The $C_6B_{12}^{2-}$ complex: A beautiful molecular wheel containing a ring of six planar tetracoordinate carbon atoms

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Abstract

We predicted by density functional theory (DFT) calculations the C–B binary wheel-like clusters: planar $C_6B_{12}^{2-}$, quasi-planar C_6B_{12} and $C_6B_{12}^{2+}$ complexes. The $C_6B_{12}^{2-}$ dianion with D_{6h} symmetry has six equivalent planar tetracoordinate carbon atoms. Remarkably, its C_6 unit is highly fluxional and rotates readily inside the boron perimeter. Based on our calculating results, we do not think that the Hückel $4n+2\pi$ electron rule is applicable to describe the aromaticity of the whole ring-in-ring systems, but suitable for each individual ring. Further analysis reveals that the multicenter σ bonding helps bind the outer boron ring to central C_6 unit.
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1. Introduction

The design of complexes with planar tetracoodinate carbon (PTC) or planar hypercoordinate carbon (PHC) center has been a 'stand alone' research goal and the recent reports mainly focused on the design and studies of the molecules with merely one PTC or PHC, which were often described as the molecular wheel [1–16], while few attention has been paid to the molecules with multi PTC or PHC centers, especially those with high symmetries. To the best of our knowledge, only the groups of Prof. Schleyer and Prof. Li Si-Dian reported some complexes with multi PTCs or PHCs, which were constructed by bridging some known clusters with single PTC or PHC center, thus, these complexes did not have high symmetry [10,17,18]. Very recently, to solve the problem that more than eight-membered boron rings are too large to bind only a carbon, Prof. Schleyer et al. introduce multi carbon atoms to the center of boron ring and find C_2B_8, $C_3B_9^{3+}$ and $C_5B_{11}^+$ species [19]. Of them, the former two complexes have D_{2h} and D_{3h} symmetries, but they have no obvious PTC or PHC; only the C_{2v} $C_5B_{11}^+$ has an unambiguous PTC. However, their works present a new thoughtway to design the wheel-like molecules

with multi PTCs or PHCs. The results of our computations reveal that for the C–B binary system, the six-membered central carbon ring will fit nicely, both geometrically and electronically, with the 12-membered outer boron ring. The suitable proportion of the numbers of carbon and boron atoms makes it potentially possible to design and then achieve the molecules with high symmetries and multi PTCs or PHCs. By means of extensive computational explorations, we studied the possibilities of C_6B_{12} species with various structures and charges and located three wheel-like (The wheels in two pictures of Fig. 1 look like each other, do not they?) stable local minima: planar $C_6B_{12}^{2-}$ dianion, quasi-planar C_6B_{12} neutral molecule and $C_6B_{12}^{2+}$ dication (Fig. 2). They have 14-, 12- and 10-π-electron, respectively. As Fig. 2A shows, D_{6h} $C_6B_{12}^{2-}$ dianion has six PTCs and the other two minima (Fig. 2B and D) both have new hexagon-in-hexagon structures.

2. Computational details

The fully optimization and imaginary frequencies analyses of $C_6B_{12}^q$ were performed at DFT B3LYP/6-311+G (2df) level and those of MC_6B_{12} (M=Mg and Ca) at B3LYP/6-31g (d) level. The DFT wave functions of C_{6v} C_6B_{12} and $C_6B_{12}^{2+}$ minima were checked to be stable, while that of $C_6B_{12}^{2-}$ minimum was unstable because of positive eigenvalues of its top six occupied orbitals. However, the dianion could be effectively stabilized by introducing metal ions into the system. As shown in Fig. 3, the cases of $C_6B_{12}Mg$ and $C_6B_{12}Ca$ were

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Fig. 1. Left wheel: the real wheel of a car, right wheel: the molecular orbital (MO) 34 of the $C_6B_{12}^{2-}$ dianion.

confirmed to have the stable wave functions as well as negative highest occupied molecular orbital (HOMO) energies of -4.46 and -4.82 eV. We estimated that the $C_6B_{12}^{2-}$ dianion could exist in its saline solution with some organic solvent such as tetrahydrofuran (THF). To examine the bonding feature and assess the aromaticity of the complex, we performed the natural bond orbital (NBO) analysis and nucleus-independent chemical shift (NICS) calculations [20], respectively, at B3LYP/6-311+G (2df) level. All calculations were performed by using GAUSSIAN 03 package [21].

3. Results and discussion

As shown in Fig. 2A, all carbon atoms in the $C_6B_{12}^{2-}$ complex are all unambiguous PTC, which is originated from the three-center two-electron bond of every CB_2 triangle. This dianion has relative higher D_{6h} symmetry (in this case, all carbon atoms are equal to each other and similar situations are met in boron atoms), together with the properly arranged atoms that make the whole molecule look like the tire steel and if the plot of its molecular orbital is added, it will look more like the real wheel as shown in Fig. 1. More significantly, similar to the situation observed in the C_2B_8, $C_3B_9^{3+}$ and $C_5B_{11}^+$ complexes, the C_6 center of the $C_6B_{12}^{2-}$ complex is also highly fluxional and rotates readily inside the boron perimeter. The barrier for counter rotation of outer boron ring and inner C_6 unit could almost be neglected. We could not locate any transition state (TS) for rotation at B3LYP/6-311+g (2df) level.

The quasi-planar C_{6v} C_6B_{12} and $C_6B_{12}^{2+}$ both have wheel-like structures, too. But their 12-membered outer boron rings

both arrange in the hexagon-like conformation, of which six boron atoms locate at the middle points of the edges and the other six locate at the vertexes. The central carbon atoms contact directly to the former. In this manner, their central carbon atoms are all planar tricoordinate. Each carbon center is too weakly bound ($r \approx 2$ Å) to its nearest two vertical boron atoms to have fully developed planar pentacoordination. Compared with that in $C_6B_{12}^{2-}$ dianion, the rotations of their central C_6 units with regard to the outer 12-memberd hexagon are extremely difficult. We locate a TS for each C_{6v} complex, but the barrier for rotation are 14.25 and 29.95 kcal/mol for C_6B_{12} and $C_6B_{12}^{2+}$, respectively, which could not be over-stepped under the normal conditions.

As these complexes are the derivatives of aromatic benzene, it is interesting to study their aromaticities. Orbital analyses reveal that the planar $C_6B_{12}^{2-}$ dianion, quasi-planar C_6B_{12} neutral molecule and $C_6B_{12}^{2+}$ dication have 14, 12 and 10 π-electrons, respectively. The lowest unoccupied molecular orbital (LUMO) and occupied π MOs of these three complexes are shown in Fig. 4. The full set of the valence orbitals are given in the Supporting Information. According to Hückel $(4n+2)$ π electron rule, the 12-π-electron C_6B_{12} complex should be an antiaromatic molecule and the other two complexes should be aromatic. To assess the aromatic characters of these complexes, we calculated the NICS for the ghost atoms located 0.0, 1.0 and 2.0 Å above the geometrical center of all unique rings employing the gauge-independent atomic orbital (GIAO) approach [22,23]. As shown in Table 1, the results show that if the whole molecule is investigated, the 10-π-electron $C_6B_{12}^{2+}$, 12-π-electron C_6B_{12}, 10-π-electron TS D_{6h} $C_6B_{12}^{2+}$ and 12-π-electron TS D_{6h} C_6B_{12} complexes are aromatic, while the whole 14-π-electron $C_6B_{12}^{2-}$ complex is antiaromatic, but its CB_2 triangles of $C_6B_{12}^{2-}$ complex are aromatic. The only difference among $C_6B_{12}^{2-}$, TS D_{6h} C_6B_{12} and TS D_{6h} $C_6B_{12}^{2+}$ is whether the MO 48 and MO 49 (Fig. 4) are occupied or not. According to Hückel $(4n+2)$ π electron rule, the sixth and seventh lowest π MO 48 and 49 should be the antibonding orbital and bonding orbital, respectively. However, as the first row of Fig. 4 shows, the pattern of the MO 48 has obvious characters of bonding orbital, so the aromaticity of the whole molecule increases when MO 48 is occupied (compare the NICS values of two TS in Table 1). In contrast,
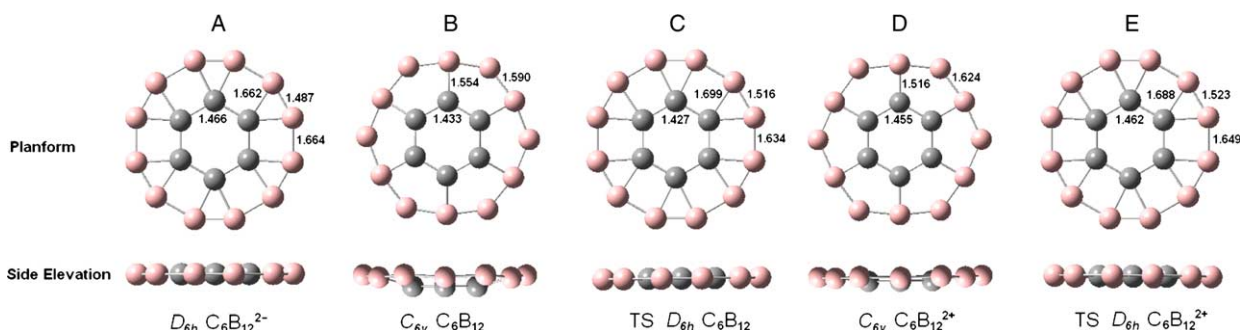

Fig. 2. Optimized structures of $C_6B_{12}^q$ ($q = -2$, 0 or $+2$) complexes with necessary bond lengths (Å). The pink balls stand for boron atoms and the gray balls for carbon atoms (for interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).
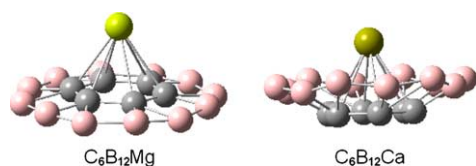
Fig. 3. Optimized structure of $C_6B_{12}Mg$ and $C_6B_{12}Ca$ (symmetry restrictions are removed).

the pattern of the MO 49 exhibits antibonding character for the whole molecule as well as C_2B_2 squares and central C_6 unit, but bonding character for CB_2 triangles. Thus, when the MO 49 is occupied, the whole molecule becomes antiaromatic, but the CB_2 triangle still keeps aromatic. It is noteworthy that similar situations are met in C_{6v} $C_6B_{12}^{2+}$ and C_{6v} C_6B_{12} complexes. The C_{6v} $C_6B_{12}^{2+}$ complex is aromatic and its occupied π orbitals have typical pattern of a 10-π-electron, Hückel, aromatic system (Third row of the Fig. 4). When MO 48 is occupied, the aromaticity increases, too (C_{6v} C_6B_{12} complex has lower NICS values than that of C_{6v} $C_6B_{12}^{2+}$ dication as shown in Table 1).

With above analyses, we do not think that the Hückel $4n+2\pi$ electron rule, which is based on the single ring system, is applicable to describe the aromaticity of the whole ring-in-ring systems, but maybe suitable for each individual ring.

These molecules all have 24 occupied σ valence orbitals and all of them are highly delocalized in the whole molecule. It is interesting that their 10 lowest occupied σ valence orbitals are similar to their typical π orbitals in both orbital patterns and energy orders. Take the situation in

$C_6B_{12}^{2-}$ dianion as an example, the pattern of σ MO 19 is similar to MO 31; MO 20, 21 to MO 35, 36; MO 22, 23 to 46, 47; MO 24 to MO 48; MO 25, 26 to MO 49 and MO 27, 28 to MO 50, 51 (see Supporting Informations).

It is noteworthy that the $C_6B_{12}^{2-}$ complex has six equal PTCs, which are originated from the electron-deficient multicenter σ bonding. Natural bond orbital analysis could confirm and explain these peculiar bonding pattern. D_{6h} $C_6B_{12}^{2-}$ has the natural atomic electronic configurations of C, [He] $2s^{0.89}2p^{3.39}(2s^{0.89}2p_x^{1.19}2p_y^{1.11}2p_z^{1.09})$ and B, [He] $2s^{0.81}2p^{2.19}(2s^{0.81}2p_x^{0.86}2p_y^{0.71}2p_z^{0.62})$, which are in agreement with the natural atomic charge of C, -0.285 and B, $-0.024|e|$. Though all carbon atoms are planar tetracoordinate and the boron atoms are planar tricoordiante, its total Wiberg bond indecies (WBI) show $WBI_C = 3.97$ and $WBI_B = 3.53$. Thus, the octet rule is not violated. To bind the central C_6 unit with outer electron-deficient boron ring, it is necessary to form the multicenter σ bonds. In fact, every CB_2 triangle in Fig. 2A could be assigned three-center two-electron character. The Wiberg bond order of C–B is $WBI_{C-B} = 0.75$, so each CB_2 triangle has the total $WBI_{C-B} = 1.5$. If the p_z valence concerning the delocalized π interaction is excluded, there leaves total $WBI_{C-B} = 1$. The existence of these multicenter bonds is essential to the stable contact of the inner and outer rings.

4. Conclusion

We predicted by DFT calculations the C–B binary wheel-like clusters: planar $C_6B_{12}^{2-}$ dianion, quasi-planar C_6B_{12} neutral
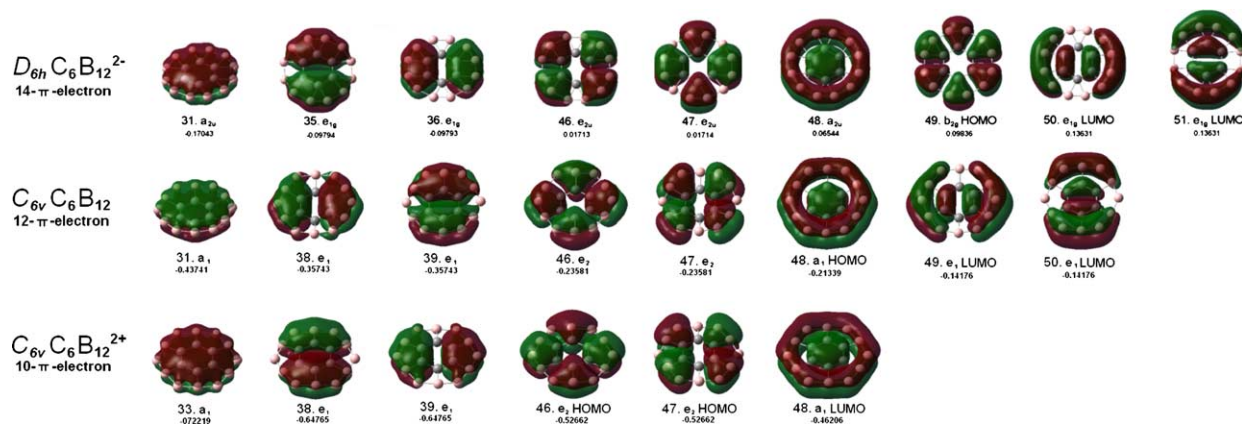

Fig. 4. Plots of the LUMO and occupied π MOs of D_{6h} $C_6B_{12}^{2-}$, C_{6v} C_6B_{12} and $C_6B_{12}^{2+}$ complexes. Orbital energies are given in Hartrees.

Table 1
The calculated NICS values (ppm)

	$C_6B_{12}^{2-}$			TS C_6B_{12}			TS $C_6B_{12}^{2+}$			C_6B_{12}		$C_6B_{12}^{2+}$	
	C_6	CB_2	C_2B_2	C_6	CB_2	C_2B_2	C_6	CB_2	C_2B_2	C_6	C_2B_3	C_6	C_2B_3
2 Å	5.02	2.96	5.14	−10.00	−5.42	−5.98	−8.32	−4.08	−4.66	−10.97	−8.08	−8.53	−4.86
1 Å	7.03	−4.30	10.97	−16.35	−15.42	−9.91	−13.54	−12.34	−7.68	−17.73	−13.33	−13.61	−8.22
0 Å	17.33	−28.52	17.36	−11.16	−28.67	−1.01	−12.07	−15.52	4.86	−9.93	−4.20	−9.64	2.21
−1 Å										−13.31	−6.13	−12.19	−5.32
−2 Å										−9.18	−3.40	−8.09	−3.25

molecule and $C_6B_{12}^{2+}$ dication. Remarkably, all carbon atoms of the $C_6B_{12}^{2-}$ dianion are planar tetracoordinate and the whole C_6 unit is highly fluxional; the inner C_6 unit and outer boron ring can rotate quite freely with regard to one another. The NBO analysis explains the peculiar structures (especially the multi-center bonding) of these complexes and NICS behaviors of the complexes reveal that the Hückel $4n + 2\pi$ electron rule, which is based on the single ring system, is not always applicable to describing the aromaticity of the ring-in-ring systems, but maybe suitable for each individual ring. These predictions await experimental confirmation, which would establish a new rule to describe the aromaticity of the complicated systems, such as the molecules with ring-in-ring structures.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2006.03.006

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