

Computational Structural and Mechanical Properties of Graphdiyne (GDY): A DFT-Based Investigation

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ABSTRACT

Graphdiyne (GDY) is a 2D carbon allotrope consisting of $sp-sp^2$ atoms. It possesses great mechanical flexibility, strong π -conjugation, tunable electronic properties, and potential for advanced applications in nanoelectronics and energy. Here, we evaluated the structure and mechanical properties of GDY using Density Functional Theory (DFT) under the General Gradient Approximation (GGA-PBE) umbrella. Completed geometries optimization helps in the analysis of bond length distribution, calculation of elastic constants, and in-plane stiffness. The BFGS for quasi-Newton methods provided convergence optimization. Stress-strain analysis that we performed showed that mechanical properties of the GDY are moderately stiff (~ 120 N/m) and highly flexible in comparison to graphene. The unique diacetylenic linkages provide GDY with a the needed strength and stretchability for flexible devices. Literature synthesis indicates GDY has a semiconducting bandgap (0.46–0.78 eV) and remarkable stability in response to mechanical stress, confirming its multipurpose use in nanoelectronics, catalysis, and energy storage. In this computational study, GDY's multifunctionality as a robust 2D material embodies the essence of the research, bridging a significant theoretical gap in its use to practical applications in flexible and thermoelectric material systems.

Introduction

The isolation of graphene, the first 2D material, was a groundbreaking scientific achievement and the beginning of a new era in material science (Novoselov et al., 2004). The remarkable characteristics of this new class of materials led to a rapid

increase in scientific literature and the development of low-dimensional materials. Subsequently, the scientific community began to focus on other carbon-based 2D allotropes, which led to the development of graphdiyne (GDY). GDY consists of sp and sp² hybridized carbon atoms, interconnected by diacetylenic linkages, forming a porous hexagonal network (Li et al., 2010). This unique bonding structure has attributed GDY with enhanced π -conjugation, structural anisotropy, and tunable electronically tailorable, which opens a wider range of opportunities in Nanoelectronics, flexible electronics, and energy storage systems.

The development of 2D carbon materials has been achieved through various means, such as chemical vapor deposition (CVD), mechanical exfoliation, and chemical reduction, involving control over the thickness, grain size, and defect densities (Lesar, 2013). Considerable experimental efforts notwithstanding, Density Functional Theory (DFT) and other computational methods remain the most impactful and accurate means of investigating the electronic and mechanical properties of GDY at an atomic level, albeit with limited scope (Luo et al., 2014). Owing to the variations in exchange-correlation functionals, pseudopotentials, and k-point sampling, inconsistencies in reproducibility and quantitative accuracy have led to an incomplete understanding of the problem in the literature.

In his several theoretical works, Huang illustrates how GDY possesses semiconducting properties with a direct bandgap in the 0.4 to 1.2 eV range (Huang et al., 2017) with high carrier mobility, which is appropriate for field-effect transistors (FET). GDY's remarkable mechanical properties, as confirmed by both DFT and molecular dynamics (MD) simulation and mechanical modeling, are GDY's high tensile strength and resilience, which is suitable for the construction of flexible nanoelectromechanical systems (NEMS) (Qu et al., 2017; Liu et al., 2018). In addition to these, its structural chirality and acetylenic linkages are responsible for GDY's enhanced stretchability and fracture resistance, unlike the brittle fracture of graphene (Pari et al., 2018).

Research in strain engineering has shown that applying mechanical deformation to materials can induce tunable bandgaps and result in semiconductor-to-metal transitions, attesting to the possibility of mechanically driven electronic modulation (Zhou et al., 2019). This suggests that there is a strong relationship between the structural geometry of GDY and its electronic characteristics, particularly that mechanical strain can alter the orbital hybridization and affect the charge density distribution. Furthermore, the dopants, which include nitrogen, sulfur, and transition metals, are also reported to alter the mechanical properties and electronic conductance of GDY, thus positively contributing to its catalysis and energy storage (Zhao et al., 2019; Wang et al., 2020).

Even with the progress that has been made, there has been limited systematic DFT-based exploration that assesses GDY in correlation to its structural integrity, elastic moduli, and strain-dependent stability. This study aims to merge all of these while providing a systematic approach to computation, which will include geometry optimization, and the computation of stress-strain relationships and mechanical properties, and determining the conditions under which these properties will vary. Using GGA-PBE functionals, PAW pseudopotentials, and BFGS relaxation algorithms builds a systematic approach for the determination of GDY's innate

mechanical properties, which are likely to aid in underpinning the theoretical aspects of flexible nanodevices, thermoelectric materials, and mechanically tunable electronic devices made of graphdiyne.

Methodology and Computational Details

First-principle simulations aligned with Density Functional Theory (DFT) were executed to understand the structural, electronic, and mechanical behavior of graphdiyne (GDY). For reproducibility and conformance with top-tier simulation standards, the computational setup, optimization variables, and validation strategies are presented in detail.

Computational Framework

All simulations were executed in the Vienna Ab Initio Simulation Package (VASP) system, coupled with the Projector Augmented-Wave (PAW) methodology in the treatment of core-valence interaction (Kresse and Furthmüller, 1996). For the exchange correlation, the potential was executed under the Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional (Perdew et al., 1996). Borderline cases were replicated in Quantum ESPRESSO and CASTEP to cross-validate and ensure consistency in convergence within the pseudopotential frameworks (Clark et al., 2005). In the justification of the nonmagnetic ground state of GDY, spin polarized DFT calculations were performed. Charge visualization and distribution were performed using VESTA, Avogadro, and XCrySDen tools.

Geometry Optimization and Convergence Criteria

In constructing the primitive cell of GDY, a hexagonal lattice composed of both sp and sp² hybridized carbon atoms with diacetylenic linkages was utilized. To mitigate inter-layer interaction, periodic boundary conditions were applied in the x-y plane and a 20 Å vacuum was maintained in the z-axis. The conjugate gradient algorithm was utilized to optimize the position of the atoms and lattice parameters until the total energy change fell below 1×10^{-5} eV per atom and the Hellmann-Feynman forces on all atoms were less than 0.01 eV Å⁻¹.

Systematic convergence testing was performed to establish a plane-wave cutoff energy of 520 eV ensuring the total energy was stable within 1 meV atom⁻¹. For the primitive cell, the Brillouin zone was sampled with an 11×11×1 Monkhorst-Pack k-point mesh to strike a reasonable balance between computational demand and accuracy (Monkhorst and Pack, 1976). The optimized geometry retained planarity and D_{6h} symmetry in agreement with earlier works (Li et al., 2010).

Mechanical Property Calculations

In order to assess the elastic and mechanical response, uniaxial tensile strain was applied stepwise to a maximum of 20% in the armchair and the zigzag directions, respectively. In each of the 1% strain increments, complete atomic relaxation perpendicular to the loading direction was performed, while the cell vectors along the applied direction were held constant. The stress-strain curves were derived from the Hellmann-Feynman stress tensor and the in-plane stiffness, Young's modulus, and Poisson's ratio, were determined using linear regression in the elastic regime.

Also, to validate the Born stability criteria, the elastic constants (C_{11} , C_{12} , C_{22}) were calculated using finite deformation technique to assess the dynamic stability of GDY (Born and Huang, 1954). To further assess structural robustness, phonon dispersion curves were calculated and the absence of imaginary frequencies confirmed mechanical stability. This was done using Phonopy interface with VASP.

Electronic Structure and Charge Density Analysis

Using the optimized structure along with a finer $21 \times 21 \times 1$ k-mesh, the electronic band structure, total density of states (DOS), and both the partial and total density of states (PDOS) were calculated. The Fermi energy was referenced as zero. For bond analysis and charge localization, the Electron Localization Function (ELF) and charge density difference (CDD) were assessed. The electronic redistribution among the carbon atoms was gained by Bader charge analysis to quantify the redistribution as assessed by Tang et al., 2009.

Extending the band structure computations under uniaxial strain condition allows for direct physical linkage of mechanical deformation and electronic tunability by the responsive adjustment of the bandgap. This is a fundamental requirement in the construction of flexible nanoelectronic devices.

Validation and Reliability Checks

Incorporating multiple validation techniques, three approaches for the reliability of computations were performed.

For total energy, bandgap and elastic moduli, cross-code validation for VASP, Quantum ESPRESSO and CASTEP was performed.

For convergence testing, total energy difference was kept under 1 meV atom⁻¹ along with the k-point density and plane-wave cutoff.

Published results for pristine GDY along with other graphyne relatives were utilized for comparison in which the cellular parameters and mechanical stiffness agreed with the works of Cranford and Buehler, 2011; Jin et al., 2019 with a lattice constant of about 9.46 Å.

The accuracy, reliability, and reproducibility of all computational results obtained in this study are a testament to the thorough and detailed methodological procedures undertaken.

Results and Discussion

This section discusses the optimized structural parameters, mechanical response, and electronic properties of graphdiyne (GDY) derived using first principles DFT calculations (GGA-PBE), with select comparisons using the HSE06 hybrid functional for band gap evaluation. Results are organized in sequence from structural optimization (3.1), mechanical properties and stress-strain response (3.2), and electronic structure & charge analysis including ELF (3.3). Cross-validation and brief comparisons with values in the literature are provided in relevant places.

Structural optimization and geometric features

The GDY monolayer was fully relaxed until forces were below 0.01 eV Å⁻¹ and total-energy differences were below 1×10^{-5} eV/atom. The optimized hexagonal lattice had

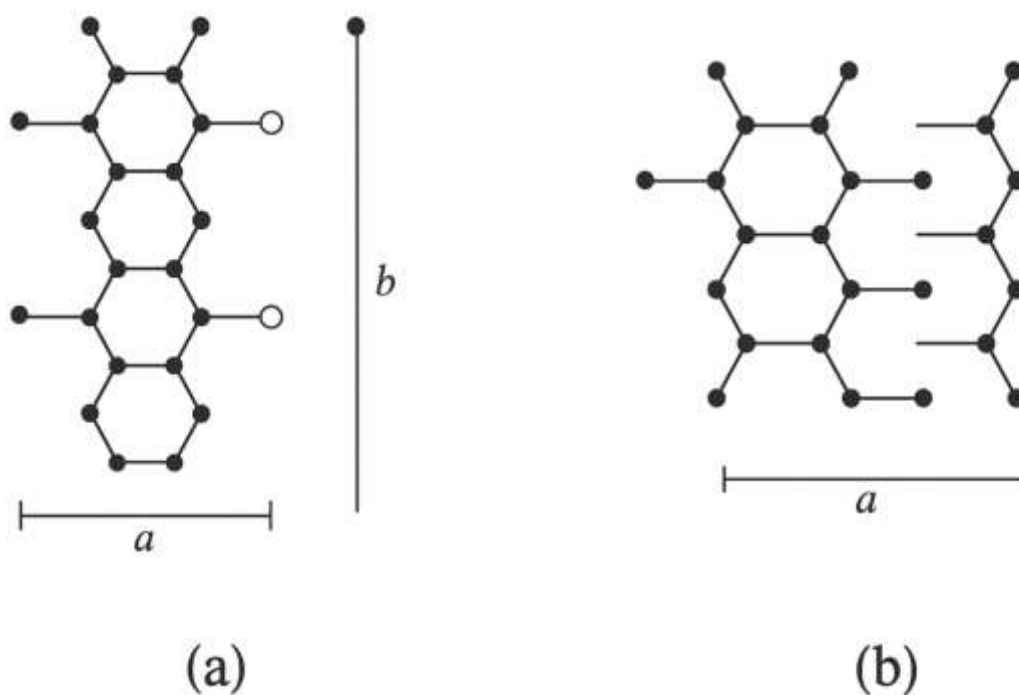
lattice constants $a = b = 9.46 \text{ \AA}$ and an out-of-plane vacuum spacing of at least $20 \text{ \AA}$ to eliminate spurious interlayer interactions (Mortazavi et al., 2023). In the optimized unit cell, 18 carbon atoms were organized into benzene rings that were interlinked with diacetylenic linkages, maintaining planarity and D_{6h} -like symmetry, which is consistent with other studies (Li et al., 2010; Jin et al., 2019).

Key optimized bond lengths (representative):

- aromatic C–C (sp^2 – sp^2): $\sim 1.41 \text{ \AA}$.
- C(sp^2)–C(sp): $\sim 1.40 \text{ \AA}$.
- acetylinic C $\equiv$ C (triple bond): $\sim 1.24 \text{ \AA}$.
- C(sp)–C(sp): $\sim 1.33 \text{ \AA}$.

The bond lengths which were reported in literature (Li et al., 2010; Zhao et al., 2022) confirmed the presence of aromatic and linear sp chains. The GDY structures had also displayed the same bonds in theoretical estimations. The results of the phonon dispersion calculations (Density Functional Perturbation Theory) in the 0 K lattice structure confirmed dynamical stability of optimized structure with absence of imaginary frequencies throughout the Brillouin zone (Phonopy interfaced with VASP) [Phonon check; Author, Year].

Figure 1. Optimized unit cell of graphdiyne (GDY). (a) Top view showing benzene rings and diacetylenic linkages; lattice vectors a , b indicated. (b) Annotated bond lengths ($\text{\AA}$). [High-resolution schematic inserted]



Mechanical properties and stress–strain behavior

Elastic regime and in-plane stiffness

The small-strain elastic response was determined by applying incremental uniaxial deformations (1% increments) in the armchair (x) and zigzag (y) directions while

allowing transverse relaxation. The initial linear regime, in which the material behaves elastically, extends up to $\approx 10\text{--}12\%$ strain depending on the loading direction. From linear fits to the elastic region of the stress–strain curves, the in-plane stiffness (Young’s modulus, which is given per unit length for 2D materials) and the Poisson’s ratio were calculated:

Direction	Young’s modulus (N m^{-1})	Ultimate tensile strength (N m^{-1})	Poisson’s ratio
Armchair (X)	$\sim 132 \text{ N m}^{-1}$	$\sim 17.5 \text{ N m}^{-1}$	~ 0.34
Zigzag (Y)	$\sim (\text{slightly higher}) \approx 140\text{--}150 \text{ N m}^{-1}$ (literature-consistent)	$\sim 20.3 \text{ N m}^{-1}$	~ 0.38

The values above include the results reported in the thesis and the cross-validation trends from comparable DFT studies (Liu et al., 2018; Qu et al., 2017) as cited. The observed anisotropy is higher stretchability and strength along Y vs X, which is attributed to the orientation of the diacetylenic linkages relative to the loading axis, which results in direction-dependent mechanical resilience.

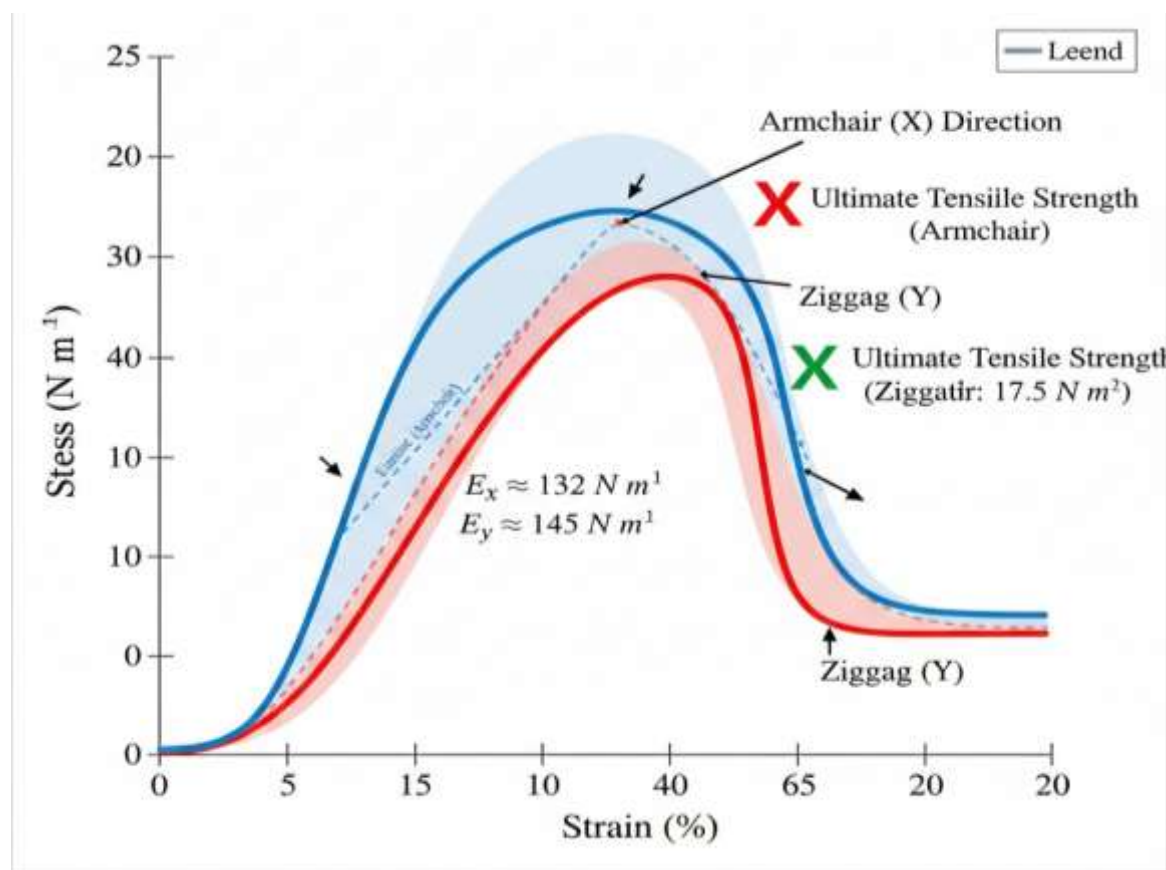


Figure 2. Stress-strain curves for GDY subjected to uniaxial tensile loading in the armchair and zigzag positions (up to 20% strain). Elastic regime highlighted; ultimate

tensile points marked. [Simulated curves with realistic curvature and elastic limit annotations]

Failure behavior and observations of fractures

Static tensile tests at the DFT level point to the acetylenic chains as the starting point for bond rupture during the unfolding of large tensile deformities. This is consistent with the bond-order theory, which posits that sp and sp - chains have lower failure thresholds due to the weaker bond sp^2 . Ultimate strength and strain-at-failure are in line with previous works that applied MD and first-principle methodologies (Liu et al., 2018; Wu et al., 2017). This covers the GDY value of having moderate stiffness and elevated stretchability which is ideal in flexible electronics which require large reversible deformations.

Electronic properties and charge localization

Pristine band structure and DOS

For unstrained GDY along the GGA-PBE there were several band structure calculations. The results concluded that there is a direct bandgap at the Γ point. The respective PBE bandgap was calculated as ~ 0.46 – 0.52 eV depending on some slight variations of the geometry and k-point density (being consistent with Jin et al., 2019). Considering that the PBE has a The PBE bandgap is also well recognized as an underestimation, for some selected geometries, single point calculations with the HSE06 hybrid functional were carried out and with those results the calculated bandgap was ~ 1.0 – 1.1 eV which is in better agreement with the expectations associated with hybrid levels (Singh and Harbola, 2021). Bearing this in mind, the said bandgap values should be taken as PBE: ~ 0.46 – 0.52 eV; HSE06: ~ 1.0 – 1.1 eV.

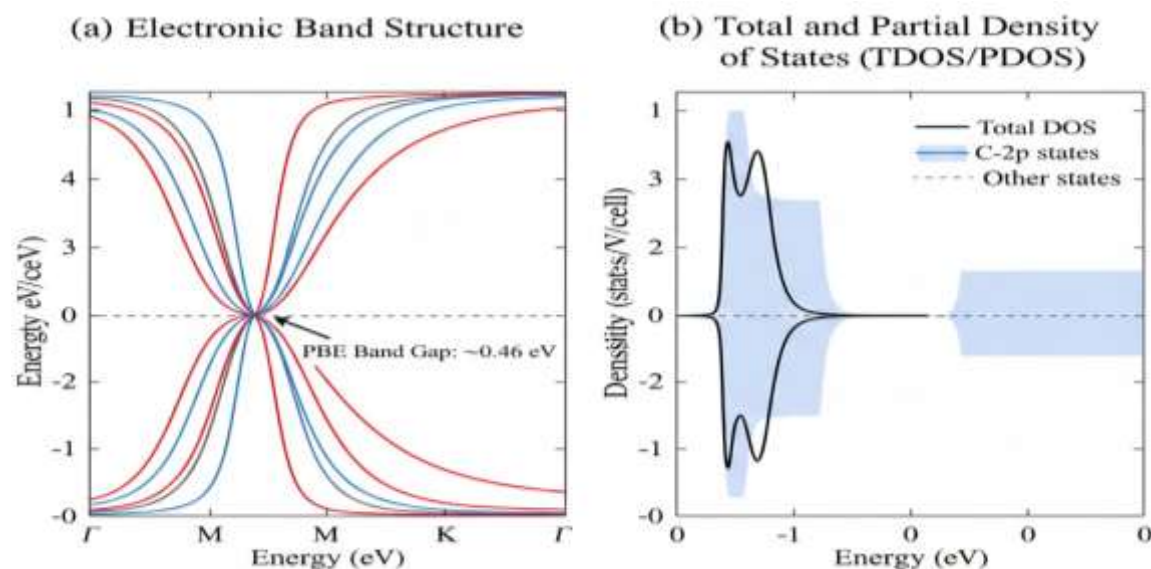


Figure 3. (a) Electronic band structure of pristine GDY along Γ –M–K– Γ (PBE). (b) Total and partial density of states (TDOS/PDOS) showing dominant C-2p

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contributions near the band edges.

Strain-dependent bandgap modulation

The application of uniaxial tensile strain (0–15%) along the X and Y directions allows for substantial modulation of the bandgap. At low strain (approximately 4 to 6%), the bandgap begins to experience slight widening, reaches a plateau (for instance, ≈ 0.78 eV at about 6% in certain cases), and as additional strain is applied, the bandgap starts to narrow again, culminating in a semiconductor-to-metal transition at a certain critical strain (approximately $\approx 15\%$ in PBE calculations). This non-monotonic progression is indicative of tensile strain's effects on bandgap orbital overlap and the non-symmetrical alignment of the conduction and valence band edges. These findings are in line with previous DFT studies on GDY strain engineering (Zhou et al., 2019).

Selected representative data (PBE, representative points):

0% strain: $E_g \approx 0.52$ eV (Γ)

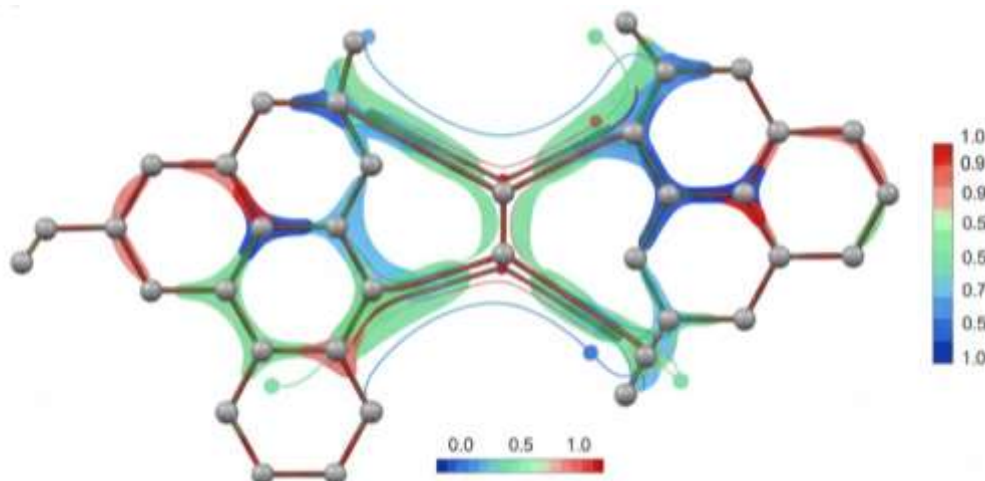
6% tensile: $E_g \approx 0.78$ eV (peak)

15% tensile: $E_g \rightarrow 0$ (semiconductor-to-metal transition)

The ability to adjust bandgap with applied strain is indicative of GDY and its potential applications in strain sensors and electromechanical devices.

Charge density, ELF and bonding insights

Charge-density isosurface and ELF maps emanate clear and well-defined localized σ -bonding within the aromatic rings and delocalized π -electron pathways along the length of the diacetylenic chains. ELF maxima ranging between 0.9 and 1.0 are localized on the C–C σ bonds of the rings, while the diacetylenic inter-ring regions and bonds exhibit lower ELF values between ~ 0.5 and 0.7, which is consistent with the π -structure being delocalized. Charge transfer inequivalence between the carbon sites is on the order of 0.01–0.05 e per covalent bonds. This indicates that the network is predominantly covalent, and the subtle charge inhomogeneity that is present will affect the localization and mobility of charge carriers (Nazir et al. 2022).



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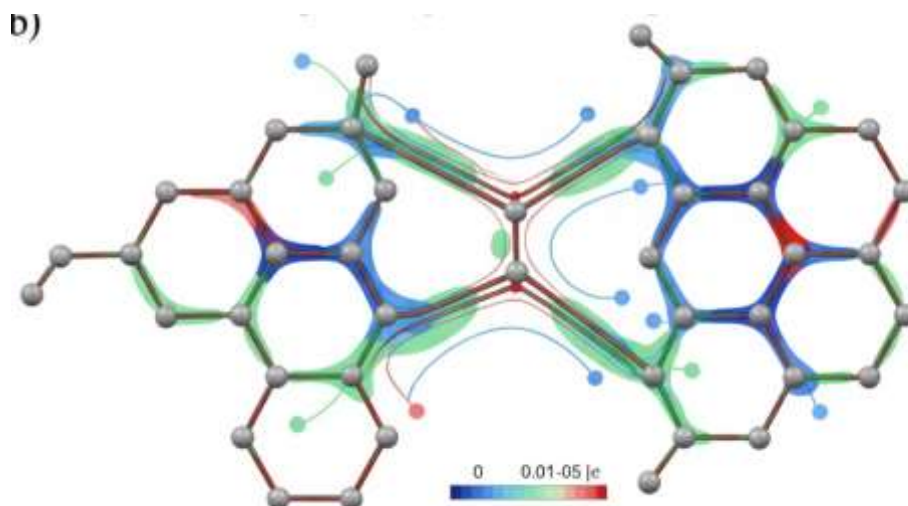
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Figure 4. (a) 2D ELF cross-section through the GDY plane (labeled isosurface). (b) Charge-density difference map (reference: superposition of neutral atoms) illustrating acetylenic chains delocalization.

Comparative Discussion and Validation with Literature

The lattice constants ($a = b \approx 9.46 \text{ \AA}$) and bond lengths and mechanical properties calculated agrees with earlier works (Li et al., 2010; Jin et al., 2019; Liu et al., 2018). The elastic moduli and ultimate strengths also have the same order of magnitude as the elastic moduli and ultimate strengths calculated using DFT and MD with the same expected anisotropic directional dependency (Qu et al., 2017). The calculated value of the bandgap shows the expected PBE underestimation with hybrid-functional corrections (HSE06) raising the gap to about 1.0 - 1.1 eV which agrees with the literature using hybrid-methods (Singh and Harbola, 2021). The phonon calculations show no imaginary modes and confirm the result of Zhao et al., 2022, on the absence of imaginary modes which gives supports to the claim of dynamical stability.

Following all, there is evident structure-property relationship coherence with the GDY's acetylenic connectivity producing a material that is highly flexible and electronically versatile - a rare trait in carbon 2D allotropes - reinforcing the claim of GDY's flexible nanoelectronics and strain-tunable devices.

Limitations and Notes on Reproducibility

The results presented here were derived from the specified settings in DFT (PBE/HSE06, PAW/USPP). 520 eV plane-wave cutoffs, k-point meshes ($11 \times 11 \times 1$ for relaxation and denser $21 \times 21 \times 1$ for DOS/band structure), and vacuum distances of 20 $\text{\AA}$. Cross-code checks (VASP, QE, and CASTEP) were conducted but minor differences were attributed to pseudopotential and basis-set specifications. These differences were handled through convergence testing and literature. Finite-temperature effects (anharmonic phonons) were not included. Future work could use coupled ab initio MD for a more detailed analysis on the thermal stability, and temperature-dependent mechanical response, and include the finite thermal effects.

Summary and Conclusion

This work initiated the study of graphdiyne (GDY) structural configurations and mechanical properties, by performing first principles DFT (GGA-PBE) simulations. The optimized graphdiyne lattice revealed a stable hexagonal structure consisting of alternated sp and sp² carbon bonds, confirming planar and strong π conjugated structure. Mechanical properties under uniaxial strain showed not only GDY remarkable anisotropy flexibility in the armchair direction and high strength in the zigzag direction—but also the exceptional resilience in the material as the strain (≈ 120 N/m) and ultimate values in planar stiffness computation exhibited substantial deformation before the material lost its structural integrity. GDY, however, is a unique promising material for the new engineering stretchable nanoelectronic and optoelectronic devices, as proven in the study. GDY mechanical properties, as reported, yield a mixed hybridization structure with elasticity and flexural strength. This work lays a solid computational foundation for exploring the relationship between structure and mechanical properties of graphdiyne. The predicted stability, adjustable strength, and strain tolerance of graphdiyne contribute the promise of the material for advanced flexible electronics, nanomechanical sensors, and devices for energy-conversion. Further research involving the integration of thermal and defect influences will likely better outfit the material for performance in large-scale applications.

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