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Synthesis and Structures of (*p*-Halogenophenoxy)phosphazenes: Comparison of the Structures of Cyclic and Linear Short-Chain Species

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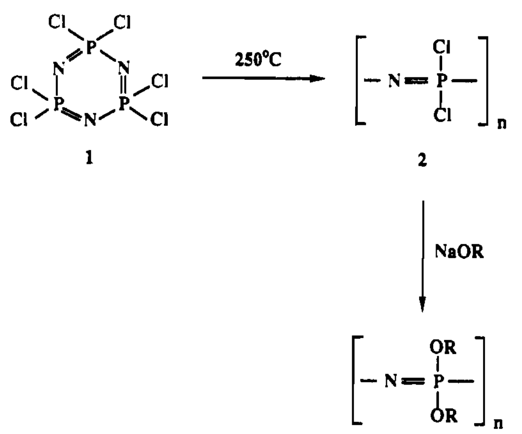
The crystal structures of $OP(OR)_2NP(OR)_3$, where OR = $O{-}C_6H_4F$-*p*, $O{-}C_6H_4Cl$-*p*, and $O{-}C_6H_4Br$-*p*, and $[NP(OR)_2]_3$, where OR = $O{-}C_6H_4F$-*p*, $O{-}C_6H_4Cl$-*p*, $O{-}C_6H_4Br$-*p* and $O{-}C_6H_4I$-*p*, were determined by X-ray crystallography. These small molecule phosphazenes are structural models for the corresponding high polymers, and their structures provide insight into the conformation and nature of bonding in the polymeric species. Crystals of $OP(O{-}C_6H_4F\text{-}p)_2NP(O{-}C_6H_4F\text{-}p)_3$ are triclinic with cell dimensions of a = 8.394(2) Å, b = 10.690(3) Å, c = 16.760(4) Å, α = 86.99(2)°, β = 84.82(2)°, γ = 69.66(2)°, space group $P\bar{1}$, Z = 2. Crystals of $OP(O{-}C_6H_4\text{-}Cl\text{-}p)_2NP(O{-}C_6H_4Cl\text{-}p)_3$ are triclinic with cell dimension of a = 10.513(6) Å, b = 12.574(3) Å, c = 13.359(5) Å, α = 91.83(3)°, β = 106.76(4)°, γ = 104.68(3)°, space group $P\bar{1}$, and Z = 2. Crystals of $OP(O{-}C_6H_4Br\text{-}p)_2NP(O{-}C_6H_4Br\text{-}p)$ are triclinic with cell dimension of a = 9.839(2) Å, b = 12.373(4) Å, c = 14.286(3) Å, α = 103.74(2)°, β = 91.76(2)°, γ = 100.89(2)°, space group $P\bar{1}$, and Z = 2. Crystals of the cyclic species are monoclinic. The unit cell dimensions are as follows: $[NP(O{-}C_6H_4F\text{-}p)_2]_3$, a = 20.860(5) Å, b = 8.085(12) Å, c = 21.813(5) Å, β = 104.62(3)°, space group $P2_1/n$, Z = 4; $[NP(O{-}C_6H_4Cl\text{-}p)_2]_3$, a = 17.746(9) Å, b = 7.623(7) Å, c = 27.856(10) Å, β = 91.76(12)°, space group $P2_1/c$, Z = 4; $[NP(O{-}C_6H_4Br\text{-}p)_2]_3$, a = 13.680(5) Å, b = 31.316(7) Å, c = 9.289(3) Å, β = 90.70(3)°, space group $P2_1/n$, Z = 4; $[NP(O{-}C_6H_4I\text{-}p)_2]_3$, a = 13.700(6) Å, b = 9.381(11) Å, c = 32.675(16) Å, β = 95.72(4)°, space group $P2_1/c$, Z = 4. The results show that the P–N bond lengths in both the short-chain and cyclic species are very similar, with an average value of 1.55 Å. Evidence for side group stacking can be detected in the crystal lattice of both the cyclic and linear oligomers, and these arrangements are analogous to those expected in polymer microcrystallites.

The thermal polymerization of hexachlorocyclotriphosphazene (**1**) yields linear high polymeric poly(dichlorophosphazene) (**2**), which can undergo nucleophilic replacement of the chlorine atoms to yield stable poly(organophosphazenes) (Scheme 1).[1] In general, the high polymers are semicrystalline materials when only a single type of substituent is present, but amorphous polymers are formed when substitution is carried out with a mixture of two or more nucleophilic reactants.[2] The effects of organic side groups on the properties of polyphosphazenes have been discussed.[3]

In order to understand the differences in the properties of different phosphazene polymers, it is necessary to examine the structural features at the molecular level and to attempt to relate the molecular structures to solid-state properties, such as materials strength, flexibility, glass transition temperature, electrical behavior, etc. A detailed analysis of the preferred conformation of the polymer chain and the influence of the side groups and bonding on chain flexibility forms an important part of this approach.

One of our approaches to determining the structure of high polymeric phosphazenes involves structural studies with small molecule linear phosphazene oligomers that may mimic the conformational behavior of the analogous high polymers. The structures of several short-chain linear phosphazenes have been reported in a previous publication.[4] In this paper, we describe the structures of three new short-chain linear phosphazenes that bear para-substituted halogenophenoxy groups, specifically the *p*-fluorophenoxy, *p*-chlorophenoxy, and *p*-bromophenoxy groups. In addition, the structures of four cyclic trimeric analogs were studied for comparison with the linear species.

Scheme 1



The main objective of this study was to determine if the *p*-halogeno groups impart a detectable structural influence that affects the conformation of the phosphazene skeleton or side group orientation. If such influences exist, it is of interest to determine if they can be related to the physical characteristics of the corresponding linear high polymers. Aryloxy side groups in high polymeric phosphazenes may form stacked arrangements, and these are related to the liquid crystalline[5] or nonlinear optical properties in related derivatives.[6]

Results and Discussion

Synthesis. The compounds discussed in this paper are species **4–6**, **9–12**, and **13–16**. The starting linear chlorophosphazene

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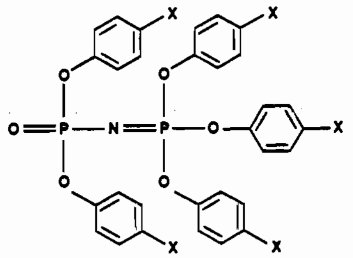
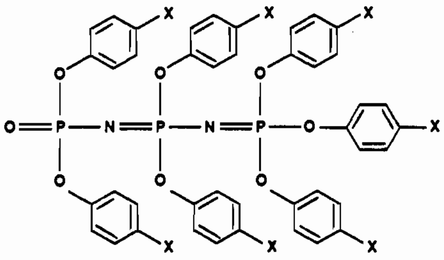
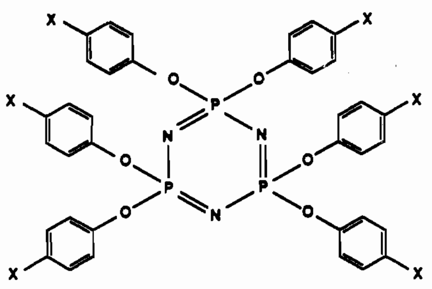


X = F (4)
Cl (5)
Br (6)
I (7)



X = F (9)
Cl (10)
Br (11)
I (12)



X = F (13)
Cl (14)
Br (15)
I (16)

dimer, $OPCl_2NPCl_3$ (**3**), was prepared by the reaction of PCl_5 and $(NH_4)_2SO_4$ in *sym*-tetrachloroethane.[8] The linear chlorophosphazene trimer $OPCl_2NPCl_2NPCl_3$ (**8**) was prepared by a block building method developed by Reisel.[7] Subsequent reactions of **3** and **8** with sodium aryloxides yielded the desired products. Crystallization of these compounds often took place only with difficulty. Species **4** was crystallized from a dichloromethane/hexane mixture at temperature below 0 °C, while **5** and **6** were recrystallized at room temperature from the same solvent. Crystals of **6** were obtained from an oil at room temperature. Compounds **9**–**12** were obtained only as oils. Compounds **13**–**16** were prepared by treatment of hexachlorocyclotriphosphazene with the appropriate sodium salts of the *p*-halogenophenols. The compounds were recrystallized from dichloromethane by slow evaporation of the solvent. All compounds studied in this paper formed clear, colorless crystals. The ^{31}P NMR chemical shifts of these compounds are shown in Table 2.

X-ray Structure Results. X-ray diffraction studies of compounds **4**–**6** and **13**–**16** were carried out in order to obtain information about molecular parameters such as bond lengths, bond angles, torsional angles, preferred conformations, and packing arrangements for the phosphazene backbone and the side groups. Data from X-ray diffraction studies of compounds **4**–**6** and **13**–**16** are shown in Table 1.

(a) Molecular Structure of $OP(O–C_6H_4F\text{-}p)_2NP(O–C_6H_4F\text{-}p)_3$ (4). Species 4 (Figure 1) contains a short-chain linear phosphazene backbone that consists of two phosphorus atoms bonded to a connecting nitrogen atom. Five *p*-fluorophenoxy groups are bonded to the phosphorus atoms through P–O–C linkages. Atom P2 also bears a monoconnected oxygen atom. The disposition of side groups allows two phenyl rings bonded to O4 and O2 to align roughly parallel to each other. The dihedral angle between these rings is 33.60 ± 0.03°. The orientation of the remaining side groups appears to be dictated by the need to maintain a maximum separation from each other for steric reasons. There are two molecules in the unit cell. The packing arrangement allows, for example, the two phenyl rings that are attached to O4 in each molecule to form a parallel orientation. The same arrangement is also obvious for other intermolecular pairs of phenyl rings. This characteristic could possibly provide for more efficient packing of molecules, yielding a tighter and stronger crystal lattice. The distance P1–N is 1.528(1) Å, and P2–N is 1.600(2) Å. The P–N–P angle is 135.39(9)°. The P–O6 distance is 1.462(1) Å, which is consistent with double bond character. The remaining P–O distances have an average value of 1.578(2) Å. These values are comparable to those found in $OP(O–C_6H_5)_2NP(O–C_6H_5)_3$.[3] Selected structural parameters are summarized in Tables 3 and 4.

(b) Molecular Structure of $OP(O–C_6H_4Cl\text{-}p)_2NP(O–C_6H_4Cl\text{-}p)_3$ (5). The structure of **5** (Figure 2) contains the same basic phosphazene skeletal unit as does **4**. Although the main structural features are very similar in the two systems, slight differences exist in side group arrangements. In **5**, the *p*-chlorophenoxy groups are disposed in a more orderly fashion. Stacking of side

Table 1. Summary of Crystal Data and Intensity Collection Parameters

	4	5	6	13	14	15	16
formula	$OP_2N(O\text{-}C_6H_4\text{-}F\text{-}p)_5$	$OP_2N(O\text{-}C_6H_4\text{-}Cl\text{-}p)_5$	$OP_2N(O\text{-}C_6H_4\text{-}Br\text{-}p)_5$	$C_{36}H_{24}N_3P_3O_6F_6$	$C_{36}H_{24}N_3P_3O_6Cl_6$	$C_{36}H_{24}N_3P_3O_6Br_6$	$C_{36}H_{24}N_3P_3O_6I_6$
fw, amu	647.44	729.71	951.99	801.54	900.25	1160.9	1448.9
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.394(2)	10.513(6)	9.839(2)	20.860(5)	17.746(9)	13.680(5)	13.700(6)
b, Å	10.690(3)	12.574(3)	12.373(4)	8.085(12)	7.624(10)	31.316(7)	9.381(11)
c, Å	16.760(4)	13.359(5)	14.286(3)	21.813(5)	27.856(10)	9.289(3)	32.675(16)
α, deg	86.99(2)	91.83(3)	103.74(2)				
β, deg	84.82(2)	106.76(4)	91.76(2)	104.62(3)	91.75(3)	90.70(3)	95.72(4)
γ, deg	69.66(2)	104.68(3)	100.89(2)				
V, Å^3	1503.9	1765.9	1739.1	3559.6	3766.8	3979.3	4178.5
Z	2	2	2	4	4	4	4
d(calcd), g/cm^3	1.532	1.491	1.912	1.495	1.587	1.948	2.303
μ, cm^{-1}	2.27	5.87	6.16	21.4	59.2	89.6	45.7
T, K	173	293	293	293	293	293	293
λ, Å	0.710 73	0.710 73	0.710 73	1.5418	1.5418	1.5418	0.710 73
R, R_w[a]	0.0336, 0.0479	0.0518, 0.0813	0.0446, 0.0647	0.0568, 0.0708	0.1008, 0.1334	0.0944, 0.1290	0.1210, 0.1390

[a] $R_w = (\sum\Delta^2/\sum wF_o^2)^{1/2}$.

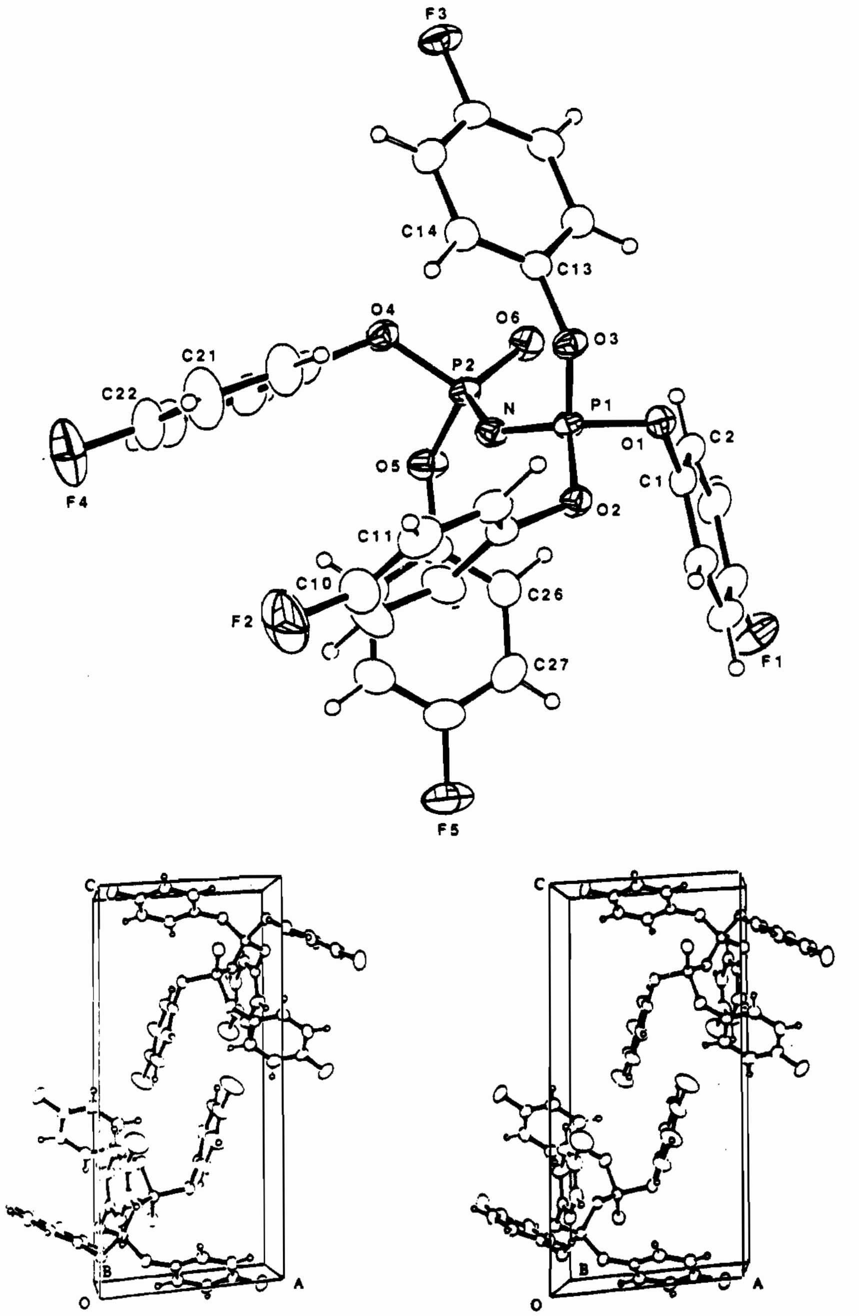


Figure 1. (a) Top: ORTEP diagram of $OP(O{-}C_6H_4F{-}p)_2NP(O{-}C_6H_4F{-}p)_3$ (**4**). (b) Bottom: Packing diagram of $OP(O{-}C_6H_4F{-}p)_2NP(O{-}C_6H_4F{-}p)_3$ (**4**).

groups can be discerned for a pair of phenyl rings that are bonded to O1 and O4. The dihedral angles between these rings is 29.74 ± 0.47°. The planes formed by these groups are also roughly parallel to the phenyl ring bonded to O2. The angle between the ring containing C1 and the ring containing C7 is only a narrow 13.48 ± 0.90°. The angle between the ring containing C23 and the ring containing C7 is 31.42 ± 0.53°. The crystal structure of **5** contains two discrete molecules in the unit cell. The packing of the molecules allows intermolecular coplanarity of some side groups. In particular, in the *a* direction of the cell, the phenyl rings bonded to O1 and O4 of a molecule are parallel to the phenyl ring bonded to O1 of the adjacent molecule, forming a continuous three-phenyl-ring coplanar arrangement. The distance P1–N is 1.515(2) Å, and P2–N is 1.581(2) Å. The P–N–P angle is 149.5(2)°. The unusually large P–N–P angle is presumably due to crystal packing forces, rather than an intramolecular influence of the side groups. The P–O6 distance is 1.450(2) Å, and the remaining P–O distances averaged to 1.578(4) Å. Selected structural parameters are summarized in Tables 5 and 6.

(c) Molecular Structure of $OP(O{-}C_6H_4Br{-}p)_2NP(O{-}C_6H_4{-}Br{-}p)_3$ (6). The structure of **6** (Figure 3) contains the same basic linear phosphazene skeletal unit as in **4** and **5**. The general structural features are similar to the former species. However, no obvious stacking of side groups can be detected in **6**. The unit cell contains two molecules. Each molecule is related to its neighbor along the *a* direction by a center of inversion. Molecules

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Table 2. ^{31}P NMR Assignments[a]

compd	no.	chem shifts[b] ppm			coupling const, Hz	
$OP(O-C_6H_4F-p)_2NP(O-C_6H_4F-p)_3$	4	$A = -22.6$	$B = -14.0$		$J_{AB} = 75.2$	
$OP(O-C_6H_4Cl-p)_2NP(O-C_6H_4Cl-p)_3$	5	$A = -22.4$	$B = -15.9$		$J_{AB} = 75.0$	
$OP(O-C_6H_4Br-p)_2NP(O-C_6H_4Br-p)_3$	6	$A = -22.6$	$B = -15.8$		$J_{AB} = 76.2$	
$OP(O-C_6H_4I-p)_2NP(O-C_6H_4I-p)_3$	7	$A = -22.0$	$B = -16.0$		$J_{AB} = 75.0$	
$OP(O-C_6H_4F-p)_2NP(O-C_6H_4F-p)_2NP(O-C_6H_4F-p)_3$	9	$A = -23.4$	$B = -17.7$	$C = -13.6$	$J_{AB} = 72.3$	$J_{BC} = 68.4$
$OP(O-C_6H_4Cl-p)_2NP(O-C_6H_4Cl-p)_2NP(O-C_6H_4Cl-p)_3$	10	$A = -23.7$	$B = -18.4$	$C = -13.4$	$J_{AB} = 72.7$ $J_{AC} = 4.9$	$J_{BC} = 67.7$
$OP(O-C_6H_4Br-p)_2NP(O-C_6H_4Br-p)_2NP(O-C_6H_4Br-p)_3$	11	$A = -24.2$	$B = -19.0$	$C = -14.5$	$J_{AB} = 71.3$ $J_{AC} = 4.9$	$J_{BC} = 67.4$
$OP(O-C_6H_4I-p)_2NP(O-C_6H_4I-p)_2NP(O-C_6H_4I-p)_3$	12	$A = -24.3$	$B = -19.3$	$C = -14.7$	$J_{AB} = 71.3$	$J_{BC} = 64.5$
$[NP(O-C_6H_4F-p)_2]_3$	13	$A = +9.10$				
$[NP(O-C_6H_4Cl-p)_2]_3$	14	$A = +8.72$				
$[NP(O-C_6H_4Br-p)_2]_3$	15	$A = +8.00$				
$[NP(O-C_6H_4I-p)_2]_3$	16	$A = +8.62$				
$[NP(O-C_6H_4Br-p)_2]_n$	17	$A = -18.0$[c]				

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

Table 3. Bond Lengths (Å) and Bond Angles (deg) for $OP(O-C_6H_4F-p)_2NP(O-C_6H_4F-p)_3$ (4)

P1–O1	1.569(1)	P2–O4	1.596(1)	P2–N	1.600(2)	O3–C13	1.413(2)
P1–O2	1.568(1)	P2–O5	1.588(1)	O1–C1	1.422(2)	O4–C19	1.404(2)
P1–O3	1.569(1)	P2–O6	1.462(1)	O2–C7	1.415(2)	O5–C25	1.392(2)
P1–N	1.528(1)						
O1–P1–O2	102.81(6)	O3–P1–N	116.17(6)	O5–P2–N	106.07(7)	P1–O2–C7	121.6(1)
O1–P1–O3	102.19(6)	O4–P2–O5	100.90(6)	O6–P2–N	119.39(7)	P1–O3–C13	121.1(1)
O1–P1–N	118.15(7)	O4–P2–O6	108.20(6)	P1–N–P2	135.39(9)	P2–O4–C19	122.7(1)
O2–P1–O3	102.84(6)	O4–P2–N	108.40(6)	P1–O1–C1	121.1(1)	P2–O5–C25	126.4(1)
O2–P1–N	112.67(7)	O5–P2–O6	112.27(7)				

Table 4. Fractional Atomic Positional Parameters for $OP(O-C_6H_4F-p)_2NP(O-C_6H_4F-p)_3$ (4)

	x	y	z	$U(1,1)$[a] Å^2		x	y	z	$U(1,1)$[a] Å^2
P1	0.13113(4)	0.27222(4)	0.13871(2)	0.0204(2)	C9	0.0873(3)	−0.0085(2)	0.3503(1)	0.072(1)
P2	0.31077(5)	0.40474(4)	0.22331(2)	0.0217(2)	C10	0.1401(2)	−0.1338(2)	0.3185(1)	0.0494(9)
F1	−0.4628(1)	0.8359(1)	0.22252(7)	0.0335(5)	C11	0.1492(2)	−0.1543(2)	0.2381(1)	0.0325(8)
F2	0.4863(2)	−0.2416(1)	0.36945(9)	0.1001(9)	C12	0.1067(2)	−0.0433(2)	0.1872(1)	0.0268(7)
F3	0.8949(1)	0.1931(1)	−0.01294(6)	0.0253(4)	C13	0.4190(2)	0.1880(2)	0.0520(1)	0.0232(6)
F4	0.7140(2)	−0.0381(1)	0.48603(8)	0.1043(9)	C14	0.5574(2)	0.0784(2)	0.0705(1)	0.0319(7)
F5	−0.3173(1)	0.4541(1)	0.49959(7)	0.0399(5)	C15	0.7914(2)	0.0802(2)	0.0484(1)	0.0256(7)
O1	0.0183(1)	0.3920(1)	0.08753(6)	0.0258(5)	C16	0.7349(2)	0.1926(2)	0.0094(1)	0.0247(6)
O2	0.0071(1)	0.1943(1)	0.16555(7)	0.0232(4)	C17	0.5980(2)	0.3018(2)	−0.0103(1)	0.0338(7)
O3	0.2553(1)	0.1809(1)	0.07268(7)	0.0232(4)	C18	0.4357(2)	0.2995(2)	0.0118(1)	0.0287(7)
O4	0.5045(1)	0.3198(1)	0.23757(7)	0.0226(4)	C19	0.5513(2)	0.2294(2)	0.3024(1)	0.0237(6)
O5	0.2424(1)	0.4631(1)	0.30991(7)	0.0314(5)	C20	0.5711(3)	0.0976(2)	0.2933(1)	0.062(1)
O6	0.3090(1)	0.5094(1)	0.16320(7)	0.0303(5)	C21	0.6263(3)	0.0070(2)	0.3556(1)	0.087(1)
N	0.2141(2)	0.3036(1)	0.20894(8)	0.0240(5)	C22	0.6587(3)	0.0561(2)	0.4249(1)	0.056(1)
C1	−0.1061(2)	0.5050(2)	0.1248(1)	0.0230(6)	C23	0.6379(2)	0.1828(2)	0.4356(1)	0.0480(9)
C2	−0.0732(2)	0.6232(2)	0.1207(1)	0.0230(6)	C24	0.5831(2)	0.2733(2)	0.3726(1)	0.0353(7)
C3	−0.1947(2)	0.7354(2)	0.1540(1)	0.0302(7)	C25	0.0975(2)	0.4563(2)	0.3546(1)	0.0281(7)
C4	−0.3432(2)	0.7245(2)	0.1896(1)	0.0257(7)	C26	−0.0575(2)	0.5538(2)	0.3439(1)	0.0358(8)
C5	−0.3775(2)	0.6075(2)	0.1932(1)	0.0227(6)	C27	−0.1985(2)	0.5523(2)	0.3928(1)	0.0272(8)
C6	−0.2566(2)	0.4949(2)	0.1597(1)	0.0270(6)	C28	−0.1797(2)	0.4537(2)	0.4506(1)	0.0332(7)
C7	0.0550(2)	0.0823(1)	0.2185(1)	0.0206(6)	C29	0.0261(2)	0.3551(2)	0.4617(1)	0.0453(8)
C8	0.0423(2)	0.1025(2)	0.2994(1)	0.0502(8)	C30	0.1150(2)	0.3563(2)	0.4123(1)	0.0321(7)

[a] The form of the anisotropic thermal parameter is $U = \exp[-2PI^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$, where a, b, and c are reciprocal lattice constants.

Table 5. Bond Lengths (Å) and Bond Angles (deg) for $OP(O-C_6H_4Cl-p)_2NP(O-C_6H_4Cl-p)_3$ (5)

P1–O1	1.568(2)	P2–O4	1.594(2)	P2–N	1.581(2)	O3–C13	1.408(3)
P1–O2	1.567(2)	P2–O5	1.588(2)	O1–C1	1.384(3)	O4–C19	1.398(3)
P1–O3	1.573(2)	P2–O6	1.450(2)	O2–C7	1.413(3)	O5–C25	1.394(3)
P1–N	1.515(2)						
O1–P1–O2	102.4(1)	O3–P1–N	112.0(1)	O5–P2–N	107.4(1)	P1–O3–C13	119.4(1)
O1–P1–O3	102.2(2)	O4–P2–O5	99.4(1)	O6–P2–N	118.7(1)	P2–O4–C19	120.6(1)
O1–P1–N	117.7(1)	O4–P2–O6	114.9(1)	P1–O1–C1	126.1(2)	P2–O5–C25	123.3(1)
O2–P1–O3	102.8(1)	O4–P2–N	104.5(1)	P1–O2–C7	119.9(2)	P1–N–P2	149.5(2)
O2–P1–N	117.5(1)	O5–P2–O6	109.9(1)				

Table 6. Fractional Atomic Positional Parameters for OP(O–C_6H_4Cl-*p*)$_2$NP(O–C_6H_4Cl-*p*)$_3$ (**5**)

	x	*y*	*z*	*U*(1,1),[a] Å^2		*x*	*y*	*z*	*U*(1,1),[a] Å^2
Cl1	0.4684(2)	0.8715(1)	0.2633(2)	0.204(2)	C9	−0.3743(3)	0.1689(3)	0.2559(3)	0.052(1)
Cl2	−0.4400(1)	0.1464(1)	0.4361(1)	0.0777(4)	C10	0.3516(3)	0.2171(3)	0.3558(3)	0.050(1)
Cl3	0.3376(1)	0.0216(1)	−0.0034(1)	0.1020(5)	C11	0.2593(3)	0.3190(3)	0.3927(3)	0.066(1)
Cl4	0.6723(1)	0.5808(1)	0.1295(1)	0.1046(5)	C12	0.1853(3)	0.3734(2)	0.3306(3)	0.054(1)
Cl5	−0.0292(1)	0.1925(1)	0.3309(1)	0.1622(8)	C13	0.0407(3)	0.1929(2)	0.0598(2)	0.054(1)
P1	0.00330(7)	0.35360(6)	0.16191(5)	0.0537(3)	C14	0.0888(3)	0.2172(3)	−0.0246(2)	0.090(2)
P2	0.19198(7)	0.37955(6)	0.38177(5)	0.0575(3)	C15	0.1797(4)	0.1630(3)	−0.0443(3)	0.098(2)
O1	0.0602(2)	0.4457(2)	0.0972(2)	0.086(1)	C16	0.2203(3)	0.0889(3)	0.0209(3)	0.066(1)
O2	−0.1324(2)	0.3802(2)	0.1672(2)	0.0642(9)	C17	0.1721(3)	0.0636(3)	0.1037(3)	0.076(2)
O3	−0.0527(2)	0.2475(2)	0.0794(1)	0.0564(9)	C18	0.0805(3)	0.1164(2)	0.1234(2)	0.067(1)
O4	0.3407(2)	0.3652(2)	0.3893(1)	0.0518(9)	C19	0.4153(3)	0.4196(2)	0.3257(2)	0.044(1)
O5	0.1461(2)	0.2871(2)	0.4523(1)	0.074(1)	C20	0.4975(3)	0.5256(2)	0.3567(2)	0.064(1)
O6	0.1925(3)	0.4865(2)	0.4259(2)	0.113(2)	C21	0.5778(3)	0.5754(2)	0.2965(2)	0.066(2)
N	0.1023(2)	0.3365(2)	0.2637(2)	0.052(1)	C22	0.5734(3)	0.5183(2)	0.2062(2)	0.060(1)
C1	0.1542(3)	0.5475(2)	0.1385(2)	0.069(1)	C23	0.4885(3)	0.4116(2)	0.1740(2)	0.066(1)
C2	0.2525(3)	0.5850(3)	0.0900(2)	0.078(2)	C24	0.4107(3)	0.3622(2)	0.2345(2)	0.053(1)
C3	0.3465(4)	0.6854(3)	0.1267(3)	0.074(2)	C25	0.1078(3)	0.1740(2)	0.4195(2)	0.058(1)
C4	0.3416(5)	0.7469(3)	0.2120(3)	0.114(3)	C26	0.2035(3)	0.1184(3)	0.4277(3)	0.051(1)
C5	0.2468(5)	0.7104(3)	0.2602(3)	0.139(3)	C27	0.1624(3)	0.0054(3)	0.3991(3)	0.085(2)
C6	0.1484(4)	0.6097(3)	0.2224(3)	0.105(2)	C28	0.0242(3)	−0.0497(3)	0.3628(2)	0.085(2)
C7	−0.2059(3)	0.3235(2)	0.2323(2)	0.048(1)	C29	−0.0708(3)	0.0072(3)	0.3547(3)	0.056(1)
C8	−0.3011(3)	0.2226(3)	0.1930(3)	0.060(1)	C30	−0.0312(3)	0.1195(2)	0.3825(2)	0.055(1)

[a] The form of the anisotropic thermal parameter is $U = \exp[-2PI^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$, where *a*, *b*, and *c* are reciprocal lattice constants.

Table 7. Bond Lengths (Å) and Bond Angles (deg) for OP(O–C_6H_4Br-*p*)$_2$NP(O–C_6H_4Br-*p*)$_3$ (**6**)

P1–O1	1.537(6)	P2–O4	1.594(6)	P2–N	1.574(6)	O3–C31	1.38(1)
P1–O2	1.544(5)	P2–O5	1.589(5)	O1–C11	1.41(1)	O4–C41	1.38(1)
P1–O3	1.555(5)	P2–O6	1.452(6)	O2–C21	1.40(1)	O5–C51	1.40(1)
P1–N	1.526(7)						
O1–P1–O2	96.8(4)	O3–P1–N	110.0(3)	O5–P2–N	105.8(3)	P1–O3–C31	129.8(5)
O1–P1–O3	108.1(4)	O4–P2–O5	99.4(3)	O6–P2–N	119.0(3)	P2–O4–C41	121.9(5)
O1–P1–N	118.5(4)	O4–P2–O6	114.5(3)	P1–O1–C11	124.2(5)	P2–O5–C51	121.6(5)
O2–P1–O3	108.7(3)	O4–P2–N	103.3(3)	P1–O2–C21	129.9(4)	P1–N–P2	131.5(5)
O2–P1–N	113.7(4)	O5–P2–O6	112.8(3)				

Table 8. Fractional Atomic Positional Parameters for OP(O–C_6H_4Br-*p*)$_2$NP(O–C_6H_4Br-*p*)$_3$ (**6**)

	x	*y*	*z*	*U*(1,1),[a] Å^2		*x*	*y*	*z*	*U*(1,1),[a] Å^2
Br1	0.5510(2)	0.0794(2)	0.2733(1)	0.122(1)	C23	1.1253(9)	−0.0190(6)	−0.4261(7)	0.090(6)
Br2	1.3457(1)	0.07848(9)	−0.52499(8)	0.0695(5)	C24	1.2239(8)	0.0774(7)	−0.4236(7)	0.056(4)
Br3	0.6155(1)	0.3846(1)	−0.4794(1)	0.1022(7)	C25	1.2344(9)	0.1739(7)	−0.3504(7)	0.084(6)
Br4	1.0750(1)	0.3780(1)	0.5563(1)	0.163(1)	C26	1.1432(9)	0.1723(7)	−0.2799(7)	0.094(6)
Br5	1.4407(1)	0.5478(1)	−0.2663(1)	0.1025(7)	C31	0.8304(8)	0.2894(7)	−0.2256(6)	0.073(5)
P1	0.9212(2)	0.1574(2)	−0.1260(2)	0.074(1)	C32	0.8497(8)	0.4013(6)	−0.2309(6)	0.066(5)
P2	1.0749(2)	0.2726(2)	0.0516(2)	0.059(1)	C33	0.7841(9)	0.4302(7)	−0.3057(6)	0.076(5)
O1	0.7759(6)	0.0958(6)	−0.1103(4)	0.077(4)	C34	0.6983(8)	0.3475(6)	−0.3731(6)	0.072(5)
O2	0.8413(6)	0.0717(4)	−0.2199(4)	0.089(4)	C35	0.6781(10)	0.2368(8)	−0.3687(7)	0.100(6)
O3	0.9070(6)	0.2708(4)	−0.1506(4)	0.124(4)	C36	0.7416(10)	0.2078(8)	−0.2920(8)	0.136(8)
O4	1.0904(6)	0.2005(4)	0.1287(4)	0.092(3)	C41	1.0866(8)	0.2451(6)	0.2262(5)	0.063(4)
O5	1.2334(5)	0.3300(5)	0.0506(4)	0.056(3)	C42	0.9669(8)	0.2719(7)	0.2650(6)	0.056(4)
O6	0.9870(5)	0.3553(4)	0.0783(4)	0.074(3)	C43	0.9649(8)	0.3121(7)	0.3628(6)	0.063(5)
N	1.0377(6)	0.1793(5)	−0.0467(5)	0.068(4)	C44	1.0810(9)	0.3247(7)	0.4219(6)	0.088(5)
C11	0.7283(8)	0.0918(7)	−0.0187(6)	0.054(4)	C45	1.2012(9)	0.3002(7)	0.3850(6)	0.074(5)
C12	0.7641(9)	0.0182(7)	0.0292(8)	0.083(5)	C46	1.2037(8)	0.2591(6)	0.2875(6)	0.052(4)
C13	0.7093(10)	0.0132(8)	0.1159(8)	0.098(6)	C51	1.2792(8)	0.3849(7)	0.0209(6)	0.046(4)
C14	0.6215(9)	0.0837(9)	0.1532(7)	0.058(5)	C52	1.2144(7)	0.4628(7)	−0.0463(6)	0.050(4)
C15	0.5870(9)	0.1561(8)	0.1011(8)	0.075(5)	C53	1.2636(8)	0.5133(7)	−0.1176(7)	0.059(5)
C16	0.6420(9)	0.1626(8)	0.0175(7)	0.083(5)	C54	1.3765(8)	0.4819(7)	−0.1652(7)	0.049(4)
C21	1.0440(8)	0.0797(7)	−0.2849(6)	0.068(5)	C55	1.4403(8)	0.4042(8)	−0.1389(8)	0.046(4)
C22	1.0343(8)	−0.0181(6)	−0.3560(6)	0.079(5)	C56	1.3921(9)	0.3539(7)	−0.0644(8)	0.059(5)

[a] The form of the anisotropic thermal parameter is $U = \exp[-2PI^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$ where *a*, *b*, and *c* are reciprocal lattice constants.

along the *c* direction have identical molecular orientations. No unusual molecular interaction could be detected. The P1–N bond distance is 1.526(7) Å, and P2–N is 1.574(6) Å. The P–N–P bond angle is 131.5(5)°, and the P–O6 distance is 1.452(6) Å. The remaining P–O distances have a mean value of 1.564(12) Å. Selected structural parameters of this compound are summarized in Tables 7 and 8.

(d) Molecular Structure of [NP(O–C_6H_4F-*p*)$_2$]$_3$ (13). Species **13** contains a cyclic trimeric phosphazene ring with two *p*-fluorophenoxy groups bonded through P–O–C linkages to each phosphorus atom (Figure 4). The aryloxy units are disposed so that they are approximately at a right angle to the plane of the phosphazene ring. In this molecule, intramolecular side group stacking is present. The PNP angles are 122.5(2), 121.3(2), and 122.3(2)°, and the variation in NPN angles is as follows: 117.2(1), 117.2(1), and 117.7(1)°. The P–N bond lengths averaged to 1.578(7) Å, and the P–O bond lengths averaged 1.581(5) Å. However, the bond lengths within the molecule varied by as much as 0.03 Å. Selected structural parameters are listed in Tables 9 and 10.

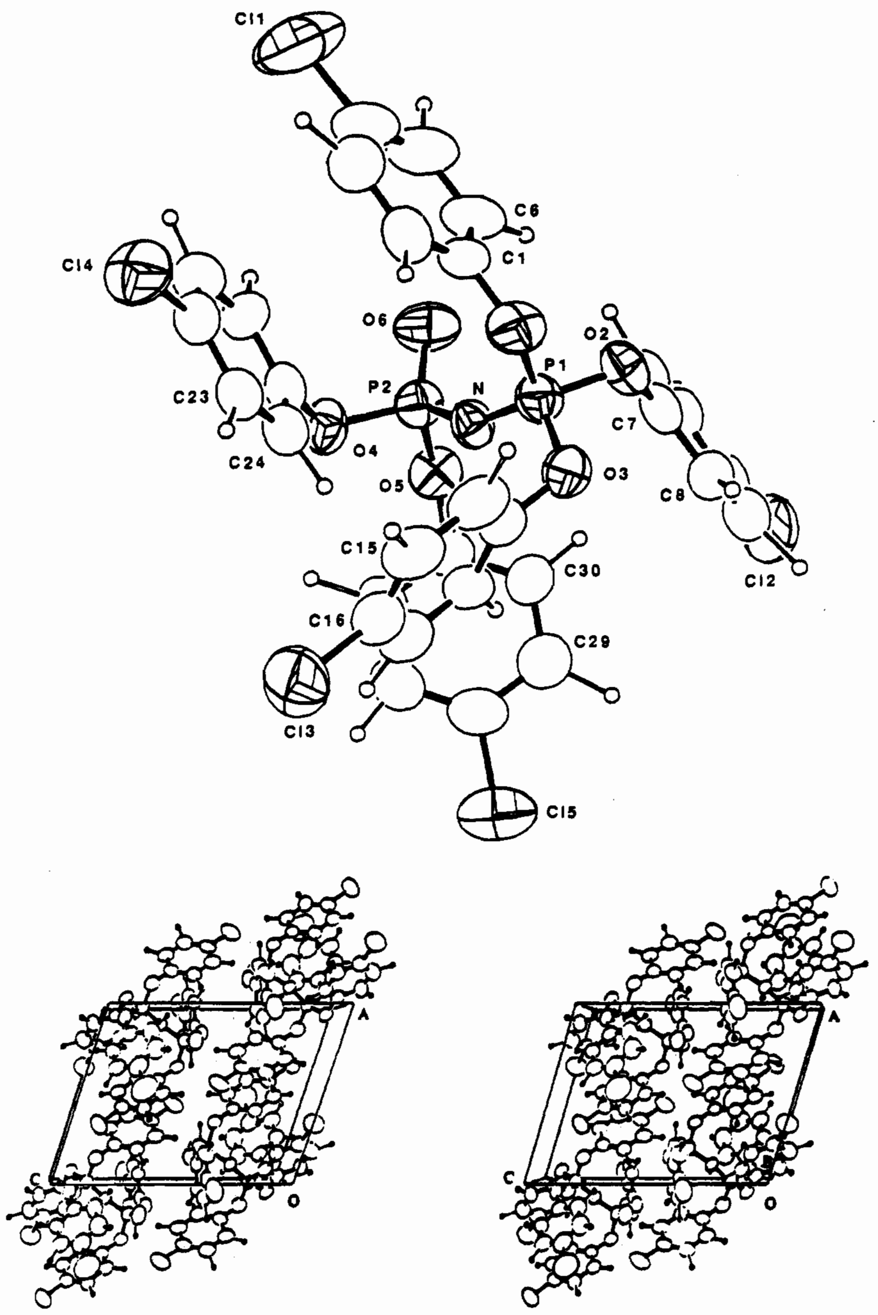

Figure 2. (a) Top: ORTEP diagram of $OP(O-C_6H_4Cl\text{-}p)_2NP(O-C_6H_4Cl\text{-}p)_3$ (**5**). (b) Bottom: Packing diagram of $OP(O-C_6H_4Cl\text{-}p)_2NP(O-C_6H_4Cl\text{-}p)_3$ (**5**).

Table 9. Bond Lengths (Å) and Bond Angles (deg) for $N_3P_3(O-C_6H_4\text{-}F\text{-}p)_6$ (**13**)

P1–O1	1.594(2)	P2–N1	1.574(3)	F1–C4	1.371(5)	O1–C1	1.397(4)
P1–O2	1.577(2)	P2–N2	1.586(3)	F2–C10	1.345(5)	O2–C7	1.397(4)
P1–N1	1.569(3)	P3–O5	1.581(3)	F3–C16	1.361(5)	O3–C13	1.407(4)
P1–N3	1.594(2)	P3–O6	1.582(2)	F4–C22	1.376(2)	O4–C19	1.392(4)
P2–O3	1.581(2)	P3–N2	1.581(3)	F5–C28	1.336(5)	O5–C25	1.396(5)
P2–O4	1.573(2)	P3–N3	1.563(3)	F6–C34	1.348(5)	O6–C31	1.384(4)
O1–P1–O2	98.9(1)	O3–P2–N1	110.8(1)	O5–P3–N3	109.8(1)	P1–O1–C1	119.7(2)
O1–P1–N1	110.4(1)	O3–P2–N2	109.6(1)	O6–P3–N2	110.8(2)	P1–O2–C7	122.9(2)
O1–P1–N3	110.3(1)	O4–P2–N1	106.1(1)	O6–P3–N3	110.2(2)	P2–O3–C13	122.9(2)
O2–P1–N1	106.7(1)	O4–P2–N2	112.5(1)	N2–P3–N3	117.7(1)	P2–O4–C19	128.8(2)
O2–P1–N3	111.8(1)	N1–P2–N2	117.2(1)	P1–N1–P2	122.5(2)	P3–O5–C25	124.2(2)
N1–P1–N3	117.2(1)	O5–P3–O6	94.7(2)	P2–N2–P3	121.3(2)	P3–O6–C31	124.1(2)
O3–P2–O4	99.2(1)	O5–P3–N2	111.2(1)	P1–N3–P3	122.3(2)		

(e) Molecular Structure of $[NP(O-C_6H_4Cl\text{-}p)_2]_3$ (14). The structure found for **14** (Figure 5) is similar to the one reported earlier by Pappalardo et al.[14] The phosphazene ring is slightly puckered. The disposition of the side groups is such that the planes of the phenoxy groups are roughly perpendicular to the phosphazene ring. The unit cell of **14** contains four molecules

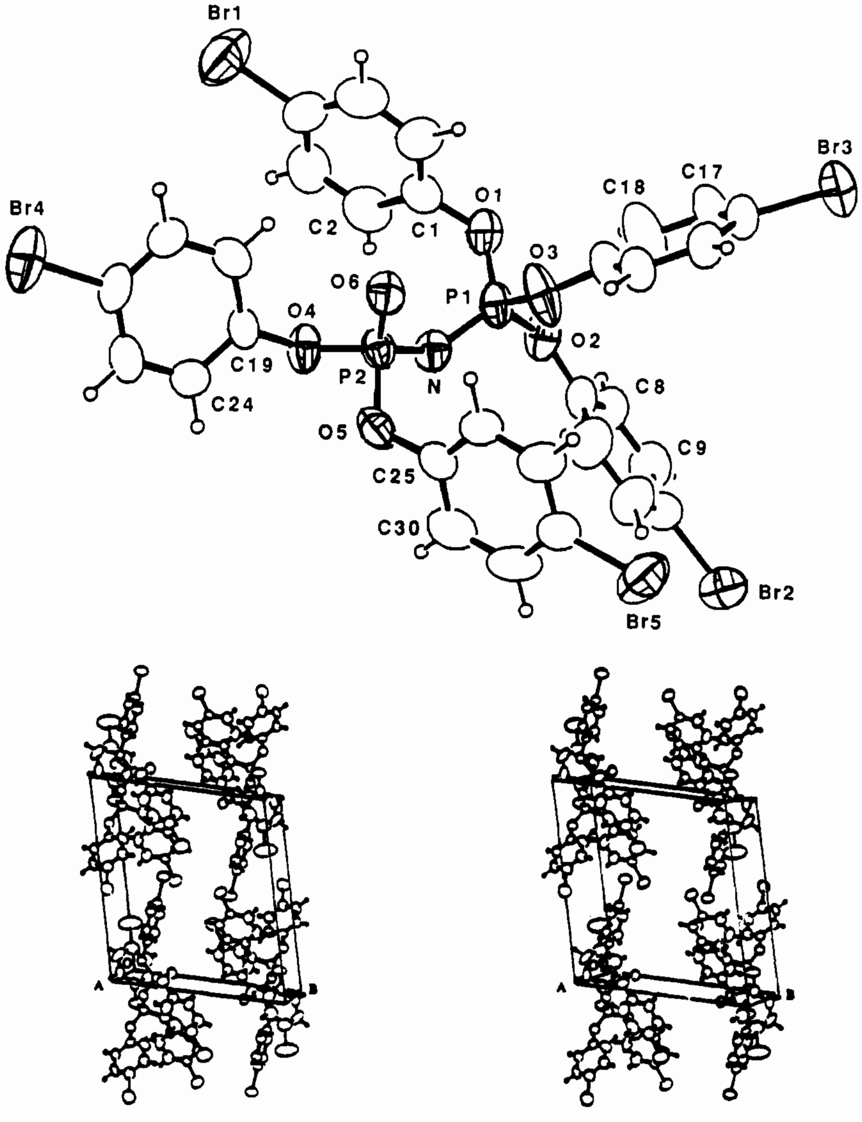

Figure 3. (a) Top: ORTEP diagram of OP(O–C_6H_4Br-*p*)$_2$NP(O–C_6H_4Br-*p*)$_3$ (6). (b) Bottom: Packing diagram of OP(O–C_6H_4Br-*p*)$_2$NP(O–C_6H_4Br-*p*)$_3$ (6).

arranged in a staggered arrangement. The longest axes of the molecules are pointed in the same direction. No obvious intra- or intermolecular stacking of side groups could be detected. The mean P–N–P angle is 122.3(5)°, and the N–P–N angle is 117.6(5)°. The P–N bond distances are about equal with an average of 1.572(12) Å. The P–O bond lengths averaged to 1.578(11) Å. The structural parameters are summarized in Tables 11 and 12.

(f) Molecular Structure of [NP(O–C_6H_4Br-*p*)$_2$]$_3$ (15). The structure of **15** is shown in Figure 6. The phosphazene ring is essentially planar. As in **13** and **14**, the aryloxy units are roughly perpendicular to the phosphazene ring. In addition, the phenyl rings bonded to O2 and O5 form a coplanar, parallel arrangement. The angle between these rings is only 19.89 ± 0.64°. The unit-cell contains four molecules arranged with the longest axis of each molecule parallel to the *b* direction of the cell. The molecule is related to its neighbor in the *b* direction by a 3-fold rotation about the molecular axis. The P–N bond lengths do not differ significantly. The mean P–N bond length value is 1.571(19) Å. The bond angles at phosphorus and nitrogen are comparable to those found for **13** and **14**. The average P–N–P and N–P–N angles are 121.7(8) and 116.6(7)°, respectively. The average P–O bond length was 1.584(5) Å. Selected structural parameters are listed in Tables 13 and 14.

(g) Molecular Structure of [NP(O–C_6H_4I-*p*)$_2$]$_3$ (16). The phosphazene ring of **16** (Figure 7) is planar. The side groups are disposed so that the planes of all the phenoxy groups are almost perpendicular to the plane formed by the phosphazene ring. Intramolecular coplanarity is obvious between the phenyl rings attached to O4 and O7. The angle between these rings is a narrow 13.68 ± 0.59°. The unit cell of **16** contains four molecules arranged in a slightly staggered manner. The overall packing arrangement is very similar to that for **15**. The longest axes of all molecules are pointed in the same direction. Intermolecular coplanarity of side groups can also be detected. The average P–N bond length is 1.57(5) Å, which is identical to that in **13**–**15**. The mean P–N–P and N–P–N angles are 121.0(2) and 118.0(2)°, respectively. These values are consistent with those of compounds **13**–**15**. The structural parameters are listed in Tables 15 and 16.

Relationships between the Structures of the Cyclic and Short-Chain Linear Phosphazenes. The main structural features of all three short-chain compounds are similar to each other. This indicates that the conformation of the P–N backbone and the orientations of the side groups are not influenced by the halogeno substituent in the para position of the phenoxy moiety. The P–N bond distances are unequal, but similar. The difference in the P–N bond distances in the same molecule ranges from 0.048(9) to 0.072(2) Å. The slight inequality in the bond distances may be influenced by strong P═O bonding. The average bond length

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(14) Bandoli, G.; Casellato, U.; Gleria, M.; Grassi, A.; Montoneri, E.; Pappalardo, G. C. *J. Chem. Soc., Dalton Trans.* **1989**, 757.

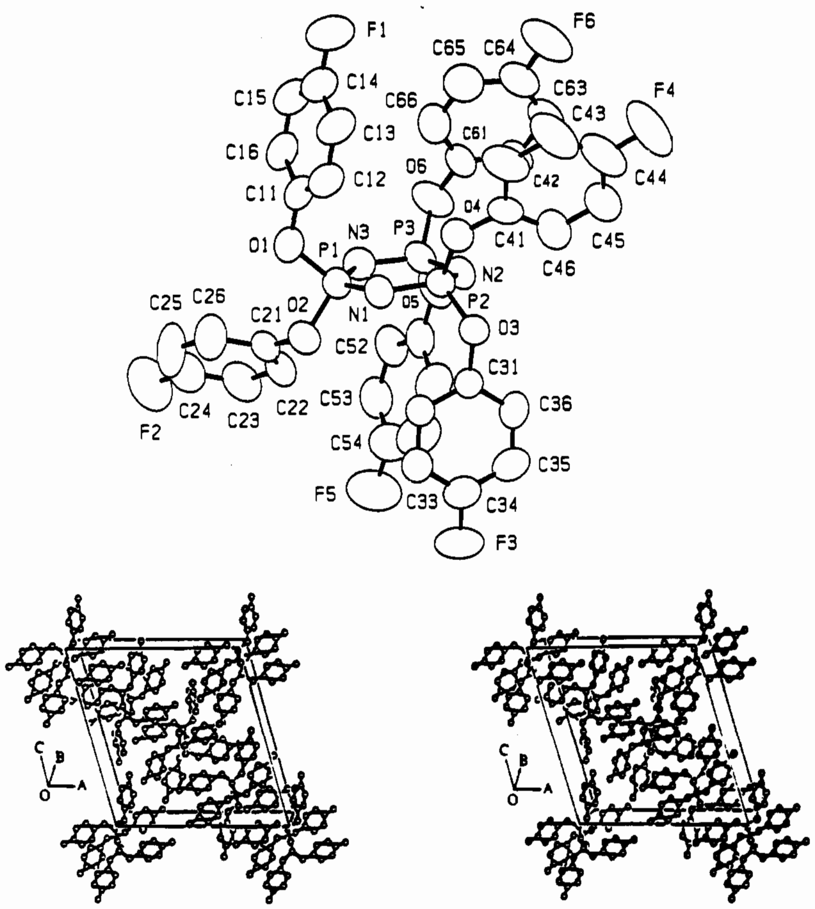

Figure 4. (a) Top: ORTEP diagram of $[NP(O{-}C_6H_4F\text{-}p)_2]_3$ (**13**). (b) Bottom: Packing diagram of $[NP(O{-}C_6H_4F\text{-}p)_2]_3$ (**13**).

Table 10. Fractional Atomic Positional Parameters (×10⁴) and Isotropic Temperature Factors U_{eq} (×10³ Å[a]) for $[NP(O\text{-}C_6H_4\text{-}F\text{-}P)_2]_3$ (**13**)

	x	*y*	*z*	U_{eq}[a]		*x*	*y*	*z*	U_{eq}[a]
P1	8618(1)	2086(1)	535(1)	55(1)	C24	7314(3)	250(7)	−1717(2)	96(3)
P2	8723(1)	2196(1)	1819(1)	52(1)	C25	7635(4)	1723(9)	−1664(2)	133(5)
P3	8885(1)	−771(1)	1251(1)	56(1)	C26	7853(3)	2425(6)	−1072(2)	102(3)
N1	8600(1)	3059(3)	1153(1)	60(2)	C31	7509(1)	2493(3)	1945(1)	53(2)
N2	8772(1)	238(3)	1836(1)	55(1)	C32	7165(2)	3206(5)	1383(2)	71(2)
N3	8794(1)	166(3)	608(1)	61(2)	C33	6496(2)	2936(6)	1178(2)	87(3)
O1	9089(1)	3001(3)	170(1)	70(1)	C34	6189(2)	2019(6)	1543(2)	84(3)
O2	7932(1)	2400(3)	44(1)	66(1)	C35	6519(2)	1363(5)	2114(2)	87(2)
O3	8193(1)	2778(3)	2179(1)	60(1)	C36	7193(2)	1596(5)	2309(2)	76(2)
O4	9356(1)	3045(3)	2252(1)	68(1)	C41	9691(2)	2666(4)	2872(2)	64(2)
O5	8463(1)	−2417(3)	1144(1)	73(1)	C42	10281(2)	3414(7)	3080(3)	95(3)
O6	9578(1)	−1689(4)	1430(1)	85(2)	C43	10651(3)	3163(9)	3698(4)	129(5)
F1	11737(1)	3646(4)	1279(2)	109(2)	C44	10406(3)	2150(8)	4067(3)	104(4)
F2	7110(2)	−423(6)	−2298(1)	155(3)	C45	9836(3)	1331(8)	3874(2)	110(4)
F3	5524(1)	1761(5)	1346(2)	123(2)	C46	9458(2)	1599(7)	3257(2)	92(3)
F4	10774(2)	1861(6)	4676(2)	156(3)	C51	7796(2)	−2500(4)	814(2)	65(2)
F5	5891(2)	−3004(5)	−182(2)	143(3)	C52	7644(2)	−3560(4)	313(2)	72(2)
F6	11667(2)	−200(6)	3390(2)	143(3)	C53	6992(2)	−3757(5)	−26(2)	81(2)
C11	9763(2)	3173(4)	460(2)	67(2)	C54	6522(2)	−2864(6)	147(3)	95(3)
C12	9970(2)	4298(4)	946(2)	74(2)	C55	6667(3)	−1765(7)	645(3)	109(3)
C13	10643(2)	4442(5)	1220(2)	88(3)	C56	7314(2)	−1604(6)	991(2)	94(3)
C14	11076(2)	3514(5)	985(2)	87(2)	C61	10101(2)	−1242(4)	1932(2)	67(2)
C15	10873(2)	2427(5)	502(2)	85(3)	C62	10158(2)	−1936(6)	2512(2)	89(3)
C16	10202(2)	2264(5)	226(2)	75(2)	C63	10681(2)	−1588(8)	3017(2)	100(3)
C21	7754(2)	1643(4)	−551(1)	59(2)	C64	11141(2)	−540(7)	2905(2)	93(3)
C22	7440(2)	142(5)	−617(2)	72(2)	C65	11099(3)	210(8)	2339(3)	111(4)
C23	7226(2)	−590(6)	−1208(2)	88(3)	C66	10563(3)	−144(7)	1842(2)	100(3)

[a] U_{eq} is one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

is 1.55(1) Å. This value is considerably shorter than the P–N single bond in sodium phosphoramidate, NaH_3NPO_3 (1.76 Å).[9] The PNP bond angle in compound **5** is unusually high (149.5(2)°). This may be a manifestation of crystal packing forces, rather than a consequence of the nature of the side groups. As discussed, even though the molecular structures of the linear oligomers are very similar, the packing arrangements of these molecules differ significantly. Because the bulk properties of a material are influenced by the way in which the molecules are packed, these differences may be translated into expected property differences between the analogous high polymers.

A comparison of the structural parameters and melting points

Table 11. Bond Lengths (Å) and Bond Angles (deg) for $[NP(O–C_6H_4Cl\text{-}p)_2]_3$ (**14**)

Cl1–C4	1.728(7)	P2–N1	1.572(5)	Cl2–C10	1.357(9)	P2–N2	1.580(5)
Cl3–C16	1.721(7)	P3–O5	1.565(5)	Cl4–C22	1.721(8)	P3–O6	1.575(5)
Cl5–C28	1.722(7)	P3–N2	1.565(5)	Cl6–C34	1.708(8)	P3–N3	1.574(5)
P1–O1	1.561(4)	O1–C1	1.417(7)	P1–O2	1.599(4)	O2–C7	1.376(7)
P1–N1	1.563(5)	O3–C13	1.395(7)	P1–N3	1.579(5)	O4–C19	1.419(7)
P2–O3	1.600(4)	O5–C25	1.403(8)	P2–O4	1.567(5)	O6–C31	1.368(8)
O1–P1–O2	99.9(2)	O3–P2–N1	110.7(3)	O5–P3–N3	110.0(3)	P2–O4–C19	124.8(4)
O1–P1–N1	105.6(3)	O3–P2–N2	110.1(3)	O6–P3–N2	110.5(3)	P3–O5–C25	126.1(4)
O1–P1–N3	112.2(3)	O4–P2–N1	106.0(3)	O6–P3–N3	110.5(3)	P3–O6–C31	127.1(4)
O2–P1–N1	109.4(3)	O4–P2–N2	112.2(3)	N2–P3–N3	117.4(3)	P1–N1–P2	122.2(3)
O2–P1–N3	110.1(2)	N1–P2–N2	117.3(3)	P1–O1–C1	126.8(4)	P2–N2–P3	122.8(3)
N1–P1–N3	118.0(3)	O5–P3–O6	95.2(3)	P1–O2–C7	120.3(4)	P1–N3–P3	122.0(3)
O3–P2–O4	99.0(2)	O5–P3–N2	111.0(3)	P2–O3–C13	121.2(4)		

Table 12. Fractional Atomic Positional Parameters for $NP(O–C_6H_4Cl\text{-}p)_2]_3$ (**14**)

	x	*y*	*z*	*U*(1,1),[a] Å²		*x*	*y*	*z*	*U*(1,1),[a] Å²
Cl1	0.4135(2)	0.4689(4)	0.22733(8)	0.124(2)	C10	0.5139(4)	0.1904(9)	0.5930(3)	0.036(4)
Cl2	0.5629(1)	0.2116(3)	0.64677(7)	0.050(1)	C11	0.4494(3)	0.0852(9)	0.5906(2)	0.029(3)
Cl3	−0.0674(1)	0.3545(4)	0.34610(8)	0.053(1)	C12	0.4083(4)	0.0734(9)	0.5474(3)	0.029(3)
Cl4	0.0840(2)	0.2448(5)	0.76001(9)	0.142(2)	C13	0.0720(3)	0.1855(9)	0.4729(2)	0.019(3)
Cl5	0.3626(2)	0.5600(4)	0.74205(8)	0.116(2)	C14	0.0051(4)	0.276(1)	0.4800(2)	0.025(3)
Cl6	0.1354(2)	0.7619(4)	0.27034(8)	0.108(2)	C15	−0.0376(4)	0.325(1)	0.4408(3)	0.032(4)
P1	0.30896(9)	0.2385(2)	0.45867(6)	0.0284(8)	C16	−0.0145(4)	0.285(1)	0.3953(3)	0.033(4)
P2	0.19730(9)	0.2058(2)	0.52413(6)	0.0275(8)	C17	0.0494(4)	0.191(1)	0.3900(3)	0.034(4)
P3	0.25242(9)	0.5335(2)	0.50207(6)	0.042(1)	C18	0.0930(4)	0.138(1)	0.4287(2)	0.038(4)
O1	0.2919(2)	0.1945(6)	0.4047(2)	0.044(3)	C19	0.1807(3)	0.1562(9)	0.6172(2)	0.036(3)
O2	0.3921(2)	0.1594(6)	0.4647(2)	0.025(2)	C20	0.1103(5)	0.113(1)	0.6258(3)	0.070(5)
O3	0.1135(2)	0.1350(6)	0.5139(2)	0.025(2)	C21	0.0776(5)	0.140(1)	0.6693(3)	0.063(5)
O4	0.2114(2)	0.1120(6)	0.5733(2)	0.042(2)	C22	0.1220(5)	0.213(1)	0.7046(3)	0.073(5)
O5	0.2947(3)	0.6607(6)	0.5378(2)	0.086(3)	C23	0.1948(5)	0.257(1)	0.6965(3)	0.090(6)
O6	0.2079(3)	0.6823(6)	0.4741(2)	0.089(3)	C24	0.2253(4)	0.229(1)	0.6520(3)	0.049(4)
N1	0.2532(3)	0.1237(7)	0.4876(2)	0.035(3)	C25	0.3106(4)	0.6292(8)	0.5867(2)	0.050(4)
N2	0.1968(3)	0.4121(7)	0.5292(2)	0.037(3)	C26	0.2664(4)	0.707(1)	0.6198(3)	0.041(4)
N3	0.3104(3)	0.4424(6)	0.4684(2)	0.029(3)	C27	0.2813(4)	0.689(1)	0.6673(3)	0.047(4)
C1	0.3253(4)	0.2727(8)	0.3644(2)	0.047(4)	C28	0.3417(4)	0.590(1)	0.6818(3)	0.065(5)
C2	0.2786(4)	0.365(1)	0.3341(3)	0.041(4)	C29	0.3886(4)	0.514(1)	0.6481(3)	0.044(4)
C3	0.3065(5)	0.428(1)	0.2922(3)	0.066(5)	C30	0.3715(4)	0.532(1)	0.6005(3)	0.039(4)
C4	0.3793(4)	0.397(1)	0.2813(2)	0.068(5)	C31	0.1932(4)	0.6915(8)	0.4257(2)	0.045(4)
C5	0.4268(4)	0.310(1)	0.3129(3)	0.052(4)	C32	0.1277(4)	0.621(1)	0.4069(3)	0.039(4)
C6	0.3992(4)	0.246(1)	0.3556(3)	0.044(4)	C33	0.1097(4)	0.641(1)	0.3585(3)	0.032(4)
C7	0.4307(3)	0.1692(8)	0.5083(2)	0.028(3)	C34	0.1576(4)	0.738(1)	0.3301(3)	0.047(4)
C8	0.4966(4)	0.272(1)	0.5119(3)	0.030(3)	C35	0.2246(4)	0.809(1)	0.3500(3)	0.047(4)
C9	0.5372(4)	0.281(1)	0.5531(3)	0.035(4)	C36	0.2412(4)	0.7873(9)	0.3980(3)	0.042(4)

[a] The form of the anisotropic thermal parameter is $U = \exp[-2PI^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$, where *a*, *b*, and *c* are reciprocal lattice constants.

Table 13. Bond Lengths (Å) and Bond Angles (deg) for $[NP(O–C_6H_4Br\text{-}p)_2]_3$ (**15**)

P1–O1	1.576(7)	P2–N1	1.585(7)	P3–O6	1.601(6)	O4–C41	1.39(2)
P1–O2	1.582(6)	P2–N2	1.564(8)	P3–N2	1.571(8)	O5–C51	1.37(2)
P1–N1	1.562(7)	P3–O5	1.564(6)	P3–N3	1.564(9)	O6–C61	1.44(2)
P1–N3	1.581(8)	Br1–C14	1.90(2)	O1–C11	1.44(2)	Br4–C44	1.89(1)
P2–O3	1.596(7)	Br2–C24	1.89(1)	O2–C21	1.39(1)	Br5–C54	1.90(2)
P2–O4	1.589(6)	Br3–C34	1.87(1)	O3–C31	1.41(1)	Br6–C64	1.91(1)
O1–P1–O2	98.6(3)	O3–P2–N1	112.6(3)	O5–P3–N3	111.8(4)	P2–O4–C41	121.6(5)
O1–P1–N1	111.0(4)	O3–P2–N2	106.7(4)	O6–P3–N2	110.7(4)	P3–O5–C51	128.3(6)
O1–P1–N3	110.2(4)	O4–P2–N1	109.8(4)	O6–P3–N3	112.1(4)	P3–O6–C61	117.1(6)
O2–P1–N1	111.2(3)	O4–P2–N2	110.2(4)	N2–P3–N3	115.9(4)	P1–N1–P2	119.7(4)
O2–P1–N3	107.2(4)	N1–P2–N2	116.8(4)	P1–O1–C11	122.5(6)	P2–N2–P3	122.9(5)
N1–P1–N3	117.1(4)	O5–P3–O6	93.1(3)	P1–O2–C21	126.6(6)	P1–N3–P3	122.5(5)
O3–P2–O4	99.5(3)	O5–P3–N2	111.1(4)	P2–O3–C31	124.8(6)		

of the compounds reported in this work is summarized in Table 17. There is a significant rise in melting point (>20 °C) for **4** compared to the parent compound $OP(O–C_6H_5)_2NP(O–C_6H_5)_3$. On the other hand, smaller melting point differences exist within the different *p*-halogenophenoxy species in the series. The structure of $OP(O–C_6H_5)_2NP(O–C_6H_5)_3$ has been reported in a previous publication.[3] The variation in melting points within the series may be attributed to increased van der Waals attraction due to greater polarizability of the heavier halide groups.

Compounds **4**–**6** were synthesized as models for the high polymeric system, and it is instructive to compare their structures to those found in the actual polymers. Single crystals and twinned crystals of $[NP(O–C_6H_4F\text{-}p)_2]_n$ have been described by Masuko and Magill,[10,11] and X-ray diffraction of a film of this polymer was investigated by Matsuzawa.[12] Both groups reported a monoclinic unit cell for the polymeric crystals, although the values quoted for the cell dimensions were different (a = 26.4 Å, b = 19.2 Å, c = 4.91 Å, β = 86° [10], a = 18.9 Å, b = 13.2 Å, c = 4.90 Å, β = 77° [12]). Our results show that crystals of **4** possess a triclinic unit cell. This suggests an obvious difference in the way the polymer molecules and the short-chain models pack. The differences may be attributed to the fact that the short-chain species possesses an end group with three aryloxy units attached to it. Thus, it does not truly mimic the structure of a high polymer.

Table 14. Fractional Atomic Positional Parameters for $[NP(O-C_6H_4Br\text{-}p)_2]_3$ (**15**)

	x	*y*	*z*	$U(1,1)$,[a] Å^2		*x*	*y*	*z*	$U(1,1)$,[a] Å^2
Br1	0.0852(2)	0.50795(4)	0.2689(2)	0.189(1)	C24	0.1407(8)	0.8515(3)	–0.0306(12)	0.067(6)
Br2	0.1298(1)	0.90683(4)	0.0490(2)	0.152(1)	C25	0.1496(11)	0.8470(3)	–0.1783(13)	0.13(1)
Br3	0.4545(1)	0.90666(3)	0.0445(2)	0.168(1)	C26	0.1557(9)	0.8057(3)	–0.2327(12)	0.107(8)
Br4	0.4641(1)	0.50950(4)	0.2931(2)	0.130(1)	C31	0.4382(6)	0.7703(2)	–0.1450(9)	0.042(5)
Br5	0.2156(1)	0.43619(4)	–0.0505(2)	0.104(1)	C32	0.4531(8)	0.7754(3)	–0.0017(10)	0.081(6)
Br6	0.2963(1)	0.84491(3)	–0.6433(2)	0.113(1)	C33	0.4597(8)	0.8170(3)	0.0572(11)	0.087(7)
P1	0.1939(2)	0.68825(6)	–0.1547(2)	0.044(1)	C34	0.4455(8)	0.8516(3)	–0.0326(12)	0.067(6)
P2	0.3928(2)	0.68773(6)	–0.1544(2)	0.044(1)	C35	0.4255(11)	0.8457(3)	–0.1768(12)	0.16(1)
P3	0.2915(2)	0.64199(6)	–0.3607(2)	0.059(1)	C36	0.4232(9)	0.8046(3)	–0.2320(11)	0.107(8)
O1	0.1115(5)	0.6757(2)	–0.0455(7)	0.053(3)	C41	0.4697(6)	0.6349(3)	0.0316(9)	0.040(5)
O2	0.1482(5)	0.7314(2)	–0.2132(7)	0.064(4)	C42	0.4176(8)	0.6329(3)	0.1615(11)	0.064(6)
O3	0.4415(5)	0.7304(2)	–0.2139(7)	0.065(4)	C43	0.4155(8)	0.5963(3)	0.2380(11)	0.077(7)
O4	0.4745(4)	0.6738(2)	–0.0406(7)	0.038(3)	C44	0.4663(8)	0.5610(3)	0.1865(11)	0.073(6)
O5	0.2917(5)	0.5933(2)	–0.3979(7)	0.085(4)	C45	0.5152(8)	0.5626(3)	0.0584(12)	0.078(7)
O6	0.2925(5)	0.6560(2)	–0.5265(7)	0.073(4)	C46	0.5174(8)	0.6008(3)	–0.0187(11)	0.079(7)
N1	0.2931(5)	0.6965(2)	–0.0745(7)	0.046(4)	C51	0.2728(7)	0.5594(3)	–0.3086(11)	0.054(5)
N2	0.3892(5)	0.6555(2)	–0.2828(9)	0.047(4)	C52	0.2388(11)	0.5221(4)	–0.3770(16)	0.111(9)
N3	0.1950(6)	0.6557(2)	–0.2847(8)	0.052(4)	C53	0.2192(12)	0.4873(4)	–0.2998(16)	0.16(1)
C11	0.1106(7)	0.6357(3)	0.0284(10)	0.046(5)	C54	0.2385(8)	0.4871(3)	–0.1568(15)	0.064(6)
C12	0.1524(8)	0.6319(3)	0.1567(11)	0.077(7)	C55	0.2723(9)	0.5226(3)	–0.0811(14)	0.082(7)
C13	0.1486(9)	0.5937(4)	0.2320(11)	0.100(7)	C56	0.2897(8)	0.5594(3)	–0.1618(12)	0.070(6)
C14	0.0953(9)	0.5606(3)	0.1684(12)	0.107(8)	C61	0.2938(7)	0.7010(3)	–0.5564(9)	0.062(5)
C15	0.0521(8)	0.5649(3)	0.0349(11)	0.084(7)	C62	0.2066(7)	0.7207(3)	–0.5755(10)	0.046(5)
C16	0.0588(8)	0.6028(8)	–0.0359(11)	0.062(6)	C63	0.2078(7)	0.7651(3)	–0.6025(10)	0.052(5)
C21	0.1485(6)	0.7706(3)	–0.1434(9)	0.041(5)	C64	0.2952(7)	0.7847(3)	–0.6113(9)	0.053(5)
C22	0.1343(8)	0.7760(3)	–0.0002(11)	0.070(6)	C65	0.3801(7)	0.7631(3)	–0.5993(10)	0.055(6)
C23	0.1294(8)	0.8170(3)	0.0577(10)	0.088(7)	C66	0.3797(6)	0.7202(3)	–0.5711(9)	0.043(5)

[a] The form of the anisotropic thermal parameter is $U = \exp[-2PI^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3))\}]$ where *a*, *b*, and *c* are reciprocal lattice constants.

Table 15. Bond Lengths (Å) and Bond Angles (deg) for $[NP(O-C_6H_4I\text{-}p)_2]_3$ (**16**)

I1–C4	2.06(2)	P1–O2	1.56(2)	P3–O5	1.58(2)	O3–C13	1.42(2)
I2–C10	2.08(2)	P1–N1	1.56(2)	P3–O6	1.55(2)	O4–C19	1.41(3)
I3–C16	2.09(2)	P1–N3	1.61(2)	P3–N2	1.59(2)	O5–C25	1.42(3)
I4–C22	2.07(2)	P2–O3	1.59(1)	P3–N3	1.54(2)	O6–C31	1.39(2)
I5–C28	2.11(2)	P2–O4	1.57(2)	O1–C1	1.34(2)	C1–C2	1.45(3)
I6–C34	2.07(2)	P2–N1	1.58(2)	O2–C7	1.31(3)	C1–C6	1.38(3)
P1–O1	1.56(1)	P2–N2	1.55(2)				
O1–P1–O2	96.8(8)	O3–P2–N1	107.0(8)	O5–P3–N3	108.4(9)	P2–O4–C19	123(1)
O1–P1–N1	110.2(9)	O3–P2–N2	111.5(8)	O6–P3–N2	110.6(9)	P3–O5–C25	119(1)
O1–P1–N3	110.2(9)	O4–P2–N1	109.0(8)	O6–P3–N3	107.7(8)	P3–O6–C31	129(1)
O2–P1–N1	111(1)	O4–P2–N2	110.7(8)	N2–P3–N3	119(1)	P1–N1–P2	122(1)
O2–P1–N3	110.4(8)	N1–P2–N2	117.8(9)	P1–O1–C1	121(1)	P2–N2–P3	120(1)
N1–P1–N3	117(1)	O5–P3–O6	98.4(7)	P1–O2–C7	135(1)	P1–N3–P3	121(1)
O3–P2–O4	99.3(7)	O5–P3–N2	110.9(8)	P2–O3–C13	126(1)		

Furthermore, the conformation assumed by the small molecules may be influenced more strongly by crystal packing forces. Conversely, at the high polymeric level, chain-packing considerations often play only a secondary role in governing the conformations assumed by molecular chains in the crystalline state. The conformation assumed by a polymer is usually the one of minimum potential energy.[15] Therefore, the crystal structures found may not reflect those of the most stable high polymeric conformers.

Bishop and Hall conducted a detailed analysis of the structure of $[NP(O-C_6H_4Cl\text{-}p)_2]_n$.[13] They suggested an orthorhombic unit cell with space group $P2_12_12_1$ and cell dimensions of $a = 13.08$ Å, $b = 20.23$ Å, and $c = 4.90$ Å. The P–N backbone was reported to be close to a planar cis–trans conformation. Their analysis also suggested that both side groups attached to a phosphorus atom stacked with similar groups attached to the next phosphorus atom along the same chain. In our investigation, we find that crystals of the corresponding short-chain species **5** have a triclinic unit cell with space group $P\bar{1}$, a different packing arrangement from that of the high polymer. Nevertheless, some similarities exists in both species. For instance, the O–P–N–P backbone of the short-chain is close to a planar conformation, and stacking of neighboring side groups clearly exists. These features were also observed for the other short-chain species. Therefore, in this respect, the short-chain models resemble the high polymer to an appreciable degree.

Comparison of the structures of the cyclic trimeric species with those of the linear short-chain molecules revealed some significant differences. First, the average P–N bond distance of the trimer (1.57(2) Å) is slightly longer than the average P–N distance in the linear species (1.55(1) Å). The other major difference involves the P–N–P bond angle. The mean P–N–P angle in the cyclic trimers is 122(1)°, compared to 138(1)° found for the linear species. This clearly illustrates the shortcoming in the use of the cyclic compounds as models for the linear polymers. The wider P–N–P angle in the linear species reflects a response to the steric requirements of the side groups. Because the side groups incur more severe steric repulsions when bonded to a linear backbone, increases in the P–N–P angle would maximize the distance between the side units. The average O–P–O bond angles (102(1)°) in the linear phosphazenes are wider than in the cyclic species (97(2)°).

In both cyclic and linear species, the observed P–O distances (average 1.57(2) Å) are shorter than the single bond value of 1.71 Å.[21] This indicates considerable π-bonding beyond the main phosphazene backbone. However, because the value of the P–O

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Table 16. Fractional Atomic Positional Parameters for $NP(O–C_6H_4I\text{-}p)_2]_3$ (**16**)

	x	y	z	$U(1,1)$,[a] Å^2		x	y	z	$U(1,1)$,[a] Å^2
I1	0.2233(1)	–0.6424(2)	0.15293(5)	0.073(1)	C10	0.241(2)	–0.190(3)	0.5081(6)	0.06(1)
I2	0.2191(1)	–0.0939(2)	0.56377(5)	0.068(1)	C11	0.220(2)	–0.336(3)	0.5028(6)	0.09(2)
I3	0.0440(1)	0.0321(2)	0.09408(5)	0.085(1)	C12	0.241(2)	–0.396(3)	0.4684(8)	0.06(1)
I4	0.1004(2)	0.2548(2)	0.49499(6)	0.105(1)	C13	0.100(1)	–0.151(2)	0.2323(6)	0.03(1)
I5	0.4550(1)	0.2944(2)	0.48760(6)	0.073(1)	C14	0.086(2)	–0.012(2)	0.2268(7)	0.05(1)
I6	0.3807(2)	0.0467(2)	0.09364(5)	0.087(1)	C15	0.070(2)	0.039(2)	0.1871(7)	0.05(1)
P1	0.2781(4)	–0.3624(6)	0.3555(2)	0.033(3)	C16	0.073(2)	–0.041(3)	0.1544(6)	0.04(1)
P2	0.1675(3)	–0.1591(6)	0.3120(2)	0.019(2)	C17	0.089(2)	–0.191(3)	0.1607(8)	0.08(2)
P3	0.3658(4)	–0.1599(6)	0.3111(2)	0.018(2)	C18	0.103(2)	–0.241(3)	0.1997(7)	0.06(1)
O1	0.273(1)	–0.520(1)	0.3403(4)	0.045(8)	C19	0.1000(1)	0.0170(1)	0.3646(5)	0.03(1)
O2	0.292(1)	–0.396(2)	0.4025(4)	0.07(1)	C20	0.0580(1)	–0.0490(2)	0.3959(4)	0.03(1)
O3	0.108(1)	–0.218(1)	0.2714(4)	0.025(6)	C21	0.0570(2)	0.0230(2)	0.4340(4)	0.05(1)
O4	0.091(1)	–0.050(2)	0.3257(5)	0.029(7)	C22	0.1040(2)	0.1530(3)	0.4388(5)	0.08(1)
O5	0.450(1)	–0.049(2)	0.3245(5)	0.029(7)	C23	0.1410(1)	0.2160(2)	0.4051(6)	0.04(1)
O6	0.403(1)	–0.212(1)	0.2703(4)	0.029(7)	C24	0.1400(2)	0.1480(3)	0.3680(5)	0.04(1)
N1	0.178(1)	–0.286(2)	0.3437(5)	0.012(7)	C25	0.4480(1)	0.0270(3)	0.3620(7)	0.03(1)
N2	0.263(1)	–0.082(2)	0.3022(5)	0.010(7)	C26	0.4010(2)	0.1530(2)	0.3616(5)	0.06(1)
N3	0.375(1)	–0.286(2)	0.3416(5)	0.034(8)	C27	0.4050(2)	0.2380(2)	0.3970(6)	0.05(1)
C1	0.264(1)	–0.551(2)	0.3000(6)	0.019(9)	C28	0.4550(2)	0.1790(2)	0.4320(7)	0.07(1)
C2	0.166(1)	–0.572(2)	0.2784(7)	0.022(9)	C29	0.5020(1)	0.0490(3)	0.4338(5)	0.05(1)
C3	0.155(2)	–0.599(3)	0.2374(7)	0.03(1)	C30	0.5020(1)	–0.0280(3)	0.3962(6)	0.03(1)
C4	0.241(1)	–0.618(2)	0.2517(6)	0.023(9)	C31	0.3930(2)	–0.1480(2)	0.2317(6)	0.016(9)
C5	0.334(1)	–0.595(3)	0.2369(7)	0.018(9)	C32	0.4000(1)	–0.0030(2)	0.2252(5)	0.05(1)
C6	0.343(1)	–0.566(2)	0.2776(6)	0.03(1)	C33	0.3960(2)	0.0530(3)	0.1862(7)	0.013(9)
C7	0.274(1)	–0.328(2)	0.4361(6)	0.029(9)	C34	0.3850(1)	–0.0330(2)	0.1529(7)	0.03(1)
C8	0.293(2)	–0.182(3)	0.4403(7)	0.04(1)	C35	0.3730(1)	–0.1770(3)	0.1588(5)	0.11(2)
C9	0.275(2)	–0.113(3)	0.4773(7)	0.05(1)	C36	0.3820(2)	–0.2350(2)	0.1982(6)	0.05(2)

[a] The form of the anisotropic thermal parameter is $U = \exp[-2PI^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$ where *a*, *b*, and *c* are reciprocal lattice constants.

Table 17. Structural Comparison of Halogenated Phenoxyphosphazenes and Their Melting Points

compd	no.	P1–N, Å	P2–N, Å	P–N–P, deg	N–P–N, deg	mp, °C
$OP(O–C_6H_5)_2NP(O–C_6H_5)_3$[a]		1.60	1.53	134		53.5
$OP(O–C_6H_4F\text{-}p)_2NP(O–C_6H_4F\text{-}p)_3$	**4**	1.600(2)	1.528(1)	135.39(9)		76.5
$OP(O–C_6H_4Cl\text{-}p)_2NP(O–C_6H_4Cl\text{-}p)_3$	**5**	1.515(2)	1.581(2)	149.5(2)		83.5
$OP(O–C_6H_4Br\text{-}p)_2NP(O–C_6H_4Br\text{-}p)_3$	**6**	1.526(7)	1.574(6)	131.5(5)		88.8
$[NP(O–C_6H_4F\text{-}p)_2]_3$	**13**	1.578(3)		122.0(2)	117.3(1)	118
$[NP(O–C_6H_4Cl\text{-}p)_2]_3$	**14**	1.572(2)		122.5(2)	117.6(2)	140
$[NP(O–C_6H_4Br\text{-}p)_2]_3$	**15**	1.571(3)		121.3(7)	116.9(2)	169
$[NP(O–C_6H_4I\text{-}p)_2]_3$	**16**	1.572(1)		121(3)	118.0(7)	184
$[NP(O–C_6H_5)_2]_3$		1.58		122	117	115
$[NPF_2]_3$[b]		1.57		120	119	28
$[NPCl_2]_3$[c]		1.59		121	118	114
$[NPBr_2]_3$[d]		1.58		121	117	191

[a] Reference 3. [b] Reference 18. [c] Reference 19. [d] Reference 20.

distances in both species is similar, the extent of electron delocalization beyond the phosphazene skeleton is insensitive to the conformation and geometry of the P–N backbone. The P–O–C bond angles are very similar in all seven compounds.

The molecular geometry of a compound is dictated by the need for each molecule to attain a minimum energy conformation. Because the geometry of a small molecule is also affected by crystal packing forces, the conformations observed for both the cyclic and linear models may not truly reflect those present in the corresponding high polymers. On the other hand, features that are shared by both cyclic and linear species may be adopted by the corresponding high polymers. For example, the intra- and intermolecular stacking of side groups found in several of the linear and cyclic species strongly suggests that such stacking may also be present in the polymeric analogues. The similarity in the P–N bond lengths found for both cyclic and linear short-chain species indicates that this parameter is relatively insensitive to the structure of the P–N skeleton. On the basis of this fact, we propose a value of about 1.55 Å for the P–N bond length in the corresponding high polymers. For the bond angles, we prefer the values derived from the short-chain structures for the reasons already discussed. The bond angle at nitrogen in the linear species is in the range of 133–134°. The N–P–N angle in the high polymers cannot be inferred from our results. However, based on previous studies, the N–P–N angle should approximate to 115°.[22] The O–P–O bond angles should assume a value of 102°, based on the results for the linear models.

The glass transition temperatures (T_g) of the corresponding polymers, namely $[NP(O–C_6H_4F\text{-}p)_2]_n$, $[NP(O–C_6H_4Cl\text{-}p)_2]_n$ and $[NP(O–C_6H_4Br\text{-}p)_2]_n$ are reported to be –4, 7, and 15 °C respectively.[23] We cannot explain these differences in terms of conformational differences between these molecules. Most likely, other factors such as the packing arrangement of polymer molecules, free volume, and polarizability of the halogen moieties would contribute significantly to the observed glass transition temperatures.

Experimental Section

Materials. 1,4-Dioxane (Baker) and tetrahydrofuran (Matheson) were distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane, hexane, and benzene were distilled from CaH_2. Phosphorus

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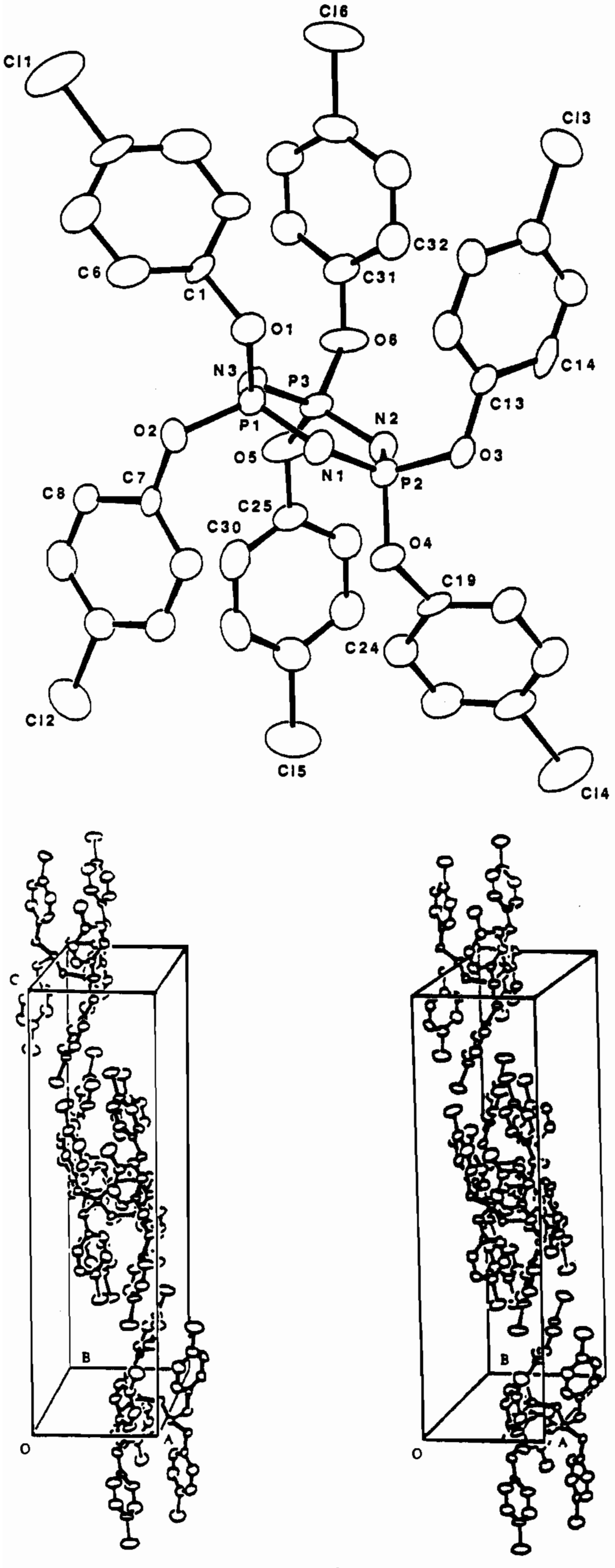

Figure 5. (a) Top: ORTEP diagram of $[NP(O\text{–}C_6H_4Cl\text{-}p)_2]_3$ (**14**). (b) Bottom: Packing diagram of $[NP(O\text{–}C_6H_4Cl\text{-}p)_2]_3$ (**14**).

pentachloride (Aldrich) was used as received. Hexachlorocylclotriphosphazene (Ethyl) was purified by fractional sublimation at 0.05 Torr. The *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodophenols were obtained from Aldrich and were purified by sublimation or recrystallization from methanol. They were dried under vacuum. All reactions were carried out under an atmosphere of dry argon.

Equipment. ^{31}P NMR spectra were obtained by use of a JEOL FX-90Q spectrometer operating at 90 MHz. Melting points were obtained by means of a Uni-melt capillary melting apparatus. X-ray diffraction was carried out with the use of an Enraf-Nonius CAD4 automated diffractometer.

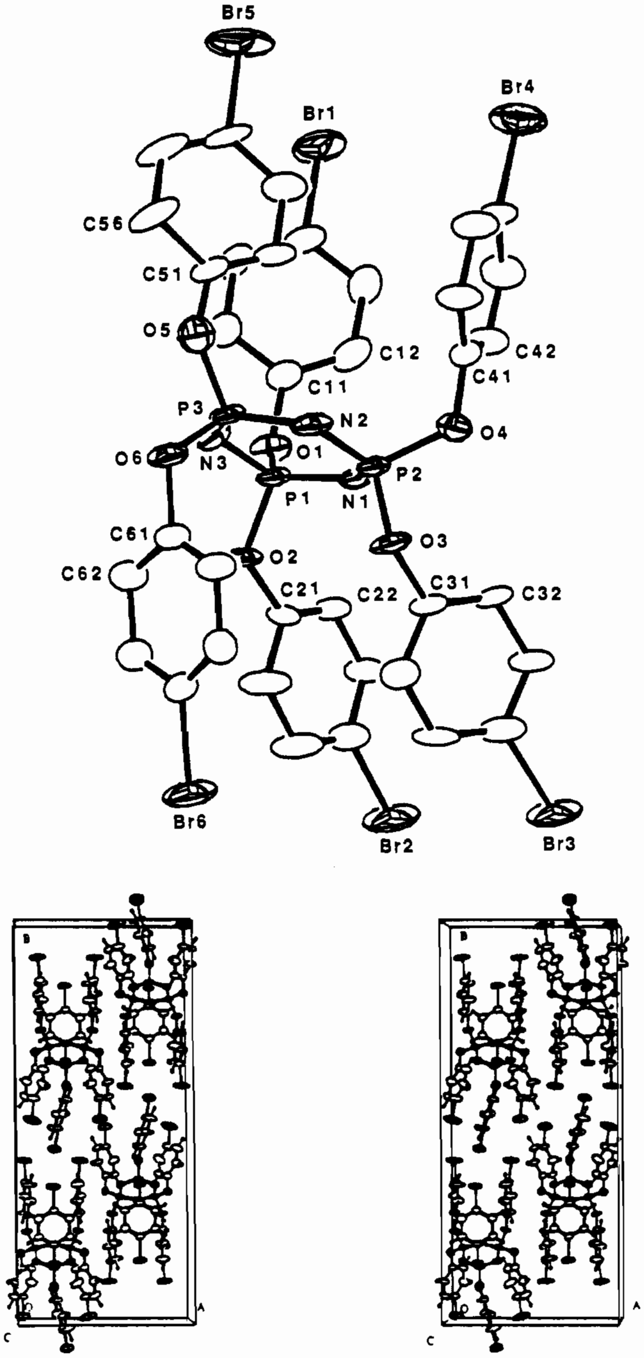

Figure 6. (a) Top: ORTEP diagram of $[NP(O\text{–}C_6H_4Br\text{-}p)_2]_3$ (**15**). (b) Bottom: Packing diagram of $[NP(O\text{–}C_6H_4Br\text{-}p)_2]_3$ (**15**).

X-ray Structure Determination Technique. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf-Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections within the range of 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method using variable scan speed (1.83–8.24° min^{-1}), scan width $(1.00 + 0.35 \tan\theta)°$, and monochromatized Mo Kα radiation in the range $2 < \theta < 25°$ or Cu Kα radiation in the range $5 < \theta < 65°$. All data sets were collected at room temperature with the exception of **4**, where data were collected at −100 °C and the crystal was sealed in a capillary.

Structures were solved by the direct methods. Refinements were by full-matrix, least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map revealed all H atoms which were included in the subsequent cycles at geometrically idealized positions (C–H 0.95 Å) and an overall isotropic temperature

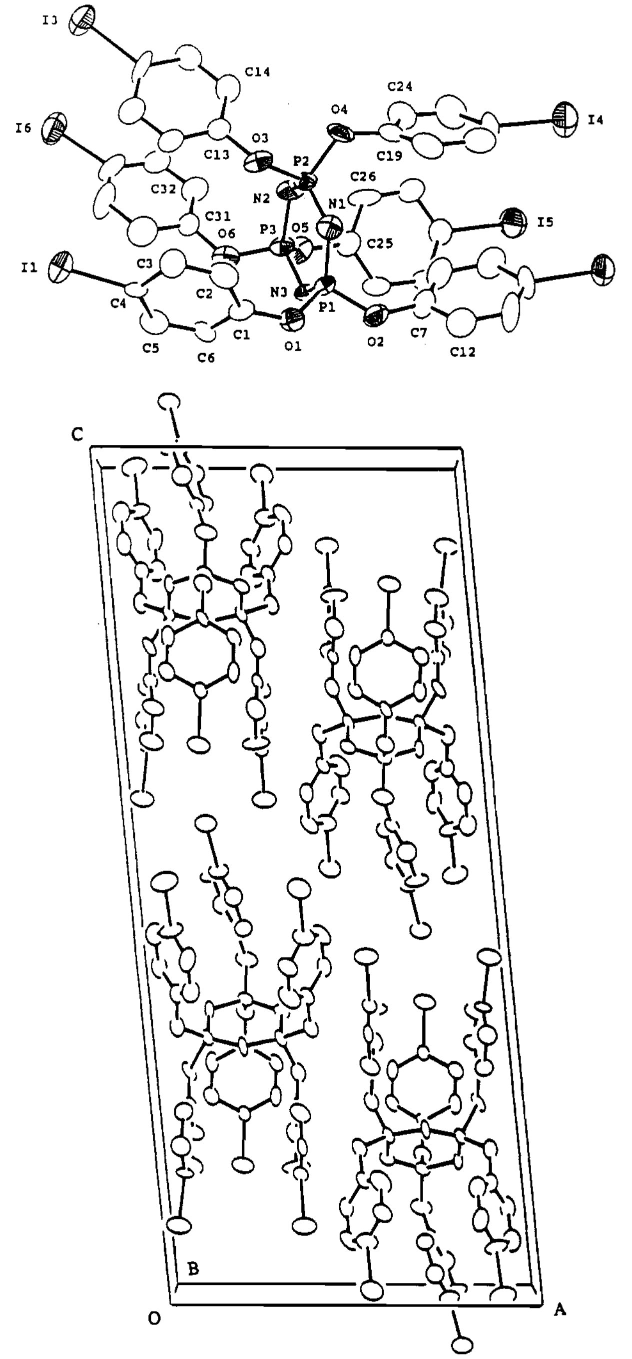

Figure 7. (a) Top: ORTEP diagram of $[NP(O-C_6H_4I-p)_2]_3$ (**16**). (b) Bottom: Packing diagram of $[NP(O-C_6H_4I-p)_2]_3$ (**16**).

factor. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann (1968)[16] and Stewart, Davidson, and Simpson (1965),[17] and allowance was made for anomalous dispersion (Cromer and Liberman, 1970).[24] A difference map calculated at the conclusion of the refinement had no chemically significant features. The computer programs used in this study were SHELX-76[25] and SHELX-86[26] (**13**) (Sheldrick, 1976 and 1986). At the conclusion of the refinements, the values of R and $R_w = [\Delta w/\Delta w F_o]$ were as follows: **4**, 0.0336 and 0.0479; **5**, 0.0518 and 0.0813; **6**, 0.0446 and 0.0647; **13**, 0.0568 and 0.0708; **14**, 0.1008 and 0.1334; **15**, 0.0944 and 0.129; **16**, 0.121 and 0.139.

Synthesis of Short-Chain Chlorophosphazenes 3 and 8. Species $OPCl_2NPCl_3$ (**3**) was prepared from PCl_5 and $(NH_4)_2SO_4$ (4.5:1 molar ratio) in *sym*-tetrachloroethane.[3] The product was purified twice by vacuum distillation to yield white crystals. $OPCl_2NPCl_2NPCl_3$ (**8**) was prepared as follows: **3** was treated with $NHSi_2Me_6$ (1:1 molar ratio) in dichloromethane and the mixture was refluxed for 12 h. A quantitative amount of PCl_5 was then added to the reaction flask, and the mixture was refluxed for another 12 h. Compound **8** was used without further purification.

Synthesis of Short-Chain Linear Phosphazenes bearing *p*-Halogenophenoxy Groups: Compounds 4–7 and 9–12. The following general procedure is typical. The short-chain chlorophosphazene **3** (1.5 g, 5.7 × 10^{-3} mol) or **9** (1.5 g, 3.9 × 10^{-3} mol) was treated with the sodium salt of the *p*-halogenophenol (4.3 × 10^{-2} mol with **3**; 4.1 × 10^{-2} mol with **9**) in dioxane (60 mL) which was cooled by means of an ice bath. The reaction mixture was stirred for about 30 min. $ClSiMe_3$ was then added to neutralize the excess salt. The reaction mixture was then filtered, and removal of the solvent yielded an oily residue. Purification was achieved by column chromatography over silica gel. Recrystallization of the oil was carried out from dichloromethane/hexane mixture. Yields ranged from 40 to 60% for the short-chain reactions.

Synthesis of Cyclic *p*-(Halogenophenoxy)phosphazene Trimers 13–16. $[NPCl_2]_3$ (3 g, 8.6 × 10^{-3} mol) was allowed to react with the sodium salt of the appropriate *para*-halogenated phenol (1.0 × 10^{-1} mol) in THF (75 mL). The reaction mixture was stirred and refluxed gently over a period of 12 h. The crude products were chromatographed on a silica gel column. Compounds **13–16** were recrystallized from CH_2Cl_2. Yields were virtually quantitative for all cyclic phosphazene reactions.

Acknowledgment. This work was supported by the U.S. Army Research Office. We also thank R. J. Fitzpatrick for supplying samples of hexakis(*p*-bromophenoxy)cyclotriphosphazene for X-ray studies.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, least squares planes, dihedral angles and derived hydrogen atom locations (60 pages). Ordering information is given on any current masthead page.

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