Study of the Molecular Geometry, Electronic Structure, and Thermal Stability of Phosphazene and Heterophosphazene Rings with ab Initio Molecular Orbital Calculations

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Received July 24, 1998

Ab initio molecular orbital calculations at the MP2/6-31G* level of theory have been used to study the molecular geometry, electronic structure, and the thermal stability of six-membered phosphazene and heterophosphazene rings. The studies included the phosphazene ring $[NPCl_2]_3$, the carbophosphazene ring $[(NCCl)(NPCl_2)_2]$, and three thionylphosphazene rings $[(NSOX)(NPCl_2)_2]$ (X = F, Cl) and $[(NSOF)(NPF_2)_2]$ and their cations $[(NPCl)(NPCl_2)_2]^+$, $[(NC)(NPCl_2)_2]^+$, and $[(NSO)(NPY_2)_2]^+$ (Y = F, Cl). The ring skeleton of the phosphazene ring, the carbophosphazene ring and of all cation rings adopt a planar conformation; the ring skeletons of the thionylphosphazene rings adopt an envelope conformation. The valence electron charge density of the molecules indicates strong charge separations along their skeleton and is in agreement with Dewar's island delocalization model. The electrostatic potential in the vicinity of the neutral heterophosphazene rings which results from their electronic structure, and the position of the HOMO indicate that a heterolytic cleavage of a ligand and the opening of the ring involving a reaction with a electrophilic cation will most likely occur at the nitrogen atoms close to the heteroatom. The thermal stability of the phosphazene ring with respect to a cleavage of chlorine from phosphorus and the thermal stability of the heterophosphazene rings with respect to the cleavage of the halogen ligand bonded to the heteroatom were studied with several model reactions. Most of the reactions are exothermic. A comparison of isodesmic reactions shows that the thionylphosphazenes molecules are the least thermally stable rings with respect to ionization and that the carbophosphazene molecules are the most thermally stable rings with respect to ionization. The energy gains during the ionization reaction of the rings correlate well with the conformational changes which occur during the reactions.

Introduction

Polymers with a main chain constructed from inorganic elements can often be synthesized from cyclic inorganic rings via a thermally induced ring opening polymerization.[1−5] The thermal ring opening polymerization of the six-membered phosphazene rings $[NPCl_2]_3$ (**1**),[5] carbophosphazene rings $[(NCCl)(NPCl_2)_2]$ (**2**), and thionylphosphazene rings $[(NSOX)(NPCl_2)_2]$ (X = F, Cl) **3a,b** (see Figure 1) yield poly(dichlorophosphazene) $[NPCl_2]_n$, poly(carbophosphazene) $[(NCCl)(NPCl_2)]_n$,[2] and poly(thionylphosphazene) $[(NSOX)(NPCl_2)]_n$ (X = F, Cl)[3,4] polymers. The polymerization mechanism is, in addition to molecular geometry and electronic structure of the rings, an area of particular interest. Initial studies suggested a cationic chain growth process with an initiation step involving the formation of a cationic ring by the heterolytic cleavage of a substituent.[5−8]

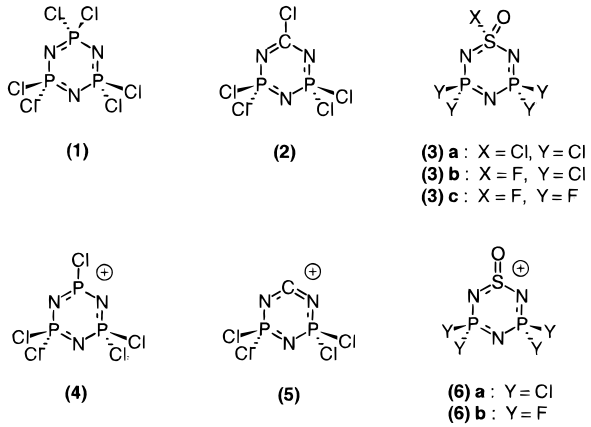

Figure 1. Phosphazene **1**, carbophosphazene **2**, and thionylphosphazene rings **3a**−**c**, and their cations **4**−**6a,b**.

In the last decades, computational methods have become important for studying the properties of molecules. Previous ab initio quantum chemical studies on the structure and bonding of cyclic and short chain linear phosphazene molecules were carried out by Trinquier[9,10] and Ferris et al.[11,12] Subsequently we performed in our group quantum chemical calculations which

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10.1021/ic980877n CCC: $18.00
Published on Web 03/04/1999

Table 1. MP2/6-31G* ab Initio Results on the Molecular Geometry of the Neutral Cyclic Molecules **1**−**3c**, E = C for **1**, and E = S for **3a**−**c**

	1	**2**	**3a**	**3b**	**3c**
$r(N_1-P_1)$ in Å	1.60	1.62	1.62	1.62	1.60
$r(P_1-N_2)$ in Å	1.60	1.60	1.60	1.60	1.58
$r(E-N_1)$ in Å	−	1.33	1.58	1.58	1.57
∠(N−P−N) in deg	118.7	117.5	117.5	117.3	117.8
∠(P−N−P) in deg	121.3	115.5	120.4	120.8	120.9
∠(E−N−P) in deg	−	118.3	120.1	119.8	121.0
∠(N−E−N) in deg	−	133.0	113.3	114.6	114.2
ξ in deg	0.0	0.0	32.1	31.5	27.5

focused on the structure and chain flexibility of linear, short chain thionylphosphazene molecules.[13−15] In this paper, we want to study the molecular geometry and the electronic structure of the six membered phosphazene and heterophosphazene rings **1**−**3a**−**c** and their cations **4**−**6a,b** and the thermal stability of the neutral rings **1**−**3a**−**c** with respect to the heterolytic cleavage of a ligand with ab initio molecular orbital calculations.

Computational Methods

Gaussian 94 ab initio calculations were carried out on Silicon Graphics Indy R4600 and Silicon Graphics O2 R10000 workstations.[16,17] The graphical presentations of the molecules were created with the Cerius^2 molecular modeling package.[18] The charge densities and molecular orbitals were plotted with the IRIS Explorer graphics package.

Calculations were carried out at the closed shell Hartree−Fock and closed shell MP2 (second-order Møller−Plesset perturbation theory) level of theory with the 6-31G* polarized split valence basis set. A comparison of experimental and calculated (RHF and MP2) molecular geometries is presented at the end of the following section.

Molecular Geometries of the Ring Molecules and their Cations

We first want to discuss structural parameters of the inorganic ring molecules. Selected bond lengths, bond angles, and dihedral angles of the ring molecules are displayed in Tables 1 and 2. The definition of the plane angle ξ and the labeling of the ring atoms E, N_1, P_1, and N_2 is shown in Figure 2. Further details on the results of the calculations (complete internal coordinates, etc.) are available in the Supporting Information.

On the basis of the geometry optimizations which we carried out, the following conclusions can be reached. The six-membered dichlorophosphazene ring adopts a planar conformation with D_{3h} symmetry. Introducing a heteroatom into the ring system or cleaving a substituent reduces the symmetry of the ring molecules: the neutral carbophosphazene rings and all cationic rings adopt a planar conformation with C_{2v} symmetry. The two different substituents which are bonded to sulfur in the thionylphosphazene rings lead to an envelope conformation of the ring skeleton. The sulfur atom is tilted out of the plane which is defined by the three nitrogen atoms (see Figure 2). The chlorinated thionylphosphazene ring shows the most pronounced envelope conformation (ξ(**3a**, MP2/6-31G*) = 32.5°, ξ(**3b**, MP2/6-31G*) = 31.5°, ξ (**3c**, MP2/6-31G*) = 27.5°). The lower symmetry of the molecular geometry of the heterophosphazene rings and the corresponding cations can be seen in alternations of the P−N bond lengths. Cleaving a substituent leads for each of the four cation rings to a more pronounced P−N bond length alternation and a widening of the N−E−N (E = P, C, S) angle where the E is the atom where the cleavage occurs. The most pronounced widening of the N−E−N bond angle is observed for the carbophosphazene ring. The N−C−N bond angle changes from 133.0° (MP2/6-31G*, neutral ring **2**) to 163.7° (MP2/6-31G*, cation **5**).

To assess the accuracy of the geometry optimizations, we compared the calculated geometries of the phosphazene and thionylphosphazene rings to results of X-ray diffraction studies.

Structural data on six-membered dichlorophosphazene rings are compiled in the review paper by Shaw et al.[19] Most of the diffraction studies found a planar conformation of the six-membered phosphazene rings with equal P−N bond lengths. An exception is found in the study of Giglio,[19,20] where a chair conformation of the ring with alternating P−N bond lengths was observed. Overall, the calculated structures which are reported in this study agree well with the experimental planar

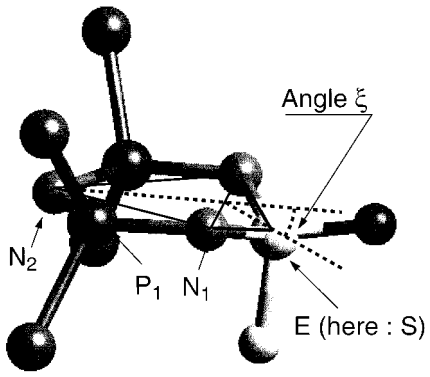

Figure 2. Thionylphosphazene ring **3b**. The definition of atoms E, N_1, P_1, and N_2 and the plane angle ξ which describes the ring tilt are shown on this model.

Table 2. MP2/6-31G* ab Initio Results on the Molecular Geometry of the Cationic Cyclic Molecules **4**−**6b**; E is the Phosphorus Atom Where the Cleavage Occurred for **4**, E = C for **5**, and E = S for **6a,b**

	4	**5**	**6a**	**6b**
$r(N_1-P_1)$ in Å	1.59	1.72	1.69	1.66
$r(P_1-N_2)$ in Å	1.68	1.70	1.59	1.57
$r(E-N_1)$ in Å	1.57	1.24	1.55	1.55
∠(N−P−N) in deg	114.6	109.4	113.6	114.2
∠(P−N−P) in deg	129.8	127.5	128.5	127.8
∠(E−N−P) in deg	116.9	105.0	120.4	120.8
∠(N−E−N) in deg	129.3	163.7	123.4	122.1
ξ in deg	0.0	0.0	0.0	0.0

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Table 3. Experimental and ab Initio Structural Data of the Ring Molecules **1** and **3a**

	1		
	RHF/6-31G*	MP2/6-31G*	expt.[19]
r(P−N) in Å	1.58	1.60	1.57−1.65
∠(N−P−N) in deg	116.2	118.7	118−121
∠(P−N−P) in deg	123.7	121.3	118−120
	3a		
	RHF/6-31G*	MP2/6-31G*	expt.[21]
$r(N_1-P_1)$ in Å	1.59	1.61	1.58
$r(P_1-N_2)$ in Å	1.61	1.63	1.60
r(S−N) in Å	1.57	1.60	1.56
∠(S−N−P) in deg	125.0	120.9	120.1
∠(P−N−P) in deg	122.7	122.0	120.4
∠(N−P−N) in deg	115.4	117.5	116.8
ξ in deg	18.6	32.2	26.2

structures with equal P−N bond lengths (see Table 3). The RHF calculations overestimate the P−N−P bond angle. Including electron correlation improves the agreement of the calculated value for the P−N−P angle with the crystal structure data.

Molecular geometries which were obtained from a X-ray diffraction study by van de Grampel[21] on the thionylphosphazene ring **3a** and selected geometrical parameters which were obtained from our calculations are also shown in Table 3. The bond lengths are in general underestimated by RHF/6-31G* and MP2/6-31G* calculations. MP2 calculations result—compared to RHF calculations—in a better description of conformational features such as bond angles and tilt angles. As a concluding remark it should be noted that calculated geometries correspond to individual molecules in the gas phase. X-ray data were obtained from molecules positioned on a crystal lattice. Conformational changes due to the packing of molecules onto a crystal lattice are not included in the ab initio calculation we carried out.

Electronic Structure and Thermal Stability of Cyclic Phosphazenes and Heterophosphazenes

A possible path for the polymerization reaction of phosphazene and heterophosphazene rings is a cationic chain growth process with an ionization of a P-Cl, a C−Cl, or a S−X (X = F, Cl) bond.[5,6] Experimental studies of van de Grampel and Manners suggest that the ionization for thionylphosphazenes occurs most likely at the S−X bond.[6−8,22] We intend to use the results of our quantum chemical calculations in order to gain further insight into possible reaction mechanisms.

The chemical reactivity of molecules is affected by several factors. The rate of reaction can, for example, be accelerated by the Coulombic attraction between two reactants. In reactions of a nucleophile with an electrophile, the interaction between the HOMO (highest occupied molecular orbital) of the nucleophile with the LUMO (lowest unoccupied molecular orbital) of the electrophile contributes to the attraction between the two reactants. Studying the electrostatic potential in the vicinity of the reactants and the spatial distribution of HOMO and LUMO of the reactants is expected to show whether or not the reaction is site-specific.[23]

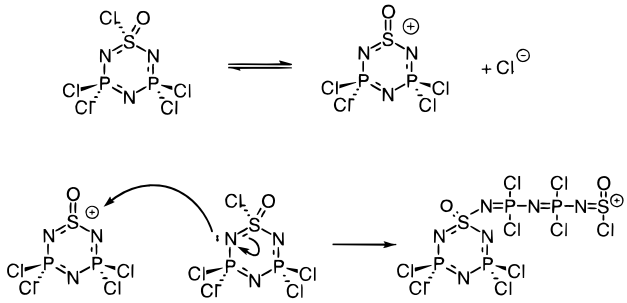

Figure 3. Suggested polymerization mechanism: initiation step (heterolytic cleavage of chlorine at sulfur) and propagation (ring opening) for the chlorinated thionylphosphazene ring.

Modeling an entire chemical reaction in detail (e.g. following the reaction path, including the effect of solvent molecules, etc.) with molecular orbital calculations would involve many calculations on large systems, and is therefore in most cases not feasible. It is, however, possible to elucidate certain aspects of a chemical reaction. The charge density, electrostatic potential, and HOMO and LUMO of an individual molecule in the gas phase will yield information on the reactivity of the molecule in an actual reaction. Calculated values for energies of model reactions in the gas phase will be different from the energies of actual reactions which occur in solution or in the melt. Comparing calculated results on a series of reactions of similar model systems (e.g. comparing reactions of phosphazene, carbophosphazene, and thionylphosphazene rings) may show trends in the reactions of these systems and can yield some insight into factors which determine their thermal stability.

We want to address two questions related to the suggested reaction mechanism depicted in Figure 3. First, we attempt to investigate whether or not the two reaction steps are site-specific, and subsequently we want want to address the issue of the thermal stability of the neutral rings with respect to a heterolytic cleavage of a halogen substituent with several model reactions.

Electronic Structure of the Phosphazene and Heterophosphazene Rings and their Cations

One result of the molecular orbital calculations is the molecular wave function of the molecules. The wave function can be used to determine the electrostatic potential in the vicinity of the rings in order to identify sites which will attract cations, and which will therefore be most likely involved in the reaction.

The representative plot of the valence electron charge densities of a neutral ring molecule is displayed in Figure 4. We observe a build-up of charge density on the nitrogen atoms and nodes at the phosphorus and heteroatoms (C and S). This charge distribution is in agreement with the island delocalization model of bonding in linear and cyclic phosphazenes elucidated by Dewar.[24] Dewar's model states that a delocalization of valence electrons occurs over only three-atom P−N−P units. This leads to an island-like structure of the charge density with nodes on phosphorus and high charge densities on nitrogen. This charge distribution results in highly polar ring skeleton. Population analysis schemes like the Natural Population Analysis[25] assign strong partial charges to the individual atoms of the ring molecules (see Table 4). The ligands bonded to the inorganic ring are all negatively charged and therefore repel each other.

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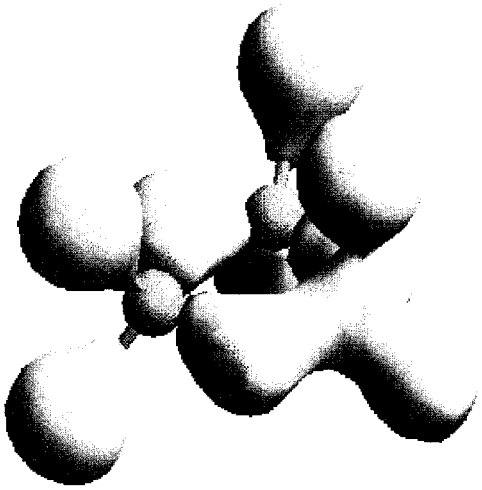

Figure 4. Valence electron charge densities of the chlorinated thionylphosphazene ring **3a**. The surfaces denote points of constant charge density.

Table 4. Partial Charges (in e) Situated on Selected Ring Atoms Which Were Determined with the Natural Population Analysis[a]

atom	**1**	**2**	**3a**	**3b**	**3c**
R	−	0.6	2.4	2.7	2.7
N_1	−1.6	−1.1	−1.4	−1.4	−1.4
P_1	2.1	2.0	2.0	2.0	2.8
N_2	−1.6	−1.6	−1.6	−1.6	−1.6
X	−	0.0	−0.2	−0.5	−0.5
O	−	−	−0.9	−1.0	−1.0
Cl/F[a]	−0.2	−0.2	−0.2	−0.2	−0.2

[a] Cl bonded to P for **1**−**3b**, and F bonded to P for **3c**.

Isopotential surfaces of the electrostatic potential of the carbophosphazene and the fluorinated thionylphosphazene rings are shown in Figure 5. The gray shaded grids are surfaces of zero potential, i.e. they separate regions where positive charges are attracted from regions where positive charges are repelled. In the space above these surfaces ($E_{pot} > 0$, on the side of the ring where the heteroatom is situated), positive charges are attracted; in the space below these surfaces ($E_{pot} < 0$), positive charges are repelled. There remains a small attractive region for positive charged ions close to the nitrogen atom opposite from the heteroatom (i.e. in the "repulsive" area). The black surfaces include areas with an electrostatic potential higher than 0.039 hartree/e. These maxima of the potential are for the carbo- and thionylphosphazene rings situated close to the nitrogen atoms bonded to the heteroatom. For the thionylphosphazene ring we find an additional area of high electrostatic potential close to the oxygen atom. Cations will be electrostatically attracted to the side of the ring where the heteroatom is situated. The sites close to the heteroatoms are therefore favored for reactions of heterophosphazenes with cations.

Both steps of the suggested polymerization mechanism involve the reaction of an electrophile (the cation) with a nucleophile (the ring molecule). The interaction of the LUMO of the cation with the HOMO of the ring plays therefore an important role in the reaction.

The electronic structure of linear and cyclic phosphazenes was previously investigated by Ferris and co-workers.[11,12] They reported that the phosphonitrilic molecules contain both π' (in-plane) and π (out-of-plane) bonding systems. We find similar results for the heterophosphazene rings. The highest occupied molecular orbital (HOMO) and the second highest occupied molecular orbital (HOMO-1) are, for all neutral rings, an out-of-plane π bonding system. HOMO-2 to HOMO-4 are—depending on the ring—either an in-plane π' or an out-of-plane π orbital.

The two degenerate highest occupied orbitals of the dichlorophosphazene ring and the HOMO of the carbophosphazene- and the chlorinated thionylphosphazene ring are shown in Figure 6.

The position of the HOMO of the neutral heterophosphazene rings can indicate at which site of the ring an electrophile attack is most likely to occur. If the energy eigenvalues of the HOMO and the second highest occupied molecular orbital are very close, the HOMO-1 must also be considered as a possible site of an electrophile attack.

This is the case for the thionylphosphazene rings **3a**−**c**. The energy difference between HOMO and HOMO-1 is small compared with the energy difference between the HOMO and LUMO or the HOMO-1 and HOMO-2. Since the HOMO and HOMO-1 of **3a**−**c** are situated at all nitrogen atoms, one cannot conclude that the HOMO/LUMO interaction will favor a specific site of the thionylphosphazene rings.

In case of the carbophosphazene ring there is a considerable energy gap (20.24 kcal/mol) between the HOMO which is a out-of-plane π bonding system centered at the nitrogen atoms close to the carbon atom, and the HOMO-1, which is situated at the nitrogen atom opposite to the carbon atom (see Table 5). We can therefore identify for the carbophosphazene ring the HOMO as a site which will be most likely involved in a reaction with a electrophile.

The LUMOs of all cation rings are located at the side of the ring where the heterolytic cleavage of a substituent occurred (i.e. at the side of the heteroatom for the heterophosphazene rings) (see Figure 7). LUMO and LUMO+1 of all cation rings are energetically well separated such that the LUMO will be mostly involved in reactions with a nucleophile.

We can summarize that the analysis of the electrostatic potential of the heterophosphazene rings showed that a reaction with a cation will most likely occur close to the heteroatom. For the carbophosphazene ring the HOMO is located close to the heteroatom. The HOMO/LUMO interaction will in this case also favor a reaction close to the carbon atom. For the cation rings the LUMOs are located at the site where the cleavage of the substituent occurred. These sites will therefore most likely participate in a reaction as electrophilic moieties.

Thermal Stability of the Cyclic Phosphazenes and Heterophosphazenes with Respect to Heterolytic Cleavage of a Substituent

The results on the electronic structure of the rings which we presented in the previous section support the experimental results of van de Grampel and Manners[6−8,22] which indicate that the heterolytic cleavage of a substituent of the heterophosphazene rings will most likely occur at the heteroatom. In this section we want to study the energy gains and losses of reactions involving the heterolytic cleavage of the halogen ligand bonded to the heteroatom of rings **2** and **3a**−**c**. These reactions are compared to the cleavage of a chlorine atom from the phosphazene ring **1**.

We used the following type of reactions for our ab initio studies:

$$\text{ring} + \text{counter-reactant}^+ \rightleftarrows \text{ring}^+ + \text{counter-reactant} \quad (1)$$

Energy gains or losses are evaluated by subtracting energies of the products from energies of the reactants. We included the

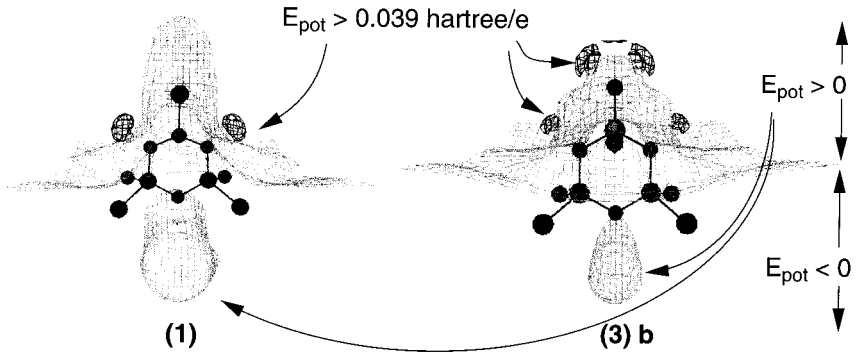

Figure 5. Isosurfaces of the electrostatic potential in the vicinity of the carbophosphazene ring **2** and fluorinated thionylphosphazene ring **3b**. The ring skeletons are situated in the plane of the drawing. The gray-shaded grids are surfaces of zero potential. The black grids show the regions of the highest electrostatic potential.

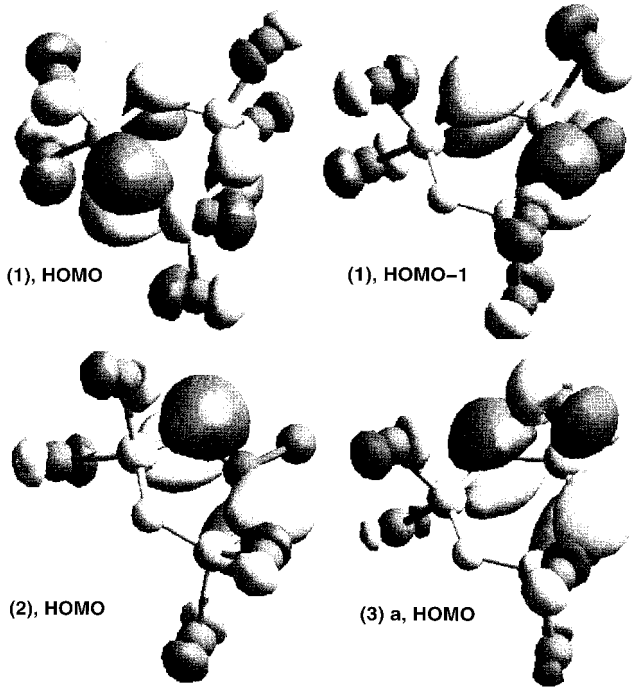

Figure 6. HOMOs (degenerate) of the phosphazene ring **1**, and HOMO of the carbophosphazene ring **2** and the thionylphosphazene ring **3a**.

Table 5. Energy Differences (in kcal/mol) between HOMO-2, HOMO-1, HOMO, and LUMO

ΔE	**1**	**2**	**3a**	**3b**	**3c**
$E_{HOMO-1} - E_{HOMO-2}$	13.08	4.24	9.48	16.44	8.45
$E_{HOMO} - E_{HOMO-1}$	0.	20.24	1.93	0.16	2.51
$E_{LUMO} - E_{HOMO}$	320.63	310.47	312.67	330.29	399.3

zero-point vibrational energy and thermal energy terms (the latter in order to obtain energy values for 298 K) into the calculation of the energy gains and losses:

$$\Delta E^{298} = \Delta E_0 + \Delta E_v^0 + \Delta(\Delta E_v^{298}) + \Delta E_r^{298} + \Delta E_t^{298} \quad (2)$$

If a suitable counter-reactant is chosen, the number of formal bonds are conserved during the reaction. This type of reaction is called an "isodesmic reaction". An example of an isodesmic reaction of the chlorinated thionylphosphazene ring and sulfonyl dichloride SO_2Cl_2 is shown in Figure 8. Since the number and type of bonds is the same on the reactant and product side of the reaction, systematic errors in the calculations of energies (e.g. incomplete treatment of electron correlation) are likely to cancel to a certain degree when the difference between the

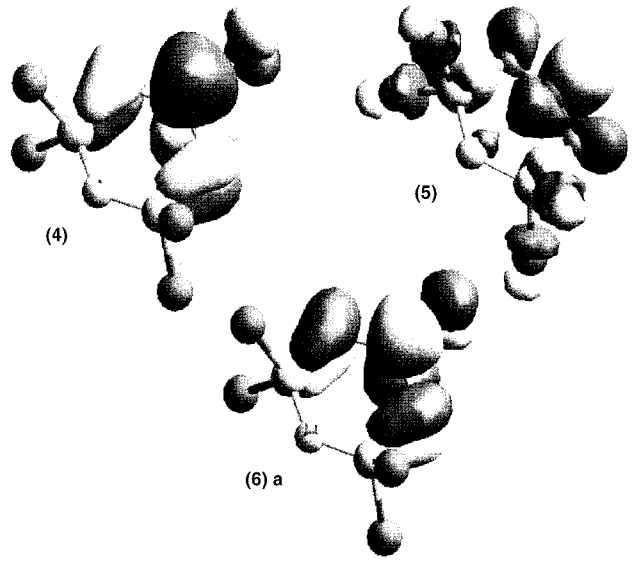

Figure 7. LUMO of the phosphazene cation **4**, the carbophosphazene cation **5**, and the thionylphosphazene cation **6a**.

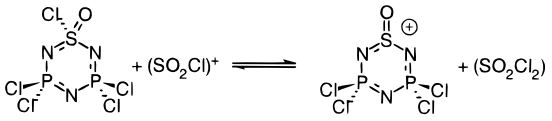

Figure 8. Isodesmic reaction of the chlorinated thionylphosphazene ring with the sulphonylchloride cation.

energy of products and reactants is determined.[26] We studied reaction with SO_2Cl_2, $POCl_3$, CCl_4, and $COCl_2$ as counter-reactants for the heterolytic cleavage of a chlorine ligand, and reactions with SO_2F_2, CF_4, and COF_2 as counter-reactants for the heterolytic cleavage of a fluorine ligand. The results for ΔE^{298} are shown in Tables 6 and 7. The results for isodesmic reactions are printed in bold face.

The RHF and MP2 calculations yield similar values for ΔE^{298} for the isodesmic reactions for dichlorophosphazene- and carbophosphazene rings (ΔE^{298}(MP2) − ΔE^{298}(RHF) ranges between 0.6 and 2.9 kcal/mol). For non-isodesmic reactions the differences between MP2 and RHF results increase to −3.8 to 11.5 kcal/mol. This is in contrast to the results for the reactions of thionylphosphazene rings. ΔE^{298}(MP2) − ΔE^{298}(RHF) lies for all thionylphosphazenes in the range between 6.5 and 7.8

(26) Hehre, W. J.; Radom, L.; v. R. Schleyer, P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; p 298.

Table 6. Energy Gains (in kcal/mol) for Reactions of Chlorinated (Hetero)phosphazene Rings and Suitable Counter-Reactants

	ΔE^{298} for **1**		ΔE^{298} for **2**		ΔE^{298} for **3a**	
	MP2/ 6-31G*	RHF/ 6-31G*	MP2/ 6-31G*	RFH/ 6-31G*	MP2/ 6-31G*	RHF/ 6-31G*
SO_2Cl_2	−19.75	−26.80	−28.86	−40.40	**−41.98**	**−48.44**
$POCl_3$	**−30.57**	**−33.48**	−39.68	−47.08	−52.80	−55.12
CCl_4	2.92	6.77	**−6.187**	**−6.83**	−19.30	−14.87
$COCl_2$	−9.40	−5.88	**−18.51**	**−19.48**	−31.63	−27.52

Table 7. Energy Gains (in kcal/mol) for Reactions of Fluorinated (Hetero)phosphazene Rings and Suitable Counter-Reactants

	ΔE^{298} for **3b**		ΔE^{298} for **3c**	
	MP2/6-31G*	RHF/6-31G*	MP2/6-31G*	RHF/6-31G*
SO_2F_2	**−63.32**	**−70.31**	**−50.89**	**−58.67**
CF_4	−60.96	−52.46	−48.52	−40.81
COF_2	−55.37	−52.63	−42.94	−40.99

kcal/mol; the differences for non-isodesmic reaction lie between −8.4 and 2.3 kcal/mol.

The results of the calculations show that the reactions are in general exothermic (with the exception of the reaction of **1** with CCl_3^+). Most of the cation rings will therefore form readily. The energy gains depend on the choice of the counter-reactants. Superimposed on the data is the propensity of the counter-reactants to form a neutral molecule by forming a bond with a halogen ion. In addition, we can state that the activation temperatures which are observed for the thermal ring opening polymerization cannot be explained by the suggested first step of the reaction, the heterolytic cleavage of a substituent on the heteroatom: since the ionization step is exothermic, no activation energy is needed. Furthermore, the order of temperatures T_{ROP} where the thermal ring opening polymerization sets in, does not correlate with the order of the energy gains (T_{ROP}(**1**) = 250 °C, T_{ROP}(**2**) = 120 °C, T_{ROP}(**3a**) = 165 °C, and T_{ROP}(**3b**) = 180 °C).[2,4,5] The experimentally observed activation barriers suggest that the ring opening reaction has to pass through some transition states (e.g. during the ring-opening of the cationic rings), whose "heights" then could explain the polymerization temperatures. Transition states which have to be overcome by an activation energy were not considered in our calculations since we considered only reactants and products of the first step of the ring opening polymerization in our calculations.

If one compares the energy gains of the phosphazene and heterophosphazene rings for the isodesmic reactions, the molecules can be organized in three groups: the highest energy gain is observed for the thionylphosphazene rings, followed by the phosphazene ring, followed by the carbophosphazene ring which showed the lowest energy gain. The energy gains correlate well with the conformational changes which occur during the heterolytic cleavage of the substituent: the carbophosphazen ring shows the smallest change in the geometry of the skeleton (essentially only the chlorine atom is removed). For the phosphazene ring, the remaining chlorine atom at the site of the cleavage moves into the plane of the P−N backbone of the ring. For the thionylphosphazene rings, the conformation of the S−N−P backbone of the ring changes from an envelope conformation to a planar conformation, and the oxygen atom bonded to sulfur moves into the plane of the ring skeleton.

The heterolytic cleavage of chlorine form **1** and chlorine or fluorine from **3a**−**c** differs in two aspects from the heterolytic cleavage of chlorine from **2**. For **1** and **3a**−**c**, the negatively charged chlorine or fluorine ligand is positioned relatively close to the negatively charged chlorine atoms bonded to the phosphorus atoms. If one ligand is removed, the electrostatic repulsion between the ligands will make a contribution to the energy which is gained during the ionization step. Secondly, the remaining substituent which is bonded to the ring atom where the cleavage occurred is moved away from the other chlorine atoms bonded to phosphorus. As a result, the electrostatic energy of the cation rings decreases further. These two effects are most pronounced for the thionylphosphazene rings. Due to the envelope conformation, the halogen atom bonded to sulfur is—compared with the phosphazene ring—closer to the other chlorine ligands. In addition, the oxygen atom bonded to sulfur is strongly negatively charged. The change from an envelope to a planar conformation and the motion of the oxygen into the ring plane will therefore lead to a significant decrease of the electrostatic repulsion between the ligands.

The result that conformational changes correlate well with energy differences in isodesmic reactions is not surprising: since the number of formal bonds is retained, essentially only change position of individual atoms with respect to each other is changed. Changes in the electrostatic energy will therefore give an essential contribution to the energy gain in these reactions.

If we do not restrict our analysis to isodesmic reactions, the energy gains or losses also include the formation and cleavage of different types of bonds (e.g. in the reaction of **1** with CCl_3^+ a Cl−P bond is cleaved and a Cl−C bond is formed). Reactions involving CCl_3^+ or $COCl^+$ as counter ion in general result in lower energy gains than reactions involving $POCl_2^+$ or SO_2Cl^+ as a counter ion. As a result, the order of the thermal stability for **1** and **2** is reversed if energy gains for one type of counter-reactant are compared: in contrast to the isodesmic reactions, **1** is the thermally most stable ring. The thionylphosphazene rings **3** remain the least thermally stable rings.

The link between energy gains of isodesmic ionization reactions and the conformational changes which occur during the reaction can be used in order to obtain a rough estimate of energy gains or losses of other isodesmic reactions involving the inorganic rings **1**−**3a**−**c**. For example, we can try to estimate whether or not an isodesmic reaction involving a cleavage of chlorine from a phosphorus atom instead of the heteroatom will result in a higher energy gain. For the thionylphosphazene rings, we would expect a lower energy gain if a Cl−P instead of a Cl−S bond is cleaved. The latter will decrease the electrostatic repulsion of the ligands to a larger extent. If chlorine is cleaved from sulfur, the remaining substituents bonded to the ring will be moved further apart, since the ring skeleton of the cation will adopt a planar conformation. In addition, the highly negative charged oxygen is moved into the ring plane. If chlorine is cleaved from phosphorus, the envelope conformation is retained, and the oxygen atom remains closer to the other ligands.

For the carbophosphazene ring, we expect the opposite result: when a chlorine atom is cleaved from phosphorus, the remaining chlorine will move into the plane of the ring skeleton, and will therefore reduce the electrostatic repulsion with the chlorine atoms bonded to the other phosphorus atoms. We expect therefore a higher energy gain for the cleavage of chlorine from phosphorus than the cleavage of chlorine from carbon.

Energy gains calculated on the RHF/3-31G* level of theory confirm this analysis: for the heterolytic cleavage of chlorine from phosphorus from **3a** with $POCl_2^+$ as counter-reactant we obtain an energy gain of −23.0 kcal/mol (in contrast to −55.1 kcal/mol for the cleavage of Cl from S with the same counter-reactant). For the cleavage of chlorine from phosphorus from **2** with $POCl_2^+$ as counter-reactant we obtain an energy gain of −27.8 kcal/mol (compared to −6.8 kcal/mol for the isodesmic

reaction with CCl_3^+, and −19.5 kcal/mol for the isodesmic reaction with $COCl^+$). For a reaction of **2** with $POCl_2^+$, the cleavage of chlorine from carbon remains the most exothermic reaction, since the energy gains resulting from the conformational changes due to the cleavage of Cl from P are outweighed by the energy gains of the cleavage of a Cl−C and the subsequent formation of a Cl−P bond.

Summary

The molecular geometry of the phosphazene- and heterophosphazene rings **1**−**3a**−**c** and their cations **4**−**6a,b** were determined with ab initio molecular orbital calculations at the MP2/6-31G* level of theory. The phosphazene and carbophosphazene ring and all cation rings adopt a planar conformation. The thionylphosphazene rings adopt an envelope conformation. The sulfur atom is tilted out of the plane which is defined by the three nitrogen atoms of the ring skeleton. The chlorinated thionylphosphazene ring **3a** adopts the most pronounced envelope conformation.

The charge density of the valence electrons of all rings is in agreement with Dewar's island delocalization model which was developed to describe bonding in phosphazenes. We observe a build-up of charge density on the nitrogen atoms, and nodes at the phosphorus and the heteroatoms. The ring skeleton is therefore highly polar. An analysis of the electrostatic potential in the vicinity of the neutral carbo- and thionylphosphazene rings showed that positively charged ions will be attracted to the side of the ring where the heteroatom is situated.

In accordance with the studies of Ferris and co-workers, all rings show in-plane and out-of-plane π bonding. It is not possible to identify a preferred side of the ring for an electrophilic attack from the spatial distribution of the HOMO of the phosphazene ring **1** and the thionylphosphazene rings **3a**−**c**. The HOMOs of **1** are situated at all three nitrogen atoms. For **3a**−**c**, the energy difference between HOMO and HOMO-1 is small, and HOMO and HOMO-1 are also situated at all three nitrogen atoms. The HOMO of the carbophosphazene ring **2** is situated close to the carbon atom, and the energy difference to the HOMO-1 is large compared to the energy difference between the HOMO and HOMO-1 of the other rings. A electrophilic attack on **2** will therefore occur most likely close to the carbon atom due to favorable HOMO/LUMO interactions. The LUMOs of all cation rings are situated close to the heteroatom, or (for **4**) the phosphorus atom where the cleavage of the chlorine atom occurred.

Based on the investigation of the electrostatic potential around the heterophosphazene rings (and the position of the HOMO for **2**), our calculations support the experimental results of Manners and van de Grampel that a heterolytic cleavage of a ligand of a heterophosphazene ring and the ring opening reaction will most likely occur close to the heteroatom.

The thermal stability of the rings with respect to the heterolytic cleavage of a chlorine atom from **1** and of the halogen ligand bonded to the heteroatom from **2**−**3a**−**c** were studied with different model reactions. All reactions which were studied are exothermic, apart from the reaction of **1** with CCl_3^+. Thus, the cation rings should generally form readily. If we compare the energy gains of isodesmic reactions, we find that the thionylphosphazenes **3a**−**c** are the least thermally stable rings with respect to ionization, and the carbophosphazene ring **2** is the most thermally stable ring with respect to ionization. The energy gains correlate well with the conformational changes which occur during the reactions. These changes move the negatively charged ligands bonded to the ring skeleton further apart, and decrease therefore the electrostatic energy of the cation ring. The most extensive conformational changes occur for the thionylphosphazene rings, followed by the phosphazene ring. The smallest conformational changes occur during the ionization of the carbophosphazene ring.

Acknowledgment. The financial support of the Nuffic exchange program (M.D.) and the University of Twente is gratefully acknowledged. It is a pleasure to thank Ms. Anne Klemperer for the help with the preparation of this paper.

IC980877N