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Chemical Physics Letters 429 (2006) 326–334
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

B_7^- as a novel ligand: Theoretical investigations on structures and chemical bonding of LiB_7 and BeB_7^+

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Received 27 March 2006; in final form 2 August 2006
Available online 9 August 2006

Abstract

Ab initio molecular orbital theory and density functional theory have been applied to investigate LiB_7 and BeB_7^+ species. Almost the same stability order as bare B_7^- occurs for both LiB_7 and BeB_7^+ species, two low-lying (C_{6v}, $^3A_1$) and (C_{2v}, $^1A_1$) structures are the lower energy minima. Natural bond orbital (NBO) and molecular orbital (MO) analyses show that the B_7^- unit in LiB_7 and BeB_7^+ is nearly identical to the pure B_7^- cluster, providing a viable possibility to use it as a novel ligand and building unit.

1. Introduction

The structures and bonding of bare boron clusters have been the objects of many previous investigations (Refs. [1–6] and references therein). A remarkable breakthrough was the characterization of planar boron clusters by a series of recent joint experimental and theoretical studies of Wang's and Boldyrev's teams [7–12]. The confirmation of the planarity or quasi-planarity could be understood in terms of the multiple aromaticity (σ and π) and antiaromaticity.

Among the pure boron clusters, the B_7^- cluster is an intriguing and complex system. On their work [11], Wang's and Boldyrev's groups found three low-lying B_7^- isomers: (1) a wheel-type twofold (σ and π) aromatic C_{6v} ($^3A_1$) global minimum (structure **A** in Fig. 1); (2) a σ-aromatic and π-antiaromatic C_{2v} ($^1A_1$) minimum (structure **B** in Fig. 1); and (3) an elongated planar doubly (σ and π) antiaromatic C_{2v} ($^1A_1$) isomer (structure **C** in Fig. 1), also have been revealed by the authors during the investigations on $B_7H_2^-$ [13] or $B_7Au_2^-$ [14].

Alexandrova et al. have studied the influence of dehydrogenation [13] theoretically, and Zhai et al. have studied the bi-gold species theoretically and experimentally [14], and it is found that an inversion in stability occurs upon addition of two H, or two Au atoms to the B_7^-. The planar $B_7H_2^-$ or $B_7Au_2^-$ formed from the doubly antiaromatic B_7^- isomer (structure **C** in Fig. 1) is significant favored as the equilibrium σ-aromatic structure. The second most stable $B_7H_2^-$ and $B_7Au_2^-$, derived from the aromatic quasi-planar wheel B_7^- (structures **A**, **B** in Fig. 1), become doubly (σ- and π-) antiaromatic and thus substantial less stable.

As discussed in the previous studies [7–12], the pure boron clusters are multiple aromaticity, and may be used as potential ligands, analogous to $C_5H_5^-$ or benzene. Among the boron clusters, B_3^-, B_8^{2-}, B_9^-, B_{10}, B_{11}^-, and B_{12} are aromatic (σ and π) species and represent the suitable candidates to be new ligands [12].

Alexandrova et al. have recently carried out the investigations on LiB_8^- [15] and LiB_6^- [16] using photoelectron spectroscopy characterization and ab initio calculations. The found of $Li^+[B_8^{2-}]$ or $Li^+[B_6^{2-}]$ as charge-transfer salt providing the first experimental proof that planar pure boron clusters can be used as new ligands and building units in chemistry. Kuznetsov and Boldyrev have predicted

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doi:10.1016/j.cplett.2006.08.025

theoretically the existence of MX_3 (M = Li–Cs; X = B–Tl) type salt molecules [17], and Li and Jin predicted a series of MB_6 (M = Be–Ca) [18] and MB_5 (M = Li–Cs) [19].

It will be interesting to extend the studies to the related compounds MB_7 (M = Li–Cs) and MB_7^+ (M = Be–Ba) clusters, additional to our previous work on the single C_{7v} structure for MB_7 (M = Li–Cs) [20] (note that the C_{7v} isomer is not the global minima).

Motivated by the work of Wang's and Boldyrev's teams involving B_6^{2-}, B_7^-, B_8^{2-} [16,11–15] lately, the theoretical efforts in the present work were made to further investigate MB_7 and MB_7^+ species with B3LYP and MP2 methods, based mainly on earlier studies [11] of analogous bare B_7^- cluster. A range of reasonable B_7^-, LiB_7 and BeB_7^+ structures have been optimized, and the structures and bonding of the lower-lying isomers are discussed.

We hope this investigation will contribute to the understanding of the planarity or quasi-planarity of B_7^- in terms of the multiple aromaticity (σ- and π-) and antiaromaticity, or a mixture of them.

2. Theoretical methods

All calculations were performed using GAUSSIAN 03 program packages [21] with B3LYP and MP2 methods. The B3LYP method is a density functional theory (DFT) method with Becke's three parameters functional and Lee et al. correlation functional [22,23]. The MP2 method is the second-order Møller–Plesset perturbation theory [24]. The 6-311+G* basis sets [25,26] are adopted for B, Li, Na, K, Be, Mg, and Ca atoms, and the relativistic effective core potential with the LANL2DZ basis sets [27] are chosen for the heavier Rb, Cs, Sr, and Ba atoms. The Natural Bond Orbital (NBO) [28–30] and molecular orbital (MO) analyses are carried out at the B3LYP/6-311G*//B3LYP/6-311+G* and B3LYP/6-311+G*//B3LYP/6-311+G* levels, respectively. The MO diagrams are made by using the MOLDEN 3.7 program [31].

3. Results and discussion

The calculated results are shown in Figs. 1–5, Tables 1–8 in this Letter, and suppl. Figs. 1 and 2 and suppl. Tables 1–12 in supplement materials section.

Just as Wang's and Boldyrev's groups reported in their work [11], the same three lowest-lying B_7^- isomers (**A**–**C** in Fig. 1) are predicted in the present work. Furthermore, the order of stability of the low-energy structures of LiB_7 (**1**, **2**, **5** in Fig. 2) was the same as that of bare B_7^-, unlike the dihydrogenation of the B_7^- to $B_7H_2^-$ or B_7^- added two Au atoms to $B_7Au_2^-$ [14], an inversion occurs in the order of energies.

Two most stable structures of LiB_7 are a triplet C_{6v} ($^3A_1$) and a singlet C_{2v} ($^1A_1$) quasi-sandwich minima (structures **1** and **2** in Fig. 2). The latter is 8 kcal/mol higher in energy than the former. The next nearest low-lying isomer is found to be a planar singlet (C_s, $^1A'$) structure (**3** in Fig. 2), 24.3 kcal/mol higher in energy, yielded from the optimization of without symmetry restrictions for the planar C_{2v} symmetric structure **5** in Fig. 2. Structure **5** is 30.1 kcal/mol higher in energy, and the mode (b_1) of another imaginary frequency leads another structure **4** (shown in Fig. 2), lying lower in energy than **5** by 5.3 kcal/mol. The another planar C_{2v} structure (**6** in Fig. 2) is predicted to have an imaginary frequency at the B3LYP/6-311+G* level, following the mode of imaginary frequency, a C_2 symmetric minimum is obtained, lying energetically higher than the global minimum **1** by 31.4 kcal/mol. However, at the MP2/6-311+G* level, structure **6** is predicted to be local minimum. The other higher-lying isomers will not be discussed here after.

The molecular properties of low-lying LiB_7 species are listed in Tables 1–3.

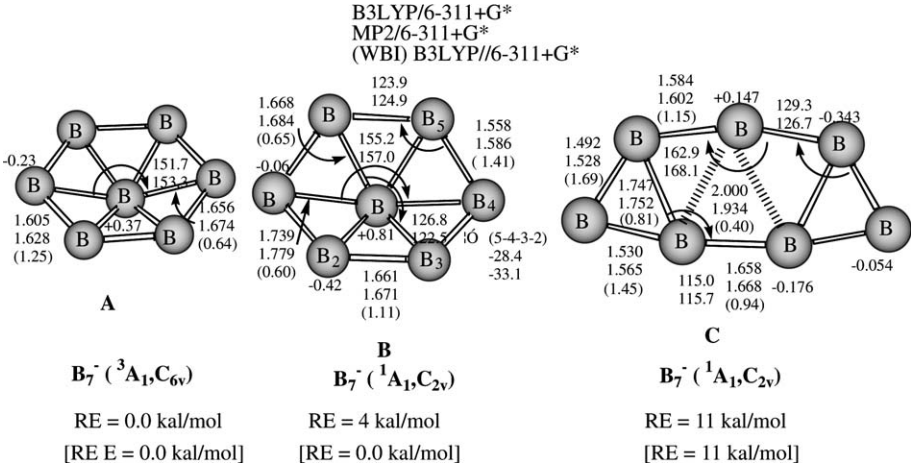

Fig. 1. Low-lying structures of B_7^- species (bond lengths in Å, bond angles in degrees) at the B3LYP/6-311+G* and MP2/6-311+G* levels, relative energies (RE) at B3LYP/6-311+G* level (relative energies computed at the MP2/6-311+G* level are shown in square brackets), and the selected Wiberg bond indices (WBI) and natural charges at B3LYP/6-311G*//B3LYP/6-311+G* level.