Biphenylene monolayer as a two-dimensional nonbenzenoid carbon allotrope: a first-principles study

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Abstract
In a very recent accomplishment, the two-dimensional form of biphenylene network (BPN) has been fabricated. Motivated by this exciting experimental result on 2D layered BPN structure, herein we perform detailed density-functional theory-based first-principles calculations, in order to gain insight into the structural, mechanical, electronic and optical properties of this promising nanomaterial. Our theoretical results reveal the BPN structure is constructed from three rings of tetragon, hexagon and octagon, meanwhile the electron localization function shows very strong bonds between the C atoms in the structure. The dynamical stability of BPN is verified via the phonon band dispersion calculations. The mechanical properties reveal the brittle behavior of BPN monolayer. The Young’s modulus has been computed as 0.1 TPa, which is smaller than the corresponding value of graphene, while the Poisson’s ratio determined to be 0.26 is larger than that of graphene. The band structure is evaluated to show the electronic features of the material; determining the BPN monolayer as metallic with a band gap of zero. The optical properties (real and imaginary parts of the dielectric function, and the absorption spectrum) uncover BPN as an insulator along the zz direction, while owning metallic properties in xx and yy directions. We anticipate that our discoveries will pave the way to the successful implementation of this 2D allotrope of carbon in advanced nanoelectronics.

Keywords: density functional theory, first-principles study, carbon allotrope, biphenylene monolayer, two-dimensional nonbenzenoid

(Some figures may appear in colour only in the online journal)

1. Introduction
Carbon can be found in a variety of allotropes. Aside from diamond and graphite, other found types with remarkable characteristics have been identified due to the carbon tendency to be present in several hybridizations. Carbon’s ability to form in a variety of shapes through different dimensions has sparked interest in discovering additional allotropic forms made up of diverse networks of rings and polygons. To clarify, researchers have identified a wide range of carbon allotropes composed of...
Several types of carbon allotropes exist, including sp\(^3\), sp\(^2\), and sp hybridized carbon atoms such as graphenylene [1], graphdiyne [2], graphyne [3], cyclocarbons [4], pentaheptite [5], graphene [6], phagraphene [7], heackelites [8], pentahexoctite [9], carbon nanotubes [10], carbon nanocone [11], and fullerene [12]. Owing to their electronic and mechanical properties, these materials have been widely advocated as a possible candidate for popularly used applications such as sensors [13], energy storage [14], nanoelectronic devices [9], thermal rectifier [15], etc. Among these forms of carbon allotropes, two-dimensional (2D) graphene and its like have been extensively studied theoretically and experimentally [16–20]. In addition, graphene has piqued the curiosity of scientists in a wide range of domains. To be more specific, this 2D material is a single, thin sheet of carbon atoms organized in a hexagonal honeycomb pattern that is one atom thick. The immense attention for graphene is due to the specific characteristics that set it apart from its 2D brethren. To exemplify, graphene’s most impressive features are thermal, electronic, and mechanical properties such as its large surface area [21], brilliant high Young’s modulus [22], excellent thermal conductivity [23], and electronic mobility [24].

Although recent technological advances have led to tremendous progress in the creation and manufacture of many carbon allotropes, there are forms in which carbon atoms themselves can be organized that have still to be discovered. This was confirmed by a very recent experimental study carried out by scholars who identified a kind of non-benzene carbon named biphenylene which is as thin as graphene and thus as thin as an atom [25]. This carbon grid is made up of octagons, hexagons, and squares of sp\(^2\) carbon atoms that were derived from a regular grid. According to the researchers, this material appeared to have fascinating electronic characteristics that differ from those of graphene. They synthesized this non-benzene carbon bottom-up approaches and used high-resolution scanning probe microscopy to establish the network’s unique structure and discovered that its electronic characteristics are significantly distinct from that of graphene. Importantly, authors found that the measured bandgap decreased with increasing the widths of biphenylene ribbon. Despite this, the form of carbon boasts metallic properties thanks to its narrow webbing stripes that are 21 atoms wide. However, a non-benzene 2D carbon polymorph containing rings that have 6 or more atoms will possibly give better anode materials in lithium–ion rechargeable batteries because of its expected higher lithium storage capacity than graphene [26]. Precisely, these stripes can be utilized as conductive wires in lithium–ion batteries and carbon-based electronic systems.

In this paper, motivated by the very recent successful experiments on the biphenylene network (BPN), we investigate the structural, mechanical, electronic and optical properties of named BPN network using first-principles simulations. The present results constitute a significant breakthrough in our knowledge of the properties of this nanostructure. We anticipate that our results will pave the way to the successful implementation of this 2D allotrope of carbon in future nanoelectronics and optoelectronic devices.

2. Method

The density-functional theory (DFT) calculations in this work are performed using the plane-wave basis projector augmented wave method along with generalized gradient approximation with Perdew–Burke–Ernzerhof (PBE) [27, 28] functional as implemented in the Vienna ab initio simulation package [29, 30]. The kinetic energy cut-off of 600 eV is set for plane-wave expansion and the energy is minimized for the structure until variation in the energy falls below 10\(^{-5}\) eV. To get optimized structures, total Hellmann–Feynman forces are reduced to 0.05 eV Å\(^{-1}\). The k-points for sampling over the Brillouin zone integration are generated using the Monkhorst-Pack scheme [31] with 19 \(\times\) 19 \(\times\) 1 \(\Gamma\) centered k-point sampling. Charge transfer analysis is accomplished using the Bader technique [32]. The vibrational properties are obtained from the small displacement method as implemented in the PHONOPY code [33]. Simulated scanning tunneling microscopy (STM) images are obtained using the Tersoff–Hamann theory [34] and are graphed using WSxM software [35].

3. Structural and mechanical properties

Top and side views of the atomic structure of the BPN monolayer with structural parameters such as bond length and bond angles displayed in figure 1(a). The lattice of BPN is orthorhombic and belongs to the space group \(Pm\) (No. 6). It has a rectangular primitive unit cell, indicated as a red dashed line rectangle. The primitive unit cell of BPN carbon lattice is formed by 6 C atoms. The lattice constants of BPN orthorhombic structure are calculated to be 3.75 Å (a) and 4.52 Å (b). In the BPN structure lattice, we can see three types of C–C rings of tetragon, hexagon and octagon. The bond lengths in the C–C tetragon ring is determined to be \(d_1 = 1.45\) Å and the bond angle is 90°. In the C–C hexagon ring, \(d_1\) is equal to 1.40 Å and the bond angle of C–C–C is 109°, while in the C–C octagon ring \(d_1\) is 1.44 Å, with the respective bond angle of the C–C–C being 125°. The optimized structure of the BPN monolayer has a planar lattice and no C atom deviates from this two dimensional sheet. The structural parameters are gathered and given in table 1. To get a better understanding of the underlying characteristics of bonding properties, the electron localization function (ELF) along the (0 0 1) plane and total charge density are quantified and illustrated as insets in figure 1(a). This sum takes a value between 0 and 0.5, where ELF = 0.5 corresponds to perfect localization. The ELF value between C atoms is around the maximum amount of 0.50, which shows a large proportion of bonds in the BPN monolayer as very strong covalent bonds. This is clearly depicted in figure 1(a), where the color red shows intense localization and in turn, a stronger bond. The dynamical stability of BPN is verified using phonon band dispersions shown in figure 1(b). As seen in this figure, the phonon band structure does not have any of the bands enter the negative realm and is therefore, stable.

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Figure 1. (a) Atomic structure and ELF; (b) phonon band dispersion, and (c) STM simulated image of the BPN monolayer. Square primitive unit cell is indicated by the red dotted line. The ELF and total charge density are indicated as inset.

Table 1. Structural and electronic parameters of the optimized BPN monolayer as shown in figure 1(a), including: lattice constants $a$ and $b$, bond lengths of C–C atoms in tetragon ring ($d_1$), hexagon ring ($d_2$) and octagon ring ($d_3$), bond angles of C–C–C atoms in tetragon ring ($\theta_1$), hexagon ring ($\theta_2$) and octagon ring ($\theta_3$), cohesive energy per atom ($E_{\text{coh}}$) and electronic states ($ES$) which are specified as metal (M). Work function $\Phi$; shear modulus (S); Young’s modulus (Y); and Poisson’s ratio ($\nu$) are also inserted into the table.

| Sys. | $a$ (Å) | $b$ (Å) | $d_{1,2,3}$ (Å) | $\theta_{1,2,3}$ (°) | $E_{\text{coh}}$ (eV/atom) | $ES$ | $\Phi$ (eV) | S (TPa) | Y (TPa) | $\nu$ |
|------|---------|---------|-----------------|-----------------|--------------------------|------|-----------|--------|---------|------|
| BPN  | 3.75    | 4.52    | 1.45,1.40,1.44  | 90,109,125      | $-7.55$                  | M    | 4.30      | 0.03   | 0.10    | 0.26 |

The phonon spectrum depicts an in-plane transverse (TA) and a longitudinal (LA) optical mode, with linear dispersion and an out-of-plane mode (ZA) in the long-wavelength limit. The slight penetration of ZA mode in negative frequencies is just noise. There is anisotropy in the slope of TA and LA branches between $\Gamma$–X and $\Gamma$–Y directions, which depicts the anisotropy as the sound velocity in this system. In addition, here, we can not recognize a striking gap between the high-frequency and low-frequency optical branches. The STM simulated image is obtained from first-principles DFT calculations in order to provide visible guidance for future experimental observations (see figure 1(c)). The atomistic structure is easily recognized from the predicted STM image, where the C atoms are brighter. The cohesive energy per atom that quantifies the stability of a material is calculated using the following equation:

$$E_{\text{coh}} = [E_{\text{tot}} - n_C E_C]/(n_C),$$ (1)

where $E_C$ represents the energy of an isolated single C atom, $E_{\text{tot}}$ represents the total energy of the BPN and $n_C$ stands for the number of C atoms in the primitive unit cell. The negative cohesive energy for this layer suggests that the free-standing state of the structure is likely to be stable, which is a very important clue for technologists in their quest for planar sp²-hybridized carbon allotropes. The calculated cohesive energy for BPN is $-7.55$ eV/atom, and is shown in table 1. It is found out that the electrostatic potential of the BPN monolayer is flat in the vacuum region. The work function of BPN is calculated using the following formula: $\Phi = E_{\text{vacuum}} - E_F$ and is determined to be 4.30 eV. The mechanical properties of the BPN monolayer evaluated using harmonic approximation indicate that all elastic constant values (13 independent elastic constants) satisfy the Born’s criteria, which confirms the mechanical stability of BPN. Young’s modulus (0.10 TPa) is smaller than the experimental (2.4 TPa) [36] and theoretical (1.0 TPa) values of graphene [37, 38]. Due to the large lattice constant, slightly larger C–C bond length, and smaller symmetry of the BPN sheet as compared to graphene. We find out that shear modulus is 0.03 TP much less than that of graphene, 0.3 TP [39] and the Poisson’s ratio is 0.26, which is larger than that of graphene (0.16) [40] and is very close to that of MoS$_2$N$_4$ (0.28) [41]. The value of Poisson’s ratio indicates
that the BPN monolayer has brittle behavior (it is less than 0.33 [42]).

4. Electronic properties

The results of the electronic structure calculations, i.e., the band structure, density of states (DOS) and projected DOS (PDOS) of the BPN monolayer are presented in figures 2(a) and (b). In the bands portrayed here, no space is seen unaltered between the VBM and the CBM, resulting in metallic features in the structure. The Dirac cone is formed slightly above the Fermi level and is severely tilted to the side. This tilt has been observed in other Dirac/Weyl materials [43–45] and the solid-state system containing this tilted cone have been interpreted as systems where the effective spacetime is non-Minkowski and it is, in turn, deformed [46]. A zoom of the band structure and the atomic structure with C atoms is illustrated in right of the panel in figure 2(a). The crossing point of energy bands at the Fermi level indicates metallicity of the BPN, which is confirmed by DOS at the Fermi level. A Dirac point was observed above the Fermi level, however, different to that of graphene. As displayed in figure 2(a), the Dirac point at a high symmetry point (between Γ–Y) was observed, but it was about 0.5 eV above the Fermi level. The corresponding Fermi velocity (v_F) of the Dirac fermions has been evaluated by linear fitting the first derivatives of the band energies near the Dirac point. The energy bands of BPN monolayer in the vicinity of the Dirac point were very different in comparison to graphene. These bands exhibit a linear dispersion in both k_x and k_y directions and one can see an anisotropic Dirac point. The slope of the energy bands near the Dirac cone, equivalent to a Fermi velocity v_F = E/k, where is the reduced Planck’s constant. The Fermi velocity for these linear dispersion bands is calculated as 0.01 and 0.14 × 10^6 m s^−1 in k_x and k_y directions, respectively. The Fermi velocities of BPN were much smaller than that of graphene (0.95 × 10^6 m s^−1), [47] but much larger than that of α-graphyne (0.67 × 10^6 m s^−1) [48]. It should be noted that the Fermi velocity at the DFT Kohn–Sham level is usually underestimated in comparison with the corresponding GW value and the experimental one [47]. This indeed multiplies the importance of the BPN monolayer and opens a path for further investigations. The total DOS of the system is also displayed in figure 2(a), with the addition of a DOS where the effects from the C_1 and C_2 atoms are seen. These atoms represent the only symmetries where the DOS is specific and all the other symmetries would be equal.
Figure 3. (a) Real (Re(\varepsilon)) and (b) imaginary (im(\varepsilon)) parts of the dielectric function, and (c) the absorption coefficient vs the photon incident energy.

atoms of the system take the same shape as one of the chosen particles. This can be understood given the mirror symmetries present in the two dimensional sheet. The noteworthy part of this DOS is near the Fermi level, where the atom of C\textsubscript{2} is in full effect, contrary to C\textsubscript{1} which gives a very little contribution. The position of these two atoms is illustrated in figure 2(a). PDOS of the indicated atoms is drawn in figure 2(b). In this shape, the s, p\textsubscript{x}, p\textsubscript{y} and p\textsubscript{z} shells are given separately. PDOS of C\textsubscript{1} and C\textsubscript{2} show striking resemblance in some sections, but are wildly different in other areas. Both atoms show a heavy involvement of p\textsubscript{z} shell near the Fermi level; while, as mentioned before, only C\textsubscript{2} is intensely contributing when it gets close to the line. It is also witnessed for both atoms that with getting further away from the Fermi level, the p\textsubscript{x} shell subsides completely and abruptly. This happens as the p\textsubscript{x} shell also ceases to exist almost completely in the atom of C\textsubscript{1} after going deep in the states, while the same thing does not happen in C\textsubscript{2} and p\textsubscript{x} continues to contribute strongly even further down the line.

5. Optical properties

The real and imaginary parts of the dielectric function of BPN monolayer are illustrated in figures 3(a) and (b). These are typically used to describe the monolayer response to the electromagnetic field. That is, wherever a part of the dielectric function is negative, electromagnetic waves become weak and absorption or reflection occurs. The real and imaginary parts of the dielectric function are connected by the Kramers–Kronig relations. The dielectric function has two interband and intraband transitions; the interband transition is due to the excitation of the absorption edges, however, the intraband
transition happens because of the volume of plasmon excitation. The imaginary part of the dielectric function is calculated by taking into account all possible transitions from occupied to unoccupied states. In figure 3(a), the static value of the real part has shown that its value is 12.5, 2.5 and 1.3 for \( xx \), \( yy \) and \( zz \) components, respectively. Many peaks appear in the \( xx \) and \( yy \) directions from 0.5 eV to 5.0 eV. Furthermore, many small peaks appear in all directions when moving past 10.0 eV. According to the imaginary part of the dielectric function (figure 3(b)), it can be seen that the value of the imaginary part in \( xx \) direction tends to be infinitely positive, which represents the extremely intense metallic behavior. Similar to the real part, the imaginary part also owns many peaks above 10.0 eV in all directions. One can notice that the value of the imaginary part is zero from 5.0 eV to 10 eV in \( yy \) direction and from 0.5 to 10.0 eV in \( zz \) direction. Optical absorption depends on the imaginary part of the dielectric tensor, where the electrons in valence band states are induced by absorbing a photon into the conduction band states. The absorption peaks in the \( yy \) direction, from 0 eV to 5 eV, are shifted towards larger energies, which are related to the behavior of real and imaginary dielectric constants. In addition, the zero absorption in the \( zz \) direction is related to the zero value of the imaginary part and a constant value of the real part within the same energy range from 0.0 eV to 10 eV. The absorption amount is very large at energies higher than 10.0 eV for all components (figure 3(c)). The \( xx \) and \( yy \) components have absorption peaks in the energy range from 0.0 eV to 7.5 eV, meanwhile there is no any contribution in the \( zz \) direction. This phenomenon dictates metallic properties in \( xx \) and \( yy \) directions and insulating behavior along \( zz \) direction.

6. Conclusion

The structural, electronic and optical properties of the BPN monolayer are investigated by means of first-principles calculations. The overall shape of the BPN is constructed from three rings of tetragon, hexagon and octagon, meanwhile the ELF shows very strong bonds between the C atoms in the structure. The phonon band dispersion provides a substantial proof for the dynamical stability of BPN, as no bands have values of less than zero. The STM simulated image has been evaluated and shows a picture that can be extremely useful in order to observe the structure in future experimental endeavors. BPN gives a cohesive energy of \(-7.55\) eV/atom, while the work function value is determined to be 4.30 eV. Mechanical properties calculations have revealed the brittle behavior of the BPN monolayer. The electronic band structure reveals the BPN as a metal with conduction and valence bands overlapping considerably on the Fermi energy level. A tilted Dirac cone does appear in the bands, slightly higher than the Fermi energy level. The optical properties, are calculated giving valuable information about where absorption or reflection is bound to happen. These two parts of the dielectric function, along with the absorption coefficient vs the photon incident energy, demonstrate the metallic properties of the BPN monolayer in \( xx \) and \( yy \) direction and insulating behavior along the \( zz \) direction.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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