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Theoretical description of benzene–fullerene and its organometallic derivative

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ABSTRACT

The ubiquitous benzene derivative of fullerene has been analyzed from a theoretical point of view. The pronounced difficulties involved in its preparation relate to the structure of the frontier orbitals of the primitive fragments (i.e. benzene and fullerene C_{60}) and their corresponding interactions. The nature of the inductive effect is studied on the basis of the nitro and amino derivatives (functional groups substituted on benzene ring). The electrophilic activation/deactivation patterns induced by substituent groups added to phenyl-fullerene molecule are studied applying the criteria of reactivity indexes in conjunction with the molecular electrostatic potential and the dipole moment of the molecules. The capacity of the resultant molecule to generate organometallic derivatives similar to the dibenzene-chromium is also studied. All structures were calculated using DFT methods.

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1. Introduction

The organo-fullerene compounds comprise a rare classification of substances because the direct reactions between fullerene and organic fragments are not common [1]. There are several methods which can be used to synthesize the so-called organohydrofullerenes where a double bond on the fullerene surface is broken to yield the substitution of a functional group and a hydrogen atom [2]. Among these, it is important to mention those compounds where the substitution makes it possible for an aromatic ring to take a substituent on one end of a double bond, and a hydrogen atom on the other [3,4], causing an elecrophilic aromatic substitution to occur. This type of compound constitutes the subject of our interest.

The phenyl-fullerene (**PF**) is presented in Fig. 1; the molecule is the only product resulting from the substitution of a benzene molecule on a (6,6) fullerene bond and its corresponding proton. The first attempt to prepare this compound was undertaken by Olah and his co-workers [5], but the problem encountered in a direct reaction lies in the possibility that a multiple substitution will take place at the surface of the C_{60}, it is thus convenient that the products should consist of a mix of several substances. The titration method [3,4] has been shown to represent a better option and the phenyl-fullerene can be synthesized in this way, however little information exists concerning its structure and reactivity.

The goal of this study is to analyze the nature of the electronic structure of this molecule from a theoretical point of view, analyzing the intrinsic properties involved in possible reactive behavior, the changes precluded by new substituents on the benzene fragment and the possibility of preparing organometallic derivatives.

2. Methods

All calculations were carried out by applying a pure DFT method for energy evaluations. In the case of structures of all derivatives of benzene, Becke's gradient corrections [6] for exchange and Perdew–Wang's for correlation [7] were applied. This is the scheme for the BPW91 method which forms part of the Gaussian 09 [8] Package. The calculations were performed using the 6-31G** basis set. The structure of complex di-benzenechromium-fullerene (**BCF**) was optimized using DFT in the generalized gradient approximation (GGA) with the Materials Studio DMol3 program [9,10] from Accelrys Inc. We employed the Perdew–Wang 1991 (PW91) exchange–correlation functional [11] with a double numerical, plus a polarization function basis set (DNP) to describe the valence electrons, in combination with Hartree–Fock effective core potentials [12,13] for the treatment of the ionic cores. The structure was relaxed until the total remaining force was below 0.002 Ha/Å, a thermal smearing of 0.05 Ha was used to optimize geometry. Finally, the structure was optimized with Gaussian 09.

Frequency calculations were carried out at the same level of theory in order to confirm that the optimized structures were at a minimum on the potential surfaces. Work strategy was selected according to that proposed in the previous fullerenocene study [11]. The bond lengths of the optimized structures were used for

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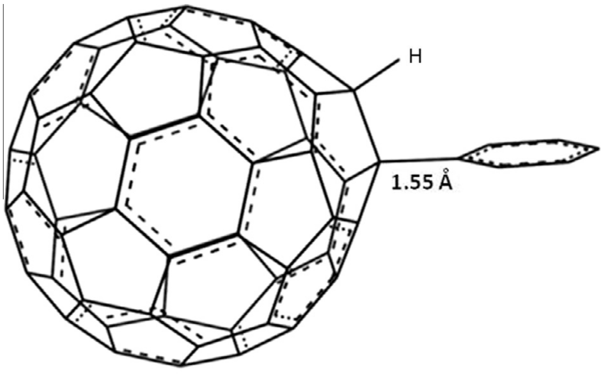

PF

Fig. 1. DFT optimized geometry BPW91/6-31G** of **PF.**

the HOMA (Harmonic Oscillator Model of Aromaticity) method [14,15] for studying aromaticity.

3. Model equations

The global eletrophilicity, ω, defined by Parr et al. [16] as $\omega = \frac{\mu^2}{2\eta}$, is evaluated in terms of the electronic chemical potential μ (the negative of Mulliken electronegativity) approached by $\mu = -\frac{(I+A)}{2}$ and the chemical hardness η defined as $\eta = (I - A)$. They are evaluated in terms of the vertical ionization potential I and electron affinity A for the ground state of the molecules, at the BPW91/6-31G** level of theory. The maximum electron flow ΔN_{max} is given as $\Delta N_{max} = -\frac{\mu}{\eta}$.

4. Results and discussion

The first molecule that was studied is **PF** presented in Fig. 1. The results suggest that the molecule is stable from a thermodynamic point of view; the frequency calculation indicates that there are not imaginary frequency values.

The nature of the **PF** molecule manifests a narrow energy gap (1.47 eV) between the HOMO and LUMO. In the fullerene (**F**) the corresponding value is 2.762 eV previously obtained [17]. This situation arises due to the new arrangement of molecular orbitals (MOs). Originally the molecular orbitals of **F** presented an arrangement portraying a threefold degenerated set for the LUMO and a fivefold degenerate set for the HOMO. In the case of benzene (**B**) it manifests the classic distribution of a twofold degenerate set for the HOMO and a near HOMO-1 which completes the sextet. Mixing both molecules produces a large set of eight delocalized and occupied MOs that are very similar in energy and exert a strong electronic influence, stronger than the one exerted by the fivefold degenerated set of the fullerene. Therefore the LUMO is attracted by this force and the gap in **PF** is lower than it is in a pure **F** molecule. All this is depicted in the interaction diagram presented in Fig. 2.

It is important to note that the energy of the HOMOs in both cases (i.e. **B**: −5.95 eV, **F**: −5.98 eV) is almost the same. It seems possible that an electronic pair originally situated on the HOMO of benzene could transfer to one of the three orbitals of the degenerated set of the fullerene LUMO and meanwhile the other four aromatic electrons from the benzene mix with the fullerene HOMO. Obviously the symmetry of the **PF** is very low and the large degeneration taking place in the parent molecules is lost. However, the new levels are very similar, suggesting electronic flow. The shapes of the molecular orbitals are presented in Fig. 2, all of them demonstrate strong fullerene participation. Indeed, the LUMO only manifests fullerene participation and the HOMO, along with the threefold degenerate set of HOMO-1 orbitals presents little participation of benzene and a bond between both fragments.

This scheme is useful for establishing the reactive nature of **PF**. A very important feature is that the LUMO represents a low energy double degeneracy which can provide the site for easy electrophilic substitution, a characteristic which varies little from that displayed by pristine fullerene which is shown to have a weak electronic acceptor nature. In contrast, **PF** is actually a strong electronic acceptor. The HOMO and HOMO-1 set also play an important role in this discussion because they offer eight electrons for interaction with a very near LUMO. Thus semiconductor behavior is addressed.

The aromaticity of the ring joined to the **F** is expected to change to some extent, so the evaluation of this possible modification was carried out by applying the HOMA method [14,15]. The result is interesting because the predicted value for free **B** is 1.0 and the value obtained for the **B** ring in our case is 0.995, therefore the change is minimal and indicates that the **F** substituent displays almost neutral behavior because the hypothetical reactivity of **B** manifests few changes.

In order to assess the last statement, new calculations were carried out involving various functional groups substituted at the *para* position on the **B** fragment to compare with the substitution on the fullerene sphere. The substituents consisted firstly of an electron releasing agent $-NH_2$ (**APF**) and secondly an electronic withdrawing agent such as the $-NO_2$ group (**NPF**) (Fig. 3). The analysis of these results is presented later in the text.

The electronic gap in the new molecules reflects the expected changes. The energy gap for the nitro substituted molecule is practically the same as that of **PF**; the value is 1.43 eV in comparison with 1.47 eV in the case of the unsubstituted one. The interesting

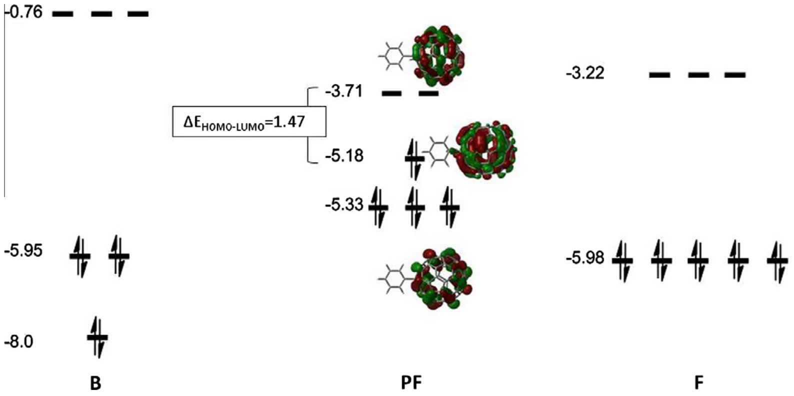

Fig. 2. Interaction molecular orbital diagram sets for **B**, **PF** and **F** (eV).

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