FIRST-PRINCIPLES INSIGHTS ON THE BONDING MECHANISM OF DIRECT-STACKED BIPHENYLENE NETWORK

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ABSTRACT

Recently, a new class of carbon-based nanomaterial (biphenylene network) was synthesized and gained much attention in the scientific community. Using first-principles method, we explored the bonding mechanism of direct-stacked biphenylene networks. Our calculations suggest that the nature of the interaction between the layers of the network is due to van der Waals interaction. This is due to the weak binding energy between the biphenylene networks and the deformed Electron Localization Function in the interface. We anticipate that this work will serve as a reference for further scientific investigation on the biphenylene network.

INTRODUCTION

The discovery of novel two-dimensional nanomaterials has led to so much research about their real applicability at the nanoscale level [6, 23-26]. In recent years, high-performance carbon-based nanomaterials have paid much attention due to the potential applications they carry in a wide area of disciplines [1, 4]. Interesting materials such as 0D, 1D, and 2D materials show promising potentials owing to their interesting quantum mechanical effects [1, 10, 31]. Carbon allotropes, particularly graphene and carbon nanotubes, have become some of the most studied nanomaterials [5, 29]. However, due to the strong van der Waals force between their graphitic surfaces, graphene and CNTs tend to agglomerate which leads to difficulty in application [3, 17]. Despite the challenges, graphene and CNTs are pursued, owing to their revolutionary potential and interesting physics.

Just recently, the Biphenylene network, a new type of carbon allotropes which is consist of eight-, six-, and four- carbon rings, was successfully synthesized by Fan and his colleagues [9]. This material has attracted much attention due to its predicted mechanical and electrical properties which are important for its applications [7, 18, 30]. For instance, Denis, P. A. [8] conducted the theoretical characterization of the stability and electronic properties of the Biphenylene network. Accordingly, it was found that the network is metallic. Peng-Fei Liu, et.al [20] studied the electronic structure and topology of the bands of the Biphenylene network showing a metallic behavior. It was revealed that a two-band Fermi surface and tilted Dirac cones are present just above the Fermi level.

However, to date, no substantial theoretical study was conducted clarifying the interaction between biphenylene networks in a multilayered system. To bridge this gap, we conducted a first-principles study exploring the bonding mechanism of a direct-stacked biphenylene network in the bilayer and trilayer configurations.

COMPUTATIONAL DETAILS

Density Functional Theory (DFT) is a well-tested computational scheme that is widely used in condensed matter physics, chemistry, and materials science for a good balance between accuracy and speed. Our prototype biphenylene network is a 2x2 supercell with a 15 Å slab. The optimization and electronic structure calculations

are conducted at DFT level using PBE parametrization and ultrasoft pseudopotential generated by GBRV library implemented in Quantum Espresso [11-14, 21]. The cut-off energy and cut-off charge density are set to 50 Ry and 250 Ry, respectively. Further, we set the force threshold to 1.0 x 10^{-4} Ry/Bohr, and the stress threshold is set to 0.05 Pa. The k-points sampling is then set to 3x3x1. We then calculated the binding energy using

$$E_{binding} = \frac{(E_{multilayer} - nE_{monolayer})}{n} \qquad \text{Eq. 1}$$

where the number of layers, binding energy, energy of the Biphenylene network, and energy of multilayers are denoted by n, $E_{binding}$, $E_{monolayer}$ and $E_{multilayer}$, respectively. To compare electron redistribution of the system, we calculated the electronic localization function and the charge density difference of the direct-stacked biphenylene network.

RESULTS AND DISCUSSION

The optimized structure of the monolayer biphenylene network is displayed in Figure 1a, with the corresponding bond lengths listed in Table 1. Here, bond lengths are in good agreement with the recent theoretical report [16].

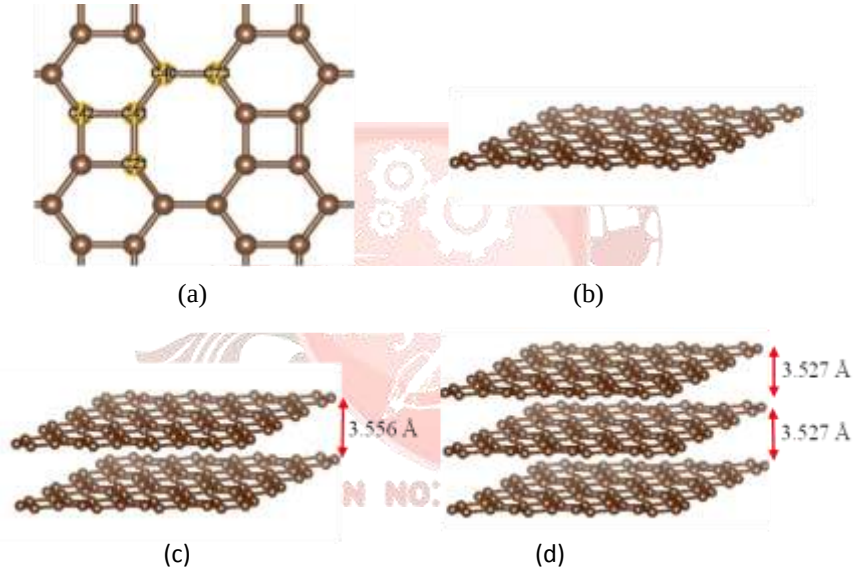


Figure 1. (a) 2x2 supercell of a biphenylene network. (b) Monolayer, (c) bilayer, and (d) trilayer biphenylene network.

Figure 1a depicts the 2x2 supercell of biphenylene which shows the eight-, six-, and four- carbon rings that make up the network. Here, the vacuum distance between the layers of the network is 3.556 Å and 3.527 Å for the bilayer and trilayer, as shown in Figure 1c and Figure 1d, respectively. This value is close to the reported spacing of stacked graphene [2, 19]. Table 1 shows the tabulated C-C bond lengths indicated in Figure 1a.

Table 1. Bond lengths of biphenylene network.

Bonds	Bond Length (Å)
C40 – C73	1.45115
C40 – C41	1.40429
C41 – C21	1.45395
C41 – C42	1.45904

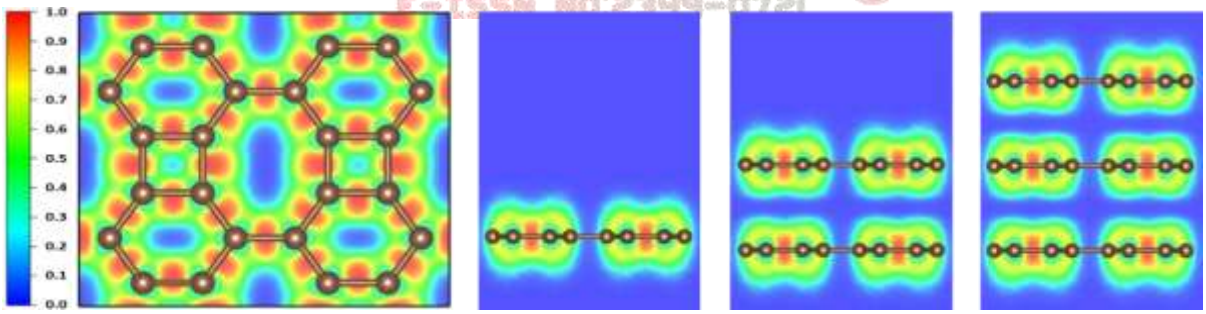
We further examine the stacking of the Biphenylene network using the Electron Localization Function (ELF). The ELF is a scalar field that is known to determine the locality of electrons between atoms and molecules [15, 23]. ELF is defined as follows,

$$ELF = n(r) = \frac{1}{1+\chi(r)} \qquad \text{Eq.2}$$

where χ is the ratio of the positive-definite local Pauli, $\tau_p(r)$, and Thomas Fermi, $\tau_h(r)$, kinetic energy densities in the given systems [27, 28] given by,

$$\chi = \frac{\tau_p(r)}{\tau_h(r)} = \frac{\frac{1}{2}\sum_{i=1}^{N}|\nabla\psi_i(r)|^2 - \frac{1}{8}\frac{|\nabla\rho(r)|}{\rho(r)}}{\frac{3}{10}(3\pi^2)^{\frac{2}{3}}\rho(r)^{\frac{5}{3}}}. \qquad \text{Eq.3}$$

ELF takes the values in the range between 0 and 1. When $n(r) > 0.7$, the electrons are characterized as localized, indicating strong covalent bonding. If $0.2 < n(r) < 0.7$, the electrons are delocalized similar to metallic bonding. Figure 2 depicts the ELF of the direct-stacked biphenylene network. In Figure 2a, we observed highly localized electron density between the C atoms. Basins are almost spherical located in the middle of the C-C bond which describes single σ bonds between atoms. These results are the characteristic definition of strong covalent bonding between atoms in the biphenylene network[15]. In Figure 2c, we can see a suppressed ELF in the interface of the bilayer system indicating an induced dipole. The same trend is observed in the trilayer system as shown in Figure 2d. The induced dipole is proportional to the number of layers of the network. According to Eq. 1, the binding energy per Biphenylene network is -0.39 eV and -0.54 eV, for bilayer and trilayer systems, respectively. The increase in the magnitude of the binding energy is attributed to a more induced dipole present in the trilayer system. This type of interaction between the biphenylene network is similar to the stacking of graphene and other hybrid systems [15, 22].



(a) (b) (c) (d)

Fig.ure2. The 2D ELF of monolayer biphenylene network (a) horizontal and (b) vertical plane monolayer Biphenylene network. (c) and (d) are the vertical 2D ELF of the bilayer and trilayer biphenylene network.

CONCLUSION

We explored the bonding mechanism of direct-stacked biphenylene network using first-principles method. The calculations reveal that the interaction between the layers of the biphenylene network is due to the van der Waals interaction indicated by the deformed ELF in the interface. This is further supported by the weak binding

energy of the direct-stacked system. We anticipate that these findings will serve as a reference for future investigation and practical use of the biphenylene network.

ACKNOWLEDGMENT

We would like to acknowledge Jose Rizal Memorial State University – Tamplisan Campus, Mindanao State University – Marawi Campus, and Mindanao State University – Iligan Institute of Technology for the support and motivation that led to the success of this paper.

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