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From Substituted Cyclotriphosphazenes to Double–Stranded Phosphazene Chains – A Quantumchemical Study[#]

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Abstract

Hybrid density functional theory methods have been used to examine the reactivity of hexafluoro– and hexachlorocyclotriphosphazene with respect to single, multiple and complete substitution with water, ammonia, phosphoric and sulfuric acid. Geometries of both educts and all substitution products have been optimized and their thermodynamic properties are discussed. Based on these results the thermodynamically most favorable reaction pathways have been determined. Starting from a basic unit, which consists of two phosphazene rings that are geminally linked by two hydrazine bridges, several possibilities to form double–stranded chains or helices containing cyclotriphosphazenes were examined by PM3 calculations.

Keywords. Substituted cyclotriphosphazene; double–stranded phosphazene chains and helices; quantumchemical calculations; thermochemical calculations.

Abbreviations and notations

B3LYP, density functional theory with B3LYP formalism
DNA, deoxyribonucleic acid
FC, frozen core approximation
HF, Hartree–Fock theory
MP2, second–order Møller–Plesset perturbation theory
NBO, natural bond orbital
PM3, Semiempirical method with a Parameterized Method 3 model hamiltonian

1 INTRODUCTION

As early as 1834 Rose investigated the reaction of phosphorus pentachloride with ammonia. Ever since then there has been considerable interest in the chemistry and bonding of phosphazene and its derivatives [1]. In an editorial comment to Rose's work J. v. Liebig describes an unknown byproduct he and F. Wöhler had isolated [2]. Later Gerhard [3,4], Laurent [5], Gladstone and Holmes [6–8], and Wichelhaus [9] were able to determine the molecular weight and chemical composition $N_3P_3Cl_6$ of this byproduct. Stokes [10–14] identified its cyclic structure and showed, that this 2,2,4,4,6,6–hexachlorocyclotriphosphazene is the beginning of a series of cyclic homologous. Schenk and Römer [15] developed a more efficient synthesis, which is still the basis

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[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.

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for todays synthesis methods. An extensive and detailed overview of the different syntheses for many halogen–, pseudohalogen–, alkyl–, alkyloxo– and arylcyclotriphosphazenes is given by Pantel and Becke–Goehring [16].

The structure of hexachlorocyclotriphosphazene was investigated by Wilson and Carroll [17], Giglio [18] and Bullen [19] by crystal structure analysis. The authors concluded from their results, that the molecule is a nearly planar hexagonal ring system with alternating phosphorus and nitrogen atoms. All nitrogen phosphorus bonds are equally long and the chlorine atoms are bond to the phosphorus atoms in pairs. The molecule has a D_{3h} symmetry (Figure 1). The experimentally observed small deviation from planarity are probably caused by electrostatic forces (lattice effects). $(NPF_2)_3$ and $(NPBr_2)_3$ form a nearly planar ring as well. Recently, a rather unusual bent structure was found in 2,2,4,4,6,6–hexaisothiocyanatocyclotriphosphazene [20]. Here the phosphazene ring system adopts a slightly distorted half–chair conformation. It is assumed that the non–planarity of the phosphazene ring indicates weak S¨S interactions of the isothiocyanate groups, as well as packing effects.

The problem of explaining the bonding arrangements in phosphazenes has occupied the attention of a number of investigators [21,22].

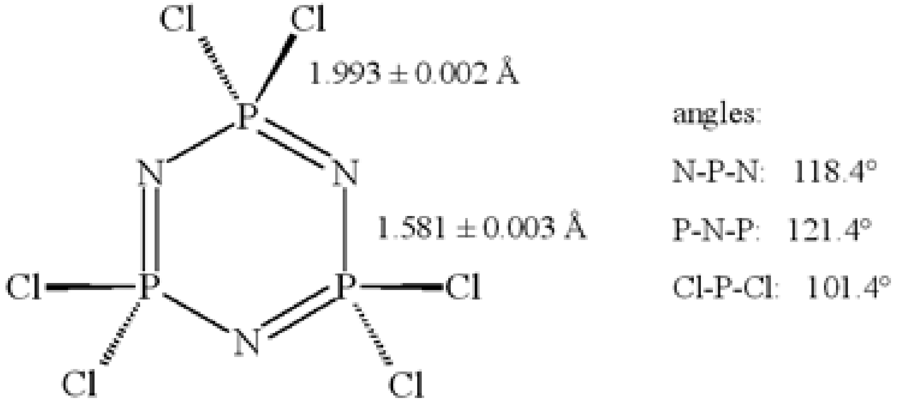


Figure 1. Structural data obtained by Bullen (crystal structure analysis) [19].

The aim of this study is to answer the rather theoretical question, whether it would be possible to build up an inorganic, *i.e.* carbon–free, information carrier similar to the double stranded DNA–helix. Therefore, the carbon–containing components of the DNA–helix – the 2–desoxy–D–ribose sugar and the different DNA bases – had to be replaced successively. We approached this rather complex task in four steps: (*i*) replacement of 2–deoxy–D–ribose by hexachlorocyclotriphosphazene $[(NPCl_2)_3]$ and to investigate the thermodynamics and substitution pattern of the isolated species $(NPCl_2)_3$ using different acids (water, ammonia, phoshoric and sulfuric acid), (*ii*) to introduce different linker species to built up a phosphazene chain such as sulphurdiimide, mono– and diphosphate, mono– and disulfate, (*iii*) to find and investigate different inorganic donor–

acceptor species as DNA bases analogues and (*iv*) to add all inorganic species together to produce an inorganic DNA analogue. Step (*i*) and (*ii*) are described in this study and we can show that it is possible to generate reasonable and stable double stranded chains or helixes after replacing the 2–desoxy–D–ribose with hexachlorocyclotriphosphazene. To study the phosphazene chains (*e.g.* the connection of two chains forming a helix) and to decrease the complexity of the supermolecule, hydrazine bridges were introduced to connect two phosphazene chains instead of the base pairs as found in the DNA. Future work deals with step (*iii*) and (*iv*) as well as with finding other alternatives for the 2–desoxy–D–ribose and evaluating different sets of inorganic information carrying molecules.

2 COMPUTATIONAL DETAILS

All calculations were performed with the quantumchemical program package Gaussian 98 [23] (revision A6 and A7) on a cluster of Linux [24] PCs. The data analyses were performed with Molden Version 3.7 [25] and GaussView 2.08 [26] on a Linux [24] PC architecture.

The computations of the substitution reactions were carried out at DFT [27–29] level using the hybrid method B3LYP which includes a mixture of Hartree–Fock exchange with DFT exchange–correlation. Becke's three parameter functional where the non–local correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used which is implemented in Gaussian 98. For a concise definition of the B3LYP functional see Ref. [30]. All geometries were fully optimized and characterized as true minima by a frequency analysis.

The energies of several substitution reactions of phosphazene were corrected for zero point vibrational energies obtained at the same level of theory (B3LYP) from unscaled harmonic vibrational frequencies. Thermal corrections also have been made to be able to estimate the free molecular enthalpy of the substitution reaction at 298.15 K and 1 atm [31].

For molecules with more than one phosphazene unit computations were carried out utilizing the PM3 level [32,33], in order to obtain a consistent set of data for all medium–sized and large oligomers. The geometry optimizations of the phosphazene oligomers were fully optimized utilizing a bottom to top approach.

Interaction energies at the PM3 level are not discussed. With respect to the interaction energies (*e.g.* stacking energies) it is assumed that there are contributions not covered by the empirical potentials or semiempirical calculations (π–π interactions, induction attraction, lone pair interactions, anisotropic short–range repulsion). We are aware that only non–empirical *ab initio* methods (including electron correlation) should be used to estimate accurate interaction energies [34]; hence we only tried to answer structural problems. In future work, we will address this question utilizing non–empirical *ab initio* methods. No doubt such *ab initio* calculation will be very tedious and time consuming.

NBO analyses [35] were carried out to investigate the bonding in monomeric species at the B3LYP level with the NBO program version 3.1, which is implemented in Gaussian. Solvent effects may play an important role. The present study concerns mainly with the gas phase oligomerization of phosphazenes without introducing any solvent effects.

3 RESULTS AND DISCUSSION

Firstly, to find a suitable, *i.e.* adequate for the problem and at the same time cost saving, combination of a quantumchemical method and a basis set to describe hexachlorocyclotri–phosphazene, optimizations with different semiempirical, *ab initio* and density functional theory methods have been done with different basis sets. In the second part we would like to discuss the thermodynamics of the entire series of substitution reactions of hexafluoro– and hexachlorocyclotriphosphazene with water, ammonia, sulfuric and phosphoric acid. The last section approaches the question whether phosphazenes are capable of forming stable double stranded chains or helixes.

3.1 Hexachlorocyclotriphosphazene

To evaluate the quality of several methods a series of computations on $(NPCl_2)_3$ using different methods such as HF, MP2(FC) [36,37], B3LYP and PM3 as well as different basis sets (4–31G, 6–31G(d), 6–311G(d), cc–pVDZ and 6–311+G(3df)) have been carried out. These results together with the experimental data are summarized in Table 1.

Table 1. Calculated / experimental geometry of $(NPCl_2)_3$ (distances in Å, angles in °).

Method	P–N bond length	P–Cl bond length	N–P–N bond angle	P–N–P bond angle	Cl–P–Cl bond angle
PM3/VSTO–3G	1.640	2.024	110.4	129.6	100.9
HF/4–31G	1.612	2.186	111.9	128.1	100.8
HF/6–31G(d)	1.577	2.000	116.2	123.8	102.8
HF/6–311G(d)	1.570	2.003	115.1	124.9	102.7
B3LYP/6–31G(d)	1.602	2.036	118.3	121.7	102.3
B3LYP/6–311G(d)	1.595	2.038	116.9	123.1	102.3
B3LYP/6–311+G(3df)	1.592	2.036	116.9	123.1	102.3
B3LYP/cc–pVDZ	1.619	2.056	120.2	119.8	101.5
MP2(FC)/6–31G(d)	1.600	2.008	118.7	121.3	102.8
crystal structure data					
A. Wilson et al. [17]	1.59	1.98	119.6	119.4	101.9
G. J. Bullen [19]	1.58	1.99	118.4	121.4	101.4

The usual D_{3h} symmetry planar arrangement of the $(NPCl_2)_3$ represents a stable structure at all levels of theory. As expected there are no non–planar stable structures. The geometries obtained at the HF, MP2 and B3LYP level of theory are in good agreement with the experimental X–ray data of Bullen [19] as long as the basis sets are large enough (6–31G(d), 6–311G(d), 6–311+G(3df) and cc–

pVDZ). It should be noted, that the computed values refer to the gas–phase whereas the experimental data refer to the solid state, which always results in small deviations due to lattice effects [31].

At the PM3 level slightly larger bond lengths are found. The Cl–P–Cl angle is in agreement with the experiment whereas a rather large deviation is found for the N–P–N and P–N–P bond angles (about 8°), which may stem from missing d functions in the basis set of the phosphorus atom. However, for the computations of large structures, PM3 had to be used because of its lower demand of computing resources. Therefore, to save computing time, we carried out our further calculations of the substitution reactions at the B3LYP level of theory and with the 6–31G(d) standard basis set. All calculations of molecules with more than one phosphazene unit were done at the PM3 level of theory.

Bonding. The $(NPCl_2)_3$ species represents a highly polarized molecule with a positive net charge of 2.07 e on phosphorus and a negative net charge of –1.61 and –0.23 e on nitrogen and chlorine, respectively. Many properties can be explained more clearly within the picture of localized bond orbitals. According to NBO analysis, both the σ and π bond system of $(NPCl_2)_3$ are strongly polarized. Only 27% of the sigma NBO of the P–N bond is on the hybrid orbital of the phosphorus atom (30% for the P–Cl bond). The P–N π bond represents almost a lone pair on the nitrogen atom since only 6% of the π NBO are localized on the phosphorus atom. The total hybridization on phosphorus is $sp^{2.09}d^{0.13}$. The calculated partial charges and the electrostatic potential indicate, that a nucleophile should preferably attack the phosphorus atom as shown in Figure 2.

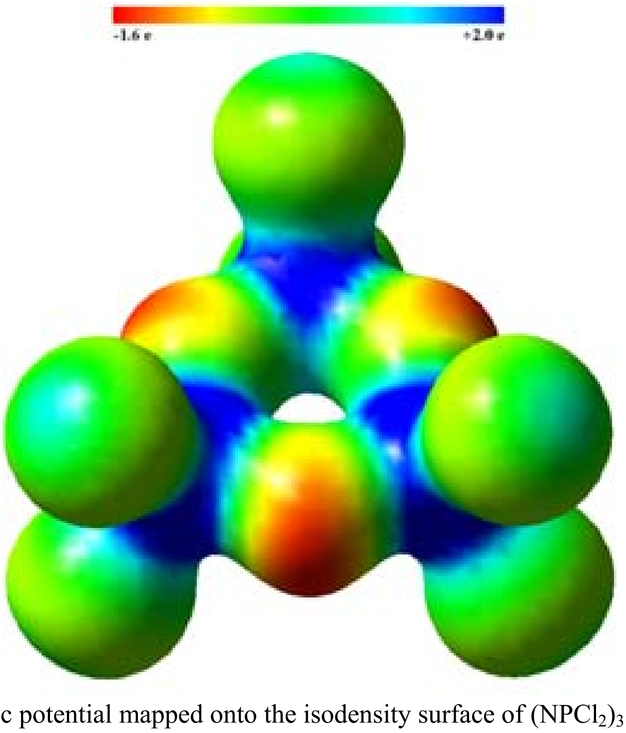


Figure 2. Electrostatic potential mapped onto the isodensity surface of $(NPCl_2)_3$ (B3LYP/6–31G(d)).

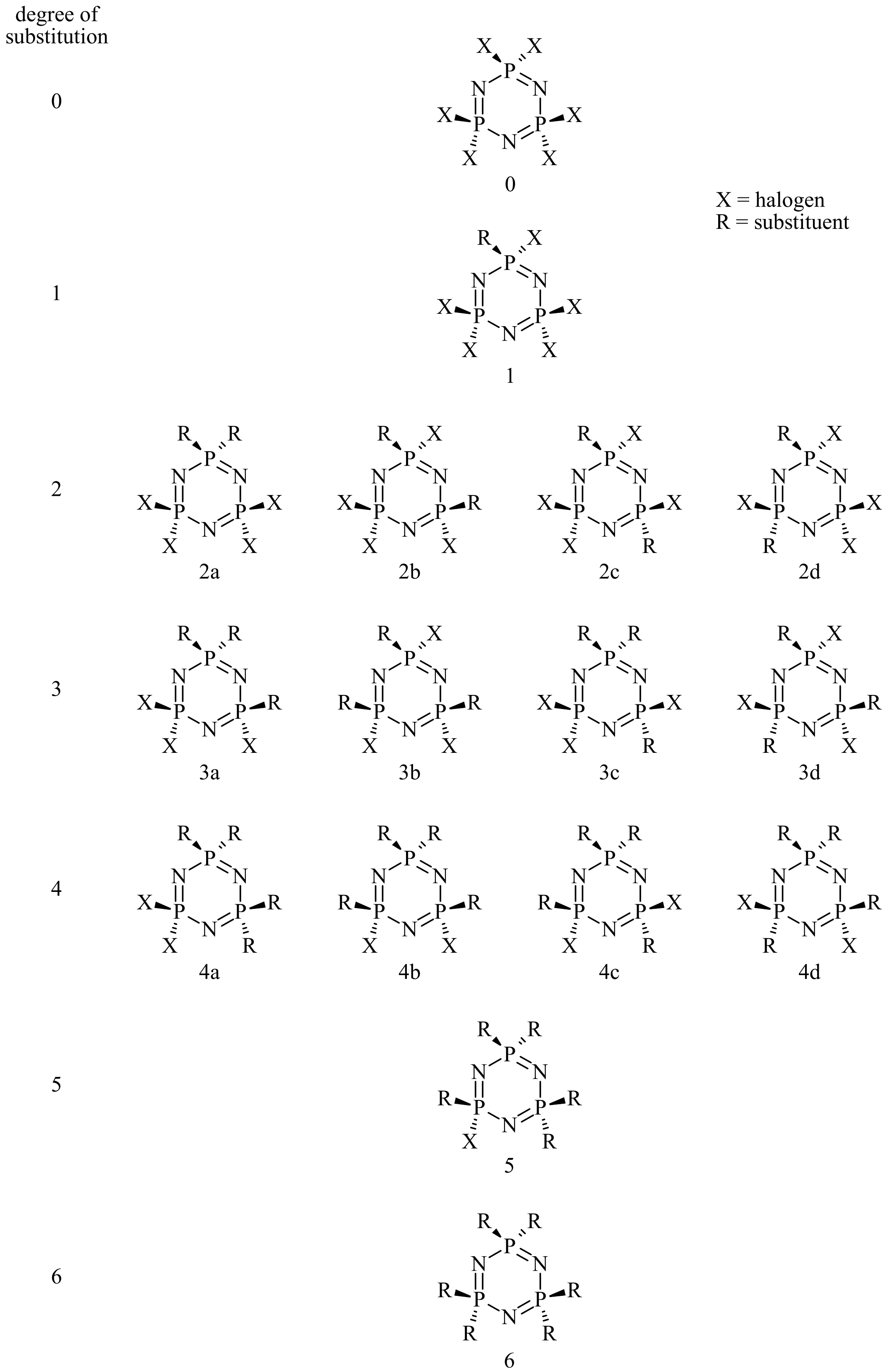


Figure 3. Possible substitution patterns of hexahalogenocyclotriphosphazene.

3.2 Substitution of Hexachlorocyclotriphosphazene

In order to design double stranded oligomers of phosphazenes several basic units composed of different phosphazene species have to be regioselectively linked together. Therefore it is necessary to get an exact image of the reactivity and the conformational space of substituted cyclotriphosphazene systems.

Substitution reactions of hexahalogenocyclotriphosphazene with nucleophils such as water and ammonia have been extensively described in literature [21]. Shaw *et al.* [38] already pointed out, that substitution reactions with cyclotriphosphazene are either always geminal or non–geminal (see Figures 4 and 5) along the entire reaction path. Whether a geminal or non–geminal path is preferred depends only on the substituent (*e.g.* non–geminal replacement pattern for ammonia and some amines, geminal substitution in case of phenylation by Friedel–Crafts reaction). In our study these two different reaction schemes have been considered for the progressive replacement of chlorine atoms in hexachlorocyclotriphosphazene. The differences depend on whether replacement occurs preferentially at phosphorus containing one chlorine atom (geminal replacement) or at phosphorus containing two chlorine atoms (non–geminal replacement). Both reaction schemes are illustrated in Figures 3, 4 and 5. Figure 3 represents an overview of all possible substitution patterns including the exact stereochemistry, whereas Figure 4 exclusively displays a geminal substitution and Figure 5 a non–geminal replacement. According to these schemes the species **2c**–**2d**, **3a**–**3c** and **4c**–**4d** are enantiomers.

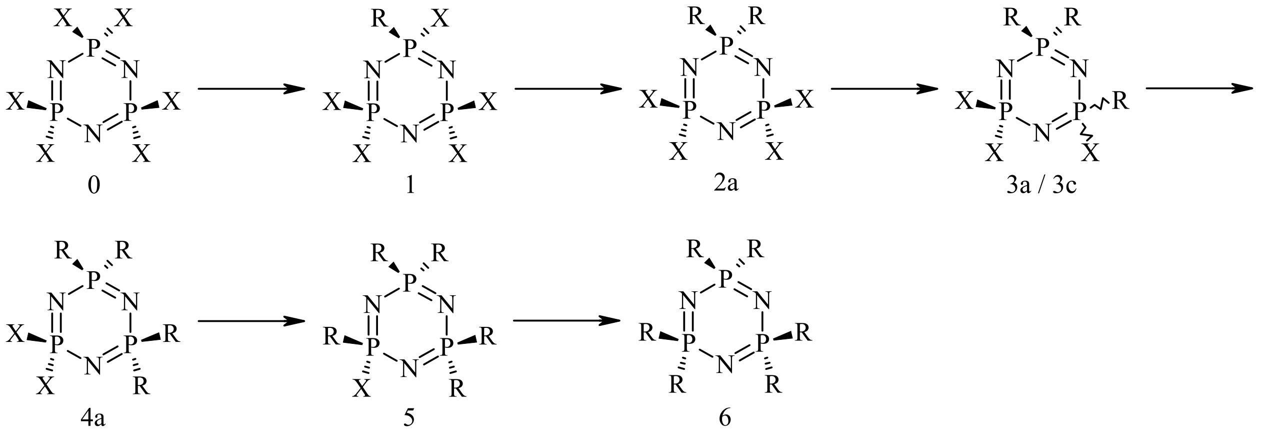


Figure 4. Geminal substitution patterns of hexahalogencyclotriphosphazene.

In order to find the thermodynamically preferred reaction path of the substitution of hexafluoro– and hexachlorocyclotriphosphazene with water, ammonia, sulfuric and phosphoric acid, for all involved phosphazene species optimizations and subsequently thermochemical calculations were performed. All calculations were carried out with a 6–31G(d) standard basis at the B3LYP level of theory. The results for all different chloro–derivates of cyclotriphosphazene are shown in Tables 2–5 and results for the fluoro–derivates of cyclotriphosphazene are given as supplementary material.

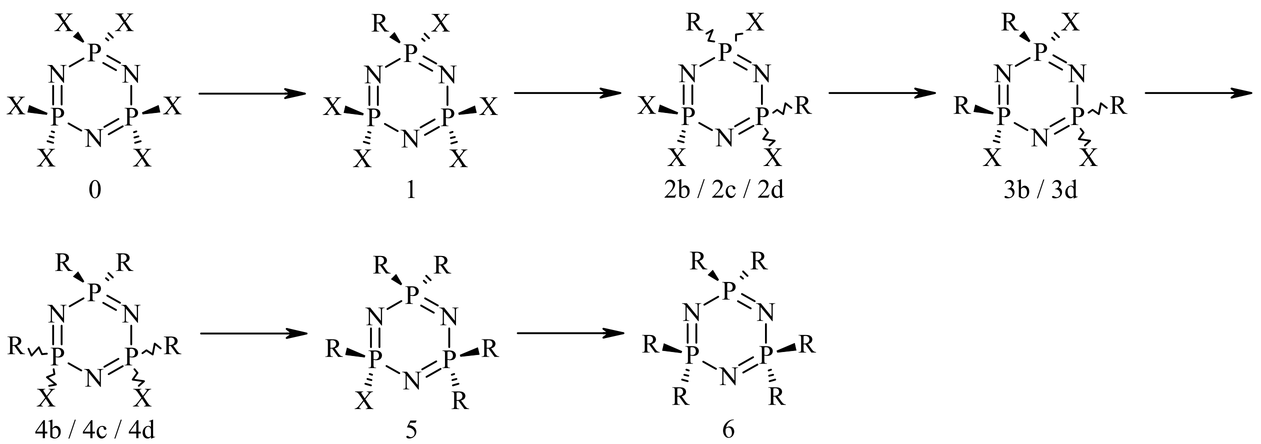


Figure 5. Non–geminal substitution patterns of hexahalogencyclotriphosphazene.

3.2.1 Water

The thermodynamical data of the replacement reactions of hexachlorocyclotriphosphazene with water according to the following reaction scheme (x = 6, 5 ... 1)

$$N_3P_3Cl_x(OH)_{6-x} + H_2O \rightarrow N_3P_3Cl_{x-1}(OH)_{6-x+1} + HCl$$

are presented in Table 2. All steps of these substitutions are exergonic with an energy gain of –45 to –62 kJ/mol. From the second step on, any further replacement can either result in the formation of a geminal or non–geminal product. However, in all cases non–geminal substituted isomers are 4 to 6 kJ/mol more favorable than the according geminal substituted isomers.

Table 2. Gibbs free energies ΔG_{298} (in kJ/mol) for the substitution with water (B3LYP/6–31G(d)). [a]

		educt														
		0	1	2a	2b	2c	2d	3a	3b	3c	3d	4a	4b	4c	4d	5
product	1	–58.6														
	2a		–54.0													
	2b		–57.9													
	2c		–57.9													
	2d		–57.9													
	3a			–56.5	–52.6	–52.6	–52.6									
	3b			–61.6	–57.8	–57.7	–57.7									
	3c			–56.5	–52.7	–52.7	–52.6									
	3d			–62.1	–58.2	–58.2	–58.2									
	4a							–48.3	–43.2	–48.3	–42.7					
	4b							–54.8	–49.6	–54.7	–49.2					
	4c							–54.6	–49.5	–54.6	–49.0					
	4d							–54.6	–49.5	–54.6	–49.0					
	5											–54.0	–47.6	–47.7	–47.7	
	6															–44.5

[a] all energy values highlighted with a gray color represent a replacement reaction, that is impossible according to the reaction path

3.2.2 Ammonia

The thermodynamical data of the replacement reactions of hexachlorocyclotriphosphazene with ammonia according to the following reaction scheme (x = 6, 5 ... 1)

$$N_3P_3Cl_x(NH_2)_{6-x} + NH_3 \rightarrow N_3P_3Cl_{x-1}(NH_2)_{6-x+1} + HCl$$

are presented in Table 3. In contrast to the reaction with water, steps 4 and 5 are endergonic although these reactions are experimentally known to be exergonic in solution [21]. This difference between theory and experiment can be attributed to solvent effects (e.g. solvation and forming of ammonia salts). Moreover, upgrading the level of theory may have an influence on the Gibbs free energy which can be in the range of 10 kJ/mol. All other steps are exergonic, however, the difference between geminal and non–geminal replacement is much larger compared to the water replacement reaction. Here the non–geminal isomers of the double substitution are 23 kJ/mol, of the triple substitution 6 to 8 kJ/mol and of the quadruple substitution 16 to 18 kJ/mol more favorable than the according geminal isomers.

Table 3. Gibbs free energies ΔG_{298} (in kJ/mol) of substitution with ammonia (B3LYP/6–31G(d)). [a]

		Educt														
		0	1	2a	2b	2c	2d	3a	3b	3c	3d	4a	4b	4c	4d	5
product	1	–31.1														
	2a		–4.2													
	2b		–26.8													
	2c		–27.5													
	2d		–27.5													
	3a			–37.8	–15.2	–14.5	–14.5									
	3b			–44.0	–21.4	–20.6	–20.6									
	3c			–38.1	–15.5	–14.7	–14.8									
	3d			–45.9	–23.3	–22.5	–22.5									
	4a							–1.7	4.5	–1.4	6.4					
	4b							–18.2	–12.0	–17.9	–10.1					
	4c							–19.1	–12.9	–18.8	–11.0					
	4d							–19.1	–12.9	–18.8	–11.0					
	5											–10.6	5.9	6.8	6.8	
	6															21.7

[a] all energy values highlighted with a gray color represent a replacement reaction, that is impossible according to the reaction path

3.2.3 Phosphoric acid

Table 4 displays the thermodynamical data of the replacement reaction of hexachlorocyclo–triphosphazene with phosphoric acid according to the following reaction scheme (x = 6, 5, ... 1)

$$N_3P_3Cl_x(OPO(OH)_2)_{6-x} + H_3PO_4 \rightarrow N_3P_3Cl_{x-1}(OPO(OH)_2)_{6-x+1} + HCl$$

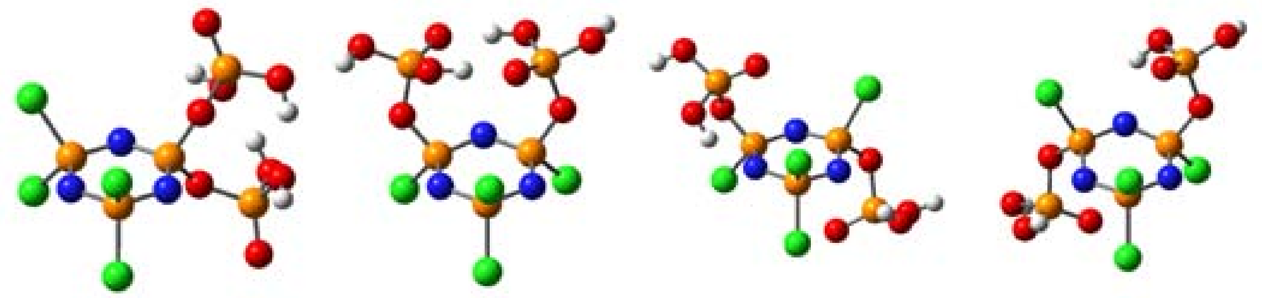


Figure 6. Hexachlorocyclotriphosphazene substituted two times with phosphoric acid (B3LYP/6–31G(d)).

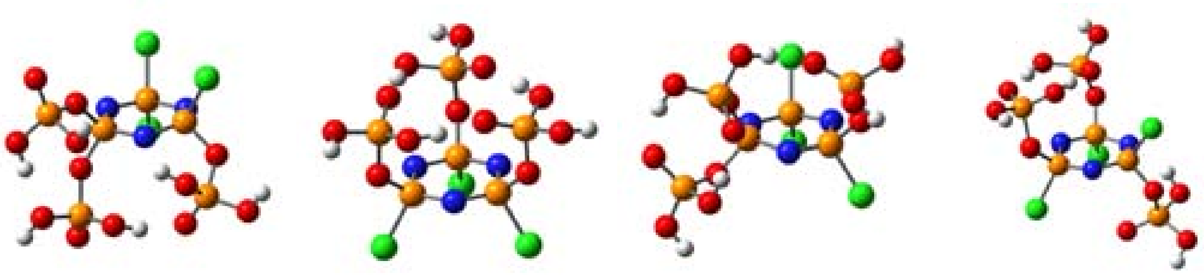


Figure 7. Hexachlorocyclotriphosphazene substituted three times with phosphoric acid (B3LYP/6–31G(d)).

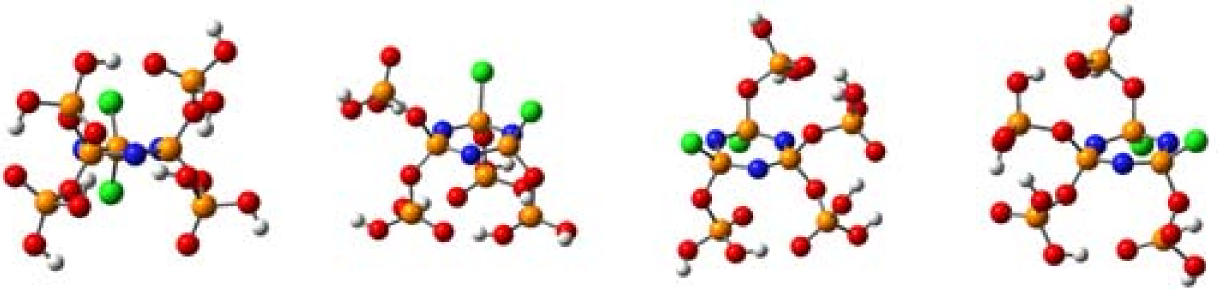


Figure 8. Hexachlorocyclotriphosphazene substituted four times with phosphoric acid (B3LYP/6–31G(d)).

Experimentally, the reaction of $(NPCl_2)_3$ with phosphoric acid is not known yet. Again, all six substitutions are exergonic, however, the magnitude of energy release is much larger compared to the reaction with water and ammonia. This can be attributed to the formation of hydrogen bonds between two or three phosphate units. Figures 6–8 show the optimized structures of di–, tri– and four–substituted phosphazenes including different isomers. In each substitution series (**2a**–**2d**, **3a**–**3d** and **4a**–**4d**) it is a striking feature, that the structures **2b**, **3b** and **4b** are energetically notably more favorable than the other isomers. A comparison of all structures of one series reveals, that structure type **b** is energetically stabilized by the formation of intramolecular hydrogen bonds. Structure **2b** is energetically about 65 to 77 kJ/mol more stable than the isomers **2a**, **2c** and **2d**. Between the two phosphate groups in structure **2b**, two hydrogen bonds are formed. Structure 3**b** is energetically about 40 to 90 kJ/mol more stable compared to isomers **3a**, **3c** and **3d**. Structure **3b** can be derived from structure **2b** by adding a third phosphate group at the same side. Hence, three hydrogen bonds are formed between the three phosphate groups in structure **3b**, in such a way, that the three units form a twelve–membered ring above the phosphazene ring. The stabilization of structure **4b** is 27 to 49 kJ/mol larger than for the isomers **4a**, **4c** and **4d**. Structure **4b** can be derived from structure **3b** by replacing one chlorine atom by an additional phospate group beneath the P_3N_3 ring maintaining the hydrogen bond stabilized twelve–membered ring above the P_3N_3 ring.

Table 4. Gibbs free energies ΔG_{298} (in kJ/mol) of substitution with phosphoric acid (B3LYP/6–31G(d)). [a]

		educt														
		0	1	2a	2b	2c	2d	3a	3b	3c	3d	4a	4b	4c	4d	5
product	1	–44.7														
	2a		–34.9													
	2b		–111.7													
	2c		–44.8													
	2d		–46.5													
	3a			–75.2	1.7	–65.3	–63.5									
	3b			–165.2	–88.4	–155.3	–153.5									
	3c			–120.1	–43.3	–110.2	–108.4									
	3d			–125.0	–48.2	–115.1	–113.4									
	4a							–110.8	–20.8	–65.9	–61.0					
	4b							–138.3	–48.3	–93.4	–88.5					
	4c							–106.1	–16.1	–61.2	–56.2					
	4d							–89.7	0.3	–44.8	–39.9					
	5											–107.5	–80.0	–112.3	–128.6	
	6															–15.2

[a] all energy values highlighted with a gray color represent a replacement reaction, that is impossible according to the reaction path

According to these thermodynamical data, a thermodynamically controlled substitution would preferably result in the formation of exclusively non–geminal products:

$$\text{type } 0 \rightarrow \text{type } 1 \rightarrow \text{type } 2b \rightarrow \text{type } 3b \rightarrow \text{type } 4b \rightarrow \text{type } 5 \rightarrow \text{type } 6$$

3.2.4 Sulfuric acid

The substitution of cyclotriphosphazene with sulfuric acid is not yet known in literature. Table 5 displays the thermodynamical data of the replacement reaction of hexachlorocyclotriphosphazene with sulfuric acid according to the following reaction scheme ($x = 6, 5, \ldots 1$)

$$N_3P_3Cl_x(OSO_2(OH))_{6-x} + H_2SO_4 \rightarrow N_3P_3Cl_{x-1}(OSO_2(OH))_{6-x+1} + HCl$$

Figures 9–11 show the optimized structures of di–, tri– and four–substituted phosphazenes including the different isomers. The structures **2a**, **3a/3c** and **4a** from the substitution with sulfuric acid have been proven to be the energetically most stable isomers. Inspection of the fully optimized structures displays again the formation of intramolecular hydrogen bonds, resulting in an additional stabilization.

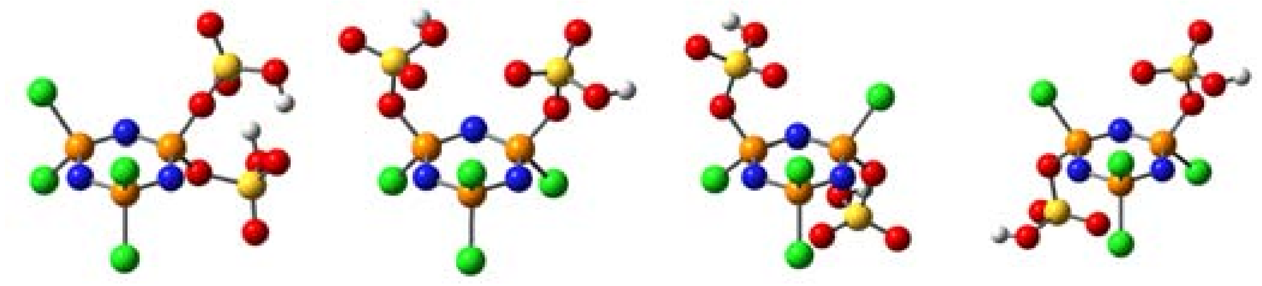


Figure 9. Hexachlorocyclotriphosphazene substituted two times with sulfuric acid (B3LYP/6–31G(d)).

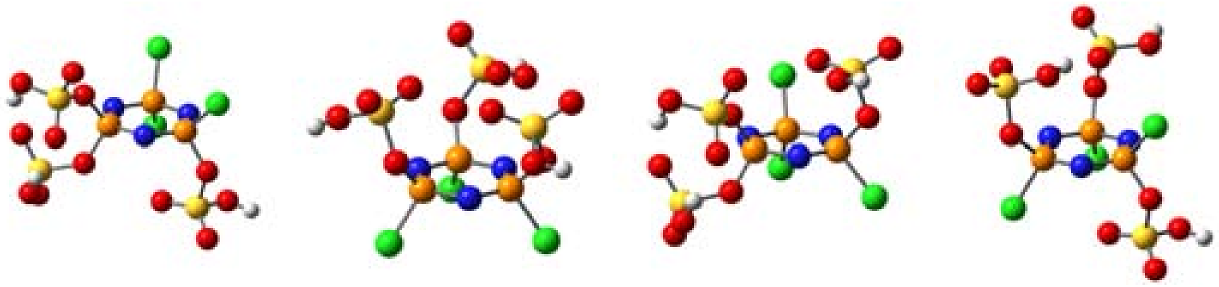


Figure 10. Hexachlorocyclotriphosphazene substituted three times with sulfuric acid (B3LYP/6–31G(d)).

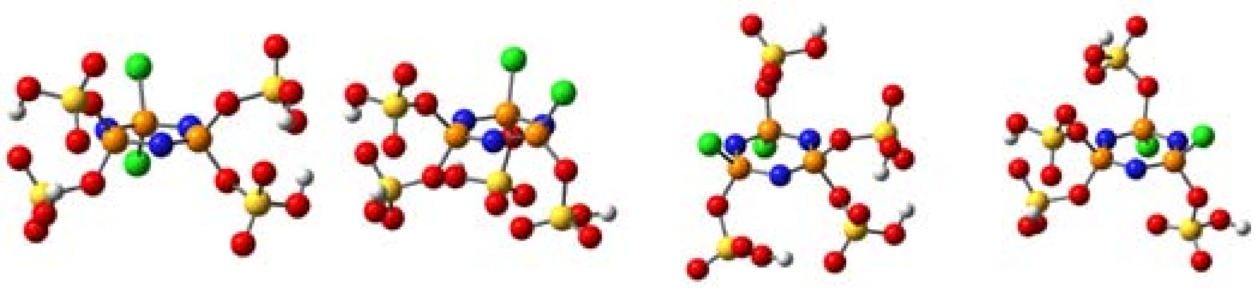


Figure 11. Hexachlorocyclotriphosphazene substituted four times with sulfuric acid (B3LYP/6–31G(d)).

Structure **2a** is energetically 20 to 28 kJ/mol more stable than the structures **2b**, **2c** and **2d**. In contrast to the substitution with phosphoric acid, where the hydrogen bonds were preferably formed between non–geminal phosphate groups, in case of the sulfate substituted products hydrogen bonds are formed between geminal sulfate groups. Structure **3a** and **3c** are 14 to 36 kJ/mol more stable than structure **3b** and **3d** due to the formation of hydrogen bonds between the geminal sulfate units. In structure **4a** hydrogen bonds can be formed between the two pairs of geminal sulfate groups resulting in a stabilization of 13 to 28 kJ/mol compared to the other isomers with only one geminally substituted phosphorus atom.

Table 5. Gibbs free energies ΔG_{298} (in kJ/mol) of substitution with sulfuric acid (B3LYP/6–31G(d)). [a]

		educt														
		0	1	2a	2b	2c	2d	3a	3b	3c	3d	4a	4b	4c	4d	5
product	1	–8.1														
	2a		–30.6													
	2b		–3.0													
	2c		–10.1													
	2d		–10.7													
	3a			–9.1	–36.8	–29.7	–29.1									
	3b			26.6 [b]	–1.1	6.0	6.6									
	3c			–10.0	–37.6	–30.5	–29.9									
	3d			4.7	–23.0	–15.9	–15.3									
	4a							–29.4	–65.1	–28.5	–43.1					
	4b							–1.4	–37.1	–0.6	–15.2					
	4c							–16.6	–52.3	–15.8	–30.4					
	4d							–4.3	–40.0	–3.5	–18.1					
	5											–10.4	–38.3	–23.2	–35.5	
	6															–28.4

[a] all energy values highlighted with a gray color represent a replacement reaction, that is impossible according to the reaction path.

[b] a positive energy value is obtained since the stabilizing hydrogen bonds of the geminal structure **2a** are not maintained in structure **3b**.

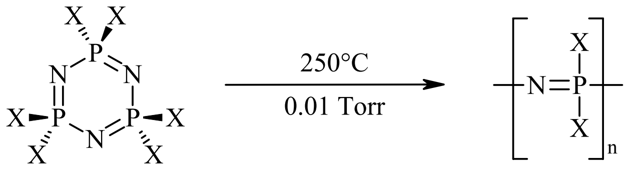
According to the two reaction paths, all steps of the substitution of cyclotriphosphazene with sulfuric acid are exergonic and in a thermodynamically controlled substitution reaction preferably geminal substitution products should be formed:

$$\text{type } 0 \rightarrow \text{type } 1 \rightarrow \text{type } 2a \rightarrow \text{type } 3c \rightarrow \text{type } 4a \rightarrow \text{type } 5 \rightarrow \text{type } 6$$

3.3 Phosphazene Oligomers

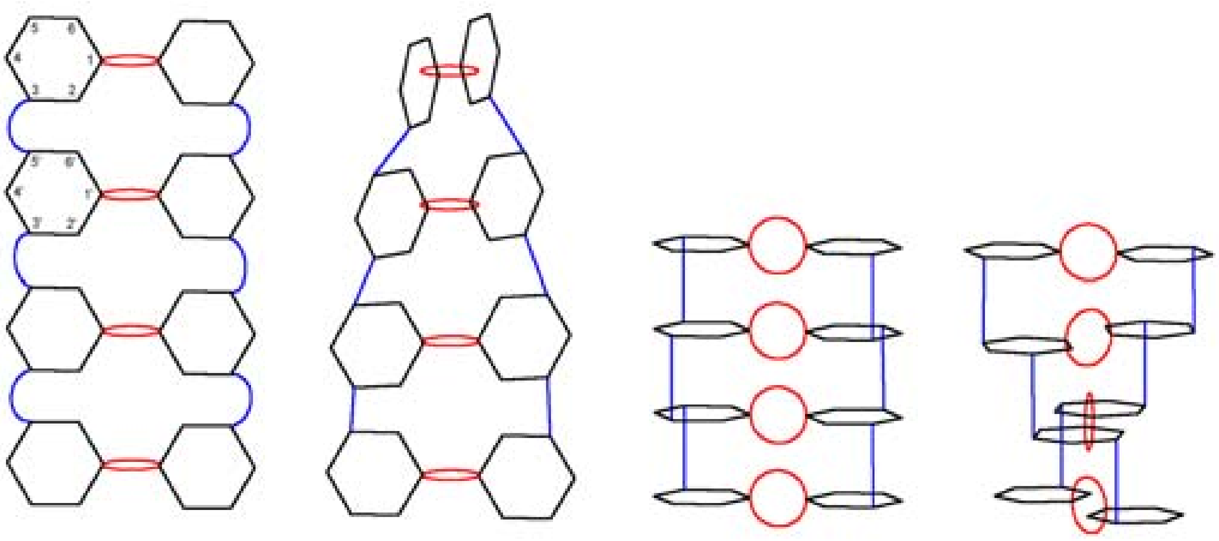
Polymeric phosphazenes are often described as a unique class of inorganic–organic materials, that offer a high degree of tailorability by variation in the synthesis procedure. Both linear polymers and cyclic small molecule phosphazenes can be functionalized with a broad range of organic substituents [39]. The most widely studied phosphazene polymer systems have a linear backbone of alternating phosphorus and nitrogen atoms with two organic groups linked to each phosphorus atom. Several hundred different polymers of this type are known [40–42]. Three types of phosphazene polymers are known: linear type macromolecules, cyclolinear polymers and cyclomatrix resins.

Pure inorganic polymers maintaining the P_3N_3 unit of the phosphazene are not known, yet. However, inorganic phosphazens also occupy a strategic place in inorganic polymer chemistry [21,43]. The rubbery chlorophosphazene high polymer, $(NPCl_2)_n$ was one of the first inorganic molecules to be recognized as a linear macromolecule. Molten hexahalogenocyclotriphosphazenes polymerize to a linear–type high polymer, when heated to 250°C. An ionic polymerization mechanism via ring opening is assumed.



X = halogen
n < 15,000

A cyclotriphosphazene ring offers six possible positions for a substition at its three phosphorus atoms. To form information carrying macromolecules from phosphazenes both the geminal and non–geminal positions of the phosphorus atoms can be used to link information carrying molecules. Hence either four or two replacement positions remain to build a chain or helix like structure. In Figure 12 several possibilities to connect phosphazenes via non–geminal linking are shown. The black hexagonal polygons represent the planar cyclotriphosphazene units. The red ellipses symbolize the information carrying molecules and the blue lines are linker molecules for the systematic construction of a polymeric cyclotriphosphazene chain.



type I **type II** **type III** **type IV**

Figure 12. Possible structures based on cyclotriphosphazene rings.

In all cases (type I – IV), the linkage of both phosphazene chains occurs via two bridges (*e.g.* hydrazine). Hence both connected phosphorus atoms are geminally substituted. The phosphazene chains themselves are always built up by linking the remaining non–geminally substituted phosphorus atoms with linker molecules (*e.g.* phosphate). For structure types I, II and IV the phosphorus atom in position 3 is assoziated by a linker molecule with the phosphorus atom in position 5' of the adjacent phosphazene ring (notation 3–5'). Structure type III shows a 3–3' linkage.

In structure type I all phosphazene rings along a chain lie in–plane and the rings are connected in a *cis–cis*–type fashion. Hence, only an untwisted double–stranded chain can be obtained. The difference between structure I and II is, that the connection between the P_3N_3 rings goes via a trans–trans–link. In this case, a double–stranded helix like structure can be formed. Structure type III displays a 3–3' linkage of horizontally arranged phosphazene rings along one chain resulting in a non–twisted double–stranded chain. Structure type IV utilizes a 3–5' linkage of horizontally arranged phosphazene rings. Hence a twisted double–stranded helix can be achieved.

The major advantage of structure type I and II over III and IV is, that there is more space left between two adjacent pairs of phosphazene rings, which means more space is available when information carrying molecules will be introduced. Our results show, that only half of the space of structure type I and II is left in structure type III and IV.

To built up structures analogous to the organic DNA and to keep, for the time being, things independent of the information carrying molecules two phosphazene molecules were geminally linked together with two hydazine bridges, as shown in Figure 13. The resulting 4,4,4",4",6,6,6",6"–octachlorocyclotriphosphazene–2–spiro–3'–cyclodi(phosphadiazane)–6'–spiro–2"–cyclotriphosphazene has already been synthesized and described by Engelhardt *et al*. [44]. In all following sections, this species is used as basic unit for the composition of several phosphazene macromolecules as shown in Figure 12. It should be noted, that those hydrazine bridges are certainly no replacement for the nucleic acids, but although they cannot be used for carrying information, they allow a temporarily stable fixation of the above discussed structure types I to IV.

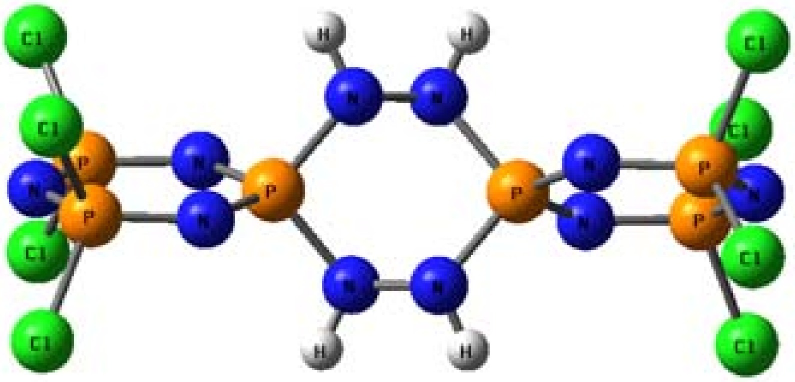


Figure 13: Spiro compound used as basic unit (optimized with PM3).

Moreover, the influence of the linker molecule has carefully been investigated since (*i*) too small species result in a large repulsion between two basic units, (*ii*) too large species lead to a large flexibility of the entire moiety. As a result, no double–stranded chain can be observed. Thus sulfurdiimide, sulfate, phosphate, disulfate and diphosphate have been examined as linker molecules.

3.3.1 Sulfurdiimide

The synthesis of –N=S=N– bridged hexafluorocyclotriphosphazenes is described by Niecke, Glemser and Thamm [45]. These –N=S=N– bridged hexafluorocyclotriphosphazenes were obtained in a two–step synthesis according to the following equations:

$$N_3P_3F_5NH_2 + SOCl_2 \rightarrow N_3P_3F_5(N{=}S{=}O) + 2\ HCl$$

$$2\ N_3P_3F_5(N{=}S{=}O) \rightarrow N_3P_3F_5(N{=}S{=}N)P_3N_3F_5 + SO_2$$

The sulfurdiimide group was now used to built macromolecules according to structure type I to IV with two basic units (Figure 14). According to our calculations there are no big differences between the total energies for all four structure types. Structure type II represents the energetically best arrangement, followed by structure type III (+22 kJ/mol). Structure type I and IV lie about 31 kJ/mol above structure type II.

Comparing all four structure types, it can be seen, that only half of the space of structure type I and II is available in structure type III and IV between the hydrazine bridges of the two basic units. [type I: d(N – N') = 7.6 Å; II: d = 5.7 Å; III: d = 3.7 Å; IV: d = 3.5 Å]. Selected structural data of two basic units linked by a NSN unit are summarized in Table 6. The dihedral angle $<(P_1N_4P_{1'}N_{4'})$ describes the deviation of two adjacent phosphazene rings of one chain from planarity. This dihedral angle quantitatively describes the deviation from an in–plane structure (with respect to the phosphazene rings) as shown in Figure 12.

Table 6. Selected structural data of two basic units linked by NSN, phosphate, sulfate, diphosphate and disulfate.

structure type	d(P–P') / Å [a]	d(N–N') / Å [b]	$<(P_1N_4P_{1'}N_{4'})$ / °
I (NSN)	5.070	7.640	22.0
II (NSN)	5.137	5.720	29.1
III (NSN)	5.382	3.710	4.7
IV (NSN)	5.381	3.533	59.4
I (phosphate)	5.122	7.627	24.3
II (phosphate)	5.146	5.831	32.3
I (sulfate)	5.023	7.474	24.4
II (sulfate)	5.175	5.886	40.4
I (diphosphate)	6.947	7.672	33.6
II (diphosphate)	6.459	7.150	9.3
I (disulfate)	6.033	7.750	19.4
II (disulfate)	6.390	7.005	25.3

[a] for structure type I, II and IV the P–atoms are linked by a 3 – 5' connection, III by a 3 – 3' connection, averaged values

[b] this N–N distance represents the smallest gap between two hydrazine bridges of two different basic units

The structures of type III and IV offer only little space between the different basic units compared to the structures of type I and II. These geometries work well with the relatively small hydrazine groups but with large information carrying molecules substantial deformations and repulsions inside the macromolecule can be expected. Hence, our further calculations were limited to the structures of type I and II.

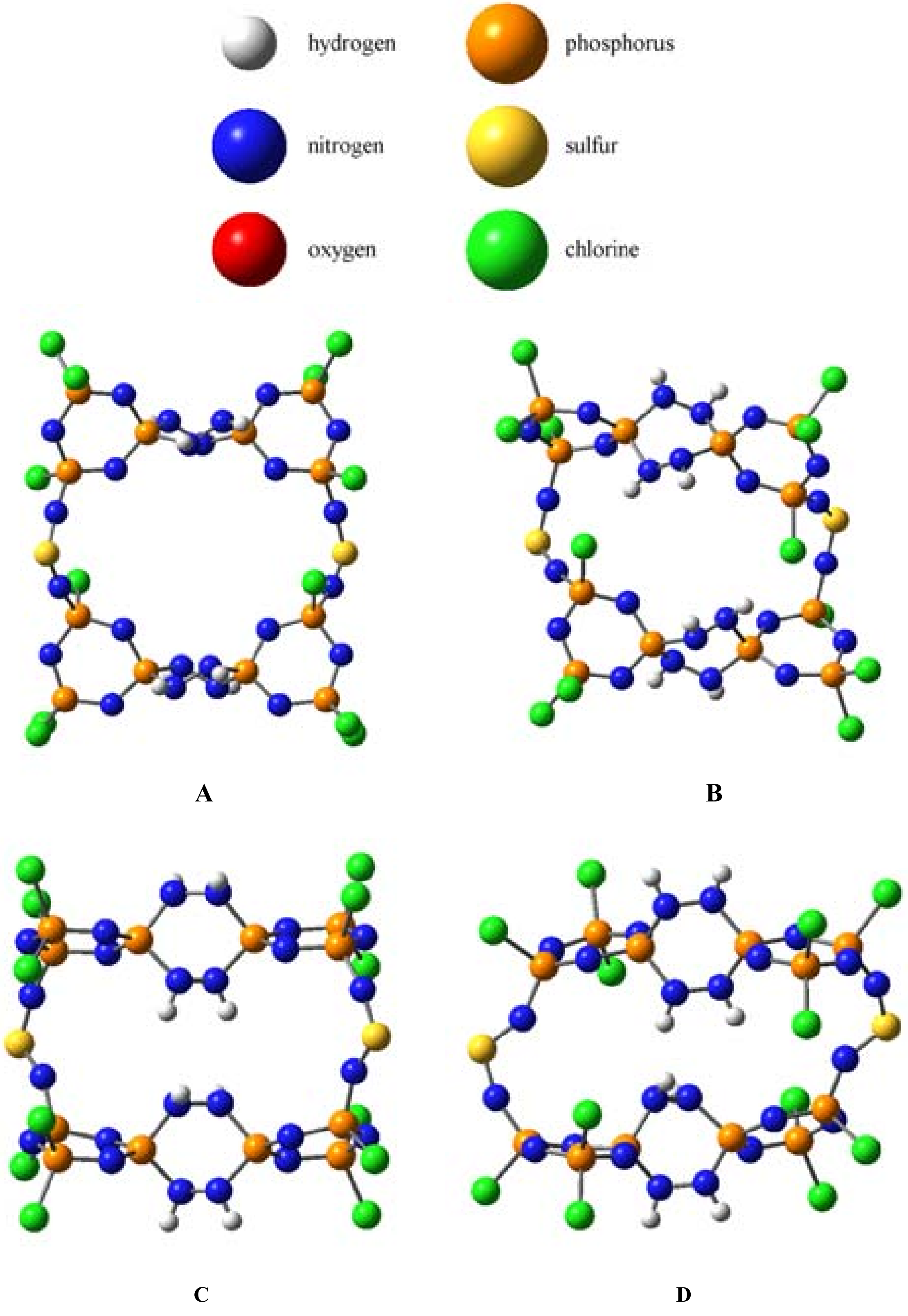


Figure 14a–d. Two stacked basic units (type I, II, III and IV) linked by a NSN group (optimized with PM3).

Since the –N=S=N– linker is strongly bent (<(NSN) = 109.2 to 115.5°), sulfurdiimide units represent suitable linker units in order to build chains of structure type I and III with non–twisted basic units. When NSN linker are used to form structures of type II and IV, a large deviation from the ideal structure is observed. In structure type II one hydrogen bond per basic unit is formed between the chlorine atom at the P–atom in position 3 of the phosphazene ring and the closest hydrogen atom of the hydrazine bridge (Figure 15). We assume that these hydrogen bridges are responsible for the above discussed large deviation from the ideal structure type and result in an additional energetical stabilization of the entire macromolecule.

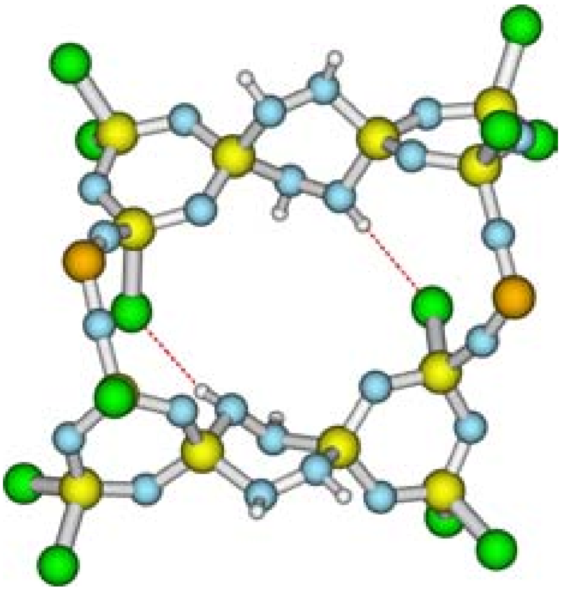


Figure 15. Hydrogen bonds in structure type II linked by a NSN group (optimized with PM3).

3.3.2 Phosphate

As an alternative to the very hydrolysis sensitive NSN linker a concatenation of the basic units with phosphate groups has been examined. The use of phosphate groups seems to be obvious, because the sugar units in the organic DNA are linked together by phosphate groups, however, such phosphazene compounds are experimentally not known, yet. The optimized structures of type I and II are shown in Figure 16. Similar to the systems linked with NSN linker, structure type II shows a fairly large deviation from the ideal structure (Table 6). However, structure type II also represents the energetically preferred structure (ΔE(type I – type II) = +24 kJ/mol). In accordance with the NSN linked system, the P–P' distances are very similar (5.12 versus 5.15 Å) for structure types I and II, whereas a large difference is observed for the gap between two hydrazine bridges of two different basic units. Moreover, structure type II is also influenced by one hydrogen bond per basic unit as discussed before for the sulfurdiimide linked system.

3.3.3 Sulfate

A second alternative is the concatenation with a sulfate group. The optimized structures of type I and II are shown in Figure 17. Similar to the systems linked with phosphate linker, structure type II shows a fairly large deviation from the ideal structure. Again, structure type II also represents the energetically preferred structure (Δ*E*(type I – type II) = +33 kJ/mol) and one hydrogen bond per basic unit was observed.

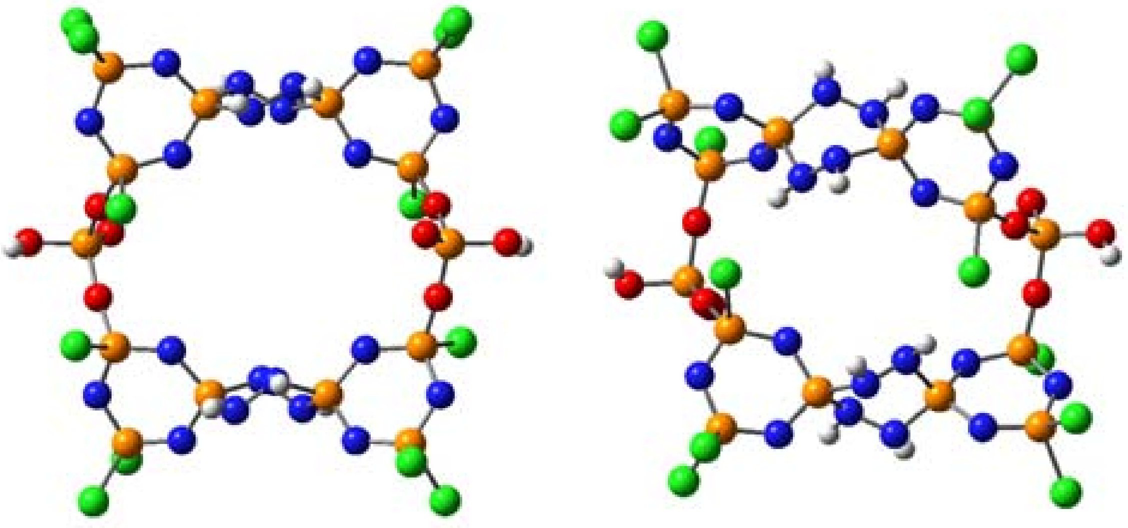


Figure 16a–b. Two stacked basic units (type I and II) linked by a phosphate group (optimized with PM3).

The P–P' distances are almost the same as found for the NSN and phosphate linked systems. Moreover, the N–N' distance is also found in the range of 7.6 Å for structure type I and 5.9 Å for structure type II.

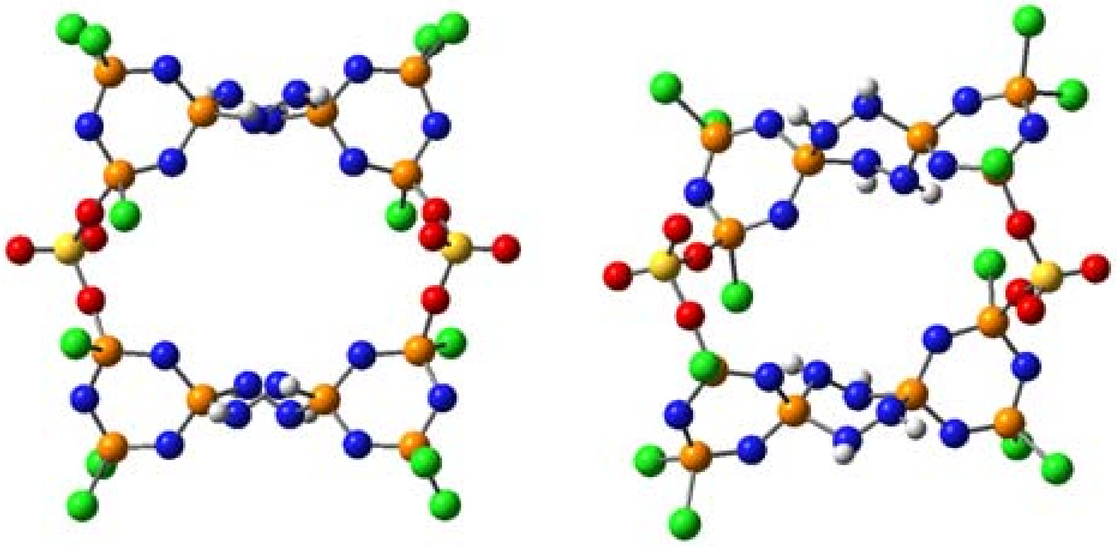


Figure 17a–b. Two stacked basic units (type I and II) linked by a sulfate group (optimized with PM3).

3.3.4 Diphosphate and disulfate

In order to increase the space between two basic units, a diphosphate and disulfate linker has been introduced to connect two basic units. It was our hope, that this would lead to smaller interactions (*e.g.* no formation of hydrogen bonds) between the two basic units. The optimized structures of the diphosphate and disulfate cluster are shown in Figures 18 and 19. For both cluster types, structure type II is energetically favored over structure type I (diphosphate: ΔE(type I – type II) = +14, disulfate: +51 kJ/mol).

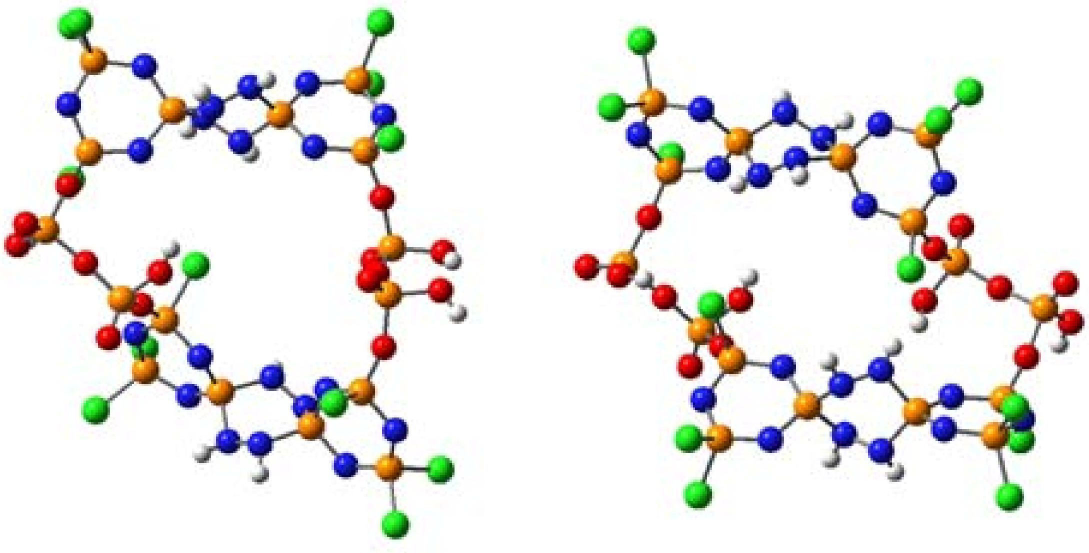


Figure 18a–b. Two stacked basic units (type I and II) linked by a diphosphate group (optimized with PM3).

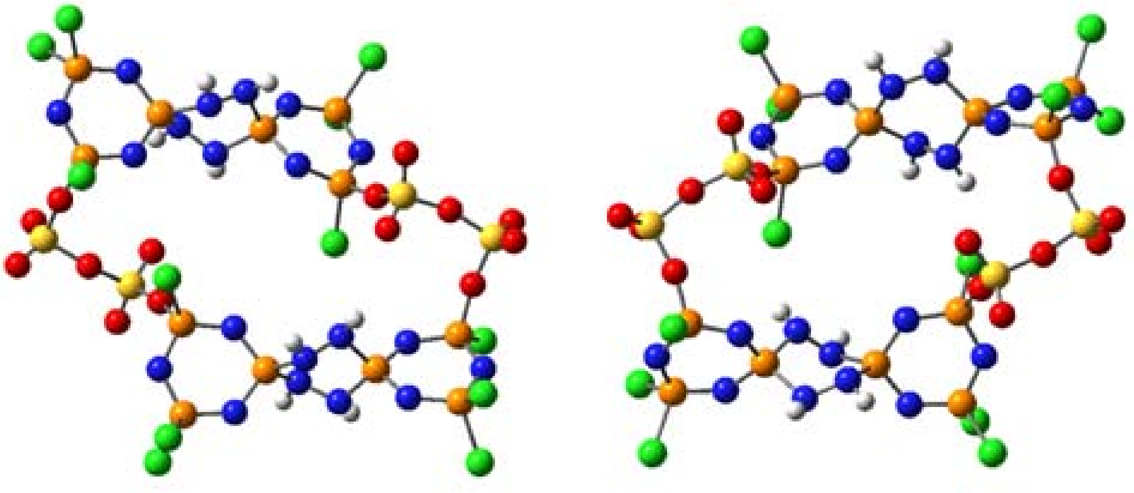


Figure 19a–b. Two stacked basic units (type I and II) linked by a disulfate group (optimized with PM3).

Exchanging the monophosphate and monosulfate linker by diphosphate and disulfate results in larger P–P' distances as expected. The computed N–N' distances display an unusual trend: for structure type I these distances are very similar to those of the monophosphate and monosulfate (7.6 versus 7.7 Å), whereas for structure type II these distances are dramatically increased (~5.8 to 7.1 Å) and lie now in the range of the distances found for structure type I (Table 6).

The deviation from the ideal structure emerges for structure type II when larger linkers such as diphosphate or disulfate are used to connect two basic units, however, at the same time, the entire cluster receives a larger structural flexibility. This finding could not be observed for structure type I.

3.3.5 Composition of larger structures of type I and II

From the DNA it is known, that 10 bases pairs are needed for one winding of the double–stranded α–helix with an averaged distance of 3.4 Å between two adjacent nucleic bases [46]. To gain further insight into the structural behavior of phosphazene oligomers of the types discussed above, the number of basic units has been increased. Figures 20 and 21 display the fully optimized structures (type I and II) of four phosphate and sulfate linked basic units.

In accordance with the two basic units structures, structure type II also represents the energetically most stable geometry for both the phosphate and sulfate linked four basic units cluster. (phosphate: ΔE(type I – type II) = +34, sulfate: +50 kJ/mol).

The sulfate and phosphate clusters of type I hardly change their regular linear geometry when the cluster size is increased from two to four basic units. Structure type II displays a rather large deviation from the ideal arrangement. Beside the expected inner twist in each chain, structures of type II show an additional strong torsion of the entire double–strand. By adding further basic units to the molecule it may be possible, that this additional torsion vanishes or at least will be repelled to the ends of the macromolecule.

Compared to the two basic units structures, the P–P' distances remain almost unchanged whereas the N–N' distance of structure type II decreases by roughly 0.7 Å (Table 7). The calculated dihedral angles $<(P_1N_4P_{1'}N_{4'})$ display an almost ideal arrangement for structure type I. In case of structure type II, dihedral angles of 34 (phosphate) and 42° (sulfate) are observed, illustrating the beginning of a twisted double–stranded helix. For the phosphate and sulfate linked clusters, the estimation of the number of basic units needed for a complete turn of the double–strand are 11 and 9, respectively.

Table 7. Selected structural data of four basic units linked by phosphate and sulfate.

structure type	*d*(P–P') / Å [a]	*d*(N–N') / Å [b]	<($P_1N_4P_{1'}N_{4'}$) / °	# of basic units per winding [c]
I (phosphate)	5.239	7.335	0.0	–
II (phosphate)	5.042	4.933	33.8	11
I (sulfate)	5.123	6.979	1.6	–
II (sulfate)	5.031	4.780	41.5	9

[a] for structure types I and II the P–atoms are linked by a 3–5' connection, averaged values

[b] this N–N distance represents the smallest gap between two hydrazine bridges of two different basic units

[c] estimated number necessary for one full (360°) twist of the double–stranded chain

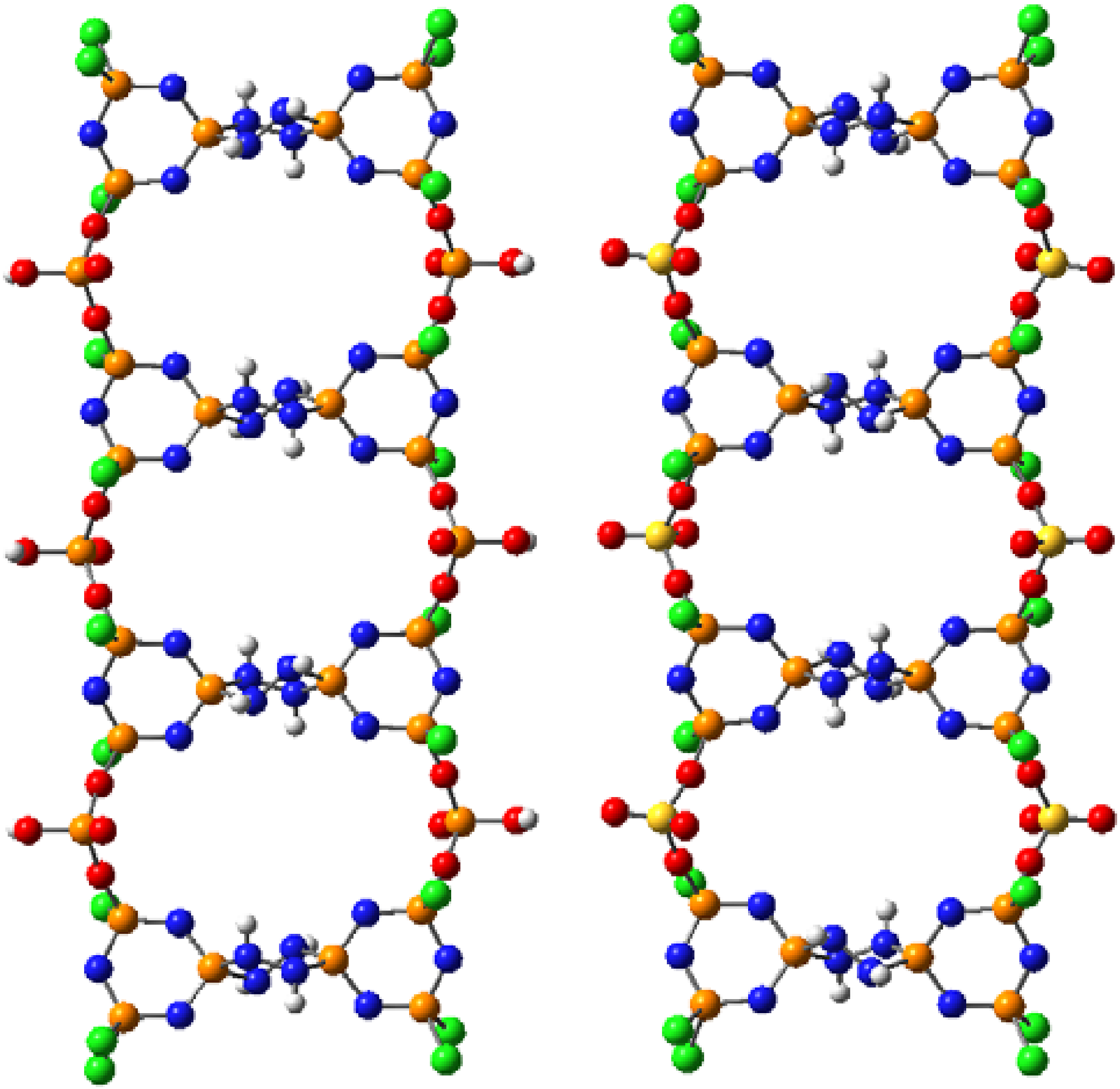


Figure 20a–b. Four stacked basic units (type I) linked by phosphate or sulfate groups (optimized with PM3).

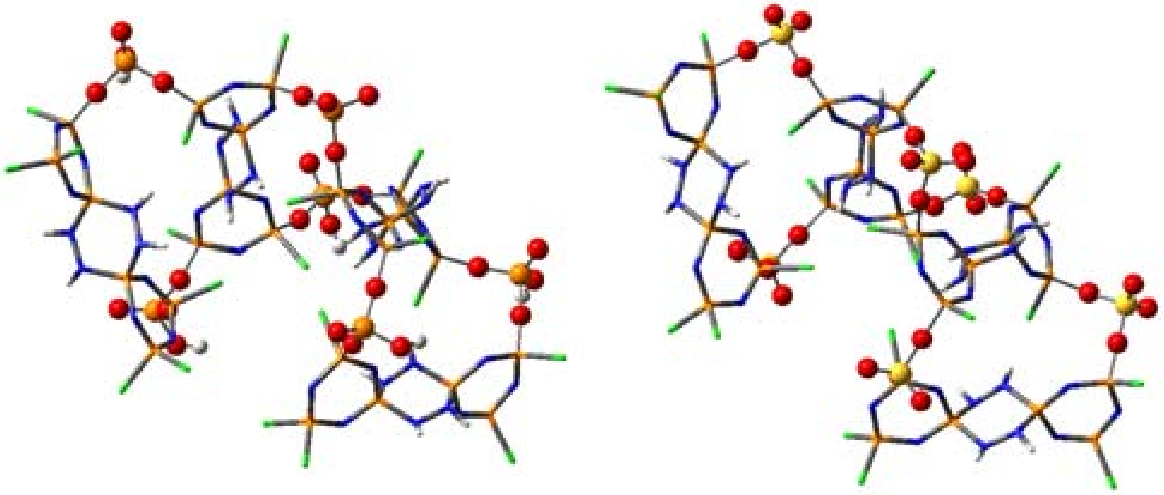


Figure 21a–b. Four stacked basic units (type II) linked with phosphate or sulfate groups (optimized with PM3).

4 CONCLUSIONS

The investigation of substitution reactions (with water, ammonia, phosphoric and sulfuric acid) displayed two exergonic thermodynamically controlled reaction schemes: An entirely geminal replacement path and an entirely non–geminal replacement path. In some cases, the formation of hydrogen bonds could be observed resulting in an additional stabilization.

Starting from a hydrazine bridged phosphazene basic unit, different cluster sizes were investigated utilizing 3–3' and 3–5' coupling via different linker (sulfurdiimide, phosphate, sulfate, diphosphate and disulfate) as well as forming *cis–cis* or *trans–trans* isomers. By this procedure four different structure types could be designed. Our computations indicate, that structure type I and II should be qualified to built either a double–stranded chain (structure type I) or a double–stranded helix (structure type II). Future work deals with the introduction of inorganic information carriers and the extension of the phosphazene cluster size. Moreover, to estimate interaction energies and to obtain more reliable geometries non–empirical *ab initio* methods will be introduced (*e.g.* RI–MP2).

Acknowledgment

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Supplementary Material

Structural data of all discussed species (xyz–coordinates) as well as frequency analyses are deposited as an archive in the supplementary material. Moreover, all analogue data of the hexafluorocyclotriphosphazene can be received from the authors.

5 REFERENCES

[1] H. Rose, Über eine Verbindung des Phosphors mit dem Stickstoff, *Annalen* **1834**, *11*, 129–139.
[2] J. v. Liebig, Über eine Verbindung des Phosphors mit dem Stickstoff – Nachtrag, *Annalen* **1834**, *11*, 139–151.
[3] C. Gerhardt, *Ann. Chim. Phys.* **1846**, *18*, 188.
[4] C. Gerhardt, Recherches sur les combinaisons du phosphore avec l'azote, *Compt. Rend. hebd. Séances Acad. Sci.* **1846**, *22*, 858.
[5] A. Laurent, Sur diverses combinaisons organiques, *Compt. Rend. hebd. Séances Acad. Sci.* **1850**, *31*, 349–356.
[6] J. H. Gladstone and J. D. Holmes, On Chlorophosphuret of Nitrogen, and its Products of Decomposition, *J. Chem. Soc.* **1864**, *17*, 225–237.
[7] J. H. Gladstone and J. D. Holmes, *Ann. Chim. Phys.* **1864**, *3*, 465.
[8] J. H. Gladstone and J. D. Holmes, *Bull. Soc. Chim. Fr.* **1865**, *3*, 113.
[9] H. Wichelhaus, Ueber Chlorphosphorstickstoff, *Ber. dtsch. chem. Ges.* **1870**, *3*, 163–166.
[10] H. N. Stokes, Ueber Chlorphosphorstickstoff und zwei seiner homologen Verbindungen, *Ber. dtsch. chem. Ges.* **1895**, *28*, 437–439.
[11] H. N. Stokes, On the Chloronitrides of Phosphorus, *Amer. chem. J.* **1895**, *17*, 275–290.
[12] H. N. Stokes, On the Chloronitrides of Phosphorus (II), *Amer. chem. J.* **1897**, *19*, 782–796.
[13] H. N. Stokes, On Trimetaphosphimic Acid and its Decomposition–Products, *Amer. chem. J.* **1896**, *18*, 629–663.
[14] H. N. Stokes, On Tetrametaphosphimic Acid, *Amer. chem. J.* **1896**, *18*, 780–789.
[15] R. Schenck and G. Römer, Über die Phosphornitrilchloride und ihre Umsetzungen (I), *Ber. dtsch. chem. Ges.* **1924**, *57B*, 1343–1355.
[16] S. Pantel and M. Becke–Goehring, *Sechs– und achtgliedrige Ringsysteme in der Phosphor–Stickstoff–Chemie*, Springer–Verlag, Berlin, 1969.
[17] A. Wilson and D.F. Carroll, Phosphonitrilic Derivatives. Part II. The Structure of Trimeric Phosphonitrilic Chloride, *J. Chem. Soc.* **1960**, 2548–2552.
[18] E. Giglio, *Ricerca Sci.* **1960**, *30*, 721.
[19] G. J. Bullen, An Improved Determination of the Crystal Structure of Hexachlorocyclotriphosphazene (Phosphonitrilic Chloride), *J. Chem. Soc.* (*A*) **1971**, 1450–1453.
[20] E. Kessenich, A. Schulz and K. Polborn, A new polymorph of 2,2,4,4,6,6–hexaisothiocyanatocyclotriphosphazene, *Acta. Cryst.* **2002**, *E58*, i15–i16.
[21] H. R. Allcock, Recent Advances in Phosphazene (Phosphonitrilic) Chemistry, *Chem. Rev.* **1972**, *72*, 315–355.
[22] M. J. S. Dewar, E. A. C. Lucken and M. A. Whitehead, The Structure of the Phosphonitrilic Halides, *J. Chem. Soc.* **1960**, 2423–2429.
[23] Gaussian 98 (Revision A.6 and Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, A. G. Baboul, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al–Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head–Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.
[24] *Linux* is a Registered Trademark of Linus Torvalds.
[25] *Molden Version 3.7*, Gijs Schaftenaar, Nijmegen, **1991**.
[26] *GaussView Version 2.08*, Semichem, Inc., Gaussian, Inc., Pittsburgh PA, **1998**.
[27] R. G. Parr and W. Yang, *Density–Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, **1989**.
[28] P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas, *Phys. Rev.* **1964**, *136* (*3B*), 864–871.
[29] W. Kohn and L. J. Sham, Self–Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev.* **1965**, *140* (*4A*), 1133–1138.
[30] (a) A. D. Becke, Density–functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* **1993**, *98*, 5648–5652; (b) A. D. Becke, Density–functional exchange–energy approximation with correct asymptotic behavior, *Phys. Rev. A* **1988**, *38*, 3098–3100; (c) C. Lee, W. Yang and R. G. Parr, Development of the Colle–Salvetti correlation–energy formula into a functional of the electron density, *Phys. Rev. B* **1988**, *37*, 785–789; (d) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200; (e) B. Miehlich, A. Savin, H. Stoll and H. Preuss, Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr, *Chem. Phys. Lett.* **1989**, *157*, 200–206.
[31] T. M. Klapötke and A. Schulz, *Ab–initio methods in Main Group Chemistry*, John Wiley & Sons, New York, 1998.

[32] J. J. P. Stewart, Optimization of Parameters for Semiempirical Methods – I. Method, *J. Comp. Chem.* **1989**, *10*, 209–220.

[33] J. J. P. Stewart, Optimization of Parameters for Semiempirical Methods – II. Applications, *J. Comp. Chem.* **1989**, *10*, 221–264.

[34] P. Hobza and J. Šponer, Structure, Energetics, and Dynamics of the Nucleic Acid Base Pairs: Nonempirical *Ab Initio* Calculations, *Chem. Rev.* **1999**, *99*, 3247–3276.

[35] (a) NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold; (b) J. E. Carpenter and F. Weinhold, Analysis of the geometry of the hydroxymethyl radical by the "different hybrids for different spins" natural bond orbital procedure, *J. Mol. Struct.* (*Theochem*) **1988**, *169*, 41–62; (c) J. P. Foster and F. Weinhold, Natural hybrid orbitals, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218; (d) A. E. Reed and F. Weinhold, Natural bond orbital analysis of near–Hartree–Fock water dimer, *J. Chem. Phys.* **1983**, *78*, 4066–4073; (e) A. E. Reed, R. B. Weinstock and F. Weinhold, Natural population analysis, *J. Chem. Phys.* **1985**, *83*, 735; (f) A. E. Reed, L. A. Curtiss and F. Weinhold, Intermolecular interactions from a natural bond orbital. donor–acceptor viewpoint, *Chem. Rev.* **1988**, *88*, 899; (g) A. E. Reed and P. v. R. Schleyer, The anomeric effect with central atoms other than carbon. 1. Strong interactions between nonbonded substituents in polyfluorinated first– and second–row hydrides, *J. Am. Chem. Soc.* **1987**, *109*, 7362; (h) A. E. Reed and P. v. R. Schleyer, The anomeric effect with central atoms other than carbon. 2. Strong interactions between nonbonded substituents in mono– and polyfluorinated first– and second–row amines, $F_nAH_mNH_2$, *Inorg. Chem.* **1988**, *27*, 3969; (i) F. Weinhold and J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum Press, New York, 1988, p. 227.

[36] C. Møller and M. S. Plesset, Note on an Approximation Treatment for Many–Electron Systems, *Phys. Rev.* **1934**, *46*, 618–622.

[37] R. J. Bartlett, Many–Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules, *Ann. Rev. Phys. Chem.* **1981**, *32*, 359–401.

[38] R. A. Shaw, B. W. Fitzsimmons and B. C. Smith, The Phosphazenes (Phosphonitrilic Compounds), *Chem. Rev.* **1962**, *62*, 247–281.

[39] H. R. Allcock, E. C. Kellam III. and M. A. Hofmann, Synthesis of Cyclolinear Phosphazene–Containing Polymers via ADMET Polymerization, *Macromolecules* **2001**, *34*, 5140–5146.

[40] (a) H. R. Allcock, *Macromolecular Design of Polymeric Materials*, Marcel Dekker, New York, 1996; (b) H. R. Allcock, The synthesis of functional polyphosphazenes and their surfaces, *Appl. Organometal. Chem.* **1998**, *12*, 659–666.

[41] H. R. Allcock, *Phosphorus–Nitrogen Compounds. Cyclic, Linear and High Polymeric Systems*, Academic Press, New York, 1972.

[42] J. E. Mark, H. R. Allcock and R. West, *Inorganic Polymers*, Prentice Hall: Englewood Cliffs, NJ, 1992.

[43] M. Gleria and R. De Jaeger, Aspects of Phosphazene Research, *J. Inorg. Organomet. Polym.* **2001**, *11*, 1–45.

[44] U. Engelhardt, U. Diefenbach and R. Damerius, Cyclotriphosphazen–2–spiro–3'–cyclodiphosphadiazan und Cyclotriphosphazen–2–spiro–3'–cyclodiphosphadiazan–6'–spiro–2''–cyclotriphosphazen – Spiroverbindungen aus Cyclotriphosphazen und Cyclodiphosphadiazanen, *Z. Naturforsch.* **1990**, *45b*, 457–460.

[45] E. Niecke, O. Glemser and H. Thamm, N–[2.4.4.6.6–Pentafluor–1.3.5.2.4.6–triazaphosphor(V)inyl–(2)]–schwefelimide ("N–Pentafluorcyclotriphosphazoschwefelimide"), *Chem. Ber.* **1970**, *103*, 2864–2867.

[46] T. A. Brown, *Moderne Genetik*, Spektrum Akademischer Verlag, Heidelberg, 1999, 2nd edition, p. 41.

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