Structural Data, Linear and Nonlinear Optical Properties of Some Cyclic Phosphazenes: A Theoretical Investigation

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Abstract: We report *ab initio* and DFT calculation 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 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.

Keywords: Mean polarizability, polarizability anisotropy, vibrational and electronic polarizability, vibrational and electronic first hyperpolarizability.

1. INTRODUCTION

Cyclicphosphazene studies in this paper are inorganic compound with the formula $(NPX_2)_n$ with n=3 and X=H, Br, Cl and 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 $(NPCl_2)_3$ [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 first synthesized recently by stepwise substitution of hexachlorocyclotriphosphazene $(NPCl_2)_3$ [4], with alkoxypoly (ethyleneglycol) and amino acid esters. Phosphazenes materials with 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 $N_3P_3Cl_6$ 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 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 electronic and 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 proceeded with theoretical calculation like HF [15, 16], DFT [17] and MP2 [18] last years.

The chemical structure of these cyclic phosphazenes studies in this work are showed in (Figure **1**).

2. COMPUTATIONAL DETAILS AND METHODS

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. The reader unfamiliar with the applied methods may refer to the vast literature on the

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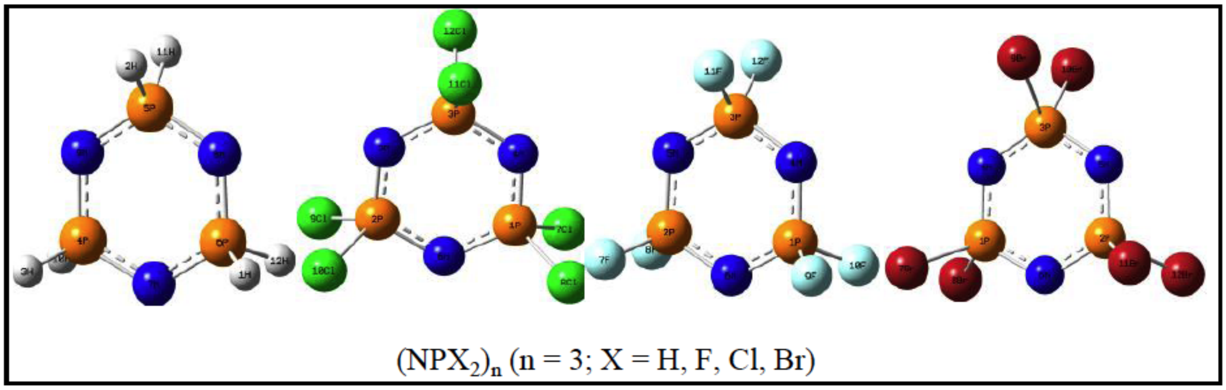

Figure 1: Chemical structure of these cyclic phosphazenes studies in this work.

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:

$$E(F) = E(0) - \mu_i F_i - \frac{1}{2!}\alpha_{ij}F_iF_j - \frac{1}{3!}\beta_{ijk}F_iF_jF_k - \frac{1}{4!}\gamma_{ijkl}F_iF_jF_kF_l \dots \tag{1}$$

μ, α, and β dipole moment, polarizability, and first to nth order hyperpolarizability, respectively.

Equation (1) 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].

$$P = P^{ele} + P^{vib} \tag{2}$$

2.1. Electronic Diagonal Polarizabilities and Electronic Static First Hyperpolarizabilities

For the calculation of electronic contributions to static firs thyperpolarizabilities, 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],

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

$$\bar{\beta} = \sum_{i=x,y,z}\frac{\mu_i\beta_i}{|\mu|} \tag{4}$$

where

$$\beta_i = \frac{1}{5}\sum_{j=x,y,z}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \tag{5}$$

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 α_v can be obtained from infrared intensities [34, 35]. In this work, the vibrational contribution α to be evaluated under the double harmonic oscillator approximation with the sum-over-modes expression [36].

$$\alpha^{v}_{ij} = \sum_{a}^{3N-6} \frac{\left(\frac{\partial\mu_i}{\partial Q_a}\right)_0 \left(\frac{\partial\mu_j}{\partial Q_a}\right)_0}{\omega_a^2} \qquad (6)$$

Where ω_a is the circular vibrational frequency of the n^{th} normal mode Q_a and $\frac{\partial\mu_i}{\partial Q_a}$ is the partial derivative of the i-component of μ with respect to Q_a evaluated at the equilibrium geometry.

A perturbation treatment of dynamic vibrational hyperpolarizabilities has been given by Bishop and Kirtman (BK) [37, 38]. This treatment is based on the general sum-over-states (SOS) formulas [39] for the total hyperpolarizability given in terms of vibronic energies and dipole moment matrix elements. Then the vibrational and electronic contributions are separated by applying a canonical or clamped nucleus approximation [40].

The vibrational first hyperpolarizability:

$$\beta^{v}_{ijk} = [\mu\alpha]^{0,0} =$$
$$\sum_{\xi}\left(\frac{1}{\omega_\xi^2}\right)\left[\left(\frac{\partial\mu_i}{\partial Q_\xi}\right)_0\left(\frac{\partial\alpha_{jk}}{\partial Q_\xi}\right)_0 + \left(\frac{\partial\mu_j}{\partial Q_\xi}\right)_0 + \left(\frac{\partial\mu_k}{\partial Q_\xi}\right)_0\left(\frac{\partial\alpha_{ij}}{\partial Q_\xi}\right)_0\right] \qquad (7)$$

Where Q_ζ denotes ζ^{th} normal vibrational coordinate of frequency ω_ζ, and $\frac{\partial\mu_i}{\partial Q_\xi}$ and $\frac{\partial\alpha_{jk}}{\partial Q_\xi}$ are the derivatives of the molecular dipole moment and polarizability with respect to normal coordinate Q_ξ respectively. Indices i, j, and k denote Cartesian coordinates. The sum in Eq. (7) extends over all normal modes of vibration.

In the present study, the vibrational contributions are evaluated using the double harmonic model. All calculations were performed with the quantum chemical program package Gaussian 09 [41]. The data analyses were performed with Gauss View 5.08 [42]. In order to find the optimized molecular geometry, the DFT/CAM-B3LYP [43] level geometry optimization were performed with the 6-311++G** basis set. No imaginary frequencies were obtained in vibrational frequencies calculation and thus confirm the equilibrium geometries that correspond to energy minima. Our results are checked with experimental results where available. Electronic and vibrational polarizability, electronic and vibrational contributions to first hyperpolarizability computations are carried out at a variety of DFT level [44, 45]. We investigate the traditional B3LYP [46, 47] and PBE [48] functional as well as the long-range corrected CAM-B3LYP, LC-BLYP [49] and wB97XD [50] functional, it is now well recognized that the electron correlation (EC) may strongly influence the values of electronic and vibrational contributions to hyperpolarizabilities [51-55].

3. RESULTS AND DISCUSSION

3.1. Structural Data

All structural results obtained for the systems under study, at HF, PBE and CAM-B3LYP levels of theory with the same basis sets 6-31G* and 6-31++G* are illustrated in Table **1**.

The PN bond in $(PNH_2)_3$ is 1.608Å at CAM-B3LYP/6-31++G*, 1.630Å at PBE/6-31++G* and 1.595Å at HF/6-31++G*. This bond is shorter than the one in the $NH_2\text{-}PO_3^{-2}$ ion (1.77Å) which corresponds to a simple PN bond [56]. Sabzyan *et al*. have reported the same results of PN bonds with 1.615Å at DFT/B3PW91 and 1.618Å at DFT/B3LYP calculation with the same basis set [57]. There are differences in the crystal data reported in the literature; the PN bond lengths vary from 1.48Å to 1.58Å [58]. These variations may be attributed to packing effects and uncertainty in the X-ray diffraction measurements.

The obtained results shown in Table **1** for $(PNH_2)_3$ at PBE level agree with those of CAM-B3LYP with errors varying between 0.02Å and 0.021Å with the same basis sets 6-31g* and 6-31g++*.

The PN bond length in HF level as compared to DFT level (1.594Å, 1.629Å) because the HF level which does not take into account the electronic correlation. With maximum size 0.001Å to 0.002Å; diffused basis set have negligible effects on the optimized structural parameters, but there is enormous effect of improper (not sufficiently large) basis set on the optimized values of structural parameters obtained for $(PNH_2)_3$ compounds using DFT with the functional PBE and CAM-B3LYP.

In this series of cyclic phosphazenes $(NPX_2)_3$ with X = H, Br, Cl and F, all identical PN bonds lengths obtained is a sign of aromaticity in this compounds.

Table 1: Structural Data of Cyclic Phosphazenes $(NPX_2)_n$ (n = 3; X = H, F, Cl and Br) from HF, PBE and CAM-B3LYP Calculations Used 6-31g* and 6-31++g* Basis Sets; Comparison with Semiempirical and Experimental Result

Parameter	AM1[c]	HF		PBE		CAM-B3LYP		Exp
		6-31g*	6-31++g*	6-31g*	6-31++g*	6-31g*	6-31++g*	
$(PNH_2)_3$								
P-N	1.497	1.59	1.595	1.629	1.630 1.615[a]	1.606	1.608 1.617[b]	
P-H	1.288	1.390	1.389	1.428 1.424[i]	1.427 1.413[a]	1.409	1.407 1.413[b]	
∠ P-N-P	134.6	123.4	123.6	119.7	120.0 121.5[a]	122.1	122.3 121.5[b]	
∠ N-P-N	105.7	116.5	116.3	120.2	119.9 118.9[a]	117.8	117.6 118.9[b]	
∠ H-N-H	97.8	101.2	101.7	100.3	101.1 101.3[a]	100.8	101.5 101.3[b]	
$(PNF_2)_3$								
P-N	1.510	1.563	1.565	1.600	1.602 1.589[a]	1.577	1.560 1.588[b]	1.57[d] 1.570[e]
P-F	1.544	1.532	1.533	1.579	1.586 1.570[a]	1.554	1.579 1.566[b]	1.52[d] 1.529[e]
∠ P-N-P	135.5	123.4	122.9	120.0	119.4 121.0[a]	122.1	121.7 120.7[b]	121.1[d] 120.4[e]
∠ N-P-N	104.6	116.5	117.0	119.9	120.5 119.0[a]	117.8	118.2 119.3[b]	119.5[d] 119.6[e]
∠ F-P-F	94.5	98.6	98.4	98.2	97.8 98.0[a]	98.5	98.1 98.0[b]	99.9[d] 99.1[e]
$(PNCl_2)_3$								
P-N	1.490	1.576	1.576	1.615	1.615 1.602[a]	1.590	1.590 1.598[b]	1.581[d] 1.65[f] 1.58[g]
P-Cl	1.944	1.999	2.000	2.041	2.041 2.038[a]	2.017	2.017 2.023[b]	1.993[d] 1.97[f] 1.99[g]
∠ P-N-P	134.6	123.7	123.7	120.1	120.1 121.7[a]	122.4	122.5 121.4[b]	121.4[d] 121.4[g]
∠ N-P-N	105.5	116.2	116.2	119.8	119.8 118.2[a]	117.5	117.4 118.6[b]	118.4[d] 118.4[h]
∠ Cl-P-Cl	102.6	102.7	102.5	102.2	102.0 102.1[a]	102.4	102.2 102.1[b]	101.4[d] 107.1[f] 101.4[g]
$(PNBr_2)_3$								
P-N		1.579	1.578	1.619	1.619 1.606[a]	1.593	1.593 1.602[b]	1.58[h] 1.576[j]
P-Br		2.173	2.175	2.207	2.209 2.209[a]	2.184	2.186 2.190[b]	2.162[j]
∠ P-N-P		123.8	123.2	120.3	119.6 121.3[a]	122.6	122.0 120.9[b]	126.8[h] 120.9[j]
∠ N-P-N		116.1	116.7	119.6	120.3 118.7[a]	117.3	117.9 119.1[b]	117[h] 118.5[j]
∠ Br-P-Br		103.2	103.6	102.5	103.2 102.6[a]	102.6	103.3 102.7[b]	102.0[h] 102.1[j]

[a,b] [57] B3PW91and B3LYP calculation.

[c] [62] AM1 calculation.

[d] [75] X ray data.

[e] [76] Electron diffraction.

[f] [71] Electron diffraction.

[g] [72] X ray data.

[h] [73, 74] X ray data.

[i] [60] B3LYP/6-31++G* for linear phosphazene.

[j] [77] X ray data.

Used Quantum chemical calculations in order to find the effect of substitution halogens atoms in PN bonds; Abdellatif *et al*. [60] have reported that the PN bond lengths in short linear phosphazenes decrease with increasing the electronegativity of (R_3PNH, R_3PNF and R_3PNOH with R=H, F). Sabzyan *et al*. have reported that the PN bond lengths in the cyclic phosphazenes decrease with increasing the electronegativity of the halogen substituent on the phosphorus atom [57]. Our calculation led to the following results: the PN bond is 1.608Å in $(PNH_2)_3$, 1.593Å in $(PNBr_2)_3$, 1.590Å in $(PNCl_2)_3$, and 1.560Å in $(PNF_2)_3$ used the CAMB3LYP/ 6-31++G* calculation; so similar results are obtained in this work.

In 1998, Sun used the COMPASS force field (condensed-phase optimized *ab initio* force field) [59] with *ab initio* RHF and density functional methods used, 6-31G* basis sets, showed the PN and PX bond lengths and ∠X-N-X angle in cyclic phosphazenes are shortened with increasing the electronegativity of the halogen atom substituted on the phosphorus atom.

The ∠P-N-P angle in $(PNH_2)_3$ is 122.3° at CAM-B3LYP/6-31++G*, 120.0° at PBE/6-31++G* and 121.7° at HF/6-31++G*, when the hydrogen atom is substituted with the halogens atoms Br, Cl and F, the ∠ P-N-P angle at CAM-B3LYP with the same basis set is 122.0°, 122.5° and 121.7° respectively, so the Fluor atom was important effect on the ∠P-N-P angle.

Trinquier using a standard *ab initio* method with the DZP basis set [61] in order to find stability and bonding in cyclotriphosphazene, Castro *et al*. [62] in 2002 used the semi empirical approach AM1 [63] and PM3 [64] to determine these structural properties, also, employing quantum computational, Sabzyan *et al*. in 2003 [57] are reported molecular structure and bonding, thermochemical stability, vibrational and NMR spectra of cyclic phosphazenes $(NPX_2)_3$, theses results of structural investigation show that all of these phosphazenes have planar structures. The remarkable discrepancies among theoretical values and available experimental data do not allow to state definite conclusions.

Table 2: Comparison of Diagonal Electronic and Vibrational Contributions to Static Polarizability Evaluated Atvarious Levels of Theory. Basis Set: 6-311++G. The Values are Given in Atomic Units**

		Vibrational			Electronic			$\alpha_{xx}^{e} / \alpha_{xx}^{v}$
		α_{xx}^{v}	α_{yy}^{v}	α_{zz}^{v}	α_{xx}^{e}	α_{yy}^{e}	α_{zz}^{e}	
$(PNH_2)_3$	HF	63.75	63.71	31.56	68.44	68.43	51.90	1.07
	PBE	30.36	30.34	34.99	76.87	76.86	54.69	2.53
	B3LYP	30.35	30.33	43.90	76.77	76.76	54.58	2.52
	CAM-B3LYP	30.26	30.24	33.64	76.62	76.62	54.28	2.53
	LC-BLYP	29.11	29.08	31.90	75.11	75.11	53.75	2.58
	wB97XD	28.97	28.97	30.78	74.00	74.02	52.87	2.55
$(PNBr_2)_3$	HF	70.11	79.22	79.30	80.25	64.32	64.21	1.14
	PBE	44.72	58.70	58.70	191.66	177.47	177.46	4.28
	B3LYP	44.62	58.59	58.59	191.52	177.32	177.34	4.92
	CAM-B3LYP	44.01	58.46	58.42	190.64	175.94	177.01	4.33
	LC-BLYP	43.23	57.37	57.36	190.00	174.11	176.43	4.39
	wB97XD	42.87	56.32	56.32	189.44	174.08	175.77	4.41
$(PNCl_2)_3$	HF	55.22	65.32	67.98	123.70	115.04	115.04	2.24
	PBE	43.01	56.98	57.05	134.09	131.05	131.58	3.11
	B3LYP	42.89	56.88	56.89	134.00	130.88	131.44	3.12
	CAM-B3LYP	42.55	56.88	56.86	133.97	130.74	130.74	3.14
	LC-BLYP	41.87	55.56	55.56	132.65	130.00	130.01	3.16
	wB97XD	40.98	54.89	54.87	132.01	129.13	129.16	3.22
$(PNF_2)_3$	HF	44.01	43.99	26.47	59.27	59.26	43.75	1.34
	PBE	33.22	30.14	18.22	75.25	75.22	69.14	2.26
	B3LYP	33.12	30.01	18.11	75.12	75.09	69.01	2.26
	CAM-B3LYP	32.29	31.32	19.32	74.25	74.00	68.04	2.29
	LC-BLYP	31.78	30.60	18.45	73.22	73.33	67.65	2.30
	wB97XD	30.45	30.01	18.01	72.21	72.87	66.11	2.37

It is apparent that our calculation at DFT is agreed with the experimental (X-ray) data and other theoretical study such as Breza *et al*. [65] and Sabzyan *et al*. [57] for this cyclic phosphazenes, and better agreement between the calculated results CAM-B3LYP and the X-ray data for the chloro-substituted cyclo-phosphazenes. The usual D_3h symmetry planar arrangement of the $(NPX_2)_3$ represents a stable structure at all levels of theory. Schulz *et al*. found the same results of the cyclic phosphazene $(NPCl_2)$ [66]. 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 [67].

3.2. Electronic and Vibrational Polarizability, Mean Polarizability and Polarizability Anisotropy

The systems that are the subject of the present investigation are given in (Figure **1**). The results presented in Table **2** are the essential basis for the further discussion on the effect of electronic and vibrational contributions to nonlinear optical properties.

The results shown in Table **2**, Figures **2** and **3** presents electronic and vibrational contributions to static polarizability for all investigated compounds, the values of the polarizabilities (α) of Gaussian 09 output are reported in atomic units (au).

Used the traditional B3LYP and PBE functionals and the long-range corrected functional like Coulomb-attenuating method CAM-B3LYP, LC-BLYP and wB97XD introduces a part of electron correlation through the use of an exchange correlation term in the energy expression, with small additional cost in the computational procedure and compared to HF observed for standard methods. The calculations show that the substitution effect of electronic correlation on α value is observed solely for the electronic counterpart; the change in the vibrational contributions to polarizability upon inclusion of electronic correlation is significant. The obtained DFT results are virtually unaffected by the change of the traditional functional PBE and B3LYP and with small error with the long-range corrected functional CAM-B3LYP, LC-BLYP and wB97XD.

The ratio between the vibrational and electronic contributions $\alpha_{xx}^{v}/\alpha_{xx}^{e}$ might depend crucially on the applied level of theory; these results are confirmed by Sucarrat *et al*. [68] and other studies for conjugated organic molecules [69].

The mean polarizability was calculated from the polarizability components as [70]:

$$\langle\alpha\rangle = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (8)$$

And the polarizability anisotropy as:

$$|\Delta\alpha| = \sqrt{\frac{1}{2}\left[\left((\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{xx}-\alpha_{zz})^2 + (\alpha_{yy}-\alpha_{zz})^2\right)\right]} \quad (9)$$

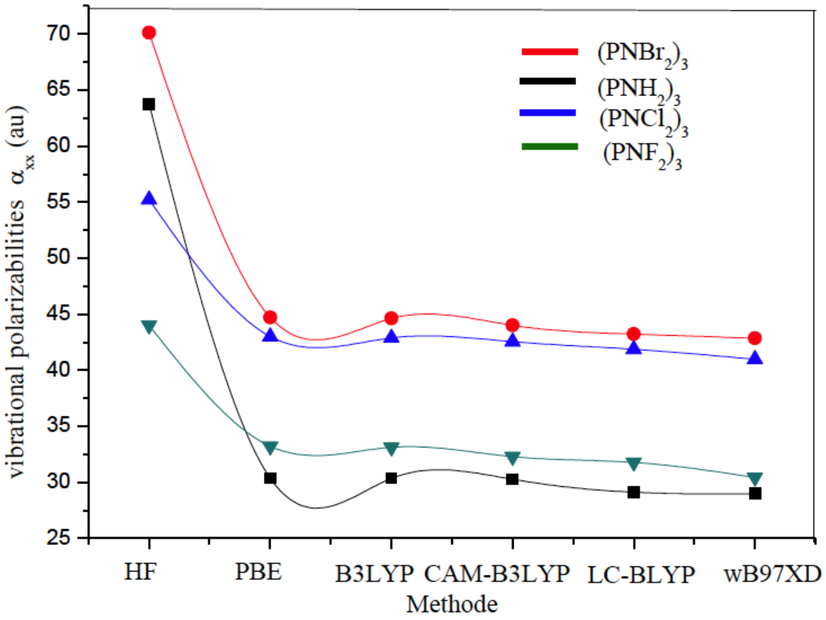

Figure 2: Vibrational contributions to static polarizability α_{xx}^{v} evaluated at various levels of theory used 6-311++G** basis set. The values are given in atomic units.

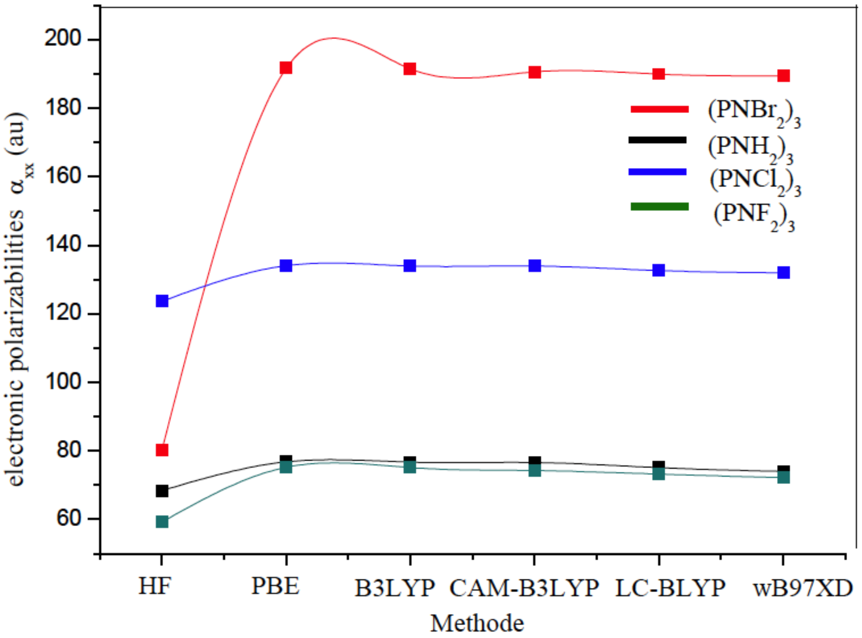

Figure 3: Electronic contributions to static polarizability α^{e}_{xx} evaluated at various levels of theory used 6-311++G** basis set. The values are given in atomic units.

Table 3: Basis Set Effects on PBE Vibrational Polarizability Responses, the Mean Polarizability and The polarizability Anisotropy of $(PNF_2)_3$. The (α) Values are given in Atomic Units (1 a.u =1.6488×10^{-41}C^{2}m^{2}J^{-1}=0.14818Å^3)

Basis set	α^{v}_{xx}	α^{v}_{yy}	α^{v}_{zz}	$\langle\alpha\rangle$	$\lvert\Delta\alpha\rvert$
6-31G	83.64	83.04	40.62	69.1	42.72
6-31G*	39.79	39.79	22.93	34.17	16.85
6-31+G	72.71	72.52	42.65	62.62	29.96
6-31+G*	41.59	41.59	24.30	35.82	17.29
6-311G	62.12	61.97	35.30	53.13	26.74
6-311G*	43.60	43.57	25.97	37.71	17.61
6-311+G*	43.42	43.39	25.66	37.49	17.73
cc-pVDZ	44.01	44.62	26.27	38.04	18.25
cc-pVTZ	44.26	44.92	26.87	38.45	19.00
Aug-cc-pVDZ	45.11	45.17	27.05	38.87	19.22

In Table **3** and Figure **4**, the polarizability components, mean polarizability and the polarizability anisotropy have been presented.

To avoid possible systematic errors in the computation of the linear optical properties, we used two basis set families of different construction as implemented in GAUSSIAN 09. The first family comprises the correlation consistent cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets, and the second one is built upon the 6-31G and 6-311G substrates, by systematically adding standard diffuse and polarization Gaussian type functions. All geometries were optimized before calculation of vibrational contributions to polarizability response α_{xx}, α_{yy} and α_{zz} mean polarizability $\langle\alpha\rangle$ and the polarizability anisotropy $\lvert\Delta\alpha\rvert$. We examined the basis set effects at PBE levels that are the least computationally demanding among the DFT levels we used.

Depending on the basis set choice, the mean polarizability varies from 69.1 (6-31G basis set) to 37.49 au (6-311++G*) at the same PBE level. These sorts of variations reveal a rather small and larger basis set effect on this property. No dramatic changes on the computed values of mean polarizability and the polarizability anisotropy $\lvert\Delta\alpha\rvert$ are noted if we used the

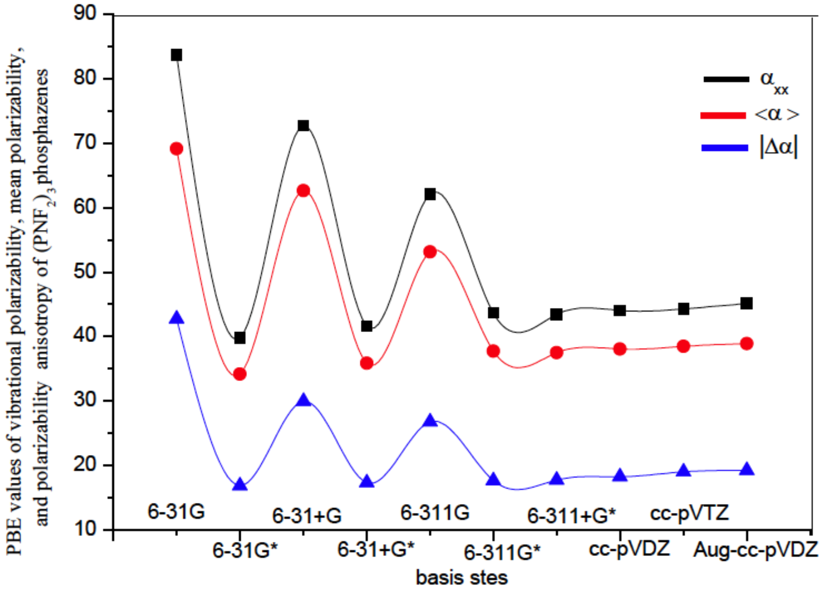

Figure 4: Basis set effects on PBE vibrational polarizability responses, the mean polarizability and the polarizability anisotropy of $(PNF_2)_3$ phosphazenes. The (α) values are given in atomic units.

correlation consistent cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets.

The results shows that for all properties; there is a good correlation between the largest extension basis sets like 6-311G*, 6-311+G*, cc-pVDZ, cc-pVTZ and Aug-cc-pVDZ. The addition of p-polarization functions tends to increase in the $\langle\alpha\rangle$ mean polarizability, and the same statement for the polarizability anisotropy. Going from double-ζ to a triple-ζ leads to smaller increase in all properties.

3.3. Dipole Moment, Electronic and Vibrational Contributions to First Hyperpolarizability

Table **4** summarizes dipole moment, electronic and vibrational contributions to first-order hyperpolarizability calculated at HF, PBE, B3LYP, CAM-B3LYP, LC-BLYP, and wB97XD levels for the geometry optimized at the CAM-B3LYP/6-311++G (d, p) level of theory. The results shows that when passing from traditional functional PBE and B3LYP to long-range corrected functional CAM-B3LYP, LC-BLYP and wB97XD calculation of electronic and vibrational contribution to first hyperpolarizabilities, only marginal effects are observed. In fact, the high symmetry of all structures $(PNH_2)_3$, $(PNBr_2)_3$, $(PNCl_2)_3$ and $(PNF_2)_3$, which present a planar cyclic arrangement, with rather small deviations from perfect planarity. This property is clearly revealed by the zero or nearly null dipole moment and null first hyperpolarizabilities calculated at *ab initio* (HF) and DFT levels for all the molecules.

4. CONCLUSIONS

In this study, we investigate structural data, *ab initio*, and DFT calculation of electronic and vibrational contribution to polarizabilities, the mean polarizability, the polarizability anisotropy, electronic and vibrational contributions to first hyperpolarizabilities of cyclic phosphazenes $(PNX_2)_3$ with n=3 and X= H, Br, Cl and F. We showed that, these numerical simulations obtaining reliable information on the geometrical structure and the substitution effect on the electronic and vibrational nonlinear optical NLO properties. In this series of cyclic phosphazenes $(NPX_2)_3$ with X= H, Br, Cl and F, all identical PN bonds lengths obtained is a sign of aromaticity in this compounds. The obtained structural data results in this paper agree with other theoretical calculation, and experimental data.

This study for this cyclic phosphazenes compounds $(NPX_2)_3$ on the basis set effect and the inclusion of electron correlation, by going from the Hartree-Fock to the DFT (PBE, B3LYP, CAM-B3LYP, LC-BLYP, and wB97XD levels), leads to largest variations of vibrational and electronic contributions to polarizability. Only marginal effects are observed when passing from the traditional functional PBE and B3LYP to long-range corrected functional CAM-B3LYP, LC-BLYP and wB97XD for calculation of linear and nonlinear optical properties of this cyclic phosphazenes.

We present an accurate investigation of the NLO properties of a series of phosphazene, focusing on the relationships between dipole moment, first

Table 4: Dipole Moment (D), Electronic and Vibrational Contributions to First-Order Hyperpolarizability Calculated for the Geometry Optimized at the CAM-B3LYP/6-311++G (d, p) Level of Theory. The Values are Given in Atomic Units

		Dipole moment	β Vibrational			β Electronic		
			β^{v}_{xxx}	β^{v}_{yyy}	β^{v}_{zzz}	β^{e}_{xxx}	β^{e}_{yyy}	β^{e}_{zzz}
$(PNH_2)_3$	HF	0.001	0.05	0.05	0.05	0.01	0.01	0.01
	PBE	0.000	0.03	0.03	0.03	0.03	0.01	0.01
	B3LYP	0.001	0.00	0.00	0.00	0.00	0.00	0.01
	CAM-B3LYP	0.000	0.03	0.03	0.03	0.03	0.01	0.01
	LC-BLYP	0.001	0.02	0.02	0.02	0.02	0.01	0.00
	wB97XD	0.001	0.01	0.01	0.01	0.01	0.01	0.00
$(PNBr_2)_3$	HF	0.001	0.01	0.05	0.00	0.01	0.00	.000
	PBE	0.000	0.03	0.03	0.00	0.03	0.01	0.01
	B3LYP	0.001	0.02	0.00	0.00	0.00	0.01	0.01
	CAM-B3LYP	0.000	0.03	0.03	0.00	0.03	0.01	0.01
	LC-BLYP	0.000	0.02	0.02	0.00	0.02	0.00	0.00
	wB97XD	0.001	0.01	0.01	0.00	0.01	0.00	0.00
$(PNCl_2)_3$	HF	0.001	0.00	0.01	0.00	0.01	0.00	0.00
	PBE	0.000	0.04	0.03	0.03	0.03	0.00	0.00
	B3LYP	0.000	0.02	0.00	0.02	0.00	0.00	0.00
	CAM-B3LYP	0.001	0.01	0.03	0.00	0.03	0.00	0.00
	LC-BLYP	0.001	0.00	0.02	0.00	0.02	0.00	0.00
	wB97XD	0.001	0.00	0.01	0.00	0.00	0.00	0.0
$(PNF_2)_3$	HF	0.001	0.02	0.01	0.02	0.01	0.02	0.00
	PBE	0.000	0.01	0.03	0.01	0.02	0.02	0.00
	B3LYP	0.001	0.01	0.00	0.01	0.00	0.01	0.00
	CAM-B3LYP	0.000	0.01	0.03	0.01	0.03	0.03	0.00
	LC-BLYP	0.000	0.00	0.02	0.00	0.02	0.02	0.00
	wB97XD	0.000	0.00	0.01	0.00	0.00	0.00	0.00

hyperpolarizabilities and the symmetry of the molecules. In this case, symmetric planar structures obtained for the whole cyclic phosphazenes, they all have null dipole moments and null first hyperpolarizabilities calculated at *ab initio* (HF) and DFT levels.

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