Boron-based binary \( \text{Be}_6\text{B}_{10}^{2-} \) cluster: three-layered aromatic sandwich, electronic transmutation, and dynamic structural fluxionality

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Boron-based nanoclusters have unique structures, bonding, and dynamic properties, which originate from boron’s electron-deficiency. We demonstrate here that pouring in extra electrons can alter such systems fundamentally. A coaxial triple-layered \( \text{Be}_6\text{B}_{10}^{2-} \) sandwich cluster is designed via global structural searches and quantum chemical calculations. It is well defined as the global minimum, which consists of a slightly elongated \( \text{B}_{10} \) monocyclic ring and two \( \text{Be}_3 \) rings, the latter forming a \( \text{Be}_6 \) trigonal-prism albeit without interlayer \( \text{Be} \)–\( \text{Be} \) bonding. The \( \text{B}_{10} \) ring shows structural and chemical integrity with respect to the \( \text{Be}_3 \) rings, and yet it differs markedly from the free \( \text{B}_{10} \) cluster and closely resembles the \( \text{C}_{10} \) cluster. The present data testify to the idea of electronic transmutation, in which a \( \text{B} \) is equivalent to \( \text{C} \) and a \( \text{B}_3 \) cluster, upon charge-transfer, is converted to and stabilized as a monocyclic ring analogous to \( \text{C}_{10} \). Chemical bonding analyses reveal that the \( \text{B}_{10} \) ring in the \( \text{Be}_6\text{B}_{10}^{2-} \) cluster has 10\( \pi \) and 10\( \sigma \) delocalization and each \( \text{Be}_3 \) ring is held together by 2\( \sigma \) electrons, collectively rendering four-fold \( \pi/\sigma \) aromaticity. The bonding pattern is in line with the formula of \( [\text{Be}_3]^{4+}[\text{B}_{10}]^{10-} [\text{Be}_3]^{4+} \) suggesting a highly charged electron-transfer complex. Furthermore, the \( \text{Be}_6\text{B}_{10}^{2-} \) cluster is dynamically fluxional with dual modes of revolution (orbiting) and rotation (twisting), being structurally robust at least up to a temperature of 1500 K.

1. Introduction

Boron as an electron-deficient element possesses new chemistry that differs from carbon, its nearest neighbor in the periodic table. Boron-based nanoclusters are of current interest in physical chemistry and materials science. Elemental boron clusters assume planar or quasi-planar (2D) geometries in a wide range of sizes, up to 40 atoms for anions, which are governed by aromaticity, antiaromaticity, or conflicting aromaticity. Planar boron clusters also show an isolobal analogy to boranes and hydrocarbons in terms of chemical bonding. These 2D clusters are dominated by close-packing triangular \( \text{B}_3 \) units, which are complemented by quadrangular, pentagonal, and hexagonal defect holes.

Notably, monocyclic boron rings are scarce in 2D boron clusters nor do they appear in low-dimensional boron nanomaterials (such as borospherenes, nanotubes, and borophenes). In contrast, boron double chains (BDCs) or BDC ribbons prevail in low-dimensional boron systems, which help compensate for electron-deficiency. Carbon clusters are known to form monocyclic ring structures, with \( \text{C}_{10} \) being a typical example. Thus, it is of interest to raise a couple of fundamental questions. Is it possible to make or stabilize monocyclic boron rings in gas-phase boron clusters? Can we chemically convert boron into carbon (or can we design a boron cluster that resembles a carbon one)? If yes, how? What is the nature of bonding in such monocyclic boron rings? What are the possible electron counting rules?

Considering the intrinsic electron deficiency of boron, a natural way to approach the above mentioned goal is to pour a sufficient number of extra electrons into a boron cluster. To this end, binary Be–B clusters are ideal systems, in which Be has a rather low electronegativity and is capable of donating up to two electrons per Be atom. Such binary clusters have been explored recently. In particular, Zhai and coworkers studied a \( \text{Be}_6\text{B}_{11}^- \) cluster, unraveling two highly competitive 3D isomeric structures: a boron helix versus a boron-based sandwich.
The latter species possesses structural fluxionality with dual dynamic modes. Fluxional clusters are intriguing in physical chemistry as well as in nanoscale and nanotechnologies. Boron is the magic element for structural fluxionality. Previous fluxional clusters are rare and they have only one dynamic mode, either as molecular Wankel motors or subnanoscale tank treads.

The \( \text{B}_{10} \) cluster is quasi-planar and features close-packed boron triangles, which have no rhombic or rectangular defect sites. The shape is anticipated to be dynamically nonfluxional. Indeed, a recent theoretical work suggests that \( \text{B}_{10} \) has a considerable energy barrier for in-plane rotation (12.7 kcal mol\(^{-1} \)) using unbiased Coalescence Kick (CK) and Minima Hopping (MH) algorithms. Some 8000 stationary points in total fluxional clusters are rare and they have only one dynamic mode, either as molecular Wankel motors or subnanoscale tank treads. Further, the \( \text{B}_{10} \) cluster turns into a monocyclic ring, which becomes part of a well-defined global-minimum (GM) \( \text{Be}_{6}\text{B}_{10}^{2-} \) cluster. Second, the \( \text{B}_{10} \) cluster maintains its chemical integrity in the alloy, except that it is now in a charged state of \([\text{B}_{10}]^{10-}\) owing to electron transfer from Be centers. Third, the alloy system cluster resembles a \( \text{C}_{10} \) cluster in terms of geometry and bonding. Note that the \( \text{C}_{10} \) cluster is dynamically nonfluxional. Indeed, a recent theoretical work suggests that \( \text{B}_{10} \) has a quasi-planar and features close-packed boron triangles, which have no rhombic or rectangular defect sites. The shape is anticipated to be dynamically nonfluxional. Indeed, a recent theoretical work suggests that \( \text{B}_{10} \) has a considerable energy barrier for in-plane rotation (12.7 kcal mol\(^{-1} \)) using unbiased Coalescence Kick (CK) and Minima Hopping (MH) algorithms. Some 8000 stationary points in total fluxional clusters are rare and they have only one dynamic mode, either as molecular Wankel motors or subnanoscale tank treads.

2. Methods

Global structural searches were conducted for \( \text{Be}_{6}\text{B}_{10}^{2-} \) cluster using unbiased Coalescence Kick (CK) and Minima Hopping (MH) algorithms. Some 8000 stationary points in total were probed on the potential energy surface. Subsequently, candidate low-lying isomers were re-optimized at the PBE0/6-311+G(d) level, with zero-point energy (ZPE) corrections. Frequency calculations were done at the same level to confirm that the reported structures are true minima unless stated otherwise. To confirm the energetics, the top-five low-lying isomers were benchmarked using single-point CCSD(T) calculations, that is, at the CCSD(T)/6-311+G(d)/PBE0/6-311+G(d) level.

To evaluate the energy barrier with regards to molecular dynamics (MD) and for comparison with the literature, the transition state (TS) structures of \( \text{Be}_{6}\text{B}_{10}^{2-} \) were also optimized at the PBE0-D3/def2-TZVP level along with the frequency calculations. QST2 and intrinsic reaction coordinate (IRC) calculations were performed at the PBE0/6-311+G(d) level to locate and confirm TS structures. Salt complex cluster \( \text{Be}_{6}\text{B}_{10}\text{Na}_{2} \) was also optimized at the PBE0/6-311+G(d) and PBE0-D3/def2-TZVP levels.

Chemical bonding was elucidated using canonical molecular orbitals (CMOs), adaptive natural density partitioning (AdNDP), and natural bond orbital (NBO) analysis at the PBE0/6-311+G(d) level; the latter offers Wiberg bond indices (WBIs). Nature charges were calculated independently using NBO 6.0. Orbital composition was analyzed by the Multiwfn program. Nucleus-independent chemical shifts (NICSs) were calculated for selected species at the PBE0/6-311+G(d) level to assess aromaticity. Born–Oppenheimer molecular dynamics (BOMD) simulations were performed using CP2K. AdNDP results were visualized using Molekel.

3. Results

3.1. Global-minimum \( \text{Be}_{6}\text{B}_{10}^{2-} \) cluster

Our computer global searches, PBE0/6-311+G(d) calculations, and CCSD(T) benchmarking lead to the GM structure of the \( \text{Be}_{6}\text{B}_{10}^{2-} \) cluster: \( \text{Be}_{6}\text{B}_{10}^{2-} \) (C\(_{2v}\), \( ^{1}\text{A}_{1} \)). Overall, cluster 1 is reasonably well defined on the potential energy surface (Fig. 1–5), being about 10 kcal mol\(^{-1} \) more stable than its nearest competitor at both the PBE0 and single-point CCSD(T) levels. Cluster 1 consists of three coaxial rings: a monocyclic \( \text{B}_{10} \) ring in the middle and two \( \text{Be}_{3} \) rings at the top and bottom (Fig. 2(a)). The two \( \text{Be}_{3} \) rings overlap spatially, forming a trigonal prism with distortion (Fig. 2(b)). Interlayer bonding between \( \text{Be}_{3} \) rings is minimal despite their closeness in space (vide infra), which justifies the assessment of cluster 1 as a sandwich.

The nature of B–B, Be–Be, and B–Be bonding in cluster 1 can be largely recognized from their bond distances. Recommended covalent radii by Pyykko give the upper limit of single B–B, double B–B, and single Be–Be bonds as 1.70, 1.56, and 2.04 Å, respectively. For further reference, a typical B–B double bond is 1.51 Å, whereas the bond distances in \( \text{Be}_{3} \) and \( \text{Be}_{3}^{+} \) are 2.44 Å (van der Waals) and 2.21 Å (half bond), respectively.

Therefore, the B–B bonds in the \( \text{B}_{10} \) ring of cluster 1 (1.55–1.60 Å) are beyond single bonds, with clear double bond characters. The Be–Be links in \( \text{Be}_{3} \) rings (2.06–2.14 Å) indicate strong bonding, probably comparable to that in \( \text{Be}_{3}^{+} \). Interlayer Be–Be distances (2.11–2.24 Å) are also short, but their WBIs are close to zero (Fig. 3(a)), suggesting that there is no bonding. Between the \( \text{Be}_{3} \) core and outer \( \text{B}_{10} \) ring, the Be–B links as depicted in Fig. 2(b) are diverse, spanning from 1.84 to 2.20 Å (not shown). Such bonds are quite ionic, with a rather weak covalent component.

One may argue that a dianion cluster such as 1 is electronically unstable, due to Coulomb repulsion between the two extra charges. Thus we also explored the neutral salt complex, \( \text{Be}_{6}\text{B}_{10}\text{Na}_{2} \), using two Na\(^{+} \) counter-ions to balance charges. Among different configurations, the lowest-energy one is a \( \text{C}_{2v} \) (\( ^{1}\text{A}_{1} \)) salt complex; see the ESI (Fig. S1). It is a true minimum, showing virtually identical geometry with respect to GM cluster 1. This structure was also optimized at the PBE0-D3/def2-TZVP level (not shown), resulting in similar geometry.

3.2. Selected isomeric and transition-state structures

Higher energy isomers of the \( \text{Be}_{6}\text{B}_{10}^{2-} \) cluster (Fig. 1) are generally unimportant in light of the reasonably defined GM \( \text{Be}_{6}\text{B}_{10}^{2-} \) (C\(_{2v}\), \( ^{1}\text{A}_{1} \)) cluster. We choose to briefly describe isomers 3 and 8 only. Isomer 3 as a local minimum (LM) differs from GM 1 by a twist of one \( \text{Be}_{3} \) ring against another, so that two \( \text{Be}_{3} \) rings are...
in a staggered fashion (Fig. 4 and 5). The energy cost is \( \sim 10 \text{ kcal mol}^{-1} \) at single-point CCSD(T). The B–B distances (1.57–1.63 Å) in 3 expand slightly as compared to GM 1, while those of Be–Be (2.06–2.10 Å) shrink slightly. These minor changes reflect the spatial constraints for rotation between two Be\(_3\) rings. Isomer 8 contains an open, helix B\(_{10}\) chain. It is \( \sim 15 \text{ kcal mol}^{-1} \) above GM 1, in contrast to our recent report on a Be\(_6\)B\(_{10}\)^{2–} cluster\(^{11}\), for which the helix isomer is energetically competitive with the sandwich cluster. Thus, chain size has a remarkable effect on the stability of a boron helix. While exploring the potential energy surface of the Be\(_6\)B\(_{10}\)^{2–} cluster, we also located certain TS structures: TS\(_1\) and TS\(_2\) (Fig. 2(c) and 4(b)).\(^6^0\)

### 3.3 Wiberg bond indices and natural charges

The above analyses based on the geometries unveil a rough bonding picture for the Be\(_6\)B\(_{10}\)^{2–} cluster. NBO analysis confirms...
this picture, using WBIs and natural atomic charges. Calculated WBI values for B–B links in the GM cluster 1 are 1.50–1.76 (Fig. 3(a)), which are well beyond single bonds, suggesting delocalized bonding in the outer B10 ring. The WBIs of Be3 rings are 0.28/0.32, hinting at a delocalized bonding system here. In contrast, the WBIs of interlayer Be–Be links are negligibly small (0.02/0.03). There is no interaction between two Be3 rings. The WBI data are in line with a triple-layered sandwich cluster 1, whose two Be3 rings are independent from each other.

Natural atomic charges in GM 1 indicate substantial interlayer charge transfers from the two Be3 rings to the middle B10 layer. Each Be center carries a positive charge of greater than 1.0, and six Be atoms collectively donate a net charge of 6.56 |e| to the B10 ring. The formal number of charges is anticipated to be even larger, resulting in a highly charged cluster system. NBO data for TS1 are similar to those of GM 1, except that the charges shift circularly with the Be centers (Fig. 3(b)). Charge transfers from Be to B in the system are rather local processes, depending sensitively on coordination with the Be centers.

4. Discussion
4.1. Chemical bonding in the sandwich Be6B10^2– cluster: four-fold \( \pi/6 \) aromaticity

It is relatively straightforward to elucidate the bonding in GM Be6B10^2– (1, \( C_{2v}, 1A_1 \)) cluster through CMO analyses. Cluster 1 is a bonding system with 44 valence electrons, which occupy 22 CMOs as depicted in Fig. 6. Here the CMOs are sorted into five subsets, according to the type of atomic orbital (AO) of which a specific CMO is composed. Subset (a) involves 10 CMOs, mainly derived from B 2s AOs in the outer B10 ring. The CMOs have 0, 1, 2, 3, 4, and 5 nodal planes, respectively, following the
construction principles. They represent a complete series of CMOs that are responsible for peripheral B–B σ bonding in the \( B_{10} \) ring, which can be transformed to and localized as two-center two-electron (2c–2e) Lewis B–B σ bonds, one for each B–B link. This subset is the only Lewis element in cluster 1, consuming 20 electrons. All of the other 24 electrons participate in delocalized bonding.

Subset (b) contains five \( π \) CMOs, which are derived primarily from \( 2p_z \) AOs; see Table S1 [ESI†] for their orbital components. Among these, HOMO–14 has the largest contribution from the \( Be_6 \) prism (38.1%), which can recombine constructively/destructively with HOMO–4 to fully recover two spatially separated “π” CMOs: one for the outer \( B_{10} \) ring and the other for the inner \( Be_6 \) prism. Subset (b) also strictly follows the building principles, with 0, 1, and 2 nodal planes that are perpendicular to the \( B_{10} \) ring; the intrinsic nodal plane associated with the p-type AO is not counted, as routine. Indeed, these CMOs show one-to-one correspondence, in terms of the spatial pattern, to the lower
energy CMOs in subset (a). The five π CMOs cannot be localized and represent a 10π aromatic subsystem, conforming to the \((4n + 2)\) Hückel rule. Subset (c) is analogous to subset (b), except that the former is \(\sigma\) in nature based on radial B 2p AO. These 10σ electrons cannot be transformed into Lewis bonds and render \(\sigma\) aromaticity to cluster 1.

Subsets (d) and (e) are mainly clouded on the inner Be₆ prism, which can be fully “purified” upon combination with HOMO−14 and HOMO−13, respectively, as mentioned earlier. The two “purified” bonds represent a constructive/destructive combination between two Be₃ rings, which are readily transformed to two 3c–2e \(\sigma\) bonds, one on each Be₃ ring. Thus a Be₃ ring in cluster 1 is held together merely by one 3c–2e \(\sigma\) bond.

In short, the sandwich cluster features four-fold electron delocalization: the B₁₀ ring has 10π and 10σ subsystems and each Be₃ ring has a 2σ subsystem, which all satisfy the Hückel rule, rendering four-fold π/σ aromaticity for cluster 1. This bonding picture is beautifully borne out using AdNDP (Fig. 7). An alternative AdNDP scheme for 10π/10σ subsystems is presented in Fig. S2 (ESI†). Since each Be₃ ring has only one 3c–2e \(\sigma\) bond, cluster 1 should be formally formulated as \(\text{[Be}_3\text{]}^{4+}\text{[B}_{10}\text{]}^{10}\text{/C}_0\text{[Be}_3\text{]}^{4+}\), a highly-charged electron-transfer complex. Indeed, NBO analysis gives an effective formula of \(\text{[Be}_3\text{]}^{1.28}\text{[B}_{10}\text{]}^{8.56}\text{[Be}_3\text{]}^{2.81}\) (Fig. 3(a)). One reviewer suggests an interesting possibility of applying charge decomposition analysis (CDA)⁶² to this charge transfer complex.

While we are aware of the fact that CDA is a partitioning scheme for donor-acceptor interactions and applies best for metal–ligand systems, we chose to accommodate the reviewer and ran preliminary CDA calculations. The results are in line with a charge-transfer complex.⁶³ We stress that the bonding picture is entirely reached via CMO analyses, further confirmed by AdNDP and NBO data. With this picture, cluster 1 is held together primarily via electrostatics between the three layers, with secondary haptic covalent bonds. The latter have WBI values of 0.11–0.16.

Interestingly, the two Be₃ rings, which have 2s electrons only, participate in both π and \(\sigma\) bonding with the B₁₀ ring. Their main CMOs are HOMO−14/HOMO−14 and HOMO−13/HOMO−5 (Fig. 6). The shape of HOMO−14 is peculiar. Two layers of Be₃ 3c–2e \(\sigma\) clouds couple out-of-phase and disguise as a “π” component, facilitating a global π bond. The B 2p \(z\) component serves as a clamp (with intrinsic thickness) and pulls the two Be₃ rings close, balanced by electrostatics between the Be₃/B₁₀/Be₃ rings. Here the Be₃–Be₃ bonding is not necessarily optimal despite short interlayer Be–Be distances, leading to an unusual situation: close and nonbonding.

NICS calculations may be used as a qualitative measure for aromaticity of a molecular system. Generally, NICSₜ is considered as a better indicator for planar molecules. The calculated NICSₜ values at the PBE0/6-311+G(d) level are highly negative for cluster 1: −77.78 ppm at the center of the B₁₀ ring and −66.01 ppm at 1 Å

![Fig. 7](image-url)
above the center (Table 1), which confirm the assessment of $\pi/\sigma$ aromaticity, in line with CMO and AdNDP analyses. It should be stressed that the NICS$_{zz}$ values herein are the collective effects of all four-fold $\pi/\sigma$ aromatic subsystems to a probing point, so that NICS$_{zz}(1)$ is not solely associated with $\pi$ aromaticity of the $B_{10}$ ring, because of the “perturbation” of $\sigma$ aromaticity of the $B_3$ ring in the vicinity. Indeed, we do not intend to disentangle the contributions of the four aromatic subsystems from each other. The NICS data serve only as an additional support of $\pi/\sigma$ aromaticity in the $Be_B_{10}^{2-}$ (1) cluster, which is a relatively minor issue of this paper.  

### 4.2. Electronic transmutation: analogy between the $Be_B_{10}^{2-}$ cluster, the carbon cluster $C_{10}$, and the hydrocarbon compound $C_{10}H_{10}$

CMO and AdNDP analyses show that 1 is a charge transfer complex: \([Be_3]^+\frac{[B_{10}]}{10} [Be_3]^{4-}\). Specifically, “antibonding” electrons from $Be_3$ rings are transferred to “bonding” CMOs of the $B_{10}$ ring. Charge-transfer not only helps compensate for boron’s electron-deficiency, but also strengthens bonding in the $B_{10}$ rings. The resultant complex cluster 1 has a sandwich shape with aromatic \([Be_3]^{3+}/[B_{10}]^{10-}/[Be_3]^{4-}\) subsystems, which are held together through electrostatics.  

In contrast to carbon, bare boron clusters do not form monoboronyl rings. The $B_{10}$ cluster is quasi-planar with two dovetailed hexagonal pyramids, which is composed solely of close-packing $B_3$ triangles.\(^\text{10}\) It has delocalized $6\pi$ and $8\sigma$ subsystems, clouding on the 2D surface. On the other hand, the $C_{10}$ cluster has monocylic geometry.\(^\text{17}\) Thus, it seems feasible that if a sufficient number of extra electrons are donated to the $B_{10}$ cluster, the latter can be transformed from a close-packed 2D sheet to a monocyclic ring (akin to $C_{10}$). This is exactly what happens for the $B_{10}$ ring in cluster 1.  

The delocalized $\pi/\sigma$ bonding of the $[B_{10}]^{10-}$ ring in cluster 1 may be compared to those of carbon-based analogs: hydrocarbon compound $D_{10h}C_{10}H_{10}$ and carbon cluster $D_{10h}C_{10}$. Note that the $C_{10}$ cluster\(^\text{17,18}\) adopts a monocyclic $D_{10h}$ structure; $D_{10h}$ is a second-order saddle point at the PBE0/6-311+G(d) level. Likewise, $D_{10h}C_{10}H_{10}$ is a model system. As shown in Fig. 8, the $10\sigma$ systems in the three species are identical, whereas the $10\pi$ system in $D_{10h}C_{10}$ also resembles that in $[B_{10}]^{10-}$. AdNDP analysis can also fully reproduce the $10\pi/10\sigma$ aromatic system in $D_{10h}C_{10}$ (Fig. S3, ESI†). The above comparison renders the sandwich $Be_B_{10}^{2-}$ cluster an analog of $D_{10h}C_{10}$ and $D_{10h}C_{10}H_{10}$. In fact, $[B_{10}]^{10-}$ is isoelectronic to $C_{10}$. Thus, cluster 1 suggests the possibility of stabilizing monocyclic boron rings via charge donation. Alternatively, it is an example of electronic transmutation,\(^\text{32–37}\) in which $B^-$ is chemically converted to $C$ in terms of cluster structure and chemical bonding.  

#### 4.3. Dynamic fluxionality of the $Be_B_{10}^{2-}$ cluster

The sandwich $Be_B_{10}^{2-}$ (1) cluster resembles the $Be_B_{11}^{2-}$ cluster\(^\text{11}\) in terms of geometry; the dynamic fluxionality of the latter was reported recently by our group. The $Be_B_{10}^{2-}$ cluster serves to address a couple of critical issues. Firstly, to demonstrate the idea that sandwich clusters can become energetically competitive in binary Be–B systems. Note that the $Be_B_{10}^{2-}$ (1) cluster is well defined as GM, whereas the prior $Be_B_{11}^{2-}$ cluster has a competitive helix versus sandwich isomers. Second, to demonstrate electronic transmutation\(^\text{32–37}\) using analogy between $[B_{10}]^{10-}$ and $C_{10}$. They not only adopt similar structures, but also have similar bonding (two-fold $10\pi/10\sigma$ aromaticity). This concept suggests further opportunities are available to stabilize monocylic boron rings in charge transfer clusters. We believe that the strategy may be explored in synthetic works and should lead to unconventional boron compounds. Third, to examine factors that affect structural fluxionality and energy barriers in dynamic cluster systems, as detailed below.  

During the global structural searches, we have identified GM cluster 1, LM 3, and two TS structures (TS1 and TS2) for the $Be_B_{10}^{2-}$ cluster, where TS structures were obtained and confirmed with the aid of QST2 and IRC calculations. The relationship between these structures is outlined in Fig. 9. As an example, chemical bonding in TS1 is analyzed using CMOs and AdNDP (Fig. S4 and S5, ESI†), which is quite similar to GM 1. With the above key structures, it is natural to ask a number of questions. Is the $Be_B_{10}^{2-}$ cluster dynamically fluxional? Can more than one modes be present in the $Be_B_{10}^{2-}$ cluster? How are its dynamic properties different from the prior $Be_B_{11}^{2-}$ cluster? What determines the energy barriers, in particular for twisting between the two $Be_3$ rings?  

Let us start with GM cluster 1. It has rhombic structural “defects” (Fig. 2[b]),\(^\text{11,13}\) which are the most flexible portion in the system and can facilitate rhombic-to-square transformation and vice versa. Vibrational analyses indicate that cluster 1 has at least three frequencies relevant to intramolecular rotation: 148.0, 133.9 and 542.4 cm\(^{-1}\) at the PBE0/6-311+G(d) level (Fig. S6, ESI†). For the 148.0 cm\(^{-1}\) frequency, the two $Be_3$ rings move in phase, counteracting the direction of the outer $B_{10}$ ring. Thus, $Be_3$ remains as a prism and the $B_{10}$ ring rotates around the prism. Such a movement deforms the rhombic defects in 1 and naturally leads to TS1, whose imaginary frequency (100.1 cm\(^{-1}\); Fig. S6(b), ESI†) is also in line with in-plane rotation. The 133.9 and 542.4 cm\(^{-1}\) frequencies of cluster 1 feature counter-rotation (that is, twisting) between the two $Be_3$ rings; the latter frequency probably suggests a higher energy barrier. The twisting movement leads to TS2, which has an imaginary frequency of 132.21 cm\(^{-1}\). In summary, cluster 1 can in principle move in two dynamic modes, revolution (orbiting) versus rotation (twisting).  

Quantitatively, the revolution barrier of cluster 1 is calculated to be 0.30 kcal mol\(^{-1}\) at the PBE0/6-311+G(d) level, which is refined to 0.36 and 0.81 kcal mol\(^{-1}\) at the PBE0-D3/def2-TZVP and CCSD(T)/def2-TZVP levels, respectively. This barrier is minor.

<table>
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<th>Species</th>
<th>$Be_B_{10}^{5-}$ (1)</th>
<th>$D_{10h}C_{10}$</th>
<th>$D_{10h}C_{10}H_{10}$</th>
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<tr>
<td>$NICS_{zz}(0)$</td>
<td>$-77.78$</td>
<td>$-71.06$</td>
<td>$-39.20$</td>
</tr>
<tr>
<td>$NICS_{zz}(1)$</td>
<td>$-66.01$</td>
<td>$-57.82$</td>
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suggesting that the B$_{10}$ ring in 1 is likely to orbit freely at moderate temperatures. Furthermore, the energy barrier for the twisting mode is calculated to be 12.56 and 12.69 kcal mol$^{-1}$ at the PBE0/6-311+G(d) and CCSD(T)/def2-TZVP levels, respectively. We also performed PBE0-D3/def2-TZVP calculations and the barrier is calculated to be 12.95 kcal mol$^{-1}$. The twisting barrier is quite high in comparison to 4.52 kcal mol$^{-1}$ for the prior Be$_6$B$_{11}$ cluster, hinting that cluster 1 can twist only at very high temperatures.

We believe that the difference between cluster 1 and Be$_6$B$_{11}$ in revolution/rotation barriers is due to subtle geometric reasons. The B$_{10}$ ring in cluster 1 is only marginally smaller than the B$_{11}$ ring in Be$_6$B$_{11}$, with a width/height of 4.81/5.05 Å for the former versus 4.94/5.31 Å for the latter. Such a tiny reduction of the ring size in cluster 1 would reinforce the confinement of the Be$_6$ prism, alter Be–B bonding as well as Be$_3$–B$_{10}$ and Be$_3$–Be$_3$ interactions, and affect the dynamic barriers (in particular for the twisting mode). Specifically, the peripheral B–B distances in cluster 1 (Fig. 2(b)) are slightly longer than those in Be$_6$B$_{11}$ (Fig. S1(b), ESI†), by 0.04 Å in average. However, the Be$_3$ rings in cluster 1 are more compact (by at least 0.1 Å). These parameters hint at discernible geometric constraints in cluster 1. In other words, the outer B$_{10}$ ring in cluster 1 seems a bit too small and the inner Be$_3$ rings are too large, which are not a perfect match for dynamics and should result in elevated barriers. Ideally, a system with slightly too large an outer ring and too small an inner

Fig. 8 Comparison of (a) delocalized $\pi$/$\sigma$ CMOs of the GM Be$_6$B$_{10}^{2-}$ (1) cluster with those of (b) $D_{10h}$ C$_{10}$H$_{10}$ and (c) $D_{10h}$ C$_{10}$. The latter two are model clusters only.
core may benefit dynamic fluxionality, because it dilutes the bonding between the outer ring and the inner core. This understanding shall benefit forthcoming rational design or discovery of dynamic systems with optimal dual-mode fluxionality.

To demonstrate dual-mode dynamic fluxionality of sandwich cluster 1, we performed BOMD simulations at different temperatures. Typical simulations are presented in the form of short movies (300, 600, and 1500 K; see ESI†), which were carried out for 20 ps using the CP2K package at the PBE0/DZVP-GTH level. Initial conditions were chosen to correspond to the microcanonical ensemble (NVE). At room temperature (300 K), the Be 6 prism in cluster 1 only jitters back and forth around its equilibrium position and the cluster never reaches the TS1 structure. Neither revolution (orbiting) nor rotation (twisting) is activated at this temperature.

At 600 K, the B 10 ring can glide freely around the Be 6 prism, like a flexible chain, and the inner Be 3 rings only jitter around their equilibrium positions. No twisting event occurs and the Be 6 prism maintains its integrity. Similar dynamics is observed at 1000 K and 1200 K, indicating that the twisting mode remains inactive. At a high temperature of 1500 K, both dynamic modes are functioning: the outer B 10 ring glides like a hula hoop, whereas the two Be 3 rings also twist occasionally against each other akin to dancing the tango. Alternatively, dual dynamic modes of revolution/rotation make an earth-moon system at the nanometer scale. It is remarkable that the B 10 and the Be 3 rings in cluster 1 are robust against fragmentation at a temperature as high as 1500 K, which may be ascribed to multifold π/σ aromaticity in the system.

5. Conclusions

We report on computational design of a coaxial triple-layered Be 6B 10 2− sandwich cluster, which is established as the global minimum of the system via machine searches and quantum chemical calculations. It features a monocyclic B 10 ring, sandwiched by two Be 3 rings on top and underneath. The latter two rings form a trigonal-prism albeit without interlayer Be–Be bonding. The B 10 ring in the Be 6B 10 2− cluster differs fundamentally from the free B 10 cluster, and yet it resembles a C 10 cluster closely. Bonding analyses show that the Be 6B 10 2− cluster possesses four-fold π/σ aromaticity: 10π and 10σ delocalization for the B 10 ring and 2σ delocalization for each Be 3 ring. The bonding picture indicates that Be 6B 10 2− is a charge transfer complex with a formula of [Be 3] 4+[B 10] 10/C 0 [Be 3] 4+. The highly charged [B 10] 10/C 0 ring is chemically converted to a C 10 cluster via “electronic transmutation”, which underlies the monocyclic boron ring in the Be 6B 10 2− cluster. Indeed, the [B 10] 10− and C 10 species are similar in geometry and bonding, including two-fold π/σ aromaticity. Lastly, the sandwich Be 6B 10 2− cluster has dynamic structural fluxionality, featuring two dynamic modes. The B 10 ring is robust against rupture or fragmentation at least up to 1500 K, owing to double π/σ aromaticity.

Conflicts of interest

There are no conflicts to declare.
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References

60 Structure TS1 is related to GM 1, following in-planar rotation of the outer B10 ring against the Be3 prism by half a B–B link. Note that the B–B and Be–Be distances in TS1 closely resemble those in GM 1, hinting at structural fluxionality for cluster 1. Likewise, TS2 corresponds to structural transformation from GM 1 to LM 3, suggesting another possible dynamic mode.
61 In this alternative AdNDP scheme, the contribution from the Be6 prism is omitted, leading to minor decreases in occupation numbers (ONs) by less than 15%. Thus, 10r/10s subsystems in cluster 1 are indeed dominated by the outer B10 ring.
63 To accommodate a reviewer, we ran complementary CDA calculations for the charge transfer complex. Specifically, we divide the Be6B102− cluster into Be66+ and B1010− segments, and the CDA results point to a final formula of [Be3]6+[B10]10−, which is qualitatively consistent with a charge transfer cluster, although the quantitative number of electrons transferred is less than those in the formal (8 | e) and NBO (6.56 | e) data. We consider the formal picture of [Be3]6+[B10]10− [Be3]4+ from CMO analyses to be fundamental, which is confirmed by AdNDP and NBO analyses. In this context, the CDA data are relatively unimportant (and indeed less reliable).
65 This argument is valid for two reasons. Firstly, the expansion of B–B distances in GM Be6B102− (1) (Fig. 2(b)) relative to Be6B11− (C2v, 1A1) (Fig. S1(b), ESI†) is not due to the dianion nature of 1, because the neutral Be6B10Na+ salt complex (Fig. S1(a), ESI†) follows the same trend. Second, species Be6B11− (C2v, 1A1), GM Be6B102− (1), and LM Be6B102− (3) (Fig. 1a) form a whole series, along which the B–B links expand systematically and the Be–Be links in the Be3 rings shrink. Using the average values, the B–B/Be–Be bonds are 1.53/2.21, 1.57/2.11, and 1.58/2.09 Å, respectively, suggesting that geometric constraints increase monotonously along the series and size mismatch between the B10 and Be3 rings does exist in GM Be6B102− (1). Such mismatch is relevant to the energy barrier for the twisting mode.