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Li$_7$(BH)$_5$$^+$: A New Thermodynamically Favored Star-shaped Molecule

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The potential energy surfaces (PESs) of Li$_n$(BH)$_5$$^{n-6}$ systems (where n = 5, 6, and 7) were explored using the gradient embedded genetic algorithm (GEGA) program, in order to find their global minima conformations. This search predicts that the lowest-energy isomers of Li$_6$(BH)$_5$ and Li$_7$(BH)$_5$$^+$ contains a (BH)$_5$$^{6-}$ pentagonal fragment, which is isoelectronic and structurally analogue to the prototypical aromatic hydrocarbon anion C$_5$H$_5$$^-$. The Li$_7(BH)_5$$^+$, along with Li$_7C_5$$^+$, Li$_7Si_5$$^+$ and Li$_7$Ge$_5$$^+$, joins a select group of clusters that adopt a seven-peak star-shape geometry, which is favored by the aromaticity in the central five-membered ring, and by the preference of Li atoms for bridging positions. The theoretical analysis of chemical bonding, based on magnetic criteria, supports the notion that electronic delocalization is an important stabilization factor in all these star-shaped clusters.

Introduction

The chemistry of the main group elements provides a number of interesting examples of atypical molecular structures, not only for the challenge of devising and synthesizing them, but also because they often stem from a type of unusual chemical bonding,[1] which defy the pre-established chemical models and concepts,[2–7] resulting in their extension and/or generalization.[8–15]

The enhanced thermodynamic stability of aromatic hydrocarbons inspired chemists to extend the aromaticity concept to inorganic chemistry with the aim of helping to rationalize, predict and synthesize stable compounds.[16–19] A simple protocol used by scientists to theoretically design inorganic aromatic compounds is the following: to build valence isoelectronic compounds to match their aromatic organic counterparts. Though this approach is simple and intuitive, its predictive capacity is rendered inefficient. For example; the Si$_6$H$_6$ (D$_{6h}$) and Si$_5$H$_5$$^-$ (D$_{5h}$), isoelectronic counterparts of the aromatic species benzene (C$_6$H$_6$) and

cyclopentadienyl anion (C$_5$H$_5$$^-$), are not even local minima on their potential energy surface (PES).[20–23] Additional factors need to be considered in order to obtain stable compounds. For the examples mentioned above, the replacement of hydrogen by lithium allows the stabilization of Li$_6$Si$_6$ (D$_{6h}$) and Li$_5$Si$_5$$^-$ (D$_{5h}$) systems. However, they are just local minima on their corresponding PES,[20,24] and therefore impractical targets for experimental detection.

We have theoretically designed a stable silicon-based C$_5$H$_5$$^-$ analogue: the Li$_7$Si$_5$$^+$ (D$_{5h}$) cluster, which is a star-like molecule in its lowest energy conformation.[20] Subsequently, it has unequivocally been shown that the five-pointed star shape is a common structural pattern for minimum energy conformation of Li$_7$E$_5$$^+$ (E = C, Si, and Ge).[25,26] This unusual high-symmetry pattern is favored by i) the aromaticity in the central five-membered ring, and by ii) the preference by Li atoms for bridging positions. Even though these cyclopentadienyl anion analogues are still theoretical predictions, Kuhn and co-workers reported both a synthesis and a crystalline Zintl phase of Li$_{12}$Si$_7$, where a Si$_5$$^{6-}$ pentagonal ring is surrounded by Li$^+$ counterions with two of them placed above and below the plane (apical positions),[27,28] just like our prediction on the Li$_7$Si$_5$$^+$ cluster.[20] These observations suggest that the Li$_7$E$_5$$^+$ star-like clusters could be viable as building blocks for new materials. Besides, these units are adequate models, due to its small size, when used to analyze chemical properties in great detail; hence the importance of their study.

Herein, we evaluate if the star-shape pattern persists when shifting to Group 13 and replacing each E atom in Li$_7$E$_5$$^+$ by a BH unit to obtain the Li$_7$(BH)$_5$$^+$ molecule. There is some evidence that suggests this possibility: according to the electronic-transmutation concept (which was originally based

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on the idea that if a boron atom acquires an extra electron, it starts to behave as a carbon atom)[12] $Li_7(BH)_5^+$ should be classified as $C_5H_5^-$ derivative. Besides, the trivalent boron has been proposed as an isolobal analogue of divalent silicon,[29–31] which also supports the analogy between $Li_7(BH)_5^+$ and the prototypical start-shaped cluster $Li_7Si_5^+$. Furthermore, Boldyrev and coworkers have shown that the most stable structure of $Li_6(BH)_6$ contains a planar hexagon $(BH)_6^{6-}$ unit, isoelectronic and isostructural to benzene.[32] However, since in cluster research nothing can be taken for granted, to propose a good candidate for global minimum is only possible through an adequate exploration of its PES.

The stability of the clusters $Li_n(BH)_5^{n-6}$ (n = 5, 6, 7), which are isoelectronic $C_5H_5^-$, was analyzed in detail using genetic algorithms to explore their PESs. Interestingly, six or seven lithiums are necessary to obtain pentagonal $(BH)_5$ rings in global minimum conformations of $Li_6(BH)_5$ (C_{2v}) and $Li_7(BH)_5^+$ (D_{5h}) clusters. This means that the ideal correspondence between organic and inorganic systems proposed in this study is affected by the presence of just one Li; showing that important factors concerning the counterion (like nature, number, and spatial distribution) need to be considered when these analogies are used to design new molecules. As a result of this work, we can conclude that the $Li_7(BH)_5^+$, along with $Li_7C_5^+$, $Li_7Si_5^+$ and $Li_7Ge_5^+$, joins a select group of clusters that adopt a seven-peak star-shape geometry and it that fulfills Hückel's rule of 4n+2 π electrons; the z component (B^{ind}_z) of the induced magnetic field (B^{ind})[33,34] supports the high degree of aromatic character in these species.

Computational Methods

First, we performed a large and nearly exhaustive exploration of the PES to ensure that geometries are true global minima. The search was performed employing the GEGA program,[35,36] using the PBE0 functional[37] and the Stuttgart/Dresden effective core potential (ECP)[38] with its respective SDD basis set for geometry optimizations. The global minima and the 30 kcal/mol lowest-energy isomers were re-optimized and characterized with the same functional and cc-pVTZ[38] basis set implemented in the Gaussian 09 program.[39] For a better description of the respective PESs, a finer energy analysis was carried out at CCSD(T)[40–42]/cc-pVTZ//PBE0/cc-pVTZ corrected with the Zero point energy at PBE0/cc-pVTZ level of theory. The T_1-diagnostic of Lee and Taylor[43] have been used to perform a standard check on the quality of the single-reference correlation method; it has been suggested that T_1 values, greater than 0.02, indicate the need for a multi-reference wave function.[43] The shielding tensors were computed at the PBE0/cc-pVTZ level using the Gauge-Independent Atomic Orbital (GIAO) method.[44,45] The structures were placed in such way that the center of the molecule was located at the origin of the coordinate system and the z-axis was identical to the highest symmetry axis. Plots of the isolines induced a magnetic field (B^{ind}) and molecular orbitals were generated using the VisIt 2.8.1[46] and VMD 1.9.1[47] programs, respectively.

Results and Discussion

Structural Analysis

The lowest-lying energy isomers of the clusters $Li_n(BH)_5^{n-6}$ (n = 5, 6, 7) are shown in Figure 1, all these minima (1, 2 and 3) are closed shell systems and have been found after the exploration of both singlet and triplet PESs. The closest triplet structures are higher in energy than the singlet ones by 1.7, 20.7 and 40.3 kcal/mol for 1, 2 and 3. The T_1 values computed for the global minima are lower than 0.02, except for 1 (0.029). This suggests the presence of some multi-reference character on 1; however, due to the fact that this isomer is not structurally related with the prototype aromatic $C_5H_5^-$ anion, a more detailed analysis about its ground state wave function has not been undertaken in this work. The structures, Cartesian coordinates and relative energies of the most stable isomers are reported in the supporting information.

$Li_5(BH)_5^-$ system can be considered as the ideal $C_5H_5^-$ analogue, according to the electronic transmutation concept.[12] However, the lowest energy isomer (1) does not contain the $(BH)_5^{6-}$ pentagonal ring; instead, it is a C_{4v} structure conformed by a $(BH)_4$ square-based pyramid with four Li atoms acting as bridging groups at the edges of the square base pyramid. The fifth Li lies opposite to the top boron of the pyramid. The second thermodynamically preferred isomer (1-B) is 6.4 kcal/mol higher in energy and it has a C_s symmetry; the structure of this system contains a trigonal-bipyramid B_5 fragment, where two axial and two equatorial B are bonded to hydrogen; and one of the equatorial B is bonded (by the Li-Li edge) to one tetrahedral Li_3H fragment. The third isomer (C_s, 1-C), which lies at 8.7 kcal/mol from the 1-A, is conformed by a planar pentagonal ring $(BH)_5$, with three Li acting as bridging groups at the B-B edges, and two lithium placed over and below the $(BH)_5$ ring. This isomer is structurally similar to the $Si_5Li_5^-$ global minimum[20] and derivative of the $C_5H_5^-$ according to the electronic transmutation concept.

The $Li_6(BH)_5$ (C_{2v}, 2) global minimum conformation is structurally analogue to the most stable isomer of Li_6Si_5 and derivative (electronic-transmutation) of $C_5H_5^-$. The lithium atoms are distributed in apical position (two of them) and in equatorial positions (four of them) bridged between the B atoms. The low symmetry isomer (2-B) is 17.4 kcal/mol higher in energy and it consists of a squared B_4 fragment (with three B-H bonds where the lithiums are placed in apical positions and two of them are bridged between the boron atoms). Finally, a BH_2 unit is bonded to one B of the square fragment to form a planar $H_2B-(BH)_3$ unit with the two remaining Li bridging the $H_2B-(BH)_3$.

The minimum energy conformation of the last explored system, $Li_7(BH)_5^+$, was manifested as a highly symmetric star-shaped structure (D_{5h}, 3), consisting of a $(BH)_5$ pentagon surrounded by seven lithiums. This system is structurally similar to the $Li_7Si_5^+$ (D_{5h})[20] and $Li_7C_5^+$ (D_{5h})[25] clusters. The next higher-energy isomer contains the same $(BH)_5$ planar-pentagonal fragment (C_s, 3-B), but with two double-bridged Li atoms leaving a free space in the molecular plane. This rearrangement of the lithium makes the 3-B isomer 26

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kcal/mol higher in energy when compared to the most stable one.
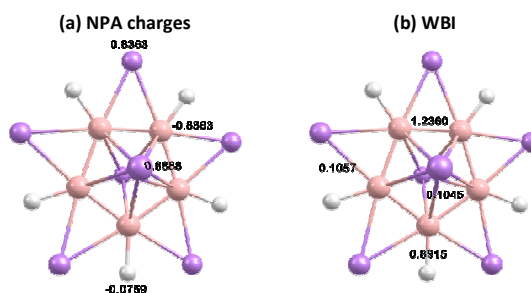
Bonding Analysis

Among the evaluated systems, just **2** ($Li_6(BH)_5$) and **3** ($Li_7(BH)_5^+$) contains a $(BH)_5$ pentagon surrounded by lithium atoms in their global minimum conformations. We would like to highlight the persistence of the star-shaped geometry in the global minimum of $Li_7(BH)_5^+$ which is no longer an exclusive structural pattern of group 14 elements and lithium, but it can also be transferable to boron clusters.

It is expected that aromaticity contribute to the stabilization of $Li_7(BH)_5^+$ based on the fact that it fulfills the Hückel's rule of $4n+2$ π electrons. To test this hypothesis, we have performed its chemical bonding analysis using different theoretical approximations. As we can see in Figure 2,according to the natural population analysis (NPA), the charges are in the range of +0.69 $|e|$ to +0.84 $|e|$ for axial and equatorial lithium, respectively. The total charge on the $(BH)_5$ fragment is of -4.6 $|e|$, stressing the dominant Li-(BH) ionic interactions in the title complex. Thus, in spite of the highly ionic character between the Li and the nonmetallic fragment, the lithium is not completely ionized, as the electronic transmutation concept requires. The WBI analysis, predicts a B-B bond order of 1.24, which suggests a partial double bond character (Figure 2). The same analysis could be extrapolated to the neutral $(BH)_5Li_6$ where the $(BH)_5$ fragment has a total charge of -4.3 $|e|$.
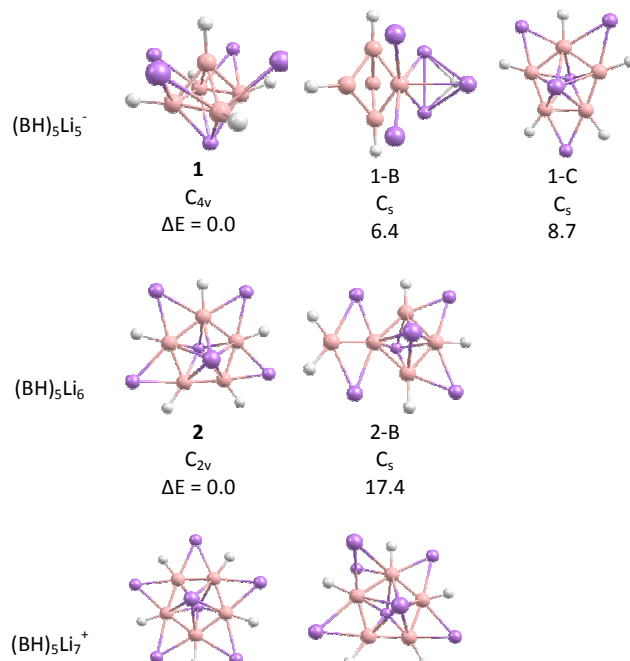
Figure 2(a) Atomic charges according to natural population analysis (NPA) and (b) bond order according to Wiberg bond indices (WBI), for $Li_7(BH)_5^+$.

In Figure 3 the $Li_7(BH)_5^+$ valence molecular orbitals are reported. There are six π-electrons distributed in a degenerate $1e_1''$ (HOMO) and one $1a_2''$ (HOMO-1) π-orbital set. Then, it is expected that through resonance each bond acquire some double-bond character in agreement with WBI analysis. As in the cyclopentadienyl anion and the star-shaped $Li_7C_5^+$ and $Li_7Si_5^+$ clusters, the $Li_7(BH)_5^+$ fulfills the $4n+2$ π-electrons requirement in the aromatic systems.

Figure 3. Molecular Orbitals of $(BH)_5Li_7^+$

The electronic delocalization is associated with the high stability of different chemical compounds. In previous works, the magnetic response of $Li_7Si_5^+$ and $Li_7C_5^+$ was reported.[20,25] Highly diatropic responses on those systems were identified by the induced magnetic field profiles. In the present work, a similar analysis was done for $C_5H_5^-$ (D_{5h}), C_4H_4 (D_{2h}), $C_5H_5^+$ (C_{2v}), $Li_7C_5^+$ (D_{5h}), $Li_7Si_5^+$ (D_{5h}), and $Li_7(BH)_5^+$ (D_{5h}). The classical $C_5H_5^-$ (aromatic) and C_4H_4 (antiaromatic) systems, as well as the planar $C_5H_5^+$ cation (antiaromatic), have been included in order to be compared. The plots of the isolines of the B^{ind}_z are depicted in Figure 4. With four π-electrons, the C_4H_4 and the $C_5H_5^+$ shows a deshielding (paratropic) elliptical-shaped region inside the molecular ring. This behavior is associated with an antiaromatic response. On the other hand, with six π-electrons, the cyclopentadienyl anion shows a shielding (diatropic) elliptical-shaped region covering the molecular ring such as in benzene. This behavior is associated with an

$(BH)_5Li_5^-$

1
C_{4v}
$\Delta E = 0.0$

1-B
C_s
6.4

1-C
C_s
8.7

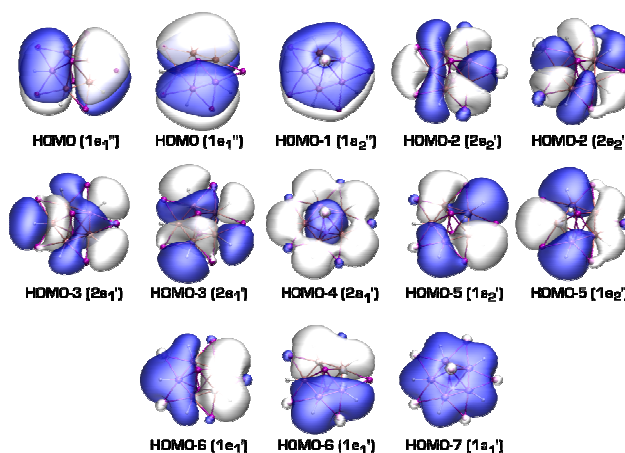$(BH)_5Li_6$

2
C_{2v}
$\Delta E = 0.0$

2-B
C_s
17.4

$(BH)_5Li_7^+$

Figure 1. Isomers of $Li_n(BH)_5^{n-6}$ (n = 5, 6 and 7). White, pink and purple spheres represent hydrogen, boron and lithium atoms, respectively. Relative energies calculated at CCSD(T)/cc-pvTZ//PBE0/cc-pvTZ are reported in kcal/mol.

aromatic response. The star-shaped $Li_7C_5^+$, $Li_7Si_5^+$, and the new $(BH)_5Li_7^+$ systems show a similar response: a diatropic region surrounding the pentagon cores. In all the $Li_7X_5^+$ systems (where X = BH, C, and Si) the lithium atoms are lying in the edge of the shielding zones. For $Li_7Si_5^+$ the shielding zone is larger, due to its molecular size. Then, the electronic delocalization can be considered as having the same nature in all these star-like clusters and their plots are comparable with the $C_5H_5^-$ isolines.

Conclusions

We have evaluated *in silico* the structures and stability of the most stable isomers of $Li_n(BH)_5^{n-6}$ (*n=5-7*) systems. The expected $(BH)_5$ pentagonal ring into the most stable conformations, according to the electronic-transmutation principles, is just to be found in $Li_6(BH)_5$ and $Li_7(BH)_5^+$ clusters. The global minimum of the $Li_5(BH)_5^-$ cluster is a C_{2v} structure that does not match these principles. The saturation of the bridging and, at least of one apical position of the B_5 ring with lithium atoms, are necessary to stabilize this conformation. According to their structural analogy, these clusters could be classified as isoelectronic analogues of Li_6Si_5 and $Li_7Si_5^+$, respectively. Moreover, following the electronic-transmutation principle, both clusters are derivatives of cyclopentadienyl anion ($C_5H_5^-$). We have shown that the stabilization of these systems is enhanced by an electron delocalization. The induced magnetic field reveals a diatropic behavior in $Li_7(BH)_5^+$, similar to the one previously reported for $Li_7C_5^+$ and $Li_7Si_5^+$; these patterns on the induced magnetic field are comparable with the one presented by the $C_5H_5^-$: the aromatic five membered ring employed as a reference.
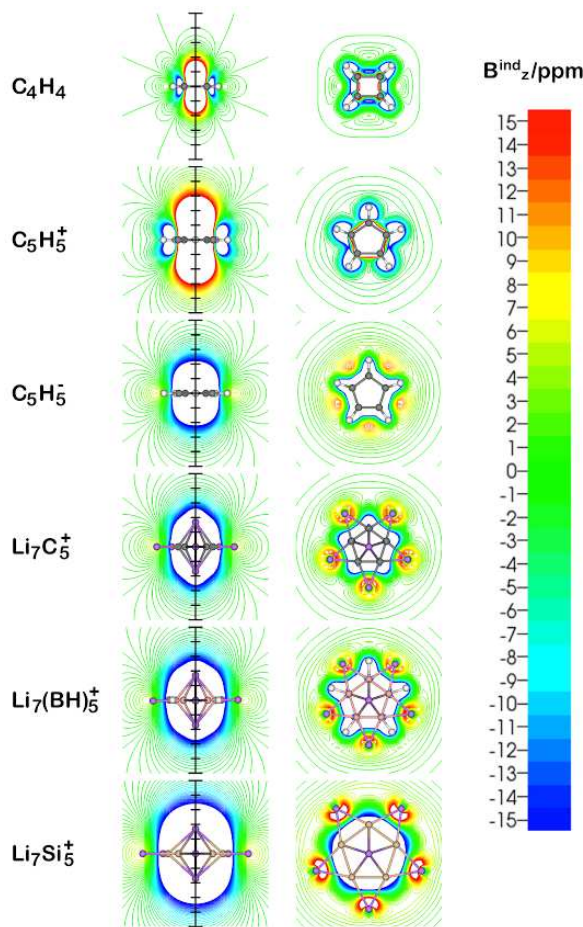
Figure 4. Isolines of the B^{ind}_z computed in isoelectronic compounds with the formula $X_5Li_7^+$, where X = (BH), C and Si, and the classic organic anion $C_5H_5^-$. Negative and positive values are associated with diatropic and paratropic regions, respectively. The scale is in ppm considering $\mathbf{B}^{ext}$ = 1 T.

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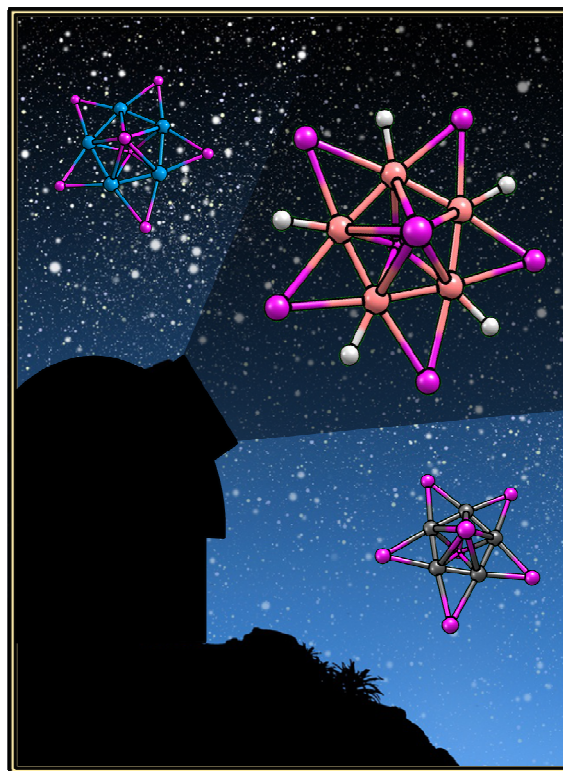
The feasibility of stabilizing a new star-shaped molecule, the $Li_7(BH)_5^+$, is demonstrated by an *in silico* investigation, combining DFT and Ab initio methods.

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