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Journal of Molecular Structure 691 (2004) 249–257

Journal of MOLECULAR STRUCTURE

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Preparation and characterization of chromophore group containing cyclotriphosphazenes: IV spectroscopic and thermal investigation of some hexakis(*p*-phenylazo-*o*-allylphenoxy)cyclotriphosphazenes

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Received 5 September 2003; revised 5 December 2003; accepted 18 December 2003

Abstract

Some new substituted cyclotriphosphazenes were prepared by the reaction of hexachlorocyclotriphosphazene and 3-allyl-4-hydroxyazo compounds such as 3-allyl-4-hydroxyazobenzene, 4′-chloro-3-allyl-4-hydroxyazobenzene, 4′-methyl-3-allyl-4-hydroxyazobenzene, 4′-bromo-3-allyl-4-hydroxyazobenzene, 4′-acetyl-3-allyl-4-hydroxyazobenzene, 3′,4′-dimethyl-3-allyl-4-hydroxyazobenzene and 4′-iodo-3-allyl-4-hydroxyazobenzene. They are characterized by UV–VIS, FT-IR, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, TG, DTG and DTA.
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Keywords: Cyclotriphosphazenes; Azo dyes; UV–VIS; IR; NMR; Thermal analysis

1. Introduction

Azo compounds are the oldest and largest class of industrial synthesized organic dyes. There are about 3000 azo dyes currently in use all over the world. The great majority of them are monoazo compounds, which have the common structure unit of the azo chromophore, –N=N–, linking two aromatic systems. The textile industry is the largest consumer of dyestuffs. Some azo dyes have been reported to be toxic but five of the nine synthetic colorants permitted in food in the United States are monoazo dyes [1,2]. Dozens of additional monoazo dyes are permitted in drugs and cosmetics [1]. Furthermore, azo compounds have been utilized as analytical reagents [3] and they can also be used as materials for non-linear optics and for storage optical information in laser disks [4]. The research of synthesizing azo compounds has received much attention over the years. Though many kinds of azo dyes have been synthesized, cyclotriphosphazene derivatives are relatively rare. Monoazo [5,6] and bis-azo [7] chromophore group carrying some cyclotriphosphazene derivatives were synthesized and some of their properties were investigated. We report herein the synthesis of 3-allyl-4-hydroxyazobenzene compounds and their cyclotriphosphazene derivatives such as methyl, acetyl, chloro, bromo, iyodo and unsubstituted ring. The new compounds have been characterized by using UV–VIS, FT-IR, ^{1}H-NMR, ^{13}C-NMR, elemental and thermal analysis techniques.

2. Results and discussion

2.1. Synthesis

Azo chromophore carrying *o*-allylphenoxycyclotriphosphazenes **5** were synthesized by the cyclotriphosphazene **4** and *p*-phenylazo-*o*-allylphenol dyes **3** which are synthesized with azo-coupling reactions of substituted benzenediazonium salts and *o*-allylphenol shown in Scheme 1 and Table 1. Substituted anilines **1** were diazotized using sodium nitrite in the presence of hydrochloric acid followed by coupling with *o*-allylphenol substrate **2** to produce *p*-phenylazo-*o*-allylphenol dyes **3** in good yield. The dyes **3** and their cyclotriphosphazene derivatives **5** were purified by recrystallization from suitable solvents and their purity was examined by thin-layer chromatography.

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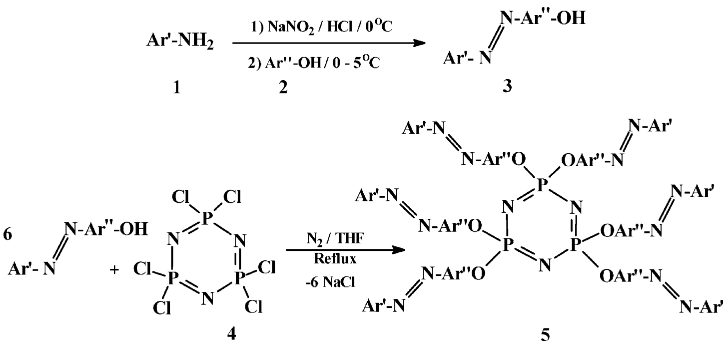
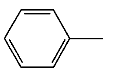
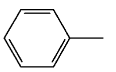
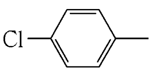
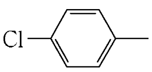
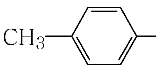
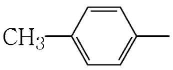
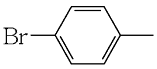
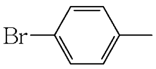
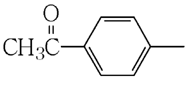
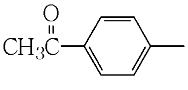
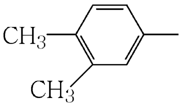
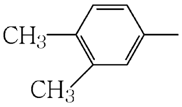
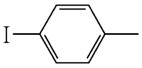
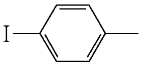
0022-2860/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2003.12.034



Scheme 1.

Table 1
Synthesized and properties of *p*-phenylazo-*o*-allylphenols **3** and its cyclotriphosphazene derivatives **5** (Ar″, *o*-allylphenol)

Compound	Ar′	Yield (%)[a]	Mp (°C)	%C calculated (found)	%H calculated (found)	%N calculated (found)
3a		75	89–91	–	–	–
5a		62	53–55[b]	69.94 (69.45)	5.01 (4.97)	13.49 (12.95)
3b		82	98–99	–	–	–
5b		55	56–58[b]	61.22 (61.38)	4.08 (4.18)	11.90 (11.21)
3c		85	84–85	–	–	–
5c		64	44–46[b]	70.20 (69.97)	5.48 (5.57)	12.80 (11.93)
3d		78	105–107	–	–	–
5d		66	58–60[b]	53.17 (53.57)	3.54 (3.60)	10.33 (9.94)
3e		78	114–115	–	–	–
5e		68	63–65[b]	67.66 (67.43)	4.97 (5.35)	11.61 (11.08)
3f		80	131–133	–	–	–
5f		76	60–62[b]	70.95 (71.05)	5.91 (5.95)	12.17 (11.74)
3g		77	134–136	–	–	–
5g		66	62–64[b]	46.69 (46.43)	3.11 (3.69)	9.08 (8.73)

[a] Isolated yields.

[b] Decomposition point.

Table 2
UV–VIS absorption bands of *p*-phenylazo-*o*-allylphenols **3** and its cyclotriphosphazene derivatives **5** in $CHCl_3$

Compound	$n \rightarrow \pi^*$ nm (ε)	$\pi \rightarrow \pi^*$ nm (ε)
3a	445 (2950)	350 (26950)
5a	**439 (3500)**	**326 (26525)**
3b	455 (3223)	357 (30320)
5b	**437 (4029)**	**332 (33685)**
3c	451 (2580)	353 (23800)
5c	**434 (4230)**	**333 (25400)**
3d	457 (2430)	358 (27390)
5d	**430 (4190)**	**335 (32430)**
3e	471 (2620)	368 (33430)
5e	**446 (3690)**	**336 (36500)**
3f	449 (3228)	355 (22168)
5f	**432 (6456)**	**338 (24383)**
3g	452 (2857)	364 (28525)
5g	**443 (3210)**	**342 (34456)**

2.2. UV–VIS absorption spectra

Typical characteristic UV–VIS absorption bands of *p*-phenylazo-*o*-allylphenols **3** and its cyclotriphosphazene derivatives **5** in $CHCl_3$ are given in Table 2. UV–VIS spectra of the azo side group carrying *o*-allylphenols **3** are found to be similar to the spectra of their cyclotriphosphazene **5** derivatives. Thus, delocalization effects between the substituents and phosphazene ring were not detected as previous researches [7–10]. Cyclotriphosphazene ring themselves do not absorb in near UV region [11], but if there were delocalization, an absorption would be seen in this region. The electronic transitions, were assigned as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ according to absorption of similar azo dyes [12]. The absorption maxima (λ_{max}) were observed in the range of 430–471 and 326–368 nm for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, respectively (Table 2). The hypsochromic shift is observed in UV–VIS absorptions, when the *p*-phenylazo-*o*-allylphenols are converted to their cyclotriphosphazene derivatives. The λ_{max} values of *p*-phenylazo-*o*-allylphenols and its cyclotriphosphazene derivatives were also affected by substituted group at phenyl ring.

2.3. IR absorption spectra

The characteristic IR absorption bands of *p*-phenylazo-*o*-allylphenols **3** and *p*-phenylazo-*o*-allylphenoxycyclotriphosphazenes **5** are determined in KBr disk. As shown in Table 3, the *p*-phenylazo-*o*-allylphenoxycyclotriphosphazene compounds have four characteristic absorption bands. These bands are shown at 1412–1438, 1151–1202, 1232–1241 and 950–961 cm^{-1} are due to N=N, P=N, P–N–$P_{(asym)}$, and P–N–$P_{(sym)}$, respectively.

When the IR spectra of *p*-phenylazo-*o*-allylphenols **3** and its derivatives *p*-phenylazo-*o*-allylphenoxycyclotriphosphazenes **5** are compared, it is seen that the OH vibration at 3125–3530 cm^{-1} region disappeared and a new band appeared at 1066–1081 cm^{-1} region of the spectrum because of P–OAr absorption (Table 3). The absorption frequency's of N=N and $C_{(aryl)}$–N of *p*-phenylazo-*o*-allylphenols **3** changed a few cm^{-1} in *p*-phenylazo-*o*-allyl phenoxycyclotriphosphazenes **5**. These changes are attributed to the replacement of H with the P atom and the hindrance of the resonance between the N=N group and the phenyl ring. Similar observations were reported for some bis-azo compounds and their derivatives [7].

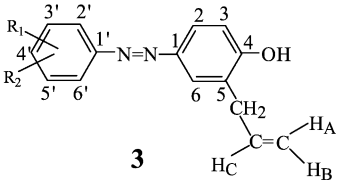
2.4. NMR investigations

In the ^{1}H-NMR spectra, all azo dyes **3** show one peak at 9.05–9.34 ppm which belongs to the hydroxyl group as cited in the previous works [5,7,8]. After the reactions mentioned above are carried out this peak disappears in this range. The ^{1}H-NMR spectra of the synthesized compounds show *dd* peaks at 5.07–5.19 ppm and *d* at 3.47–3.57 ppm and *ddt* at 5.97–6.09 ppm, which are attributed to allyl

Table 3
FT-IR bands (cm^{-1}) of *p*-phenylazo-*o*-allylphenols **3** and *p*-phenylazo-*o*-allylphenoxycyclotriphosphazenes **5** (KBr disk)

Compound	OH	N=N	Ar–N=	C=C (allyl)	P–N–P (asym)	P–N–P (sym)	P=N	P–OAr	C=O
3a	3350–3250	1425	1137	1639	–	–	–	–	–
5a	–	**1437**	**1120**	**1636**	**1235**	**950**	**1191–1165**	**1072**	–
3b	3520–3275	1412	1125	1642	–	–	–	–	–
5b	–	**1418**	**1122**	**1639**	**1233**	**957**	**1193–1165**	**1066**	–
3c	3490–3125	1428	1130	1644	–	–	–	–	–
5c	–	**1435**	**1128**	**1638**	**1232**	**956**	**1196–1151**	**1075**	–
3d	3460–3125	1425	1135	1646	–	–	–	–	–
5d	–	**1432**	**1133**	**1638**	**1232**	**952**	**1191–1155**	**1080**	–
3e	3530–3272	1412	1145	1637	–	–	–	–	1675
5e	–	**1422**	**1142**	**1645**	**1234**	**956**	**1197–1164**	**1081**	**1682**
3f	3522–3187	1430	1125	1634	–	–	–	–	–
5f	–	**1438**	**1123**	**1638**	**1241**	**961**	**1202–1164**	**1079**	–
3g	3351–3180	1432	1138	1635	–	–	–	–	–
5g	–	**1436**	**1133**	**1638**	**1236**	**953**	**1192–1163**	**1078**	–

Table 4
^{1}H-NMR spectral data of **3a–g** compounds in aceton-d$_6$



3

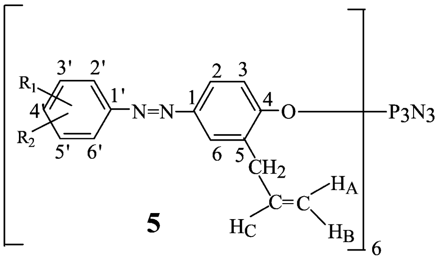
a) R_1=R_2=H; **b)** R_1=4 -Cl, R_2=H; **c)** R_1=4 -CH_3, R_2=H; **d)** R_1=4 -Br, R_2=H;
e) R_1=4 -CH_3C=O, R_2=H; **f)** R_1=3 -CH_3, R_2=4 -CH_3; **g)** R_1=I, R_2=H

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
–OH	9.25 (s)	9.34 (s)	9.30 (s)	9.30 (s)	9.34 (s)	9.05 (s)	9.31 (s)
H$_A$	5.15 (dd) $J_{A,B} = 2.95$ $J_{A,C} = 16.92$	5.16 (dd) $J_{A,B} = 1.96$ $J_{A,C} = 17.62$	5.18 (dd) $J_{A,B} = 1.92$ $J_{A,C} = 17.13$	5.16 (dd) $J_{A,B} = 1.92$ $J_{A,C} = 17.05$	5.16 (dd) $J_{A,B} = 1.91$ $J_{A,C} = 17.04$	5.16 (dd) $J_{A,B} = 1.97$ $J_{A,C} = 15.45$	5.15 (dd) $J_{A,B} = 1.98$ $J_{A,C} = 17.10$
H$_B$	5.08 (dd) $J_{B,A} = 2.95$ $J_{B,C} = 10.17$	5.09 (dd) $J_{B,A} = 1.96$ $J_{B,C} = 10.05$	5.09 (dd) $J_{B,A} = 1.92$ $J_{B,C} = 10.11$	5.07 (dd) $J_{B,A} = 1.92$ $J_{B,C} = 10.07$	5.08 (dd) $J_{B,A} = 1.91$ $J_{B,C} = 10.21$	5.08 (dd) $J_{B,A} = 1.97$ $J_{B,C} = 10.13$	5.08 (dd) $J_{B,A} = 1.98$ $J_{B,C} = 10.12$
H$_C$	6.09 (ddt) $J_{C,CH_2} = 6.65$ $J_{C,A} = 16.92$ $J_{C,B} = 10.17$	6.08 (ddt) $J_{C,CH_2} = 6.60$ $J_{C,A} = 17.62$ $J_{C,B} = 10.05$	6.08 (ddt) $J_{C,CH_2} = 6.64$ $J_{C,A} = 17.13$ $J_{C,B} = 10.11$	6.05 (ddt) $J_{C,CH_2} = 6.64$ $J_{C,A} = 17.05$ $J_{C,B} = 10.07$	6.09 (ddt) $J_{C,CH_2} = 6.62$ $J_{C,A} = 17.04$ $J_{C,B} = 10.21$	6.08 (ddt) $J_{C,CH_2} = 6.63$ $J_{C,A} = 15.45$ $J_{C,B} = 10.13$	6.07 (ddt) $J_{C,CH_2} = 6.64$ $J_{C,A} = 17.10$ $J_{C,B} = 10.12$
–CH$_2$–	3.49 (d) $J_{CH_2},C = 6.65$	3.49 (d) $J_{CH_2},C = 6.60$	3.50 (d) $J_{CH_2},C = 6.64$	3.49 (d) $J_{CH_2},C = 6.64$	3.50 (d) $J_{CH_2},C = 6.62$	3.48 (d) $J_{CH_2},C = 6.63$	3.49 (d) $J_{CH_2},C = 6.64$
CH$_3$–	–	–	2.42 (s)	–	2.64 (s)	2.35 (s) and 2.32 (s)	–
H2	7.60–7.44 (m)	7.46 (dd) $J_{2,3} = 8.36$ $J_{2,6} = 1.96$	7.36 (dd) $J_{2,3} = 8.42$ $J_{2,6} = 1.90$	7.52 (dd) $J_{2,3} = 8.39$ $J_{2,6} = 1.90$	7.76 (dd) $J_{2,3} = 8.40$ $J_{2,6} = 1.96$	7.28 (dd) $J_{2,3} = 8.43$ $J_{2,6} = 1.95$	7.34 (dd) $J_{2,3} = 8.38$ $J_{2,6} = 1.96$
H3	7.06 (d) $J_{3,2} = 8.37$	7.06 (d) $J_{3,2} = 8.36$	7.05 (d) $J_{3,2} = 8.42$	7.05 (d) $J_{3,2} = 8.39$	7.07 (d) $J_{3,2} = 8.40$	7.02 (d) $J_{3,2} = 8.43$	7.05 (d) $J_{3,2} = 8.38$
H6	7.60–7.44 (m)	7.76 (d) $J_{6,2} = 1.96$	7.70 (d) $J_{6,2} = 1.90$	7.77 (d) $J_{6,2} = 1.90$	7.83 (d) $J_{6,2} = 1.96$	7.56 (d) $J_{6,2} = 1.95$	7.75 (d) $J_{6,2} = 1.96$
H2$'$, H6$'$	7.88 (m) $J_{2',3'} = 8.19$ $J_{2',6'} = 1.98$	7.58 (dd) $J_{2',3'} = 8.70$ $J_{2',6'} = 2.06$	7.79 (dd) $J_{2',3'} = 8.37$ $J_{2',6'} = 2.06$	7.81 (dd) $J_{2',3'} = 8.99$ $J_{2',6'} = 2.00$	7.94 (dd) $J_{2',3'} = 8.55$ $J_{2',6'} = 2.00$	7.75 (d) (*H2$'$*) $J_{2',6''} = 2.37$ 7.64 (dd) (*H6$'$*) $J_{5',6''} = 7.61$ $J_{6',2'} = 2.37$	7.66 (dd) $J_{2',3'} = 8.65$ $J_{2',6'} = 1.83$
H3$'$, H5$'$	7.75 (m) $J_{3',2'} = 8.19$ $J_{3',5'} = 1.98$	7.87 (dd) $J_{3',2'} = 8.70$ $J_{3',5'} = 2.06$	7.75 (dd) $J_{3',2'} = 8.37$ $J_{3',5'} = 2.06$	7.72 (dd) $J_{3',2'} = 8.99$ $J_{3',5'} = 2.00$	8.14 (dd) $J_{3',2'} = 8.55$ $J_{3',5'} = 2.00$	7.71 (d) $J_{5',6'} = 7.61$	7.94 (dd) $J_{3',2'} = 8.65$ $J_{3',5'} = 1.83$
H4$'$	7.75 (m) $J_{3',2'} = 8.19$ $J_{3',5'} = 1.98$	–	–	–	–	–	–

group. The phenyl groups were also observed in the 7.02–8.14 ppm region, as given in Tables 4 and 5. Various protons of azo dyes **3** have appeared in their usual pattern [5] but with a slight chemical shift compared to the phosphazene derivatives **5**. The peaks of substituted methyl groups are also given in Tables 4 and 5.

The ^{13}C-NMR spectra of azo dyes **3** have shown the characteristic chemical shift with slight shift compared to its phosphazene derivatives **5** (Tables 6 and 7). Considering all dyes synthesized, it is clearly seen that *p*-hydroxyazobenzene derivatives exist exclusively in the azo form and do not form any intramolecular hydrogen bond [12–14]. As can be observed from the values of C4 atoms of the dyes that the chemical shift values are 158.76–159.87 ppm and it is in 151.01–152.16 ppm region for the phosphazene derivatives depending on the chemical environment of the carbon [12]. In addition, the C4 carbon signals in *p*-phenylazo-*o*-allylphenoxycyclotriphosphazenes (**5a–g**) appear as false doublet which this carbon atoms are coupled with the nearest phosphorus.

Table 5
^{1}H-NMR spectral data of **5a–g** compounds in aceton-d_6



5

a) R_1=R_2=H; **b)** R_1=4 -Cl, R_2=H; **c)** R_1=4 -CH_3, R_2=H; **d)** R_1=4 -Br, R_2=H;
e) R_1=4 -CH_3C=O, R_2=H; **f)** R_1=3 -CH_3, R_2=4 -CH_3; **g)** R_1=I, R_2=H

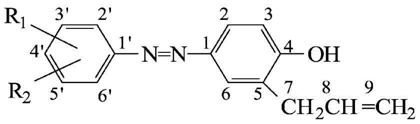
	5a	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
$\mathbf{H}_A$	5.14 (dd) $J_{A,B} = 2.94$ $J_{A,C} = 17.58$	5.14 (dd) $J_{A,B} = 1.98$ $J_{A,C} = 17.97$	5.17 (dd) $J_{A,B} = 1.90$ $J_{A,C} = 17.43$	5.15 (dd) $J_{A,B} = 1.90$ $J_{A,C} = 16.98$	5.19 (dd) $J_{A,B} = 1.94$ $J_{A,C} = 16.98$	5.15 (dd) $J_{A,B} = 1.95$ $J_{A,C} = 16.58$	5.17 (dd) $J_{A,B} = 1.93$ $J_{A,C} = 16.99$
$\mathbf{H}_B$	5.09 (dd) $J_{B,A} = 2.94$ $J_{B,C} = 10.91$	5.08 (dd) $J_{B,A} = 1.98$ $J_{B,C} = 10.05$	5.08 (dd) $J_{B,A} = 1.90$ $J_{B,C} = 10.23$	5.09 (dd) $J_{B,A} = 1.90$ $J_{B,C} = 10.16$	5.12 (dd) $J_{B,A} = 1.94$ $J_{B,C} = 10.23$	5.09 (dd) $J_{B,A} = 1.95$ $J_{B,C} = 10.22$	5.08 (dd) $J_{B,A} = 1.93$ $J_{B,C} = 10.03$
$\mathbf{H}_C$	5.98 (ddt) $J_{C,CH_2} = 6.66$ $J_{C,A} = 17.58$ $J_{C,B} = 10.91$	5.98 (ddt) $J_{C,CH_2} = 6.62$ $J_{C,A} = 17.97$ $J_{C,B} = 10.05$	5.97 (ddt) $J_{C,CH_2} = 6.62$ $J_{C,A} = 17.43$ $J_{C,B} = 10.23$	5.98 (ddt) $J_{C,CH_2} = 6.68$ $J_{C,A} = 16.98$ $J_{C,B} = 10.16$	5.97 (ddt) $J_{C,CH_2} = 6.64$ $J_{C,A} = 16.98$ $J_{C,B} = 10.23$	6.02 (ddt) $J_{C,CH_2} = 6.62$ $J_{C,A} = 16.58$ $J_{C,B} = 10.22$	5.98 (ddt) $J_{C,CH_2} = 6.68$ $J_{C,A} = 16.99$ $J_{C,B} = 10.03$
–CH_2–	3.52 (d) $J_{CH_2},C = 6.66$	3.53 (d) $J_{CH_2},C = 6.62$	3.47 (d) $J_{CH_2},C = 6.62$	3.48 (d) $J_{CH_2},C = 6.68$	3.57 (d) $J_{CH_2},C = 6.64$	3.47 (d) $J_{CH_2},C = 6.62$	3.50 (d) $J_{CH_2},C = 6.68$
CH_3–	–	–	2.43 (s)	–	2.66 (s)	2.36 (s) and 2.31 (s)	–
H2	7.50–7.33 (m)	7.40 (dd) $J_{2,3} = 8.40$ $J_{2,6} = 1.95$	7.31 (dd) $J_{2,3} = 8.43$ $J_{2,6} = 1.90$	7.49 (dd) $J_{2,3} = 8.36$ $J_{2,6} = 1.89$	7.52 (dd) $J_{2,3} = 8.43$ $J_{2,6} = 1.95$	7.25 (dd) $J_{2,3} = 8.46$ $J_{2,6} = 1.97$	7.32 (dd) $J_{2,3} = 8.41$ $J_{2,6} = 1.95$
H3	7.18 (d) $J_{3,2} = 8.30$	7.16 (d) $J_{3,2} = 8.40$	7.15 (d) $J_{3,2} = 8.43$	7.14 (d) $J_{3,2} = 8.36$	7.20 (d) $J_{3,2} = 8.43$	7.17 (d) $J_{3,2} = 8.46$	7.11 (d) $J_{3,2} = 8.41$
H6	7.50–7.33 (m)	7.68 (d) $J_{6,2} = 1.95$	7.66 (d) $J_{6,2} = 1.90$	7.68 (d) $J_{6,2} = 1.89$	7.76 (d) $J_{6,2} = 1.95$	7.49 (d) $J_{6,2} = 1.97$	7.73 (d) $J_{6,2} = 1.95$
H2′, *H6′*	7.80 (m) $J_{2',3'} = 8.21$ $J_{2',6'} = 1.96$	7.53 (dd) $J_{2',3'} = 8.68$ $J_{2',6'} = 2.05$	7.75 (dd) $J_{2',3'} = 8.35$ $J_{2',6'} = 2.04$	7.79 (dd) $J_{2',3'} = 8.96$ $J_{2',6'} = 1.98$	7.85 (dd) $J_{2',3'} = 8.57$ $J_{2',6'} = 1.98$	7.75 (d) (H2′) $J_{2',6''} = 2.35$ 7.58 (dd) (*H6′*) $J_{5',6''} = 7.65$ $J_{6',2'} = 2.35$	7.56 (dd) $J_{2',3'} = 8.68$ $J_{2',6'} = 1.85$
H3′, H5′	7.67 (m) $J_{3',2'} = 8.21$ $J_{3',5'} = 1.96$	7.80 (dd) $J_{3',2'} = 8.68$ $J_{3',5'} = 2.05$	7.70 (dd) $J_{3',2'} = 8.35$ $J_{3',5'} = 2.04$	7.64 (dd) $J_{3',2'} = 8.96$ $J_{3',5'} = 1.98$	8.07 (dd) $J_{3',2'} = 8.57$ $J_{3',5'} = 1.98$	7.70 (d) $J_{5',6'} = 7.65$	7.88 (dd) $J_{3',2'} = 8.68$ $J_{3',5'} = 1.85$
H4′	7.67 (m) $J_{3',2'} = 8.21$ $J_{3',5'} = 1.96$	–	–	–	–	–	–

The chemical shifts of the other C atoms show similar behavior and this changing are presented in Fig. 1 as examples.

2.5. Thermal decomposition studies

The thermal behavior of the studied compounds except to **5d** were investigated by employing thermoanalytical TG-DTG, DTA methods simultaneously in the temperature range of 20–1000 °C in static air atmosphere. The thermoanalytical results obtained are given in Table 8. Thermal analysis curves of **5a** are presented in Fig. 2 as an example. All compounds under investigation showed three-stage decomposition as a common feature. The first decomposition stage of the compounds occurs in temperature range of 172–343 °C (DTG curve) by giving

Table 6
^{13}C-NMR chemical shifts **3a–g** compounds in aceton-d_6

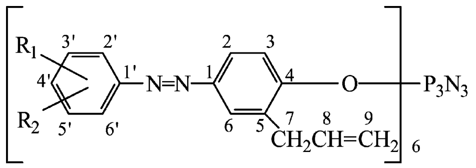


3

a) R_1=R_2=H; **b)** R_1=4 -Cl, R_2=H; **c)***R_1= 4 -CH_3, R_2=H; **d)** R_1=4 -Br, R_2=H;
e) ** R_1=4 -CH_3C=O, R_2=H; **f)***** R_1=3 -CH_3, R_2=4 -CH_3; **g)** R_1=I, R_2=H

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
C1	147.29	147.14	147.28	147.16	147.40	147.38	147.14
C2	123.13	124.11	123.15	124.18	123.12	120.84	124.21
C3	116.09	116.15	116.05	116.15	116.20	116.06	116.16
C4	159.11	159.35	158.88	159.53	159.87	158.76	159.50
C5	128.36	128.41	128.29	125.66	125.89	131.05	128.49
C6	125.52	125.66	123.68	124.89	124.49	123.61	125.72
C7	34.76	34.72	34.78	34.73	34.72	34.80	34.72
C8	137.43	136.26	137.50	137.37	137.33	138.16	137.36
C9	116.24	116.21	116.20	116.33	116.37	116.19	116.29
C10	–	–	21.31	–	26.83	19.81	–
C11	–	–	–	–	197.34	19.69	–
C1′	153.76	152.30	151.84	152.66	156.15	152.21	153.23
C2′	123.89	124.63	130.54	133.18	128.60	128.28	124.97
C3′	129.96	130.11	125.36	124.61	130.18	137.53	139.11
C4′	131.06	137.36	141.46	128.51	138.99	140.13	96.66
C5′	129.96	130.11	125.36	124.61	130.18	125.39	139.11
C6′	123.89	124.63	130.54	133.18	128.60	124.22	124.97

Table 7
^{13}C-NMR chemical shifts of **5a–g** compounds in aceton-d_6



5

a) R_1=R_2=H; **b)** R_1=4 -Cl, R_2=H; **c)***R_1= 4 -CH_3, R_2=H; **d)** R_1=4 -Br, R_2=H;
e) ** R_1=4 -CH_3C=O, R_2=H; **f)***** R_1=3 -CH_3, R_2=4 -CH_3; **g)** R_1=I, R_2=H

	5a	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
C1	150.74	151.03	150.75	150.58	150.87	150.91	151.03
C2	122.64	122.77	123.56	122.77	122.98	121.78	122.90
C3	121.83	122.59	121.97	121.85	121.88	121.33	122.37
C4	151.42	151.76	151.30	151.75	151.52	151.01	152.16
C5	130.05	130.26	128.97	126.22	126.45	131.10	129.96
C6	126.06	126.29	124.15	125.95	123.59	122.34	126.29
C7	35.08	35.15	35.14	35.10	35.17	35.14	35.15
C8	136.36	136.15	136.42	136.30	136.28	138.26	136.13
C9	117.38	117.50	117.31	117.46	117.54	117.38	117.52
C10	–	–	21.47	–	26.88	19.81	–
C11	–	–	–	–	197.32	19.67	–
C1′	153.43	151.82	151.47	152.20	155.49	151.92	152.62
C2′	123.64	125.06	130.46	134.16	130.13	125.95	125.26
C3′	132.03	133.30	125.28	125.25	134.24	136.32	139.41
C4′	134.07	137.58	142.56	133.31	139.76	141.29	98.39
C5′	132.03	133.30	125.28	125.25	134.24	124.69	139.41
C6′	123.64	125.06	130.46	134.16	130.13	122.47	125.26

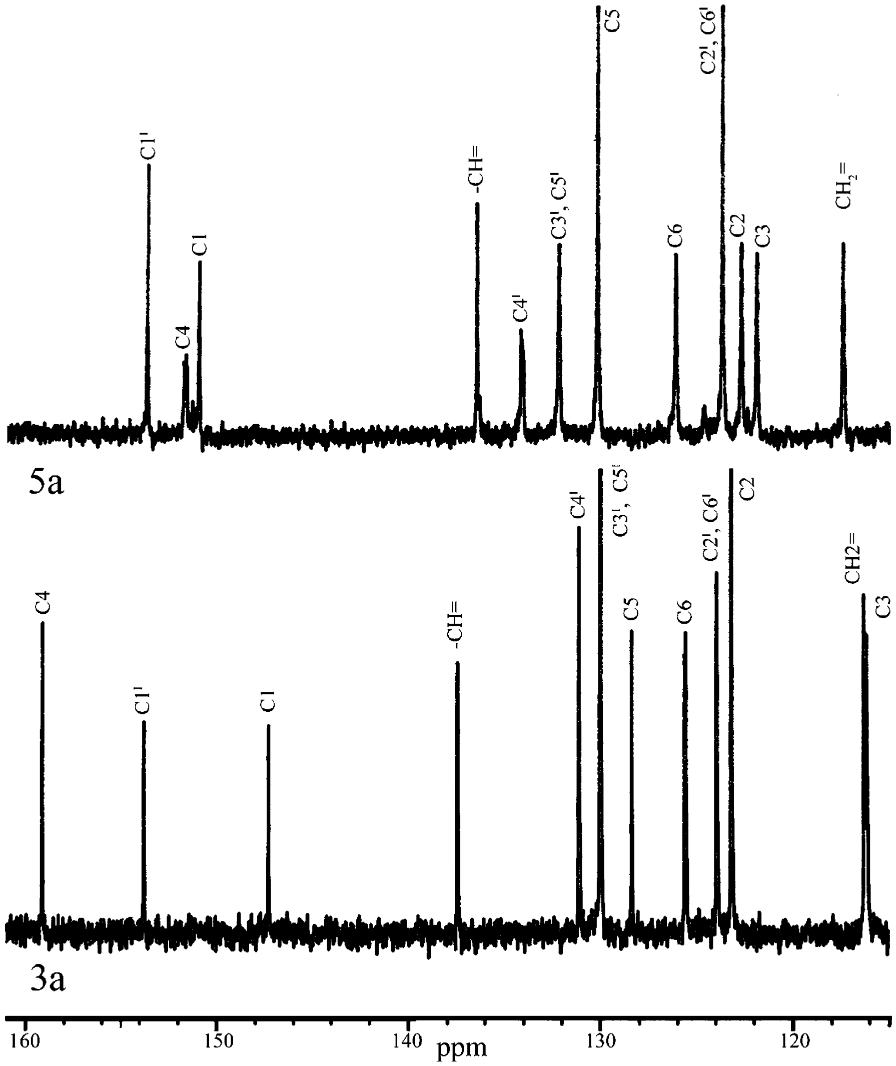


Fig. 1. The ^{13}C-NMR spectra of *p*-phenylazo-*o*-allylphenol (**3a**) and hexakis(*p*-phenylazo-*o*-allylphenoxy)cyclotriphosphazene (**5a**).

exothermic effect (DTA curve). This exothermic effect on the DTA curves (Fig. 2) was also observed in the dynamic nitrogen atmosphere (80 ml min^{-1}). Calculations indicated that the observed weight loss (around 10%) might be attributed to liberation of exothermic N_2 in the first decomposition stage [7]. Calculated weight loss for the first stage was close to the found values (Table 8). Despite the similarity of the chemical structure of compounds, **5g** shows a different thermal behavior in the curves. The weight loss observed in the first decomposition stage of **5g** is actually a combination of two sub-steps (DTG_{max}: 189 and 271 °C). The second decomposition stages for the all compounds were observed in the temperature range of 330–530 °C in static air atmosphere. In this endothermic stage, some volatile products are liberated. The third stage of decomposition is associated with an exothermic oxidation process in the temperature range of 527–588 °C (DTA curve). In this stage, the organic part of the compounds is oxidized and turned into colorless and stable final products from 730 to 1000 °C depending on the compound. The releasing of the volatile products such as aliphatic and aromatic substituents and then oxidation in static air atmosphere results in to the polymerization of the compounds. The polymerization of the similar compounds was also observed by Levchik et al. in previous studies [15].

3. Experimental

3.1. Instrumentation

All melting points were taken with an electrothermal melting point apparatus. FT-IR spectra were recorded on a Mattson 1000 FT-IR spectrometer calibrated with polystyrene film using the KBr disc. Absorption spectra in chloroform were determined on UV–VIS spectrometer. The ^{1}H-NMR and ^{13}C-NMR spectra were taken on a BRUKER AC 200 MHz spectrometer, reference tetramethylsilane as internal standard. TG,

Table 8
Thermoanalytical results for **5** compounds in static air atmosphere

Compound	Temperature range (°C)	DTG_{max}[a] (°C)	Weight loss %		Total weight loss
			Found	Calculated	
*$C_{96}H_{78}N_{15}O_6P_3$ (**5a**)*					
1	226–343	280 (−)	11.33	10.79	
2	380–530	488 (+)	18.93		
3	531–900	565 (−)	57.46		87.72
*$C_{90}H_{72}N_{15}Cl_6O_6P_3$ (**5b**)*					
1	225–333	270 (−)	11.33		
2	330–450	400 (+)	9.85	9.52	
3	451–570	527 (-)	10.48		
4	571–900	–	47.08		78.74
*$C_{96}H_{90}N_{15}O_6P_3$ (**5c**)*					
1	215–314	280 (-)	8.43	10.24	
2	360–520	485 (+)	20.46		
3	521–900	563 (-)	52.96		81.85
*$C_{102}H_{90}N_{15}O_{12}P_3$ (**5e**)*					
1	208–282	254 (−)	2.09		
2	403–522	439 (+)	12.32	9.30	
3	523–654	588 (−)	18.09		
4	655–950	−	52.45		84.95
*$C_{102}H_{102}N_{15}O_6P_3$ (**5f**)*					
1	25–70	36 (+)	1.21		
2	228–332	287 (−)	10.22	9.74	
3	355–495	454 (+)	20.35		
4	496–730	542 (−)	46.40		78.18
*$C_{90}H_{72}N_{15}I_6O_6P_3$ (**5g**)*					
1	30–65	55 (+)	1.37		
2	103–171	150 (+)	2.34		
3	172–256	189 (−)	8.96	7.25	
	256–360	271 (−)	1.94		
4	362–444	−	26.04		
5	445–753	549 (−)	46.60		87.25

[a] Exothermic and endothermic processes are denoted by (−) and (+), respectively.

DTG and DTA curves were recorded simultaneously on Rigaku TG 1810 thermal analyser combined with a TAS 100 thermogravimetric analyser. The experiments were performed in static air atmosphere with a heating rate of 10 °C min^{-1} from room temperature to 1000 °C in platinum crucibles. The samples weighed approximately 10 mg and highly sintered α-Al_2O_3 was used as a reference material. The DTG sensitivity was 0.05 mg s^{-1}. Elemental analysis was recorded by TUBITAK Marmara Research Center.

3.2. Dye synthesis and purification

3-Allyl-4-hydroxyazobenzene compounds were prepared by the method of Saunders [16]. A mixture of aniline (2.79 g, 0.03 mol), 30 ml water and concentrated hydrochloric acid (7.5 ml, 0.09 mol) was heated while stirring until a clear solution was obtained. This solution was cooled to 0–5 °C and a solution of sodium nitrite (2.21 g, 0.032 mol) in water added dropwise, maintaining the temperature below 5 °C. The resulting mixture was stirred for 30 min in an ice bath. The excess nitrite was buffered with solid sodium acetate.

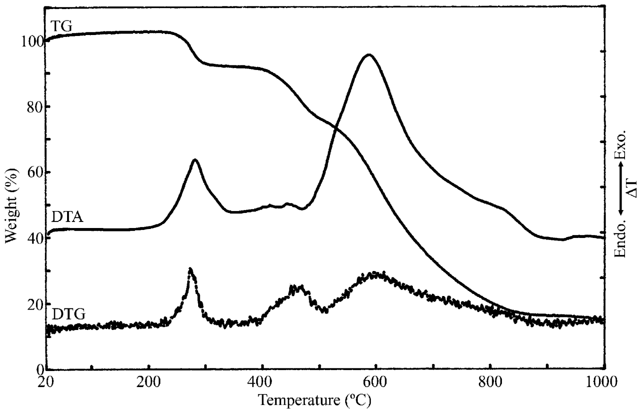


Fig. 2. Thermoanalytical curves of the hexakis(*p*-phenylazo-*o*-allylphenoxy)cyclotriphosphazene (**5a**) in static air atmosphere.

All the other substituted anilines were diazotized in a similar manner to that describe above.

The 2-allylphenol (4.02 g, 0.03 mol) was gradually added to the solution of cooled benzenediazoniumchloride prepared as described above and the resulting mixture was continually stirred at 0–5 °C for 2 h in an ice bath. The resulting product was recrystallized from ethyl alcohol–water or glacial acetic acid–water mixture to give a solid (**3a**), Mp 89–91 °C (yield: 75%).

All the other dyes were synthesized in a similar manner to that described above (Table 1).

*3.3. Preparation of hexakis(p-phenlyazo-o-allylphenoxy)cyclotriphosphazene (**5a**)*

Hexakis(*p*-phenlyazo-*o*-allylphenoxy)cyclotriphosphazene (**5a**) was prepared by modifying the method of Allcock and Kim using the following steps [17];

A solution of hexachlorocyclotriphosphazene (1.04 g, 0.003 mol) in THF was added to a THF solution of sodium *p*-phenylazo-*o*-allylphenoxide which was prepared from 3-allyl-4-hydroxyazobenzene (4.28 g, 0.018 mol) and sodium (0.414 g, 0.018 mol) in an atmosphere of dry nitrogen. After 96 h at reflux, the reaction mixture was filtrated. The product isolated by column chromatography and was purified by recrystallization from acetonitrile–aceton (2:1). Physical properties of compound **5a** and other cyclotriphosphazenes are given in Table 1.

Other compounds were prepared by similar methods and identified by UV–VIS, FT-IR, ^{1}H-NMR, ^{13}C-NMR, elemental and thermal analysis techniques.

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