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The synthesis and characterization of 4-isopropylanilino derivatives of cyclotriphosphazene

Aylin Uslu *, Şule Şahin Ün, Adem Kılıç, Şükriye Yılmaz, Fatma Yuksel, Ferda Hacıvelioğlu

Department of Chemistry, Gebze Institute of Technology, PB. 141, 41400 Kocaeli, Turkey

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ABSTRACT

Hexachlorocyclotriphosphazene $N_3P_3Cl_6$ and gem-disubstituted cyclotriphosphazene derivatives $N_3P_3Cl_4X_2$ (X = Ph, PhS, PhNH) were reacted with 4-isopropylaniline to give geminal tetra and hexa substituted compounds (**1a–4a**, **1b–4b**). The compounds (**1a–4a**, **1b–4b**) were separated by column chromatography on silica gel and analyzed by elemental analysis, mass spectrometry, and ^{31}P and ^{1}H NMR spectroscopies, and also crystal structures of **2a** and **3b** were determined by X-ray crystallography. Compounds were prepared to cover the normal ranges of C-, S- and N-substituents in cyclophosphazene (X = Cl, Ph, SPh, NHPh). Compounds (**1a–4a**, **1b–4b**) were reported for the first time. We additionally investigated the effect of substituent (Cl, Ph, SPh, NHPh) on ^{31}P NMR chemical shifts of neighboring phosphorus atoms.

1. Introduction

Phosphazenes are cyclic or linear molecules that contain a framework of alternating phosphorus and nitrogen atoms with two substituent groups attached to each phosphorus atom [1]. Cyclic phosphazenes are an important family of inorganic ring systems [2,3] which have attracted the attention of inorganic chemists in recent years because of their applications as flame retardants, antimicrobial agents, lithium-ion batteries, liquid crystals, organic light emitting diodes, membrane hydrogels, drug carriers, surfactants and phase transfer catalysts [4–16]. Also the preparation of new cyclophosphazene derivatives is very straightforward by a substitution reaction of chlorine atoms on the phosphorus and their physical and chemical properties can be tailored via appropriate selection of substituted groups of phosphorus atoms [17–20].

In this work, we report the synthesis of the geminal 4-isopropylanilino substituted derivatives of cyclotriphosphazenes $N_3P_3Cl_4X_2$ (X = Cl, Ph, PhS, PhNH). The structures of obtaining compounds (**1a–4a**, **1b–4b**) were characterized by elemental analysis, mass spectrometry, and ^{31}P and ^{1}H NMR spectroscopies and crystal structures of **2a** and **3b** were also confirmed by X-ray crystallography. In addition, relationships between substituents effect (Cl, Ph, SPh, NHPh) on phosphazene ring and ^{31}P NMR chemical shifts of 4-isopropylanilino substituted phosphorus were obtained for compounds (**1a–4a**) and (**1b–4b**).

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd.) was purified by fractional crystallization from hexane. The following chemicals were obtained from Merck; triethylamine (>99%), *n*-hexane (>96%), benzene (⩾99.5%), thiophenol (>98.0%), aniline (>99%), tetrahydrofuran (THF) (⩾99.0%), dichloromethane (⩾99.0%), diethyl ether (⩾99.0%), anhydrous sodium sulfate (⩾99.0%) ethyl acetate (⩾99.0%) and chloroform-d1, from Alfa Aesar; 4-isopropylaniline (>99%) and toluene (>99%). Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh and, Kieselgel 60, 70–230 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).

2.2. Equipment

Elemental analyses were carried out using a Thermo Finnigan Flash 1112 Instrument. Mass spectra were recorded on a Bruker MicrOTOF LC–MS spectrometer with the electrospray ionization method. ^{31}P and ^{1}H NMR spectra were recorded in $CDCl_3$ solutions on a Varian INOVA 500 MHz spectrometer using 85% H_3PO_4 as an external reference for ^{31}P and TMS as an internal reference for ^{1}H.

2.2.1. X-ray crystallography

Intensity data were recorded on a Bruker APEX II QUAZAR diffractometer. Absorption correction by multi-scan has been applied [21] and space groups were determined using XPREP implemented

* Corresponding author. Tel.: +90 262 6053129; fax: +90 262 6053101.
E-mail address: aylin@gyte.edu.tr (A. Uslu).

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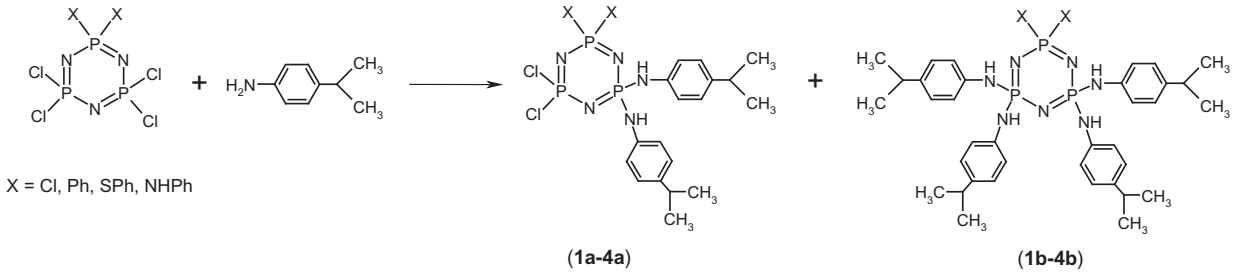

X =	Cl	(**1a**)	Cl	(**1b**)
	Ph	(**2a**)	Ph	(**2b**)
	SPh	(**3a**)	SPh	(**3b**)
	NHPh	(**4a**)	NHPh	(**4b**)

Scheme 1. The synthesis scheme of compounds (**1a**–**4a**, **1b**–**4b**).

in APEX2 [22]. Structures were determined using the direct methods procedure in SHELXS-97 [23] and refined by full-matrix least squares on F^2 using SHELXL-97 [23]. All non-hydrogen atoms were refined with anisotropic displacement parameters and C–H hydrogen atoms were placed in calculated positions and allowed to ride on the parent atoms. The final geometrical calculations and the molecular drawings were carried out with PLATON [24], and MERCURY [25] programs. Structure determinations have been deposited with the Cambridge Crystallographic Data Centre with references CCDC-886526 for structure **2a** and CCDC-886527 for structure **3b**.

2.3. Syntheses

The cyclotriphosphazene derivatives $N_3P_3Cl_4X_2$, (X = Ph, SPh, NHPh), which we used as starting compounds were prepared as given in the literature [26–28]. The reactions of cyclotriphosphazene and gem-disubstituted derivatives of cyclotriphosphazene with 4-isopropylaniline were done and compounds (**1a**–**4a**, **1b**–**4b**) (Scheme 1) were obtained.

2.3.1. Reaction of $N_3P_3Cl_6$ with 4-isopropylaniline to give compounds *1a* and *1b*

Triethylamine (1.60 mL,11.52 mmol) and 4-isopropylaniline (1.58 mL, 11.52 mmol) in 20 mL dry THF were added to a stirred solution of $N_3P_3Cl_6$ (1 g, 2.88 mmol) dissolved in 20 mL dry THF at room temperature under an argon atmosphere. The reaction mixture was refluxed for 8 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:ethylacetate (3:1) to give compounds **1a** (0.86 g, 54.9%, mp. 161.3 °C) and **1b** (0.08 g, 3.7%, mp. 212.3 °C).

2.3.2. Reaction of $N_3P_3Cl_4Ph_2$ with 4-isopropylaniline to give compounds *2a* and *2b*

Triethylamine (0.81 mL, 5.80 mmol) and 4-isopropylaniline (0.79 mL, 5.80 mmol) in 10 mL dry toluene were added to a stirred solution of $N_3P_3Cl_4(Ph)_2$ (0.5 g, 1.16 mmol) dissolved in 10 mL dry toluene at room temperature under an argon atmosphere. The reaction mixture was refluxed for 5 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:ethylacetate (8:1) to give compounds **2a** (0.23 g, 31.6%, mp. 155.0 °C) and **2b** (0.46 g, 48.1%, mp. 212.3 °C). Compound **2a** was crystallized from hexane-dichloromethane (1:4).

2.3.3. Reaction of $N_3P_3Cl_4(SPh)_2$ with 4-isopropylaniline to give compounds *3a* and *3b*

Triethylamine (0.70 mL, 5.05 mmol) and 4-isopropylaniline (0.68 mL, 5.05 mmol) in 10 mL dry THF were added to a stirred solution of $N_3P_3Cl_4(SPh)_2$ (0.5 g, 1.01 mmol) dissolved in 10 mL dry THF at room temperature under an argon atmosphere. The reaction mixture was refluxed for 10 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:THF (8:1) to give compounds **3a** (0.25 g, 35.8%, oily) and **3b** (0.07 g, 7.8%, mp. 206.5 °C). Compound **3b** was crystallized from hexane–dichloromethane (1:2).

2.3.4. Reaction of $N_3P_3Cl_4(NHPh)_2$ with 4-isopropylaniline to give compounds *4a* and *4b*

Triethylamine (0.76 mL, 5.43 mmol) and 4-isopropylaniline (0.74 mL, 5.43 mmol) in 10 mL dry toluene were added to a stirred solution of $N_3P_3Cl_4(NHPh)_2$ (0.5 g, 1.09 mmol) dissolved in 10 mL dry toluene at room temperature under an argon atmosphere. The reaction mixture was refluxed for 5 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:ethylacetate (3:1) to give compounds **4a** (0.24 g, 15.3%, mp. 209.3 °C) and **4b** (0.36 g, 16.8%, mp. 129 °C).

3. Results and discussion

3.1. Syntheses and characterizations of compounds *1a*–*4a*, *1b*–*4b*

Compounds **1a**–**4a** and **1b**–**4b** were obtained from the reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ and gem-disubstituted cyclotriphosphazene derivatives, $N_3P_3Cl_4X_2$ (X = Ph, PhS, PhNH) with 4-isopropylaniline (Scheme 1). In present work, compounds were prepared to cover the normal ranges of Cl-, C-, S- and N-substituents in di- or tetra- substituted 4-isopropylanilino derivatives

Table 1
^{31}P NMR parameters of compounds (**1a–4a**, **1b–4b**).[a]

Compound	Chemical shifts (ppm)			X	^{2}J(PP)/Hz		
	>PCl_2 (1)	>PX_2 (2)	>$P(NHR)_2$ (3)		1,2	1,3	2,3
1a	21.76		−1.86	Cl		48.30	
1b	24.35		0.98			53.10	
2a	21.14	19.47	−0.77	Ph	18.40	37.30	2020
2b		19.25	2.39				22.4
3a	21.46	45.95	−1.47	SPh	6.60	45.00	11.00
3b		45.64	1.57				17.90
4a[b]	24.15	0.66	0.99	NHPh	53.24	53.45	49.33
4b[c]		4.48	4.79				50.41

[a] 202, 38 MHz ^{31}P NMR measurements in $CDCl_3$ solutions at 293 K. Chemical shifts referenced to external H_3PO_4.
[b] ABX spin system, the parameters were obtained from simulation analysis.
[c] AB_2 spin system, the parameters were obtained from simulation analysis.

Table 2
^{1}H NMR chemical shifts (ppm) of compounds (**1a–4a**, **1b–4b**).[a]

Compound	Aromatic peaks of 4-isopropylaniline	CH_3	CH	NH	Aromatic peaks of substituent	
1a	d; 7.11 d; 7.00	d; 1.21	m; 2.85	4.99	Cl	
1b	m; 6.96 m; 6.91	m; 1.13	m; 2.75	4.89	Cl	
2a	d; 7.02 d; 6.99	d; 1.20	m; 2.82	5.03	Ph	m; 7.74 m; 7.46 m; 7.37
2b	m; 6.98 m; 6.93	m; 1.19	m; 2.80	5.31	Ph	m; 7.62 m; 7.36 m; 7.22
3a	d; 6.95 d; 6.76	d; 1.11	m; 2.73	4.42	SPh	m; 7.46 m; 7.29 m; 7.19
3b	m; 6.99 m; 6.90	m; 1.20	m; 2.82	5.30	SPh	m; 7.40 m; 7.31 m; 7.13
4a	d; 6.99 d; 7.03	d; 1.19	m; 2.82	5.14 5.06	NHPh	m; 7.17 m; 7.04 m; 6.93
4b	m; 6.97 m; 6.97	m; 1.20	m; 2.80	5.07 4.99	NHPh	m; 7.10 m; 7.00 m; 6.87

[a] ^{1}H NMR measurements at 499,95 MHz in $CDCl_3$ solution with chemical shifts referenced to internal TMS.

Table 3
Microanalysis and MS of compounds (**1a–4a**, **1b–4b**).

Compound	MH^+(*m*/*z*)(calc)	C(%) (calc)	H(%)(calc)	N(%) (calc)	Empirical formula
1a	546.68 (543)	39.48(39.66)	4.23(4.44)	12.58(12.85)	$C_{18}H_{24}C_{l4}N_5P_3$
1b	745.15 (741)	57.98(58.22)	6.28(6.51)	12.96(13.20)	$C_{36}H_{48}C_{l2}N_7P_3$
2a	626.12 (627)	57.28(57.34)	5.38(5.45)	11.08(11.14)	$C_{30}H_{34}C_{l2}N_5P_3$
2b	824.39 (825)	69.75(69.80)	7.05(7.08)	11.79(11.87)	$C_{48}H_{58}N_7P_3$
3a	692.60 (691)	51.87(52.03)	4.79(4.95)	09.87(10.11)	$C_{30}H_{34}C_{l2}N_5P_3S_2$
3b	890.79 (889)	64.58(64.77)	6.43(6.57)	10.89(11.02)	$C_{48}H_{58}N_7P_3S_2$
4a	658.65 (657)	54.67(54.72)	5.44(5.51)	14.76(14.89)	$C_{30}H_{36}C_{l2}N_7P_3$
4b	857.29 (855)	67.33(67.35)	7.05(7.07)	14.62(14.73)	$C_{48}H_{60}N_9P_3$

of cyclophosphazenes to investigate substituent effects on phosphorus chemical shifts. Although a mixture of mono-, di-, tri- and tetra-4-isopropylanilino substituted derivatives was formed, only di- and tetra-substituted products were isolated to provide a related set of compounds for comparison. The yields of the isolated compounds were low because of forming mixed substitution. All compounds were characterized by elemental analysis, mass spectrometry, and ^{31}P and ^{1}H NMR spectroscopies. In addition, the crystal structure of **2a** and **3b** were also confirmed by X-ray crystallography. The phosphorus chemical shifts, phosphorus–phosphorus coupling constants and ^{1}H NMR spectroscopy results were summarized in Tables 1 and 2, respectively, and the other analytical information was given in Table 3.

The spin systems of the compounds were interpreted as A_2X, AMX and ABX from the ^{1}H-decoupled ^{31}P NMR spectra of **1a**, **2–3a** and **4a**, respectively. The ^{31}P NMR spectrum of compound **4a** showed the ABX pattern due to the similar chemical environment of anilino substituted phosphorus atoms. ^{31}P NMR spectra showed the AX_2 and AB_2 spin systems for compounds **1–3b** and **4b**, respectively. The proton-decoupled ^{31}P NMR spectra of the

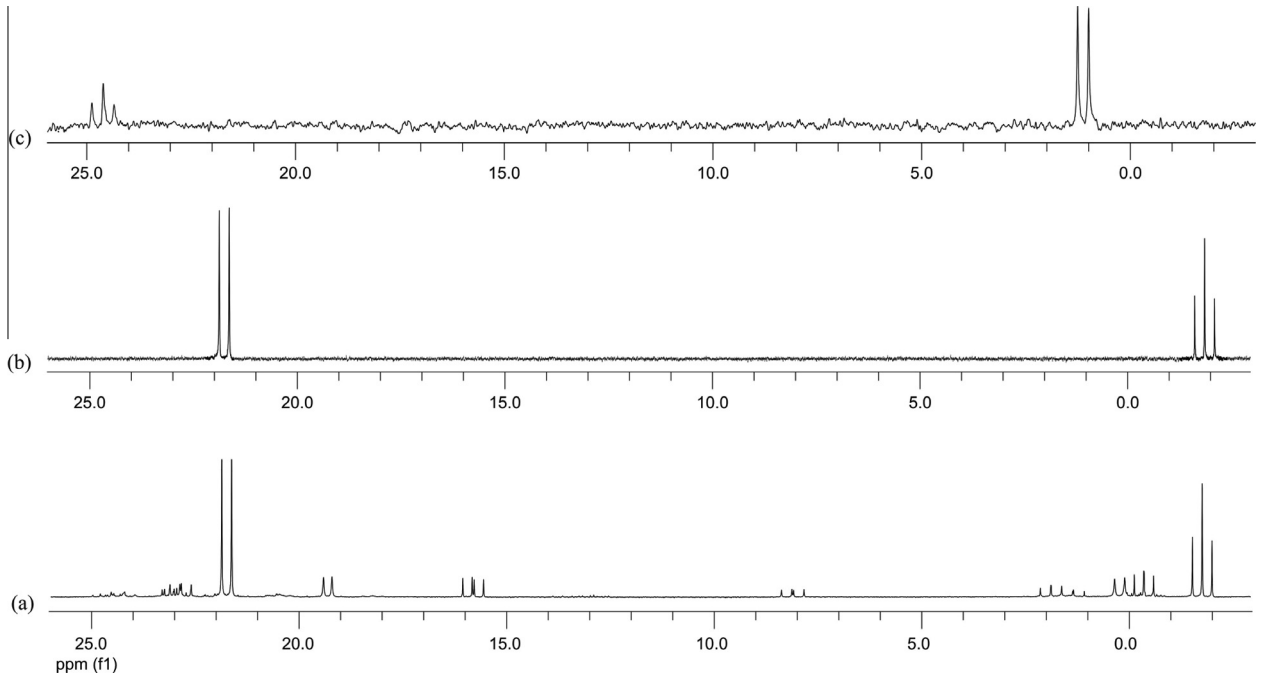

Fig. 1. Proton decoupled ^{31}P NMR spectra of (a) reaction mixture of **1a** and **1b** (b) compound **1a** (c) compound **1b**.

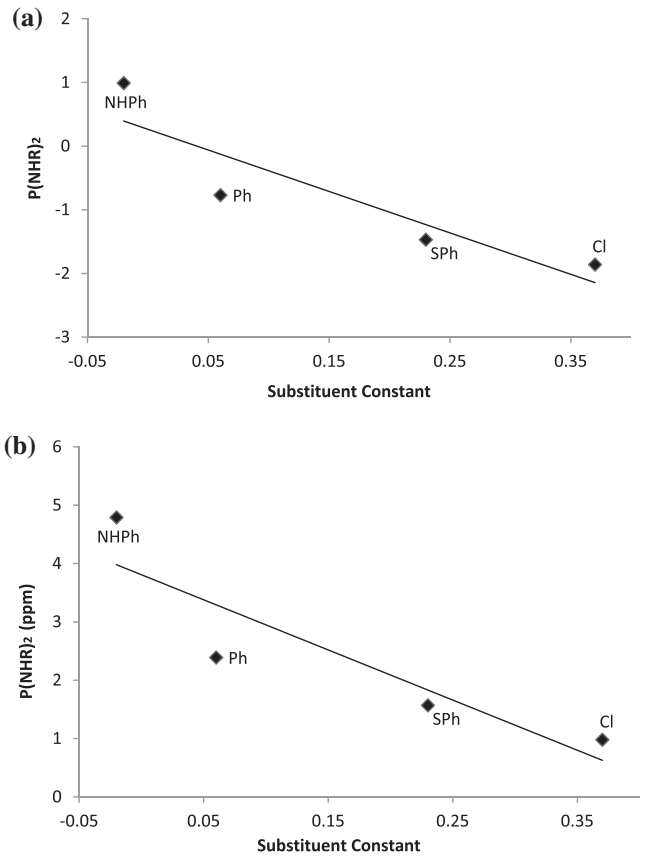

Fig. 2. Variations of the substituent constants – ^{31}P chemical shifts of >P(NHR)$_2$ (ppm) for (a) compounds (**1a**–**4a**); (b) compounds (**1b**–**4b**).

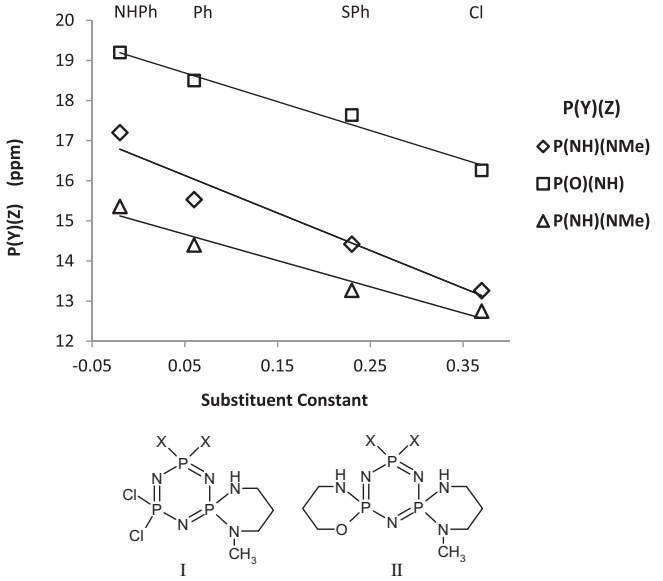

Fig. 3. Variations of the substituent constants – ^{31}P chemical shifts of P(Y)(Z) (ppm) for compounds **I** and **II** (trans) [29c]. (P(Y)(Z) chemical shift value is for >P(NH)(NMe) on compound **I**. P(Y)(Z) are >P(NH)(NMe) and >P(NH)(O) for compound **II**. X groups on PX_2 are Cl, SPh, Ph, NHPh groups).

reaction mixture of $N_3P_3Cl_6$ with 4-isopropylaniline and the spectra of the isolated compounds **1a** and **1b** from the reaction mixture were given as an example in Fig. 1. The spectra of the resulting reaction mixture showed the predominance of A_2X spin system due to the formation of the di-substituted 4-isopropylanilino phosphazene derivative **1a** and the minor product **1b** in AX_2 spin system. The remaining multiple small peaks can be attributed to the mono-, tri- and penta-4-isopropylanilino substituted compounds (Fig. 1a).

The electron withdrawing or releasing nature of the substituent on the cyclophosphazene ring can effect the ^{31}P chemical shift of neighboring phosphorus atoms and electron withdrawing or releasing behavior of the substituted group can be compared in geminal substituted cyclophosphazenes [29–30]. This substituent effect on neighboring phosphorus chemical shifts can be attributed

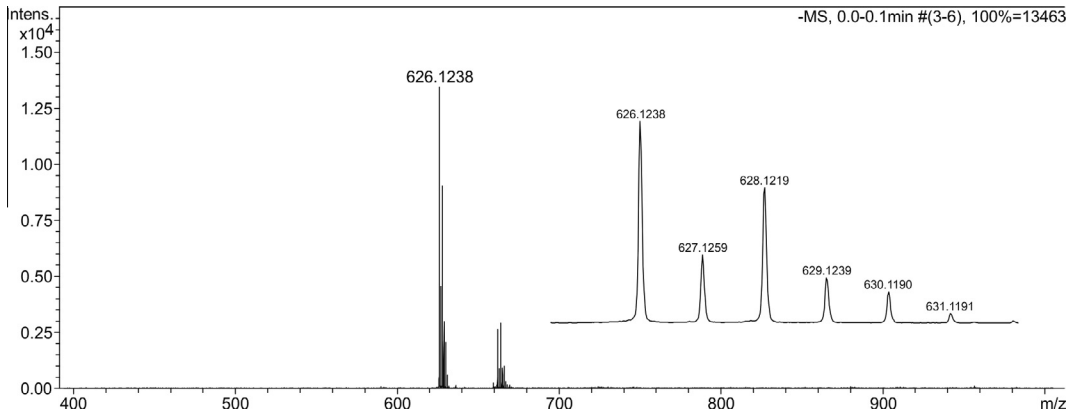

Fig. 4. Mass spectra of compound **2a**.

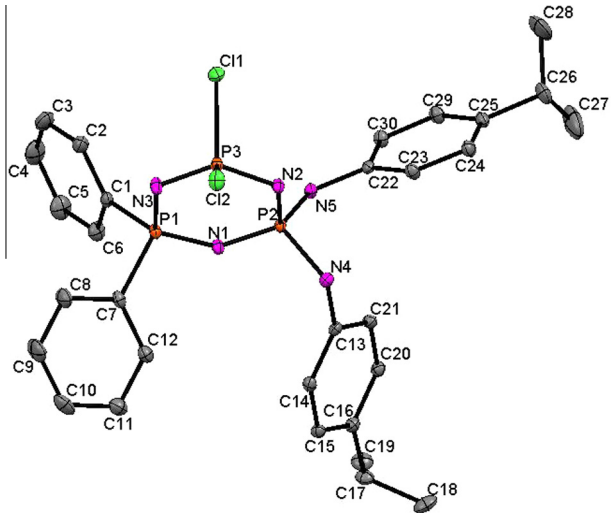

Fig. 5. Crystal structure of compound **2a** with the atom-numbering scheme. The hydrogen atoms have been omitted for clarity.

to negative hyperconjugative interactions [31]. The ^{31}P chemical shifts of 4-isopropylanilino substituted phosphorus (>P(NHR)$_2$) data for compounds **1a**–**4a** and **1b**–**4b** were evaluated with the Hammett substituent constants (σ) values of groups on neighboring phosphorus atom and variations between them were shown in Fig. 2 [32]. The substituent effects on the neighboring phosphorus chemical shifts for similar compounds reported in the literature were plotted as an example and the same trend in Fig. 3 was observed for these compounds [29c].

The mass spectrum of compound **2a** was given as an example in Fig. 4. It showed a molecular ion peak at m/z 626.12 and contained an isotope pattern indicating the presence of two chlorine atoms in the structure of **2a** (Fig. 4).

3.2. X-ray crystallographic characterizations of *2a* and *3b*

The molecular structures of compounds **2a**, and **3b** have been established by single crystal X-ray diffraction and their molecular structures are presented in Figs. 5 and 6, respectively. The compound **2a** gives monoclinic crystals, space group $C2/c$, while compound **3b** gives triclinic crystals, space group $P\bar{1}$. Other appropriate crystallographic data are summarized in Table 4. Furthermore, the molecular structure of compound **2b** was confirmed by X-ray. However, the crystal structure did not give a good refinement presumable due to poor crystal quality.

Compound **2a** contains the six-membered (N_3P_3) cyclophosphazene ring whose phosphorus atoms are gem-substituted with two phenyl, two chlorine and two 4-isopropylanilino-moieties (Fig. 5).

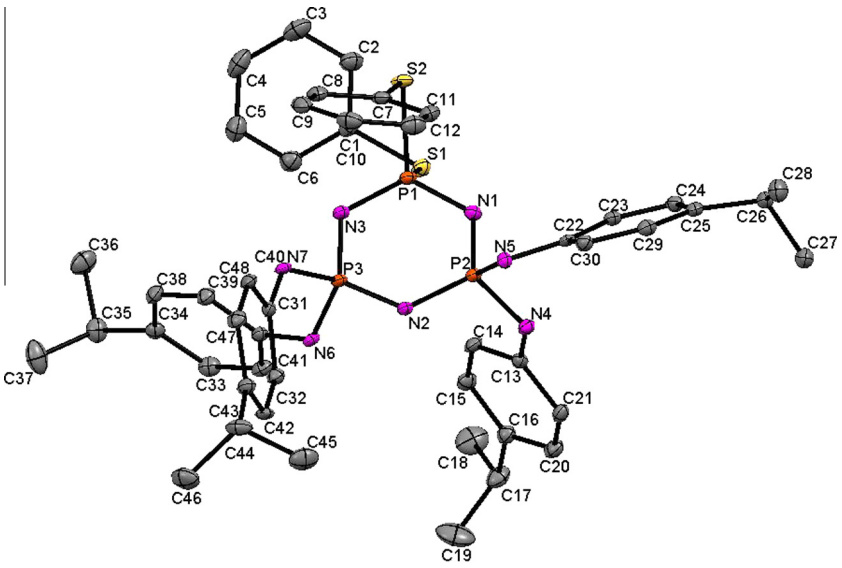

Fig. 6. Crystal structure of compound **3b** with the atom-numbering scheme. The hydrogen atoms have been omitted for clarity.

Table 4
Crystalographic data of compounds (**2a** and **3b**).

Compound	**2a**	**3b**
Empirical formula	$C_{30}H_{34}Cl_2N_5P_3$	$C_{48}H_{58}N_7P_3S_2$
Formula weight	628.43	890.04
T (K)	120(2)	120(2)
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	18.9842(9)	12.2067(7)
b (Å)	29.5057(14)	13.4508(8)
c (Å)	11.6680(6)	16.3160(10)
α (°)		70.953(4)
β(°)	100.851(2)	76.783(4)
γ (°)		72.268(4)
V (Å^3)	6418.9(5)	2387.0(2)
Z	8	2
D_{calc} (Mg/m^3)	1.301	1.238
Absorption coefficient (mm^{-1})	0.380	0.253
F(000)	2624	944
Crystal size (mm^3)	0.21 × 0.27 × 0.43	0.08 × 0.11 × 0.62
θ_{max} (°)	28.31	25.03
Reflections collected	29890	27132
Independent reflections	7978	8429
R_{int} (merging R value)	0.0261	0.0660
Parameter	371	561
R ($F^2 > 2\sigma F^2$)	0.0361	0.0501
wR (all data)	0.0985	0.1265
Goodness-of-fit (GOF) on F^2	1.029	1.031
$\Delta\rho$ Maximum/minimum (e Å^{-3})	1.342/−0.549	0.471/−0.578

The six-membered (N_3P_3) phosphazene ring is nearly planar with maximum deviation from the plane of the ring being only 0.0543 (14) Å (N3). The P–N bond lengths of N_3P_3 ring of **2a** are in the range of 1.5664(14)–1.6256(14) Å. Although these values are found within the normal range for those similar cyclophosphazene derivatives [29c,33–36], there is significant difference in P–N bond lengths for bonds involving PPh_2 [1.5932(14), and 1.6218(14) Å], and P(4-isopropylanilino)$_2$ [1.5906(14), and 1.6256(14) Å], compared to those involving PCl_2 groups [1.5744(13), and 1.5664(14) Å]. Similarly, the P(R$_1$)$_2$–N1–P(R$_2$)$_2$ [124.47(9)°; where R$_1$: Ph, R$_2$: 4-isopropylanilino] bond angle is slightly greater than those involving PCl_2 groups, P(R$_1$)$_2$–N3–PCl_2 [120.52(9)°] and P(R$_2$)$_2$–N2–PCl_2 [120.32(8)°]. Additionally, N–P–N bond angle belonging to PCl_2 phosphorus atom [121.52(7)°] is greater than other N–P–N bond angles [116.34(7)°, and 116.21(7)°] of cyclotriphosphazene ring. These behaviors were observed in previous structures [29c,37–39] and which was attributed to negative hyperconjugation [31a,b,e].

The crystal structure investigations of compound **2a** showed that weak inter-molecular hydrogen bonds and CH···Cg interactions between aromatic rings probably improve the stabilization of crystal packing (Table 5). The crystal structure of compound **3b** confirms that molecule contains the six-membered (N_3P_3) cyclophosphazene ring whose phosphorus atoms are gem-substituted with two thiophenyl-, and four 4-isopropylanilino- moieties (Fig. 6). The six-membered (N_3P_3) phosphazene ring is nearly planar in compound **3b** with maximum deviation from the plane of the cyclophosphazene ring being only 0.0693(12) Å (P3). In the N_3P_3 ring, The P–N bond lengths [1.585(3)–1.600(3) Å], P–N–P bond angles [122.97(16)–121.46(16)°] and N–P–N bond angles [116.48(13)–118.50(13)°] of are found in the normal ranges for many cyclotriphosphazenes [29c,33,37–40]. The variation in these values is not large compared to those in compound **2a** and there is no significant difference between those P(SPh)$_2$ and P(4-isopropylanilino)$_2$ moieties on the contrary of **2a**. This observation probably caused by similar steric and electron releasing or withdrawing effect of thiophenyl-, and 4-isopropylanilino-substituents on cyclotriphosphazene ring. Furthermore, the crystal packing of compound **3b** is stabilized by weak inter-molecular hydrogen bonds and CH···Cg interactions between aromatic rings as given in Table 5.

4. Conclusion

In this paper we report the synthesis and characterization of a series of 4-isopropylanilino derivatives of cyclotriphosphazene (**1a**–**4a**, **1b**–**4b**). All compounds have been fully characterized by standard spectroscopic techniques. The compounds **2a** and **3b** have been also determined by X-ray crystallography. It was seen that ^{31}P chemical shifts of >P(isopropylanilino)$_2$ nuclei of compounds (**1a**–**4a**, **1b**–**4b**) moved downfield with the substituents of neighboring phosphorus atom in the order Cl < SPh < Ph < NHPh.

Acknowledgement

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Table 5
Selected inter-molecular interactions for compound **2a**, and **3b**.

D–H···A	D–H	H···A	D···A	DHA	Symmetry code
2a					
N4–H1···N2	0.864(15)	2.308(15)	3.1628(19)	170.2(16)	1 − x, y, 3/2 − z
C2–H3···N3	0.95	2.61	3.034(2)	107	
C12–H12···N1	0.95	2.60	3.036(2)	108	
C18–H18c···Cg1[a]		2.74	3.696(2)	167	1 − x, y, 1/2 − z
C20–H20···Cg2[b]		2.85	3.6104(17)	138	1/2 − x, 1/2 − y, 1 − z
C30–H30···Cg1[a]		2.77	3.6970(19)	165	1/2 − x, 1/2 − y, 1 − z
3b					
N4–H1···N2	0.86 (2)	2.35(3)	3.155(4)	157(3)	1 − x, 2 − y, −z
C39–H39···N7	0.95	2.57	3.261(4)	130	
C14–H15···Cg3[c]		2.60	3.337(3)	135	x, y, z
C21–H21···Cg4[d]		2.66	3.382(4)	132	1 − x, 2 − y, −z
C30–H30···Cg5[e]		2.79	3.652(4)	152	1 − x, 2 − y, −z
C33–H33···Cg6[f]		2.81	3.713(4)	160	1 − x, 1 − y, 1 − z

[a] Centroid of ring C13/C14/C15/C16/C20/C21 in compound **2a**.
[b] Centroid of ring C1/C2/C3/C4/C5/C6 in compound **2a**.
[c] Centroid of ring P1/N1/P2/N2/P3/N3 in compound **3b**.
[d] Centroid of ring C40/C41/C42/C43/C47/C48 in compound **3b**.
[e] Centroid of ring C13/C14/C15/C16/C20/C21 in compound **3b**.
[f] Centroid of ring C1/C2/C3/C4/C5/C6 in compound **3b**.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.05.031.

References

[1] C.W. Allen, Chem. Rev. 9 (1991) 119.
[2] M. Gall, M. Breza, Polyhedron 28 (2009) 521.
[3] V. Chandrasekhar, S. Nagendran, Chem. Soc. Rev. 30 (2001) 193.
[4] İ. Ün, H. İbişoğlu, A. Kılıç, Ş. Şahin Ün, F. Yuksel, Inorg. Chim. Acta 387 (2012) 226.
[5] K. Tao, J. Li, L. Xu, X. Zhao, L. Xue, X. Fan, Q. Yan, Polym. Degrad. Stab. 96 (2011) 1248.
[6] P. Dallas, V.K. Sharma, R. Zbori, Adv. Colloid Interface Sci. 166 (2011) 119.
[7] S.V. Sazhin, M.K. Harrup, K.L. Gering, J. Power Sources 196 (2011) 3433.
[8] J. Jimenez, A. Laguna, A.M. Molter, J.L. Serrano, J. Barbera, L. Oriol, Chem. Eur. J. 17 (2011) 1029.
[9] M.S. Soh, S.A.G. Santamaria, E.L. Williams, J. Polym. Sci., Part B: Polym. Phys. 49 (2011) 531.
[10] Y.J. Jun, U.S. Toti, H.Y. Kim, J.Y. Yu, B.J. Jeong, M.J. Jun, Y.S. Sohn, Angew. Chem., Int. Ed. 45 (2006) 6173.
[11] B. Baroli, G. Delogu, A.M. Fadda, G. Podda, C. Sinico, Int. J. Pharm. 183 (1999) 101.
[12] D.E. Brown, K. Ramachandran, K.R. Carter, C.W. Allen, Macromolecules 34 (2001) 2870.
[13] Y. Zhu, J. Fu, L. Zhu, X. Tang, X. Huang, Polym. Int. 57 (2008) 449.
[14] S.T. Feia, R.M. Wooda, D.K. Leea, D.A. Stonea, H.L. Changb, H.R. Allcock, J. Membr. Sci. 320 (2008) 206.
[15] N.R. Krogman, M.D. Hindenlang, L.S. Nair, C.T. Laurencin, H.R. Allcock, Macromolecules 41 (2008) 8467.
[16] M. Gümüşderelioğlu, A. Gür, React. Funct. Polym. 52 (2002) 71.
[17] B. Çoşut, S. Yeşilot, Polyhedron 35 (2012) 101.
[18] B. Çoşut, M. Durmuş, A. Kılıç, S. Yeşilot, Inorg. Chim. Acta 366 (2011) 161.
[19] S. Sudhakar, A. Sellinger, Macromol. Rapid Commun. 27 (2006) 247.
[20] S. Beşli, M. Durmuş, H. İbişoğlu, A. Kılıç, F. Yuksel, Polyhedron 29 (2010) 2609.
[21] Bruker, SADABS, Bruker AXS Inc, Madison, Wisconsin, USA, 2005.
[22] Bruker APEX2 (Version 2011.4-1). Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
[23] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112–122.
[24] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
[25] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, S.J. Towler, J. Appl. Crystallogr. 39 (2006) 453.
[26] V.B. Desai, R.A. Shaw, B.C. Smith, J. Chem. Soc. (1970) 2023.
[27] K.G. Alcock, R.A. Shaw, F.B.G. Wells, J. Chem. Soc. (1964) 121.
[28] A.P. Carroll, R.A. Shaw, J. Chem. Soc. (1966) 914.
[29] (a) B. Çoşut, H. İbişoğlu, A. Kılıç, S. Yeşilot Inorg, Chim. Acta 362 (2009) 4931; (b) S. Yeşilot, B. Çoşut, Inorg. Chem. Commun. 10 (2007) 88; (c) Ş. Şahin Ün, A. Uslu, S. Yeşilot, İ. Ün, B. Çoşut, F. Yuksel, A. Kılıç, Polyhedron 30 (2011) 1587.
[30] (a) H.S. Wu, S.S. Meng, Ind. Eng. Chem. Res. 37 (1998) 675; (b) P.J. Harris, Inorg. Chim. Acta 71 (1983) 233.
[31] (a) D.G. Gilheany, Chem. Rev. 94 (1994) 1339; (b) A.B. Chaplin, J.A. Harrison, P.J. Dyson, Inorg. Chem. 44 (2005) 8407; (c) M. Calichman, A. Derecskei-Kovacs, C.W. Allen, Inorg. Chem. 46 (2007) 2011; (d) K.R. Carter, M. Calichman, C.W. Allen, Inorg. Chem. 48 (2009) 7476; (e) A. Okumuş, Z. Kılıç, T. Hökelek, H. Dal, L. Açık, Y. Öner, L.Y. Koç, Polyhedron 30 (2011) 2896.
[32] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 97 (1991) 165.
[33] J.F. Bickley, R. Bonar-Law, G.T. Lawson, P.I. Richards, F. Rivals, A. Steiner, S. Zacchini, Dalton Trans. (2003) 1235.
[34] G.Y. Ciftci, H. Dal, E.T. Ecik, T. Hökelek, A. Kılıç, E. Şenkuytu, Polyhedron 29 (2010) 1209.
[35] S. Bilge, S. Demiriz, A. Okumuş, Z. Kılıç, B. Tercan, T. Hökelek, O. Büyükgüngör, Inorg. Chem. 45 (2006) 8755.
[36] B. Tercan, T. Hökelek, S. Bilge, A. Natsagdorj, S. Demiriz, Z. Kılıç, Acta Crystallogr., Sect. E 60 (60) (2004) o795.
[37] G.Y. Çitfçi, E. Şenkuytu, E.T. Eçik, A. Kılıç, F. Yuksel, Polyhedron 30 (2011) 2227.
[38] N. Asmafiliz, E.E. Ilter, M. Işıklan, Z. Kılıç, B. Tercan, N. Çaylak, T. Hökelek, O. Büyükgüngör, J. Mol. Struct. 832 (2007) 172.
[39] N.V. Mani, F.R. Ahmed, W.H. Barnes, Acta Crystallogr. 21 (1966) 375.
[40] M. Krishnaiah, L. Ramamurthy, H. Manohar, S.S. Krishnamurthy, T.S. Cameron, Acta Crystallogr., Sect. A 40 (1984) C220.