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Syntheses and Structures of Cyclic and Short-Chain Linear Phosphazenes Bearing 4-Phenylphenoxy Side Groups

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Abstract: A series of cyclic and short-chain linear phosphazenes bearing the 4-phenylphenoxy side group has been synthesized. These compounds are models for the corresponding linear high polymer. The X-ray structures of $[NP(O-C_6H_4-C_6H_5\text{-}p)_2]_3$ (1), $[NP(O-C_6H_4-C_6H_5\text{-}p)_2]_4$ (2), and $OP_3N_2(O-C_6H_4-C_6H_5\text{-}p)_7$ (6) are reported. Compound 6 represents the first three-phosphorus linear oligomeric phosphazene-bearing aryloxy side group to be described. The molecular structure of 6 showed that the linear phosphazene skeleton assumes a distorted cis-trans conformation. Crystals of 1 are monoclinic with space group $P2_1/c$ with $a = 23.296$ (6) Å, $b = 7.762$ (4) Å, $c = 34.666$ (7) Å, $\beta = 90.14$ (2)°, $V = 6268.4$ Å^3, and $Z = 4$. Crystals of 2 are triclinic of space group $P1$ with $a = 10.462$ Å, $b = 16.433$ Å, $c = 23.326$ Å, $\alpha = 94.25$ (2)°, $\beta = 91.03$ (3)°, $\gamma = 103.59$ (3)°, $V = 3883.9$ Å^3, and $Z = 2$. Finally, crystals of 6 are monoclinic with space group $P2_1/n$ with $a = 10.413$ (9) Å, $b = 23.425$ (9) Å, $c = 36.359$ (12) Å, $\beta = 96.27$ (6)°, $V = 8815.77$ Å^3, and $Z = 4$.

High polymeric phosphazenes form a class of inorganic/organic macromolecules that possess a wide range of unusual properties.[1] The type of side group attached to the polyphosphazene chain has a powerful effect on the physical and chemical characteristics.[2] As part of our program to better understand the structure–property relationships in poly(organophosphazenes), we have synthesized a series of small-molecule cyclic and linear phosphazenes as structural models for the corresponding high polymers. The value of small-molecule phosphazene models for devising synthetic routes for the high polymers, and as tools to probe the possible structure of polymers, has been illustrated previously.[3-6] In the present work, we report the syntheses of a series of cyclic and linear oligomeric phosphazenes that bear the 4-phenylphenoxy side group. In particular, the structures of $[NP(O-C_6H_4-C_6H_5\text{-}p)_2]_3$ (1), $[NP(O-C_6H_4-C_6H_5\text{-}p)_2]_4$ (2), and $OP_3N_2(O-C_6H_4-C_6H_5\text{-}p)_7$ (6) are reported. The study of these compounds was guided by the following questions: (a) What is the effect of bulky aryloxy side groups on the bond lengths, bond angles, and conformation of a cyclophosphazene ring or a linear phosphazene backbone? (b) What is the preferred conformation of a linear phosphazene backbone? (c) Can evidence be found for the "stacking" of side groups in a way that might indicate possible liquid crystalline or nonlinear optical properties in related derivatives? (d) How closely will these model compounds mimic the structure and chemical properties of the high polymer? In this paper, the structural features of these compounds are compared and implications for the structure of the corresponding high polymer are discussed.

Results and Discussion

Syntheses. The reaction sequence used for the synthesis of the cyclophosphazenes is outlined in Scheme I. The cyclic model compounds were prepared by treatment of hexachlorocyclotriphosphazene or octachlorocyclotetraphosphazene with sodium 4-phenylphenoxide to yield the cyclic phosphazenes 1 and 2, respectively.

The reaction sequence for the synthesis of short-chain linear phosphazenes is summarized in Schemes II and III. The linear species, pentachlorooxodiphosphazene (3) was prepared by the reaction of phosphorus pentachloride with ammonium sulfate.[7] Heptachlorooxotriphosphazene (5) was prepared from 4 by use of a chain-building process.[8] Treatment of the respective chlorooxophosphazenes with sodium 4-phenylphenoxide gave compounds 4 and 6. Compound 7 was prepared by the reaction of $[P_4N_3Cl_{10}]^+Cl^-$ with sodium 4-phenylphenoxide.

Structural Characterization. The ^{31}P NMR and mass spectra of compounds 1, 2, 4, 6, and 7 are listed in Table VII. Microanalysis data are listed in Table VIII. The ^{31}P NMR spectra of the cyclic species were singlets, while those of the linear species were multiplets, reflecting the different chemical environment of the phosphorus atoms in these compounds. The chemical shifts of the $-P(OR)_2-$ units in the linear species showed a close similarity to those in the high polymeric system, suggesting a strong correlation in structure between the linear models and the corresponding high polymer. However, the main structural characterization was by means of X-ray single-crystal analysis.

Crystal and Molecular Structure of $[NP(O-C_6H_4-C_6H_5\text{-}p)_2]_3$ (1). Compound 1 contains a cyclic trimeric phosphazene ring, with six 4-phenylphenoxy groups attached through P–O–C linkages to P(1), P(2), and P(3) of the phosphazene skeleton (Figure 1). The phosphazene ring is slightly puckered: the phosphorus atoms are located above and the nitrogen atoms are below the plane of the ring. (The displacements of the atoms from this plane are as follows: P(1), 0.089; P(2), 0.057; P(3), 0.043; N(1), -0.085; N(2), -0.035, and N(3), -0.068 Å.) By contrast, the phosphazene ring of $[NP(OPh)_2]_3$ is planar.[12] Thus, extension of the side chains by one phenyl group, as in compound 1, appears to have only a minor effect on the conformation of the ring. However, the disposition of the biphenyl units is complex. On one side of the phosphazene ring, three side chains are aligned with their longest axes at right angles to the plane of the inorganic ring. On the other side of the phosphazene ring, three side chains are oriented so that their longest axes are slanted at approximately 68° to the ring. While no direct stacking of side groups was detected *within* a molecule, *inter*molecular stacking of side groups is clearly shown in the packing diagram. The two phenyl rings of the 4-phenylphenoxy units are twisted relative to each other. The smallest angle of twist is for the C(49)–C(54) and C(55)–C(60) planes (2.58°). For the other side groups, the dihedral angles between planes of the rings in the biphenyl unit range between 18.02° and

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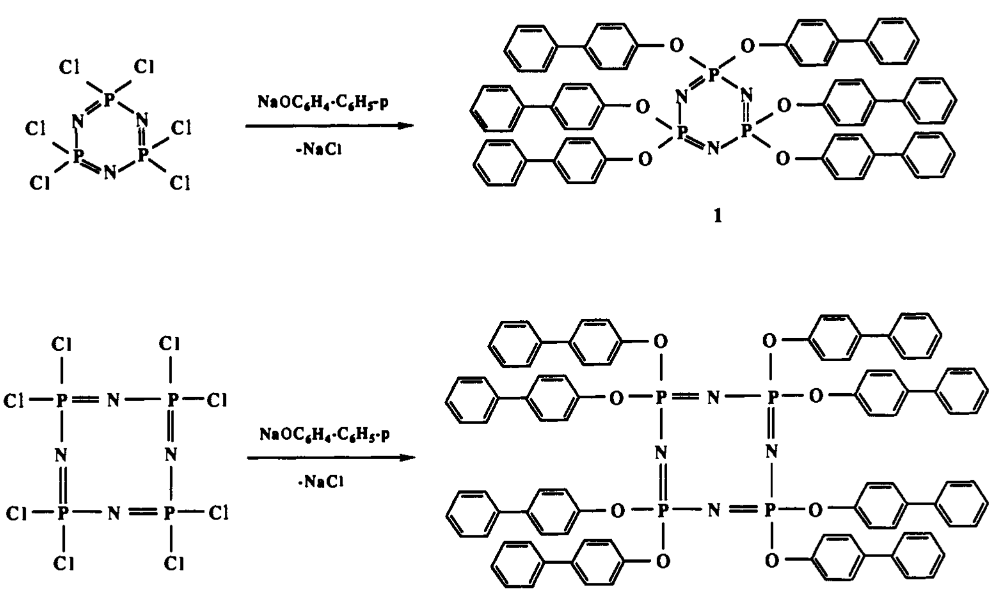
Scheme I



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Scheme II

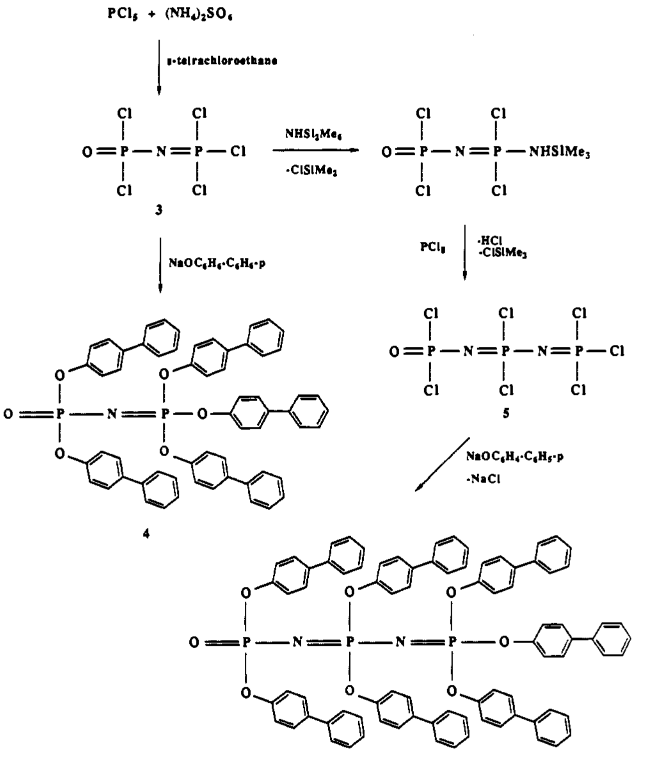

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Table I. Bond Lengths (Å) and Bond Angles (deg) for $[NP(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_3$ (1)[a,b]

P(1)-O(1)	1.559 (6)	O(1)-C(1)	1.363 (8)
P(1)-O(2)	1.575 (6)	O(2)-C(13)	1.360 (8)
P(2)-O(3)	1.592 (6)	O(3)-C(25)	1.355 (8)
P(2)-O(4)	1.556 (6)	O(4)-C(37)	1.379 (8)
P(3)-O(5)	1.580 (6)	O(5)-C(49)	1.369 (9)
P(3)-O(6)	1.578 (6)	O(6)-C(61)	1.352 (8)
P(1)-N(1)	1.561 (7)	C(4)-C(7)	1.483 (9)
P(1)-N(3)	1.581 (7)	C(16)-C(19)	1.485 (9)
P(2)-N(1)	1.568 (8)	C(28)-C(31)	1.495 (10)
P(2)-N(2)	1.602 (7)	C(40)-C(43)	1.485 (9)
P(3)-N(2)	1.554 (7)	C(52)-C(55)	1.500 (10)
P(3)-N(3)	1.570 (7)	C(64)-C(67)	1.502 (9)
N(1)-P(1)-N(3)	115.1 (4)	O(4)-P(2)-N(1)	107.2 (4)
N(1)-P(2)-N(2)	116.4 (4)	O(4)-P(2)-N(2)	111.0 (4)
N(2)-P(3)-N(3)	118.0 (4)	O(5)-P(3)-O(6)	97.8 (3)
P(1)-N(1)-P(2)	123.2 (4)	O(5)-P(3)-N(2)	110.4 (4)
P(2)-N(2)-P(3)	120.9 (5)	O(5)-P(3)-N(3)	109.6 (4)
P(3)-N(3)-P(1)	122.3 (4)	O(6)-P(3)-N(2)	112.1 (4)
O(1)-P(1)-O(2)	92.9 (3)	O(6)-P(3)-N(3)	107.0 (4)
O(1)-P(1)-N(1)	122.4 (4)	P(1)-O(1)-C(1)	131.2 (5)
O(1)-P(1)-N(3)	110.5 (4)	P(1)-O(2)-C(13)	120.6 (5)
O(2)-P(1)-N(1)	111.8 (4)	P(2)-O(3)-C(25)	126.0 (5)
O(2)-P(1)-N(3)	112.0 (4)	P(2)-O(4)-C(37)	123.4 (5)
O(3)-P(2)-O(4)	98.3 (3)	P(3)-O(5)-C(49)	120.2 (5)
O(3)-P(2)-N(1)	112.5 (4)	P(3)-O(6)-C(61)	128.8 (5)
O(3)-P(2)-N(2)	109.9 (4)		

[a] Aromatic C–C distances were constrained to be 1.395 Å. [a] Aromatic C–C–C angles were constrained to be 120.0°.

Table II. Angles between Phenyl Rings of Biphenyl Units in 1

atoms in ring		angle between rings (deg)
C(1)-C(6)	C(7)-C(12)	28.70
C(13)-C(18)	C(19)-C(24)	25.55
C(25)-C(30)	C(31)-C(36)	18.02
C(37)-C(42)	C(43)-C(48)	29.53
C(49)-C(54)	C(55)-C(60)	2.58
C(61)-C(66)	C(67)-C(72)	27.73

28.70°. The unit cell contains four molecules arranged in such a manner that the longest axis of each molecule is pointed in the same direction. This orientation allows maximum stacking of side groups between neighboring molecules. The unit cell also contains four molecules of *m*-xylene, a solvent used for crystallization.

The bond angles and bond distances for structure of 1 are shown in Table I. The average P–N bond distances range from 1.554 (7) to 1.602 (7) Å with a mean value of 1.572 (7) Å. The P–N–P angles range between 120.9 (5)° and 123.2 (4)° with an average value of 122.1 (4)°, and the N–P–N angles vary from 115.1 (4)° to 118.0 (4)° with a mean value of 116.5 (4)°. These values are similar to those found in $[NP(OPh)_2]_3$. The average P–O bond distances range between 1.556 (6) and 1.592 (6) Å with a mean value of 1.573 (6) Å. This is shorter than the P–O single bond (1.61 Å), which suggests some exocyclic delocalization of electrons. The mean O–P–O bond angles range from 92.9 (3)° to 97.8 (3)° and average to 96.3 (3)°. The angles of twist between the phenyl rings of the biphenyl units are listed in Table II.

Crystal and Molecular Structure of $[NP(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_4$ (2). Molecules of $[NP(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_4$ contain an eight-

Scheme III

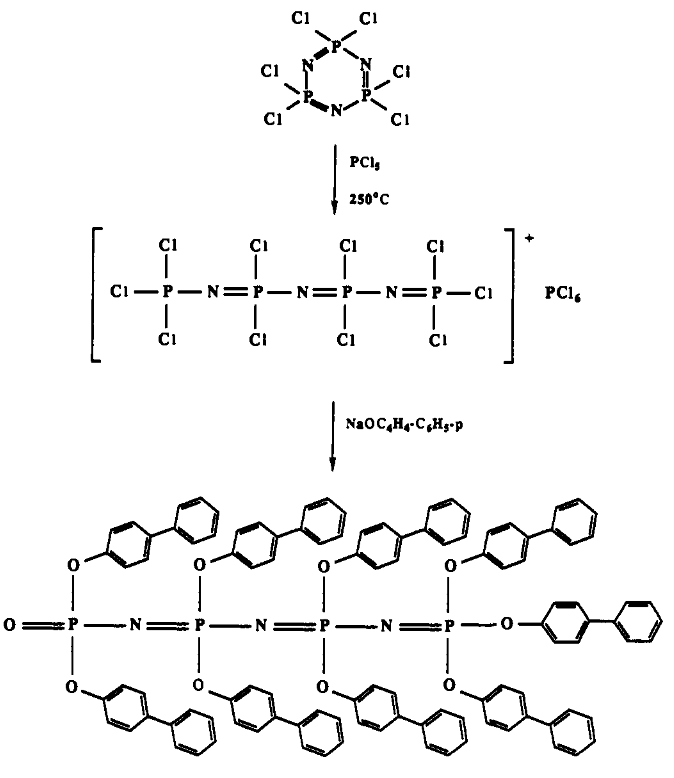

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Table III. Bond Lengths (Å) and Bond Angles (deg) for [NP(O–C_6H_4–C_6H_5-*p*)$_2$]$_4$ (**2**)

P(1)–O(1)	1.596 (9)	P(4)–O(7)	1.583 (9)
P(1)–O(2)	1.575 (8)	P(4)–O(8)	1.601 (7)
P(1)–N(1)	1.539 (9)	P(4)–N(3)	1.570 (16)
P(1)–N(4)	1.569 (8)	P(4)–N(4)	1.553 (9)
P(2)–O(3)	1.565 (8)	O(1)–C(101)	1.40 (1)
P(2)–O(4)	1.579 (9)	O(2)–C(201)	1.40 (2)
P(2)–N(1)	1.572 (9)	O(3)–C(301)	1.41 (1)
P(2)–N(2)	1.571 (8)	O(4)–C(401)	1.38 (1)
P(3)–O(5)	1.579 (7)	O(5)–C(501)	1.38 (1)
P(3)–O(6)	1.575 (8)	O(6)–C(601)	1.40 (1)
P(3)–N(2)	1.529 (9)	O(7)–C(701)	1.41 (1)
P(3)–N(3)	1.552 (15)	O(8)–C(801)	1.36 (1)
N(1)–P(1)–N(4)	121.4 (5)	O(4)–P(2)–N(1)	105.5 (5)
N(1)–P(2)–N(2)	121.3 (5)	O(4)–P(2)–N(2)	109.0 (4)
N(3)–P(3)–N(3)	119.5 (5)	O(5)–P(3)–O(6)	99.1 (4)
N(3)–P(4)–N(4)	120.5 (5)	O(5)–P(3)–N(2)	109.7 (5)
P(1)–N(1)–P(2)	133.1 (5)	O(5)–P(3)–N(3)	105.6 (4)
P(2)–N(2)–P(3)	138.7 (6)	O(6)–P(3)–N(2)	112.1 (4)
P(3)–N(3)–P(4)	132.1 (6)	O(6)–P(3)–N(3)	108.7 (5)
P(1)–N(4)–P(4)	132.5 (6)	O(7)–P(4)–O(8)	99.0 (4)
O(1)–P(1)–O(2)	102.5 (4)	O(7)–P(4)–N(3)	109.2 (6)
O(1)–P(1)–N(1)	106.4 (5)	O(7)–P(4)–N(4)	107.0 (5)
O(1)–P(1)–N(4)	108.5 (4)	O(8)–P(4)–N(3)	112.3 (5)
O(2)–P(1)–N(1)	110.1 (4)	O(8)–P(4)–N(4)	106.6 (5)
O(2)–P(1)–N(4)	106.5 (4)	P(1)–O(1)–C(101)	121.7 (7)
O(3)–P(2)–O(4)	104.6 (4)	P(1)–O(2)–C(201)	129.8 (7)
O(3)–P(2)–N(1)	110.5 (4)	P(2)–O(3)–C(301)	130.6 (8)
O(3)–P(2)–N(2)	104.9 (5)	P(2)–O(4)–C(401)	123.7 (7)
P(3)–O(5)–C(501)	126.0 (7)	P(3)–O(6)–C(601)	126.1 (7)
P(4)–O(7)–C(701)	122.5 (8)	P(4)–O(8)–C(801)	124.3 (8)

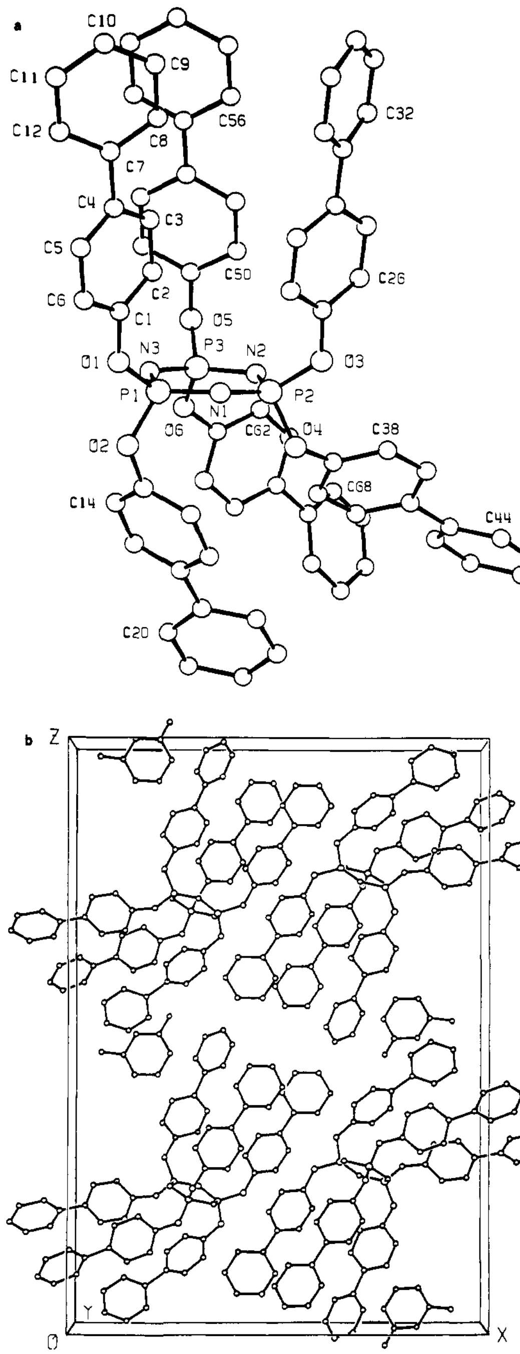

Figure 1. (a) ORTEP and (b) packing diagrams for [NP(O–C_6H_4–C_6H_5-*p*)$_2$]$_3$ (**1**).

membered phosphazene ring that assumes a boat conformation (Figure 2). Two 4-phenylphenoxy groups are attached to each phosphorus atom through P–O–C linkages. On one side of the phosphorus–nitrogen ring, three side chains from P(2), P(3), and P(4) are oriented with their longest axes approximately perpendicular to the ring. On the other side of the ring, three other side chains from P(1), P(2), and P(3) have their longest axes less than 90° to the plane of the inorganic ring. This conformation is very similar to that of the trimeric analogue **1**, which suggests that the side-chain conformation is not dependent on the size of the phosphazene ring. It is interesting to note that one of the side groups (from P(1)) is disposed so that it is coplanar with the phosphazene ring. As in **1**, no *intra*molecular stacking of side groups was detected. However, the four molecules of **2** in the unit cell are arranged to permit long-range stacking of side groups between neighboring molecules. The bond angles and bond distances of compound **2** are shown in Table III. The P-N bond distances range from 1.529 (9) to 1.571 (8) Å with a mean of 1.554 (11) Å. The P-N-P angles range from 132.1 (6)° to 138.7 (6)° with a mean value of 134.1 (6)°, and the N-P-N angles vary between 119.5 (5)° and 121.4 (5)° with an average of 120.7 (5)°. The P–O distances range between 1.565 (8) and 1.601 (7) Å with a mean of 1.582 (8) Å. The O–P–O angles are between 99.0 (4)° and 104.6 (4)° with an average of 101.3 (4)°, which is significantly wider than that found in the cyclic trimeric species. As in **1**, the phenyl rings of the biphenyl units are not coplanar. The dihedral

Table IV. Angles between Phenyl Rings of Biphenyl Units in **2**

atoms in ring		angle between rings (deg)
C(1)–C(6)	C(7)–C(12)	43.17
C(13)–C(18)	C(19)–C(24)	34.68
C(25)–C(30)	C(31)–C(36)	34.08
C(37)–C(42)	C(43)–C(48)	32.44
C(49)–C(54)	C(55)–C(60)	131.95
C(61)–C(66)	C(67)–C(72)	36.00
C(73)–C(78)	C(79)–C(84)	137.91
C(85)–C(90)	C(91)–C(96)	135.02

Table V. Bond Lengths (Å) and Bond Angles (deg) for $OP_3N_2(O–C_6H_4–C_6H_4\text{-}p)_7$ (**6**)[a,b]

P(1)–O(1)	1.483 (12)	O(3)–C(13)	1.41 (2)
P(1)–O(2)	1.559 (11)	O(4)–C(25)	1.41 (2)
P(1)–O(3)	1.584 (11)	O(5)–C(37)	1.37 (2)
P(1)–N(1)	1.571 (14)	O(6)–C(49)	1.46 (2)
P(2)–N(1)	1.570 (13)	O(7)–C(61)	1.40 (2)
P(2)–N(2)	1.533 (13)	O(8)–C(73)	1.37 (2)
P(2)–O(4)	1.585 (10)	C(4)–C(7)	1.54 (2)
P(2)–O(5)	1.592 (10)	C(16)–C(19)	1.47 (2)
P(3)–N(2)	1.524 (13)	C(28)–C(31)	1.50 (2)
P(3)–O(6)	1.545 (11)	C(40)–C(43)	1.51 (2)
P(3)–O(7)	1.532 (12)	C(52)–C(55)	1.49 (2)
P(3)–O(8)	1.537 (11)	C(64)–C(67)	1.52 (2)
O(2)–C(1)	1.40 (2)	C(76)–C(79)	1.51 (2)
N(1)–P(2)–N(2)	114.3 (7)	O(6)–P(3)–O(7)	111.3 (6)
P(1)–N(1)–P(2)	127.8 (8)	O(6)–P(3)–O(8)	103.0 (6)
P(2)–N(2)–P(3)	142.6 (10)	O(6)–P(3)–N(2)	105.5 (7)
O(1)–P(1)–O(2)	103.6 (6)	O(7)–P(3)–O(8)	103.2 (6)
O(1)–P(1)–O(3)	112.8 (6)	O(7)–P(3)–N(2)	115.9 (7)
O(1)–P(1)–N(1)	124.0 (7)	O(8)–P(3)–N(2)	117.4 (6)
O(2)–P(1)–O(3)	98.4 (6)	P(1)–O(1)–C(1)	123.6 (9)
O(2)–P(1)–N(1)	108.1 (6)	P(1)–O(3)–C(13)	122.8 (9)
O(3)–P(1)–N(1)	106.7 (7)	P(2)–O(4)–C(25)	123.1 (8)
O(4)–P(2)–O(5)	100.2 (6)	P(2)–O(5)–C(37)	122.4 (9)
O(4)–P(2)–N(1)	116.1 (6)	P(3)–O(6)–C(49)	119.0 (10)
O(4)–P(2)–N(2)	108.4 (7)	P(3)–O(7)–C(61)	129.5 (10)
O(5)–P(2)–N(1)	107.0 (6)	P(3)–O(8)–C(73)	125.2 (9)
O(5)–P(2)–N(2)	109.7 (6)		

[a] Aromatic C–C constrained to be 1.395 Å. [b] Aromatic C–C–C constrained to be 120.0°.

angles between planes of the phenyl rings range between 32.44° and 48.05°. The angles of twist between the phenyl rings of the biphenyl units are listed in Table IV.

Crystal and Molecular Structure of $OP_3N_2(O–C_6H_4–C_6H_5)_7$ (6). The structure of **6** provided a considerable amount of useful information. The structure is the first short-chain phosphazene with three phosphorus atoms that bears aryloxy side groups (Figure 3). The phosphazene backbone assumes a slightly distorted cis–trans conformation. The torsion angles are P(1)–N(1)–P(2)–N(2) = −174° and N(1)–P(2)–N(2)–P(3) = 31°. The slight deviation of the backbone from exact planarity may be due to crystal-packing forces. The side groups are oriented to maintain a maximum distance of separation. However, certain groups appear to be arranged approximately parallel to each other. This can be seen for two pairs of side groups from [P(1),P(3)] and [P(2),P(3)]. The asymmetric unit of **6** is composed of a phosphazene molecule and two molecules of *n*-pentane (a solvent used for crystallization), one of which is disordered. In the crystal structure, the planes formed by the P–N backbones of each molecule are approximately parallel to each other. Intermolecular stacking of side groups in the *a* direction of the unit cell can be also be observed. The four solvent molecules are trapped in a cavity formed by four molecules of **6**. The guest molecules apparently do not influence the conformation of **6** since the global structural features of **6** compare well with those of related compounds, such as $OP_3N_2Cl_7$ and $OP_3N_2(NHC_6H_5)_7$.[6] The highly disordered *n*-pentane molecules may contribute to the relatively high *R* value of the crystal structure of **6**.

Table VI. Angles between Phenyl Rings of Biphenyl Units in **6**

atoms in ring		angle between rings (deg)
C(1)–C(6)	C(7)–C(12)	23.74
C(13)–C(18)	C(19)–C(24)	18.54
C(25)–C(30)	C(31)–C(36)	15.76
C(37)–C(42)	C(43)–C(48)	13.73
C(49)–C(54)	C(55)–C(60)	39.93
C(61)–C(66)	C(67)–C(72)	38.33
C(73)–C(78)	C(79)–C(84)	31.68

Table VII. ^{31}P NMR Chemical Shift Assignments[a]

compd	chemical shift (ppm)	coupling constant (Hz)
$[NP(O–C_6H_4–C_6H_4\text{-}p)_2]_3$ (**1**)	+8	
$[NP(O–C_6H_4–C_6H_5\text{-}p)_2]_4$ (**2**)	−12	
$OP_2N(O–C_6H_4–C_6H_5\text{-}p)_5$[b] (**4**)	A = −21.6, B = −15.1	J_{AB} = 72.3
$OP_3N_2(O–C_6H_4–C_6H_5\text{-}p)_7$[b] (**6**)	A = −23.2, B = −18.2 C = −13.1	J_{AB} = 64.0, J_{BC} = 69.8, J_{AC} = 4.4
$OP_4N_3(O–C_6H_4–C_6H_5\text{-}p)_9$[b] (**7**)	A = −22.9, B = −19.5 C = −17.4, D = −13.3	J_{AB} = 69.0, J_{CD} = 59.5

[a] In CH_2Cl_2. [b] The phosphorus atom designations are the following: atom A bears the terminal oxygen atom; atom B is the next one along the chain; etc.

Table VIII. Elemental Analysis Data

		% calcd	% found
$[NP(O–C_6H_4–C_6H_5\text{-}p)_2]_3$ (**1**)	C	75.20	75.55
	H	4.70	4.66
	N	3.66	3.68
$[NP(O–C_6H_4–C_6H_5\text{-}p)_2]_4$ (**2**)	C	75.19	75.20
	H	4.73	4.82
	N	3.65	3.68
$OP_2N(O–C_6H_4–C_6H_5\text{-}p)_5$ (**4**)	C	76.80	76.65
	H	4.80	5.11
	N	1.50	1.19
$OP_3N_2(O–C_6H_4–C_6H_5\text{-}p)_7$ (**6**)	C	76.36	76.76
	H	4.77	5.05
	N	2.12	2.21
$OP_4N_3(O–C_6H_4–C_6H_5\text{-}p)_9$ (**7**)	C	76.10	76.53
	H	4.76	4.84
	N	2.47	2.49

The P–N bond lengths are similar but not equal. P(1)–N(1) and P(2)–N(1) have almost identical lengths of 1.571 (4) Å. Bonds P(2)–N(2) and P(3)–N(2) have very similar values of 1.533 (13) and 1.524 (13) Å, respectively. For all practical purposes, no separation into discrete single and double P–N bonds was detected. The average P–N bond distance is 1.558 (13) Å. The P–N–P bond angle at N(2) is unusually large at 142.6 (10)°. This may be due to the need for the side groups at P(3) to maintain a maximum distance from those at P(2). In effect, the angle at N(2) is widened to achieve this end. The angle at N(1) is 127.8 (8)° and the N(1)–P(2)–N(2) angle is 114.3 (7)°. The latter is similar to those found in cyclic phosphazenes, again suggesting that the N–P–N angle is less flexible than the P–N–P angle. The dihedral angles between the phenyl rings of the side group range between 13.73° and 39.93°.

The bond lengths and bond angles are shown in Table V. The angles of twist between the phenyl rings of the biphenyl units are listed in Table VI.

Significance of the Structures. A purpose of this work was to examine the relationships and trends in the structures of cyclic and linear short-chain phosphazenes. The comparison of the structures studied in this work with those of related compounds would permit the identification of structural trends. This information might allow reasonable predictions to be made about the conformation and packing behavior of the high polymer. The structural parameters for several cyclic and linear phosphazenes are listed in Table IX.

Table IX. Structural Comparison of Cyclic and Linear Phosphazene Models

	P-N	P-N-P	N-P-N	O-P-O	P-O	P-O-C	O-C
$(NPF_2)_3$[a]	1.56	121	119				
$(NPF_2)_4$[b]	1.51	147.2	122.7				
$(NPCl_2)_3$[c]	1.59	120	120				
$(NPCl_2)_4$[d]	1.67	123	117				
$[NP(Ph)_2]_3$[e]	1.597	122.1	117.8				
$[NP(OPh)_2]_3$[f]	1.575	121.9	117.3	97.20	1.582	123.2	1.406
$[NP(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_3$	1.572	122.1	116.5	96.30	1.573	125.1	1.363
$[NPO(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_4$	1.554	134.1	120.7	101.3	1.582	125.6	1.393
OP_2NCl_5[g]	1.542	146.2					
$OP_3N_2Cl_7$[g]	1.542	136.5	116.8				
$OP_2N(OPh)_5$[g]	1.561	133.9		104.6	1.574	124.9	1.402
$OP_3N_2(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_7$	1.558	135.2	114.3	103.2	1.563	123.7	1.400

[a] Reference 20. [b] Reference 21. [c] Reference 22. [d] Reference 23. [e] Reference 24. [f] Reference 12. [g] Reference 6.

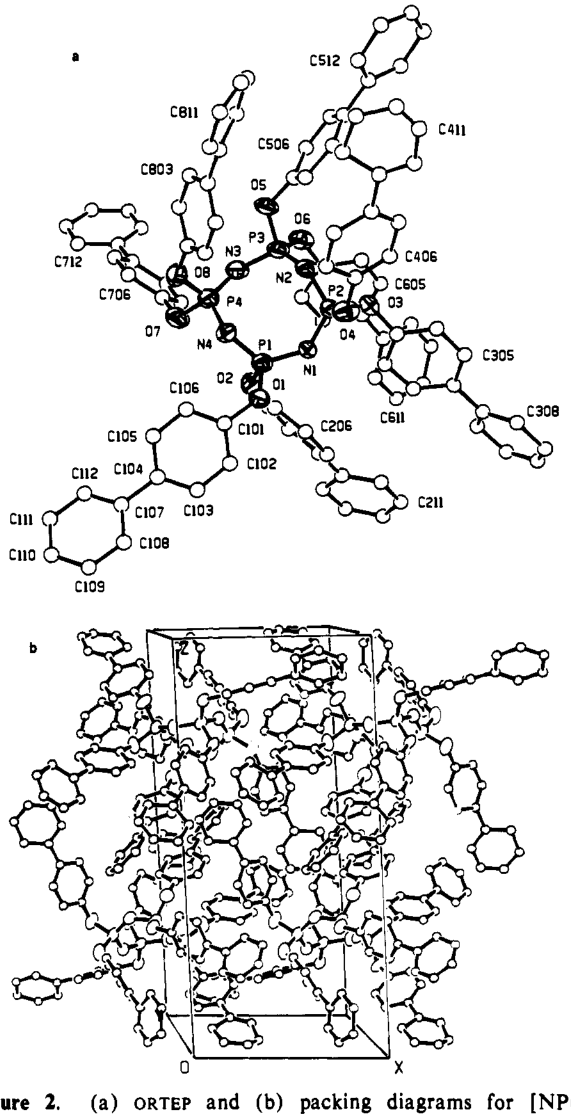

Figure 2. (a) ORTEP and (b) packing diagrams for $[NP(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_4$ (**2**).

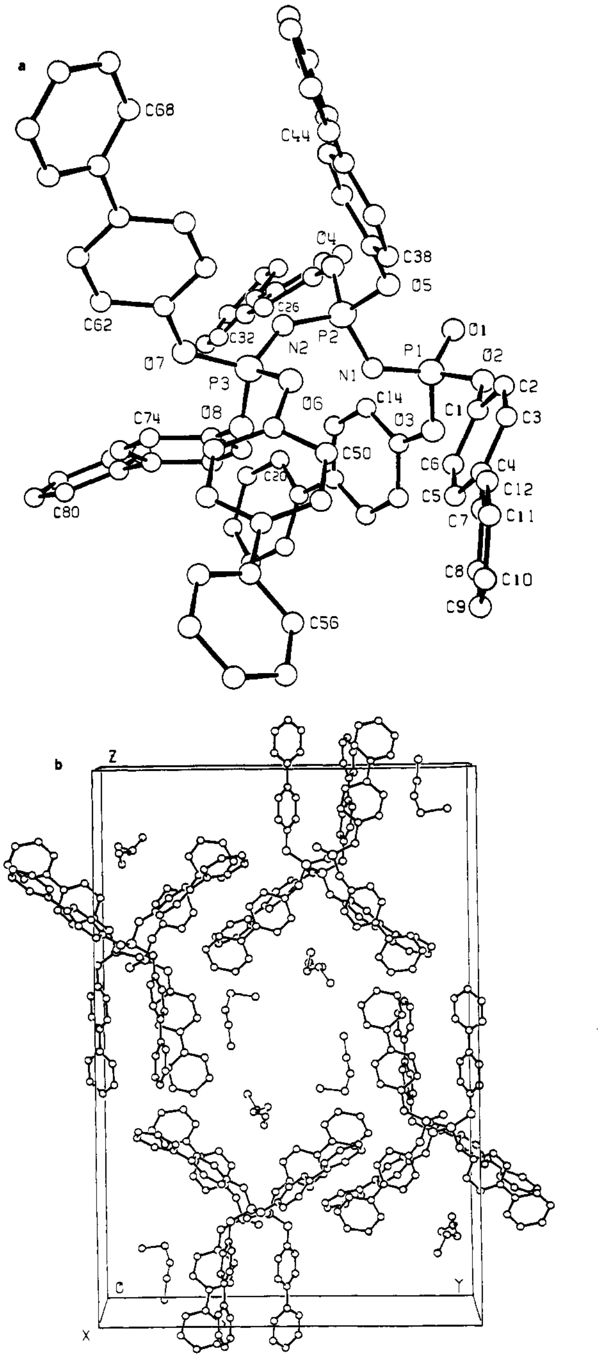

Figure 3. (a) ORTEP and (b) packing diagrams for $OP_3N_2(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_7$ (**6**).

The comparison of **1** with $[NP(OPh)_2]_3$ is of primary interest. First, what effect does the replacement of phenyl groups in **1** by biphenyl units have on the structure of the phosphazene ring? The present results indicate that no significant difference exists between the two ring structures. Therefore, at least for this side-group variation, the conformation of the ring is independent of the length of the aromatic side chain.

Second, what structural differences exist between the trimeric, tetrameric, and linear derivatives? Inspection of the structural data shows that, although some variation exists in the value of P-N bond lengths in each compound, the skeletal bonds obviously have some multiple-bond character. The values of 1.572 (7), 1.554 (11), and 1.558 (13) Å for **1**, **2**, and **6** are all shorter than the P-N single bond found in sodium phosphoramidate, NaH_3NPO_3 (1.76 Å),[13] and $(NH_2)_3PBH_3$ (1.65 Å).[14] Thus, the P-N bond

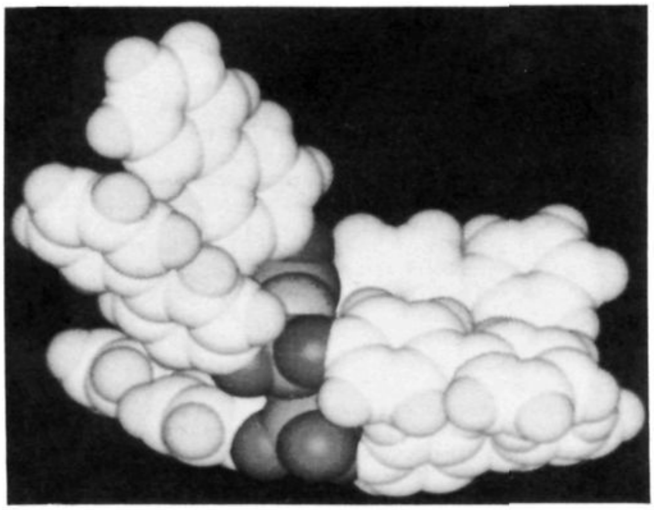

Figure 4. Space-filling model for $OP_3N_2(O-C_6H_4-C_6H_5\text{-}p)_7$ (**6**).

distance in the corresponding high polymer is expected to be in the range of 1.55–1.56 Å. Next, consider the bond angles. The angles at nitrogen are clearly sensitive to the overall structure of the skeleton. The P–N–P angles in **1**, **2**, and **6** are 122.1°, 134.1°, and 135.2°, respectively. On the other hand, the variation in N–P–N angles is less. It is interesting to note that the N–P–N angle in **6** is narrower than those in the cyclic analogues. These results suggest that the main centers of angular flexibility of the P–N backbone may be concentrated at the nitrogen atoms. Because the variation of P–N–P angles between **2** and **6** is small, we propose that this angle in the corresponding polymer should be in the region of 135°. The N–P–N angle in the polymer may approximate to 115°.

Perhaps the most significant result of this study is from the structure of **6**. Although a previous study reported X-ray data from a phosphazene high polymer with 4-phenylphenoxide side groups, on the basis of a single crystal of the polymer,[15] no conclusions were drawn about the conformation of the side groups or backbone or of the detailed structural parameters. The structure of **6** provides an insight into the possible arrangement of relatively large side chains about the phosphazene backbone, as well as the conformation of the backbone itself. The most striking feature of this molecule is the near planarity of the P–N skeleton. With skeletal torsion angles of −174° and 31°, the P–N backbone occupies a distorted cis–trans conformation. Chain planarity was also found for a short-chain phosphazene with chloro side groups[6] in which the backbone also assumes a near-cis–trans planar structure. Thus, the results of this study suggest that this skeletal conformation may be maintained for wide variations in the size of side groups attached to the phosphazene skeleton. A cis–trans planar conformation for a number of high polymeric phosphazenes has been proposed by several investigators, including ourselves.[6,16-18] The present results serve to reinforce these findings.

The orientation of the side groups about the backbone in **6** is also interesting. Although stacking of side chains within the same molecule is not obvious, a tendency does exists for the side chains to form colinear arrangements. This feature may serve to enhance the crystallinity of the material. Furthermore, close inspection of the structure also revealed that very little free volume exists in the crystal that might allow movement by the side groups. For example, rotation of the bond between N(2)–P(3) would generate interference between the side chains attached to P(3) and the side chains of P(2). This creates an energetically unfavorable condition. Thus, the flexibility of the molecule is restricted. To further illustrate this point, a space-filling model of **6** was constructed from its crystal data (Figure 4).[25] The model clearly shows the tightness of packing of the side groups around the P–N skeleton. This finding is compatible with the properties of the corresponding polymer. The glass transition temperature (T_g) of $[NP(O-C_6H_4-C_6H_5\text{-}p)_2]_n$ ranges from 73[15] to 93 °C.[2] The restricted motion of side groups found for **6** and their interference with skeletal bond torsion would explain this high T_g. Comparison of **6** with related compounds, namely OP_3NCl_7 and $OP_2N(OPh)_5$ showed no significant differences in bond lengths and bond angles.

Table X. Summary of Crystal Data and Intensity Collection Parameters

	1	**2**	**6**
formula	$C_{72}H_{54}N_3P_3O_6\cdot C_7H_8$	$C_{96}H_{72}N_4P_4O_8$	$C_{84}H_{63}N_2P_3O_8\cdot 2C_5H_{12}$
fw (amu)	1242.35	1533.60	1453.62
space gp	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	23.296 (6)	10.462 (4)	10.413 (9)
b (Å)	7.762 (4)	16.433 (6)	23.425 (9)
c (Å)	34.666 (7)	23.326 (6)	36.359 (12)
α (deg)		94.25 (2)	
β (deg)	90.14 (2)	91.03 (3)	96.27 (6)
γ (deg)		103.59 (3)	
V (Å^3)	6268.4	3883.9	8815.77
Z	4	2	4
d(calcd) (g/cm^3)	1.316	1.311	1.104
T (K)	293	293	293
radiation	Mo Kα	Mo Kα	Cu Kα
λ (Å)	0.71073	0.71073	1.5418
μ (cm^{-1})	1.14	1.548	9.60
θ_{max} (deg)	23	20	50
ω-scan width	$1.25 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$	$1.00 + 0.14 \tan\theta$
scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
crystal decay[a] (%)	3.4	none	4.74
data measured	4549	7763	9072
data used	4051	4959	3591
R, wR	0.082, 0.095	0.108, 0.146	0.1354, 0.1361
data/param	9.6	9.4	7.8
$(\Delta/\sigma)_{max}$	<0.2	0.3	<0.2
$\Delta\rho$ (e A^{-3})	0.44	0.47	0.62
p in weighing scheme[b]	0.023	0.060	0.023

[a] Data corrected by appropriate scaling. [b] $w = (1/\sigma^2F + pF^2)$.

In all structures, the P–O bond distances are shorter than the single bond value of 1.61 Å.[19] This suggests that the delocalization of skeletal electrons is extended beyond the inorganic ring or chain.

Experimental Section

Analytical Techniques. ^{31}P NMR (^1H-decoupled) spectra were obtained with a JEOL FX-90Q NMR spectrometer operated at 36.2 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. X-ray crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer controlled by a PDP 11/44 computer. The structures were solved by the SDP programs installed on the PDP 11/44. Elemental analyses were obtained by Galbraith Laboratories.

X-ray Structure Determination Technique. The structures were solved by direct methods using MULTAN82.[9] In each case, the first E-map revealed the position of most of the non-hydrogen atoms; the remaining atoms were located from the subsequent Fourier maps. For compound **2**, anisotropic thermal parameters were allowed for P, O, and N atoms, while C atoms were refined isotropically. For **1** and **6**, all the non-hydrogen atoms were refined anisotropically. Difference Fourier syntheses,

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calculated toward the end of the refinement, showed a few maxima consistent with the expected positions of hydrogen atoms in all the structures. In **1** and **6**, hydrogen atoms were included at geometrically idealized positions with C–H bond distance at 1.08 Å. Hydrogen atoms were not included in **2**. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[10] and those for hydrogen atoms from Stewart and Davidson.[11] At the conclusion of the refinements, the values of R were 0.082, 0.108, and 0.1354 for **1**, **2**, and **6**, and $wR = [\sum w\Delta^2/\sum wF_0^2]$ were 0.095, 0.146, and 0.1361, respectively. In the refinements, weights were derived from the counting statistics. The programs used in the structure determination were Enraf Nonius SDP for **2** and SHELX76 for **1** and **6**.

Bond lengths and bond angles (Tables I, III, and V) are given in the text. Positional parameters are provided as supplementary material. A summary of crystal data is provided in Table X.

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. and was purified by recrystallization from hexane and sublimation at 50 °C (0.05 mmHg). Tetrahydrofuran (THF) (Fisher) and 1,4-dioxane (Fisher) were dried over sodium benzophenone ketyl. Hexane and methylene chloride were dried over calcium hydride. *sym*-Tetrachloroethane was dried over anhydrous calcium carbonate. All solvents were distilled in an atmosphere of dry nitrogen before use. 4-Phenylphenol (Aldrich) was purified by sublimation. Hexamethyldisilazane (Aldrich) was distilled and stored over molecular sieves. Phosphorus pentachloride (Aldrich) was used as received.

Synthesis of $[NP(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_3$ (1). A solution of sodium 4-phenylphenoxide was prepared by the reaction of sodium (1.06 g, 4.6 × 10^{-2} mol) with a solution of 4-phenylphenol (7.9 g, 4.6 × 10^{-2} mol) in tetrahydrofuran (30 mL). The 4-phenylphenoxide solution was decanted from unreacted sodium, and a solution of hexachlorocyclotriphosphazene $(NPCl_2)_3$ in tetrahydrofuran was added to it dropwise with vigorous stirring. After the solution was refluxed for 21 h under a nitrogen atmosphere, the solvent was removed on the rotary evaporator at room temperature and the residue was washed with water to yield a white product. This product was recrystallized from *m*-xylene; mp 202–203 °C. The isolated yield was 84%.

Synthesis of $[NP(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_2]_4$ (2). The synthesis of **2** was essentially similar to that of **1**. Octachlorocyclotetraphosphazene, $(NPCl_2)_4$ (2.0 g, 4.3 × 10^{-3} mol) was allowed to react with sodium 4-phenylphenoxide (6.7 × 10^{-2} mol) in tetrahydrofuran (60 mL). The reaction conditions and workup procedure were similar to those in the preparation of **1**; mp 156–158 °C. The isolated yield was 80%.

Synthesis of OP_2NCl_5 (3). Compound **3** was synthesized by a method previously reported.[7] Typically, PCl_5 (187 g, 0.90 mol) was reacted with $(NH_4)_2SO_4$ (26.4 g, 0.20 mol) in *sym*-tetrachloroethane (400 mL). The product **3** was purified by vacuum distillation twice to yield colorless crystals.

Synthesis of OP_3NCl_7 (5). Species **5** was synthesized by the method of Riesel.[8] Species **3** (2.0 g, 7.4 × 10^{-3} mol) was reacted with $NHSi_2Me_6$ (1.2 g, 7.4 × 10^{-3} mol) in CH_2Cl_2 (40 mL). The reaction mixture was refluxed for 12 h. PCl_5 was then added to the reaction flask via a Schlenk addition tube, and the mixture was refluxed for an additional 12 h. The product was used in subsequent reactions without further purification.

Synthesis of $OP_2N(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_5$ (4) and $OP_3N_2(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_7$ (6). The syntheses of **4** and **6** follow the same general procedure. The compounds were prepared by the reaction of **3** (1.5 g, 5.6 × 10^{-3} mol) and **5** (2.9 g, 7.4 × 10^{-3} mol), respectively, with sodium 4-phenylphenoxide (4.2 × 10^{-2} mol with **3**; 7.8 × 10^{-2} mol with **5**) in dioxane (60 mL). The reaction mixture was cooled with an ice bath and was allowed to warm to room temperature while stirred. The whole process required ~30 min. After the reaction, the solvent was removed and the product was chromatographed on a silica gel column. The products isolated were oils initially. Species **4** was recrystallized from hexane–methylene chloride to give white powders; mp 165–167 °C. Isolated yield was 35%. These failed to form crystals suitable for X-ray analysis. Compound **6** was recrystallized from pentane–methylene chloride to yield white crystals: mp 83–85 °C. The isolated yield was 30%.

Synthesis of $OP_4N_3(O\text{-}C_6H_4\text{-}C_6H_5\text{-}p)_9$ (7). Compound **7** was synthesized by treating the ionic short-chain species $[P_4N_3Cl_{10}]^+PCl_6^-$ (2.0 g, 2.6 × 10^{-3} mol) with sodium 4-phenylphenoxide (5.2 × 10^{-2} mol) in dioxane (75 mL). The reaction and workup procedures were identical with those used in the syntheses of **4** and **6**. Compound **7** was recrystallized from hexane–methylene chloride to give white powders. Isolated yield was 20%. However, all attempts to grow single crystals of **7** acceptable for X-ray analysis were unsuccessful.

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Supplementary Material Available: Tables of selected least-squares planes and distances of atoms from those planes and thermal parameters (18 pages); listing of observed and calculated structure factor amplitudes (96 pages). Ordering information is given on any current masthead page.

Novel Oligo(phenylenevinylenes): Models for the Charging of Extended π Chains

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Abstract: The syntheses as well as the chemical and electrochemical reduction of a series of novel oligo(phenylenevinylenes) are described. The extended π chains are built up by sequences of Wittig reactions, and the corresponding polyanions are generated by electron-transfer reactions and characterized by NMR spectroscopy and quenching experiments. The charge-storage capacity, the charge distribution, and the stereodynamic behavior of the anions are examined as a function of the chain length, the linkage of the stilbene subunits, and the presence of phenyl substituents. The reduction of the title compounds serves as a suitable model experiment for the doping of the corresponding poly(phenylenevinylenes).

1. Introduction

Poly(*p*-phenylenevinylene) (**1**) is the subject of continuing experimental and theoretical efforts, with the emphasis being on the design of battery electrodes and of electrically conducting materials.[1,2] The existence of molecular weight distributions and the insolubility of polymer **1** in organic solvents along with occurring structural inhomogeneities have severely inhibited detailed studies of the charge-storage mechanisms of **1** and of the structures of charged species derived from **1**. In the present work, we have, therefore, considered well-defined oligomeric model systems for

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