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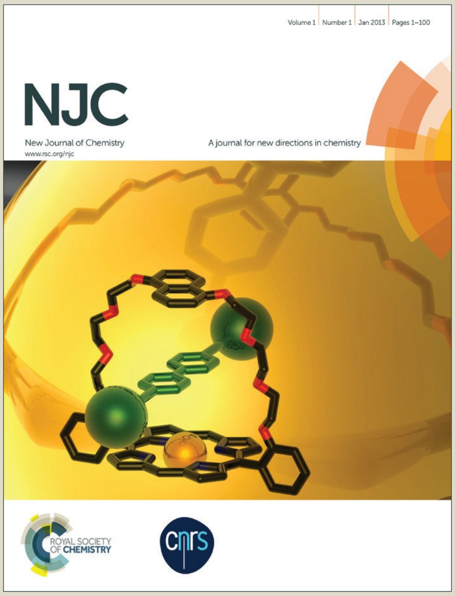

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ARTICLE

Boron avoids cycloalkane-like structures in the $Li_nB_nH_{2n}$ series

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The stability of the $Li_nB_nH_{2n}$ (n=3-6) series was analyzed using quantum chemical calculations, and it was found that cyclic isomers are not energetically favored. This is different to what happens in their organic counterparts (C_nH_{2n}), where cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}) are the low-lying isomers. Apparently, aromaticity is a key-stabilizing factor that needs to be considered for designing stable lithium-boron hydrides analogues of cyclic organic compounds. This is verified in the $Li_3B_3H_3^+$ system, which has been designed as the smallest aromatic carbocation ($C_3H_3^+$) analogue. The global minimum structure of the $Li_3B_3H_3^+$ contains a triangular $B_3H_3^{2-}$ moiety, which has structural and chemical bonding features similar to its organic counterpart. Besides, this new cluster is classified as aromatic according to both, the 4n+2 Hückel rule and the analysis of the induced magnetic field. This theoretical evidence leads us to propose this cluster as a viable target for experimental detection in gas phase.

Introduction

The ability of carbon to form long hydrocarbon chains and rings like benzene, where carbons are linked through covalent bonds, is the reason for the vast presence of organic compounds in nature. This so-called homocatenation is not exclusive of carbon; several other main group elements catenate to form chains and rings, but not so easily and in such a versatile way as carbon does. For instance: boron, despite having significant homonuclear σ-bond enthalpy, examples of boron catenation are extremely rare.[1] To date, it is known that boron prefers to participate in multicenter bonds, avoiding sp^2 hybridization and classical structures;[2] as in polyhedral boranes,[3] pure boron clusters[4-8] and, in the two-dimensional boron lattice (known as α-sheet).[9]

In recent years, several theoretical investigations suggest that the isoelectronic principle could be successfully used to achieve the boron catenation.[10-15] Thirteen years ago, due to the resistance of boron hydrides to form planar aromatic structures, Boldyrev and coworkers posed the following question: "Can we force deltahedral boranes to become planar by reducing and thus making them isoelectronic to aromatic hydrocarbons?" The authors explored, *in silico*, the viability of this proposal by reducing the octahedron $B_6H_6^{2-}$ (representative molecules of deltahedral boranes) to make it isoelectronic to benzene (representative molecule of aromatic hydrocarbons). After an exhaustive search on the potential energy surface (PES), ab initio calculations predicted that the most stable structure of $Li_6B_6H_6$ consists of a planar and hexagonal $B_6H_6^{6-}$ anion (structurally analogue to benzene) surrounded by Li^+ counterions.[10] Later on, Olson and Boldyrev introduced the electronic transmutation (ET) concept, which is based on the idea that if a boron atom acquires an extra electron, it starts to behave like a carbon atom.[11] This concept is a narrowed definition of the isoelectronic principle,[16, 17] and has been recently extended to propose a new class of aluminum homocatenated compounds ($Li_nAl_nH_{2n+2}$).[18] It also supports the $Li_6B_6H_6$ viability mentioned above, and it has been successfully used to design lithium borohydrides, which are analogues of homocatenated small saturated hydrocarbons.[11] More recently, we have shown that $Li_7B_5H_5^+$ (D_{5h}) is a thermodynamically favored star-shaped molecule, which has structural and chemical bonding analogies with the aromatic $C_5H_5^-$ (D_{5h}) anion.[19] Moreover, there are other important works where the isoelectronic equivalence between carbon and B^- has been discussed.[12-15, 20, 21]

Another important concept in chemistry, put forward by Baeyer[22] over 100 years ago, is the ring strain,[23, 24] which has proven quite useful in understanding the chemical reactivity of a number of biologically significant cyclic compounds.[25, 26] The introduction of strained rings into a molecular environment can have a profound effect on the chemistry of the overall system, providing an avenue to have control of properties on new designed materials. For instance, the strain modulation

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replacing one or more carbons by silicon in small cycloalkanes, has been systematically analyzed in the past.[27, 28]

In the light of the already mentioned studies, in this work we will analyze (*in silico*) the viability of boron compounds obtained after complete carbon replacement by B^- in the series of small cycloalkanes (C_nH_{2n}, n=3-6). The motivation behind this proposal is: on the one hand, to test the efficiency of the ET concept to design these non-aromatic rings and; on the other hand, to diversify the series of stable boron compounds where B^- behaves like C. Similarly to the strategy used by Boldyrev group,[10, 11, 14] we have also used Li as electron donor to design organic-like structures with the formula: $Li_nB_nH_{2n}$ (n=3-6). Two main aspects should affect the stability of these boron compounds. First: the ring strain, which is expected to decrease (as it does in their organic counterparts)[29] as the size increases. Second: the extremely high repulsion between extra charges.[30]

The stability of the title clusters was analyzed in detail using genetic algorithms to explore their PESs. Interestingly, the cyclic structures are not energetically favored, different to what happens in their organic counterparts (C_nH_{2n}), where cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}) are the low-lying isomers. These findings conjointly with the high stability reported for the $Li_6B_6H_6$ (D_{6h}) and $Li_7B_5H_5^+$ (D_{5h}), suggest that aromaticity is a key-stabilizing factor that needs to be considered for design stable lithium boron hydrides analogues of cyclic organic compounds. This is verified in the analogue of the smallest aromatic carbocation ($C_3H_3^+$), the $Li_3B_3H_3^+$ system. According to our calculations, the global minimum isomers of this cluster involves a triangular $B_3H_3^{2-}$ moiety, which has structural and chemical bonding features similar to its organic counterpart. Additionally, Hückel's rule of 4n+2 π electrons and, the analysis of the z component ($B^{ind}{}_z$) of the induced magnetic field (**B**^{ind})[31, 32] predicts that this cluster is aromatic.

To our best knowledge, this kind of compounds has not yet been systematically studied; then, we hope that our study can complement the recent advances in the chemistry of boron catenation using lithium as a reducing agent.

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 two methods, the GEGA program,[33, 34] and the Kick Coalescence (CK) program[35] written by B. B. Averkiev based in Saunders Kick method[36]. In the GEGA procedure we have used 4N as initial population (N is the number of atoms in the system), and almost three independent searches have been performed for each system. In the CK method we have used a population of 1000 individuals in each search. In both searches, the geometries were optimized using the PBE0 functional[37] with the Stuttgart pseudopotentials and their respective basis set (SDDALL).[38] Then, the geometry of the lowest energy isomers (within an energy range of 30 kcal.mol^{-1}) were refined using the more complete Def2-TZVP basis set.[39, 40] A frequency analysis has also been performed, at this level of theory, to ensure that each structure was a minimum on the PES. Finally, finer energy computations were performed at CCSD(T)[41-43] /Def2-TZVP (single-point calculations) using the geometries and the zero-point energy corrections obtained at PBE0/Def2-TZVP. In this way, it is ensured that we obtain the most accurate possible relative energies among the reported isomers. The T_1-diagnostic of Lee and Taylor[44] 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.[44]

Born-Oppenheimer Molecular-Dynamics (BO-MD)[45-47] simulations were done at 900 K for 20 picoseconds (ps) with a time steep of 1fs (the corresponding movie is included in the supporting information). To ensure that the temperature remained constant, it was verified that the nuclear kinetic energy remains constant throughout the simulation; to accomplish this, all velocities were rescaled at each step.

Chemical bonding analysis was performed with the adaptive natural density partitioning (AdNDP) method[5] at the PBE0/Def2-TZVP level of theory. The AdNDP method analyzes the first-order reduced density matrix and represents the electronic structure in terms of n-center–two-electron (nc–2e) bonds in order to recover both Lewis bonding elements (1c–2e or 2c–2e, i.e., lone pairs or two-center two-electron bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity.

The shielding tensors were computed at the PBE0/cc-pVTZ level using the Gauge-Independent Atomic Orbital (GIAO) method.[48, 49] 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.

As an alternative way to measure aromaticity, we calculated the multi-center delocalization index (MCI)[50-52] according to the equation:

$$\delta(A, B, C \ldots H) = 4 \sum_i \sum_j \sum_k \ldots \sum_q S_{ij}(A) S_{jk}(B) S_{kl}(C) \ldots S_{qi}(H) \qquad (1)$$

where $S_{ij}(A)$ means that the overlap integral between the occupied molecular orbitals *i* and *j* is computed over the basin of atom A.

Geometry optimizations, frequency analysis, single point energy calculations and BOMD simulations were done with the Gaussian 09 program.[53] Calculation of the MCI and the AdNDP analysis were performed with the Multiwfn program.[54] Plots of the isolines of the **B**^{ind} and localized orbitals were generated using the Visit 2.8.1[55] and VMD 1.9.1[56] programs, respectively.

Results and Discussion

Stability and Structural Analysis

Our investigation began with an exhaustive PES exploration of the proposed systems. This procedure has been performed using the gradient embedded genetic algorithm (GEGA) program.[34, 57] In order to test the reliability of the GEGA

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results, we have performed an alternative PES exploration using the CK program for the systems $Li_3B_3H_3$ and $Li_4B_4H_4$. The two searches provided us with the same set of low lying isomers (see Tables S1 and S2 in the supporting information).

The cyclic and the most stable isomer of the C_nH_{2n} organic compounds, their relative energies, their symmetry point group and their ground electronic state along with their corresponding boron analogues, are presented in Figure 1. The structures of other higher energy isomers are available in the supporting information (SI, tables S1-S4). All structures presented in Figure 1 are singlet; the triplet PES has also been exhaustively explored for the $Li_3B_3H_6$ cluster; for the larger clusters, we have optimized in triplet multiplicity the most stable structures obtained from singlet PES exploration. The calculations show that triplet state is not energetically favored in any of the analyzed systems. For instance, the most stable triplet for $Li_3B_3H_6$ is higher in energy than the most stable singlet by more than 40.2 kcal.mol^{-1}; and, for larger clusters, the triplet is about 50.0 kcal.mol^{-1} above the most stable singlet.

As Figure 1 shows, the cyclic structure is not energetically favored when the size of the $Li_nB_nH_{2n}$ systems increases, opposite to what happens in their organic counterparts. Therefore, the ET concept did not lead to a thermodynamically viable boron-based cyclic isomer. However, it is important to remark the predictive capability of the ET concept in the smallest cluster of this series. Not only it predicts the most stable boron-based isomers, but also their relative stability (the energy difference between the two most stable isomers of $Li_3B_3H_6$ (I'.1 and I'.2) is of 11.2 kcal.mol^{-1}, which is comparable with the energy difference between propene (I.1) and cyclopropane (I.2) molecules.

For $Li_4B_4H_8$, the cyclic isomer is located 41.8 kcal.mol^{-1} above the global minimum; in contrast to cyclobutane, which is only 10.8 kcal.mol^{-1} above the global minimum (2-methylpropene). However, it is important to remark that ET concept succeeds in accurately predicting the global minimum structure. As we can see in Figure 1, the structural analogy of B_4H_8 fragment in II'.1 with the 2-methylpropene (II.1) is evident.

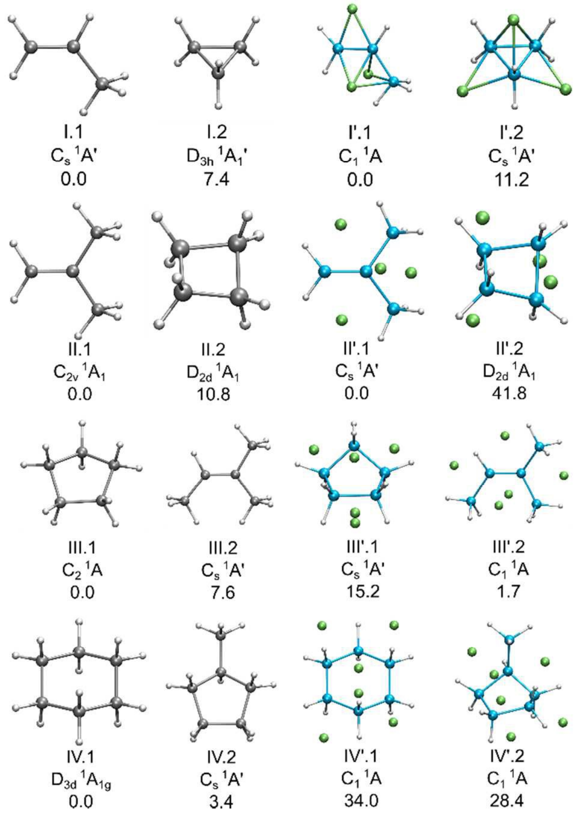

Figure 1. Structures, symmetry point-groups, ground electronic state and relative energy at the CCSD(T)/Def2-TZVP//PBE0/Def2TZVP level of theory of the lowest energy isomers of the C_nH_{2n} (n=3-6), and their corresponding boron analogues ($Li_nB_nH_{2n}$ (n=3-6)). Here and elsewhere spheres in grey, white, light blue and green represent C, H, B and Li, respectively.

The drastically reduced strain in C_5H_{10} and C_6H_{12},[58, 59] promote the stabilization of cyclopentane and cyclohexane, which are the global minimum isomers. In contrast, their boron analogues, structures III'.1 and IV'.1, are 15.2 and 34.0 kcal.mol^{-1} higher in energy isomers. As in the previously described small clusters, a classic non cyclic structure is energetically favored in $Li_5B_5H_{10}$ (III'.2), which is the analogue of 2-methyl-2-butene (III.2). However, in $Li_6B_6H_{12}$, neither of the two most stable organic-like structures (IV'.1 and IV'.2) is energetically favored.

The results discussed above show that, among the cyclic structures, the small system ($Li_3B_3H_6$) is the most energetically favored. However, this is not the global minimum isomer, disabling it as a viable target for experimental detection (in gas phase). On the other hand, the aromatic rings $Li_6B_6H_6$ and $Li_7B_5H_5^+$ (D_{5h}), have been reported as global minimum isomers.[10, 19] This suggests that aromaticity is a key-stabilizing factor that needs to be considered for designing stable lithium boron hydrides analogues of cyclic organic compounds. We decided to verify this hypothesis designing the analogue of the smallest aromatic carbocation ($C_3H_3^+$), the $Li_3B_3H_3^+$ system. It should be noted that this system as well as other isoelectronic species have been proposed in the past as aromatic rings,[60, 61] however in those works these clusters have not been

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confirmed as global minima. As it is shown in figure 2, such global minimum (V'.1), obtained from PES search, is singlet and contains a B_3H_3 fragment, which is structurally analogue to the cyclopropenyl cation (V.1). The second most stable isomer of $Li_3B_3H_3^+$ (V'.2) also has structural similarities with the second most stable isomer of $C_3H_3^+$ (V.2). However, there are small deviations, the C-C-C angle in V.2 is 180°, whereas the B-B-B angle in V'.2 is 161°. Similar deviations have been observed in alkane-analogue aluminum homocatenated compounds, where distortions maximize the interaction of terminal hydrogen with the Li^+ counterions.[18] Despite all that, the energy difference between the two most stable isomers follows the same order: 27.6 $kcal.mol^{-1}$ and 25.3 $kcal.mol^{-1}$, for the organic and inorganic analogues, respectively. The structures of other higher energy isomers of the $Li_3B_3H_3^+$ cluster are available in the supporting information (SI, Table S5). In order to check for a possible multi-configurational character in the wave function of the analyzed isomers, the T1 diagnosis was performed.[44] According to this analysis, if T1 is less than 0.02, the wave function has no significant multi-configurational character. All of the T1 values obtained for the reported systems (in figure 2) were lower than 0.02, indicating that there is no need for a multi-configurational treatment. This finally validates the reliability of our DFT and CCSD(T) computations.

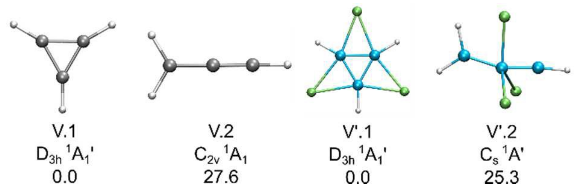

Figure 2. Structures, symmetry point-groups, ground electronic state and relative energy at the CCSD(T)/Def2-TZVP//PBE0/Def2TZVP level of theory of the lowest energy isomers of the $C_3H_3^+$ and those of their corresponding boron analogue $Li_3B_3H_3^+$.

In order to complement the stability analysis of the $Li_3B_3H_3^+$ cluster, Born-Oppenheimer Molecular-Dynamics (BO-MD) simulations were done at 900 K for 20 picoseconds (ps) with a time steep of 1fs (the corresponding movie is included in the supporting information). The system maintained its structure (V'.1) at 900K during the complete time interval considered for the simulation. There are some fluctuations in the positions of the lithium atoms; however, the boron-hydrogen skeleton of this system remained intact. This analysis ensures the persistence of structure even at elevated temperatures.

Bonding Analysis

As in previous successful predictions of the ET concept, it is expected that structural analogies between organic with their boron counterparts coincide in their chemical bonding. In order to check this, we have used the adaptive natural density partitioning (AdNDP) method. The organic systems have been also included in the analysis in order to be compared. As representative examples, we reported here the chemical bonding analysis for the cyclic isomers of C_3H_6 and $C_3H_3^+$ and their corresponding boron analogues.

For cyclopropane, AdNDP distributed the electron density in classical two-center two-electron (2c-2e) σ bonds (three C-C and six C-H bonds) each with an occupation number (ON)=1.99 |e| (Figure 3-a), which completely agrees with the classical representation of this molecule. For the boron analogue (I'.2), AdNDP predicts three 2c-2e B-B σ bonds with ON between 1.88 and 1.93 |e|. Additionally, the analysis indicate the presence of six 2c-2e B-H σ bonds with an ON between 1.93 and 1.95 |e| (Figure 2-b). The small discrepancies between the ON, for the same kind of chemical bonds, could be justified by the asymmetrical distribution of the Li^+ counterions.

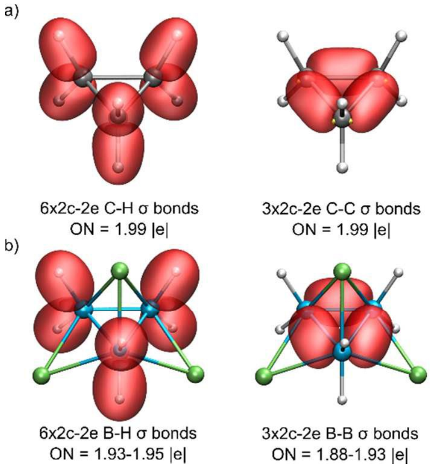

Figure 3. Results of the AdNDP analysis at the PBE0/Def2-TZVP level of theory of systems a) I.2 and b) I'.2. ON stands for occupation number.

In the case of the cyclopropenyl cation ($C_3H_3^+$), AdNDP distributes the valence electrons into: three 2c-2e C-C σ bonds (ON=1.98|e|), three 2c-2e C-H σ bonds (ON=1.99|e|) and one delocalized 3c-2e π bond (ON=2.00|e|); supporting the aromatic character of this cation (see Figure 4-a). As it is shown in part b of Figure 4, for the boron analogue of the cyclopropenyl cation ($Li_3B_3H_3^+$, V'.1), AdNDP distributes their valence electrons into: three 2c-2e B-B σ bonds (ON=1.95|e|), three 2c-2e B-H σ bonds (ON=1.98|e|) and one delocalized 3c-2e π bond (ON=1.97|e|). The π bond is mainly delocalized around the B_3 fragment.

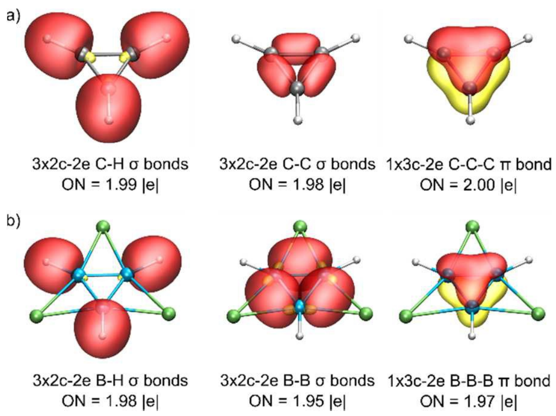

Figure 4. Results of the AdNDP analysis at the PBE0/Def2-TZVP level of theory of systems a) II.1 and b) II'.1. ON stands for occupation number.

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The chemical bonding analysis shows striking similarities between C-C and C-H with B-B and B-H, respectively. Even the presence of a delocalized π bond, symptom of an aromatic character of the $C_3H_3^+$, is also found in their boron counterpart. The AdNDP results for the noncyclic isomers (I'.1 and V'.2) are reported in Figures S1 and S2 in the supporting information. Similarly to what happens with the cyclic isomers, the analogy between organic and inorganic structures coincide with their chemical bonding. Moreover, it is important to note that all AdNDP localized orbitals have ON values close to the ideal value of 2.0 |e|, which validates these chemical bonding representations. In order to complement this analysis, we have performed calculations of atomic charges using the Natural Population Analysis (NPA), which confirms that in both boron-containing compounds ($Li_3B_3H_6$ and $Li_3B_3H_3^+$), boron has acquired one electron from each lithium atom and has electronically been transmuted into their carbon analogues: q(Li_3 fragment) = +2.553 in I'.2 and q(Li_3 fragment) = +2.862 in V'.1. Interestingly, similar trends were found for the other low energy isomers (see Tables S6 and S7 in the supporting information).

Finally, with the aim of performing a more rigorous comparative analysis of chemical bonding between the aromatic species V.1 and V'.1, we have evaluated their magnetic response through the analysis of the *z*-component of the induced magnetic field (B^{ind}_z). The plots of the isolines of the B^{ind}_z are depicted in Figure 5. The cyclopropenyl cation, with two delocalized π-electrons, shows a shielding (diatropic) region covering the molecular ring (as for benzene, this behavior is associated with an aromatic response). Strikingly, the new $B_3H_3Li_3^+$ system shows a similar response: a diatropic region surrounding the triangular B_3H_3 core, and the lithium atoms lying at the edge of the shielding zones. We are aware that aromaticity is currently described as a multidimensional phenomenon implying that it cannot be quantified using a single index,[62-65] for this reason we used an alternative aromaticity descriptor based in electronic delocalization estimation,[66] the multi-center delocalization index (MCI).[50-52] MCI gives an idea of the electron sharing between all atoms in the ring. The more positive the MCI value is the more aromatic the ring.[52, 67, 68] The MCI and MCI_π values obtained for $Li_3B_3H_3^+$ (D_{3h}) are 0.175 and 0.108 e, respectively, not far from the values 0.221 and 0.144 e, obtained for its organic counterpart ($C_3H_3^+$, D_{3h}). Then, electronic delocalization can be considered as having the same nature in both the cyclopropenyl cation and its boron analogue.

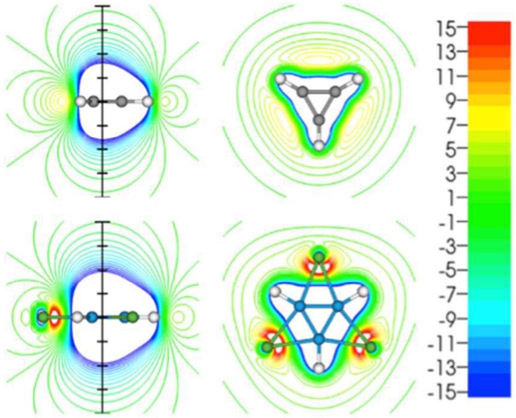

Figure 5. Isolines of the B^{ind}_z computed for $C_3H_3^+$ (top) and for $Li_3B_3H_3^+$ (bottom). At the left are the planes that bisect the molecular plane, and at the right the molecular planes. Negative and positive values are associated with diatropic and paratropic regions, respectively. The scale is in ppm considering $\mathbf{B}^{ext}$ = 1 T. The vertical axis (on the left) ranges from -4 to 4 Å, divided into intervals of 1 Å.

Conclusions

In summary, boron avoids cycloalkane-like structures in the $Li_nB_nH_{2n}$ (n=3-6) series, which is different in their organic counterparts (C_nH_{2n}), where cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}) are the low-lying isomers. It appears that aromaticity is a key stabilizing factor that needs to be considered in the design of cyclic lithium boron hydrides. This was verified here, through the design of a cyclopropyl cation analogue, the $Li_3B_3H_3^+$ (D_{3h}) cluster, which is the lowest-lying energy form on the corresponding PES. This raises expectations that this cluster can be prepared experimentally in the gas phase. We are aware of the limitations present in experimental synthesis, in a condensed phase, of compounds containing boron rings.[1, 69-71] But it opens the possibility of designing stable and aromatic compounds by reducing boron hydrides with lithium molecules (in gas phase); and producing lithium boron hydrides isoelectronic and isostructural to aromatic hydrocarbons.

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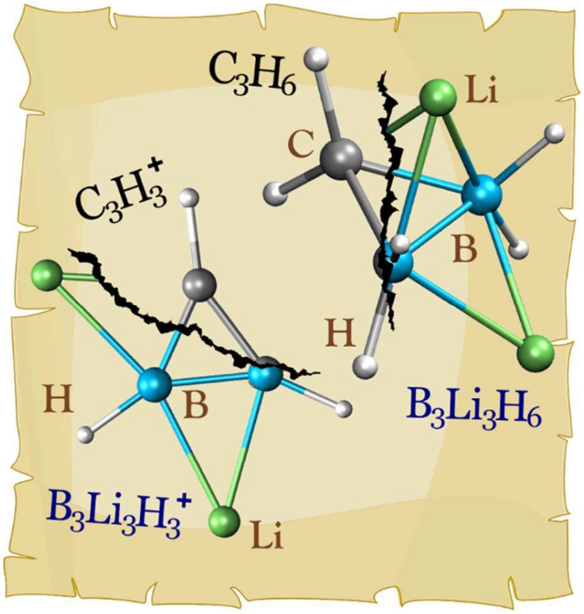
The stability of cycloalkane-like structures in the series $Li_nB_nH_{2n}$ is analyzed using ab-initio calculations. Neither of these cyclic species is energetically favored, contrary to what happens with aromatic lithium boron hydride rings



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