

A quantum chemical ab initio study of the polymerization to polyhydridophosphazenes

Rebecca Fondermann ^{a,*}, Michael Dolg ^a, Michael Raab ^b,

Edgar Niecke ^b

^a*Universität zu Köln, Institut für Theoretische Chemie, Greinstraße 4, D-50939*

Köln, Germany

^b*Universität Bonn, Institut für Anorganische Chemie, Gerhard-Domagk-Straße 1,*

D-53121 Bonn, Germany

Abstract

Quantum chemical ab initio calculations on the polymerization to polyhydridophosphazenes were carried out using mainly Møller - Plesset perturbation theory. Considering finite clusters of increasing size modeling the infinite system suggests that the isolated polyhydridophosphazenes prefer helical structures. A small bond alternation of 0.02 Å was found, whereas amino substituted hydridophosphazenes show a little larger bond alternation of 0.04 Å. Our study suggests that a substituent on the phosphorus atom with an electronegativity of about 3, e.g. amino substituents, makes the polymerization energetically favorable. This agrees excellently with the experiments on the polymerization of trisaminophosphanes to polyhydridophosphazenes. The theoretical investigations also support a recently proposed polymer-

ization mechanism.

Key words: Polymers, Polyhydridophosphazenes, Finite cluster approach,

Reaction mechanism

1 Introduction

Polyhydridophosphazenes (figure 1) are of special synthetic interest. They should potentially provide the possibility to obtain new types of polyphosphazenes by means of an electrophilic substitution of the proton. This is in contrast to the “classical” polyphosphazenes, in which the halogene atom can be substituted nucleophilically [1]. Therefore polyhydridophosphazenes should allow access to polymers with new material properties.

Polymeric hydridophosphazenes were first formulated as a by-product of condensation reactions of phosphanes bearing sterically demanding diorganylamino-substituents ($N(i - \text{Pr})_2$, $N(c - \text{Hex})_2$, $N\text{Ph}_2$, $N(i - \text{Bu})_2$). The isolation and unambiguous characterization of the polymers failed due to the small selectivity of the reactions [2]. Using sterically less demanding diorganylamino-substituents, the polymeric product becomes the main product [3, 4]. In contrast to previously reported experiments on the condensation reactions of such species [5], our studies of the reaction products show a nearly quantitative formation of the polyhydridophosphazenes [6].

* Corresponding author.

Email address: r.fondermann@uni-koeln.de (Rebecca Fondermann).

The mechanism of the polymerization is difficult to investigate experimentally. In the present contribution the polymerization mechanism to the polyhydridophosphazenes is investigated by applying quantum chemical ab initio methods, i. e., MP2 (Møller - Plesset second order perturbation theory) and CCSD(T) theory (singles and doubles coupled cluster with a perturbative estimate of triples). Moreover, we studied the structures and especially the bond alternation of the polyhydridophosphazenes theoretically. Thus, the primary goal of the present study is to extend our understanding of the molecular structure and the polymerization mechanism of polyhydridophosphazenes by performing high level theoretical calculations against the background of accompanying experimental studies, published elsewhere [6].

The organization of this paper is as follows: In section 2, the theoretical framework is briefly described. The results are then presented and discussed in section 3. Finally, a summary is given in section 4.

2 Theoretical framework

Hartree - Fock (HF) solutions for periodic systems can be routinely obtained nowadays with standard program packages, such as CRYSTAL [7], whereas difficulties arise when going beyond this level. The most widely used approach to include electron correlation effects in electronic structure calculations of polymers is density functional theory (DFT) [8, 9a-b]. These calculations be-

came routine with the implementation of DFT in the CRYSTAL program package. The main advantage of DFT is the speed with which the computations can be carried out. However, in contrast to ab initio methods there is no possibility for systematic improvement towards the exact result.

In this paper a straight-forward wavefunction-based quantum chemical method for calculating polymers, the finite cluster approach, is outlined (in the following) and applied (section 3.2).

In principle the total energy E_{tot} or the correlation energy E_{corr} per unit cell U of a polymer U_∞ can be obtained as the limit:

$$E = \lim_{n \rightarrow \infty} \Delta E_n = \lim_{n \rightarrow \infty} [E(R(U_{n+1})R') - E(R(U_n)R')] \quad (1)$$

i.e., by performing a series of molecular calculations for increasingly long oligomers $R(U_n)R'$, where the dangling bonds at both ends have been saturated by end groups R and R' (which are usually hydrogen atoms). A unit cell in the middle of such an oligomer is assumed to be virtually in the same environment as a corresponding unit cell in a polymer of infinite length. The energy per unit cell can be obtained by taking the differences ΔE_n of the energies of two oligomers differing by one unit cell and extrapolating them to the limit $n = \infty$. The convergence of ΔE_n with respect to the number of unit cells, n , is much faster for the dynamic correlation energy than for the HF energy, due to the local character of electron correlations (in contrast to

the long-range character of the mean-field interactions). Equation (1) may be applied at any level of the theory, which is size-extensive, e.g., HF, MBPT or CC.

It is interesting to see how the simple finite cluster approach is related to the so-called incremental scheme, devised first for 3D solids [10, 11] and later also applied to polymers [12]. In the incremental approach using localized orbitals, the correlation energy per unit cell is expanded as

$$E_{corr} = \Delta\epsilon_i + \sum_{i<j} \Delta\epsilon_{ij} + \sum_{i<j<k} \Delta\epsilon_{ijk} + \dots, \quad (2)$$

where the summation over i involves groups of localized orbitals in the reference cell, while those over j and k include all the groups of localized orbitals of the crystal.

The “one-body” increments

$$\Delta\epsilon_i = \epsilon_i \quad (3)$$

are calculated by correlating each group of the localized orbitals in turn, while others are kept frozen at the HF level. The “two-body” increments $\Delta\epsilon_{ij}$ are determined by considering pairs of groups, and performing correlated calculations for each chosen pair. Excitations are allowed only from the orbitals belonging to this pair, keeping the rest of the orbitals frozen.

The “two-body” increments are defined as

$$\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j), \quad (4)$$

where ϵ_{ij} is the correlation energy obtained by correlating orbitals i and j . “Three-body” - and higher “m-body” - increments are defined analogously. Summing up all the increments with the appropriate weight factors determined by the occurrence in the unit cell, one obtains the exact (referring to a given one-particle basis set and the chosen correlation method) correlation energy per unit cell of the infinite system as given in equation (2). This equation is in principle valid for any kind of correlation treatment. However size-extensivity is required in order to achieve convergence in practical applications. For periodic systems with well-localized orbitals usually at most “three-body” increments and at most next-nearest neighbours interactions are needed to recover more than 98% of the correlation energy.

The relation between the incremental scheme and the finite cluster approach becomes obvious by disregarding the end groups in the latter and assuming that the “ideal” oligomer (starting at cell i and ending at cell n) can be considered to be a part of the polymer. As an approximation to the correlation energy E_{corr} per unit cell one obtains

$$\begin{aligned}
 E_{unit\ cell}^{corr} &\approx E_{corr}(n+1) - E_{corr}(n) \\
 &= \epsilon_i + \sum_{i<j} \Delta\epsilon_{ij} + \sum_{i<j<k} \Delta\epsilon_{ijk} + \dots + \Delta\epsilon_{ijk\dots(n+1)}
 \end{aligned}
 \tag{5}$$

The error in the correlation energy per unit cell, for a convergent incremental expansion, should be smaller than the “two-body” term $\Delta\epsilon_{i,n+1}$, which decays as $1/(n+1)^6$ for large n due to van der Waals type correlation contributions. When building the difference in equation (5), the additional “two-body” con-

tributions of the terminal rests R and R' (eq. 1) in the finite cluster approach almost completely cancel out. The exception are those terms which refer to one rest and the cell most remote to it in the longer oligomer, as well as the difference in the R-R' increments for oligomers of length $n + 1$ and n . All these corrections should for suitable choices of R and R' be smaller than $\Delta\epsilon_{i,n+1}$ due to the larger distances involved. Similar arguments hold for higher-order terms involving the terminal rests R and R', which are usually much smaller and do not determine the error resulting from eqn. 5. The main advantage of this method is that it can readily be applied to any size-extensive correlation treatment working in canonical orbitals with standard molecular quantum chemistry program packages.

The finite cluster approach was previously used successfully in calculations for the three isomers of polyacetylene (*all-trans*, *cis-transoid* and *trans-cisoid*) [12], the two boron-nitrogen systems polyaminoborane and polyiminoborane [13] as well as polymethineimine [14]. In order to perform a consistent study of the polymerization mechanism, by treating monomers, intermediates as well as the polymeric products on equal footing, we adopt this approach in the following.

All compounds which are important for the polymerization process were studied in C_1 symmetry at the MP2 level using 6-31G** basis sets [15]. Full geometry optimizations were carried out for all systems. The program package MOLPRO [16] was used for the calculations.

In order to investigate in more detail the conceivable reaction pathways for the polymerization to **I**, the monomers **1a** and **2a** (figure 2) were fully optimized also at the CCSD(T) level using correlation-consistent polarized valence quadruple-zeta basis sets (cc-pVQZ) [17]. These optimized structures were used as the basis for the following calculations.

We then estimated the influence of different substituents R at phosphorus on the position of the equilibrium **1b** \leftrightarrow **2b** in the following way: An attractive (more electronegative substituents) or a repulsive (less electronegative substituents) local pseudopotential of Gaussian form was added to one hydrogen atom bonded to the phosphorus atom. The coefficient of the potential was chosen for a fixed exponent of 1.0 in such a way that at the CI level using the aug-cc-pVQZ hydrogen basis set (spdf) the electronegativity (EN), assumed to be proportional to the sum of the ionization potential (IP) and the electron affinity (EA) according to the Mulliken formula

$$EN = \text{factor} \cdot (IP + EA), \quad (6)$$

ranges between 1.60 and 4.13, when the value for hydrogen is set to 2.10 per definition. For the applied basis sets the factor was appointed to be 0.1464. The results for the EN change by less than 10^{-2} when an uncontracted aug-cc-pV5Z basis set (spdfg) is applied. The energy of the resulting substituted systems **1b** and **2b** was determined by single point calculations at the CCSD(T) level using once again the cc-pVQZ basis sets.

3 Results and discussion

3.1 The aminophosphane/imino-phosphorane system

The prototrope equilibrium between the phosphazene and the phosphazane - form of the monomer is normally shifted to the left side (see figure 2). The aminophosphanes (“*NH*- form”) are therefore stable compounds where no shifting of the hydrogen atom from the nitrogen to the phosphorus can be observed, i.e., the imino-phosphorane (“*PH*-form”) is not formed. One central step in the polymerization to the hydridophosphazene polymers is the shifting of the equilibrium to the right side.

Almost two decades ago *Gonbeau* analysed the electronic properties of the regular system H_2PNH_2 **1a** and its isomer H_3PNH **2a** [18]. At the HF/4-31G* level the isomer **1a** was found to be by 16.25 kcal/mol more stable than the isomer **2a**. In 1991 *Sudhakar* and *Lammertsma* studied the NPH_4 system considering also electron correlation effects at the MP2/6-31G* [19]. Isomer **1a** was calculated to be 29.64 kcal/mol more stable than isomer **2a** and the activation energy of the hydrogen shift was determined to be 50.19 kcal/mol. The authors also examined the tautomeric phosphinoammoniumylid HPNH_3 , which was found to be even less energetically favorable than **2a** and 32.27 kcal/mol less stable than isomer **1a**.

Theoretical investigations on the influence of different substituents to the po-

sition of the equilibrium, have, to our best knowledge, not been published yet. At the CCSD(T) level using cc-pVQZ basis sets we calculated **1b** and **2b** (using pseudopotentials as described in section 2) to model substituents of different electron affinity. The resulting energy differences between the aminophosphane and the iminophosphorane are shown in figure 3. We fitted the resulting curve for the energy difference ΔE (in kcal/mol) depending on the electronegativity x . The minimum calculated from this fitted curve using the Newton method corresponds to an electronegativity of about 3. This result implies that the most suitable compounds for the synthesis of the polymeric hydridophosphazenes are those where the phosphorus has a substituent with an electronegativity of about 3. These theoretical studies correspond to the results of our experimental investigations. The formation of polyhydridophosphazenes works well with diorganylamino-substituents as educts, i.e., a substituent with an electronegativity of about 3 [3, 4, 6]. For the unsubstituted case we find isomer **1a** to be 25.57 kcal/mol more stable than isomer **2a** in excellent agreement with the results of *Sudhakar* and *Lammertsma* [19].

3.2 Polyaminophosphanes **3** and polyiminophosphanes **4**

All published studies discuss only the “classical” polyiminophosphoranes, but not the corresponding polyaminophosphanes. These theoretical investigations of the polyphosphazenes confine mainly to the bond lengths between the phosphorus and the nitrogen atom. The center of interest is the question,

if there are alternating bond lengths. Theoretical studies to the polymeric hydridophosphazenes are still not carried out.

First we calculated the polyaminophosphane **3** as well as the polyiminophosphorane **4** using the finite cluster approach described in section 2. For both we optimized the geometry parameters starting from four different model structures taken from *Allcock et al.* [23]: a *cis-trans*-planar conformation (i.e. with the dihedral angles N-P-N-P = 180.0° and P-N-P-N = 0.0°), a twisted *cis-trans*-planar conformation (N-P-N-P = 156.0° and P-N-P-N = 14.0°), a *helical* conformation (N-P-N-P = 75.5° and P-N-P-N = 75.5°) and an alternative *helical* conformation with dihedral angles N-P-N-P = 42.5° and P-N-P-N = 86.5°. This set of models was chosen in order to provide a broad range of possible conformations. From the energetic most favorable conformation we determined first the energy per unit cell and substituted then a hydrogen atom on every phosphorus by an NH₂-group. We optimized the bond parameters again and appointed the energy per unit cell.

3.2.1 The polyaminophosphane **3a**

The optimization of the *helical* conformation with the dihedral angles N-P-N-P = 75.5° and P-N-P-N = 75.5° led to the most stable conformer of **3a** (see figure 5). The calculated energies per unit cell are listed in table 1 and the optimized geometry parameters in table 2. The convergence of the energy E per unit cell is for low n already more than an order of magnitude better than the

typical accuracy of periodic HF calculations (e.g. CRYSTAL [7], accuracy 10^{-3} Hartree per heavy atom). A fit gave the energy of the polyaminophosphanes for $n = \infty$ to be $E = -396.6265$ au. We assume that the accuracy of this value allows the determination of polymerization energies with an uncertainty of less than 0.1 kcal/mol for the applied computational model (MP2/6-31G**).

3.2.2 The polyiminophosphorane **4a**

The lowest energy for the various conformers of **4a** we obtained for the optimization of the *helical* conformation with the dihedral angles N-P-N-P = 42.47° and P-N-P-N = 86.5° (see figure 6). The calculated energies per unit cell are listed in table 1. The optimized geometry parameters are shown in table 3. The fitted energy of the polyphosphazenes for $n = \infty$ is $E = -396.6124$ au. We estimated the accuracy of this extrapolated result to be better than 10^{-3} Hartree. An uncertainty of less than 0.6 kcal/mol results for the relative stability compared to **3a**. In view of an energy difference of 8.9 kcal/mol this small uncertainty of 7% or less appears to be acceptable. In summary, the finite cluster approach used here leads to a fast convergence of the energy per unit cell and to sufficiently accurate results.

3.2.3 The polyaminophosphane **3b** and the polyiminophosphorane **4b**

After substitution of one hydrogen atom on the phosphorus centre by an NH_2 group we optimized the geometrical parameters for **3b** and **4b** (see table 4

and 5). The optimized dihedral angles prove the *helical* conformation to be the energetically most stable conformation. In similar polyphosphazenes of the type $\text{H}(\text{PX}_2\text{N})_n\text{H}$ with $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$ *Sun* also found the *helical* conformation to be most stable [20]. The author explained his result by considering the electrostatic interactions within the polymer chain. As illustrated in figure 7, four electrostatic interactions (four short interaction lines) between non-bonded phosphorus and nitrogen atoms (1-4 interactions) are favoured in the *helical* conformation. In contrast the *cis-trans*-planar conformation exhibits only two interactions. However it has to be emphasized that the calculated energy differences between the *helical* and the *cis-trans* planar conformations are very small. For the polyiminophosphorane **4a** the difference amounts to 2.3 kcal/mol and for the polyaminophosphane **3a** to 6.0 kcal/mol. This suggests that the order of stability in the solid state might be reverse due to possible interactions between polymer chains. Because of this we decided to carry out solid state calculations. For these calculations the X-ray data of the structures are essential. Because for the polyhydridophosphazenes X-ray data is not available, we calculated the “classical” poly(dichlorophosphazene) .

The “classical” poly(dichlorophosphazene) conformation is controversially discussed in the literature. In respect to X-ray analysis *Meyer et al.* suggested first a regular helical conformation [21]. A second X-ray analysis was reported by *Giglio* [22], who proposed a slightly distorted *cis-trans* planar chain conformation, which was in 1980 confirmed by *Allcock* [23].

All early theoretical investigations used semiempirical methods to calculate the conformational structures. *Tanaka et al.* performed one-dimensional tight binding SCF energy calculations at CNDO/2 level [24]. These single point calculations proved the *cis-trans* planar structure to be the most stable conformation. MNDO optimizations with symmetry constraints on the two molecules $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{POCl}_2$ und $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{PCl}_3][\text{PCl}_6]$, $n = 1,2$, led to the same result [25]. As already mentioned *Sun* carried out geometry optimizations in C_s symmetry at DFT level for the isolated poly(dichlorophosphazene) [20]. He proposed that the *helical* twisted conformation is more stable than the *cis-trans* planar conformation.

Like in the work from *Tanaka et al.* [24] we started from the nine models from *Allcock et al.* [23] based on X-ray analysis and fully optimized all of them. For this geometry optimization we applied the ksh-Script "LoptCG" from *C.M. Zicovich-Wilson* in addition to the program CRYSTAL 98 [7]. All calculations were done at the post-HF DFT-level within the local density approximation for the correlation energy (Hartree-Fock-exchange and the correlation functional of Vosko, Wilk and Nusair [26]). Furthermore we used the 6-31G basis set, whereas the exponents of the most diffuse s- and p-functions were set to a value of 0.272 for nitrogen, 0.160 for phosphorus and 0.203 for chlorine in order to avoid linear dependencies.

Our solid state optimizations provide two different conformations, one *helical* and one *cis-trans* planar structure. The *cis-trans* planar conformation is slightly more stable than the *helical* one. This result confirms the prediction

of *Allcock* based on X-ray data and of *Tanaka* based on semiempirical investigations and implies that the interactions between the polymer chains indeed play an important role in the solid state. However, as in the isolated molecules, the energy difference between these two conformations is very small ($\Delta E = 6.2$ kcal/mol) [27] which is obviously the reason for the controversially discussed conformations in the literature.

From the calculated energies per unit cell we derived the energy differences between the tautomers **3a** (more stable) and **4a** ($\Delta E = 8.9$ kcal/mol) and between **3b** and **4b** (more stable) ($\Delta E = -1.7$ kcal/mol). As it could already be expected from the results of the model calculations in section 3.1, more electronegative substituents on the phosphorus atom shift the equilibrium strongly in the direction of the polyhydridophosphazenes **4b**. Our results indicate that the hydridophosphazene **4b** will be more stable than the corresponding polyaminophosphane **3b** from a chain length greater than 6 - 8 unit cells. The use of species with “nitrogen substituents” on every phosphorus atom should therefore facilitate the polymerization to **4b**. These theoretical results are in line with our experimental findings (see section 3.1) and in excellent agreement with the results of *Koppel et al.* [28].

3.2.4 Bond alternation

Theoretical studies regarding the bond alternation were first carried out by *Ferris* [30a–b]. He optimized geometries of planar *cis-trans* phosphazene oligomers $\text{H}_3\text{P}(\text{NPH}_2)_n\text{NH}$, $n = 1-4$ with C_S -symmetry using the Hartree-Fock method, ECPs and LP-31G* basis sets. In 1997 *Sun* optimized these systems in C_S -symmetry by using the DFT method (nonlocal exchange functional of Becke [29] and local correlation functional of Vosko, Wilk and Nusair [26] in combination with double numerical basis sets, B+VWN/DNP) [20].

We now once again optimized these species ignoring all symmetry constraints at the MP2 level using the 6-31G** basis. The obtained differences of bond lengths are shown in figure 8 in comparison with the data from *Ferris* and *Sun*. Similar to the well-known *all-trans* polyacetylene [12, 31] electron correlation reduces the bond alternation. Furthermore the bond alternation decreases as the size of the oligomers increases. This result is in excellent agreement with the data from *Ferris* and *Sun*. While the value at the DFT level converges to 0.024 Å at $n = \infty$, the corresponding MP2 value is 0.016 Å. The amino substituted hydridophosphazenes show a little larger bond alternation of 0.04 Å at the MP2 level.

How does the bond alternation change in dependence on the substituents? On the basis of the P-N and P=N bond lengths for the $[\text{NH}_2]$ -polyphosphazene **4b**, it is obvious that in contrast to the P-N distance the P=N bond length is corre-

lated with the electronegativity of the element/group attached to phosphorus. The more electronegative the element/group is, the shorter the corresponding P=N bond will be. The bond alternation in the [NH₂]-polyphosphazene **4b** is therefore more pronounced than in the [H]-polyphosphazene **4a**. This is in accordance with the results of former investigations of *Sun* [20].

3.3 The reaction scheme

Finally, we suggest for the polymerization mechanism an anionic polymerization initiated by anionic or neutral bases. The initial step for this mechanism should be the tautomerization of aminophosphine P(NH₂)₃ to its PH-form, (H₂N)₂P(H) = NH. Abstraction of the NH-hydrogen by the solvent ammonia (or dimethylamine) leads to a phosphazene anion, [(H₂N)₂P(H) = N]⁻, which attacks the phosphorus atom of the starting aminophosphine via the negatively charged nitrogen atom. Elimination of amine yields a aminophosphanylhydridophosphazene, (H₂N)₂P(H) = N – P(NH₂) – NH₂. The tautomerization of this species to the diphosphazene, (H₂N)₂P(H) = N – P(NH₂) = NH, followed by deprotonation to the diphosphazene anion and subsequent reaction with aminophosphine propagates the chain to give (H₂N)₂P(H) = N – [P(H)(NH₂) = N]_n – H. We calculated the relative stabilities of these aminophosphine/phosphazene tautomers. The calculated energy values are listed in table 6. The results derived from these *ab initio* calculations are shown in figure 9 and demonstrate that the increased energetic preference of the phosphazene in comparison to

the corresponding aminophosphine from the tautomers **5/6** and **7/8** results in a nearly balanced energetic situation for three PN units **9/10**. The formation of the polymer **11** shows a stabilization energy of 5.4 kcal per PN-unit, which underlines operational conjugative effects by delocalization. The formation of an experimentally observed cyclic trimer as a byproduct is 2.5 kcal per PN-unit less favored than the polymerization. A detailed analysis of the nature of bonding in linear conjugative $\lambda^5 - P = C$ bond systems attributed the stabilization to an effective one-way PC-interaction [32]. Under the conditions of chain propagation the formation of an iminophosphorane moiety is energetically preferred over the aminophosphine unit.

4 Conclusions

The ab initio finite cluster approach developed for one-dimensional periodic systems has first been applied to polyhydridophosphazenes. Together with corresponding molecular calculations on monomers and oligomers these investigations yield results which are in excellent agreement with experimental evidence. Thus a substituent with an electronegativity of about three was found to make the polymerization energetically favorable. This confirms the experimental investigations on the polymerization of trisaminophosphanes to polyhydridophosphazenes. The geometrical data for the calculated polyhydridophosphazene show that the polymer exhibits a *helical* conformation with

small bond alternation. Finally a theoretical study on a potential polymerization mechanism was presented. The calculated energy values are in accordance with the proposed anionic polymerization initiated by anionic or neutral bases . However, the reaction becomes more complex due to the competitive polymerization and depolymerization reaction.

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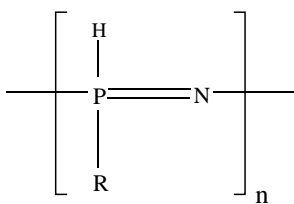
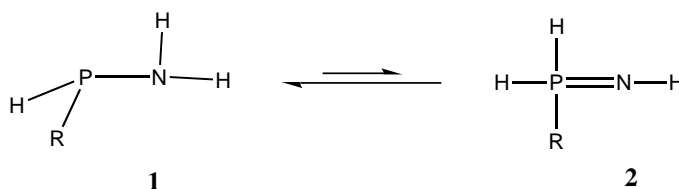


Fig. 1. The polyhydridophosphazene.



- a** R = H
b R = H + pseudopotential

Fig. 2. The prototype equilibrium between aminophosphane and iminophosphorane.

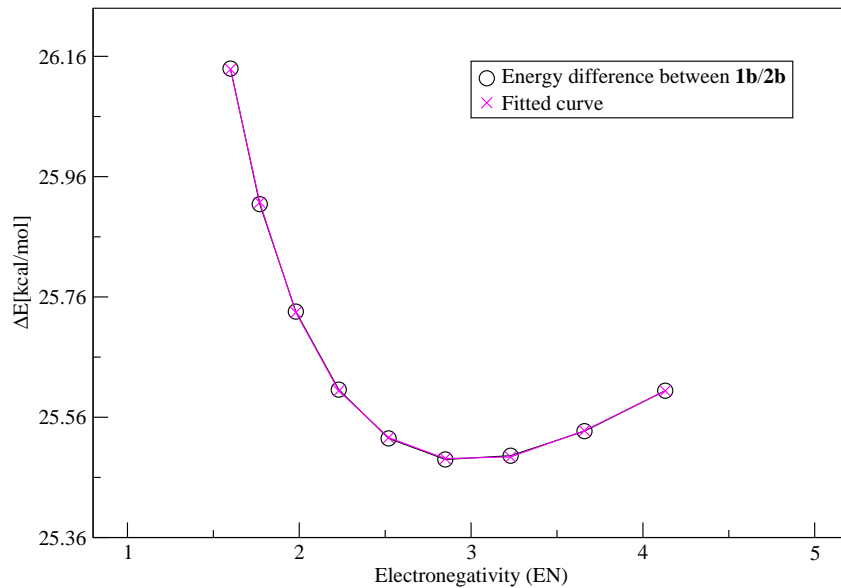


Fig. 3. Energy differences between the aminophosphane **1b** and the iminophosphorane **2b** depending on the electronegativity of the substituent on phosphorus.

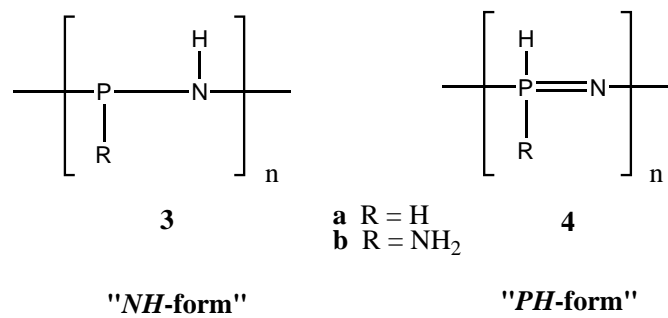


Fig. 4. The polyaminophosphane **3** and the polyhydridophosphazene **4**.

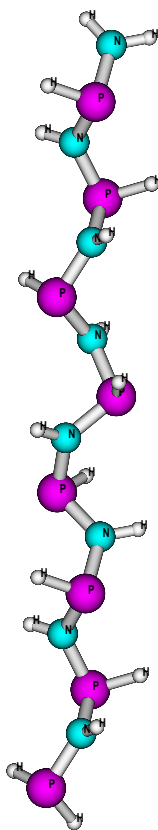


Fig. 5. The optimized structure of the polyaminophosphane **3a** for $n=7$.

Table 1

Energy (Hartree) per unit cell for the polyaminophosphane **3a** and the polyiminophosphorane **4a**.

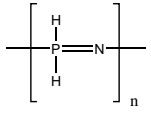
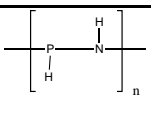
n	3	4	5	6	7
	-396.609753	-396.610986	-396.611682	-396.611818	-396.612230
	-396.626414	-396.626442	-396.626447	-396.626455	-396.626462

Table 2

Optimized bond lengths [\AA] and angles [$^\circ$] of **3a**.

geometrical parameters	n = 3	n = 4	n = 5	n = 6	n = 7
P-N	1.723	1.723	1.723	1.723	1.723
P-N-P	125.94	125.94	125.94	125.94	125.95
N-P-N	107.20	107.19	107.20	107.18	107.17
P-N-P-N	74.06	73.78	73.53	73.24	72.96
N-P-N-P	114.33	114.84	115.46	115.75	115.90

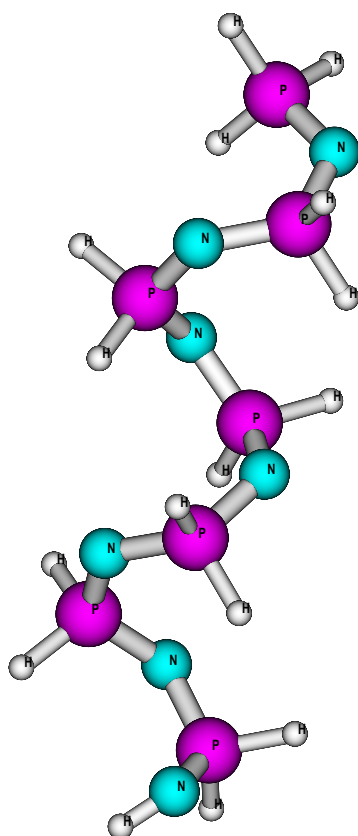


Fig. 6. The optimized structure of the polyiminophosphorane **4a** for $n=7$.

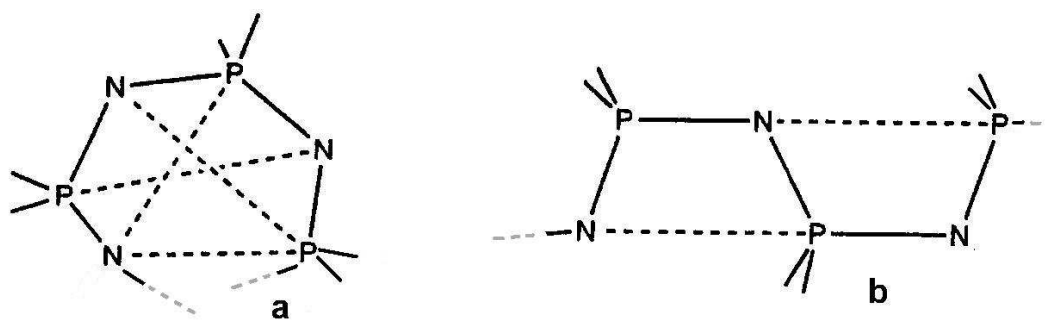


Fig. 7. Electrostatic interactions in the *helical* (a) and in the *cis-trans* planar conformation (b) [20].

Table 3

Optimized bond lengths [\AA] and angles [$^\circ$] of **4a**.

geometrical parameters	n = 3	n = 4	n = 5	n = 6	n = 7
P-N	1.598	1.602	1.603	1.604	1.606
N-P	1.638	1.634	1.628	1.627	1.625
P-N-P	123.88	123.47	124.68	124.74	124.57
N-P-N	120.28	120.13	120.66	120.69	120.62
P-N-P-N	79.33	79.06	77.56	77.66	77.51
N-P-N-P	0.000	0.000	0.000	0.000	0.000

Table 4

Optimized bond lengths [\AA] and angles [$^\circ$] of **3b**.

geometrical parameters	n = 3	n = 4
P-N	1.725	1.725
P-N-P	126.48	126.48
N-P-N	105.70	105.69
P-N-P-N	63.64	63.50
N-P-N-P	91.90	91.80

Table 5

Optimized bond lengths [\AA] and angles [$^\circ$] of **4b**.

geometrical parameters	n = 3	n = 4
P-N	1.594	1.598
N-P	1.640	1.636
P-N-P	126.71	126.04
N-P-N	120.84	120.86
P-N-P-N	64.47	64.42
N-P-N-P	0.000	0.000

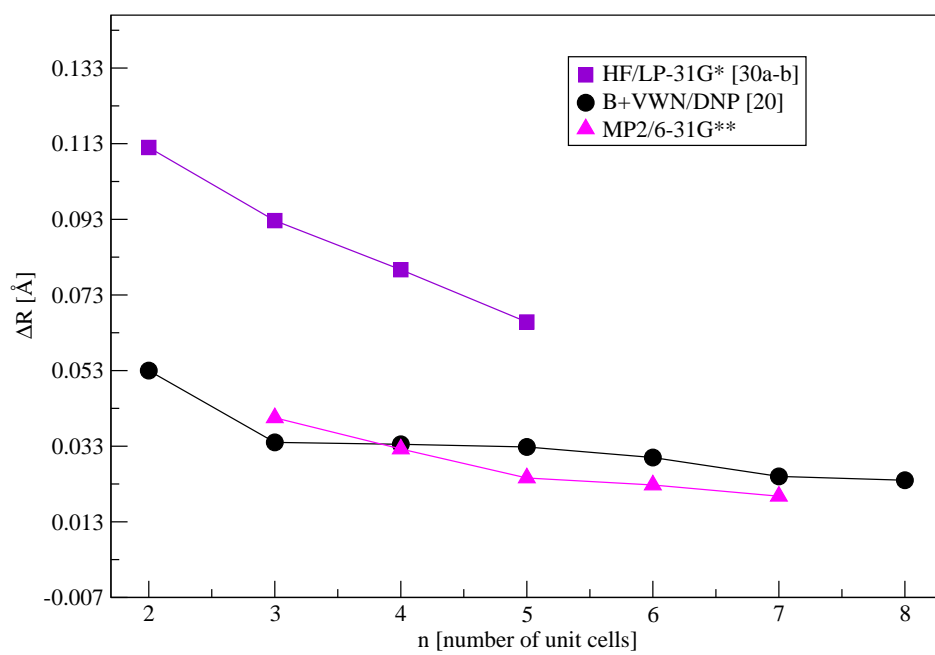


Fig. 8. Calculated bond-length alternations (ΔR) of the oligomers $H_3P(NPH_2)_nNH$, $n = 1-7$ at different theoretical levels.

Table 6

Energy values of the compounds **5** - **12** at the MP2/6-31G** level.

Compound	5	6	7
Energy [a.u.]	-508.212049	-508.192575	-960.053347
Compound	8	9	10
Energy [a.u.]	-960.045600	-1411.892484	-1411.888665
Compound	11	12	NH₃
Energy [a.u.]	-451.839809 per PN-unit	-451.844501 per PN-unit	-56.380984

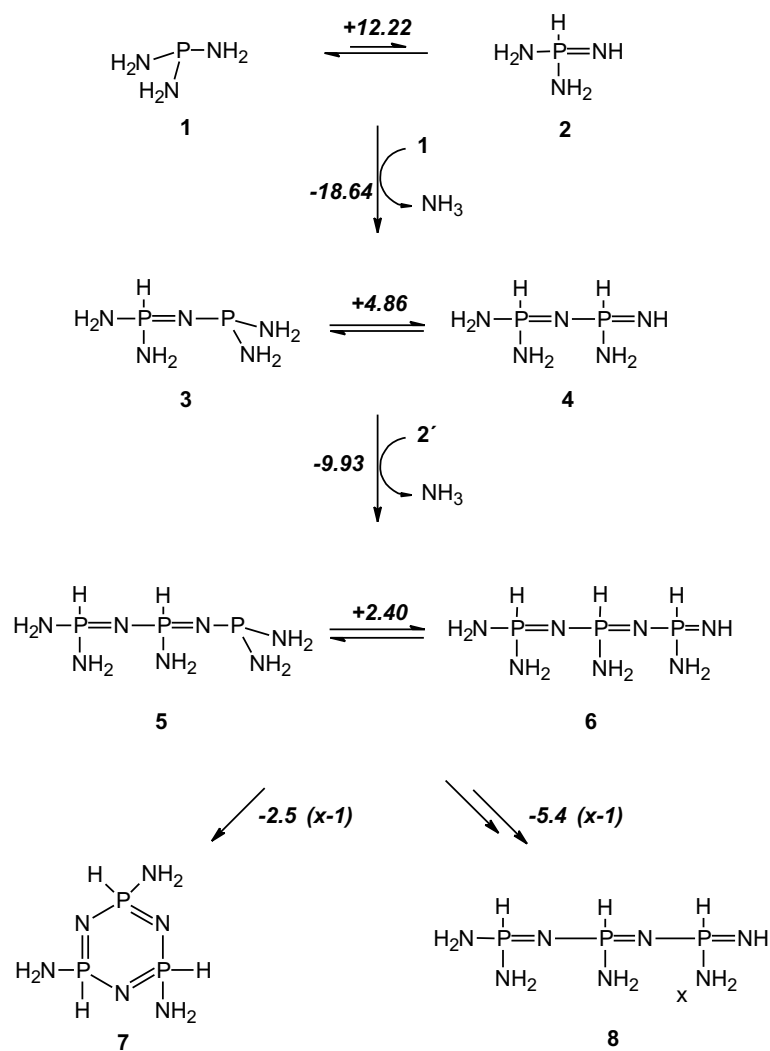


Fig. 9. Proposed mechanism of the polymerization reaction. The energy values are given in kcal/mol.