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# Why nanoscale tank treads move? Structures, chemical bonding, and molecular dynamics of a doped boron cluster $B_{10}C^{+}$

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Planar boron clusters form dynamic rotors, either as molecular Wankel motors or subnanoscale tank treads, the latter being exemplified by an elongated B<sub>11</sub><sup>-</sup> cluster. For an in-depth mechanistic understanding of the rotors, we investigate herein a doped boron cluster, B<sub>10</sub>C, in which a C atom isovalently substitutes B<sup>-</sup> in the  $B_{11}^{-}$  tank tread. Two critical structures are achieved: the  $C_s$  (<sup>1</sup>A') global minimum (GM) with C positioned in the peripheral ring and the  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) local minimum (LM) with C in the diatomic core. In the GM the C atom completely halts the rotation of  $B_{10}C$ , whereas in the LM the dynamic fluxionality remains. The energy barriers for in-plane rotation differ markedly: 12.93/18.31 kcal mol<sup>-1</sup> for GM versus 1.84 kcal mol<sup>-1</sup> for LM at the single-point CCSD(T) level. The GM rotates via two transition states (TS), compared to one for the LM. Chemical bonding in the structures is elucidated via canonical molecular orbital (CMO) analysis, adaptive natural density partitioning (AdNDP), electron localization functions (ELFs), and Wiberg bond indices (WBI). Electron delocalization is shown to be essential for structural fluxionality. In particular, the variation of WBI from the GM or LM geometries to their TS structures correlates positively with the energy barrier, which offers a quasiquantitative measure of the barrier height and hence controls the dynamics. This finding may be extended to all molecular rotors. It also helps rationalize why a strongly covalently bound system can behave dynamically in a manner similar to a weakly bound one; it is the latter that is generally anticipated to be structurally fluxional.

## Introduction

Dynamic structural fluxionality<sup>1–8</sup> in nanoclusters has emerged as a hot topic in physical chemistry and in nanoscience and nanotechnologies. Boron appears to be the magic element for molecular rotors, owing to its intrinsic elec-

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tron-deficiency and the potency of boron clusters to adopt novel quasi-planar (2D) structures for a wide range of sizes up to 40 atoms, which is unprecedented for any element in the periodic table.<sup>9-17</sup> Specifically, an array of boron-based molecular Wankel motors and subnanoscale tank treads were discovered recently. The latter species<sup>4</sup> are sort of beyond intuitive imagination for chemists, because in a tank-tread-shaped cluster the elongated inner core seems to be a "bar" that should halt the intramolecular rotation.

Therefore, it is important to gain an in-depth mechanistic understanding of molecular rotors in general and nanoscale tank treads in particular. Structural fluxionality is normally anticipated for weakly bound systems only, whereas boronbased clusters possess rather strong covalent chemical bonding. So why are such covalent species structurally fluxional? What governs the in-plane rotational barrier? How to control the barrier? In this communication, we attempt to address these questions using a simple, doped, elongated boron cluster: B<sub>10</sub>C. The system offers both a halted globalminimum (GM) structure and a fluxional local minimum (LM), which differ markedly in the height of the rotational barrier. These two structures turn out to be ideal models for the dynamic fluxionality of nanoscale tank treads. It is found that the change of the Wiberg bond index (WBI) during the rotation process correlates closely with the height of the rotational barrier. The finding should be extended to and applicable for all molecular rotors. It also elucidates why a strongly covalently bound nanosystem and a weakly bound one can behave similarly. We note that boron chemistry has been a rapidly expanding field in recent years, which notably features flat boron clusters,<sup>9-16</sup> borospherenes,<sup>14,17-19</sup> and borophenes,<sup>20–23</sup> among others.

### Methods

We searched for the GM and isomeric structures of  $B_{10}C$  using the unbiased Coalescence Kick (CK) method<sup>24,25</sup> at the density-functional theory (DFT) level. Low-lying candidate

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structures were then fully reoptimized at PBE0/6-311+G\* 26,27 and their relative energies evaluated, using the Gaussian 09 package.<sup>28</sup> Vibrational frequencies were calculated to ensure that all structures presented are true minima on the potential energy surface. QST3 calculations were performed to search the transition states (TS) for intramolecular rotation. Intrinsic reaction coordinate (IRC) calculations were carried out to confirm that the TS structures are truly associated with the GM or LM. To benchmark their relative energies, the GM, LM, and TS structures were further refined at the single-point CCSD(T)/ 6-311G\*//PBE0/6-311+G\* level.<sup>29</sup> Born-Oppenheimer molecular dvnamics (BOMD) simulations were carried out using the CP2K software package.<sup>30</sup> Bonding analyses were performed via canonical molecular orbitals (CMOs), electron localization functions (ELFs),<sup>31</sup> and adaptive natural density partitioning (AdNDP).<sup>32</sup> Since AdNDP analyses are not sensitive to the level of theory or the basis set used, we chose the PBE0/6-31G level for AdNDP calculations. Natural bond orbital (NBO) calculations were performed at the PBE0/6-311G\* level. Visualization of ELF and AdNDP data was realized using the Molekel 5.4.0.8 program.<sup>33</sup>

#### **Results and discussion**

#### The B10C cluster: global minimum versus local minimum

The B<sub>10</sub>C cluster is relevant to the prototypical nanoscale tank tread, B<sub>11</sub><sup>-,4</sup> *via* isovalent substitution of a C atom for B<sup>-</sup> in the latter. B<sub>10</sub>C is a relatively small cluster and the powerful and unbiased CK method<sup>24,25</sup> is anticipated to be able to reliably solve the structural problem. Specifically, we carried out the CK searches at the DFT level, with a total of 3000 stationary points being examined. Alternatively, the isomeric structures of B<sub>10</sub>C can also be constructed manually on the basis of B<sub>11</sub><sup>-</sup> *via* C substitution (or B<sub>10</sub>/B<sub>10</sub><sup>-</sup> by attachment of a C atom)<sup>10</sup> at various possible sites. These efforts allow the establishment of  $C_s$  (<sup>1</sup>A') as the GM of the system, according to the energetics at both PBE0 and single-point CCSD(T) levels; see Fig. 1a. The Cartesian coordinates are presented in Table S1 in the ESI.<sup>†</sup>

Overall, the GM has a  $B_2$  bar enclosed inside a  $B_8C$  ring, resulting in an elongated shape of the tank tread. Compared to  $B_{11}^{-4,10}$  the C atom in the  $B_{10}C$  cluster occupies a position in the peripheral ring, which induces a slight structural deformation and lowers the symmetry from  $C_{2v}$  to  $C_s$ . Additional low-lying structures are displayed in Fig. S1 (ESI†). Note that the closest structure is roughly 1 eV above the GM and the energetics at PBE0 and CCSD(T) are highly consistent with each other, suggesting that the GM is rather well-defined on the potential energy surface.

Among the isomers is a  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) structure, which assumes a perfect 2D geometry and is labeled as LM in Fig. 1b, being 1.65 eV above the GM at CCSD(T). The two structures are similar in shape, except that the C atom in the LM constitutes part of the inner diatomic bar. A prior work<sup>34</sup> suggested that in a B–C binary 2D cluster system, the C atom prefers to



**Fig. 1** Optimized structures of (a)  $C_s$  (<sup>1</sup>A') global minimum (GM) of  $B_{10}C$ , (b)  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) local minimum (LM), and their transition states (TS) for in-plane rotation at the PBE0/6-311+G\* level.

occupy the outer ring in order to avoid hypercoordination. The present structural data seem to support this idea. Indeed, among the top ten low-lying isomers of  $B_{10}C$ , nine have the C atom in the peripheral ring.

#### **BOMD** simulations

A primary motivation of the present study is to use the  $B_{10}C$  cluster as a model system to shed light on the mechanism of structural fluxionality of molecular rotors. Now that the  $C_s$  (<sup>1</sup>A') GM and  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) LM structures (Fig. 1) are established for  $B_{10}C$  and they do not deviate much from  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) GM of  $B_{11}^{-,4,10}$  will the dynamic properties of the three species be similar? Or, will they differ markedly in structural fluxionality?

Vibrational frequency analyses show that the GM and LM of  $B_{10}C$  each possess a low-frequency soft mode for in-plane rotation: 143.7 and 112.4 cm<sup>-1</sup>, respectively. These modes are similar to that of 148.7 cm<sup>-1</sup> in  $B_{11}$ <sup>-,4</sup> Following the 143.7 cm<sup>-1</sup> mode of the GM, two TS structures were located (TS<sub>1</sub> and TS<sub>2</sub> for clockwise and anti-clockwise rotations, respectively; Fig. 1a), both of which have  $C_{2v}$  symmetry and one imaginary frequency (201.3*i* cm<sup>-1</sup> for TS<sub>1</sub>; 223.0*i* cm<sup>-1</sup> for TS<sub>2</sub>). In contrast, the LM has only one TS structure (TS<sub>LM</sub>; Fig. 1b) with an imaginary frequency of 202.9*i* cm<sup>-1</sup>. The imaginary frequencies of TS<sub>1</sub>, TS<sub>2</sub>, and TS<sub>LM</sub> are also related to the in-plane rotation. IRC calculations at PBE0 confirmed that the TS structures are truly associated with the GM or LM.

Aided with TS structures, the barriers for rotation can be evaluated straightforwardly: the GM of  $B_{10}C$  has a barrier of 13.52 *versus* 16.95 kcal mol<sup>-1</sup> for TS<sub>1</sub> and TS<sub>2</sub>, respectively, at PBE0 with zero-point energy (ZPE) corrections, which are refined to 12.93 *versus* 18.31 kcal mol<sup>-1</sup> at single-point CCSD (T). The barrier for LM amounts to 1.48 kcal mol<sup>-1</sup> at PBE0 and 1.84 kcal mol<sup>-1</sup> at CCSD(T). Thus, the GM has rather high barriers, which can certainly prevent its peripheral ring from in-plane rotation or gliding around the inner core. In contrast, the LM has a low barrier (one order of magnitude smaller), hinting nearly free in-plane rotation at an appropriate temperature. These barriers should be compared to that of the  $B_{11}^{-}$  cluster,<sup>4</sup> which is 0.42 kcal mol<sup>-1</sup> at PBE0. In short, despite being isovalent and sort of isostructural with each other, the  $C_{\rm s}$  (<sup>1</sup>A') GM of  $B_{10}$ C,  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) LM of  $B_{10}$ C, and  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) GM of  $B_{11}^{-}$  possess quite different in-plane rotational barriers. The LM of  $B_{10}$ C should be structurally fluxional akin to  $B_{11}^{-}$ , whereas the GM of  $B_{10}$ C can be rigid for in-plane rotation.

BOMD simulations fully support the above assessments; see the extracted short movies in the ESI<sup>†</sup> for the GM and LM structures. The simulations were performed at the PBE/DZVP-GTH level, starting from the equilibrium geometry with random velocities assigned to atoms. The systems were equilibrated at 300, 600 and 900 K using a Nosé–Hoover thermal bath for 20 ps, after which a set of 30 ps trajectories were computed. Only the BOMD data at 600 K are presented in the ESI.<sup>†</sup> Indeed, the LM behaves vividly like a nanotank, whereas the GM is rigid and nonfluxional.

#### Dynamic structural evolutions

With the GM, LM, and TS structures being identified (Fig. 1), we can readily map out their in-plane rotation processes. Note that structure-wise this is also doable for the GM; its dynamic nonfluxionality is only due to the insurmountable barriers at limited temperatures. A whole loop of rotation for the GM is illustrated in Fig. 2, assuming that the system moves clockwise. At the initial GM<sub>1</sub>, the C atom (labeled as C9) is located at the top right corner, where the B10C9 link turns out to be the most rigid part of the structure. As the peripheral atoms move clockwise following the soft vibrational mode, the whole ring adjusts accordingly around the inner core, leading to  $TS_{1-2}$ , which corresponds to  $TS_1$  in Fig. 1a. Passing the barrier, the GM<sub>2</sub> is reached, which is equivalent to GM<sub>1</sub> with a 180° out-plane rotation around the B11B10 axis. From GM<sub>1</sub> to GM<sub>2</sub>, the C atom moves by as much as three links.

Further rotation of C9 clockwise reaches  $TS_{2-3}$  and subsequently recovers  $GM_3$ , with an overall movement of two links. Here  $TS_{2-3}$  corresponds to  $TS_2$  in Fig. 1a, whereas  $GM_3$  is an enantiomer of  $GM_2$ , being equivalent to  $GM_1$  with a 180° in-plane rotation. Next two steps from  $GM_3$  to  $GM_4$  and from  $GM_4$  to  $GM_5$  are exactly in the spirit of the prior steps, allowing the accomplishment of the remaining half loop. Thus, the GM rotates by "giant" steps (3 or 2 links per step) *via* two kinds of TS structures ( $TS_1$  and  $TS_2$ ; Fig. 1a) and accomplishes a full loop within as few as four steps. Qualitatively speaking, such an oversimplified process means a long, uphill path for every step of rotation, which contributes to the high barrier and makes the movement impractical.

On the other hand, the structural evolution of the LM proceeds *via* a single TS, as illustrated in Fig. S2 (ESI<sup>†</sup>). For one step, the ring rotates by one link. After 9 times of repetition, every atom in the system completely recovers its initial position. As a reference, the  $B_{11}^{-}$  cluster<sup>4</sup> manages to move by even smaller steps: half a link per energy barrier. In summary, the structural evolutions of  $B_{10}C$  GM,  $B_{10}C$  LM, and  $B_{11}^{-}$  clusters with respect to the in-plane rotation differ in (i) the kind of TS structure: 2, 1, and 1, respectively; (ii) step length: 3 or 2 links, 1 link, and half a link, respectively; and (iii) the number of steps for a full loop: 4, 9, and 18. These numbers appear to correlate inversely with the height of the rotation barrier, which qualitatively explains why  $B_{10}C$  GM is nonfluxional,  $B_{10}C$  LM rotates as a tank tread, and the  $B_{11}^{-}$  cluster moves freely like a nanotank with negligible barrier.

#### Mechanism behind tank treads: chemical bonding in B<sub>10</sub>C

To gain a deeper understanding of the dynamics of  $B_{10}C$ , in particular the difference between its GM and LM structures, we performed chemical bonding analyses *via* the CMOs, ELFs, and AdNDP. All occupied CMOs of  $B_{10}C$  GM are depicted in



Fig. 2 Schematic structural evolution processes of the  $C_s$  (<sup>1</sup>A') GM of B<sub>10</sub>C, assuming in-plane rotation clockwise. A full loop is accomplished in only 4 steps. Two kinds of TS structures (TS<sub>1-2</sub>/TS<sub>3-4</sub> versus TS<sub>2-3</sub>/TS<sub>4-5</sub>) are present, which correspond to TS<sub>1</sub> and TS<sub>2</sub> in Fig. 1a, respectively.



Fig. 3 Canonical molecular orbitals (CMOs) of the  $C_s$  (<sup>1</sup>A') GM of B<sub>10</sub>C. (a) Nine localized  $\sigma$  bonds; (b) five delocalized  $\sigma$  bonds; (c) three delocalized  $\pi$  bonds. The 10 $\sigma$  and 6 $\pi$  electron-countings in (b) and (c) conform to the (4n + 2) Hückel rule for aromaticity.

Fig. 3, which are sorted to three subsets according to the type of atomic orbital (AO) and its orientation.<sup>35</sup> Subset (a) includes nine  $\sigma$  CMOs, composed of s/p hybridized AOs of B/C (tangential to the ring), which can be localized as peripheral twocenter two-electron (2c-2e)  $\sigma$  bonds. Subset (b) has five  $\sigma$  CMOs, which mainly originate from the p AOs of B/C, orienting radially toward the center of the cluster. This subset of CMOs has an increasing number of nodal planes from zero up to 2, showing one-to-one correspondence with the deeper CMOs in subset (a). The  $10\sigma$  subsystem is essentially delocalized and cannot be transformed to lone-pairs or 2c-2e bonds, thus rendering  $\sigma$  aromaticity to the GM according to the (4n + 2) Hückel rule. Likewise, the three CMOs in subset (c) constitute a delocalized  $6\pi$  subsystem and render  $\pi$  aromaticity to the GM, akin to benzene. Therefore, the B10C GM cluster possesses ( $\pi$  and  $\sigma$ ) double aromaticity with  $6\pi$  and  $10\sigma$ electrons, respectively.

The above assessment does not differ much from that of  $B_{11}^{-}$  (and the  $B_{10}C$  LM has a similar CMO pattern; see Fig. S3, ESI<sup>†</sup>),<sup>4</sup> suggesting that the distinctly different dynamics of  $B_{10}C$  GM and  $B_{11}^{-}$  lies in the subtle difference in bonding. To this end, the ELF data offer key insights. The  $B_{10}C$  GM,  $B_{10}C$  LM, and  $B_{11}^{-}$  clusters differ in particular in their spatial continuity in the ELF<sub> $\pi$ </sub> pattern (Fig. 4, right panels). The  $\pi$  cloud in

the  $B_{11}^{-}$  cluster is continuous and smoothly distributed on the peripheral ring, and the pattern largely maintains in  $B_{10}$ C LM. However, the  $ELF_{\pi}$  pattern of  $B_{10}$ C GM appears to be somewhat segmented around the C site (Fig. 4a), so that the electron flow can be less continuous during the in-plane rotation. A prior report uses a peripheral C atom to stop the rotation of a  $B_{19}^{-}$  Wankel motor.<sup>36</sup> Thus, the  $ELF_{\pi}$  pattern helps differentiate the three systems, correlating closely with their dynamic fluxionality.

Fig. 5a shows the AdNDP bonding pattern of  $B_{10}C$  GM. Firstly, AdNDP fully recovers nine peripheral 2c–2e  $\sigma$  bonds, which are associated with the CMOs in Fig. 3a. Second, the  $6\pi$ aromatic subsystem in Fig. 3c is reproduced (Fig. 5a, second row). Third and most importantly, AdNDP can offer an island view for the 10 $\sigma$  subsystem in Fig. 3b and describes it in terms of a combination of two 2c–2e bonds and three 3c–2e bonds (see Fig. 5a, first row). Of course, this island description is approximate as reflected from the relatively low occupation number (ON) of 1.59|*e*|, in particular for the 2c–2e bonds. An ultimately localized approximation is shown in Fig. 5b, which indicates that the B10–C9 bond has a markedly higher ON value than other diagonal 2c–2e bonds. Indeed, the island view suggests that the B10–C9 bond is the most robust among all bonds in between the diatomic core and the outer ring;



considering the bond strengths of typical B–C *versus* B–B single bonds, the robustness of the B10–C9 bond in the GM is further reinforced. The primary reason is that the C center is more electronegative (C 2.55 *versus* B 2.04 at the Pauling scale) and thus the B10–C9 bond is largely localized. The ON of 1.59|e| for B10–C9 indicates a reasonable Lewis 2c–2e bond. For the LM structure, the diagonal island  $\sigma$  bonds are more even and delocalized; see Fig. 5c. Intuitively, a localized B10–C9 bond in B<sub>10</sub>C GM is anticipated to serve as a rigid bar that blocks its in-plane rotation, explaining why the GM and LM of B<sub>10</sub>C have different BOMD behaviors (see movies in the ESI†).

#### A semi-quantitative description of the rotational barrier?

Which factor governs the in-plane rotational barrier? Can we quantitatively describe the barrier? Table 1 compares the calculated WBIs, as well as the changes of WBI (that is,  $\Delta$ WBI) during rotation, for the three systems: B<sub>10</sub>C GM, B<sub>10</sub>C LM, and B<sub>11</sub><sup>-</sup>. For a cluster to rotate, the electronic clouds need to be delocalized so that they flow instantaneously in response to the moves of the atoms. At the TS, certain bonds in the system reach their maximum in terms of stretching or compressing. Thus the change of WBI for the most robust bonds between the GM or LM and the TS is a measure of the degree of difficulty for rotation, which should reflect the barrier.



3×11c-2e

ON=2.00|e|

As shown in Table 1,  $B_{10}C$  GM,  $B_{10}C$  LM, and  $B_{11}^{-}$  have  $\Delta$ WBI values of 0.2234/0.2984, 0.0137, and 0.0068, respectively, which are 30.4/40.6, 1.6, and 0.9 percent of their WBI values in the GM or LM. Note that the  $\Delta$ WBI for  $B_{10}C$  GM is substantially greater than those of  $B_{10}C$  LM and  $B_{11}^{-}$ ; the latter two having comparable values. This trend correlates rather well with that in their calculated barriers: 13.52/16.95, 1.48, 0.42 kcal mol<sup>-1</sup>. We believe that  $\Delta$ WBI can be used as a quasi-quantitative description for the rotational barrier of nanoscale tank treads. This finding shall hold the key to the structural fluxionality of covalently bound nanosystems, including molecular Wankel motors and tank treads. In this regard, a strongly covalently bound species is no different from a weakly bound system. It is the extent of bond variation that matters in dynamics, not the absolute bond strength.

**Table 1** Calculated Wiberg bond indices (WBIs) of the global-minimum (GM) and local-minimum (LM) structures of B<sub>10</sub>C and their rotational transition states (TS) at the PBE0/6-311G\* level, compared to those of B<sub>11</sub><sup>-</sup>. Calculated energy barriers ( $\Delta E$ , in kcal mol<sup>-1</sup>) at PBE0 are also presented

Species	Structure	Bond <sup>a</sup>	WBI	$\Delta \mathrm{WBI}^b$	$\Delta \mathrm{WBI}^{b}(\%)$	$\Delta E$
GM	$\begin{array}{c} \text{GM} \\ \text{TS}_1 \\ \text{TS}_2 \end{array}$	B10-C9 B10-C9 B10-C9	0.7348 0.9582 0.4364	0.2234 0.2984	30.4 40.6	13.52 16.95
LM	LM TS <sub>LM</sub>	C10-B1 C10-B1	0.8448 0.8311	0.0137	1.6	1.48
B <sub>11</sub> <sup>-</sup>	GM TS	B11–B6 <sup>c</sup> B11–B6	0.7344 0.7276	0.0068	0.9	0.42

<sup>*a*</sup> Atomic labels are shown in Fig. 1. All of the bonds listed here are the most robust between the inner core and peripheral ring. <sup>*b*</sup>  $\Delta$ WBI is defined as the difference of the WBI values of a specific bond in GM or LM and TS structures;  $\Delta$ WBI (%) is the ratio of  $\Delta$ WBI over WBI of the GM or LM. <sup>*c*</sup> Atomic labels for B<sub>11</sub><sup>-</sup> are based on ref. 4.

## Conclusions

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In conclusion, we have presented a mechanistic study of the dynamics of nanoscale tank treads, using a doped boron cluster  $B_{10}C$  as the model system. Both  $C_s$  (<sup>1</sup>A') globalminimum and  $C_{2v}$  (<sup>1</sup>A<sub>1</sub>) local-minimum structures are investigated, the former having C positioned in the peripheral ring and the latter with C in the diatomic core. The GM is rigid and nonfluxional, whereas the LM moves dynamically like a tank tread. Their energy barriers for in-plane rotation amount to 12.93/18.31 and 1.84 kcal mol<sup>-1</sup>, respectively, at single-point CCSD(T), differing by one order of magnitude. Bonding analyses suggest that electron delocalization is essential for structural fluxionality, and the change of the Wiberg bond indices between the GM or LM and their TS structures shall serve as a semi-quantitative measure of the rotational barrier. A single B-C bond with C in the peripheral ring is enough to reduce the extent of electron delocalization in B<sub>10</sub>C and markedly elevate the rotational barrier, halting its dynamic fluxionality. The current mechanism should be applicable for all molecular rotors.

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