Cyclic and Short-chain Linear Phosphazenes with Hindered Aryloxy Side Groups†

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A series of short-chain and cyclic phosphazenes bearing *o*-dichloro- and *o*-dimethyl-phenoxy groups have been synthesised, and their structures studied by X-ray crystallography. These compounds are small-molecule models for the corresponding linear high polymers. Structural parameters: $N_3P_3Cl_5(OC_6H_3Cl_2\text{-}o)$ **1**, $a = 8.081(4)$, $b = 8.074(2)$, $c = 25.868(3)$ Å, $\beta = 91.11(2)°$, space group $P2_1/c$, $Z = 4$; *gem*-$N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2$ **2**, $a = 18.856(5)$, $b = 8.002(2)$, $c = 16.124(2)$ Å, $\beta = 114.89(2)°$, space group $P2_1/c$, $Z = 4$; $N_3P_3Cl_2(OC_6H_3Cl_2\text{-}o)_4$ **4**, $a = 7.975(3)$, $b = 18.373(4)$, $c = 22.225(3)$ Å, $\beta = 90.35(2)°$, space group $P2_1/n$, $Z = 4$; $[NP(OC_6H_3Cl_2\text{-}o)_2]_3$ **5**, $a = 12.021(4)$, $b = 19.938(5)$, $c = 18.379(11)$ Å, $\beta = 90.84(5)°$, space group $P2_1/n$, $Z = 4$; *gem*-$N_4P_4Cl_4(OC_6H_3Cl_2\text{-}o)_4$ **6**, $a = 10.806(2)$, $b = 10.861(2)$, $c = 17.075(7)$ Å, $\alpha = 89.33(4)$, $\beta = 80.79(3)$, $\gamma = 68.44(2)°$, space group $P1$, $Z = 2$; *gem*-$N_3P_3Cl_4(OC_6H_3Me_2\text{-}o)_2$ **7**, $a = 9.470(3)$, $b = 18.481(12)$, $c = 13.087(8)$ Å, $\beta = 94.56(4)°$, space group $P2_1/n$, $Z = 4$; $[NP(OC_6H_3Me_2\text{-}o)_2]_3$ **8**, $a = 20.560(5)$, $b = 20.580(9)$, $c = 22.085(4)$ Å, $\alpha = \beta = \gamma = 90.0°$, space group $P4/ncc$, $Z = 8$; $OPCl_2NP(OC_6H_3Cl_2\text{-}o)_3$ **9**, $a = 14.319(4)$, $b = 16.837(4)$, $c = 20.660(8)$ Å, space group $Pbca$, $Z = 8$; $OPCl(OC_6H_3Me_2\text{-}o)NPCl(OC_6H_3Me_2\text{-}o)NP(OC_6H_3Me_2\text{-}o)_3$ **10**, $a = 15.212(3)$, $b = 18.965(1)$, $c = 14.559(2)$ Å, $\beta = 102.96(2)°$, space group $P2_1/c$, $Z = 4$. Despite the bulkiness of the *o*-dichloro- and *o*-dimethyl-phenoxy groups, their introduction into the phosphazene structure followed a geminal substitution pathway during the early stages of the reaction. In the reactions with the linear short-chain oligomers these nucleophiles preferentially attacked at the terminal PCl_3 rather than at the PCl units in the middle of the chain or those associated with the phosphoryl group. The structure of compound **10** revealed a distorted *trans-trans* conformation for the PN skeleton, in contrast to the *cis-trans* arrangement generally believed to exist for linear phosphazene high polymers.

The nucleophilic halogen-replacement reactions of various nucleophiles with halogenophosphazenes have been investigated in much detail and the subject was recently reviewed.[1] The reactions of $(NPCl_2)_3$ with aryloxide ions or secondary amines generally follow non-geminal pathways,[2–6] while those with benzenethiolate, ethenethiolate and primary amines proceed *via* geminal substitution.[7,8] The geminal introduction of bulky aryloxy groups is less well known. Here, we report the syntheses and structures of a series of short-chain linear and cyclic phosphazenes that bear the bulky *o*-dichloro- and *o*-dimethyl-phenoxy side groups. These are model reactions for the synthesis of highly polymeric phosphazenes that bear these same aryloxy side groups. The objectives of this study were three-fold: (1) to determine the effect of relatively hindered side groups on the synthesis and structure of the cyclic and short-chain linear phosphazenes; (2) to relate the structures of these model compounds to the preparation and properties of the analogous highly polymeric phosphazenes; and (3) to determine the influence of steric and electronic factors on the nucleophilic substitution patterns found for cyclic and linear phosphazenes.

Results and Discussion

Syntheses.—Compounds **1**–**10** are described in this paper. Cyclic phosphazenes **1**–**8** were prepared by treatment of hexachlorocyclotriphosphazene $(NPCl_2)_3$ or the cyclic tetramer $(NPCl_2)_4$ with the sodium salts of *o*-dichloro- or *o*-dimethylphenol in the ratios needed to obtain the desired degree of substitution. Compound **9** was prepared by the reaction of $OPCl_2NPCl_3$[9] with the sodium salt of *o*-dichlorophenol, and **10** was prepared by the reaction of $OPCl_2NPCl_2NPCl_3$[10] with the sodium salt of *o*-dimethylphenol. The ^{31}P NMR chemical shifts, melting point and analytical data are in Table 1. The compounds were recrystallized from a mixture of methylene chloride and hexane.

X-Ray Crystal Structures.—(*a*) $N_3P_3Cl_5(OC_6H_3Cl_2\text{-}o)$ **1**. The structure of compound **1** consists of a planar six-membered ring of alternating phosphorus and nitrogen atoms (Fig. 1). Two chlorine atoms are bonded to each of atoms P(2) and P(3), and one chlorine atom is linked to P(1); the latter is also connected to a $o\text{-}Cl_2C_6H_3O$ group through a P–O linkage. The average P–N bond distance is 1.573(3) Å, and the N–P–N and P–N–P angles assume mean values of 118.9(2) and 121.0(2)° respectively. All the P–Cl bond distances are similar to each other, with an average value of 1.981(1) Å. The structural data are listed in Tables 2 and 3.

(*b*) $N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2$ **2**. The molecule of **2** contains a planar six-membered phosphazene ring, (Fig. 2). Each of the P(2) and P(3) atoms are bonded to two chlorine atoms, while two $o\text{-}Cl_2C_6H_3O$ groups are attached to P(1) through P–O linkages. The planes of the aryloxy groups are oriented roughly perpendicular to each other and to the phosphazene ring. The P–N bond distances are essentially equivalent with a mean value of 1.575(3) Å. The average N–P–N and P–N–P bond angles are 118.4(2) and 121.0(2)° respectively. The P–Cl bond lengths are equivalent and have a value near 1.98(1) Å. The structural data are listed in Tables 4 and 5.

(*c*) $N_3P_3Cl_2(OC_6H_3Cl_2\text{-}o)_4$ (*cis*) **4**. Compound **4** contains a planar six-membered ring (Fig. 3). Two *o*-dichlorophenoxy groups are bonded to P(1). Each P(2) and P(3) atom is connected to one such moiety (non-geminal structure), and a chlorine atom. The disposition of the side groups is such that, at P(1), the planes of the two *o*-dichlorophenoxy groups are perpendicular to each other. The aryloxy group bonded to O(2)

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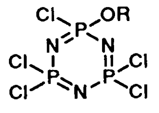
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



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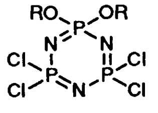

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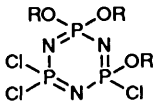

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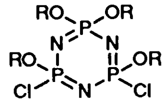

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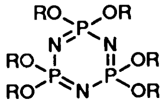

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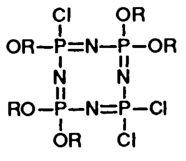

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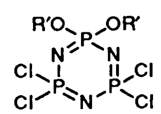

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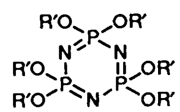

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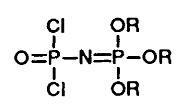
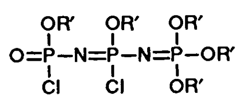


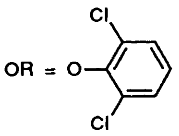
$O{=}PCl_2{-}N{=}P(OR)_3$

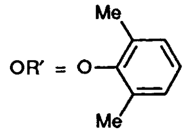
9



$O{=}P(OR')Cl{-}N{=}P(OR')Cl{-}N{=}P(OR')_3$

10





is coplanar with the phosphazene ring. The planes of the *o*-dichlorophenoxy groups bonded to P(2) and P(3) are parallel to each other, forming a stacked arrangement, and are also perpendicular to the phosphazene ring. It is interesting that all the aryloxy groups are oriented so that their planes are mutually perpendicular. The average N–P–N and P–N–P angles are 117.7(1) and 121.6(1)° respectively. The average P–N bond distance is 1.574(2) Å. The structural parameters are listed in Tables 6 and 7.

(*d*) $[NP(OC_6H_3Cl_2\text{-}o)_2]_3$ **5**. Molecules of **5** (Fig. 4) contain a six-membered phosphazene ring that is slightly puckered. Six *o*-$Cl_2C_6H_3O$ groups are attached to the phosphazene ring through P–O linkages. The orientation of the aryloxy groups around the phosphazene ring is as follows: the aryl rings bonded to O(4) and O(1) are almost coplanar with the phosphazene

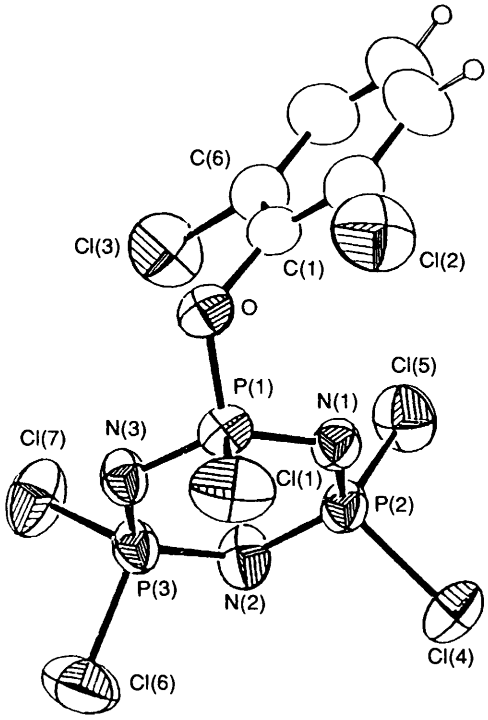


Fig. 1 An ORTEP diagram for $N_3P_3Cl_5(OC_6H_3Cl_2\text{-}o)$ **1**

Table 1 Characterization data

	^{31}P NMR		Analysis (%)				
Compound	δ	*J*/Hz	C	H	N	Cl	M.p. (°C)
1	A_2 +21, B +12.5	J_{AB} 60	15.75 (15.75)	0.65 (0.65)	9.15 (9.15)	54.2 (54.15)	86
2	A_2 +22.8, B −1.3	J_{AB} 70	23.95 (24.00)	1.05 (1.40)	7.05 (7.00)	47.35 (47.20)	179
3	A +22.6, B +1.2, C +13.8	J_{AB} 77, J_{BC} 82, J_{AC} 76	29.80 (29.75)	1.75 (1.25)	5.70 (5.80)	43.10 (43.85)	144
4	A_2 +23.7, B −1.2	J_{AB} 83	33.80 (33.75)	1.40 (1.40)	4.90 (4.90)	41.30 (41.50)	195
5	A +3.3	—	39.10 (39.05)	1.70 (1.65)	3.85 (3.80)	38.75 (38.45)	>280
6	A −18.5, B_2 −29.6	J_{AB} 83	29.60 (29.75)	1.30 (1.25)	5.85 (5.80)	44.10 (43.85)	140
7	A −8.00	—	37.05 (37.00)	3.45 (3.50)	8.15 (8.10)	27.45 (27.30)	120
8	A +3.7	—	66.95 (66.90)	6.25 (6.30)	4.95 (4.90)		266
9	A −22.0, B −16.0	J_{AB} 68	36.05 (36.00)	1.55 (1.50)	2.40 (2.35)	47.30 (47.20)	85
10	A −23.7, B −10.9, C +29.8	J_{AB} 58.7, J_{BC} 88.5	59.00 (52.05)	5.60 (5.60)	3.40 (3.45)	9.00 (8.70)	140

Note: For compounds **1**–**8** A = PCl_2, B = $P(OR)_2$; for **9** and **10** A is the phosphorus bound to oxygen, B and C are the next phosphorus atoms along the chain.

Table 2 Bond lengths (Å) and angles (°) for $N_3P_3Cl_5(OC_6H_3Cl_2\text{-}o)$ **1**

Cl(1)–P(1)	1.982(1)	P(2)–N(2)	1.575(3)
Cl(2)–C(2)	1.718(5)	P(3)–N(2)	1.574(3)
Cl(3)–C(6)	1.731(4)	P(3)–N(3)	1.562(3)
Cl(4)–P(2)	1.977(1)	O–C(1)	1.390(4)
Cl(5)–P(2)	1.989(1)	C(1)–C(2)	1.372(6)
Cl(6)–P(3)	1.989(1)	C(1)–C(6)	1.381(5)
Cl(7)–P(3)	1.969(1)	C(2)–C(3)	1.386(6)
P(1)–O	1.581(2)	C(3)–C(4)	1.365(9)
P(1)–N(1)	1.580(3)	C(4)–C(5)	1.377(8)
P(1)–N(3)	1.578(3)	C(5)–C(6)	1.390(6)
P(2)–N(1)	1.571(4)		
Cl(1)–P(1)–O	101.1(1)	N(2)–P(3)–N(3)	119.4(2)
Cl(1)–P(1)–N(1)	110.3(1)	P(1)–O–C(1)	123.0(2)
Cl(1)–P(1)–N(3)	107.6(1)	P(1)–N(1)–P(2)	121.3(2)
O–P(1)–N(1)	109.4(1)	P(2)–N(2)–P(3)	120.4(2)
O–P(1)–N(3)	109.1(1)	P(1)–N(3)–P(3)	121.4(2)
N(1)–P(1)–N(3)	118.0(2)	O–C(1)–C(2)	120.1(4)
Cl(4)–P(2)–Cl(5)	101.36(6)	O–C(1)–C(6)	120.1(3)
Cl(4)–P(2)–N(1)	108.6(1)	C(2)–C(1)–C(6)	119.7(3)
Cl(4)–P(2)–N(2)	109.8(1)	Cl(2)–C(2)–C(1)	120.0(3)
Cl(5)–P(2)–N(1)	108.3(1)	Cl(2)–C(2)–C(3)	120.2(3)
Cl(5)–P(2)–N(2)	108.1(1)	C(1)–C(2)–C(3)	119.8(4)
N(1)–P(2)–N(2)	119.3(2)	C(2)–C(3)–C(4)	119.8(4)
Cl(6)–P(3)–Cl(7)	101.4(7)	C(3)–C(4)–C(5)	121.7(5)
Cl(6)–P(3)–N(2)	108.7(1)	C(4)–C(5)–C(6)	117.9(4)
Cl(6)–P(3)–N(3)	109.2(1)	Cl(3)–C(6)–C(1)	119.1(3)
Cl(7)–P(3)–N(2)	108.5(1)	Cl(3)–C(6)–C(5)	119.7(3)
Cl(7)–P(3)–N(3)	108.2(1)	C(1)–C(6)–C(5)	121.1(4)

Table 3 Final positional parameters for $N_3P_3Cl_5(OC_6H_3Cl_2\text{-}o)$ **1**

Atom	x	y	z
Cl(1)	0.792 8(2)	0.202 7(1)	0.170 96(5)
Cl(2)	0.787 0(2)	0.251 2(1)	0.033 16(5)
Cl(3)	0.562 1(2)	−0.353 8(1)	0.079 74(5)
Cl(4)	1.235 7(1)	−0.214 6(2)	0.177 52(5)
Cl(5)	1.040 5(1)	−0.432 9(1)	0.100 80(4)
Cl(6)	0.770 9(2)	−0.218 1(2)	0.295 20(4)
Cl(7)	0.578 2(1)	−0.452 5(1)	0.223 06(5)
P(1)	0.760 5(1)	−0.029 2(1)	0.147 74(3)
P(2)	1.005 4(1)	−0.263 9(1)	0.155 46(3)
P(3)	0.743 9(1)	−0.274 1(1)	0.220 65(4)
O	0.640 5(3)	−0.003 9(3)	0.099 4(1)
N(1)	0.929 6(3)	−0.105 0(4)	0.129 2(1)
N(2)	0.911 2(3)	−0.349 1(4)	0.201 0(1)
N(3)	0.664 8(3)	−0.123 5(4)	0.191 4(1)
C(1)	0.678 5(4)	−0.057 6(4)	0.050 0(1)
C(2)	0.746 1(5)	0.050 2(5)	0.015 3(1)
C(3)	0.776 0(6)	−0.002 0(7)	−0.034 7(2)
C(4)	0.743 5(7)	−0.162 0(8)	−0.048 6(2)
C(5)	0.677 7(7)	−0.273 8(6)	−0.014 4(2)
C(6)	0.645 0(5)	−0.218 7(5)	0.035 3(2)

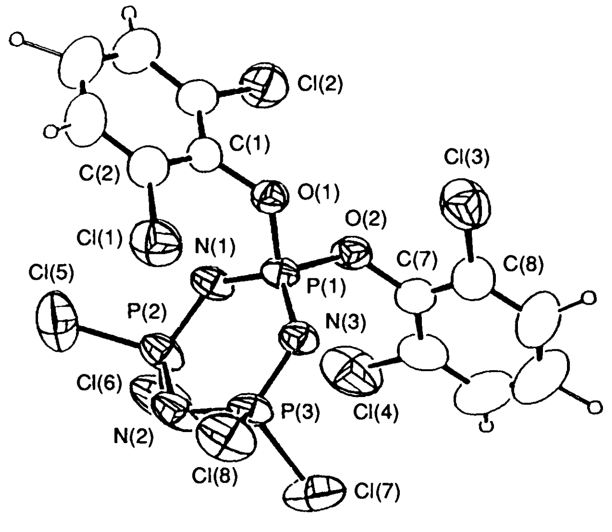


Fig. 2 An ORTEP diagram for $N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2$ **2**

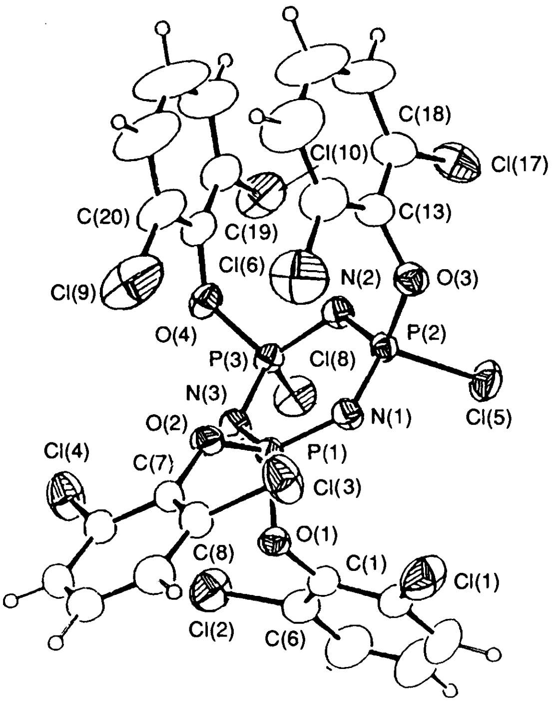


Fig. 3 An ORTEP diagram for $N_3P_3Cl_2(OC_6H_3Cl_2\text{-}o)_4$ **4**

ring, while the remaining aryloxy groups are oriented roughly perpendicular to the phosphazene ring. The aryloxy groups are arranged almost like a propeller to allow the sterically hindered *o*-dichloro moieties to fit together in a manner that minimizes steric repulsions. No intramolecular stacking of side groups was detected. The P–N bond distances are similar, with an average value of 1.58(2) Å. The N–P–N and P–N–P angles averaged to 117.7(3) and 121.8(4)° respectively. The structural data are listed in Tables 8 and 9.

(*e*) *gem*-$N_4P_4Cl_4(OC_6H_3Cl_2\text{-}o)_4$ **6**. The skeleton of compound **6** consists of an eight membered ring of alternating phosphorus and nitrogen atoms (Fig. 5). Two chlorine atoms are bonded to each of P(2) and P(4), while P(1) and P(3) are each bonded to two *o*-$Cl_2C_6H_3O$ groups. Two molecules **6a** and **6b** with slightly different conformations were found to exist in the unit cell. In each of the conformers an inversion centre exists in the centre of the ring. As a result the geometry and conformation on one half of the ring is duplicated by inversion on the other half. Consequently, two coplanar pairs of aryloxy groups exist in each molecule. The main difference between **6a** and **6b** lies in the orientation of the P–O–C linkages between the phosphazene ring and the aryloxy groups. In **6a** the planes formed by the P–O–C linkages from each phosphorus atom are perpendicular to each other, while in **6b** these linkages are coplanar. In **6a** part of one aryloxy group from each phosphorus atom is directly above and below the phosphazene ring. No such feature exists in the structure of **6b**. The relevant bond angles and bond lengths are: **6a**, N–P–N 120.3(2), P–N–P 129.8(2)°, P–N 1.552(3) Å; **6b**, N–P–N 120.5(3), P–N–P 143.9(2)°, P–N 1.548(4) Å. The structural data are listed in Tables 10 and 11.

(*f*) *gem*-$N_3P_3Cl_4(OC_6H_3Me_2\text{-}o)_2$ **7**. The structural of compound **7** is very similar to that of **2**. The molecule consists of a six-membered ring formed by alternating phosphorus and nitrogen atoms (Fig. 6). Two chlorine atoms are bonded to phosphorus atoms P(2) and P(3). Two *o*-$Me_2C_6H_3O$ groups

Table 4 Bond lengths (Å) and angles (°) for $N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2$ **2**

Cl(1)–C(2)	1.726(4)	P(1)–O(1)	1.579(2)	P(3)–N(3)	1.565(3)	C(5)–C(6)	1.376(6)
Cl(2)–C(6)	1.720(4)	P(1)–O(1)	1.571(3)	O(1)–C(1)	1.382(3)	C(7)–C(8)	1.396(7)
Cl(3)–C(8)	1.701(4)	P(1)–N(1)	1.579(3)	O(2)–C(7)	1.391(4)	C(7)–C(12)	1.361(5)
Cl(4)–C(12)	1.746(5)	P(1)–N(3)	1.579(3)	C(1)–C(2)	1.379(5)	C(8)–C(9)	1.388(6)
Cl(5)–P(2)	1.981(1)	P(2)–N(1)	1.568(3)	C(1)–C(6)	1.379(5)	C(9)–C(10)	1.371(9)
Cl(6)–P(2)	1.984(1)	P(2)–N(2)	1.580(3)	C(2)–C(3)	1.381(6)	C(10)–C(11)	1.356(9)
Cl(7)–P(3)	1.986(1)	P(3)–N(2)	1.576(4)	C(3)–C(4)	1.359(7)	C(11)–C(12)	1.363(7)
Cl(8)–P(3)	1.974(1)			C(4)–C(5)	1.353(7)		
O(1)–P(1)–O(2)	99.4(1)	Cl(7)–P(3)–Cl(8)	101.3(1)	O(1)–C(1)–C(6)	119.8(3)	O(2)–C(7)–C(12)	121.6(4)
O(1)–P(1)–N(1)	108.6(1)	Cl(7)–P(3)–N(2)	109.1(1)	C(2)–C(1)–C(6)	119.4(3)	C(8)–C(7)–C(12)	119.2(3)
O(1)–P(1)–N(3)	110.5(1)	Cl(7)–P(3)–N(3)	108.3(2)	Cl(1)–C(2)–C(1)	119.4(3)	Cl(3)–C(8)–C(7)	119.9(3)
O(2)–P(1)–N(1)	110.7(1)	Cl(8)–P(3)–N(2)	108.4(1)	Cl(1)–C(2)–C(3)	121.0(3)	Cl(3)–C(8)–C(9)	120.6(4)
O(2)–P(1)–N(3)	108.8(1)	Cl(8)–P(3)–N(3)	109.5(1)	C(1)–C(2)–C(3)	119.5(4)	C(7)–C(8)–C(9)	119.6(4)
N(1)–P(1)–N(3)	117.5(2)	N(2)–P(3)–N(3)	118.9(2)	C(2)–C(3)–C(4)	120.0(4)	C(8)–C(9)–C(10)	118.4(6)
Cl(5)–P(2)–Cl(6)	100.3(1)	P(1)–O(1)–C(1)	124.7(2)	C(3)–C(4)–C(5)	121.0(4)	C(9)–C(10)–C(11)	122.3(5)
Cl(5)–P(2)–N(1)	108.3(2)	P(1)–O(2)–C(7)	122.8(2)	C(4)–C(5)–C(6)	119.8(4)	C(10)–C(11)–C(12)	118.9(5)
Cl(5)–P(2)–N(2)	108.0(1)	P(1)–N(1)–P(2)	121.6(2)	Cl(2)–C(6)–C(1)	119.4(2)	Cl(4)–C(12)–C(7)	118.5(4)
Cl(6)–P(2)–N(1)	110.3(1)	P(2)–N(2)–P(3)	119.6(2)	Cl(2)–C(6)–C(5)	120.4(3)	Cl(4)–C(12)–C(11)	120.0(4)
Cl(6)–P(2)–N(2)	109.5(1)	P(1)–N(3)–P(3)	121.8(3)	C(1)–C(6)–C(5)	120.2(4)	C(7)–C(12)–C(11)	121.6(5)
N(1)–P(2)–N(2)	118.9(2)	O(1)–C(1)–C(2)	120.6(3)	O(2)–C(7)–C(8)	119.2(4)		

Table 5 Final positional parameters for $N_3P_3Cl_4(OC_6H_3Cl_2\text{-}o)_2$ **2**

Atom	*x*	*y*	*z*
Cl(1)	0.111 14(6)	0.445 3(2)	0.763 62(7)
Cl(2)	0.230 24(7)	−0.154 9(1)	0.750 24(8)
Cl(3)	0.426 80(7)	0.283 4(2)	0.834 19(8)
Cl(4)	0.402 10(9)	0.021 0(2)	1.126 08(7)
Cl(5)	0.067 10(7)	0.121 1(2)	0.947 41(10)
Cl(6)	0.211 39(7)	0.023 0(2)	1.117 62(6)
Cl(7)	0.348 20(9)	0.501 0(2)	1.134 84(7)
Cl(8)	0.218 74(7)	0.678 0(1)	0.974 07(8)
P(1)	0.272 33(5)	0.193 7(1)	0.911 04(5)
P(2)	0.181 38(5)	0.160 9(1)	1.005 81(6)
P(3)	0.259 34(6)	0.451 9(1)	1.015 71(6)
O(1)	0.236 2(1)	0.195 9(3)	0.803 2(1)
O(2)	0.350 4(1)	0.097 7(3)	0.930 9(1)
N(1)	0.217 5(2)	0.086 7(3)	0.942 1(2)
N(2)	0.195 2(2)	0.351 2(4)	1.033 3(2)
N(3)	0.292 9(2)	0.376 5(4)	0.950 1(2)
C(1)	0.162 1(2)	0.140 0(5)	0.746 8(2)
C(2)	0.098 9(2)	0.246 5(5)	0.718 9(2)
C(3)	0.026 6(2)	0.191 5(6)	0.656 7(3)
C(4)	0.018 3(3)	0.034 3(7)	0.622 4(3)
C(5)	0.079 7(3)	−0.072 0(6)	0.649 9(3)
C(6)	0.152 0(2)	−0.020 1(5)	0.712 5(2)
C(7)	0.423 6(2)	0.160 7(5)	0.987 6(2)
C(8)	0.466 2(2)	0.248 7(6)	0.949 1(3)
C(9)	0.540 3(3)	0.307 5(7)	1.004 8(4)
C(10)	0.568 9(3)	0.279 3(7)	1.097 1(4)
C(11)	0.528 2(3)	0.192 4(7)	1.134 9(3)
C(12)	0.456 0(2)	0.133 0(6)	1.079 4(3)

are bonded to P(1) through P–O linkages. The planes of the phenoxy groups are roughly perpendicular to each other and those formed by the P–O–C linkages are nearly coplanar. The crystal possess four molecules in the unit cell. Two layers of molecules can be identified, those in each layer assuming similar general orientations. In other words the phosphorus atoms that bear the two aryloxy groups are pointed in the same direction. On the other hand, molecules in the adjacent layer are oriented so that the phosphorus atom that bears the aryloxy groups is directed 180° away from its neighbouring counterpart. No direct intermolecular stacking of side groups was detected.

Slight differences exist in the values of the P–N bond distances. The average of P(1)–N(1) and P(1)–N(3) is 1.59 Å, slightly longer than the average P–N bond distance in the rest of the ring (1.57 Å). The N(1)–P(1)–N(3) angle, at 116.4°, is also slightly smaller than N(2)–P(3)–N(3) and N(1)–P(3)–N(2) (average 119.1°). The P–N–P angles averaged to 121.6(2)°. The structural data are listed in Tables 12 and 13.

(*g*) $[NP(OC_6H_3Me_2\text{-}o)_2]_3$ **8**. The structure of compound **8** consists of six *o*-$Me_2C_6H_3O$ groups bonded through P–O linkages to a non-planar six-membered phosphazene ring (Fig. 7). The molecule possesses a C_2 rotational axis going through P(2) and N(3). The arrangement of side groups around the phosphazene ring is unexceptional. However, the P–N bond lengths are unequal. The difference between the longest (1.79 Å) and the shortest bond (1.36 Å) amounts to as much as 0.4 Å. Similarly, the N–P–N bond angles vary from 111.0(2) to 119.6(3)°, while the P–N–P bond angles vary from 122.8(5) to 125.5(3)°. As a consequence the phosphazene ring is puckered. Selected structural parameters are listed in Tables 14 and 15.

(*h*) $OPCl_2NP(OC_6H_3Cl_2\text{-}o)_3$ **9**. Compound **9** is a short-chain linear phosphazene with an O–P–N–P backbone (Fig. 8). Two chlorine and an oxygen atom are bonded to P(1), while three *o*-$Cl_2C_6H_3O$ groups are bonded to P(2). The structure is the first example of a partially substituted short-chain phosphazene to be described, and serves to illustrate the initial site of nucleophilic replacement, which is the terminal PCl_3 unit. The planes formed by the three aryloxy groups are oriented mutually perpendicular to each other. This conformation appeared to allow the bulky side groups to be separated from each other to the greatest degree possible.

The P–N bond distances are unequal: P(1)–N is 1.515(4) and P(2)–N is 1.567 Å. The large value may reflect the fact that P(2) is connected to three *o*-$Cl_2C_6H_3O$ groups, which exert a strong electron-withdrawing effect on the phosphazene skeleton, causing a net decrease of electron density and thereby weakening the bonding between P(2) and skeletal nitrogen. The P–N–P bond angle is 142.4(4)°. Selected structural data are listed in Tables 16 and 17.

(*i*) $OPCl(OC_6H_3Me_2\text{-}o)NPCl(OC_6H_3Me_2\text{-}o)NP(OC_6H_3Me_2\text{-}o)_3$ **10**. The crystal structure of compound **10** consists of four molecules in the unit cell. The molecules are arranged in a staggered arrangement. Intermolecular stacking of side groups is not obvious. The molecule consists of a short-chain linear phosphazene with an O–P–N–P–N–P backbone (Fig. 9). One chlorine atom and a *o*-$Me_2C_6H_3O$ group are bonded to P(2) and P(3). An oxygen atom is also bonded to P(3). Three *o*-$Me_2C_6H_3O$ groups are also connected to P(1). Intramolecular stacking of aryloxy groups clearly exists: the aryloxy rings that include O(3) [bonded to P(1)], O(4) [bonded to P(2)], and O(5) [bonded to P(3)] are coplanar and form a stacking arrangement. As in **9** the three *o*-$Me_2C_6H_3O$ groups bonded to P(1) are mutually perpendicular to each another. The phosphazene skeleton assumes a non-planar *trans-trans* conformation.

The P–N bond lengths are non-equivalent and can be separated into long and short ones: P(1)–N(1) and P(2)–N(2) are similar at about 1.535(3) Å, while P(2)–N(1) and P(3)–N(2) are about 1.576(4) Å. The P(1)–N(1)–P(2) angle is 143.8(2)° and P(2)–N(2)–P(3) is 135.3(2)°. The N(1)–P(2)–N(2) angle is 114.9(2)°. The structural data are listed in Tables 18 and 19.

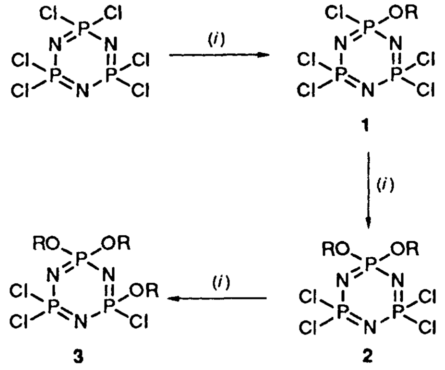
Significance of the Structures.—Many examples exist of geminally substituted cyclic phosphazene trimers, even though the exact mechanisms that lead to the formation of such products is not well understood. In this paper attempts are made to probe the influence of steric and electronic factors on the nucleophilic replacement reactions carried out with cyclic and short-chain chlorophosphazenes. Compounds **1**–**6** are cyclic phosphazenes that bear the *o*-$Cl_2C_6H_3O$ side group which is relatively bulky and strongly electron-withdrawing. The work described here provided an opportunity to examine the structure of cyclic phosphazenes formed at different stages in the nucleophilic substitution. It is also of interest to understand the effect of the electron-withdrawing ability of the *o*-$Cl_2C_6H_3O$ group on the electronic environment of the phosphazene ring. It should be noted that the compounds described represent major products that were isolated and crystallized. In all cases they were not the only products obtained from the reaction mixtures. It is possible that other configurational isomers may be present as minor products, but failed to crystallize.

Table 6 Bond lengths (Å) and angles (°) for $N_3P_3Cl_2(OC_6H_3Cl_2\text{-}o)_4$ **4**

P(1)–O(1)	1.595(2)	P(3)–N(2)	1.584(2)
P(1)–O(2)	1.582(2)	P(3)–N(3)	1.571(2)
P(1)–N(1)	1.576(2)	P(2)–Cl(5)	1.999(2)
P(1)–N(3)	1.569(2)	P(3)–Cl(8)	2.009(1)
P(2)–O(3)	1.582(2)	O(1)–C(1)	1.375(3)
P(2)–N(1)	1.562(2)	O(2)–C(7)	1.383(3)
P(2)–N(2)	1.582(2)	O(3)–C(13)	1.378(3)
P(3)–O(4)	1.581(3)	O(4)–C(19)	1.377(3)

O(1)–P(1)–O(2)	98.42(9)	Cl(8)–P(3)–N(2)	109.97(9)
O(1)–P(1)–N(1)	111.5(1)	Cl(8)–P(3)–N(3)	107.28(9)
O(1)–P(1)–N(3)	110.9(1)	O(4)–P(3)–N(2)	109.1(1)
O(2)–P(1)–N(1)	108.8(1)	O(4)–P(3)–N(3)	111.2(1)
O(2)–P(1)–N(3)	109.9(1)	N(2)–P(3)–N(3)	118.8(1)
N(1)–P(1)–N(3)	116.0(1)	P(1)–O(1)–C(1)	123.4(2)
Cl(5)–P(2)–O(3)	97.86(8)	P(1)–O(2)–C(7)	127.7(2)
Cl(5)–P(2)–N(1)	107.34(9)	P(2)–O(3)–C(13)	125.9(2)
Cl(5)–P(2)–N(2)	110.46(9)	P(3)–O(4)–C(19)	126.1(2)
O(3)–P(2)–N(1)	111.3(1)	P(1)–N(1)–P(2)	123.2(1)
O(3)–P(2)–N(2)	109.6(1)	P(2)–N(2)–P(3)	118.9(1)
N(1)–P(2)–N(2)	118.4(1)	P(1)–N(3)–P(3)	122.7(2)
Cl(8)–P(3)–O(4)	98.66(8)		

Compound **1** possesses a single *o*-$Cl_2C_6H_3O$ group attached to the trimeric ring. The bond lengths and angles are normal. In particular, all the P–Cl bonds are of similar length. Thus, the linkage of an *o*-$Cl_2C_6H_3O$ group to P(1) did not induce a shortening of the geminal P(1)–Cl bond, which suggests that the electronic environment of the phosphazene ring is not greatly altered by the presence of an *o*-$Cl_2C_6H_3O$ group. Further substitution (Scheme 1) generates a geminally disubstituted derivative **2**, even though the phosphorus atom P(1) already possesses one bulky *o*-$Cl_2C_6H_3O$ unit. This behaviour is unusual, because steric arguments would suggest that subsequent substitution steps should occur at a less-crowded phosphorus atom, which in this case is either P(2) or P(3). Does the electron-withdrawing ability of the *o*-$Cl_2C_6H_3O$ group in same way cause a weakening of the P(1)–Cl bond, thereby rendering the latter more susceptible to further nucleophilic substitution? This appears not to be the case in compound **1**. The bond distance of P(1)–Cl is 1.98 Å, while the bond lengths of the remaining P–Cl bonds average to 1.98 Å. This suggests that all the P–Cl bonds have the same electron density and should have equivalent reactivity. These facts seem to rule out an electronic influence as the driving force behind the geminal reaction pathway.



Scheme 1 (*i*) NaOR

Table 7 Final positional parameters for $N_3P_3Cl_2(OC_6H_3Cl_2\text{-}o)_4$ **4**

Atom	*x*	*y*	*z*
Cl(1)	0.362 3(1)	0.109 62(5)	0.505 16(5)
Cl(2)	−0.260 5(1)	0.090 32(5)	0.414 79(5)
Cl(3)	0.255 7(1)	0.282 06(5)	0.591 99(4)
Cl(4)	−0.370 9(1)	0.266 73(5)	0.505 08(5)
Cl(5)	0.456 2(1)	0.209 65(4)	0.333 93(3)
Cl(6)	0.322 1(2)	0.424 46(6)	0.485 57(4)
Cl(7)	0.478 9(1)	0.398 61(5)	0.252 47(4)
Cl(8)	−0.084 4(1)	0.203 02(4)	0.266 35(3)
Cl(9)	−0.145 6(2)	0.426 72(6)	0.418 63(4)
Cl(10)	−0.089 5(2)	0.382 34(6)	0.181 97(4)
P(1)	0.047 58(8)	0.238 81(4)	0.445 04(3)
P(2)	0.297 87(8)	0.283 08(3)	0.367 98(3)
P(3)	−0.026 14(9)	0.278 63(4)	0.328 37(3)
O(1)	0.023 1(2)	0.162 25(9)	0.477 62(7)
O(2)	−0.005 8(2)	0.289 98(9)	0.498 88(8)
O(3)	0.427 4(2)	0.347 6(1)	0.376 3(8)
O(4)	−0.149 8(2)	0.340 8(1)	0.306 85(9)
N(1)	0.237 5(3)	0.253 5(1)	0.430 05(9)
N(2)	0.161 1(3)	0.305 2(1)	0.319 50(9)
N(3)	−0.079 1(3)	0.247 6(1)	0.391 3(1)
C(1)	0.061 7(4)	0.096 8(2)	0.451 2(1)
C(2)	0.218 8(4)	0.065 7(2)	0.459 9(1)
C(3)	0.257 0(5)	−0.000 9(2)	0.434 9(2)
C(4)	0.136 1(6)	−0.037 3(2)	0.402 4(2)
C(5)	−0.019 5(5)	−0.010 0(2)	0.395 3(2)
C(6)	−0.058 4(4)	0.057 5(2)	0.420 1(1)
C(7)	−0.062 5(3)	0.269 4(1)	0.555 0(1)
C(8)	0.046 1(4)	0.265 4(2)	0.603 4(1)
C(9)	−0.012 5(5)	0.249 1(2)	0.660 2(1)
C(10)	−0.179 9(4)	0.237 3(2)	0.668 8(1)
C(11)	−0.290 1(4)	0.241 9(2)	0.621 5(1)
C(12)	−0.232 3(4)	0.258 1(2)	0.564 3(1)
C(13)	0.394 3(4)	0.420 5(2)	0.367 6(1)
C(14)	0.352 8(5)	0.463 5(2)	0.416 4(2)
C(15)	0.337 9(8)	0.538 8(2)	0.408 6(2)
C(16)	0.364(1)	0.569 1(2)	0.353 3(2)
C(17)	0.408 3(7)	0.526 3(2)	0.305 0(2)
C(18)	0.423 0(5)	0.451 8(2)	0.312 3(1)
C(19)	−0.109 5(4)	0.413 1(2)	0.299 3(1)
C(20)	−0.111 3(6)	0.460 9(2)	0.347 8(1)
C(21)	−0.087 9(8)	0.534 3(2)	0.339 0(2)
C(22)	−0.059(1)	0.559 6(2)	0.282 0(2)
C(23)	−0.055 9(7)	0.513 8(2)	0.233 8(2)
C(24)	−0.081 6(5)	0.440 7(2)	0.242 8(2)

Further substitution leads to the formation of the trisubstituted species $N_3P_3Cl_3(OC_6H_3Cl_2\text{-}o)_3$ **3**. Attempts to solve the crystal structure of **3** have been unsuccessful because the crystals appeared to be disordered. The lowered melting point of **3**, relative to compounds **1** and **2**, also supports the argument that the crystal is disordered.

Replacement of the fourth chlorine atom followed a non-geminal pathway to give structure **4**, in which P(2) and P(3) both possess one $o\text{-}Cl_2C_6H_2O$ group and one chlorine atom. The $o\text{-}Cl_2C_6H_3O$ groups at these positions are *cis* to and coplanar with each other. It appears that a different substitution mechanism operates at this stage in the reaction. In spite of the fact that an S_N1 process might be anticipated at this stage, steric factors seem to predominate in the replacement of the fourth chlorine atom, since substitution at a non-geminal site serves to minimize the crowding of the aryloxy groups. The resultant structure also allows intramolecular stacking of side groups. The synthesis of the hexasubstituted compound **5** required more forcing reaction conditions, which reflects the steric hindrance associated with the side groups.

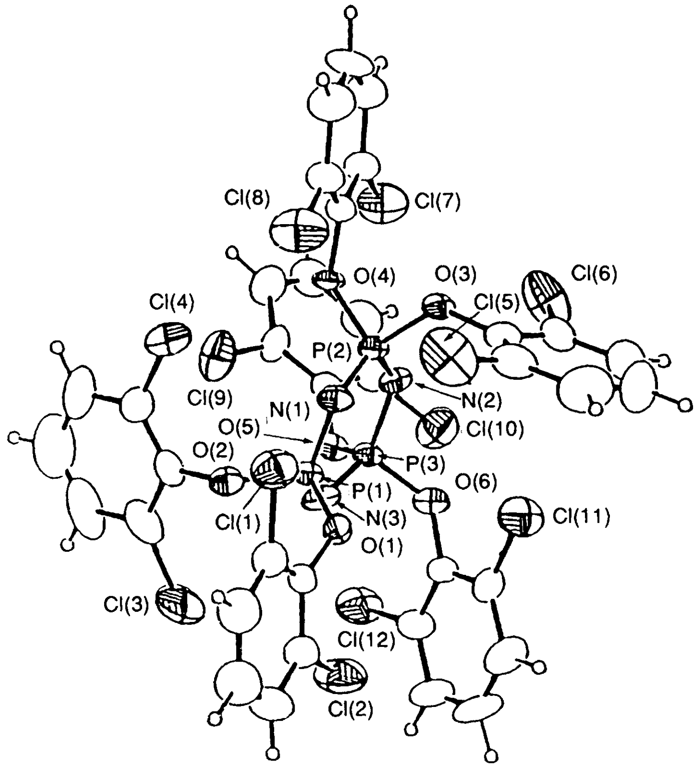


Fig. 4 An ORTEP diagram for $[NP(OC_6H_3Cl_2\text{-}o)_2]_3$ **5**

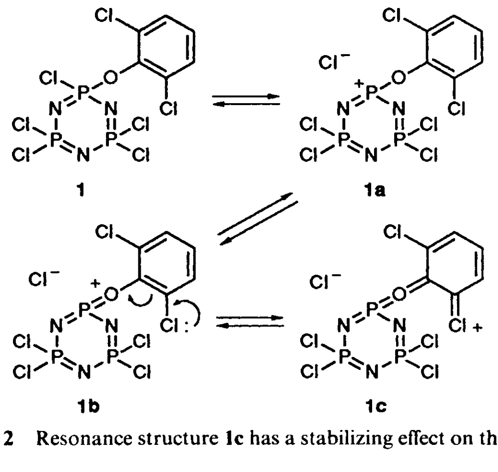
Table 8 Bond lengths (Å) and angles (°) for $N_3P_3(OC_6H_3Cl_2\text{-}o)_6$ **5**

P(1)–O(1)	1.58(1)	P(3)–O(6)	1.59(1)
P(1)–O(2)	1.60(1)	P(3)–N(2)	1.58(1)
P(1)–N(1)	1.57(1)	P(3)–N(3)	1.59(1)
P(1)–N(3)	1.55(1)	O(1)–C(1)	1.38(1)
P(2)–O(3)	1.60(1)	O(2)–C(7)	1.41(2)
P(2)–O(4)	1.58(1)	O(3)–C(13)	1.39(1)
P(2)–N(1)	1.58(1)	O(4)–C(19)	1.39(1)
P(2)–N(2)	1.57(1)	O(5)–C(25)	1.39(1)
P(3)–O(5)	1.58(1)	O(6)–C(13)	1.38(1)
O(1)–P(1)–O(2)	97.8(3)	O(5)–P(3)–N(2)	108.7(3)
O(1)–P(1)–N(1)	106.3(3)	O(5)–P(3)–N(3)	109.2(3)
O(1)–P(1)–N(3)	111.6(3)	O(6)–P(3)–N(2)	108.9(3)
O(2)–P(1)–N(1)	111.6(3)	O(6)–P(3)–N(3)	109.1(3)
O(2)–P(1)–N(3)	110.6(4)	N(2)–P(3)–N(3)	119.3(4)
N(1)–P(1)–N(3)	117.4(4)	P(1)–O(1)–C(1)	129.0(6)
O(3)–P(2)–O(4)	97.1(3)	P(1)–O(2)–C(7)	127.3(5)
O(3)–P(2)–N(1)	112.5(3)	P(2)–O(3)–C(13)	126.7(5)
O(3)–P(2)–N(2)	109.9(3)	P(2)–O(4)–C(19)	131.0(5)
O(4)–P(2)–N(1)	109.1(3)	P(3)–O(5)–C(25)	126.7(5)
O(4)–P(2)–N(2)	110.2(3)	P(3)–O(6)–C(31)	126.0(5)
N(1)–P(2)–N(2)	116.4(3)	P(1)–N(1)–P(2)	123.8(4)
O(5)–P(3)–O(6)	99.8(3)	P(2)–N(2)–P(3)	120.6(5)
		P(1)–N(3)–P(3)	120.9(4)

In compound **5** the side groups are arranged in a propeller-like fashion that leaves very little space for movement by an individual side group. Despite the bulkiness of the side groups, the phosphazene ring maintains a planar structure. The P–N bond distances, and the N–P–N and P–N–P bond angles, are within normal ranges. By comparison, the *o*-dimethylphenoxy analogue **8** contains a non-planar phosphazene ring. Hence, despite the similarity of the side groups, their effect on the structure of the phosphazene ring is significantly different. Compound **6** is a cyclotetrameric phosphazene. The four $o\text{-}Cl_2C_6H_3O$ groups are bonded geminally to two phosphorus atoms in the ring. This structure further illustrates the preference for a geminal substitution pathway.

Compound **7** is analogous to **2**, but with the $o\text{-}Cl_2C_6H_3O$ units replaced by $o\text{-}Me_2C_6H_3O$ groups. The two methyl groups in the *ortho* positions provide an electron supply toward the inorganic ring. This provides a means to determine if the substitution mechanism is strongly influenced by the electronic properties of the side units. As the structure of **7** shows, formation of this compound also follows a geminal route. This reinforces the view that electronic factors are not a major contributor to the geminal substitution mechanism. The arrangement of the $o\text{-}Me_2C_6H_3O$ groups around the phosphazene ring is almost identical to that in **2**. However, the geometry of the phosphazene ring in **7** shows a slight deviation from planarity. The electron-donating effect of the $o\text{-}Me_2C_6H_3O$ groups, coupled with the electron-withdrawing effect of the PCl_2 units, results in an electronic push–pull effect. This causes a lengthening of the P–N bonds in P(1)–N(1) and P(1)–N(3) (1.59 Å), where P(1) is bonded to the two $o\text{-}Me_2C_6H_3O$ groups. At the same time, electrons are pulled toward the opposite end of the phosphazene ring. This brings about a slight shortening of the remaining P–N bond distances (1.57 Å). The N(1)–P(1)–N(3) angle (116°) is narrowed slightly in comparison to the other two N–P–N angles (119°). This may be the consequence of the scissoring action induced by the $o\text{-}Me_2C_6H_3O$ groups. The P–N–P angles maintained a normal value of 122°.

Why do these bulky aryloxy groups enter the molecule *via* a geminal substitution pathway? Nucleophilic substitution can be achieved by either S_N1 or S_N2 mechanisms. An S_N2 mechanism requires that the bulky nucleophile must attack the phosphorus atom in synchrony with the departure of chlorine. A low probability exists that this will occur because of the steric crowding imposed by the bulky group already bonded to the phosphorus atom. An S_N1 mechanism, in general, is favoured by



Scheme 2 Resonance structure **1c** has a stabilizing effect on the cation

Table 9 Final positional parameters for $N_3P_3(OC_6H_3Cl_2\text{-}o)_6$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1)	0.9240(2)	0.1873(1)	0.8626(2)	C(7)	0.6759(8)	0.2363(4)	1.0339(5)
Cl(2)	0.5614(3)	0.0304(1)	0.8838(2)	C(8)	0.6168(9)	0.1959(5)	1.0801(6)
Cl(3)	0.5737(3)	0.1177(2)	1.0554(2)	C(9)	0.5983(10)	0.2193(7)	1.1508(6)
Cl(4)	0.7960(3)	0.3435(1)	0.9985(2)	C(10)	0.6349(10)	0.2799(7)	1.1724(6)
Cl(5)	0.8077(2)	0.2839(2)	0.6894(2)	C(11)	0.6941(10)	0.3200(6)	1.1267(6)
Cl(6)	0.3963(2)	0.3849(2)	0.6644(2)	C(12)	0.7169(9)	0.2970(5)	1.0563(6)
Cl(7)	0.4293(2)	0.4997(1)	0.8303(2)	C(13)	0.5954(7)	0.3267(4)	0.6733(5)
Cl(8)	0.8551(2)	0.4187(2)	0.8333(2)	C(14)	0.6829(9)	0.2879(5)	0.6453(5)
Cl(9)	0.4789(2)	0.3673(2)	1.0178(2)	C(15)	0.6662(11)	0.2554(6)	0.5798(6)
Cl(10)	0.1202(2)	0.3144(1)	0.8505(2)	C(16)	0.5674(12)	0.2627(7)	0.5417(6)
Cl(11)	0.4685(2)	0.1682(1)	0.6945(1)	C(17)	0.4861(10)	0.3008(6)	0.5682(6)
Cl(12)	0.2213(2)	0.1364(1)	0.9319(2)	C(18)	0.4994(8)	0.3341(5)	0.6341(5)
P(1)	0.6331(2)	0.2183(1)	0.8910(1)	C(19)	0.6455(8)	0.4666(4)	0.8312(4)
P(2)	0.5858(2)	0.3367(1)	0.8176(1)	C(20)	0.5688(8)	0.5165(4)	0.8209(5)
P(3)	0.4177(2)	0.2574(1)	0.8682(1)	C(21)	0.6008(9)	0.5821(5)	0.8033(6)
O(1)	0.6821(5)	0.1550(3)	0.8506(3)	C(22)	0.7107(10)	0.5944(5)	0.7962(6)
O(2)	0.7040(5)	0.2117(3)	0.9649(3)	C(23)	0.7881(9)	0.5459(5)	0.8033(6)
O(3)	0.6137(5)	0.3616(3)	0.7373(3)	C(24)	0.7574(8)	0.4812(4)	0.8224(5)
O(4)	0.6125(5)	0.4047(2)	0.8579(3)	C(25)	0.2951(7)	0.3479(4)	0.9367(4)
O(5)	0.3327(5)	0.2825(3)	0.9272(3)	C(26)	0.3528(8)	0.3900(5)	0.9814(5)
O(6)	0.3364(5)	0.2135(3)	0.8184(3)	C(27)	0.3097(9)	0.4554(5)	0.9954(5)
N(1)	0.6692(5)	0.2810(3)	0.8459(4)	C(28)	0.2097(10)	0.4718(5)	0.9669(6)
N(2)	0.4585(5)	0.3199(3)	0.8228(4)	C(29)	0.1508(9)	0.4305(5)	0.9222(6)
N(3)	0.5070(6)	0.2098(3)	0.9059(4)	C(30)	0.1955(8)	0.3675(4)	0.9069(5)
C(1)	0.7483(7)	0.1042(4)	0.8783(4)	C(31)	0.3409(7)	0.1447(4)	0.8097(5)
C(2)	0.8619(7)	0.1120(4)	0.8868(5)	C(32)	0.3919(7)	0.1169(4)	0.7493(5)
C(3)	0.9276(9)	0.0594(5)	0.9084(6)	C(33)	0.3847(9)	0.0487(5)	0.7369(6)
C(4)	0.8798(9)	−0.0012(5)	0.9248(7)	C(34)	0.3279(9)	0.0084(5)	0.7838(7)
C(5)	0.7666(10)	−0.0113(5)	0.9175(7)	C(35)	0.2787(9)	0.0346(4)	0.8442(6)
C(6)	0.7005(8)	0.0415(4)	0.8951(5)	C(36)	0.2837(8)	0.1029(4)	0.8559(5)

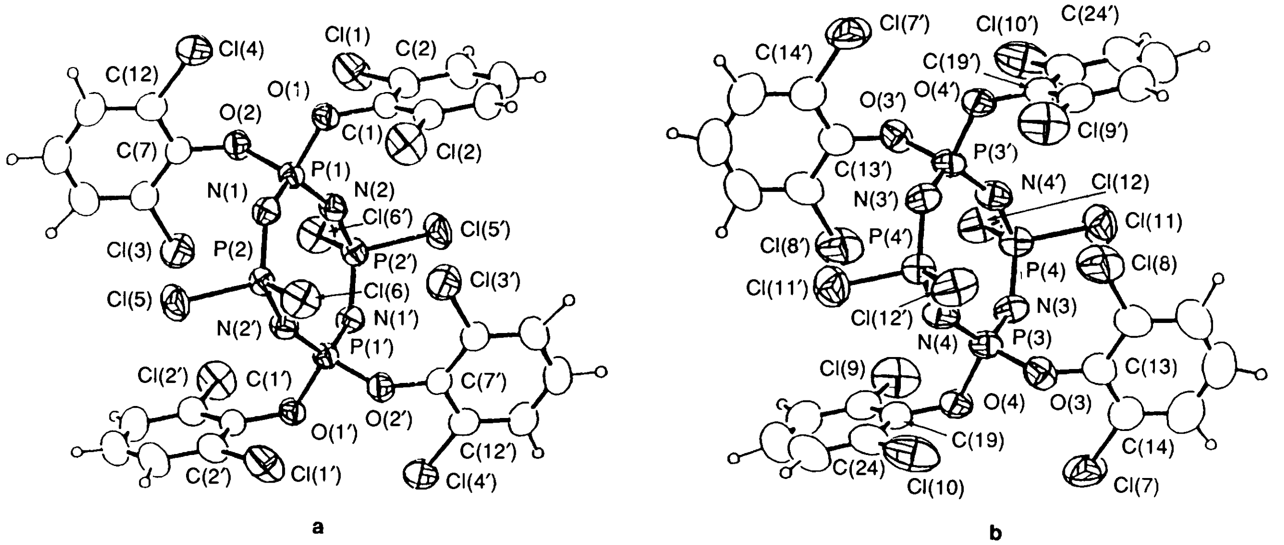


Fig. 5 An ORTEP diagram for $N_4P_4Cl_4(OC_6H_3Cl_2\text{-}o)_4$ **6**

a hindered substrate.[11] By this mechanism, the leaving group departs with its bonding electron pair, followed rapidly by an attack by the organic nucleophile on the positively charged substrate. A strong steric effect by the bulky side group will thus favour an S_N1 mechanism. The positive charge formed on the substituted phosphorus atom can also be stabilized by the electron-donating ability of groups such as *o*-dimethylphenoxy. In the case of *o*-dichlorophenoxy derivatives, even though the chlorine atoms are electron withdrawing by induction, they possess π-electron donating character. The stabilizing effect of the chlorine atom on the cation is illustrated in Scheme 2, where the resonance species **1c** stabilizes the cation. This effect may be sufficient to stabilize a cationic intermediate. Thus, the large attacking nucleophile will tend to interact with the phosphorus atom that already bears a ligand, leading to a geminally disubstituted product. This mechanism is postulated in an attempt to explain our experimental observations. However, without more detailed investigation, it is not possible to rule out other mechanisms.

Compounds **9** and **10** are two short-chain models for the corresponding highly polymeric analogues. The structures of these linear oligomers are probably more accurate representations of their polymeric analogues than are the cyclic counterparts. Compound **9** possesses three $o\text{-}Cl_2C_6H_3O$ groups linked to one of the terminal phosphorus atoms, while the chlorine atoms on the phosphoryl phosphorus remained unchanged. The formation of this compound indicates that the preferred site of nucleophilic substitution on a short-chain chlorophosphazene is at the terminal PCl_3 unit. Similarly, in **10**, the terminal phosphorus P(1) is bonded to three $o\text{-}Me_2C_6H_3O$

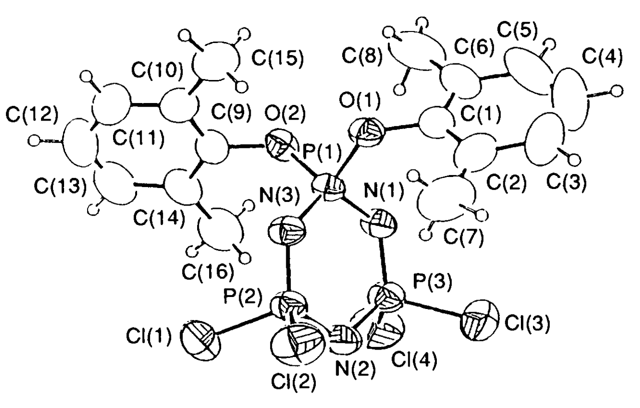


Fig. 6 An ORTEP and packing diagram for $N_3P_3Cl_4(OC_6H_3Me_2\text{-}o)_2$ **7**

Table 10 Bond lengths (Å) and angles (°) for $N_4P_4Cl_4(OC_6H_3Cl_2\text{-}o)_4$ **6**

P(2)–Cl(5)	2.000(2)	P(3)–O(3)	1.585(2)
P(2)–Cl(6)	2.002(1)	P(3)–O(4)	1.585(3)
P(4)–Cl(11)	1.995(2)	P(3)–N(3)	1.560(4)
P(4)–Cl(12)	2.000(1)	P(3)–N(4)	1.539(4)
P(1)–O(1)	1.590(3)	P(4)–N(3)	1.559(3)
P(1)–O(2)	1.582(3)	P(4)–N(4)	1.535(3)
P(1)–N(1)	1.569(4)	O(1)–C(1)	1.391(5)
P(1)–N(2)	1.535(3)	O(2)–C(7)	1.380(5)
P(2)–N(1)	1.553(2)	O(3)–C(13)	1.387(5)
		O(4)–C(19)	1.393(5)
O(1)–P(1)–O(2)	100.9(1)	N(3)–P(3)–N(4)	119.7(2)
O(1)–P(1)–N(1)	107.6(1)	Cl(11)–P(4)–Cl(12)	100.7(1)
O(1)–P(1)–N(2)	107.4(1)	Cl(11)–P(4)–N(3)	107.1(1)
O(2)–P(1)–N(1)	108.7(2)	Cl(11)–P(4)–N(4)	107.8(1)
O(2)–P(1)–N(2)	110.6(2)	Cl(12)–P(4)–N(3)	108.5(1)
N(1)–P(1)–N(2)	120.0(1)	Cl(12)–P(4)–N(4)	109.4(1)
Cl(5)–P(2)–Cl(6)	101.5(1)	N(3)–P(4)–N(4)	121.3(3)
Cl(5)–P(2)–N(1)	108.3(1)	P(1)–O(1)–C(1)	123.4(3)
Cl(6)–P(2)–N(1)	107.2(1)	P(1)–O(2)–C(7)	124.7(2)
O(3)–P(3)–O(4)	100.2(1)	P(3)–O(3)–C(13)	125.5(3)
O(3)–P(3)–N(3)	109.2(2)	P(3)–O(4)–C(19)	124.3(2)
O(3)–P(3)–N(4)	109.9(2)	P(1)–N(1)–P(2)	129.8(2)
O(4)–P(3)–N(3)	108.2(2)	P(3)–N(3)–P(4)	130.5(2)
O(4)–P(3)–N(4)	107.9(2)	P(3)–N(4)–P(4)	157.2(2)

groups, while P(2) and P(3) are each only partially substituted by a $o\text{-}Me_2C_6H_3O$ group. This suggests that the PCl_2 middle units in the phosphazene skeleton have comparable reactivity towards nucleophilic substitution. The structure of **10** is also consistent with that of cyclic trimer **4**, in which nucleophilic substitution follows a non-geminal route when the phosphazene backbone already bears two side groups. The most interesting feature of the structure of **10** is the conformation of the P–N backbone. The torsional angles are N(2)–P(2)–N(1)–P(1) 130.71° and N(1)–P(2)–N(2)–P(3) −135.62°. These values correspond to a distorted *trans-trans* conformation of the skeleton, in contrast to the *cis-trans* conformation generally proposed for highly polymeric phosphazene skeletons.[12] Thus a conformation other than *cis-trans* planar may be allowed for the phosphazene skeleton when the molecule is only partially substituted. This unusual geometry is almost certainly a consequence of the presence of bulky side groups. A *trans-trans* conformation appears to allow the side groups to maintain a maximum separation from each other. The P–N bond distances in **9** and **10** are similar, but not equivalent. However, the value of

Table 12 Bond lengths (Å) and angles (°) of *gem*-$N_3P_3Cl_4(OC_6H_3\text{-}Me_2\text{-}o)_2$ **7**

Cl(1)–P(2)	1.998(1)	P(1)–N(3)	1.581(2)
Cl(2)–P(2)	1.976(1)	P(2)–N(2)	1.566(3)
Cl(3)–P(3)	1.991(1)	P(2)–N(3)	1.570(2)
Cl(4)–P(3)	1.983(1)	P(3)–N(1)	1.559(2)
P(1)–O(1)	1.566(2)	P(3)–N(2)	1.576(3)
P(1)–O(2)	1.563(2)	O(1)–C(1)	1.419(4)
P(1)–N(1)	1.594(3)	O(2)–C(9)	1.420(4)
O(1)–P(1)–O(2)	101.4(1)	Cl(3)–P(3)–N(1)	109.9(1)
O(1)–P(1)–N(1)	109.4(1)	Cl(3)–P(3)–N(2)	107.8(1)
O(1)–P(1)–N(3)	109.8(1)	Cl(4)–P(3)–N(1)	109.0(1)
O(2)–P(1)–N(1)	109.3(1)	Cl(4)–P(3)–N(2)	108.5(1)
O(2)–P(1)–N(3)	109.4(1)	N(1)–P(3)–N(2)	119.2(1)
N(1)–P(1)–N(3)	116.4(1)	P(1)–O(1)–C(1)	125.3(2)
Cl(1)–P(2)–Cl(2)	100.51(6)	P(1)–O(2)–C(9)	126.0(2)
Cl(1)–P(2)–N(2)	108.0(1)	P(1)–N(1)–P(3)	122.2(2)
Cl(1)–P(2)–N(3)	110.0(1)	P(2)–N(2)–P(3)	120.5(2)
Cl(2)–P(2)–N(2)	108.4(1)	P(1)–N(3)–P(2)	122.1(2)
Cl(2)–P(2)–N(3)	109.3(1)	O(1)–C(1)–C(2)	118.0(3)
N(2)–P(2)–N(3)	119.0(1)	O(1)–C(1)–C(6)	117.3(3)
Cl(3)–P(3)–Cl(4)	100.99(6)		

Table 11 Final positional parameters for $N_4P_4Cl_4(OC_6H_3Cl_2\text{-}o)_4$ **6**

Atom	*x*	*y*	*z*
Cl(1)	0.2209(1)	0.4629(1)	0.9826(1)
Cl(2)	0.1954(1)	0.1599(1)	1.2300(1)
Cl(3)	0.4559(1)	−0.0343(1)	0.8097(1)
Cl(4)	−0.0440(1)	0.1953(1)	0.9721(1)
Cl(5)	0.3978(1)	−0.2841(1)	0.9639(1)
Cl(6)	0.4074(1)	−0.2171(1)	1.1381(1)
Cl(7)	0.1709(2)	0.8745(1)	0.3157(1)
Cl(8)	0.2194(2)	0.7093(1)	0.6099(1)
Cl(9)	0.6040(2)	0.4439(1)	0.2256(1)
Cl(10)	0.5911(2)	0.8773(1)	0.3783(1)
Cl(11)	0.1881(1)	0.4277(1)	0.4977(1)
Cl(12)	0.4479(1)	0.2479(1)	0.3904(1)
P(1)	0.3015(1)	0.1248(1)	1.0044(1)
P(2)	0.4521(1)	−0.1478(1)	1.0294(1)
P(3)	0.4337(1)	0.6414(1)	0.4183(1)
P(4)	0.3786(1)	0.4119(1)	0.4618(1)
O(1)	0.1869(2)	0.2327(2)	1.0650(1)
O(2)	0.2407(2)	0.1575(2)	0.9249(1)
O(3)	0.3145(2)	0.7765(2)	0.4502(2)
O(4)	0.4806(2)	0.6797(3)	0.3318(1)
N(1)	0.3035(2)	−0.0152(3)	1.0297(2)
N(2)	0.4300(3)	0.1562(3)	0.9986(2)
N(3)	0.3742(3)	0.5321(3)	0.4101(2)
N(4)	0.5502(3)	0.6154(3)	0.4654(2)
C(1)	0.2118(3)	0.3221(3)	1.1119(2)
C(2)	0.2261(4)	0.4348(4)	1.0818(2)
C(3)	0.2480(4)	0.5238(4)	1.1292(3)
C(4)	0.2503(4)	0.5013(4)	1.2082(3)
C(5)	0.2343(4)	0.3912(4)	1.2402(2)
C(6)	0.2146(3)	0.3016(4)	1.1914(2)
C(7)	0.2001(3)	0.0735(3)	0.8846(2)
C(8)	0.2880(3)	−0.0166(4)	0.8261(2)
C(9)	0.2457(4)	−0.0920(4)	0.7814(3)
C(10)	0.1120(4)	−0.0785(4)	0.7959(3)
C(11)	0.0222(4)	0.0084(4)	0.8546(3)
C(12)	0.0663(4)	0.0849(4)	0.8985(2)
C(13)	0.1784(4)	0.7962(3)	0.4647(2)
C(14)	0.0990(4)	0.8468(4)	0.4084(3)
C(15)	−0.0380(5)	0.8779(4)	0.4245(3)
C(16)	−0.0961(5)	0.8563(5)	0.4981(4)
C(17)	−0.0183(5)	0.8033(4)	0.5553(3)
C(18)	0.1202(4)	0.7737(4)	0.5386(2)
C(19)	0.6145(4)	0.6556(4)	0.2988(2)
C(20)	0.6830(4)	0.5475(4)	0.2470(2)
C(21)	0.8145(5)	0.5218(5)	0.2095(3)
C(22)	0.8732(5)	0.6077(6)	0.2250(3)
C(23)	0.8086(5)	0.7161(5)	0.2766(3)
C(24)	0.6770(4)	0.7404(4)	0.3139(3)

Table 13 Final positional parameters for *gem*-$N_3P_3Cl_4(OC_6H_3Me_2$-*o*$)_2$ **7**

Atom	*x*	*y*	*z*
Cl(1)	0.090 71(11)	0.087 50(5)	0.548 91(9)
Cl(2)	0.050 09(11)	0.157 78(7)	0.337 22(8)
Cl(3)	0.095 83(11)	0.398 36(6)	0.504 68(11)
Cl(4)	0.113 58(12)	0.322 20(7)	0.713 45(8)
P(1)	0.408 71(8)	0.237 71(4)	0.520 23(6)
P(2)	0.146 06(8)	0.176 19(5)	0.474 40(7)
P(3)	0.165 79(8)	0.306 89(5)	0.571 31(7)
O(1)	0.510 2(2)	0.268 7(1)	0.442 2(1)
O(2)	0.516 6(2)	0.201 9(1)	0.601 6(2)
N(1)	0.330 3(3)	0.302 9(1)	0.572 0(2)
N(2)	0.073 5(3)	0.242 8(2)	0.522 4(2)
N(3)	0.310 6(3)	0.177 3(1)	0.466 6(2)
C(1)	0.520 3(3)	0.342 6(2)	0.414 3(2)
C(2)	0.438 8(4)	0.366 2(2)	0.330 1(3)
C(3)	0.457 8(5)	0.439 1(3)	0.302 5(4)
C(4)	0.553 2(7)	0.483 0(3)	0.358 0(4)
C(5)	0.632 5(5)	0.455 5(2)	0.439 4(4)
C(6)	0.619 1(4)	0.384 8(2)	0.471 2(3)
C(7)	0.334 8(5)	0.317 6(3)	0.271 8(3)
C(8)	0.707 0(4)	0.355 1(3)	0.561 6(3)
C(9)	0.522 3(3)	0.127 5(2)	0.628 3(2)
C(10)	0.610 0(3)	0.083 4(2)	0.575 2(3)
C(11)	0.624 4(4)	0.012 5(2)	0.608 8(3)
C(12)	0.557 4(5)	−0.011 9(2)	0.689 2(4)
C(13)	0.470 0(5)	0.033 1(2)	0.740 4(3)
C(14)	0.450 0(4)	0.105 5(2)	0.710 9(3)
C(15)	0.686 1(4)	0.111 3(3)	0.487 8(3)
C(16)	0.359 3(5)	0.155 9(3)	0.765 7(3)

Table 14 Bond lengths (Å) and angles (°) for $N_3P_3(OC_6H_3Me_2$-*o*$)_6$ **8**

P(1)–O(1)	1.593(3)	P(2)–O(3)	1.570(4)
P(1)–O(2)	1.601(3)	P(2)–O(3′)	1.495(4)
P(1)–N(3)	1.791(4)	P(1)–N(1)	1.598(4)
P(1′)–N(3)	1.357(5)	P(1)–N(1′)	
P(1′)–O(1′)	1.593(3)	O(1)–C(11)	1.407(6)
P(1′)–O(2′)	1.601(3)	O(2)–C(21)	1.412(6)
P(2)–N(1)	1.578(6)	O(3)–C(31)	1.441(6)
P(2)–N(1′)	1.481(6)		
O(3)–P(2)–O(3′)	99.3(2)	N(1′)–P(1′)–N(3)	119.6(3)
O(1)–P(1)–N(2)	99.1(2)	O(3′)–P(2)–N(1)	114.4(4)
O(1)–P(1)–N(1)	111.5(2)	O(3′)–P(2)–N(1′)	109.4(4)
O(1′)–P(1′)–N(3)	109.0(3)	N(1)–P(2)–N(1′)	116.8(2)
O(1)–P(1)–N(3)	114.0(2)	P(1)–O(1)–C(11)	126.4(4)
O(2)–P(1)–N(1)	110.8(2)	P(1)–O(2)–C(21)	129.6(3)
N(1)–P(1)–N(3)	111.0(2)	P(2)–O(3)–C(31)	126.5(4)
O(2)–P(1)–N(3)	109.8(2)	P(2)–O(3′)–C(31′)	129.2(4)
O(2′)–P(1′)–N(3)	104.6(3)	P(1′)–N(3)–P(1)	122.8(5)
O(3)–P(2)–N(1)	110.1(3)	P(1)–N(1)–P(2)	122.9(3)
O(3)–P(2)–N(1′)	104.9(3)	P(1′)–N(1′)–P(2)	125.5(3)

about 1.55 Å is still shorter than a P–N single-bond value,[13] and suggests multiple-bond character. The P–N–P bond angle in **9** is 142°, and in **10**, they are 143° and 135°. The P–N–P angle in the middle of the phosphazene skeleton is 135°. We propose that this value may model the analogous angle in the corresponding highly polymeric phosphazenes. The N–P–N angle is constant at 115°, which would also be expected in a highly polymeric analogue.

Table 20 summarizes the structural parameters of the phosphazene skeleton for the compounds studied in this work. The values for the cyclic trimeric species are essentially identical. As the ring expands the P–N–P angle changes most significantly. A shortening of the P–N bond length was also detected. This perhaps reflects the more efficient delocalization of the π electrons along the P–N skeleton of the higher cyclic and linear species.

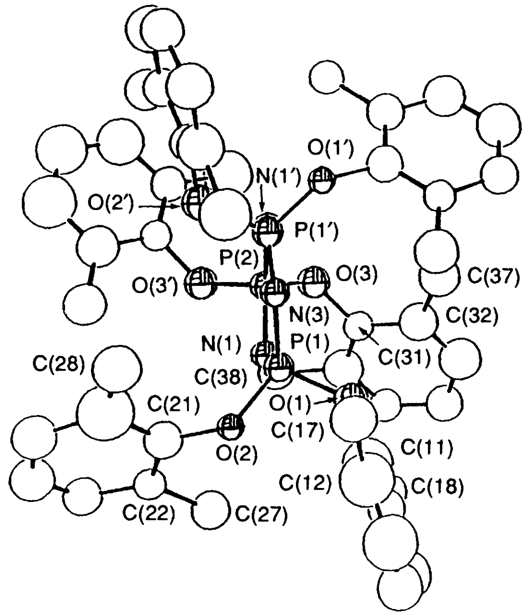


Fig. 7 An ORTEP diagram for $[NP(OC_6H_3Me_2$-*o*$)_2]_3$ **8**

Table 15 Final positional parameters for $N_3P_3(OC_6H_3Me_2$-*o*$)_6$ **8**

Atom	*x*	*y*	*z*
P(1)	0.589 09(6)	0.093 68(6)	0.187 33(5)
P(2)	0.488 6(1)	0.507 6(1)	0.252 4(3)
O(1)	0.645 5(2)	0.079 5(2)	0.139 8(1)
O(2)	0.556 6(2)	0.155 1(2)	0.155 2(1)
O(3)	0.435 5(2)	0.015 5(2)	0.247 9(2)
N(1)	0.538 9(2)	0.034 8(2)	0.191 1(2)
N(3)	0.617 6(3)	0.115 7(3)	0.261 1(2)
C(11)	0.674 8(3)	0.019 1(3)	0.128 4(2)
C(12)	0.737 4(3)	0.005 5(3)	0.162 6(3)
C(13)	0.768 4(3)	−0.056 0(4)	0.141 4(3)
C(14)	0.738 0(4)	−0.092 2(4)	0.095 2(3)
C(15)	0.680 7(4)	−0.083 6(4)	0.069 8(3)
C(16)	0.651 9(3)	−0.022 1(3)	0.080 6(3)
C(17)	0.763 8(3)	0.047 0(4)	0.207 5(3)
C(18)	0.588 2(4)	−0.000 1(4)	0.046 2(3)
C(21)	0.574 5(3)	0.187 2(2)	0.101 2(2)
C(22)	0.629 6(3)	0.228 4(3)	0.098 9(3)
C(23)	0.639 7(3)	0.262 1(3)	0.048 6(3)
C(24)	0.612 5(3)	0.251 1(4)	0.000 4(3)
C(25)	0.551 2(4)	0.213 8(3)	−0.003 2(3)
C(26)	0.532 0(3)	0.175 5(3)	0.051 2(2)
C(27)	0.665 0(3)	0.243 1(4)	0.159 6(4)
C(28)	0.475 1(4)	0.136 8(4)	0.053 2(3)
C(31)	0.541 5(2)	−0.103 9(3)	0.300 3(2)
C(32)	0.500 3(3)	−0.124 3(3)	0.348 3(2)
C(33)	0.525 4(3)	−0.167 5(3)	0.391 0(3)
C(34)	0.587 3(3)	−0.192 2(3)	0.389 5(3)
C(35)	0.627 3(3)	−0.167 9(3)	0.338 5(3)
C(36)	0.603 8(3)	−0.128 0(3)	0.296 4(2)
C(37)	0.433 8(3)	−0.096 7(3)	0.351 7(3)
C(38)	0.652 2(3)	−0.101 5(3)	0.246 6(3)

In conclusion, we have shown that the nucleophilic replacement of P–Cl units in cyclic phosphazene oligomers by *o*-$Cl_2C_6H_3O$ and *o*-$Me_2C_6H_3O$ units initially follows a geminal pathway. This mechanism may be explained by a simple S_N1 process. However, steric considerations become a major factor in the later stage of the reaction. Further nucleophilic attack occurs at sites that will generate the least sterically hindered molecule. The results from the short-chain study suggest that the linear phosphazene skeleton can assume a conformation other than *cis-trans* planar. The conformation of the backbone depends both on the types of side groups present and on the disposition of bulky side groups.

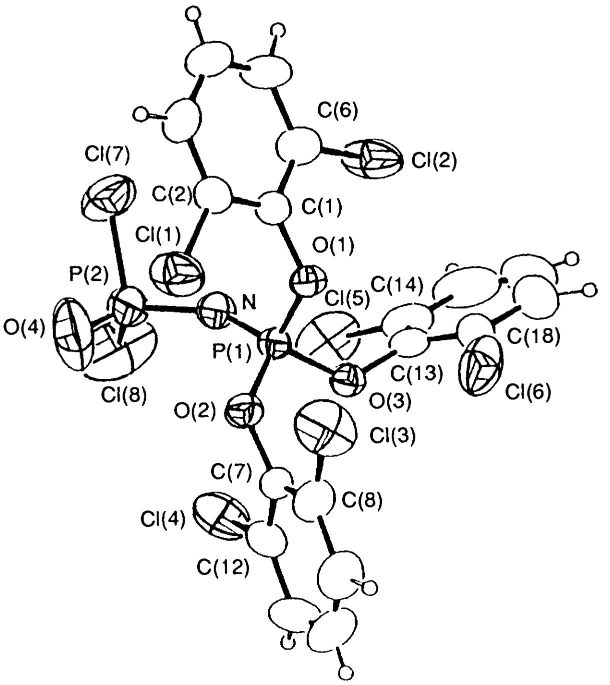


Fig. 8 An ORTEP diagram for $O{=}PCl_2N{=}P(OC_6H_3Cl_2\text{-}o)_3$ **9**

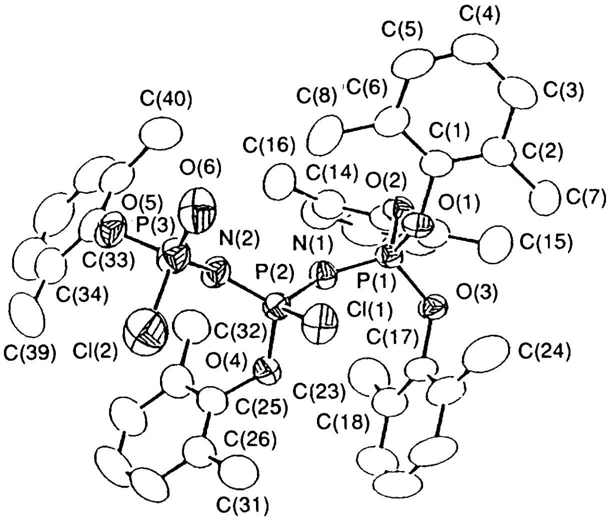


Fig. 9 An ORTEP diagram for $OPCl(OC_6H_3Me_2\text{-}o)NPCl(OC_6H_3Me_2\text{-}o)NP(OC_6H_3Me_2\text{-}o)_3$ **10**

Table 16 Bond lengths (Å) and angles (°) for $O{=}PCl_2N{=}P(OC_6H_3Cl_2\text{-}o)_3$ **9**

P(1)–O(1)	1.571(4)	P(2)–Cl(7)	1.999(2)
P(1)–O(2)	1.559(3)	P(2)–Cl(8)	1.980(3)
P(1)–O(3)	1.567(3)	O(1)–C(1)	1.398(5)
P(1)–N	1.515(4)	O(2)–C(7)	1.385(5)
P(2)–N	1.567(4)	O(3)–C(13)	1.385(6)
P(2)–O(4)	1.423(6)		
O(1)–P(1)–O(2)	108.0(2)	Cl(7)–P(2)–N	104.8(2)
O(1)–P(1)–O(3)	104.2(2)	Cl(8)–P(2)–O(4)	112.3(3)
O(1)–P(1)–N	111.2(2)	Cl(8)–P(2)–N	105.7(2)
O(2)–P(1)–O(3)	100.8(2)	O(4)–P(2)–N	121.1(3)
O(2)–P(1)–N	114.6(3)	P(1)–O(1)–C(1)	122.6(3)
O(3)–P(1)–N	116.9(3)	P(1)–O(2)–C(7)	129.3(4)
Cl(7)–P(2)–Cl(8)	100.5(1)	P(1)–O(3)–C(13)	126.4(3)
Cl(7)–P(2)–O(4)	110.5(2)	P(1)–N–P(2)	142.4(4)

Table 17 Final positional parameters for $O{=}PCl_2N{=}P(OC_6H_3Cl_2\text{-}o)_3$ **9**

Atom	*x*	*y*	*z*
Cl(1)	0.9390(1)	0.2186(1)	0.7911(1)
Cl(2)	0.7457(1)	0.3242(1)	0.5872(1)
Cl(3)	1.0668(1)	0.4056(1)	0.7873(1)
Cl(4)	1.2232(1)	0.2731(1)	0.5789(1)
Cl(5)	0.9818(2)	0.3002(1)	0.4601(1)
Cl(6)	0.9512(1)	0.5088(1)	0.6539(1)
Cl(7)	0.8806(1)	0.0661(1)	0.5922(1)
Cl(8)	1.0642(2)	0.0977(1)	0.5211(1)
P(1)	0.9948(1)	0.2915(1)	0.6346(1)
P(2)	1.0023(1)	0.1224(1)	0.6044(1)
O(1)	0.9077(2)	0.3183(2)	0.6753(1)
O(2)	1.0819(2)	0.2925(2)	0.6799(2)
O(3)	1.0163(2)	0.3647(2)	0.5902(2)
O(4)	1.0514(4)	0.0904(3)	0.6583(3)
N	0.9771(3)	0.2129(2)	0.6011(2)
C(1)	0.8347(3)	0.2665(3)	0.6909(2)
C(2)	0.8392(3)	0.2186(3)	0.7452(2)
C(3)	0.7647(4)	0.1713(3)	0.7616(2)
C(4)	0.6857(3)	0.1707(3)	0.7254(3)
C(5)	0.6803(4)	0.2161(4)	0.6714(3)
C(6)	0.7549(4)	0.2652(3)	0.6546(2)
C(7)	1.1549(3)	0.3464(3)	0.6825(3)
C(8)	1.1572(4)	0.4013(3)	0.7335(3)
C(9)	1.2321(4)	0.4504(3)	0.7409(3)
C(10)	1.3022(4)	0.4467(4)	0.6971(4)
C(11)	1.3042(4)	0.3939(4)	0.6473(3)
C(12)	1.2274(3)	0.3418(3)	0.6403(3)
C(13)	0.9522(3)	0.4071(3)	0.5537(3)
C(14)	0.9298(4)	0.3844(4)	0.4927(3)
C(15)	0.8681(5)	0.4278(5)	0.4570(3)
C(16)	0.8303(5)	0.4941(4)	0.4815(4)
C(17)	0.8544(5)	0.5205(4)	0.5423(4)
C(18)	0.9166(4)	0.4777(3)	0.5790(3)

Table 18 Bond lengths (Å) and angles (°) of compound **10**

P(1)–O(1)	1.550(2)	P(3)–O(6)	1.558(3)
P(1)–O(2)	1.555(3)	P(3)–N(2)	1.576(4)
P(1)–O(3)	1.566(2)	O(1)–C(1)	1.419(4)
P(1)–N(1)	1.528(3)	O(2)–C(9)	1.430(4)
P(2)–O(4)	1.572(3)	O(3)–C(17)	1.440(5)
P(2)–N(1)	1.575(3)	O(4)–C(25)	1.409(4)
P(2)–N(2)	1.542(3)	O(5)–C(33)	1.385(5)
P(3)–O(5)	1.589(3)		
O(1)–P(1)–O(2)	102.5(1)	O(5)–P(3)–N(2)	106.2(2)
O(1)–P(1)–O(3)	106.0(1)	O(6)–P(3)–N(2)	119.9(2)
O(1)–P(1)–N(1)	114.9(2)	P(1)–O(1)–C(1)	132.0(2)
O(2)–P(1)–O(3)	104.8(1)	P(1)–O(2)–C(9)	126.1(2)
O(2)–P(1)–N(1)	114.0(1)	P(1)–O(3)–C(17)	123.3(2)
O(3)–P(1)–N(1)	113.5(2)	P(2)–O(4)–C(25)	129.0(2)
O(4)–P(2)–N(1)	104.8(2)	P(3)–O(5)–C(33)	128.7(3)
O(4)–P(2)–N(2)	112.8(2)	P(1)–N(1)–P(2)	143.8(2)
N(1)–P(2)–N(2)	114.9(2)	P(2)–N(2)–P(3)	135.3(2)
O(5)–P(3)–O(6)	108.3(2)		

Experimental

Materials.—Dioxane (Baker) was distilled under nitrogen from sodium–benzophenone, methylene chloride, hexane, benzene and acetonitrile from CaH_2. Phosphorus pentachloride (Aldrich) was used as received. Hexachlorocyclotriphosphazene (Ethyl) and octachlorocyclotetraphosphazene were purified by sublimation and recrystallization from hexane. All phenols were obtained from Aldrich and were purified by sublimation.

Equipment.—The ^{31}P NMR spectra were obtained with the use of a JEOL FX-90Q spectrometer. Melting points were obtained using a Uni-melt capillary melting apparatus. X-Ray

Table 19 Final positional parameters for $OP_3N_2Cl_2(OC_6H_3Me_2\text{-}o)_5$ **10**

Atom	*x*	*y*	*z*
Cl(1)	0.439 22(7)	0.024 27(6)	0.324 05(8)
Cl(2)	0.435 14(9)	−0.080 80(9)	0.101 2(1)
P(1)	0.251 16(6)	0.046 04(5)	0.433 39(6)
P(2)	0.309 40(6)	0.009 02(5)	0.259 43(7)
P(3)	0.358 01(8)	−0.121 90(6)	0.182 98(9)
O(1)	0.329 0(2)	0.014 5(1)	0.509 6(2)
O(2)	0.166 2(2)	0.024 5(1)	0.469 4(2)
O(3)	0.258 0(2)	0.127 9(1)	0.446 7(2)
O(4)	0.289 1(2)	0.073 1(1)	0.189 4(2)
O(5)	0.294 1(2)	−0.174 9(1)	0.113 9(2)
O(6)	0.419 6(2)	−0.165 7(2)	0.262 6(2)
N(1)	0.249 1(2)	0.022 3(2)	0.332 7(2)
N(2)	0.294 7(2)	−0.062 9(2)	0.208 8(2)
C(1)	0.329 8(2)	−0.034 8(2)	0.583 1(3)
C(2)	0.342 2(2)	−0.008 5(2)	0.673 1(3)
C(3)	0.352 8(3)	−0.057 8(3)	0.745 8(3)
C(4)	0.353 1(3)	−0.129 1(3)	0.727 1(4)
C(5)	0.338 4(3)	−0.152 1(2)	0.635 9(4)
C(6)	0.326 3(3)	−0.106 4(2)	0.560 9(3)
C(7)	0.347 7(3)	0.068 3(2)	0.694 3(3)
C(8)	0.310 6(4)	−0.132 5(2)	0.462 2(4)
C(9)	0.075 6(2)	0.046 5(2)	0.430 4(3)
C(10)	0.043 1(3)	0.103 2(2)	0.471 8(3)
C(11)	−0.046 7(3)	0.122 9(2)	0.435 5(4)
C(12)	−0.099 8(3)	0.085 6(3)	0.361 6(4)
C(13)	−0.064 8(3)	0.028 5(3)	0.323 7(3)
C(14)	0.023 6(3)	0.005 9(2)	0.358 0(3)
C(15)	0.099 4(3)	0.144 0(2)	0.552 6(3)
C(16)	0.059 0(3)	−0.059 4(3)	0.320 3(3)
C(17)	0.296 3(3)	0.173 8(2)	0.387 2(3)
C(18)	0.240 2(3)	0.200 4(2)	0.308 3(3)
C(19)	0.279 6(4)	0.243 7(3)	0.250 9(4)
C(20)	0.370 4(4)	0.257 9(3)	0.274 7(4)
C(21)	0.424 5(3)	0.232 7(2)	0.357 7(4)
C(22)	0.387 8(3)	0.189 6(2)	0.416 6(3)
C(23)	0.141 2(4)	0.186 0(3)	0.284 3(4)
C(24)	0.444 3(3)	0.164 1(3)	0.507 9(4)
C(25)	0.266 6(3)	0.072 7(2)	0.090 1(3)
C(26)	0.328 6(3)	0.100 9(2)	0.044 7(3)
C(27)	0.303 4(4)	0.108 4(3)	−0.051 9(3)
C(28)	0.218 7(4)	0.087 0(4)	−0.099 5(4)
C(29)	0.160 0(4)	0.058 0(3)	−0.052 9(3)
C(30)	0.181 1(3)	0.049 9(2)	0.044 0(3)
C(31)	0.420 7(3)	0.125 3(3)	0.096 5(4)
C(32)	0.114 3(3)	0.019 3(3)	0.094 5(3)
C(33)	0.202 0(3)	−0.170 3(2)	0.077 6(3)
C(34)	0.171 7(4)	−0.151 1(3)	−0.018 2(3)
C(35)	0.080 9(4)	−0.151 1(3)	−0.057 0(4)
C(36)	0.021 9(4)	−0.169 3(3)	−0.003 6(5)
C(37)	0.050 6(4)	−0.188 5(3)	0.089 4(4)
C(38)	0.142 5(3)	−0.190 3(2)	0.132 3(4)
C(39)	0.239 4(5)	−0.131 2(4)	−0.075 5(4)
C(40)	0.176 3(4)	−0.213 5(3)	0.232 2(4)

Table 20 Summary of structural parameters

Compound	P–N/Å	N–P–N/°	P–N–P/°
1	1.573(3)	118.9(2)	121.0(2)
2	1.575(3)	118.4(2)	121.0(2)
4	1.574(2)	117.7(1)	121.6(1)
5	1.58(2)	117.7(3)	121.8(4)
6a	1.552(3)	120.3(2)	129.8(2)
6b	1.548(4)	120.5(3)	143.9(2)
7	1.574(3)	118.2(1)	121.6(2)
8	1.561(5)	115.8(2)	123.7(4)
9	1.541(4)	—	142.4(4)
10	1.548(3)	114.9(2)	139.6(2)

Table 21 Molecular ratios and product yields in the preparation of cyclic phosphazenes

Cmpd.	Yield (%)	Cyclic phosphazene (amount, g/mmol)	NaOR (mmol)
1	60	$(NPCl_2)_3$ (2, 5.7)	$Na(OC_6H_3Cl_2\text{-}o)$ (5.7)
2	56	$(NPCl_2)_3$ (2, 5.7)	$Na(OC_6H_3Cl_2\text{-}o)$ (11)
3	52	$(NPCl_2)_3$ (2, 5.7)	$Na(OC_6H_3Cl_2\text{-}o)$ (18)
4	53	$(NPCl_2)_3$ (2, 5.7)	$Na(OC_6H_3Cl_2\text{-}o)$ (23)
5	64	$(NPCl_2)_3$ (2, 5.7)	$Na(OC_6H_3Cl_2\text{-}o)$ (68)
6	71	$(NPCl_2)_4$ (1, 2.2)	$Na(OC_6H_3Cl_2\text{-}o)$ (8.8)
7	59	$(NPCl_2)_3$ (2, 5.7)	$Na(OC_6H_3Me_2\text{-}o)$ (11)
8	62	$(NPCl_2)_3$ (2, 5.7)	$Na(OC_6H_3Cl_2\text{-}o)$ (68)

diffraction data were obtained by use of an Enraf-Nonius four-circle CAD4 automated diffractometer.

Preparation of Sodium salts of Phenols.—In general, sodium or sodium hydride was allowed to react with the phenols in dioxane. A slight excess of phenol was used to ensure complete consumption of the sodium. The resulting salt solutions were used immediately in the subsequent reactions with the halogenophosphazenes.

Preparation of Compounds **1**–**8**.—The cyclic phosphazenes were prepared by treatment of hexachlorocyclotriphosphazene $(NPCl_2)_3$ with the sodium aryloxide in the molecular ratios listed in Table 21. All reactions except for **5** and **8** were carried with the use of dioxane (75 cm^3) as a solvent. In the preparation of **5** and **8**, 2,5,8-trioxanonane (diglyme) (50 cm^3) was used as the solvent. The reaction mixtures for compounds **1**, **2**, **4**, **6** and **7** were refluxed for 12 h, those for **5** and **8** for 48 h. Typically, at the end of reaction, the reaction mixture was filtered through Fuller's earth and the crude product was chromatographed on a silica gel column, using a mixture of methylene chloride (30–60%) and hexane as eluent. The compounds were recrystallized from a mixture of hexane and methylene chloride to yield colourless crystals.

Preparation of Compounds **9** *and* **10**.—The starting chlorophosphazenes, $OPCl_2NPCl_3$ and $OPCl_2NPCl_2NPCl_3$, were prepared by literature methods.[9] Treatment of $OPCl_2NPCl_3$ (1.5 g, 5.6 × 10^{-3} mol) with $Na(OC_6H_3Cl_2\text{-}o)$ (5.6 × 10^{-2} mol) and of $OPCl_2NPCl_2NPCl_3$ (1.5 g, 3.9 × 10^{-3} mol) with $Na(OC_6H_3Me_2\text{-}o)$ (5.4 × 10^{-2} mol) yielded the desired products. In both cases the reaction mixtures were refluxed overnight. The crude products were purified by chromatography on a silica gel column, using methylene chloride (30–60%) and hexane as eluent. The compounds were recrystallized from a mixture of hexane and methylene chloride to yield colourless crystals. Yields are: **9**, 72; **10**, 69%.

X-Ray Structure Determinations.—The structures were solved by direct methods using MULTAN 82. In each case the first E map revealed the positions of all non-hydrogen atoms which were refined anisotropically. Hydrogen atoms were calculated and refined isotropically. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[14] and those for hydrogen atoms from Stewart *et al.*[15] In the refinements weights were derived from the counting statistics. A summary of the crystal data and intensity collection parameters is given in Table 22.[16]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 22 Summary of crystal data and intensity collection parameters

	1	2	4	5	6	7	8	9	10
Formula	$C_6H_3Cl_7N_3OP_3$	$C_{12}H_6Cl_8N_3O_2P_3$	$C_{24}H_{12}Cl_{10}N_3O_4P_3$	$C_{36}H_{18}Cl_{12}N_3O_6P_3$	$C_{24}H_{12}Cl_{12}N_4O_4P_4$	$C_{16}H_{18}Cl_4N_3O_2P_3$	$C_{48}H_{54}N_3P_3O_6$	$C_{18}H_9Cl_8NO_4P_2$	$C_{40}H_{45}N_2Cl_2P_3O_6$
M	474.20	600.75	853.83	1106.92	969.72	519.07	861	648.85	813.64
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Tetragonal	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P4/ncc$	$Pbca$	$P2_1/c$
a/Å	8.081(4)	18.856(5)	7.975(3)	12.021(4)	10.806(2)	9.470(3)	20.560(5)	14.319(4)	15.212(3)
b/Å	8.074(2)	8.022(2)	18.373(4)	19.938(5)	10.861(2)	18.481(12)	20.560(5)	16.837(4)	18.965(1)
c/Å	25.868(3)	16.124(2)	22.225(3)	18.379(11)	17.075(7)	13.087(8)	22.085(4)	20.660(8)	14.559(2)
α/°					89.33(4)		90.00(2)	—	—
β/°	91.11(2)	114.89(2)	90.35(2)	90.85(4)	80.79(3)	94.56(4)	90.00(2)	—	102.96(2)
γ/°					68.44(2)		90.00(3)	—	—
U/Å^3	1687.6	2212.4	3256.7	4404.5	1837.3	2283.2	9344.9	4981.1	4093.2
Z	4	4	4	4	2	4	8	8	4
D_c/g cm^{-3}	1.866	1.803	1.741	1.669	1.753	1.510	1.220	1.730	1.320
$F(000)$	928	1184	1696	2208	960	1056	3648	2576	1704
Crystal size (mm)	0.60 × 0.54 × 0.27	0.54 × 0.35 × 0.45	0.70 × 0.29 × 0.40	0.35 × 0.45 × 0.25	0.70 × 0.45 × 0.45	0.54 × 0.51 × 0.45	0.50 × 0.45 × 0.20	0.22 × 0.27 × 0.35	0.47 × 0.42 × 0.38
T/K	293	293	293	293	293	293	293	293	293
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Cu-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Cu-Kα
λ/Å	0.710 73	0.710 73	0.710 73	1.5418	0.710 73	0.710 73	0.710 73	0.710 73	1.5418
μ/cm^{-1}	14.61	12.556	10.45	85.70	11.214	7.452	17.04	10.648	29.58
θ_{max}/°	25	23	27	65	24	25	25	25	65
ω-Scan width	0.75 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	1.00 + 0.14 tan θ	1.00 + 0.35 tan θ	0.90 + 0.35 tan θ	1.00 + 0.35 tan θ	1.00 + 0.35 tan θ	1.00 + 0.14 tan θ
Variable scan speed/° min^{-1}	1.20–8.24	1.3–3.3	1.0–5.5	1.65–5.5	1.27–3.3	1.18–3.30	1.18–3.30	1.27–3.30	2.1–5.5
Crystal decay[a] (%)	None	2.3	2.4	3.2	1.5	0.8	1.5	4.2	2.8
Empirical absorption correction[b]									
maximum coefficient	0.9996	0.9991	0.9980	0.9982	0.9987	1.000	0.9967	0.9884	—
minimum coefficient	0.9195	0.8258	0.9355	0.7006	0.8570	0.9866	0.9835	0.8840	
Data measured	3217	3066	7841	8275	5760	4014	9157	4868	7231
Data used, $I > 3\sigma(I)$	2355	2575	5456	3789	3995	2920	2191	2537	5150
R, R'	0.0379, 0.0693	0.0512, 0.0759	0.0367, 0.0656	0.0699, 0.0872	0.0347, 0.0455	0.0414, 0.0641	0.062 91, 0.056 51	0.0473, 0.0717	0.0596, 0.0873
Data/parameters	13	9.5	13.5	7.0	9.2	11.5	6.1	7.8	10.8
$(\Delta/\sigma)_{max}$	0.00	0.02	0.02	0.02	0.01	0.00	0.58	<0.1	<0.05
$\Delta\rho$/e Å^{-3}	0.37	0.44	0.577	0.725, −0.635	0.32, −0.29	0.243	12.675	0.57, −0.55	0.561
p in weighting scheme[c]	0.080	0.080	0.100	0.070	0.040	0.080	0.050	0.080	0.080
Error in weights, S	1.554	1.773	1.179	1.689	1.560	1.366	4.501	1.48	1.732

[a] Data corrected by appropriate scaling. [b] Calculated using the program included in the SDP package.[16] [c] $w^{-1} = \sigma^2(F) + pF^2$.

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References

1 C. W. Allen, *Chem. Rev.*, 1991, **91**, 119.
2 E. T. McBee, K. Okuhara and C. J. Morton, *Inorg. Chem.*, 1966, **5**, 450.
3 D. Dell, B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 1965, 4070.
4 D. Dell, B. W. Fitzsimmons, R. Keat and R. A. Shaw, *J. Chem. Soc. A*, 1966, 1680.
5 R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.
6 R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1966, 908.
7 R. A. Shaw, *Z. Naturforsch., Teil B*, 1976, **31**, 641.
8 D. J. Lingley, R. A. Shaw, M. Woods and S. S. Krishnamurthy, *Phosphorus Sulfur*, 1978, **4**, 379.
9 J. Emsley, J. Moore and P. B. Udy, *J. Chem. Soc. A*, 1971, 2863.
10 L. Riesel and R. Somiesi, *Z. Anorg. Allg. Chem.*, 1975, **411**, 148.
11 J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1935, 236; A. M. Ward, *J. Chem. Soc.*, 1927, 2285; E. D. Hughes, C. K. Ingold and C. S. Patel, *J. Chem. Soc.*, 1933, 526.
12 H. R. Allcock, N. M. Tollefson, R. A. Arcus and R. R. Whittle, *J. Am. Chem. Soc.*, 1985, **107**, 5166; E. Giglio, F. Pompa and A. Ripamonti, *J. Polym. Sci.*, 1962, **59**, 293.
13 E. Hobbs, D. E. C. Corbridge and B. Raistrick, *Acta Crystallogr.*, 1953, **6**, 621; C. E. Nordman, *Acta Crystallogr.*, 1960, **13**, 535.
14 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
15 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3178.
16 Enraf-Nonius Structure Determination Package (SDP Plus version 1.0), Enraf-Nonius, Delft, 1982.

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