



Simulation of [2]rotaxane and [2]catenane compounds containing fullerene fragments. Influence of the fullerene moiety



Roberto Salcedo*, Olivia Monroy, Anabel Ruiz-Espinoza, Lioudmila Fomina

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n, Coyoacán, 04510 Ciudad de México, Mexico

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ABSTRACT

A direct covalent bond joins fullerene molecules to chains which form [2]rotaxane and [2]catenane molecules. The chains are directly connected to the fullerene surface by a covalent C–C bond, enabling all electronic riches from fullerenes to be shared with the chains. We carried out this simulation in two stages; the first consisted in designing the “ball and chain” molecules in order to reveal the nature of the bonds and the frontier molecular orbitals. During this stage, notoriously strong dispersion bonds are formed between the fullerene sphere and the body of the chain. During the second stage, [2]rotaxane and [2]catenane are formed. Fullerenes significantly influence the resultant compounds and we also discuss their thermodynamic stability and electronic behavior.

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1. Introduction

Catenane [1] and rotaxane [2,3] molecules are highly ordered supramolecular species in which large chains are interlocked to form linked rings in the first case or threaded trapped rods in the second. In both instances, mechanical, covalent and weak bonds are present and these sustain a complex structure. These kinds of compounds have been the object of important studies because evidently they can participate in biochemical, energy storage and catalysis procedures [4–6].

In isolation, fullerenes are discrete carbon molecules with spheroidal shape and a large number of electrons. Since their initial discovery, fullerenes (C₆₀) [7] have revolutionized the world of chemistry and are studied in a great variety of fields; including both medicine and electronics [8].

Only in a few instances have fullerenes been included in the chemistry of rotaxanes and catenanes [9–13] and in all these cases, the link between fullerene and chain appears at the lateral ring adduct of the fullerene and not on the sphere itself. This type of fullerene reaction seems to be very popular for obtaining organic derivatives [14–16].

In this instance, we simulated some [2]rotaxane molecules with fullerene as stoppers and also [2]catenane molecules containing

fullerene in their chains. A novel proposition to alter the geometry of these derivatives entailed direct bonds linking fullerene and other fragments to the sphere. This scheme provided us with several new definitions relating to the supramolecular structure of the proposed species. This study considers the following: firstly the nature of the bond fullerene-chain, secondly, the construction of the “ball and chain” molecules prior to the formation of [2]rotaxanes and [2]catenanes and finally the description of certain [2]rotaxanes and [2]catenanes formed by the interlock of the designed ball and chain species. Likewise, we analyzed the nature of the frontier molecular orbitals of all species.

2. Methods

The optimization process of all designed species was carried out in two steps. First a 100,000 steps Molecular Mechanics conformational search using Amber force field with Amber parameters set [17,18] was performed in order to achieve the global minimum, in this step the NWChem version [19] was used. After M062X and M06L methods [20,21], as implemented in the Gaussian09 package [22] were used to optimize all geometries and in all calculations, the 6-31G** basis set was used. Grimme's empirical dispersion corrections (G3) were used for evaluating the π -stacking interactions, by means of the DFT-D3 method [23]. Considering that M06 family has built on dispersion, our Grimme analysis only considers part of the large distance interactions, however those values are enough to have an interesting qualitative analysis.

* Corresponding author.

E-mail address: salcevitch@gmail.com (R. Salcedo).

3. Results and discussion

3.1. Covalent interaction between fullerene and an organic chain

Synthesis of fullerene 1,4 or 1,2 di-organo-derivatives is not commonly undertaken, however Zhou and his coworkers [24] made a very valuable contribution by taking advantage of a palladium (0) catalyst used to carry out a mono-addition reaction, selectively yielding 1,4 substituted fullerene organic derivatives. Previously, our group had theoretically studied the nature of phenyl substituted fullerenes and their intrinsic characteristics [25]. However in that work, the analyzed compounds were in all cases mono-substituted in 1,2 fashion, with respect to the associated hydrogen atom. In contrast, this study investigates the nature of di-substituted fullerene organic derivatives.

The chosen compound is the same as that prepared by Zhou [24], and we also carried out a comparison with the 1,2 isomer. The shapes of the calculated molecules (molecules **1** and **2**) are shown in Fig. 1.

We have approximated the energy values for both isomers, revealing a difference of only 3.77 kJ/mol, which accounts for a Boltzmann distribution of 78% that favors the 1,4 isomer. A first challenge is to establish the reason why the 1,2 substitution shows this difference, with two items of evidence backing up this assumption. Firstly, the short distance between both substituents gives place simply to steric factors. A calculation of the force dispersions on both isomers shows a repulsion energy of 8.5 kJ/mol in the 1,2 isomer, which is a low energy value but may be small enough for the other isomer to predominate. Molecular orbital analysis provides a further source of evidence.

The molecular orbital diagrams show accidental degenerated sets for HOMO and LUMO for the 1,4 isomer, a phenomenon which is a throwback to the pristine fullerene, considered as a parent molecule of this compound. The accidental degeneracy is four-folded for the HOMO and double-folded for the LUMO. The shapes of the frontier molecular orbitals of this species are shown in Fig. 2. Notably, almost all the functions are concentrated on the fullerene sphere, with the exception of the carbon atom coming from the substituents. This carbon atom is directly joined to the fullerene and appears in the HOMO or the LUMO. Another feature to consider as a legacy of C_{60} is the energy gap between HOMO and LUMO, which has a low value of 1.48 eV.

The 1,2 isomer can be described in a similar way, the only difference being that the joined carbon atoms from the substituents do not appear in the HOMO or the LUMO. This situation results from a strange phenomenon related to the weakness of the fuller-

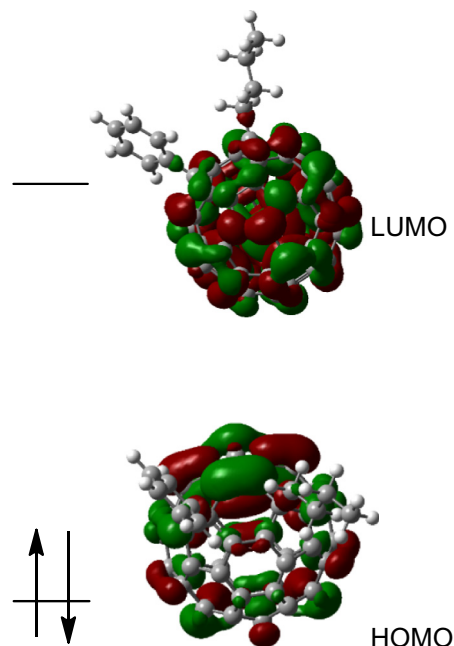


Fig. 2. Frontier molecular orbitals of the 1,4 isomer.

ene bond which supports the substituents; the bond length in this region is 1.65 Å, which is very large for a single bond. These factors may explain why the 1,4 isomer is predominant.

On the basis of these results, the lateral chains joined to the fullerene molecules in the simulated compounds have been substituted in conformation 1,4 with respect to a second chain (in the catenane cases) or an associated hydrogen atom (in the rotaxane compound) and in all cases there is a direct C–C bond; a C atom from fullerene and another C atom from the substituent.

3.2. Ball and chain molecules

Fig. 3 shows molecules **3** and **4**; the first of these has two fullerene spheres at the ends of a central chain; the idea is to simulate a [2]rotaxane, by putting a substituent on the chain, attached by a mechanical bond. Meanwhile molecule **4** has only one fullerene, which bears two chains joined to two different points at the surface of the fullerene sphere. Again, the idea is to join both chains

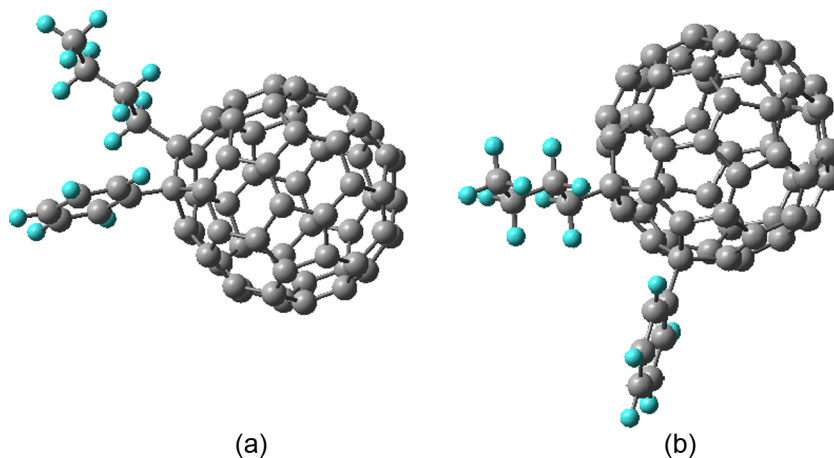


Fig. 1. (a) 2,3-1-Butyl-phenyl-[60]fullerene; (b) 1,4-1-butyl-phenyl-[60]fullerene.

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