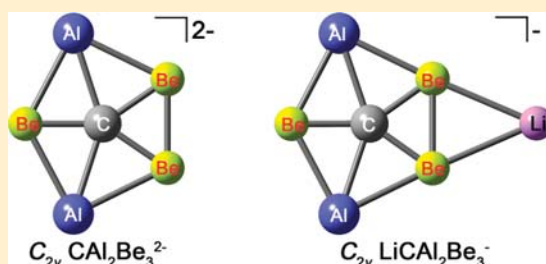


CAI₂Be₃²⁻ and Its Salt Complex LiCAI₂Be₃⁻: Anionic Global Minima with Planar Pentacoordinate Carbon

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Supporting Information

ABSTRACT: Following the isoelectronic relationship in global minima planar pentacoordinate carbon (ppC) species (cationic CAI₅⁺, neutral CAI₄Be, and monoanionic CAI₃Be₂⁻), we designed a dianionic ppC species C_{2v} CAI₂Be₃²⁻ (**1a**) and its salt complex C_{2v} LiCAI₂Be₃⁻ (**2a**) in this work. In combination with DFT and high-level ab initio calculations (CCSD(T)), the extensive exploration on their potential energy surfaces indicates that they are the global minima. Their kinetic stability was proved by two sets of 100 ps ab initio Born–Oppenheimer molecular dynamic simulations at the B3LYP/6-31+G(d) level. The detailed analyses indicate that the introduction of Li⁺ into **1a** only influences the electrovalent bonding (through changing of the charge distribution) and the σ aromaticity (through changing of the in-plane ring current), while the structures, the bonding properties, the π aromaticity, and so forth are almost unchanged. Nevertheless, the MO energy levels, the HOMO–LUMO gaps, and the values of vertical detachment energies (VDEs) all verify that the lithiation significantly improves the stability. We think the ppC dianion **1a** is possible to detect directly in the gas-phase experiments, but it can be detected as its salt complex **2a** more easily.



1. INTRODUCTION

The planar tetracoordinate carbon (ptC), where carbon and its four ligand atoms are in the same plane, was first reported by Monkhorst in 1968 as a transition state (TS) of the interconversion of enantiomer with an asymmetry carbon without breaking bonds.¹ In 1970, Hoffmann, Alder, and Wilcox sponsored the project of stabilizing the ptC.² They analyzed the electron structure of planar methane, based on which they proposed a couple of strategies to stabilize the ptC. After the Schleyer and Pople groups reported the first feasible ptC molecule, 1,1-dilithiocyclopropane,³ a number of ptC species were reported.^{4–9} The concept of ptC was extended to planar pentacoordinate and hexacoordinate carbon (ppC and phC) in 2000–2001 by the Schleyer group.^{10,11} Planar tetracoordinate or hypercoordinate arrangements with other main group atoms (e.g., N, O, and Si) or transition metals (e.g., Ag, Au, Co, Ru, Cd, and Hg) have also been reported.^{12–21}

In 1991, Schleyer and Boldyrev designed the first examples of pentaatomic ptC species, *cis*- and *trans*-CSi₂Al₂,¹² whose isoelectronic species NaCAI₄⁻, CAI₃Si⁻, and CAI₃Ge⁻ with a C_{2v} point group had been detected in the photoelectron spectroscopy by the Wang–Boldyrev group in 1999–2000.^{22–24} It is found that the planar structure is stabilized by 18 valence electrons. Remarkably, under their gas-phase experimental conditions, the thermodynamic favorable isomers (especially the global minima) will be strongly enriched. The combined theoretical analysis also proved that these ptC

species are the global minima on their potential energy surfaces (PESs). The experimental results attracted the attention on searching for the global minima planar hypercoordinate carbon species. The CCu₄²⁺, CCu₃Ni⁺, CCu₂Ni₂, CAI₃Sn⁻, CAI₃Pb⁻, CB₄⁺, CE₄²⁺ (E = Al, Ga, In, Tl), CBAl₃²⁻, CNAl₃, and so forth were found to be the global minima with a ptC.^{25–29} We found that D_{5h} C₅Al₅⁻ is nearly a global minimum with five ptCs.³⁰ In 2008, the Zeng–Schleyer group reported the first ppC global minimum, the D_{5h} CAI₅⁺ cation.³¹ In 2009, we found that D_{2h} C₂Al₄ is a simplest neutral global minimum with two ptCs³² and established a rational relationship among CAI₄²⁻, CAI₅⁺, and C₂Al₄. Adding two electrons to tetrahedral CAI₄ neutral molecule will result in the planar molecules with planar hypercoordinate carbon; the electrons are added directly in CAI₄²⁻, while they are added by introducing an Al⁺ in CAI₅⁺ and by introducing a C atom in C₂Al₄ (two electrons for C–C bonding). Following this electron rule, the neutral and monoanionic ppC species CAI₄Be and CAI₃Be₂⁻ with C_{2v} point group were found to also be the global minima in 2010.³³ Note that C₂Al₄ had been detected experimentally by single photon ionization spectroscopy in 2010.³⁴

Recently, the experimental and theoretical search for small, stable, multiply charged anions in the gas phase and the

Received: January 10, 2012

Revised: March 1, 2012

Published: March 19, 2012



examination of their geometric and electronic properties have quickly become the topic of a rapidly developing research field.^{35–39} Within the planar carbon chemistry, the dianionic ptC and phC species had been reported,^{10,23,29,40,41} of which the CAL_4^{2-} had been detected in the form of its salt complex NaCAL_4^- in the photoelectron spectroscopy.²³ However, to our knowledge, no ppC dianion has been reported. Can the intrinsic good electron structure in global minima ptC and ppC species (D_{4h} CAL_4^{2-} , D_{5h} CAL_5^+ , D_{2h} C_2Al_4 , C_{2v} CAL_4Be , and C_{2v} $\text{CAL}_3\text{Be}_2^-$) be used to design the dianionic species with novel ppC bonding? The answer turned out to be yes. Bearing the isoelectronic relationship of the above-mentioned species and the diagonal relationship between Al and Be in mind, we have explored the possibility of the isoelectronic $\text{CAL}_2\text{Be}_3^{2-}$ system having the ppC structure. The extensive explorations on the $\text{CAL}_2\text{Be}_3^{2-}$ PES suggest that its global minimum (**1a**; see Figure 1) has a ppC in the center. Moreover, we verify that the global

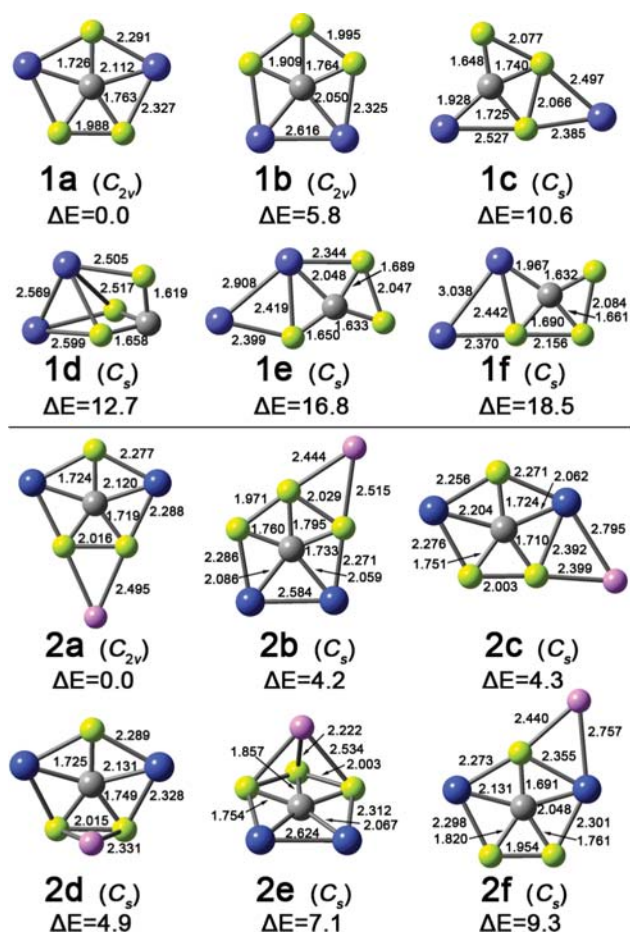


Figure 1. The CCSD(T)/aug-cc-pVTZ optimized structures of the six lowest isomers of $\text{CAL}_2\text{Be}_3^{2-}$ and $\text{LiCAL}_2\text{Be}_3^-$ with the relative energies (ΔE , in kcal/mol) and necessary bond lengths (in Å). Color codes: C: gray; Al: blue; Be: yellow; Li: purple.

minimum of $\text{LiCAL}_2\text{Be}_3^-$ (**2a**; see Figure 1) has an **1a** ppC moiety and an attached Li. The ab initio Born–Oppenheimer molecular dynamics (BOMD) simulations unveiled that **1a** and **2a** are both kinetically stable. We think the ppC dianion **1a** can possibly be detected in the gas-phase experiment, while its salt complex **2a** is even more promising than **1a**.

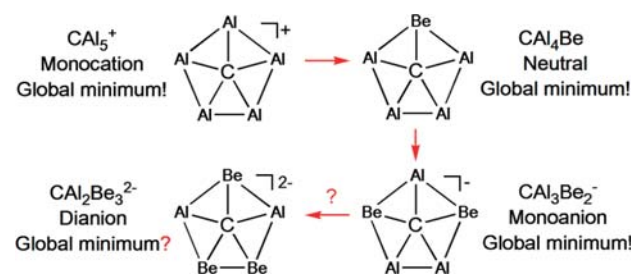
2. METHODS

The PESs of $\text{CAL}_2\text{Be}_3^{2-}$ and $\text{LiCAL}_2\text{Be}_3^-$ were explored using the stochastic search^{32,42} method (random Cartesian coordinates), which was coded in the GXYZ program.⁴³ Three sets of parallel searches for the singlet surface and two sets for the triplet surface were run to guarantee the convergence of PES exploration. For each set of stochastic searches, we initially generated a pool of random structures, which would be subjected to geometry optimization at the B3LYP/6-31+G(d) level. The low-lying isomers from all five sets of searches were optimized, and the harmonic vibrational frequencies were analyzed at the B3LYP/aug-cc-pVTZ level. The wave function stability of the concerned isomer was checked at the same level. The geometries of six lowest isomers of $\text{CAL}_2\text{Be}_3^{2-}$ and $\text{LiCAL}_2\text{Be}_3^-$ were further refined at the CCSD(T)/aug-cc-pVTZ level, and the refined geometries and energetic results were discussed. Two sets of BOMD simulations^{44,45} (at 4 and 298 K) were performed at the B3LYP/6-31+G(d) level for the global minima (**1a** and **2a**) to examine their kinetic stability. The natural bond orbital (NBO) analyses⁴⁶ were performed at the B3LYP/aug-cc-pVTZ level to deepen the understanding of the electron structures, and the nucleus-independent chemical shift (NICS)^{47,48} and electron localization function (ELF)⁴⁹ analyses were carried out to verify the aromaticity. The vertical detachment energies (VDEs) and electron affinity (EA) were calculated using the outer-valence Green's function (OVGF) procedure⁵⁰ in combination with the aug-cc-pVTZ basis set (i.e., at the OVGF/aug-cc-pVTZ level). The CCSD(T)/aug-cc-pVTZ optimization was performed by using the Molpro 2006.1 package,⁵¹ while other calculations were carried out by using the Gaussian 03⁵² and Gaussian 09 packages.⁵³

3. RESULTS AND DISCUSSION

As shown in Scheme 1, in the previous studies, one or two Al atoms in the cationic ppC global minimum D_{5h} CAL_5^+ was/were

Scheme 1



replaced with Be atoms, which resulted in the first neutral and monoanionic ppC global minima CAL_4Be and $\text{CAL}_3\text{Be}_2^-$.³¹ To acquire the dianionic species, we further replaced an Al atom in $\text{CAL}_3\text{Be}_2^-$ with a Be atom in this work. Two possible structures (see **1a** and **1b** in Figure 1) with ppC were both confirmed to be the energy minima at the B3LYP/aug-cc-pVTZ level. Though the HOMO–LUMO gaps are only 0.94 and 0.76 eV for **1a** and **1b** (see Table 1), respectively, their wave functions are stable. The CCSD(T)/aug-cc-pVTZ optimization gives very similar geometries. We then explored the PES of $\text{CAL}_2\text{Be}_3^{2-}$ using the stochastic search algorithm. At the final CCSD(T)/aug-cc-pVTZ level, **1a** was found to be the global minimum on the singlet surface, while **1b** was the second lowest isomer and 5.8 kcal/mol higher in energy than **1a**. The

Table 1. Lowest Vibrational Frequencies (ν_{\min} , in cm^{-1}), the Energy Levels of HOMOs (in eV), the HOMO–LUMO Gaps (in eV), and the VDE/EA Values (in eV) of **1a**, **1b**, **2a**, $\text{CAL}_3\text{Be}_2^-$, CAL_4Be , and CAL_5^+

	ν_{\min}	HOMO	gap	VDE/EA
1a	131	2.60	0.94	−1.10
1b	131	2.60	0.76	−1.18
2a	94	−0.74	1.79	2.28
$\text{CAL}_3\text{Be}_2^-$	110	−0.18	2.56	2.85
CAL_4Be	77	−5.40	2.60	7.03
CAL_5^+	69	−9.99	2.81	−4.69

structures of the third to sixth lowest isomers are given in Figure 1 as **1c–1f**, which are 10.6, 12.7, 16.8, and 18.5 kcal/mol, respectively, higher in energy than **1a**. In **1c–1f**, only **1d** has the 3D structure, while the other three isomers are all planar and have CALBe_3 ppC units and an attached Al atom. The lowest triplet isomer has a similar geometry to **1c**, but it is 4.9 kcal/mol higher in energy than **1c** (15.5 kcal/mol higher than **1a**); therefore, the triplet isomers are disregarded.

Though **1a** is the global minimum, this does not suffice for experimental viability predictions because the high net charge may lead to the strong trend to detach the extra electron. Such a trend can be verified by the positive energy levels of the five highest occupied molecular orbitals and the calculated negative VDE (−1.10 eV; see Table 1). In the experimental realization of multiple charged anions, the alkali metals were often employed to reduce the high net charge. For example, in the realization of CAL_4^{2-} , a Na^+ was added to counteract the high net charge (i.e., CAL_4^{2-} was detected as its salt complex NaCAL_4^-).²³ In this work, we used a Li^+ to counteract with the $\text{CAL}_2\text{Be}_3^{2-}$. The structures of $\text{LiCAL}_2\text{Be}_3^-$ isomers were obtained by the exploration of the PES at the B3LYP/6-31+G(d) level. After the refinement at B3LYP/aug-cc-pVTZ (optimization and frequency analyses) and CCSD(T)/aug-cc-pVTZ (optimization) levels, an isomer (**2a**; see Figure 1) with a Li atom bonded to the Be–Be bridge of **1a** was found to be the global minimum on the $\text{LiCAL}_2\text{Be}_3^-$ surface. The second lowest isomer (**2b**) has a **1b** ppC unit with a Li atom binding on the Be–Be bridge. The third to sixth lowest isomers are given in Figure 1 as **2c–2f**. It is interesting that these isomers all have a **1a** or **1b** ppC core and an attached Li atom.

Let us focus on the global minimum **2a**. Compared to **1a**, it just has an additional Li atom, which does not obviously affect the geometries of the **1a** unit (see the bond lengths of **1a** and **2a** in Figure 1). However, the net charge decreases from −2 in **1a** to −1 in **2a**, and this significantly affects the molecular stability. For example, the energies of all occupied molecular orbitals become negative. Correspondingly, the calculated first VDE is positive (2.28 eV; see Table 1), suggesting that the trend of automatic detachment of the extra electron is partly eliminated. In addition, the HOMO–LUMO gap increases from 0.94 eV in **1a** to 1.79 eV in **2a** (see Table 1). The stability comparisons suggest that **2a** is more realizable than **1a**.

The thermodynamic stability only controls the abundance of the isomers, while the kinetic stability controls the persistent capability of each isomer. The kinetic stability of **1a** and **2a** was studied by two sets of BOMD simulations (at 4 and 298 K, respectively). The structural undulation is depicted by the curves of the root-mean-square deviation (RMSD, in Å) versus simulation time. As shown in Figure 2, the RMSD curves for the simulations of both **1a** and **2a** have no sharp increase, which

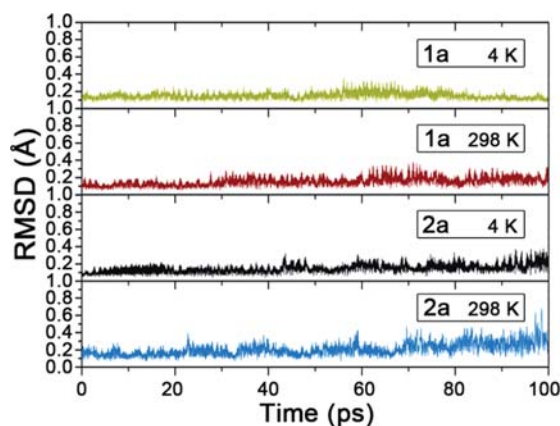


Figure 2. The RMSD versus time in the BOMD simulations of **1a** and **2a** at 4 and 298 K, respectively.

suggests that both of them are capable of maintaining the ppC structures during the 100 ps simulation at two different temperatures. The simulation result of **2a** is consistent with our expectation, while that of **1a** is beyond our expectation because there is a strong electrostatic repulsion, which may cause the Coulomb explosion. Remarkably, the fluctuation of all of the RMSD curves is very small, implying the very rigid ppC structures. The dynamic simulations reveal that **1a** and **2a** are kinetically stable.

1a and **2a** are the global minima with high kinetic stability; therefore, it is potentially possible to detect these two anionic ppC species in the gas-phase experiment. In the following discussion, we will focus on these two global minima. As shown in Figure 1, the C–Al and C–Be bond lengths in **1a** are 2.112 and 1.763/1.726 Å, respectively, at the CCSD(T)/aug-cc-pVTZ level, which are a little longer than the typical C–Al and C–Be bond lengths (~2.000 and ~1.650 Å) but close to the C–Al distance (2.120 Å) in CAL_5^{+31} and the C–Be distance (1.725 Å) in $\text{CAL}_3\text{Be}_2^{-33}$ at the same level. The structure of the CAL_2Be_3 ppC core in **2a** is close to **1a** (the differences for C–Al and C–Be bond lengths are less than 0.05 Å), which suggests that the introduction of Li^+ does not influence the structure of the ppC core obviously.

As shown in Table S1 in the Supporting Information, the NBO analysis reveals that the natural charge distributions on C, Al, and Be (Q_C , Q_{Al} , and Q_{Be}) in **1a** are −2.43, 0.27, and −0.03/−0.06 lel, respectively, while those in **2a** are −2.37, 0.51, and −0.17/0.05 lel, respectively, which suggest the obvious charge redistribution when Li^+ is added. Thus, the electrovalent bonding in **1a** is somewhat different from that in **2a**. However, this does not affect the covalent bonding notably. The total Wiberg bond index values (see Table S1, Supporting Information) for C, Al, and Be (WBI_C , WBI_{Al} , and WBI_{Be}) and Wiberg bond orders of C–Al and C–Be (WBI_{C-Al} and WBI_{C-Be}) in **1a** are very similar to those in **2a**. It is interesting that the Q_C values in **1a** and **2a** are smaller than those in CAL_5^+ (−2.80 lel), CAL_4Be (−2.61 lel), and $\text{CAL}_3\text{Be}_2^-$ (−2.48 lel), and this may be caused by two additional electrons that disperse the electron cloud through the Coulomb repulsion remarkably. Such dispersion can be concretely proved by the pictures of molecular orbitals shown in Figure 3. The MO pictures also suggest that the introduction of Li^+ only alters the shape of the LUMO and exchanges the energy order of HOMO−2 and HOMO−3; therefore, the electronic structure of **2a** is not essentially different from that of **1a**.

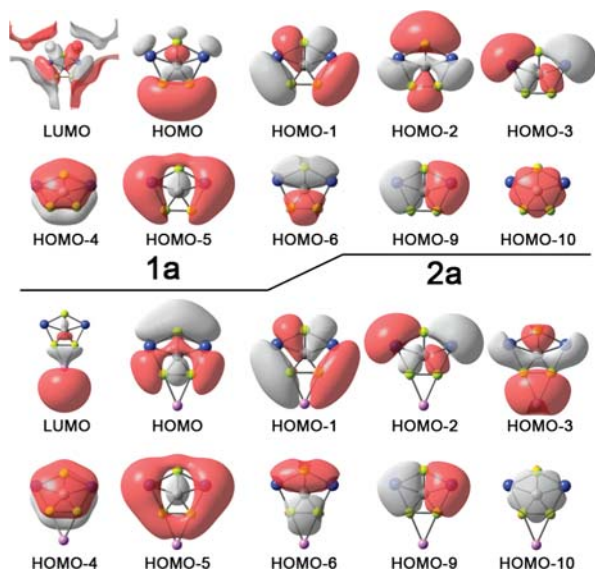


Figure 3. HOMO, LUMO, and occupied valence molecular orbitals of **1a** and **2a**. The isovalue for LUMO of **1a** is 0.002, and those for other MOs are 0.02.

NBO analysis also reveals that the total π electron occupancies for **1a** and **2a** are both 1.97 lel. The occupancy in **1a** comes from C, Al, and Be by 1.47, 0.08, and 0.10/0.13 lel, respectively, and that in **2a** comes from C, Al, Be, and Li by 1.44, 0.07, 0.12/0.14, and 0.00 lel, respectively, which reveals that the Li atom does not contribute to the out-of-plane π bonding. In both **1a** and **2a**, the $2p_z$ orbitals of C dominate such bonding, which is consistent with the stabilization strategy proposed by Hoffmann et al.² The total number of π electrons (close to 2.00) satisfies the Hückel $4n + 2$ π electron rule ($n = 0$); therefore, **1a** and **2a** should be the aromatic species. The aromaticity can also be verified by the negative NICS and NICS_{zz} values (see the Figure S14 in the Supporting Information) and an out-of-plane π orbital (see two HOMO-4 in Figure 3). Remarkably, the aromaticity can be proved quantitatively by the electron localization function (ELF). The ELF analyses on various organic and inorganic systems established that the molecules with average bifurcation values (ELF_{av}) greater than 0.70 on the interval of (0,1) can be considered to be aromatic.^{49,56–58} As shown in Figure S1 (Supporting Information), our ELF analyses on **1a** give the ELF _{σ} , ELF _{π} , and ELF_{av} values of 0.88, 0.99, and 0.94, respectively. Thus, according to ELF criteria, **1a** possesses σ and π double aromaticity. The ELF_{av} value of 0.94 is much larger than the threshold of 0.70, which, together with the large NICS(1) value, reveals the strong aromaticity. The introduction of Li⁺ in **2a** observably affects the in-plane ring current, and thus, the ELF _{σ} value decreases to 0.63, but it does not affect the out-of-plane ring current, and the ELF _{π} value does not change (being also 0.99). Thus, ELF_{av} for **2a** is 0.81. Therefore, **2a** is σ antiaromatic, π aromatic, and overall aromatic. We think that the aromaticity (especially the π aromaticity) contributes to stabilizing the planar pentacoordinate bonding of carbon.

4. CONCLUSION

In summary, following the isoelectronic relationship among ppC global minima D_{5h} CaI_5^+ , C_{2v} CaI_4Be , and C_{2v} $CaI_3Be_2^-$, we have designed a dianionic ppC species C_{2v} $CaI_2Be_3^{2-}$ (**1a**)

and its salt complex C_{2v} $LiCaI_2Be_3^-$ (**2a**). Thermodynamically, the stochastic search algorithm together with DFT and high-level ab initio calculations reveal that **1a** and **2a** are the global minima on their PESs. Kinetically, the BOMD investigations prove that their structures are well-maintained during 100 ps simulations. The introduction of a Li⁺ into **1a** (to form **2a**) does not obviously affect the molecular structure of the CaI_2Be_3 ppC core. The NBO analyses suggest that adding Li⁺ into **1a** observably influences the electrovalent bonding, but it does not significantly affect the covalent bonding. Though the π electron counting, NICS(1) value, and MO analyses suggest that **1a** and **2a** are both overall aromatic, the ELF analyses unveiled that **1a** is σ and π double aromatic, while **2a** is σ antiaromatic but π and overall aromatic. We think that **1a** is a promising dianionic ppC species that can be detected in the gas-phase experiments, and because the introduction of Li⁺ into **1a** does not essentially change the molecular properties but significantly improves the stability, the ppC dianion can be alternatively realized in the form of its salt complex **2a**.

■ ASSOCIATED CONTENT

Supporting Information

The CCSD(T)/aug-cc-pVTZ optimized geometries (in Cartesian coordinates) of $CaI_2Be_3^{2-}$ and $LiCaI_2Be_3^-$ isomers (**1a–1f** and **2a–2f**), the table summarizing the NBO results, the pictures and table describing the NICS and NICS_{zz} values, the pictures of ELF densities, and the full form of refs S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project is supported financially by NSFC (Grants 21003086 and 20973197) and SXNSF (Grant 2009021016-3) and Shanxi University. The authors thank Prof. Zhi-Xiang Wang for constructive discussion.

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