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# A Combined NMR/IGLO/Ab Initio Study of the $C_2B_{10}H_{13}^-$ Isomers

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The $C_2B_{10}H_{12}^{2-}$ precursor dianion of the two known forms of $C_2B_{10}H_{13}^-$, the "unreactive" (**1**, $C_s$) and the "reactive" isomer (two possibilities: **2**, $C_s$ and **3**, $C_1$), have all been characterized computationally. The unsymmetrical, fluctuating structure (**3**) of the reactive isomer in solution is firmly established by means of IGLO chemical shift calculations. The calculated geometries of **1** and **3** (ab initio: HF/3-21G) are in good agreement with X-ray data. At the MP2/6-31G*//3-21G + ZPE level, the "unreactive" isomer (**1**) is 6.7 kcal/mol more stable than the "reactive" isomer (**3**) which is known to rearrange into the former. IGLO $^{11}B$ NMR chemical shifts for **1** and **3** (averaged), but not **2**, agree well with experiment. As the energy of **2** is computed to be 11.5 kcal/mol higher than that of **3**, it should be possible to "freeze out" dynamic NMR behavior of the "reactive" isomer (**3**) at lower temperatures.

## Introduction

The carborane *closo*-1,2-$C_2B_{10}H_{12}$, undergoes a two-electron reduction[1] to form a *nido*-$C_2B_{10}H_{12}^{2-}$ carborane dianion presumably with an open six-membered face. Protonation of this dianion resulted in the formation of two monoanions of formula $C_2B_{10}H_{13}^-$.[2] The two isomers are designated as "reactive" and as "unreactive" because of the marked difference in their propensity to undergo typical reactions with transition metals to form organometallic complexes.[3] The "reactive" isomer is the kinetic product and rearranges to the thermodynamically more stable "unreactive" form at moderate temperatures. X-ray structures of *nido*-$R_2C_2B_{10}H_{11}$ ($R = CH_3, C_6H_5$), which are closely related to the "unreactive" isomer, were reported in 1973 by Churchill and DeBoer[4] (CD) and by Tolpin and Lipscomb[5] (TL).[6] These structures are characterized by an open five-membered face, a bridging methylene group, and an approximate symmetry plane. Despite the obvious interest in the second isomer, it was not until 1990 that Getman, Knobler, and Hawthorne[7] solved the X-ray structure of the "reactive" form. The structure has an open six-membered face with the "extra" hydrogen asymmetrically bridging two borons in the open face. Perhaps even more interesting is the presence of a quadrilateral B–B–B–C face which results in a chiral ($C_1$) point group and forces one carbon to be above and the other below the open six-membered face. Since most carboranes without substituents have at least a plane of symmetry,[8] it is of interest to determine whether crystal-packing forces or electronic effects are responsible for the distortion and whether the same structural preference persists in solution.

The room temperature NMR spectra of both isomers have been assigned recently.[3] Two possibilities were considered for the "reactive" isomer, which (in terms of the number of signals) has effective $C_s$ symmetry at least on the NMR time scale. Either the "reactive" isomer possesses a static, $C_s$ structure or a fluxional set of $C_1$ enantiomers which interconvert rapidly (in $CD_2Cl_2$ at 294 K) via a $C_s$ transition state. Unfortunately, a decision could not be reached as both interpretations were consistent with the experimental data. We now provide decisive evidence in favor of the latter possibility.

## Methods

All calculations employed the GAUSSIAN 88[9] or GAUSSIAN 90[10] program systems.[11] Geometries were optimized fully at the HF/3-21G level. Force constants were calculated analytically at that level to establish the nature of the stationary point as well as to provide the zero point energy (ZPE) corrections (0.9 scaling factor). Single-point calculations at MP2/6-31G* provided the final energies. The latter calculations involved 206 basis functions for the $C_2B_{10}H_{13}^-$ species and would not have been possible without the development of direct methods which eliminate the need to store the two-electron integrals.[12] While it is technically possible to optimize the $C_2B_{10}H_{13}^-$ isomers at HF/6-31G* or even at MP2/6-31G*, we did not deem this expenditure of computer time to be necessary. The geometries would be expected to improve, but this could hardly bring any better agreement between the computed (IGLO) and the experimental chemical shifts.

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**Table I.** Absolute (hartrees) and Relative Energies (kcal/mol) of $C_2B_{10}H_{13}^-$ and $C_2B_{10}H_{12}^{2-}$ Species

| compound | structure | sym | HF/3-21G | HF/6-31G* | MP2/6-31G* | ZPE/3-21G[a] |
|---|---|---|---|---|---|---|
| | | | Absolute Energies | | | |
| $C_2B_{10}H_{13}^-$ | **1** | $C_s$ | −328.34506 | −330.20170 | −331.42953 | 122.03(0) |
| | **2** | $C_s$ | −328.31941 | −330.17820 | −331.39506 | 118.23(2) |
| | **3** | $C_1$ | −328.33471 | −330.19784 | −331.41643 | 120.37(0) |
| $C_2B_{10}H_{12}^{2-}$ | **4** | $C_1$ | −327.64150 | −329.49183 | −330.71653 | 110.81(0) |
| | | | Relative Energies | | | |
| $C_2B_{10}H_{13}^-$ | **1** | $C_s$ | −6.5 | −2.4 | −8.2 | −6.7[b] |
| | **2** | $C_s$ | 9.6 | 12.3 | 13.4 | 11.5[b] |
| | **3** | $C_1$ | 0.0 | 0.0 | 0.0 | 0.0[b] |
| $C_2B_{10}H_{12}^{2-}$ | **4** | $C_1$ | 435.0 | 443.0 | 439.2 | 430.6[b] |

[a] Zero-point energy at the HF/3-21G level (kcal/mol) and number of imaginary frequencies in parentheses. [b] The MP2/6-31G* relative energies are corrected with zero-point energies adjusted by a 0.9 factor to account for the overestimation of vibrational frequencies.

**Table II.** Comparison of Calculated (HF/3-21G*) and Experimental X-ray Distances (Å) in **1**

| group | | calcd | exptl (CD[a]) | exptl (TL[b]) |
|---|---|---|---|---|
| $CH_2$ bridge | $B_1C_1$ | 1.643 | 1.642 | 1.67 |
| top ring | $B_1B_2$ | 1.900 | 1.847 | 1.86 |
| | $B_2B_3$ | 1.934 | 1.865 | 1.88 |
| | $B_3C_2$ | 1.630 | 1.625 | 1.66 |
| bottom ring | $B_5B_6$ | 1.844 | 1.796 | 1.84 |
| | $B_6B_7$ | 1.789 | 1.765 | 1.78 |
| | $B_7B_8$ | 1.764 | 1.743 | 1.74 |
| apex | $B_5B_{10}$ | 1.766 | 1.757 | 1.85 |
| | $B_6B_{10}$ | 1.825 | 1.788 | 1.82 |
| | $B_7B_{10}$ | 1.796 | 1.775 | 1.78 |
| ring to ring | $B_1B_5$ | 1.829 | 1.799 | 1.84 |
| | $B_2B_6$ | 1.832 | 1.794 | 1.81 |
| | $B_3B_6$ | 1.751 | 1.728 | 1.76 |
| | $B_3B_7$ | 1.846 | 1.797 | 1.83 |
| | $C_2H_7$ | 1.710 | 1.670 | 1.71 |
| $CH_2$ fold angle | $\alpha$ | 71.2 | 73.8 | |

[a] Reference 4. [b] Reference 5.

**Table III.** Calculated (HF/3-21G) (Å) in **2**

| group | | calcd |
|---|---|---|
| $H_b$ bridge | $B_1H_b$ | 1.212 |
| | $B_2H_b$ | 1.915 |
| top ring | $B_1B_2$ | 1.920 |
| | $B_2C_1$ | 1.640 |
| | $C_1B_3$ | 1.533 |
| bottom ring | $B_5B_6$ | 1.849 |
| | $B_6B_7$ | 1.764 |
| | $B_7B_8$ | 1.863 |
| apex | $B_5B_{10}$ | 1.831 |
| | $B_7B_{10}$ | 1.760 |
| | $B_8B_{10}$ | 1.774 |
| ring to ring | $B_1B_5$ | 1.807 |
| | $B_2B_6$ | 1.748 |
| | $B_2B_7$ | 1.821 |
| | $C_1B_7$ | 1.737 |
| | $C_1B_8$ | 1.988 |
| | $B_3B_8$ | 2.065 |

The IGLO (individual gauge for localized orbitals) method was used[13] to calculate $^{11}B$ chemical shifts. An extensive evaluation of boranes and carboranes has shown that 3-21G geometries are sufficiently accurate to yield computed $^{11}B$ chemical shifts which are in quite reasonable accord with the experimental shifts.[14,15] In addition, it has been demonstrated that the agreement (or disagreement) between calculated and experiment NMR shifts provides strong evidence for deciding among borane and carborane structural candidates. Good agreement between the theoretical chemical shifts for a molecule (even though computed in the isolated state at equilibrium) and the experimental chemical shifts measured at ambient temperatures in solution can be expected to establish the solution-phase structure reliably. As also will be soon below, it is possible to differentiate between a single minimum and a rapidly equilibrating pair of minima.[14b,15a]

Absolute energies (in hartrees), zero-point energies (kcal/mol), and relative energies (kcal/mol) are given in Table I. Unless otherwise indicated, the energy differences discussed are at the MP2/6-31G*//3-21G + ZPE level of theory. The absolute chemical shieldings (relative to the bare nucleus) are calculated (IGLO) with the double-ζ basis set of Huzinaga.[16] These were then put on the usual chemical basis as follows. The relative $^{11}B$ chemical shifts were computed vs. $B_2H_6$. The experimental chemical shift of $\delta(B_2H_6) = 16.6$ ppm with respect to the experimental standard of $BF_3{\cdot}OEt_2$[17,18] was then employed. Likewise, the $^{13}C$ chemical shifts were computed relative to $CH_4$. This has an experimental shift of $\delta(CH_4) = -2.3$ ppm with respect to the experimental standard, TMS.[19]

## Results and Discussion

The calculated geometry of the "unreactive" isomer is compared with the X-ray structures of CD[4] and of TL[5] in Table II. The distances are organized within groups to facilitate comparisons: distances within the open face, distances within the lower five-membered ring, distances to the apex, and, finally, distances between the open face and the lower ring. While the degree of agreement is reasonable, the HF/3-21G level systematically overestimates the B–B and B–C distances. However, the relative trends are well reproduced. Theory and experimental both identify the longest bonding interaction ($B_2B_3$, calcd 1.934 Å; X-ray, 1.865[4] or 1.88[5] Å) as well as the shortest distance ($B_3C_2$, calcd 1.630 Å; X-ray, 1.625[4] or 1.66[5] Å). Also, the dihedral angle between the three-membered ring and the five-membered open face agrees with experiment (calcd 71.2°; X-ray,[4] 73.8°).

We computed alternative geometries of the "reactive" isomer; data for the $C_s$ symmetry structure with a triple bridging hydrogen (**2**) are given in Table III and for the $C_1$ form with its asymmetric double bridging hydrogen (**3**) in Table IV. The geometry computed for **3** is in reasonable agreement with the X-ray structure although the B–B and B–C bond distances again are overestimated at HF/3-21G. The shortest bonding distances, $B_3C_2$ and $C_2B_4$, involve carbon in the open six-membered face. The distances from $B_3$ to $B_8$ and $B_9$, all members of the unique quadrilateral

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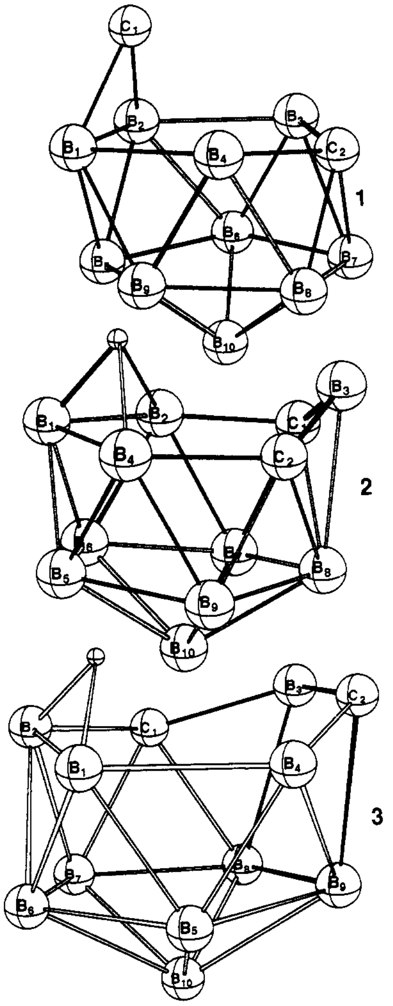

**Figure 1.** Three-dimensional structures of **1**–**3** generated from the calculated Cartesian coordinates. The quadrilateral face in **3** is emphasized by making the enclosing bonds bold.

**Table IV.** Comparison of Calculated and Experimental Distances (Å) in **3**

| group | | calcd | exptl[a] | group | | calcd | exptl[a] |
|---|---|---|---|---|---|---|---|
| $H_b$ bridge | $B_1H_b$ | 1.263 | 1.43 | ring to ring | $B_1B_5$ | 1.775 | 1.741 |
| | $B_2H_b$ | 1.390 | 1.43 | | $B_1B_6$ | 1.769 | 1.746 |
| top ring | $B_1B_2$ | 1.867 | 1.846 | | $B_2B_6$ | 1.840 | 1.809 |
| | $B_2C_1$ | 1.650 | 1.648 | | $B_2B_7$ | 1.861 | 1.816 |
| | $C_1B_3$ | 1.615 | 1.638 | | $C_1B_7$ | 1.702 | 1.668 |
| | $B_3C_2$ | 1.518 | 1.506 | | $C_1B_8$ | 1.730 | 1.679 |
| | $C_2B_4$ | 1.515 | 1.513 | | $B_3B_8$ | 2.005 | 1.858 |
| | $B_4B_1$ | 1.930 | 1.885 | | $B_3B_9$ | 2.294 | 2.093 |
| bottom ring | $B_5B_6$ | 1.804 | 1.786 | | $C_2B_8$ | 2.810 | 2.816 |
| | $B_6B_7$ | 1.777 | 1.759 | | $C_2B_9$ | 1.843 | 1.796 |
| | $B_7B_8$ | 1.757 | 1.729 | | $B_4B_9$ | 1.960 | 1.929 |
| | $B_8B_9$ | 1.909 | 1.892 | | $B_4B_5$ | 1.782 | 1.762 |
| | $B_9B_5$ | 1.900 | 1.874 | | | | |
| apex | $B_5B_{10}$ | 1.776 | 1.762 | | | | |
| | $B_6B_{10}$ | 1.828 | 1.806 | | | | |
| | $B_7B_{10}$ | 1.778 | 1.753 | | | | |
| | $B_8B_{10}$ | 1.738 | 1.722 | | | | |
| | $B_9B_{10}$ | 1.833 | 1.807 | | | | |

[a] Supplementary material from ref 7.

**Table V.** Comparison of Calculated (DZ/IGLO//3-21G) $^{11}B/^{13}C$ and Experimental $^{11}B$ NMR Chemical Shifts (ppm) for **1**[a]

| $^{11}B/^{13}C$ | calcd | exptl[b] | Δ |
|---|---|---|---|
| $C_1$ | 68.4 | | |
| $C_2$ | 39.8 | | |
| $B_1/B_2$ | −14.6 | −16.2 | 1.6 |
| $B_3/B_4$ | 18.6 | 16.0 | 2.6 |
| $B_5$ | 13.7 | 11.1 | 2.6 |
| $B_6/B_9$ | −23.4 | −22.8 | −0.6 |
| $B_7/B_8$ | −7.3 | −6.3 | −1.0 |
| $B_{10}$ | 0.9 | 0.2 | 0.7 |

[a] The calculated chemical shifts for carbon are compared to $CH_4$ and then reported with respect to the experimental standard, TMS, by using the experimental chemical shift of $CH_4$ ($\delta = -2.3$ ppm).[c] Likewise, the calculated chemical shifts for boron are compared to $B_2H_6$ and then reported with respect to the experimental standard, $BF_3{\cdot}OEt_2$, by using the experimental chemical shift of $B_2H_6$ ($\delta = 16.6$ ppm).[d] [b] Reference 3. [c] Reference 19. [d] Reference 17.

B–B–B–C face, are about 0.2 Å too long (Table IV). The transformation from **2** to **3** can be thought of as a diamond–square–diamond (DSD) rearrangement[20] where the $B_3B_8B_9C_2$ diamond (the $C_2B_8$ diagonal distance in **2** is 1.988 Å) is converted into another diamond with the opposite diagonal connected ($B_3B_9$, 2.293 Å) in **3**.

The computed relative energies of **1**–**3** are rather insensitive to the inclusion of polarization functions (6-31G*) or electron correlation (MP2). (This also justifies our decision not to reoptimize the geometries at these higher levels.) The "unreactive" isomer (**1**) is predicted to be 6.7 kcal/mol more stable than the "reactive" structure in $C_1$ symmetry. This result agrees with the known facile conversion of the "reactive" $C_2B_{10}H_{13}^-$ form into the "unreactive" form under mild conditions.[3] The energy of **2**, with its triply bridged hydrogen in $C_s$ symmetry, is predicted to be 11.5 kcal/mol higher than **3** with a asymmetrical doubly bridged hydrogen. This result is unusual. Most parent (.i.e, unsubstituted) carboranes have at least a plane of symmetry, although exceptions are known.[8,15a]

However, comparing the "architectural patterns"[21,22] of the two structures **2** and **3** is instructive. Using Williams' perspective,[21,22] carbon prefers to be in an "electron-poor environment" and tends to "preempt 2c–2e bonds". While both carbons in **2** are in unfavorable "electron-rich environments", **3** is better since only one carbon ($C_1$) is so located.

The $^{11}B$ NMR spectra for **1** and **3**[3] were determined in $CD_2Cl_2$ at room temperature and assignments were made with the help of COSY correlations. Table V compares the calculated (DZ(IGLO)//3-21G) with the experimental chemical shifts. The average IGLO chemical shift deviation from the measured values is only 1.5 ppm. This supports the experimental assignments stongly.

Although no general relationship between NMR chemical shifts and atomic charges can be expected,[15] correlations in related cases may be found.[23] We note that the downfield shift of $B_3/B_4$ vs the significant upfield shift of $B_6/B_9$ is consistent with the HF/6-31G* Mulliken charges on the BH units, +0.06 vs −0.10 e⁻, respectively.

The measured chemical shifts of the "reactive" isomer are compared with the computed values for **2** and **3** in Table VI. The experimental results could not differentiate between a rapidly equilibrating pair of $C_1$ isomers (**3**) or a static $C_s$ structure (**2**). The calculated chemical shifts identify the $C_1$ structure unambiguously as the "reactive" isomer in solution. The deviations of the calculated chemical shifts for the symmetric form **2** are so large that this structure can be excluded.[14] In contrast, the agreement between theory and experiment for the $^{11}B$ chemical shifts of the asymmetric form **3** (after averaging the computed

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**Table VI.** Comparison of Calculated (DZ/IGLO//3-21G) $^{11}B/^{13}C$ and Experimental $^{11}B$ NMR Chemical Shifts (ppm) for **2** and **3**[a]

| $^{11}B/^{13}C$ | **3**, $C_1$ | **2**, $C_s$ | exptl[b] | **3**, $C_1$ (av) | Δ |
|---|---|---|---|---|---|
| $C_1,C_2$ | 29.3/114.3 | 32.1 | | 71.8 | |
| $B_3$ | 17.2 | 41.4 | 12.7 | 17.2 | 4.5 |
| $B_2,B_4$ | −7.8/17.7 | 7.1 | 2.5 | 5.0 | 2.5 |
| $B_1$ | −20.3 | −51.2 | −20.1 | −20.3 | −0.2 |
| $B_8$ | −5.6 | −1.2 | −4.7 | −5.6 | −0.9 |
| $B_7,B_9$ | −6.8/−41.8 | −28.7 | −21.4 | −24.3 | −2.9 |
| $B_5,B_6$ | 7.2/−28.9 | −12.7 | −7.9 | −10.9 | −3.0 |
| $B_{10}$ | −15.6 | −46.3 | −17.7 | −15.6 | 2.1 |

[a] The calculated chemical shifts for carbon are compared to $CH_4$ and then reported with respect to the experimental standard, TMS, by using the experimental chemical shift of $CH_4$ ($\delta = -2.3$ ppm).[c] Likewise, the calculated chemical shifts for boron are compared to $B_2H_6$ and then reported with respect to the experimental standard, $BF_3{\cdot}OEt_2$, by using the experimental chemical shift of $B_2H_6$ ($\delta = 16.6$ ppm).[d] [b] Reference 3. [c] Reference 19. [d] Reference 17.

shifts of equivalent borons) is very good (average deviation = 2.3 ppm). Keeping the reservations stated above in mind, we note that the sizable downfield (+17.2 ppm) shift of $B_3$ and the very large upfield shift (−41.8 ppm) of $B_7$ are at least in qualitative accord with the Mulliken BH charges, +0.15 and −0.14 $e^-$, respectively.

Note the large difference in the two $^{13}C$ chemical shifts of in **3**. The carbon in the formally four-coordinate "classical" position ($C_2$, $\delta = 114.3$ ppm) has a remarkably large downfield shift, also relative to the five-coordinate "nonclassical" carbon ($C_1$, $\delta = 29.3$ ppm). However, the $C_2$–$B_9$ distance (ca. 1.8 Å) is quite long and $C_2$ has considerable "unsaturated" character. The behavior of $C_1$ has many precedents in electron-deficient carbon compounds, e.g., carbocations. The large HOMO–LUMO gaps involving hypercoordinated carbons generally result in upfield $^{13}C$ chemical shifts.[13c,14]

Why is the distorted **3** favored over the symmetrical **2**? This is not due primarily to the presence of the "extra" hydrogen but to the preference of carbon for an electron-poor environment. Therefore, the interpretation should be applicable to the dianion $C_2B_{10}H_{12}^{2-}$ as well. To test this prediction, the geometry of the dianion was optimized without symmetry (**4**, $C_1$) and compared with an earlier calculation[25] of the same dianion ($2,4\text{-}C_2B_{10}H_{12}^{2-}$) in $C_s$ symmetry (both at 3-21G). Single point energies were then obtained. At the highest level (MP2/6-31G*//3-21G + ZPE), the unsymmetrical dianion **4** ($C_1$) is 10.4 kcal/mol more stable than the $C_s$ form. This energy difference can be compared to the 11.5 kcal/mol preference for the isomer with the $C_1$ point group in the protonated forms (Table I). Indeed, the "extra" hydrogen in **2** and **3** appears to have little influence. In this context, we note that Lee's recent claim based on "second moment scaling" that symmetrical $B_{12}H_{12}^{4-}$ and $C_4B_8H_{12}$ "should be isostructural with their isoelectronic analogs"[26] is not supported by our results on $C_2B_{10}H_{12}^{2-}$.

The heat of reaction of eq 1 (Table I) is quite endothermic (430.6 kcal/mol) due to the electrostatic attraction of the dianion

$$C_2B_{10}H_{13}^-\ (C_1) \rightarrow C_2B_{10}H_{12}^{2-} + H^+\ (C_1) \qquad (1)$$

for the positive charge. This protonation energy is quite high and may be compared with the value of 413.1 kcal/mol computed recently for the protonation of $B_8H_8^{2-}$.[27]

## Conclusions

Ab initio theory provides a reasonable description of the behavior of the $C_2B_{10}H_{13}^-$ system. Even the geometries computed with the modest 3-21G basis set agree well with the X-ray structures. The relative energies correspond with the known tendency of the "reactive" isomer (**3**) to rearrange to the "unreactive" form (**1**), as well as with the preference of **3** over the symmetrical alternative, **2**. The IGLO results for **1** and **3** are particularly satisfying. The good agreement between the calculated and measured chemical shifts for **3** allow the unsymmetrical structure of the "reactive" isomer to be established unambiguously in solution. Computations on the parent $C_2B_{10}H_{12}^{2-}$ dianion (which has not been characterized experimentally) also favor an unsymmetrical geometry.

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