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Inclusions of Si-atoms in Graphene nanostructures: a computational study on the ground-state electronic properties of Coronene and Ovalene

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Abstract. We present a computational study on graphene nanostructures, focusing our attention on Coronene ($C_{24}H_{12}$) and Ovalene ($C_{32}H_{14}$) molecules and their Si-atoms substituted counterparts. We used density functional theory to quantify the effects of the chemical modifications. For all the modified geometries (with single silicon atoms, dimers and trimers) we record an increase of the energy stability. Concerning the structural properties, the effect caused by Si-trimers is, in some configurations, for both the molecules under study, a deformation of the original structure associated with a loss of the flatness, typical of the pure systems.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) in their crystalline and thin-film state are widely used as active elements in several opto-electronic devices, such as organic thin-film field-effect transistors, light-emitting diodes, photovoltaic cells, and liquid crystals [1]. Among them, the Circumacenes (Coronene, Ovalene, Circumanthracene, Circumtetracene, and Circumpentacene) have recently attracted attention [2, 3]. Coronene is made by the union of six benzene rings (with chemical formula $C_{24}H_{12}$), while Ovalene ($C_{32}H_{14}$) is obtained from Coronene by the addition of three benzene rings. The first one occurs naturally as the very rare mineral Carpathite, which is characterized by flakes of pure Coronene embedded in sedimentary rock and it can be tractable through hydrocracking processes [4]; the latter is a reddish-orange compound that can be synthesized, as Coronene, via the hydrocracking process of petroleum refining.

When compared with polymers, small molecules offer several advantages, such as the possibility to be easily purified by various techniques and processed both by evaporation and from solution [5, 6]. These molecules are here considered for their interesting properties: they are the smallest in size among the Circumacenes, but they qualify as nanometric systems and they are moreover characterized by a symmetric structure with a planar geometry.

These systems are of strong interest both for fundamental research (e.g. in astrochemistry and in condensed matter) and for solid state applications. Our choice to deal with this set of PAHs is mainly justifiable by the following reasons: (i) they present both a rigid backbone and an energy gap of moderate size rapidly converging with the size of the molecule [7]; (ii) their molecular packing in thin films might extremely differ from the classical herringbone structure found for the corresponding (oligo)acenes and thus might provide more efficient pathways for charge transport;



and (iii) the synthesis of Circumanthracene [8] as well as other versatile related molecules [9] has been successfully reported in the literature. Hence, these low-dimensional carbon structures could be considered as promising candidates for new emergent technologies [10].

The aim of this work consists in the study of the effects that silicon-atoms substitutions induce in Coronene and in Ovalene molecules with respect to their ground-state properties. This work follows other previous studies related to inclusion of Si atoms in Graphene [11, 12]. We consider initially one atom substitutions, double atoms substitutions (dimers) and triple substitutions (trimers) of Si, analyzing their effects on the morphological and electronic properties, using the Density Functional Theory (DFT)[13]. We will compare our results with existing data after previous theoretical and experimental works and concerning the ground-state electronic properties we will try to find possible trends.

2. Computational Methods

Following previous studies [2, 3], we performed geometry optimizations using the hybrid exchange-correlation functional B3LYP [14, 15, 16], in combination with the $6-31G^*$ basis-set, a valence double- ζ set augmented with d polarization functions for each atom. We used the B3LYP XC potential, since with respect to other possible choices (e.g. the PBE (Perdew-Burke-Ernzerhof)[17]), it has been proved to reproduce for different families of PAHs molecules better results, either for ground-state and the excited one [2, 18, 19, 20]. All the molecular relaxations have been performed without symmetry constraints. Geometry optimizations were obtained using tight convergence criteria, specified by maximum and root mean square gradient thresholds of $1.5 \cdot 10^{-5}$ and $1.0 \cdot 10^{-5}$ atomic units, respectively, and maximum and root mean square thresholds of the Cartesian step respectively of $6.0 \cdot 10^{-5}$ and $4.0 \cdot 10^{-5}$ atomic units. We employed NWChem [21], that is an all-electron gaussian-based computational package, to evaluate the general properties of Coronene and Ovalene substitutional clusters. The code is based on a numerical resolution of the Khon-Sham equations after a DFT Hamiltonian [13]. The exchange and correlation effects are treated using a particular functional entering in the Hamiltonian after the B3LYP scheme [14, 15, 16].

3. Si-atoms Insertions

According to the molecular symmetries, the possible non-equivalent insertions of silicon atoms are the following (see Fig. 1):

- 6 (9) configurations after single Si atom substitutions in Coronene (Ovalene);
- 4 (9) configurations after Si-dimer substitutions in Coronene (Ovalene);
- 4 (10) configurations after Si-trimer substitutions in Coronene (Ovalene).

We have found that, in the case of Coronene, the configurations number is reduced from 6 to 3, because of the equivalence between A-F, B-E and C-D atoms. On the other hand, considering the Ovalene structure, the addition of three benzene rings increases the possible configurations, entailing a gradual loss of the molecular symmetry. The configurations of substituted species were found to preserve the planar geometry of their parent molecules, after single and double Si-atoms inclusions. On the contrary, for both Coronene and Ovalene, the insertion of a trimer, in some case, breaks their planar symmetry (see fig. 3). This effect appears to be more pronounced for Ovalene than for Coronene as shown by the variation in interatomic distances connecting Si-C atoms. On the contrary, we verified that single and dimer substitutions, as for Coronene and Ovalene, preserve the flatness typical of the original systems: the deformations are planar and only localized.

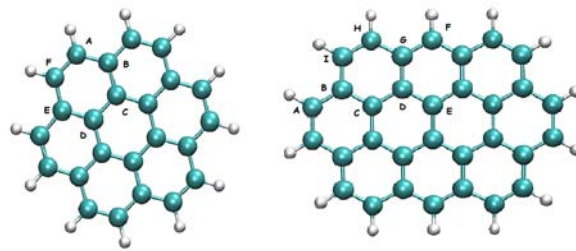


Figure 1. Coronene and Ovalene molecules. The Carbon atoms selected to be replaced by Silicon atoms are indicated by letters from A to F for Coronene (left), while from A to I for Ovalene (right). Dimers and trimers will be composed by the union of the adjacent single ones.

Table 1. Unsubstituted-systems ground-state total energies (E_0^n) and ground-state total energy differences $E_0^s - E_0^n$ (see equation 1). The percentage deviation Δ is also reported.

	Total Energy Differences (keV)	Δ (%)
Coronene	($E_0^n = -25.1$)	–
single-substitution	-6.837	27.3
dimer-substitution	-14.678	58.5
trimer-substitution	-20.518	81.2
Ovalene	($E_0^n = -33.4$)	–
single-substitution	-6.838	20.5
dimer-substitution	-13.678	40.9
trimer-substitution	-20.518	61.4

4. Ground-state Total Energies

Tab. 1 reports the computed data of the ground-state energy (E_0^n) for Coronene and Ovalene pure neutral systems and their substituted counterparts. In particular, the first column shows the energy differences between the original molecules and each substituted one. Because of the large configurations number, we have selected for each insertion (single, double and trimer) the most energetically stable structure among all the possibilities, to make a comparison with its corresponding pure parent. This comparison can be evaluated calculating the percentage change (Δ) passing from the pure system to the substituted one for each type of insertion, namely:

$$\Delta = \frac{E_0^s - E_0^n}{E_0^n} \quad (1)$$

where E_0^s and E_0^n are respectively the ground-state total energies for the substituted system and the unsubstituted one. We note that, from the energetic point of view, all Ovalene configurations show deeper energies than those of Coronene (that is an increase, in absolute value, of the ground-state total energy, E_0^n) and this is a consequence of the increase in the number of electrons, while the (Δ) variations are lower than in the case of Coronene. In particular, the most energetically favourable configurations are, for Coronene (Ovalene) the following ones: the single substitution corresponding to the insertion indicated by letter C (H); for the double substitution, the dimer composed by letter A-F (H-I); for the triple insertion, the trimer consisting of F-A-B (H-I-B). In general, the energy stability tends to decrease from the external to the inner molecular region:



Figure 2. Coronene (a, c) and Ovalene (b, d) with single Si-atom inclusions and Si-dimers ones.

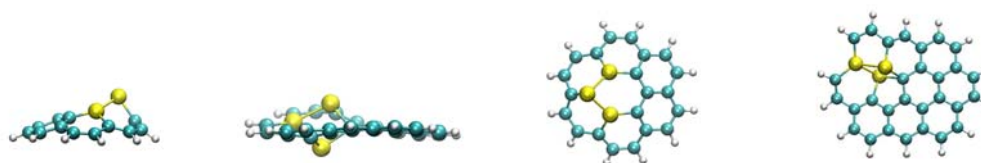


Figure 3. Coronene (a,c) and Ovalene (b,d) with a Si-trimer substitution placed in an internal molecular region.

this means that, in general, the most stable configurations are those in which the substitutional site is placed in the peripheral molecular areas, rather than in the inner part of the molecules (the only exception is the single substituted Coronene).

5. Morphological Properties

In this section we select an example for each species to show the effects induced on the structural properties by the Si-atoms insertions and what are the consequences as a function of the numbers of C-atoms replaced. In particular, we focus our attention on the trimer substitution for both the molecules. In fact, this modified configuration largely loses the flatness typical of the pure Circumacenes (see fig. 3). For Coronene, we selected the configuration in which the trimer substitution is made on the central ring (corresponding Si atoms are represented in yellow and indicated by numbers 1,2,3). For Ovalene the modified trimer is composed by the atoms labeled by B, C, D. Interatomic bond lengths are shown in Table 2, where Si-C, Si-Si, C-C atomic distances are reported for these two specific configurations, labeling the selected atoms as indicated by fig. 4. Also the percentage changes of interatomic distance between C-C atoms that compose the parent molecules are shown (the medium value of C-C bond length for the unsubstituted compounds ($C - C_{\text{unp}}$) is 1.43 \AA). We analyzed quantitatively how the distances in the ring in which Silicon atoms are inserted have been modified in comparison to the original structures. In the case of trimer substitutions, it is possible to see that the distortions are consistent and they concern the global structure, that loses noticeably its planar appearance. On the contrary, in the case of some single and double substitutions, after the present calculations, minor deformations of the rigid structure take place, but in general, for both Coronene and Ovalene, the deformations are only local and they determine a change of the interatomic bond lengths, without any loss of planar feature.

Table 2. Interatomic bond lengths between C-Si, Si-Si and C-C atoms for the two selected substituted molecules with a trimer. The percentage changes (Δ) with respect to the C-C unperturbed distance ($C - C_{\text{unp}}$) are also shown.

Coronene	\AA	$\Delta(\%)$	Ovalene	\AA	$\Delta(\%)$
$C - C_{\text{unp}}$	1.43	—	$C - C_{\text{unp}}$	1.43	—
$C^1 - \text{Si}^1$	1.78	19.7	$C^1 - \text{Si}^{\text{B}}$	1.84	22.3
$C^2 - \text{Si}^1$	1.80	25.9	$C^2 - \text{Si}^{\text{B}}$	1.84	22.3
$C^5 - \text{Si}^2$	1.92	25.5	$C^4 - \text{Si}^{\text{D}}$	1.92	25.5
$C^6 - \text{Si}^3$	1.80	25.9	$C^6 - \text{Si}^{\text{C}}$	1.92	25.5
$C^4 - \text{Si}^3$	1.78	19.7	$C^5 - \text{Si}^{\text{D}}$	2.04	29.9
$\text{Si}^1 - \text{Si}^2$	2.22	35.6	$\text{Si}^{\text{B}} - \text{Si}^{\text{C}}$	2.68	46.6
$\text{Si}^2 - \text{Si}^3$	2.22	35.6	$\text{Si}^{\text{B}} - \text{Si}^{\text{D}}$	2.69	46.8
$C^2 - C^3$	1.45	1.37	$C^2 - C^3$	1.37	-4
$C^3 - C^6$	1.45	1.37	$C^3 - C^4$	1.45	1.38
			$C^4 - C^7$	1.37	-4

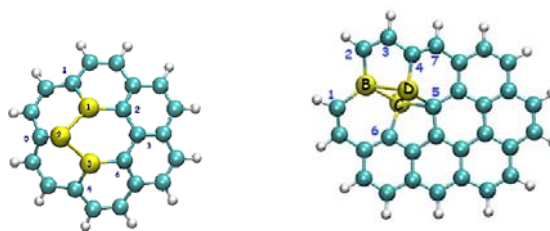


Figure 4. Coronene (a) and Ovalene (b) with a Si-trimer substitution in which Si and C atoms are labeled by letters and numbers, as reported in Table 2.

In particular, modifications imply that for Coronene the percentage change of the C-Si bond with respect to the corresponding C-C bond of the unsubstituted system goes from $\sim 20\%$ to 26% . Likewise, a similar situation is recorded for Ovalene, where the percentage change of the C-Si bond in comparison with the C-C one results between the range of $22\% - 30\%$. Moreover, the distance connecting two silicon atoms (Si-Si bond) is larger in the case of Ovalene (with an increase of about $\sim 47\%$ compared to the C-C bond) if compared to that of Coronene ($\sim 36\%$), confirming a greater deformation induced by the insertion in Ovalene molecule. On the contrary, the length of the C-C bond, in the case $C^2 - C^3$ and $C^4 - C^7$, in the substituted Ovalene is subjected to a reduction of about $\sim 4\%$ compared to the pure geometry, while for Coronene the C-C bond for $C^2 - C^3$ and $C^3 - C^6$ show a negligible variation of about $\sim 1.4\%$. This effect proves that the chemical modification implies different results depending on the position in which it has been made as well as on the system under study. After the here presented results for Si-atoms insertions the here considered isolated molecules seem to offer a different scenario in comparison to the infinite Graphene sheet [11, 12]. This point therefore deserves additional focused experimental studies associated with other theoretical ones to be fully understood.

Conclusions

We presented a systematic comparative study of Coronene and Ovalene in their unsubstituted and substituted forms, with Silicon single atoms, dimers and trimers insertions. In the

framework of DFT calculations, we found larger values of ground-state energies compared to the original structures, in both Coronene and Ovalene molecules as a consequence of the chemical modification.

Dealing with morphological properties, we observed that some trimer insertions (as for Coronene and Ovalene) are the substitutions which deform consistently the molecule in the out-of-plane directions. Other calculations, performed with different substitutional sites, have shown different behaviours in terms of out-of-plane distortions: for example, some peripheral substitutions did not present this effect. We expect that as the number of Si atoms substituted increases, there would be larger or morphologically different molecular distortions. The present systematic quantitative evaluation of the effect of Si-atoms substitutions on the structural properties of the two first members of the Circumacenes can be considered the preliminar step for future studies on the electronic (ground and excited) states and the optical properties of these systems.

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