

Opto-Electronic properties of BN-ring insertions in Circumacenes: the case of Coronene and Ovalene

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Abstract. We report a comparative computational analysis on the electronic and optical properties of some emblematic carbonaceous planar molecules after BN substitutions. In particular, we focused on Coronene ($C_{24}H_{12}$) and Ovalene ($C_{32}H_{14}$) molecules (belonging to the Circumacenes family) after different hexagonal-Boron-Nitride-ring insertions. We have performed all-electrons Density Functional Theory and Time Dependent DFT calculations using a localized Gaussian basis-set combined with the hybrid exchange-correlation functional B3LYP. For all the systems, we calculate the main molecular electronic and optical properties and we discuss if the mixed C-BN-ring-substituted clusters could be a potential attractive alternative or integration with respect to their C-made compounds, for both fundamental and application research.

1. Introduction

Not so long, the class of Polycyclic Aromatic Hydrocarbons (PAHs) has stimulated a considerable attention in optoelectronics, covering a significant position, from fundamental physics research to the development of several applications. These small molecules, in fact, are usually employed as active elements in many optoelectronic devices (from light-emitting diodes (LEDs) and photovoltaic cells to liquid crystals and organic thin-film field-effect transistors [1]). Among these compounds, we selected the Circumacenes¹, since they possess attractive novel properties [2, 3]. Moreover, these symmetric and planar molecules can be considered as finite portions (with a nanometric size) of Graphene, their infinite counterpart [4]. The success of Graphene and C-based material research has stoked a deep interest in the investigation of other 2D nanomaterials such as, the 2D Nitrides class (GaN, AlN, InN, TiN..) and the 2D Boron-Nitride (BN) compounds [5, 6].

The BN compound is formed by the union of B and N atoms in the same percentage and has various crystalline forms, isoelectronic with respect to the elementary C-made structure, among which the cubic form (*c*-BN) which is the counterpart of diamond and the hexagonal form (*h*-BN) analogous of the C-made graphite [7]. Furthermore, actually, the BN compound is well-known to be one of the most resistant materials among those existing from both the thermal and chemical points-of-view [7]. Despite of the structural similarities between the two species, many differences characterize the BN-made compounds with respect to the C-based

¹ Coronene, Ovalene, Circumanthracene, Circumtetracene, and Circumpentacene are the first five members of the Circumacenes family.

ones, especially from a physical-chemical point of view. These divergences are mostly due to the different nature of the chemical bonds involved and imply different properties for the two materials (for example, while graphite is a conductive semimetal, *h*-BN is an insulator). 2D BN-based nanostructures are believed to be promising candidates for many forefront applications and devices: in microelectronics, as wear-resistant lubricants for vacuum technology and x-ray lithography masks, as deep UV LED for graphene-engineering [10] and finally also in the biomedical field [8, 9]. Moreover, interesting experimental works, after theoretical predictions, have been reported for the successful synthesis of hetero-junctions between *h*-BN domains and Graphene. These experimental results address attention to the possibility of the design and fabrication of different hybrid systems with interesting electronic and transport properties [11, 12].

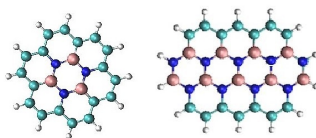


Figure 1. Coronene (left) and Ovalene (right) in their BN-ring substituted forms (ring (R) and stripe (S), respectively). C atoms are indicated in light-blue, H in white, N in blue and B in pink.

In what follows we propose a comparative computational analysis on the electronic and optical properties of these BN-substituted molecules thanks to their interesting properties for potential applications in solid-state physics domain [13, 14, 15]. In particular, we pay our attention on the first two members of the Circumacenes (see Fig. 1), after two different BN-rings insertions: namely, BN-ring substitution of the central core (R, which consists of 1 ring for Coronene and 2 rings for Ovalene) and by BN-stripe (S, which consists of 3 adjacent rings for Coronene and 4 adjacent rings for Ovalene). This new form of BN/C-hybrid materials could be useful in bandgap-engineering applications having electronic and optical properties distinguished from those of either Graphene or *h*-BN [16].

2. Computational Methods

Building on recent works [1, 2, 17], we performed geometric optimizations once selected a localized gaussian basis-set, $6 - 31 + G^*$, coupled with a hybrid exchange correlation (XC) functional B3LYP [18, 19, 20]. The basis-set is composed by a valence double- ζ set augmented with d polarization functions for each atom (the + sign indicated the presence of the diffuse functions) [21]. As XC potential, the B3LYP has been chosen, because as compared to other possibilities (e.g. the PBE - Perdew-Burke-Ernzerhof [22]), it is able to reproduce better results for different class of PAHs, for either the ground-state or the excited one, as shown by previous studies [1, 23, 24].

We performed all electrons DFT [25] and Time dependent DFT (TDDFT) [26] calculations, as implemented in the *Gaussian16* computational package[21]. To obtain the ground-state electronic properties the DFT technique has been employed. Subsequently, through TDDFT we calculate the optical properties, producing the absorption spectra from the IR up to the UV range (covering the middle ultraviolet (MUV [4.13-6.20 eV]) and part of far ultraviolet (FUV [6.20-10.16 eV])). These spectra are based on the computation of the poles of the polarizability function in the frequency space, through the Casida scheme: these poles correspond to the vertical excitation energies, while their intensities represent the oscillator strengths [27].

The vertical electron affinities (EA_V) and ionization energies (IE_V) have been calculated as differences between the ground-state total energy of the neutral system, E_0^0 , and the energies of the charged species (the anion E_-^0 and the cation E_+^0 , respectively), at the neutral geometry.

According to the ΔSCF method [28], we obtain the QP gap (or "fundamental gap" E_{gap}), defined by:

$$E_{gap} = IE_V - EA_V = (E_+^0 - E_0^0) - (E_0^0 - E_-^0). \quad (1)$$

Related to this, knowing the value of E_{opt} , the first optically active transition in the absorption spectrum, an estimate of the exciton-binding energy could be given by the difference: $E_{bind} = E_{gap} - E_{opt}$ [24, 29, 30].

Here, we address also the calculation of some transport coefficients entering the *Marcus* model for transport which is valid in the hopping regime [31]. We limit our study on the calculations of the molecular reorganization energies, which are defined by the following expression, according to the *four-points-method* [32, 33]

$$\lambda = \lambda_1 + \lambda_2 = (E_0^\pm - E_0) + (E_\pm^0 - E_\pm) \quad (2)$$

where, E_0 (E_\pm) is the energy at the optimized geometry of the neutral (charged) systems, E_0^\pm (E_\pm^0) is the single-point energy of the neutral (charged) molecule at the charged (neutral) geometry.

3. Electronic and Optical Properties

In the following discussion the molecules under study will be recalled respectively by the acronyms in brackets, which indicate the original and BN-substituted configurations (R= ring and S= stripe): Coronene (C), BN-Coronene-ring (BNC-R) and BN-Coronene-stripe (BNC-S) (similarly for Ovalene).

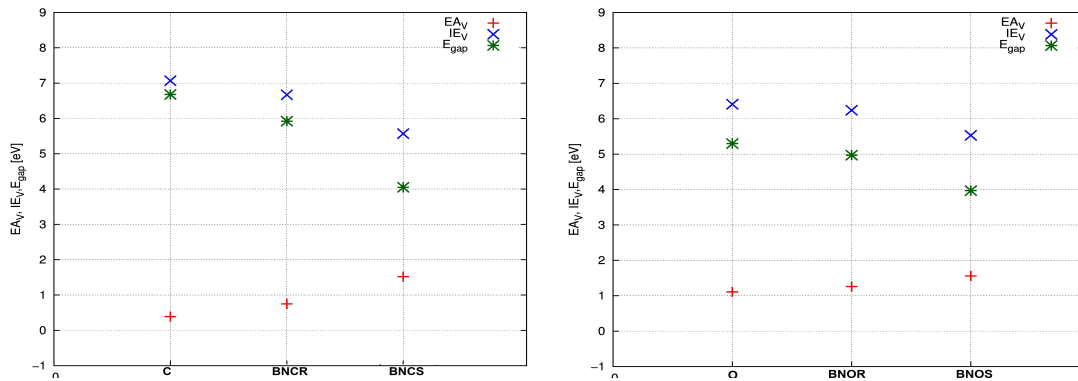


Figure 2. Computed electronic properties for Coronene (left) and Ovalene (right) in their BN-ring substituted configurations: vertical electron affinity (EA_V), vertical ionization energy (IE_V) and quasi-particle energy gap (E_{gap}). All data are in eV.

All the computed electronic and optical properties are reported in Tab.1. Firstly, we propose a description concerning the behavior of the electronic properties analyzed, separately, from one side within Coronene family and on the other inside Ovalene one, followed by a final comparison between the two hybrid clusters ². From Fig. 2 we noted that a general decrease of IE_V (up to $\sim 21\%$ for C and $\sim 14\%$ for O) and E_{gap} (up to $\sim 40\%$ for C and $\sim 25\%$ for O) takes place. On the contrary, a general increase of EA_V (up to ~ 3 times for C and up to $\sim 100\%$ for O) take place for both Coronene and Ovalene.

² Note that we compare a symmetric molecule (Coronene) with one with a different symmetry (Ovalene), obtained by the addition of three lateral benzene rings, to evaluate the "size-effects".

Table 1. Vertical electron affinity (EA_V), vertical ionization energy (IE_V), energies relative to the main peak position (M.P.P.), optical onset (E_{opt}) [with the corresponding oscillator strength (O.S.)] and exciton-binding energy (E_{bind}) for C (O), BNC-R (BNO-R) and BNC-S (BNO-S). The (%) variation of each observable is computed with respect to the original C-made molecule. All the values are in eV.

| Molecule | EA_V | IE_V | M.P.P. [O.S.] | E_{opt} [O.S.] | E_{bind} |
|--------------|---------------|----------------|----------------------|-----------------------|---------------|
| C | 0.39 | 7.07 | 4.09 [0.69] | 4.09 [0.69] | 2.59 |
| BNC-R | 0.75 (+34.2%) | 6.67 (-5.7%) | 3.60 [0.89](-12%) | 3.60 [0.89] (-12%) | 2.32 (-10.4%) |
| BNC-S | 1.52 (+289 %) | 5.57 (-21.2 %) | 6.87 [0.42](+68%) | 1.02 [0.055](-75%) | 3.03 (+17%) |
| O | 1.11 | 6.41 | 3.68 [1.08] | 2.69 [0.17] | 2.61 |
| BNO-R | 1.26 (+13.5%) | 6.24 (-2.6%) | 3.06 [1.18] (-16.7%) | 1.99 [0.0035] (-26%) | 1.98 (-24.1%) |
| BNO-S | 1.56 (+40.5%) | 5.53 (-13.7%) | 3.47 [1.08] (-5.7%) | 0.98 [0.002] (-63.6%) | 2.99 (+14.5%) |

Considering the switching from BNC-R (BNC-S) to BNO-R (BNO-S) we found an increase of $\sim 70\%$ ($\sim 3\%$) for EA_V , a decrease of $\sim 7\%$ ($\sim 1\%$) for IE_V and a reduction of $\sim 16\%$ ($\sim 2\%$) for E_{gap} . Finally, we verified that the behavior of the above mentioned electronic properties are almost similar, considering the two molecular structures.

It seems that increasing number of BN atoms determines a closure of E_{gap} , as defined in Eq. 1. For an optical characterization, we measure the optical properties, reproducing the optical absorption spectra for Coronene (left) and Ovalene (right) and their BN-ring substituted counterparts using TDDFT calculations (Fig. 3).

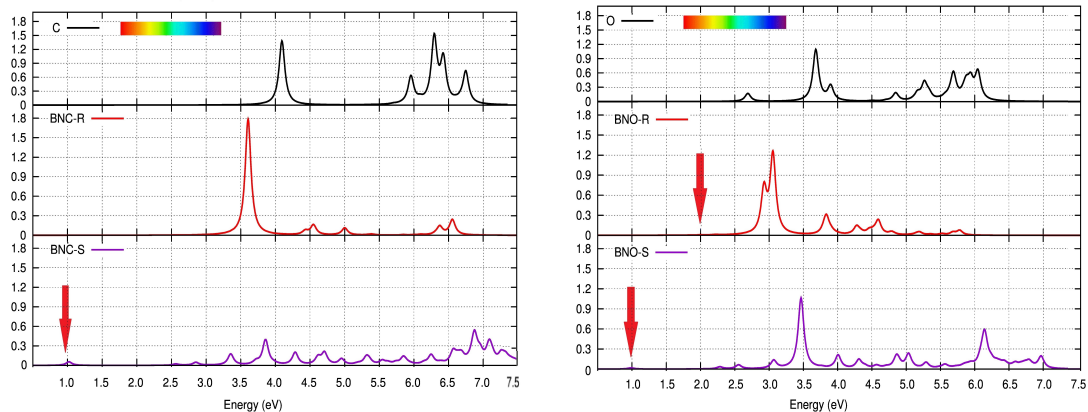


Figure 3. Absorption cross-section [a.u.] as a function of energy [eV] for Coronene (left) and Ovalene (right) families. The visible range is highlighted with a color bar.

In Coronene clusters the absorption begins in the IR (from 1.02 eV that is the optical onset of BNC-S up to the UV, over 7.5 eV). The characteristic main peak at the onset region (present in C and BNC-R spectra) is not present in BNC-S, which presents an absorption structure with more lower amplitude peaks shifted toward the UV. BNC-R and BNC-S E_{opt} are redshifted with respect to that of C. The dominant peaks (onsets energies) range is included between 3.60-6.87 eV (1.02-4.09 eV).

we found a similar behavior in the case of Ovalene family: the characteristic main peaks at the onset region, for O and BNO-R, in the case of BNO-S is not present, being replaced by a UV centered less intense structure. BNO-R and BNO-S E_{opt} are redshifted with respect to that

of O. The overall absorption takes place from the IR (~ 1 eV) up to the FUV (~ 7 eV). The dominant peaks are in the range included between the visible (3.06 eV) and the UV (3.68 eV). Comparing BNC-S and BNO-S spectra, aside from the main peak position, the spectra look rather similar, while BNC-R and BNO-R show spectra with noticeable differences. Regarding the exciton binding-energy, in Tab.1, we found that the two hybrid structures with the BN-stripe substitution (BNC-S and BNO-S) present larger values as compared with their corresponding carbon molecules. The variation with respect the parent molecule oscillates in the range $\sim -4/ + 17\%$ for Coronene and $\sim -8/ + 15\%$ for Ovalene. Moreover, switching from BNC-R (BNC-S) to BNO-R (BNO-S) we found a redshift of the order of 45% (49%) for both the M.P.P. and for E_{opt} of 15% ($\sim 4\%$) and a reduction of E_{bind} around $\sim 18\%$ ($\sim 1.3\%$).

4. Transport Properties: Molecular Reorganization Energies

Fig. 4 show the molecular reorganization energies for electrons (λ_e) and holes (λ_h) as a function BN-substitution-size (Ring, Stripe) for Coronene and Ovalene, as obtained through the so-called *four-point-method*.

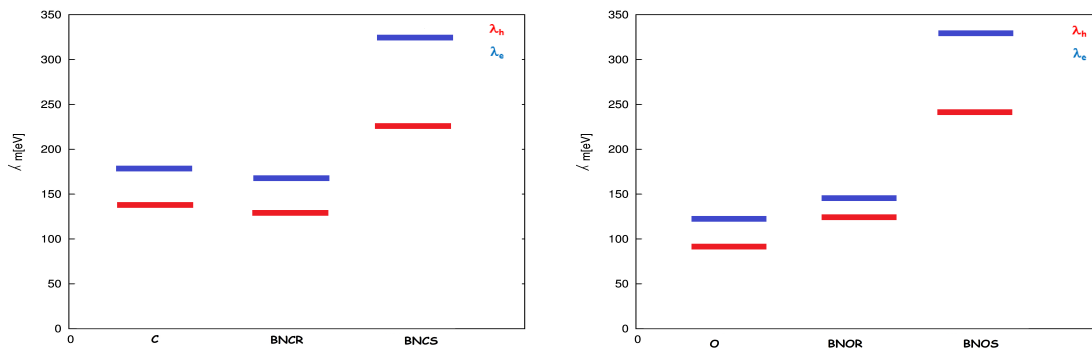


Figure 4. Molecular reorganization energies for electron λ_e (blue lines) and holes λ_h (red lines), for Coronenes (left) and Ovalenes (right), after BN-rings insertions.

Molecular reorganization energies have a central position in the calculation of the mobility within the *Marcus Theory* for the transport in the hopping regime: since λ coefficient enters in the argument of an exponential (see Refs. [32, 33]), it exercises a high influence in the hopping rate and consequently on the mobility. For the λ coefficients, we found that the values for the electrons (λ_e) are always larger with respect to the holes (λ_h) cases. For both λ_e and λ_h a general increase as a function on BN-rings substitutions with respect to the C-based original parents takes place (the only exception is BNC-R, which shows a slight decrease of λ coefficients, as compared to C). Moreover, switching from BNC-R to BNO-R a reduction of $\sim 12\%$ for λ_e occurs, with a coincidence in λ_h ; on the other hand, going from BNC-S to BNO-S λ_e increase by around 3%, while for λ_h the rise is near to 10%. On the contrary, for the original parent molecule, from C to O, both λ_e and λ_h decrease of -29% and -31% , respectively. In the case of S-type substitution a consistent increase of both λ_e and λ_h take place.

We conclude that the BN/C-hybrid systems here considered with respect to the λ coefficients will show a worsening of transport properties with respect to their C-pure analogous. However, to address completely this issue, one should perform a complete evaluation of all the parameters entering the hopping regime description [23].

Conclusions

We presented a comparative study of Coronene and Ovalene after BN-ring insertions using DFT and TDDFT methods. Regarding the electronic and optical properties, we have found a similar behavior for the physical observables under exam, both for Coronene and Ovalene.

Regarding the optical properties, we observed that the absorption begins in the IR for both the families after S-type-substitutions, unlike their C-made parents which absorb in the visible (except C). Basically, no substantial differences exist between C and O and their corresponding BN-rings modified shapes, showing that at fixed substitution-type, the consequences are of the same order of magnitude even comparing a symmetric molecule with one of a different symmetry: there is a negligible dependence on size effects. Our results reveal that, at this level of evaluation (only esteeming λ coefficients), C-made compounds present better charge transport properties than the BN/C-mixed hybrid systems in the hopping regime.

Acknowledgments

P M gratefully acknowledges the PhD school of "Università degli studi di Cagliari". G C acknowledges partial financial support from IDEA-AISBL Bruxelles.

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