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The impact of lead on structural, electronic, and vibrational properties of pristine C36 and its boron, nitrogen-dopant C36 on pentagonal and hexagonal rings

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ABSTRACT

In this work, lead's impacts on the structural, electronic, and vibrational characteristics of pure C36 and C36 doped with boron and nitrogen on pentagonal and hexagonal rings are calculated using the DFT method. We provide an in-depth examination of these characteristics and how lead affects them. The adsorption energy, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and electrostatic potentials at the isosurface (EPI) have been studied in detail. Assess the ring dependence of the lead adsorption energy for the hexagonal and pentagonal rings of pristine C36 and B and N impurities at the substitutional site. The adsorption energy for the Pb on pristine C36 is endothermic; however, it is exothermic for the Pb on NBdoped C36 but has different values on the pentagonal and hexagonal rings. The results demonstrate that nitrogen and boron doping significantly increased the Pb atom's adsorption energy when the dopants occupied pentagonal sites. In addition, the bond lengths surrounding the impurity and the bond lengths of Pb atoms placed on pristine C36, BN-doped hexagonal ring, and BN-doped pentagonal ring in C36 are investigated. The electrostatic potential isosurface (EPI) surrounding the BN-doped hexagonal and pentagonal rings of C36 is described. The Mulliken charge transfer analysis demonstrates that the interaction between NB-doped C36 fullerene and lead (Pb) has a substantial effect on the charge transfer process and the reactivity of the doped system towards lead. However, the quantity of charge transmitted depends on the impurity's location on the hexagonal and pentagonal rings. These findings aid in the atomistic understanding of the interaction between a single Pb atom on the surface of C36 and BN-doped C36 at various rings. Our findings not only shed light on the complex interplay between lead and C36 but also offer valuable insights into potential applications in materials engineering and environmental remediation.

1. Introduction

In recent years, pentagon-hexagon carbon frameworks (Cn with n < 60) have been investigated for their unique structures and potential applications as lower fullerenes. Despite the fact that these fullerene structures are less well-known than C60 or C70, they still possess intriguing properties and applications [1-3] C36 is one of the first experimentally realized fullerene structures [4]. Numerous isomers are conceivable for a 36-atom carbon lattice with hexagonal and pentagonal faces, as demonstrated [5]. Consequently, high reactivity, substantial steric strain, and a small HOMO-LUMO gap are predicted [6]. The C36 molecule is significantly more reactive chemically than the C60

molecule [4,7]. It is believed that this fullerene and its derivatives constitute a class of exciting substances with novel structure and electronic properties, including high reactivity, covalent bonding, significant steric strain, high strength, a small gap, and superconductivity [8]. Therefore, research interest in C36 fullerene seems to be rapidly increasing. C36 fullerenes have the most favourable and energetic structures (D6h and D2d); they are effectively isoenergetic [9]. Piskoti et al. [4] constructed C36 crystalline using the arc-discharge approach; this is the first time a fullerene smaller than C60 has been mass-produced. Lan-Feng Yuan et al. [10] determined that the D6h anion is more stable than the D2d anion, while the D2d cation has less energy than the D6h cation. B. Mortazavi et al. [11] utilized density

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functional theory to confirm that the anticipated C36 fullerene network possesses exceptional thermal stability at temperatures above 1500 K and an elastic modulus of 266 GPa. Multiple authors have reported on the substitutional modification of fullerenes. Additionally, substitution can influence the strength of chemical bonds, particularly in curved and stressed areas. Fateme Nattagh et al. [12] investigated the impact of B and N doping, or codoping, on the aspirin adsorption behavior of C60 fullerene. Using density functional theory, Zhongfang Chen et al. [13] and Zuoyin Yang et al. [14] investigated the characteristics of N- and B-doped low fullerenes. L. Viani [15] demonstrated that replacing carbon atoms with nitrogen and boron, both dopants, diminished the formation energy of non-doped lower fullerenes compared to C60. Dr. Miguel Reina and colleagues [1] studied the adsorption of neuroprotective medications on C36 and C35E (E = N and B) in the gas phase using density functional theory. Recently, nanomaterials have been used for many application especially of the treatment of heavy metal-contaminated water and environmental cleaning [16-20] and there is limited research on the interaction of heavy metals with nitrogen and boron-doped C36 (fullerene) or lower fullerene [21], as C36 fullerene is a less studied and less prevalent variant of fullerene compared to C60 fullerene. A water molecule, together with Rb, Cs, and Pb, did not want to be enclosed inside the fullerene, as demonstrated by Tiangtrong P. [22]. Additionally, an external force must be provided to form endofullerene with a single water molecule or Rb, Cs, and Pb within.

However, nitrogen and boron doping can alter the electronic and structural properties of fullerene, making it more reactive to heavy metals. Navaratnarajah et al. [23] used density functional theory with dispersion correction (DFT + D) to predict the structures and energies of Cd captured by C60. Lead (Pb) pollution is a major environmental concern due to its toxicity and negative impact on human health. There is an increasing demand for lead sensors that can accurately detect and quantify lead in various environmental matrices. Monika Srivastava [24] employed DFT examination of nitrogen- and boron-doped graphene sheets to serve as lead detection devices, whereas Josefa R. Baena et al. [25] determined the speciation of lead in water from the environment by preconcentration on a novel fullerene derivative. According to Milanpreet Kaur et al.'s [26] construction of a fullerene-based biological marker for detecting lead impurities, the current and conductance of the fullerene molecule increased with increasing defects, suggesting that it can be used in medical diagnostics. Fullerene was first utilized in a mini-column to determine the prior concentration of Pb in the preparation of samples [27]. Another instance of the use of a fullerene column for Pb species (inorganic Pb and ionized alkyl Pb substances) was performed on rainwater [28], with the goal of preparing the solution of Pb-producing diethyldithiocarbamate (DDTC) compounds before employing FAAS as a screening strategy utilizing C60 fullerenes. Utilizing density functional theory, Behrooz Abbaszadeh [29] studied the transport parameters of the molecular conductance of a C36 cluster situated between two Al electrodes. The encapsulation (atoms situated inside) and adsorption (atoms placed outside) of atoms of metal have recently received considerable practical and theoretical attention to optimize the applicability of C60 [30-32]. Matetskiy [33] and Li et al. [34] studied the interaction between C60 and Pb atoms. In this paper, density functional theory (DFT) is used to examine equilibrium structure, electronic structure, vibrational properties, and the adsorption capability of a single Pb atom on the surface of pristine and substitutional B and N doping on the hexagonal and pentagonal rings on the surface of C36.

The objective of the study Understand the unique behaviors and interactions of lead (Pb) on pentagonal rings pristine C36 fullerenes, as well as on C36 cluster doped with nitrogen and boron, and we contrast these results with the behavior of lead on hexagonal rings in the pristine C36 and BN-doped C36 structures. The secondary aim was to offer an understanding of the lead-induced structural, electrical, and vibrational characteristics of these materials, elucidating how dopant components affect their behavior. By achieving this goal, we aim to contribute to the broader understanding of the unique properties, potential applications, and environmental consequences of these carbon-based nanostructures. The novelty of the work is the interaction of lead with C36 cluster, which is an area that hasn't been extensively examined in previous studies. The focus on the influence of lead on clusters with both pentagonal and hexagonal ring configurations is a distinctive feature. The findings may lead to insights into practical applications of these materials also potentially beneficial in various industries, such as nanotechnology and materials science.

2. Method of calculation

To determine the structure and electronic properties of Pb interaction with C36 and Boron and nitrogen-doped at different rings, Quantum Espresso/PBE DFT and Gaussian/B3LYP approach models were used effective convergence standardsIn the geometry optimizations of C36 fullerene, two carbon atoms in the hexagonal ring of C36 are replaced by boron and nitrogen atoms, and two carbon atoms in the pentagonal ring of C36 are replaced by boron and nitrogen atoms, naming them the NBC34-Hexa and NBC34-Penta-ring, respectively, as depicted in Figs. 1 and 2. DFT calculations were performed utilizing the periodic planewave framework included in the Quantum Espresso package [35] Utilizing the Perdew-Burke-Ernzerhof (PBE) functional in conjunction with pseudopotentials [36], was studied for structural relaxations, the wavefunction with charge density cutoff of 30 Ry and 300 Ry was utilized. In numerous investigations, the efficiency of this computational setup was demonstrated [37,38]. The QuantumEspresso code is an open-source program that is available for free and is used for electronic structure computations and related materials modeling techniques. In order to simplify the handling of infinite crystalline systems, Quantum Espresso codes are built using periodic boundary conditions. Pb interactions with C36-Hexa-ring, C36-Penta-ring, NBC34-Hexa-ring and NBC34-Penta-ring, denoting them PbC36-Hexa-ring, PbC36-Penta-ring, PbNBC34-Hexa-ring, and PbNBC34-Penta-ring, are optimized using the same computing estimate levels, as shown in Fig. 3. The electronic properties, Mulliken charge distribution, and EPI were computed using the Gaussian 16 approach [39,40] and hybrid B3LYP [41,42] and LANL2DZ with core potential basis sets that are efficient for Pb ion and 6-31G(d,p) [43] for C, B and N atoms was used. [21], A collection of software packages for computational chemistry called Gaussia provides a range of theoretical approaches that can tackle systems with different degrees of precision and in different molecular states and chemical environments. Using the GaussView16 softwar, several molecular structures were represented in all calculations, the imaginary is equal to zero. RMS Displacement (0.0003). Also the Gaussian 16/B3LYP/gen in addition to the Quantum Espresso/PBE-GGA since B3LYP is more suited for calculations including optical properties (HOMO and LUMO) and vibration characteristics. The impact of Pb position on the gap price was evident in both level hypotheses. By two different methods Quantum ESPRESSO (plane-wave basis sets to represent the wavefunctions of electrons) and Gaussian09 (Gaussian basis sets) can provided The Impact of Lead on Structural, Electronic, and Vibrational Properties of Pristine C36 and its Boron, Nitrogen-dopant C36 on Pentagonal and Hexagonal Rings.

3. Result and discussion

3.1. Structural and electronics characteristics of pristine C36, NBC34-Hexa, and NBC34-Penta-ring

The C36 structure consists of separate hexagons at the north and south poles, two rings of six pentagons, and one ring of six hexagons at the equator. The hexagonal and pentagonal rings of C36 are depicted in Fig. 1 to illustrate the equilibrium geometry of the C36 carbon cage derived by analyzing bond lengths with the quantum espresso code. In



Fig. 1. Geometrical optimization for C36 with indication of the two different types of C—C bonds in hexagonal rings and pentagonal rings by using DFT/Quantum ESPRESSO.



Fig. 2. Geometrical optimization for a: NBC34-Hexa and b: NBC34-Penta-ring with indication of bond length by using DFT/Quantum ESPRESSO.

the pentagonal and hexagonal rings of C36, there are two distinct forms of C—C bonding. There are no double bonds in pentagonal rings, as the double bonds are located at the north and south poles. The calculated bond lengths of C—C and C—C are distinct, as shown in Fig. 1 and Table 1. The bond lengths of pristine C36 in a hexagonal ring (C1-C2, C2-C3, C3-C4, C4-C5, and C5-C6) are determined to be identical and equal to 141 pm; however, the bond lengths in a pentagonal ring (C1-C2, C2-C3, C3-C4, and C4-C5) are 143, 150, 141, and 150 pm.

Previous studies [7,9,44] have investigated the influence of N and B doping on bond lengths at the impurity site. L. Viani [15]demonstrated that for boron, modifications in the local geometry around the dopant are bond elongation and nonuniformity; nevertheless, nitrogen substitution relaxes the structure to provide more uniform bond lengths around the dopant, namely C—N bonds. Due to the electron-withdrawing nature of N atoms and the electron-donating nature of B atoms, H. R. Jiang et al. [45] demonstrated that the average N—C bond length is longer than the B-C bond length. Bond lengths in hexagonal and pentagonal rings are investigated as a function of the nitrogen and boron positions in their activity as part of the study. Compared to the NBC34-Hexa-ring and NBC34-Penta-ring, the NB-dopant at the Hexagonal ring exhibited the highest defect gap as shown in Table 1.

In the case of N and B doped fullerenes C36 at the hexagonal ring (NBC34-Hexa-ring), however, the bond lengths of the dopant atom along with the surrounding carbon atom are B-C2, C6-B, C3-N, and N—C5, which are 151, 151, 142, and 142 pm, respectively. Compared to NBC34-Penta-ring, the bond lengths (B-C2, C5-B, C3-N, and N—C5) are displaced upwards by 152, 156, 149, and 139 pm, respectively, causing a structural distortion on the carbon surface, as depicted in Fig. 2a and b. Compared to pristine C36, the bond length around B and N is increased by 7%, 7%, 0.6%, and -0.141%, respectively, for B-C2, C6-B, C3-N, and N—C5, in the NBC34-Hexa-ring. However, in the NBC34-Penta-ring, the fractional bond lengths of B-C2, C5-B, C3-N, and N—C5 are 6.29%, 4.66%, -1.428%, and -0.66%, respectively.

3.2. Structure and adsorption energy of PbNBC34-Hexa and PbNBC34-Penta-rings

The geometrical optimization for a. PbC36-Hexa-ring, b. PbC36-Penta-ring, c. PbNBC34-Hexa-ring and d. PbNBC34-Penta-ring is depicted in Fig. 3. In PbC36-Hexa-ring the Pb created bond length with different C3, and C6, Pb-C3 and Pb-C6 is equal to 245 and 297 pm respectively. Trigonal pyramid shapes are formed by the Pb and C atoms respectively in n the PbC36-Penta-ring; the bond lengths Pb-C1, Pb-C2



Fig. 3. Geometrical optimization for (a) PbC36-Hexa-ring b)(PbC36-Hexa-ring, (c)PbNBC34-Hexa, and (d) PbNBC34-Penta-ring by using DFT/Quantum ESPRESSO.

Table 1

Bond lengths [pm unit] of C36 and varied configuration substitutional-NB doping (NBC34) clusters at various rings, derived by optimizing the geometry for each bond's length surrounding the impurity, as shown in Figs. 1 and 2.

Bond- types	Pristine C Hexa- ring	36 Penta- ring	B–N doped Bond- types	l C36 NBC34–Hexa	NBC34–Penta
C1C2	141.1	143	B-C2	151	152
C2–C3	141.1	143	C2–C3	138	141
C3–C4	141.1	150	C3–N	142	149
C4–C5	141.1	141	N-C5	142	139
C5-C1		150	C5–C6	138	
C5–C6	141.1		C5–B		156
C6C1	141.1		C6–B	151	
номо	-3.313		-3.264		-3.055
[eV]			-2.52		
LUMO	-2.257		0.733		-2.420
[eV]					
Eg[eV]	0.4320				0.465

and Pb-C3 equal 233, 249 and 298 pm respectively. As shown in Table 2. The distance between Pb-B atoms in the PbNBC34-Hexa and PbNBC34-Penta-ring structures is approximately 250 and 240 pm, respectively, as shown in Table 2. B-C2 and C6-B have identical bond lengths of 152 pm for PbNBC34-Hexa-ring, whereas C2-B and C6-B for PbNBC34-Penta-ring are 157 and 159 pm, respectively. Adsorption energy can be calculated using the equation [46]

$$E_{AE(BSSE)} = E_{Pb-C34NB \text{ at Hexa or penta-ring}} - E_{C34NB \text{ at Hexa or penta-ring}} - E_{Pb} + E(BSSE)$$

 $E_{AE(BSSE)}$ is the correct adsorption energy with; $E_{Pb-C34NB}$ at Hexa or $P_{Penta-ring}$ is the entire energy of heavy metal, and N-B doped C36 at the hexagonal or pentagonal ring; E_{C34NB} at Hexa or $P_{enta-ring}$ is the overall energy of N-B doped C36 at the hexagonal or pentagonal ring; E_{Pb} represents the entire energy of an isolated heavy metal; and E(BSSE) is the energy of the basis set superposition error. It should be noted that the

Adsorption energies have been adjusted using the counterpoise approach for the basis set superposition error (BSSE) [47,48].

The negative calculated adsorption energies indicate that BNC34 may be capable of adsorbing heavy metal ions. Also, they demonstrate the high-strength nature of the interaction between the Pb ion and the NBC34 cluster, which is dependent on the impurity's position at the various hexagonal and pentagonal rings in C36. As shown in Table 2, the first Pb adsorbs on the hexagonal rings of PbNBC34-Hexa with an adsorption energy of -2.297 eV and a bond length of 250 pm, as opposed to the PbNBC34-Penta-ring, where the adsorption energy is -2.601 eV, and the bond length is 240 pm. The findings reveal that the PbNBC34-Hexa-ring interacts with the Pb atom more strongly than the PbNBC34-Hexa-ring, which can be attributed to its higher adsorption energies of PbC36-Hexa-ring and PbC36-Hexa-ring equal 2.768 and 1.643. Negative and positive adsorption of Pb interaction with pure graphene and N- and B- doped C35 observed [24,49].

3.3. The density of states (DOS), HOMO, LUMO and EPI of C36, PbC36-Hexa-ring and PbC36-Hexa-ring cluster by using Gaussian 16/B3LYP

Finding the energy gap for pure C36 by Quantum ESPRESSO /PBE is equal to 0.432 eV Also; the energy gap is different when B and N are placed in hexagonal and pentagonal rings (Table 1), but due to the underestimated band gap by Quantum ESPRESSO /PBE the Gaussian 06 has been used to calculate the energy band gap. Gaussian-16 program was used to compute the density of state (DOS) to analyze the electronic properties of pure C36. Fig. 4a depicts the electronic density of states (DOS) for pristine C36, PbC36-Hexa-ring and PbC36-Penta-ring; the dotted lines in each plot indicate the position of the Fermi level, which can be described as the average value of the HOMO and LUMO energies. The C36 fullerene cluster had HOMO-LUMO gaps of 1.0239 eV, with the HOMO at -5.432 eV and the LUMO at -4.920 eV These outcomes are consistent with [7,8,11,44,50-52] Fig. 4b depicts the distinct HOMO-LUMO distribution around the hexagonal and pentagonal rings of C36. The HOMO and LUMO orbitals in the pentagonal ring are

Table 2

Bond lengths [pmunit] and adsorption energies [eV] of various configurations are compared. Pb interaction with pristine C36 and NB doped C34 (NBC34) at distinct rings was observed by adjusting the geometry for every bond length, as shown in Fig. 3.

		B–N doped C36		
Bond-types	PbC36–Hexa–ring	PbC36–Penta–ring	PbNBC34–Hexa–ring	Pb NBC34–Penta–ring
C1-C2	149	152		
B-C2			152	157
C2–C3	142	142	152	139
C3–C4	147	1474		
C4–C5	147	149		
C3–N			140	147
N–C5			142	142
C5—C6	142		142	
С5–В				159
C6-C1	159			
С6-В			152	
Pb–B			250	240
Pb–C1		233		
Pb-C2		249		
Pb–C3	245	298		
Pb–C6	297			
E _{AE(BSSE)} [eV]	2.768	1.643	-2.297	-2.601



Fig. 4. a) The density of states [DOS] of (a) pristine C36, PbC36 and PbC36; vertical dotted lines represent Fermi levels of energy; HOMO and LUMO of: (b) pure C36 (c) PbC36-Hexa-ring and (d) PbC36-Penta-ring by using Gaussian 16/B3LYP.

predominantly across the ring and neighbouring carbon. According to Fig. 4a, The HOMO-LUMO gaps in the PbC36-Hexa-ring and PbC36-Hexa-ring clusters, which are 1.0239 and 0.89 eV and 1.0201 eV, respectively. At the top of the valence band and the bottom of the conduction band, there is a slight orbital mixing in the pentagonal ring. In the PbC36-Penta-ring, the LUMOs are distributed around the metal atom, but in the PbC36-Hexa-ring, the Pb atom is devoid of any density in HOMO and LUMO. It might be claimed that Pb's location on the ring affects how much the carbon framework overlaps with Pb.as shown in Fig. 4b and c.

The EPI and the distribution of charges provide insight into C36. Observing regions of color allows for a qualitative evaluation of chemical reactivity. Consequently, these maps are visually engaging. Blue and red or yellow regions correspond, correspondingly, to areas with low and high electron densities. The EPI surrounding the hexagonal and pentagonal rings of C36 is depicted in Fig. 5 Based on the (EPI) analysis,

each carbon atom within C36 has a modestly negative potential, with a minor positive potential in the core of each ring.

3.4. DOS, HOMO, and LUMO, and EPI of NBC34-Hexa-ring and NBC34-Penta-ring

To comprehend the effect of boron and nitrogen on the structure and electronic features of C36, first-principles calculations based on density functional theory were performed for two distinct configurations: one for the impurity located in the hexagonal ring and the other in the pentagonal ring. Fig. 6a depicts the density of states (DOS) of the NBC34-Hexa-ring and NBC34-Penta-ring, with the dashed line representing the fermi energy between the HOMO and LUMO. The density of states associated with B and N elements is depicted in black and red in Fig. 6a. In NBC34-Hexa-ring, three peaks were observed around [-3–0] and two peaks around [0–2] eV; in NBC34-Penta-ring, three peaks were



Fig. 5. Electrostatic potential isosurfaces (EPS) of C36 by using Gaussian 16/B3LYP.



Fig. 6. a) The density of states (DOS) of the NBC34-Hexa-ring and the NBC34-Penta-ring; the vertical dotted lines relate to the Fermi energy level; b) HOMO and LUMO of the NBC34-Hexa-ring; and c) HOMO and LUMO of the NBC34-Penta-ring.

observed around [-3-0] and one broad peak around [0-2] eV. In addition, the maximal density of the state in the NBC34-Hexa-ring is greater than that in the NBC34-Penta-ring. Furthermore, the band gap is largely unaffected, whereas the valence and conduction bands change,

which can influence the quantum transport of electrons and holes. The computed findings show that for C36, NBC34-Hexa-ring, and NBC34-Penta-ring, the (H-L) gap is equivalent to 1.0239, 1.029, and 1.044 eV, respectively. Consequently, upon doping at the pentagonal ring, the



Fig. 7. Electrostatic potential isosurfaces of (a) NBC34-Hexa-ring and (b) NBC34-Penta-ring.

(H-L) gap widened. The HOMO and LUMO (NBC34-Hexa-ring) and the HOMO and LUMO (NBC34-Penta-ring) are depicted in Fig. 6b and c, respectively. In the case of NBC34-Penta-ring, computed HOMO and LUMO are localized on the B, N, and adjacent rings, as illustrated in Fig. 6c compared to Fig. 6b The HOMO and LUMO wave functions are primarily localized around the equator ring, whereas the LUMO wave function is primarily localized at the B dopant. As depicted in Fig. 7a and b, it is common knowledge that the physical and chemical characteristics of most molecules are related to their EPI. EPI correspond to electronic density and is a very helpful descriptor for understanding electrophilic and nucleophilic reaction sites. The EPI diagram of NBC34-Hexa-ring is depicted in Fig. 7a; across N and B impurities, the negative and positive contribute to the reduced and enlarged bond lengths of N-C and B-C compared to the same C-C bond length of 141 pm in the pure C34 cluster. In the case of BNC34-Penta-ring, as shown in Fig. 7b, the pentagonal ring and the closest neighbor rings are predominantly positive, and the charge surrounding the B is more positive than that surrounding the B at the BNC34-Hexa-ring, with a small quantity of negative charge surrounding the N. The findings show that although NB doped in the hexagonal ring is more electronegative and rich in electrons (Lewis base), the NB in the pentagonal ring is deficient in electrons (Lewis acid).

3.5. DOS, HOMO, and LUMO, as well as EPI of PbNBC34-Hexa-ring PbNBC34-Penta-ring

Fig. 8a depicts the density of states (DOS) spectra by representing the Fermi energy level (EF) with dotted red lines. The band gap decreased more in the Pb NBC34-Penta-ring system (0.756 eV) than in the Pb NBC34-Hexa-ring system (0.938 eV), indicating that the Pb metal on the NBC34-Hexa-ring is less reactive. In the Pb-NBC36-Penta-ring system, the HOMO and LUMO are highly localized around Pb and NBC34 compared with the Pb-NBC36-Hexa-ring system. This is evident from Fig. 8b and c. HOMO is more concentrated on the Pb atom than LUMO, indicating electron conduction through NBC34. This distinguishes the electronic properties of Pb deposited on a pentagonal ring from those of pb on a hexagonal ring of C36 and NBC34. The variation of HOMO-LUMO energy (Eg) values is greater for Pb adsorbed on a hexagonal ring, as demonstrated in Fig. 8a. HOMO 0.4 eV has shifted in PbNBC34-Penta-ring toward the Fermi level, which is a considerable difference between Pb BNC34-Hexa-ring and Pb BNC34-Penta-ring.

3.6. Chemical hardness(η) and chemical potential(μ) of PbC36-Hexaring, PbC34-Penta-ring, PbNBC34-Hexa-ring and PbNBC34-Penta-ring

It is widely known that the HOMOLUMO border orbitals and energies are well-liked quantum mechanical descriptors that play a significant part in regulating a wide range of chemical interactions. According to Koopman's theorem [53,54], the two most important parameters for determining the system's chemical reactivity are chemical hardness and chemical potential. Chemical potential (μ) is equal to -(HOMO-+LUMO)/2 and chemical hardness(η) is equal to (LUMO—HOMO)/2. It is obvious from the hardness data that systems with Single lead atoms on the C36-Hexa-ring and PbC36-Penta-ring are harder than the PbNBC34-Hexa-ring and PbNBC34-Penat-ring. NBC34-Penat-ring structure after Pb adsorption, chemical hardness, energy gap and chemical potential were reduced compared with PbC36-Hexa-ring and PbC34-Penta-ring of PbNBC34-Hexa-ring, as shown in Fig. 9(a and b).

3.7. Mulliken atomic charge populations and natural bond orbital of C36, PbC36-Hexa-ring, and PbC36-Penta-ring, NBC34-hexa-ring, NBC34-penta-ring, PbNBC34-Hexa-ring, and PbNBC34-Penta-ring

This study also examined the interaction between Pb and C36, NBC34, emphasizing the effect of charge transfer, and utilized the Mulliken charge distribution method to determine the charge transfer between Pb and C36, NBC34 at various rings. Calculated Mulliken atomic charge populations of C36, PbC36-Hexa-ring, and PbC36-Pentaring, NBC34-Hexa-ring, and NBC34-Penta-ring, at the B3LYP/6-31 G level are depicted in Fig. 10 (in color online). The color of the atoms indicates the number of electrons in the Mulliken atomic charge. As shown in the figure, green, black, and red represent the positive, neutral, and negative charges, respectively, located on the fullerene surface. The result determined by Mulliken indicates that the surface of pure fullerene (Fig. 10) is neutral, particularly in hexagonal rings compared to pentagonal rings. Comparing the Mulliken population analyses of NBC34-Hexa-ring and NBC34-Penta-ring demonstrates that the N and B atoms accept the negative and positive charges introduced into the system.

The value of the Mulliken charge B in the NBC34-Hexa-ring is equal to 0.316, and the two carbon atoms surrounding it are negatively charged (-0.05 e and -0.05 e, respectively), while the value of N is equal to -0.564, and the two carbon atoms surrounding it are positively charged (0.165 e and 0.165 e, respectively). In contrast, in the NBC34-Penta-ring, B is equal to -0.552 and its two surrounding carbon atoms



Fig. 8. a) Density of states (DOS) of PbNBC34-Hexa-ring and PbNBC34-Penta-ring; the vertical dotted lines represent the Fermi energy level; b) HOMO and LUMO of the PbNBC34-Hexa-ring; and c) PbNBC34-Penta-ring.



Fig. 9. Chemical potential and Reactivity index hardness (η) PbNBC34-Hexa-ring and PbNBC34-Penta-ring.



Fig. 10. Mulliken atomic charge populations of C34, PbC36-Hexa-ring, PbC36-Penta-ring, NBC34-Hexa-ring, NBC34-Penta-ring, PbNBC34-Hexa-ring, and PbNBC34-Hexa-ring.

are negatively charged (-0.053e and 0.082e, respectively), while N is -0.552 and its surrounding carbon atom is positively charged (0.125e), as shown in Fig. 10. In the Pb-NBC34-Hexa-ring, the Mulliken charge on Pb is equal to 0.542, and B equals 0.209. In addition, the partial charges of the neighbouring B atoms (-0.403e, and the other side in neutrality is equal to 0.046), as well as in the case of Pb located on the pentagonal ring (Pb-NBC34-Penta-ring), are equal to 0.466, while the partial charges of the two carbon atoms surrounding B have increased to 0.190e and 0.182e. At the Pentagonal Ring, when a Pb atom adsorbs BN-doped C34, the absolute amount of charge transfer is larger than PbNB-Hexa-ring. The Mulliken population analysis of the PbC36-Hexa-ring and PbC36-Penta-ring is compared, and the results show that the Pb atom effectively accepts the system's added negative charge. The insertion of the negative charge has affected the Mulliken atomic charge of the C atom in the pentagonal and hexagonal ring in the neutral state, but as

shown in Fig. 10, the charges on the C atoms have not changed

Table 3

Natural bond orbital (NBO) analysis (Values in units of the electron) of PbC36-Hexa-ring and PbC36-Penta-ring.

Atom (PbC36- Hexa- ring)	Before adsorption	After adsorption	Atom (PbC36- Penta- ring)	Before adsorption	After adsorption
Pb	0	0.432	Pb	0	0.308
C1	0.002	-0.318	C1	0.01	0.029
C2	0.002	-0.169	C2	0.01	-0.037
C3	0.002	-0.038	C3	-0.056	0.037
C4	0.002	-0.037	C4	0.05	-0.169
C5	0.002	-0.134	C5	-0.06	-0.318
C6	0.002	-0.211			

appreciably. Tables 3 and 4 present the findings of Natural bond orbital (NBO) population analysis for PbC36-Hexa-ring, PbC36-Penta-ring, PbNBC34-Hexa-ring, and PbNBC34-Penta-ring structures, both prior to and following Pd adsorption. These results showed that charge transfers have been occurred from NB-doped C36 to Pb atom adsorbed. The PbC36-Hexa-ring and PbC36-Penta ring are less suitable for the adsorption of Pb atoms, as it exhibit an endoergic binding energy and a small charge transfer. We anticipate that this theoretical prediction can stimulate experiments to validate and apply these materials for adsorbing Pb atoms.

3.8. Vibrational Raman spectra

Researchers have effectively reproduced and analyzed the Raman spectra of lower fullerene using DFT [10,55], thereby enhancing their understanding of its vibrational modes and molecular structure. Alternatively, according to research, [7,52,56] the position of the radial respiration mode of fullerene is highly dependent on its size and doping. As shown in Fig. 11a-c, the pristine C36, Pb C36-Hexa-ring, C36-Penta-ring, PbNBC34-Hexa-ring and PbNBC34-Penta-ring have been calculated. Numerous prominent peaks can be observed in the Raman spectrum of C36 fullerene. As indicated by the asterisk (*), all spectra contain four features: two in the range $300-700 \text{ cm}^{-1}$ and two peaks in the range 1000–1700 cm^{-1} . The first peak is approximately 358 cm^{-1} in height. This peak represents numerous axial deformations of the C36 fullerene. The second characteristic is detected at approximately 628 cm⁻¹ and is associated with an entirely symmetric radial breathing mode (RBM) of fullerene C36. Within the range of $1000-1700 \text{ cm}^{-1}$, the G-mode is observed at approximately 1448 cm^{-1} owing to the E2g mode at the Γ -point. The G-band is a characteristic of all sp2 carbon systems and results from the elongation of the C—C bond in graphitic materials. The d-band, a significant prominence in the Raman spectrum of C36 fullerene, results from defects or irregularities in the carbon lattice, defect-related d-band (1254 cm⁻¹). The Raman characteristics of doping effects are optimally monitored by [57–61] and the interaction of heavy metal with fullerene is reported by [62-65]. The Raman spectra of BNC34-Penta-ring, PbC36-Hexa-ring, BNC34-Hexa-ring, and PbC36-Penta-ring PbBNC34-Hexa-ring, and PbBNC34-Penta-ring are calculated in Fig. 11b and c. Substituting a carbon atom with boron and nitrogen breaks the C36 fullerene's translational symmetry. The (RBW) and G modes for the NBC34-Hexa-ring and NBC36-Penta-ring clusters have shifted significantly towards lower frequencies. Additionally, the peaks of BNC34 are less intense than those of C36. Due to the presence of Pb, a new set of Raman peaks associated with carbon vibrations can be observed (Fig. 11b and c). In addition, the substantial shift of the RBM and G modes in the PbBNC34-Penta-ring was greater than in the PbBNC34-Hexa-ring. Significant alterations in the local bonding environment can be attributed to the adsorption of Pb in the hexagonal and pentagonal rings.

4. Conclusions

The structure, stability, electronic, and vibrational properties of Pb on C36, BN-doped C36 at the hexagonal ring, and Pb on C36, BN-doped C36 at the pentagonal ring were investigated by employing density

functional calculations. Our primary findings are outlined below:

- The adsorption energy of Pb on the BNC34-Penta-ring is equal to -2.531 eV, and the bond length (Pb-B) is equal to 159 pm. In comparison to Pb on the BNC34-Hexa-ring, the adsorption energy and bond length of B-Pb is equal to -2.219 eV and 152 pm, respectively. PbNBC34-Hexa and PbNBC34-Penta-ring's negative adsorption energies demonstrate that the reaction is exothermic and thermodynamically stable. However, PbC36-Hexa-ring and PbC36-Penat-ring have positive adsorption energy.
- The small HOMO-LUMO gaps estimated for each PbNBC36 exhibit a high level of reactivity, which varies depending on the impurity position on the hexagonal and pentagonal rings. As predicted, owing to the highest binding energy of the Pb on NBC34 at the Pentagonal ring, there is a substantial decrease in the magnitude of the HOMO-LUMO gap when compared to the Pb C36 -Hexa-ring, Pb C36 -Hexaring and PbNB-Hexa-ring
- According to the Mulliken population analysis, the C atoms in the pentagonal ring coordinated with Pb get slightly negative charges, and the Pb atom in the PbNBC34-Penta-ring has a greater positive charge than the PbNBC34-Hexa-ring.
- The Pb atom on BN-doped C36 at the pentagonal ring has high adsorption energy, low chemical hardness, and low chemical potential in comparison to the PbNBC34-Penta-ring, according to the findings of the current study.
- The changes in the peak frequencies of the C36 and NBC34 were examined before and after the adsorption of Pb at different rings. The red shift in the G bond is varied depending on the locations of pb on hexagon and pentagon rings for C36 and BNC36.

Overall, the study suggests that the ring dependence of nitrogen and boron doping in C36 fullerene nanoclusters plays a crucial role in their interaction with lead, which should be considered in developing future lead-potential application technologies. We expect this theoretical prediction to stimulate experiments to apply these materials (C36 and NBdoped C36) for absorption pb that can used for different applications.

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CRediT authorship contribution statement

Shaida Anwer Kakil: Writing – original draft, Formal analysis. Hewa Y. Abdullah: Supervision, Investigation, Project administration. Tahseen G. Abdullah: Conceptualization, Validation, Visualization.

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.

Table 4

Natural bond orbital (NBO) analyses (Values in units of the electron) of PbNBC34-Hexa-ring and PbNBC34-Penta-ring -ring.

Atom (PbNBC34-Hexa-ring)	Before adsorption	After adsorption	Atom (PbNBC34-Penta-ring)	Before adsorption	After adsorption
Pb	0	0.782	Pb	0	0.562
В	0.416	0.209	В	0.443	0.185
C2	-0.055	-0.046	C2	0.009	-0.357
C3	0.195	0.141	N	-0.562	0.182
N	-0.596	-0.562	C4	0.185	-0.568
C5	0.195	0.227	C5	-0.059	0.113
C6	-0.005	-0.413			



Fig. 11. Depicts the calculated Raman spectra of a: C36, b and c: BNC34-Hexa-ring, BNC34-Penta-ring, PbC36-Hexa-ring, PbC36-Penta-ring, PbBNC34-Hexa-ring, and PbBNC34-Penta-ring at 300–700 cm⁻¹ and 1300–1700 cm⁻¹, respectively.

Data availability

No data was used for the research described in the article.

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