Theoretical Study on Phosphorus Substitutionally Doped Fullerenes

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ABSTRACT. Since Karfunkel predicted the stability of azafullerenes by semiempirical calculation, a sustaining effort was paid to quantum-chemical calculation of substitutionally dopped fullerenes. While the N and B hetero-fullerenes are the most known, in the last years Si, Co, Ni, Fe, Rh, Ir dopped C_{60} have been modeled.[4-6]

This paper reports semiempirical PM3 calculations of phosphorus substituted fullerenes $C_{60-n}P_n$, n = 1-6. The C by P replacement appears to not dramatically influence the thermal stability of substituted C_{60} but electronic structure is changed. The degeneracy of HOMO and LUMO levels is reduced or destroyed while the HOMO-LUMO gap is, in some cases, as high as in the parent C_{60} and consistent with a good kinetic stability. The difference between C and P electronegativity determines the partial positive charge at phosphorus and a negative charge at the neighboring C atoms. The displacement of a number of phosphorus atoms on the same polygon diminishes the positive charge at phosphorus. Angles at phosphorus are larger when phosphorus is on a hexagon. The reverse situation is found for bond length that increases for P-C [5,6] with respect to [6,6] bonds. The bonding energy of P-dopped fullerenes decrease with increasing the number of phosphorus atoms, as the strength of P-C bonds decreases with respect to C-C bonds. From energetic considerations, we can draw the conclusion that phosphorus dopped fullerenes may be stable molecules.

1. INTRODUCTION

In the last years much attention was focused on developing fullerenes macroscopic synthesis methods due to their very interesting electronic, optic, magnetic, self-assembly and chemical properties, very promising for new materials.[1-7] The synthesis of a variety of endhohedral, substitutional and exohedral dopped fullerenes was a challenge for chemists that would expect to obtain compounds with enhanced chemical reactivity or special electro-optic properties.[2,3,8] Buckminster fullerene $C_{60,}$ with icosahedral symmetry, is the most studied with respect to the substitution pattern and chemical reactivity. Fullerenes show, in general, electron deficient properties similar to polyalkenes, with a weak conjugation. The main reactions are complexation, addition and cycloaddition (mainly at the 6-6 double bond), hydrogenation, hydroboration, hydrometalation and halogenation.[9-13] Upon the addition reaction, a series of changes are induced such as the cage deformation, the appearance of nonequivalent C atoms, the lowering of symmetry, etc.[14]

Since the stability of azafullerenes were predicted by semiempirical calculation, an intensive effort was undertaken to theoretical and quantum-chemical calculation of hetero fullerenes.[15-28] Among the most known heterofullerenes, there are aza and bora fullerenes $C_{60-n}N_n$(n=1 to 12), $C_{60-n}B_n$(n=1 to 6), $C_{58}BN$ but also the heterofullerene $C_{58}Si_2$ was obtained and characterized by photoionization mass spectra.[2,3,5,8,23] Up to now, a number

of theoretical calculations have been done on N, B, BN, Si, Ge, Sn, Al, P substituted fullerenes. The substitution modifies the chemical reactivity of the parent fullerene while the three-dimensional structure of the framework is preserved. The frontier orbitals belong to the π system, which is weak and perpendicular to the surface but, due to the curvature, there is a mixing with the σ system, that is very stable and confers the stability to the whole molecule. The pyramidalization of the sp^2 hybridized carbon atoms is a result of the strain occurring in fullerene cages. Reuther[3] appreciates that 80% of the fullerene ΔH_f is strain energy. In C_{60}, HOMO is of h_u symmetry, five fold degenerated and angular momentum $l =5$, LUMO is t_u symmetry, three fold degenerated and has the same angular momentum. Due to the molecular dimensions of C_{60}, the LUMO is stabilized and fullerene is easily reduced but hardly oxidized.[11,19] Theoretical calculations on monomeric $C_{59}N$ demonstrated that the additional electron is localized at N atom while in $(C_{59}N)_2$ charge density is distributed near the N atom and on the intermolecular bond. The skeletal substitution by N and B does not change significantly the shape of the fullerene surface but the heavier silicon atom deforms the fullerene geometry and localize it at the heteroatom.[8] This paper is focused on the study of geometry, electronic structure and thermodynamic stability of a series of phospha-fullerenes, by using semiempirical PM3 calculations. In the literature, there is only one example of theoretical investigation of phosphorus substituted fullerenes, namely the MNDO calculation on $C_{55}P_5$, by A. Chistyakov *et al.*[27]

2. METHOD

Full optimization of the molecular geometries was performed with the Hyper-Chem 5.11 software program.[29] A pre-optimization by molecular mechanics MM+ force field, was done while the final optimization of all molecules was carried out by the semiempirical procedure PM3-RHF, for the F operator.[30] The method of accelerate convergence with a convergence limit of 10^{-5} SCF was chosen. The molecules were considered in vacuum and the optimization algorithm was the Polack-Ribiere conjugated gradient, with 0,01Kcal/Åmol.

3. RESULTS AND DISCUSSIONS

The parameters derived from PM3 calculations are shown in table 1.

Table 1. Semiempirical PM3 data for phosphorus substitutionally doped fullerenes.

No	Structure	HOMO LUMO Gap (eV)	HOMO (eV)	HF/atom (kcal/mol)	Binding E (kcal/mol)	Charge on P
1	C_{60}	6.595	-9.481	13.511	-9442.683	-
2	$C_{59}P_1\bullet$	6.605	-9.230	13.274	-9361.627	P_1 0.846
3	$C_{58}P_2$	3.644	-7.684	14.148	-9213.840	P_{34} 0.826, P_{35} 0.826
4	$C_{58}P_2$ m	5.102	-8.368	13.827	-9233.093	P_{23} 0.845, P_{49} 0.847
5	$C_{58}P_2$ p	2.449	-7.086	14.335	-9202.632	P_{16} 0.855, P_{37} 0.855
6	$C_{58}P_2$ 12 [6,6]	6.352	-9,184	13.165	-9272.832	P_{18} 0.490, P_{30} 0.490
7	$C_{58}P_2$ 12 [5,6]	5.829	-8.941	13.514	-9251.862	P_{35} 0.529, P_{37} 0.529

Table 1. (continued).

8	$C_{58}P_2$ 13	4.541	-8.099	13.935	-9226.609	P_{23} 0.830, P_{30} 0.832
9	$C_{58}P_2$ 14	6.332	-9.047	13.193	-9271.131	P_9 0.818, P_{41} 0.818
10	$C_{56}P_4$ [5,6]	4.920	-7.899	13.985	-9032.996	P_{43} 0.568, P_{44} 0.575, P_{51} 0.564, P_{53} 0.567
11	$C_{56}P_4$ [6,6]	6.320	-9.042	12.814	-9103.245	P_5 0.486, P_7 0.489, P_{53} 0.486, P_{60} 0.489
12	$C_{56}P_4$ p1	4.833	-8.161	14.385	-9008.973	P_{14} 0.814, P_{20} 0.814 P_{34} 0.814, P_{35} 0.814
13	$C_{56}P_4$ p 2	5.862	-8.868	13.169	-9081.945	P_2 0.486, P_2 0.487, P_{41} 0.526, P_{43} 0.526
14	$C_{55}P_5$•	6.428	-8.830	12.50	-9026.402	P_7 0.785, P_{25} 0.791, P_{28} 0.787, P_{32} 0.789, P_{35} 0.788
15	$C_{54}P_6$ h	5.522	-8.893	11.994	-8961.799	$P_2$0.193, P_{21}0.197, P_{24} 0.197, P_{25}0.194, P_{32}0.195, P_5 0.194
16	$C_{54}P_6$ m	4.697	-7.878	13.655	-8862.174	P_6 0.800, P_{24} 0.830, P_{30} 0.831, P_{34}0.803, P_{45} 0.805, P_{46} 0.803
17	$C_{54}P_6$ c	3.651	-7.206	15.614	-8744.595	$P_2$0.847, P_{12}0.815 P_{27}0.813, P_{39}0.848, P_{50} 0.835, P_{55} 0.834
18	$C_{54}P_6$ p 135	4.295	-7.752	14.675	-8800.958	$P_2$0.793, P_{23} 0.791, P_{28} 0.793, P_{38} 0.791, P_{41} 0.787, P_{57} 0.789
19.	$C_{54}P_6$[6,6]	6.333	-8.950	12.459	-8933.906	P_1 0,482, P_{13} 0,487, P_{20} 0,482, P_{26} 0,482, P_{35} 0,487, P_{52} 0,487
20.	$C_{54}P_6$ [5,6]	5.640	-8.680	13.515	-8870.526	P_8 0,527, P_{10} 0,528, P_{16} 0,530, P_{20} 0,523, P_{58} 0,522, P_{59} 0,525
21.	P_{60}	4.069	-8.947	-10.625	-5171.754	-

Distance between P atoms in polysubstituted fullerenes: m-medium, p-pole, c-central, h-hexagon. In the same polygon, 1,2-ortho, 1,3-meta, 1,4-para, 1,3,5-simetrical substitution

3.1. GEOMETRY

The introduction of the phosphorus atom in the fullerene network results in the prominence of the site of the heteroatom due to the changes in the bond length and bond angles (Figure 1). In phosphorus substituted fullerenes, the longer P-C bonds due to the larger covalent radius of phosphorus require small valence angles at phosphorus. The 3pπ-2pπ overlap between phosphorus and carbon, lower than the carbon-carbon 2pπ-2pπ overlap, leads to larger bonds and lower bond energies.[31] As the number of heteroatoms increases, the surface shape is drastically changed, as it can be seen in the Figure 1. P-C bonding status in the all the investigated 21 phosphorus doped fullerenes is: P-C [6,6]

bond length is in the range 1.813 ÷ 1.871 Å, while P-C [5,6] bonds are 1.831 ÷ 1.959 Å. P-P [6,6] bond length is between 2.153 and 2.156 Å, while P-P [5,6] is somewhat larger, 2.159 to 2.160 Å. The above data were compared with those supplied by the gas phase phosphabenzene geometry, P-C 1,73 Å and hexaphosphabenzene P-P bond length of 2.17 Å, crystallogaphically measured in the [CpMo(P)$_6$MoCp] complex.[32,33] Based on a bond length criterion, an important aromatic character is assigned to phosphafullerenes. The valence angles at phosphorus are 90,11 ÷ 99.50 degrees in the hexagon, smaller than in aromatic phosphorus compounds, *e.g*., 101° in phosphabenzene and 84.05°÷89.67° in the pentagon. P-P-C angles in a hexagon are 103.38 ÷104.56°, while in the pentagon are in the range 93.97 ÷ 94.59°. P-C-C angles are 106.84÷116.80° in pentagon, smaller than those in hexagon 122.82÷131.12°.

(a)　　　　　　　　　　　　　　　　　　　　(b)

(c)　　　　　　　　　　　　　　　　　　　　(d)
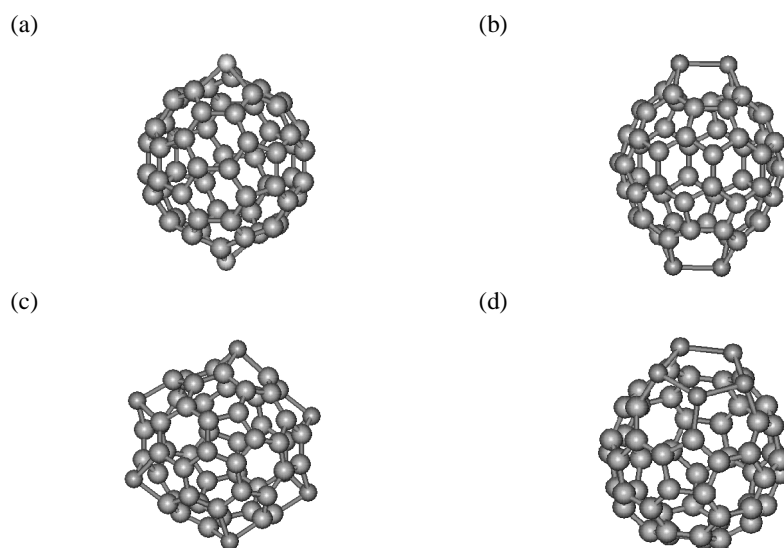
Figure 1. The geometries of phosphorus poly-substituted fullerenes: (a)$C_{58}P_2p$; (b) $C_{56}P_4p2$; (c) $C_{54}P_6c$; (d) $C_{54}P_6$

3.2. THERMODYNAMIC STABILITY

Thermodynamic stability was appreciated on the ground of the heat of formation HF/atom and binding energy (Figure 2 and 3). The introduction of phosphorus atoms in fullerene framework does not change dramatically the thermodynamic stability. Regitz *et al*.[35] affirmed that "after carbon, phosphorus is the second element with the most pronounced ability to form element-element bonds".

In the case of a hexagon substituted with phosphorus the stability of that isomer is greater than of all the studied isomers (Table 1, entry 15, in italics). When the substitution occurs at 6,6 positions, the isomers are more stable than those in the position 5,6. In the case of di-substitution on the same hexagon, the 1,4 isomer is the most stable, in agreement with previous calculations for the silicon substituted fullerene, but in contrast with theoretical and practical observation of 1,4-diphosphabenzene that is the most unstable isomer.[8,34] However, the rest of the cage seems to confer stability to the heterofullerene. The distance between heteroatoms has no constant influence on isomer stability, just in case of the pole substitution. For example, the isomers of the

heterofullerenes $C_{58}P_2$ $C_{56}P_4$, $C_{54}P_6$ substituted at pole are the least stable. Another less favorable situation is when the substitution takes place at isolated central positions in the fullerene $C_{54}P_6c$. The lower stability may be explained because of the multiple highly charged centers. Note the stability of the radicals $C_{59}P_1^{.}$ and $C_{55}P_5^{.}$ from thermodynamic point of view. In literature is noticed that aromatic stabilization of phosphacyclopentadienide anions $C_nR_nP_{5-n}$ n=1-5 are similar to cyclopentadienide anion.[36]

Figure 2. Variations of HF/atom function of the number of P atoms and relative position.

Figure 3. The influence of C by P substitution on binding energy of $C_{60-n}P_n$.

The decrease of binding energy along with the increase of the number of phosphorus atoms is consistent with respect to the decrease of the P-C bond strength.[37,38]

Atomic charges

The introduction of the more electropositive phosphorus atom, with respect to the carbon atom, leads to a partial positive charge on phosphorus atoms and a negative charge at vicinal carbon atoms. In the rest of the cage, the charges of carbon atoms are very small positive or negative. In the case of polysubstitution, if the phosphorus atoms are situated on the same hexagon the positive charge at phosphorus decreases and conversely, the charge increases when phosphorus atoms are situated on a pentagon, but the charge of vicinal carbon does not changes significantly. If the phosphorus atoms are separated by carbon atoms the charge at phosphorus increases and the charge at carbon remains practically unchanged. The displacement of a number of phosphorus atoms on the same polygon diminish the positive charge at phosphorus and increase the stability. When the substitutional sites are separated by at least three C-C between phosphorus atoms, the charge on phosphorus increases and stability is diminished.

3.3. HOMO-LUMO GAP

The electronic properties of phosphorus atom influence the energy of molecular orbitals. The perturbation induced by the substitution determines the increase of HOMO energy and decrease of LUMO energy (Figure 4). In consequence, the HOMO-LUMO gap reduces and the chemical reactivity is expected to increase, with respect to the parent fullerene (Figure 5).
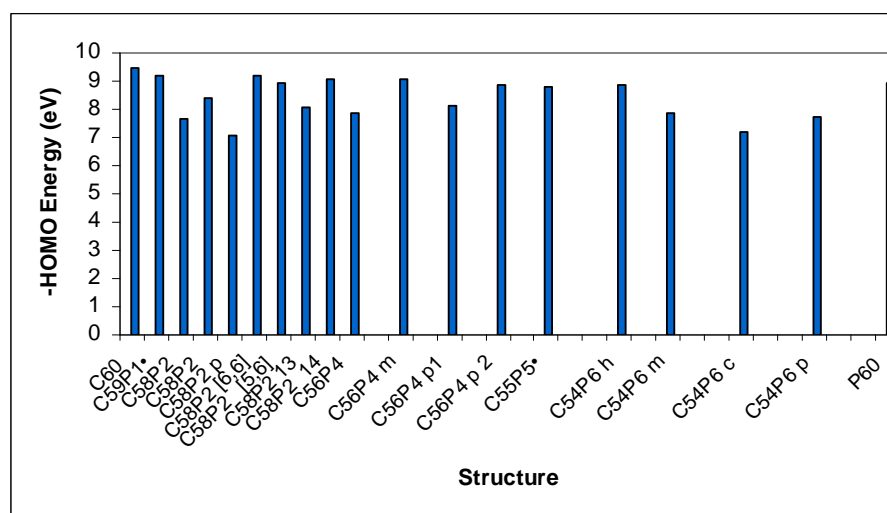
Figure 4. The effect of introduction of P atom on HOMO energy (eV) in phosphorus substituted C_{60}.

This implies an easier oxidation and a more difficult reduction, in contrast with C_{60}. It is well known that the phosphorus atom, in a sp^2 hybridization state, displays very interesting coordination chemistry, namely the very low LUMO enhances the retro-donating ability. Thus, it is possible that phosphorus skeletally doped fullerenes to

undergo complexation reaction with different metallic centers. The lowered HOMO-LUMO gap may favor the electron excitation from the HOMO to the LUMO level.

Figure 5. HOMO-LUMO gap of $C_{60-n}P_n$.

The degeneracy of HOMO and LUMO levels is reduced or destroyed but the HOMO-LUMO gap is, in some cases, namely $C_{59}P_1$, $C_{58}P_2$ [6,6], $C_{56}P_4$ [6,6], $C_{55}P_5$, $C_{54}P_6$ [6,6], as high as for the parent C_{60} and consistent with a good kinetic stability. It seems like the substitutional pattern influences the orbital energies. The thermodynamic stability it is known to correlate with the HOMO-LUMO gap: isomers with a larger gap are supposed to have smaller values of the HF/atom.

Our results showed that the most stable isomers have the largest HOMO-LUMO gap. In the case of $C_{58}P_2$ isomers, the [5,6] substitution is associated with a reduced HOMO-LUMO gap, while [6,6] substitution provides a larger gap.

CONCLUSIONS

The semiempirical PM3 calculations of the equilibrium geometries, heat of formation, and HOMO-LUMO gap, for a number of phosphorus substitutionally doped fullerenes was carried out. The substitution with the more bulky phosphorus atom deforms the cage more dramatically than nitrogen does. The thermodynamic data showed that skeletally substituted fullerenes are in some cases as stable as the parent C_{60} . The site of substitution influences all the calculated parameters, HF/atom, binding energy, HOMO-LUMO gap, and charge on phosphorus. Always, the [5,6] substitution is less favorable than the [6,6] substitution and the larger the distance between heteroatoms, the more unstable isomer is expected. The phosphorus substituted fullerenes have a higher HOMO and smaller LUMO energies, thus being more easily oxidable than the parent C_{60}. Based on the above considerations, we could appreciate that substitutionally doped fullerenes are stable, possible molecules.

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