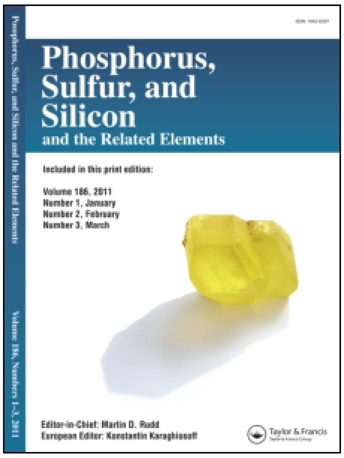

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Mustafa Odabaşoğlu[a]; Şükriye Çakmak[a]; Günseli Turgut[a]; Hasan İçbudak[a]
[a] Ondokuz Mayts University, Samsan, Turkey

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PREPARATION AND CHARACTERIZATION OF CHROMOPHOR GROUP CONTAINING CYCLOTRIPHOSPHAZENES: III BIS-AZO CHROMOPHOR CARRYING SOME CYCLOTRIPHOSPHAZENES

Mustafa Odabaşoğlu, Şükriye Çakmak, Günseli Turgut,
and Hasan İçbudak
Ondokuz Mayts University, Samsan, Turkey

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Some new substituted cyclotriphosphazenes were prepared by reaction of hexachlorocyclotriphosphazene and phenylazophenylazophenol compounds such as p-*[*p-*phenylazo-phenylazo]phenol,* p-*[*p-*(*o-*chlorophenylazo)phenylazo]phenol,* p-*[*p-*(*p-*chlorophenylazo)-phenylazo]phenol,* p-*[*p-*(*p-*methylphenylazo)phenylazo]phenol, and tetrazobenzene-β-naphtol. They are characterized by UV-Vis, FT IR, elemental analysis, and TG, DTG, and DTA.*

Keywords: Bis-azocompounds; cyclotriphosphazenes; MS; phenylazophenoxycyclotriphosphazenes; thermal analysis

INTRODUCTION

Azobenzene derivatives have been the most widely used class of dyes due to their versatile application in various fields, such as dyeing textile fibers, biomedical studies, advanced applications in organic synthesis, and high technology areas as laser, liquid crystalline displays, electro-optical devices, and ink-jet printers.[1–3] Furthermore, phophazene-bound dye systems are of interest in photochemical research, in photographic processes, and in a number of biologically related applications.[4–7] As part of our general interest in the reaction of cyclic phosphazenes, we have examined the possibility whether Schiff's

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Address correspondence to Mustafa Odabaşoğlu, Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139, Kurupelit, Samsun, Turkey. E-mail: muodabas@omu.edu.tr

bases-linked[8] and monoazodyes-linked cyclic phosphazenes[9] can be prepared by side-group construction reactions carried out on a performed cyclic organophosphazenes.

Although, azochromophors carrying some poly and cyclotriphosphazenes have been synthesized and the structures have been identified by a variety of techniques previously,[4,9] bis-azo chromophore carrying have not been reported. In this work, we report the synthesis of bis-azo chromophore group carrying cyclotriphosphazenes with unsubstituted ring and substituents like chloro and methyl on the ring. The new compounds have been characterized by using FT IR and UV-Vis spectroscopic techniques, thin-layer chromatography, elemental analysis, and thermal analysis techniques.

RESULT AND DISCUSSION

All bis-azo dyes were synthesized by azo-coupling reactions of substituted benzenediazonium salts and phenol. The prepared bis-azo dyes and their cyclotriphosphazene derivatives are listed in Table I. The dyes and their cyclotriphosphazene derivatives were purified by recrystallization from suitable solvents and their purity was examined by thin-layer chromatography.

The FT IR spectra of substituted and unsubstituted hexakis[*p*-(*p*-phenylazo)phenylazo-phenoxy]cyclotriphosphazene compounds have four characteristic absorption bands. These bands are shown at 1468–1416 cm^{-1}, 1253–1145 cm^{-1}, 1269–1243 cm^{-1}, and 971–950 cm^{-1} and are due to —N=N—, —P=N—, P—N—P (sym), and P—N—P (asym) respectively (Table II).

TABLE I The Characterization and Elemental Analysis of **VI–X**

Compound	% C Calculated[a] (found)	% H Calculated[a] (found)	m.p. (°C)	Yield (%)
VI	66.76 (66.42)	4.27 (4.31)	154[b]	60
VII	60.54 (58.67)	3.60 (3.97)	185[b]	45
VIII	60.54 (62.08)	3.60 (3.94)	162[b]	55
IX	67.52 (69.05)	4.67 (5.06)	150[b]	60
X	70.56 (71.31)	4.23 (4.45)	175	40

[a] Every compound has 1 mole THF.

[b] Decomposition point.

TABLE II FT IR Bands of Compounds **I–X** (cm^{-1})

Compound	O—H	—N=N—	—C—N=	P—N—P$_{(asym)}$	P—N—P$_{(sym)}$	P=N	P—OAr
I	3445–3164	1426	1148	—	—	—	—
VI	—	1468	1112	1243	960	1236–1145	1014
II	3475–3075	1416	1125	—	—	—	—
VII	—	1442	1110	1269	954	1222–1175	1017
III	3440–3040	1434	1138	—	—	—	—
VIII	—	1442	1112	1243	950	1214–1177	1018
IV	3434–3018	1440	1142	—	—	—	—
IX	—	1460	1122	1253	971	1253–1156	1029
V	3400–3334	1438	1154	—	—	—	—
X	—	1455	1154	1255	960	1236–1150	1019

When the FT IR spectra of *p*-(*p*-phenylazophenylazo)phenol (I) and its derivative hexakis-[*p*-(*p*-phenylazo)phenylazophenoxy]cyclotriphosphazene (VI) are compared, it is seen that the OH vibration at 3445–3164 cm^{-1} disappeared and a new band at 1014 cm^{-1} due to P-OAr appeared in the spectrum VI (Table II). Significant shifts in the absorptions of —N=N— at 1426 cm^{-1} and —C—N= at 1148 cm^{-1} were observed in the spectrum of VI. 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 noted for the other bis-azo compounds and their derivatives (Table II).

UV-Vis spectra of the bis-azo side group carrying compound synthesized are found to be similar to the spectra of their cyclotriphosphazene derivatives. The electronic transitions, were assigned as $n \to \pi^*$ and $\pi \to \pi^*$ (Table III).

UV-Vis spectra of Sudan III (tetrazobenzene-β-naphtol) show an absorption of $n \to \pi^*$ and $\pi \to \pi^*$ at 518 and 356 nm respectively. The

TABLE III UV-Vis Absorption Bands of Compounds **I–X** (nm)

Compound	$n \to \pi^*$	$\pi \to \pi^*$
I	—	402
VI	450 (shoulder)	368
II	623	401
VII	620	396
III	618	414
VIII	605	405
IV	606	390
IX	582	387
V	518	356
X	509	350

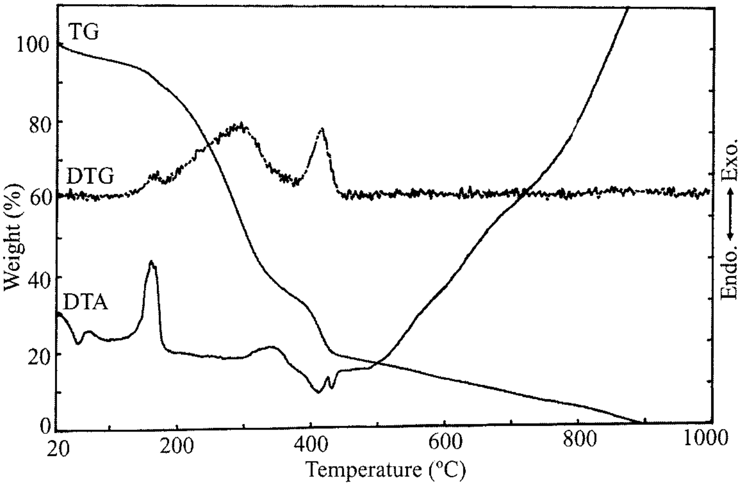


FIGURE 1 DTA, TG, and DTG curves of **VIII**.

same transitions were observed at 509 and 350 nm for its cyclotriphosphazene derivative (**X**). The other bis-azo compounds and their derivatives exhibit similar transitions.

The TG-DTG and DTA curves of hexakis {*p*-[*p*-(*p*-chlorophenylazo)-phenylazo]phenoxy}-cyclotriphosphazene (**VIII**) and hexakis (tetrazobenzene-β-naphtoxy)-cyclotriphosphazene (**X**) are shown in Figures 1

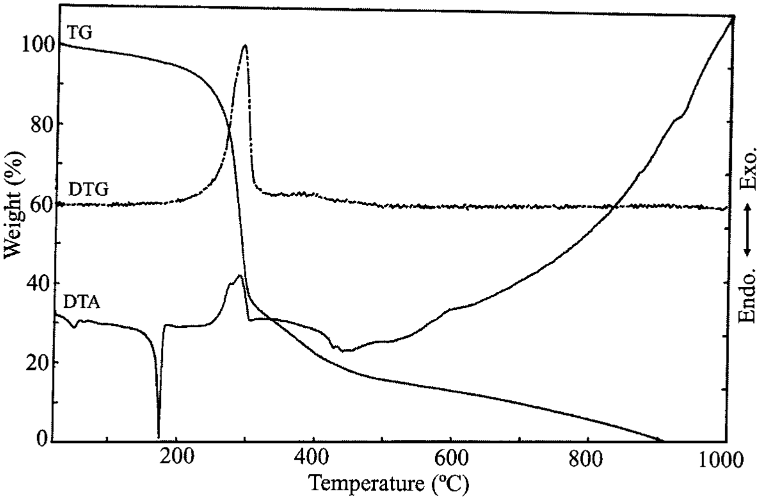


FIGURE 2 DTA, TG, and DTG curves of **X**.

TABLE IV Thermoanalytical Results for the Cyclotriphosphazene Compounds **VI**, **VIII–X**

Compound	Temperature range (°C)	DTG_{max} (°C)	Weight loss %		Removed product
			Found	Calculated	
VI					
1	29–110	52	3.87	3.57	C_4H_8O
2	126–173	154	31.28	31.29	$C_6H_4N_2$
3	173–292	254	14.46	—	—
4	292–415	366	10.59	—	—
VIII					
1	22–73	52	3.34	3.22	C_4H_8O
2	110–191	162	7.90	7.52	N_2
3	191–374	320	56.52	57.80	$C_{12}H_8N_2Cl$
4	374–451	418	19.97	20.54	C_6H_4
IX					
1	24–130	46	3.52	3.43	C_4H_8O
2	130–191	150	32.50	34.05	$C_6H_4N_2$
3	191–450	270			
4	350–600	521	48.90	—	—
X					
1	22–144	48	3.29	3.16	C_4H_8O
2	194–330	291	61.70	57.81	$C_{12}H_8N_4$
3	336–500	380	16.0	—	—

and 2; temperature ranges, and experimental and calculated weight losses of all compounds are summarized in Table IV.

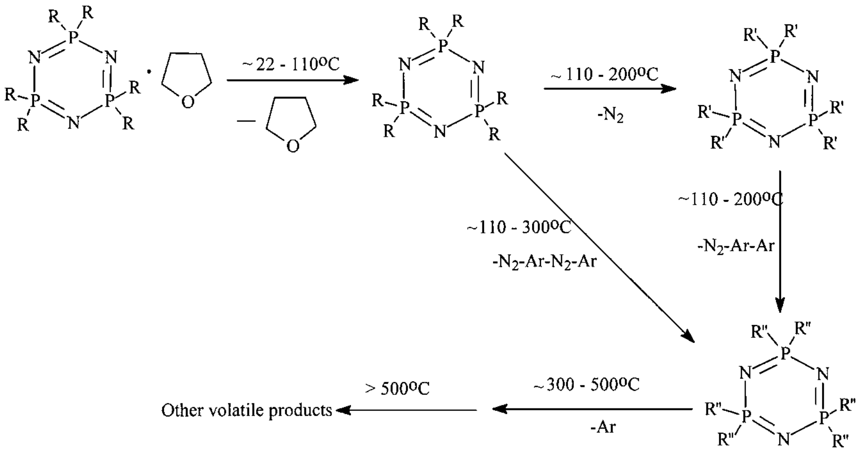
When we look at the Figure 1 for the thermal decomposition of the VIII four different decomposition steps have been observed. The weight loss starts at low temperatures such as 22°C and continuous to well above to 900°C. In the first step an endothermic weight loss (3.34%), which is seen as a peak minimum at 52°C in DTA curve, can be attributed to removal of solvent (THF) which has been hold on to the crystals. Also, the mass spectra, detects the mass due to THF (m/e = 73). Similar decompositions have been observed by different researches.[10–11] For the second step 110–191°C calculations indicate that the weight loss might be due to exothermic N_2 loss (exp. 7.90%; calcd. 7.52%). In the 191–374°C step a weight loss corresponding to release of the $C_{12}H_8N_2Cl$ group that is the 56.52% of the weight loss (calcd: 57.80%) has been observed. Two endothermic processes have been observed at 412°C and 433°C in the DTA curve which can be due to decompose remaining hydrocarbon parts of the **VIII**.

Three decomposition steps have been observed for hexakis-(tetrazobenzene-β-naphtoxy)cyclotriphosphazene (X) (Figure 2). The first endothermic peak at 48°C corresponds to the removal of solvent. The second endothermic peak at 175°C, without any weight loss, clearly represents a physical process and is attributed to the melting of hexakis-(tetrazobenzene-β-naphtoxy)cyclotriphosphazene. In the following step in the temperature range 194–330°C, the phenylazo group ($C_{12}H_8N_4$) is removed by giving exothermic effect (exp. 61.70%; calcd. 57.81%). The mass spectrum is consistent with the TG-DTG/DTA data. The mass spectrum shows that $C_{12}H_8N_4$ (m/e = 209) is detected.

Similar decompositions processes have been observed for the other compounds, which are listed in the Table IV.

MS spectra of VI were recorded at 150°C and 250°C, and probable products are shown in Figures 3 and 4 respectively. These observations are consistent with the results reported by Enrico.[12] The MS data of compound VI are also in agreement with data obtained by TG-DTG/DTA. Furthermore, the m/e values of IX and X are consistent with the TG-DTG/DTA data. [(m/e values of IX: 77, 91, 105, 119, 167 at 150°C; 73, 91, 119, 135, 209, 223, 299 at 250°C); (m/e values of IX: 77, 105 at 150°C; 73, 91, 135, 149, 209, 335 at 250°C)].

According to thermal analysis and mass spectral studies, the decomposition mechanism of bis-azo chromophore side group carrying cyclotriphosphazenes in nitrogen atmosphere may be as shown below.



SCHEME 1

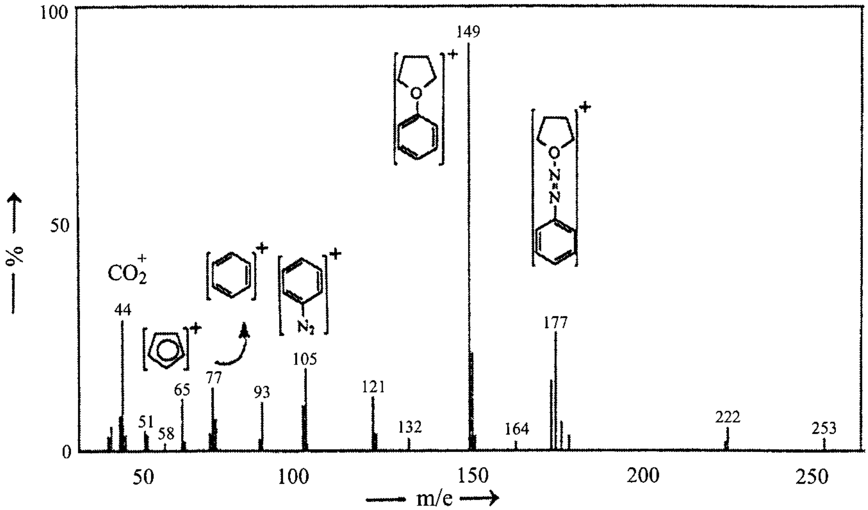


FIGURE 3 MS spectrum of **VI** at 150°C.

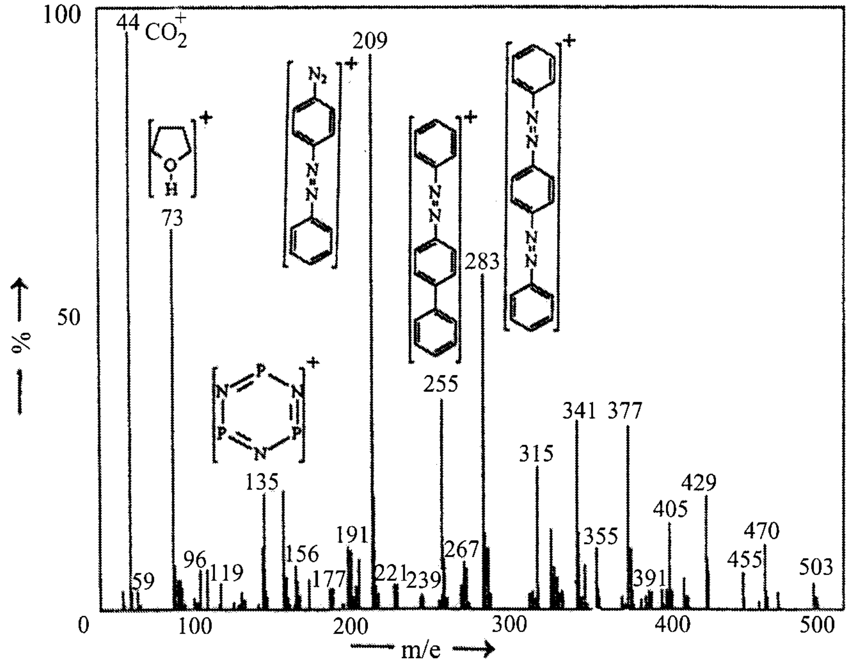


FIGURE 4 MS spectrum of **VI** at 250°C.

EXPERIMENTAL

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 acetone were determined on a Unicam UV-Vis spectrophotometer. TG, 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 nitrogen atmosphere (80 ml min^{-1}) with a heating rate of 10 K 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 and MS spectra were recorded by TUBITAK Marmara Research Center.

Dye Synthesis and Purification

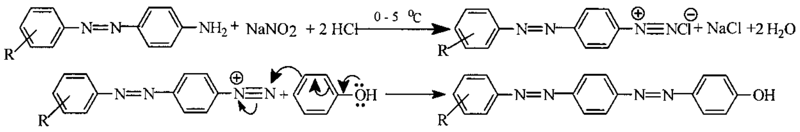
Diazoaminobenzenes and *p*-aminoazobenzenes, were prepared by the method of Voge,[13] *p*-phenylazophenylazophenols by the method of Saunders[14] and Sudan III (tetrazobenzene-β-naphthol), (V) was purchased from Merck company.

Synthesis of p-*[*p*-Phenylazophenylazo]phenol (I)*

A mixture of *p*-aminoazobenzene (4.925 g, 0.025 mol), 50 ml water (or water-alcohol) and 5 ml concentrated hydrochloric acid was heated while stirring until a clear solution was obtained. This solution was cooled to 0–5°C and a solution of sodium nitrite (2.070 g, 0.30 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 destroyed by addition of urea.[14] This solution was buffered with solid sodium acetate.

All the other substituted *p*-aminoazobenzenes were diazotized in a similar manner to that describe above.

The crystalline phenol (2.350 g, 0.025 mol) gradually was added to the solution of the cooled *p*-aminoazobenzenediazoniumchloride prepared as described above and the resulting mixture was stirred at 0–5°C for 60 min in an ice bath. The resulting product was recrystallized from an absolute alcohol-benzene mixture to give solid *p*-[*p*-phenylazophenylazo]phenol, m.p. 158°C (yield: 72%).



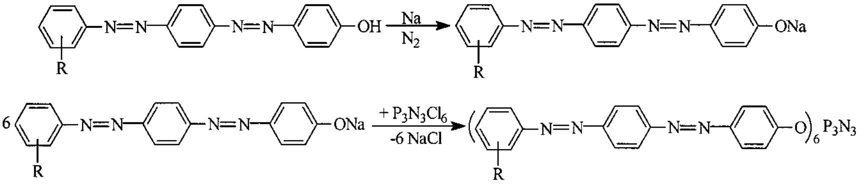
I: R = H
II: R = *o*-Cl
III: R = *p*-Cl
IV: R = *p*-CH_3

SCHEME 2

All other substituted *p*-[*p*-phenylazophenylazo]phenols were synthesized in a similar manner to that describe above.

Preparation of Hexakis[p-(p-Phenylazophenylazo)-phenoxy]cyclotriphosphazene (VI)

Hexakis[*p*-(*p*-phenylazophenylazo)phenoxy]cyclotriphosphazene was prepared by modifying the method of Allcock and Kim using the following steps.[12]



VI: R = H
VII: R = o-Cl
VIII: R = p-Cl
IX: R = p-CH_3

SCHEME 3

A solution of hexachlorocylotriphosphazene (1.39 g, 0.004 mol) in THF was added to a THF solution of *p*-[*p*-phenylazophenylazo]-phenoxide which was prepared from *p*-[*p*-phenylazophenylazo]phenol (7.248 g, 0.024 mol) and sodium (0.552 g, 0.024 mol) in an atmosphere of dry nitrogen. After 20 h at reflux, the reaction mixture was filtrated. The product (**VI**) was isolated by column chromatography and was purified by recrystallization from acetonitrile (m.p. 154°C, yield 40%).

VI–IX were prepared by similar methods and hexakis(tetrazobenzene-β-naphtoxy)cyclotriphosphazene (**X**) was also prepared from tetrazobenzene-β-naphtol (**V**).

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