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Stabilizing carbon-lithium stars†

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We have explored *in silico* the potential energy surfaces of the $C_5Li_n^{n-6}$ ($n = 5, 6, \text{ and } 7$) clusters using the Gradient Embedded Genetic Algorithm (GEGA) and other computational strategies. The most stable forms of $C_5Li_5^-$ and C_5Li_6 are two carbon chains linked by two lithium atoms in a persistent seven membered ring capped by two Li atoms. The other Li atoms are arrayed on the edge of the seven membered ring. In contrast, the global minimum structure for $C_5Li_7^+$ is a bicapped star of D_{5h} symmetry. The molecular orbital analysis and computed magnetic field data suggest that electron delocalization, as well as the saturation of the apical positions of the five-membered carbon ring with lithium atoms in $C_5Li_7^+$ plays a key role in the stabilization of the carbon-lithium star. In fact, the planar star sub-structure for the carbon ring are unstable without the apical caps. This is also what has been found for the Si analogues. The split of the B_z^{ind} in its σ - and π -contribution indicates that $C_5Li_7^+$ is a π -aromatic and σ -nonaromatic system.

Introduction

During the last two decades, several groups have been interested in the stabilization of the perlithiated analogue of the cyclopentadienyl (Cp^-) anion, $C_5Li_5^-$.¹⁻⁴ Bretschneider-Hurley and Winter claimed the formation of the perlithiation product of ruthenocene $Ru(C_5Li_5)_2$ in 1994.¹ The $C_5Li_5^-$ ring substituent would be an intriguing species, if stable, but because of the ionic character of the C–Li bonding,⁵ lithium evidently prefers bridging positions⁶⁻⁹ and, therefore, the structure of the ligand can hardly be expected to follow classical expectations (or satisfy our own biases towards the aesthetically pleasing symmetries in Fig. 1).³

In 1997, Jemmis *et al.* studied the structures and energies of lithiated cyclopropenyl cations computationally.¹⁰ They found that the most stable form of $C_3Li_3^+$ is a triply bridged trilithiocyclopropenium ion with a beautiful starlike D_{3h} geometry containing three planar tetracoordinate carbon (ptC) atoms (see Fig. 1). Later on, the group of Minkin proposed a series

of planar starlike perlithioannulenes (see Fig. 1), including the D_{5h} $C_5Li_5^-$ cluster.³ These systems were shown to be local minima, but the authors did not explore in detail the potential energy surfaces of these binary clusters. So, it is unclear whether these star-like isomers are the thermodynamically preferred arrangement of the atoms in those $C_nLi_n^x$ species. Quite recently, the $C_5Li_5^-$ unit has been used as a ligand, in analogy to Cp^- , to assemble on paper some novel series of metallocenes.^{2,4} However, in that contribution as well the assumption was made that $C_5Li_5^-$ is stable compared to other potential isomers.

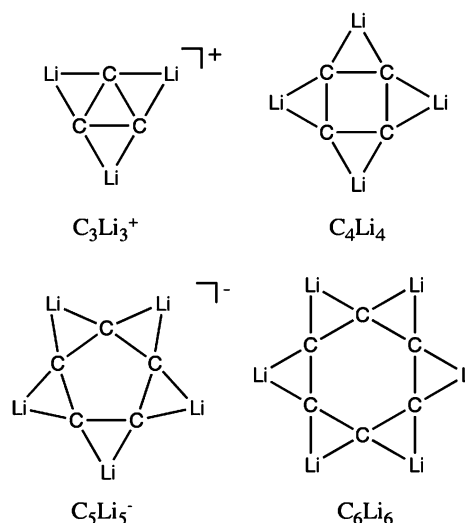


Fig. 1 Carbon-lithium molecular stars.

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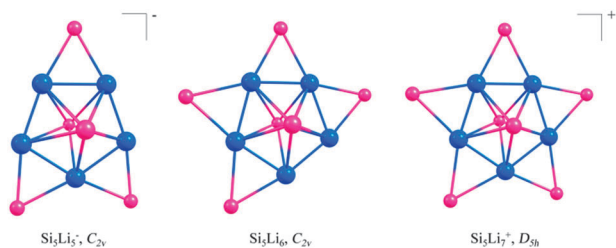


Fig. 2 Lowest energy structures of Si₅Li₅⁻, Si₅Li₆, and Si₅Li₇⁺ calculated at the B3LYP/def2-TZVPP level.

Two years ago, three of the current authors and others explored the potential energy surfaces of some silicon-lithium clusters with formula Si₅Li_{*n*}^{*n*-6} (*n* = 5–7) (See Fig. 2).¹¹ All of them preserve a bicapped five-membered ring (Si₅Li₂) fragment, with the other Li atoms in bridging positions on the periphery coplanar with the five membered ring (Fig. 2). For Si₅Li₇⁺, the five extra lithium atoms occupy all the vacant bridges, maintaining the silicon ring skeleton and forming a perfect global minimum starlike structure. Surprisingly, later on, a study of the slightly larger Si₆Li₆ system showed that the global minimum of that cluster does not contain a silicon ring,¹² indicating that the capped star bonding pattern is not necessarily transferable to larger rings.

Organic chemistry teaches us that high energy isomers may be just as interesting as global minima (*e.g.*, cubane *vs.* styrene in the C₈H₈ family).¹³ However, for clusters such as C₅Li₅⁻, the assortment of products obtained in the gas-phase under “annealing” conditions tend to contain primarily the low-energy isomers. So, for these exotic clusters experimental confirmation would only be anticipated for the lowest energy-lying isomers.

In this paper, we analyse in detail the stability, the electronic structure, and the bonding patterns of three carbon-lithium clusters: C₅Li₅⁻, C₅Li₆, and C₅Li₇⁺. The main goal is to establish rules governing the stability of the carbon-lithium starlike molecule(s). We find that the most stable form of C₅Li₅⁻ is not the D_{5h} one. So, how to stabilize a carbon-lithium star? We converge on such a system only when *n* = 7.

Our results show that the stability of a three-dimensional starlike carbon-lithium structure mandates the capping fragment as a pre-requisite due to the relative stability of the five fold (half-sandwich) interaction of Li with the entire C₅⁻ ring compared to the formation of a Li–C bond in the plane of the ring. We demonstrate that the most stable structure for C₅Li₇⁺ has a perfect D_{5h} seven-peak starlike structure.

Computational details

Potential energy surfaces were explored using the gradient embedded genetic algorithm (GEGA) program.^{14,15} We used the B3LYP^{16,17} functional as implemented in the Gaussian 03 program¹⁸ with the SDD¹⁹ basis set for energy, gradient, and force calculations. We reoptimized geometries and calculated frequencies at the B3LYP/def2-TZVPP²⁰ level for all the isomers that were found. Total energies were also recalculated at the CCSD(T)²¹/def2-TZVPP//B3LYP/def2-TZVPP level. The energy differences presented include the zero point energy

corrections obtained at the B3LYP/def2-TZVPP level. To analyse the bonding mechanism, a natural population analysis (NPA)²² was done. Additionally, the nature of the bonding in structures 3-A and 3-C was analysed using an Energy Decomposition Analysis (EDA); both systems were divided into two fragments, C₅Li₂⁴⁻ and Li₅⁵⁺, whose structures were taken from the Gaussian 03 geometry optimizations. The EDA computations were carried out using the exchange functional of Becke²³ in conjunction with the correlation functional of Perdew²⁴ in ADF2009.01.^{25,26} The basis set has triple- ζ quality augmented by two sets of polarization, that is, d and f functions for carbon and lithium atoms.

In order to evaluate the electron delocalization present in the C₅Li₇⁺ cluster discussed herein we performed an induced magnetic field analysis²⁷ using the PW91²⁸ functional in conjunction with the IGLO-III basis set for carbon and IGLO-II for lithium. The shielding tensors were computed using the IGLO method.²⁹ The deMon-2k program³⁰ was used to compute the molecular orbitals and the deMon-NMR package³¹ was employed for the shielding tensors. Induced magnetic fields were computed in ppm of the external field applied perpendicularly to the molecular plane. Assuming an external field of 1.0 T, the unit of the induced field is 1.0 mT, which is equivalent to 1.0 ppm of the shielding tensor.

The C₅Li₅⁻ anion

Fig. 3 shows the several isomers found within 15.0 kcal·mol⁻¹ above the lowest energy structure (see ESI for details concerning cartesian coordinates, energy and zero-point correction). Calculations reveal that the most stable isomer of the C₅Li₅⁻ assemblies is the singlet three-dimensional C_s structure 1-A, which is a bicapped seven membered ring build up from a

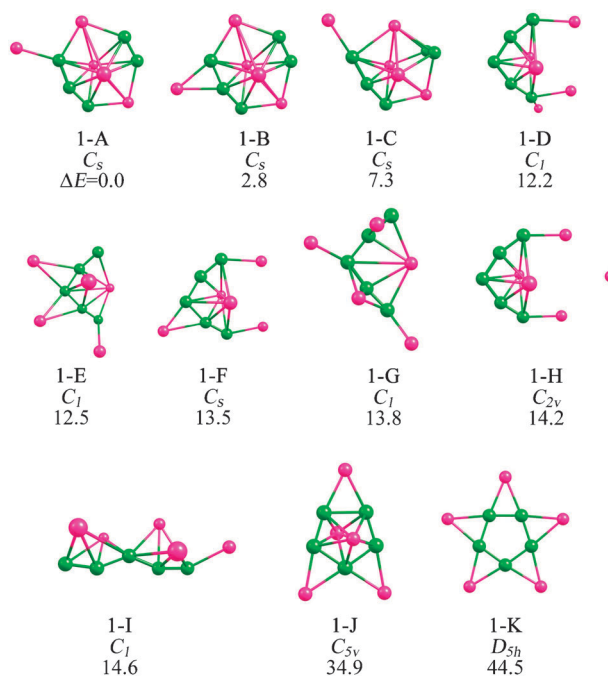


Fig. 3 Isomers for C₅Li₅⁻. Relative energies calculated at the CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP level with respect to structure 1-A are given in kcal·mol⁻¹.

3-carbon chain and a 2-carbon chain mediated by two lithium atoms, with a Li atom above and below the ring. The final Li atom is bonded to one C in the C₃ fragment. This species and others based on it such as **1-B** and **1-C** may be viewed as complexes involving a C₂²⁻ and a C₃⁴⁻ subunit interacting with the array Li⁺ ions in the system. The second most stable isomer, **1-B**, is 2.8 kcal·mol⁻¹ higher in energy than **1-A**. It arises from the movement of the final Li atom in **1-A** to a bridging position; while the third most stable isomer, **1-C**, comes up from the 90 degrees rotation of the two-carbon fragment. We also found isomers with a five-membered carbon chain (**1D-1I**), each of which is less stable than the global minimum for at least 12.0 kcal·mol⁻¹. Intentionally, we added two more arrangements, **1-J** and **1-K**. The first one is analogous to the global minimum for Si₅Li₅⁻, and the second is the one proposed by Minkin and coworkers.³ Both are considerably higher in energy than **1-A**, by 34.9 and 44.5 kcal·mol⁻¹, respectively. So, like the Si analogue, the basic rule of thumb that the cap is more stable than the edge applies for the C₅Li₅⁻ structure, too, even if the Li inserts itself into the ring as well.

C₅Li₆

The most stable structure for C₅Li₆ (**2-A**) is also asymmetrical (see ESI for details), with two carbon chains bridged by lithium atoms. The global minimum is 2.6 kcal·mol⁻¹ more stable than the second most stable isomer (**2-B**). The fourth most stable structure (**2-D**) is a beautiful C_{5v} molecular star that is only 5.7 kcal·mol⁻¹ higher in energy. This isomer is hardly surprising since the half-sandwich Cp-Li in which the equatorial Li atoms in **2-D** are replaced by terminal H atoms is known to be stable.³² Structure **2-E**, the analogue of the Si₅Li₆ global minimum, is only 10.4 kcal·mol⁻¹ less stable than **2-A** (See Fig. 4).

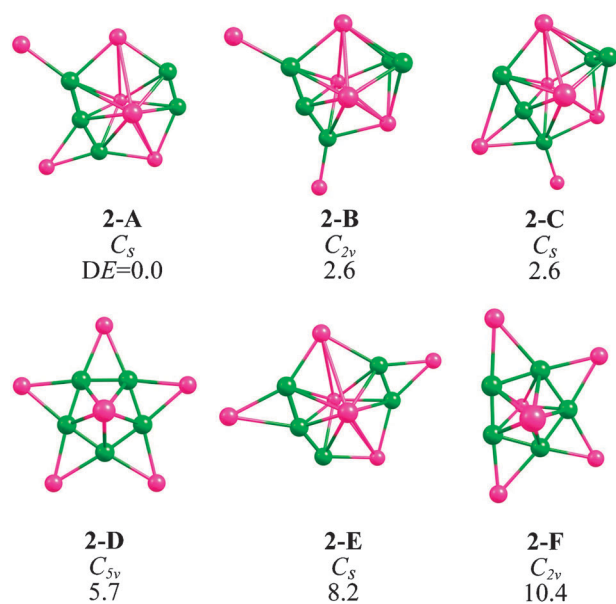


Fig. 4 Isomers for C₅Li₆. Relative energies calculated at the CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP level with respect to structure **2-A** are given in kcal·mol⁻¹.

The C₅Li₇⁺ cation

The last chance for stabilizing a star structure in C₅Li_n analogous to those identified previously for the Si₅Li_n systems is at n = 7, where all the C edges are saturated. Our results show that it is only under these conditions—where the caps are in place and the C edges are identically saturated—that the carbon pentagon star is stabilized. Notice that the bridging Li arrangement is far more stable in C₅Li₆ than it is in C₅Li₅⁻ if we compare, for example, the energy difference between **1-A** and **1-K** on the one hand vs. the energy difference between **2-A** and **2-D**. This suggests that the stability of the three-center C–Li–C in plane fragments (as in **2-D** in Fig. 4) is a function of the number of the Li atoms in the systems. Put another way, the bridges become increasingly stable as the bonding environment of the C atoms in the ring become more and more similar. This characteristic may be mandated by the increasing aromaticity of the systems when the C sites are equivalent. As one reviewer suggests as well, the decrease in the total Li–Li repulsion by disrupting the Li₄ unit in the **3-B** isomer helps to explain why **3-A** is the preferred isomer of the C₅Li₇⁺ cation. Moreover, the relocation of two of these Li atoms to the C-skeleton reduces the net charge negative on the C₃ and C₂ fragments as well, and makes the closure of the 5-membered ring much more favourable. From that perspective, it is rather unsurprising, therefore, that for the C₅Li₇⁺ monocation the most stable structure, **3-A**, is a perfect seven-point three-dimensional molecular star (see ESI for details). This structure is reminiscent, too, of the inverse Li sandwich systems such as C₄H₄Li₂.³³ Within the range of 15 kcal·mol⁻¹, only one other isomer (**3-B**) was detected (See Fig. 5). It is 10.5 kcal·mol⁻¹ higher than **3-A**.

Other arrangements were found as well, but they are more than 20 kcal·mol⁻¹ less stable than the global minimum. The most stable triplet structure is 39.7 kcal·mol⁻¹ higher in energy than the global minimum **3-A**, which excludes further considerations on high-spin species.

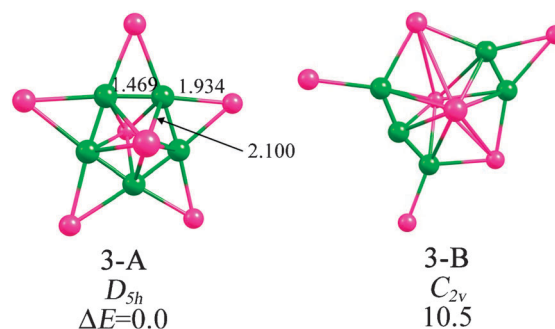


Fig. 5 Isomers for C₅Li₇⁺. The relative energies calculated at the CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP level with respect to **3-A** are given in kcal·mol⁻¹. The bond lengths are in Å.

Structure and bonding in C₅Li₇⁺

Each carbon atom in **3-A** is tetracoordinate in the equatorial plane of the molecule and interacts directly with the two Li atoms in the axial positions. So, the C atom is nominally hypercoordinate. This is not to suggest, however, that the

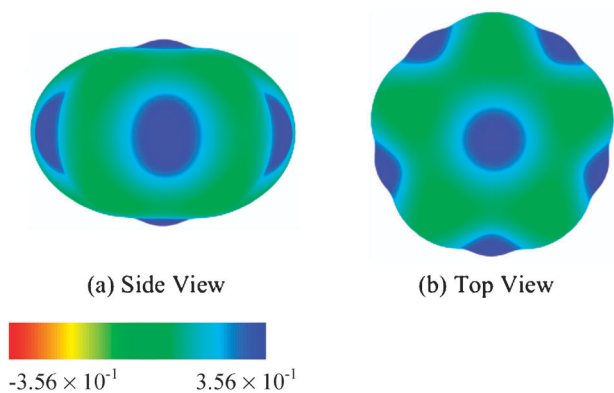


Fig. 6 Electrostatic potential map (with the scale in atomic units) for $C_5Li_7^+$ on the 0.001 electrons/bohr³ isodensity surface.

apical Li atoms form five covalent bonds to the Cp ring. The apical Li atoms form a single multi-center bond to the ring. Despite the higher coordination, the C–C bond lengths of 1.469 Å in **3-A** (see Fig. 5) are comparable with those in cyclopentadienyl anion (1.470 Å) obtained at the B3LYP/def2-TZVPP. This geometrical insensitivity to the Li bridges suggests that electron delocalization plays a significant role in the stabilization of the $C_5Li_7^+$ comparable to its role in Cp^- .

Moreover, an assessment of the C–C Wiberg bond index (WBI) gives a value of 1.42 in **3-A**. This formal bond order is extremely close to that which we obtain for the cyclopentadienyl anion (1.41) and benzene (1.44)! These results help us to appreciate the significant stability of the **3-A** structure in which every bridging and apical position of the five membered carbon ring is occupied with a lithium atom (compared to the **3-B** alternative, for example). Analysis of the bonding in this system, performed by natural population analysis (NPA), turns up rather large point charges for the Li atoms

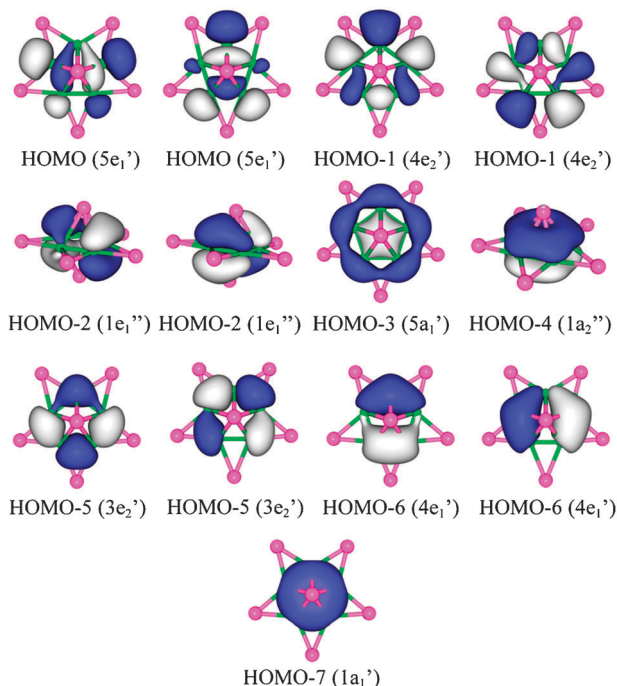


Fig. 7 Molecular orbitals of $C_5Li_7^+$.

Table 1 Energy decomposition analysis of $C_5Li_7^+$ at the BP86/TZ2P level. energies are given in kcal·mol⁻¹

	3-A	3-C
ΔE_{int}	-1613.4	-1554.6
ΔE_{Pauli}	163.2	113.2
ΔV_{elstat}	-1460.3	-1422.5
ΔE_{oi}	-316.2	-245.4

(+0.88|e| for the bridging lithiums, and +0.93|e| for the capping top and bottom lithiums). These large charges for the Li centres and a -1.06|e| charge for the carbon centres, indicates the dominance of the C–Li ionic interactions in **3-A**.⁵

The significant polarity of the C–Li bonds in the molecule is indicated as well by the dramatic variations in the electrostatic potentials across the isodensity surface in Fig. 6.

A side view (left) and a top view (right) are shown. The surface becomes increasingly blue as the electrostatic potential becomes more positive. The most intensely blue regions coincide with the Li centers in the structure.

In order to get some deeper insights into the nature of the C–Li interaction, we performed an Energy Decomposition Analysis (EDA) for **3-A** and for the hypothetical structure **3-C** where lithium atoms are not in bridging positions, but are instead, in the classical terminal positions. This **3-C** structure was optimized at the B3LYP/def2-TZVPP level, and was found to be a third order saddle point, and 72.9 kcal·mol⁻¹ less stable than **3-A** at the CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP level. $C_5Li_2^{4-}$ and Li_5^{5+} were taken as the two interacting fragments to analyse the in-plane equatorial C··Li bonding interactions. Table 1 summarizes the results. As expected, the total interaction energy between $C_5Li_2^{4-}$ and Li_5^{5+} is lower (more negative) for **3-A** than it is for **3-C** by 58.8 kcal·mol⁻¹. The Pauli repulsion term for **3-A** is higher by 50.0 kcal·mol⁻¹. However, this excess in the Pauli repulsion is well compensated for by the electrostatic and orbital terms, which are 37.8 kcal·mol⁻¹ and 70.8 kcal·mol⁻¹, respectively, lower for **3-A** compared to **3-C**. These results suggest that the electrostatic stabilization plus the orbital contributions to the interaction energy are the important drivers behind the preference for the bridged structure.

A look at the $C_5Li_7^+$ (**3-A**) molecular orbitals proves to be very instructive. The highest occupied molecular orbital (HOMO) is a doubly occupied degenerated σ orbital ($5e_1'$). As in benzene and cyclopentadienyl, there are six π -electrons distributed in the HOMO-2 ($1e_1''$ degenerated π orbital set) and in the HOMO-4 ($1a_2''$) levels (see Fig. 7). The stability of the obviously planar ' C_5Li_5 ' fragment in $C_5Li_7^+$ can be partially attributed to the influence of the six highly delocalized π -electrons and the stability of the σ -skeleton with its six σ -type radial electrons. These are exactly the same molecular orbitals as in $Si_5Li_7^+$, where the only difference is the ordering of the energy levels (see Fig. 7).

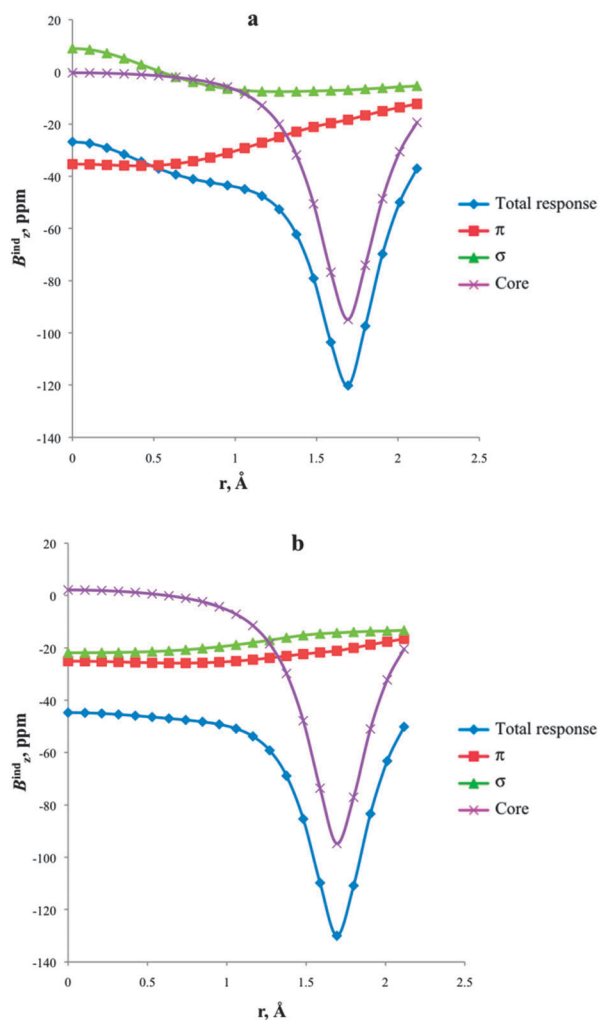


Fig. 8 B_z^{ind} profiles of (a) C_5Li_7^+ and (b) Si_5Li_7^+ calculated at the PW91/IGLO level. The total response, σ -, π -, and core-contributions are shown.

Aromaticity

The aromatic stabilization hypothesis, pointed out in the previous section, has been tested by an in-depth analysis of the induced magnetic field \mathbf{B}^{ind} . Using this technique, we have been able to explain electron delocalization in a plethora of exotic molecules.^{34–42} We have previously shown by the induced magnetic field analysis (\mathbf{B}^{ind}) that aromaticity plays an important role in the stabilization of the $\text{Si}_5\text{Li}_n^{n-6}$ systems.¹¹

In order to evaluate electron delocalization in the C_5Li_7^+ cluster, we performed an induced magnetic field analysis²⁷ using the PW91²⁸ functional in conjunction with the IGLO-III basis set for carbon and IGLO-II for lithium. Note that the z-component of the induced magnetic field is mathematically equal to the NICS_{zz} .⁴³

Fig. 8 depicts the B_z^{ind} profiles for the global minimum structures of C_5Li_7^+ and Si_5Li_7^+ , respectively. The B_z^{ind} value at the centre of the C_5 ring in C_5Li_7^+ is about -26.8 ppm, which is comparable to that in benzene and Cp^- . However, this value is less negative than the one in the Si_5Li_7^+ systems (-44.7 ppm). These results confirm that electron

delocalization is hardly attenuated in the carbon-lithium C_5Li_7^+ cluster (compared to the Cp^- case itself), and that this delocalization substantially enhances the stability of the C_5Li_7^+ cation.

We have plotted in Fig. 8 the contributions of the σ -, π -, and core-electrons for both systems to the B_z^{ind} at the center of the ring and above it up to 2.00 \AA . The dramatic dip in B_z^{ind} arises because we pass through the axial Li center around $1.65\text{--}1.80 \text{ \AA}$ above the ring in both the C and Si systems. As it is also shown in Fig. 8, the π -contribution to the B_z^{ind} at the centre of the ring is around 10 ppm higher for C_5Li_7^+ than it is for Si_5Li_7^+ . Nevertheless, for the σ -contribution the trend changes drastically. While σ - and π -contributions in Si_5Li_7^+ are almost the same, resulting in a two-fold aromatic system, C_5Li_7^+ can be considered as a π -aromatic and σ -nonaromatic system.

Conclusions

We have explored in detail the potential energy surfaces of the $\text{C}_5\text{Li}_n^{n-6}$ ($n = 5\text{--}7$) systems. We find that the saturation of the bridging and apical positions of a carbon ring with lithium atoms leads to a stable structure containing several hyper-coordinate carbon centers, and we show that this stabilization is enhanced by electron delocalization. Given that the structures here reported are global minima on their corresponding potential energy surfaces, we propose them as good candidates for experimental detection. The apical positions, we find, must be occupied in the Si and the C systems in preference to the equatorial sites. For this reason, in the C systems at least, the star type multi-center bonding between the C and Li atoms and the stability of the planar tetracoordinated carbon centers is accomplished only when the apical atoms are in position and the equatorial positions are identically bridged.

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