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NUCLEAR MAGNETIC RESONANCE STUDIES OF ICOSAHEDRAL CARBORANES AND SELECTED ICOSAHEDRAL CARBORANE DERIVATIVES

by

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FOREWORD

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I also wish to thank the members of my research group for their help and especially for their friendship.

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1.0 BACKGROUND

1.1 General

Many of the members of the boron hydride family were first prepared and characterized by Alfred Stock[1] in the early 1900's. Development of boron hydride chemistry continued slowly during the 1930's and 1940's. The structures of many of the hydrides were not determined until the late 1940's. Schlesinger and Burg,[2] in 1942, and Schlesinger and Brown,[3] in 1953, reviewed much of this early work, which was concerned primarily with the lower hydrides.

The two decades following World War II saw a great expansion of knowledge about boron hydride chemistry. The expansion was fueled by Government money searching for exotic propellants and for new drugs for medicine. The success of these researches resulted primarily from two advances in widely differing areas.

The application of nuclear magnetic resonance methods (NMR) to the boron hydrides provides a method for obtaining detailed information on molecular symmetry, positions of substitution, and number of hydrogens attached to each boron in relatively short times. Previously, structural information came primarily from more laborious

---

[1] A. Stock, Hydrides of Boron and Silicon, Cornell University Press, Ithaca, New York, 1933.

[2] H. I. Schlesinger and A. B. Burg, Chem. Rev. 31, 1 (1942).

[3] H. I. Schlesinger, H. C. Brown, et al, J. Am. Chem. Soc. 75, 186 (1953).

methods such as single-crystal x-ray diffraction, electron diffraction and spectral studies. ^{11}B NMR can provide structural information on liquids, gases, and samples in solution. ^{1}H NMR is also often useful for structural determinations, particularly with the lighter hydrides.

In a series of papers published during the period 1959-1962, Lipscomb[1] devised a theory of bonding which is both systematic and comprehensive. The theory utilizes 3-center bonds and the equations of balance, and a set of rules based on common structural features of known hydrides. The success of the theory is shown by the fact that previously unknown compounds were predicted to exist, and subsequently several have been prepared experimentally.

Much of the work of the past two decades has been based either upon decaborane(14) itself, or upon derivatives of decaborane(14). The present research is based upon derivatives of decaborane(14), the icosahedral carboranes. The structures and electron distributions of decaborane(14) and the icosahedral carboranes are similar. It appears instructive to discuss briefly in outline the chemistry of decaborane(14) before describing the chemistry of the carboranes. We shall also discuss current theories of the electron distribution in the carboranes, and nuclear magnetic resonance theory in some detail before reporting results to date.

---

[1] W. N. Lipscomb, Boron Hydrides, W. A. Benjamin, Inc., New York, 1963.

1.2 Specific

1.21 Decaborane(14)

Decaborane(14) is a white, crystalline solid with a characteristic offensive odor. The structure and numbering convention[1] is given in Figure 1A. There are four symmetrically related sets of boron atoms: (6,9), (5,7,8,10), (2,4), and (1,3). Theory[2] predicts that the order of electron density is: (2,4) > (1,3) > (5,7,8,10) > (6,9). With the exception of the bridge protons, decaborane(14) chemistry is characterized by substitution reactions, formally similar to the substitution reactions of aromatic chemistry.

The chemistry of decaborane(14) may be divided into three classifications. The bridge hydrogens have a partially positive charge, and are acidic. One classification, therefore, is the acid-base chemistry of decaborane(14). Second, the (2,4) and (1,3) borons are electron rich, relative to the rest of the molecule. These are the sites of expected electrophilic attack. Our second classification, therefore, is electrophilic reactions of decaborane(14). The (6,9) boron atoms are the most positive borons. The third classification is nucleophilic reactions of decaborane(14).

1.211 Decaborane(14) as a Brønstead Acid. Decaborane(14) is an acid and can be titrated to an end-point in water, water-ethanol,

---

[1]The Nomenclature of Boron Compounds, Inorg. Chem. 7, 1945 (1968).

[2]W. N. Lipscomb, Boron Hydrides, W. A. Benjamin, Inc., New York, 1963.

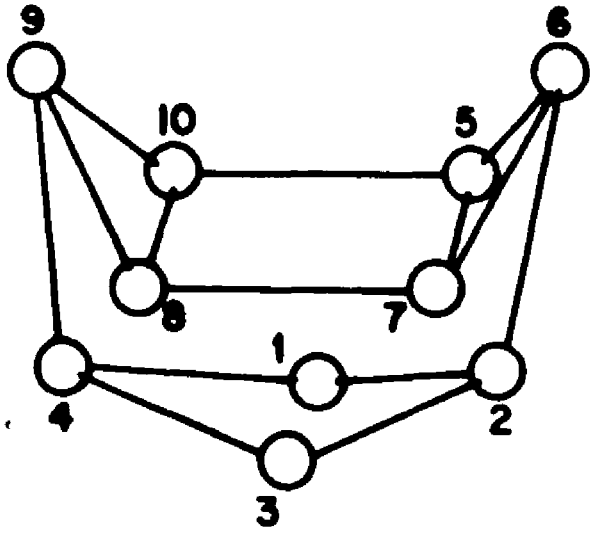

Figure 1(a). Structure and Numbering System of Decaborane(14).

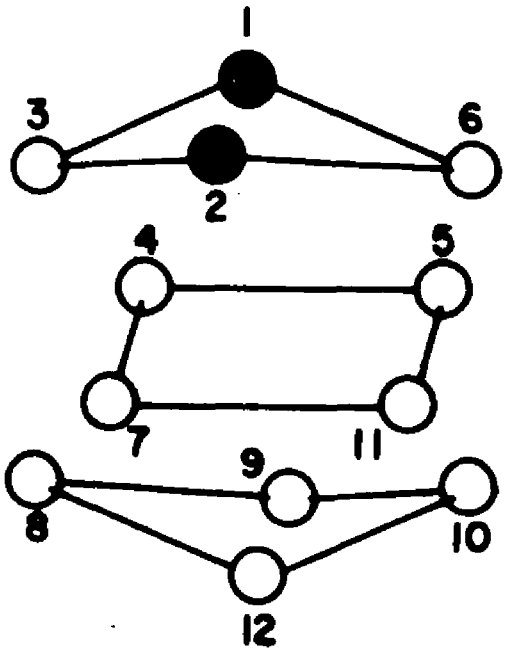

Figure 1(b). Structure and Numbering System of o-Carborane.

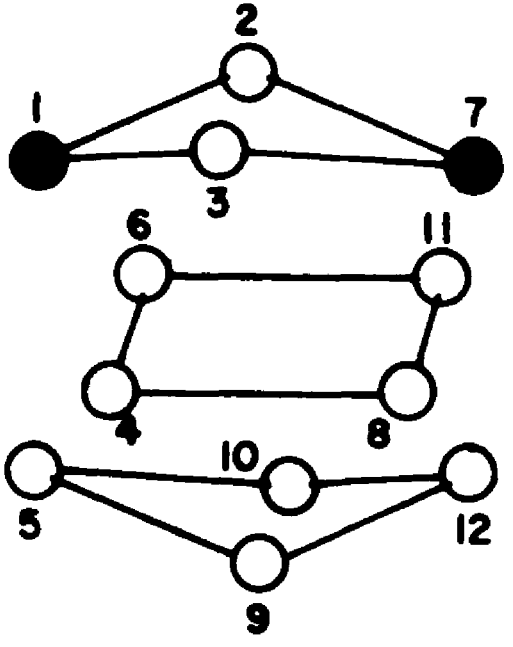

Figure 1(c). Structure and Numbering System of m-Carborane.

and water-dioxane using sodium hydroxide.[1] The original decaborane(14) can be regenerated using hydrogen chloride. It has been shown by deuterium isotope studies that a bridge proton is lost.[2] The structure of the salt has not been unequivocally determined, probably because the solvent is intimately involved in the reaction.[3] With excess sodium hydride, or with potassium hydride in tetrahydrofuran(THF), the dibasic salt was reported.[4] The $B_{10}H_{12}^{2-}$ ion was also reported as a constituent of the product from the reaction of transition metal halides with sodium decaboronate(13).[5]

1.212 Electrophilic Reactions of Decaborane(14). The reaction of decaborane(14) with halogens in the presence of an electrophilic catalyst such as Al_2Cl_6 results in the formation primarily of 2-halo-substituted decaborane(14), with a major impurity being 1-halo-substituted decaborane(14).[6] The conditions of the reaction are similar to the well-known Friedel-Crafts reactions of aromatic chemistry.

The Friedel-Crafts alkylation of aromatic molecules is matched by the "Friedel-Crafts" alkylation of decaborane(14).[7-9] The alkylation

---

[1] G. A. Guter and G. W. Schaeffer, J. Am. Chem. Soc. 78, 3546 (1956).

[2] W. N. Lipscomb, J. Inorg. Nucl. Chem. 11, 1 (1959).

[3] R. L. Hughes, I. C. Smith, and E. W. Lawless, Production of Boranes and Related Research, Academic Press, New York and London, 1967.

[4] J. C. Carter and P. H. Wilks, J. Am. Chem. Soc. 88, 3441 (1966).

[5] F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, Inorg. Chem. 7, 2072 (1968).

[6] M. Hillman, J. Inorg. Nucl. Chem. 12, 383 (1960).

[7] N. J. Blay, J. W. Williams, R. L. Williams, J. Chem. Soc. 424 (1960).

[8] N. J. Blay, I. Dunstan, R. L. Williams, J. Chem. Soc. 430 (1960).

[9] R. L. Williams, I. Dunstan, N. J. Blay, J. Chem. Soc. 5006 (1960).

of decaborane(14) is difficult to control; several alkylated derivatives result, with the 1,2,3,4, and even 5 positions being attacked. Pure products are difficult to obtain in any quantity.

Deuterium exchange with decaborane(14) under electrophilic conditions occurs at the (1,2,3,4) positions.[1] A slight difference in rate of exchange was detected for these four positions.[2] Additional exchange with the (5,7,8,10) borons occurs under electrophilic catalysis, but only with very long reaction times[1] or with high pressures of DCl.[3] The second method has been used to prepare 1,2,3,4,5,7,8,10-d_8-$B_{10}H_{14}$.

In dioxane, DCl exchanges with the bridge hydrogens, with all four hydrogens exchanging.[1] With D_2O in dioxane, the (6,9) boron atoms also exchange hydrogen for deuterium, along with a competing hydrolysis reaction.[4] Exchange of the (6,9) hydrogens is followed by a slower equilibrium reaction, where the (5,7,8,10) hydrogens exchange for the deuterium of the (6,9) borons. Completely or selectively deuterated decaborane(14) can thus be prepared by a judicious choice of reaction conditions.

1.213 Nucleophilic Reactions of Decaborane(14). Electron-rich substances react with decaborane(14) displacing hydrogen, and forming decaborane(12) diligand compounds. The first decaborane(12) diligand

---

[1] J. A. Dupont and M. F. Hawthorne, J. Am. Chem. Soc. 84, 1804 (1962).

[2] G. M. Bodner and L. G. Sneddon, Inorg. Chem. 9, 1421 (1970).

[3] L. S. Kogut, Ph.D. Thesis, University of Pittsburgh, Pittsburgh, Pennsylvania, 1970.

[4] I. Shapiro, M. Lustig, and R. E. Williams, J. Am. Chem. Soc. 81, 838 (1959).

compound formed was $B_{10}H_{12}\cdot 2CH_3CN$.[1] Single-crystal x-ray determinations[2] have shown that the ligands are attached to the (6,9) positions of decaborane, and that there has been little other structural change in the boron framework. Other ligands which form diligand compounds are triphenyl phosphine, pyridine, amines, and thioethers. The oxygen ethers are weaker bases than the thioethers, and do not result in loss of hydrogen upon mixing with decaborane(14). They are probably strongly coordinated to the (6,9) borons.

The decaborane(12) diligand compounds are important intermediates in boron chemistry. The action of strong bases, such as trialkylamines, results in cage closure and formation of the polyhedral borane anions $B_9H_9^{-2}$, $B_{10}H_{10}^{-2}$, $B_{11}H_{11}^{-2}$, and $B_{12}H_{12}^{-2}$.[3] All the anions are very stable, both chemically and thermally. $B_{12}H_{12}^{-2}$, a regular icosahedron, can be boiled in concentrated sulfuric acid and recovered intact, and its cesium salt can be heated to 810°C without decomposition.[4] By comparison, decaborane(14) decomposes at 160°C, and reacts destructively with alcohols.

1.22 Icosahedral Carboranes

During the course of investigations of boron hydrides as possible high energy fuels, the reactions of small boron hydrides with acetylenes

---

[1] R. Schaeffer, J. Am. Chem. Soc. 79, 1006 (1957).

[2] J. Reddy and W. N. Lipscomb, J. Chem. Phys. 31, 610 (1959).

[3] E. L. Muetterties and W. H. Knoth, Polyhedral Boranes, Marcel Dekker, Inc., New York, 1968.

[4] E. L. Muetterties, J. H. Balthis, Y. T. Chien, W. H. Knoth, and H. C. Miller, Inorg. Chem. 3, 444 (1964).

were studied. The products were carboranes, compounds containing carbon, boron, and hydrogen, and appeared promising as fuels.[1] The best carborane preparations were ligand catalyzed. The drawbacks were low yields and the difficulties of working with the very reactive small boranes.

1.221 Preparation and Properties of the Icosahedral Carboranes. Almost simultaneously, researchers at several chemical corporations working on the development of advanced fuels decided to attempt the reaction of acetylene with decaborane(12) diligand compounds. The results were first reported in 1963 after declassification of the research.

The reaction of vinyl acetylene with decaborane(12) bisacetonitrile produces 1-vinyl-1,2-dicarba-closo-dodecahydrododecaborane:[2]

$$CH_2{=}CH{-}C{\equiv}C{-}H \;+\; B_{10}H_{12}\cdot 2CH_3CN \xrightarrow[\text{Benzene}]{80^\circ C} CH_2{=}CH{-}\underset{\underset{B_{10}H_{10}}{\backslash 0 /}}{C{-}C}{-}H \;+\; H_2 \;.$$

The reaction is general. Almost any acetylene can be used, provided its substituents do not degrade the decaborane cage, and any ligand that coordinates with decaborane(14) can act as a catalyst; even the weak base THF has been used. The decaborane(12) diligand intermediate need not be isolated, nor must stoichiometric amounts of ligand be employed.

The icosahedral carboranes are isoelectronic with $B_{12}H_{12}^{-2}$, and exhibit strong thermal and chemical stability. 1,2-dicarba-closo-dodeca-

---

[1] R. L. Hughes, I. C. Smith, and E. W. Lawless, Production of Boranes and Related Research, Academic Press, New York and London, 1967.

[2] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, Inorg. Chem. 2, 1089 (1963).

hydrododecaborane, ortho carborane, can be heated to 475°C before any change occurs. At 475°C, ortho carborane isomerizes to 1,7-dicarba-closo-dodecahydrododecaborane, meta carborane.[1] The meta isomer is stable to over 620°C, at which temperature isomerization to 1,12-dicarba-closo-dodecahydrododecaborane, para carborane, occurs along with competing polymerization and decomposition reactions.[2]

Chemically, all three are resistive even to raw fluorination. Ortho carborane is least stable but 30% of the original ortho carborane can be recovered as decafluoro-o-carborane.[3] The remainder of the original ortho carborane can be found as small boron fluoride molecules. The meta and para isomers are more resistive to chemical degradation, with 60 and 85 percent, respectively, being recovered as decafluoro carborane upon fluorination.

1.222 Structures of the Carboranes. The question of the structure of the carboranes has been answered in some detail. Single-crystal x-ray diffraction studies of several carboranes have shown that the carboranes are nearly regular icosahedra. The first two correct reports of the structures utilized 1,2-bisbromomethyl-o-carborane[4] and octachloro-o-carborane.[5] Octachloro-o-carborane has

---

[1] D. Grafstein and J. Dvorak, Inorg. Chem. 2, 1128 (1963).

[2] S. Papetti and T. L. Heying, J. Am. Chem. Soc 86 2295 (1964)

[3] S. Kongpricha and H. Schroeder, Inorg. Chem. 8, 2449 (1969).

[4] D. Voet and W. N. Lipscomb, Inorg. Chem. 3, 1679 (1964)

[5] J. A. Potenza and W. N. Lipscomb, Inorg. Chem. 3, 1673 (1964).

chlorine atoms bonded to all borons except those two closest to the carbons.

The positions of substitution of three brominated o-carboranes have been established. The correct structures are 9-bromo-o-carborane, 9,12-dibromo-o-carborane,[1] and 8,9,12-tribromo-o-carborane.[2] The structure of 1,2-dimethyl-8,9,10,12-tetrabromo-o-carborane has also been established.[3]

The structure of m-carborane has also been established. Decachloro-m-carborane was the first m-carborane determined.[4] All boron atoms are labeled with chlorine atoms and the carbon atoms are not adjacent. The structure of 9,10-dibromo-m-carborane has also been determined.[5] The 9,10 boron atoms are the only boron atoms in m-carborane that are not bonded directly to at least one carbon atom. Structures and numbering conventions[6] for o-carborane and m-carborane are given in Figures 1-B and 1-C, respectively.

1.223 Theory of Electron Distribution in Carboranes. Two theories of bonding currently enjoy popularity among chemists. The valence bond method examines essentially localized two electron bonds,

---

[1]J. A. Potenza and W. N. Lipscomb, Inorg. Chem. 5, 1471 (1966).

[2]J. A. Potenza and W. N. Lipscomb, Inorg. Chem. 5, 1478 (1966).

[3]J. A. Potenza and W. N. Lipscomb, Inorg. Chem. 5, 1483 (1966).

[4]J. A. Potenza and W. N. Lipscomb, Proc. Natl. Acad. Sci. U.S. 56, 1917 (1966).

[5]H. Beall and W. N. Lipscomb, Inorg. Chem. 6, 874 (1966).

[6]The Nomenclautre of Boron Compounds, Inorg. Chem. 7, 1945 (1968).

extending over two or three atoms. For large aromatic molecules determination of the total number of essentially similar possible arrangements is usually all that is attempted, although estimates of charge distributions and stabilities are also possible. The molecular orbital method delocalizes the valence electrons throughout the entire molecule. For large aromatic molecules, factorization is used to reduce the calculations to reasonable proportions.

For most aromatic molecules, overlap integrals are considered only between nearest-neighbors. This is incorrect for boron-hydrides in general, and polyhedral boranes in particular. For boron polyhedra, third and fourth nearest-neighbor overlap integrals need to be considered.[1]

A complete calculation of $B_{12}X_{12}^{2-}$ or $C_2B_{10}H_{12}$ icosahedra involves the four orbitals for each boron and one orbital from each X: a 5N x 5N problem. This involves the diagonalization of a 5N x 5N matrix, in this case 60 x 60. The X orbitals will form essentially localized bonds, and may be factored out (ignored). This leaves a 4N x 4N matrix to be diagonalized. Additional factorization can be carried out. The boron orbitals may be hybridized (sp,p^2), (sp^2,p), or (sp^3). One of these orbitals must be used to bond to the external atoms, in essentially localized bonds. This orbital may also be neglected, which leaves a 3N x 3N problem.[1]

---

[1] R. Hoffman and W. N. Lipscomb, J. Chem. Phys. 36, 2179 (1962).

When the boron orbitals are hybridized (sp,p^2), the p orbitals lie along the surface of the molecule. There is a strong temptation to separate these two p orbitals from the sp orbital pointing into the boron cage. The assumption is that these two sets of orbitals do not interact. This further factorization leads to errors in the order of the energy levels, however, and the conclusion is that the "surface" orbitals do interact with the "in" orbitals.[1]

The results of several calculations were reported in Boron Hydrides by Lipscomb,[2] and are reproduced in Table I. More recent calculations[3,4] have not altered the calculated order of electron distribution. The results of these calculations indicate that the (9,12) boron atoms are the most negative, followed by the (8,10) borons, then the (4,5,7,11) borons, and the (3,6) borons are the most positive. For meta carborane, the (9,10) boron atoms are the most negative, followed by the (5,12) borons, then the (4,6,8,11) borons and the (2,3) boron atoms are the most positive.

Lipscomb[2] has derived a relatively quick and simple topological theory to account for the bonding in boron hydrides. The theory is an application of the valence bond method, and involves the calculation of STYX numbers. For a molecule or ion $(B_pH_{p+q+c})^c$, S is the number of BHB bridges, T is the number of BBB three-centered

---

[1] R. Hoffmann and W. N. Lipscomb, J. Chem. Phys. 36, 2179 (1962).

[2] W. N. Lipscomb, Boron Hydrides, W. A. Benjamin, Inc., New York, 1963.

[3] C. S. Cheung, R. A. Beaudet, and G. A. Segal, J. Am. Chem. Soc. 92, 4158 (1970).

[4] T. F. Koetzle and W. N. Lipscomb, Inorg. Chem. 9, 2743 (1970).

bonds, either open or central, Y is the number of BB single bonds, and X is the number of BH_2 groups. The equations of balance are:

$$S + X = q + c$$

$$S + T = p + c$$

$$T + Y = p - c - q/2 \quad .$$

With four unknowns, but only three equations, several possible STYX numbers often result. Of more importance to us, however, is that for a given STYX number, many possibilities may exist for the distribution of the bonds.

For $B_{12}H_{12}^{2-}$, or for $B_{10}C_2H_{12}$, the solutions of the equations of balance yield as the only STYX number 0·10·3·0, i.e., there are 10 three-centered bonds and three single bonds for the boron-carbon framework, but no BHB bridges or BH_2 units. The 10 three-centered bonds may be open or central, or a combination of both. In the icosahedral carboranes, the three single bonds are biased, one being between the two carbon atoms in ortho carborane. In meta and para carborane, two single bonds are constrained to originate on a carbon. Considering now all possibilities, we find that ortho carborane has 10 structures involving open three-centered bonds, and 27 structures involving closed three-centered bonds, for a total of 37 structures. Meta carborane has 17 open and 76 central structures, for a total of 93, and a para carborane has 85 open and 36 central structures for a total of 121. The minimum conclusion from this is that the order of stabilities is expected to be ortho < meta < para. Charge distributions may also be calculated. The results[1] of such

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[1] W. N. Lipscomb, Boron Hydrides, W. A. Benjamin, Inc., New York, 1963.

Table I

Calculations of Framework Charges of Icosahedral Carboranes and Decaborane(14)

	Net Atomic Charges[a]			
o-Carborane	1b	1c	4b	5b
B-3	+0.08	+0.02	+0.05	+0.07
B-4	-0.03	-0.12	+0.03	+0.03
B-8	-0.16	-0.26	+0.01	-0.14
B-9	-0.16	-0.11	+0.02	-0.16
m-Carborane	1b	1c	4b	5b
B-2	+0.10	-0.09	+0.04	+0.10
B-4	-0.03	-0.11	+0.03	+0.03
B-5	-0.03	-0.10	+0.04	+0.02
B-9	-0.16	-0.21	+0.01	-0.16
Decaborane(14)	2b	3c	3b	
B-6	+0.09	+0.29	+0.33	
B-5	+0.00	+0.10	+0.12	
B-1	+0.05	-0.03	-0.04	
B-2	-0.14	-0.45	-0.10	

[a] In units of electronic charge.

[b] Molecular orbital calculation

[c] Valence-bond 3-center resonance calculation

[1] R. Hoffmann and W. N. Lipscomb, J. Chem. Phys. 36, 3480 (1962).

[2] F. P. Boer, M. D. Newton, and W.N. Lipscomb, J. Am. Chem. Soc. 88, 2361 (1966).

[3] W. N. Lipscomb, Boron Hydrides, W. A. Benjamin, Inc., New York and Amsterdam, 1963.

[4] C. S. Cheung, R. A. Beaudet, and G. A. Segal, J. Am. Chem. Soc. 92, 4158 (1970).

[5] T. F. Koetzle and W. N. Lipscomb, Inorg. Chem. 9, 2743 (1970).

a calculation are reported in Table I. Also given in Table I is the calculated electron distribution of decaborane(14).

Figure I gives the structures of decaborane(14), ortho carborane, and meta carborane, with boron atoms with comparable electronic charges in the same relative positions. The figure pictorially illustrates the similarities in electronic distributions and suggests that decaborane(14) may be a model for the boron chemistry of the carboranes.

1.23 Chemistry of the Carboranes

An extensive derivative chemistry of the carboranes has been developed over the past several years. The scope of this derivative chemistry is so vast that we can only skim the surface in this report. Several reviews of the chemistry of the carboranes have been written. The reviews by Onak,[1] Bregadze and Okhlobystin,[2] and Grimes[3] are highly recommended.

1.231 Derivatives Bonded to Carbon. Most of the derivative chemistry of the carboranes involves substitution at the carbon. Only four main types of reactions are required to produce the large number of derivatives.

With only a few exceptions, any acetylene will react with decaborane(12) diligand to yield an o-carborane. If a suitably substituted acetylene can be obtained, the correspondingly substituted

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[1]T. P. Onak, Advan. Organometal. Chem. 3, 263 (1965).

[2]V. I. Bregadze and O. Y. Okhlobystin, Organometal. Chem. Rev. A4, 345 (1969).

[3]R. N. Grimes, Carboranes, Academic Press, New York and London, 1970.

o-carborane can be produced. Thus, methylacetylene reacts with decaborane(12) diligand to produce 1-methyl-o-carborane.[1]

The method is not often the reaction of choice, however. The yields may be low; 1-methyl-o-carborane is produced in 30% yield.[2] Symmetrical acetylenes in general give very low yields. Only a trace of 1,2-dimethyl-o-carborane is produced from the reaction of 2-butyne with decaborane(12) diligand.[3] On the other hand, high yields of 1,2-bis(chloromethyl)-o-carborane resulted from the reaction of 1,4-dichloro-2-butyne with decaborane(12) diligand.[3] If the substituent on the acetylene reacts with decaborane, no carborane formation is possible. Thus, 1,4-diol-2-butyne reacts explosively with decaborane(12) diligand.[3] Acids and alcohols can be prepared using the appropriate acetylene ester, and hydrolyzing the resulting carborane ester.

A second method for preparing derivatives of carboranes utilizes the acidic nature of the hydrogen atoms bonded to the carbons. Strong bases such as butyl lithium react to form either the mono- or di-lithio-carborane, depending upon stoichiometry. The lithio-carborane then will react with halo-organics or other covalently bonded halogen compounds to form lithium halide and the substituted carborane.

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[1]T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, Inorg. Chem. 2, 1089 (1963).

[2]V. I. Stanko, V. V. Kopylov, and A. I. Klimova, J. Gen. Chem. U.S.S.R. 35, 1437 (1965).

[3]M. Fein, D. Grafstein, J. Paustian, J. Bobinski, B. Lichstein, N. Mayes, N. Schwartz, and M. Cohen, Inorg. Chem. 2, 1115 (1962).

The reactions[1] of 1-lithio-o-carborane with iodomethane, and of 1-lithio-o-carborane with chlorotrimethylsilane, produce 1-methyl-o-carborane and 1-trimethylsilyl-o-carborane, respectively.

The major difficulty with this method is that even with a one to one butyl-lithium to o-carborane ratio, some dilithio-carborane is formed, probably by a solvent-assisted disproportionation. A typical preparation of monolithio-o-carborane in ethyl ether will yield 75-80% monolithio-o-carborane, 10-12% dilithio-o-carborane, and 10-12% unreacted o-carborane.[2] The need for purification of the product reduces yields below the 100% conversion. Use of non-solvating solvents such as the alkanes improves the percentage of monolithio-o-carborane, but the reactions are slower because ortho carborane is less soluble in alkanes than in ethers.

An important synthetic intermediate is 1-bromomethyl-o-carborane, obtainable pure in about 90% yield from the reaction of propargylbromide with decaborane(14) in acetonitrile.[3] A normal Grignard reaction is formed by 1-bromomethyl-o-carborane. The highest yield of 1-methyl-o-carborane is obtained by the reaction sequence:[4]

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[1] T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, Inorg. Chem. 2, 1097 (1963).

[2] L. I. Zakharkin, A. V. Grebennikov, and A. V. Kazantsev, Izv. Akad. Nauk. S.S.S.R., Ser. Khim., 2077 (1967).

[3] E. L. Muetterties, Ed., Inorg. Syn., Vol. X, McGraw-Hill Book Co., New York, San Francisco, Toronto, London, Sydney, 1967, p. 100.

[4] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M Cohen, and M. Fein, Inorg. Chem. 2, 1120 (1963).

$$HC{\equiv}C\text{-}CH_2Br + B_{10}H_{12}\cdot 2CH_3CN \rightarrow 1\text{-}BrCH_2\text{-}CB_{10}H_{10}CH + H_2\uparrow$$

$$1\text{-}BrCH_2\text{-}CB_{10}H_{10}CH + Mg \xrightarrow{(C_2H_5)_2O} 1\text{-}BrMgCH_2CB_{10}H_{10}CH$$

$$1\text{-}BrMgCH_2\text{-}CB_{10}H_{10}CH + HCl \xrightarrow{H_2O} 1\text{-}CH_3\text{-}CB_{10}H_{10}CH + MgBrCl$$

The total yield, based on the initial decaborane(14), is greater than 70%.

THF has also been used as solvent and works well for the preparation of 1-methyl-o-carborane. It is not suitable for preparing longer carbon chains, because the disproportionation reaction

$$BrMgCH_2\text{-}CB_{10}H_{10}CH \xrightarrow{THF} CH_3\text{-}CB_{10}H_{10}C\text{-}MgBr$$

occurs. The addition of allylbromide to the above mixture results in good yields of 2-methyl-1-allyl-o-carborane.[1] The disproportionation is solvent assisted,[2] occurring slightly in ethyl ether, but to a much greater extent in THF.

Grignard reagents react with o-carborane itself[1] to produce new Grignard reagents suitable for synthetic intermediates. This reaction sequence is not used

$$HCB_{10}H_{10}CH + C_2H_5MgBr \rightarrow BrMgCB_{10}H_{10}CH + C_2H_6\uparrow$$

$$BrMgCB_{10}H_{10}CH + CH_3I \rightarrow CH_3CB_{10}H_{10}CH + MgBrI$$

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[1] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. Cohen, and M. Fein, Inorg. Chem. 2, 1120 (1963).

[2] V. I. Stanko and G. A. Anorova, J. Gen. Chem. U.S.S.R. 38, 2719 (1968).

as often as the other reactions described.

Substituted m- and p-carboranes can also be prepared by the above set of reactions, except that the direct synthesis is impossible. As an alternative to the direct synthesis, thermal isomerization is used. Heating an ortho carborane to 450-500°C in a sealed tube or autoclave, either under an inert atmosphere or under vacuum, for twenty-four hours, results in essentially complete conversion to the corresponding m-carborane.[1] An alternate procedure is to heat the carborane to 600°C for a few seconds in a flow system.[2] Longer reaction times decrease the yield of meta carborane and increase the yield of p-carborane and polymeric products.[3]

The isomerization temperature is dependent upon the substituent on the carbon, and can be lowered extensively if the substituents are large, with large steric requirements. Thus, 1,2-bis(trimethylsilyl)-o-carborane converts to the meta isomer at 275°C.[4]

The mechanism of the isomerization appears to involve a cube-octahedral intermediate. The sequence is depicted in Figure 2. An analysis of the mechanism indicates that the isomerization of 9-bromo-o-carborane should lead to m-carborane with the bromine atom bonded to any one of the ten boron atoms. Thermal isomerization of 9-bromo-

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[1] D. Grafstein and J. Dvorak, Inorg. Chem. 2, 1128 (1963).

[2] S. Papetti, C. Obenland, and T. L. Heying, Ind. Eng. Chem., Prod. Res. Dev. 5, 334 (1966).

[3] V. I. Stanko, Y. V. Gol'tyapin, A. I. Klimova, I. S. Astakhova, Y. T. Struehkov, and T. P. Klimova, J. Gen. Chem. U.S.S.R. 39, 796 (1969).

[4] R. M. Salinger and C. L. Frye, Inorg. Chem. 7, 1815 (1965).

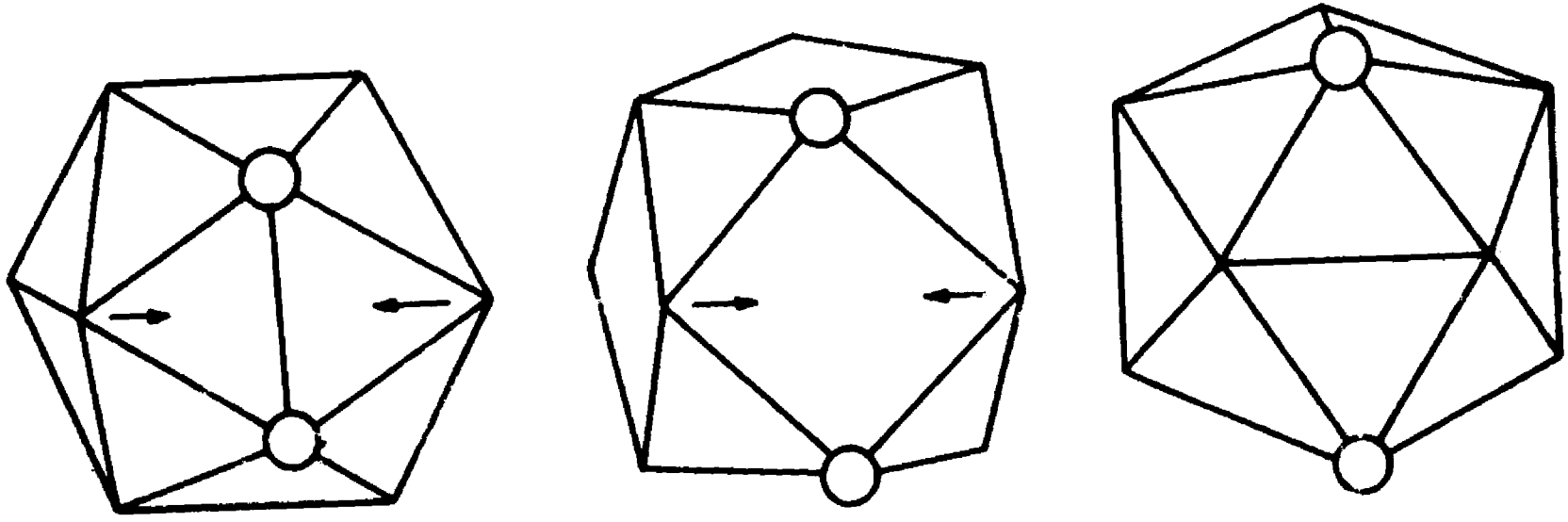

Figure 2. Cube-Octahedral Rearrangement of o-Carborane to m-Carborane.

o-carborane at 400°C for four hours and identification of the products by gas chromatography showed[1,2] that all possible B-bromo-o- and -m-carborane isomers were produced.

The one product not possible by the cube-octahedral mechanism is p-carborane. The isomerization of m-carborane to p-carborane occurs at 615°C with a twenty-four hour residence time,[3] but in low yield. Polymerization also occurs at this temperature. The best preparation of p-carborane is via a flow system at 700°C.[4]

1.232 B-halo-carboranes. Boron substituted carborane derivatives have been much less extensively studies. Some derivatives have been prepared from substituted decaborane(14).[5-7] Pure substituted decaboranes are not always easy to obtain, so this method is limited.

Halogenation of the carboranes occurs readily. The products obtained with a particular carborane isomer reflect the reactivity of the halogens, whereas the products obtained with a particular halogen reflect the differing stabilities of the carborane isomers.

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[1]H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, J. Am. Chem. Soc. 89, 4218 (1967).

[2]L. I. Zakharkin and V. N. Kalinin, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 542 (1969).

[3]S. Papetti and T. L. Heying, J. Am. Chem. Soc. 86, 2295 (1964).

[4]S. Papetti, C. Obenland, and T. L. Heying, Ind. Eng. Chem., Prod. Res. Dev. 5, 334 (1966).

[5]T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, Inorg. Chem. 2, 1089 (1963).

[6]L. I. Zakharkin and V. N. Kalinin, Izv. Akad. Nauk. U.S.S.R. 1946 (1966).

[7]J. Plesek, V. Gregor, S. Hĕrmánek, Collect. Czech. Chem. Commun. 35, 346 (1970).

Raw fluorination proceeds rapidly with all three carboranes.[1] The only identifiable fluoro-carborane products are the three decafluoro-o-, -m-, and -p-carboranes, regardless of the amount of fluorine used. All boron atoms of the three carboranes are apparently substituted at the same rate. Upon complete fluorination, 30% of the original o-carborane is recovered as decafluoro-o-carborane, the rest of the original carborane appearing as degraded fluoroboranes. The other two isomers are more stable, with 60% and 85% of the original carboranes being recovered as decafluoro-m-carborane and decafluoro-p-carborane, respectively.

Chlorination proceeds readily at 70°C with U.V. light as initiator.[2] The reaction is difficult to control until four chlorine atoms have been substituted, although two dichloro, one trichloro, and at least one tetrachloro derivatives of o-carborane have been isolated. Further chlorination occurs with longer reaction times. The products are difficult to obtain pure. The reaction rate is rapid, especially for the first four to six chlorine atoms substituted. Subtle differences in temperature, concentration, and reaction times are necessary to prepare the desired chlorinated carborane. In addition, the chloro-carboranes form mixed crystals, which are difficult to separate by recrystallization.

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[1] S. Kongpricha and H. Schroeder, Inorg. Chem. 8, 2449 (1969).

[2] H. Schroeder, T. L. Heying, and J. R. Reiner, Inorg. Chem. 2, 1092 (1963).

In contrast to the first two halogens, bromine requires a catalyst,[1] usually Al_2Br_6 or Al_2Cl_6. The reaction is clean, easily controlled, and results in formation of mono-, di-, or tribromo-o-carborane, depending upon the molar ratio of bromine to o-carborane. Tetrabromo-o-carborane cannot be prepared by this method, although tetrabromo-1,2-dimethyl-o-carborane can be synthesized. The bromocarboranes can be further halogenated with chlorine.

One or two bromine atoms can be readily substituted on m-carborane,[1] but further bromination does not occur. Tribromo-1,7-dimethyl-m-carborane can be prepared.

The positions of substitution have been determined by single-crystal x-ray diffraction. The (9,12) positions of o-carborane are attacked first.[2] Tribromo-o-carborane is 8,9,12-tribromo-o-carborane.[3] Dibromo-m-carborane is 9,10-dibromo-m-carborane.[4] The order of electrophilic attack thus follows the order predicted by theory.[5]

Iodination of the carboranes occurs at 180-200°C in the absence of a catalyst,[6] or at 70-80°C with a catalyst.[7] Mono-, di-

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[1]H. D. Smith, J. A. Knowles, and H. Schroeder, Inorg. Chem. 4, 107 (1965).

[2]J. A. Potenza and W. N. Lipscomb, Inorg. Chem. 5, 1471 (1966).

[3]J. A. Potenza and W. N. Lipscomb, Inorg. Chem. 5, 1478 (1966).

[4]H. Beall and W. N. Lipscomb, Inorg. Chem. 6, 874 (1967).

[5]R. Hoffmann and W. N. Lipscomb, J. Chem. Phys. 36, 3489 (1962).

[6]L. I. Zakharkin, J. I. Stanko, and A. I. Klimova, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 1946 (1966).

[7]V. I. Stanko, A. I. Klimova, and T. P. Klimova, J. Gen. Chem. U.S.S.R. 37, 2123 (1967).

and tetraiodo-o- and -m-carboranes have been isolated. The order of electrophilic iodination for the first two iodine atoms substituted is the same as that found for bromine substitution.[1]

1.233 B-Alkyl-Carboranes. The reaction of o-carborane, Al_2Cl_6, and the halo-alkanes methyl and ethyl bromide has been reported.[2] The reaction was reported to produce a mixture of B-alkyl-o-carboranes with from one to six alkyl groups substituted for hydrogen atoms. The positions of substitution were not determined.

Both 1-isopropenyl-o-carborane and 1-methyl-o-carborane were reported[3] to undergo Friedel-Crafts alkylation with ethyl bromide in carbon disulfide solvent. However, o-carborane itself was reported not to alkylate under these conditions. The reaction of methylene chloride, chloroform, or carbon tetrachloride with o-carborane and fused Al_2Br_6 at 135-145°C was reported[3] to produce polymers. However, similar conditions were used[4,5] to prepare chlorinated o- and m-carboranes.

Substitution on the boron atom of the 3(6) position of o-carborane, and at the 2(3) position of m-carborane, can be accomplished readily. The synthesis proceeds through several steps.

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[1]L. I. Zakharkin and V. N. Kalinin, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 2014 (1966).

[2]S. L. Clark and D. J. Mangold, U. S. Patent 3,092,664 (1963).

[3]D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. Cohen, and M. Fein, Inorg. Chem. 2, 1120 (1963).

[4]L. I. Zakharkin, O. Y. Okhlobystin, G. K. Semin, and T. A. Babushkina, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 1913 (1965).

[5]L. I. Zakharkin and U. N. Kalinin, Dokl. Akad. Nauk. U.S.S.R. 169, 590 (1966).

Alcoholic base degrades o-carborane and m-carborane[1] relatively rapidly with abstraction of a boron atom adjacent to the carbons. Further degradation occurs much more slowly. The initial product can be isolated as the monobasic salt, $NaC_2B_9H_{12}$. For synthetic purposes, the dibasic salt, $Na_2C_2B_9H_{11}$, is prepared *in situ*. Addition of a dihaloborane restores the carborane cage.[2,3]

$$RBX_2 + Na_2C_2B_9H_{11} \rightarrow 2NaX + 3\text{-}R\text{-}C_2B_{10}H_{11}$$

The substituent R has been aliphatic,[3,4] aromatic,[2] amino,[5] and ethoxy[5] groups, and halogen[6] atoms. Aluminum halides have also been used, to form 3-alumino-carboranes.[7] Be,[8] Ge,[9] Pb,[9] and Sn[9] have also been introduced into the carborane cage by similar reactions.

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[1] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, J. Am. Chem. Soc. 90, 862 (1968).

[2] M. F. Hawthorne and P. A. Wegner, J. Am. Chem. Soc. 87, 4392 (1965).

[3] M. F. Hawthorne and P. A. Wegner, J. Am. Chem. Soc. 90, 896 (1968).

[4] B. M. Mikhailov and T. V. Topapova, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 1629 (1967).

[5] T. V. Topapova and B. M. Mikhailov, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 2367 (1967).

[6] J. S. Roscoe, S. Kongpricha, and S. Papetti, Inorg. Chem. 9, 1561 (1970).

[7] B. M. Mihailov and T. V. Topapova, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 1153 (1968).

[8] G. Popp and M. F. Hawthorne, J. Am. Chem. Soc. 90, 6553 (1968).

[9] R. L. Voorhees and R. W. Rudolph, J. Am. Chem. Soc. 91, 2173 (1969).

Deuterium exchange has been attempted with o-carborane.[1] Deuterium exchange occurred with the hydrogens bonded to carbon in basic solution, and the hydrogens bonded to boron exchanged with deuterium in acid. The positions of exchange were not determined more explicitly.

The carborane moiety acts as a substituent with a large negative I, or electron withdrawing effect with substantial steric requirements. An analysis[2] of the pKa's of several m- and p-substituted anilinium ions indicated that o-carborane has a stronger negative I effect than the halogens. Of the substituents studied, only the nitro group has a stronger negative I effect. Similar results were found[2,3] for the pKa's of a series of m- and p-substituted benzoic acids. A study[2] of ^{19}F chemical shifts of a series of m- and p-substituted fluorobenzene derivatives indicated that o-carborane has a stronger negative I effect than does m-carborane, and that m-carborane has a negative I effect slightly stronger than chlorine.

Substitution of benzoic acids or fluorobenzene derivatives at the 3(6) boron atom of o-carborane can be accomplished by Hawthorne's insertion reaction.[4] Studies of the pKa's of the benzoic acids,[3]

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[1] V. N. Setkina, I. G. Malakhova, V. I. Stanko, A. I. Klimova, and L. I. Zakharkin, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 1627 (1966).

[2] M. F. Hawthorne, T. E. Berry, and P. A. Wegner, J. Am. Chem. Soc. 87, 4746 (1965).

[3] L. I. Zakharkin, V. N. Kalinin, and I. P. Shepilov, Dokl. Akad. Nauk. U.S.S.R. 174, 606 (1967).

[4] M. F. Hawthorne and P. A. Wegner, J. Am. Chem. Soc. 90, 890 (1968).

and of the ^{19}F NMR chemical shifts,[1] indicated that o-carborane has a smaller negative I effect when substituted at the 3(6) boron atom than when substituted at the carbon atom of either o-carborane or m-carborane.

1.24 Nuclear Magnetic Resonance

1.241 General. The general rules of NMR apply to ^{11}B NMR. The use of the p orbitals of boron in bonding restricts the rotation of the electron cloud around the nucleus, thus increasing the paramagnetic contribution to the shielding. The paramagnetic contribution to the shielding of the boron nucleus in the icosahedral carboranes was concluded[2] to dominate the diamagnetic shielding. When the paramagnetic contribution dominates the shielding, it is inaccurate and misleading to rely upon such cureall of proton spectra as electronegativity and electron density for interpreting spectra.

With a nuclear spin quantum number I = 3/2, ^{11}B has a quadrupole moment, which generally affords a rapid and efficient relaxation mechanism. The spectra of boranes show broad resonances, with peak widths at half-height on the order of 50 Hz. The broadness of the peaks obscures all but the largest coupling. Thus, coupling of ^{11}B to ^{11}B,

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[1] R. G. Adler and M. F. Hawthorne, J. Am. Chem. Soc. 92, 6174 (1970).

[2] F. P. Boer, R. A. Hegstrom, M. D. Newton, J. A. Potenza, and W. N. Lipscomb, J. Am. Chem. Soc. 88, 5340 (1968).

or ^{10}B to ^{11}B, is not directly observed, nor is long-range coupling of ^{11}B to any other magnetic nucleus observed. Coupling is observed for ^{11}B bonded directly to ^{1}H, ^{19}F, or ^{31}P, all spin 1/2 nuclei. ^{11}B-^{1}H coupling constants range from 80-200 Hz, apparently increasing with increasing s character of the boron-hydrogen bond. Bridge hydrogen coupling to boron is observed only with the small boranes, diborane(6) or tetraborane(10). Interpretation of ^{11}B spectra of boranes and carboranes can be difficult because the coupling constants and peak widths are of the same order. When, as for the icosahedral carboranes at 19.3 MHz, the entire spectrum covers only about 300 Hz, interpretation is nearly impossible. An increase in magnetic field will cause changes in the magnitude of the chemical shift in Hertz, but will not affect the coupling constant.

Coupling of ^{1}H to ^{11}B follows the usual $(2nI + 1)$ multiplicity rule, where I is the spin quantum number of the nucleus coupled, and n is the number of nuclei, generally 1 for ^{11}B in ^{1}H spectra of boranes. ^{11}B spectra therefore can indicate the number of hydrogen atoms bonded to boron when peaks are resolvable. ^{1}H spectra will show quartets for protons bonded to boron. The rapid relaxation of ^{11}B broadens the ^{1}H resonance lines. All peaks of the quartet will be the same height and width, because the probability of the boron nucleus being in one of its four energy states is the same for all four states. Protons coupled to ^{10}B, with $I = 3$, will show a septet. The septet has a smaller coupling constant and smaller width than the quartet of ^{11}B-^{1}H coupling. In addition, the intensities will be less, because ^{10}B is only 20% of naturally

occurring boron and also because of the difference in multiplicities. The result is that ^{10}B-^{1}H coupling in ^{1}H spectra reduces the resolvability.

When resolvable, ^{1}H and ^{11}B spectra of the same compound are complementary. Coupling constants should be the same in both spectra, but may be more clearly seen in ^{1}H spectra. The chemical shifts of proton spectra will reflect the diamagnetic shielding, and thus the electron density around the proton. The ^{11}B chemical shifts will reflect the paramagnetic contribution to the shielding of the boron nucleus, and therefore the restriction of the electron cloud rotation about the nucleus. As the theory becomes developed, this may yield information about excited states of the molecule.

1.242 ^{11}B and ^{1}H Spectra of the Icosahedral Carboranes. Both o-carborane and m-carborane have four sets of symmetrically equivalent boron atoms, and should give four doublets of relative areas 2:2:4:2. In the ^{11}B NMR spectra of o-carborane at 19.3 MHz, however, only three sets of doublets can be found, and these only by ^{1}H double resonance.[1,2] The ^{11}B spectrum at 19.3 MHz of decachloro-o-carborane[3,4] shows only two resonance peaks. The ^{11}B NMR spectra of 9-bromo-o-

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[1]J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, J. Am. Chem. Soc. 88, 628 (1966).

[2]G. D. Vickers, H. Agahigian, E. A. Pier, and H. Schroeder, Inorg. Chem. 5, 693 (1966).

[3]H. Schroeder, T. L. Heying, and J. R. Reiner, Inorg. Chem. 2, 1092 (1963).

[4]H. Schroeder and G. D. Vickers, Inorg. Chem. 2, 1317 (1963).

carborane, 9,12-dibromo-o-carborane, and 8,9,12-tribromo-o-carborane[1] were obtained at 19.3 MHz, and a tentative assignment made. With ^{1}H double resonance, the 32.1 MHz ^{11}B NMR spectrum of o-carborane shows[2] four peaks corresponding to the four sets of symmetrically equivalent boron atoms. The ^{11}B NMR spectra of three dihalo-o-carboranes, 9,12-dichloro-o-carborane, 9,12-dibromo-o-carborane, and 9,12-diiodo-o-carborane were studied[2] at 32.1 MHz with ^{1}H double resonance, and a tentative assignment made. This assignment was made on the basis of the observed data and upon the assumption that the (3,6) boron atom resonance must be at higher field than the (8,10) boron atom resonance because of the greater electronegativity of the carbon atoms adjacent to the (3,6) boron atoms. No proof of this assumption was advanced nor were any (3,6) or (8,10) substituted o-carborane derivatives studied. The ^{11}B NMR spectra of decaborane(14) show that this assumption is not justified for decaborane(14).

Chlorine and bromine substitution in decaborane(14) causes large downfield chemical shifts.[3,4] Iodine substitution causes large upfield chemical shifts.[4] These shifts could result in undetectable changes in the relative positions of resonances in a narrow spectrum.

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[1] J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, J. Am. Chem. Soc. 88, 628 (1966).

[2] V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, Zh. Strukt. Khim. 11, 627 (1970).

[3] M. Hillman and D. J. Mangold, Inorg. Chem. 4, 1357 (1965).

[4] R. Schaeffer, J. N. Shoolery, and R. Jones, J. Am. Chem. Soc. 80, 2670 (1958).

In view of the narrowness of the spectrum of o-carborane at 19.3 MHz, and because no spectra of (8,10) or (3,6) substituted o-carborane derivatives were obtained during the study at 32.1 MHz, the assignments at these frequencies can at best be considered to be good guesses.

Spectra of o-carborane have been obtained at 60 MHz,[1] and at 64.2 MHz.[2] In these spectra, four doublets are detectable. The relative areas of these four doublets, in the order of increasing field, are 2:2:4:2. Unfortunately, no substituted o-carboranes were investigated. The unequivocal assignment of the ^{11}B NMR spectrum of o-carborane must be considered incomplete.

The 19.3 MHz ^{11}B NMR spectrum of m-carborane shows only three resonances with ^{1}H double resonance[2] or upon substitution of ten chlorine atoms.[3] The ^{11}B NMR spectrum of 9,10-dibromo-o-carborane was obtained[4] at 15 MHz. The spectrum is very poorly resolved but the authors believe that the (9,10) boron atom resonance is not at lowest field.

Four resonance peaks are observed in the ^{1}H double-irradiated 32.1 MHz ^{11}B NMR spectrum of m-carborane.[5] The ^{1}H double-irradiated

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[1] R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, Proc. Chem. Soc. 402 (1964).

[2] G. D. Vickers, H. Agahigan, E. A. Pier, and H. Schroeder, Inorg. Chem. 5, 693 (1966).

[3] H. Schroeder and G. D. Vickers, Inorg. Chem. 2, 1317 (1963).

[4] H. Beall and W. M. Lipscomb, Inorg. Chem. 6, 874 (1967).

[5] V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, Zh. Struht. Khim. 11, 627 (1970).

32.1 MHz ^{11}B NMR spectra of three dihalo-m-carboranes, 9,10-dichloro-m-carborane, 9,10-dibromo-m-carborane, and 9,10-diiodo-m-carborane, were also obtained and an assignment made.[1] The assignment assumed that the (9,10) boron atoms were at lowest field, and that the (2,3) boron atoms were at highest field. The data were interpreted on the basis of this assumption. No spectra of other m-carborane derivatives have been obtained, and no unequivocal assignment can be made.

The ^{11}B NMR spectrum of m-carborane at 64.2 MHz has been obtained[2] and shows the same increase in resolution that was found for o-carborane. All four doublets are resolved. No substituted m-carboranes have been studied at high magnetic fields.

The ^{1}H spectra of the carboranes have been obtained at 60 MHz[3-7] and at 220 MHz.[8] All studies have been concerned either with the proton

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[1] V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, Zh. Strukt. Khim. 11, 627 (1970).

[2] G. D. Vickers, H. Agahigan, E. A. Pier, and H. Schroeder, Inorg. Chem. 5, 693 (1966).

[3] M. F.Hawthorne and P. A. Wegner, J. Am. Chem. Soc. 87, 4392 (1965).

[4] R. L. Voorhees and R. W. Rudolph, J. Am. Chem. Soc. 91, 2173 (1969).

[5] G. Popp and M. F. Hawthorne, J. Am. Chem. Soc. 90, 6553 (1968).

[6] K. M. Harmon, A. B. Harmon, and B. C. Thompson, J. Am. Chem. Soc. 89, 5309 (1967).

[7] N. K. Hota and D. S. Matteson, J. Am. Chem. Soc. 90, 3570 (1968).

[8] V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, Zh. Strukt. Khim. 11, 542 (1970).

resonances of substituents on the carbons or with the hydrogens attached to the carborane carbons. A small, unresolved blob at about two ppm downfield from tetramethylsilane(TMS) is assumed to be due to hydrogens attached to boron. No attempt has been made to assign the ^{1}H spectra of the carboranes.

2.0 STATEMENT OF THE PROBLEM

At present, the most widely used method of structural determination for the carboranes is single-crystal x-ray diffraction. Assignment of the ^{11}B NMR spectra of o- and m-carborane could lead to another, more rapid method for determination of the positions of substitution of derivatives of the carboranes. High magnetic fields will be required for the assignment of the spectra. The construction of a 60 Kgauss NMR spectrometer under NIH Facilities Grant FR 00292 to the MPC Corporation affords a means of obtaining spectra at high enough field to permit assignment of the spectra.

The assignment of the ^{1}H NMR spectra of the carboranes could yield information complementary to that obtained from ^{11}B NMR spectra. Large magnetic fields are also needed for these assignments. The 60 Kgauss NMR operates at 80.2 MHz for ^{11}B and 250 MHz for ^{1}H, and should allow the assignment of many of the ^{1}H NMR spectra of the carboranes.

We have proposed that decaborane(14) chemistry could be a model for the boron chemistry of the carboranes. As a test for this model, deuterium isotope exchange experiments were carried out. The positions of exchange were determined from the ^{11}B NMR spectra of the products. As an additional test, "Friedel-Crafts" alkylation of the carboranes was attempted.

Interesting and unusual results were found upon variation of RF power while obtaining ^{11}B NMR spectra of halogen-substituted carboranes. An investigation of these results was carried out.

3.0 RESULTS AND DISCUSSION

^{11}B chemical shifts and ^{11}B-^{1}H coupling constants found for the o-carborane derivatives studied are given in Table II. Table III presents ^{11}B chemical shifts and ^{11}B-^{1}H coupling constants found for the m-carborane compounds studied, and Table IV give ^{1}H chemical shifts and ^{11}B-^{1}H coupling constants found at 250 MHz for o-carborane and m-carborane. All ^{11}B chemical shifts are reported relative to trimethoxyborane(TMB) as an external standard, and all ^{1}H chemical shifts are reported relative to tetramethylsilane(TMS) as an external standard.

3.1 Ortho Carborane

3.11 Assignment of the ^{11}B NMR Spectrum of Ortho Carborane

The structure and numbering convention for o-carborane is given in Figure 1-B. There are four sets of symmetrically equivalent boron atoms: the (3,6), (4,5,7,11), (9,12), and (8,10) positions. The 80.2 MHz ^{11}B NMR spectrum of o-carborane given in Figure 3 shows four doublets with relative areas 2:2:4:2 with increasing field.

The spectrum may be completely assigned by considering molecular symmetry, relative peak areas, and data on 9-bromo-o-carborane, 9,12-dibromo-o-carborane, and 8,9,12-tribromo-o-carborane, whose structures have been determined by single-crystal x-ray diffraction techniques. The only resonance of relative area four must be assigned to the four symmetrically equivalent boron atoms (4,5,7,11). The

Table II[a]

80.2 MHz ^{11}B NMR Chemical Shifts and $^{11}B-^{1}H$ Coupling Constants of o-Carborane and Selected Derivatives

Compound	J_{BH}[b] 9,12	δ[c] 9,12	J_{BH}[b] 8,10	δ[c] 8,10	J_{BH}[b] 4,5,7,11	δ[c] 4,5,7,11	J_{BH}[b] 3,6	δ[c] 3,6
o-carborane	151	+21.1	151	+28.0	163	+32.5	178	+33.7
9-bromo-o-carborane	--- 150	+19.4 +20.5	151	+27.1	165	+32.4 +33.3	175	+34.6
9,12-dibromo-o-carborane	---	+18.9	154	+26.5	166	+33.6	176	+36.5
8,9,12-tribromo-o-carborane	---	+19.1	--- 160	+24.4 +27.8	168	+31.7 +36.0	192	+36.7 +40.3
tetrachloro-o-carborane	---	+13.2	---	+19.2	162	+34.7	188	+41.1
octachloro-o-carborane	---	+16.1	---	+23.4	---	+29.6	196	+41.9
9,12-diiodo-o-carborane	---	+33.1	158	+24.7	(165)	+31.8	(178)	+33.7
1-bromomethyl-o-carborane	(151)	+21.5 +23.8	(151)	+27.7	(163)	+29.5 +31.5	(178)	+30.7
1-methyl-o-carborane	154	+21.0 +25.9	(154)	+28.2	(163)	+29.7 +32.1	(178)	+30.3
1-vinyl-o-carborane	(151)	+21.0 +23.6	(151)	+27.8	(163)	+29.7 +31.5	(178)	+29.8
1-bromomethyl-o-carborane-d_4 in acetone	---	+21.4 +23.7	---	+27.7	(163)	+29.0 +31.1	(178)	+30.3
1-bromomethyl-o-carborane-d_4 in $CDCl_3$	---	+21.5 +24.1	---	+27.9	(163)	+29.6 +32.0	(178)	+31.8
1,2-dimethyl-o-carborane	151	+24.4	(151)	+27.8	(163)	+28.7	(178)	+29.6

(continued)

Table II[a] (continued)

Compound	J_{BH}[b] 9,12	δ[c] 9,12	J_{BH}[b] 8,10	δ[c] 8,10	J_{BH}[b] 4,5,7,11	δ[c] 4,5,7,11	J_{BH}[b] 3,6	δ[c] 3,6
3-phenyl-o-carborane[d]	152	+21.6	154	+27.7	?	?	---	+24.3
			?	?			?	?
5-bromo-o-carborane	152	+23.2	(150)	+30.2	---	+32.8	176 ± 4	+36.5
	148	+24.1		+31.4	168 ± 4	+33.4	176 ± 2	+39.7
						+35.7[e]		
o-carborane-d_4[f]	---	+21.6	---	+28.1	164	+32.7	178	+33.9
B-methyl-o-carbone	---	+11.1	137	+25.3	?	?[g]	?	?
	137	+19.8						

[a]Values of J_{BH} in parenthesis are assumed.

[b]J_{BH} is given in Hertz and are accurate to ± 2 Hz unless otherwise noted.

[c]δ is given in ppm relative to trimethoxy borane as an external standard and are accurate to ± 0.1 ppm.

[d]Only the (9,12), 8(10), and 3 boron atoms could be assigned.

[e]Doublet of relative area two.

[f]Prepared by Friedel-Crafts type reaction.

[g]Center of the remaining peaks of relative area six is +31.1 ppm.

9-bromo-o-carborane and 9,12-dibromo-o-carborane data indicate the position of the (9,12) boron resonance; the 8,9,12-tribromo-o-carborane data then locates the (8,10) boron atom resonance. In addition, the three brominated derivatives establish that no unusual changes occur in either chemical shift or coupling constant for non-substituted boron atoms. The only two remaining boron atoms, (3,6), are assigned to the only remaining doublet of area two. Thus, the doublet at +21.1 ppm, J = 151 Hz, is assigned to boron atoms (9,12), the doublet at +28.0 ppm, J = 151 Hz, to boron atoms (8,10), the doublet at +32.5 ppm, J = 163 Hz, to boron atoms (4,5,7,11), and the doublet at +33.7 ppm, J = 178 Hz, to boron atoms (3,6). Each of the compounds will now be considered separately.

The 80.2 MHz ^{11}B NMR spectra of 9-bromo-o-carborane and 9,12-dibromo-o-carborane are shown in Figures 4 and 5, respectively. These spectra show the progressive collapse of the lowest field doublet to a singlet at +18.8 ppm. The spectrum of 9-bromo-o-carborane shows that the singlet of relative area one at +19.4 ppm overlaps the doublet of relative area one at +20.5 ppm. This shows that there has been no major change in position of resonance upon bromine substitution, and establishes that the low field doublet of relative area two, at +21.1 ppm and J = 151 Hz in the o-carborane spectrum is due to the (9,12) boron atoms. These atoms are opposite the carbon atoms in the cage.

Substitution at the 9 position reduces the symmetry of the molecule. The (4,5) boron atoms are no longer symmetrically equivalent to the (7,11) boron atoms. The symmetrical equivalence of the

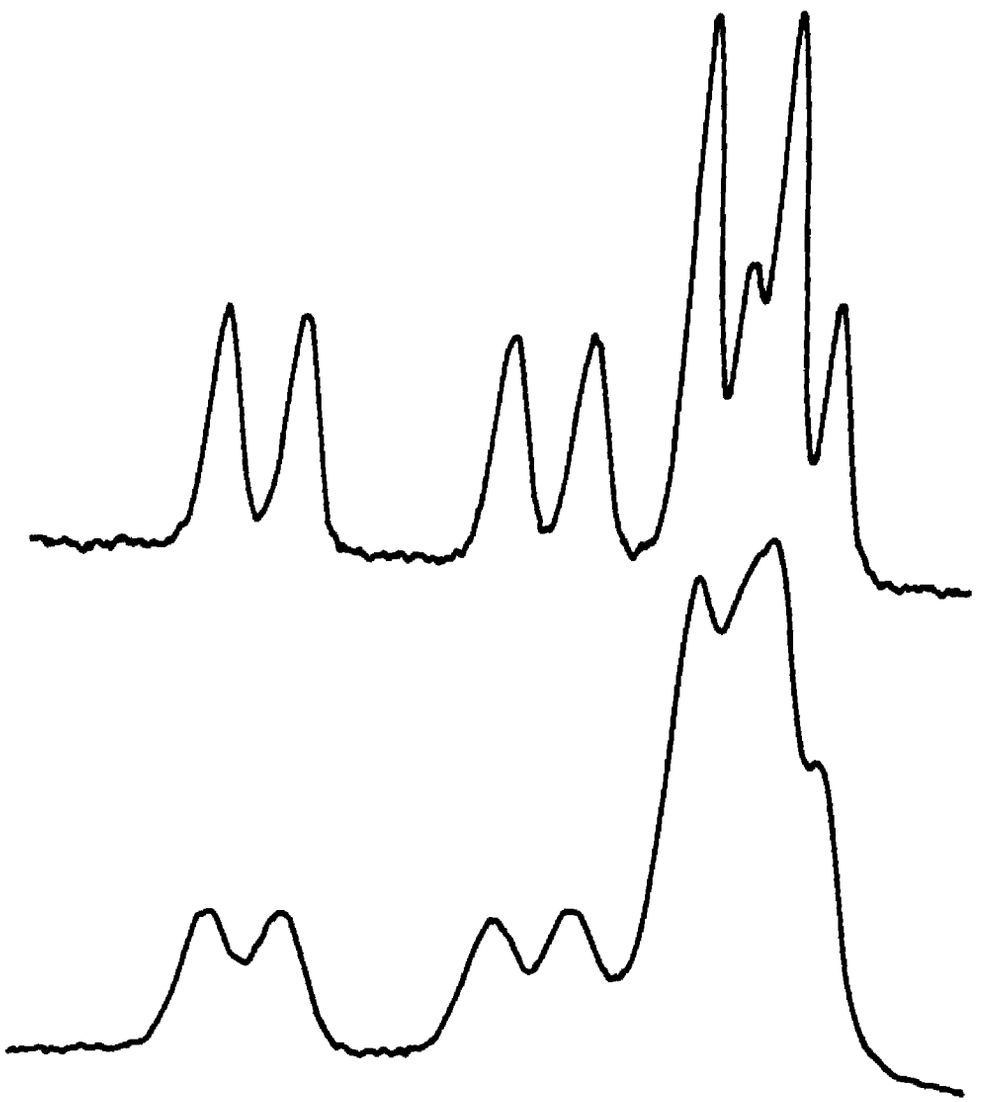

Figure 3. ^{11}B NMR Spectra of o-Carborane at 80.2 MHz.

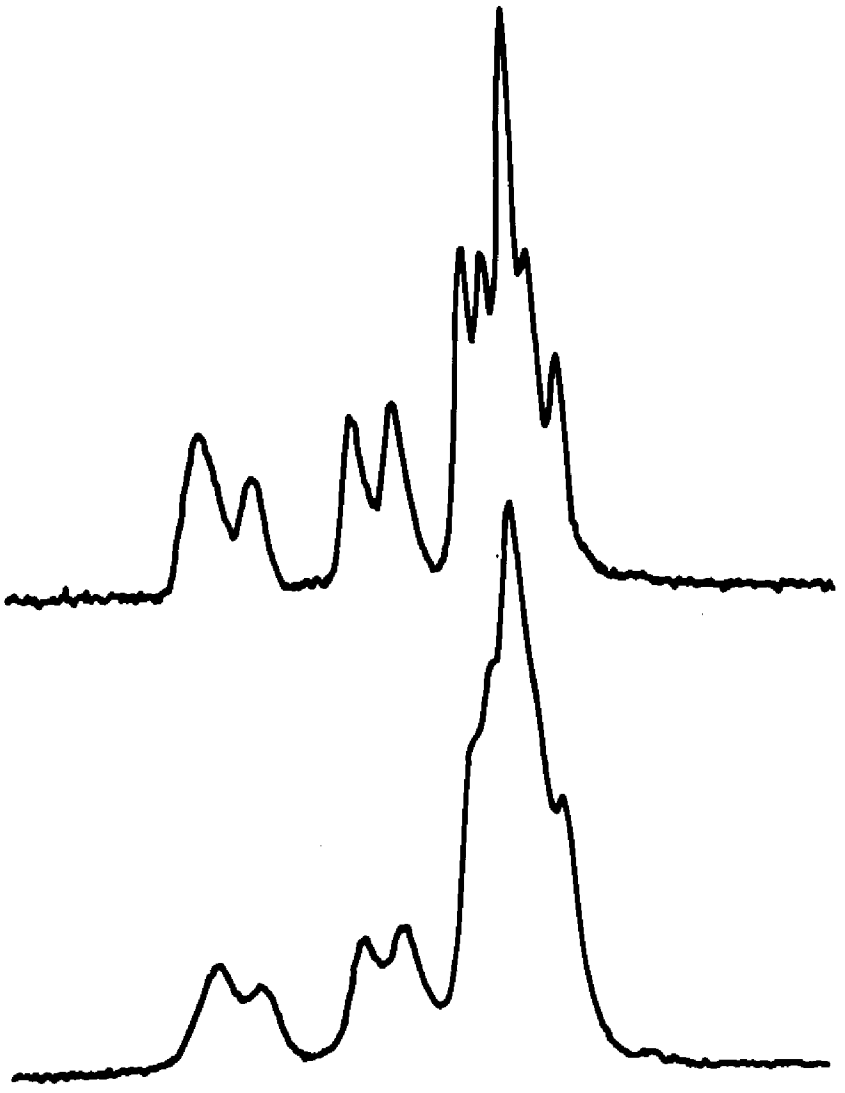

Figure 4. ^{11}B NMR Spectra of 9-Bromo-o-Carborane at 80.2 MHz.

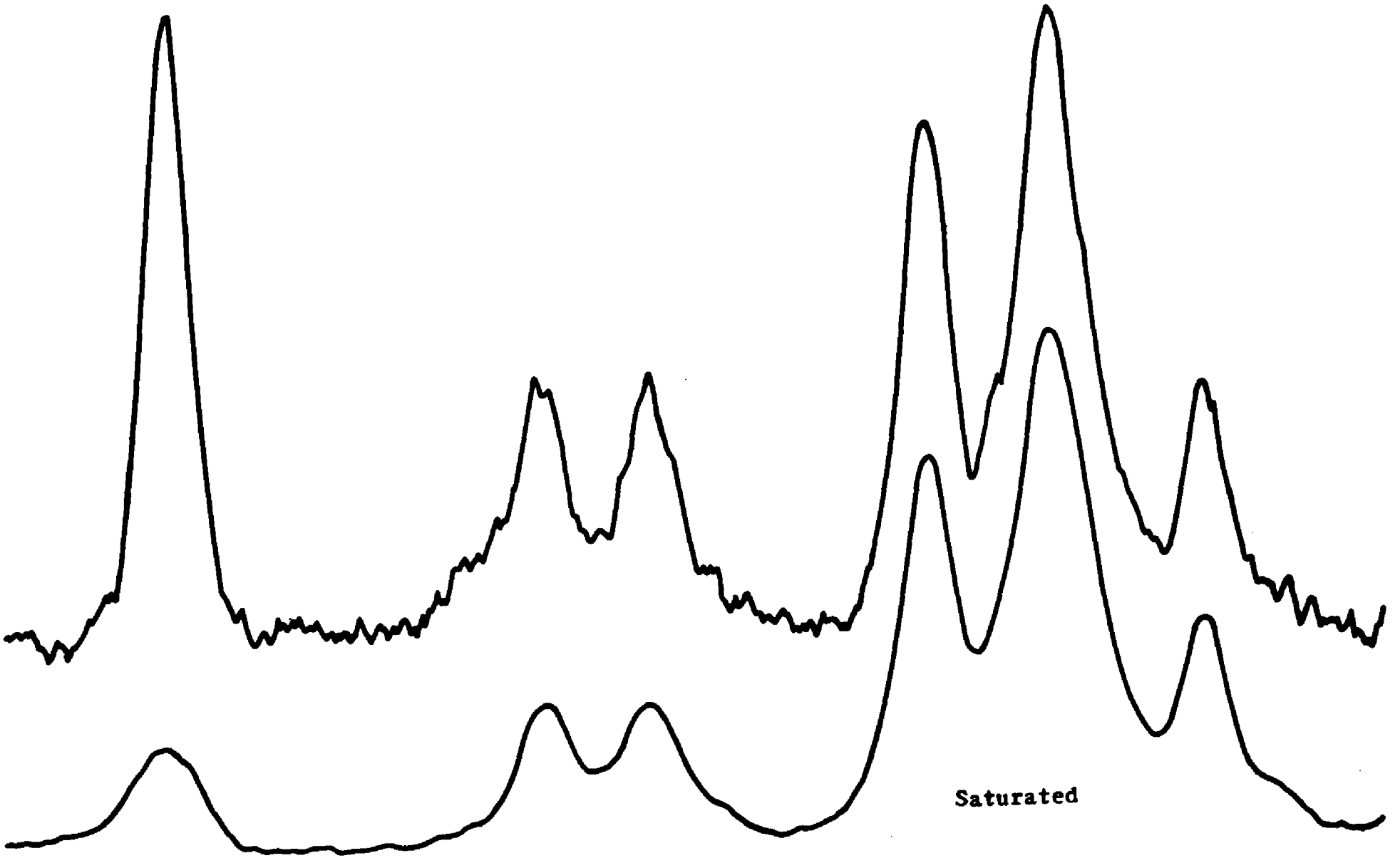

Figure 5. ^{11}B NMR Spectra of 9,12-Dibromo-o-Carborane at 80.2 MHz.

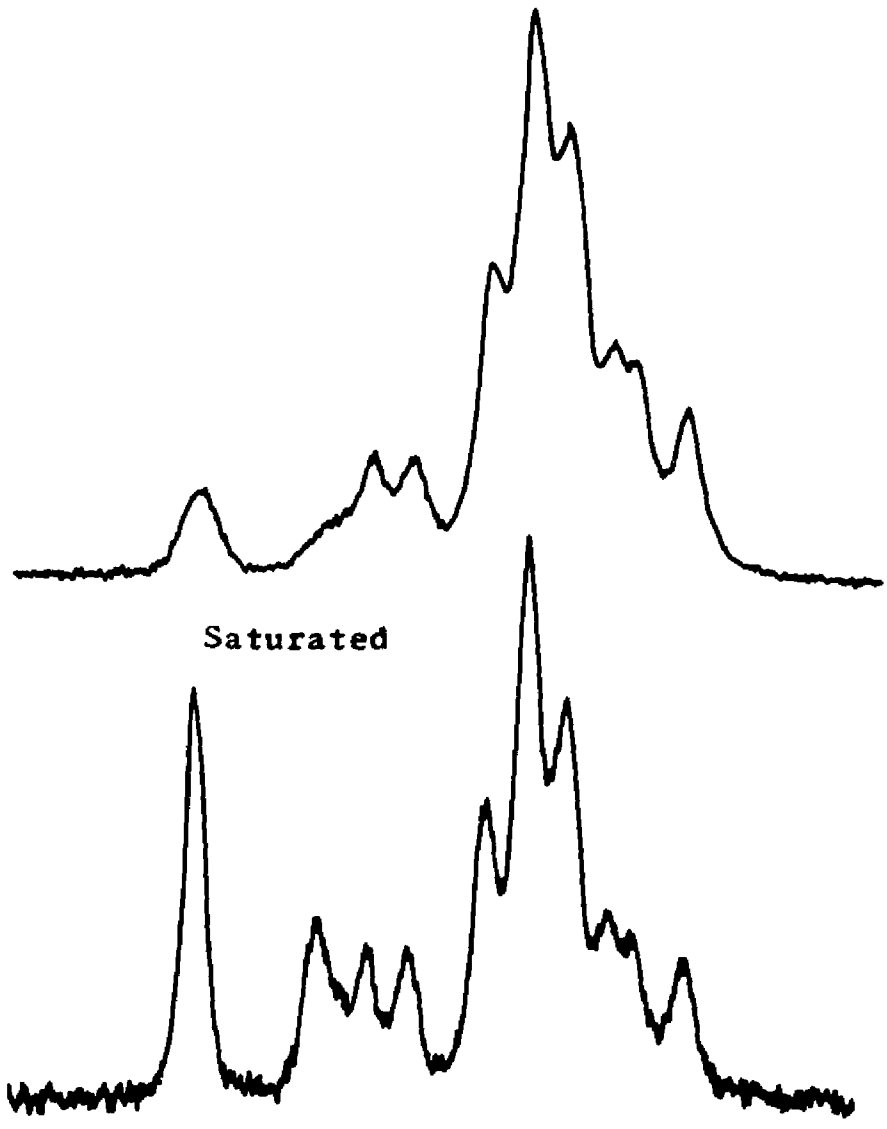

Figure 6. ^{11}B NMR Spectra of 8,9,12-Tribromo-o-Carborane at 80.2 MHz.

(8,10) boron atoms, and that of the (3,6) boron atoms, is not affected by the substitution. The spectrum shows four doublets of relative area two, in addition to the singlet and doublet of relative area one each at lowest field. The spectrum shows a slight downfield shift for the (8,10) boron atoms, no change in the average chemical shift of the two doublets assigned to the (4,5,7,11) borons, and a slight upfield shift of the (3,6) boron atoms.

Substitution at the (9,12) boron atoms does not change the symmetry of the molecule, and the spectrum, Figure 5, shows three doublets, of relative areas 2:4:2, in addition to the singlet of relative area two at lowest field. The high field doublet of relative area two overlaps the doublet of relative area four. For this reason, there is one less peak visible in the spectrum than was expected. The downfield shift of the (8,10) boron atom doublet, at + 26.5 ppm, has increased with the substitution of a second bromine atom. An upfield shift of the (4,5,7,11) boron atom doublet, and a further increase in the upfield shift of the (3,6) boron atom doublet observed in the 9-bromo-o-carborane spectrum is also apparent. The changes in coupling constants for 9-bromo-o-carborane, and for 9,12-dibromo-o-carborane, given in Table II, are not considered to be significant because they are within $\pm$ 2 Hz which is the error associated with the determination of peak centers.

Figure 6 presents the ^{11}B NMR spectrum of 8,9,12-tribromo-o-carborane. Substitution at the 8 position reduces the symmetry of the molecule. The symmetrical equivalence of the (9,12) boron atoms is not affected. However, the (4,7) boron atoms are no longer

symmetrically equivalent to the (5,11) boron atoms, nor is the (3) boron atom symmetrically equivalent to the (6) boron atom. The spectrum is expected to show, in order of increasing field, a singlet of relative area two at lowest field, a singlet of relative area one, a doublet of relative area one, two doublets of relative areas two, and two doublets of relative areas one.

The spectrum does show a singlet of relative area two at + 19.1 ppm, assigned to the (9,12) boron atoms, a singlet of relative area one at + 24.4 ppm, assigned to 8(10) boron atom, a doublet of relative area one at + 27.8 ppm with J_{BH} = 160 Hz, assigned to the 10(8) boron atom, two doublets of relative areas two at + 31.7 ppm and + 36.0 ppm, respectively, and with J_{BH} = 168 Hz for both, assigned to the 4,7(5,11) and 5,11(4,7) boron atoms, and two doublets of relative areas one, at + 36.7 ppm and + 40.3 ppm with J_{BH} = 192 Hz for both, assigned to the 3(6) and 6(3) boron atoms.

We are confident of our assignment of the (8,10) boron atoms because the chemical shift changes upon bromine substitution in the mono- and dibromo-o-carborane spectra discussed above were small. In addition, the changes in coupling constants observed in the spectrum of 8,9,12-tribromo-o-carborane are all increases. It would be extremely difficult to rationalize a change in coupling constant for the 3(6) boron atom of - 18 Hz, a change in coupling constant for the 10(8) boron atom of + 40 Hz, a downfield shift of the 3(6) boron atom of 9 ppm from the chemical shift found for the highfield doublet in the spectrum of 9,12-dibromo-o-carborane, and an upfield shift of the 10(8) boron atom of 16 ppm from the chemical shift found for the low-

field doublet in the spectrum of 9,12-bromo-o-carborane. These changes are contrary to the trends observed for bromine substitution at the 9 and 12 positions of o-carborane.

Comparing the ^{11}B NMR spectra of the three bromo-o-carboranes with that of o-carborane enables us to assign unequivocally the ^{11}B NMR spectrum of o-carborane. The four doublets observed in the o-carborane spectrum are assigned as follows: the (9,12) boron atoms are assigned to the doublet at + 21.1 ppm with J = 151 Hz; the (8,10) boron atoms are assigned to the doublet at + 28.0 ppm with J = 151 Hz; the (4,5,7,11) boron atoms are assigned to the doublet at + 32.5 ppm with J = 163 Hz; and the (3,6) boron atoms are assigned to the doublet at + 33.7 ppm with J = 178 Hz. Using this assignment as a basis, we shall proceed to the interpretation of the ^{11}B NMR spectra of the other substituted o-carboranes studied.

3.12 Ortho Carborane Derivatives

3.121 Halogenated Ortho Carborane Derivatives. Figure 7 presents the ^{11}B NMR spectrum obtained for 8,9,10,12-tetrachloro-o-carborane. There is an impurity believed to be trichloro-o-carborane. The two singlets of relative areas two, at + 13.17 ppm and +19.23 ppm, are assigned to the (9,12) and (8,10) boron atoms, respectively. The chemical shift changes observed relative to those found in o-carborane are in the direction found with the bromo-o-carboranes, although larger. The same trends are observed upon comparison of ^{11}B NMR spectra of bromo- and chloro-decaborane(14) with the ^{11}B NMR spectra of decaborane(14).[1,2]

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[1] M. Hillman and D. J. Mangold, Inorg. Chem. 4, 1357 (1965).

[2] R. Schaeffer, J. N. Shoolery, and R. Jones, J. Am. Chem. Soc. 80, 2670 (1958).

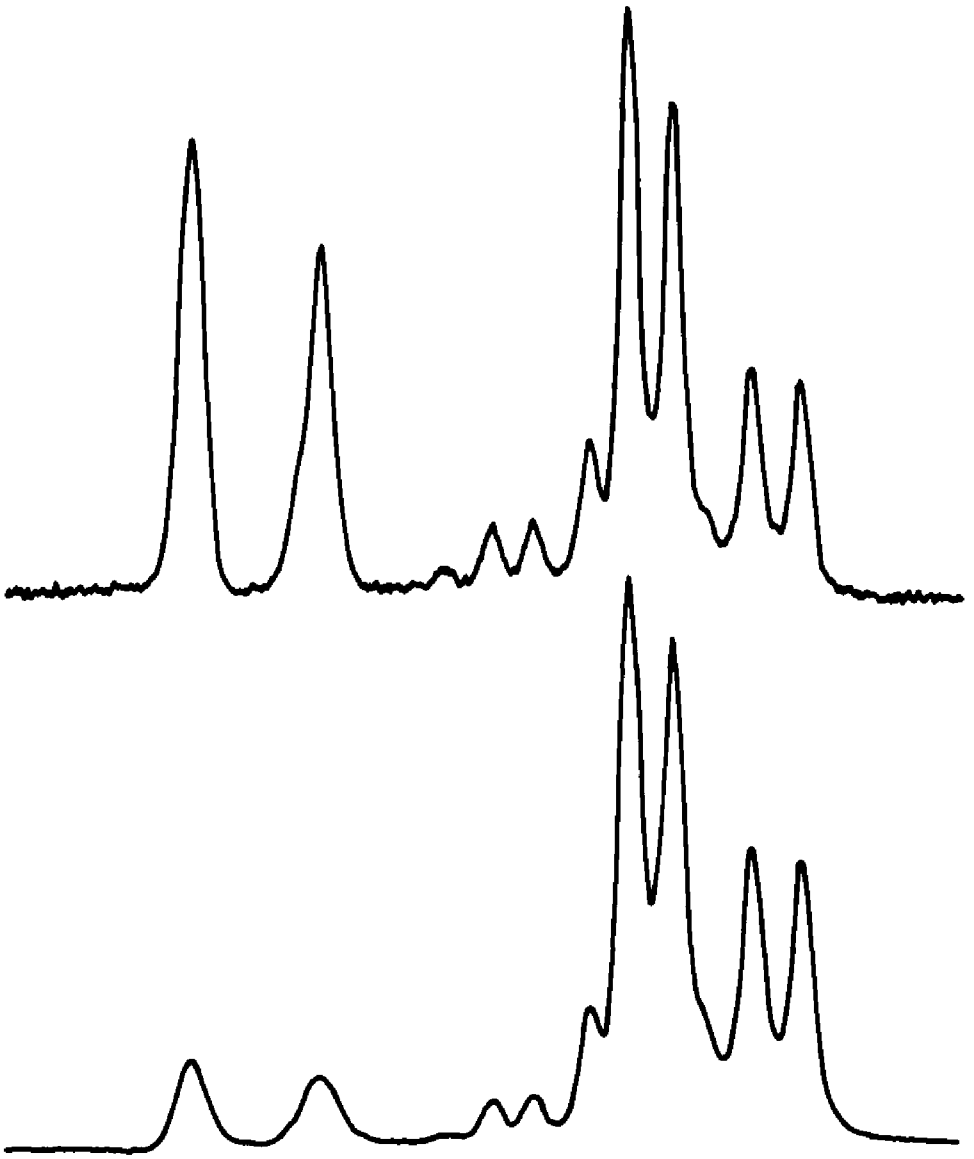

Figure 7. ^{11}B NMR Spectra of Tetrachloro-o-Carborane at 80.2 MHz.

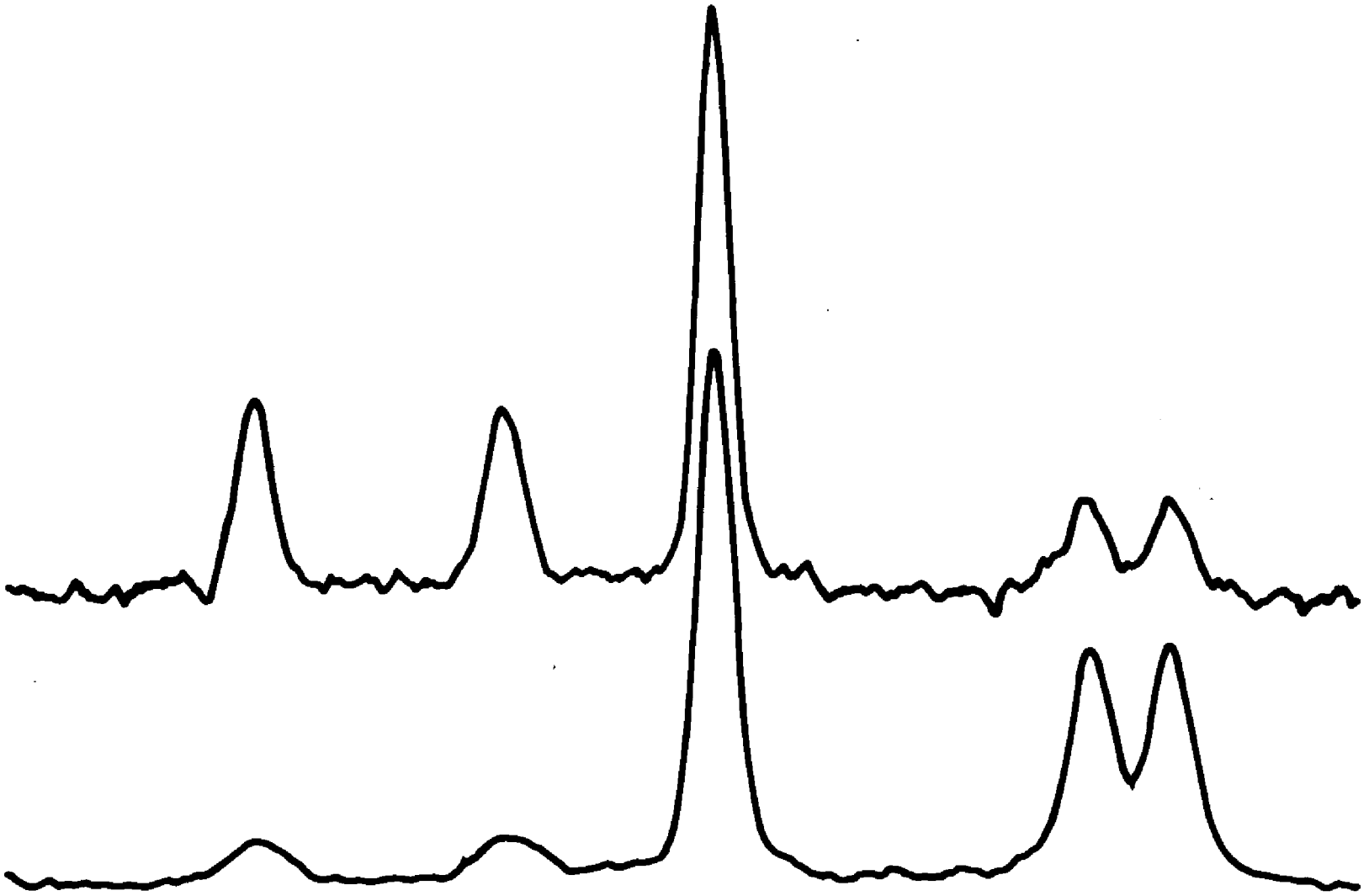

Figure 8. ^{11}B NMR Spectra of Octachloro-o-Carborane at 80.2 MHz.

No transposition of the relative positions of the chemical shifts of the (9,12) and (8,10) boron atoms in the bromo-carboranes was observed and is not expected upon chlorine substitution.

The doublet of relative area four at + 34.7 ppm with J_{BH} = 162 Hz is assigned to the (4,5,7,11) boron atoms, and the doublet of relative area two, at + 41.1 ppm with J_{BH} = 188 Hz is assigned to the (3,6) boron atoms. Both doublets are shifted upfield relative to the chemical shifts observed for them in o-carborane. In addition, the $^{11}B-^{1}H$ coupling constant of the (3,6) boron atoms has increased. These observations are consistent with the trends observed with the bromo-o-carboranes.

The interpretation of the octachloro-o-carborane spectrum shown in Figure 8 is straight forward. All boron atoms are chlorine substituted except the (3,6) boron atoms. The spectrum shows a singlet of relative area two at + 16.1 ppm, assigned to the (9,12) boron atoms, a singlet of relative area two at + 24.0 ppm, assigned to the (8,10) boron atoms, a singlet of relative area four at + 29.6 ppm, assigned to the (4,5,7,11) boron atoms, and a doublet of relative area two at + 41.9 ppm with J_{BH} = 196 Hz, assigned to the (3,6) boron atoms.

The substitution of chlorine for hydrogen causes a large downfield shift of the boron atoms substituted relative to the chemical shifts observed for o-carborane. There is also a significant increase in the $^{11}B-^{1}H$ coupling constant of the (3,6) boron atoms. Bromine and chlorine are more electronegative than hydrogen, and are expected to have some effect upon the circulation of the electron cloud within

the carborane cage, and some effect upon the distribution of electronic charge. Theory is not advanced enough to predict the extent of these changes, nor what effect they may have upon the NMR spectrum.

In contrast to bromine or chlorine substitution, iodine substitution on decaborane(14) causes an upfield shift.[1] This is expected to occur in iodo-o-carborane. The ^{11}B NMR spectrum of 9,12-diiodo-o-carborane given in Figure 9 is deceptively simple. Only five peaks are observable, with relative areas 1:1:2:5:1. The two peaks of relative areas one each at lowest field form a doublet of area two at + 24.7 ppm with J_{BH} = 158 Hz. This doublet is assigned to the (8,10) boron atoms because the coupling constant and chemical shift are similar to the coupling constants and chemical shifts found for the (8,10) boron atoms in o-carborane and the three bromo-o-carboranes.

Substitution of iodine atoms at the 9 and 12 boron atoms will not affect the symmetry of the molecule. The (4,5,7,11) boron atoms will therefore produce a doublet of relative area four. One half of this doublet is visible in the peak of relative area two; the other half must be part of the peak of relative area five. The (3,6) will produce a doublet of relative area two. The highfield peak of relative area one is one-half of this doublet. The other half must be part of the peak of relative area five. Subtracting a relative

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[1] R. Schaeffer, J. N. Shoolery, and R. Jones, J. Am. Chem. Soc. 80, 2670 (1958).

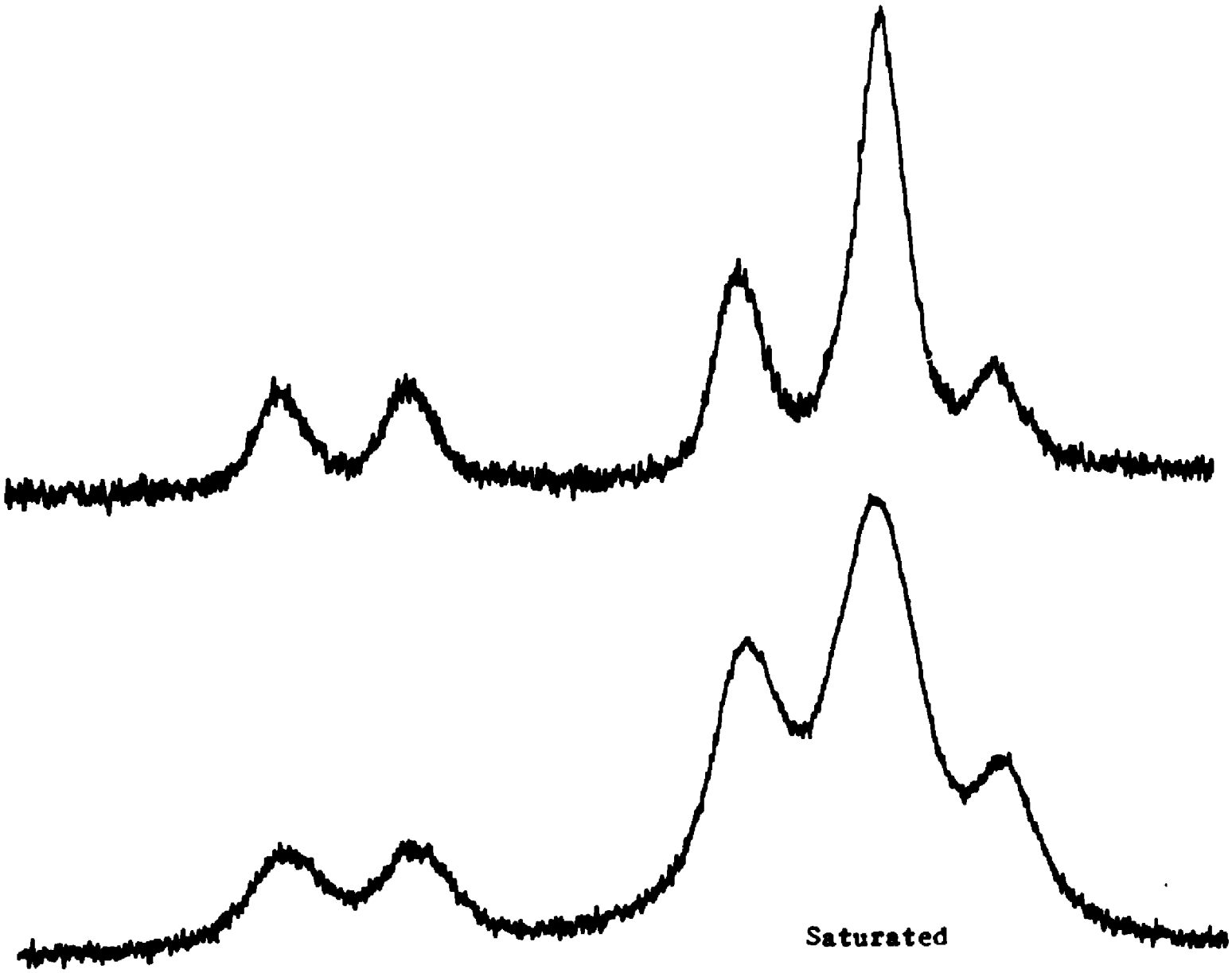

Figure 9. ^{11}B NMR Spectra of 9,12-Diiodo-o-Carborane at 80.2 MHz.

area two and a relative area one from this peak of relative area five to represent the overlapped halves of these two doublets, leaves a singlet of relative area two which is assigned to the (9,12) boron atoms which were iodine substituted.

The overlap of one-half of the doublet of relative area four with one-half of the doublet of relative area two and with the singlet of relative area two prevents an accurate determination of the coupling constants. The chemical shifts given in Table II were obtained assuming J_{BH} = 165 Hz for the (4,5,7,11) boron atoms and J_{BH} = 178 Hz for the (3,6) boron atoms. These coupling constants do fit the observed spectrum; changing the coupling constants by as much as 16 Hz will change the chemical shift by only 0.1 ppm. This is an estimated upper limit of the error in the chemical shift resulting from the uncertainty in determination of the center of overlapped peaks.

Stanko, et al.,[1] assigned the (9,12) boron atom reasonance of the ^{1}H double irradiated 32.1 MHz ^{11}B NMR spectrum of 9,12-diiodo-o-carborane to the peak at + 24.0 ppm. They argued that the (8,10) boron atom resonance was shifted far upfield due to overlap of the $p\pi$ orbitals of iodine with the π orbitals of the (8,10) boron atoms. Their assignment is incorrect. Substitution of iodine at the (9,12) boron atoms causes a downfield shift of the (8,10) boron atom resonance and a large upfield shift of the (9,12) boron atom resonance.

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[1] V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, Zh. Strukt. Khim. 11, 627 (1970).

3.122 Carbon-Substituted Ortho Carborane Derivatives. Substitution at the 1 position of o-carborane reduces the symmetry of the molecule. The 9 boron atom is no longer symmetrically equivalent to the 12 boron atom, and the (4,5) boron atoms are not symmetrically equivalent to the (7,11) boron atoms. The symmetrical equivalence of the (8,10) boron atoms, and of the (3,6) boron atoms, is not affected. The ^{11}B NMR spectrum of 1-substituted o-carborane is expected to show two doublets of relative area one at lowest field, due to the 9,12 boron atoms, and four doublets of relative areas two each.

The ^{11}B NMR spectra of 1-bromomethyl-o-carborane, 1-methyl-o-carborane, and 1-vinyl-o-carborane are given in Figures 10, 11, and 12, respectively. All three show two doublets of relative areas one at lowest field. In the spectrum of 1-methyl-o-carborane, one of the doublets of area one is clearly visible at + 21.0 ppm with J_{BH} = 154 Hz. The spectra of 1-bromomethyl-o-carborane and 1-vinyl-o-carborane show the overlap of the two lowfield doublets of relative areas one each into an apparent triplet. The central peak is broad compared to the two wings of this apparent triplet. This indicates that the triplet is actually two overlapping doublets. The ^{11}B-^{1}H coupling constants for the (9,12) boron atoms in these two cases, 1-vinyl-o-carborane and 1-bromomethyl-o-carborane, cannot be determined accurately. They were assumed to be 151 Hz, and the chemical shifts calculated accordingly.

As discussed above, large changes in coupling constants, which are not observed in J_{BH} for the 9(12) boron atom in 1-methyl-o-carborane, have no effect upon the chemical shift, within experimental error. Therefore, we have confidence in the chemical shifts calculated

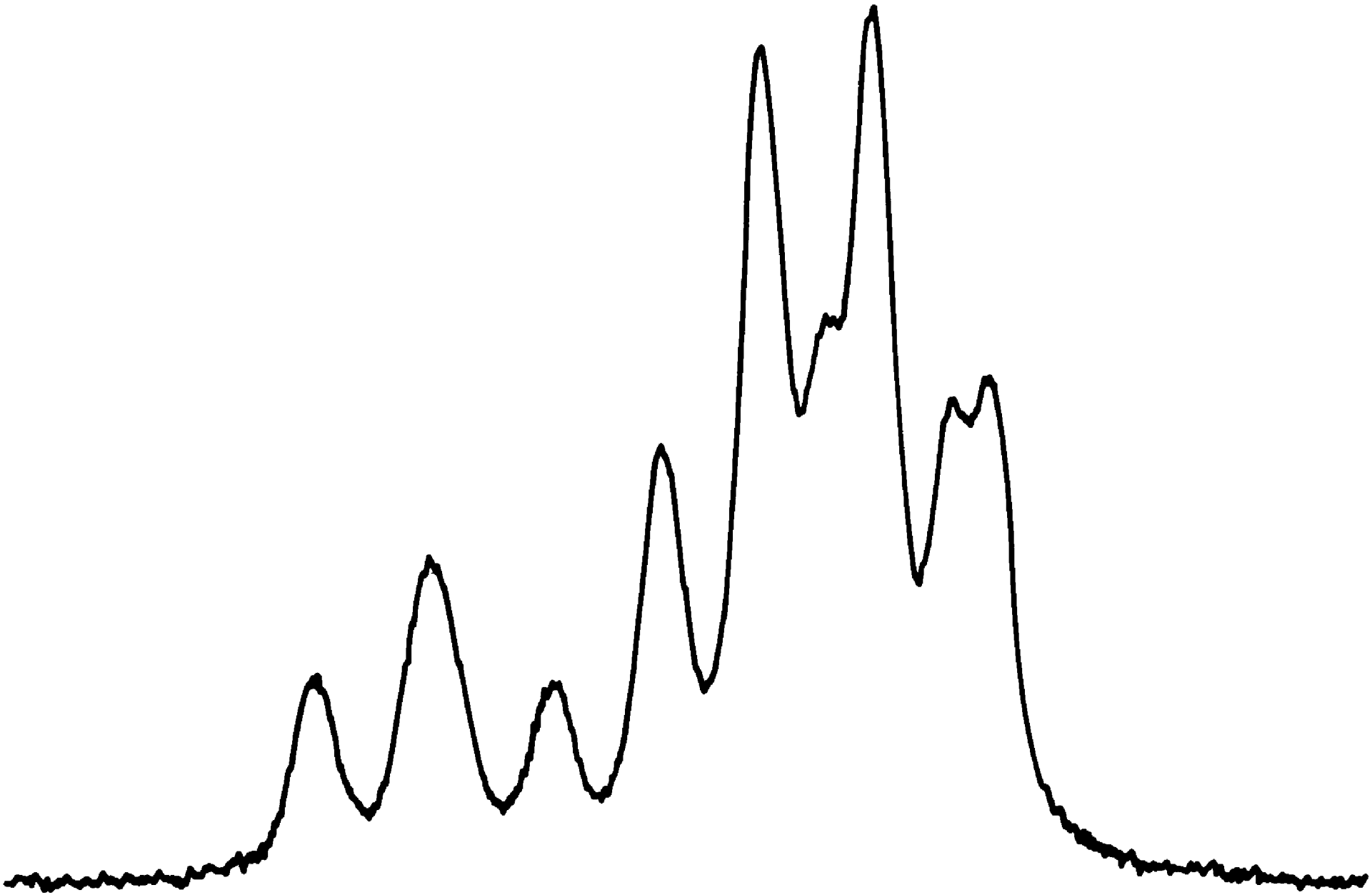

Figure 10. ^{11}B NMR Spectrum of 1-Bromomethyl-o-Carborane at 80.2 MHz.

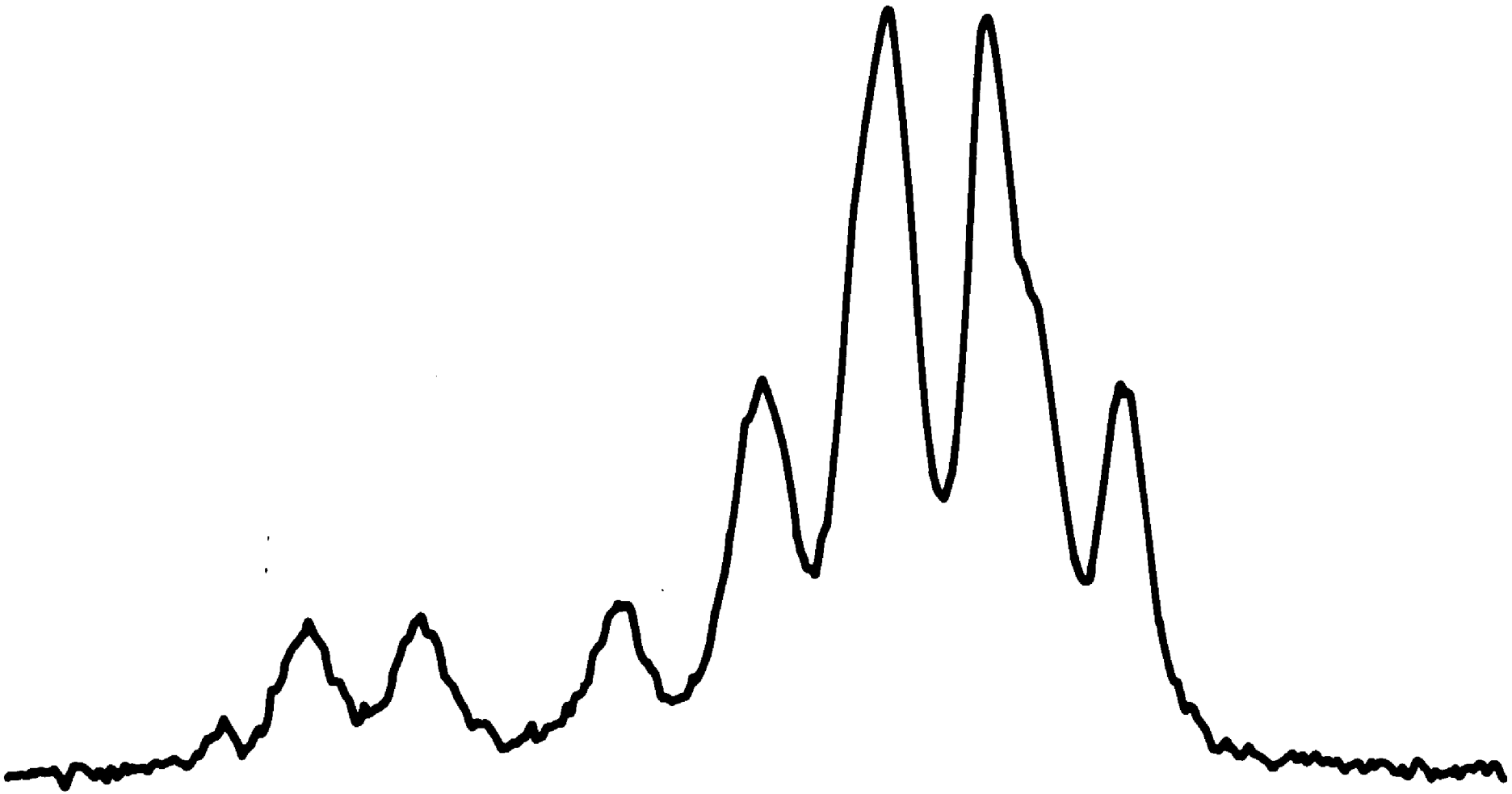

Figure 11. ^{11}B NMR Spectrum of 1-Methyl-o-Carborane at 80.2 MHz.

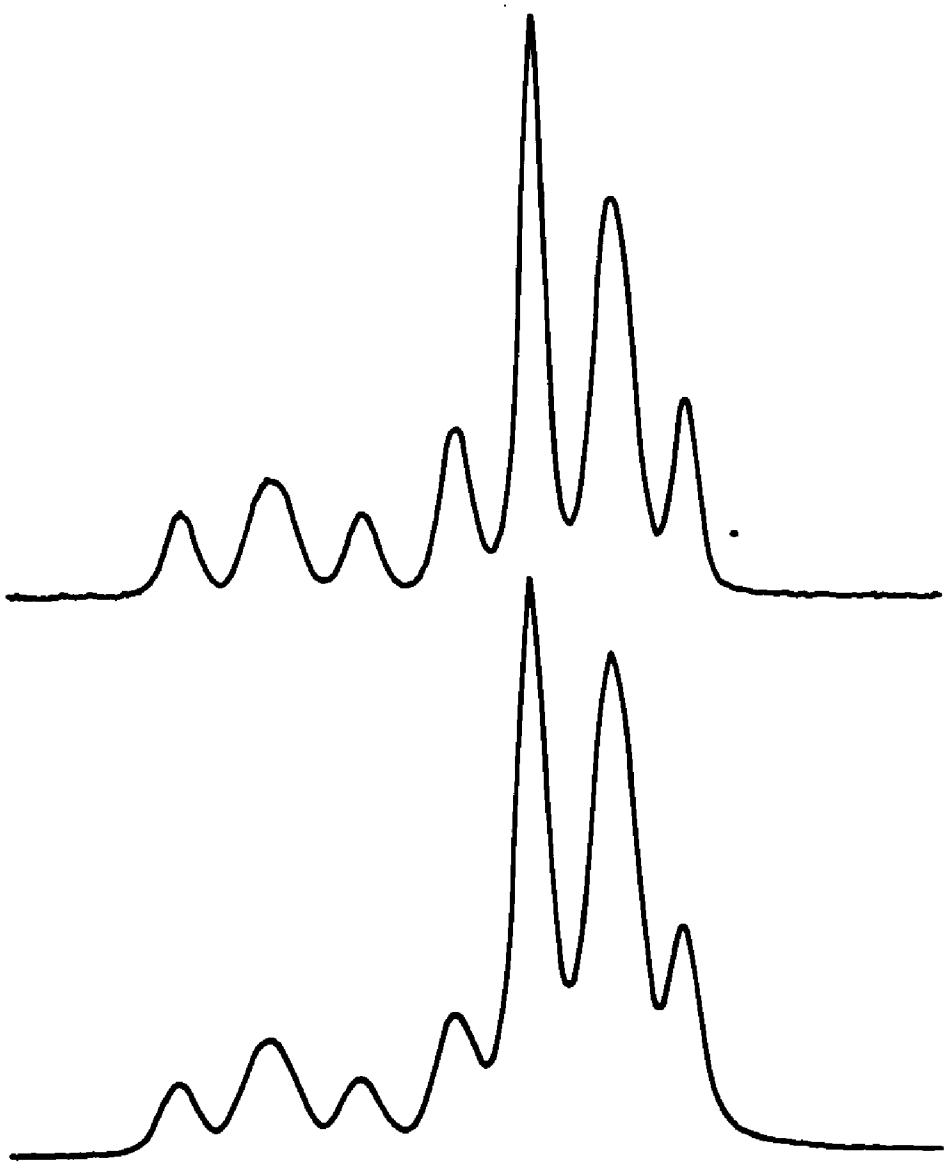

Figure 12. ^{11}B NMR Spectra of 1-Vinyl-o-Carborane at 80.2 MHz.

and reported in Table II for the 9 and 12 boron doublets.

The assignment of the remaining four doublets of relative areas two in these three spectra is not as straightforward. The doublet appearing at + 27.9 ± 0.2 ppm in all three spectra is assigned to the (8,10) boron atoms. This doublet appears at + 28.0 ppm in the o-carborane spectrum. The chemical shift of this doublet was calculated assuming no change in J_{BH} from that found for this doublet in o-carborane.

The remaining three doublets, each of relative area two, show extensive overlap in all three spectra, and we shall therefore consider this region in each spectrum in detail.

The spectrum of 1-bromomethyl-o-carborane shows the most detail in this region. The two peaks which are separated by 178 ± 4 Hz are <u>not</u> at highest field. The centers of the two tallest peaks are separated by 160 ± 4 Hz, the center of the highest-field peak is 165 ± 4 Hz from the center of one of these two tallest peaks.

Therefore, we assign the ^{11}B NMR spectrum of 1-bromomethyl-o-carborane as follows: the 9(12) boron atom is assigned to the doublet at + 21.5 ppm with J_{BH} = 151 Hz; the 12(9) boron atom is assigned to the doublet at + 23.8 ppm with J_{BH} = 151 Hz, the (8,10) boron atoms are assigned to the doublet of + 27.7 ppm with J_{BH} = 151 Hz; the 4,5(7,11) boron atoms are assigned to the doublet at + 29.5 ppm with J_{BH} = 163 Hz; the (3,6) boron atoms are assigned to the doublet at + 30.7 ppm with J_{BH} = 178 Hz; and the 7,11(4,5) boron atoms are assigned to the doublet at + 31.5 ppm with J_{BH} = 163 Hz. All coupling constants were assumed to be the same as were found in o-carborane.

The ^{11}B-^{1}H coupling constant of the 9(12) boron atom in 1-methyl-o-carborane could be determined and was found to be 154 Hz, a change within the experimental error in J_{BH}. The ^{11}B-^{1}H coupling constant of the (9,12) boron atoms in the spectrum of 1,2-dimethyl-o-carborane, discussed below, could also be determined and was found to be 151 Hz.

An alternate assignment of these three upfield doublets is possible. However, it involves the assumption that J_{BH} for the (4,5, 7,11) boron atoms increases by 8 to 10 Hz at the same time that J_{BH} for the (3,6) boron atoms decreases by 8 to 10 Hz. This assumption would maintain the order of chemical shifts the same as found in o-carborane. The spectrum is narrower than the o-carborane spectrum, and the (4,5) and (7,11) boron atoms are split. It appears reasonable to maintain coupling constant changes small because the changes, where directly observable, are small.

The spectrum of 1-methyl-o-carborane is not as clear. The assignments for the (4,5,7,11) and (3,6) boron atoms given in Table II were made assuming that the spectrum should be similar to that of 1-bromomethyl-o-carborane. This assumption, with $J_{BH} = 163 \pm 2$ Hz for the (4,5,7,11) boron atoms and $J_{BH} = 178 \pm 2$ Hz for the (3,6) boron atoms, does fit the observed spectrum. However, the assumption that the (4,5) and (7,11) boron doublets lie below the doublet due to the (3,6) boron atoms, and with the ^{11}B-^{1}H coupling constants as above, also fits the data.

The ^{11}B NMR spectrum of 1-vinyl-o-carborane shows only seven peaks of relative areas 0.5:1:0.5:1:3:3:1. The three low-field peaks

form an apparent triplet, actually two overlapping doublets, and has been assigned above to the 9 and 12 boron atoms. The central peak of the seven, of relative area one, was assigned above as one-half of the doublet of relative area two due to the (8,10) boron atoms. The other half appears as one-third of the sharp peak of relative area three. The sharpness of this peak must result from coincidental overlap of one-half of three different doublets of relative area two. One of these doublets has been assigned: the (8,10) boron doublet. If the other two doublets are the (4,5) and (7,11) doublets, then these two would coincide exactly because J_{BH} should be the same for the (4,5) and (7,11) doublets. This would mean that the vinyl group substituted at the 1 position does not split the (4,5,7,11) boron atoms, as expected, but does split the (9,12) boron atoms. The alternate assignment is given in Table II. This assignment does maintain coupling constants to $\pm$ 2 Hz, and does split the (4,5) and (7,11) boron atoms, as well as the (9,12) boron atoms.

The spectra of the three 1-substituted o-carboranes cannot be assigned unequivocally. The (9,12) and (8,10) boron atoms can be assigned unequivocally, but the remaining three doublets cannot. The assignments given in Table II are each only one possible assignment. Of the three, we are most confident of the assignment of the spectrum of 1-bromomethyl-o-carborane because the peaks are most discernable, and coupling constants accurate to $\pm$ 4 Hz can be obtained.

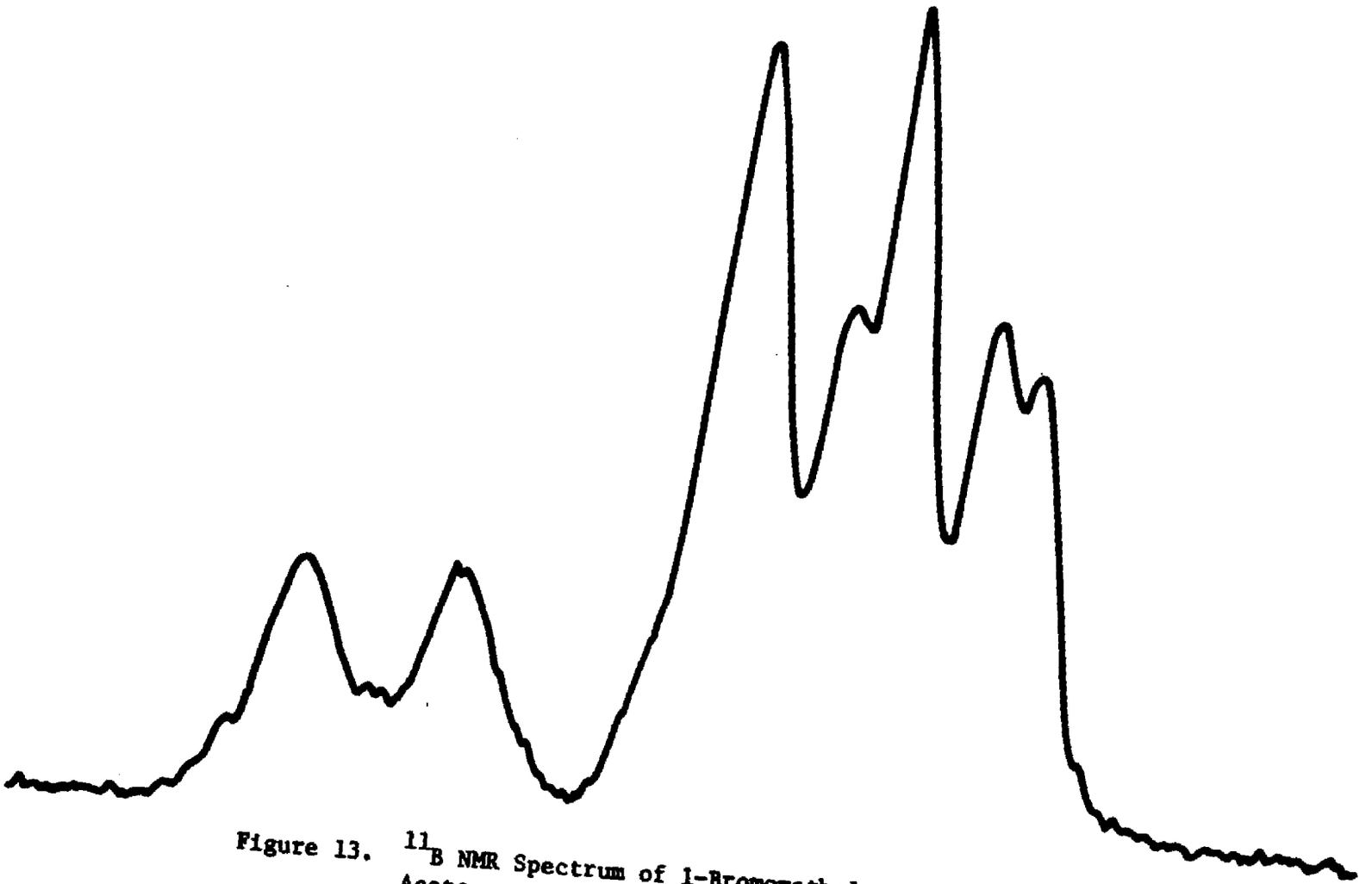

Figure 13. ^{11}B NMR Spectrum of 1-Bromomethyl-o-Carborane-d_4 in Acetone at 80.2 MHz.

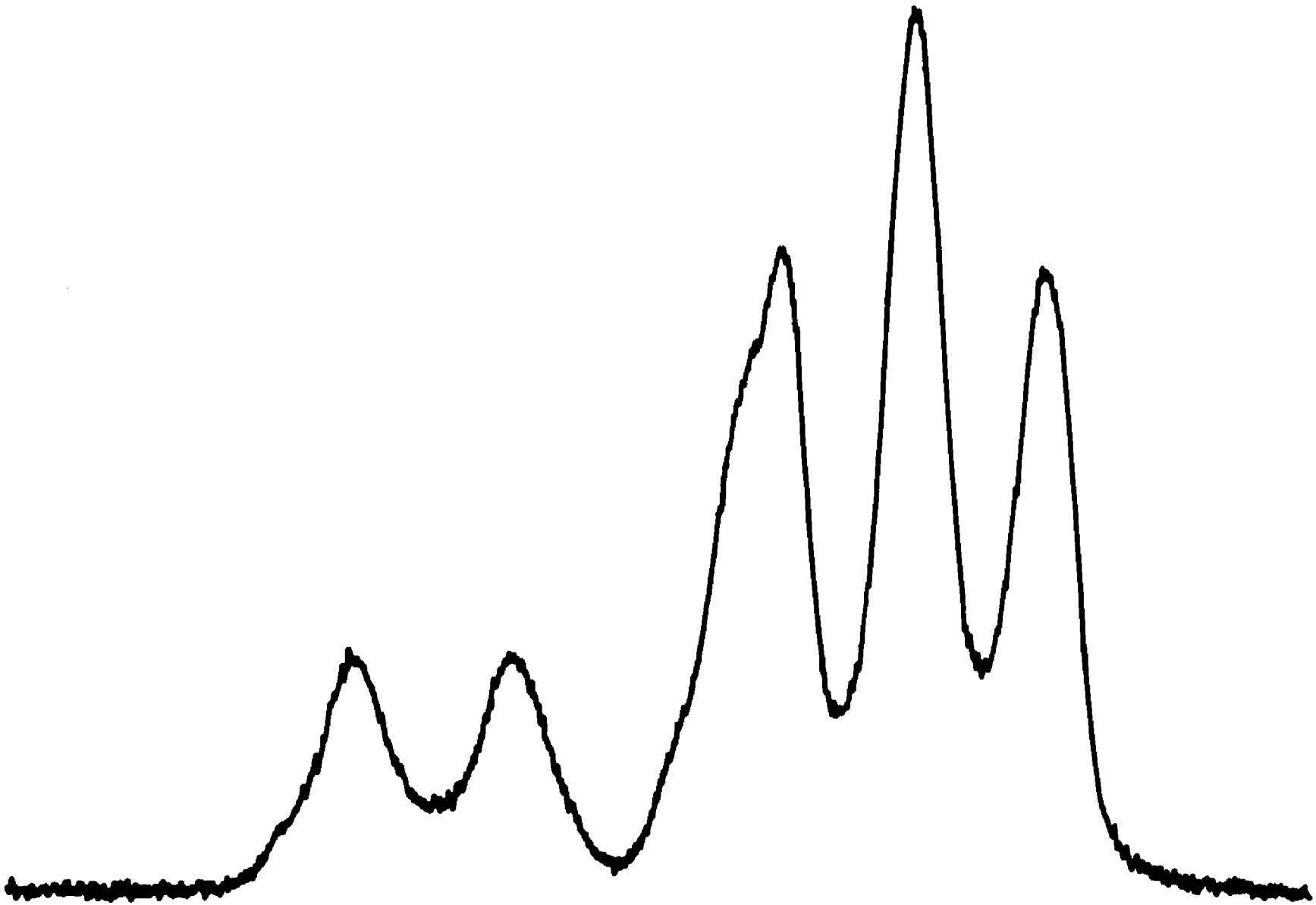

Figure 14. ^{11}B NMR Spectra of 1-Bromomethyl-o-Carborane-d_4 in Deuterochloroform at 80.2 MHz.

8,9,10,12-d_4-1-bromomethyl-o-carborane was prepared from 1,2,3,4-d_4-decaborane(14) by a literature preparation.[1] The ^{11}B NMR spectrum of 8,9,10,12-d_4-1-bromomethyl-o-carborane in acetone is given in Figure 13. The two lowfield doublets of area one each have collapsed to two singlets of area one each, at + 21.4 ppm and + 23.7 ppm. In addition, the doublet of area two at + 27.7 ppm has disappeared. A singlet of area two is expected at + 27.7 ppm; this position is just to the left of the tall peak at + 28.1 ppm, and is not discernable as a separate peak although relative area studies demonstrate its presence. The remainder of the spectrum is exactly like the spectrum of undeuterated 1-bromomethyl-o-carborane.

The effect of a solvent change can be seen by comparison of the spectrum of 8,9,10,12-d_4-1-bromomethyl-o-carborane in acetone, Figure 13, with the spectrum of the same compound in deuterochloroform, Figure 14. The 9 and 12 boron atoms appear as singlets at + 21.5 ppm and + 24.1 ppm. The singlet due to the (8,10) boron atoms is now visible as a shoulder and appears at + 27.9 ppm. The remaining three doublets of relative area two overlap to give an apparent triplet. The relative areas of the triplet indicate that the (3,6) and 7,11(4,5) boron atom doublets almost exactly coincide; the 4,5(7,11) boron atom doublet is at lower field than these two doublets. The alternate assignment is that the (4,5,7,11) doublet of area four is not split into two doublets of area two and that

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[1] E. L. Muetterties, Inorganic Synthesis, Vol. X, McGraw-Hill Book Company, New York, San Francisco, Toronto, London, Sydney, 1967, p. 100.

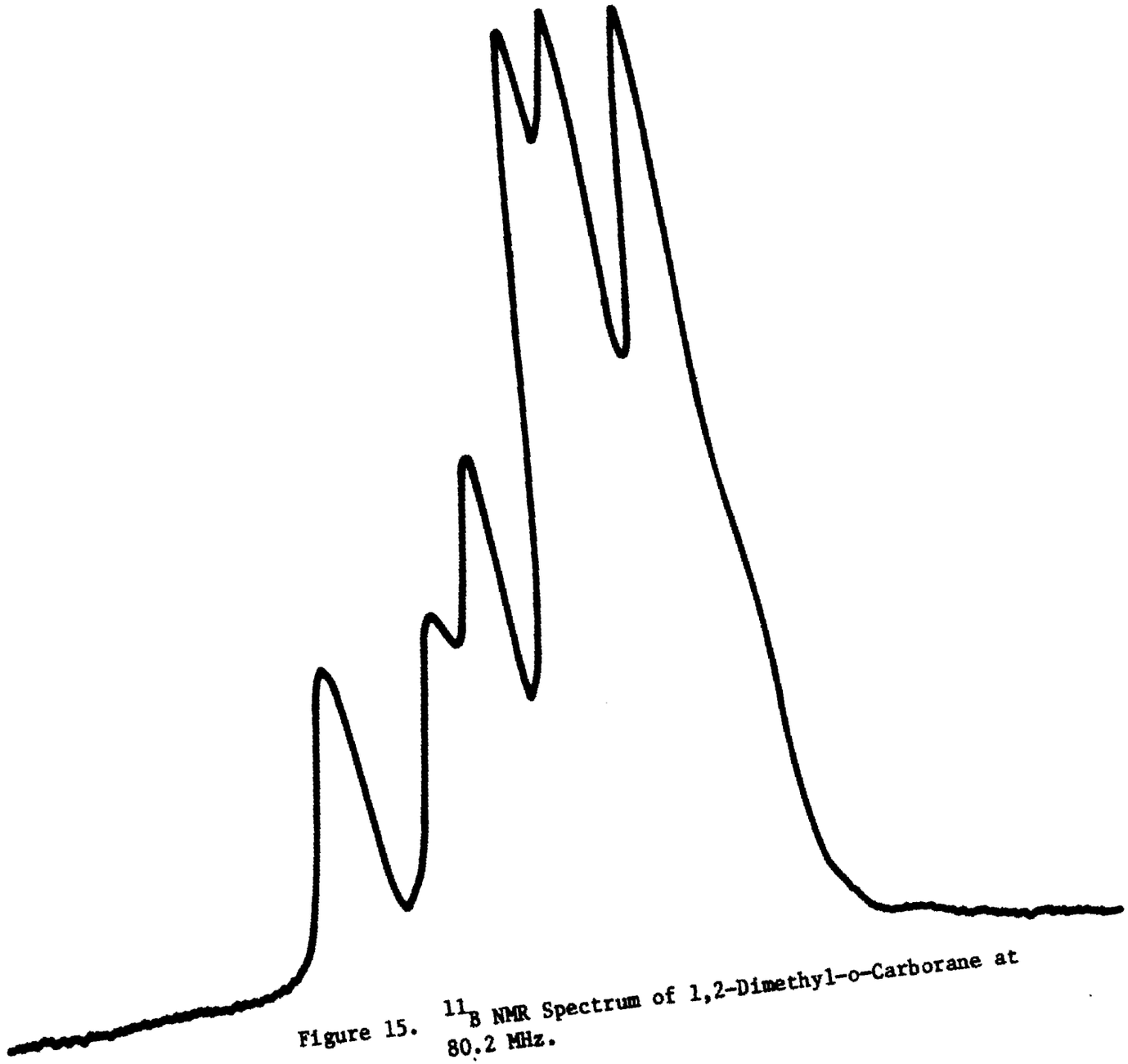

Figure 15. ^{11}B NMR Spectrum of 1,2-Dimethyl-o-Carborane at 80.2 MHz.

it appears at higher field than the (3,6) boron atom doublet. A more complete assignment of the 1-substituted o-carboranes awaits further work.

Substitution of a methyl group on each of the carbons of o-carborane results in a considerable compression of the ^{11}B spectrum which is shown in Figure 15. The entire spectrum covers only 5 ppm, and there is extensive overlap. The symmetry of the molecule has not been affected by substitution on both of the carbons, and no transposition of chemical shifts is expected. The doublet of area two at + 24.4 ppm with J_{BH} = 151 Hz is assigned to the (9,12) boron atoms. The doublet due to the (8,10) boron atoms overlaps the remainder of the spectrum too much for the coupling constant to be accurately measured. Assuming it to be 151 $\pm$ 2 Hz, the chemical shift is + 27.8 ppm. This is very close to that found for the (8,10) boron atoms in the o-carborane spectrum. The (4,5,7,11) boron atoms are assigned to the doublet of area four at + 28.7 ppm with J_{BH} = 163 $\pm$ 4 Hz assumed. The (3,6) boron atoms are assigned to the doublet of area two at + 29.5 ppm with J_{BH} = 178 $\pm$ 4 Hz assumed.

Methyl groups in organic chemistry are considered to be electron-releasing. The methyl groups attached to the carbon atoms in o-carborane may be releasing electrons into the cage, causing a change in the electron circulation and electron distribution within the carborane cage. The theory is not sufficiently developed to allow us to predict the extent or direction of the changes to be expected in the ^{11}B NMR spectrum.

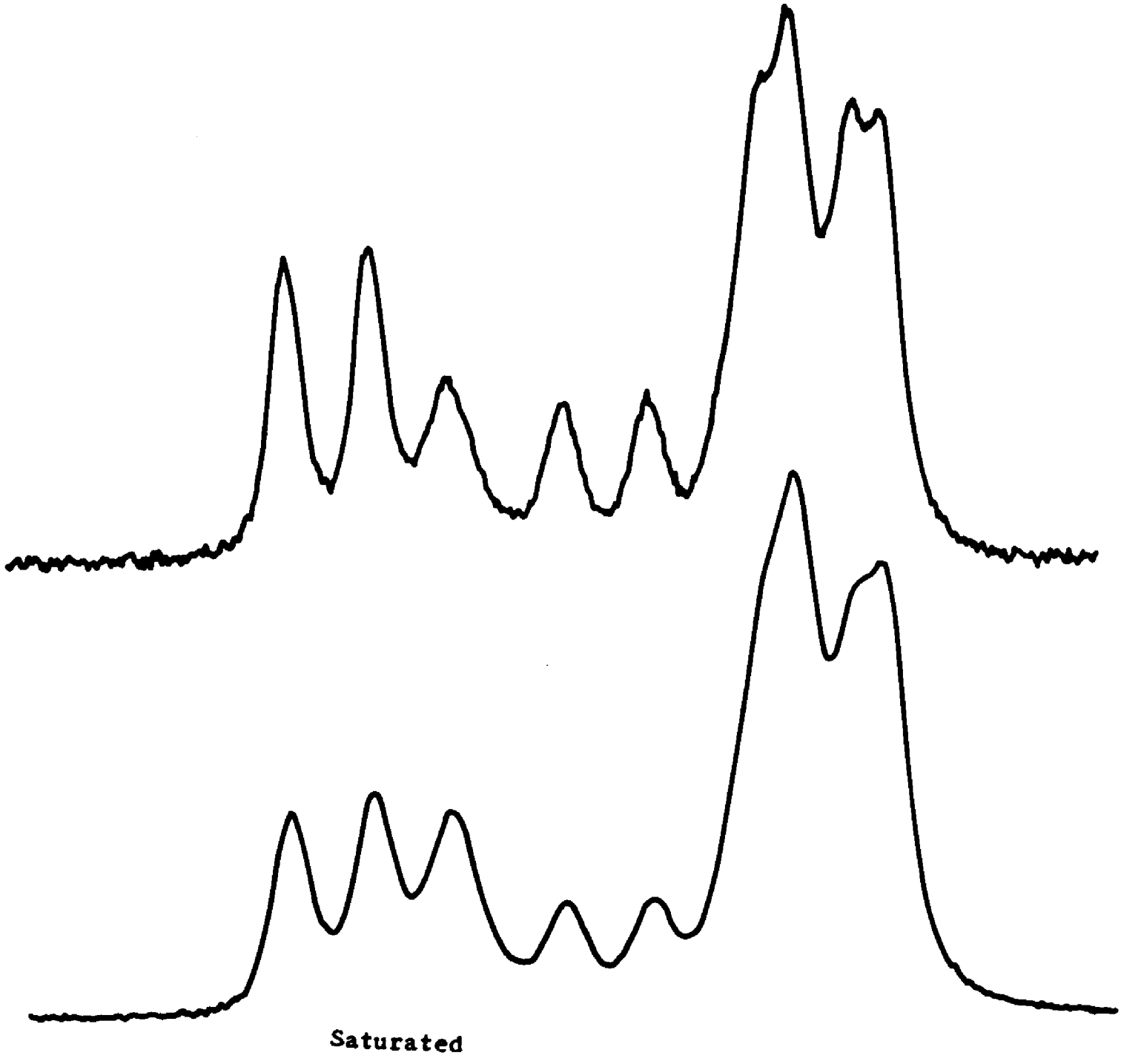

Figure 16. ^{11}B NMR Spectra of 3-Phenyl-o-Carborane at 80.2 MHz.

3.123 3-Phenyl-o-Carborane. Figure 16 presents the ^{11}B NMR spectrum of 3-phenyl-o-carborane obtained from Dr. S. Hêrmánek of the Czechoslovak Academy of Sciences. Substitution at the 3 position reduces the symmetry of the molecule. The (9,12) boron atoms are still symmetrically equivalent. The other sets of symmetrically equivalent boron atoms are the (4,5) and the (7,11) boron atoms The 6, 8, and 10 boron atoms are all unique and each will produce a doublet of relative area one. The spectrum shows a doublet of relative area two at + 21.6 ppm with J_{BH} = 152 Hz which is assigned to the (9,12) boron atoms. The singlet at + 24.3 ppm is assigned to the 3 boron atom. The doublet of relative area one at + 27.7 ppm with J_{BH} = 154 Hz is assigned to the 8(10) boron atom because the chemical shift and coupling constant are similar to those found for the (8,10) boron atoms of o-carborane. The remainder of the spectrum shows such extensive overlap that no assignment can be made.

3.2 Meta Carborane

3.21 Assignment of the Meta Carborane Spectrum

The structure and numbering convention for m-carborane are given in Figure 1-C. There are four sets of symmetrically equivalent boron atoms: the (2,3), the (4,6,8,11), the (9,10), and the (5,12) boron atoms. The 80.2 MHz ^{11}B NMR spectrum of m-carborane given in Figure 17 shows four doublets of relative areas 2:2:4:2.

The spectrum may be completely assigned by considering molecular symmetry, relative areas, and data on 9-bromo-m-carborane and

9,10-bromo-m-carborane, whose structures have been determined by single-crystal x-ray diffraction techniques. The only resonance of relative area four must be assigned to the four symmetrically equivalent boron atoms (4,6,8,11). The 9,10-bromo-m-carborane data indicate the position of the (9,10) boron atom resonance and also establishes that no unusual changes in coupling constants or chemical shifts occur for non-substituted boron atoms. The 9-bromo-m-carborane data establish the positions of the (5,12) and (2,3) boron atom resonances because the (2,3) boron atoms are not symmetrically equivalent. In addition, the 9-bromo-m-carborane data confirms that no unusual changes occur in either chemical shifts or coupling constants for non-substituted boron atoms. Thus, the doublet at + 25.2 ppm, J_{BH} = 162 Hz, is assigned to boron atoms (5,12), the doublet at + 29.4 ppm, J_{BH} = 151 Hz, is assigned to boron atoms (9,10), the doublet at + 32.3 ppm, J_{BH} = 164 Hz, is assigned to boron atoms (4,6,8,11), and the doublet at + 36.2 ppm, J_{BH} = 178 Hz, is assigned to boron atoms (2,3). Each of the compounds will now be considered separately.

The ^{11}B NMR spectrum of 9,10-bromo-m-carborane is shown in Figure 18. The doublet of relative area two at + 29.4 ppm with J_{BH} = 151 Hz in the m-carborane spectrum has disappeared and is replaced by a singlet at + 26.4 ppm. This singlet overlaps the highfield side of the doublet of area two at + 25.4 ppm. For this reason, the ^{11}B-^{1}H spin-spin coupling constant of the (5,12) boron atoms cannot be accurately determined but may be estimated to be 155 $\pm$ 10 Hz. The chemical shift found for the (5,12) boron

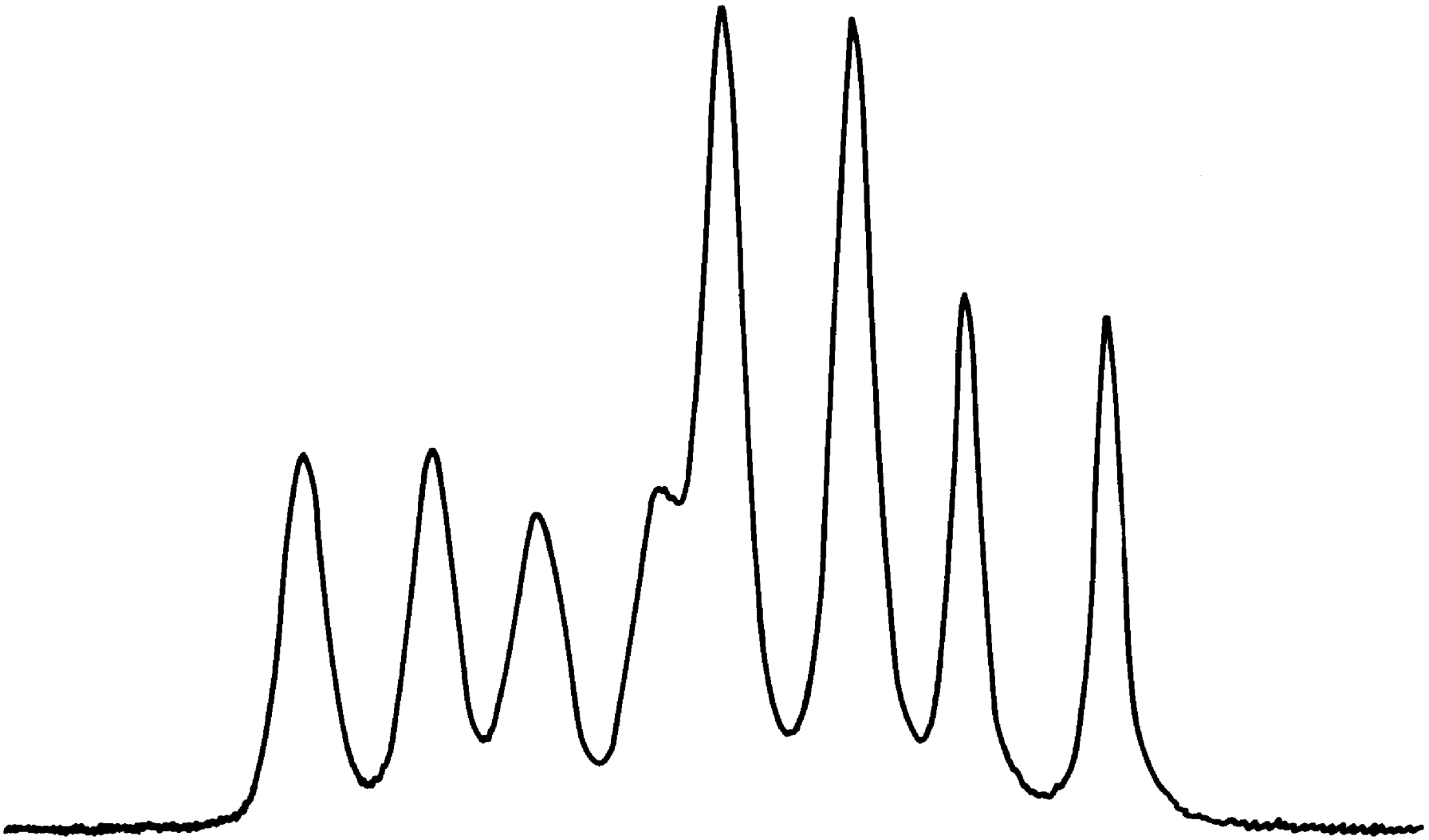

Figure 17. ^{11}B NMR Spectrum of m-Carborane at 80.2 MHz.

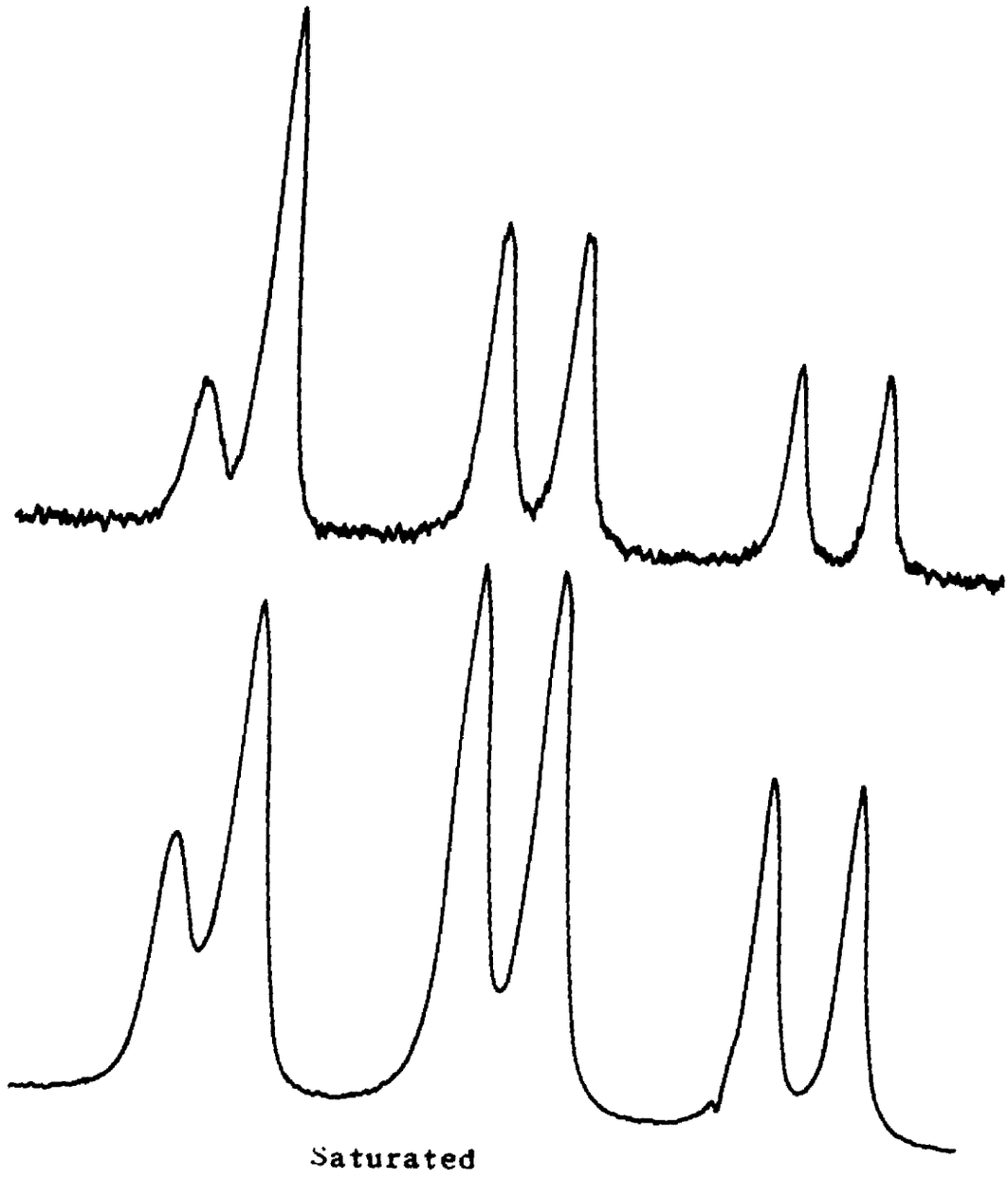

Figure 18. ^{11}B NMR Spectra of 9,10-Dibromo-m-Carborane at 80.2 MHz.

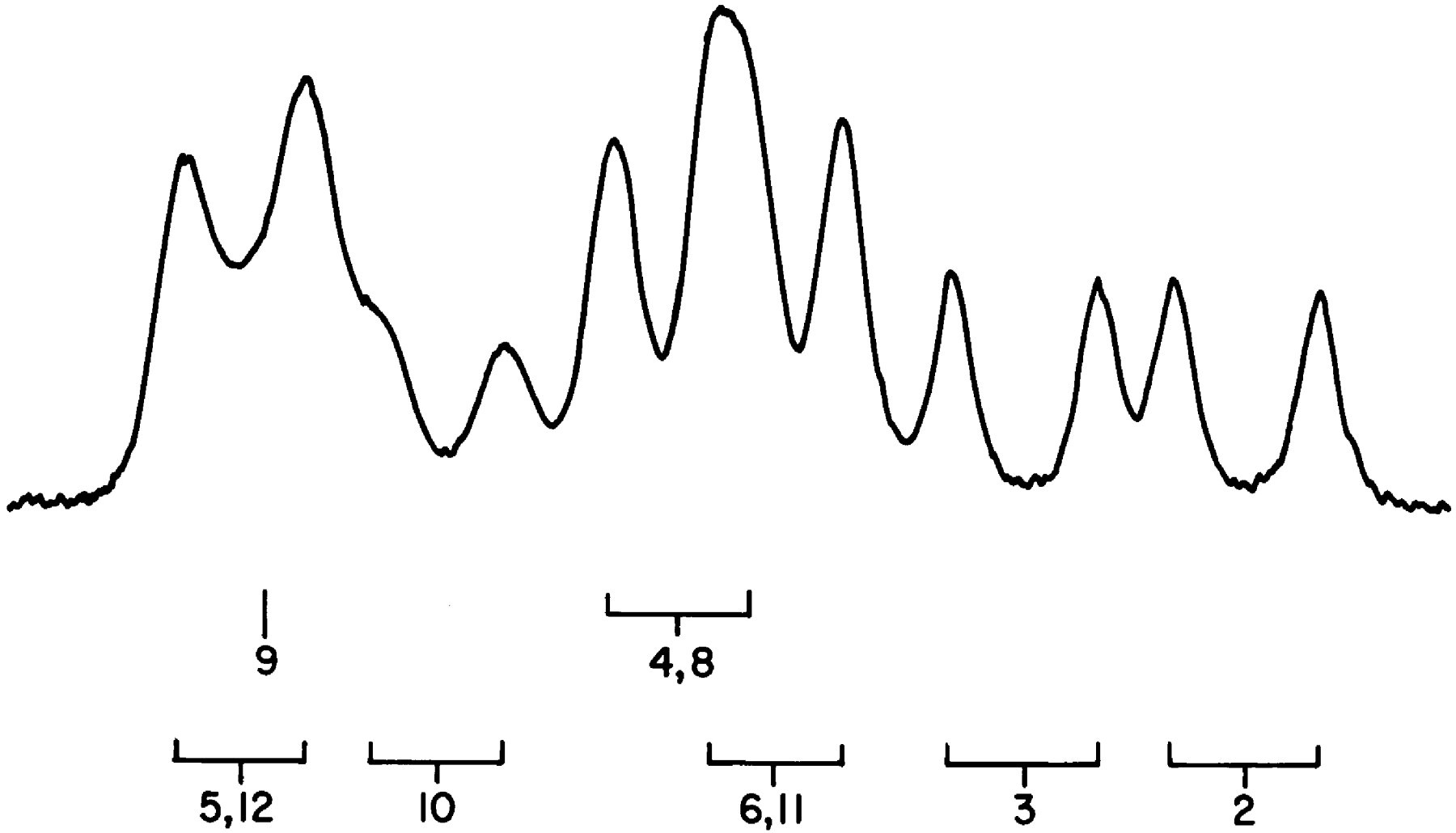

Figure 19. ^{11}B NMR Spectrum of 9-Bromo-m-Carborane at 80.2 MHz.

atom resonance in 9,10-bromo-m-carborane is the same as the chemical shift found for the (5,12) boron atoms in m-carborane, within experimental error. It is unlikely that the (9,10) boron atoms are at lowest field in m-carborane. If they were, bromine substitution would require not only an upfield shift, which has not been observed before, but also a large downfield shift of the doublet at + 29.4 ppm. The (9,10) boron atom resonance in m-carborane, therefore, is assigned to the doublet at + 29.4 ppm with J_{BH} = 151 Hz. The remainder of the assignment is given in Table III.

Substitution at the 9 position of m-carborane reduces the symmetry of the molecule. The (5,12) boron atoms are symmetrically equivalent. The (4,6) boron atoms are no longer symmetrically equivalent to the (8,11) boron atoms, nor is the 2 boron atom symmetrically equivalent to the 3 boron atom. The ^{11}B NMR spectrum of 9-bromo-m-carborane is shown in Figure 19. The doublet of relative area two at + 25 ppm is assigned to the (5,12) boron atoms. The singlet of relative area one due to the 9(10) boron atom is at + 26.0 $\pm$ 0.2 ppm and is partially hidden by overlap of the doublet due to the (5,12) boron atoms. The overlap prevents a more accurate determination of its chemical shift. The doublet of relative area one at + 28.3 ppm is assigned to the 10(9) boron atom. The overlap of this doublet with the doublet at + 25.3 ppm prevents accurate determinations of the coupling constants but they may be estimated to be J_{BH} = 150 $\pm$ 10 Hz for the (5,12) boron doublet and J_{BH} = 155 $\pm$ 5 Hz for the 10(9) boron doublet.

Table III[a]

80.2 MHz ^{11}B NMR Chemical Shifts and $^{11}B-^{1}H$ Coupling Constants of m-Carborane and Selected Derivatives

Compound	J_{BH}[b] 5,12	δ[c] 5,12	J_{BH}[b] 9,10	δ[c] 9,10	J_{BH}[b] 4,6,8,11	δ[c] 4,6,8,11	J_{BH}[b] 2,3	δ[c] 2,3
$m-C_2H_2B_{10}H_{10}$	162	+25.2	151	+29.4	164	+32.3	178	+36.2
$m-C_2H_2B_{10}H_8Br_2$	155 ± 10	+25.4	---	+26.4	168	+34.1	178	+41.1
$m-C_2H_2B_{10}H_9Br$	150 ± 10	+25.3	--- 155 ± 5	+26.0 ± 0.2 +28.3	(165)	+32.0 +33.4	180	+37.6 +40.8
$m-(CH_3)_2C_2B_{10}H_{10}$	(162)	+26.6	(151)	+24.3	(140)	+29.1	(178)	+31.4
$m-C_2H_2B_{10}H_8D_2$	166	+25.4	---	+29.4	164	+32.2	178	+35.9

[a] Values of J_{BH} in parenthesis are assumed.

[b] Values of J_{BH} in Hertz.

[c] Values of δ in ppm relative to trimethoxyborane.

The doublets of relative areas two at + 32.0 ppm and + 33.4 ppm are assigned to the 4,8(6,11) and 6,11(4,8) boron atoms, respectively. The doublets overlap to form an apparent triplet. The broadness of the central peak demonstrates that the triplet is actually two overlapping doublets. The coupling constants cannot be determined accurately. The chemical shifts were calculated assuming the coupling constants for the two doublets to be 165 Hz. The two doublets of relative areas one each at + 37.6 ppm and + 40.8 ppm with J_{BH} = 180 Hz for both are assigned to the 2 and 3 boron atoms.

The doublet at + 25.2 ppm in the m-carborane spectrum can be assigned to the (5,12) boron atoms with some confidence because it is unchanged in the 9-bromo-m-carborane spectrum. The doublet at +36.2 ppm with J_{BH} = 178 Hz in the m-carborane spectrum is assigned to the (2,3) boron atoms because it is split into two doublets of relative areas one each in the 9-bromo-m-carborane spectrum. The spectrum also shows that bromine substitution does not cause any unusual changes in either chemical shifts or coupling constants for non-substituted boron atoms. The chemical shift and ^{11}B-^{1}H coupling constant of the 10(9) boron resonance are similar to those found for the (9,10) boron atoms in the m-carborane spectrum.

We can therefore assign completely and unequivocally the ^{11}B NMR spectrum of m-carborane. The doublets, in order of increasing field, are attributed to boron atoms (5,12), (9,10), (4,6,8,11), and (2,3). This assignment contradicts the assignment of Stanko, et al.,[1]

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[1] V. I. Stanko, V. V. Khrapov, A. I. Klimova, and J. N. Shoolery, Zh. Strukt. Khim. 11, 542 (1970).

and agrees with the assignment of the (9,10) boron atom resonance of Beall and Lipscomb.[1] The assignment by Stanko, et al., did not utilize ^{11}B-^{1}H coupling constants as an aid to interpretation of the spectra. The analysis of (9,10) substituted m-carborane ^{11}B NMR spectra alone is not sufficient for an unequivocal assignment of the ^{11}B NMR spectrum of m-carborane because the positions of resonance of the (5,12) and (2,3) boron atoms cannot be unequivocally assigned. In addition, the data of Stanko, et al., seems to indicate that the (9,10) boron atom resonance is not at lowest field. A peak at + 25 ppm relative to TMB is found in all m-carborane ^{11}B NMR spectra obtained by Stanko, et al., and is unchanged upon halogen substitution. The peak of relative area four in all of their m-carborane ^{11}B NMR spectra also shows only small changes in chemical shift upon halogen substitution, and the peak of relative area two at highest field in the ^{1}H double-irradiated 32.1 MHz ^{11}B NMR spectrum of m-carborane is shifted upfield slightly upon halogen substitution. The only peak of relative area two that is significantly changed upon halogen substitution is the peak at about + 29 ppm in the m-carborane spectrum. This peak shows large changes in chemical shift upon halogen substitution, and is found at + 25 ppm in the ^{1}H double-irradiated 32.1 MHz ^{11}B NMR spectrum of 9,10-dibromo-m-carborane. It, therefore, coincides with the peak at + 25 ppm in

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[1] H. Beall and W. N. Lipscomb, Inorg. Chem. 6, 874 (1966).

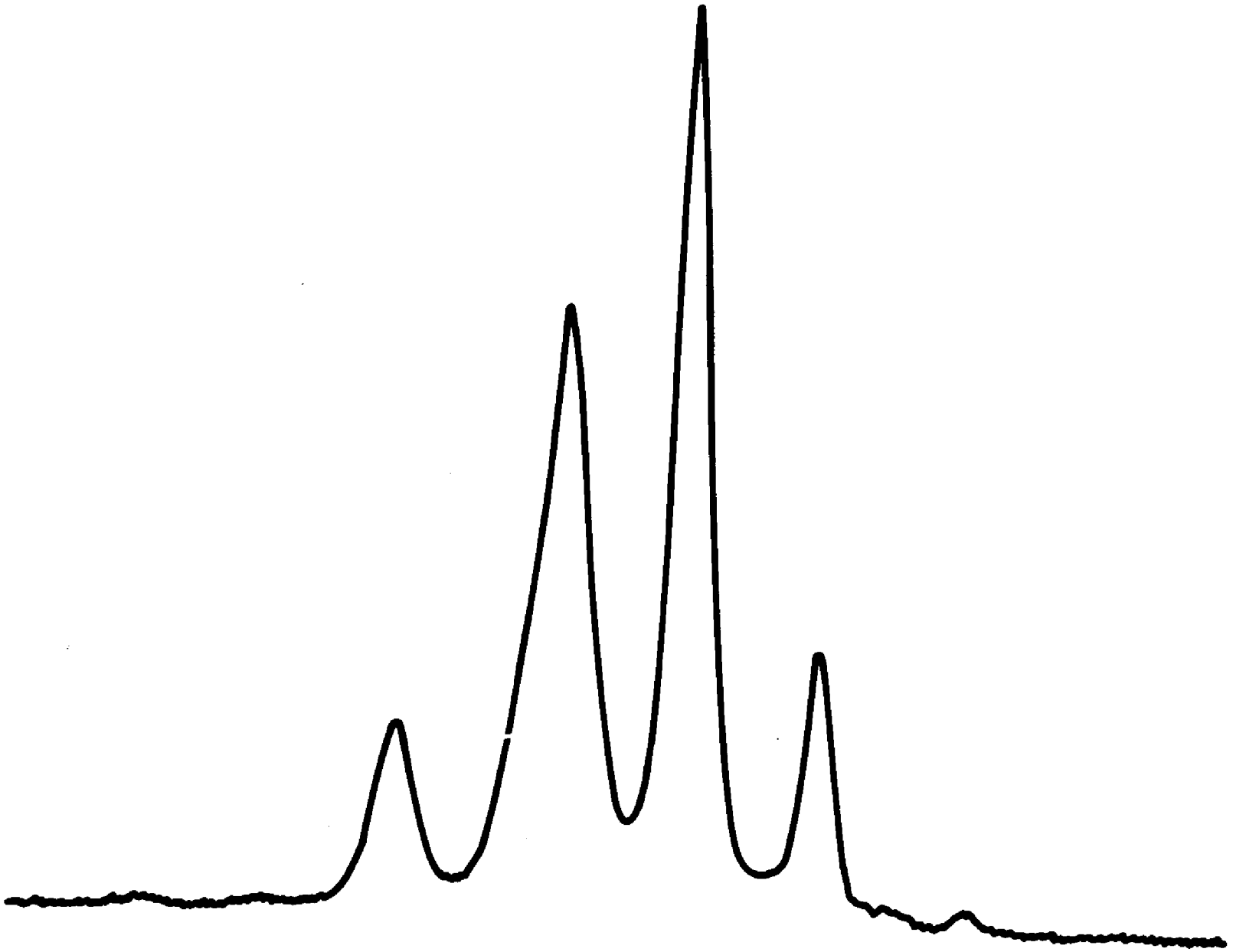

Figure 20. ^{11}B NMR Spectrum of 1,7-Dimethyl-m-Carborane at 80.2 MHz.

the m-carborane spectrum. The ^{1}H double-irradiated 32.1 MHz ^{11}B NMR spectrum of 9,10-dibromo-m-carborane has two resonances of relative area four. The data of Stanko, et al., therefore seem to show that the (9,10) boron resonance is not at lowest field.

3.22 Meta Carborane Derivatives

The 80.2 MHz ^{11}B NMR spectrum of 1,7-dimethyl-m-carborane is shown in Figure 20. The spectrum is deceptively simple. Only four peaks are discernable, of relative areas 1:4:4:1. There is extensive overlap and coupling constants cannot be determined accurately. Substitution at both carbon atoms does not affect the symmetry of the molecule. No change in the relative order of the four doublets is expected. Therefore, the (5,12) boron atoms are assigned to a doublet at + 26.6 ppm; the doublets due to the (9,10) and (4,6,8,11) boron atoms accidently coincide at + 29.2 ppm, and the (2,3) boron atoms are assigned to a doublet at + 31.4 ppm. The chemical shifts were calculated assuming no change in the ^{11}B-^{1}H coupling constants found in the m-carborane spectrum.

3.3 Deuterium Isotope Exchange

Decaborane(14) exchanges deuterium for hydrogen under electrophilic conditions. The calculated electron distribution in the icosahedral carboranes is similar to that calculated for decaborane(14). With decaborane(14) as a model for carborane reactions, deuterium chloride is expected to exchange deuterium for the hydrogens bonded to boron of carboranes using aluminum chloride as a catalyst.

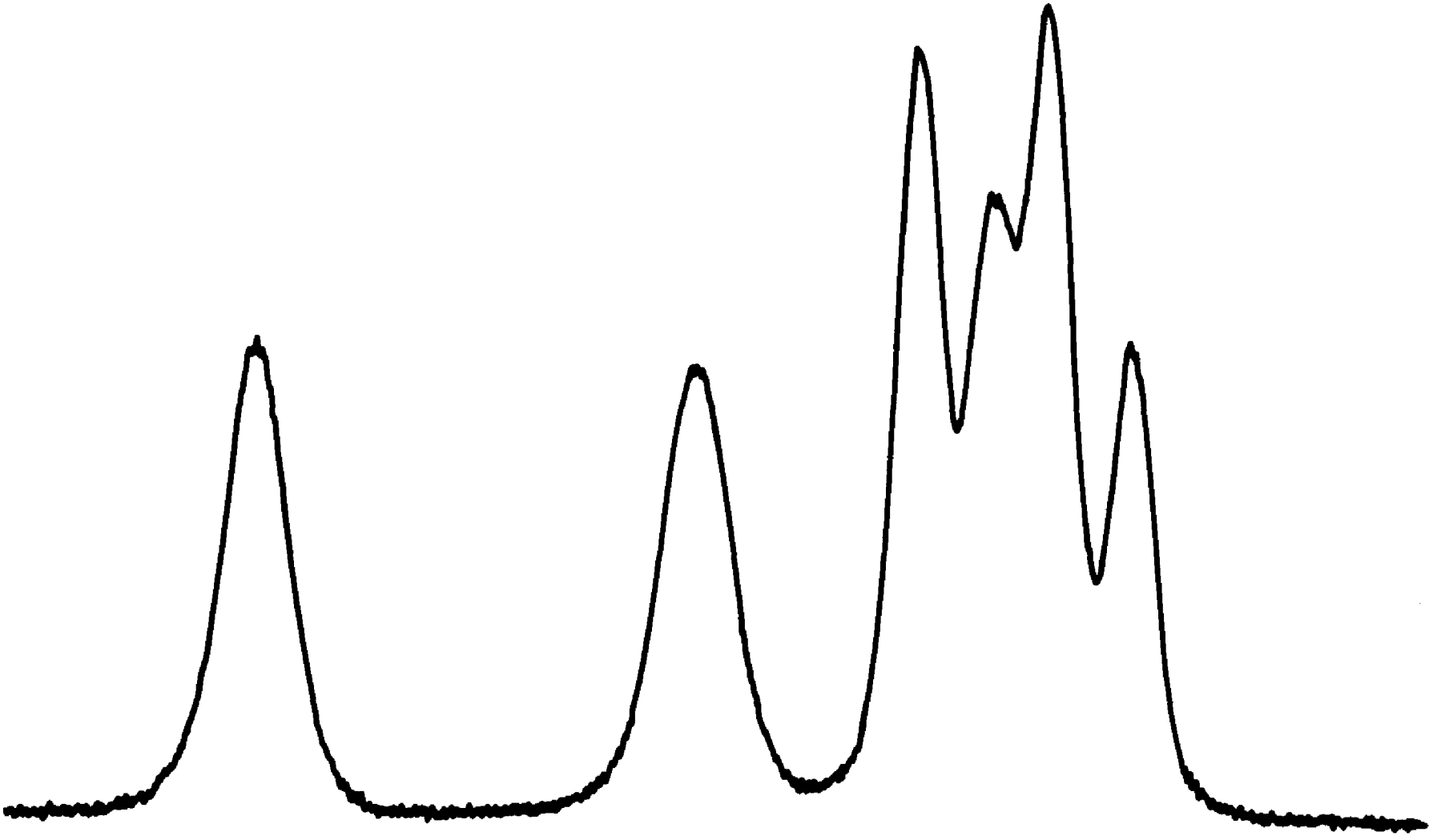

Figure 21. ^{11}B NMR Spectra of o-Carborane-d_4 at 80.2 MHz.

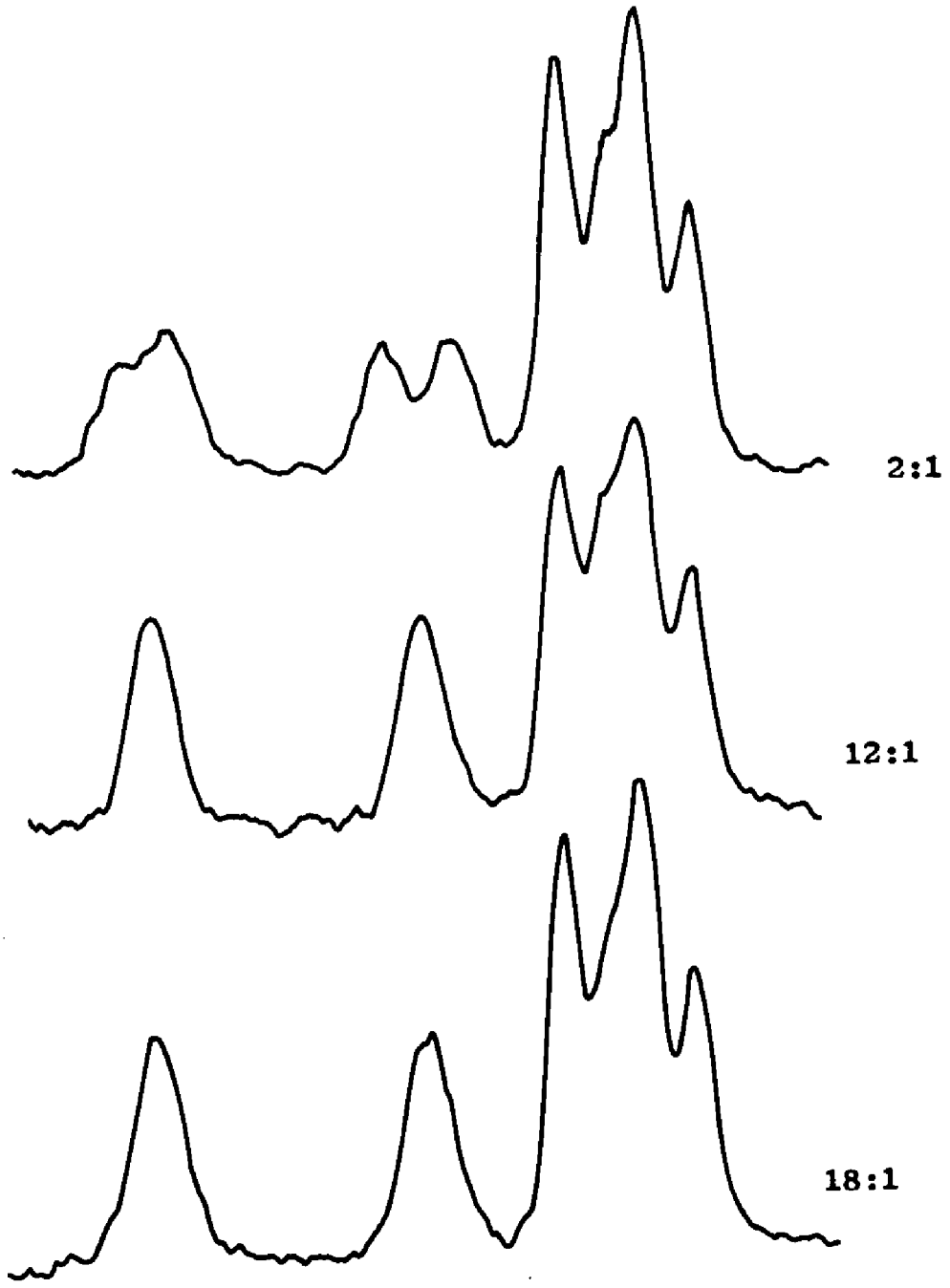

Figure 22. ^{11}B NMR Spectra of o-Carborane-d_4 at 80.2 MHz: Kinetics Study.

Deuterium isotope exchange does occur with both o-carborane and m-carborane under electrophilic conditions. The same conditions were used for the exchange as are routinely used for decaborane(14) deuterium exchange at the 1,2,3,4 positions.

Figure 21 shows that deuterium isotope exchange with o-carborane occurs at the (8,9,10,12) positions. Figure 22 shows a composite of several ^{11}B NMR spectra obtained after partial deuteration of o-carborane. There may be a slight difference in the rate of exchange of the (9,12) and (8,10) boron atoms. This difference in rate of exchange is not large enough to allow isolation of 9,12-d_2-o-carborane. This behavior is analogous to the deuterium exchange of decaborane(14), where differences in rate of exchange for the (1,2,3,4) boron atoms are difficult to detect.[1] There is no evidence of any further deuterium exchange at the (4,5,7,11) and (3,6) boron atoms under these conditions.

Decaborane(14) does exchange deuterium at the (5,7,8,10) boron atoms with high DCl pressures and Al_2Cl_6 catalyst. Further deuterium exchange also occurs with o-carborane at high DCl pressures, as is shown in Figure 23. Complete exchange has not occurred but exchange is proceeding at the (4,5,7,11) boron atoms. There is no evidence of exchange at the (3,6) boron atoms.

Deuterium isotope exchange occurs with m-carborane under electrophilic conditions. Figure 24 shows ^{11}B NMR spectra of several partially deuterated m-carborane samples. The difference in rate of deuterium exchange between the (9,10) and (5,12) boron atoms is sufficient to

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[1] G. M. Bodner and L. G. Sneddon, Inorg. Chem. 9, 1421 (1970).

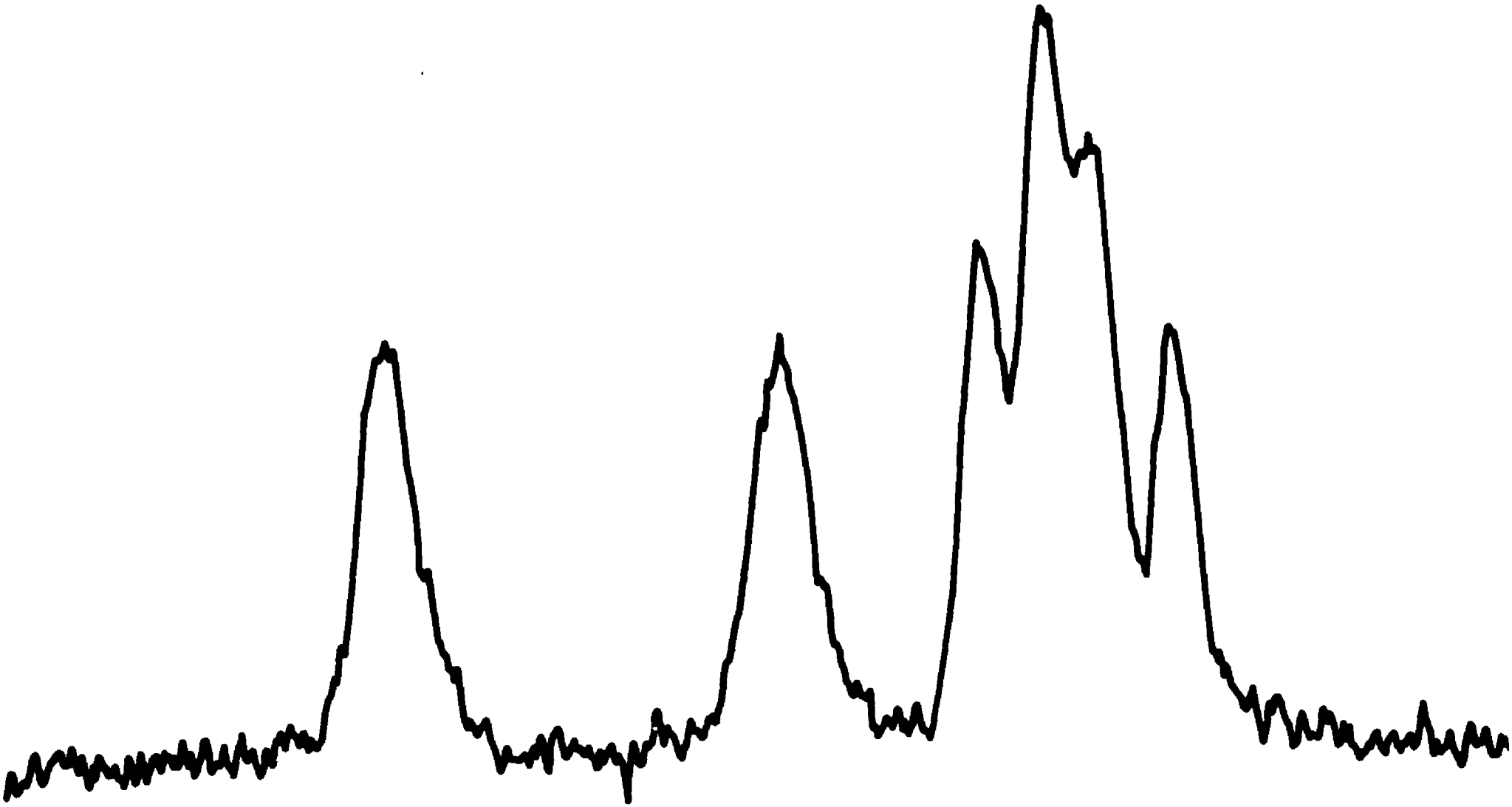

Figure 23. ^{11}B NMR Spectrum of o-Carborane-d_8 at 80.2 MHz.

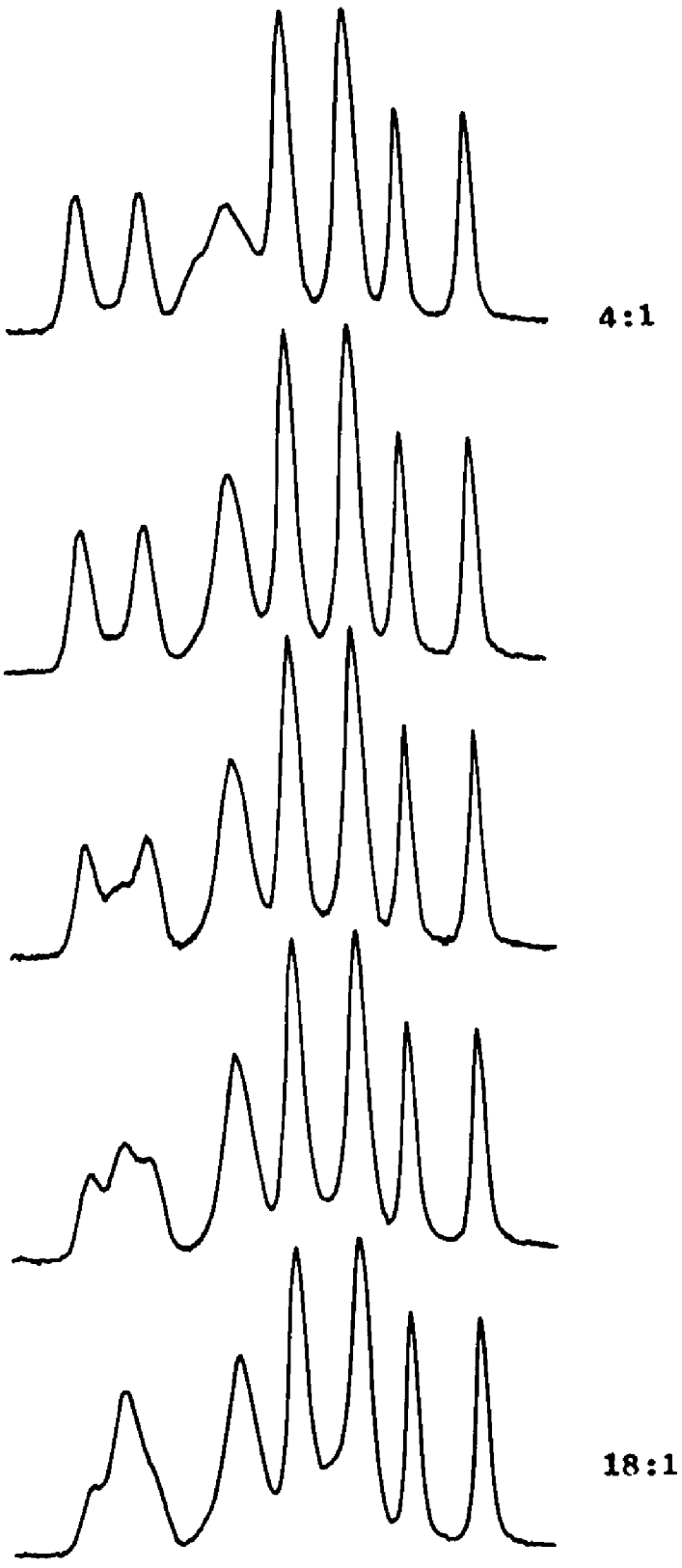

Figure 24. ^{11}B NMR Spectra of m-Carborane-d_4 at 80.2 MHz: Kinetics Study.

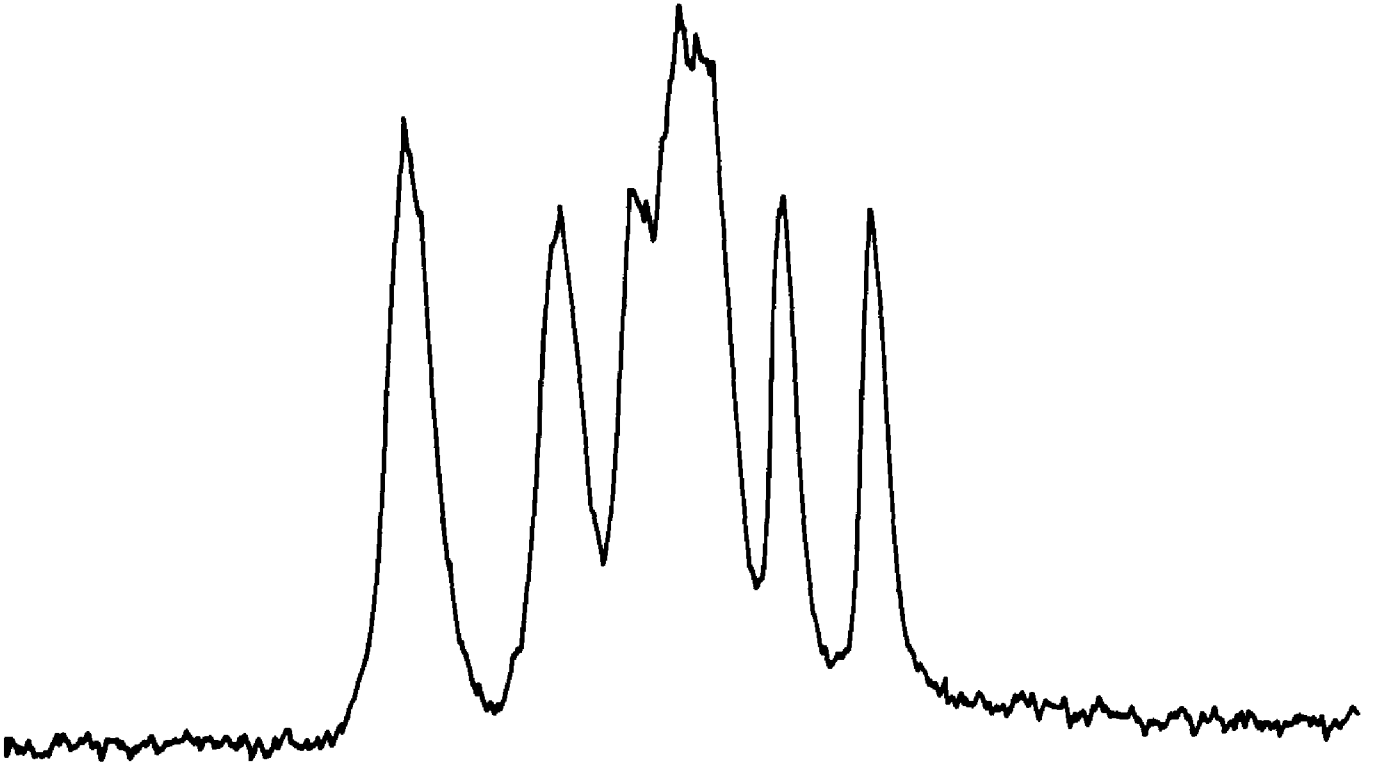

Figure 25. ^{11}B NMR Spectrum of m-Carborane-d_8 at 80.2 MHz.

allow isolation of relatively pure 9,10-d_2-m-carborane. The relative rates of exchange decrease in the order (9,10) > (5,12) > (4,6,8,11) > (2,3). Further deuterium exchange occurs largely at the (5,12) positions. However, the rate of deuterium exchange at the (4,6,8,11) boron atoms is rapid enough that isolation of 5,9,10,12-d_4-m-carborane, with no exchange at the (4,6,8,11) boron atoms, is not possible. No evidence of exchange at the (2,3) boron atoms was found.

With high DCl pressures, deuterium exchange occurs at the (4,6,8,11) boron atoms to give 4,5,6,8,9,10,11,12-d_8-m-carborane. Figure 25 shows the ^{11}B NMR spectrum of an extensively deuterated m-carborane. Complete deuterium exchange at the (4,6,8,11) positions has not yet occurred. Again, no evidence is seen for exchange at the (2,3) positions.

Deuterium exchange also occurs at the (8,9,10,12) boron atoms of 1-bromomethyl-o-carborane. The ^{11}B NMR spectrum of 8,9,10,12-d_4-1-bromomethyl-o-carborane, prepared by the "Friedel-Crafts" deuterium exchange, is identical in all respects with the ^{11}B NMR spectrum of 8,9,10,12-d_4-1-bromomethyl-o-carborane prepared from 1,2,3,4-d_4-decaborane(14).

3.4 ^1H NMR Spectra

The ^1H spectra of both o-carborane and m-carborane should show four sets of quartets due to coupling of boron with the protons by the $(2nI + 1)$ rule, and a singlet due to the protons bonded to carbon. The ratio of the relative areas of the quartets should be 2:2:4:2, and the ^{11}B-^1H coupling constants should be the same as those found from the corresponding ^{11}B spectra.

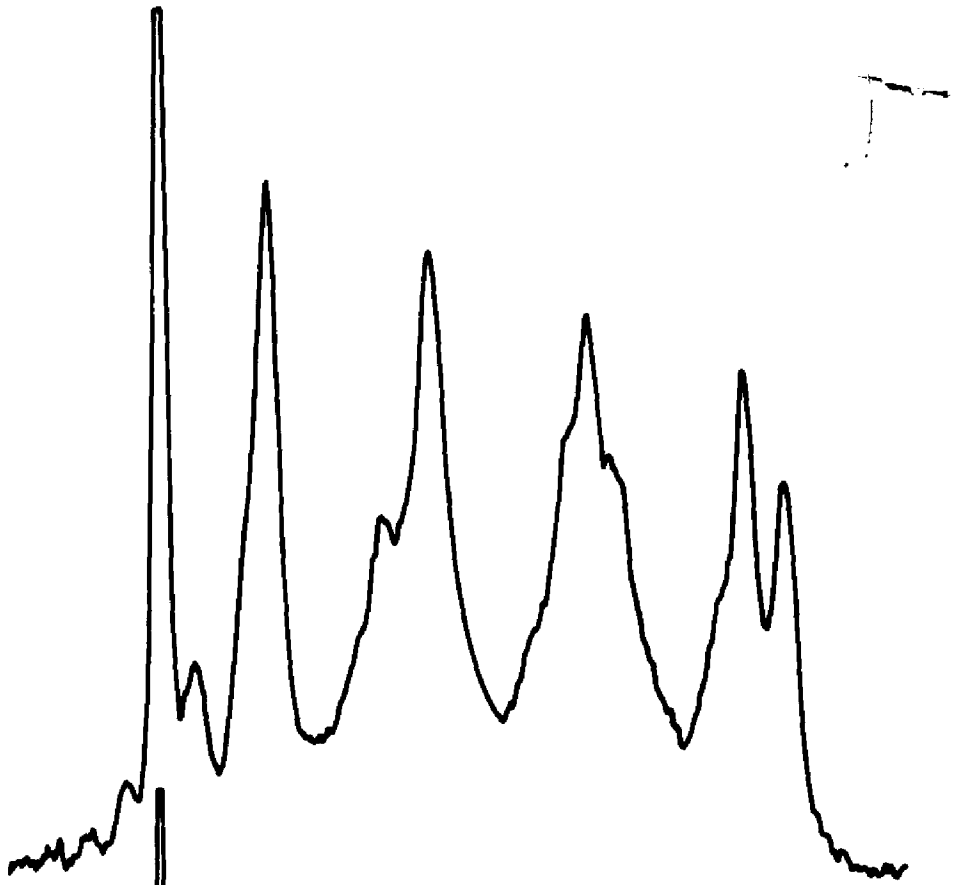

Figure 26(a). ^{1}H NMR Spectrum of o-Carborane at 250 MHz.

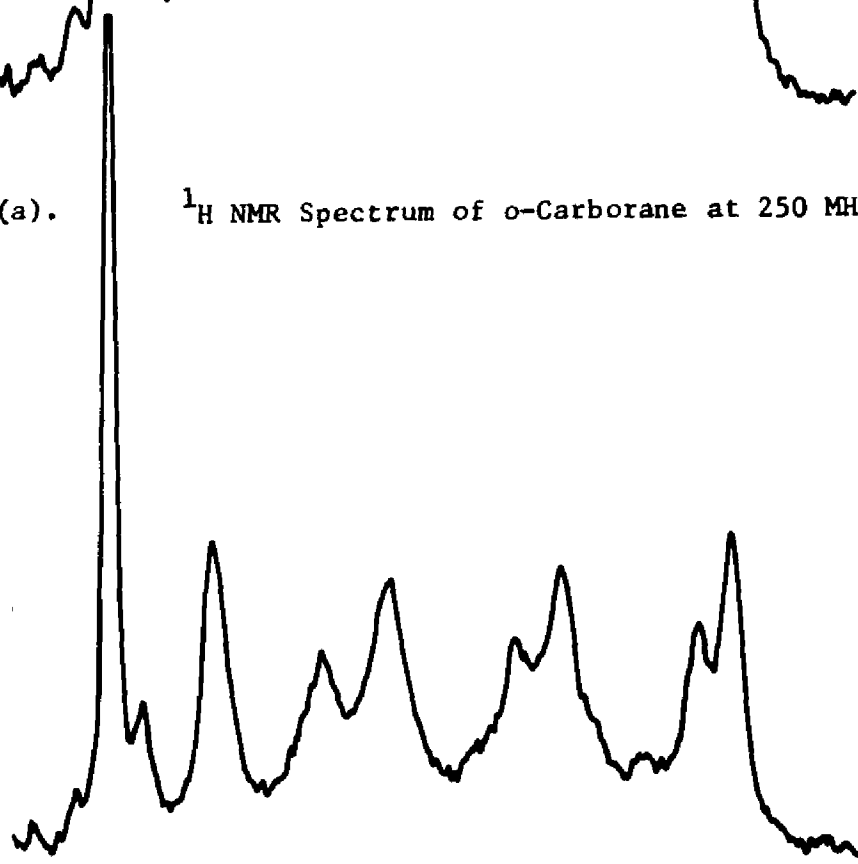

Figure 26(b). ^{1}H NMR Spectrum of o-Carborane-d_4 at 250 MHz.

3.41 Ortho Carborane

The 250 MHz ^{1}H NMR spectrum of o-carborane is given in Figure 26A. The C-H peak is found at -3.81 ppm from TMS as an external standard. No other assignment can be made from this spectrum. The 250 MHz ^{1}H NMR spectrum of 8,9,10,12-d_4-o-carborane, prepared from o-carborane by "Friedel-Crafts" deuterium exchange, is given in Figure 26B. Peaks at 911 Hz, 733 Hz, 555 Hz, and 377 Hz downfield from TMS have a relative area of two, and are assigned to protons bonded to the (3,6) boron atoms. The ^{11}B-^{1}H coupling constant is 178.2 Hz, and the center of the quartet is -2.58 ppm from TMS. The quartet centered at -2.39 ppm with J_{BH} = 164.5 Hz is assigned to protons coupled to the (4,5,7,11) boron atoms.

Subtracting these peaks from the ^{1}H spectrum of o-carborane, Figure 26A, leaves peaks at 842 Hz, 692 Hz, 542 Hz, and 392 Hz with J_{BH} = 150.4 Hz. The relative area of the quartet appears to be four. It would seem, therefore, that the proton resonances due to the hydrogen atoms bonded to the (8,10) and (9,12) boron atoms accidentally coincide. The data do not allow us to separate the peaks any further. The assignment is given in Table IV.

3.42 Meta Carborane

The 250 MHz ^{1}H NMR spectrum of m-carborane is given in Figure 27A. Figure 27B gives the ^{1}H spectrum of 9,10-d_2-m-carborane, and Figures 27C and D give ^{1}H spectra of m-carborane-$d_{2.5}$ and m-carborane-d_3, respectively. The C-H peak is at -3.12 ppm from TMS.

An analysis of all four proton spectra shows that the peaks at 1007 Hz and 451 Hz downfield from TMS are unchanged by deuterium

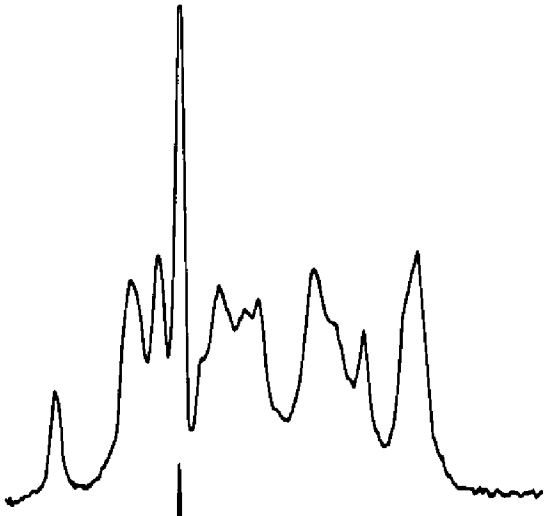

Figure 27(a). ^1H NMR Spectrum of m-Carborane

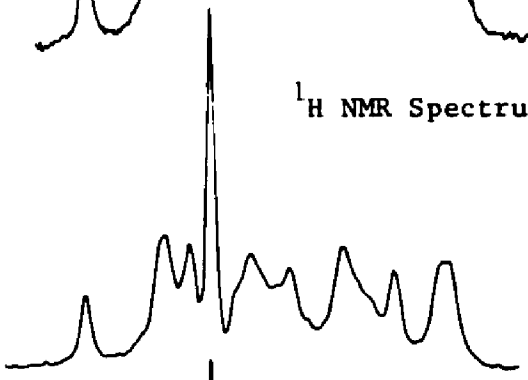

Figure 27(b). ^1H NMR Spectrum of m-Carborane-d_2

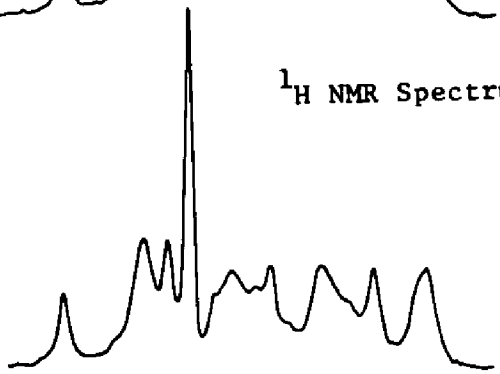

Figure 27(c). ^1H NMR Spectrum of m-Carborane-$d_{2.5}$

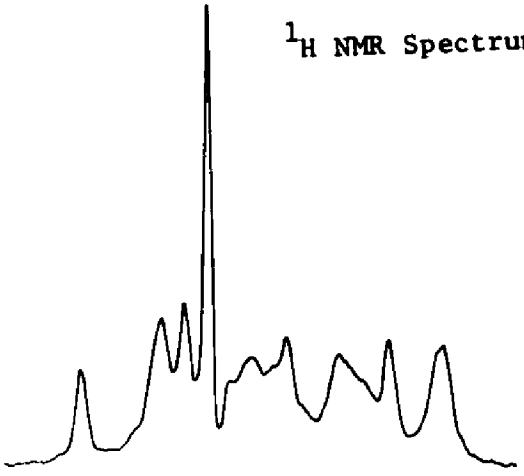

Figure 27(d). ^1H NMR Spectrum of m-Carborane-d_3

exchange. These peaks are of relative area 2, and with J = 178.6 Hz, are assigned to the hydrogens bonded to the (2,3) boron atoms. The remaining two peaks of the quartet are at 818 Hz and 640 Hz downfield from TMS, so that the center of the quartet is at -2.92 ppm from TMS.

The peaks at 819 Hz, 668 Hz, 518 Hz, and 367 Hz downfield from TMS in the m-carborane spectrum are much diminished in the 9,10-d_2-m-carborane spectrum. These are assigned to the protons bonded to the (9,10) boron atoms. The chemical shift of the quartet is -2.37 ppm with J_{BH} = 150.8 Hz.

The peak at 872 Hz is larger than that of 668 Hz in 9,10-d_2-m-carborane, and that at 384 Hz is the same size as the peak at 363 Hz. Figures 28C and D show that additional deuterium exchange causes a decrease in size of the 872 Hz and 384 Hz peaks relative to the adjacent peaks. These two peaks, therefore, are assigned to the hydrogens bonded to the (5,12) boron atoms. The ^{11}B-^{1}H coupling constant is 162.9 Hz. The remaining peaks of the quartet are therefore at 710 Hz and 548 Hz downfield from TMS with a chemical shift of the quartet of -2.51 ppm.

Subtracting the three quartets already determined from the ^{1}H spectrum leaves peaks of relative area four at 363 Hz, 529 Hz, 694 Hz, and 860 Hz downfield from TMS. The ^{11}B-^{1}H coupling constant is 165.7 Hz and the chemical shift is -2.45 ppm. The complete assignment is given in Table IV.

Table IV

250 MHz ^{1}H NMR Chemical Shifts and Coupling Constants of o-Carborane and m-Carborane

Compound	J_{BH}[a]	δ[b]	J_{BH}[a]	δ[b]	J_{BH}[a]	δ[b]	J_{BH}[a]	δ[b]	δ[b]
	9,12/5,12		8,10/9,10		4,5,7,11/4,6,8,11		3,6/2,3		C-H
o-$C_2H_2B_{10}H_{10}$	150.4	-2.47	150.4	-2.47	164.5	-2.39	178.2	-2.58	-3.81
m-$C_2H_2B_{10}H_{10}$	162.9	-2.51	150.8	-2.37	165.7	-2.45	178.6	-2.92	-3.12

[a]Values of J_{BH} in Hertz.

[b]Values of δ in ppm relative to tetramethyl silane.

3.5 Saturation Studies

3.51 General

Boron 11 has a nuclear spin quantum number of 3/2 and hence has an electric quadrupole moment. Nuclei with electric quadrupole moments generally have efficient, rapid relaxation mechanisms, and hence short spin-lattice relaxation times, T_1. The saturation factor is $(1 + \gamma^2 H_1^2 T_1 T_2)^{-1}$, where γ is the magnetogyric ratio of the nucleus, H_1 is the applied RF power, and the spin-spin relaxation time T_2 is assumed to be approximately equal to T_1. Inspection shows that increasing RF power, or increasing T_1, will increase the saturation. From theory,[1] the contribution to the relaxation time T_1 of the quadrupole moment is given by the equation

$$\frac{1}{T_1} = \frac{3}{8} \frac{(eq)^2 (eQ)^2}{\hbar^2} \tau_g \quad .$$

The electric field gradient is eq, eQ is the electric quadrupole moment, and τ_g is the correlation time of the molecule. The correlation time depends upon how rapidly the molecule rotates or tumbles.

The contribution to the relaxation time T_1 of the electric quadrupolar interaction normally dominates the contribution arising from the magnetic dipolar interactions. However, if the electric quadrupole moment is small, the contribution of the electric quadrupole moment is small. The electric field gradient is small for symmetrical

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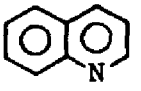
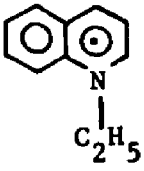
[1] J. A. Pople, W. G. Schneider, and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, McGraw-Hill Book Company, New York, Toronto, London, 1959.

electric fields. In cases where the electric field is symmetrical, relaxation times are long, and saturation could occur more readily than in cases where the field is asymmetric.

Nitrogen 14 has a nuclear spin quantum number I = 1 and an electric quadrupole moment. In ammonia and most other nitrogen compounds, the rapid relaxation resulting from the interaction of the electric quadrupole moment with the fluctuating electric field gradient gives a short T_1. Protons coupled to ^{14}N in these compounds show broad resonances, and the splitting of the proton resonance into three peaks may be obscured or even wiped out by the rapid relaxation.[1] However, the proton spectrum of NH_4^+ shows a very sharp triplet.[1] The tetrahedral arrangement of the orbitals results in a symmetrical electric field gradient, and hence a long relaxation time, because the electric quadrupole moment does not interact with the electric field. Similarly, quinoline,  , shows a broad ^1H resonance for the proton alpha to the nitrogen.[2] Quaternization, however, for example in  I^-, results in a sharp alpha proton resonance, and longer ^{14}N relaxation times. The electric field gradient is nearly tetrahedral, and the electric quadrupole moment is ineffective as a relaxation mechanism.

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[1] J. A. Pople, Mol. Phys. 1, 168 (1958).

[2] J. P. Kintzinger and J. M. Lehn, Mol. Phys. 14, 133 (1968).

Most boranes show broad resonances of both ^{1}H and ^{11}B nuclei but coupling is normally observable. Pople[1] and Suzuki and Kubo[2] have shown that for very rapid relaxation times, no apparent coupling will be detectable because the proton will see the average orientation of the rapidly relaxing nucleus. That ^{11}B-^{1}H coupling is observed, even though the peaks are broad, suggests that the relaxation times of the boron atoms are relatively long. Saturation will distort the spectrum, and a check of possible RF saturation should always be made.

3.52 Results and Discussion

Chronologically, the first two carborane spectra obtained at 80.2 MHz were those of o-carborane and tetrachloro-o-carborane. Saturation studies done while obtaining these spectra indicated that boron atoms bonded to chlorine atoms saturated very rapidly, but boron atoms bonded to hydrogen did not.

All subsequent spectra obtained with halocarboranes included a saturation study. In addition, saturation studies were carried out with several selected o- and m-carborane derivatives. The saturation effects conceivably could have been caused by some interaction of the quadrupole moments of the halogen and the boron nuclei. To check this possibility, several deuterated samples were studied because deuterium nuclei have quadrupole moments. The results of the saturation studies are given in Table V.

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[1] J. A. Pople, Mol. Phys. 2, 108 (1958).

[2] M. Suzuki and R. Kubo, Mol. Phys. 6, 201 (1963).

Table V

Saturation Studies of the Carboranes

A. Halo-o-Carborane Derivatives - Relative Areas of Peaks

RF Power Attenuation and Pulse Duration	12 db 2 μ sec				0 db 2 μ sec			
Compound	(3,6)	(4,5,7,11)	(8,10)	(9,12)	(3,6)	(4,5,7,11)	(8,10)	(9,12)
$o\text{-}C_2B_{10}H_{11}Br$	6.00		1.64	1.64[a]	6.00		1.34	1.02
$o\text{-}C_2B_{10}H_{10}Br_2$	6.00		2.16	2.16	6.00		1.36	0.46
$o\text{-}C_2B_{10}H_9Br_3$	6.00		1.69	1.23[a]	6.00		0.99	0.32
$o\text{-}C_2B_{10}H_8Cl_4$	2.00	4.04	2.00	2.32	2.00	3.17	0.34	0.36
$o\text{-}C_2B_{10}H_4Cl_8$	2.00	4.34	1.51	1.51	2.00	2.11	0.25	0.25
$o\text{-}C_2B_{10}H_{10}I_2$[b,c]	1.00	2.11	2.11	5.05[a] (1.95)	1.00	1.91	1.08	3.15 (0.24)

(continued)

Table V (continued)

B. o-Carborane Derivatives

RF Power Attenuation and Pulse Duration	12 db 2 μ sec			6 db 2 μ sec			0 db 3 μ sec		
Compound	(3,4,5, 6,7,11)	(8,10)	(9,12)	(3,4,5, 6,7,11)	(8,10)	(9,12)	(3,4,5, 6,7,11)	(8,10)	(9,12)
$o\text{-}C_2B_{10}H_{12}$	6.00	1.96	1.88	6.00	1.74	1.74	6.00	1.37	1.22
$o\text{-}C_2B_{10}H_8D_4$				6.00	1.63	1.60[d]	6.00	1.37	1.19
$1\text{-}BrCH_2\text{-}o\text{-}C_2B_{10}H_7D_4$	6.00		2.00[a]	6.00		1.57[d]	6.00		1.34
$1\text{-}C_2H_3\text{-}o\text{-}C_2B_{10}H_{11}$	6.00		2.00				6.00		1.68[e]

Compound	(Standard)	(3-φ)	8(10)	(9,12)[f]	(Standard)	(3-φ)	8(10)	(9,12)[g]
$3\text{-}C_6H_5\text{-}o\text{-}C_2B_{10}H_{11}$	6.00	0.90	1.04	2.09	6.00	0.99	0.97	1.69

Compound	(Standard)	(8,10,5, ½7)	[5]	(9,12)[f]	(Standard)	(8,10,5, ½7)	[5]	(9,12)[h]
$5\text{-}o\text{-}C_2B_{10}H_{11}Br$	4.50	3.52	(10)	1.92	4.50	2.49	(0.5)	1.50

(continued)

Table V (continued)

C. m-Carborane Derivatives

RF Power Attenuation and Pulse Duration	12 db 2 μ sec				0 db 2 μ sec			
Compound	(2,3)	(4,6,8,11)	(9,10)	(5,12)	(2,3)	(4,6,8,11)	(9,10)	(5,12)
$m\text{-}C_2B_{10}H_{10}Br_2$	2.00	4.01	3.92		2.00	3.94	2.82	
$1,7\text{-}(CH_3)_2\text{-}m\text{-}C_2B_{10}H_{10}$ [i]	1.00	3.69	3.86	0.93	1.00	3.96	4.02	1.18

[a] 10 db attenuation.

[b] The areas of only one-half the (3,6) and (4,5,7,11) doublets could be obtained independently of the (9,12) singlet. The (9,12) column has the area of the tallest peak and in parenthesis the presumed area due to the (9,12) boron singlet.

[c] All at 3 μ sec pulse duration.

[d] 5 db attenuation.

[e] 2 μ sec pulse duration.

[f] 8 db attenuation, 2 μ sec pulse duration.

[g] 0 db attenuation, 3 μ sec pulse duration.

[h] 5 db attenuation, 2 μ sec pulse duration.

[i] Only four peaks discernable.

The power levels given show the attenuation of the applied RF power. Thus, 12 db attenuation is a lower power level than 6 db attenuation, as more power has been removed from the exciting pulse in the former. The exciting frequency is applied at a certain power level for a certain length of time. The power is then turned off, and the detector turned on. Therefore, a second method of increasing applied power is to increase the duration of the exciting pulse. Thus, a zero db attenuated pulse applied for two microseconds is a lower power level than a pulse at zero db attenuation applied for three microseconds.

The spectrometer magnet and power levels are quite stable over a period of several hours, but do vary slightly. In addition, sample tubes vary slightly, as does sample volume. The total susceptabilities will change between samples. The total power applied for a particular power setting has also not been calibrated. For these reasons, no strictly quantitative comparisons may be made between different samples. With the same sample, the only change is the power level. Thus, o-carborane at 0 db, 2 μsec can be compared with some confidence to o-carborane at 12 db, 2 μsec, but a comparison to o-carborane-d_4 can only be approximate because the measurements were made on different days.

Examination of spectra for a particular compound at several different power settings indicated that some peaks were either saturating slowly or not at all. These peaks were then selected as standards and were assumed not to saturate. The relative areas of the standard peaks were assumed to be equal to the number of boron atoms responsible for the resonance. The areas of all peaks in the spectrum

were then obtained and are reported relative to the standard peaks.

For example, the o-carborane spectra obtained suggested that the (4,5,7,11) and (3,6) boron doublets did not saturate under the conditions of the experiment. The relative area of these two doublets was defined as six. The two doublets overlap, especially at high power levels, and therefore, both doublet were used together. After obtaining the areas of all doublets in the spectrum, the areas of the (9,12) and (8,10) doublets are reported relative to the (4,5,7,11) and (3,6) doublets defined as six.

For 1-bromomethyl-o-carborane-d_4, the (8,10) boron atom peak could not be readily separated from the peaks due to the (4,5,7,11) and (3,6) boron atoms. In this case, the areas of the (9,12) boron atom peaks were subtracted from the remaining total area. Our assumption was that the (8,10) boron atoms saturated at the same rate as the (9,12) boron atoms. The same procedure was used with the 1-vinyl-o-carborane spectra.

The (9,12) singlet in 9,12-I_2-o-carborane overlaps with one-half the doublets due to the (4,5,7,11) and (3,6) boron atoms. At low power levels, the relative areas of the five peaks visible are 1:1:2:5:1. One-half the doublet due to the (3,6) boron atoms is visible at highest field and was defined to be 1.00. The areas of the other four peaks were measured and are reported relative to this peak. In addition, the area of the (3,6) peak visible and the area of the part of the (4,5,7,11) doublet which is visible were subtracted from the overlap peak. This was presumed to give the area of the (9,12) boron singlet.

One caution should be mentioned. The areas of the peaks where overlap occurred depend upon how well a curve could be drawn to fit the observed spectra. The curves were drawn to give what appeared to give a good fit to the overlapping peaks. The use of a curve resolver did not appreciably change the relative areas. We are reasonably confident that our curves are accurate to a few percent in most cases, but at high power levels overlap was more extensive and our error is probably increased.

All halogen compounds show rapid saturation of boron atoms bonded to halogen. There is a difference in saturation rates between the set (8,9,10,12) and the set (4,5,7,11) in octachloro-o-carborane. The (9,12) and (8,10) boron atoms saturate most rapidly. The (3,6) boron atoms do not appear to saturate.

Comparing now the (9,12) and (8,10) boron atoms bonded to the same halogen, these four boron atoms appear to saturate at the same rate. Our data are not accurate enough for the differences sometimes observed to be significant. Change of halogen from chlorine to bromine or iodine also does not seem to have much effect upon the rate of saturation of the (9,12) boron atoms.

Our data suggests that the presence of a halogen bonded to boron could be detected, at least in the carboranes, by a saturation study. To test this idea, a saturation study of 9,10-bromo-m-carborane was carried out. The (9,10) peak, whose position was known, showed the same type of saturation effects as were observed in the halo-o-carboranes, although the rate of saturation was different.

A real test was presented by the spectrum of 5-bromo-o-carborane, so named by Dr. S. Hermánek, who prepared it from 5-bromodecaborane(14). There are no symmetrically equivalent boron atoms, although it appears as if the 4 and 11 boron atoms may be nearly equivalent, and may have similar chemical shifts.

The saturation study indicated that the peak at + 32.8 ppm, of approximate relative area two, is associated with the 5 boron. The remaining assignments are based primarily on coupling constants. The set of peaks at lowest field can be resolved into two overlapping doublets of area one each at + 23.2 ppm and + 24.1 ppm with J_{BH} = 150 $\pm$ 2 Hz. These doublets are assigned to the 9 and 12 boron atoms. The 8 and 10 boron atoms are found at + 30.2 ppm and + 31.4 ppm, overlapping doublets of relative area one each with J_{BH} = 152 $\pm$ 2 Hz. The 3 and 6 boron atoms are assigned to two doublets of relative area one at + 36.5 ppm and + 39.7 ppm with J_{BH} = 176 $\pm$ 2 Hz. Relative areas at low power show that one of the remaining doublets of relative area one can be found at + 33.4 ppm with one of its two peaks coinciding with the singlet due to the 5 boron. The ^{11}B-^{1}H coupling constant found is 168 $\pm$ 4 Hz. The remaining two doublets accidently coincide at + 35.7 ppm with J_{BH} = 168 $\pm$ 4 Hz.

The relative area of the high field peaks, those with chemical shifts greater than + 32.8 ppm, was defined as 4.50. The areas of the remaining peaks were obtained and are reported in Table V relative to the high field set defined as 4.50. A curve which is believed to represent the peak due to the 5 boron atom singlet, and also to consist of contributions from the doublets

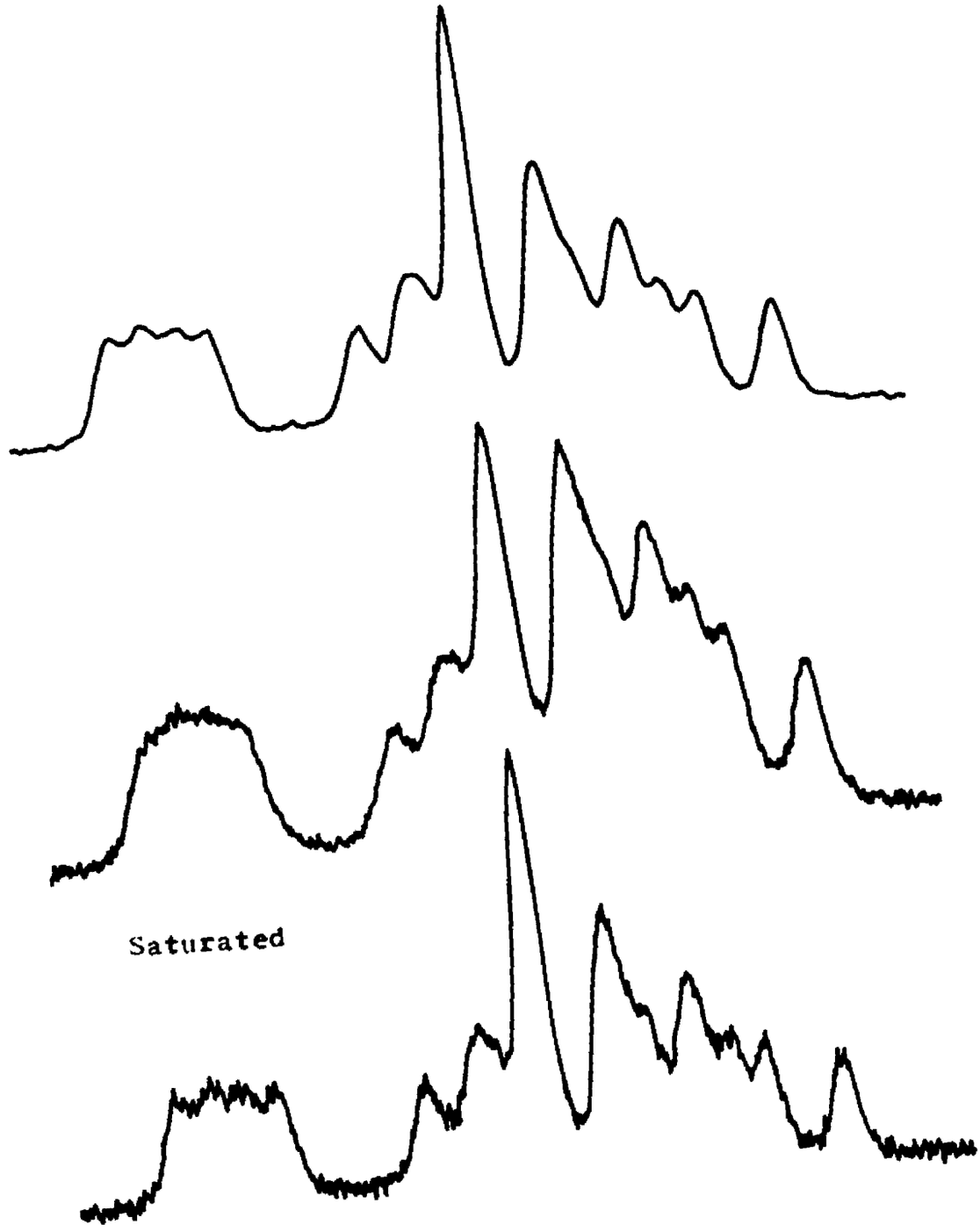

Figure 28. ^{11}B NMR Spectra of 5-Bromo-o-Carborane at 250 MHz.

due to the 10(8) and 7 boron atoms was drawn, and the area calculated and reported relative to the high field boron atoms. The relative areas calculated are pleasing, but cannot be considered accurate enough to draw profound conclusions. We can state, however, that knowing the chemical shift of the 5 boron atom aided greatly in assigning the spectrum. It appears that a saturation study of halocarboranes, and perhaps of haloboranes, can be a diagnostic tool for interpreting spectra.

The results of the saturation studies on o-carborane, o-carborane-d_4, and 1-bromomethyl-o-carborane-d_4 show that the rate of saturation of boron bonded to hydrogen is the same as that for boron bonded to deuterium, within experimental error. This demonstrates that there are no profound interactions of the quadrupole moment of deuterium or halogen with the quadrupole moment of boron.

The saturation effects observed are due to a change in the electric field gradient around the boron atoms bonded to halogen. All the halogens are more electronegative than hydrogen and are expected to attract the electron cloud more strongly than hydrogen. Substitution of deuterium for hydrogen would have no effect upon the electron cloud.

Substitution of halogen for hydrogen on carboranes results in a more symmetrical distribution of electrons about the boron nucleus. This reduces the electric field gradient, and hence lengthens T_1, and cause a change in saturation rate.

It appears that halogen substitution has a measurable effect only upon the boron atoms bonded directly to the halogen. The saturation rate of the (8,10) boron atoms in 9-bromo-o-carborane, 9,12-dibromo-o-carborane, o-carborane, and o-carborane-d_4 are all about the same. Intuitively, one would expect that changes in the electron cloud would be transmitted throughout the cage. However, no evidence for changes in saturation rates was observed for other than borons bonded directly to halogen.

The effect of substitution on the carbon was not extensively studied. 1-Bromomethyl-o-carborane-d_4 showed the same relative rates of saturation that were found for o-carborane and o-carborane-d_4. 1-Vinyl-o-carborane does seem to show a change from o-carborane. The rate of saturation of the (9,12) boron atoms in 1-vinyl-o-carborane does appear to be slower than in o-carboranes.

3-Phenyl-o-carborane was also studied. The 3 boron atom does not appear to saturate nor does the 8(10) boron atom. The (9,12) boron atoms do appear to saturate but at a slower rate than in o-carborane. The singlet due to the 3 boron is broad and overlaps both the (9,12) doublet and the 8(10) doublet. Fitting curves for determination of the areas of the peaks is less certain, and the relative areas are less accurate. We can state that the 3 boron does not appear to saturate because the peak height increases relative to the height of the (9,12) boron doublet.

The only other carbon-substituted carborane studied was 1,7-dimethyl-o-carborane. The spectrum is quite compressed and consists

of four peaks. The relative areas do not change significantly upon changing RF power.

3.6 Friedel-Crafts Alkylation

Decaborane(14) can be alkylated at the 1,2,3,4 and even 5 positions by a "Friedel-Crafts" alkylation using a haloalkane and aluminum chloride catalyst. The formation of boron-alkylated carboranes has been reported[1,2] via reactions similar to the decaborane reaction. Reactions under similar conditions have been reported[3,4] to produce halocarboranes. Therefore, it was decided to try to prepare a B-methyl-o-carborane by a Friedel-Crafts type reaction.

A Fischer-Porter pressure reaction tube was charged with o-carborane, a large excess of Al_2Cl_6, an excess of methyl bromide, and carbon disulfide for solvent. The reaction mixture was maintained at 55°C for 24 hours. HCl and HBr were released by the reaction and were identified from the infrared spectrum of the gaseous mixture. The major component in the gas mixture was HCl. The HCl and HBr mixture was collected from the reaction tube and allowed to react with NH_3. The NH_4Br and NH_4Cl mixture produced was weighed, and the weight collected indicated that about 25%

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[1] S. L. Clark and D. J. Mangold, U. S. Patent 3,092,664 (1963).

[2] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. Cohen, and M. Fein, Inorg. Chem. 2, 1120 (1963).

[3] L. I. Zakharkin, O. Y. Okhlobystin, G. K. Semin, and T. A. Babushkina, Izv. Akad. Nauk. U.S.S.R., Ser. Khim. 1913 (165).

[4] L. I. Zakharkin and V. N. Kalinin, Dokl. Akad. Nauk. U.S.S.R. 169, 590 (1966).

of the methyl bromide had reacted.

The percent of methyl bromide that reacted increased with increasing amounts of aluminum chloride catalyst. The percent of methyl bromide that reacted did not appear to increase with increasing amounts of o-carborane or of methyl bromide.

The product, alkylated o-carborane, was a dense oily red liquid, soluble in aromatic solvents. The product is not a halo-o-carborane because all halogen derivatives of o-carborane are solids with melting points in excess of 170°C. The product was partially purified by washing with n-hexane. The alkane-soluble portion consisted of a mixture of undetermined nature. The product was not soluble in n-hexane.

A ^{11}B NMR of the residue was taken. The spectrum appeared in the same region as that of o-carborane. Chemical shifts, relative areas, and coupling constants, where determinable, are given in Table II, and the best spectrum is given in Figure 29.

It appears that o-carborane can be alkylated by methyl bromide in a Friedel-Crafts type reaction. The ^{11}B NMR spectrum is consistent with alkylation at the 9(12) position. These positions are most active in electrophilic halogenation.

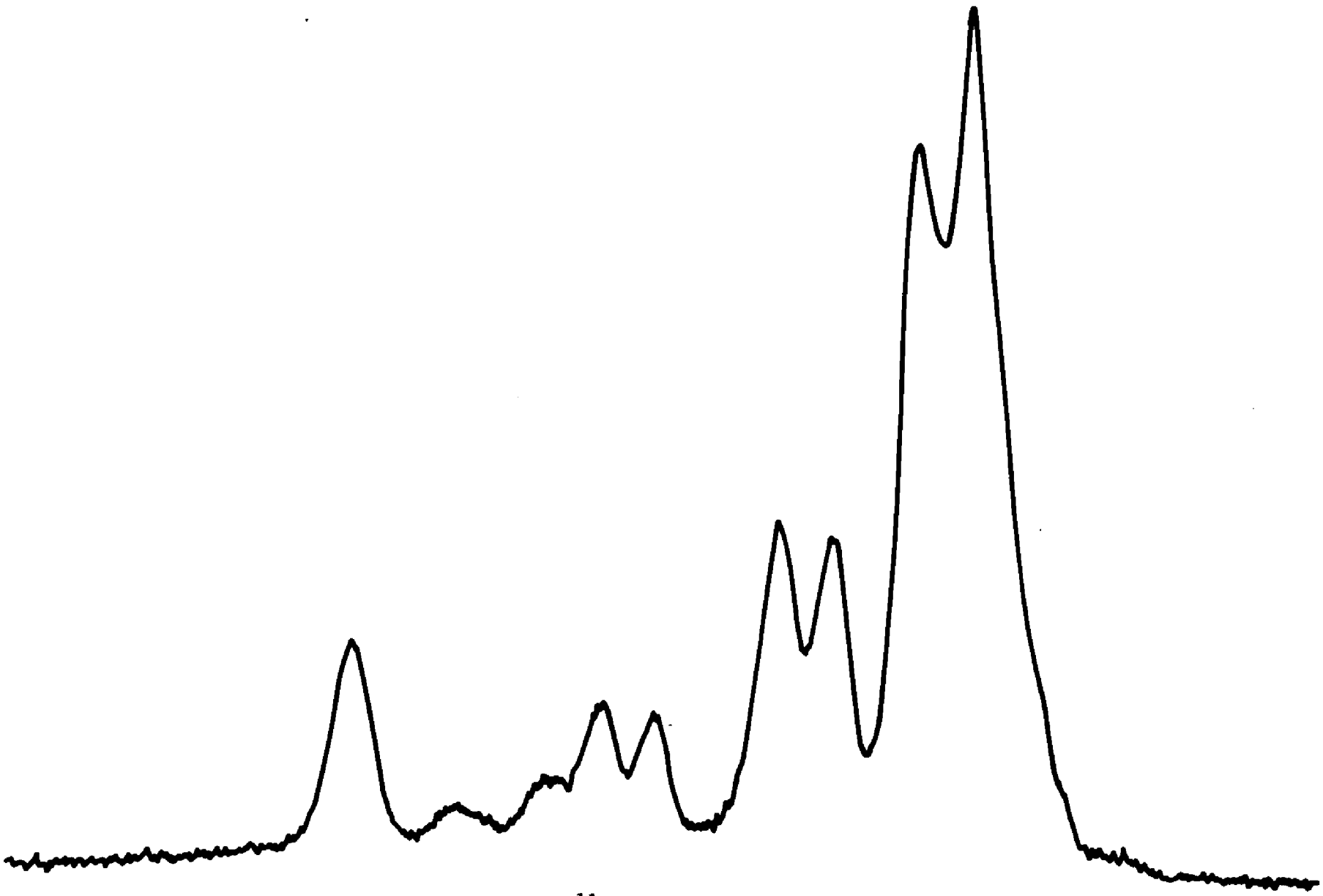

Figure 29. ^{11}B NMR Spectrum of B-Methyl-o-Carborane

4.0 SUMMARY

The ^{11}B NMR spectra of o- and m-carborane, and of selected derivatives of o- and m-carboranes, were obtained at 80.2 MHz. The ^{11}B NMR spectra of o- and m-carborane were assigned, and values of coupling constants and chemical shifts are reported. The ^{11}B NMR spectra of selected derivatives of o- and m-carborane are interpreted on the basis of these assignments. It was established that o- and m-carborane undergo deuterium isotope exchange under electrophilic conditions at both normal and high pressures of deuterium chloride, and the positions of exchange were determined by ^{11}B NMR spectral studies. The ^{1}H NMR spectra of o- and m-carborane, and of selectively deuterated o- and m-carborane, were obtained at 250 MHz, and were assigned. Values of coupling constants and chemical shifts are reported. Interesting and unusual effects were found upon variation of RF power while obtaining ^{11}B NMR spectra of halogen substituted o- and m-carboranes. It was established that saturation studies are an aid to the interpretation of ^{11}B NMR spectra of halogen substituted o- and m-carboranes. Attempted syntheses of B-alkyl o- and m-carborane are also reported.

5.0 EXPERIMENTAL

5.1 Preparative Techniques

5.11 Deuterated Carboranes

5.111 8,9,10,12-d_4-o-$B_{10}C_2H_{12}$. In a typical experiment, a 500 ml round-bottom flask equipped with a stirring bar, "O" ring seal, and a Teflon stopcock was charged with 3 millimoles of ortho-carborane, 5 millimoles of aluminum chloride, and 15 ml of carbon disulfide. The flask was joined to a vacuum line, and evacuated at -78°C. 6 millimoles of DCl were then condensed into the flask. The reaction mixture was stirred for two to three hours at room temperature, then cooled to -78°C, and the HCl/DCl mixture was removed. 6 millimoles more of DCl were then condensed into the flask, and the exchange continued for two to three more hours. The process was continued until two successive infrared spectra of the gaseous HCl/DCl mixture showed no change in the relative intensities of the HCl/DCl absorptions. This required 54 to 60 millimoles of DCl.

5.112 8,9,10,12-d_4-1-$BrCH_2B_{10}C_2H_{11}$. The same procedure was used to prepare 8,9,10,12-d_4-1-bromomethyl-ortho-carborane. 8,9,10,12-d_4-1-bromomethyl-ortho-carborane was also prepared from 1,2,3,4-d_4-decaborane(14) by literature methods.[1]

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[1] Earl L. Muetterties, Ed., Inorganic Synthesis, Vol. X, McGraw-Hill Book Company, New York, 1967, p. 100.

5.113 9,10-d_2-m-$C_2B_{10}H_{12}$. The same procedure was also used to prepare 9,10-d_2-meta-carborane. In this case, infrared spectra of the gaseous HCl/DCl mixture are not useful for determining the end-point of the exchange, because further deuterium exchange occurs slowly at the 5,12 boron atoms. A kinetic study indicated that, starting with 3 millimoles of meta-carborane, 36 millimoles of DCl added as above, section 5.111, will produce 9,10-d_2-meta-carborane of high purity as determined by its ^{11}B NMR spectrum. Continued addition of DCl results in deuterium exchange at the 5,12 boron atoms, and some exchange at the 4,6,8,11 boron atoms.

5.114 8,9,10,12,4,5,7,11-d_8-o-$C_2B_{10}H_{12}$. In a typical experiment, 3 millimoles of 8,9,10,12-d_4-ortho-carborane were placed in a Fischer-Porter tube with a small stirring bar, 5 millimoles of aluminum chloride, and 15 ml of carbon disulfide. After evacuation of the tube, 42 millimoles of DCl were condensed into the tube. The reaction mixture was stirred at room temperature for 24 hours at a total DCl pressure of 90 psig. The DCl/HCl mixture was removed and an additional 42 millimoles of DCl were added. The process was continued until a total of 168 millimoles of DCl had been added. The product was estimated to have exchanged a total of about 6 or 7 deuterium atoms per molecule from its ^{11}B NMR spectrum.

5.115 9,10,5,12,4,6,8,11-d_8-m-$C_2B_{10}H_{12}$. The same procedure as in section 5.114, above, was used for the preparation of a meta-carborane which had exchanged about 6 or 7 deuterium atoms per molecule. The ^{11}B NMR spectrum of the product showed that complete exchange at the 5,12 and 9,10 boron atoms had occurred.

5.12 Alkylated Carboranes

5.121 B-Methyl-Ortho-Carborane. In a typical experiment, 3 millimoles of ortho-carborane, a stirring bar, 10 millimoles of aluminum chloride, and 15-20 ml of carbon disulfide were placed in a Fischer-Porter tube. The system was evacuated and 24 millimoles of methylbromide were condensed into the tube. The reaction mixture was stirred at 60°C for 36 hours. The tube was rejoined to a vacuum line, and the materials volatile at -78°C were removed. The tube was then opened and the solution filtered from the solid materials. The solids were treated with water and the product, a red oily liquid, was extracted from the water with ethyl ether. The ether was evaporated from the product on a rotary evaporator. The product was then washed three times with 5 ml portions of n-hexane. The ^{11}B NMR spectrum of the product indicated the presence of some impurity. Sublimation at 80°C on a vacuum line did not seem to improve the purity of the product.

5.122 B-Methyl-Meta-Carborane. A methylated meta-carborane was prepared by the same procedure described in section 5.122 except that no sublimination was carried out.

5.13 Literature Preparations

The bromo carboranes,[1] the chloro carboranes,[2] 9,12-diiodo-

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[1] Hampton D. Smith, Thomas A. Knowles, and Hansjuergen Schroeder, Inorg. Chem. 4, 107 (1965).

[2] H. Schroeder, T. L. Heying, and J. R. Reiner, Inorg. Chem. 2, 1092 (1963).

ortho-carborane,[1] the methyl and dimethyl carboranes,[2,3] and 1-bromomethyl-ortho-carborane[4] were all prepared by literature methods. Purity was determined from melting point determinations and, where infrared spectra were reported,[5-7] from the infrared spectra. Ortho-carborane, meta-carborane, and 1-vinyl-ortho-carborane were obtained from Alfa Inorganics. 5-Bromo-ortho-carborane and 3-phenyl-ortho-carborane were obtained from Dr. S. Hêrmánek of the Czechoslovak Academy of Sciences.

5.2 Description of the Spectrometer

The NMR spectrometer used has been described by Dr. Dadok.[8] The magnet is a 60 Kg superconducting solenoid constructed by

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[1] L. I. Zakharkin and V. N. Kalinin, Izv. Akad. Nauk. U.S.S.R., 908 (1967).

[2] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. Fein, Inorg. Chem. 2, 1120 (1963).

[3] T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S.I. Trotz, Inorg. Chem. 2, 1097 (1963).

[4] E. L. Muetterties, Ed., Inorganic Synthesis, Vol. X, McGraw-Hill Book Co., New York, 1967, p. 100.

[5] H. Schroeder, T. L. Heying, and J. R. Reiner, Inorg. Chem. 2, 1092 (1963).

[6] L. A. Leites, L. E. Vinogradov, V. N. Kalinin, and L. I. Zakharkin, Izv. Akad. Nauk. U.S.S.R. 1016 (1968).

[7] V. I. Stanko, A. I. Klimova, and T. P. Klimova, J. Gen. Chem. U.S.S.R. 37, 2123 (1967).

[8] J. Dadok, Abstracts, 10th Experimental NMR Conference, Pittsburgh, Pa., February 1969; J. Dadok, R. F. Sprecher, A. A. Bothner-By, and T. Link, Abstracts, 11th Experimental NMR Conference, Pittsburgh, Pa., April 1970; J. Dadok, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1971.

Westinghouse. The shim coils for improving field homogeneity were designed by Dr. Dadok. Resolution on proton samples is better than 0.1 Hz (locked) and field stability is approximately 1 to 2 Hz without the locking system engaged. The RF portion of the spectrometer uses a frequency synthesizer and a single coil, time shared system developed by Dr. Dadok. Samples are measured in spinning 5 mm Wilmad precision NMR tubes at ambient temperature.

5.3 Reagents Used

Aluminum chloride (anhydrous) was obtained from Fischer Scientific Company and was used as supplied.

Acetonitrile (Baker Analyzed) was obtained from J. T. Baker Chemical Company.

Benzoyl chloride (Reagent Grade) was obtained from Mallinckrodt Chemical Works and used without further purification.

Benzene (Certified Reagent) was obtained from Fischer Scientific Company and was dried over calcium hydride and distilled prior to use.

Bromine was obtained from J. T. Baker Chemical Company.

Butyl lithium was obtained from Foote Mineral Company and used as supplied.

Ortho-carborane was obtained from Alfa Inorganics and was used as supplied.

Meta-carborane was obtained from Alfa Inorganics and was used as supplied.

Vinyl-o-carborane was obtained from Alfa Inorganics and was used as supplied.

Carbon disulfide (Baker Analyzed) was obtained from J. T. Baker Chemical Company and was dried over type 4A molecular sieves prior to use.

Chloroform-d_1 (99.5% deuterium) was obtained from Stohler Isotopic Chemicals.

Deuterium chloride was obtained from the reaction of benzoyl chloride and deuterium oxide[1] and was distilled in a vacuum line prior to use.

Deuterium oxide (99.88 mole %) was obtained from Bio-Rad Laboratories.

Decaborane(14) (Triply Sublimed) was obtained from Callery Chemical Company and was used without further purification.

Ethyl ether (anhydrous - Baker Analyzed) was obtained from J. T. Baker Chemical Company and was dried over calcium hydride and distilled prior to use.

Heptane (Practical Grade) was obtained from Eastman Organics.

Hexane (Certified Reagent) was obtained from Fischer Scientific Company

Methyl bromide was obtained from the Matheson Company, Inc., and was distilled in a vacuum line prior to use.

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[1] H. C. Brown and G. Groot, J. Am. Chem. Soc. 64, 2223 (1942).

Methyl iodide (Certified Reagent) was obtained from Fischer Scientific Company and was dried over type 4A molecular sieves and distilled prior to use.

Propargyl bromide was obtained from Aldrich Chemical Corporation and was used as supplied.

Trimethoxy borane was obtained from Alfa Inorganics.

Tetramethyl silane was obtained from Aldrich Chemical Corporation and was dried over type 4A molecular sieves prior to use.

Chlorine was obtained from The Matheson Company, Inc.

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