ATLANTIS PRESS

Advances in Engineering Research, volume 120

International Forum on Energy, Environment Science and Materials (IFEESM 2017)

Structures and bonding of anionic B_7Cl^- cluster

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Keywords: density functional theory (DFT); boron cluster; structure

Abstract. Ab initio molecular orbital theory and density functional theory have been applied to investigate B_7Cl^- cluster. It is found that almost an inversion in stability occurs upon addition of one Cl to B_7^- cluster. Two low-lying planar(C_s,$^2A'$) structures are the lower energy minima, and the quasi-planar geometry (C_s, $^2A''$) exhibit the next stability. Natural bond orbital (NBO) analysis show that the B_7^- unit in B_7Cl^- is different from the pure B_7^-, providing a viable possibility to flattening the distorted pentagonal bipyramid $B_7Cl_7^-$ structure by a successive stripping of Cl.

Introduction

Boron compounds have attracted great interest because of their wide applications and unique physiochemical properties [1-3]. It is long known that $B_nX_n^{2-}$ (n = 6−12, X = H, halogen) in large scale technically employed Lewis acids, and exhibit three-dimensional (3D) structures. It was supposed that the $B_nX_n^-$ species should also form deltahedral geometries similar to the doubly charged anions. However, the recent joint experimental and computational investigations have demonstrated that B_n^-(n = 3-30, 35, 36) anionic clusters favor planar or quasi-planar (2D) structures [refer 4 and references therein], in contrast to 3D bulk phase. Due to electron deficiency, boron has a strong propensity to form multicenter bonds, which renders aromaticity or antiaromaticity to the systems [5–7]. The 2D B_{36}, B_{35}^- borophenes [5, 8], and a 3D cage-like $B_{40}^{-/0}$ and chiral B_{39}^- borospherenes [9, 10] have been observed recently, extending the analogy between boron and carbon, and uncovering an interesting 2D–3D structural evolution in boron clusters[11, 12]. It is well accepted that the doped atoms can dramatically affect structures and properties of pure clusters. For the non-metal monovalent dopants of $B_n^{0/-}$, Bai and Li [13] reported a systematic investigation on the effect of hydrogenation of $B_{12}^{0/-}$ clusters and found that there exists a 2D−3D transition between n = 3 and 4 in $B_{12}H_n^{0/-}$(n = 1−6), Li et al.[14] reported systematic study of $B_nH_2^{0/-}$ (n = 3-12) even electron systems. Li et al. [15]in a joint experimental and theoretical study of the $B_nH_2^-$ clusters for n = 8-12 have demonstrated that they have planar ladder structures. They stated that the boron dihydride clusters are similar to conjugated alkenes. Olson and Boldyrev also reported studies of the $B_6H_n^-$(n = 2−4) clusters[16]. Alexandrova et al. computationally showed that $B_7H_2^{0/-}$ are planar[17].

The B_7^- cluster is known to be planar or quasi-planar[18], while $B_7X_7^-$ is a distorted pentagonal bipyramid 3D structure. Thus, one should expect that the 2D−3D transition should occur at some degree of halogenation along the $B_7X_n^-$ series. In this article, we show the preliminary results of investigation: the geometries, stability, and bonding of halogen-doped B_7Cl^- cluster.

Computional methods

The B3LYP and B3PW91 schemes of density functional theory (DFT) and ab initio molecular orbital theory (MP2) combining with the 6-311+G(d) basis sets were selected to perform the optimization of geometries and the calculatations of the total energies and vibrational frequencies. The natureal bond

orbital (NBO) analysis was carried out at the B3LYP/6-311+G* level. All calculations were performed using GAUSSIAN03 package programs [19].

Results and discussion

Fig. 1 sketches the relevant comformations of B_7Cl^- cluster at the B3LYP, B3PW9, and MP2 levels using 6-311+G(d) basis sets. The bonding distances, NBO charges and Wiberg bond indices (B3LYP level) between adjacent atoms were also listed.

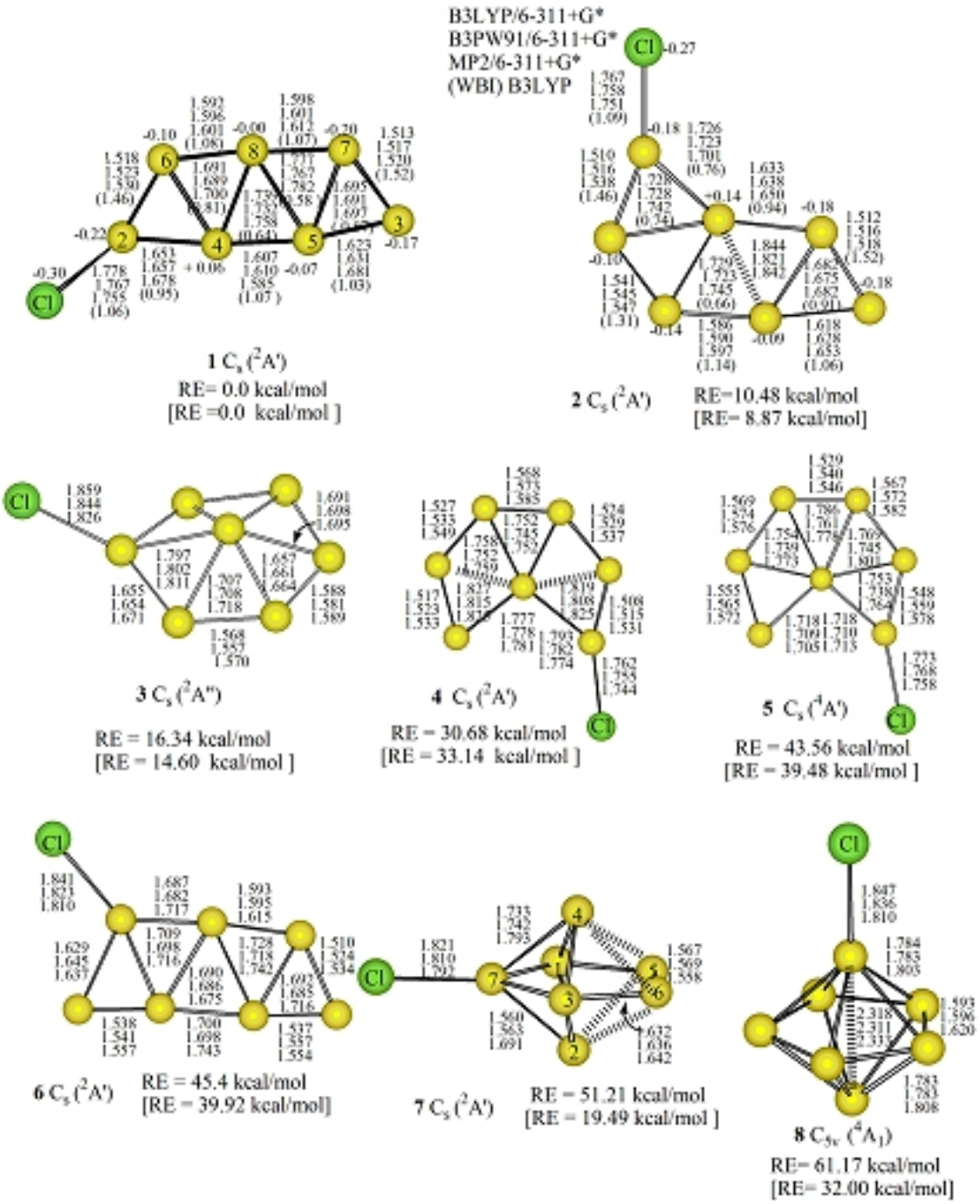

Fig.1. Low-energy isomers (1-8) of B_7Cl^- cluster and WBIs (B3LYP/6-311+G*) (relative energie of B3LYP and MP2 (in square brackets) methods)

Using the computation scheme described above, a number of low-lying isomers have been explored and the lowest-energy structures for B7Cl- clusters is determined. In contrast to the bare B_7^-,

the planar structure (**1** in Fig. 1) is the global minimum of B_7Cl^-; it originates from the planar bare B_7^- cluster (the third stability) with Cl atom bonded to an end boron atom of the cluster, being in agreement with the results of the previous investigations for similar species. The average peripheral B–B bond lengths is about 1.57 Å, and B–Cl bond length of 1.78 Å, consistent with the experimental results [20]. NBO analysis indicate that there are 3c–2e or multi-centered bonds in its structure. The WBI of the B-B bonds are between 1.52 (B3–B7, etc.), 1.03 (B3–B5, etc.), and 0.95 (B3–B5, etc.), and WBI of the B-Cl bond is 1.06, which show the delocalization of the electrons of ring. The predicted vertical detachment energy (VDE), binding energy(to B_7^- + Cl), and HOMO-LUMO gap are 3.8, 4.8, and 3.41 eV respectively at the B3LYP/6-311+G* level. The NBO analysis show the natural charge of Cl is -0.19, show the higher electronegativity Cl attracts the electrons and induce shift of electron clouds. Both the global minimum structure and the next lowest isomer for B_7Cl^- have different planar structures (**1** and **2** in Fig. 1). The second stability structure (**2** in Fig. 1) has an planar B_6^- kernel with one B-Cl (iso-electronic with CO) bridge-connected to two boron atoms. The next quasi-planar structure (**3** in Fig. 1) may be Cl bonded on to one boron atom of the peripheral of the global $B_7^-(C_{6v},{}^3A_1)$ or the second $B_7^-(C_{2v},{}^1A_1)$, and lies energetically higher than the global planar by 16.3 or 14.6 kcal/mol at B3LYP/6-311+G* or MP2/6-311+G*level. Other isomers include typical planar and 3D structures (**4-6** and **7, 8** in Fig. 1), less stability than the global minimum by 30.7-61.2 kcal/mol with B3LYP method, and 19.5-39.9 kcal/mol with MP2 method, whereas the stability orders are slightly different, as DFT-B3LYP computes electron correlation via general functionals of the electron density, while MP2 therory adds higher excitations to Hartree-Fock theory as a non-iterative correlation.

Conclusions

In this work, the effection of chlorination on the relative stability of the low-lying species of B_7^- was investigated theoretically. The previous studies showed that the bare B_7^- has a doubly aromatic $C_{6v}({}^3A_1)$ quasi-planar wheel-like triplet global minimum, a low-lying quasi-planar $C_{2v}({}^1A_1)$ sturucture and a planar doubly antiaromatic $C_{2v}({}^1A_1)$ isomer. However, upon chlorination, an inversion in the stability occurs. The planar(C_s,${}^2A'$) structures **1**, come from the addition of Cl to the planar doubly antiaromatic $C_{2v}({}^1A_1)$ isomer, become the global minimum structure, and the chlorination of the global quasi-planar $C_{6v}({}^3A_1)$ triplet distorted completely to the wheel-like planar structure **4, 5**, which lie higher energies than 1 by 30.7 and 43.6 kcal/mol respectively.

Acknowledgements

This work was supported by the Undergraduates Research Training Programs (URTs: 2017J00156, 2017J00026 and 2016J00017) of China National Education Commission, and Dawn TC4000 High-Performance Computation Platform in Beijing Institute of Petro-Chemical Technology.

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