Synthesis and Structure of Small-molecule Phosphazene Rings bearing Fused-ring Aryloxy Side Groups: Models for Optically Useful 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 cyclic tri- and tetra-meric phosphazenes $[NP(OR)_2]_n$ (n = 3 or 4), $N_3P_3(OR)Cl_5$ and $N_3P_3(OR)_4Cl_2$ has been prepared with 1- or 2-naphthyloxy, 1-naphthylmethyloxy, 1-naphthylethyloxy, 9-anthryloxy and 9-phenanthryloxy side groups OR. These syntheses are model processes for the preparation of the corresponding phosphazene high polymers. The small-molecule compounds were characterized by a combination of ^{31}P NMR and mass spectroscopy, elemental analysis and crystal structures of six compounds. Attempts to synthesize the corresponding phosphazene high polymers by similar substitution techniques were, in general, successful, with high-temperature reaction conditions needed to overcome steric hindrance effects.

Of all the small-molecule and high polymeric phosphazenes that exist or are accessible using known techniques, those that bear aryloxy side groups generate some of the most interesting and potentially useful properties. High polymeric phosphazenes with aryloxy side groups are of interest as high refractive index glasses,[1,2] ferroelectric and non-linear optical polymers,[3,4] liquid-crystalline materials[5-9] and photoactive polymers.[10-17] In general, it can be argued that the refractive index and other optical and electronic properties become more interesting as the aryloxy side groups contain two or more fused aromatic rings because of the resultant electron delocalization. Moreover, the opportunities that exist for side groups to assume coplanarity with their counterparts elsewhere in a solid-state system may favour the generation of microcrystalline domains, which would constitute scattering centres in an optical glass. With these facts in mind, we have been involved in a project to design and synthesize a broad range of different fused-ring aryloxy-substituted phosphazene polymers and to study their properties. For example, refractive index values as high as 1.75 have recently been generated by the linkage of iodo-2-naphthyloxy side groups to a high polymeric phosphazene chain.[2]

Most poly(organophosphazenes) are synthesized by macromolecular substitution reactions in which organic nucleophiles are allowed to react with poly(dichlorophosphazene). These reactions were discovered in our program[18-21] and the synthesis method is now well established. However, because these macromolecular substitution reactions are of the S_N2 type, they are affected by the steric characteristics of both the organic nucleophile and the organic side groups introduced during the earlier stages of the reaction. This is a particular problem when the nucleophile is a fused-ring aromatic species. For this reason, the development of new macromolecular reactions of this type requires that the substitution processes should be attempted first with small-molecule model systems. Moreover, because of the inherent difficulties in the detailed structure determination of high polymers, it is essential that primary molecular structural information be obtained from the small-molecule model systems and then applied judiciously to the high polymeric counterparts. This paper deals with a number of these small-molecule model reactions and with the structures of several of the products. It also illustrates the transposition of these reactions to the high polymer level.

Four questions were kept in mind throughout this work: (1) can all the chlorine atoms linked to a phosphazene ring or polymer chain be replaced by bulky, fused-ring aryloxy units without significant skeletal cleavage or other side reactions? (2) If only partial chlorine replacement is possible, which halogen sites are the least reactive, and why? (3) To what extent can the special characteristics of the model reactions be expected to persist when the reactions are transposed to the high polymeric level? (4) Do any unusual structural features exist for these ring systems that might be important for the behaviour of the analogous linear high polymers?

Results and Discussion

Synthesis and Characterization of Cyclic Trimeric and Tetrameric Fused-ring Aryloxyphosphazenes.—The reaction sequence used for the synthesis of these compounds is shown in Schemes 1 and 2, together with the specific aryloxy units studied. The reactions involve the nucleophilic replacement of chlorine atoms in hexachlorocyclo-$2\lambda^5,4\lambda^5,6\lambda^5$-triphosphazene **1** or octachlorocyclo-$2\lambda^5,4\lambda^5,6\lambda^5,8\lambda^5$-tetraphosphazene **5** by aryl oxide ions to introduce side groups **a**–**f**. In a few cases, partly substituted species such as **2** or **3** were isolated and characterized as well as fully substituted species. No fully substituted species corresponding to **4e** was isolated, presumably for reasons of steric hindrance. In all cases, the reaction yields ranged from 70 to 85%.

The products were identified initially by ^{31}P NMR analysis, elemental microanalysis, infrared spectroscopy and mass spectrometry as summarized in Table 1. Specifically, the ^{31}P NMR spectra of fully substituted species **4a**–**4d**, **4f**, **6a** and **6b** consisted of a single peak, with the chemical shift varying with the different side groups (Table 1). The spectra of compounds **2e** and **3e** consisted of AB spin systems (A_2B or AB_2) which were consistent with the structures shown in Scheme 1. Infrared spectra showed absorbances in the 1100–1200 cm^{-1} range characteristic of P=N bonded cyclic skeletal systems. Except for compound **4c**, the mass spectra showed parent ions corresponding to the expected molecular weights. More extensive characterization of compounds **4a**, **4b**, **2e**, **3e**, **6a** and **6b** was obtained from single-crystal X-ray diffraction studies. The remaining products were not studied by X-ray techniques

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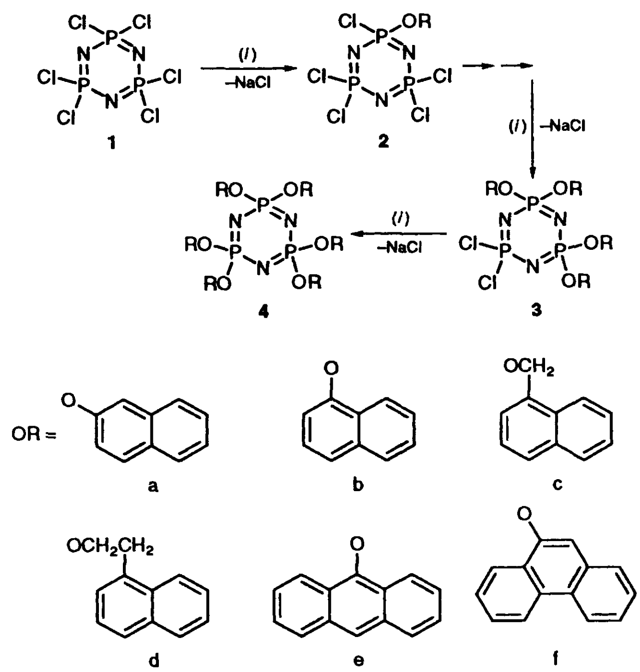
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

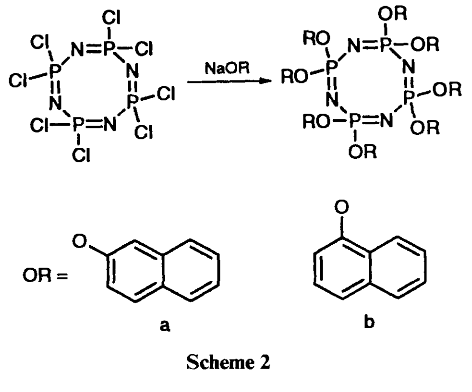
Table 1 Characterization data

Compound	M.p./°C	Mass spectral data (molecular ion mass)[a]	Analysis (%)[a] C	H	N	^{31}P NMR Chemical shifts (δ) PCl_2	$P(OR)_2$
4a	166.5–168	993	72.35	4.40	4.25		8.49
		(993)	(72.50)	(4.25)	(4.25)		
4b	111–112	993	72.60	4.35	4.40		9.34
		(993)	(72.50)	(4.25)	(4.25)		
4c	119–121	*b*	73.35	5.25	4.20		17.98
		(1077)	(73.50)	(5.05)	(3.90)		
4d	Oil	1161	74.00	5.50	4.20		17.82
		(1161)	(74.40)	(5.70)	(3.60)		
4f	131[c]	1293	77.80	4.40	3.25		9.3
		(1293)	(77.95)	(4.15)	(3.25)		
2e[d]	161–162	505	32.70	1.80	8.25	21.97	
		(505)	(33.25)	(1.80)	(8.30)		
3e[e]	> 300	977	63.60	3.65	3.30	24.60	3.20
		(977)	(68.70)	(3.70)	(4.30)		
6a	131–132	1324	72.20	4.60	4.15		−11.9
		(1324)	(72.20)	(4.25)	(4.25)		
6b	147–148	1324	69.00	4.40	4.00		−13.8
		(1324)	(72.20)	(4.25)	(4.25)		

[a] Calculated values in parentheses. [b] Unresolved. [c] With decomposition. [d] δ 13.37 for PCl(OR). [e] Discrepancies in the microanalyses reflect the presence of carbon tetrachloride or dichloromethane in the crystal lattice.



Scheme 1 (*i*) NaOR



Scheme 2

because single crystals of sufficiently high quality were not obtained.

Crystal and Molecular Structures.—Compound **4a**. Compound **4a** is the only derivative in this series that has been reported previously. Its crystal structure was previously determined by Bandoli *et al.*,[22] to an *R* factor of 0.090. We had independently carried out a structure determination to $R = 0.062$ which agrees with the general features of that study. Our results are reported here for direct comparison with the other structures studied. The structure is characterized by a slightly puckered cyclotriphosphazene ring with an average P–N bond length of 1.576(2) Å and individual values of 1.568(2), 1.579(2), 1.578(2) (two) and 1.577(2) Å (two). The average N–P–N ring angle is 117.1(1)° with individual values of 118.4(1), 117.8(1) and 116.9(1)°. The average P–N–P bond angle is 121.5(2) Å with individual values of 121.6(2), 121.8(1) and 121.2(1)°. The naphthalene rings are normal in all respects, with P–O–C connecting links having an average bond angle of 124.7(2)° with individual values of 128.3(2), 124.2(2), 119.1(2), 129.2(2), 121.4(2) and 125.9(2)°. The average O–P–O angle is 99.0(1)° with individual values of 98.9(1), 99.1(1) and 99.0(1)°. As shown in Fig. 1, the side groups are oriented in a quasi-collinear fashion above and below the plane of the phosphazene ring, leaving the edge of the phosphazene ring relatively exposed. However, the naphthyloxy units are *not* coplanar with each other. The packing diagram shown in Fig. 2 illustrates that some *inter*molecular side-group coplanarity can be discerned of a type that suggests the possibility of polymer excimer interactions if the arrangement persists in a high polymeric counterpart. Selected bond lengths and angles for **4a** are listed in Table 2.

Compound **4b**. The structure of compound **4b** was solved to $R = 0.076$. The phosphazene ring is essentially planar, with an average P–N bond length of 1.575(4) Å and individual values of 1.565(4), 1.583(3), 1.576(4), 1.593(4), 1.555(4) and 1.570(4) Å. The average N–P–N ring angle is 117.3(2)° with individual values of 117.2(2)°, 116.7(2) and 118.0(2)°. The P–N–P average ring angle is 122.7(2)° with individual values of 123.1(2), 122.6(2) and 122.4(2)°. The naphthyloxy groups are normal. The P–O–C connecting angles average 126.2(3)° with individual values of 122.7(3), 126.5(3), 126.4(3), 124.2(3), 129.8(4) and 127.6(3)°. The O–P–O angles have an average of 98.0(2)° with individual values of 98.6(2), 93.0(2) and 102.7(2)°. The variations in these angles probably reflect differences in steric

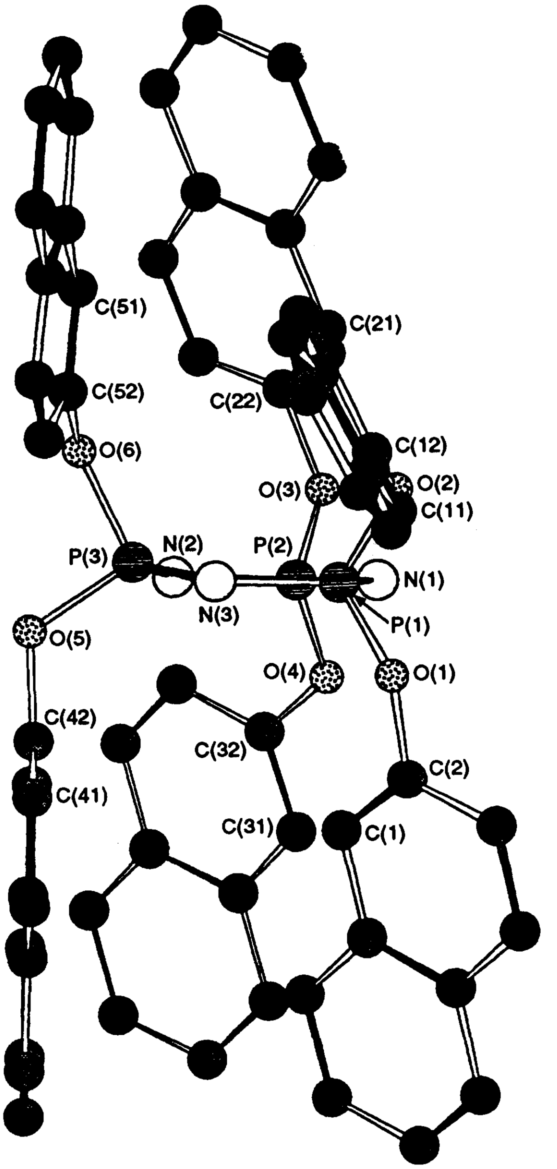


Fig. 1 An ORTEP[23] diagram of the molecular structure of $N_3P_3(2\text{-}OC_{10}H_7)_6$ **4a**

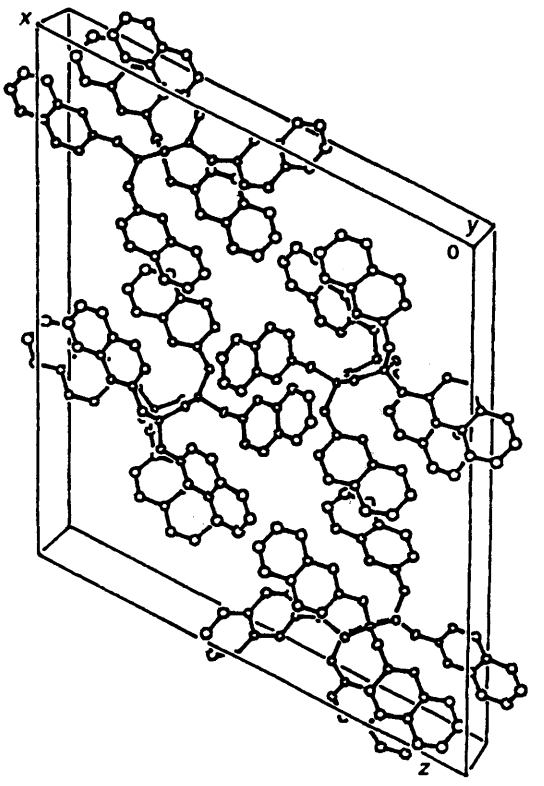


Fig. 2 Unit-cell packing arrangement of $N_3P_3(2\text{-}OC_{10}H_7)_6$ **4a**

Table 2 Bond distances (Å) and angles (°) for compound **4a**

P(1)–O(1)	1.591(2)	P(3)–O(6)	1.584(2)
P(1)–O(2)	1.585(2)	P(3)–N(2)	1.577(2)
P(1)–N(1)	1.568(2)	P(3)–N(3)	1.577(2)
P(1)–N(3)	1.579(2)	O(1)–C(2)	1.394(3)
P(2)–O(3)	1.594(2)	O(2)–C(12)	1.415(3)
P(2)–O(4)	1.564(2)	O(3)–C(22)	1.414(3)
P(2)–N(1)	1.578(2)	O(4)–C(32)	1.406(3)
P(2)–N(2)	1.578(2)	O(5)–C(42)	1.408(3)
P(3)–O(5)	1.581(2)	O(6)–C(52)	1.405(3)
O(1)–P(1)–O(2)	98.9(1)	P(2)–O(3)–C(22)	119.1(2)
O(1)–P(1)–N(1)	111.5(1)	P(2)–O(4)–C(32)	129.2(2)
O(1)–P(1)–N(3)	109.0(1)	P(3)–O(5)–C(42)	121.4(2)
O(2)–P(1)–N(1)	105.6(1)	P(3)–O(6)–C(52)	125.9(2)
O(2)–P(1)–N(3)	111.6(1)	P(1)–N(1)–P(2)	121.6(2)
N(1)–P(1)–N(3)	118.4(1)	P(2)–N(2)–P(3)	121.8(1)
O(3)–P(2)–O(4)	99.1(1)	P(1)–N(3)–P(3)	121.2(1)
O(3)–P(2)–N(1)	111.3(1)	O(1)–C(2)–C(1)	125.2(2)
O(3)–P(2)–N(2)	109.1(1)	O(1)–C(2)–C(3)	112.6(2)
O(4)–P(2)–N(1)	105.6(1)	O(2)–C(12)–C(11)	120.6(2)
O(4)–P(2)–N(2)	112.4(1)	O(2)–C(12)–C(13)	116.7(2)
N(1)–P(2)–N(2)	117.8(1)	O(3)–C(22)–C(21)	121.0(2)
O(5)–P(3)–O(6)	99.0(1)	O(3)–C(22)–C(23)	116.9(2)
O(5)–P(3)–N(2)	110.0(1)	O(4)–C(32)–C(31)	114.8(2)
O(5)–P(3)–N(3)	109.6(1)	O(4)–C(32)–C(33)	122.4(2)
O(6)–P(3)–N(2)	107.3(1)	O(5)–C(42)–C(41)	120.2(2)
O(6)–P(3)–N(3)	112.6(1)	O(5)–C(42)–C(43)	117.2(2)
N(2)–P(3)–N(3)	116.9(1)	O(6)–C(52)–C(51)	116.7(3)
P(1)–O(1)–C(2)	128.3(2)	O(6)–C(52)–C(53)	120.7(2)
P(1)–O(2)–C(12)	124.2(2)		

Numbers in parentheses are estimated standard deviations in the least significant digits. Naphthyloxy (anthryloxy in Tables 4 and 5) ring carbons are set to a 1.395 Å C–C bond distance and a 120.0° C–C–C bond angle in the refinement program.

factors and packing orientations rather than electronic differences. Little or no evidence was found for intra- or intermolecular side-group coplanarity or stacking in this system (Figs. 3 and 4). Selected bond lengths and angles are listed in Table 3.

Compound **2e**. Compound **2e**, with a single 9-anthryloxy unit linked to the cyclic trimeric ring platform, was solved to *R* 0.030 (Fig. 5). The phosphazene ring is planar. The average P–N bond length is 1.579 Å. Although the individual bond lengths are very similar, they do fall into two groups. Those that are adjacent to the site of organic substitution and those most distant from the site of substitution and are similar in length, being 1.586(3), 1.587(3), 1.580(3) and 1.583(3) Å respectively, but with the remaining P–N bonds being shorter at 1.569(3) and 1.572(3) Å. This follows a pattern repeated for many asymmetrically substituted cyclotriphosphazenes and may reflect electronic influences within the ring. The phosphazene ring N–P–N angles have an average value of 118.0(2)°, with individual values being 116.6(2), 118.6(2) and 119.0(2)° and with the narrowest of these angles being at the site of substitution. The P–N–P angles average 121.0(2)°, with individual values being 121.3(2), 120.3(2) and 121.4(2)°. The anthracene ring appears to be normal in its planarity and its

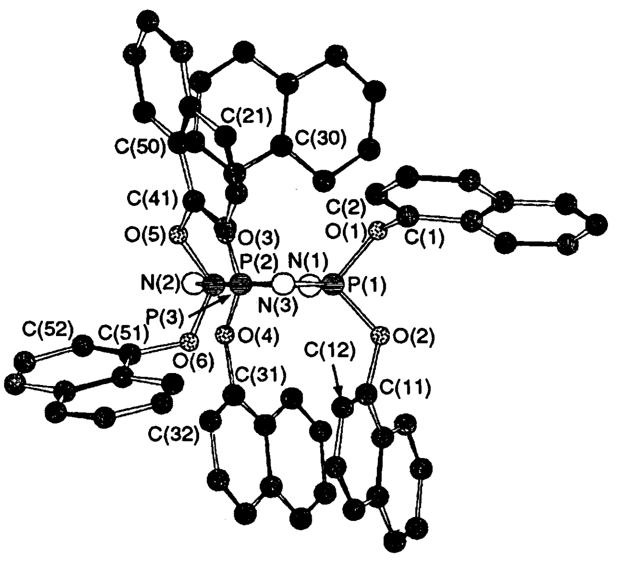


Fig. 3 An ORTEP diagram of the molecular structure of $N_3P_3(1\text{-}OC_{10}H_7)_6$ **4b**

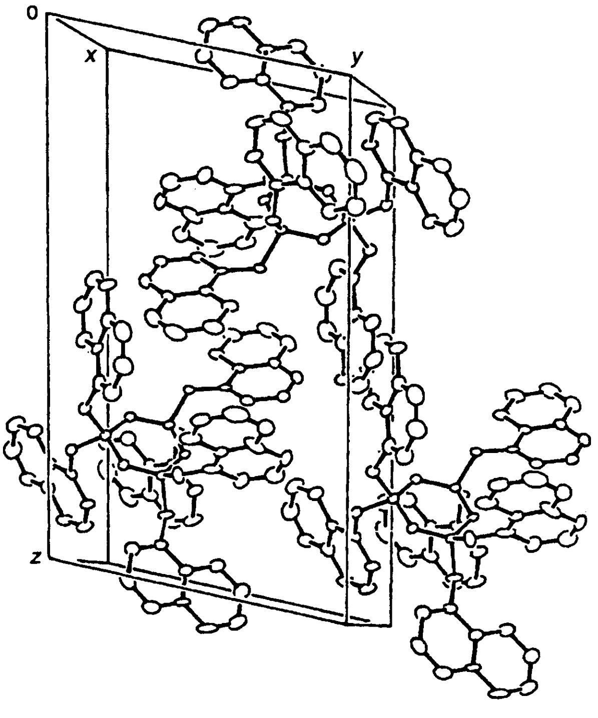


Fig. 4 Unit-cell packing arrangement of $N_3P_3(1\text{-}OC_{10}H_7)_6$ **4b**

Table 3 Bond distances (Å) and angles (°) for compound **4b**

P(1)–O(1)	1.584(3)	P(3)–O(6)	1.594(3)
P(1)–O(2)	1.591(3)	P(3)–N(2)	1.555(4)
P(1)–N(1)	1.565(4)	P(3)–N(3)	1.570(4)
P(1)–N(3)	1.583(3)	O(1)–C(1)	1.391(5)
P(2)–O(3)	1.588(3)	O(2)–C(11)	1.408(5)
P(2)–O(4)	1.583(3)	O(3)–C(21)	1.408(5)
P(2)–N(1)	1.576(4)	O(4)–C(31)	1.413(5)
P(2)–N(2)	1.593(4)	O(5)–C(41)	1.374(7)
P(3)–O(5)	1.564(3)	O(6)–C(51)	1.400(6)
O(1)–P(1)–O(2)	98.6(2)	P(2)–O(3)–C(21)	126.4(3)
O(1)–P(1)–N(1)	107.1(2)	P(2)–O(4)–C(31)	124.2(3)
O(1)–P(1)–N(3)	111.7(2)	P(3)–O(5)–C(41)	129.8(4)
O(2)–P(1)–N(1)	110.3(2)	P(3)–O(6)–C(51)	127.6(3)
O(2)–P(1)–N(3)	110.3(2)	P(1)–N(1)–P(2)	123.1(2)
N(1)–P(1)–N(3)	117.2(2)	P(2)–N(2)–P(3)	122.6(2)
O(3)–P(2)–O(4)	93.0(2)	P(1)–N(3)–P(3)	122.4(2)
O(3)–P(2)–N(1)	112.2(2)	O(1)–C(1)–C(2)	121.3(4)
O(3)–P(2)–N(2)	111.0(2)	O(1)–C(1)–C(10)	117.6(4)
O(4)–P(2)–N(1)	110.5(2)	O(2)–C(11)–C(12)	120.4(5)
O(4)–P(2)–N(2)	111.1(2)	O(2)–C(11)–C(20)	117.0(5)
N(1)–P(2)–N(2)	116.7(2)	O(3)–C(21)–C(22)	119.4(7)
O(5)–P(3)–O(6)	102.7(2)	O(3)–C(21)–C(30)	118.6(5)
O(5)–P(3)–N(2)	106.2(2)	O(4)–C(31)–C(32)	121.0(4)
O(5)–P(3)–N(3)	113.3(2)	O(4)–C(31)–C(40)	114.8(5)
O(6)–P(3)–N(2)	111.2(2)	O(5)–C(41)–C(42)	119.5(6)
O(6)–P(3)–N(3)	104.5(2)	O(5)–C(41)–C(50)	123.4(6)
N(2)–P(3)–N(3)	118.0(2)	O(6)–C(51)–C(52)	121.5(5)
P(1)–O(1)–C(1)	122.7(3)	O(6)–C(51)–C(60)	116.4(5)
P(1)–O(2)–C(11)	126.5(3)		

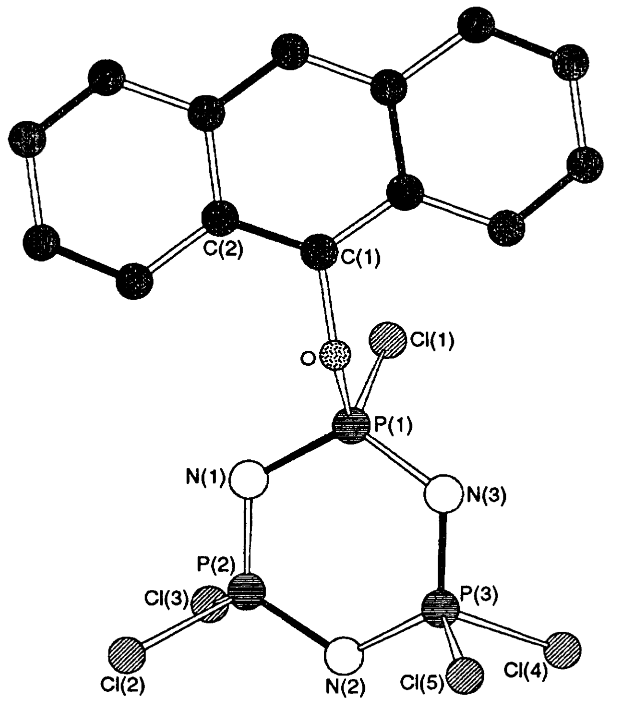


Fig. 5 An ORTEP diagram of the molecular structure of $N_3P_3(OC_{14}H_9)Cl_5$ **2e**

bond lengths and angles. The P–O–C connecting bond has an angle of 129.5(2)° and the Cl–P–O angle is 105.3(1)°. The crystal-packing diagram (Fig. 6) reveals intermolecular coplanarity between the anthracene units which, if translated to the high-polymer level, may be a predictor of microcrystallinity, liquid crystallinity or possible excimer effects. Selected bond lengths and angles of **2e** are listed in Table 4.

Compound **3e**. The phosphazene ring in compound **3e** bears four geminal 9-anthryloxy side groups (Fig. 7). The structure was solved to *R* 0.104, a value that reflects the disorder generated by two and a half molecules of carbon tetrachloride in each unit cell. The phosphazene ring is planar with an average P–N bond distance of 1.573(8) Å. Individual values were 1.586(9), 1.560(8), 1.556(8), 1.546(8), 1.613(9) and 1.578(8) Å. The shortest of these bonds are adjacent to the PCl_2 unit. The N–P–N angles average to 117.1(4)°, with specific values being 117.1(4), 119.3(4) and 114.9(4)°. The P–N–P angles average to 122.8(5)° with individual values of 121.4(5), 122.5(5) and 124.4(5)°. Again, the anthracene rings are planar and normal in all respects. The P–O–C angles average to 124.7(6)° with individual values of 126.0(6), 122.3(6) and 125.3(5)° (two). The O–P–O angle average is 99.0(3)° with individual values of 99.8(3) and 98.1(4)°. The Cl–P–Cl angle is 100.2(2)°. No intramolecular coplanarity was detected between

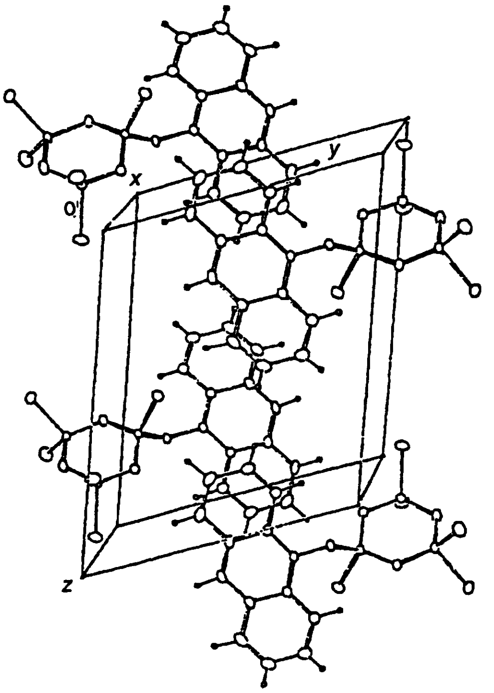


Fig. 6 Unit-cell packing arrangement of $N_3P_3(OC_{14}H_9)Cl_5$ **2e**

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

Cl(1)–P(1)	1.995(1)	P(1)–N(3)	1.587(3)
Cl(2)–P(2)	1.992(1)	P(2)–N(1)	1.569(3)
Cl(3)–P(2)	1.996(1)	P(2)–N(2)	1.580(3)
Cl(4)–P(3)	1.989(1)	P(3)–N(2)	1.583(3)
Cl(5)–P(3)	1.997(1)	P(3)–N(3)	1.572(3)
P(1)–O	1.570(2)	O–C(1)	1.415(3)
P(1)–N(1)	1.586(3)		
Cl(1)–P–O	105.29(9)	Cl(4)–P(3)–Cl(5)	101.20(6)
Cl(1)–P(1)–N(1)	107.7(1)	Cl(4)–P(3)–N(2)	108.4(1)
Cl(1)–P(1)–N(3)	110.5(1)	Cl(4)–P(3)–N(3)	109.3(1)
O–P(1)–N(1)	110.3(1)	Cl(5)–P(3)–N(2)	109.0(1)
O–P(1)–N(3)	105.8(1)	Cl(5)–P(3)–N(3)	108.5(1)
N(1)–P(1)–N(3)	116.6(2)	N(2)–P(3)–N(3)	119.0(2)
Cl(2)–P(2)–Cl(3)	100.68(6)	P(1)–O–C(1)	129.5(2)
Cl(2)–P(2)–N(1)	108.4(1)	P(1)–N(1)–P(2)	121.3(2)
Cl(2)–P(2)–N(2)	109.5(1)	P(2)–N(2)–P(3)	120.3(2)
Cl(3)–P(2)–N(1)	109.9(1)	P(1)–N(3)–P(3)	121.4(2)
Cl(3)–P(2)–N(2)	108.3(1)	O–C(1)–C(2)	117.8(3)
N(1)–P(2)–N(2)	118.6(2)	O–C(1)–C(14)	117.3(3)

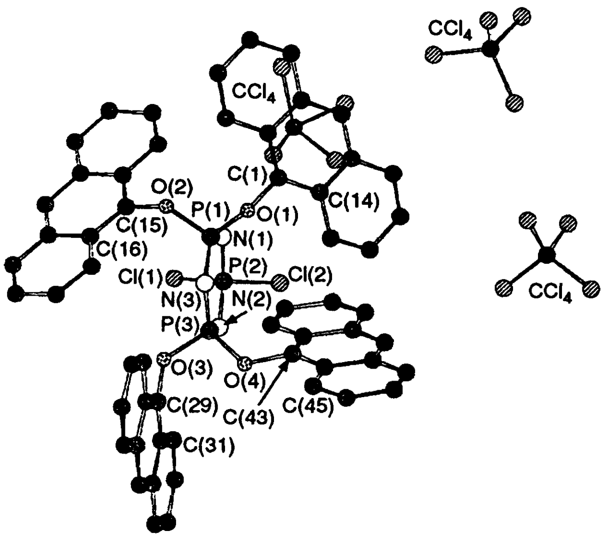


Fig. 7 An ORTEP diagram of the molecular structure of $N_3P_3(OC_{14}H_9)_4Cl_2$ **3e**

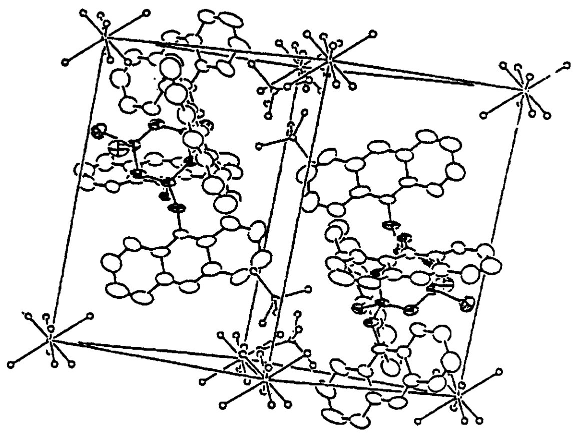


Fig. 8 Unit-cell packing arrangement of $N_3P_3(OC_{14}H_9)_4Cl_2$ **3e**

anthracene units but intermolecular coplanarity was identified from the packing diagram (Fig. 8). Selected bond lengths and angles of **3e** are listed in Table 5.

Compound **6a**. The structure of the cyclic tetrameric octakis(2-naphthyloxy) compound **6a** was solved to *R* 0.096. The structure consists of a cyclic tetrameric phosphazene ring puckered in a boat conformation, to which are attached eight 2-naphthyloxy groups. The average P–N bond length is 1.556(7) Å with individual values of 1.565(6), 1.560(6) (two), 1.564(7), 1.532(8), 1.563(7), 1.554(6) and 1.552(6) Å. The average N–P–N angle is 120.4(3)° with individual values of 121.7(3), 118.4(4), 121.5(4) and 120.3(3)°. The average P–N–P angle is 134.3(5)°, with specific values of 132.4(5), 133.9(6), 134.4(5) and 136.6(5)°. The naphthalene rings are normal. The P–O–C angles average to 125.3(5)°, with individual values of 126.5(4), 122.5(6), 120.8(4), 127.5(5) (two), 125.4(5), 122.0(5) and 130.7(6)°. The average O–P–O angle is 99.0(2)° with specific values of 99.2(3), 94.0(3), 104.6(4) and 99.4(3)°. Within each molecule, the side groups are oriented in a roughly collinear manner above and below the average plane of the phosphazene ring (Fig. 9) but with little discernible coplanarity of the naphthyloxy units. This situation is similar to that found in the cyclic trimeric analogue. Packing of the molecules in the unit cell (Fig. 10) leads to intermolecular collinearity of the side groups but again with little evidence of coplanarity or side-group stacking. Selected bond lengths and angles of **6a** are listed in Table 6.

Compound **6b**. The cyclic tetramer **6b**, octakis(1-naphthyloxy)cyclo-$2\lambda^5,4\lambda^5,6\lambda^5,8\lambda^5$-tetraphosphazene), is an isomer of compound **6a** and its crystal structure was solved to *R* 0.051. The structure consists of a slightly puckered, boat-shaped, cyclic tetrameric phosphazene ring with two 1-naphthyloxy groups attached to each phosphorus atom. The average P–N bond length was 1.545(6) Å with individual values of 1.553(6), 1.537(6) (two), 1.546(6) (two), 1.540(6), 1.552(6) and 1.550(6) Å. The average N–P–N angle is 123.3(3)° with individual values of 122.8(3), 123.1(3), 123.6(3) and 123.4(3)°. The P–N–P average angle is 144.5(4)°, with specific values of 144.7(4), 143.9(4), 144.5(4) and 144.8(4)°. The naphthalene rings are normal with an average P–O–C angle of 124.1(4)° and individual values of 121.8(4), 126.7(4), 126.8(4), 127.1(4) (two), 121.4(4), 120.8(4) and 121.0(4)°. The average O–P–O angle is 105.4(3)° with specific values of 105.4(3), 105.2(3) (two) and 105.7(3)°. Within each molecule, the side groups are oriented in a paddle wheel-like arrangement when viewed normal to the phosphazene ring (Fig. 11). Although there is no crystallographic symmetry in

Table 5 Bond distances (Å) and angles (°) for compound **3e**

Cl(1)–P(2)	2.003(4)	P(3)–O(3)	1.579(5)
Cl(2)–P(2)	1.985(4)	P(3)–O(4)	1.582(7)
P(1)–O(1)	1.564(6)	P(3)–N(2)	1.613(9)
P(1)–O(2)	1.592(7)	P(3)–N(3)	1.578(8)
P(1)–N(1)	1.586(9)	O(1)–C(1)	1.40(1)
P(1)–N(3)	1.560(8)	O(2)–C(15)	1.46(1)
P(2)–N(1)	1.556(8)	O(3)–C(29)	1.38(1)
P(2)–N(2)	1.546(8)	O(4)–C(43)	1.44(1)
O(1)–P(1)–O(2)	99.8(3)	N(2)–P(3)–N(3)	114.9(4)
O(1)–P(1)–N(1)	112.6(3)	P(1)–O(1)–C(1)	126.0(6)
O(1)–P(1)–N(3)	105.9(4)	P(1)–O(2)–C(15)	122.3(6)
O(2)–P(1)–N(1)	110.0(4)	P(3)–O(3)–C(29)	125.3(5)
O(2)–P(1)–N(3)	109.9(4)	P(3)–O(4)–C(43)	125.3(5)
N(1)–P(1)–N(3)	117.1(4)	P(1)–N(1)–P(2)	121.4(5)
Cl(1)–P(2)–Cl(2)	100.2(2)	P(2)–N(2)–P(3)	122.5(5)
Cl(1)–P(2)–N(1)	108.7(3)	P(1)–N(3)–P(3)	124.4(5)
Cl(1)–P(2)–N(2)	108.6(3)	O(1)–C(1)–C(2)	119.4(8)
Cl(2)–P(2)–N(1)	110.0(3)	O(1)–C(1)–C(14)	118.2(8)
Cl(2)–P(2)–N(2)	108.3(3)	O(2)–C(15)–C(16)	114.6(9)
N(1)–P(2)–N(2)	119.3(4)	O(2)–C(15)–C(28)	118.4(7)
O(3)–P(3)–O(4)	98.1(4)	O(3)–C(29)–C(30)	119.8(9)
O(3)–P(3)–N(2)	108.4(4)	O(3)–C(29)–C(42)	116.8(8)
O(3)–P(3)–N(3)	109.3(3)	O(4)–C(43)–C(44)	116.0(7)
O(4)–P(3)–N(2)	111.7(4)	O(4)–C(43)–C(56)	118.1(8)
O(4)–P(3)–N(3)	113.0(4)		

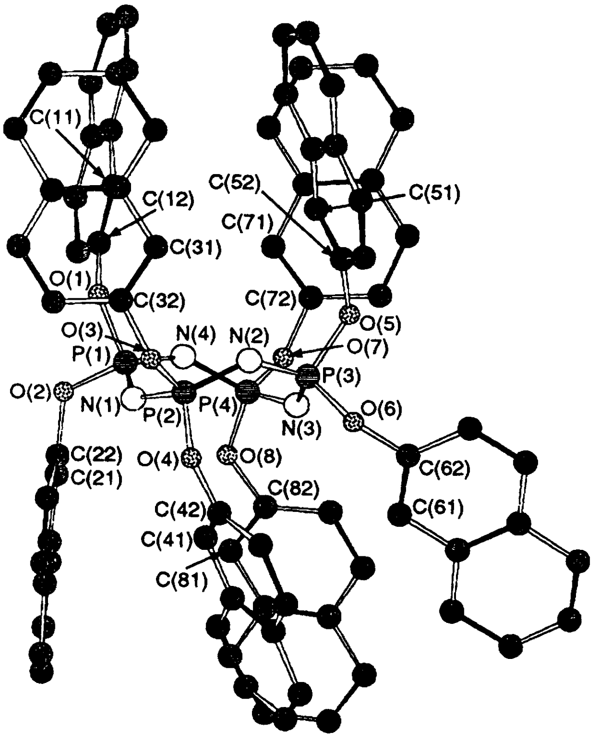


Fig. 9 An ORTEP diagram of the molecular structure of $N_4P_4(2\text{-}OC_{10}H_7)_8$ **6a**

the unit cell (space group $P\bar{1}$), there appears to be a great deal of intramolecular stacking within the molecule. Selected bond lengths and angles of **6b** are listed in Table 7.

Relationship to Phosphazene Polymer Chemistry.—Synthesis reactions were also attempted between an excess of the same fused-ring nucleophiles and high-molecular-weight poly(dichlorophosphazene), $(NPCl_2)_n$. Complete replacement of all the chlorine atoms in $(NPCl_2)_n$ was found to be difficult, presumably because of steric constraints. The use of high-temperature (150 °C) reactions in pressure vessels using dioxane as a reaction solvent increased the degree of replacement considerably, but small amounts of chlorine were still detected in a few cases (1.8% for side group **e**, and 0.5% for **b**). More complete replacement was achieved when a second, less-hindered co-substituent was introduced. For example, total replacement occurred during the synthesis of $[NP(OR)_x(OCH_2CF_3)_{2-x}]_n$ (R = 1-naphthyl), $[NP(OR)_{0.5}(OPh)_{1.5}]_n$ or $[NP(OR)_{1.58}(OCH_2CF_3)_{0.42}]_n$ (R = 9-phenanthryl). Overall, the steric constraints detected in the model compound chemistry are certainly present at the high-polymer level, but they do not impose serious barriers to the

Table 6 Bond distances (Å) and angles (°) for compound **6a**

P(1)–O(1)	1.583(5)	P(4)–O(7)	1.588(6)
P(1)–O(2)	1.589(7)	P(4)–O(8)	1.570(7)
P(1)–N(1)	1.565(6)	P(4)–N(3)	1.554(6)
P(1)–N(4)	1.560(6)	P(4)–N(4)	1.552(6)
P(2)–O(3)	1.593(5)	O(1)–C(12)	1.391(8)
P(2)–O(4)	1.573(5)	O(2)–C(22)	1.39(1)
P(2)–N(1)	1.564(7)	O(3)–C(32)	1.40(1)
P(2)–N(2)	1.532(8)	O(4)–C(42)	1.385(9)
P(3)–O(5)	1.578(7)	O(5)–C(52)	1.39(1)
P(3)–O(6)	1.588(5)	O(6)–C(62)	1.41(1)
P(3)–N(2)	1.560(6)	O(7)–C(72)	1.40(1)
P(3)–N(3)	1.563(7)	O(8)–C(82)	1.411(9)
O(1)–P(1)–O(2)	99.2(3)	O(8)–P(4)–N(4)	105.5(4)
O(1)–P(1)–N(1)	108.3(3)	N(3)–P(4)–N(4)	120.3(3)
O(1)–P(1)–N(4)	108.5(3)	P(1)–O(1)–C(12)	126.5(4)
O(2)–P(1)–N(1)	107.3(4)	P(1)–O(2)–C(22)	122.5(6)
O(2)–P(1)–N(4)	109.8(4)	P(2)–O(3)–C(32)	120.8(4)
N(1)–P(1)–N(4)	121.7(3)	P(2)–O(4)–C(42)	127.5(5)
O(3)–P(2)–O(4)	94.0(3)	P(3)–O(5)–C(52)	125.4(5)
O(3)–P(2)–N(1)	109.3(3)	P(3)–O(6)–C(62)	127.5(5)
O(3)–P(2)–N(2)	109.4(4)	P(4)–O(7)–C(72)	122.0(5)
O(4)–P(2)–N(1)	109.5(4)	P(4)–O(8)–C(82)	130.7(6)
O(4)–P(2)–N(2)	113.5(3)	P(1)–N(1)–P(2)	132.4(5)
N(1)–P(2)–N(2)	118.4(4)	P(2)–N(2)–P(3)	133.9(6)
O(5)–P(3)–O(6)	104.6(4)	P(3)–N(3)–P(4)	134.4(5)
O(5)–P(3)–N(2)	108.2(4)	P(1)–N(4)–P(4)	136.6(5)
O(5)–P(3)–N(3)	106.6(3)	O(1)–C(12)–C(11)	116.7(7)
O(6)–P(3)–N(2)	105.2(4)	O(1)–C(12)–C(13)	119.1(8)
O(6)–P(3)–N(3)	109.6(3)	O(2)–C(22)–C(21)	118.0(7)
N(2)–P(3)–N(3)	121.5(4)	O(2)–C(22)–C(23)	118.9(7)
O(7)–P(4)–O(8)	99.4(3)	O(3)–C(32)–C(31)	120.2(9)
O(7)–P(4)–N(3)	110.4(4)	O(3)–C(32)–C(33)	115.2(9)
O(7)–P(4)–N(4)	108.3(3)	O(4)–C(42)–C(41)	123.8(7)
O(8)–P(4)–N(3)	111.0(3)	O(4)–C(42)–C(43)	113.5(7)
O(5)–C(52)–C(51)	118.4(8)	O(7)–C(72)–C(71)	118.8(9)
O(5)–C(52)–C(53)	118.4(7)	O(7)–C(72)–C(73)	115.9(7)
O(6)–C(62)–C(61)	119.1(9)	O(8)–C(82)–C(81)	113.5(7)
O(6)–C(62)–C(63)	114.4(8)	O(8)–C(82)–C(83)	121.8(8)

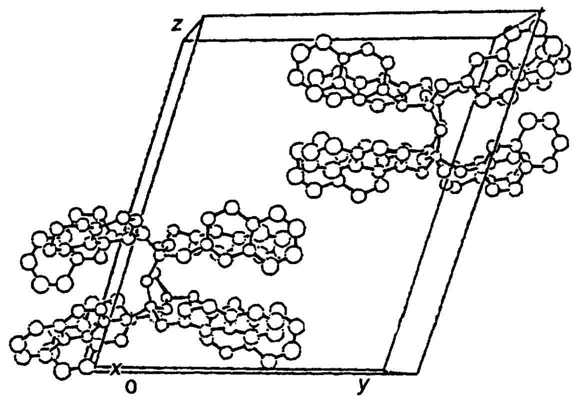


Fig. 10 Unit-cell packing arrangement of $N_4P_4(2\text{-}OC_{10}H_7)_8$ **6a**

synthesis of related high polymers. Molecular structural data for the high polymers were difficult to obtain. However, the molecular weights, estimated by GPC analysis, were in the range 1×10^6–5×10^6. Glass transition temperatures were in the range 20–70 °C for the single-substituent polymers. The introduction of OCH_2CF_3 co-substituent groups for the naphthyloxy polymers lowered the T_g to −3.7 °C. The ^{31}P NMR shifts for the naphthyloxy derivatives were of the order of δ −20. The interposition of aliphatic spacer groups between the aromatic units and the phosphazene chain lowers the steric barriers to substitution and markedly enhances the solubility of the polymers.[2]

Although these cyclic species provide a good first approximation to the corresponding high polymeric structures, previous work[24] has shown that the related linear short-chain species come much closer to approximating the macromolecular structures. The linear small molecules possess an angular flexibility not found in the cyclic systems. The crystal structures of linear short chains also reveal the near planarity of the short-chain backbones and the conformation-directing influence of the side groups. However, linear short-chain species are more difficult to synthesize and crystallize than are their cyclic tri- or tetra-meric counterparts and, hence, the cyclic models provide critical data that cannot be obtained from other sources.

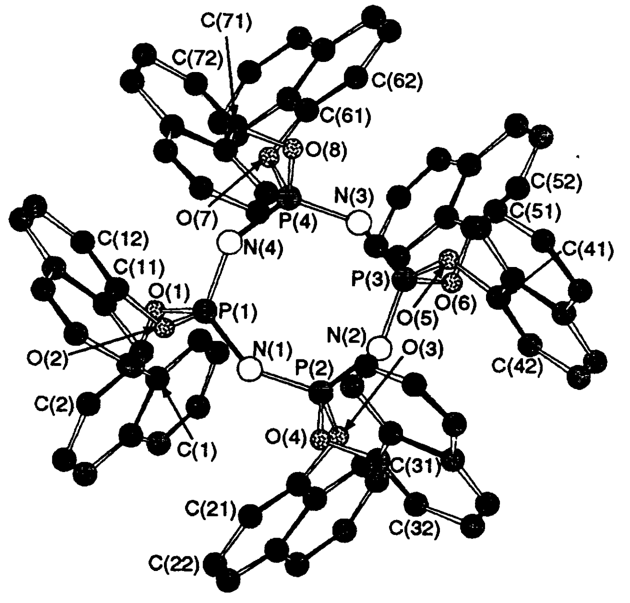


Fig. 11 An ORTEP diagram of the molecular structure of $N_4P_4(1\text{-}OC_{10}H_7)_8$ **6b**

Table 7 Bond distances (Å) and angles (°) for compound **6b**

P(1)–O(1)	1.590(5)	P(4)–O(7)	1.578(5)
P(1)–O(2)	1.567(5)	P(4)–O(8)	1.590(5)
P(1)–N(1)	1.553(6)	P(4)–N(3)	1.546(6)
P(1)–N(4)	1.540(6)	P(4)–N(4)	1.550(6)
P(2)–O(3)	1.580(5)	O(1)–C(1)	1.399(8)
P(2)–O(4)	1.569(5)	O(2)–C(11)	1.411(8)
P(2)–N(1)	1.537(6)	O(3)–C(21)	1.401(8)
P(2)–N(2)	1.552(6)	O(4)–C(31)	1.406(8)
P(3)–O(5)	1.580(5)	O(5)–C(41)	1.418(8)
P(3)–O(6)	1.604(5)	O(6)–C(51)	1.417(9)
P(3)–N(2)	1.537(6)	O(7)–C(61)	1.413(9)
P(3)–N(3)	1.546(6)	O(8)–C(71)	1.426(8)
O(1)–P(1)–O(2)	105.4(3)	O(8)–P(4)–N(4)	108.1(3)
O(1)–P(1)–N(1)	107.5(3)	N(3)–P(4)–N(4)	123.4(3)
O(1)–P(1)–N(4)	105.3(3)	P(1)–O(1)–C(1)	121.8(4)
O(2)–P(1)–N(1)	105.2(3)	P(1)–O(2)–C(11)	127.1(4)
O(2)–P(1)–N(4)	109.4(3)	P(2)–O(3)–C(21)	126.7(4)
N(1)–P(1)–N(4)	122.8(3)	P(2)–O(4)–C(31)	121.4(4)
O(3)–P(2)–O(4)	105.2(3)	P(3)–O(5)–C(41)	126.8(4)
O(3)–P(2)–N(1)	109.2(3)	P(3)–O(6)–C(51)	120.8(4)
O(3)–P(2)–N(2)	104.8(3)	P(4)–O(7)–C(61)	127.1(4)
O(4)–P(2)–N(1)	105.7(3)	P(4)–O(7)–C(71)	121.0(4)
O(4)–P(2)–N(2)	107.7(3)	P(1)–N(1)–P(2)	144.7(4)
N(1)–P(2)–N(2)	123.1(3)	P(2)–N(2)–P(3)	144.5(4)
O(5)–P(3)–O(6)	105.2(3)	P(3)–N(3)–P(4)	143.9(4)
O(5)–P(3)–N(2)	109.3(3)	P(4)–N(3)–P(1)	144.8(4)
O(5)–P(3)–N(3)	104.8(3)	O(1)–C(1)–C(2)	120.7(8)
O(6)–P(3)–N(2)	105.2(3)	O(1)–C(1)–C(10)	116.3(7)
O(6)–P(3)–N(3)	107.4(3)	O(2)–C(11)–C(12)	123.6(7)
N(2)–P(3)–N(3)	123.6(3)	O(2)–C(11)–C(20)	114.4(6)
O(7)–P(4)–O(8)	105.7(3)	O(3)–C(21)–C(22)	123.9(7)
O(7)–P(4)–N(3)	108.6(3)	O(3)–C(21)–C(30)	113.8(7)
O(7)–P(4)–N(4)	104.7(3)	O(4)–C(31)–C(32)	120.9(8)
O(8)–P(4)–N(3)	105.2(3)	O(4)–C(31)–C(40)	115.9(7)
O(5)–C(41)–C(42)	123.5(7)	O(7)–C(61)–C(62)	123.9(7)
O(5)–C(41)–C(50)	113.6(7)	O(7)–C(62)–C(70)	114.1(6)
O(6)–C(51)–C(52)	121.4(8)	O(8)–C(71)–C(72)	120.8(8)
O(6)–C(51)–C(60)	116.1(7)	O(8)–C(71)–C(80)	115.8(7)

Table 8 Summary of crystal data and intensity collection parameters

	4a	**4b**	**2e**	**3e**	**6a**	**6b**
Formula	$C_{60}H_{42}N_3O_6P_3$	$C_{60}H_{42}N_3O_6P_3$	$C_{14}H_9Cl_5N_3OP_3$	$C_{56}H_{36}Cl_2N_3O_4P_3\cdot 2.5CCl_4$	$C_{80}H_{56}N_4O_8P_4$	$C_{80}H_{56}N_4O_8P_4\cdot 0.5C_6H_{14}$
M	993.94	993.94	505	977	1324	1324
Space group (no.)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$C2/c$ (15)	$P1$ (1)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
a/Å	24.885(4)	11.202(7)	7.837(2)	12.418(3)	21.116(4)	13.138(8)
b/Å	7.717(4)	11.271(4)	10.744(1)	15.511(2)	15.628(3)	13.146(4)
c/Å	27.732(2)	20.130(11)	12.627(2)	16.094(1)	21.111(5)	13.155(3)
α/°		79.62(4)	111.47(3)	103.55(1)		114.66(2)
β/°	115.89(1)	76.76(5)	92.38(2)	96.94(1)	95.70(2)	106.91(3)
γ/°		88.82(4)	98.84(1)	94.34(1)		106.93(4)
U/Å^3	4791.0	2433.0	972.1	2974(3)	6932.2	1738(1)
Z	4	2	2	2	4	1
D_c/g cm^{-3}	1.38	1.36	1.38	1.09, 1.52 (obs.)	1.271	1.31 (with 1/2 hexane included)
μ/cm^{-1}	1.77	1.742	10.04	64.37	1.48	1.7
F(000)	2062	1032	504	1378	2752	713
Radiation (λ/Å)	Mo-Kα (0.710 69)	Cu-Kα (1.5418)	Cu-Kα (1.5418)	Cu-Kα (1.5418)	Cu-Kα (1.5418)	Mo-Kα (0.710 69)
$R, R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.062, 0.077	0.076, 0.095	0.030, 0.041	0.104, 0.128	0.096, 0.096	0.051, 0.067
p In weighting scheme	0.030	0.060	0.020	0.100	0.030	0.017

Table 9 Positional parameters for compound **4a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
P(1)	0.313 53(5)	0.078 9(2)	0.387 94(4)	C(25)	0.352 6(2)	0.052 2(8)	0.158 6(2)
P(2)	0.201 39(5)	−0.014 9(2)	0.313 41(4)	C(26)	0.309 0(2)	0.122 4(8)	0.111 2(2)
P(3)	0.236 29(5)	0.327 4(2)	0.323 61(4)	C(27)	0.251 7(2)	0.131 8(7)	0.103 2(2)
O(1)	0.339 6(1)	0.055 0(5)	0.451 1(1)	C(28)	0.233 5(2)	0.069 7(7)	0.142 2(2)
O(2)	0.371 3(1)	0.028 5(4)	0.380 7(1)	C(29)	0.174 3(2)	0.075 8(8)	0.136 0(2)
O(3)	0.184 6(1)	−0.119 8(4)	0.259 2(1)	C(30)	0.158 6(2)	0.014 2(8)	0.174 0(2)
O(4)	0.157 2(1)	−0.103 8(4)	0.332 1(1)	C(31)	0.097 3(2)	−0.063 4(6)	0.318 6(2)
O(5)	0.209 2(1)	0.495 1(4)	0.337 3(1)	C(32)	0.077 6(2)	−0.115 9(6)	0.354 8(2)
O(6)	0.247 6(1)	0.401 9(5)	0.275 6(1)	C(33)	0.017 1(2)	−0.081 2(7)	0.344 4(2)
N(1)	0.266 0(1)	−0.063 7(5)	0.357 1(1)	C(34)	−0.004 6(2)	−0.132 0(8)	0.382 1(2)
N(2)	0.186 7(1)	0.183 0(5)	0.299 8(1)	C(35)	−0.063 6(2)	−0.091 0(9)	0.370 7(2)
N(3)	0.296 0(1)	0.275 2(5)	0.373 4(1)	C(36)	−0.100 6(2)	−0.005 1(9)	0.323 8(2)
C(1)	0.308 7(2)	0.018 0(6)	0.481 4(2)	C(37)	−0.080 7(2)	0.042 1(7)	0.287 3(2)
C(2)	0.251 6(2)	0.063 2(6)	0.468 2(2)	C(38)	−0.020 9(2)	0.004 3(7)	0.296 8(2)
C(3)	0.225 4(2)	0.015 8(7)	0.502 4(2)	C(39)	0.002 4(2)	0.054 9(7)	0.260 4(2)
C(4)	0.164 6(2)	0.053 7(7)	0.489 5(2)	C(40)	0.060 2(2)	0.021 7(7)	0.270 5(2)
C(5)	0.140 1(2)	0.002 7(8)	0.523 0(2)	C(41)	0.185 5(2)	0.491 0(6)	0.375 1(2)
C(6)	0.175 8(2)	−0.083 3(8)	0.571 2(2)	C(42)	0.130 4(2)	0.425 2(7)	0.361 5(2)
C(7)	0.233 0(2)	−0.120 2(8)	0.585 3(2)	C(43)	0.105 7(2)	0.432 7(7)	0.398 5(2)
C(8)	0.260 1(2)	−0.073 2(7)	0.551 1(2)	C(44)	0.047 9(2)	0.365 6(8)	0.386 4(2)
C(9)	0.319 5(2)	−0.116 2(7)	0.563 0(2)	C(45)	0.026 1(2)	0.371 3(9)	0.424 2(2)
C(10)	0.344 3(2)	−0.070 9(7)	0.529 5(2)	C(46)	0.060 5(2)	0.445 0(9)	0.474 4(2)
C(11)	0.421 8(2)	0.137 3(6)	0.395 0(2)	C(47)	0.115 2(2)	0.512 3(8)	0.487 4(2)
C(12)	0.458 6(2)	0.169 7(6)	0.447 5(2)	C(48)	0.140 1(2)	0.505 2(7)	0.449 8(2)
C(13)	0.508 8(2)	0.279 4(6)	0.460 1(2)	C(49)	0.197 4(2)	0.570 6(7)	0.462 1(2)
C(14)	0.547 7(2)	0.324 4(7)	0.513 9(2)	C(50)	0.220 4(2)	0.564 2(7)	0.425 8(2)
C(15)	0.593 5(2)	0.437 0(8)	0.524 0(2)	C(51)	0.300 5(2)	0.480 8(7)	0.280 1(2)
C(16)	0.603 6(2)	0.510 8(8)	0.483 6(2)	C(52)	0.316 3(2)	0.450 4(7)	0.239 8(2)
C(17)	0.567 4(2)	0.469 6(8)	0.431 2(2)	C(53)	0.371 0(2)	0.535 1(7)	0.243 5(2)
C(18)	0.518 6(2)	0.351 9(7)	0.417 6(2)	C(54)	0.388 5(2)	0.510 0(8)	0.202 7(2)
C(19)	0.480 6(2)	0.308 3(7)	0.364 5(2)	C(55)	0.440 6(2)	0.588 4(9)	0.207 7(2)
C(20)	0.432 3(2)	0.203 5(7)	0.352 8(2)	C(56)	0.474 9(2)	0.687 8(8)	0.252 4(2)
C(21)	0.203 0(2)	−0.054 7(7)	0.221 2(2)	C(57)	0.459 3(2)	0.716 9(8)	0.292 0(2)
C(22)	0.260 7(2)	−0.064 9(7)	0.229 6(2)	C(58)	0.404 0(2)	0.637 0(7)	0.288 6(2)
C(23)	0.277 4(2)	−0.003 5(7)	0.190 3(2)	C(59)	0.385 1(2)	0.664 7(8)	0.327 8(2)
C(24)	0.337 5(2)	−0.011 5(7)	0.197 2(2)	C(60)	0.333 2(2)	0.589 9(7)	0.323 3(2)

Table 10 Positional parameters for compound **4b** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
P(1)	0.936 0(2)	0.232 0(2)	0.699 68(9)	C(25)	0.655 9(7)	0.702(7)	0.525 5(4)
P(2)	0.773 8(2)	0.037 8(2)	0.747 34(9)	C(26)	0.713 9(11)	0.057 0(9)	0.457 6(4)
P(3)	0.724 8(2)	0.248 1(2)	0.799 92(9)	C(27)	0.818 1(12)	−0.009 5(9)	0.450 5(6)
O(1)	0.960 1(4)	0.299 5(4)	0.621 5(2)	C(28)	0.867 0(10)	−0.061 2(8)	0.502 2(5)
O(2)	1.072 1(4)	0.237 7(4)	0.710 3(2)	C(29)	0.817 6(8)	−0.047 5(7)	0.569 8(5)
O(3)	0.697 1(4)	−0.020 4(4)	0.703 6(2)	C(30)	0.707 7(8)	0.022 5(6)	0.581 5(4)
O(4)	0.798 6(4)	−0.089 1(4)	0.789 8(2)	C(31)	0.876 2(6)	−0.106 2(6)	0.836 9(3)
O(5)	0.609 9(4)	0.326 3(4)	0.792 7(3)	C(32)	0.860 3(7)	−0.043 7(6)	0.889 7(4)
O(6)	0.739 4(4)	0.258 2(4)	0.875 6(2)	C(33)	0.935 0(8)	−0.070 2(8)	0.935 6(4)
N(1)	0.897 6(5)	0.098 8(4)	0.701 0(3)	C(34)	1.017 5(8)	−0.158 3(8)	0.932 5(4)
N(2)	0.688 8(5)	0.117 2(4)	0.796 5(3)	C(35)	1.036 9(7)	−0.224 7(7)	0.876 3(4)
N(3)	0.847 0(5)	0.304 9(4)	0.750 2(3)	C(36)	1.122 5(8)	−0.315 2(8)	0.869 1(4)
C(1)	0.997 2(6)	0.420 1(6)	0.601 1(3)	C(37)	1.140 3(8)	−0.375 1(8)	0.816 8(5)
C(2)	0.919 7(7)	0.510 2(6)	0.618 8(4)	C(38)	1.069 2(9)	−0.348 0(8)	0.766 0(5)
C(3)	0.955 3(7)	0.629 4(6)	0.595 0(4)	C(39)	0.983 7(7)	−0.260 4(7)	0.770 5(4)
C(4)	1.067 5(8)	0.658 8(6)	0.551 7(4)	C(40)	0.962 7(6)	−0.197 2(6)	0.827 0(4)
C(5)	1.148 8(6)	0.566 5(6)	0.531 4(4)	C(41)	0.603 2(7)	0.446 4(8)	0.765 5(4)
C(6)	1.263 2(8)	0.595 5(8)	0.485 7(5)	C(42)	0.685 3(7)	0.530 4(7)	0.776 6(5)
C(7)	1.338 9(8)	0.508 0(10)	0.467 5(5)	C(43)	0.669 5(9)	0.648 4(9)	0.751 3(5)
C(8)	1.308 1(7)	0.388 9(8)	0.492 8(4)	C(44)	0.593 2(8)	0.698 2(7)	0.715 1(5)
C(9)	1.197 0(7)	0.354 9(7)	0.537 6(4)	C(45)	0.501 4(8)	0.607 4(8)	0.703 5(5)
C(10)	1.115 2(6)	0.446 8(6)	0.557 2(3)	C(46)	0.430 1(9)	0.656 4(7)	0.665 8(5)
C(11)	1.107 4(6)	0.218 7(7)	0.774 1(4)	C(47)	0.340 3(9)	0.571 9(11)	0.652 9(5)
C(12)	1.078 3(7)	0.298 9(7)	0.817 3(4)	C(48)	0.350 7(7)	0.452 1(9)	0.677 8(4)
C(13)	1.126 5(9)	0.281 9(9)	0.877 6(4)	C(49)	0.426 3(8)	0.402 9(10)	0.716 9(5)
C(14)	1.203 5(8)	0.191 0(10)	0.889 2(4)	C(50)	0.518 3(6)	0.490 9(6)	0.729 6(3)
C(15)	1.232 2(7)	0.106 8(8)	0.846 1(4)	C(51)	0.646 2(6)	0.257 4(6)	0.935 4(4)
C(16)	1.308 3(8)	0.013 4(9)	0.860 4(5)	C(52)	0.554 3(7)	0.174 3(7)	0.954 3(4)
C(17)	1.334 7(9)	−0.068 8(9)	0.818 7(6)	C(53)	0.467 5(8)	0.173 7(8)	1.017 6(5)
C(18)	1.283 4(8)	−0.062 1(8)	0.760 2(5)	C(54)	0.472 7(7)	0.257 3(8)	1.057 9(4)
C(19)	1.209 2(7)	0.030 7(7)	0.744 4(4)	C(55)	0.567 7(6)	0.346 2(7)	1.037 0(3)
C(20)	1.181 2(6)	0.118 9(7)	0.787 6(4)	C(56)	0.573 0(7)	0.433 9(8)	1.076 5(4)
C(21)	0.651 8(7)	0.039 9(7)	0.648 3(4)	C(57)	0.664 0(8)	0.521 1(8)	1.054 0(5)
C(22)	0.547 9(8)	0.105 4(8)	0.661 2(5)	C(58)	0.751 5(8)	0.521 6(8)	0.993 1(5)
C(23)	0.497 9(8)	0.154 1(10)	0.606 7(5)	C(59)	0.750 9(7)	0.436 2(7)	0.953 9(4)
C(24)	0.546 0(8)	0.142 0(9)	0.541 6(5)	C(60)	0.655 9(6)	0.344 5(6)	0.975 1(3)

Table 11 Positional parameters for compound **2e** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cl(1)	−0.058 9(1)	0.133 64(8)	0.627 07(7)
Cl(2)	−0.255 4(1)	−0.050 8(1)	0.984 58(7)
Cl(3)	−0.481 0(1)	−0.048 4(1)	0.780 95(8)
Cl(4)	−0.119 1(1)	−0.354 62(8)	0.518 66(7)
Cl(5)	0.116 2(1)	−0.317 46(9)	0.733 52(8)
P(1)	0.026 5(1)	0.057 31(7)	0.737 21(6)
P(2)	−0.238 6(1)	−0.061 20(7)	0.824 69(6)
P(3)	−0.041 2(1)	−0.220 56(7)	0.676 70(7)
O	0.204 9(3)	0.151 6(2)	0.796 5(2)
N(1)	−0.109 6(4)	0.067 7(2)	0.828 3(2)
N(2)	−0.204 0(4)	−0.206 4(3)	0.747 5(3)
N(3)	0.070 4(3)	−0.089 0(2)	0.670 8(2)
C(1)	0.273 5(4)	0.283 4(3)	0.801 0(2)
C(2)	0.257 9(4)	0.393 9(3)	0.899 3(2)
C(3)	0.172 5(4)	0.381 6(3)	0.993 4(3)
C(4)	0.172 5(5)	0.493 7(4)	1.089 0(3)
C(5)	0.253 2(5)	0.625 0(4)	1.096 2(3)
C(6)	0.331 5(5)	0.640 3(3)	1.007 8(3)
C(7)	0.339 8(4)	0.526 6(3)	0.905 7(3)
C(8)	0.428 3(4)	0.538 6(3)	0.816 2(3)
C(9)	0.446 9(4)	0.426 3(3)	0.720 7(3)
C(10)	0.547 8(5)	0.437 1(4)	0.631 4(3)
C(11)	0.570 7(5)	0.325 4(4)	0.542 4(3)
C(12)	0.494 9(5)	0.195 6(4)	0.536 0(3)
C(13)	0.395 0(4)	0.177 5(3)	0.616 7(3)
C(14)	0.368 4(4)	0.292 3(3)	0.712 1(2)
H(3)	0.123(4)	0.291(3)	0.996(3)
H(4)	0.125(5)	0.480(3)	1.149(3)
H(5)	0.246(5)	0.709(4)	1.166(3)
H(6)	0.368(5)	0.729(4)	1.007(3)
H(8)	0.476(5)	0.619(4)	0.814(3)
H(10)	0.589(6)	0.527(4)	0.639(4)
H(11)	0.664(6)	0.330(5)	0.497(4)
H(12)	0.518(6)	0.122(4)	0.480(4)
H(13)	0.353(4)	0.089(3)	0.614(3)

Conclusion

The most significant result is that no difficulties were encountered with the introduction of six of the naphthalene units **a**–**d** into the cyclic trimer system, or eight of units **a** and **b** into the cyclic tetramer. This suggested that phosphazene high polymers which bear two of these groups on every repeating unit should be accessible by the appropriate macromolecular substitution techniques, and this was found to be the case. The steric hindrance incurred with the introduction of the 9-anthryloxy groups to the trimer system was apparently too large to permit hexasubstitution, although almost complete substitution to give $[NP(OR)_{1.6}Cl_{0.4}]_n$ (R = 9-anthryl) occurred at the high polymer level. However, six 9-phenanthryloxy groups could be linked to the trimeric ring in spite of the severe hindrance that might be expected, and more than 75% of the chlorine atoms in the high polymer could be replaced by the same organic groups. One result that seems clear from this work is that the torsional flexibility associated with the P–O–C linkage unit allows a surprising number of bulky fused di- or tri-aromatic units to be accommodated around the phosphazene rings and chains, and this provides an optimistic scenario for the development of a wide range of high polymers that are of interest as advanced optical materials.

Experimental

Analytical Techniques.—The ^{31}P NMR (^1H decoupled) spectra were obtained with a JEOL FX-90Q spectrometer operated at 36.2 MHz; the chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive values downfield from the reference. Infrared spectra were recorded with a Perkin-Elmer model 283B grating spectrometer, and ion-impact mass spectra with an AEC/MS 902 mass spectrometer. Elemental analyses were obtained by Galbraith Laboratories.

Materials.—Hexachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazene and octachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazene were obtained from Ethyl Corporation and were 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. 1-Naphthol, 2-naphthol, anthracen-9-ol, phenanthren-9-ol, naphthalene-1-methanol and naphthalene-2-ethanol were obtained from Aldrich, and purified by sublimation. Sodium, sodium hydride and tetra-*n*-butylammonium bromide (Aldrich) were used as received. All reactions were carried out in an atmosphere of dry nitrogen.

Syntheses.—$[NP(2\text{-}OC_{10}H_7)_2]_3$ **4a**. A solution of sodium 2-naphthyl oxide [prepared from NaH (11.16 g, 2.89 × 10^{-1} mol) and 2-naphthol (41.74 g, 2.89 × 10^{-1} mol) in tetrahydrofuran (thf) (300 cm^3)] was added slowly to a stirred solution of $(NPCl_2)_3$ (10 g, 2.89 × 10^{-2} mol) in thf (100 cm^3) under an atmosphere of dry nitrogen. The mixture was refluxed for 48 h, and then cooled to room temperature. Filtration and removal of the solvent left a solid white product. It was dissolved in toluene to remove unreacted naphthol, then filtered and evaporated to dryness. The product was purified by recrystallization from a dichloromethane–hexane mixture.

The compound $[NP(1\text{-}OC_{10}H_7)_2]_3$ **4b** was prepared similarly except that 1- was used in place of 2-naphthol.

$[NP(OCH_2C_{10}H_7)_2]_3$ **4c**. A solution of $(NPCl_2)_3$ (1.0 g, 2.89 × 10^{-3} mol) in thf (30 cm^3) was added slowly to a stirred solution of sodium 1-naphthylmethyl oxide (2.3 × 10^{-2} mol) at room temperature. The mixture was then heated at reflux for 18 h. The solvent was removed under reduced pressure and the product extracted with dichloromethane. Compound **4c** was separated and purified by gradient elution through a silica gel chromatography column with a dichloromethane–hexane mixture.

$[NP(OCH_2CH_2C_{10}H_7)_2]_3$ **4d**. A solution of $(NPCl_2)_3$ (1.92 g, 5.57 × 10^{-3} mol) in thf (75 cm^3) was added to a solution of sodium 1-naphthylethyl oxide [prepared from naphthalene-2-ethanol (7.03 g, 4.45 × 10^{-2} mol) and a molar excess of NaH] at 56 °C. The reaction was stirred at this temperature for 24 h and the mixture then cooled to room temperature. Filtration and removal of the solvent from the filtrate left a solid product. This compound was purified by silica gel chromatography using a dichloromethane–hexane mixture as eluent.

$[NP(OC_{14}H_9)_2]_3$ **4f**. A solution of $(NPCl_2)_3$ (1.0 g, 2.89 × 10^{-3} mol) in thf (50 cm^3) was added dropwise to a stirred solution of sodium 9-phenanthryl oxide [prepared from phenanthren-9-ol (4.46 g, 2.3 × 10^{-2} mol) and a molar excess of NaH]. The mixture was refluxed for 48 h and then cooled to room temperature. Filtration and removal of the solvent left a solid product. The compound was purified by gradient elution chromatography through a silica gel column with dichloromethane–hexane mixture as eluent.

$N_3P_3(OC_{14}H_9)Cl_5$ **2e** *and* $N_3P_3(OC_{14}H_9)_4Cl_2$ **3e**. The compound $(NPCl_2)_3$ (2.89 × 10^{-3} mol) in thf (150 cm^3) was treated with a solution of sodium 9-anthryl oxide [prepared from anthracen-9-ol (6.67 g, 3.44 × 10^{-2} mol) and a molar excess of NaH] and the mixture was refluxed for 48 h. After removal of the solvent, the crude product was chromatographed through a silica gel column with a dichloromethane–hexane mixture as eluent. Products **2e** and **3e** were isolated and further purified by recrystallization from a dichloromethane–hexane mixture or from carbon tetrachloride.

$[NP(2\text{-}OC_{10}H_7)_2]_4$ **6a**. A solution of $(NPCl_2)_4$ (1.97 g, 4.3 × 10^{-3} mol) in dioxane (25 cm^3) was added dropwise to a stirred solution of sodium 2-naphthyl oxide [prepared from 2-naphthol (9.94 g, 6.9 × 10^{-2} mol) and a molar excess of NaH] and

Table 12 Positional parameters for compound **3e** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1)	−0.0684(2)	0.7830(2)	0.6522(2)	C(19)	0.1268(14)	0.4321(8)	0.5191(9)
Cl(2)	0.0286(3)	0.9784(2)	0.7009(2)	C(20)	0.0568(12)	0.4362(7)	0.5744(8)
Cl(3)	0.3610(4)	1.3786(3)	1.1544(2)	C(21)	0.0654(9)	0.5043(7)	0.6503(7)
Cl(4)	0.2537(4)	1.2322(3)	1.1993(3)	C(22)	−0.0062(11)	0.5079(8)	0.7089(8)
Cl(5)	0.2903(4)	1.3999(3)	1.3191(2)	C(23)	0.0052(9)	0.5743(7)	0.7869(7)
Cl(6)	0.4695(4)	1.3023(4)	1.2820(4)	C(24)	−0.0652(11)	0.5736(8)	0.8471(9)
Cl(7)	0.3618(4)	1.5475(2)	0.8570(3)	C(25)	−0.0490(9)	0.6369(10)	0.9239(9)
Cl(8)	0.3857(4)	1.4095(3)	0.9436(3)	C(26)	0.0404(12)	0.7080(8)	0.9407(7)
Cl(9)	0.2175(6)	1.5208(5)	0.9712(4)	C(27)	0.1065(9)	0.7100(6)	0.8818(6)
Cl(10)	0.2086(5)	1.3975(4)	0.8146(4)	C(28)	0.0947(9)	0.6436(6)	0.8039(6)
Cl(11)	0.0745(7)	0.9475(6)	0.9314(5)	C(29)	0.2361(8)	0.7067(6)	0.4014(5)
Cl(12)	0.0811(8)	1.0714(7)	0.9583(6)	C(30)	0.1696(9)	0.7277(6)	0.3363(6)
Cl(13)	0.0527(13)	1.0921(7)	1.0707(9)	C(31)	0.0709(9)	0.7694(7)	0.3501(6)
Cl(14)	0.1224(10)	0.9502(9)	1.0951(9)	C(32)	0.0073(11)	0.7868(8)	0.2831(8)
P(1)	0.2613(2)	0.7958(2)	0.7324(1)	C(33)	0.0391(14)	0.7697(9)	0.1996(7)
P(2)	0.0755(2)	0.8570(2)	0.6682(2)	C(34)	0.1276(13)	0.7298(9)	0.1836(7)
P(3)	0.2304(2)	0.8060(2)	0.5614(1)	C(35)	0.1994(9)	0.7087(6)	0.2515(6)
O(1)	0.3608(5)	0.8507(4)	0.7970(3)	C(36)	0.2914(10)	0.6673(7)	0.2362(6)
O(2)	0.2590(5)	0.7048(4)	0.7622(3)	C(37)	0.3601(9)	0.6460(6)	0.3024(6)
O(3)	0.2064(5)	0.7208(4)	0.4831(3)	C(38)	0.4602(11)	0.6046(8)	0.2899(7)
O(4)	0.3015(5)	0.8671(4)	0.5178(3)	C(39)	0.5235(11)	0.5858(8)	0.3539(8)
N(1)	0.1505(7)	0.8385(5)	0.7453(4)	C(40)	0.4980(10)	0.6069(8)	0.4385(8)
N(2)	0.1162(7)	0.8448(5)	0.5795(4)	C(41)	0.4053(9)	0.6450(6)	0.4548(6)
N(3)	0.2970(6)	0.7813(4)	0.6409(4)	C(42)	0.3336(9)	0.6664(6)	0.3889(6)
C(1)	0.3556(8)	0.9109(6)	0.8760(5)	C(43)	0.3606(8)	0.9522(6)	0.5614(5)
C(2)	0.3754(8)	0.8834(6)	0.9525(6)	C(44)	0.3040(8)	1.0273(6)	0.5600(5)
C(3)	0.3982(9)	0.7939(7)	0.9542(6)	C(45)	0.1932(9)	1.0249(6)	0.5246(6)
C(4)	0.4163(12)	0.7721(8)	1.0302(7)	C(46)	0.1455(10)	1.1009(7)	0.5259(7)
C(5)	0.4191(11)	0.8336(9)	1.1087(7)	C(47)	0.2088(11)	1.1856(7)	0.5659(7)
C(6)	0.3955(10)	0.9213(8)	1.1102(6)	C(48)	0.3119(11)	1.1910(7)	0.5985(7)
C(7)	0.3774(8)	0.9476(7)	1.0328(6)	C(49)	0.3677(9)	1.1128(6)	0.5976(6)
C(8)	0.3564(9)	1.0335(7)	1.0325(6)	C(50)	0.4750(9)	1.1167(7)	0.6307(6)
C(9)	0.3372(9)	1.0598(6)	0.9563(6)	C(51)	0.5306(9)	1.0420(7)	0.6315(6)
C(10)	0.3087(11)	1.1490(7)	0.9544(8)	C(52)	0.6411(9)	1.0461(8)	0.6640(6)
C(11)	0.2874(12)	1.1707(7)	0.8805(8)	C(53)	0.6910(10)	0.9708(9)	0.6601(7)
C(12)	0.2897(11)	1.1114(7)	0.8010(7)	C(54)	0.6320(10)	0.8859(9)	0.6238(7)
C(13)	0.3158(9)	1.0275(7)	0.7977(6)	C(55)	0.5250(8)	0.8781(7)	0.5918(6)
C(14)	0.3346(8)	0.9992(6)	0.8751(6)	C(56)	0.4664(8)	0.9542(6)	0.5938(5)
C(15)	0.1617(9)	0.6406(6)	0.7429(6)	C(57)	0.3420(11)	1.3298(9)	1.2387(8)
C(16)	0.1575(9)	0.5723(6)	0.6674(6)	C(58)	0.2910(11)	1.4672(8)	0.8967(9)
C(17)	0.2321(9)	0.5647(6)	0.6087(6)	C(59)	0	1.0	1.0
C(18)	0.2211(12)	0.4974(7)	0.5368(8)				

Table 13 Positional parameters for compound **6a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
P(1)	0.6278(2)	0.1761(1)	0.2164(1)	C(46)	0.931(1)	−0.2965(6)	0.3733(5)
P(2)	0.6345(2)	0.0982(1)	0.3636(1)	C(47)	0.959(1)	−0.3113(6)	0.3090(6)
P(3)	0.9197(2)	0.0983(1)	0.3325(1)	C(48)	0.920(1)	−0.2520(7)	0.2485(6)
P(4)	0.9192(2)	0.1203(1)	0.1850(1)	C(49)	0.845(1)	−0.1740(6)	0.2531(5)
O(1)	0.5535(5)	0.2657(3)	0.2202(3)	C(51)	0.9159(9)	0.3062(5)	0.3192(4)
O(2)	0.5463(6)	0.1634(3)	0.1638(3)	C(52)	0.9455(9)	0.2309(5)	0.3610(4)
O(3)	0.5126(5)	0.1363(3)	0.4166(3)	C(53)	0.929(1)	0.2138(5)	0.4351(5)
O(4)	0.6259(6)	0.0072(3)	0.4069(3)	C(54)	0.885(1)	0.2784(6)	0.4669(5)
O(5)	0.9984(6)	0.1668(3)	0.3296(3)	C(55)	0.8554(9)	0.3596(5)	0.4240(4)
O(6)	0.9763(6)	0.0211(4)	0.3912(3)	C(56)	0.811(1)	0.4284(6)	0.4552(5)
O(7)	1.0338(6)	0.1657(3)	0.1304(3)	C(57)	0.784(1)	0.5062(7)	0.4117(6)
O(8)	0.9202(5)	0.0541(3)	0.1468(3)	C(58)	0.797(1)	0.5221(7)	0.3402(6)
N(1)	0.5892(6)	0.1157(4)	0.2906(3)	C(59)	0.839(1)	0.4559(7)	0.3062(6)
N(2)	0.7665(6)	0.1240(4)	0.3641(3)	C(61)	1.1194(9)	−0.0963(5)	0.3591(4)
N(3)	0.9640(6)	0.0796(4)	0.2583(3)	C(62)	1.1045(9)	−0.0308(5)	0.3849(4)
N(4)	0.7794(6)	0.1787(4)	0.1798(3)	C(63)	1.201(1)	−0.0168(6)	0.4196(5)
C(11)	0.5808(9)	0.3997(5)	0.2002(4)	C(64)	1.325(1)	−0.0705(6)	0.4203(5)
C(12)	0.5845(8)	0.3384(4)	0.1725(4)	C(65)	1.345(1)	−0.1382(5)	0.3926(5)
C(13)	0.6031(9)	0.3466(5)	0.0985(4)	C(66)	1.476(1)	−0.1973(6)	0.3961(5)
C(14)	0.6251(9)	0.4227(5)	0.0532(4)	C(67)	1.493(1)	−0.2609(7)	0.3670(6)
C(15)	0.6264(9)	0.4879(5)	0.0807(4)	C(68)	1.400(1)	−0.2744(6)	0.3348(5)
C(16)	0.652(1)	0.5648(6)	0.0326(5)	C(69)	1.271(1)	−0.2197(6)	0.3332(5)
C(17)	0.654(1)	0.6265(7)	0.0614(6)	C(71)	1.0032(9)	0.3081(5)	0.1151(4)
C(18)	0.631(1)	0.6186(7)	0.1329(6)	C(72)	1.0716(9)	0.2324(5)	0.1406(4)
C(19)	0.602(1)	0.5444(6)	0.1804(5)	C(73)	1.191(1)	0.2140(6)	0.1730(5)
C(21)	0.611(1)	0.0769(5)	0.0877(5)	C(74)	1.230(1)	0.2806(6)	0.1810(5)
C(22)	0.5551(9)	0.0873(5)	0.1529(4)	C(75)	1.1644(9)	0.3610(5)	0.1566(4)
C(23)	0.494(1)	0.0270(6)	0.2083(5)	C(76)	1.209(1)	0.4281(6)	0.1653(5)

Table 13 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(24)	0.506(1)	−0.0492(6)	0.1971(5)	C(77)	1.141(1)	0.5065(7)	0.1422(6)
C(25)	0.571(1)	−0.0620(6)	0.1318(5)	C(78)	1.032(1)	0.5235(7)	0.1083(6)
C(26)	0.585(1)	−0.1443(7)	0.1210(6)	C(79)	0.984(1)	0.4581(6)	0.0992(5)
C(27)	0.646(1)	−0.1529(8)	0.0545(7)	C(81)	0.9898(8)	−0.0540(5)	0.0943(4)
C(28)	0.690(1)	−0.0882(7)	−0.0037(6)	C(82)	1.0180(8)	−0.0159(5)	0.1380(4)
C(29)	0.681(1)	−0.0127(6)	0.0076(5)	C(83)	1.1288(9)	−0.0426(5)	0.1721(4)
C(31)	0.5048(9)	0.2747(5)	0.4125(4)	C(84)	1.215(1)	−0.1159(5)	0.1644(5)
C(32)	0.4533(9)	0.2193(5)	0.3979(4)	C(85)	1.1892(9)	−0.1596(5)	0.1209(4)
C(33)	0.334(1)	0.2372(5)	0.3690(5)	C(86)	1.281(1)	−0.2364(6)	0.1144(5)
C(34)	0.260(1)	0.3161(6)	0.3548(5)	C(87)	1.252(1)	−0.2766(6)	0.0699(5)
C(35)	0.308(1)	0.3748(5)	0.3695(5)	C(88)	1.145(1)	−0.2464(6)	0.0336(6)
C(36)	0.230(1)	0.4607(7)	0.3539(6)	C(89)	1.055(1)	−0.1709(6)	0.0394(5)
C(37)	0.284(1)	0.5193(7)	0.3653(6)	C(110)	0.6032(9)	0.4780(5)	0.1524(4)
C(38)	0.404(1)	0.5000(7)	0.3941(6)	C(210)	0.6197(9)	−0.0010(5)	0.0756(4)
C(39)	0.481(1)	0.4185(7)	0.4113(6)	C(310)	0.428(1)	0.3591(5)	0.3964(5)
C(41)	0.7377(9)	−0.0780(5)	0.3290(4)	C(410)	0.813(1)	−0.1563(5)	0.3218(5)
C(42)	0.7084(9)	−0.0634(5)	0.3925(4)	C(510)	0.8706(9)	0.3742(5)	0.3496(4)
C(43)	0.7505(9)	−0.1231(5)	0.4543(4)	C(610)	1.2479(9)	−0.1520(5)	0.3608(4)
C(44)	0.822(1)	−0.1990(6)	0.4467(5)	C(710)	1.0513(9)	0.3766(5)	0.1230(4)
C(45)	0.8546(9)	−0.2163(5)	0.3827(4)	C(810)	1.0806(9)	−0.1283(5)	0.0858(4)

Table 14 Positional parameters for compound **6b** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
P(1)	0.9682	0.9019	0.2237	C(36)	0.889(1)	0.973(2)	0.803(1)
P(2)	0.8876(2)	0.7318(2)	0.3071(2)	C(37)	0.942(2)	1.083(2)	0.818(2)
P(3)	1.1409(2)	0.8214(2)	0.4771(2)	C(38)	0.949(1)	1.090(1)	0.722(1)
P(4)	1.2217(2)	0.9852(2)	0.3880(2)	C(39)	0.9063(10)	0.985(1)	0.6048(10)
O(1)	0.9437(5)	0.8465(5)	0.0810(5)	C(40)	0.8470(8)	0.861(1)	0.5807(8)
O(2)	0.9108(5)	0.9929(5)	0.2500(6)	C(41)	1.1585(7)	0.8746(8)	0.7037(7)
O(3)	0.8227(5)	0.5821(5)	0.2157(5)	C(42)	1.0931(8)	0.7542(8)	0.6681(8)
O(4)	0.7996(5)	0.7618(6)	0.3619(5)	C(43)	1.0609(9)	0.735(1)	0.753(1)
O(5)	1.1991(5)	0.9058(5)	0.6267(5)	C(44)	1.0950(10)	0.834(1)	0.869(1)
O(6)	1.1655(5)	0.7019(5)	0.4463(5)	C(45)	1.1637(9)	0.958(1)	0.9079(9)
O(7)	1.2869(5)	0.9581(6)	0.3037(5)	C(46)	1.205(1)	1.068(2)	1.034(1)
O(8)	1.3092(5)	1.1277(5)	0.5065(5)	C(47)	1.272(2)	1.190(2)	1.063(1)
N(1)	0.8909(5)	0.7905(6)	0.2278(5)	C(48)	1.303(1)	1.210(1)	0.979(1)
N(2)	1.0028(5)	0.7653(6)	0.4182(6)	C(49)	1.2668(10)	1.1084(9)	0.8598(9)
N(3)	1.2190(5)	0.9024(6)	0.4439(6)	C(50)	1.1955(7)	0.9809(9)	0.8222(7)
N(4)	1.1066(5)	0.9806(6)	0.3056(6)	C(51)	1.2804(7)	0.7132(7)	0.4615(9)
C(1)	0.8311(7)	0.7479(8)	−0.0222(7)	C(52)	1.3753(8)	0.7755(8)	0.5771(10)
C(2)	0.7362(8)	0.770(1)	−0.0548(8)	C(53)	1.4819(10)	0.775(1)	0.586(1)
C(3)	0.6259(9)	0.670(1)	−0.163(1)	C(54)	1.491(1)	0.717(1)	0.481(2)
C(4)	0.617(1)	0.554(1)	−0.231(1)	C(55)	1.398(1)	0.654(1)	0.362(1)
C(5)	0.713(1)	0.530(1)	−0.1994(9)	C(56)	1.397(2)	0.582(2)	0.238(2)
C(6)	0.711(2)	0.407(1)	−0.271(1)	C(57)	1.305(2)	0.525(2)	0.130(2)
C(7)	0.802(2)	0.391(2)	−0.238(2)	C(58)	1.203(2)	0.528(1)	0.121(1)
C(8)	0.912(2)	0.488(1)	−0.133(1)	C(59)	1.187(1)	0.588(1)	0.226(1)
C(9)	0.922(1)	0.6049(10)	−0.0581(9)	C(60)	1.2872(8)	0.6518(8)	0.349(1)
C(10)	0.8249(8)	0.6284(8)	−0.0902(7)	C(61)	1.3948(7)	0.9488(7)	0.3345(7)
C(11)	0.9511(7)	1.1103(7)	0.2601(7)	C(62)	1.4798(8)	1.0030(9)	0.4540(8)
C(12)	1.0176(8)	1.1416(8)	0.2058(9)	C(63)	1.5850(8)	0.992(1)	0.474(1)
C(13)	1.0528(10)	1.261(1)	0.218(1)	C(64)	1.6034(9)	0.928(1)	0.376(1)
C(14)	1.0171(10)	1.3407(10)	0.280(1)	C(65)	1.517(1)	0.8713(10)	0.252(1)
C(15)	0.9466(9)	1.3106(8)	0.3370(10)	C(66)	1.535(2)	0.804(2)	0.143(2)
C(16)	0.901(1)	1.3930(10)	0.409(1)	C(67)	1.445(2)	0.750(2)	0.023(2)
C(17)	0.839(1)	1.359(2)	0.462(2)	C(68)	1.333(1)	0.756(1)	−0.001(1)
C(18)	0.811(1)	1.243(1)	0.455(1)	C(69)	1.3160(10)	0.8223(10)	0.1007(9)
C(19)	0.8459(9)	1.1601(10)	0.3874(10)	C(70)	1.4078(8)	0.8796(8)	0.2291(9)
C(20)	0.9142(7)	1.1921(7)	0.3286(8)	C(71)	1.3141(7)	1.2324(7)	0.4958(7)
C(21)	0.7163(7)	0.5061(7)	0.0993(7)	C(72)	1.3682(9)	1.2640(8)	0.4334(8)
C(22)	0.6303(7)	0.5411(8)	0.0678(8)	C(73)	1.379(1)	1.373(1)	0.434(1)
C(23)	0.5242(8)	0.457(1)	−0.052(1)	C(74)	1.330(1)	1.440(1)	0.494(1)
C(24)	0.5078(9)	0.341(1)	−0.1321(9)	C(75)	1.2727(10)	1.4082(9)	0.556(1)
C(25)	0.5942(10)	0.3006(9)	−0.1006(8)	C(76)	1.223(1)	1.479(1)	0.626(2)
C(26)	0.582(2)	0.174(1)	−0.184(1)	C(77)	1.175(2)	1.450(2)	0.683(2)
C(27)	0.670(2)	0.146(1)	−0.151(1)	C(78)	1.163(1)	1.342(1)	0.685(1)
C(28)	0.776(2)	0.232(1)	−0.035(1)	C(79)	1.2057(10)	1.2666(9)	0.621(1)
C(29)	0.793(1)	0.3500(9)	0.0480(10)	C(80)	1.2627(8)	1.2997(7)	0.5565(8)
C(30)	0.7035(8)	0.3863(8)	0.0174(7)	C(81)	0.5523	1.2548	1.2473
C(31)	0.7952(7)	0.7473(9)	0.4608(8)	C(82)	0.5399	1.1497	1.1827
C(32)	0.7421(8)	0.6305(10)	0.439(1)	C(83)	0.5611	1.1678	1.1243
C(33)	0.734(1)	0.622(1)	0.540(2)	C(84)	0.5916	1.0751	1.0857
C(34)	0.778(1)	0.725(2)	0.654(1)	C(85)	0.5129	1.0291	1.0109
C(35)	0.8348(10)	0.845(1)	0.6785(10)	C(86)	0.5477	0.9586	0.9494

dioxane (75 cm^3) at room temperature. The mixture was heated to reflux and the progress of the reaction was followed by ^{31}P NMR spectroscopy. After 72 h the reaction mixture was cooled to room temperature and solvent was removed. The residual product was dissolved in dichloromethane and filtered through silica gel. The dichloromethane was removed under vacuum, and the oily residue dissolved in toluene and extracted with 1 mol dm^{-3} NaOH to remove residual sodium salts. The toluene was removed and the reaction product further purified by column chromatography using a dichloromethane–hexane mixture as the eluent.

$[NP(1\text{-}OC_{10}H_7)_2]_4$ **6b**. The procedure was identical to that used for the preparation of **6a** except for the addition of tetra-*n*-butylammonium bromide to the reaction mixture after 40 h reflux to aid in the nucleophilic substitution. 1-Naphthol was used in place of 2-naphthol.

General Procedure for Polymer Reactions.—The following is a typical synthesis of the polymers described in this paper. $[NP(1\text{-}OC_{10}H_7)_2]_n$. A solution of $(NPCl_2)_n$ (3.45×10^{-2} mol, 4.0 g) in dioxane (300 cm^3) and a solution of sodium 1-naphthyl oxide [prepared from Na (4.76 g, 2.07×10^{-1} mol) and 1-naphthol (36.0 g, 2.49×10^{-1} mol) in dioxane (200 cm^3)] were placed in an autoclave reaction vessel. The mixture was heated to 150 °C for 48 h and then cooled to room temperature. The reaction mixture was concentrated and the product was isolated by precipitation into water. It was soluble in thf and further purified by repeated precipitations from a thf solution into water and hexane. The polymer was purified further by Soxhlet extraction with methanol (72 h) and hexane (72 h), and dried under vacuum.

X-Ray Structure Determination Techniques.—Our general X-ray structural technique has been described in earlier papers[25,26] and only the details related to the present work will be given here. The data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer controlled by a PDP 11/44 computer. The structures were solved by direct methods using SDP[27] installed on the PDP 11/44 and also using a SHELX-MULTAN 82[28] program installed on the Pennsylvania State University IBM-VMS computer. Structures were also solved using the TEXSAN crystal solution package[29] at the University of Calgary, Canada. The ORTEP diagrams were generated using the Chem3D molecular modelling system software. Other programs employed were DIFABS (a program for empirical absorption correction),[30] SIR 92 (a direct methods analysis program)[31] and DIRDIF 92 (a Fourier techniques analysis program).[32] In each case, the first E map revealed the positions of all non-hydrogen atoms. Anisotropic thermal parameters were allowed for P, O and N atoms while C atoms were refined isotropically in compound **4a**. In **4b**, **2e**, **3e**, **6a** and **6b** all the non-hydrogen atoms were refined anisotropically. Fourier difference syntheses calculated toward the end of the refinements showed maxima consistent with the expected positions of hydrogen atoms in all the structures. In **4a**, **4b**, **3e**, **6a** and **6b** hydrogen atoms were included at geometrically idealized positions with overall isotropic thermal parameters. In **2e** the hydrogen atoms were allowed to refine isotropically. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[33] and those for hydrogen atoms from Stewart *et al.*[34] The weighting scheme used was of the form $w^{-1} = \sigma^2(F) + pF^2$. The crystal and refinement data are summarized in Table 8, atomic coordinates in Tables 9–14.

Additional material available from the Cambridge Crystallographic Centre comprises thermal parameters and remaining bond lengths and angles.

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