Table III. Crystallographic Data for $Cl_2Hg(\mu\text{-}Cl)_2HgIr(CO)Cl(dpm)(\mu\text{-}dpmAuCl)\cdot 1.5CH_3OH$

$C_{52.5}H_{44}AuCl_6Hg_2IrO_{2.5}P_4$	fw = 1841.8
a = 10.594 (7) Å	$P2_1/c$ (No. 14), monoclinic
b = 25.12 (2) Å	T = 130 K
c = 21.397 (13) Å	λ(Mo Kα) = 0.71073 Å
β = 91.04 (5)°	μ(Mo Kα) = 106.9 cm^{-1}
V = 5698 (7) $Å^3$	d_{calcd} = 2.147 $Mg\cdot m^{-3}$
Z = 4	transm factors = 0.52–0.70
$R(F_o)^a$ = 0.066	$R_w(F_o)^a$ = 0.061

[a] $R = \sum||F_o| - |F_c||/|F_o|$; $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_ow^{1/2}|$; $w^{-1} = \sigma^2|F| = 0.0003F^2$.

longer present. This solution was stable for at least 2 h when excess boron trifluoride was present. When the solvent was evaporated or when diethyl ether was added to precipitate the complex, the color of the sample returned to orange and only unreacted **1** was recovered. When a similar experiment was conducted with **2**, the $^{31}P\{^1H\}$ NMR spectrum of the colorless solution showed loss of resonances of **2** and appearance of 10 singlets between 40 and -65 ppm. Attempts to recover **2** from this mixture were unsuccessful.

Observation of Intermediates in the Reaction of 1 and 2 with Mercury(II) Chloride. A solution of **1** (5 mM) in dichloromethane was prepared in a 5-mm NMR tube. The sample was cooled to −78 °C in an acetone/dry ice bath. Three equivalents of solid mercury(II) chloride were added to the cold sample, which was vigorously shaken. This solution was transferred to the previously cooled probe of the NMR spectrometer, and the data in Figure 1 were collected. Attempts to isolate the adduct by crystallization through diffusion of either to the sample at −78 °C were unsuccessful. Similarly, a 5 mM acetone solution of **2** was prepared and cooled to −78 °C. Addition of solid mercury(II) chloride gave the sample which was used to obtain the data shown in Figure 3. This sample was stable to warming to 10 °C. At 23 °C the resonances of the intermediate were lost and new resonances of a species similar to **5** developed (δ_1 = 18 ppm, δ_2 = 17 ppm (J(P,P) = 289 Hz), δ_3 = −47 ppm (J(P,P) = 280 Hz), δ_4 = −61 ppm) along with singlets at 19, −22, −25, and −48 ppm. The signal to noise ratio did not allow mercury satellites to be observed.

X-ray Data Collection. Ivory parallelepipeds of the complex were coated with a light hydrocarbon oil, mounted on a glass fiber with silicon grease, and placed in the 130 K nitrogen stream of a Siemens R3m/V diffractometer that was equipped with a locally modified low-temperature apparatus. Unit cell parameters were determined by least-squares refinement of 28 reflections with 10° < 2θ < 21°. The unique space group $P2_1/c$ (No. 14) was determined by the following conditions: $0k0$, $k = 2n$; $h0l$, $l = 2n$. Two check reflections showed only random (<2%) fluctuation in intensity during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table III. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[26]

Solution and Structure Refinement. Calculation were performed using the Siemens SHELXTL PLUS system of programs. The structure was solved by direct methods. The carbon atoms of the dpm ligands and the carbon and oxygen atoms of methanol were refined isotropically, while all other atoms were refined anisotropically. Hydrogen atoms were included in the refinement model. Their positions were calculated by the use of a riding mode with C–H distance fixed at 0.96 Å and a thermal parameter of U = 0.05 Å.[2] An absorption correction was applied.[17]

Acknowledgment. We thank the National Science Foundation (Grant CHE 9022909) for support and Johnson-Matthey, Inc., for a loan of precious metal salts.

Supplementary Material Available: Tables of crystal data, atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for **5** (10 pages); a listing of structure factors for **5** (27 pages). Ordering information is given on any current masthead page.

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(26) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(27) The method obtains an empirical absorption tensor from an expression relating F_o and F_c: Moezzi, B. Ph.D. Thesis, University of California, Davis, 1987.

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Synthesis and Structure of Small-Molecule Cyclic Phosphazenes Bearing Ortho-Substituted Aryloxy and Phenoxy Substituents

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A series of cyclic trimeric and tetrameric phosphazenes with ortho-substituted aryloxy side groups have been synthesized. The ortho substituents are methyl and phenyl groups. These compounds are structural models for the corresponding linear high-polymeric phosphazenes. X-ray structural analysis of the cyclic tetrameric species $[NP(OC_6H_4CH_3\text{-}2)_2]_4$ (**3**), $[NP(OC_6H_4C_6H_5\text{-}2)_2]_4$ (**4**), and $[NP(OC_6H_5)_2]_4$ (**5**) are reported. Crystals of **3** are triclinic with space group $P\bar{1}$, with a = 11.494 (3) Å, b = 12.348 (2) Å, c = 30.181 (5) Å, α = 80.88 (1)°, β = 88.19 (2)°, γ = 71.23 (1)°, V = 4003.6 $Å^3$, and Z = 3. Crystals of **4** are orthorhombic with space group $Pna2_1$, with a = 25.177 (2) Å, b = 20.472 (3) Å, c = 17.256 (3) Å, V = 8894.1 $Å^3$, and Z = 4. Finally, crystals of **5** are triclinic with space group $P\bar{1}$, with a = 11.514 (2) Å, b = 11.567 (2) Å, c = 17.761 (1) Å, α = 79.21 (1)°, β = 79.87 (1)°, γ = 81.21 (1)°, V = 2269.8 $Å^3$, and Z = 2.

High-polymeric phosphazenes comprise a broad class of inorganic/organic hybrid macromolecules with the general formula $[NPR_2]_n$ (where n = 15000). The specific physical or chemical properties of these polymers are imposed by the structure of the organic, inorganic, or organometallic side group.[1,2] For example, different side groups generate properties such as liquid-crystallinity,[3] nonlinear optical character,[4] or utility as biomedical materials.[5]

In an earlier paper, we reported the synthesis of a series of poly((aryloxy)phosphazenes) with phenylphenoxy and related

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(1) (a) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216. (b) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709. (c) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716. (d) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.

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Table I. Cyclophosphazene Characterization Data

compd[a]	^{31}P NMR, ppm[b]	^{1}H NMR, ppm[b]	mass spectral data, *m/e* calcd	mass spectral data, *m/e* found	mp, °C	elemental anal. element	elemental anal. calcd, %	elemental anal. found, %
1	8.8 (s)	7.1–6.9 (m, ArH), 2.1 (s, CH_3)	778	778	58–59	C	64.86	64.20
						H	5.44	5.30
						N	5.40	5.34
2	6.7 (s)	7.3–6.7 (m, ArH)	1149	1149	*c*	C	75.19	74.57
						H	4.73	5.23
						N	3.65	3.78
3	−14.5 (s)	7.1–6.9 (m, ArH), 2.0 (s, CH_3)	1036	1036	152–153	C	64.86	64.49
						H	5.44	5.59
						N	5.40	5.09
4	−14.2 (s)	7.2–6.9 (m, ArH)	1533	1533	390–392	C	75.19	75.16
						H	4.73	4.50
						N	3.65	3.65

[a] See Scheme I for structures. [b] In $CDCl_3$ solution. [c] Highly viscous oil.

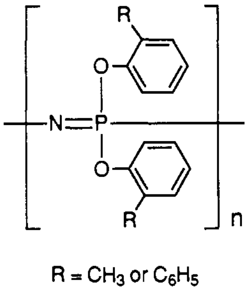


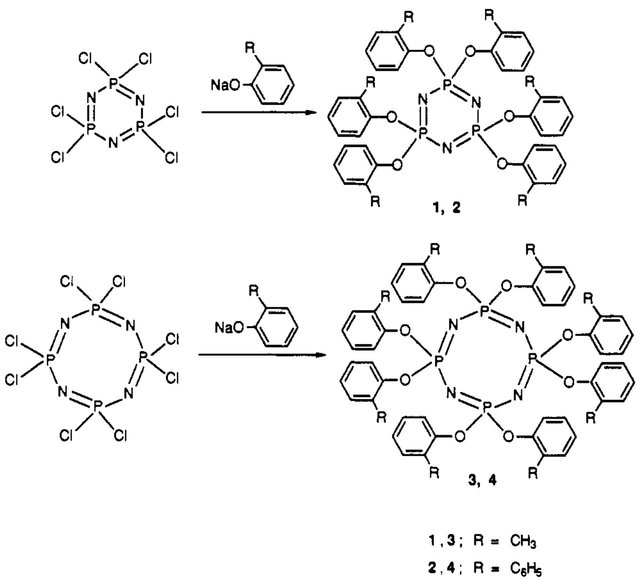
Figure 1. Polyphosphazene bearing ortho-substituted aryloxy groups.

bulky side groups.[6] The emphasis in that work was on the variation in thermal transition and optical properties of the polymers as a function of changes in the aryloxy side group structure. In addition, the steric limits for side groups linked to a polyphosphazene chain were explored, with a particular emphasis on ortho-substituted aryloxy nucleophiles.

Specifically, the synthesis of 2-methylphenoxy- and 2-phenylphenoxy-substituted polyphosphazenes was attempted. The general structure of the desired high-polymeric species is shown in Figure 1. Complete replacement of the chlorine atoms by the appropriate aryloxy nucleophiles could not be achieved. A maximum loading of only ca. 85% for the 2-methylphenoxy group and ca. 76% for the 2-phenylphenoxy group could be accomplished. Surprisingly, in spite of the presence of unreacted P–Cl bonds, these polymers were stable even after repeated precipitations into water and after exposure to atmospheric moisture. Less shielded P–Cl bonds would have hydrolyzed to P–OH units and formed crosslinks under the same conditions. This result emphasizes the difficulty involved in the replacement of a chlorine atom geminal to a bulky ortho-substituted aryloxy group, even by an unhindered nucleophile such as water. Note that single-substituent polyphosphazenes can be synthesized with phenoxy side groups or with meta- and para-substituted aryloxy units.[6,7]

In the present work, we report the syntheses of a series of small-molecule cyclic phosphazenes that bear ortho-substituted aryloxy side groups. Specifically, the synthesis of the cyclic trimeric species $[NP(OC_6H_4CH_3\text{-}2)_2]_3$ (**1**) and $[NP(OC_6H_4C_6H_5\text{-}2)_2]_3$ (**2**) and the tetrameric compounds $[NP(OC_6H_4CH_3\text{-}2)_2]_4$ (**3**) and $[NP(OC_6H_4C_6H_5\text{-}2)_2]_4$ (**4**) are reported, and the molecular structures of compounds **3** and **4** are presented. In addition, the molecular structure of a related cyclic tetramer, $[NP(OC_6H_5)_2]_4$ (**5**), is included for comparison. Compounds **1**–**5** are shown in Figure 2. The primary objective of this work was to gain an insight into the influence of the ortho-substituted aryloxy side groups on the bond lengths, bond angles, and conformation of the cyclophosphazene ring. These species are structural models which may assist in understanding the steric limitations associated with the synthesis of the corresponding linear macromolecules.[8]

Scheme I



Results and Discussion

Synthesis of Cyclic (Aryloxy)phosphazenes. The synthesis of the ortho-substituted (aryloxy)cyclophosphazenes is summarized in Scheme I. In the preparation of compounds **1** and **2**, hexachlorocyclotriphosphazene was allowed to react with an excess of sodium 2-methylphenoxide or sodium 2-phenylphenoxide, respectively, in dioxane in the presence of tetra-*n*-butylammonium bromide. The analogous reactions between octachlorocyclotetraphosphazene and sodium 2-methylphenoxide or sodium 2-phenylphenoxide yielded compounds **3** and **4**, respectively. In all four cases, total replacement of chlorine atoms by the aryloxy units occurred within 48 h at 100 °C.

Characterization of Cyclic (Aryloxy)phosphazenes. The structures of compounds **1**–**4** were examined by NMR spectroscopy, mass spectrometry, and elemental analysis. The characterization data are listed in Table I. The ^{31}P NMR spectra of **1**–**4** consisted of singlet resonances, which was indicative of complete chlorine replacement. The ^{31}P NMR resonances for cyclic trimers **1** and **2** were at 8.8 and 6.7 ppm, respectively, while the resonances for cyclic tetramers **3** and **4** were at ca. −14 ppm. In each case, the mass spectral and elemental analysis data were compatible with the proposed structures. However, the main structural characterization was by means of X-ray single-crystal analysis.

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(7) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972; and references cited therein.

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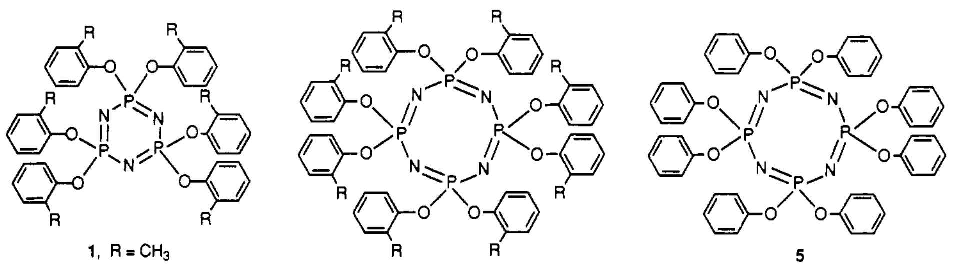

1, R = CH_3
2, R = C_6H_5

3, R = CH_3
4, R = C_6H_5

5

Figure 2. Structures of compounds **1–5**.

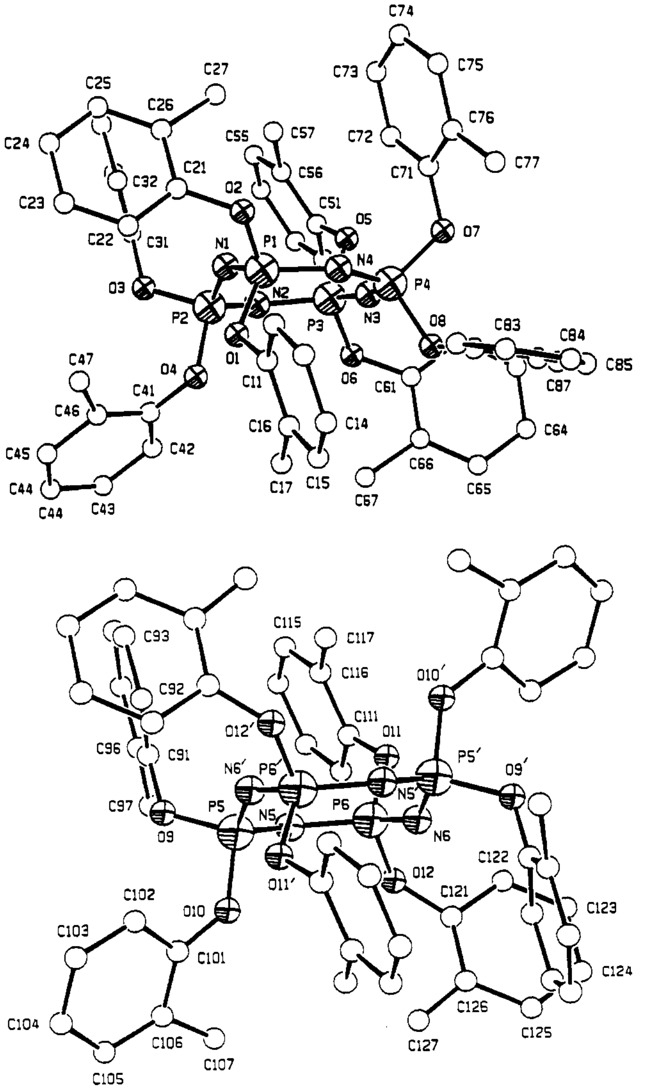

Figure 3. (a) Top: Molecular structure of $[NP(OC_6H_4CH_3\text{-}2)_2]_4$ (**3a**). (b) Bottom: Molecular structure of $[NP(OC_6H_4CH_3\text{-}2)_2]_4$ (**3b**).

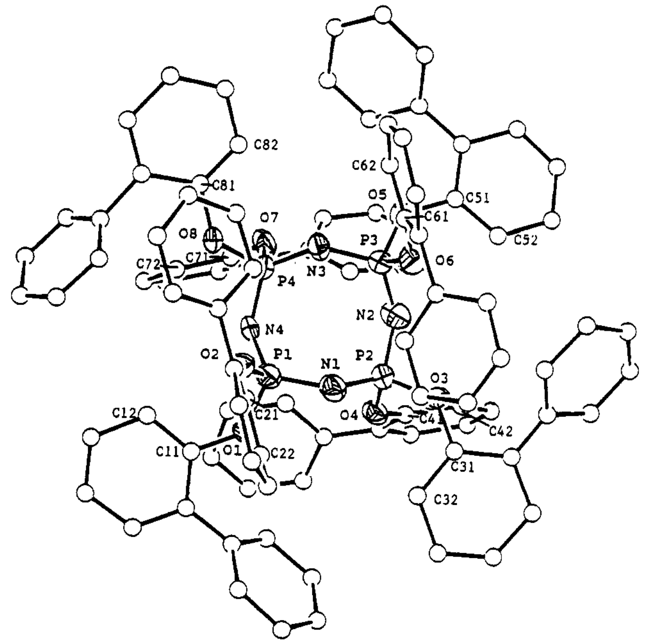

Figure 4. Molecular structure of $[NP(OC_6H_4C_6H_5\text{-}2)_2]_4$ (**4**).

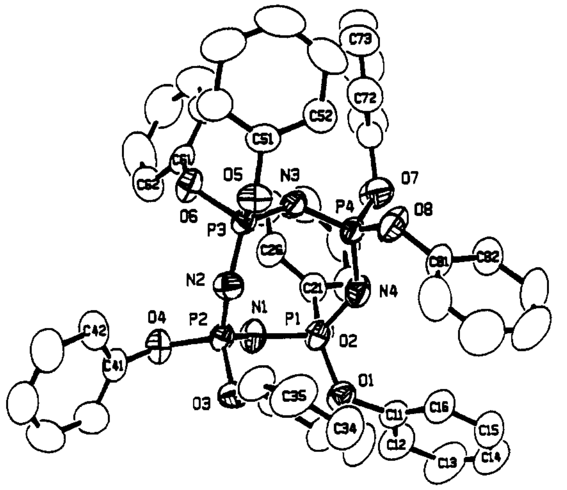

Figure 5. Molecular structure of $[NP(OC_6H_5)_2]_4$ (**5**).

X-ray Analysis. The X-ray crystallographic investigation was carried out in order to explore the effect of the ortho-substituted aryloxy group on the structural parameters of the phosphazene ring. Molecular structure determinations were carried out for ortho-substituted aryloxy tetramers $[NP(OC_6H_4CH_3\text{-}2)_2]_4$ (**3**) and $[NP(OC_6H_4C_6H_5\text{-}2)_2]_4$ (**4**) and the phenoxy tetramer $[NP(OC_6H_5)_2]_4$ (**5**). Compound **5**, prepared as described previously,[7] provided a comparison between the structural influences of the aryloxy and ortho-substituted aryloxy groups on the tetramer ring.

The molecular structures of species **3a,b** (vide infra), **4**, and **5** are shown in Figures 3–5, respectively. A summary of cell constants and data collection parameters is included in Table II. Selected bond lengths and angles are listed in Tables III and IV, respectively. In order to simplify structural comparisons among compounds **3–5**, selected average bond lengths and angles are summarized in Table V. Selected final fractional atomic coordinates are listed in Table VI.

Molecular Structure of $[NP(OC_6H_4CH_3\text{-}2)_2]_4$ (3). The molecular structure of compound $[NP(OC_6H_5CH_3\text{-}2)_2]_4$ (**3**) consists of two distinct molecules, which are shown as **3a** (Figure 3a) and **3b** (Figure 3b). Molecule **3a** is noncentric, while molecule **3b** has an inversion center. In **3b**, the atoms labeled with a prime (for example, P(5′) and P(6′)) were generated by symmetry. Both molecules contain an eight-membered phosphazene ring that assumes a slightly puckered conformation. Two 2-methylphenoxy

Table II. Summary of Crystal Data and Intensity Collection Parameters

	3	**4**	**5**
formula	$P_4N_4O_8C_{56}H_{56}$	$P_4N_4O_8C_{96}H_{72}$	$P_4N_4O_8C_{48}H_{40}$
fw	1036.93	1533.46	924.72
cryst size, mm	0.63 × 0.48 × 0.50	0.45 × 0.37 × 0.45	0.40 × 0.38 × 0.32
space group	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a, Å	11.494 (3)	25.177 (2)	11.514 (2)
b, Å	12.348 (2)	20.472 (3)	11.567 (2)
c, Å	30.181 (5)	17.256 (3)	17.761 (1)
α, deg	80.88 (1)		79.21 (1)
β, deg	88.19 (2)		79.87 (1)
γ, deg	71.23 (1)		81.21 (1)
V, Å^3	4003.6	8894.1	2269.8
Z	3	4	2
d(calcd), g/cm^3	1.290	1.234	1.353
θ limits, deg	2–25	5–50	2–25
μ, cm^{-1}	1.925	20.87	2.180
radiation (λ, Å)	Mo Kα (0.71073)	Cu Kα (1.5418)	Mo Kα (0.71073)
T, K	293	293	293
scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
ω-scan width, deg	0.80 + 0.35 tan θ	0.60 + 0.14 tan θ	0.60 + 0.35 tan θ
cryst decay, %	none	1.4	none
empirical abs cor			
min cor factor	0.9071	0.9230	0.9692
max cor factor	0.9998	0.9994	0.9991
no. of unique data msd	14072	4761	7962
no. of data used [$I > 3\sigma(I)$]	9663	3618	6419
data:param ratio	10	6	11
R, R_w ($=(\sum\Delta^2/\sum wF_o^2)^{1/2}$)	0.084, 0.120	0.084, 0.117	0.048, 0.074
$(\Delta/\sigma)_{max}$ in last cycle	<0.1	<0.2	<0.3
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.37	0.936	0.47
p (weighting factor)	0.05	0.200	0.060
error in weights	3.69	1.2	2.122

Table III. Selected Bond Distances (Å) for Compounds **3**–**5**

	3a	**4**	**5**
P(1)–N(1)	1.563 (4)	1.572 (9)	1.561 (2)
P(1)–N(4)	1.562 (4)	1.560 (9)	1.548 (2)
P(1)–O(1)	1.594 (3)	1.595 (7)	1.577 (1)
P(1)–O(2)	1.581 (3)	1.595 (8)	1.582 (1)
P(2)–N(1)	1.546 (4)	1.568 (9)	1.566 (1)
P(2)–N(2)	1.576 (4)	1.571 (9)	1.563 (2)
P(2)–O(3)	1.575 (4)	1.579 (8)	1.584 (1)
P(2)–O(4)	1.584 (3)	1.570 (7)	1.581 (1)
P(3)–N(2)	1.552 (4)	1.551 (9)	1.561 (1)
P(3)–N(3)	1.534 (4)	1.58 (1)	1.560 (1)
P(3)–O(5)	1.592 (3)	1.575 (8)	1.587 (1)
P(3)–O(6)	1.574 (3)	1.586 (8)	1.587 (1)
P(4)–N(3)	1.543 (4)	1.56 (1)	1.560 (1)
P(4)–N(4)	1.556 (4)	1.579 (9)	1.557 (2)
P(4)–O(7)	1.582 (3)	1.591 (7)	1.579 (1)
P(4)–O(8)	1.585 (3)	1.582 (8)	1.581 (1)
O(1)–C(11)	1.415 (6)	1.38 (1)	1.400 (2)
O(2)–C(21)	1.412 (6)	1.40 (1)	1.389 (2)
O(3)–C(31)	1.403 (5)	1.36 (1)	1.403 (2)
O(4)–C(41)	1.376 (7)	1.40 (1)	1.405 (2)
O(5)–C(51)	1.406 (6)	1.40 (1)	1.398 (2)
O(6)–C(61)	1.403 (6)	1.40 (1)	1.402 (2)
O(7)–C(71)	1.411 (5)	1.43 (1)	1.395 (2)
O(8)–C(81)	1.397 (6)	1.40 (1)	1.403 (2)
	3b		
P(5)–N(5)	1.573 (6)	P(5)–N(6′)	1.561 (5)
P(5)–O(9)	1.577 (4)	P(5)–O(10)	1.539 (5)
P(6)–N(5)	1.534 (6)	P(6)–N(6)	1.551 (6)
P(6)–O(11)	1.584 (6)	P(6)–O(12)	1.596 (5)
O(9)–C(91)	1.356 (9)	O(10)–C(101)	1.265 (8)
O(11)–C(111)	1.394 (10)	O(12)–O(121)	1.340 (9)

groups are attached to each phosphorus atom through P–O–C linkages.

A comparison of the molecular structures of **3a** and **3b** shows that the molecules differ in several conformational features of the 2-methylphenoxy substituents relative to the phosphazene ring. The significant variations are at atoms P(2) and P(4) in **3a** in comparison to atoms P(5) and P(5′) in **3b**, respectively. Specifically, the orientation of the substituent that is attached to P(2) through O(4) differs from that at P(5) by rotation around bond O(4)–C(21) in **3a**. This difference is illustrated clearly by the location of the methyl ortho substituent. Similarly, both 2-methylphenoxy groups attached to P(4) in **3a** have different orientations compared to the groups at P(5′) in **3b**. The differences involve rotation around bonds P(4)–O(7) and P(4)–O(8). There is also some thermal disorder in the methylphenoxy groups of **3b**. This disorder is indicated by the large temperature factors of the methylphenoxy groups of **3b** as opposed to those in **3a**.

The specific structural features for molecules **3a** and **b** are similar. The average P–N bond distance for **3a** is 1.554 Å and for **3b** is 1.555 Å. In **3a**, the P–N–P bond angles vary from 130.0 to 161.4°, with an average value of 141.2°, while, in **3b**, the P–N–P angles range from 130.9 to 140.6°, with a mean value of 135.8°. Note that the P–N–P bond angle at N(3) in **3a** is exceptionally large at 161.4°. The analogous angle at N(5′) in **3b** is 130.9°. The difference in the bond angles at N(3) and N(5′) may result from the generation of a less crowded steric environment on rotation of the two 2-methylphenoxy substituents at P(4). The average N–P–N bond angles for **3a**,**b** are very similar, at 120.6 and 120.9°, respectively.

The mean P–O bond distance is 1.583 Å for **3a** and 1.574 Å for **3b**. This is shorter than a P–O single bond (1.61 Å),[9] and this suggests some exocyclic delocalization of electrons. The O–P–O bond angles average 102.7° for **3a** and 103.4° for **3b**. Interestingly, in **3a**, the O–P–O bond angles alternate in the following manner: 105.2° (P(1)), 100.2° (P(2)), 105.4° (P(3)), and 100.1° (P(4)). This pattern of narrowing and widening at the exocyclic angle may reflect different steric environments around the phosphazene ring.

Molecular Structure of $[NP(OC_6H_4C_6H_5\text{-}2)_2]_4$ (4). Molecules of $[NP(OC_6H_4C_6H_5\text{-}2)_2]_4$ (**4**) contain an eight-membered phosphorus–nitrogen ring that assumes a boat conformation (Figure 4). Two 2-phenylphenoxy groups are attached to each phosphorus atom through P–O–C linkages. The disposition of the two side groups is similar at each phosphorus atom in the ring, with one of the groups extended out from the tetramer ring, while the other is extended either above or below the ring. This molecular

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[9] Cruickshank, D. W. J. *J. Chem. Soc.* **1961**, 5486.

Table IV. Selected Bond Angles (deg) for Compounds **3**–**5**

	3a	**4**	**5**
N(1)–P(1)–N(4)	122.4 (2)	121.3 (5)	120.16 (8)
N(1)–P(1)–O(1)	106.6 (2)	104.6 (4)	107.09 (8)
N(1)–P(1)–O(2)	108.5 (2)	108.4 (4)	107.76 (8)
N(4)–P(1)–O(1)	109.3 (2)	107.9 (4)	109.34 (8)
N(4)–P(1)–O(2)	103.6 (2)	108.0 (4)	110.71 (8)
O(1)–P(1)–O(2)	105.2 (2)	105.6 (4)	99.81 (7)
N(1)–P(2)–N(2)	116.7 (2)	120.7 (5)	120.56 (8)
N(1)–P(2)–O(3)	110.5 (2)	107.5 (5)	112.32 (8)
N(1)–P(2)–O(4)	108.8 (2)	106.3 (4)	101.71 (7)
N(2)–P(2)–O(3)	107.6 (2)	105.7 (5)	107.43 (7)
N(2)–P(2)–O(4)	111.7 (2)	109.2 (4)	112.63 (8)
O(3)–P(2)–O(4)	100.2 (2)	106.6 (4)	100.33 (7)
N(2)–P(3)–N(3)	123.8 (2)	121.0 (4)	121.32 (8)
N(2)–P(3)–O(5)	108.6 (2)	109.3 (5)	101.70 (7)
N(2)–P(3)–O(6)	103.5 (2)	106.9 (5)	110.69 (8)
N(3)–P(3)–O(5)	105.5 (2)	104.7 (5)	113.32 (8)
N(3)–P(3)–O(6)	108.8 (2)	108.0 (4)	106.96 (7)
O(5)–P(3)–O(6)	105.4 (2)	106.0 (4)	101.04 (7)
N(3)–P(4)–N(4)	119.5 (2)	120.7 (5)	122.52 (8)
N(3)–P(4)–O(7)	111.1 (2)	107.3 (4)	108.40 (8)
N(3)–P(4)–O(8)	105.2 (2)	108.5 (4)	106.31 (8)
N(4)–P(4)–O(7)	108.3 (2)	108.3 (5)	102.91 (9)
N(4)–P(4)–O(8)	110.9 (2)	105.6 (5)	108.15 (8)
O(7)–P(4)–O(8)	100.1 (2)	105.5 (5)	107.9 (1)
P(1)–N(1)–P(2)	140.3 (2)	128.9 (6)	133.4 (1)
P(2)–N(2)–P(3)	130.0 (3)	129.3 (6)	131.8 (1)
P(3)–N(3)–P(4)	161.4 (3)	130.3 (6)	135.10 (9)
P(1)–N(4)–P(4)	132.9 (3)	127.9 (6)	135.3 (1)
P(1)–O(1)–C(11)	122.9 (3)	126.9 (7)	124.4 (1)
P(1)–O(2)–C(21)	120.7 (3)	125.3 (7)	125.9 (1)
P(2)–O(3)–C(31)	124.4 (3)	127.7 (7)	126.6 (1)
P(2)–O(4)–C(41)	125.3 (4)	130.7 (7)	123.6 (1)
P(3)–O(5)–C(51)	122.1 (3)	128.6 (7)	122.5 (1)
P(3)–O(6)–C(61)	124.7 (3)	125.5 (7)	124.6 (1)
P(4)–O(7)–C(71)	122.1 (3)	126.6 (6)	127.4 (1)
P(4)–O(8)–C(81)	123.8 (2)	129.1 (7)	124.9 (1)

3b

N(5)–P(5)–N(6′)	118.3 (3)	N(5)–P(5)–O(9)	107.8 (3)
N(5)–P(5)–O(10)	107.0 (3)	N(6′)–P(5)–O(9)	108.4 (3)
N(6′)–P(5)–O(10)	112.7 (4)	O(9)–P(5)–O(10)	101.2 (3)
N(5)–P(6)–N(6)	123.4 (3)	N(5)–P(6)–O(11)	108.0 (3)
N(5)–P(6)–O(12)	102.6 (3)	N(6)–P(6)–O(11)	108.8 (3)
N(6)–P(6)–O(12)	106.9 (3)	O(11)–P(6)–O(12)	105.6 (3)
P(5)–N(5)–P(6)	130.9 (4)	P(5′)–N(6)–P(6)	140.6 (3)
P(5)–O(9)–C(91)	124.9 (4)	P(5)–O(10)–C(101)	140.9 (5)
P(6)–O(11)–C(111)	125.0 (5)	P(6)–O(12)–C(121)	127.1 (5)

Table V. Average Selected Bond Distances (Å) and Angles (deg) for Compounds **3**–**5**

	3a	**3b**	**4**	**5**
	Bond Distances			
P–N	1.554	1.555	1.57	1.560
P–O	1.583	1.574	1.584	1.582
O–C	1.403	1.339	1.40	1.400
	Bond Angles			
P–N–P	141.2	135.8	129.1	133.9
N–P–N	120.6	120.9	120.9	121.1
O–P–O	102.7	103.4	105.9	102.3
P–O–C	123.3	129.5	127.6	125.1

Table VI. Selected Final Fractional Atomic Coordinates for **3**–**5**

atom	*x*	*y*	*z*
	$[NP(OC_6H_4CH_3)_2]_4$ (**3a,b**)		
P(1)	0.65988 (9)	0.18371 (9)	0.81439 (4)
P(2)	0.4259 (1)	0.17713 (9)	0.78163 (4)
P(3)	0.30958 (9)	0.26365 (9)	0.85889 (4)
P(4)	0.54141 (9)	0.30905 (9)	0.88413 (4)
N(1)	0.5576 (3)	0.1348 (3)	0.8020 (1)
N(2)	0.3171 (3)	0.2101 (3)	0.8153 (1)
N(3)	0.4128 (3)	0.3007 (3)	0.8761 (1)
N(4)	0.6512 (3)	0.2468 (3)	0.8559 (1)
O(1)	0.6811 (2)	0.2652 (2)	0.7705 (1)
O(2)	0.7848 (3)	0.0802 (2)	0.8229 (1)
O(3)	0.4052 (3)	0.0839 (2)	0.7555 (1)
O(4)	0.4155 (3)	0.2794 (3)	0.7414 (1)
O(5)	0.2809 (2)	0.1775 (2)	0.8995 (1)
O(6)	0.1894 (3)	0.3717 (2)	0.8514 (1)
O(7)	0.5808 (3)	0.2722 (2)	0.9355 (1)
O(8)	0.5225 (3)	0.4435 (2)	0.8784 (1)
P(5)	0.1010 (2)	−0.0266 (1)	0.44353 (5)
P(6)	0.1555 (2)	−0.0067 (2)	0.53195 (6)
N(5)	0.1808 (4)	−0.0108 (5)	0.4819 (2)
N(6)	−0.0415 (4)	0.0291 (5)	0.4446 (2)
O(9)	0.1471 (4)	0.0220 (3)	0.3972 (1)
O(10)	0.1411 (7)	−0.1570 (4)	0.4410 (2)
O(11)	0.1639 (4)	0.1122 (4)	0.5426 (2)
O(12)	0.2739 (5)	−0.1042 (6)	0.5557 (2)
	$[NP(OC_6H_4C_6H_5)_2]_4$ (**4**)		
P(1)	0.6615 (1)	0.0695 (1)	0.8381 (2)
P(2)	0.6792 (1)	0.1300 (1)	0.9834 (2)
P(3)	0.6512 (1)	0.2496 (1)	0.9130 (2)
P(4)	0.6778 (1)	0.1923 (1)	0.7679 (2)
O(1)	0.6940 (3)	0.0027 (3)	0.8394 (5)
O(2)	0.6070 (3)	0.0533 (3)	0.7950 (4)
O(3)	0.6499 (3)	0.1258 (4)	1.0641 (4)
O(4)	0.7357 (3)	0.0991 (3)	0.9954 (4)
O(5)	0.6750 (3)	0.3207 (4)	0.9134 (5)
O(6)	0.5944 (3)	0.2551 (4)	0.9524 (5)
O(7)	0.7312 (3)	0.2321 (3)	0.7541 (4)
O(8)	0.6492 (3)	0.1899 (4)	0.6863 (4)
N(1)	0.6490 (3)	0.0841 (4)	0.9257 (5)
N(2)	0.6854 (4)	0.0250 (4)	0.9658 (5)
N(3)	0.6428 (4)	0.2330 (4)	0.8246 (6)
N(4)	0.6929 (4)	0.1192 (4)	0.7871 (5)
	$[NP(OC_6H_5)_2]_4$ (**5**)		
P(1)	1.14838 (6)	0.05686 (5)	0.72658 (3)
P(2)	1.15054 (5)	0.25780 (5)	0.79965 (3)
P(3)	0.90512 (5)	0.33115 (5)	0.78909 (3)
P(4)	0.91784 (5)	0.15848 (5)	0.68904 (3)
O(1)	1.2726 (2)	0.0588 (1)	0.6724 (1)
O(2)	1.1549 (2)	−0.0802 (1)	0.7604 (1)
O(3)	1.2630 (1)	0.3130 (2)	0.7497 (1)
O(4)	1.1802 (2)	0.2500 (1)	0.88419 (9)
O(5)	0.8516 (1)	0.4575 (1)	0.7487 (1)
O(6)	0.8386 (2)	0.3289 (1)	0.8755 (1)
O(7)	0.8409 (2)	0.0544 (2)	0.6949 (1)
O(8)	0.8967 (2)	0.2499 (2)	0.6131 (1)
N(1)	1.1538 (2)	0.1238 (2)	0.7942 (1)
N(2)	1.0384 (2)	0.3481 (2)	0.7836 (1)
N(3)	0.8686 (2)	0.2260 (2)	0.7585 (1)
N(4)	1.0477 (2)	0.0956 (2)	0.6764 (1)

structure approximates to a "pin-wheel" arrangement of the 2-phenylphenoxy groups. No intramolecular stacking of the side groups was detected. Note that the two phenyl rings of the 2-phenylphenoxy units are twisted relative to each other. The unit cell of **4** also contains two molecules of chloroform (a solvent used for recrystallization), one of which is disordered.

The P–N bond distances for **4** are similar and are in the range from 1.551 to 1.579 Å, with an average value of 1.57 Å. The P–N–P bond angles range between 127.9 and 130.3°, with a mean value of 129.1°. The variation in the N–P–N bond angles is small, with a range from 120.7 to 121.3° and an average value of 120.9°. The P–O bond distances vary between 1.570 and 1.595 Å, with a mean value of 1.584 Å. The O–P–O bond angles are all wide, with values between 105.5 and 106.6° and an average value of 105.9°. This wide bond angle may be necessary in order to accommodate the bulky phenyl group in the ortho position of the aryloxy substituents.

Molecular Structure of $[NP(OC_6H_5)_2]_4$ (5). The molecular structure of $[NP(OC_6H_5)_2]_4$ (**5**) contains a tetrameric phosphazene ring with two phenoxy units attached to each phosphorus atom. The phosphorus–nitrogen ring assumes a boat conformation. No repetitive arrangement of the phenoxy units relative to the tetramer ring was detected.

The P–N bond distances for **5** vary in the range from 1.548 to 1.566 Å, with an average value of 1.560 Å. The P–N–P bond angles range from 131.8 to 135.3°, with an average of 133.9°. In addition, the N–P–N bond angles are similar and range between

120.16 and 122.52°, with a mean value of 121.1°. The P–O bond distances are equivalent, with a range from 1.577 to 1.587 Å and an average value of 1.582 Å. A large variation in the O–P–O bond angles was detected, with a range from 99.8 to 107.9° and an average value of 102.3°.

Comparison of the Molecular Structures of 3–5. The incorporation of an *o*-methyl substituent (**3**) or an *o*-phenyl substituent (**4**) into phenoxy-substituted tetramer (**5**) does not bring about a significant change in conformation of the phosphorus–nitrogen ring. In each case, a puckered or a boat conformation was detected. Since a wide array of ring conformations can be adopted by tetrameric phosphazene rings,[7,10] the similarity between these structures is striking. The P–N bond distances did not vary more than 0.045 Å and, therefore, are unaffected by the ortho substituent. No alternation of bond lengths around the phosphazene ring was detected.

A significant variation over a range of 33.5° was detected in the P–N–P bond angles for **3**–**5**. This variation can be accounted for by the exceptionally large P–N–P bond angle of 161.4° for P(3)–N(3)–P(4) in **3a**. This angle reflects the slightly puckered conformation of the tetramer ring in **3a**, in comparison with the boat conformations for **3b**, **4**, and **5**. A variation of only ca. 7.1° was detected for the N–P–N bond angles.

The P–O bond distances were equivalent within 0.056 Å, which is anticipated on the basis of similarities in the electronic features of the phenoxy and substituted-phenoxy groups. The O–P–O bond angles were similar, with a variation of 6.1°. The C–C bond lengths and C–C–C bond angles in the aromatic substituents were unexceptional.

A striking and important feature of the molecular structures of **3**–**5** is the increase in free volume near the skeletal ring in $[NP(OC_6H_5)_2]_4$ (**5**) in comparison to the corresponding *o*-methyl (**3a,b**) and *o*-phenyl (**4**) species. The steric crowding is particularly evident in compound **4** (see Figure 4), where the phosphazene ring is shrouded in phenoxy and ortho-substituted phenyl units.

Significance of the Structures. The purpose of this work was to examine the effect of phenoxy ortho substituents (methyl and phenyl) on the molecular structures of phosphazene cyclic tetramers. The overall goal was to extend the conclusions to the macromolecular level, in order predict the steric limits for substituents attached to a high-polymeric phosphazene chain.

This work demonstrated that full replacement of chlorine atoms in $(NPCl_2)_3$ and $(NPCl_2)_4$ can be accomplished under relatively mild conditions with the use of sodium 2-methylphenoxide and sodium 2-phenylphenoxide. The molecular structures of the cyclic tetrameric species confirmed the complete P–Cl substitution. In addition, the molecular structures indicated that the ortho substituents do not significantly distort the skeletal phosphorus–nitrogen ring or associated parameters.

The primary structural change that accompanies the introduction of ortho substituents is an increase in steric crowding near the phosphazene ring for compounds **3** and **4**. This feature, which can be seen in the ORTEP structures of the small molecules, is probably responsible for the steric shielding of unreacted P–Cl bonds in the corresponding high-polymeric phosphazenes. A correlation exists between the size of the ortho substituent and the number of chlorine atoms replaced in poly(dichlorophosphazene), since 85% replacement is achieved with 2-methylphenoxide versus 76% substitution with 2-phenylphenoxide.[6]

Experimental Section

Materials. Hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene (provided by Ethyl Corp.) were separated and purified by fractional sublimation before use. 2-Methylphenol (Aldrich) was purified by distillation under reduced pressure. 2-Phenylphenol (Aldrich) was purified by sublimation. All other reagents (Aldrich) were used as received. Compound **5**, $[NP(OC_6H_5)_2]_4$, was prepared according to procedures described previously.[7] Solvents were dried and distilled under nitrogen by standard methods. All reactions were carried out under an atmosphere of dry argon or nitrogen by using standard Schlenk and drybox techniques.

Equipment. ^{31}P (36.23 MHz) NMR spectra were recorded with use of a JEOL FX90Q NMR spectrometer. ^{1}H (360 MHz) NMR spectra were recorded with use of a Brucker WM360 spectrometer. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or tetramethylsilane (^{1}H). All heteronuclear NMR spectra were proton decoupled. Electron-impact mass spectra were obtained with the use of a Kratos MS9/50 spectrometer. X-ray crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer controlled by a PDP 11/44 computer. Elemental microanalysis were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of $[NP(OC_6H_4CH_3\text{-}2)_2]_3$ (1). To a suspension of sodium metal (4.76 g, 0.21 mol) and tetra-*n*-butylammonium bromide (0.20 g, 6.2 mmol) in dioxane (100 mL) was added slowly a solution of 2-methylphenol (23.4 mL, 0.23 mol, 10% excess) in dioxane (50 mL). The mixture was heated at 100 °C for 12 h and was then added to a solution of hexachlorocyclotriphosphazene (3.00 g, 8.63 mmol) in dioxane (75 mL). The reaction mixture was heated at 100 °C for 48 h. The solvent was removed by rotary evaporation, and the residue was dissolved in methylene chloride, extracted with 10% aqueous NaOH (3 times), washed with water (2 times), and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation to yield tan-colored solids. Attempts to grow single crystals of **1** acceptable for X-ray analysis were unsuccessful. Yield: 4.56 g, 68%. Characterization data for **1** are listed in Table I.

Synthesis of $[NP(OC_6H_4C_6H_5\text{-}2)_2]_3$ (2). Compound **2** was prepared from 2-phenylphenol by following the same procedure described for compound **1**. Compound **2** was a tan-colored, viscous oil. Yield: 57%. Characterization data for **2** are listed in Table I.

Synthesis of $[NP(OC_6H_4CH_3\text{-}2)_2]_4$ (3). Compound **3** was prepared from octachlorocyclotetraphosphazene by following the same procedure described for compound **1**. Yield: 64.9%. Crystals of **3** were grown by recrystallization from hot *n*-hexane. Characterization data for **3** are listed in Table I.

Synthesis of $[NP(OC_6H_4C_6H_5\text{-}2)_2]_4$ (4). Compound **4** was prepared from octachlorocyclotetraphosphazene and 2-phenylphenol by following the same procedure described for compound **1**. Yield: 54.7%. Crystals of **4** were grown by recrystallization from hot *n*-hexane/chloroform. Characterization data for **4** are listed in Table I.

X-ray Structure Determination Technique. Our general technique is described elsewhere,[11] and only details related to the present work will be given here. The structures were solved by direct methods using MULTAN '82[12] and Fourier methods. In compound **3**, all non-hydrogen atoms were refined anisotropically. In compound **4**, carbon atoms were refined isotropically, and all other non-hydrogen atoms (P, O, N) were refined anisotropically. In compound **5**, all non-hydrogen atoms were refined anisotropically. In compound **5**, hydrogen atoms were included in the refinements at their geometrically idealized positions with isotropic temperature factors. Hydrogen atoms were not included in **3** and **4**.

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Registry No. **1**, 106437-01-8; **2**, 141377-23-3; **3**, 141377-24-4; **4**, 141377-25-5; **5**, 992-79-0; hexachlorocyclotriphosphazene, 940-71-6; octachlorocyclotetraphosphazene, 2950-45-0; 2-methylphenol, 95-48-7; 2-phenylphenol, 90-43-7.

Supplementary Material Available: Complete tables of bond distances and angles, final fractional atomic coordinates, and anisotropic thermal parameters for **3**–**5** (47 pages); tables of calculated and observed structure factors for **3**–**5** (204 pages). Ordering information is given on any current masthead page.

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