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# A Molecular Orbital Study of Monomeric Metaphosphate. Density Surfaces of Frontier Orbitals as a Tool in Assessing Reactivity

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**Abstract:** The geometry, bonding, charge distribution and reactivity of monomeric metaphosphate, a unique anionic Lewis acid, are explored with ab initio and semiempirical MO calculations. Comparison with calculations on the isostructural and congeneric nitrate anion places many of these features in perspective. Among the key findings are: (1) a large contribution from 2p–3d π bonding affects not only the P–O overlap population but also the bond length; (2) 2p–3p π bonding is significantly (but not drastically) diminished in $PO_3^-$ relative to 2p–2p π bonding in $NO_3^-$; (3) the electrophilic reactivity of this unstable intermediate may be ascribed to the presence of a low lying unoccupied acceptor orbital of σ symmetry which is nearly degenerate with the usual π* MO. Isodensity surface plots and plots of density in a plane are presented for the acceptor orbitals of $PO_3^-$ and $NO_3^-$; these allow a thorough qualitative perturbation theory analysis of their relative reactivities. Extensions of this analysis to other systems are suggested.

The monomeric metaphosphate anion is believed to be a key intermediate in many of the phosphoryl transfer reactions occurring in biological systems.[1] Both kinetic[2] and trapping[3] experiments have amply demonstrated a finite lifetime for this and closely related species; recently in fact, the preparation[4] and x-ray structure determination[5] of some highly substituted neutral analogues were reported.
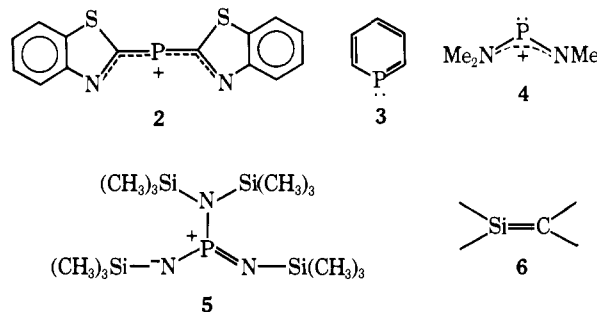
The use of theory to examine unstable species can provide accurate predictions of potential experimental results. In this work we probe the properties of this experimentally elusive anion via several molecular orbital techniques including an ab initio SCF–MO method using a Gaussian orbital basis set. Most importantly, examination of the low energy unoccupied MO's suggests some interesting aspects of the reactivity of $PO_3^-$ and its analogues, including the surprisingly strong electron acceptor properties of their σ systems. This is achieved with the aid of computer-generated three-dimensional probability density plots and exemplifies an approach of potentially broad applicability. While the major thrust of our work is based on qualitative examinations of the calculations, the derived geometry and charge distribution, although approximate, will allow better informed speculations on the conditions under which the intermediate is stabilized.

In addition to these properties, the calculations reveal the nature of the bonding in this unique anionic Lewis acid. Specifically, its electronic structure is examined for the importance of 2p–3p π bonding as illustrated by resonance structures **1**.



**1a**   **1b**   **1c**
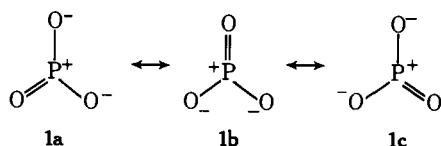
The origin of the apparent ineffectiveness of π bonds between second and third period elements has long been the subject

of theoretical[6] and experimental[7] interest. A recent surge of activity in this field has included the preparation of phosphamethine cyanines,[8] **2**, phosphabenzene,[9] **3**, bis(dimethyla-



mido)phosphinium cation, **4**,[10] a metaphosphordiimidic amide, **5**,[11] and the detection of a silaethylene, **6**, by low temperature infrared spectroscopy.[12] Semiempirical and ab initio MO calculations of systems **3**[13,14] and **6**[15,16] have also appeared and aid considerably in the correlation of spectroscopic data and relative reactivities. In this work the general problem of 2p–3p π bonding is probed by direct comparison of the bonding in $PO_3^-$ with the results of similar calculations on the congeneric $NO_3^-$.

The system also provides a new environment for assessing the importance of d-orbital participation. This, too, has been the subject of much recent effort and controversy with cases being made for[17] and against[18] depending on the system studied or the criterion chosen for judgement. It might be expected that for our system the electron deficiency of the central phosphorus could cause a contraction of d orbitals leading to substantial π interaction with unshared electron pairs on the oxygens (structures **7**). Examination of d-orbital effects in nitrate ion provides a good frame of reference as well as an
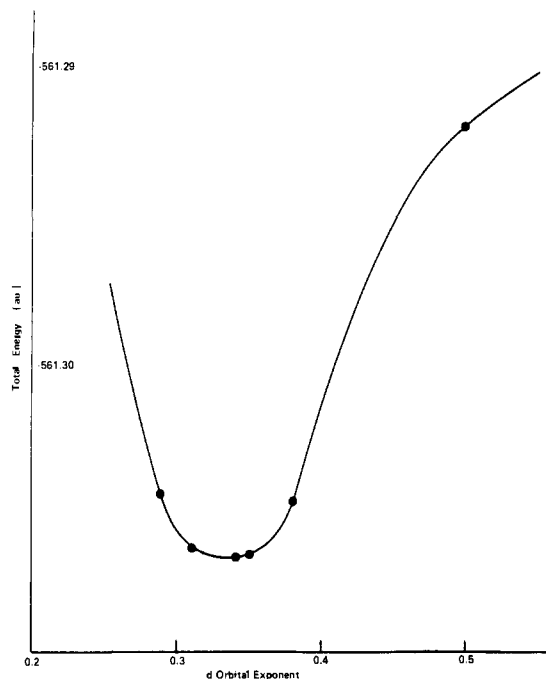
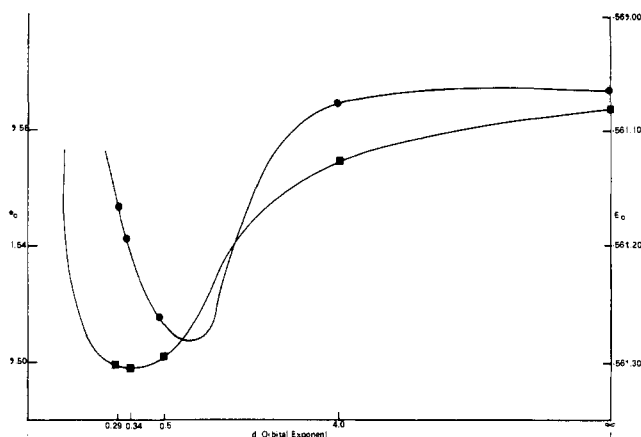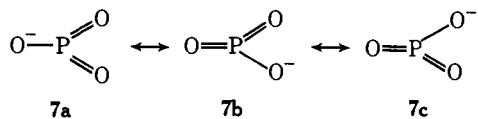Figure 1. Optimization of d-orbital exponent.



Figure 2. Minimum energy P–O distances (●) and their corresponding energies (■) as a function of d-orbital exponent (logarithmic abscissa).



interesting case for the importance of polarization in second period elements.

## Calculational Details

Ab initio SCF–MO calculations were performed on an IBM 370/158 computer using the program IBMOL-V[19] with basis sets of Gaussian orbitals. For phosphorus, the primary basis consisted of 9s, five sets of p, and one set of d primitive Gaussians, which were contracted to sets of 6s, 3p, and 1d. The primary nitrogen basis consisted of 6s, 3p, and 1d contracted to 3s, 2p, and 1d. The oxygen basis followed the same scheme as nitrogen but did not contain a d set. The s and p orbital exponents are from the compilation of Huzinaga.[20] The d orbital exponent on nitrogen (0.95) is obtained by an extrapolation procedure suggested by Roos and Siegbahn.[21] The N–O bond distance was set at the experimental value of 1.22 Å.[22] The P–O bond distance and the value of the exponent of the d set
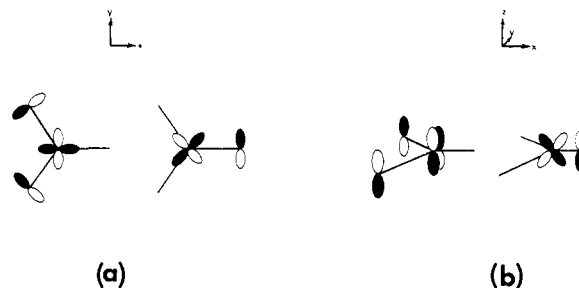


Figure 3. (a) In-plane (E′) d–p π bond. (b) Perpendicular (E″) d–p π bond.

on phosphorus were obtained by iterative minimization of the total energy with respect to both these parameters (vide infra). Unless stated otherwise, results refer to the ab initio calculations.

Semiempirical calculations were performed using the program ICON, Version 8,[23] for the extended Huckel[24] method and CNINDO[25] for the CNDO/2[26] method.

A new approach for the generation of three-dimensional isodensity surfaces was developed for this work. Briefly, it involves calculation of distances in the direction of the line of sight to the surface from a plane safely in front of it. These distances are determined at regular intervals of the horizontal and vertical dimensions of the plane. This generates a small matrix which is then used to initiate the same search procedure for an expanded matrix to give the resolution desired. The "hidden line problem"[27] is thus circumvented and computation is not wasted calculating points which will not be used. Each of these matrix elements is then transformed to the coordinate system of the molecule (which has been rotated with respect to the plotter coordinates to enhance perspective). The superposition of two-dimensional contour plots in each of these three molecular Cartesian coordinates yields the final product. The contour plotting subroutine was kindly provided by N. Timofeeff of the SUNY at Binghamton Department of Geography.

The program for generating plots of electron density in a plane is a standard one and was also provided by Professor Timofeeff. A Calcomp Model 563 plotter was used to produce all the graphics.

## Results and Discussion

**d-Orbital Effects.** Since the value of the optimal d-orbital exponent ($\alpha_d$) in $PO_3^-$ is a function of P–O distance (vide infra) a reasonable guess of 0.29 was made in order to initiate the geometry optimization. The P–O distance thus derived (1.554 Å) was then used to determine a new $\alpha_d$ (Figure 1) and this iterative procedure continued. The final P–O distance is 1.543 Å and the exponent is 0.34 with convergence after only two cycles. These calculations are summarized in Figure 2.

One of the most striking features of Figure 2 is the manner in which the P–O bond distance decreases as $\alpha_d$ increases in the vicinity of the energy minimum. This indicates that the oxygens are following the d orbitals as they shrink in toward the P nucleus. For very large values of $\alpha_d$ this interaction ceases due to the dominance of other forces (i.e., electron–electron and nuclear–nuclear repulsions) and the P–O bond relaxes to its length in the absence of d orbitals (1.595 Å). This tendency of the bond lengths to follow the d-orbital size may prove to be a general criterion for the importance of d orbitals in bonding.

A more traditional criterion is the response of the Mulliken population analysis[28] to the presence of d orbitals. In particular, 1E″ and 5E′ are oxygen lone pair molecular orbitals of the proper symmetries ("local" π symmetry for E′) for d–p π

**Table I.** Overlap Population Analysis

| | PO₃⁻ | PO₃⁻ (−d) | NO₃⁻ | NO₃⁻ (−d) |
|---|---|---|---|---|
| $d\pi$–$p\pi$ population[a,b] | 0.449 | | 0.100 | |
| $p\pi$–$p\pi$ population[a] | 0.163 | 0.167 | 0.181 | 0.181 |
| $\sigma$ population[a] | 1.008 | 0.566 | 0.702 | 0.645 |
| Total population[a] | 1.362 | 0.733 | 0.925 | 0.826 |
| Charge on central atom | +1.35 | +1.48 | +0.25 | +0.47 |

[a] Overlap population per bond. [b] Sum of d–p populations for 1E″ and the highest energy MO of E′ symmetry.

**Table II.** Orbital Energies (au)

| | NO₃⁻ | NO₃⁻ (−d)[a] | PO₃⁻ | PO₃⁻ (−d)[a] |
|---|---|---|---|---|
| A₁′* | 0.7982 | 0.7884 | 0.4119 | 0.4288 |
| A₂″* | 0.4298 | 0.4031 | 0.3902 | 0.3355 |
| A₂′ | −0.1617 | −0.1760 | −0.1981 | −0.2098 |
| E″ | −0.1801 | −0.1811 | −0.2233 | −0.2069 |
| E′ | −0.2340 | −0.2324 | −0.2451 | −0.2219 |
| E′ | −0.4462 | −0.4559 | −0.3371 | −0.3413 |
| A₂″ | −0.5008 | −0.5207 | −0.3417 | −0.3662 |
| A₁′ | −0.5268 | −0.5335 | −0.4576 | −0.4654 |
| E′ | −1.1046 | −1.1217 | −1.0190 | −1.0340 |
| A′ | −1.3827 | −1.3998 | −1.1169 | −1.1461 |
| E′ | | | −5.2815 | −5.3872 |
| A₂″ | | | −5.2820 | −5.3852 |
| A₁′ | −15.5912 | −15.6200 | −7.5154 | −7.6206 |
| A₁′ | −20.2331 | −20.2465 | −20.2558 | −20.2403 |
| E′ | −20.2335 | −20.2468 | −20.2560 | −20.2404 |
| A′ | | | −79.7078 | −79.8018 |
| Total energy | −277.3762 | −277.2708 | −561.3076 | −561.0724 |

[a] d orbital removed from basis.

bonding (Figure 3) and contribute a d–p overlap population for one P–O bond of 0.191 and 0.258, respectively. While these values do seem quite large in an absolute sense, it was felt that their significance could be assessed most effectively by comparison with the congeneric nitrate anion; here no special d-orbital effect on bonding is to be expected. Indeed the d–p overlap populations for the N–O bond are only 0.040 in the 1E″ MO and 0.060 in the 4E′ MO.

The gross populations are also very sensitive to d orbitals in PO₃⁻ while relatively insensitive in NO₃⁻ according to the result summarized in Table I. For the calculation in which the d orbitals were removed from the phosphorus basis, all the populations are remarkably lowered with a decrease of over 0.6 electron in the total population per bond. This is to be contrasted with the drop of 0.1 in the NO₃⁻ case.[29] These comparisons with NO₃⁻ argue against the possibility that the d orbitals are simply compensating for an insufficient number of p and s functions in our admittedly moderately sized basis set. Furthermore, the d-orbital effects are even more pronounced in the semiempirical calculations.

The addition of d orbitals to a basis set will of necessity lower the calculated total energy of any system. As pointed out by Coulson,[30] it is vital, therefore, to discriminate between this "polarization" effect and actual involvement of d orbitals in bonding. The penetrating studies by Wolfe et al.[18] on the interaction of sulfur or phosphorus with an adjacent carbanionic center led to conformational potential surfaces totally "irrelevant" to the p–d π-bonding concept which had so commonly been used to rationalize experimental observations. This insensitivity of the geometry to d-orbital inclusion was complemented by only minor changes in overlap populations. It is clear that these criteria lead to opposite conclusions when applied to PO₃⁻; both the bond distance and the population analysis are sensitive to d-orbital participation.

This contrast in the behavior of the two systems can be rationalized with the help of perturbation theory. The electronegative oxygen can inductively lower the energy of the d orbitals on phosphorus. A withdrawal of $\sigma$ electrons by oxygen will, conversely, raise the energy of its lone pair electrons because of electron–electron repulsion. The net effect of these first-order perturbations is to close the energy gap between the oxygen p orbitals and the phosphorus d orbitals. The second-order mixing of these levels (being inversely proportional to the size of the energy gap) is thus enhanced, strengthening the 2p–3d π bond between oxygen and phosphorus. One can even envisage a series of higher order effects whereby this electron transfer increases the effective electronegativity of the oxygen, decreasing the energy gap, and thus increasing the (2p–3d) coupling still further. This is similar to the back-bonding model often used to rationalize transition metal bonding to ligands with both $\sigma$-donor and $\pi$-acceptor properties. The cooperative action of $\sigma$ withdrawal and $\pi$ donation by oxygen is absent in the sulfur–carbon systems treated by Wolfe. Carbon (especially with a formal negative charge) does not withdraw $\sigma$ electrons from sulfur; it appears that such inductive withdrawal may be a necessary prerequisite for effective 2p–3d π conjugation.

**2p–3p π Bonding.** As expected there is some indication of weakened 2p–3p π bonding in PO₃⁻ relative to NO₃⁻. The molecular orbitals corresponding to this bond are 1A₂″ in NO₃⁻ and 2A₂″ in PO₃⁻. As is seen from Figure 4 and Table II the energy of the π electrons is considerably higher in the latter. The overlap populations are 0.181 and 0.163 electron per bond, respectively; these are not terribly different but again indicate a weakened π bond in PO₃⁻. The 2p–3p overlap populations in both anions are quite insensitive to the presence of d orbitals in the basis sets (cf. Table I).

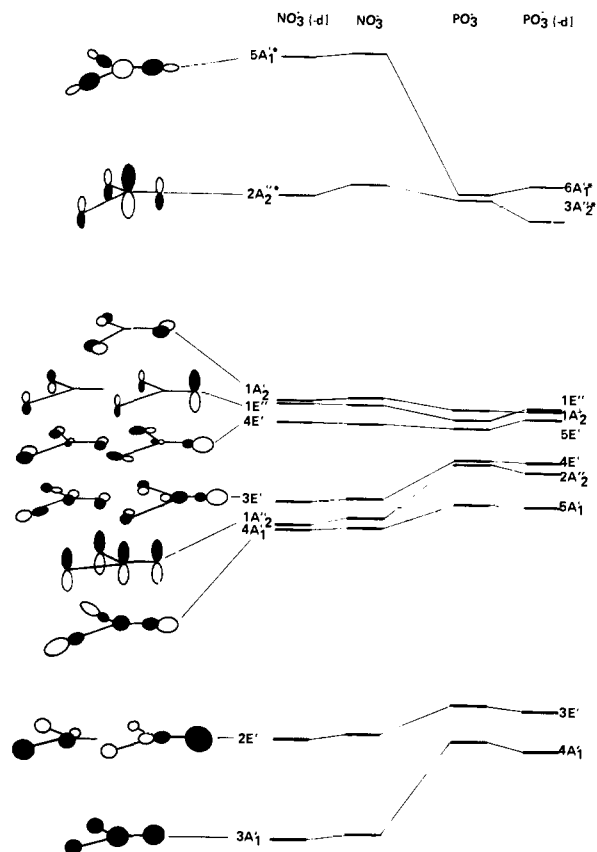On the other hand, can one be completely satisfied that this

**Figure 4.** Valence shell molecular orbital energy levels for $PO_3^-$ and $NO_3^-$ with the full and the d-orbital depleted (−d) basis sets.



**Figure 5.** Interaction diagram for approach of an occupied donor orbital toward the unoccupied acceptor orbitals of $PO_3^-$.



**Figure 6.** Probability density of the $2A_2''$ ($\pi^*$) MO of nitrate in a plane containing one oxygen and the nitrogen and perpendicular to the molecular plane; the $x$ and $z$ dimensions are 10 au each and the resolution is 100 points/au².

weakening of the 2p-3p $\pi$ component of the P-O bond is sufficient to explain the instability of $PO_3^-$? After all the 2p-2p $\pi$ bond of ethylene is less stable than the corresponding $\sigma$ bond in polyethylene; yet, polymerization requires thermal or catalytic activation. $PO_3^-$ adds water or polymerizes spontaneously, while $NO_3^-$ is absolutely inert. Indeed, when the entire P-O bond is examined its relative stability becomes even more ambiguous. The total overlap population is much greater for the P-O bond than for the N-O bond in $NO_3^-$ (Table I); this arises from d-orbital participation as already discussed. A recent calculation on $(HO)_3PO^{31}$ with a similar basis set[32] allows comparison of the P-O bond in $PO_3^-$ with an ordinary phosphoryl linkage. The phosphoryl bond contains 0.2 electron less, despite its status as among the strongest of single bonds; although this is not an ideal comparison, it again indicates that 2p-3p $\pi$ bonding is contributing significantly in $PO_3^-$. These troublesome inconsistencies led to a search for a more subtle source of the reactivity of monomeric metaphosphate.

**Reactivity.**[33] Electrophilicity centered at the third period element is a feature quite common to 2p-3p $\pi$-bonded systems. $PO_3^-$ is rather unique in its role as an anionic Lewis acid. Because of its negative charge, $PO_3^-$ falls clearly into the class of "soft"[34] or "orbital controlled"[35] electrophiles. A "charge controlled"[35] process is further negated by the observation that $H_3PO_4$, while a much weaker electrophile, bears a larger positive charge at phosphorus (+1.76[31] vs. +1.35 from population analyses).

Klopman's[35] treatment for orbital controlled reactivity is based on the size of the interaction between occupied (donor) orbitals of the nucleophile and unoccupied (acceptor) orbitals of the electrophile. According to perturbation theory, this interaction is proportional to the squared matrix element coupling the donor and acceptor levels and inversely proportional to the difference in their energies. The latter accounts for the
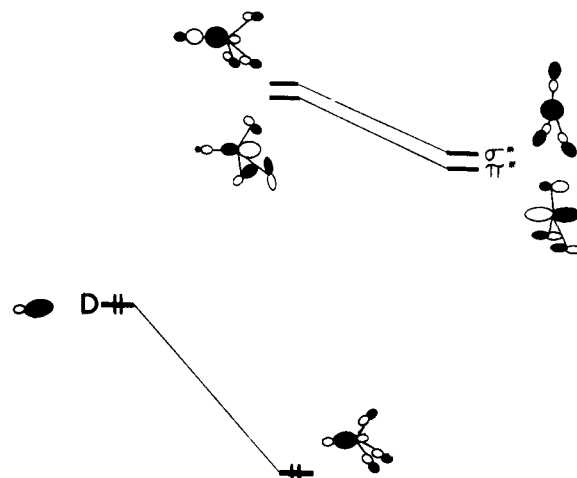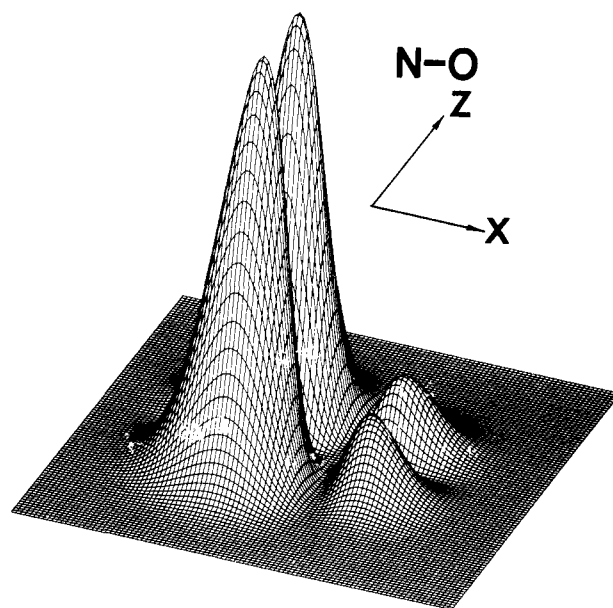
importance of the lowest energy acceptor orbitals in determining electrophilicity. The matrix element is approximately proportional to the overlap of the interacting orbitals. It follows that the electrophilic center in a molecule is at the atom with the largest acceptor orbital probability density; the more highly localized this density, the greater the "electron deficiency" at this center. But localization does not imply concentration. In fact, a diffuse acceptor orbital will allow substantial overlap with an approaching donor orbital at distances too large for appreciable closed shell repulsion.

These considerations can be qualitatively applied to assess the electrophilic reactivity of $PO_3^-$ with $NO_3^-$ as a reference. For ordinary $\pi$ systems like $NO_3^-$ the acceptor orbital is always an antibonding $\pi^*$, the lowest $\sigma^*$ level being energetically inaccessible to the donor electrons. This is clearly the situation for $NO_3^-$ (Figure 4 and Table II), with the unoccupied $2A_2''$ level well below the $5A_1'$ level. A dramatic lowering of the $\sigma^*$ level in $PO_3^-$ is pictured in Figure 4, placing it only 0.02 hartree above the $\pi^*$ level. This lowering is found for all the calculational methods used; the CNDO results actually place the $6A_1'$ ($\sigma^*$) orbital below the $3A_2''$ ($\pi^*$) orbital in $PO_3^-$. The
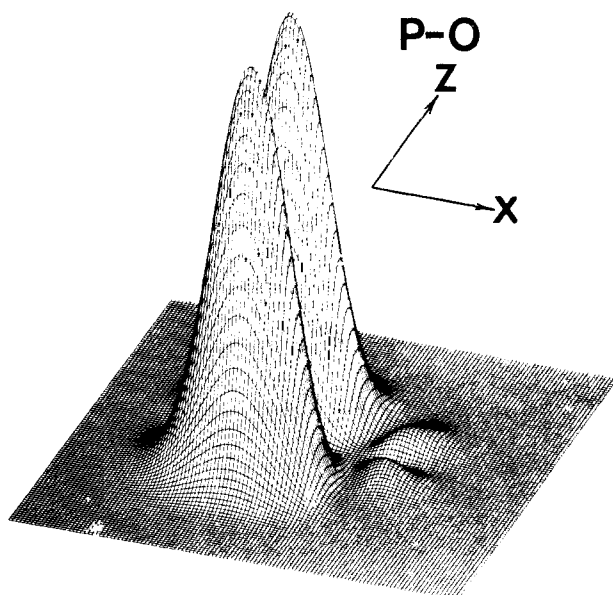
Figure 7. Probability density of the $3A_2''$ ($\pi*$) MO of metaphosphate. The $x$ and $z$ dimensions are 12 au each and the resolution is 100 points/au$^2$.
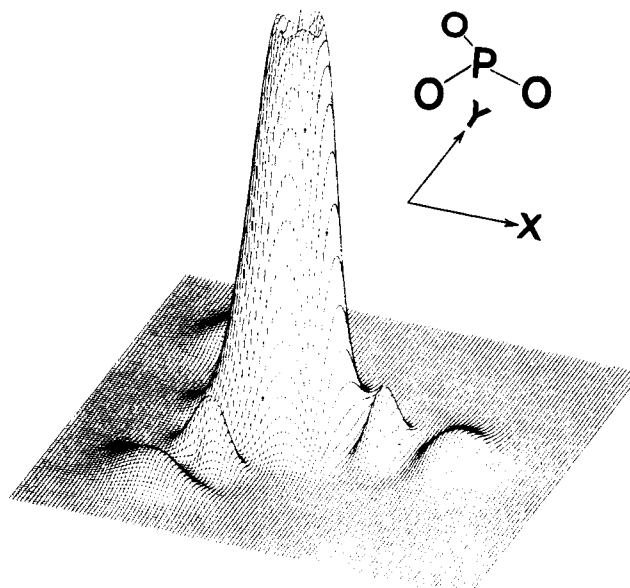


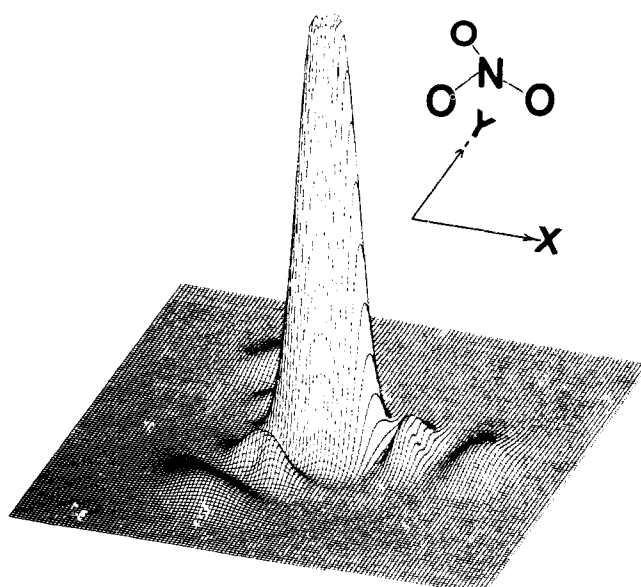Figure 9. The $6A_1'$ ($\sigma*$) MO of $PO_3^-$ as in Figure 8.



Figure 8. Probability density of the $5A_1'$ ($\sigma*$) MO of $NO_3^-$ in the molecular plane. The $x$ and $y$ dimensions are 12 au each and the resolution is 100 points/au$^2$.
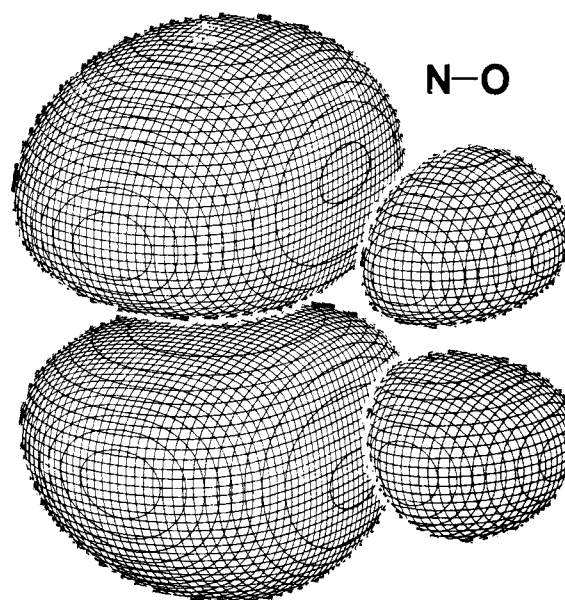


Figure 10. The isodensity surface at a probability of 0.01 au$^{-3}$ for the $\pi*$ MO of $NO_3^-$ (only one N–O bond is shown).

"reality" of these virtual orbital energies was further checked by examining the two lowest energy doubly excited configurations;[36] these correspond to excitation of the $1A_2'$ electrons to the $6A_1'$ and $3A_2''$ levels, respectively. These configurations are only 4 × 10$^{-3}$ hartree apart! Thus, the near degeneracy of the $6A_1'*$ and $3A_2''*$ orbitals allows both to contribute to the electrophilic reactivity of $PO_3^-$. The symmetry breaking perturbation of an approaching donor orbital will allow effective mixing of these MO's leading ultimately to a strongly bonding occupied orbital and a pair of unoccupied antibonding MO's (Figure 5). The theory can be stretched, therefore, to account for the stability of the tetrahedral product as well as the reactivity of the trigonal reactant.

We have dealt so far only with the inverse relation of reactivity with acceptor orbital energy. Figures 6 through 13 allow us to compare the overlap of the acceptor orbitals in monomeric metaphosphate and in nitrate with a hypothetical donor (the nitrate $\sigma*$ level is eliminated as an effective acceptor because

of its high energy; it is included only for comparison). Figures 6, 7, 8, and 9 are maps of the total probability density in a plane; Figures 10, 11, 12, and 13 are the three-dimensional surfaces at which the probability density is 0.01 (au$^{-3}$). These different representations of the orbital shapes provide complementary rather than redundant assessments of reactivity. The following conclusions can be drawn:

(1) Figures 6 through 13 clearly indicate that the acceptor orbitals are much more localized on the central atom in $PO_3^-$. This leads to a larger value of the matrix element coupling the acceptor orbitals to a donor orbital approaching the phosphorus (i.e., lowered activation enthalpy).

(2) Figures 6 through 9 indicate that the density decays more slowly for $PO_3^-$ in both the $\pi$ and the $\sigma$ orbitals. Thus, a donor orbital will begin to interact at relatively large distances with minimal closed shell (i.e., steric) repulsions between nucleophile and electrophile. This manifests itself in both a higher entropy and lower enthalpy of activation for $PO_3^-$.

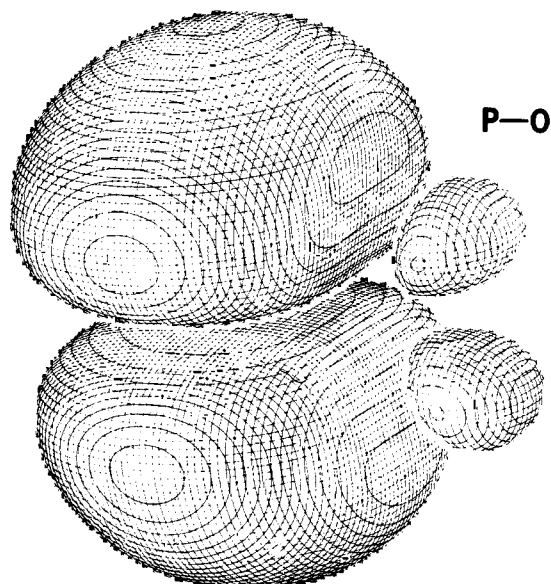(3) Figures 11 and 13 indicate that the preferred mode of

P—O

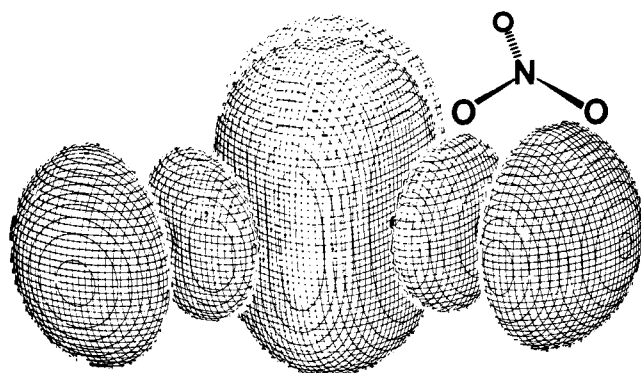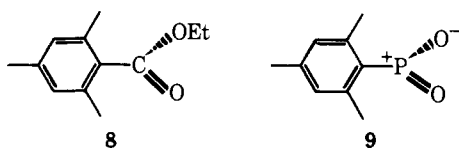Figure 11. The $\pi^*$ isodensity surface of $PO_3^-$ (as is Figure 10).



Figure 12. The $\sigma^*$ isodensity surface of $NO_3^-$ (0.01 au$^{-3}$).

approach of a nucleophile is along a path perpendicular to the molecular plane. This is the usual case for ordinary $\pi$ systems and has been recently supported by several calculations of potential hypersurfaces for such reactions.[37] There is a key difference, however: second period $\pi$ systems have only their $\pi^*$ MO's to rely upon for electrophilicity; an in-plane approach is absolutely precluded since the molecular plane contains zero acceptor density. $PO_3^-$ has its $\sigma^*$ level available to accept electrons in the molecular plane (Figure 13). While this is not the most preferred mode of approach, its greater availability and that of intermediate paths should provide a shallower potential surface and a more favorable activation entropy than an analogous reaction involving a second period $\pi$ electrophile. This difference might also manifest itself in an insensitivity to steric effects. For example, although ethyl mesitoate, **8**, cannot undergo saponification via the normal addition–elimination mechanism, phosphonomesitylene, **9**, polymerizes even at dry ice temperatures.[38]



**8**                    **9**

To summarize, we have shown that a careful examination of the unoccupied low energy orbitals of $PO_3^-$ and comparison with the congeneric $NO_3^-$ can provide insight into the origin
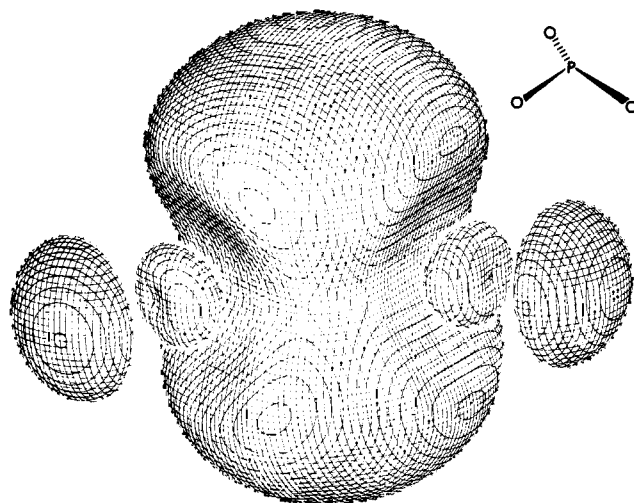


Figure 13. The $\sigma^*$ isodensity surface of $PO_3^-$ (0.01 au$^{-3}$).

of the former's reactivity. It should be noted that this can be accomplished without recourse to the ab initio calculations. We have used the extended Hückel[24] and CNDO/2[26] methods to generate the molecular orbitals of both systems. While geometries and charge distributions are poor, these methods virtually duplicate the general shapes and energy level spacings of the ab initio MO's. There is evidence for the generality of this particular success of the semiempirical methods.[39] It thus becomes possible to extend the detailed analysis of orbital shapes to more complex systems such as delocalized nucleophiles,[40] transition metal complexes,[41] carbonium ions,[42] or cycloaddends.[43]

Indeed, extension of the analysis to other 3p–2p $\pi$ systems has been initiated with semiempirical calculations on $SO_3$ (isoelectronic with $PO_3^-$), thioformaldehyde, and silaethylene. Preliminary results are completely consistent with the finding of a $\sigma$ component in the reactivity of $PO_3^-$. For example, according to an extended Hückel calculation of silaethylene,[44] the lowest unoccupied $\sigma$ level is only 1.2 eV above the lowest unoccupied $\pi$ level; for ethylene the difference is 11.1 eV. Furthermore, these $\pi^*$ and $\sigma^*$ orbitals in silaethylene are 90 and 92% localized on silicon, respectively. The corresponding figures for carbon in ethylene are 50 and 24%, respectively. Further investigation is necessary to establish the complete generality of this phenomenon for 2p–3p $\pi$-bonded systems.

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# Some Observations on the ESCA Spectra of Plastocyanins

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**Abstract:** The core level spectra of a number of plastocyanins have been investigated by means of ESCA. The higher binding energy component in the $S_{2p}$ levels observed for particular samples is shown to arise from extraneous sulfur present in a high oxidation state rather than from coordination of sulfur-containing amino acids to the metal ion, as has previously been claimed.

Solomon et al.[2a] have recently reported the results of an ESCA study on the "blue" copper protein plastocyanin. A single peak at 164 eV binding energy in the $S_{2p}$ region of the spectrum was observed for the apoprotein, while an additional peak shifted by about 5 eV to higher binding energy was observed in that of the Cu and Co proteins. The bean (*Phaseolus vulgaris*) plastocyanin studied, contains two methionine and one cysteine[12] residues,[2b] and since the ratio of the intensity of the $S_{2p}$ peak at higher binding energy to that at the lower binding energy component was about 1:2, the spectra were interpreted as indicating that one of the sulfur atoms, probably

that of the single cysteine residue, binds to the metal atom in the plastocyanin.

We have used the ESCA technique to examine a number of proteins including the copper proteins, plastocyanin, and hemocyanin; our results and those of a number of previously published studies lead us to suggest that the higher binding energy component is due to sulfate or some other form of oxidized sulfur present in the metalloprotein preparations. ESCA is essentially a surface technique (the mean free paths through a solid of electrons photoemitted by Al or Mg $K\alpha$ x rays being of the order of a few tens of ångströms or less). Fur-