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Endohedral dibenzenechromium

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ABSTRACT

The possibility of having a metallocene species, in which metal atoms as well as the corresponding aromatic rings appear within a fullerene sphere, is analyzed from a theoretical point of view. The complexes were simulated by joining a $Cr(C_6H_6)$ fragment to the inner wall of a C_{116} (T_h) fullerene. The large cage of this fullerene makes it possible to place two of these fragments within the sphere, so that several possibilities for isomers can be contemplated, and the mono-endo, di-endo, mono-endo-mono-exo and di-exo geometries can be modeled and compared.

1. Introduction

Since the discovery of fullerene [1,2], the study of this kind of substance has become one of the most popular themes in scientific research [3,4]. Endohedral complexes of fullerene are species, where an atom or a small cluster of atoms are confined within the shell of a fullerene [5]. This particular study topic constitutes one of the most investigated areas in Chemistry, Physics and Material Sciences [6].

The nature of the species confined within the shell can be very variable; they may only be metal atoms (mainly from the lanthanide family) [5] or small clusters containing metal atoms joined to nitrogen, oxygen or carbon atoms [7,8]; however there are very few reports describing endohedral fullerene cages containing transitional elements; to the best of our knowledge, the only exception is titanium [9,10]. The presence of a chromium atom within a fullerene would therefore be very notorious.

The objective in this work is to simulate an endohedral species where a chromium atom and a complete benzene ring are found within the cage of a large fullerene, aiming to produce an endohedral analog of a dibenzene-chromium. However this fragment would not be separated from the inner wall, as one of the two benzene rings belongs to the fullerene itself. The only similar investigation was proposed by Chistyakov and Stankevich [11], who simulated an analog of ferrocene, with the iron atom at the center of a little cage (for example $C_{40}H_{30}$), and both five-member rings at the polar extremities of the sphere, with direct bonds through the central iron atom.

There are several discussions concerning the possibility of metal atoms being joined to fullerene cages with different hapticities [12]. The case of η^5 exohedral complexes has been theoretically studied by several groups [13–18] and experimentally solved by Nakamura and his group [19–21]. It has been claimed that the formation of stable η^5-complexes between fullerenes and transition metals is highly improbable because the conjugated system is strongly delocalized, and the polarization of the atoms of the five-member face is weak [12]; however the formation of a “fence” of five organic groups around the five-member ring can help to localize the electrons and enable the simulation of the charge present in the cyclopentadienyl ion; indeed this was the strategy employed by Nakamura and his group, who managed to solve the problem [22].

All these problems arise mainly because the bond between iron and the cyclopentadienyl moiety has a strong electrostatic component. However a collateral study of similar structures would involve sandwich compounds from chromium, because the archetypical species of this metal, i.e., dibenzene-chromium has a bond based on covalent interactions due to zero oxidation for the central chromium atom. An experimental exo η^6 analog of this metal does not yet exist, but there are theoretical propositions [23] which demonstrate the possibility of its existence. Therefore the proposed molecules studied in the present work have chromium as the central species and the entire discussion is focused on the thermodynamic stability of these species, while also comparing them.

2. Methods

All calculations were carried out by applying a pure DFT method for energy evaluations. For the structures of all derivatives, Becke’s

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gradient corrections [24] for exchange and Perdew–Wang's for correlation [25] were applied. This is the scheme for the B3PW91 method, which forms part of the GAUSSIAN09 [26] Package. Calculations were performed using the 6-31G** basis set and full optimizations were carried out for all structures, as well as frequency calculations that were useful for achieving the absolute energy minima in each case.

3. Results and discussion

Since its discovery [27], dibenzene-chromium has been the object of several monographs [28,29] and studies [30,31]. It represents the model structure for the arene organometallic compounds and the reference molecule (together with ferrocene) for π organometallic chemistry. One of its most important characteristics is the Cr(0) condition at the metal center, as described previously. In the present work, it has been embedded within fullerene geometry.

The general description of the molecules being studied is as follows; a large fullerene structure can be part of a bis(benzene)chromium, sharing a six-member ring (or more) with a $Cr(C_6H_6)$ fragment. The chosen fullerene was C_{116} (6061) (**1**), a cage which was deliberately chosen for three main reasons: first it is large enough to comfortably receive one organometallic fragment or even two, second, it has an IPR structure that has been indicated as very possibly representing a stable molecule [32], and finally it has effective symmetry, belongs to the T_h point group and presents significant advantages for quickly producing stable optimized structures. The shape of this molecule can be seen in Fig. 1.

The C_{116} (T_h) has several sets which consists in a six membered face joint to six rings, four of them are other six membered cases and there are also two opposite five membered rings. The particular symmetry of this species allows to connect one of this sets with other similar by means a proper C_2 axis, the substitution of the fragment $Cr(C_6H_6)$ was made with a η^6 hapticity on one of this sets in the case of a mono-substitution or in two opposite connected by symmetry sets in the cases of di-substitution. Therefore there are several isomers that can be studied regarding their thermodynamic stability; however there is only one possibility studied here concerning the position of the metallocene into the sphere.

All the resultant molecules in which the host is the C_{116} (T_h) fullerene cage are the following:

- A mono-substituted endo complex.
- A mono substituted exo complex.
- A di-substituted endo complex.
- A di-substituted endo and exo (same time) complex.
- A di-substituted exo complex.

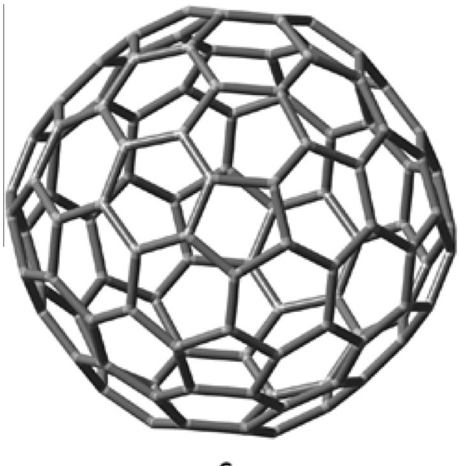

Fig. 1. Empty cage of C_{116} fullerene (**1**).

The description of these substances will be presented and analyzed in the following sections.

3.1. Mono substituted complexes

The first case corresponds to the mono-substituted endo complex (**2**), the shape of which can be seen in Fig. 2; the atoms corresponding to the embedded di-benzene-chromium are highlighted.

Free di-benzene-chromium (**3**) was calculated under the same conditions, for the purpose of comparison. The first important feature to consider is that the stable fullerene complex has a staggered di-benzene-chromium in strong contrast to (**3**), which is always found as an eclipsed species. This feature results from the influence of the electrons within the cage.

The distance between both aromatic rings also varies, as in the case of dibenzene-chromium, leading to a very symmetric (D_{6h}) and regular species. The bond length is almost the same in all cases and is about 3.184 Å. In contrast, in the case of the fullerene endo complex, the average for this value measured from edge to edge is 3.459 Å (the free aromatic ring is slightly sloping). This result is obviously the consequence of the distortion of the $Cr(C_6H_6)$ unit, but likewise it is important to consider that the top of the di-benzene-chromium that comes from the cage is distorted, due to the intrinsic curvature of the fullerene. Furthermore the free aromatic ring is immersed in an electron environment, which can also cause distortions.

The exo analog was also simulated; its shape can be seen in Fig. 2b, representing an analog similar to that studied previously with a C_{60} fullerene [23]. The energy comparison between both exo and endo structures reveals that the exo form is more stable than the endo, with a difference of 37.83 kcal/mol.

The molecular orbitals (MO) scheme, corresponding to di-benzene-chromium is shown in Fig. 3 and compared with both exo and endo species, as presented in Fig. 4.

The general shape of both interaction diagrams is more or less the same; indeed neither belong to a clear point group, although the geometry of the exo complex somewhat resembles the Cs point group. However, the position has few differences, possibly because of the position of the $(C_6H_6)Cr$ moiety, but mainly because the endo is a staggered species, whereas the exo is almost an eclipsed one. There is an interesting analysis that compares the nature of the bond in ferrocene and di-benzene-chromium [33]. This study concludes from the irreducible representations involved in the frontier molecular orbitals that the bond in ferrocene is mainly π in nature, whereas the equivalent in di-benzene-chromium is predominantly δ. In the present case, serious difficulties are encountered when carrying out a similar analysis, because of the lack of symmetry of these molecules and the concomitant absence of labels in the molecular orbitals. However, a qualitative analysis, based mainly on the HOMO's shape, suggests that in both cases the nature of the bond is π. The shapes of the frontier molecular orbitals for both species are shown in Fig. 5. This same phenomenon has been noted in the description of frontier molecular orbitals of other fullerene molecules that were simulated as having bonds with η^6 hapticity [23].

The form of the HOMO and HOMO − 1 orbitals coming from di-benzene-chromium is shown in Fig. 6 and the δ nature of the bond is demonstrated. This particular behavior is caused by the interaction of the dz^2 orbital from the chromium atom and the aromatic functions from the benzene rings. The double degenerated system corresponding to the HOMO − 1 set shows however the π interaction which appears to resemble those that appear as HOMO in the