



# Reactions of cyclotriphosphazene with 1,6-diaminohexane and 1,8-diaminooctane: Mono-ansa, double- and triple-bridged derivatives



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## ABSTRACT

The reactions of hexachlorocyclotriphosphazene,  $N_3P_3Cl_6$  (**1**), with 1,6-diaminohexane (**2a**) and 1,8-diaminooctane (**2b**), having long carbon chains, in acetonitrile have been investigated. The reactions gave three different types of products, whose structures have been characterized by elemental analysis, mass spectrometry,  $^1H$  and  $^{31}P$  NMR spectroscopy, viz. the triple-bridged compounds  $N_3P_3Cl_3[NH(CH_2)_nNH]_3N_3P_3Cl_3$  [ $n = 6$  (a series);  $n = 8$  (b series)] (**3a**, **3b**), the mono-ansa compounds  $N_3P_3Cl_4[NH(CH_2)_nNH]$  (**4a**, **4b**) and the double-bridged compounds  $N_3P_3Cl_4[NH(CH_2)_nNH]_2N_3P_3Cl_4$ , (**5a**, **5b**). X-ray crystallographic studies confirmed the structures of the two ansa compounds (**4a**, **4b**) and the meso-anti double-bridged compounds (**5a**, **5b**). The results of both reactions were compared with previous work on the reaction of compound **1** with the same diamines (**2a**, **2b**).

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## 1. Introduction

Cyclophosphazenes are an important group of inorganic heterocyclic compounds containing the  $[N = PX_2]$  repeating unit. They have active phosphorus-halogen bonds that can be replaced with nucleophiles, leading to the formation of different types of product which could be region or stereo isomers. The most common members of this family of compounds are hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene, and these compounds serve as the starting materials for the synthesis of new compounds and materials. Especially, amino derivatives of cyclophosphazenes have been used in a variety of applications in science and technology, such as anti-cancer reagents [1–4], tumor growth inhibitors [5,6], biologically active molecules [7], flame retardants [8] and antimicrobial reagents [9].

Nucleophilic substitution reactions of cyclotriphosphazenes with di-functional reagents give different types of products, such as open chain, spiro, ansa, bridged and their isomers. For this reason, lots of researchers have concentrated on the reactions of cyclotriphosphazenes with di-functional reagents [10–28]. The formation of bridged species is quite complex. Intermolecular bridged derivatives are entropically favoured over intramolecular cyclizations. It is likely that the formation of bridged derivatives with long chain diols and diamines result from the flexibility of the longer chain

of the mono-substituted intermediate such that the terminal alkoxy group preferentially reacts with the P–Cl group of a neighboring cyclotriphosphazene molecule (intermolecular reaction) [24–27] rather than an intramolecular reaction to form either a spiro or ansa derivative.

In our previous work, triple bridged aminocyclotriphosphazene derivatives were synthesized according to the literature [11] for use as starting compounds. Although only the formation of triple bridged derivatives are mentioned in this literature, we have seen that the formation of also other derivatives (mono-ansa and double-bridged derivatives) under the same conditions (a 1:3.3 molar ratio, in acetonitrile solution, at 0 °C, for 4 days) (Scheme 1). These new derivatives were isolated and characterized. The crystal structures of the mono-ansa derivatives (**4a**, **4b**) and double bridged compounds (**5a**, **5b**) have been determined by single crystal X-ray diffractometry for the first time.

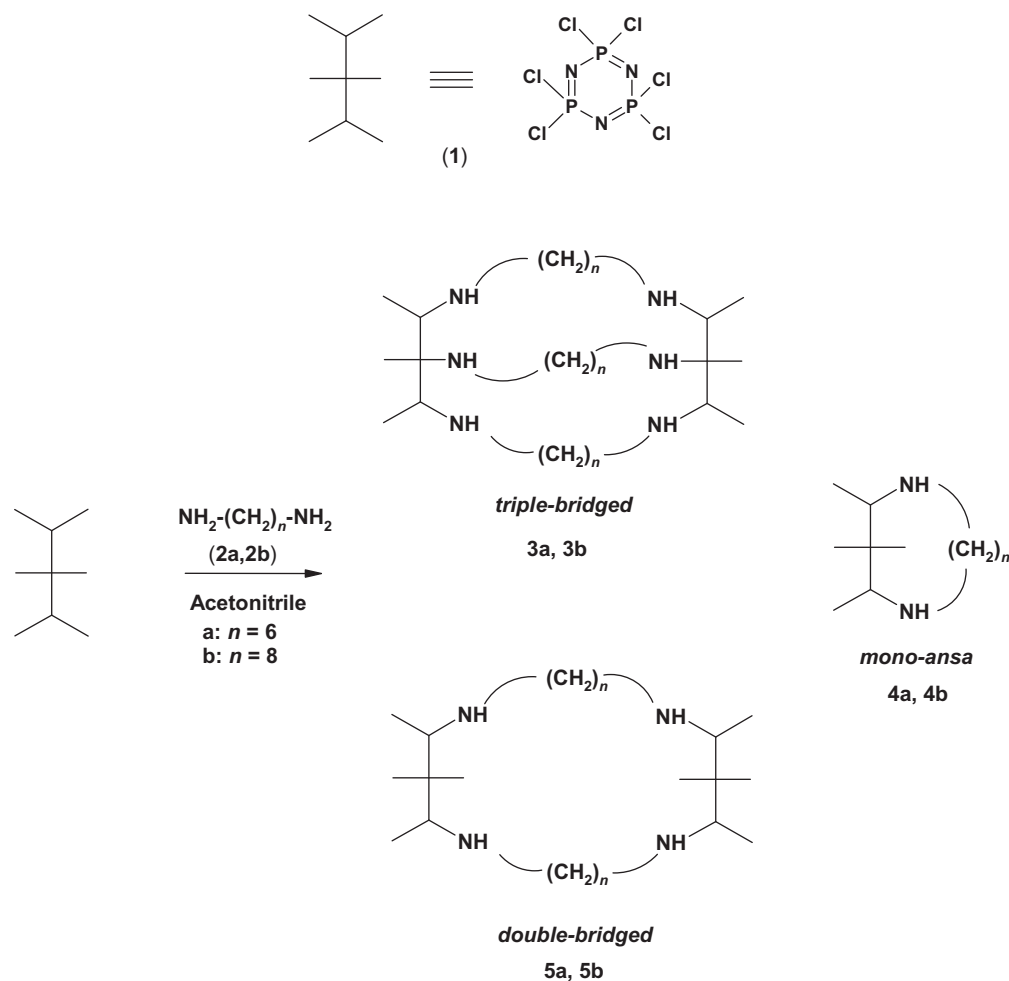
## 2. Experimental

### 2.1. Method

Hexachlorocyclotriphosphazene (Aldrich) was purified by fractional crystallization from hexane. Sodium hydride, 60% dispersion in mineral oil (Merck) was removed by washing with dry heptane (Merck) followed by decantation. Acetonitrile (Merck) was dried over a molecular sieve under an atmosphere of dry argon. Hexane, dichloromethane, 1,6-diaminohexane, 1,8-diaminooctane were obtained from Merck and used as received. Silica gel (Merck 60,

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**Scheme 1.** The reactions of cyclotriphosphazene (1) with diamines (2a, 2b) and the structures of the products.

0.063–0.200 mm) was used for column chromatography. All reactions were performed under a dry argon atmosphere.

## 2.2. Materials

Thin layer chromatography (TLC) was performed on Merck Silica gel plates (Merck 60, 0.25 mm thickness) with F254 indicator. Column chromatography was performed on silica gel (Merck 60, 0.063–0.200 mm; 150 g silica gel was used in a column 2 cm in diameter and 120 cm in length). Elemental analyses were obtained using a Thermo Finnigan Flash 1112 series, Italy instrument. The mass analyzer was a Bruker Daltonics Micro TOF LC-MS spectrometer with an electrospray ionization (ESI) source. The instrument was operated in the positive or negative ion mode using a range of  $m/z$  50–3000. Analytical  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded in  $\text{CDCl}_3$  solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for  $^1\text{H}$  NMR, and 85%  $\text{H}_3\text{PO}_4$  as an external reference for  $^{31}\text{P}$  NMR.

## 2.3. Synthesis

### 2.3.1. Reaction of hexachlorocyclotriphosphazene (1) with 1,6-diaminohexane (2a) [11]

Hexachlorocyclotriphosphazene (1) (3.48 g, 10 mmol) was dissolved in 500 mL of anhydrous acetonitrile in a 1000 mL three-necked round bottomed flask under an argon atmosphere and the reaction was cooled to  $0^\circ\text{C}$ . A solution of 1,6-diaminohexane (2a) (3.80 g, 33 mmol) in 150 mL of acetonitrile was prepared and

the solution was added dropwise into the reaction flask under an argon atmosphere. The reaction mixture was stirred for 4 days at  $0^\circ\text{C}$ . The reaction mixture was filtered to remove amine salts or some insoluble materials, and then the solvent was evaporated at reduce pressure. White solids formed at the bottom of the flask when dichloromethane was added to dissolve the crude reaction mixture. The precipitated solid part was filtered and the triple bridged cyclotriphosphazene derivative (3a), was obtained (0.97 g, 23%, mp  $> 300^\circ\text{C}$ ) [29]. The filtrated part of the reaction mixture was investigated by TLC on silica gel plates using  $n$ -hexane–THF (3:1) as the mobile phase and two new products were observed. This soluble part in dichloromethane was subjected to column chromatography, using  $n$ -hexane–THF (3:1) as the mobile phase. The first product is the mono-ansa derivative,  $\text{N}_3\text{P}_3\text{Cl}_4[\text{NH}(\text{CH}_2)_6\text{NH}]$  (4a) (0.11 g, 5%, mp  $246.7^\circ\text{C}$ ). *Anal. Calc.* for  $\text{C}_6\text{H}_{14}\text{Cl}_4\text{N}_5\text{P}_3$  (M, 390.95): C, 18.43; H, 3.61; N, 17.91; P, 23.77. Found ( $[\text{M}-\text{H}]^+$ , 389.94): C, 18.38; H, 3.53; N, 17.87; P, 23.75%.  $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 298 K,  $\delta$ : 1.46–1.60 (m, 8H,  $-\text{NHCH}_2\text{CH}_2$  and  $-\text{NHCH}_2\text{CH}_2$ ), 3.07, 3.25 (m, 4H,  $-\text{NHCH}_2$ ), 3.18 (m, 2H,  $-\text{NH}$ ). The second product was the double bridged derivative,  $[\text{N}_3\text{P}_3\text{Cl}_4]_2[\text{NH}(\text{CH}_2)_6\text{NH}]_2$  (5a) (0.32 g, 12%, mp  $238^\circ\text{C}$ ). *Anal. Calc.* for  $\text{C}_{12}\text{H}_{28}\text{Cl}_8\text{N}_{10}\text{P}_6$  (M, 781.89): C, 18.43; H, 3.61; N, 17.91; P, 23.77. Found ( $[\text{M}+\text{Na}]^+$ , 804.90): C, 31.65; H, 5.94; N, 18.39; P, 20.41%.  $^1\text{H}$  NMR,  $d_8$ -THF, 298 K,  $\delta$ : 1.99–2.07 (m, 8H,  $-\text{NHCH}_2\text{CH}_2\text{CH}_2$ ), 2.78–2.80 (m, 8H,  $-\text{NHCH}_2\text{CH}_2$ ), 3.84–3.92 (m, 8H,  $\text{NHCH}_2$ ), 3.31 (br, 4H,  $\text{NH}$ ). Suitable crystals for X-ray crystallography were obtained for compounds 4a and 5a from  $n$ -hexane–THF (3:1).

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