Short Communication

2D boron nitride incorporating homonuclear boron bonds: stabilized in neutral, anionic and cationic charge

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Abstract

In this work, by means of molecular simulation, we propose two new armchair boron nitride (BN) nanosheets with homonuclear boron bonds with chemical compositions: $B_{30}N_{24}H_{18}$ and $B_{33}N_{21}H_{18}$ under the scheme of the density functional theory at the level HSEh1PBE/6–311 + + g(d,p). The main characteristic that these nanosheets contain is that the homonuclear boron bonds are concentrated at the central zone and the periphery of the central hexagon (B_3N_3) of the nanosheets, forming pentagonal and triangular geometries. These structural arrangements generate high cohesion energy (for neutral charge − 10.94 and − 10.10 eV/atom, respectively) compared to the nanosheet with heteronuclear bonds (pristine). Also, as a result of quantum simulations, these nanosheets present an insulator (pristine BNNs)—semiconductor ($B_{30}N_{24}H_{18}$ nanosheet)—conductor-like ($B_{33}N_{21}H_{18}$ nanosheet) transition. In addition, it is revealed high polarity (in range of 0.30–4.55 D) and possible magnetic behavior for $B_{33}N_{24}H_{18}$ composition (2.0 magneton bohr). The two nanosheets are stabilized with global neutral charge, anion (− 1|e|) and cation (+ 1|e|), which could be of great interest in the adsorption process and drug delivery.

Article highlights

(1) We report boron nitride nanosheets containing homonuclear boron bonds.
(2) The inclusion of more boron atoms in the boron nitride nanosheets causes an improvement in electrical conductivity.
(3) A magnetic behavior is presented in the boron nitride nanosheet with chemical composition $B_{33}N_{24}H_{18}$.

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1 Introduction

The 2D boron nitride (BN) with hexagonal symmetry and heteronuclear boron-nitrogen bonds was reported for the first time in 2005 [1] with electronic behavior of insulator (5.9–6.1 eV) [2]. The hexagonal BN nanosheets have similar structure to graphene with sp^2 hybridization, as well as B–N bond length of 1.44 Å, which is comparable to the C–C bond length of 1.42 Å in graphene. This nanosheet has gained great interest due to, first, its intrinsic properties [3] and, second, to its various technological applications recently reported [4–7].

However, in the search for new and/or better properties of this 2D BN system, it is essential to propose nanosheets rich of boron and nitrogen atoms (homonuclear bonds) with the chemical composition $B_{30}N_{24}H_{18}$ and $B_{24}N_{30}H_{18}$, respectively, such as it was reported in 2017 [8]. These are stabilized in anionic charge ($Q = -1|e|$) and doublet state ($M = 2$) due to the position of boron atoms forming a linear chain of homonuclear boron bonds. So far, only a few theoretical reports are available on 0D [9, 10], 1D [11, 12] and 2D [13] nanostructures considering these homonuclear bonds and inferring changes in their electronic properties as well as a possible synthesis routes in the case of 0D systems [10].

In this sense, this short investigation reports an electronic structure analysis of two novel boron nitride nanosheets containing homonuclear boron bonds in a specific geometry and the chemical compositions $B_{30}N_{24}H_{18}$ and $B_{33}N_{21}H_{18}$ using de density functional theory (DFT) for the quantum simulations. This study or quantum analysis allows us to propose this nanosheet as adsorber and possible vehicle for drug delivery, and that perhaps it can give us indications of its possible synthesis since it was reported for fullerene-like structures [10].

This work is divided as follows: Sect. 2—Methodology addresses information on the level of DFT theory used to perform quantum simulations, as well as the characteristics of the analyzed systems. In Sect. 3, the analysis was carried out through quantum descriptors typical of DFT theory, to visualize their possible applications, and finally the conclusions are reported.

2 Quantum simulations: computational details

Quantum simulations using density-functional were developed to propose two novel armchair modified boron nitride nanosheets (BNNs) constructed from hexagonal BN patterns. The chemical compositions were: $B_{30}N_{24}H_{18}$ and $B_{33}N_{21}H_{18}$ for a BN nanosheets generating homonuclear boron bonds (see Fig. 1). These systems are generated through the re-emplacement of a central hexagon and periphery by boron atoms. The size of these systems was determined in such manner that the calculated cohesion energy and the |HOMO–LUMO| gap energy are in concordance with the reported experimental and theoretical results [2, 14]. Neutral ($Q = 0$), anionic ($Q = -1|e|$) and cationic ($Q = +1|e|$)) systems were considered in this study (see Supplementary material). Furthermore, two spin-states, defined by multiplicity values ($M = 2S_T + 1$; $S_T = $ total spin) of 1 and 2, they were addressed for the hexagonal BN nanosheet/rich in boron atoms. The full geometry optimization for the BN nanostructures were performed with the HSEh1PBE hybrid functional, coupled with $6-311 + + g(d,p)$ orbital basis sets, as it is implemented in the quantum chemistry Gaussian-09 software [15]. The HSEh1PBE functional, being derived from the Perdew- Burke-Ernzerhof exchange–correlation method (PBE), can describe the non-covalent interactions reasonably well. This functional includes 25% of the exact Hartree–Fock exchange energy [16, 17]. The electronic gap using DFT descriptors [18] was approached as the energetic difference between the frontier orbitals: HOMO (Highest Occupied Molecular orbital) and LUMO (Lowest Unoccupied Molecular Orbital) for case spin no-polarized, and Gap_{HL} spin up $\uparrow = |(\varepsilon_{HOMO} \uparrow - \varepsilon_{LUMO} \uparrow)/2| \approx |\varepsilon_{HOMO} \uparrow - \varepsilon_{LUMO} \uparrow|$ and Gap_{HL} spin down $\downarrow = |(\varepsilon_{HOMO} \downarrow - \varepsilon_{LUMO} \downarrow)/2| \approx |\varepsilon_{HOMO} \downarrow - \varepsilon_{LUMO} \downarrow|$ [19] for open-shell systems. The cohesion energy of these structures was determined as follows: $E_{Coh} = E_T$(BN nanosheets/Rich in Boron)$-kE_T$ (Boron)$-pE_T$(Nitrogen)$-mE_T$ (Hydrogen)$/(k + p + m)$, where E_T represents the total energy for the most stable structures of neutral ($Q = 0$, multiplicity = 1 or 3) or charged ($Q = -1|e|$), multiplicity = 2) nanosheets. While E_T (Boron or nitrogen) represents the total energy for the ground state of the boron or nitrogen atoms. The labels k, p and m represent the number of boron, nitrogen and hydrogen atoms in the structures.

3 Results and discussion

For the new proposals of BN nanosheets, these are stabilized in neutral, anionic ($-1|e|$) and cationic ($+1|e|$) charge, due to the introduction of a greater amount of boron atoms (55.56% more than chemical composition $B_{30}N_{24}$ and 61.11% for $B_{33}N_{21}$, respectively) than pristine BN structure (50/50% of boron/nitrogen). The geometry presented by this nanosheet is influenced by global charge, that is, for chemical composition $B_{30}N_{24}H_{18}$ exhibits pentagonal and triangular geometry at the central zone, as result of

Fig. 1 Boron nitride nanosheets in the chemical composition **a**, **b** $B_{30}N_{24}H_{18}$ (neutral and cation charge); **c**, **d** $B_{33}N_{21}H_{18}$ (neutral charge)
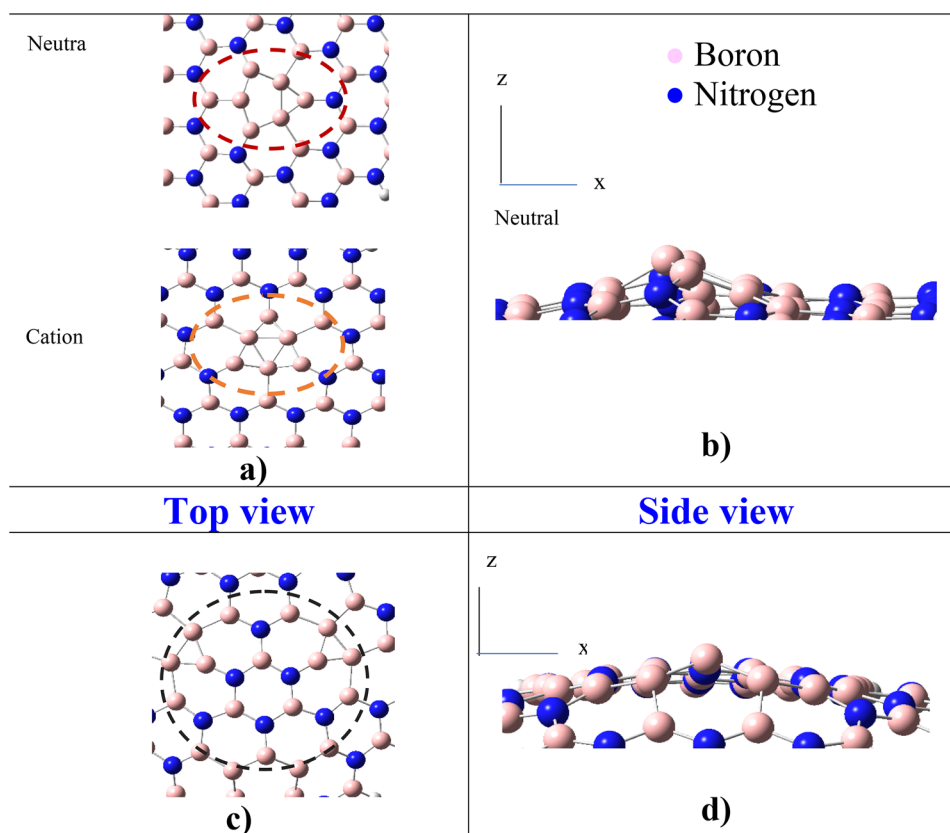
the geometric optimization, see Fig. 1a-top view, versus the hexagonal geometry in the rest of the nanosheet. It is noteworthy that the energetic difference between this nanosheet and that reported in reference 8 (but different arrangement, that is a linear chain of boron atoms) at the same level of theory used in this work is $\Delta E = 1.60$ eV, indicating that we have found it to be more stable the composition and ordering reported in this work. See Table S1—Supporting Information.

The range of values for B–B bond length is larger (1.56–1.79 Å) than those of reported for the other nanosheets rich in boron atoms of the same chemical composition [8]. Here a convexity is also observed in the central zone, see Fig. 1b-top side. Similar situation of increasing occurs for the B–N heteronuclear bond, this range is from 1.40 to 1.47 Å. Therefore, a lot of flexibility is observed in these types of bonds, which may provoke improvements in their mechanical properties. For this same chemical composition with cationic charge (Fig. 1a), a completely triangular geometry is observed at the central hexagon analogous to the boron nanostructures [20], and also this structural change is attributed to the effect of the global charge and multiplicity or spin magnetic moment, as it has been already reported in the literature in the case of a cluster of B_6 being adsorbed on a fullerene-like structure [21].

For the second nanosheet, $B_{33}N_{21}H_{18}$ (see Fig. 1c—top view) chemical composition, the bond distance of B–B is 1.52 to 1.70 Å and 1.44 to 1.48 Å for B–N. Similarly, this nanosheet has a concavity at the central area, see Fig. 1d—top side. Here, around the central zone, a geometry combination of hexagons, pentagons and triangles is observed, this is in the second ring (coronene-like structure).

According to these latter structural features, the new nanosheets improve considerably their stability, as can be seen in Table 1 according to the cohesion energy with a value of -10.94 eV/atom for $B_{30}N_{24}H_{18}$ in neutral charge and of -10.10 eV/atom for $B_{33}N_{21}H_{18}$ also in neutral charge compared to the value reported for BCN nanosheet (-7.4 eV [22]) and graphene -7.8 eV/atom [23], so its structural and chemical stability is guaranteed. Furthermore, to guarantee the determination of local minima, vibrational calculations also as a criterion of structural stability, within the harmonic approximation, were carried out for the lowest energy structures, obtaining positive values, see Fig. 2.

In the same way, this small variation or introduction of a greater number of boron atoms makes it more stable than the previously reported BN nanosheet, which contains a linear chain of homonuclear boron bonds, whose value was found to be -5.48 eV/atom [8].

On the other hand, analyzing their electronic properties such as the value of |HOMO–LUMO| energy gap as

Table 1 Bond length (Å), HOMO−LUMO gap (eV), Dipole moment (Debye), Chemical potential (eV), Moment magnetic (μB) and cohesion energy (eV/atom) for pristine hBNNs, hBNNs/Rich in Boron

Nanosheets	Bond length	|HOMO–LUMO|energy Gap	Dipolar Moment	Cohesion energy	Magnetic Moment	Ionization Potential	Electronic Affinity
BNNs		5.92^a		-7.05^{21}	0.90 (B)/0.83 (N)^{22}		
$B_{27}N_{27}$Ns	1.44 (B-N) ^{b}	5.79^b 5.89^c	0.01^b 0.00^c	-5.64^b -5.59^c	–		
BNNs/B[7]	1.45 (B-N) 1.62,1.63 (B-B)	2.21	1.64	−5.48	1.0		
BNNs/N[7]	1.45 (N–N) 1.43–1.45 (N–N)	1.09	2.01	−5.33	1.0		
$B_{30}N_{24}$Ns/B Neutral^c	1.40–1.47 (B-N) 1.56–1.79 (B-B)	2.10	1.55	−10.94	–	5.82	1.71
Anion^c		1.16↑ 1.36↓ 1.26 average	1.88	−5.44	1.0	–	–
Cation^c		0.91↑ 1.74↓ 1.33 average	0.30	−5.34	1.0	–	–
$B_{33}N_{21}$Ns/B Neutral^c	1.44–1.48 (B-N) 1.52–1.70 (B-B)	0.71↑ 0.19↓ 0.45 average	1.76	−10.10	2.0	5.22	3.48
Anion^c		0.23↑ 2.65↓ 1.44 average	1.90	−5.32	1.0	–	–
Cation^c		2.62↑ 0.22↓ 1.42 average	4.55	−5.20	1.0	–	–

^{a}Experimental value

^{b}Reference 13

^{c}This work

^{A}Neutral charge

^{B}Anionic (− 1) charge

^{C}Cationic charge

a qualitative measure of its electrical conductivity indicates two important transitions: (i) insulator (pristine BN nanosheet) → semiconductor ($B_{30}N_{24}H_{18}$ nanosheet) and (ii) insulator (pristine BN nanosheet) → conductor ($B_{33}N_{21}H_{18}$) transition. This information is corroborated by means of the density of state plot (Fig. 3) obtained from periodic calculations, the conductor-like electronic behavior is clearly observed since it does not present an energy gap. This same electronic transition (insulator-conductor) is also observed in fullerenes with large chemical composition $B_{47}N_{53}$ [23] and $B_{116}N_{124}$ [24] due to the combination of heteronuclear and homonuclear bonds causing its stability.

The value of their polarity (1.55 to 1.88 D) indicates their affinity with solvents such as water (1.85 D). This

effect leads to propose them as sensors or vehicles for drug delivery. In addition, this parameter as a vector (for these cases they point out to the central hexagon with the largest number of boron atoms) tells us how the electric charge distribution is, causing reactive sites, unlike to the pristine structure which it has a null dipole moment.

Also, it is highlighted the fact that the nanosheet in $B_{33}N_{21}H_{18}$ chemical composition is stabilized in global neutral charge and multiplicity 3 (see Table S1—Supporting Information) it is inferred possible magnetism, that is, a magnetic moment of 2.0 μB coming from the atoms of boron hybridized to the nitrogen atoms in the middle of the nanosheet as it is observed in the total spin density, see Fig. 4. This magnetic moment is compared with previous reports for the BN nanoribbons with values of
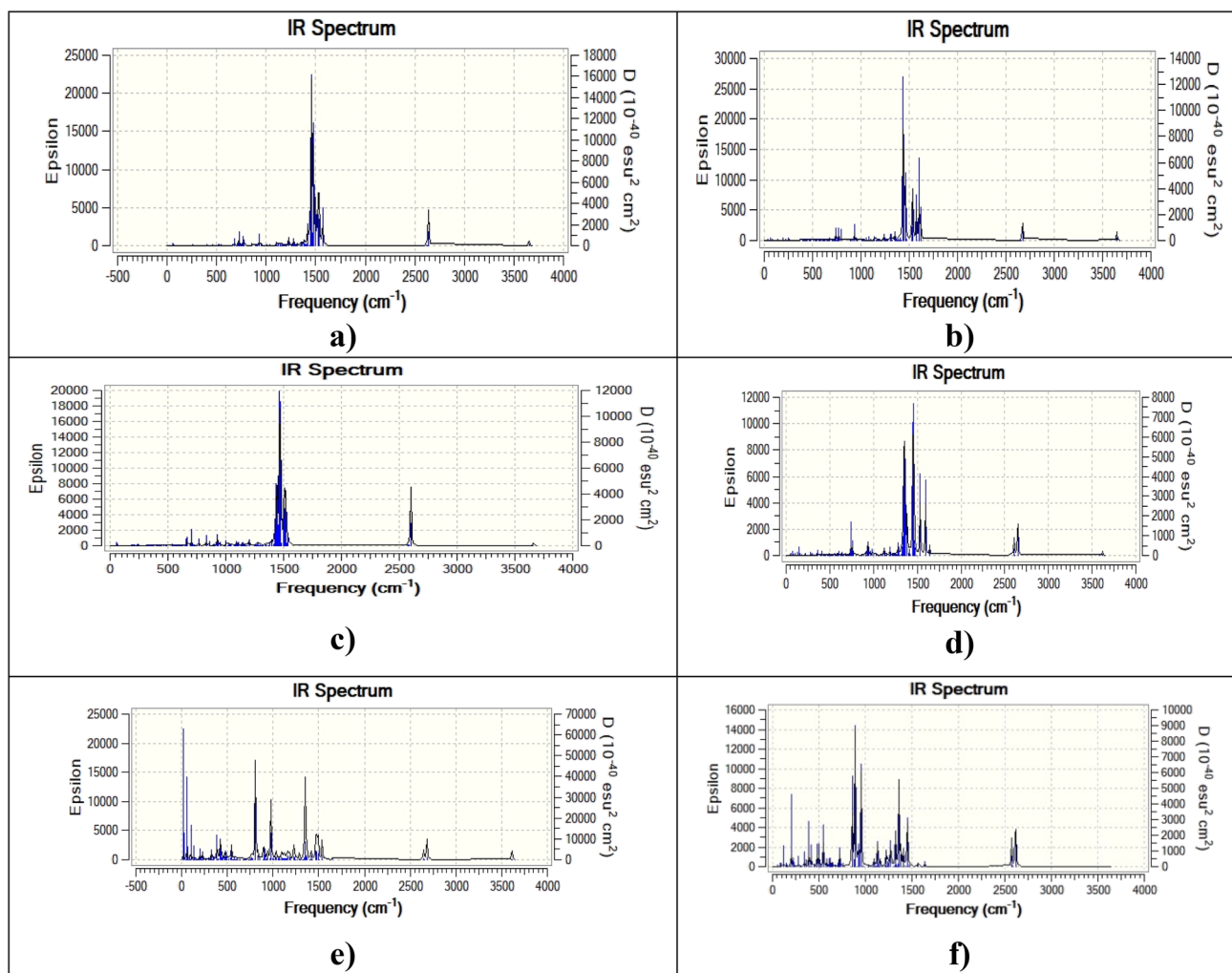
Fig. 2 Vibrational spectrum for nanosheets with neutral, cation and anion charge, **a**, **b**, **c** $B_{30}N_{24}H_{18}$; **d**, **e**, **f** $B_{33}N_{21}H_{18}$
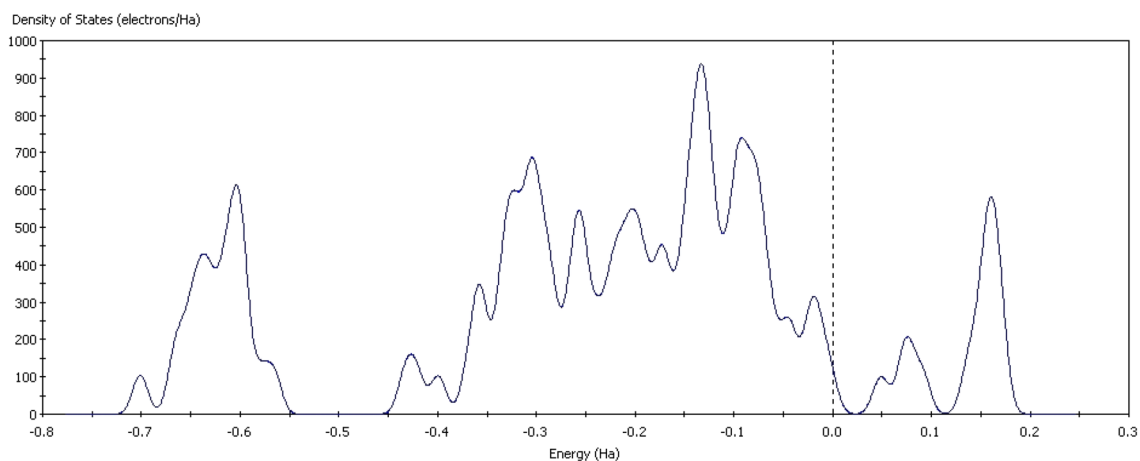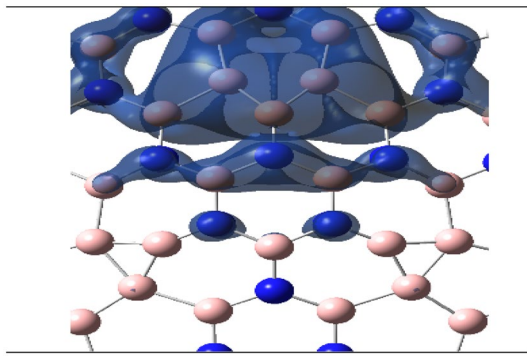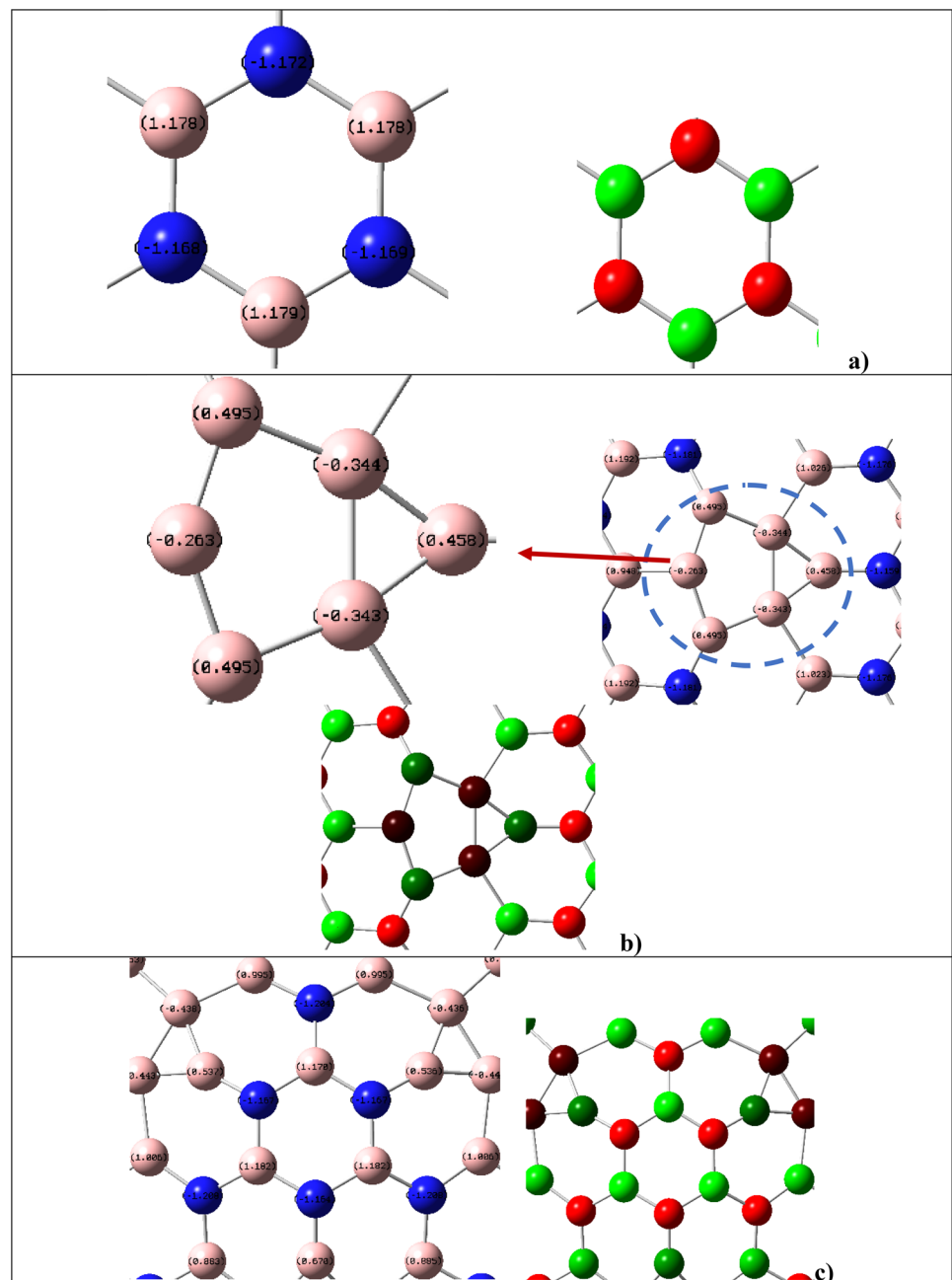

Fig. 3 Total DOS of boron nitride nanosheet ($B_{33}N_{21}H_{18}$-in neutral charge and multiplicity 3)

Fig. 4 Total spin density for chemical composition $B_{33}N_{21}H_{18}$ nanosheet in neutral charge

Fig. 5 Atomic charges of **a** BN nanosheet pristine, **b** $B_{30}N_{24}H_{18}$ nanosheet, and **c** $B_{33}N_{21}H_{18}$ nanosheet. In red and deep red: negative; green: positive

0.90 (for boron) and 0.83 (for nitrogen) µB [25]. Therefore, under these characteristics, it is feasible that we can propose these nanosheets as sensors and/or vehicles for drug delivery due to their richness in the number of boron atoms. As an example of this situation, it is presented in the BN nanosheets that when the pristine is compared versus those containing homonuclear boron bonds, these improve the adsorption of DNA nucleobases on their surface [26] or the possible degradation and activation of contaminants by considering in $B_{12}N_{12}$ fullerenes these types of bonds [9, 27] due to a re-distribution of charge, that is, considering areas with negative and positive charge on boron atoms (Fig. 5) that become attracting sites for

various molecules, also the high polarity, low chemical reactivity and magnetic behavior. This magnetism could favorably influence the adsorption process of various molecules.

Finally, the low value of their electronic affinity/ionization potential (1.71/5.82 eV) indicates that it is feasible for the nanosheet to behave as a charge acceptor/electrodonating, consistent with their nature as a semiconductor/conductor according to their gap energy, respectively.

4 Conclusions

DFT calculations were developed to propose two novel armchair boron nitride nanosheets with heteronuclear and homonuclear boron bonds which were stabilized with neutral, anionic and cationic charge and semiconductor and conductor-like behavior. These were more stable than the pristine $B_{27}N_{27}$ nanosheet (50/50% in boron/nitrogen atoms or heteronuclear bonds) according to their cohesion energy, the dependence is observed in the position where it is doped with boron atoms. They also present high polarity and possible magnetic behavior for the composition $B_{30}N_{24}H_{18}$ (55.56% in boron atoms) and $B_{33}N_{21}H_{18}$ (61.11% in boron atoms) in global neutral charge. According to these electronic properties, these nanosheets are proposed to improve applications for drug sensing and/or transport processes due to higher negative charge (concentrated in boron atoms) that causes areas of attraction for various molecules.

Declarations

Conflict of interest The author declares that he has no conflict of interest.

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