

Flattening the $B_6H_6^{2-}$ Octahedron. Ab Initio Prediction of a New Family of Planar All-Boron Aromatic Molecules

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Boron is a neighbor of carbon, and yet their structural chemistries are very different. The favored geometry in boron hydrides is the polyhedron (deltahedron) that has all faces equilateral or nearly equilateral triangles. The structural chemistry of boron hydrides enjoys a long history of great discoveries.^{1–5} In carbon structural chemistry, planar aromatic structures are more abundant than are polyhedral structures. Aromaticity in hydrocarbons also continues to fascinate chemists and to be a center of discussion.^{6–8} The representative molecules of deltahedral boranes and planar aromatic hydrocarbons are the octahedron $B_6H_6^{2-}$ and benzene C_6H_6 . Boron differs from carbon by one electron, and substitution of B^- for C may result in a stable molecule such as the very common BH_4^- , which can be viewed as a derivative of CH_4 . The question is, can we force deltahedral boranes to become planar by reducing and thus making them isoelectronic to aromatic hydrocarbons? For example, can we reduce a $B_6H_6^{2-}$ octahedron into a planar aromatic $B_6H_6^{6-}$ hexagon which is isoelectronic to benzene? At first glance, such reduction is highly unfavorable. Both the electropositivity of B and a very large HOMO–LUMO gap (>14 eV) in $B_6H_6^{2-}$ ⁹ do not favor the highly charged $B_6H_6^{6-}$ anion. However, even more highly charged anions of more electropositive atoms such as Ga_6^{8-} are known to be stable in the external field provided by counter-cations.¹⁰ Therefore, we had hope that aromatic planar all-boron species might exist. We were not able to find any experimental or computational data on the existence of the planar aromatic $B_6H_6^{6-}$ hexagon structure in the literature and decided to perform our own ab initio calculations in order to test the viability of such species.

First, we performed ab initio calculations on a wide variety of structures of $Li_6B_6H_6$ in search of the global minimum using three different theoretical methods.^{11–13} We found that the most stable structure for $Li_6B_6H_6$ was a bipyramid (Figure 1A,B) consisting of two Li^+ cations coordinated above and below a planar hexagon $B_6H_6^{6-}$ unit with four other Li^+ cations located in the plane. The distortions imposed on the $B_6H_6^{6-}$ hexagon by the cations are rather small. All B–B–B angles inside of the hexagon are close to 120.0° (within 0.5°), and all B–B bonds in the hexagon are close to one another in length (within 0.05 Å). Optimized bond lengths and valence angles vary little (0.02 Å and 0.5° , respectively) at three different levels of theory (Figure 1Sa and Table 1S, Supporting Information). The Hartree–Fock wave function was found to be dominant ($C_{HF} = 0.963$) in the CASSCF expansion, ensuring that the B3LYP, MP2, and CCSD(T) calculations are reliable. Other isomers (their structures and harmonic frequencies are presented in the Supporting Information) were also located (chemical bonding in alternative structures will be discussed elsewhere), but all had higher energies than the bipyramidal structure. Therefore, we conclude that the bipyramidal structure detailed in Figure 1 is the global minimum for the $Li_6B_6H_6$ species.

The planar hexagon $B_6H_6^{6-}$ unit is undoubtedly isoelectronic to benzene. There is a great deal of charge transfer from the lithium atoms to the B_6H_6 structural unit, yielding a total formal charge

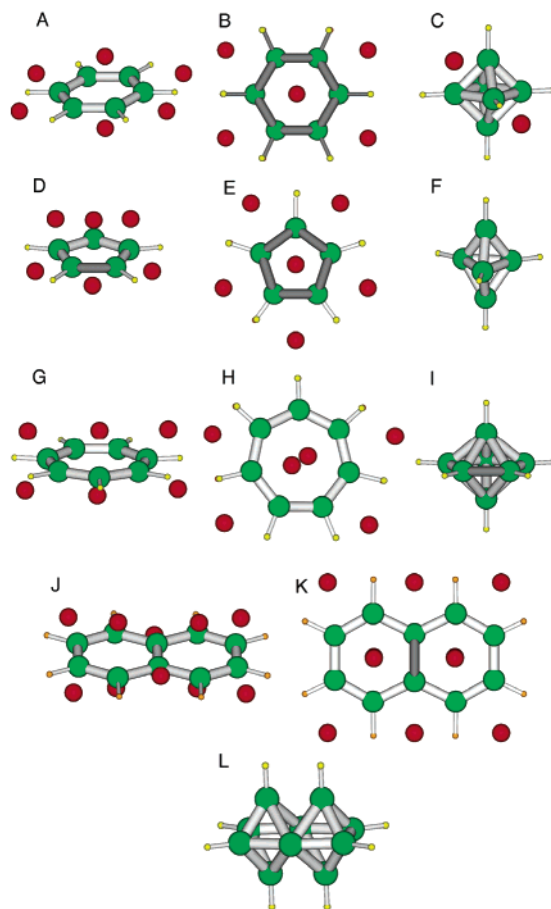
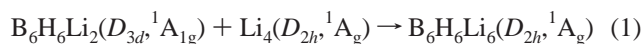


Figure 1. Optimized structures of $B_6H_6Li_6$ ($D_{2h}, ^1A_g$), side view (A); $B_6H_6Li_6$ ($D_{2h}, ^1A_g$), front view (B); $B_6H_6Li_2$ ($D_{3d}, ^1A_{1g}$) (C); $B_5H_5Li_6$ ($C_{3v}, ^1A'$), side view (D); $B_5H_5Li_6$ ($C_{3v}, ^1A'$), front view (E); $B_5H_5^{2-}$ ($D_{3h}, ^1A_1'$) (F); $B_7H_7Li_6$ ($C_{1v}, ^1A$), side view (G); $B_7H_7Li_6$ ($C_{1v}, ^1A$), front view (H); $B_7H_7^{2-}$ ($D_{5h}, ^1A_1'$) (I); $B_{10}H_8Li_{10}$ ($D_{2h}, ^1A_g$), side view (J); $B_{10}H_8Li_{10}$ ($D_{2h}, ^1A_g$), front view (K); and $B_{10}H_8^{4-}$ ($D_{2h}, ^1A_g$) (L).

close to -6 (NBO analysis). The $B_6H_6^{6-}$ anion also has the same set of occupied molecular orbitals as benzene. π -MOs of $Li_6B_6H_6$ and C_6H_6 are presented in Figure 2, thus providing theoretical proof that the $B_6H_6^{6-}$ hexagon is indeed aromatic. We also calculated NICS indices for $Li_6B_6H_6$. NICS indices were introduced by Schleyer^{14–16} as a simple probe for aromaticity. We found that the NICS index for $Li_6B_6H_6$ at the center of the $B_6H_6^{6-}$ hexagon is negative (-7.2 ppm) and close to the NICS index in benzene (-8.0 ppm) at the same level of theory (B3LYP/6-311++G**), thus providing additional proof of aromaticity in $Li_6B_6H_6$.

We evaluated the exothermicity of the four-electron reduction of $B_6H_6^{2-}$ to $B_6H_6^{6-}$ involved in the gas-phase reaction 1.



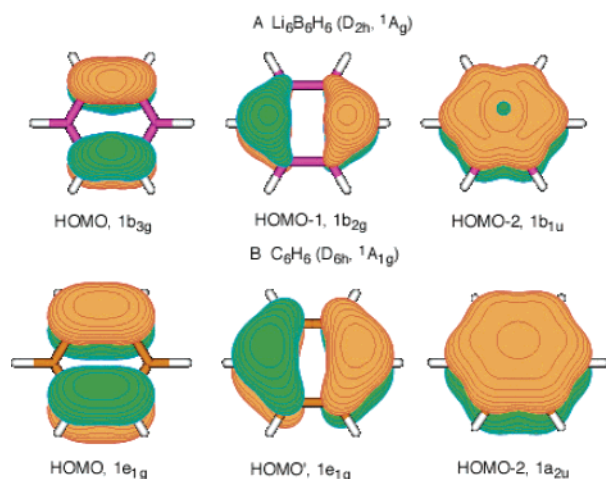


Figure 2. π -Molecular orbital pictures of $B_6H_6Li_6$ (D_{2h} , $1A_g$) and C_6H_6 (D_{6h} , $1A_g$).

Surprisingly, we found that this gas-phase reaction is highly exothermic ($\Delta E = -53$ kcal/mol at the CCSD(T)/6-311++G** level of theory). It is known, however, that $M_2B_6H_6$ solid salts are difficult to reduce.^{1–5} The high stability of closo-boranes, $B_nH_n^{2-}$, has been attributed to their three-dimensional aromaticity.^{1–5,17,18} Therefore, our calculated high exothermicity for reaction 1 requires some explanation. The stability of the $B_6H_6^{2-}$ octahedron comes from two types of bonding. A pairwise overlap of the six pairs of the p_x, p_y tangential B orbitals results in bonding over the two-dimensional surface of the octahedron. Additional bonding comes from the global mutual overlap of the six $s-p_z$ hybrid B orbitals. This last bonding is responsible for the aromatic stabilization in $B_6H_6^{2-}$.^{4,17} In the $B_6H_6^{6-}$ anion, six classical two-center, two-electron B–B σ -bonds and the resonance of the three two-electron, two-center π -bonds are responsible for chemical bonding in the planar hexagon. Apparently, the formation of the six B–B σ -bonds, which are rather strong ($D_e(B-B) = 101$ kcal/mol from the dissociation B_2H_4 into two BH_2 fragment), together with formation of the three π -bonds and their resonance, provide the extra stability for the aromatic $B_6H_6^{6-}$ structure.

Is the $Li_6B_6H_6$ salt molecule a lucky strike of the delicate balance between aromatic stabilization in $B_6H_6^{6-}$, the extremely high repulsion between six extra charges, and the external stabilizing field of six extra counteranions? We tested other planar aromatic all-boron molecules which satisfy the $4n + 2$ aromatic rule. We found that $Li_6B_5H_5$ (Figure 1D), $Li_6B_7H_7$ (Figure 1G), and $Li_{10}B_{10}H_8$ (Figure 1J), containing $B_5H_5^{6-}$ (isoelectronic analogue of $C_5H_5^-$), $B_7H_7^{6-}$ (isoelectronic analogue of $C_7H_7^+$), and $B_{10}H_8^{10-}$ (isoelectronic analogue of naphthalene, $C_{10}H_8$) respectively, are all true minima, clearly showing a general trend for all-boron planar aromaticity. NICS indices calculated for these planar boron species (-2.0 ppm for $Li_6B_5H_5$, -93.2 ppm for $Li_6B_7H_7$, and -54.2 ppm for $Li_{10}B_{10}H_8$, all at the center of the polygon) provide us further proof of their aromaticity. We believe that all deltahedral boranes can be further reduced to yield planar aromatic boranes.

In this work, we theoretically predicted the existence of a new class of planar aromatic boranes. Ab initio calculations show that the reduction of a three-dimensional $B_6H_6^{2-}$ octahedron (in $Li_2B_6H_6$), a $B_5H_5^{2-}$ trigonal bipyramid (in $Li_2B_5H_5$), a $B_7H_7^{2-}$ pentagonal bipyramid (in $Li_2B_7H_7$), and a $B_{10}H_8^{4-}$ biocahedral with a joint edge (in $Li_4B_{10}H_8$) leads to the formation of perfectly stable, planar structures. Planar $B_6H_6^{6-}$ hexagon (in $Li_6B_6H_6$), planar pentagon $B_5H_5^{6-}$ (in $Li_6B_5H_5$), planar heptagon $B_7H_7^{6-}$ (in $Li_6B_7H_7$), and naphthalene-like $B_{10}H_8^{10-}$ (in $Li_{10}B_{10}H_8$) were found to be

aromatic and stable species. Certainly, synthesis of planar all-boron aromatic molecules such as $(M^+)_6[B_6H_6^{6-}]$ and $(M^+)_{10}[B_{10}H_8^{10-}]$ will represent a challenge; otherwise, they would have been synthesized a long time ago. However, we hope that chemists will find a way to make these new compounds, and we expect that these species may have surprising properties like their now famous “cousin”, MgB_2 .¹⁹

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Supporting Information Available: Geometries and vibrational frequencies of all planar aromatic species found and their low-lying isomers, as well as full molecular orbital picture of $Li_6B_6H_6$ and C_6H_6 species (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Lipscomb, W. L. *Boron Hydrides*; W. A. Benjamin, Inc.: New York, 1963.
- (2) Meuterties, E. L., Ed. *Boron Hydride Chemistry*; Academic Press: New York, 1975.
- (3) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999.
- (4) King, R. B. *Chem. Rev.* **2001**, *101*, 1119.
- (5) Jemmis, E. D.; Balakrishnarajan, M. N.; Pancharatna, P. D. *Chem. Rev.* **2002**, *102*, 93.
- (6) Bergman, E. D.; Pullman, B., Eds. *Aromaticity, Pseudoaromaticity, Antiaromaticity*; Israel Academy of Science and Humanities: Jerusalem, 1971.
- (7) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994.
- (8) Schleyer, P. v. R., Guest Editor. *Chem. Rev.* **2001**, *101* (5), 1115 (introduction to the thematic issue on Aromaticity).
- (9) Fowler, P. W. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 61.
- (10) Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 5178.
- (11) We initially optimized geometries and calculated frequencies of $Li_2[B_6H_6]$, $Li_6[B_6H_6]$, $Li_6[B_5H_5]$, $Li_6[B_7H_7]$, and $Li_{10}[B_{10}H_8]$ species using analytical gradients with polarized split-valence basis sets (6-311++G**) and a hybrid method known in the literature as B3LYP. An extensive search for the global minimum structure has been performed for the $Li_6[B_6H_6]$ species. Alternative structures are presented in Supporting Information. We then refined geometries at the second-order Møller–Plesset perturbation theory (MP2) level and at the complete active space self-consistent field (CASSCF(8,8)) level of theory using the same basis sets. The energies of the most stable structures were refined using the CCSD(T) method and the 6-311++G** basis sets. Core electrons were kept frozen in treating the electron correlations at the MP2, CASSCF, and CCSD(T) levels of theory. All calculations were performed using the Gaussian 98 program¹² on 63-nodes Birch–Retford Beowulf cluster computer built at USU by K. A. Birch and B. P. Retford. Molecular orbitals' pictures were made using the MOLDEN3.4 program.¹³
- (12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (13) Schaftenaar, G. *MOLDEN3.4*; CAOS/CAMM Center: The Netherlands, 1998.
- (14) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
- (15) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.
- (16) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454.
- (17) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.
- (18) Aihara, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 3339.
- (19) Namatsu, J.; Nakagawa, N.; Muranaka, T.; Zenitani, Y.; Akimitsu, J. *Nature* **2001**, *410*, 63.

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