

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236867562>

The response of selected isomers of B80 buckyball toward NH₃ adsorption: A density functional theory investigation

ARTICLE *in* STRUCTURAL CHEMISTRY · OCTOBER 2012

Impact Factor: 1.84 · DOI: 10.1007/s11224-012-0159-z

CITATIONS

2

READS

42

5 AUTHORS, INCLUDING:



Aidin Bahrami

Tarbiat Modares University

7 PUBLICATIONS 17 CITATIONS

SEE PROFILE



Sirous Yourdkhani

University of Warsaw

13 PUBLICATIONS 38 CITATIONS

SEE PROFILE



Mehdi D Esrafil

University of Maragheh

180 PUBLICATIONS 901 CITATIONS

SEE PROFILE



Milad Bahrami

Polytechnique Montréal

6 PUBLICATIONS 13 CITATIONS

SEE PROFILE

The response of selected isomers of B₈₀ buckyball toward NH₃ adsorption: a density functional theory investigation

Aidin Bahrami · Sirous Yourdkhani ·
Mehdi D. Esrafil · Milad Bahrami ·
Nasser L. Hadipour

Received: 15 August 2012 / Accepted: 25 October 2012
© Springer Science+Business Media New York 2012

Abstract Density functional theory calculations at the B3LYP/6-31G(d) and B3LYP/6-31+G(d) levels were carried out for the adsorption of NH₃ on three symmetric isomers of B₈₀ {C₁, T_h, I_h}. To investigate the binding features of B₈₀ isomers with NH₃, different studies including the structural and electronic parameters, the ¹⁴N electric field gradient tensors and the atoms in molecules (AIM) properties were considered. The calculated parameters by these investigations can be used as powerful tools to find out some of the unknown aspects of electronic structures of the boron buckyball and its isomers. According to previous studies, boron buckyball as an amphoteric and a hard molecule has two distinct reactive sites defined as cap and frame which act as an acid and a base, respectively. Regarding the obtained results in this study, all the isomers had the same exposure when NH₃ molecule reacted with the external wall of B₈₀. For instance, the stability of N–B bond in the cap site was significantly more than the stability of N–B bond in the frame. Moreover, the adsorption of NH₃ on frame site showed a considerable reduction in HOMO–LUMO energy gap. According to AIM theory, an electrostatic nature was observed for N–B interaction. Concerning the selected

isomers of buckyball, the capability of the NH₃–B₈₀ complexes to localize electron at the N–B bond critical points depend on the reaction sites significantly. In general, ¹⁴N nuclear quadruple coupling constants and asymmetry parameter reveal a remarkable effect of NH₃ adsorption on electronic structure of the B₈₀.

Keywords Adsorption · B₈₀ boron buckyball · DFT · HOMO–LUMO · ¹⁴N quadruple coupling tensors · Atoms in molecules

Introduction

The electron deficiency of boron gives it a unique property so that chemistry is going to focus on this subject [1–3]. Regarding boron's characteristic, one electron less than its neighbor (carbon), other strategies must be pursued to form interboron covalent or noncovalent bonds.

Since few experimental studies have been performed on B₈₀ and its isomers, the main part of our knowledge about boron buckyballs comes from theoretical analyzes. Computational studies such as ab initio methods and their predictions about Boron derivatives have changed our attitude toward the concepts of chemical bonding [4, 5]. The wide variety of boron clusters as novel solids [6, 7], quasiplanar clusters [8], nanosheets [9, 10], nanotubes [11, 12], nanoropes [13], nanospheres [14, 15], nanowires [16, 17], nanobelts [18], nanoribbons [19, 20], nanochains, and quasi-crystals [21, 22] are available due to their special molecular structures and spectroscopic properties.

A recent density functional theory (DFT) study by Szwacki et al. proposed a fullerene-like hollow cage composed of 80 boron atoms with 20 extra boron atoms in the centers of all hexagons called B₈₀ boron fullerene or

A. Bahrami · S. Yourdkhani · N. L. Hadipour (✉)
Department of Chemistry, Tarbiat Modares University,
14115-175, Tehran, Iran
e-mail: nasser.hadipour@gmail.com; hadipour@modares.ac.ir

M. D. Esrafil
Laboratory of Theoretical Chemistry, Department of Chemistry,
University of Maragheh, Maragheh, Iran

M. Bahrami
Department of Technology and Engineering, Islamic Azad
University, Tabriz Branch, Tabriz, Iran

boron buckyball [13, 23, 24]. B₈₀ fullerene is energetically one of the most favorable boron clusters that have been studied so far. If becoming operational, B₈₀ will be found many usages in material sciences, medicine, pharmaceuticals, and electronic industries [25, 26]. What is more, generally boron clusters have been used in cancer therapy for years [27].

It is proved that B₈₀ buckyball has various isomers which three of them are close to each other in terms of energy and geometrical conditions. Visually, their geometrical conditions are almost identical. However, a detailed analysis has revealed significant differences in their symmetries. Namely, one of them does not have any symmetry called C₁. The other two have similar symmetries to icosahedral (I_h) and tetrahedral (T_h) [28]. In addition, the analysis of the interaction between B₈₀ and the adsorbed molecules on its surface has paramount importance to clarify some structural and electronic properties of B₈₀ buckyball. It is known that NH₃ as one of the toxic gaseous molecules has low boiling point and it is volatile. Therefore, recognition and development of new sensitive compounds to detect the gaseous NH₃ molecules has a great deal of importance.

According to the best of our knowledge, a few studies have been carried out about adsorption of gaseous molecules on pure boron nanostructures [29]. However, some literatures have investigated adsorption of gaseous molecules by mixture of boron with other elements [30, 31]. The main purpose of this study is investigation of NH₃ adsorption on B₈₀ symmetric isomers to find out how they respond to the adsorption of a molecule on their external wall. The results of this study give some view points about symmetry effects on electronic and chemical structures of B₈₀ buckyball during the adsorption of ammonia molecule on the surface of its different isomers.

Computational methods

DFT calculations

The Gaussian 98 suits program was employed for electronic structure calculations [32]. For the B₈₀ isomers as being pristine and adsorbent, the geometrical parameters were fully optimized with symmetry constraints at the B3LYP functional [33, 34] and 6-31G* basis set [35].

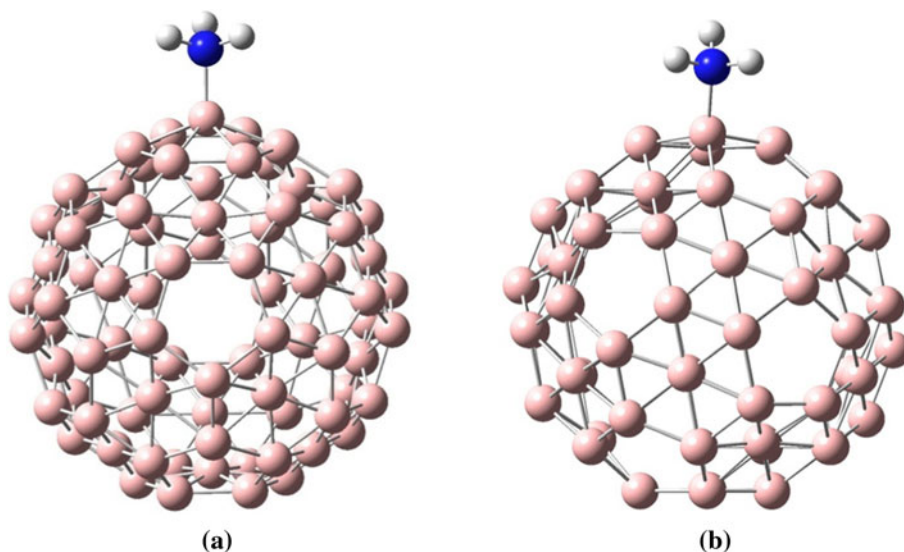
Since our focus was on the external surface of B₈₀ isomers, two types of boron including cap and frame atoms were investigated. In this study, all orientations of NH₃ molecule to approach B₈₀ were considered. Moreover, all these combinations have been used for T_h, I_h, and C₁ symmetries to probe the effect of symmetry changing on the adsorption parameters.

It should be mentioned that all calculations were performed at B3LYP/6-31G* to obtain the most stable complex. Based on the results, one of the optimized complex structures in any isomers seems to be more stable than the others thermodynamically (Fig. 1). This result is in completely agreement with Lewis acid–base interaction. The group V hydride molecules such as NH₃ are electron-rich bases which have one lone pair electrons to interact with B₈₀ as a Lewis acid. According to Fig. 1, a strong noncovalent bond is formed between nitrogen and boron atoms. Atoms in molecules and nuclear quadruple resonance calculations are just performed on the most stable structure to obtain useful information about the nature of interactions.

Atoms in molecules (AIM) calculations

AIM analysis was performed using AIM 2000 code [36]. For atom–atom interplay such as intermolecular interactions or valence bonds, the characteristics of the bond

Fig. 1 Equilibrium geometries and pictorial view of the NH₃ adsorption on **a** cap and **b** frame sites of T_h isomer of B₈₀ boron buckyball



critical point (BCP) are very essential [37] to determine the electron density ρ_C and its Laplacian $\nabla^2\rho_C$. The energetic properties of BCPs are often regarded as the electron energy density at BCP (H_C). It is worth mentioning that H_C has two components: the kinetic electron energy density (K_C) and the potential electron energy density (V_C) and there is a relation between these energetic characteristics, $H_C = K_C + V_C$.

From the virial theorem, it is also concluded that $1/4\nabla^2\rho_C = 2K_C + V_C$. The negative value of the $\nabla^2\rho_C$ at BCP determines the concentration of the electron charge among the nuclei of the interacting atoms and it is typical of covalent bonds-shared interactions. In addition, in some studies it has been mentioned that the interaction can be considered as partly covalent in nature when $\nabla^2\rho_C > 0$ and $H_C < 0$ [38]. In the case that $\nabla^2\rho_C$ and H_C are positive, there is a decline in electron charge between the atoms which indicates an interaction of closed shell systems: ions, van der Waals interactions, or H-bonds. Therefore, the Bader theory provides the characteristics of BCPs that depends on the covalent or noncovalent nature of interaction.

Results and discussion

Analysis of binding energies and structural parameters

The 2p valence shell of boron is occupied by only one electron and the remaining p orbitals are vacant and ready themselves to get lone pair electrons. The cap atoms transfer three electrons to the nearest frame atoms [39]. Hence, the caps atoms become more acidic while a slight increase occurs in the electron density of the frame atoms due to this interplay. Since the value of the transferred electrons is not adequate to compensate the electron deficiency of the frame, the boron atoms in B_{80} mostly behave as Lewis acids.

The cap atoms are divided into couple groups viz. the outward and the inward, depending on the value of their radial distance from the center. It is proved that when nucleophilic ligands approach to the cap atoms, the initial orientation of the attacking nucleophiles toward exo or endo caps has no influence on the final geometrical conditions [40]. Therefore, NH_3 molecule can be located outside the cage (exo- B_{80}). It should be mentioned that all the calculations have been performed on these two cap sites, however, the average of the results has been shown in tables.

Exohedral complexes

These complexes are characterized by bond distances among heteroatom nitrogen with the boron and boron–boron bond

near the interaction site which are shown in Table 1. Although, distance differences of N–B bonds among three isomers are not perceptible, the results show that the interaction of N with boron in the cap site is stronger than the frame one. It is clear that the nearest B–B to N–B bond in the cap site becomes longer than the similar bond in the frame site. Moreover, the analysis of the results related to the binding energy reveals differences among the isomers obviously. According to Table 2, the comparison between two coordinates confirms pervious results. For instance, the values of the binding energy in NH_3 -cap are approximately 44, 45, and 48 % more than those of NH_3 -frame coordinates for T_h , I_h , and C_1 isomers, respectively. Hence, it can be concluded that the cap complexes are more stable than the frame ones. This result is also proved by the slight shortening of B–N bond distances in NH_3 -cap in comparison with NH_3 -frame complexes (Table 1).

The stabilities of all investigated complexes in this study can also be discussed on the basis of their HOMO–LUMO gaps with regard to the maximum hardness principle [41]. According to Fig. 2, the LUMO has a small contribution to the cap and a great contribution to the frame atoms, whereas the HOMO is more localized on the frame. The study of NH_3 – B_{80} interaction reveals that the HOMO of the NH_3 consisting of lone pair which interacts with the

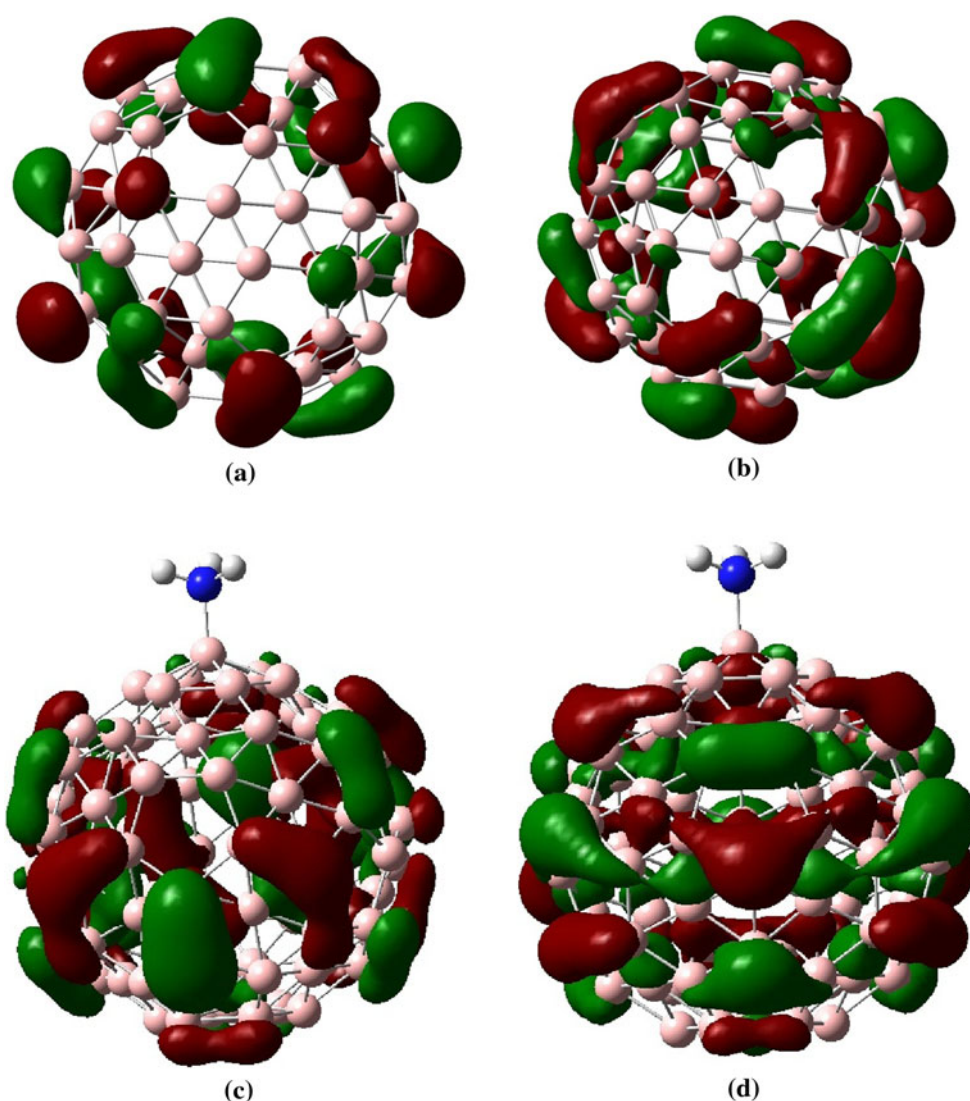
Table 1 The B–B, B–N, and N–H bond distances (Å) for the most stable complexes of B_{80} different isomers

Isomer	Status	B–B	B–B	B–N	N–H
C_1	NH_3 -cap	1.700	1.829	1.633	1.025
	NH_3 -frame	1.738	1.799	1.654	1.025
Tetrahedral	NH_3 -cap	1.714	1.833	1.633	1.025
	NH_3 -frame	1.743	1.804	1.656	1.026
Icosahedral	NH_3 -cap	1.704	1.828	1.633	1.025
	NH_3 -frame	1.737	1.804	1.659	1.026

Table 2 The calculated HOMO and LUMO energies, HOMO–LUMO energy gap (E_g), energy of adsorption (E_b), for NH_3 adsorption on the pristine and adsorbent B_{80} isomers

Isomer	Status	E_b (eV)	HOMO (eV)	LUMO (eV)	E_g (eV)
C_1	Pristine	–	–5.47	–3.59	1.88
	NH_3 -cap	–1.15	–5.11	–3.20	1.91
	NH_3 -frame	–0.60	–4.88	–3.27	1.61
Tetrahedral	Pristine	–	–5.43	–3.48	1.95
	NH_3 -cap	–1.13	–5.21	–3.34	1.87
	NH_3 -frame	–0.63	–4.86	–3.21	1.65
Icosahedra	Pristine	–	–5.53	–3.59	1.94
	NH_3 -cap	–1.13	–5.11	–3.23	1.88
	NH_3 -frame	–0.62	–4.88	–3.27	1.61

Fig. 2 HOMO–LUMO molecular orbitals of T_h isomer of B_{80} and NH_3 -cage when NH_3 approaches on cap site in T_h isomer; **a** HOMO of T_h isomer, **b** LUMO of T_h isomer, **c** HOMO of NH_3 - T_h , **d** LUMO of NH_3 - T_h



LUMO of the buckyball. Because of borons low electronegative feature the polarization of the N–B bond is illustrated in HOMO and LUMO of NH_3 - T_h (Fig. 2c, d) by the localization of an orbital lobe close to N along the B–N bond. Moreover, the values of HOMO–LUMO energy and HOMO–LUMO energy gap in both NH_3 -cap and NH_3 -frame complexes change due to NH_3 adsorption (Table 2). In spite of the fact that the energy level of HOMO–LUMO in both cap and frame complexes has increased (Table 2), our results show a decrease in HOMO–LUMO gaps in comparison with pristine. It is worth noting that the scale of this reduction is not significant for NH_3 -cap while it is noticeable for frame complexes. For instance, in the case of T_h isomer the HOMO–LUMO gap has changed about 15 % from pristine to adsorbent. In addition, these decreases are shown to be 17 and 12 % for I_h and C_1 , respectively.

According to the results, it can be concluded that the boron atoms localized on the cap are hard and the

hard–hard interaction between NH_3 and cap atoms is expected to be stronger than that of frame.

^{14}N quadruple coupling tensors

NQR parameters of nitrogen atoms are also changed due to this adsorption. Table 3 shows the average of ^{14}N EFG eigenvalues, their associated nuclear quadruple coupling constants, C_Q (^{14}N), and asymmetry parameter η_Q , at the nitrogen positions of NH_3 when it approaches to three isomers of B_{80} (C_1 , T_h , and I_h). The intermolecular bond between nitrogen and boron atoms on two sites of B_{80} (cap and frame) is expected to strongly affect the electronic environment at the nuclei involved in the interaction. Thus, the bond effects in electronic structure made by N–B formation influence the EFG properties of the ^{14}N nuclei in B_{80} complexes.

Table 3 The calculated electric field gradient tensors diagonal components (q_{xx} , q_{yy} , q_{zz}), C_Q (MHz) and η_Q parameters for three isomers of B_{80} and single NH_3 molecule

Isomer	Status	q_{xx}	q_{yy}	q_{zz}	C_Q	η_Q
C_1	NH_3 -cap	-0.1514	-0.1509	0.3024	1.2649	0.0016
	NH_3 -frame	-0.1827	-0.1737	0.3564	1.4908	0.0252
Tetrahedral	NH_3 -cap	-0.1335	-0.1330	0.2665	1.1148	0.0016
	NH_3 -frame	-0.1728	-0.1646	0.3373	1.4112	0.0243
Icosahedra	NH_3 -cap	-0.1510	-0.1507	0.3016	1.2617	0.0010
	NH_3 -frame	-0.1816	-0.1729	0.3544	1.4826	0.0245
NH_3	—	-0.40346	-0.40346	0.806912	3.3757	0.0000

Moreover, these findings reveal that C_Q and η_Q values of ^{14}N sites are modified by NH_3 adsorption. According to Table 3, with respect to the formation of N–B bond, the obtained results from B3LYP method including q_{zz} and consequently C_Q tend to decrease, whereas the η_Q shows an opposite trend in comparison with the same parameters of NH_3 molecule. More specifically, the C_Q (^{14}N) value decreases from 3.38 MHz for NH_3 to 1.11 and 1.41 MHz in NH_3 -cap and NH_3 -frame, respectively, in the T_h isomer (67 and 58 % reduction). Correspondingly, the asymmetry parameter η_Q (^{14}N) has shown an increase (by 0.0001–0.025 U) from single NH_3 molecule to complexes due to NH_3 -cage interaction. Also the amount of the reduction of C_Q in T_h isomer is more significant than the one in C_1 and I_h . In addition, it is revealed that the value of C_Q (^{14}N) increases at the B3LYP level with the greatest jump from cap to frame coordinate when NH_3 approaches them. Furthermore, the results show that the changes in η_Q values in frame coordinate is more considerable than those of cap complexes. For instance, in T_h isomer, the η_Q value in frame site changes ~ 93 % more than the cap coordinate value.

Thus, it seems that although the interaction of N with cap boron is stronger than the one with frame boron, this interaction influences the symmetry of electronic environment of frame more than cap coordinate.

Atoms in molecules analysis

Bader theory has been applied here to analyze the characteristics of N–B BCPs at two different interaction sites (cap and frame) of B_{80} isomers. In the equilibrium geometrical condition, an interatomic interaction line is regarded as a bond path [37]. For such an equilibrium molecular structure, there is a virial path for each bond of the interacting atoms [42]. Molecular graphs of the optimized I_h isomer are depicted in Fig. 3. For N–B and B–B interactions, there are corresponding bond paths and critical points (BCPs) within the equilibrium structures. As indicated in previous studies, the characteristics of donor–acceptor BCPs are very useful to obtain a profound perception of the nature of interactions. Parameters such as electron density at the donor–acceptor BCP (ρ_C) and its Laplacian ($\nabla^2\rho_C$) often correlate with the bond energy or

Fig. 3 Molecular graphs of the fully optimized systems: **a** the complex of NH_3 on cap site of I_h isomer and **b** the complex of NH_3 on frame site of I_h isomer. Graphs were obtained at the B3LYP/6-31+G* level. Big circles correspond to atoms and small ones to critical points

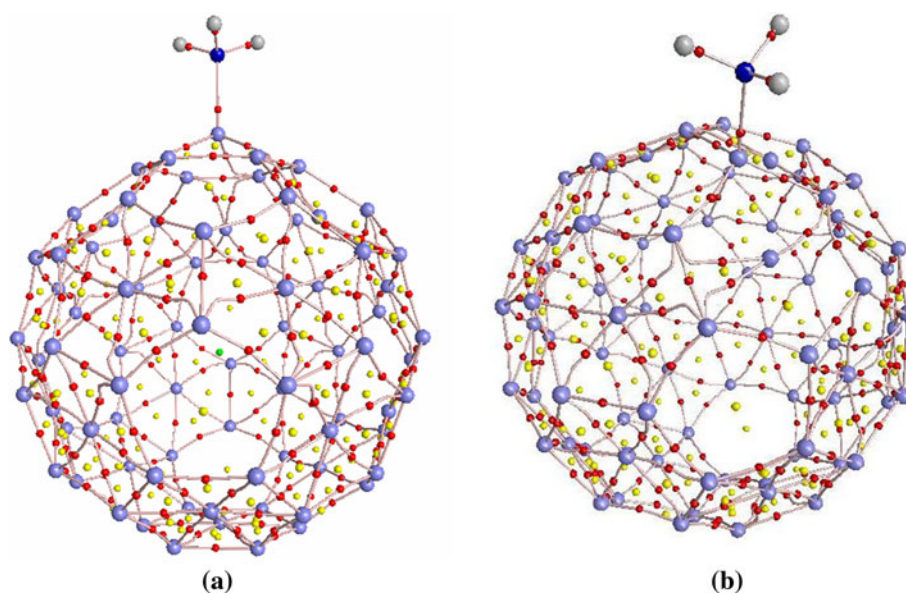


Table 4 Topological parameters (all in atomic units) for the optimized three isomers of B₈₀ analyzed here

Isomer	Interaction	Coordinate	ρ_C	$\nabla^2\rho_C$	K_C	V_C	H_C	$-\frac{K_C}{V_C}$
C ₁	N...B	Cap	0.124	0.249	-0.0925	0.123	0.0304	0.752
		Frame	0.113	0.293	-0.0784	0.084	0.006	0.933
Tetrahedral	N...B	Caps	0.124	0.248	-0.0925	0.123	0.0303	0.752
		Frame	0.113	0.291	-0.0782	0.084	0.005	0.931
Icosahedral	N...B	Caps	0.124	0.248	-0.0924	0.123	0.0306	0.751
		Frame	0.112	0.285	-0.0779	0.085	0.007	0.916

other parameters like donor–acceptor distance, etc. [42]. According to Table 4, the calculated electron densities at N–B BCPs are found to be about 0.124 and 0.113 au in cap and frame complexes, respectively, and these values do not show a significant difference among these three isomers. In agreement with the previous results, it can be concluded that the value of electron density in N–B BCP decreases when NH₃ approaches to frame coordinate at three isomers. For instance, the average value of ρ_C (0.124 au) for the N–B bond in NH₃-cap in T_h isomer is ~9 % more than the one in NH₃-frame complex (0.113 au). Also the capacity of the B₈₀ isomers to concentrate electrons at the N–B BCP is sensitive to the interaction site on the external surface of cage. The calculated electron density properties of the isomers demonstrate that the N–B bonding has high ρ , and positive $\nabla^2\rho_C$ values (ranging from 0.248 to 0.293). These properties are typical of closed shell interactions and clarify electrostatic features of the N–B bonding. It is claimed that in case of positive $\nabla^2\rho_C$ and negative H_C , the interaction is partly covalent in nature, but in case of positive H_C the nature of interaction is electrostatic [39]. H_C is the electron energy density at BCP which is equal to the sum of kinetic electron energy density (K_C) and potential electron energy density (V_C). In the B₈₀ isomers, the V_C value is positive while K_C value is negative. The balance between these values determines the nature of the interaction. Therefore, the characteristics of $-K_C/V_C$ can determine covalent and noncovalent interactions. According to the results, the N–B interaction at three isomers of B₈₀ has a noncovalent nature and due to the less amount of $-K_C/V_C$, the N–B bond in NH₃-cap shows more considerable electrostatic nature in comparison with NH₃-frame complex.

Conclusion

In this study, the responses of symmetric isomers of B₈₀ with two distinct reactive sites localized on cap and frame to the adsorption of NH₃ have been investigated. It is found that the differences between equilibrium geometries and

interaction energies of the three isomers are not very significant. Nonetheless, all electronic and structural parameters depend on the reactive sites considerably. The results confirm that the cap boron atoms as hard acids form the stronger interaction than the frame atoms with group NH₃. In agreement with this finding, nuclear quadruple resonance calculations indicate that the NQR parameters of nitrogen atoms change with varying of sites. Furthermore, the capacity of the isomers to concentrate electrons at the N–B BCP increases when NH₃ approaches the cap in comparison with frame atoms. Moreover, AIM calculations have detected an electrostatic nature for N–B interaction in more details. The obtained results can enhance our perception about the nature of B₈₀ as an adsorbent to rationalize the common occurrence of similar interactions in boron buckyballs.

References

- Muetterties EL (ed) (1975) Boron hydride chemistry. Academic Press, New York
- Liebman JF, Greenberg A, Williams RE (eds) (1988) Advances in boron and boranes. VCH Publishers, New York
- Siebert W (ed) (1997) Advances in boron chemistry. The Royal Society of Chemistry, Cambridge
- Alexandrova AN, Boldyrev AI, Zha HJ, Wang LS (2006) Coord Chem Rev 250:2811
- Quandt A, Boustani I (2006) ChemPhysChem 6:2001
- Oganov AR, Chen JH, Gatti C, Ma YZ, Ma YM, Glass CW, Liu ZX, Yu T, urakevych OO, Solozhenko VL (2009) Nature 457:863
- Yu E, Dubrovinsky L, Dubrovinskaia N, Miyajima N, Filinchuk Y, Chernyshov D, mitriev V (2008) Sci Technol Adv Mater 9:044209
- Boustani I (1997) Phys Rev B 55:16426
- Boustani I (1997) Surf Sci 370:355
- Lau KC, Pandey R (2007) J Phys Chem C 111:2906
- Boustani I, Quandt A, Hernandez E, Rubio A (1999) J Chem Phys 110:3176
- Tang H, Ismail-Beigi S (2007) Phys Rev Lett 99:115501
- Szwacki NG, Sadrzadeh A, Yakobson B (2007) Phys Rev Lett 98:166804
- Prasad DVK, Jemmis ED (2008) Phys Rev Lett 100:165504
- Mukhopadhyay S, He H, Pandey R, Yap YK, Boustani I (2009) J Phys Conf Ser 176:012028
- Kunstmann J, Quandt A (2005) Chem Phys Lett 402:21

17. Zhang Y, Ago H, Yumura M, Ohshima S, Uchida K, Komatsu T, Iijima S (2004) *Chem Phys Lett* 385:177
18. Tian J, Cai J, Hui C, Zhang C, Bao L, Shen C, Gao H (2008) *Appl Phys Lett* 93:122105
19. Wang Z, Shimizu Y, Sasaki T, Kawaguchi K, Kimura K, Koshizaki N (2003) *Chem Phys Lett* 368:663
20. Xu TT, Zheng JG, Wu N, Nicholls AW, Roth JR, Dikin DA, Ruoff RS (2004) *Nano Lett* 4:963
21. Ding Y, Yang X, Ni J (2008) *Appl Phys Lett* 93:043107
22. Boustani I, Quandt A, Kramer P (1996) *Europhys Lett* 36:583
23. Gopukumar G, Nguyen MT, Ceulemans A (2008) *Chem Phys Lett* 450:175
24. Ceulemans A, Tshishimbi Muya J, Gopukumar G, Nguyen MT (2008) *Chem Phys Lett* 461:226
25. Grimes RNJ (2004) *Chem Educ* 81:657
26. Sivaev IB, Bregadze VV (2009) *Eur J Inorg Chem* 11:1433
27. Hawthorne MF (1991) *Pure Appl Chem* 63:327334
28. Szwacki NG, Sadrzadeh A, Yakobson BI (2008) *Phys Rev Lett* 100:159901
29. Wu G, Wang J, Zhang X, Zhu L (2009) *J Phys Chem C* 113:7052
30. Sun Q, Wang Q, Jena P (2005) *Nano Lett* 5:1273
31. Durgun E, Jang YR, Ciraci S (2007) *Phys Rev B* 76:073413
32. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery Jr JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) *Gaussian 03 revision C.01*, Gaussian, Inc., Wallingford
33. Becke ADJ (1993) *Chem Phys* 98:5648
34. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785
35. Hehre WJ, Ditchfield R, Pople JAJ (1972) *Chem Phys* 56:2257
36. Biegler-Konig F, Schonbohm J, Bayles D (2001) *J Comput Chem* 22:545
37. Bader RFW (1990) *Atoms in molecules a quantum theory*. Oxford University Press, New York
38. Esrafil MD (2012) *J Mol Model* 18:2003
39. Muya JT, Nguyen MT, Ceulemans A (2009) *Chem Phys Lett* 483:101
40. Muya JT, De Proft F, Geerlings P, Nguyen MT, Ceulemans A (2011) *J Phys Chem A* 115:9069
41. Chattaraj PK, Lee H, Parr RG (1991) *J Am Chem Soc* 113:1855
42. Keith TA, Bader RFW, Aray Y (1996) *Int J Quantum Chem* 57:18