Ab initio simulation of the effects of substitutional doping of oxygen in the semifullerene (C$_{30}$)

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Abstract. Using first principles calculations, we studied the effects of substitutionally doping a 30-atom semifullerene (C$_{30}$) with oxygen atoms, within the Density Functional Theory (DFT) and the pseudopotential formalism. We analyzed two C$_{30}$ structures, one with a pentagonal and one with a hexagonal base. In both cases, the substitutionally absorbed oxygen atoms break the bonds between pentagons and hexagons of the semifullerene. We show that each semifullerene breaks into two geometrically flat structures, one of them being consistent with a known ring isomer of the fullerene C$_{20}$. We used the Quantum ESPRESSO package code and the generalized gradient corrected Perdew-Burke-Ernzerhof (PBE) approximation for the exchange and correlation functional.

1. Introduction
Since their discovery, fullerenes have shown interesting physical and chemical properties [1]. Many studies have focused on their geometry, energetic stability, spectra, and interactions with other molecules. But theoretical and experimental investigations of fullerene molecules can be quite challenging, due in part to the large number of fullerene geometrical isomers. Hence, it is important to fully understand the factors determining the structures and stabilities of smaller carbon clusters [2-4]. Differences in geometry and topology between various fullerene isomers can lead to great differences in their chemical and physical properties [5-6]. For example, fullerene C$_{20}$, –the smallest possible– has three isomers: cage, bowl and ring, with different properties [4].

In this work, we used DFT calculations to study a proposed heterofullerene compound [7] that includes oxygen atoms. We started with the C$_{30}$ semifullerene, which results from the splitting in half of a C$_{60}$ fullerene. After a structural relaxation of the pentagonal-based semifullerene (figure 1a), the bond length between a pentagon and a hexagon, labeled as (5,6), is equal to 1.425 Å. The bond length between two adjacent hexagons, labeled as (6,6), is 1.360 Å. Structural relaxation of the hexagonal-based semifullerene (figure 1b) results in a different structure consisting of four rectangle-shaped rings, in addition to the pentagons and hexagons already present. The bond length between a pentagon and a rectangle, labeled (5,4), is 1.540 Å, while the bond length between a hexagon and a rectangle, labeled (6,4), is 1.375 Å.
We also found for this second structure, that the bond length between two hexagons (6,6) and the bond length between one pentagon and one hexagon (5,6), were 1.436 Å and 1.485 Å respectively. All the former are average values over the set of available bonds. The experimental average values are 1.391 Å for the (6,6) and 1.455 Å for the (5,6) bond lengths [8].

Figure 1. YZ-plane views of the final configurations of (a) the pentagonal-based and (b) the hexagonal-based C$_{30}$ semifullerene, after a structural relaxation. The figure shows the bonds between pentagons and hexagons (left), and between pentagons, hexagons and rectangles (right).

2. Computational methods
Self-consistent field calculations were used in this study, based on the Density Functional Theory (DFT) [9, 10] and using the pseudopotential formalism. The Quantum Espresso code was used [11]. This package considers a plane-wave expansion for the electronic wave functions, and periodic boundary conditions. For the carbon and oxygen atoms, we used Martin-Troulliers norm-conserving pseudopotentials [12]. The Perdew-Burke-Ernzerhof (PBE-GGA) exchange and correlation functional was used [13]. The following valence electronic states were considered: for carbon C, $2s^2 2p^2$ and for oxygen O, $2s^2 2p^4$.

The Monkhorst-Pack [13] scheme for k-point sampling was used for integration over the first Brillouin zone. The Kohn-Sham energy functional was directly minimized using the conjugate gradient method. For the k-point sampling, a $4 \times 4 \times 4$ grid was used, as well as a cut-off energy for the plane-wave set of 80 Ry ($\approx$1100 eV). The convergence threshold for the energy was $1.2 \times 10^{-5}$ eV. Previous studies [14], lead us to use non-relativistic, non-polarized spin calculations, as they produce reliable results for this type of carbon-based materials. For crystal visualization purposes, we used the XCrySDen package [15].

3. Results and discussion
3.1. Semifullerene bowl with a pentagonal base
We considered the pentagonal-based semifullerene of 30 carbon atoms. This corannulene-like structure forms part of the C$_{60}$ cage [3]. We first doped it substitutionally with five oxygen atoms, symmetrically placed around the carbon atoms forming the pentagonal base (see figure 2). After a structural relaxation of the system, we found that it splits into two separate systems. One of those new systems could be identified as the ring isomer of the fullerene C$_{20}$. 
Figure 2. Structural relaxation of the semifullerene (pentagonal base) substitutionally doped with five oxygens. The figure shows the initial and final configurations as well as a plot of the difference in the total energy of the system, taking the final value as the reference. The semifullerene breaks up in two separate systems.

Figure 3. a) XY-plane view of the initial configuration of the semifullerene C30 substitutionally decorated with five oxygen atoms. b) XY-plane view of the final configuration of the system, after a structural relaxation is performed.

The planes of the two structures obtained after the relaxation (figure 3) are essentially parallel and separated by 2.85 Å. The bond lengths of the C$_{20}$ ring obtained, range between 1.27 Å and 1.29 Å.

3.2. Semi-fullerene bowl with a hexagonal base
The second case considered was the system with a hexagonal base. This sumanene-like structure forms part of the C$_{60}$ cage as well [16]. We doped it substitutionally with 9 oxygen atoms as shown in figure 1.
After being geometrically optimized, the structure breaks up again into two systems, one of which is a ring formed by 9 carbons (figure 5).

![Figure 4](image_url)  
**Figure 4.** Structural relaxation of the semifullerene (hexagonal base) substitutionally doped with nine oxygens. The semifullerene breaks up into two systems as well.

![Figure 5](image_url)  
**Figure 5.** a) XY-plane view of the initial configuration of the hexagonal-based semifullerene C\textsubscript{30}. b) XY-plane view of the final configuration of the semifullerene C\textsubscript{30}.

The two structures obtained are separated by 3.80 Å (figure 5). As in the previous case, their planes are parallel and here the bond lengths of the smaller ring, composed of nine carbon atoms, range between 1.28 Å and 1.33 Å.

The results obtained in this work, particularly for the C\textsubscript{20} isomer structure, are consistent with previous studies [17, 18]. These types of small carbon clusters are also potential candidates for carbon-based superconductors [19].
4. Conclusions

In this work we studied the effects that substitutional oxygen atoms can have in the structure of two different C$_{30}$ semifullerene isomers. In the two cases considered (pentagonal and hexagonal bases) the structural relaxation shows that the oxygen atoms catalyze the splitting of the system into two parts. In the case of the pentagonal-based semifullerene, a C$_{20}$ ring, which is a known semifullerene isomer, is found.

This process could hence be found to be a way of obtaining C$_{20}$ isomers.

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