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Graphenyldiene: A new sp²-graphene-like nanosheet



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ABSTRACT

The race and the discovery of novel two-dimensional (2D) carbon-based materials have been intensified because many are suitable for energy storage systems, thermoelectric devices, and catalysis applications. Therefore, this study introduces to the scientific community a novel 2D nanosheet named graphenyldiene (GPD), which is formed by arranging cyclobutadiene and bi-phenyl groups to create a monolayer with octadecagonal, hexagonal and tetragonal rings. The cohesive energy of GPD is only 1.37 and 0.65 eV/atom higher than graphene and biphenylene, respectively. Molecular dynamics simulations confirmed its structural and thermal stability. The GPD monolayer remains stable, with no significant deformations at around 1000 K, and the disintegration of the geometry occurs only at a temperature of 1500 K, which is characterized by the formation of an amorphous graphdiyne. The GPD electronic structure shows a direct band gap transition, 1.26 eV, at the Γ point. GPD is a promising alternative to electronic devices due to its carrier mobility of around 10^3 .cm²/V.s. Also, the GPD satisfies the Born-Huang criterion for mechanical stability with elastic constants $C_{11} = 157.62$ N/m, $C_{12} = 53.66$ N/m and $C_{66} = 51.98$ N/m. The Bader's topological analysis indicated that all bonds have strong shared shell characteristics. Finally, the vibrational analysis identified 54 modes, where 21 are Raman active, with A_{1g} and E_{2g} modes dominating the spectrum at 1347, 1685 and 1697 cm⁻¹.

1. Introduction

The discovery and development of new sp²-graphene-like structures have attracted significant interest in recent years [1–6]. These materials possess unique properties such as high conductivity [7,8], mechanical strength [9–11], and thermal stability [12,13], making them attractive for various applications such as energy storage [13–17], thermoelectric devices [18–21], and catalysis [22]. To achieve novel two-dimensional (2D) carbon allotropes with remarkable properties, high-throughput computational simulations [23–26] in conjunction with artificial intelligence (AI) have shown themselves to be promising strategies [1, 27–29].

Combining density functional theory (DFT) and machine learning algorithms has proven to be a promising strategy for generating new carbon-based structures. Morresi et al. [23], employing an algorithm based on the augmentation of regular and semi-regular planar tessellations, predicted sp^2 -bonded carbon allotropes with the lowest density, toughness, and strength comparable to graphene. Xie et al. [30] performed a generalization of patterning Stone-Walse defects manipulation by adding (or removing) carbon pairs on pristine graphene, resulting in

20 2D-carbon allotropes between them, and well-known nanosheets such as pentaheptites, T-graphene, OPGs, and 13 non-reported structures. Regarding the 2D planar sp² carbon lattices, a DFT-based high-throughput framework identified and characterized 190 Dirac semimetals, 241 semiconductors and 683 normal metals in a carbon allotrope scan [31]. These findings can stand in the real world through chemical vapor deposition (CVD) or bottom-up approaches using low-dimensional carbon building blocks [32].

Unprecedented performance and functionality by combining the unique properties of $sp^{2-}carbon$ -based nanosheets with their tunable porosity can be noticed [33], resulting in porous 2D structures such as QPHT-graphene [34], DHP-graphene [35], TPDH-graphene [36], graphenylene [37], triphenylenes [38], naphthylenes [39,40] and tripentaphenes [41,42]. Zhang et al. [43] verified that the Li and K anchorage could modify the naphthylenes to generate a hydrogen storage capacity of 11.07 wt%. The N-triphenylene-graphdiyne [44] showed promising as an anode material for Na-, K-, Mg-, and Ca-ion storage with ultrahigh capacities of 1439, 1871, 2159, and 4319 mAh/g, respectively. Following energy storage applications, the DHP-graphene monolayer was investigated for H₂ purification under

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Fig. 1. Building blocks of the graphenyldiene crafting: (a) the expansion of biphenylene via cyclobutadiene addition resulting in (b) the biphenyldiene (6–4–4–6 arene system), as two benzene rings joined together by two cyclobutadiene, and (c) the conjunction of six biphenyldienes in a hexagonal lattice to obtain (d) the graphenyldiene monolayer.

mechanical strain, being noted that the H₂ permeance met the industrial standard for 6 % of strain, at which the H₂ selectivities over CO₂, CO, N₂, and CH₄ are 3.78×10^{30} , 1.46×10^{31} , 3.61×10^{32} , and 1.91×10^{72} , respectively, at 300 K [45].

Over the past few years, numerous bottom-up chemical pathways have emerged to search for novel nanocarbon structures by strategically selecting molecular precursors [46–51]. This feature can be illustrated by the recent synthesis of biphenylene-like moieties in an octagonal [52] and dodecagonal expansion [53], called 4–6–8 membered biphenylene, and graphenylene, respectively. The biphenylene moiety is characterized by linking two benzene rings with one cyclobutadiene, assuming different topologies depending on the fusion, with prominent circular-membered rings. Regarding the precursors, 4,4″-dibromo-2,2′, 2″,5,5′,5″-hexafluoro-1,1′:4′,1″-terphenyl is used as a building block of the biphenylene via lateral dehydrofluorination (HF-zipping) reaction on Au(111) [52]. On the other hand, Du et al. [53] prepared the graphenylene by the dehydration and polymerization reactions using the 1, 3,5-trihydroxybenene precursor, finding a dodecagonal ring diameter of 5.8 Å that is very closer to the theoretical reports [54].

Given this, a small expansion of 1,3,5-trihydroxybenzene molecules can be proposed through the addition of one cyclobutadiene in the biphenylene group (Fig. 1a), obtaining a new functional group named herein biphenyldiene (Fig. 1b). By arranging these groups in a hexagonal 2D lattice, it is possible to construct a monolayer named graphenyldiene (or $h4^{6}6^{2}18^{1}$, according to the polygon-based symbol proposed by Girão et al. [1]) with octadecagonal, hexagonal and tetragonal rings (GPD) (Fig. 1c and d).

Therefore, this paper is dedicated to presenting the GPD monolayer to the scientific community for the first time. Its viability was theoretically demonstrated via the DFT approach. Its properties were investigated in terms of density of states, band structure, topological and vibrational analysis, and thermal and dynamical stabilities. This study is expected to trigger experimental investigations to synthesize this new 2D material, and its properties can be understood, confirmed and employed in new nanodevices.

2. Methodology

The computational simulations were carried out using the DFT implemented in the CRYSTAL17 package [55]. CRYSTAL17, in conjunction with the HSE06 hybrid functional [56], has been used to

simulate several applications in materials science, chemistry, and condensed matter physics. It investigates the electronic properties of semiconductors, insulators, metals, and complex molecular systems. The double-zeta valence with polarization (DZVP) [57] basis set was adopted to describe the C atoms. The HSE06 functional can accurately account for predicting band gaps, charge transfer processes and reduced self-interaction error [56]. The precision of the infinite Coulomb and HF exchange series is controlled by five α_i parameters with i = 1, 2, 3, 4 and 5, where α_1 is the overlap, α_2 is the penetration for Coulomb integrals, α_3 is the overlap for HF exchange integrals and α_4 and α_5 are the pseudo-overlaps (HF exchange series). The two-electron contributions are neglected when the overlap between atomic functions is lower than $10^{-\alpha_i}$. For the calculations, the five α_i parameters were set to 8, 8, 8, 8, and 16, respectively. The convergence criteria for the electronic energy were set to 10^{-6} a.u./cell for all calculations.

For periodic systems, the only mandatory parameter is the shrinking factor, which generates a proportional grid of k-points in reciprocal space according to the Monkhorst-Pack method used in an $8 \times 8 \times 1$ (36 \times 36 \times 1 for band structure, Density of States (DOS) and Crystal Orbital Hamilton population (COHP) calculations) k-point mesh in the irreducible Brillouin zone.

The vibrational modes at the Γ point were evaluated using the numerical second derivatives of the total energies estimated with the coupled perturbed HF/Kohn–Sham (CPHF/KS) algorithm [58].

The quantum theory of atoms in molecules (QTAIM), proposed by Bader [59] and extended for crystals by Gatti [59,60], is implemented in the CRYSTAL17, and adopted here to understand the nature of chemical bonds based on the electronic density ($\rho(\mathbf{r})$) at the bond critical points (BCPs). Some topological parameters, such as the electronic density laplacian ($\nabla^2 \rho(\mathbf{r})$), the potential energy density (V(r)), the kinetic energy density (G(r)), and the total electronic energy density (H(r) = V(r) + *G*(r)), when evaluated on the BCPs, can provide valuable information regarding the type of bond interaction. The chemical bonds can be classified based on whether the electrons in the bond formation come from shared electron pairs or closed electron shells of one of the atoms. These two types of bonds are known as covalent bonds (shared electron pairs) and ionic bonds (closed shells).

The elastic constants (C_{ij}) were calculated as the second derivative of the energy (E) concerning the strain component $(\epsilon_i \text{ and } \epsilon_j)$ according to the following expression $C_{ij} = \partial^2 E / \partial \epsilon_i \partial \epsilon_j$.

The cohesive energy (E_{coh}) was calculated to confirm and compare



Fig. 2. (a) Unit cell with different bond lengths (l_1 , l_2 , l_3 and l_4) and angles (δ , θ and Δ) represented, (b) phonon dispersion bands, (c) the octadecagonal ring and (d) simulated STM image ($3 \times 3 \times 1$ supercell) of GPD monolayer.

the structural stability of the GPD by the equation [61], $E_{coh} = (E_{monolayer} - n_C E_C)/n_C$, where $E_{monolayer}$ is the total energy of the respective monolayer, and E_C is the energy of each isolated atom, and n_C is the number of C atoms.

The carrier mobility (μ_{2D}) was calculated with the phonon limited scattering mode and effective masses fittings through the deformation potential theory, given from the expression $\mu_{2D} = (e\hbar^3 C_{2D})$ $/(k_B Tm^* m_d(E_1)^2)$, where *e* is the elementary charge, \hbar is the reduced Planck constant, k_B is the Boltzmann constant, T the temperature (in this work T = 300 K), m^* is the effective mass of the charge carrier along the transport direction (m_x or m_y for the x and y directions, respectively), m_d is the equivalent density-of-state mass defined as $m_d = \sqrt{m_x^* m_y^*}$, and E_1 is the deformation potential computed mimicking the lattice deformation due to the carrier-phonon interaction by compressing/dilating the lattice constant and relaxing the atomic positions. E_1 is given by $E_1 = \Delta E$ $\Delta l/l_0$, where ΔE is the energy change of the band (valence band maximum for hole and conduction band minimum for electron) under small lattice deformation (i.e., $\Delta l/l_0 = -1\%, -0.5\%, 0.5\%, 1\%$), l_0 is the lattice parameter in the transport direction, and Δl is the l_0 deformation, C_{2D} is the elastic constant of the longitudinal strain in the propagation direction (x or y) of the longitudinal acoustic wave, which is calculated as $(E - E_0)/A_0 = (C_{2D}/2)/(\Delta l/l_0)^2$, where *E* and *E*₀ are the system energy with and without deformation and A_0 is the area of the 2D lattice in equilibrium.

The effective masses were calculated by a parabolic fitting in the conduction bands minimum and valence bands maximum according to the expression, $(1/m^*) = (1/\hbar) \cdot (d^2 E_n(k)/dk^2)$, where E_n is the band energy dispersion, and k is the point along the Brillouin zone.

The DFTB approximation in its self-consistent-charge (SCC)-DFTB [62] implemented in the DFTB+ code [63] was used to verify the thermodynamic stability of the monolayer. DFTB+Molecular Dynamics (MD) simulations were conducted using the Verlet algorithm and a Berendsen thermostat [64] employing a $4 \times 4 \times 1$ GPD supercell. It utilizes the matsci-0–3 parametrization implemented in the matsci Slater-Koster files [65]. The thermal stability was performed at 300 K for 10 ps with a timestep of 1 fs. Following, to verify the temperature of GPD rupture, the temperature was increased from 300 K up to the breakdown employing the same timestep. The simulated scanning tunneling

microscopy (STM) image was obtained using the Quantum Espresso software [66].

3. Results and discussion

3.1. Structural Properties and Stability

Fig. 2a shows the planar Graphenvldiene (GPD) monolaver with a hexagonal unit cell with the P6/mmm space group (No. 191) and lattice parameters a = b = 9.28 Å and $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$ The unit cell can be described in terms of two non-equivalent atoms in C_1 (0.67283, 0.49097, 0.00000) and C₂ (0.57493, 0.00000, 0.00000) positions, which comprises two bonded central quadrilaterals with hexagons in the extremities. A weak distortion is verified for the hexagons with two different bonds, $l_2 = 1.52$ Å and $l_3 = 1.35$ Å, and the internal angles $\theta =$ 120° For the central quadrilaterals, another distortion is also noticed with $l_1 = 1.46$ Å, $l_2 = 1.52$ Å and $l_4 = 1.39$ Å bonds, and two angles $\delta =$ 93° and $\Delta = 87^{\circ}$ In particular, the average bond length of GPD (1.43 Å) is very close to the calculated in the present work for graphene (1.42 Å) and graphenylene (1.43 Å) nanosheets. Furthermore, the simulations revealed that GPD has an octadecagonal ring with a diameter of 8.32 Å, a much superior ring size than the dodecagonal ring of graphenylene (5.51 Å), indicating a promising use for gas separation and energy storage applications [67]. The cohesive energy of the GPD $(h4^{6}6^{2}18^{1})$ is -7.30 eV/atom, in agreement with the calculated for other 2D-carbon which exhibit the GPD counterparts (quadrilateral and hexagonal rings), as can be seen in the polygon-based symbols: graphene $(h6^1)$ (-8.47 eV/atom), graphenvlene $(h4^{3}6^{2}12^{1})$ (-8.28 eV/atom), porous-graphene ($h6^{2}18^{1}$) (-6.93 eV/atom), α - ($h4^{6}6^{6}9^{2}12^{1}$) (-7.85 eV/atom) and β - ($c4^26^210^1$) (-7.84 eV/atom) naphthylenes, T-graphene $(t4^{1}8^{1})$ (-7.87 eV/atom), and biphenylene $(r4^{1}6^{1}8^{1})$ (-7.95 eV/atom). The results above show that E_{coh} of the GPD is only 1.37 and 0.65 eV/atom higher than graphene and biphenylene, both experimentally reported. These findings attest to the GPD stability from energetic point of view.

Phonon dispersion can be used to assess the dynamical stability of two-dimensional structures. The dispersion relation describes how the phonon energy changes with momentum in the Brillouin zone. The



Fig. 3. Molecular Dynamics snapshots of GPD at (a) 300 K, (b) 600 K, (c) 1000 K, (d) 1044 K, (e) 1200 K, (f) 1400 K, (g) 1500 K, and (h) 1700 K temperatures, and (i) Crystalline Graphdiyne.



Fig. 4. (a) Band structure and (b) Density of States (DOS) of GPD nanosheet.

phonon dispersion should exhibit smooth and well-defined curves in a stable structure, indicating coherent and predictable vibrational modes. Anomalies or irregularities in the dispersion curves, such as imaginary frequencies or the absence of well-defined branches, were not noticed, which indicates high dynamical stability and the absence of structural defects. The phonon dispersion along the high symmetry directions is shown in Fig. 2b, which was obtained using the Phonopy package [68].

Fig. 2d shows the simulated STM image of the $3 \times 3 \times 1$ GPD supercell at a bias voltage of -1 V. The dark regions depict the octadecagonal, hexagonal and square rings, and the brighter spots are the C—C bonds. One can see that the C—C intra-ring bonds (l_4) has a smoother, larger bright area than other connections, which occurred due to the charge concentration in the region mentioned.

Regarding thermal stability, MD simulations were performed from 300 K up to 1700 K (the video animations are available in supplementary material). It was noticed that the GPD nanosheet is stable at around 1000 K, and there are no broken bonds or geometric reconstructions, as displayed in the MD snapshots in Fig. 3. At 1044 K, the first bond breakages occur, and at 1300 K, the formation of some fragments of

graphdiyne is displayed. The GPD disappears completely at about 1500 K. For higher temperatures, amorphous graphdiyne is obtained, and the formation of more graphdiyne rings is not observed. These results unravel the conversion of GPD into an amorphous form of graphdiyne through controlled heating.

3.2. Electronic Properties

The band structure and the total DOS are depicted in Fig. 4. The GPD is a semiconductor with a direct band gap energy transition (at Γ point) of 1.26 eV. The valence band maximum (VBM) and conduction band minimum (CBM) are almost flattened bands between the Γ and K points. An interval with bands absence can be observed in the VB region around -7.50 to -6.00 eV. The bands are more dispersed in the conduction band, which characterizes relatively high carrier mobility compared to the valence band.

To study the carrier mobility along the x (zigzag) and y (armchair) directions, it is necessary to transform the GPD hexagonal lattice into an orthorhombic (Fig. 5i), as can be seen in Fig. 5. Are presented the in-



Fig. 5. VBM (E_{VB}) and CBM (E_{CB}) shift with respect to the lattice dilation or compression in the (a and b) zigzag and (d and e) armchair directions, strain energy (E- E_0) curves along the (c) zigzag and (f) armchair directions, (g) band structure and (i) corresponding Brillouin Zone in (h) an orthorhombic lattice.

Table 1
Carrier effective masses (m_x^* and m_y^*), potential constants ($E_{1,x}$ and $E_{1,y}$, in eV), 2D elastic constants ($C_{2D,x}$ and $C_{2D,y}$ in N/m) and carrier mobilities ($\mu_{2D,x}$ and $\mu_{2D,y}$ in
$10^3 {\rm cm^2/V.s}$).

Carrier	m_x^*	m_y^*	E_{1_x}	E_{1_y}	C_{2D_x}	C _{2D_y}	μ_{2D_x}	$\mu_{2D_{-y}}$
electron	0.618	0.417	1.989	1.981	157.47	157.45	2.711	4.044
hole	0.395	0.389	8.142	8.121	-	-	0.327	0.334

plane uniaxial strain for zigzag (ε_x) and armchair (ε_y) orientations (Fig. 5h). From the band structure calculated in the orthorhombic lattice (Fig. 5 g), notice that the CBM is more dispersive than the VBM, agreeing with the result obtained for the hexagonal lattice, indicating greater electron mobility than the holes. The energy shift of the band edges for zigzag and zigzag strains are plotted in Fig. 5a, b, d and e. The deformation potential constant (E_1) for electrons and holes along the corresponding directions can be obtained from a linear data fitting.

To obtain the elastic constant C_{2D} , the strain energy $(E - E_0)$ was calculated as a function of the lattice compression and dilatation in the x

and y directions and plotted in Fig. 5c and f, respectively. Employing a parabolic fitting the curve of the strain energy versus lattice deformation (ε_x or ε_y), were obtained the following elastic constants $C_{2D_-x} = 157.47 \text{ N/m}$ and $C_{2D_-y} = 157.45 \text{ N/m}$. The equilibrium area (A_0) utilized was 149.11 Å². The R^2 values in Fig. 5a–f indicate the square of the sample correlation coefficient between the calculated values and the fittings, so that $R^2 = 1$ indicates the predictions perfectly fit the data.

The results are summarized in Table 1, where the calculated effective carrier masses $(m_x^* \text{ and } m_y^*)$ and carrier mobilities $(\mu_{2D_x} \text{ and } \mu_{2D_y})$ are also present. The GPD exhibits anisotropic behavior concerning the



Fig. 6. (a) Crystal Orbital Hamilton Population (COHP), (b) partial Density of States (pDOS), (c) Highest Occupied Crystalline Orbital (HOCO), and (d) Lowest Unoccupied Crystalline Orbital (LUCO) for GPD nanosheet.



Fig. 7. (a) Laplacian of the charge density $(\nabla^2 \rho(r))$ surface, (b) all the four different bond lengths (in Å), and (c) single- and double-bond configuration for GPD structure.

carrier effective masses and mobility, mainly concerning the electrons (CB). For zigzag direction $\mu_{2D} = 2.71$ and $0.33 \ 10^3 \text{.cm}^2/\text{V.s}$, while for armchair orientation, $\mu_{2D} = 4.04$ and $0.33 \ 10^3 \text{.cm}^2/\text{V.s}$, for electrons and holes, respectively. These values corroborate the suggested highest carrier mobility at the conduction bands from the band electronic dispersion. Furthermore, GPD is a promising alternative to electronic devices due to its comparable carrier mobility to other 2D materials such as MoS₂ (~200 cm²/(V.s)) [69], phosphorene (~10⁴ cm²/(V.s)) [70], tetrahex-C (~10⁴ cm²/(V.s)) [71], GaSe and GaTe (~ 10³ cm²/(V.s)) [72].

Table 2

Topological parameters based on the Quantum Theory of Atoms in Molecules and Crystals (QTAIMC) analysis for l_1 , l_2 , l_3 and l_4 bonds, where $\rho(r)$ is the charge density, $\nabla^2 \rho(r)$ is the Laplacian of the charge density, $\nabla(r)/G(r)$ is the ratio between the virial (V(r)) and the kinetic density energy (G(r)), and $H(r)/\rho(r)$ is the bond degree all calculated on the bond critical points (BCPs).

Bond	$\rho(\mathbf{r})$	$\nabla^2 \rho(\mathbf{r})$	V(r) /G(r)	H/ ho(r)
l_1	0.25	-0.51	3.65	-0.81
l_2	0.25	-0.52	4.03	-0.79
l_3	0.32	-0.78	3.56	-0.99
l4	0.33	-0.85	3.90	-0.98

Fig. 6a presents the COHP analysis, which determines bonding and antibonding states in a crystal lattice, providing insights into the nature of chemical bonding and the materials' stability. Negative and positive COHP values indicate bonding and antibonding interactions, respectively. For lower energies at valence bands, l_2 , l_3 and l_4 are bonding while l_1 is antibonding. The l_2 exhibits the highest bonding character. Closer to the maximum of valence bands, l_4 and l_3 are bonding, and l_2 becomes antibonding, which agrees with the highest occupied crystalline orbital (HOCO) (Fig. 6c), where for l_4 and l_3 bonds, it is possible to note the orbital overlap along the bond axis. For the conduction bands minimum, it is verified that l_1 and l_2 are bonding, aligned with the lowest unoccupied crystalline orbital (LUCO) (Fig. 6d), where the orbital overlap occurs on these bonds.

The partial density of states (pDOS) of GPD monolayer is depicted in Fig. 6b. For VB lower energies, many states are associated with p orbitals. Closer to the VBM and CBM, the p_z orbitals dominate the distribution with high amount of states. These data demonstrate that the bonds are of π -type, characterizing a great carrier mobility and the high dispersion around the CBM observed in the band structure plot (Fig. 3).

3.3. Bond Topological Analysis

The QTAIMC analysis was employed to understand the chemical character of the GPD bonds. From the analysis of the Laplacian $(\nabla^2 \rho)$ surface, plotted in Fig. 7a and the displayed values of Table 2, it is possible to note a strongly shared shell character for all bonds evaluated. Notice that the l_3 and l_4 are significantly lower than l_1 and l_2 (Fig. 7b), and it is verified highest $\rho(\mathbf{r})$ and very negative $\nabla^2 \rho(\mathbf{r})$, which can be associated with the higher π character of these bonds, resulting in the representative scheme in Fig. 7c, where these interactions are double covalent bonds and the others are single. This is corroborated by the HOCO (Fig. 6c), where it is possible to see the π states resulting from these bonds. Consequently, the cyclobutadiene addition in the biphenylene counterpart generates a charge density accumulation in the l_4 intra-ring bond, evidenced by the higher values of V/G ratio and H/ $\rho(\mathbf{r})$.

3.4. Mechanical Properties

The standard Voigt notation was used to analyze the mechanical stability of the GPD structure, with 1-xx, 2-yy and 6-xy, corresponding to the elastic strain per area ($U(\varepsilon)$), which can be given by $U(\varepsilon) = \frac{1}{2}C_{11}\varepsilon_{xx}^2 + \frac{1}{2}C_{22}\varepsilon_{yy}^2 + C_{12}\varepsilon_{xx}\varepsilon_{yy} + 2C_{66}\varepsilon_{xy}^2$, where C_{11} , C_{12} , C_{22} and C_{66} are components of the elastic modulus tensor, corresponding to the second partial derivative of strain energy.

The Born-Huang criteria play a crucial role in the study and understanding of the stability of materials, especially when dealing with novel and nanoscale 2D materials. Following this criterion, the elastic constants must satisfy the condition, $C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$. Due to the hexagonal symmetry of GPD, this condition is reduced to $C_{11} > |C_{12}|$ and $C_{66} > 0$. The calculated GPD elastic constants are $C_{11} = 157.62$ N/ m, $C_{12} = 53.66$ N/m and $C_{66} = 51.98$ N/m, which satisfies the Born-Huang criterion [73].

The Poisson's ratio (v) and the in-plane Young Modulus (Y) are two

Table 3

Elastic constants (C_{11} and C_{12}) in N/m, Young Modulus (Y) in N/m, and Poisson Ratio (v) for other sp²-carbon-based materials.

Material	<i>C</i> ₁₁ (N/m)	C ₁₂ (N/ m)	Y (N/m)	υ
Graphene (h6 ¹)	355.08	102.56	325.46	0.289
Graphenylene (h4 ³ 6 ² 12 ¹)	248.71	71.69	228.04	0.288
Porous-graphene (<i>h</i> 6 ² 18 ¹)	151.55	62.50	125.77	0.279
T-graphene (t4 ¹ 8 ¹)	324.65	63.44	312.24	0.195
Biphenylene (r4 ¹ 6 ¹ 8 ¹)	307.49/	93.21	273.46/	0.366/
	255.63		227.35	0.303
Naphthylene- α ($h4^{6}6^{6}9^{2}12^{1}$)	259.79	83.84	232.74	0.323
Naphthylene- β ($c4^{2}6^{2}10^{1}$)	243.83	73.92	221.42	0.323
Graphenyldiene (h4 ⁶ 6 ² 18 ¹)	157.62	51.98	140.48	0.330

important mechanical properties used to describe the behavior of materials, especially when subjected to mechanical loads or deformations. Therefore, it is reported that *Y*, which can be given by $Y = (C_{11}^2 - C_{12}^2)/C_{11}$, is calculated to be 140.48 N/m. At the same, the ν , obtained by the relation $v = C_{12}/C_{11}$, is found at about 0.330. These results are summarized in Table 3 for GPD and other 2D carbon-based materials. Due to the anisotropy present on biphenylene, were represented the C_{11}/C_{22} and the Y and ν in zigzag and armchair directions (Y_x/Y_y , and ν_x/ν_y , respectively) and the previously mentioned equations are not used.

It is possible to note that the GPD presents Y lower to those obtained for other carbon membranes listed in Table 3, being a material more flexible than ones, which can be due to its highest pore (8.32 Å), however, is more rigid than porous-graphene ($h6^{2}18^{1}$) that also exhibits octadecagonal carbon rings (7.23 Å, considering the highest C—C distance). In general, the *v* values are closer to 0.300, for all sp²-carbon 2D structures evaluated (except for T-graphene ($t4^{1}8^{1}$)), including for GPD, indicating moderate lateral expansion when the material is under axial deformation.

3.5. Vibrational Analysis

Vibrational modes provide unique fingerprints for different nanostructures. Analyzing the vibrational spectrum allows identifying and characterizing the specific arrangement of atoms in a carbon-based structure. Vibrational modes are directly related to the symmetry operations present in a structure. The vibrational analysis was carried out via the CPKS method [74], indicating the existence of 54 vibrational modes $\Gamma_{vibrational} = 3A_{1g} + 3A_{2g} + A_{1u} + 2A_{2u} + B_{1g} + 2B_{2g} + 3B_{1u} + 3B_{2u} + 12E_{1u} + 6E_{2u} + 6E_{1g} + 12E_{2g}$. The GPD exhibits the C_2 , C_3 , C_6 , I, σ_h , S_6 and σ_v symmetry operations, which results in A_{1u} , A_{2g} , B_{1g} , B_{2g} , B_{1u} , B_{2u} , E_{2u} acoustic modes (inactive in both infrared and Raman), and 21 Raman active modes, $\Gamma_{Raman} = 3A_{1g} + 6E_{1g} + 12E_{2g}$. The A modes are single degenerate and symmetric concerning rotation axis, and E modes are doubly degenerated with two vibrations for each mode, both A and E modes in GPD are symmetric with respect to the inverse (indicated by g subscript). Fig. 8 represents the Raman spectrum of the GPD with the three most intense peaks noticed for 1347, 1685 and 1697 cm⁻¹ with A_{1g} and E_{2g} vibrational modes, respectively. The vibrations associated with these peaks are in plane symmetric stretchings.

4. Conclusion

The graphenyldiene (GPD) structure was characterized by its structural, mechanical, topological and vibrational properties. The cohesive energy of -7.30 eV/atom, phonon dispersion and molecular dynamic simulations demonstrate the energetic, dynamical and thermal stabilities of GPD. Molecular Dynamics simulations indicate the GPD structure is stable up to approximately 1000 K, with lower deformations and no broken bonds. However, at around 1140 K, the first breaks appear, leading to a complete geometry reconstruction of GPD at 1500 K and the formation of amorphous graphdiyne. The electronic structure calculations reveal a direct band gap transition at Γ point with an energy of 1.26 eV, thus being a new 2D semiconductor carbon allotrope. This new structure exhibits anisotropic behavior concerning the carrier effective masses and mobility, mainly concerning the electrons (CB). For zigzag direction $\mu_{2D} = 2.71$ and 0.33 10^3 cm²/V.s, while for armchair orientation, $\mu_{2D} = 4.04$ and 0.33 10^3 cm²/V.s, for electrons and holes, respectively. It is possible to note that the GPD presents Young Modulus lower to those obtained for other sp²-carbon membranes, being a material more flexible than ones.

The COHP analysis exhibits variations across different energy levels of valence and conduction bands. Our description of these bonding and antibonding patterns was reinforced by the plot of crystalline orbitals (HOCO and LUCO), characterizing them as π -type bonds with implications for enhanced carrier mobility. The GPD exhibits covalent bonds marked by strong shared shell characteristics, with particular emphasis on the l_3 and l_4 (intra-ring) bonds, which is produced by the charge accumulation on the cyclobutadiene-like regions.

The vibrational analysis demonstrates the existence of 54 vibrational modes, with 21 Raman active modes. The Raman spectrum has exposed dominant peaks at 1347, 1685 and 1697 cm⁻¹, corresponding to A_{1g} and



Fig. 8. Raman spectra calculated via the CPKS method for the GPD nanosheet and the vibration modes associated with the most intense peaks highlighted.

 E_{2g} modes, respectively. Unveiling the remarkable characteristics of GPD, these findings are expected to motivate experimentalists and theoreticians to compare or confirm our analysis to harness the potential of this novel 2D material.

CRediT authorship contribution statement

José A.S. Laranjeira: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. Nicolas F. Martins: Data curation, Formal analysis, Visualization, Writing – review & editing. Pablo A. Denis: Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – review & editing. Julio R. Sambrano: Data curation, Formal analysis, Funding acquisition, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.cartre.2024.100321.

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