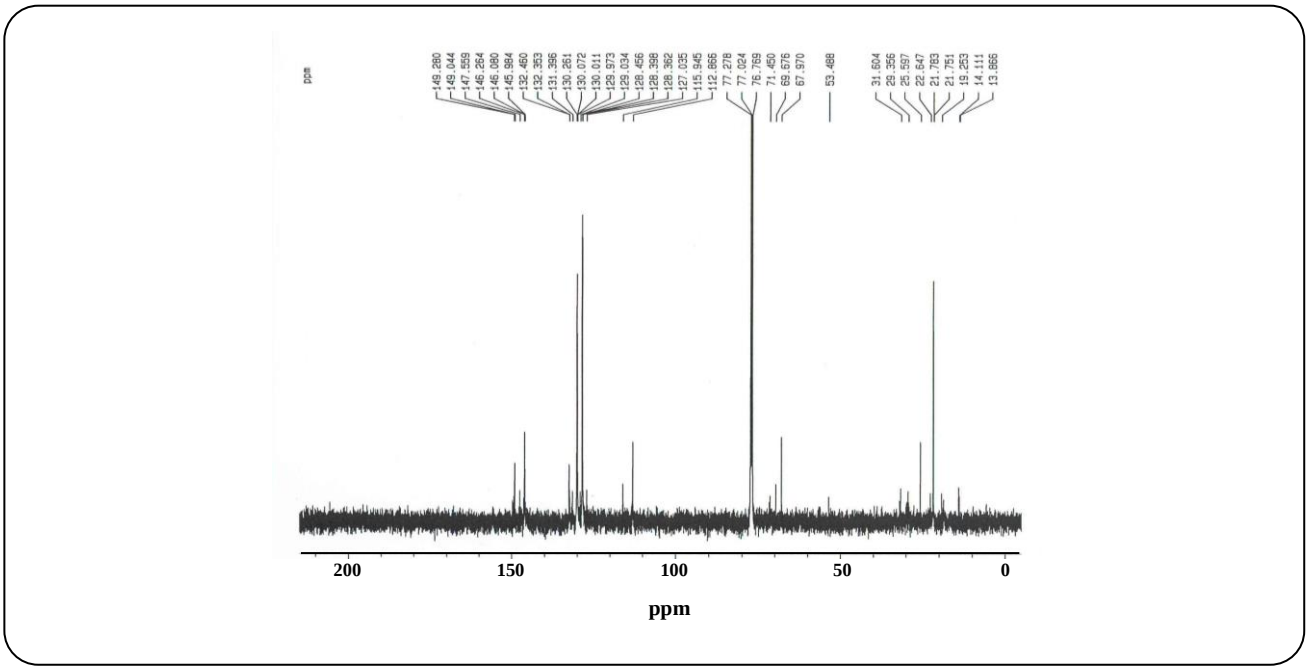

Fig. 4: ^{13}CNMR spectrum of final product.

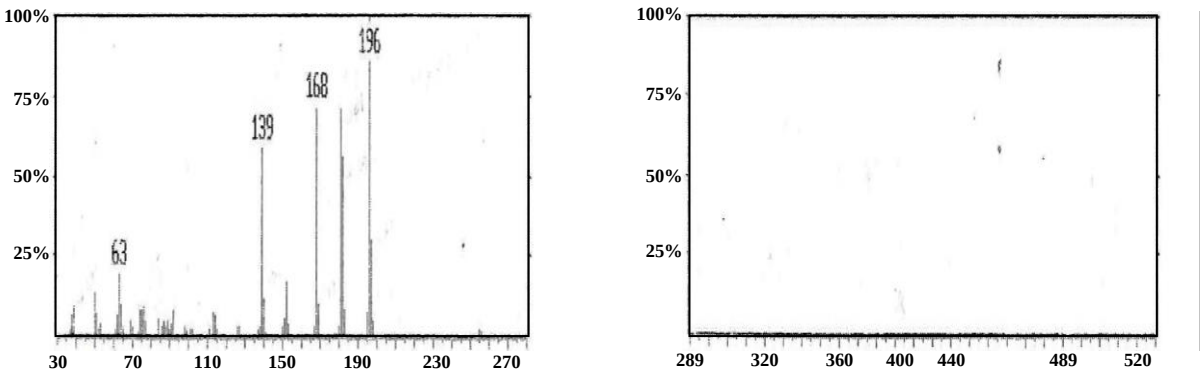

Fig. 5: Mass spectrum of final product.

are assigned to hydrogen atoms in aromatic ring of tosylate group. Since the number of electronegative atoms attached to be aromatic ring is lower than that of phloroglusine ring, peaks shift is lower. Peaks in the range of 2.34-2.39 ppm are assigned to the hydrogen atoms in methyl group attached to the aromatic ring of tosylate group as well as OMe group attached to the aromatic ring of phloroglusine. Peaks in the range of 0-2 ppm are assigned to the THF solution remained in crystalline structure of the product. Moreover, phosphorus atom has a minor effect on splitting due to the long distance from the nearest hydrogen atom (4 bonds) (Fig. 3).

Analysis of ^{13}CNMR of final product

Peaks in the range of 129.97-130.07 ppm are assigned to carbon atoms in aromatic ring of phloroglusine.These peaks shift towards lower fields because of the attachment of three oxygen atoms to the ring. Peaks in the range of 128.36-128.45 ppm are assigned to carbon atoms

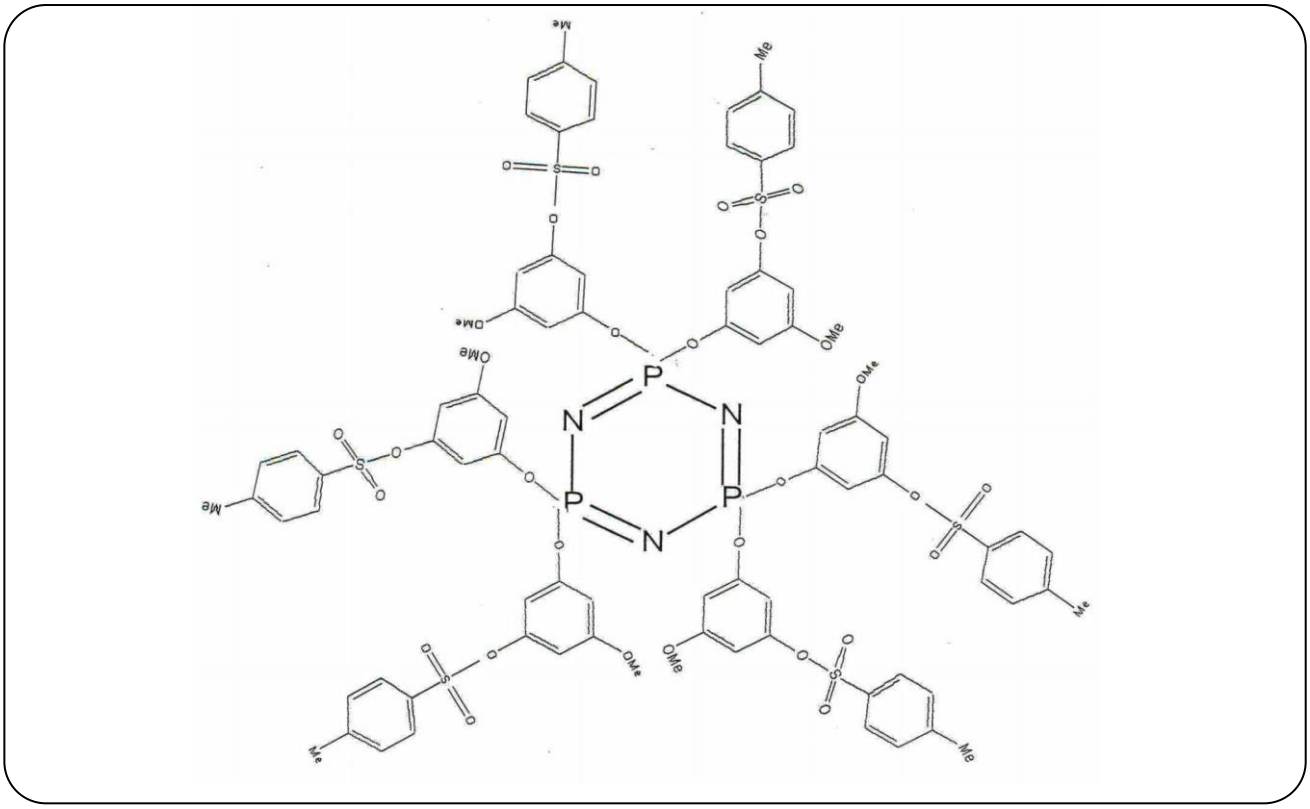

Fig 6: Chemical structure of final product.

in aromatic ring of tosylate group. Three peaks with equal intensity at 77 ppm are assigned to carbon atoms to in $CDCl_3$ solvent. Carbons of OMe group attached the phloroglusine ring create a peak at 67.97 ppm. In addition, carbon atoms in methyl group attached to tosylate ring reflect a peak at 25.97 ppm. The peak around 0 ppm is assigned to the final product. This peak is a relatively sharp single peak, indicating that the oxygen atom in the ligand is attached to phosphorous atom and all chlorine atoms are substituted with the ligand and all phosphorous atoms have identical position (Fig. 4).

Analysis of mass spectrum of final product

The base peak (m/z=91) is assigned to $[C_7H_7]^+$ segment. Other notable peaks (m/z= 123,155,246) are assigned to $[C_{13}H_{10}O_3S]^+$, $[C_7H_7O_2S]^+$ and $[C_6H_3O_3]^+$ segments, respectively(Fig. 5).

CONCLUSIONS

According to the results obtained from various characterization tests, molecular structure shown in Fig. 6 can be proposed for the prepared compound. Analysis of the product implies that the proposed structure includes a symmetric triphosphazene in which all phosphorus and nitrogen atoms have the same position.

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