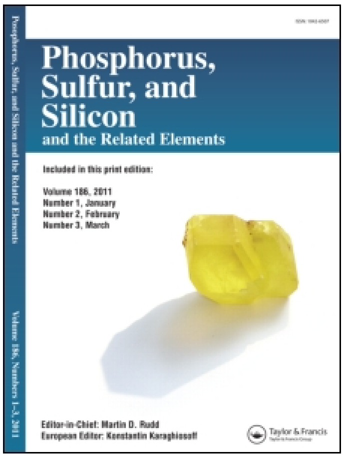

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Synthesis and Characterization of Tris[2,3-di(o-oxyphenylene)quinoxalin]cyclotriphosphazene--A Novel Spiroheterocyclophosphazene

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SYNTHESIS AND CHARACTERIZATION OF TRIS[2,3-DI(O-OXYPHENYLENE)QUINOXALIN] CYCLOTRIPHOSPHAZENE—A NOVEL SPIROHETEROCYCLOPHOSPHAZENE

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Hexachlorocyclotriphosphazene $(NPCl_2)_3$*, reacted with 2,3-di(o-hydroxyphenylene)quinoxalin in the presence of a base, to yield tris[2,3-di(o-oxyphenylene)quinoxalin]cyclotriphosphazene. The synthesis of 2,3-di(o-hydroxy phenylene)quinoxaline was carried out through three steps: benzoin condensation, oxidation, and reaction of diketone with diamine. The products were characterized by* ^{1}*HNMR,* ^{31}*PNMR, IR, and mass spectral data.*

Keywords: Cyclotriphosphazene; quinoxalin; salicylaldehyde; spectral data; synthesis

Chlorocyclophosphazenes form an important class of inorganic heterocyclic ring systems and lie at the interface between organic and inorganic chemistry.[1] The nucleophilic substitution reaction, involving replacement of labile P—Cl bonds by nucleophiles such as aliphatic and aromatic amines, alcohols, and phenols have been extensively investigated.[2–8] The synthesis, characterization, polymerization, inclusion behavior and preliminary crystal structure of tris(o-phenylenedioxy)cyclotriphosphazen tris(diphenyl-2,2′-dioxy)cyclotriphosphazene, and tris(o-phenylenediamino) cyclotriphosphazene previously were reported.[9–12]

The clathration host properties of several spirocyclophosphazenes including tris(2,3-naphtalenedioxy)-cyclotriphosphazene[13–15]

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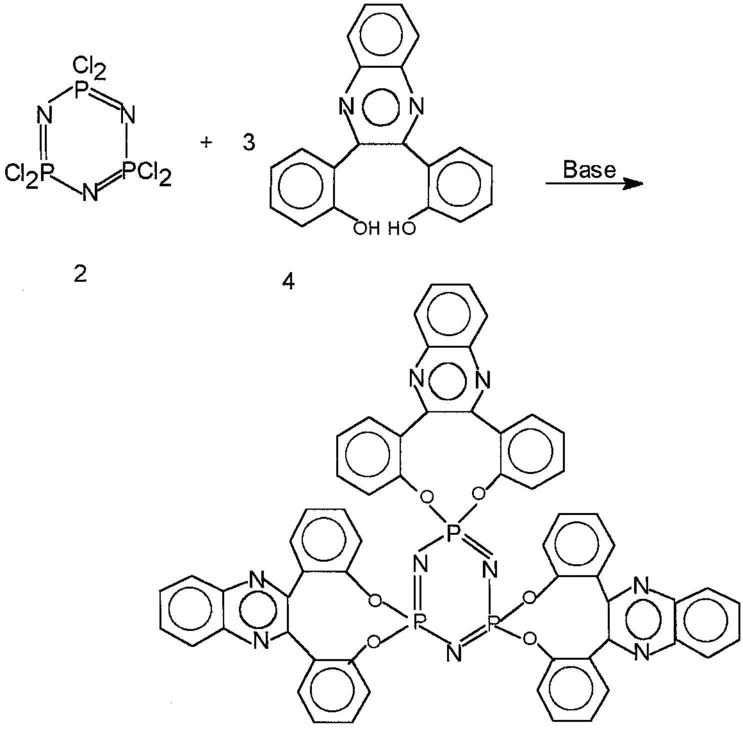
tris(1,8-naphtalenedioxy)cyclotriphosphazene,[16] tris(3,6-dimethylphenylenedioxy)-cyclotriphosphazene[17] also are known.

This article describes the synthesis and characterization of another trimeric phosphazene which contains cyclic groups attached to the phosphorus atoms that form a 9-member, spiro-heterocyclic ring compound, tris[2,3-di(o-oxyphenylene) quinoxalin]cyclotriphosphazene, **1**.

RESULTS AND DISCUSSION

Synthesis and Characterization of Tris[2,3-di(o-oxyphenylene)quinoxalin] Cyclotriphosphazene 1

The general reaction scheme used for the preparation of the cyclized compound is the typical reaction of hexachlorotriphosphazene with an aromatic difunctional phenol in the presence of a base.[18,19]



2

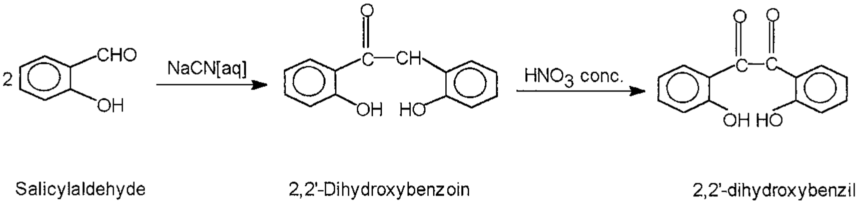
4

1

Accordingly, hexachlorocyclotriphosphazene **2** was treated with three molar equivalents of 2,3-di(o-hydroxyphenylene)quinoxaline **4** in the presence of solvent and base, to yield tris[2,3-di(o-oxyphenylene)quinoxaline]cyclotriphosphazene **1**.

The ability of tris(o-phenylenedioxy)cyclotriphosphazene, 2,3-dioxynaphthyl compound, and others to polymerize by phosphazene ring cleavage when heated above 250°C were reported previously,[11] whereas the compound **1**, tris[2,3-di(o-oxyphenylene) quinoxaline] cyclotriphosphazene, was resistant to polymerization or decomposition at tempratures up to 300°C. In this case, steric widening of the O—P—O angle may serve to stabilize the cyclic trimeric structure relative to the large cyclic or open-chain homologies.[20]*

The synthesis of 2,3-di(o-hydroxyphenylene)quinoxaline was carried out through three steps: (1) benzoin condensation of salicylaldehyde, where aromatic aldehydes treated with an alkali metal cyanide, usually in aqueous solution, undergo condensation to yield the hydroxyketone or benzoin; (2) oxidation, where oxidation of α-hydroxyketone with concentrated nitric acid yields the diketone; and (3) reaction of the resultant diketone with o-phenylenediamine yields 2,3-di(o-hydroxyphenylene)quinoxaline.



Spectral Data

The principal infrared bands for **1** to **4** as KBr plates are shown in Table I.

An important feature of the spectra concerns the position of the phosphorus–nitrogen stretching peak (asymmetrical ring stretching mode) in the 1200 cm^{-1} region. In general, electron withdrawal by the side groups should raise the frequency of this band partly due to the bond strengthening which results from the greater $d_\pi - P_\pi$ character in these circumstance.[21–22] The ^{1}HNMR data for the compounds **1**, **3**, **4** and ^{31}PNMR data for **1** obtained in suitable solvents are shown in Table II.

*X-ray diffraction results show that the O—P—O angle in tris (o-phenylenedioxy) cyclotriphosphazene is 97°. Compare this with the value of 102° reported for $(NPCl_2)_3$.

TABLE I Infrared Bands for Compounds **1–4**

Compound number	Infrared data (cm^{-1})
1	1555, 1487 (C=N); 1625, 1425 (C=C aromatic); 1374–1284 (C—O) 935 (P—O—Ar); 1170, 1202 (P=N); 750, 880 (C—H aromatic)
2	519, 610 (PCl$_2$); 837, 1177 (P=N)
3	3500 (O—H); 3000–2800 (C—H, CHOH); 1700 (C=O); 770–730 (C—H aromatic)
4	3500–3200 (O—H); 1550–1450 (C=N); 1470, 1380 (C=C aromatic); 680, 740 (C—H aromatic)

Proton NMR spectra were used to confirm the structures of compound number **1**, **3**, and **4**. The spectrum of **3** showed aromatic protons with chemical shifts at 7.5–8.5 ppm, phenolic —OH protons, alcoholic —OH protons and none-aromatic —CH protons in the ratio of 8:2:1:1 respectively. The spectrum of **4** also showed aromatic protons with chemical shifts at 7.8–9 ppm and phenolic —OH protons in the ratio of 12:2.

The spectrum of **1** showed only aromatic protons .The aromatic pattern could be rationalized in terms of 1,2-substitution.[23] The ^{31}PNMR of the final product, **1**, indicated the presence of a single enviroment for the phosphorus atom.

The mass spectrum also was employed to confirm the structure of **4**. The spectrum of 2,3-di(o-hydroxyphenylene)quinoxaline showed the stable radical-cation or cation species might be formed from the fragmentation of molecular ion[$C_{20}H_{14}N_2O_2$]$^+$ with m/e = 314.

The fragmentation of **4** was as follows:

$$\begin{tikzcd}
 & {[C_{14}H_9N_2O]^+ \ \text{m/e=221} \quad + \quad [C_6H_5O]^\cdot} \\
{[C_{20}H_{14}N_2O_2]^{+\cdot} \ \text{m/e=314}} \arrow[ur] \arrow[dr] & \\
 & {[C_{14}H_9N_2O]^\cdot \quad + \quad [C_6H_5O]^+ \ \text{m/e=93}}
\end{tikzcd}$$

$$[C_6H_5O]^+ \ \text{m/e=93} \xrightarrow{-CO} [C_5H_5]^+ \ \text{m/e=65}$$

$$[C_{14}H_9N_2O]^+ \ \text{m/e=221} \longrightarrow \text{m/e=128} + \text{m/e=93}$$

Owing to the high melting point of **1**, reliable mass data were not obtained for this compound.

TABLE II NMR Spectra Data for Compounds **1**, **3**, and **4**

Compound number		NMR data (chemical shift in ppm)[a]
1	^{1}HNMR	7.8–9, m (in CCl_4)
	^{31}PNMR	−4.5 (in $CCl_4 + CS_2$)
3	^{1}HNMR	7.5–8.5 (8H, m); (2H, s), 4.9 (1H, s); 2.4 (1H, s) (in CD_3COCD_3)
4	^{1}HNMR	7.8–9 (12H, m); 5.3 (2H, s) (in $CCl_4 + CS_2$)

[a] ^{1}H and ^{31}PNMR data in ppm relative to TMS and phosphoric acid respectively.

EXPERIMENTAL

Material

Hexachlorocyclotriphosphazene was synthesized from the reaction of phosphorus pentachloride (99%, Merck) with ammonium chloride (99%, Merck) in dichlorobenzene (99%, Merck) as a solvent.[18] Petroleum ether (b.p. = 50–70°C, Merck), sodium cyanide (95%, Merck), ethanol (99%, Merck), salicylaldehyde (PROLABO), nitric acid (65%, Merck), o-phenylenediamine (98%, Merck), sodium carbonate (99.5%, Merck), tetrahydrofurane (99%, Merck), and xylene (>99%, Merck) were purchased.

2,2′-Dihydroxy Benzoin

In a 100 ml beaker was placed 10.1 ml (0.1 mmol) of salicylaldehyde (d = 1.16 g/ml), 25 ml of ethanol and a solution of 1 g (0.02 mmol) of sodium cyanide in 50 ml of water. The mixture was stirred and cooled in an ice bath.

The crude product was filtered, washed with 50% ethanol-water, drained, and dried. Melting point of crude 2,2′-dihydroxy benzoin, which is yellow in color, is 158–159°C (yield 90%).

2,2′-Dihydroxy Benzil

11.5 g (0.047 mmol) of crude 2,2′-dihydroxy benzoin and 50 ml of concentrated nitric acid were heated on a boilling water bath with occasional shaking until the evolution of nitrogen dioxides has ceased (about 45 min). The reaction mixture was poured into 140 ml of cold water and stirred well until it crystallized completely as a yellow solid. The crude 2,2′-dihydroxy benzil was filtered and washed thoroughly with cold water to remove the nitric acid. Recrystallization from 40 ml of ethanol (95%). Melting point of 2,2′-dihydroxy benzil is 118–119°C (yield 85%).

2,3-Di(o-hydroxy phenylene)quinoxaline

To a warm solution of 2.42 g (0.01 mmol) of 2,2′-dihydroxybenzil in 8 ml of absolute ethanol was added a solution of 1.1 g (0.01 mmol) of o-phenylenediamine in 8 ml of absolute ethanol. It was warmed in a water bath for 30 min, then water was added until a slight cloudiness formed; it was then allowed to cool. Filteration and recrystallization from aqueous ethanol, had a m.p. of 145–146°C (yield 50%).

Tris [2,3-Di(o-oxyphenylene)quinoxaline]-cyclotriphosphazene

A mixture of hexachlorocyclotriphosphazene (5 g, 0.0144 mmol) 2,3-di(o-hydroxyphenylene) quinoxaline (12.56 g, 0.0432 mmol), sodium carbonate (9.16 g, 0.0864 mmol), and tetrahydrofurane (500 ml) was refluxed for a total of 17 h and was stirred at 25°C for a further 40 h. The white residue was then filtered off and washed with a large excess of water until the washing were no longer basic to litmus. A portion of the residue was recrystallized from xylene at 200°C. It produced white-yellow crystals of tris[2,3-di(o-oxyphenylene) quinoxaline] cyclotriphosphazene which did not melt up to 300°C (yield 38%).

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