An ab initio and force field study on the conformation and chain flexibility of the dichlorophosphazene trimer

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SUMMARY:

Ab initio molecular orbital calculations have been used to study the conformation, valence electron charge density, and chain flexibility of a dichlorophosphazene trimer ($\text{CH}_3[\text{NP}(\text{Cl}_2)]_3\text{CH}_3$). The calculations were carried out at the restricted Hartree-Fock level with the 6–31 G* basis set. The dichlorophosphazene trimer adopts a planar *trans-cis* conformation. The valence electron charge distribution indicates strong charge separations along the backbone of the molecule, and is in agreement with Dewar's island delocalization model for bonding in linear and cyclic phosphazenes. In order to determine the height of the torsional barrier (2,5 kcal/mol), the torsional potential of a central P–N bond of the trimer was studied with a rigid rotor scan and geometry optimizations of selected rotamers. The flexibility of the P–N–P bond angle contributes significantly to the chain flexibility. Based on the results of the ab initio calculations, an empirical force field for the dichlorophosphazene trimer was developed. The energy expression includes bond stretch, angle bend, electrostatic, van der Waals, and torsional potential terms. A relaxed scan with the force field achieves good agreement with the ab initio results for the torsional potential in the vicinity of the stable conformation, and an excellent agreement with the ab initio results on changes in the $\text{P}^2\text{N}^2\text{P}^3$ bond angle and the $\text{N}^1\text{P}^2 - \text{N}^2\text{P}^3$ dihedral angle during a full rotation around the $\text{N}^2 - \text{P}^3$ bond.

Introduction

Recently, interest in the design of novel, high value added materials with specific chemical or physical characteristics has been increasing. Most of the commercially used polymeric materials are carbon-based. In searching for novel polymers, it is therefore important to investigate the synthesis and physical properties of macromolecules which have inorganic elements in the main chain in order to evaluate their potential for technological applications.

Compared to organic polymers, inorganic macromolecules have interesting and unusual chemical, mechanical, electronic, and/or thermal properties. The unique properties of polymeric materials (like the large reversible deformability of elastomers, or the high impact strength of thermoplastics) are due to the variety of different conformations which the polymer chains can adopt¹⁾. Knowledge of the stable conformation and the flexibility of the polymer main chain (i.e., the energy barriers between different conformations) is therefore essential to understand the physical properties of polymers. A molecular geometry which differs from the geometry of a carbon-based backbone (e.g., larger bond lengths and bond angles), and a highly flexible main chain cause the exceptional properties of some inorganic polymers²⁾.

The glass transition temperature of a polymer is influenced by the chain flexibility³⁻⁵. For example, the flexibility of the poly(dimethylsiloxane) ($[\text{Si}(\text{CH}_3)_2\text{O}]_n$) backbone leads to an extraordinarily low glass transition temperature $T_g = -126^\circ\text{C}$. Low glass transition temperatures of some polyphosphazenes ($[\text{PR}_2\text{N}]_n$) are also attributed to the high torsional mobility of the phosphazene backbone.

Computational techniques have recently become more important for studying polymer structures and properties^{6,7}. In this paper we present a computational study of the structure and chain flexibility of a trimer of poly(dichlorophosphazene) (PDCP), $(\text{PCl}_2)_n$ (see Figs. 1 and 2).

Fig. 1. Chemical repeat unit of the poly(dichlorophosphazene) polymer. The crystallographic repeat unit consists of two monomers. Single and double P—N bonds are in terms of their length and electronic structure — unlike C—C single and double bonds — almost identical

Fig. 2. Chemical structure of the dichlorophosphazene trimer

The synthesis of phosphazene polymers was pioneered by Allcock and coworkers. Ab initio molecular orbital calculations on the structure and bonding of cyclic and short chain linear phosphazene molecules have been carried out by Trinquier^{8,9}) and Ferris et al.¹⁰⁻¹²). Several authors reported on the development of empirical force fields for phosphazene molecules¹³⁻¹⁶). The parameterization of these force fields was based on experimental data.

We use ab initio molecular orbital calculations in order to study the structure, torsional potentials, charge density distributions, and force constants of the dichlorophosphazene trimer which is used as a short chain analogue of PDCP. Based on the ab initio results, we develop and parameterize an empirical force field for the dichlorophosphazene trimer which simulates the flexibility of the phosphazene main chain.

Method of computation

We used a HP 755 workstation and an Indigo SGI RS 4000 workstation in order to perform the Gaussian 92 ab initio molecular orbital calculations^{17,18}). The calculations were carried out at the restricted Hartree-Fock (RHF) level of theory. We used the 6-31G* basis set for the Gaussian orbital wave functions. The program employs a gradient method for geometry optimizations.

The graphic representations of the molecules were created with the CERIU molecular modeling software package¹⁹) and the IRIS Explorer graphics package.

We developed a Fortran 77 routine for the force field calculations. The program uses a conjugate-directions algorithm for the geometry optimizations which was written by R. P. Brent. The routine was obtained through the internet by the 'Guide to Available mathematical Software' which is maintained by the National Institute of Standards and Technology.

Ab initio results and discussion

Conformation and charge density distribution of the dichlorophosphazene trimer

The molecular geometry of the dichlorophosphazene trimer (see Fig. 2) was restricted to a conformation with C_s symmetry for the geometry optimizations. The mirror plane contained the backbone atoms (i.e., the phosphorus, nitrogen, and carbon atoms). We carried out a frequency calculation on the molecular geometry which resulted from the geometry optimization in order to verify that the optimized geometry corresponds to a minimum and not to a transition state of the potential energy surface (PES). The dichlorophosphazene trimer adopts a planar *trans-cis* conformation (see Fig. 3). The bond lengths, bond angles, and dihedral angles of the stable conformation are shown in Tab. 1. We observe a slight alternation in P—N bond lengths (up to 0,1 Å). The longer, 'single' P—N bonds are parallel to the direction of the main chain, and the shorter, 'double' P=N bonds form an angle with the direction of the main chain. The energy of the *trans-cis* conformation of the dichlorophosphazene trimer with respect to the quantum chemical standard state (i.e., the state where all electrons and nuclei are infinitely separated) is $E(\text{RHF}/6-31\text{G}^*) = -2523680,9 \text{ kcal/mol}$.

Fig. 3. 'Ball and stick' model of the stable conformation of the dichlorophosphazene trimer

Tab. 1. Molecular geometry of the dichlorophosphazene trimer. The dihedral angles which are marked with the symbol * were kept fixed during the geometry optimization

Bond lengths in Å			
P ¹ – C ¹	1,7971	Cl ¹ – P ¹	2,0075
N ¹ – P ¹	1,5369	Cl ³ – P ²	2,0097
P ² – N ¹	1,5995	Cl ⁵ – P ³	2,0514
N ² – P ²	1,5376	H ¹ – C ¹	1,0815
P ³ – N ²	1,6034	H ² – C ¹	1,0829
N ³ – P ³	1,5079	H ⁴ – C ²	1,0832
C ² – N ³	1,4396	H ⁵ – C ²	1,0877
Bond angles in degree			
∠N ¹ P ¹ C ¹	110,81	∠Cl ³ P ² N ²	114,54
∠P ² N ¹ P ¹	135,34	∠Cl ⁵ P ³ N ³	115,74
∠N ² P ² N ¹	113,37	∠H ¹ C ¹ P ¹	110,83
∠P ³ N ² P ²	134,31	∠H ² C ¹ P ¹	108,30
∠N ³ P ³ N ²	115,97	∠H ⁴ C ² N ³	108,90
∠C ² N ³ P ³	131,61	∠H ⁵ C ² N ³	112,24
∠Cl ¹ P ¹ N ¹	115,19		
Dihedral angles in degree			
∠Cl ¹ P ¹ – N ¹ C ¹	119,6	∠N ² P ² – N ¹ P ¹	0,0*
∠Cl ³ P ² – N ² N ¹	120,8	∠P ³ N ² – P ² N ¹	180,0*
∠Cl ⁵ P ³ – N ³ N ²	-122,2	∠N ³ P ³ – N ² P ²	0,0*
∠H ² C ¹ – P ¹ H ¹	120,9	∠C ² N ³ – P ³ N ²	180,0*
∠H ⁵ C ² – N ³ H ³	119,1	∠H ¹ C ¹ – P ¹ N ¹	180,0*
∠P ² N ¹ – P ¹ C ¹	180,0*	∠H ⁴ C ² – N ³ P ³	180,0*

The charge density of the valence electrons of the dichlorophosphazene trimer is displayed in Fig. 4. The valence electron density exhibits nodes at phosphorus, and a build-up of electron density at nitrogen. The charge distribution is in agreement with the classical picture of bonding in linear and cyclic phosphazenes involving the island delocalization model elucidated by Dewar²⁰. This model states that a delocalization of valence electrons occurs over only three-atom P–N–P units.

The charge distribution of the dichlorophosphazene trimer indicates that the PDCP polymer will possess a highly polar backbone. Based on the pronounced charge separation, we anticipate that electrostatic attraction and repulsion will give a significant contribution to the intra- and intermolecular interactions. We used the 'Natural Population Analysis' (NPA) in order to assign partial atomic charges to the atoms of the dichlorophosphazene trimer²¹. Results of the NPA are shown in Tab. 2.

Our results on the stable geometry, the bond length alternation, and the charge distribution are in agreement with the results of Ferris and co-workers^{10–12}. Ferris et al. carried out a detailed ab initio study on the bond structure and bond lengths alter-

Fig. 4. Charge density of the valence electrons of the dichlorophosphazene trimer. The surface denotes the volume which includes 85% of the charge density of the valence electrons

nations of small cyclic and linear phosphazene molecules with hydrogen and fluorine as substituents bonded to phosphorus. Based on the results for bond length alternations of a series of linear phosphazene molecules with increasing molecular weight, Ferris and co-workers suggest bond lengths which alternate by 0,05 Å for the polymer. Although chemical bonding in linear phosphazene backbones cannot be interpreted in terms of single and double bonds, small bond length alternations can have a significant influence on the vibrational and electronic properties of polymers (consider, e.g., bond length alternations in polyenes²¹⁾). However, the electronic structure of phosphazenes differs from the electronic structure of a potential conductor such as polyacetylene. The smallest possible repeat unit of PDCP consists of a PCl_2 moiety and a nitrogen atom. The phosphorus and the nitrogen atom each contribute one electron to the highest occupied band, and this band is therefore filled. A Peierls distortion (like in polyacetylene) will not occur, since a half-filled conducting band is required for this phenomenon.

Tab. 2. Partial atomic charges q_i for the dichlorophosphazene trimer which were assigned with the Natural Population Analysis. The numbering of the atoms corresponds to Fig. 2

Atom	q in e	Atom	q in e
P ¹	1,913	Cl ⁵	-0,340
N ¹	-1,610	Cl ⁶	-0,340
P ²	2,135	C ¹	-1,042
N ²	-1,626	C ²	-0,392
P ³	2,110	H ¹	0,271
N ³	-1,232	H ²	0,280
Cl ¹	-0,247	H ³	0,280
Cl ²	-0,247	H ⁴	0,212
Cl ³	-0,258	H ⁵	0,195
Cl ⁴	-0,258	H ⁶	0,195

The torsional flexibility of the dichlorophosphazene trimer

The ab initio molecular orbital method is well-suited for determining the energy which is needed to rotate parts of a molecule around a given bond. As a first step, the stable conformation of the molecule is determined. Starting from the stable conformation, the energies of the conformers which form during a given rotation around a bond (the 'rotamers') are calculated. The energy values as a function of the dihedral angle which defines the rotation are the torsional potential.

We used two approaches to study the torsional potentials. In order to gain a first impression of the torsional flexibility of a molecule, we performed a 'rigid rotor scan'. In the 'rigid rotor' approximation, all bond lengths, bond angles and remaining dihedral angles are kept fixed while part of the molecule is rotated around a bond. This means that the rigid rotor approximation yields an upper limit for the actual torsional potential.

In addition, we compared the results of the rigid rotor scan with results of a 'fully optimized' or 'relaxed' scan. In the 'relaxed' scan the energies of fully optimized structures which form during a rotation are determined. Therefore, the relaxed scan will yield shapes of torsional potentials which are close to those in reality.

Compared to the relaxed scan, the rigid rotor scan is significantly less time-consuming, since geometry optimizations are omitted while one part of the molecule is rotated around a bond. The rigid rotor approximation is not successful in determining absolute barrier heights and shapes of torsional potentials, since adjustments of the molecular geometry which reduce strains (e.g., bending of bond angles or rotation of side groups) during the rotation of a part of the molecule are not considered. A comparison of the result of a rigid rotor scan and the energies of the geometry optimized rotamers (relaxed scan) will show the contribution of the flexibility of the bond angles to the torsional mobility of the PDCP backbone.

The P²N² – P³N³ dihedral angle of the dichlorophosphazene trimer was rotated from 0° to 180° in 15° steps during a rigid rotor scan – a full rotation was not neces-

sary owing to the C_s symmetry of the molecule. In addition, we carried out geometry optimizations for selected rotamers which form during a rotation around the $N^2 - P^3$ bond. The results of the rigid-rotor and the relaxed scan are shown in Fig. 5.

Fig. 5. Torsional potential of the $N^2 - P^3$ bond (angle in degree). Open symbols denote results of rigid-rotor scans; filled symbols denote results of relaxed scans. The torsional angle $\phi = 0^\circ$ corresponds to the *cis* conformation

The torsional potential which was obtained with the rigid rotor approximation exhibits three maxima. The local maxima at $\angle P^2N^2 - P^3N^3 \approx 100^\circ$ and 260° occur at conformations with minimal distance between one chlorine atom bonded to phosphorus atom P^2 and another chlorine atom bonded to phosphorus atom P^3 . The global maximum at $\angle P^2N^2 - P^3N^3 = 180^\circ$ corresponds to the eclipsed conformation.

The height of the torsional barrier which resulted from the relaxed scan (2,5 kcal/mol) is significantly lower than the barrier which was obtained with the rigid rotor approximation (8,2 kcal/mol). The $P^2N^2P^3$ bond angle undergoes a significant variation during a full rotation (see Fig. 8). The bond angle opens up to $24,0^\circ$. The widening of the $P^2N^2P^3$ bond angle decreases the repulsive interaction between the PCl_2 moieties, and therefore lowers the torsional barrier. The flexibility of the $P-N-P$ bond angles contributes therefore significantly to the flexibility of the phosphazene backbone.

We want to discuss two results of our previous ab initio molecular orbital study on the structure and chain flexibility of halogenated poly(thionylphosphazene)s $[(NSOX)(NPCl_2)_2]_n$, $X = F$ or Cl , which are of significance for the present study on the chain flexibility of $PDCP^{23}$. In this work it was concluded that electron correlation has a negligible influence on the height of the torsional barriers of halogenated poly(thionylphosphazene)s (electron correlation reduces the barrier by 3%). In addition, the torsional flexibility of a bond of the main chain is governed by its immedi-

ate 'molecular environment'. The torsional potential for a rotation around a P—N bond of the 'phosphazene end' of the poly(thionylphosphazene) monomer unit differs at most by 5% from the torsional potential of a central P—N bond in the dichlorophosphazene trimer. This observation justifies the significance of the calculations on low molecular weight analogues for the polymeric system.

An empirical force field for the dichlorophosphazene trimer

The *ab initio* molecular orbital technique, which was used in the previous section, requires time-consuming calculations. *Ab initio* calculations on 'larger' molecules (e.g. macromolecules or molecules with larger side groups) are currently not feasible, since the required computer time increases sharply with the number of atomic orbitals which are used to carry out the calculations²⁴. A possible solution to this problem is to use 'classical mechanical' or 'empirical' force field calculations for larger molecules^{7,25}. Force field calculations approximate the potential energy surface (PES) $E(\mathbf{r}, \boldsymbol{\theta}, \boldsymbol{\varphi})$ with an analytical expression (the 'energy expression') which is composed of a sum of energy terms. $\mathbf{r} = (r_2, \dots, r_N)$ denotes the bond-lengths, $\boldsymbol{\theta} = (\theta_3, \dots, \theta_N)$ the bond-angles, and $\boldsymbol{\varphi} = (\varphi_4, \dots, \varphi_N)$ the dihedral angles which are necessary to define the molecular geometry. The various energy terms represent changes in the energy of the molecule which are caused by particular internal motions or interactions^{26,27}. Previous results (e.g. experimental and/or *ab initio* results) are absolutely necessary for a parameterization of the various energy term of the energy expression.

Energy expression and parameterization

We tried to develop an empirical force field which simulates the flexibility of the PDCP main chain. We used the *ab initio* results on the dichlorophosphazene trimer (molecular structure, partial atomic charges, torsional barriers, and force constants for bond stretch and angle bend motions) in order to parameterize and test the energy expression of the force field. The energy expression includes harmonic terms for bond stretch (1) and angle bend (2) motions, electrostatic (3) and van der Waals (4) potentials for the non-bonded intramolecular interaction, and torsional potential terms (5) for selected torsional motions:

$$E(\mathbf{r}, \boldsymbol{\theta}, \boldsymbol{\varphi}) = \sum_{i=2}^N \frac{1}{2} k_i^s (r_i - r_i^0)^2 \quad (1)$$

$$+ \sum_{i=3}^N \frac{1}{2} k_i^b (\theta_i - \theta_i^0)^2 \quad (2)$$

$$+ \frac{\alpha}{4\pi\epsilon_0} \sum_{i < j} \frac{q_i q_j}{r_{ij}} \quad (3)$$

$$+ \sum'_{i < j} D_{ij}^0 \left[\left(\frac{r_{ij}^0}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right] \quad (4)$$

$$+ \sum_{i=4,6,8} k'(1 - \cos(2\varphi_i)) \quad (5)$$

r_i^0 denotes the 'zero-strain' values for bond lengths, k_i^s the force constant for bond stretching, θ_i^0 the zero-strain values for bond angles, and k_i^b the force constant for bond angle bending. α is an adjustable parameter, ϵ_0 denotes the permittivity of the vacuum, w_i are NPA partial atomic charges, and r_{ij} are the inter-nuclear distances. r_{ij}^0 denotes the inter-nuclear distance at which the Lennard-Jones potential reaches its minimum value D_{ij}^0 . Pairs of atoms which are covalently bonded or which form a bond form a bond angle with a third covalently bonded atom are not included in the summation $\sum'_{i < j}$ in the energy terms of non-bonded interactions. The contribution of covalently bonded atoms to the non-bonded interaction will be included in the 'bond-stretch' terms, and the contribution of two atoms which form a bond angle with a third atom is included in the 'angle-bend' energy term. The torsional potential terms (5) restrict the mobility of torsional motion around the dihedral angles $\varphi_4 = \angle C^1P^1 - N^1P^2$, $\varphi_6 = \angle N^1P^2 - N^2P^3$, and $\varphi_8 = \angle C^2N^3 - P^3N^2$.

We used the parameters D_{ij}^0 and r_{ij}^0 of the Lennard-Jones 12-6 potential which are implemented in the Dreiding II force field⁽²⁸⁾ (see Tab. 3). The geometric means $D_{A,B}^0 = \sqrt{D_{A,A}^0 D_{B,B}^0}$ and $r_{A,B}^0 = \sqrt{r_{A,A}^0 r_{B,B}^0}$ of the parameters for like atoms were used for the parameters of pairs of unlike atoms.

Tab. 3. Parameters r^0 and D^0 for the Lennard-Jones 12-6 potential

Atom	r^0 in Å	D_0 in kcal/mol
P	4,15	0,32
N	3,66	0,077
Cl	3,95	0,283
C	4,15	0,25
H	3,20	0,015

The atomic centered charges w_i were based on partial atomic charges, which were assigned with the Natural Population Analysis (see Tab. 2). A common scaling factor $\sqrt{\alpha}$ was applied to all charges since the magnitude of partial atomic charges depends on the population analysis scheme⁽²⁹⁾. We used a non-linear regression of a rigid rotor scan around the $P^2 - N^3$ bond in order to determine the scaling factor $\alpha = 0,348$ (see Fig. 6).

Ab initio RHF/6-31G* geometry optimizations and frequency calculations were used in order to determine the constants k_i^s and k_i^b and the zero-strain bond lengths r_i^0 and bond angles θ_i^0 .

Fig. 6. Non-linear fit of an ab initio rigid rotor scan around the $P^2 - N^3$ bond (angle in degree) with electrostatic and van der Waals potentials. The scaling factor α of the electrostatic term is an adjustable parameter

The geometry optimization yields a stationary point of the PES, i.e.

$$\frac{\partial E}{\partial r_i} = 0 \quad \frac{\partial E}{\partial \theta_j} = 0 \quad \frac{\partial E}{\partial \varphi_l} = 0 \quad (6)$$

and the frequency calculation determines the second derivatives of the potential energy surface at the stationary point:

$$\frac{\partial^2 E}{\partial r_i^2} = H_{ii} \quad \frac{\partial^2 E}{\partial \theta_j^2} = H_{jj} \quad \frac{\partial^2 E}{\partial \varphi_l^2} = H_{ll} \quad \frac{\partial^2 E}{\partial r_i \partial \theta_j} = H_{ij} \quad \dots \quad (7)$$

The ab initio results include contributions from non-bonded interactions, which are accounted for separately in the force field calculation. Therefore, the influence of the non-bonded interactions on the geometry optimized bond lengths r_i and bond angles θ_j , and on the elements H_{ij} of the matrix of second derivatives of the PES has to be removed in order to obtain the zero-strain values r_i^0 , θ_j^0 , k_i^s , k_j^b

$$\frac{\partial E}{\partial r_i} = 0 = k_i^s(r_i - r_i^0) + \frac{\partial}{\partial r_i}[E_{\text{estat}} + E_{\text{vdW}}] \quad (8)$$

$$\frac{\partial E}{\partial \theta_j} = 0 = k_j^b(\theta_j - \theta_j^0) + \frac{\partial}{\partial \theta_j}[E_{\text{estat}} + E_{\text{vdW}}] \quad (9)$$

$$\frac{\partial^2 E}{\partial r_i^2} = H_{ii} = k_i^s + \frac{\partial^2}{\partial r_i^2} [E_{\text{estat}} + E_{\text{vdW}}] \quad (10)$$

$$\frac{\partial^2 E}{\partial \theta_j^2} = H_{jj} = k_j^b + \frac{\partial^2}{\partial \theta_j^2} [E_{\text{estat}} + E_{\text{vdW}}] \quad (11)$$

$$\Rightarrow k_i^s = H_{ii} - \frac{\partial^2}{\partial r_i^2} [E_{\text{estat}} + E_{\text{vdW}}] \quad r_i^0 = r_i - \frac{\frac{\partial}{\partial r_i} [E_{\text{estat}} + E_{\text{vdW}}]}{H_{ii} - \frac{\partial^2}{\partial r_i^2} [E_{\text{estat}} + E_{\text{vdW}}]} \quad (12)$$

$$\Rightarrow k_j^b = H_{jj} - \frac{\partial^2}{\partial \theta_j^2} [E_{\text{estat}} + E_{\text{vdW}}] \quad \theta_j^0 = \theta_j - \frac{\frac{\partial}{\partial \theta_j} [E_{\text{estat}} + E_{\text{vdW}}]}{H_{jj} - \frac{\partial^2}{\partial \theta_j^2} [E_{\text{estat}} + E_{\text{vdW}}]} \quad (13)$$

where E_{estat} refers to term (3), and E_{vdw} refers to term (4) of the energy expression.

The geometry optimized bond length r_i and bond angles θ_j , the second derivatives of the PES at the optimized geometry H_{ij} , the zero-strain bond length r_i^0 and zero-strain bond angles θ_j^0 , and the constants k_i^s and k_j^b are shown in Tabs. 4 and 5. The values which are shown in the tables were calculated with the constants for the van der Waals interaction, the partial charges, and the scaling constant α , which were discussed above.

The harmonic approximation for the bond-stretch and angle-bend potentials yielded satisfactory results for small variations of bond lengths and bond angles. However, the $\text{P}^2\text{N}^2\text{P}^3$ bond angle undergoes large changes (24°) during a torsion around the $\text{N}^2 - \text{P}^3$ bond. We therefore adjusted the values of H_{jj} for the $\text{P}-\text{N}-\text{P}$ bond angle bending motion to $0.05 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{degree}^{-2}$.

Geometry optimizations with an energy expression which includes only the terms (1)–(4) (i.e., without the torsional potential terms (5)) show that the force field is able to capture certain characteristics of the PES. The force field determines the planar *trans-cis* conformation as a minimum of the PES in an unconstrained geometry optimization, and a geometry optimization of the eclipsed conformation (which corresponds to a $\text{P}^2\text{N}^2 - \text{P}^3\text{N}^3$ dihedral angle of 180°) yields values of the torsional barrier and the $\text{P}^2\text{N}^2\text{P}^3$ bond angle bend which are close to those determined with an ab initio relaxed scan — provided that the molecule is restricted to the planar (i.e., it is restricted to adopt the C_s symmetry).

If an unconstrained geometry optimization is carried out starting with an initial guess which is 'far away' from the *trans-cis* conformation (e.g. an all-*trans* conformation), the force field finds a *gauche* conformation as ground state conformation ($\angle \text{P}^2\text{N}^1 - \text{P}^1\text{C}^1 = -63.6^\circ$ instead of 180.0°). The planar *trans-cis* conformation is a

Tab. 4. Geometry optimized bond lengths r_i , zero-strain bond lengths r_i^0 , second derivatives of the PES H_{ii} , and constants k_i^s for the dichlorophosphazene trimer

Bond	r_i	r_i^0	H_{ii}	k_i^s
	in Å		in kcal·mol ⁻¹ ·Å ⁻²	
C ¹ – P ¹	1,797	1,905	158,356	154,377
P ¹ – N ¹	1,537	1,637	370,342	366,750
N ¹ – P ²	1,600	1,740	273,965	278,549
P ² – N ²	1,538	1,660	367,714	362,835
N ² – P ³	1,603	1,740	269,013	273,083
P ³ – N ³	1,508	1,492	411,140	378,749
N ³ – C ²	1,440	1,368	249,796	222,711
Cl ¹ – P ¹	2,008	1,937	145,491	109,253
Cl ² – P ¹	2,008	1,937	145,491	109,253
Cl ³ – P ²	2,010	2,033	143,889	143,085
Cl ⁴ – P ²	2,010	2,033	143,889	143,085
Cl ⁵ – P ³	2,051	2,068	117,014	113,284
Cl ⁶ – P ³	2,051	2,068	117,014	113,284
H ¹ – C ¹	1,082	1,093	243,024	243,511
H ² – C ¹	1,083	1,093	241,151	239,981
H ³ – C ¹	1,083	1,093	241,151	239,981
H ⁴ – C ²	1,083	1,074	236,372	235,058
H ⁵ – C ²	1,088	1,076	228,429	227,102
H ⁶ – C ²	1,088	1,076	228,429	227,102

local minimum of the force field approximation of the PES. This *gauche* conformation was also found with a RHF/6–31G* ab initio geometry optimization. However, the ab initio results show that the *gauche* conformation corresponds to a local minimum of the PES, and the planar *trans-cis* conformation corresponds to the global minimum of the PES.

An unrestricted geometry optimization of the eclipsed conformation with the force field shows that the eclipsed conformation corresponds to a transition state with respect to the dihedral angle N¹P² – N²P³ (the transition state lies between stable conformations corresponding to dihedral angles $\angle$ N¹P² – N²P³ = 126,2° and $\angle$ N¹P² – N²P³ = 233,8°). Ab initio geometry optimizations found no indication of local minima of the PES which correspond to these two conformations. In addition, the ab initio calculations showed that the planar eclipsed conformation corresponds to a minimum of the PES with respect to variations of the N¹P² – N²P³ dihedral angle.

An energy expression which only includes the terms (1)–(4) overestimates the torsional flexibility of P–N bonds which form an angle with the main chain (i.e., the ‘double’ bonds). This leads to a de-stabilization of *trans* conformations and to the prediction of spurious stable conformations.

The introduction of torsional potential terms (5) with $k' = 0,5$ kcal/mol for these bonds resolves the problems which were discussed above. The *gauche* conformation corresponds to a local minimum of the PES, and the planar eclipsed conformation

Tab. 5. Geometry optimized bond angles θ_j , zero-strain bond angles θ_j^0 , second derivatives of the PES H_{jj} , and constants k_j^b for the dichlorophosphazene trimer

Angle	θ_j	θ_j^0	H_{jj}	k_j^b
	in degree		in kcal · mol ⁻¹ · degree ⁻²	
$\angle C^1 P^1 N^1$	110,81	114,37	0,385	0,403
$\angle P^1 N^1 P^2$	135,34	140,05	0,050	0,530
$\angle N^1 P^2 N^2$	113,37	117,99	0,501	0,544
$\angle P^2 N^2 P^3$	134,31	165,66	0,050	0,080
$\angle N^2 P^3 N^3$	115,97	118,50	0,504	0,533
$\angle P^3 N^3 C^2$	131,61	92,89	0,105	0,033
$\angle Cl^1 P^1 N^1$	115,19	117,90	0,413	0,343
$\angle Cl^2 P^1 N^1$	115,19	117,90	0,413	0,343
$\angle Cl^3 P^2 N^2$	114,54	114,60	0,425	0,420
$\angle Cl^4 P^2 N^2$	114,54	114,60	0,425	0,420
$\angle Cl^5 P^3 N^3$	115,74	114,80	0,414	0,389
$\angle Cl^6 P^3 N^3$	115,74	114,80	0,414	0,389
$\angle H^1 C^1 N^1$	110,83	111,59	0,233	0,230
$\angle H^2 C^1 N^1$	108,30	109,97	0,228	0,230
$\angle H^3 C^1 N^1$	108,30	109,97	0,228	0,230
$\angle H^4 C^2 N^3$	108,90	108,35	0,299	0,294
$\angle H^5 C^2 N^3$	112,24	110,85	0,295	0,278
$\angle H^6 C^2 N^3$	112,24	110,85	0,295	0,278
$\angle Cl^1 P^1 C^1$	119,58	119,61	0,311	0,291
$\angle Cl^2 P^1 Cl^1$	120,84	115,58	0,314	0,217
$\angle Cl^3 P^2 N^1$	120,83	120,83	0,352	0,355
$\angle Cl^4 P^2 Cl^3$	118,34	117,37	0,314	0,316
$\angle Cl^5 P^3 N^2$	122,21	122,21	0,338	0,349
$\angle Cl^6 P^3 Cl^5$	115,59	114,42	0,339	0,345
$\angle H^2 C^1 H^1$	120,85	120,22	0,195	0,193
$\angle H^3 C^1 H^1$	120,85	120,22	0,195	0,193
$\angle H^5 C^2 H^4$	119,09	119,67	0,205	0,205
$\angle H^6 C^2 H^4$	119,09	119,67	0,205	0,205

corresponds to a minimum (instead of a transition state) with respect to torsions around the $P^2 - N^2$ bond, if the torsional potential terms are included in the energy expression.

Results and discussion

The results of a relaxed scan around the $N^2 - P^3$ bond with the force field with torsional potential energy terms, and the ab initio molecular orbital calculations are shown in Figs. 7–9. The force field calculations reproduce the torsional potential of the $N^2 - P^3$ bond well for torsional motions within $\pm 100^\circ$ of the planar *trans-cis* conformation. The force field over-estimates the torsional barrier by approximately 0,8 kcal/mol, and predicts that the eclipsed conformation is a transition state (with

Fig. 7. Relaxed scan around the $N^2 - P^3$ bond (angle in degree) with the force field. The filled symbols refer to results of the ab initio molecular orbital calculations

Fig. 8. Change in the $P^2N^2P^3$ bond angle during a relaxed scan around the $N^2 - P^3$ bond with the force field. The filled symbols refer to results of the ab initio molecular orbital calculations. Angles are given in degree

respect to a rotation around the $N^2 - P^3$ bond) instead of a local minimum of the PES. The variation of the $P^2N^2P^3$ bond angle and the $N^1P^2 - N^2P^3$ dihedral angle during a rotation around the $N^2 - P^3$ bond are in excellent agreement with the results of the ab initio molecular orbital calculations.

Fig. 9. Change in the $N^1P^2 - N^2P^3$ dihedral angle during a relaxed scan around the $N^2 - P^3$ bond with the force field. The filled symbols refer to results of the ab initio molecular orbital calculations. Angles are given in degree

Further developments and improvements of the force field should take its future applications into account. The force field which is introduced in the previous section focuses on the ability to reproduce ab initio results on stable conformations and relaxed scans around the central P—N bond in a dichlorophosphazene trimer. In order to achieve a good agreement between force field and ab initio results for conformers which form during a rotation, the torsional potential terms were introduced. The torsional potential terms improve the performance of the force field in the vicinity of the conformations which were studied with the ab initio technique. This emphasizes that previous ab initio studies of the regions of the PES which are investigated with the force field are essential for obtaining reliable results with the force field technique. Since the torsional potentials which were studied with the ab initio technique and bond-stretch and angle bend force constants are largely determined by the immediate molecular environment of a bond²³, the parameterization for the trimer can be extended to a parameterization for larger molecules.

This force field is well-suited to study main chain motions of larger molecules for which the conformation of a local chain segment remains close to the stable conformation (e.g. one could consider a 'twist' motion of a chain which is created by concerted small variations of dihedral angles)^{30,31}. In addition, it is well-suited for studying motions which involve full rotations around main chain bonds (e.g. crankshaft-type motions)^{32,33}.

However, one should proceed with caution if this force field is used for conformational studies of molecular geometries which are far away from the conformations which were studied with the ab initio technique. The calculation of conformational entropies can be problematic as it involves extensive scans of the PES^{4,5}.

A first step in order to extend the reliability of the force field is to investigate the physical and/or chemical origins of the torsional potential terms (5). The following approximations which were used to develop the force field can provide an explanation for the torsional potential terms:

(a) The electrostatic interaction of electrons and nuclei is approximated by the electrostatic interaction of nuclear centered point charges (i.e., we only consider the interaction of electrostatic monopoles). A more accurate description of the electrostatic interaction would include higher multipole moments.

(b) Throughout the whole rotation of a part of the molecule around a bond, we use partial atomic charges which were derived from the ground state conformation. We therefore neglect the polarizability of the charge distribution. A rigid rotor scan (RHF/6-31+G*) showed that the NPA partial atomic charges of the substituents vary only slightly (up to 6%) during torsional motion. The polarizability of the charge distribution will most likely lead to the variations in higher multipole moments during a rotation. The polarizability of selected regions of the molecular electron density (e.g. the polarizability of an 'electron cloud' in the vicinity of a substituent) can be studied by investigating changes in higher multipole moments during a torsion.

Nuclear centered multipole moments can be determined from ab initio results by the 'distributed multipole analysis'³⁴⁾ or by a least squares fit of the electrostatic potential of the molecule with a multipole expansion³⁵⁾.

(c) Previous studies suggest that the bond structure of a P—N bond results in no intrinsic barrier to rotation (due to a $p_\pi(\text{N}) - d_\pi(\text{P})$ overlap)³⁶⁾. An imperfect $p_\pi(\text{N}) - d_\pi(\text{P})$ overlap can lead to an intrinsic barrier to rotation around the P—N bonds. Although we were able to fit the results of the rigid rotor scan around a single bond entirely with the electrostatic and the van der Waals interaction (see Fig. 6), we can not rule out that the torsional barriers include small contributions from intrinsic barriers to rotation.

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