Reactivity Indices for the Coronene Nanocrystals and Their Derivatives: Modeling Approach

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ABSTRACT

The modeling approach was applied for the study of the reactivity of pristine and the substitution and absorption of doped coronene nanocrystals with nitrogen and boron under different cases. The reactivity indices of doped coronene molecules were investigated by adopting the Density Function Theory (DFT) code under the SIESTA and Hückel method schemes, which were performed using WebMO. We calculated reactivity indices that were placed into an orbital molecular frame. The results showed that the replacement and absorption of the effects of the doped coronene molecule with nitrogen increased the reactivity of the coronene nanocrystals. The pure coronene molecule is the molecule that has the largest energy gap. The hardness value of doped coronene substituted with a nitrogen atom decreases. The magnitude of chemical potential and electrophilicity for doped coronene with a nitrogen molecule has higher values than all compound cases studied. Moreover, the reactivity indices for the para position are low, so the compound will be less stable and highly reactive compared to the other positions. Therefore, substitution and absorption of doped coronene nanocrystals with nitrogen, and also the para position for doping with nitrogen and boron cases, will be a candidate for studying reactivity in the future.

1. Introduction

In recent years, the attention given to organic crystals has increased due to their low heaviness and price tag, which can be shown by substituting transition raw material oxides within large amounts of available carbon-based crystals (Devi *et al.,* 2020; Lee *et al.,* 2018; Mauger *et al.,* 2019; Vadehra *et al.,* 2014; Zhu *et al.,* 2018). Graphene-based materials are at present widely valued for their possible uses as devices and adsorbents. The electronic properties and reactivity of graphene can be improved by doping with transition metals or heteroatoms. Coronene composites can be employed as small graphene quantum dots (Malček and Cordeiro, 2018). Coronene nanocrystals have been used in the creation of graphene (Kato *et al,* 2021; Saha and Bhattacharyya, 2018). The properties of pure coronene and its boron nitride substitution were considered (Dosso *et al.,* 2020; Kurita, 2000; Vessally *et al.,* 2017). Lithium as a dopant has already been reported to reduce the stability of coronene more than three times (Forozmand and Biglari, 2021). The substitution and absorption of doped coronene nanocrystals with nitrogen are of interest in scientific circles concerning their use in the field of nanomaterial science, biosensors, environmental pollution remediation, drug delivery, and several other areas (Kato *et al.,* 2021).

Molecular modeling is the best-developed field to simulate any molecule or system to recognize and predict its behavior. It has further uses in engineering and material sciences, including nanoscience materials and electronics, which cover numerous areas of investigation dealing with things that are scaled in nanometers and that are expected to change the manufacturing sector in the coming decades (Müller and Gubbins, 1998; MacDonell and Schuurman, 2018; Cygan, 2001; Mekky, 2020). Computational software has proven to be an important exploratory tool, and our plan is to bring this technology to the classroom and apply it to examining the doping of nitrogen and boron into carbon compounds (Amin and Deraz 2000; Petrushenko, 2019; Zhu *et al.,* 2018).

The examination of the adsorption actions of the graphene, fullerene, carbon, and coronene ring complexes' theoretical composites can provide important data about their reactivity and electronic and structural tracts (Almuqrin *et al.,* 2021; Wiśniewski and Gauden, 2009).

The reactivity descriptors widely used by computational scientists contain the highest occupied molecular orbital (HOMO) energies, global hardness or chemical hardness, electrophilicity, and chemical potential, as shown by Koopmans' formulas (Bassi *et al.,* 2020). A thorough consideration of the stability of a doped system as visualized in the previous studies requires assessing the above descriptors for discovering potential synthetic uses in the future (Belghiti *et al.,* 2016; Bhawsar *et al.,* 2015; Jaufeerally *et al.,* 2013; Mujica-Martínez and Arce, 2010; Qiang *et al.,* 2016; Yadav *et al.,* 2016; Mekky, 2018).

In this paper, we propose that substitution and absorption of doped coronene nanocrystals with nitrogen, as well as the para position for doping with nitrogen and boron cases, will be a candidate for studying reactivity in the future.

2. Methods and Calculations

Calculations were carried out using the Density Function Theory (DFT) in the SIESTA code. It is used to obtain the relaxed geometry of the considered composites, the optimum structural geometry of the fragments shown in Figures 1, 2, and 3 come to be reached up to all forces in general on atoms are lesser than 0.05 V/Ang. Energy with a cutoff of 200 Ry is measured in the SIESTA calculations and to carry out the measurements to examine electronic properties.

Once the inter-atom forces were smaller than 40 me V/A, the systems were measured completely optimized. The last step was to compute the mean-field Hamiltonians of the full junctions after fixing the geometry of the junctions. SIESTA is a self-consistent density functional theory method that uses norm-conserving pseudo-potentials and a linear combination of atomic orbital basis (LCAOB) to execute effective calculations (Soler *et al.,* 2002; Sozykin, 2021).

WebMO is a web-based interface for computational physics and chemistry packages (Perri and Weber, 2014; Schmidt and Polik, 2021)**.** It allows the user to set up, run, and visualize physical and chemical calculations from a web browser, smartphone, or tablet. It is used to model and study the reactivity parameters of coronene nanocomposites and their derivatives. Substitution and absorption of doped coronene nano molecules by nitrogen and boron (with ortho and meta and para) positions are displayed in Figures 1 and 2. All models involved in this study are presented in Figures 1 and 2.

Figure 1: Structure of (a) pure coronene, substitutional doped coronene with (b) nitrogen, and (c) boron molecules and absorbed (d) nitrogen, and (e) boron molecules inside coronene.
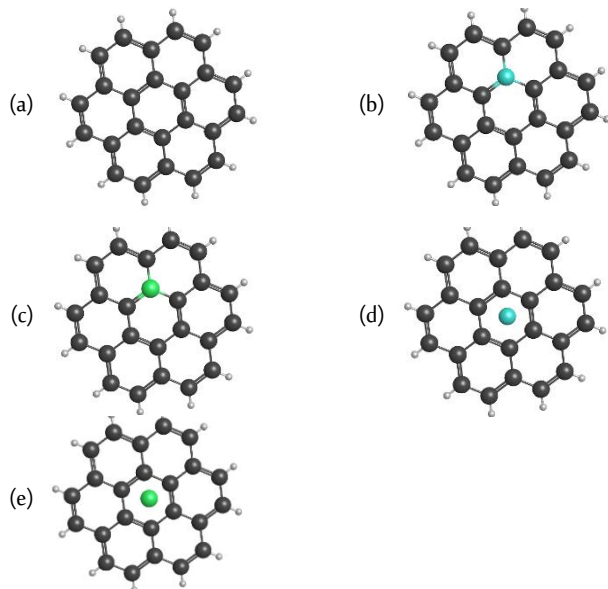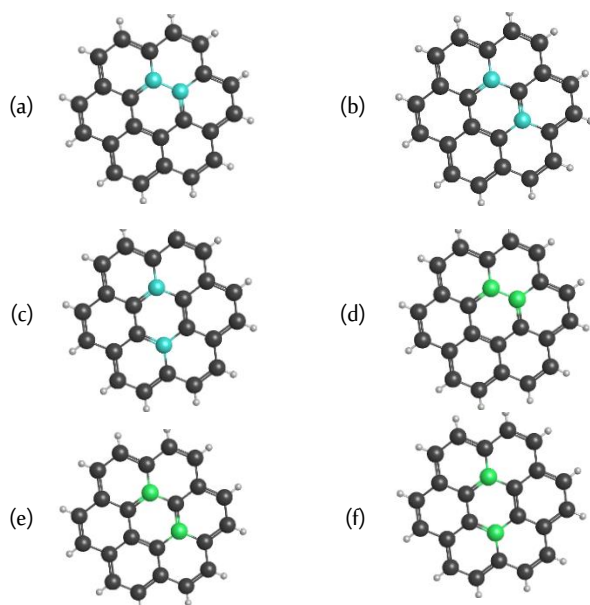

Figure 2: Structure of substitutional doped coronene with nitrogen (a, b, and c), and boron (d, e, and f) molecules at the (ortho & meta & para) positions.

These have been examined by assuming the Hückel method. Merging mechanic cleanups through a Hückel orbital scheming is a rapid approach to optimizing geometry and assessing molecular orbitals devoid of exhausting a computational engine. To show molecular orbitals, WebMO uses the Extended Hückel Theory (EHT) Molecular Orbital method. The Hückel Molecular Orbital (HMO) concept is a very simple theorem for examining both sigma and pi-molecular orbitals of carbon systems.

EHT covers the important components of the molecular orbital principle at a minimum level. Typically, EHT with a very low computational request suggests a qualitatively valuable explanation of the electronic structure of molecules.

The objective of WebMO's EHT execution is computational efficiency.

3. Results and Discussion

Reactivity is the impetus by which material needs to undergo a chemical reaction with an overall flow of energy, either alone or with other substances. The reactivity index is the traditional theoretical quantity used to calculate the relative rate of identical reactions occurring at various positions in a compound or in different compounds.

For the calculations of inclusive identifiers of reactivity, the Lowest Unoccupied Molecular Orbital (LUMO) and HOMO energies are used. The reactivity indices are hardness, energy gap, electrophilicity, and chemical potential, symbolled as η, ΔE, ω, and μ, respectively (Mekky, 2014; Islam *et al.,* 2019) These are determined using the formulas below, based on E_{HOMO} and E_{LUMO}:

$$\Delta E = E_{gap} = (E_{LUMO} - E_{HOMO}) \tag{1}$$

where

$$\mu = (E_{LUMO} + E_{HOMO}) / 2, \tag{2}$$

$$\eta = (E_{LUMO} - E_{HOMO}) / 2, \text{ and} \tag{3}$$

$$\omega = \mu^2 / 2\,\eta. \tag{4}$$

The doping of nitrogen and boron atoms in coronene is performed to obtain the worked models. For the heterostructure, only in the central ring of coronene, we replace C atoms with B and N. It is worth noting that the purpose of this paper is to examine the replacement and absorption effects of the doped coronene molecule on coronene reactivity indices. The energy gap (E_{LUMO}-E_{HOMO}) is a significant stability index that maintenances telling the reactivity (stability) of the studied molecule. The reactivity is different from the kind with dopants. The substitution of doped coronene by a nitrogen atom has the lowest energy gap, as shown in Figure 3(a). It allows this lower gap to be the softest molecule and more reactive than all the cases studied. The pure coronene molecule is the molecule that has the largest energy gap.

Figure 3: (a) energy gaps, (b) hardness, (c) chemical potential, and (d) electrophilic of coronene and its substituted N and B derivatives.
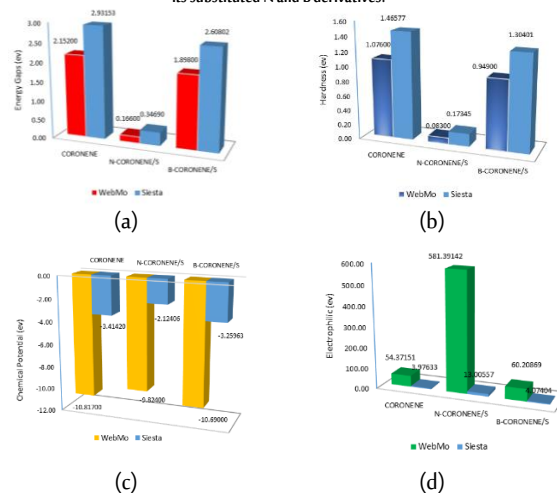
As shown in Figure 3(b), among all other molecules in the study case, the hardness value of doped coronene substitution with the nitrogen

atom is lower. Thus, it is observed that coronene doped with nitrogen is more reactive than in other recent cases.

From SIESTA and WebMO simulations, the hardness of the pure coronene molecule is estimated to be 1.47 and 1.08 eV, respectively (Figure 3[b]), and the value decreases due to the replacement of carbon with nitrogen and boron atoms. In the case of nitrogen substitution, the lower value of chemical hardness means that the stability of the studied system decreases, and it will come to be more reactive.

Generally, the chemical potential is defined as the negative of electronegativity, and it describes the trend of gaining electrons in the direction of the molecule. Electrons in general flow from low to high electronegativity areas up to the electronegativity value of the constituent system neutralizes. The magnitude of chemical potential for doped coronene with nitrogen molecules has higher values than all compound cases studied (figure 3[c]) when determined using SIESTA and WebMO calculations.

The coronene compound doped with a nitrogen atom has nearly as high an electrophilicity value as all compound cases studied (Figure 3[d]). The results illustrate the compound that has the slightest energy gap. Therefore, it is polarizable and is associated with a greater chemical reactivity and smaller stability, and it is labeled as a soft molecule.

As shown in Figure 2, we found several possible formations for both the nitrogen and boron atoms occupying the central ring of the coronene model. The two substituent atoms are adjacent at the ortho substitution. If there is one C atom between the two atoms, then it is in the meta substitution, whereas para substitution inserts two C atoms between the two atoms.

The meta and para substitution slightly decreases the energy gaps of N and B of the doped coronene in comparison to the ortho position. Figures 4(a) and 5(a) summarize these effects. This illuminates the dependence of energy gaps on the sites N and B of the doped coronene molecules.

The LUMOs−HOMOs gap explains the reactivity and stability of the composites. At the para position, the energy gap is lower than in the two other positions; the compound at the para position is less stable and more reactive. Correspondingly, the energy gap at the ortho position is large, so the compound will be highly stable and less reactive compared to the other positions.

As shown in Figures 4(b) and 5(b), the nitrogen and boron substitutions lead to a decrease in meta and para position hardness compared with the ortho position hardness. On the other hand, the lowest single value for hardness is the para doped B and N system position. So, the coronene that dopes with nitrogen is the more reactive.

In Figures 4(c) and 5(c), the most chemical-potential molecule value is coronene doped with N and B at the ortho position, but the lowest chemical-potential molecule value in each is at the para position. The more reactive one is the compound structure at the para position.

Assuming SIESTA yields better results, the N and B substitution becomes equally good in terms of reactivity, which is described in Figures 4(a) and 5 (a) by similar ΔE values of 0.225 eV and 0.231 eV.

Figure 4: (a) energy gaps, (b) hardness,(c) chemical potential, and (d) electrophilic of coronene and its substituted N derivatives for (ortho or meta & para) positions.
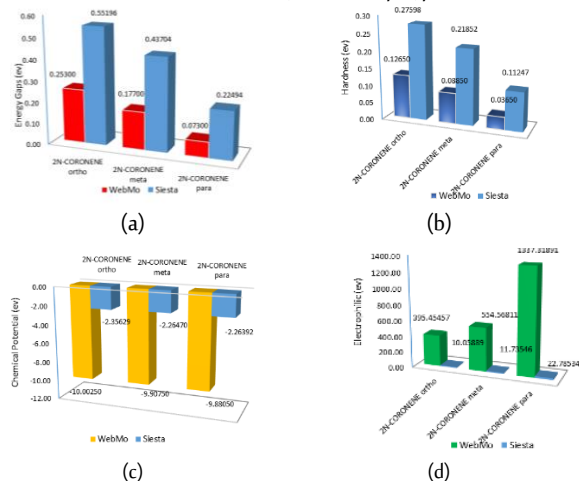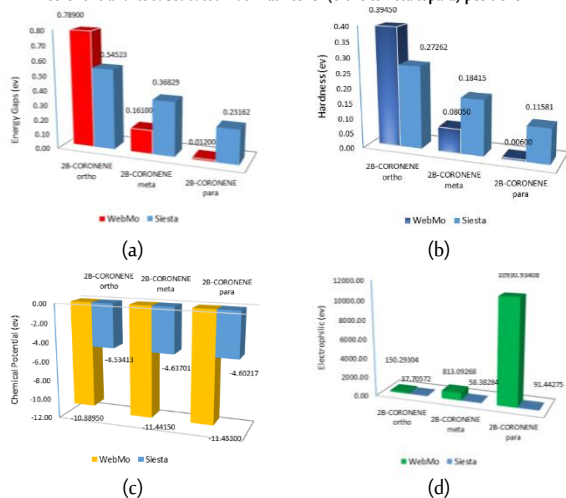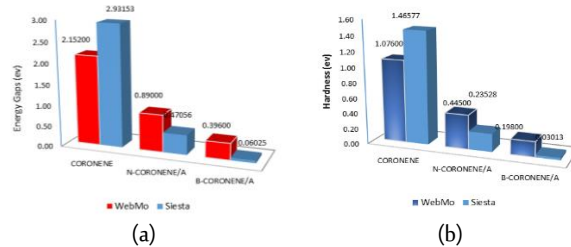

(a)

(b)

(c)

(d)

Figure 5: (a) energy gaps, (b) hardness,(c) chemical potential, and (d) electrophilic of coronene and its substituted B derivatives for (ortho & meta & para) positions.
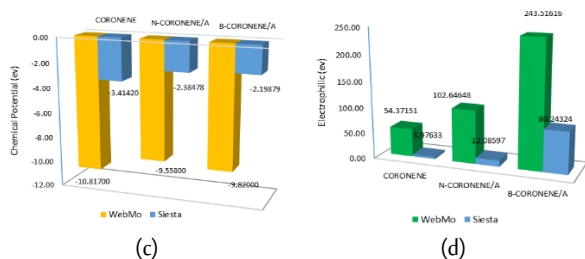

(a)

(b)

(c)

(d)

The electrophilicity of the modified coronene rises from ortho to para, which once again confirms the reduction in chemical stability, as shown in Figures 4(d) and 5(d), supporting the theory of optimal electrophilicity. Because the molecule of the para position system becomes less stable than that of the other position systems, this will demonstrate a higher propensity to accumulate extra electronic charges from the surroundings.

As shown earlier in Figures 1 (b) and (c), we identified the hollow absorption sites to demonstrate that the hollow positions are the most favorable for the absorption of nitrogen and boron atoms. Doping with the B atom does not increase the energy gap from Figure 6(a), whereas the addition of the N atom to the molecule's central ring results in a decrease, with the weakest energy gap being lower than pristine coronene, as seen in Figure 6(a). This narrower gap makes it more reactive than in other situations. The largest energy difference is present in the pure coronene compound.

Figure 6: (a) energy gaps, (b) hardness, (c) chemical potential, and (d) electrophilic of coronene and its absorbed N and B molecules inside coronene.

(a)

(b)

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(c)

(d)

The most reactive and unstable compound in this sequence, as shown in Figure 6(b), was absorbed by coronene B, and its reactivity was also accompanied by lower hardness values. The most stable compound was the pure coronene compound, which is also confirmed by its elevated hardness values.

The chemical potential of coronene and its absorbed N and B derivatives are shown in Figure 6(c). For pristine coronene, the highest value was observed, and for coronene absorbed B, the lowest value was measured.

It has been observed from Figure 6(d) that the highest electrophilicity index value of the coronene absorbed B molecule is obtained from the considered molecules.

4. Conclusions

A modeling approach is performed using the Density Function Theory (DFT) and the Extended Hückel Theory (EHT) methods to study the reactivity indices for pristine coronene and doped coronene with nitrogen and boron atoms and the position of doping in the molecule. The results obtained for the reactivity indices show that the most reactive study case is the most stable, depending on the values of the energy gap ($E_{LUMO}-E_{HOMO}$). Assuming SIESTA yields better results, the N and B substitutions become equally good in terms of reactivity. The studies show that doping decreases some of the above reactivity indices significantly while some increase occurs compared to pure coronene, suggesting that one can induce a significant change in doped coronene reactivity with nitrogen and the para position doping.

Biography

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