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## A computational investigation on the electronic and optical properties of Coronene and its **Boron-Nitride and perfluorinated** counterparts

#### P Mocci, R Cardia and G Cappellini

Department of Physics, University of Cagliari, S.P. Monserrato-Sestu Km 0,700 I-09042 Monserrato (CA), ITALY

E-mail: paola.mocci@dsf.unica.it

Abstract. We present a computational study on the electronic and optical properties of a representative C-made and Boron-Nitride-made (BN) planar molecule of interest for potential applications in the solid state domain. In particular, we analyzed the case of Coronene  $(C_{24}H_{12})$ in its BN and perfluorinated analogues. We performed all electrons Density Functional Theory (DFT) and Time Dependent-DFT (TD-DFT) calculations using a localized Gaussian basis-set in combination with a hybrid exchange-correlation functional. For all the systems we have calculated different electronic properties and the optical absorption spectra. A discussion on the possible implications of the general trends, observed for the BN-made clusters properties as compared to their C-based parents, will be given.

#### 1. Introduction

During the recent past, in the optoelectronics branch, a high interest and a deep attention has been covered by small molecules, known as Polycyclic Aromatic Hydrocarbons (PAHs), playing a meaning role for both the unrestrainable growth of the modern application areas and the theoretical research field. These systems are commonly employed as active elements in several optoelectronic devices, from light-emitting diodes and photovoltaic cells to liquid crystals and organic thin-film field-effect transistors [1]. Indeed, they present various advantages, such as: the possibility to be easily purified through evaporation and solution processings, accompained with their tunable electronic and optical features. In particular, among these compounds, the position occupied by the Circumacenes (Coronene, Ovalene, Circumanthracene, Circumtetracene, and Circumpentacene are the first five members of the family) has recently shown up, thanks to their attractive properties [2, 3]. Aside from their characteristic planar and symmetric geometry, these molecules potentially play a significant role as finite portions (with a nanometric size) of an infinite system widely studied and analyzed: the Graphene [4].

Furthermore, related to the surge of Graphene and Carbon-based material research, a vivid interest in the investigation of other 2D nanomaterials has soon manifested, for example on the 2D Boron-Nitride (BN) [5]. Bulk-BN, in fact, occupies a unique position, sharing many of its properties, structures, processing and applications with carbon. In particular, for cubic-BN (c-BN), its extreme hardness, wide energy band gap, low dielectric constant, and high

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thermal conductivity are also very near to those of diamond [6]. 2D BN-based nanostructures are therefore considered as promising candidates for different technologic devices and applications: ranging from vacuum technology, microelectronic devices, wear-resistant lubrificants to x-ray lithography masks, deep UV LED, graphene-engineering [6] and biological and medical fields applications [7]. In this last context, the synthesized BN-nanotubes (BNNTs) were investigated for their potential use in biomedical applications as gene and drug transporter or tissue scaffolds after the evaluation of their non-toxicity and their biocompatibility [8]. The BN compound, formed by the union of Boron and Nitrogen atoms in the same percentage, shows up as a thermally and chemically resistant material. It presents various crystalline forms, isoelectronic with respect to the elementaty Carbon-made structure, among which:

- the hexagonal form (*h*-BN), that is the counterpart of the graphite (the most stable and soft form among BN polymorphs, usually employed as lubrificant, additive to cosmetic products, ceramics..);
- the cubic form (*c*-BN) which is the diamond analogue (softer than diamond but with a superior thermal and chemical stability, usually used as abrasive);

On the other hand, the differences between the BN-made compounds and the C-based ones are mostly due to the different nature of their chemical bond: for example, while the h-BN is an insulator, the graphite is a conductive semimetal [9].



Figure 1. Coronene molecule (I) in its BN (II), perfluorinanted (III) and perfluorineted-BN-made (IV) counterparts. C atoms are indicated in grey, H in white, F in light-blue, N in blue and B in pink.

In the present work we expose a computational comparative analysis on the electronic and optical properties of some representative BN planar molecules of interest for potential applications in condensed matter physics domain [10, 11, 12]. In particular, we have selected the Coronene molecule (the first member among the Circumacenes family), studying its BN-made and perfluorinated counterparts <sup>1</sup>. We have performed Density Functional Theory (DFT)[13] and the Time Dependent-DFT (TD-DFT) calculations [14] to obtain the ground-state electronic properties and the excited-ones, respectively. We will discuss our results with existing previous theoretical and experimental data from the literature, focusing on the possible implications of the BN clusters properties in comparison with their C-made counterpart.

<sup>&</sup>lt;sup>1</sup> The perfluorination corresponds to the total substitution of H atoms with F atoms in the peripheral molecular areas. A similar analysis has been made by Ref. [15].

#### 2. Computational methods

According to previous works [1, 2, 16], geometry optimizations have been performed using a localized gaussian basis-set,  $6-31+G^*$ , combined with a hybrid exchange-correlation functional B3LYP [17, 18, 19], within an all electrons computational code, *Gaussian*16 [20]. The selected basis-set is composed by a valence double- $\zeta$  set augmented with *d* polarization functions for each atom (the + sign indicate the presence of the diffuse functions). The choice for the B3LYP as exchange-correlation potential, has been justyfied, because, with respect to other possibilities (e.g. the PBE - Perdew-Burke-Ernzerhof [21]), it has been demonstred to reproduce better results for different clusters of PAHs molecules, for both the ground-state and the excited one [1, 23, 25, 27, 28].

We have performed the DFT [13] and Time dependet-DFT (TD-DFT) [14] calculations implemented in the *Gaussian*16 computational package [20]. In particular, through the DFT scheme we have obtained the ground-state and the electronic properties (e.g electron affinities, ionization energies and quasi-particle (QP) gaps) for all the systems under study. While, the time-dependet counterpart of this method has allowed us to calculate the optical properties (optical onsets, exciton binding energies) and obtain the absoption spectra in the visible up to the middle ultraviolet (MUV) and far ultraviolet (FUV). In particular, we used the Casida computational scheme which computes the poles of the polarizability in the frequency domain (these poles correspond to the vertical excitation energies, while their strenghts represent the oscillator strenghts [22]).

Finally, we used the  $\Delta SCF$  scheme [26, 29]. Within this method the vertical electron affinities  $(EA_V)$  and ionization energies  $(IE_V)$  can be calculated as differences between the ground-state total energy of the neutral system,  $E_n^0$ , and the energies of the charged species (the anion  $E_a^0$  and the cation  $E_c^0$ , respectively), in correspondence of the neutral geometry.

This permits the evaluation of the quasi-particle (QP) gap (known also as "fundamental gap"), which in the  $\Delta SCF$  scheme is defined as follows:

$$E_{gap} = IE_V - EA_V = (E_c^0 - E_n^0) - (E_n^0 - E_a^0)$$
(1)

In addition, knowing the first optically active transition from the absorption spectrum,  $E_{opt}$ , we could give an estimate of the exciton-binding energy through the difference:  $E_{bind} = E_{gap} - E_{opt}$ .

#### 3. Electronic properties

In the following discussion, for brevity, the analyzed molecules will be indicated respectively by the acronyms in brackets: Coronene (C), BN-Coronene (BNC), perfluorinated-Coronene (p-C) and perfluorinated-BNCoronene (p-BNC). Tab. 1 presents the computed data of the electronic properties for all the molecules under study. For each observable the percentage variation, calculated with respect to the original parent (C), has been reported in brackets (for further details see the footnote <sup>2</sup>). Some of the data (vertical electron affinity  $(EA_V)$ , vertical ionization energy  $(IE_V)$  and fundamental gap  $(E_{gap})$  are shown in Fig.2 (A) through a diagrammatic representation.

In what follows, we have decided to focus in detail only in a comparative description on the electronic properties behavior, analyzing, in particular, what happens in the passage from C to BNC and from BNC to p-BNC. Considering the vertical electron affinity, going from C to BNC, a decrease nearly  $\sim$ -200% takes place. On the other hand, the perfluorination effect in BNC determines a large increase (of the order of +200%) of the same observable. On the contrary, for the vertical ionization energy, in the passage from C to its BN-counterpart, we have registered a rise of about 20%. For this observable, the presence of Fluorine (F) atoms

 $<sup>^{2}</sup>$  We report our calculated data with two significant digits since the precision of the experimental values available in the literature are of the order of 10 meV.

**Table 1.** Vertical electron affinity  $(EA_V)$ , vertical ionization energy  $(IE_V)$  and fundamental gap  $(E_{gap})$  for C, BNC, p-C and p-BNC. The (%) variation of each observable is computed with respect to the original C-made molecule (C). All the values are given in eV.

Molecule	$\mathbf{EA_V}$	$IE_V$	$\mathrm{E_{gap}}$
C BNC	0.39	7.07 8.45 (±19.5%)	6.68 8 71 (+30.4%)
p-C	1.77 (+354%)	8.45 (+19.5%) 8.25 (+16.7%)	6.49 (-2.8%)
p-BNC	0.35~(-10.3%)	9.68 (+36.9%)	9.33 (+39.7%)

produced a rise of similar entity in p-BNC (of about 15%) as compared to the corresponding original parent (BNC). For what concerns the fundamental gap, we observed an increase of  $\sim$  +30% from C to BNC. In this case, for p-BNC the fundamental gap increases of  $\sim$ +7% with respect to its original analogue (BNC). Globally, the transition from the C-made molecule to the BN-made one provokes a lowering in the vertical affinity, an increase of the ionization energy and a consequent rise of the QP gap. The perfluorination effect going to BNC to p-BNC provokes a general raise of all the above mentioned observables.



Figure 2. (A)Vertical electron affinities (red lines), vertical ionization energies (blue lines) and fundamental gaps (black arrows) for C, BNC, p-C and p-BNC, from left to right, respectively.

(B) Fundamental gaps (green lines), optical onsets (light-blue lines) and exciton binding energies (black arrows) for C, BNC, p-C and p-BNC, from left to right, respectively.

#### 4. Optical properties

Tab. 2 reports the results for the optical properties, as obtained after TD-DFT calculations, while Fig. 2 (B) shows the trend of some of the previous observables through a diagramatic representation. Also in this case, we focus in detail on the comparison between C and BNC and BNC and p-BNC (the others molecular comparisons could be found referring to Tab. 2).

From the computed data we noted that both the main peak and the optical onset of BNC are blueshifted of  $\sim 80\%$  and  $\sim 50\%$ , respectively, as compared to those of C. For what concerns the perfluorination effect, the presence of F-atoms implicates a redshift of the optical onset and the dominant peak in the p-BNC with respect to BNC and respectively of the order of 2% and 14%. Globally, the absorption edge takes place in the UV for all the examined molecules, accompained with a blueshift and a remodeling of the absorption structure for the BN-systems with respect to that of their C-made original parent.

**Table 2.** Energies relative to the main peak position (M.P.P.), optical onset  $(E_{opt})$  and exciton-binding energy  $(E_{bind})$  for C, BNC, p-C and p-BNC. The% variation of each observable is calculated with respect to the original C-made parent molecule. All values are given in eV.

Molecule	M.P.P.	$\mathbf{E_{opt}}$	$\mathbf{E}_{\mathbf{bind}}$
С	4.09	4.09	2.59
BNC	7.44 (+82%)	6.22 (+52%)	2.49~(-4%)
p-C	6.44 (+57%)	3.91~(-4%)	2.59 (-)
p-BNC	6.38~(+56%)	6.07 (+48%)	3.26 (+26%)

For what concerns the exciton-binding energy this observable remains almost constant from a molecule to an other: in particular, a negligible reduction ( $\sim 4\%$ ) from C to BNC takes place, while a rise of  $\sim 26\%$  is determined as a consequence of the perfluorination in BNC.



Figure 3. Absorption spectra (absorption cross-section [a.u.] vs energy [eV]) for C, BNC, p-C and p- BNC, from the top to the bottom, respectively.

Moreover, from Fig. 3 the optical onsets of the BNC and p-BNC are blueshifted with respect to their C-made original parents: the absorption is mainly translated towards the UV region. The typical absorption structure of the C-based material, with a peak in the region close to 4 eV, disappears in the BN-made molecules spectra, with a redistribution of the intensity at higher energies. The presence of F-atoms in the BN-system, produces a redshift for both the main peak (from 7.44 to 6.38 eV) and for the optical onset (6.22 from to 6.07 eV), as previously discussed.

#### Conclusions

We have presented a comparative study of Coronene and its BN and perfluorinated forms in the context of DFT and TD-DFT techniques. Dealing with the electronic properties, we have found that a lowering of the vertical electron affinities and a rise of the ionization energies and QP gaps take place passing from the C-made to the BN-based systems.

For what concerns the optical properties, we observed that the absorption is localized in the UV for all the molecules under study, with a blueshift of the optical onsets and the dominant peaks for the BN-made molecules with respect to the original C-made parents. Moreover, the perfluorination effect has similar entity either for the Carbon and the Boron-Nitride compounds. This quantitative comparison on the electronic and optical properties of these compounds, could open future ways on a theoretical level, in order to take full advantages in many application fields as emerging novel materials. The high chemical inertia, thermal stability, the tunable electronic and optical properties, no-toxicity, make these BN-nanostructures as promising candidates for different technologic devices, complementary but also innovative with respect to the successfull Carbon-based counterpart [7]. In particular, thanks to their UV-absorption feature here analysed, these BN nanomaterials keep a promising role in the technology linked to UV optoelectronics.

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