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Synthesis, Characterization, and Fluorescence Phenomena of 1-Naphthoxy and 1-Naphthylamino Substituted Cyclotriphosphazenes

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ABSTRACT: *The reactions of hexachlorocyclotriphosphazene $N_3P_3Cl_6$ (**1**) with 1-naphthol and 1-naphthylamine have been examined. The reaction of* **1** *with sodium 1-naphthoxy gave the hexakis(1-naphthoxy)cyclotriphosphazene (**2**) in high yield. Geminal 2,2-di(1-naphthylamino)-4,4,6,6-tetrachlorocyclotriphosphazene (**3**) was obtained from the reaction of* **1** *with 1-naphthylamine. The structures of phosphazene derivatives were defined by elemental analysis, FTIR, UV–visible, and ^1H, ^{13}C, ^{31}P NMR spectroscopy. The fluorescence intensity of the compounds was measured in THF and CH_2Cl_2.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:158–162, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20400

INTRODUCTION

Phosphazenes are made up of a range of linear short chain or cyclic molecules and high polymers [1]. They play an important role in the chemistry of heteroatom compounds. Cyclophosphazene derivatives and organocyclophosphazenes have attracted great interest in the last three decades and have been reviewed over the years [2]. Up to now, more than 5000 different cyclic and linear phosphazene derivates have been known and characterized [3]. The compounds are starting materials for the preparations of poly(organo)phosphazene substrates [2,3]. The phosphazene compounds have stimulated a major research effort in recent years for use in a wide range of applications in a number of fields such as battery, biomaterials, full cell, flame resistant, photonic materials, and so on [4–9].

Photophysical properties of hexakis(2-naphthyloxy) cyclotriphosphazene [10], chiral binaphthoxyphosphazene polymers [11], hexakis(2-naphthoxy) cyclotriphosphazene [12], $N_3P_3\{[O(CH_2)_3NH]$-$[O(CH_2CH_2O)_4](2\text{-naphthoxy})_2\}$ [13], poly[bis(2-naphthoxy)]phosphazene [14], molecular characterization of poly[bis(β-naphthoxy)phosphazene] [15], the fluorescence phenomena of hexakis(4-aminophenoxy)cyclotriphosphazene [16], the eximer emission of hexaaryloxy-substituted cyclophosphazenes [17] have been reported. Hexakis(*p*-phenylazo-α-naphthoxy)cyclotriphosphazene [18], 6-*N*,*N*′-dimethylamino-α-naphthol or 6-*N*,*N*′-diethylamino-α-naphthol-substituted polyphosphazenes [19] have been synthesized and characterized.

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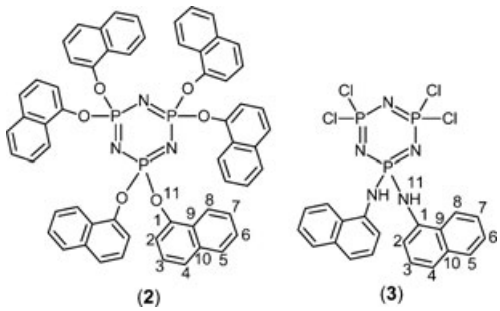
In this study, we report the reactions of **1** with sodium salts of 1-naphthol and 1-naphthylamine. Hexakis(1-naphthoxy) cyclotriphosphazene (**2**) and geminal disubstituted 2,2-di(1-naphthylamino) cyclotriphosphazene (**3**) were obtained.

RESULTS AND DISCUSSION

Hexachlorocyclotriphosphazene was reacted with 6 equiv. of 1-naphthol as sodium salt and 1-naphthylamine in dry THF at the mentioned temperatures in the Experimental section. Triethylamine in the synthesis of compound **3** was used for the formation of $NEt_3 \cdot HCl$ with the elevated HCl. The compounds are stable in air and moisture as white solids. Hexakis(1-naphthoxy) cyclotriphosphazene was obtained from the reaction of **1** with 1-naphthol. Progress of the reactions was monitored by TLC technique. The samples were taken from the reaction flask from time to time and controlled. The reaction was continued until the formation of hexasubstituted phosphazene was complete. The complete substitution of chlorine atoms by the α-naphthoxy groups was achieved for 5 days. But it is reported that the synthesis of poly[bis (α-naphthoxy)phosphazene], complete substitution of chlorine atoms by the α-naphthoxy group, was not achieved neither in the polymer nor in the trimer hexachlorocyclotriphosphazene, presumably due to steric hindrance [15]. Geminal 2,2-di(1-naphthylamino)-4,4,6,6-tetrachlorocyclotriphosphazene was also obtained from 1-naphthylamine. The primary amines show an increased tendency to geminal substitution with increased steric bulk and may exhibit incoming group control of the reaction pathway [20].

The structures of compounds **2** and **3** were determined by using elemental analysis, IR, UV–vis, ^1H, ^{13}C, and ^{31}P NMR spectroscopies. These results are given in the Experimental section. The IR spectrum of **3** shows the N—H stretching vibration at 3395 cm^{-1}. The P=N bonds, which are characteristic for phosphazenes, give strong infrared peaks at 1206 for **2** and **3**. The aryl C—H stretching vibrations of **2** and **3** were observed at 3055 and 3050 cm^{-1}, respectively. P—O—C_{aryl} vibration at 1082 cm^{-1} for **2** and P—N—C_{aryl} vibration at 1182 cm^{-1} for **3** were observed.

The proton-decoupled ^{31}P NMR spectra of compounds were interpreted as A_3 for **2** and AB_2 for **3** spin systems. All phosphorus atoms in skeleton of **2** have the same environments. As expected, only one peak is observed in the ^{31}P NMR spectrum of **2** at 9.24 ppm. There are two phosphorus signals for **3** because of the two different phosphorus environments in geminal-disubstituted phosphazene. Chemical shifts appeared at 0.44 ppm as a triplet for PNHR and at 21.80 ppm as a doublet for PCl_2. Compared to **1**, the substituted phosphorus signals for both compounds are shifted to the higher field.



SCHEME 1 The structures of the compounds **2** and **3**.

The ^1H and ^{13}C NMR data also confirm the structures of **2** and **3** (Scheme 1). In the ^1H NMR spectra (in the Experimental section), the aromatic protons for both compounds appear between 6.89 and 8.00 ppm. H^8 protons are observed at the lowest downfield as doublets. For **3**, a NH proton was observed at 5.31 and 5.29 ppm as two peaks. It is expected that the NH proton is not split because there are not protons on adjacent carbon atoms. The nonequivalence protons on the nitrogen atom, due to the difference resonance structures, cause two peaks. The resonance structures of the amino-α-naphthoxy group are shown in Fig. 1. Since the electron density on the nitrogen atom is shifted to carbon atom by resonance (in **b**), the NH proton signal appears at the lower downfield (at 5.31 ppm). The proton in (**a)** appears at 5.29 ppm.

In the ^{13}C NMR spectra, the ipso carbon atoms are observed at the lowest downfield at 146.4 ppm for **2** and 134.2 ppm for **3**. Other carbon atoms are observed between 128.2 and 121.6 ppm for **2**, and 129.1 and 119.9 ppm for **3**. The carbon signals for **3** appeared at upper field than **2**.

In the electronic spectrum of 1-naphthole, the bands at 237 (E_1-band), 275 (E_2-band), and 310 (B-band) nm in dichloromethane can be attributed to $\pi \rightarrow \pi^*$ transitions. Hexachlorocyclotriphosphazene shows absorption maxima at 175 nm [1]. Hexakis(1-

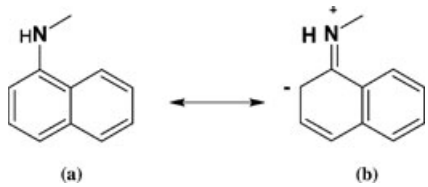


FIGURE 1 The resonance structures of **3**.

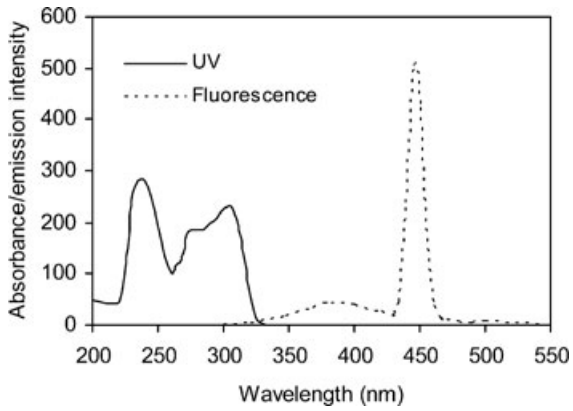


FIGURE 2 Absorption (solid line) and fluorescence (dotted line) spectra of **2** in CH_2Cl_2.

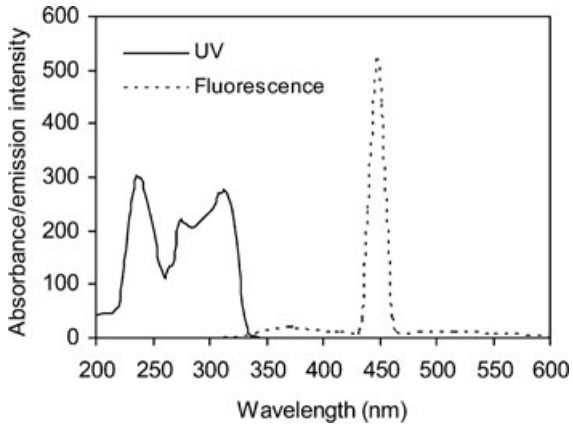


FIGURE 3 Absorption (solid line) and fluorescence (dotted line) spectra of **3** in CH_2Cl_2

naphthoxy)cyclotriphosphazene shows absorption maxima at 238, 275, and 305 nm. It is understood that the B-band is shifted to higher energy. There are three bands at 237 (E_1-band), 308 (E_2-band), and 320 (B-band) nm in dichloromethane

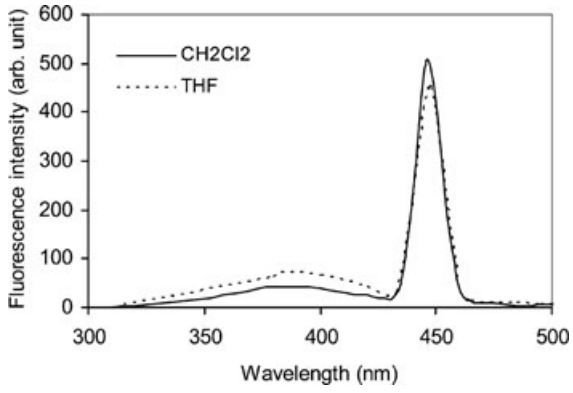


FIGURE 4 The fluorescence spectra of **2** in CH_2Cl_2 and THF.

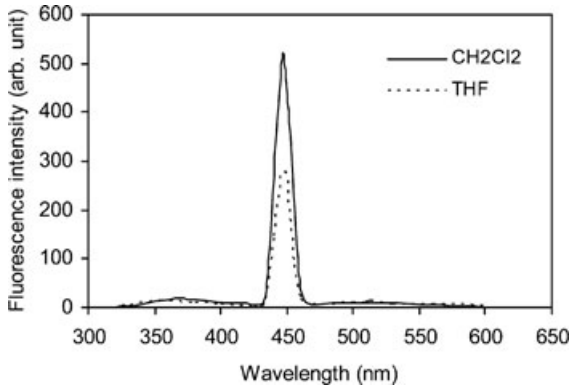


FIGURE 5 The fluorescence spectra of **3** in CH_2Cl_2 and THF.

for 1-naphthylamine. Compound **3** shows absorption maxima at 237, 276, and 314 nm. $E_2$and B-bands are shifted to higher energy for **3**.

The absorption and fluorescence spectra for **2** and **3** in CH_2Cl_2 are shown in Figs. 2 and 3. Although the absorption maxima were observed at 238, 275, and 305 nm for **2**, and at 237, 276, and 314 nm for **3**, the maximum fluorescence emission band was observed at 447 nm for **2** and **3**. The variation of the fluorescence intensity with solvents is shown in Figs. 4 and 5. Cyclotriphosphazene rings are photochemically inert and do not have any low-energy absorption band of their own. Hence, they do not interfere with the photophysical properties associated with the attached chromophores [10]. 1-Naphthoxy and 1-naphthylamino groups are the electron donors, when the molecules were exited by light, the delocalized π electrons can undergo a transition from the ground state to the excited state [16]. It is reported that the fluorescence intensity increased with the increase in the solvent polarity [10,16]. It is observed that the fluorescence intensity of **3** is higher than **2** in CH_2Cl_2, which of **2** is higher approximately two times than **3** in THF.

EXPERIMENTAL

All reactions were performed under dry argon atmosphere using standard Schlenk techniques. The tetrahydrofuran (THF, used as solvent) was distilled under argon atmosphere from sodium benzophenone prior to use. Hexachlorocyclotriphosphazatriene (99%) was purchased from Aldrich Ltd., Munich, Germany and purified by recrystallization from *n*-hexane and characterized by IR and ^{31}P NMR techniques. 1-Naphthol (99%) and 1-Naphthyl amine (99%) were purchased from Fluka

Ltd., Munich, Germany and used as purchased. Sodium salt was prepared from the reaction of 1-naphthol with metallic sodium. Hexachlorocyclotriphosphazene was purchased and purified by recrystallization from *n*-hexane, and characterized by IR and ^{31}P NMR techniques. The P=N, P–N–P, and P–Cl vibrations were observed at 1215, 873, and 600 cm^{-1} in the IR spectrum of **1**, respectively. Only one peak appeared at 21.20 ppm in the ^{31}P NMR spectrum of **1** [1,21].

All reactions were monitored by using Kieselgel 60 F254 (silica gel) precoated TLC plates, and the separating conditions were determined. The separation of products was carried out by column chromatography using Kieselgel 60 (60–230 mesh).

IR spectra were recorded with a Perkin Elmer RXI FTIR spectrophotometer as KBr disks and were reported in cm^{-1} units. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker DPX-400 high-performance digital FT-NMR spectrometer operating at 400.13, 100.63, and 161.98 MHz, respectively. All data were recorded for solutions in $CDCl_3$. The ^{1}H and ^{13}C chemical shifts were measured using $SiMe_4$ as an internal standard, the ^{31}P chemical shifts, using 85% H_3PO_4 as an external standard. Chemical shifts downfield from the standard are assigned positive δ values. Melting points were measured in open capillary with a Stuart Scientific melting point apparatus. Microanalysis was carried out by LECO 932 CHNS-O apparatus. The UV–vis spectra of the compounds as solutions in CH_2Cl_2 were obtained with Schimadzu 1610 spectrometer. Fluorescence measurements were carried out by Shimadzu Rf-1501 spectrofluorophotometer with solutions of 1×10^{-2} M in CH_2Cl_2 and THF.

Synthesis of **2**

1-Naphthol (2.87 g, 18.98 mmol) in THF (20 mL) was adde over a period of 30 min to small pieces of Na (80.44 g, 18.98 mmol) in THF (40 mL) with stirring at room temperature, with argon being passed over the reaction mixture. Excess sodium was removed by filtration. To this solution, **1** (1.00 g, 2.88 mmol) in THF (20 mL) was added to it dropwise with vigorous stirring. The solution was refluxed for 5 days under argon atmosphere. After the reaction was complete, the precipitated NaCl was filtered off and the solvent was removed by the rotary evaporator under vacuum. The residue was chromatographed (R_f: 0.57, CH_2Cl_2/*n*-hekzan 1:1). The compound **2** [hexakis(1-naphthoxy)cyclotriphosphazene] was obtained in 85% yield (2.43 g), mp 65°C. $N_3P_3(OC_{10}H_7)_6$ (993.9 g). Calcd: C 72.51, H 4.26, N 4.23; Found: C 71.98, H 4.10, N 4.05. IR (KBr, cm^{-1}): 3055 (C–H, aryl), 1597 (C=C), 1206 (P=N), 1082 (P–O–C_{aryl}). ^{1}H NMR ($CDCl_3$, ppm): 8.00 δ (H^8, d, $^{5}J_{POCH}$: 8.38 Hz), 7.80 δ (H^5, d, $^{6}J_{POCH}$: 8.07 Hz), 7.55 δ (H^4, d, $^{6}J_{POCH}$: 8.16 Hz), 7.47 δ (H^3, t, $^{5}J_{POCH}$: 7.26 Hz), 7.34 δ (H^6, t, $^{7}J_{POCH}$: 7.61 Hz), 7.17 δ (H^2, d, $^{3}J_{POCH}$: 7.56 Hz), 6.98 δ (H^7, t, $^{6}J_{POCH}$: 7.93 Hz). ^{13}C NMR ($CDCl_3$, ppm): C^1: 146.4, C^{10}: 134.7, 128.2–121.6 δ (C_2–C_9). ^{31}P NMR ($CDCl_3$, ppm): 9.24 δ (A_3, s).

Synthesis of **3**

A solution of $N_3P_3Cl_6$ (1.00 g, 2.88 mmol) in dry THF (60 mL) was added dropwise to a mixture of 1-naphthyl amine (2.72 g, 19 mmol) and NEt_3 (2.40 mL, 19 mmol) in dry THF (40 mL). After the mixture was allowed to reach ambient temperature, it was refluxed by stirring for 5 days with argon being passed over the reaction mixture. After the reaction was complete, the precipitated amine hydrochloride was filtered off and the solvent was removed by the rotary evaporator under vacuum. The residue was chromatographed (R_f: 0.37, CH_2Cl_2/*n*-hekzan 1:2). The compound **3** [2,2-di(1-naphthylamino)-4,4,6,6-tetrachclorocyclotriphosphazene] was obtained in 12% yield (0.20 g), mp 190°C, $N_3P_3Cl_4(NHC_{10}H_7)_2$(454.38 g). Calcd: C 42.81, H 2.87, N 12.48; Found: C 42.78, H 2.81, N 12.05. IR (KBr, cm^{-1}): 3395 (N–H), 3050 (C–H, aryl), 1594 (C=C), 1206 (P=N), 1182 (P–N–C_{aryl}), 588 (P–Cl). ^{1}H NMR ($CDCl_3$, ppm): 7.80 δ (H^8, d, $^{5}J_{PNCH}$: 7.60 Hz), 7.70 δ (H^5, d, $^{6}J_{PNCH}$: 8.38 Hz), 7.66 δ (H^4, d, $^{6}J_{PNCH}$: 7.45 Hz), 7.63 δ (H^3, t, $^{5}J_{POCH}$: 8.41 Hz), 7.45–7.35 δ (H^2, H^6, H^7, m, J_{PNCH}: 4 Hz), 5.31 and 5.29 δ (H^{11}), ^{13}C NMR ($CDCl_3$, ppm): C^1 134.2, C^{10} 133.1, 129.1–119.9 δ (C_2-C_9). ^{31}P NMR ($CDCl_3$, ppm, AB_2 pattern): 21.80 δ (PCl_2, d, J_{PNP}: 48.61 Hz), 0.44 δ (PNHR, t, J_{PNP}: 48.33 Hz).

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