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Atoms-in-Molecules and Electron Localization Function Study of the Phosphoryl Bond

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Calculations at the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level involving the atoms-in-molecules (AIM) and electron localization function (ELF) methods have been carried out for a variety of PO-bond-containing molecules in an effort to further characterize the phosphoryl bond. One cannot distinguish the phosphoryl bond from a conventional PO double bond by comparing bond distances. Both the bond breaking energies and delocalization indices do divide into the three classes of single, double, and phosphoryl and tend to parallel each other. On the basis of the PO bond in HPO having a reference bond order of 2.0, the phosphoryl bond has a bond order of about 1.3. Examination of localized orbitals confirm our ideas that the phosphoryl bond is highly polar as, indeed, are the other PO bonds. What sets the phosphoryl bond apart is the high degree of back-bonding that contributes to the delocalization index (and covalent bond order) and provides for its stronger-than-single-bond character and short bond distance.

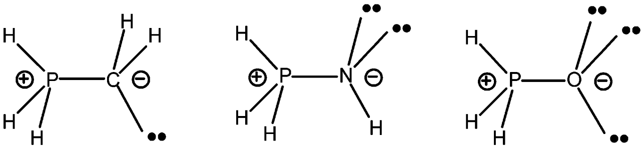
Introduction

The nature of the phosphoryl bond in phosphine oxides (R_3PO) continues to be of interest. In his extensive reviews Gilheany[1,2] points out that both experiment and ab initio calculations generally agree that the PO bond is strong, polar, and as short as conventional PO double bonds. The role of d functions as polarization functions rather than primary valence orbitals is well-established.[3,4] Where differences arise has been in the interpretation of the bond based on different perspectives.

The bonding has been viewed as a donor−acceptor interaction[5] with superimposed oxygen π orbital back-bonding with the degenerate H_3P moiety antibonding orbitals (negative hyperconjugation[6]), while localized orbital approaches yield pictures both as one strong PO σ_j bond and three equivalent oxygen orbitals characterized primarily as lone pairs polarized toward phosphorus and staggered with respect to the PR bonds,[7−9] as well as one that involves 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,[7,10,11] a picture supported by GVB−SOPP calculations.[12] Nyulászi et al.[13] have presented arguments that the multiple bond in H_3PCH_2 has many similarities to the conventional multiple bond in $HPCH_2$.

Ab initio nuclear magnetic resonance (NMR) calculations on the effect of correlation on phosphorus shielding in the phosphine oxides[14] clearly suggest the absence of *conventional* multiple bonding in the PO bond. In this study the atoms-in-molecules[15,16] (AIM) approach yielded localized molecular orbitals[17−19] that indicated one highly polarized σ bond plus strong back-bonding of the oxygen π orbitals. While it has been argued that the strong character of the PO bond in the phosphine oxides is conveyed best by the $R_3P{=}O$ formula, this investigation suggested that the situation is better pictured as $R_3P^+{-}O^-$. These results are in agreement with conclusions reached by Rai and Symons[20] and by Power[21] on the basis of experimental ESR and NMR data, respectively. The theoretical studies of Dixon and Smart[22] support a zwitterionic structure, and Bachrach[23] concludes from the pyramidal structure about the carbon bound to phosphorus in the ylides that it must be carbanionic in nature.

CHART 1



A key question has been the disposition of the oxygen lone pairs. Using Bader's AIM approach involving the Laplacian of the electron density, MacDougall and Hall[24] and more recently Dobado et al.[25] concluded the presence of three nonbonded maxima behind the oxygen atom (away from phosphorus) and staggered with respect to the R_3P bonds to indicate the lone pair positions. This picture is in agreement with our early study[26] involving the electron localization function (ELF).[27−34]

More recently we examined the bonding in the four-coordinate H_3XCH_2, H_3XNH, and H_3XO compounds where X = N, P, emphasizing the ELF approach by focusing on changes in bond basin populations as the bonding types were changed.[35] That study supported an ionic plus covalent bonding picture shown in Chart 1 and led us to propose the name *cov-ionic* for this particular kind of chemical bond.

Yet another measure of bond type is given by the delocalization index of Fradera et al.,[36] which purports to measure the degree of electron pair sharing between two AIM atomic basins and, to a degree, the covalent bond order of the bond between the two atoms, and it is this approach that we emphasize here.

We have suggested that while bonding parameters involved in ELF basin populations and AIM delocalization indices may not in an absolute sense reflect our simple ideas of bond orders, ratios of these parameters referenced to a suitable standard may

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be a more viable measure of the bonding situation.[37] We applied this to all two-heavy-atom hydrides of the first and second row elements and found that a division into classes of clearly defined formal bond order was clear for the AIM delocaliztion index and apparent though less clear for the ELF bond basin populations. This approach had been successfully used earlier in the characterization of the bonds in the various Si_2H_2 isomers[38] and led to the characterization of the Si−Si bond in trans-bent HSiSiH as triple and the trans-bent HGaGaH hydride as having a bond order intermediate between two and three.[39]

In the present paper we continue our study of the PO bond with emphasis on the phosphoryl bond in R_3PO species. Our results are consistent with previous studies and suggest that the phosphoryl bond order is approximately 1.3.

Theoretical Background

The two approaches used here to characterize the nature of bonding interactions are the *delocalization index* of Fradera et al.[36] based on the electron pair density in the AIM approach[15,16] and ELF isosurfaces and *bond basin populations* in the approach of Becke and Edgecombe[27] as extensively developed by Savin and Silvi and co-workers.[28−34] In the AIM approach atomic basins are derived from the scalar field of the electron density, $\rho(\vec{r})$, while ELF basins arise from a potential which is based on strong physical arguments regarding the Fermi hole[40,41] and the corresponding tendency of electron pairs to occupy different regions of space.

In Bader's atoms-in-molecules approach[15,16] the gradient field of the electron density, $\boldsymbol{\rho}(\vec{r})$, defines atomic basins over which one can integrate to obtain AIM atomic basin electron populations, N_i. (While we talk about both AIM and ELF basin populations in this work, the context should make clear which one is being referenced.) The delocalization index[36] is defined in terms of the electron pair density as it relates to the AIM atomic basins. The (spinless) electron pair density,[40,41] $P_2(\vec{r}_1,\vec{r}_2)$, is the diagonal part of the reduced second-order density matrix and is normalized as

$$\int d\vec{r}_1 \int d\vec{r}_2\, P_2(\vec{r}_1,\vec{r}_2) = \int d\vec{r}_1 (N-1)\, \rho(\vec{r}_1) = N(N-1) \tag{1}$$

where $\rho(\vec{r}_1)$ is the electron number density and N the total number of electrons. It proves convenient to define the pair density in terms of a quantity that accentuates the role of correlation by introducing the *correlation factor* $f(\vec{r}_1,\vec{r}_2)$

$$P_2(\vec{r}_1,\vec{r}_2) = \rho(\vec{r}_1)\, \rho(\vec{r}_2)[1 + f(\vec{r}_1,\vec{r}_2)] \tag{2}$$

so that

$$\frac{P_2(\vec{r}_1,\vec{r}_2)}{\rho(\vec{r}_2)} - \rho(\vec{r}_1) = \rho(\vec{r}_1)\, f(\vec{r}_1,\vec{r}_2) \tag{3}$$

The quantity on the left is the *conditional probability density* of finding an electron at $\vec{r}_1$ *given* that there is one at $\vec{r}_2$, minus the number density at $\vec{r}_1$, $\rho(\vec{r}_1)$. This expression (either side of eq 3) defines the *exchange-correlation hole* associated with the reference electron at $\vec{r}_2$; for a single determinant wave function such as we employ, only the exchange part is present as the *Fermi hole.*[40,41]

If we integrate the two coordinates of the pair density over two AIM basins, Ω_i and Ω_j, we obtain the interbasin pair number, N_{ij}, and, using eq 2, can write[16,42,43]

$$\begin{aligned} N_{ij} &= \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2\, P_2(\vec{r}_1,\vec{r}_2) \\ &= \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2\, \rho(\vec{r}_1)\, \rho(\vec{r}_2)[1 + f(\vec{r}_1,\vec{r}_2)] \\ &= N_i N_j + \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2\, \rho(\vec{r}_1)\, \rho(\vec{r}_2)\, f(\vec{r}_1,\vec{r}_2) \\ &= N_i N_j - F_{ij} \end{aligned} \tag{4}$$

where N_i and N_j are the AIM basin populations (electron numbers) and where, here, in contrast to Fradera et al.,[36] we have explicitly introduced the negative sign in the definition of F_{ij} because it is generally positive.

It is the sum of the off-diagonal terms, $F_{ij} + F_{ji} = 2F_{ij} \equiv \delta_{ij}$, in the AIM approach that Fradera et al.[36] define as the *delocalization index* and propose as a quantitative measure of electron pair sharing between basins Ω_i and Ω_j; they also denote F_{ii} as the *atomic localization index*.

In the density functional approach used here, we approximate the system wave function by the Kohn−Sham single determinant. For such a single determinant wave function (as also in the Hartree−Fock self-consistent-field approach), the delocalization index, δ_{ij}, for a closed-shell system may be written as

$$\delta_{ij} = 4\sum_{\mu,\nu} \langle \varphi_\nu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega i} \langle \varphi_\mu(\vec{r})|\varphi_\nu(\vec{r})\rangle_{\Omega j} \tag{5}$$

where one sums over the doubly occupied orbitals, μ and ν. This is, as both Fradera et al.[36] and Ángyán et al.[44] point out, invariant to unitary transformations and is closely related to the covalent bond order presented by Cioslowski and Mixon[19] in which only the diagonal terms, $\boldsymbol{\mu} = \boldsymbol{v}$, of eq 5 are kept. Cioslowski and Mixon's expression is not invariant to a unitary transformation, but, as Ángyán et al.[44] point out, on the basis of the population-localized orbitals Cioslowski and Mixon use, the neglected off-diagonal terms become small and, for strictly localizable systems, may be negligible. We shall see in our study here that the results of the two expressions are, indeed, nearly identical.

The representation of the delocalization index at the single determinant level as a covalent bond order is of considerable interest. Fradera et al.[36] state that the delocalization index or electron pair sharing function is nonarbitrary, being determined by the second-order density matrix at all levels of theory, and in general cannot be associated with a bond order. They comment that only in the case of *equal* sharing will δ_{ij} indicate the number of pairs of electrons involved in the bond and that in the case where polarization effects are present (ionic character of the bond) it will be reduced. However, the fact that the delocalization index at the single determinant level may be taken as a measure of *covalent bond order* is well worth noting; that is to say, the idea of covalent bond order as defined by Ángyán et al.[44] and by Cioslowski and Mixon[19] does explicitly take into account the fact that a particular bond may be polarized and have significant ionic character. Our discussion here based on the density functional approach (single Kohn−Sham determinant) will be interpreted in this way.

ELF is a robust descriptor of chemical bonding based on topological analyses of local quantum mechanical functions related to the Pauli exclusion principle. For a closed shell single determinantal wave function built from Hartree−Fock or Kohn−Sham orbitals, φ_j, ELF, $\eta = \eta(\vec{r})$, is *defined* as

$$\eta = \frac{1}{1 + (D/D_h)^2} \tag{6}$$

where

$$D = \frac{1}{2}\sum_{j=1}^{N}|\nabla\varphi_j|^2 - \frac{1}{8}\frac{|\nabla\rho|^2}{\rho}$$

$$D_h = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3}$$

$$\rho = \sum_{j=1}^{N}|\varphi_j|^2 \tag{7}$$

and where the scaling factor is arbitrarily chosen to be the homogeneous electron gas kinetic energy density of a system of the same electron density. D is the local Pauli kinetic energy density, the excess kinetic energy electrons have been (due to the Pauli exclusion principle) compared to a system of bosons of the same density.[29,30] The ELF function can be viewed as a local measure of the Pauli repulsion between electrons due to the exclusion principle and allows one to define regions of space that are associated with different electron pairs in a molecule or solid.

Using the vector field of the gradient of the electron localization function, the topology of the ELF function can be used to define basins within which electron pairs can be found.[29−31,34] ELF basins are labeled as either core or valence basins. Inner core basins contain or surround a nucleus while valence basins do not; hydrogen basins are taken as exceptions since, although they contain a proton, they are taken to represent a shared pair interaction. A valence basin is characterized by its number of connections to core basins, referred to as its synaptic order. Basins are connected if they are bounded by part of a common surface.

The population of an ELF basin Ω_i, N_i, is given by integrating the total electron density, $\rho(\vec{r})$, over the basin volume (eq 8). The ELF basin populations are particularly important in that they tend to reflect delocalization effects and, in the case of bond basins, the bond order.

$$N_i = \int_{\Omega_i}\rho(\vec{r})\,\mathrm{d}\vec{r} \tag{8}$$

Often the ELF bond basin population is taken as a measure of the order of the bond involved, but this, just as for the delocalization index, is usually not straightforward because of polarization effects and the tendency sometimes found of contributions both to or from the bond basin population from/to neighboring lone pair basins. Care must be taken, and it will usually be better to compare *relative* basin populations as we have suggested.[37]

Theoretical Details

The structures employed here used optimized geometries found in the B3LYP approach[45,46] with a 6-311+G(d,p) basis using Gaussian 98.[47] The AIM and ELF calculations were carried out by employing the TopMod Package of Noury and co-workers,[48] also in the B3LYP/6-311+G(d,p) approach. Step sizes of 0.1 au and box sizes that extended 5.0 au from the outermost atomic coordinates in each direction were used. The TopMod package sacrifices some accuracy for efficiency and, according to the authors, is thought to be accurate to a few percent, sufficient for comparative studies.

The anti form (hydroxyl hydrogen syn to the phosphorus lone pair) of $HOPH_2$ was employed here, although it is but 0.6 kcal/mol higher than the syn form in this work. More accurate calculations[49] indicate the difference may be even smaller, of the order of 0.2 kcal/mol.

TABLE 1: Optimized Bond Distances (R_{PO}, Å) and PO-Bond-Breaking Energies (ΔE, kcal/mol)[a]

	R_{PO}	ΔE
A. Formal Single Bonds		
$HOPH_2$	1.690	88.9
HOPO	1.637	103.1
$HOPO_2$	1.600	105.7
$(HO)_3P$	1.652	104.2
$(HO)_3PO$	1.606	121.4
B. Formal Double Bonds		
HPO	1.497	163.5
HOPO	1.483	182.5
C. Phosphoryl Bonds		
$HOPO_2$[b]	1.468	115.7
$HOPO_2$[c]	1.462	118.3
H_3PO	1.493	109.6
$(CH_3)_3PO$	1.500	132.8
$(NH_2)_3PO$	1.486	127.6
$(HO)_3PO$	1.476	143.7
F_3PO	1.450	130.2
Cl_3PO	1.465	123.0

[a] The data have been divided into formal single (A), double (B), and phosphoryl (C) bonds. [b] Oxygen syn to the OH hydrogen. [c] Oxygen anti to the OH hydrogen.

Results and Discussion

Bond Distance and Energy Data. Table 1 exhibits the optimized PO bond distances and bond breaking energies as determined by the G2MP2 method.[50] One can readily see that the bond distances resolve into two classes, one involving what we think of as formal single bonds and the other containing both formal double bonds and phosphoryl bonds whose bond order is yet to be determined. The R_3PO PO bond is short and of the order of what one considers to be a conventional PO double bond, such as in HPO. Clearly on the basis of these distances, phosphoryl and double bonds are equivalent.

On the other hand, such is not the case for the bond breaking energies. Here the three indicated classes in the table are distinguishable, with the phosphoryl bond-breaking energies intermediate between the single and double bond data. We often use both bond distances and bond energies to characterize the order of a bond, and usually these two criteria are consistent with each other. Such is not the case here. As many have noted before, the phosphoryl bond is unusual.

ELF Data. For reasons discussed below we emphasize the AIM delocalization index analysis in this work. It provides a measure of covalent bond order in the single determinant density functional theory approach we employ and yields results that we conclude are consistent and less ambiguous than those of the ELF approach. Nonetheless the electron localization function provides data which should be taken into account in the overall analysis of the bonding situation of the PO phosphoryl bond.

The ELF data are presented in Table 2 for basin populations for the PO bond and the O lone pairs. The bond basin populations for both the single and double bonds are less than that classically expected (two and four, respectively), and this signals the polarized nature of both bonds. On the basis of a single phosphorus-donated electron pair in the phosphoryl bond, the phosphoryl bond population might be considered somewhat high. Both the singly and double bound oxygen lone pair populations are larger than expected (four in both cases), while the phosphoryl oxygen population is on average about 0.23 electron smaller than the classically expected value of six

TABLE 2: ELF Bond Basin (N_{bb}) and Oxygen Lone Pair Basin (Nlp(O)) Populations[a]

	N_{bb}	Nlp(O)
A. Formal Single Bonds		
$HOPH_2$	1.34	4.61
HOPO	1.61	4.35
$HOPO_2$	1.73	4.39
$(HO)_3P$	1.46	4.62
$(HO)_3PO$	1.60	4.55
B. Formal Double Bonds		
HPO	1.98	5.36
HOPO	2.01	5.44
C. Phosphoryl Bonds		
$HOPO_2$[b]	2.07	5.82
$HOPO_2$[c]	2.04	5.85
H_3PO	1.89	5.85
$(CH_3)_3PO$	1.91	5.85
$(NH_2)_3PO$	2.05	5.80
$(HO)_3PO$	2.12	5.83
F_3PO	2.36	5.57
Cl_3PO	2.21	5.62

[a] The data have been divided into formal single (A), double (B), and phosphoryl (C) bonds. [b] Oxygen syn to the OH hydrogen. [c] Oxygen anti to the OH hydrogen.

corresponding to three isolated lone pairs. We think that the lessened values of the single and double bond basins in the PO bond are due in part to the bonding electrons appearing in the associated lone pair basin. We note that the ratio of the PO bond population in HPO to that of $HOPH_2$ is close to 1.5, in line with our earlier results, which indicated that ELF bond basin population ratios are not as accurate in measuring relative bond order as is the delocalization index.[37] The reduced value of the phosphoryl oxygen lone pair population is consistent with back-bonding to phosphorus.

The polarized nature of the bonds can also be seen from the fact that the relative distances of the bond basin attractors is very close to 40% of the way from oxygen to phosphorus in *all* the bonds studied, both HOP and PO types. Of equal interest is the fact that, again in *all* the cases studied here, the AIM bond critical point is very close to 60% of the way from oxygen to phosphorus. Accordingly, the majority of the ELF bond basin most likely resides in the oxygen AIM basin. Raub and Jansen[51] have recently studied the quantitative disposition of this effect in several small molecules and use it to define a quantitative measure of the polarity of a bond, that is to say, its ionic character. Parts a−c of Figure 1 exhibit ELF isosurfaces in $HOPH_2$, HPO, and H_3PO; core, hydrogen, and lone pair basins are readily recognized, and one can see that the PO bond basins are located rather close to the oxygen atomic core and its lone pair basins.

But the key observation at this point is that *if* we take the ratio of bond populations to measure bond order and *if* HPO is our standard for the PO bond of order 2, then all the R_3PO PO bonds are also of order 2. As we shall see, this is in conflict with the AIM delocalization index results. Because we believe the AIM data more properly describe the phosphoryl bond, the above result may be considered a shortcoming of the ELF interpretation in this case.

AIM Data. Table 3 contains the AIM delocalization index information. If we take the PO bond in HPO to have order 2.0, then, with the exception of the OH bond in $(HO)_3PO$, PO single bonds are of order 1 as expected, while the R_3PO bonds are larger than unity but noticeably smaller than 2, on average about 1.3. We note that the PO "multiple" bonds in $HOPO_2$ are also of this magnitude. The π system for this molecule is a three-center four-electron one where each multiple bond would be expected to be about order 1.5, close to the observed relative delocalization index of 1.42. It may also be viewed as a resonance hybrid involving the species shown in Scheme 1 below. Note that the P^+O^- localized bond in this representation can be viewed as back-bonding to the π antibonding orbital on the other PO fragment, a picture equivalent to that of the three-center, four-electron bond. This type of back-bonding is, however, different from that in the R_3PO species in that in the latter case the back-bonding involves the antibonding R_3P orbitals, generally higher in energy than would be the PO antibonding π^* orbital of the PO π system. Thus, the back-bonding in the three-center, four-electron case is expected to be significantly larger, as indeed it is. Because the characteristics

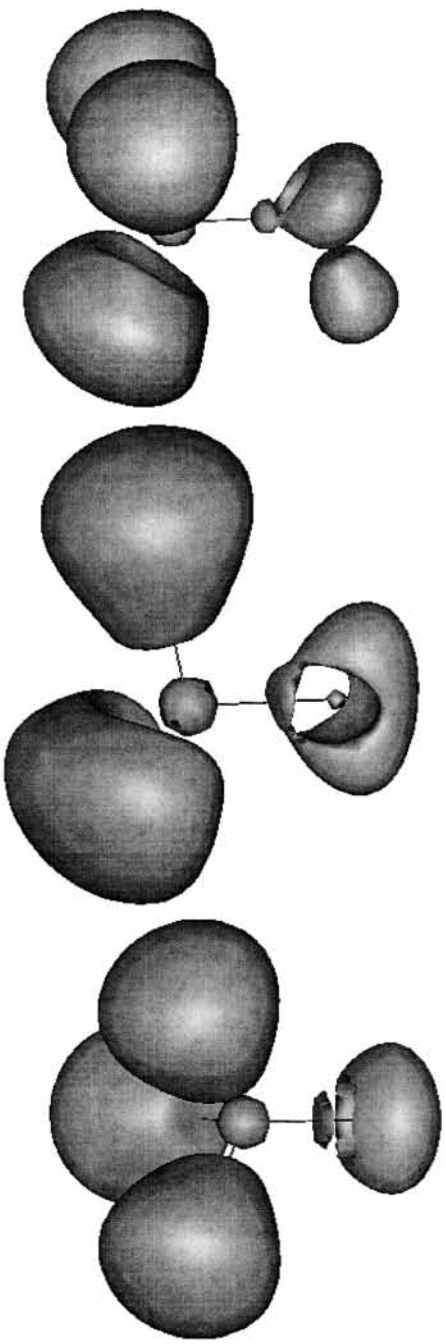


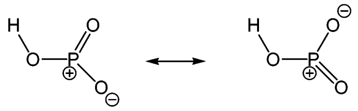
Figure 1. ELF isosurfaces for (a, top) $HOPH_2$ ($\eta = 0.83$), (b, middle) HPO ($\eta = 0.82$), and (c, bottom) H_3PO ($\eta = 0.80$). Core, hydrogen, bond, and lone pair basins are readily identified. Note that the close proximity to the oxygen atom of the PO bond isosurfaces is in all cases.

TABLE 3: AIM Absolute (δ) and Relative ($\delta^{rel}_{HPO} \equiv 2.0$) Delocalization Indices for the PO Bonds[a]

	δ	δ^{rel}
A. Formal Single Bonds		
$HOPH_2$	0.83	1.07
HOPO	0.90	1.16
$HOPO_2$	0.69	0.90
$(HO)_3P$	0.78	1.01
$(HO)_3PO$	0.60	0.70
B. Formal Double Bonds		
HPO	1.54	(2.00)
HOPO	1.40	1.82
C. Phosphoryl Bonds		
$HOPO_2$[b]	1.10	1.42
$HOPO_2$[c]	1.01	1.32
H_3PO	1.06	1.37
$(CH_3)_3PO$	0.98	1.27
$(NH_2)_3PO$	0.88	1.14
$(HO)_3PO$	0.96	1.24
F_3PO	1.01	1.31
Cl_3PO	1.12	1.46

[a] The data have been divided into formal single (A), double (B), and phosphoryl (C) bonds. [b] Oxygen syn to the OH hydrogen. [c] Oxygen anti to the OH hydrogen.

SCHEME 1



of the multiple bonds in $HOPO_2$ so closely resemble those of the more conventional phosphine oxides, we have included them in this classification in the tables.

To illustrate the nature of the ionic character and back-bonding in these molecules, we have employed the delocalized orbitals of Cioslowski and Mixon.[19] They defined a natural bond order in the atoms-in-molecules picture using a localization procedure[17,18] based on the idea of atomic overlap matrices. For a closed-shell system of doubly occupied orbitals they partition the total number of electrons in the molecule over the AIM basins Ω_i as

$$\begin{aligned} N &= 2\sum_{\mu}\sum_{i}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega I} \\ &= 2\sum_{\mu}\sum_{i}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega I}\sum_{j}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega j} \\ &= 2\sum_{\mu}\sum_{i,j}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega I}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega j} \\ &= 2\sum_{\mu}\sum_{i}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega i}{}^{2} + \\ &\qquad 4\sum_{\mu}\sum_{i<j}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega I}\langle\varphi_\mu(\vec{r})|\varphi_\mu(\vec{r})\rangle_{\Omega j} \\ &= N_{\text{atomic}} + N_{\text{diatomic}} \end{aligned} \tag{9}$$

where it is the second, N_{diatomic}, term that they take as a measure of the covalent bondorder, $p(i,j)$, between atoms defined by the AIM basins i and j. We have commented earlier on this bond order definition and the more general (and invariant) one due to Ángyán et al.[44] The Cioslowski−Mixon localized orbitals 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.[17,18] These bond orders generally relate well to conventional ideas of single and multiple covalent bonds, as they also do in the more general and invariant form due to Ángyán et al.

TABLE 4: Atomic Occupancies of the Localized Orbitals in $HOPH_2$, HPO, and H_3PO

$HOPH_2$

orbital	H1	O2	P3	H4	H5	orbital type
1	0.00000	0.00000	1.00000	0.00000	0.00000	core
2	0.00000	1.00000	0.00000	0.00000	0.00000	
3	0.00000	0.00003	0.99993	0.00002	0.00002	
4	0.00001	0.00132	0.99850	0.00009	0.00009	
5	0.00000	0.00012	0.99897	0.00006	0.00085	
6	0.00000	0.00012	0.99897	0.00085	0.00006	
7	0.00296	0.98913	0.00590	0.00101	0.00101	O lone pair
8	0.00779	0.95382	0.02693	0.00573	0.00573	O lone pair
9	0.00426	0.82405	0.15654	0.00758	0.00758	OP bond
10	0.19924	0.78539	0.01109	0.00213	0.00213	HO bone
11	0.00090	0.02879	0.92303	0.02364	0.02364	P lone pair
12	0.00067	0.01922	0.26105	0.69795	0.02112	PH bond
13	0.00067	0.01922	0.26105	0.02112	0.69795	PH bond

HPO

orbital	H1	P2	O3	orbital type
1	0.00000	1.00000	0.00000	core
2	0.00000	0.00000	1.00000	
3	0.00003	0.99993	0.00004	
4	0.00019	0.99653	0.00328	
5	0.00054	0.99898	0.00048	
6	0.00005	0.99941	0.00055	
7	0.00026	0.00170	0.99803	O lone pair
8	0.00655	0.14967	0.84378	PO bond
9	0.01303	0.04382	0.94315	O lone pair
10	0.01235	0.22793	0.75971	PO bond
11	0.02255	0.94786	0.02959	P lone pair
12	0.70422	0.27013	0.02565	HP bond

H_3PO

orbital	O1	P2	H3	H4	H5	orbital type
1	0.00000	1.00000	0.00000	0.00000	0.00000	core
2	1.00000	0.00000	0.00000	0.00000	0.00000	
3	0.00370	0.99604	0.00009	0.00009	0.00009	
4	0.00034	0.99855	0.00005	0.00101	0.00005	
5	0.00034	0.99855	0.00101	0.00005	0.00005	
6	0.00034	0.99855	0.00005	0.00005	0.00101	
7	0.99679	0.00175	0.00048	0.00049	0.00049	O lone pair
8	0.80824	0.16794	0.00789	0.00797	0.00797	PO bond
9	0.91502	0.06164	0.01270	0.00532	0.00532	O lone pair
10	0.91502	0.06164	0.00293	0.01021	0.01021	O lone pair
11	0.01794	0.23717	0.01675	0.01675	0.71139	PH bond
12	0.01794	0.23717	0.01675	0.71139	0.01675	PH bond
13	0.01793	0.23719	0.71137	0.01675	0.01675	PH bone

We first present in Table 4 atomic occupancies of the localized orbitals of Cioslowski and Mixon for the three prime cases illustrating single- ($HOPH_2$), double- (HPO), and phosphoryl-bond-containing (H_3PO) molecules. Similar data were presented in our earlier work,[14] but we repeat it here for the present level of theory and to view it alongside our current AIM and ELF results. In the table, core and valence orbitals are separated, and an inspection of the occupancies clearly reveals the orbital types as listed in the right-hand column. We note that in all cases the orbitals characterized as PO bonds (orbital 9 for $HOPH_2$, 8 and 10 for HPO, and 8 for H_3PO) are highly ionic with the preponderance of charge residing on the oxygen atom. Cioslowski and Mixon[19] define the ionic character of such bonds by taking the difference of occupancies divided by their sum (as a normalization), so that for the aforementioned bonds one has ionicities of 68, 70, 54, and 66%, respectively; these are clearly very polar bonds. There are two such bonds in HPO corresponding to its designation as a double bond with σ and π parts. In each of the molecules there is one oxygen lone pair

TABLE 5: Significant Bond and Lone Pair Contributions to the PO Covalent Bond Order from the Cioslowsky−Mixon[19] Localized Orbitals[a]

	PO bond	lone pairs	subtotal	total	δ
		A. Formal Single Bonds			
$HOPH_2$	0.516	0.209 (2)	0.725	0.830	0.83
HOPO	0.406	0.404[b]	0.811	0.925	0.90
$HOPO_2$	0.384	0.120	0.504	0.574	0.69
$(HO)_3PO$	0.404	0.090	0.494	0.582	0.60
		B. Formal Double Bonds			
HPO	1.198 (2)	0.277 (2)[c]	1.475	1.527	1.54
HOPO	1.049 (2)	0.347 (2)[d]	1.396	1.431	1.40
		C. Phosphoryl Bonds			
$HOPO_2$[e]	0.478	0.416 (2)	0.894	0.937	1.10
$HOPO_2$[f]	0.481	0.424 (2)	0.905	0.945	1.01
H_3PO	0.543	0.451 (2)	0.994	1.071	1.06
$(CH_3)_3PO$	0.512	0.401 (2)	0.912	0.978	0.98
$(NH_2)_3PO$	0.484	0.376 (2)	0.860	0.905	0.88
$(HO)_3PO$	0.490	0.411 (2)	0.901	0.946	0.96
F_3PO	0.514	0.481 (2)	0.995	1.036	1.01

[a] The number of contributing orbitals is given in parentheses. The total covalent bond order contains all contributions, while the delocalization index[36] (δ) is that found in the present study. The data have been divided into formal single (A), double (B), and phosphoryl (C) bonds. [b] From one oxygen lone pair (0.265) and one phosphorus lone pair (0.139). [c] From one oxygen lone pair (0.165) and one phosphorus lone pair (0.112). [d] From one oxygen lone pair (0.224) and one phosphorus lone pair (0.123). [e] Oxygen syn to the OH hydrogen. [f] Oxygen anti to the OH hydrogen.

orbital of virtually unit occupancy (7 in all three cases) relatively uninvolved in the bonding. The other oxygen lone pairs (8 in $HOPH_2$, 9 in HPO, and 9 and 10 in H_3PO have ionicities of 95, 91, 87, and 87%, respectively; the phosphorus lone pair orbitals (11 in $HOPH_2$ and HPO) likewise are highly polar as expected, with ionicities of 94% in each case. Yet, these seemingly small transfers of charge from oxygen to phosphorus (and from phosphorus to oxygen for the P lone pairs) make a significant contribution to the covalent bond order (and the delocalization index) and are characteristic of the importance of back-bonding in these molecules.

This is illustrated further by the data of Table 5 which list the major contributions to the covalent bond order (and delocalization index) by the PO bonds and back-bonding O and P lone pairs. First, note that the Cioslowski−Mixon bond order ("total") is essentially equal to the delocalization index (δ) for all cases studied; clearly in our study the terms Cioslowski and Mixon neglect are negligible. Second, as noted above both the single and phosphoryl species have essentially one (polar) PO bond while the double bonds in HPO and HOPO have two, each contributing approximately the same amount to the covalent bond order. The fact that the double bonds in HPO and HOPO have double the contribution that the other species have is consistent with our ideas of double bonds. Third, note that *all* species have nonnegligible contributions from the lone pairs, both those on oxygen and, where appropriate, those on phosphorus. But, fourth and most important, note that the phosphoryl species have twice as many back-bonding orbitals contributing to the bonding, although they are not as strong contributors as the (σ) PO bonding orbitals. This is why the phosphoryl species have a higher covalent bond order than the single bond species (such as $HOPH_2$) but one that is smaller than the conventionally doubly bound cases.

Finally, we comment on the involvement of "lone pairs" in the PF bond in PF_3 and F_3PO as an example of lone pair bonding involvement in other than the PO bond. Orbitals, however localized, will generally overlap into adjacent atomic basins and as such will contribute to the covalent bond order. In both PF_3 and F_3PO the fluorine lone pairs make up about 28% of the significant contributions to the PF covalent bond order. In addition, in PF_3 the phosphorus one pair contributes about 17%. Clearly the contributions of lone pairs to covalent bonding is quite general. It is the fact that it is so large in the R_3PO phosphoryl bond that accords that bond its special characteristics.

Summary

One cannot distinguish the phosphoryl bond from a conventional PO double bond by comparing bond distances. This is true as well when examining the ELF PO bond basin populations. Because the ratio of multiple bond basin populations to those corresponding to single bonds is not as high as we would expect, we put less trust on this approach to characterize the phosphoryl bond. Both the bond breaking energies and delocalization indices do nicely divide into the three classes of single, double, and phosphoryl and, indeed, tend to parallel each other. On the basis of the PO bond in HPO having a bond order of 2.0, the phosphoryl bond has a bond order of about 1.3. Examination of localized orbitals confirm our ideas that the phosphoryl bond is highly polar as, indeed, are the other PO bonds. What sets the phosphoryl bond apart is the high degree of back-bonding that contributes to the delocalization index (and covalent bond order) and provides for its stronger-than-single-bond character and short bond distance.

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