

The Origin of Endocyclic Bond Length Variations in Disubstituted Cyclotriphosphazenes

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Intraannular ring alternation in heterogeneously substituted cyclotriphosphazenes is investigated using both *ab initio* and density functional methods. Comparisons of the calculated geometries for $N_3P_3X_6$ ($X = H, F, Cl, Me, Ph$) and $N_3P_3X_4Y_2$ ($X = F, Cl; Y = Me, Ph, X, Cl$) with experimental X-ray data establish the utility of the 6-31G* basis for use with both Hartree–Fock and the B3LYP and B3PW91 functionals. Analysis of orbitals and charges shows that the bonding is best described using a polarized bond model rather than the previous explanation of asymmetric nitrogen-lone-pair donation into the phosphorus–nitrogen bond.

Introduction

The nature of the bonding in the phosphazene ring has remained unsettled for years. The extent of conjugation through the ring, as well as the roles of hyperconjugation and d orbital participation, has been debated. The widely utilized “island” model¹ proposed by Dewar describes the bonding in three parts, a σ backbone of the ring and combinations of the p and d orbitals to form out-of-plane π and in-plane π' systems. This model proposes a buildup of electron density at the ring nitrogen atoms, with π - and π' -bonding nodes at the phosphorus atoms. The advent of widespread applications of *ab initio*^{2,3} and, more recently, density functional theory (DFT)⁴ to compounds containing second-row or heavier elements has led to extensive interest in applying these methods to the study of phosphazenes.^{5–9} This work has led to emphasis on alternative proposals,^{3,10} including the importance of polarized or ionic bonding as the primary mode and contributions from substituent lone pairs into P–N σ^* orbitals (negative hyperconjugation).¹¹

Table 1. Selected Geometrical Parameters for $P_3N_3R_6$

R	method	$r(P-N)$	$r(P-X)$	$\angle PNP$	$\angle NPN$	
F	calcd ^a	1.563	1.533	123.4	116.6	
		1.584	1.561	121.6	118.4	
		1.587	1.564	121.5	118.5	
Cl	exptl ²⁵	1.590	1.543	121.4	118.6	
		calcd ^a	1.577	2.001	123.8	116.2
			1.599	2.022	121.5	118.5
Me	calcd ^a	1.602	2.036	121.7	118.3	
		1.581	1.985	121.3	118.4	
		1.601	1.815	124.4	115.7	
Ph	exptl ²⁶	1.620	1.824	122.2	117.8	
		calcd	1.623	1.830	122.4	117.5
			1.605	1.809	112.6	116.8
Ph	exptl ²⁸	1.599	1.820	124.1	115.9	
		1.622 ^b	1.829 ^b	122.4 ^b	117.5 ^b	
		1.601	1.808	122.2	117.2	

^a Row 1, HF/6-31G*; row 2, B3PW91/6-31G*; row 3, B3LYP/6-31G*.
^b B3LYP/6-31G*.

Some years ago, X-ray diffraction studies of the mixed cyclophosphazene 2,2-diphenyl-4,4-tetrafluorocyclotriphosphazene¹² showed significant differences in the P–N bond lengths within the ring. The longest P–N bond length is at the diphenyl phosphorus atom; the adjacent intraannular bond is the shortest, and the length of the bonds to the nitrogen opposite the ring from the diphenyl phosphorus atom is intermediate between the two. This pattern of bond length alternation has proved to be general for geminal disubstituted cyclophosphazene derivatives.^{13,14} At the time, the results were explained as a consequence of favorable competition

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- (1) Dewar, M. J. S.; Lucken, E. A. C.; Whitehead, M. A. *J. Chem. Soc.* **1960**, 2423.
- (2) Magnussen, E. *J. Am. Chem. Soc.* **1993**, *115*, 1051.
- (3) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339.
- (4) Cotton, F. A.; Cowley, A. H.; Fenj, X. *J. Am. Chem. Soc.* **1998**, *120*, 1795.
- (5) Trinquier, G. *J. Am. Chem. Soc.* **1986**, *108*, 568.
- (6) Haddon, R. C. *Chem. Phys. Lett.* **1985**, *120*, 372.
- (7) Ferris, K. F.; Friedman, P.; Friedrich, D. M. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1988**, 207.
- (8) Breza, M.; Biskupič, S. *THEOCHEM* **1994**, *309*, 305.
- (9) Manners, I. *Coord. Chem. Rev.* **1994**, *137*, 109.
- (10) Magnussen, E. *J. Am. Chem. Soc.* **1993**, *115*, 1051.

- (11) Chaplin, A. B.; Harrison, J. A.; Dyson, P. J. *Inorg. Chem.* **2005**, *44*, 8407.
- (12) Allen, C. W.; Faught, J. B.; Moeller, T.; Paul, I. C. *Inorg. Chem.* **1969**, *8*, 1719.

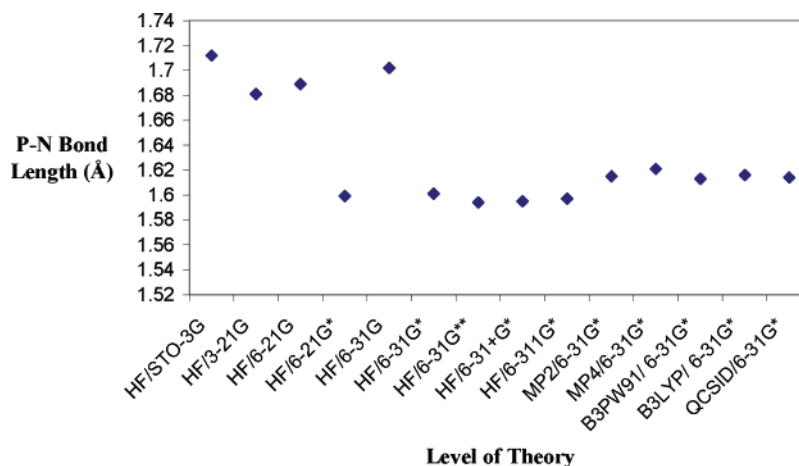


Figure 1. Intraannular bond length of $P_3N_3H_6$ calculated at levels of theory.

of the fluorinated phosphorus atoms over the phenylated phosphorus atoms for the nitrogen lone pairs, leading to more double bond character between the nitrogen and the phosphorus atoms with fluorine substituents and more single bond character between the phenyl-substituted phosphorus atom and its ring neighbors. The P–N bonds between the two PF_2 centers would equally share nitrogen lone pairs.

Research in our group has included interest in the use of spectroscopic¹⁵ and computational^{16,17} methods for problems of electronic structure and reactivity in cyclophosphazene chemistry. Previous and recent computational studies^{5–9,11} have focused exclusively on persubstituted cyclophosphazenes. In this paper, we probe the validity of the preferential donation of the endocyclic lone-pair hypothesis using modern calculation methods to examine disubstituted cyclophosphazene derivatives.

Computational Details

The compounds were modeled using the Gaussian¹⁸ suite of programs using standard desktop PC computers. Computations were also run on a cluster of Power Macs with dual processors (head node: 2GHz G5 XServe, 1 GB RAM; 4 cluster nodes: dual 2GHz G5 XServe, 1 GB RAM; 2.3 Tb XServe RAID). Unless otherwise noted, calculations consisted of geometry optimizations followed by orbital analysis, including natural bond order calculations. Geometries were validated by a frequency analysis, with the

assessment of six zero-normal modes authenticating the presence of a structural energy minimum. Structures were not symmetry constrained in the geometry optimizations. As is typically noted in computational studies, with a larger basis set and a more sophisticated model, the calculations better approach experimental values. It is important to use d orbitals for phosphorus, as it significantly improves the molecular geometry. Even split valence basis sets perform poorly unless polarization functions are included on the heavy atoms. Omission of d orbitals also leads to a nonplanar ring geometry. Further splitting of the valence orbitals does not change the geometry significantly; there was less than 0.01 Å difference in the P–N distances when the basis set was improved from 6-31G* to 6-311G*, in contrast with the 0.1 Å difference between the results of 6-31G and 6-31G* (addition of heavy-atom d orbitals) calculations. Addition of diffuse orbitals (6-31+G* basis) or hydrogen p orbitals (6-31G**), likewise, resulted in only a small alteration to the bond length. Nonlocal density functional calculations using the most commonly used functionals, B3PW91 or B3LYP, yielded geometries in good agreement with the Møller–Plesset (ab initio perturbation theory) procedure, while they required approximately half of the computational time. As shown in the Supporting Information (Table S1), our results are comparable with those previously published in the literature.

Results and Discussion

Basis set effects were investigated on the simple hypothetical model system, hexahydrocyclophosphazene ($P_3N_3H_6$). Selected geometrical values for each level of theory are shown in the Supporting Information (Table S1), along with the corresponding values found in previous computational studies. The variation in the P–N intraannular bond length with basis sets is displayed in Figure 1, which shows that, above the 6-31G* level, only incremental variations are noted. This convergence of computed and experimental parameters over a more limited range of levels of theory is shown for the structurally characterized species $P_3N_3X_6$ ($X = F, Cl, Me, Ph$) in Table 1. A wider range of calculated parameters may be found in the Supporting Information (Tables S2 and S3). The results for the persubstituted halogen and methyl derivatives are consistent with previous calculations.¹¹ The calculations for the organophosphazenes, N_3P_3 -

- (13) Allen, C. W. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haidue, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 2, Chapter 20, p 501.
- (14) (a) Allen, C. W. In *Organophosphorous Chemistry*; Royal Society of Chemistry: London, 1986–1997; Vols. 16–28. (b) van de Grampel, J. In *Organophosphorous Chemistry*; Royal Society of Chemistry: London, 1998–2005; Vols. 29–34.
- (15) Allen, C. W.; Worley, S. D. *Inorg. Chem.* **1999**, *38*, 5187.
- (16) Calichman, M.; Hernandez-Rubio, D.; Allen, C. W. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 1811.
- (17) Freund, A. S.; Calichman, M.; Allen, C. W. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2059.
- (18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

- (19) Allen, C. W. Unpublished observations.

Table 2. Selected Internuclear Distances for $P_3N_3X_4R_2^a$

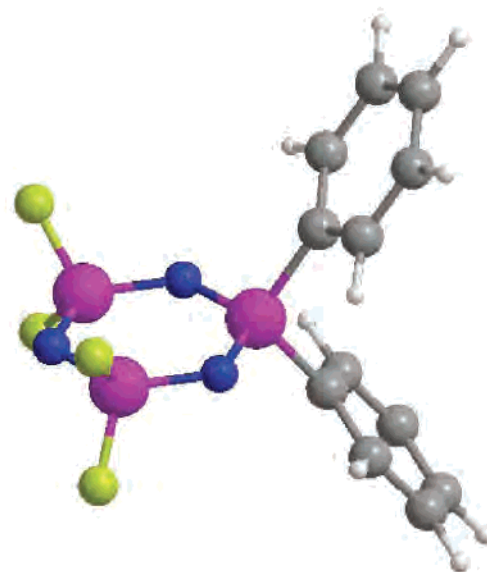
X	R	method	P_2N_1	P_6N_1	P_6N_5	PR	PX
F	Me	calcd ^b	1.612	1.552	1.567	1.804	1.541
			1.631	1.573	1.587	1.809	1.571
		exptl ²⁹	1.601	1.552	1.560	1.77	1.525
F	Ph	calcd ^c	1.611	1.552	1.566	1.806	1.542
			1.631	1.573	1.587	1.808	1.571
		exptl ¹²	1.617	1.539	1.558	1.789	1.527
Cl	Ph	calcd ^c	1.612	1.561	1.579	1.807	2.013
			1.687	1.585	1.604	1.814	2.053
		exptl ³⁰	1.615	1.555	1.578	1.788	1.998
Cl	F	calcd ^d	1.585	1.597	1.599	2.020	1.563
F	Cl	calcd ^d	1.598	1.585	1.583	2.019	1.562

^a Phosphorus atom in PR₂ is P₂ with N₁, N₃ adjacent nitrogen atoms.
^b Row 1, HF/6-31G*; row 2, B3PW91/6-31G*. ^c Row 1, HF/6-31G*; row 2, B3LYP/6-31G*. ^d B3PW91/6-31G*.

Ph₆, have not previously been reported. These data show the predictive power of computational approaches using only desktop or small cluster computers for the structure of cyclophosphazenes with large and electronically complex substituents.

With the establishment of the level of theory most effective in balancing accuracy and computational efficiency for homogeneously substituted cyclotriphosphazenes, the question of structure and bonding in the heterogeneously substituted systems could be addressed. A simple species with known structural parameters, 2,2-dimethyl-4,4,6,6-tetrafluorocyclophosphazene $P_3N_3F_4Me_2$, was investigated. The relevant computed and experimental internuclear distances are summarized in Table 2. The calculations not only reproduce the systematic bond length alternations common to geminally substituted cyclophosphazenes but also provide reasonable approximations of the observed bond lengths. In fact, the Hartree–Fock (HF) level calculations for the endocyclic P–N bond lengths are within the statistical range of the experimental values. The HF calculations slightly overestimate the exocyclic bond lengths. The density functional methods predict slightly longer bond lengths than the HF procedure, reflecting the explicit incorporation of electron correlation, and, therefore, greater electron–electron repulsion.

The next system chosen for investigation was the geometrically and electronically more complex molecule 2,2-diphenyl-4,4,6,6-tetrafluorocyclophosphazene, $P_3N_3F_4Ph_2$. The computed structure is shown in Figure 2, and selected interatomic distances are found in Table 2. A wide range of geometrical parameters calculated for this and related compounds can be found in the Supporting Information (Tables S3–S6). Again, the computational methods reproduce the pattern of bond length variations and provide a close approximation to the experimental distances and angles. Both density functional procedures calculate longer bond lengths than those reported in the crystal structure, while the HF method gives shorter bond lengths than the others. The intraannular angles are better reproduced with the density functionals, however. The observed relative orientation of the phenyl rings with respect to each other is reproduced in the calculations. However, all of the computations predict a flat phosphazene ring, in contrast to the observed structure in which the substituted phosphorus atom is out of the plane

**Figure 2.** 2,2-Diphenyl-4,4,6,6-tetrafluorocyclophosphazene.

of the remaining five endocyclic atoms.¹² The ¹⁹F NMR spectrum of the diphenyltetrafluorophosphazene remains unchanged at low temperatures,¹⁹ which indicates that the barrier to deformation of the planar structure is low. Thus, it is reasonable to suggest that the nonplanar structure may be the result of solid-state forces, while the computations yield the gas-phase structure.

Previous investigations^{20,21} have utilized molecular modeling (force field) approaches for the prediction of cyclophosphazene structures. The current demonstration that ab initio and DFT methods can give good approximations to observed geometrical structures provides a useful tool for determination of the structure for cyclophosphazenes which resist crystallization. Examples of interest include many alkoxy and aryloxy derivatives, which tend to be oils and inseparable mixtures of isomers. The success in reproducing the patterns of bond length variations also suggests that these methods will allow for an understanding of the factors that lead to the observed structures.

The natural bond order (NBO) subprogram²² was used to analyze the bonding situation in these molecules. This procedure expresses the bonding in terms of one and two centered orbitals, rather than as molecular orbitals delocalized over the entire ring. Thus, it is useful to investigate the local effects, such as the lone pairs of the nitrogen atoms, and the possibility of the electron density differentials within the

(20) Verduyck, K.; Vidal, C.; Labarre, J.-F. *Main Group Chem.* **2000**, *3*, 91.

(21) Allcock, H. R.; Ngo, D. C. *Macromolecules* **1992**, *25*, 2802.

(22) For NBO Version 3.1, see: (a) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *J. Mol. Struct.: THEOCHEM* **1988**, *169*, 41. (b) Carpenter, J. E. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1987. (c) Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (e) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (f) Reed, A. E.; Weinhold, F.; Weinstock, R. B. *J. Chem. Phys.* **1985**, *83*, 735. (g) Reed, A. E.; Weinhold, F.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899. (h) Carpenter, J. E.; Weinhold, F. In *The Structures of Small Molecules and Ions*; Naaman, R., Vager, Z., Eds.; Plenum: New York, 1988, p 227.

Table 3. Selected Natural Electron Populations and NBO Charges for N₃P₃X₄R₂

X	R	P ₂		P ₄		N ₁		N ₅	
		3p ^a	charge	3p ^a	charge	2p ^a	charge	2p ^a	charge
F	F	0.461	2.799	—	—	1.486	-1.615	—	—
		0.489							
		0.439							
Me	Me	0.574	2.274	—	—	1.736	-1.648	—	—
		0.541							
		0.692							
F	Me	0.618	2.259	0.492	2.810	1.569	-1.636	1.772	-1.640
		0.492		0.460		1.715		1.500	
		0.701		0.447		1.778		1.767	
F	Ph	0.614	2.302	0.492	2.812	1.572	-1.634	1.772	-1.639
		0.688		0.447		1.782		1.776	
		0.493		0.460		1.715		1.500	
Cl	Ph		2.107		2.3036		-1.618		-1.616
Cl	F		2.54		1.84		-1.45		-1.43
F	Cl		1.83		2.54		-1.45		-1.47

^a p_x, p_y, p_z down the column.

Table 4. Wiberg Bond Order of Selected Bonds in N₃P₃X₄R₂

X	R	P ₂ N ₁	P ₆ N ₁	P ₆ N ₅	P ₂ C	P ₆ F
F	F	1.037	1.037	1.037		0.677
Me	Me	0.952	1.098	1.028	0.876	0.657
F	Me	0.947	1.092	1.028	0.840	0.657
Ph	Ph	0.995	0.995	0.995	0.841	
F	Ph	0.947	1.092	1.028	0.840	0.657
Cl	Ph	0.933	1.086	1.009	0.843	0.873

endocyclic nitrogen centers. Additionally, the calculated NBO charges are useful parameters in the estimation of relative bond polarities.

A selection of orbital populations and changes of the mixed systems is shown in Table 3. Additional details can be found in the Supporting Information (Tables S7–S9).

The dimethyl- and diphenyltetrafluorophosphazenes show similar charges and populations. Selected orbital populations of the ring atoms are shown in detail in Table 3. The fluorine atoms strongly withdraw electron density from the phosphorus 3p orbitals. In the mixed rings, the nitrogen atoms, however, show little variation in the orbital populations, with only a difference of 0.02 e in the 2p population. Similar effects are seen in 3s and 2s orbitals

There is little difference in electron density between the 2p_z orbitals in the nitrogen atoms. This is in marked contrast to the phosphorus atoms, where the change in substituent gives rise to a difference in the 3p_z population by 0.25 e. The difference in the phosphorus (3p_x, 3p_y) electron density is 0.16 e, which is also significant. By way of contrast, the corresponding difference among the nitrogen 2p_x, 2p_y orbital density is only 0.013 e, a marginal quantity. These observations strongly suggest that the electron withdrawal is primarily an inductive effect through the σ backbone and that there is little, if any, differential π interaction of the nitrogen lone pairs with the separate phosphorus centers.

A similar analysis of the hexafluoro- and hexamethylcyclophosphazene orbital electronic populations is also shown in Table 3. As demonstrated previously in this Article, the fluorine substituents strongly withdraw electron density from the phosphorus valence orbitals. The differential in the valence electronic population at phosphorus varies from 2.706 to 2.182 e. The nitrogen 2p_z orbitals, on the other hand,

are relatively unaffected, changing only from 1.799 to 1.762 e population upon going from the hexafluoro to the hexamethyl derivative. A comparison of disubstituted with the homogeneously substituted rings (Table 3) shows that the orbital populations of the phosphorus atoms in the mixed phosphazenes depend solely upon their directly bonded substituents.

The electron populations of the in-plane lone pairs of all of the nitrogen ring atoms in the persubstituted and disubstituted derivatives are virtually unchanged, ranging from 1.836 to 1.845, despite differing substituents on the vicinal phosphorus centers. The Wiberg bond order of the P–F bond (Table 4) shows a low covalent bond order, indicating considerable ionic character. The bond orders of the mixed phosphazenes correlate well with the bond order of the homogeneous phosphazene substituents; for example, in the hexaphenyl derivative, the P₂–N₁ bond order is similar to the bond order in the hexamethyl species, while the P₆–N₁ bond resembles that in the hexafluoro species, and the P₆–N₅ bond has an intermediate value. The bond orders are never more than minimally above 1.0.

The high formal charges and low bond orders indicate a significant ionic content to the endo- and exocyclic bonds. This ylid type of character has been increasingly favored over traditional π electron descriptions in recent calculations.¹¹ In this model, the endocyclic bond length variations have their origins in the relative charges at the phosphorus centers. Thus, an increase in the electron-withdrawing capacity of an exocyclic substituent leads to an increased positive charge on the phosphorus atom, which, in turn, leads to increased electrostatic attraction to the negative nitrogen center. This attraction is manifested in a shortening of the P–N bond length. Previous experimental studies have noted correlations between the electron-releasing properties of substituents, as measured by basicity and structural parameters of the phosphazene ring.^{23,24}

- (23) Besli, S.; Coles, S. J.; Davies, D. B.; Hursthouse, M. B.; Kilie, A.; Mayer, T. A.; Shaw, R. A.; Uslu, A. *Acta Crystallogr., Sect. B* **2002**, *58*, 545.
- (24) Coles, S. J.; Davies, D. B.; Hursthouse, M. B.; Kiliç, A.; Mayer, T. A.; Shaw, R. A.; Yenilmez-Ciftci, G. *Acta Crystallogr., Sect. B* **2004**, *60*, 739.

In both the hexafluoro and hexamethyl derivatives, the HOMO corresponds to the $2p_z$ orbitals on the nitrogen atoms, with negligible contributions from phosphorus-centered atomic orbitals. Thus, they correspond to lone pairs in a Lewis structure description of the molecule. This is also true in the dimethyltetrafluoro species. The full details of the coefficients of the atomic orbitals in the HOMO and the differences of their absolute magnitudes can be found in the Supporting Information (Table S10). The coefficients of the nitrogen atoms are little changed in going from the hexafluorinated to dimethyltetrafluorocyclotriphosphazene. In all three compounds, the contributions of the phosphorus orbitals to the HOMO are minimal.

The molecular orbital that corresponds most closely to the in-plane, sp^2 -hybrid nitrogen lone pairs (in the Lewis structure scheme) is the HOMO-3 orbital in the hexafluoro and hexamethyl species. The coefficients of these atomic orbitals are provided in the Supporting Information (Table S11). In these two molecules, there is a slight difference in coefficients, mostly owing to a small contribution from the phosphorus atomic orbitals.

The NBO procedure factors the global molecular orbitals into localized bonds and lone pairs. This is useful to investigate localized effects in the molecule. The natural localized molecular orbital (NLMO) analysis of the two lone pairs for the hexafluoro and hexamethyl derivatives indicates that the in-plane nitrogen lone pair has some contributions from the neighboring phosphorus atomic orbitals (Supporting Information Table S12). There is little change in going from the hexafluorinated to the dimethylphosphazenes, however.

For both the dimethyl- and diphenylphosphazenes, there is little change in the negligible contributions of the phosphorus center orbitals to the HOMO. There is a significant increase in the amount of contribution of the nitrogen atoms' p_z orbitals (Supporting Information Table S13). These interact directly with the orbitals on the methyl and phenyl groups. The atomic orbitals with components in the z axis have interactions with the substituent orbitals in the HOMO. This is especially notable with the nitrogen orbitals vicinal to the methyl or, especially, the phenyl groups. These have significant energy matching which, along with the appropriate symmetry, allow significant interactions to occur.

These results imply no significant π conjugation throughout the ring. The relatively constant population of the nitrogen p orbitals implies that there is little polarization of the lone pairs into the P–N bond. Instead, to explain the differing bond lengths, we propose that the higher partial charge of the fluorinated phosphorus results in increased electrostatic attraction, reducing the bond length. The orga-

nosubstituted phosphorus atom is more electron-rich and has less ionic attraction, leading to longer bonds.

These results predict that intraannular bond alternation effects in the chlorinated analogue $N_3P_3Cl_4Ph$ would be less than those in the fluoro analogue. The experimental and computed geometrical data are presented in Table 2. Similar to the fluorinated phosphazene, the crystal structure shows deviance from phosphazene ring planarity, but the computed structures are flat. Both the HF and B3LYP density functional overestimate bond lengths. The HF calculation is closer to the experimental lengths, but the B3LYP functional method reproduces the bond angles better.

As in the fluorinated system, the phosphazene ring shows alternation in bond lengths. The fluoro trimer has a deviance of 5.0% from the mean phosphorus–nitrogen length, while in the chloro trimer, the range is 3.8% of the mean. This is a result of the lessened electronegativity of the chlorine substituents, resulting in a reduced amount of charge difference of the phosphorus centers. The charges and bond orders are shown and contrasted with the fluorinated analogue in Tables 2 and 4. A comparison of the HF and DFT results can be found in the Supporting Information (Table S14). The HF procedure calculates larger charges than the density functional. Interestingly, the phenylated phosphorus center is calculated to have a higher charge than the chlorinated center at the B3LYP level. This is also the case when using the B3PW91 functional and at the MP2 level of theory, although to a lesser extent. This must be a result of correlation of the electrons since, in the HF procedure, electron correlation is not explicitly considered. In all cases, the charges of the ring nitrogens are similar, implying that the lone pairs are not being polarized into the bonds. The bond orders are also similar, leading to the same conclusions.

If orbital overlap played a major role, the better energy and size matching of the chlorine atom orbitals with those of the phosphorus atoms would imply a larger effect on intraannular bond deviance. The correlation of bond lengths with electronegativities supports the model of polarized charges and bonding dominated by electrostatics. The observation that the atomic $3p_z$ orbitals of the phosphorus centers do not contribute significantly to the HOMO, which is comprised of the nitrogen $2p_z$ along with orbitals on the carbon substituents, provides further evidence for polarized σ bonding in the phosphazene ring and not vicinal N–P π bonds to any large extent.

The structurally uncharacterized mixed-halogen rings 2,2-difluoro-4,4,6,6-tetrachlorocyclotriphosphazene and 2,2-dichloro-4,4,6,6-tetrafluorocyclotriphosphazene have been investigated at the HF, B3PW91, and B3LYP levels, using the 6-31G* basis set. The geometry was optimized, and the charges were investigated using the NBO scheme.

The equilibrium structures of the mixed-halogen phosphazene rings are described in Table 2. All of the rings are planar, and there is remarkable continuity of geometrical parameters of the hexahalogen (Table 1) and mixed-halogen derivatives (Table 2). The bond lengths and angles at the phosphorus centers are constant among the same substituents but are unaffected by the substituents on the other phosphorus

- (25) Davis, M. I.; Paul, J. W. *J. Mol. Struct.* **1971**, *9*, 478.
 (26) Oakley, R. T.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 420632.
 (27) Bullen, G. J. *J. Chem. Soc.* **1971**, 1450.
 (28) Ahmed, F. R.; Singh, P.; Barnes, W. H. *Acta Crystallogr., Sect. B* **1969**, *25*, 316.
 (29) Cordes, A. W.; Swepston, P. N.; Oakley, R. T.; Paddock, N. L.; Ranganathan, T. N. *Can. J. Chem.* **1981**, *59*, 2364.
 (30) Mani, N. V. Ahmed, F. R.; Barnes, W.-H. *Acta Crystallogr.* **1965**, *19*, 696.

centers on the ring. Thus, a fluorinated phosphorus center has bond lengths to the neighboring nitrogen atom almost exactly the same as those in the hexafluorinated phosphazene. The ring P–N lengths and P–N–P angles do vary slightly, depending on whether the phosphorus atom has fluorine or chlorine substituents. The length of the P–X bond is invariant in relation to that of the specific compound.

The NBO charges, shown in Table 3, are constant across a phosphorus center. As in the mixed alkyl/halogen compound, the identity of the compound as a whole does not influence the charge, but only influences the substituents upon the phosphorus. Thus, the fluorinated phosphorus atoms all have NBO charges of 2.54, notwithstanding if the molecule is totally or only partially fluorinated. The computed charges of the halogen substituents are virtually unchanged across the row.

As with the *gem*-organosubstituted heterocyclophosphazenes, it is possible to compare the populations of the nitrogen atom, in-plane lone pairs (details can be found in the Supporting Information (Table 5)). The electronic occupation of the orbitals is bracketed by those of the hexafluoro (1.843) and hexachloro derivatives (1.832). The more electronegative substituent on the phosphorus center results in a slightly larger population of the lone pair. This is not well-explained by the model of lone-pair donation into the P–N bond, but it is compatible with the scheme of polarized intraannular bonding.

Conclusions

The experimental geometries of *gem*-heterosubstituted cyclotriphosphazenes have been reproduced, including observed intraannular bond length alternation, at the *ab initio* (Hartree–Fock) and density functional (B3LYP, B3PW91) levels, utilizing the 6-31G* basis. Detailed analysis of the bonding, using the NBO method, does not support the previous hypothesis¹² of in-plane N-lone-pair polarization into the P–N ring σ backbone. Instead, polarized bonds, leading to expanded or contracted phosphorus center orbitals, appear to be the origin of the bond alternation effects.

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Supporting Information Available: Selected geometrical parameters, natural electron populations, natural atomic orbital electronic occupancies, natural atomic valence orbital electronic occupancies, comparisons of orbital contributions, natural localized molecular orbital analyses, ring orbital contributions, and computed NBO charges. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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