## Non-existence Fullerene Compounds

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**Abstract:**
A brief summary about the research lines of our group is presented. The common factor in all the
propositions is the fullerene in a chemical reactive role. The chemistry proposed is novel and can
yield interesting results.

## 1. Introduction:

Fullerenes have been the object of intensive research for the last twelve years [1-3]. There are
several features to consider when studying these fascinating molecules because they can be
approached from a physical, chemical or even biological point of view, and during their short life
(as a full characterized species) they have been found to be useful or applicable in several
different fields; for example electronics, communications or even pharmacy.

One important feature that strongly accounts for this diversity is the particular and novel
reactivity of these species [4]. In spite of their ambiguous aromatic character [5] (which itself is
an important topic for study), the reactions of fullerenes are somewhat different to those of
classic polyaromatic hydrocarbons or even those pertaining to normal olefins. In this sense, it is
relatively easy to find sigma substituted organic derivatives [6]; endohedral [7] and also
exohedral [8] organometallic complexes, adducts of biomolecules [6] or porphyrin and also
phtalocyanine derivatives [9].

Theoretical calculations have been very useful for this research [4]. The precise models
for new species and comparisons with experimental and spectroscopic data have been
demonstrated to represent a very important tool for the design, search or application of the large
quantity of fullerene derivatives known today.

Our research group has been working on the design of very different fullerene
compounds. We have proposed new species that have been theoretically studied and we have
found thermodynamic evidence of stability, suggesting that many of these new molecules can be
prepared and may even have potentially important applications.

Our propositions are divided into five main groups:

a). Fullerenocene.

b). $C_{80}$ exohedral $\eta^6$ compounds.

c). Cycloadditioned fullerene compounds.

d). Phenyl-fullerene.

e). Symmetrically nested (matrushka) endohedral fullerenes.

## 2. Results.

a). **Fullerenocene [10].**

Di-benzene-chromium [11] (figure 1) is a well known $\pi$ compound. This type of
molecule was previously considered to be a very important example of an organometallic
compound, where the bond between the metal atom and the aromatic fragments is formed only

by $\pi$ interactions. In another context, the aromaticity of fullerenes has been the object of very different studies and there is no conclusive argument to indicate whether or not they are aromatic. Thus it is not possible to establish the interaction between all the carbon atoms of a six member fullerene ring and a metal atom (or ion), indeed no definitive experimental study exists where a $\eta^6$ fullerene organometallic complex has been characterized, however a theoretical study does exist and one of the species focused on in this study is the fullerenocene (see figure 2a).
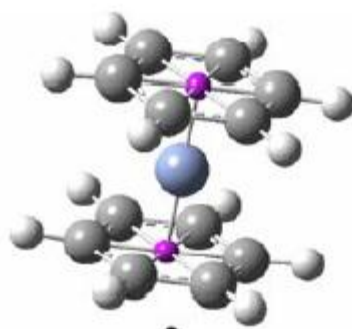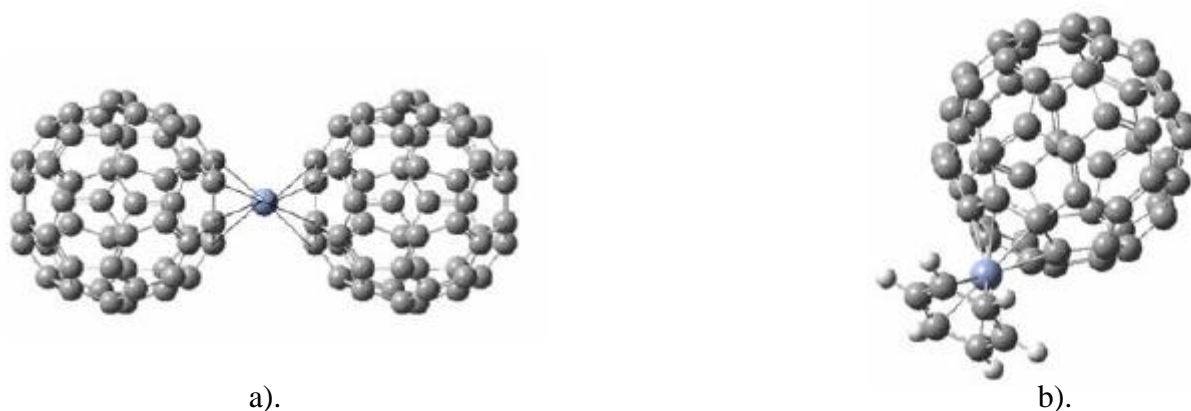


Figure 1. Dibenzene-chromium.



a).                                                                                       b).

Figure 2. a). Fullerenocene, b). Hybrid compound of fullerene and benzene.

Fullerenocene and the hybrid compound $\eta^6$ phenyl-chromium- $\eta^6$ –fullerene [13] (figure 2b) indicate that they are theoretically stable compounds with very interesting electronic properties. Some typical methods (HOMA and NICS) were used to measure and quantify the possible aromaticity of both these species and the result was astonishing; in both cases the fullerene fragments manifested a strong aromatic character, even stronger than that obtained for the pristine fullerene itself. Besides, the large electronic delocalization and narrow HOMO-LUMO gap suggest semiconductor behavior, where again this feature manifests better results in the case of organometallic complexes, than fullerene on its own (with the hybrid complex being dominant).

This kind of compounds can exist but they are yet elusive, however the theoretical study has been accepted by the scientific community and there are experimental work in this area, in short time will have news about this or other $\eta^6$ complexes of this type.

## b). $C_{80}$ exohedral $\eta^6$ compounds [12].

The sphericity of $C_{60}$ causes a pyramidalization angle which puckers the ring; therefore this is one of the factors which negates $\eta^6$ hapticity.  It has been suggested that this $\eta^6$ bond between fullerene and a metal atom can be improved if the six member rings are flatter than those in $C_{60.}$ One possibility for improving this is to prepare the organometallic compounds using larger fullerenes because there will be more carbon atoms and the pyramidalization angle will be shorter. However there is another factor to consider when contemplating this compound. All the larger fullerenes that match the IPR (isolated pentagon rule) [13] have several isomers [4] (with the exception of $C_{70}$) and depending on the different symmetries it is possible to get very different values for the pyramidalization angle, as well as very different energy values for stability, and this was the object of the second investigation.

The seven possible isomers of the $\eta^6$ phenyl-chromium- $\eta^6$ –fullerene $C_{80}$ were studied theoretically (actually only six because there are two belonging to the $C_{2v}$ point group that have almost the same energy value and only one is included, see figure 3); the result is very interesting because it would first appear that the smaller the pyramidalization angle, the better the overlap among the six carbon atoms of the ring with a resulting intrinsically improved aromatic character, however in the case of the model this appears to be very different because the favored isomers of the $\eta^6 \pi$ organometallic $C_{80}$ complexes are those with a larger pyramidalization angle. A qualitative explanation of this phenomenon involves the $p_z$ orbitals that belong to the six carbon atoms of the ring, which on puckering have a tendency to slope with respect to the perpendicular position of a flatter benzen ring. These orbitals show a strong interaction with the toroidal ring of the $d_z{}^2$ orbital corresponding to the metal center and this interaction is found on the very close LUMO of the systems. The best overlap corresponds to the isomers, where the $C_{80}$ fragment belongs to the $C_{2v}$, $D_2$, $D_{5d}$ and $D_3$ point groups in this order, whereas the $I_h$ and $D_{5h}$ (which are the unstable species) show smaller angles and diminished stability.



(a) $C_{2v}$    (b) $D_2$    (c) $D_{3d}$

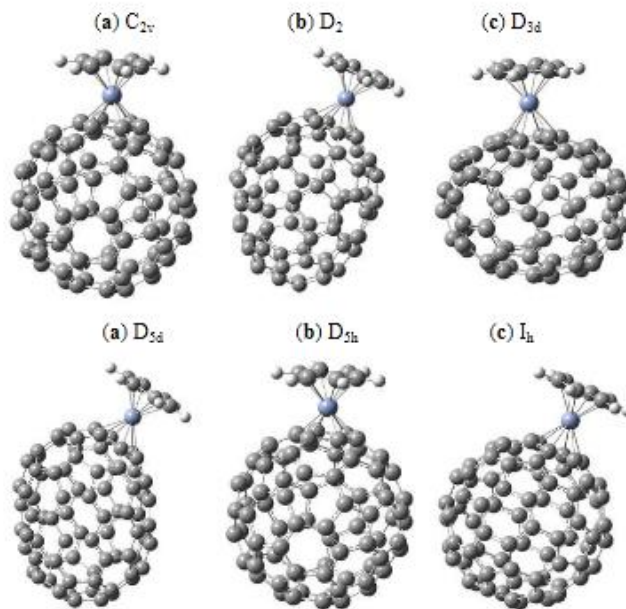(a) $D_{5d}$    (b) $D_{5h}$    (c) $I_h$

Figure 3. The six isomers of exohedral organometallic complexes of $C_{80}$ with chromium.

c). **Cycloadditioned fullerene compounds.**

Another important characteristic of the fullerenes is that they can offer unoccupied molecular orbitals (MO's) with low energy (figure 4), therefore it is easy to generate anions of fullerene and considering the triple degenerated set of MO's corresponding to the LUMO of the $I_h$ symmetry group of $C_{60}$, this molecule is easily able to adopt six electrons (and therefore the hexa-anion is very common). This electron affinity might be useful for designing chemical reactions which would be apt for the extraction of electrons; a peculiarity which was applied to exploring a known reaction, constituting a recognized health problem.
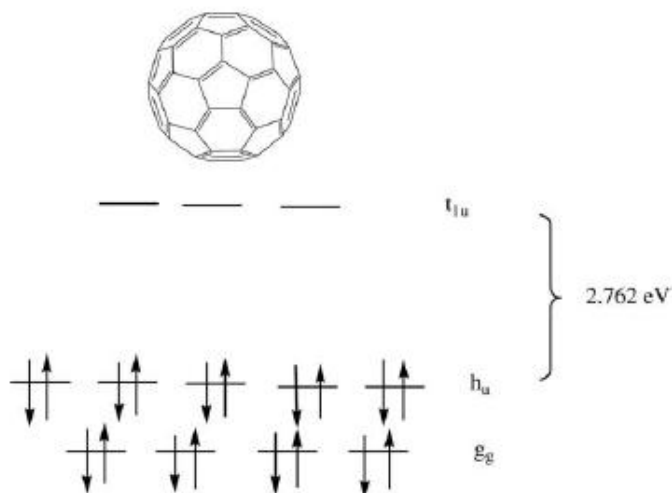


Figure 4. Molecular Orbital scheme of fullerene $C_{60}$.

Estradiol is a known molecule that is part of the female hormonal system. Young women have the necessary enzymes for converting this into estrone, but after menopause women lose these particular enzymes and as a result their estradiol is no longer converted; therefore it accumulates in the body and may cause undesirable reactions. One of these reactions is the insertion between two puric bases of the DNA chain giving place to a mistake in the replication process which causes a type of cancer [14].

Estradiol can be oxidized and thus lose its ability to produce the epoxide form which is the substance that participates in the damaging DNA process. However for this to occur, it is necessary to submit it to a reaction with an electron withdrawing molecule, for example fullerene $C_{60}$. For this reason, we have simulated the interaction between both these molecules.

The result from this experiment was rather different from the one we were expecting, as a reaction took place but this was a cycloaddition reaction (figure 5), or rather the double bond of the epoxidized ring of estradiol interacted with a double bond of a six member ring on the fullerene surface yielding a cycloadditioned compound which continues to incorporate the epoxide group, but has lost its intrinsic reactivity for participating in the process of insertion within the DNA causing subsequent damage.
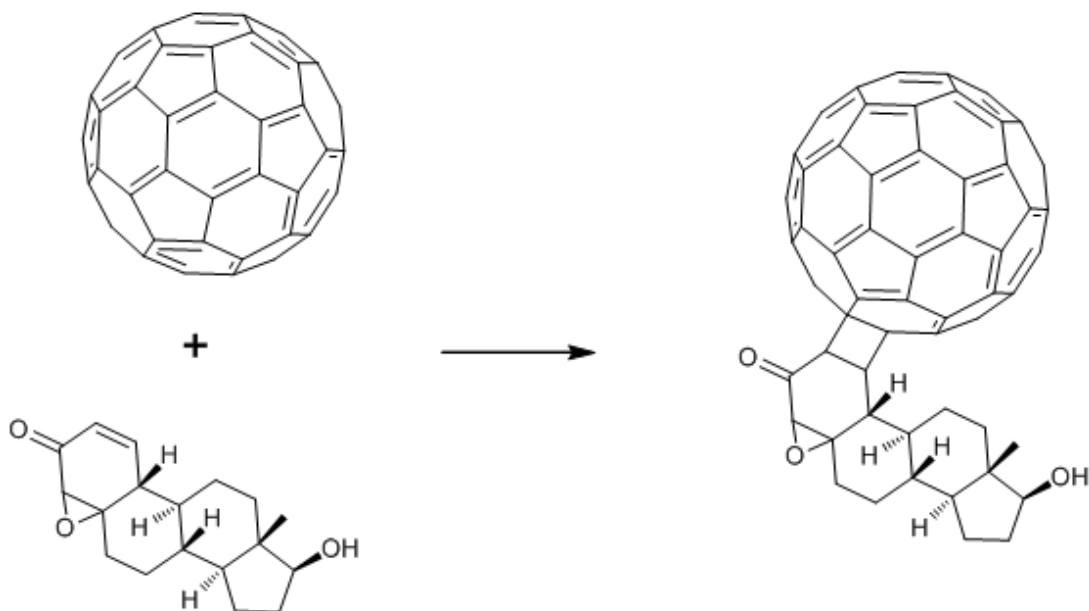
Figure 5. Cycloadition reaction between fullerene and epoxide of estradiol.

d). **Phenyl-fullerene.**

A number of fullerene compounds in which the sphere is directly joined to an organic fragment have been prepared. Those compounds in which long aliphatic chains are joined to the sphere are particularly valuable because these decorative chains provide the fullerenes with optimum solubility properties. However the synthesis of a compound where a benzene ring was directly joined to the sphere has only been performed once and the yield is poor, as is information about the compound formed [15]. Thus we have investigated all these topics and likewise the characteristics of similar compounds containing nitro-benzene, aniline or ferrocene rather than benzene, and results indicate that several of these species may be useful for the design of electronic devices (figure 6).



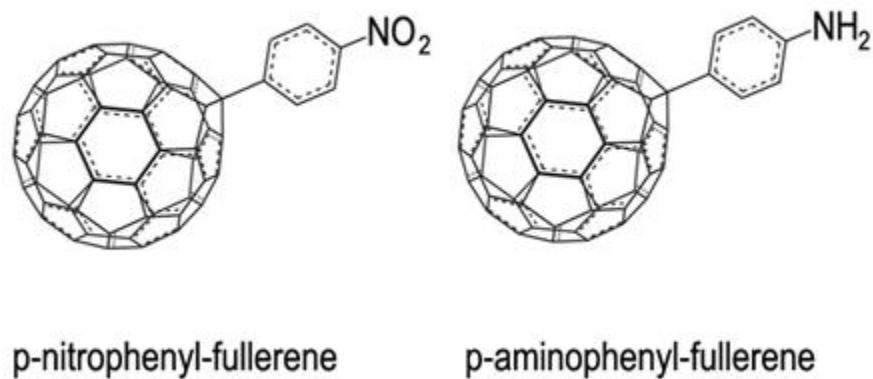p-nitrophenyl-fullerene          p-aminophenyl-fullerene

Figure 6. Derivatives of phenyl-fullerene.

e). **Symmetrically nested (matrushka) endohedral fullerenes.**

And finally, endo complexes constitute one of the most famous derivatives of fullerene, where metal ions or small clusters with a positive charge can be trapped in a large fullerene. Recently there has been much interest in new species in which the inner fragments may consist of small metallic salts; in a different context people studying large nanostructures have shown deference to very large clusters named "onions" of which large fullerenes include some with little molecular weight, however this type of nanomaterial obeys the $60n^2$ rule (where n represents the number of layers) [16], implying that the first core must be $C_{60}$, that the following one will be $C_{240}$, the third $C_{540}$ and so on. We decided to study the intermediate species between the endo complexes and the onions; this indicated complexes where a large fullerene comprises a smaller one, not however conforming to the $60n^2$ rule, but only following the symmetry of the cages.

Two complexes have been studied, the first one is that which at first sight indicates large symmetry, it is the $C_{60}$ sphere put into a $C_{180}$ cage where both systems belong to the $I_h$ symmetry group (figure 7). The second one is the combination of the $I_h$ $C_{20}$ (that is unstable and does not obey the IPR rule) and then there is the $T_h$ $C_{116}$ (not yet known as an isolated species); in both cases the results are very interesting.



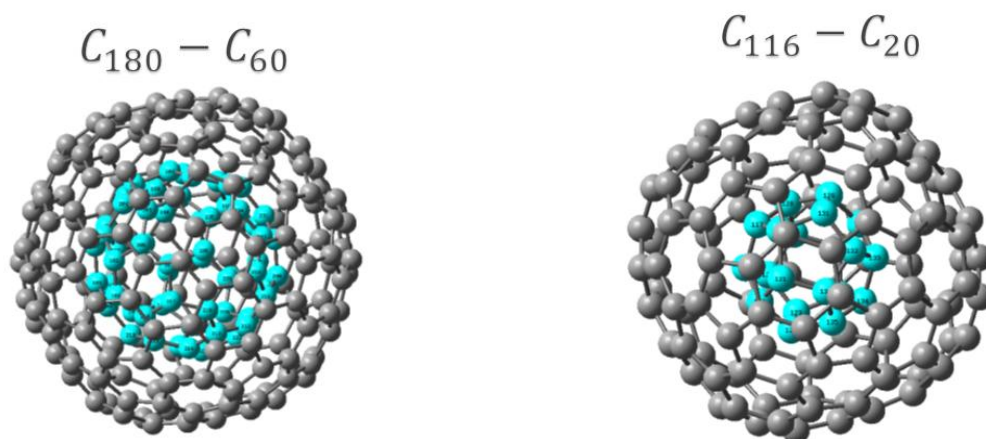$$C_{180} - C_{60} \qquad C_{116} - C_{20}$$

Figure 7. Nested fullerene complexes.

In the first instance, the resultant nested fullerene lost the original symmetry in the subsequent guest and host interaction, i.e., the final cage shows that the fullerene $C_{60}$ rotates from an ideal position to an alternative one manifesting less energy), this is a kind of distortion that resembles those from Jahn-Teller although in the present case it is not so notorious because the inner fullerene does not change its geometry, but only its position with respect to the outer sphere.

An interesting point to note is that the interaction between both spheres seems to represent a favorable energetic process, table 1 shows the total energy values for $C_{180}$, $C_{60}$ and the complex (in hartrees), the difference between the value of the complex and the sum of the values of the isolated species indicate that the complex has the minimum value (equaling -3.994 eV), therefore the complex is a stable species. Furthermore it is important to note that there is a strong electronic exchange between both cages, but the result is unexpected, as the largest

electronic density is found at the geometrical center of the entire complex, i.e. at the center of the inner $C_{60}$ (figure 8).

The other case is very different; this manifests behavior resembling that of the classic endohedral complexes, there is a net transfer of charge from the inner sphere to the outer one, but curiously this is completely localized on the equatorial zone of the outer sphere. Likewise, the combination of both these species also gives place to a more stable species.
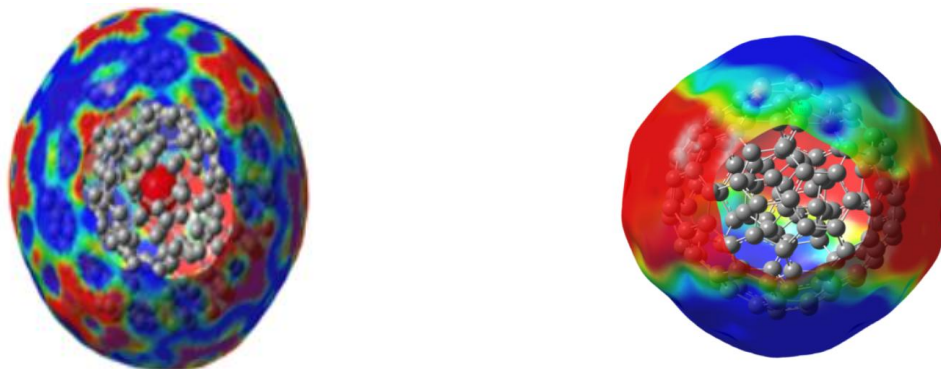


Figure 8. Electrostatic potential of the both nested fullerene complexes.

### 3. Conclusions:

Five new items for study into the chemistry of fullerenes are shown, the ideal resulting species can have interesting applications in several areas as can be: conductivity, catalysis or even pharmacy, the next step is the laboratory activity, if these experiments match with the theoretical results there will be a large collection of new and interesting substances in which fullerene fragments will have the main role.

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