Anisotropic-Cyclicgraphene: A New Two-Dimensional Semiconducting Carbon Allotrope

Marcin Mażdziarz 1,*, Adam Mrozek 2, Wacław Kuś 3 and Tadeusz Burczyński 1

1 Institute of Fundamental Technological Research Polish Academy of Sciences, Pawińskiego 5B, 02-106 Warsaw, Poland; tburczynski@ippt.gov.pl
2 Department of Applied Computer Science and Modelling, AGH University of Science and Technology, Mickiewicza 30, 30-059 Cracow, Poland; amrozek@agh.edu.pl
3 Institute of Computational and Mechanical Engineering, Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland; Waclaw.Kus@polsl.pl

* Correspondence: mmazdz@ippt.pan.pl; Tel.: +48-22-826-12-81

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Abstract: A potentially new, single-atom thick semiconducting 2D-graphene-like material, called Anisotropic-cyclicgraphene, has been generated by the two stage searching strategy linking molecular and ab initio approach. The candidate was derived from the evolutionary-based algorithm and molecular simulations was then profoundly analysed using first-principles density functional theory from the structural, mechanical, phonon, and electronic properties point of view. The proposed polymorph of graphene (rP16-P1m1) is mechanically, dynamically, and thermally stable and can achieve semiconducting with a direct band gap of 0.829 eV.

Keywords: carbon; graphene; graphyne; ab initio calculations; Semiconductors

1. Introduction

Carbon is probably the most versatile element of the periodic table due to the possibility of creating (C–C) bonds with different atom hybridization (sp$^1$, sp$^2$, and sp$^3$) [1] and its allotropes occur in all possible dimensionalities (0D-3D). The Samara Carbon Allotrope Database (SACADA) [2] has now gathered more than five hundred 3D carbon allotropes.

The Nobel Prize for Physics in 2010, “for groundbreaking experiments regarding the two-dimensional material graphene”, has attracted tremendous interest in this polymorph of carbon [3] due to its extraordinary physical properties [4,5]. Graphene is a zero-gap semiconductor with linear energy band dispersion close to the Fermi level. The absence of a band gap in the electronic spectrum of graphene can prohibit the direct implementation of this material in electronics and that is why scientists and engineers have started to look for ways to improve this. It was found that mechanical deformations of graphene can give rise to a band gap of up to 1 eV and narrow graphene ribbons may possess the properties of semiconductors, where their band gaps are narrowed as the ribbons become wider [6]. Graphene armchair nanotubes are metallic, whereas zigzag and chiral nanotubes can be also semiconducting with a band gap depending inversely on its diameter [7]. Patterned defects can be utilised to disrupt the sublattice symmetry of graphene so as to widen the band gap up to 1.2 eV [8].

Undoubtedly the blossoming of studies on graphene has accelerated interest in exploring graphene-like materials, see [9–12]. A huge number of types of 2D carbon networks have been proposed, for example, by replacing some (or all) (C=C) bonds in graphene, sp$^2$ hybridization type, by acetylene (–C≡C–) linkages, sp$^1$ hybridization type, see [1,5,6,13,14]. Among these several dozens of 2D carbon allotrops, only a few are semiconductors and we will focus on those here. Optimized geometries and electronic structures of graphyne and its family were proposed and analysed theoretically in [15,16]. Graphyne can be seen as a 6-fold symmetry lattice of benzene rings connected by acetylene (–C≡C–)
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linkages. The structures proposed therein are, according to linear combination of atomic orbitals (LCAO) calculations, semiconductors with moderate band gaps. More than 30 years later, some of these structures, called graphdiyne and Ene-yne, were synthesized in [17,18]. Semiconducting carbon allotrope named C$_z$ with a band gap of 0.858 eV, consisting of 4, 6, 8, 12, 14 and 18 atom rings was proposed in [19] and similar Coro-graphene, consisting of 4, 6 and 10 rings, with a direct band gap $\sim$0.63 eV was found in [20]. Graphenylene, consisting of 4, 6 and 12 rings, with a direct and narrow band gap (0.025 eV) was found in [21]. T-Graphene, 2D carbon allotrope with C$_8$ and C$_4$ rings in [22] is metallic, in [23] as a planar structure is metallic but, even as nanoribbon, is semiconducting with 0.7–0.15 eV direct band gap. However, in [24] the same planar carbon sheet can be semiconducting with a band gap, depending on the calculation method, between 0.43 and 1.01 eV. A pza-C$_{10}$ allotrope consisting of alternating parallel zigzag and armchair chains (C$_5$ + C$_6$ + C$_7$ carbon rings) was proposed in [25], where electronic structure was studied and calculated band gap to be 0.31 (0.71) eV with gradient (hybrid) functionals.

In addition to the single-atom thick 2D structures mentioned above, multi-atom structures were also proposed. The twin graphene (with thickness, $t_{12}$ = 1.55 Å) was analysed both by first-principles methods and classical molecular dynamics simulations in [26]. Its band gap was found to be around 1 eV. Theoretical two-atom thick semiconducting carbon sheet, $H$-net, with indirect band gap of 0.88 eV was postulated in [27].

Even a 2D metastable carbon allotrope $p$-net-graphene, 2D sheet with a total thickness of 1.2 Å and calculated quasi-direct band gap 2.3 (4.3) eV with generalized gradient (Green’s function) approximations was proposed in [28,29] but questioned by [30] because of occurrence of there tetrahedral $sp^3$-carbon linkers. While consistent with experiment stable crystalline carbon polytypes contain only one hybridization state of carbon (either $sp^2$ or $sp^3$).

The present paper is focused on an in-depth analysis of new, one-atom thick 2D carbon semiconducting material, called Anisotropic-cyclicgraphene and is organised as outlined below: Section 2.1 references to the memetic algorithm and molecular methods used to generate Anisotropic-cyclicgraphene, Section 2.2 briefly describes the computational ab initio methods utilised in examination of the new structure, Section 2.3 demonstrates the results of computations, and Section 3 draws conclusions.

2. Computational Methods

2.1. Prediction of Two-Dimensional Materials

A description and application of the memetic algorithm [31,32] and molecular methods [33–36] using the semi-empirical potential for optimal searching for the new stable 2D graphene-like carbon structures with predefined mechanical properties was shown in [37]. The results obtained there, with two rectangular, primitive with 8 atoms in unit cell and P1 plane group symmetry structures: $rP8$-P1, wherein the designations mean: 2D Pearson symbol, 2D space group, have served here as input for more accurate and reliable first-principles calculations. Consequently, the first that structure with dimensions 6.42 $\times$ 6 Å from first-principles calculations found to be metallic, so quite common 2D carbon material, but the second with dimensions 3.922 $\times$ 8.472 Å found to be semiconducting, so quite rare and interesting one and for this reason, it was decided to analyse only this one of them.

2.2. Ab Initio Computations

First-principles calculations with the use of density functional theory (DFT) [38,39] within the pseudopotential, plane-wave approximation (PP-PW) have been made using the Cambridge Serial Total Energy Package (CASTEP) [40]. For structural, mechanical and phonon calculations the modified Perdew-Burke-Ernzerhof generalized gradient approximation for solids (PBEsol GGA) was applied as an exchange-correlation functional [41] whereas for band structure computations the hybrid exchange-correlation functional HSE06 [42–44]. The calculation settings and methodology was taken from [45].
2.3. Finite Temperature Stability-Molecular Dynamics Calculations

The thermal stability of 2D structures is typically examined by performing ab initio molecular dynamics (AIMD) or classical molecular dynamics (MD) with the use of interatomic potentials. Due to the significant calculation cost of AIMD, simulations are limited to only 200 atoms and a few ps (∼10,000 steps) in NVT (constant number of atoms, volume, and temperature) ensemble; see [24,28]. However, to achieve reliable accuracy of the phase space sampling at least 10^7 steps is required [46], which is still too large a number for AIMD, but not for classical MD [47].

All the molecular simulations in this work have been performed by using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [33] and the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential for hydrocarbons [48], and visualized through the use of the Open Visualization Tool (OVITO) [49].

In all computations, periodic boundary conditions were applied to a 2D sheet, consisting of 10 × 10 Anisotropic-cyclicgraphene conventional supercells in the plane of the model, and non-periodic and shrink-wrapped in the normal direction to the model [33], thus atoms could vibrate in 3 dimensions. Molecular dynamics simulations covered the time span of 20 ns (2 × 10^7 MD steps, one step = 1 fs). At a given temperature and zero pressure, NPT (constant number of atoms, pressure and temperature) a Nose-Hoover style barostat was used [33,34]. Thermodynamic information was computed and outputted every 1 ps (1000 MD steps). Similar settings were used in [47] to examine thermal stability of graphyne.

Applying the methodology outlined in Section 2.2, the first stage in our computations was geometric optimization of a potentially new polymorph of graphene. Whereas, the initial unit cell was rectangular, primitive with 8 atoms in unit cell and P1 plane group symmetry: rP8-P1, see Table A3 after DFT optimization it was obtained oblique, primitive with 8 atoms in unit cell and P1m1 plane group symmetry: oP8-P1m1, see Table A2, which corresponds to, rP16-P1m1 conventional unit cell, see Table A1.

2.4. Structural Properties

For Anisotropic-cyclicgraphene-rP16-P1m1 (C3 + C17 carbon rings), where the basic cell is portrayed in Figure 1a and recorded in Table A1, our lattice parameters, i.e., a = 3.822 Å and b = 16.967 Å, are slightly smaller than those obtained from molecular calculations, see Table 1. It is worth mentioning that 2D non-traditional carbon materials employing a three-membered ring, i.e., C3 + C12, C3 + C24, C3 + C36 carbon rings, were theoretically investigated in [50], but were found to be dynamically unstable and metallic. Previously, the mechanical properties of the C3 + C12 carbon rings structure, named cyclicgraphene, was studied by classical molecular dynamics simulations in [51].

Unlike other single-atom thick 2D carbon semiconductors, our structure contains only such odd type of rings. Due to very low symmetry of the proposed structure the bond lengths vary, in the three-membered ring: 1.39–1.41 Å and in the long carbon chain: 1.24–1.39 Å. A general principle from organic chemistry says, that the more s character the bond has, the more tightly held the bond will be and carbon bonds in representative hydrocarbons, \( sp^2 = sp^2 \approx 1.40 \text{ Å}, \ sp = sp \approx 1.37 \text{ Å}, \ sp^2 – sp^2 \approx 1.34 \text{ Å}, \ sp^{\equiv}sp \approx 1.20 \text{ Å} \), see [52]. Similarly here, \( sp^2 \) bonds in the three-membered ring are longer than \( sp \) bonds in long carbon chain.

If we look at the calculated cohesive energy in Table 1 we see that for Anisotropic-cyclicgraphene \( E_{coh} \approx -6.823 \text{ eV/Atom} \). Cohesive energies derived from the molecular calculations are ∼0.5 eV/Atom higher. The relative energy of Anisotropic-cyclicgraphene with respect to pristine graphene is \( E_{rel} \approx 0.967 \text{ eV/Atom} \), a value similar to that of other graphynes [27,53] and almost identical to other 2D non-traditional carbon materials employing three-membered ring as building blocks [50], i.e., \( E_{rel} \approx 0.96 \text{ eV/Atom} \) for the C3 + C12 carbon rings and \( E_{rel} \approx 1.03 \text{ eV/Atom} \) for C3 + C24 rings and C3 + C36 rings, respectively.
Figure 1. Anisotropic-cyclicgraphene—(a) conventional and (b) primitive cell.

Table 1. Lattice parameters of conventional and primitive cell (Å), cohesive energy $E_{\text{coh}}$ (eV/Atom), relative energy $E_{\text{rel}}$ (eV/Atom) with respect to pristine graphene, and elastic constants $C_{ij}$ (N/m) of Anisotropic-cyclicgraphene.

| Source | DFT | MD |
|--------|-----|----|
| $a$    | 3.822 (3.822) | 3.936 (3.936) |
| $b$    | 16.967 (8.701) | 17.544 (9.000) |
| $\gamma$ | 90.0° (77.166°) | 90.0° (77.17°) |
| $E_{\text{coh}}$ | −6.823 | −6.292 |
| $E_{\text{rel}}$ | 0.967 | 1.133 |
| $C_{11}$ | 80.54 | 71.17 |
| $C_{22}$ | 294.46 | 257.45 |
| $C_{12}$ | 47.19 | 46.41 |
| $C_{66}$ | 5.38 | 2.79 |

2.5. Mechanical and Phonon Properties

The in-plane elastic constants $C_{ij}$ of analysed structure are listed in Table 1. It can be seen that all $C_{ij}$ are lower for Anisotropic-cyclicgraphene than for pristine graphene, which has $C_{11} = C_{22} = 352.7$, $C_{12} = 60.9$, $C_{66} = 145.9$ (N/m) [54]. Elongated character of the basic cell, Figure 1, manifests itself in anisotropy of elastic properties. The studied structure have positive definite 2D elasticity tensor ($C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$) [28] and is in-plane mechanically stable. The results of molecular calculations are slightly lower than those of DFT. For other graphynes it is known that an increase in the number of acetylenic linkages corresponds to degradation of the stiffness [55].

Phonon dispersion curves for investigated structure, plotted along the high symmetry k-points, $\Gamma (0.00, 0.00, 0.00) \rightarrow Y (0.50, 0.00, 0.00) \rightarrow S (0.50, 0.50, 0.00) \rightarrow X (0.00, 0.50, 0.00) \rightarrow \Gamma (0.00, 0.00, 0.00)$.
0.00) → S (0.50, 0.50, 0.00), are drawn in Figure 2. Analysis of calculated curves allows one to say that, phonon modes have positive frequencies and Anisotropic-cyclic graphene is not only mechanically but also dynamically stable.

![Figure 2. Anisotropic-cyclic graphene—(a) phonon dispersion and (b) density of phonon states.](image)

2.6. Electronic Properties

The electronic band structure (EBS) and density of states (DOS), total and partial, for the analysed structure are plotted along the high symmetry $k$-points, $\Gamma$ (0.00, 0.00, 0.00) → Y (0.50, 0.00, 0.00) → S (0.50, 0.50, 0.00) → X (0.00, 0.50, 0.00) → $\Gamma$ (0.00, 0.00, 0.00) → S (0.50, 0.50, 0.00), in Figure 3 for the GGA functional and in Figure 4 for the HSE06 hybrid functional. The integrated total and partial density of states for both functionals are presented in Figure 5. The overall pattern of the valence band (VB) and conduction band (CB) of the analysed structure is quite similar for both functionals, however, it should be noted, that for HSE06 hybrid functional the VB is a bit wider and the CB is wider and shifted slightly upwards than for GGA functional, see Figures 3b and 4b. A direct band gap is $E_g = 0.418$ eV for the functional PBEsol, while $E_g = 0.829$ eV for the HSE06 at the $\Gamma$ point of the first Brillouin zone. Analysis of integrated total and partial density of states in Figure 5 shows that from the energy level of approximately $-11$ eV, the s-states minimally contribute to the total DOS and it is clearly evident that the p-states are primarily responsible for the formation of VB and CB near to the Fermi level. The calculated Fermi energy for Anisotropic-cyclic graphene system equals $-4.243$ eV with the PBEsol GGA functional and $-3.106$ eV with the HSE06 hybrid functional.
Figure 3. *Anisotropic-cyclic graphene*—(a) electronic band structure and (b) total and partial density of states (GGA functional). The Fermi level $E_F$ is set to 0.

Figure 4. *Anisotropic-cyclic graphene*—(a) electronic band structure and (b) total and partial density of states (HSE06 functional). The Fermi level $E_F$ is set to 0.
Figure 5. Anisotropic-cyclicgraphene—integrated total and partial density of states—(a) (GGA functional) and (b) (HSE06 functional). The Fermi level $E_F$ is set to 0.

2.7. Finite Temperature Stability

We see in Figure 6 that the total energy for $T = 800$ K fluctuate around average value throughout the simulation, whereas for $T = 900$ K it decreases slowly until a considerable change at a time $\sim 18$ ns. By analysing snapshots of the structures at given temperature in Figure 7, we see that for $T = 800$ K the topology of Anisotropic-cyclicgraphene does not change and atoms vibrate around equilibrium positions. At $T = 900$ K topological changes occur and many smaller rings appear. We therefore conclude that the polymorph is thermally stable up to a temperature of 800 K.

Figure 6. Anisotropic-cyclicgraphene—total energy for 800 K and 900 K.
Figure 7. Anisotropic-cyclicgraphene—snapshots of the structures at 800 K and 900 K after 20 ns.

3. Conclusions

The extensive analysis of potentially new polymorph of graphene consisting of C3+C17 carbon anisotropic rings within the framework of DFT from point of view of the structural, mechanical, phonon, and electronic properties was carried out in the paper. All above calculations have been completed using ultra-fine quality settings, the modified PBEsol GGA for solids exchange-correlation functional and additionally for electronic band structure computations the hybrid exchange-correlation functional HSE06. In addition the thermal stability of the proposed Anisotropic-cyclicgraphene was examined by performing a series of classical molecular dynamics simulations.

The following conclusions can be stated:

• The proposed polymorph of graphene (rP16-P1m1) is mechanically and dynamically stable contrary to other C3-cyclicgraphenes.
• The proposed structure is thermally stable up to a temperature of at least 800 K.
• The relative energy of Anisotropic-cyclicgraphene with respect to pristine graphene is similar to other graphynes and cyclicgraphenes.
• Anisotropic-cyclicgraphene can be semiconducting, with a direct band gap with a value of 0.829 eV.
• The semi-empirical potential AIREBO seems to be surprisingly suitable for carbon structures.

Some results in this paper are unique and we trust that they will be verified by other works. Naturally, the synthesis of the proposed structure is a separate task and goes beyond the area of this work. The effect of carbon rings anisotropy and chain lengths on the properties of potentially new 2D structures will be the subject of further research.

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Author Contributions: Marcin Mażdziarz carried out the ab initio calculations. Adam Mrozek, Waclaw Kuś and Tadeusz Burczyński performed molecular simulations. All the authors prepared the manuscript, discussed the results and commented on the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. Unit Cells

The following tables present crystallographic data for Anisotropic-cyclicgraphene-rP16-P1m1.

Table A1. Lattice parameters (Å) and fractional coordinates of atoms of Anisotropic-cyclicgraphene-rP16-P1m1-conventional cell, Figure 1a.

| Atom Number | Fractional coordinates of atoms |
|-------------|---------------------------------|
| 1           | 0.50000 0.28603                 |
| 2           | 0.50000 0.36811                 |
| 3           | 0.50000 0.44107                 |
| 4           | 0.00000 0.78603                 |
| 5           | 0.00000 0.86811                 |
| 6           | 0.00000 0.94107                 |
| 7           | 0.18150 0.24436                 |
| 8           | 0.68150 0.74436                 |
| 9           | 0.81850 0.24436                 |
| 10          | 0.31850 0.74436                 |
| 11          | 0.00000 0.17228                 |
| 12          | 0.00000 0.01941                 |
| 13          | 0.00000 0.09259                 |
| 14          | 0.50000 0.67228                 |
| 15          | 0.50000 0.51941                 |
| 16          | 0.50000 0.59259                 |

Table A2. Lattice parameters (Å) and fractional coordinates of atoms of Anisotropic-cyclicgraphene-oP8-P1m1-primitive cell, Figure 1b.

| Atom Number | Fractional coordinates of atoms |
|-------------|---------------------------------|
| 1           | 0.13221 0.59914                 |
| 2           | 0.85619 0.51591                 |
| 3           | 0.49331 0.51566                 |
| 4           | 0.05066 0.76329                 |
| 5           | 0.97724 0.90920                 |
| 6           | 0.74632 0.37162                 |
| 7           | 0.82547 0.21225                 |
Table A3. Lattice parameters (Å) and fractional coordinates of atoms of initial cyclicgraphene-rP8-P1-primitive cell [37].

| Lattice Parameters |  |
|--------------------|---|
| \(a\)              | 3.922 |
| \(b\)              | 8.472 |
| \(\gamma\)         | 90.0° |

| Atom Number | Fractional coordinates of atoms |
|-------------|---------------------------------|
| 1           | 0.15902 0.60266                 |
| 2           | 0.85954 0.52400                 |
| 3           | 0.45448 0.52020                 |
| 4           | 0.14158 0.76639                 |
| 5           | 0.02079 0.91373                 |
| 6           | 0.67188 0.35866                 |
| 7           | 0.89386 0.05964                 |
| 8           | 0.77916 0.20769                 |

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