Spectrochimica Acta Part A 74 (2009) 881–886

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Structural and fluorescence properties of phenolphthalein bridged cyclotriphosphazatrienes

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

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

ARTICLE INFO

Article history:
Received 13 April 2009
Received in revised form 31 July 2009
Accepted 7 August 2009

Keywords:
Cyclophosphazenes
Hexachlorocyclotriphosphazatriene
Phenolphthalein
Fluorescence
FT-IR
NMR

ABSTRACT

This study dealt with the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (trimer) (**1**) with phenolphthalein (**2**) to give the phenolphthalein bridged compounds **3**, **4** and **5**. The phenolphthalein bridged cyclotriphosphazatriene derivatives are reported for the first time. The new compounds (**3**–**5**) are characterized by elemental analysis, mass spectrometry, UV–vis, FT-IR, ^1H, ^{31}P NMR and fluorescence spectroscopy. The more bridged phenolphthalein groups show the higher intensity of the absorption bands in the UV–vis spectra. Fluorescence spectrum of compound **3** shows a small band in the lower spectral range, while the spectra of compounds **4** and **5** show more intense and a band in higher spectral range.

1. Introduction

Phosphazenes are important compounds from which a large number of organophosphazenes can be derived by the reaction with nucleophiles. Organophosphazenes find a variety of applications in science and technology [1]. Phosphazenes are made up of a range of linear short chain or cyclic molecules and high polymers. The chemical and physical properties of phosphazenes change with the substituted side groups. For example, it is possible to design materials with special properties such as inflammable textile fibers and advanced elastomers [2], anticancer agents [3–5], hydraulic fluids and lubricants [6,7], electrical conductivity [8], fertilizers [9,10], flame retardant [11,12] and liquid crystalline [13–16] properties.

The reactions of hexachlorocyclotriphosphazatriene with difunctional alcohols are widely studied [17–19]. The four types of products (spiro, ansa, open chain and bridged compounds) derived from the reactions of **1** with diols are well established [20]. Reaction of **1** with ethane-, 1,3-propane-, and 1,4-butane-diols (in the presence of pyridine to neutralize the HCl formed) predominantly gave spiro derivatives with 5-, 6-, 7-membered phosphate rings, respectively whereas ansa derivatives were obtained only in small yields [21]. A bridged derivative was observed as a minor product with butanediol, indicating that chain length was a contributing factor in determining the type of the compound [20]. It was also found that ansa-derivatives are formed using sodium salts of diols as reagents in polar solvents such as tetrahydrofuran (THF) [22,23].

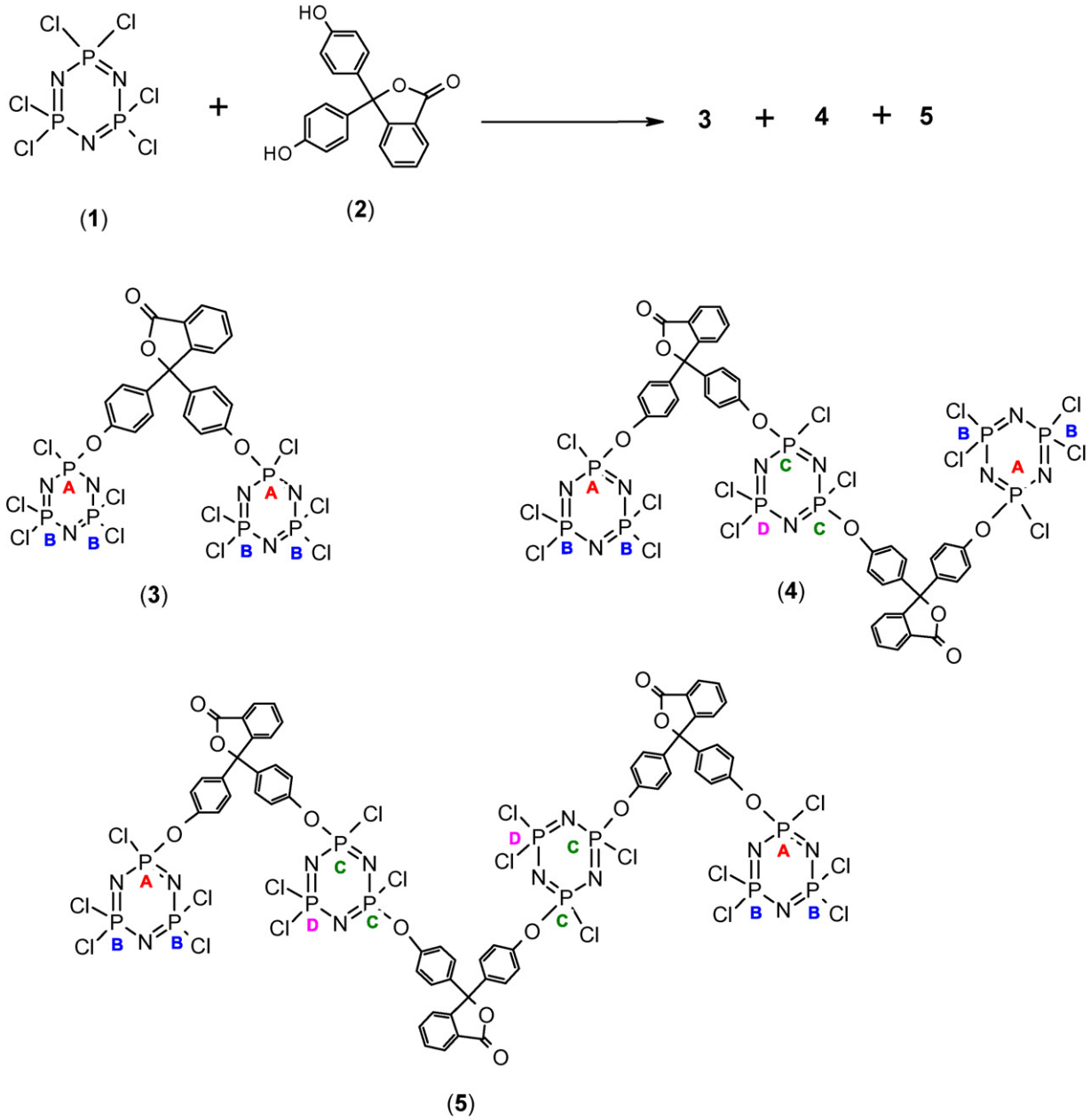
The reaction of 2,2-dioxybiphenyl groups with the hexachlorocyclotriphosphazatriene are well known [24,25] and mono spiro and mono ansa products are isolated from the reaction between **1** and 2,2-dioxybiphenyl [25]. There are also some works reported in the literature about the reaction of **1** with some phenol and phenol derivatives [26,27] and their fluorescence properties [28]. Information on the reactions between **1** and polyphenols is not well known and bridged products are found rarely [29]. Some phenoxy phosphazene derivatives are found in the literature about a potential candidate of new type of dendritic emitting structures for solution processed and hybrid organic light emitting diode (OLED) devices [30].

Phenolphthalein is found in a variety of ingested products as well as in some scientific applications such as food industry. It can be incorporated easily in tablets, powders, and liquids due to being odorless and tasteless. It has been commonly used as a laxative, available worldwide as an over-the-counter chocolate or gum laxative product [31]. Although there were several studies including the phenolphthalein groups in the literature [32a,b], there is no study which has been done about the reaction of phenolphthalein with cyclophosphazenes.

This study aims to investigate for fluorescence properties of the phenolphthalein bridged cyclotriphosphazatriene derivatives. For this purpose, reaction of phenolphthalein with trimer in THF is investigated and some phenolphthalein bridged cyclotriphosphazatriene compounds (**3**–**5**) (Scheme 1) are characterized.

* Corresponding author. Tel.: +90 262 6053110; fax: +90 262 6053101.
E-mail address: yenilmez@gyte.edu.tr (G.Y. Çiftçi).

1386-1425/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2009.08.028



Scheme 1.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazatriene (Otsuka Chemical Co. Ltd.) was purified by fractional crystallization from *n*-hexane. Sodium hydride (60% dispersion in mineral oil, Merck; prior to use the oil was removed by washing with dry heptane followed by decantation). Phenolphthalein (>99%), tetrahydrofuran (THF) (≥99.0%), dichloromethane (≥99.0%), *n*-hexane (≥95.0%) were obtained from Merck. THF was distilled over a sodium–potassium alloy under an atmosphere of dry argon. All reactions were performed under a dry argon atmosphere. Silica gel 60 (230–400 mesh) for column chromatography was obtained from Merck. $CDCl_3$ for NMR spectroscopy are obtained from Goss Scientific.

2.2. Methods

Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Mass spectra were recorded on a Bruker MicrOTOF LC–MS spectrometer using the electrospray ionization (ESI) method; ^{35}Cl values were used for calculated masses. Analytical Thin Layer Chromatography (TLC) was performed 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 used in a column of 3 cm in diameter and 60 cm in length). ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ 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. The FT-IR spectra were recorded with Bio-Rad 175 FTS. The spectrum resolution was

Table 1
Analytical data of cyclotriphosphazatrienes (**3**–**5**).

Comp.	Empirical formula	Analytical data (%)						Mass[a]	
		Calculated			Found			M	$[M+Na]^+$
		N	C	H	N	C	H		
3	$C_{20}H_{12}Cl_{10}N_6O_4P_6$	8.93	25.54	1.29	8.92	25.52	1.28	940	962.8
4	$C_{40}H_{24}Cl_{14}N_9O_8P_9$	8.22	31.32	1.58	8.21	31.32	1.57	1533	1555.7
5	$C_{60}H_{36}Cl_{18}N_{12}O_{12}P_{12}$	7.90	33.88	1.71	7.91	33.87	1.70	2126	2150.7

[a] The ESI-MS spectra of compounds (**3**–**5**) show the $[M+Na]^+$ and M molecular ion peaks.

Table 2
Selected FT-IR vibrations of compounds **3**–**5**.

Compound	$\nu_{(C-H)arom}$	$\nu_{(C=O)}$	$\nu_{(C=C)}$	$\nu_{(P=N)}$	$\nu_{(P-Cl)}$	$\nu_{(P-O)}$
(**1**)	–	–	–	1258; 1169 s	532; 608 s	–
(**2**)	3061 m	1740 vs	1514 s	–	–	–
(**3**)	3070 m	1778 s	1503 s	1286; 1163 s	524; 601 s	1242; 1162 s
(**4**)	3060 m	1776 s	1505 s	1288; 1165 s	536; 604 s	1246, 1160 s
(**5**)	3058 m	1774 s	1503 s	1288; 1163 s	526; 600 s	1162, 1242 s

s: strong; m: medium; vs: very strong.

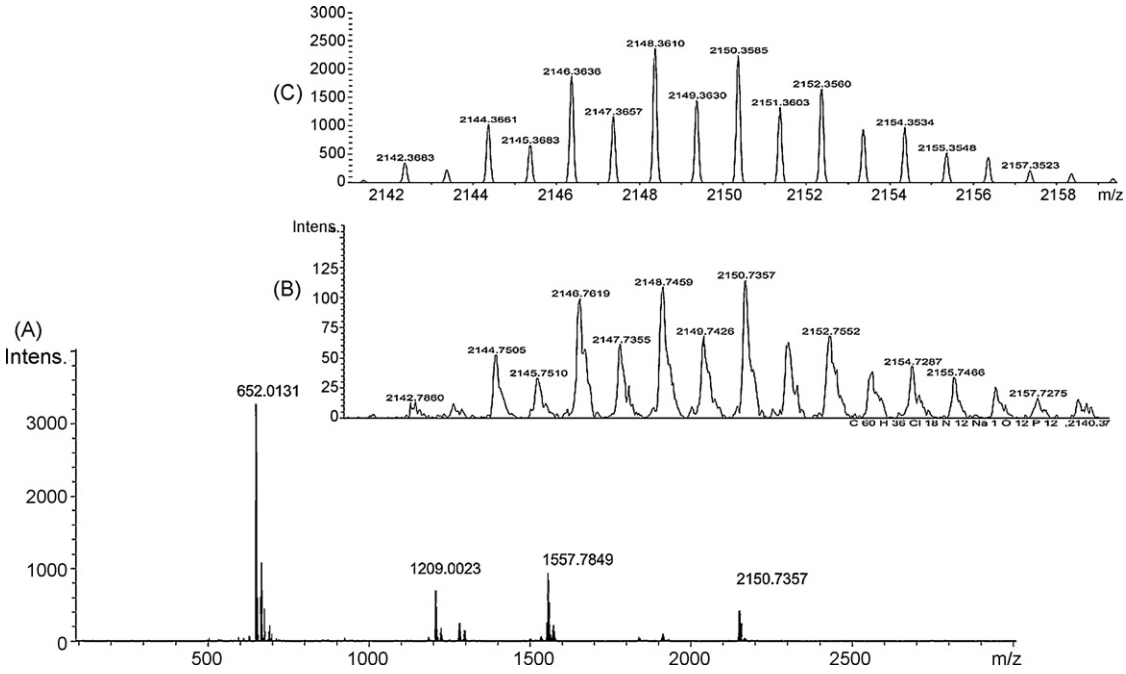


Fig. 1. (A) Mass spectrum compound of **5**; (B) chloro pattern of compound **5**; (C) computer analyzing of chloro pattern of compound **5**.

$2\,cm^{-1}$ and 16 scans were recorded for all samples. The spectra were recorded on the base of KBr pellet technique. UV–vis spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluoremeter using 1 cm pathlength cuvettes at room temperature.

2.3. Synthesis

2.3.1. Reaction of *1* with *2* in a 2:1 ratio to form compounds *3*–*5*

Hexachlorocyclotriphosphazatriene (**1**) (5.0 g, 14.4 mmol) and phenolphthalein (**2**) (1.94 g, 7.2 mmol) were dissolved in 100 mL of dry THF under an argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.57 g, 14.4 mmol) in 40 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 5 days at room temperature and the reaction followed on TLC silica gel plates using *n*-hexane–THF (2:1) as eluent. Four products were observed on TLC. The reaction mixture was filtered to remove the sodium chloride formed and the solvent removed under reduced pressure. The resulting colorless oil was subjected to column chromatography, using *n*-hexane–THF (2:1) as eluent. The first product was starting material $N_3P_3Cl_6$ (0.6 g, 12%), Rf = 0.82. The second product was the mono-phenolphthalein bridge derivative (**3**) (1.26 g, 9.3%, m.p.

Table 3
$^{31}P\{^1H\}$ NMR parameters for compounds **3**–**5** in $CDCl_3$.

Comp.	δ (^{31}P NMR) (ppm)				Spin system	^2J(PP) (Hz)	
	P(OCl)		PCl_2			A, B	C, D
	A	C	B	D			
(**3**)	13.2		23.5		A_2X	61.6	
(**4**)	13.2	16.2	23.6	25.7	A_2X, $A'X'_2$	61.6	64.9
(**5**)	12.4	14.6	22.5	24.6	A_2X, $A'X'_2$	60.8	64.4

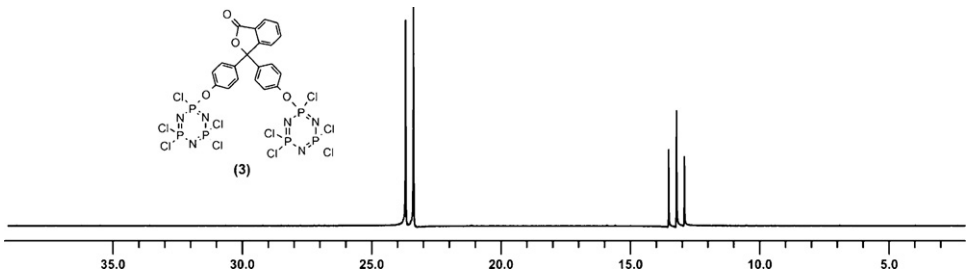


Fig. 2. Proton-decoupled ^{31}P NMR spectrum of the compound **3** in $CDCl_3$.

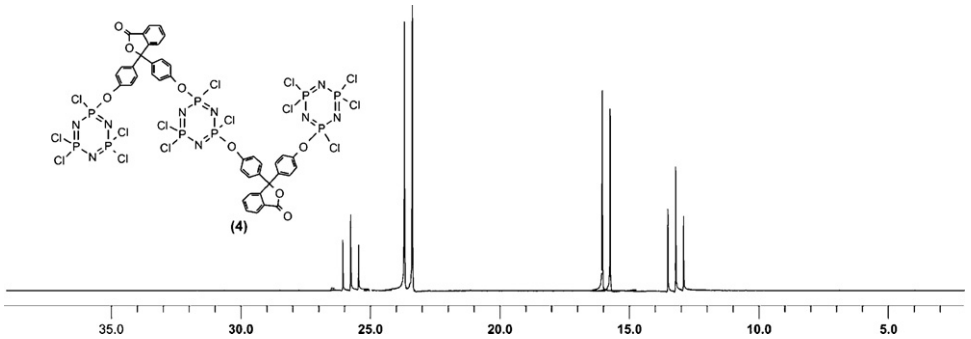


Fig. 3. Proton-decoupled ^{31}P NMR spectrum of the compound **4** in $CDCl_3$.

58 °C), Rf = 0.64. The third product was the bis-phenolphthalein bridge derivative (**4**) (0.32 g, 1.4%, oily), Rf = 0.43. The fourth product was the isomeric tris-phenolphthalein bridge derivative (**5**) (0.25 g, 0.8%, m.p. 120 °C), Rf = 0.35 [*n*-hexane–THF (2:1)]. Analytical data of cyclotriphosphazatrienes (**3**–**5**) were listed in Table 1. The elemental analyses results and mass values were in agreement with the proposed structures. The ESI-MS spectrum of compound (**5**) was given in Fig. 1. Table 1 gives the empirical formula, molecular weights (mass) and elemental analyses for the compounds (**3**–**5**).

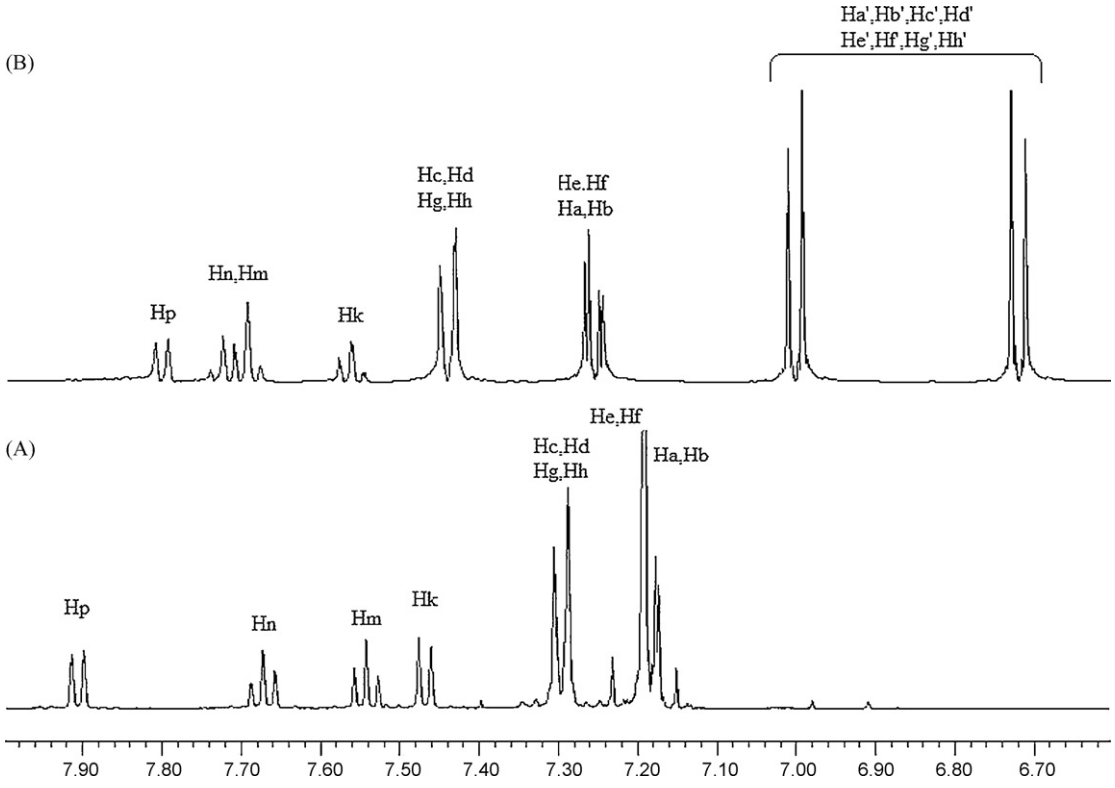
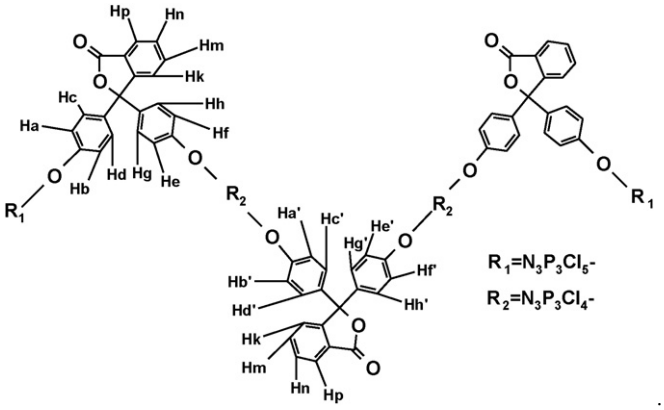


Fig. 4. ^{1}H NMR spectra of (A) compound **3** and (B) compound **5** between 6.6 and 8 ppm in $CDCl_3$.

Table 4
^{1}H NMR spectral data of compounds **3**–**5** in $CDCl_3$.



	Compounds		
	3	**4**	**5**
Ha, Hb, He, Hf	7.15–7.20	7.27–7.31	7.24–7.28
Ha′, Hb′, He′, Hf′	–	6.91–7.18	6.71–7.02
Hm	7.54 (td, 1H) [$^3J_{HnHk-Hm}$ = 7.51]	7.76–7.82	7.68–7.74
Hk	7.47 (d, 1H) [$^3J_{Hk-Hm}$ = 7.76]	7.67 (d, 1H) [$^3J_{Hk-Hm}$ = 7.94]	7.56 (td, 1H) [$^3J_{Hpk-Hm}$ = 7.82]
Hn	7.67(td,1H) [$^3J_{HpHm-Hn}$ = 7.09]	7.76–7.82	7.68–7.74
Hc′, Hd′, Hg′, Hh′	–	6.91–7.18	6.71–7.02
Hc, Hd, Hg, Hh	7.30 [$^3J_{HH}$ = 8.45]	7.52–7.62	7.45 (d, 1H) [$^3J_{HH}$ = 8.52]
Hp	7.90 (d, 1H) [$^3J_{Hp-Hn}$ = 7.67]	7.91(d,1H) [$^3J_{Hp-Hn}$ = 7.91]	7.80 (d, 1H) [$^3J_{Hp-Hn}$ = 7.66]

3. Results and discussion

3.1. IR spectroscopy

FT-IR frequencies of various diagnostic bands for the compounds (**3**–**5**) were given in Table 2. FT-IR spectra of the compounds **3**–**5** showed characteristic stretching bands of $\nu_{(C-H)arom}$ and $\nu_{(C=O)}$ between 3070–3058 cm^{-1} and 1740–1778 cm^{-1}. The vibration bands assignable to the stretching of the –P=N– and P–Cl bands for compounds **3**–**5** were observed at frequency in the range of 1163–1286 and 524–604 cm^{-1}, respectively. These data were in accordance with the reported values for phosphazene derivatives [33].

3.2. NMR spectroscopy

The proton-decoupled ^{31}P (^{31}P $\{^1H\}$) NMR spectral data of bridge phenolphthalein derivatives of hexachlorocyclotriphosphazatriene (**3**–**5**) were given in Table 3. Compound **3** had two different phosphorus environments within the molecule. ^{31}P $\{^1H\}$ NMR spectrum of compound **3** had A_2X spin systems and a typical example was shown in Fig. 2. In $^{31}P\{^1H\}$ NMR spectra, the resonance belonging to the POCl group was observed at 13.2 ppm as triplet and PCl_2 group was observed at 23.5 ppm as doublet. In general, resonance of PORCl group should be observed at *ca.* 30 ppm [23] but the compound **3** showed this resonance at 13.2 ppm may be due to the shielding effect. The chemical shift values of PORCl groups for compound **4** were observed at 13.2 and 16.2 ppm, and PCl_2 groups for compound **4** were observed at 23.6 and 25.7 ppm, respectively (Table 3 and Fig. 3). The ^{31}P $\{^1H\}$ NMR spectral data of compounds **4** and **5** were very similar. The chemical shift values of PORCl groups for compound **5** were observed at 12.4 and 14.6 ppm, and PCl_2 groups were observed at 22.5 and 24.6 ppm, respectively. The coupling constants of all compounds were very similar, *i.e.*, about 61–64 Hz because of all coupling constants between PCl_2 and [P(OR)Cl] groups (Table 3).

The ^{1}H NMR data also confirmed the structures of **3**–**5**. The aromatic protons for all the compounds were observed between 6.72 and 7.90 ppm and some of them were distinguishable from each other, ^{1}H NMR spectra of **3** and **5** were shown as an example in Fig. 4. In aromatic groups for **3**, Hp, Hn, Hm, Hk protons were resonated at 7.90, 7.67, 7.54, 7.47 ppm, in which those have three bond-coupling constants, average of *ca.* $^3J_{HH}$ = 7.5 Hz (Fig. 4). The chemical shifts of some aromatic protons and coupling constants were shown in Table 4. Values of chemical shifts for **3** were consistent with the literature values [34].

3.3. Ground state electronic absorption and fluorescence spectra

The absorption and fluorescence spectra of phosphazene derivatives were measured with diluted solutions (1×10^{-5} mol dm^{-3}) in dichloromethane (DCM). Compounds **3**–**5** were excited at 240 nm for fluorescence emission studies. The absorption bands were observed at 275 nm for all studied phenolphthalein bridged cyclotriphosphazatriene compounds **3**–**5** in dichloromethane (Fig. 5). The trend of absorption maximum among the corresponding cyclotriphosphazatriene compounds was increased with respect to number of the phenolphthalein group in dichloromethane (Fig. 5). Fluorescence emission spectra of phenolphthalein bridged cyclotriphosphazatriene compounds in DCM were shown in Fig. 6. Fluorescence emission peaks at 311 nm

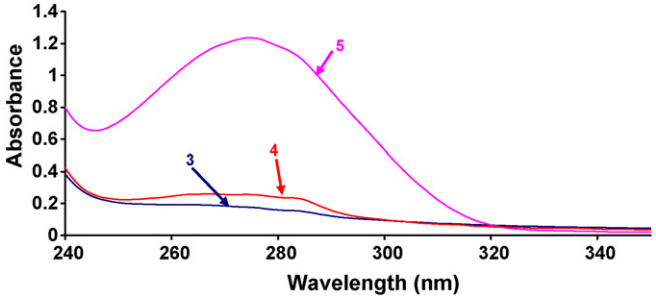


Fig. 5. The absorption spectra of **3**, **4** and **5** in dichloromethane. Concentration: 1×10^{-5} mol dm^{-3}.

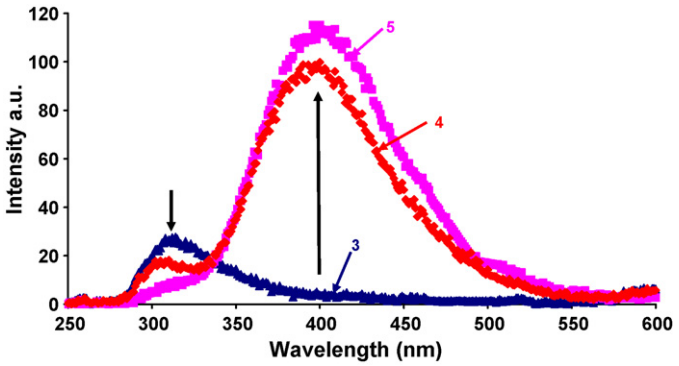


Fig. 6. The fluorescence emission spectra of **3**, **4** and **5** in dichloromethane. Concentration: 1×10^{-5} mol dm^{-3}; excitation wavelength: 240 nm.

for compound **3**, 311 and 400 nm for compound **4** and 400 nm for compound **5** were observed. The increase of the phenolphthalein group on cyclotriphosphazatriene ring caused the red shift from 311 to 400 nm in fluorescence emission of cyclotriphosphazatriene compounds in DCM. Compound **5** showed a higher fluorescence emission behaviour than that of compounds **3** and **4**. Increasing of the fluorescence behaviour with increasing of the number of the phenolphthalein group was explained by the non-covalent π–π interactions between aromatic double bonds of phenolphthalein group. These interactions have previously proposed for other phosphazene derivatives and that a detailed study of eximer formation [35–39]. The phenolphthalein bridged cyclotriphosphazatrienes (**3**–**5**) might lead to some applications for developing of OLED materials.

Acknowledgement

The author thanks the Shin Nisso Kako Co. Ltd. for gifts of $N_3P_3Cl_6$ and Gebze Institute of Technology Research Fund for partial support.

References

[1] M. Gleria, R.D. Jaeger, J. Inorg. Org. Polym. 11 (2001) 1–45.
[2] H.R. Allcock, M.E. Napierala, C.G. Cameron, S.J.M. O'Connor, Macromolecules 29 (1996) 1951–1956.
[3] J.L. Sassus, M. Graffeuil, P. Castera, J.F. Labarre, Inorg. Chim. Acta 108 (1985) 23–27.
[4] S. In, A.D. Lann, F. Oksman, E.L. Fournie, J.F. Labarre, H. Benoist, G.J. Fournie, Int. J. Immunopharm. 14 (1992) 871–876.
[5] K. Brandt, Z. Jedlinski, Makromol. Chem. Suppl. 9 (1985) 169–174.
[6] R.E. Singler, A.J. Deome, D.A. Dunn, M.J. Bieberich, Ind. Eng. Chem., Prod. Res. Dev. 25 (1986) 46–57.
[7] M.A. Keller, C.S. Saba, Anal. Chem. 68 (1996) 3489–3492.
[8] K. Inoue, T. Yamauchi, T. Itoh, E. Ihara, J. Inorg. Organomet. Polym. Mater. 17 (2007) 367–375.
[9] W. Vanek, Angew. Chem. Int. Ed. Engl. 8 (1969) 617–630.
[10] S.S. Krishnamurty, A.C. Sau, M. Woods, Adv. Inorg. Chem. Radiochem. 21 (1978) 41–112.
[11] C.W. Allen, in: I. Haiduc, B.D. Sowerby (Eds.), The Chemistry of Inorganic Homo- and Hetero-Cycles, Academic Press, London, vol. 2, 1987, p. 501.
[12] C.W. Allen, J. Fire Sci. 11 (1993) 320–328.
[13] K. Moriya, T. Masuda, S. Yano, T. Suzuki, M. Kajiwara, Mol. Cryst. Liq. Cryst. 318 (2001) 267–277.
[14] K. Moriya, T. Suzuki, S. Yano, S. Miyajima, J. Phys. Chem. B 105 (2001) 7920–7927.
[15] K. Moriya, T. Yamane, T. Suzuki, T. Masuda, H. Mizusaki, S. Yano, M. Kajiwara, Phosp. Sulfur Silicon 177 (2002) 1427–1432.
[16] J. Barber, M. Bardaj, J. Jimnez, A. Laguna, J. Martnez, L. Serrano, I. Zaragozano, J. Am. Chem. Soc. 127 (2005) 8994–9002.
[17] M.G. Muralidhara, N. Grover, V. Chandrasekhar, Polyhedron 12 (1993) 1509–1513.
[18] S. Besli, S.J. Coles, D.B. Davies, M.B. Hursthouse, A. Kılıç, R.A. Shaw, J. Chem. Soc. Dalton Trans. (2007) 2792–2801.
[19] N. Satish Kumar, K.C. Kumara Swamy, Polyhedron 23 (2004) 979–985.
[20] H.A. Al-Madfa, A.H. Alkubaisi, H.G. Parkers, R.A. Shaw, Heterocycles 28 (1989) 347–358.
[21] S. Beşli, S.J. Coles, D.B. Davies, R.J. Eaton, A. Kılıç, R.A. Shaw, Polyhedron 25 (2006) 963–974.
[22] K. Brandt, T. Kupka, J. Drozd, J.C. van de Grampel, A. Meetsma, A.P. Jekel, Inorg. Chim. Acta 228 (1995) 187–192.
[23] S.J. Coles, D.B. Davies, R.J. Eaton, M.B. Hursthouse, A. Kılıç, R.A. Shaw, G. Yenilmez Çiftçi, Polyhedron 25 (2006) 953–962.
[24] M.E. Amato, G.A. Carriedo, F.J. Garcia Alonso, J.L. García-Alvarez, G.M. Lombardo, G.C. Pappalardo, J. Chem. Soc. Dalton Trans. (2002) 3047–3053.
[25] S. Begec, Heteroatom. Chem. 18 (2007) 372–375.
[26] E.W. Ainscough, A.M. Brodie, A.B. Chaplin, J.M. O'Connor, C.A. Ottor, Dalton Trans. (2006) 1264–1266.
[27] (a) D. Dell, B.W. Fitzsimmons, R.A. Shaw, J. Chem. Soc. (1965) 4070–4073;
(b) G. Bandoli, U. Casellato, M. Gleria, A. Grassi, E. Montoneri, G.C. Pappalardo, J. Chem. Soc. Dalton Trans. (1989) 757–760.
[28] (a) F. Aslan, O. Halcı, M. Arslan, Heteroatom. Chem. 19 (2008) 158–162;
(b) F. Aslan, Z. Demirpence, R. Tatsiz, H. Turkmen, A.I. Ozturk, M. Arslan, Z. Anorg. Allg. Chem. 634 (2008) 1140–1144.
[29] V. Chandrasekhar, G. Thangavelu, S. Andavan, R. Azhakar, B.M. Pandian, Tetrahedron Lett. 47 (2006) 8365–8368.
[30] H.J. Bolink, E. Barea, R.D. Costa, E. Coronado, S. Sudhakar, C. Zhen, A. Sellinger, Org. Electron. 9 (2008) 155–163.
[31] S. Budavari, The Merck Index, 12th ed., Merck & Company Inc., Whitehall, NJ, 1996.
[32] (a) C. Wu, S. Bo, M. Siddiq, G. Yang, T. Chen, Macromolecules 29 (1996) 2989–2993;
(b) M. Strukelj, A.S. Hay, Macromolecules 25 (1992) 4721–4729.
[33] H. Dal, Y. Süzen, Spectrochim. Acta Part A 67 (2007) 1392–1397.
[34] B. Zhang, Z. Wang, X. Zhang, Polymer 50 (2009) 817–824.
[35] M. Gleria, F. Barigelletti, S. Dellonte, S. Lora, F. Minto, P. Bortolus, Chem. Phys. Lett. 83 (1981) 559–563.
[36] L. Flamigni, N. Camaioni, P. Bortolus, F. Minto, M. Gleria, J. Phys. Chem. 95 (1991) 971–975.
[37] M. Gleria, F. Minto, S. Lora, L. Busulini, P. Bortolus, Macromolecules 19 (1986) 574–578.
[38] B. Çoşut, F. Hacıvelioğlu, M. Durmuş, A. Kılıç, S. Yeşilot, Polyhedron 28 (2009) 2510–2516.
[39] G. Marcelo, E. Saiz, F. Mendicuti, G.A. Carriedo, F.G. Alonso, J.L. García-Alvarez, Macromolecules 39 (2006) 877–885.