Theoretical Study on the Aromaticity of the Pyramidal MB_6 (M = Be, Mg, Ca, and Sr) Clusters

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A series of metal−polyboron clusters with the general formula MB_6 (M = Be, Mg, Ca, and Sr) were investigated using ab initio self-consistent field and density functional theory (DFT) methods. Calculation results show that the two clusters of BeB_6 and MgB_6 have C_{6v} pyramidal structure with M^{2+} cation interacting with a planar hexagonal B_6^{2-} dianion. Whereas the other two CaB_6 (C_1) and SrB_6 (C_S) clusters possess quasi-pyramidal structure with M^{2+} cation interacting with a chairlike B_6^{2-} dianion. Molecular orbital (MO) analysis and nucleus-independent chemical shifts (NICS) further reveal that the four MB_6 species all have three delocalized π MOs and two delocalized σ MOs and therefore exhibit the multiple-fold aromaticity.

1. Introduction

The concept of aromaticity originally developed from two-dimensional polygonal molecules often refers to cyclic, planar, or conjugated organic compounds with $4n + 2$ delocalized π electrons.[1,2] In recent years this concept has been successfully extended from traditional organic molecules into pure all-metal clusters.[3−10] Li and co-workers[3] presented evidence of aromaticity for MAl_4^- (M = Li, Na, and Cu) purely metallic systems. The Al_4^{2-} dianion in a series of bimetallic clusters was found to possess two delocalized π electrons conforming to the $4n + 2$ electron counting rule for aromaticity. Similar aromaticity is found in Ga_4^{2-} and In_4^{2-} dianions[4] in the gaseous $NaGa_4^-$ and $NaIn_4^-$ clusters due to the presence of two delocalized π electrons. Li et al.[5] investigated the possibility of aromaticity in the heterocyclic four-membered ring XAl_3^- systems and found that the cyclic planar XAl_3^- (X = Si, Ge, Sn, and Pb) species have delocalized π electrons and therefore aromaticity. Aromaticity was also proposed in the 10 valence electrons B_3^-, Al_3^-, and Ga_3^- systems to explain the geometrical and electronic properties.[6] The structural and electronic stability of the square-planar Hg_4^{6-} and Al_4^{2-} was attributed not only to π aromaticity due to the presence of the two π electrons, but also to σ aromaticity due to the occupation of the two four-center σ bonding orbitals.[7] Zhan et al.[9] first proposed the orbital analysis approach of the multiple-fold aromaticity for the square-planar Al_4^{2-} structure which can be determined by three independent delocalized (π and σ) bonding systems. Alexandrova et al.[10] extended the σ aromaticity concept to small σ-aromatic alkali metal and alkaline metal clusters to explain relative stability of Li_3^+ and Li_3^- ions.

Boron's remarkable abilities of forming three-center or multi-center bonds compensate for its electron deficiency. A lot of papers have been published on the pure boron clusters B_n.[11−23] A few of the theoretical investigations in the literature have been reported on the metal−polyboron compounds.[24−26] The best-known example of the metal−polyboron compounds is the structure of CaB_6 showed by Longuet-Higgins and Roberts[27] many years ago in which the two electrons are donated by the calcium atom to satisfy the bonding requirements of the boron octahedral. For rare-earth metal borides, LaB_6 is an emitter of electron source, CeB_6 is known as a dense-Kondo material,[28] and SmB_6 is a so-called Kondo semiconductor with tiny energy gap.[29] In these solid-state metal borides, B_6 constitutes an octahedron B_6 cage and forms a three-dimensional network with metal atoms. However, the pyramidal metal borides have not been reported previously.

In the present paper, a series of the pyramidal MB_6 (M = Be, Mg, Ca, and Sr) species are theoretically investigated with ab initio and DFT methods. Molecular orbital (MO) analysis and the nucleus-independent chemical shifts (NICS)[30−33] provide insight into the multiple-fold aromaticity of the pyramidal MB_6 clusters. The present study shows that the planar B_6^{2-} dianion (D_{2h}) with four π electrons is antiaromatic. Alexandrova et al.[22] carried out the structure and bonding of B_6, B_6^-, and B_6^{2-} and established the antiaromatic nature of chemical bonding for B_6^- and B_6^{2-}. In addition, Ma et al.[23] also studied the dianionic B_6 cluster, and found the most stable B_6^{2-} (D_{2h}) having four π electrons is antiaromatic. Our results show that the pyramidal MB_6 (M = Be, Mg, Ca, and Sr) species have the multiple-fold aromaticity. It is an interesting thing that an antiaromatic B_6^{2-} dianion could be transformed into an aromatic one under the influence of the metal ions.

2. Computational Methods

All calculations were performed using the Gaussian 98 program package.[34] We initially optimized geometries and calculated frequencies of B_6^{2-}, BeB_6, MgB_6, and CaB_6 species at the B3LYP/6-311+G* level of theory, where B3LYP is a DFT method using Becke's three parameter nonlocal exchange functional[35] with the nonlocal correlation of Lee, Yang, and Parr[36] and 6-311+G* is a split-valence triple-ζ plus polarization basis set augmented with diffuse functions.[37] We further studied B_6^{2-}, BeB_6, MgB_6, and CaB_6 using the second-order Moller-plesset perturbation theory (MP2).[38] For the SrB_6 species, we optimized at the B3LYP and MP2 levels of theory, where the 6-311+G* basis set was used for boron and the LANL2DZ basis set was used for the heavier metal atom Sr (Z = 38). Minima were characterized with zero imaginary frequency and first-order saddle point with one imaginary frequency.

Molecular orbitals (MOs) for four MB_6 species were calculated by the HF method with the corresponding basis set. All MO pictures were made using the MOLDEN 3.4 program.[39]

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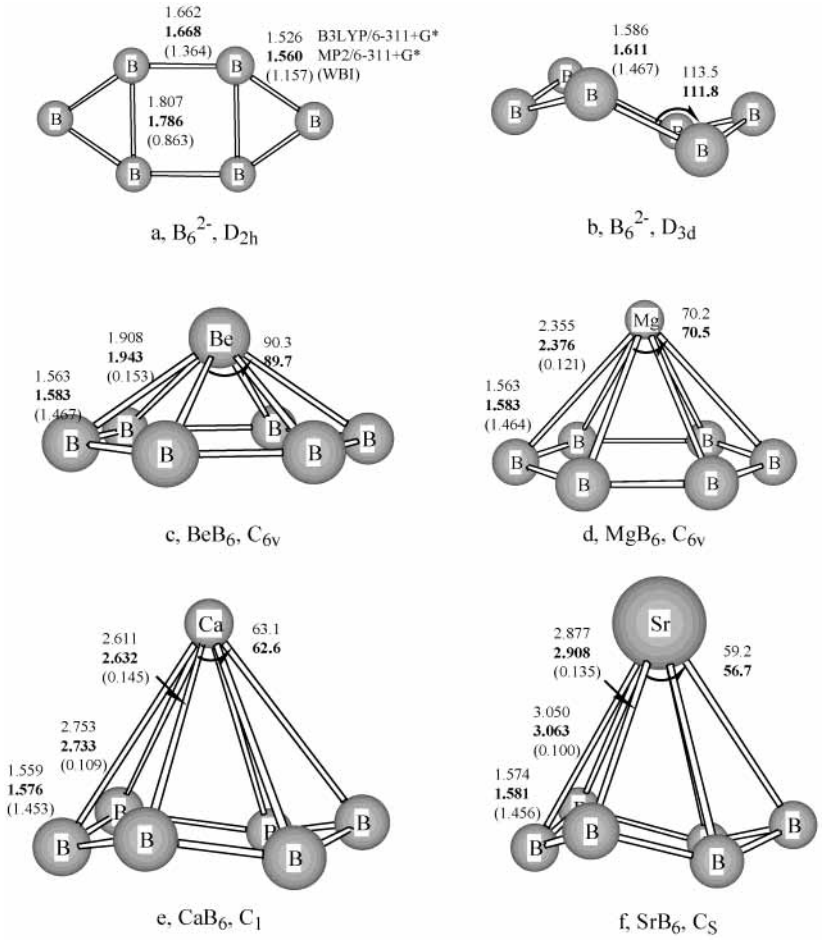

Figure 1. Optimized geometries (bond lengths in Å, bond angles in degrees) and the Wiberg bond indices (WBI) for BeB_6, MgB_6, CaB_6, and SrB_6 species at the B3LYP and MP2 (bold font) methods.

TABLE 1: Total Energies (*E*),[a] Zero-Point Energy (ZPE),[b] and the Number of Imaginary Frequencies (NImag) for the BeB_6, MgB_6, CaB_6, and SrB_6 Species[c,d]

	B3LYP			MP2		
species	*E*	ZPE	NImag	*E*	ZPE	NImag
B_6^{2-}, (D_{6h})	−148.822932	12.72	0	−147.564183	12.36	0
B_6^{2-}, (D_{3d})	−148.696511	9.62	3	−147.562043	13.56	0
BeB_6, (C_{6v})	−163.590033	15.89	0	−162.415881	15.49	0
MgB_6, (C_{6v})	−348.905732	13.60	0	−347.350407	13.63	0
CaB_6, (C_1)	−826.433001	13.01	0	−824.985832	13.45	0
SrB_6, (C_S)	−179.234988	12.48	0	−178.388943	12.98	0

[a] Total energies in Hartrees. [b] Zero-point energies in kcal/mol. [c] The 6-311+G* basis set was used for B, Be, Mg, and Ca, and the LANL2DZ basis set was used for the heavier metal Sr ($Z = 38$). [d] The listed total energies, ZPE, and NImag for CaB_6 are calculated at the MP2/6-31+G* level of theory.

NICS values for the four MB_6 species were calculated with the GIAO-HF//B3LYP method, where the 6-311+G* basis set was used for B, Be, Mg, and Ca, and the LANL2DZ basis set was used for Sr. The natural bond orbital (NBO)[40−43] analysis was also performed to provide insight into the bonding nature and aromaticity of these species, and therein lies the explanation of the stability of the MB_6 species.

3. Results and Discussion

The optimized geometric structures and the Wiberg bond indices (WBI) for the four MB_6 species and B_6^{2-} dianion have been shown in Figure 1. Total energies, zero-point vibrational energies (ZPE), and number of imaginary frequencies of all species are summarized in Table 1. The vibrational frequencies of the BeB_6, MgB_6, CaB_6, and SrB_6 species at the B3LYP and MP2 methods are shown in Table 2. Calculated bond lengths (in Å), covalent radii of atom (in Å), and relative stability for BeB_6, MgB_6, CaB_6, and SrB_6 species (B3LYP/6-311+G*) are listed in Table 3. The calculated NICS values are given in Table 4. MOs pictures for four MB_6 species are exhibited in Figure 2.

3.1. Geometric Structures and Vibrational Frequencies. We performed ab initio and DFT methods on a wide variety of structures and found that all the ground-state pyramidal structures are local minimum with all real frequencies at the B3LYPand MP2 methods. Both BeB_6 and MgB_6 species have C_{6v} pyramidal structures with M^{2+} cations interacting with a planar hexagonal B_6^{2-} dianion. However, CaB_6 (C_1) and SrB_6 (C_S) possess quasi-pyramidal structures with M^{2+} cations interacting with a chairlike B_6^{2-} dianion.

TABLE 2: Calculated Vibrational Frequencies[a,b] (in cm^{-1}) for the BeB_6, MgB_6, CaB_6, and SrB_6 Species

	B3LYP						MP2					
species	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
BeB_6, (C_{6v})	296	390	461	536	587	697	285	321	451	503	582	664
MgB_6, (C_{6v})	190	233	340	364	421	461	120	268	341	398	423	435
CaB_6, (C_1)	156	224	273	318	353	414	255	262	269	339	366	389
SrB_6, (C_S)	170	245	252	258	358	474	221	241	255	295	339	397

[a] The 6-311+G* basis set was used for B, Be, Mg, and Ca, and the LANL2DZ basis set was used for the heavier metal Sr. [b] Calculated vibrational frequencies for CaB_6 are calculated at the MP2/6-31+G* level of theory.

TABLE 3: Calculated Bond Lengths (in Å), Covalent Radii (in Å), and Zero-Point Corrected B3LYP Energies ΔE (in kcal/mol) for Hypothetical $MB_6 \rightarrow M + B_6$ Reactions

	BeB_6, C_{6v}	MgB_6, C_{6v}	CaB_6, C_1	SrB_6, C_S
B−B	1.563	1.563	1.559	1.574
M−B	1.908	2.355	2.611	2.877
sum of covalent radii of metal and boron	1.77	2.25	2.62	2.79
ΔE	68.2	1.5	29.5	5.6

TABLE 4: Calculated NICS Values (in ppm) with GIAO-HF//B3LYP Method for the BeB_6, MgB_6, CaB_6, and SrB_6 Species

	BeB_6	MgB_6	CaB_6	SrB_6
NICS	−51.32	−44.27	−33.67	−29.56

[a] Calculated NICS at the geometrical centers of the pyramidal structures.

Theoretical studies on various B_6^{2-} dianions showed that the planar hexagonal (D_{2h}) ring (Figure 1a) is the most stable dianion at the B3LYP/6-31+G*.[22,23] The B−B bonds are not identical in the most stable D_{2h} planar structure. Chairlike D_{3d} structure (Figure 1b) is a third-order saddle point at the B3LYP/6-311+G* level of theory, while it is a local minima at the MP2/6-311+G* level of theory. There does exist a change in B−B bond distance in the MB_6 species and the B_6^{2-} dianion. For the pyramidal MB_6 species, all B−B distances are identical and slightly shorter than the average bond distance in the corresponding B_6^{2-} dianion (Figure 1a and b), and the extent of shortening shows a decreasing trend from Be to heavier metal atoms. This indicates that the lighter the metal atom is, the more important are the M^{2+} effects on the B_6^{2-} dianion.

As shown in Figure 1, the distances between metal atom and boron atom (1.908−2.877 Å) are much larger than those of the B−B (1.563−1.574 Å) in all the geometries of MB_6 species. Moreover, the larger the atomic number of the metal is, the longer the distance between metal and boron is and the smaller the angle of B−M−B is. The bond lengths of B−B in the four MB_6 species change slightly at the B3LYP and MP2 methods. The B−B bond lengths (1.563−1.574 Å) in the four MB_6 species are much shorter than the sum of covalent radii of two boron atoms (1.76 Å), indicating the existence of stronger B−B bonding. The M−B bond lengths in the four MB_6 species are longer than the sum of covalent radii of the corresponding metal atom and boron atom except for CaB_6. The covalent radii for the metal atoms and boron atom are 0.89, 1.37, 1.74, 1.91, and 0.88 Å for Be, Mg, Ca, Sr, and B, respectively.[44] In addition, the structures of CaB_6 and SrB_6 have chair conformation with identical B−B distances of 1.559 and 1.574 Å at the B3LYP method, respectively.

The calculated harmonic vibrational frequencies given in Table 2 show that the lowest frequencies of the BeB_6, MgB_6, CaB_6, and SrB_6 species are 296, 190, 156, and 170 cm^{-1} at the B3LYP method and 285, 120, 255, and 221 cm^{-1} at the MP2 method. The lowest vibrational frequencies calculated for the four MB_6 species are larger enough to prove the minimum. The vibrational frequencies agree well at the B3LYP and MP2 methods for the four species (shown in Table 2).

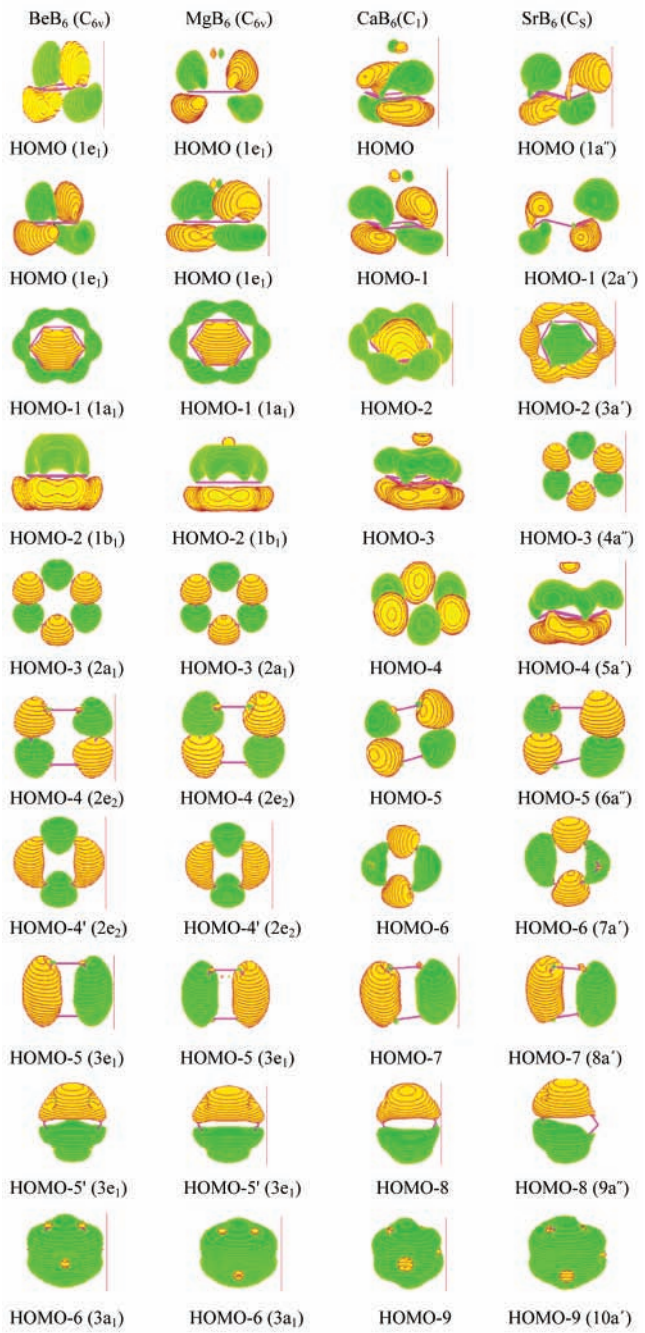

Figure 2. Molecular orbital pictures of the BeB_6, MgB_6, CaB_6, and SrB_6 species, showing the HOMO down to the ninth valence molecular orbital.

3.2. Stability of the MB_6 Species. Natural population analysis indicates that alkaline earth metal atoms have positive charge

and boron atoms have negative charge in the four MB_6 species. The MB_6 species can be regarded as complexes of the B_6^{2-} dianion and metal M^{2+} cation. Bonding is due to electrostatic attraction effect between M^{2+} and B_6^{2-}. The charges on the metal ions are Q(Be) = +1.49 e (BeB_6), Q(Mg) = +1.58 e (MgB_6), Q(Ca) = +1.61 e (CaB_6), and Q(Sr) = +1.65 e (SrB_6) (all are computed at the B3LYP/6-311+G*). NBO analysis shows that every WBI between metal and boron are 0.11−0.15, suggesting that M^{2+} cations have a role of stabilizing the B_6^{2-} dianion. The B_6^{2-} dianion might be stabilized in the form of a planar hexagonal (D_{6h}) ring by the interaction of its π system with Be and Mg atoms. However, the heavier alkaline earth metals cations Ca^{2+} and Sr^{2+} have effects on the electronic structure of the B_6^{2-} dianion. That induces changing of geometry of B_6^{2-} into the chairlike D_{3d} structure from the most stable planar (D_{2h}) ring structure. The calculated adjacent B−B WBI of the four MB_6 species is around 1.46, which is intermediate of the standard values of single-bond (1.0) and double-bond (2.0), indicating the existence of delocalization of electrons in the B_6^{2-} dianion.

The zero-point corrected B3LYP energies for hypothetical reactions $MB_6 \rightarrow M + B_6$ are given in Table 3. The reaction is endothermic, indicating that the four MB_6 species are stable toward decomposition. The MB_6 species lie about 1.5−68.2 kcal/mol above the energy of a ground-state metal and the most stable B_6 (C_{2h}) cluster[23] at the B3LYP method. A simply energetic comparison of the MB_6 and B_6 cluster shows a substantial energy stabilization of the MB_6 species as compared to the bare B_6 cluster. On the basis of the above analysis, it is reasonably believed that the four MB_6 species have a quiet possibility of existence.

3.3. Aromaticity of the MB_6 Species. *3.3.1. Nucleus-Independent Chemical Shifts (NICS).* Aromaticity is often definable via magnetic criteria, such as NICS, which is based on the negative value of the magnetic shielding computed at or above the geometrical centers of rings or clusters. NICS is a simple and efficient aromaticity criterion in a wide range of molecules. Aromaticity is characterized by the negative NICS values (given in ppm), antiaromaticity is shown by positive NICS values, and nonaromatic compounds have NICS values close to zero.[30−33] The more negative the NICS, the more aromatic the molecule is. In this study we calculated NICS values at the geometrical centers of the pyramidal structures for providing a direct measure of the ring current effects. NICS values of the BeB_6, MgB_6, CaB_6, and SrB_6 species at the GIAO-HF//B3LYP method are −51.3, −44.3, −41.5, and −29.6 ppm, respectively. NICS values for the four MB_6 species are all negative, suggesting the existence of delocalization and aromaticity in the four species. The antiaromaticity of the planar B_6^{2-} (D_{2h}) dianion with a positive NICS value above (by 1.0 Å) the geometric centers of the boron six-membered ring have been recently reported.[23] Here we have also calculated the NICS value of the planar B_6^{2-} (D_{2h}) dianion, which has a positive NICS value with the GIAO-B3LYP//B3LYP/6-311+G* level of theory above (by 1.0 Å) the geometric centers of the boron six-membered ring. Therefore, the plane B_6^{2-} (D_{2h}) dianion is antiaromaticity. When the metal ions are added to B_6^{2-} to form MB_6, the interaction of π system of B_6^{2-} dianion with the metal atoms occurs. This results in transformation of antiaromatic B_6^{2-} dianion into an aromatic one under the influence of the metal cations. We also found that NICS values for the four species increase with the increasing atomic number of the metal atom, indicating the decreasing of aromaticity of MB_6 species. For BeB_6 and MgB_6 species, the six boron atoms are locating in a plane and easily forming cyclic π and σ electrons delocalization. Though the six boron atoms in CaB_6 species are not in a plane and have a chairlike structure, NICS value is −41.5 ppm at the GIAO-HF//B3LYP/6-311+G* level of theory and exhibit aromaticity due to the delocalization of π electrons and σ electrons.

3.3.2. Presence of $4n + 2$ π Electrons and σ Electrons. In an orbital picture, three π delocalized MOs are first observed in the higher occupied molecular orbitals. As exhibited in Figure 2, the highest occupied molecular orbital (HOMO, $1e_1$) of BeB_6 species includes two degenerated orbitals formed from the out-of-plane p orbitals. The two degenerate HOMO ($1e_1$) orbitals are delocalized π bonding MOs which render π aromaticity. The HOMO-1 ($1a_1$) and HOMO-3 ($2a_1$), formed from the in-plane p orbitals, are two six-center delocalized σ bonding orbitals that render σ aromaticity. The HOMO-2 ($1b_1$), formed from the out-of-plane p orbitals, is a delocalized π bonding orbital that renders π aromaticity. The two degenerated HOMO-4 ($2e_2$) MOs are linear combinations of s and p orbitals. The other three MOs are formed primarily from orbitals. In these occupied orbitals, HOMO (including two degenerated orbitals) and HOMO-2 are three delocalized π-bonding orbitals, containing six π electrons. HOMO-1 ($1a_1$) and HOMO-3 ($2a_1$) are σ delocalized MOs we would like to call σ-aromatic MO, each of the σ delocalized bonding systems containing two σ electrons. σ-Aromaticity initially introduced in hydrocarbons[2,45,46] has been extended to metal, nonmetal, and metal−nonmetal clusters.[7,9,10,23] The number of π electrons and σ electrons of BeB_6 species both satisfy the famous $4n + 2$ electron counting rule and it is expected to have the multiple-fold aromaticity. The presence of delocalized π and σ orbitals have also played an important role in the stabilization of the metal−polyboron species. The MgB_6 species has a MO picture similar to that of the BeB_6 species.

For CaB_6 and SrB_6 species, the six boron atoms are not in a plane. The nonplanar B_6^{2-} diaion is greatly influenced by the heavier alkaline earth metal atoms. Even though CaB_6 and SrB_6 species with chairlike B_6^{2-} diaion have MOs similar to those of BeB_6 and MgB_6 except for the slight difference in ordering. But the MOs are distorted due to the presence of the heavier cations and showing the characteristic of chairlike B_6^{2-} structure. MO analysis shows that CaB_6 and SrB_6 species both have three π delocalized MOs and two σ delocalized MOs.

By comparing in Table 2 the MOs of B_6^{2-} reported in the literature[23] with the MOs of the four MB_6 species in this study, we found that the MOs of MB_6 and B_6^{2-} are different. For the D_{2h} B_6^{2-} diaion, the HOMO (B_{2g}) and HOMO-4 (B_{3u}) are π bonding MOs, containing four π electrons. It is seen to be a 4π system conforming with the $4n$ electron counting rule and therefore antiaromatic.[22,23,47] It is obvious that MB_6 has three occupied π MOs; two of them are the degenerated HOMO MOs, the other one is the HOMO-2 for BeB_6 and MgB_6, and HOMO-3 and HOMO-4 for CaB_6 and SrB_6, respectively. Thus, the four pyramid MB_6 species are seen to be 6π systems conforming with the $4n + 2$ electron counting rule and therefore aromatic.

On the basis of the above MO analysis, π delocalized MOs and σ delocalized MOs contribute the property of the multiple-fold aromaticity for the four pyramidal MB_6 species, due to the presence of six π electrons and two σ electrons which follow the $4n + 2$ electron counting rule. The delocalized π and σ MOs played an important role in stabilizing the four pyramidal BeB_6, MgB_6, CaB_6, and SrB_6 species.

4. Conclusion

We investigated a series of alkaline earth metal−polyboron clusters with the general formula MB_6 (M = Be, Mg, Ca, and

Sr) using ab initio and DFT methods, for which no report is found so far. Our calculation results showed that BeB_6 and MgB_6 possess C_{6v} pyramidal structures with a planar hexagonal B_6^{2-} dianion. Whereas CaB_6 (C_1) and SrB_6 (C_S) possess quasi-pyramidal structures with a chairlike B_6^{2-} dianion. From molecular orbital (MO) analysis and nucleus-independent chemical shifts (NICS) analysis, it is known that each of the four species has three delocalized π MOs and two independent delocalized σ MOs. Each of the delocalized chemical bonding systems satisfies the $4n + 2$ electron counting rule and therefore exhibits characteristic of the multiple-fold aromaticity.

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