



# Molecular structure, linear and nonlinear optical properties of some cyclic phosphazenes: A theoretical investigation



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## ABSTRACT

We report *ab initio* and density functional theory calculations of structural data, dipole moment, diagonal vibrational and electronic contributions to polarizability, vibrational and electronic contributions to first hyperpolarizability of some cyclic phosphazenes. The electronic structure of substituted cyclic phosphazenes has been investigated using Hartree-Fock and density functional theory. The vibrational and electronic contributions to polarizabilities and first hyperpolarizability of these molecules were calculated with HF method, and different DFT levels used the traditional B3LYP and PBE functional and the long-range corrected functional like Coulomb-attenuating method CAM-B3LYP, LC-BLYP and wB97XD used different basis sets. These cyclic phosphazenes adopts a planar structure. The chosen level of theory was found to describe satisfactory the molecular structure (r. m. s. of the relative deviations). The study reveals that the cyclic phosphazenes derivatives have large vibrational contribution to static first hyperpolarizability values. The results obtained from this work will provide into the electronic properties of this important class of inorganic polymers.

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## 1. Introduction

Cyclic phosphazene are inorganic compound with the formula  $(\text{NPX}_2)_n$  with  $n = 3$  and  $X = \text{H, Br, Cl}$  and  $\text{F}$ . These molecules have a cyclic backbone consisting of alternating phosphorus and nitrogen atoms. The chemistry of the phosphazenes goes back to 1834 when Liebig and Wöhler isolated a small of an unidentified crystalline product from the reaction of ammonia and phosphorus pentachloride [1]. The first phosphazene which was synthesized and isolated, was  $(\text{NPCI}_2)_3$  [2]. In 1895, Stokes suggested a cyclic structure for this compound [3]. The cyclic phosphazenes are of interest to both theoretical and experimental chemists. For example, a new class of thermo-sensitive cyclotriphosphazenes has been synthesized recently by stepwise substitution of hexachlorocyclotriphosphazene  $(\text{NPCI}_2)_3$  [4], with alkoxy poly (ethylene glycol) and amino acid esters. Phosphazenes materials have interesting properties, for example, they exhibit fire-retardant

properties, have high refractive indices, and might find application in nonlinear optics, as ferro-electric materials, as liquid crystals or as photoactive materials [5–11]. They also possess a number of characteristics such as biomedical properties and applications due to their strong antitumor activity. Magnetic properties for the new complexes are prepared in one step functionalization; coordination used cyclic phosphazene  $\text{N}_3\text{P}_3\text{Cl}_6$  by Spodine et al. [12]. Biologically; important substrates such as anti-cancer agents, insect chemosterilants, pesticides, fertilizers, and supports for catalysts, dyes, and crown ether-phase transfer catalysts for nucleophilic substitution reactions. Application for cyclic and polymeric phosphazene as solid state template for the formation of  $\text{RuO}_2$  nanoparticles such as the work of Spodine et al. [13], and in application of Boratophosphazene like synthesis of Borazine-phosphazene hybrid cations such as the work of Rheingold et al. [14].

For some systems and processes the vibrational properties are even more important than the corresponding electronic ones, together both contributions govern nonlinear optical NLO behavior. A large number of the vibrational calculations have preceded with theoretical calculation like HF [15,16] DFT [17] and MP2 [18] last years.

In this work the aim was to compare structural theoretical

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calculation with the experimental data of these cyclic phosphazenes, and was to calculate linear and nonlinear optical properties used different level of theories such us Hartree-Fock and density functional theory. Reasonably-sized basis sets are used which are already known to give ‘high quality’ polarizabilities for molecules under gas-phase conditions. In this contribution we summarize selected electric properties, mostly dipole moment, static dipole polarizabilities and hyperpolarizabilities for these molecules. Results are compared to similar molecules whenever appropriate.

## 2. Computational details

In this section we will present only brief description of the calculation methods used to calculate electronic and vibrational contributions to static polarizability and electronic and vibrational contributions to static first hyperpolarizabilities for these cyclic phosphazene (Fig. 1, Fig. 2). The reader unfamiliar with the applied methods may refer to the vast literature on the subject. Analytical calculation of electrical properties are not carry out in this work, Interested on the static properties.

In the presence of a uniform electric field, the total energy of molecule can be expressed as a Taylor series:

$$E(F) = E(0) - \mu_i F_i - \frac{1}{2!} \alpha_{ij} F_i F_j - \frac{1}{3!} \beta_{ijk} F_i F_j F_k - \frac{1}{2!} \gamma_{ijkl} F_i F_j F_k F_l \dots \quad (1)$$

$\mu$ ,  $\alpha$ , and  $\beta$  are dipole moment, polarizability, and first to nth order hyperpolarizability, respectively.

Equation (1) is used for calculations of electric dipole (hyper) polarizabilities. Within the Born Oppenheimer approximation and, for a non-rotating and non-translating molecule, the hyperpolarizability can be split into electronic and vibrational contributions, a number of research groups have focused their attention recently on the evaluation of vibrational hyperpolarizabilities [19].

$$P = P^{ele} + P^{vib} \quad (2)$$

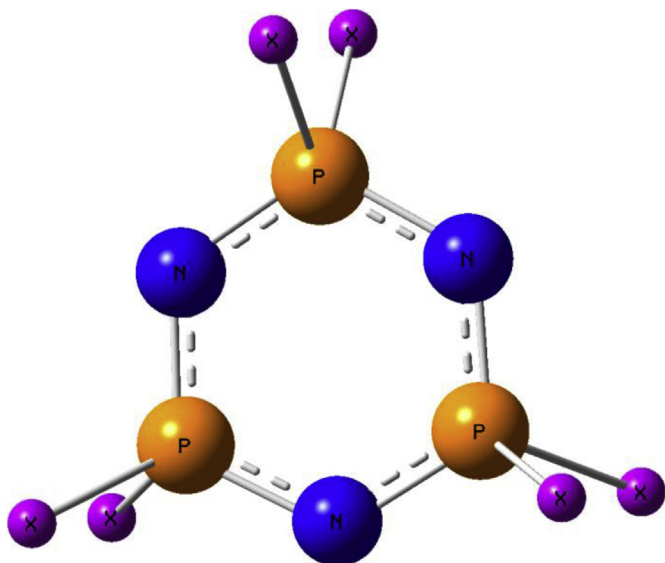


Fig. 1. Chemical structure of cyclic phosphazenes  $(NPX_2)_n$  with  $n = 3$  and  $X = H, Br, Cl$  and  $F$  studies in this work.

### 2.1. Electronic diagonal polarizabilities and electronic static first hyperpolarizabilities

For the calculation of electronic contributions to static first hyperpolarizabilities, we followed the procedure outlined by Kurtz et al. [20,21] and used equation (1) for numerical differentiation of the total energy of the molecular system with respect to the electric field. Our calculations were performed using *ab initio* and density functional theory (DFT) methods. The performances of traditional and novel long-range corrected DFT levels were explored. Long-range corrected DFT functionals can be competitive to traditional DFT functionals and *ab initio* methods to calculate linear and nonlinear response electric properties, owing to accuracy and minor computational demand. Indeed, recent studies have demonstrated that long-range corrected DFT methods are largely superior to traditional functionals, with results comparable to *ab initio* levels in predicting (hyper) polarizabilities [22–30]. In the case of orientationally invariant hyperpolarizabilities [31],

$$\bar{\alpha} = \frac{1}{3} \sum_{i=x,y,z} \alpha_{ii} \quad (3)$$

$$\bar{\beta} = \sum_{i=x,t,z} \frac{\mu_i \beta_i}{|\mu|} \quad (4)$$

where

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jjj} + \beta_{jji}) \quad (5)$$

and static first hyperpolarizabilities  $\langle \beta \rangle$  can be computed as

$$\langle \beta \rangle = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (6)$$

The value of the field amplitude (equal to 0.001 a.u) was assumed. In the case of diagonal tensor elements; the Romberg differentiation procedure was employed [32]. The Romberg procedure was also used to remove the higher order hyperpolarizability contaminations.

The diagonal components were determined according to equation (5) from second-order derivatives of the energy with respect to the relevant components of the field, using a second-order polynomial least square shift over energies obtained after embedding the target of interest in homogenous electric fields in the  $x$ ,  $y$  and  $z$  directions.

### 2.2. Diagonal vibrational polarizabilities and vibrational first hyperpolarizabilities

The mean polarizabilities value  $\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$  is usually determined from the refractive index or from dielectric measurements [33], while vibrational polarizabilities  $\alpha_v$  can be obtained from infrared intensities [34,35]. In this work, the vibrational contribution  $\alpha_v$  to be evaluated under the double harmonic oscillator approximation with the sum-over-modes expression [36].

$$\alpha_{ij}^v = \sum_a \frac{3N-6}{\omega_a^2} \left( \frac{\partial \mu_i}{\partial Q_a} \right)_0 \left( \frac{\partial \mu_j}{\partial Q_a} \right)_0 \quad (7)$$

where  $\omega_a$  is the circular vibrational frequency of the  $n^{\text{th}}$  normal mode  $Q_a$  and  $\frac{\partial \mu_i}{\partial Q_a}$  is the partial derivative of the  $i$ -component of  $\mu$

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