$D_{\infty h}$ $B_2(BS)_2^{-/2-}$ and T_d $B(BS)_4^-$: Boron Sulfide Clusters Containing BB Multiple Bonds and B^- Tetrahedral Centers

WEN-ZHI YAO,[1] JIN-CHANG GUO,[2] HAI-GANG LU,[1] SI-DIAN LI[1,2]

[1]*Institue of Molecular Sciences, Shanxi University, Taiyuan, Shanxi 030001, People's Republic of China*

[2]*Institute of Materials Sciences and Department of Chemistry, Xinzhou Teachers' University, Xinzhou, Shanxi 034000, People's Republic of China*

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ABSTRACT: A density functional theory investigation on the geometrical and electronic properties of $B_4S_2^{0/-/2-}$ ($B_2(BS)_2^{0/-/2-}$) and $B_5S_4^{0/-}$ ($B(BS)_4^{0/-}$) clusters has been performed in this work. Both the doublet $B_2(BS)_2^-$ ($[S{=}B{-}B\stackrel{\cdots}{=}B{-}B{=}S]^-$) ($D_{\infty h}$, $^2\Pi_u$) and the singlet $B_2(BS)_2^{2-}$ ($[S{=}B{-}B{\equiv}B{-}B{=}S]^{2-}$) ($D_{\infty h}$, $^1\Sigma_g^+$) proved to have perfect linear ground-state structures containing a multiply bonded BB core ($B\stackrel{\cdots}{=}B$ or $B{\equiv}B$) terminated with two BS groups, while T_d $B(BS)_4^-$ turned out to possess a perfect B^- tetrahedral center directly corrected to four BS groups, similar to the corresponding boron hydride molecules of $D_{\infty h}$ $B_2H_2^-$, $D_{\infty h}$ $B_2H_2^{2-}$, and T_d BH_4^-, respectively. B_4S_2 and B_5S_4 neutrals, however, appeared to be much different: they favor a planar fan-shaped C_{2v} B_4S_2 (a di-S-bridged B_4 rhombus) and a planar kite-like C_{2v} B_5S_4 (a di-S-bridged B_3 triangle bonded to two BS groups), respectively. One-electron detachment energies and symmetrical stretching vibrational frequencies are calculated for $D_{\infty h}$ $B_2(BS)_2^-$ and T_d $B(BS)_4^-$ monoanions to facilitate their future characterizations. Neutral salts of $B_2(BS)_2Li_2$ with an elusive $B{\equiv}B$ triple bond and $B(BS)_4Li$ containing a tetrahedral B^- center are predicted possible to be targeted in experiments. ©2009 Wiley Periodicals, Inc. Int J Quantum Chem 110: 2689–2696, 2010

Key words: boron sulfide clusters; ab initio calculations; geometries; electronic structures; electron detachment energies; photoelectron spectroscopy

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Correspondence to: S.-D. Li; e-mail: lisidian@yahoo.com

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1. Introduction

Boron oxide clusters B_xO_y have attracted considerable attention in recent years because of their importance in both fundamental research and materials sciences. In four recent articles [1–4], Zhai, Yao, Li, and Wang performed combined photoelectron spectroscopy (PES) and ab initio theory investigations on a series of boron oxide clusters in gas phases, including the linear $C_{\infty v}$ BO^- and $D_{\infty h}$ BO_2^- [1], linear $D_{\infty h}$ $B(BO)_2^-$ and triangular D_{3h} $B(BO)_3^-$ [2], linear $D_{\infty h}$ $B_2(BO)_2^{0/-/2-}$ [3], and tetrahedral T_d $B(BO)_4^-$ [4]. These studies confirmed the existence of BO groups (boronyls) and BB multiple bonds (B═B, $\mathrm{B}\overset{\cdots}{=}\mathrm{B}$, and B≡B) in a wide range of boron oxide clusters and revealed a clear structural link between boron oxide clusters $B_m(BO)_n$ and the corresponding boron hydride molecules B_mH_n. Recent theoretical studies performed by other groups well support this conclusion [5, 6]. Considering the similarities between S ($3s^23p^4$) and O ($2s^22p^4$) in valence electron configurations, our group performed recently a density functional theory (DFT) investigation on linear BS^-, BS_2^-, and $B(BS)_2^-$ and triangular $B(BS)_3^-$ [7]. Close similarities were obtained between BS and BO σ-radicals and $B(BS)_n^{0/-}$ and $B(BO)_n^{0/-}$ ($n = 2, 3$) microclusters. However, there have been no experimental or theoretical investigations on $B_m(BS)_n$ clusters with $m > 1$ or $n > 3$ reported in literature [7, 8]. In this work, we extend the research at ab initio levels to novel boron sulfide clusters including $B_4S_2^{0/-/2-}$ ($B_2(BS)_2^{0/-/2-}$) and $B_5S_4^{0/-}$ ($B(BS)_4^{0/-}$) at different charged states. Both $D_{\infty h}$ $B_2(BS)_2^-$ monoanion ($[\mathrm{S{=}B{-}B\overset{\cdots}{=}B{-}B{=}S}]^-$) and $D_{\infty h}$ $B_2(BS)_2^{2-}$ dianion ($[\mathrm{S{=}B{-}B{\equiv}B{-}B{=}S}]^{2-}$) turned out to possess perfect linear ground-state structures containing a multiply bonded BB core ($\mathrm{B}\overset{\cdots}{=}\mathrm{B}$ or B≡B) terminated with two BS groups, while $B(BS)_4^-$ proved to have a perfect tetrahedral geometry with a B^- center directly bonded to four BS groups, similar to the corresponding boron hydride molecules of $D_{\infty h}$ $B_2H_2^-$, $D_{\infty h}$ $B_2H_2^{2-}$, and T_d BH_4^-, respectively. However, the ground states of their neutrals proved to be much different: B_4S_2 favored a planar fan-shaped C_{2v} structure (a di-S-bridged B_4 rhombus), while B_5S_4 possessed a planar kite-like C_{2v} geometry (a di-S-bridged B_3 triangle connected to two BS groups). These molecular fragments could be relevant for matrix spectroscopy or possibly in mass spectroscopy of boron sulfide solids. As B─S binary compounds were more volatile than their B─O analogies and investigation of their structures and thermodynamic properties was believed to be greatly facilitated [8], the boron sulfide clusters theoretically studied in this work are expected to be synthesized and characterized in future experiments.

2. Computational Methods

DFT structural optimizations and frequency analyses of boron sulfide clusters were performed using the hybrid B3LYP procedure [9] with the Dunning's all-electron basis (aug-cc-pVTZ) [10] implemented in Gaussian 03 program [11]. Extensive structure searches have been performed on these small clusters to determine their ground-state structures, starting from either the geometries of the corresponding boron oxide clusters [3, 4] without symmetry constrains or arbitrarily designed initial structures with specific symmetries. Energy refinements were achieved using the coupled cluster method including triple excitations (CCSD(T)) [12] at the B3LYP structures with the same basis to determine the relative stabilities of the low-lying isomers more accurately. Adiabatic detachment energies (ADEs) were calculated as the energy differences between the anions and the corresponding neutrals at their ground-state structures, while the vertical detachment energies (VDEs) as the energy differences between the anions and their neutrals at the ground-state structures of the anions. One-electron detachment energies of the monoanions were also approximated with the outer valence Green function approach (OVGF(full)) [13]. Figure 1 shows the ground-state structures of linear $B_2(BS)_2^{-/2-}$ and the fan-shaped B_4S_2. Figure 2 depicts the low-lying isomers of $B_4S_2^{0/-/2-}$ at different charged states. Figure 3 illustrates the π and σ BB multiple bonding within the B_2 cores and the B─B σ single bonds between the B_2 core and the two BS terminals in linear $B_2(BS)_2^{0/-/2-}$. Figure 4 shows the transition state of D_{2h} $B_4S_2Li_2$ and the ground state of C_{2h} $B_4S_2Li_2$ which contain a B≡B triple bond at the center. Figure 5 depicts the ground-state structures of tetrahedral T_d $B(BS)_4^-$, tetrahedral T_d $C(BS)_4$, the Li^+-bridged C_{2v} B_5S_4Li, and the planar kite-like B_5S_4, while Figure 6 shows the low-lying isomers of $B_5S_4^{0/-}$. The four B─B σ orbitals of T_d $B(BS)_4^-$ are illustrated in Figure 7. Table I summarizes the calculated electronic properties and

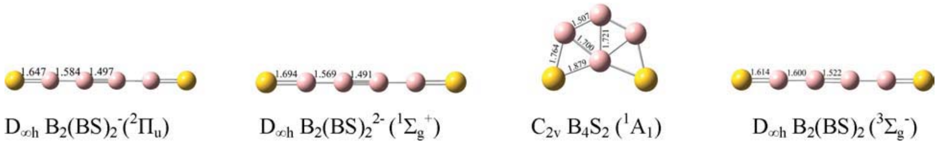


FIGURE 1. Ground-state structures of linear $B_2(BS)_2^-$, linear $B_2(BS)_2^{2-}$, and the fan-shaped C_{2v} B_4S_2 at B3LYP with bond lengths indicated in Å. Linear triplet $B_2(BS)_2$ is also shown for comparison. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

symmetrical stretching vibrational frequencies of the most concerned high symmetry clusters. Table II tabulates the calculated one-electron detachment energies of $D_{\infty h}$ $B_2(BS)_2^-$ and T_d $B(BS)_4^-$.

3. Results and Discussion

3.1. $B_2(BS)_2^-$, $B_2(BS)_2^{2-}$, AND B_4S_2

We start from boron sulfide anions possible to be observed in PES experiments first. As can be seen from Figures 1 and 2, analogous to $D_{\infty h}$ $B_2(BO)_2^-$ and $D_{\infty h}$ $B_2(BO)_2^{2-3}$, both the ground states of doublet $D_{\infty h}$ $B_2(BS)_2^-$ $(^2\Pi_u)$ and singlet $D_{\infty h}$ $B_2(BS)_2^{2-}$ $(^1\Sigma_g^+)$ possess a perfect linear geometry (1) lying at least 0.38 and 0.78 eV lower than other low-lying isomers (**2**–**8**). For $B_4S_2^-$ monoanion, C_{2v} **2** and C_{2v} **6** both contain an S- or SBS-bridged B_3 triangle [14], while all other low-lying isomers (**3**, **4**, **5**, **7**, and **8**) possess a rhombus B_4 core [14] with S bridges or S terminals. $B_4S_2^{2-}$ dianion possesses similar low-lying structures in a different energy order. However, unlike B_4O_2 which has a clear linear triplet ground state [O═B─B═B─B═O] [3], the ground state of B_4S_2 neutral turned out to be the planar fan-shaped C_{2v} **7** $(^1A_1)$ (a di-S-bridged rhombus B_4), with the linear triplet $D_{\infty h}$ $B_2(BS)_2$ (**1**, $^3\Sigma_g^-$) serving as a local minimum lying 0.55 eV higher in energy. In fact, both the di-S-bridged C_{2v} B_4S_2 (**4**) and C_{2v} B_4S_2 (**8**) also lay lower than linear $D_{\infty h}$ $B_2(BS)_2$ (**1**) by 0.18 eV and 0.34 eV, respectively. Concerning the bond length variations in the optimized linear $[S═B─B≡B─B═S]^{0/-/2-}$ chains, it is interesting to notice that, with the molecular net charges increasing from 0, −1, to −2, the BB multiple bond lengths within the B_2 core decease from 1.522 Å, 1.497 Å, to 1.491 Å, the B─B single bonds between the B_2 core and BS groups decrease from 1.600 Å, 1.584 Å, to 1.569 Å, while the B─S distances within the BS groups increase from 1.614 Å, 1.647 Å, to 1.694 Å (see Fig. 1). This situation is very similar to that observed in $B_2(BO)_2^{0/-/2-}$

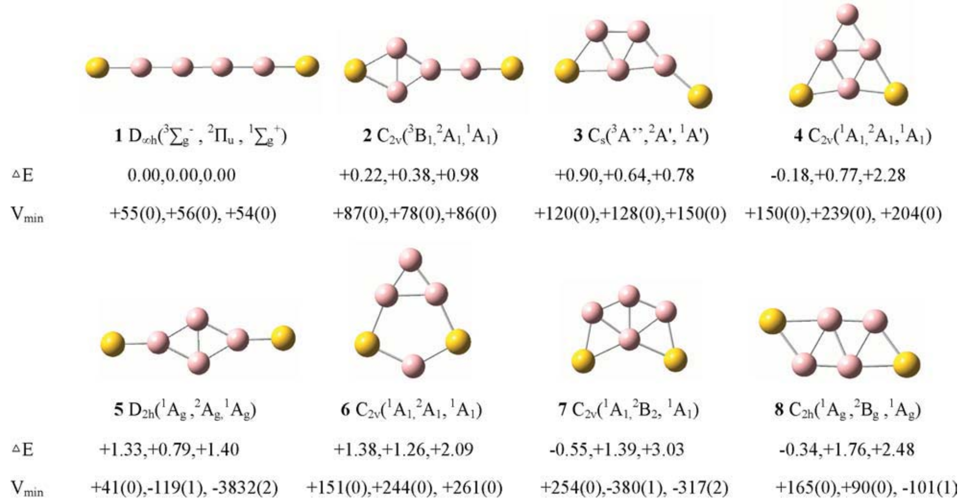


FIGURE 2. Low-lying isomers obtained $B_4S_2^{0/-/2-}$ clusters in the increasing energy order of $B_4S_2^-$, with energies relative to the linear **1** (Δ*E*, eV) indicated at CCSD(T)//B3LYP level. The lowest vibrational frequencies (V_{min}, cm^{-1}) and the number of imaginary frequencies (quoted in parentheses) are also indicated at B3LYP. Notice, the first, second, and the third numbers stand for B_4S_2, $B_4S_2^-$, and $B_4S_2^{2-}$, respectively. [Color figure can be viewed in the online issue, which is available at at wileyonlinelibrary.com.]

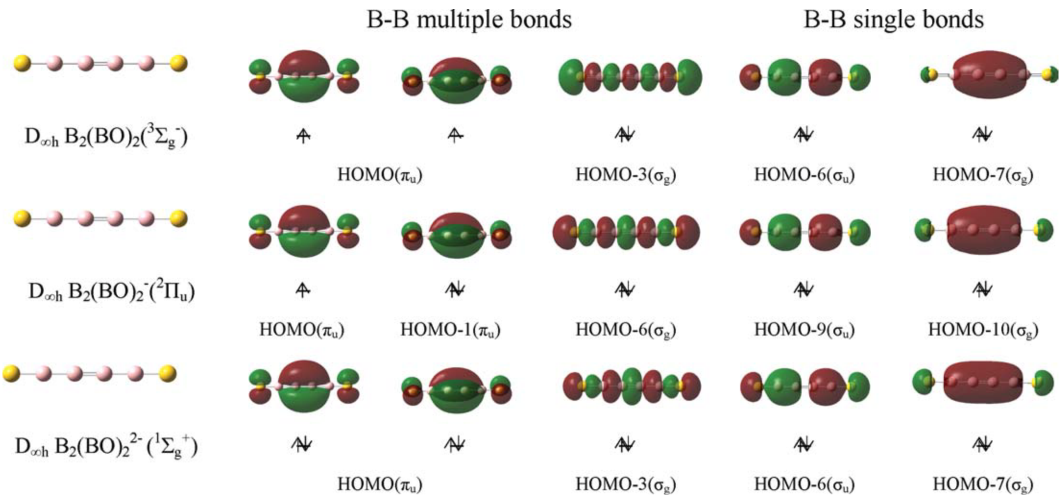


FIGURE 3. Pictures of the selected occupied molecular orbitals responsible for the BB multiple bonds within the B_2 cores and the B—B single bonds between B_2 core and the two BS terminals in linear $D_{\infty h}$ $B_2(BO)_2^{0/-/2-}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

series (**3**), confirming the existence of formal B=B, B$\overset{\cdots}{=}$B, and B≡B multiple bonds in linear $B_2(BS)_2^{0/-/2-}$ series and further supporting the isolobal relationship between —H, —BO, and —BS groups [7].

As mentioned earlier, the di-S-bridged C_{2v} B_4S_2 (**4**), C_{2v} B_4S_2 (**7**), and C_{2v} B_4S_2 (**8**) all turned out to be more stable than linear $B_2(BS)_2$ (**1**), with C_{2v} B_4S_2 (**7**) being the global minimum of the neutral. Other low-lying B_4S_2 neutral isomers (**2**, **3**, **5**, **6**) with bridging or terminal BS group(s) or a bridging SBS group appeared to lie at least 0.22 eV higher than $D_{\infty h}$ $B_2(BS)_2$ (**1**). Bridging S atoms are favored over BS groups in B_4S_2 neutral isomers which prefer to contain a rhombus B_4 core. This situation is different from B_4O_2 which clearly favors the linear triplet $D_{\infty h}$ $B_2(BO)_2$ containing a B_2 core terminated with two BO groups [3], in line with the fact that a BS group possesses a lower bond energy (132 Kcal/mol at B3LYP) than that (194 Kcal/mol) of a BO group.

The linear structures of $[S{=}B{-}BB{-}B{=}S]^{0/-/2-}$ series originate from the triplet ground state of the B_2 core ($^3\Sigma_g^-$) [14] and the σ radical nature of the two terminal BS groups [7] and can be understood in terms of the unique orbital occupations of the linear systems (see Fig. 3). The triplet low-lying linear $[S{=}B{-}B{=}B{-}B{=}S]$ ($^3\Sigma_g^-$) possesses the valence electronic configuration of $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^2$. The half-filled degenerate HOMOs ($2\pi_u$) and the fully occupied HOMO-3 ($4\sigma_g$) mainly contribute to the B=B double bond interaction which has the formal bond order of 2, while the doubly occupied HOMO-6 ($2\sigma_u$) and HOMO-7 ($2\sigma_g$) form the two B—B σ single bonds between B_2 core and the two BS terminal groups. With one or two extra electrons successively added into the degenerate HOMOs ($2\pi_u$), $[S{=}B{-}B\overset{\cdots}{=}B{-}B{=}S]^-$ monoanion ($^2\Pi_u$: $1\sigma_g^2 1\sigma_u^2 21\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^3$) and $[S{=}B{-}B{\equiv}B{-}B{=}S]^{2-}$ dianion ($^1\Sigma_g^+$: $1\sigma_g^2 1\sigma_u^2 21\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^4$) possess the formal BB bond orders of 2.5 and 3 within the B_2 core, respectively. With the bond orders increasing from 2, 2.5, to 3, the BB multiple bond lengths within the B_2 core decrease gradually from $D_{\infty h}$ $B_2(BS)_2$, $D_{\infty h}$ $B_2(BS)_2^-$, to $D_{\infty h}$ $B_2(BS)_2^{2-}$ (see discussion above). However, the bond length decreasing of 0.006 Å from B$\overset{\cdots}{=}$B in $[S{=}B{-}B\overset{\cdots}{=}B{-}B{=}S]^-$ to B≡B in $[S{=}B{-}B{\equiv}B{-}B{=}S]^{2-}$ is obviously too small.

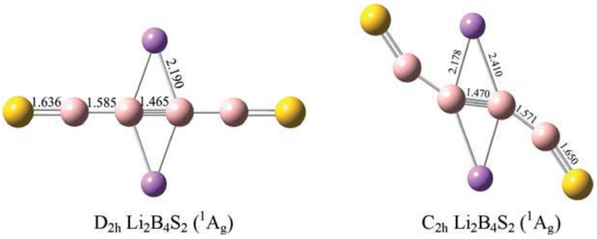
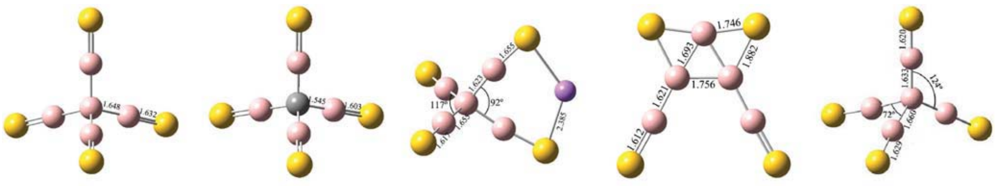
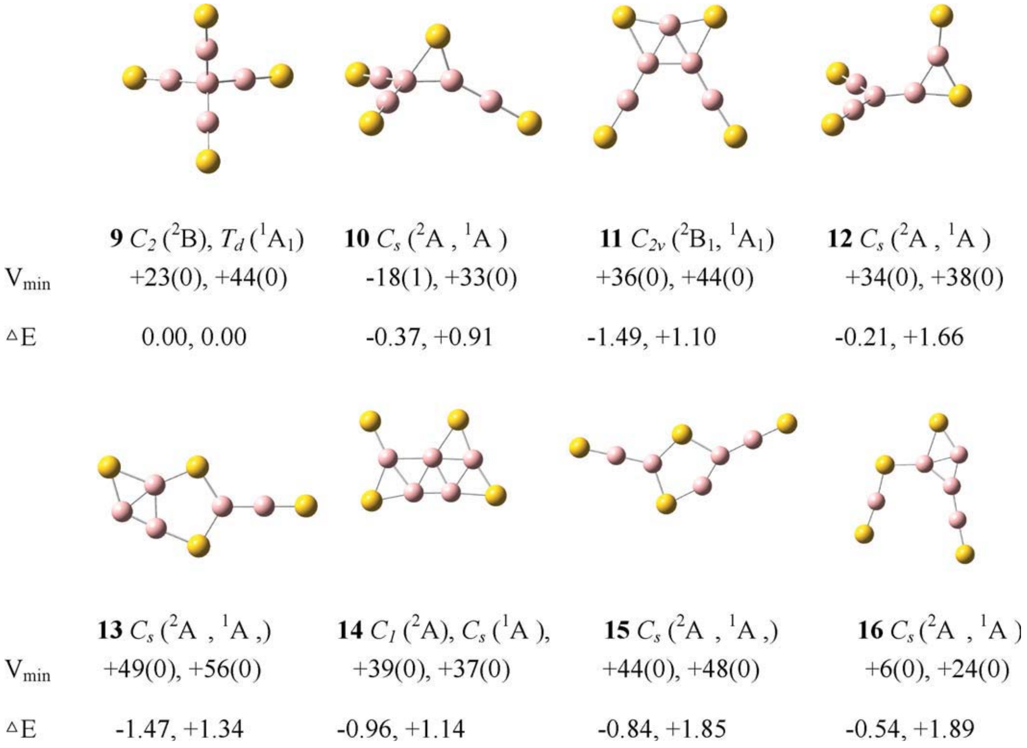


FIGURE 4. Optimized structures of D_{2h} $Li_2B_4S_2$ and C_{2h} $Li_2B_4S_2$ at B3LYP with bond lengths indicated in Å at B3LYP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



T_d $B(BS)_4^-$ ($^1A_1$) T_d $C(BS)_4$ ($^1A_1$) C_{2v} $B(BS)_4Li$ ($^1A_1$) C_{2v} B_5S_4 ($^2B_1$) C_2 $B(BS)_4$ (^2A)

FIGURE 5. Ground-state structures of T_d $B(BS)_4^-$, T_d $C(BS)_4$, C_{2v} $B(BS)_4Li$, C_{2v} B_5S_4 at B3LYP with bond lengths indicated in Å. The local minimum structure of C_2 $B(BS)_4$ is also depicted for comparison. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

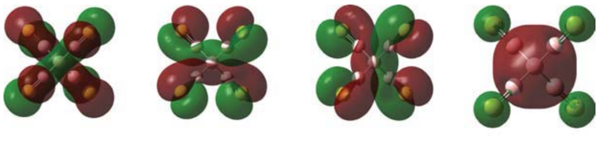


	9 C_2 (^2B), T_d ($^1A_1$)	**10** C_s (^2A , ^1A)	**11** C_{2v} ($^2B_1$, $^1A_1$)	**12** C_s (^2A , ^1A)
V_{min}	+23(0), +44(0)	-18(1), +33(0)	+36(0), +44(0)	+34(0), +38(0)
ΔE	0.00, 0.00	-0.37, +0.91	-1.49, +1.10	-0.21, +1.66

	13 C_s (^2A , ^1A ,)	**14** C_1 (^2A), C_s (^1A),	**15** C_s (^2A , ^1A ,)	**16** C_s (^2A , ^1A)
V_{min}	+49(0), +56(0)	+39(0), +37(0)	+44(0), +48(0)	+6(0), +24(0)
ΔE	-1.47, +1.34	-0.96, +1.14	-0.84, +1.85	-0.54, +1.89

FIGURE 6. Low-lying isomers of $B_5S_4^{0/-}$ clusters in the increasing energy order of $B_5S_4^-$, with energies relative to the tetrahedral **9** (ΔE, eV) indicated at CCSD(T)//B3LYP level. The lowest vibrational frequencies (V_{min}, cm^{-1}) and the number of imaginary frequencies (quoted in parentheses) at B3LYP are also indicated. The first and second numbers stand for B_5S_4 and $B_5S_4^-$, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Coulomb repulsion in the highly charged $[S{=}B{-}B{\equiv}B{-}B{=}S]^{2-}$ dianion partially cancels the B≡B covalent triple bond and eventually makes the calculated B≡B bond length slightly longer (0.03 Å) than the expected value of $r_{B\equiv B}$ =1.46 Å [15]. This situation can be effectively changed by introducing two Li^+ countercations into $B_2(BS)_2^{2-}$ dianion to form a $B_2(BS)_2Li_2$ neutral, as shown in Figure 4. The transition state of D_{2h} $B_2(BS)_2Li_2$ (^1A_g) (with an imaginary vibrational frequency of



HOMO(t_2) HOMO(t_2) HOMO(t_2) HOMO-6(a_1)

FIGURE 7. Pictures of the four σ molecular orbitals between B center and its four BS ligands in T_d $B(BS)_4^-$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I

Calculated natural atomic charges (q_X, |e|) and total Wiberg bond indexes (WBI_X) of the central B/C atoms, bond orders of X—B single bonds (WBI_{X-B}), B=S double bonds ($WBI_{B=S}$), and BB multiple bonds (WBI_{BB}), and the symmetrical stretching vibrational frequencies (ν, cm^{-1}) of the high symmetry species at B3LYP level

	State	q_X	WBI_X	WBI_{X-B}	$WBI_{B=S}$	WBI_{BB}	ν
$D_{\infty h}$ $B_2(BS)_2$	$^3\Sigma_g^-$	0.06	2.65	1.13	2.38	1.40	301(σ_g), 1224(σ_g), 1572(σ_g)
$D_{\infty h}$ $B_2(BS)_2^-$	$^2\Pi_u$	−0.25	3.26	1.23	2.12	1.78	307(σ_g), 1188(σ_g), 1606(σ_g)
$D_{\infty h}$ $B_2(BS)_2^{2-}$	$^1\Sigma_g^+$	−0.53	3.88	1.37	1.84	2.06	305(σ_g), 1098(σ_g), 1626(σ_g)
T_d $B(BS)_4^-$	$^1A_1$	−1.69	3.93	0.93	2.27		298(a_1), 1293(a_1)
C_{2v} $B(BS)_4Li$	$^1A_1$	−1.63	3.94	0.89, 0.98	2.11, 2.40		302(a_1), 1278(a_1), 1347(a_1)
C_2 $B(BS)_4$	^2A	−1.24	3.79	0.94	2.33		309(a), 1227(a), 1300(a)
T_d $C(BS)_4$	$^1A_1$	−1.54	3.42	0.82	2.48		353(a_1), 1427(a_1)

-52 cm^{-1}) lies 0.09 eV higher than the distorted ground state of C_{2h} $B_2(BS)_2Li_2$ (^1A_g) and the B≡B triple bond lengths in these neutral structures are reduced to 1.46–1.47 Å. $B_2(BS)_2Li_2$ salt is predicted possible to be synthesized in experiments to prepare the elusive B≡B-containing compounds [3]. It should also be mentioned that, similar to the B≡O triple bonds discussed in our previous articles [1–3], the calculated B—S bond lengths between 1.61 and 1.69 Å in the $B_2(BO)_2^{0/-/2-}$ series within the BS groups (see Fig. 1) turned out to be quite close to the expected B≡S triple bond lengths of 1.68 Å [15].

Natural bonding orbital analyses further help to qualitatively understand the bonding situation in $[S{=}B{-}BB{-}B{=}S]^{0/-/2-}$ linear chains. The Wiberg bond indexes (WBI) of BB multiple interactions within the B_2 cores increase from $WBI_{BB} = 1.40$, 1.78, to 2.06 from linear $B_2(BS)_2$, $B_2(BS)_2^-$, to $B_2(BS)_2^{2-}$, with the corresponding total bond orders of the central B atoms increasing from $WBI_B = 2.65$, 3.26, to 3.88. These values qualitatively support the BB multiple bond length decreasing discussed above. Interestingly, the bond orders of the B—B interactions between the B_2 core and the two BS groups also increase from $WBI_{B-B} = 1.13$, 1.23, and 1.37, indicating that these B—B interactions possess certain double bond characteristics (especially in $B_2(BS)_2^{2-}$ in which the B—B bond length possesses the lowest value of 1.569 Å). This agrees with the observation that the HOMO (π_u) of the systems has been partially delocalized along the B_4 chains at the centers of the $[S{=}B{-}BB{-}B{=}S]^{0/-/2-}$ structures (see Fig. 3).

3.2. $B(BS)_4^-$ AND B_5S_4

Similar to the geometries of T_d BH_4^- and T_d $B(BO)_4^-$ [4], $B_5S_4^-$ anion proved to have a perfect tetrahedral ground state of T_d $B(BS)_4^-$ (**9**,$^1A_1$), in which the four BS groups were directly connected to the negatively charged B center, with the B—B bond lengths of 1.648 Å and B=S bond lengths of 1.632 Å (see Figs. 5 and 6). Replacing the negative B center in **9** with a C atom produces the T_d $C(BS)_4$ neutral ($^1A_1$) which is a BS substitute of CH_4 with the bond lengths of $r_{C-B} = 1.545$ Å and $r_{B=S} = 1.603$ Å. Other 2D and 3D $B_5S_4^-$ isomers (**10**–**16**) analogous to the low-lying isomers of $B_5O_4^-$ [4] lie at least 0.91 eV higher than T_d $B(BO)_4^-$ (**9**), suggesting that a B^- tetrahedral center is strongly favored in a $B(BO)_4^-$ anion. The results obtained here on T_d $B(BS)_4^-$ and T_d $C(BS)_4$ strongly support the B^-/C analog noticed in our previous work [4]. A perfect squared D_{4h} $B_5S_4^-$ (with a planar tetracoordinate B at the center) similar to the ground state of D_{4h} $Al_5O_4^-$ [16]

TABLE II

Calculated ADEs (eV) and VDEs (eV) of $D_{\infty h}$ $B_2(BS)_2^-$ and T_d $B(BS)_4^-$ at B3LYP and CCSD(T) levels and their vertical one-electron detachment energies at OVGF (full) with pole-strengths greater than 0.80

	Final state	B3LYP	CCSD(T)/ B3LYP	OVGF(full)/ B3LYP
$D_{\infty h}$ $B_2(BS)_2^-$				
ADE	$^3\Sigma_g^-$	3.05	3.01	
VDE (X)	$^3\Sigma_g^-$	3.11	3.09	3.04
A	$^1\Delta_g$			3.28
B	$^1\Sigma_g$			3.77
C	$^3\Sigma_g^-$			6.19
T_d $B(BS)_4^-$				
ADE	^2B	5.32	5.61	
VDE(X)	$^2T_2$	5.87	6.63	6.33
A	$^2T_1$			6.70
B	^2E			7.11
C	$^2T_2$			8.17

proved to lie very higher in energy (>15 eV). Introducing a bridging Li^+ cation to T_d $B(BO)_4^-$ produces the Li^+-bridged C_{2v} $B(BO)_4Li$ ($^1A_1$) which is the global minimum of the neutral (see Fig. 5). Tetrahedral B center is well maintained in C_{2v} $B(BO)_4Li$ ion-pair, suggesting the possibility of synthesizing $B(BO)_4Li$ salt containing tetrahedral B^- centers in experiments.

Given the BS/H isolobal relationship [4], the high stability of tetrahedral T_d $B(BS)_4^-$ can be understood in its molecular orbitals shown in Figure 7 which represent the four B—B σ bonds between the B center and its BS ligands. In fact, the electronic configuration of B $2s^{0.95}2p^{3.68}$ in T_d $B(BS)_4^-$ anion qualitatively agrees with C $2s^{1.17}2p^{4.28}$ in T_d $C(BS)_4$ neutral, indicating that the B center in T_d $B(BS)_4^-$ with the negative atomic charge of $q_B = -1.69$ |e| behaves similar to the C center in T_d $C(BS)_4$ which has the net charge of $q_C = -1.54$ |e|. The calculated B—B bond order of $WBI_{B-B} = 0.93$ and the total bond order of the central B atom $WBI_B = 3.93$ well support the B sp^3 hybridization pattern in T_d **9**.

Detaching one electron from the perfect tetrahedral T_d $B(BS)_4^-$ (15) involves a John-Teller process to produce the severely distorted local minimum of C_2 $B(BS)_4$ (see Fig. 5) which lies 1.49 eV higher than the ground state of the neutral system—a planar kite-like C_{2v} B_5S_4 (**11**, $^2B_1$). C_{2v} B_5S_4 contains a di-S-bridged B_3 triangle [14] bonded to two BS groups. All the other low-lying isomers of B_5S_4 shown in Figure 6 also proved to be more stable than C_2 B_5S_4, indicating that a tetrahedral B center directly bonded to four BS groups in B_5S_4 neutral is extremely unstable. C_{2v} B_5S_4 (**11**) appeared to be also much different from the ground state of the Y-shaped C_s B_5O_4 in which BO groups are basically maintained [4], further indicating that bridging S atoms are more energetically favored in B_5S_4 neutral than bridging O in B_5O_4 and BS groups are obviously less robust in boron sulfide clusters than BO units in boron oxide counterparts.

3.3. ONE-ELECTRON DETACHMENT ENERGIES AND SYMMETRICAL STRETCHING VIBRATIONAL FREQUENCIES

As shown in Table II, B3LYP, OVGF(full), and CCSD(T) methods produced consistent one-electron detachment energies for $D_{\infty h}$ $B_2(BS)_2^-$ and T_d $B(BS)_4^-$ anions possible to be characterized in PES experiments. $D_{\infty h}$ $B_2(BS)_2^-$ is predicted to have one strong X band ($^3\sum_g^-$) at 3.09 eV, two closely located weak bands with A ($^1\Delta_g$) at 3.28 eV and B ($^1\sum_g^-$) at 3.77 eV, and one strong C band ($^1\sum_g^-$) at 6.19 eV. As the structural relaxation from $D_{\infty h}$ $B_2(BS)_2^-$ to $D_{\infty h}$ $B_2(BS)_2$ is very small (see Fig. 1), the X band of $B_2(BS)_2^-$ is expected to be a sharp peak with close ADE (3.01 eV) and VDE (3.09 eV) values, similar to the situation of $D_{\infty h}$ $B_2(BO)_2^{-3}$. Besides, the symmetrical stretching vibrations of B—B bond at 301 cm^{-1} (σ_g), B=S bond at 1224 cm^{-1} (σ_g), and B=B bond at 1572 cm^{-1} (σ_g) in neutral $D_{\infty h}$ $B_2(BS)_2$ (see Table I) are expected to be resolved as vibrational progressions in high resolution PES. It is also possible to observe the symmetrical stretching vibrations of the $D_{\infty h}$ $B_2(BS)_2^-$ anion (Table I) in the hot bands of its PES.

The PES spectrum of T_d $B(BS)_4^-$ is predicted to contain broad bands for the reason that significant structural changes are involved from T_d $B(BS)_4^-$ to C_2 $B(BS)_4$ (see Fig. 5) when the extra electron is detached. This prediction agrees with the huge energy difference (≈1.0 eV) between the calculated ADE (5.61 eV) and VDE (6.63 eV) at CCSD(T) level. The symmetrical stretching vibrations of B—B at 309 cm^{-1} and B=S at 1227 cm^{-1} and 1300 cm^{-1} predicted for C_2 $B(BS)_4$ may be resolved in high resolution PES of T_d $B(BS)_4^-$. It is also possible to observe the B—B stretching at 298 cm^{-1} and B=S stretching at 1293 cm^{-1} obtained for T_d $B(BS)_4^-$ in the hot bands of its PES. Besides, it should be pointed out that the first VDE ($^2T_2$) of T_d $B(BS)_4^-$ located between 6.3 and 6.6 eV appears to be considerably lower than the corresponding value of 7.8–8.1 eV predicted for T_d $B(BO)_4^-$ [7].

4. Summary

We have presented an ab initio investigation on the geometrical and electronic properties of $B_4S_2^{0/-/2-}$ ($B_2(BS)_2^{0/-/2-}$) and $B_5S_4^{0/-}$ ($B(BS)_4^{0/-}$) at different charged states in this work. Both the ground states of linear $D_{\infty h}$ $B_2(BS)_2^-$ and $D_{\infty h}$ $B_2(BS)_2^{2-}$ prove to contain a multiply bonded BB core terminated with two BS groups, while T_d $B(BS)_4^-$ is predicted to possess a perfect tetrahedral B^- center directly connected to four BS groups. Their neutrals, on the other hand, possess the planar fan-shaped C_{2v} B_4S_2 and planar kite-like C_{2v} B_5S_4 geometries with two bridging S atoms, respectively. Inorganic neutral salts of $B_2(BS)_2Li_2$ with B≡B triple bonds and $B(BS)_4Li$ with tetrahedral B^- centers are predicted possible to be synthesized in experiments.

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