PNL-SA--16623

DE89 014460

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May 1989

To be published in the Proceedings
of the 1989 Sanibel Symposia
held April 1-8, 1989
St. Augustine, Florida

Work supported by the
U. S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Chemical Bonding in Phosphonitrilic Systems - Comparison of the Electronic Structures of $(F_2PN)_3$, $(F_2PN)_4$ and $OP(F_2)NP(F_2)NPF_3$

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Abstract

The electronic structure of phosphonitrilic systems contain both π' (in-plane) and π (out-of-plane) bonding systems. Earlier work in this laboratory has indicated that the d-orbital involvement in these systems affects primarily the electronic structure, and is modulated by ligand electronegativity. *Ab initio* molecular orbital calculations were performed on a series of small phosphazene molecules [$(F_2PN)_3$, $(F_2PN)_4$ and $OP(F_2)NP(F_2)NPF_3$] to elucidate the electronic and molecular structure of these small molecules as models for polymeric systems. The chemical bonding and charge distribution in the phosphonitrilic trimers, tetramers and these small fragments is highly polarized, primarily through the π and π' bonding networks. Our results indicate that while the majority of the electronic aspects of $OP(F_2)NP(F_2)NPF_3$ can be described by analogies to $(F_2PN)_3$ and $(F_2PN)_4$, major geometric differences such as bond alternation are evident. The opening of the P-N-P bond angles in the linear fragment results in reduced overlap over multiple centers, promoting 'islands of delocalization' first proposed by Dewar et al.[2]

Introduction

Phosphonitrilic compounds have emerged from the general class of inorganic polymers because of a series of unique properties that renders them as potentially useful candidates for optical, high-temperature, and ceramic processing applications. Many of these properties are simply the result of the P-N backbone in these species giving rise to the unusual chemical bonding characteristics between second and third row elements. 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.

The past controversies on phosphazenes have focused on the out-of-plane $d_\pi(P)$ and p_π (N) bond formation in the trimer, tetramer and polymer. In earlier work, we have shown that the $d_\pi(P)$ and p_π (N) out-of-plane bond focus is complicated by the interaction of the nitrogen lone pairs mixing with d-orbitals on phosphorus to give an in-plane π' system[3]. The involvement of d-functions in the electronic structure of these species is modulated by the ligand electronegativity, and follows the symmetry requirements for d-orbital involvement in earlier proposals by Dewar et al. For the major geometric features of these molecules, the effect of d-orbitals is reduced with high ligand electronegativity. However, for these same cases, there are marked enhancements in both the π and π' bonding systems with the inclusion of d-orbitals.

The P-N bond lengths for the fluorophosphonitrilic polymer $(NPF_2)_n$ are 1.52 Å oriented in a cis-trans planar chain as shown in Figure 1, with N-P-N and P-N-P bond angles being 119.0° and 136.0°, respectively. One of the more unusual aspects of the polyphosphonitrilic system is the equal bond lengths along the P-N backbone with no apparent terminal group effects. Recently, Allcock et al.[4] have developed a series of short chain linear phosphazenes, which they have proposed for models of polymeric systems. The X-ray crystal structures of $OP(Cl_2)NPCl_3$ and $[Cl_3PNP(Cl_2)NP(Cl_2)NPCl_3]^{1+}$ as reported by Allcock et al. had indicated a bond alternation of ~0.06 Å, which they interpreted as insignificant in light of the single bond length for P-N in sodium phosphoramidate being 1.77 Å with triply bonded P≡N being 1.491 Å for PN. In addition, no bond alternation (<0.01 Å) was apparent for $OP(R_2)NP(R_2)NPR_3$. One unresolved question is whether this small degree of bond alternation is real, and why such alternation was not seen for $OP(Cl_2)NP(Cl_2)NPCl_3$ in light of the evidence pointing to such alternation in smaller and longer repeat-unit short-chain fragments.

As a consequence, it has become necessary to develop a fundamental understanding of the structural and electronic properties of these materials. *Ab initio* calculations on phosphonitrilic systems illustrate the classical bonding problems between second and third row elements. There are large size and electronegativity differences between these two rows of the periodic table; these differences result in highly polarized π bonding. Because of the large number of heavy atoms in these systems, previous theoretical investigations have primarily utilized semiempirical methods[5] or small molecule models[6]. Trinquier[6b] has provided an excellent review of correlating monomer, dimer and trimer properties with respect to electronic structure. However, these systems have fallen short of providing us with models for the polyphosphonitrilic system itself.

In this paper, we report the results of electronic structure calculations on a series of phosphonitrilic systems ($(F_2PN)_3$, $(F_2PN)_4$ and $OP(F_2)NP(F_2)NPF_3$) using *ab initio* molecular orbital methods to ascertain their value as models for polymeric systems. We have used molecular orbital contour analysis to graphically interpret their chemical bonding, and to correlate these results with those known for the polymeric system.

Computational Methods

Ab initio molecular orbital calculations were performed at the Pacific Northwest Laboratory[1] using the GAUSSIAN 82 computer program[7] modified for use with *ab initio* pseudopotentials. All geometries were energy minimized using a force relaxation method[8]. Molecular orbital contour plots were generated using QCPE program #340[9] that was modified to allow the user to delete the contribution of individual atomic centers from the molecular orbital plot.

The electronic structure of the molecules $(F_2PN)_3$ and $(F_2PN)_4$ were calculated at both the 3-21G* split-valence basis set level[10] and with the same basis using a pseudopotential[11] method to reduce the computational requirements. The linear fragment model $OP(F_2)NP(F_2)NPF_3$ was treated with the same basis using the pseudopotential method. Earlier electronic structure calculations for siloxane and pyrosilicic acid have shown the need for d-polarization functions on the bridging oxygen[12]. Preliminary calculations using the 3-21G* basis set both with and without pseudopotentials have shown that this constraint is shared for the linear phosphonitrilic species, $OP(F_2)NP(F_2)NPF_3$. Thus, the nitrogen basis set was augmented with polarization functions using the exponent value from the 6-31G* basis set[13] and is designated as LP-21G*+. As a basis for comparison on the P-N structure, the energy optimized LP-31G*[14] basis set without d-polarization functions on the fluorines was also used for the linear fragments. Molecular geometries for the cyclic phosphazenes were not constrained during geometry optimization, the resulting structures still maintained D_3 and D_4 symmetries. For the linear fragment species, the P-N backbone was constrained to be planar, consistent with experimental evidence for the chlorinated derivative[4], with the oxygen atom of the terminal $-P(F_2)O$ group rotated to maintain a plane of symmetry.

Results and Discussion

Structural Considerations

The optimized molecular geometries for the phosphonitrilic trimer and tetramer were determined at the 3-21G*, LP-21G*+ and LP-31G* basis set levels and are given in Table I. Energy optimized structural information for the short-chain linear fragment, $OP(F_2)NP(F_2)NPF_3$, was determined at the LP-21G*+ and LP-31G* basis set levels and is given in Table II.

The geometric predictions of P-N bond lengths for the cyclic trimer and tetramer systems were within 3% of the experimental values reported by Shaw[15]. Greater variation was noted for the P-F bond lengths along this same series. The LP-31G* basis gave the longest P-F bond lengths; however, this was expected since the d-functions on the fluorine were dropped from these calculations. The bond angles for these systems were fairly well reproduced regardless of basis set, and confirms the general wideness of the P-N-P bond angle when not constrained by a ring. Such observations were expected from our previous work on the phosphonitrilic trimer, as we would have expected VSEPR type considerations to be sufficient to describe the flexibility of the P-N-P bond angle. As such, the larger-membered ring compound, $(F_2PN)_4$, would appear to be a better model for the polymer because the P-N-P bond angles are sufficiently wide to decrease the lone pair interactions of the nitrogens found for the cyclic trimer.

The calculated molecular structure of the linear species was in reasonable agreement with the experimental structure for the short-chain linear fragments, but causes concern regarding their value as models for the polymer. We found small bond alternations of ~0.07 Å (taken as the difference between the N2-P3 and P3-N4 bond lengths); this result is consistent with the structures reported for $OP(R_2)NPR_3$ and $[R_3PNP(R_2)NP(R_2)NPR_3]^{1+}$, but such alternations are absent in the direct analog, $OP(R_2)NP(R_2)NPR_3$. The reported bond lengths for $OP(Cl_2)NPCl_3$ and $[Cl_3PNP(Cl_2)NP(Cl_2)NPCl_3]^{1+}$ range from 1.52 to 1.58 Å and 1.50 to 1.58 Å, respectively, which are in relatively close agreement with our calculated values. Using the LP-31G* basis set, the bond length alternation persisted, although at slightly larger bond lengths. When the ligand electronegativity was switched by changing the ligand atoms from fluorine to hydrogen, the bond length alternation still persisted. The bond lengthening noted for the terminal $-N-PCl_3$ of $OP(Cl_2)NP(Cl_2)NPCl_3$ of 0.05 Å is apparently propagated along the P-N backbone, and we predict that other short repeat unit analogs would also show such bond alternations. Further, such bond alternation implies that the π electron system in these species is not as fully delocalized as had been previously proposed by Allcock et al. While the chemical bonding in these systems cannot be interpreted in terms of discrete single and double bonds, there are inequivalent interactions that distinguish them from the polymer.

Electronic Structure

In Figure 2, the molecular orbital contours for the in-plane π' interactions by the nitrogen lone pairs are shown for the fluorophosphonitrilic tetramer $(F_2PN)_4$. In Figure 3, the corresponding π and π' orbital contours for the trimer, tetramer and linear fragment are given . For space and clarity considerations, the completely symmetric combination is only shown for the π' bonding systems, and the completely antisymmetric combination for the π bonding network.

The charge distribution in the phosphonitrilic system can be described by three bonding systems - the bond axis oriented σ bonds, the in-plane π bonds from the nitrogen lone pairs, and the out-of-plane π bonds from p_z interactions. The general chemical bonding pattern of the phosphonitrilic series is dominated by the P-N bond polarity, which results in P(δ+)-N(δ-) type state. This pattern has been noted by Trinquier for $(H_2PN)_n$ n=1,2,3, and is accentuated by ligands of increasing electronegativity such as $(F_2PN)_n$. Both of the π systems are highly polarized, as evidenced by the atomic charges reported in Tables III, and better yet for sake of illustration, orthogonal to each other. As a result, the π bonding in phosphazenes can be described in terms of nodal planes in a manner reminiscent of Huckel orbital theory as shown in Figure 2 for the fluorotetramer.

This simple picture of the chemical bonding in phosphonitrilic systems holds the key to their physical and chemical properties. One might consider that the fluorotetramer is a four node Huckel system. Symmetry constraints require that the interactions of the π systems result in the highest filled molecular orbital alternating between a single and doubly degenerate orbital depending upon whether n is odd or even for $(F_2PN)_n$ where n=3,4,5... One obvious result of these interactions is the oscillation of the first ionization potentials for the cyclic phosphonitrilic species, which results from an e type orbital symmetry in $(X_2P\text{-}N)_n$ systems where n is an odd number. In ascending the fluorophosphazene homologous series, $(F_2PN)_{3\text{-}8}$, there is an alternation of ionization potential with those species with odd numbers of monomer units having higher values than those with even numbers of monomer units (n=3 IP=11.4 eV, n=4 IP=10.7 eV, n=5 IP=11.4 eV, ...)[16]. Such trends had been rationalized in the past in terms of an electron being removed during cation formation being derived from a bonding orbital rather than a nonbonding pair. Given that the fluorotrimer is relatively reactive to nucleophilic reagents as compared to the fluorotetramer, one interesting open question is whether this oscillating pattern of orbital interactions determines the reactivity of larger ring systems (than trimers and tetramers).

The emerging picture of the electronic structure for cyclic phosphonitrilic systems is that the high molecular symmetry and the charge transfer between the P and N centers make their electronic structure particularly amenable to interpretation in terms of symmetry arguments. Insofar as d-orbital participation is concerned, these arguments do not necessarily require d-orbital participation in the chemical bonding of P and N, although inclusion of d-functions are necessary for the calculation[17]. The role of d-orbitals at this level is primarily to shape the orbital interactions more sensitively in chemical bonding areas where the split-valence basis set used was not complete.

Small molecule models such as the linear fragment $OP(F_2)NP(F_2)NPF_3$ complicate this description. In addition to breaking the molecular symmetry, there are substantive end group effects with the limited number of repeat units. These effects can be seen in both the π (out-of-plane) and π' (in-plane) bonding interactions. As shown in the molecular orbitals in Figure 3, there is significant charge redistribution along the P-N backbone resulting from the terminal $-POF_2$ group. Combined with the decrease in P-N-P bond angle for the short chain linear fragment as compared to the tetramer, there is a tendency to localize charge at individual sites along the chain, thus creating "islands." Still, these chemical bonding arguments can be viewed as perturbations of the simple picture developed above because of the large degree of charge transfer between the nitrogen and phosphorus centers.

Cyclic Compounds and Linear Fragments as Model Systems for the Polymer

Phosphonitrilic systems considered here are characterized by large charge transfer in the π and π' bonding networks, which results in the electronic structure being dominated by the nitrogen lone pair interactions. We see no change in these trends in moving to the large cyclic systems or to the small linear fragments, and would anticipate such trends to be reproduced for the polymer.

However, with regards to which system would be a good candidate for polymeric phosphazenes, the main body of experimental evidence suggests that the search is still on. On the basis of both the electronic and structural information for the trimer, tetramer, and linear compounds considered here, there are significant differences for each of these with the polymer. The phosphonitrilic trimer is a poor candidate given that the six-membered ring imposes the geometric constraints that the P-N-P bond angles are now ~120° instead of the ~135-40° seen in the polymer. As such, the nitrogen-nitrogen interactions are exaggerated compared with the linear fragment and polymeric systems (Figure 3). We would expect that models for the polymer based upon the phosphonitrilic trimer might have exaggerated nitrogen-based properties.

On the other hand, the linear fragments in the range of the investigation reported here (2-1/2 repeat units) also do not emerge as significantly better candidates. There are significant perturbations to the electronic structure because of the terminal $-P(F_2)O$ group, which tends to exaggerate the charge distribution on the neighboring phosphorus site. In addition, the bond alternation in these species is not observed in the polymeric system.

The tetrameric systems $(F_2P\text{-}N)_4$ is the survivor in this series. The bond length calculated for tetramer was 1.54 Å as compared with the experimental 1.52 Å value, and the bond angles 148.6° (P-N-P) and 121.4 (N-P-N) agreed reasonably well with the experimental values for the fluorophosphonitrilic polymer (136.0° and 119.0°, respectively). In one sense, cyclic systems as a general class might seem to be better candidates for the polymer. The molecular symmetry of the cyclic systems defines equivalent sites, which are also the experimental observables for the polymer. However, the question that lies unresolved for this case is the electronic structure of the polymer. The Huckel delocalization energies per electron for heteromorphic and homomorphic interactions of $(X_2P\text{-}N)_n$ can be viewed as a function of number of monomeric units[18], and approaches a limiting value as $n \dashrightarrow \infty$. The majority of the delocalization energy available is found for the n=4 case, but not this limiting value. Similar arguments were made above using Huckel theory to explain the alternating interactions of the nitrogen lone pairs with respect to high-lying molecular orbitals and oscillating first ionization potentials. Thus, given the substantive differences between the electronic structure of the trimer with respect to the tetramer, the data from these two cases is insufficient to determine whether the electronic picture has converged.

Conclusions

Cyclic systems are best characterized by their molecular symmetry which lends itself to simple orbital interpretations of their electronic structure. These descriptions result directly from the highly polarized nature of the chemical bonding in the phosphonitrilic systems, which leads to equivalent P-N bond lengths. On a strictly geometric basis, the larger P-N-P bond angles for the tetramer and linear fragments causes the charge on their nitrogen sites to be localized to a greater extent.

As models for the phosphonitrilic polymer, serious deficiencies exist for both the trimer and small chain linear fragments in terms of both their electronic and molecular structure. For the phosphonitrilic trimer, the small P-N-P bond angles (when compared against the polymer) result in enhanced nitrogen-nitrogen interactions. Terminal group effects result in both bond alternation and non-symmetric charge distributions for the small-chain linear fragments. Tetrameric fluorophosphazene is the best candidate of the series considered, with the major difference being the wider P-N-P bond angle. Considerable differences exist between the trimer and tetramer, and convergence upon a band description of a number of states found in the polymer is not certain. Thus, it is not clear whether the electronic structure picture based upon fluorophosphonitrilic tetramer is a sufficiently accurate model for the fluorophosphonitrilic polymer.

Acknowledgments

The authors would like to thank the group members of the Molecular Interactions Task Force for stimulating discussions during the preparation of this manuscript. This work has been supported by the U.S. Department of Energy, Office of Basic Energy Sciences under contract DE-AC06-76-RLO 1830.

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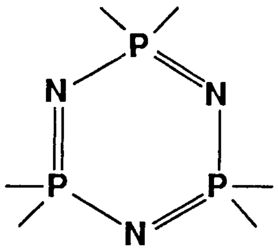
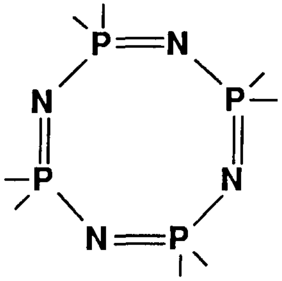
Table I. Geometric Parameters for the Cyclic Phosphonitrilic Molecules

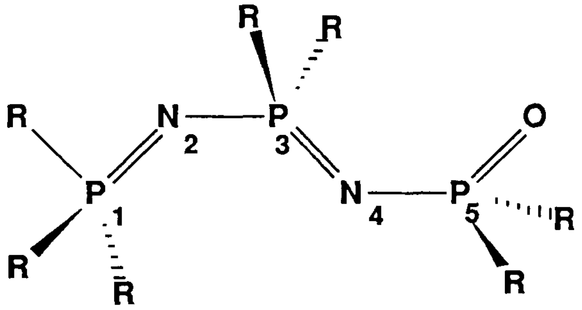


$(F_2P\text{-}N)_3$	$r_{P\text{-}N}$(Å)	$r_{P\text{-}F}$(Å)	P-N-P(°)	N-P-N(°)	F-P-F(°)
LP-21G*+	1.557	1.503	123.3	116.7	99.2
LP-31G*	1.574	1.578	122.1	117.9	98.1
3-21G*	1.557	1.533	126.8	113.2	99.1
6-31G*[6a]	1.560	1.546	127.2	112.8	99.1
experimental[15]	1.570	1.529	120.4	119.6	99.1



$(F_2P\text{-}N)_4$	$r_{P\text{-}N}$(Å)	$r_{P\text{-}F}$(Å)	P-N-P(°)	N-P-N(°)	F-P-F(°)
LP-21G*	1.538	1.506	148.6	121.4	99.3
LP-31G*	1.556	1.581	147.0	123.0	98.7
3-21G*	1.534	1.536	152.5	117.5	99.2
experimental[15]	1.507	1.514	147.2	122.7	99.9

Table II. Geometric Parameters (Å and °) for OP(R2)NP(R2)NPR3



	R=F LP-21g*+	R=F LP-31G*	R=H LP-21G*+
Bond Lengths (Å)			
P1-N2	1.50	1.51	1.55
P3-N2	1.59	1.61	1.61
P3-N4	1.52	1.53	1.55
P5-N4	1.59	1.62	1.61
PO	1.44	1.45	1.45
PF(average)	1.50	1.56	1.39
PF(range)	1.49-1.50	1.56-1.59	1.39-1.40
Bond Angles (°)			
P1-N2-P3	131.12	136.76	125.77
N2-P3-N4	114.02	115.42	112.25
P3-N4-P5	130.83	132.90	132.64

Table III - Mulliken Populations for Cyclic and Linear Phosphonitrilic Molecules

$(F_2P\text{-}N)_3$	P	N	F
3-21G*	13.3791	7.9414	9.3398
LP-21G*+	4.1046	5.7792	7.0581
LP-31G*	3.610	5.765	7.312

$(F_2P\text{-}N)_4$	P	N	F
3-21G*	13.3089	7.9822	9.3544
LP-21G*+	4.1023	5.7627	7.0675
LP-31G*+	3.5774	5.787	7.318

$OP(R_2)NP(R_2)NPR_3$

	P1	N2	P3	N4	P5	O	R (range)
R=F / LP-21G*+	4.181	5.734	4.116	5.818	4.463	6.217	7.05-7.10
R=H / LP-21G*+	3.979	5.705	3.903	5.796	4.216	6.250	1.23-1.10

Note: 'LP' designation denotes use of a pseudopotential. Core electrons were omitted from population analysis.

Figure Captions

Figure 1 - Molecular structure of cyclic trimer, tetramer, and linear phosphonitrilic compounds

Figure 2 - Molecular orbital contours (LP-21G*+, level=0.065) for the π' interactions in $(F_2PN)_4$. The ligand atom contributions have been omitted for clarity.

Figure 3 - Molecular orbital contours (LP-21G*+, level=0.05) for π and π' interactions in $(F_2PN)_3$, $(F_2PN)_4$ and $OP(F_2)NP(F_2)NPF_3$. The molecules are shown from above the plane of the P-N network and have the ligand atom contributions omitted for clarity.

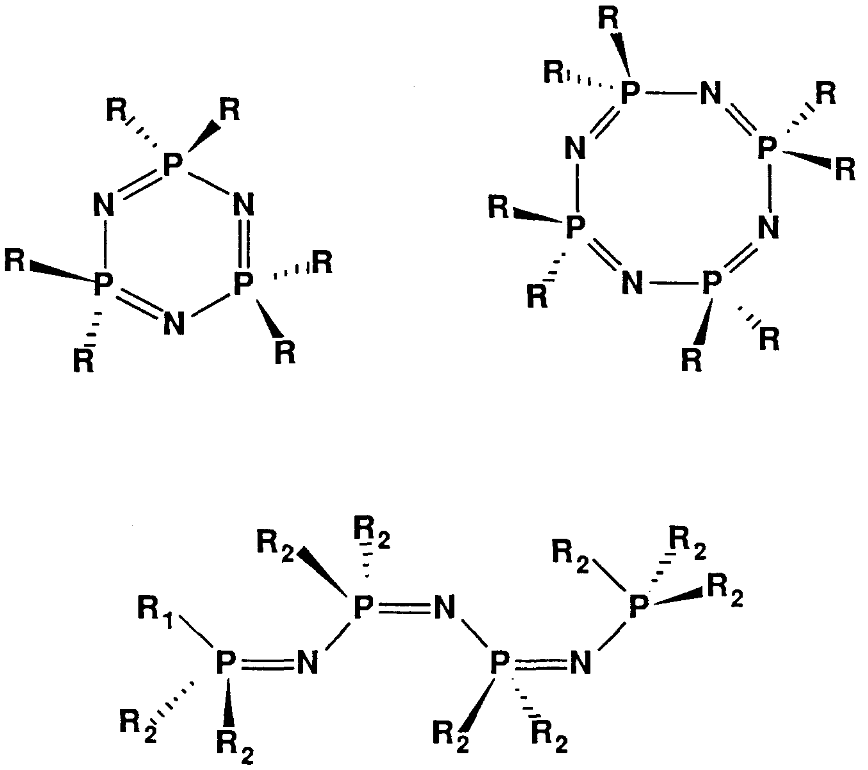


Figure 1 - Molecular Structure of Cyclic Trimer, Tetramer, and Linear Phosphonitrilic Compounds

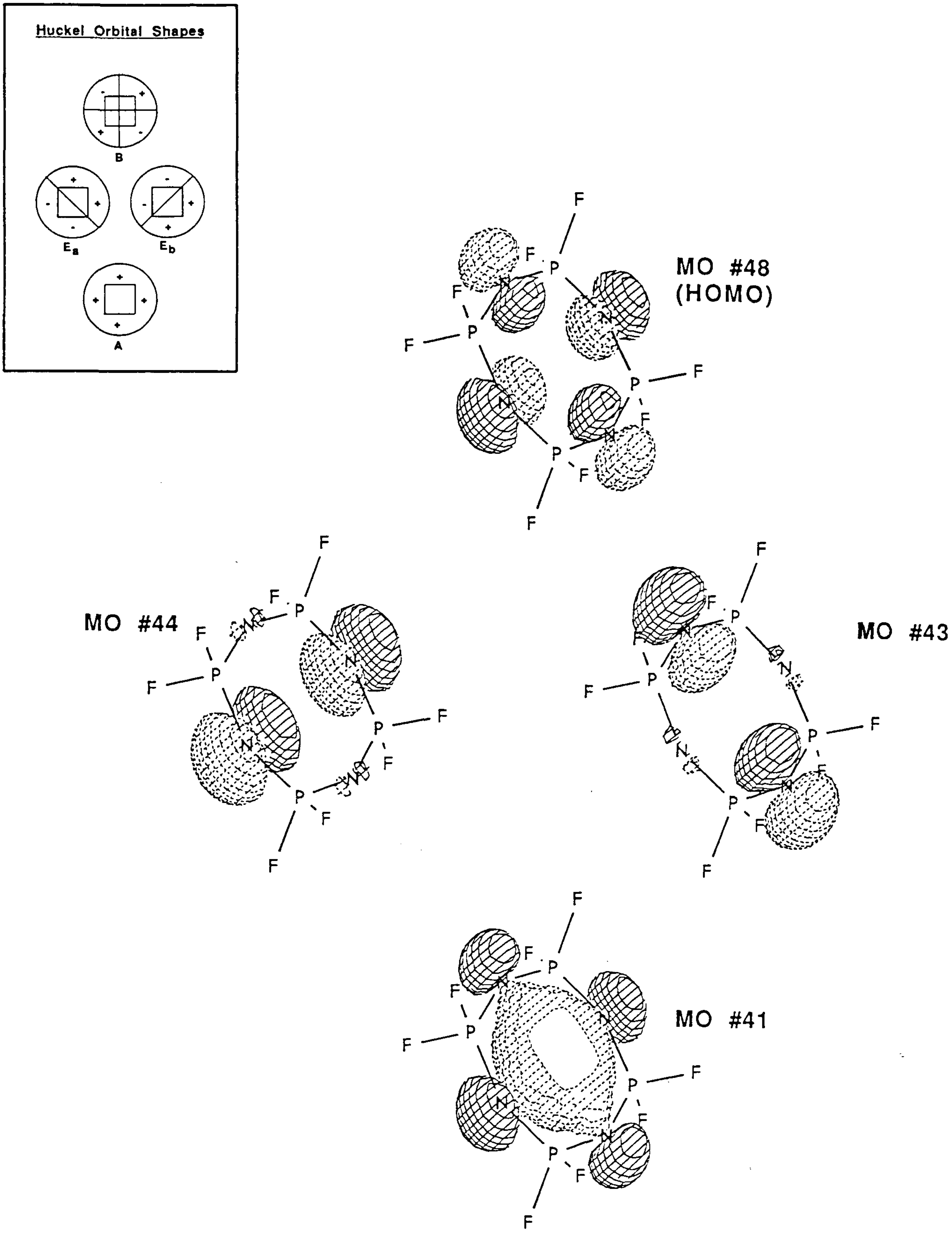


Figure 2

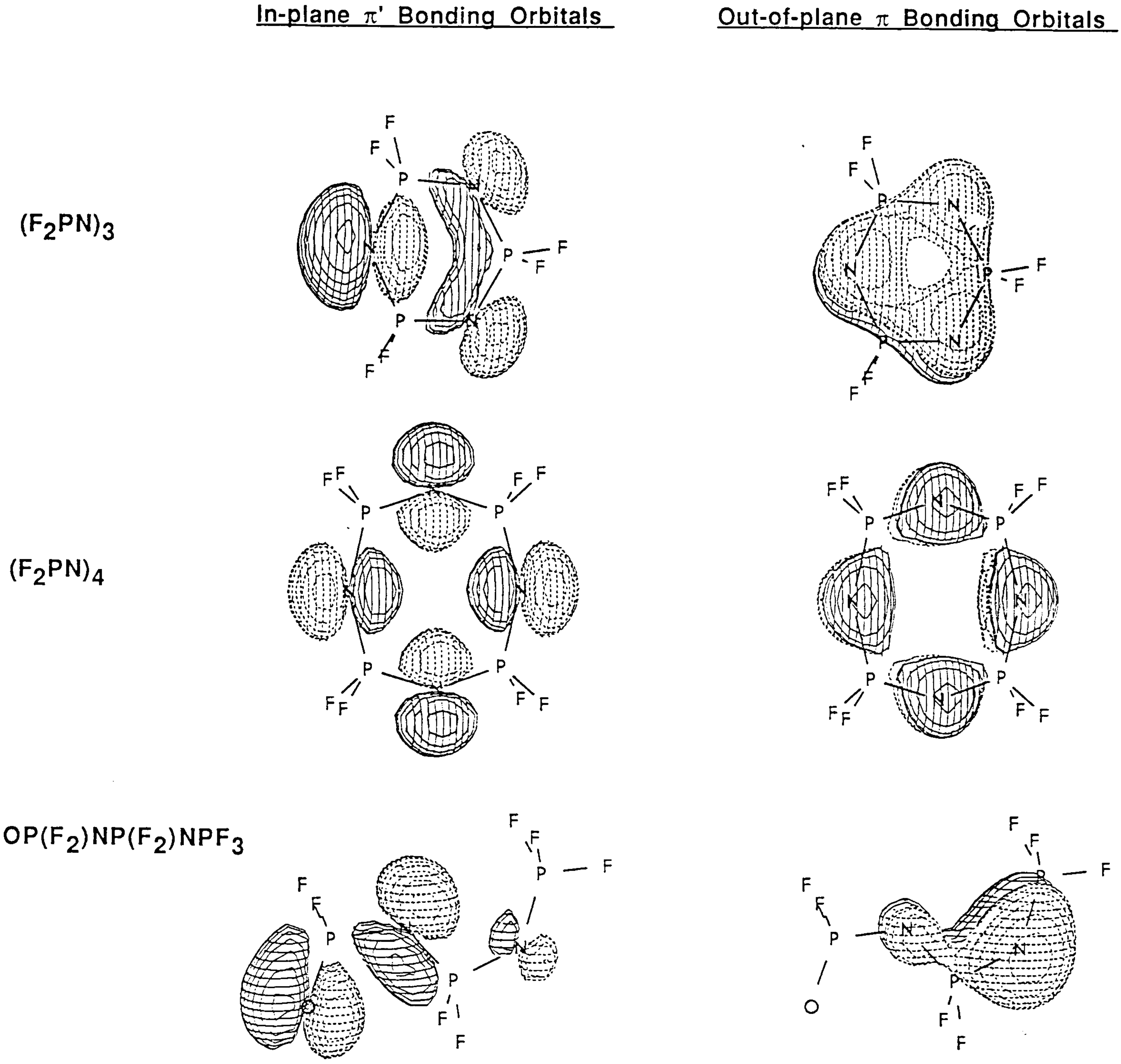

In-plane π' Bonding Orbitals
Out-of-plane π Bonding Orbitals
(F₂PN)₃
(F₂PN)₄
OP(F₂)NP(F₂)NPF₃
F
P
N
O

Figure 3