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Small-molecule model phosphazenes with *para*-substituted phenoxy side groups: synthesis, crystal structures and comparisons with corresponding high polymers

Harry R. Allcock,* Saman Al-Shali, Dennis C. Ngo, Karyn B. Visscher and Masood Parvez

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

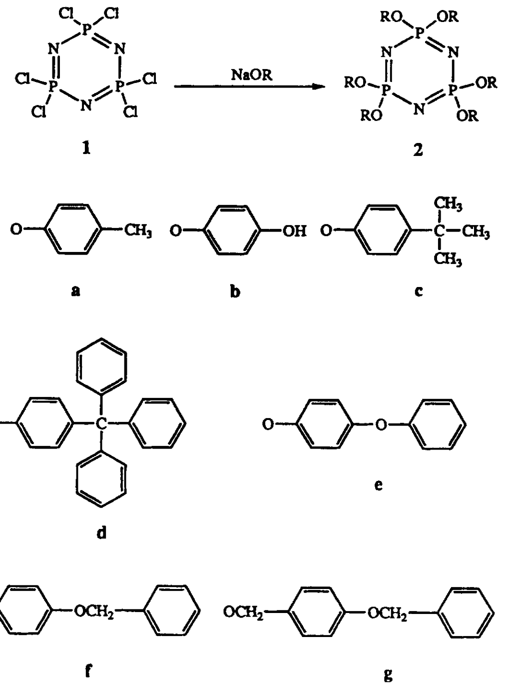
A series of new cyclic phosphazenes and a linear short-chain phosphazene have been synthesized as models for the preparation of the corresponding phosphazene high polymers. Several of the high polymers were also prepared. The small molecule compounds were characterized by a combination of ^{31}P NMR, mass spectrometry and elemental analysis. The crystal and molecular structures of $N_3P_3(OC_6H_4R\text{-}4)_6$ (R = CH_3, OH, OPh or OCH_2Ph), $N_4P_4(OC_6H_4OPh\text{-}4)_8$ and $OP(OC_6H_4Bu^t\text{-}4)_2NP(OC_6H_4Bu^t\text{-}4)$ were investigated by single-crystal X-ray diffraction techniques. High polymers, $[NP(OC_6H_4R\text{-}4)_2]_n$, (R = OPh, OCH_2Ph or Bu^t), $[NP(OC_6H_4CPh_3\text{-}4)_{1.5}Cl_{0.5}]_n$, and $[NP(OCH_2C_6H_4OCH_2Ph\text{-}4)_2]_n$ were also prepared and their structures confirmed by a variety of techniques including ^{1}H and ^{31}P NMR spectroscopy, elemental analysis and differential scanning calorimetry.

Aryloxy-substituted phosphazene high polymers are of interest as high-refractive glasses,[1,2] liquid-crystalline,[3–7] non-linear optical[8] and ferroelectric species[9] and, in some cases, as photoreactive polymeric materials.[10–17] The optical properties, in particular, are affected by the groups linked to the phenoxy side groups. For example, phenylphenoxy side groups generate high-refractive-index materials, and a polymer with 4-(4-iodophenyl)phenoxy side units has a refractive index as high as 1.664.[2] The mechanical properties of the polymers also depend on the nature of the units linked to phenoxy side groups and on the presence of one, two or more different co-substituent groups attached to the phosphazene backbone.

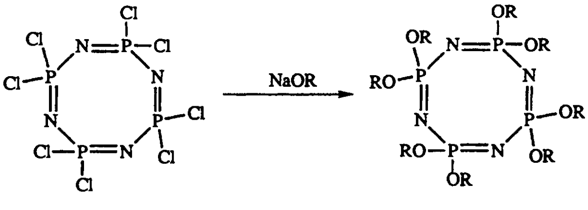
Polymers of this type are prepared by replacement of the halogen atoms in poly(dichlorophosphazene), $(NPCl_2)_n$, by reactions with aryl oxides,[18–21] with the ease of substitution being dependent on both the steric and electronic characteristics of the aryloxy units. Thus, bulky or electronically deactivated nucleophiles under mild reaction conditions may replace only a fraction of the available chlorine atoms, and a subsequent treatment with a second, more reactive, nucleophile is required in order to ensure the absence of hydrolytically sensitive PCl units in the final polymer.

Macromolecular substitution reactions are more complicated than the corresponding reactions at the small-molecule level. In a typical macromolecular reaction the replacement of 30 000 chlorine atoms per polymer molecule must be induced. Hence, a prudent protocol in this type of research is to examine prospective polymer reactions first at the small-molecule model compound level. The small-molecule systems allow characterization by NMR, mass spectrometry and X-ray techniques that are difficult or impossible for high polymers.

In this paper we discuss the reactions of the model cyclic trimer **1** with a variety of *para*-substituted aryl oxides. The products are listed in Scheme 1 as species **2a**–**2g**. In addition, a cyclic tetrameric model, **4a**, was prepared by the route shown in Scheme 2. In one case a linear short-chain phosphazene compound was also prepared and studied as a model for the corresponding high polymer. Several of the same substitution reactions were also investigated at the high-polymer level. All the organic substituted products were examined by microanalysis, NMR, and mass spectrometric techniques. Six of these compounds were also studied by single-crystal X-ray crystallography. The other three could not be so examined because they did not yield crystals of suitable quality.



Scheme 1



Scheme 2 **a**, OR = 4-Phenoxyphenoxy

Results and Discussion

Synthesis of the small-molecule model compounds

Replacement of all the chlorine atoms in compounds **1** and **3** by all the nucleophiles occurred relatively easily if a high boiling

Table 1 Characterization data

Compound	M.p. (°C)	Mass spectrum, m/z[a,b]	Analysis (%)[a] C	H	N	$\delta(^{31}P)$ for $P(OR)_2$
2a[c]	116–117	777 (777)	64.8	5.50	5.40	9.2
			(64.9)	(5.40)	(5.40)	
2b[d]	241–243	789 (789)	54.6	3.90	5.20	8.0
			(54.75)	(3.80)	(5.30)	
2c	*e*	1029 (1029)	*e*			8.7
2d	144[f]	Unresolved	83.25	5.55	2.90	8.6
			(83.9)	(5.35)	(1.95)	
2e	201–202	1149 (1149)	75.55	4.65	3.70	9.3
			(75.2)	(4.70)	(3.65)	
2f	100–101	1245 (1245)	69.55	4.65	3.20	9.3
			(69.4)	(4.35)	(3.35)	
2g	125–127	1413 (1413)	71.82	5.20	3.05	9.8
			(70.4)	(5.00)	(3.15)	
4a	68	1661 (1661)	68.65	4.10	3.40	−11.8
			(69.4)	(4.35)	(3.35)	
6a	85–87	837 [856 (**6a** + H_2O)]	73.50	7.85	0.60	−22.24 [$P(OR)_3$]
			(71.65)	(7.80)	(1.65)	−15.99

Compound	T_g/°C	T_1/°C	10^{-6} M	Analysis (%)[a] C	H	Cl	N	$\delta(^{31}P)$
8c	50	135	2.5	69.8	7.30	0.5	4.05	−19
				(69.95)	(7.65)	(0)	(4.10)	
8d[g]	(48)	—	1.0	80.1	5.15	2.00	2.90	−21.4
				(79.65)	(5.00)	(1.85)	(2.45)	
8e	17	126	4.6	68.75	4.50	0.03	3.40	−18.2
				(69.4)	(4.35)	(0)	(3.35)	
8f	30	145	3.5	70.25	5.35	0.00	3.20	−21.4
				(70.55)	(5.00)	(0)	(3.15)	

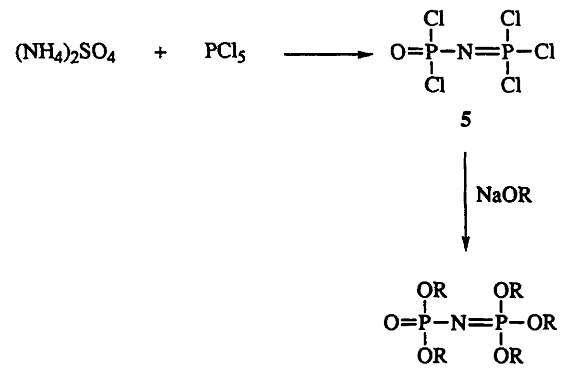
[a] Calculated values in parentheses. [b] Molecular ion. [c] Prepared and characterized previously as in ref. 25. [d] Prepared and characterized previously as in ref. 26. [e] Data not obtained. [f] Decomposition. [g] Actual structure is $[NP(OR)_{1.5}Cl_{0.5}]_n$.

ether solvent such as dioxane was employed. This suggests that, provided the terminal unit occupies the 4 position of the aryloxy group, the steric hindrance effects are comparable to that of an unsubstituted phenoxy unit. Hence, the transposition of these reactions to the high-polymer level should be relatively straightforward, and this was generally found to be the case (see later).

The reaction sequence used for the synthesis of the cyclotriphosphazenes is outlined in Scheme 1. The cyclic model compounds were prepared by treatment of hexachlorocyclotriphosphazene **1** with the sodium aryl oxides to yield cyclic phosphazenes with 4-methyl-, 4-*tert*-butyl-, 4-(triphenylmethyl)-, 4-phenoxy-, 4-benzyloxy-phenoxy and 4-benzyloxybenzyloxy side units. The cyclic trimer with 4-hydroxyphenoxy side units was prepared by a two-step process, with the second step involving the oxidation of methoxy units of hexakis(4-methoxyphenoxy)cyclotriphosphazene using BCl_3. In all these and the following reactions complete replacement of the chlorine atoms by the aryloxy groups occurred and reaction yields ranged from 70 to 85%.

The reaction used for the synthesis of the cyclotetraphosphazene is outlined in Scheme 2. Treatment of octachlorocyclotetraphosphazene **3** with the sodium aryl oxide yielded a cyclic phosphazene tetramer with 4-phenoxyphenoxy side units. Complete replacement of chlorine atoms was achieved.

The protocol for the synthesis of the linear, short-chain phosphazene is illustrated in Scheme 3. The preparation of $OPCl_2NPCl_3$ **5** has been described elsewhere.[22–24] The reaction of **5** with sodium 4-*tert*-butylphenoxide yielded product **6a**. Complete replacement of the chlorine atoms was achieved.



Scheme 3 **a**, OR = 4-*tert*-Butylphenoxy

Structural characterization of small-molecule cyclic and linear phosphazenes

Species **2a**–**2g**, **4a** and **6a** were characterized by a combination of ^{31}P NMR, mass spectrometry and elemental analysis (Table 1). The ^{31}P NMR spectra of compounds **2a**–**2g** and **4a** were singlets with the chemical shift position varying with the nature of the substituent group. The presence of a singlet in the ^{31}P NMR spectrum is consistent either with full substitution, or with the presence of only one environment for the phosphorus atoms as would be generated by non-geminal partial substitution. Compound **6a** gave an AB spin pattern due to the two different phosphorus environments within the molecule. Infrared spectra contained the absorbances expected for cyclophosphazenes, with maxima in the 1100–1200 cm^{-1} range characteristic of the P=N bond. All the compounds, except for **2d**, yielded mass spectra that contained a parent ion consistent with the expected molecular weights. More extensive characterization of compounds **2a**, **2b**, **2e**, **2f**, **4a** and **6a** was obtained from single-crystal X-ray diffraction studies. Compounds **2c**, **2d** and **2g** were not so studied due to the difficulty of obtaining single crystals of sufficiently high quality.

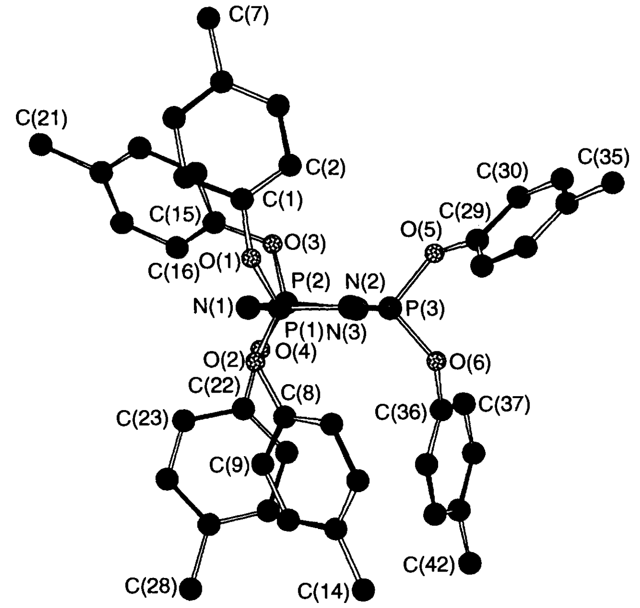


Fig. 1 An ORTEP[27] diagram of the molecule $N_3P_3(OC_6H_4CH_3\text{-}4)_6$ **2a**

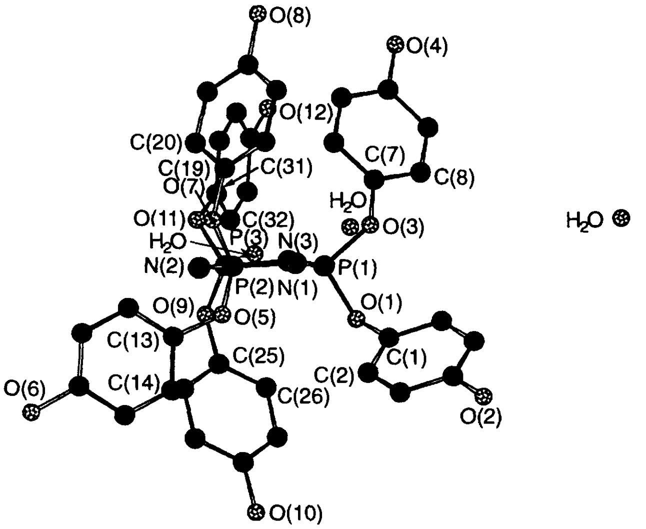


Fig. 2 An ORTEP diagram of the molecule $N_3P_3(OC_6H_4OH\text{-}4)_6$ **2b**

Table 2 Pertinent bond distances (Å) and angles (°) for compound **2a**

P(1)–O(1)	1.584(3)	P(3)–O(6)	1.575(4)
P(1)–O(2)	1.595(3)	P(3)–N(2)	1.570(4)
P(1)–N(1)	1.570(3)	P(3)–N(3)	1.566(4)
P(1)–N(3)	1.583(4)	O(1)–C(1)	1.425(5)
P(2)–O(3)	1.583(4)	O(2)–C(8)	1.402(5)
P(2)–O(4)	1.584(2)	O(3)–C(15)	1.399(6)
P(2)–N(1)	1.589(4)	O(4)–C(22)	1.416(5)
P(2)–N(2)	1.568(4)	O(5)–C(29)	1.376(5)
P(3)–O(5)	1.583(3)		
O(1)–P(1)–O(2)	94.5(1)	P(2)–O(3)–C(15)	123.3(3)
N(1)–P(1)–N(3)	116.9(2)	P(2)–O(4)–C(22)	124.1(3)
O(3)–P(2)–O(4)	99.3(2)	P(3)–O(5)–C(29)	127.4(3)
N(1)–P(2)–N(2)	117.6(2)	P(3)–O(6)–C(36)	126.7(4)
O(5)–P(3)–O(6)	100.5(2)	P(1)–N(1)–P(2)	122.0(2)
N(2)–P(3)–N(3)	117.2(2)	P(2)–N(2)–P(3)	122.0(2)
P(1)–O(1)–C(1)	123.5(2)	P(1)–N(3)–P(3)	123.7(2)
P(1)–O(2)–C(8)	122.9(3)		

Numbers in parentheses are estimated standard deviations in the least significant digits. Bond lengths and angles for phenoxy ring carbons were set to 1.395 Å and 120.0° in the crystal refinement program (also in Tables 3, 4 and 7).

Table 3 Pertinent bond distances (Å) and angles (°) for compound **2b**

P(1)–O(1)	1.565(2)	O(1)–C(1)	1.400(4)
P(1)–O(3)	1.586(2)	O(2)–C(4)	1.386(4)
P(1)–N(1)	1.574(3)	O(3)–C(7)	1.399(4)
P(1)–N(3)	1.584(3)	O(4)–C(10)	1.357(4)
P(2)–O(5)	1.574(2)	O(5)–C(13)	1.409(5)
P(2)–O(7)	1.562(3)	O(6)–C(16)	1.375(4)
P(2)–N(1)	1.572(3)	O(7)–C(19)	1.393(3)
P(2)–N(2)	1.581(3)	O(8)–C(22)	1.377(4)
P(3)–O(9)	1.577(2)	O(9)–C(25)	1.417(3)
P(3)–O(11)	1.572(2)	O(10)–C(28)	1.383(4)
P(3)–N(2)	1.585(3)	O(11)–C(31)	1.404(3)
P(3)–N(3)	1.579(2)	O(12)–C(34)	1.382(4)
O(1)–P(1)–O(3)	100.7(1)	P(2)–O(5)–C(13)	121.0(2)
N(1)–P(1)–N(3)	116.2(1)	P(2)–O(7)–C(19)	127.1(2)
O(5)–P(2)–O(7)	101.5(1)	P(3)–O(9)–C(25)	116.7(2)
N(1)–P(2)–N(2)	118.1(1)	P(3)–O(11)–C(31)	126.5(3)
O(9)–P(3)–O(11)	100.6(1)	P(1)–N(1)–P(2)	122.8(2)
N(2)–P(3)–N(3)	117.1(1)	P(2)–N(2)–P(3)	121.1(2)
P(1)–O(1)–C(1)	129.3(3)	P(1)–N(3)–P(3)	123.7(2)
P(1)–O(3)–C(7)	118.6(2)		

Compound 2a. The structure of compound **2a** was solved to an *R* factor of 0.085. As shown in Fig. 1, the cyclotriphosphazene ring is slightly puckered, with an average P–N bond length of 1.574(4) Å. The average N–P–N ring angle is 117.2(2)° and the average P–N–P ring angle 122.5(2)°. The phenoxy rings are normal in all respects with an average P–O–C angle of 124.6(3)°. The *p*-methyl groups on the phenoxy rings have an average C–C bond distance of 1.510(7) Å. Individual bond distances and angles are shown in Table 2.

Compound 2b. The structure of the hexakis(4-hydroxyphenoxy) cyclic trimer, **2b**, was solved to an *R* factor of 0.050. This system contains 3 molecules of water per unit cell. The six-membered phosphazene ring shows a slight boat distortion from planarity. Six 4-hydroxyphenoxy side groups are linked to the phosphorus atoms of the ring (Fig. 2) which has an average P–N bond length of 1.579(3) Å. The average N–P–N ring angle is 117.1(2)° with individual angles of 116.2(1), 118.1(1) and 117.1(1)°. The average P–N–P and O–P–O angles are 122.5(2) and 100.9(1)°. The phenoxy rings are normal in all respects with an average P–O–C angle of 123.2(3)°. The *p*-hydroxy groups on the phenoxy rings have an average C–O ••• (H) bond distance of 1.377(4) Å, which is typical for phenolic groups. No evidence was found that the crystal structure was stabilized by hydrogen bonding. Individual bond distances and angles are shown in Table 3.

Compound 2e. This structure was solved to an *R* factor of 0.0348. The cyclic trimeric phosphazene ring is slightly puckered in a chair conformation. The average P–N bond length is 1.582(2) Å. The average N–P–N and P–N–P ring angles are 116.7(2) and 122.3(1)°. The average O–P–O angle is 96.80(8)° with individual angles of 98.39(9), 93.16(7) and 98.86(7)°. The narrowest of these angles is probably due to crystal-packing forces. The P–O–C angles ranged from 122.6(1) to 131.2(1)°, average 125.3(2)°, and are considered to be normal, as indeed are the C–O–C angles which range from 117.1(2) to 120.1(2)°, average 118.8(2)°. The aryl rings are planar with normal dimensions. The orientation of the side groups is interesting, with four of the units oriented roughly normal to the phosphazene ring plane (Fig. 3) and two disposed approximately parallel to and away from the inorganic ring. The stereoview of the packing diagram (Fig. 4) illustrates the way in which the side-group torsional flexibility around the P–O–C and C–O–C units allows an efficient use by the side groups of the available unit-cell volume. By contrast, earlier

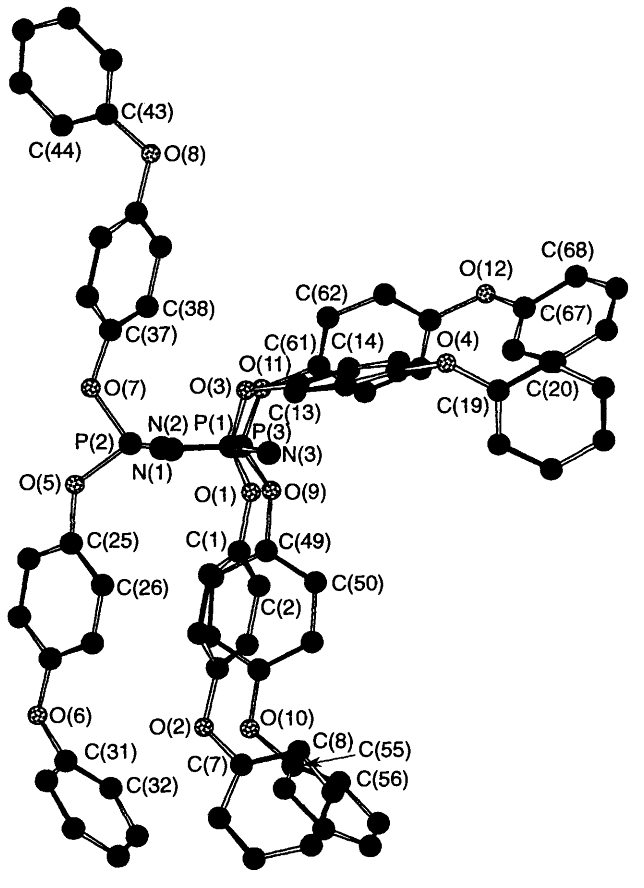


Fig. 3 An ORTEP diagram of the molecule $N_3P_3(OC_6H_4OPh\text{-}4)_6$ **2e**

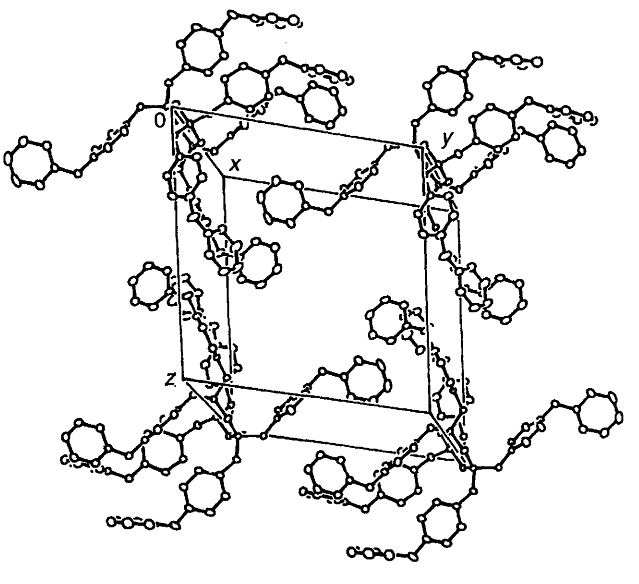


Fig. 4 Unit-cell packing diagram of the molecule **2e**

structure solutions of $[NP(OC_6H_4Ph)_2]_3$ and analogous short-chain species showed that the side-group conformation was significantly constrained by the rigidity of the structure.[28] Individual bond distances and angles are shown in Table 4.

Compound 2f. The structure of compound **2f** was solved to an *R* factor of 0.057. One phenyl ring showed high thermal parameters and this suggests a degree of thermal motion in this unit. The phosphazene ring is almost planar but with a slight chair distortion. The P–N bond distances range from 1.562(4) to 1.588(5) Å, average 1.577(5) Å. The average N–P–N ring angle is 117.8° and the average P–N–P bond angle 121.2(3)°. The average O–P–O angle is 96.2(2)°. All the benzenoid rings appear to be normal. The P–O–C angles [average 124.5(4)°] are within expected limits. So too are the C–O–C angles [in the range of 115.5(6) to 119.1(5)°] with the exception of one narrower angle of 100(1)°. Again, crystal-packing forces may explain this anomaly. The orientation of side groups (Fig. 5) is interesting, with maximum extension of each unit being favoured, and with four of the groups oriented almost normal to the phosphazene ring and the remaining two disposed away from the ring at roughly 45°. The packing diagram (Fig. 6) further illustrates this structure. Individual bond distances and angles are listed in Table 5.

Table 4 Pertinent bond distances (Å) and angles (°) for compound **2e**

P(1)–O(1)	1.583(2)	O(3)–C(13)	1.417(3)
P(1)–O(3)	1.582(1)	O(4)–C(16)	1.394(3)
P(1)–N(1)	1.574(2)	O(4)–C(19)	1.375(2)
P(1)–N(3)	1.569(2)	O(5)–C(25)	1.400(2)
P(2)–O(5)	1.565(1)	O(6)–C(28)	1.381(3)
P(2)–O(7)	1.577(1)	O(6)–C(31)	1.394(4)
P(2)–N(1)	1.582(2)	O(7)–C(37)	1.403(2)
P(2)–N(2)	1.572(2)	O(8)–C(40)	1.395(3)
P(3)–O(9)	1.583(1)	O(8)–C(43)	1.389(3)
P(3)–O(11)	1.579(2)	O(9)–C(49)	1.410(2)
P(3)–N(2)	1.574(2)	O(10)–C(52)	1.379(3)
P(3)–N(3)	1.583(2)	O(10)–C(55)	1.395(3)
O(1)–C(1)	1.407(2)	O(11)–C(61)	1.407(2)
O(2)–C(4)	1.397(3)	O(12)–C(64)	1.393(3)
O(2)–C(7)	1.381(3)	O(12)–C(67)	1.380(4)
O(1)–P(1)–O(3)	98.39(9)	C(28)–O(6)–C(31)	120.0(2)
N(1)–P(1)–N(3)	116.8(1)	P(2)–O(7)–C(37)	126.4(1)
O(5)–P(2)–O(7)	93.16(7)	C(40)–O(8)–C(43)	117.7(2)
N(1)–P(2)–N(2)	116.27(9)	P(3)–O(9)–C(49)	123.5(1)
O(9)–P(3)–O(11)	98.86(7)	C(52)–O(10)–C(55)	120.1(2)
N(2)–P(3)–N(3)	117.0(1)	P(3)–O(11)–C(61)	122.8(2)
P(1)–O(1)–C(1)	125.5(2)	C(64)–O(12)–C(67)	118.9(2)
C(4)–O(2)–C(7)	118.6(2)	P(1)–N(1)–P(2)	122.9(1)
P(1)–O(3)–C(13)	122.6(1)	P(2)–N(2)–P(3)	122.3(1)
C(16)–O(4)–C(19)	117.1(2)	P(1)–N(3)–P(3)	121.8(1)
P(2)–O(5)–C(25)	131.2(1)		

Compound 4a. Compound **4a** contains eight phenoxyphenoxy side groups attached to a cyclic, tetrameric phosphazene ring. The crystal structure exhibits two different molecular conformations (designated as molecules a and b) and was solved to an *R* factor of 0.0567 (Fig. 7). One phenyl ring showed evidence of large thermal parameters, attributed to thermal disorder. In both molecules the phosphazene ring is puckered into a boat-shaped conformation. Within molecule a the P–N bond lengths range from 1.556(5) to 1.562(5) Å, average 1.559(5) Å, within b 1.552(5) to 1.570(5) Å, average 1.560(5) Å. The N–P–N ring angles for molecule a range from 120.5(3) to 121.4(3)°, average 120.9(3)°, for molecule b from 120.7(3) to 121.6(3)°, average 121.1(3)°. The P–N–P angles for molecule a range from 134.9(3) to 136.0(3)°, average 135.5(3)°, for molecule b from 133.1(3) to 136.3(3)°, average 134.6(3)°. The average O–P–O angle is 99.1(3)° for molecule a, range 98.2(3)–99.7(3)°, 99.5(3)° for b range 98.9(2)–100.0(3)°.

The phenoxy rings are normal in all respects, with an average P–O–C angle for molecule a of 124.1(3)° and for b of 123.9(3)°. Throughout the two molecules the values range from 120.9(3) to 126.6(3)°. The C–O–C angles that connect the phenyl rings within the side-group structures have average values of 118.7(5)° for molecule a and 118.3(5)° for b, with a range throughout the two molecules of 116.9(6)–120.3(4)°.

As shown in Fig. 7, the differences in the molecular conformations arise from twisting within the side groups. In general, the side units extend in a perpendicular manner from the tetramer ring. There appears to be some intramolecular side-group stacking or organization *within* the molecule. Owing to the complex nature of the packing diagram (Fig. 8) it is

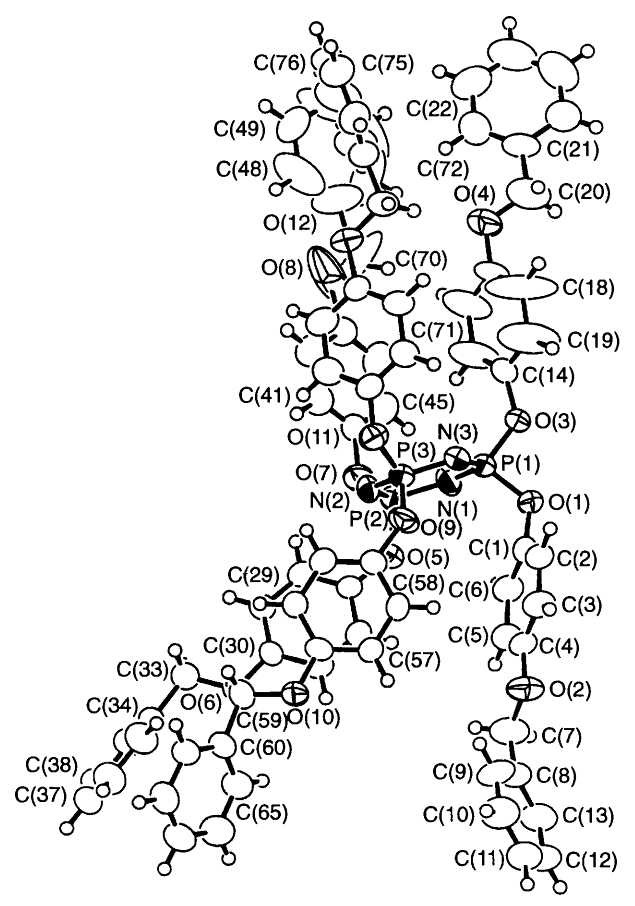


Fig. 5 An ORTEP diagram of the molecule $N_3P_3(OC_6H_4OCH_2Ph\text{-}4)_6$ **2f**

difficult to discern stacking *between* molecules. Individual bond distances and angles are shown in Table 6.

Compound 6a. Compound **6a** is a short-chain linear phosphazene that contains two phosphorus atoms linked to a central nitrogen atom (Fig. 9). Atom P(2) is bonded to two 4-*tert*-butylphenoxy groups and an oxygen atom, P(1) to three 4-*tert*-butylphenoxy groups. The structure was solved to an *R* factor of 0.0918. This large *R* factor is attributed to a slight degree of disorder within the *tert*-butylphenoxy side groups. The P–N bond distances were not identical, P(1)–N 1.495 and P(2)–N 1.578 Å. Although different, these are shorter than the single-bond value, and this suggests some form of electron delocalization within the P–N skeleton. The bond P(2)–O(6) has a length of 1.449 Å, shorter than the average P–O bond distances of 1.56 Å, suggesting some double-bond character. The P–N–P angle has a value of 157°, which is wide compared to other short-chain species.[22–24] It is assumed that this reflects the influence of the bulky *tert*-butyl moiety. The orientation of the side units is probably dictated by the need for them to maintain a maximum distance from each other. This effect should also be expected at the high polymeric level. The phenoxy rings appeared normal in all respects and no side-group stacking could be detected. Individual bond distances and angles are listed in Table 7.

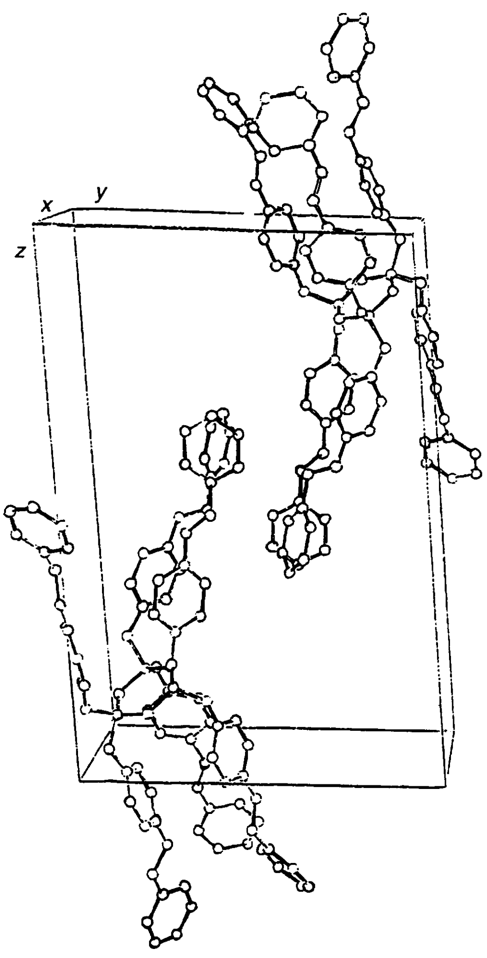


Fig. 6 Unit-cell packing diagram of the molecule **2f**

Table 5 Pertinent bond lengths (Å) and angles (°) for compound **2f**

P(1)–O(1)	1.589(4)	P(1)–O(3)	1.553(4)
P(1)–N(1)	1.588(5)	P(1)–N(3)	1.584(5)
P(2)–O(5)	1.594(4)	P(2)–O(7)	1.596(4)
P(2)–N(1)	1.562(4)	P(2)–N(2)	1.569(5)
P(3)–O(9)	1.584(4)	P(3)–O(11)	1.589(4)
P(3)–N(2)	1.586(5)	P(3)–N(3)	1.573(4)
O(1)–C(1)	1.404(7)	O(2)–C(4)	1.367(7)
O(2)–C(7)	1.397(7)	O(3)–C(14)	1.394(7)
O(4)–C(17)	1.384(7)	O(4)–C(20)	1.398(9)
O(5)–C(27)	1.392(6)	O(6)–C(30)	1.364(6)
O(6)–C(33)	1.418(7)	O(7)–C(40)	1.398(7)
O(8)–C(43)	1.58(1)	O(8)–C(46)	1.398(2)
O(9)–C(53)	1.398(6)	O(10)–C(56)	1.377(6)
O(10)–C(59)	1.427(7)	O(11)–C(66)	1.411(7)
O(12)–C(69)	1.369(7)	O(12)–C(72)	1.418(8)
O(1)–P(1)–O(3)	92.8(2)	P(1)–N(3)–P(3)	121.5(3)
O(5)–P(2)–O(7)	98.4(2)	N(2)–P(3)–N(3)	118.2(3)
O(9)–P(3)–O(11)	97.4(2)	C(4)–O(2)–C(7)	119.1(5)
P(1)–O(1)–C(1)	121.0(3)	C(17)–O(4)–C(20)	115.5(6)
P(1)–O(3)–C(14)	128.6(4)	C(30)–O(6)–C(33)	117.5(4)
P(2)–O(5)–C(27)	124.9(3)	C(43)–O(8)–C(46)	100(1)
P(2)–O(7)–C(40)	123.7(4)	C(56)–O(10)–C(59)	117.4(4)
P(3)–O(9)–C(53)	128.3(4)	C(69)–O(12)–C(72)	117.7(6)
P(3)–O(11)–C(66)	120.2(4)	P(2)–N(2)–P(3)	120.1(3)
P(1)–N(1)–P(2)	122.1(3)		

Synthesis and characterization of high polymers

Poly(organophosphazenes) with the same *para*-substituted aryloxy side groups as employed in small molecules **2c**–**2g** were also prepared. These polymers have the general structure shown in **8**, and were prepared by the route shown in Scheme 4. The macromolecular substitution reactions were carried out at 150 °C using a pressurized reactor, with the use of dioxane as a solvent. These forcing reaction conditions were needed in order to overcome the steric hindrance involved, and favour a high degree of chlorine replacement. However, some chlorine remained in a few cases (one for every twenty repeat units for side group **c**, approximately one chlorine atom for every two repeat units in **8d**, and essentially no chlorine remained in **8e** and **8f**). The polymers were characterized by elemental analysis,

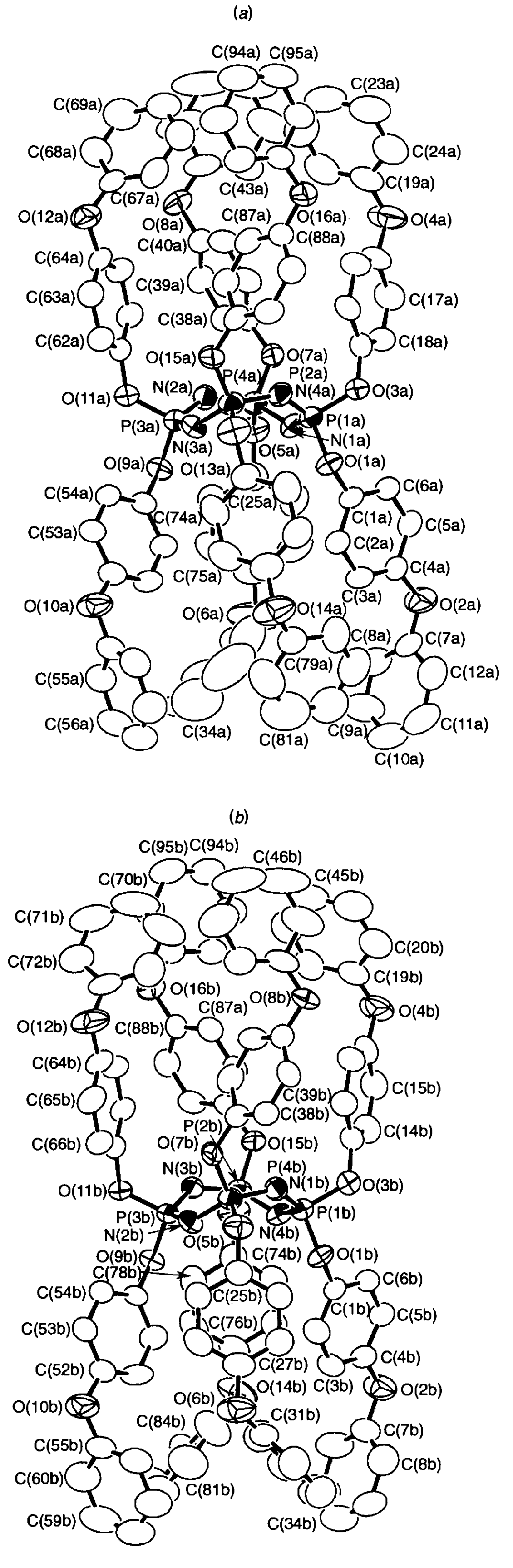


Fig. 7 An ORTEP diagram of the molecule $N_4P_4(OC_6H_4OPh\text{-}4)_8$ **4a** showing molecules a and b

^1H and ^{31}P NMR spectroscopy, differential scanning calorimetry to determine T_g and T_1 values, and gel permeation chromatography to estimate molecular weights (Table 1).

Polymer **8c** was formed with approximately 98% of the side groups being aryloxy units and only 2% unreacted chlorine atoms. This indicates that the presence of the *tert*-butyl group in the *para* position of the aryloxy nucleophile exerts little if any inhibition to the halogen-replacement process. However, the glass transition temperature is approximately 60 °C higher than the value for $[NP(OPh)_2]_n$, and this reflects the influence of the terminal group in inhibiting the thermally induced torsional motions of the polymer chain. The T_1 or microcrystalline melting temperature of 135 °C found is lower than the 160 and 390 °C reported for the phenoxy derivative and this probably reflects disorder introduced by the terminal group. The ^{31}P NMR shift is almost identical to that of $[NP(OPh)_2]_n$. The GPC average molecular weight of 2.5×10^6 is in the same range as values found for the phenoxy-substituted polymers.

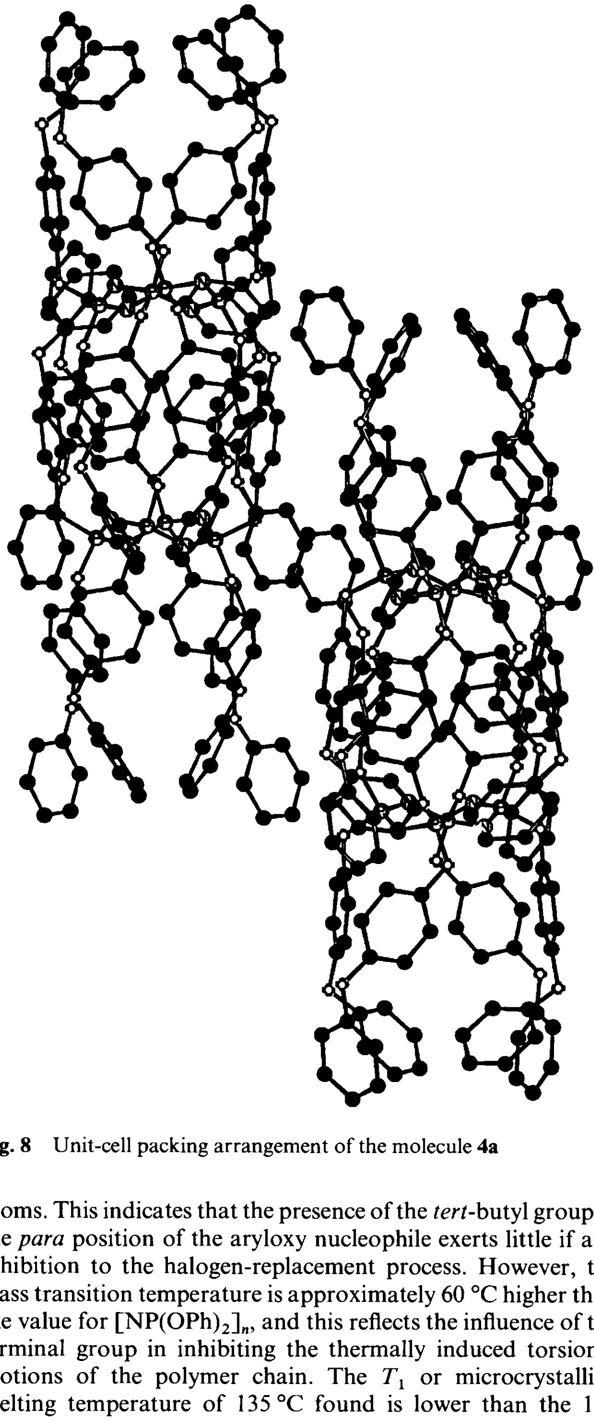


Fig. 8 Unit-cell packing arrangement of the molecule **4a**

The side groups in polymer **8d** are among the bulkiest that have been linked to a polyphosphazene chain and it is not surprising that roughly 25% of the chlorine atoms are not replaced even after forcing conditions. Indeed, it is surprising that the macromolecular substitution reaction proceeds beyond the 50% replacement stage. The steric hindrance imparted by the organic side groups is so strong that the remaining chlorine atoms are protected not only from reaction with the aryl oxide, but also from reaction with water. A glass transition temperature value of approximately 48 °C was measured for this polymer, but the DSC scan revealed only an indistinct transition and this value may not be accurate. No melting temperature was detected, perhaps a consequence of the disorder generated by the presence of two types of side groups.

Table 6 Pertinent bond distances (Å) and angles (°) for compound **4a**

P(1a)–N(1a)	1.559(5)	P(3a)–N(2a)	1.557(5)	P(1b)–N(1b)	1.557(5)	P(3b)–N(3b)	1.552(5)
P(1a)–N(4a)	1.561(5)	P(3a)–N(3a)	1.559(5)	P(1b)–O(1b)	1.569(4)	P(3b)–N(2b)	1.552(5)
P(1a)–O(1a)	1.579(4)	P(3a)–O(9a)	1.576(4)	P(1b)–N(4b)	1.570(5)	P(3b)–O(9b)	1.581(4)
P(1a)–O(3a)	1.581(4)	P(3a)–O(11a)	1.587(4)	P(1b)–O(3b)	1.591(4)	P(3b)–O(11b)	1.594(4)
P(2a)–N(2a)	1.556(5)	P(4a)–N(4a)	1.559(5)	P(2b)–N(1b)	1.561(5)	P(4b)–N(4b)	1.553(5)
P(2a)–N(1a)	1.556(5)	P(4a)–N(3a)	1.562(5)	P(2b)–O(7b)	1.565(4)	P(4b)–N(3b)	1.563(5)
P(2a)–O(7a)	1.561(4)	P(4a)–O(15a)	1.564(4)	P(2b)–N(2b)	1.569(5)	P(4b)–O(15b)	1.574(4)
P(2a)–O(5a)	1.578(4)	P(4a)–O(13a)	1.585(5)	P(2b)–O(5b)	1.581(4)	P(4b)–O(13b)	1.578(4)
N(1a)–P(1a)–N(4a)	120.5(3)	C(37a)–O(7a)–P(2a)	126.6(3)	N(1b)–P(1b)–N(4b)	121.6(3)	C(37b)–O(7b)–P(2b)	125.4(3)
O(1a)–P(1a)–O(3a)	99.7(2)	C(43a)–O(8a)–C(40a)	117.6(5)	O(1b)–P(1b)–O(3b)	98.9(2)	C(43b)–O(8b)–C(40b)	117.5(5)
N(2a)–P(2a)–N(1a)	120.8(3)	C(49a)–O(9a)–P(3a)	123.6(3)	N(1b)–P(2b)–N(2b)	120.7(3)	C(49b)–O(9b)–P(3b)	125.6(3)
O(7a)–P(2a)–O(5a)	99.7(3)	C(55a)–O(10a)–C(52a)	120.3(4)	O(7b)–P(2b)–O(5b)	100.0(3)	C(55b)–O(10b)–C(52b)	118.4(4)
N(2a)–P(3a)–N(3a)	121.4(3)	C(61a)–O(11a)–P(3a)	124.1(3)	N(3b)–P(3b)–N(2b)	121.1(3)	C(61b)–O(11b)–P(3b)	122.5(3)
O(9a)–O(3a)–O(11a)	98.7(2)	C(67a)–O(12a)–C(64a)	117.9(4)	O(9b)–P(3b)–O(11b)	99.3(2)	C(67b)–O(12b)–C(64b)	117.5(5)
N(4a)–P(4a)–N(3a)	120.8(3)	C(73a)–O(13a)–P(4a)	124.8(3)	N(4b)–P(4b)–N(3b)	120.9(3)	C(73b)–O(13b)–P(4b)	122.1(3)
O(15a)–P(4a)–O(13a)	98.2(3)	C(79a)–O(14a)–C(76a)	119.4(5)	O(15b)–P(4b)–O(13b)	99.6(3)	C(76b)–O(14b)–C(79b)	118.6(5)
C(1a)–O(1a)–P(1a)	124.5(3)	C(85a)–O(15a)–P(4a)	124.5(3)	C(1b)–O(1b)–P(1b)	124.0(3)	C(85b)–O(15b)–P(4b)	125.9(3)
C(7a)–O(2a)–C(4a)	120.0(5)	C(91a)–O(16a)–C(88a)	119.0(4)	C(7b)–O(2b)–C(4b)	119.4(4)	C(91b)–O(16b)–C(88b)	118.4(4)
C(13a)–O(3a)–P(1a)	124.0(3)	P(2a)–N(1a)–P(1a)	134.9(3)	C(13b)–O(3b)–P(1b)	123.5(3)	P(2b)–N(1b)–P(1b)	134.9(3)
C(19a)–O(4a)–C(16a)	118.7(5)	P(2a)–N(2a)–P(3a)	135.7(3)	C(19b)–O(4b)–C(16b)	118.5(5)	P(3b)–N(2b)–P(2b)	134.1(3)
C(25a)–O(5a)–P(2a)	120.9(3)	P(3a)–N(3a)–P(4a)	136.0(3)	C(25b)–O(5b)–P(2b)	122.1(3)	P(3b)–N(3b)–P(4b)	136.3(3)
C(31a)–O(6a)–C(28a)	116.9(6)	P(4a)–N(4a)–P(1a)	135.4(3)	C(31b)–O(6b)–C(28b)	117.9(5)	P(4b)–N(4b)–P(1b)	133.1(3)

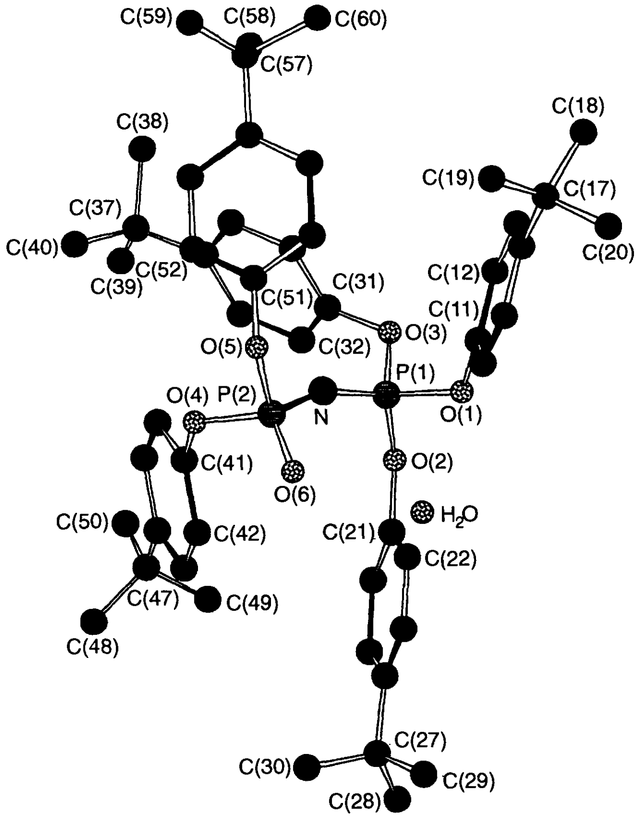
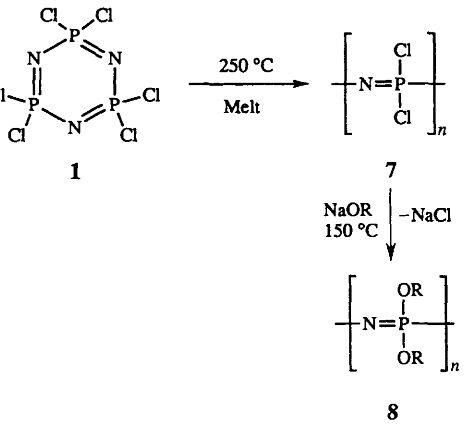


Fig. 9 An ORTEP diagram of the molecule OP(OC$_6$H$_4$Bu^t-4)$_2$NP(OC$_6$H$_4$Bu^t-4)$_3$ **6a**

Table 7 Pertinent bond distances (Å) and angles (°) for compound **6a**

P(1)–N	1.495(4)	P(2)–O(6)	1.449(5)
P(1)–O(1)	1.548(3)	O(1)–C(11)	1.408(4)
P(1)–O(2)	1.539(3)	O(2)–C(21)	1.410(5)
P(1)–O(3)	1.562(4)	O(3)–C(31)	1.398(5)
P(2)–N	1.578(5)	O(4)–C(41)	1.388(6)
P(2)–O(4)	1.578(4)	O(5)–C(51)	1.378(5)
P(2)–O(5)	1.582(3)		
N–P(1)–O(1)	118.8(2)	N–P(2)–O(6)	119.4(2)
N–P(1)–O(2)	118.4(2)	O(4)–P(2)–O(6)	114.4(2)
O(1)–P(1)–O(2)	101.4(2)	O(5)–P(2)–O(6)	106.5(3)
N–P(1)–O(3)	113.3(2)	P(1)–N–P(2)	157.0(3)
O(1)–P(1)–O(3)	102.1(2)	P(1)–O(1)–C(11)	121.3(2)
O(2)–P(1)–O(3)	101.1(3)	P(1)–O(2)–C(21)	127.0(3)
N–P(2)–O(4)	106.3(2)	P(1)–O(3)–C(31)	121.2(3)
N–P(2)–O(5)	109.2(2)	P(2)–O(4)–C(41)	121.5(3)
O(4)–P(2)–O(5)	99.2(2)	P(2)–O(5)–C(51)	124.5(4)



Scheme 4 OR = **c**–**g** as in Scheme 1

The ^{31}P NMR shift at δ −21.4 is similar to that of [NP(OPh)$_2$]$_n$. The measured molecular weight of 1 × 10^6 suggests that little or no depolymerization occurred during the synthesis and purification of the polymer.

Polymer **8e** contained essentially no unreacted chlorine and this is consistent with the use of a nucleophile that generates only minimum steric constraints due to its elongated profile and flexibility at the ether linkage. The T_g value of 17 °C is similar to that of **8c** (and **8f**) and for similar reasons. Microcrystallinity was evident from the T_1 value at 126 °C. Again, the ^{31}P NMR shift at δ −18.2 is similar to that of [NP(OPh)$_2$]$_n$.

The introduction of an OCH$_2$ unit in place of an -O- linkage between the phenyl rings does not affect the ease of halogen replacement. Polymer **8f** contained essentially no residual chlorine. Its ^{31}P NMR spectrum and molecular weight were similar to those of polymer **8e**, but the T_g value of 30 °C indicated slightly less molecular flexibility than in **8e**.

Polymer **8g** proved to be difficult to synthesize, and this was attributed to a possible instability of the P–O–alkyl linkage at the elevated temperatures required for substitution, and to a possible reduced nucleophilicity of the alkoxide compared to the aryl oxides used for the other syntheses. The products from these reactions also cross-linked during purification, and this suggested the presence of appreciable ratios of residual reactive P–Cl bonds.

Conclusion

Phenoxy-substituted phosphazene cyclic trimers and tetramers were some of the earliest organophosphazenes to be synthesized and characterized[29] and a phenoxy-substituted phosphazene high polymer was one of the first stable phosphazenes to be reported.[18–21] Since that time high polymers with various alkyl and aryl substituent groups linked to the phenoxy side units have played a major role in the industrial development of polyphosphazene elastomers and in the exploration of phosphazenes as structural, fibrous and optical materials. Yet many of these macromolecular developments have occurred in the absence of fundamental data about the influence of the terminal groups linked to aryloxy units on reaction pathways and molecular conformations.

In this paper we have shown that, provided the terminal unit is at the *para* position of the aryl oxide nucleophile, few steric hindrance constraints exist that would limit the number of accessible reactions at the small-molecule level. The preliminary results described here and in other recent papers[1,2] suggest that this situation persists at the level of macromolecular substitution also, provided the steric hindrance close to the reactive terminus of the aryl oxide is not excessive.

It could be argued that molecular structural information obtained for small-molecule cyclic trimers and tetramers is only of peripheral value for understanding the forces that control conformation and chain packing at the high-polymer level. Nevertheless, data from small molecule rings provide virtually the only structural information accessible at this time that can be used to analyse the behaviour of high polymers. The use of phosphazene short chains such as **6a** offers information that may be more relevant to linear high polymers, but even here the structural features are probably dominated by the end groups in ways that are not pertinent to molecules that may contain 15 000 or more repeating units for every two end units. The answer clearly lies in the study of longer linear oligomeric phosphazenes, as we have attempted to do in earlier publications,[22–24] but these species provide a special challenge with respect to synthesis and crystallization for X-ray studies. Perhaps the most important structural conclusions to be derived from this paper are related to the orientation of the various aryloxy side groups and their intramolecular interactions. These interactions and the cone-angle volumes swept out by the side units appear to dominate the small-molecule structures, and will presumably exert an even more profound influence on the conformations and packing of the highly flexible long chains found in the macromolecules.

Experimental

Analytical techniques

The ^{31}P NMR (^1H-decoupled) spectra were obtained with the use of a JEOL FX-90Q NMR spectrometer operated at 36.2 MHz; chemical shifts are relative to 85% H_3PO_4 at δ 0 with positive values downfield from the reference. Glass transition temperatures (T_g) were recorded with the use of a Perkin-Elmer DSC-7 unit equipped with a PE 7500 computer. The samples (10–30 mg) were analysed in crimped aluminium pans: a heating rate of 40 °C min^{-1} and a helium flow of 10 cm^3 min^{-1} were used. The instrument was calibrated with a cyclohexane standard, with thermal transitions at −87.06 and 6.54 °C. Infrared spectra were recorded with the use of a Perkin-Elmer model 283B grating spectrometer, and ion-impact mass spectra with an AEC/MS 902 mass spectrometer. Molecular weight data were obtained with a Hewlett-Packard 1090 liquid chromatograph equipped with an HP 1037A refractive-index detector and using a polystyrene standard. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Materials

Hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene were provided by Ethyl Corporation and purified by recrystallization from hexane and sublimation at 50 °C (0.05 mmHg, *ca.* 6.65 Pa). All solvents were dried either over sodium–benzophenone or calcium hydride and were distilled in an atmosphere of dry nitrogen before use. 4-Benzyloxyphenol, 4-benzyloxybenzyl alcohol, *p*-cresol and 4-methoxyphenol were obtained from Aldrich and purified by sublimation. Boron trichloride, sodium and sodium hydride (Aldrich) were used as received. All reactions were carried out in an atmosphere of dry nitrogen.

Syntheses

$[NP(OC_6H_4CH_3\text{-}4)_2]_3$ 2a.[25] The compound $(NPCl_2)_3$ (2.03×10^{-2} mol) in dioxane (150 cm^3) was added slowly to a stirred solution of the sodium salt of *p*-cresol (0.23 mol) in dioxane (400 cm^3). The mixture was heated at reflux for 48 h after which time it was cooled and filtered through silica gel. The filtrate was concentrated, dissolved in toluene and extracted with 1 mol dm^{-3} NaOH (3 ×) and distilled deionized water (2 ×). After extraction the filtrate was concentrated and the remaining residue recrystallized from hexanes. The product was purified by column chromatography using a dichloromethane eluent.

$[NP(OC_6H_4OH\text{-}4)_2]_3$ 2b.[26] (*a*) $[NP(OC_6H_4OCH_3\text{-}4)_2]_3$. The compound $(NPCl_2)_3$ (3.4×10^{-2} mol) was dissolved in dioxane (150 cm^3). To this solution was added a solution of sodium 4-methoxyphenoxide (0.564 mol) in dioxane (600 cm^3). The mixture was refluxed for 24 h, then cooled to room temperature, filtered through silica gel, and concentrated. The oily residue was dissolved in diethyl ether and extracted with 1 mol dm^{-3} NaOH (3 ×) and distilled deionized water (3 ×). The resulting product was recrystallized twice from methanol.

(*b*) $[NP(OC_6H_4OH\text{-}4)_2]_3$. The compound $[NP(OC_6H_4\text{-}OCH_3\text{-}4)_2]_3$ (5.79×10^{-3} mol) was dissolved in dry methylene chloride (20 cm^3). A boron trichloride solution (150 cm^3 of 1 mol dm^{-3} BCl_3 in CH_2Cl_2) was added by syringe and the mixture stirred at room temperature for 48 h. It became dark amber. The reaction mixture was then quenched by addition of methanol and then sodium hydrogencarbonate, gravity filtered, passed through silica gel and concentrated. The final product was purified by column chromatography using tetrahydrofuran (thf)–dichloromethane (1 : 1) as eluent.

$[NP(OC_6H_4Bu^t\text{-}4)_2]_3$ 2c. The compound $(NPCl_2)_3$ (2.87×10^{-2} mol) in thf (150 cm^3) was allowed to react with a solution of sodium 4-*tert*-butylphenoxide (0.344 mol) and boiled at reflux for 12 h. After filtration and reduction of the solvent volume, the crude product was chromatographed through a silica gel column using a dichloromethane–hexane mixture as eluent. The product was recrystallized from a dichloromethane–hexane solution.

$[NP(OC_6H_4CPh_3\text{-}4)_2]_3$ 2d. A solution of $(NPCl_2)_3$ (2.87×10^{-2} mol) in dioxane (75 cm^3) was added dropwise to a solution of sodium tritylphenoxide (2.3×10^{-2} mol) at 80 °C. The reaction mixture was boiled at reflux for 7 h. The solvent was then removed under reduced pressure and the residual product extracted with dichloromethane. It was recrystallized from a dichloromethane–hexane solution.

Table 8 Summary of crystal data and intensity-collection parameters[a]

	2a	**2b**	**2e**	**2f**	**4a**	**6a**
Formula	$C_{42}H_{42}N_3O_6P_3$	$C_{36}H_{30}N_3O_{12}P_3 \cdot 3H_2O$	$C_{72}H_{54}N_3O_{12}P_3$	$C_{78}H_{66}N_3O_{12}P_3$	$C_{96}H_{72}N_4O_{16}P_4$	$C_{50}H_{65}NO_6P_2 \cdot H_2O$
M	777.7	843.6	1246.2	1330.3	1661.5	856
a/Å	9.791(2)	9.577(5)	15.348(2)	9.297(5)	16.728(1)	13.058(5)
b/Å	11.399(4)	10.147(2)	15.567(3)	15.551(4)	20.516(9)	14.467(2)
c/Å	18.495(3)	20.395(6)	16.035(2)	23.342(4)	25.760(2)	14.840(11)
α/°	97.86(2)	77.65(2)	77.02(2)	84.12(2)	106.04(3)	70.07(3)
β/°	95.33(1)	85.45(3)	66.55(3)	89.44(3)	93.55(6)	84.38(4)
γ/°	102.85(2)	84.03(2)	59.87(4)	80.55(2)	101.33(1)	74.55(3)
U/Å^3	1977.2	1922.5	3038.2	3311.3	8266.9	2540.2
Z	2	2	2	2	4	2
D_c/g cm^{-3}	1.306	1.463, 1.457 (obs)	1.362	1.33	1.335, 1.33 (obs)	1.12
μ/cm^{-1}	1.79	2.2	1.604	1.58	1.64	10.65
Radiation (λ/Å)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Cu-Kα (1.5418)
$R, R'_w = (\Sigma\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.085, 0.112	0.050, 0.050	0.0348, 0.0447	0.057, 0.065	0.0567, 0.151	0.0918, 0.1066
Unique data	6725	5339	5654	6786	16 307	9601
Data used	4319	4224	4981	4342	9584	6030
Number of parameters	487	489	811	865	1777	328
Data/parameter	8.87	8.64	6.1	5[b]	5.5[b]	18.40[b]
$(\Delta/\sigma)_{max}$ in last cycle	< 0.1	< 0.1	0.01	0.16	0.13	< 0.1
$\Delta\rho$/e Å^{-3} in final ΔF map	0.40	0.40	0.32	0.30	0.33	0.488

[a] Details in common: triclinic, space group $P\bar{1}$. [b] Structure was refined in blocks due to its size.

$[NP(OC_6H_4OPh\text{-}4)_2]_3$ 2e. A solution of $(NPCl_2)_3$ (2.87×10^{-2} mol) in dioxane (20 cm^3) was added dropwise to a stirred solution of sodium 4-phenoxyphenoxide (2.15×10^{-2} mol) at room temperature. The mixture was refluxed for 20 h, and then cooled to room temperature. Filtration and removal of the solvent left an oily product. The compound was purified by gradient elution through a silica gel chromatography column with dichloromethane as solvent. It was recrystallized from toluene and hexane.

$[NP(OC_6H_4OCH_2Ph\text{-}4)_2]_3$ 2f. A solution of $(NPCl_2)_3$ (4.31×10^{-3} mol) in dioxane (25 cm^3) was added dropwise to a stirred solution of sodium 4-benzyloxyphenoxide (3.6×10^{-2} mol) in dioxane (150 cm^3). The mixture was boiled at reflux for 17 h, and then cooled to room temperature. Filtration and removal of the solvent left a solid product. This compound was purified by gradient elution through a silica gel column with a thf–hexane mixture. It was recrystallized from a dichloromethane–hexane mixture.

$[NP(OCH_2C_6H_4OCH_2Ph\text{-}4)_2]_3$ 2g. The compound $(NPCl_2)_3$ (2.30×10^{-2} mol) in dioxane (25 cm^3) was added slowly to a stirred solution of sodium 4-benzyloxybenzyloxide (2.02×10^{-2} mol) in dioxane (125 cm^3) at room temperature. After the mixture had been stirred for 17 h the solvent was removed by rotary evaporation. The product was purified by column chromatography using a dichloromethane–hexane mixture as eluent.

$[NP(OC_6H_4OPh\text{-}4)_2]_4$ 4a. A solution of $(NPCl_2)_4$ (4.3×10^{-3} mol) in dioxane (30 cm^3) was added to a stirred solution of sodium 4-phenoxyphenoxide (6.9×10^{-2} mol) in dioxane (75 cm^3) at room temperature. The reaction mixture was refluxed for 24 h, then cooled to room temperature and the solvent removed. The product was dissolved in dichloromethane and was filtered through silica gel. The dichloromethane was removed and the residue dissolved in toluene and extracted with aqueous 1 mol dm^{-3} NaOH. The toluene was removed and the product purified by column chromatography using a dichloromethane–hexane mixture as eluent.

$OP(OC_6H_4Bu^t\text{-}4)_2NP(OC_6H_4Bu^t\text{-}4)_3$ 6a. A solution of $OPCl_2NPCl_3$ (7.4×10^{-2} mol) in dioxane (100 cm^3) was treated with a solution of sodium 4-*tert*-butylphenoxide (7.4×10^{-2} mol) in dioxane (100 cm^3). The reaction mixture was stirred at room temperature for 3 h. After filtration and reduction of the solvent volume, the crude product was chromatographed through a silica gel column using a dichloromethane–hexane mixture as eluent. It was recrystallized from hexane by slow evaporation.

High polymers. The following procedure for $[NP(OC_6H_4OPh\text{-}4)_2]_n$ is a typical synthesis of the polymers discussed. A solution of $(NPCl_2)_n$ (3.0 g, 5.3×10^{-2} mol) in dioxane (250 cm^3) and a solution of sodium 4-phenoxyphenoxide [prepared from Na (5.59 g, 0.243 mol) and 4-phenoxyphenol (47.28 g, 0.245 mol) in dioxane (300 cm^3)] were placed in an autoclave. The mixture was heated to 150 °C for 40 h, then cooled to room temperature. It was concentrated, and the polymer recovered by precipitation into water. The reaction product was soluble in thf and was purified by repeated precipitations into water and hexane from a thf solution. It was further purified by Soxhlet extraction against methanol (72 h) and hexane (72 h), then dried under vacuum.

Crystallography

Our general X-ray diffraction technique has been described in earlier papers[30,31] and only details related to the present work will be given here. Crystals were cut to be roughly equidimensional with ≈0.25–0.5 mm along each edge. Crystallographic data were collected at 293 K with the use of an Enraf-Nonius CADIV diffractometer controlled either by a PDP 11/44 computer or by the CAD4PC program installed on a Gateway 2000 386 mb computer. The structures were solved by direct methods using the program SDP[32] installed on the PDP 11/44 and also SHELXS and MULTAN[33] installed on the Pennsylvania State University IBM-VMS computer. Structure **4a** was refined using SHELXL with F^2 employed in the refinements and with the benzene rings constrained as regular hexagons; **2f** was refined using TEXSAN. Several of the ORTEP diagrams were generated using CHEM3D molecular modelling software.

In each case, the first E map revealed the position of all non-hydrogen atoms. In compounds **2a**, **2b**, **2e** and **6a** all the non-hydrogen atoms were refined anisotropically. Fourier-difference syntheses, calculated towards the end of the refinements, showed maxima consistent with the expected positions of hydrogen atoms in all the structures. In all structures hydrogen atoms were included at geometrically idealized positions with overall isotropic thermal parameters. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[34] and those for hydrogen atoms from Stewart *et al.*[35] At the conclusion of refinement the ΔF maps were essentially featureless. Crystal data and intensity collection parameters are summarized in Table 8.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/120.

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