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The 2D-to-3D geometry hopping in small boron clusters: The charge effect

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**Abstract**

DFT TPSSh/6-311+G(d) calculations are carried out on a series of 2D and 3D forms of \( B_n \), \( n = 20, 22 \) and 24 in different charge states. For a certain size, the relative energy within a pair of two-dimensional quasi-planar (2D) and three-dimensional staggered double-ring (3D) boron cluster isomers may shift the sign as they reach a certain charge state. Specifically, electron addition tends to enhance the stability of the 2D over the corresponding 3D isomer irrespective of the available electrons. Linear correlations between 2D–3D relative energy and net charge are established. Along with 2D-to-3D geometry hopping at critical size, our results suggest a local 2D–3D geometry hopping via critical charge.

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1. Introduction

Boron is well-known to exist in solid state in the forms of amorphous, \( \alpha \)- and \( \beta \)-rhombohedral allotropies, and in other boron-rich compounds such as boranes. A number of these materials have important applications in, among others, high temperature semiconductors at up to 530 °C [1], super-conductors at abnormal conditions of 6 K and 175–250 GPa [2], and/or high density energy fuels [3]. Recent discoveries of boron clusters [4], boron sheets and boron nanotubes [5,6] have opened up new horizons of boron-based materials with many interesting characteristics. A boron paradox is that it has one electron less than carbon to form cluster bonds but prefers highly coordinated centers. A peculiar feature of finitesize boron clusters is their aromaticity which has intensively been studied during the last decade [7]. Such aromaticity apparently reveals a nano-confinement effect, i.e., properties that exist at a nanoscale but are not found in solid bulk. For instance, while the dominant cells in bulky boron materials are three-dimensional (3D) cages, low-lying energetic isomers of small boron clusters mostly adapt two-dimensional (2D) quasi-planar (QP) or perfectly planar structures [8–14]. This characteristic was initially introduced for the global minimum of the \( B_{13}^+ \) cluster which was presented with a perfect 2D planar structure instead of a 3D cage as previously assumed [14,15]. The \( \pi \)-electron delocalization was identified as a factor facilitating the planarity and aromaticity. Electron delocalization of the planar \( B_{13}^+ \) isomer was subsequently confirmed by its molecular orbital framework [14,15].

Small boron clusters were found to have not only \( \pi \)- but also \( \sigma \)-aromaticity, called a double aromaticity. For instance, the global minima of \( B_{15}^+ \) and \( B_{15}^- \) clusters exhibit both \( \pi \) and \( \sigma \) electrons obeying the classical Hückel (4\( N \) + 2) electron rule [7,16]. They are altogether responsible for the interesting planar wheel structures with highly coordinated central boron atom. While small boron clusters \( B_n \) with \( n \) being up to 23, have planar or quasi-planar structures resembling unsaturated hydrocarbons [4,7,17–21], the well-known boron hydrides \( B_{16}H_{16} \) prefer cage-formed 3D structures [22]. For circular and elongated structures, a trend of boron clusters is to adapt \( \pi \)-electron patterns of unsaturated hydrocarbons. Accordingly, the \( B_{16–18} \) neutral and negatively charged clusters were known to resemble naphthalene [18,19], that of \( B_{16}^– \), with 10-annulene [17], and \( B_{22}^– \) and \( B_{23}^– \) clusters with anthracene and phenanthrene [4], respectively. Recently, the concept of disk aromaticity [21] has been introduced to rationalize the electronic structure of the \( B_{25}^+ \) dianon. It appears that for circular species, the classical Hückel electron count is a particular case of the more general disk aromaticity.

Furthermore, the aromatic character has also been anticipated to be involved in the 2D-to-3D geometry hopping of boron clusters as they reach a transition size, i.e., size at which the global minimum shifts from a 2D to a 3D structure. For instance, at the size of 20-atoms, the global minimum of the neutral boron cluster has a 3D staggered double-ring (SDR) structure [10,23]. The geometry hopping was implicitly assigned for a marvelous double aromaticity of 3D SDR structure contributed from two separate tangential and radial MO stacks, whose occupied electrons obeying the Hückel count [11]. This geometrical transition was confirmed by the fact that 3D SDR structures remain the global minima for the immediately larger sizes [12,13,24].
However, the critical size for 2D-to-3D geometry hopping, quantitatively represented by the 2D–3D relative energy, turns out to vigorously vary with respect to the implemented net charge. For instance, the critical size of the $B_{20}$ system is solely applicable for the neutral state. In the cationic state, a geometrical transition was found to occur earlier, i.e., the 3D SDR isomer is already the global minimum of $B_{19}$ clusters [15, 25]. In the anionic state, the 2D QP isomers, however, remain iso-energetic with 3D SDR structures for $B_{19}$ and $B_{20}$ [21, 26]. By adding one extra electron giving a dianionic state, the 2D QP structure becomes a distinguishable global minimum with large energy gap with respect to the 3D SDR isomer [21, 26]. Boron clusters of larger sizes, containing 22–24 atoms could have a global minimum having either a 2D QP [4] or a 3D SDR structure [13], apparently depending on the implemented charge of the system. Thus, the 2D–3D relative energy, which intuitively depends on their charged state, is likely to directly be affected by the number of itinerant electrons. However, to the best of our knowledge, no previous study has analyzed a charge effect on 2D–3D relative energies of boron clusters. Most of them mainly considered the geometrical transition at a specific charged state for a critical size. In this context, we set out to elucidate such an effect by investigating a series of 2D and 3D boron clusters $B_n$ in a range of $n = 20–24$ atoms with an effective net charge varying from $+2$ (dication) to $-2$ (dianion).

2. Computational methods

The present Letter mainly concentrates on the relative stability between both 2D QP and 3D SDR isomers of a size with respect to the implemented net charges. All electronic structure calculations are performed at the same level for the purpose of comparison. For each pair, relevant structures are obtained, when available, from the literature [10]. When a structure at a certain size and charge is missing, we carry out a search for its global minimum. Both low-lying 2D QP and 3D SDR structures can be built up either manually starting from the highest symmetry and then relaxed to their optimized structures are subjected to normal mode vibrational analyses. The additional module aims to eliminate fragmented and/or superpositioned structures by assigning each atom with avoiding and valence spheres. Both spheres have radii that are equal to the half of the possibly shortest and longest valence bonds. By counting the number of superpositioned (Figure 1a), normal (Figure 1b) and fragmented (Figure 1c) overlaps, unphysical structures can thus be eliminated. Using the kick algorithm [27,28], another simple bash shell script is also implemented to automatically build inputs from guessed geometries, and compute their energies at a desired theoretical level [28]. In eliminating the failed and redundant points, a new set of possible structures can be considered for higher level computations.

For 2D isomers, many degrees of freedom can be reduced by keeping the structures strictly planar ($C_2$ point group). All optimized structures are subjected to normal mode vibrational analyses at the same level. Imaginary frequencies are eliminated by geometry reoptimization slipping along the corresponding normal modes.

Due the large size of the clusters considered, high accuracy MO methods such as the second-order perturbation theory (MP2) and/or coupled-cluster theory (CCSD(T)) could not be applied within our limited computational resource. In order to obtain relatively reliable energy but with more reasonable computational costs, density functional theory (DFT) is used. Instead of the popular hybrid B3LYP functional, the TPSSh functional [29] is used in conjunction with the 6-31G(d) basis set for initial computations, and the 6-31+G(d) basis set for refined structural and energetic determinations. Extensive recent benchmark computations demonstrated that the B3LYP functional tends to underestimate the energy differences between 2D and 3D boron clusters [25,26,30–32]. The TPSSh functional has also been calibrated and shown to give better relative energies for boron clusters than other available functionals, as compared to results obtained from high level MO methods (CCSD(T)). All calculations are carried out using the Gaussian 09 suite of program [33].

3. Results and discussion

3.1. The 20-atoms boron clusters

The $B_{20}$ system was previously found to be a critical point of the 2D-to-3D geometrical transition of pure boron clusters. For the neutral, the 3D SDR isomer was identified by DFT computations as the global minimum, which is also the possible thinnest embryo of boron nanotube [10]. This result was subsequently confirmed by coupled-cluster (CCSD(T)) calculations.

DFT calculations at the TPSSh/6-31+G(d) level show that the pairs of low-lying 2D QP and 3D SDR isomers for $B_{20}$ are similar to the previously reported ones [10,25,26,34] (Figure 2a). Similar results on 2D–3D relative stabilities are also obtained with calculated relative energies presented in Table 1. This quantity appears to be noticeably sensitive to the actual net charge. For instance, neutral and positively charged 3D SDR isomers consistently remain the energetically lowest-lying isomers with about 10–30 kcal/mol lower than 2D QP counterparts [25,34]. In the anionic state, it becomes ambiguous to assign the global minimum as the 2D–3D energy difference is faded within the range of expected error margin of DFT computations of about 4–5 kcal/mol [21,26]. However, such

Figure 1. Three typical relative position between a pair of atoms (green points) in term of avoiding (red) and valence (blue) spheres. (a) The superposition position with the superposition overlap between two avoiding spheres; (b) the normal position with normal overlap between two valence spheres; and (c) the fragmented position with no (fragmented) overlap between two valence spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
a result appears to be in agreement with the fact that only the anionic 2D QP isomers were detected by photoelectron spectroscopy under experimental conditions [26]. By adding one extra electron, the dianionic 2D QP isomers are now found to be 18–20 kcal/mol clearly more stable than the 3D SDR ones [21].

3.2. The 22-atoms boron clusters

The 2D–3D geometry transition identified for the size of 20-atoms is confirmed as the B_{22} system keeps the 3D SDR isomer as the global minimum of the neutral state. In varying the net charge from cationic to anionic states, SDR isomers are always calculated to be 8–50 kcal/mol higher in energy than the 2D QP isomer [12].

Our results obtained from an extensive structural search using the genetic algorithm are generally consistent with the literature reports [12] in which the global minimum of either the neutral B_{22} or the positively charged B_{22} boron clusters have a 3D SDR structure (Figure 2b). The corresponding 2D–3D energy difference varies from 7 to 37 kcal/mol as shown in Table 1. Similarly to B_{22} system, the 2D QP isomer in the anionic B_{22} clusters is nearly iso-energetic with the 3D SDR counterpart, e.g., energy difference being equal to about 1.0 kcal/mol (cf. Table 1). As one more electron is added to form the dianionic state, the elongated isomer B_{22}-QP-1 becomes much more stable than 3D SDR one, the former being 18.0 kcal/mol lower in energy than the latter. The second 2D isomer of the dianion B_{22}-QP-2 remains even iso-energetic with the 3D SDR structure.

3.3. The 24-atom boron clusters

Structures of the B_{24} clusters have recently been determined including certain geometries of monocycles, 3D SDR and other forms [24]. The 3D SDR isomer was found as the most stable neutral form.

The two low-lying 2D QP isomers, namely the B_{24}-QP-1 and B_{24}-QP-2 shown in Figure 2c, are calculated to be less stable than their 3D SDR isomers not only for the positively charged and neutral states but also for the anionic state. In contrast to the B_{20} and B_{22} systems, the 3D SDR anions of B_{24} turn out to be more stable than the corresponding 2D QP anions. In this charged state, 3D structures are about 9–42 kcal/mol lower in energy than their 2D QP isomers. There is no iso-energetic domain between 2D and 3D structures for B_{24} clusters as it is the cases of B_{20} and B_{22} clusters. When adding one extra electron to form the doubly negatively charged state, 2D QP isomers are now energetically less favored than 3D SDR structure by up to 11–19 kcal/mol (Table 1).

3.4. An analysis of the geometrical transition

In observing the evolution of various pairs of 2D and 3D boron clusters having different size and charge, the corresponding 2D–3D relative energy and their trend of variation with respect to the implemented net charge can be established. Geometry and electronic structure of the clusters considered also provide us with some insights into the driving force for the energetic changes.

Our calculated results point out an intrinsic interdependency between shape (2D versus 3D) and charge (from dicationic to dianionic states) in a small range of size from 20 to 24 B-atoms. The 20-atom boron cluster is now firmly established as the transition point where neutral 3D SDR structure becomes more stable than the 2D QP isomers. Such a geometrical transition generally occurs early for positively charged states, and later for negatively charged states. In other words, calculated results point out that the 2D–3D relative stability inherently depends on the implemented charge of the clusters. Figure 3 shows a plot illustrating the variation of 2D–3D relative energy with respect to net charge. The correlation between 2D–3D relative stability and implemented charge indicates that addition of electrons tend to stabilize the 2D QP over the 3D SDR isomers. Furthermore, such a 2D–3D stability dependency can be

<table>
<thead>
<tr>
<th>Charge</th>
<th>B_{20}-QP-1</th>
<th>B_{20}-QP-2</th>
<th>B_{22}-QP-1</th>
<th>B_{22}-QP-2</th>
<th>B_{24}-QP-1</th>
<th>B_{24}-QP-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>22.6 (10, aar)</td>
<td>30.4 (10, aar)</td>
<td>36.9 (12, ar)</td>
<td>32.4 (12, ar)</td>
<td>41.6 (12, aar)</td>
<td>38.5 (12, aar)</td>
</tr>
<tr>
<td>1</td>
<td>18.5</td>
<td>24.6</td>
<td>30.6</td>
<td>20.4</td>
<td>36.2</td>
<td>37.8</td>
</tr>
<tr>
<td>0</td>
<td>14.1 (12, ar)</td>
<td>9.9 (12, ar)</td>
<td>14.9 (14, aar)</td>
<td>7.2 (14, aar)</td>
<td>26.7 (14, ar)</td>
<td>32.7 (14, ar)</td>
</tr>
<tr>
<td>−1</td>
<td>−3.6</td>
<td>−5.0</td>
<td>−0.9</td>
<td>0.9</td>
<td>8.5</td>
<td>10.2</td>
</tr>
<tr>
<td>−2</td>
<td>−20.9 (14, aar)</td>
<td>−18.4 (14, aar)</td>
<td>−17.8 (14, ar)</td>
<td>−3.2 (14, ar)</td>
<td>−11.0 (16, aar)</td>
<td>−18.7 (16, aar)</td>
</tr>
</tbody>
</table>

These values are calculated using a 2D QP structure is more stable than the corresponding 3D SDR isomer with a negative relative energy. Total number π of electrons and corresponding aromaticity (ar)/anti-aromaticity (aar) of the 2D QP isomer according to Hückel rule are presented in parentheses.

In Figure 2, Geometries of the 2D QP and 3D SDR isomers of boron clusters considered.
Clusters are considered as, for example, geometrical clusters is plotted in Figure 5. In the neutral state, the B20-1 to B24-2 transition is supported upon planarization with conservative boundary obviously increases the planarity. While internal atoms are more vigorously reordered to adapt the molecular planes, most of the peripheral bonds are saturated with two electrons giving 2c–2e bond systems. The planarization with conservative boundary obviously increases the atomic repulsion significantly. Such a pattern is expectedly stabilizing the structure by maximizing the exchange energy obtained from \( \pi \)-electron delocalization within molecular planes [7]. In a sense, the planarity is favored as more electrons are added. For instance, while the cationic B24-2D-1 isomer remains buckled, the corresponding neutral 3D SDR isomer is almost planar. Nevertheless, the dicationic B24-2D-1 isomer becomes also perfectly planar and this might come from a side effect of Coulomb repulsion [36].

The 2D QP structures are iteratively supported upon planarization and the consequent delocalization of \( \pi \)-electrons heading toward the classical Hückel rule for aromaticity, and the resemblance with unsaturated hydrocarbon in their \( \pi \) patterns [4,7,18,19,35]. The first step of aromatizing and resembling electronic structure of hydrocarbons is to flatten the B-clusters facilitating an overlap of \( \pi \)-atomic orbitals. To observe geometrical changes of 2D isomers as being charged, the peripheral bonds and side-projected geometry of 2D QP of the B24 clusters are considered as for an example. Geometrical and structural parameters of B24 are depicted in Figure 4. With change in the charged state, Figure 4 shows that both the bond-length and corresponding occupancy of the peripheral bonds tend to be conserved. While internal atoms are more vigorously reordered to adapt the molecular planes, most of the peripheral bonds are saturated with two electrons giving 2c–2e bond systems. The planarization with conservative boundary obviously increases the atomic repulsion significantly. Such a pattern is expectedly stabilizing the structure by maximizing the exchange energy obtained from \( \pi \)-electron delocalization within molecular planes [7]. In a sense, the planarity is favored as more electrons are added. For instance, while the cationic B24-2D-1 isomer remains buckled, the corresponding neutral anion is almost planar. Nevertheless, the dicationic B24-2D-1 isomer becomes also perfectly planar and this might come from a side effect of Coulomb repulsion [36].

The 2D QP structures are iteratively supported upon planarization and the consequent delocalization of electrons occupying \( \pi \)-, or even \( \sigma \)-MO. Intuitively, the total number of \( \pi \) electrons is expected to obey the Hückel count as a prerequisite for energetically favorable electron delocalization. Interestingly, the Hückel electron count seems not always to correlate with the 2D–3D relative stability. As for a typical example, the \( \pi \)-system of the well-known \( B_{20} \) clusters is plotted in Figure 5. In the neutral state, the B20-QP-1 isomer is found to be anti-aromatic with a total number of 14 \( \pi \) electrons, while the corresponding neutral 3D SDR isomer features a double aromaticity [11]. This gives rise to a suitable 2D–3D relative energy, i.e., the neutral B20-QP-1 being about 14 kcal/mol higher in energy than the 3D SDR isomer (cf. Table 1). With two additional electrons yielding the dianionic state, the B20-QP-1 isomer is now Hückel aromatic with 14 \( \pi \) electrons, while the 3D SDR

\[
\Delta E^{0.98} = 12.73C + 8.31 \quad (B20-1)
\]

\[
\Delta E^{0.91} = 10.92C + 6.17 \quad (B20-2)
\]

\[
\Delta E^{0.98} = 14.09C + 12.73 \quad (B22-1)
\]

\[
\Delta E^{0.95} = 9.09C + 11.546 \quad (B22-2)
\]

\[
\Delta E^{0.95} = 13.30C + 20.40 \quad (B24-1)
\]

\[
\Delta E^{0.83} = 14.20C + 20.09 \quad (B24-2)
\]

While B20-1 denotes the linearly fitted equation for B20-QP-1 isomer, \( \Delta E \) (in kcal/mol) is the 2D–3D relative energy formulated in such a way that a 2D QP isomer is more stable than the corresponding 3D SDR with a negative value and vice versa. The actual net charge is denoted with capital C varying in the range of \([2^-, +2]\). The superscript given on the \( \Delta E \) 2D–3D relative energy is the correlation coefficient of the fitted equation. In all cases studied, the correlation between relative energy and implemented charge are relatively high. The lowest correlation coefficient amounts to 0.83 (Eq. B24-2), whereas the highest one of 0.98 (Eqs. B20-1 and B22-1) is very close to unity.

The magnitude of the slopes and intercepts of the fitted lines represents the dependency of 2D–3D relative stability on implemented charge, i.e., the larger the slope, the higher the dependency, and conversely for the intercept value. As seen in equations B20-1 to B24-2, all slopes are positive, and relatively larger than the intercepts. The positive slope values prove that electron addition consistently decreases the stability of the 3D SDR isomer as compared to its corresponding 2D QP isomer. This rationalizes the finding of an early geometrical hopping for positively charged states (e.g. for the cationic state, the critical size being around 16-atom system [15,25]), while it becomes later for negatively charged states (e.g. a critical size being larger than 20-atom in anionic state). Therefore, the 2D-to-3D geometry hopping of boron clusters occurs not only at a critical size but also with a critical charge. With a certain size the relative stability of a pair of 2D–3D isomers could changes as the system reaches a critical charge. Accordingly, a full description of geometry hopping of small boron clusters needs to include a coupling of both critical size and charge parameters.
contains a mixed aromatic radial (10π electrons) and anti-aromatic tangential (12π electrons) stack of MOs [11]. This reverses the energy ordering in favor of the negatively charged state, e.g. the B20-QP-1 isomer becoming now 21 kcal/mol lower in energy than the 3D SDR. On the contrary, upon removal of two electrons from the neutral, the dication B20-QP-1 becomes aromatic (e.g. with 10π electrons shown in Figure 5). The dicationic 3D SDR isomer again contains a mixed aromatic radial (10π electrons) and anti-aromatic tangential (8π electrons) MO stacks. However, the B20-QP-1 dication is calculated to be 23 kcal/mol higher in energy than the corresponding 3D SDR cation, in contrast to the prediction based on the classical electron count.

By performing the similar MO analyses on the π-systems of the other 2D QP isomers, the added electrons are found to occupy π-MOs in priority inducing a π-delocalization favoring planarization [8,9]. Total numbers of counted π electrons of 2D QP isomers and the assigned aromaticity (ar) as well as the anti-aromaticity (aar) in term of Hückel rule are presented in Table 1. It can be seen that assignment of Hückel aromatic character does not always correlate with energy ordering. This result is consistent with previous analyses [21,37] where the Hückel aromaticity for π-delocalization are not always applicable to boron clusters.

4. Concluding remarks

In the present theoretical investigation, we carried out DFT calculations on a series of pairs of energetically lower-lying 2D QP and 3D SDR structures of small boron clusters having different sizes from 20 to 24 atoms and net charges (from dication to dianion). The 2D–3D relative energy is generally found to linearly vary with respect to the actual charge of the cluster, i.e., a 2D QP isomer becomes stabilized, or even more stable, as compared to its corresponding 3D SDR following addition of extra electrons. Our results thus unveil the underlying background for the early 2D-to-3D geometry hopping for positively charged boron clusters, and reversely for the negatively charged counterparts.
Planarization of the molecular skeleton appears obviously as a driving force facilitating electron delocalization in 2D structures. Within the range of implemented charge of $[2^-, 2^+]$, the added electrons to 2D structures tend to reinforce the $\pi$-MOs and thereby stabilize planar structures irrespective of the classical Hückel electron count.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2013.05.041.

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