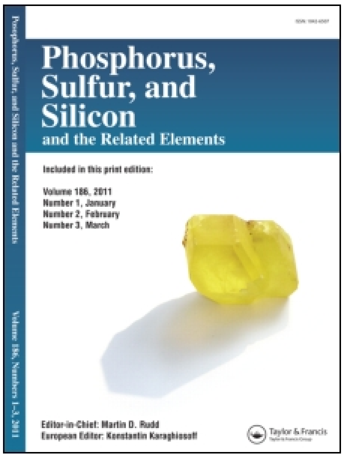

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PREPARATION AND CHARACTERAZATION OF CHROMOPHOR GROUP CONTAINING CYCLOTRIPHOSPHAZENES: II AZO CHROMOPHOR CARRYING SOME CYCLOTRIPHOSPHAZENES

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To cite this Article Odabaşoğlu, Mustafa , Turgut, Günseli and Kocaokutgen, Hasan(1999) 'PREPARATION AND CHARACTERAZATION OF CHROMOPHOR GROUP CONTAINING CYCLOTRIPHOSPHAZENES: II AZO CHROMOPHOR CARRYING SOME CYCLOTRIPHOSPHAZENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 152: 1, 27 — 34

To link to this Article: DOI: 10.1080/10426509908031614

URL: http://dx.doi.org/10.1080/10426509908031614

Phosphorus, Sulfur and Silicon, 1999, Vol. 152, pp. 27-34
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PREPARATION AND CHARACTERAZATION OF CHROMOPHOR GROUP CONTAINING CYCLOTRIPHOSPHAZENES: II AZO CHROMOPHOR CARRYING SOME CYCLOTRIPHOSPHAZENES

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(Received 26 November, 1998; In final form 14 December, 1998)

Some new substituted cyclotriphosphazenes were prepared by the reaction of hexachlorocyclotriphosphazene and 4-hydroxyazo compounds such as 4-hydroxyazobenzene, 4′-ethyl-4-hydroxyazobenzene, 4′-*tert*butyl-4-hydroxyazobenzene, 4′-methoxy-4-hydroxyazobenzene, 3′,4′-dichloro-4-hydroxyazobenzene, 2′-chloro-4-hydroxyazobenzene and 2′-methoxy-5′-chloro -4-hydroxyazobenzene. The structure of the compounds with the general formula $[NP(OC_6H_4N=N\text{-}Ar)_2]_3$. was determined by UV-VIS, IR, ^{1}H-NMR and elemental analysis.

Keywords: Cyclotriphosphazenes; azo compounds; hexachlorocyclotriphosphazene; chromophor group; azo dyes; phenlyazophenoxycyclotriphosphazenes

INDRODUCTION

Azobenzene derivatives have been the most widely used class of dyes due to their versatile application in various fields, such as dyeing textile fibber, 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

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photographic processes, and in a number of biologically related aplications[4–7]. As part of our general interest in the reaction of cyclic phosphazenes[8], we have examined the possibility whether Schiff's bases-linked cyclic phosphazenes can be prepared by side-group construction reactions carried out on a performed cyclic organophosphazenes.

Althought, azochromophors carrying some poly and cyclotriphosphazenes have been synthesised and the structures have been identified by a variety of techniques previously, a limited number of research on substituted azo dyes which have substituted groups in different positions such as chloro, methoxy, ethyl, *tert*-butyl have not been reported[4]. In this work, we report the synthesis of azo chromophor group carrying cyclotriphosphazenes with the substituents like chloro, methoxy, *tert*-buthyl and ethyl on the ring and have been characterised by using IR, UV-VIS and ^{1}H-NMR spectroscopic techniques, thin-layer chromatography (TLC) and elemental analysis.

RESULTS AND DISCUSSION

All the azo dyes were synthesized by azo-coupling reactions of substituted benzenediazonium salts and phenol. The prepared 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 as can be seen from the values in Table I. The structures of the compounds were identified by UV-VIS, IR and ^{1}H-NMR spectroscopic techniques.

The IR spectra of substituted phenylazophenoxycyclotriphosphazene compounds have four characteristic absorption bands. These bands are shown at 1422–1416 cm^{-1}, 1225–1141 cm^{-1}, 1303–1263 cm^{-1} and 960–931 cm^{-1} and are due to -N=N-, -P=N-, P-N-P (sym) and P-N-P (asym), respectively (Table III).

TABLE I The characterisation and elemental analysis of the azo chromophors carrying some cyclotriphosphazenes

Compound	*Yield(%)*	*m.p (°C)*	*%C (calculate-found)*	*%H (calculate-found)*
Ia	80	151–153	-	-
VIa	82	177–179	65.62–65.38	4.10–4.19
Ib	72	118–119	-	-
VIb	76	95–97	67.88–68.00	5.25–5.74
Ic	62	120–122	-	-
VIc	58	90–91	69.69–69.36	6.17–5.78
Id	75	132–134	-	-
VId	66	148–150	62.52–62.71	4.41–4.48
II	71	117–120	-	-
VIe	68	192–193	49.91–50.82	2.43–3.09
III	62	101–103	-	-
VIf	55	153–155	56.69–57.23	3.15–3.01
IV	68	160–162	-	-
VIg	62	94–96	54.93–54.48	3.52–3.85

When the IR spectra of 4-hydroxyazobenzene and its derivative hexakis-4-phenylazophenoxycyclotriphosphazene are compared, it is seen that the OH vibration at 3400–3115 cm^{-1} disappeared and a new band at 1014 cm^{-1} due to P-OAr appeared in the spectrum of hexakis-4-phenylazophenoxycyclotriphosphazene. Significant shifts in the absorptions of -N=N- at 1416 cm^{-1} and -C-N= at 1145 cm^{-1} were observed in the spectrum of hexakis-4-phenylazophenoxycyclotriphosphazene. These changes are attributed to the replacement of H with the P atom and the hinderance of the resonance between the -N=N- group and the phenyl ring. Similar observations were noted for the other azo compounds and their derivatives (Table III).

UV-VIS spectra of the azo compound synthesized are found to be similar to the spectra of their cyclotriphosphazene derivatives. The electronic transitions were assigned as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (Table II).

TABLE II UV-VIS absorbtion bands of all the synthesised compounds (nm.)

Compound	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
Ia	447	350
VIa	439	324
Ib	443	353
VIb	430	335
Ic	445	353
VIc	430	331
Id	443	358
VId	439	350
II	469	361
VIe	443	336
III	452	358
VIf	440	331
IV	465	375
VIg	370	315

UV-VIS spectra of 4-hydroxyazobenzene show an absorption of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ at 447 and 350 nm., respectively. The same transitions were observed at 439 and 324 nm. for its cyclotriphosphazene derivative. The other azo compounds and their derivatives exhibit similar transitions.

When the ^{1}H-NMR spectra of Ia and VIa are compared, it is seen that the OH peak appears 5.35 ppm. This peak is absent in the spectra of cyclophosphazene derivatives and the protons of the aromatic ring resonances are at a lower field. The ^{1}H NMR results of the compounds are given in Table IV.

EXPERIMENTAL SECTION

General

All melting points were taken with an electrothermal melting point apparatus. IR spectra were recorded on a Mattson 1000 FTIR spectrometer calibrated with polystrene film using the KBr disc. Absorbtion spectra in $CHCl_3$ were determined on a Unicam UV-VIS spectrophotometer. The ^{1}H-NMR spectra were taken on a Varian EML NMR 200 MHz spectrometer, reference tetramethylsilane as internal standard. Elemental analysis were performed by TUBITAK Marmara Research Center.

TABLE III IR bands of all the synthesised compounds (cm^{-1})

Compound	*O-H*	*-N=N-*	*-C-N=*	*P-N-P(asy.)*	*P-N-P(sym.)*	*P=N*	*P-OAr*
Ia	3400–3135	1416	1145	-	-	-	-
VIa	-	1438	1110	1275	960	1232–1177	1014
Ib	3404–3016	1440	1114	-	-	-	-
VIb	-	1442	1110	1269	954	1223–1176	1019
Ic	3500–3180	1438	1154	-	-	-	-
VIc	-	1426	1112	1265	950	1236–1179	1017
Id	3404–3000	1438	1154	-	-	-	-
VId	-	1440	1120	1303	960	1255–1141	1036
II	3586–3016	1428	1125	-	-	-	-
VIe	-	1416	1123	1263	953	1253–1180	1015
III	3450–3201	1428	1154	-	-	-	-
VIf	-	1434	1148	1277	954	1222–1175	1018
IV	3456–3165	1438	1134	-	-	-	-
VIg	-	1436	1122	1274	950	1214–1177	1029

TABLE IV ^{1}H-NMR chemical shifts of all the synthesised compounds (δ)

Compound	*O-H*	*C-H (aromatic)*	*-OCH$_3$*	*-CH$_2$-*	*-CH$_3$*	*-C(CH$_3$)$_3$*
Ia	5.35	6.92–7.89	-	-	-	-
VIa	-	7.12–7.80	-	-	-	-
Ib	5.55	6.88–7.87	-	2.70	1.27	-
VIb	-	7.11–7.74	-	2.72	1.29	-
Ic	5.34	6.88–7.88	-	-	-	1.37
VIc	-	7.08–7.81	-	-	-	1.39
Id	5.40	6.90–7.90	3.88	-	-	-
VId	-	6.88–7.78	3.88	-	-	-
II	5.37	6.93–7.98	-	-	-	-
VIe	-	6.98–7.88	-	-	-	-
III	5.34	6.92–7.95	-	-	-	-
VIf	-	7.17–7.84	-	-	-	-
IV	5.48	6.90–7.89	4.00	-	-	-
VIg	-	6.93–7.80	3.96	-	-	-

in $CDCl_3$.

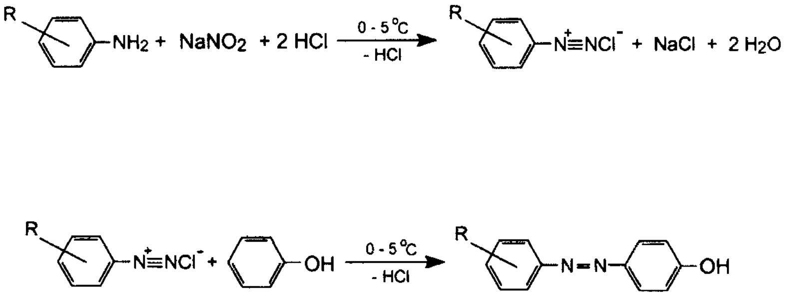
Dye Synthesis and Purification

A mixture of aniline (4.74g., 0.051mol), water (50ml.) and concentrated hydrochloric acid (25ml., 0.28mol) was heated while stirring until a clear solution was obtained. This solution was cooled to 0–5°C and a solution of sodium nitrite (2.42g., 0.35mol) in water was then 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[9]. This solution was buffered with solid sodium acetate.

All the other substituted anilines were diazotized in a similar manner to that describe above (Scheme 1).

The crystalline phenol (4.70g., 0.05mol) was gradually added to the solution of the cooled benzenediazoniumchloride prepared as described above and the resulting mixture was continually stirred at 0–5°C for 60 min. in an ice bath. The resulting product was recrystallized from ethylalcohol-water mixture to give a solid (Ia) of m.p 151–153°C.

All the other dyes were synthesized in a similar manner to that describe above.



I a) R= H
b) R= p-C_2H_5
c) R= p-$(CH_3)_3C$
d) R= p-CH_3O

II R= 3,4-Cl_2
III R= 2-Cl
IV R= 2-CH_3O-5-Cl

SCHEME 1

Preparation of $N_3P_3(OC_6H_4N{=}NC_6H_5)_6$

$N_3P_3(OC_6H_4N{=}NC_6H_5)_6$ was prepared by modifying the method of Allcock and Kim using the following steps,[10] (Scheme 2):

A solution of hexachlorocylotriphosphazene (1.39g., 4.00mmol) in THF was added to a THF solution of (4-phenylazo)sodiumphenoxide which was prepared from 4-(phenyl)azobenzene (7.14g., 36mmol) and sodium (0.83g., 36mmol) in an atmosphere of dry nitrogen. After 20h at reflux, the reaction mixture was filtrated. The product (VIa) was isolated by column chromatography and was purified by recrystallization from acetonitrile (Yield 82%).

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

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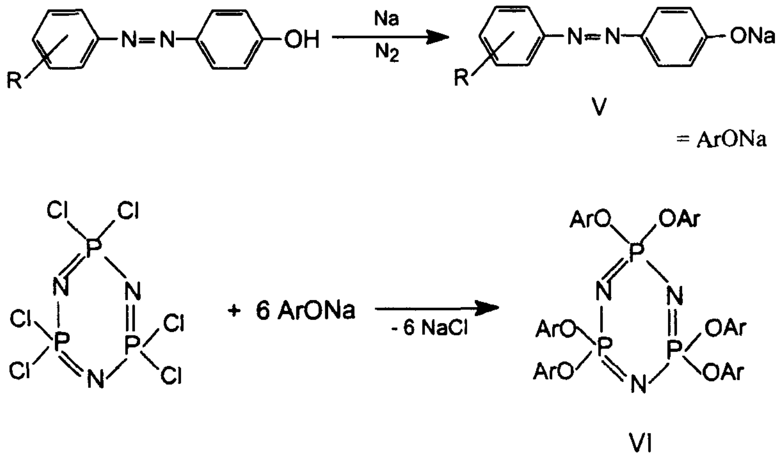

a) R= H
b) R= 4-C_2H_5
c) R= 4-$(CH_3)_3C$
d) R= 4-CH_3O
e) R= 3,4-Cl_2
f) R= 2-Cl
g) R= 2-CH_3O-5-Cl

SCHEME 2

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