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Adsorption of nitrogen dioxide on $C_{30}B_{15}N_{15}$ heterofullerene: AIM and NBO study via DFT

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ABSTRACT

Adsorption of nitrogen dioxide on the exterior surface of $C_{30}B_{15}N_{15}$ through B atom of adsorbent is studied using the DFT-B3LYP/6-31G* level. Independent to the orientation, the NO_2 molecule presents strong chemisorption with large charge transfer from $C_{30}B_{15}N_{15}$ to adsorbed gas. NBO (natural electron configuration of adsorbing B atom), AIM analysis and spin density distributions indicate that the chemisorption of NO_2 on the $C_{30}B_{15}N_{15}$ in all studied complexes are covalent in nature.

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1. Introduction

Since its discovery in 1985 [1], the hollow spherical form of carbon allotropes has attracted increasing attention due to its potential applications. This allotrope was named fullerene. C_{60} is the most plentiful and smallest stable fullerene with I_h symmetry. The construction principle of the fullerenes is an outcome of the isolated pentagon rule (IPR) [2] and Euler theorem. Based on these principles, for the closure of each spherical network with n hexagons, 12 pentagons are required ($n \neq 1$) and none of the pentagons are in contact with each other. Compared to graphene sheets and carbon nanotubes (CNTs), the structures of these three-dimensional systems are wonderful and attractive. Spherical shape of fullerenes is due to the pentagons which are absent in graphene and CNT. Due to the spherical shape of C_{60} , the conjugate π bond should be less effective on the wall of a C_{60} and there is hybridization between the π and σ orbitals. Therefore,

conjugate π bonding among the carbon atoms is limited and this phenomenon causes high reactivity of C_{60} . On-ball doped (dopant is included in the fullerene shell) fullerenes in which one or more of carbon atoms that form the cage structure are replaced by heteroatoms are called heterofullerenes [2–4]. BN is a binary compound made of Group III and Group V elements in the periodic table that is much closer to the carbon system. BN materials are the best candidates to replace carbon because they are isoelectronic with their all-carbon analogues. Therefore, the inclusion of nitrogen and boron dopants for the formation of heterofullerenes with the general formula of $C_{60-2n}B_nN_n$ is a promising way to modify the physical and chemical properties of fullerenes [3–5]. Existence of atoms with different electronegativities indicates the high ionicity of the heterofullerenes. The chemical functionalization of nano structures is an effective way to enhance their solubility and change their electronic properties [6]. Moreover, the results of these studies are very important on account of application of these materials for sensing and/or filtering of many hazardous molecules such as CO, HCOH, NH_3 , NO_x , etc. Over the past decade, functionalization of various nanotubes has been extensively studied,

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while the functionalization of heterofullerenes has been less considered. As one of the early pioneers of theoretical study of functionalized heterofullerenes, the author has studied the chemical functionalization of heterofullerenes with NH_3 and NO_2 [7–10].

Nitrogen dioxide (NO_2) is one of a group of highly reactive oxidant and corrosive gasses known as nitrogen oxides (NO_x). This toxic gas is mainly emitted from the motor vehicle exhaust, burning of fossil fuels, petrol and metal refining, power plants, gas stoves, etc. [11–13]. Nitrogen dioxide is an important air pollutant because it contributes to the formation of ground-level ozone, a major component of photochemical smog, which can have significant impacts on human health. NO_2 is linked with a number of adverse effects on the respiratory system and is a precursor to nitrates, which contribute to increased respirable particle levels in the atmosphere [14,15]. As a radical, the reaction with NO_2 [16] is an interesting test of the reactivity of heterofullerenes. According to my knowledge, no prior theoretical investigations have been reported on the covalent/electrostatic nature of addend-heterofullerene interactions. The present work is a DFT study of functionalization of $\text{C}_{30}\text{B}_{15}\text{N}_{15}$ with NO_2 on the different adsorption sites, with a careful examination of a number of configurations. To get more information about the nature of the interaction, energy densities at the bond critical points (BCP) from Bader's [17] quantum theory of atoms in molecules (QTAIM) [18,19], and natural electron configuration of adsorbing atom using natural bond orbital analysis (NBO) [20] were calculated.

2. Model system and computational details

The initial geometry of C_{60} was adopted for construction of $\text{C}_{30}\text{B}_{15}\text{N}_{15}$ as model adsorbent by replacing 15 carbon atoms by nitrogen atoms and another 15 carbon atoms by boron atoms (Fig. 1). Geometry optimizations and calculation of their electronic wave functions were

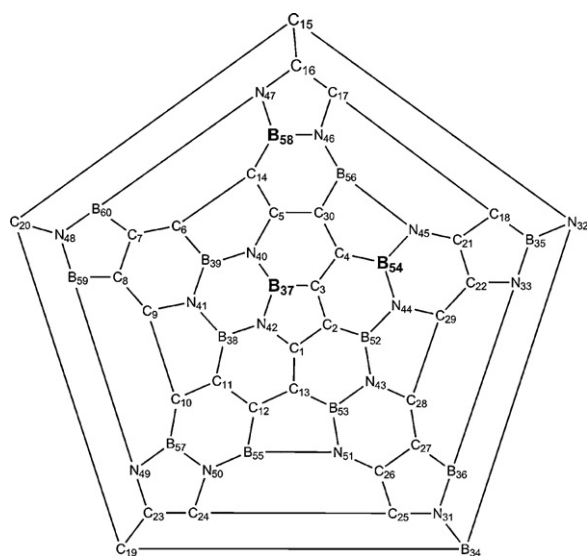


Fig. 1. Schlegel diagram showing the C_{60} core C-atoms, and the dopant atoms of nitrogen and boron.

performed at the 6-31G* basis set with B3LYP functional [21,22], using Gaussian 03 software package [23]. This model chemistry for adsorption study in pi-extended systems is economical and accurate with respect to other model chemistries and used in many articles [7–10,24–26]. The AIM computations were carried out using the AIM 2000 program [18,19]. An NBO calculation was performed with the use of the NBO program version 5.0 [20] by the B3LYP method and 6-31G* standard basis set in the optimized structures in order to evaluate the natural electron configuration of adsorbing atom and electron charge transfer between bound gas molecule and $\text{C}_{30}\text{B}_{15}\text{N}_{15}$.

3. Results and discussion

For a careful investigation of NO_2 adsorption on the exterior surface of a $\text{C}_{30}\text{B}_{15}\text{N}_{15}$ heterofullerene, different adsorption positions and orientation of the triangular shaped NO_2 relative to the $\text{C}_{30}\text{B}_{15}\text{N}_{15}$ surface must be taken into consideration. Three different adsorption sites for adsorption of NO_2 are available, adsorbed gas nearest to a C atom, N atom and B atom. Full geometrical optimization of $\text{NO}_2\text{-C}_{30}\text{B}_{15}\text{N}_{15}$ complexes with different orientation, including individual N or O atoms of adsorbed gas or both of them close to the surface, at several adsorption sites show that in the most stable configurations, the adsorbed gas is close to a B atom of $\text{C}_{30}\text{B}_{15}\text{N}_{15}$. Hence, the same labelling and numbering of C_{60} as the Schlegel diagram was used to show the three-adsorption sites (Fig. 1). In this figure, adsorption sites pointed out in bold. Other boron sites could be considered but they are equivalent to those three, in such a manner that boron atoms labelled 34, 35, 36, 38 and 39 are in equivalent positions as B.37 (site I) and those at 53, 55, 56, 59 and 60 are equivalent to B.54 (site II). At last, boron atoms of sites 52 and 57 are equivalent to B.58 (site III). Equivalent sites indicate similarity in position symmetry and binding to neighbouring atoms with those three considered sites. On the other hand, there are three possible orientations for adsorption of NO_2 on the exterior of a $\text{C}_{30}\text{B}_{15}\text{N}_{15}$, as schematically illustrated in Figs. 2–4. In the nitro configuration (A), the NO_2 molecule is bonded to the surface with the nitrogen end. Bonding with one oxygen end produces the trans-nitrite configuration (B), while bonding with both oxygen ends produces the cis-nitrite configuration (C). For assurance that optimized $\text{NO}_2\text{-C}_{30}\text{B}_{15}\text{N}_{15}$ complexes are in global minimum, rotation of adsorbed molecule around the C₂ axis was performed, then complexes in minimum state reoptimized at the spin-unrestricted B3LYP/6-31G* level of theory. To evaluate the interaction between a NO_2 molecule with different orientations and those three sites of $\text{C}_{30}\text{B}_{15}\text{N}_{15}$ heterofullerene, binding energies (E_b) computed, according to following:

$$E_b = E_{(\text{C}_{30}\text{B}_{15}\text{N}_{15}-\text{NO}_2)} - E_{(\text{C}_{30}\text{B}_{15}\text{N}_{15})} - E_{(\text{NO}_2)}$$

where $E_{(\text{C}_{30}\text{B}_{15}\text{N}_{15}-\text{NO}_2)}$ is the total energy of a NO_2 molecule adsorbed on the $\text{C}_{30}\text{B}_{15}\text{N}_{15}$ surface and $E_{(\text{C}_{30}\text{B}_{15}\text{N}_{15})}$ and $E_{(\text{NO}_2)}$ are the total energy of the free surface and gas phase

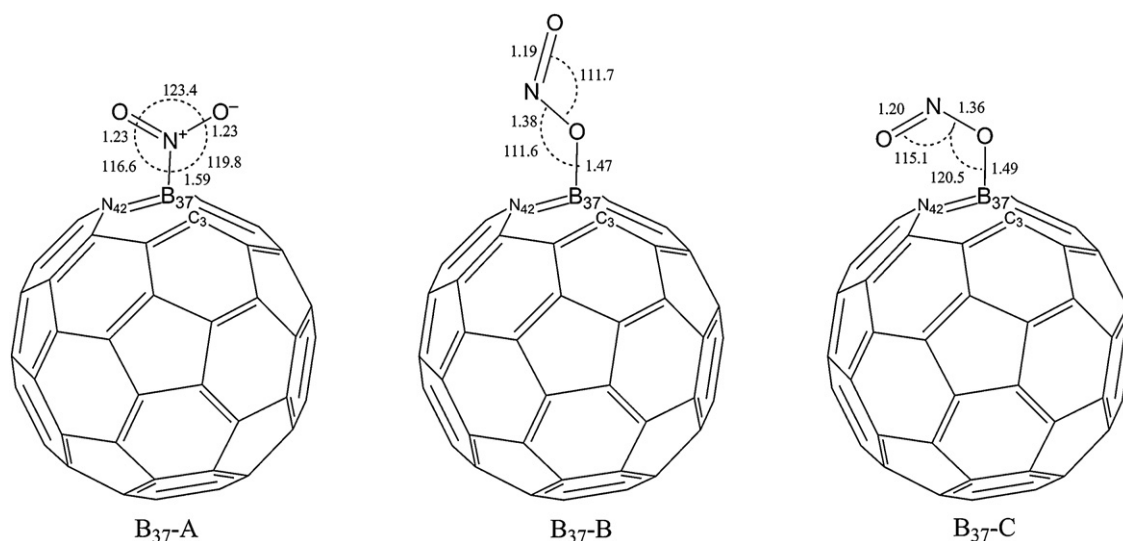


Fig. 2. Adsorption of NO₂ on the exterior surface of C₃₀B₁₅N₁₅ heterofullerene through B₃₇. The distances shown are in angstroms.

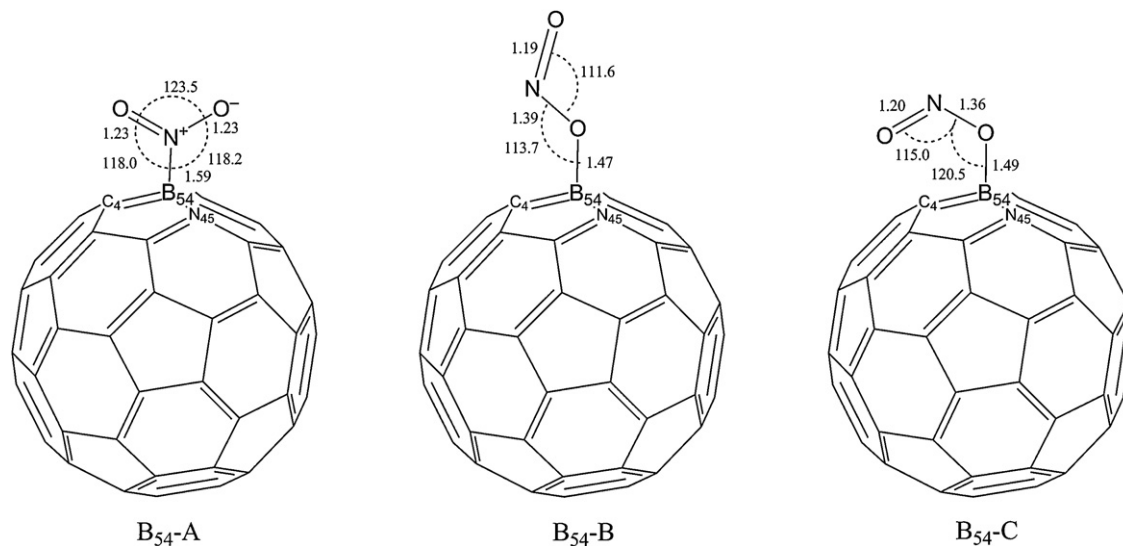


Fig. 3. Adsorption of NO₂ on the exterior surface of C₃₀B₁₅N₁₅ heterofullerene through B₅₄. The distances shown are in angstroms.

molecule, respectively. By the definition, negative values of E_b correspond to exothermic adsorption. The bond length and bond angle of optimized free NO₂ in the gas phase are 1.20 Å and 133.8°, respectively. Geometrical parameters of pristine model and 9 configurations of NO₂-C₃₀B₁₅N₁₅ complexes are gathered in Table 1 and Figs. 2–4. More detailed information including total electronic energies, binding energies and charge transfer based on NPA analysis are listed in Table 2. In the all 9 investigated NO₂-C₃₀B₁₅N₁₅ complexes, the adsorption energies are more negative than -10 kcal/mol, indicating that the adsorption process is chemical in nature. The geometric structure of C₃₀B₁₅N₁₅ at the adsorption site significantly deformed after the sorption of NO₂, where the adsorbing boron atom is slightly pulled out from the spherical surface

and the corresponding bonds of adsorbing boron with three nearby atoms are elongated. Local structural deformation at the adsorption site is due to change in the local hybridization of the adsorbing boron atom with a charge transfer from C₃₀B₁₅N₁₅ to NO₂. Natural electron configuration of adsorbing B atom affords a proper picture about the nature of interaction between C₃₀B₁₅N₁₅ and NO₂. Natural electron configuration of adsorbing B atom for bare model and nine NO₂-C₃₀B₁₅N₁₅ complexes are tabulated in Table 3. Rehybridization of adsorbing B atom with increase in p character was predictable from flexible long bonds around the adsorbing atom. It is known that in covalent functionalization, the hybridization type of adsorbing atom is changed but in noncovalent (electrostatic) functionalization, the hybridization type of

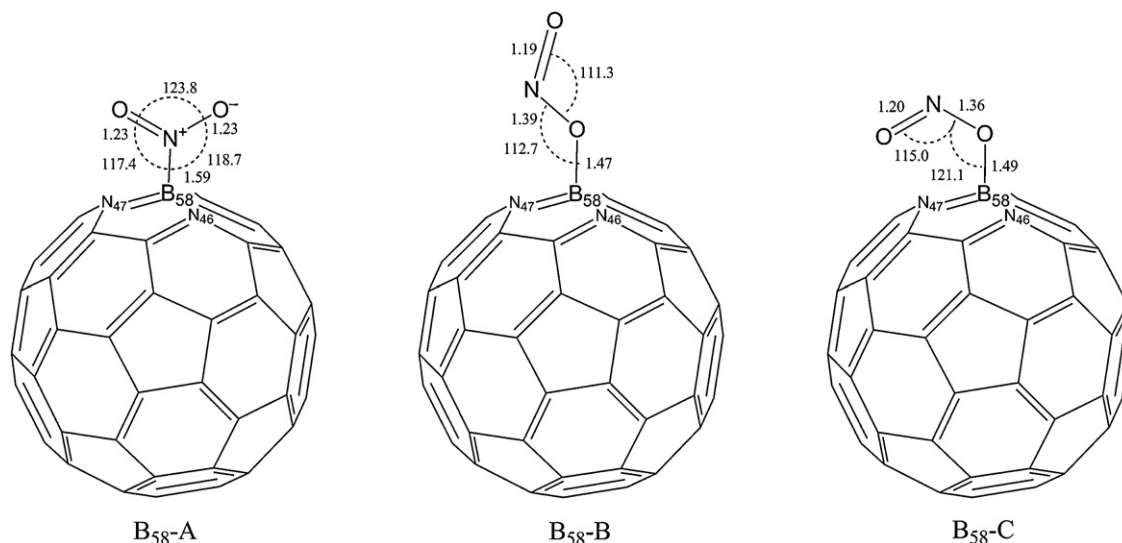


Fig. 4. Adsorption of NO₂ on the exterior surface of C₃₀B₁₅N₁₅ heterofullerene through B₅₈. The distances shown are in angstroms.

Table 1
Calculated structural parameters (the distances are in angstroms).

Model (Configuration)	B.37–C.3	B.37–N.40	B.37–N.42	B.54–C.4	B.54–N.44	B.54–N.45	B.58–C.14	B.58–N.46	B.58–N.47
Bare model	1.54	1.43	1.47	1.55	1.44	1.47	1.55	1.45	1.46
B ₃₇ -A	1.60	1.53	1.57						
B ₃₇ -B	1.60	1.55	1.59						
B ₃₇ -C	1.60	1.54	1.59						
B ₅₄ -A				1.63	1.53	1.55			
B ₅₄ -B				1.64	1.55	1.57			
B ₅₄ -C				1.64	1.55	1.57			
B ₅₈ -A							1.61	1.54	1.56
B ₅₈ -B							1.63	1.56	1.59
B ₅₈ -C							1.63	1.56	1.59

adsorbing atom is unchanged. Therefore these interactions have mainly covalent character. To further examine this issue, AIM analysis performed on the nine studied NO₂-C₃₀B₁₅N₁₅ complexes. Quantum theory of atom in molecules is a powerful method to study the nature of

interactions [17]. Nature of chemical bonds and other valuable information about chemical bonding can be described by analysis of total electronic density, $\rho(r)$, and its corresponding Laplacian, $\nabla^2\rho(r)$, at corresponding bond critical point (BCP). Thus, at the BCP the first derivative of the charge density, $\rho(r)$, is zero [17,27]. The Laplacian of total electronic density is related to the bond interaction energy by a local expression of the virial theorem at critical points [17]:

$$\frac{1}{4}\nabla^2\rho(r) = 2G(r) + V(r)$$

where $G(r)$ and $V(r)$ are electronic kinetic and electronic potential energy densities, respectively. Negative and positive $\nabla^2\rho(r)$ values are associated with shared-electron (covalent) interactions and closed-shell (electrostatic) interactions, respectively. For $2G(r) > |V(r)| > G(r)$, above description is not valid. Therefore, in this case total energy density, $H(r)$, is a good indicator for bonding interactions:

$$H(r) = G(r) + V(r)$$

For negative $H(r)$, the local potential energy density will dominate and an accumulation of electronic charge in the

Table 2
Calculated total electronic energies, adsorption energies and charge transfer for adsorption of NO₂ on the exterior surface of C₃₀B₁₅N₁₅ heterofullerene.^a

Model (Configuration)	Total Electronic Energy (a.u.)	E_b (kcal/mol) ^c	Q_T (e) ^b
Bare Model	-2338.1525321		
B ₃₇ -A	-2543.2828574	-36.47	-0.449
B ₃₇ -B	-2543.2947684	-43.94	-0.508
B ₃₇ -C	-2543.2954393	-44.36	-0.485
B ₅₄ -A	-2543.2879756	-39.68	-0.445
B ₅₄ -B	-2543.3000198	-47.24	-0.499
B ₅₄ -C	-2543.2998987	-47.16	-0.489
B ₅₈ -A	-2543.2891551	-40.43	-0.439
B ₅₈ -B	-2543.3003500	-47.45	-0.505
B ₅₈ -C	-2543.3003660	-47.46	-0.486

^a $E_{\text{ele}}(\text{NO}_2) = -205.0722062$ Hartree.

^b Charge transfer from C₃₀B₁₅N₁₅ to NO₂ molecule.

^c The binding energy between the NO₂ molecule and C₃₀B₁₅N₁₅.

Table 3
Calculated natural electron configuration of adsorbing B atom.

Model (Configuration)	Natural Electron Configuration		
	B ₃₇	B ₅₄	B ₅₈
Bare Model	[core] 2S ^{0.52} 2p ^{1.44} ≈ sp ^{2.77}	[core] 2S ^{0.52} 2p ^{1.45} ≈ sp ^{2.79}	[core] 2S ^{0.52} 2p ^{1.42} ≈ sp ^{2.73}
A	[core] 2S ^{0.51} 2p ^{1.61} ≈ sp ^{3.15}	[core] 2S ^{0.51} 2p ^{1.61} ≈ sp ^{3.15}	[core] 2S ^{0.52} 2p ^{1.60} ≈ sp ^{3.07}
B	[core] 2S ^{0.49} 2p ^{1.50} ≈ sp ^{3.06}	[core] 2S ^{0.49} 2p ^{1.48} ≈ sp ^{3.02}	[core] 2S ^{0.50} 2p ^{1.46} ≈ sp ^{2.92}
C	[core] 2S ^{0.49} 2p ^{1.52} ≈ sp ^{3.10}	[core] 2S ^{0.50} 2p ^{1.50} ≈ sp ^{3.00}	[core] 2S ^{0.51} 2p ^{1.49} ≈ sp ^{2.92}

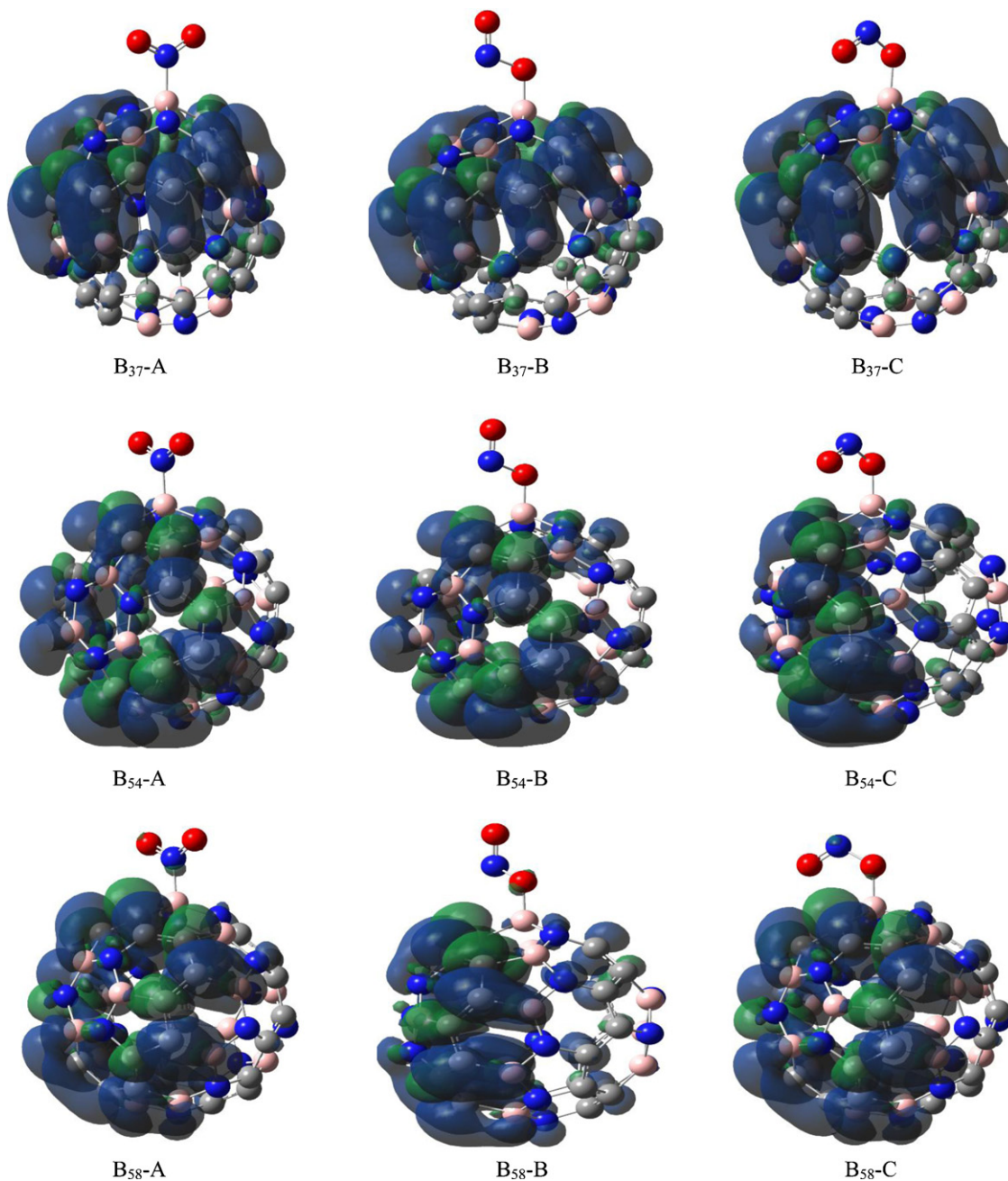


Fig. 5. Visualized spin density distribution of NO₂-C₃₀B₁₅N₁₅ complexes.

Table 4

Topological parameters calculated at the BCP between NO₂ and C₃₀B₁₅N₁₅ on the B3LYP/6-31G* wave functions.

Model (Configuration)	$\nabla^2\rho(r)$ e/a ³	G(r) eV	V(r) eV	H(r) eV
B ₃₇ -A	0.243418	4.881	-8.107	-3.226
B ₃₇ -B	0.591966	6.883	-9.739	-2.856
B ₃₇ -C	0.528393	6.271	-8.947	-2.676
B ₅₄ -A	0.214331	4.710	-7.962	-3.252
B ₅₄ -B	0.612923	7.043	-9.917	-2.874
B ₅₄ -C	0.51732	6.266	-9.013	-2.747
B ₅₈ -A	0.207357	4.674	-7.938	-3.264
B ₅₈ -B	0.582856	6.880	-9.795	-2.915
B ₅₈ -C	0.511881	6.242	-9.001	-2.759

In all configurations $2G(r) > |V(r)| > G(r)$.

internuclear region will be stabilizing. This case is a covalent bond. For zero or positive $H(r)$, there will be closed-shell or electrostatic interactions [28]. The values of $\nabla^2\rho(r)$, $G(r)$, $V(r)$ and $H(r)$ are presented in Table 4. For nine studied NO₂-C₃₀B₁₅N₁₅ complexes, the Laplacian of total electronic densities at BCPs are positive and reveals that electronic charges are depleted in the interatomic path, which is characteristic of closed-shell interactions, but according to above theoretical background, this discussion is not valid because in the all studied cases $2G(r) > |V(r)| > G(r)$. Negative values of $H(r)$ emphasizing that interaction of NO₂ and C₃₀B₁₅N₁₅ in all studied gas-heterofullerene complexes are covalent in nature.

The results of natural electron configuration and AIM analysis were confirmed by spin density distribution analysis. Spin density is one of the diagnostic tools to determine the nature of the interaction between NO₂ and C₃₀B₁₅N₁₅. Spin density distributions of nine studied NO₂-C₃₀B₁₅N₁₅ complexes are visualized using GaussView software [29]. The visualized spin density distributions presented in Fig. 5. For all 9 studied NO₂-C₃₀B₁₅N₁₅ complexes, the spin densities are located somewhere other than the B-NO₂ units. In the NO₂-C₃₀B₁₅N₁₅ complexes, where the gas molecule interacted with B₃₇ and B₅₄ of C₃₀B₁₅N₁₅ heterofullerene, spin densities on the B-NO₂ units not observed. For adsorption of NO₂ through B₅₈ of C₃₀B₁₅N₁₅ heterofullerene, spin density distributions on the B-NO₂ units are very small. Spin density distributions of 9 studied NO₂-C₃₀B₁₅N₁₅ complexes show that the interactions between NO₂ and C₃₀B₁₅N₁₅ are covalent in nature.

4. Conclusions

The interaction between NO₂ and C₃₀B₁₅N₁₅ with different orientation of adsorbed gas investigated on the basis of density functional theory calculations. The results imply that NO₂ can be chemically adsorbed on the exterior surface of C₃₀B₁₅N₁₅ heterofullerene with a charge transfer from adsorbent to adsorbed gas. The results of NBO (natural electron configuration of adsorbing B atom), AIM analysis and spin density distributions revealed that the interaction of NO₂ and C₃₀B₁₅N₁₅ in all studied complexes are covalent in nature. From a qualitative aspect, all

consequences are not dependent on the orientation of adsorbed gas.

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