Polyhedron 77 (2014) 1–9

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Investigation of the structural properties of 2-naphthylamine substituted cyclotetraphosphazenes

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ARTICLE INFO

Article history:
Received 10 February 2014
Accepted 30 March 2014
Available online 13 April 2014

Keywords:
Octachlorocyclotetraphosphazene
Tetramer
2-Naphthylamine
^{31}P NMR spectroscopy
X-ray crystallography

ABSTRACT

In the present study, 2-naphthylamine substituted cyclotetraphosphazenes were synthesized and characterized for the first time. The reaction of octachlorocyclotetraphosphazene (**1**) with 2-naphthylamine (**2**) was performed in a THF solution and gave eight products (**3**–**10**). All the 2-naphthylamine substituted cyclotetraphosphazene compounds (**3**–**10**) were fully characterized by elemental analysis, MALDI-TOF mass spectrometry, ^{1}H, ^{13}C and ^{31}P NMR spectroscopies. The molecular structure of the non-geminal bis-substituted 2-naphthylamine cyclotetraphosphazene compound **3** (2-*trans*-6) was also determined by X-ray crystallography. Compounds **3**, **4** and **8** could be formed by an S_N2 mechanism. Compounds **5**–**7**, **9** and **10** might be formed by both S_N1 and S_N2 reaction mechanisms. These mechanisms were supported by ^{31}P NMR and X-ray crystallography results.

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1. Introduction

Cyclophosphazenes as a type of phosphazene compound are an important family of inorganic heterocyclic rings with a large variation in ring size. The six membered hexachlorocyclotriphosphazene (trimer) and eight membered octachlorocyclotetraphosphazene ($N_4P_4Cl_8$, **1**, tetramer) have been investigated in terms of (a) nucleophilic substitution reactions at phosphorus, (b) ring-opening polymerization to linear polymers and (c) utility as a support for building multisite coordination ligands [1–6]. Substitution reactions of the reactive P–Cl bonds on the phosphazene group have been shown to create cyclophosphazene compounds that have several applications. For example, cyclophosphazenes could form a base from which to synthesize a variety of compounds that can be utilized as biomedical materials, anticancer and antimicrobial agents [7–11], liquid crystals [12–14] and organic light emitting diodes [15–18].

While the reactions of the trimer with aromatic amines have been studied in detail by researchers [19–24], studies on tetramer with aromatic amines are rather limited [25,26], mainly because of the much larger number of products, their low yields and consequent difficulty in structure determination [27–29]. Additionally, the reactions of primary amines with the trimer lead to the formation of geminal structures, whereas the reactions of tetramer with primary amines proceed via a non-geminal path for the replacement of chlorine atoms [1,6]. Geminal and non-geminal reactions take place concurrently and competitively via separate reaction mechanisms. The mechanism for the non-geminal substitution is associative (S_N2), while the geminal reaction appears to involve a rate determining ionization step prior to attack by the nucleophile (S_N1) [18,30].

Naphthylamine is an important industrial material and is used as a chemical intermediate for certain dyes, rubber and in the synthesis of a large number of chemicals, such as certain herbicides [31,32]. Naphthylamine and its derivatives have also attracted the attention of researchers due to their fluorescent properties [26]. Although the reactions of naphthylamine with various ligands have been studied [31–33], there is only one study regarding the synthesis of a 1-naphthylamino substituted cyclotetraphosphazene compound [26]. To the best of our knowledge, there is no report on the reactions of 2-naphthylamine with cyclophosphazenes so far.

In this work, 2-naphthylamine substituted cyclotetraphosphazenes were synthesized by the reactions of 2-naphthylamine with tetramer in THF using triethylamine as a base. Newly synthesized compounds (**3**–**10**), which are the first examples of 2-naphthylamine substituted cyclotetraphosphazenes, were obtained in the current study (Scheme 1). These compounds have been fully characterized by MALDI-TOF mass spectrometry, ^{1}H, ^{13}C and ^{31}P NMR spectroscopies, elemental analysis and X-ray crystallography (**3**).

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http://dx.doi.org/10.1016/j.poly.2014.03.062
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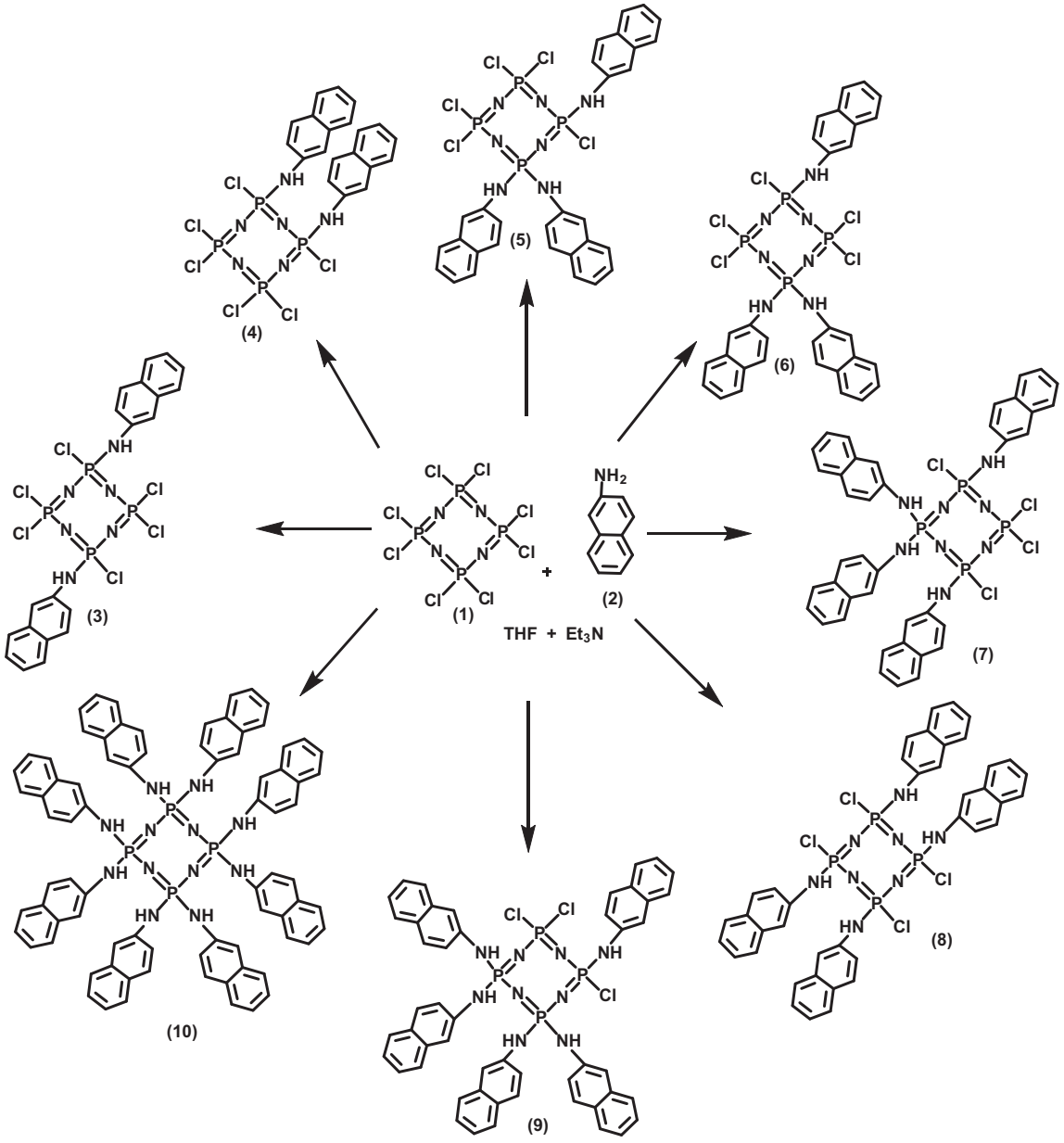

Scheme 1. 2-Naphthylaminocyclotetraphosphazene derivatives.

Table 1
$^{31}P\{^{1}H\}$ NMR parameters for compounds **3**–**10**.

Comp.	δ (^{31}P NMR) (ppm)							Spin system	^{2}J(PP) (Hz)								
	A	A′	B	B′	C	C′	X		$^{2}J_{AX}$	$^{2}J_{AB}$	$^{2}J_{AA'}$	$^{2}J_{AB'}$	$^{2}J_{BB'}$	$^{2}J_{BC}$	$^{2}J_{BC'}$	$^{2}J_{A'C}$	$^{2}J_{AC}$
(**3**)[a]	−2.79 (PCl_2)	–	–	–	–	–	−12.11 (PClR)	A_2X_2	39.85	–	–	–	–	–	–	–	–
(**4**)[a]	−5.65 (PCl_2)	−5.65 (PCl_2)	−8.57 (PClR)	−8.57 (PClR)	–	–	–	AA′BB′	–	37.92	13.83	–	13.90	–	–	–	–
(**5**)[a]	−4.38 (PCl_2)	−6.82 (PCl_2)	−9.41 (PR_2)	–	−13.79 (PClR)	–	–	AA′BC	–	37.51	30.71	–	–	43.89	–	38.21	–
(**6**)[a]	−3.76 (PCl_2)	–	−10.31 (PR_2)	–	−16.82 (PClR)	–	–	A_2BC	–	36.83	–	–	–	–	–	–	38.45
(**7**) [a]	−3.89 (PCl_2)	–	−5.40 (PR_2)	–	−8.63 (PClR)	−8.63 (PClR)	–	ABCC′	–	–	–	–	–	47.77	50.96	–	37.88
(**8**)[b]	−6.71 (PClR)	–	–	–	–	–	–	A_4	–	–	–	–	–	–	–	–	–
(**9**)[a]	−3.15 (PCl_2)	–	−4.58 (PR_2)	−7.40 (PR_2)	−13.96 (PClR)	–	–	ABB′C	–	–	–	35.22	48.53	51.50	–	–	38.56
(**10**)[a]	−8.43 (PR_2)	–	–	–	–	–	–	A_4	–	–	–	–	–	–	–	–	–

[a] 202.38 MHz ^{31}P NMR chemical shifts (ppm) in $CDCl_3$.
[b] 202.38 MHz ^{31}P NMR chemical shifts (ppm) in THF-d8.

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