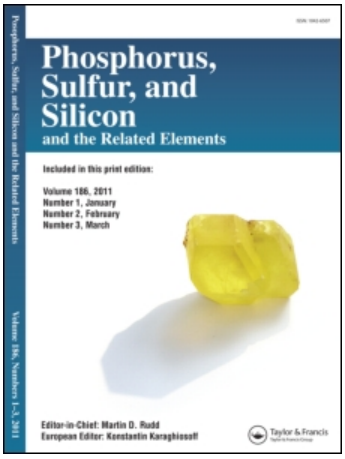

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SYNTHESIS AND CHARACTERIZATION OF NEW 3-NITROPHTHALIMIDOPHENOXY- AND 4-NITROPHTHALIMIDOPHENOXY-CYCLOTRIPHOSPHAZENE MONOMERS AND INTERMEDIATES

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SYNTHESIS AND CHARACTERIZATION OF NEW 3-NITROPHTHALIMIDOPHENOXY- AND 4-NITROPHTHALIMIDOPHENOXY-CYCLOTRIPHOSPHAZENE MONOMERS AND INTERMEDIATES

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Synthesis of novel monomers and polymer precursors: hexakis[4-(3′-nitrophthalimido)phenoxy]cyclotriphosphazene (**VIIa**), hexakis[4-(4′-nitrophthalimido)phenoxy]cyclotriphosphazene (**VIIb**), tris[4-(3′-nitrophthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**VIIIa**) and tris[4-(4′-nitrophthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**VIIIb**) has been performed by two efficient methods. In method 1, hexakis(4-aminophenoxy)cyclotriphosphazene (**III**) and tris(4-aminophenoxy)tris(phenoxy)cyclotriphosphazene (**IV**) are reacted in a single step with 3-nitro- and 4-nitrophthalic anhydride in refluxing phenol and toluene. In method 2, **III** and **IV** are condensed with 3-nitro- and 4-nitrophthalic anhydride in an aprotic solvent followed by *in situ* thermal cyclodehydration of the intermediate respective phthalamic acids. These compounds are yellow crystalline substances and soluble in THF and aprotic solvents. The structure of all the novel compounds has been confirmed by infrared (IR), proton and phosphorus-31 nuclear magnetic resonance (NMR) spectroscopy, elemental analysis and differential thermal analysis (DTA). Thermogravimetric analysis (TGA) of the synthesized compounds **VIIIa** and **VIIIb** showed their thermal stability at 395°C and 32% char yield in air at 800°C. These compounds are potential candidates for the preparation of heat-and fire-resistant polymers and resins.

Key words: Hexakis-, tris- aminophenoxycyclotriphosphazene; 3-nitro- and 4-nitrophthalimidophenoxy-cyclotriphosphazenes; monomers, synthesis; structural assignments.

INTRODUCTION

There is a growing demand for fire-resistant and heat-resistant polymeric materials for civil and defense applications. However, most commercially available polymers lack structural integrity and fire retardancy at high temperatures and also give off smoke and toxic gases when burned in air. In the past decade, cyclolinear and cyclomatrix poly(organo)phosphazenes have formed a class of heat- and fire-resistant ablative polymer systems useful as structural adhesives and coatings.[1–10] We have reported successful synthesis of polyimides,[8] polybismaleimides,[3–7] epoxy matrix resins[9,10] and demonstrated that the cyclotriphosphazene containing polymers are better materials than other reported phosphorus containing polymers[1,2,11] for use as composites and adhesives. The particular enhanced properties obtained were high char yield of polymers in air and nitrogen and 100% limited oxygen index (LOI) of their graphite cloth laminates. These attractive properties of the

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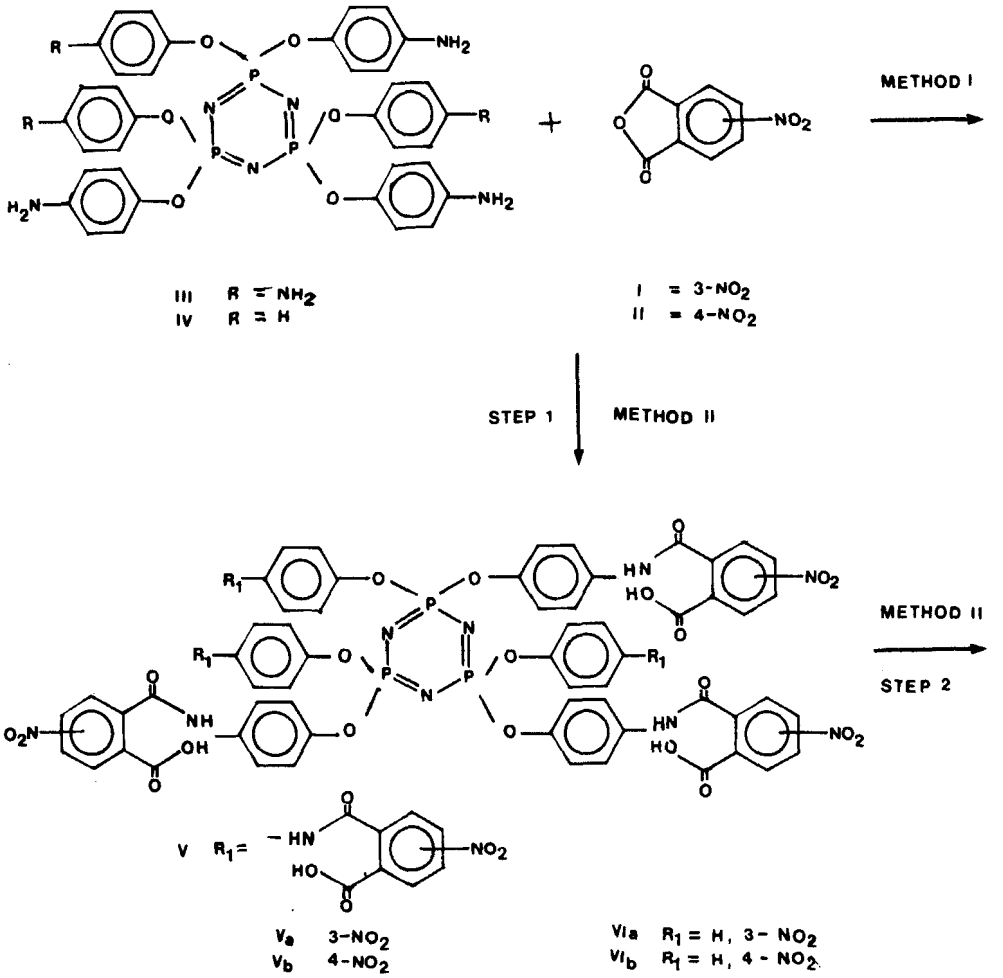
cyclotriphosphazene containing matrix resins prompted further our efforts to improve upon their thermal stability, flexibility and toughness without deteriorating their fire-resistant characteristics.

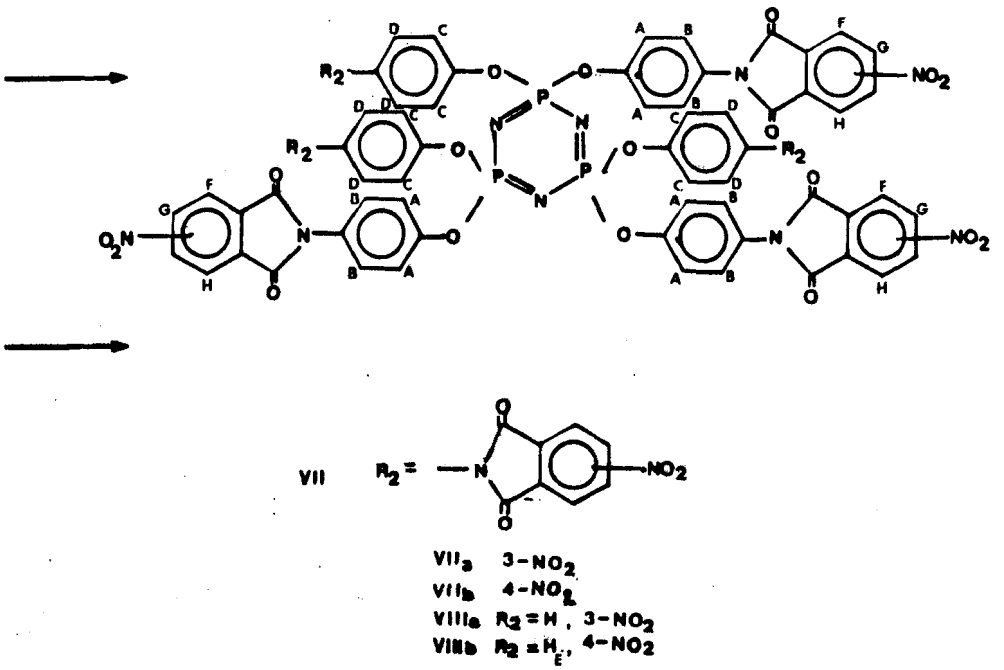
In this paper we present synthesis and characterization of 3-nitrophthalimido- and 4-nitrophthalimido-cyclotriphosphazene monomers and intermediates. These monomers are of considerable interest and useful for developing heat- and fire-resistant polyetherimides by nitro displacement method.

RESULTS AND DISCUSSION

The specific reaction sequences used for the synthesis of 3-nitrophthalimidophenoxy- and 4-nitrophthalimidophenoxycyclotriphosphazene polymer precursors and intermediates are outlined in Scheme I. Hexakis(4-aminophenoxy)cyclotriphos-



SCHEME I



SCHEME I *Continued*

phazene (**III**) and tris(4-aminophenoxy)tris(phenoxy)cyclotriphosphazene (**IV**) have been prepared utilizing the procedures reported earlier by us.[3,12]

Hexakis(4-aminophenoxy)cyclotriphosphazene (**III**) was reacted with 3-nitrophthalic anhydride (**I**) and 4-nitrophthalic anhydride (**II**) by two methods. In method 1, hexakis[4-(3′-nitrophthalimido)phenoxy]cyclotriphosphazene (**VIIa**) was synthesized in good yield by the reaction of **I** and **III** in refluxing toluene and phenol. The structure of **VIIa** was determined by infrared, proton NMR, phosphorus-31 NMR spectroscopy and elemental analysis. In the Table I there are presented ^{1}H-NMR, ^{31}P-NMR and IR spectral data for **VIIa**. The infrared spectra showed characteristics[15] cyclic phosphazene —P=N— skeleton and the presence of phthalimide group, also the bands at 1530 and 1380 cm^{-1} were observed, characteristic of nitro group asymmetrical and symmetrical stretchings. The NMR spectra showed presence of AB coupled 24 aromatic protons. The observation of deshielding of 12 aromatic protons as doublet at 7.30 ppm indicated the presence of imide ring. Further downfield shift of the aromatic protons to 7.80 and 8.15 ppm showed the presence of 3-nitrophthalimido group. Its ^{31}P-NMR spectra showed a A_3 spin singlet at 14.18 ppm indicating the presence of magnetically equivalent phosphorus atoms of the P_3N_3 ring. The differential thermal analysis (DTA) of **VIIa** showed a sharp endotherm at 298°C due to its melting. In method 2, the reaction of **I** and **III** in DMSO at room temperature (Step 1) gave hexakis[4(3′-nitrophthalimic acid)phenoxy]cyclotriphosphazene (**Va**), which on cyclodehydration in step 2 at 160–165°C gave hexakis[4-(3′-nitrophthalimido)phenoxy]cyclotriphosphazene (**VIIa**), identical to that obtained in method 1. The structure of **Va** was consistent to infrared

TABLE I

Spectral data of compounds **VIIa**, **VIIb**, **VIIIa** and **VIIIb**

compound	m.p. (°C) DTA	IR(KBr pellet)ν[cm^{-1}] carbonyl imide	nitro	P=N	P-OC$_{ar}$	O-C$_{ar}$	HC$_{ar}$	^{1}H-NMR in DMSO-d$_6$(δ)* CH$_{ar}$	^{31}P-NMR in DMSO-d$_6$(δ)
VIIa	298°	1780(sh) 1720(s) 705	1530(Assym) 1380(Sym)	1199 1168	1160	1240	1500 1480	7.05(d, 12H$_A$, J_{AB}=10H$_Z$), 7.30(d, 12H$_B$, J_{AB}=J_{BA}=10H$_Z$), 7.55(m, 12H$_{CD}$), 8.15(dd, 6H$_E$, J_{ED}=10H$_Z$ and J_{EC}=2.5H$_Z$)	14.18
VIIb	340°	1780(sh) 1720(S) 705	1525(Assym) 1375(Sym)	1200 1170	1160	1240	1500 1475	7.05(d, 12H$_A$, J_{AB}=10H$_Z$), 7.30(d, 12H$_B$, J_{BA}=10H$_Z$), 7.85(d, 6H$_C$, J_{CD}=10H$_Z$), 7.95 (d, 6H$_E$, J_{ED}=2.5J_Z) 8.50(dd, 6H$_D$,J_{DC}=10H$_Z$, J_{DE}=2.5H$_Z$)	
VIIIa	150°	1780(Sh) 1720(S) 706	1530(Assym) 1390(Symm)	1195 1170	1160	1260	1500 1475	6.91-7.24(m, 18H$_{ABC}$, ortho to ether and imido groups), 7.31-7.42 (m, 9H$_{DEF}$, meta and para to ether groups), 7.98-8.15 (m, 6H$_{GH}$) 8.25-8.35 (m, 3H$_I$)	14.20
VIIIb	172°	1781(Sh) 1720(S) 708	1525(Assym) 1378(Sym)	1199 1172	1160	1245	1502 1479	7.05 (d, 6H$_A$, J_{AB}=10H$_Z$), 7.20 (d, 6H$_B$, J_{BA}=10H$_Z$), 7.15-7.22 (m, 15H$_{CDE}$), 7.95-8.50 (m, 9H$_{FGH}$)	14.15

* Assigned alphabets for the protons of the compound VIIIb are labelled in the shown scheme.

and proton NMR spectra and the data is presented in Table II. The presence of phthalamic acid was seen in NMR and confirmed by D_2O exchange of carboxylic and amido protons. In a similar fashion, hexakis[4-(4′-nitrophthalimido)phenoxy]cyclotriphosphazene (**VIIb**) was synthesized by the reaction of **II** and **III** in refluxing toluene-phenol (method 1) or in DMSO (method 2). The structure of **VIIb** has seen consistent to IR and NMR and the spectral data is presented in Table I. The DTA analysis of **VIIb** showed a sharp endotherm at 340°C due to its melting. The intermediate hexakis[4-(4′-nitrophthalamic acid)phenoxy]cyclotriphosphazene (**Vb**) was characterized and the spectral data is presented in Table II.

Tris[4-(3′-nitrophthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**VIIIa**) was synthesized in good yield by two methods. In method 1, tris(4-aminophenoxy)tris(phenoxy)cyclotriphosphazene (**IV**) was reacted with 3-nitrophthalic anhydride (**I**) in refluxing phenol and toluene. The structure of **VIIIa** was determined by infrared, proton NMR, phosphorus-31 NMR and elemental analysis, the data is presented in Table I. The infrared spectra showed the presence of nitro, imido and phosphazene ring. The proton NMR spectrum showed a 3:3 substitution of

TABLE II

Spectral Data for compounds **Va**, **Vb**, **VIa** and **VIb**

Compound	IR(KBr pellet) ν[cm^{-1}] nitro	=P=N-	P-O$_{ar}$	O-C$_{ar}$	-COOH	-CONH-	HC$_{ar}$	^{1}H-NMR in DMSO-d$_6$(δ) CH$_{ar}$
Va	1525(Assym) 1199 1380(Sym) 1171		1160	1255	3000 1700	1650	1500 1480	7.10 (d,2H$_A$, J_{AB}=10Hz), 7.50 (d, 12H$_B$, J_{BA}=10Hz), 7.80 (m, 12H$_{CD}$), 8.15 (dd, 6H$_E$,J_{ED}=10Hz, J_{EC}=2.5Hz), 9.80-10.20 (broad S,6H, -NHCO-, exchangeable to D_2O) 10.58 (S, 6H, -COOH, exchangeable to D_2O)
Vb	1525(Assym) 1199 1380(Sym) 1171	1160	1254	3000 1702	1648	1500 1480		7.10 (d, 12H$_A$, J_{AB}=10Hz), 7.65 (d, 12H$_B$, J_{BA}=10Hz), 7.90 (d, 6H$_C$, J_{CD}=10Hz), 8.40 (d, 6H$_E$, J_{ED}=2.5Hz), 8.52 (dd, 6H$_D$, J_{DC}=10Hz, J_{DE}=2.5Hz), 9.80-10.20 (broad S, 6H, -NHCO-, exchangeable to D_2O) 10.58 (S, 6H, -COOH exchangeable to D_2O)
VIa	1525(Assym) 1199	1160	1255	3000	1650	1505		6.45(d, 6H$_A$,J_{AB}=10Hz), 6.75 (d, 6H$_B$, J_{BA}=10Hz) 6.77-7.15(m, 15H$_{CDE}$) 7.40-8.15 (m, 9H$_{FGH}$), 9.70-10.10 (broad S,3H, -NHCO- exchangeable to D_2O), 10.40 (S, 3H, -COOH, exchangeable to D_2O)
VIb	1525 (Assym) 1199 1375 (Sym) 1171	1160	1255	3000 1700	1650	1502 1480		6.45 (d, 6H$_A$, J_{AB}=10Hz), 6.79 (d, 6H$_B$, J_{BA}=10Hz), 6.80-7.15 (m, 15H$_{CDE}$), 7.45-8.70 (m, 9H$_{FGH}$), 9.75-10.10(braod S, 3H, -NHCO-, exchangeable to D_2O), 10.40 (S,3H,-COOH, exchangeable to D_2O)

phenoxy and nitrophthalimidophenoxy groups. The observation of a downfield shift of aromatic protons due to the deshielding of the nitro group confirmed its structure. Its phosphorus-31 NMR showed a A_3 spin singlet at 14.20 ppm indicating magnetic equivalence of phosphorus atoms of the P_3N_3 ring. This confirmed a non geminal substitution of the phenoxy and 3-nitrophthalimidophenoxy groups. In method 2, compound **IV** and **I** are reacted at room temperature in DMSO and the obtained tris[4(3′-nitrophthalamic acid)phenoxy]tris(phenoxy)cyclotriphosphazene (**VIa**) was cyclodehydrated thermally at 160–165°C. The compound **VIIIa** obtained by method 2 was found identical to that obtained in method 1. The structure of intermediate phthalamic acid (**VIa**) was seen consistent to IR and ^{1}H-NMR spectra (Table II). The DTA analysis of **VIIIa** showed a single endothermic transition at 150°C. Its dynamic thermogravimetric analysis in air indicated that this compound is thermally stable. A three step decomposition was observed (Table III). The first decomposition starting at 395°C may be due to the loss of phenoxy group(s) and the second decomposition due to the imide linkage(s) starting at 460°C. The third decomposition was slow even in air and the char yield was 50% at 700°C and 32% at 800°C. The observed high char yield is a characteristic[2–4] of the cyclotriphosphazene moiety and makes these compounds attractive for preparation of variety of polymers. Similarly, tris[4-(4′-phthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**VIIIb**) was synthesized by two methods and was seen consistent to its spectral data. The IR and proton NMR data of **VIIIb** and the intermediate tris[4-(4′-phthalamic acid)phenoxy]tris(phenoxy)cyclotrisphosphazene (**VIb**) are presented in Tables I and II, respectively. The DTA analysis of **VIIIb** showed a single endotherm at 172°C.

The revealed ease of preparation of compounds **VIIa**, **VIIb**, **VIIIa**, and **VIIIb** can be extended for the preparation of various mono-, di-, tetra- and penta-functional monomers. These monomers and intermediates are potential candidates for the preparation of heat- and fire-resistant polymers and materials. A preliminary study performed in our laboratory has demonstrated the use of these monomers for the preparation of heat- and fire-resistant polyetherimides and the results are part of another publication.

EXPERIMENTAL

All melting points were determined in an open-end capillary using optical microscope melting point apparatus and are uncorrected. Differential thermal analysis (DTA) and dynamic thermogravimetric analysis (TGA) were performed on a Rigaku PTC 10A thermal analyzer system with a heating rate of 10°C min. The elemental analysis were performed on a Heraeus CHN elemental analyzer. Infrared (IR) spectra were recorded on a Shimadzu spectrometer IR-435 on a KBr disk or a pellet. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on Perkin Elmer R-32(90 MHz)NMR spectrometer. The chemical shifts (δ) is given in ppm with tetramethylsilane (TMS) as an internal standard. ^{31}P-NMR spectra chemical shift (δ) is given in parts per million with 85% aqueous H_3PO_4 as an external standard.

Hexachlorocyclotriphosphazene (Nippo Soda, Japan) was purified by fractional vacuum sublimation at 80–85°C and crystallized from n-heptane. Hexakis(4-aminophenoxy)cyclotriphosphazenes (**III**), m.p. 177–179°C, was synthesized using our earlier method.[3] Tris(4-aminophenoxy)tris(phenoxy)cyclotriphosphazene (**IV**), m.p. 103–107°C, was synthesized as described earlier by us.[12] 3-Nitrophthalic anhydride (**I**), m.p. 163–164°C, was synthesized[13] by the nitration of phthalic anhydride to 3-nitrophthalic acid, m.p. 216–218°C, followed by cyclodehydration of the later using acetic anhydride. 4-Nitrophthalic anhydride (**II**), m.p. 120°C was synthesized[14] by the nitration of phthalimide followed by hydrolysis. The obtained 4-nitrophthalic acid was cyclodehydrated by refluxing in acetic anhydride.

TABLE III

Analytical and thermal characteristics of compounds **VIIb**, **VIIIa**, and **VIIIb**

Compound	mp (°C)	Yield (%)	Formula		Elemental analysis C(%)	H(%)	N(%)	TGA decomposition temperature (°C) PDT	PTD_{max} (W^*)a	Char yield (%) 700°C	800°C
VIIb	340-342	86	$C_{84}H_{42}O_{30}N_{15}P_3$	Calcd.	54.90	2.29	11.40	--			
				Found	55.41	2.63	11.28				
VIIIa	148-150	82.5	$C_{60}H_{36}O_{18}N_9P_3$	Calcd.	58.70	2.85	9.98	395(1st)	400(80)	50	32
				Found	58.76	3.02	9.84	460(2nd)	540(60)		
VIIIb	170-172	80	$C_{60}H_{36}O_{18}N_9P_3$	Calcd.	58.70	2.85	9.98				
				Found	58.90	3.09	10.30				

PDT = Temperature at which weight loss starts

PDT_{max} = Temperature at which maximum weight loss occurs

[a]W^* = Weight remaining at that temperature

Toluene was dried over sodium metal and distilled before use. Phenol was distilled. N,N-dimethylsulfoxide (DMSO) was distilled over phosphorus pentoxide.

Synthesis

Reaction of hexakis(4-aminophenoxy)cyclotriphosphazene (**III**) *with 3-nitrophthalic anhydride* (**I**).

Method I: To a three necked flask equipped with a nitrogen inlet, magnetic stirrer, thermometer and a Dean Stark condenser, hexakis(4-aminophenoxy)cyclotriphosphazene (**III**) (1 g, 0.0012 mole) was dissolved in phenol (1.5 ml) and toluene (10 ml). To this stirring solution 3-nitrophthalic anhydride (**I**) (1.5 g, 0.0077 mole) was added. The reaction was heated in an oil bath at 100°C. The refluxing toluene was continuously collected in a Dean and Stark's condensor until the reaction temperature reaches to 140°C. The heating of the reaction was continued for 2 h. At this stage Dean and Stark condenser was replaced with another trap filled with molecular sieves. The refluxing was continued for another 1 h to ensure complete dehydration. The reaction mixture was diluted with toluene (2–3 ml) and poured in cold methanol. A pale yellow compound was collected by filtration. It was boiled for 15 min in acetone:methanol (1:1). The obtained solid ws recrystallized from o-dichlorobenzene and dried in vaccum to give hexakis[4(3'-nitrophthalimido)phenoxy]cyclotriphosphazene (**VIIa**), m.p. 298–300°C. Yield 83%.

Anal: Calcd for $C_{84}H_{42}N_{15}O_{30}P_3$: C, 54.90% H, 2.29%; N, 11.40%. Found: C, 55.40%; H, 2.45%; N, 11.00%.

Method II: Step 1: In a round-bottom flask, hexakis(4-aminophenoxy)cyclotriphosphazene (**III**) (0.34 g, 0.0004 mole) was dissolved in dimethylsulfoxide (5 ml) and the solution was allowed to stir. To this stirring solution 3-nitrophthalic anhydride (**I**) (0.53 g, 0.0026 mole) was added in one lot and the stirring continued for 1 h to give the corresponding phthalamic acid (**Va**).

Step 2: The reaction solution of step 1 was transferred to a petri-dish and placed in a preheated air oven maintained at 50–60°C for overnight and the solvent was removed by evaporation. Further heating at 160–165°C in a vacuum oven for 30 min afforded a yellow solid (**VIIa**), mp 298–300°C. It was found similar to compound **VIIa**, synthesized above in method I.

Hexakis[4-(4'-nitrophthalimido)phenoxy]cyclotriphosphazene (**VIIb**), was similarly synthesized by method I and II involving the reaction of hexamine III with 4-nitrophthalic anhydride and its analytical data is given in Table III.

Reaction of tris(4-aminophenoxy)tris(phenoxy)cyclotriphosphazene (**IV**) *with 3-nitrophthalic anhydride* (**I**) and 4-nitrophthalic anhydrides (**II**).

Method I: The reaction of tris(4-aminophenoxy)tris(phenoxy)cyclotriphosphazene (**IV**) (1.37 g, 0.0019 mole) with 3-nitrophthalic anhydride (**I**) (1.15 g, 0.0059 mole) was similarly performed in phenol and toluene. The obtained solid was purified from methanol and dried to give tris[4-(3'-nitrophthalimido)phenoxy)tris(phenoxy)cyclotriphosphazene (**VIIIa**). It was also synthesized by method II and found identical.

Tris[4-(4-nitrophthalimido)phenoxycyclotriphosphazene (**VIIIb**) was similarly synthesized by method I and II by the reaction of trisamine (**IV**) and 4-nitrophthalic anhydride. The analytical data is given in Table III.

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