

## Bonding of Atomic Phosphorus to Polycyclic Hydrocarbons and Curved Graphitic Surfaces

Santiago Melchor,<sup>†</sup> Jose A. Dobado,<sup>†</sup> J. Andreas Larsson,<sup>\*,‡</sup> and James C. Greer<sup>‡</sup>

*Contribution from Grupo de Modelización y Diseño Molecular, Departamento Química Orgánica, Campus Fuentenueva, Universidad de Granada, 18071 Granada, Spain, and NMRC, University College, Lee Maltings, Prospect Row, Cork, Ireland*

Received July 1, 2002; E-mail: alarsson@nmrc.ucc.ie

**Abstract:** We present a theoretical study of the bonding of atomic phosphorus to planar hydrocarbons and to curved graphite-like surfaces. We find that bonding of phosphorus to planar polycyclic hydrocarbons induces curvature away from the phosphorus atom, as defined by the pyramidalization angle. Similarly, bonding of atomic phosphorus to the [5,5] fulvalene–circulene semifullerene and buckminsterfullerene is only possible on the convex side of the carbon surface. On the other hand, we find the interaction of atomic phosphorus with the concave side of fullerene-like surfaces to be nonbonding for both quartet and doublet spin states. We find the prerequisite for stable epoxy-type bonds within these systems is the ability of the carbon atoms to maintain or induce curvature away from the  $P\cdots C=C$  bond.

### I. Introduction

The interaction between phosphorus and carbon based materials is of interest for many fields of chemistry as varied as organic synthesis, doping of carbon systems, and fullerene chemistry. The bonding of atomic phosphorus to double bonds, conjugated double bonds, and aromatic bonds has not been fully explored. This is true in particular for the newer forms of carbon: the fullerenes and nanotubes. Our study examines the bonding of phosphorus to buckminsterfullerene (**1**), the [5,5] fulvalene–circulene semifullerene (**2**),<sup>1–5</sup> pyracyclene (**3**), pyrene (**4**), and ethene (**5**).

The molecules considered vary in their geometric and electronic structures. We find, however, that there are generic effects associated with phosphorus bonding to these molecules in terms of bond energies, magnitude of charge transfer, electronic densities, and pyramidalization angles. Our choice of molecules allows us to reasonably extrapolate the behavior we observe to a broader set of organic and fullerene systems. We will relate our findings to recent studies of the nonbonding interaction of nitrogen and phosphorus with the inside of fullerene cages.<sup>6–18</sup> Many endohedral dopant atoms from the first and second rows of the periodic table, and for metallic dopants studied, reveal that endohedral dopant atoms bond to

the inside wall of the fullerene, with the exception of the noble gas atoms and, as recently observed, nitrogen and phosphorus. The latter two dopant atoms, like the rare gases, occupy a central position in the fullerene cage. Experimental and theoretical findings confirm that the properties of endohedral group V atoms are only slightly perturbed by the surrounding  $C_{60}$  cage;<sup>6–8,14–15</sup> the dopant atom and host's chemical and electronic properties are largely undisturbed. There are recent semiempirical studies indicating bonding interactions for endohedral phosphorus doping of buckminsterfullerene;<sup>19–21</sup> however, these calculations are in conflict with experimental studies<sup>6–13</sup> and ab initio calculations.<sup>14–16</sup> Recently it has been shown that the internal curvature of  $C_{60}$  inhibits covalent bonding of fluorine, and that the F atom prefers to bond to the exterior of (5,5) single wall nanotubes.<sup>22</sup>

\* To whom correspondence should be addressed. Phone: +353 (0)21 490 4166. Fax: +353 (0)21 427 0271.

<sup>†</sup> Universidad Granada.

<sup>‡</sup> NMRC, University College Cork.

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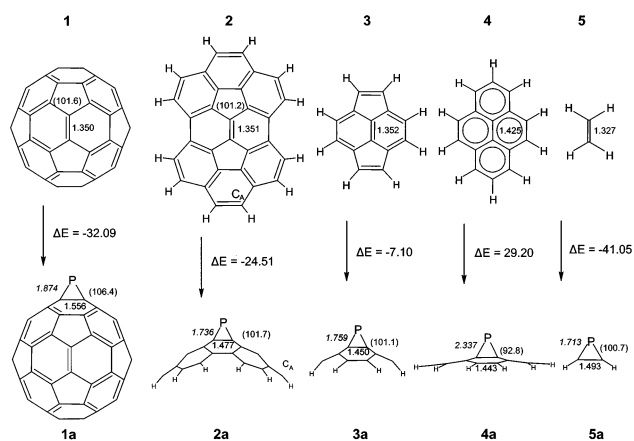
Many atoms,<sup>23–25</sup> including phosphorus,<sup>26–27</sup> chemically react with the exterior of the buckminsterfullerene cage to form epoxy-like bonds,<sup>28</sup> yet, as noted above, this bonding is not observed for atomic phosphorus within C<sub>60</sub>. The difference between the  $\pi$ -system for the interior and the exterior of the C<sub>60</sub> carbon network is the curvature of the fullerene surface. This raises the question: is the inability to bond with the interior of the carbon cage for the endohedral atoms in P@C<sub>60</sub> and N@C<sub>60</sub> purely a consequence of the curvature of the  $\pi$ -system? We investigate this point and assess the general role of curvature in bonding of phosphorus to carbon double bonds in organic molecules and graphite-like surfaces.

## II. Computational Details

Density functional calculations using the Becke three-parameter Lee, Yang, and Parr (B3-LYP)<sup>29–30</sup> exchange and correlation density functional have been used in all energy and geometry optimization calculations. Fully relaxed (geometry optimized) configurations were calculated for molecules (1–5) and the phosphorus bonded systems (1a–5a) using the 6-311G(d) polarized valence triple  $\zeta$  Gaussian basis set.<sup>31</sup>

Phosphorus bonding to the molecules (1a–5a) is displayed in Figure 1. To quantify the curvature of the graphite surface, the  $\pi$ -orbital axis vector (POAV) analysis<sup>32</sup> has been used to give a quantitative measure of curvature in terms of pyramidalization angles. The electronic density has been examined using the atoms in molecules (AIM) analysis<sup>33</sup> to determine bond critical points (BCP),<sup>34</sup> and the electronic density and corresponding Laplacian field have been calculated to examine the strength of the covalent bonding within these systems.<sup>35</sup>

The interaction between P and C<sub>60</sub> has been calculated using a polarized valence triple  $\zeta$  (TZVP) Gaussian basis set<sup>36–38</sup> and a relativistic effective core potential (ECP)<sup>39</sup> on phosphorus.



**Figure 1.** Equilibrium bond distances (Å) and pyramidalization angles (deg) for molecules 1–5 and 1a–5a at the UB3LYP/6-311G(d)/UB3LYP/6-311G(d) level of theory. The pyramidalization angles for structures 3–5 are all 90°. The C–C bond lengths are given in normal text, the distance between phosphorus and the center of the double bond is given in italics, and the pyramidalization angle is given in parentheses. Binding energies  $\Delta E$  (kcal/mol) are given with respect to the isolated quartet P and molecules 1–5.

The energy is calculated as atomic phosphorus is displaced along a C<sub>2</sub> axis, perpendicular to a double bond of the C<sub>60</sub> cage; the geometry of the C<sub>60</sub> has been held fixed in its optimized *I<sub>h</sub>* geometry determined for P@C<sub>60</sub>. The hemifullerene was allowed to relax in C<sub>2v</sub> symmetry using a 6-311G(d) basis set. This relaxed structure was held rigid for the total energy calculations with the phosphorus atom positioned at different distances relative to the two surfaces of the bucky-bowl along the C<sub>2</sub> axis (henceforth referred to as the interior and exterior of the semifullerene, in analogy to buckminsterfullerene). Energy calculations were performed for both the quartet and doublet spin states.

## III. Results and Discussion.

C–C and C–P bond distances, pyramidalization angles, and the binding energies are displayed within Figure 1; the corresponding data for the isolated hydrocarbons and buckminsterfullerene are included for comparison. Electronic data at bond critical points and Mulliken charges are listed in Tables 1 and 2. Potential energy curves for phosphorus interacting with the curved surfaces of 1 and 2 are presented. The electronic structure of bonding and repulsive phosphorus interactions is discussed. Cross-sections of the Laplacian of the electronic density for molecules 2 and 2a are examined to clarify the nature of bonding.

**A. Curvature Changes upon Phosphorus Bonding.** All the systems 1a–5a considered display increased curvature after bond formation as determined by the pyramidalization angle, independently of whether the isolated molecule's geometry is curved or planar. The largest pyramidalization angle is found for 1a, P bonded to buckminsterfullerene at 106.4°, larger than even the value of a tetrahedron. A large increase in the pyramidalization angle is not seen for 2a, i.e., for P bonded to the semifullerene. This difference in geometry upon bonding is due to the lack of freedom in C<sub>60</sub> to change the overall structure in the carbon skeleton relative to C<sub>30</sub>H<sub>12</sub>. In C<sub>60</sub>, the change in the cage geometry due to the bonding to phosphorus is thus primarily local. In 2a, there is likewise a local bond change; the central C–C bond is longer and the pyramidalization angle

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**Table 1.** Electronic Data for the C–C and C–P at Bond Critical Points. Electron Density,  $\rho(r)$  ( $e/a_0^3$ ), Its Laplacian,  $\nabla^2\rho(r)$  ( $e/a_0^5$ ), the Ellipticity,  $\epsilon$ , and Electronic Energy Density  $E_d(r)$  (hartree/ $a_0^3$ ) Computed at the B3LYP/6-311G(d) Level

	CC				CP		
	$\rho(r)$	$\nabla^2\rho(r)$	$\epsilon$	$E_d(r)$	$\rho(r)$	$\nabla^2\rho(r)$	$E_d(r)$
<b>1</b>	0.308	−0.844	0.221	−0.315			
<b>1a</b>	0.222	−0.388	0.259	−0.092	0.135	−0.166	−0.114
<b>2</b>	0.337	−1.031	0.206	−0.377			
<b>2a</b>	0.261	−0.583	0.212	−0.232	0.131	−0.155	−0.105
<b>3</b>	0.322	−0.951	0.162	−0.343			
<b>3a</b>	0.275	−0.664	0.200	−0.257	0.127	−0.133	−0.097
<b>4</b>	0.294	−0.788	0.161	−0.284			
<b>4a</b>	0.283	−0.728	0.159	−0.264	0.042	−0.077	−0.004
<b>5</b>	0.343	−1.010	0.329	−0.390			
<b>5a</b>	0.249	−0.521	0.223	−0.209	0.273	−0.893	−0.260

**Table 2.** Mulliken Charges for the Phosphorus and the Nearest Carbon Atoms

	C	P	C	P
<b>1a</b>	−0.42	0.46	<b>4</b>	−0.05
<b>2</b>	−0.02		<b>4a</b>	−0.35
<b>2a</b>	−0.44	0.40	<b>5</b>	−0.41
<b>3</b>	−0.02		<b>5a</b>	−0.61
<b>3a</b>	0.26	0.22		0.24

increases. However within the semifullerene, the rest of the carbon frame is able to adjust with greater freedom to the changes in the C–C bond, in such a way that the distance from the outermost carbon ( $C_A$  in Figure 1) to the  $C_2$  axis becomes longer. This distance can be used as a measure of the overall curvature change when phosphorus bonds to the semifullerene. Without P-bonding (**2**), this distance is 5.09 Å and it becomes 5.20 Å upon bonding (**2a**). Since such a distortion is hindered in the  $C_{60}$  cage, the local perturbation to the carbon atoms that bond to P is larger in **1a** than for **2a**.

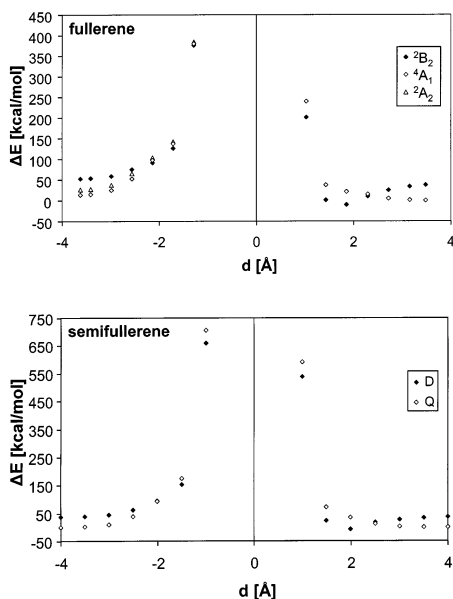
For pyracyclene and ethene, the bonding interaction produces substantial curvature away from the P atom, relative to these hydrocarbons' planar equilibrium conformations. In the case of pyracyclene, the P interaction with the central double bond is stabilizing enough to produce a large deformation, leading to a pyramidalization angle of 101.1°. For the reaction of P with pyrene, there is an induced curvature that is small, but clearly a result of the bonding, resulting in a pyramidalization angle of 92.8°. Note that in pyrene, the stable aromatic bonding of the hexagon rings strongly inhibits induced curvature and significantly effects the stability of the bonding, a point we return to in the next section.

**B. Phosphorus Binding Energies.** For all systems studied, a bonding configuration is found with C–P bond lengths ranging between 1.713 and 2.337 Å. Note, however, the bonding configuration for pyrene is metastable. The curvature due to phosphorus bond formation can be correlated to the strength of the bonding and the electronic characteristics of the central C–C bond. The weakest and strongest interaction with P correspond to compounds **4a** and **1a**, respectively, in terms of binding energy, reduction of C–C charge density, ellipticity, and (absolute) electronic energy density. In complex **1a**, the central C–C bond has the least double bond character of all, showing the lowest values of electronic density and the value of the Laplacian at the bond critical point (see Table 1). The central C–C bond in complex **1a** is extremely weakened upon P-bonding, with the electronic density lower than for an ethane single bond. The ellipticity value remains unchanged, reflecting

that anisotropy remains unaffected. The isolated systems **1–3** have a central C=C bond with similar and relatively strong double bond character. For P bonded to pyrene **3a**, the phosphorus binding energy is low, but in molecules **1a** and **2a**, P bonding results in a much higher degree of stabilization. The lack of relative stabilization in **3a** is due to the energy gained due to bond formation being canceled by the energy needed to deform the carbon structure from its planar equilibrium configuration. In contrast, for the fullerene structures **1** and **2**, curvature is created due to the presence of the pentagons inserted into the hexagonal carbon network. Hence, there is less energetic opposition to the interaction between the P atom and the C=C bond, resulting in a subsequently higher stabilization energy. In ethene, the energy loss due to the pyramidalization of the carbon atoms is not large, as only reorientation of C–H bonds is required. The reason for the weaker C–P bonds and less pronounced curvature in phosphorus bonded to pyrene is that the molecule is composed exclusively by six-membered carbon rings, showing a higher degree of aromaticity and stability; the study of the aromaticity of fullerenes and their building blocks is well-developed and can be found in the literature.<sup>39,40</sup> This can be seen in the approximately equidistant and longer C–C bonds and with the weakest double character of the central C–C bond (electronic density of 0.294  $e/a_0^3$  and ellipticity of 0.161, the lowest values for isolated graphitic molecules in this study). Nevertheless, the interaction of phosphorus with pyrene produces a bound doublet state, but with differing characteristics: a much longer P–C bond distance, lower induced curvature, and a positive binding (thermodynamically unstable) energy. Furthermore, the resulting complex (**4a**) is dissociative since the quartet state is energetically more stable (by 4.8 kcal/mol at the doublet equilibrium geometry) than the doublet state. The lower energy quartet state is nonbonding at all bond lengths. These results indicate that curvature or the ability to induce curvature into graphite-like surfaces is a necessity for bonding of atomic phosphorus.

**C. Phosphorus Interaction Potential with Fullerene and Semifullerene.** The requirement of curvature away from the bonded phosphorus is central to the understanding of the repulsive nature of group V atoms inside  $C_{60}$ . To shed light on the inability of the group V atoms nitrogen and phosphorus to bond with the inside of  $C_{60}$ , the interaction between phosphorus relative to structures **1** and **2** has been studied. The energy dependence of the phosphorus displacement has been calculated in the doublet and quartet spin states, for both the interior and

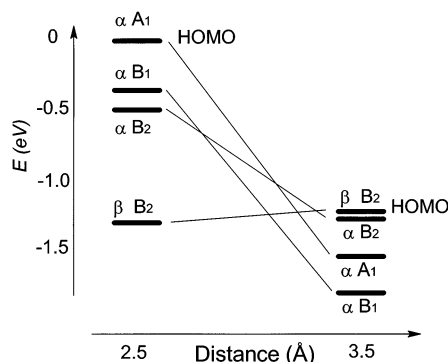
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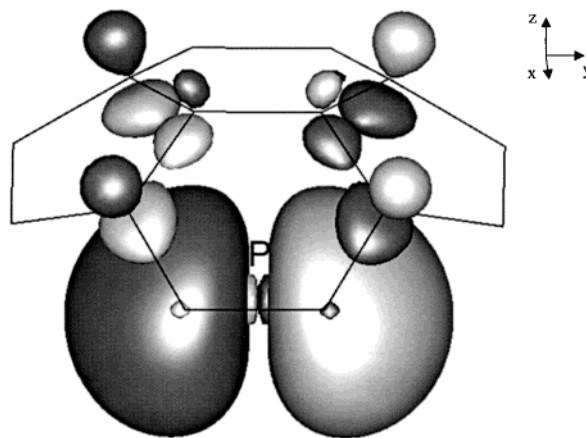
**Figure 2.** Bond energy between phosphorus at both the interior and exterior of fullerene **1** and semifullerene **2**, with the phosphorus atom constrained to lie along the  $C_2$  axis, at a distance  $d$  from the central  $C=C$  bond. (a)  $C_{60}$  geometry fixed at the  $P@C_{60}$  equilibrium structure, calculated with TZVP basis set and a relativistic effective core potential for phosphorus. (b) [5,5] fulvalene–circulene geometry fixed in its equilibrium structure, calculated with 6-311G(d) basis set.

exterior of the  $C_{60}$  cage, and for semifullerene **2**. The resulting potential energy curves are depicted in Figure 2. For  $C_{60}$ , as well as for the bucky bowl, both the interior and exterior fullerene surfaces repel the phosphorus in the quartet state. In contrast, the doublet-state interaction with the fullerene and semifullerene is very different for the inside and outside surfaces. At a distance of approximately 2 Å, there is a potential energy minimum corresponding to a bonding state at the outer surface. The two energy curves, shown in Figure 2, also indicate that the quartet states are energetically favorable at longer distances from the carbon double bond, but, in the approximate range of  $-2.0$  to  $+2.0$  Å, the doublet interaction is lower in energy. The crossing of the quartet and doublet curves shows a change in the nature of interaction with the fullerene and semifullerene molecules, with bonding interaction on the outside but repulsive interaction on the inside. This is true for both the  $^2A_2$  and the  $^2B_2$  electronic states of P (corresponding to the  $^2D$  and  $^2P$  states of phosphorus) on the inside of  $C_{60}$ , which can be seen in Figure 2a. This is consistent with the observation<sup>13</sup> that the atoms of group V inside the fullerene cage do not bond but are trapped within the cage and are thermodynamically metastable. Additionally, we have performed Hartree–Fock calculations to ensure that the shape of the potential energy curves for phosphorus with regard to the fullerene molecules (Figure 2) is not due to an artifact of density functional theory (DFT) at long interaction distances. The same general behavior is found with Hartree–Fock calculations.

From the energy of the quartet state inside the semifullerene, the strength of the repulsive interaction between P and  $C_{60}$  in  $P@C_{60}$  can be estimated, and the thermodynamic instability of  $P@C_{60}$  can be verified. The energy for phosphorus at a distance of 3.544 Å from  $C_{30}H_{12}$  (which equals the radius of  $P@C_{60}$ ) is 3.09 kcal/mol higher than at infinite separation. The equilibrium energy of  $P@C_{60}$  is 13.91 kcal/mol higher in energy than the



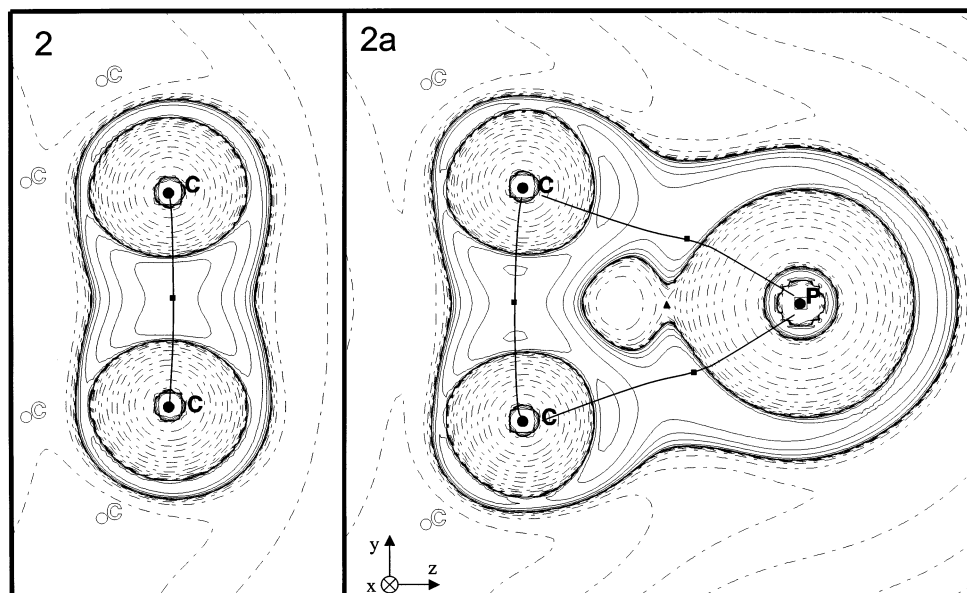
**Figure 3.** Plot of the four highest (for P located at 2.5 Å) quartet spin-state orbital eigenvalues for the P atom located inside the [5,5] fulvalene–circulene **2**, evaluated at distances of 2.5 and 3.5 Å, calculated at the UB3LYP/6-311G(d) level, showing the three orbitals corresponding to P, lifted over the HOMO at 2.5 Å due to repulsion.



**Figure 4.** Three-dimensional isosurface plots of HOMO-2, at a cut-off value of 0.03, in structure **2** with a phosphorus atom located inside at a distance of 2.5 Å, representative of the repulsive interaction together with HOMO and HOMO-1.

free atom and cage. The repulsive energy for  $P@C_{60}$  is naturally larger, since  $C_{60}$  constitutes two semifullerene units (excluding the hydrogens) and has a uniform spherical curvature with a lower mean distance to the phosphorus atom.

**D. Electronic Structure of Endohedral Phosphorus:  $P@C_{60}$ .** It has been shown previously that in both  $N@C_{60}$  and  $P@C_{60}$  the half-filled endohedral valence  $p$ -orbital energy levels lie below the highest occupied molecular orbital (HOMO) of the endohedral complex. This is seen using both unrestricted and restricted open shell Hartree–Fock and with DFT calculations.<sup>14,15</sup> In this work, we have further studied the relative position of the phosphorus atoms 3p orbitals with regard to the semifullerene energy levels. In the quartet spin state with the phosphorus atom positioned relative to the interior surface of the bucky bowl, for distances 3 Å and longer, the 3p levels are below the HOMO of the semifullerene. At a distance of 2.5 Å from the central double bond of the semifullerene, the repulsive interaction has lifted the P 3p levels high enough in energy to constitute the HOMO of the complex; this effect is shown diagrammatically in Figure 3. Since the distance to the center of the cage in  $P@C_{60}$  (and  $N@C_{60}$ ) is longer than the interaction distance at which the repulsion becomes dominant (2.5 Å), the p levels remain well below the HOMO of the  $P@C_{60}$  (and  $N@C_{60}$ ). Thus, the existence of buried open-shell levels in these molecules<sup>14,15</sup> is clearly to be expected. In Figure 4, the (HOMO-



**Figure 5.** Two-dimensional plots of the electronic density Laplacian in compounds **2** and **2a**. Negative values corresponding to the charge concentration areas are shown as continuous lines, while positive values indicating charge depletion areas are marked with dashed lines. The plane of the plot contains the  $C_{2v}$  symmetry axis and the central C=C bond.

2) half-occupied molecular orbital of the quartet state of the phosphorus interacting with the inside of the bucky bowl for a distance of 2.5 Å is shown. There is a clear antibonding interaction between P and the bowl, also evident in the interaction of the remaining two p-orbitals of phosphorus (HOMO and HOMO-1). This repulsive interaction with the inside surface of **2** is also found for the phosphorus 3p orbitals in the doublet state, with energies lower than the HOMO of the complex at large distances from the bowl.

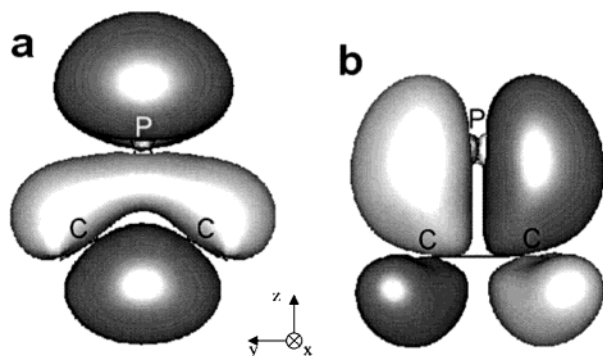
#### E. Nature of Phosphorus Bonding to Graphitic Molecules.

The phosphorus–fullerene and –semifullerene complexes show distinct differences, in bonding parameters and in overall changes to the carbon structure, as can be seen in Table 1. The C–P bonds in **1a** are unique in that they display the highest charge density occurring for all the polycyclic P-complexes considered. Inspection of the Mulliken charges (see Table 2) suggests there exist a common charge transfer from the phosphorus to the carbons (excluding the metastable complex **4a**). Phosphorus loses charge to the two neighboring carbons, but the charge gained by these carbon atoms is higher than the charge transfer from the phosphorus. This is accommodated by charge rearrangement within the atoms directly surrounding the bonding carbon atoms.

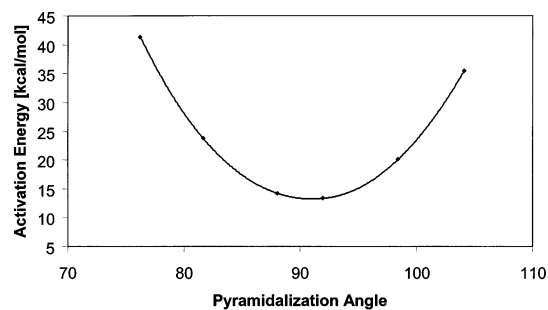
In Figure 5, valence shell charge concentration (VSCC) regions are shown with solid lines, while the depletion zones are marked with dashed lines for the semifullerene structure. It can be observed in Figure 5 that, for the isolated semifullerene molecule, for the regions near the central C atoms, the charge concentration basins (as revealed by positive values in the Laplacian of the electronic density) are displaced to the outside of the bond path. This indicates that the electron pair of the central C=C bond moves toward the outer region and is more accessible from outside of the bond and is suitable to interact with electrophilic substituents. The curved geometry makes the creation of charge concentration zones on the interior surface energetically unfavorable.

The curvature induced by bonding of phosphorus to the double bonds in **3a**, **4a**, and **5a** can also be understood through the VSEPR model. The two C–P bonds that are formed, and their subsequent charge concentration basis repel the contiguous bonds (C–H in case of ethene or C–C in the two other cases), resulting in a pyramidalization of the central carbon atoms. The induced curvature is explained by the creation of two new charge concentrations, extracting charge from the (formerly) carbon–carbon double bond; this mechanism is responsible for the observed reduction in the double bond character. The resulting new charge basins are directed toward the phosphorus, thereby repelling the bonded electron pairs of the carbon atoms' other neighbors. In the Laplacian diagrams, it is observed that the interaction between the P atom and the C–C double bond in **2a** produces two relatively small charge concentration zones near the P–C bond paths, next to the carbon atoms. The negative values of the Laplacian at the bond critical points of the C–P bond indicates that the bond is covalent, but the small magnitude of the charge density of  $0.261 \text{ e/a}_0^3$  reveals that bonding is only weakly covalent.

We have discussed bonding from a detailed analysis of the charge density and the formation of charge basins. However, the same results can be understood from a more intuitive picture based upon a molecular orbital analysis. As shown in Figure 4, the orbital interaction between phosphorus and the interior (concave surface) of buckminsterfullerene and the semifullerene is repulsive. If the electronic structure of P bonded to a C=C bond is examined (ethene (**5a**) is shown for clarity, in Figure 6, but the conclusion is generic), one can see that two orbitals are responsible for bonding. As can be seen in Figure 6a,b, the  $14a_1$  orbital accounts for the bending of the structure and the  $15b_2$  orbital is responsible for the C–C bond length increase. Since bonding of phosphorus requires a lengthening of the C=C bond and a pyramidalization of  $sp^2$  hybridized carbon atoms (or preexisting curvature in the carbon surface), it is clearly anticipated that phosphorus will not covalently bond to the inside



**Figure 6.** Three-dimensional isosurface plots of molecular orbitals at a value of 0.03. (a) HOMO-2 of compound **5a**, responsible for the bending of the structure. (b) HOMO-1 of compound **5a**, responsible for the elongation of the C=C bond.



**Figure 7.** Activation energy of the reaction between phosphorus and ethene (91.9°) and at constrained pyramidalization angles, both convex and concave, calculated with B3LYP using the TZVP basis set and a relativistic effective core potential for phosphorus.

surface of C<sub>60</sub>. In cases where the graphitic surface is curved toward the phosphorus (the interiors of fullerene and the bucky bowl within our study), only bond lengthening can be accommodated, but the curvature away from the phosphorus atom cannot be fulfilled. The pyramidalization of the carbon atom of a planar system plays an important role for the reaction with phosphorus. In Figure 7, we show the activation energy of the reaction between phosphorus and ethene. The transition state for this reaction is only slightly pyramidal (pyramidalization angle = 91.9°). If this pyramidalization angle is reversed, to

study the reaction with a system that is slightly bent in an unfavorable direction, the activation energy increases by 1 kcal/mol. On the other hand, it can be seen in Figure 7, that the activation energy for larger pyramidalization angles has a larger difference between the convex and concave side, favoring the convex side.

#### IV. Conclusions

We have studied the interaction of phosphorus with graphitic surfaces and small polycyclic hydrocarbons. We conclude that curvature about the C=C bond is a prerequisite condition for bonding of atomic phosphorus, whether the curvature is preexisting or induced by the bond formation. If induced curvature is not possible within the molecule, stable bonding will not result.

Phosphorus bonds to the exteriors (convex surface) of buckminsterfullerene and to the bucky bowl ([5,5] fulvalene–circulene). Bonding to a fullerene double bond has been investigated and reveals two equivalent C–P bonds are formed and the C=C double bond is reduced to a single bond. We have shown that the bonding of phosphorus to planar hydrocarbons induces curvature, both in ethene and in pyracyclene, and to a much lesser extent in pyrene. In pyrene, an unstable bonding configuration results as a consequence of the inability of the molecule to sustain curvature.

We have studied the interaction of phosphorus with graphitic systems with preexisting curvature and clarified the mechanism preventing bonding of atomic phosphorus to concave graphitic surfaces. In particular, we have shown that phosphorus does not bond to the interiors of C<sub>60</sub> or the [5,5] fulvalene–circulene semifullerene. The interaction between the interior surfaces of these two molecules with atomic phosphorus, in both quartet and doublet states, is repulsive.

**Acknowledgment.** This work was partially financed by INTAS Project 97-30810, the Marie Curie Training Site Fellowship (Grant HPMT-CT-2000-00091), and Improving Human Potential (IHP) Research and Training Network (RTN) ATOMCAD (Grant HPRN-CT-2000-00028).

JA027520+