First-principle Investigation of Boron Nitride Nanobelt

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In this paper, we report a new boron nitride molecular structure called BN-nanobelt, an inorganic analog of (12)cyclophenacene synthesized in 2017. An extensive investigation using Density Functional Theory (DFT) and Quantum Molecular Dynamics (QMD) calculations showed that BN-nanobelt is a structurally and thermally stable molecule with all positive vibrational frequencies. BN-nanobelt behaves as an insulator, and it absorbs in the ultraviolet region, suggesting a potential application as a UV detector. All results presented in this paper indicate structural stability and the possibility of its synthesis. We hope that the proposed BN-nanobelt structure could stimulate further experimental investigations on its synthesis and bring potential novel technological applications.

I. INTRODUCTION

Over the last half-century, theoretical and experimental research of a new kind of organic molecules has been made. Heilbronner [1] was the first who introduce a new class of aromatic molecules called carbon nanobelt. His studies dealt with the orbital structure in the hypothetical (n)cyclacenes [2]. These aromatic belts predict radially oriented p orbitals and interesting photoluminescence properties confirmed by experiment [3, 4]. Since Heilbronner inaugurates aromatic carbon nanobelt investigations, other groups proposed new aromatic nanobelts of (n)cyclacene type [5–7], however, they have faced some difficulties in its synthesis due to strain and high reactivity [8]. Carbon nanobelt follows the same symmetry nomenclature patterns of the nanotubes (armchair and zigzag) and consists of a loop of fully fused benzene rings. Nanobelt of (n)cyclacene type follows a zigzag pattern and (n)cyclophenacene type follows armchair pattern. Vögtle proposed and attempted the synthesis of a new kind of armchair carbon nanobelt called Vögtle’s belts [8, 9], unfortunately, the synthesis was unsuccessful. Other groups [10–13] pursued other ways to make armchair nanobelts, but they have not succeeded.

In 2017, a new armchair carbon nanobelt called (12)cyclophenacene was synthesized by Itami, and Segawa’s group [3] which represent segments of an armchair nanotube (6,6). This achievement

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opens a new way of materials synthesis. Inspired by Itami and Segawa’s achievement, Kwan Yin Cheung et al. [4] recently reported the synthesis of two carbon nanobelts, which represent sidewall segments of an armchair and chiral carbon nanotubes (CNTs), (12,12) and (18,12), respectively. In 2021 an achievement in materials science has been reported, the synthesis of a zigzag carbon nanobelt [14]. Zigzag carbon nanobelts are considered the most difficult to synthesize between these two symmetry types (Armchair and Zigzag). This difficulty is due to the high reactivity of zigzag nanobelts [8, 14, 15]. Most recently, nitrogen-doped nanobelts were synthesized [16]. Based on these recent synthetic achievements, we can see the importance of the conjugated carbon nanobelts. In this work, encouraged by these discoveries, we propose a boron nitride nanobelt \((B_{24}N_{24}H_{24})\) with the same geometry as (12)cyclophenacene as shown in Figure 1.

To describe this new structure, an extensive study was carried out using the Density Functional Theory method [17, 18] by calculating electronic, optical, thermodynamic properties and quantum dynamics. It is hoped that BN-nanobelt investigation could serve as seeds to open a new way to synthesize boron nitride nanotubes. This study is organized as follows: In Section 2, the computational methodologies used to obtain all the properties of the proposed structure. Section 3 discusses the results obtained, including structural and thermal stability, electronic properties, optical absorption, vibrational properties, thermodynamics potentials, and quantum dynamics simulation. In Section 4 are presented the concluding remarks.
II. METHODOLOGIES

BN-nanobelt was modeling through molecular software DMol³ [19, 20]. The full geometry optimization was performed using LDA-PWC [21] and GGA-PBE [22] functional. We used the Double Numerical Plus Polarization (DNP) basis set, which includes a polarization p function on all hydrogen atoms. Furthermore, for an appropriate convergence, we considered a maximum energy change below $1.0 \times 10^{-5} H \epsilon$, maximum force of $2.0 \times 10^{-3} \frac{H \epsilon}{\text{Å}}$ and a maximum displacement not exceeding $5.0 \times 10^{-3} \text{Å}$. In all calculations, we employed the DFT semi-core pseudopotentials (DSPP) [23] method to core electrons treatment which rewrites the core electrons by a single effective potential.

After obtaining the optimized molecular nanostructure through the DMol³ code, the infrared and Raman frequencies were evaluated together with the Raman spectrum considering only the GGA-PBE functional due to the geometry optimization criteria were more stringent than other functionals. The vibrational properties to the boron nitride nanobelt ($B_{24}N_{24}H_{24}$) will be presented and compared with other literature results.

The optical absorption was evaluated for both LDA-PWC and GGA-PBE functionals using the DNP basis set and considering the 80 first excited states. In addition, the COSMO solvation model was applied to evaluate solvent effects on the optical absorption [24]. The dichloromethane solvent, with dielectric constant $\varepsilon=9.08$, was considered. The adiabatic local exchange functional approximation (ALDA) [25] was used with time-dependent functional theory (TDDFT) [26]. The BN-nanobelt thermodynamic properties were calculated through only PBE functional and DNP basis sets. All calculations are done at 0K than to estimate thermodynamic properties at finite temperature, and it was necessary considering translational, rotational, and vibrational components to determine enthalpy, entropy, free energy, and heat capacity at constant pressure [27, 28].

To verify the stability of the BN-nanobelt structure under high temperatures, we carried out fully atomistic quantum molecular dynamics (QMD) simulations using SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [29] in an NVT ensemble with Nose thermostat, with temperatures ranging from 1000 to 5000K, in steps of 500K, time step 1fs, and the production time of 2.0ps. To fine-tuning the temperature of rupture, we carried out a QMD from 3000 to 4000K range in steps of 100K. For Boron, Nitrogen, and Hydrogen atoms, we replaced the atomic core for a non-relativistic pseudopotential of Ceperly-Alder [30] without core-correction, where the electronic ground state configuration $[2s^22p^1]$, $[2s^22p^3]$ and $[1s^1]$ were used respectively. A mesh-cutoff of 50 Rydberg ($\sim$680 eV) for 3D grid calculation for some integrals.
III. RESULTS AND DISCUSSION

A. Structural stability and electronic properties

The total energy and the binding energy (energy needed to dissociate the molecular structure) for BN-nanobelt were found and compared with (12)cyclophenacene [3, 15] molecule using the GGA-PBE approach as shown in Table I. This table shows that BN-nanobelt’s total energy is smaller than (12)cyclophenacene, about 1.45 times. This difference can be explained when we look for the electronic Hamiltonian, which describes each one of the molecular systems. BN-nanobelt has more electrons than (12)cyclophenacene, which decreases the system energy. Binding energy results show that BN binding energy is lesser when compared to (12)cyclophenacene; this indicates that carbon-carbon bonds are stronger and requires higher energies to dissociate than the boron-nitrogen bonds. Analyzing the results, we can see the good electronic stability of BN-nanobelt.

In order to support our calculations, we have calculated the borazine (B$_3$H$_6$N$_3$) bond length and bond angle comparing with the available experimental results. The mean borazine bond length is 1.429(1) Å [31] while our results are 1.423 and 1.437 Å considering PWC and PBE functional respectively in the DNP basis set. The borazine mean interbond angles of the six-membered ring are 117.1(1) degrees at the boron atoms and 122.9(1) degrees at the nitrogen atoms [31] while our results show interbond angles are 116.8 degrees at the boron atoms and 123.1 degrees at the nitrogen atoms (mean values) for both PWC and PBE functional. These results are consistent with the BN-nanobelt bonds length and angle (see Table II). It seems that BN-nanobelt consists of fully borazine rings.

The calculated bond lengths for the BN-nanobelt were also carried out through PWC and PBE and are compared in Table II. Our results for the calculated BN-nanobelt bond lengths are in good agreement with the two-dimensional hexagonal boron nitride (h-BN) bond length 1.45 Å [32] and boron nitride nanotubes (BNNTs) bond lengths which is between 1.437 Å and 1.454 Å [33].

The HOMO (highest occupied molecular orbital), LUMO (Lowest unoccupied molecular orbital), and GAP (HOMO-LUMO) energies are shown in Table III for both molecular systems. The hardness ($\eta$) can be approximated using Koopman’s theorem [34] as follows [35, 36]:

$$\eta = \frac{\epsilon_{LUMO} - \epsilon_{HOMO}}{2}$$ (1)
Table I: Total Energy and Binding Energy (in Hartree) of (12)cyclophenacene and BN-nanobelts considering PWC and PBE functionals and DNP basis sets.

| Molecule         | (12)cyclophenacene | BN-nanobelt |
|------------------|--------------------|-------------|
| **Functional**   | PWC                | PBE         | PWC         | PBE         |
| **Basis set**    | DNP                | DNP         | DNP         | DNP         |
| **Total Energy** | -1827.47           | -1841.83    | -1910.95    | -1925.47    |
| **Binding Energy** | -17.56            | -15.79      | -15.81      | -14.11      |

Hard molecules have a large HOMO-LUMO GAP, and soft molecules have a small HOMO-LUMO gap \[37\]. The hardness has an important role in chemical reactivity wherein high HOMO-LUMO GAP is responsible for high kinetic stability, and small HOMO-LUMO GAP indicates low chemical stability \[38\], this suggests that the BN-nanobelt is a very stable structure. From Table III the GAP results suggest that BN-nanobelt presents an insulator property. This insulator behavior was expected since other boron nitride structures as nanotubes (BNNTs) are insulators with a wide bandgap (5-6eV) \[33, 39–41\]. The representation of the frontier molecular orbitals is exhibited in Figure 2. From Figure 2, it is clear the HOMO preference in nitrogen atoms. This preference is due to electronegativity since the nitrogen atom is more electronegative than the boron atom.

To investigate the electronic properties of the proposed BN-nanobelt, we calculated the gap energy, the total density of states (DOS), and the partial density of states (PDOS) after the optimization of geometry using LDA-PWC and GGA-PBE functionals. The DOS of a molecular system describes the number of states allowed to be occupied at each energy range.

From total DOS, Figure 3 can be concluded the insulation character of BN-nanobelt through the analysis of Fermi level whereas the Fermi level is taken to be 0 eV. We find that p orbital has a great contribution to the DOS around the Fermi level. From PDOS it can be inferred that the atomic p orbitals contribute more in the valence region and in the conduction region the p and d orbitals contribute predominantly.
Figure 2: BN-nanobelt frontier molecular orbitals calculated at PBE/DNP (Isovalue 0.015). a) BN-nanobelt HOMO representation and b) BN-nanobelt LUMO representation. Blue and yellow colors represent the positive (module square of real part of wavefunction) and negative (module square of imaginary part of wavefunction), respectively. The boron, nitrogen and hydrogen atoms are illustrated by pink, blue, and white spheres, respectively.

Figure 3: BN-nanobelt total DOS and PDOS a) LDA-PWC, b) GGA-PBE.
Table II: Calculated bond length (Å) and bond angle (degree) of BN-nanobelt considering PWC and PBE functional in DNP basis set.

| Bond (Å) | PWC | PBE | Bond Angle (degree) | PWC | PBE |
|----------|-----|-----|---------------------|-----|-----|
| B1-N1    | 1.413 | 1.426 | B1-N1-B3            | 121.011 | 121.004 |
| B1-N2    | 1.444 | 1.459 | B3-N4-B2            | 117.736 | 117.555 |
| B2-N2    | 1.453 | 1.468 | B2-N2-B1            | 119.863 | 119.771 |
| B2-N4    | 1.446 | 1.461 | N2-B1-N1            | 118.048 | 117.949 |
| B3-N1    | 1.437 | 1.451 | N1-B3-N4            | 117.985 | 117.963 |
| B3-N3    | 1.425 | 1.439 | N4-B2-N2            | 119.446 | 119.459 |
| B3-N4    | 1.451 | 1.465 | B3-N3-B5            | 119.493 | 119.744 |
| B4-N4    | 1.436 | 1.453 | B5-N6-B4            | 119.562 | 118.696 |
| B4-N6    | 1.427 | 1.443 | B4-N4-B3            | 118.492 | 118.135 |
| B5-N3    | 1.428 | 1.443 | N4-B3-N3            | 118.830 | 118.878 |
| B5-N5    | 1.446 | 1.461 | N3-B5-N6            | 117.061 | 116.613 |
| B5-N6    | 1.453 | 1.468 | N6-B4-N4            | 120.160 | 120.164 |
| B6-N6    | 1.444 | 1.459 | B5-N5-B7            | 117.692 | 117.556 |
| B6-N7    | 1.413 | 1.426 | B7-N7-B6            | 120.933 | 120.965 |
| B7-N5    | 1.451 | 1.465 | B6-N6-B5            | 119.846 | 119.718 |
| B7-N7    | 1.437 | 1.451 | N6-B5-N5            | 119.444 | 119.556 |

B. Vibrational properties

The DMol³ code generate a Hessian matrix, a matrix of Cartesian second derivatives, using this to perform a frequency calculation. Harmonic vibrational frequencies are computed by diagonalizing the mass-weighted second-derivative matrix, \( \mathbf{F} \) [42]. The elements of \( \mathbf{F} \) are given by
Table III: HOMO, LUMO, GAP and Hardness ($\eta$) energies (in eV) of (12)cyclophenacene [15] and BN-nanobelts considering PBE and PWC functionals with DNP basis sets.

| Molecule        | (12)cyclophenacene | BN-nanobelt |
|-----------------|---------------------|-------------|
| Functional      | PWC                 | PBE         | PWC         | PBE         |
| Basis set       | DNP                 | DNP         | DNP         | DNP         |
| $\epsilon$ HOMO | -4.84               | -4.64       | -6.14       | -5.92       |
| $\epsilon$LUMO | -3.04               | -2.85       | -1.58       | -1.30       |
| GAP             | 1.80                | 1.79        | 4.56        | 4.62        |
| Hardness ($\eta$)| 0.90                | 0.89        | 2.28        | 2.31        |

Eq. 2:

$$F_{ij} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E}{\partial q_i \partial q_j},$$

being that, $q_i$ and $q_j$ represent two Cartesian coordinates of atoms $i$ and $j$, and $m_i$ and $m_j$ are the masses of the atoms. The square roots of the eigenvalues of $F$ are the harmonic frequencies.

To carry out the calculations of the infrared (IR) intensities of a given mode, this can be evaluated as a square of all transition moments of this mode and expressed in terms of the $A$ (atomic polar tensors) matrix and eigenvectors of the mass-weighted Hessian, according to the Eq. 3 [42]:

$$I_i = \left( \sum_{j,k} F'_{i,j} A_{j,k} \right)^2.$$

$F'$ are eigenvectors of the normal mode, $i$.

The Raman spectrum is based on the Raman effect of inelastic scattering of monochromatic light, resulting in the energy of incident photons being shifted up or down, employed to study the vibrational, rotational, and other low-frequency modes. The energy shift is defined by the vibrational frequency and the proportion of the inelastically scattered light is defined by the spatial
derivatives of the macroscopic polarization \[43\], as also described in previous works to others types of systems following this same scheme \[28, 44–48\]. However, after calculating Raman activities, the DMol\(^3\) code can display corresponding Raman cross sections (intensity) for the Stokes component of the \(i^{th}\) mode for a given experiment incident light frequency and temperature using the Eq. 4 \[43\]:

\[
\frac{d\sigma}{d\Omega} = \frac{(2\pi v_s)^4}{c^4} \frac{h (n_i + 1) I_{Ram}}{8\pi^2 v_c 45},
\]

being that, \(v_s\) is the frequency of scattered light, \(c\) is the speed of light, \(h\) is Planck constant, \(n_i\) is the Bose-Einstein statistical factor, and \(I_{Ram}\) is the Raman activity of the given mode. The parameter \(v_s\) can be obtained from the frequency of incident light \(v_0\), i.e., \(v_s = v_0 - v_i\), we can calculate Raman intensities in experimental conditions \(T\) and \(v_0\).

The symmetry group of the molecule of boron nitride nanobelt \((B_{24}N_{24}H_{24})\) is \(S_6\) with about 106 active modes for both IR and Raman. The calculated frequencies for the nanobelt molecule through GGA approach are shown in Table IV, with some frequencies close to theoretical calculations and experimental results, despite being related to periodic structures of the single-wall boron nitride nanotubes \[49–55\]. Looking to the IR theoretical frequencies, according to the Table IV, in the low-frequency region from 26 to 100 cm\(^{-1}\), characterized by the stretching movement of N-H and B-H bonds, bending of H-B-N, N-B-N, and H-N-B bonds, and the torsional motion of B-N-B-N, H-B-N-B, H-N-B-N bonds. In the region from 100 to 211 cm\(^{-1}\) being related to the stretching movement of N-H and B-H bonds, bending of N-B-N, H-N-B and H-B-N bonds, the torsional motion of H-B-N-B, B-N-B-N, and H-N-B-N bonds, and the out-of-plane torsional motion of N-N-N-B and B-B-B-N bonds. Between frequencies 223 and 390 cm\(^{-1}\) it also includes a stretching movement of B-N bonds, in addition to those mentioned in the previous region. The region between 448 and 1200 cm\(^{-1}\) (with Raman and IR active modes \[52\]), the vibrational modes are represented by: stretching movement of N-H, B-H and B-N bonds, bending of N-B-N, H-N-B, and H-B-N bonds, the torsional motion of H-B-N-B, B-N-B-N, H-N-B-N, and N-B-N-B (additional mode) bonds, and out-of-plane torsional motion of N-N-N-B and B-B-B-N bonds. In the 1224-1500 cm\(^{-1}\) range at medium frequencies (with Raman and IR active modes \[52\]), the vibrational modes are related to the stretching movement of N-H, B-H, and B-N bonds, bending of N-B-N, H-N-B and H-B-N bonds, the torsional motion of H-B-N-B, B-N-B-N, H-N-B-N, and N-B-N-B bonds, and out-of-plane torsional motion of N-N-N-B and B-B-B-N bonds, with emphasis on the stronger stretching movement of B-N bonds. In the region from higher frequencies, between 1500 and 2610 cm\(^{-1}\),
approximately, the modes are assigned to the very strong stretching movement of H-B bonds, bending of N-B-N, H-N-B, and H-B-N bonds, the torsional motion of H-B-N-B, B-N-B-N, H-N-B-N, and N-B-N-B bonds, and out-of-plane the torsional motion of N-N-N-B and B-B-B-N bonds. From 3500 cm$^{-1}$, the vibrational modes are related with a very strong stretching movement of H-N bonds, bending of N-B-N, H-N-B, and H-B-N bonds, and torsional motion of H-B-N-B, B-N-B-N, H-N-B-N, and N-B-N-B bonds.

Figure 4: Raman spectrum of nanobelt in the 0-3600 cm$^{-1}$ range using the GGA-PBE exchange-correlation functional.

Figure 4 presents the calculated Raman scattering spectrum, using the GGA-PBE functional. In the 0-1600 cm$^{-1}$ range, the most intense peak at 26.8 cm$^{-1}$, in the low-frequency regime, is assigned to the movements of stretching of N-H bonds, bending of H-B-N, N-B-N, and H-N-B bonds, and torsional motion of B-N-B-N bonds. The second most intense peak appears at 123.5 cm$^{-1}$ is related to the stretching movement of N-H and B-H bonds, bending of N-B-N, H-N-B, and H-B-N bonds, the torsional motion of H-B-N-B, B-N-B-N, and H-N-B-N bonds, and out-of-plane torsional motion of N-N-N-B and B-B-B-N bonds. The third most intense peak occurs at 305.9 cm$^{-1}$, corresponding
to the stretching movement of N-H, B-H, and B-N bonds, bending of N-B-N, H-N-B, and H-B-N bonds, the torsional motion of H-B-N-B, B-N-B-N, and H-N-B-N bonds, and out-of-plane torsional motion of N-N-N-B and B-B-B-N bonds. There is a fourth intense peak in 1360.3 cm\(^{-1}\) (1364.7, 1376, 1365, and 1366 cm\(^{-1}\), associated with tangential modes at high frequencies for periodic structures of h-BN, which is the main peak in spectra) that can be mainly associated with a stronger stretching movement of B-N bonds and a bending of N-B-N, H-N-B, and H-B-N bonds. Smaller peaks can be seen up to 1600 cm\(^{-1}\) related with the vibrational modes in the same range as the IR active modes. In the 2500-3600 cm\(^{-1}\) range, for higher frequencies, the most intense peak occurs at 2607.5 cm\(^{-1}\) mainly associated with a very strong stretching movement of H-B bonds.

C. Optical properties

Figure 5 shows the BN-nanobelt optical absorbance peak. The calculations were performed using LDA-PWC (red dashed line) and GGA-PBE (solid black line) functional considering the DNP basis set and the molecule immersed in dichloromethane. The result presents all the excited states. The HOMO-LUMO transitions are the first two small peaks in the energy range between 4.8 eV (258 nm) and 5.0 eV (248 nm). The maximum absorption peaks are between 5.0 eV (248 nm) and 5.3 eV (234 nm). The second largest absorption peaks are around at 5.95 eV (208 nm). BN-nanobelt absorbance calculated here is in excellent agreement with previous work on boron nitride nanotubes’ experimental optic properties, which indicates absorbance peaks at 4.45, 5.5, and 6.15 eV [56]. These optical results suggest that BN-nanobelt has potential for applications in optoelectronic as a UV detector.

D. Thermodynamic properties

In Figure 6 it is represented the thermodynamic potentials. The calculated entropy as a function of the temperature in the range of 0-1000 K, Figure 6 a). The BN-nanobelt has a higher entropy when compared to the (12)cyclophenacene nanobelt. This fact suggests that BN-nanobelt reacts a little bit more to temperature changes than (12)cyclophenacene.

The Figure 6 b) presents the heat capacity at a constant pressure of both molecular systems. It is possible to view that the curves are well similar; this result implies that BN-nanobelt slightly absorbs more heat than (12)cyclophenacene, this means that BN-nanobelt needs more energy to raise the temperature by 1 K. BNNTs are known for their high thermal conductivity [57], so it is
| N  | k (cm⁻¹) IR Raman | N  | k (cm⁻¹) IR Raman | N  | k (cm⁻¹) IR Raman | N  | k (cm⁻¹) IR Raman |
|----|------------------|----|------------------|----|------------------|----|------------------|
| 1  | 26.8 Y N 54 512.3 Y N 107 887.1 Y N 160 1297.0 N Y | 2  | 30.9 Y N 55 550.5 N Y 108 887.2 N Y 161 1301.1 N N |
| 3  | 35.3 Y N 56 551.3 N Y 109 889.4 Y N 162 1301.8 Y Y |
| 4  | 47.0 Y N 57 553.6 N Y 110 891.8 Y N 163 1329.2 N Y |
| 5  | 75.9 Y N 58 559.0 Y N 111 895.0 N Y 164 1342.0 N Y |
| 6  | 78.2 Y N 59 561.8 Y N 112 901.8 Y N 165 1347.1 Y N |
| 7  | 82.2 N Y 60 564.6 N Y 113 904.3 Y N 166 1349.9 Y N |
| 8  | 89.3 N Y 61 596.6 N Y 114 925.7 N N 167 1352.5 Y N |
| 9  | 123.5 N Y 62 601.0 Y N 115 978.1 N Y 168 1353.8 N Y |
| 10 | 126.1 N N 63 604.1 Y N 116 981.8 Y N 169 1360.3 N Y |
| 11 | 134.0 Y N 64 619.3 N Y 117 995.2 N Y 170 1391.4 Y N |
| 12 | 135.2 Y N 65 622.0 N Y 118 997.0 Y Y 171 1395.0 Y N |
| 13 | 157.7 Y N 66 626.2 N Y 119 1005.0 Y Y 172 1398.2 N Y |
| 14 | 171.0 N N 67 632.7 Y N 120 1006.4 N Y 173 1402.6 N Y |
| 15 | 177.6 N N 68 633.5 Y N 121 1009.7 N Y 174 1414.0 Y N |
| 16 | 186.6 Y N 69 639.7 N Y 122 1061.8 Y N 175 1417.5 N Y |
| 17 | 187.0 N N 70 640.5 Y N 123 1065.5 Y N 176 1429.2 Y N |
| 18 | 192.1 N N 71 642.2 N N 124 1066.3 N Y 177 1437.3 Y N |
| 19 | 192.2 Y N 72 642.7 Y N 125 1077.3 Y N 178 1447.0 N Y |
| 20 | 204.7 N Y 73 648.3 N Y 126 1079.6 N Y 179 1455.7 N Y |
| 21 | 211.3 Y N 74 656.7 Y N 127 1080.1 N Y 180 1463.4 Y N |
| 22 | 223.8 Y N 75 658.7 Y N 128 1082.4 Y N 181 1466.0 N N |
| 23 | 237.2 Y N 76 673.0 Y N 129 1091.9 N Y 182 1467.0 Y N |
| 24 | 240.5 N Y 77 675.7 N Y 130 1095.2 Y N 183 1478.8 Y N |
| 25 | 273.8 Y N 78 675.9 N Y 131 1103.0 Y N 184 1486.1 N Y |
| 26 | 285.0 N Y 79 689.5 Y N 132 1106.3 N Y 185 1493.8 N Y |
| 27 | 291.3 N N 80 692.7 Y N 133 1124.3 Y N 186 1497.8 Y N |
| 28 | 291.4 N Y 81 693.0 N N 134 1129.2 N Y 187 2527.4 N Y |
| 29 | 294.7 Y N 82 693.7 N Y 135 1130.7 N Y 188 2527.48 Y Y |
| 30 | 305.9 N N 83 696.3 Y N 136 1135.0 N Y 189 2545.9 N Y |
| 31 | 310.1 N N 84 697.7 N Y 137 1138.3 Y N 190 2546.4 Y Y |
| 32 | 313.8 Y N 85 700.7 N Y 138 1139.8 Y N 191 2547.3 Y Y |
| 33 | 320.7 Y N 86 704.3 N Y 139 1157.1 Y N 192 2547.6 N N |
| 34 | 327.5 Y N 87 707.0 Y N 140 1163.5 N Y 193 2551.6 N Y |
| 35 | 343.3 N N 88 710.5 Y N 141 1168.2 N Y 194 2551.7 Y N |
| 36 | 350.8 N Y 89 715.6 Y N 142 1183.2 Y N 195 2568.9 N Y |
| 37 | 351.5 Y N 90 719.5 N Y 143 1184.1 Y N 196 2569.2 Y Y |
| 38 | 354.5 Y N 91 724.8 Y N 144 1200.5 N Y 197 2607.58 Y Y |
| 39 | 354.7 N Y 92 740.5 N Y 145 1224.1 Y Y 198 2607.58 Y Y |
| 40 | 356.1 N N 93 741.3 N Y 146 1225.8 N Y 199 3527.03 N Y |
| 41 | 358.4 N Y 94 752.0 Y N 147 1238.1 Y Y 200 3527.08 Y Y |
| 42 | 364.6 N N 95 755.7 Y N 148 1240.7 N Y 201 3531.11 N Y |
| 43 | 367.7 Y Y 96 761.8 N N 149 1242.0 N N 202 3531.16 Y Y |
| 44 | 386.4 Y N 97 796.5 Y N 150 1242.4 Y Y 203 3532.0 N N |
| 45 | 389.9 Y N 98 823.5 N Y 151 1246.4 Y Y 204 3532.1 Y Y |
| 46 | 407.6 N N 99 826.6 N Y 152 1247.9 N Y 205 3540.08 Y Y |
| 47 | 412.2 N Y 100 848.4 Y N 153 1250.7 Y N 206 3540.69 N Y |
| 48 | 448.8 Y N 101 851.1 N Y 154 1255.3 N Y 207 3544.10 Y Y |
| 49 | 451.6 Y N 102 851.2 Y Y 155 1258.8 N Y 208 3544.12 N Y |
| 50 | 456.7 Y N 103 854.4 N Y 156 1271.6 N Y 209 3554.73 Y Y |
| 51 | 459.2 N Y 104 865.3 Y N 157 1273.9 Y N 210 3554.74 N Y |
| 52 | 483.2 N N 105 869.0 N Y 158 1277.1 Y N - - - |
| 53 | 489.6 N Y 106 878.3 Y N 159 1284.5 Y N - - - |

Table IV: IR and Raman assignment table of BN-nanobelt
expected that BN-nanobelt also presents a high thermal conductivity.

The enthalpy is represented as a function of the temperature in Figure 6 c). The enthalpy of both molecular systems has an exponential behavior as far as temperature increases. We can see in the temperature range of 0-1000K that BN-nanobelt enthalpy (square-blue) is less compared with (12)cyclophenacene; in other words, BN-nanobelt requires less energy to be synthesized than (12)cyclophenacene.

Finally, Figure 6 d) presents the free energy of both molecules. The results show that in the range of 0-1000K, the free energy is positive; in other words, there is not spontaneous formation. For comparison, at 1000 K, BN-nanobelt free energy is 6.1 kcal/mol, and for (12)cyclophenacene free energy at 1000 K is 59.9 kcal/mol. Despite all this, BN-nanobelt presents the lowest free energy compared with (12)cyclophenacene, which indicates a more favorable possibility of its synthesis.

For both molecular structures mentioned here, the entropy and enthalpy increase as temperature increases, indicating that all these reactions are endothermic. Furthermore, BN-nanobelt has a smaller enthalpy and free energy than (12)cyclophenacene, suggesting a potential synthesis. However, we cannot guarantee that synthesis would occur. The process of synthesis is complex due to many factors. Only additional research from an experimental and thermochemical point of
view could confirm our findings.

![Thermodynamic potentials](image)

**Figure 6:** (12)cyclophenacene (circles-red) and BN-nanobelt (square-blue) thermodynamic potentials: a) Entropy, b) Heat Capacity, c) Enthalpy and d) Free energy.

E. Quantum dynamics properties

Using SIESTA code [29], we performed quantum molecular dynamics to analyze the stability of BN-nanobelt in high temperatures. Figure 7 below presents frames for molecular dynamics simulation indicating the frames where this molecular structure starts to break. We observed that BN-nanobelt suffers a rupture at 3000K (∼2727°C), indicating high thermal stability for this structure.

IV. CONCLUSIONS

In this paper, we proposed the BN-nanobelt. We performed *ab initio* calculations within the DFT approach to calculate electronic, optical, and thermodynamics properties. The BN-nanobelt stability was verified through a vibrational frequencies analysis wherein all frequencies are positives. We verified that BN-nanobelt possesses an insulation character with an estimated gap of
around 4.6 eV. The hardness analysis for BN-nanobelt showed high chemical stability. The optical absorption spectra revealed that BN-nanobelt is an excellent UV absorber, suggesting that this molecule could be employed as a UV detector. The calculated thermodynamics potentials indicate that BN-nanobelt could also be synthesized. The calculated IR and Raman frequencies show the following assignments of its active modes, stretching, bending, and torsion of the bonds. The calculated Raman spectrum exhibits the most intense peak at 26.8 cm\(^{-1}\), in the low-frequency regime, corresponding to movements of stretching of N-H bonds, bending of H-B-N, N-B-N and H-N-B bonds, and torsional motion of B-N-B-N bonds. Finally, quantum molecular dynamics results indicated that BN-nanobelt presents high stability at a very high temperature (around 3000 K).

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