Reactions of Experimentally Known Closo-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10} with Bases. A Computational Study

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Abstract: On the basis of the direct transformations of closo-1,2-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10} with OH\textsuperscript{(-)} and NH\textsubscript{3} to arachno-1,6,9-OC\textsubscript{2}B\textsubscript{8}H\textsubscript{13}(-) and arachno-1,6,9-NC\textsubscript{2}B\textsubscript{8}H\textsubscript{13}, respectively, which were experimentally observed, the DFT computational protocol was used to examine the corresponding reaction pathways. This work is thus a computational attempt to describe the formations of 11-vertex arachno clusters that are formally derived from the hypothetical closo-B\textsubscript{13}H\textsubscript{13}(2-). Moreover, such a protocol successfully described the formation of arachno-4,5-C\textsubscript{2}B\textsubscript{6}H\textsubscript{11}(-) as the very final product of the first reaction. Analogous experimental transformations of closo-1,6-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10} and closo-1,10-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10}, although attempted, were not successful. However, their transformations were explored through computations.

Keywords: carboranes; DFT; reaction pathways

1. Introduction

Polyhedral borane and heteroborane clusters are known for the presence of delocalized electron-deficient bonding \[1,2\] and characterized by forming three-center, two-electron (3c-2e) bonds. This bonding is quite different from organic chemistry that is dominated by classical two-center two-electron (2c-2e) bonds. The trigonal faces of boranes and carboranes are assembled to create three-dimensional shapes such as icosahedron and bicapped-square antiprism \[2\] appearing in closo systems. The preparation and subsequent reactivity of these clusters have been extensively studied by experiments \[1,2\]. In particular, the 12-vertex icosahedral closo clusters have been one of the main targets. In contrast to well-understood reaction mechanisms in organic chemistry, those in boron cluster chemistry can be very complex because there are very small energy differences between many intermediates and transition states. On that basis, the reaction of boron hydrides may involve many competing pathways \[3\]. For that reason, relatively little progress has so far been made in the understanding of the reaction mechanisms of boron hydrides and carboranes of various molecular shapes \[4–6\]. To our knowledge, the reaction pathways associated with ten-vertex closo carboranes, for instance closo-1,2-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10} (see Scheme 1), have not yet been explored.
The C$_2$B$_8$H$_{10}$ molecular shape of a bicapped-square antiprism exists in seven positional isomers, only three of which (1,2-, 1,6- and 1,10-isomers) are known experimentally [2]. The most stable one is the 1,10-isomer and the least stable one is the 2,3-isomer [7]. The 1,6-isomer has recently been examined experimentally [8]. In addition, a new synthetic pathway for the preparation of the 1,2-isomer has also been outlined, including some mechanistic considerations [9]. Mutual isomerizations of all the possible closo-C$_2$B$_8$H$_{10}$ have been studied computationally [10]. As to the observed reactivity of the 1,2-isomer, its direct closo to arachno transformations have been experimentally observed [11,12], with the resulting arachno structural motif being based on the hypothetical closo-B$_{13}$H$_{13}$ (2-) as also seen from the corresponding atomic numberings (see also Scheme 1) [13]. Since no computational work has been reported in the area of the reactions of 10-vertex closo carboranes, we have undertaken a computational study of the experimentally known isomers of closo-C$_2$B$_8$H$_{10}$ with the Lewis bases OH(−) and NH$_3$. Both bases are hard in terms of the HSAB theory of acids and bases [14] with OH(−) being harder than NH$_3$ on the HSAB scale.

2. Methods

All of the stationary points in the reactions of closo-1,2-, 1,6-, and 1,10-C$_2$B$_8$H$_{10}$ with OH(−) were optimized and frequencies were calculated at the SMD(water) [15,16]/B3LYP/6-311+G(2d,p) level, a model chemistry well-established for this class of materials [4–6]. The entries in Table 1 for B3LYP/6-311+G(2d,p) are single-point energies at SMD(water)/B3LYP/6-311+G(2d,p)-optimized geometries. The reactions of the same carborane with neutral NH$_3$ were optimized at the B3LYP/6-311+G(2d,p) level without taking solvation effects into account, which is quite reasonable for neutral species. Moreover, unlike the investigation of organic reaction mechanisms where the bonding is 2c–2e and bond-breaking reaction steps can cause the wave function to become unstable with respect to symmetry-breaking, in the investigation of electron deficient reactions, the bonding scheme fluidly changes between different patterns of multi-center bonding. While dynamic electron correlation is important (and described by the B3LYP approach used in this study), non-dynamic (i.e., static) electron correlation (caused by near degeneracy effects) is not important. All of the transition states were relaxed in terms of the application of the intrinsic reaction coordinate (IRC) approach at the SMD(water)/B3LYP/6-31+G(d) level for the reactions with OH(−) and at the B3LYP/6-31G(d) level for the reactions with NH$_3$, and the structures obtained are very similar to those obtained with the 6-311+G(2d,p) basis set. In order to check the possible influence of dispersion corrections, the wB97XD/6-311+G(2d,p), model chemistry was also employed for some stationary points. All the computations were performed using Gaussian09, in which the above model chemistries and basis sets are incorporated [17].
Table 1. Solvation free energies (kcal·mol$^{-1}$), and free energies relative to the appropriate reference. The small “c” refers to ortho (1,2-) $C_2B_8H_{10}$. The capital letters “A”, “B”, “C”, etc. and “TS#” are related to individual intermediates and transition states, respectively. If there were two conformations possible, two letters are used to differentiate between them (e.g., $oG/G′-O$, $oK/K′-O$ and $oM/M′-O$). The capital “-O” and “-N” distinguish between the reactions of OH$^{-}$ and NH$_3$, respectively. Wherever the intermediate is relatively stable (and already isolated or possibly trappable), “P1”, “P2”, “P3”, etc. are used instead of “A”, “B”, “C”.

| Notation | $\Delta G$ (solv)$^1$ | $\Delta G$ (aq,298K)$^2$ | Notation | $\Delta G$ (solv)$^1$ | $\Delta G$ (aq,298K)$^2$ |
|----------|------------------------|------------------------|----------|------------------------|------------------------|
| $C_2B_8H_{10} + OH^{-}(c)$ | -94.76 | -3.67 | $C_2B_8H_{10} + NH_3$ | 4.70 | 32.1 |
| OH$^-$ | -94.76 | -3.67 | H$_2$O | -2.05 | -1.24 |
| H$_2$BOH | -3.82 | -3.82 | oTS1-N | -4.70 | 32.1 |
| OBOH | -14.65 | -14.65 | oA-N | -11.06 | 15.8 |
| B(OH)$_3$ | -1.43 | -1.43 | oTS2-N | -0.43 | 50.3 |
| oTS1-O | -53.74 | 27.2 | oP1-N | -3.75 | -1.3 |
| oA-O | -46.19 | 2.0 | oTS3-N | -0.64 | 43.8 |
| oTS2-O | -42.59 | 10.0 | oB-N | -0.39 | 23.8 |
| oB-O | -44.80 | 1.8 | oTS4-N | -1.46 | 32.8 |
| oTS3-O | -39.89 | 14.5 | oC-N | -0.34 | 24.4 |
| oP1-O | -40.16 | -18.4 | oTS5-N | -0.01 | 32.3 |
| 4,5-$C_2B_8H_{11}^-$ | -39.67 | -50.7 | oD-N | 0.27 | 31.2 |
| oC-O | -41.59 | -18.2 | oTS6-N | 0.81 | 39.5 |
| oTS4-O | -45.21 | 18.5 | P2-N | -3.48 | 7.3 |
| oD-O | -47.70 | -2.2 | oTS7-N | -1.01 | 38.3 |
| oTS5-O | -48.36 | 9.1 | oE-N | -0.55 | 29.5 |
| oE-O | -47.59 | 0.0 | oTS8-N | 0.49 | 36.4 |
| oTS6-O | -47.61 | 0.2 | oP3-N | -3.20 | 11.1 |
| oF-O | -45.17 | -1.2 | oTS9-N | -3.06 | 32.1 |
| oTS7-O | -43.15 | 8.8 | oF-N | -3.30 | 29.7 |
| oP2-O | -45.07 | -18.8 | oTS10-N | -6.51 | 29.8 |
| oTS8-O | -58.47 | 6.2 | oG-N | -2.08 | 25.1 |
| oG-O | -63.94 | 1.6 | oTS11-N | -2.74 | 35.0 |
| oG$^+$ | -63.85 | 1.6 | oH-N | -2.77 | 26.5 |
| oTS9-O | -50.19 | 7.9 | oTS12-N | -2.22 | 39.1 |
| oH-O | -53.32 | 4.6 | oI-N | -1.85 | 32.0 |
| oTS10-O | -51.94 | 5.7 | oTS13-N | -1.97 | 32.8 |
| oI-O | -66.84 | 0.1 | oP4-N | -2.27 | -5.5 |
| oj-O | -60.59 | -1.1 | |
| oTS11-O | -58.96 | -1.5 | |
| oK-O | -48.64 | -27.9 | |
| oK$^+$ | -44.34 | -26.8 | |
| oTS12-O | -45.37 | -19.5 | |
| oL-O | -51.68 | -26.9 | |
| oM-O | -56.47 | -28.4 | |
| oM$^+$ | -53.96 | -29.2 | |
| oTS13-O | -58.13 | -4.2 | |
| 4,5-$C_2B_8H_{11}^+$ | -39.43 | -41.7 | |

$^1$ Solvation free energies (the energy difference between B3LYP/6-311+G(2d,p) and SMD/B3LYP/6-311+G(2d,p) at 298.15 K (kcal·mol$^{-1}$). $^2$ Relative free energies in kcal·mol$^{-1}$ (where the references are 1,2-$C_2B_8H_{10}^++OH^-$ for OH$^{-}$ and 1,2-$C_2B_8H_{10}^++NH_3$ for NH$_3$ reactions). The ΔG(aq,298K) and ΔG(solv) for 1,2-$C_2B_8H_{10}^+$ are 0.0 kcal·mol$^{-1}$ and -0.5 kcal·mol$^{-1}$, respectively. The solvation free energy of H$_2$O is taken from the experiment (-2.05 kcal·mol$^{-1}$). In some cases, H$_2$NBH$_3$ is added for mass balance. In the formation of $C_2B_8H_{11}^-$, the comparison is made with respect to 1,2-$C_2B_8H_{10}^++OH^-$+3H$_2$O. $^3$ Geometry optimizations and frequencies calculated at the SMD(water)/B3LYP/6-311+G(2d,p) level of theory. $^4$ Geometry optimizations and frequencies calculated at the B3LYP/6-311+G(2d,p) level of theory.
3. Results and Discussion

3.1. The Reaction with Hydroxides

The first part of the reaction of 1,2-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10} with OH\textsuperscript{(-)} is a quite straightforward process. This experimentally verified reaction, with the oP1-O final product, arachno-1,6,9-OC\textsubscript{2}B\textsubscript{8}H\textsubscript{13}(−) (Scheme 1), proceeds through three transition states (TSs) and two intermediates, with the latter still bearing OH\textsuperscript{(-)} (see Figure 1). The B-H-B bridge is a result of H migration to the B(7)-B(8) position in the final step of this reaction cascade. However, when one molecule of H\textsubscript{2}O is added to oP1-O, the cluster further degrades and through seven TSs an intermediate oI-O is obtained, which is prone to further degradation, when another water molecule is added to the O-B-O-H chain through two hydrogen bonds. This initiation results, via selective degradation of B(3,6)-cage atoms, in the formation of arachno-C\textsubscript{2}B\textsubscript{8}H\textsubscript{11}(−) through a number of TSs and intermediates, this arachno system being also isolated experimentally (see Figures 1 and 2 and Table 1) \[18\]. Note that the first barrier associated with oTS1-O was also examined with wB97XD/6-311+G(2d,p) and no significant difference from the B3LYP/6-311+G(2d,p) value was found, i.e., 24.9 kcal·mol\textsuperscript{-1} vs. 27.2 kcal·mol\textsuperscript{-1} as seen from Table 1. The potential energy surface attributed to the reaction of 1,6-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10} + OH\textsuperscript{(-)} was rather difficult to follow. Since this reaction was not observed experimentally, we moved this computational effort to Supplementary Materials (see Figures S1 and S2). The geometrical shape of the final product mP3-O bears a slight resemblance to the nido-11 vertex geometry, but not with the open pentagonal belt because the OH\textsuperscript{(-)} group migrates through the entire process without any indication of the insertion of oxygen into the cage boron atoms (see Figure S1). The mechanism of the reaction of the 1,10 isomer with OH\textsuperscript{(-)}, also not observed experimentally, is even more complex. Interestingly, the final product (pP1-O, see Figures S3 and S4) of the latter reaction is of the same molecular shape, i.e., with a B-O-B bridge, as in the case of the reaction of 1,2-C\textsubscript{2}B\textsubscript{8}H\textsubscript{10} with OH\textsuperscript{(-)} (oP1-O), but it originates through five TSs instead of three.
Figure 1. Cont.
Figure 1. Individual stationary points as determined in the reaction pathway of the reaction of closo-1,2-C$_2$B$_8$H$_{10}$ with OH$^-(\cdot)$.  

Figure 2. Cont.
3.2. The Reaction with Amines

The reaction of \( \textit{closo}-1,2-C_2B_8H_{10} \) with \( \text{NH}_3 \) has been experimentally known to provide \textit{arachno}-1,6,9-NC\( _2B_8H_{13} \) (Scheme 1) [11,17]. The initiation of this reaction is based on the attack of \( \text{NH}_3 \) on the most positive boron within the cage, i.e., B(3), which forms a triangle with both C vertices. The highest free energy barrier (50.3 kcal·mol\(^{-1}\)) is TS\( _2-N \), through which the \( \text{NH}_3 \) group becomes NH\( _2 \) in the 1,6,9 isomer denoted as oP\( _1-N \) in the reaction pathway (see Figures 3 and 4 and Table 1). However, this experimentally known part of the entire reaction (see above) occurs without any large intervening barriers and, consequently, the oP\( _1-N \) isomer is obtained through two transition states and one intermediate. The same is apparently true for various amines of the \( R_1R_2NH \) type [19]. This reaction proceeds through a series of intermediate steps to the known 1,8,11-isomer (oP\( _2-N \)), experimentally available by another procedure [20]. To our knowledge, there is no experimental evidence of the conversion of oP\( _2-N \) to oP\( _1-N \), although this process is computed to be exothermic (\( \Delta G = -8.6 \) kcal·mol\(^{-1}\)). Note that the experimentally detected \textit{arachno}-1,6,9-NC\( _2B_8H_{13} \) originates under less exothermic conditions than its oxygen analog. In analogy with the reaction of 1,2-C\( _2B_8H_{10} \) with \( \text{OH}^- \), we also examined the first barrier using wB\( 97XD/6-311+G(2d,p) \) and again no significant difference from the B3LYP/6-311+G(2d,p) value was computed, i.e., 28.3 kcal·mol\(^{-1}\) vs. 32.1 kcal·mol\(^{-1}\) as provided by Table 1. When the 1,6,9-isomer (oP\( _1-N \)) was examined computationally in terms of searching for another TS, i.e., oTS\( _7-N \), it isomerizes to a new isomer, oP\( _3-N \), through two TSs and one intermediate, oE-N, with the C–C bond remains intact as judged by a separation of 1.565 Å. When the
C–C separation was increased, another TS and intermediate, i.e., oTS9-N and oF-N, respectively, were located with much longer C ... C separations of 2.409 and 2.774 Å, respectively. This significant geometrical change initiates a continuation of the reaction through other four subsequent TSs to the next known isomer, i.e., oP4-N. The reaction of the 1,6-isomers (see Figures S5 and S6) was a result of the simultaneous initial attack of NH₃ on B(3) and C(6); the N atom forms a cap above the B(2)B(3)C(6) triangle in the transition state with a free energy barrier of 34.6 kcal·mol⁻¹. The second free energy barrier was even higher, 52.0 kcal·mol⁻¹ and might account for the fact that this reaction does not occur experimentally. Interestingly, when the common product of the reactions of closo-1,2-C₂B₈H₁₀ and closo-1,6-C₂B₈H₁₀ with NH₃, i.e., oP4-N, is reached (see also Figure S5), both reactions proceed in the same way and closo-C₂B₇H₉ is obtained, where the two carbon atoms are separated from each other. Basically, there are five isomers of closo-C₂B₇H₉. The isomerization barrier between the most stable Cᵥ (C ... C separation) and the third most stable C₁ (C–C bond) forms is quite high (36 kcal·mol⁻¹). The high barrier is not unusual as isomerizations involving the C–C bond in carboranes often have rather high barriers. This type of closo/closo isomerization can also be described [21] in a more detailed way in terms of the consecutive double-Diamond-Square-Diamond (DSD) mechanism [10,22]. These two closo isomers have already been discussed by Schleyer [7] favoring the Cᵥ-symmetrical 4,5-isomer as well.

![Figure 3. Cont.](image-url)
Figure 3. Individual stationary points on the PES of the reaction of closo-1,2-C$_2$B$_8$H$_{10}$ with NH$_3$. 
The reaction of the 1,10 isomer with NH₃ is rather complex and proceeds through a cascade of TSs. The initial attack of NH₃ simultaneously takes place at the boron atoms of both CB₈ hemispheres (pTS1-N) with an initial free energy barrier of more than 60 kcal·mol⁻¹ and closo-C₂B₈H₁₀ originating as the final product in the endothermic reaction, which is entirely the same as above (see Figures S7 and S8). The experimental reaction of neither the 1,6- nor the 1,10-isomer of C₂B₈H₁₀ with NH₃ have been successfully carried out.

4. Conclusions

The reaction pathways of the experimentally known reactions of closo-1,2-C₂B₈H₁₀ with both OH(−) and NH₃ were computed using the DFT protocol. The final predicted products from the extensive search of the potential energy surfaces correspond to the same products detected experimentally. Both the closo-1,6-C₂B₈H₁₀ and the closo-1,10-C₂B₈H₁₀ isomers were allowed to react with the OH(−) and NH₃ bases, without any defined products being observed. Finally, this work represents a computational attempt to study the debor reaction, in contrast to the debor principle [23] (the successive elimination of vertices), where boron vertices are removed in the course of the reaction as illustrated by obtaining arachno-C₂B₈H₁₁(−) as the very final product from the reaction of closo-1,2-C₂B₈H₁₀ with OH(−).
Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/10/896/s1:
Figure S1: Individual stationary points as detected in the reaction pathway of the reaction of closo-1,6-C2B10H10 with OH−. Figure S2: Relative free energies (kcalmol−1) of the individual stationary points on the PES of the reaction of closo-1,6-C2B10H10 with OH−. Figure S3: Individual stationary points as detected in the reaction pathway of the reaction of closo-1,10-C2B10H10 with OH−. Figure S4: Relative free energies (kcalmol−1) of the individual stationary points on the PES of the reaction of closo-1,10-C2B10H10 with OH−. Figure S5: Individual stationary points as detected in the reaction pathway of the reaction of closo-1,6-C2B10H10 with NH3. Figure S6: Relative free energies (kcalmol−1) of the individual stationary points on the PES of the reaction of closo-1,10-C2B10H10 with NH3. Figure S7: Individual stationary points as detected in the reaction pathway of the reaction of 1,10-C2B10H10 with NH3. Figure S8: Relative free energies (kcalmol−1) of the individual stationary points on the PES of the reaction of closo-1,10-C2B10H10 with NH3. Table S1: Number of imaginary frequencies, zero-point energies (kcalmol−1), heat capacity correction (kcalmol−1), entropies (calmol−1K−1), solvation free energies (kcalmol−1), and free energies relative to the appropriate reference. Small o, m, or p refer to ortho (1,2-), meta (1,6-), or para (1,10-)C2B10H10, respectively. Capital letters “A”, “B”, “C”, etc. or “TS#” are related to individual intermediates or transition states, respectively. If there were two conformations possible, two letters are used to discern them (e.g., oG/G’-O, oK/K’-O, or oM/M’-O). Capital “-O” or “-N” distinguish between the reactions of OH(−) or NH3, respectively. In cases where the intermediate is relatively stable (and already isolated or possibly trappable), “P1”, “P2”, “P3”, etc. is used instead of “A”, “B”, “C”. Table S2: Cartesian coordinates of all species in Table S1

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