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C₆₀-like boron carbide and carbon nitride fullerenes: Stability and electronic properties obtained by DFT methods

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ABSTRACT

The structural stability, electronic and magnetic properties of novel boron carbide and carbon nitride fullerenes, of chemical compositions: C₃₆B₂₄ and C₂₄B₃₆ (CBF) and C₃₆N₂₄ and C₂₄N₃₆ (CNF), rich in carbon, boron and nitrogen atoms, were determined by means of density functional theory based-methods. Calculations were done using a exchange–correlation functional developed by Heyd-Scuseria-Ernzerhof, within the generalized gradient approximation (HSEh1PBE-GGA) in concert with 6–311G(d,p) basis sets. The DFT simulation results for the neutrals, cations and anions reveal structural stability for the four chosen compositions. Several spin multiplicities were determined for each system. Although distorted, the located low-lying states preserve the basic fullerene features. In the addressed compositions, the lowest energy structures occur for the anions, which behave as semi-metallic and magnetic nanomaterials. Indeed, they have HOMO-LUMO gaps of 0.55, 0.66, 0.34 and 2.17 eV and 3.0, 5.0, 1.0 and 3.0 magneton bohrs, respectively. These CB and CN hybrid fullerenes show high polarity and low-chemical reactivity. Additionally, they have low-work functions, which is crucial for the design of electronic devices.

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1. Introduction

The recently discovered allotropic form of carbon: C₆₀ fullerene presenting 20 hexagons and 12 pentagons in sp² hybridization and semiconductor behavior, with a gap of 1.86 eV, is of great interest due to its novel properties.^[1–3] Currently, several attempts are realized for the design and synthesis of new compounds of such low-dimensional form, presenting the required structural, electronic and energetic properties. For example, boron-carbon nitride hybrid fullerenes,^[4–8] boron-carbon systems of different compositions,^[9–13] and silicon carbide species, showing semiconductor behavior in different stoichiometry,^[14–20] appear to be promising.

The synthesis of CN_x (0 < x ≤ 0.3) fullerene-like compounds was done for the first time in 1995 by Sjöström *et al.*^[21] Other studies confirm the synthesis of Carbon Nitride fullerenes, with a low content of nitrogen atoms.^[22–24] More recently, a Boron Carbide fullerene-like structure, of different composition to that of C₆₀, was reported in 2010 by Jemmis *et al.*^[25] Motivated by the design of new materials of fullerene form, in this work will be studied several C₆₀ compounds, exploring different stoichiometries.

The boron and nitrogen atoms are the nearest neighbors to the carbon atom. Hence, it will be interesting to search for the structural stability of the prototypical C₆₀ fullerene through the doping of boron and nitrogen atoms, which have one less (B) and one more (N) electron than the carbon atom. The

proposed non-stoichiometric systems, C₃₆B₂₄ and C₂₄B₃₆ and C₃₆N₂₄ and C₂₄N₃₆, allow determining the changes of the physicochemical properties for this kind of new fullerene-doped systems. By means of density functional theory (DFT) based-methods,^[26] we will be characterized the structural, electronic, and energetic properties of the proposed C₆₀ non-stoichiometric compounds: boron carbide (C₃₆B₂₄ and C₂₄B₃₆) and carbon nitride (C₃₆N₂₄ and C₂₄N₃₆) in gas phase. Specifically, all-electron calculations are made for the determination of the stability and physicochemical properties of the CB and CN fullerene systems. As quoted below, DFT based-methods contained in the Gaussian software were used.^[27]

2. Simulation models and methods

The structural, electronic and magnetic properties of new C₆₀-like boron carbide and carbon nitride fullerenes, CBF and CNF, with the C₃₆B₂₄, C₂₄B₃₆, C₃₆N₂₄ and C₂₄N₃₆ composition being rich in carbon, boron and nitrogen atoms, are studied by means of first principles DFT total energy calculations. The next structural details characterize this kind of nanostructures, which are similar to those previously reported.^[13] It contains 7 C–C, 1 C–C–C and 2 C–C–C–C bonds; aside from the absence of B–B and N–N bonds for C₃₆B₂₄ and C₃₆N₂₄, respectively. Appears also hexagons formed by 5 C and 1B and 5 C and 1 N atoms. For C₂₄B₃₆ and C₂₄N₃₆ fullerenes, we consider:

7 B–B or N–N, 1 B–B–B or N–N–N and 2 B–B–B–B or N–N–N–N bonds, see figure 1. This is the criteria used for the construction of the candidate geometries of these non-stoichiometric compounds, which after a relaxation procedure present structural stability.

In this work, all structures are optimized using the hybrid HSEh1PBE functional; which is derived from the PBE method and includes 25% of exact Hartree-Fock exchange.^[28,29] The HSEh1PBE method, able to describe non-covalent interactions, is available in the quantum chemistry software GAUSSIAN-09.^[27] Source of errors from the basis sets were studied using the valence split 6-311G(d,p) set for the simulations, negligible changes appear for the structural parameters and for the HOMO–LUMO gaps. Several spin multiplicities ($M = 2S_T + 1$, where S_T is the total spin) were inspected for each system. For example, doublet, quartet and sextet were calculated for the anions of the $C_{36}B_{24}$ and $C_{24}B_{36}$ species. In Tables S1 and S2 are reported the multiplicities all the studied neutral and charged compositions. Tight convergence criteria was required in the stage of the geometry optimization. Employing an ultrafine grid, strict convergence was required for the total energy, minimized to 10^{-8} a. u. The geometries were optimized with a 10^{-4} a. u. threshold and for the RMS forces a 10^{-6} a. u. threshold was employed. Also in this way and for guarantee the determination of local minima, vibrational calculations within the harmonic approximation were done for the low-lying states, obtaining positive values. On the other hand, the spin contamination for the studied systems was quite small. For instance, for the sextet, quart, doublet, and quart state of the $C_{24}B_{36}$, $C_{36}B_{24}$, $C_{36}N_{24}$, and $C_{24}N_{36}$ systems, the obtained value

for the S^2 operator is of 8.7546, 3.8311, 0.8359, and 3.7505 which differs by 0.5, 8.11, 8.59, and 0.05% from the exact value. The structures having the lowest total energies are shown in Table 1 and Table S1 and S2 in the supplementary information.

Let us to mention that not all the possible isomers for each composition were determined. This task will require enormous amounts of computational time. However, under the used bonded criteria (of the B, C and N atoms criteria for the construction of the structures all the currently identified isomers present structural stability. As quoted above, we carefully studied the effects of the charge and spin multiplicity for each system. Interestingly, the anions, mostly in high spin-states, are the ones that define the lowest energy states for the chosen compositions. It is expected that these results may exemplifies the kind of properties that may present these type of doped fullerene systems

The analysis is realized in terms of quantum descriptors, obtained within the DFT framework.^[30] The electronic gap was considered as the energetic difference of the frontier orbitals: HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). The chemical potential, μ , being a measure of global chemical reactivity, was estimated as the (HOMO+LUMO)/2 arithmetic mean, since for a free electron gas it is equal to the Fermi level, and is considered the center of such energy gap.

For the design of optoelectronic devices, it is important to determine the work function (WF).^[31] This property defines the minimal energy needed for removing an electron from a solid to a point immediately outside the surface or the cost of

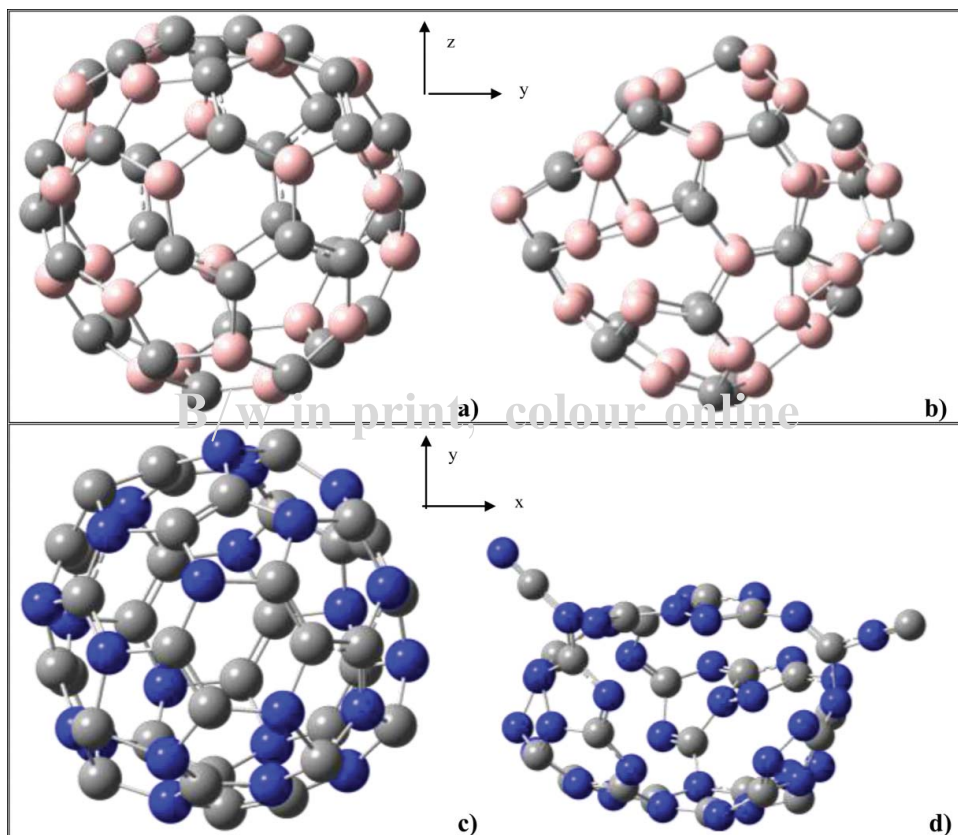


Figure 1. Lowest energy structures for a) $C_{36}B_{24}$ fullerene ($Q = -1$; $M = 4$), b) $C_{24}B_{36}$ fullerene ($Q = -1$; $M = 6$), c) $C_{36}N_{24}$ fullerene ($Q = -1$; $M = 2$) and d) $C_{24}N_{36}$ fullerene ($Q = -1$; $M = 4$).

Table 1. Bond length (Å), HOMO-LUMO gap (eV), Dipolar moment (Debye), Chemical potential (eV), Work function (eV), Moment magnetic (μ_B), Cohesion energy (eV), Electronic affinity (eV), Ionization potential (eV) for Boron Carbide and Carbon Nitride fullerenes.

Fullerenes	Bond length	HOMO-LUMO Gap	Dipolar Moment	Chemical potential	Work Function	Magnetic Moment	Cohesion energy	Electronic Affinity	Ionization Potential
C ₆₀	1.41 [†] (C–C)	1.86 [48]	0.61 [36]	−4.78	—	—	−7.04 [49]	2.66 [38]	7.58 [39]
C ₃₆ Si ₂₄ [50]	1.40-1.47 (C–C)	0.89	1.16	−5.75	0.45	—	−7.38	—	—
B ₂₄ N ₃₆ [45]		0.59	3.80	−6.07	0.29	1.0	—	—	—
C ₃₆ B ₂₄ ; Q = 0, M = 3	1.37-1.42 (C–C)	0.53	2.07	−9.06	0.26				
Q = −1, M = 4*	1.53-1.60 (B–C)	0.55	1.46	−9.08	0.28	3.0	−6.02	4.24	11.54
Q = +1, M = 2		0.25	1.22	−9.21	0.12				
C ₂₄ B ₃₆ ; Q = 0, M = 3	1.42-1.65 (B–C)	0.20	2.11	−8.71	0.11				
Q = −1, M = 6*	1.56-1.86 (B–B)	0.66	0.84	−8.71	0.33	5.0	−5.77	3.00	9.04
Q = +1, M = 4		0.39	3.59	−8.81	0.20				
C ₃₆ N ₂₄ ; Q = 0, M = 3	1.32-1.46 (C–C)	0.36	4.23	4.60	0.18				
Q = −1, M = 2*	1.32-1.53 (C–N)	0.34	2.25	−4.59	0.17	1.0	−5.34	2.30	5.20
Q = +1, M = 4		0.82	2.67	−4.81	0.41				
C ₂₄ N ₃₆ ; Q = 0, M = 3	1.42-1.44 (N–N)	0.35	4.64	−4.72	0.17				
Q = −1, M = 4*	1.30-1.45 (C–N)	2.17	17.48	−5.93	1.05	3.0	−5.02	26.37	14.33
Q = +1, M = 4		1.99	15.68	−5.74	0.99				

[†]Experimental data.

*Minimal energy structure.

energy for to move an electron from the Fermi energy level into vacuum. The work function was roughly determined as the difference of the potential energy of the empty LUMO level and the Fermi energy (or chemical potential). The cohesion energy of these structures was obtained as follows: $E_{\text{Coh}} = E_{\text{T}}(\text{C}_{36}\text{B}_{24}, \text{C}_{24}\text{B}_{36}, \text{C}_{36}\text{N}_{24} \text{ or } \text{C}_{24}\text{N}_{36}) - kE_{\text{T}}(\text{Carbon}) - pE_{\text{T}}(\text{Boron or Nitrogen}) / (k + p)$, where E_{T} represents the total energy for the most stable structures of charged ($Q = -1$, multiplicity = 4, 6, 2 and 4) fullerenes. While E_{T} (Carbon, Boron or Nitrogen) represents the total energy for the ground state of the Carbon, Boron or Nitrogen atoms. The labels “k” and “p” represent the amount of Carbon, Boron, and Nitrogen atoms in the structures.

Lastly, the MEPs surfaces (Molecular Electrostatics Potentials) were determined as described in the literature.^[32] These surfaces are usually associated with the lone pairs of the more electronegative atom.

3. Results and discussion

3.1 Stability and structural properties

The fully relaxation process indicates that the boron carbide fullerene of composition C₃₆B₂₄ has a lowest energy state for the anion ($Q = -1$, in figure 1 a), producing magnetic behavior, because a quartet ($M = 4$) was found for the ground state; Table S1—complementary material. The stability of this rich in carbon system was obtained by means of a vibrational analysis, done under the harmonic approximation. Indeed, the frequencies for the vibrational modes have positive values; the whole IR spectrum of these systems are shown in figure 2. The structural stability of these species was also done using at the M06 (the hybrid functional of Truhlar and Zhao)^[33] and VSXC (van Voorhis and Scuseria’s τ -dependent gradient-corrected correlation method),^[34] levels of theory. Similar results were found as those using HSEh1PBE. Strongest bands appears for the CB systems. In the C₃₆B₂₄ fullerene the strong peaks occurs at 407.4 and 751.9 cm^{−1}, which corresponds to the wagging of the whole structure; see figure 2 a. For the rich in boron C₂₄B₃₆ nano-cage, stabilized for an anionic ($Q = -1$) charge of

multiplicity 6, figure 1b, such band emerges at 1320.7 and 1565.7 cm^{−1} (figure 2b). It has signatures of stretching vibrations throughout the B-C bonds. For the C₃₆N₂₄ fullerene rich in carbon atoms which stabilized for an anionic ($Q = -1$) charge and multiplicity 2, see figure 1 c and Table S2—complementary material), the peak leaders appears at 342.9 and 1492.0 cm^{−1} and corresponds to wagging modes over the whole net. Other band was found at 1670.6 cm^{−1}, being assigned to stretching modes of the C-C bonds, see figure 2 c.

Note that larger content of nitrogen atoms, as in C₂₄N₃₆, produce also nano-cage-like structures, which are stabilized for an anionic charge ($Q = -1$) and multiplicity 4, figure 1 d, and with the peculiarity that the C-N and N-N bonds are dissociated. The estimated IR spectrum of C₂₄N₃₆ presents main bands at: 939.2, 1103.4, 1255.8, 1318.7, 1557.6 and 2208.6 cm^{−1}, mainly assigned to stretching movements of the N-N and C-N bonds.

Regarding the bond distances, the rich in carbon C₃₆B₂₄ dot present 1.37 – 1.42 Å and 1.53 – 1.60 Å for the C-C and B-C bonds, respectively. The dimensions of this structure are: 0.75 nm along the “x” axis, 0.74 nm along the “y” axis, and 0.67 nm along “z”. With an inverse composition, C₂₄B₃₆ has also nano-cage-like shape, but with larger bond lengths: 1.42 – 1.65 Å and 1.56 – 1.86 Å for the B-C and B-B bonds, respectively. Consistently, the dimensions of this structure are of 0.83 nm for the “x” axis, 0.75 nm along the “y” axis an 0.65 nm for the “z” axis.

For the poor in nitrogen system, the bond lengths are: 1.32 – 1.46 Å and 1.32 – 1.53 Å for the C-C and C-N bonds, respectively. The dimension of this structure are: 0.71 nm, 0.66 nm, and 0.69 nm along the “x”, “y” and “z” axis, respectively. Lastly, the C₂₄N₃₆ nanocage-like structure, shows N-N and C-N bond lengths of 1.42 – 1.44 Å and 1.30 – 1.45 Å, respectively. See Table 1, for a resume of the properties.

3.2 Electronic properties

The estimated cohesion energies indicate values of −6.02 eV/atom for C₃₆B₂₄, −5.77 eV/atom for C₂₄B₃₆, −5.34 eV/atom for C₃₆N₂₄, and −5.02 eV/atom for C₂₄N₃₆, implying high stability for these

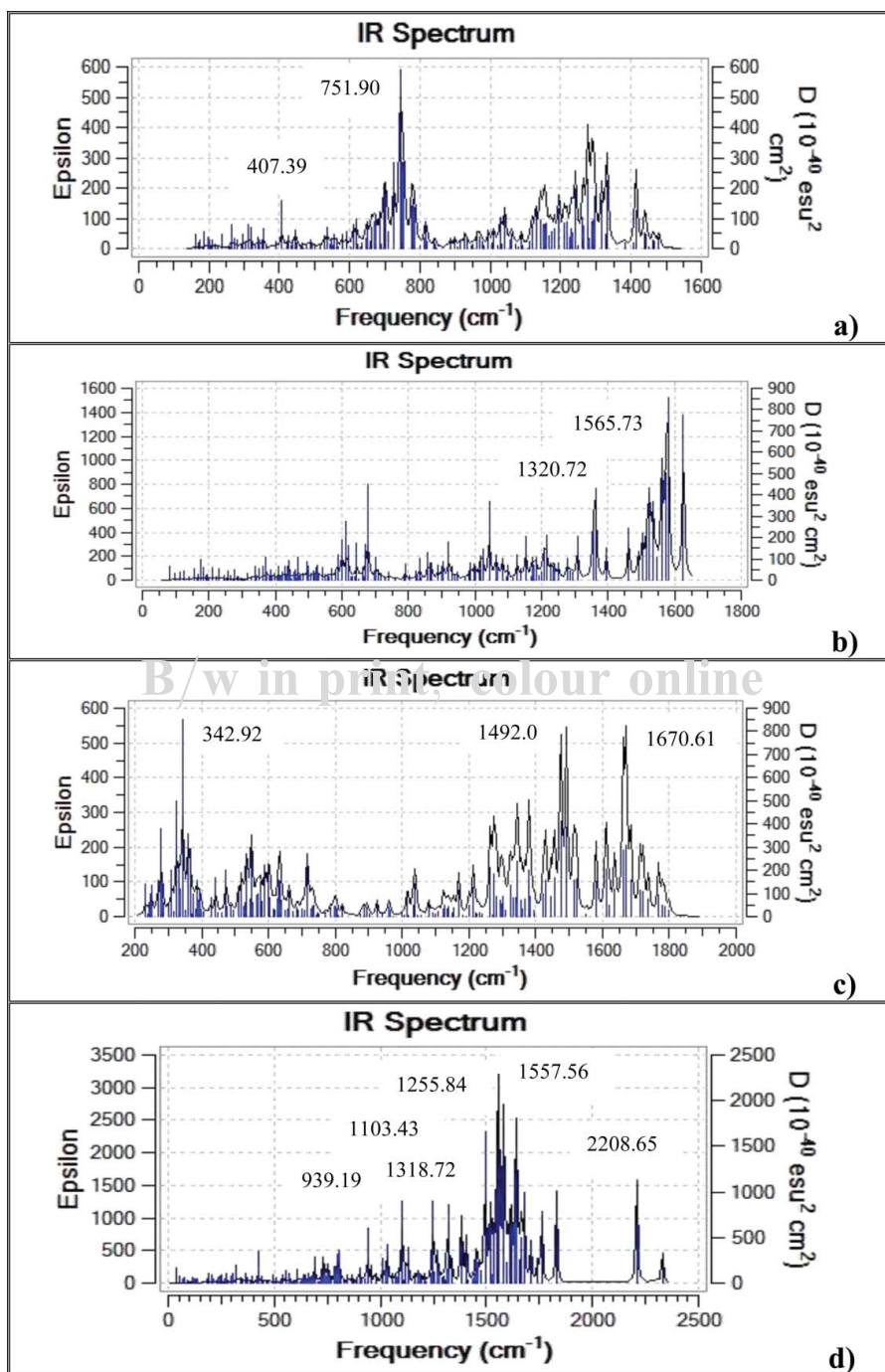


Figure 2. Infrared spectra for a) $C_{36}B_{24}$ fullerene ($Q = -1$; $M = 4$), b) $C_{24}B_{36}$ fullerene ($Q = -1$; $M = 6$), c) $C_{36}N_{24}$ fullerene ($Q = -1$; $M = 2$), d) $C_{24}N_{36}$ fullerene ($Q = -1$; $M = 4$).

anionic compounds, which is even comparable to that, 7.04 eV, of the prototypical C_{60} fullerene, see Table 1.

The analysis of the electronic properties reveals drastic reduction of the HOMO–LUMO gap, of 1.31 eV ($C_{36}B_{24}$) and 1.20 eV ($C_{24}B_{36}$), as referred to that, 1.86 eV, of pristine C_{60} . In fact, these rich in carbon and boron nanomaterials reach semi-metallic behavior, as they have gaps of 0.55 and 0.66 eV; see Table 1. Remarkably, the $C_{36}N_{24}$ fullerene presents a considerable small gap, of 0.34 eV. These behaviors are mainly originated from the bonding effects: formation of homonuclear carbon or boron bonds may improve the conductivity of these non-stoichiometric nanostructures. The N–N bond formation

is reflected in the rich in nitrogen $C_{24}N_{36}$ fullerene anion, which undergoes a significant increase in the gap (2.17 eV), behaving thus as a semiconductor nanostructure. Qualitative insight of the conductor behavior may be obtained through the formula: $\sigma = \alpha \exp(-E_g/kT)$, where E_g is equal to the HOMO–LUMO gap, “k” is the Boltzmann constant and “T” is the absolute temperature.^[35] As shown in Table 1, the HOMO–LUMO gap for the rich in carbon neutral species, $C_{36}B_{24}$ and $C_{36}N_{24}$, is similar to that of the respective anions. However, the gap for the rich in boron and nitrogen neutral species, $C_{24}B_{36}$ and $C_{24}N_{36}$, differs from that of the anions. The effects of the charge and composition on the conductivity are shown by these results.

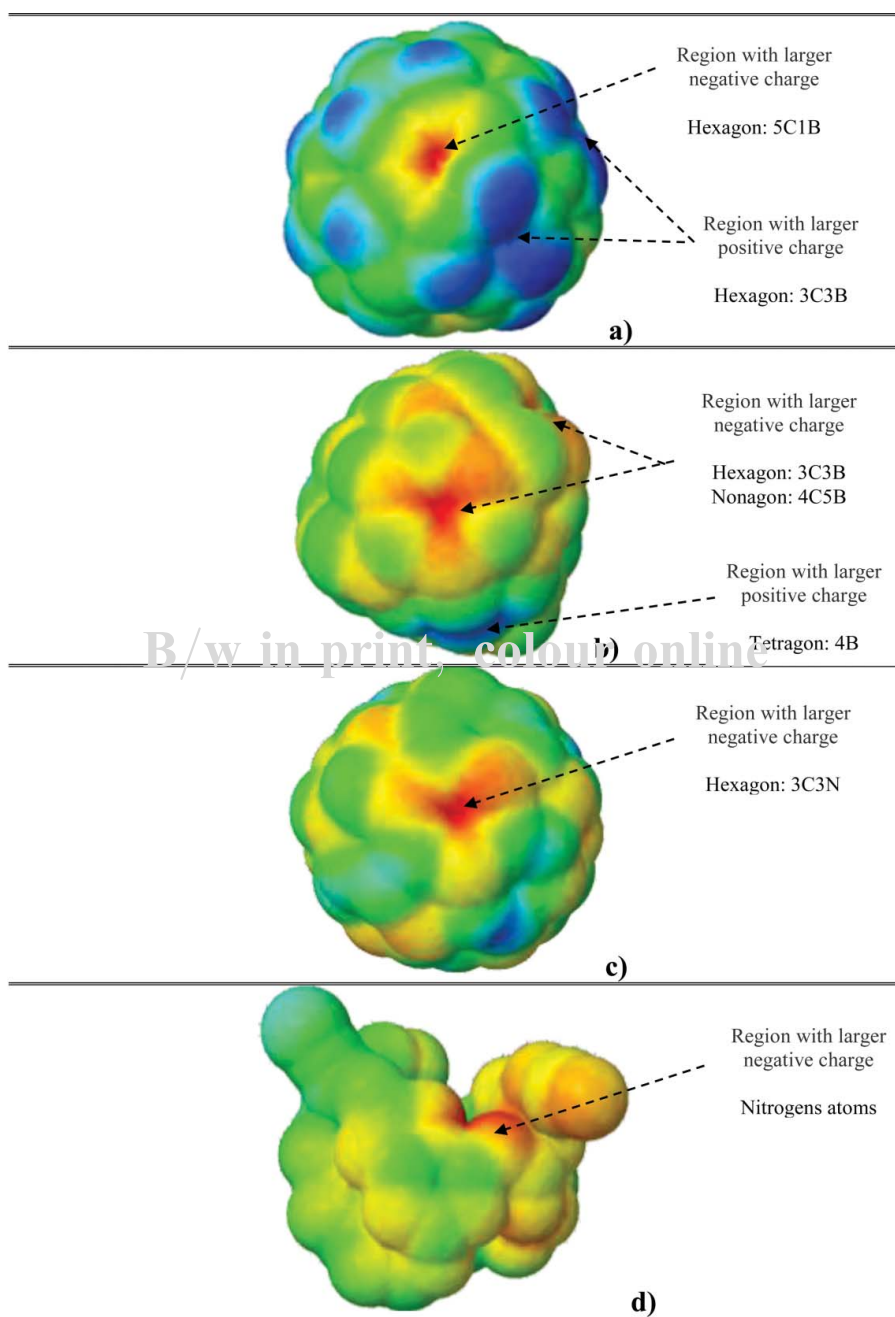


Figure 3. MEPs surfaces of the a) $C_{36}B_{24}$ fullerene ($Q = -1$; $M = 4$), b) $C_{24}B_{36}$ fullerene ($Q = -1$; $M = 6$), c) $C_{36}N_{24}$ fullerene ($Q = -1$; $M = 2$), d) $C_{24}N_{36}$ fullerene ($Q = -1$; $M = 4$).

Noticeably, it was determined an increase in the polarity of these boron carbide fullerenes in the gas phase. Indeed, dipole moments of 1.46 D and 0.84 D appear for the $C_{36}B_{24}$ and $C_{24}B_{36}$ anions, respectively. For carbon nitride fullerenes, we have values of 2.25 D for $C_{36}N_{24}$ and of 17.48 D for the $C_{24}N_{36}$ fullerene. Such increase reflects the polarization ability of the electronic clouds (promoted by the C-B, C-N and homo-nuclear C-C, B-B and N-N bonds) making feasible the solubility of such fullerenes. This behavior differs from the one of pristine C_{60} , having an average dipole moment of 0.61 D.^[36]

Therefore, the polarity increase of the non-stoichiometric CB and CN systems made viable their potential application in biological process. Particularly is the transportation of pharmaceutical molecules presenting negatively charged surfaces, as it

is reported in the literature, where it is studied the adsorption of dopamine with, negatively charged, membrane.^[37]

Concerning the chemical potential, there are observed reductions of 4.3 and 3.93 eV for the $C_{36}B_{24}$ and $C_{24}B_{36}$ fullerenes, which reaches smaller values, of -9.08 and -8.71 eV, as compared to the one, -4.78 eV, for C_{60} . For the $C_{24}N_{36}$ fullerene a reduction of 1.15 eV was determined. Such decrease implies lower reactivity for the non-stoichiometric systems. Unexpectedly, a small increase (0.19 eV) of reactivity is predicted for the $C_{36}N_{24}$ cage, since it has a chemical potential of -4.59 eV.

Note that the electron affinity and ionization potential are equal to 4.24 eV and 11.54 eV for $C_{36}B_{24}$ and 3.00 eV and 9.04 eV for $C_{24}B_{36}$. These results for the neutral compounds are clearly larger than those, 2.66 eV^[38] and 7.58 eV,^[39] for

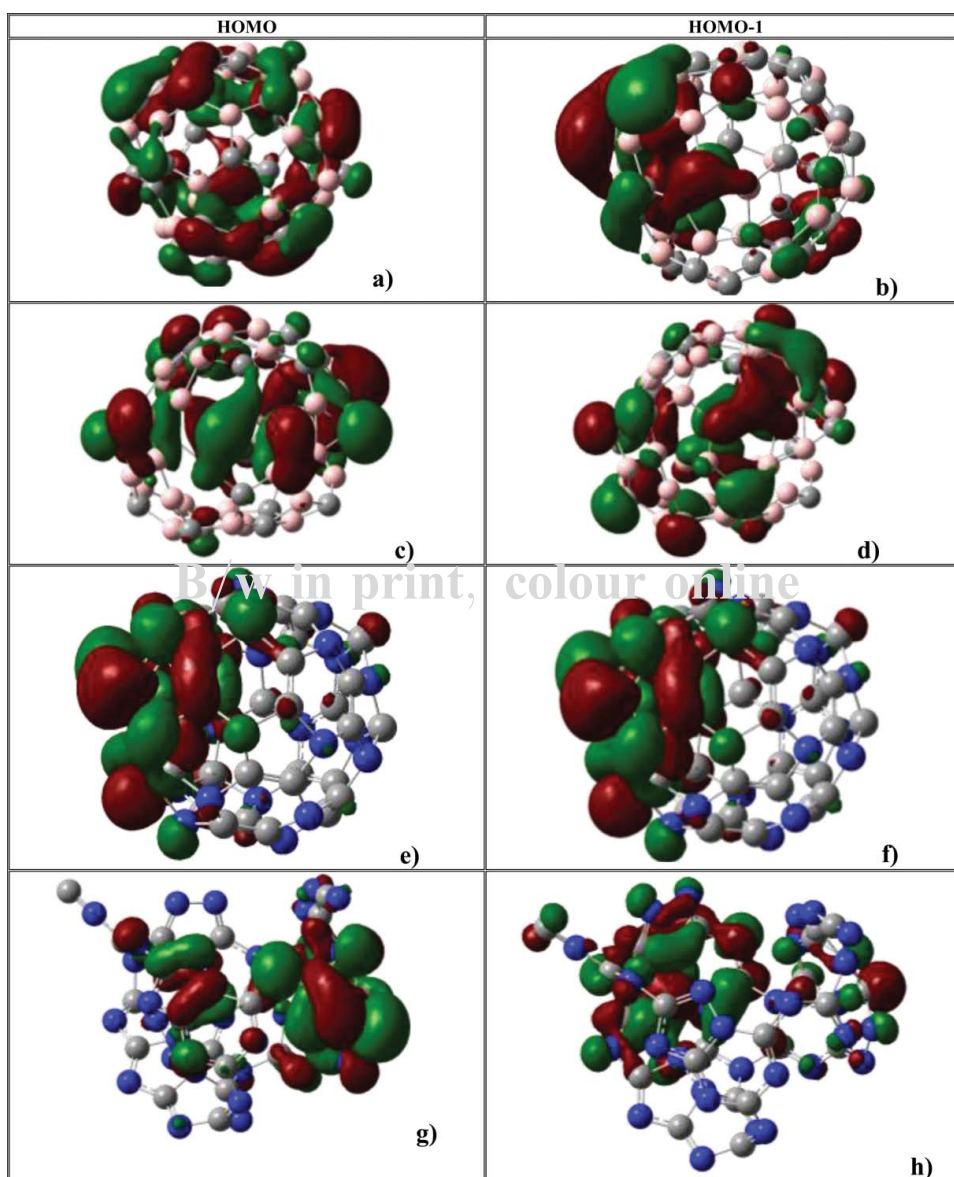


Figure 4. Frontier orbitals HOMO and HOMO-1 of: a, b) $C_{36}B_{24}$ fullerene ($Q = -1$; $M = 4$), c, d) $C_{24}B_{36}$ fullerene ($Q = -1$; $M = 6$), e, f) $C_{36}N_{24}$ fullerene ($Q = -1$; $M = 2$), g, h) $C_{24}N_{36}$ fullerene ($Q = -1$; $M = 4$).

pristine C_{60} fullerene, respectively. Whereas visibly smaller values, 2.30 eV and 5.20 eV, were found for the $C_{36}N_{24}$ poor in nitrogen system. Unexpectedly, larger values, 26.37 eV and 14.33 eV, appear for the rich in nitrogen $C_{24}N_{36}$ system; see Table 1. Thus, detachment and addition of electrons is quite sensitive on the chosen composition for these systems.

The charge distribution for the CB and CN fullerenes shows regions of negative or positive charge, mainly located on the hexagons with high content of carbon, boron or nitrogen atoms; see the MEPS isosurfaces reported in figure 3.

These electronic features suggest that fullerenes with the $C_{36}B_{24}$ and $C_{24}B_{36}$ composition, rich in carbon atoms, may be feasible for catalytic processes, since they presents π -bonds on the C-B and B-B inter-nuclear regions (figure 4 a-4 d), in a similar way as the 1D and 2D nanostructures formed or doped by carbon atoms.^[40,41]

Lastly, the work function is of paramount importance for the design of electronic devices.^[42] In this sense, it is observed a

reduction of this property, due to the intramolecular transfer-
ences of charge, from the boron to the carbon and from the carbon
to the nitrogen atoms. Similar mechanism of charge
transfer has been reported in the literature for this kind of sys-
tems.^[43] Work functions of 0.28, 0.33, 0.17 and 1.05 eV were
obtained for the $C_{36}B_{24}$, $C_{24}B_{36}$, $C_{36}N_{24}$ and $C_{24}N_{36}$ anions,
respectively. The neutral species present also low work
functions, see Table 1; the lowest value takes place for the
 $C_{24}B_{36}$ composition. Accordingly, these systems are promising
candidates for electronic technological applications such as
sensors.^[44]

Magnetic moments of 3.0, 5.0, 1.0 and 3.0 μ_B were found for
 $C_{36}B_{24}$, $C_{24}B_{36}$, $C_{36}N_{24}$ and $C_{24}N_{36}$ fullerenes, respectively.
Notably, the rich in boron $C_{24}B_{36}$ cage produces a large mag-
netic moment, 5 μ_B , even comparable to those of superpara-
magnetic clusters of transition metal (Fe, Co, and Ni) atoms.^[45]
This magnetic moment is build up from the localized px orbitals
of the boron, carbon and nitrogen atoms, as it is depicted

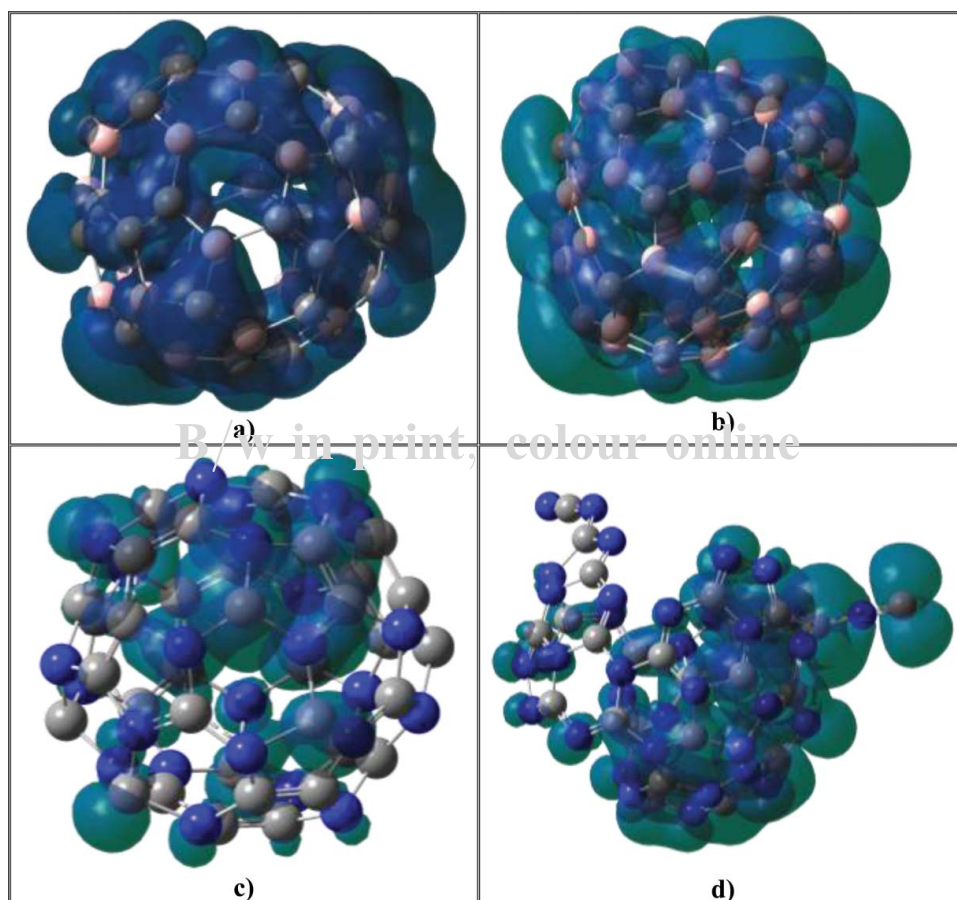


Figure 5. Spin density for a) $C_{36}B_{24}$ fullerene ($Q = -1$; $M = 4$), b) $C_{24}B_{36}$ fullerene ($Q = -1$; $M = 6$), c) $C_{36}N_{24}$ fullerene ($Q = -1$; $M = 2$), d) $C_{24}N_{36}$ fullerene ($Q = -1$; $M = 4$).

from the contourplots of the respective HOMO and HOMO-1 orbitals see figure 4 a to 4 h and spin density surfaces figure 5. Even more, these magnetic moments are larger than those determined for Boron Nitride fullerene with homonuclear bonds ($1.0 \mu_B$),^[46] see Table 1. These results points out the importance of chemical composition in the design of hybrid fullerenes with desired electronic properties. The magnetism of these kind of fullerenes is useful for applications in drug delivery, as it is reported in the literature for the case of oxide nanoparticles.^[47]

4. Conclusions

The structural, electronic and magnetic properties of boron carbide and carbon nitride fullerenes were studied by means of DFT calculations. The rich in carbon, boron or nitrogen fullerenes show stability in anionic forms, where magnetic moments emerges. The magnetism is large for the $C_{24}B_{36}$ anion, marking the importance of structure and composition. Overall, the homo-nuclear carbon, boron or nitrogen bonding plays an important role in the exhibited properties of these mixed nano-materials. Low chemical reactivity and an increase in polarity, in the gas phase, were determined for the CB and CN hybrid fullerenes, suggesting their feasibility for applications in the transportation of pharmaceutical compounds. Although with a higher reactivity, a larger polarity was determined also for the rich in nitrogen $C_{24}N_{36}$ nano-cage. Due to the surface B-B and

C-B π -bonds the $C_{36}B_{24}$ and $C_{24}B_{36}$ dots, with a high content of carbon and boron, may be used in catalytic process. Improvement in the conductivity is predicted for the CB and CN systems; being produced by homonuclear carbon, boron or nitrogen bonds, making them viable candidates for the design of electronic devices. This is also implied by the obtained reduction of the work function for this kind of boron carbide and carbon nitride systems.

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