

Density functional investigation of $X@B_nH_n$ ($X = B^+, Be; n = 5-8$)

Lifen Li, Chang Xu, Longjiu Cheng*

Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China

ARTICLE INFO

Article history:

Received 8 May 2013

Received in revised form 1 July 2013

Accepted 1 July 2013

Available online 9 July 2013

Keywords:

Borane cluster

Aromaticity

Density functional theory

ABSTRACT

The stability of $X@B_nH_n$ ($X = B^+, Be; n = 5-8$) is investigated by density functional theory. Geometry optimization shows that both the radius of the center atom and the ring size make contribution to the stability of $X@B_nH_n$ structure. All the optimized structures are thermodynamics stable according to the large HOMO–LUMO gap, bonding energy, vertical ionization potential and vertical electron affinity. Nuclear independent chemical shift reveals that the (quasi-)planar structures are π aromatic, which is confirmed by chemical bonding analysis.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Boron and boron-based clusters have attracted much attention in the past 20 years owing to their interesting physical and chemical properties. Experiment and theory studies over the last decades have demonstrated that positively charged boron clusters are shown to become 3D at B_{16}^+ [1–3], while negatively charged and neutral boron clusters are still planar at B_{23}^- and B_{21} [4–14], respectively, except for B_{14} [15]. The in-plane σ and the out-of-plane π bonding are found in the planar boron clusters, each of which follows the $(4n + 2)$ Huckel rule for aromaticity. The delocalized bonding results in multiple aromaticity and enhances the stability of the planar clusters, such as molecular wheel-type clusters $D_{7h} B@B_7^{2-}$ and $D_{8h} B@B_8^-$ [16]. In the $B@B_7^{2-}$ and $B@B_8^-$ molecular wheels, two electrons contribute to the B–B peripheral covalent bonds by each B atom in the circumference and one electron to the delocalized bonds by the central B atom. Both species are doubly aromatic with 6σ and 6π delocalized electrons and have closed shell electronic configurations, rendering these clusters with enhanced stability. Pure boron clusters have been proposed as novel building blocks of solid materials, and recently a series of planar tetra-, penta-, and hexa-coordinate carbon–boron mixed clusters has been reported by numerous theoretical reports [17–23].

Lots of hydrogenated small boron clusters were reported [24–27], however, most boron hydrides adopt three-dimensional aromatic structures. In 2009, Yu and co-workers [28] presented a borane cation $B_6H_5^+$ in D_{5h} symmetry, which is the global minimum according to their calculation. A question arises: how do the structure and the bonding change when the ring size increases?

And can we replace the central boron atom with isoelectronic atom Be?

Therefore, we adopted density functional theory (DFT) method to investigate the stability of $X@B_nH_n$ ($X = B^+, Be; n = 5-8$) clusters. The three valence electrons of the peripheral boron formed three σ bonding among B_nH_n , and the p_z orbitals of the peripheral boron are empty due to the electron deficiency of boron. The electronic number occupied the π molecular orbital is decided on the valence electronic number of the center atom. The two valence electrons of B^+ and Be, which delocalized on the π molecular orbital combined with the p_z atom orbitals of the center atom and the peripheral boron, are satisfied the Huckel aromatic rule. The calculated results show that the stability of $[B@B_nH_n]^+$ reduces as the rings increasing due to the small radius of boron and that of $Be@B_nH_n$ raises up to $n = 8$. Besides, $[B@B_5H_5]^+$, $[B@B_6H_6]^+$ and $Be@B_8H_8$ are aromatic according to the electronic analysis.

2. Computational details

The geometries of $X@B_nH_n$ ($X = B^+, Be; n = 5-8$) were optimized by using the TPSSh functional [29]. The structures of $[B@B_5H_5]^+$ and $[B@B_6H_6]^+$ were investigated using the method combining the genetic algorithm (GA) with DFT implemented in our group [30–33]. All the optimization and the calculations of the energies and HOMO–LUMO gaps are performed at the TPSSh/6-311+G** level. The TPSSh functional was proven to give reasonably accurate energetic properties of boron and boron-based clusters [15,33–36]. To confirm the stability of structures, we analyzed the vibrational frequencies. If an imaginary vibrational mode was found, a relaxation along the coordinates of this mode should be carried out until the true local minimum is obtained. Thus, all isomers for each cluster are true local minima. The binding energy of the compound Eb

* Corresponding author. Tel.: +86 551 5107342; fax: +86 551 5107342.
E-mail address: clj@ustc.edu (L. Cheng).

($X@B_nH_n$) is defined as $E(X@B_nH_n) - E(X) - E(B_nH_n)$. Then, vertical electron affinity (VEA) of $[B@B_nH_n]^+ = E([B@B_nH_n]^+) - E(B@B_nH_n)$, VEA of $Be@B_nH_n = E(Be@B_nH_n) - E([Be@B_nH_n]^-)$ and the vertical ionization potential (VIP) of $Be@B_nH_n = E([Be@B_nH_n]^+) - E(Be@B_nH_n)$ are given out. All calculations are carried out using the GAUSSIAN 09 package [37].

3. Results and discussion

We optimized D_{nh} $X@B_nH_n$ ($X = B^+$, Be; $n = 5-8$) at TPSSH/6-311+G** level. Fig. 1 plots the local minima of $X@B_nH_n$ ($X = B^+$, Be; $n = 5-8$) from two sides. The bonding energy of $X@B_nH_n$, energy gap, VEA of $X@B_nH_n$ and benzene, VIP of $Be@B_nH_n$ and benzene, and nucleus-independent chemical shifts (NICS) value [38] above the molecular plane 1 Å of $[B@B_5H_5]^+$, $[B@B_6H_6]^+$, $Be@B_8H_8$ and benzene are listed in Table 1. The planar structures may not be global minima, so we performed global optimization on $[B@B_5H_5]^+$ and $[B@B_6H_6]^+$ using the method combining GA with DFT. The results show that the global minimum of $[B@B_5H_5]^+$ is the planar structure in D_{5h} symmetry, whereas that of $[B@B_6H_6]^+$ is 3D structure (see Supporting Information). The interesting bonding style between the center atom and ligand boron attract our attention due to the electron deficiency of boron. We infer there may be delocalized π and/or σ bonds in the molecules. Thus, we focus on only the (quasi-)planar structures hereby instead of the global minimum one.

3.1. Geometry structures

The optimized $[B@B_5H_5]^+$, the same as Yu and co-workers reported, is in D_{5h} symmetry. The $B_{cen}-B_{per}$ (B_{cen} and B_{per} represent for center B and the peripheral B, respectively) bond length is 1.58 Å and the $B_{per}-B_{per}$ bond length is 1.85 Å. A small distortion is happened after the optimization of $[B@B_6H_6]^+$ (D_{3d}), of which the hydrogenated cyclic boron presented chair-like model. The $B_{cen}-B_{per}$ and the $B_{per}-B_{per}$ bond length are 1.68 Å and 1.71 Å, respectively. As the ring size increasing, the symmetry of $[B@B_7H_7]^+$ (C_s) and $[B@B_8H_8]^+$ (C_2) are broken completely. Replaced the center B atom with Be atom, $Be@B_5H_5$ (C_s), $Be@B_6H_6$ (C_s) and $Be@B_7H_7$ (C_2) distorted seriously due to the large radius of Be atom. Crown-shaped $Be@B_8H_8$ is in D_{4d} symmetry with $B_{cen}-B_{per}$ and the $B_{per}-B_{per}$ bond length of 2.05 Å and 1.63 Å respectively.

3.2. Stability

The stability of those local minima was evaluated theoretically. First, all the minima are verified to be true local minima by

Table 1

Energy gap, bonding energy, vertical ionization potential, vertical electron affinity and NICS(1) values of structures for $X@B_nH_n$ ($X = B^+$, Be; $n = 5-8$) and benzene.

	$\Delta E_{HI}/eV$	E_b/eV	VIP/eV	VEA/eV	NICS(1)/ppm
$[B@B_5H_5]^+$	3.78	11.24		6.87	-8.55
$[B@B_6H_6]^+$	4.32	9.49		6.45	-14.17
$[B@B_7H_7]^+$	3.28	10.23		6.70	
$[B@B_8H_8]^+$	3.46	9.97		6.78	
$Be@B_5H_5$	3.57	5.83	9.39	1.05	
$Be@B_6H_6$	3.78	6.00	9.19	1.17	
$Be@B_7H_7$	3.43	5.69	8.89	1.41	
$Be@B_8H_8$	3.39	4.49	8.18	0.94	-11.90
C_6H_6	5.89		9.17	1.33	-10.19

frequency check. Second, the fairly large HOMO–LUMO energy gaps (3.28–4.32 eV) strongly suggest high stability of those systems. In the last, the VEA values (6.45–6.87 eV) of $[B@B_nH_n]^+$ are smaller than the VIP (8.18–9.39 eV) values of $Be@B_nH_n$, and the VEA (0.94–1.41 eV) and VIP (8.18–9.39 eV) values of $Be@B_nH_n$ are similar to benzene (1.33 eV and 9.17 eV, respectively), which indicates that the cations of $B@B_nH_n$ and the natural molecules of $Be@B_nH_n$ are stable. Note that we did not expect the minima to keep good chemical stability under ambient atmospheric conditions because therein most of the borohydride molecules are active.

3.3. Aromaticity

$[B@B_5H_5]^+$, $[B@B_6H_6]^+$ and $Be@B_8H_8$ are (quasi-)planar, which is always associated with delocalized electrons. Are there delocalized electrons in those structures? Since delocalization is always associated with aromaticity, we focus on the aromaticity of those clusters. NICS is an easy and efficient criterion to identify aromatic nature. A large negative NICS at the ring center (or inside and above the molecular plane) implies the presence of diamagnetic ring currents. Hereby, we calculated NICS values above the molecular plane 1 Å ($NICS(1) = -8.55$, -14.17 and -11.90 ppm for $[B@B_5H_5]^+$, $[B@B_6H_6]^+$ and $Be@B_8H_8$, respectively). Such large negative NICS(1) values indicate that the (quasi-)planar structures are aromatic as a comparison with the NICS(1) value of benzene (-10.19 ppm).

3.4. Electronic structures

According to the aromaticity of above structures, we infer that there must be delocalized electrons among the clusters. In order

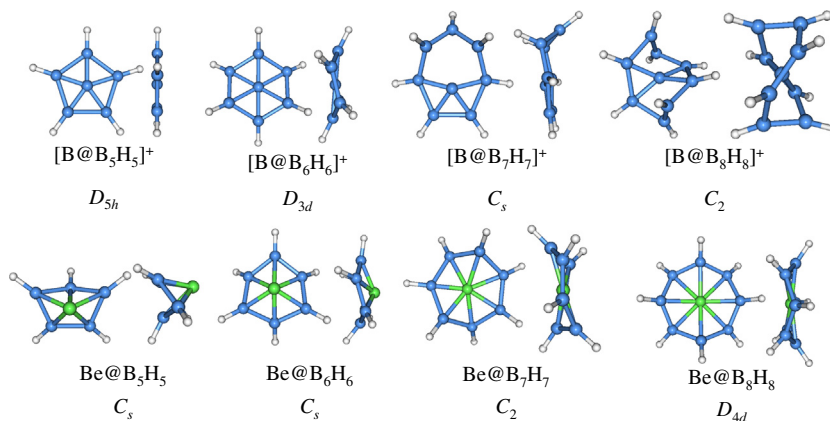


Fig. 1. Local minima of $X@B_nH_n$ for $X = B^+$, Be and $n = 5-8$. The symmetry is labeled in figure (two sides of views are given); H-white, B-blue, Be-green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

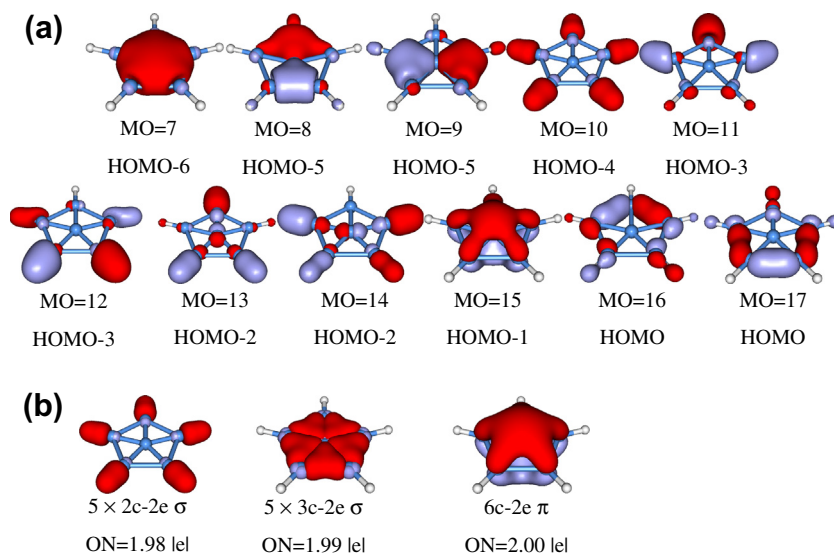


Fig. 2. (a) Canonical molecular orbitals and (b) AdNDP localized bonding patterns of $[B@B_5H_5]^+$.

to get insight into the delocalized orbital and bonding style of those clusters, canonical molecular orbital (CMO) analysis and Adaptive natural density partitioning (AdNDP) is adopted. AdNDP is a new theoretical tool developed by Zubarev and Boldyrev [39] for analysis of chemical bonding and has been successfully applied recently to the analysis of chemical bonding in clusters, such as boron based clusters [15,33,35,40,41]. In the following we discuss their electronic structures based on CMO and AdNDP analysis.

Yu and co-workers [28] have given the CMO analysis of $[B@B_5H_5]^+$ (D_{5h}) and pointed out the π orbital (MO = 15 showed in Fig. 2a). However, it is indistinct to identify other orbitals. In order to gain more insights into bonding style of $[B@B_5H_5]^+$, we presented the AdNDP analysis of $[B@B_5H_5]^+$ in Fig. 2b. The AdNDP analysis shows that there are five two-center two-electron ($2c-2e$) σ -BH bonds, five $3c-2e$ σ -BBB bonds, and one $6c-2e$ π bond with occupy number (ON) of 1.98 |e|, 1.99 |e|, and 2.00 |e|, respectively. On the basis of the above AdNDP analysis, we suppose that all of the boron atoms are in sp^2 hybridization. One hybridized

orbital of B_{per} interacts with the $1s$ orbital of the adjacent H atom, which forms a σ -BH bond; and the other two hybridized orbitals of B_{per} overlap the three hybridized orbitals of B_{cen} composing five $3c-2e$ σ -BBB bonds. The π MO is comprised of the six B p_z orbitals, which is occupied by the two electrons of B_{cen} .

$[B@B_6H_6]^+$ is in D_{3d} symmetry which contained a planar hexacoordinated B atom. The difference between the $B_{\text{cen}}-B_{\text{per}}$ bond length (1.68 Å) and the $B_{\text{per}}-B_{\text{per}}$ (1.71 Å) bond length is smaller than that of D_{5h} $[B@B_5H_5]^+$ (1.58 Å and 1.85 Å, respectively). CMO analysis reveals that there is also a π MO in the molecule (MO = 17 in Fig. 3a). The AdNDP analysis shows that there are six $2c-2e$ σ -BH bonds, six $3c-2e$ σ -BBB bonds, and one $7c-2e$ π bond (ON = 1.93 |e|, 1.95 |e|, and 2.00 |e|, respectively). Thus it can be seen that the three valence electrons of peripheral B form a $2c-2e$ σ -BH bond and two $3c-2e$ σ -BBB bonds, and the two valence electrons of the center B delocalized in the molecule.

Be and B^+ are isoelectronic. As the ring size increasing, $Be@B_8H_8$ is quasi-planar in D_{4d} symmetry with the peripheral B showing a

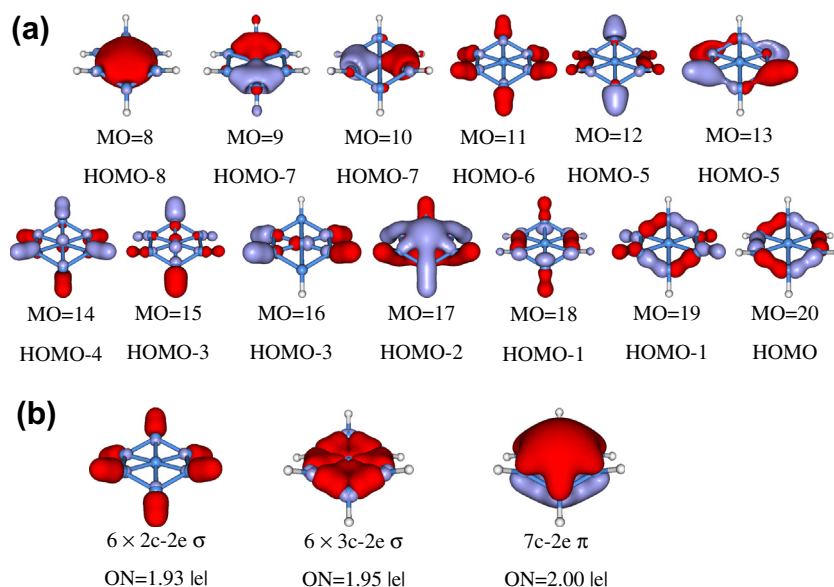


Fig. 3. (a) Canonical molecular orbitals and (b) AdNDP localized bonding patterns of $[B@B_6H_6]^+$.

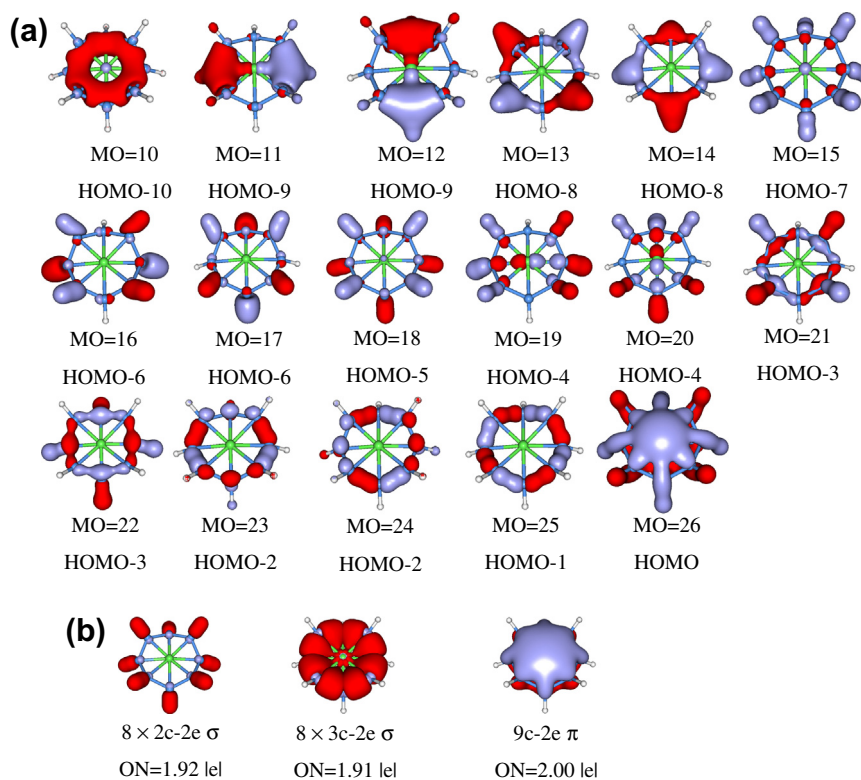


Fig. 4. (a) Canonical molecular orbitals and (b) AdNDP localized bonding patterns of Be@B₈H₈.

crow shape. The CMOs are given in Fig. 4a. A π molecular orbital (MO = 26) is found in the CMO analysis and the other MOs are unrecognizable. Again, in order to gain more information for the bonding style of Be@B₈H₈, we performed AdNDP analysis of Be@B₈H₈ in Fig. 4b, which suggests that Be@B₈H₈ possesses eight 2c–2e σ -BH bonds, eight 3c–2e σ -BBBe bonds, and one 9c–2e π bond with ON of 1.92 |e|, 1.91 |e|, and 2.00 |e|, respectively. Similar to [B@B₅H₅]⁺ and [B@B₆H₆]⁺, one valence electron of the peripheral B contribute to the 2c–2e σ -BH bond and the other two contribute to the two 3c–2e σ -BBBe bonds. The p_z orbitals of the peripheral and center boron atoms form π MO which stores the rest of two valence electrons of the center B atom.

Based on the analysis above, we can conclude that the bonding type of [B@B₅H₅]⁺, [B@B₆H₆]⁺ and Be@B₈H₈ are composed of n 2c–2e σ -BH bonds, n 3c–2e σ bonds and one $(n + 1)$ c–2e π bond. However, the center atoms of [B@B₅H₅]⁺, [B@B₆H₆]⁺ and Be@B₈H₈ contribute different electrons to the 3c–2e σ bonds according to the natural bond orbital (NBO) analysis. The ONs of B_{per}–B_{per} of [B@B₅H₅]⁺ and [B@B₆H₆]⁺ are 1.54 |e| and 1.60 |e|, respectively; while that of Be@B₈H₈ is 1.81 |e|. That is, compared with the ONs of 3c–2e σ bonds of [B@B₅H₅]⁺, [B@B₆H₆]⁺ and Be@B₈H₈ (1.99 |e|, 1.95 |e| and 1.91 |e|, respectively), the center boron of [B@B₅H₅]⁺ and [B@B₆H₆]⁺ contribute 0.45 |e| and 0.35 |e| to the 3c–2e σ bond, while the center Be of Be@B₈H₈ contribute 0.10 |e|. The reason for the difference between the 3c–2e bonds may be as follows: (1) the electronegative of B is larger than Be; (2) the energy of the sp² hybrid orbitals of the three centers for [B@B₅H₅]⁺ and [B@B₆H₆]⁺ are matching better than that for Be@B₈H₈.

4. Conclusions

In summary, we optimized X@B_nH_n (X = B⁺, Be; $n = 5-8$) at TPSSH/6-311+G** level. Besides of D5h [B@B₅H₅]⁺ reported by Yu, we gained two other stable planar minima D3d [B@B₆H₆]⁺ and

D4d Be@B₈H₈. Just like many ring-like hypercoordinated planar molecules proposed, the peripheral and central atomic radius must fit each other harmoniously. NICS value reveals that the D5h [B@B₅H₅]⁺, D3d [B@B₆H₆]⁺ and D4d Be@B₈H₈ are aromatic, which is confirmed by MO and AdNDP analysis. The [B@B₅H₅]⁺, [B@B₆H₆]⁺ and Be@B₈H₈ possess π MO and are analog of benzene, which makes those species be good ligands possible.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant No. 21273008), by 211 project of Anhui University. The calculations are carried out on the High-Performance Computing Center of Anhui University. We acknowledge Professor Boldyrev for the AdNDP codes.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2013.07.001>.

References

- [1] T.B. Tai, N.M. Tam, M.T. Nguyen, The Boron conundrum: the case of cationic clusters B_n⁺ with $n = 2-20$, *Theor. Chem. Acc.* 131 (2012) 1241.
- [2] J. Zhang, A.P. Sergeeva, M. Sparta, A.N. Alexandrova, B₁₃⁺: a photodriven molecular wankel engine, *Angew. Chem., Int. Ed.* 51 (2012) 8512.
- [3] G. Martinez-Guajardo, A.P. Sergeeva, A.I. Boldyrev, T. Heine, J.M. Ugalde, G. Merino, Unravelling phenomenon of internal rotation in B₁₃⁺ through chemical bonding analysis, *Chem. Commun.* 47 (2011) 6242.
- [4] T.B. Tai, N.M. Tam, M.T. Nguyen, Structure of boron clusters revisited, B_n with $n = 14-20$, *Chem. Phys. Lett.* 530 (2012) 71.
- [5] T.B. Tai, A. Ceulemans, M.T. Nguyen, Disk Aromaticity of the planar and fluxional anionic boron clusters B₂₀²⁻, *Chem.-Eur. J.* 18 (2012) 4510.
- [6] A.P. Sergeeva, D.Y. Zubarev, H.J. Zhai, A.I. Boldyrev, L.S. Wang, Photoelectron spectroscopic and theoretical study of B₁₆⁻ and B₁₆²⁻: an all-boron naphthalene, *J. Am. Chem. Soc.* 130 (2008) 7244.

- [7] A.P. Sergeeva, Z.A. Piazza, C. Romanescu, W.L. Li, A.I. Boldyrev, L.S. Wang, B_{22}^- and B_{23}^- : all-boron analogues of anthracene and phenanthrene, *J. Am. Chem. Soc.* 134 (2012) 18065.
- [8] A.P. Sergeeva, B.B. Averkiev, H.J. Zhai, A.I. Boldyrev, L.S. Wang, All-boron analogues of aromatic hydrocarbons: B_{17}^- and B_{18}^- , *J. Chem. Phys.* 134 (2008) 7244.
- [9] C. Romanescu, D.J. Harding, A. Fielicke, L.S. Wang, Probing the structures of neutral boron clusters using infrared/vacuum ultraviolet two color ionization: B_{11} , B_{16} , and B_{17} , *J. Chem. Phys.* 137 (2012) 014317.
- [10] Z.A. Piazza, W.L. Li, C. Romanescu, A.P. Sergeeva, L.S. Wang, A.I. Boldyrev, A photoelectron spectroscopy and *ab initio* study of B_{21}^- : negatively charged boron clusters continue to be planar at 21, *J. Chem. Phys.* 136 (2012) 104310.
- [11] Y. Nakagami, N.Y. Suzuki, R. Sekine, T. Matsuura, J. Aihara, The occurrence of *pi* molecular orbitals in planar boron clusters, *Bull. Chem. Soc. Jpn.* 85 (2012) 475.
- [12] W. Huang, A.P. Sergeeva, H.J. Zhai, B.B. Averkiev, L.S. Wang, A.I. Boldyrev, A concentric planar doubly *pi*-aromatic B_{19}^- cluster, *Nat. Chem.* 2 (2010) 202.
- [13] B.C. Hikmat, T. Baruah, R.R. Zope, Low-lying planar isomers of neutral and charged B_{22} clusters, *J. Phys. B-At. Mol. Opt. Phys.* 45 (2012) 225101.
- [14] R. Casillas, T. Baruah, R.R. Zope, Geometry and electronic structure of neutral and charged B_{21} clusters, *Chem. Phys. Lett.* 557 (2013) 15.
- [15] L.J. Cheng, B_{14} : an all-boron fullerene, *J. Chem. Phys.* 136 (2012) 104301.
- [16] H.-J. Zhai, A.N. Alexandrova, K.A. Birch, A.I. Boldyrev, L.-S. Wang, Hepta- and octacoordinate boron in molecular wheels of eight- and nine-atom boron clusters: observation and confirmation, *Angew. Chem., Int. Ed.* 42 (2003) 6004.
- [17] B.B. Averkiev, L.-M. Wang, W. Huang, L.-S. Wang, A.I. Boldyrev, Experimental and theoretical investigations of CB_8^- : towards rational design of hypercoordinated planar chemical species, *Phys. Chem. Chem. Phys.* 11 (2009) 9840.
- [18] B.B. Averkiev, D.Y. Zubarev, L.-M. Wang, W. Huang, L.-S. Wang, A.I. Boldyrev, Carbon avoids hypercoordination in CB_6^- , CB_8^{2-} , and $C_2B_5^-$ planar carbon-boron clusters, *J. Am. Chem. Soc.* 130 (2008) 9248.
- [19] L.-M. Wang, W. Huang, B.B. Averkiev, A.I. Boldyrev, L.-S. Wang, CB_7^- : experimental and theoretical evidence against hypercoordinate planar carbon, *Angew. Chem., Int. Ed.* 46 (2007) 4550.
- [20] K. Ito, Z.F. Chen, C. Corminboeuf, C.S. Wannere, X.H. Zhang, Q.S. Li, P.V. Schleyer, Myriad planar hexacoordinate carbon molecules inviting synthesis, *J. Am. Chem. Soc.* 129 (2007) 1510.
- [21] Z.-X. Wang, P.v.R. Schleyer, Construction principles of "Hyparenes": families of molecules with planar pentacoordinate carbons, *Science* 292 (2001) 2465.
- [22] R.M. Minyaev, T.N. Gribanova, A.G. Starikov, V.I. Minkin, Octacoordinated main-group element centres in a planar cyclic B_8 environment: an *ab initio* study, *Mendeleev Commun.* 11 (2001) 213.
- [23] K. Exner, P.v.R. Schleyer, Planar hexacoordinate carbon: a viable possibility, *Science* 290 (2000) (1937).
- [24] W.L. Li, C. Romanescu, T. Jian, L.S. Wang, Elongation of planar boron clusters by hydrogenation: boron analogues of polyenes, *J. Am. Chem. Soc.* 134 (2012) 13228.
- [25] D.Z. Li, H.G. Lu, S.D. Li, Planar *pi*-aromatic C_{3h} $C_6H_3^-$ and *pi*-antiaromatic C_{2h} $B_8H_2^-$: boron hydride analogues of D_{3h} $C_3H_3^+$ and D_{2h} C_4H_4 , *J. Mol. Model.* 18 (2012) 3161.
- [26] D.Z. Li, Q. Chen, Y.B. Wu, H.G. Lu, S.D. Li, Double-chain planar D_{2h} B_4H_2 , C_{2h} B_8H_2 , and C_{2h} $B_{12}H_2$: conjugated aromatic borenes, *Phys. Chem. Chem. Phys.* 14 (2012) 14769.
- [27] Q. Chen, S.D. Li, *Pi*-aromatic $B_{16}H_6$: a neutral boron hydride analogue of naphthalene, *J. Cluster Sci.* 22 (2011) 513.
- [28] H.L. Yu, R.L. Sang, Y.Y. Wu, Structure and aromaticity of $B_6H_5^+$ cation: a novel borohydride system containing planar pentacoordinated boron, *J. Phys. Chem. A* 113 (2009) 3382.
- [29] J. Tao, J.P. Perdew, V.N. Staroverov, G.E. Scuseria, Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids, *Phys. Rev. Lett.* 91 (2003) 146401.
- [30] Y. Yuan, L.J. Cheng, Theoretical prediction for the structures of gas phase lithium oxide clusters: $(Li_2O)_n$ ($n = 18$), *Int. J. Quantum Chem.* 113 (2013) 1264.
- [31] L. Ren, L.J. Cheng, Y. Feng, X.M. Wang, Geometric and electronic structures of $(BeO)_N$ ($N = 2-12, 16, 20$, and 24): rings, double rings, and cages, *J. Chem. Phys.* 137 (2012) 014309.
- [32] R. Li, L.J. Cheng, Structural determination of $(Al_2O_3)_n$ ($n = 1-7$) clusters based on density functional calculation, *Comput. Theor. Chem.* 996 (2012) 125.
- [33] L.F. Li, L.J. Cheng, First principle structural determination of $(B_2O_3)_n$ ($n = 1-6$) clusters: from planar to cage, *J. Chem. Phys.* 138 (2013) 094312.
- [34] Y. Yuan, L.J. Cheng, Ferrocene analogues of sandwich B_{12} center dot Cr center dot B_{12} : a theoretical study, *J. Chem. Phys.* 138 (2013) 024301.
- [35] Y. Yuan, L.J. Cheng, B_{14}^{2+} : a magic number double-ring cluster, *J. Chem. Phys.* 137 (2012) 044308.
- [36] E. Oger, N.R.M. Crawford, R. Kelting, P. Weis, M.M. Kappes, R. Ahlrichs, Boron cluster cations: transition from planar to cylindrical structures, *Angew. Chem., Int. Ed.* 46 (2007) 8503.
- [37] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B. 01, Gaussian, Inc., Wallingford CT, 2009.
- [38] P. Von Rague Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R. Van Eikema Hommes, Nucleus-independent chemical shifts: a simple and efficient aromaticity probe, *J. Am. Chem. Soc.* 118 (1996) 6317.
- [39] D.Y. Zubarev, A.I. Boldyrev, Developing paradigms of chemical bonding: adaptive natural density partitioning, *Phys. Chem. Chem. Phys.* 10 (2008) 5207.
- [40] I.A. Popov, A.I. Boldyrev, Computational probing of all-boron $Li_{2n}B_{2n}H_{2n+2}$ polyenes, *Comput. Theor. Chem.* 1004 (2013) 5.
- [41] J.K. Olson, A.I. Boldyrev, Planar to 3D transition in the $B_6H_6^-$ anions, *J. Phys. Chem. A* 117 (2013) 1614.