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Rearrangements in icosahedral boranes and carboranes revisited

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Abstract The structure, stability, and intermolecular rearrangements between ortho-, meta-, and para-C\(_2\)B\(_{10}\)H\(_{12}\) and B\(_{12}\)H\(_{12}\)\(^{2–}\) were investigated using the hybrid density functional B3LYP/6-31G(d) for vibrational frequencies, as well as B3LYP/6-311+G(2d,p) for single-point electronic energies. The general trends in free energies of rearrangement between ortho-C\(_2\)B\(_{10}\)H\(_{12}\) to meta-C\(_2\)B\(_{10}\)H\(_{12}\) and meta-C\(_2\)B\(_{10}\)H\(_{12}\) to para-C\(_2\)B\(_{10}\)H\(_{12}\) presented here are consistent with experimental reaction temperatures. In addition, the majority of the rearrangements can be viewed in terms of concerted diamond–square–diamond steps and triangular face rotations.

Keywords Deltahedron · Carboranes · Icosahedral · Triangular face rotation · Diamond–square–diamond

Introduction

The roots of modern boron cluster chemistry originated in a few seminal works by Wade [1, 2], Hart and Lipscomb [3–6], and Williams [7–9]. These compounds, which are characterized by their electron deficiencies, form non-classical three-center two-electron bonds and have been the topic of numerous texts [10–14]. This leads to the very familiar deltahedron geometries for closo-C\(_2\)B\(_{10}\)H\(_{12}\)+x with \(n+1\) skeletal electron pairs, nido-C\(_2\)B\(_{10}\)H\(_{12}\)+x with \(n+2\) skeletal electron pairs, and arachno-C\(_2\)B\(_{10}\)H\(_{12}\)+x with \(n+3\) skeletal electron pairs, determined empirically by Wade’s Rules [1, 2, 15, 16]. Although a great deal of time has been spent in comparing and contrasting carborane systems of varying size in terms of stability, rearrangement, and reactivity [7, 8, 17–23], a special effort has been expended in understanding closo-B\(_{12}\)H\(_{12}\)\(^{2–}\), closo-C\(_2\)B\(_{10}\)H\(_{12}\), and their respective derivatives [21, 24–29], which is due primarily to their unusually high stability. An eclectic array of mechanisms have been quite naturally suggested for the intermolecular rearrangement of closo-C\(_2\)B\(_{10}\)H\(_{12}\), from those involving highly symmetric cubeoctahedral and anticubeoctahedral transition states to those with relatively simple triangular face rotations (TFRs) and diamond–square–diamond (DSD) steps [4, 5, 20, 25, 30–36]. Rearrangements in substituted icosahedral C\(_2\)B\(_{10}\)H\(_{12}\) have been studied experimentally by way of \(^{10}\)B-labeling, halogen substitution, methyl substitution, and even tethered linkages [3, 24, 28, 36, 37] in the hopes that the electronic structure of the cage will be preserved.

Despite previous theoretical work on the stability of large carboranes and their derivatives and the aforementioned experimental work on intermolecular rearrangements in closo-C\(_2\)B\(_{10}\)H\(_{12}\), there has been relatively little rigorous computational work in verifying whether any of the proposed mechanisms play a role in these intermolecular rearrangement reaction pathways. The present work confirms the presence of a TFR pathway in both the carborane and the borane case. Another pathway, which consists of concerted DSD steps and the opening of the cage into a pseudo-nido intermediate, is also described for both cases.

Methodology

The following calculations were done using the Gaussian03 program [38]. Species were optimized and vibrational frequencies were calculated at the B3LYP/6-31G(d) level, leading to their characterization as stationary points. In

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\text{closo-C}_2\text{B}_{10}\text{H}_{12}^{2–}, \quad \text{closo-C}_2\text{B}_{10}\text{H}_{12}, \quad \text{closo-C}_2\text{B}_{10}\text{H}_{12}^{2–}, \quad \text{closo-C}_2\text{B}_{10}\text{H}_{12}
\]
addition, zero-point energies, integrated specific heat corrections at constant pressure, and entropies were calculated at this level. Once a continuous reaction pathway was determined, single-point electronic energies were calculated for the pertinent species at the B3LYP/6-311+G(2d,p) level. The enthalpies for the species at 500 and 800 K were approximated to be the same as the enthalpy at 298 K. These values were then used to determine the absolute free energy at 298, 500, and 800 K. The change in free energies at 298, 500, and 800 K for the species in the carborane rearrangement are relative to ortho-C₂B₁₀H₁₂ and, similarly, the species in the borane rearrangement are relative to B₁₂H₁₂²⁻.

Results and discussion

The reaction pathways between ortho-, meta-, and para-C₂B₁₀H₁₂, and B₁₂H₁₂²⁻ are shown in Figs. 1 and 2, with representative geometries in Figs. 3 and 4, respectively. At first glance, some common features between Figs. 1 and 2 should be apparent. The arrangement of the vertices and edges for both C₂B₁₀H₁₂ and B₁₂H₁₂²⁻ are very similar (Figs. 1 and 2). Both have two distinct pathways operating the TFR pathway and the non-TFR pathway (the non-TFR pathway is actually quite complicated and cannot be succinctly described). In addition to the graphical similarities in the schemes, the representative geometries in Figs. 3 and 4 are analogs. The ortho- to meta-C₂B₁₀H₁₂ case mimics the meta- to para-C₂B₁₀H₁₂ case, which mimics the B₁₂H₁₂²⁻ case. These similarities will prove to be useful when discussing the mechanisms of the pathways in detail.

General trends

Before discussing rearrangement mechanisms, it is important to establish some confidence by way of general trends between the stabilities and geometries of the three carborane isomers. Pertinent electronic and thermodynamic data can be found in Tables 1 and 2. Notice that the ΔG (298 K) for the three isomers decreases from ortho- to meta- to para-C₂B₁₀H₁₂, which is consistent with experimental observation [39]. Furthermore, the approximate transition temperatures of 450 °C for the ortho- to meta- C₂B₁₀H₁₂ rearrangement and 620 °C for the meta- to para-C₂B₁₀H₁₂ rearrangement are qualitatively consistent with the barrier heights in Fig. 1 [39–41]. Besides trends in stability, two recent gas-phase electron diffraction (GED) studies have made it possible to compare the calculated unique bond distances in the three isomers to the
experimentally determined unique bond distances (see Table 3 and Fig. 5) [42, 43]. In almost all of the bonds, the difference between the calculated distance and the most recent experimentally determined distance (GED at 463 K) is around 0.01 Å.

Fig. 3 Geometries for ortho-, meta-, and para-C$_2$B$_{10}$H$_{12}$. The nomenclature is as follows: the first two letters separated by a dash indicate which carboranes are being rearranged (e.g., m-p corresponds to a meta to para rearrangement species). An italicized T indicates a TFR pathway species. The last letters (and possible number) indicates the type of stationary point of the species.
Table 1  Total electronic energies (in hartrees), zero-point energies (kJ/mol), heat capacity corrections to 298 K, and entropies (J/mol K) for species on the C$_2$B$_{10}$H$_{12}$ and B$_{12}$H$_{12}$ $^2-$ potential energies surfaces

| Structures       | Total energy | Zero-point energy | $\int Cp$ | Entropy |
|------------------|--------------|-------------------|----------|---------|
| ortho-C$_2$B$_{10}$H$_{12}$ | -332.17455   | 466.1             | 22.7     | 347.1   |
| meta-C$_2$B$_{10}$H$_{12}$  | -332.20059   | 468.0             | 22.4     | 345.5   |
| para-C$_2$B$_{10}$H$_{12}$  | -332.20500   | 468.0             | 22.4     | 345.7   |
| o–m-TS1          | -332.04031   | 445.7             | 26.6     | 372.2   |
| o–m-INT          | -332.10921   | 455.1             | 26.8     | 373.7   |
| o–m-TS2          | -332.07899   | 451.5             | 25.4     | 363.8   |
| o–m-T-TS         | -332.08224   | 448.5             | 26.7     | 373.5   |
| o–o-T-TS         | -332.01780   | 444.1             | 27.6     | 380.3   |
| m–m-T-TS         | -332.09144   | 449.5             | 26.7     | 372.2   |
| m–p-TS1          | -332.06051   | 448.2             | 26.3     | 370.2   |
| m–p-TS1*         | -332.10091   | 452.5             | 25.1     | 362.4   |
| m–p-INT          | -332.12258   | 455.5             | 26.6     | 371.5   |
| m–p-TS2          | -332.08274   | 451.5             | 25.6     | 365.8   |
| m–p-T-TS         | -332.05341   | 446.7             | 27.3     | 378.8   |
| p–p-T-TS         | -332.03032   | 444.5             | 27.7     | 379.4   |
| B$_{12}$H$_{12}^2-$ | -305.77394   | 439.1             | 23.1     | 348.7   |
| b–b-T-TS         | -305.60815   | 418.6             | 28.3     | 383.6   |
| b–b-T-INT        | -305.60974   | 419.7             | 29.6     | 373.2   |
| b–b-TS1          | -305.58691   | 419.4             | 27.4     | 377.1   |
| b–b-INT1         | -305.63168   | 423.9             | 26.0     | 367.4   |
| b–b-TS2          | -305.63167   | 423.9             | 26.0     | 367.4   |
| b–b-INT2         | -305.63167   | 423.9             | 26.0     | 367.5   |
| b–b-TS3          | -305.61911   | 422.4             | 26.6     | 374.5   |

Fig. 4  Geometries of B$_{12}$H$_{12}^2-$ species. The nomenclature system is analogous to the carborane case. Consult Fig. 3 for a description.
Table 2  Relative enthalpies (kJ/mol), entropies (J/K·mol), and free energies (kJ/mol) for species on the $\text{C}_2\text{B}_{10}\text{H}_{12}$ and $\text{B}_{12}\text{H}_{12}^2$ potential energy surfaces

| Structures | $\Delta H$ (0 K) | $\Delta H$ (298 K) | $\Delta S$ | $\Delta G$ (298 K) | $\Delta G$ (500 K) | $\Delta G$ (800 K) |
|------------|------------------|-------------------|-----------|-------------------|-------------------|-------------------|
| $\text{o-m-TS1}$ | 332.1 | 336.0 | 25.1 | 328.5 | 323.4 | 315.9 |
| $\text{o-m-INT}$ | 160.6 | 164.7 | 26.6 | 156.8 | 151.4 | 143.4 |
| $\text{o-m-TS2}$ | 236.3 | 239.0 | 16.7 | 234.0 | 230.6 | 225.6 |
| $\text{o-o-T-TS}$ | 224.7 | 228.8 | 26.4 | 220.9 | 215.5 | 207.6 |
| $\text{o-o-T-S}$ | 389.6 | 394.5 | 33.3 | 384.6 | 377.9 | 367.9 |
| $\text{m-m-T-TS}$ | 201.6 | 205.6 | 25.1 | 198.1 | 193.1 | 185.5 |
| $\text{m-p-T-S}$ | 281.6 | 285.1 | 23.1 | 278.2 | 273.6 | 266.6 |
| $\text{m-p-T-S}$ | 358.3 | 361.3 | 18.7 | 355.7 | 351.9 | 346.3 |
| $\text{m-p-T-S}$ | 471.4 | 475.7 | 28.4 | 467.2 | 461.5 | 453.0 |
| $\text{m-p-T-S}$ | 532.1 | 536.0 | 31.7 | 528.3 | 524.6 | 519.9 |
| $\text{B}_{12}\text{H}_{12}^2$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

Ortho- to meta-carborane rearrangement

TFR pathway

Figure 6 illustrates the ortho- to meta-$\text{C}_2\text{B}_{10}\text{H}_{12}$ TFR mechanism where the structures of the stationary points are similar to those in the ortho-$\text{C}_2\text{B}_{10}\text{H}_{12}$ to ortho-$\text{C}_2\text{B}_{10}\text{H}_{12}$ degenerate TFR, the meta-$\text{C}_2\text{B}_{10}\text{H}_{12}$ to para-$\text{C}_2\text{B}_{10}\text{H}_{12}$ TFR, and the borane TFR rearrangement. The left column in Fig. 6 displays the geometric progression through the reaction and the right column shows a two-dimensional projection of the pertinent atoms and bonds of the corresponding geometry on the left. As can be seen in the left column, a TFR acts by taking an equilateral triangle of three atoms, lifting them up slightly, rotating them by 120° (counter-clockwise in this case), and lowering them back down. The projective graphs display unequivocally that the mechanism is, in fact, a sequence of concerted diamond–square–diamonds. The transition state graph corresponding to o–m-T-TS shows the three simultaneous square faces.

Non-TFR pathway

Figure 7 illustrates the non-TFR mechanism. The first step in this mechanism is for one of the ortho-$\text{C}_2\text{B}_{10}\text{H}_{12}$ carbons, situated at the apex of a pentagonal cap, to break three of its bonds, while performing a DSD transition on the lower diamond. The square face in the DSD transition can be seen in the lower part of the graph corresponding to o-m-TS1. As the carbon migrates and forms the bond in the DSD, the species approaches a pseudo-nido geometry, which is displayed graphically in brackets. This geometry, in which the carbon lies approximately in a hexagonal plane, is never realized because other stabilizing forces exert themselves and propel the species towards the geometry in o-m-INT. The geometry displays two pentagonal faces in lieu of the hexagonal face of the pseudo-nido geometry. The last transition state o-m-TS2 is due to two adjacent DSD transitions on the opposite side of the cluster. In one direction, the species minimizes to o-m-INT. In the other direction, the molecule minimizes to meta-$\text{C}_2\text{B}_{10}\text{H}_{12}$.

Meta- to para-carborane rearrangement

TFR pathway

See “TFR pathway” subsection under “Ortho- to meta-carborane rearrangement”.

$^2$David Wales has two examples of carborane rearrangements that illustrate the necessary movement: (1) rearrangement from the icosahedral 1,2-carborane to a higher energy C$_5$ isomer (http://www.ch.cam.ac.uk/SGTL/teach/djw1.html) and (2) rearrangement from the 1,7-icosahedral carborane to a higher energy isomer based on an anticuboctahedron (http://www.ch.cam.ac.uk/SGTL/teach/djw2.html).

$^3$All of these pathways operate in essentially the same manner, except for slight deviations in geometry due to juxtaposition of boron with carbon and vice versa.
The non-TFR mechanism for the meta- to para-rearrangement (Fig. 8) mimics the ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} rearrangement except that there is a second possible transition state m–p-TS\textsubscript{1}* which is lower in energy than the analogous ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} transition state (m–p-TS\textsubscript{1}, Table 1). The structural change from meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} to m–p-TS\textsubscript{1} is exactly the same as in the ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} case, except that only a boron vertex moves from the apex of a pentagonal cap opening a face in the cluster. Just as with the ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} rearrangement, a "nido" geometry is never reached, leading instead to m–p-INT. The more thermodynamically favorable pathway is through m–p-TS\textsubscript{1}* which can be described as two adjacent concerted DSD steps. The second half of the rearrangement is analogous to the ortho-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} rearrangement: two concerted adjacent DSD steps occur on the opposite side of the cluster (see m–p-TS\textsubscript{2}) and para-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} results.

### Table 3

Comparison of calculated distances [B3LYP/6-31G(d)] with distances from two gas-phase electron diffraction studies for ortho-, meta-, and para-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12}

| Bond | B3LYP/6-31G(d) | GED [42] | GED [43] |
|------|---------------|----------|----------|
| C(1)–C(2) | 1.625 | 1.624(8) | 1.653(49) |
| C(1)–B(3) | 1.720 | 1.734(7) | 1.711(14) |
| C(1)–B(4) | 1.700 | 1.700(6) | 1.711(14) |
| B(3)–B(4) | 1.780 | 1.788(6) | 1.802(13) |
| B(4)–B(5) | 1.786 | 1.794(8) | 1.802(13) |
| B(3)–B(8) | 1.765 | 1.774(9) | 1.789(9) |
| B(5)–B(9) | 1.778 | 1.787(6) | 1.789(9) |
| B(7)–B(8) | 1.781 | 1.796(6) | 1.789(9) |
| B(8)–B(9) | 1.793 | 1.808(8) | 1.789(9) |
| B(9)–B(12) | 1.784 | 1.787(9) | 1.789(9) |
| C(1)–B(2) | 1.694 | 1.678(5) | 1.720(9) |
| C(1)–B(4) | 1.715 | 1.730(4) | 1.720(9) |
| C(1)–B(5) | 1.712 | 1.704(8) | 1.720(9) |
| B(2)–B(3) | 1.789 | 1.786(9) | 1.831(52) |
| B(2)–B(6) | 1.768 | 1.771(6) | 1.791(15) |
| B(4)–B(5) | 1.783 | 1.801(5) | 1.791(15) |
| B(4)–B(9) | 1.781 | 1.780(6) | 1.817(13) |
| B(5)–B(9) | 1.778 | 1.783(6) | 1.817(13) |
| B(4)–B(8) | 1.771 | 1.778(9) | 1.817(13) |
| B(9)–B(10) | 1.793 | 1.795(9) | 1.817(13) |
| C(1)···C(7) | 2.608 | 2.575(9) | |
| C–B | 1.708 | 1.698(3) | 1.710(11) |
| B–B tropical | 1.790 | 1.784(1) | 1.792(7) |
| B–B meridional | 1.767 | 1.774(4) | 1.772(13) |
| C(1)···C(12) | 3.057 | 3.029(5) | 3.05(5) |

### Non-TFR pathway

The non-TFR mechanism for the meta- to para-rearrangement (Fig. 8) mimics the ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} rearrangement except that there is a second possible transition state m–p-TS\textsubscript{1}* which is lower in energy than the analogous ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} transition state (m–p-TS\textsubscript{1}, Table 1). The structural change from meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} to m–p-TS\textsubscript{1} is exactly the same as in the ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} case, except that only a boron vertex moves from the apex of a pentagonal cap opening a face in the cluster. Just as with the ortho- to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} rearrangement, a “nido” geometry is never reached, leading instead to m–p-INT. The more thermodynamically favorable pathway is through m–p-TS\textsubscript{1}* which can be described as two adjacent concerted DSD steps. The second half of the rearrangement is analogous to the ortho-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} to meta-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} rearrangement: two concerted adjacent DSD steps occur on the opposite side of the cluster (see m–p-TS\textsubscript{2}) and para-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} results.

### Borane rearrangement

TFR pathway

See “TFR pathway” subsection under “Ortho- to meta-carborane rearrangement”. There is one exception in the B\textsubscript{12}H\textsubscript{12} case. There is a D\textsubscript{3h} intermediate b–b-T-INT that is lower than b–b-T-INT in enthalpy at 298 K by 1.7 kJ/mol. When entropic effects are taken into account, the intermediate b–b-T-INT is actually higher in free energy at 298, 500, and 800 K.

### Non-TFR pathway

Figure 9 illustrates the non-TFR mechanism in the B\textsubscript{12}H\textsubscript{12} case. There is one exception in the B\textsubscript{12}H\textsubscript{12} case. There is a D\textsubscript{3h} intermediate b–b-T-INT that is lower than b–b-T-INT in enthalpy at 298 K by 1.7 kJ/mol. When entropic effects are taken into account, the intermediate b–b-T-INT is actually higher in free energy at 298, 500, and 800 K.
the apex of a pentagonal cap migrates, breaking three bonds, and performs a DSD step on the lower diamond. The geometry again progresses towards a pseudo-nido geometry but does not quite achieve it. Another bond begins to form, which acts to prevent the cluster from opening, resulting in $b-b$-INT1. An interesting feature of the pathway is that there is an additional minimum ($b-b$-TS2) and transition state ($b-b$-INT1) along the reaction pathway that disappear when zero-point corrections are included. From $b-b$-TS2, two adjacent concerted DSD steps are needed to reach $b-b$-TS3 which then leads directly to icosahedral $\text{B}_{12}\text{H}_{12}^{2-}$.

The free energy of activation in the gas phase for rearrangement of the boron vertices at 800 K is 398.5 kJ/mol via $b-b$-INT (Fig. 2). The free energy barrier is much higher than calculated for rearrangement in the isoelectronic carboranes (Fig. 1). In fact, the barrier is higher than for fragmentation of a B–H bond, which implies that $\text{B}_{12}\text{H}_{12}^{2-}$ should undergo decomposition rather than rearrangement. In a recent study of the boron hydride monoanions, $\text{B}_{12}\text{H}_{12}^{2-}$ was determined to be the smallest boron hydride dianion with a positive adiabatic ionization potential [22]. It is still unlikely that both electrons would remain attached at elevated temperatures.

Experimental verification

There is one very interesting anomaly that emerges with respect to carborane rearrangements. The lowest free
energy carborane barrier is a degenerate rearrangement meta- to meta-C$_2$B$_{10}$H$_{12}$, which is 185.5 kJ/mol at 800 K. This process may prove useful in rationalizing products obtained from rearrangement of the substituted carborane. In addition, because the barrier is lower than the barrier for rearrangement to ortho- and para-C$_2$B$_{10}$H$_{12}$, if one were able to synthesize a substituted meta-C$_2$B$_{10}$H$_{12}$ with a methyl group on a boron atom adjacent to carbon, then, at a moderate temperature, one would expect to see migration of the methyl group to a boron position non-adjacent to carbon. We offer this prediction as a means of testing the rearrangement mechanism in the gas phase.
Conclusion

The rearrangement mechanism in C$_2$B$_{10}$H$_{12}$ and B$_{12}$H$_{12}^{2-}$ has been explored using density functional theory methods. From ortho-C$_2$B$_{10}$H$_{12}$, the lowest free energy pathway to meta-C$_2$B$_{10}$H$_{12}$ is via a triangular-face-rotation mechanism with a barrier of 207.6 kJ/mol. From meta- to para-C$_2$B$_{10}$H$_{12}$, the lowest-energy rearrangement mechanism is non-TFR which might loosely be described as a closo to nido to closo mechanism as the transition state is much more open than the reactant or product. The free energy barrier is 279.9 kJ/mol, 72.3 kJ/mol lower in free energy.

Fig. 7 The ortho- to meta-C$_2$B$_{10}$H$_{12}$ non-TFR rearrangement pathway.
Fig. 8  The meta- to para-$C_2B_{10}H_{12}$ non-TFR rearrangement pathway
than the ortho to meta process. The rearrangement of B_{12}H_{12}^{2-}, which would scramble labeled vertices, has a free energy barrier of 398.5 kJ/mol. For B_{12}H_{12}^{2-}, the preferred process in the gas phase would be to emit an electron or cleave a B–H bond.

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Fig. 9 The B_{12}H_{12}^{2-} to B_{12}H_{12}^{2-} non-TFR rearrangement pathway
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