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EFFECTS OF IN-PLANE π' BONDING ON ELECTRONIC TRANSITION ENERGIES FOR INORGANIC POLYMERS

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ABSTRACT

The electronic structure of organic and inorganic polymeric systems are well described in terms of their molecular symmetry, even with the large bond polarity shown by such systems as polyphosphazenes. We have performed calculations using the semi-empirical CNDO/1 method to determine the valence electronic structure for a series of model phosphonitrilic and organic compounds. The optical transition energies for phosphonitrilic compounds are greater than their organic counterparts as a result of in-plane π' bonding interactions. The extent of these interactions is modulated by the electronegativity of the substituent groups on the phosphorus atoms. We report values for the vertical ionization energy and electronic absorption wavelengths, and use molecular orbital contour analysis to show the effects of ligand electronegativity on the π' network.

INTRODUCTION

Phosphonitrilic compounds have emerged from the general class of inorganic polymers because of a set of unique properties which makes them potentially useful candidates for optical applications. Many of these properties are simply the result of the unusual chemical bonding characteristics between first and second row elements constituting the P-N backbone in these species. Other important properties stem from the ease with which substituent groups on the phosphorus may be altered, resulting in markedly different physical characteristics [1].

The nature of the P-N bonding gives rise to two independent π networks; the normal out-of-plane π network as is seen in organic polymers, and an in-plane π' network. The presence of the second network is largely responsible for the large increase in optical transition energies, keeping the polymer transparent in the visible region. The conjugation of these π networks is also responsible for the large non-linear optical properties recently observed and calculated for these polymers [2]. The generally better materials properties of these inorganic polymers, however, means these materials may be more useful than organic polymers for fabricating practical devices such as optical switches and power limiters.

Our approach to understanding and predicting the physical properties of these systems is to develop a fundamental picture of these materials based upon their molecular and electronic structure. In this paper, we report the results of electronic structure calculations on a series of phosphonitrilic systems ($(F_2PN)_3$, $(F_2PN)_4$ and $(F_2PN)_5$) and organic systems (C_5H_5N and $C_3H_3N_3$) using the CNDO/1 formalism with configuration interaction, in order to compare orbital interactions and electronic transitions in these materials. The two principal electronic features examined are the vertical ionization potentials and ultraviolet absorption spectra, while orbital contour diagrams will be presented to show some of the unique bonding interactions of the π' network.

METHODS

Semiempirical valence electron molecular orbital methods were used to evaluate the electronic structure of ($(F_2PN)_3$, $(F_2PN)_4$, C_5H_5N and $C_3H_3N_3$) and were compared to *ab initio* results [3] where applicable. Vertical ionization potentials for the molecules were estimated from the one-electron orbital eigenvalues using Koopman's theorem. Molecular orbital contour plots were generated using QCPE program #340 [4] that was modified to allow the user to delete the contribution of individual atomic centers from the molecular orbital plot. UPS spectra were simulated using the superpositions of gaussian absorption profiles with a FWHM=0.35 eV and the dielectric relaxation model in ref.[5]. Coulomb integrals were evaluated using the Mataga-Nishimoto interpolation formula[6], and the Pople-Segal formalism[7] was used for core Hamiltonian matrix terms. One center gamma integrals and vertical ionization potentials were taken from the MINDO/3 parameterization in MOPAC 4.0 (QCPE #455). For the phosphonitrilic species, the ratio of s and p orbital exponents was kept constant while they were being re-optimized to reproduce the electronic structure determined by ab initio computations and experimental vertical ionization potential data. Ultraviolet absorption transitions were evaluated using a 4x4 configuration interaction scheme for organic species, and an 8x8 for inorganics. Further details on the electronic structure method are available in ref [8].

RESULTS AND DISCUSSION

Typical organic polymers are constituted of first row elements in the polymer backbone, with classical chemical bonding interactions characterized by the small electronegativity differences between adjacent bonding pairs. On the other hand, common inorganic species, such as carbides, nitrides and oxides, invoke chemical bonding situations in which there are large size and electronegativity differences along the polymer backbone. The involvement of lone pair orbitals on bridging atoms in the backbone can perturb classical π type interactions, and create in-plane p orbital interactions which have been described as π' bonding.

In order to clarify the organic vs. inorganic backbone and π vs. π' bonding interaction issues, molecular orbital calculations were performed on the small cyclic molecules, ($(F_2PN)_3$, $(F_2PN)_4$, C_5H_5N and $C_3H_3N_3$), as models for organic and inorganic systems. For pyridine, the calculated vertical ionization potentials (Table 1) and orbital ordering ($1a_2$ (π), $11a_1(\sigma,n)$, $2b_1(\pi)$ ...) were in good agreement with the experimental values reported by Batich et.al.[9]. The electronic transition energy was calculated to be ~267 nm compared against 286 nm measured experimentally[10]. Previous estimates for pyridine by Duke et.al. [5] had used a $1a_2(\pi)$, $2b_1(\pi)$, $11a_1(\sigma,n)$ ... orbital ordering in order to compare against the measured ionization potentials for pyridine and its alkyl substituted derivatives. The presence of high lying π molecular orbitals results in the π-π^* optical transition observation in a manner similar to benzene. Analysis of our optical transition eigenfunctions shows that the orbital transitions are essentially 100% n-π^* for pyridine and 87% n-π^* for triazine, consistent with the experimental measurements of Innes[11], and later calculations by Ridley and Zerner[12].

The vertical ionization potentials for triazine are given in Table 1, and also show good agreement with the experimental values reported by Gleiter et.al.[13]. The orbital interactions of the nitrogen lone pairs is defined by the molecular symmetry, which results in the $e'(\sigma,n)$ linear combination being the uppermost orbital in the occupied orbital manifold. Such patterns recur in the phosphonitrilic systems as described below. For triazine, the first electronic transition energy was 259 nm compared to an experimental value of 274 nm [10].

Table 1 - Vertical ionization potentials(eV) for C_5H_5N and $C_3H_3N_3$

C_5H_5N		$C_3H_3N_3$	
Calculated	Experimental[9]	Calculated	Experimental[13]
9.7 (π)	9.7 (π)	10.37 e'(σ,n)	10.37 e'(σ,n)
9.82 (σ,n)	9.8 (σ,n)		
10.8 (π)	10.5 (π)	11.82 e"(π)	11.67 e"(π)
11.5 (σ)	12.5 (σ)		
14.6 (π)	12.6 (π)	13.97 (σ,n)	13.2 (σ,n)

The electronic structure of organic polymers is characterized by σ and out-of-plane π bonding networks, while inorganic polymers may also exhibit in-plane π'bonding interactions. Electronegativity differences along the backbone have been shown to play an important part in determining the interaction of the in-plane nitrogen orbitals. However, the molecular symmetry of the phosphonitrilic systems also offer the interesting contrasts for the electronic transitions with organic compounds. As opposed to benzene, pyridine, and the triazines where the ligand attached to the ring backbone remains coplanar with the ring, the phosphonitrilic ligands are oriented above and below the ring. These orientations present a possible π-like path for electronic transitions which would formally be called a charge transfer (CT) transition, nitrogen π to ligand.

Table 2 - Vertical ionization potentials (eV) for $(NPF_2)_n$, n=3,4,5 [14].

n=3		n=4		n=5	
Calculated	Expt'l	Calculated	Expt'l	Calculated	Expt'l
--	--	10.7	10.7	--	--
11.4	11.4	11.6	11.5	11.4	11.4
--	---	12.6	12.5	12.7	12.5
13.0	13.1	13.5	13.6	14.6	13.3
--	--	14.9	14.9	--	
14.8	15.4	--	--		

The vertical ionization potentials for the cyclic phosphonitrilic series are given in Table 2. Given the orthogonality of the π and π' networks, simple molecular symmetry arguments determine the orbital pattern of the uppermost occupied molecular orbitals. For example, the first ionization potential for the cyclic trimer corresponds to the pair of doubly degenerate orbitals (e' and e"), one of which contains the in plane π' interactions, the other, the out-of-plane π orbital. Higher ionization potentials arise from singly degenerate π and π' interactions, and the P-N σ network respectively. In comparison with the organic species, the UPS simulation plays an critical role in determining the quality of the calculated vertical ionization data. The differences in electronegativity and size between the first and second rows of the period table result in π interactions weaker than for their organic counterparts. Thus, the orbital manifold described by the possible nitrogen p orbital interactions contains both degenerate and nearly degenerate linear combinations. Degenerate and nearly degenerate orbital eigenvalues become unresolvable with the finite linewidths seen with normal experimental measurements.

Figure 1 - Orbital contour for π' interactions in (a) $(F_2PN)_3$ and (b) $(H_2PN)_3$. Ligand orbital contributions omitted for clarity.

Ligand electronegativity has significant effects on the electronic transitions of these species. Previous work[3] has shown that the location of the π orbitals in the occupied orbital manifold is particularly sensitive to these effects, becoming higher in energy with decreased ligand electronegativity. The interactions of the π' orbitals become less pronounced under these conditions (Figure 1). The net effect is to decrease the π-LUMO energy difference, and subsequently the electronic transition energy becomes smaller. The experimental values for electronic absorption for the series $(X_2P\text{-}N)_3$, X=F,Cl,Br changes from ~149 nm to 195 nm respectively[1].

In Table 3, we report the lowest electronic transition for the phosphonitrilic systems. In more descriptive terms, this transition has been defined as a charge transfer band between the π system and ligands. The one-electron eigenfunction analysis shows that the π orbital is a classical out-of-plane bonding orbital involving nitrogen p-orbitals polarized in a manner consistent with the electronegativity difference between the P and N atoms. Participation of the phosphorus orbitals is affected by similar energetic and symmetry concerns.

Table 3 - Electronic absorption wavelengths (nm) for $(NPF_2)_n$

	Calculated	Experimental [15]
$(NPF_2)_3$	149	149
$(NPF_2)_4$	162	148
$(NPF_2)_5$	155	---

SUMMARY

The electronic structure of both organic and inorganic materials can be well described using semiempirical molecular orbital methods. There are many similarities between conventional organic species and phosphonitrilic systems, with the electronic structure of both systems characterized by their molecular symmetry, even with the large bond polarity shown by the phosphonitrilic systems. A major difference is the extent of interaction of the the π' bonding networks and its effect on electronic transition energies. These effects are strongly dependent on the electronegativity of the ligand attached to the phosphorus. Thus, phosphonitrilic materials offer comparable electronic and tunable optical properties to organic materials.

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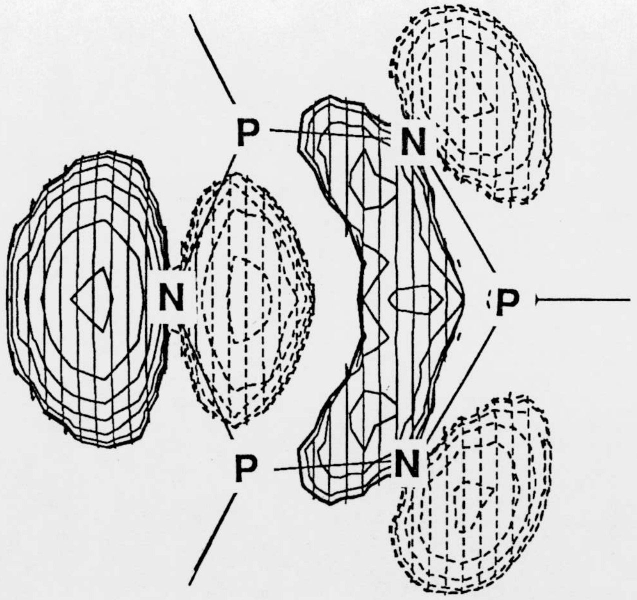

Figure 1A

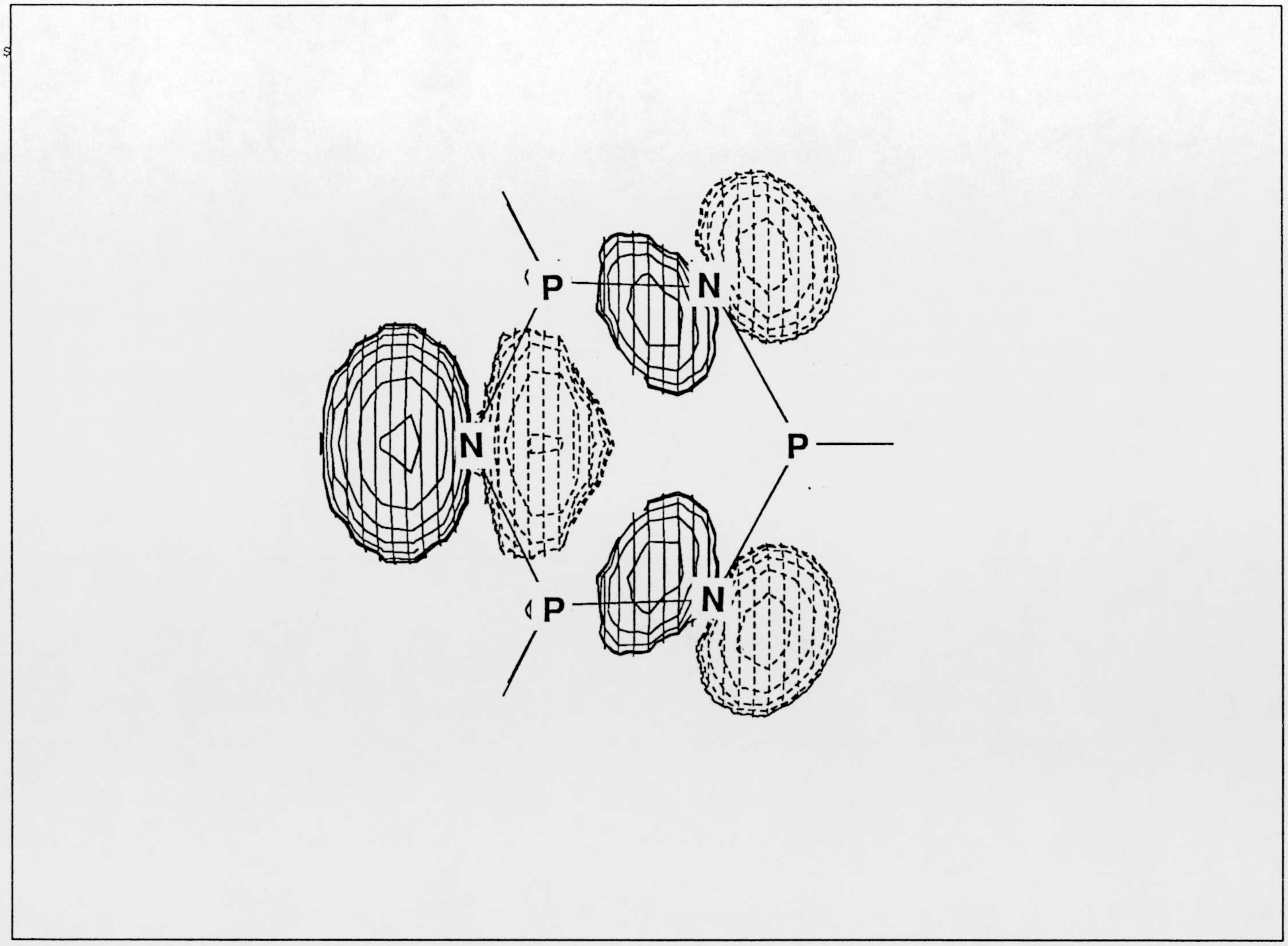

Figure 1B