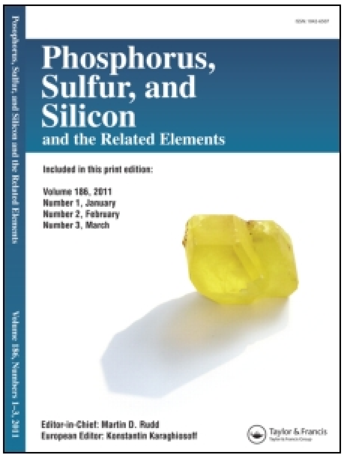


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PREPARATION AND CHARACTERIZATION OF CHROMOPHOR GROUP CONTAINING CYCLOTRIPHOSPHAZENES: I IMINO CHROMOPHOR CARRYING SOME CYCLOTRIPHOSPHAZENES

Mustafa Odabaşoğlu[a]; Günseli Turgut[a]; Hatice Karaer[b]
[a] Science and Arts Faculty, Department of Chemistry, Ondokuz Mayis University, Kurupelit, Samsun, Turkey [b] Amasya Education Faculty, Department of Chemistry Amasya, Ondokuz Mayis University, Turkey

To cite this Article Odabaşoğlu, Mustafa , Turgut, Günseli and Karaer, Hatice(1999) 'PREPARATION AND CHARACTERIZATION OF CHROMOPHOR GROUP CONTAINING CYCLOTRIPHOSPHAZENES: I IMINO CHROMOPHOR CARRYING SOME CYCLOTRIPHOSPHAZENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 152: 1, 9 — 25

To link to this Article: DOI: 10.1080/10426509908031613

URL: http://dx.doi.org/10.1080/10426509908031613

Phosphorus, Sulfur and Silicon, 1999, Vol. 152, pp. 9-25
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATION AND CHARACTERIZATION OF CHROMOPHOR GROUP CONTAINING CYCLOTRIPHOSPHAZENES: I IMINO CHROMOPHOR CARRYING SOME CYCLOTRIPHOSPHAZENES

MUSTAFA ODABAŞOĞLU[a]*, GÜNSELI TURGUT[a] and
HATICE KARAER[b]

[a]*Ondokuz Mayis University, Science and Arts Faculty, Department of Chemistry 55139, Kurupelit Samsun, Turkey and* [b]*Ondokuz Mayis University, Amasya Education Faculty, Department of Chemistry Amasya, Turkey*

(Received 03 November, 1998; In final form 14 December, 1998)

Some new substituted cyclotriphosphazenes were prepared by the reaction of hexachlorocyclotriphophazene and 4-hydroxy or 4′-hydroxy Schiff bases as 4′-hydroxybenzylideneaniline, 4′-hydroxy-4-chlorobenzylideneaniline, 4′-hydroxy-2-chlorobenzylidenaniline, 4′-hydroxyfurfurylidenaniline, 4-hydroxybenzylidene-2′-methylaniline, 4-hydroxybenzylidene-2′,6′-dimethylaniline, 4-hydroxybenzylidene-2′-chloroaniline, 4-hydroxybenzylidene-4′-tert-butylaniline, 4′-hydroxybenzylidene-3,4–15-Crown-5-aniline. The structure of compounds with a general formula $[NP(OC_6H_4CH{=}N\text{-}Ar)_2]_3$ or $[NP(OC_6H_4N{=}CH\text{-}Ar)_2]_3$, was determined by IR, UV, ^{1}H-NMR and elemental analysis. IR spectra of all compounds showed four characteristic bands located at 1633–1601cm^{-1}, 1242–1150cm^{-1}, 1278–1261cm^{-1} and 958–943cm^{-1}, respectively, corresponding to CH=N, P=N, P-N-P (asymmetric) and P-N-P (symmetric) vibrations. Charasterictic UV bands, named as Band I, Band II, Band III and Band IV located at 346–308nm, 294–271nm, 262–216nm and 240–210nm respectively, are due to electronic transitions. The ^{1}H-NMR spectra of 4-hydroxyfurfurylidene and the phosphazene derivative shows cis-trans izomerization below 305°K and 295°K.

Keywords: Cyclotriphosphazenes; Schiff bases; phosphazenes; cromophor group; imino group; hexachlorocyclotriphosphazenes

---

* Correspondence Author.

INDRODUCTION

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, is a noteworthy halophosphazane and is a key material to the synthesis of the majority of other halophosphazenes and various side group phosphazenes. In a number of papers published in recent years, scientists have explored mixed-substituted polymers containing p-methoxy groups and rigid, aromatic Schiffs bases side groups[1] and they pointed out the possibility of bioactive molecules which might be attached to poly[aryloxyphosphazenes] through a hydrolyzable Schiff base linkage[2]. The reactions reported, are prototypes since the use of aryloxy cosubstituent groups precludes the possibility of total biodegradation of these polymers. On the other hand, the synthesis and complexing properties of open-chain ligands (podands) have been studied extensively in recent years and some interesting reviews in this field have appeared[3]. Moreover, some examples of the application of new ligands, which contain polyether chains and thus a higher number of donor atoms, are reported to be phase-transfer catalysts in anion promoted reactions[4].

In this study, hexachlorocylotriphosphazenes are caused to react with 4-hydroxy and 4′-hydroxy Schiff bases in THF. This process resulted in the formation of cyclotriphosphazenes containing imino chromophor groups. The spectroscopic properties of cyclotriphosphazenes are also investigated. The aim of our study was to synthesize and examine the characteristics of the new derivatives of cyclotriphosphazenes containing a chromophor group, with was used in the above mention field.

RESULT and DISCUSSION

In the IR spectra of all substituted anilines used as condensation components, the doublet stretching vibration was observed between 3400–3200cm^{-1} that belongs to the amino group and aldehydes have a strong stretching vibration due to the carbonyl group between 1710–1685cm^{-1} region which are in agreement with literature values[5]. The characteristic disappearance of carbonyl and amino groups and the appearance of C=N in the region 1633–1601cm^{-1} and broad OH absorption in the region 3500–3300cm^{-1} were indicative of Schiff's base formation. The cyclotrimeric products, which were obtained after the treatment of $P_3N_3Cl_6$ with OH group substituted Schiff's bases, showed broad bands as expected. The compounds VI and VII showed a characteristic P=N stretching absorption band between 1242–1150cm^{-1}. Furthermore, these compounds give two other characteristic infrared bands. The strongest band in the 1278–1261cm^{-1} region corresponds to a P-N-P asymmetric vibration or a degenerate ring-stretching mode. The second characteristic band in the 958–943cm^{-1} region can be attributed to P-N-P symmetric stretch.

The absorption band for hexachlorocyclotriphosphazene is at about 885cm^{-1} [6], but this vibrational frequency has been increased by the 4-iminophenoxy groups. All the characteristic IR bands are shown in Table III.

TABLE I The characterisation and elemental analysis of the imino chromophor carrying cyclotriphosphazenes

Compound	*Yield (%)*	*m.p (°C)*	*%C*	*%C*	*%H*	*%H*
			Calculate	*Found*	*Calculate*	*Found*
Ia	72	186–188	-	-	-	-
VIa	65	163–165	71.39	70.42	4.57	4.45
Ib	85	183–185	-	-	-	-
VIb	58	228–230	61.66	61.95	3.56	3.55
Ic	76	149–150	-	-	-	-
VIc	62	154–156	61.66	61.55	3.56	3.87
II	63	183–185	-	-	-	-
VId	58	73–75	63.31	62.11	3.84	3.42
IIIa	82	194–196	-	-	-	-
VIIa	68	145–147	71.39	71.62	4.58	5.59
IIIb	85	187–189	-	-	-	-
VIIb	62	80–81	73.02	73.55	5.68	5.57
IIIc	78	174–175	-	-	-	-
VIIc	48	78–80	72.26	71.71	5.16	5.78
IIId	82	172–175	-	-	-	-
VIId	54	73–75	61.66	61.31	3.56	3.50
IIIe	68	153–155	-	-	-	-
VIIe	45	195–196	74.43	74.96	6.56	7.18
IV	76	121–122	-	-	-	-
VIIf	64	110–112	63.23	62.71	6.41	6.35
V	73	186–188	-	-	-	-
VIIg	81	74–75	75.97	75.29	4.47	4.17

TABLE II UV-VIS absorbtion bands of all the synthesised compounds

Compound	*Band I*	*Band II*	*Band III*	*Band IV*
Ia	339(20512)	273(17888)	240(21616)	209(17008)
VIa	316(63200)	264(104080)	220(83200)	212(83200)
Ib	345(9120)	279(10400)	243(8608)	-
VIb	319(60480)	271 (98240)	-	-
Ic	349(9480)	282(7768)	244(10624)	207.5(8558)
VIc	327(37280)	279(63040)	228(113120)	-
II	343(10468)	293(9256)	269(4222)	207(4435)
VId	312(100000)	292(106320)	262(69333)	229(46363)
IIIa	336(6300)	318(6660)	258(5852)	240(4258)
VIIa	308(49400)	294(56750)	251(65700)	-
IIIb	316(3238)	291(12184)	265(13632)	-
VIIb	335(11870)	290(17540)	247(32600)	-
IIIc	312(17760)	294(22344)	268(15840)	238(10392)
VIIc	324(60040)	290(82400)	250(129600)	210(46560)
IIId	-	301(6661.5)	268(4206)	238(3558)
VIId	308(37714)	292(51340)	252(66145)	-
IIIe	313(19619)	294(20536)	260(13560)	238(10880)
VIIe	321(30140)	289(32780)	265(42160)	240(30540)
IV	339(11392)	293(10888)	268(8212)	239(6980)
VIIf	336(37340)	292(48940)	246(65357)	-
V	342(7296)	293(2285)	278(9856)	-
VIIg	346(48580)	284(58285.7)	250(68200)	-

The UV-VIS spectral behaviour of Schiff's bases and their cyclotriphosphazene derivatives were investigated in THF. As can be seen in Table II, the substituted cyclotriphosphazenes give the spectra VIa similar to Ia, VIIg similar to V (see also Figure 1). Thus, delocalization effects between the substituents and the phosphazene ring were not detected [7,8]. Cyclophosphazene rings themselves do not absorb in the near UV region[9], but if there were delocatization, an absorption would be seen in this region.

The spectra of components VI are closely similar to that of Schiff's bases, (Figure 1a); It is clearly seen that the band I shifts to longer wavelengths, while other bands shift to shorter wavelengths. These results are related with the nonplanar structure and the conjugation of Schiff's bases. The pair of electrons on the nitrogen atom can conjugate with the N-phenyl

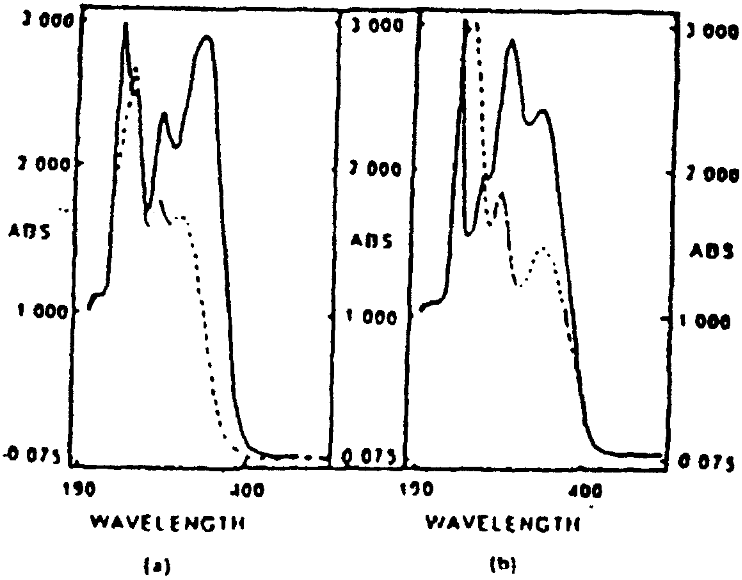


FIGURE 1 The UV-VIS spectra of the compounds, Ia, VIa, V and VIIg a) – Ia ... VIa; b) – V ...VIIg

ring, Ph_N. This implies a noncoplanar molecular structure, since Ph_N can only conjugate with the nitrogen lone pair if the Ph_N is rotated out of the plane of the conjugated system consisting of the C-phenyl group, Ph_C, and the azo-methine group. In the latter the π-conjugation extends over the whole molecule but the nitrogen lone-pair electrons do not take part in the π-conjugation and exhibit repulsion with neighbouring hydrogen atoms[10].

Band I is sensitive to Ph_N substitution and corresponds to a transition to a benzene $^1B_{2u}$-type state in the aniline part of the molecule. A transition to a benzene $^1B_{2u}$-type state in the benzal part of the molecule is hidden under more intense transitions. Band II is sensitive to Ph_N substitution and is interpreted as a transition to a charge-transfer state in which the azo-metine groups acts as electron acceptors and the Ph_C ring as electron donors.

Band III appears to be sensitive to Ph_N substitution and may correspond to the charge-transfer band of the aniline part. This band of aniline has appreciable local-excited-state character corresponding to a benzene $^1B_{1u}$-type state. Band IV is sensitive to Ph_C substitution and is interpreted as the perturbated $^1B_{1u}$ band of the benzal part.

TABLE III IR bands of all the synthesised compounds

Compound	*O-H*	*-CH=N-*	*C-O*	*P-N-P(asy.)*	*P-N-P(sym.)*	*P=N*	*P-OAr*
Ia	3300–3200	1633	1373	-	-	-	-
VIa	-	1631	1364	1272	953	1241–1179	1015
Ib	3500–3250	1630	1276	-	-	-	-
VIb	-	1628	1298	1267	957	1205–1174	1019
Ic	3500–3250	1614	1380	-	-	-	-
VIc	-	1628	1364	1276	958	1215–1177	985
II	3503–3430	1635	1386	-	-	-	-
VId	-	1636	1351	1274	950	1208–1150	1017
IIIa	3250	1601	1385	-	-	-	-
VIIa	-	1634	1360	1272	958	1242–1164	1017
IIIb	3350–3274	1624	1388	-	-	-	-
VIIb	-	1639	1380	1278	945	1186–1167	1019
IIIc	3456–3300	1614	1388	-	-	-	-
VIIc	-	1634	1369	1272	949	1203–1164	1017
IIId	3575–3341	1620	1399	-	-	-	-
VIId	-	1633	1368	1270	946	1201–1162	976
IIIe	3610–3484	1614	1369	-	-	-	-
VIIe	-	1630	1369	1276	953	1213–1172	1015
IV	3493–3442	1611	1362	-	-	-	-
VIIf	-	1624	1360	1261	943	1184–1162	1020
V	3500–3430	1610	1294	-	-	-	-
VIIg	-	1623	1363	1276	951	1200–1168	1016

One should point out here that bands I and III, which correspond to electronic transitions involving the Ph_N, do not appear in N-benzlimines where the Ph_N is replaced with an aliphatic group.

In the ^1H-NMR spectra all substituted Schiff's bases used as side groups of cylotriphosphazenes, show one peak at 9.42–10.12 ppm which belongs to the hydroxyl groups, as cited in the literature[11]. After the reactions mentioned above are carried out this peak disappears in this range. The ^1H-NMR spectra of the synthesised compounds show a shape singlet at 1.34 ppm, which is attributed to tert-butyl group. The phenyl groups were also observed in the 6.55–8.22 ppm region, as given in Table IV. The peaks of $=CH-$, $-CH_3$, $-CH_2CH_2-$ are also given.

^1H-NMR spectra at 305°K of II and at 295°K of VId exhibited a dublet signal at 8.38 ppm which is attributed to the =CH group.

There is a weak peak in the spectra shifting with temperature. The cis-trans izomerization shows the same behaviour, in furfural[11]. Similarly, the compounds synthesised in this work using furfural, show the cis-trans izomerization below definite temperatures. Figure 2 indicates that this izomerization occurs below 305°K for compound II and below 295°K for compound VI d.

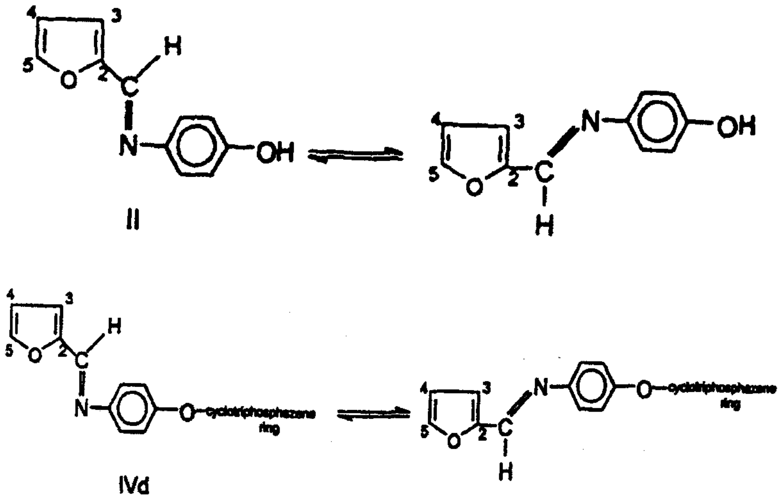


FIGURE 2 Cis-trans izomerization of compounds II and VId

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

Compound	*O-H*	*C-H(arom)*	*CH=N*	$-CH_3$	$-C(CH_3)_3$
Ia	9.55	6.77–7.99	8.56	-	-
VIa	-	7.01–7.78	8.62	-	-
Ib	9.58	6.78–7.86	8.53	-	-
VI	-	6.97–7.74	8.54	-	-
Ic	9.75	6.79–7.18	8.83	-	-
VIc	-	6.98–8.05	8.74	-	-
*II	-	6.64–7.77	8.43	-	-
**VId	-	6.62–7.80	8.37	-	-
IIIa	10.12	6.86–7.78	8.44	-	-
VIIa	-	6.55–7.85	8.53	-	-
IIIb	10.11	6.86–7.78	8.13	2.11	-
VIIb	-	6.80–7.92	8.30	2.49	-
IIIc	10.11	6.85–7.79	8.32	2.48	-
**VIIc	-	6.86–7.77	8.29	2.34	-
IIId	9.80	6.87–7.84	8.29	-	-
VIId	-	7.11–7.88	8.48	-	-
IIIe	9.42	6.80–7.74	8.40	-	1.33
VIIe	-	7.06–7.33	8.42	-	1.34
IV	9.77	6.90–7.92	8.54	-	-
VIIf	-	6.85–8.22	8.59	-	-
V	10.10	6.70–7.75	8.46	3.97	-
**VIIg	-	6.71–7.73	8.38	*3.75	-

* Aseton-d_6, ** $CDCl_3$, DMSO-d_6.

The spectrum of compound II at 295°K is shown in Figure 3, and the 8.0–10 ppm region at various temperatures is shown in Figure 4. Also the spectrum of compound VId at 295°K is shown in Figure 5, and the 8.5–10 ppm region at various temperatures is shown in Figure 6. The VId compound, which is obtained after replacing the hydrogen atom of the OH group of compound II with a phosphorus atom can not have a hydrogen band, and shows cis-trans isomerization at lower temperatures.

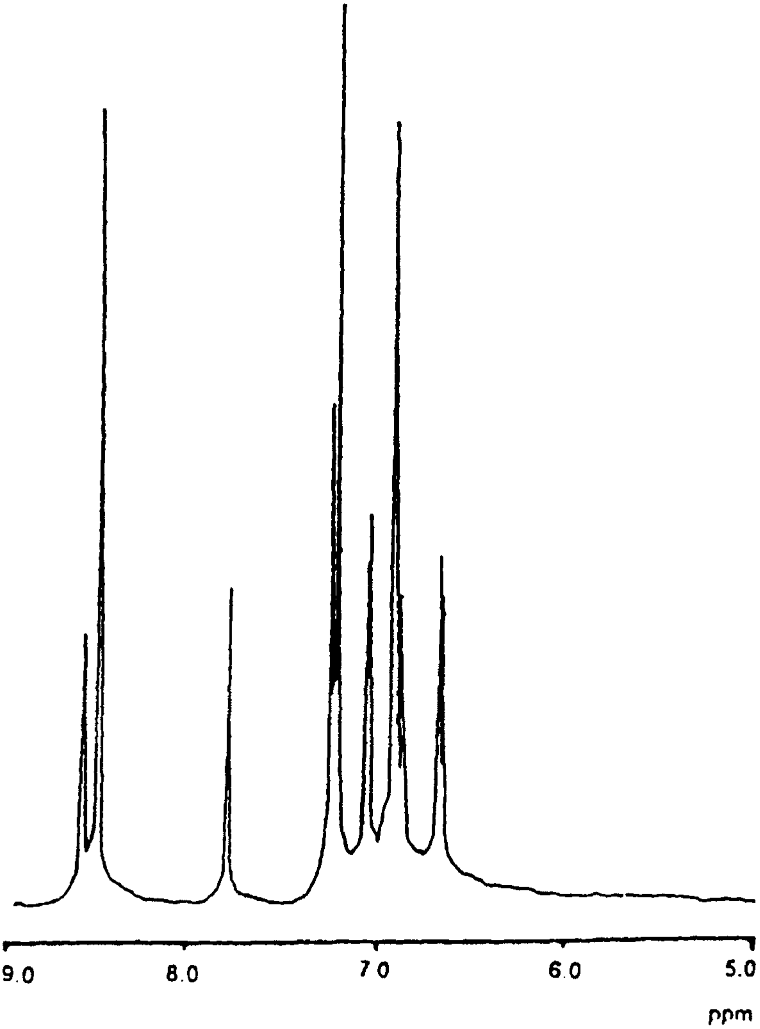


FIGURE 3 The ^{1}H-NMR spectra of compound II at 295°K

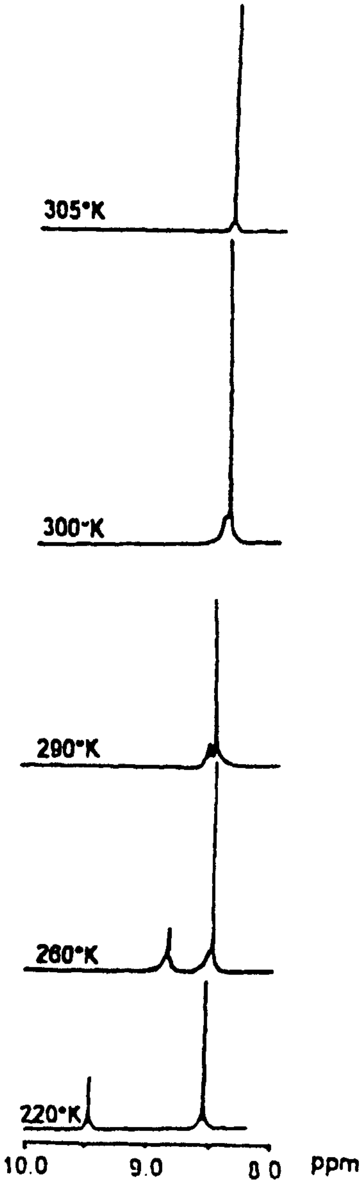


FIGURE 4 The ^{1}H-NMR spectra of compound II at various temperatures (the 10.0–8.0 ppm region)

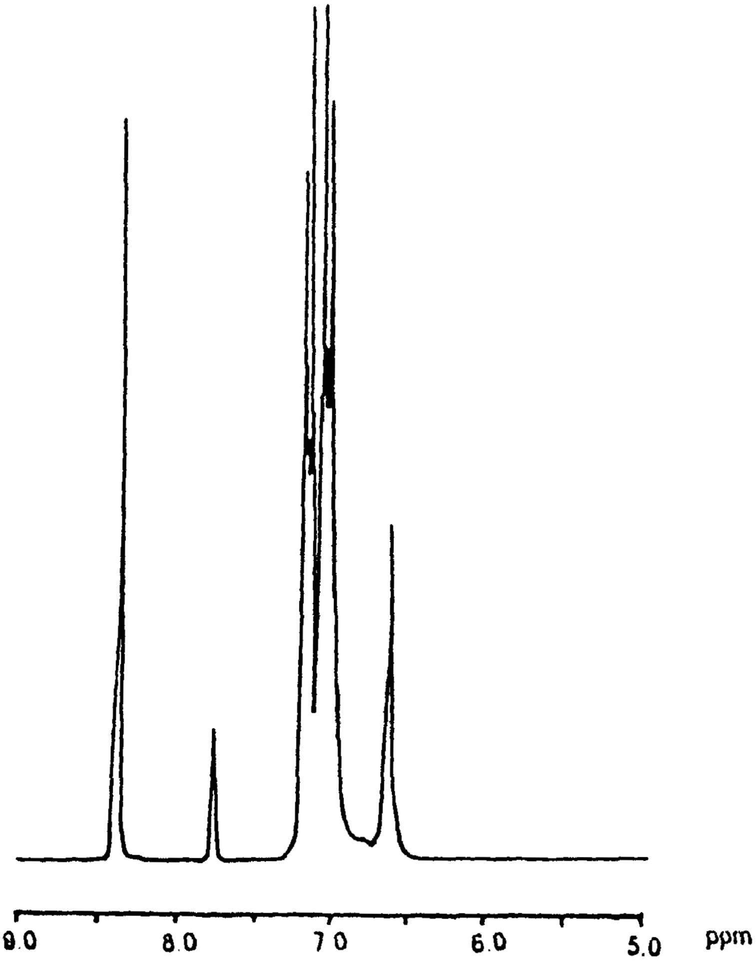


FIGURE 5 The ^1H-NMR spectra of compound VId at 295°K

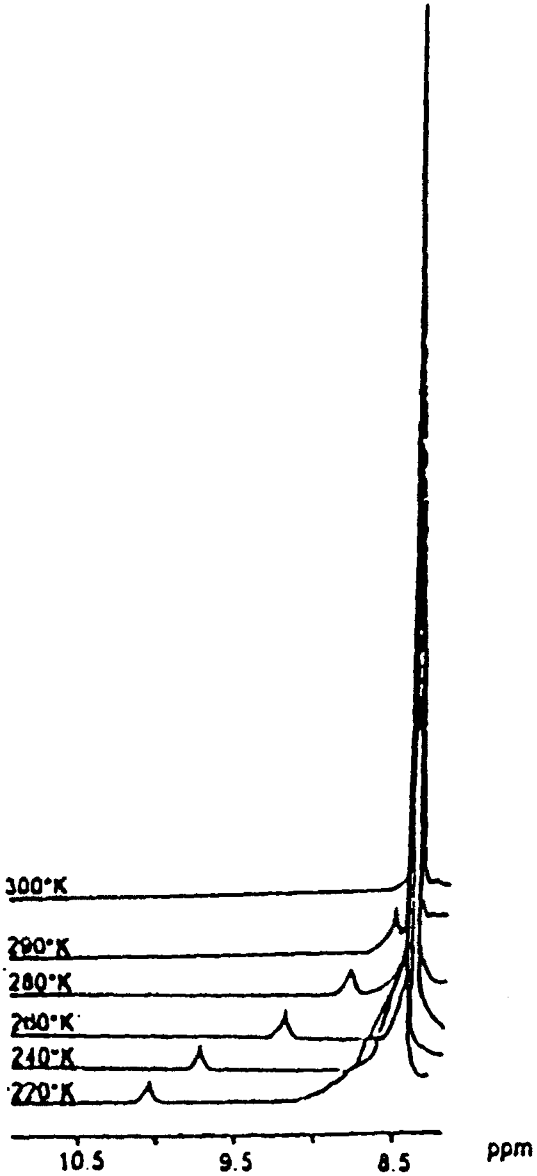


FIGURE 6 The ^{1}H-NMR spectra of compound at VId various temperatures (the 10.0–8.5 ppm)

EXPERIMENTAL SECTION

Reagents and Solvents

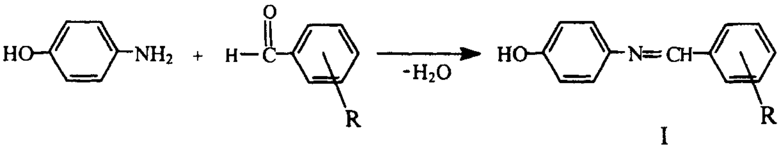
Hexachlorocyclotriphosphazene (99%), 2,6-dimethylaniline (99%) and o-toluidine (99%) were purchased from Aldrich Chemical Company; 4-hydroxybenzaldehyde (>95%), 4′-aminobenzo-15-Crown-5 (>97%), and 4-amino phenol (>99%) were purchased from Fluka AG Chemical Company; Aniline (>99%), 2-chloroaniline (>98%), naphtyl-1-amine (99%), n-hexane (99%), acetonitrile (99%), tetrahydrofuran extra pure (>99%) and acetone (99%) were purhased from Merck Chemical Company; Benzaldehyde (99%) was purchased from Riedel-deHaén AG Chemical Company; Ethlyalcohol was purchased from Tekel. n-Hexan and tetrahydrofuran were refluxed with metallic sodium and distilled prior to use.

Analytical Techniques

All of the compounds were purified by recrystalization, then were chromatographed on neutral alumina with tetrahydrofuran and their purities were monitored by Thin Layer Chromatography. The melting points (m.p) of the compounds were measured with a Gallenkamp Electrothermal melting point aparatus. IR spectra were recorded on a Mattson 1000 FTIR Spectrometer calibrated with polystrene film. Absorption spectra in THF were determined on a Unicam UV-VIS Spectrophotometer. The ^{1}H-NMR spectra were recorded with a Varian EML NMR 200 MHz. Reference tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed by TUBITAK, Marmara Research Centre and TUBITAK Ankara Instrumental Laboratories.

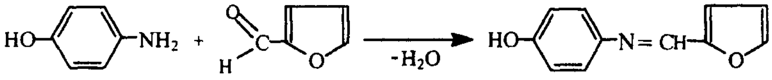
The Synthesis of Schiff's Bases

Preparation of Schiff's bases was reported in previous papers[12–15] using the following reactions:

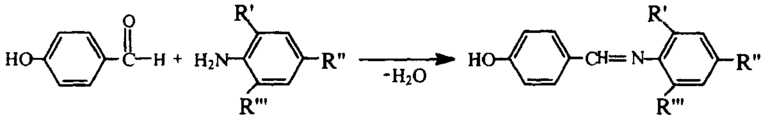


I

a) R= H
b) R= p-Cl
c) R= o-Cl



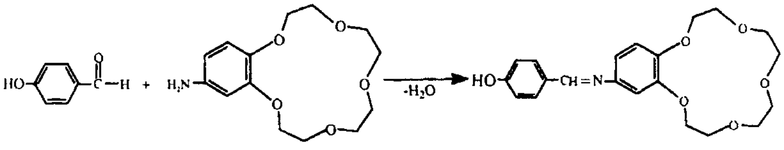
II



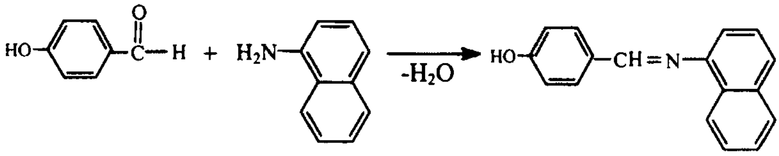
III

a) $R'=R''=R'''=H$
b) $R'=R'''=CH_3$ $R''=H$
c) $R'=CH_3$ $R''=R'''=H$
d) $R'=Cl$ $R''=R'''=H$
e) $R'=R'''=H$ $R''=(CH_3)_3C$

In a preparative experiment, 0.2 mole of amine and the appropriate amount of aldehyde were heated for 4–6 hours under reflux in ethanol containing 4 drops of piperidine. The products crystallised on cooling and were recrystallized from ethanol several times for purification. Similarly, the compounds I-V were prepared using the same set up.



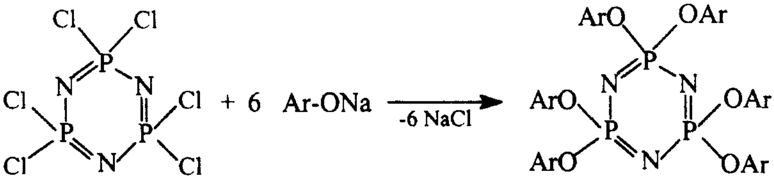
IV



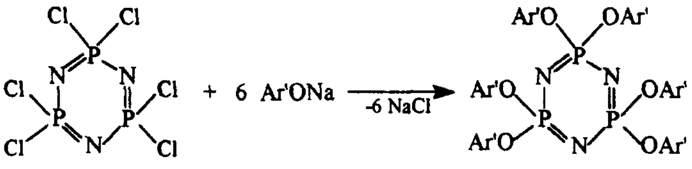
V

The Synthesis of Substitued Phenoxy Cyclotriphosphazenes

Cyclotriphosphazenes (VI,VII) were prepared by modifying the method of Allcock[6,16]. (VI,VII) were obtained by the reaction of hexachlorocylotriphosphazene with Schiffs bases containing hydroxy groups.

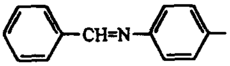


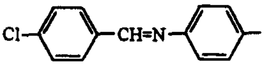
VI

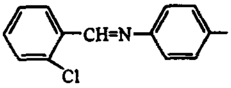


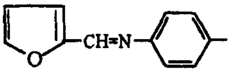
VII

VI

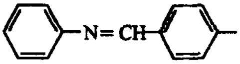
a) Ar =


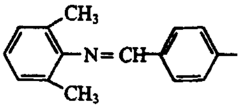
b) Ar =


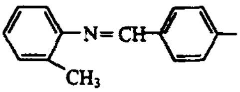
c) Ar =


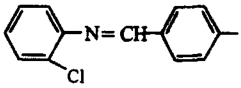
d) Ar =


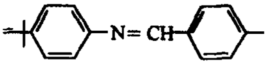
VII

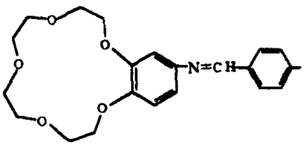
a) Ar' =


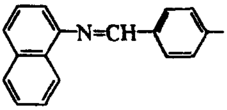
b) Ar' =


c) Ar' =


d) Ar' =


e) Ar' =


f) Ar' =


g) Ar' =


Schiffs base-sodium pheonoxide derivative (Ia) is prepared from 0.3 mole Schiffs base and 0.3 mole sodium under a dry nitrogen atmosphere. A solution of hexachlorotriphosphazene (0.05 mole) in 100 ml THF is prepared and added to the above solution while stirring it continuously. The mixture is then refluxed for 8 hours and then kept for 56 hours at 25°C. Afterwords NaCl is filtered. The filtrate is then evaporated and the residual mixture is precipitated in an acetone-water mixture. The yield of the reaction is a slightly yellow solid. The product is recrystallized twice from acetonitrile for further purification and chromotographed on neutral alumina. The filtrate is evaporated in vacum oven at 60°C. The resulting compound is VIa with 65% yield and with melting point of 163–164°C.

Other compounds (VI,VII) were prepared by similar methods and identified by IR, UV-VIS, ^1H NMR spectroscopic techniques. The analytical data (C and H) with melting points and yields are give in Table I.

References

[1] H.R. Allcock, M.S. Connolly, J.J. Sisko and S. Al-Shali, Macromolecules. **21**, 323–334 (1988).
[2] H.R. Allcock and P.E. Austin, Macromolecules. **14**, 1616–1612 (1981).
[3] F. Vögtle and J. Weber, Angew. Chem. Int. Ed. Engl. **18**, 753 (1979).
[4] M.P. Bullitta, E. Maccioni, L. Cordo and G. Podda, J. Heterocyclic Chem. **30**, 93 (1993).
[5] R.M. Silverstein, G.C. Bassler and T.C. Morrill, "Spectrometric Identification of Organic Compounds." 4th press, John Wiley and Sons, New York (1981).
[6] H.R. Allcock , "Phosphorus – Nitrogen Compounds" Academic Press, Inc. New York (1972).
[7] H.R. Allcock, J. Amer. Chem. Soc. **86**, 2591 (1964).
[8] H.R. Allcock and R.L. Kugel, Inorg. Chem. **2**, 896 (1963).
[9] H.R. Allcock, K.L. Kugel and K.J. Valan, Inorg. Chem. **5**, 1709 (1966).
[10] M.A. El-Bayoumi, M. El-Aasser and F. Abdel-Halim, J. Amer. Chem. Soc. **93**, 586 (1971).
[11] A.D. Bain, G.J. Dungs, F. Rathgeb and J.J. Vanderlet, Phys. Chem. **99**, 17338 (1995).
[12] H. Karaer and I.E. Gümrükçoğlu, Tr. J. of Chemistry. **23**, 67 (1999).
[13] J.W. Jr. Ledbetter, J. Phys. Chem. **70**, 2245 (1967).
[14] J.W. Jr. Ledbetter, J. Phys. Chem. **71**, 445 (1963).
[15] R.E. Kirk, D.F. Otmer, Encylopedia of Chemical Technolog. 2, ABD (1954).
[16] H.R. Allcock and R.J. Best, Can. J. Chem. **42**, 447 (1964).