# Cycloalkylaminocyclo- and Polyphosphazenes: X-ray Crystal Structures of *gem*-Tetrakis(cyclohexylamino)dichlorocyclotriphosphazene and Octakis(cyclopropylamino)cyclotetraphosphazene

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The reactions of chlorocyclophosphazenes $N_3P_3Cl_6$ (**1**) and $N_4P_4Cl_8$ (**2**) and polydichlorophosphazene (**3**) with cyclohexylamine, cyclopentylamine, and cyclopropylamine have been studied. The major product with **1** is the geminal tetrakis derivative $N_3P_3Cl_2(NHR)_4$, while **2** gives the completely substituted derivative, $N_4P_4(NHR)_8$. X-ray crystal structure determinations of $N_3P_3Cl_2(NHC_6H_{11})_4$ (**1a**) and $N_4P_4(NHC_3H_5)_8$ (**2c**) have been carried out. **1a** crystallizes in a triclinic space group, $P\bar{1}$, with $a = 11.2330(13)$ Å, $b = 11.4269(16)$ Å, $c = 13.4055(12)$ Å, $\alpha = 72.211(10)°$, $\beta = 72.150(9)°$, $\gamma = 81.777(11)°$, $V = 1557.3(3)$ Å$^3$, and $Z = 2$. **2c** crystallizes in a monclinic space group, $P2_1/n$, with $a = 12.433(3)$ Å, $b = 20.484(4)$ Å, $c = 12.645(3)$ Å, $\beta = 92.81(2)°$, $V = 1557.3(3)$ Å$^3$, and $Z = 4$. The cycloalkylamino-substituted polyphosphazenes contain a small amount of residual chlorine atoms. These have high glass transition temperatures.

## Introduction

Cyclophosphazenes have attracted the attention of researchers for three main reasons. One, attention has centered around the substitution of the P−Cl bonds of chlorocyclophosphazenes with many nucleophilic reagents. The stereo- and regioselectivities involved in these reactions have been a subject of intense scrutiny.[2] Two, the use of cyclophosphazenes as ligands for transition metals is another area of interest. Coordination through a ring nitrogen atom and/or an appropriately substituted ligating group can lead to a number of interesting structures.[3,4] We and others have recently shown that pyrazolyl-substituted cyclophosphazenes can function as extremely versatile multisite ligands, and unprecedented coordination modes have been observed with these systems.[5] Three, the ring opening polymerization of $N_3P_3Cl_6$ (**1**) to the linear polymer $[NPCl_2]_n$ (**3**) has provided a viable route for the preparation of more than 700 different types of polyphosphazenes, making this the single largest family of polymers that does not contain a carbon backbone.[6] More recently, other methods of preparing the linear polyphosphazenes have become available. These are based on the condensation polymerization of phosphoranimines.[7,8]

Although several polyphosphazenes containing amino substituents are known, the number of examples with primary amino substituents are still quite few, and only one example with a cycloalkylamino substituent is known.[9] Among the primary

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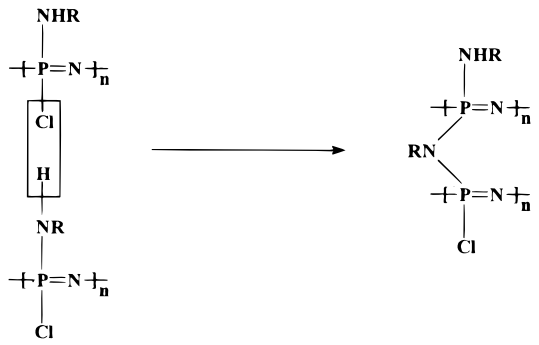
**Scheme 1**




amino-substituted polyphosphazenes, the methylamino-substituted polymer is known to be water soluble and can function as a ligand for platinum(II). This macromolecular complex has also been shown to be active against certain forms of cancer.[10] Another important aspect of primary amino substitution on polydichlorophosphazene is the tendency for cross-linked product formation[11] (Scheme 1). It has been suggested that increasing the steric bulk of the primary amine can inhibit such intermolecular cross-linking.[11] Allcock and co-workers have also recently prepared (adamantylamino)polyphosphazenes that are expected to possess useful properties. To understand the behavior of cycloalkylamines (which are intermediate between simple primary alkylamines and the sterically encumbered adamantylamine), we have chosen to investigate the reactions of cyclopropylamine, cyclopentylamine, and cyclohexylamine with chlorocyclophosphazenes and polydichlorophosphazene. Also, recently, it has been shown that sterically hindered primary amino substituents on cyclophosphazenes[12] and cyclophosphazanes[13] can be deprotonated in a facile manner, affording novel alkylamido metal complexes. Successful assembly of cyclic (alkylamino)polyphosphazenes would pave the way for the generation of a new family of polymeric alkylamido ligands.

Using the protocol developed by Allcock and co-workers,[2d] the reactions of the cycloalkylamines were first studied with the ring systems $N_3P_3Cl_6$ and $N_4P_4Cl_8$ and then applied to the polymeric system $[NPCl_2]_n$. Representative X-ray crystal structure investigations were carried out on one six-membered ring compound, *gem*-$N_3P_3Cl_2(NHC_6H_{11})_4$, and one eight-membered ring compound, $N_4P_4(NHC_3H_5)_8$.

## Experimental Section

**Reagents and General Procedures.** All operations were carried out in an inert atmosphere of nitrogen or argon. The solvents were purified and dried according to standard procedures.[14] Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**) (Aldrich) and octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (**2**) (Nippon Soda, Japan), were purified by recrystallization from hexane. Triethylamine (Qualigens, India) was dried over KOH and freshly distilled before use. Cyclohexylamine, cyclopentylamine, cyclopropylamine, and diazabicycloundecane (DBU) were obtained from Fluka, Switzerland and were used as such. Polydichlorophosphazene was prepared according to a literature procedure.[15]

**Instrumentation.** Infrared spectra were recorded as KBr or CsI pellets on KBr windows by using a Perkin-Elmer IR 1320 spectrophotometer. $^1$H NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz using tetramethylsilane as the internal standard. $^{31}$P NMR spectra were recorded on a Bruker WM 400 spectrometer operating at 135 MHz. Phosphoric acid (85%) was used as the external standard. Mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using xenon (6 kV, 10 mA) as the FAB gas. C, H, and N analyses were carried out at the Central Drug Research Institute's (Lucknow, India) regional instrumentation facility. The polymeric

**Table 1.** Experimental Details of the Rections of $N_3P_3Cl_6$ (**1**) and $N_4P_4Cl_8$ (**2**) with Cycloalkylamines

Reaction with $N_3P_3Cl_6$

| amine (mmol) | $N_3P_3Cl_6$ (mmol) | $Et_3N$ (mmol) | solvent | reaction condition[a] | product (% yield)[b] |
|---|---|---|---|---|---|
| $C_6H_{11}NH_2$ (86.4) | 14.4 | 86.4 | benzene | A | **1a** (41.0%) |
| $C_6H_{11}NH_2$ (86.4) | 14.4 | 86.4 | $CH_3CN$ | A | **1a** (41.0%) |
| $C_6H_{11}NH_2$ (86.4) | 14.4 | 86.4 | $CHCl_3$ | A | **1a** (41.0%) |
| $C_6H_{11}NH_2$ (86.4) | 14.4 | 86.4 | THF | A | **1a** (41.0%) |
| $C_6H_{11}NH_2$ (57.0) | 6.0 | 57.0 | $CHCl_3$ | B | **1a** (41.0%) |
| $C_6H_{11}NH_2$ (57.0) | 6.0 | 57.0 | benzene | B | **1a** (41.0%) |
| $C_5H_9NH_2$ (86.4) | 14.4 | 86.4 | benzene | A | **1b** (50.0%) |
| $C_5H_9NH_2$ (86.4) | 14.4 | 86.4 | THF | A | **1b** (47.5%) |
| $C_5H_9NH_2$ (60.0) | 6.0 | 60.0 | benzene | B | **1b** (50.5%) |
| $C_5H_9NH_2$ (60.0) | 6.0 | 60.0 | $CHCl_3$ | B | **1b** (48.5%) |
| $C_3H_5NH_2$ (86.4) | 14.4 | 86.4 | benzene | A | **1c** (62.0%) |
| $C_3H_5NH_2$ (86.4) | 14.4 | 86.4 | THF | A | **1c** (58.0%) |
| $C_3H_5NH_2$ (60.0) | 6.0 | 60.0 | benzene | B | **1c** (55.0%) |

| amine (mmol) | $N_3P_3Cl_6$ (mmol) | DBU (mmol) | solvent | reaction condition[a] | product (% yield)[b] |
|---|---|---|---|---|---|
| $C_6H_{11}NH_2$ (70.0) | 10 | 80.0 | $CHCl_3$ | C | **1d** (6.8%) |
| $C_5H_9NH_2$ (70.0) | 10 | 80.0 | $CHCl_3$ | C | **1e** (6.5%) |
| $C_3H_5NH_2$ (80.0) | 10 | 80.0 | $CHCl_3$ | C | **1f**[c] |

Reaction with $N_4P_4Cl_8$

| amine (mmol) | $N_4P_4Cl_8$ | $Et_3N$ | solvent | reaction condition[a] | product (% yield)[b] |
|---|---|---|---|---|---|
| $C_6H_{11}NH_2$ (39.3) | 4.3 | 39.5 | benzene | D | **2a** (29.0%) |
| $C_6H_{11}NH_2$ (39.3) | 4.3 | 39.5 | THF | D | **2a** (27.5%) |
| $C_5H_9NH_2$ (39.3) | 4.3 | 39.5 | benzene | D | **2b** (36.0%) |
| $C_5H_9NH_2$ (39.3) | 4.3 | 39.5 | THF | D | **2b** (31.0%) |
| $C_3H_5NH_2$ (39.3) | 4.3 | 39.5 | benzene | D | **2c** (34.0%) |
| $C_3H_5NH_2$ (39.3) | 4.3 | 39.5 | THF | D | **2c** (32.0%) |

[a] A = 12 h of stirring at room temperature followed by 12 h of heating under reflux. B = 6 h of stirring at room temperature followed by 72 h of heating under reflux. C = addition at ambient temperature followed by 8 days of heating under reflux with stirring. D = 8 h of stirring at room temperature followed by 14 h of heating under reflux. [b] Yields refer to actual isolated yields after column chromatography. Other products formed in the reaction could not be isolated. [c] Could not be isolated in a pure form.

samples did not give reproducible analytical data owing perhaps to incomplete combustion. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were done on a Perkin-Elmer DSC 7 and a Dupont 9900 thermal analyzer at a heating rate of 10 °C/min. Dilute solution viscosity measurements were carried out on a Schott-Gerate viscometer in dry benzene at 26 °C using an Ubbholde viscometer (capillary size, 0.46 mm).

**Synthesis.** The complete experimental details of the reactions carried out in the present study are summarized in Table 1. Given below are typical procedures.

**a. 2,2-Dichloro-4,4,6,6-tetrakis(cyclohexylamino)cyclotriphosphazene, $N_3P_3Cl_2(NHC_6H_{11})_4$ (1a).** To a stirred solution of hexachlorocyclotriphosphazene (**1**) (5.00 g, 14.38 mmol) in benzene (100 $cm^3$) was added a mixture of cyclohexylamine (8.50 g, 85.7 mmol) and triethylamine (8.70 g, 86.0 mmol) also dissolved in benzene (100 $cm^3$). The addition was done dropwise over a period of 30 min at room temperature. The reaction mixture was stirred at room temperature for 12 h and then heated under reflux for another 12 h. The amine hydrochloride formed in the reaction was filtered, and the solvent was removed from the filtrate in vacuo affording an oil. This was subjected to column chromatography over silica gel. Elution with a mixture of ethyl acetate and hexane (1:1) afforded the desired product (3.50 g, 40.7%). mp: 158 °C. $^1$H NMR ($CDCl_3$): 3.00 (m, 4H, NH−C*H*), 2.40 (broad signal, 4H, N*H*), multiplets centered at 1.90, 1.70, and 1.20 (44H, cycloalkyl protons). $^{31}$P NMR ($CDCl_3$): 22.6 (t, $PCl_2$), 20.9 (d, $P(NHC_6H_{11})_2$, $^2J(P-N-P) = 49.4$ Hz). Anal. Calcd for $C_{24}H_{48}N_7P_3Cl_2$: C, 48.16; H, 8.08; N, 16.38. Found: C, 48.05; H, 8.10; N, 16.10. FAB-MS: 598 (parent ion).

The synthesis of the other compounds **1b** and **1c** were carried out in a similar way as that described above. Data relating to these compounds are given below.

**b. 2,2-Dichloro-4,4,6,6-tetrakis(cyclopentylamino)cyclotriphosphazene, $N_3P_3Cl_2(NHC_5H_9)_4$ (1b).** Yield: 50%. mp: 144 °C. $^1$H NMR ($CDCl_3$): 3.60 (m, 4H, N*H*), centers of multiplets at 2.30,1.90,1.50, 1.40 (36H, cyclopentyl signals). $^{31}$P NMR ($CDCl_3$): 23.9 (t, $PCl_2$), 11.4 (d, $P(NHR)_2$, $^2J(P-N-P) = 48.2$ Hz). Anal. Calcd for $C_{20}H_{40}N_7P_3Cl_2$: C, 44.29; H, 7.43; N, 18.08. Found: C, 44.16; H, 7.51; N, 17.96. FAB-MS: 542 (parent ion, base peak).

**c. 2,2-Dichloro-4,4,6,6-tetrakis(cyclopropylamino)cyclotriphosphazene $N_3P_3Cl_2(NHC_3H_5)_4$ (1c).** Yield: 62%. mp: 138 °C. $^1$H NMR ($CDCl_3$): 2.80 (broad singlet, 4H, N*H*), 2.42 (m, 4H, N−C*H*), 0.60 (d, 8H, N−C−C$H_2$, $^3J$(H−H) = 3.1 Hz). $^{31}$P NMR ($CDCl_3$): 23.8 (t, $PCl_2$), 14.4 (d, $P(NHR)_2$, $^2J(P-N-P) = 46.7$ Hz). Anal. Calcd for $C_{12}H_{24}N_7P_3Cl_2$: C, 33.50; H, 5.62; N, 22.79. Found: C, 33.16; H, 5.45; N, 22.45. FAB-MS: 430 (parent ion).

**d. Hexakis(cyclohexylamino)cyclotriphosphazene, $N_3P_3(NHC_6H_{11})_6$ (1d).** To a stirred solution of hexachlorocyclotriphosphazene (**1**) (3.48 g, 10 mmol) in chloroform (100 $cm^3$) was added cyclohexylamine (6.943 g, 70.0 mmol) and DBU (12.18 g, 80.0 mmol) dropwise via a syringe. The reaction mixture was then heated under reflux with stirring for about 8 days. The solvent was removed in vacuo to afford an oil, which was subjected to column chromatography over silica gel. Elution with a mixture of ethyl acetate and benzene (20:80) afforded the compound **1a** (30.0%), and continued elution (50:50) gave the desired product. Yield: 0.49 g, 6.8%. mp: 230 °C. $^{31}$P NMR ($CDCl_3$): 10.33 (s). Anal. Calcd for $C_{36}H_{72}N_9P_3$: C, 59.72; H, 10.02; N, 17.41. Found: C, 59.58; H, 9.85; N, 17.35. FAB-MS: 724 (parent ion).

The syntheses of the other compounds **1e** and **1f** were carried out in a similar way as that described above. Data relating to these compounds are given below.

**e. Hexakis(cyclopentylamino)cyclotriphosphazene, $N_3P_3(NHC_5H_9)_6$ (1e).** Yield: 6.5%. mp: 212 °C (d). $^{31}$P NMR: 10.0 (s). Anal. Calcd for $C_{30}H_{60}N_9P_3$: C, 56.32; H, 9.45; N, 19.70. Found: C, 56.18; H, 9.05; N, 19.35. FAB-MS: 641 (parent ion).

**f. Hexakis(cyclopropylamino)cyclotriphosphazene, $N_3P_3(NHC_3H_5)_6$ (1f).** It was not possible to isolate the pure compound. However, the EI mass of the reaction mixture showed a peak at 472 corresponding to the hexakis derivative. The phosphorus NMR of the mixture also showed a peak at 10.0 similar to those observed for **1d** and **1e**.

**g. Octakis(cyclohexylamino)cyclotetraphosphazene, $N_4P_4(NHC_6H_{11})_8$ (2a).** To a stirred solution of octachlorocyclotetraphosphazene, **2** (2.00 g, 4.32 mmol) in benzene (75 $cm^3$), was added a mixture of cyclohexylamine (3.90 g, 39.32 mmol) and triethylamine (4.00 g, 39.53 mmol) dissolved in benzene (50 $cm^3$) dropwise at room temperature. The mixture was stirred at room temperature for 8 h and then heated under reflux for 14 h. After the reaction mixture was allowed to attain ambient temperature, the amine hydrochloride that

**Table 2.** Crystal, Data Collection, and Refinement Parameters

| | 1a | 2c |
|---|---|---|
| formula | $P_3N_7Cl_2C_{24}H_{44}$ | $P_4N_{12}C_{24}H_{48}$ |
| fw | 594.48 | 628.61 |
| cryst size, mm | 0.24 × 0.14 × 0.32 | 0.38 × 0.58 × 0.66 |
| cryst color | colorless | colorless |
| cryst mount | fiber with silicone rubber | glass fiber with silicone glue |
| *a*, Å | 11.2330(13) | 12.433(3) |
| *b*, Å | 11.4269(16) | 20.484(4) |
| *c*, Å | 13.4055(12) | 12.645(3) |
| α, deg | 72.211(10) | |
| *β*, deg | 72.150 (9) | 92.81 (2) |
| *γ*, deg | 81.777(11) | |
| *V*, Å$^3$ | 1557.3(3) | 3216.5(13) |
| cell detn, refls | 25 | 25 |
| cell detn, 2*θ* range, deg | 28−29 | 28−28.8 |
| *d* (calcd), g $cm^{-3}$ | 1.268 | 1.298 |
| space group | *P*1 | $P2_1/n$ |
| Z | 2 | 4 |
| *F*000 | 633.22 | 1345.83 |
| radiation | Mo Kα, graphite monochr | Mo Kα, graphite monochr |
| *λ*, Å | 0.7107 | 0.7107 |
| temp, K | 293 | 293 |
| linear abs coeff, $mm^{-1}$ | 0.38 | 0.278 |
| diffractometer | Enraf-Nonius CAD-4 | Enraf-Nonius CAD-4 |
| scan technique | *θ*−2*θ* | *θ*−2*θ* |
| scan width, deg | 1.0 + 0.35 tan *θ* | 1.0 + 0.35 tan *θ* |
| 2*θ* range, deg | 4−40 | 4−50 |
| *h*, *k*, *l* ranges | −10, 10; 0, 10; −11, 12 | −14, 14; 0, 24; 0,15 |
| std refl indices | −7 2 0; −4−7−5; −1 4 8 | 1, −6, 10; 2, 5, 5; 3, 4, 4 |
| drift of stds, % | 1.5 | 1.5 |
| absorption correction | analytical | analytical |
| absorption range | 0.840−0.999 | 0.89−0.90 |
| reflns measured | 5055 | 5916 |
| unique reflns | 2883 | 5647 |
| *R* for merge | 0.029 | 0.013 |
| data with $I > 3\sigma(I)$ | 1935 | 3725 |
| solution method | direct methods | direct methods |
| parameters refined | 326 | 361 |
| $R(F^2)$, $R_w(F^2)$ | 0.045, 0.065 | 0.043, 0.069 |
| GOF | 1.13 | 1.14 |
| *p*, $w^{-1} = [\sigma^2(I) + pI^2]/(4F^2)$ | 0.05 | 0.05 |
| largest $\Delta/\sigma$ | 0.00 | 0.00 |
| extinction correction | 0.9384 | |
| final diff map, e $A^{-3}$ | −0.22(5), +0.44(5) | −0.34(6), +0.45(6) |

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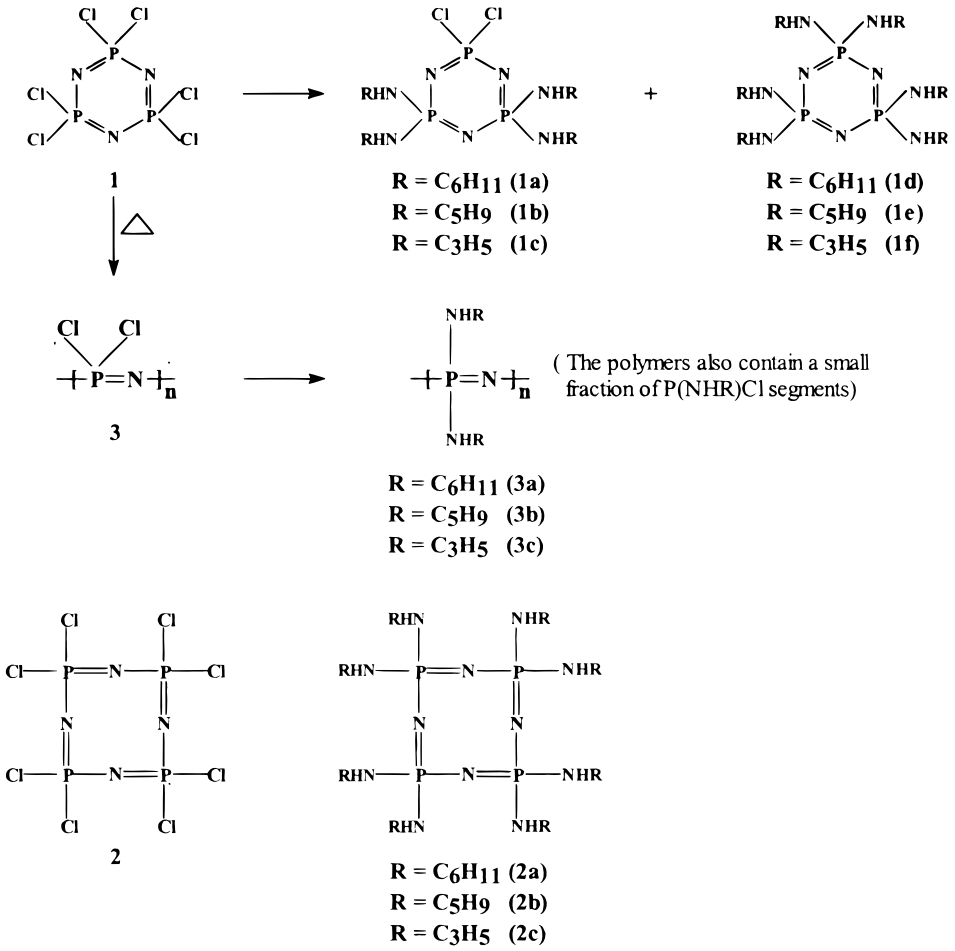
**Scheme 2**




formed was filtered off and the solvent was removed from the filtrate in vacuo affording an oil. This was chromatographed over silica gel. Elution with an ethyl acetate/hexane (25:75) mixture afforded **2a**. Yield: 1.2 g, 29%. mp: 182 °C. $^1$H NMR ($CDCl_3$): 3.00 (broad singlet, 8H, N*H*), centers of multiplets at 2.00, 1.60, and 1.30 (88H, cyclohexyl signals). $^{31}$P NMR ($CDCl_3$): 3.7 (s). Anal. Calcd for $C_{48}H_{96}N_{12}P_4$: C, 59.73; H, 10.02; N, 17.41. Found: C, 59.57; H, 9.82; N, 17.13. FAB-MS: 966 (parent ion). Data for other octakis products **2b** and **2c** are as follows.

**h. Octakis(cyclopentylamino)cyclotetraphosphazene, $N_4P_4(NHC_5H_9)_8$ (2b).** Yield: 36%. mp: 136 °C. $^1$H NMR ($CDCl_3$): 3.50 (broad singlet, 8H, N*H*), 1.60 (m, 72*H*, cyclopentyl signals). $^{31}$P NMR ($CDCl_3$): 3.9 (s). Anal. Calcd for $C_{40}H_{80}N_{12}P_4$: C, 56.32; H, 9.45; N, 19.70. Found: C, 56.01; H, 9.41; N, 19.24. FAB-MS: 854 (parent ion).

**i. Octakis(cyclopropylamino)cyclotetraphosphazene, $N_4P_4(NHC_3H_5)_8$ (2c).** Yield: 34%. mp: 130 °C. $^1$H NMR ($CDCl_3$): 2.80 (broad singlet, 8H, N*H*), 2.30 (m, N−C*H*), 0.60 (d, 32H, N−C−C$H_2$, $^3J$(H−H) = 3.0 Hz). $^{31}$P NMR ($CDCl_3$): 6.7 (s). Anal. Calcd for $C_{24}H_{48}N_{12}P_4$: C, 45.86; H, 7.70; N, 26.74. Found: C, 45.23; H, 7.45; N, 26.13. FAB-MS: 629 (parent ion).

**j. Poly[bis(cyclohexylamino)phosphazene], $[NP(NHC_6H_{11})_2]_n$ (3a).** To a stirred solution of polydichlorophosphazene (2.8 g, 24.4 mmol) in THF (100 cm$^3$) a dilute solution of cyclohexylamine (4.9 g, 49.4 mmol) and triethylamine (5.0 g, 49.4 mmol) was added dropwise. The clear solution of polydichlorophosphazene turned turbid, indicating the formation of amine hydrochloride. The reaction mixture was stirred at room temperature for 6 h and then heated under reflux for 14 h. After the reaction mixture was allowed to cool to room temperature, it was filtered and the solvent was removed in vacuo from the filtrate to afford an oily liquid. This was poured into a large excess of ethanol to afford a solid. Repeated reprecipitations were carried out to obtain a pure sample. $T_g$: 219 °C. $\eta$ (int): 11.8 cm$^3$ g$^{-1}$. $^{31}$P NMR ($CDCl_3$): 1.46.

**k. Poly[bis(cyclopentylamino)phosphazene], $[NP(NHC_5H_9)_2]_n$ (3b).** $T_g$: 217 °C. $\eta$ (int): 34.7 cm$^3$ g$^{-1}$. $^{31}$P NMR ($CDCl_3$): 2.17 (major peak); 8.3 (minor peak).

**l. Poly[bis(cyclopropylamino)phosphazene], $[NP(NHC_3H_5)_2]_n$ (3c).** $T_g$: 92 °C. $\eta$ (int): 11.0 cm$^3$ g$^{-1}$. $^{31}$P NMR ($CDCl_3$): 1.84.

**X-ray Crystallography.** The structures of **1a** and **2c** were solved by direct methods (SHELX86).[16] Refinements of the structures were performed by the full-matrix least-squares method, first with isotropic and subsequently with anisotropic temperature factors for the non-hydrogen atoms. Hydrogen atoms were included with their positions calculated using idealized sp$^3$ or sp$^2$ hybridization at the appropriate C atom with a fixed C−H distance of 0.95 Å (for N−H a fixed distance of 0.90 Å was used). These were included in the subsequent cycles of refinement with isotropic temperature factors. Refinements converged with $R = 0.045$ and $R_w = 0.065$, for compound **1a**, and $R = 0.043$ and $R_w = 0.069$, for compound **2c**. In the refinement cycles, weights were derived from counting statistics. Scattering factors were taken from ref 17. The final difference map calculated at the conclusion of the refinement had no chemically significant features. The computer program used was NRC386 (PC version of NRCVAX).[18] The crystal data, data collection methodology, and refinement parameters information for **1a** and **2c** is given in Table 2.

(16) Sheldrick, G. M. *SHELX86: Program for the Automatic Solution of Crystal Structure*; University of Gottingen: Germany, 1986.
(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(18) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr*. **1989**, *22*, 383.

**Table 3.** $^{31}$P NMR Data for the Cycloalkylaminocyclo- and Polyphosphazenes and Related Compounds

| compound | $\delta PCl_2$ | $\delta P$ $(NRR')_2$ | $^2J(P-N-P)$ Hz | ref |
|---|---|---|---|---|
| *gem*-$N_3P_3Cl_2(NHC_6H_{11})_4$ | 22.6 | 9.9 | 49.4 | this work |
| *gem*-$N_3P_3Cl_2(NHC_5H_9)_4$ | 23.9 | 11.4 | 48.2 | this work |
| *gem*-$N_3P_3Cl_2(NHC_3H_5)_4$ | 22.4 | 13.4 | 46.7 | this work |
| *gem*-$N_3P_3Cl_2$(NH adamantyl)$_4$ | 19.3 | 3.4 | *a* | 9 |
| *gem*-$N_3P_3Cl_2(NHPr^i)_4$ | 22.2 | 9.4 | 49.4 | 19 |
| *gem*-$N_3P_3Cl_2(NHBu^t)_4$ | 19.7 | 3.9 | 52.6 | 19 |
| *gem*-$N_3P_3Cl_2(NH(CH_2)_3NH)_2$ | 23.1 | 12.3 | 43.7 | 20 |
| $N_3P_3$ $(NHC_6H_{11})_6$ | | 10.3 | | this work |
| $N_3P_3$ $(NHC_5H_9)_6$ | | 10.0 | | this work |
| $N_3P_3$ $(NHC_3H_5)_6$ | | 10.0 | | this work |
| $N_3P_3$ (NH adamantyl)$_6$ | | 7.2 | | 9 |
| $N_3P_3$ $(NHPr^i)_6$ | | 12.6 | | 19 |
| $N_3P_3$ $(NHEt)_6$ | | 18.0 | | 19 |
| $N_4P_4$ $(NHC_6H_{11})_8$ | | 3.68 | | this work |
| $N_4P_4$ $(NHC_5H_9)_8$ | | 3.90 | | this work |
| $N_4P_4$ $(NHC_3H_5)_8$ | | 6.70 | | this work |
| $N_4P_4$(NH adamantyl)$_8$ | | −4.4 | | 9 |
| $N_4P_4$ $(NHMe)_8$ | | 11.1 | | 10 |
| $N_4P_4$ $(NHEt)_8$ | | 4.3 | | 21 |
| $N_4P_4$ $(NHBu^t)_8$ | | −3.1 | | 22 |
| $[NP(NHC_6H_{11})_n]^b$ | | 1.46 | | this work |
| $[NP(NHC_5H_9)_2]_n^b$ | | 2.17 | | this work |
| $[NP(NHC_3H_5)_2]_n^b$ | | 1.84 | | this work |
| $[NP(NHC_2H_5)_2]_n$ | | 4.0 | | 11b |
| $[NP(NHC_3H_7)_2]_n$ | | −3.9 | | 11b |

[a] The value of $^2J(P-N-P)$ is not given in the original reference. [b] Minor peaks centered around $\delta = +8.0$ ppm.

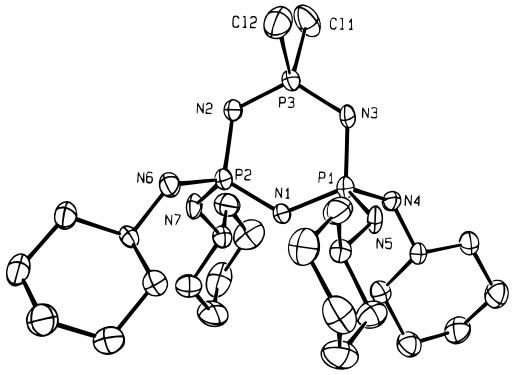



**Figure 1.** ORTEP diagram of $N_3P_3Cl_2(NHC_6H_{11})_4$ (**1a**).

## Results and Discussion

**Reactions of Chlorocyclophosphazenes with Cycloalkylamines.** The reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**) and octachlorocylotetraphosphazene, $N_4P_4Cl_8$ (**2**), with the cycloalkylamines were carried out with the view to isolate the fully substituted derivatives. Since the synthesis of polyphosphazenes involves substitution of chlorine atoms on the macromolecule $[NPCl_2]_n$ (**3**), it is advantageous to obtain information on reaction conditions suitable for such substitution by first carrying out the same reaction on the small molecule. In view of the fact that $N_4P_4Cl_8$ (**2**) is puckered and therefore structurally more similar to the linear polymer, it was also chosen for the model reactions.

In all the reactions of **1** with cycloalkylamines (as detailed in Table 1), the major product that was isolated was the incompletely substituted product, the geminal tetrakis derivative $N_3P_3Cl_2(NHR)_4$. The fully substituted derivative $N_3P_3(NHR)_6$ was formed only in minor yield. Prolonged reaction conditions and the use of DBU as a base only marginally improved the yields of these derivatives. In this regard, the reactivity of these cycloalkylamines compares very well with that of adamantylamine rather than with those of amines such as isopropylamine. Allcock and co-workers have also reported that the reaction of adamantylamine with **1** affords only the geminal tetrakis derivative in major yield.[9] In contrast to the reactivity behavior of **1**, the more flexible and reactive eight-membered ring **2** reacts with all the cycloalkylamines affording only the fully substituted octakis derivatives, $N_4P_4(NHR)_8$. The reactions of the chlorocyclophosphazenes with the cycloalkylamines and the products obtained are summarized in Scheme 2.

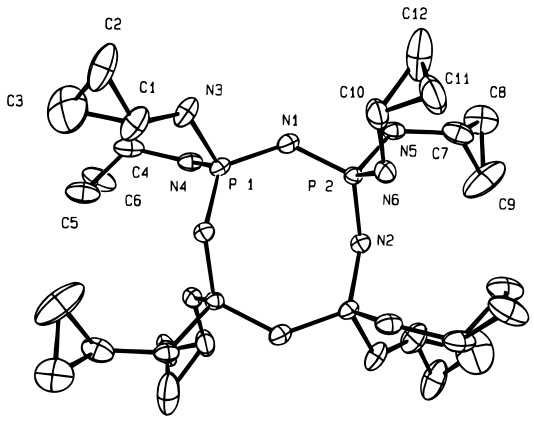



**Figure 2.** ORTEP diagram of $N_4P_4(NHC_3H_5)_8$ (**2c**).

**Table 4.** Selected Bond Length and Angle Data for $N_3P_3Cl_2(NHC_6H_{11})_4$ (**1a**)

| cyclophosphazene ring distances (Å) | exocyclic distances (Å) |
|---|---|
| P(1)−N(1), 1.589(5) | P(3)−Cl(1), 2.011(2) |
| P(2)−N(1), 1.581(5) | P(3)−Cl(2), 2.027(3) |
| P(1)−N(3), 1.622(5) | P(1)−N(4), 1.632(5) |
| P(2)−N(2), 1.621(5) | P(1)−N(5), 1.622(5) |
| P(3)−N(3), 1.553(5) | P(2)−N(6), 1.641(5) |
| P(3)−N(2), 1.561(5) | P(2)−N(7), 1.619(5) |

Cyclophosphazene Ring Bond Angles (deg)

| | |
|---|---|
| N(1)−P(1)−N(3), 114.2(2) | P(1)−N(1)−P(2), 127.3(3) |
| N(1)−P(2)−N(2), 113.7(2) | P(2)−N(2)−P(3), 120.8(3) |
| N(2)−P(3)−N(3), 121.3(3) | P(3)−N(3)−P(1), 121.2(3) |

Exocyclic Bond Angles

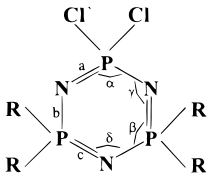
Cl(2)−P(1)−Cl(1), 98.34(12)
N(4)−P(1)−N(5), 103.1(3)
N(6)−P(2)−N(7), 102.3(3)

FAB mass spectra of all the tetrakis derivatives (**1a**−**1c**) show major peaks due to a sequential loss of amino substituents, indicating a geminal substitution pattern, which was confirmed by other techniques. The phosphorus NMR spectra of compounds **1a**−**1c** showed an $AX_2$ type of spectra (Table 3), and the geminal structure of these compounds has been confirmed by a single-crystal X-ray structural analysis of **1c** (vide infra). It is to be noted that, despite the large body of work that has been carried out on the aminolysis reactions of chlorocyclotriphosphazenes, the number of geminal isomers isolated particularly at the higher stages of chlorine substitution is still very few.

The $\equiv PCl_2$ resonances in **1a**−**1c** are downfield and nearly invariant in comparison with the $\equiv P(NHR)_2$ resonance. This trend compares well with other related derivatives known in the literature (Table 3).[19,20] Further, the $\equiv P(NHR)_2$ resonances

(19) Keat, R.; Shaw, R. A.; Woods, M. *J. Chem. Soc., Dalton. Trans.* **1976**, 1582.

**Table 5.** Comparison of the Bond Parameters of **1a** with Those of Related Geminal Tetrakis(amino)dichlorocyclotriphosphazene Derivatives



| no. | R | ring conformation | ring P−N bond distances[a] (Å) *a, b, c* | bond angles (deg)[a] N−P−N α, *β* | bond angles (deg)[a] P−N−P *γ*, *δ* | ref |
|---|---|---|---|---|---|---|
| 1 | $C_6H_{11}NH$ | planar | 1.557(5); 1.622(5); 1.585(5) | 121.3(3)<br>114.0(3) | 121.0(3)<br>127.3(3) | this work |
| 2 | $NHPr^i$ | nonplanar | 1.562(3); 1.635(3); 1.588(3) | *b* | *b* | 2e |
| 3 | $NC_2H_4$ | planar | 1.558(3); 1.610(3); 1.584(3) | 120.9(2)<br>114.0(3) | 121.1(2)<br>124.2(2) | 2c |

[a] Average values. [b] Not given.

observed for **1a** and **1b** are very close to that observed for $N_3P_3Cl_2(NHPr^i)_4$.[19] The corresponding resonance for **1c** appears at $\delta = +13.4$ ppm. It is of interest to note that the phosphorus chemical shifts of the tetrakis adamantylamino derivative $N_3P_3Cl_2(NH\ adamantyl)_4$[9] are more similar to those of the other sterically encumbered, *tert*-butylamino-substituted derivative, $N_3P_3Cl_2(NHBu^t)_4$[19], than to those of **1a, 1b**, or **1c**. The $\equiv P(NHR)_2$ resonance with the sterically hindered substituents is considerably upfield shifted (Table 3). All the fully substituted derivatives, $N_3P_3(NHR)_6$ (**1d**−**1f**) and $N_4P_4(NHR)_8$ (**2a**−**2c**), show single lines in their $^{31}P$ NMR because of the chemical shift equivalence of all the phosphorus nuclei. The chemical shifts of the eight-membered ring system are considerably upfield in comparison with those of the six-membered systems. The phosphorus resonances for the polymeric derivatives **3a**−**3c** also are upfield in comparison with the those of six-membered analogues in accordance with literature precedents.[4]

**X-ray Crystal Structures of $N_3P_3Cl_4(NHC_6H_{11})_4$ (1a) and $N_4P_4(NHC_3H_5)_8$ (2c).** The ORTEP drawings of **1a** and **2c** with atomic numbering schemes are shown in Figures 1 and 2, respectively. Despite the rich structural data available on cyclophosphazenes, there are not many examples of X-ray structures of geminal tetrakisamino-substituted cyclotriphosphazenes or fully substituted cyclotetraphosphazenes.

The six-membered ring in **1a** is very nearly planar with only one atom N(2) being out of plane by about 0.16 Å. Since the molecule contains four geminal substituents of one type and two geminal substituents of another type, there exist three types of ring P−N bond lengths (Tables 4 and 5). The bond length *a* is the shortest while the bond length *b* is the longest; viz., the bond lengths follow the order $b > c > a$. These bond length variations are rationalized in terms of different degrees of $\pi$ bonding present within the cyclophosphazene ring. The strongly electron-withdrawing chlorine substituents assist in increased $\pi$ bonding in the relevant N−P−N ring segment, making these bond lengths the shortest. There is a depletion of electron density for $\pi$ bonding in segment b, and hence the corresponding P−N bond lengths are longest. The situation is intermediate for the segment c. A comparison with other known geminally substituted tetrakis derivatives also indicates the above findings. The exocyclic P−N bond lengths (av 1.629 Å) are longer than the ring P−N bond lengths but are shorter than the ideal P−N single-bond value[2e] of 1.77 Å, indicating the presence of some multiple-bond character in this segment also. The endocyclic bond angles at phosphorus and nitrogen in the inorganic ring are largest at P3 (121.3°) and N(1) (127.3°), respectively. In general, the variation of bond angles is such that $\alpha > \beta$ and $\delta > \gamma$. Such a trend is also observed for other geminally substituted derivatives as listed in Table 5.

**Table 6.** Selected Bond Length and Angle Data for $N_4P_4(NHC_3H_5)_8$ (**2c**)[a]

| molecule 1 | length 1 (Å) | molecule 2 | length 2 (Å) |
|---|---|---|---|
| P1···P2 | 2.8953(13) | P11···P12 | 2.8657(13) |
| P1···P2a | 2.9166(14) | P11···P12b | 2.9455(13) |
| P1−N1 | 1.582(3) | P11−N11 | 1.582(3) |
| P1−N2 | 1.569(3) | P11−N12 | 1.579(3) |
| P2−N1 | 1.583(3) | P12−N11 | 1.591(3) |
| P2−N2 | 1.586(3) | P12−N12 | 1.588(3) |

[a] For comparison the average metric parameters of $N_4P_4(NMe_2)_8$ are ring P−N distance = 1.58 Å, P−N−P = 133.0°, N−P−N = 120.0° (from ref 23).

The X-ray structure of **2c** represents the first example of a cyclotetraphosphazene fully substituted with primary amino groups. **2c** consists of two crystallographically independent molecules, each located on an inversion center. The ORTEP diagram of one of these molecules is shown in Figure 2. The molecule is nonplanar. Thus, in molecule 1 of **2c** with respect to the plane of P1, P2, P1a and P2a the atom N2 is out of the plane by +0.610(3) Å. In comparison, molecule 2, with reference to the plane defined by P11, P12, P11b, and P12b, the atoms N11 and N12 are out of the plane by 0.180(3) and 0.553(3) Å, respectively. The metric parameters for the two molecules of **2c** are summarized in Table 6. The average ring P−N bond distance is 1.582(11) Å, while the average exocyclic P−N bond distance is 1.661(18) Å. The average ring P−N−P bond angle is 133(4)°, while the N−P−N bond angle is 120(2)°. The exocyclic N−P−N angle is 107(6)°. These bond parameters compare very well with those observed for $N_4P_4(NMe_2)_8$.[22]

**Polyphosphazenes Containing Cycloalkylamino Substituents.** Polydichlorophosphazene (**3**) prepared by the thermal polymerization of **1** was allowed to react with the cyclic alkylamines in the presence of the hydrogen chloride scavenger triethylamine to afford the polymers **3a**−**3c** (Scheme 2). These polymers are isolated as white powders, which are soluble in organic solvents such as THF. Also, they are completely insoluble in water, in contrast to the other primary amino-substituted polymer, $[NP(NHMe)]_n$,[10] Dilute solution viscosity measurements on the polymers reveal that they are high

(20) Chandrasekhar, V.; Krishnamurthy, S. S.; Vasudeva Murthy, A. R.; Shaw, R. A.; Woods, M. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 181.
(21) Krishnamurthy, S. S.; Sau, A. C.; Vasudeva Murthy, A. R.; Keat, R.; Shaw, R. A.; Woods, M. *J. Chem. Soc., Dalton. Trans.* **1976**, 1405.
(22) Sau, A. C.; Krishnamurthy, S. S.; Vasudeva Murthy, A. R.; Keat, R.; Shaw, R. A.; Woods, M. *J. Chem. Soc., Dalton. Trans.* **1977**, 1980.
(23) Bullen, G. J. *J. Chem. Soc.* **1962**, 3193.

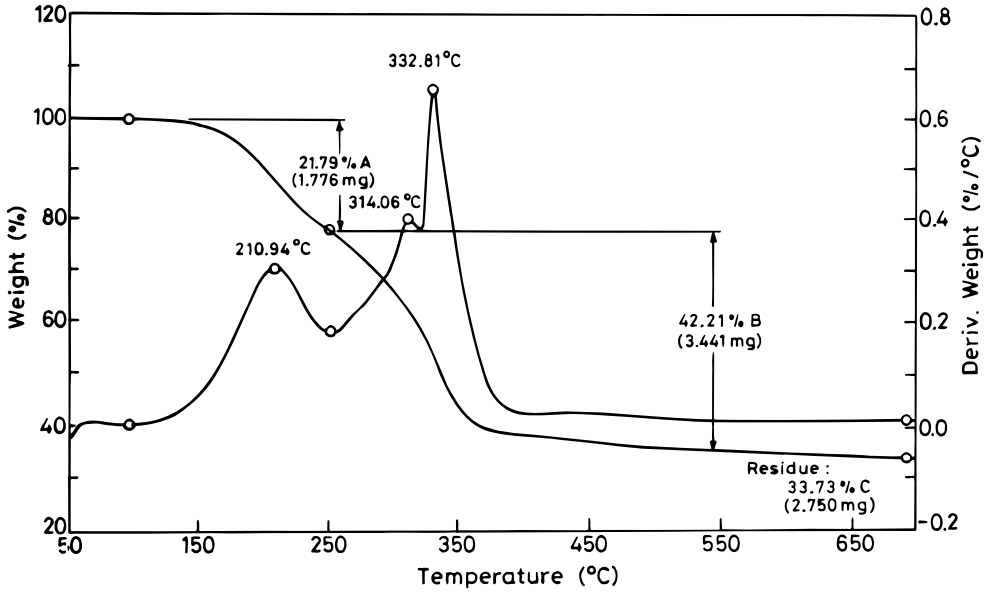



**Figure 3.** TGA trace for **3a**.

molecular weight materials. Under the reaction conditions as described vide supra a small amount of residual chlorine atoms was noted in all the polymers, consistent with the model reactions of the cyclic alkylamines with **1**. As a result of this, the polymers tend to cross-link on standing and lose their solubility properties. This can be obviated by substitution of the remaining chlorine atoms by groups such as trifluoroethoxy, which we are investigating currently. The $^{31}$P NMR spectra of **3a**−**3c** contain a large peak for the [NP(NHR)$_2$] segment and a minor peak for the [NP(NHR)Cl] segment. The latter is downfield. The $^{31}$P NMR data are summarized in Table 3. It can be seen that the chemical shifts of **3a**−**3c** are downfield shifted in comparison with those of the sterically less encumbered methylamino-substituted polymer. The $T_g$ values of **3a** (219), **3b** (217), and **3c** (92) suggest that these polymers are less flexible than other amino-substituted polyphosphazenes owing to the steric constraints of the substituent as well as perhaps to intermolecular N−H···N interactions. The polymers decompose by a three-step process. Figure 3 gives the TGA trace of **3a**, which has a fairly high char yield of 33.7% at 700 °C. Further investigations on the polymers are in progress.

**Acknowledgment.** We are thankful to CSIR (New Delhi) and DST (New Delhi) for financial support.

**Supporting Information Available:** Listings of additional interatomic distances and angles, atomic parameters $x$, $y$, $z$, and $B_{eq}$, atomic parameters for hydrogen atoms, and anisotropic thermal parameters for **1a** and for **2c** (10 pages). Ordering information is given on any current masthead page.

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