Cp-Graphyne: A Low-Energy Graphyne Polymorph with Double Distorted Dirac Points

Naga Venkateswara Rao Nulakani†‡*, and Venkatesan Subramanian†*,‡‡

†Inorganic & Physical Chemistry Department, CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India
‡Academy of Scientific and Innovative Research (AcSIR), CSIR-CLRI Campus, Chennai 600020, India

Supporting Information

ABSTRACT: In the present investigation, we have proposed a novel form of two-dimensional (2D) carbon allotropes with the aid of first-principle density functional theory-based calculations. The carbon polymorph is mainly composed of carbon pentagons (cp) and acetylenic linkers and hence named cp-graphyne. This 2D material is energetically more preferable than the rest of the semimetals of graphyne family, including graphdiyne monolayer. Close inspection of lattice dynamics and thermal and mechanical properties demonstrates the excellent dynamic, thermal, and mechanical stabilities of cp-graphyne. Interestingly, cp-graphyne exhibits a semimetallic nature and possesses double distorted Dirac points in the electronic band spectrum. The Fermi velocities ($v_F$) of cp-graphyne are highly anisotropic and are predicted to be in the range of $1.50 \times 10^5$–$8.20 \times 10^5$ m/s. Furthermore, the analysis of structural and electronic properties of the cp-graphyne bilayer discloses the presence of self-doped Dirac-like points nearer to the Fermi level in the electronic spectrum.

1. INTRODUCTION

The success of graphene1–3 in various fields, including chemistry and materials science and technology, provokes the researchers to develop multifunctional two-dimensional (2D) materials.4–10 For example, a broad range of 2D materials have been reported in the literature, including the elemental allotropes of C,11–14 Si,15 Ge,16,17 Sn,18,19 B,20,21 Al,22 and P,23 and their 2D alloys with different stoichiometric ratios using both theoretical and experimental strategies. However, graphene is exceptional among all of these materials due to its topological properties,11–14 when compared with those of other 2D materials. The unique electronic properties of graphene, including massless Dirac fermions,27 half-integer quantum Hall effect,28 Klein paradox,29 ultrahigh carrier mobility, and other topological properties,30,31 are mainly attributed to linear band dispersion in proximity of the Fermi level around the high-symmetry special points, $K$ ($K'$). The linear dispersion in the valence band (VB) and conduction band (CB) leads to the formation of double Dirac cones. The vertices of the two Dirac cones meet each other at only one contact point, $K$ ($K'$), on the Fermi level in the hexagonal Brillouin zone. This contact point is called the Dirac point of graphene. Similar electronic systems are well-defined by the relativistic Dirac equation rather than by the usual Schrödinger equation. The 2D or three-dimensional (3D) materials coupled with these properties are grouped into a special case of materials, the Dirac materials.32,33

Numerous 2D materials have been reported in the literature33 within the context of Dirac materials with linear band dispersion and associated Dirac points. For example, the other members of group IV elements such as silicon and germanium also form stable 2D materials, namely, silicene and germanene, respectively. Recently, single and multilayers of silicene and germanene have been synthesized on metallic substrates. Excitingly, the 2D monolayers of silicene15,34 and germanene35 show linear band crossing at the Fermi level similar to that in graphene. Furthermore, the electronic structure of a 2D alloy of silicon and germanium, that is, silicon germanide35 monolayer, was also characterized by the Dirac cones in the proximity of the Fermi level. The boron counterparts, such as Pmnn-boron36 and striped boron sheet (hr-sB),37 depict the Dirac states in their electronic band spectrum. Furthermore, the two-dimensional transition metal diborides, which include $m$-TiB$_2$38 and FeB$_2$,39 have linear band dispersion in their electronic band structure. Distinct from those in graphene, the Dirac states in these 2D materials are primarily originated from the d-orbitals of transition metal atoms. Similar to the $m$-TiB$_2$ and FeB$_2$, so-MoS$_2$,40 also uses its d-orbitals for the formation of linear band dispersion in the proximity of the Fermi level. Interestingly, the massless Dirac fermions in so-MoS$_2$ coexist with the massive fermions. The monolayer of black phosphorus is a semiconductor with a
direct band gap of 1.00 eV at the center of the Brillouin zone. However, it is plausible to achieve Dirac states in the multilayered black phosphorus by the application of an optimal external electric field. The planar Be5C2 and quasi-planar Be5C6 monolayers have recently been predicted to exhibit semimetallic nature with Dirac-like points. A broad range of 2D networks of conjugated polymers also demonstrates conical valence and conduction bands in their electronic fingerprints analogous to those of graphene. The heteroatomic networks (janugraphene and chlorographene)\textsuperscript{11} coupled with the rectangular lattices and nonequivalent bonds also possess Dirac points. Graphene with nitrogen line defects, Ni2C18H12, and Co2C18H12\textsuperscript{47} are some of the 2D materials with linear band dispersion relation in their electronic band structures. This indicates that there is an immense interest in exploring novel materials with Dirac points.

In addition to these heteroatomic 2D architectures, there is another class of Dirac materials, which includes only pure carbon allotropes. The pure carbon-based Dirac materials are mainly composed of sp- and sp\textsuperscript{2}-hybridized C atoms. For instance, phagraphene\textsuperscript{12} is a 2D carbon network, which is mainly composed of sp\textsuperscript{2}-hybridized 5-6-7 carbon polygons. Furthermore, phagraphene is familiar for its outstanding thermodynamic feasibility and distorted Dirac cones. Similarly, S-graphene, D-graphene, E-graphene, and ph-graphene\textsuperscript{49} mostly comprise sp\textsuperscript{2}-hybridized C atoms in their 2D architectures. These materials also have linear band dispersion and consequent Dirac points at the Fermi level. On the other hand, most of the graphyne\textsuperscript{50} networks, such as α-, β-, δ-, α\textsuperscript{-}, and γ-graphyne\textsuperscript{54} are included in the family of Dirac materials. Distinct from graphene, graphynes and graphynes\textsuperscript{14} and α-graphdiyne,\textsuperscript{54} are in the family of Dirac materials. Distinct from graphene, graphynes, and graphynes\textsuperscript{14} and α-graphdiyne\textsuperscript{54} are all made up of sp\textsuperscript{2}-hybridized C atoms in their 2D architectures and consequent Dirac points at the Fermi level.

The ratio of sp-hybridized C atoms in the monolayer gives an intuition regarding the structural stability\textsuperscript{13} and experimental feasibility of the 2D graphene network. The presence of sp-hybridized C atoms in these graphynes makes them relatively less favorable when compared with graphene. However, the energetic stability of γ-, δ-, and 6,6,12-graphynes is slightly higher than that of the recently fabricated graphdiyne\textsuperscript{55} monolayer. This implies that γ-, δ-, and 6,6,12-graphyne monolayers may be synthesized using the experimental methods in the future. Furthermore, γ-graphyne has higher energetic preference rather than that of δ- and 6,6,12-graphynes. However, γ-graphyne is a narrow direct band gap\textsuperscript{56} semiconductor. Hence, it is highly inevitable to predict novel members with high energetic preference and graphene-like electronic energy dispersion.

In the present study, we have proposed a novel 2D carbon polymorph using the state-of-the-art theoretical methods. The carbon polymorph is mainly composed of carbon pentagons and acetylenic linkers. This 2D material has higher energetic preference than that of most of the graphynes which are reported till date including δ- and 6,6,12-graphynes. The comprehensive study on dynamic, thermal, and mechanical stabilities exposes the prospects for the practical existence of this 2D material. Furthermore, the same carbon sheet is furnished with esthetically pleasing double distorted Dirac points and anisotropic charge carrier mobilities. We have also studied the structural and electronic properties of the bilayer of this 2D material. The most stable stacking mode of the cp-graphyne bilayer shows self-doped Dirac points.

### 2. COMPUTATIONAL DETAILS

All calculations were performed using the Vienna ab initio simulation package\textsuperscript{57–59} within the framework of density functional theory (DFT). The electron–electron interaction was calculated by the generalized gradient approximation\textsuperscript{60} parameterized by Perdew–Burke–Ernzerhof. The electron–ion interaction was described by the projector augmented wave\textsuperscript{61} method. The plane waves were extended with a kinetic energy cutoff of 520 eV. A 4 × 4 × 1 Monkhorst–Pack\textsuperscript{62} k-mesh was included in the energy minimization of the 2D carbon lattice. The energy difference between two consecutive steps was set to less than 10\textsuperscript{−8} eV in the self-consistent iterative technique. The residual Hellmann–Feynman force was set to less than 10\textsuperscript{−3} eV/atom. The static self-consistent calculations were performed with a denser mesh of 8 × 8 × 1 k-point set. The phonon band spectrum was calculated using the open source Phonopy package.\textsuperscript{63} The thermal stability was analyzed by performing the first-principles finite temperature molecular dynamics (FPMD) simulations. The total simulation was carried out for 5 ps at room temperature (300 K) with a time step of 1 fs using an NVT ensemble. The optimal interlayer distance in all of the bilayers was explored using van der Waals-corrected density functional theory (vdW-DF2).\textsuperscript{64} A vacuum of 15 Å was included along the z direction to avoid interlayer interactions.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural Properties

This section describes the structural properties of the novel 2D carbon allotrope. The
optimized crystal structure of the carbon pentagon-based 2D material is presented in Figure 1a. This 2D material exhibits \textit{P4/mmb} (\textit{D}_{4h}^{5}) symmetry and belongs to the tetragonal space group (space group no. 127). The equilibrium lattice parameters of the unit cell of this 2D carbon allotrope are predicted to be $a = b = 12.365$ Å. Furthermore, the unit cell is composed of 40 carbon atoms. Among these 40 C atoms, 20 are incorporated to form four five-membered rings and the remaining C atoms are utilized to form 10 acetylenic linkers. The carbon pentagons are joined together by the acetylenic linkers. Hence, we named this novel 2D material cp-graphyne, which stands for carbon pentagons with ethyne linkers. The cp-graphyne exhibits slightly altered bond lengths and bond angles from the regular sp and sp$^2$ bond parameters, which are found in graphene and graphynes.\textsuperscript{50} For example, the calculated bond lengths are in the range of 1.44–1.46 and 1.23–1.38 Å around the five-membered rings and along the acetylenic-type linker, respectively, as observed from Table 1. The central acetylenic-type C–C bond is the shortest (1.23 Å) among all of the C–C bonds of cp-graphyne. Furthermore, the bond angles are in the range of 107–109 and 121–132° in the interior and exterior of the carbon pentagon of cp-graphyne, respectively. Some of the acetylenic linkers also slightly distorted from the linear structure and show a bond angle of $\sim$168°. It is evident from Figure 1b that higher charge density is accumulated at the middle of the acetylenic linker, followed by its end C–C bonds and the carbon pentagons. This is in close association with the C–C bond lengths in cp-graphyne. The Wycko positions of six inequivalent C atoms of cp-graphyne are presented in the Figure S1, Supporting Information.

### 3.2. Structural Stabilities

#### 3.2.1. Energetic Stability

The altered bond lengths and bond angles of cp-graphyne increase the total energy, which leads to suspect the structural stability of the system. Hence, we have calculated the cohesive ($E_c$) and formation ($E_f$) energies of cp-graphyne to understand the structural stability. Furthermore, the cohesive and formation energies of cp-graphyne are also compared with those of previously reported 2D graphyne lattices to understand its relative stability and thermodynamic feasibility. Results show that the cohesive energy of cp-graphyne ($\sim$7.30 eV/atom) is higher than that of all other previously reported graphyne systems, including α– (\textit{−7.04 eV/atom}), β– (\textit{−7.12 eV/atom}), δ– (\textit{−7.22 eV/atom}), R– (\textit{−7.15 eV/atom}), and 6,6,12-graphyne (\textit{−7.23 eV/atom}), square graphynes (\textit{−7.04 to −7.14 eV/atom}), and graphdiyne (\textit{−7.20 eV/atom}), and closer to that of γ-graphyne (\textit{−7.33 eV/atom}) (see Table S1). This indicates that cp-graphyne is the strongly bonded carbon network when compared with the graphdiyne monolayer and all other 2D

| bond lengths (Å) | bond angles (deg) |
|-----------------|-----------------|
| **in carbon pentagon** | **interior of carbon pentagon** |
| C1–C2 | 1.44 | C5–C1–C2 | 107.53 |
| C1–C5 | 1.44 | C1–C2–C2 | 107.87 |
| C2–C2 | 1.46 | C1–C5–C1 | 109.20 |
| **along the acetylenic-type linker** | **exterior of carbon pentagon** |
| C1–C4 | 1.38 | C4–C1–C2 | 131.40 |
| C2–C3 | 1.38 | C1–C2–C3 | 126.07 |
| C3–C4 | 1.24 | C3–C2–C2 | 126.06 |
| C5–C6 | 1.37 | C4–C1–C5 | 121.08 |
| C6–C6 | 1.23 | C1–C5–C6 | 125.40 |
| **along the acetylenic-type linker** | **along the acetylenic-type linker** |
| C1–C4 | 1.44 | C1–C4–C3 | 167.75 |
| C2–C3 | 1.38 | C4–C3–C2 | 179.72 |
| C3–C4 | 1.24 | C5–C6–C6 | 180.00 |
graphynes (except γ-graphyne) included in this study. Furthermore, the computed formation energies of some of these graphyne layers are plotted with respect to the formation energy of graphene in Figure 2a. It is important to mention here that large-area graphdiyne films have been fabricated on the surface of copper using experimental methods. Hence, we have considered the formation energy of the graphdiyne monolayer as a reference point (represented by the black dashed line) to address the experimental feasibility of all of these graphyne monolayers including cp-graphyne (see Figure 2a). It shows that all other graphyne monolayers are energetically less favorable when compared with the graphdiyne. However, the experimental realization of a graphyne system can be expected for those 2D lattices with the formation energy lower than that of the graphdiyne monolayer. This indicates that δ-, 6,6,12-, cp-, and γ-graphynes are energetically more favorable than the graphdiyne monolayer and their practical applications may be plausible in the future. In particular, cp-graphyne is energetically more viable than the reference point by about 94 meV/atom, δ-graphyne, by about 76 meV/atom, and 6,6,12-graphyne, by about 67 meV/atom. It could be noted here that, indeed the γ-graphyne is slightly favorable than cp-graphyne, it is a direct band gap semiconductor. Hence, cp-graphyne can be considered as the first low-energy carbon polymorph in the family of semimetallic graphynes (see Table S1).

3.2.2. Dynamic Stability. The lattice dynamics of cp-graphyne was analyzed by computing phonon band dispersion using the supercell approach as implanted in the open source Phonopy package. We have used a $2 \times 2 \times 1$ supercell to calculate the vibrational modes of cp-graphyne along the high-symmetry k-points throughout the first Brillouin zone. It is clear from Figure 2b that the 2D lattice is free from imaginary modes in the first Brillouin zone. This feature endorses the dynamical stability of cp-graphyne.

3.2.3. Thermal Stability. We have analyzed the thermal stability of cp-graphyne by performing first-principles molecular dynamics (FPMD) simulations at room temperature for 5 ps. The calculated results are presented in Figure 2c. It shows that the total energy is fluctuating around a constant value throughout the simulation. Furthermore, the snapshot taken at the end of simulation is depicted in Figure S2. It shows that the C atoms of cp-graphyne are slightly displaced from their equilibrium positions in the course of the simulation. However, the C–C bonds are rigid enough to retain the original structure of cp-graphyne. This indicates that cp-graphyne is thermally stable at room temperature.

3.2.4. Mechanical Stability. Finally, we have tested the mechanical stability of cp-graphyne using density functional theory-based methods. We have applied the in-plane tensile strain along the uniaxial and biaxial directions to examine the mechanical stability of cp-graphyne. The in-plane strain has increased in steps of 1% by varying the equilibrium lattice constants of cp-graphyne. The corresponding stress values are rescaled by $Z/d^2$ to obtain the equivalent stress $\sigma_{eq}$ similar to the previous studies. Here, $Z$ is the vacuum length between the periodic images and $d^2$ (3.6 Å) is the optimal interlayer distance between the cp-graphyne layers in its 3D bulk structure. It is evident from Figure 3a that cp-graphyne can withstand up to a maximum stress of 25 GPa, which occurs at 17% of the uniaxial strain. On the other hand, the same sheet can sustain up to a maximum stress of 32 GPa, which occurs at 11% of the biaxial strain. The rupture of the C–C bond in the carbon pentagons is the rationale behind the mechanical instability of cp-graphyne after the 17% uniaxial and 11% biaxial strains, as evident from Figure S3. The strain calculations have also been performed by giving small perturbations in the carbon positions without any symmetry constrains to test the stability of cp-graphyne. However, the 2D system is stable with the same geometrical features and the uniaxial and biaxial mechanical strengths are not varied. Furthermore, the mechanical stability of 2D materials can also be estimated by evaluating the independent elastic stiffness tensor components. According to the Born criteria, the elastic constants of a mechanically stable tetragonal system need to satisfy the following conditions: $C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $C_{11} - C_{33} > 0$, $C_{11} + C_{33} - 2C_{13} > 0$, $2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0$. It is evident from Table 2 that cp-graphyne satisfies all of the above-mentioned conditions. These results corroborate the mechanical stability of cp-graphyne. The estimated Young’s modulus (Y) of cp-graphyne (81 GPa nm) is quite low when compared to that of graphene (347 N/m). The low areal density (0.26 atom/Å²) and highly porous nature of cp-graphyne are responsible for such a low Young’s modulus. On the other hand, the Poisson’s

Table 2. Calculated Elastic Constants $C_{ij}$ (GPa nm) of cp-Graphyne

| $C_{ij}$ | GPa nm |
|---------|--------|
| $C_{11}$ | 90.23  |
| $C_{33}$ | 1.35   |
| $C_{44}$ | 0.81   |
| $C_{66}$ | 24.11  |
| $C_{12}$ | 27.92  |
| $C_{13}$ | -0.71  |
Figure 4. Calculated electronic structure of cp-graphyne. (a) Full and irreducible Brillouin zone (shaded with red color) along which the bands are plotted. (b) Two-dimensional electronic band structure. Three-dimensional electronic band structure of VB and CB around Dirac points (c) D1 and (d) D2. The Fermi level is set as zero in all cases.

Figure 5. Calculated electronic properties of cp-graphyne. (a) Total and partial density of states. Partial charge densities corresponding to the (b) valence band (VB) and (c) conduction band (CB) in the vicinity of the Fermi level. (d) D2. The Fermi level is set as zero in all cases.
Figure 6. Structural and electronic properties of the cp-graphyne bilayer. (a) AA-stacking mode, (b) AB-stacking mode, and (c) most stable AC-stacking mode of the cp-graphyne bilayer. (d) Electronic band structure, (e) amplification of the bands around the self-doped Dirac-like points, and (f) 3D band structure of the valence and conduction bands of the cp-graphyne bilayer around the self-doped Dirac-like points. The Fermi level is set as zero in all cases (carbon spheres are presented with different color codes in (a)–(c) for clarity).

\(v_f = 3.39 \times 10^4 \text{ m/s and } 3.98 \times 10^5 \text{ m/s, for electrons})\) when approaching Dirac point D2 from high-symmetry special points M and \(\Gamma\). In addition to this, the 2D contour plots of both valence and conduction bands also substantiate that the energy distribution is asymmetric around Dirac points D1 and D2 (see Figure S4). These results suggest that cp-graphyne contains two pairs of distorted Dirac cones around Dirac points D1 and D2 in the vicinity of the Fermi level. These distorted Dirac cones facilitate highly anisotropic electronic properties in cp-graphyne. Overall, cp-graphyne has eight distorted Dirac points (four pairs of D1 and D2) in the first Brillouin zone, as given in Figure 4a. The four Dirac points either at D1 or at D2 are related to each other by rotational symmetry \((C_2)\). Hence, among the four pairs of distorted Dirac points, only a pair of Dirac points is symmetrically independent.

We have computed the total density of states (TDOS) and partial density of states (PDOS) to understand the origin of linear band dispersion around the Dirac points. The TDOS completely vanishes at the Fermi level and linearly increases around the Fermi level, as indicated in Figure 5a. This feature also supports the presence of Dirac states and substantiates the semimetallic nature of cp-graphyne. Furthermore, it is clear from the PDOS that the \(p_z\) states of C atoms are mainly responsible for the formation of linear valence and conduction bands in the vicinity of the Fermi level. The partial charge density plots corresponding to VB and CB (see Figure 5b,c) also suggest that the \(\pi\) and \(\pi^*\) orbitals of C atoms are solely responsible for the formation of linear band dispersion nearer to Dirac points D1. The partial charge density plots are almost similar even for the other Dirac point that is located at D2 (see Figure S5).

3.4. Structural and Electronic Properties of Bilayers. Recently, the layered materials or van der Waals solids \(^{75-76}\) of homogeneous as well as heterogeneous monolayers have gained a great deal of attention from the scientific community due to their one-to-one effect on engineering the electronic properties of individual monolayers. In this context, we have studied the different stacking modes of cp-graphyne with one another. Initially, we have considered AA-stacking mode, in which the atoms of one cp-graphyne monolayer are exactly placed on those of another, as presented in Figure 6a. In addition to this, we have also considered AC-stacking mode in which one monolayer is slightly shifted horizontally with respect to another monolayer. We have glided one of the cp-graphyne monolayers along the \(x\) direction and \(y\) direction in steps of 2.06 Å (one-sixth of the lattice constant) till the identical conformation has been repeated. This technique almost covers all favorable stacking modes including AB-stacking, which was shown in Figure 6b. Overall, the optimal interlayer distance between the two cp-graphyne monolayers has been evaluated for one AA-, one AB-, and 11 AC-stacking modes, as given in Figure 6c. The most stable AC-stacking mode between two cp-graphyne monolayers has been presented in Figure 6c. This is similar to one of the most stable stacking modes \(A\alpha\) of the \(\alpha\)-graphyne\(^{75}\) bilayer and also to that of \(\beta\)-graphyne.\(^{76}\) It is obvious that AA-stacking is not favorable than AB or AC-stacking due to interelectronic repulsions. In the most stable AC-stacking mode, two cp-graphyne monolayers are stacked together with a maximum binding energy of 42 meV/atom at an optimal interlayer distance of 3.6 Å. Furthermore, we have also computed the electronic band structure of the cp-graphyne bilayer and is presented in Figure 6d. The VB and CB of the cp-graphyne bilayer crosses at two distinct points (D1' and D2') in the \(\Gamma\rightarrow X\) high-symmetry line segment. Furthermore, these two bands exhibit almost linear band dispersion around the two crossing points, as indicated in Figure 6e. In addition to this, the 3D band picture (see Figure 6f) of VB and CB also confirms the presence of Dirac cone-like features to these bands around the crossing points. Hence, we conclude these crossing points as Dirac-like points. The interlayer interaction between the cp-graphyne monolayer may be responsible for the emergence of Dirac cones in the double layer of cp-graphyne. Excitingly, the two Dirac-like points are situated at above and below the Fermi level, indicating the p-type and n-type self-doping character of the cp-graphyne bilayer. As a result, the holes act as the charge carriers at Dirac point D1', whereas the electrons act as charge carriers at Dirac point D2' even without doping effects. Hence, cp-graphyne may be a promising 2D material for high-speed electronic applications. It is important to mention here that the synthetic accessibility is the major
concern to the graphyne-based research. However, dehydrotribenzo[12]annulenes, dehydrotribenzo[18]-annulenes, perethynlated expanded radiallynes, and cyclo[12]carbon are considered as the possible candidates for the synthesis of small graphyne flakes\(^7,^8\) using the most promising metal-catalyzed cross-coupling reactions, alkyne metathesis, and templated synthesis techniques. In the same direction, [5]radiallynes, acetylenic scaffolds of cyclopentane, and cyclic carbon cluster di-anions may serve as starting materials for the experimental synthesis of cp-graphyne.

4. CONCLUSIONS

In this investigation, a novel 2D carbon allotrope has been predicted using the state-of-the-art theoretical methods. The ideal arrangement of carbon pentagons and acetylenic linkers led to the development of this 2D material. It utilizes both sp- and sp\(^2\)-hybridized C states similar to the other graphyne networks. Thus, this novel 2D carbon sheet is named cp-graphyne based on its structural features. The structural stability is confirmed by the comprehensive investigation on the dynamic, thermal, and mechanical properties of cp-graphyne. The higher energetic favorability than that of the graphdiyne monolayer corroborates the experimental feasibility of the cp-graphyne monolayer in the future. Computed results show that double distorted Dirac points and anisotropic carrier mobilities are the dominant features in the electronic structure of cp-graphyne. Excitingly, a p- and n-type self-doping character has been found in the electronic fingerprint of the cp-graphyne bilayer.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00513.

Total, cohesive, and formation energies of different carbon allotropes; inequivalent Wyckoff positions; snapshot of FPMD simulation; mechanical instability; contour plots of highest occupied VB, lowest unoccupied CB, and charge density; and different stacking modes of the bilayer of cp-graphyne (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: subuchem@hotmail.com, subbu@crl.res.in. Tel: +91 44 24411630. Fax: +91 44 24911589.

**ORCID**

Naga Venkateswara Rao Nulakani: 0000-0002-1127-3069

Venkatesan Subramanian: 0000-0003-2463-545X

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge the Design and Development of Two-Dimensional van der Waals Solids and their Applications project (No. EMR/2015/000447) funded by DST and the Multi-Scale Simulation and Modelling (MSM) project (No. CSC0129) funded by CSIR, for financial support. One of the authors (N.V.R.N.) wishes to thank DST for SRF.

**REFERENCES**

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. Science 2004, 306, 666–669.

(2) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. Nature 2005, 438, 197–200.

(3) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. Nat. Mater. 2007, 6, 183–191.

(4) Butler, S. Z.; Hollen, S. M.; Cao, L.; Cui, Y.; Gupta, J. A.; Gutiérrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Ismach, A. F.; et al. Progress, Challenges, and Opportunities in Two-Dimensional Materials beyond Graphene. ACS Nano 2015, 7, 2989–2926.

(5) Sun, Y.; Gao, S.; Lei, F.; Xiao, C.; Xie, Y. Ultrathin Two-Dimensional Inorganic Materials: New Opportunities for Solid State Nanotechnology. Acc. Chem. Res. 2015, 48, 3–12.

(6) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-Dimensional Atomic Crystals. Proc. Natl. Acad. Sci. U.S.A. 2005, 102, 10451–10453.

(7) Bhimanapati, G. R.; Lin, Z.; Meunier, V.; Jung, Y.; Cha, J.; Das, S.; Xiao, D.; Son, Y.; Strano, M. S.; Cooper, V. R.; et al. Recent Advances in Two-Dimensional Materials beyond Graphene. ACS Nano 2015, 9, 11509–11539.

(8) Miró, P.; Audiffred, M.; Heine, T. An Atlas of Two-Dimensional Materials. Chem. Soc. Rev. 2014, 43, 6537–6554.

(9) Zou, X.; Yakobson, B. I. An Open canvas—2D Materials with Defects, Disorder, and Functionality. Acc. Chem. Res. 2015, 48, 73–80.

(10) Xu, M.; Liang, T.; Shi, M.; Chen, H. Graphene-like Two-Dimensional Materials. Chem. Rev. 2013, 113, 3766–3798.

(11) Ma, Y.; Dai, Y.; Huang, B. Dirac Cones in Two-Dimensional Lattices: Janugraphene and Chlorographene. J. Phys. Chem. Lett. 2013, 4, 2471–2476.

(12) Wang, Z.; Zhou, X.-F.; Zhang, X.; Zhu, Q.; Dong, H.; Zhao, M.; Oganov, A. R. Phagraphene: A Low-Energy Graphene Allotrope Composed of S-6-7 Carbon Rings with Distorted Dirac Cones. Nano Lett. 2015, 15, 6182–6186.

(13) Zhao, M.; Dong, W.; Wang, A. Two-Dimensional Carbon Topological Insulators Superior to Graphene. Sci. Rep. 2013, 3, No. 3532.

(14) Zhang, L. Z.; Wang, Z. F.; Wang, Z. M.; Du, S. X.; Gao, H.-J.; Liu, F. Highly Anisotropic Dirac Fermions in Square Graphynes. J. Phys. Chem. Lett. 2015, 6, 2959–2962.

(15) Vogt, P.; De Padova, P.; Quaresima, C.; Avila, J.; Frantzeskakis, E.; Asenjo, M. C.; Resta, A.; Eallet, B.; Lay, G. L. Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon. Phys. Rev. Lett. 2012, 108, No. 155501.

(16) Dávila, M. E.; Lay, G. L. Few Layer Epitaxial Germanene: A Novel Two-Dimensional Dirac Material. Sci. Rep. 2016, 6, No. 20714.

(17) Ma, Y.; Dai, Y.; Niu, C.; Huang, B. Halogenated Two-Dimensional Germanium: Candidate Materials for Being of Quantum Spin Hall State. J. Mater. Chem. C. 2012, 22, 12587–12591.

(18) Zhu, F.-f.; Chen, W.-j.; Xu, Y.; Gao, C.-l.; Guan, D.-d.; Liu, C.-h.; Qian, D.; Zhang, S.-c.; Jia, J.-f. Epitaxial Growth of Two-Dimensional Stanene. Nat. Mater. 2015, 14, 1020–1025.

(19) Ma, Y.; Dai, Y.; Guo, M.; Niu, C.; Huang, B. Intriguing Behavior of Halogenated Two-Dimensional Tin. J. Phys. Chem. C 2012, 116, 12977–12981.

(20) Wu, X.; Dai, J.; Zhao, Y.; Zhuo, Z.; Yang, J.; Zeng, X. C. Two-Dimensional Boron Monolayer Sheets. ACS Nano 2012, 6, 7443–7453.

(21) Zhang, Z.; Yang, Y.; Gao, G.; Yakobson, B. I. Two-Dimensional Boron Monolayers Mediated by Metal Substrates. Angew. Chem., Int. Ed. 2015, 54, 13022–13026.

(22) Dai, J.; Wu, X.; Yang, J.; Zeng, X. C. AlC Monolayer Sheets: Two-Dimensional Networks with Planar Tetracoordinate Carbon and Potential Applications as Donor Materials in Solar Cell. J. Phys. Chem. Lett. 2014, 5, 2058–2065.
(23) Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tománek, D.; Ye, P. D. Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility. ACS Nano 2014, 8, 4033–4041.

(24) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science 2008, 321, 385–388.

(25) Sheka, E. F. The Uniqueness of Physical and Chemical Natures of Graphene: Their Coherence and Conflicts. Int. J. Quantum Chem. 2014, 114, 1079–1095.

(26) Neto, A. H. C.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. Rev. Mod. Phys. 2009, 81, 109–162.

(27) Novoselov, K. S.; Morozov, S. V.; Mohindin, T. M. G.; Ponomarenko, L. A.; Elias, D. C.; Yang, R.; Barbolina, I. I.; Blake, P.; Booth, T. J.; Jiang, D.; et al. Electronic Properties of Graphene. Phys. Status Solidi B 2007, 244, 4106–4111.

(28) Zhang, T.; Tan, Y.-W.; Stormer, H. L.; Kim, P. Experimental Observation of the Quantum Hall Effect and Berry’s Phase in Graphene. Nature 2005, 438, 201–204.

(29) Katsnelson, M. I.; Novoselov, K. S.; Geim, A. K. Chiral Tunneling and the Klein Paradox in Graphene. Nat. Phys. 2006, 2, 620–625.

(30) Qi, X.-L.; Zhang, S.-C. Topological Insulators and Superconductors. Rev. Mod. Phys. 2011, 83, 1057–1110.

(31) Hasan, M. Z.; Kane, C. L. Colloquium: Topological Insulators. Rev. Mod. Phys. 2010, 82, 3045–3076.

(32) Wehling, T. O.; Black-Schaffer, A. M.; Balatsky, A. V. Dirac Materials. Adv. Phys. 2014, 63, 1–76.

(33) Wang, J.; Deng, S.; Liu, Z.; Liu, Z. The Rare Two-Dimensional Materials with Dirac Cones. Natl. Sci. Rev. 2015, 2, 22–39.

(34) Florene, A.; Friedlein, R.; Ozaki, T.; Kawai, H.; Wang, Y.; Yamada-Takamura, Y. Experimental Evidence for Epitaxial Silicene on Diboride Thin Films. Phys. Rev. Lett. 2012, 108, No. 245501.

(35) Zhou, H.; Zhao, M.; Zhang, X.; Dong, W.; Wang, Z.; Zhong, J.-X.; Chen, Y.-P. R-Graphene: A New Two-Dimensional Carbon Allotrope with Versatile Dirac-like Point in Nanoribbons. J. Mater. Chem. A 2013, 1, 5341–5346.

(36) Zhang, H.; Duan, W.; Liu, Z. The Existence/Absence of Dirac Cones in Graphynes. New J. Phys. 2013, 15, No. 023004.

(37) Niu, X.; Mao, X.; Yang, D.; Zhang, Z.; Shi, M.; Xue, D. Dirac Cone in α-Graphyne: A First-Principles Study. Nanoscale Res. Lett. 2013, 8, 469.

(38) Li, G.; Li, Y.; Liu, H.; Guo, Y.; Li, Y.; Zhu, D. Architecture of Graphydiene Nanoscale Film. Chem. Commun. 2010, 46, 3256–3259.

(39) Kim, B. G.; Choi, H. J. Graphyne: Hexagonal Network of Carbon with Versatile Dirac Cones. Phys. Rev. B 2012, 86, No. 115435.

(40) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B 1996, 54, 11169–11186.

(41) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. Comput. Mater. Sci. 1996, 6, 15–50.

(42) MedeA-VASP (Materials Design Inc.) is a commercial pack that provides a graphical interface to set up, run, and analyze VASP calculations under the Windows environment.

(43) Peredew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.

(44) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953–17979.

(45) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. Phys. Rev. B 1976, 13, 5188–5192.

(46) Togo, A.; Oba, F.; Tanaka, I. First-Principles Calculations of the Ferroelectric Transition between Rutile-Type and CaCl2-Type SiO2 at High Pressures. Phys. Rev. B 2008, 78, No. 134106.

(47) Lee, K.; Murray, É. D.; Kong, L.; Landqvist, B. I.; Langreth, D. C. Higher-Accuracy van der Waals Density Functional. Phys. Rev. B 2010, 82, No. 81101(R).

(48) Garg, P.; Choudhuri, I.; Mahata, A.; Pathak, B. Band Gap Opening in Stanene Induced by Patterned B–N Doping. Phys. Chem. Chem. Phys. 2017, 19, 3660–3669.

(49) Li, T. Ideal Strength and Phonon Instability in Single-Layer MoS2. Phys. Rev. B 2012, 85, No. 235407.

(50) Garg, P.; Kumar, S.; Choudhuri, I.; Mahata, A.; Pathak, B. Hexagonal Planar CdS Monolayer Sheet for Visible Light Photocatalysis. J. Phys. Chem. C 2016, 120, 7052–7060.

(51) Born, M.; Huang, K. Dynamical Theory of Crystal Lattices; Oxford University Press, 1954.

(52) Peng, Q.; Ji, W.; De, S. Mechanical Properties of Graphyne Monolayers: A First-Principles Study. Phys. Chem. Chem. Phys. 2012, 14, 13385–13391.

(53) Yu, J.; Sun, Q.; Kawazoe, Y.; Jena, P. Stability and Properties of 2D Porous Nanosheets Based on tetraoxa[8]circulene Analogues. Nanoscale 2014, 6, 14962–14970.
(71) Cadelano, E.; Palla, P. L.; Giordano, S.; Colombo, L. Elastic Properties of Hydrogenated Graphene. *Phys. Rev. B* **2010**, *82*, No. 235414.

(72) Yang, D. Z.; Si, M. S.; Zhang, G. P.; Xue, D. S. Crystal Momentum-Dependent Anisotropy of the Dirac Cone in the Rectangular Carbon Allotropes. *Europhys. Lett.* **2014**, *107*, No. 20003.

(73) Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Neto, A. H. C. 2D Materials and van der Waals Heterostructures. *Science* **2016**, *353*, No. aac9439.

(74) Geim, A. K.; Grigorieva, I. V. Van Der Waals Heterostructures. *Nature* **2013**, *499*, 419–425.

(75) Leenaerts, O.; Partoens, B.; Peeters, F. M. Tunable Double Dirac Cone Spectrum in Bilayer α-Graphyne. Tunable Double Dirac Cone Spectrum in Bilayer α-Graphyne. *Appl. Phys. Lett.* **2013**, *103*, No. 013105.

(76) León, A.; Pacheco, M. Electronic Properties of β-Graphyne Bilayers. *Chem. Phys. Lett.* **2015**, *620*, 67–72.

(77) Haley, M. M. Synthesis and properties of annulenic subunits of graphyne and graphdiyne nanoarchitectures. *Pure Appl. Chem.* **2008**, *80*, 519–532.

(78) Gholami, M.; Tykwinski, R. R. Oligomeric and Polymeric Systems with a Cross-conjugated π-Framework. *Chem. Rev.* **2006**, *106*, 4997–5027.