Inorganica Chimica Acta 423 (2014) 489–495

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Structural and fluorescence properties of 2-naphthylamine substituted cyclotriphosphazenes

Gönül Yenilmez Çiftçi *, Elif Şenkuytu, Mahmut Durmuş, Fatma Yuksel, Adem Kılıç

Department of Chemistry, Gebze Institute of Technology, Gebze 41400, Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form 21 July 2014
Accepted 1 September 2014
Available online 8 September 2014

Keywords:
Hexachlorocyclotriphosphazene
Cyclophosphazene
Fluorescence
2-Naphthylamine
^{31}P NMR spectroscopy
X-ray crystallography

ABSTRACT

The reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (trimer) (**1**), with 2-naphthylamine (**2**) in tetrahydrofuran solution were studied and six new 2-naphthylamine substituted cyclotriphosphazene compounds (**3**–**8**) were obtained in this study. All of these compounds were fully characterized by elemental analyses, MALDI-TOF mass spectrometry, ^{1}H, ^{13}C, ^{31}P NMR, electronic absorption and fluorescence spectroscopies. The molecular structure of compounds; mono- (**3**), geminal bis (**4**) and tetrakis (**6**) 2-naphthylaminocyclotriphosphazenes were also determined by X-ray crystallography. The fluorescence properties of newly synthesized compounds (**3**–**8**) were investigated and compared in tetrahydrofuran solution. The fluorescence quantum yield (Φ_F) values of newly synthesized 2-naphthylamine substituted cyclotriphosphazenes (**3**–**8**) were also determined and compared in this solution.

1. Introduction

Luminescent compounds have important applications, such as emitting materials for organic light emitting diodes, light harvesting materials for photocatalysis, fluorescent sensors for organic or inorganic analytes and photovoltaic devices [1–7]. The substituted cyclic phosphazenes have high thermal stability and they do not break down even under very aggressive chemical conditions. Cyclotriphosphazenes have many applications including organic light emitting diodes [8–15], biomedical materials, anticancer and antimicrobial agents [16–25] and liquid crystals [26–31]. In most cases, cyclotriphosphazene (hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, **1**) can be readily modified with a variety of substituents *via* nucleophilic substitution reactions [32,33].

Naphthylamine and its derivatives have also attracted the attention of researchers due to their fluorescent properties. In one study, Sun and co-workers synthesized naphthylamine rhodamine hybrid materials for ratiometric and colorimetric fluorescent probes and they investigated their photophysical properties [34]. In another study, İbisoğlu and co-workers synthesized a 1-naphthylamine substituted tetrameric phosphazene derivative and investigated the fluorescent behavior of this compound [35].

To the best of our knowledge, there is no report on the 2-naphthylamine substituted cyclotriphosphazenes so far. This study aims to investigate the fluorescence properties of the newly synthesized 2-naphthylamine substituted cyclotriphosphazene derivatives. For this purpose, the reactions of 2-naphthylamine with $N_3P_3Cl_6$ were investigated in THF using triethylamine as a base. Six products (**3**–**8**) which were the first examples of 2-naphthylamine substituted cyclotriphosphazenes were obtained (Scheme 1). These compounds were fully characterized by elemental analyses, MALDI-TOF mass spectrometry, ^{1}H, ^{13}C and ^{31}P NMR, electronic absorption, fluorescence spectroscopies and X-ray crystallography (for compounds **3**, **4** and **6**). In addition, the fluorescence properties of all these novel compounds were investigated and compared in THF solution.

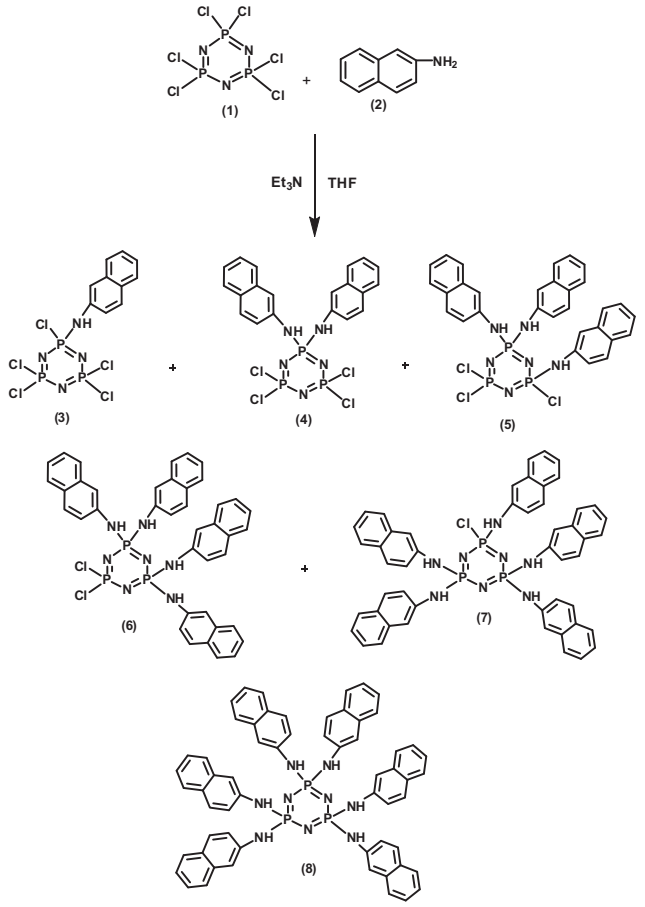
2. Experimental

2.1. Materials and methods

Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd) was purified by fractional crystallization from *n*-hexane. 2-Naphthylamine (99%) was obtained from Aldrich. Tetrahydrofuran (⩾99.0%), dichloromethane (⩾99.0%), *n*-hexane (⩾95.0%), petroleum ether (⩾99.0%), triethylamine (99.0%) were obtained from Merck. THF was distilled over sodium–potassium alloy under an atmosphere of dry argon. Silica gel 60 (230–400 mesh) for column chromatography was obtained from Merck. $CDCl_3$ and THF-d_8 for NMR spectroscopy were obtained from Goss Scientific. Elemental analytical data was obtained using a Thermo Finnigan Flash 1112

* Corresponding author. Tel.: +90 262 6053011; fax: +90 262 6053101.
E-mail address: yenilmez@gyte.edu.tr (G. Yenilmez Çiftçi).

http://dx.doi.org/10.1016/j.ica.2014.09.001
0020-1693/



Scheme 1. Synthesis of 2-naphthylaminocyclotriphosphazene derivatives (**3**–**8**).

Instrument. Positive ion and linear mode MALDI-MS of complexes were obtained in 2,5-dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. All reactions were monitored using thin-layer chromatography (TLC) on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g. crude mixture, 100 g. Silica gel was filled in a column of 3 cm in diameter and 60 cm in length). All reactions were carried out under an argon atmosphere. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ and THF-d_8 solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^{1}H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR. Absorption spectra in the UV–Vis region were recorded with a Shimadzu 2101 UV–Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvette at room temperature.

2.2. X-ray crystallography

Intensity data were recorded on a Bruker APEX II QUAZAR diffractometer using monochromatized Mo Kα x-radiation (λ = 0.71073 Å). Absorption correction was performed by multi-scan method implemented in SADABS [36] and space groups were determined using XPREP implemented in APEX2 [37]. Structures were determined using direct methods procedure in SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 [38]. All non-hydrogen atoms were refined with anisotropic displacement factors. The C–H hydrogen atoms were placed in calculated positions, while the N–H protons were determined from a difference map and the displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2 U_{eq} (for CH) and 1.5 U_{eq} (for NH) of their parent atoms. In the unit cell of **6**, some larger electron peaks due to a solvent molecule(s) was found the rest molecules were refined without the effect of the solvent molecule(s) by using SQUEEZE command of PLATON [39]. There is one cavity of volume 955 Å^3 per unit cell and total void electron count is 195. The final geometrical calculations were carried out with PLATON [39], and MERCURY [40] programs and the molecular drawings were done with DIAMOND [41] program. Structure determinations were deposited with the Cambridge Crystallographic Data Centre with references CCDC 954526–954528 for compounds **3**, **4** and **6**, respectively.

2.3. Synthesis

2.3.1. Synthesis of compounds *3* and *4*

Hexachlorocyclotriphosphazene (**1**), (3.0 g, 8.62 mmol) and triethylamine (2.4 mL, 17.24 mmol) were dissolved in 50 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and 2-naphthylamine (**2**) (2.46 g, 17.24 mmol) in 10 mL of dry THF was added to this stirred solution under an argon atmosphere. The reaction mixture was stirred for 4 days at room temperature and the reaction followed on TLC silica gel plates using *n*-hexane–CH_2Cl_2 (5:1) as eluent. Two products were observed on TLC. The reaction mixture was filtered to remove the formed triethylamine hydrochloride and the solvent was removed under reduced pressure. The resulting colorless oil was subjected to column chromatography, using *n*-hexane–THF (5:1) as eluent. The first product was 2-(2-naphthylamino)-2′,4,4′,6,6′-pentachlorocyclotriphosphazene (**3**), (0.20 g, 0.44 mmol, 5%, m.p. 159 °C), Rf = 0.75, *n*-hexane–CH_2Cl_2 (5:1). This compound (**3**) was re-crystallized from *n*-hexane–THF (5:1) and obtained as white crystals which were suitable for X-ray crystallography. Elemental analyses: Calc. for $C_{10}H_8Cl_5N_4P_3$: C, 26.43; H, 1.77; N, 12.33, Found: C, 26.18; H, 1.55; N, 12.12%. MS (MALDI-TOF) *m*/*z*: Calc. 454, found 455 [M+H]$^+$. ^{1}H NMR, $CDCl_3$, 298 K: δ ppm, 7.83 d, 1H, Hb ($^{3}J_{Hb-Hc}$ = 8.43 Hz); 7.81 d, 1H, Hf ($^{3}J_{Hf-Hk}$ = 8.48 Hz); 7.82 d, 1H, He ($^{3}J_{He-Hd}$ = 8.33 Hz); 7.62 s, 1H, Ha; 7.52 t, 1H, Hc ($^{3}J_{Hc-Hb}$ = 8.43 Hz, $^{3}J_{Hc-Hd}$ = 7.90 Hz); 7.44 t, 1H, Hd ($^{3}J_{Hd-He}$ = 8.33 Hz, $^{3}J_{Hc-Hd}$ = 7.90 Hz); 7.29 dd, 1H, Hk ($^{3}J_{Hk-Hf}$ = 8.48 Hz, $^{4}J_{Hk-NH}$ = 2.40 Hz), 5.72 d, 1H, NH ($^{2}J_{P-NH}$ = 10.56 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ ppm, 134.20 (s, C_3), 133.81 (s, C_8), 130.62 (s, C_9), 129.67 (s, C_4), 127.72–126.89 (C_5, C_6, C_7), 125.35 (s, C_1), 120.48 (d, $^{3}J_{PC}$ = 8.13 Hz, C_{10}), 117.17 (d, $^{3}J_{PC}$ = 7.37 Hz, C_2). The second product was 2,2′-bis(2-naphthylamino)-4,4′,6,6′-tetrachlorocyclotriphosphazene (**4**), (2.4 g, 4.27 mmol, 50%, m.p. 212 °C), Rf = 0.53, *n*-hexane–CH_2Cl_2 (5:1). This compound (**4**) was re-crystallized from *n*-hexane–THF (4:1) and obtained as white crystals which were suitable for X-ray crystallography. Elemental analyses: Calc. for $C_{20}H_{16}Cl_4N_5P_3$: C, 42.81; H, 2.87; N, 12.48. Found: C, 42.72; H, 2.81; N, 12.38%. MS (MALDI-TOF) *m*/*z*: Calc. 561, found 562 [M+H]$^+$. ^{1}H NMR, $CDCl_3$, 298 K: δ ppm, 7.73 d, 2H, Hb ($^{3}J_{Hb-Hc}$ = 8.09 Hz); 7.69 d, 2H, Hf ($^{3}J_{Hf-Hk}$ = 8.65 Hz); 7.68 d, 2H, He ($^{3}J_{He-Hd}$ = 7.32 Hz); 7.55 s, 2H, Ha; 7.45 t, 2H, Hc ($^{3}J_{Hc-Hb}$ = 8.09 Hz, $^{3}J_{Hc-Hd}$ = 8.10 Hz); 7.35 t, 2H, Hd ($^{3}J_{Hd-He}$ = 7.32 Hz, $^{3}J_{Hd-Hc}$ = 8.10 Hz); 7.19 dd, 2H, Hk ($^{3}J_{Hk-Hf}$ = 8.65 Hz, $^{4}J_{Hk-NH}$ = 2.08 Hz), 5.47 t, 2H, NH ($^{2}J_{P-NH}$ = 10.22 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ ppm, 135.66(s, C_3), 133.91 (s, C_8), 130.13 (s, C_9), 129.36 (s, C_4), 127.63–126.64 (C_5, C_6, C_7), 124.78 (s, C_1), 120.43 (d, $^{3}J_{PC}$ = 7.71 Hz, C_{10}), 116.07 (d, $^{3}J_{PC}$ = 6.33 Hz, C_2).