

Molecular Structures and Conformations of Polyphosphazenes—A Study Based on Density Functional Calculations of Oligomers

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Abstract: Density functional calculations were carried out on a series of oligomers of polyphosphazenes to characterize molecular structures and conformational properties of the polymers in isolation. Polyphosphazenes are found to have alternating P–N bond lengths in the planar cis–trans backbone conformation. The magnitude of the alternation is in the range of 0.03–0.07 Å, depending on the substituents. The P–N bond alternations are not present in the optimized helical chains. Rotation around the P–N bond is very flexible; the barrier height to rotation of the P–N bond in monophosphazene is about 2 kcal/mol. Systematic study of conformational properties of the oligomers suggests that isolated polyphosphazenes prefer twisted helical structures. The energy differences between the twisted and planar cis–trans chains are ca. 5 kcal/mol per repeat unit. Intramolecular electrostatic interactions are found to be the dominant forces which determine the conformational states. The impact of different side chain substituents (halogen and organo side groups) was also studied. A study of the electronic structures of phosphazene suggests that the P–N bonding consists of an ionic σ bond and a π bond mainly induced by negative hyperconjugation: $\pi(\text{N}) \rightarrow \sigma^*(\text{P}-\text{X})$. The new bonding model supercedes earlier ones and explains the structural and conformational properties reported in this and previous work on phosphazenes.

I. Introduction

Polyphosphazenes, $-(\text{NPX}_2)_n-$, as a new class of inorganic polymers, have drawn considerable interest recently.¹ Simple polyphosphazenes, such as poly(halophosphazenes), are elastomers over a broad range of temperature. However, due to easy hydrolysis, these polymers have not found practical uses. The most active area in the chemistry and engineering of polyphosphazenes is related to the numerous possibilities for replacing the halogen atoms with different organo groups. The common side groups are alkyl, aryl, alkoxy, aryloxy, amino, and their halogen derivatives. By varying the side groups, one may obtain useful mechanical, electrical, optical, and biological properties.¹

Characterizing molecular structures and conformational properties at the atomistic level provides a fundamental route to understanding the macroscopic properties of molecules. Since the discovery of polyphosphazenes, many studies have been focused on molecular structures and conformational behavior of these materials. However, even for the simplest form, dihalophosphazene, controversies over these properties are found in the literature.

Most structural parameters reported in the literature are based on X-ray diffraction measurements of crystalline phosphazenes^{2–7} and polyphosphazenes.^{8–12} Early work, mostly on small cyclic

phosphazenes,^{2–7} suggested that all P–N bonds are equal in length. The reported structural parameters for phosphazenes and polyphosphazenes vary significantly. The P–N bond lengths range approximately from 1.48 to 1.58 Å, the PNP angles are from 121° to 159°, and NPN angles are from 116° to 123°.

The assumption of equal P–N bond length has been used to interpret X-ray diffraction data of linear polyphosphazenes.^{9–11} However, the validity of extrapolating parameters from cyclic oligomers to linear polymers has been challenged by several groups recently.^{13,14} Allcock et al.,¹³ synthesized a number of short chain linear phosphazenes and analyzed their X-ray diffraction data. They found that the structural parameters obtained for these molecules are sometimes significantly different from those of small cyclic compounds. In particular, the P–N bonds reported by these authors are slightly alternating in length, with a difference of about 0.07 Å.¹³ Using ab initio calculations on short chain model phosphazenes, Ferris et al.¹⁴ found a similar difference of ca. 0.05 Å between adjacent P–N bonds.

The bond alternation model has been applied recently to solve the crystal structure of high polyphosphazenes with X-ray diffraction by Chatani et al.¹² These authors reported that adjacent P–N bonds in crystalline poly(dichlorophosphazene) (PDCP) differ by as much as 0.22 Å. Dielectric measurements of poly(diphenoxyphosphazene) in dilute benzene solution

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conducted by Uzaki et al.¹⁵ suggested that the dipole moment of each repeat unit of the polymer is aligned in the same direction parallel to the chain contour. This finding supports the bond alternation model.

Regarding molecular conformations, Meyer et al.⁸ first proposed a helical conformation for crystalline PDCP. Later, Giglio et al.⁹ suggested a different 2/1 helix with a slightly distorted cis–trans chain conformation. Allcock et al. reported their X-ray diffraction measurements of PDFP¹⁰ and PDCP.¹¹ Two polymorphs were found for PDFP at different temperatures. Conformer A, existing in the temperature range of –36 °C to 25 °C, has chain repeat distance of 6.49 Å. A helical chain structure was suggested.¹⁰ Conformer B, observed near –56 °C, has a repeat distance of 4.86 Å. The chain conformation has been assigned to a cis–trans planar structure.¹⁰ A cis–trans planar structure, with chain repeat distance of 4.92 Å, was found to be the most plausible conformer of nine proposed models for PDCP.¹¹ Similar results were reported for short chain phosphazenes.¹³ However, Chatani et al.¹² recently proposed a glide trans–cis conformation (–T'–C'–T'–C'–) with internal rotations of 175°(T') and 31°(C') for PDCP.

Semiempirical calculations have been applied to calculate the conformational structures. Tanaka et al.¹⁶ performed one-dimensional tight-binding SCF energy calculations at CNDO/2 level for the nine models proposed by Allcock.¹¹ Their results show that the cis–trans planar structure is the most stable conformation. Bougeard et al.¹⁷ carried out MNDO optimization with symmetry constraints on two molecules: Cl₃PN(PCI₂N)_n–POCl₂ and [Cl₃PN(PCI₂N)_nPCI₃][PCI₆], where *n* = 1, 2. Planar cis–trans conformers were found to be the most stable. Boehm¹⁸ performed comprehensive structure optimizations for series of ring and linear clusters of diphenoxyphosphazene using the MNDO method. A helical structure was proposed for poly(diphenoxyphosphazene).¹⁸

Because PDCP and some of the related polyphosphazenes have very low glass transition temperatures (T_g), it is speculated that the participation of d orbitals of phosphorus in the delocalized P–N bonds leads to a very small barrier to rotation. Using this model, Allcock et al.¹⁹ proposed a simple empirical force field which consists of only nonbonded interactions (Lennard-Jones 12–6 function and Coulombic terms) to study the conformational stability of halogen and organo phosphazenes. They found that the Φ–Ψ energy maps of rotations of adjacent P–N bonds along the backbone are very flat. There are many local minima with a fraction of kcal/mol difference in energy, and these minima are linked with low energy barriers, generally below 1.5 kcal/mol. This approach was followed by Saiz²⁰ who reparametrized the model and carried out RIS calculations for polyphosphazenes. Boyd et al.²¹ developed an empirical force field with flexible bond, angle, torsion, and nonbonded terms. The parameters were determined by fitting to available experimental data—vibrational frequencies and crystal structure parameters, mostly of cyclic compounds.

The primary goal of the present study is to extend our understanding of molecular structures and conformational properties of polyphosphazenes by performing high level theoretical calculations. So far, computational studies reported

in the literature are based on empirical,^{19–21} semiempirical,^{16–18} and low level ab initio methods.¹⁴ This may be partly responsible for the controversial results obtained. Another source of confusion is that some of these calculations were experiment-biased, in which experimental data were used as constraints in the calculations. The problem is that experimental data for phosphazenes are exclusively available for molecules in condensed phases (crystals or liquids), while the calculations were normally performed on isolated molecules. Despite the uncertainty of the experimental data, some molecular properties, such as conformations, are largely influenced by molecular environment. Hence it is not valid to use the parameters obtained for molecules in condensed phases to predict the properties of isolated molecules. In this study, we focus on isolated molecules only, trying to characterize the molecular properties with validated ab initio calculation methods. This study also serves as the first step toward developing an ab initio, consistent force field (CFF).^{22–26} With the force field, molecular properties in condensed phases can be studied using MM or MD simulations. In this paper, the results of ab initio calculations are presented.

II. Computational Methods

Recent progress in the density functional theory²⁷ provides a powerful computational approach which appears to be more efficient than traditional Hartree–Fock (HF) and Møller–Plesset perturbation (MPn) calculations. In this work, HF, MP2 and DFT calculations were performed in comparison studies. The HF and MP2 calculations were carried out using Turbomole;²⁸ the DFT calculations were conducted using the software package DMOL.²⁸ Several different functionals were used with DMOL: local exchange correlation functional VWN²⁹ and Becke's nonlocal exchange functional³⁰ was used with local and nonlocal correlation functionals in the combinations B+VWN, B+PW,³¹ and B+LYP.³² The basis set used in all DFT calculations was the double numerical basis set argued with polarization functions, DNP, supplied with DMOL.²⁸ For the HF and MP2 calculations, the 6-31G*,³³ DZ2P, and TZ2PF³⁴ basis sets were used.

In preparation for the larger study, several candidate DFT methods were compared with HF and MP2 calculations using a model compound; monophosphazene, HNPH₃. The results are given in the next section. Using the selected method, DFT VWN/DNP, calculations were performed on isolated oligomers of polyphosphazenes, H(NPX₂)_nH, with the number of repeat units (*n*) ranging from 1 to 8 to study the structural and conformational properties of polyphosphazenes in isolation. One

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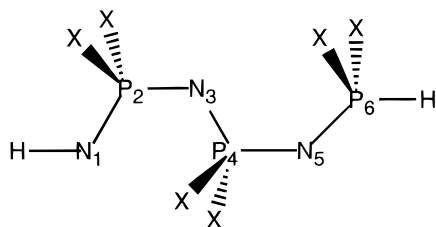


Figure 1. An illustration of the model compounds calculated—triphosphazene, $\text{H}(\text{NPX}_2)_3\text{H}$, in trans—cis conformation.

of these oligomers, triphosphazene ($n = 3$), is sketched in Figure 1. The largest oligomer calculated (octamer) has a straight end-to-end length of about 20 Å. To study the substitution effects on molecular structures and conformations, several substituents, including halogen, methyl, phenyl, hydroxy, and amine groups, were considered in the calculations. In the study of electronic structures of the chemical bonding between phosphorus and nitrogen, the model compounds, HNPH and H_2NPH_2 , in addition to HNPH_3 , were calculated.

III. Results and Discussions

1. Comparison of Computational Methods. Two conformers of monophosphazene (HNPH_3), staggered and eclipsed, depending on the relative positions of the hydrogen atoms bonded to nitrogen and phosphorus atoms, respectively, were calculated using different computational methods. The staggered is a stable conformation, while the eclipsed is a transition state of rotation about the P—N bond. The optimized structural parameters and energy differences of these two conformers (ΔE) are summarized in Table 1.

Although strict comparison between the DFT and HF or MP2 results is not valid due to different basis sets used, by comparing the data listed in Table 1, one can see that DFT results are generally close to the MP2 results. The bond lengths of HF calculations are smaller than those of MP2 and DFT. There are also significant differences in bond angles between the HF and MP2 or DFT. The DFT method with local correlation functional VWN and DNP basis set yields very similar structural parameters to those of MP2/DZ2P. The P—N bond lengths calculated with functionals including Becke's nonlocal exchange term (B+VDW, B+PW, B+LYP) are slightly longer than those of VWN and the HF and MP2 calculations. The energy barriers calculated using different methods scatter from 1.7 to 2.6 kcal/mol. The DFT results are quite stable, around ca. 2.0 kcal/mol. The VWN value is only slightly below the values obtained in other DFT calculations with nonlocal exchange functionals.

The best theoretic level considered in this study is the MP2/TZ2PF. This combination yields very good structural and energetic results in our previous study²⁶ of disiloxane for which extensive gas-phase experimental data are available for comparison. It is speculated that this level of theory should be good for phosphazenes as well because both siloxanes and phosphazenes contain isoelectronic moieties consisting of bonding pairs of first and second row elements. In comparison with the MP2/TZ2PF results, we see that the P—N bond lengths obtained using VWN/DNP are about 0.02 Å too long. (Similar deviations can be found for MP2/6-31G* and MP2/DZ2P). The bond angles and energies, however, are in good agreement with the MP2/TZ2PF results. Comparison of the VWN/DNP structural parameters with experimental data, which have been measured for crystalline cyclic-tri(halo)phosphazene, is given in Table 2. As expected, the bond lengths calculated are (on average) about 0.02 Å longer than the experimental values, but good agreement is obtained for bond angles.

In Table 1, we also list the CPU time for each optimization cycle on a IBM/RISC-550 workstation. Due to its superior CPU performance and reasonable accuracy, VWN/DNP appears to be the most efficient method for the purpose of this study. Consequently, this functional was used for most calculations reported in this paper.

2. Bond Length Alternation (Peierls Distortion). Bond length alternation has been extensively studied for polyacetylene in which the adjacent C—C bond lengths are different.^{35–37} It is understood that this phenomenon, the Peierls distortion, has its physical origin in electron—electron interactions,^{35,36} although the terminal effect and lattice-electron correlation play roles as well. Similar to the Jahn-Teller effect, the most stable structure corresponds to a symmetry-broken 2-fold degenerate state. Because of this, electron correlation and basis sets are critical issues in the calculation of the bond alternation phenomenon for polyacetylenes.^{33,36}

Ferris et al.¹⁴ studied the bond alternation phenomenon in polyphosphazenes by optimizing geometries of planar cis—trans phosphazene oligomers $\text{HN}(\text{PH}_2\text{N})_n\text{PH}_3$ ($n = 1–4$) using the Hartree—Fock method. They found that, similar to polyacetylenes, polyphosphazene has different bond lengths for adjacent P—N bonds along the backbone. The differences decrease as the size of the cluster increases. They estimated that the alternation size converges to about 0.05 Å. Since electron correlation, which would normally reduce the gap, was not included in their calculations, it is not clear to what extent the bond alternation obtained is due to lack of electron correlation and insufficiencies of the basis sets.

In extending the calculations to larger molecules with different substituents using density functional methods, oligomers of polyphosphazenes $\text{H}(\text{PX}_2\text{N})_n\text{H}$ ($n = 2–8$) in which the substituents X are H, F, Cl, and Br were studied. We first focus our attention on the planar, cis—trans conformation that is reported repeatedly for crystalline polyphosphazenes. The bond alternation with different chain conformations will be addressed later in this paper. Using the VWN/DNP method, we optimized the molecular structures with C_s symmetry constraint only, and calculated the bond alternations by subtracting the values of adjacent bond lengths in the middle of the chain. The results obtained are plotted in Figure 2, together with data reported by Ferris et al.¹⁴ (results of HF/LP-31*) for comparison.

As expected, the magnitude of the bond alternation found with VWN/DNP is smaller than that of the Hartree—Fock method. The bond alternation decreases as the size of the oligomers increases. The value converges to 0.024 Å at $n = 8$.

In order to assess how important the bond alternation is, we performed similar calculations for polyacetylene, which has been well studied both experimentally and computationally. The best estimated ab initio value in the literature is 0.08 Å.³⁵ The value obtained in this work is 0.04 Å. Comparing with the experimental value of 0.06 Å,³⁷ we see that the VWN/DNP method yields a reasonable agreement with the experimental data for polyacetylene. Assuming the same level of accuracy for phosphazenes, we conclude that the magnitude of the alternation in polyphosphazene is about half of that of polyacetylene.

3. Substitution Effects on Molecular Structures. The substitution effect on bond alternation was studied by performing calculations on tetraphosphazene $\text{H}(\text{NPH}_2)_4\text{H}$ and its halogen derivatives. Organo groups were not included, because they might complicate the problem by introducing side chain

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Table 1. Structural and Energetic Properties of Monophosphazene Calculated Using Different Computational Methods^a

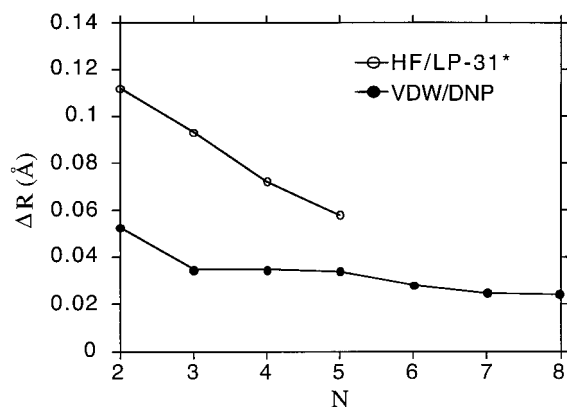
method	staggered			eclipsed			ΔE	CPU ^b
	P-N	H-N-P	N-P-H	P-N	H-N-P	N-P-H		
HF/6-31G ^b	1.548	118.6	110.0	1.543	120.6	120.6	2.13	89
HF/DZ2P	1.549	116.2	110.5	1.546	117.2	120.7	2.03	459
HF/TZ2PF	1.531	120.0	110.6	1.526	122.7	120.5	1.70	2727
MP2/6-31G ^b	1.571	116.4	108.7	1.563	119.1	122.7	2.62	130
MP2/DZ2P	1.572	113.7	109.4	1.567	115.1	123.1	2.45	1248
MP2/TZ2PF	1.553	115.5	109.7	1.548	117.6	122.1	2.14	9578
VWN/DNP	1.574	114.8	108.6	1.568	116.0	123.7	1.93	38
B+VDW/DNP	1.604	114.5	108.0	1.595	115.1	123.7	2.04	53
B+PW/DNP	1.593	114.1	108.2	1.587	114.5	123.4	2.06	156
B+LYP/DNP	1.602	114.5	108.1	1.595	115.3	123.8	2.04	53

^a Bond lengths are in Å, angles are in deg, and the energies, $\Delta E = E_{\text{staggered}} - E_{\text{eclipsed}}$, are in kcal/mol. ^b In s/cycle, approximate cpu time on IBM/RISC-6000/550 workstation.

Table 2. Comparison of Calculated and Experimental Structural Parameters of Cyclic Triphosphazenes (NPX₂)₃^a

-X =	-F		-Cl	
	calc	expt. ²	calc.	expt. ³
N-P	1.582	1.546-1.572	1.595	1.575
P-N-P	119.4	119.4	120.3	121.5/121.2
N-P-N	120.6	121.1/119.6	119.7	118.3/118.5

^a The bond lengths are in Å, angles are in deg.

**Figure 2.** Calculated bond-length alternations of polyphosphazene. HF/LP-31¹⁴ and DFT VWN/DNP results are compared for various chain lengths N.

conformations. For the same reason, planar cis-trans structures were assumed for the backbone using symmetry constraints. As shown in Table 3, the P-N bond lengths, N-P-N angles and P-N-P angles are correlated to the substituents. The bond alternations, which are the differences between the central adjacent P-N bonds, are ca. 0.03 Å (H), 0.07 Å (F), 0.05 Å (Cl), and 0.05 Å (Br).

More data on the effect of substituents were obtained for substituted monophosphazene (Table 4). Combining the data of Tables 3 and 4, one sees that different substituents have pronounced effects on the molecular structures. It appears that the P-N bond lengths are correlated with the electronegativities of the elements attached to phosphorus—the more electronegative, the shorter the corresponding P-N bond. For example, in substituted monophosphazenes, the P-N bond lengths range from 1.523 Å (F) to 1.571 Å (H). For most common substituents, the values are in the range of 1.54 Å to 1.57 Å. There is also a large variation for HNP angles, ranging from 114.5° to 123.7°; similar values are found for the P-N-P angle of the tetraphosphazenes (Table 3). The N-P-N angles are smaller, in the range of 108° to 115°.

4. Chain Conformations. The rotation energy profile of monophosphazene is shown in Figure 3. This curve consists

Table 3. Optimized Planar Structural Parameters of Tetraphosphazene and Its Halogenated Derivatives H(NPX₂)₄H^a

	-H	-F	-Cl	-Br
Bonds (Å)				
N1-P2	1.579	1.534	1.546	1.549
N3-P4	1.607	1.546	1.565	1.567
N5-P6	1.606	1.553	1.571	1.579
N7-P8	1.595	1.535	1.561	1.570
P2-N3	1.639	1.623	1.626	1.625
P4-N5	1.642	1.616	1.619	1.622
P6-N7	1.642	1.617	1.628	1.632
P2-X	1.440	1.592	2.062	2.246
P4-X	1.424	1.568	2.023	2.203
P6-X	1.424	1.561	2.009	2.187
P8-X	1.426	1.550	2.002	2.185
Angles (deg)				
N1-P2-N3	108.9	115.1	114.3	114.5
N3-P4-N5	107.9	113.9	113.2	112.4
N5-P6-N7	108.2	113.0	111.7	111.4
P2-N3-P4	114.1	123.2	124.0	126.7
P4-N5-P6	116.2	123.7	125.0	124.0
P6-N7-P8	112.5	119.7	121.8	121.8

^a The numbering of heavy atoms (P and N) is on the order of the backbone sequence, as illustrated in Figure 1.

of energy points calculated using torsion-constrained optimizations in which the dihedral angle H-P-N-H was fixed at given values, while all other degrees of freedom were relaxed. The energy profile has three minima corresponding to the staggered conformations and three maxima corresponding to the eclipsed conformations. (See section 1 and Table 1 above.) The barrier height calculated (VWN/DNP) is about 2.0 kcal/mol. Note that this value is even smaller than the barrier height of a typical single bond; e.g., the barrier to rotation of the C-C bond in ethane is 2.88 kcal/mol.³⁸

The rotation profile of diphosphazene, HNPH₂NPH₃, as shown in Figure 4, is much more complicated. The energy curve is plotted as a function of the N-P-N-P dihedral angle. The minimum energy structure is cis (0°), local minima are found around 120° and 240°, and the barrier height for a complete rotation is 9.49 kcal/mol, which is the relative energy of the trans conformation.

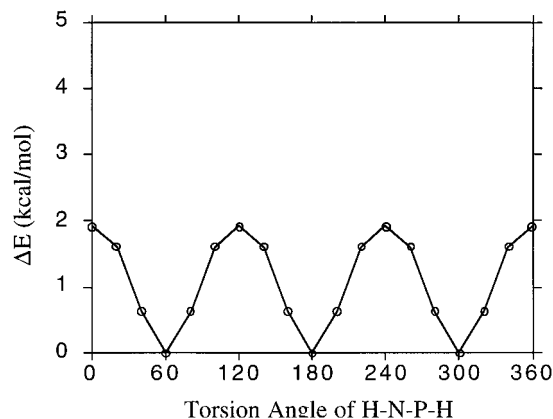
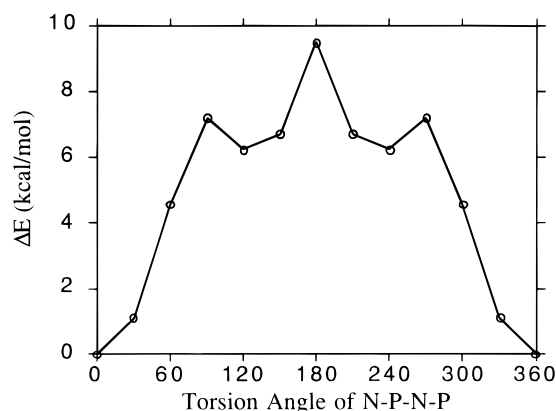
Since rotation about the P-N bond in HNPH₃ costs less than 2 kcal/mol, the large barrier height found in diphosphazene must be due to the intramolecular nonbonded interaction. Because of the differences in the sizes and electronegativities of nitrogen and phosphorous, there is a significant charge separation between P-N bonds. Atomic partial charges calculated by

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Table 4. Comparison of Optimized Structures of Monophosphazene HNPH_3^a

-X	-H	-F	-Cl	-Br	-Me	-Ph	-OH	-NH ₂
H-N	1.031	1.027	1.030	1.031	1.030	1.030	1.031	1.030
N-P	1.571	1.523	1.539	1.545	1.568	1.568	1.546	1.555
P-H	1.417	1.401	1.409	1.412	1.419	1.422	1.409	1.413
P-X	1.442	1.596	2.053	2.231	1.812	1.812	1.622	1.693
H-N-P	114.5	123.7	119.8	119.1	116.2	115.8	117.6	116.5
N-P-H	109.0	111.1	109.6	109.1	106.9	108.7	106.3	105.3

^a Bond lengths are in Å, angles are in deg.

**Figure 3.** Energy profile of rotation about the P-N bond in monophosphazene: HNPH_3 .**Figure 4.** Energy profile of rotation of the central P-N bond of diphosphazene, $\text{HNPH}_2\text{NPH}_3$.

fitting to the HF/6-31G* electrostatic potential (ESP)³⁹ for monophosphazene are 0.96e for P and -1.07e for N. An alignment of two opposite charge centers (1-4 interaction) can be found in the cis conformation but not in the trans. Considering the large energy difference between the trans and cis (the vdW intramolecular forces normally contribute much less), we deduce that the electrostatic interactions are the dominant forces to stabilize the cis conformation.

Triphosphazene, $\text{H}(\text{NPH}_2)_3\text{H}$, has three torsion angles along the backbone if rotations on both ends are ignored. To find all minimum energy conformations, we conducted a systematic search by initializing the three dihedral angles $\{\Phi_i, \Phi_j, \Phi_k\}$ with four values $\{0^\circ, 90^\circ, -90^\circ, 180^\circ\}$. Thus there are a total of $4^3 = 64$ initial isomeric states. Among them, 27 states are redundant due to symmetry. So, full geometry optimizations were conducted with 37 initial conformations. MOPAC with the PM3 Hamiltonian was used to prescreen these candidates before the DFT optimizations to speed up the search. Three conformers were found finally. The corresponding dihedral

Table 5. Three Stable Conformations of Triphosphazene, Fully Optimized with the VWN/DNP Method^a

conf	torsion angles			ΔE
cgg-	-14.4	59.2	-49.7	-11.3
ccc	-1.5	-4.8	6.2	-10.5
ctc	-8.1	-177.5	1.9	0.0

^a The energies (in kcal/mol) are relative to the cis-trans-cis (ctc) conformer.

angles and relative energies of the optimized conformations are listed in Table 5.

The most stable conformation that we found for triphosphazene is labeled as cis-gauche-gauche(-) (cgg-) in Table 5. Hessian analysis (the second derivatives of the total energy surface) confirms that this conformation is a minimum energy state. The result is striking, because the most widely accepted chain conformation of polyphosphazenes, based on X-ray diffraction studies, is planar, cis-trans. Instead, our results show that the slightly distorted cis-trans-cis conformer is 11.3 kcal/mol less stable than the cgg-, and a small negative frequency of -68.3 cm^{-1} is associated with this conformation. The cis-cis-cis (ccc) conformer, which is only 0.8 kcal/mol higher in energy than the cgg-, has a negative frequency of -97.6 cm^{-1} .

Considering the electrostatic force that stabilizes the cis conformation of diphosphazene, we find it easy to understand the results obtained for the triphosphazene. Apparently, as illustrated in Figure 5, there are four favorable electrostatic interactions (four short interaction lines) between nonbonded phosphorus and nitrogen atoms (1-4 interaction) in both cgg- and ccc conformations, while in the ctc conformation, only two such interaction lines can be drawn.

The cgg- conformation can be extended to chains longer than three repeat units only with a modification to the first (cis) torsion angle. In fact, by setting the first dihedral angle to a gauche position, one can make a helical chain with repeat segments of ggg- conformation. Since rotation of the P-N bond costs little energy, the twisted conformation should be stable.

To assess whether the twisted conformation is indeed more stable than the planar cis-trans, we constructed helical structures for each of the model chain phosphazenes with the number of repeat units ranging from 4 to 8 and carried out full geometry optimization using these structures as initial states. The initial conformations were set to $(55^\circ, 55^\circ, -55^\circ)$ repeatedly along the backbone. The optimized torsional angles and the energy differences per repeat unit relative to their planar trans-cis counterparts are listed in Table 6. From tetramer to octamer, the twisted conformations are overall ca. 5 kcal/(mol, repeat unit) lower in energy than the planar cis-trans conformers.

It should be pointed out that the optimized structures listed in Table 6 do not necessarily correspond to global minima. They are just a set of arbitrarily optimized structures from the initial (ggg-)_n states following the minimization paths. That explains the fluctuation of energies and the variety of torsional angles listed in Table 6. Thus, the true minima may be more stable

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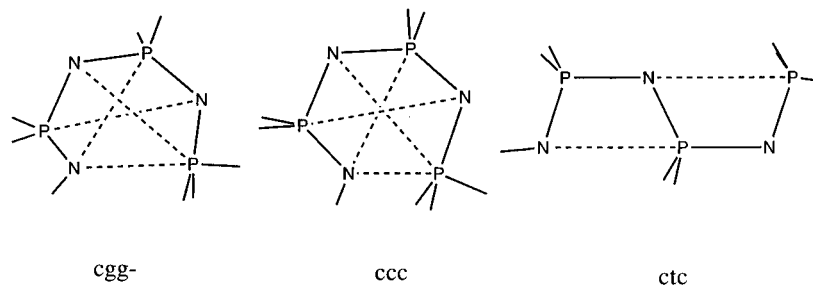


Figure 5. Optimized conformational structures of triphosphazene. In the cgg- and ccc conformations, one can draw four strong interaction (dashed) lines between nonbonded nitrogen and phosphorus atoms separated by three valence bonds (1–4 interactions). Only two strong interaction (dashed) lines can be drawn for the ctc conformation.

Table 6. Summary of the Optimized Twisted Chain Conformations of Phosphazenes with 4–8 Repeat Units^a

<i>N</i>	$\Delta E/N$	Φ
4	-5.93	-38, 65, -51, 85, 64
5	-5.20	-16, 72, -95, 119, -54, 65, -19
6	-5.07	-19, 69, -71, 101, -54, 155, -27, 69, -39
7	-4.06	-12, 81, -44, 163, -60, -7, 57, 42, -52, 147, -7
8	-4.59	-33, 69, -51, 88, -54, 154, -17, -29, 44, 60, -48, 142, -10

^aThe energies are relative to corresponding trans–cis planar conformations, normalized to one repeat unit. Optimized torsion angles are given in the order of the backbone atom sequence.

than those listed in Table 6. In addition, the data in Table 6 suggest that very complicated rotational isomeric states can be found for polyphosphazenes. This can be viewed as a consequence of the intramolecular electrostatic interactions which can be approximately represented by pairwise, point interactions.

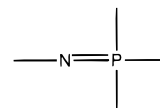
5. Substitution Effects on Conformations. The substitution effect on the conformations were investigated by performing similar geometry optimizations for halogen substituted triphosphazenes. The optimized torsion angles and total energies are listed in Table 7. For comparison, data for triphosphazene are also included.

Two conformers for each molecule were calculated: ctc and cgg-. As indicated in the table, the cgg- structures are more stable than the ctc. The energy differences between the conformers, however, are quite different for different substituents. Fluoro substitution creates the largest energy difference, 24.1 kcal/mol. The chloro substitutions behave similarly to the simple phosphazene in total relative energies, i.e., 11.2 and 11.3 kcal/mol, respectively, and the two bromo conformers are separated by 8.6 kcal/mol. Note that all of the optimized ctc conformers are distorted from a planar structure in which the torsion angles should be 0°, 180°, and 0°. The torsional angles of cgg- conformers of chloro- and bromotriphosphazenes are similar to those of simple triphosphazene, but the fluoro compound is close to a ccc conformation, presumably due to the small size of fluorine atoms.

6. Bond Alternation and Conformations. Data in Table 7 illustrate that the bond lengths and angles are strongly correlated to the chain conformations. The variations of P–N bond lengths are in the range of ca. 0.03–0.06 Å as the conformation changes from ctc to cgg-. Note that these differences are about the same magnitudes as the bond alternations found in the planar, cis–trans chains. In fact, the P–N bonds are distorted in the twisted conformations, and consequently, the alternation pattern disappears. There are also large variations in bond angles between the different conformations.

7. Electronic Structure of the Bonding Between Phosphorus and Nitrogen. Traditionally, phosphazenes are represented by a formal valence model in which the phosphorus and

nitrogen have five and three valence bonds respectively:



Note that the Lewis rare-gas rule (“Lewis octet”) is violated. A common explanation for this phenomenon is the participation of d-orbital in the hybridized valence bond scheme, e.g., dsp^3 .

The nonalternation of bond lengths in small ring molecules indicates that the formal valence picture does not represent the actual structure. The electronic system appears to be delocalized in some way. Based on a study of the theoretical and experimental evidence on the structure of the ring phosphazenes, Allcock⁴¹ has concluded that an “island-type” π structure which has phosphorus d-orbital participation is favored. It is speculated^{19,21} that the π bond may be cylindrically symmetrical about the P–N bond, which leads to a very low rotation barrier. However, the nature of the π bonding is an unresolved issue.

This problem is actually related to a well-studied phenomenon of stereoelectronic interaction, namely, the generalized anomeric effect.^{42,43} For electron-rich molecules that have a general form of X_nAY_m in which Y has one or more lone pair (π) orbitals, the lone pair electrons could be delocalized to σ^* bonds of X–A, to build π -bond character into bonds that normally have only σ character. Since the electron donation is in a reversed direction of “normal” hyperconjugation, which is from a σ bond to a π^* (a classic example is ethyl cation in which the C–H σ bond donates electrons to the π^* of the carbon), this phenomenon is referred to *negative hyperconjugation* in the literature. Reed and Schleyer⁴³ studied a group of molecules of X_3AY type (CF_4 , F_3NO , O_3ClF , O_3PS^{3-} , F_3SN , etc.) and found that, for these molecules, the A–Y bonds are highly ionic, and negative $\pi(Y) \rightarrow \sigma^*(A-X)$ type conjugation is the primary contributor to π -(A–Y) bonding, while $\pi(Y) \rightarrow d(A)$ overlap is secondary. The function of the d-orbitals of atom A is mainly to polarize the $\sigma^*(A-X)$ bond which enforces the negative hyperconjugation.

Inspired by Reed and Schleyer’s work,⁴³ we conducted a comparison study of the electronic structures of three species that contain P–N bonds: H_2NPH_2 , $HNPH$, and $HNPH_3$. The HF/6-31G* calculations were performed in conformity with data reported in the literature.^{42–44} The calculated bond lengths, energy barriers to rotation of the P–N bond, Roby-Davidson electron numbers of P–N bond (N_b),⁴⁵ which is a measurement

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Table 7. Comparison of Optimized Conformers of Halogen Substituted Triphosphazenes, H(NPX₂)₃H^a

prop.	-H		-F		-Cl		-Br		
	ctc	cgg-	ctc	cgg-	ctc	cgg-	ctc	cgg-	
	Bonds (Å)								
N1-P2	1.578	1.611	1.534	1.590	1.546	1.600	1.548	1.611	
N3-P4	1.613	1.617	1.546	1.591	1.565	1.603	1.571	1.612	
N5-P6	1.595	1.608	1.538	1.592	1.563	1.598	1.574	1.606	
P2-N3	1.641	1.611	1.627	1.567	1.628	1.589	1.628	1.591	
P4-N5	1.648	1.614	1.621	1.557	1.630	1.584	1.634	1.588	
	Angles (deg)								
N1-P2-N3	108.0	110.1	114.7	116.6	114.0	113.8	114.8	113.8	
N3-P4-N5	107.0	122.2	114.5	122.2	111.7	119.8	110.8	120.0	
P2-N3-P4	113.2	112.3	122.7	116.2	124.0	114.2	127.3	113.8	
P4-N5-P6	112.3	126.1	126.6	133.3	122.3	130.2	119.9	128.4	
	Torsion Angles (deg)								
Φ1	-8.1	-14.4	-16.2	-15.6	-15.6	-22.8	-38.4	-19.6	
Φ2	-177.5	59.2	174.9	24.4	-175.1	46.6	-168.4	45.2	
Φ3	1.9	-49.7	-5.8	-25.2	-2.5	-41.0	15.0	-47.1	
	ΔE (kcal/mol)								
	0.0	-11.3	0.0	-24.1	0.0	-11.2	0.0	-8.6	

^a The numbering of atoms and torsional angles is in the order of backbone atom sequence, as illustrated in Figure 1. The energies are relative to the corresponding cis-trans-cis conformer for each of the molecules.

Table 8. Comparison of HF/6-31G* Calculated Bond Lengths (*R*), Roby-Davidson Electron Numbers of P-N Bond (*N_b*), Energy Barriers to Rotation of P-N Bond (*ΔE*), Potential Derived Partial Charges (ESP), and Localized Molecular Orbitals (LMOs) of Three P-N Bonded Molecules^c

	H ₂ NPH ₂	HNP	HNP ₃
<i>R</i> (Å)	1.706	1.544	1.548
<i>N_b</i> (e)	1.336	2.195	2.358
Δ <i>E</i> (kcal/mol)	6 ^a	44 ^b	2
ESP charges (e)			
P	-0.17	0.14	0.94
N	-0.72	-0.62	-1.07
H(P)	0.10	0.10	-0.08
H(N)	0.34	0.38	0.41
LMO energies and atomic population numbers			
-9.88 P(2.047)		-10.17 P(2.050)	-9.66 N(1.795)
-11.00 N(1.961)		-11.60 P(0.789)-N(1.229)	-10.81 N(1.794)
-14.63 P(0.953)-H(1.089)		-14.62 P(0.789)-N(1.229)	-15.43 P(0.982)-H(1.068)
-15.87 P(0.747)-N(1.400)		-15.96 N(1.983)	-15.83 P(0.905)-H(1.137)
-18.33 N(1.352)-H(0.675)		-21.50 P(0.904)-H(1.117)	-17.11 N(1.073)-P(0.962)
-22.50 P(0.925)-H(1.118)		-31.63 N(1.314)-H(0.693)	-23.22 P(0.905)-H(1.137)
-31.60 N(1.354)-H(0.671)			-30.46 N(1.287)-H(0.703)

^a Reference 42. ^b SOCI/6-31G(d) result, ref 44. ^c The LMO orbital energies are in atomic units; the atomic population numbers of LMOs are given in parentheses following the symbols of atoms.

of the bond order, electrostatic partial charges (ESP),³⁹ and Boys localized Molecular orbitals⁴⁵ are given in Table 8.

Clearly, H₂NPH₂ and HNP are typical single and double bonded molecules, respectively. This conclusion can be justified by comparing the bond lengths (1.706 Å vs 1.544 Å), barrier height (6 vs 44 kcal/mol), and the bond order (1.336 vs 2.195) listed in Table 8. In comparison, HNP₃ has some double bond characters: the short bond length of 1.548 Å and large bond order of 2.358, both are close to that of HNP. However, the energy barrier height to rotation about the PN bond is very low, only ca. 2 kcal/mol.

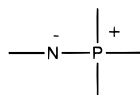
The ESP atomic partial charges in Table 8 indicate that the P-N bonds in HNP₃ is highly polarized. Specifically, both phosphorus and nitrogen atoms bear nearly unit electronic charges with opposite signs. The charge separations between phosphorus and nitrogen in both H₂NPH₂ and HNP are much smaller, however.

More features of the bonding structures can be revealed by analyzing the Boys localized molecular orbitals (LMO) of these molecules. The orbital energies and atomic populations of valence LMOs are given in Table 8. Note that only the major contributions of the populations are given. For the single bonded H₂NPH₂, we obtained seven valence orbitals: two lone

pairs for phosphorus and nitrogen respectively, two P-H bonds, two N-H bonds, and one P-N bond. The population of the lone-pair orbitals are 1.961 for nitrogen and 2.047 for phosphorus. For the double bonded HNP, we obtained six valence orbitals: two lone-pairs for nitrogen and phosphorus, respectively, with very similar populations (1.983 and 2.050) to that for the former species, two P-N bonds (one σ and one π), one N-H bond, and one P-H bond. So far, all of these agree with our chemical intuition; common Lewis structures can be drawn for both molecules. However, for HNP₃, the seven valence orbitals obtained are one P-N bond, three P-H bond, one N-H bonds, and two (the first and second HOMOs) depleted lone-pairs on the nitrogen atom. It is important to note that the populations of the lone-pair orbitals are significantly smaller than 2.0 (1.795 and 1.794, respectively). Close examination of the coefficients of the atomic orbitals of the two lone-pair wave functions reveals that both orbitals are delocalized with major contributions (in addition to that of nitrogen) from phosphorus p-orbitals and small contributions from s-orbitals of hydrogens and d-orbitals of phosphorus.

From this analysis, we can draw the conclusion that the electronic structure of HNP₃ falls into the pattern suggested by Reed and Schleyer for X_nAY_m molecules.⁴³ The P-N

bonding in HNP₃H consists of an ionic σ bond and a π bond induced largely by negative hyperconjugation that involves electron donation from the lone-pair $\pi(\text{N})$ orbitals to $\sigma^*(\text{P}-\text{H})$ bonds. In contrast to the earlier proposed model,^{21,41} the participation of d-orbitals in the π bonding is insignificant. A better valence structure of polyphosphazene, which obeys the Lewis rule, can be represented by



With this valence model, we can explain the observations made in this and previously published work.

Because the π bonding is actually induced by the delocalization of the lone-pair orbitals of nitrogen, which are mostly confined in the vicinity of the P–N–P region, we corroborate the “island π bonding” proposed earlier by Allcock.⁴¹ But, in contrast to Allcock’s model, we find little contribution from phosphorus d-orbitals.

The π system of polyphosphazenes is very different from that of the “normal” conjugated molecules like polyacetylene. However, when the polyphosphazenes are forced to a planar conformation, we do see a similar bond alternation pattern in both systems. The similarity can be explained in the following ways: (1) When the end-group effect can be neglected, both systems are translationally symmetric. (2) Both systems have delocalized π electrons, although the extent and mechanism of the delocalization between the two systems are different. (3) The electron–electron interaction is the origin of bond alternation, which exists in both systems despite the difference in the conjugation. The electron–electron interaction in polyphosphazene is presumably weaker than that in the polyacetylene due to the restriction of the π orbitals in the formal system (the “island” π bonding), hence, the size of alternation is smaller in polyphosphazene than that in polyacetylene.

Since the π bonding is a consequence of the electron donation from the $\pi(\text{N})$ to the $\sigma^*(\text{P}-\text{X})$ orbitals, the strength of the π bonding is correlated to the relative position of the lone-pair orbitals of nitrogen and the P–X σ^* orbitals. Consequently, we conclude: (1) the molecular backbone does not necessarily favor planar conformation like the normal π conjugations and (2) the energy barrier to rotation of the P–N bond must be low. The ionic σ bonding, corresponding to large charge separation between the phosphorus and nitrogen atoms, leads naturally to the finding in this study that the electrostatic interaction is the dominating force which controls the rotational isomeric states of polyphosphazenes.

Because polarization of the P–X bond promotes the negative hyperconjugation which reinforces the π bonding system, we found that more electronegative side groups cause shorter P–N bonds (Tables 3, 4, and 7). For example, fluorine derivatives have the shortest P–N bonds in comparison with other substitutions. The stronger π bonding also strengthens the conjugation effect and the electron–electron interaction in the π system, which leads to larger bond alternation (Table 7).

IV. Summary and Remarks

(1) Comparison of DFT calculations of different functionals with HF and MP2 methods shows that the DFT method VWN/DNP yields comparable valence properties to MP2/DZ2P calculations with much less CPU time. Consequently, the VWN/DNP method was used with confidence to study molecular structures and conformations of polyphosphazenes.

(2) The optimized structures of planar trans–cis phosphazene oligomers of chain sizes from 1 to 8 show a converging pattern of systematic alternating P–N bond lengths. Since the electron correlation effect, which is a critical component for describing the electron–electron interaction, is included in the DFT calculations, the size of alternation obtained in this study is about half of that obtained using HF methods.¹⁴ The magnitude of the alternation is smaller than that of polyacetylene,³⁵ in the range of 0.03–0.07 Å depending on substituents. The alternations only exist in the planar structures which have been found in crystals.

(3) Rotation of the backbone P–N bond is very flexible as suggested previously by other research groups.^{19–21} The calculated energy barrier height to rotation of the P–N bond of monophosphazene is found to be ca. 2 kcal/mol, which is less than that for the C–C bond in ethane.

(4) There is a significant charge separation between the phosphorus and nitrogen atoms. Consequently, the intramolecular (nonbonded) electrostatic interaction dominates the energies of rotational isomeric states of polyphosphazenes. One consequence of this phenomenon is that the classic RIS model, which includes short-range interactions only, may not be sufficient to describe the statistics of polyphosphazenes. Another consequence is that any model representing the molecular interactions of polyphosphazene must include the electrostatic terms and must be parametrized carefully.

(5) These calculations for isolated linear phosphazenes and halophosphazenes with up to eight repeat units show that the twisted backbone structure is more stable than the planar trans–cis structure. This finding disagrees with many other calculations reported in the literature,^{14–17} which were mostly limited optimizations done with a planarity constraint. The accuracy level of computational methods is probably another source of the disagreement.

(6) Following Reed and Schleyer’s work,⁴³ a valence model is proposed for chemical bonding in phosphazenes and polyphosphazenes based on a comparison study of the electronic structures of model compounds that contain P–N bonds. The P–N bonding in phosphazene consists of an ionic σ bond and a π bond induced by *negative hyperconjugation*. This new model supercedes earlier ones and explains the structural and conformational properties reported in this and previous work.

(7) All calculations reported in this paper were performed on isolated molecules. The conformational properties obtained disagree in some respects with those measured for crystalline polyphosphazenes using X-ray diffraction. As seen in many other polymers, the packing effect may have a strong impact on the chain conformations in crystals. For example, isolated poly(dimethylsilanes) (PDMS) are helices, but the chain conformations in crystals are planar, all trans.^{25,40} Due to the large charge separation between phosphorus and nitrogen atoms in phosphazenes, it is reasonable to expect a strong intermolecular electrostatic interaction that can significantly influence chain conformations in bulk systems. To study the chain conformation in crystals, 3-D crystal calculations using an ab initio method such as DFT or a molecular force field method is required. Work in this area is ongoing in our research group.

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