

## Synthesis and Analysis of Isotopically Pure *closo*-1, 2-Dicarbadoecaborane

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### Abstract

Accomplishing a successful hydrogen economy requires solutions to many logistical problems that researchers currently face. The storage of hydrogen for transportation uses is one of the most challenging due to problems with low hydrogen weight percentages for currently used metal hydrides. Lighter elements, such as boron, are currently being researched because of its high H wt%; however, more research must be done on the dehydrogenation and re-hydrogenation of these boron compounds in order to make conclusions about the catalysis ability of these compounds. Researching the B-H bonds of boron containing compounds requires the use of different instruments including Temperature Programmed Desorption (TPD), Infrared analysis (IR), and Reflective Absorption Infrared Spectroscopy (RAIRS). However, the existence of two boron isotopes in nature unnecessarily complicates the analysis of these compounds. Therefore, the synthesis of isotopically pure compounds to be used for analysis is necessary to effectively research these compounds. Multiple paths exist to synthesize carborane, current compound of interest for hydrogen storage; however, the path outlined by Schlesinger et al. is the one used, which converts boric acid to sodium borohydride. The sodium borohydride is then converted to decaborane and finally to carborane; however, the specific intermediate conversions depend on the specific path that is followed.

## Introduction

Realizing a hydrogen economy requires many advances in current research and technology. One of the most important and possibly the most challenging is the storage of hydrogen for transportation. Low volumetric hydrogen densities and hydrogen weight percentages are some of the problems encountered during the research of this problem. Researchers attempted to solve this problem by introducing complex hydrides as a means for hydrogen storage; however, these compounds produce a new problem of being too heavy. The use of the currently researched hydrides would be impractical because the new weight introduced would counter-balance the additional hydrogen storage. The transportation vehicle would not gain any energy because it would be compensating for the additional weight of the compound.

Using other lighter elements that form hydrides for hydrogen storage is a possibility instead. Boron is one of these possible elements. This element has a fairly low atomic mass of 10.81g/mol compared to  $\text{LaNi}_5$ , which has a favorable volumetric hydrogen density, but lanthanum alone has an atomic mass of 138.9 g/mol. Various boron hydrides have good hydrogen weight percentages around 9% compared to  $\text{LaNi}_5$ , which has an H wt% of 1.49%. An example of one of these hydrides is  $\text{LiBH}_4$ , which is 18.5% hydrogen by weight and has a volumetric hydrogen density of 122g/L compared to liquid hydrogen, which has a density of 70g/L. [5] The high volumetric densities and H wt% of these boron hydrides supports the hypothesis that further research into the use of these compounds for hydrogen storage.

Many unknowns about the interactions of these compounds exist, including understanding the B-H bonds, determining the reactivity with other compounds, and

researching the reactions of these compounds with surfaces. The last unknown is very important because researchers must understand how the compound will dehydrogenate and/or re-hydrogenate to understand carborane's catalytic capabilities. Studying the boron compound at the surface while increasing the temperature allows for analysis of the breaking of the B-H bonds and dehydrogenation. After investigation of this process is complete the re-hydrogenation process can be researched.

## **Background**

Many different boron hydrides exist; however, carborane, *closo*-1, 2-dicarbadoecaborane, was chosen to begin this research because it has a fairly low weight, which will allow for a high H wt% and volumetric hydrogen density. The stability of the B-H bonds and the surface chemistry of these bonds on a transition metal surface is not widely studied. To further understand the surface chemistry of this compound, researchers investigate the compound using Reflective Absorption Infrared Spectroscopy (RAIRS) and temperature programmed Desorption (TPD). These instruments measure the absorption or desorption of energy from the bonds. However, there is a complication when studying this compound because boron has two isotopes,  $^{11}\text{B}$  and  $^{10}\text{B}$ , in nature and the presence of these isotopes complicates the spectra making them difficult to analyze. The synthesis of isotopically pure carborane would help to simplify the spectra when doing the analysis of this compound.

## Experimental Method

### *Conversion of Boric Acid to Methyl Borate*

Many steps are required in the preparation of isotopically pure carborane to ensure no contamination with naturally abundant boron occurs. The synthesis begins with isotopically pure boric acid, easily obtained from Sigma-Aldrich. The boric acid is then reacted with methanol in a round-bottom flask under reflux to produce methyl borate. The methyl borate is washed with small portions of sulfuric acid and then purified through distillation. The equation  $\text{H}_3^{10}\text{BO}_3 + 4\text{CH}_3\text{OH} \rightarrow [(\text{CH}_3\text{O})_3^{10}\text{B} + \text{CH}_3\text{OH}] + 3\text{H}_2\text{O}$  summarizes this reaction. Written in this reaction is the B-10 isotope, but either B-10 or B-11 may be used. [6]

### *Conversion of Methyl Borate to Sodium Borohydride*

The methyl borate is then heated under reflux with sodium hydride, which produces sodium borohydride, summarized in the following reaction.  $4\text{NaH} + ^{10}\text{B}(\text{OCH}_3)_3 \rightarrow \text{Na}^{10}\text{BH}_4 + 3\text{NaOCH}_3$  The sodium borohydride is washed with isopropylamine, which was dried over barium oxide and distilled from sodium hydride. The mixture is then heated gently under reflux to purify; impurities are removed by filtration with a sintered glass disc. The distillate is then washed again with isopropylamine, and then the amine is removed by distillation at atmospheric pressure. [7]

### Synthesis of Carborane from Sodium Borohydride

At this point in the synthesis, two different paths produce isotopically pure decaborane, which can then be reacted to produce carborane.

**Path A***Conversion of Sodium Borohydride to  $^{10}\text{B}_{11}\text{H}_{14}^-$* 

The borohydride is mixed with sodium iodide and 1-chloropentane and heated under a constant argon purge to maintain a positive inert atmosphere. After the mixture cools, water is added, which produces hydrogen gas. Once all the gas has evolved, more water is added with orthophosphoric acid to remove impurities. The solid product,  $^{10}\text{B}_{11}\text{H}_{14}^-$  anion, is collected through vacuum filtration using a coarse glass frit.

*Conversion of  $^{10}\text{B}_{11}\text{H}_{14}^-$  to Decaborane*

The solid anion is then mixed with mineral oil and placed in an ice bath to maintain a temperature of 35°C or less. Water and hexane is then added sequentially to the flask. Then sulfuric acid is slowly added. After mixing, ferrous sulfate heptahydrate and hydrogen peroxide are slowly added such that the temperature is maintained at 35°C or less. The mixture is allowed to cool and the hexane layer is separated in a separatory funnel. This hexane layer is then washed with water and dried with anhydrous magnesium sulfate. The hexane solution is then passed through a silica gel to remove impurities. The resulting hexane solution contains  $^{10}\text{B}$ -decaborane and is stable for storage or shipping. [4]

**Path B***Conversion of Sodium Borohydride to  $\text{Na}[^{10}\text{B}_3\text{H}_8] \cdot 3(\text{C}_4\text{H}_8\text{O}_2)$*

In the second path, the sodium borohydride is mixed with diglyme, and this mixture is reacted with I<sub>2</sub> and heated to 95°C. The product, Na[<sup>10</sup>B<sub>3</sub>H<sub>8</sub>].3(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>), is then collected with vacuum filtration and anhydrous dioxane is used to purify through recrystallization as shown in the following reaction.  $3\text{Na}^{10}\text{BH}_4 + \text{I}_2 \rightarrow \text{Na}^{10}\text{B}_3\text{H}_8 \cdot 3(\text{C}_4\text{H}_8\text{O}_2) + 2\text{H}_2 + 2\text{NaI}$

*Conversion of Na[<sup>10</sup>B<sub>3</sub>H<sub>8</sub>].3(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) to Pentaborane*

The product is then mixed with NiCl<sub>2</sub> in a dry box with mineral oil. The mixture is heated in a warm oil bath to 110°C overnight, while the reaction  $2\text{Na}^{10}\text{B}_3\text{H}_8 \cdot 3(\text{C}_4\text{H}_8\text{O}_2) + \text{NiCl}_2 \rightarrow ^{10}\text{B}_5\text{H}_9 + 2\text{H}_2 + \text{C}_4\text{H}_8\text{O}_2 \cdot ^{10}\text{BH}_3$ , takes place. The noncondensable gas is then removed, and the mixture is fractionated out through a series of traps held at 0, -45, -64, -94, and -196°C to collect pure <sup>10</sup>B-pentaborane. [2]

*Conversion of Pentaborane to Na<sup>10</sup>B<sub>5</sub>H<sub>8</sub>*

The pentaborane must then be reacted to make Na<sup>10</sup>B<sub>5</sub>H<sub>8</sub>,  $^{10}\text{B}_5\text{H}_9 + \text{NaH} \rightarrow \text{Na}^{10}\text{B}_5\text{H}_8$ , to obtain the required reactant for the decaborane synthesis. This reaction takes place by mixing pentaborane with NaH and stirring. The solution is then condensed by stirring at -78°C and then slowly warmed to room temperature. The mixture is filtered quickly and the solid product, Na<sup>10</sup>B<sub>5</sub>H<sub>8</sub>, is washed with n-hexane to remove impurities.

*Conversion of Na<sup>10</sup>B<sub>5</sub>H<sub>8</sub> to Decaborane*

Method I

The synthesis of decaborane with  $\text{Na}^{10}\text{B}_5\text{H}_8$  as a reactant can be performed using four different methods. The first method, summarized in the reaction  $\text{Na}^{10}\text{B}_5\text{H}_8 + \text{NiCl}_2 \rightarrow {}^{10}\text{B}_{10}\text{H}_{14}$ , begins by mixing  $\text{Na}^{10}\text{B}_5\text{H}_8$  with anhydrous benzene. The mixture is then quickly poured onto anhydrous  $\text{NiCl}_2$  and stirred. The product is collected through vacuum filtration, purified through sublimation, and captured in a u-trap held at  $0^\circ\text{C}$ .

### Method II

A second method to synthesize decaborane is to react  $\text{Na}^{10}\text{B}_5\text{H}_8$  with  $\text{FeCl}_3$  ( $\text{Na}^{10}\text{B}_5\text{H}_8 + \text{FeCl}_3 \rightarrow {}^{10}\text{B}_{10}\text{H}_{14}$ ) in a flask with dry benzene at  $0^\circ\text{C}$ . The product is separated with vacuum filtration, purified through sublimation at  $100^\circ\text{C}$ , and then collected in a u-trap held at  $0^\circ\text{C}$ .

### Method III

In a third method, the  $\text{Na}^{10}\text{B}_5\text{H}_8$  is mixed with anhydrous dioxane in a dry box. Dry dioxane and  $\text{C}_5\text{H}_{11}\text{Br}$  is then added to the flask, while the entire reaction ( $\text{Na}^{10}\text{B}_5\text{H}_8 + \text{C}_5\text{H}_{11}\text{Br} \rightarrow {}^{10}\text{B}_{10}\text{H}_{14}$ ) is under a constant purge of  $\text{N}_2$ . The mixture is then heated to  $100^\circ\text{C}$  and stirred for two hours. The mixture is allowed to cool to room temperature and all of the solvent is removed in vacuo over a period of 4-5 hours to isolate a solid product in a u-trap held at  $0^\circ\text{C}$ .

### Method IV

The fourth and final method for the synthesis of decaborane mixes the  $\text{Na}^{10}\text{B}_5\text{H}_8$  and dioxane in a dry box.  $\text{Br}_2$  is then added with anhydrous dioxane, while the mixture is maintained at  $-78^\circ\text{C}$ . The reaction, summarized in the equation  $\text{Na}^{10}\text{B}_5\text{H}_8 + \text{Br}_2 \rightarrow$

$^{10}\text{B}_{10}\text{H}_{14}$ , is then stirred for 4 hours at room temperature and all the volatiles are removed at  $0^\circ\text{C}$ . The product is then collected through sublimation in vacuo at room temperature.

[3]

*Conversion of Decaborane to 1,2-Bis(Acetoxyethyl)-closo-1,2-Dicarbadoecaborane(12)*

The isotopically pure decaborane is then used to synthesize 1,2-Bis(Acetoxyethyl)-closo-1,2-Dicarbadoecaborane(12). The first step of this procedure is to reflux dimethyl sulfide, benzene, and sublimed decaborane for six hours. The reaction flask is then cooled to room temperature and 2-butyne-1,4-diol diacetate is added. The reagent is washed down with dry benzene. The mixture is stirred until the reaction subsides and then allowed to reflux for another 10 hours. The dimethyl sulfide and benzene is removed under vacuum with a rotary evaporator. Methanol is then added to the remaining solution, stirred at room temperature for five hours, and then cooled to  $-10^\circ\text{C}$ . The product is recrystallized with methanol to purify the product. During the previous reflux two reactions occur. The first is represented by the equation  $^{10}\text{B}_{10}\text{H}_{14} + 2(\text{CH}_3)_2\text{S} \rightarrow [(\text{CH}_3)_2\text{S}]_2^{10}\text{B}_{10}\text{H}_{12} + \text{H}_2$  and this reaction involves the formation of an intermediate product. The second reaction,  $[(\text{CH}_3)_2\text{S}]_2^{10}\text{B}_{10}\text{H}_{12} + \text{CH}_3\text{COOCH}_2\text{C} \rightarrow 1,2\text{-Bis(acetoxyethyl)-closo-1,2-Dicarbadoecaborane(12)} + 2(\text{CH}_3)_2\text{S} + \text{H}_2$ , converts this intermediate product to the desired product, 1,2-Bis(Acetoxyethyl)-closo-1,2-Dicarbadoecaborane(12).

*Conversion of 1,2-Bis(Acetoxyethyl)-closo-1,2-Dicarbadoecaborane(12) to Carborane*

Once the 1,2-Bis(Acetoxyethyl)-closo-1,2-Dicarbadoecaborane is purified and thoroughly dried the product is mixed with potassium hydroxide solution and stirred at room temperature for five hours. The reaction flask is cooled and finely divided potassium permanganate is added while stirring over an 8-hour period. During this period the final reaction, represented in the equation  $1,2\text{-Bis(acetoxyethyl)-closo-1,2-Dicarbadoecaborane(12)} + 10\text{KOH} + 8\text{KMnO}_4 \rightarrow 3^{10}\text{B}_{10}\text{C}_2\text{H}_{12} + 6\text{CH}_3\text{COOK} + 8\text{MnO}_2 + 6\text{K}_2\text{CO}_3 + 8\text{H}_2\text{O}$ , of this synthesis occurs. Following the addition of the potassium permanganate, potassium disulfite is added at 0°C and then ice-cold sulfuric acid. The solid that forms is mixed with 8-mesh anhydrous calcium chloride, and the mixture is extracted with n-pentane for 28 hours using a Soxhlet extractor. The carborane product is isolated from pentane by filtration and allowed to thoroughly dry.

**Results/Discussion**

Two paths were identified for the synthesis of decaborane from sodium borohydride; however, path A is the method that would be preferred. Path A is a much safer synthesis because it avoids the production of the intermediate pentaborane, which is a very harsh and unsafe compound. Pentaborane is highly toxic by inhalation, skin absorption and ingestion, and this compound may also spontaneously ignite in air. In addition to these hazards, Path B also requires the use of a dry box, which further complicates the synthesis. Path A avoids all of these problems and is the most logical synthesis for decaborane.

Once the synthesis is complete, the sample of carborane produced must be analyzed with the different instruments mentioned above, RAIRS and TPD. Also, before the completion of the synthesis, a calculated infrared spectrum of the naturally abundant decaborane intermediate compound is used to estimate the complexity of the naturally abundant carborane spectrum. The results of this calculation are in Appendix I with the corresponding spectra in Appendix IV. Calculations were done for decaborane molecules containing all B-11, all B-10, two B-10, and four B-10 atoms in different positions. The probability of how many B-10 molecules could be in the decaborane molecule was also determined and that data is in Appendix III. The most probable number of B-10 atoms to be in the decaborane molecule was two, which had a 30.2 percent probability. However, the results are not dependent on position or symmetry.

The calculated infrared spectrum is quite different for each combination of boron isotopes. The spectrum that had all B-11 boron atoms and the spectrum that had all B-10 atoms are the most dissimilar. For example, the intensities of the two spectra are dramatically different with the maximum intensity for the all B-11 being 207.83 and the maximum for all B-10 being 212.46, which shows that the intensities for the B-10 spectrum are higher. The frequencies obtained for the B-10 spectrum are higher than the B-11 one as well. For example, the corresponding frequency for the peak with an intensity of 207.83 is  $2690.23\text{ cm}^{-1}$  on the B-11 spectrum, but it is  $2702.03\text{ cm}^{-1}$  with an intensity of 212.46 on the B-10 spectrum. These results are logical because the all B-10 molecule is lighter than the all B-11 molecule and would therefore have higher frequencies.

Four different spectra were calculated with two B-10 atoms in different positions. These spectra separate into two groups. The first group includes two spectra with B-10 atoms at positions five and six and the other with B-10 atoms at positions two and seven. (A diagram of the decaborane molecule with labeled boron atoms is in appendix II). Group one has very similar spectra to the all B-11 spectra except for one peak that has a higher intensity. The spectra with B-10 atoms at positions two and seven has a more intense peak at  $2698\text{ cm}^{-1}$  and the spectra with B-10 at positions five and six has a more intense peak at  $2690\text{ cm}^{-1}$ . Group two, however, has two peaks that have a higher intensity and a higher frequency than the all B-11 spectrum. This occurs at  $2696\text{ cm}^{-1}$  and  $2700\text{ cm}^{-1}$ . One final spectrum was calculated with two B-10 atoms at positions one and ten; however, this spectrum does not fit into either one of the previous groups. This spectrum has one peak that is the same as the all B-11 spectrum, one peak that has a higher frequency and intensity at  $2690\text{ cm}^{-1}$ , and the final peak has a higher frequency but a lower intensity at  $2709\text{ cm}^{-1}$ .

One final set of calculations were completed with four B-10 atoms in the decaborane molecule. All calculations involved two B-10 atoms at positions one and ten and the final two rotated among the final positions. Two groups were also seen in this final set with the first group containing spectra with B-10 atoms at positions one, ten, five, and six and the second spectra with B-10 atoms at positions one, ten, two, and seven. The spectra with B-10 atoms at positions five and six had one peak with a higher frequency and intensity than the all B-11 spectrum. The second peak had the same frequency and intensity as the second peak on the spectrum with two B-10 atoms at positions five and six, and the third peak had the same frequency and intensity as the

spectrum with two B-10 atoms at positions one and ten. The same results occurred for the second spectra in this first group; however, the third peak had the same frequency as the one and ten spectra but had a slightly higher intensity.

The second group of this final set of calculations is unique from the first group because all of these spectra had four intense peaks instead of three. The first spectrum taken had B-10 atoms at positions one, ten, four and nine. This spectrum had all of the same differences as the spectrum with B-10 atoms at positions four and nine except that the middle peak at  $2690\text{ cm}^{-1}$  was split into two peaks at  $2691\text{ cm}^{-1}$  and  $2701\text{ cm}^{-1}$ . The same results occurred on the spectra with B-10 atoms at positions one, ten, three, and eight.

Experimental infrared and mass spectra analysis of naturally abundant decaborane was performed on a sample and the results are found in appendices V and VI respectively. The experimental spectrum of the decaborane molecule has two main groups of peaks. The first group has two peaks around  $2600\text{ cm}^{-1}$ , one at  $2588\text{ cm}^{-1}$  and the other at  $2606\text{ cm}^{-1}$ , both are due to B-H and  $\text{BH}_2$  stretches. The second group has one peak at  $1523\text{ cm}^{-1}$ , which is due to B-H-B bridged hydrogen stretches. As the sample heats from 90 K to 400 K all of the peaks shrink until at 400 K there are no peaks. This supports the idea that decaborane dehydrogenates when heated. Also, when a mass spectrum was taken on the sample to confirm the presence of decaborane the experimental spectrum, Appendix VI, is very similar to the reference spectrum, which supports the idea that decaborane is present.

## Conclusions

The research recorded in this report is one step toward a hydrogen economy. Before this new mode of transportation is used, researchers must address the logistical problems. The storage of hydrogen is one of the most difficult problems to solve because of low volumetric hydrogen densities and H wt%. More specifically understanding the surface chemistry of these compounds (carborane and decaborane) is essential to obtaining effective and efficient hydrogen burning transportation. In order to study and analyze carborane and decaborane as efficiently as possible an isotopically pure sample must first be obtained through synthesis. This molecule must then be tested for purity and can then be used for testing on surfaces and spectroscopy. Boron containing compounds may be the solution to the hydrogen storage problem, but researchers must first understand reactivity and catalysis properties.

## References

- 1) C. Kotal, D. Owen, L. Todd, "closo-1,2-Dicarbadoecaborane(12)", *Inorganic Syntheses*. Vol.11 (1968) 19-23
- 2) L. Adams, S. Tomlinson, J. Wang, S. Hosmane, J. Maguire, N. Hosmane, "A New Synthetic Route to boron-10 Enriched Pentaborane(9) from Boric Acid and its Conversion to anti- $^{10}\text{B}_{10}\text{H}_{22}$ ", *J. Am. Chem Soc.* 124 (2002), 7292-7293
- 3) L. Adams, S. Tomlinson, J. Wang, S. Hosmane, J. Maguire, N. Hosmane, "Novel approach to boron-10 enriched decaborane(14): an important advance in synthetic boron hydride chemistry", *Inor Chem Comm.* 5 (2002), 765-767
- 4) R.Cowan, D.M. Ginosar, G.B. Dunks, "Methods of Synthesizing Enriched Decaborane for Use in Generating Boron Neutron Capture Therapy Pharmaceuticals", U.S. Pat. No. 6,086,837 (2000).
- 5) Trenary, Michael. Reversible Dehydrogenation of Boron Nanoclusters. Proposal to the Department of Energy. 2005
- 6) H.I. Schlesinger, H.C. Brown, D.L. Mayfield, J.R. Gilbreath, "Procedures for the Preparation of Methyl Borate", *J. Amer. Chem. Soc.*, 75, 213 (1953)
- 7) H.I. Schlesinger, H.C. Brown, A.E. Finholt, "The Preparation of Sodium Borohydride by the High Temperature Reaction of Sodium Hydride and Borate Esters", *J. Amer. Chem. Soc.*, 74, 205 (1953)

## Acknowledgements

- 1) NSF EEC-0453432 Grant, Novel Materials and Processing in Chemical and Biomedical Engineering (Director C.G. Takoudis)
- 2) NSF CTS-0533499 & 0434201 GOALI: Atomic-scale Investigation of High Dielectric Constant Thin Films Using In Situ and Other Techniques, (Director C.G. Takoudis)

## Appendix I

**B<sub>10</sub>H<sub>14</sub>-2&7 B10 -  
66 modes**

	Freq	IR Intensity
1	230.3955	0.0001
2	337.0008	1.194
3	369.1952	4.4953
4	436.9413	0.5461
5	439.2598	1.275
6	518.6885	0
7	547.6546	0.0141
8	559.2391	0.013
9	583.3324	0
10	600.0652	0.0728
11	623.27	6.2514
12	637.0255	0.0061
13	639.1583	0.0056
14	658.3435	1.0367
15	668.0772	0.0002
16	696.2919	0.0727
17	706.4788	2.9354
18	712.3738	5.765
19	728.0141	0.0003
20	730.0527	12.5742
21	733.4177	17.0068
22	751.8021	0.3956
23	759.0878	4.9275
24	770.1411	0
25	776.5739	0.2625
26	776.9061	0.0454
27	782.2706	23.1581
28	838.3885	12.3813
29	838.7088	2.7759
30	872.269	0
31	881.4998	1.7087
32	887.5312	16.6778
33	920.7438	7.7364
34	925.0795	0.0393
35	929.774	0.0002
36	945.8064	0.0003
37	947.453	14.2008
38	956.6981	4.3094
39	968.4461	11.202

40	971.3235	0
41	978.2587	4.2603
42	996.6755	5.1724
43	1034.554	13.1173
44	1039.74	21.7432
45	1054.432	0.0004
46	1084.295	1.2532
47	1096.854	0.5434
48	1151.556	0.919
49	1567.063	0.0016
50	1594.875	32.0557
51	1617.247	163.9089
52	1686.905	26.541
53	1957.353	0.0006
54	1975.068	0.0215
55	2003.949	23.0651
56	2022.637	27.8874
57	2657.518	22.7135
58	2661.782	43.0945
59	2682.712	2.7124
60	2685.244	0.0022
61	2686.171	15.6715
62	2689.222	22.9954
63	2690.241	207.8851
64	2691.69	91.0106
65	2698.947	189.8179
66	2703.616	0.2838

**B<sub>10</sub>H<sub>14</sub>-4&9 B10 -**  
**66 modes**

Freq	IR Intensity
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1	233.1785	0.0006
2	337.3495	1.1821
3	373.9703	4.6164
4	442.568	1.2251
5	443.2604	0.6112
6	514.4892	0.0021
7	545.2479	0.0044
8	557.4147	0.0092
9	585.7807	0.0051
10	601.5405	0.0815
11	619.3229	6.7624
12	637.603	0.0139
13	641.0064	0.1422
14	649.6411	1.3236
15	666.8393	0.0006
16	697.0883	0.4674
17	703.9437	2.8539
18	713.9212	6.2956
19	731.8371	2.9889
20	736.2351	12.9052
21	738.2245	14.6953
22	752.7679	3.5119
23	754.821	0.0702
24	770.7598	0.0069
25	775.2205	0.0727
26	777.7103	0.7593
27	786.0166	22.4532
28	830.2083	14.2124
29	837.9621	3.5313
30	870.2939	1.3561
31	877.0769	1.5341
32	890.3029	12.3308
33	918.9635	0.0131
34	921.7169	7.1085
35	927.6188	0.0038
36	946.2612	4.1591

37	947.7685	0.2573
38	948.8062	9.9329
39	960.7322	6.6422
40	967.4627	0.0117
41	977.5984	2.1898
42	986.3797	10.8768
43	1037.439	13.8866
44	1039.989	24.8347
45	1055.7	0.2955
46	1081.927	0.9289
47	1097.648	0.4277
48	1152.504	1.0106
49	1567.674	0.0073
50	1595.192	32.0374
51	1617.893	163.8553
52	1687.203	26.6138
53	1959.081	0.0236
54	1976.48	0.0297
55	2005.949	23.4268
56	2024.359	28.357
57	2657.573	24.7237
58	2661.269	30.5981
59	2677.141	40.8904
60	2679.063	84.4003
61	2684.501	16.0378
62	2689.704	84.5361
63	2693.789	16.1727
64	2696.562	119.3658
65	2700.363	141.7553
66	2706.563	38.1465

**B<sub>10</sub>H<sub>14</sub>-5&6 B10 -****66 modes**

Freq	IR Intensity
------	--------------

1	230.2723	0.0001
2	337.7711	1.18
3	371.4972	4.4963
4	436.3623	0.5344
5	438.4479	1.259
6	511.1187	0
7	545.1975	0.0118
8	558.4601	0.0055
9	591.601	0
10	608.2402	1.2499
11	627.3348	6.123
12	631.9761	0.015
13	638.5917	0.0599
14	652.7411	1.8524
15	663.0873	0.0007
16	691.9617	0.0141
17	703.0536	4.574
18	725.1756	6.0161
19	728.0609	0.0025
20	733.6188	18.7675
21	736.1554	9.9586
22	753.4883	1.6214
23	759.2164	2.24
24	774.4584	3.6032
25	775.9943	0.1756
26	777.0859	0
27	787.339	19.3795
28	834.3446	12.9271
29	835.7667	3.8834
30	870.9494	1.8795
31	873.0407	0.0002
32	883.6167	13.4358
33	924.6632	9.7916
34	925.6171	0.0468
35	929.3281	0.0001

36	944.8217	11.2423
37	945.0238	0.0828
38	946.9752	2.4497
39	959.5151	7.7402
40	974.784	0
41	986.1108	2.5028
42	997.2901	8.8539
43	1044.133	12.6347
44	1044.382	24.1979
45	1055.141	0.0005
46	1081.565	1.9331
47	1096.901	0.5056
48	1150.937	0.938
49	1567.138	0.0015
50	1594.892	32.062
51	1617.399	163.7335
52	1686.884	26.488
53	1957.374	0.0006
54	1975.082	0.0208
55	2003.93	22.978
56	2022.577	27.9852
57	2668.633	14.1876
58	2670.634	6.8056
59	2676.883	32.9429
60	2679.673	85.5222
61	2683.991	29.3272
62	2685.243	0.0006
63	2690.303	54.0286
64	2690.557	216.5383
65	2697.932	152.3338
66	2702.445	3.7512

**B<sub>10</sub>H<sub>14</sub>-1&10 B10 -**  
**66 modes**

	Freq	IR Intensity
1	231.2532	0.0001
2	346.175	1.29
3	369.1618	4.5972
4	437.1629	0.4882
5	443.9201	1.3142
6	512.2	0
7	546.1631	0.0013
8	557.0673	0
9	586.6691	0
10	600.1192	0.0383
11	626.065	6.2635
12	633.9544	0.0697
13	635.4174	0.03
14	651.5961	1.4855
15	663.3394	0.0003
16	695.4861	0.1488
17	702.329	2.9108
18	711.8102	6.1134
19	729.7855	11.9497
20	730.3506	0.0011
21	739.3431	17.9732
22	752.3113	2.7161
23	762.2518	0.9979
24	772.2494	1.1466
25	772.5419	0
26	777.4969	0.2244
27	787.8144	21.5988
28	836.4627	4.0758
29	838.8273	14.4066
30	875.6133	0.0001
31	880.1202	1.3674
32	883.727	13.6604
33	922.2827	0.1992
34	922.7052	7.5436

35	926.0964	0.0001
36	945.6972	10.4273
37	946.4444	3.3739
38	947.7761	0.0005
39	959.7373	7.3412
40	967.2764	0
41	977.6913	4.3101
42	990.025	8.7568
43	1037.698	15.5731
44	1037.808	24.1239
45	1055.906	0.0004
46	1083.987	1.0793
47	1098.414	1.0155
48	1151.641	0.8476
49	1568.345	0.0015
50	1596.278	32.0705
51	1618.438	165.9285
52	1688.223	26.5047
53	1959.562	0.0006
54	1977.675	0.0995
55	2006.404	23.0457
56	2025.187	27.8191
57	2657.517	22.7258
58	2661.193	31.492
59	2676.902	34.0169
60	2678.576	73.8554
61	2684.921	57.1841
62	2685.246	0.0035
63	2690.243	207.682
64	2692.243	22.3551
65	2708.896	125.6003
66	2711.098	22.3027

**B<sub>10</sub>H<sub>14</sub>-1, 10, 2, &7**  
**B10 - 66 modes**

Freq	IR Intensity
------	--------------

1	231.3648	0.0001
2	346.5862	1.2981
3	369.6105	4.5644
4	438.61	0.5126
5	444.6946	1.3311
6	519.7493	0
7	552.2357	0
8	562.9495	0.0203
9	587.7817	0
10	600.1201	0.0409
11	630.8718	5.7729
12	639.5818	0.0077
13	639.9473	0.0032
14	660.6973	1.1417
15	668.7984	0.0005
16	701.2897	0.0908
17	708.695	3.1044
18	714.1454	5.8513
19	730.1439	13.1587
20	730.4182	0.005
21	739.7405	17.4428
22	754.5896	2.3257
23	765.7521	2.9399
24	775.3189	0
25	777.3205	0.653
26	780.2418	0.3689
27	787.8255	21.565
28	840.1959	2.9931
29	846.9718	11.6212
30	877.2175	0
31	888.1536	17.3869
32	891.2143	1.6138
33	922.7065	7.6755

34	929.9592	0.0001
35	930.4248	0.0002
36	948.7926	13.6027
37	948.9413	0.0412
38	957.2703	4.6287
39	968.6526	11.2119
40	971.3257	0.0001
41	979.7171	4.7908
42	1002.209	5.0137
43	1038.553	14.6527
44	1040.158	21.1409
45	1055.909	0.0004
46	1088.4	1.2868
47	1098.444	1.0051
48	1152.438	0.8572
49	1568.345	0.0015
50	1596.307	32.1587
51	1618.487	166.1455
52	1688.256	26.5385
53	1959.569	0.0006
54	1977.676	0.0985
55	2006.484	23.0612
56	2025.248	27.7467
57	2657.518	22.7264
58	2661.784	43.4067
59	2683.037	4.5767
60	2685.247	0.0024
61	2686.41	27.9879
62	2690.246	207.7278
63	2690.567	72.8962
64	2695.363	64.8405
65	2709.199	140.2296
66	2711.637	14.3854

**B<sub>10</sub>H<sub>14</sub>-1, 10, 3, &8**  
**B10 - 66 modes**

Freq	IR Intensity
------	--------------

1	234.1921	0.0006
2	346.9041	1.2851
3	374.4051	4.6858
4	444.9167	0.5832
5	448.0146	1.2745
6	515.8802	0.0021
7	549.8231	0.0032
8	560.7692	0.0056
9	589.8071	0.0057
10	601.5791	0.0511
11	626.3715	6.2945
12	639.3279	0.0677
13	641.5943	0.1437
14	652.2498	1.412
15	667.5586	0.0006
16	703.1509	0.0079
17	706.3477	3.0618
18	715.1698	6.4577
19	734.3337	0.8621
20	736.3805	13.4094
21	743.168	17.71
22	753.8529	2.6833
23	763.4994	0.7497
24	776.3677	0
25	777.9882	2.0547
26	779.12	0.0441
27	792.7034	20.0378
28	838.8673	3.7989
29	839.2942	14.6625
30	881.5323	2.3513
31	881.5781	2.1465
32	891.4072	10.6255

33	923.4732	6.9532
34	923.8548	0.2077
35	927.9205	0.0019
36	946.7496	4.2436
37	949.3871	9.5166
38	950.883	0.329
39	961.0158	6.2591
40	967.4895	0.0129
41	979.1251	4.2665
42	992.059	9.3369
43	1040.621	24.1385
44	1041.661	15.3866
45	1057.151	0.2717
46	1085.738	1.0746
47	1099.124	0.8438
48	1153.336	0.9437
49	1568.953	0.0067
50	1596.622	32.1378
51	1619.132	166.0987
52	1688.554	26.6125
53	1961.296	0.0236
54	1979.085	0.0915
55	2008.481	23.4199
56	2026.966	28.2112
57	2657.573	24.7381
58	2661.272	30.9126
59	2677.183	43.1821
60	2679.087	81.5631
61	2685.066	31.244
62	2691.301	119.3195
63	2696.103	7.4635
64	2701.059	101.4749
65	2709.368	135.124
66	2712.383	24.1823

**B<sub>10</sub>H<sub>14</sub>-1, 10, 4, & 9****B10 - 66 modes**

Freq	IR Intensity
------	--------------

1	234.1918	0.0006
2	346.9041	1.2851
3	374.4076	4.6859
4	444.9138	0.5831
5	448.0161	1.2744
6	515.8801	0.002
7	549.8226	0.0032
8	560.7683	0.0056
9	589.8076	0.0057
10	601.5794	0.0511
11	626.3713	6.294
12	639.3284	0.0681
13	641.5954	0.1441
14	652.2499	1.4119
15	667.555	0.0006
16	703.1481	0.0078
17	706.3497	3.0608
18	715.1681	6.4594
19	734.3384	0.8631
20	736.3814	13.408
21	743.1675	17.7106
22	753.8529	2.6829
23	763.4992	0.7494
24	776.3706	0.0001
25	777.988	2.055
26	779.1189	0.044
27	792.7036	20.0376
28	838.8668	3.8006
29	839.295	14.6609
30	881.5202	2.5347
31	881.5783	1.9721

32	891.4171	10.6164
33	923.4731	6.9555
34	923.8534	0.2056
35	927.9207	0.0019
36	946.7495	4.2438
37	949.387	9.5157
38	950.8826	0.3303
39	961.0165	6.2584
40	967.4892	0.0127
41	979.1249	4.2665
42	992.0584	9.3367
43	1040.623	24.1407
44	1041.662	15.3865
45	1057.151	0.2691
46	1085.737	1.075
47	1099.124	0.8438
48	1153.335	0.9437
49	1568.952	0.0072
50	1596.622	32.1377
51	1619.132	166.0974
52	1688.554	26.6133
53	1961.297	0.023
54	1979.085	0.0917
55	2008.48	23.4204
56	2026.966	28.2112
57	2657.573	24.7378
58	2661.272	30.9132
59	2677.184	43.1915
60	2679.088	81.5651
61	2685.071	31.2315
62	2691.306	119.3179
63	2696.099	7.4703
64	2701.055	101.4835
65	2709.367	135.1202
66	2712.382	24.1731

**B<sub>10</sub>H<sub>14</sub>-1, 10, 5, & 6**  
**B10 - 66 modes**

Freq	IR Intensity
------	--------------

1	231.2532	0.0001
2	347.3831	1.2805
3	371.907	4.5665
4	438.0569	0.5083
5	443.9205	1.3135
6	512.3583	0
7	549.4086	0.0001
8	561.4707	0.0032
9	596.0891	0
10	609.2201	0.6332
11	633.961	2.1073
12	633.9789	4.2897
13	639.622	0.0663
14	655.0173	1.912
15	663.7806	0.0012
16	696.5134	0.1961
17	705.7999	4.9556
18	726.0368	6.182
19	730.6147	0.0005
20	736.1678	9.7411
21	741.274	19.1753
22	758.4723	3.6925
23	765.017	0.0033
24	774.5097	4.2366
25	780.3616	0.0016
26	782.011	0
27	793.2017	18.0127
28	836.5554	4.1998
29	842.5181	13.2378
30	877.9192	0.0001

31	882.5608	1.8442
32	883.8869	13.5447
33	927.1521	9.7819
34	929.8374	0.0001
35	930.6943	0.0156
36	945.7231	10.4782
37	947.3246	2.9358
38	948.2616	0.0006
39	959.7606	7.4433
40	974.8366	0
41	991.856	1.7072
42	997.9129	10.2284
43	1044.661	23.7392
44	1047.835	13.9324
45	1056.589	0.0005
46	1085.433	2.0011
47	1098.46	0.9865
48	1151.818	0.874
49	1568.421	0.0015
50	1596.322	32.1607
51	1618.64	165.9699
52	1688.234	26.4868
53	1959.59	0.0006
54	1977.689	0.0972
55	2006.471	22.9727
56	2025.192	27.8418
57	2668.633	14.2032
58	2670.658	7.4614
59	2676.903	33.9756
60	2679.676	86.4326
61	2684.926	57.1708
62	2685.247	0.0037
63	2690.562	216.3945
64	2693.424	37.5389
65	2708.899	125.6118
66	2711.232	19.2292

**B<sub>10</sub>H<sub>14</sub>- all B11 - 66**  
**modes**

Freq	IR Intensity
------	--------------

1	230.2723	0.0001
2	336.6613	1.1882
3	368.7628	4.5289
4	435.5291	0.5181
5	438.4478	1.2591
6	511.0127	0
7	541.8574	0.0065
8	553.8204	0.0007
9	582.4659	0
10	600.0648	0.0759
11	618.8492	6.6903
12	631.9614	0.0154
13	634.6814	0.0343
14	649.1027	1.385
15	662.4992	0.0001
16	690.7863	0.0256
17	699.7402	2.7267
18	710.4609	6.0286
19	727.9917	0.0003
20	729.7376	11.596
21	732.3939	17.801
22	751.6394	1.3292
23	752.9207	2.4634
24	767.546	0
25	771.4817	0.0651
26	773.7828	0.0008
27	782.1766	23.6868
28	829.6105	14.1575
29	835.731	3.8143

30	868.702	1.4283
31	870.4393	0.0002
32	883.3772	13.5921
33	917.4788	0.0107
34	920.7448	7.7324
35	925.6866	0.0001
36	944.3893	0.0252
37	944.7094	11.1599
38	946.0141	3.0021
39	959.5008	7.6383
40	967.2694	0
41	976.0061	2.273
42	984.8566	10.261
43	1033.56	14.0609
44	1037.207	24.8177
45	1054.429	0.0004
46	1080.142	0.9565
47	1096.829	0.5505
48	1150.754	0.911
49	1567.063	0.0015
50	1594.847	31.97
51	1617.199	163.6955
52	1686.873	26.506
53	1957.345	0.0006
54	1975.066	0.0219
55	2003.864	23.0512
56	2022.572	27.9628
57	2657.517	22.7129
58	2661.189	31.1307
59	2676.882	32.983
60	2678.568	75.4788
61	2683.988	29.3509
62	2685.242	0.0005
63	2689.459	34.8367
64	2690.237	207.8269
65	2697.928	152.3123
66	2701.96	7.9993

**B<sub>10</sub>H<sub>14</sub>-B10 - 66**  
**modes**

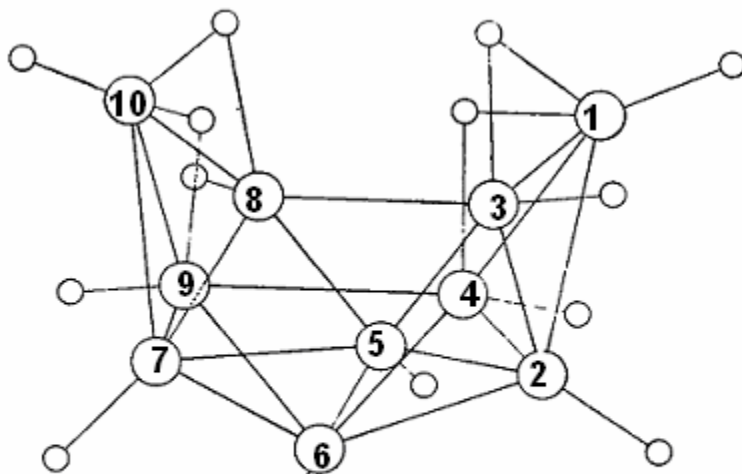
Freq	IR Intensity
------	--------------

1	237.3549	0.0001
2	349.3291	1.2628
3	384.1812	4.8235
4	453.1268	1.2563
5	454.2572	0.6288
6	527.9242	0
7	563.4091	0
8	576.7198	0.0029
9	604.6655	0
10	612.5678	0.6782
11	640.2233	6.1395
12	651.0529	0.0057
13	656.5214	0.1863
14	666.8181	1.2143
15	677.5832	0.0003
16	716.8313	0.7758
17	719.0989	6.4475
18	736.0587	7.1122
19	739.1416	0.0014
20	747.0078	12.662
21	749.5198	18.6003
22	764.2756	4.4289
23	769.756	0.1145
24	785.3703	0.1101
25	788.5665	5.2399
26	791.0315	0

27	803.7907	15.0846
28	844.3964	2.7427
29	851.4591	11.032
30	894.9535	0.0011
31	896.6573	1.6924
32	897.1338	17.127
33	929.0148	8.3541
34	939.2057	0.0001
35	943.7989	0.0466
36	956.8214	13.7914
37	957.2564	0.0234
38	959.2589	4.2188
39	970.1658	9.4665
40	977.6093	0
41	1000.929	1.3925
42	1008.865	8
43	1051.065	21.896
44	1056.067	13.1187
45	1058.962	0.0007
46	1094.126	2.3417
47	1100.023	0.5886
48	1155.985	1.0744
49	1569.645	0.0016
50	1597.028	32.3995
51	1620.082	166.5482
52	1688.922	26.7224
53	1963.22	0.0006
54	1980.619	0.0475
55	2010.55	23.7791
56	2028.702	28.5894
57	2668.894	21.9604
58	2672.837	30.7701
59	2688.775	30.29
60	2690.45	75.2196
61	2695.703	28.1957
62	2696.948	0.0005
63	2701.295	38.4201
64	2702.036	212.46
65	2710.149	159.5785
66	2714.375	6.6564

## Appendix II

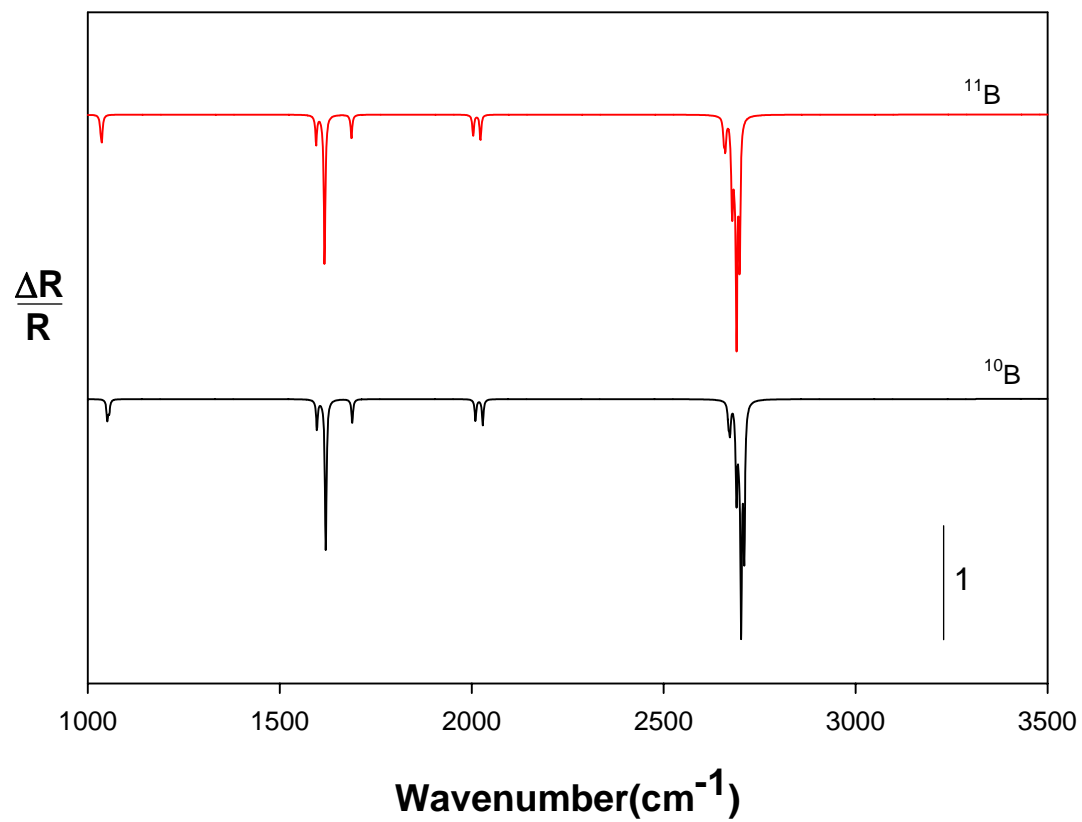
### Molecular Structure of Decaborane

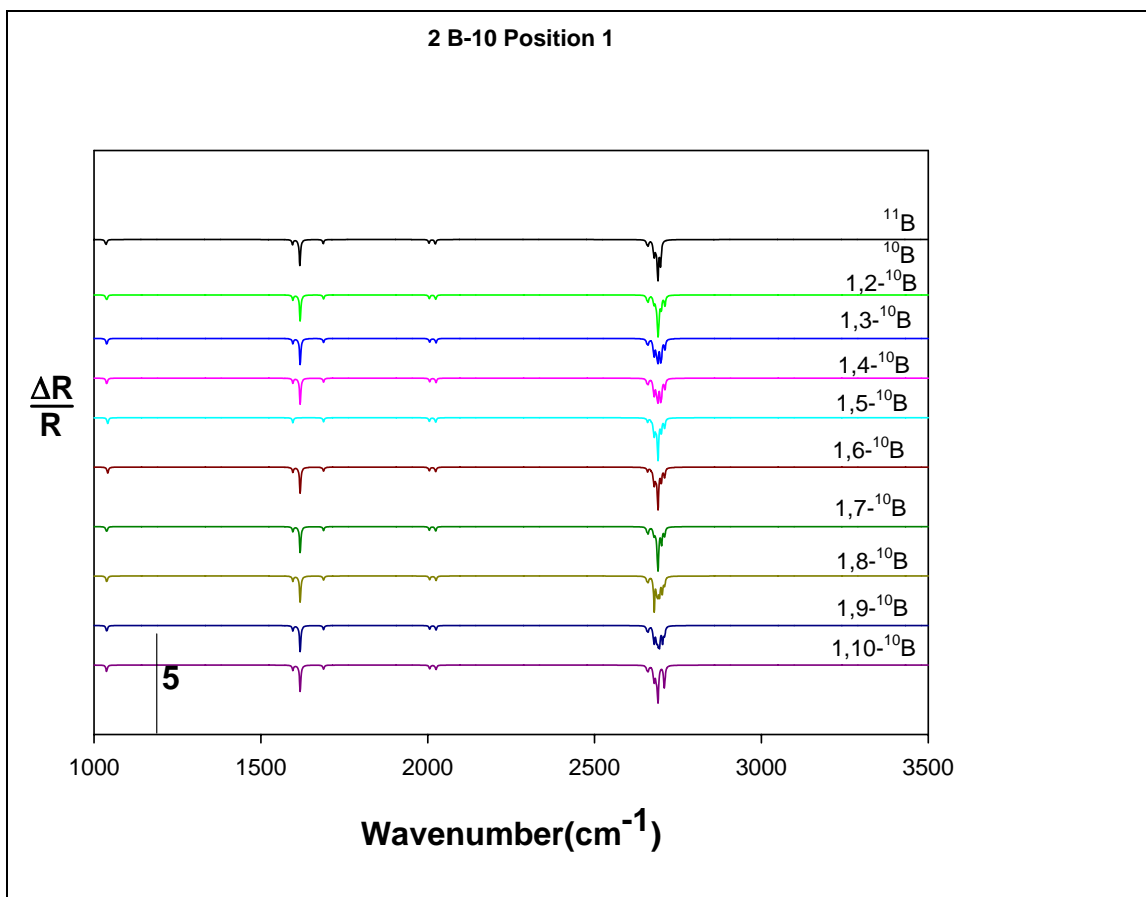


## Appendix III

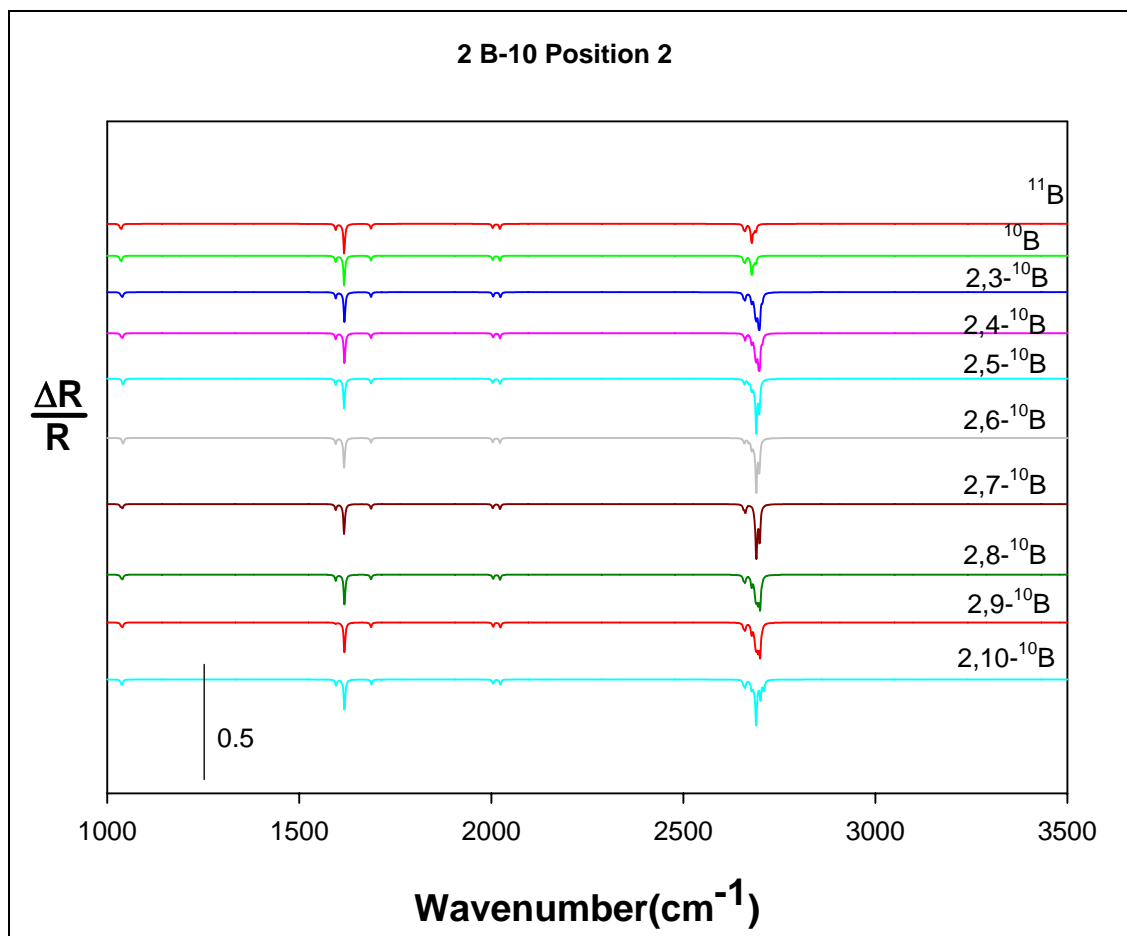
### Probability of Isotope, B-11 and B-10 Combinations

B-11	B-10	probability
10	0	0.1087
9	1	0.2701
8	2	0.30198
7	3	0.200064
6	4	0.086981
5	5	0.025932
4	6	0.005369
3	7	0.000762
2	8	0.000071
1	9	0.000004
0	10	9.74E-08

**Appendix IV****Calculated Infrared Spectra** $^{11}\text{B}$  &  $^{10}\text{B}$ 

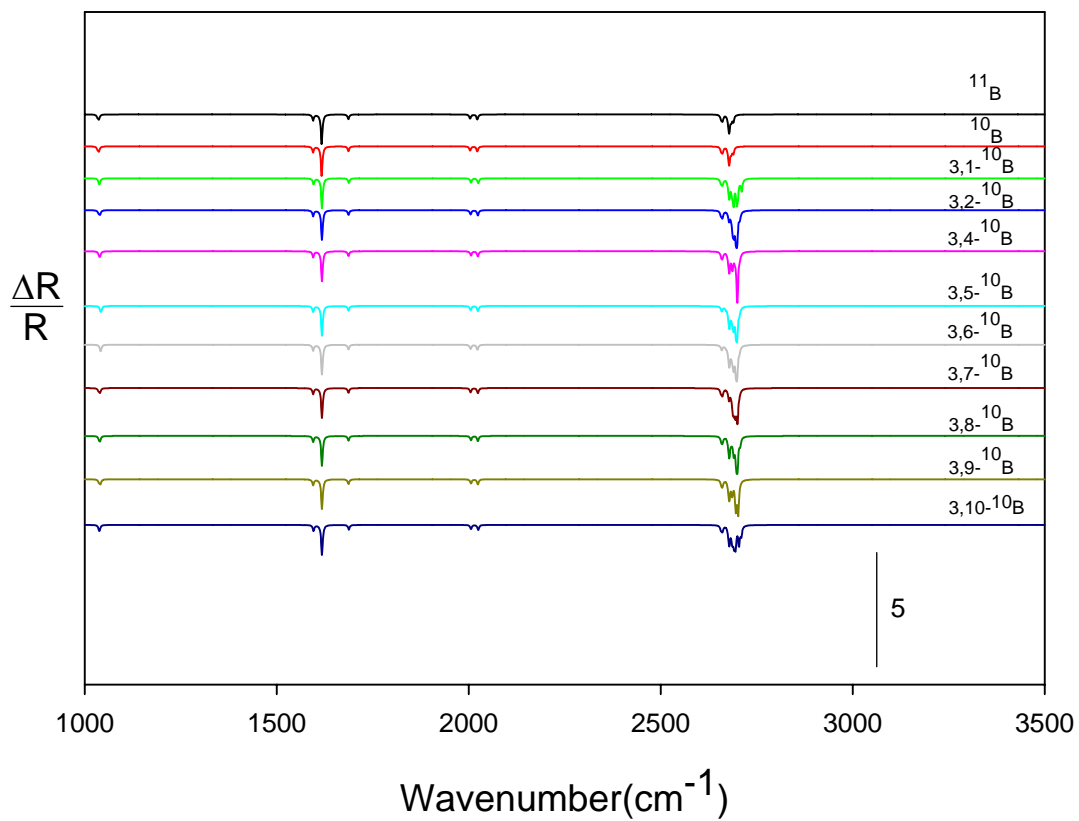


\*Each label represent the position of the B-10 atom within the decaborane molecule.  
(Example:  $1,2-^{10}\text{B} = ^{10}\text{B}$  atoms at positions one and two within the molecule)



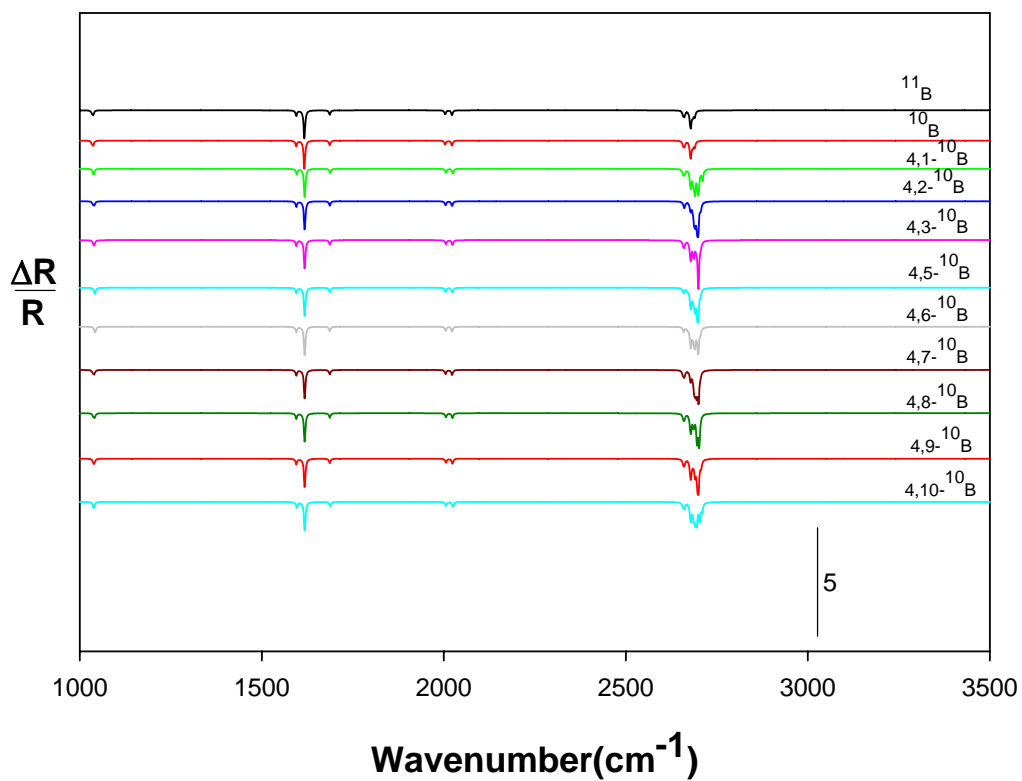
\*Each label represents the position of the B-10 atom within the decaborane molecule.  
(Example:  $2,3-^{10}\text{B}$  =  $^{10}\text{B}$  atoms at positions two and three within the molecule)

## 2 B-10 Position 3

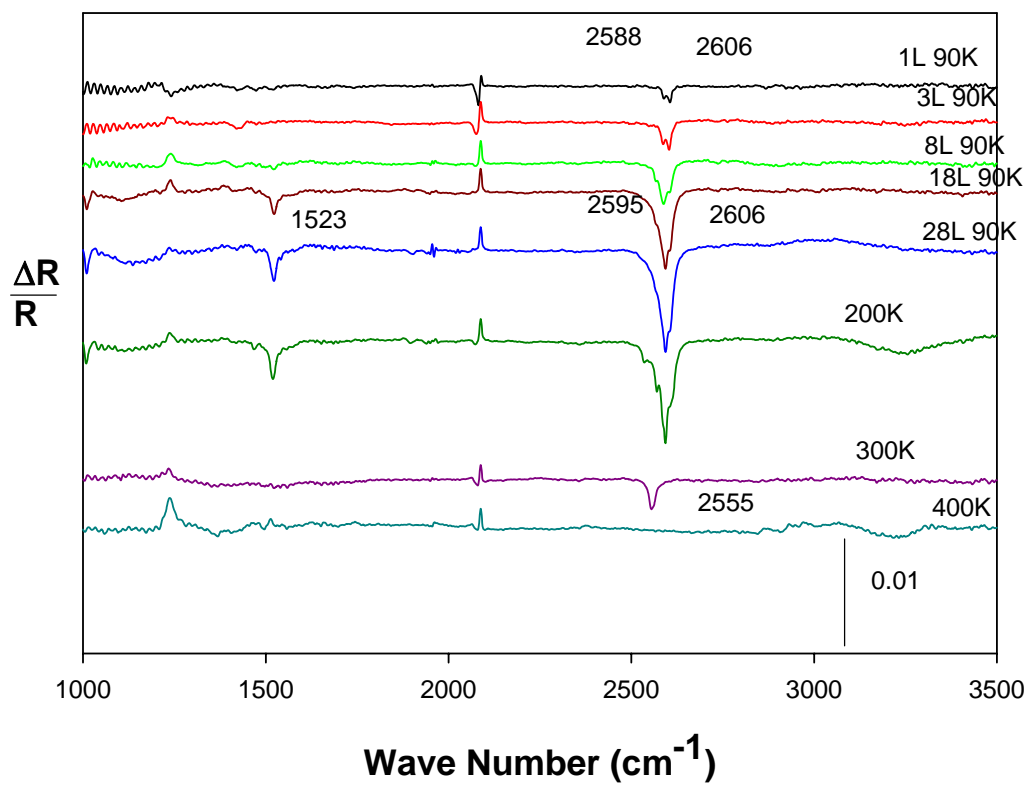


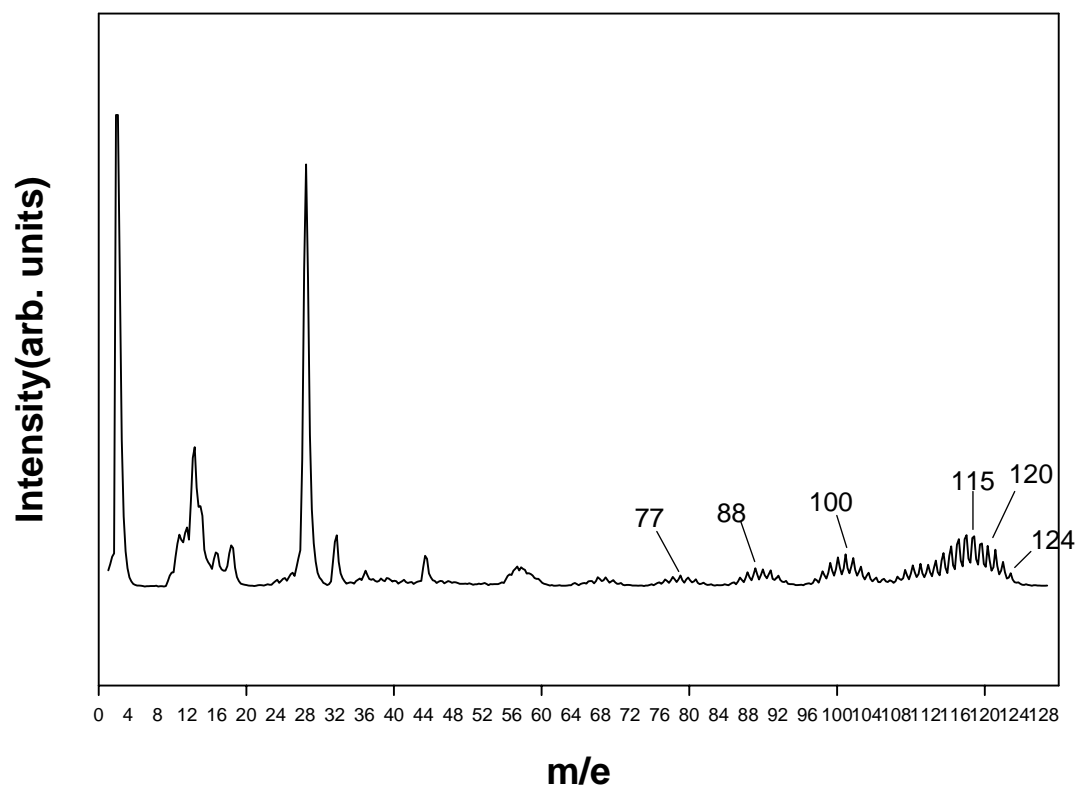
\*Each label represents the position of the B-10 atom within the decaborane molecule.  
(Example:  $3,1-^{10}\text{B} = ^{10}\text{B}$  atoms at positions three and one within the molecule)

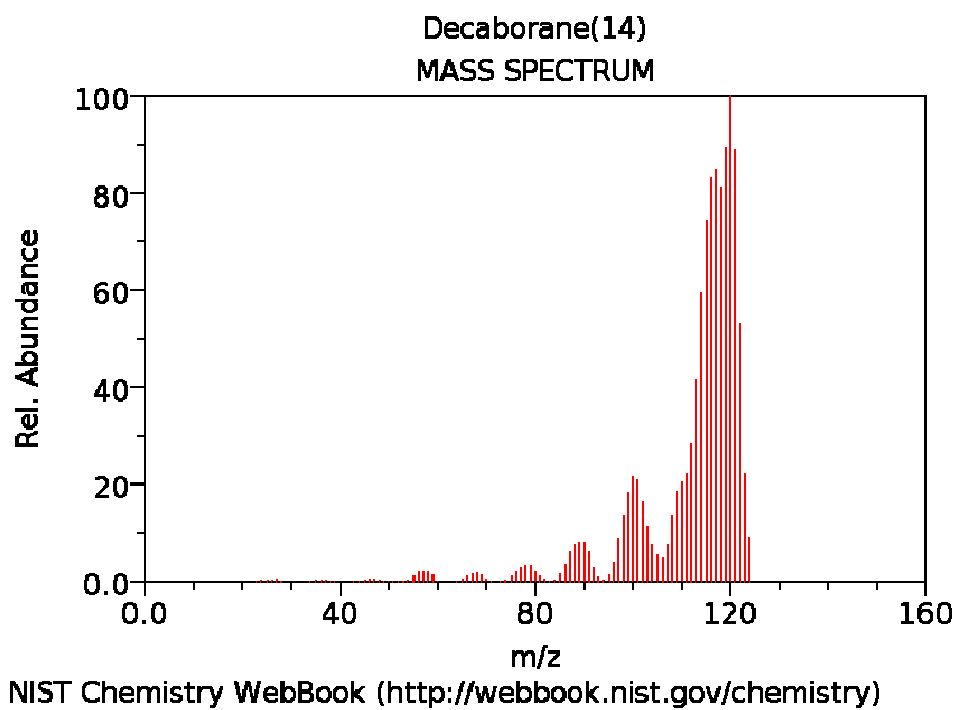
## 2-B10 Position 4



\*Each label represents the position of the B-10 atom within the decaborane molecule.  
(Example: 4,1-<sup>10</sup>B = <sup>10</sup>B atoms at positions four and one within the molecule)

**Appendix V****Experimental Infrared Spectrum****Decaborane**

**Appendix VI****Experimental and Reference Mass Spectra****B<sub>10</sub>H<sub>14</sub>-Mass Spectrum****Experimental Mass Spectrum**



**Reference Mass Spectrum**