SELÇUK
ÜNİVERSİTESİ
MÜHENDİSLİK FAKÜLTESİ

STRUCTURAL AND ELECTRONIC PROPERTIES OF $B_{6-n}C_nH_n$ (n=0-6) SERIES UPON THE SUBSTITUTION OF BORON ATOMS BY THE C-H GROUPS: A DENSITY FUNCTIONAL THEORY STUDY

İskender MUZ

Department of Mathematics and Science Education, Nevşehir Hacı Bektaş Veli University, 50300 Nevşehir, Turkey
iskendermuz@yahoo.com

ABSTRACT: In this study, the structural and energetic properties of $B_{6-n}C_nH_n$ (n=0-6) series were investigated using Density Functional Theory (DFT) approach. Adiabatic ionization potential (AIP), vertical ionization potential (VIP), adiabatic electron affinity (AEA), vertical electron affinity (VEA), vertical detachment energy (VDE), HOMO-LUMO energy gap (E_g) and binding energy (E_b) have been investigated at the B3LYP/6-311++G** level of theory and discussed for the most stable isomers. Charge distribution and nucleus independent chemical shift (NICS) analysis were also performed. $B_2C_4H_4$ and C_6H_6 series are the most stable among considered series by calculating ionization potentials (IPs), electron affinities (EAs) and E_g. The benzene-like structure is found to be the most stable isomer for n=5 (BC_5H_5), and it can be as aromatic as benzene.

Key Words: Aromaticity, Carboranes, Density Functional Theory (DFT), Electronic structure, Stability

C-H Grupları ile Bor Atomlarının Yer Değiştirmesi Sonucunda $B_{6-n}C_nH_n$ (n=0-6) Serilerinin Yapısal ve Elektronik Özellikleri: Bir Yoğunluk Fonksiyonel Teori Çalışması

ÖZ: Bu çalışmada $B_{6-n}C_nH_n$ (n=0-6) serilerinin yapısal ve enerji özellikleri yoğunluk fonksiyonel teorisi kullanılarak araştırıldı. Adyabatik iyonizasyon potansiyeli (AIP), doğrudan iyonizasyon potansiyeli (VIP), adyabatik elektron ilgisi (AEA), doğrudan elektron ilgisi (VEA), doğrudan ayrılma enerjisi (VDE), HOMO-LUMO enerji aralığı (E_g) ve bağlanma enerjisi B3LYP/6-311++G** teori seviyesinde incelendi ve en kararlı izomerler tartışıldı. Yük dağılımı ve çekirdekten bağımsız kimyasal kayma analizleri de gerçekleştirildi. $B_2C_4H_4$ and C_6H_6 serileri IP, EA ve E_g hesaplamaları sonucunda en kararlı seriler olarak bulunmuştur. Benzen tipi yapı BC_5H_5 (n=5) serisi için en kararlı isomer olarak bulunmuştur ve bu yapı benzen kadar aromatik olabilir.

Anahtar Kelimeler: Aromatiklik, Elektronik yapı, Kararlılık, Karboranlar, Yoğunluk Fonksiyonel Teorisi

INTRODUCTION

Boron is only the non-metal element of IIIA group in the periodic table and possesses a richness of chemistry second only to carbon (Smith, 1990; Jemmis, 2002). Boron and carbon are capable of forming various stable compounds with hydrogen due to their strong chemical bonding characteristics. Hydrogenated boron-carbon or carborane compounds are of great interest for both experimental and theoretical chemists. Moreover, they have been declared as appropriate pioneers for the formation of carboranes (Williams, 1976; Grimes, 2013). The unique physical and chemical properties of carboranes

have led to using them extensively in materials science (El-Zaria et al., 2011), polymer chemistry (Jiang et al., 1996; McLemore et al., 1999) organometallic and coordination chemistry (Westerhausen et al., 2001; Spokoyny et al., 2011), medicine (Soloway et al., 1998; Barth et al., 2005) and medicinal chemistry (Valliant et al., 2002; Scholz and Hey-Hawkins, 2011) applications.

The benzene-like structures have been attracted due to high resonance stability, nonclassical bonding, aromaticity and the benzene-like reactivity (Galeev and Boldyrev, 2011; Ivanov and Boldyrev, 2012; Ivanov et al., 2012; Muz and Atis, 2016). Recently, the aromaticity and antiaromaticity of some carbon based compounds such as borabenzene, silabenzene and phosphabenzene have been discussed in detail (Galeev and Boldyrev, 2011; Ivanov and Boldyrev, 2012; Ivanov et al., 2012; Muz and Atis, 2016). Moreover, these studies have been concluded that some benzene-like structures exhibit aromatic properties. More interestingly, it was found that the replacement of a phosphorus atom by the C-H group in the $C_xH_xP_{6-x}$ (x=0-6) series cause the transition from three-dimensional (3D) structures to two dimensional (2D) structures (Galeev and Boldyrev, 2011).

The exchange of different group atoms by carbon atom in the carborane compounds provides extra or deficit electron(s). Thus, it can significantly change the structural and electronic properties of the system. In literature, there is a limited number of research on the structural properties of various carborane compounds (Takano et al., 1992; Jemmis et al., 1997; Schleyer and Najafian, 1998; Li, 2017). To the best of our knowledge, there is no study investigating the substitution of a boron atom by the C-H group in the carboranes and their derivatives. Therefore, this study aims to investigate the structural and electronic properties in the $B_{6-n}C_nH_n$ (n=0-6) series upon the replacement of boron atoms by the valence isoelectronic C-H groups. Another motivation is also to detect possible structural transitions in the considered series with the replacement of a boron atom by the C-H group.

COMPUTATIONAL DETAILS

The low-lying isomers of $B_{6-n}C_nH_n$ (n=0-6) series were performed using density functional theory (DFT). For the geometry optimizations, the low-lying isomers (Dinadayalane et al., 2004) of C_6H_6 stoichiometry were first carried out. Then, the initial geometries of other series were typically constructed by substituting one boron atom by C-H group in C_6H_6 stoichiometry. This procedure continues until each C-H group takes up the boron atom. Thus, new isomers and their permutational isomers were obtained for each series.

The singlet and triplet electronic states of all possible structural configurations for considered series were initially optimized by B3LYP (Becke, 1993) and 3-21G level of theory. To increase the reliability of the calculated results, the low-lying isomers for each series were reoptimized at B3LYP/6-311++G** level of theory. To check the stability of optimized structures of all isomers, the frequency calculations were also performed at the same level of theory. All electronic structure calculations and structural visualizations were performed utilizing the Gaussian 09 (Frisch et al., 2009) and Gauss View 5.0.9 (Dennington et al., 2009) programs, respectively.

RESULTS and DISCUSSIONS

In this study, the substitution of B atoms by the C-H groups in the $B_{6-n}C_nH_n$ (n=0-6) series is investigated at B3LYP/6-311++G** level of theory. The three low-lying isomers were shown in Figure 1. In addition, the low-lying isomers and their relative energies (ΔE<40 kcal/mol) were available in Supporting Information (Figure S1). Note that there is no imaginary frequency for optimized structures reported in this study.

B₆ Isomers. According to calculations for singlet (m1) and triplet (m3) ground states, the triplet B_6 structure is the most stable isomer with planar geometry and C_{2h} point group symmetry (see Figure 1). Moreover, it has 2.70 kcal/mol lower energy than the pentagonal pyramidal geometry (second isomer) with singlet state and C_{5v} point group symmetry. The third isomer is very like the first isomer with quasi-planar geometry and C_2 point group symmetry, but it has 9.17 kcal/mol higher energy than the

global minimum. These three isomers were previously reported by Alexandrova et al. (Alexandrova et al., 2003). According to their calculations at B3LYP/6-311+G* level of theory, the second and third isomers have 1.2 and 9.1 kcal/mol higher energy than the global minimum, respectively. Therefore, the results from this current study were reinforced by findings in the literature.

B₅CH Isomers. The global minimum of B_5CH is very like the first isomer of B_6. Here, only difference is the substitution of one B atom by the C-H group. The second isomer with singlet state and C_s point group symmetry has 5.77 kcal/mol higher energy than the most stable isomer. The triplet B_5CH structure is found to be the third isomer, and it has 11.03 kcal/mol higher energy than the global minimum.

B₄C₂H₂ Isomers. The first isomer is clearly reminiscent of the global minimum of B_5CH, and it has a planar geometry with C_{2h} point group symmetry. Here, the second isomer grows from the third isomer of B_5CH. Additionally, the third isomer prefers a linear geometry with D_∞ point group symmetry. The second and third isomers have 12.27 and 14.62 kcal/mol higher energy than the global minimum, respectively.
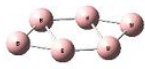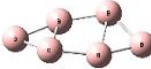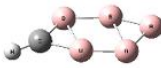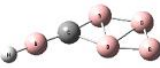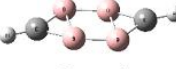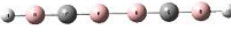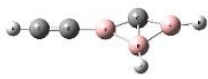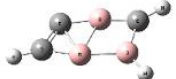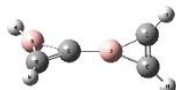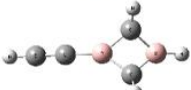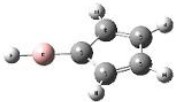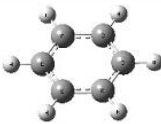

Figure 1. For B₆-nCnHn (n=0-6) series, the three low-lying isomers with relative energies (kcal/mol) at B3LYP/6-311++G** level of theory.

B₃C₃H₃ Isomers. In this series, the global minimum has a different geometry than the previous series. The second isomer grows from the global minimum of the $B_4C_2H_2$. It is also now higher (by 4.57 kcal/mol) energy than the most stable isomer. The third isomer has 4.67 kcal/mol above the most stable

isomer. The second and third isomers were very close to each other as energy. The third isomer of the $B_3C_3H_3$ series, benzene-like structure, also grows from the fifth isomer of the $B_4C_2H_2$ by replacing B atom by the C-H group (see Figure S1, Supporting Information).

$B_2C_4H_4$ Isomers. In this series, the most stable isomer has C_s point group symmetry with singlet electronic ground state, and it has 1.65 kcal/mol lower energy than the second isomer. The second isomer is very like global minimum in the $B_3C_3H_3$ series. The third isomer of this series, benzene-like structure, has also a planar geometry with C_{2v} point group symmetry. It is now only higher (by 2.12 kcal/mol) energy than the global minimum. Obviously, it grows from the three isomers of the $B_3C_3H_3$ by replacing one B atom by the C-H group. In here and subsequent series, there is no structure like the most stable isomer of B_6, B_5CH and $B_4C_2H_2$ series as well as the second isomer of $B_3C_3H_3$ series.

BC_5H_5 Isomers. The lowest-lying isomer of this series is the monoborabenzene structure with planar geometry (C_{2v} point group symmetry). The global minimum, benzene-like structure, is now more stable than the second isomer by 19.60 kcal/mol. Apparently, the substitution of five B atoms by five C-H groups in triplet planar structure (the global minimum of B_6) switched the relative stabilities of benzene-like and other structures. The third isomer has 21.94 kcal/mol above the most stable isomer.

C_6H_6 Isomers. A total of 215 isomers on the potential energy surface for C_6H_6 series were reported by Dinadayalane et al. They were provided that benzene structure is lower in energy than other isomers. In our previous paper, it is also reported as found the most stable isomer with planar D_{6h} point group symmetry.[15] For this reason, the most stable isomer is presented in this study.

To examine the structural stabilities of $B_{6-n}C_nH_n$ (n=0-6) series, the binding energy per atom (E_b) is calculated by taking into account the most stable isomers. The binding energy of a structure is also a measure of its relative stability. E_b is defined as:

$$E_b(B_{6-n}C_nH_n)=[(6-n)E(B)+(n)E(C)+(n)E(H)-E(B_{6-n}C_nH_n)]/(n+6) \qquad (1)$$

where n is from 0 to 6 the cluster-size, $E(B_{6-n}C_nH_n)$ is the cluster energy. $E(B)$, $E(C)$ and $E(H)$ are the energies of atomic boron, carbon and hydrogen, respectively. Figure 2 shows the binding energy per atom as a function of cluster-size. The values were also summarized in Table 1. The E_b increases with the substitution of B atoms by the C-H groups in $B_{6-n}C_nH_n$ (n=0-6) series. The E_b values of $B_2C_4H_4$ and BC_5H_5 series are 0.34 and 0.19 eV lower than that of C_6H_6 (5.55 eV) with 5.21 and 5.36 eV, respectively. However, the stability of B_6 is the lowest with 3.79 eV.

Table 1. Binding energy per atom (E_b), adiabatic ionization potential (AIP), vertical ionization potential (VIP), adiabatic electron affinity (AEA), vertical electron affinity (VEA), vertical detachment energy (VDE) and HOMO-LUMO energy gap (Eg). All values are in eV.

Structure	E_b	AIP	VIP	AEA	VEA	VDE	E_g
B_6	3.79	8.41	9.12	2.26	2.19	2.71	2.26
B_5CH	4.43	8.40	8.59	2.17	2.54	2.85	2.51
$B_4C_2H_2$	4.97	8.87	9.08	0.48	0.86	1.22	4.62
$B_3C_3H_3$	5.10	8.50	8.98	0.59	0.80	1.29	4.40
$B_2C_4H_4$	5.21	8.95	9.70	-0.67	-0.32	0.31	6.72
BC_5H_5	5.36	8.24	8.36	0.09	0.82	1.55	4.35
C_6H_6	5.55	9.13	9.28	-0.60	-0.60	-0.60	6.60

Structural and Electronic Properties of B6-nCnHn (n=0-6) Series upon the Substitution of Boron Atoms by the C-H Groups: A Density Functional Theory Study
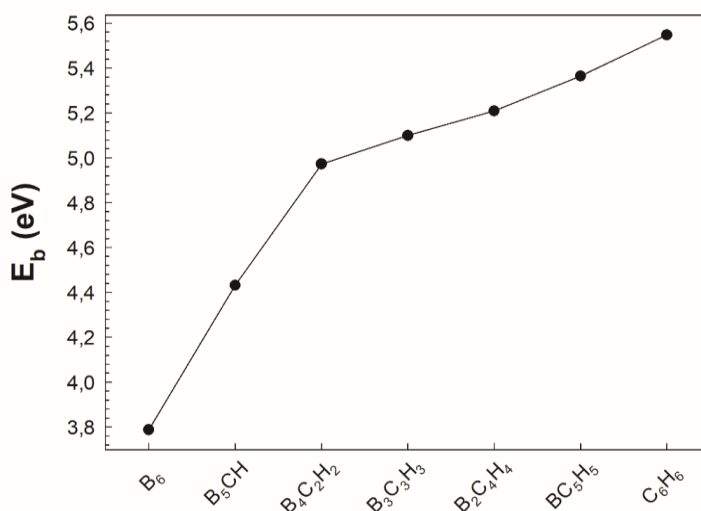
471

Figure 2. The binding energy per atom of $B_{6-n}C_nH_n$ (n=0-6) series.

The capability of clusters to obtain or remove an electron is investigated by calculations of their ionization potentials and electron affinities. To examine the electronic properties of $B_{6-n}C_nH_n$ (n=0-6) series, the adiabatic ionization potential (AIP), vertical ionization potential (VIP), adiabatic electron affinity (AEA), vertical electron affinity (VEA), vertical detachment energy (VDE) and HOMO-LUMO energy gap (E_g) were calculated by considering the most stable isomers. Ionization potentials (IPs) and electron affinities (EAs) are defined as follows:

$$IPs(B_{6-n}C_nH_n)=[E(B_{6-n}C_nH_n)^{cation}]-[E(B_{6-n}C_nH_n)^{neutral}] \tag{2}$$

$$EAs(B_{6-n}C_nH_n)=[E(B_{6-n}C_nH_n)^{neutral}]-[E(B_{6-n}C_nH_n)^{anion}] \tag{3}$$

The ionization potential (IPs) parameters such as AIP and VIP are calculated separately from Equation (2). AIP is the energy difference between cationic and neutral structures at their respective equilibrium geometries. VIP is the energy difference between the ground state of neutral and cationic structures, at optimized geometry of the neutral. The AIP and VIP are drawn in Figure 3 and tabulated Table 1. As seen in Figure 3, the AIP and VIP exhibit even-odd oscillations with maxima for even n. The ionization potentials show that the stability of odd-n series is lower than their neighboring even-n series. Note that VIP values are higher than the AIP values because of orbital relaxation.
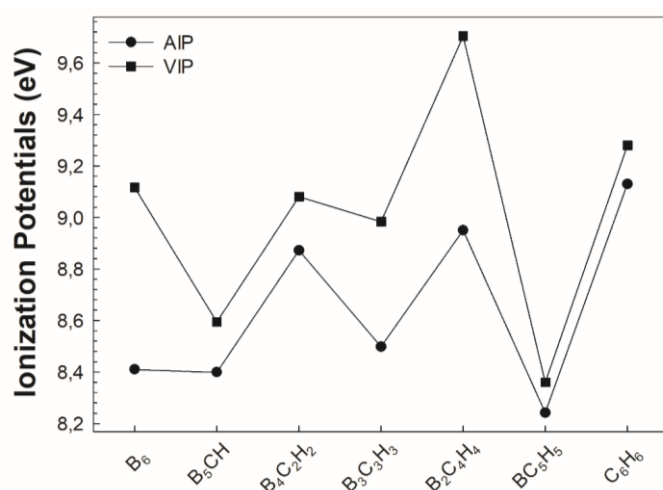
Figure 3. Size dependence of adiabatic ionization potential (AIP) and vertical ionization potential (VIP) for the most stable isomers of the $B_{6-n}C_nH_n$ (n=0-6) series.
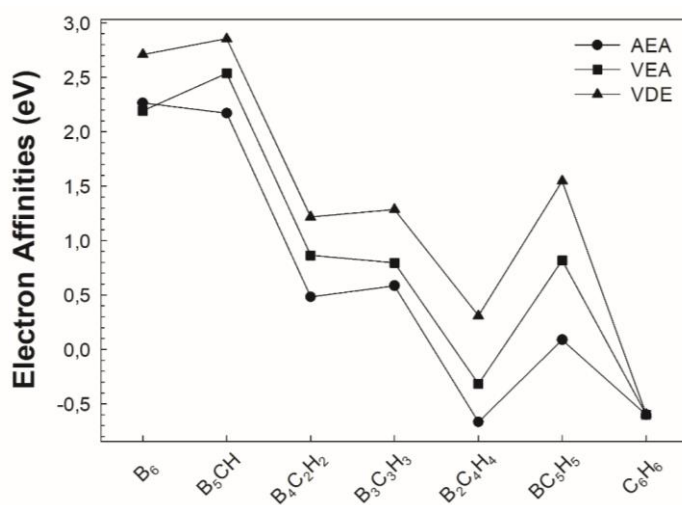
Figure 4. Size dependence of adiabatic electron affinity (AEA), vertical electron affinity (VEA) and vertical detachment energy (VDE) for the most stable isomers of the $B_{6-n}C_nH_n$ (n=0-6) series.

On the other hand, the electron affinities (EAs) parameters such as AEA, VEA and VDE are calculated separately from Equation (3). AEA is the energy difference between anionic and neutral structures at their respective equilibrium geometries. VEA is the energy difference between the ground state of neutral and anionic structures, at optimized geometry of the neutral. VDE is the energy difference between the ground state of neutral and anionic structures, at optimized geometry of the anion. The AEA, VEA and VDE are illustrated in Figure 4 and listed Table 1. The AEA, VEA and VDE decrease generally with the substitution of B atoms by the C-H groups in $B_{6-n}C_nH_n$ (n=0-6) series, and they exhibit even-odd oscillations with maxima for odd n (see in Figure 4).

Figure 5. Variation of the HOMO–LUMO gaps for the most stable isomers of the $B_{6-n}C_nH_n$ (n=0-6) series.

Another way of ensuring the stability criteria is to calculate the difference energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Additionally, the structures must have large HOMO-LUMO energy gap (E_g) and high ionization potential (IP). The E_g is illustrated in Figure 5 and tabulated in the Table 1. As seen in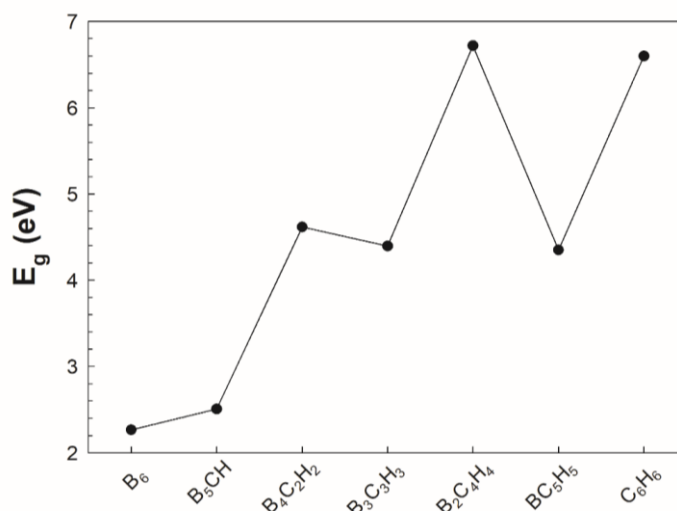 Figure 5, the E_g increases with the substitution of B atoms by the C-H groups, and it exhibits even-odd oscillations with maxima for even n (except n=1). $B_{6-n}C_nH_n$ (n=0-6) series with even-n have larger E_g and higher absolute value of IPs. Therefore, the chemical stabilities of even-n series are stronger than their neighboring odd-n series. It is consistent with the results from Figure 3. Since the most stable isomer of B_6 structure (for n=1) has open shell (triplet state) electronic configuration, its chemical stability is weaker than B_5CH structure (for n=2), which has close shell (singlet state) electronic configuration. Note that the $B_2C_4H_4$ and C_6H_6 series are the most stable among considered series by calculating IPs, EAs and E_g.

The HOMO and LUMO pictures of the $B_{6-n}C_nH_n$ (n=0-6) series are presented in Figure 6. The HOMO and LUMO localizations are found to be nearly symmetric over the most stable isomers.

The natural population analysis (NPA) and electro-static potential (ESP) charge distributions are also investigated in this study. The atomic charge distributions of the B, C and H atoms in the $B_{6-n}C_nH_n$ (n=0-6) series are shown in Figure 7(a-b). The charges on B and H atoms are positive in range of n=1-5, but C atoms are negative. Therefore, charges are transferred from B and H atoms to C atoms. Additionally, all the charge is on the H atoms for C_6H_6 series. Charges are transferred from H to C. The B atom acts generally as an electron donor for $B_{6-n}C_nH_n$ (n=1-5) series, whereas, the C atom acts as an electron acceptor.
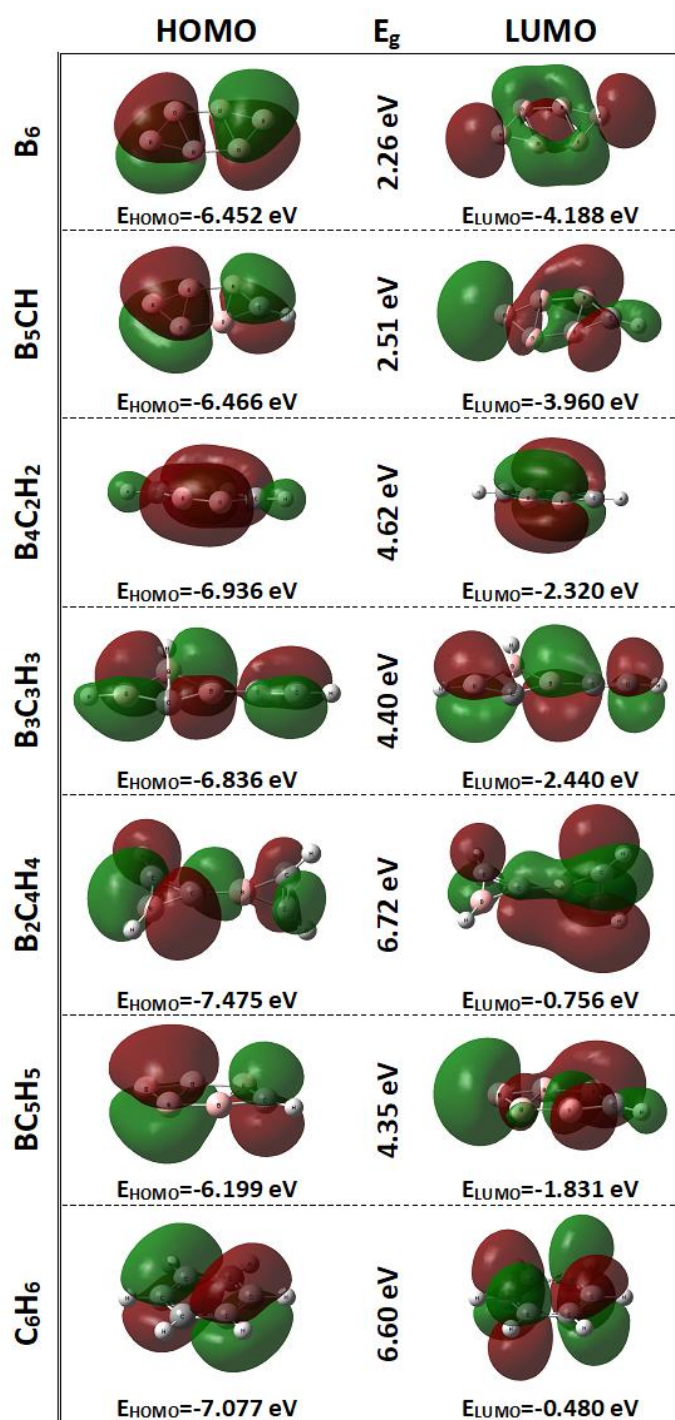
Figure 6. HOMO and LUMO pictures of the $B_{6-n}C_nH_n$ (n=0-6) series. Green and red colors represent the positive and negative isosurfaces for HOMO and LUMO, respectively.

Structural and Electronic Properties of B6-nCnHn (n=0-6) Series upon the Substitution of Boron Atoms by the C-H Groups: A Density Functional Theory Study

475

Table 2. NICS and NICSzz values for benzene and benzene-like structure. All values in ppm.

Distance (Å)	BC_5H_5		C_6H_6	
	NICS	**$NICS_{zz}$**	**NICS**	**$NICS_{zz}$**
0.0	-12.292	-17.978	-8.065	-14.492
0.2	-12.260	-19.009	-8.469	-16.264
0.4	-12.091	-21.501	-9.399	-20.571
0.6	-11.655	-24.125	-10.257	-25.213
0.8	-10.884	-25.715	-10.575	-28.336
1.0	-9.825	-25.808	-10.231	-29.252
1.2	-8.600	-24.579	-9.371	-28.244
1.4	-7.343	-22.494	-8.232	-25.998
1.6	-6.159	-20.017	-7.025	-23.170
1.8	-5.107	-17.487	-5.888	-20.228
2.0	-4.209	-15.105	-4.889	-17.444
2.2	-3.463	-12.970	-4.047	-14.947
2.4	-2.854	-11.110	-3.354	-12.777
2.6	-2.362	-9.519	-2.792	-10.926
2.8	-1.966	-8.172	-2.337	-9.363
3.0	-1.646	-7.037	-1.969	-8.051
3.2	-1.388	-6.082	-1.670	-6.950
3.4	-1.179	-5.279	-1.425	-6.026
3.6	-1.008	-4.602	-1.225	-5.249
3.8	-0.868	-4.029	-1.059	-4.592
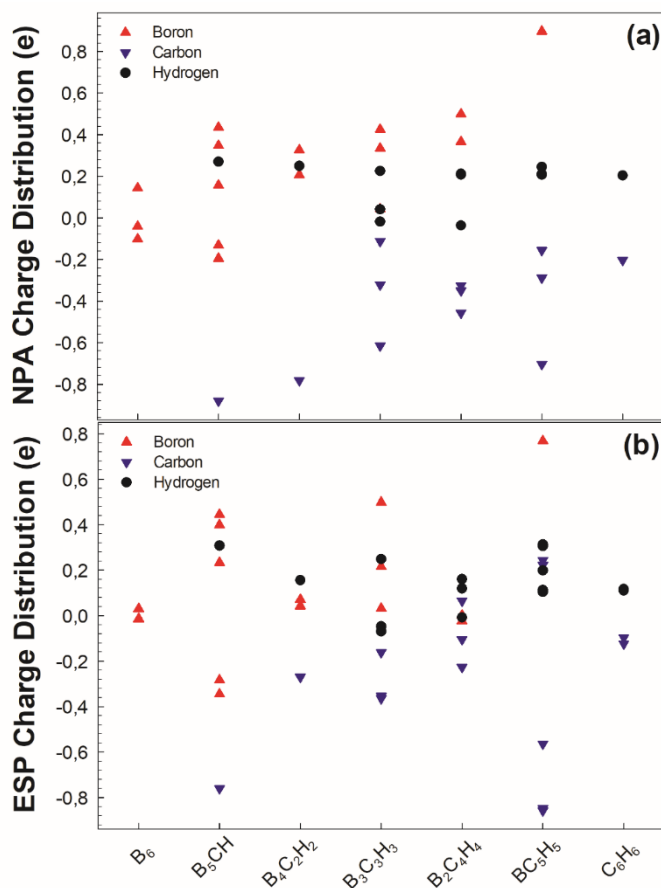
Figure 7. NPA (a) and ESP (b) charge distributions of $B_{6-n}C_nH_n$ (n=0-6) series.

The nucleus independent chemical shift (NICS) analysis is also performed to interpret whether the benzene-like structures are aromatic. In planar structures, chemical shielding or absolute magnetic shielding can be computed at ring centers, and at point above (Schleyer et al., 1996). In this study, the

NICS and $NICS_{zz}$ values calculated for benzene (C_6H_6) and benzene-like (BC_5H_5) structures in range of 0-3.8 Å (at ring centers and at point above) are tabulated in Table 2. According to NICS analyses, the BC_5H_5 structure has very high negative values. This result also indicates that BC_5H_5 structure can be an aromatic structure.

CONCLUSIONS

In this work, the substitution of boron atoms by the valence isoelectronic C-H groups in the $B_{6-n}C_nH_n$ (n=0-6) series is investigated within density functional theory DFT-B3LYP/6-311++G** level of theory. All possible isomers for each series have been searched considering the singlet and triplet electronic ground states. The most stable isomers except B_6 have singlet electronic ground state. According to calculations, the substitution of the B atoms by the C-H groups obviously contributes to strengthen the stability of considered series. The IPs, EAs and E_g results show that the $B_2C_4H_4$ and C_6H_6 series are the most stable among considered series. Additionally, the E_b values of $B_2C_4H_4$ and BC_5H_5 series are 0.34 and 0.19 eV lower than that of C_6H_6 (5.55 eV) with 5.21 and 5.36 eV, respectively. The global minimum of BC_5H_5 structure is a stable planar structure with C_{2v} point group symmetry. According to NICS analysis, the planar BC_5H_5 structure has very high negative values, and thus it can be aromatic as character. In addition, it can qualify to be an aromatic compound as much as the benzene molecule.

Structural stability of compounds allows their presence in nature and afterwards to synthesize them in experiments. Therefore, I hope that this study will help guide future efforts aimed at synthesizing novel compounds based on carboranes and their derivatives.

REFERENCES

Alexandrova AN, Boldyrev AI, Zhai HJ, et al (2003) Structure and bonding in B6(-) and B6: Planarity and antiaromaticity. J Phys Chem A 107:1359–1369. doi: 10.1021/jp0268866

Barth RF, Coderre JA, Vicente MGH, Blue TE (2005) Boron neutron capture therapy of cancer: Current status and future prospects. Clin Cancer Res 11:3987–4002. doi: 10.1158/1078-0432.CCR-05-0035

Becke AD (1993) A new mixing of hatree-fock and local density functional theories. J Chem Phys 98:1372–1377. doi: 10.1063/1.464304

Dennington R, Keith TA, Millam JM (2009) GaussView 5.0.9

Dinadayalane TC, Priyakumar UD, Sastry GN (2004) Exploration of C6H6 potential energy surface: A computational effort to unravel the relative stabilities and synthetic feasibility of new benzene isomers. J Phys Chem A 108:11433–11448. doi: 10.1021/jp0467696

El-Zaria ME, Arii H, Nakamura H (2011) m-Carborane-Based Chiral NBN Pincer-Metal Complexes: Synthesis, Structure, and Application in Asymmetric Catalysis. Inorg Chem 50:4149–4161. doi: 10.1021/ic2002095

Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision B.01.

Galeev TR, Boldyrev AI (2011) Planarity takes over in the CxHxP6-x (x=0-6) series at x=4. Phys Chem Chem Phys 13:20549–20556 . doi: 10.1039/c1cp21959f

Grimes RN (2013) Synthesis and serendipity in boron chemistry: A 50 year perspective. J Organomet Chem 747:4–15. doi: 10.1016/j.jorganchem.2013.04.018

Structural and Electronic Properties of B6-nCnHn (n=0-6) Series upon the Substitution of Boron Atoms by the C-H Groups: A Density Functional Theory Study

477

Ivanov AS, Boldyrev AI (2012) Si6-nCnH6 (n=0-6) series: when do silabenzenes become planar and global minima? J Phys Chem A 116:9591–9598. doi: 10.1021/jp307722q

Ivanov AS, Bozhenko K V, Boldyrev AI (2012) Peculiar Transformations in the CxHxP4-x (x=0-4) Series. J Chem Theory Comput 8:135–140. doi: 10.1021/ct200727z

Jemmis ED, Balakrishnarajan MM, Pancharatna PD (2002) Electronic requirements for macropolyhedral boranes. Chem Rev 102:93–144. doi: 10.1021/cr990356x

Jemmis ED, Kiran B, Coffey D (1997) Ab initio studies on disubstituted closo-icosahedral heteroboranes, X2B10H10 (X=CH, SiH, N, P, and Sb). Chem Berichte-Recueil 130:1147–1150. doi: 10.1002/cber.19971300818

Jiang W, Chizhevsky IT, Mortimer MD, et al (1996) Carboracycles: Macrocyclic compounds composed of carborane icosahedra linked by organic bridging groups. Inorg Chem 35:5417–5426. doi: 10.1021/ic960354k

Li X (2017) Structural, electronic and spectral properties of carborane-containing boron dipyrromethenes (BODIPYs): A first-principles study. Spectrochim Acta Part A-Molecular Biomol Spectrosc 185:149–154. doi: 10.1016/j.saa.2017.05.047

McLemore DK, Dixon DA, Strauss SH (1999) Density functional theory and fluorocarboranes I. Trends in B-H and B-F distances and dissociation energies for CB11H12-nFn- anions (n=0, 1, 6, 11). Inorganica Chim Acta 294:193–199. doi: 10.1016/S0020-1693(99)00285-6

Muz I, Atis M (2016) Structural transformations in the carborane series: CnB6-nH6 (n=0-6) upon substitution of boron by carbon. Inorganica Chim Acta 453:626–632. doi: 10.1016/j.ica.2016.09.035

Schleyer P V, Maerker C, Dransfeld A, et al (1996) Nucleus-independent chemical shifts: A simple and efficient aromaticity probe. J Am Chem Soc 118:6317–6318. doi: 10.1021/ja960582d

Schleyer P V, Najafian K (1998) Stability and three-dimensional aromaticity of closo-monocarbaborane anions, CBn-1Hn-, and closo-dicarboranes, C2Bn-2Hn. Inorg Chem 37:3454–3470. doi: 10.1021/ic980110v

Scholz M, Hey-Hawkins E (2011) Carbaboranes as Pharmacophores: Properties, Synthesis, and Application Strategies. Chem Rev 111:7035–7062 . doi: 10.1021/cr200038x

Smith K (1990) Synthetic Chemistry-Boron Molecular Gymnastics. Nature 348:115–116. doi: 10.1038/348115b0

Soloway AH, Werner Tjarks, Beverly A. Barnum, et al (1998) The Chemistry of Neutron Capture Therapy. Chem Rev 98:1515–1562. doi: 10.1021/cr941195u

Spokoyny A ~M., Machan C ~W., Clingerman D ~J., et al (2011) A coordination chemistry dichotomy for icosahedral carborane-based ligands. Nat Chem 3:590–596. doi: 10.1038/nchem.1088

Takano K, Izuho M, Hosoya H (1992) Abinitio Molecular-Orbital Study of Electronic-Structures of Closo-Borane Anions Bnhn2- and Closo-Carboranes C2bn-2hn. J Phys Chem 96:6962–6969. doi: 10.1021/j100196a021

Valliant JF, Guenther KJ, King AS, et al (2002) The medicinal chemistry of carboranes. Coord Chem Rev 232:173–230. doi: 10.1016/S0010-8545(02)00087-5

Westerhausen M, Guckel C, Schneiderbauer S, et al (2001) The first barium-carborate complex: Synthesis and structural investigation. Angew Chemie-International Ed 40:1902–1904 . doi: 10.1002/1521-3773(20010518)40:10<1902::AID-ANIE1902>3.0.CO;2-V

Williams RE (1976) Coordination Number Pattern Recognition Theory of Carborane Structures*. In: Emeléus HJ, Sharpe AG (eds). Academic Press, pp 67–142