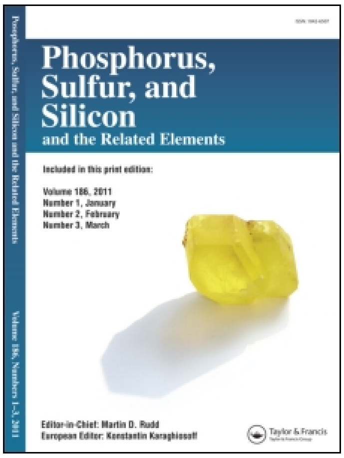

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Preparation and Characterization of Hexakis[2-methoxy-4-(2,3-dimethylphenylimino)phenylato]cyclotriphosphazene

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PREPARATION AND CHARACTERIZATION OF HEXAKIS[2-METHOXY-4-(2,3-DIMETHYLPHENYLIMINO) PHENYLATO]CYCLOTRIPHOSPHAZENE

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Hexakis[2-methoxy-4-(2,3-dimethylphenylimino)phenylato]cyclotriphosphazene was prepared by the reaction of hexakis[2-methoxy-4-formylphenoxy]cyclotriphosphazene and 3,4-dimethylaniline. The structure of new cyclotriphosphazene derivative was determined by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR spectra, thermal analysis, and X-ray diffraction.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

KEYWORDS Dendrimers; hexakis[2-methoxy-4-formylphenoxy]cyclotriphosphazene; phosphazenes; Schiff bases; X-ray diffraction

INTRODUCTION

Cyclotriphosphazenes are an important class of inorganic ring systems for two main reasons. The first reason is substitution of P-X bonds in $[NPX_2]_n$ (X = Cl or F; n = 3,4) by many nucleophilic reagents to synthesize a variety of organocyclophosphazenes. The specific physical or chemical properties of these compounds are imposed by the structures of different side groups. The second reason of interest in these compounds stems from the close relationship that exists between these ring systems with the high molecular weight polyphosphazenes, the largest family of inorganic polymers known.[1]

Reactions at the exocyclic group of a substituted cyclophosphazene have become a major synthetic methodology for producing new phosphazene derivatives that have a bulky-side group. In addition, the multifunctional nature of chlorocylophosphazenes allows these compounds to be utilized as dendrimer cores. $N_3P_3Cl_6$ offers six branching points, which is significantly more than those available with conventional organic cores, permitting the

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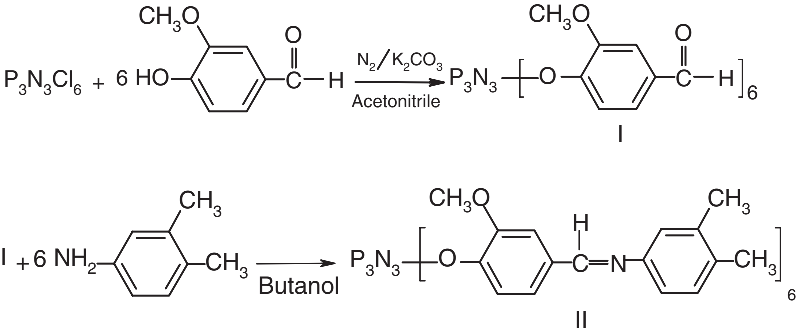
ready accommodation of a larger number of peripheral units around the cyclophopshazene framework.[2]

In this article, we report the synthesis of a Schiff base derivative of hexakis[2-methoxy-4-formylphenoxy]cyclotriphosphazene (**I**), which can be described as a dendrimeric core.[2] Cyclophosphazenes such as **I** and its Schiff base derivative, hexakis[2-methoxy-4-(2,3-dimethylphenylimino)phenylato]cyclotriphosphazene (**II**), have been used as preliminary models for polyphosphazenes.[3,4] The structure of **II** was determined by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR spectra, thermal analysis, and X-ray diffraction. The crystal structure of **I** has been published previously.[5]

RESULTS AND DISCUSSION

Synthesis of II

The synthesis of **II** is summarized in Scheme 1. In the preparation of compound **II**, **I** was allowed to react with 3,4-dimethylaniline in butanol. The mixture was refluxed for 5 days. The product was purified by recrystallization.[6,7]



Scheme 1

Characterization of II

The characteristic IR absorption bands of **I** and **II** were determined using KBr disc. When the IR spectra of **I** and **II** are compared, it is seen that the C=O vibration at 1697cm^{-1} region disapperared, and a new band appeared at the 1629 cm^{-1} region of the spectrum because of C=N vibration. **II** has four characteristic absoption bands. These bands are shown at 1191–1150 cm^{-1}, 1285 cm^{-1}, 1035 cm^{-1}, and 962 cm^{-1} and are due to P=N, P—N—P$_{(asym)}$, P—N—P$_{(sym)}$, and P—OAr, respectively.

^{1}H NMR and ^{13}C NMR spectra of **II** are taken in DMSO-d$_6$. The ^{1}H NMR spectrum of **II** shows one singlet at 8.45 ppm corresponding to the hexa-equvalent imine protons CH=N (6H). The phenyl and methoxy protons were also observed in the 6.92–7.52 and 3.79 ppm regions, respectively.

In the ^{13}C NMR spectra of **II**, the C=N peak is in the 158.39 ppm region. The methoxy and phenyl carbons were also observed in the 55.79 and 111.36–150.59 ppm regions, respectively.[4,8]

X-Ray Analysis

Crystallography. The molecular structure of the title compound **II** is shown Figure 1. The molecule comprises a cyclotriphosphazene core and six terminal 2-methoxy-4-(2,3-dimethylphenylimino) phenylato groups. The crystal is monoclinic, space group $P2_1/c$, with $a = 27.0435(6)$ Å, $b = 19.2212(4)$ Å, $c = 17.8449(5)$ Å, α, $\gamma = 90°$ and $\beta = 108.15(2)°$, $V = 8814.4(4)$ Å^3, $Z = 4$ (shown in Table I). The phosphazene rings are not planar, with a total puckering parameter of $Q_T = 0.241(3)$ Å. Literature values for puckering of the phosphazene ring are $Q_T = 0.255(2)$ Å.[5] The conformation of the phosphazene ring is twisted-boat [$q_2 = 0.241(3)$ Å, $q_3 = -0.010(2)$ Å, $\Phi_2 = 266.1(7)°$ and $\theta_2 = 92.42(71)°$]. The principal mean square atomic displacements U of the some of atoms such as C31, C91, C92, C93, and C96 are higher than the other atoms in the compound. According to cif results, this means U values are admitted. The R1 and wR2 indices are obtained higher than expected due to high U displacements of some atoms.

Selected geometric parameters are listed in Table S1 (Supplemental Materials, available online). In the phosphazene ring, for the angles nearest to the macrocycle, viz. the endocyclic α (N1−P1−N3, N2−P2−N1, N2−P3−N3) [116.61(18)°, 116.72(19)°, 117.2(2)°] and exocyclic α' (O11−P1−O9, O5−P2−O7, O3−P3−O1) [94.83(18)°, 99.41(17)°, 99.34(19)°], respectively, these values deviate slightly from those found in the standard compound $N_3P_3Cl_6$ [α 118.3(2)° and α' 101.2(1)°].[9,10]

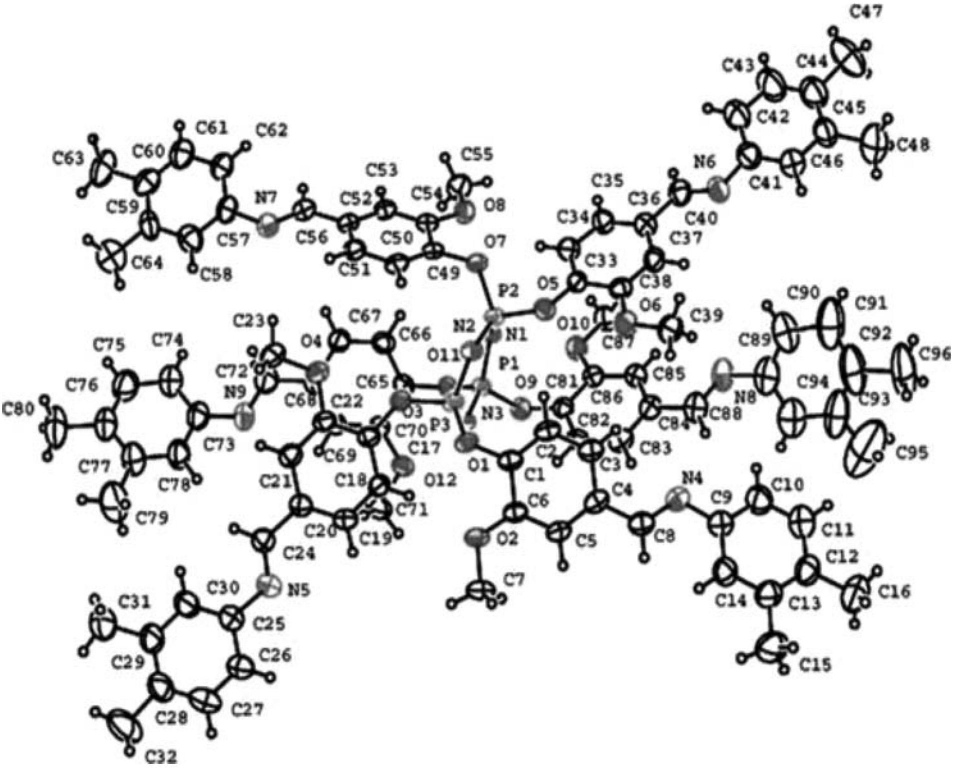


Figure 1 The molecular structure of **II**.

Table I Crystallographic data for **II**

Empirical formula	$P_3N_3(C_{16}NO_2H_{16})_6$
Molecular weight	1660.8
Temperature, T (K)	296
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Crystal size (mm^3)	0.62 × 0.40 × 0.09
Space group	P21/c
a (Å)	27.0435(6)
b (Å)	19.2212(4)
c (Å)	17.8449(5)
α (°)	90
β (°)	108.150(20)
γ (°)	90
Volume, V (Å^3)	8814.40(608)
Z	4
T_{min}, T_{maks}	0.937, 0.988
Calculated density (Mg m^{-3})	1.25
θ range (°)	1.3–25.7
Index ranges	h = –32→32, k = –23→23, l = –21→21
Measured reflections	44280
Independent reflections	16413
Observed reflections (I > 2σ)	6729
Goodness-of-fit on *F 2*	0.938
R index (I > 2σ)	0.078
wR2 index (I > 2σ)	0.149

The crystal structure of **II** is stabilized by C—H···O hydrogen bonding. This intermolecular hydrogen bond forms a C(13) graph-set chain,[11] viz. C7—H7A···O10—C86—C81—O9—P1—N3—P3—O1—C1—C6—O2, running along the [010] direction with screw axis symmetry (–x, $\frac{1}{2}$+y, $\frac{1}{2}$–z) (shown in Figures S1 and S2, Supplemental Materials) and by translation (x, y+n, z) (n is integer) of the molecule at (x, y, z). On the other hand, as can be seen from Table S2 (Supplemental Materials), the intramolecular hydrogen bonding, C18—H18···O1/ O2 and C34—H34···O8, may affect crystal packing. Aside from this, C—H···π and π—π interactions are also effective in the crystal packing.

Thermal Decomposition Studies

The thermal behavior of the cyclophosphazene derivative **II** was investigated by employing thermoanalytical TG, DTG and DTA methods simultaneously in the temperature range of 20–1000°C in a static air atmosphere. As shown in Figure S3, the endothermic peak at 167.49°C in the DTA curve, without any weight loss, clearly represents a physical process and is attributed to the melting of **II**. As shown in the TG curve of **II**, the weight loss starts at 292°C and continues to 979°C. The stages of decomposition are associated with decomposition of organic groups and an exothermic oxidation process in the temperature range of 292–979°C (DTG *max*: 319, 340, 450, 537, and 721°C). The release of the volatile products such as aliphatic and aromatic substituents and then oxidation in static air atmosphere results in the polymerization of the compound. The final decomposition product is a cross-linked structure of phosphorus and nitrogen.[12,13]

EXPERIMENTAL

Instrumentation

Melting points were recorded on electrothermal melting point apparatus. FT-IR spectra were recorded on a Mattson 1000 FT-IR spectrometer calibrated with polystyrene film using the KBr disc. The ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker AC 200 MHz spectrometer, referenced to tetramethylsilane as an internal standard. DT, DTG, and DTA curves were recorded simultaneously on a thermal analyzer. The experiments were performed in static air atmosphere with a heating rate of 10°C/min^{-1} from room temperature to 1000°C in platinum crucibles. The samples weighed approximately 10 mg, and highly sintered α-Al_2O_3 was used as a reference material. The DTG sensitivity was 0.05 mg s^{-1}. Elemental analysis was recorded by the Tubitak Atal Research Center in Ankara.

Crystallographic Analysis

The suitable crystals of compound **II** for X-ray analysis were obtained by recrystallization from acetonitrile:n-hexane (1:1) mixtures. Data collection was performed on a Stoe IPDSII image plate detector using Mo K_α radiation ($\lambda = 0.71019$ Å). Details of the crystal structure are given in Table I. Other details are as follows: Data collection: Stoe X-AREA.[16] Cell refinement: Stoe X-AREA.[14] Data reduction: Stoe X-RED.[15] The structure was solved by direct methods using SHELXS-97,[16] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97.[16] Molecular drawing was done using ORTEP-III.[18] In the title compound, the hydrogen atoms on C were placed at calculated positions (C–H = 0.93 Å, 0.96 Å for methyl groups) and were allowed to ride on the parent atom [$U_{iso}(H) = 1.2U(C)$ for CH groups and $U_{iso}(H) = 1.5U(C)$ for methyl groups]. The maximum difference density of 0.74 eÅ^{-3} indicated the presence of a possible atom site.

Synthesis and Purification

A butanol solution of hexakis[2-methoxy-4-formylphenoxy]cyclotriphosphazene (1.00 g, 0.096 mmol), which was prepared according to the published procedure,[5] was added dropwise to a solution of 3,4-dimethylaniline (0.697 g, 0.576 mmol) in dry acetonitrile (20 mL) over a period of 1 h, and then the mixture was refluxed for 5 d. The residue was washed with acetonitrile and n-hexane twice. The white product was purified by recrystallization from acetonitrile:n-hexane(1:1) mixtures, mp 165–167°C, 1.23 g (72%) yield. Anal. Calc. for $C_{96}H_{96}N_9P_3O_{12}$: C 69.43, H 5.83, N 7.59; found: C 69.78, H 5.01, N 7.85.

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