# Molecular Structures of Cyclic Mono- and Di-(phosphoranylidene)aminophosphazenes: Small-molecule Models for High Polymers†

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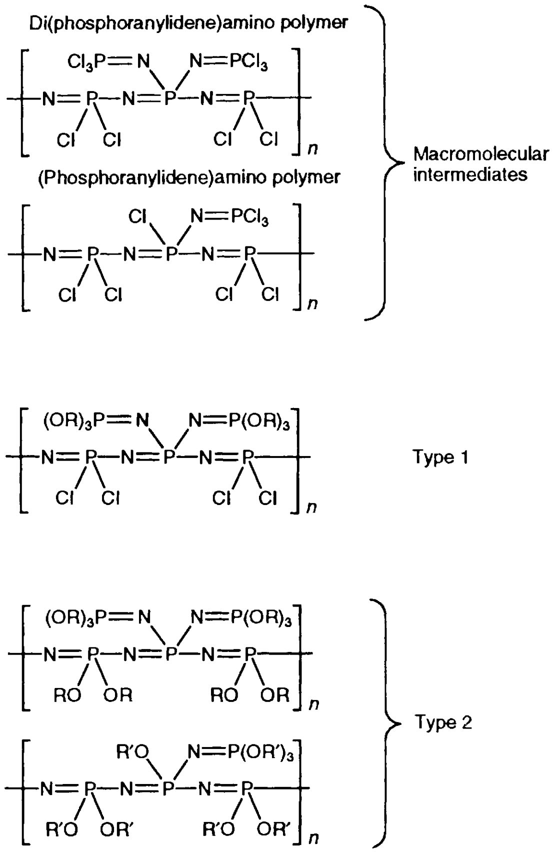
The molecular structures of four cyclic (phosphoranylidene)aminophosphazenes were determined. These compounds are small-molecule models for the corresponding high polymeric phosphazenes. The solid-state structures of *gem*-$N_3P_3Cl_4[NP(OPh)_3]_2$ **4**, *gem*-$N_3P_3(OPh)_4[NP(OPh)_3]_2$ **5**, $N_3P_3(OPh)_5NP(OPh)_3$ **6** and $N_3P_3(NHPr)_5NP(NHPr)_3{\cdot}HCl$ **7** were determined by single crystal X-ray diffraction. Structural parameters: **4**, triclinic, space group $P\bar{1}$, $a$ = 12.900(2), $b$ = 13.035(1), $c$ = 14.349(6) Å, $\alpha$ = 67.85(2), $\beta$ = 80.68(3), $\gamma$ = 67.73(1)°, $Z$ = 2; **5**, monoclinic, space group $P2_1/n$, $a$ = 20.844(12), $b$ = 13.679(3), $c$ = 22.488(4) Å, $\beta$ = 116.91(3)°, $Z$ = 4; **6**, triclinic, space group $P\bar{1}$, $a$ = 18.511(11), $b$ = 23.206(26), $c$ = 10.701(4) Å, $\alpha$ = 98.67(5), $\beta$ = 95.32(4), $\gamma$ = 97.68(6)°, $Z$ = 4 with two distinct molecular conformations; **7**, triclinic, space group $P\bar{1}$, $a$ = 13.187(10), $b$ = 14.014(13), $c$ = 14.335(4) Å, $\alpha$ = 96.41(4), $\beta$ = 115.76(5), $\gamma$ = 115.12(5)°, $Z$ = 2. Two interesting features of compound **7** are the presence of two long P–N bonds 1.686(9) and 1.676(8) Å, and two narrowed N–P–N angles, 108.9(4) and 109.7(5)°, in the phosphazene ring.

High polymeric phosphazenes form a class of inorganic/organic macromolecules in which the properties are determined mainly by the characteristics of the side groups present.[1,2] Previously, we have made extensive use of small-molecule phosphazene models to devise synthetic routes to the corresponding high polymers.[3–7] Cyclic tri- and tetra-meric phosphazenes are often easier to synthesize, purify and characterize than are the analogous high polymers that contain the same repeating units. Thus, the models may be used to explore the feasibility of synthetic routes to the high polymers. The model compound approach is also useful for studying reaction mechanisms, such as the pattern of halogen replacement.[8,9] Because fundamental molecular structural data for high polymers are difficult to obtain, crystal structure work carried out on small-molecule model compounds can provide vital information that assists the development of structure–property correlations at the high polymer level.

Cyclic (phosphoranylidene)aminophosphazenes are phosphazene rings that bear one or more exocyclic $N{=}PX_3$ units bonded to the phosphorus ring atoms. The small-molecule chemistry of this class of compounds has been well studied.[10–15] Interest in the basicity of (triphenylphosphoranylidene)aminocyclotriphosphazenes has led to the examination of the molecular structures of many of these cyclic trimers.[16–20] In particular, Shaw and co-workers[21–24] have studied the relationship between the molecular conformations and basicity of these compounds. We are interested in the structures of the $NPX_3$-substituted cyclic trimers as they relate to their macromolecular counterparts.

In two earlier papers,[25,26] we described the synthesis of a series of mono- and di-(phosphoranylidene)aminophosphazene high polymers and explored the effect of bulky $NPX_3$ units on chain flexibility and glass-transition temperatures. In the present work, we report the solid-state structures of four small-molecule cyclic (phosphoranylidene)aminophosphazenes as structural models for their high polymeric analogues. The primary objectives were to gain insight into the influence of the $NPX_3$ units on bond lengths, bond angles and conformation of the cyclic phosphazene ring and to apply that information to the macromolecular species in an attempt to correlate polymer structure with physical or chemical properties.

The structures of the poly[bis{(phosphoranylidene)amino}phosphazenes] shown below are of two general types. Type 1 consists of polymers where only the $NPX_3$ chlorine atoms have been replaced by organic units, and $P–Cl_2$ bonds remain along the polymer backbone. In the type 2 structures, all the chlorine atoms in the polymer have been



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

replaced. Both type 1 and 2 phosphazene high polymers have been synthesized.[25] Therefore two corresponding models were examined. The first is a trimer where only the $NPX_3$ chlorine atoms have been replaced by phenoxy groups (trimer **4**). The second model, trimer **5**, contained phenoxy side groups only. The mono(phosphoranylidene)amino polymers synthesized previously had a structure of type 2. Two cyclic trimer models for this system were also examined, one with bulky phenoxy substituents and one with less bulky, propylamino substituents (trimers **6** and **7**, respectively).

## Results and Discussion

*Preparation of Cyclic Trimers.*—The reactions of hexachlorocyclotriphosphazene **1** with sodium aryloxides, sodium alkoxides or primary amines in the presence of a hydrogen chloride acceptor are well known (see Scheme 1).[27] A similar route was used in this work to prepare trimers **4**–**7**. The general synthetic route to the substituted (phosphoranylidene)amino trimers is shown in Scheme 2.

*Phenoxy-substituted trimers.* For trimer **4**, only the exocyclic P–Cl bonds were replaced. Six equivalents of sodium phenoxide were added to trimer **2** and the reaction mixture in 1,4-dioxane was stirred at room temperature for 12 h. In the second case, for trimers **5** and **6**, an excess of sodium phenoxide was used with trimers **2** and **3** respectively, and the reactions were heated to reflux at 102 °C in 1,4-dioxane.

*Propylamino-substituted trimer.* Trimer **7** was synthesized by the addition of cyclic trimer **3**, in toluene, to an excess of propylamine. The reaction mixture was heated at reflux at 111 °C for 3 d.

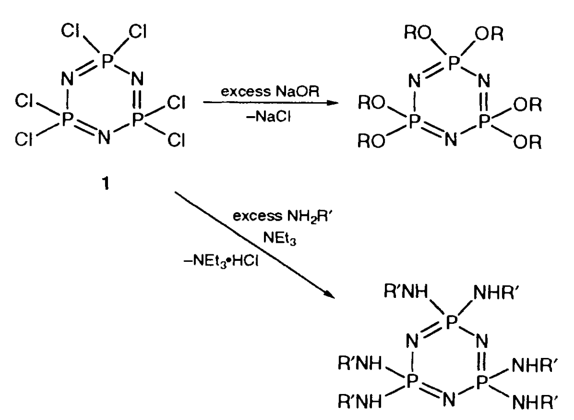
*Reactivity of Exocyclic* $PCl_3$ *Units.*—In agreement with earlier observations,[25,26,28] the exocyclic $PCl_3$ units are more reactive to nucleophilic substitution than the ring $PCl_2$ units. At room temperature, the nucleophiles react preferentially at the exocyclic P–Cl sites. This behaviour was found for both trimers **2** and **3**[25,26] and provides a simple route to product **4**.

*Characterization of Cyclic Trimers.*—The structures of compounds **4**–**7** have been examined by NMR spectroscopy, mass spectrometry and elemental analysis.[25,26] In each case the NMR spectroscopic, mass spectral and elemental analysis data were compatible with the proposed structures. However, the main structural characterization was by single-crystal X-ray analysis.

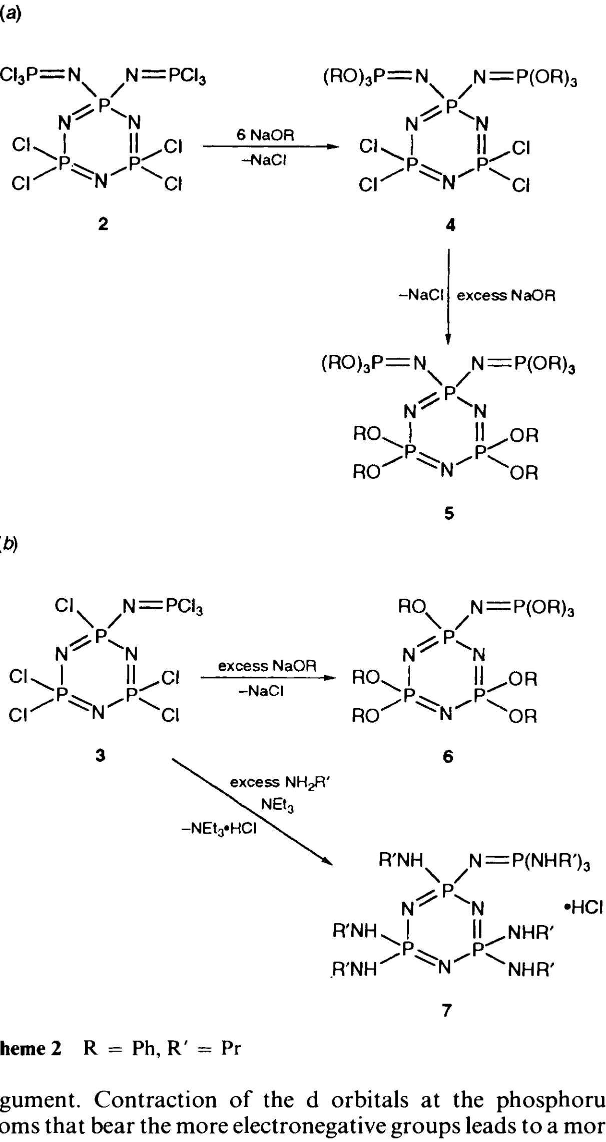
*Crystal Structure Determinations.*—The solid-state structures of **4**–**7** were determined by X-ray crystallography and are shown in Figs. 1–4. Cell constants and intensity collection parameters are shown in Table 1. Selected bond lengths and bond angles are listed in Tables 2–5 and atomic coordinates in Tables 6–9.

$N_3P_3Cl_4[NP(OPh)_3]_2$ **4**. The structure of compound **4** consists of a six-membered ring of alternating phosphorus and nitrogen atoms. Phosphorus ring atoms P(2) and P(3) each bear two chlorine atoms, while two $NP(OPh)_3$ units are attached to P(1) through N–P linkages (Fig. 1).

The phosphazene ring is characterized by three different pairs of P–N distances. The two bonds adjacent to the $NP(OPh)_3$-substituted phosphorus atom P(1) are the longest, with an average length of 1.631(7) Å. The bonds adjacent to these, N(1)–P(2) and N(3)–P(3) are the shortest [mean 1.546(7) Å], while the remaining two bonds, N(2)–P(2) and N(2)–P(3), are intermediate [mean 1.579(8) Å]. This pattern of varying bond lengths has been observed previously for phosphazene trimers such as $N_3P_3Cl_5(NPPh_3)$ and *gem*-$N_3P_3Cl_4Ph_2$.[16–18,29] The difference in the bond lengths can be correlated with the nature of the substituents at the phosphorus atoms; the shorter skeletal P–N bond distances are adjacent to the more electronegative substituents.[27,30] This can be rationalized by an orbital overlap argument. Contraction of the d orbitals at the phosphorus atoms that bear the more electronegative groups leads to a more efficient overlap of the phosphorus and nitrogen atom orbitals. This results in an increase in the bond strength and a decrease in the bond length.



**Scheme 1** R = Ph or $CH_2CF_3$, R′ = Pr or Ph



**Scheme 2** R = Ph, R′ = Pr

The exocyclic P–N bonds which join the $NP(OPh)_3$ group to the phosphazene ring, P(1)–N(4) and P(1)–N(5), have an average length of 1.606(7) Å. The $N{=}P(OPh)_3$ bonds P(4)–N(4) and P(5)–N(5) have a mean length of 1.525(7) Å, which is significantly shorter. This suggests that the electrons within the exocyclic P–N–P segment are not delocalized.

The acyclic P–N–P bond angles are 128.7(3) and 143.3(4)°.

**Table 1** Summary of crystal data and intensity collection parameters*

| | 4 | 5 | 6 | 7 |
|---|---|---|---|---|
| Formula | $C_{36}H_{30}Cl_4N_5O_6P_5$ | $C_{60}H_{50}N_5O_{10}P_5$ | $C_{48}H_{40}N_4O_8P_4$ | $C_{24}H_{64}N_{12}P_4$·HCl |
| $M$ | 925.24 | 1155.40 | 924.32 | 681.02 (+HCl) |
| Space group | $P\bar{1}$ (No. 2) | $P2_1/n$ (No. 14) | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) |
| Crystal system | Triclinic | Monoclinic | Triclinic | Triclinic |
| Crystal size/mm | 1.4 × 1.2 × 1.0 | 1.2 × 1.0 × 1.0 | 1.3 × 1.0 × 1.0 | 2.0 × 1.0 × 1.0 |
| $a$/Å | 12.900(2) | 20.844(12) | 18.511(11) | 13.187(10) |
| $b$/Å | 13.035(1) | 13.679(3) | 23.206(26) | 14.014(13) |
| $c$/Å | 14.349(6) | 22.488(4) | 10.701(4) | 14.335(4) |
| $\alpha$/° | 67.85(2) | | 98.67(5) | 96.41(4) |
| $\beta$/° | 80.68(3) | 116.91(3) | 95.32(4) | 115.76(5) |
| $\gamma$/° | 67.73(1) | | 97.68(6) | 115.12(5) |
| $U$/Å$^3$ | 2068.00 | 5717.67 | 4473.54 | 2012.39 |
| $Z$ | 2 | 4 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.428 | 1.34 | calc. = 1.373, exp. = 1.359 | calc. = 1.121, exp. = 1.122 |
| $F(000)$ | 944 | 2400 | 1920 | 370 |
| $\mu$/cm$^{-1}$ | 4.69 | 1.78 | 1.82 | 1.22 |
| Data measured | 7258 | 10 043 | 9720 | 7080 |
| Data used | 4532 | 2829 | 7344 | 2896 |
| $R'$ [= $(\Sigma\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$] | 0.0583<br>($R_g = R_m = 0.0663$) | 0.0884<br>($R_g = R_m = 0.1021$) | 0.0556<br>($R_g = R_m = 0.0585$) | 0.0846<br>($R_g = 0.1019$, $R_m = 0.1020$) |

* Details in common: Mo-Kα radiation (λ = 0.710 73 Å); $T$ = 293 K.

**Table 2** Selected bond distances (Å) and angles (°) for *gem*-$N_3P_3Cl_4[NP(OPh)_3]_2$ **4** with estimated standard deviations (e.s.d.s) in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cl(1)–P(2) | 2.003(3) | P(4)–O(1) | 1.577(4) | P(1)–N(5) | 1.596(5) | O(1)–C(11) | 1.397(5) |
| Cl(2)–P(2) | 2.010(3) | P(4)–O(2) | 1.567(4) | P(2)–N(1) | 1.547(5) | O(2)–C(21) | 1.381(5) |
| Cl(3)–P(3) | 2.011(3) | P(4)–O(3) | 1.572(5) | P(2)–N(2) | 1.578(6) | O(3)–C(31) | 1.375(5) |
| Cl(4)–P(3) | 2.020(3) | P(5)–N(5) | 1.516(5) | P(3)–N(2) | 1.579(6) | O(4)–C(41) | 1.383(5) |
| P(1)–N(1) | 1.625(5) | P(5)–O(4) | 1.578(4) | P(3)–N(3) | 1.544(5) | O(5)–C(51) | 1.386(5) |
| P(1)–N(3) | 1.636(5) | P(5)–O(5) | 1.564(4) | P(4)–N(4) | 1.533(5) | O(6)–C(61) | 1.391(5) |
| P(1)–N(4) | 1.616(5) | P(5)–O(6) | 1.565(4) | | | | |
| N(1)–P(1)–N(3) | 111.6(3) | N(5)–P(5)–O(6) | 113.3(3) | N(2)–P(3)–C(14) | 106.8(3) | O(1)–C(11)–C(12) | 118.7(2) |
| N(1)–P(1)–N(4) | 110.2(3) | O(4)–P(5)–O(6) | 107.7(2) | N(3)–P(3)–C(13) | 110.4(2) | O(1)–C(11)–C(16) | 121.2(2) |
| N(3)–P(1)–N(4) | 110.7(3) | O(5)–P(5)–O(6) | 102.5(2) | N(3)–P(3)–C(14) | 109.8(2) | O(2)–C(21)–C(22) | 117.1(2) |
| N(1)–P(1)–N(5) | 108.1(3) | P(1)–N(1)–P(2) | 124.6(3) | N(2)–P(3)–N(3) | 121.1(3) | O(2)–C(21)–C(26) | 122.8(2) |
| N(3)–P(1)–N(5) | 109.8(3) | P(2)–N(2)–P(3) | 118.1(3) | N(4)–P(4)–O(1) | 118.6(5) | O(3)–C(31)–C(32) | 121.0(2) |
| N(4)–P(1)–N(5) | 106.3(3) | P(1)–N(3)–P(3) | 123.4(3) | N(4)–P(4)–O(2) | 112.7(3) | O(3)–C(31)–C(36) | 118.9(2) |
| Cl(1)–P(2)–Cl(2) | 99.9(1) | P(1)–N(4)–P(4) | 128.7(3) | O(1)–P(4)–O(2) | 102.0(2) | O(4)–C(41)–C(42) | 124.5(2) |
| N(1)–P(2)–Cl(1) | 110.1(2) | P(1)–N(5)–P(5) | 143.3(4) | N(4)–P(4)–O(3) | 113.4(3) | O(4)–C(41)–C(46) | 115.5(2) |
| N(1)–P(2)–Cl(2) | 111.1(2) | P(4)–O(1)–C(11) | 121.0(3) | O(1)–P(4)–O(3) | 101.0(2) | O(5)–C(51)–C(52) | 116.1(2) |
| N(2)–P(2)–Cl(1) | 107.0(3) | P(4)–O(2)–C(21) | 127.1(3) | O(2)–P(4)–O(3) | 107.9(3) | O(5)–C(51)–C(56) | 123.9(2) |
| N(2)–P(2)–Cl(2) | 107.1(3) | P(4)–O(3)–C(31) | 125.8(3) | N(5)–P(5)–O(4) | 115.2(3) | O(6)–C(61)–C(62) | 119.4(4) |
| N(1)–P(2)–N(2) | 119.9(3) | P(5)–O(4)–C(41) | 127.9(3) | N(5)–P(5)–O(5) | 116.6(3) | O(6)–C(61)–C(66) | 120.5(2) |
| C(13)–P(3)–C(14) | 99.2(1) | P(5)–O(5)–C(51) | 128.4(3) | O(4)–P(5)–O(5) | 100.0(2) | | |
| N(2)–P(3)–C(13) | 107.1(3) | P(5)–O(6)–C(61) | 124.9(3) | | | | |

The average endocyclic angle at P(2) and P(3) is 120.5(4)°. The endocyclic bond angle at the geminally substituted phosphorus P(1) is significantly narrower, 111.6(3)°, possibly due to the presence of the less electronegative side groups or to a 'scissoring' effect induced by the mutual steric repulsion by the two (phosphoranylidene)amino units. The geometry about P(1) is roughly tetrahedral. The narrow endocyclic bond angle at P(1) suggests the presence of ring strain that may play a role in the ring-opening polymerization of the parent trimer $N_3P_3Cl_4(NPCl_3)_2$. Previous molecular modelling work[25] suggested a narrowed bond angle at the $NPX_3$-substituted phosphorus atom for trimer **2**.

$N_3P_3(OPh)_4[NP(OPh)_3]_2$ **5**. Trimer **5** also contains a six-membered ring of alternating phosphorus and nitrogen atoms. Two of the phosphorus ring atoms, P(2) and P(3), each bear two phenoxy groups; the third ring phosphorus, P(1), bears two $NP(OPh)_3$ units (Fig. 2).

As in trimer **4**, the phosphazene ring bears two different substituents arranged in a geminal manner. The same pattern of long, short and intermediate bonds about the phosphazene ring might be expected here also. However, because the phenoxy units are less electronegative than chlorine, the differences in bond lengths about the ring are lessened. Distinctions between the bond lengths in trimer **5** are not as clear as in **4**. The longest bond, P(1)–N(1) [1.618(16) Å], is still adjacent to the $NP(OPh)_3$-substituted phosphorus. As seen in trimer **4**, the $N{=}P(OPh)_3$ bonds are significantly different from the N–P bonds that connect the (triphenoxyphosphoranylidene)amino group to the cyclic trimer. For example, P(1)–N(5) is 1.621(13) Å in length whereas N(5)–P(5) is only 1.527(13) Å. The same trend is seen for the second $NP(OPh)_3$ substituent. The exocyclic P–N bonds P(1)–N(5) and P(1)–N(4) have the same average length, within error, as trimer **4**, 1.606(18) Å. The exocyclic bond lengths N(5)–P(5) and N(4)–P(4), with an average of 1.529(20) Å, were also similar to trimer **4**.

The acyclic P–N–P bond angles at the $NP(OPh)_3$ groups are 138.8(9) and 134.0(11)°. The average endocyclic angle at P(2) and P(3) is 118.9(11)°. In contrast to trimer **4**, the bond angle N(1)–P(1)–N(3) is 114.0(6)° and is closer to the values of the angles at the other ring phosphorus atoms.

$N_3P_3(OPh)_5NP(OPh)_3$ **6**. The structure of compound **6** consists of a six-membered ring of alternating phosphorus and nitrogen atoms. Two of the ring phosphorus atoms bear two phenoxy side groups each. The remaining ring phosphorus

**Table 3** Selected bond distances (Å) and angles (°) for *gem*-$N_3P_3(OPh)_4[NP(OPh)_3]_2$ **5** with e.s.d.s in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P(1)–N(1) | 1.618(16) | P(4)–O(7) | 1.553(11) | P(3)–N(2) | 1.580(16) | O(4)–C(41) | 1.355(15) |
| P(1)–N(3) | 1.585(15) | P(5)–N(5) | 1.527(13) | P(3)–N(3) | 1.584(11) | O(5)–C(51) | 1.398(18) |
| P(1)–N(4) | 1.591(13) | P(5)–O(8) | 1.605(14) | P(3)–O(3) | 1.587(13) | O(6)–C(61) | 1.383(15) |
| P(1)–N(5) | 1.621(13) | P(5)–O(9) | 1.575(13) | P(3)–O(4) | 1.596(13) | O(7)–C(71) | 1.384(14) |
| P(2)–N(1) | 1.548(11) | P(5)–O(10) | 1.555(14) | P(4)–N(4) | 1.530(15) | O(8)–C(81) | 1.373(17) |
| P(2)–N(2) | 1.573(16) | O(1)–C(11) | 1.365(14) | P(4)–O(5) | 1.572(12) | O(9)–C(91) | 1.378(14) |
| P(2)–O(1) | 1.623(12) | O(2)–C(21) | 1.344(12) | P(4)–O(6) | 1.583(16) | O(10)–C(101) | 1.373(15) |
| P(2)–O(2) | 1.581(13) | O(3)–C(31) | 1.371(12) | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1)–P(1)–N(3) | 114.0(6) | P(1)–N(4)–P(4) | 134.0(11) | O(3)–P(3)–O(4) | 98.1(7) | O(3)–C(31)–C(36) | 118.4(10) |
| N(1)–P(1)–N(4) | 110.5(8) | P(1)–N(5)–P(5) | 138.8(9) | N(4)–P(4)–O(5) | 112.1(8) | O(4)–C(41)–C(42) | 118.2(9) |
| N(3)–P(1)–N(4) | 106.4(8) | P(2)–O(1)–C(11) | 124.0(10) | N(4)–P(4)–O(6) | 120.4(7) | O(4)–C(41)–C(46) | 121.6(10) |
| N(1)–P(1)–N(5) | 107.1(8) | P(2)–O(2)–C(21) | 128.6(8) | O(5)–P(4)–O(6) | 99.6(7) | O(5)–C(51)–C(52) | 116.7(11) |
| N(3)–P(1)–N(5) | 108.4(8) | P(3)–O(3)–C(31) | 126.4(9) | N(4)–P(4)–O(7) | 113.9(7) | O(5)–C(51)–C(56) | 123.1(11) |
| N(4)–P(1)–N(5) | 110.4(6) | P(3)–O(4)–C(41) | 120.3(11) | O(5)–P(4)–O(7) | 108.3(6) | O(6)–C(61)–C(62) | 115.1(11) |
| N(1)–P(2)–N(2) | 119.1(8) | P(4)–O(5)–C(51) | 125.2(10) | O(6)–P(4)–O(7) | 100.8(8) | O(6)–C(61)–C(66) | 120.0(10) |
| N(1)–P(2)–O(1) | 112.7(7) | P(4)–O(6)–C(61) | 125.4(12) | N(5)–P(5)–O(8) | 116.2(9) | O(7)–C(71)–C(72) | 117.9(9) |
| N(2)–P(2)–O(1) | 107.8(7) | P(4)–O(7)–C(71) | 125.3(9) | N(5)–P(5)–O(9) | 114.5(7) | O(7)–C(71)–C(76) | 122.1(12) |
| N(1)–P(2)–O(2) | 105.9(7) | P(5)–O(8)–C(81) | 121.2(9) | O(8)–P(5)–O(9) | 102.3(6) | O(8)–C(81)–C(82) | 117.6(10) |
| N(2)–P(2)–O(2) | 111.3(7) | P(5)–O(9)–C(91) | 124.5(9) | N(5)–P(5)–O(10) | 116.7(7) | O(8)–C(81)–C(86) | 122.3(9) |
| O(1)–P(2)–O(2) | 98.0(7) | P(5)–O(10)–C(101) | 130.8(9) | O(8)–P(5)–O(10) | 100.6(7) | O(9)–C(91)–C(92) | 121.7(12) |
| N(2)–P(3)–N(3) | 118.6(8) | O(1)–C(11)–C(12) | 125.2(9) | O(9)–P(5)–O(10) | 104.6(8) | O(9)–C(91)–C(96) | 118.2(10) |
| N(2)–P(3)–O(3) | 111.9(6) | O(1)–C(11)–C(16) | 114.8(10) | P(1)–N(1)–P(2) | 124.1(10) | O(10)–C(101)–C(102) | 115.7(9) |
| N(3)–P(3)–O(3) | 106.6(7) | O(2)–C(21)–C(22) | 116.3(9) | P(2)–N(2)–P(3) | 120.4(7) | O(10)–C(101)–C(106) | 124.0(10) |
| N(2)–P(3)–O(4) | 108.5(7) | O(2)–C(21)–C(26) | 123.7(11) | P(1)–N(3)–P(3) | 123.7(10) | | |
| N(3)–P(3)–O(4) | 111.2(7) | O(3)–C(31)–C(32) | 121.4(10) | | | | |

**Table 4** Selected bond distances (Å) and angles (°) for $N_3P_3(OPh)_5NP(OPh)_3$ **6**, two conformations, with e.s.d.s in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P(1)–N(1) | 1.581(4) | P(5)–N(5) | 1.570(5) | P(4)–N(4) | 1.525(5) | P(8)–N(8) | 1.520(5) |
| P(1)–N(3) | 1.566(5) | P(5)–N(7) | 1.579(4) | P(4)–O(6) | 1.564(4) | P(8)–O(14) | 1.562(4) |
| P(1)–O(1) | 1.582(4) | P(5)–O(9) | 1.583(4) | P(4)–O(7) | 1.565(4) | P(8)–O(15) | 1.567(4) |
| P(1)–O(2) | 1.593(4) | P(5)–O(10) | 1.596(4) | P(4)–O(8) | 1.567(4) | P(8)–O(16) | 1.561(4) |
| P(2)–N(1) | 1.580(4) | P(6)–N(5) | 1.592(5) | O(1)–C(11) | 1.367(5) | O(9)–C(91) | 1.370(5) |
| P(2)–N(2) | 1.563(5) | P(6)–N(6) | 1.590(4) | O(2)–C(21) | 1.382(5) | O(10)–C(101) | 1.385(5) |
| P(2)–O(3) | 1.584(4) | P(6)–N(8) | 1.596(5) | O(3)–C(31) | 1.357(6) | O(11)–C(111) | 1.368(5) |
| P(2)–O(4) | 1.587(4) | P(6)–O(11) | 1.606(4) | O(4)–C(41) | 1.377(5) | O(12)–C(121) | 1.383(4) |
| P(3)–N(2) | 1.588(4) | P(7)–N(6) | 1.570(5) | O(5)–C(51) | 1.364(5) | O(13)–C(131) | 1.352(5) |
| P(3)–N(3) | 1.589(4) | P(7)–N(7) | 1.576(5) | O(6)–C(61) | 1.382(4) | O(14)–C(141) | 1.368(5) |
| P(3)–N(4) | 1.596(5) | P(7)–O(12) | 1.585(4) | O(7)–C(71) | 1.378(5) | O(15)–C(151) | 1.381(5) |
| P(3)–O(5) | 1.596(4) | P(7)–O(13) | 1.580(4) | O(8)–C(81) | 1.372(5) | O(16)–C(161) | 1.374(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1)–P(1)–N(3) | 118.4(2) | N(5)–P(5)–N(7) | 118.8(2) | P(1)–N(3)–P(3) | 122.3(2) | P(5)–N(7)–P(7) | 120.1(3) |
| N(1)–P(1)–O(1) | 111.5(2) | N(5)–P(5)–O(9) | 106.9(2) | P(3)–N(4)–P(4) | 133.7(3) | P(6)–N(8)–P(8) | 136.2(3) |
| N(3)–P(1)–O(1) | 107.1(2) | N(7)–P(5)–O(9) | 110.7(2) | P(1)–O(1)–C(11) | 125.1(3) | P(5)–O(9)–C(91) | 122.5(3) |
| N(1)–P(1)–O(2) | 109.4(2) | N(5)–P(5)–O(10) | 110.1(2) | P(1)–O(2)–C(21) | 119.6(3) | P(5)–O(10)–C(101) | 118.4(3) |
| N(3)–P(1)–O(2) | 109.9(2) | N(7)–P(5)–O(10) | 109.9(2) | P(2)–O(3)–C(31) | 125.8(3) | P(6)–O(11)–C(111) | 127.4(3) |
| O(1)–P(1)–O(2) | 98.8(2) | O(9)–P(5)–O(10) | 98.4(2) | P(2)–O(4)–C(41) | 125.0(3) | P(7)–O(12)–C(121) | 121.8(3) |
| N(1)–P(2)–N(2) | 118.2(2) | N(5)–P(6)–N(6) | 115.9(2) | P(3)–O(5)–C(51) | 128.6(3) | P(7)–O(13)–C(131) | 129.3(3) |
| N(1)–P(2)–O(3) | 110.2(2) | N(5)–P(6)–N(8) | 112.4(2) | P(4)–O(6)–C(61) | 122.8(3) | P(8)–O(14)–C(141) | 125.7(3) |
| N(2)–P(2)–O(3) | 110.4(2) | N(6)–P(6)–N(8) | 111.3(2) | P(4)–O(7)–C(71) | 125.8(3) | P(8)–O(15)–C(151) | 121.1(3) |
| N(1)–P(2)–O(4) | 111.9(2) | N(5)–P(6)–O(11) | 103.7(2) | P(4)–O(8)–C(81) | 124.0(3) | P(8)–O(16)–C(161) | 123.3(3) |
| N(2)–P(2)–O(4) | 105.1(2) | N(6)–P(6)–O(11) | 108.8(2) | O(1)–C(11)–C(12) | 118.6(3) | O(9)–C(91)–C(92) | 121.2(3) |
| O(3)–P(2)–O(4) | 99.5(2) | N(8)–P(6)–O(11) | 103.5(2) | O(1)–C(11)–C(16) | 121.2(3) | O(9)–C(91)–C(96) | 118.6(3) |
| N(2)–P(3)–N(3) | 115.3(2) | N(6)–P(7)–N(7) | 117.9(2) | O(2)–C(21)–C(22) | 119.1(3) | O(10)–C(101)–C(102) | 118.6(3) |
| N(2)–P(3)–N(4) | 111.0(2) | N(6)–P(7)–O(12) | 110.6(2) | O(2)–C(21)–C(26) | 120.9(3) | O(10)–C(101)–C(106) | 121.3(3) |
| N(3)–P(3)–N(4) | 113.0(3) | N(7)–P(7)–O(12) | 109.5(2) | O(3)–C(31)–C(32) | 119.6(4) | O(11)–C(111)–C(112) | 124.3(3) |
| N(2)–P(3)–O(5) | 109.1(2) | N(6)–P(7)–O(13) | 112.3(2) | O(3)–C(31)–C(36) | 120.3(4) | O(11)–C(111)–C(116) | 115.6(3) |
| N(3)–P(3)–O(5) | 103.3(2) | N(7)–P(7)–O(13) | 106.1(2) | O(4)–C(41)–C(42) | 120.9(3) | O(12)–C(121)–C(122) | 118.5(3) |
| N(4)–P(3)–O(5) | 104.2(2) | O(12)–P(7)–O(13) | 98.6(2) | O(4)–C(41)–C(46) | 119.0(4) | O(12)–C(121)–C(126) | 121.2(3) |
| N(4)–P(4)–O(6) | 117.1(2) | N(8)–P(8)–O(14) | 114.4(2) | O(5)–C(51)–C(52) | 124.9(3) | O(13)–C(131)–C(132) | 115.5(3) |
| N(4)–P(4)–O(7) | 111.7(2) | N(8)–P(8)–O(15) | 117.9(2) | O(5)–C(51)–C(56) | 115.1(3) | O(13)–C(131)–C(136) | 124.5(3) |
| N(4)–P(4)–O(8) | 119.2(2) | N(8)–P(8)–O(16) | 112.0(3) | O(6)–C(61)–C(62) | 119.5(3) | O(14)–C(141)–C(142) | 117.0(3) |
| O(6)–P(4)–O(7) | 104.5(2) | O(14)–P(8)–O(15) | 101.6(2) | O(6)–C(61)–C(66) | 120.3(3) | O(14)–C(141)–C(146) | 122.8(3) |
| O(6)–P(4)–O(8) | 96.7(2) | O(14)–P(8)–O(16) | 107.8(2) | O(7)–C(71)–C(72) | 120.8(3) | O(15)–C(151)–C(152) | 120.1(3) |
| O(7)–P(4)–O(8) | 105.7(2) | O(15)–P(8)–O(16) | 101.9(2) | O(7)–C(71)–C(76) | 119.2(3) | O(15)–C(151)–C(156) | 119.8(3) |
| P(1)–N(1)–P(2) | 120.6(3) | P(5)–N(5)–P(6) | 120.8(3) | O(8)–C(81)–C(82) | 118.7(3) | O(16)–C(161)–C(162) | 116.8(3) |
| P(2)–N(2)–P(3) | 123.4(3) | P(6)–N(6)–P(7) | 122.1(3) | O(8)–C(81)–C(86) | 121.3(3) | O(16)–C(161)–C(166) | 123.2(3) |

atom bears a phenoxy and a $NP(OPh)_3$ unit. Two molecular conformations, **6a** and **6b**, were detected in the unit cell (Fig. 3).

Most of the structural features of molecules **6a** and **6b** are similar. The average ring P–N bond distance for **6a** is 1.578(11) Å and for **6b** is 1.580(11) Å. For molecule **6a** the mean length of P(3)–N(3) and P(3)–N(2) is 1.589(6) Å; P(1)–N(3) and P(2)–N(2) are the shortest bonds in the ring with an average length of 1.565(7) Å. The mean distance of N(1)–P(1) and N(1)–P(2) is

**Table 5** Selected bond distances (Å) and angles (°) for $N_3P_3(NHPr)_5NP(NHPr)_3{\cdot}HCl$ **7** with e.s.d.s in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P(1)–N(1) | 1.582(9) | P(4)–N(4) | 1.572(8) | P(2)–N(6) | 1.663(10) | N(7)–C(71) | 1.491(14) |
| P(1)–N(3) | 1.686(9) | P(4)–N(10) | 1.649(9) | P(2)–N(7) | 1.642(10) | N(8)–C(81) | 1.456(17) |
| P(1)–N(4) | 1.589(9) | P(4)–N(11) | 1.665(9) | P(3)–N(2) | 1.579(9) | N(9)–C(91) | 1.455(17) |
| P(1)–N(5) | 1.633(10) | P(4)–N(12) | 1.660(10) | P(3)–N(3) | 1.676(8) | N(10)–C(101) | 1.489(14) |
| P(2)–N(1) | 1.591(8) | N(5)–C(51) | 1.476(15) | P(3)–N(8) | 1.648(11) | N(11)–C(111) | 1.490(13) |
| P(2)–N(2) | 1.606(8) | N(6)–C(61) | 1.422(15) | P(3)–N(9) | 1.659(10) | N(12)–C(121) | 1.480(15) |
| | | | | | | | |
| N(1)–P(1)–N(3) | 108.9(4) | N(10)–P(4)–N(12) | 100.4(5) | N(6)–P(2)–N(7) | 106.5(6) | P(4)–N(10)–C(101) | 118.0(7) |
| N(1)–P(1)–N(4) | 114.3(5) | N(11)–P(4)–N(12) | 115.1(5) | N(2)–P(3)–N(3) | 109.7(5) | P(4)–N(11)–C(111) | 120.4(8) |
| N(3)–P(1)–N(4) | 106.2(5) | P(1)–N(1)–P(2) | 126.9(5) | N(2)–P(3)–N(8) | 111.4(6) | P(4)–N(12)–C(121) | 121.9(8) |
| N(1)–P(1)–N(5) | 109.4(5) | P(2)–N(2)–P(3) | 125.7(6) | N(3)–P(3)–N(8) | 111.2(5) | N(5)–C(51)–C(52) | 105.4(11) |
| N(3)–P(1)–N(5) | 109.7(5) | P(1)–N(3)–P(3) | 129.5(6) | N(2)–P(3)–N(9) | 115.8(5) | N(6)–C(61)–C(62) | 119.7(13) |
| N(4)–P(1)–N(5) | 108.2(5) | P(1)–N(4)–P(4) | 137.4(6) | N(3)–P(3)–N(9) | 107.4(5) | N(7)–C(71)–C(72) | 107.7(13) |
| N(1)–P(2)–N(2) | 117.7(5) | P(1)–N(5)–C(51) | 121.6(8) | N(8)–P(3)–N(9) | 101.0(6) | N(8)–C(81)–C(82) | 116.1(15) |
| N(1)–P(2)–N(6) | 102.9(5) | P(2)–N(6)–C(61) | 121.6(10) | N(4)–P(4)–N(10) | 119.1(5) | N(9)–C(91)–C(92) | 109.5(14) |
| N(2)–P(2)–N(6) | 112.7(5) | P(2)–N(7)–C(71) | 120.8(9) | N(4)–P(4)–N(11) | 107.9(5) | N(10)–C(101)–C(102) | 108.8(10) |
| N(1)–P(2)–N(7) | 113.0(5) | P(3)–N(8)–C(81) | 123.8(9) | N(10)–P(4)–N(11) | 105.7(5) | N(11)–C(111)–C(112) | 106.6(12) |
| N(2)–P(2)–N(7) | 103.9(5) | P(3)–N(9)–C(91) | 123.6(9) | N(4)–P(4)–N(12) | 108.8(5) | N(12)–C(121)–C(122) | 108.7(11) |

**Table 6** Atomic coordinates for $N_3P_3Cl_4[NP(OPh)_3]_2$ **4** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Cl(1) | 0.5902(2) | −0.3235(2) | 0.3514(2) | C(23) | 0.0767(3) | 0.2598(3) | 0.5338(3) |
| Cl(2) | 0.5123(2) | −0.0869(2) | 0.3863(2) | C(24) | 0.1503(3) | 0.3176(3) | 0.5279(3) |
| Cl(3) | 0.1763(2) | −0.1273(2) | 0.5492(1) | C(25) | 0.2427(3) | 0.3072(3) | 0.4617(3) |
| Cl(4) | 0.2238(2) | −0.3657(2) | 0.5258(2) | C(26) | 0.2614(3) | 0.2389(3) | 0.4015(3) |
| P(1) | 0.2551(1) | −0.0923(1) | 0.2448(1) | C(31) | 0.0222(3) | 0.2976(3) | 0.1559(3) |
| P(2) | 0.4485(1) | −0.1918(2) | 0.3597(1) | C(32) | −0.0672(3) | 0.2877(3) | 0.2237(3) |
| P(3) | 0.2537(2) | −0.2132(2) | 0.4526(1) | C(33) | −0.1741(3) | 0.3228(3) | 0.1881(3) |
| P(4) | 0.2129(1) | 0.1411(1) | 0.2365(1) | C(34) | −0.1917(3) | 0.3679(3) | 0.0848(3) |
| P(5) | 0.1800(1) | −0.2079(1) | 0.1406(1) | C(35) | −0.1023(3) | 0.3779(3) | 0.0171(3) |
| N(1) | 0.3888(4) | −0.1299(5) | 0.2577(4) | C(36) | 0.0046(3) | 0.3427(3) | 0.0526(3) |
| N(2) | 0.3836(5) | −0.2432(6) | 0.4588(4) | C(41) | 0.3426(3) | −0.4183(3) | 0.1844(3) |
| N(3) | 0.1943(4) | −0.1491(5) | 0.3506(4) | C(42) | 0.3603(3) | −0.4303(3) | 0.2819(3) |
| N(4) | 0.1974(4) | 0.0499(4) | 0.2021(4) | C(43) | 0.4448(3) | −0.5289(3) | 0.3391(3) |
| N(5) | 0.2387(4) | −0.1379(5) | 0.1613(4) | C(44) | 0.5116(3) | −0.6155(3) | 0.2987(3) |
| O(1) | 0.3273(4) | 0.1644(4) | 0.2106(3) | C(45) | 0.4939(3) | −0.6035(3) | 0.2012(3) |
| O(2) | 0.2045(4) | 0.1075(4) | 0.3537(3) | C(46) | 0.4094(3) | −0.5048(3) | 0.1440(3) |
| O(3) | 0.1270(4) | 0.2694(4) | 0.1891(3) | C(51) | 0.1461(3) | −0.1069(3) | −0.0562(2) |
| O(4) | 0.2599(4) | −0.3253(4) | 0.1224(3) | C(52) | 0.0663(3) | −0.0640(3) | −0.1294(2) |
| O(5) | 0.1096(3) | −0.1462(4) | 0.0429(3) | C(53) | 0.0954(3) | −0.0218(3) | −0.2310(2) |
| O(6) | 0.0920(4) | −0.2402(4) | 0.2244(3) | C(54) | 0.2043(3) | −0.0225(3) | −0.2595(2) |
| C(11) | 0.3673(3) | 0.1959(3) | 0.1115(2) | C(55) | 0.2840(3) | −0.0654(3) | −0.1863(2) |
| C(12) | 0.4530(3) | 0.1096(3) | 0.0806(2) | C(56) | 0.2550(3) | −0.1076(3) | −0.0847(2) |
| C(13) | 0.4997(3) | 0.1397(3) | −0.0163(2) | C(61) | 0.0231(3) | −0.2991(3) | 0.2216(3) |
| C(14) | 0.4616(3) | 0.2562(3) | −0.0823(2) | C(62) | 0.0554(3) | −0.4211(3) | 0.2706(3) |
| C(15) | 0.3768(3) | 0.3426(3) | −0.0514(2) | C(63) | −0.0161(3) | −0.4802(3) | 0.2735(3) |
| C(16) | 0.3302(3) | 0.3124(3) | −0.0455(2) | C(64) | −0.1198(3) | −0.4173(3) | 0.2274(3) |
| C(21) | 0.1877(3) | 0.1811(3) | 0.4074(3) | C(65) | −0.1521(3) | −0.2954(3) | 0.1784(3) |
| C(22) | 0.0954(3) | 0.1916(3) | 0.4736(3) | C(66) | −0.0806(3) | −0.2363(3) | 0.1755(3) |

1.581(6) Å. For conformation **6b** the ring bonds adjacent to the $NP(OPh)_3$ phosphorus atom are the longest and have a mean value of 1.591(6) Å; N(5)–P(5) and N(6)–P(7) have an average length of 1.570(7) Å; P(5)–N(7) and N(7)–P(7) have an average distance of 1.578(6) Å. The average ring N–P–N bond angles for **6a** and **6b** are very similar, 117.3(3) and 117.5(3)°, respectively. For both molecules the smallest N–P–N angle is at the phosphorus atoms P(3) and P(6) [$NP(OPh)_3$ sites] and has a value of approximately 115°.

The exocyclic P–N bond which connects the $NP(OPh)_3$ group to the phosphazene ring has a length of 1.596(5) Å for both conformations. The $N{=}P(OPh)_3$ bond lengths, P(4)–N(4) for **6a** and P(8)–N(8) for **6b**, were also similar at 1.525(5) Å and 1.520(5) Å respectively.

A comparison of the molecular structures of **6a** and **6b** shows that the molecules differ in several conformational features of the phenoxy substituents relative to the phosphazene ring. For example, at the ring phosphorus atom P(1) in **6a**, the phenoxy group attached through O(1) differs from the one attached to P(5) through O(9) in **6b** by rotation about O(1)–C(11). Similarly, the phenoxy units attached to P(2) in **6a** have different orientations compared to the groups attached to P(7) in **6b**. The differences involve rotation around P(2)–O(3)–C(31) and P(2)–O(4)–C(41). In addition, the orientation of the substituent attached to P(4) through O(8) on the $NP(OPh)_3$ unit differs from that at P(8) by rotation about the P(4)–O(8)–C(81) bond in **6a**. Another conformational difference is the greater amount of twisting of the cyclic ring of **6b** compared to **6a**.

$N_3P_3(NHPr)_5NP(NHPr)_3{\cdot}HCl$ **7**. Trimer **7** contains a six-membered ring of alternating phosphorus and nitrogen atoms. Two of the ring phosphorus atoms, P(2) and P(3), bear two propylamino side groups each, while the remaining phosphorus, P(1), bears a propylamino group and a $NP(NHPr)_3$ unit. In addition, a molecule of hydrogen chloride is associated with the compound (Fig. 4).

Replacement of the chlorine atoms with propylamino groups allows an examination of the effects of less sterically hindered, electron-donating side groups on the phosphazene ring. The

**Table 7** Atomic coordinates for $N_3P_3(OPh)_4[NP(OPh)_3]_2$ **5** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| P(1) | 0.2540(2) | 0.0026(3) | 0.9974(2) |
| P(2) | 0.3199(2) | −0.0123(3) | 1.1365(2) |
| P(3) | 0.4018(2) | −0.0300(3) | 1.0702(2) |
| P(4) | 0.1255(3) | −0.1119(4) | 0.9296(2) |
| P(5) | 0.1883(3) | 0.1556(4) | 0.8953(2) |
| N(1) | 0.2525(7) | 0.0018(11) | 1.0687(6) |
| N(2) | 0.3951(7) | −0.0290(9) | 1.1375(6) |
| N(3) | 0.3313(6) | −0.0154(10) | 1.0021(6) |
| N(4) | 0.2032(7) | −0.0809(10) | 0.9502(6) |
| N(5) | 0.2260(7) | 0.1093(9) | 0.9644(6) |
| O(1) | 0.3293(6) | 0.0738(8) | 1.1894(5) |
| O(2) | 0.3010(6) | −0.0985(8) | 1.1727(5) |
| O(3) | 0.4586(6) | 0.0479(8) | 1.0709(5) |
| O(4) | 0.4440(6) | −0.1265(8) | 1.0686(6) |
| O(5) | 0.1050(6) | −0.2085(9) | 0.8871(5) |
| O(6) | 0.1008(7) | −0.1409(9) | 0.9843(6) |
| O(7) | 0.0690(6) | −0.0323(8) | 0.8903(5) |
| O(8) | 0.1100(6) | 0.2009(9) | 0.8747(6) |
| O(9) | 0.1734(6) | 0.0832(8) | 0.8360(5) |
| O(10) | 0.2264(6) | 0.2447(8) | 0.8820(5) |
| C(11) | 0.3439(5) | 0.1692(6) | 1.1823(5) |
| C(12) | 0.3341(5) | 0.2127(6) | 1.1227(5) |
| C(13) | 0.3519(5) | 0.3108(6) | 1.1218(5) |
| C(14) | 0.3796(5) | 0.3654(6) | 1.1805(5) |
| C(15) | 0.3895(5) | 0.3219(6) | 1.2402(5) |
| C(16) | 0.3716(5) | 0.2238(6) | 1.2411(5) |
| C(21) | 0.3340(5) | −0.1234(7) | 1.2375(4) |
| C(22) | 0.2896(5) | −0.1389(7) | 1.2680(4) |
| C(23) | 0.3193(5) | −0.1676(7) | 1.3346(4) |
| C(24) | 0.3934(5) | −0.1808(7) | 1.3709(4) |
| C(25) | 0.4379(5) | −0.1653(7) | 1.3405(4) |
| C(26) | 0.4082(5) | −0.1367(7) | 1.2738(4) |
| C(31) | 0.5283(5) | 0.0578(6) | 1.1190(5) |
| C(32) | 0.5446(5) | 0.0959(6) | 1.1818(5) |
| C(33) | 0.6161(5) | 0.1128(6) | 1.2277(5) |
| C(34) | 0.6712(5) | 0.0916(6) | 1.2108(5) |
| C(35) | 0.6550(5) | 0.0535(6) | 1.1481(5) |
| C(36) | 0.5835(5) | 0.0366(6) | 1.1021(5) |
| C(41) | 0.4135(6) | −0.2157(7) | 1.0634(6) |
| C(42) | 0.4418(6) | −0.2772(7) | 1.1188(6) |
| C(43) | 0.4151(6) | −0.3719(7) | 1.1141(6) |
| C(44) | 0.3601(6) | −0.4051(7) | 1.0540(6) |
| C(45) | 0.3319(6) | −0.3436(7) | 0.9985(6) |
| C(46) | 0.3586(6) | −0.2489(7) | 1.0032(6) |
| C(51) | 0.1164(5) | −0.2255(8) | 0.8313(4) |
| C(52) | 0.1143(5) | −0.3227(8) | 0.8116(4) |
| C(53) | 0.1207(5) | −0.3450(8) | 0.7540(4) |
| C(54) | 0.1291(5) | −0.2701(8) | 0.7160(4) |
| C(55) | 0.1312(5) | −0.1729(8) | 0.7357(4) |
| C(56) | 0.1248(5) | −0.1507(8) | 0.7933(4) |
| C(61) | 0.1241(7) | −0.2214(7) | 1.0259(5) |
| C(62) | 0.0709(7) | −0.2690(7) | 1.0363(5) |
| C(63) | 0.0883(7) | −0.3510(7) | 1.0776(5) |
| C(64) | 0.1590(7) | −0.3853(7) | 1.1085(5) |
| C(65) | 0.2122(7) | −0.3377(7) | 1.0980(5) |
| C(66) | 0.1947(7) | −0.2557(7) | 1.0567(5) |
| C(71) | −0.0048(5) | −0.0427(8) | 0.8649(5) |
| C(72) | −0.0376(5) | −0.0036(8) | 0.9016(5) |
| C(73) | −0.1119(5) | −0.0118(8) | 0.8779(5) |
| C(74) | −0.1553(5) | −0.0591(8) | 0.8175(5) |
| C(75) | −0.1205(5) | −0.0982(8) | 0.7809(5) |
| C(76) | −0.0462(5) | −0.0900(8) | 0.8046(5) |
| C(81) | 0.1019(6) | 0.2911(7) | 0.8972(6) |
| C(82) | 0.0520(6) | 0.3550(7) | 0.8512(6) |
| C(83) | 0.0430(6) | 0.4485(7) | 0.8710(6) |
| C(84) | 0.0840(6) | 0.4780(7) | 0.9370(6) |
| C(85) | 0.1339(6) | 0.4141(7) | 0.9831(6) |
| C(86) | 0.1429(6) | 0.3206(7) | 0.9632(6) |
| C(91) | 0.1476(6) | 0.1110(7) | 0.7702(4) |
| C(92) | 0.0741(6) | 0.1192(7) | 0.7281(4) |
| C(93) | 0.0500(6) | 0.1446(7) | 0.6613(4) |
| C(94) | 0.0996(6) | 0.1618(7) | 0.6367(4) |
| C(95) | 0.1731(6) | 0.1536(7) | 0.6788(4) |
| C(96) | 0.1971(6) | 0.1282(7) | 0.7456(4) |
| C(101) | 0.2966(5) | 0.2754(8) | 0.9142(5) |
| C(102) | 0.3081(5) | 0.3744(8) | 0.9076(5) |
| C(103) | 0.3781(5) | 0.4110(8) | 0.9337(5) |
| C(104) | 0.4365(5) | 0.3485(8) | 0.9664(5) |
| C(105) | 0.4251(5) | 0.2495(8) | 0.9730(5) |
| C(106) | 0.3551(5) | 0.2129(8) | 0.9469(5) |

presence of electron-supplying substituents enhances the basicity of the ring nitrogens.[27] Previous work has shown that the basicity of the ring may be higher than that of the parent amine.[22,31,32] This appears to be true for trimer **7** as well. The position of the chlorine atom from HCl is depicted in Fig. 4. The nearest ring nitrogen atom is N(3). Propylamino nitrogen atom N(11) is the nearest acyclic nitrogen to that chlorine atom.

The bonds P(1)–N(3) [1.686(9) Å] and P(3)–N(3) [1.676(8) Å] are lengthened considerably compared to the other endocyclic bonds. For example, P(1)–N(1) and P(3)–N(2) are significantly shorter, with bond lengths of 1.582(9) and 1.579(9) Å, respectively. The increased bond distances adjacent to N(3) are evidence for the protonation of this ring nitrogen atom. Similar endocyclic P–N bond distances exist adjacent to the protonated ring nitrogen in the cyclic trimer $N_3P_3Cl_2(NHPr^i)_4{\cdot}HCl$.[32] Further evidence of ring protonation can be obtained by examining the $^{31}P$ NMR spectrum of trimer **7**. At 20 °C, there are three phosphorus environments [Fig. 5(*a*)]: a doublet at approximately $\delta$ 12 corresponding to the $NP(NHPr)_3$ phosphorus atom, a multiplet at $\delta$ −1.3 corresponding to the branch point phosphorus atom and a broad peak at $\delta$ 14 corresponding to the remaining two ring phosphorus atoms. At this temperature, P(2) and P(3) are roughly equivalent, possibly due to a rapid proton exchange between the two equivalent nitrogen atoms. Fig. 5(*b*) depicts the same sample when the temperature is lowered to −60 °C. At lower temperatures the intermolecular proton exchange would be much slower, leading to the inequivalence of P(2) and P(3) observed in the spectrum. Similar $^{31}P$ NMR results were observed for the HCl adduct of *gem*-$N_3P_3(NMe_2)_4(NPPh_3)_2$.[33]

The exocyclic P–N bonds which join the propylamino groups to the phosphazene ring have a mean distance of 1.649(23) Å. The P(4)–N(10–12) bonds have an average length of 1.658(16) Å. Both exocyclic P–N bonds associated with the $NP(NHPr)_3$ group are significantly shorter than the P–N bonds at the propylamino groups. The P–N bond which joins the $NP(NHPr)_3$ group to the ring, P(1)–N(4), is 1.589(9) Å; the P(4)–N(4) bond is 1.572(8) Å. Unlike trimers **4**–**6**, the exocyclic P–N–P bonds are not significantly different in length. The increase in the P(4)–N(4) bond length is presumably due to the presence of three electron-donating propylamino substituents which would supply electron density to the bond and would increase the bond distance.

The endocyclic bond angle at P(1) [$NP(NHPr)_3$ site] is the narrowest of the four trimers examined [108.9(4)°]. The angle at P(3) is also narrowed [109.7(5)°]. The angle at P(2) is significantly wider than the other endocyclic N–P–N bonds of trimer **7**, with an angle of 117.7(5)°. In contrast, the endocyclic P–N–P bond angles show significant widening. The angles at N(1) and N(2) are 126.9(5) and 125.7(6)°, respectively. The angle at N(3) is even greater, with a value of 129.5(6)°. The increases in these angles may be related to the alleviation of ring strain.

The $NP(NHPr)_3$ group is oriented in a position that is more parallel to the ring than the units in trimers **4**–**6**. The angle P(1)–N(4)–P(4) is 137.4(6)°.

**Table 8** Atomic coordinates for $N_3P_3(OPh)_5NP(OPh)_3$ **6** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| P(1) | 0.2303(1) | 0.9004(1) | 0.8717(1) | C(63) | −0.0039(2) | 0.6060(1) | 0.8971(3) |
| P(2) | 0.2841(1) | 0.9498(1) | 1.1183(1) | C(64) | 0.0623(2) | 0.6324(1) | 0.9690(3) |
| P(3) | 0.1557(1) | 0.8693(1) | 1.0698(1) | C(65) | 0.0990(2) | 0.6848(1) | 0.9421(3) |
| P(4) | 0.1777(1) | 0.7561(1) | 1.1302(1) | C(66) | 0.0697(2) | 0.7108(1) | 0.8433(3) |
| P(5) | 0.2670(1) | 0.4111(1) | 0.2797(1) | C(71) | −0.0100(2) | 0.7364(2) | 1.4030(3) |
| P(6) | 0.2099(1) | 0.3667(1) | 0.4802(1) | C(72) | 0.0210(2) | 0.7722(2) | 1.5173(3) |
| P(7) | 0.3225(1) | 0.4610(1) | 0.5239(1) | C(73) | 0.0964(2) | 0.7917(2) | 1.5378(3) |
| P(8) | 0.2452(1) | 0.2542(1) | 0.5310(2) | C(74) | 0.1408(2) | 0.7754(2) | 1.4440(3) |
| N(1) | 0.2895(2) | 0.9440(2) | 0.9702(4) | C(75) | 0.1099(2) | 0.7396(2) | 1.3297(3) |
| N(2) | 0.2158(2) | 0.9150(2) | 1.1636(4) | C(76) | 0.0345(2) | 0.7200(2) | 1.3092(2) |
| N(3) | 0.1709(2) | 0.8589(2) | 0.9247(4) | C(81) | 0.3440(2) | 0.7300(1) | 1.2963(3) |
| N(4) | 0.1381(2) | 0.8094(2) | 1.1248(4) | C(82) | 0.3854(2) | 0.7373(1) | 1.4151(3) |
| N(5) | 0.2212(2) | 0.3602(2) | 0.3331(4) | C(83) | 0.3881(2) | 0.7890(1) | 1.5022(3) |
| N(6) | 0.2675(2) | 0.4146(2) | 0.5742(4) | C(84) | 0.3495(2) | 0.8334(1) | 1.4705(3) |
| N(7) | 0.3128(2) | 0.4643(2) | 0.3771(4) | C(85) | 0.3081(2) | 0.8261(1) | 1.3517(3) |
| N(8) | 0.2010(3) | 0.3048(2) | 0.5293(4) | C(86) | 0.3054(2) | 0.7744(1) | 1.2646(3) |
| O(1) | 0.1882(2) | 0.9344(2) | 0.7775(3) | C(91) | −0.2304(2) | 0.5150(1) | 0.8653(3) |
| O(2) | 0.2708(2) | 0.8623(2) | 0.7711(3) | C(92) | −0.2670(2) | 0.5149(1) | 0.9738(3) |
| O(3) | 0.2946(2) | 1.0172(2) | 1.1811(3) | C(93) | −0.2814(2) | 0.4631(1) | 1.0244(3) |
| O(4) | 0.3530(2) | 0.9305(2) | 1.1918(4) | C(94) | −0.2592(2) | 0.4114(1) | 0.9666(3) |
| O(5) | 0.0797(2) | 0.8948(2) | 1.0645(3) | C(95) | −0.2226(2) | 0.4115(1) | 0.8582(3) |
| O(6) | 0.1671(2) | 0.7082(2) | 1.0074(3) | C(96) | −0.2082(2) | 0.4633(1) | 0.8075(3) |
| O(7) | 0.1533(2) | 0.7214(2) | 1.2378(3) | C(101) | −0.3810(2) | 0.6355(2) | 0.7722(3) |
| O(8) | 0.2636(2) | 0.7653(2) | 1.1483(3) | C(102) | −0.4477(2) | 0.5978(2) | 0.7559(3) |
| O(9) | 0.2122(2) | 0.4341(2) | 0.1825(3) | C(103) | −0.5121(2) | 0.6172(2) | 0.7120(3) |
| O(10) | 0.3183(2) | 0.3844(2) | 0.1808(3) | C(104) | −0.5098(2) | 0.6743(2) | 0.6845(3) |
| O(11) | 0.1298(2) | 0.3859(2) | 0.4847(3) | C(105) | −0.4431(2) | 0.7119(2) | 0.7008(3) |
| O(12) | 0.3249(2) | 0.5248(2) | 0.6037(4) | C(106) | −0.3787(2) | 0.6926(2) | 0.7446(3) |
| O(13) | 0.4051(2) | 0.4532(2) | 0.5577(4) | C(111) | −0.0980(2) | 0.5942(1) | 1.4097(3) |
| O(14) | 0.3301(2) | 0.2736(2) | 0.5545(4) | C(112) | −0.1252(2) | 0.5973(1) | 1.2851(3) |
| O(15) | 0.2371(2) | 0.2068(2) | 0.4074(4) | C(113) | −0.0891(2) | 0.5754(1) | 1.1833(3) |
| O(16) | 0.2233(2) | 0.2156(2) | 0.6332(4) | C(114) | −0.0257(2) | 0.5503(1) | 1.2062(3) |
| C(11) | 0.2205(2) | 0.9685(1) | 0.6984(3) | C(115) | 0.0015(2) | 0.5472(1) | 1.3309(3) |
| C(12) | 0.2124(2) | 0.9468(1) | 0.5680(3) | C(116) | −0.0346(2) | 0.5691(1) | 1.4326(3) |
| C(13) | 0.2395(2) | 0.9824(1) | 0.4835(3) | C(121) | −0.2684(2) | 0.4425(1) | 0.4122(3) |
| C(14) | 0.2747(2) | 1.0397(1) | 0.5295(3) | C(122) | −0.2766(2) | 0.3986(1) | 0.4878(3) |
| C(15) | 0.2828(2) | 1.0614(1) | 0.6600(3) | C(123) | −0.2227(2) | 0.3625(1) | 0.4995(3) |
| C(16) | 0.2557(2) | 1.0258(1) | 0.7444(3) | C(124) | −0.1606(2) | 0.3703(1) | 0.4355(3) |
| C(21) | 0.3077(2) | 0.8187(1) | 0.8085(3) | C(125) | −0.1525(2) | 0.4142(1) | 0.3599(3) |
| C(22) | 0.2724(2) | 0.7604(1) | 0.7846(3) | C(126) | −0.2064(2) | 0.4504(1) | 0.3482(3) |
| C(23) | 0.3089(2) | 0.7157(1) | 0.8210(3) | C(131) | −0.4391(2) | 0.5576(2) | 0.3324(3) |
| C(24) | 0.3806(2) | 0.7291(1) | 0.8814(3) | C(132) | −0.5131(2) | 0.5634(2) | 0.3334(3) |
| C(25) | 0.4159(2) | 0.7874(1) | 0.9053(3) | C(133) | −0.5534(2) | 0.5735(2) | 0.2240(3) |
| C(26) | 0.3794(2) | 0.8321(1) | 0.8689(3) | C(134) | −0.5197(2) | 0.5779(2) | 0.1136(3) |
| C(31) | 0.2896(2) | 1.0632(2) | 1.1177(3) | C(135) | −0.4457(2) | 0.5721(2) | 0.1126(3) |
| C(32) | 0.3535(2) | 1.0970(2) | 1.0937(3) | C(136) | −0.4054(2) | 0.5620(2) | 0.2220(3) |
| C(33) | 0.3490(2) | 1.1463(2) | 1.0347(3) | C(141) | −0.3799(2) | 0.7573(2) | 0.3935(4) |
| C(34) | 0.2807(2) | 1.1618(2) | 0.9996(3) | C(142) | −0.4199(2) | 0.7309(2) | 0.2771(4) |
| C(35) | 0.2168(2) | 1.1281(2) | 1.0235(3) | C(143) | −0.4708(2) | 0.7603(2) | 0.2180(4) |
| C(36) | 0.2213(2) | 1.0788(2) | 1.0826(3) | C(144) | −0.4817(2) | 0.8161(2) | 0.2753(4) |
| C(41) | 0.4742(2) | 0.9553(2) | 1.1314(3) | C(145) | −0.4417(2) | 0.8425(2) | 0.3917(4) |
| C(42) | 0.5452(2) | 0.9862(2) | 1.1616(3) | C(146) | −0.3908(2) | 0.8131(2) | 0.4508(4) |
| C(43) | 0.5641(2) | 1.0249(2) | 1.2767(3) | C(151) | −0.1690(2) | 0.8214(1) | 0.6496(3) |
| C(44) | 0.5121(2) | 1.0328(2) | 1.3617(3) | C(152) | −0.1299(2) | 0.7968(1) | 0.7408(3) |
| C(45) | 0.4411(2) | 1.0018(2) | 1.3316(3) | C(153) | −0.0631(2) | 0.8270(1) | 0.8038(3) |
| C(46) | 0.4221(2) | 0.9631(2) | 1.2164(3) | C(154) | −0.0353(2) | 0.8819(1) | 0.7757(3) |
| C(51) | 0.0561(2) | 0.9028(1) | 1.2875(3) | C(155) | −0.0744(2) | 0.9066(1) | 0.6845(3) |
| C(52) | 0.0121(2) | 0.9219(1) | 1.3799(3) | C(156) | −0.1412(2) | 0.8763(1) | 0.6215(3) |
| C(53) | −0.0464(2) | 0.9510(1) | 1.3475(3) | C(161) | −0.1966(2) | 0.7627(1) | 0.2562(3) |
| C(54) | −0.0610(2) | 0.9510(1) | 1.2227(3) | C(162) | −0.1309(2) | 0.7929(1) | 0.2300(3) |
| C(55) | −0.0170(2) | 0.9419(1) | 1.1304(3) | C(163) | −0.1001(2) | 0.7731(1) | 0.1200(3) |
| C(56) | 0.0415(2) | 0.9128(1) | 1.1627(3) | C(164) | −0.1351(2) | 0.7230(1) | 0.0363(3) |
| C(61) | 0.0036(2) | 0.6844(1) | 0.7714(3) | C(165) | −0.2009(2) | 0.6928(1) | 0.0626(3) |
| C(62) | −0.0332(2) | 0.6320(1) | 0.7983(3) | C(166) | −0.2316(2) | 0.7127(1) | 0.1725(3) |

The molecular structures of trimers **4**–**7** share several similar features. (*i*) In general, the $N{=}PX_3$ distances were shorter than the N–P bonds that connect the units to the ring. The exocyclic P=N bonds, which ranged in length from 1.516(5) to 1.572(8) Å, were also generally shorter than the P–N bonds in the respective phosphazene rings. This provides some evidence of the multiple-bond character of the $N{=}PX_3$ bond. The exception is trimer **7**, in which the P(4)–N(4) and N(4)–P(1) bond lengths are not significantly different. Also, two of the phosphazene ring bond lengths, P(1)–N(1) and N(2)–P(3), were similar to the lengths in the $NPX_3$ unit. This result is due to the increased length of the $N{=}PX_3$ bond in **7**. (*ii*) The endocyclic angle at the

**Table 9** Atomic coordinates for $N_3P_3(NHPr)_5NP(NHPr)_3{\cdot}HCl$ **7** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| P(1) | 0.4454(3) | 0.0867(3) | 0.2896(2) |
| P(2) | 0.1674(3) | −0.0069(3) | 0.1727(2) |
| P(3) | 0.2676(3) | −0.0319(3) | 0.0383(2) |
| P(4) | 0.6624(3) | 0.0908(3) | 0.4799(2) |
| N(1) | 0.3109(8) | 0.0526(8) | 0.2826(6) |
| N(2) | 0.1559(9) | −0.0352(8) | 0.0555(7) |
| N(3) | 0.4113(8) | 0.0317(8) | 0.1615(7) |
| N(4) | 0.5271(8) | 0.0403(8) | 0.3667(7) |
| N(5) | 0.5398(9) | 0.2243(8) | 0.3367(8) |
| N(6) | 0.0793(9) | −0.1219(9) | 0.1902(8) |
| N(7) | 0.097(1) | 0.0675(9) | 0.1635(8) |
| N(8) | 0.225(1) | −0.1598(9) | −0.0264(8) |
| N(9) | 0.295(1) | 0.033(1) | −0.0452(8) |
| N(10) | 0.6780(8) | 0.1465(7) | 0.5965(7) |
| N(11) | 0.7805(9) | 0.1937(8) | 0.4730(7) |
| N(12) | 0.6858(9) | −0.0137(9) | 0.5037(7) |
| C(51) | 0.487(1) | 0.294(1) | 0.291(1) |
| C(52) | 0.561(2) | 0.403(2) | 0.390(2) |
| C(53) | 0.523(2) | 0.482(2) | 0.351(2) |
| C(61) | −0.060(1) | −0.192(1) | 0.117(1) |
| C(62) | −0.112(2) | −0.299(2) | 0.073(2) |
| C(63) | −0.247(2) | −0.379(2) | 0.004(2) |
| C(71) | 0.074(1) | 0.099(1) | 0.251(1) |
| C(72) | 0.131(2) | 0.223(2) | 0.287(1) |
| C(73) | 0.107(2) | 0.262(2) | 0.368(2) |
| C(81) | 0.184(2) | −0.254(1) | 0.010(1) |
| C(82) | 0.074(2) | −0.362(2) | −0.076(2) |
| C(83) | 0.081(2) | −0.401(2) | −0.159(2) |
| C(91) | 0.361(1) | 0.155(1) | −0.015(1) |
| C(92) | 0.476(2) | 0.198(1) | −0.026(2) |
| C(93) | 0.529(2) | 0.320(2) | −0.007(2) |
| C(101) | 0.665(1) | 0.246(1) | 0.610(1) |
| C(102) | 0.710(1) | 0.297(1) | 0.730(1) |
| C(103) | 0.688(2) | 0.396(1) | 0.744(1) |
| C(111) | 0.922(1) | 0.252(1) | 0.565(1) |
| C(112) | 0.990(1) | 0.369(1) | 0.563(1) |
| C(113) | 1.135(2) | 0.439(2) | 0.646(2) |
| C(121) | 0.667(1) | −0.099(1) | 0.416(1) |
| C(122) | 0.803(2) | −0.060(2) | 0.430(1) |
| C(123) | 0.783(2) | −0.164(2) | 0.346(1) |
| Cl | 0.2872(4) | 0.8548(4) | 0.7760(3) |

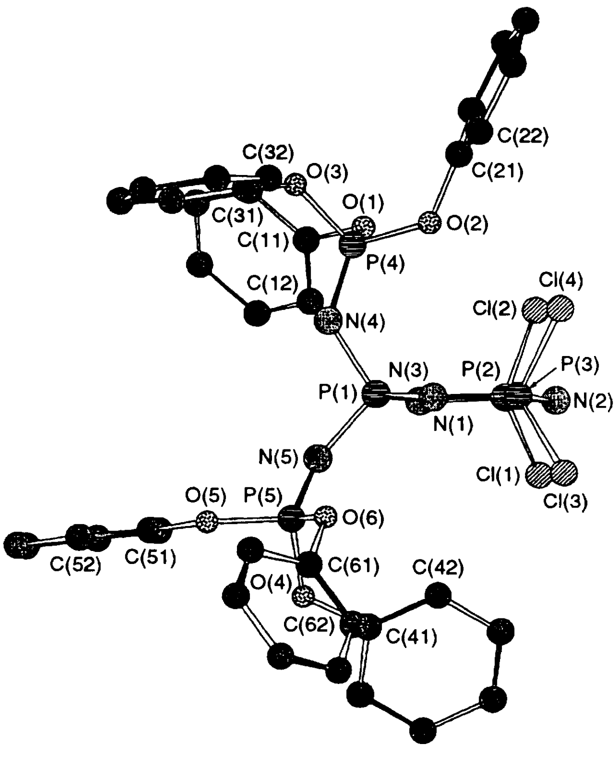


**Fig. 1** Molecular structure of *gem*-$N_3P_3Cl_4[NP(OPh)_3]_2$ **4**

$NPX_3$-bearing phosphorus in trimers **4**–**7** ranged from 108.9(4) to 115.9(2)°. These angles are significantly narrowed from the ideal angle of 120° or the average N–P–N angle of 118.4(2)° in $N_3P_3Cl_6$.[34]

*Comparison with* (*Triphenylphosphoranylidene*)*aminophosphazenes.*—As stated earlier, the structures of several cyclic (triphenylphosphoranylidene)aminophosphazenes have been determined by X-ray crystallography. The exocyclic P–N bond lengths and the dihedral angles of five such trimers and compounds **4**–**7** are listed in Table 10. The conformations of the $NPR_3$ unit, indicated by the dihedral angles, vary widely. For example, in $N_3P_3Cl_4PhNPPh_3$ and trimer **7** (dihedral angle −178 and 9°, respectively) the N–P component of the $NPX_3$ substituent is approximately perpendicular to the local ring N–P–N segment. In contrast, in $N_3P_3Cl_5NPPh_3$ (dihedral angle −83°) the $NPPh_3$ group projects parallel to the local N–P–N segment.

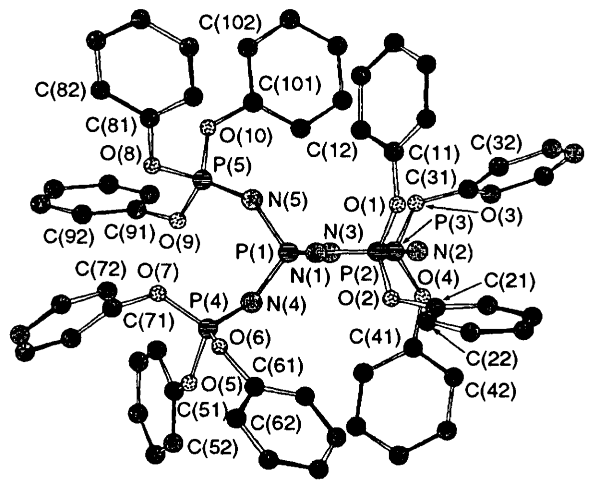


**Fig. 2** Molecular structure of *gem*-$N_3P_3(OPh)_4[NP(OPh)_3]_2$ **5**

The range of values for the $P_{ring}$–$NPX_3$ bond lengths is not significantly different when the $NPX_3$ unit bears phenyl substituents rather than phenoxy or propylamino units. In general, the N=$PX_3$ bond length is somewhat longer when X = Ph. For three of the trimers bearing triphenyl substituents [$N_3P_3Cl_5NPPh_3$, $N_3P_3Cl_4PhNPPh_3$ and $N_3P_3Cl_4(NEt_2)$-$NPPh_3$] the two exocyclic bonds lengths are not significantly different. This is indicative of electron delocalization along the acyclic P–N=P segment.[16,18,19] Of trimers **4**–**7**, only trimer **7**, with electron-donating propylamino substituents, was similar.

*Significance of the Structures.*—The purpose of this work was to examine the effect of the $NPX_3$ substituents on the molecular structures of cyclic trimeric phosphazenes and to extend the conclusions to the macromolecular level in order to aid in the understanding and prediction of polymer properties.

*Trimers* **4** *and* **5**. Partial or full replacement of the chlorine atoms in $N_3P_3Cl_4(NPCl_3)_2$ can be accomplished under relatively mild conditions with the use of sodium phenoxide as a nucleophile.[25] The molecular structure of trimer **4** confirms that the exocyclic chlorine atoms are substituted in preference to the ring phosphorus–chlorine units. The polymer [N=$PCl_2$–

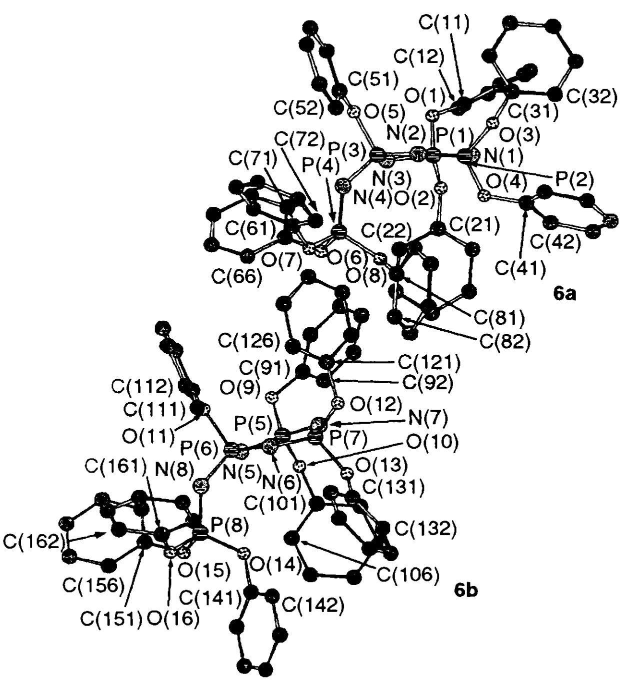


**Fig. 3** Molecular structure of $N_3P_3(OPh)_5NP(OPh)_3$ **6**, two conformations

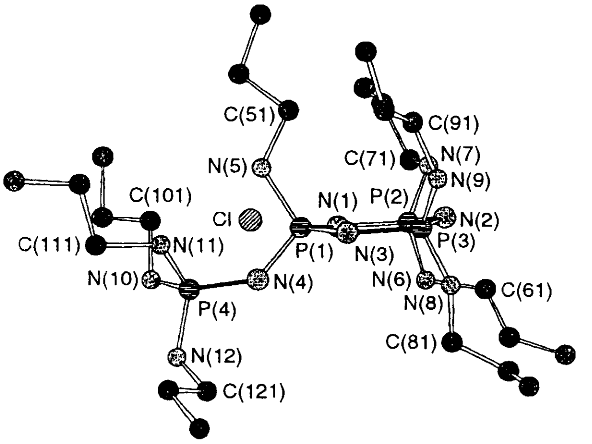


**Fig. 4** Molecular structure of $N_3P_3(NHPr)_5NP(NHPr)_3{\cdot}HCl$ **7**

$N{=}P(NPCl_3)_2{-}N{=}PCl_2]_n$ reacts in a similar manner with sodium phenoxide to replace the $NPCl_3$ chlorine atoms first.[25] Polymers of type 1 contained $NP(OR)_3$ units with $PCl_2$ groups remaining along the polymer backbone. As seen in Fig. 1, the $NP(OPh)_3$ units are rather bulky, but they are not exceptionally close to the remaining chlorine atoms. In the cyclic trimer, the side groups on different phosphorus atoms point away from each other and minimize steric effects. By contrast, despite the possibility of extended conformations assumed by the high polymer, the side groups would be closer to each other or oriented toward the nearby skeletal atoms. Thus, in the polymer, bulky substituent groups already present would exert a powerful shielding effect on the nearby P–Cl bonds. This shielding effect is probably responsible for the hydrolytic stability of the $NPX_3$-bearing polymers of structure type 1, which contain PCl units that might be expected to be quite reactive to water.[25]

Unlike the model trimer **5**, it was found that full chlorine replacement of the di(phosphoranylidene)aminophosphazene polymer with phenoxide or other bulky nucleophiles was difficult.[25] Poly[bis{(phosphoranylidene)amino}phosphazene] appears to be more sensitive to side group steric effects than are the cyclic trimers, due mainly to the differences in conformation, as stated earlier. Fig. 2 illustrates the increase in steric crowding near the phosphazene ring as the number of phenoxy groups increases. This crowding would most likely be more serious at the linear high polymer level. Thus, complete substitution of poly[bis{(phosphoranylidene)amino}phosphazene] under the given reaction conditions is difficult.

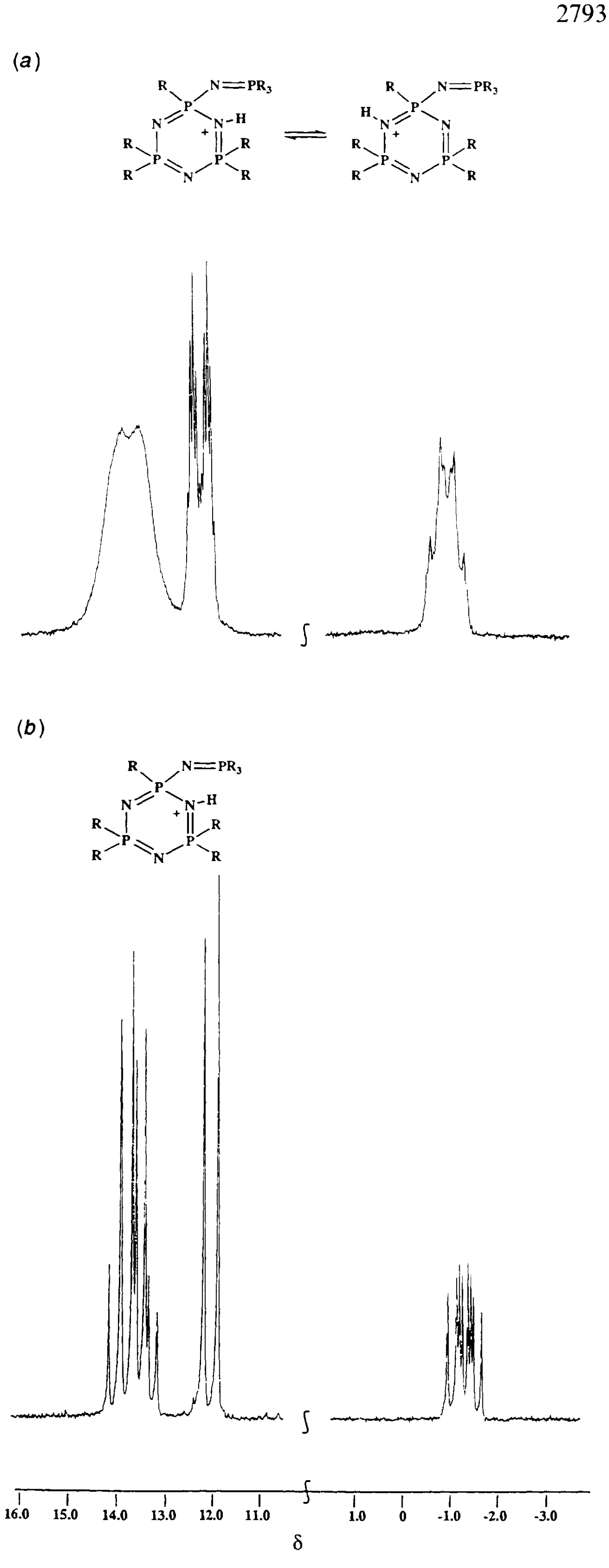


**Fig. 5** Variable-temperature $^{31}P$ NMR spectra of trimer **7** in $CD_3OD$ at (*a*) 20 and (*b*) −60 °C

*Trimers* **6** *and* **7**. Complete replacement of the chlorine atoms

**Table 10** Comparison of exocyclic P–N bond distances (Å) and dihedral angles (°) of compounds **4**–**7** and related compounds

| | | Exocyclic bonds/Å | | |
|---|---|---|---|---|
| Trimer | Ref. | $P_{ring}$–N | N=$PR_3$ | Dihedral angle/°* |
| **4** *gem*-$N_3P_3Cl_4[NP(OPh)_3]_2$ | This work | 1.616(5) | 1.533(5) | −163 |
| | | 1.596(5) | 1.516(5) | −113 |
| **5** *gem*-$N_3P_3(OPh)_4[NP(OPh)_3]_2$ | This work | 1.591(13) | 1.530(15) | −69 |
| | | 1.621(13) | 1.527(13) | −32 |
| **6** $N_3P_3(OPh)_5NP(OPh)_3$ | This work | 1.596(5) | 1.525(5) | 165 |
| | | 1.596(5) | 1.520(5) | 167 |
| **7** $N_3P_3(NHPr)_5NP(NHPr)_3$ | This work | 1.589(9) | 1.572(8) | 9 |
| *gem*-$N_3P_3Cl_4(NPPh_3)_2$ | 17 | 1.602(7) | 1.558(7) | 7 |
| | | 1.599(7) | 1.559(7) | −177 |
| $N_3P_3Cl_5NPPh_3$ | 16,19 | 1.614(9) | 1.597(9) | −83 |
| $N_3P_3(NC_2H_2)_5NPPh_3$ | 35 | 1.590(3) | 1.557(3) | 15 |
| *gem*-$N_3P_3Cl_4PhNPPh_3$ | 18,19 | 1.585(6) | 1.576(6) | −178 |
| *gem*-$N_3P_3Cl_4(NEt_2)NPPh_3$ | 19 | 1.585(12) | 1.563(12) | 154 |

* Conformation of the –N=$PR_3$ unit with respect to the phosphazene ring.

in $N_3P_3Cl_5NPCl_3$ can be achieved under relatively mild reaction conditions with the use of sodium phenoxide or propylamine. The molecular structures of the cyclic trimers **6** and **7** confirm the total replacement of the chlorine atoms.

Compared to trimer **5**, fully-substituted trimer **6** is less bulky. However, as shown in Fig. 3, significant steric crowding still exists around the phosphazene ring. High polymers of structure type 2 contained $[NP(OPh)_3](OPh)$ and $(OPh)_2$ units along the backbone as well as some residual chlorine. It was postulated that the residual chlorine was geminal to the $NP(OPh)_3$ unit.[26] This position would allow the $NP(OPh)_3$ group to shield the chlorine and would account for the hydrolytic stability of this polymer.

The molecular structure of trimer **7** confirmed its co-ordination to HCl. Fig. 4 indicates that much less steric hindrance exists about the phosphazene ring compared to trimer **6**. Thus, it is believed that the chlorine atoms in $[N{=}PCl_2{-}N{=}PCl(NPCl_3){-}N{=}PCl_2]_n$ can be completely replaced by propylamine, but that HCl may co-ordinate to the polymer chain. From all of these results, it appears that the steric bulk of the nucleophile and of the groups linked to the polymer chain is a major factor in determining the degree of chlorine substitution as the reaction proceeds.

## Experimental

*Materials.*—Hexachlorocyclotriphosphazene **1** was supplied by Ethyl Corp. and was purified by one recrystallization from heptane and two vacuum sublimations at 0.05 Torr ($\approx$6.66 Pa). Phenol (Aldrich) was purified by vacuum sublimation before use. Sodium (Aldrich), sodium hydride (60% dispersion in mineral oil, Aldrich), phosphorus pentachloride (Aldrich) and ammonia (anhydrous, Liquid Carbonic) were used as received. Propylamine was distilled from barium oxide and stored over 4 Å molecular sieves in the dark. 1,4-Dioxane (anhydrous, Aldrich) was distilled into the reaction flask from sodium–benzophenone in an atmosphere of dry argon or nitrogen. Heptane and triethylamine (Baker) were dried and distilled from $CaH_2$ into the reaction flask in an atmosphere of dry argon or nitrogen. All glassware was dried overnight in an oven or flame dried under vacuum before use. All reactions were performed using standard Schlenk techniques utilizing an atmosphere of dry argon.

*Equipment.*—The $^{31}P$ NMR spectra were recorded on a JEOL FX90Q spectrometer operated at 36.2 MHz or a Bruker WM-360 instrument at 146 MHz; chemical shifts are relative to 85% phosphoric acid as an external reference with positive shift values downfield from the reference. The $^{1}H$ and $^{13}C$ NMR spectra were recorded with a Bruker WM-360 spectrometer operated at 360 or 90.27 MHz respectively; spectra were referenced to internal $CDCl_3$ or $(CD_3)_2CO$. Elemental microanalyses were obtained from Galbraith Laboratories, Knoxville, TN. X-Ray data were collected with the use of an Enraf-Nonius CAD4 diffractometer using CAD4PC software on a Macintosh computer.

*Synthesis of Cyclic Trimers.*—$N_3P_3Cl_4(NPCl_3)_2$ **2** *and* $N_3P_3Cl_5NPCl_3$ **3**. Trimers **2** and **3** were prepared by standard literature procedures.[36] Typical yields for these and the following compounds were 65–75%.

$N_3P_3Cl_4[NP(OPh)_3]_2$ **4**. The synthesis of trimer **4** has been reported previously.[25] Trimer **2** (2.0 g, 3.4 mmol) was dissolved in dioxane (50 $cm^3$). Sodium phenoxide (21.0 mmol) in dioxane (75 $cm^3$) was then added dropwise to the trimer solution. The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered through Fuller's earth, and the filtrate was concentrated by rotary evaporation to yield a yellow oil. The crude product was purified by column chromatography using a silica gel column, with a mixture of hexane and methylene chloride (1 : 1) as the eluent. The purified product was obtained as colourless crystals.

$N_3P_3(OPh)_4[NP(OPh)_3]_2$ **5**. The synthesis of trimer **5** has been reported previously.[25] Trimer **2** (2.0 g, 3.4 mmol) was dissolved in dioxane (50 $cm^3$). This solution was added dropwise to a solution of sodium phenoxide (100 mmol) in dioxane and the reaction mixture was refluxed for 5 d. The mixture was then filtered through Fuller's earth and the solvent was removed by rotary evaporation. The crude product was redissolved in diethyl ether and extracted with 10% NaOH solution. The ethereal layer was collected and dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was purified by column chromatography on silica gel with methylene chloride as the eluent. The product was isolated as a white solid.

$N_3P_3(OPh)_5NP(OPh)_3$ **6**. The synthesis of trimer **6** has been reported previously.[26] Trimer $N_3P_3Cl_5NPCl_3$ **3** (2.0 g, 4.3 mmol) in freshly distilled dioxane (50 $cm^3$) was added dropwise to a solution of sodium phenoxide (1.7 g, 43 mmol NaH; 3.9 g, 41 mmol phenol) in dioxane (150 $cm^3$). The reaction mixture was heated to reflux for 48 h. The product was isolated by filtration through Fuller's earth and was concentrated by rotary evaporation. The product was dissolved in diethyl ether (250 $cm^3$) and was washed with 10% NaOH (3 × 100 $cm^3$), dried over $MgSO_4$, and concentrated by rotary evaporation to yield a brown oil. Final purification was by column chromatography through silica gel using hexane and methylene chloride (1 : 9) as eluents to yield a clear, slightly yellow oil from which colourless crystals were obtained.

$N_3P_3(NHPr)_5NP(NHPr)_3{\cdot}HCl$ **7**. The synthesis of trimer **7** has been reported previously.[26] Trimer **3** (4.5 g, 9.7 mmol) in toluene (100 $cm^3$) was added dropwise to a solution of propylamine (13.7 g, 232 mmol) in toluene (150 $cm^3$). The reaction mixture was heated to reflux for 3 d. The precipitated salts were then removed by centrifugation. The supernatant liquid was decanted and concentrated to obtain a yellow oil. The oil was purified by column chromatography using alumina as the stationary phase and methanol as the eluent. The clear, colourless oil crystallized on standing to form clear, colourless crystals.

*Crystal Structure Determinations.*—Unit-cell parameters were determined using an Enraf-Nonius CAD4 diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\lambda$ = 0.710 73 Å) by a least-squares refinement of the setting angles of 25 reflections with $\theta$ in the range 10–15°. Intensity data were collected by the $\omega$–2$\theta$ scan method in the range $2 < \theta < 25°$, with $\omega$ scan width = $1.00 + 0.35 \tan \theta$. The intensities of three reflections, chosen as standards, were monitored at regular intervals over the course of the data collection; any decay was corrected for by appropriate scaling. Data were corrected for Lorentz and polarization factors and for empirical absorption.

The structures were solved by direct methods.[37] Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters for the non-hydrogen atoms, and with hydrogens in calculated positions. Programs and computers used in this study are described in ref. 38 Additional refinements for the structures were performed using the MULTAN 80 refinement package.

Crystals of trimer **4** were grown from methylene chloride–hexane and were clear and colourless. A difference map calculated at the conclusion of this refinement, and those of the other structures, had no chemically significant features. Crystals of trimers **5** and **6** were grown from methylene chloride–hexane and were clear and colourless. The crystal density of **6** was determined by buoyancy (hexane–$CCl_4$). Crystals of trimer **7** were grown from methanol–hexane and were clear and colourless. The crystal density was determined by buoyancy (hexane–$CCl_4$).

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

## Acknowledgements

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