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An investigation of hydrogen bonded neutral B_4H_n ($n = 1$–11) and anionic $B_4H_{11}^{(-1)}$ clusters: Density functional study

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Abstract

In this study, detailed analysis of the structural stability of hydrogen bonded four-atom boron clusters within the framework of density functional theory (DFT) is presented. Effects of the number of hydrogen atoms on the structural stability of B_4, binding energy of the clusters, and also on the boron–hydrogen binding energy are investigated. Attention is also paid to the determination of energetically the most stable geometries of B_4H_n ($n = 1$–11) boron hydrides, and to their isomers. The lower-lying electronic states of the B_4H_n structures are investigated. In addition natural electron configurations of the most stable clusters and charge transfer between the atoms in the cluster are also analyzed. Furthermore, the stability of anionic form of $B_4H_{11}^{(-1)}$ cluster is examined.

Keywords: Boron; Hydrogen storage; Boron hydrides; Density functional calculations; Cluster compounds

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1. Introduction

Study of small clusters is an active area of research in physics and chemistry because of their differences from their bulk counterparts [1]. Geometrical arrangements and electronic properties of small clusters are significantly different from their bulk properties, which can be changed further by mixing the clusters with other species [2,3]. Due to their practical applications in different fields rapidly increasing interest has prompted for further investigation of their unknown physical and chemical behaviors and properties, and for clarifying their growth and formation mechanisms.

The boron forms ring structures with electron-donor atoms, and can link three or more atoms due to hybridization of the valence s^2p^1 electrons to sp^2 and to different levels of electron deficiency forms. This yields large coordination numbers, short covalent radius, and strong directed chemical bonds. The compositions and structures of metal borides are exceedingly varied and range from metal-rich to boron-rich compounds. These materials, due to their unique solid-state architectures and physical properties, are attractive to modern technology. Therefore, the ground-state structures of the borides and boron hydride series have been actively studied [2,4–13]. Because of the consideration of hydrogen as an ideal energy carrier the binary boron–hydrogen compounds, or boranes, are at the core of hydrogen storage [9], which is an extremely rich area of boron-based cluster chemistry. Some of the typical studies are for instance; Quong et al.[10] investigated boron hydride analogues of fullerenes, particularly focusing on B_nH_n for $n = 4$, 12, 32, and 60 by using electronic-structure method based upon the local-density-fuctional approximation (LDA). Minyaev et al. [11] studied structure and stability of closo-hexaborane by MP2(full)/6-311+G(d, p) level of theory and the density functional (B3LYP/6-311+G(d, p)) method. By using the B3LYP/6-31+G* basis set and the higher level of DFT, McKee et al. [12] have also

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investigated hypercloso boron hydrides, B_nH_n, for $n = 5$–13, 16, 19, and 22. Additionally, in a recent work of Tian [13], results of ab initio and electron propagator theory studies of several neutral and cationic boron hydrides (BH_3, B_2H_6, B_3H_7, B_4H_{10}, B_5H_9, and B_5H_{11}) for predicting their geometrical, energetical, and vibrational properties were reported. These studies show that the theoretical quantum mechanical methods are reliable for describing the intermolecular interactions.

In this work, hydrogen bonded boron complexes are reported. We have focused on the detailed analysis of the isomers of neutral B_4H_n ($n = 1$–11) clusters to understand their electronic properties as well as the geometrical structures, stabilities, growth paths, and the variations of the binding energies as n (number of hydrogen atoms) increases. The natural bond orbital (NBO) analysis [14] shows that the B_4H_n clusters prefer different levels of hybridization with different n values. Furthermore small amount of charge transfers are observed among the atoms in the clusters. Fragmentation of the complex is observed when $n = 11$ while distortions in the rhombic shape of the B_4 starts to occur at the $n = 2$. Additionally, the anion, $B_4H_{11}^{(-1)}$, is studied to test the ability of complex to stay together when the number of electrons in the complex is increased by one. These objectives show that our present work is different than above mentioned literatures, and contains original parts.

2. Methodology

All calculations were carried out by solving the Kohn–Sham equations in the DFT [15] framework. We have employed generalized gradient approximations (GGA) using the functionals of Becke's three-parameter hybrid exchange functional [16] and the Lee–Yang–Parr (LYP) non-local correlation functional [17]. In the present study, 6-311++G(d, p) basis set is employed in order to optimize the geometries and calculate all the physical quantities. For these calculations we have followed the same procedure as in Ref. [18] (for B_2–B_{12} clusters). All computations were carried out using the Gaussian-03 [19] installed on our parallel computing laboratory. Single point (SP) energy calculations were also performed on the fully optimized geometries at the same level of theory. From these data the total binding energy of the cluster is calculated from,

$$E_b[B_4H_n] = -E_{tot}[B_4H_n] + 4E[B] + nE[H] \tag{1}$$

in which the $-E[B]$ (671.105 eV) and $-E[H]$ (13.667 eV) are the energies of single boron and single hydrogen atoms with the zero-point-energy (ZPE) corrections, respectively. One may define the total B–H binding energy in the cluster as a function of n as

$$E_b\{[B_4][H_n]\} = -E_{sp}[B_4H_n] + E_{sp}[B_4] + E_{sp}[H_n] \tag{2}$$

where the $E_{sp}[B_4]$ and $E_{sp}[H_n]$ are the SP energies of the four-atom boron of the optimized complex (without the hydrogen atoms), and that of the n-atom hydrogen (without the boron atoms) configuration in the optimized cluster, respectively. The second finite difference, the stability function of the total energy of the optimized clusters, is calculated:

$$\Delta_2 E = E_{tot}[B_4H_{n+1}] + E_{tot}[B_4H_{n-1}] - 2E_{tot}[B_4H_n] \tag{3}$$

as a function of the number of hydrogen atoms. To investigate the structural properties of the clusters, the mean values of the distances of B and H atoms from the center of mass (c.m.) of the B_4 in the optimized isomers for all the complexes are calculated from

$$r_i = \left|\vec{R}_i - \vec{R}_{c.m.}\right|, \quad \vec{R}_{c.m.} = \frac{1}{4}\sum_{i=1}^{4}\vec{R}_i \tag{4}$$

in which the $\vec{R}_i$ being the position of the ith atom, and the $\vec{R}_{c.m.}$ being the position vector of the c.m. of the B_4.

3. Results and discussion

The molecular structures of B_4H_1–B_4H_{11} binary hydrides with their several isomers are depicted in Figs. 1–5 respectively. Detailed analysis has been carried out for the lower-lying electronic states: such as singlet, doublet, triplet, quartet, quintet, and hexad states of the B_4H_n. From this analysis it is observed that the most stable configurations dominantly are from the singlet and doublet states. We have reported here only several lower-lying electronic states, which yield energetically lower isomers (different electronic states which yield energetically higher isomers are not presented). In the figures, as we will discuss, the isomers are ordered with respect to their total energies (from the most to the least stable forms) and their corresponding multiplicities are given below the figures.

The most stable structure of the B_4H_1 borane has a planar configuration as shown in the Fig. 1 (isomer I). Distance between the hydrogen and its neighboring boron is 1.18 Å. The other boron atoms are arranged at 1.55, 1.60, and 1.69 Å apart from each other. These distances, in the rhombic form of the B_4 cluster without any hydrogen, are 1.52 and 1.88 Å at the B3LYP/6-311++G(d, p) level of calculation [18].

Distance between the two boron atoms in B_2 for the triplet state is 1.57 Å with the same level of calculation. The experimental value is 1.59 Å [20]. The B_3 (equilateral triangle) has 1.55 Å distance between the atoms for the doublet state. As seen in Fig. 1, hydrogen bonding with one boron atom is more stable than bonding of the hydrogen with two boron atoms. The other isomers of this putative hydride are 2.531 and 2.544 eV above the energy of the most stable one, respectively. For all these three isomers the B_4 keeps its rhombic shape in the complexes. The mean values of the B–B distances, for the three isomers, are 1.598, 1.618, and 1.620 Å, respectively. The smallest boron–hydrogen (B–H) bond lengths in isomers II and III are 1.44 and 1.42 Å, respectively, which are longer than that of the first isomer. The distance of B–H dimer is