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四角锥形结构化合物 BeB_4X_4(X=H,F,Cl),HBB_4H_4 与 $BB_4H_4^+$中 B_4 平面环的半芳香性

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摘要：选用 6-311++G(3d*f*,2*p*)基组,在二级微扰的理论下,对四角锥形结构化合物 BeB_4X_4(X=H,F,Cl),HBB_4H_4 与 $BB_4H_4^+$的分子振动频率,及原子间的相互作用进行了计算,作用能的计算使用了 CCSD(T)方法。结果显示 HBB_4H_4 与 $BB_4H_4^+$是违反韦德规则的另两个特例,它们表现稳定的原因与芳香性有关。

关键词：韦德规则；核独立化学位移；硼氢化合物；芳香性；离域电子
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One Kind of B_4 Plane Ring in the Square Pyramidal Clusters BeB_4X_4 (X=H, F, Cl), HBB_4H_4 and $BB_4H_4^+$ with Special Half Aromaticity

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Abstract: Using the 6-311++G(3d*f*,2*p*) basis set, the clusters BeB_4X_4 (X=H, F, Cl), HBB_4H_4 and $BB_4H_4^+$ which all have a square pyramidal shape were got at the second-order Mller-Plesset perturbation (MP2) level with all frequencies real. The vertexes of these square pyramidal clusters are Be, BH and B separately. They all act as a two electron donor for B_4X_4, and the B_4X_4 act as a bowl to accommodate the pair of electrons. The interaction energies between the vertexes and the B_4X_4 bowls were calculated at the CCSD(T) level. The interactions between bowls with different terminal atoms and transferred electrons were discussed. The character of the B_4 ring is affected deeply with the terminal atoms. For HBB_4H_4 and $BB_4H_4^+$, they are four and six electrons short of the Wade magic electron count, but they all have their strong bonding here.

Key words: Wade′s rules; NICS; boron hydride; aromaticity; delocalized electrons

0 Introduction

The study of boron hydrides has been a classic field in inorganic chemistry since their first preparation by Stock[1]. Because of the electron deficiency of the boron hydrides, the description of their bonding was a problem in theoretical chemistry for many years. In the early 1960s, Lipscomb applied the concept of the three-center bond to the higher boron hydrides and developed a simple method for describing and predicting the topology of such compounds[2-3]. Further progress in studying the relationship between structure and electron count have led, from Lipscombs styx-rules, to the generalized

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electron-count schemes known as Wade′s rules [4-6], today a lot of works are still focus on the electron-counting rules and tried to make it more perfect[7-9].

In general, Wade′s rules divide clusters into several groups with respect to the number of electron pairs associated with cage bonding. A famous exception to Wade′s rules is B_4H_4[2-10] In the tetrahedral geometry it has an open-shell triplet ground state. Oxidation of the tetrahedral dianion leads to the neutral cluster B_4H_4 which is known for a tetrahedral shape with a closed-shell singlet ground state[11-12]. Recently, some other structurally stable B_4H_4 isomers were pointed out[13-14]. Among them a D_{2d}-symmetric B_4H_4 isomer caused us much attention. In the following works, the dianion entity $B_4H_4^{2-}$ which also have a D_{2d}-symmetry was got[15]. Although the $B_4H_4^{2-}$ was calculated unstable, the derivatives $B_4(CN)_4^{2-}$ and $B_4(BO)_4^{2-}$ were predicted to be observable in suitable experiments. The similar researches about this kind of four member ring [16-19] provides the idea that the four p_z atomic orbitals from four B atoms formed a π-molecular orbital which is occupied with an excess electron pair.

Since some $B_4X_4^{2-}$ cluster with a D_{2d}-symmetric shape can exist stable, the netural B_4 ring should have a strong willing to get an excess electron pair. A Be atom has an electron pair located on its outside 2*s* orbital. If a Be atom close to a netural cluster B_4X_4 with B_4 ring. There should have a strong interaction between them. Recently the similar study about metal-polyboron compounds[20] MB_6 (M=Be, Mg, Ca, and Sr) species have shown some special interaction between metal and B_6 planar ring. The B_6^{2-} which is proved to be antiaromatic[21-22] could be transformed into an aromatic one under the influence of the metal ions[20]. In this present paper, the interaction between the well known boron hydride B_4H_4 (and its derivatives) and the metal Be was studied, the effects of the terminal atoms which is connected to the B atoms was discussed. And the aromaticity of the clusters BeB_4X_4 (X=H, F, Cl) were studied by the nucleus-independent chemical shifts (NICS)[23-26] method.

At last, if the Be atom was a successful electron pair donor, the similar electron pair donor BH and B^+ should also be test. And the clusters HBB_4H_4 and $BB_4H_4^+$ may be another two exceptions to Wade′s rules.

1 Computation details

The geometric optimizations of the clusters BeB_4X_4 (X =H, F, Cl), HBB_4H_4 and $BB_4H_4^+$ were performed at the second-order Mller-Plesset perturbation theory (MP2) level. With the 6-311++G(3d*f*,2*p*) basis set the stationary points were got. The vibratinal frequencies calculated are all real for these clusters. The similar cluster MgB_4H_4 was also calculated.

For the BeB_4X_4 (X=H, F, Cl) clusters, the natural bond orbitals (NBO)[27] methods were used to analyze their populations and atomic charges. Just from the charges of the Be atom, the message about the electrons transfer can be got.

The interaction energy between B_4X_4 ring and metal Be were calculated at the CCSD (T)/6-311++G (3d*f*,2*p*) level and the counterpoise procedure[28] was employed to remove basis-set superposition error (BSSE).

The distance between the geometric center of the B_4 plane and the Be atom are frozen at 0.1, 0.2, 0.3 nm. The four B atoms are forced on one plane. Then the structure of the BeB_4H_4 are optimized to study the interactions between Be and B_4H_4. In another optimization the Be atoms were frozen at its optimized position for BeB_4H_4 and BeB_4F_4, but the electron pairs were removed to study the effects of the terminal atoms.

NICS values for the BeB_4X_4 (X=H, F, Cl) clusters were calculated at the GIAO-HF//MP2 method with the 6-311++G (3d*f*,2*p*) basis set. Five points were selected to calculate the absolute shielding. They are the center of the B_4 plane (defined as BC), 0.05 nm out of the plane (BC−0.05 is the point close to the Be atom, BC+0.05 is the point far to the Be atom), 0.1 nm out of the plane (BC−0.1 is the point close to the Be atom, BC+0.1 is the point far to the Be atom).

For all the clusters, their two- or three -dimensional plots of molecular orbitals were generated with the Molden program[29]. All the calculations were performed with the GAUSSIAN 03 program package[30].

2 Results and discussion

2.1 Geometrical characteristics

The optimized structures of BeB_4X_4 (X=H, F, Cl) are shown in Fig.1 and Fig.2. The corresponding geometric parameters are listed in Table 1. It shows that the four B atoms located just on one plane and formed a square. The Be atom is on one side and the four X atoms are on the other side of the B_4 plane. This kind of cluster gives a square pyramidal shape with C_{4v}-symmetriy. While just for the B_4X_4 or $B_4X_4^{2-}$ clusters without the Be atom the four B atoms were not on one plane. Here the Be atom locate very close to the B_4 ring. The distance between the geometric center of the B_4 plane and the Be atom are 0.127 nm for BeB_4H_4, 0.135 nm for BeB_4F_4 and 0.133 nm for BeB_4Cl_4. It shows that the terminal X atoms are repulsed by the Be atom and they are not located on the same plane of the B_4 ring. The optimized structure of the Mg-B_4H_4 cluster is also given in Fig.2. It just shows a C_{4v}-symmetriy, and don′t have the square pyramidal shape. The Mg atom is a bit far from the B_4H_4 ring.

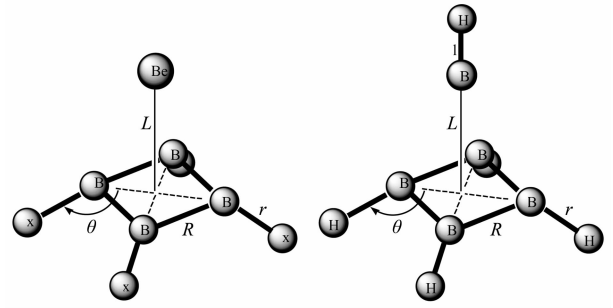


Fig.1 Definition of the geometrical parameters for the optimized geometries of the BeB_4X_4 (X=H, F, Cl), HBB_4H_4 and $BB_4H_4^+$ clusters

The highest occupied molecular orbital (HOMO) of the BeB_4H_4 in Fig.3. shows that the B_4H_4 part of the cluster act just as a bowl which accommodate the electrons transferred from the Be atom. For the three clusters B_4X_4 (X=H, F, Cl) the shapes of the B_4X_4 bowls have some difference. The θ angle shown in Fig.1. is 147.6° for B_4H_4, the same angle for B_4F_4 is 11.3° larger. Then the B_4H_4 bowl looks smaller than the B_4F_4 one.

When the Be atom were replaced by BH or B^+,

Table 1 Geometrical parameters for BeB_4X_4 (X=H, F, Cl) cluster at MP2 level with the 6-311++G(3d*f*,2*p*)

	r / nm	*R* / nm	*L* / nm	*θ* / (°)
BeB_4H_4	0.118	0.174	0.127	147.6
BeB_4Cl_4	0.173	0.174	0.133	154.7
BeB_4F_4	0.132	0.175	0.135	158.9

Table 2 Geometrical parameters for HBB_4H_4 and $BB_4H_4^+$ cluster with square pyramidal shape at MP2/6-311++G(3df,2p) level

	r / nm	*R* / nm	*L* / nm	*l* / nm	*θ* / (°)
$BB_4H_4^+$	0.117	0.185	0.085		151.0
HBB_4H_4	0.118	0.170	0.122	0.119	155.6

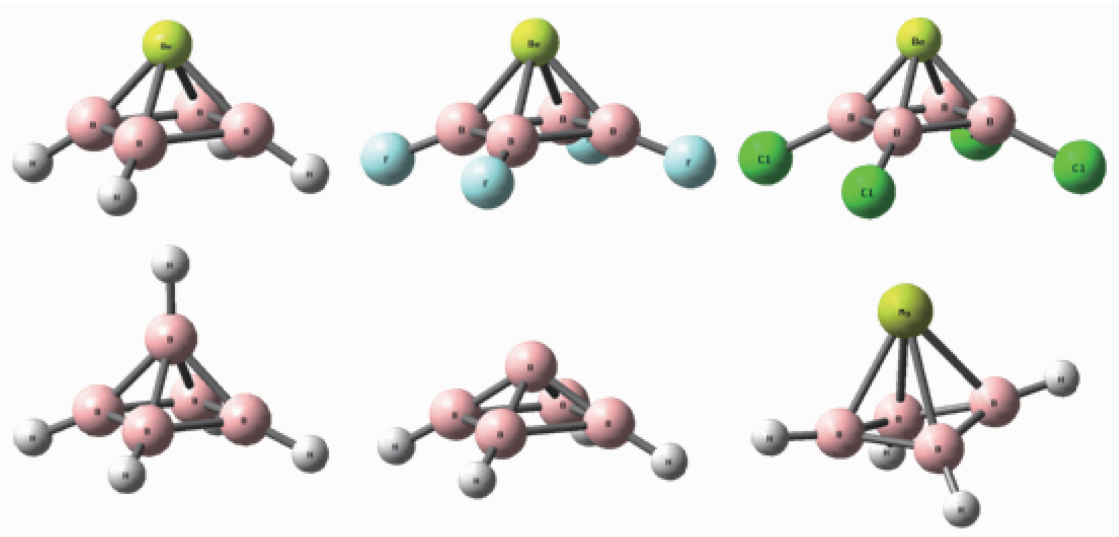


Fig.2 Optimized geometry of the BeB_4X_4 (X=H, F, Cl), Mg-B_4H_4, HBB_4H_4 and $BB_4H_4^+$ clusters

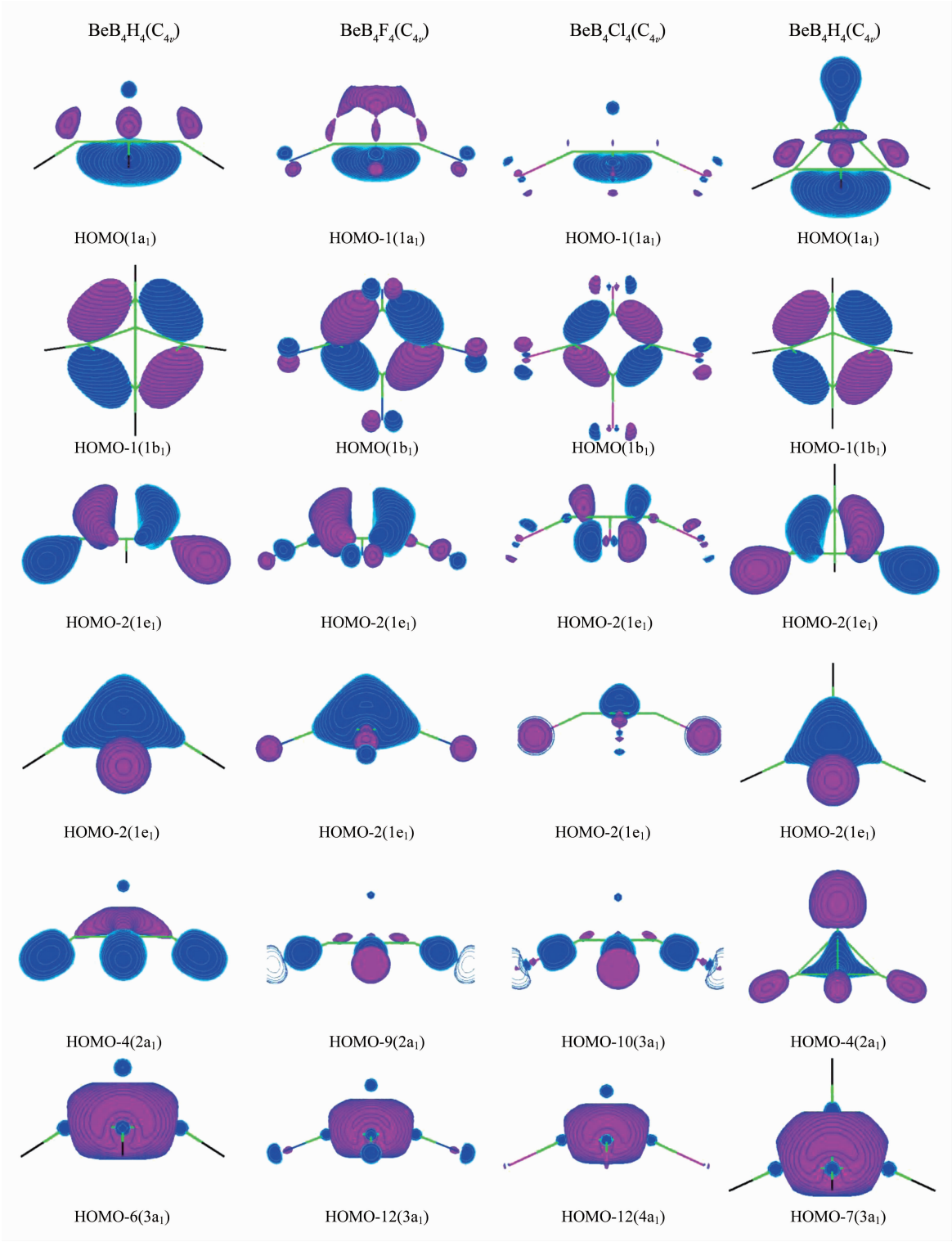


Fig.3　Delocalized higher occupied molecular orbitals of the BeB_4X_4 (X=H, F, Cl) and HBB_4H_4

the stable clusters HBB_4H_4 and $BB_4H_4^+$ were also got in the square pyramidal shape. They are also shown in Fig.2. The geometric parameters are listed in Table 2. According to the Wade magic electron count rule, they are short of four and six electrons respectively. But they all act stable here.

2.2　Effects of the terminal atoms

From the NBO calculations, the natural charges of the Be atoms were got for the clusters BeB_4X_4 (X= H, F, Cl). They are 1.39 for BeB_4H_4, 1.21 for BeB_4F_4

and 1.35 for BeB_4Cl_4. That means for the BeB_4H_4 cluster there are 1.39 electrons transferred from the Be atom to the B_4 ring, that is the largest number in these three cluster. While for the BeB_4F_4 cluster which have the strong electron pulling terminal atoms F, the transferred electrons from the Be atom to the B_4 ring are only 1.21, which is the smallest one in the three cluster. Since there are electrons in the bowls, the X (H, F, Cl) atoms should have a direction interaction with the electrons. The corresponding positive charged H atoms should close to the electron cloud and the corresponding negative charged F atoms will leave away. Then the shape of the bowl can be in control. And the largest electrons transferred from the Be atom to the B_4 ring for BeB_4H_4 is obviously owes to the direct interaction between the electrons in B_4H_4 bowl and the four H atoms nearby. And because of this H-e interaction the Be atom locate more close to the B_4 plane in the BeB_4H_4 cluster than the other two.

The interaction energies between Be and B_4X_4 (X=H, F, Cl) calculated are listed in Table 3. At the CCSD (T) level. It is 6.235 eV for BeB_4H_4, 3.643 eV for BeB_4F_4 and 4.196 eV for BeB_4Cl_4. The BeB_4H_4 cluster which has the shortest Be and B_4 plane distance (0.127 nm) get the largest interaction energy. And in the BeB_4H_4 cluster the Be atom also has the largest natural charge. On the contrary, the BeB_4F_4 cluster which has the smallest charge on its Be atom get the smallest interaction energy, and the distance between its B_4 plane and the Be atom is the longest one (0.135 nm). There is a strong correlation between the electrons transfer and the direct X-e interactions, the electrons transfer brings the X-e interaction, and for the BeB_4H_4 cluster the H-e interaction promote the electrons transfer effect.

When the distance between the geometric center of the B_4 plane and the Be atom are frozen at 0.1, 0.2, 0.3 nm. The optimized structures of the BeB_4H_4 cluster are shown in Fig.3. It is clear that the electrons transfer is so sensitive to the distance. When the distance is frozen at 0.3 nm, there are few electrons transferred from the Be atom to the B_4 ring. And the bowl shape B_4H_4 cluster turns to a plane shape without the special H-e interactions.

In another test the Be atoms were frozen at its optimized position for BeB_4H_4 and BeB_4F_4, but the electron pairs were removed to study the effects of the terminal atoms. When two electrons were removed from the BeB_4H_4 cluster, the θ angle of the cluster changes from 147.6° to 168.1°. it increased about 20.5° and becomes larger than that of the BeB_4F_4 cluster. For the BeB_4F_4 its θ angle changes little when one electron pair was removed. Since its HOMO-1 is our interested orbital, we removed two electron pairs, and the θ angle of the BeB_4F_4 changes from 158.9° to 139.0°. it decreased 19.9°. Now the B_4H_4 bowl turns larger than the B_4F_4 one without the special X-e interactions.

Table 3 Interaction energies between Be and B_4X_4 (X=H, F, Cl)

	HF	MP2	CCSD(T)
BeB_4H_4 / a.u.	−115.585 285 602	−116.063 424 257 91	−116.126 724 16
Be / a.u.	−14.571 978 591 7	−14.601 106 059 965	−14.617 842 982
B_4H_4 / a.u.	−100.849 760 052	−101.207 619 934 88	−101.279 760 52
BeB_4H_4 Interaction energy / eV	4.450	6.931	6.235
BeB_4F_4 / a.u.	−511.393 850 887	−512.846 004 429 37	−512.913 228 06
Be / a.u.	−14.571 975 861 6	−14.601 086 331 428	−14.617 837 266
B_4F_4 / a.u.	−496.743 543 736	−498.089 535 917 40	−498.161 506 13
BeB_4F_4 Interaction energy / eV	2.132	4.228	3.643
BeB_4Cl_4 / a.u.	−1 951.509 707 49	−1 952.722 038 644 9	−1 952.850 062 9
Be / a.u.	−14.571 976 288 0	−14.601 094 964 115	−14.617 838 588
B_4Cl_4 / a.u.	−1 936.839 449 90	−1 937.937 362 890 4	−1 938.078 0138
BeB_4Cl_4 Interaction energy / eV	2.674	4.996	4.196

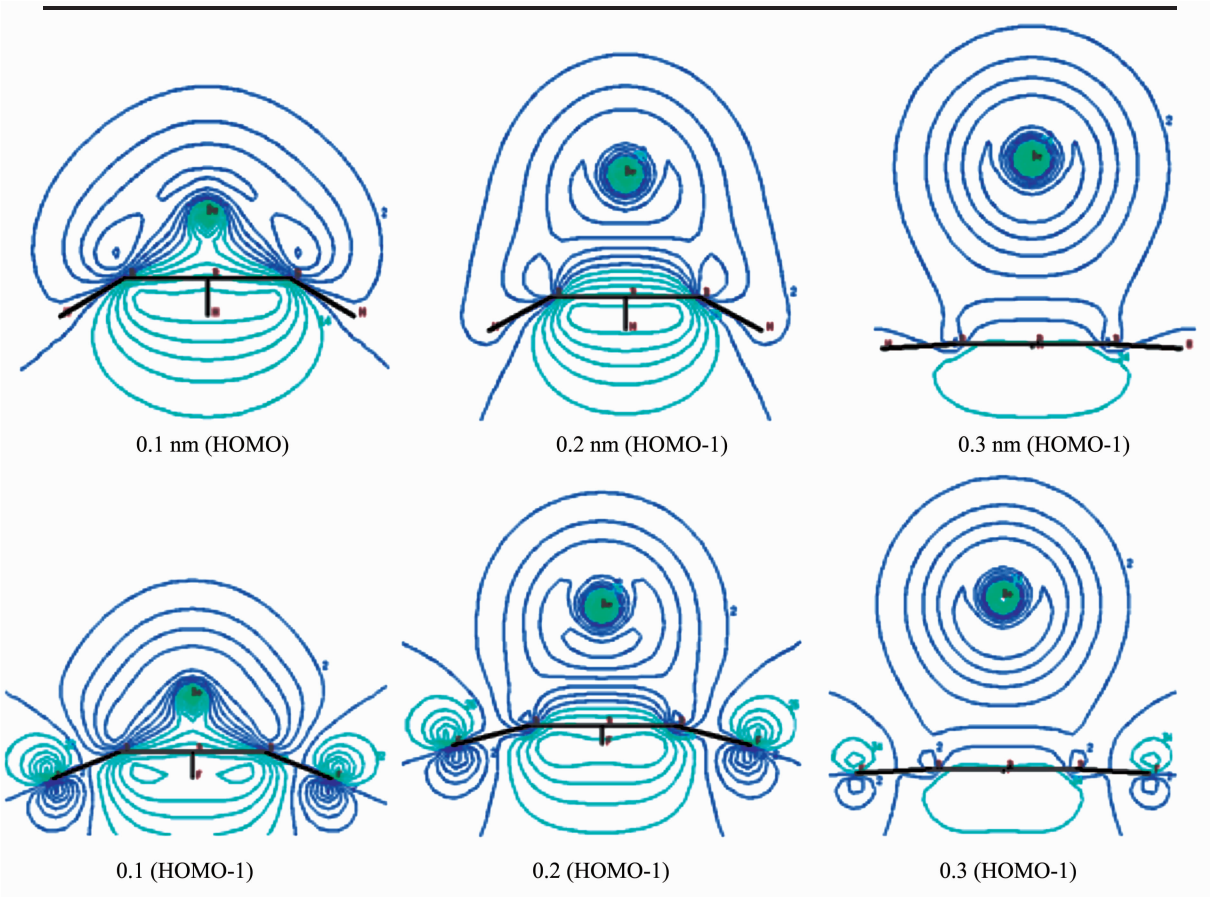
2.3 Aromaticity

NICS is a simple and efficient aromaticity criterion in a wide range of molecules. It is based on the negative value of the magnetic shielding computed at or above the geometrical centers of rings or clusters. 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[23-26]. The more negative the NICS, the more aromatic the molecule is.

In this study, The NICS values were calculated at five different points on and above the B_4 plane (described in the computation details part). The results were listed in Table 4. For the three BeB_4X_4 clusters, The NICS values are different on the two sides of the B_4 plane. On the Be atom side the NICS values calculated are all positive, while on the four terminal atoms side the NICS values calculated are negative. At the center of the B_4 ring, the NICS value is −19.887 1 ppm for BeB_4H_4 and −7.209 0 ppm for BeB_4Cl_4 which is suggesting the existence of delocalization and aromaticity. And for BeB_4F_4 the NICS values is 0.375 3 ppm, which indicate that the BeB_4F_4 is a nonaromatic compound.

Table 4　Calculated NICS values (ppm) with GIAO-HF//MP2/6-311++G(3*df*,2*p*) method for the BeB4X4 (X=H, F, Cl) clusters

NICS (in ppm)	BeB_4H_4	BeB_4F_4	BeB_4Cl_4	HBB_4H_4
BC-0.1	19.423 8	19.464 9	21.802 5	126.915 6
BC-0.05	2.972 6	5.197 1	5.382 9	45.257 4
BC	−19.887 1	0.375 3	−7.209 0	32.207 3
BC+0.05	−29.998 0	−10.265 3	−18.449 8	−8.1985
BC+0.1	−19.979 1	−9.523 2	−13.649 7	−21.086 6



Highly occupied molecular orbital from the optimized geometry

Fig.4　Frozen the distance between Be and B_4H_4 at 0.1, 0.2, 0.3 nm

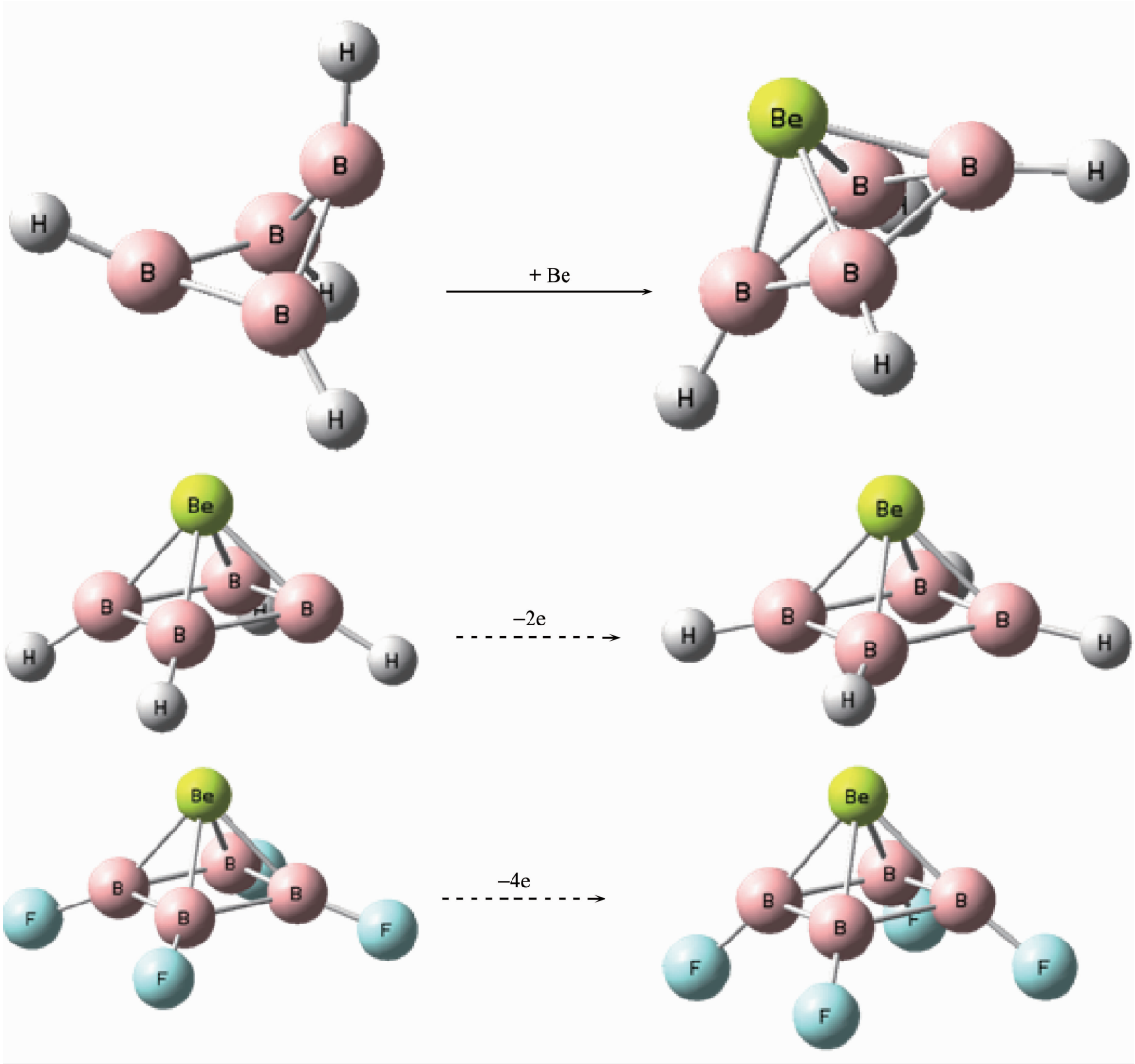


Fig.5 Structure changes when electrons were removed

Some delocalized higher occupied molecular orbitals of the BeB_4X_4 (X=H, F, Cl) and HBB_4H_4 were shown in Fig.2. For the BeB_4H_4 cluster the highest occupied molecular orbital (HOMO, $1a_1$) is rather special. It is a combination of the in-plane 4-center σ bond ($\sigma p1$) and the out-of-plane π bond. The HOMO-1 ($1b_1$) is another in-plane 4-center σ bond ($\sigma p2$). These two kind of 4-center σ bonds have been discussed by Zhan et al[31]. ($\sigma p1$ was shown in Fig.3 and $\sigma p2$ was shown in Fig.2 in the reference 31) in their article. Zhan et al. 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 (σ and π) bonding systems. While in this BeB_4H_4 cluster the multi-center σ and π orbital which should be independent are combined together in HOMO. The HOMO-2 ($1e_1$) includes two degenerated orbitals formed from the out-of-plane p orbitals. The HOMO-4 ($2a_1$) includes some parts of the in-plane 4-center σ bond ($\sigma p1$) as that type in HOMO. The HOMO-6 ($3a_1$) is another 4-center σ bond which was made from the s orbitals of each B atoms.

The σ-Aromaticity initially introduced in hydrocarbons[32-34] has been extended to metal, nonmetal, and metal-nonmetal clusters[31,35-37]. In the BeB_4H_4 cluster, the HOMO-1 and HOMO-6 are two independent delocalized σ-bonding orbitals. Each of the two σ

delocalized bonding systems containing two σ electrons that renders σ aromaticity. The delocalized σ-bonding component in HOMO-4 takes only a small part. For the delocalized π-bonding systems the HOMO-2 with two degenerated orbitals contains four π electrons. If the HOMO was regard as a π bonding orbital, the π electrons will be six and satisfy the famous 4n+2 electron counting rule. From the HOMO picture it shows clear that the main electron cloud are localized down the B_4 plane on the four legends side. Then in a simple word, there are four π electrons active above the B_4 plane on the Be atom side, and there are six π electrons active down the B_4 plane on the other side. That maybe explains the different sign NICS values on the two sides of the B_4 plane. And the B_4 ring here has both the aromaticity and antiaromaticity. This is called half Aromaticity in brief here.

The molecular orbital picture of the BeB_4F_4 cluster is similar to the BeB_4H_4 cluster except the consequence of the HOMO and HOMO-1. The corresponding orbital picture of the BeB_4Cl_4 cluster is similar to the BeB_4F_4 cluster, but the (HOMO-7, $2a_1$) for BeB_4Cl_4 which has little components of the multicenter bond was not list. And for the HBB4H4 cluster, its molecular orbital picture is adjacent to the BeB_4H_4 cluster.

3 Summary

Here the BeB_4X_4 (X =H, F, Cl), HBB_4H_4 and $BB_4H_4^+$ clusters were calculated to be stable and all have the square pyramidal shape. The vertexes of these clusters Be, BH and B act as electron pair donors. And the B_4X_4 (X =H, F, Cl) part act as electron pair accepters. The B_4X_4 part looked just like a bowl to accommodate the electron pair.

For the BeB_4X_4 (X =H, F, Cl) clusters the interaction energies between Be and B_4X_4 (X=H, F, Cl) part decrease in the sequence of BeB_4H_4>BeB_4Cl_4> BeB_4F_4, the charges of the Be atoms decrease in the same sequence. A direct interaction between the terminal atoms X(H, F, Cl) and the electrons in bowls maybe owns to this phenomenon. The shape of the B_4X_4 bowls are also affected through these X-e interactions. With the positive charged Be atom and the electron cloud in the B_4X_4 bowl, the stable BeB_4X_4 (X =H, F, Cl) clusters should have some special character when act with other reagents.

From the NICS values and the phenomenon that two delocalized electrons were forced on one side of the B_4 plane in B_4X_4 bowl, The B_4 plane here was proved to have the half Aromaticity.

The stable clusters HBB_4H_4 and $BB_4H_4^+$ are another two exceptions to the Wade's rules.

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