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An Ab Initio Nuclear Magnetic Resonance and Atoms-in-Molecules Study of the PO Bond in Phosphine Oxides

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Abstract: Ab initio nuclear magnetic resonance (NMR) calculations on the effect of correlation on phosphorus shielding in the phosphine oxides clearly suggest the absence of conventional multiple bonding in the PO bond. Atoms-in-molecules (AIM) studies that yield AIM-based localized molecular orbitals indicate one highly polarized σ bond plus strong back-bonding of the oxygen π orbitals, a picture consistent with a number of prior investigations. While it has been argued that the strong character of the PO bond in the phosphine oxides is highlighted best by the $R_3P{=}O$ formula, the present study indicates that the situation is better pictured as $R_3P^+{-}O^-$.

Introduction

The nature of the bonding in the PO bond of phosphine oxides (R_3PO) has been of great interest for many years; Gilheany[1,2] has written several clear and exhaustive reviews on both the experimental and theoretical aspects of these unusual molecules. Both experiment and ab initio calculations generally agree that the PO bond is strong, polar, and short, as short as conventional PO double bonds. The role of d functions as polarization functions rather than primary valence orbitals is now well established, the work of Magnusson[3,4] cited as being particularly illuminating. Where differences arise is in the *interpretation* of the bond based on different approaches.

What Gilheany refers to as the “traditional” view involving one σ and two π back-bonds is thoroughly reviewed and discussed in the paper by Reed and Schleyer.[5] Taking H_3PO as an example, the bonding is viewed as a donor−acceptor interaction with superimposed back-bonding of the oxygen π orbitals with the degenerate (e-symmetry) antibonding orbitals on the H_3P moiety, this latter type of interaction called negative hyperconjugation by Schleyer and Kos.[6] Gordon and co-workers[7−9] picture the bond as involving a single σ bond and three π back-bonds, basically a strong ionic interaction with polarization of the charge on oxygen. This description is derived from the energy-localized orbitals[10−12] (those orbitals which minimize interorbital repulsion) that together involve three equivalent PH bonds, one strong PO σ bond, and three equivalent oxygen orbitals characterized primarily as lone pairs polarized toward phosphorus and staggered with respect to the PR bonds.

Using the Boys localization scheme[13,14] (those orbitals which maximize the sum of the squares of the distances between the orbital centroids) Guest et al.[15] and later Wallmeier and Kutzelnigg[16] found the expected three PH bond orbitals, a single lone pair orbital on oxygen pointing *away* from the H_3P group in H_3PO, and three bent or banana bonds strongly polarized toward oxygen. This was also the picture found by Schmidt, Yabushita, and Gordon,[7] who carried out both energy and Boys localization schemes but choose to accept the former as a proper description of the bonding in H_3PO.

Still another partitioning approach is that using a natural population analysis as illustrated in the work of Reed and Schleyer.[5] This method is based on natural localized molecular orbitals[17,18] derived from a natural bond order analysis.[19] Reed and Schleyer concluded that the bonding was dominated by ionic interactions and negative hyperconjugation. As have others, they concluded that d-orbitals do play an essential role in polarizing the valence orbitals of the central atom both to enhance bonding and to diminish antibonding interactions. Strong ionic bonding was exhibited by large positive charges on the central atom on the R_3AY species they investigated.

The fact that three quite different orbital schemes arise from basically the same Hartree−Fock (HF) density points out the arbitrary nature of this subdivision of charge; any and all unitary transformations of the Hartree−Fock canonical molecular orbitals are valid, and it is clearly a matter of chemical intuition and taste that leads one to prefer one picture over another in anticipation of a better description of the molecule as one moves to post-Hartree−Fock levels.

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The approximate generalized valence bond (GVB-SOPP) method also leads to three bent bonds between P and O in H_3PO.[20] Although a set of unique orbitals is given by the valence bond approach, the full GVB and approximate GVB-SOPP can yield different descriptions of the bonds.[21,22] As is the case with the various transformations of the Hartree−Fock density, the value of one picture relative to another is in its conceptual utility. However, Shultz and Messmer[22] point out that when the more robust GVB approach is taken bent bonds generally result as opposed to the $\sigma-\pi$ picture. Since Hartree−Fock theory is a limiting case of the generalized valence bond approach, this is a convincing argument for this picture.

It is, of course, desirable where possible to study bonding situations with approaches based on experimental observations. This is the case in the work of Rai and Symons,[23] who studied radicals of the type $R_3PX^\bullet$ having an unpaired electron in a $p-\pi$ orbital on the X ligand. In their ESR studies of the uncomplexed $PhPS^{\bullet+}$ radical cation they found the ^{31}P hyperfine coupling to be very small (about 22 G) and almost isotropic. From this they concluded that the unpaired spin is basically localized in the ligand orbital with the phosphorus coupling arising from spin polarization of the PX σ electrons, much as in the case of the ethyl radical. The ESR spectra for ethyl and related radicals have been interpreted in terms of hyperconjugation ($\sigma-\pi$ delocalization).[24,25] Rai and Symons go on to conclude that in the case of the R_3PX molecules the alternative is true, namely reverse hyperconjugation (negative hyperconjugation) involving donation from the π unit into antibonding R_3P orbitals.

Nuclear magnetic resonance (NMR) is one of the more important probes of electronic structure. Currently we are able to calculate NMR chemical shieldings rather accurately, to approximately 3−4% of a nucleus' shielding range in the Hartree−Fock approach and somewhat better using second-order Møller−Plesset (MP2) and more advanced levels of theory.[26−28] While Hartree−Fock theory tends to yield shieldings that are too low (too paramagnetic), the inclusion of correlation in MP2 is generally known to overestimate the correction to this effect.[29−32] The corrections due to correlation are especially pronounced when conventional multiple bonds are present; π orbitals in self-consistent-field theory generally lie closer to the HOMO-LUMO gap than do σ orbitals and are thus more likely to be involved in mixing with the virtual orbitals and to thus give rise to significant changes in the electronic structure when correlation is included. We make use of this fact here in analyzing the Hartree−Fock and MP2 contributions to chemical shielding in phosphine oxides and conventional phosphorus compounds to show that the multiple bonding in the oxides is *not* of the conventional type. In addition, we have carried out an atoms-in-molecules (AIM) treatment[33,34] with the associated atomic overlap matrix covalent bond order defined by Cioslowski and Mixon[35] on a variety of phosphorus compounds in an effort to shed more light on the unusual PO bond in the phosphine oxides. The electron density is clearly one of the most important observables defining molecular structure so that a partitioning of charge and a bond order definition based on it seem most appropriate.

Theoretical Methods

The structures employed in the present study were all optimized at the MP2 (frozen core) level of theory with the 6-31+G(d, p) basis set[36] as implemented in the Gaussian 94 program.[37] Diffuse functions were included on the heavy atoms since significant transfer of charge occurs in many of the species. Unless otherwise noted, the AIM calculations were done at the restricted Hartree−Fock level with use of the MP2 optimized geometries. While the structure optimizations employed only a single set of d polarization functions for heavy atoms (and a single set of p functions for hydrogen), the chemical shielding calculations included two sets of d functions for phosphorus with the basis sets of Schäfer, Horn, and Ahlrichs,[38] using the HF and MP2 (full) implementation of Ditchfield's gauge including atomic orbital (GIAO) method[39] found in the ACES II code;[40] the basis sets are tzp for hydrogen (3s,p) and elements of the first long row of the periodic table (4s,3p,d), and tz2p (7s,5p,2d) for phosphorus. All the calculations represent absolute shieldings such that a bare nucleus would have a shielding of zero; chemical shifts, or shieldings with respect to a standard, may be determined by taking differences of the appropriate absolute shieldings. All of our calculations were carried out on Cray T-90 and T3E platforms located in the North Carolina Supercomputing Center.

It has recently been observed that in a number of cases where many-body perturbation theory is appropriate (that is, where perturbation theory appears to be converging) the various orders of Møller−Plesset theory NMR shieldings seem to be converging as a geometric series with a ratio of successive terms of approximately −0.5.[41] Under the assumption that this is true for all orders, one may sum the infinite perturbation series so that, with the knowledge of HF (σ_{HF}) and MP2 (σ_{MP2}) isotropic shieldings, the estimated Møller−Plesset infinite order (EMPI) shielding, σ_{EMPI}, is given by

$$\sigma_{EMPI} = \sigma_{HF} + {}^2/_3(\sigma_{MP2} - \sigma_{HF}) \qquad (1)$$

Applying this method to cited literature calculations provided NMR shieldings that were as accurate as available MP4 and coupled cluster calculations and in good agreement with experiment. The EMPI shieldings are reported in our tables; since the difference between the HF and MP2 results is also given, one may, if desired, reproduce the shieldings directly calculated at the HF and MP2 levels, shieldings available from the ACES II code.

A selection of molecular parameters resulting from the current optimizations may be obtained from the Supporting Information.

Results and Discussion

Ab Initio NMR Studies. Chemical shielding is caused by magnetic fields induced in a molecule by the application of an

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Table 1. Calculated Isotropic Shieldings (EMPI) and the Difference between the MP2 and Hartree−Fock (HF) Approaches, $\Delta\sigma^{(2)}_{\mathrm{corr}} = \sigma^{\mathrm{MP2}}_{\mathrm{calc}} - \sigma^{\mathrm{HF}}_{\mathrm{calc}}$, for Representative Molecules Containing Conventional Carbon, Nitrogen, Oxygen, and Phosphorus Single and Multiple Bonds[a]

molecule	σ_{calc}	$\Delta\sigma^{(2)}_{\mathrm{corr}}$
carbon		
C_2H_6	188.5	3.8
C_2H_4	71.7	14.0
CO	−6.1	47.7
nitrogen		
H_3N	279.6	14.3
N_2	−84.1	102.7
oxygen		
H_2O	346.1	19.0
CO	−78.3	58.9
phosphorus		
H_2PPH_2	572.3	26.0
HPPH	−207.9	241.3

[a] All the data are in ppm on an absolute scale.

external magnetic field. As one turns on the external magnetic field the ground state charge clouds are set in rotation, giving rise to internal fields in opposition to the external field. The external field also effects a mixing in to the ground state of excited states that relieves the usual quenching of orbital angular momentum, providing additional currents leading to internal field contributions that add to the external field. While the ground state charge cloud rotation is responsible for the generally large diamagnetic contribution to shielding, it is the mixing in of orbitals not represented in the ground state of the system by the application of the field, the so-called paramagnetic contribution, that dominates NMR shielding *differences* for a given nucleus. This paramagnetic contribution comes about from the scalar coupling of the electrons' angular momentum and the external field ($\mathbf{H}\cdot\mathbf{L}_j$) between orbitals, the $\mathbf{H}\cdot\mathbf{L}_j$ operators acting as rotation operators giving rise to net currents about the nucleus in question. Because the theoretical approach involves perturbation theory, the coupling between orbitals is generally a function of the difference in their orbital energies, small energy differences leading to large paramagnetic (negative) contributions to the shielding. Orbitals which lie near the Hartree−Fock HOMO-LUMO energy gap will be particularly important in this regard. Our understanding of why multiply bonded systems generally exhibit large paramagnetic effects is based on our picture of local π and π^* orbitals lying closer to this energy gap than do their σ and σ^* counterparts, the energy gap between the π and π^* orbitals being smaller than those of the σ and σ^* orbitals.

As mentioned in the Introduction, Hartree−Fock theory tends to yield shieldings that are too low (too paramagnetic), while the inclusion of correlation at the MP2 level generally overestimates the correction to this effect. The effect of inclusion of correlation at the MP2 level will be more noticeable in those systems containing conventional multiple bonds. This is illustrated by the data in Table 1 where shieldings (calculated at the EMPI level) and the differences between the MP2 and Hartree−Fock shieldings are listed for representative molecules containing carbon, nitrogen, oxygen, and phosphorus. The change in shielding due to correlation will be different for different nuclei and will scale approximately as the range of the chemical shift involved. As the table illustrates, while a change in shielding due to correlation of 14 ppm is significant for carbon, it is not for nitrogen; the effect of the presence of double bonds containing oxygen as illustrated by CO in the table is quite significant and much larger than the effect on oxygen in water. So, too, in phosphorus moving from the phosphorus singly bonded in H_2PPH_2 to the doubly bonded HPPH molecule results in a large increase in the effect of correlation. In short, by looking at $\Delta\sigma^{(2)}_{\mathrm{corr}} = \sigma^{\mathrm{MP2}}_{\mathrm{calc}} - \sigma^{\mathrm{HF}}_{\mathrm{calc}}$ in the calculated NMR shielding of a nucleus, we may generally determine if it is part of what we think of as a conventional multiple bond.

Table 2. EMPI Calculated Isotropic Shieldings, σ_{calc}, and the Difference between the MP2 and Hartree−Fock (HF) Approaches, $\Delta\sigma^{(2)}_{\mathrm{corr}} = \sigma^{\mathrm{MP2}}_{\mathrm{calc}} - \sigma^{\mathrm{HF}}_{\mathrm{calc}}$ [a]

molecule	σ_{calc}	$\Delta\sigma^{(2)}_{\mathrm{corr}}$	molecule	σ_{calc}	$\Delta\sigma^{(2)}_{\mathrm{corr}}$
phosphorus			carbon		
H_3P	602.0	28.5	H_3PCH_2	225.5	4.5
H_2PPH_2	572.3	26.0	$(CH_3)_3P$	179.6	2.2
H_3PBH_3	477.5	19.5	$(CH_3)_3PO$	178.7	1.0
PH_4^+	475.3	12.1	HCP	37.3	36.3
H_3PCH_2	453.0	12.6	nitrogen		
H_3PNH	431.3	7.5	H_3PNH	288.3	7.9
$(CH_3)_3P$	422.1	0.3	PN	−340.9	357.6
H_3PO	403.5	−0.9	oxygen		
HCP	376.2	80.9	H_2POH	374.3	23.3
F_3PO	366.9	−11.9	H_3PO	337.8	12.5
$(CH_3)_3PO$	323.2	−9.5	$(CH_3)_3PO$	246.9	−3.3
H_2POH	315.5	−8.2	HO^*PO_2	226.3	14.4
$HOPO_2$	261.5	31.3	F_3PO	208.8	10.4
PO_3^-	233.6	29.0	PO_3^-	161.1	23.8
F_3P	214.5	−35.1	HOPO*2 (anti)	154.2	35.3
HOPO	47.1	96.0	HOPO*2 (syn)	136.0	28.1
PN	34.1	367.8	HO*PO	108.8	9.8
HPPH	−207.9	241.3	HOPO*	−187.9	100.6
P_2	−257.5	336.8	HPO	−698.3	263.7
HPO	−329.2	195.0	fluorine		
boron			F_3PO	280.8	−8.0
H_3PBH_3	157.8	1.3	F_3P	234.0	−18.7

[a] All the data are in ppm.

EMPI calculated isotropic shieldings and the differences between the MP2 and Hartree−Fock approaches, $\Delta\sigma^{(2)}_{\mathrm{corr}} = \sigma^{\mathrm{MP2}}_{\mathrm{calc}} - \sigma^{\mathrm{HF}}_{\mathrm{calc}}$ are given for a large number of phosphorus compounds in Table 2 not only for phosphorus but also for the other heavy nuclei involved. An inspection of $\Delta\sigma^{(2)}_{\mathrm{corr}} = \sigma^{\mathrm{MP2}}_{\mathrm{calc}} - \sigma^{\mathrm{HF}}_{\mathrm{calc}}$ for a nucleus will clearly distinguish between those molecules in which we believe it to be involved in a conventional single bond and those in which it is involved in a conventional double or triple bond. This effect holds true for phosphorus and the atoms to which phosphorus is bonded. For example, the correlation effect in HOPO is large (96.0 ppm) for phosphorus and also for the doubly bonded oxygen (100.6 ppm), while the oxygen in the PO single bond in that molecule has a MP2 correlation effect of only 9.8 ppm.

It is clear from the table that the phosphine oxides and related molecules (H_3PCH_2 and H_3PNH) behave as *not* containing conventional multiple bonds. $HOPO_2$ and PO_3^- likewise do not show a large value of $\Delta\sigma^{(2)}_{\mathrm{corr}} = \sigma^{\mathrm{MP2}}_{\mathrm{calc}} - \sigma^{\mathrm{HF}}_{\mathrm{calc}}$ relative to those molecules containing conventional phosphorus multiple bonds. The lack of a correlation effect is also evident when looking at the atom(s) to which phosphorus is bonded. For example, in H_3PO and F_3PO the oxygen shielding changes are small and clearly not indicative of conventional multiple bonding. We can conclude from this that, in the case of the phosphine oxides, while partial multiple bonding may occur (vide infra), the presence of conventional multiple bonds is clearly *not* indicated by the NMR calculations. As far as the data in Table 2 are concerned, the bond between phosphorus and oxygen in these systems is more consistent with a conventional single bond.

We can continue the analysis a bit further by focusing on the shieldings in phosphine oxide and its imine and methylene counterparts. If the bond between phosphorus and oxygen (or nitrogen or carbon) in these cases is more like a single bond than a conventional double bond, then there is obviously considerable polarization to the bond and in an oversimplified picture one might well represent phosphorus as having a unit charge and oxygen (or carbon or nitrogen) having a unit negative charge, $R_3P^+X^-$. Indeed, this picture is consistent with the shieldings calculated for OH^-, NH_2^-, and CH_3^-. Comparing the shieldings for the substituent atom in these three cases one obtains 337.8 and 360.2 ppm for phosphine oxide and OH^-, 288.4 and 320.4 ppm for the imine and NH_2^-, and 225.5 and 243.0 ppm for the methylene derivative and CH_3^-, respectively. The shieldings of the substituent atoms in these cases are at the high (positive) end of their shielding scales where diamagnetic effects dominate.

Neither of these arguments rule out the presence of additional bonding between phosphorus and its bonded oxygen (or other atom), but suggest that it is more likely an ionic type of interaction rather than a conventional multiple bond. We address this question in the next section where an atoms-in-molecules (AIM) treatment is presented.

Atoms-in-Molecules Studies. The prior section on the NMR characterization of the PO bond in phosphine oxides is consistent with the structure $R_3P^+O^-$, but it does not provide any particular details of the bonding or distribution of charge in the system. Bader's atoms-in-molecules (AIM) approach,[33,34] a theoretical interpretation of the quantum mechanical electron density in molecules, should be a useful approach in that it is based on the electron density, obviously a key observable in a molecule's description. AIM is based on the notion long held by chemists that molecules may be viewed as a collection of atoms held together by a network of chemical bonds. In Bader's approach molecular subsystems are defined in terms of the vector field of the gradient of the electron density, $\nabla\rho$. Zero-flux surfaces ($\vec{n}\cdot\nabla\rho = 0$, where $\vec{n}$ is the unit vector normal to the surface) enclose the subsystems. Each particular gradient path starts and ends at what are called *critical points*, and nuclei act as *attractors* for gradient paths within each subsystem. The region of three-dimensional space traversed by all gradient paths that terminate at a given attractor defines the *basin* of the attractor; each attractor and its associated basin are called "atoms" by Bader.

The contribution to the electron number from the occupied orbital $|i\rangle$ in the basin Ω_A is given by

$$\langle i|i\rangle_A = \int_{\Omega_A} \langle i|i\rangle \, d\vec{r} \tag{2}$$

In the Hartree−Fock approach (which we employ here in the AIM studies) the charge, $q(A)$, associated with a nuclear attractor in the A basin is given by summing over all the orbital contributions $\langle i|i\rangle_A$ and subtracting from the associated nuclear charge.

$$q(A) = Z_A - \sum_i \langle i|i\rangle_A \tag{3}$$

Following Bader's approach, Cioslowski and Mixon[35] have defined a natural bond order in the atoms-in-molecules picture using a localization procedure due to Cioslowski[42,43] based on the idea of atomic overlap matrices. They show that the total number of electrons in the molecule may be naturally partitioned as

$$N = \sum_i \sum_A \langle i|i\rangle_A^2 + 2\sum_i \sum_{A<B} \langle i|i\rangle_A \langle i|i\rangle_B = N_{\text{atomic}} + N_{\text{diatomic}} \tag{4}$$

so that the *covalent bond order*, $p(AB)$, between atoms A and B is given by

$$p(AB) = 2\sum_i \langle i|i\rangle_A \langle i|i\rangle_B \tag{5}$$

The localized orbitals $|i\rangle$ are found by maximizing the atomic contribution, N_{atomic}, while maintaining the first-order density matrix constant, an example of what Cioslowski calls an *isopycnic* transformation.[42,43] These bond orders relate well to conventional ideas of single and multiple covalent bonds.

Table 3 shows the Bader charges (q) and the covalent bond orders (p) for the molecules studied in the present work. Metaphosphoric acid and the metaphosphate anion are shown separately as drawings in Part D of that table for clarity of presentation. One notes that the phosphine oxides are characterized by a rather large charge on phosphorus ($q > +3$) and a covalent bond order less than one, in the range of 0.7 to 0.8. The same is true of those cases where oxygen is replaced by an NH or CH_2 group (see Part B of Table 3), but clearly not in the BH_3 case. The strong ionic character of the PO bond is clearly illustrated by the charges shown in the table. Part A of that table shows that moving from the R_3P to the R_3PO species essentially results in a net transfer of charge from phosphorus to oxygen with a concomitant reduction in the covalent bond order of the PR bond. The type of results exhibited by the ordinary phosphine oxides are also present in metaphosphoric acid and the metaphosphate anion. The ionic character of the PO bond in general is shown in Part C where the covalent bond order in H_2POH is significantly less than one and that for HPO, normally viewed as a conventional double bond, is significantly less than two.

As has been pointed out by Cioslowski and Mixon,[44] the inclusion of electron correlation tends to reduce the absolute values of the atomic charges and to increase the covalent bond orders, in agreement with the observation that bond ionicities are exaggerated at the Hartree−Fock level.[45−47] These changes, however, are not large as is shown by some representative calculations performed here on H_3P, H_3PO, F_3P, and F_3PO. In these cases charges were reduced by the order of 5% compared to the Hartree−Fock numbers, covalent bond orders increased by about 7%, and the electron density at critical points was left virtually unchanged (perhaps a small (1%) reduction). Accordingly, the Hartree−Fock charges and covalent bond orders presented here are clearly representative of the systems being studied.

The nature of the bonding in these compounds is best illustrated by a detailed analysis of orbital populations illustrated in Table 4 for the singly bonded H_2POH, the double bonded HPO, and the H_3PO phosphine oxide. As in the Gaussian 94 output, the orbitals in these tables are arranged in order of decreasing kinetic energy, one way of measuring localization of an orbital. For completeness and also because it is known experimentally, Table 5 shows the same type of data for F_3PO. Cioslowski and Mixon define the localization, L_i, and ionic

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Table 3. Charges (*q*) and Covalent Bond Orders (*p*)

A. R_3P and R_3PO Species

molecule	*q*(R)	*q*(P)	*q*(O)	*p*(PO)	*p*(PR)
F_3PO	−0.84	+4.06	−1.54	0.746	0.374
F_3P	−0.85	+2.56			0.537
$(CH_3)_3PO$	−0.64[a]	+3.55	−1.61	0.733	0.564[b]
$(CH_3)_3P$	−0.62[a]	+1.86			0.750[b]
H_3PO	−0.64	+3.51	−1.58	0.805	0.592
H_3P	−0.61	+1.84			0.807

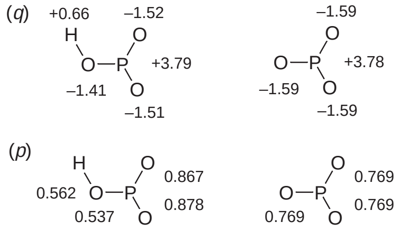
B. H_3PXH_n Molecules

molecule	*q*(H)	*q*(P)	*q*(X)	*q*(H_n)	*p*(PX)
H_3PO	−0.64	+3.51	−1.58		0.805
H_3PNH	−0.64[c]	+3.39	−1.85	+0.39	0.907
H_3PCH_2	−0.64[c]	+3.19	−1.21	−0.03	1.009
H_3PBH_3	−0.62	+1.95	+2.00	−0.70	0.333

C. Some Other Phosphorus-Containing Molecules

molecule	*q*(P)	*p*($PX^{(1)}$)	*p*($PX^{(2)}$)	*p*(PH)
$HO^{(1)}PO^{(2)}$	+2.28	0.737	1.157	
$HOPH_2$	+2.04	0.680		0.758
H_2PPH_2	+1.24	0.938		0.869[d]
HPO	+2.04	1.273		0.770
HPPH	+0.62	1.875		0.940
PN	+1.47	2.377		
HCP	+1.25	2.449		
P_2	0.0	3.079		

D. Charges (*q*) and Covalent Bond Orders (*p*) for $HOPO_2$ and PO_3^-



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[a] CH_3 group. [b] PC bond. [c] Average of PH hydrogens. [d] Average of the two distinct PH bonds.

Table 4. Atomic Occupancies of the Localized Orbitals in H_2POH, HPO, and H_3PO (Blank Lines Separate Core from Valence Orbitals)

	H_2POH					
orbital	H	O	P	H	H	orbital type
1	0.0000	0.0000	1.0000	0.0000	0.0000	core
2	0.0000	1.0000	0.0000	0.0000	0.0000	
3	0.0000	0.0000	0.9990	0.0000	0.0000	
4	0.0000	0.0001	0.9985	0.0001	0.0012	
5	0.0000	0.0016	0.9981	0.0001	0.0001	
6	0.0000	0.0001	0.9985	0.0012	0.0001	
7	0.0018	0.9927	0.0036	0.0009	0.0009	O lone pair
8	0.0049	0.9691	0.0164	0.0047	0.0047	O lone pair
9	0.0028	0.8582	0.1215	0.0088	0.0088	PO bond
10	0.1706	0.8163	0.0085	0.0023	0.0023	HO bond
11	0.0007	0.0314	0.9122	0.0278	0.0278	P lone pair
12	0.0004	0.0208	0.2102	0.0236	0.7450	PH bond
13	0.0004	0.0208	0.2102	0.7450	0.0236	PH bond

	HPO			
orbital	H	P	O	orbital type
1	0.0000	1.0000	0.0000	core
2	0.0000	0.0000	1.0000	
3	0.0000	0.9999	0.0001	
4	0.0002	0.9965	0.0033	
5	0.0010	0.9986	0.0005	
6	0.0001	0.9993	0.0006	
7	0.0002	0.0009	0.9988	O lone pair
8	0.0084	0.1251	0.8665	PO bond
9	0.0096	0.0270	0.9633	O lone pair
10	0.0147	0.1756	0.8098	PO bond
11	0.0265	0.9413	0.0322	P lone pair
12	0.7585	0.2142	0.0272	HP bond

	H_3PO					
orbital	O	P	H	H	H	orbital type
1	0.0000	1.0000	0.0000	0.0000	0.0000	core
2	1.0000	0.0000	0.0000	0.0000	0.0000	
3	0.0038	0.9958	0.0001	0.0001	0.0001	
4	0.0004	0.9980	0.0001	0.0014	0.0001	
5	0.0004	0.9983	0.0001	0.0001	0.0014	
6	0.0004	0.9980	0.0014	0.0001	0.0001	
7	0.9982	0.0009	0.0003	0.0003	0.0003	O lone pair
8	0.8405	0.1358	0.0079	0.0079	0.0079	PO bond
9	0.9438	0.0375	0.0098	0.0044	0.0044	O lone pair
10	0.9438	0.0375	0.0027	0.0080	0.0080	O lone pair
11	0.0195	0.1812	0.0187	0.7620	0.0187	PH bond
12	0.0195	0.1812	0.0187	0.0187	0.7620	PH bond
13	0.0195	0.1812	0.7620	0.0187	0.0187	PH bond

character, I_i, of a bond AB described by molecular orbital i by

$$L_i^{(AB)} = \langle i|i\rangle_A + \langle i|i\rangle_B$$

$$I_i^{(AB)} = \frac{\langle i|i\rangle_A - \langle i|i\rangle_B}{\langle i|i\rangle_A + \langle i|i\rangle_B} \tag{6}$$

We use these definitions in discussing the examples illustrated in Tables 4 and 5.

Consider first the case of H_2POH where the PO bond is thought of as a conventional single bond. Beyond the highly localized core orbitals one can clearly recognize oxygen lone pairs (orbitals 7 and 8), a phosphorus lone pair (orbital 11), two PH bonding orbitals (orbitals 12 and 13), one PO bond (orbital 9), and one OH bond (orbital 10). Both the PO and HO bonds are strongly localized but are also strongly ionic, 75.2% in the case of the PO bond, and 65.4% for the OH bond.

The situation in doubly bonded HPO is similar. Outside the core the oxygen and phosphorus lone pair orbitals are readily identified (orbitals 7, 9, and 11) as are those orbitals involved in the HP bond (orbital 12) and the two bonding orbitals involving phosphorus and oxygen (orbitals 8 and 10). Again all of these bonding orbitals are highly localized in the sense of eq 6, but again have ionicities which are quite large, 74.8 and 64.4% for the PO bonds and 56.0% for the PH bond. Clearly the high polar character of PO bonds is not restricted to the phosphine oxides.

Finally, we analyze the key example of H_3PO. The PH bonds are readily recognized along with the presence of three oxygen lone pairs (orbitals 7, 9, and 10) and one PO bond (orbital 8). The PO bonding orbital is again highly localized and highly ionic (72.2%). The oxygen lone pairs are of two types: first is the highly localized lone pair of orbital 7 and then the two equivalent, somewhat lesser localized lone pairs of orbitals 9 and 10. One can, of course, never completely localize an orbital in a given basin although those orbitals representing the atomic cores come close (to the number of significant figures given). One may pose the question of when a lone pair becomes a highly ionic bonding orbital, a question for which the answer is arbitrary and not obvious. As we shall see the small but noticeable orbital population on phosphorus in orbitals 9 and 10 of H_3PO represents back-bonding from oxygen to phosphorus and plays a key role in characterizing the phosphine oxides

Table 5. Atomic Occupancies of the Localized Orbitals in F_3PO. (A Blank Line Separates Core from Valence Orbitals)

	F_3PO					
orbital	O	P	F	F	F	orbital type
1	0.0000	1.0000	0.0000	0.0000	0.0000	core
2	0.0000	0.0000	1.0000	0.0000	0.0000	
3	0.0000	0.0000	0.0000	0.0000	1.0000	
4	0.0000	0.0000	0.0000	1.0000	0.0000	
5	1.0000	0.0000	0.0000	0.0000	0.0000	
6	0.0044	0.9950	0.0002	0.0002	0.0002	
7	0.0005	0.9965	0.0026	0.0002	0.0002	
8	0.0005	0.9965	0.0002	0.0002	0.0026	
9	0.0005	0.9965	0.0002	0.0026	0.0002	
10	0.0001	0.0002	0.9994	0.0001	0.0001	F lp
11	0.0001	0.0002	0.0001	0.9994	0.0001	F lp
12	0.0001	0.0002	0.0001	0.0001	0.9994	F lp
13	0.0037	0.0093	0.0019	0.0071	0.9780	F lp
14	0.0037	0.0093	0.0019	0.9780	0.0071	F lp
15	0.0037	0.0093	0.9780	0.0019	0.0071	F lp
16	0.0037	0.0093	0.9780	0.0072	0.0019	F lp
17	0.0037	0.0093	0.0072	0.0019	0.9780	F lp
18	0.0037	0.0093	0.0072	0.9780	0.0019	F lp
19	0.9986	0.0007	0.0002	0.0002	0.0002	O lp
20	0.0073	0.0764	0.0084	0.8995	0.0084	PF bond
21	0.0073	0.0764	0.0084	0.0084	0.8995	PF bond
22	0.0073	0.0764	0.8995	0.0084	0.0084	PF bond
23	0.8509	0.1248	0.0080	0.0081	0.0082	PO bond
24	0.9358	0.0383	0.0047	0.0107	0.0104	O lp
25	0.9358	0.0383	0.0126	0.0065	0.0068	O lp

Table 6. PO Bond and P and O Lone Pair (lp) Contributions to Covalent Bond Orders, *p*

A. PO Bonds

	PO	O lp	P lp	*p*(total)
HPO	1.002	0.108	0.121	1.273
HOPO*	0.852	0.146	0.132	1.157
HOPO*$_2$[a]	0.461	0.382		0.878
HOPO*$_2$[b]	0.457	0.372		0.867
H_3PO	0.457	0.286		0.805
PO_3^-	0.433	0.300		0.769
F_3PO	0.425	0.290		0.746
HO*PO	0.343	0.187	0.140	0.737
$(CH_3)_3PO$	0.427	0.253		0.733
H_2POH	0.417	0.078	0.115	0.680
HO*PO2	0.361	0.119		0.537

B. Other PX bonds

	PX	X lp	P lp	*p*(total)
P_2	3.000		0.075	3.076
HCP	1.314		0.084	2.450
PN	2.258	0.005	0.096	2.377
HPPH	1.774		0.073	1.875
H_3PCH_2	0.672	0.243		1.009
H_2PPH_2	0.806		0.097	0.938
H_3PNH	0.549	0.259		0.907
H_3PBH_3	0.269			0.332

C. Comparison of the H_3PX Species

	PX	X lp	P lp	*p*(total)
H_3PCH_2	0.672	0.243		1.009
H_3PNH	0.549	0.259		0.907
H_3PO	0.457	0.286		0.805
H_3PBH_3	0.269			0.332

[a] Anti oxygen. [b] Syn oxygen.

relative to other phosphorus species. The analysis of F_3PO in Table 5 is similar to that given above for H_3PO. Here there are nine F lone pairs and, again, the key, back-bonding oxygen lone pairs of orbitals 24 and 25.

The situation is clarified in Table 6, which contains the contribution to the covalent bond orders of what we have characterized as PO bonds and phosphorus and oxygen lone pair orbitals. What we note in Part A of the table is that those molecules which we have previously characterized as behaving as though singly bound with significant transfer of charge ($HOPO_2$, H_3PO, PO_3^-, F_3PO, and $(CH_3)_3PO$) all show much larger contributions to the overall covalent bond order from the oxygen lone pair orbitals than do the other cases illustrated. In Part B we note this is also true for the H_3PCH_2 and H_3PNH species but not (see Part C of Table 6) the H_3PBH_3 molecule where, of course, there are no lone pairs on boron to become involved. This significantly larger involvement of the oxygen lone pair orbitals is clearly indicative of back-bonding and provides the rational for the behavior of the unusual PO bond in the phosphine oxides and related molecules. Namely, while back-bonding does occur in other species (see the other entries in Table 6), it is significantly larger in the phosphine oxides. In conjunction with the highly polar "normal" PO bond, the back-bonding involved explains the short PO bond distance and its strength greater than that of the corresponding conventional single bond.

Our conclusions are in basic qualitative agreement with those of Reed and Schleyer,[5] who argue for the importance of negative hyperconjugation (back-bonding) on the basis of the large depletion of the oxygen $p-\pi$ lone pair occupations; their numbers relating charges and depletion of lone pair orbital populations differ from those here because their approach (a natural population analysis) differs from our atoms-in-molecules approach. Our conclusions are also consistent with the views of Streitwieser and co-workers,[48,49] who carried out studies involving integrated spatial electron populations that approximate (but are not the same as) Bader's atomic basin charges.

Note that the current analysis does not invoke atomic orbital populations (p or d or other atomic orbitals) but rather characterizes orbital involvement as being of a bonding or lone pair type. This is clearly an advantage of the Cioslowski and Mixon approach to the analysis of the electronic structure of molecules. A detailed decomposition into atomic orbitals is unnecessary provided the overall basis set is capable of reproducing the structure observed and the electronic energy.

An advantage of Cioslowski's localized orbitals is that a tabular representation of the atomic populations such as given in Tables 4 and 5 allows one to describe the bonding taking place in a molecule without resort to graphical presentations. A disadvantage is that one cannot see the details of the orbital distribution from the tabulation of populations. Nonetheless, from the apparent symmetries and equivalencies of the orbital populations one can propose reasonable interpretations. For example, from the tabulation in Table 4 of H_3PO and in Table 5 of F_3PO one is able to clearly discern the differences among the oxygen lone pairs as well as the nature of the PO bonding orbital. For H_3PO the PO bonding orbital clearly has σ-type symmetry as does the lone pair in molecular orbital 7. The oxygen lone pairs in orbitals 9 and 10 are equivalent but different from that in molecular orbital 7. A similar situation obtains for F_3PO with regard to the PO bonding orbital (23), the unique oxygen lone pair (orbital 19) and the two equivalent lone pairs of orbitals (24 and 25). The Cioslowski localized orbitals are consistent then with a $\sigma-\pi$ picture with significant back-bonding

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(48) Streitwieser, A., Jr.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987**, *109*, 4184.

(49) Streitwieser, A., Jr.; McDowell, R. S.; Glaser, R. *J. Comput. Chem.* **1987**, *8*, 788.

Table 7. NO Distances (R (Å), Optimized), Bond Critical Point Densities (ρ_b, au), Charges (q, au), Total Covalent Bond Orders (p(total)) and Their Major Contributors (NO Bond, O and N Lone Pairs) for H_2NOH, H_3NO, HNO, F_3NO, and NO^+

property	H_2NOH	H_3NO	HNO	F_3NO	NO^+
R	1.4512	1.3753	1.2376	1.1603	1.1034
ρ_b	0.287	0.341	0.486	0.591	0.672
charges					
q(O)	−0.88	−0.68	−0.46	−0.37	−0.32
q(N)	−0.55	−0.60	+0.10	+1.25	+1.32
q(H:NH)	+0.40,[a] +0.63[b]	+0.43	+0.37		
q(F)				−0.29	
NO covalent bond orders					
p(total)	1.194	1.313	2.098	1.941	2.517
major contributors					
p(NO bond)	0.914	0.939	1.870	0.979	2.447
p(O lp)	0.094	0.290	0.111	0.917[c]	0.004
p(N lp)	0.069		0.057		0.066

[a] H in the NH bond. [b] H in the OH bond. [c] This contribution could also be considered to be from two highly ionic (72%) NO bonds rather than oxygen lone pairs.

of two of the oxygen lone pairs to the phosphorus atom. This picture is again consistent with the work of Reed and Schleyer[5] and is inconsistent with the energy-localized picture given in the work of Schmidt, Yabushita, and Gordon[7] where there are three equivalent oxygen lone pairs. It is also obviously inconsistent with the Boys picture (also given in the same paper), which shows three oxygen orbitals strongly polarized toward the phosphorus atom, a picture involving bent or banana bonds; this latter description is also the picture that Messmer[20] derives from his GVB-SOPP treatment. Cioslowski[42,43] points out that in planar systems his approach does *not* permit the mixing of σ and π canonical molecular orbitals so that banana bonds are not possible. As mentioned before, the structures of the atomic population seen in Tables 4 and 5 would seem to indicate that in the case of the R_3PO systems studied here bent bonds also do not occur.

Although an extensive analysis of R_3NO compounds where nitrogen replaces phosphorus was not carried out, we did carry out calculations on H_2NOH, H_3NO, HNO, F_3NO, and NO^+ with the key results shown in Table 7. H_2NOH has the expected "normal" single bond between nitrogen and oxygen and exhibits a covalent bond order of 1.19. The oxygen lone pair orbitals in this compound contribute very little to the covalent bond order, and the NO distance is what one would expect for a normal nitrogen−oxygen single bond. The NO bond in H_3NO is significantly shortened, the covalent bond order modestly increased to 1.31, and the oxygen lone pairs now provide a noticeable contribution to the covalent bond order, a contribution of about the same order as shown in the analogous phosphorus compounds. The NO bond distance is shorter than that in H_2NOH but significantly longer than the double bond in HNO and clearly is not close to the double bond appearance found for the PO bond in the R_3PO cases. We note furthermore that the charge on nitrogen in this compound is negative. In contrast to the situation with the analogous phosphorus molecules, the F_3NO molecule is much different than H_3NO. It exhibits an NO bond distance that is midway between doubly bonded HNO and the triple bond in NO^+, shows a covalent bond order of 1.94, and has contributions from the oxygen lone pairs that are nearly equal to that found for the NO σ localized molecular orbital bond. The charge on nitrogen in this case is highly positive due to the presence of the highly electronegative fluorine atoms, so that this molecule more nearly parallels the behavior in F_3PO (and H_3PO) than does H_3NO. For H_3NO one would describe the shortened bond distance and increased covalent bond order as due to a small degree of back-bonding from oxygen to nitrogen, but one is forced to describe F_3NO as showing the equivalent of at least a double bond between nitrogen and oxygen, the contributions from the oxygen lone pairs being so large. Note in Table 7 the parallel behavior of the bond critical point density (ρ_b) and the (optimized) equilibrium bond distance, a generally observed behavior in Bader's atoms-in-molecules approach.[50] A similar relationship holds for the PO bond set.

We note finally that all of the nitrogen analogue molecules investigated showed only small effects of correlation in MP2 NMR calculations, like the phosphine oxides consistent with the picture of the amine oxides *not* containing conventional multiple bonds.

Summary and Conclusions

Our ab initio NMR calculations on the effect of correlation on phosphorus (and nitrogen) shielding in the phosphine oxides (amine oxides) clearly suggest the absence of conventional multiple bonding in the PO (NO) bond. Our AIM studies indicate one highly polarized σ bond plus strong back-bonding of the oxygen π orbitals, a picture consistent with a number of prior investigations.[5,16,23,48,49] The π back-bonding is responsible for the apparent PO (NO) multiple bond character, leading to a bond that would otherwise be classed as double in the PO cases and as triple for F_3NO. While the localized orbitals which lead to this picture[42,43] are arbitrarily defined, they are based on the electron density in Bader's model,[33,34] a key quantum mechanical observable. While Gilheany has argued that the unusual character of the PO bond in the phosphine oxides should be represented by the $R_3P{=}O$ formula, we rather believe the situation is better pictured as $R_3P^+{-}O^-$, where both σ and ionic bonds are explicitly shown.

Acknowledgment. I am indebted to the North Carolina Supercomputing Center for providing CPU time on the Cray T-916 and T3E platforms that allowed these calculations to be carried out and to Professor L. D. Quin for pointing out this interesting problem and for helpful discussions.

Supporting Information Available: A brief listing of the MP2(fc)/6-31+G(d,p)-optimized energies, bond distances and angles, and dipole moments for 15 of the X_3A and X_3AY molecules studied in this investigation (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9822198

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