



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



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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.

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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-

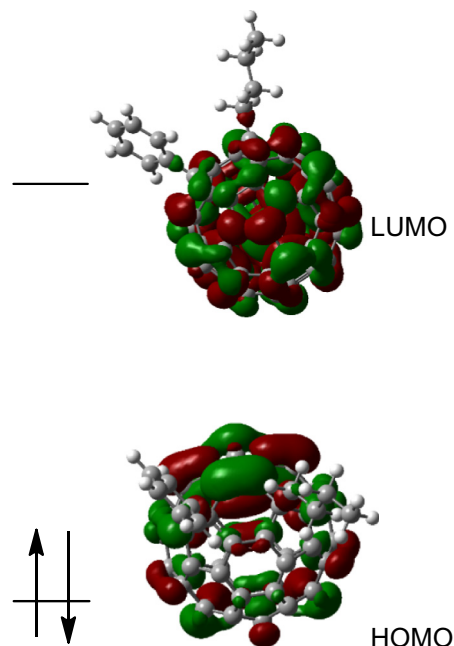


Fig. 2. Frontier molecular orbitals of the 1,4 isomer.

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

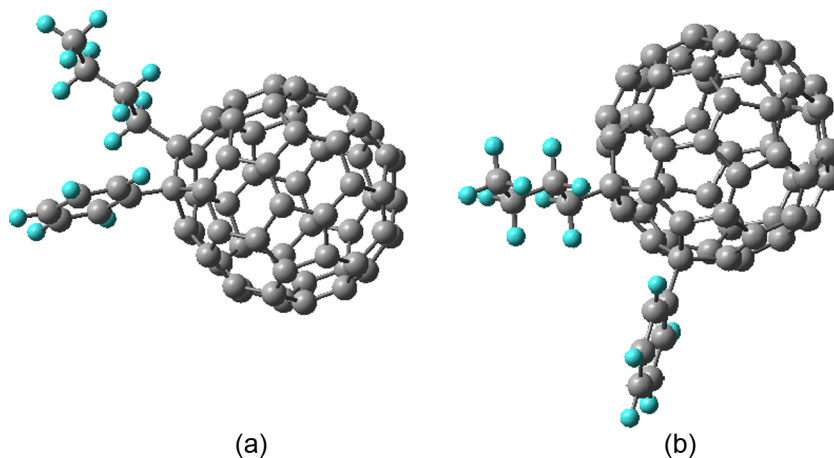


Fig. 1. (a) 2,3-1-Butyl-phenyl-[60]fullerene; (b) 1,4-1-butyl-phenyl-[60]fullerene.

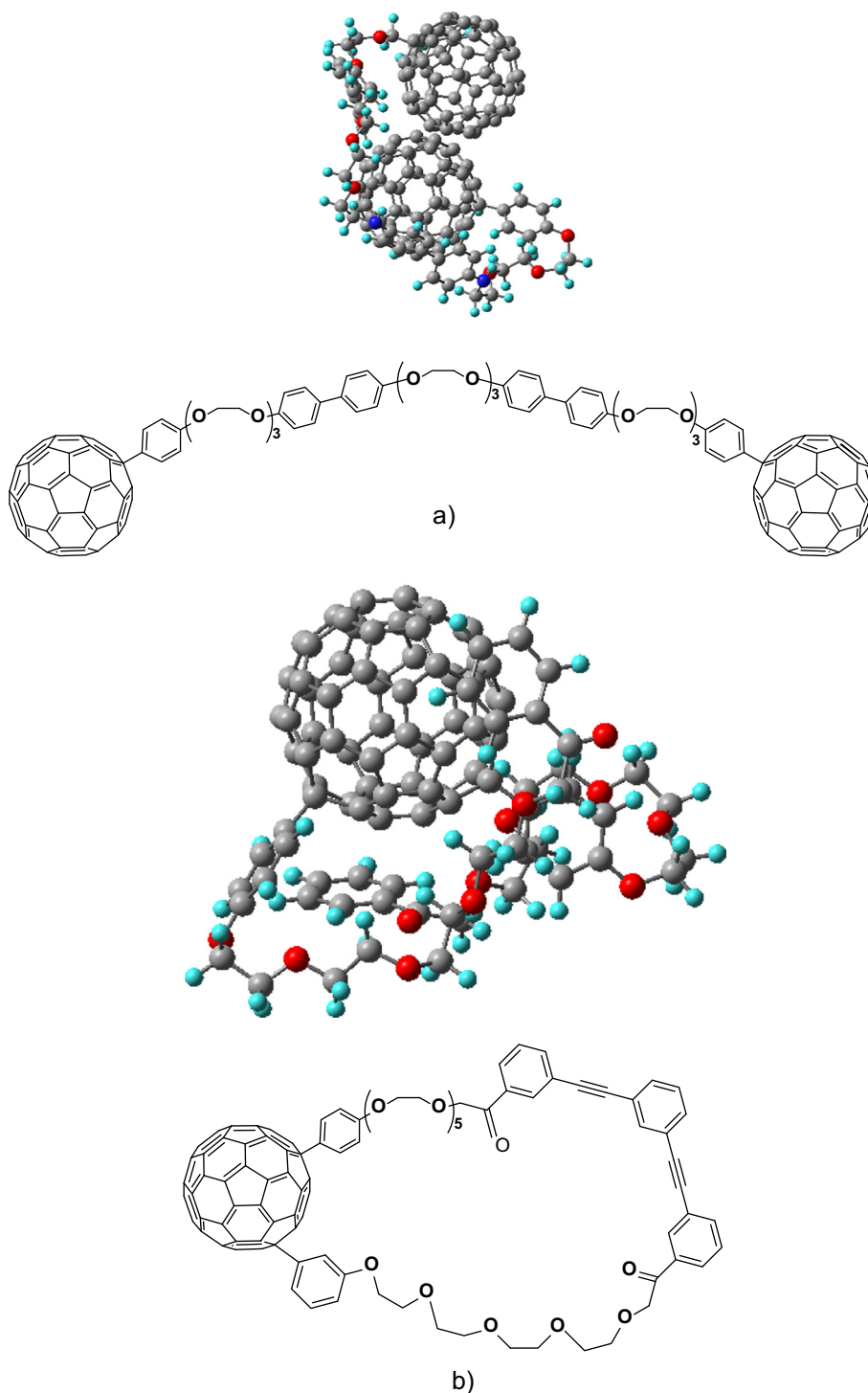


Fig. 3. “Ball and chain molecules”. (a) A chain bonded to two fullerene molecules as stoppers (**3**); (b) a chain bonded to two points on the surface of a fullerene (**4**).

in order to form a large ring with a substituent inserted into the chain.

The simulated chains are the same as those that have been used for several experimental groups [26], in each case tri-alkoxy units are joined to aniline aromatic rings and the series can grow to a defined size.

The first notable characteristic for both cases in Fig. 3 is the crooked chain. This is the fullerene joined to a single chain (**3**), which is the precursor of the rotaxane and the fullerene bearing two chains (**4**). This then gives place to the catenanes, but several attempts revealed it was impossible to attain a linear conformation

for compound **3** or an extended shape for compound **4**. The reason is that fullerene attracts the aromatic rings of the chains, resulting in a kind of π -stacking bond. This feature results in a very congested arrangement, in which an aromatic ring from the chain adopts a conformation that is almost parallel to a six-membered ring at the surface of the fullerene. The average distances between both rings is 3.5 Å and the energy contribution calculated using the dispersion forces model is 11.5 kJ/mol for each interaction. All these values concur well with others reported previously [27].

This feature is corroborated by the molecular orbitals analysis of compound **3**, where again there is an accidental degeneration

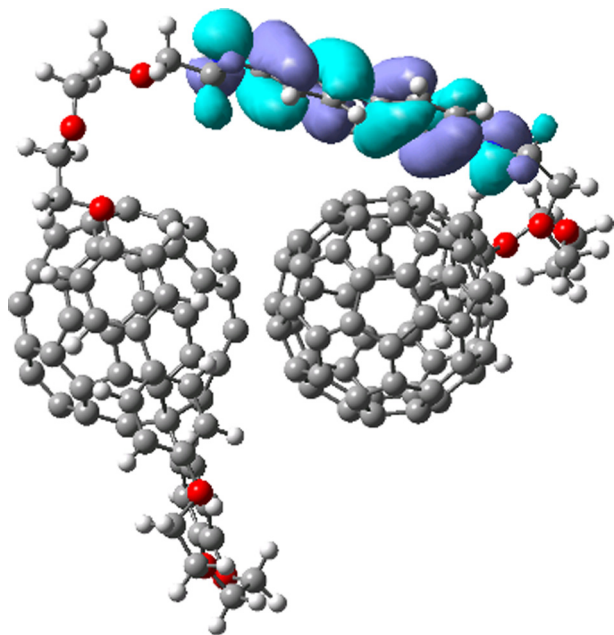


Fig. 4. HOMO of compound 3.

on the LUMO caused by the large symmetry of C_{60} . However the HOMO is a single non-degenerated orbital and is located on the chain, in the precise region where π -stacking occurs. Considering that the LUMO belongs completely to the fullerene and that the energy gap is 3.55 eV, some kind of electronic flow between the chain and the fullerene may exist. Another conspicuous aspect is that HOMO-1 is an accidental degenerated four-folded orbital, whose effect on the fullerenes is totally focused and has a separation of 0.78 eV with respect to the HOMO. It may also function as a source of electrons. The shape of the HOMO is shown in Fig. 4.

The molecular orbital analysis of molecule 4 is something different because the double substitution results in greater lack of

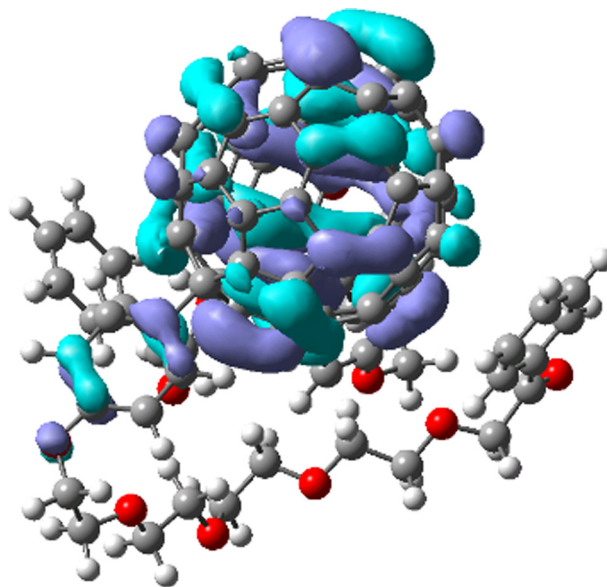


Fig. 5. HOMO-1 from compound 4, showing the interaction between fullerene and the chain

symmetry. This means there is little accidental degeneration and the HOMO and LUMO show functions related to the fullerene fragment. The energy gap between these two is 2.32 eV and the contribution coming from the lateral chains is found at HOMO-1 function, indicating the same phenomenon of electron transit but in a different pathway. The shape of HOMO-1 is illustrated in Fig. 5.

3.3. The [2]rotaxane

Once the precedents of the supramolecular species have been designed, the analysis of the rotaxane and catenane species is achieved. There is an excellent review about molecules containing

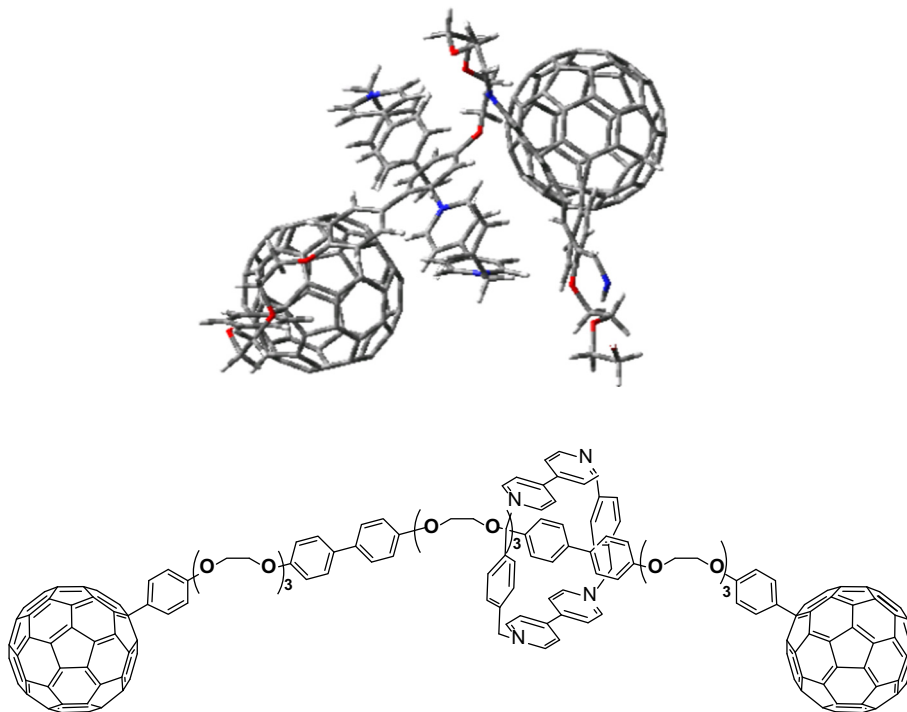


Fig. 6. The designed [2]rotaxane (6).

fullerene and rotaxanes or catenanes [28], the compounds studied here shows very different bonds and properties and the only relation with those shown in that document is the nature of the fragments which conforms the molecules. The physical properties predicted by these simulations are also different.

There are several theoretical reports in which [2]rotaxanes are involved and the theoretical tools have demonstrated to be very useful to study them [29,30]. The shape of the [2]rotaxane molecule (5) is shown in Fig. 6; the chain adopts a very different conformation because in this instance, an organic link forms a mechanical bond with it. This link is the bis pyridylpyridinium tetra-ion, which has also been used in several rotaxane or catenane molecules [9,31]. Notably, the π - π stacking interaction between the chain and the fullerene found in the ball and chain compound is not present in this derivative. The immediate consequence is that the ball and chain species becomes 117.2 kJ/mol more stable than the [2]rotaxane. Other important differences are outlined below.

The molecular orbital analysis of rotaxane is presented in Fig. 7. The LUMO pertains completely to the bis pyridylpyridinium tetra-ion, whereas the HOMO in itself comprises a very large combination of ten orbitals, indicating an accidental degenerated state and producing a mostly metallic bond. Interestingly, the energy gap in this system is 1.27 eV and the nature of the frontier molecular orbitals indicates it is a semiconductor species, in which the electrons come from the ball and chain fragment to the bis pyridylpyridinium tetra-ion, by means of the mechanical bond.

It is important to emphasize the influence of fullerene on both species, i.e. both the ball and chain and the rotaxane. In the first case, there is a tendency for the fullerene to trap the chain by means of weak non-covalent bonds, after this the formation of the [2]rotaxane gives place to the rupture of these weak bonds and the presence of renewed electronic flow, which involves the spheres, the chain and possibly also the mechanical bond.

3.4. The catenanes

Theoretical studies involving catenanes are arising in these days [32,33]. Two different [2]catenane-like species are obtained in this study. The reason is that different procedures can be used to form the mechanical bond between the two conformational chains of these species. The first one shows a similar shape to that from the [2]rotaxane in this study, which is a fullerene with a crown ether chain, but in this case the chain has two bonds on the fullerene surface, and the catenane is formed with the inclusion of the bis pyridylpyridinium link (see Fig. 8).

There is a very strong energetic difference between the [2]catenane and their separated links, and in this case the latter predom-

inates. The addition of the corresponding energy values from the ball and chain species and the lone bis pyridylpyridinium ion makes these 113.78 kJ/mol more stable than the catenane itself. This phenomenon results from the fact that intramolecular interactions take place in the ball and chain species, and these cease when [2]catenane is formed.

The molecular orbital analysis of this compound manifests typical semiconductor behavior or may act as quite an effective conductor in practical terms. The energy gap between its frontier molecular orbitals is 0.61 eV. Both HOMO and LUMO are single

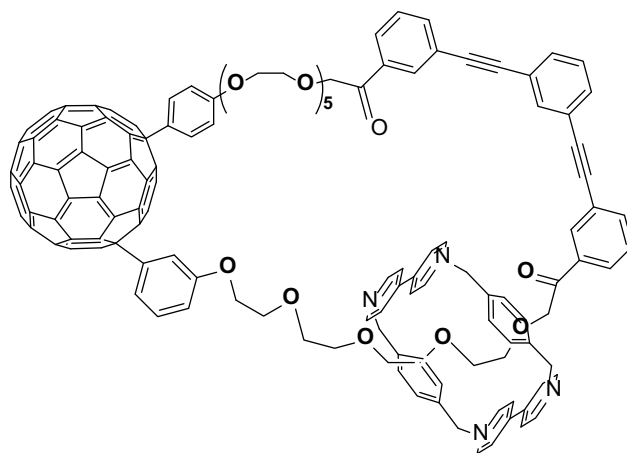
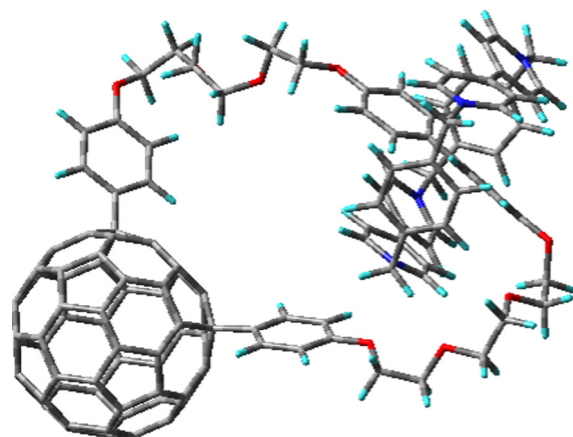


Fig. 8. The designed [2]catenane molecule (6).

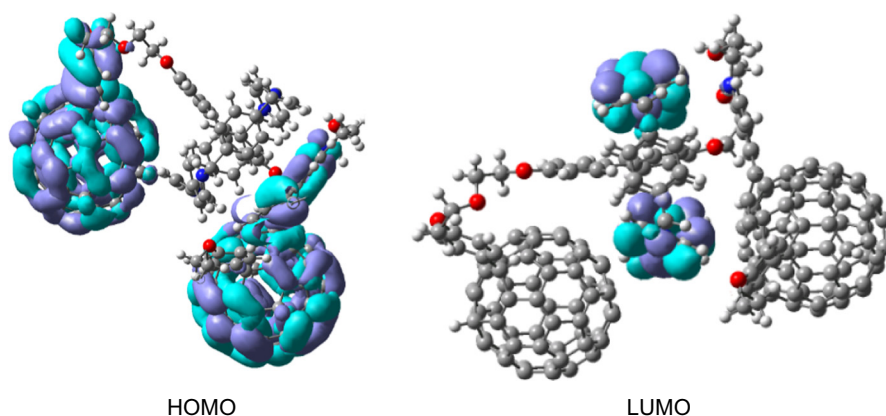


Fig. 7. Frontier molecular orbitals of molecule 5.

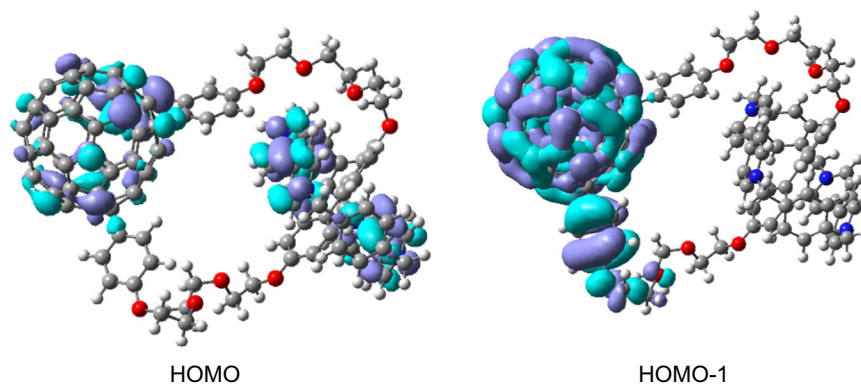


Fig. 9. Selected molecular orbitals of the [2]catenane 6.

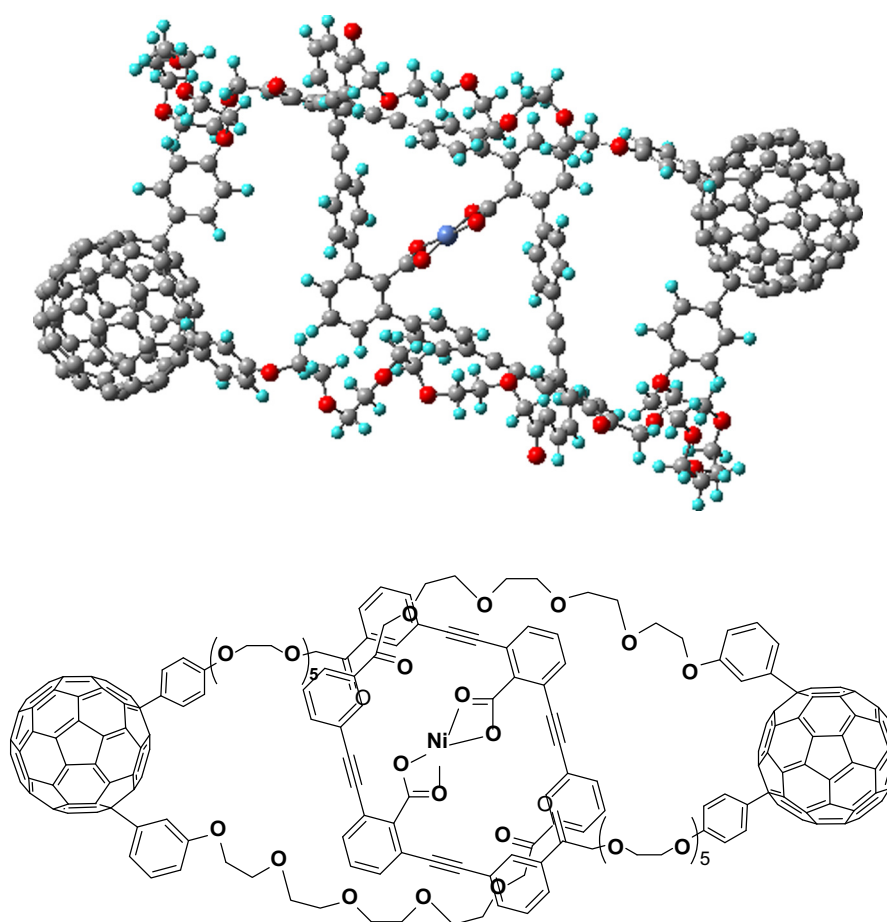


Fig. 10. [2]Catenano with a coordinated Ni ion (7).

molecular orbitals and both are centered on the fullerene and the bis pyridylpyridinium ion. Meanwhile HOMO-1 function is an accidental five-fold degenerated species, which involves the fullerene and the chain (see Fig. 9. The energy difference between this set and the HOMO is 1.88 eV).

The design of the second [2]catenano (7) is inspired by those compounds prepared by Sauvage and Weiss [34,35]. In this case, the interlocked rings are joined to a metal ion by phenantroline or acetyl type ligands. Some differences are apparent when synthesized compounds are considered; firstly in the present case, the metal is nickel instead of copper and obviously the chains in these

are closed by fullerene fragments. The coordinated ligands are acetyl bonded to a Ni(II) ion.

The shape of molecule 7 is shown in Fig. 10, where the first interesting feature is that the central metal atom and its environment form a square planar complex, as would be expected for a d^8 metal ion. However, notoriously the square is perfect with an angle of 179.98° and several attempts to obtain the tetrahedral isomer have produced only unstable and fragile structures (see Fig. 11).

Molecular orbital analysis reveals other typical semiconductor species, with an energy gap between HOMO and LUMO of

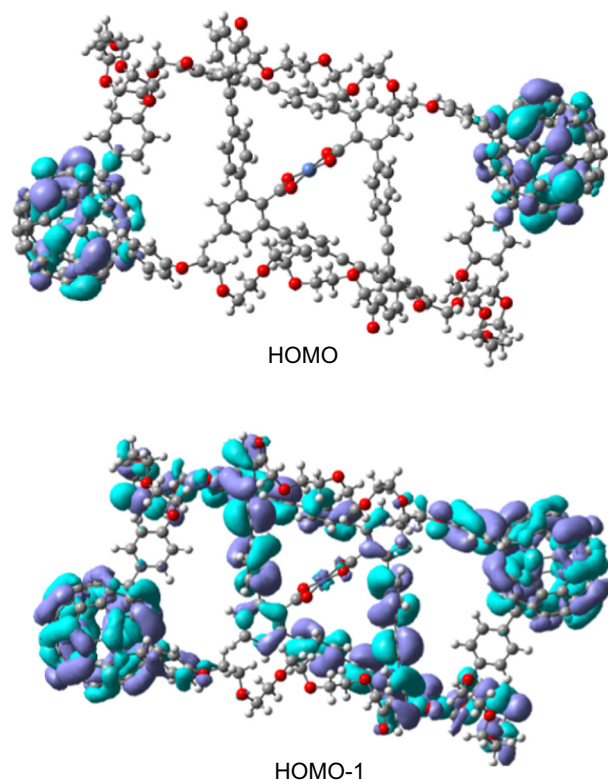


Fig. 11. Selected orbitals of [2]catenane 7.

1.07 eV and with both frontier molecular orbitals centered completely on the fullerene ends. However the HOMO-1 function is again an accidental quasi-degenerated set which covers the fullerenes as well as the chains and even involves little participation of the metal ion. This orbital is only separated from the HOMO by 0.82 eV, so this compound should also display interesting electronic behavior.

4. Conclusions

We propose new rotaxane and catenane substances which will contain fullerene fragments. The bond between fullerene and the organic chains of the designed species is joined directly to the sphere in all cases. The ball and chain species, i.e. the molecules without the bis pyridylpyridinium ion, tend to form non-covalent bonds, providing great stability. The fullerene in rotaxane functions as a stopper and as the support of the chains in the catenanes, however its electron riches cause modification to characteristics in the proposed substances. In all the cases is found typical semiconductor behavior.

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