

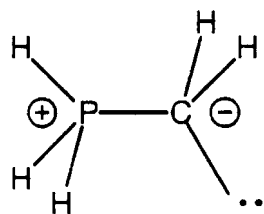
An Electron Localization Function Investigation of Bonding in Some Simple Four-Coordinate Nitrogen and Phosphorus Compounds

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ABSTRACT: *The bonding in some simple four-coordinate species involving nitrogen and phosphorus has been studied by the electron localization function (ELF) approach and compared to that in their conventionally singly and doubly bonded counterparts. Despite evidence suggesting the presence of a conventional multiple bond in certain cases of the four-coordinate species, the ELF study shows this not to be the case. Rather, the situation is better pictured as, for example, in the case of H_3PCH_2 as*



where both ionic and covalent interactions are present, a type of bond we term cov-ionic. While the ionic interaction is generally strong, the covalent part can be weak, as in the case of the four-coordinate nitrogen compounds, or strong, as in the case of the four-coordinate phosphorus species. The quantum mechanically determined properties of the cov-ionic bonded compounds are consistent with this picture. © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:341–352, 2000

INTRODUCTION

An Unusual Bonding Situation

The nature of the bonding in the PO bond of phosphine oxides (R_3PO) has been of great interest for many years. It has been reviewed extensively by Gilheany [1,2], who 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 is in the interpretation of the bond based on different approaches.

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 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 $HPCH_2$.

More recently 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. Atoms-in-molecules [15,16] (AIM) studies yield-localized molecular orbitals [17–19] that indicate one highly polarized σ bond plus strong back-bonding of the oxygen π orbitals. Although 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 latter study 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] based on 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.

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 non-bonded maxima behind the oxygen atom (away from phosphorus) and staggered with respect to the R_3P bonds to indicate the lone pairs. This picture has received strong support from our own recent electron localization function (ELF) study [26].

In the present work we examine the bonding in the four-coordinate (hereafter designated as 4cor) H_3XCH_2 , H_3XNH , and H_3XO compounds, where $X = N, P$, emphasizing the ELF approach. Although the 4cor nitrogen systems are not known experimentally, we feel that by studying both nitrogen and phosphorus compounds we will gain better insight into the unusual bonding in these molecules. Our study supports an ionic plus covalent bonding and leads us to propose a new name for this particular kind of chemical bond.

The Electron Localization Function

The ELF is a robust descriptor of chemical bonding based on topological analysis of local quantum mechanical functions related to the Pauli exclusion principle. It was first introduced by Becke and Edgecombe [27] and has been developed and applied extensively by Savin and Silvi and their collaborators [28–36]. The local maxima of the function define localization attractors corresponding to core, bonding (located between the core attractors of different atoms) and nonbonding electron pairs and their spatial arrangement.

Becke and Edgecombe pointed out that the conditional-pair probability for same spin electrons has the form

$$P_{\text{cond}}^{\sigma\sigma}(\bar{r}, s) = \frac{1}{3} \left[\sum_j^{\sigma} |\nabla\varphi_j|^2 - \frac{1}{4} \frac{|\nabla\rho_{\sigma}|^2}{\rho_{\sigma}} \right] s^2 + \dots \quad (1)$$

for a spin at point \bar{r} and another a distance s away (averaged over a spherical shell of radius s). The coefficient of the quadratic term is the local Pauli kinetic energy density; the excess kinetic energy electrons have compared to a bosonic system of the same density due to the Pauli exclusion principle [30]. When it is small, the Fermi hole at \bar{r} is large, and one would expect to find pairs of electrons of opposite spin in the region; when it is large, the converse is true.

For a single determinantal wavefunction built from Hartree-Fock or Kohn-Sham orbitals, φ_j , the ELF function of position \bar{r} is defined as

$$\eta = \frac{1}{1 + \left(\frac{D}{D_h}\right)^2} \quad (2)$$

where

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

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

$$\rho = \sum_{j=1}^N |\varphi_j|^2 \quad (3)$$

and where the scaling factor was chosen to be the homogeneous electron gas kinetic energy density of a system of the same density. The ELF localization 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. The position where η attains a maximum value (the attractor) can be used as an electron pair's signature [33].

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 one or more electron pairs are to be found [29,31–34]. These subsystems are defined in terms of zero-flux surfaces; the gradient paths ends at what are called attractors 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. The ELF basins are labeled as either core or valence basins. Core basins contain a nucleus, and valence basins do not; hydrogen basins

are taken as exceptions because although they contain a proton, they do 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. A simple covalent bond basin would be connected to two core basins and be of synaptic order two; a lone-pair basin would be monosynaptic. More complex bonding basins can be polysynaptic.

The electron population of a basin Ω_i , N_i , is given by integrating the total electron density, $\rho(\vec{r})$, over the basin.

$$N_i = \int_{\Omega_i} \rho(\vec{r}) d\vec{r} \quad (4)$$

whereas the basin variance (or fluctuation), σ_i^2 , is given by

$$\begin{aligned} \sigma_i^2 &= N_i - N_i^2 + \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_i} P(\vec{r}_1, \vec{r}_2) d\vec{r}_2 \\ &= N_{ii} - N_i(N_i - 1) \end{aligned} \quad (5)$$

where $P(\vec{r}_1, \vec{r}_2)$ is the spinless pair function, that is, the probability of finding one electron at position \vec{r}_1 and another at \vec{r}_2 [34]. N_{ii} is the actual number of electron pairs within Ω_i , whereas $N_i(N_i - 1)$ is the number of pairs in an isolated system containing N_i particles.

THEORETICAL DETAILS

The quantum mechanical calculations were done using the Gaussian suite of programs [37], while the ELF calculations employed the TopMod package of Noury et al. [38]. The various properties studied here were determined with a variety of basis sets and theoretical levels found to be appropriate from past experience; in all cases we employed sets of six d-polarization and seven f-polarization functions. Structures were optimized at the MP2(FC)/6-31+G(d,p) level. Wavefunctions used for the ELF studies were obtained from B3LYP/6-311+G(3df,2pd)//MP2(FC)/6-31+G(d,p) calculations [39,40]. The NMR shieldings and dipole moments calculations used two sets of d-polarization functions for phosphorus and single sets of polarization functions for the other atoms at the MP2(FC)/6-311+G(d,p)//MP2(FC)/6-31+G(d,p) and RHF/6-311+G(d,p)//MP2(FC)/6-31+G(d,p) levels, respectively. The shielding calculations were done in the GIAO approach [41] with our estimated Møller-Plesset infinite order (EMPI) approach [42] based on the apparent convergence of the various orders of Møller-Plesset theory as a geometric series. The

EMPI shielding, σ_{EMPI} , is a combination of Hartree-Fock and MP2, shieldings and is given by:

$$\sigma_{\text{EMPI}} = \sigma_{\text{HF}} + \frac{2}{3} (\sigma_{\text{MP2}} - \sigma_{\text{HF}}) \quad (6)$$

The EMPI shieldings are reported in our tables; because the difference between the HF and MP2 results are also given, one may, if desired, reproduce the shieldings directly calculated at the HF and MP2 levels; shieldings directly available from the Gaussian code. Calculations to determine relative energies for the various species, including the transition state structures, were carried out at the B3LYP/6-311++G(3df,2p)//B3LYP/6-31+G(d,p) level with zero-point and thermal corrections to the energies taken directly from the B3LYP/6-31+G(d,p) optimizations with no scaling. This approach to determining energies has proven to be competitive [43] with those involving more conventional high-accuracy methods [44–47] and is significantly faster.

RESULTS AND DISCUSSION

Quantum Mechanical Properties

One of the main points of interest in the 4cor phosphorus compounds is that the heavy atom bond distances are often reduced from what one would expect for a normal covalent single bond to essentially that characteristic of a normal double bond. It was pointed out recently [14] that this multiple bond cannot be of the conventional type in that large correlation effects in the NMR shielding seen in normal doubly bonded systems are absent. Table 1 shows some new and some recalculated chemical shieldings for conventional single bonded species (first column), conventional double bonded species (third column), and the 4cor nitrogen and phosphorus species (second column). In all cases the 4cor species exhibit small correlation effects much more like their single bonded counterparts rather than the double bonded compounds. In the latter case, one understands the impact of correlation on the shielding to arise from the reduced energy gap due to π bonds and the σ - π orbital mixing (in the presence of a magnetic field) that leads to significant changes relative to the Hartree-Fock level of theory. The data in Table 1 clearly indicate that, while some sort of multiple bonding may be present in the 4cor species, it is not of the conventional type.

The optimized heavy atom bond distances are given in Table 2 so we can compare the conventional single and double bond cases to the 4cor species (middle column). All of the 4cor phosphorus compounds show bond distances that are essentially

equal to that of their conventional double bonded counterparts. In the case of 4cor nitrogen, a bond reduction is seen for H_3NO , but not for H_3NNH nor H_3NCH_2 , the latter compound actually showing an increase of some 0.09 Å compared to its singly bonded precursor. The strength of bonding involved in the two cases, nitrogen versus phosphorus, is obviously different.

TABLE 1 Chemical Shielding (ppm) for the Nitrogen and Phosphorus Species^a

Nitrogen Species						
	H_2NXH_n		$H_3NX_{(n-1)}$		$HNXH_{(n-1)}$	
	N	X	N	X	N	X
$XH_n = CH_3$	257.7	166.4	225.6	138.8	-82.1	31.8
	10.6	1.4	4.7	1.7	69.3	20.2
NH_2	218.0	218.0	201.6	140.4	-326.4	-326.4
	7.8	7.8	-1.1	23.5	218.5	218.5
OH	150.4	275.9	174.4	184.6	-791.3	-1835.0
	6.8	4.5	-8.1	50.6	899.7	1499.5

Phosphorus Species						
	H_2PXH_n		$H_3PX_{(n-1)}$		$HPXH_{(n-1)}$	
	P	X	P	X	P	X
$XH_n = CH_3$	519.6	198.2	448.5	224.1	108.8	15.7
	18.0	5.8	10.2	5.9	53.2	37.9
NH_2	426.3	279.4	426.1	286.1	-216.3	-254.3
	2.8	15.4	4.9	10.0	194.7	248.1
OH	311.5	364.7	399.3	352.1	-959.2	-919.8
	-12.5	21.3	-3.9	15.7	-739.6	-61.5

^aThe first row of each entry is the EMPI isotropic shielding, and the second row is the isotropic MP2 shielding minus the SCF isotropic shielding. The three sets of columns correspond to the single bonded species, the four-coordinate species, and the double bonded species, respectively.

TABLE 2 Optimized NX and PX Bond Distances (Å) for the Nitrogen and Phosphorus Species^a

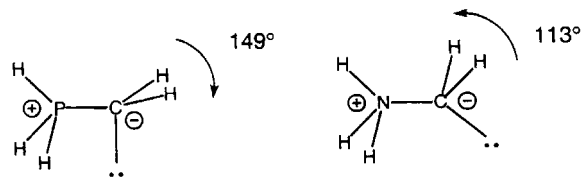
Nitrogen Species			
	H_2NXH_n	$H_3NX_{(n-1)}$	$HNXH_{(n-1)}$
	$XH_n = CH_3$	1.4641	1.5540
NH_2	1.4336	1.4652	1.2655
OH	1.4512	1.3753	1.2376

Phosphorus Species			
	H_2PXH_n	$H_3PX_{(n-1)}$	$HPXH_{(n-1)}$
	$XH_n = CH_3$	1.8589	1.6820
NH_2	1.7241	1.5773	1.6086
OH	1.6921	1.5039	1.5220

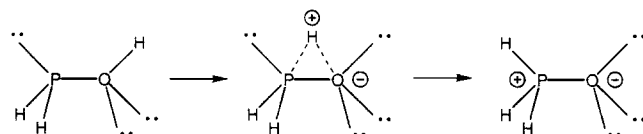
^aThe three columns correspond to the single bonded species, the four-coordinate species, and the double bonded species, respectively.

Some hint of the difference in bonding in these two cases can be seen from the arrangement of the hydrogens on the X-atom in these compounds. For the cases of H_3PCH_2 and H_3PNH , the carbon and nitrogen protons are bent back from the XP bond compared to the single bond species, a configuration that would allow the orbitals involved with the lone pairs to be more actively involved in the region of the bond; just the opposite is true for H_3NCH_2 and H_3NNH , where the CH_2 and NH protons are actually bent closer to the heavy atom bond, suggesting that the lone pair orbitals in these cases prefer to be further away from that bond. This situation is illustrated schematically in Scheme 1 for H_3PCH_2 and H_3NCH_2 . Whereas for an ideal tetrahedral arrangement, the bisector of the HCH bonds makes an angle of 125° , this angle is increased to 149° in H_3PCH_2 and reduced to 113° in the H_3NCH_2 case. We shall return to this picture and its implications after our discussion of the ELF isosurfaces.

The formation of the 4cor species from their conventional parent molecules results from the transfer of a proton from one half of the molecule to the lone pair on either the 4cor phosphorus or nitrogen atom as schematically shown in Scheme 2 for the example of H_3PO . This simplistic picture puts a formal charge of +1 on the H_3P portion of the molecule and a corresponding charge of -1 on the other half of the molecule. This picture is provided some support from the data in Table 3 that compares the dipole moments for the conventional single- and double-bonded species (columns one and three in Table 3) and the 4cor species (column two in Table 3). The dipole moments for all of the 4cor species are significantly larger than both their conventional single and double-bonded counterparts. The apparent lack of involvement of the lone pairs in 4cor nitrogen is much in evidence as the dipole moments in these



SCHEME 1



SCHEME 2

species are reproduced by essentially unit charges at the nitrogen and other heavy atom centers (the n_q values). On the other hand, for the 4cor phosphorus compounds, the dipole moments are smaller and exhibit an increase in the methylene, imine, and oxide sequence.

There is further data supporting the assertion that the bond in the 4cor phosphorus compounds is much stronger than that in the 4cor nitrogen species. Table 4 gives bond breaking reaction enthalpies for both the conventional single bonded molecules (reaction R1) and for their 4cor counterparts (reaction R2). Breaking the conventional single bonds in both the nitrogen and phosphorus species requires from 60 to 80 kcal/mol, whereas the bond breaking energies in the 4cor species are much larger. This latter,

TABLE 3 Dipole Moments (debye) for the Nitrogen and Phosphorus Species^a

Nitrogen Species					
	H_2NXH_n	$H_3NX_{(n-1)}$	$H NXH_{(n-1)}$	n_q	
$XH_n =$	CH_3	1.490	5.830	2.435	0.781
	NH_2	2.143	5.803	0.0	0.825
	OH	0.808	5.900	2.149	0.893
Phosphorus Species					
	H_2PXH_n	$H_3PX_{(n-1)}$	$H PXH_{(n-1)}$	n_q	
$XH_n =$	CH_3	1.242	2.817	1.015	0.349
	NH_2	1.637	3.684	1.776	0.486
	OH	1.044	4.515	3.208	0.625

^a n_q represents the charge (positive and negative) located at the heavy atoms necessary to reproduce the calculated dipole moment for the $H_3NX_{(n-1)}$ and $H_3PX_{(n-1)}$ compounds. The first three columns correspond to the single-bonded species, the four-coordinate species, and the double-bonded species, respectively.

TABLE 4 Bond-Breaking Reactions Involving Three- and Four-Coordinate Nitrogen and Phosphorus Compounds^a

$H_2RXH_n \rightarrow H_2R \cdot + \cdot XH_n$ (R1)				
$H_3RXH_{n-1} \rightarrow (H_3R \cdot)^+ + (\cdot XH_{n-1})^-$ (R2)				
		(R1)	(R2)	$\Delta(R2-R1)$
R = N	$XH_n = CH_3$	78.9	238.9	160.1
	$= NH_2$	60.5	231.6	171.1
	$= OH$	59.4	232.4	173.0
R = P	$XH_n = CH_3$	65.7	260.5	194.8
	$= NH_2$	70.5	277.2	206.7
	$= OH$	83.9	295.8	211.9

^aThe enthalpy differences (kcal/mol) for reactions R1 and R2 and their difference ($\Delta(R2-R1)$) were calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level with thermal corrections to the enthalpy taken from the unscaled B3LYP/6-31+G(d,p) calculations. The UB3LYP method was employed for the doublet state species.

large energy required to break the bond involves breaking not only the covalent bond present but also separating the two charged particles, a significant energy quantity. For example, two unit electronic charges separated by 1.4 Å require some 237 kcal/mol to be separated.

The data in Table 4 show that the heavy atom bonds in the 4cor nitrogen species are weaker than those in the phosphorus compounds, as might be expected on the basis of the significant bond length reduction exhibited by the latter and missing in the former. The overall large value of the bond breaking energies is due, of course, to the fact that one is separating charged ions and overcoming a very large coulomb attraction. If one calculates the energy required to separate positive and negative charges initially located at the positions of the heavy atoms in these compounds, one obtains values of 214, 227, and 241 kcal/mol for the CH_3 , NH_2 , and OH nitrogen species, respectively, and 197, 211, 221 kcal/mol for the corresponding phosphorus compounds. While the energies required to break the bonds in the R2 nitrogen reactions are comparable to the electrostatic energies, those for the 4cor phosphorus species are some 60 to 80 kcal/mol higher. Although in both cases we think in terms of covalent plus ionic interactions, the bonding in the phosphorus compounds is clearly stronger.

The stability of the 4cor species relative to their conventionally single bonded counterparts is shown in Table 5, which contains the relative enthalpies of

TABLE 5 Relative Enthalpies of the Equilibrium Three- and Four-Coordinate Nitrogen and Phosphorus Species (kcal/mol)^a

Nitrogen Species						
	H_{min}	H_2NXH_n	Transition State	$H_3NX_{(n-1)}$	ΔH^+	
$XH_n =$	CH_3	-95.83325	0.0	79.2	63.4	15.8
	NH_2	-111.86225	0.0	62.2	43.0	19.2
	OH	-131.73332	0.0	48.2	23.3	24.8
Phosphorus Species						
	H_{min}	H_2PXH_n	Transition State	$H_3PX_{(n-1)}$	ΔH^+	
$XH_n =$	CH_3	-382.45254	0.0	77.6	44.1	33.5
	NH_2	-398.51843	0.0	72.4	22.8	49.7
	OH	-418.41294	0.12	59.3	0.0	59.1

^aEnergies were calculated at the B3LYP/6-311++G(3df,2p)//B3LYP/6-31+G(d,p) level with (unmodified) thermal corrections taken from frequencies calculated at the B3LYP/6-31+G(d,p) level. ΔH^+ represents the enthalpy of activation of the more enthalpic equilibrium species, and the absolute enthalpy of the lowest enthalpy structure is given by H_{min} (au).

the equilibrium structures for the 3- and 4- coordinate compounds, as well as the transition states whereby a proton is being transferred to either nitrogen or phosphorus. The observed transition states (one imaginary frequency) have an appearance much like that shown for the central structure in Scheme 2. There is a clear sequence of increasing stability as one moves from the CH_3 , to NH_2 , to the OH compounds, with again the phosphorus compounds being significantly lower in energy (approximately 20 kcal/mol) than their nitrogen counterparts. As pointed out in earlier work [43], the H_3PO and H_2POH compounds are virtually equi-energetic.

Also included in the table are the enthalpies of activation required to take the 4cor species to their corresponding transition states. According to simple transition state theory, the rate of a single reactant proceeding to a single product is given by

$$k_r = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (7)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy of activation. If we ignore the entropy term, the half-life of the reactant will be

$$t_{1/2} = \ln(2) \frac{h}{k_B T} \exp\left(+\frac{\Delta H^\ddagger}{RT}\right) \quad (8)$$

The half-life is a sensitive function of the enthalpy of activation and varies from 51 seconds for $\Delta H^\ddagger = 20$ kcal/mol to 35 years for $\Delta H^\ddagger = 30$ kcal/mol. When $\Delta H^\ddagger = 25$ kcal/mol the half-life is 2.7 days. For purposes of argument, in what follows we shall consider any enthalpy of activation greater than 25–30 kcal/mol to indicate a kinetically stable species capable of isolation in the laboratory.

For all of the nitrogen compounds the enthalpy of activation is such that we would regard these species as unstable. Indeed, there is no experimental evidence of their existence. On the other hand, the enthalpies of activation for the 4cor phosphorus compounds are all in that range where one might expect to be able to isolate the compounds involved. To date there is only experimental evidence for the oxide, H_3PO , studied in an argon matrix at very low temperatures [48].

The ELF Representations

The use of ELF in describing chemical bonding is useful not only in the visual representation of the isosurfaces involved but also in the basin populations. Although one might project from the Pauli exclusion principle that two electrons should occupy each basin, there is no a priori reason for this, and, indeed, deviations from this figure are common. It

is remarkable, indeed, that basin populations do roughly correspond to our chemical expectations, as we shall see in the following. A number of articles discussing ELF bond characterization and the associated basin populations have appeared [30,31,34] and some of this work has been repeated here in order to be able to discuss our results with a consistent set of ELF potentials.

Kohout and Savin [31] showed that atomic shells in the Li to Sr sequence are nicely separated from each other by ELF minima and that the integration of the electron density in a shell gives electron numbers in good agreement with the ones expected from the periodic table. These authors showed that for carbon, nitrogen, and oxygen, populations in the K-shell were typically 2.1, this increase coming at the expense of the electron population of the L-shell. Similarly for phosphorus, the K-shell value was 2.2, and the L-shell value was 7.9, so that the core population in phosphorus is 10.1, just slightly greater than that expected on basic principles. As we shall see, because of some of these complexities in basin populations, it proves useful to look at changes in basin populations as one moves from one type of molecule to a related one.

Some data for carbon compounds is given in section A of Table 6 where it is seen that the carbon core basins typically have populations of approximately 2.1 and that the hydrogen basins (denoted there as CH) are generally somewhat greater than 2 as well. These increased values for the core and hydrogen basins thereby detract from the electron populations in the other bonds in the molecules. The carbon-carbon single-bond basin population is nearly uniform at a population of 1.90, while the double- and triple-bond basins have values of 3.40 and 5.04, significantly smaller than that which we might expect on the basis of double and triple chemical bonds. Clearly, the basin boundaries which affect the corresponding basin populations are shifting the “ideal” populations from heavy atom bonds to core and hydrogen atom basins.

Figure 1 illustrates the qualitative nature of the ELF isosurfaces for ethane, propene, and cyclobutadiene, compounds with conventional single and double bonds. The shape of the bond basin for the single bond is roughly spherical, while that for the double bond resembles a prolate spheroid elongated above and below the molecular plane. We can use this qualitative difference between single and double bonds to analyze more complicated systems. Although not so evident in Figure 1, a view down onto the molecular plane in cyclobutadiene shows that both single and double bond basin centers are slightly displaced from the square arrangement of

TABLE 6 Electron Basin Populations (Number of Electrons) of Conventional Single and Multiple Heavy Atom Bonds^a

Carbon Compounds					
	CC	C=C	C≡C	Core	CH
H ₃ CCH ₃	1.90	—	—	2.09	1.99
H ₂ CCH ₂	—	3.36	—	2.10	2.10
HCCH	—	—	5.04	2.09	2.37
cyclopropane	1.82	—	—	2.10	2.05
propene	1.96	3.45	—	2.10	2.04 (mean)
C ₄ H ₄	1.93	3.38	—	2.09	2.24

Formal Double Bonds				
Bond	N lp	O lp	P lp	
H ₂ CCH ₂	—	—	—	
H ₂ CNH	2.86	2.69	—	—
H ₂ CO	2.46	—	5.06	—
HNNH	2.34	2.67	—	—
HNO	1.97	2.61	5.12	—
HPCH ₂	2.96	—	—	2.62
HPNH	2.57	2.70	—	2.51
HPO	2.02	—	5.41	2.30

Formal Triple Bonds			
Bond	C lp	N lp	
HCCH	5.04	—	—
HCN	4.21	—	3.21
NN	3.28	—	3.26
CN	3.41	2.83	3.48

^aThe notation CH and lp refer to electron populations corresponding to hydrogen and lone pair basins, respectively.

the nuclear framework, indicating the presence of some “bentness” to both types of bonds in this highly constrained system.

Section B of Table 6 gives basin populations for the heavy atom bonds and the lone pairs involved in a series of molecules that we would definitely consider doubly bonded. Figures 2c and 3c show the isosurfaces for HNCH₂ and HPCH₂ where we can see not only the occurrence of the double-bond shape in the heavy atom bond but also the presence of basins representing the lone pairs on nitrogen and phosphorus, respectively. The data in 6B exhibits a significant progression in the bond population as one changes the electronegativity of one heavy atom relative to its neighbor. In the sequence ethylene, methyleneimine, and formaldehyde, the formally double-bond basin populations (in the nitrogen and oxygen cases) are significantly reduced, while the lone-pair populations in the nitrogen and oxygen cases are significantly larger than would be expected in terms of our simple chemical pictures. One can note the same progression in the other sets of similarly related molecules in the table. It is at first tempting to describe

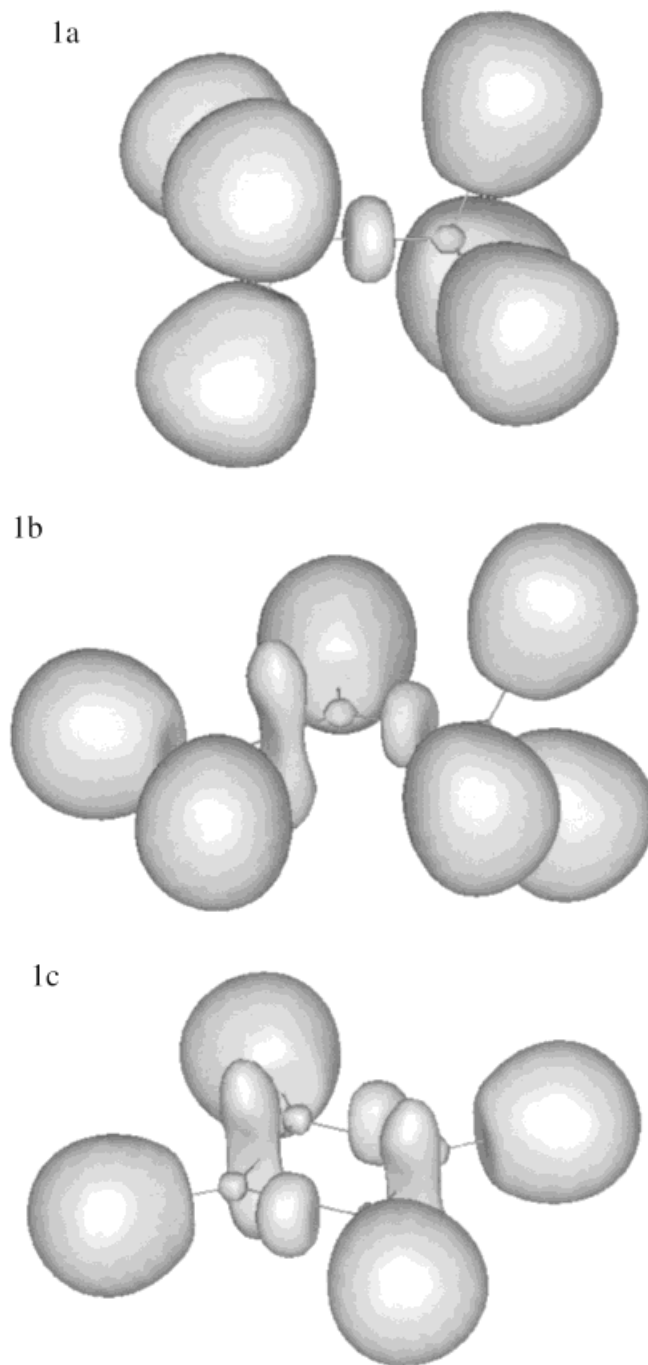


FIGURE 1 The $\eta = 0.85$ isosurfaces for (a) ethane, (b) propene, and (c) cyclobutadiene as examples of molecules containing conventional single and double bonds.

the reduction in the heavy atom bond population and the increase in the lone-pair populations as a polarization effect, that is, an effect which gives rise to ionic character to the bond. That this oversimplifies the case is illustrated by HNNH which, aside from some NH effects, should not be ionic yet has a significantly larger than “normal” lone-pair popula-

tion on nitrogen. Although not given in Table 6, similar effects arise in the molecules HOOH, HSSH, H₂PPH₂, and H₂NNH₂ where the bond and lone-pair populations are 0.74, 4.80 (HOOH), 1.47, 4.23 (HSSH), 1.43, 2.17 (H₂NNH₂), and 1.79, 2.04 (H₂PPH₂). Although not focused on explicitly here, similar effects are present for triple bonds where lone pairs are also involved as shown in section C of Table 6. The bond basin populations are significantly less than the value six we might expect, again at the expense of increased lone-pair populations.

In short, with or without lone pairs, our understanding of multiple bonds as given by the ELF populations must be modified compared to our simple (and sometimes simplistic) chemical pictures. What we can do and proceed to do in the remaining discussion is to accept populations in conventionally single and multiply bonded cases as reference points and look at changes from these as deviations from conventional character.

In our discussion we shall refer to those molecules in which conventional single bonds between heavy atoms are present to be singly bonded, while those with conventional double bonds are designated as doubly bound. Basin populations for the formally singly and doubly bonded nitrogen and phosphorus compounds and their 4cor species are contained in Table 7. Bond and lone-pair basin populations are given along with the changes in the bond population (Δ bond) and total lone-pair population (Δ lp) taking the singly bonded species as base. From our simple chemical pictures of lone pairs, we would expect that the number of lone-pair electrons would be conserved for the proton transfer reaction as illustrated in Scheme 2 and, for that matter, for the doubly bound species as well, in the doubly bound species, CH bonds are broken and an extra heavy atom bond formed but no lone pairs modified; changes in this quantity then reflect the type of bonding involved.

We see here that the changes occurring in the ELF populations as we move from singly to doubly bonded systems are just what we noted in our earlier discussion. Bond populations increase significantly (as, of course, they should, but with an increase significantly less than two) with the deficit showing up as increases in the lone-pair populations.

Such is generally not the case for the 4cor species. Here one sees relatively small increases in bond populations with a generally large decrease in lone-pair populations. The sum of these two populations need not be conserved, but, since the sum of all the populations must correspond to the number of electrons present, the difference must show up elsewhere. For the isoelectronic singly bound and 4cor

TABLE 7 Electron Basin Populations (Number of Electrons) of for the Four-Coordinate Nitrogen and Phosphorus Species and their Normal Single and Double Bond Counterparts^a

<i>Nitrogen Compounds</i>							
	<i>Bond</i>	<i>C lp</i>	<i>N lp</i>	<i>O lp</i>		Δ bond	Δ lp
H ₂ NCH ₃	1.73	—	2.06	—			
H ₃ NCH ₂	1.77	1.96	—	—		0.04	-0.10
HNCH ₂	2.86	—	2.69	—		1.13	0.63
H ₂ NNH ₂	1.43	—	2.17 (2)	—			
H ₃ NNH	1.56	—	4.22	—		0.16	-0.12
HNNH	2.34	—	2.67 (2)	—		0.91	0.50
HONH ₂	1.05	—	2.25	4.68			
ONH ₃	1.39	—	—	6.18		0.34	-0.75
HNO	1.97	—	2.61	5.12		0.92	0.80
<i>Phosphorus Compounds</i>							
	<i>Bond</i>	<i>C lp</i>	<i>N lp</i>	<i>O lp</i>	<i>P lp</i>	Δ bond	Δ lp
H ₂ PCH ₃	1.87	—	—	—	2.08		
H ₃ PCH ₂	2.42	1.31	—	—	—	0.55	-0.77
HPCH ₂	2.96	—	—	—	2.62	1.09	0.58
H ₂ PNH ₂	2.18	—	1.92	—	2.01		
H ₃ PNH	2.24	—	3.66	—	—	0.06	-0.27
HPNH	2.57	—	2.70	—	2.51	0.39	1.28
HOPH ₂	1.34	—	—	4.73	2.07		
OPH ₃	2.00	—	—	5.72	—	0.66	-1.08
HPO	2.02	—	—	5.41	2.30	0.68	0.91

^aThe notation lp is used for electron populations corresponding to lone pairs. Δ bond and Δ lp correspond to the population changes in the heavy atoms bond and the lone-pairs sum relative to the conventionally singly bonded molecule.

species studied here the difference is made up by increases in the hydrogen basin populations.

The appearance of the ELF isosurfaces also shows that the 4cor species are different from the double bonded molecules. Figure 2 shows the H₂NCH₃, H₃NCH₂, and HNCH₂ cases and is fairly typical of the nitrogen cases. There the single and double bond cases are what we have come to expect, whereas the 4cor molecule is qualitatively very much like the single-bond case. The analogous case for phosphorus is shown in Figure 3 for H₂PCH₃, H₃PCH₂, and HPCH₂. Again the single- and double-bond isosurfaces are the expected ones, whereas that for H₃PCH₂ is quite unusual and different from its conventionally bonded counterparts. This particular case is atypical of the 4cor phosphorus species in general, as one can see by examining Figure 4 where the isosurfaces for H₃PCH₂, H₃PNH, and H₃PO are shown.

The unusual isosurface for H₃PCH₂ tends to suggest the presence of a conventional double bond; yet from the other evidence presented we know that this

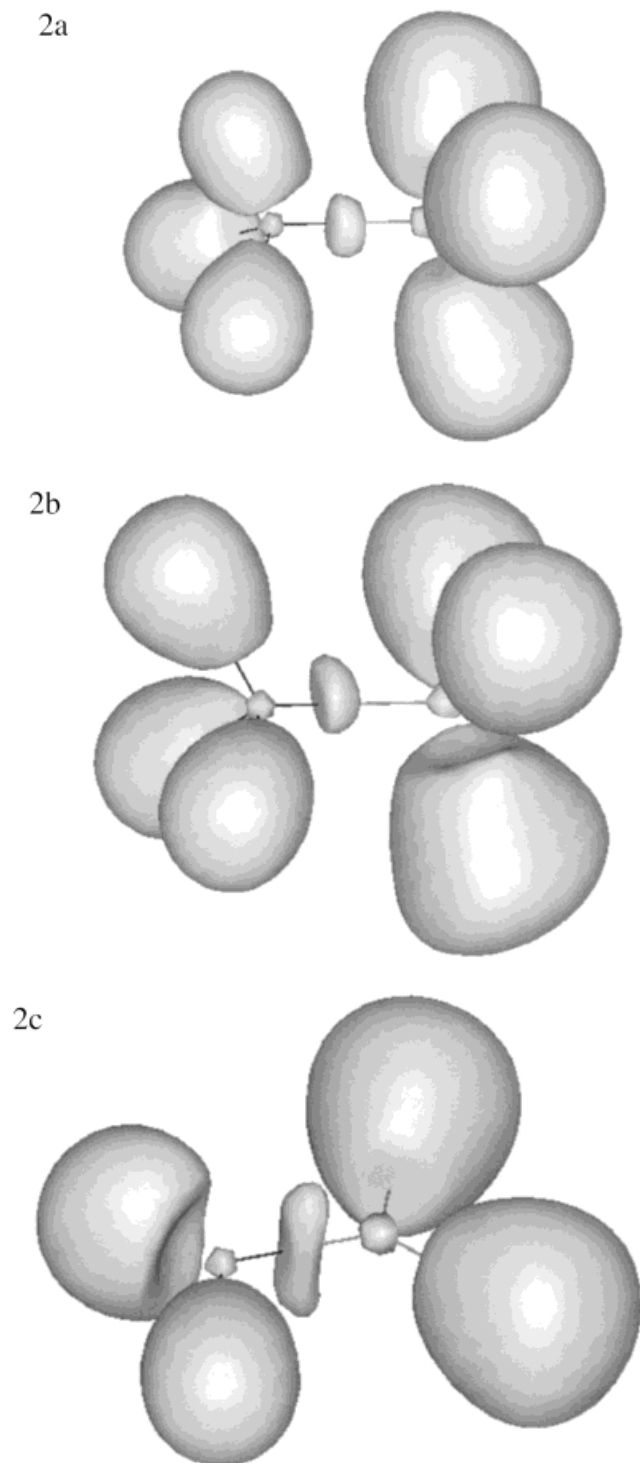


FIGURE 2 The $\eta = 0.85$ isosurfaces for (a) H_2NCH_3 , (b) H_3NCH_2 , and (c) HNCH_2 . In each example the nitrogen part of the molecule is on the left.

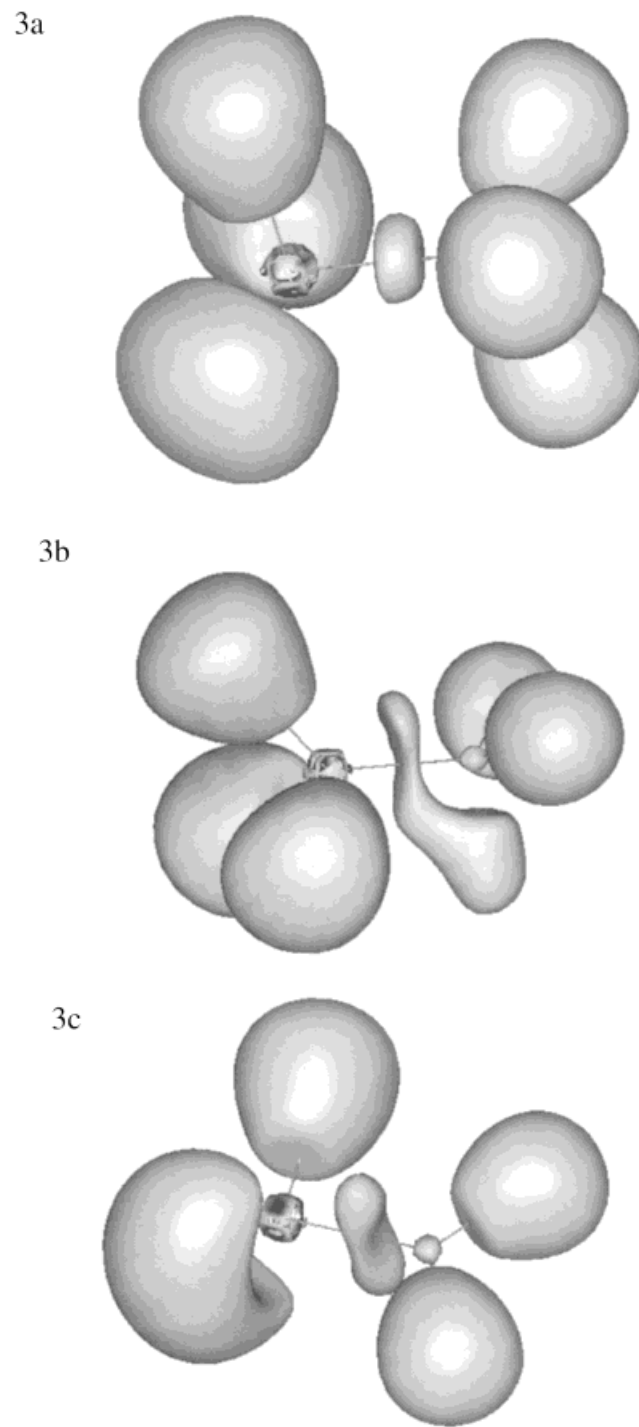


FIGURE 3 The $\eta = 0.85$ isosurfaces for (a) H_2PCH_3 , (b) H_3PCH_2 , and (c) HPCH_2 . In each example the phosphorus part of the molecule is on the left.

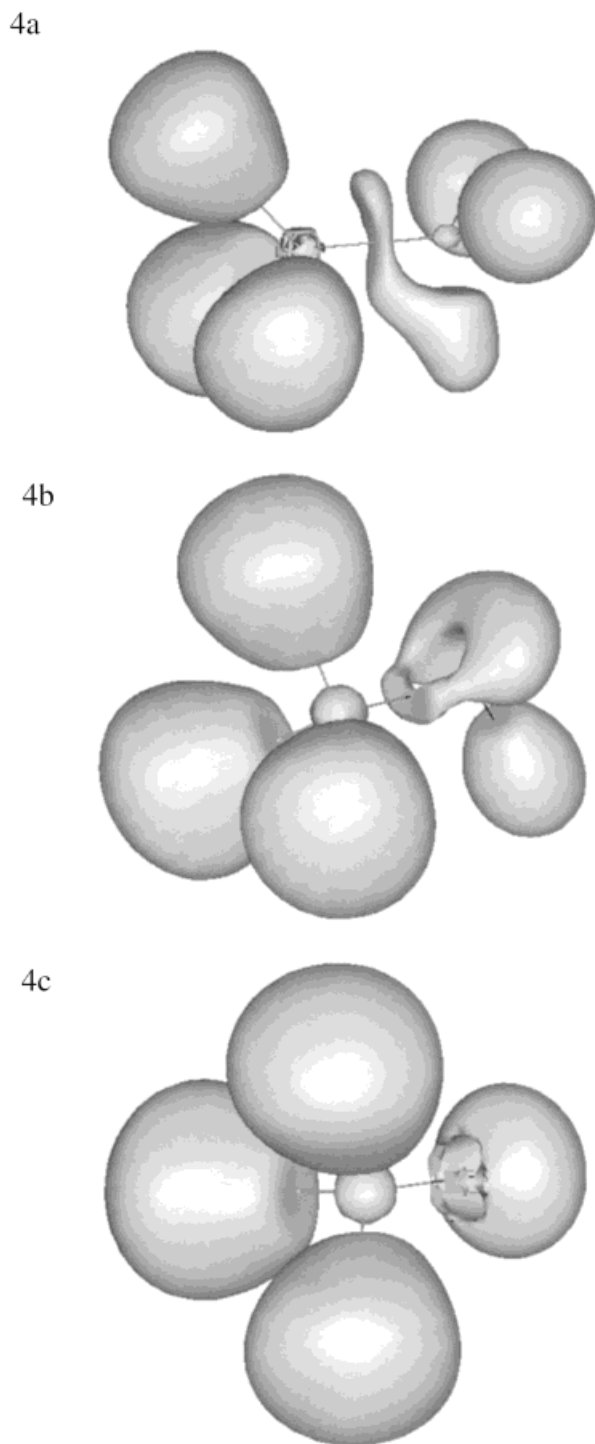


FIGURE 4 Isosurfaces for the 4cor phosphorus species: (a) H_3PCH_2 at $\eta = 0.85$, (b) H_3PNH at $\text{ELF} = 0.83$, and (c) H_3PO at $\eta = 0.796$. In each example the phosphorus part of the molecule is on the left.

cannot be the case. The unusual appearance of this isosurface appears to be due to the composition of the lone pair molecular orbital in this molecule, previously investigated by several others [49–52]. A simple STO-3G RHF calculation shows that the HOMO is lone-pair dominated, and that the carbon orbital involved is almost pure p in character. This is in contrast to the HOMO in H_3NCH_2 , also lone-pair dominated, but essentially sp^2 in character. Figure 5 shows the MOs dominated by the lone pairs in both H_3PCH_2 and H_3NCH_2 from a B3LYP/6-31+G(d,p)//MP2(FC)/6-31+G(d,p) calculation. The figure shows what may be taken to be a conventional lone-pair orbital on carbon in H_3NCH_2 (5a), situated below and directed away from the NC bond and consistent with the geometry of this molecules as illustrated in Scheme 1. That for H_3PCH_2 (5b) is similar in ap-

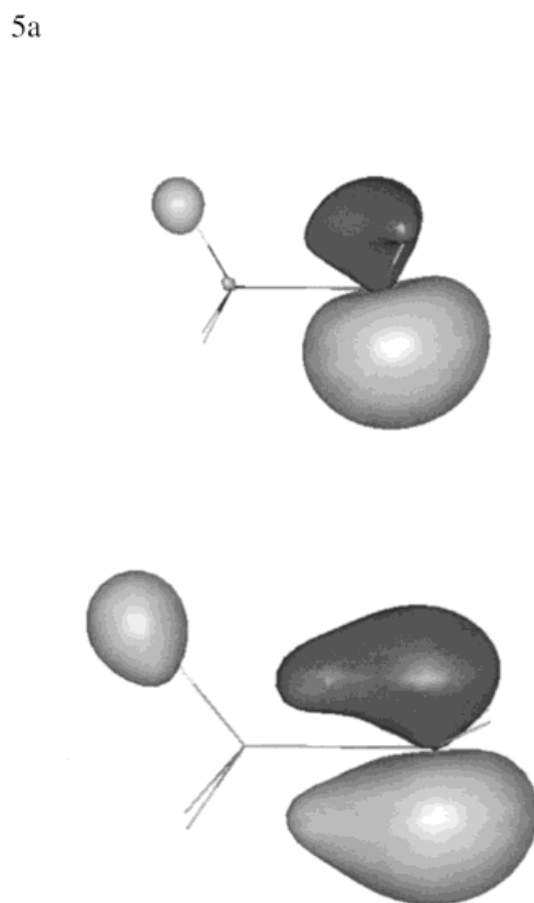


FIGURE 5 The lone-pair-dominated HOMOs for (a) H_3NCH_2 , and (b) H_3PCH_2 . The isosurfaces correspond to a density of 0.08 electrons per cubic Ångstrom from B3LYP/6-31+G(d,p)//MP2(FC)/6-31+G(d,p) calculations. The different shading indicates the different phases of the molecular orbitals, and in each case the carbon atom is on the right hand side.

pearance but more nearly perpendicular to the PC bond and has a significant extension toward the phosphorus atom, as one also sees from Scheme 1, which illustrates the nearly flattened CH₂ group. Apparently it is this unusual extension of the lone pair MO in H₃PCH₂ plus the covalent bonding that give rise to the unusual appearance of the ELF basin iso-surfaces in the PC bond region in this particular case.

The bonding between heavy atoms in the 4cor species is clearly different from both their singly and doubly bound counterparts. We can schematically picture the 4cor species as below in Scheme 3. We are then talking about both covalent character, possibly polarized, and basic ionic character. We propose to call this hybrid type of bond *cov-ionic*, indicating the presence of both types of interaction. The ionic interaction is obviously stabilizing and likely accounts for the fact that energy minima are found for the 4cor species, even though they are higher in overall energy (and enthalpy) than their single-bonded precursors. The strength of the covalent part of the bond will then determine whether the species may be further stabilized or weakened. Because the bond-breaking energies for the nitrogen cases are close to that of a simple ionic bond, we think the covalent character for them must be weak. This is also consistent with their relatively small bond length changes. On the other hand, the covalent character for the 4cor phosphorus compounds must be strong; they exhibit marked decreases in bond lengths and have bond enthalpies in excess of what might be expected on the basis of ionic-only interactions.

One further piece of evidence tends to corroborate this picture. The location of the heavy atom bond basin attractor can be used as an indicator of the polarization of the bond. For the phosphorus compounds, the single-bond attractor is a fraction 0.59 of the bond length from phosphorus in the singly bonded compounds and only slightly reduced to 0.57 in the 4cor species; that is to say, the bond is polarized toward the more electronegative partner (as expected) and essentially does not change in going from single bond to cov-ionic bond. The covalent part of the bond must, therefore, maintain its

strength. On the other hand, for nitrogen, the single-bond attractor is a fraction 0.50 of the bond length between heavy atoms (no polarization) in the single bond case and is reduced to 0.40 in the 4cor species, that is, is closer to the 4cor nitrogen atom: that is to say, for nitrogen the bond becomes more polarized in the cov-ionic case and can therefore be expected to be weaker. The polarization towards the 4cor nitrogen atom further increases the polarity of the molecule and helps to account for the large dipole moments seen in these cases.

SUMMARY

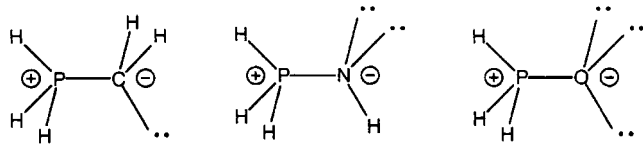
The bonding in some simple four-coordinate species involving nitrogen and phosphorus has been studied by the electron localization function approach and compared to that in their conventionally singly and doubly bonded counterparts. Despite evidence suggesting the presence of a conventional multiple bond in certain cases of the four-coordinate species, the ELF study shows this not to be the case. Rather, the situation is better pictured as, for example, H₃P⁺CH₂⁻ where both ionic and covalent interactions are present, a type of bond we term *cov-ionic*. While the ionic interaction is generally strong, the covalent part can be weak, as in the case of the four-coordinate nitrogen compounds, or strong, as in the case of the four-coordinate phosphorus species. The quantum mechanically determined properties of the cov-ionic bonded compounds are consistent with this picture.

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SCHEME 3

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