



Research paper

Structural transformations in the carborane series: $C_nB_{6-n}H_6$ ($n = 0-6$) upon substitution of boron by carbonİskender Muz^{a,*}, Murat Atiş^b^a Faculty of Education, Department of Science Education, Nevsehir Haci Bektas Veli University, 50300 Nevsehir, Turkey^b Institute for Computational Engineering and Sciences, The University of Texas Austin, Austin, TX 78712, USA

ARTICLE INFO

Article history:

Received 22 June 2016

Received in revised form 9 September 2016

Accepted 18 September 2016

Available online 20 September 2016

Keywords:

Carboranes

Stochastic search

Carbon doping

Stability

ABSTRACT

In this paper we examined a structural transition from three-dimensional to two-dimensional in the $C_nB_{6-n}H_6$ ($n = 0-6$) series. The searches for all the isomers of clusters were performed using the stochastic search algorithm at the B3LYP/6-31G level of theory. Subsequent geometry optimizations at the hybrid density functional B3LYP/6-311++G** level of theory along with single-point CCSD(T) calculations were carried out to estimate relative energies. We found that 3D-2D transition occurs at $n = 5$ ($C_5B_1H_6$). Moreover, the stability of clusters is discussed on the basis of the binding energy per atom, second-order energy difference, adiabatic ionization potential, HOMO-LUMO energy gap and polarizability. Based on the simultaneous criteria of high binding energy, high band gap, high adiabatic ionization potential and low polarizability, it is found that $C_2B_4H_6$ cluster has a higher stability.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Carboranes refers to any member of a class of organometallic compounds composed of carbon, boron and hydrogen. Carbon and boron are the most refractory materials owing to their strong chemical bonding capacities as well as the most versatile element being capable to form various stable compounds with hydrogen. The hydrogenated carbon-boron compounds can serve as useful and versatile starting materials for the generation of novel carboranes. Because of unique properties of hydrogenated carbon boron compounds, determining physical and chemical properties of carborane clusters can be also interesting for science and engineering. Carboranes have used widely in chemical engineering and petrochemistry as superacids [1], in materials science and crystallography [2] as building blocks, in organometallic and coordination chemistry as ligands, in medicine as a source of boron [3,4] and in medicinal chemistry as pharmacophores [5].

Recently, only a few types of carbon-containing compounds such as silabenzene and phosphabenzene were studied due to high resonance stability, nonclassical bonding, aromaticity and the benzene-like reactivity [6–8]. These studies have been concentrated on the substitution of carbon with materials such as silicon and phosphorus. It is concluded that a two-dimensional/three-dimensional

(2D-3D) transition was observed in series of SiC_5H_6 and $C_4H_6P_2$ where benzene-like structures become significantly more stable than the other structures. Moreover, some studies have shown that substitution of carbon atoms for boron atoms in boron-carbon mixed clusters (boron carbides) leads to a structural transition [9,10]. For more than half a century, various carborane compounds have been studied both theoretically and experimentally [11–19]. However, there are no reports on the structural transition of carboranes and their derivatives. Since the substitution of a carbon atom for a boron atom in carborane clusters provides one additional electron [20], it could induce a significant change in structural and electronic properties of the system. On the basis of these preliminary data, we plan to investigate the transition from 3D to 2D structures in $C_nB_{6-n}H_6$ ($n = 0-6$) clusters and to carry out the analyses of energetic and structural stabilities of the global minimums of these clusters using the stochastic search method [21].

2. Computational details

We at first carried out all possible isomer searches in the $C_nB_{6-n}H_6$ ($n = 0-6$) series with n ranging from 0 to 6, using the stochastic search method [21]. Briefly, the stochastic search method subjects randomly moving all the atoms of a structure placed to origin as an initial geometry in which case each atom is gradually kicked and new structure is optimized to the nearest local minimum. In this study, the stochastic search calculations

* Corresponding author.

E-mail address: iskender.muz@nevsehir.edu.tr (İ. Muz).

were performed using the B3LYP functional in the 6-31G basis set [22]. After low-lying isomers were sorted up to 100 kcal/mol as regards the global minimum structure, they were re-optimized with follow up frequency calculations at the B3LYP/6-311++G** level of theory. The subsequent single point calculations were performed using the CCSD(T) method in the 6-311++G**, aug-cc-pVDZ and aug-cc-pVTZ basis sets [23]. We used to frozen-core approximation that is satisfy to enough accuracy for many applications [24]. All calculations were performed using the Gaussian 09 software package [25]. Additionally, MOLDEN 5.2 [26] program was used for the structure visualization.

3. Results and discussion

In this study, we investigated a structural transition in the $C_nB_{6-n}H_6$ ($n = 0-6$) series upon replacing boron atoms by carbon atoms. All studied isomers are calculated at B3LYP/6-311++G**, CCSD(T)/6-311++G**, CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels of theory and are ordered according to energies at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G** level of theory. To ensure whether or not all the calculated structures reside in local minima on the potential energy surface, the vibrational frequencies of optimized geometries are also calculated. All calculations are performed considering the singlet/triplet spin states (for clusters with even number of atoms) and doublet/quadruplet spin states (for clusters with odd number of atoms). The low-lying isomer geometries and their relative energies ($\Delta E < 50-100$ kcal/mol) are presented in Supporting Information (Figs. S1–S7). However, only some selected 3D and benzene-like structure that could show 3D to 2D transition are presented in Fig. 1.

B₆H₆ isomers. Five isomers for B₆H₆ stoichiometry: I.1, I.4, I.6, I.37 and I.46 are given in Fig. 1(a). The lowest-lying isomer of B₆H₆ cluster is structure I.1, which is very analog to benzvalene structure and it has 5.8 kcal/mol lower energy than the fourth isomer with quasi-planar form. The sixth lowest isomer (structure I.6) has octahedral geometry with the most stable isomer lying 10.6 kcal/mol above the global minimum. The tetracyclic-type structure I.37 is also 34.9 kcal/mol higher than the most stable isomer. The benzene-like planar structure I.46 is not a minimum but is a three-order saddle point. Geometry optimization along the imaginary frequency mode leads to distorted different isomer. The D_{2h} benzene-like planar structure is 129.9 kcal/mol higher in energy than the first isomer.

CB₅H₆ isomers. Five isomers for CB₅H₆ stoichiometry: II.1, II.2, II.3, II.5 and II.41 are presented in Fig. 1(b). The most stable isomer of CB₅H₆ cluster is structure II.1 with octahedral geometry (3D) and it is very similar to the sixth lowest isomer of B₆H₆ cluster. The only difference is that one B is substituted by the C atom. Benzvalene-like structure II.2, analog of which has been global minima in B₆H₆ stoichiometry, is 27.0 kcal/mol higher energy than the first isomer. Structures II.3 and II.5 have 3D form with the first isomer lying 28.2 kcal/mol and 29.4 kcal/mol above the global minimum, respectively. Additionally, the benzene-like nonplanar structure II.41 is now a local minimum and is 72.2 kcal/mol higher than the global minimum.

C₂B₄H₆ isomers. Five isomers for C₂B₄H₆ stoichiometry: III.1, III.3, III.4, III.5 and III.36 are shown in Fig. 1(c). The first isomer of C₂B₄H₆ cluster (III.1) is clearly reminiscent of the most stable isomer of CB₅H₆ cluster with octahedral geometry (3D), where one B atom is replaced by the C atom. The second isomer of C₂B₄H₆ cluster (1,2-C₂B₄H₆), structure III.2 (Fig. S3, Supporting Information), is 8.3 kcal/mol (at CCSD(T)/aug-cc-pVTZ level) higher energy than the most stable isomer (1,6-C₂B₄H₆). Moreover, it is a permutational isomer of the global minimum with one carbon atom located left side the other carbon atom. On the other hand the first

carbaborane isomers, which had the general formula C₂B₄H₆, were synthesised in 1963 [27]. 1,2 and 1,6-C₂B₄H₆ structures as known dicarba-closo-hexaboran have attracted interest for decades [12,15,17–19]. The first and second stable isomers presented in this paper (Fig. S3) are in excellent agreement with structures (as 1,6-C₂B₄H₆ or sym-C₂B₄H₆ and 1,2-C₂B₄H₆ or unsym-C₂B₄H₆ isomers) reported by these studies. For example, Ababsa et al. [17] obtained these two isomers and calculated the energy difference between the isomers to be 9.2 kcal/mol at the B3LYP/6-311++G (d,p) level of theory. In this study, the energy difference is found to be 8.7 kcal/mol with the same level of theory, as seen in Fig. S3 (Supporting Information). Therefore, our results are in good agreement with previously reported the experimental and theoretical datas. Structures III.4 and III.5 have 3D form with the first isomer lying 31.5 kcal/mol and 41.1 kcal/mol above the most stable isomer, respectively. Moreover, the benzene-like nonplanar structure III.36 (1,4-C₂B₄H₆) is 79.3 kcal/mol higher in energy than the global minimum.

C₃B₃H₆ isomers. In this study we weren't detect the isomer with octahedral structure, which are analogous to structures I.6, II.1 and III.1, in range of $n = 3-6$ for $C_nB_{6-n}H_6$ series. Therefore, in this and subsequent series (except C₆H₆), we only presented four isomers. Four isomers for C₃B₃H₆ stoichiometry: IV.1, IV.2, IV.12, IV.24 are given in Fig. 1(d). Accordingly, the lowest-lying isomer of C₃B₃H₆ cluster is structure IV.1 with pentagonal pyramid geometry (3D). The second lowest isomer of C₃B₃H₆ cluster is structure IV.2 with tetracyclic-type geometry, being just 4.7 kcal/mol higher in energy. Structure IV.12 in C₃B₃H₆ cluster is reminiscent of the fourth isomer of C₂B₄H₆ cluster with one B is substituted by the C atom, and it has 41.2 kcal/mol lower energy than the global minimum structure. Additionally, the benzene-like nonplanar structure IV.24 (1,2,3-C₃B₃H₆) is 50.2 kcal/mol higher in energy than the global minimum.

C₄B₂H₆ isomers. Four isomers for C₄B₂H₆ stoichiometry: V.1, V.4, V.15 and V.20 are given in Fig. 1(e). The most stable isomer of C₄B₂H₆ cluster is structure V.1 with quasi-planar geometry (3D). It is reminiscent of the first isomer of C₃B₃H₆ cluster. However, the benzene-like structure V.4 (1,2,4,5-C₄B₂H₆) is a close-lying (28.0 kcal/mol) to the second lowest isomer of this series. Moreover, it is now lower in energy than benzvalene structure. Additionally, the tetracyclic-type structure (V.15) and benzvalene structure (V.20) are 47.3 kcal/mol and 76.6 kcal/mol higher in energy than the global minimum, respectively.

C₅BH₆ isomers. Four isomers for C₅BH₆ stoichiometry: VI.1, VI.10, VI.21 and VI.22 are given in Fig. 1(f). The lowest-lying isomer of C₅BH₆ cluster is structure VI.1 with planar geometry (2D). According to our systematic computational study, the 3D to 2D transition occurs in C₅BH₆ clusters. The benzvalene structure VI.21 is higher in energy than the global minimum by 53.7 kcal/mol, but it is now lower in energy than tetracyclic-type structure. As regards our results, it seems that the 3D-2D transition occurs only at $n = 5$, which benzene-like planar structure (2D) becomes much more stable than the 3D structures.

C₆H₆ isomers. Dinadayalane et al. [28] proposed that a total of 215 isomers with C₆H₆ stoichiometry were located on the potential energy surface. Thus, they were provided the most exhaustive account of relative stabilities of C₆H₆ stoichiometry. In this study, we report three isomers of C₆H₆ (as benzene, benzvalene structure and tetracyclic-type structure) in Fig. 1(g). The benzene structure for C₆H₆ stoichiometry are found to be lower in energy than all the other isomers, as reported literature. As regards our calculations, the benzvalene structure (VII.2) is lower in energy than the tetracyclic-type structure (VII.3). Additionally, the benzvalene structure (VI.2) and tetracyclic-type structure (VII.3) are analogous to structures I.1, II.2, III.4, IV.12, V.20, VI.21 and I.3, II.4, III.7, IV.2, V.15, VI.22 in the $C_nB_{6-n}H_6$ series, respectively. The relative

Download English Version:

<https://daneshyari.com/en/article/7751068>

Download Persian Version:

<https://daneshyari.com/article/7751068>

[Daneshyari.com](https://daneshyari.com)