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Structure and Conformation of the Medium-Sized Chlorophosphazene Rings

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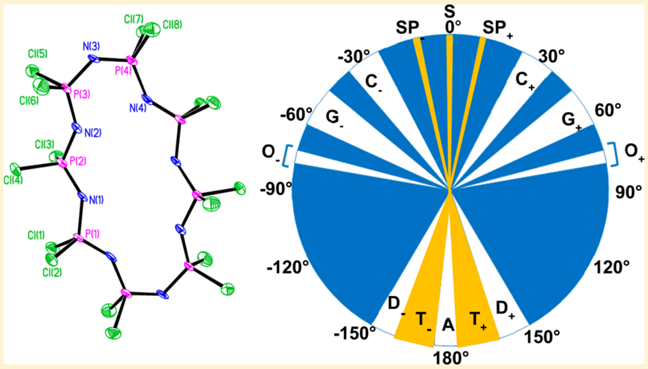
Supporting Information



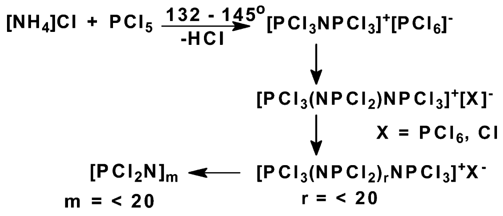
ABSTRACT: Medium-sized cyclic oligomeric phosphazenes $[PCl_2N]_m$ (where $m = 5-9$) that were prepared from the reaction of PCl_5 and NH_4Cl in refluxing chlorobenzene have been isolated by a combination of sublimation/extraction and column chromatography from the predominant products $[PCl_2N]_3$ and $[PCl_2N]_4$. The medium-sized rings $[PCl_2N]_m$ have been characterized by electrospray ionization−mass spectroscopy (ESI-MS), their ${}^{31}P$ chemical shifts have been reassigned, and their T_1 relaxation times have been obtained. Crystallographic data has been recollected for $[PCl_2N]_5$, and the crystal structures of $[PCl_2N]_6$, and $[PCl_2N]_8$ are reported. Halogen-bonding interactions were observed in all the crystal structures of cyclic $[PCl_2N]_m$ ($m = 3-5$, 6, 8). The crystal structures of $[P(OPh)_2N]_7$ and $[P(OPh)_2N]_8$, which are derivatives of the respective $[PCl_2N]_m$, are also reported. Comparisons of the intermolecular forces and torsion angles of $[PCl_2N]_8$ and $[P(OPh)_2N]_8$ with those of three other octameric rings are described. The comparisons show that chlorophosphazenes should not be considered prototypical, in terms of solid-state structure, because of the strong influence of halogen bonding.

■ INTRODUCTION

Polyphosphazenes encompass the largest class of inorganic backbone oligomers and polymers, and applications for these systems continue to accumulate.[1,2] By way of substitution reactions, chlorophosphazenes are utilized as precursors to most of the hundreds of other phosphazene compounds. The array of promising applications that exist for phosphazene oligomers and polymers is attributed to the wide range of substituents that can be placed on the P−N backbone.[1,2] Therefore, chlorophosphazene chemistry is central to the phosphazene field. Irreproducibility and other difficulties associated with the synthesis and storage of chlorophosphazenes, especially high polymeric $[PCl_2N]_n$, have limited commercial use of the entire class of polyphosphazenes. Thus, fundamental research of chlorophosphazenes is essential to overcome these problems.

Classically, cyclic chlorophosphazenes of the formula $[PCl_2N]_m$ (where m = oligomer = <20) are synthesized via the reaction of PCl_5 and NH_4Cl in the presence of a high boiling (∼132−145 °C) halogenated solvent (Scheme 1).[3] Such reactions have been known since the 19th century[4] and give a mixture of cyclic and linear species.[5] The cyclic species $[PCl_2N]_3$ and $[PCl_2N]_4$ are the major products from Scheme 1. These rings are important precursors to high polymeric $[PCl_2N]_n$, because of their ability to undergo thermal ring-opening polymerization at elevated temperatures.[6] The medium-sized cyclic oligomeric phosphazenes $[PCl_2N]_m$, with $m \geq 5$, often have been foreshadowed by the lower-molecular-weight homologues and are usually considered byproducts of Scheme 1.

Scheme 1. Classic Synthesis of a Mixture of Cyclic and Linear Chlorophosphazenes[a]



[a] Data taken from ref 3. The species that adds to the cationic intermediates has been suggested to be $Cl_3P{=}NH$.

As part of a reinvestigation of Scheme 1, herein we report a study of the medium-sized cyclic oligomeric chlorophosphazenes $[PCl_2N]_m$, with $m = 5-9$. There were several reasons why we chose to investigate the medium-sized $[PCl_2N]_m$ rings. An

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early motivation concerned certain NMR parameters. There was confusion in the literature with respect to the ^{31}P NMR chemical shift of several $[PCl_2N]_m$. In addition, quantification of the products from Scheme 1 often had been done via integration of ^{31}P NMR signals. The underlying assumption behind the use of integration is that the relaxation time T_1 is similar for all products. As part of our reinvestigation of Scheme 1, it was important to correctly identify the products from Scheme 1 and determine their relative quantities.

This work on medium-sized $[PCl_2N]_m$ rings also addresses basic questions of structure and conformation and considers how cyclic phosphazenes compare to other cyclic molecules such as hydrocarbons, polysilanes, and polysiloxanes. Cyclic phosphazenes are typically drawn with alternating single and double P−N bonds. However, the bonds usually are all an intermediate length, between those expected for single and double bonds, and large P−N−P angles are observed. Two bonding descriptions have been advanced for the multiple bond character: one is based on P−N dπ−pπ bonding[7] and, more recently, the other is a combination of an ionic attraction between charges on the ring coupled with hyperconjugation effects.[8] Either bonding description is rather different than those applied to rings such as $[CR_2]_{2m}$ and $[SiR_2]_{2m}$.[9] More similar to phosphazene rings are the various bonding descriptions that have been applied to the isoelectronic siloxane rings.[10−13] In addition, steric considerations play an important role in the conformations of rings. Unlike $[CR_2]_{2m}$ and $[SiR_2]_{2m}$ that have a substituent on every atom of the ring, $[SiMe_2O]_m$ and $[PCl_2N]_m$ have functional groups at every other atom of the ring, thereby leading to different backbone alignments. For these reasons, we were interested in determining the conformations of the ring bonds of medium-sized $[PCl_2N]_m$.

Although the crystal structures and the configuration of the P−N backbones of $[PMe_2N]_m$ rings with m values in the range 3−12 have been described,[14] the picture was far less complete for the important $[PCl_2N]_m$ rings, from which the $[PMe_2N]_m$ rings were derived. Only the crystal structures of $[PCl_2N]_3$,[15] $[PCl_2N]_4$,[16] and $[PCl_2N]_5$[17] had been obtained. The unit cells of the hexameric and octameric $[PCl_2N]_m$ rings were known for many years (as early as 1897!),[18,19] but their crystal structures or that of $[PCl_2N]_7$ had not been reported. As West and coworkers have done for polysilanes,[20] we expected that comparisons among the structures of the medium-sized cyclic $[PCl_2N]_m$ rings and the $[PCl_2N]_n$ high polymer would provide important insights. The medium-sized rings should be better models for the structure of the high polymer $[PCl_2N]_n$[21,22] than the smaller $[PCl_2N]_m$, because of the marked increase in flexibility and the lower ring strain as the cyclics become larger. By comparing the structures of the $[PCl_2N]_m$ medium-sized rings with rings in which the chlorides are substituted with organic groups, we hoped to obtain insights into the structures of the respective polymers. Another motivation to study the structures of $[PCl_2N]_m$ concerned halogen bonding. Halogen bonds are intermolecular interactions that are due to asymmetric electron distributions on halogen atoms and have been compared to hydrogen bonds.[23] The asymmetric electron distribution creates a σ-hole so that the Cl atoms of the P−Cl bonds are capable of acting as acceptors of lone pairs on neighboring molecules. Recent computational studies indicate the existence of halogen bonds between $[PCl_2N]_3$ and a variety of Lewis basic substrates.[24] Although we did not discuss this point in our publication,[25] there are short contacts in the crystal structures of Group 13 Lewis acid adducts of $[PCl_2N]_3$, which suggest the presence of halogen bonding. Considering these precedents, we wondered whether halogen bonding might play a more general role in chlorophosphazene chemistry, including its role in determining the conformations of rings and polymers.

■ EXPERIMENTAL SECTION

General Procedures. All glassware was dried in an oven overnight (~115 °C) before use and reaction apparati were assembled hot. The glassware used for the experiments was made with virtually greaseless Fisher-Porter Solv-seal glass joints and high-vacuum valves on the flasks were purchased from Kimble-Kontes.

Materials. Chlorobenzene, hexanes, and THF (Fisher Scientific) were dried and deoxygenated by alumina and copper columns in the Pure Solv solvent system (Innovative Technologies, Inc.). Heptane (ACS reagent grade), dodecanol (Fisher Scientific), pentane, aniline, pyridine, PCl_5, potassium hydride (Sigma−Aldrich), and $CDCl_3$ (Cambridge Isotopes, 99.8%) were used as received. NH_4Cl (Fisher Scientific) was crushed with a mortar and pestle. Phenol was recrystallized from petroleum ether and dried *in vacuo*. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with SiO_2 (IB2-F). Column chromatography was conducted using or SiO_2 (60−200 mesh) from Sorbent Technologies.

NMR Spectroscopy. Routine NMR spectra were obtained using a Varian Gemini 300 MHz or VNMRS 500 MHz instruments at 25 °C. ^{31}P NMR spectra were referenced to an external reference of 0.15 M H_3PO_4 solution in a deuterated solvent (0 ppm). ^{1}H NMR and ^{13}C NMR spectra were referenced to the residual protons (7.24 ppm) and the ^{13}C atoms (77.23 ppm) in the $CDCl_3$ solvent. Integrations of ^{31}P NMR spectra were performed on a Varian Model VNMRS 500 MHz instrument with a relaxation delay (d1) of 70 s. The ^{31}P T_1 experiment was performed with the inversion−recovery (relaxation-180°−τ−90°-acquire) technique. The experiment was performed with a spectral window of 26 kHz, 20 s relaxation delay, 1.6 s acquisition time, and a 13.6 μs (90°) pulse width, with gated ^{1}H (WALTZ-16, $\gamma B_H/2\pi$ = 2.9 kHz) decoupling. A total of 17 τ delays ranging from 0.05 to 50.0 s (which were randomized) were used. Data were fitted to an exponential function using a three-parameter fit. The quantitative ^{31}P NMR spectrum was obtained with an 13.7 kHz spectral window with inverse-gated ^{1}H decoupling (to suppress NOEs in order to retain quantitative accuracy) using WALTZ-16 modulation ($\gamma B_H/2\pi$ = 2.9 kHz). For the purpose of quantitation, a 70.0 s relaxation delay (corresponding to 5 times the longest measured T_1), a 1.6 s acquisition time, and a 13.6 μs (90°) pulse width were used. The data were zero-filled to 128 K, and line broadening was set to 0.5 Hz before Fourier transformation.

ESI-MS. ESI spectra were acquired in both positive and negative mode, to detect the positive or negative ions, respectively, generated at the source. The mass spectrometer utilized in this study was a SYNAPT HDMS hybrid quadrupole/time-of-flight (Q/oa-ToF) mass spectrometer (Waters, Beverly, MA) equipped with a Z-spray electrospray source operated in both positive- and negative-ion mode. The instrumental settings were tuned in order to optimize both signal and resolution as follows: capillary voltage, 3.5 kV; cone voltage, 35−40 V; and sampling cone voltage, 3−4 V. The source temperature and the desolvation gas temperature were held to 90−60 °C and 240−110 °C, respectively. The sample solution was electrosprayed at a flow rate of 15 μL/min. The data acquisition, data processing, and theoretical isotope distribution generation were performed using Waters' MassLynx 4.1 software.

X-ray Crystallography. Crystal structure datasets were collected on a Bruker SMART Apex or Bruker ApexII Duo diffractometers. Unit-cell determination was achieved by using reflections from three different orientations. An empirical absorption correction and other corrections were done using multiscan SADABS. Structure solution, refinement, and modeling were accomplished using the Bruker SHELXTL package.[26] The structures were obtained by full-matrix least-squares refinement of F^2 and the selection of appropriate atoms from the generated difference map. X-ray wavelength, crystal data, and structure refinement for $[PCl_2N]_6$, $[P(OPh)_2N]_7$, $[PCl_2N]_8$, and $[P(OPh)_2N]_8$ are given in Table 1, and data for $[PCl_2N]_3$, both forms of $[PCl_2N]_4$, and $[PCl_2N]_5$ are given in the Supporting Information.

Synthesis and Isolation of a Crude Mixture of the Medium-Sized Rings $[PCl_2N]_m$ (m = 5−9). A mixture of cyclic and linear chlorophosphazenes was synthesized in a chlorobenzene solution at 10%−20% scale of a literature procedure.[27] In a representative reaction, NH_4Cl (0.672 g, 0.0126 mol), PCl_5 (2.09 g, 0.0100 mol), and dry chlorobenzene solvent (∼15 mL) was added to a 100-mL Schlenk flask containing a 1-in. stir bar. A reflux condenser topped with a drying tube containing Drierite was connected to the flask. The flask was placed on a heating mantle and refluxed for ∼12 h. *[Caution: This literature procedure should be carefully monitored to ensure that sublimation of PCl_5 does not plug the narrower parts of the apparatus and result in pressure buildup from the gaseous HCl product. Such pressure buildup can lead to an explosion.]* The pale yellow solution was filtered from a solid, presumably unreacted NH_4Cl. The volatile components were removed under reduced pressure at 0.1 Torr resulting in a yellow slurry. At this point and by ^{31}P NMR, the yields of individual rings for a representative reaction were as follows: $[PCl_2N]_3$, 64%; $[PCl_2N]_4$, 5%; $[PCl_2N]_5$, 7%; $[PCl_2N]_6$, 6%; $[PCl_2N]_7$, 3%; and $[PCl_2N]_{8,9}$, 2%. The remainder of the mixture (∼13%) was a mixture of linear oligomeric chlorophosphazenes. Individual reactions gave variable total yields of cyclics $[PCl_2N]_m$ (m = 3−9) in the range of 60%−92%. $[PCl_2N]_3$ and most of the $[PCl_2N]_4$ were separated from the yellow slurry by sublimation at 60 °C for 6 days with a vacuum line whose ultimate vacuum was $\sim 10^{-4}$ Torr. The unsublimed material was extracted with hexane in air to separate the soluble medium-sized rings $[PCl_2N]_m$ from the insoluble linear oligomers. The crude medium-sized rings, which, at this point, still contain small amounts of $[PCl_2N]_4$ and several higher-molecular-weight species, were collected from ∼25 such reactions (total of ∼3 g), combined, and stored in air (maximum exposure of ∼6 months).

Chromatographic Isolation of the Medium-Sized Rings $[PCl_2N]_m$ (m = 5−9) in Air. The combined crude medium-sized rings (see above) were extracted with ∼50 mL heptane; the solution was filtered, and the volatiles were removed under vacuum to give 2.5 g of a slightly brown oily solid. A concentrated heptane (∼5 mL) solution of the oily solid was placed on a silica gel column (61 cm in length, 4 cm in diameter). Chromatography of the mixture on silica gel with heptane eluent resulted in the isolation of each cyclic species. Thin-layer chromatography was used to monitor the separations and determine R_f values (for $[PCl_2N]_4$, R_f = 0.44; for $[PCl_2N]_5$, R_f = 0.38; for $[PCl_2N]_6$, R_f = 0.36; for $[PCl_2N]_7$, R_f = 0.32; for $[PCl_2N]_8$, R_f = 0.24; and for $[PCl_2N]_9$, R_f = 0.22) and visualization of the cyclic oligomers was achieved by staining with a 2:1 (v/v) aniline−pyridine mixture.[28] A total of 1.308 g of medium-sized rings was isolated. Yields, crystallization procedures (in air unless otherwise indicated), and characterizational data for each medium-sized ring $[PCl_2N]_m$ (m = 5−9) are given below. By collecting further heptane fractions, several other higher-molecular-weight oligomeric species (m values up to ∼17, as determined by mass spectrometry) were also collected (total of 0.067 g). A toluene flush was collected and an additional mixture of chlorophosphazenes was isolated (0.02 g). Full characterization of the individual products in the last heptane fractions and the toluene fraction was not possible, because of the small quantity of material. There was a yellow band of material that never moved more than approximately one-third of the distance down the column, and eventually the band turned green.

$[PCl_2N]_5$. Crystals suitable for X-ray crystallography were obtained by recrystallization from hexane. Colorless solid (0.407 g, 16%), R_F = 0.38; ^{31}P NMR (500 MHz, $CDCl_3$) −15.1 ppm (s); ESI-MS (THF): for $[PCl_2N]_5^-$, m/z 574.568; for $[P_5Cl_9N_5O]^-$, m/z 555.615; and for $[P_5Cl_9N_5]^-$, m/z 539.624.

$[PCl_2N]_6$. Evaporation of the volatile components from the fraction with R_F = 0.36 gave a colorless solid (0.392 g, 16%). Triclinic crystals suitable for X-ray crystallography were obtained by recrystallization from hexane or $CHCl_3$. Monoclinic crystals suitable for X-ray crystallography were obtained during an attempt to isolate a derivative by protonation of the ring. Using standard anaerobic techniques, a solution of $[PCl_2N]_6$ (0.100 g, 0.144 mmol), HCl (measured in a known volume on the vacuum line: 55 mmHg, 295.75 K, 0.050 L, 0.15 mmol) and $SbCl_5$ (0.019 mL, 0.148 mmol) in $CHCl_3$ (10 mL) was prepared and stirred for 12 h. After removal of the volatile components on a vacuum line whose ultimate vacuum was $\sim 10^{-4}$ Torr, a colorless solid was obtained. A ^1H NMR spectrum in $CDCl_3$ taken immediately after the solid was isolated indicated protonation of the ring (δ NH = 6.13 ppm). After storage in the glovebox for 1 week, recrystallization by slow removal of $CHCl_3$ *in vacuo* at 0 °C yielded colorless crystals of monoclinic $[PCl_2N]_6$ among a brown gelatinous solid. Colorless solid; R_F = 0.36, ^{31}P NMR (500 MHz, $CDCl_3$) −15.3 ppm (s); ESI-MS (THF): for $[PCl_2N]_6^-$, m/z 689.485; for $[P_6Cl_{11}N_6O]^-$, m/z 670.516; and for $[P_6Cl_{11}N_6]^-$, m/z 654.535.

$[PCl_2N]_7$. Colorless liquid (0.322 g, 13%); R_F = 0.32; ^{31}P NMR (500 MHz, $CDCl_3$) −17.0 ppm (s); ESI-MS (THF): for $[PCl_2N]_7^-$, m/z 804.390; for $[P_7Cl_{13}N_7O]^-$, m/z 785.424; and for $[P_7Cl_{13}N_7]^-$, m/z 769.435.

$[PCl_2N]_8$. Crystals suitable for X-ray crystallography were obtained by recrystallization from heptane. Colorless solid (0.140 g, 6%); R_F = 0.24; ^{31}P NMR (500 MHz, $CDCl_3$) −17.7 ppm (s); ESI-MS (THF): for $[PCl_2N]_8^-$, m/z 919.307; for $[P_8Cl_{15}N_8O]^-$, m/z 900.314; and for $[P_8Cl_{15}N_8]^-$, m/z 884.327.

$[PCl_2N]_9$. Colorless liquid (0.047 g, 2%); R_F = 0.22; ^{31}P NMR (500 MHz, $CDCl_3$) −17.7 ppm (s); ESI-MS (THF): for $[PCl_2N]_9^-$, m/z 1034.239; for $[P_9Cl_{17}N_9O]^-$, m/z 1015.247; and for $[P_9Cl_{17}N_9]^-$, m/z 999.250.

Synthesis of $[P(OPh)_2N]_7$. In the glovebox, KH (0.015 g, 0.37 mmol) and 10 mL of dry THF were added to a 100-mL Schlenk flask containing a 1-in. stir bar. $[PCl_2N]_7$ (0.022 g, 0.19 mmol) and phenol (0.036 g, 0.38 mmol) were placed in separate vials and each was dissolved in 5 mL of dry THF. Using standard Schlenk techniques, the phenol solution was added to the Schlenk flask under nitrogen. The solution immediately evolved a gas, presumably H_2, and became pink. When gas evolution ceased, the $[PCl_2N]_7$ solution was added under nitrogen. The flask was equipped with a condenser topped with a bubbler and the contents were heated to reflux for ∼24 h. The pink solution was filtered in air and the volatile components were removed under reduced pressure at ∼0.1 Torr. The product was washed with water (20 mL × 4) to remove unreacted KOPh and phenol. The product was dried *in vacuo*, giving $[P(OPh)_2N]_7$ as a viscous colorless oil. Yield: 86%. Crystals suitable for X-ray diffraction (XRD) were obtained by adding a 50:50 heptane/*n*-dodecanol mixture to the oil. The heptane was evaporated and the room temperature was cooled below the melting point of dodecanol, leaving a small amount of a colorless solid that was manually removed from the solid dodecanol. ^{31}P NMR ($CDCl_3$) δ −18.8 ppm (s). ^1H NMR ($CDCl_3$) δ 6.88 (d, 28 H) 6.96−7.02 (m, 42 H). ^{13}C NMR ($CDCl_3$) δ (ppm): 121.5(s), 123.9(s), 129.1(s), 152.0(s).

Synthesis of $[P(OPh)_2N]_8$. $[P(OPh)_2N]_8$ was synthesized utilizing the same procedure as for $[P(OPh)_2N]_7$, but using 0.020 g of $[PCl_2N]_8$ (0.022 mmol), 0.014 g of KH (0.35 mmol), and 0.034 g of phenol (0.36 mmol). $[P(OPh)_2N]_8$ was obtained as colorless crystals. Crystals suitable for XRD were obtained by recrystallization from chloroform. Yield: 90%. Mp: 109−111 °C. ^{31}P NMR ($CDCl_3$) δ (ppm): −20.1(s). ^1H NMR ($CDCl_3$) δ 6.83 (d, 32 H) 6.91−6.98 (m, 48 H). ^{13}C NMR ($CDCl_3$) δ (ppm): 121.2(s), 123.8(s), 129.0(s), 152.0(s).

Synthesis of $[P(OPh)_2N]_9$. $[P(OPh)_2N]_9$ was synthesized using the same procedure as for $[P(OPh)_2N]_7$, but using 0.030 g of $[PCl_2N]_9$ (0.029 mmol), 0.060 g of KH (1.50 mmol), and 0.034 g of phenol (0.36 mmol). Yield: 87%. ^{31}P NMR ($CDCl_3$) δ (ppm): −21.2(s). ^1H NMR ($CDCl_3$) δ 6.79 (d, 36 H) 6.85−6.95 (m, 54 H). ^{13}C NMR ($CDCl_3$) δ (ppm): 121.2(s), 123.4(s), 128.7(s), 151.7(s).

RESULTS AND DISCUSSION

Synthesis and Spectral Characterization of Medium-Sized Ring $[PCl_2N]_m$. Mixtures of oligomeric $[PCl_2N]_m$ and $[Cl_3PN(PCl_2N)_rPCl_3^+]X^-$ (X = Cl or PCl_6) were prepared from the reaction of PCl_5 and NH_4Cl in refluxing

Table 1. Crystal Data and Structure Refinement for Monoclinic $[PCl_2N]_6$, $[P(OPh)_2N]_7$, $[PCl_2N]_8$, and $[P(OPh)_2N]_8$

parameter	Value/Remark			
	$[PCl_2N]_6$	$[P(OPh)_2N]_7$	$[PCl_2N]_8$	$[P(OPh)_2N]_8$
empirical formula	$Cl_{12}N_6P_6$	$C_{84}H_{70}N_7O_{14}P_7$	$Cl_{16}N_8P_8$	$C_{96}H_{80}N_8O_{16}P_8$
formula weight	695.28	1618.26	927.04	1849.44
temperature	100(2) K	100(2) K	100(2) K	100(2) K
wavelength	0.71073 Å	0.71073 Å	1.54178 Å	0.71073 Å
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*Cc*	*P*2(1)2(1)2(1)	*C*2/*c*	*P*2(1)/*c*
unit-cell dimensions	18.5934(7) Å	13.3660(5) Å	24.8803(15) Å	11.6548(16) Å
a				
b	10.5874(4) Å	18.0227(7) Å	6.1382(5) Å	25.761(3) Å
c	23.5344(9) Å	31.6490(12) Å	20.3292(15) Å	14.643(2) Å
β	112.095(2)°		111.114(5)°	94.047(5)°
volume	4292.6(3) $Å^3$	7624.0(5) $Å^3$	2896.2(4) $Å^3$	4385.5(10) $Å^3$
Z	8	4	4	2
density (calculated)	2.152 Mg/m^3	1.410 Mg/m^3	2.126 Mg/m^3	1.401 Mg/m^3
absorption coefficient	1.997 mm^{-1}	0.235 mm^{-1}	18.267 mm^{-1}	0.233 mm^{-1}
F(000)	2688	3360	1792	1920
crystal size	0.23 mm × 0.14 mm × 0.11 mm	0.31 mm × 0.20 mm × 0.08 mm	0.41 mm × 0.01 mm × 0.01 mm	0.15 mm × 0.08 mm × 0.04 mm
theta range for data collection	3.52°–27.30°	1.30°–28.31°	3.81°–65.78°	1.58°–27.30°
index ranges	$-23 \leq h \leq 18$, $-13 \leq k \leq 11$, $-29 \leq l \leq 30$	$-16 \leq h \leq 17$, $-23 \leq k \leq 24$, $-42 \leq l \leq 42$	$-28 \leq h \leq 28$, $-7 \leq k \leq 7$, $-23 \leq l \leq 16$	$-15 \leq h \leq 15$, $-33 \leq k \leq 20$, $-18 \leq l \leq 18$
reflections collected	13073	99054	7237	37504
independent reflections	8609 [*R*(int) = 0.0262]	18909 [*R*(int) = 0.0550]	2367 [*R*(int) = 0.0594]	9867 [*R*(int) = 0.1546]
completeness to θ = 28.31°	99.8%	99.8%	93.8%	99.9%
absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
maximum and min inum transmissions	0.8058 and 0.6512	0.9815 and 0.9308	0.8243 and 0.0506	0.9919 and 0.9668
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
number of data/ restraints/ parameters	8609/2/433	18909/0/1009	2367/0/145	9867/0/577
goodness-of-fit on F^2	1.018	1.034	1.025	1.113
final *R* indices [$I > 2\text{sigma}(I)$]	*R*1 = 0.0247, *wR*2 = 0.0516	*R*1 = 0.0368, *wR*2 = 0.0727	*R*1 = 0.0557, *wR*2 = 0.1385	*R*1 = 0.0705, *wR*2 = 0.0891
R indices (all data)	*R*1 = 0.0275, *wR*2 = 0.0526	*R*1 = 0.0523, *wR*2 = 0.0771	*R*1 = 0.0681, *wR*2 = 0.1489	*R*1 = 0.1932, *wR*2 = 0.1120

Table 1. continued

parameter	Value/Remark			
	$[PCl_2N]_6$	$[P(OPh)_2N]_7$	$[PCl_2N]_8$	$[P(OPh)_2N]_8$
absolute structure parameter	0.02(5)	−0.01(4)		
largest diff peak and hole	0.373 and −0.325 e $Å^{-3}$	0.304 and −0.370 e $Å^{-3}$	0.900 and −0.829 e $Å^{-3}$	0.388 and −0.486 e $Å^{-3}$

chlorobenzene (Scheme 1). The following separation methods were chosen such that the temperature did not exceed ~100 °C, because it has been suggested that ring−ring conversions, such as interconversion of $[PCl_2N]_3$ and $[PCl_2N]_6$, can occur above 100 °C.[5a,29] After $[PCl_2N]_3$ and $[PCl_2N]_4$ were largely removed by sublimation at 60 °C under vacuum, the residue was extracted with hexane in order to isolate the mixed $[PCl_2N]_m$ rings from the insoluble $[Cl_3PN(PCl_2N)_rPCl_3^+]X^-$. At this point, the mixture of $[PCl_2N]_m$ rings can be stored in dry air for long periods. Whereas sublimation and recrystallization are popular techniques for purification of $[PCl_2N]_3$ and $[PCl_2N]_4$, they are less useful in separating the higher $[PCl_2N]_m$ rings from each other. We decided to test reports that state that the separation of the higher $[PCl_2N]_m$ rings can be done via thin-layer chromatography (TLC) on silica (hydrocarbon elutants),[30] despite a report that suggests that surface silanol groups could displace Cl atoms in the rings, leading to covalent binding to the surface of the silica.[31] We found that both TLC and column chromatography on silica with pure heptane eluent of the mixture of higher $[PCl_2N]_m$ rings can be used to isolate $[PCl_2N]_5$, $[PCl_2N]_6$, $[PCl_2N]_7$, $[PCl_2N]_8$, and $[PCl_2N]_9$ in air. Instead of heptane, hexanes also can be used as an elutant, but the separation is not as good, with no separation of $[PCl_2N]_4$ and $[PCl_2N]_5$. According to NMR, MS and X-ray crystallographic data, which will be described below, the $[PCl_2N]_m$ (m = 5−9) rings eluted in order of molecular weight, with the smallest ring coming off first. Several reports indicate that Scheme 1 produces cyclic oligomeric chlorophosphazenes that are larger than dodecamers.[32] Further elution of the column with heptane and then toluene gave materials of higher molecular weights but in quantities too small for complete characterization. Some decomposition was evident because a yellow band of material remained on the column.

The crude product mixture from Scheme 1 appears to contain acidic impurities, and the polymer $[PCl_2N]_n$ develops acidic impurities upon storage.[33] We have observed significantly greater air sensitivity when the rings $[PCl_2N]_m$ are impure; this may be due to the presence of the more air-sensitive $[Cl_3PN(PCl_2N)_rPCl_3^+]X^-$ or acidic impurities. Upon long-term storage of the impure higher rings in air, degradation begins to occur, as evidenced by the presence of $POCl_3$, H_3PO_4, and related impurities (by ^{31}P NMR spectroscopy[34]). Sublimation or filtration through a pad of silica are effective methods to remove any acidic impurities or $[Cl_3PN(PCl_2N)_rPCl_3^+]X^-$ that may be present. Therefore, the success of the column chromatography may be due, in part, to the destruction of some impurities by the silica. Although the purified medium-sized rings are fairly stable to air (~1−2 months), we recommend that they be stored under a dry gas to eliminate any degradation.

Previous reports of ^{31}P chemical shifts for the medium-sized cyclics $[PCl_2N]_m$ are unclear and several reports are contradictory,[19,35] which includes incorrect assignments by our group based on ^{31}P DOSY NMR spectroscopy.[36] Because the chromatography allowed us to isolate each species and confirm its identity with MS and X-ray crystallography (see below), the ^{31}P NMR chemical shifts now can be assigned unambiguously. Figure 1 shows the ^{31}P NMR spectrum of each isolated cyclic $[PCl_2N]_m$ in order of elution from the chromatographic column. The ^{31}P chemical shifts were assigned as follows: $[PCl_2N]_5$ at −15.1 ppm, $[PCl_2N]_6$ at −15.3 ppm, $[PCl_2N]_7$ at −17.0 ppm, $[PCl_2N]_8$ at −17.7 ppm, and $[PCl_2N]_9$ at −17.7 ppm. The ^{31}P chemical shift moves upfield as the ring gets

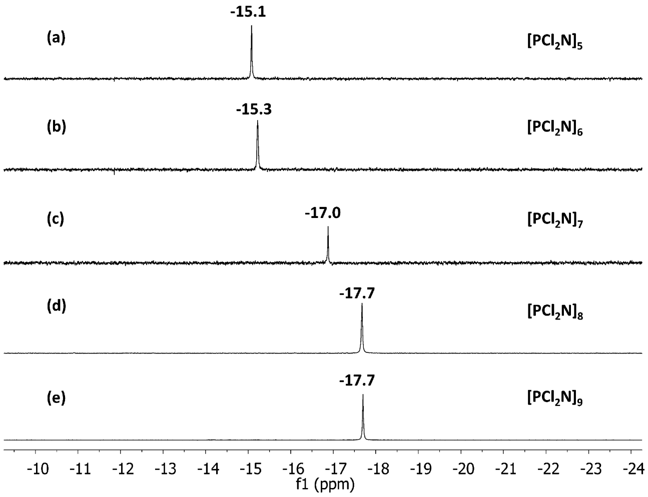

Figure 1. ^{31}P NMR spectra of (a) the cyclic pentamer $[PCl_2N]_5$, (b) the cyclic hexamer $[PCl_2N]_6$, (c) the cyclic heptamer $[PCl_2N]_7$, (d) the cyclic octamer $[PCl_2N]_8$, and (e) the cyclic nonamer $[PCl_2N]_9$, in order of elution from a silica gel column.

larger, but it levels off for the higher rings. This general trend is also observed for the rings $[P(OPh)_2N]_m$[37] and largely for $[PMe_2N]_m$ and $[PF_2N]_m$.[14g,38] The reassigned resonances of $[PCl_2N]_m$ offer evidence that $[PCl_2N]_8$ and $[PCl_2N]_9$ behave most similarly to the high-molecular-weight polymer $[PCl_2N]_n$ in solution, because the ^{31}P chemical shifts for the three substances are virtually identical.

When several cyclic chlorophosphazene species are present in a sample, integration of ^{31}P NMR spectra has been used to quantify the relative amount of each ring present.[5,35,39] However, strained $[PCl_2N]_3$ and $[PCl_2N]_4$ would be expected to have longer relaxation times than the unstrained larger rings. A spin−lattice relaxation time (T_1) ^{31}P NMR spectroscopy experiment for a sample of purified rings $[PCl_2N]_m$ ($m = 3−9$) in $CDCl_3$ was completed and these data are shown in the Supporting Information. The relaxation delay value is the minimum relaxation delay time required to obtain accurate integration values, and it is five times the largest T_1 value. $[PCl_2N]_4$ has the longest relaxation time at 14.0 s. The T_1 value for the remaining rings decreases as the rings increase in size: $[PCl_2N]_3$, 13.4 s; $[PCl_2N]_5$, 11.2 s; $[PCl_2N]_6$, 8.2 s; and $[PCl_2N]_7$, 7.8 s. The unresolved signal for $[PCl_2N]_8$ and $[PCl_2N]_9$ relaxes with the shortest T_1 value of 3.2 s. Therefore, for accurate quantification of mixtures of $[PCl_2N]_m$ ($m = 3−9$), a relaxation delay time of 70 s ($5T_1$ of $[PCl_2N]_4$) is required, which drastically lengthens the time required to obtain a spectrum. Based on several runs of the reaction in Scheme 1, ^{31}P NMR spectra that are integrated without the proper relaxation delay can result in great overestimation of the yields of the higher $[PCl_2N]_m$ ($m > 5$). All integrations reported in this paper were run with a 70-s delay.

There are some important ramifications that result from the above NMR studies. The reassignment of ^{31}P NMR chemical shifts of the medium-sized rings indicates that some earlier mechanistic suggestions, with regard to the process in Scheme 1, may be in error. Because of the similarity of the T_1 values, reported relative quantities of $[PCl_2N]_3$ to $[PCl_2N]_4$ obtained from the integrations of ^{31}P NMR spectra are relatively accurate, irrespective of the relaxation delay that was used to obtain the spectrum. However, the relative quantities of the medium-sized rings compared to those of $[PCl_2N]_3$ or $[PCl_2N]_4$ are exaggerated, unless a long relaxation delay was used. To the best of our knowledge, this was not done in earlier studies.

Except for an ESI-MS study of $[PCl_2N]_3$,[40] several decades have passed since the last report of the characterization of chlorophosphazene rings by mass spectrometry.[41] For this reason, and to obtain unambiguous NMR assignments, the samples used for NMR characterization were further diluted and characterized by high-resolution electrospray ionization mass spectrometry (ESI-MS). A few ions were observed from the various $[PCl_2N]_m$ in the positive ESI mode, but these data were less useful than data obtained in the negative mode. As an example, Figure 2 shows the high-resolution ESI spectrum of the $[PCl_2N]_7$ in the negative ion mode. The highest mass signal arises from addition of one electron to neutral $[PCl_2N]_7$ to give the radical anion $[PCl_2N]_7^-$. The next highest mass signal at 18.97 Da lower mass has been assigned as the monooxygenated heptamer $[P_7Cl_{13}N_7O]^-$, which arises by displacement of one Cl atom of $[PCl_2N]_7^-$ by an O atom, whose source presumably would be water. The third signal at 34.97 Da lower mass from that of $[PCl_2N]_7^-$ is formed by loss of a Cl atom and is assigned to $[P_7Cl_{13}N_7]^-$. All isolated $[PCl_2N]_m$ rings ($m = 5−9$) showed $[P_mCl_{2m}N_m]^-$, $[P_mCl_{2m-1}N_mO]^-$, and $[P_mCl_{2m-1}N_m]^-$ species in the negative mode ESI-MS (see the Supporting Information) as the predominant species. This observation suggests that no ring−ring equilibrium occurs in the gas phase with any of the isolated cyclics, even under high-energy conditions, and suggests that the medium-sized cyclic oligomers have a relatively high level of stability toward ionization. All the signals observed for $[PCl_2N]_m$ rings ($m = 5−9$) in the negative ESI mode showed the expected isotope distributions (error between 3−15 ppm).

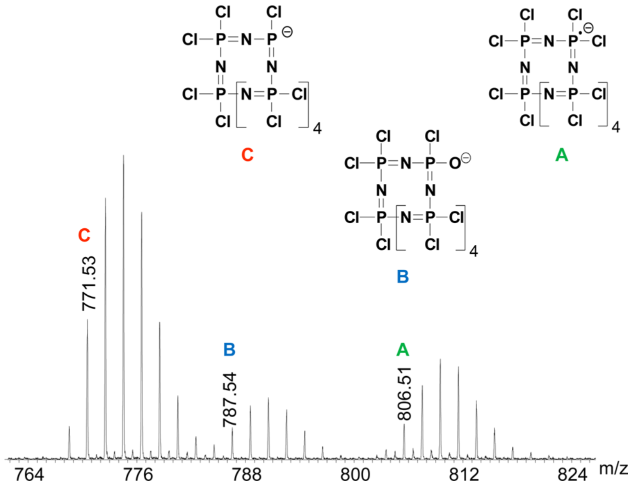

Figure 2. Negative-ion mode, ESI mass spectrum of the cyclic heptamer $[PCl_2N]_7$. The cyclics $[PCl_2N]_m$ (m = 5, 6, 8, 9) show similar product ion patterns, and their spectra can be found in the Supporting Information.

Single-Crystal X-ray Diffraction Studies of $[PCl_2N]_m$ or Their Derivatives. Crystallographic data were collected for $[PCl_2N]_3$, as well as both forms of $[PCl_2N]_4$, $[PCl_2N]_5$, $[PCl_2N]_6$, $[PCl_2N]_8$, $[P(OPh)_2N]_7$, and $[P(OPh)_2N]_8$. The structures of the first three are known,[15−17] but they were redetermined in order to make comparisons of crystal structures obtained under the same conditions and with structures that have better R-values (see the Supporting

Information). Crystal data and structure refinement parameters for $[PCl_2N]_6$, $[PCl_2N]_8$, $[P(OPh)_2N]_7$, and $[P(OPh)_2N]_8$ are shown in Table 1, and complete lists of bond lengths and angles can be found in the Supporting Information. The crystal structure of $[PCl_2N]_6$ was particularly challenging to obtain. An orthorhombic form of $[PCl_2N]_6$, known since 1897, and two triclinic forms of $[PCl_2N]_6$ had been reported, but none of the crystal structures had been solved.[18,19] Initially, triclinic crystals of $[PCl_2N]_6$ were obtained that had a unit cell that was the same as that reported by Paddock and co-workers.[19] Our efforts to solve the triclinic structure were unsuccessful, because of high thermal motion of the Cl and N atoms even at low temperatures. In order to obtain a derivative, $[PCl_2N]_6$ was treated with HCl/$SbCl_5$. NMR data showed that the protonation reaction was successful. However, the protonated crystals degraded in the glovebox over a week and monoclinic crystals of $[PCl_2N]_6$ were obtained.[42] The structure of the monoclinic crystals of $[PCl_2N]_6$ was solved, over a century after the first reported unit cell! Crystals of $[PCl_2N]_8$ were solved in the same unit cell as that reported by Paddock in 1960.[19] We looked for the possibility of two crystalline forms for $[PCl_2N]_8$, because the ring has an unusual shape (see below) but did not find a second form. Because $[PCl_2N]_7$ and $[PCl_2N]_9$ are oils at room temperature, their phenoxide derivatives were prepared by reaction with excess KOPh. Only the crystals of $[P(OPh)_2N]_7$ were suitable for X-ray diffraction. The derivative $[P(OPh)_2N]_8$ was made from $[PCl_2N]_8$ to provide an additional example for a study on how the crystal structure of octameric rings is related to the substituent (see below).

The thermal ellipsoid plot of one of the two molecules of monoclinic $[PCl_2N]_6$ is shown in Figure 3, and selected bond distances and angles are given in Tables 2 and 3. The overall shapes of the two molecules are similar, but there are slight differences in the structural parameters of the two rings. Halogen bonding interactions may be responsible for the slight differences (see below). Although the average P−N distances in the two rings are similar (1.566 Å vs 1.567 Å), there are significant differences in the ranges of distances [1.561(3)−1.575(3) Å vs 1.556(3)−1.583(3) Å]. The nonplanar, bowl-shaped molecules of $[PCl_2N]_6$ have rather differently shaped rings than the double tub structures of $[P(OMe)_2N]_6$[43] and $[PMe_2N]_6$[14d] but are similar to one of the two structural isomers of the 12-membered ring of the thionyl phosphazene $[(PCl_2N)_2SOClN]_4$.[44]

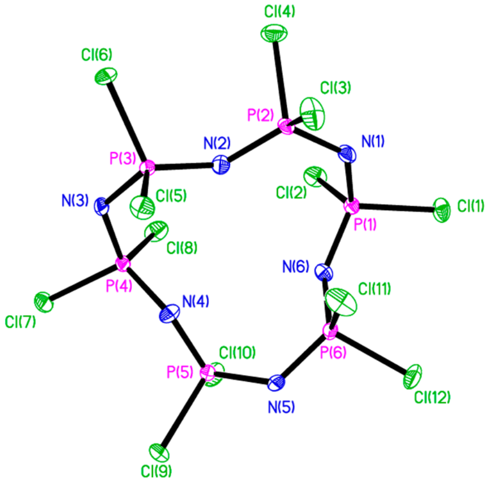

Figure 3. Thermal ellipsoid plot of one of the two molecules of the crystal structure of $[PCl_2N]_6$ drawn at the 50% probability level.

The thermal ellipsoid plot of the crystal structure of $[PCl_2N]_8$ is shown in Figure 4, and selected bond distances and angles are given in Tables 2 and 3. The ring is elongated and is nearly planar. This ring shape is rather different from those observed for the crystal structures of other octameric phosphazene rings,[14f,45,46] including that of $[P(OPh)_2N]_8$ (see Figure 7 below). Some of the larger P−N distances are statistically different from the smaller ones, but there is no alternating or other pattern to the different lengths, including whether the bond is part of the more linear segment of the ring or at the bent ends, which will be referred to as the kinks.

Average bond lengths and angles for the crystallographically characterized $[PCl_2N]_m$ ($m = 3-6, 8$) rings are shown in Tables 2 and 3, respectively. The P−N bond distances (Table 2) are toward the longer end of the range of distances characteristic of cyclophosphazenes and polyphosphazenes (1.47−1.62 Å).[47] With the exception of $[PCl_2N]_6$, the P−N bond lengths become shorter as the cyclics become larger. This correlates with the observation that the larger rings have little or no ring strain and thereby more idealized bonding between P and N may occur. Except for $[PCl_2N]_3$, the average N−P−N angle decreases as the ring size increases. No clear trend in the average P−N−P angle and the size of the ring was observed, and the average Cl−P−Cl and N−P−Cl angles vary little with ring size. Interesting trends are observed from the ranges of particular angles for the cyclic oligomers. Consistent with the expectation that the larger rings are more flexible than the smaller homologues, the range of N−P−N angles is ∼0° for $[PCl_2N]_3$ and $[PCl_2N]_4$ (boat), ∼2° for $[PCl_2N]_4$ (chair), ∼4° for $[PCl_2N]_5$, ∼6°$[PCl_2N]_6$, and ∼6° for $[PCl_2N]_8$. However, this trend is not observed for the P−N−P angle. The P−N−P angles are highly variable in $[PCl_2N]_5$ and $[PCl_2N]_6$ and are in the range of 22° and ∼18°, respectively. In contrast, the range of P−N−P angles is ∼10° for $[PCl_2N]_8$ and ∼7° for $[PCl_2N]_4$ (chair), and the range for either $[PCl_2N]_3$ or $[PCl_2N]_4$ (boat) is <1°.

The crystal structure of highly stretched fibers of the polymer $[PCl_2N]_n$ has been reported by two different groups.[21,22] Because one structure determination had problems with disorder or crystal twinning, bond distances and angles from the better-resolved structure are given in Tables 2 and 3. The structural parameters for $[PCl_2N]_n$ are most similar to those of the larger rings, especially to those of $[PCl_2N]_8$. In contrast to the structure of $[PCl_2N]_n$,[22] no significant alternation in the length of the P−N bonds is observed for either $[PCl_2N]_6$ or $[PCl_2N]_8$.

In the crystal structures of the homologous series $[PCl_2N]_m$ ($m = 3-6, 8$), two different types of halogen bonds are observed: P−Cl···Cl and P−Cl···N. The halogen bonding interactions of each ring can be seen in Figure 5, and their distances and the number per molecule are given in Table 4. The distances in the halogen bonds fall within the sum of the van der Waals radii, which are 3.6 and 3.3 Å for P−Cl···Cl and P−Cl···N interactions, respectively. P−Cl···Cl halogen bonds are consistently observed in all the rings, but the P−Cl···N halogen bond is only observed for $[PCl_2N]_3$, $[PCl_2N]_5$, and $[PCl_2N]_6$. The shortest P−Cl···Cl interactions are found in $[PCl_2N]_6$, whereas the shortest P−Cl···N interactions are found in $[PCl_2N]_3$. Halogen bonding is most prevalent in monoclinic $[PCl_2N]_6$, where 12 or 14 separate interactions occur with the two forms and least prevalent in the chair form of $[PCl_2N]_4$. It

Table 2. Average Bond Lengths and Ranges in $[PCl_2N]_m$ (m = 3–6, and 8) and $[PCl_2N]_n$[22]

	average P–N distance (range, Å)	average P–Cl distance (range, Å)
$[PCl_2N]_3$	1.58092 [1.5794(17)–1.5818(17)]	1.9920 [1.9875(7)–1.9961(11)]
$[PCl_2N]_4$ (boat)	1.5710 [1.5710(12)–1.5711(12)]	1.9952 [1.9951(7)–1.9952(6)]
$[PCl_2N]_4$ (chair)	1.565 [1.561(2)–1.570(2)]	1.997 [1.9902(9)–2.0028(9)]
$[PCl_2N]_5$	1.5584 [1.547(3)–1.568(3)]	1.9980 [1.9889(12)–2.0068(12)]
$[PCl_2N]_6$	1.567 [1.556(3)–1.583(3)]	1.9987 [1.9870(12)–2.0097(12)]
$[PCl_2N]_8$	1.555 [1.544(5)–1.564(5)]	2.002 [1.993(2)–2.0109(19)]
$[PCl_2N]_n$[a]	1.56 [1.44, 1.67]	2.01 [1.97, 2.04]

[a] Values taken from ref 22.

Table 3. Bond Angles of $[PCl_2N]_m$ (m = 3–6, and 8) and $[PCl_2N]_n$[a]

	N–P–N avg. (range, deg)	P–N–P avg. (range, deg)	Cl–P–Cl avg. (range, deg)	N–P–Cl avg. (range, deg)
$[PCl_2N]_3$	118.38 [118.34(12)–118.41(10)]	121.20 [120.98(15)–121.41(11)]	101.75 [101.40(4)–102.09(3)]	108.74 [108.12(9)–109.27(7)]
$[PCl_2N]_4$ (chair)	120.20 [119.21(13)–121.18(13)]	134.70 [131.12(14)–138.27(15)]	103.38 [103.21(4)–103.55(4)]	107.97 [105.10(8)–111.15(9)]
$[PCl_2N]_4$ (boat)	120.46 [120.46(8)]	130.91 [130.91(8)]	103.19 [103.19(2)]	107.97 [105.02(5)–111.89(5)]
$[PCl_2N]_5$	117.43 [115.49(14)–119.93(15)]	140.3 [129.92(17)–152.0(2)]	102.49 [100.99(5)–103.56(5)]	108.95 [105.05(11)–112.28(12)]
$[PCl_2N]_6$	116.84 [114.72(15)–120.77(14)]	133.79 [123.61(16)–141.30(19)]	102.53 [101.71(6)–103.59(5)]	109.12 [104.74(10)–112.62(11)]
$[PCl_2N]_8$	114.5 [111.7(2)–117.5(2)]	138.3 [133.9(3)–143.1(3)]	101.46 [101.11(9)–102.26(8)]	110.0 [107.4(2)–111.8(2)]
$[PCl_2N]_n$[a]	115	131	99	110[b] [108–113][b]

[a] Values taken from ref 22. [b] Values calculated from data reported in ref 22.

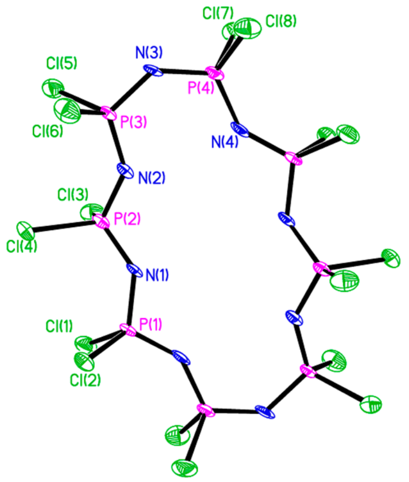

Figure 4. Thermal ellipsoid plot of the cyclic octamer $[PCl_2N]_8$ drawn at the 50% probability level.

is interesting to note that the more favored boat conformation of $[PCl_2N]_4$ shows four halogen bonds per molecule, whereas the less stable chair form only has two. The boat form of $[PCl_2N]_4$ has longer average P–N bonds than the chair form, whereas the $[PCl_2N]_6$ ring with the larger number of interactions also has the greater range of P–N distances within the ring. More intermolecular interactions would help to stabilize a crystal, and, therefore, halogen bonding appears to be responsible for the ranges in distances and angles and for the preference of a particular conformation in $[PCl_2N]_m$ rings. There was no clear correlation between any of the bond lengths and angles and the number of halogen bonds. The P–N framework of the various $[PCl_2N]_m$ rings may be flexible enough that each molecule could have several different ways of maximizing the number of halogen bonds. To probe these possibilities, it would be useful to have the P–N bond distances of $[PCl_2N]_4$ or $[PCl_2N]_6$ in the absence of halogen bonding. However, the available theoretical studies of $[PCl_2N]_4$ give a range of P–N bond distances of 1.545–1.614 Å,[48] depending on the method used in the calculation, and no studies could be found for $[PCl_2N]_6$. In the crystal structure of *stretched* fibers of polymeric $[PCl_2N]_n$, Cl⋯Cl contacts of 3.61, 3.72, 3.79, and 3.84 Å are observed that are equal to or longer than the sum of the van der Waals distances. Therefore, no halogen bonds are observed in *stretched* $[PCl_2N]_n$.[22]

The thermal ellipsoid plots of the structures of $[P(OPh)_2N]_7$ and $[P(OPh)_2N]_8$ are shown in Figures 6 and 7, respectively. There are intermolecular C–H⋯O and C–H⋯π interactions in both structures. Selected distances and angles are shown in Table 31 of the Supporting Information, and parameters for the crystal structures of $[P(OPh)_2N]_3$ and $[P(OPh)_2N]_4$ are included therein for comparison.[49] The shape of the P–N ring of $[P(OPh)_2N]_7$ has an irregular tublike conformation, in contrast to the spear-tip-shaped ring of $[PMe_2N]_7$.[14e] The P–N ring of $[P(OPh)_2N]_8$ has two fairly planar regions separated by a skewed step, somewhat like that of $[P(OMe)_2N]_8$[46] (see Figure 8 below). The bond distances for $[P(OPh)_2N]_8$ are similar to those of $[P(OPh)_2N]_7$, where the difference in average P–N, P–O, and O–C bond distances are all less than 0.008 Å. The difference for average bond angles are <2°. As with the chloro rings, the P–N distance of $[P(OPh)_2N]_m$ decreases as the ring becomes larger. The P–O bond distances are shorter than a P–O single bond, which has been attributed to partial double-bond character.[50]

Structural Comparisons among Phosphazene Octamers with Different Substituents. For historical and synthetic reasons, many discussions of phosphazenes begin with the chlorophosphazenes. This perspective gives the impression that chlorophosphazenes are the prototypical phosphazene. However, in several instances above, the P–N ring shape of medium-sized $[PCl_2N]_m$ is rather different than those of other phosphazenes. This suggests chlorophosphazenes may not be prototypical in terms of structure. Because there now are five crystallographically characterized octamers, $[PCl_2N]_8$, $[P(OPh)_2N]_8$, $[P(OMe)_2N]_8$,[46] $[P(NMe_2)_2N]_8$,[45] and $[PMe_2N]_8$,[14f] a comparison of their structures, including the

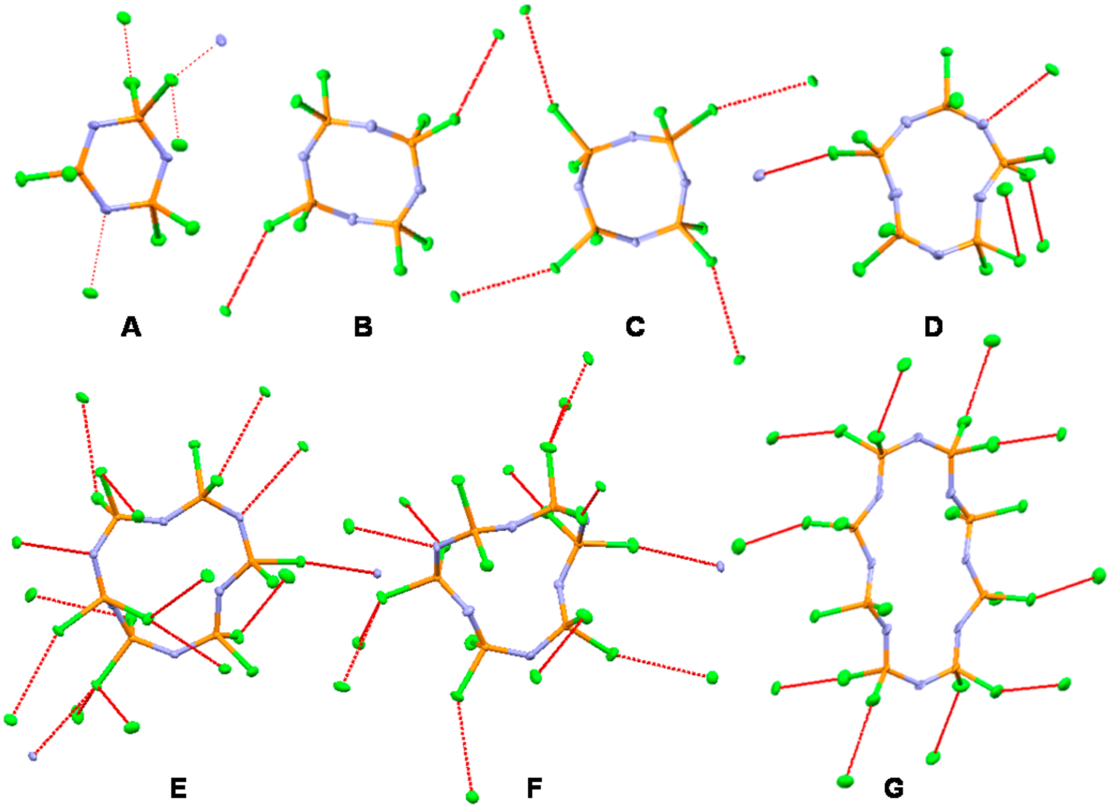

Figure 5. Halogen bonding (red dashed lines) in the crystal structures of $[PCl_2N]_3$ **A**, $[PCl_2N]_4$ (chair **B**) and (boat **C**), $[PCl_2N]_5$ **D**, $[PCl_2N]_6$ **E** and **F** (two molecules within the unit cell) and $[PCl_2N]_8$ **G**.

Table 4. Halogen Bond Distances from the Crystal Data for Cyclic $[PCl_2N]_m$

	P−Cl···Cl		P−Cl···N	
	number of contacts	avg. (range, Å)	number of contacts	avg (range, Å)
$[PCl_2N]_3$, **A**	2	3.453 (3.453)	2	3.141 (3.141)
$[PCl_2N]_4$ (chair), **B**	2	3.480 (3.480)		
$[PCl_2N]_4$ (boat), **C**	4	3.497 (3.497)		
$[PCl_2N]_5$, **D**	2	3.409 (3.409)	2	3.213 (3.213)
$[PCl_2N]_6$, **E**	10	3.427 (3.381−3.486)	4	3.267 (3.251−3.283)
$[PCl_2N]_6$, **F**	10	3.407 (3.291−3.486)	2	3.250 (3.250)
$[PCl_2N]_8$, **G**	10	3.414 (3.399−3.421)		

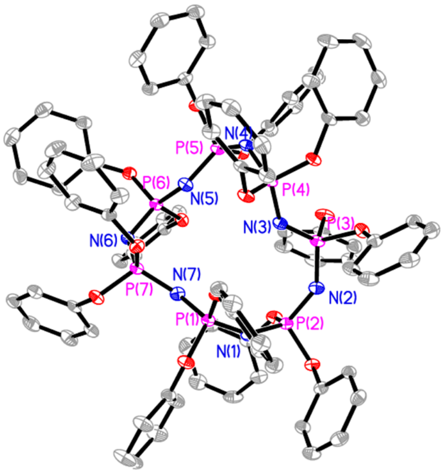

Figure 6. Thermal ellipsoid plot of $[P(OPh)_2N]_7$ drawn at the 50% probability level. Hydrogen atoms omitted for clarity.

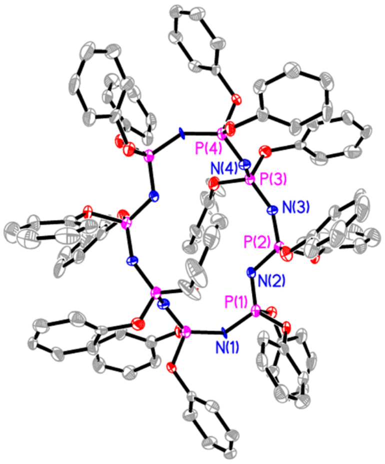

Figure 7. Thermal ellipsoid plot of $[P(OPh)_2N]_8$ drawn at the 50% probability level. Hydrogen atoms omitted for clarity.

Table 5. Conformations of the Ring P−N Bonds for Phosphazene Octamers[a]

	$[PCl_2N]_8$		$[P(OPh)_2N]_8$		$[P(OMe)_2N]_8$		$[PMe_2N]_8$		$[P(NMe_2)_2N]_8$	
	number of ω	range (deg)	number of ω	range (deg)	number of ω	range (deg)	number of ω	range (deg)	number of ω	range (deg)
S, SP	4	±0−12								
C			2	±31	4	±28−34	4	±28	4	±27−39
G			8	±50−61	4	±54−61	4	±61	2	±64
O					2	±79	4	±77	4	±79
D	6	±158−160	4	±154−157	2	±153	4	±157	4	±153−155
T	2	±167			4	±164−170				
A	4	±175−176	2	±177					2	±178

[a] Dihedral angles for $[P(OMe)_2N]_8$,[46] $[P(NMe_2)_2N]_8$,[45] and $[PMe_2N]_8$[14f] were determined from the CIF files associated with the references in the Cambridge Crystallographic Data Centre. The columns are arranged in order of increasing basicity.

configuration of the P−N chain in the ring, was undertaken. Selected distances and angles and a summary of intermolecular interactions for the five octamers are shown in Table 32 of the Supporting Information (Table SI32). Based on the trend observed for similarly substituted trimers,[51] the columns in Table SI32 (and in Table 5 and Figure 8 below) are arranged in order of increasing basicity, starting with the weakly basic $[PCl_2N]_8$ to highly basic $[P(NMe_2)_2N]_8$. This was done to aid in the discernment of electronic factors that may be involved in determining the structures of the octamers, which is a factor that has been considered by two theoretical studies of chlorophosphazenes.[52,53]

The average metrical parameters in Table SI32 in the Supporting Information for the five octameric rings show no clear dependence on the basicity of the nitrogen atom in the ring, electronegativity of the substituent, or sterics. Except for the structure of $[P(OMe)_2N]_8$, which has the largest estimated standard deviations, the longer and shorter P−N bond distances within each octameric ring are slightly different from one other. The most variable angle among the octamers is the P−N−P angle. However, the average P−N−P angles are all within 2° of 138°, except the angle for $[P(NMe_2)_2N]_8$ (156.5°). Perhaps this larger angle is caused by steric hindrance among substituents, but the next largest angle is for $[PMe_2N]_8$, which contains small substituents. The average N−P−N angle for $[PCl_2N]_8$ is 2°−4° less than the average angles of the other four octamers. The average N−P−N angle (within the ring) for the other octamers vary from each other by no more than a degree. The average N−P−X (X = substituent and N is within the ring) angles for the five octamers are similar and have a range of only 1.1°. The average X−P−X angles encompass a 3.6° range of values but the differences are not explained by simple steric or electronic arguments.

The shapes of the P−N rings and views perpendicular to the planes of the P−N rings for the five octamers are shown in Figure 8. The relative basicity of the ring nitrogen shows no discernible effect on the structure of the ring. As described above, $[PCl_2N]_8$ shows 10 Cl···Cl halogen bonds. The structures of $[P(OPh)_2N]_8$ (eight C−H···O and 11 C−H···π interactions) and $[P(OMe)_2N]_8$ (four CH···O interactions) show contacts between molecules that are shorter than the sum of the van der Waals radii. The most common shape of the P−N rings among the five octamers is a chairlike or step structure, in which there are two roughly planar regions of the ring. Both $[P(NMe_2)_2N]_8$ and $[P(OMe)_2N]_8$ have step structures and $[P(OPh)_2N]_8$ shows a twisted-step structure. A combination of steric interactions and intermolecular forces may be responsible for the distortions observed in $[P(OPh)_2N]_8$ from a more regular step structure. Of the five different substituents of the octamers, chloride and methyl are the smallest and they are roughly the same size.[54] $[PMe_2N]_8$ has a crown-like ring that is very different from the oblong, nearly planar ring in $[PCl_2N]_8$. The latter, approximately planar ring stands apart from the nonplanarity of the other four octameric rings. The only factor that seems to account for the unusual structure of $[PCl_2N]_8$ is halogen bonding.

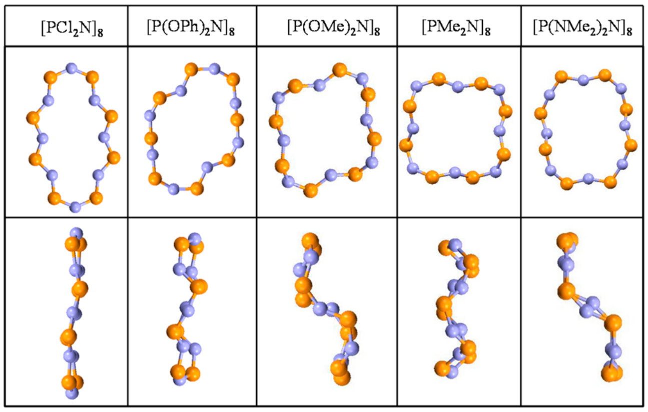

Figure 8. Two views of the P−N rings of $[PCl_2N]_8$, $[P(OPh)_2N]_8$, $[P(OMe)_2N]_8$, $[P(NMe_2)_2N]_8$, and $[PMe_2N]_8$ (P = yellow, N = blue). The top view is of the best planes of the rings. The bottom view is roughly perpendicular to the top view. The columns are arranged in order of increasing basicity of the ring N atom. The substituents have been removed for clarity. The drawings for $[P(OMe)_2N]_8$,[46] $[P(NMe_2)_2N]_8$,[45] and $[PMe_2N]_8$[14f] were generated from the CIF files associated with their references in the Cambridge Crystallographic Data Centre.

The shapes of the five octamers can be compared to those of nonphosphazene rings. As Paddock and co-workers have pointed out, the distinctive crown shape of $[PMe_2N]_8$ is similar that of $[SiMe_2O]_8$, but there are some subtle differences.[55] Unfortunately, the crystal structures of other appropriately substituted octameric siloxanes are not available to make further comparisons. Paddock also noted that the shape of the $[PMe_2N]_m$ (m = 7−12) rings are related to the shapes of the respective $[CH_2]_m$ hydrocarbons rings, especially for the even values of m. In these comparisons, each PMe_2N unit is being associated with a single CH_2 unit. Except for the shape of $[PCl_2N]_8$, the shapes of the other four phosphazene octamers are similar to those of the higher-energy structures $[CH_2]_8$.[56] There seems to be no agreement as to the most stable structures of $[CH_2]_{16}$, but a rectangular structure similar to that of $[PCl_2N]_8$ is a higher-energy form of $[CH_2]_{16}$ in some calculations.[57] The shape of $[SiMe_2]_{16}$ is different from any shape exhibited by the five octamers.[20]

Paddock and co-workers considered the conformations of several medium-sized $[PMe_2N]_m$ (m = 8, 9, 12) rings.[14f,g] However, the nomenclature system they used does not describe all the conformations of the five phosphazene octamers. Therefore, the Michl–West system (**A**, anti, $\omega \approx \pm180°$; **T**, transoid, $\omega \approx \pm165°$; **D**, deviant, $\omega \approx \pm150°$; **O**, ortho, $\omega \approx \pm90°$; **G**, gauche, $\omega \approx \pm60°$; **C**, cisoid, $\omega \approx \pm30°$; S, syn, $\omega \approx 0°$; **E**, eclipsed, $\omega \approx \pm120°$)[58] and one additional conformation (**SP**, syn-periplanar, $0° < \omega > \pm30°$[59]) will be used to describe the five octameric phosphazene rings in Table 5 (pie-chart representations are given in the graphical abstract and in Figure 14 of the Supporting Information). The structure of $[PCl_2N]_8$ has two very different types of torsion angles; large **D**, **T**, and **A** angles for the linear portion of the molecule and S and SP for the kinks. Once derivatized with organic functional groups, the **S** and **SP** conformations are no longer observed and there are fewer **D**, **T**, or **A** conformations. In their place, **C** and **G** conformations are observed for the four organo-octamers and **O** conformations are observed for all but $[P(OPh)_2N]_8$.

Does the above structural analysis of the five octamers provide insights into the structures of the polymeric phosphazenes? Unusual features in the structure of $[PCl_2N]_8$ include the nearly planar P–N ring, the conformations of the P–N bonds, and the large number of intermolecular interactions in the form of halogen bonding. The linear fragment of the $[PCl_2N]_8$ molecule is close to ideal all-trans(oid), a conformation that is so unlike those observed in the other four octamers and of most polymers. Most experiments and calculations on the structures of the polymers $[PCl_2N]_n$ (**C**: 31°, **A**: 175° for *stretched* fibers),[22] $[PMe_2N]_n$ (**S**: 2.39° and **A**: 174.1°),[60] $[P(OPh)_2N]_n$,[61] and other polyphosphazenes indicate that alternating cis–trans(oid) (**S**-**A**) or distorted cis–trans(oid) (**C**-**A**) conformations are the most stable.[62,63] The cis–trans conformation is favored because it minimizes steric interactions among the substituents on adjacent P atoms that are separated by a N atom that has no substituents. Interestingly, a molecular dynamics calculation of *unstretched* $[PCl_2N]_n$ indicates that, on average, the P–N chain contains segments of roughly three (2.7) P–N bonds in trans(oid) conformations that alternate with single cis–trans units and result in a globular structure.[53] This calculated structure shares some similarity to the pattern of conformations observed for the P–N bonds in the $[PCl_2N]_8$ ring. Each half of the ring can be described as two cis–trans P–N bonds separated by a segment of six trans(oid) P–N bonds. Therefore, the structure of $[PCl_2N]_8$, which appears to be stabilized by halogen bonds, may be a better model for the structure of *unstretched* rather than *stretched* $[PCl_2N]_n$. As mentioned earlier, no halogen bonds are observed in the crystal structure of *stretched* fibers of polymeric $[PCl_2N]_n$.[22] Because there is no compelling reason to believe that $[PCl_2N]_n$ would not form halogen bonds like other chlorophosphazenes, the lack of halogen bonds in *stretched* fibers of $[PCl_2N]_n$ could indicate that stretching ~8 times from the original length disrupted the halogen bonding in *unstretched* $[PCl_2N]_n$. If *unstretched* $[PCl_2N]_n$ is globular, then a constantly changing network of Cl⋯Cl halogen bonds may be present, somewhat reminiscent of the hydrogen-bonding network in liquid water. This could occur because each chloride can act as both an acid and a base in a halogen bond, and because there would be the possibility of many such interactions due to the high chlorine content. Lastly, the usefulness of the Michl–West notations for conformations[58] of the phosphazene octamers is notable and surprising. In contrast to phosphazenes, the polysilanes that inspired the Michl–West notations have two substituents at *every* chain atom and all-trans(oid) conformations are the more stable.

■ SUMMARY

Isolation of the individual medium-sized cyclic chlorophosphazenes $[PCl_2N]_m$ (m = 5–9) has been completed through a combination of separation techniques, where complete separation was accomplished via column chromatography. Each $[PCl_2N]_m$ has been characterized by ^{31}P NMR (chemical shifts and relaxation times), ESI-MS, and if possible by crystallographic data of it or a derivative. The crystal structures of all the $[PCl_2N]_m$ rings (m = 3, 4, 5, 6, 8) show that halogen bonding interactions are present and, for most of the rings, there are many interactions per ring. The conformations of the P–N bonds for five octameric phosphazene rings largely can be described by the Michl–West notations. The ring shape and conformations of nearly planar $[PCl_2N]_8$ are quite different from those of nonplanar $[P(OPh)_2N]_8$, $[P(OMe)_2N]_8$, $[PMe_2N]_8$, and $[P(NMe_2)_2N]_8$, and halogen bonding appears to be the major contributing factor in the differences. The data reported herein suggests that the medium-sized cyclic chlorophosphazene $[PCl_2N]_8$ is a good model compound for *unstretched* $[PCl_2N]_n$. The structures of chlorophosphazenes should not be considered as prototypical of other phosphazenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR and mass spectra, X-ray diffraction data for all crystal structures, a table of comparisons among phenoxy $[P(OPh)_2N]_m$ (m = 3, 4, 7, 8), and a figure showing comparisons among the five octameric phosphazene rings $[P(X)_2N]_8$ (X = Cl, OPh, OMe, NMe_2, Me). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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