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THEORETICAL DETERMINATION OF THE NONLINEAR OPTICAL PROPERTIES OF INORGANIC POLYMERS

S. M. Risser
K. F. Ferris

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Pacific Northwest Laboratory
Richland, Washington 99352

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Theoretical Determination of the Nonlinear Optical Properties of Inorganic Polymers

Steven M. Risser and Kim F. Ferris
Pacific Northwest Laboratory[1], Materials and Chemical Sciences Center, Richland WA 99352

ABSTRACT

Third order hyperpolarizabilities were calculated using the Huckel Hamiltonian and third order perturbation theory for a series of phosphonitrilic compounds, $(X_2P-N)_n$, as a function of bond length alternation, ligand substitution and backbone conformation. Phosphonitrilic compounds show hyperpolarizabilities comparable to those reported for organic species, and are modulated by ligand group electronegativity. In contrast to organic polyenes, the difference in π orbital energy between phosphorus and nitrogen is critical to determining the onset of saturation and the magnitude of the hyperpolarizability. Conformation effects are smaller than those seen in polyenes.

Keywords: Nonlinear, hyperpolarizability, inorganic polymers, optical properties, phosphazenes

1.0 INTRODUCTION

While the search for materials with large macroscopic nonlinear properties has often focused on conjugated organic molecules, inorganic polymers feature many similar chemical bonding interactions and should also be viewed as viable candidates. Recent experiments on polyphosphazenes have shown that these polymers exhibit large bulk nonlinearities and high laser damage thresholds[2]. These properties combined with their transparency in the visible spectrum mark these compounds as potential alternatives for use in fabricating optical devices.

Most of the electronic properties of the polyenes, such as absorptions and both the linear and nonlinear optical properties[3], are governed by the conjugated π bonding electrons. Inorganic polymers such as the phosphonitrilic system feature two independent π-bonding networks, the normal π network which is constructed from out of the plane p_z orbitals, and a

second, less highly conjugated π' network lying in the plane of the molecule[4]. The interaction of the two conjugated π electron systems has large effects on the electronic properties of the polyphosphazenes, increasing the optical transition energies of the out-of-plane π electrons[5] as compared to organic molecules, and making intrinsic contributions to the electronic hyperpolarizabilities of the molecule.

The similarities in the chemical bonding between organic and inorganic polymers would indicate that some features which affect the nonlinear optical properties of polyenes, such as degree of bond alternation and chain conformation, should be considered for their potential influences on inorganic polymers. In addition, characteristics such as the large electronegativity differences between atoms along the polymer backbone which are unique to the inorganic polymers, may also have large effects on the hyperpolarizabilities. This electronegativity difference may restrict the delocalization of the π electrons and decrease the magnitude of the hyperpolarizabilities.
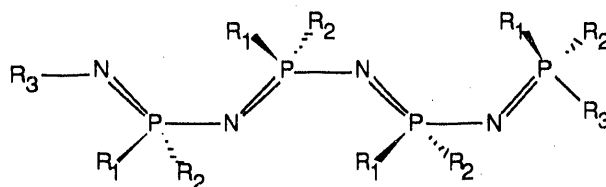

Figure 1. Schematic of phosphazene tetramer

We have calculated third order hyperpolarizabilities for a series of phosphazenes, $(X_2PN)_n$ (tetramer shown in Figure 1), as a function of its molecular parameters, that is, ligand substitutions, bond alternation and chain conformation. These effects of these parameters on the hyperpolarizability are compared to similar calculations for polyenes, and are interpreted in terms of the electronic structure and chemical properties of the phosphazene.

2.0 <u>METHODS</u>

The nonlinear optical properties of organic molecules are dominated by the conjugated π electrons, allowing them to be treated in a predictive sense by a π electron Hamiltonian for the determination of their hyperpolarizabilities[6]. The Huckel Hamiltonian was selected for this

work based upon two features: 1) The chemical bonding of phosphonitrilic systems are dominated by π bonding interactions, and 2) The simplicity of the Hamiltonian allows also for calculation of the hyperpolarizabilities for a range of molecular parameters.

The Huckel Hamiltonian is a tight-binding π electron Hamiltonian allowing interactions between near neighbor atoms. In second quantized form, this Hamiltonian can be written as:

$$\hat{H} = \sum_{i,\sigma} \alpha_i c_{i\sigma}^\dagger c_{i\sigma} + \sum_{\substack{i=j \\ \sigma}} \beta_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma})$$

where c_i ($c_i^\dagger$) is the destruction (creation) operator, which destroys (creates) a π electron on atom i. The second summation is restricted to bonded pairs of atoms i,j. Atomic p_z orbitals are assumed to be orthogonal, and molecular eigen states are formed as linear combinations of the atomic p_z orbitals. The ground state of the molecule is formed from the Slater determinant of the occupied molecular eigen states.

There are two sets of matrix elements which define the Hamiltonian, the Coulomb term α_i which is approximately equal to the ionization energy of a p electron atom i, and the hopping term β_{ij} describing the transfer of an electron from atom i to atom j. Ligand group effects at the phosphorus site were modelled by using a range of differences in the π orbital energy ($\Delta\alpha$) between the nitrogen and phosphorus centers. Structural parameters for the polyphosphazenes were taken from recent *ab initio* calculations for $(F_2PN)_4$. Because of the large role bond alternation plays in calculations of the hyperpolarizability for polyenes and the existence of bond length alternation in short chain length phosphazenes[4b,7], we have performed calculations for a series of bond length alternations (0.00 $\beta_{PN} \equiv$ no bond alternation).

The third order hyperpolarizability can be determined by expanding the energy of the molecule in a Taylor series, and using perturbation theory to calculate the coefficients of the expansion. Thus, the third order hyperpolarizability can be shown to be:

$$\gamma_{\alpha\beta\lambda\delta} = P\left\{ \sum_{ijk=0} \frac{\langle 0|\mu_\alpha|i\rangle\langle i|\mu_\beta|j\rangle\langle j|\mu_\lambda|k\rangle\langle k|\mu_\delta|0\rangle}{(E_i-E_0)(E_j-E_0)(E_k-E_0)} \right.$$

$$- \sum_{ij=0} \frac{\langle 0|\mu_\alpha|i\rangle\langle i|\mu_\beta|0\rangle\langle 0|\mu_\lambda|j\rangle\langle j|\mu_\delta|0\rangle}{(E_i-E_0)(E_i-E_0)(E_k-E_0)}$$

$$- 2\sum_{ij=0} \frac{\langle 0|\mu_\alpha|0\rangle\langle 0|\mu_\beta|i\rangle\langle i|\mu_\lambda|j\rangle\langle j|\mu_\delta|0\rangle}{(E_i-E_0)(E_i-E_0)(E_k-E_0)}$$

$$\left. + \sum_{i=0} \frac{\langle 0|\mu_\alpha|0\rangle\langle 0|\mu_\beta|0\rangle\langle 0|\mu_\lambda|i\rangle\langle i|\mu_\delta|0\rangle}{(E_i-E_0)(E_i-E_0)(E_i-E_0)} \right\}$$

where α, β, λ, and δ refer to Cartesian coordinates in the molecular reference frame, P being the permutation operator for α, β, λ, δ; μ the one electron dipole operator, $|0\rangle$ is the ground state wavefunction, $|i\rangle$ $|j\rangle$ $|k\rangle$ are excited state wavefunction, E_0 the ground state energy and E_i the excited state energy. Summations extend over all possible excited states. Because of the nature of the dipole operator, it is possible to restrict the first summation to single and double electron excitations. The latter three summations are restricted to single electron excitations.

3.0 RESULTS

The focus of the current investigation is to provide a theoretical basis for the nonlinear optical properties of phosphonitrilic polymers. While there are a number of similarities in the electronic properties between the organic and phosphonitrilic systems, one of the significant differences is the charge distribution along the polymer backbone. Although polarized chemical bonding situations are well known to exist in organic polymer systems, larger electronegativity differences are still possible when second row elements are included in the polymer backbone. The effects of these changes in the electron distribution and their interactions with bond alternation contributions are examined in the following discussion on the hyperpolarizability of the polyphosphonitrilic system.

Molecular Structure and Conformation

Crystallographic studies of the chloro-substituted polymer have shown the bonds to be of equal length within the resolution of the measurements[8], while recent *ab initio* calculations have shown the existence of bond length alternation in the small linear phosphonitrilic compounds. The existence or non-existence of bond alternation may be vital, as bond alternation has been firmly established as a principal factor in theoretical calculations of the third order hyperpolarizabilities in polyenes. Previous theoretical calculations of the hyperpolarizability of trans and cis polyenes have shown that the magnitude of bond alternation plays a crucial role in deciding not only the magnitude but also the sign of the average hyperpolarizability[6]. The effects of possible bond alternation on the third order hyperpolarizability for a fixed difference in orbital energies ($\Delta\alpha=0.6\beta_{PN}$) are shown in Figure 2. The average hyperpolarizability per repeat unit for the cis-trans conformation is shown for five distinct amounts of bond alternation. The inclusion of bond length alternation has no qualitative effects on the third order hyperpolarizability, and causes only a slight decrease in magnitude. This is in contrast to the cis-trans polyenes, where greater degrees of bond alternation have been shown to increase the average hyperpolarizability.
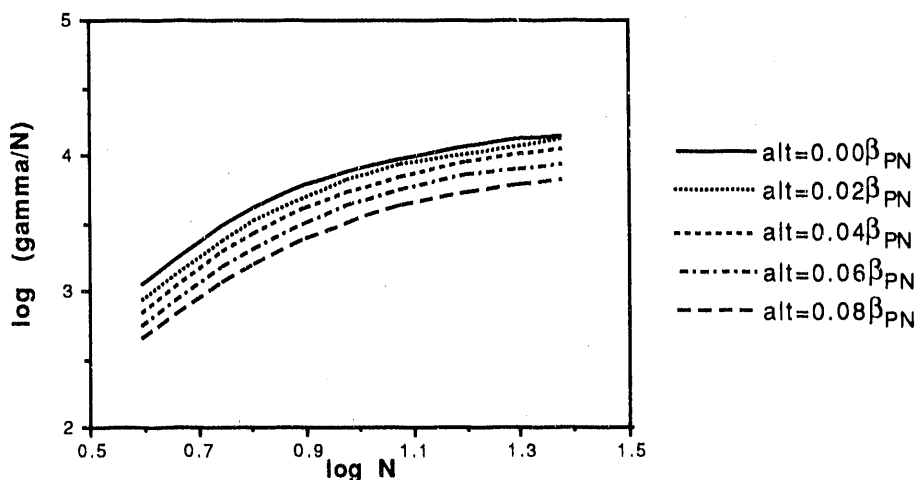

Figure 2. Hyperpolarizability per repeat unit of cis-trans conformation vs. number of repeat units. The energy difference between p_z orbitals is held constant at $\Delta\alpha=0.6\beta_{PN}$.

The large amount of flexibility in the backbone of inorganic polymers gives rise to more than one possible conformation for the polymer. Both experimental and theoretical determinations of the hyperpolarizability of polyenes have shown that the hyperpolarizability per repeat unit is dependent on the conformation of the polyene, but the magnitudes of the hyperpolarizability for the all-trans and cis-trans conformations are almost exactly identical per unit length along the primary axis of the molecule. Since inorganic systems commonly assume trans, cis-trans, and helical conformations due to their high backbone flexibility, the phosphazene conformation may also be significant in determining the hyperpolarizability of phosphazenes. To determine whether this same length dependence exists in phosphazenes, we have also performed calculations on the trans conformation of the polyphosphazene. The structural parameters were kept the same as for the cis-trans phosphazene. The hyperpolarizability per repeat unit for the trans conformation with varying degrees of bond
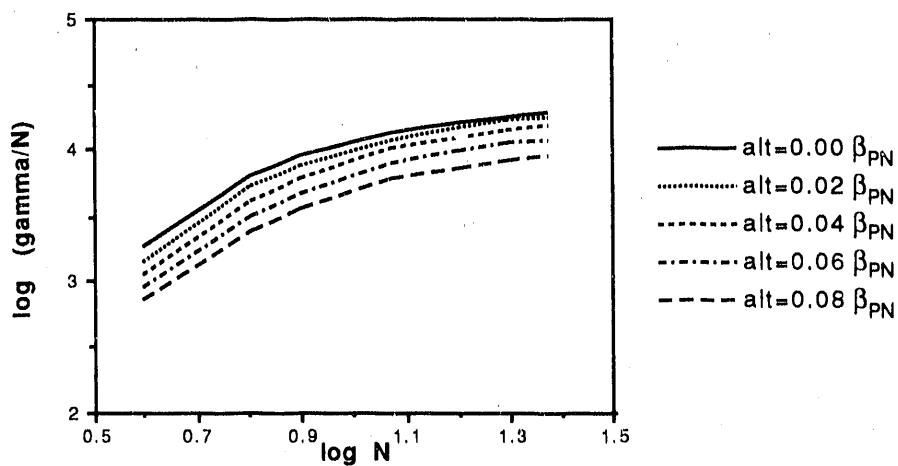

Figure 3. Hyperpolarizability per repeat unit of trans conformation vs. number of repeat units. The energy difference between p_z orbitals is held constant at $\Delta\alpha=0.6\beta_{PN}$.

alternation is shown in Figure 3. The difference in orbital energies was held constant at $\Delta\alpha=0.6\beta_{PN}$ to allow for direct comparisons with the cis-trans results in Figure 2. The magnitudes of the hyperpolarizability per repeat unit for the trans conformation are comparable to those of the cis-trans conformation indicating that the length of the conjugated system, and not the backbone conformation, is also the important feature for inorganic polymers.

The onset of saturation and the increase in nonlinearity per repeat unit determines the bulk nonlinearity for large molecular weight polymers. The rapid increase in the hyperpolarizability observed for small number of repeat units as shown in Figure 2 does not continue indefinitely, but instead quickly reaches saturation, where the nonlinearity becomes linearly dependent on the number of repeat units. Previous research in organic polymers has shown that the nonlinear optical properties saturate at a small number of repeat units, with the degree of bond alternation included in theoretical models being the key ingredient in determining when the models show saturation. The similarity of the shapes of the curves in Figures 2 and 3 indicate that bond alternation has no effect on the onset of saturation for the phosphonitrilic system. The decrease in the magnitude of the curves when bond alternation is included show that the existence of bond alternation in the polymer will decrease the magnitude of the bulk nonlinearity for either conformation of the polymer.

Electronic Interactions

The chemical bonding in phosphazenes has distinctly different electronic properties from organic polymers which may play a large role in determining their hyperpolarizabilities. Perhaps most important of these is the interaction of the substituent groups attached to the phosphorus with the in-plane and out-of-plane π bonding networks. The effects of varying substituent groups on the hyperpolarizability of phosphazenes was represented through variations in the energy of a p_z electron on the phosphorus atoms. Figure 4 shows the hyperpolarizability per repeat unit plotted against the number of repeat units for a number of energy differences, $\Delta\alpha$, between the nitrogen and phosphorus p_z orbitals, with the bond alternation held constant at $0.04\beta_{PN}$. Changing the energy difference between orbitals has a very large effect on the hyperpolarizability. Decreasing the orbital energy difference increases both the magnitude of the hyperpolarizability and its rate of growth with increasing number of repeat units. This is most evident for the $\Delta\alpha=0.0$ curve, where the hyperpolarizability curve still exhibits significant curvature even for 60 repeat units.

The effects of conformation on these electronic influences were investigated by performing similar calculations on the trans conformation of the phosphazenes. Figure 5 shows the hyperpolarizability per repeat unit of the trans conformation plotted against the number of repeat units for a number of values for $\Delta\alpha$, with the bond alternation held constant at
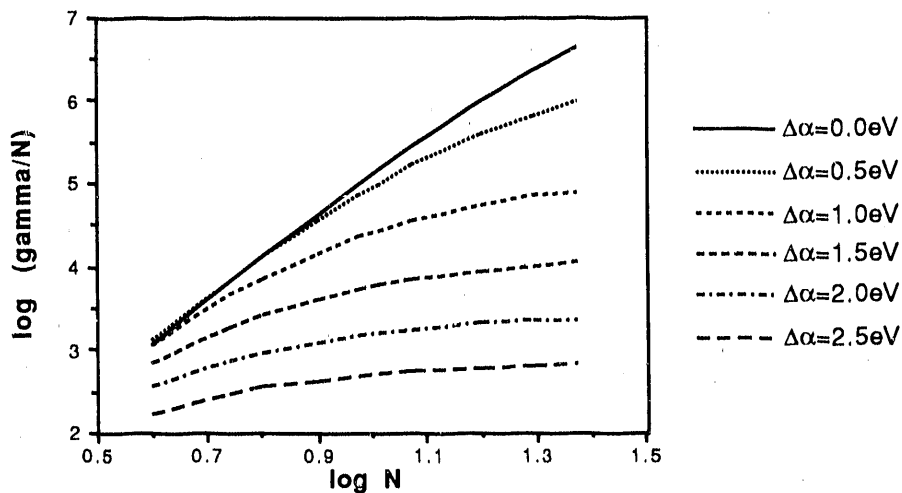
Figure 4. Hyperpolarizability per repeat unit of cis-trans conformation polyphosphazene vs. number of repeat units for various energy differences between p_z orbitals on nitrogen and phosphorus. The bond alternation is held at $0.04\beta_{PN}$.
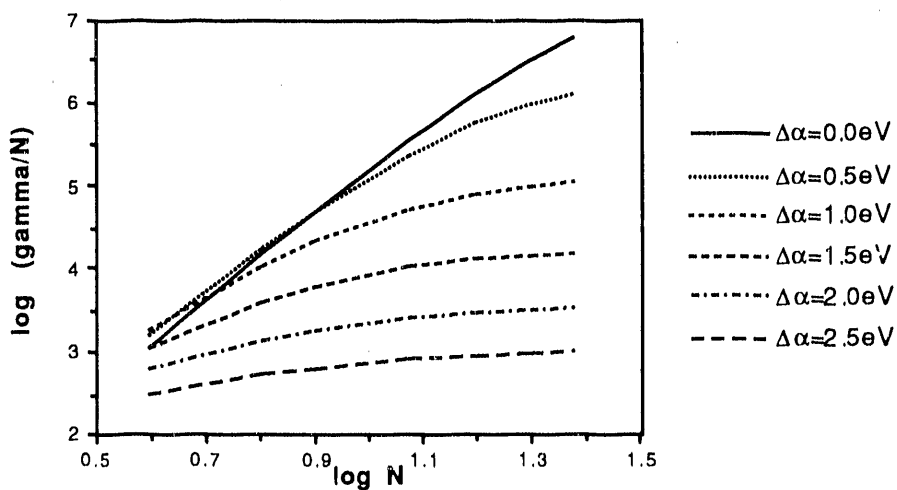

Figure 5. Hyperpolarizability per repeat unit of trans conformation polyphosphazene vs. number of repeat units for various energy differences between p_z orbitals on nitrogen and phosphorus. The bond alternation is held at $0.04\beta_{PN}$.

a value of $0.04\beta_{PN}$. The curves appear very similar to those of Figure 4, with the exception of for very small number of repeat units, where the $\Delta\alpha=0.0$ curve drops noticeably below that for the 0.5 eV curve.

4.0 CONCLUSIONS

We have calculated the third order hyperpolarizability for phosphazenes of increasing length using the Huckel Hamiltonian and third order perturbation theory, using a series of possible bond alternations and representations of different substituent groups on the phosphorus. These calculations have shown that bond alternation does not appear to play a large role in determining the saturation of polyphosphazenes, in contrast to the results observed for organically based polyenes. Substituent effects on the electronic structure play crucial roles in determining the hyperpolarizability, with the largest magnitudes coming with weakly electron drawing groups.

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CONCLUSIONS

The optical properties of both organic and inorganic materials are a direct function of their electronic structure, and can be related to structural, conformational and ligand electronegativity effects. While the electronic structure of both systems can be well described by their molecular symmetry, the large electronegativity differences possible with inorganic systems complicates simple interpretations of their electronic structure. The major difference between organic and inorganic systems is the extent of orbital interaction in the π' bonding networks which are modulated by ligand electronegativity, and its effect on electronic transition energies. Substituent electronegativity effects also play a major role in determining the hyperpolarizability of the phosphonitrilic system, with the largest magnitudes arising from weakly electron accepting groups.

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