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Dyes and Pigments 70 (2006) 117–125
DYES and PIGMENTS
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Preparation and characterization of chromophore group containing cyclotriphosphazenes: V. Spectroscopic investigation of some hexakis(*p*-phenylazo-α-naphtoxy)cyclotriphosphazenes

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Received 19 November 2004; received in revised form 11 February 2005; accepted 2 May 2005
Available online 6 July 2005

Abstract

Some new substituted cyclotriphosphazenes were prepared by the reaction of hexachlorocyclotriphosphazene and 4-phenylazo-1-naphthol compounds such as 4-phenylazo-1-naphthol, 4-(2-chlorophenylazo)-1-naphthol, 4-(3-chlorophenylazo)-1-naphthol, 4-(4-chlorophenylazo)-1-naphthol, 4-(4-florophenylazo)-1-naphthol, 4-(4-bromophenylazo)-1-naphthol, 4-(4-iyodophenylazo)-1-naphthol, 4-(4-acetylphenylazo)-1-naphthol, 4-(4-methylphenylazo)-1-naphthol, 4-(4-ethylphenylazo)-1-naphthol, 4-(3,4-dimethylphenylazo)-1-naphthol, 4-(2,4-dichlorophenylazo)-1-naphthol, 4-(2,6-dichlorophenylazo)-1-naphthol and 4-(2,6-dimethylphenylazo)-1-naphthol. The structure of these compounds with a general formula $[NP(OC_{10}H_6N{=}NAr)_2]_3$, was determined by UV–vis, FT-IR, ^{1}H NMR and elemental analysis.

Keywords: Cyclotriphosphazenes; Azo dyes; Chromophore group; UV–vis; IR; NMR

1. Introduction

Azo compounds have been the most widely used class of organic dyes, due to their versatile application in various field, such as the dyeing of textiles, and fibers, the coloring of different materials, and high-technology areas, such as laser, electro-optical devices, liquid crystalline displays and ink-jet printers [1–3]. 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. Phosphazene-bound dye systems are of interest in photochemical research, in photographic processes, and in a number of biologically related applications [4–7]. Monoazo and bis-azo chromophore group carrying some cyclotriphosphazene derivatives were synthesized and investigated for some of their properties [8–10]. We report herein the synthesis of 4-phenylazo-1-naphthol compounds and their cyclotriphosphazene derivatives such as methyl, ethyl, acetyl, floro, chloro, bromo, iyodo and unsubstituted ring. The new compounds have been characterized by using UV–vis, FT-IR, ^{1}H NMR and elemental analysis techniques.

2. Experimental

2.1. Synthesis

Azo chromophore carrying α-naphtoxycyclotriphosphazenes **5** were synthesized by the cyclotriphosphazene

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0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.05.005

4 and *p*-phenylazo-α-naphthol dyes **3** which are synthesized with azo-coupling reactions of substituted benzenediazonium salts and α-naphthol 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 α-naphthol substrate **2** to produce *p*-phenylazo-α-naphthol dye **3** in good yield. The dye **3** and its cyclotriphosphazene derivative **5** was purified by recrystallization from suitable solvents and its purity was examined by thin-layer chromatography.

2.2. Physical measurements

All melting points were taken with an electrothermal melting point apparatus. FT-IR spectra of 4-phenylazo-1-naphthol compounds and their cyclotriphosphazene derivatives were recorded in the region of 4000–400 cm^{-1}, using a Mattson 1000 FT-IR Spectrometer (KBr pellets). Absorption spectra in $CHCl_3$, absolute EtOH, DMSO were determined on a Unicam UV–vis Spectrometer. ^1H NMR data in DMSO–d_6 were acquired on a Bruker AC 200 Spectrometer. Elemental analyses were recorded by TUBITAK Marmara Research Center.

3. Results and discussions

3.1. UV–vis absorption spectra

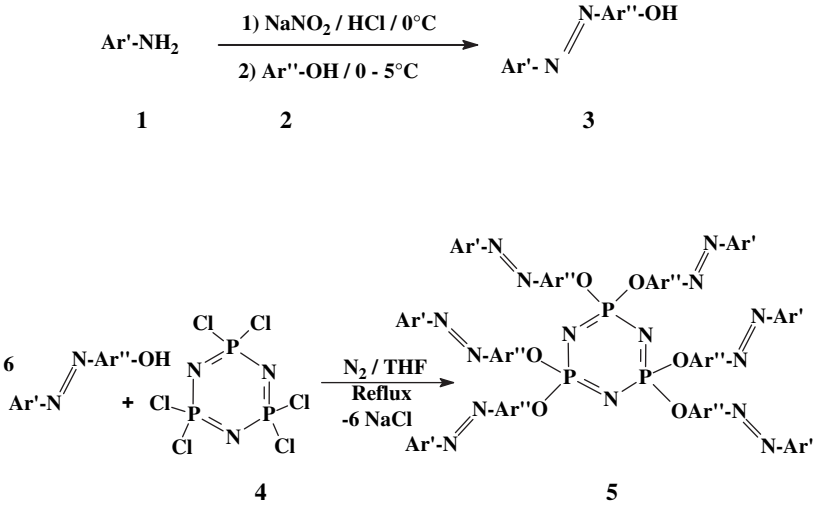
In particular, azo dyes that contain a naphtholic hydroxy group conjugated with the azo linkage exist in aqueous solution as an equilibrium mixture of two chemically distinct tautomers, the azo or hydrazone forms [11]. The forms have characteristically different visible spectra with azo form absorbing typically at 400–440 nm (yellow) and hydrazone at 475–510 nm (orange/red) [11–13]. The factors influencing the relative stabilities of the two tautomeric forms are subtle and complex, and include, among others, the polarity of the solvent, substituents in the molecule, the hydrogen bonding properties of the solvent, and temperature of the solution [12,14,15]. Therefore, UV–vis spectra of synthesized *p*-phenylazo-α-naphthols (**3**) were taken in different polarity solvents as chloroform, absolute ethanol, dimethylsulphoxide and azo-hydrazone tautomeric equilibrium were investigated in this solvents. Typical characteristic UV–vis absorption bands of *p*-phenylazo-α-naphthols (**3**) in $CHCl_3$, absolute EtOH and DMSO are given in Table 2. As shown in Table 2, while *p*-phenylazo-α-naphthols (**3**) are found only in azo form in DMSO, *p*-(*p*-acethylphenylazo)-α-naphthol (**3h**) is found in hydrazone form in DMSO. This result is in accordance with literature [15,16].

UV–vis spectra of synthesized *p*-phenylazo-α-naphthols (**3**), except for **3b**, **3c** and **3n**, have been determined both tautomeric forms in $CHCl_3$. In generally investigated, except for **3h** and **3n**, tautomeric equilibrium of synthesized *p*-phenylazo-α-naphthols (**3**) have been shifted from hydrazone to azo in turn in order $CHCl_3$ < absolute EtOH < DMSO (Fig. 1 and Table 2).

The UV–vis spectra taken in chloroform ($CHCl_3$) and dimethylsulfoxide (DMSO) showed that hexakis(*p*-phenylazo-α-naphthoxy)cyclotriphosphazene derivative (**5**) existed only in the azo form and absorption bands of the cyclotriphosphazene derivatives (**5**) shifted to blue region of the spectra comparing with the starting azo compound (**3**) (Fig. 2 and Table 3). It is shown that, *p*-phenylazo-α-naphthol compounds (**3**) were connected to cyclotriphosphazene on azo form.

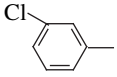
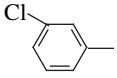
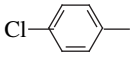
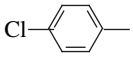
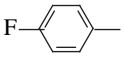
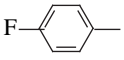
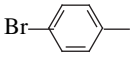
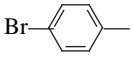
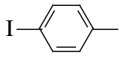
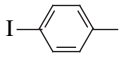
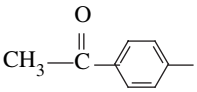
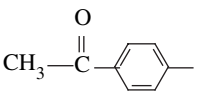
3.2. IR absorption spectra

While arylazophenols exist only in the azo form, the arylazonaphthols exist in both the azo and the



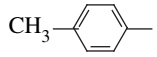
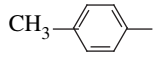
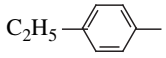
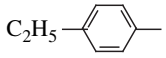
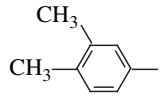
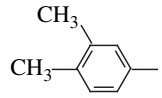
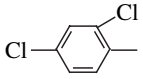
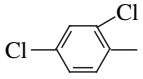
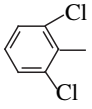
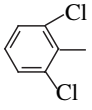
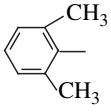
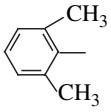
Scheme 1.

Table 1
Synthesized and properties of *p*-phenylazo-α-naphthol dyes **3** and its cyclotri phosphazene derivatives **5** (Ar″, α-naphthol)

Compound	Ar′	Yield (%)[a]	Mp (°C)	%C Calculated (Found)	%H Calculated (Found)	%N Calculated (Found)
3a		78	184–186	–	–	–
5a		64	122–124[b]	71.24 (71.95)	4.08 (4.65)	12.98 (12.62)
3b		72	176–178	–	–	–
5b		58	133–135[b]	63.16 (62.86)	3.29 (3.97)	11.51 (11.22)
3c		75	197–199	–	–	–
5c		62	137–139[b]	63.16 (63.04)	3.29 (3.52)	11.51 (10.85)
3d		71	233–235	–	–	–
5d		60	138–140[b]	63.16 (62.64)	3.29 (4.05)	11.51 (10.87)
3e		68	200–201	–	–	–
5e		54	132–134[b]	66.78 (66.22)	3.48 (3.95)	12.17 (11.98)
3f		73	228–230	–	–	–
5f		56	137–139[b]	55.09 (55.18)	2.87 (3.14)	10.04 (9.83)
3g		74	227–229	–	–	–
5g		55	134–135[b]	48.55 (48.91)	2.53 (2.97)	8.85 (8.36)
3h		75	232–234	–	–	–
5h		68	156–158[b]	69.34 (68.98)	4.17 (4.27)	11.24 (11.54)

(*continued on next page*)

Table 1 (*continued*)

Compound	Ar′	Yield (%)[a]	Mp (°C)	%C Calculated (Found)	%H Calculated (Found)	%N Calculated (Found)
3i		63	196–197	–	–	–
5i		67	132–135[b]	71.95 (71.68)	4.58 (5.08)	12.34 (12.45)
3j		60	198–200	–	–	–
5j		56	136–139[b]	72.61 (71.98)	5.04 (5.56)	11.77 (11.65)
3k		58	206–208	–	–	–
5k		54	127–129[b]	72.61 (71.95)	5.04 (5.20)	11.76 (11.26)
3m		74	196–198	–	–	–
5m		68	124–126[b]	56.72 (57.31)	2.66 (3.14)	10.34 (9.92)
3n		76	150–152	–	–	–
5n		66	120–122[b]	56.72 (56.47)	2.66 (3.17)	10.34 (9.95)
3o		67	122–125	–	–	–
5o		62	109–110[b]	72.61 (71.97)	5.04 (4.52)	11.77 (11.97)

[a] Isolated yields.
[b] Decomposition point.

hydrazone forms or only hydrazone form. From a color point of view, azo–hydrazone tautomerism is quite important, since the two tautomeric forms will, in general, have different spectroscopic properties [17–19]. The IR spectra of the tautomeric forms of arylazonaphthols show significant differences. Band characteristic of the hydroxyl and azo groups appear in the spectrum of the azo form and should be replaced by hydrazone and carbonyl bands in the spectrum of the hydrazone form [20]. Infrared spectra of arylazonaphthols have shown azo–hydrazone tautomerism analysed by the associated C=O formation with carbonyl bands in the

Table 2
UV–vis absorption bands of *p*-phenylazo-α-naphthols (**3**) in DMSO, absolute EtOH and $CHCl_3$ (nm, $\varepsilon_H/\varepsilon_A$)

Compound	$CHCl_3$		Absolute EtOH		DMSO	
	A	H	A	H	A	H
3a	411(31167) $\varepsilon_H/\varepsilon_A = 1.29$	464(40167)	406(33667) $\varepsilon_H/\varepsilon_A = 0.87$	472(29167)	411(29667) Azo	–
3b	– Hydrazone	456(45000)	418(27667) Azo	–	424(31500) Azo	–
3c	– Hydrazone	454(33167)	428(20333) $\varepsilon_H/\varepsilon_A = 1.07$	455(21667)	425(26167) Azo	–
3d	418(24667) $\varepsilon_H/\varepsilon_A = 1.05$	456(25833)	417(13333) $\varepsilon_H/\varepsilon_A = 0.96$	456(12833)	423(39000) Azo	–
3e	405(24000) $\varepsilon_H/\varepsilon_A = 0.75$	462(18000)	406(39167) $\varepsilon_H/\varepsilon_A = 0.55$	474(21500)	412(37500) Azo	–
3f	426(23333) $\varepsilon_H/\varepsilon_A = 1.04$	455(24167)	419(16000) $\varepsilon_H/\varepsilon_A = 0.91$	470(14500)	425(26333) Azo	–
3g	432(20833) $\varepsilon_H/\varepsilon_A = 1.10$	461(23000)	418(17550) $\varepsilon_H/\varepsilon_A = 0.94$	470(16500)	424(42333) Azo	–
3h	377(14167) $\varepsilon_H/\varepsilon_A = 1.54$	461(21833)	410(9667) $\varepsilon_H/\varepsilon_A = 1.36$	469(13167)	– Hydrazone	468(39000)
3i	404(29167) $\varepsilon_H/\varepsilon_A = 0.93$	469(27167)	406(24667) $\varepsilon_H/\varepsilon_A = 0.65$	474(16000)	411(41833) Azo	–
3j	404(30167) $\varepsilon_H/\varepsilon_A = 0.97$	470(29167)	406(37833) $\varepsilon_H/\varepsilon_A = 0.66$	474(24833)	410(34167) Azo	–
3k	405(35500) $\varepsilon_H/\varepsilon_A = 0.94$	474(33500)	399(23000) $\varepsilon_H/\varepsilon_A = 0.59$	480(13667)	412(29167) Azo	–
3m	384(15333) $\varepsilon_H/\varepsilon_A = 2.49$	456(38167)	428(28167) Azo	–	435(39000) Azo	–
3n	418(27667) Azo	–	396(32000) Azo	–	401(36000) Azo	–
3o	388(21500) $\varepsilon_H/\varepsilon_A = 0.78$	459(16833)	387(36833) $\varepsilon_H/\varepsilon_A = 0.47$	470(17167)	392(27167) Azo	–

A: azo, H: hydrazone.

1615–1650 cm^{-1} region. But C=N (hydrazone) bands have not been observed because these bands have remained under of the C=O bands [21].

The characteristic IR absorption bands of *p*-phenylazo-α-naphthol compounds **3** and their cyclotriphosphazene derivatives **5** are determined in KBr disk. It can be seen that the IR spectrum of *p*-phenylazo-α-naphthol compounds **3** agrees with the azo–hydrazone tautomerism (Table 4). There is an overlapped band at 3351–3116 cm^{-1} which is assigned to –NH/–OH stretching modes. Hydrazone structure is further supported by the presence of a strong carbonyl band at 1633–1619 cm^{-1}. The appearance of N=N bands at 1416–1408 cm^{-1} and Ar–N= bands at 1158–1149 cm^{-1}, encountered in the IR spectrum of many azo compounds [22], shows that *p*-phenylazo-α-naphthol compounds **3** also contain azo tautomer [20]. This stretching band supports the presence of azo–hydrazone tautomerism in the solid state [20].

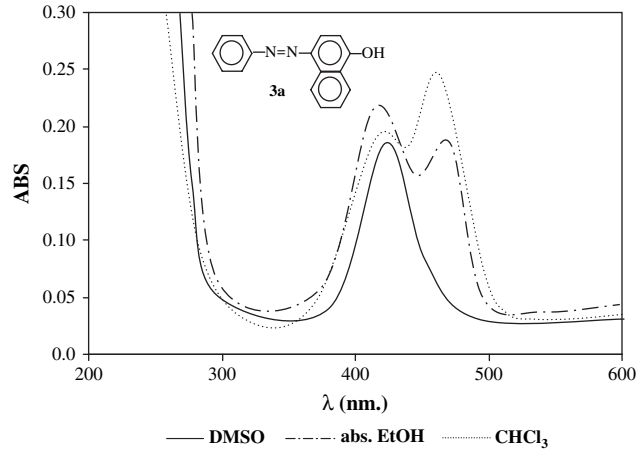


Fig. 1. UV–vis spectra of *p*-phenylazo-α-naphthol (**3a**) in DMSO, absolute EtOH and $CHCl_3$.

As shown in Table 4, the *p*-phenylazo-α-naphtoxycyclotriphosphazene compounds **5** have four characteristic absorption bands. These bands shown at 1432–1423 cm^{-1}, 1232–1203 cm^{-1}, 1273–1253 cm^{-1}, and 928–912 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-α-naphthols **3** and its derivatives *p*-phenylazo-α-naphthoxycyclotriphosphazenes **5** are compared, it is seen that the –NH/–OH vibration at 3351–3116 cm^{-1} region and C=O vibration at 1633–1619 cm^{-1} region disappeared and a new band appeared

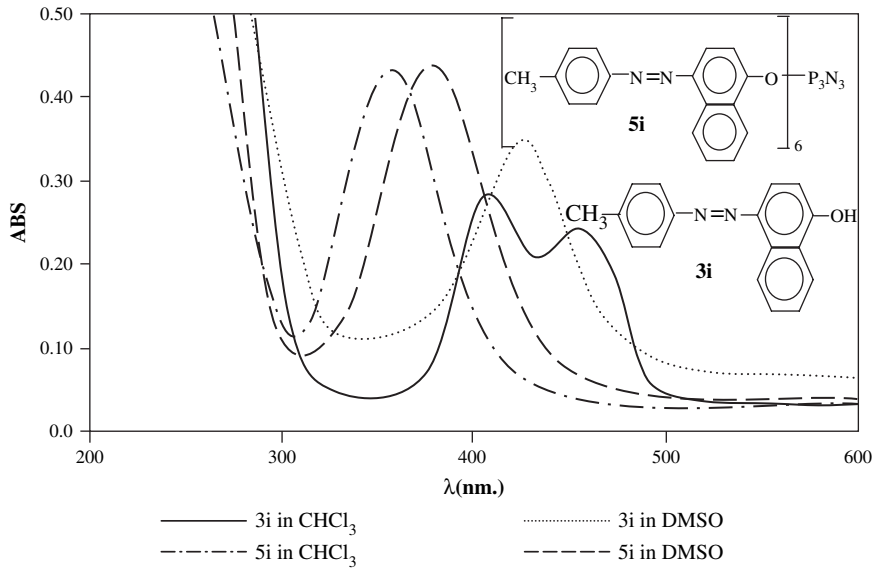


Fig. 2. UV–vis spectra of *p*-(*p*-methylphenylazo)-α-naphthol (**3i**) and hexakis[*p*-(*p*-methylphenylazo-α-naphthoxy)]cyclotriphosphazene (**5i**) in $CHCl_3$ and DMSO.

at 1065–1034 cm^{-1} region of the spectrum because of P–OAr absorption (Table 4, Fig. 3). The absorption frequencies of N=N and $C_{(aryl)}$–N= of *p*-phenyl azo-α-naphthols **3** changed a few cm^{-1} in *p*-phenylazo-α-naphthoxycyclotriphosphazenes **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 the some bis-azo compounds and their derivatives [22,23].

Table 3
UV–vis absorption bands of *p*-phenylazo-α-naphthols (**3**) and its cyclotriphosphazene derivatives (**5**) in $CHCl_3$ and DMSO (nm, ε_{max})

Compound	$CHCl_3$ (A)	$CHCl_3$ (H)	DMSO (A)	DMSO (H)
3a	411(31,167)	464(40,167)	411(29,667)	–
5a	378(6000)	–	378(75,500)	–
3b	–	456(45,000)	424(31,500)	–
5b	386(54,333)	–	387(87,500)	–
3c	–	454(33,166)	425(26,166)	–
5c	382(83,000)	–	384(54,500)	–
3d	418(24,667)	456(25,833)	423(39,000)	–
5d	382(83,833)	–	384(69,833)	–
3e	405(24,000)	462(18,000)	412(37,500)	–
5e	375(57,333)	–	377(97,667)	–
3f	426(23,333)	455(24,167)	425(26,333)	–
5f	384(93,000)	–	385(50,833)	–
3g	432(20,833)	461(23,000)	424(42,333)	–
5g	385(61,500)	–	385(98,750)	–
3h	377(14,167)	461(21,833)	–	468(39,000)
5h	395(89,333)	–	391(60,833)	–
3i	404(29,167)	469(27,167)	411(41,833)	–
5i	378(43,500)	–	382(76,667)	–
3j	404(30,167)	470(29,167)	410(34,167)	–
5j	374(59,167)	–	379(88,667)	–
3k	405(35,500)	474(33,500)	412(29,167)	–
5k	378(47,500)	–	384(29,333)	–
3m	384(15,333)	456(38,167)	435(39,000)	–
5m	392(62,667)	–	399(62,667)	–
3n	418(27,667)	–	401(36,000)	–
5n	368(50,000)	–	368(54,833)	–
3o	388 (21,500)	459(16,833)	392(27,167)	–
5o	362(61,000)	–	366(69,333)	–

Table 4
FT-IR bands (cm^{-1}) of *p*-phenylazo-α-naphthols **3** and its derivatives *p*-phenylazo-α-naphthoxycyclotriphosphazenes **5** (KBr disk)

Compound	−NH/−OH	N=N	C=O	Ar−N=	P−N−P (asym)	P−N−P (sym)	P=N	P−OAr	CH_3−C=O
3a	3247−3197	1415	1622	1155	–	–	–	–	–
5a	–	1423	–	1147	1254	928	1227−1205	1060	–
3b	3343−3127	1412	1622	1157	–	–	–	–	–
5b	–	1423	–	1145	1253	926	1227−1205	1058	–
3c	3251−3125	1414	1626	1155	–	–	–	–	–
5c	–	1423	–	1147	1272	912	1231−1207	1065	–
3d	3245−3193	1415	1628	1153	–	–	–	–	–
5d	–	1425	–	1147	1254	928	1228−1205	1055	–
3e	3249−3145	1416	1628	1149	–	–	–	–	–
5e	–	1423	–	1145	1265	926	1230−1203	1053	–
3f	3245−3185	1415	1628	1154	–	–	–	–	–
5f	–	1423	–	1147	1263	926	1227−1205	1065	–
3g	3241−3178	1413	1627	1153	–	–	–	–	–
5g	–	1425	–	1145	1265	925	1228−1203	1049	–
3h	3239−3184	1408	1630	1158	–	–	–	–	1672
5h	–	1425	–	1151	1263	928	1228−1205	1034	1684
3i	3243−3197	1414	1624	1151	–	–	–	–	–
5i	–	1423	–	1147	1255	926	1227−1205	1052	–
3j	3237−3190	1410	1624	1152	–	–	–	–	–
5j	–	1423	–	1147	1257	926	1226−1205	1054	–
3k	3230−3116	1410	1620	1151	–	–	–	–	–
5k	–	1423	–	1145	1255	918	1224−1205	1052	–
3m	3303−3125	1410	1633	1153	–	–	–	–	–
5m	–	1426	–	1149	1262	926	1226−1205	1053	–
3n	3330−3135	1413	1619	1156	–	–	–	–	–
5n	–	1432	–	1146	1255	926	1227−1205	1052	–
3o	3351−3122	1408	1620	1157	–	–	–	–	–
5o	–	1425	–	1141	1273	915	1232−1205	1052	–

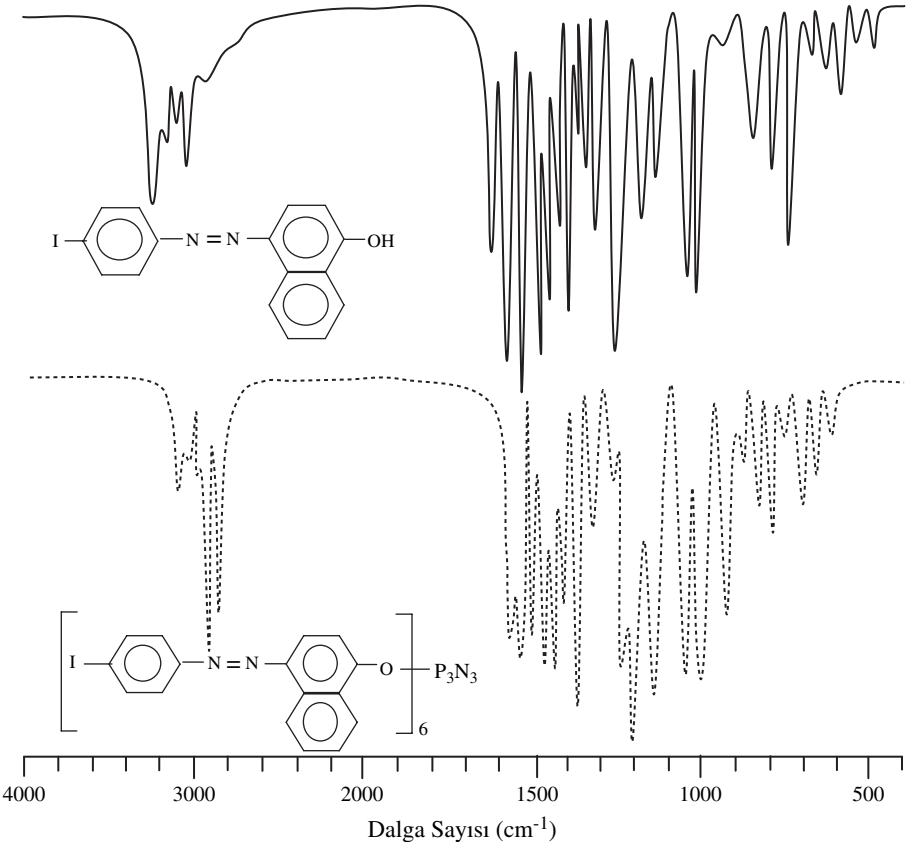
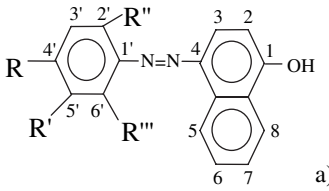


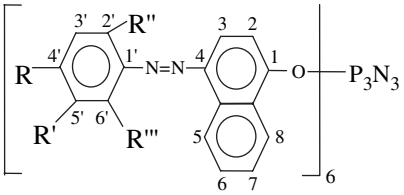
Fig. 3. IR spectra of *p*-(*p*-iyodophenylazo)-α-naphthol (3 g) and hexakis[*p*-(*p*-iyodo phenylazo-α-naphthoxy)]cyclotriphosphazene (5 g) in KBr disk.

Table 5
^{1}H NMR spectral data of *p*-phenylazo-α-naphthols **3** and its derivatives *p*-phenylazo-α-naphthoxycyclotriphosphazenes **5** in DMSO–d_6



3

a) R,R',R",R"'= H
b) R"= Cl, R, R', R"'= H
c) R'= Cl, R, R",R"'= H
d) R= Cl, R',R",R"'= H
e) R= F,R',R",R"'= H
f) R= Br,R',R",R"'= H
g) R=I,R',R",R"'= H
h) R= CH_3CO, R', R",R"'= H
i) R= CH_3, R', R",R"'=H
j) R= CH_3CH_2, R', R",R"'= H
k) R,R'= CH_3, R",R"'= H
m) R",R= Cl, R',R"'= H
n) R",R"'= Cl, R',R= H
o) R",R"'= CH_3, R',R= H



5

Compound	OH/NH*	H2	H3	H5	H6 H7	H8	H2′	H3′	H4′ H5′	H6′	CH_3–	CH_2–
3a	11.15	7.02	7.95	8.89	7.66–7.74	8.23	7.86		7.55–7.60	7.86	–	–
5a	–	7.15	7.93	8.70	7.63–7.71	8.05	7.83		7.48–7.55	7.83	–	–
3b	11.32	7.05	7.91	8.92	7.56–7.75	8.25	–		7.46–7.54	7.83	–	–
5b	–	7.18	7.88	8.73	7.59–7.73	8.02	–		7.43–7.58	7.78	–	–
3c	11.40	6.93	7.94	8.79	7.67–7.76	8.17	7.42–7.61	–	7.42–7.61	7.82	–	–
5c	–	7.15	7.87	8.78	7.61–7.70	8.06	7.48–7.57	–	7.48–7.57	7.74	–	–
3d	11.24	7.03	7.97	8.88	7.66–7.72	8.23	7.89	7.59	– 7.59	7.89	–	–
5d	–	7.18	7.94	8.80	7.66–7.74	8.19	7.83	7.58	– 7.58	7.83	–	–
3e	11.26	6.98	8.02	8.84	7.53–7.73	8.21	7.40	7.93	– 7.93	7.40	–	–
5e	–	7.10	7.97	8.73	7.52–7.64	8.16	7.33	7.87	– 7.87	7.33	–	–
3f	11.21	7.02	7.96	8.80	7.50–7.68	8.19	7.78	7.74	– 7.74	7.78	–	–
5f	–	7.13	7.91	8.79	7.51–7.65	8.03	7.75	7.68	– 7.68	7.75	–	–
3g	11.23	7.02	8.01	8.84	7.57–7.84	8.28	7.93	7.31	– 7.31	7.93	–	–
5g	–	7.20	7.90	8.71	7.58–7.75	8.30	7.87	7.32	– 7.32	7.87	–	–
3h	10.17*	6.80	8.16	8.65	7.46–7.74	8.25	7.98	8.08	– 8.08	7.98	2.56	–
5h	–	7.13	8.02	8.68	7.40–7.70	8.23	7.82	7.91	– 7.91	7.82	2.58	–
3i	11.25	6.97	7.88	8.84	7.47–7.72	8.21	7.80	7.38	– 7.38	7.80	2.41	–
5i	–	7.14	7.90	8.70	7.45–7.71	8.19	7.82	7.34	– 7.34	7.82	2.46	–
3j	11.09	7.01	7.89	8.88	7.55–7.73	8.23	7.80	7.43	– 7.43	7.80	1.24	2.71
5j	–	7.11	7.86	8.75	7.48–7.68	8.12	7.74	7.38	– 7.38	7.74	1.26	2.73
3k	11.03	6.97	7.85	8.86	7.53–7.62	8.21	7.71	–	– 7.33	7.64	2.34(p), 2.29(m)	–
5k	–	7.12	7.84	8.87	7.50–7.60	8.18	7.71	–	– 7.35	7.64	2.34(p), 2.30(m)	–
3m	11.25	7.05	7.94	8.90	7.52–7.76	8.28	–	7.52–7.76	– 7.52–7.76	7.86	–	–
5m	–	7.18	7.78	8.65	7.53–7.73	8.12	–	7.53–7.73	– 7.53–7.73	7.68	–	–
3n	11.40	7.07	7.89	8.68	7.56–7.76	8.26	–		7.34–7.42	–	–	–
5n	–	7.25	7.79	8.55	7.51–7.68	8.05	–		7.31–7.44	–	–	–
3o	11.08	7.03	7.81	8.68	7.53–7.68	8.24	–		7.18–7.38	–	2.38	–
5o	–	7.15	7.80	8.60	7.56–7.64	8.15	–		7.17–7.35	–	2.34	–

* 3h has been hydrazone form in DMSO–d_6.

3.3. ^{1}H NMR spectra

^{1}H NMR spectra of both starting azo compounds and their phosphazene derivatives are taken in DMSO–d_6. Because, in DMSO–d_6 azo compounds (**3**) except to **3h** are found only in azo tautomer form, which has been found from UV–vis data to display azo form in DMSO.

In the ^{1}H NMR spectra studied azo dyes (**3**) except **3h** show one peak at 11.40–11.03 ppm, which belongs to the hydroxyl group as cited in the work [24]. After the reactions mentioned above are carried out this peak disappears in this range. The phenyl and naphthyl groups were also observed in the 7.17–8.08 ppm and 6.80–8.92 ppm regions, respectively (Table 5). Various protons of azo dyes **3** have appeared in their usual pattern [15,16,20,22] but with a slight chemical shift compared to the phosphazene derivatives **5**. The peaks of substituted groups are also given in Table 5.

^{1}H NMR spectra of *p*-(*p*-acethylphenylazo)-α-naphthol (**3h**) show difference from the other *p*-phenylazo-α-naphthol compounds **3** in DMSO–d_6. The singlet peak at 10.17 ppm belonging to –NH proton in ^{1}H NMR spectra in Fig. 4 shows that this compound (**3h**) has been the hydrazone form. This result is harmonious with its UV–vis spectra in DMSO [11,16,25].

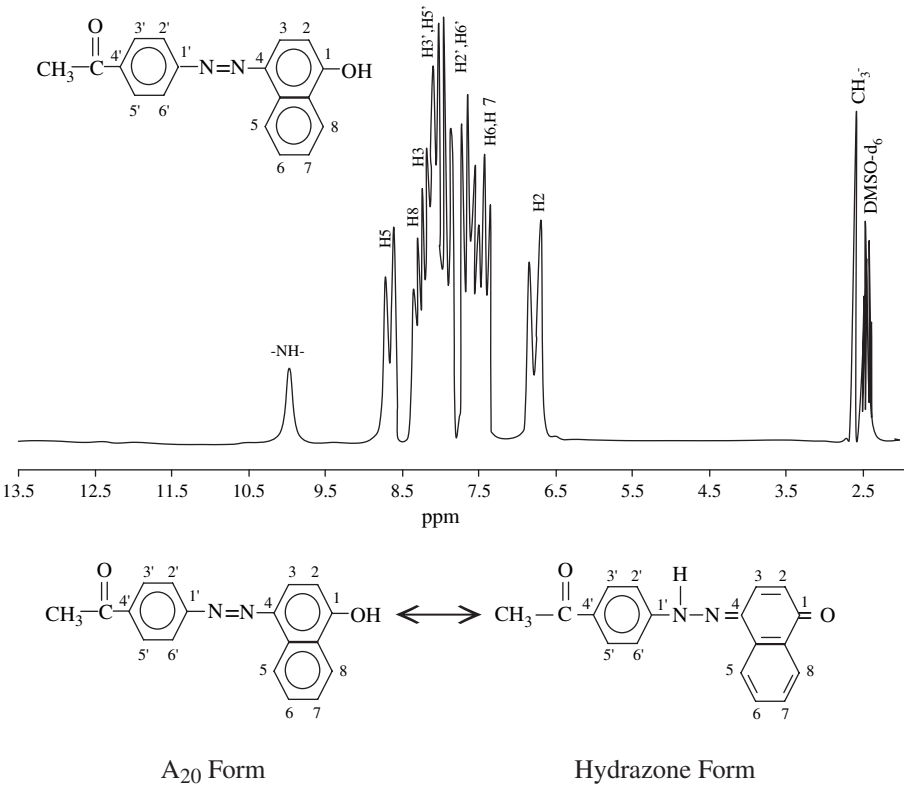


Fig. 4. ^{1}H NMR spectra of *p*-(*p*-acethylphenylazo)-α-naphthol (**3h**) in DMSO–d_6.

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