# Synthesis of a Novel Cyclotriphosphazene by Using Xanthydrol Oxygen Containing Ligand

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**ABSTRACT:** *A new derivative of Cyclotriphosphazene with xanthydrol as the oxygen-containing ligand was synthesized. Firstly Hexaclorocyclotriphosphazene was obtained Hexaclorocyclotriphosphazene from ammonium chloride and phosphorus pentachloride reaction and then the deprotonated xanthydrol was reacted with Hexaclorocyclotriphosphazene in the ratio of 6:1 in dry toluene as the solvent. All of the Cl atoms were substituted with hydroxyl groups of ligand to give a new product with* $(NP\,(C_{14}H_{10}O)_2)_3$ *formula. This product was identified by a series of spectroscopic techniques including FTIR,* $^{31}P$ *NMR,* $^{13}C$ *NMR,* $^{1}H$ *NMR and mass spectroscopy. Analyses were performed to confirm the formation of the designed product and structure.*

**KEYWORDS:** *Hexaclorocyclotriphosphazene; Oxygen containing ligand; Xanthydrol.*

## INTRODUCTION

Over the recent decades, the border between organic and inorganic chemistry has attracted advanced studies, which can also be noted for phosphorous- nitrogen compounds. The study of cyclic and open-chain phosphazenes (phosphonitriles) has been of interest in the field of synthesis and analysis of the mechanism. Synthesis chemistry of most popular cyclic and polymeric phosphazenes is based on the reaction of HCTP (known also as phosphonitric chloride trimer) (Fig.1a) and octachlorocyclotetraphosphazene (OCTP) (Fig.1b).

Over 1000 compounds have been synthesized by these two parent compounds [1]. *Liebig* and *Wöhler* obtained small amounts of HCTP from the reaction of ammonium chloride and phosphorus pentachloride in 1839 [2]. Later *Gerhardt, Laurent, Holmz,* and *Wichhelhaus* determined the molecular weight, composition and thermal behavior of these compounds [3]. Further developments were achieved by applying techniques for the replacement of a halogen in halophosphazene with organic substituents and producing organophosphazenes [4].

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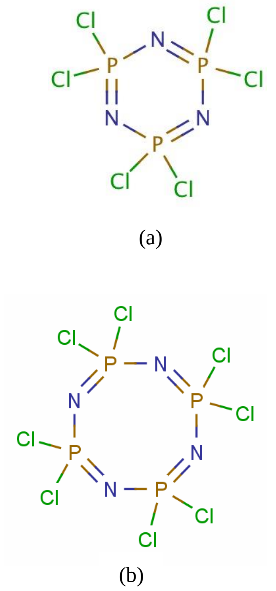

(a)

(b)

***Fig. 1: Molecular structure of HCTP (a) and OCTP (b).***

The structure of these compounds has been carefully analyzed by several characterization tests including X-ray diffraction, vibrational spectroscopy, nuclear magnetic resonance and other physical methods [5]. Previous structural studies are essential for that they provide information to understand the electronic structure of phosphazenes and pseudo aromatic synthesis linked to them [6-9]. Many synthesis studies on the chemistry of phosphazenes have been attractive to develop the chemistry of inorganic polymers [10-15].

In general, synthesis methods of phosphazenes are: (1) the reaction of ammonium chloride and phosphorous pentachloride, (2) the reaction of ammonium halides with other halophosphors, (3) synthesis by azide intermediates, (4) cyclization of linear phosphazenes, (5) dehydrohalogenation of aminochlorophosphorane and (6) chloramination 0[5].

In the reaction of ammonium chloride and phosphorus pentachloride, which is used more frequently than other methods, these compounds react in a boiling solvent such as symmetric tetrachloroethane and a mixture of linear and cyclic phosphazenes and HCl is produced as the product [4].

$$nNH_4Cl + n\,PCl_5 \rightarrow (NPCl)_n + 4n\,HCl$$

This reaction is more applicable for the synthesis of chlorophosphazenes which are used as raw materials to produce almost all organic phosphazenes. P-N ring in cyclic phosphazenes which is either planar or nonplanar, has a negligible effect on the stability of the ring molecules, in contrast with organic aromatic compounds. Most cyclic tetramers and larger compounds are non-planar, except $(NPF_2)_4$ and cyclic $(NPCl_2)_4$. Single bond length of P-N in phosphazenes is typically reported about 1.77 to 1.78 Å, while the bond lengths in cyclic and polymeric phosphazenes are near 1.42 to 1.62 Å. If substituents exist symmetrically around the ring, all P-N bonds lengths will be equal. N-P-N angel, which depends partially on polymerization degree is about 120° in most polymeric or cyclic phosphazenes. Phosphazenes have are applicable in many productions such as glass, ceramic and metal thinner, an additive for lubricants, pesticides and softeners and resin modifiers (resins, prepared from chlorophosphazenes and a polyhydric phenol, as thermally stable coatings, softeners, protective materials, mold making materials and fire proof materials.

## EXPERIMENTAL SECTION

All chemicals were purchased in lab grade from Merck Company. For $^1H$ NMR and $^{13}C$ NMR spectra, samples were dissolved in $CDCl_3$ and TMS that used as reference. For $^{31}P$ NMR samples were dissolved in $CDCl_3$ and $H_3PO_4$ (85%) that used as a reference. All of the spectra were acquired by a Bruker Avance DPZ-500 spectrometer. The FTIR spectra of the sample were recorded by 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 40hr. The HCl gas generated during the reaction was removed. The flask was then cooled and the excess ammonium chloride was separated by filtration. The obtained solution was then vacuum dried to remove the solvent and obtain a yellowish solid. A mixture of cyclophosphazenes consists of trimers, tetramers, pentamers, and of the oligomers. Petroleum ether was added to the product and after mixing, the resulting mixture was decanted. The remaining dark portion

***Table 1: FT-IR data of synthesized HCTP.***

| Absorption bond ($cm^{-1}$) | groups |
|---|---|
| 517.204 and 600.286 | Stretching vibration of $PCl_2$ |
| 874.35, 1184.54 and 1216.76 | Absorption bands assigned to P=N vibration (ring stretch vibrations) |

of the mixture was again mixed with petroleum ether and the clear portion was separated. To the clear solution, concentrated sulfuric acid was added, leading to the formation of 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 solvent of the ether phase, white crystals of octachlorocyclotetraphosphazene with a melting point of 120°C were formed. The acid phase was washed with distilled water and petroleum ether was then added to the washed product. After separating ether and aqueous phases, petroleum ether was added to the lower phase (aqueous) which was 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. The remaining compound above the filter contains tetramers, which are insoluble in ethanol. Trimers, which are soluble in ethanol, pass through the filter. Ethanol is removed from the filtered mixture, and white crystals of HCTP with a melting point of 112°C are obtained.

### *Preparation of xanthydrol ligand*

An ampoule containing 10 wt. % solution of xanthydrol in methanol was broken and after removing the methanol by slow evaporation colorless, needle-like crystals of xanthydrol appeared. In order to deprotonate xanthydrol and use it as a ligand, it must be first dissolved with a stoichiometric amount of sodium in an appropriate solvent (dry THF or toluene) at a specific reflux to convert the aliphatic OH group to ONa.

### *Addition of xanthydrol ligand to HCTP*

A mixture of HCTP in dry toluene solution (1:6 HCTP: toluene) was added dropwise to a flask containing xanthydrol salt. The mixture was stirred vigorously at 100°C, at reflux for 3 days until the NaCl precipitate and get filtered (according to the reference the boiling points of toluene is 111°C and the reflux time is 3 days). The filtered solvent evaporated slowly and to purify the remaining solid, it was washed with petroleum ether, resulting in a milky solid with a melting point of 108°C.

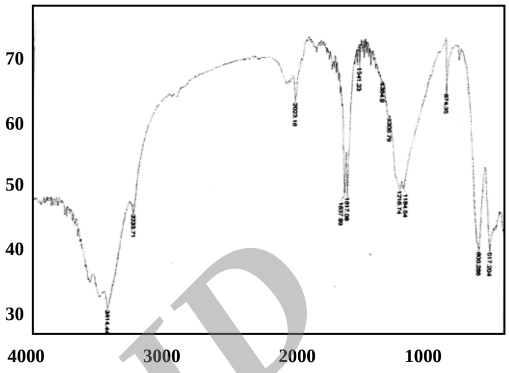

***Fig. 2: FT-IR spectrum of synthesized Hexaclorocyclotriphosphazene (KBr pellet)***

## RESULTS AND DISCUSSION

### *FT-IR spectrum of HCTP*

Important absorption bonds of HCTP are listed in Table 1 and FT-IR spectrum of synthesized Hexaclorocyclotriphosphazene (KBr pellet) is shown in Fig. 2.

### *$^{31}$P NMR spectrum of synthesized HCTP*

$^{31}$P NMR spectrum of HCTP shows a sharp single peak at 20.3 ppm, which is compatible with the reference spectrum, indicating that all phosphorus atoms in the compound are in the same chemical position. $^{31}$P NMR spectrum of synthesized hexaclorocyclotriphosphazene is shown in Fig. 3.

### *The FT-IR spectrum of xanthydrol ligand*

Important absorption bonds of xanthydrol ligands FTIR spectrum are presented in Table 2 and the analysis of FTIR spectrum of xanthydrol is shown in Fig. 4.

### *Analysis of $^{1}$H NMR spectrum of xanthydrol ligand*

Xanthydrol structure consists of two symmetric aromatic rings, which have four hydrogen atoms. Each ring has hydrogen with the same chemical position of the other ring. The structure also contains aliphatic and alcoholic hydrogens. Therefore, there are 6 types of hydrogen,

**Table 2: FT-IR data of xanthydrol ligand.**

| Absorption band, cm-1 | assignment |
|---|---|
| 751.085 | Stretching vibration of Aliphatic C-H bond (phenyl) (out- of- plane vibration) |
| 1258 | The symmetric vibration of C-O-C angle |
| 1337 | Stretching vibration of C-O bond |
| 1458.7 and 1476.41 | Bending vibration of C-H bond |
| 1573.82 | Bending vibration of C=C bond |
| 1605.2 | Stretching vibration of C=C bond |
| 1212.43 | Bending vibration of C-H bond |
| 2916.45 | Stretching vibration of Aliphatic C-H bond |
| 3032.43 | Bending vibration of alcoholic O-H bond |
| 3004.64 | Bending vibration of Phenyl C-H bond |
| 3406.05 | Stretching vibration of alcoholic O-H bond |

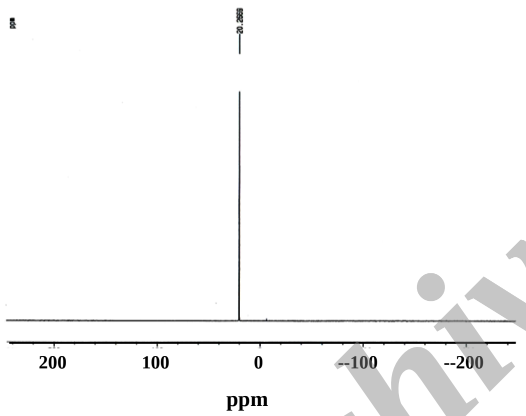

*Fig. 3: 31P NMR spectrum of synthesizad Hexaclorocyclotriphosphazene.*

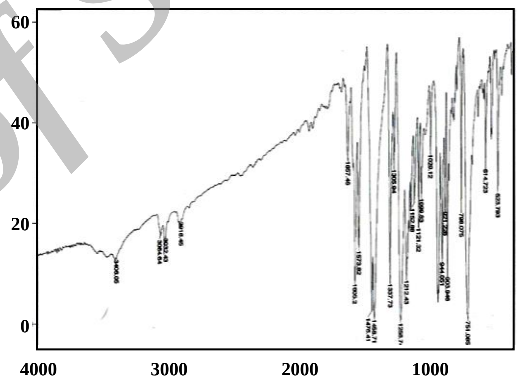

*Fig. 4: FT-IR spectrum of xanthydrol.*

resulting in 6 groups of peaks. $^1$H NMR spectrum of xanthydrol is shown in Fig. 5. There are at least 10 groups of peaks for this xanthydrol sample. Singlet peak at 3.98 ppm is assigned to aliphatic hydrogen adjacent to the alcoholic functional group. Two peaks at 5.7 ppm and near 6.83-8.2 ppm are assigned to OH alcoholic group and aromatic ring hydrogens, respectively. The peak at 8.28 ppm can be assigned to two hydrogens in the ring which has minimum distances.

The tendency towards the lower field due to the high influence of

The electronegative oxygen atom. Singlet peak at 7.27 ppm is assigned to the chloroform in $CDCl_3$

### *Analysis of $^{13}$C NMR spectrum of xanthydrol*

Analysis of $^{13}$C NMR spectrum of xanthydrol is shown in Fig. 6. Xanthydrol contains 13 carbons, which six of them are in the aromatic ring. Therefore, peaks in the range of 116-134 ppm are assigned to aromatic ring carbons. Similar to $^1$H NMR spectrum. The peak at 68.4 ppm can be assigned to the alcohol group.

### *Analysis of FTIR spectrum of the final product*

Important absorption bonds obtained from FT-IR spectrum are listed in Table 3 and two FT-IR spectrums of final product (dry THF solvent and KBr pellet) are shown in Fig. 7 and Fig. 8.

**Table 3: FT-IR data of final product.**

| Absorption band (cm-1) | assignment |
|---|---|
| 756.037 | Stretching vibration of Aliphatic C-H bond(phenyl) (out-of-plane vibration) |
| 1209.23 | Bending vibration of C-H bond |
| 1261.2 | The asymmetric vibration of C-O-C angle |
| 1345.19 | Stretching vibration of C-O bond |
| 1480 and 1485 | Bending vibration of C-H bond |
| 1581.51 | Bending vibration of C=C bond |
| 1656.82 | Stretching vibration of C=C bond |
| 2832.67 | Stretching vibration of Aliphatic C-H bond |
| 3032.43 | Stretching vibration of Phenyl C-H bond |

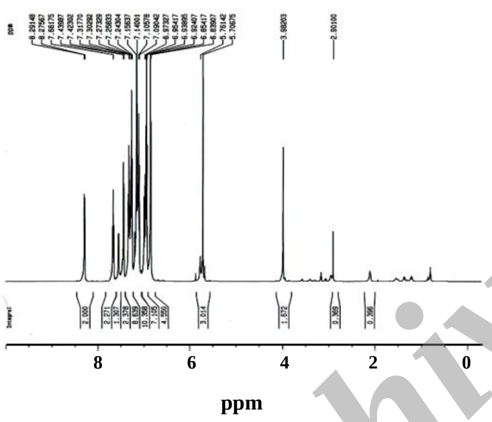

Fig. 5: 1H NMR spectrum of xanthydrol.

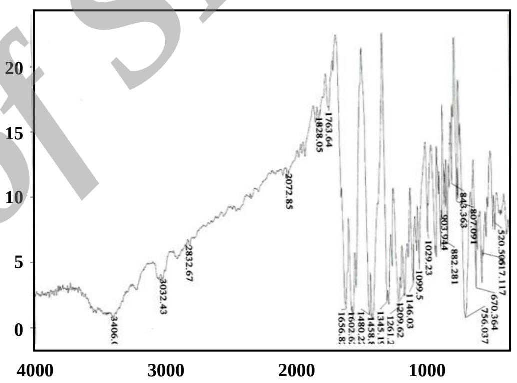

Fig. 7: FT-IR spectrum of the final product (KBr pellet).

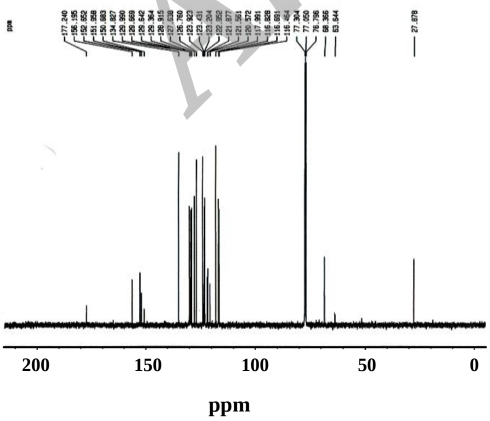

Fig. 6: 13C NMR spectrum of xanthydrol.

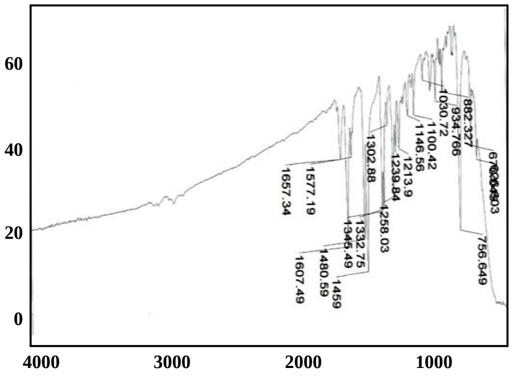

Fig. 8: FT-IR spectrum of the final product (dry THF solvent).

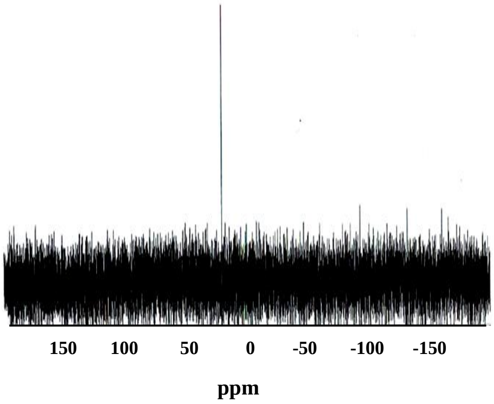

*Fig. 9: $^{31}$P NMR spectrum of the final product*

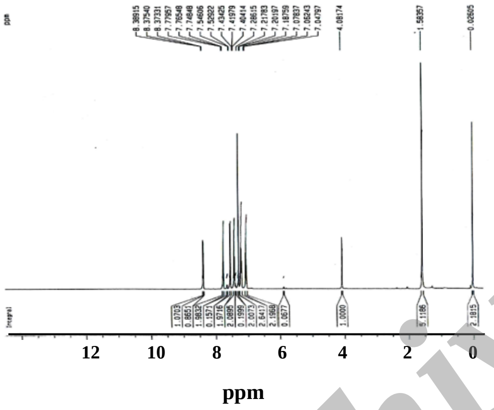

*Fig. 10: 1H NMR spectrum of final product.*

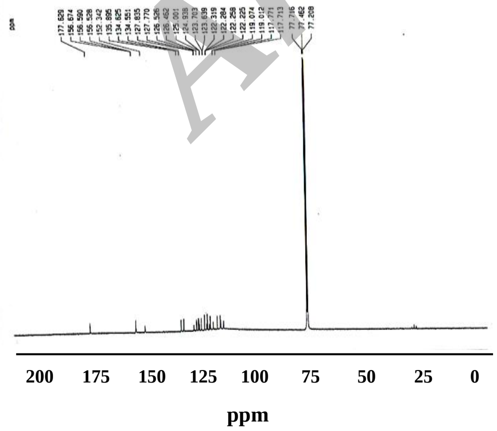

*Fig. 11: 13C NMR spectrum of final product.*

Fig. 8 FT-IR spectrum of the final product (dry THF solvent)

Interestingly, the absorption band at 3406.05 cm$^{-1}$, which is assigned to stretching vibration of alcoholic OH, has completely disappeared indicating that the ligand is attached to the desired chemical position and no free ligand presents in the reaction environment. Moreover, there are two absorption bonds at 882.327 and 1261.2 cm$^{-1}$ which are respectively assigned to asymmetric stretching vibration of P-N and stretching vibration of P=N in phosphazene ring. It should be noted that attaching the oxygenic ligand causes the absorption bonds to shift to higher frequencies because ligand is attached to phosphazene by an electronegative oxygen atom, which decreases the electron density on phosphazene ring by forming P-O bonds.

The peak at 5.7 ppm, which is assigned to alcoholic OH, disappeared because of the attachment of a ligand to the trimer by forming P-O bonds. The peak at 4.08 ppm is assigned to an aliphatic hydrogen atom. This peak shifted from its initial frequency (3.98ppm) due to the attachment of hydrogen to phosphorus.

Peaks in the range of 117-126ppm are assigned to carbon atoms in the aromatic ring. Three high peaks with the same intensity at 77ppm are assigned to CDCl3 solvent. A high peak at 27.87 ppm is assigned to aliphatic C-H.

### *Analysis of $^{31}$P NMR spectrum of the final product*

$^{31}$P NMR spectrum of the final product is shown in Fig. 9. According to the Fig. 9 a singlet peak at 15 ppm shows that the oxygen in ligand structure is attached to the phosphorus atom and all chlorine atoms are substituted with the ligand. It also indicates that the reaction forms a single product and all phosphorus atoms have the same chemical environments.

### *3.8 Analysis of $^{1}$H NMR spectrum of the final product*

Analysis of $^{1}$H NMR spectrum of the final product is shown in Fig. 10. Peaks appeared in the range of 7.03-8.39 ppm are assigned to hydrogens in aromatic rings. Attaching the ligand to the phosphorus atom shifts peaks of the product to lower field. The peak observed around 8.37 ppm is assigned to the hydrogen in each aromatic ring, which is the closest to the etheric oxygen, resulting in a higher chemical shift towards lower fields.

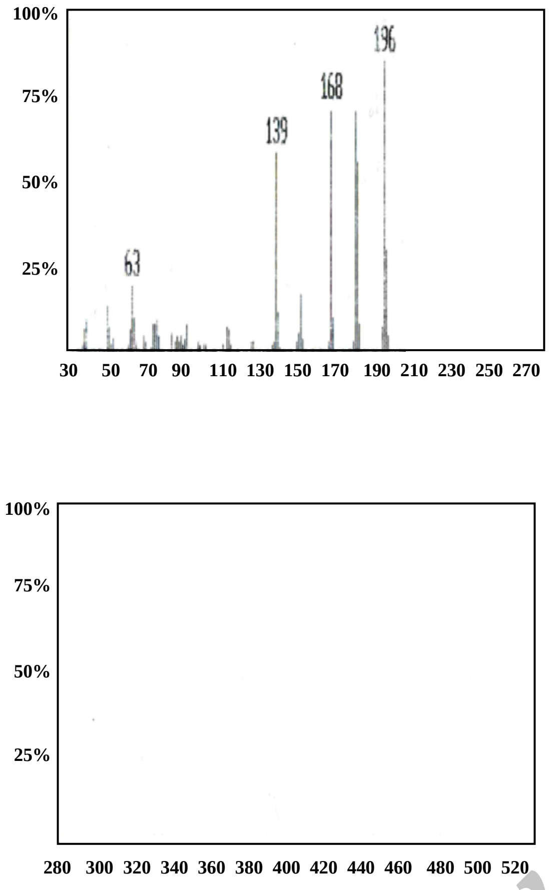

*Fig. 12: Mass spectrum of final product.*

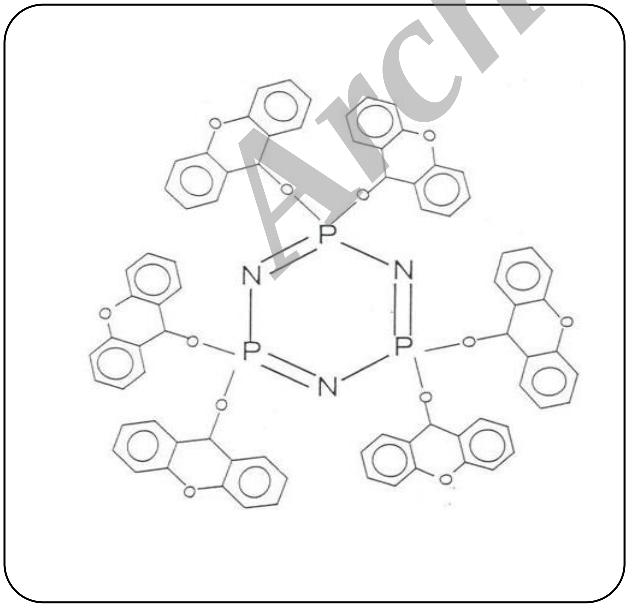

*Fig.13: Chemical structure of the final product.*

### *Analysis of $^{13}$C NMR of the final product*

Analysis of $^{13}$C NMR spectrum of the final product is shown in Fig. 11. Peaks appeared in a range of 117-126 ppm are assigned to aromatic carbon atoms. Tree peaks with the same height of 77 ppm are assigned to $CDCl_3$ solvent. The single peak that's appeared in 27.87 ppm is assigned to aliphatic C-H.

### *Mass spectrum of the final product*

Fig. 12 shows the analysis of the Mass spectrum of final product. Base peak (m/z= 196) is assigned to $[C_{13}H_8O_2]^+$ fragment. Other distinct peaks (m/z= 139, 168) are assigned to $[C_{12}H_8O]^+$ and $[C_4H_2O_2PN_2]^+$ fragments, respectively.

## CONCLUSIONS

The molecular structure illustrated in Fig. 13 can be proposed for the synthesized complex based on results obtained from various structural characterization tests. The structure consists of a symmetric triphosphazene in which all phosphorus and nitrogen atoms have the same chemical environment.

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