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REACTIONS OF PENTABORANE(9) AND ITS DERIVATIVES WITH AMINES

by

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A DISSERTATION

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UNIVERSITY, ALABAMA

1971

DEDICATION

This dissertation is dedicated to my wife, Patricia, who has given me much understanding and encouragement during my years of graduate study.

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Dr. Christopher L. Bramlett for his assistance and guidance throughout this research.

The author also wishes to acknowledge the graduate teaching assistantships provided him by the Department of Chemistry at the University of Alabama.

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INTRODUCTION

The chemistry of the boron hydrides began with the now classical work of Alfred Stock.[1] It was not until about 1912, at which time Stock had developed vacuum-line techniques for handling small amounts of volatile, air-reactive materials, that mixtures of the boron and silicon hydrides could be separated and characterized. During the following twenty years Stock and his co-workers isolated and studied the physical and chemical properties of B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$.

These compounds are said to be "electron-deficient", i.e., they contain insufficient bonding electrons to form conventional two-electron bonds between all the atom-pairs that are within a bonding distance. A characteristic of most of the boranes is the hydrogen bridge bond, and this type of bond can best be regarded as a three-center bond. Similar three-center bonds between three boron atoms can be used in combination with normal bonds to describe the bonding in boranes.

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

The accepted structure for pentaborane(9), B_5H_9, is based upon the crystal structure study of Dulmage and Lipscomb[2,3] in which the molecule was found to have C_{4v} symmetry. Hydrogen atoms were located by subtraction of the boron contribution. This structure was verified by the electron diffraction study of Hedberg, et al.[4] and by the microwave studies of Hrostowski et al.[5]

The boron skeleton shown in Figure 1 can be considered as a fragment of an octahedron, and actually forms a square pyramid. Each of the boron atoms has a terminally bonded hydrogen, and the remaining four hydrogens are located below the plane of the base in bridging positions. These bridge hydrogens form an external dihedral angle of about 193°.

Pentaborane(9) can be examined from a simplified molecular orbital approach.[6] Apical boron atoms are considered to be sp hybridized, with two unhybridized p orbitals, while the four basal boron atoms are sp^3 hybridized.

---

[2]W. J. Dulmage and W. N. Lipscomb, J. Am. Chem. Soc., 73, 3539, (1951).

[3]W. J. Dulmage and W. N. Lipscomb, Acta Cryst., 5, 260, (1952).

[4]H. Hedberg, M. E. Jones, and V. Schomaker, J. Am. Chem. Soc., 73, 3539, (1951).

[5]H. H. Hrostowski, R. J. Meyers and G. C. Pimentel, J. Chem. Phys., 20, 518, (1952).

[6]W. N. Lipscomb, Boron Hydrides, The W. A. Benjamin Company, New York, New York, 1963.

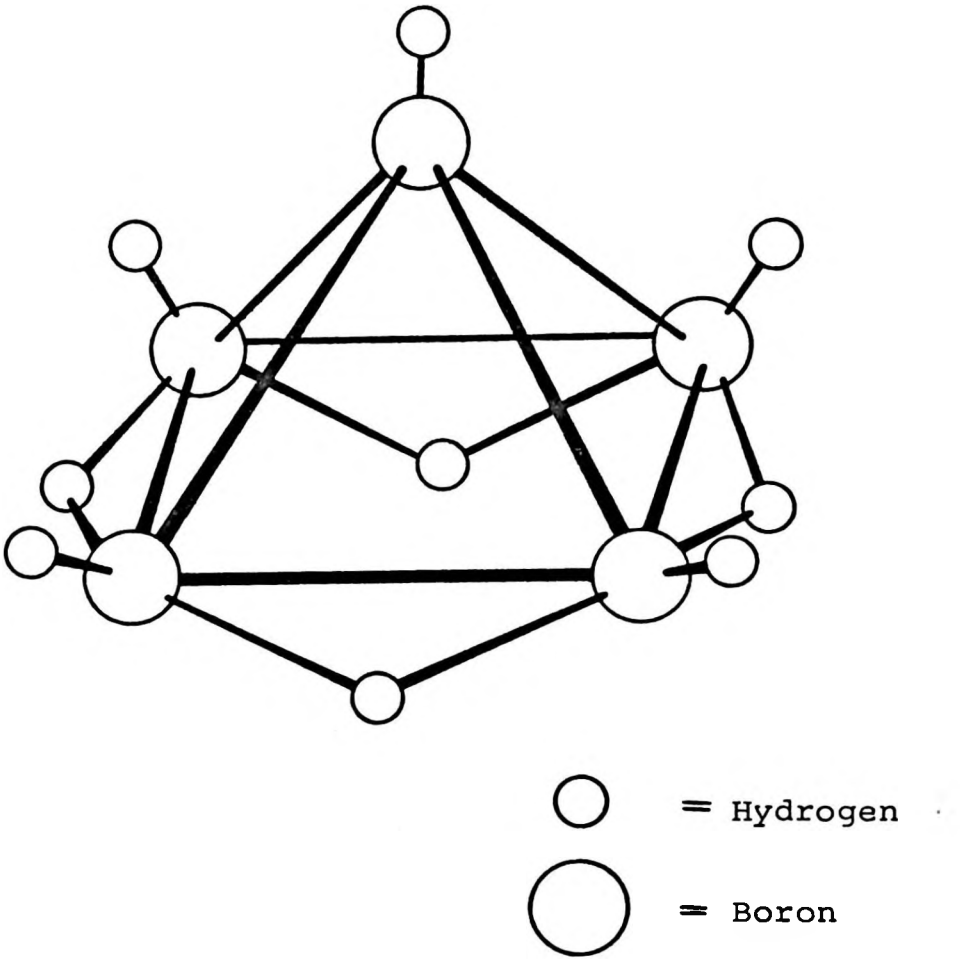


Figure 1. Spatial arrangement of atoms in pentaborane(9).

Each boron atom contributes four atomic orbitals and three electrons, giving a total of twenty atomic boron orbitals and fifteen electrons for bonding. There are nine 1s orbitals and the same number of electrons contributed by hydrogen atoms. After isolating the external electron pair B-H bonds, and the 4 B-H-B bridge bond, the cage framework can be considered as held together by the remaining six electrons occupying molecular orbitals spread over the framework of cage boron atoms. In other words, the bonding electrons of the cage system are largely delocalized over the entire cage framework.

During the past several years a considerable number of reactions involving reaction at external positions on the B_5H_9 cage system have been reported consistent with the results of calculations made by Lipscomb.[6] Nearly all substitutions at the apex of B_5H_9 have been affected using conditions[7] reminiscent of aromatic electrophilic substitution reactions. Ryschkewitsch *et al.*[8] found that olefins and alkyl halides react with B_5H_9 to give the apically substituted organoborane when catalyzed with a Lewis acid such as $AlCl_3$, anhydrous $FeCl_3$, or $SnCl_4$. Further alkylation did not occur even with excess olefins or alkylhalide, indicating

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[7]T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, Inorg. Chem., 6, 1465, (1965).

[8]G. E. Ryschkewitsch, L. W. Harris, E. J. Mezey, H. H. Sisler, E. A. Weilmuenster and A. B. Garrett, Inorg. Chem., 2, 890, (1963).

that attack at the apical boron atom, which has the most electron density, is exclusive under electrophilic conditions. The apically substituted organoborane will isomerize to a basal position establishing that the latter position is thermodynamically more stable. For example, thermal rearrangements of 1-RB_5H_8 to 2-RB_5H_8 where R=CH_3 or C_2H_5, occur at 200°[9]. About 80% rearrangement of 1-DB_5H_8 to 2-DB_5H_8 is found in 20 hours at 145°[10]. The question of the nature of mechanism of isomerization is complicated by the fact that there is little evidence that this intramolecular rearrangement takes place at a lower temperature than the intermolecular H atom exchange.[11]

Ryschkewitsch et al.[12] have established that, under nucleophilic conditions, olefins will attack the somewhat electropositive basal boron atoms[6,7]. Cyclopropane and B_5H_9 were found by Overton[13] to react thermally at 200° to give two alkylated pentaborane products, the 1-isopropylpentaborane and the 2-n-propylpentaborane. The basal isomer

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[9]T. P. Onak and F. J. Gerhart, Inorg. Chem., 1, 742, (1962).

[10]T. P. Onak and F..J. Gerhart, J. Am. Chem. Soc., 81, 3554, (1959).

[11]I. Shapiro and B. Keilin, J. Am. Chem. Soc., 77, 2663, (1955).

[12]G. E. Ryschkewitsch, E. J. Mezey, C. R. Altwicker, H. H. Sisler, and A. B. Garrett, Inorg. Chem., 2, 892, (1963).

[13]E. B. Overton, Doctoral Dissertation, University of Alabama, 1970.

was, by far, the major reaction product. It was suggested that the reaction path involves the nucleophilic attack of cyclopropane at the basal boron atoms of B_5H_9 in the formation of 2-alkyl isomer. The presence of a small amount of the 1-isomer was accounted for by the possibility of isomerization. Onak et al.[14] observed a 22% yield of the basal chlorinated derivatives, but no apically chlorinated derivatives from the reaction of methyl chloride with 2-methylpentaborane using $AlCl_3$ as a catalyst.

The theoretical calculations by Lipscomb et al.[6] have also indicated that bridge hydrogens are more positive than the terminal hydrogens leading to a prediction that bridge hydrogens are more hydrolytic. This has been supported by Shore, et al.[15], who found that B_5H_9 and B_6H_{10} reacted with suitable bases such as $LiCH_3$, LiC_4H_9, and KH, to form the salt MB_5H_8 in ether solution. The boron hydride, in both cases, loses a bridge hydrogen, with the larger boron hydride salt solution being quite stable. These ionic materials can undergo further reactions in order to form boron hydrides containing various substituents in the briding position. Gaines et al.[16] found that LiB_5H_8 and compounds of the

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[14]P. M. Tucker, T. Onak, and J. Leach, Inorg. Chem., 9, 1430, (1970).

[15]H. D. Johnson, R. A. Geanangel, S. G. Shore, Inorg. Chem., 9, 908, (1970).

[16]D. F. Gaines, T. V. Iorns, J. Am. Chem. Soc., 90, 6617 (1967).

general formula XMR_3 react at low temperature to give u-$R_3MB_5H_8$ which isomerizes to 2-$R_3MB_5H_8$ at room temperature. X was Cl, Br, or I while M could be Si, Ge, Sn or Pb.

Since the early work of Stock[1], the observations that at low temperatures each of the hydrides of boron forms molecular compounds with ammonia (borane·$(NH_3)_n$ with n-2,4,6) have led to the casual surmise that the boranes behave like "acids". It is now evident that the mere stoichiometry of condensation does not demonstrate acid-base behavior.

Many of the early attempts to account for the electron deficiency of diborane involved the suggestion that the molecule contains potentially acidic hydrogens. These arguments culminated in Wiberg's[17] representation of diborane as an ethylene analog and in Pitzer's[18] protonated bridge bond based on the now well supported bridge model.

The formation of the "diammoniate of diborane" was originally cited as evidence supporting the latent acidic character of diborane, but the exchange experiments of Burg[19] and the tracer study of Shore, Girardot and Parry[20] show conclusively that the formation of this compound, $H_2B(NH_3)_2^+BH_4^-$ in no way reflects such acidic behavior.

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[17] E. Wiberg, Ber., 69, 2816, (1936).

[18] K. S. Pitzer, J. Am. Chem. Soc., 67, 1126, (1945).

[19] A. B. Burg, J. Am. Chem. Soc., 69, 747, (1957).

[20] S. G. Shore, P. R. Girardot, R. W. Parry, J. Am. Chem. Soc., 80, 20, (1958).

Parry and Shore[21] found that when diborane and ammonia are allowed to interact slowly at about -120°C, it is possible to get diborane absorption and loose compound formation as indicated by a drop in B_2H_6 pressure, but they were also able to separate some B_2H_6 and NH_3 from the mixture by distillation. They pictured such ammonia addition as resulting from ammonia coordination to the weakly acidic hydrogen located in the bridge. Kodama[22] made similar postulates for the system B_4H_{10}-NH_3 in which he interpreted his observations as suggesting low temperature addition of ammonia to the very weakly acidic hydrogen bridges without bridge rupture. On standing, the bridge bonds opened, and a new product, $B_4H_{10}\cdot 2NH_3$, was formed. Shore et al.[23] reported that ammonia reacts with hexaborane(10) in a deprotonation reaction to form the compound, $NH_4^+B_6H_9^-$. It has also been shown unequivocally that the bridge hydrogens of decaborane are acidic in character.[24] Similarly the observations of Fitch and Laubengayer[25] on

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[21]R. W. Parry and S. G. Shore, J. Am. Chem. Soc., 80, 19, (1958).

[22]G. Kodama, Doctoral Dissertation, University of Michigan.

[23]G. L. Brubaker, M. L. Denniston, S. G. Shore, J. C. Carter, and F. Swicker, J. Am. Chem. Soc., 92, 7216 (1970).

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

[25]S. J. Fitch and A. W. Laubengayer, J. Am. Chem. Soc., 80, 5911, (1958).

the system dimethylamine-decaborane can be interpreted in terms of amine addition to the acid decaborane bridge without formation of an ionic methylammonium salt. The volatility of the product and the easy regeneration of the amine by acid indicated association of amine and borane without cleavage of the borane molecule. When the product is heated, decomposition interpretable as bridge opening occurs.

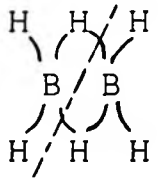
In general, the presence of bridge hydrogens in boranes appears to be one major determinant of the chemical and physical characteristics of boranes. The bridge hydrogens are apparently more hydrolytic than terminal hydrogens (but the reactivity of the hydrogens depend considerably on the physical state and especially on the solvent), and acid strength increases with increased polyhedral framework size.

As a result of the strong "Lewis Acid" character of the boron hydrides, the manner of their reactions with various bases of different electron donor properties such as the amines is of great interest. Stock[1] noted the reaction of B_2H_6, B_4H_{10}, B_5H_9 and $B_{12}H_{12}$ with a number of amines and suggested possible structures for the addition type compounds. Since then, the size of the field of boron-nitrogen chemistry has grown immensely. Wiberg[26] classified boron-nitrogen derivatives in accordance with the nature of the boron-nitrogen bond.

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[26]E. Wiberg, Naturwissenschaften, 35, 182, (1948).

Amine-boranes are addition compounds of amines with the borane unit, BH_3, or substituted boranes, ($R_3N \longrightarrow BH_3$). This structure is roughly comparable to that of alkanes, in the sense that in alkanes two carbon atoms are linked by a single two-electron bond. Compounds such as salts containing the bisamine-boronium cation, $(R_3N)_2BR_2^+X^-$ should also be considered as members of the amine-boranes. The reaction of amines with diborane at low temperatures normally results in symmetrical cleavage of the diborane and ready formation of



$$+ \quad 2NR_3 \longrightarrow 2R_3N \cdot BH_3$$

an amine-borane. This symmetrical cleavage of the boron-hydrogen bridge system is typical of the reactions of most Lewis bases with diborane. Relatively few examples of unsymmetrical cleavage have been reported. Direct reaction of ammonia with diborane produces $H_2B(NH_3)_2^+BH_4^-$, the best documented example of unsymmetrical cleavage by a nitrogen base. Shore *et al.*[27] have also shown that diborane reacts directly with excess CH_3NH_2 or $(CH_3)_2NH$ at low temperatures to produce unsymmetrical as well as symmetrical cleavage. The predominant product was found to be that of the unsymmetrical cleavage.

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[27] S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, *87*, 2755, (1965).

Burg[28] and Schlesinger reported that diborane reacts with acetonitrile to yield the adduct $CH_3CN \cdot BH_3$. This data was verified by Emeleus and Wade[29] who also studied the reactions:

$$B_2H_6 + EtCN \longrightarrow EtCN \cdot BH_3$$

$$B_2H_6 + CH_2{=}CH{-}CN \longrightarrow CH_2{=}CH{-}CN \cdot BH_3$$

$$B_2H_6 + \text{Cyanogen} \longrightarrow \text{products not identified}$$

$$B_2H_6 + HCN \longrightarrow \text{products not identified}$$

Aminoboranes differ from amineboranes in that the boron and nitrogen are linked together by one normal covalent bond. It is possible for the unshared electron pair of the nitrogen to participate somewhat in this linkage, thereby introducing a degree of double bond character analogous to the alkenes. The parent compound of the aminoborane system, $H_2N{-}BH_2$, is not known in monomeric form but is highly associated and unstable. The extent of association of aminoborane decreases as hydrogen is replaced by organic groups. Thus methylaminoborane, $CH_3HN{-}BH_2$, exists as a stable trimer.[30] Reversible

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

[29] H. J. Emeleus and K. Wade, J. Chem. Soc., 2614, (1960).

[30] T. C. Bissot and R. W. Parry, J. Am. Chem. Soc., 77, 3481, (1955).

monomer-dimer equilibria have been demonstrated for dimethylaminoborane.[31] Preparations are based on the fact that amine-boranes decompose at elevated temperatures in accordance with the general equation:

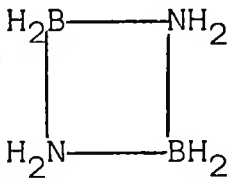
$$R_3N \cdot BR_3' \longrightarrow R_2NBR_2' + RR'$$

In other reactions, interesting heterocyclics have been formed, including the following:

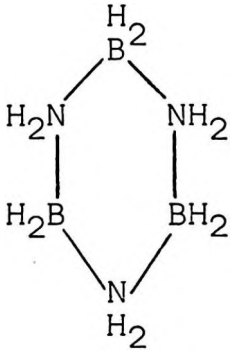
Boddecker, Shore, and Bunting[32]

$$(NH_3)_2BH_2^+BH_4^- + NaNH_2 \longrightarrow (BH_2NH_2)_n + NaBH_4 + 2NH_3$$

for n=2,



for n=3,

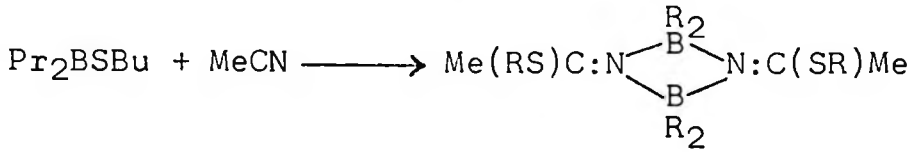


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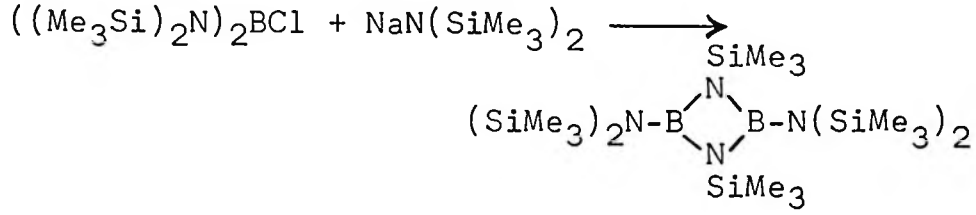
[31] E. Wiberg, H. Bolz and P. Buchheit, Z. Anorg. Allg. Chem., 256, 285, (1948).

[32] K. W. Boddecker, S. G. Shore and R. K. Bunting, J. Am. Chem. Soc., 88, 4496, (1966).

Mikhailov, Dorokhov, and Yakovlev[33]

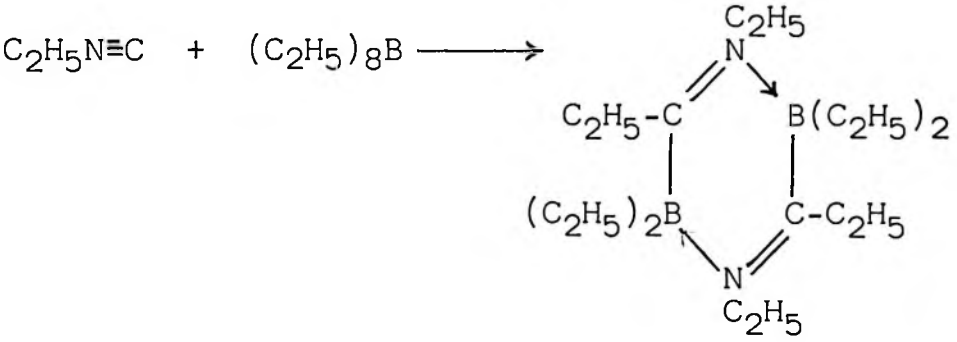


and Geymayer and Rochow[34]



Reactions involving isocyanides have also led to the formation of heterocyclics:

Bresadola, Canaro, Pecile, and Turco[35]



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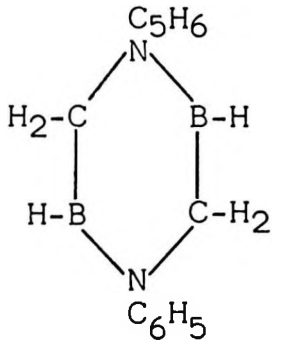
[33]B. M. Mikhailov, V. A. Dorokhov, I. P. Yakovlev, Izv. Akad. Nawk. SSSR, Ser. Khim., 332, (1966).

[34]P. Geymayer and E. G. Rochow, Monatsh. Chem., 97, 429, (1966).

[35]S. Bresadola, G. Carraro, C. Pecile, and A. Turco, Tetr. Letters, 43, 3185, (1964)

Tanaka and Carter[36]

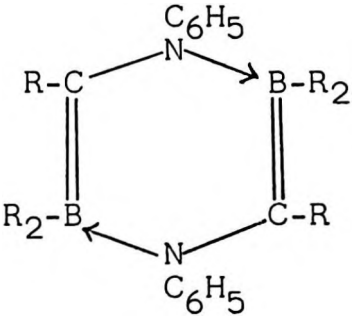
$C_6H_5N{\equiv}C + B_2H_6 \longrightarrow$



Hesse and White[37]

$R_3B + C_6H_5NC \longrightarrow$

$R{=}C_2H_5$ or n-C_4H_9



Burg[38] demonstrated that the hexane-like ring compound $((CH_3)_2NBH_2)_3$ can be formed in major yields from the trimerization of $(CH_3)_2NBH_2$ in the presence of B_5H_9. A mechanism was proposed in which as $(CH_3)_2NBH_2 \cdot B_4H_6$ complex is involved as an intermediate.

$$B_5H_9 + (CH_3)_2NBH_2 \longrightarrow (CH_3)_2NB_2H_5 + (CH_2)_4NBH_2 \cdot B_4H_6$$

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[36]J. Tanaka and J. C. Carter, Tetr. Letters, 5, 329, (1965).

[37]G. Hesse and H. White, Angew. Chem., 75, 791, (1963).

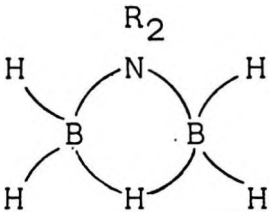
[38]A. B. Burg and J. S. Sandha, J. Am. Chem. Soc., 89, 1926, (1967).

$$(CH_3)_2NBH_2 \cdot B_4H_6 + 3(CH_3)_2NBH_2 \longrightarrow ((CH_3)_2NBH_2)_4 \cdot B_4H_6$$

$$((CH_3)_2NBH_2)_4 \cdot B_4H_6 \longrightarrow ((CH_3)_2NBH_2)_3 + (CH_3)_2NBH_2)_4 \cdot B_4H_{10}$$

The μ-aminodiboranes, compounds in which an amino group replaces one of the bridge hydrogens in the diborane structure can be conveniently prepared from aminoboranes and B_2H_6.[39,40]

$$(R_2NBH_2)_2 + B_2H_6 \longrightarrow 2$$



The third major group of boron-nitrogen compounds comprises the cyclic borazines which are of particular interest in that they are isoelectronic and isostructural with aromatic carbon compounds. Borazine, $B_3N_3H_6$ has a superficial resemblance to benzene particularly with respect to its physical and chemical properties. In benzene, however, the carbon-carbon bonds are nonpolar and the nucleus is very resistant to addition reactions, whereas the borazine nucleus because of its polarities is fairly reactive.

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[39] A. B. Burg and C. L. Randolph, J. Am. Chem. Soc., 71, 345, (1949).

[40] K. Hedberg and A. J. Stosick, J. Am. Chem. Soc., 74, 954, (1952).

Stock and Pohland[41] first prepared borazine from the addition compound of ammonia and diborane. They found that when the diammoniate of diborane is rapidly heated to 200° in a closed tube the relatively stable, volatile compound $B_3N_3H_6$ is obtained in about 50% yields. Schlesinger[42], Burg, and co-workers prepared the B-methyl derivatives of $B_3N_3H_6$ by heating mixtures of ammonia and various substituted diboranes at 200°. A vigorous reaction occured yielding the mono, di and trimethyl derivatives of $B_3N_3H_6$ as the major products. Only the reaction of monomethyldiborane with ammonia gave a higher yield of the B-unsymmetrical derivatives, (mono and dimethyl) than of the B-symmetrical derivative, (trimethyl), but as the alkyl substituents were increased on diborane the trend was found be have reversed. No B-unsymmetrical derivatives were reported in the reaction of tri and tetramethyldiborane with ammonia. The N-methyl derivatives were prepared in an analogous manner[43] by the reactions of diborane with mixtures of ammonia and methylamine. If ammonia is absent, only the N-trimethyl derivative is produced in the reaction. If the proportions of ammonia and methylamine are such that

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[41] A. Stock and Pohland, Ber., 59, 2216, (1926).

[42] H. I. Schlesinger, L. Horvitz and A. B. Burg, J. Am. Chem. Soc., 58, 409, (1936).

[43] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, J. Am. Chem. Soc., 60, 1296, (1938).

there is an excess of ammonia, the principal product is the N-mono derivative along with smaller quantities of the other compounds. When methylamine is slight in excess, however, there is obtained a mixture in which no one of the derivatives predominates.

One of the most intriguing problems in borazine chemistry is the synthesis of the unsymmetrically substituted derivatives. Only a limited number of borazine derivatives unsymmetrically substituted with respect to one or both of the annular atoms have been reported. Because they were difficult to obtain, very little was known about these compounds until recently when Beachley[44] reported new synthetic methods for the four unsymmetrically substituted N-methyl and B-methyl borazines along with their boron-11 and proton nmr, infrared and mass spectra.

The reactions of amines and other bases with B_5H_9 have not been fully elucidated. The low-temperature reactions lead to adducts which undergo transformations when the temperature is raised. Some products in which the B_5 unit remains intact can also be obtained by carefully controlling reactions at moderate temperatures. Higher temperatures or strong bases lead to cleavage reactions. In general, the reaction appears to be exceptionally complex. The ratio of reactants often determines the final product, since initial

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[44]O. T. Beachley, Jr., Inorg. Chem., 8, 981, (1969).

products are prone to react further. The products of the reaction also appear to depend upon the strength of the base.

Stock[1] reported that the liquid ammonia-B_5H_9 reaction was relatively slow at about -80°, but at higher temperatures 1 mole of B_5H_9 readily added 4 moles of NH_3 to form a very stable, salt-like adduct, $B_5H_9 \cdot 4NH_3$. Characterization of the compound, however, was not complete. When warmed at 200° the adduct yielded the nitrogenous compound $B_3N_3H_6$, together with nonvolatile substances. A diammoniate was also indicated when reaction was carried out for short times in liquid ammonia. Reaction between dilute gaseous reactants at room temperature proceeded only very slowly.

The low temperature reaction of ammonia in an etheral solution of B_5H_9 has been restudied recently by Kodama[45] and rather than the tetraammoniate reported by Stock, the diammoniate of pentaborane was characterized to have the formula, $(H_2B(NH_3)_2^+)(B_4H_7^-)$. The $B_4H_7^-$ anion had not been isolated previously.

The reaction of B_5H_9 with dimethylamine reported by Burg[19] led to the isolation of several aminoboron hydrides; $(CH_3)_2NH_2H_5$, $(CH_3)_2NBH_2$, $((CH_3)_2N)_2BH$, and $((CH_3)_2N)_2B_4H_6$.

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[45]G. Kodama, J. Am. Chem. Soc., 92, 3482, (1970).

Hough, Edwards and Stang[46] reported the preparation of the salt $(CH_3)_2NH^+RB_5H_7^-$ from the reaction of 1-ethylpentaborane(9) and trimethylamine. Isolation of this ion is extremely important, as it is thought to be the key intermediate for the isomerization of 1-alkylpentaborane(9) to 2-alkylpentaborane(9) in the presence of 2,6-dimethylpyridine reported by Onak.[47] However, efforts to duplicate the preparation of the $(CH_3)_3NH^+RB_5H_7^-$ ion have been unsuccessful.

B_5H_9 has been found to react with trimethylamine[20,48] to form an adduct which on heating with excess base yields two moles of $(CH_3)_3NBH_3$ per mole of B_5H_9. Burg[19] proposed a mechanism in which the two amine molecules remove two BH_3 units from the base of the B_5H_9 system leaving $(BH)_3$ to form a polymeric material. After studying the reaction of B_5H_9 with a weaker base $(CH_3)_2S$, however, Burg[49] et al. suggested a different mechanism in which the base $-B_4H_6$ unit condensed to a resin and the BH_3 is captured by another molecule of base.

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[46]W. V. Hough, L. J. Edwards, and A. F. Stang, J. Am. Chem. Soc., 85, 831, (1963).

[47]T. P. Onak, J. Am. Chem. Soc., 83, 2584, (1961).

[48]J. E. Field, Doctoral Dissertation, Tulane University, 1957.

[49]I. B. Mishra and A. B. Burg, Inorg. Chem., 9, 2188, (1970).

In another study[50] trimethyl- or triethylamine was found to react with B_5H_9 in a 2:1 ratio (amine-to-B_5H_9) at 0°, but the corresponding dialkylamines gave complexes containing ratios from 2:1 up to 5:1. All the complexes evolved hydrogen at higher temperatures and alkylaminodiboranes or alkylaminoboranes were formed. Decomposition of the dimethylamine - B_5H_9 adduct gave hydrogen, dimethylaminodiborane, and yellow solids of approximate composition, $B_9H_{12}(NMe_2)$. Partial reversibility has been noted for the trimethylamine-B_5H_9[19] and dimethylamine-B_5H_9 system[51] at -80°.

Very little is known about the cleavage of the B_5H_9 cage system, largely because the fragments resulting from such a cleavage are immensely reactive. Consequently an unidentifiable polymeric resin is usually obtained as the final product of these reactions.

In this study the reaction of pentaborane(9) with amines was undertaken in order to extend our understanding as to the modes of cleavage of the pentaborane cage skeleton. Basically, two types of reactions have been examined. In each reaction, attention was concentrated on the volatile products; the non-volatile, highly viscous liquids were not characterized. First, the reactivity of

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[50]Ye Zhigach, B. Kazakova and I. S. Antonov, Zh. Khim., 27, 1655, (1956).

[51]R. W. Parry and L. J. Edwards, J. Am. Chem. Soc., 81, 3554, (1959).

pentaborane(9) towards ammonia and monomethylamine was investigated under a variety of conditions, and the borazine systems found in the reactions were firmly established. In addition, the pyrolysis of µ-methylaminodiborane was examined in order to demonstrate its use as an intermediate in the formation of the borazine derivatives. Secondly, the reactivity of 1-methyl- and 2-methylpentaborane(9) towards ammonia and monomethylamine was investigated in order to establish the nature of amine attack on the pentaborane molecule, i.e., electrophilic attack at the apical boron versus nucleophilic attack at a basal boron. This was accomplished by characterizing and quantitatively measuring the different borazine systems formed in the reactions. It was expected that substituent groups on the borazine system would give insight into the source of specific B-atoms from the pentaborane cage.

INTERPRETATION OF SPECTRA

Infrared spectra were obtained using a Perkin-Elmer 337 Infracord grating spectrophotometer. Gaseous samples were recorded in a special Pyrex glass cell fitted with NaCl windows. The cell, which was 9 cm long and 1 cm in diameter, was equipped with a condensation finger. Gaseous samples could thus be concentrated into the volume of the cell and, therefore, smaller sample sizes were required.

Infrared spectra were used for both functional group analysis and finger-print comparison with known samples. The spectrum of gaseous B_5H_9 is given in figure 2. Representive information about boron hydrides can be obtained from the interpretation of the spectrum of B_5H_9. The absorption in the region 2500-2600 cm^{-1} is characteristic of the BH stretching frequencies and can be used to verify the presence of non-bridge hydrogens. The absorption in the region 1800-2140 cm^{-1} is characteristic of the BHB stretching frequencies and can be used to verify the presence of bridge hydrogens. The infrared spectra of B_2H_6 (figure 3), B_4H_{10} (figure 4), 1-$CH_3B_5H_8$ (figure 5), 2-$CH_3B_5H_8$ (figure 6), 1,2-$(CH_3)_2B_5H_7$ (figure 7),

u-$(CH_3)NHB_2H_5$ (figure 8), and $C_2B_4H_8$ (figure 9) are included for comparison of the characteristic borane frequencies. The normal BH and BH_2 stretching modes always fall in the range 2630-2350 cm^{-1}. The BH_2 group can be distinguished by the doubling due to asymmetric and symmetric vibration modes. No difference can be detected between the stretching frequencies of the terminal and apical BH groups in compounds such as B_5H_9

The apical and basal BH frequencies in the substituted pentaboranes (figures 5, 6 and 7) have not been characterized sufficiently to determine the type of substitution. It is, however, possible to distinguish between apical and basal substitution on the basis of the complexity of the spectra. The infrared spectrum of apically substituted pentaborane resembles the spectrum of pentaborane(9) more closely than does the spectrum of the basal-substituted product. The latter compound has a more complex spectrum because it is less symmetrical, this feature causing splittings of the bridge hydrogen absorptions. Strong bands near 1320 cm^{-1} indicate B-methyl substitution, while bands at approximately 1450 cm^{-1} are characteristic of C-methyl deformation. The C-H stretching absorption in CH_3 groups should occur at 2900 cm^{-1}.

The B-H stretching frequency in the infrared spectrum of carboranes, for example, $C_2B_4H_8$ (figure 9) at 2560 cm^{-1} does not vary appreciably from the frequency in the boron hydrides. A single, sharp band near 3020 cm^{-1} is

characteristic of a cage CH stretch. This absorption is present in all carboranes and can be used to determine the degree of substitution on the carbon atoms, as the relative intensities of CH_3 (2900 cm^{-1}) and BH (2500 cm^{-1}) stretching bands are a qualitative indication of the number of functional groups present in the molecule. In addition to these band assignments, there is usually a close resemblance between the infrared absorptions of most carboranes in the 700-1100 cm^{-1} region characteristic of cage vibrations.

The infrared spectrum of μ-methylaminodiborane (figure 8) has several absorption frequencies similar to diborane (figure 3), but the BH absorption of μ-methyl-aminodiborane is shifted about 50 cm^{-1} to lower wave number when compared with diborane. In addition, the spectra of u-aminodiboranes generally exhibit NH absorption near 3460 cm^{-1}, BN stretching at 1625 cm^{-1}, and a weak bridge hydrogen symmetric stretch in the 1800-1900 cm^{-1} region.

Table 1 contains the interpreted absorption position of the more common functional groups found in boron hydrides, carboranes and μ-aminodiboranes. Variations are to be expected with some changes in structural environments. This compilation of characteristic group absorptions versus structural type is particularly useful when the spectrum of an unknown material has been obtained. For example, if the spectrum contains a sufficiently strong band at 1840 cm^{-1}, the compound almost certainly contains a bridge hydrogen.

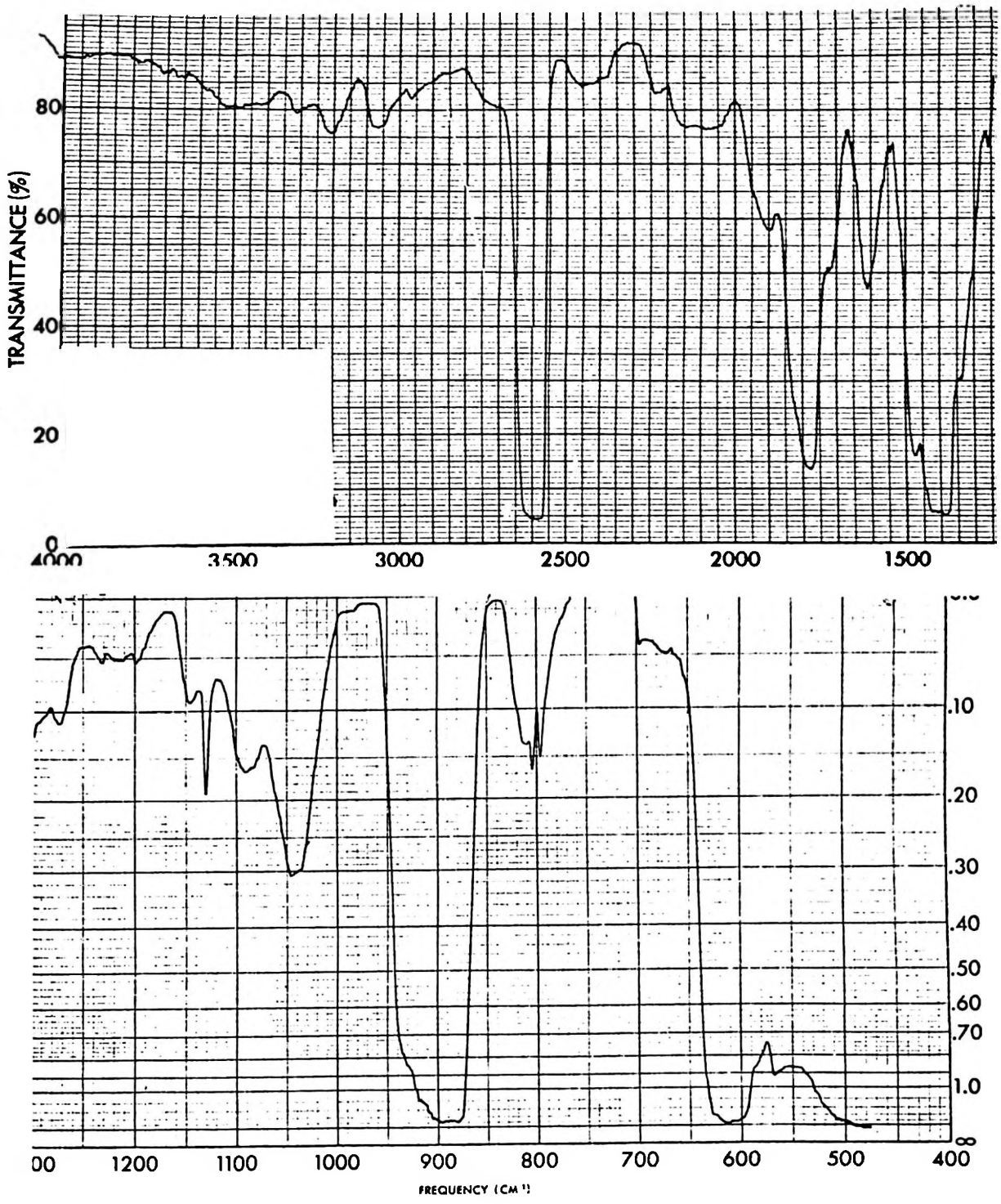


Figure 2. Infrared spectrum of pentaborane(9).

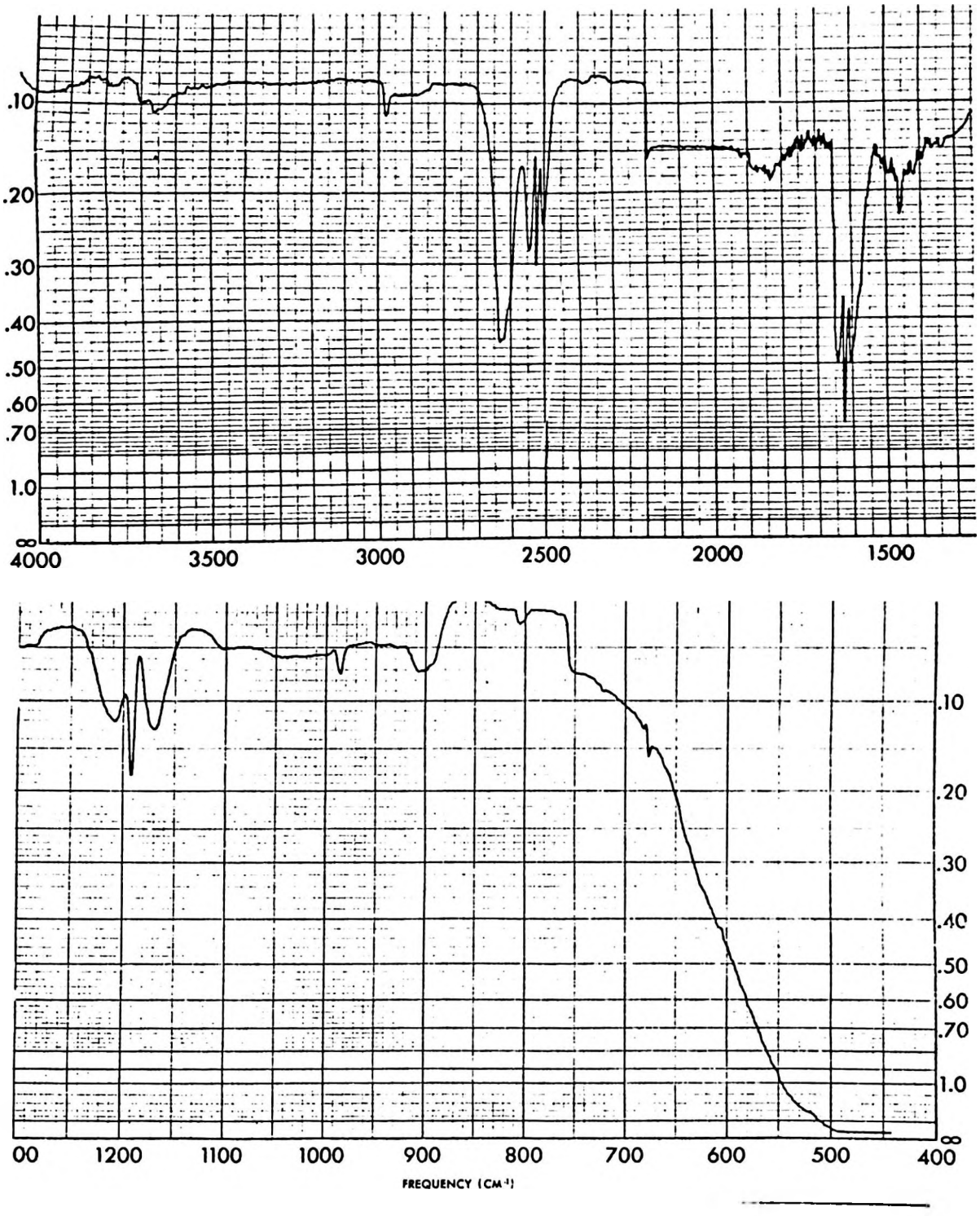


Figure 3. Infrared spectrum of diborane(6).

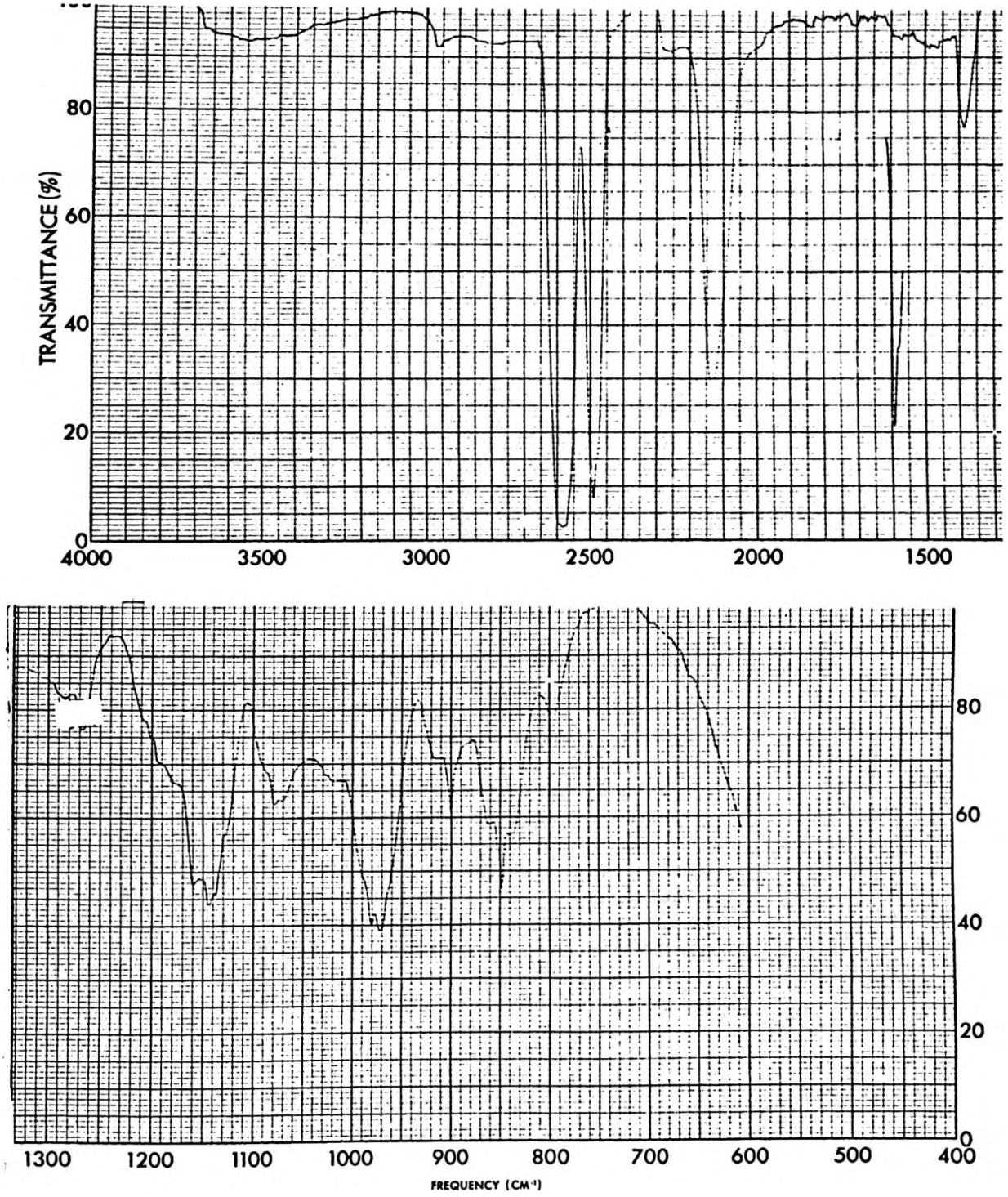


Figure 4. Infrared spectrum of tetraborane(10).

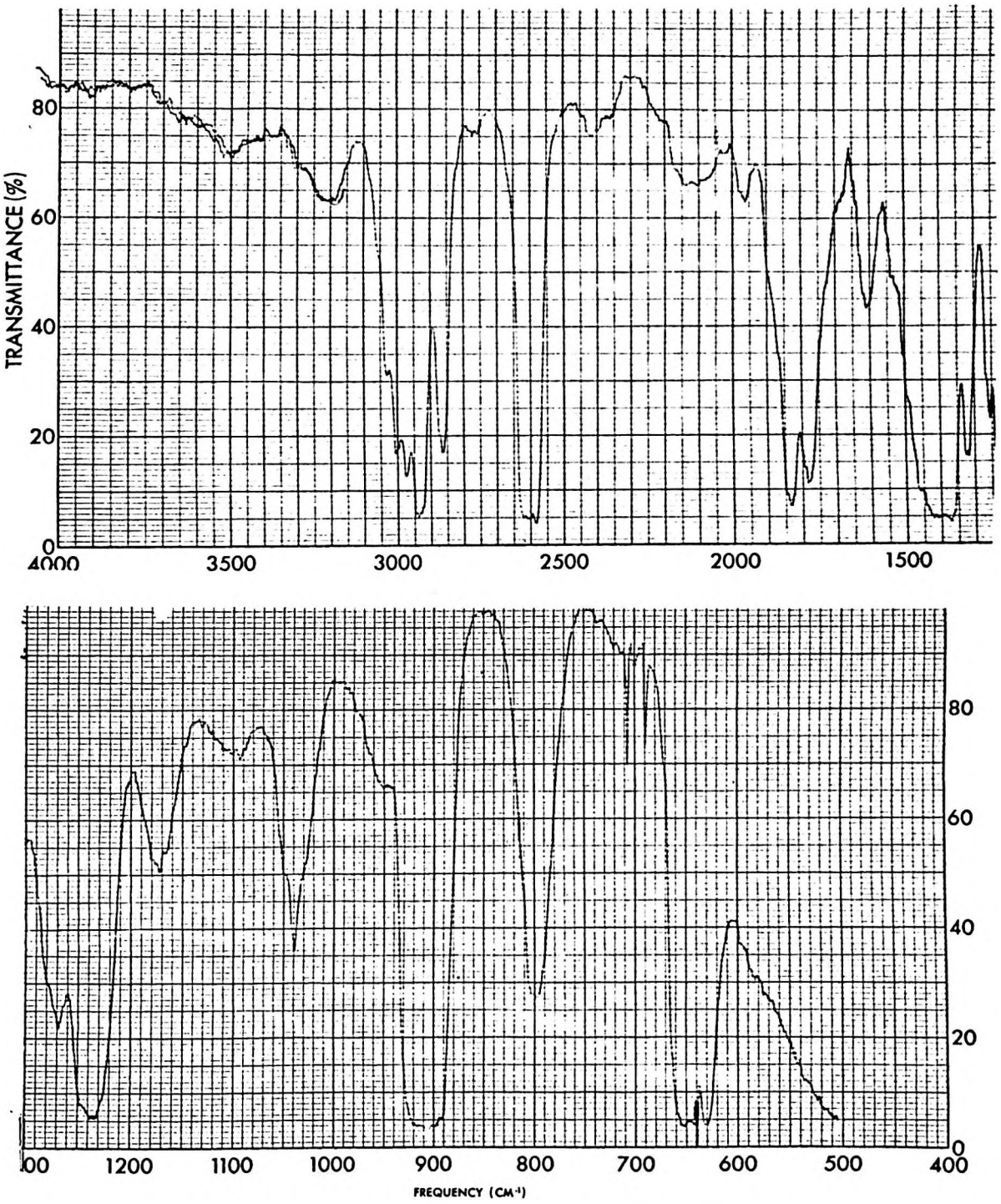


Figure 5. Infrared spectrum of 1-methylpentaborane(9).

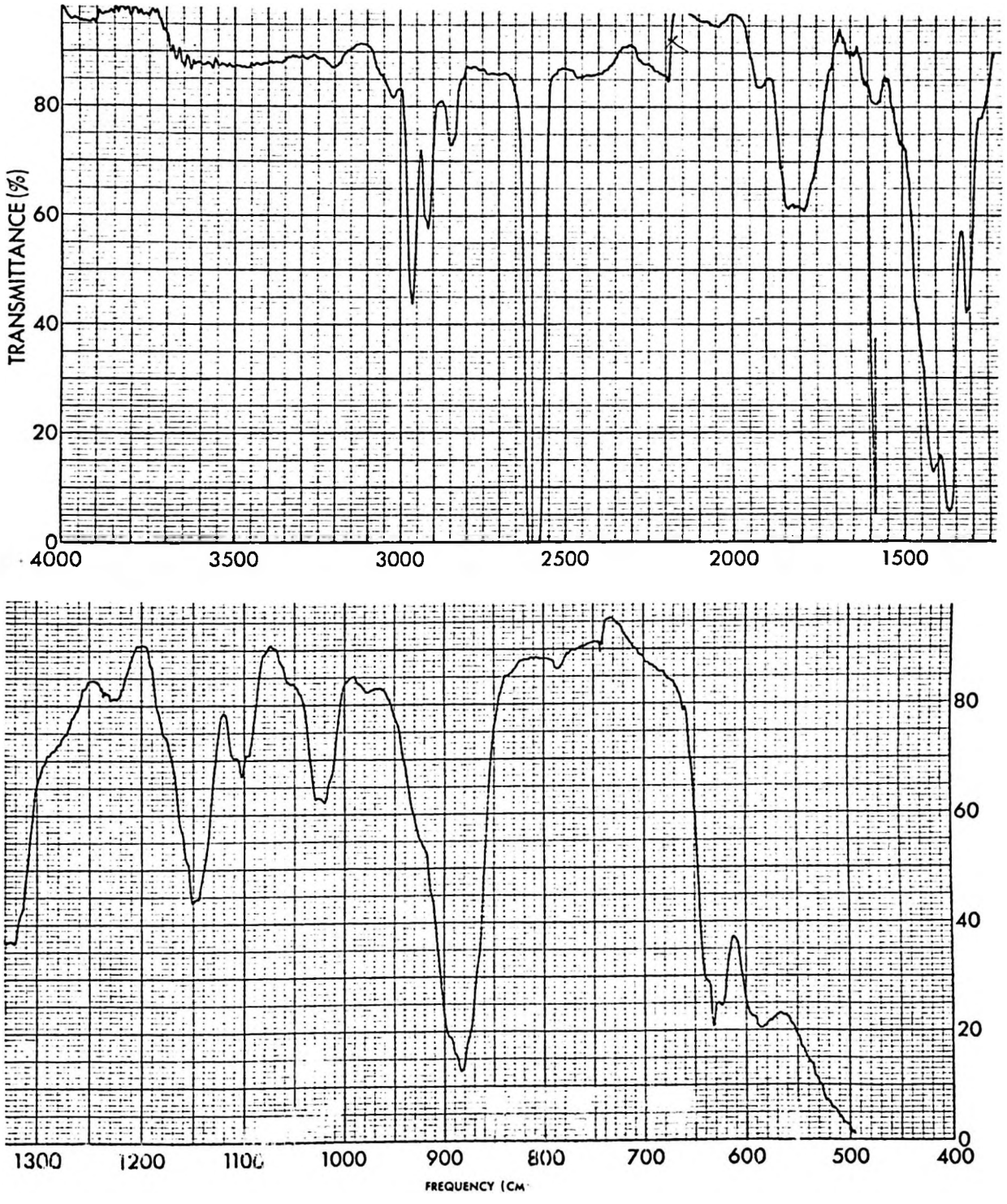


Figure 6. Infrared spectrum of 2-methylpentaborane(9).

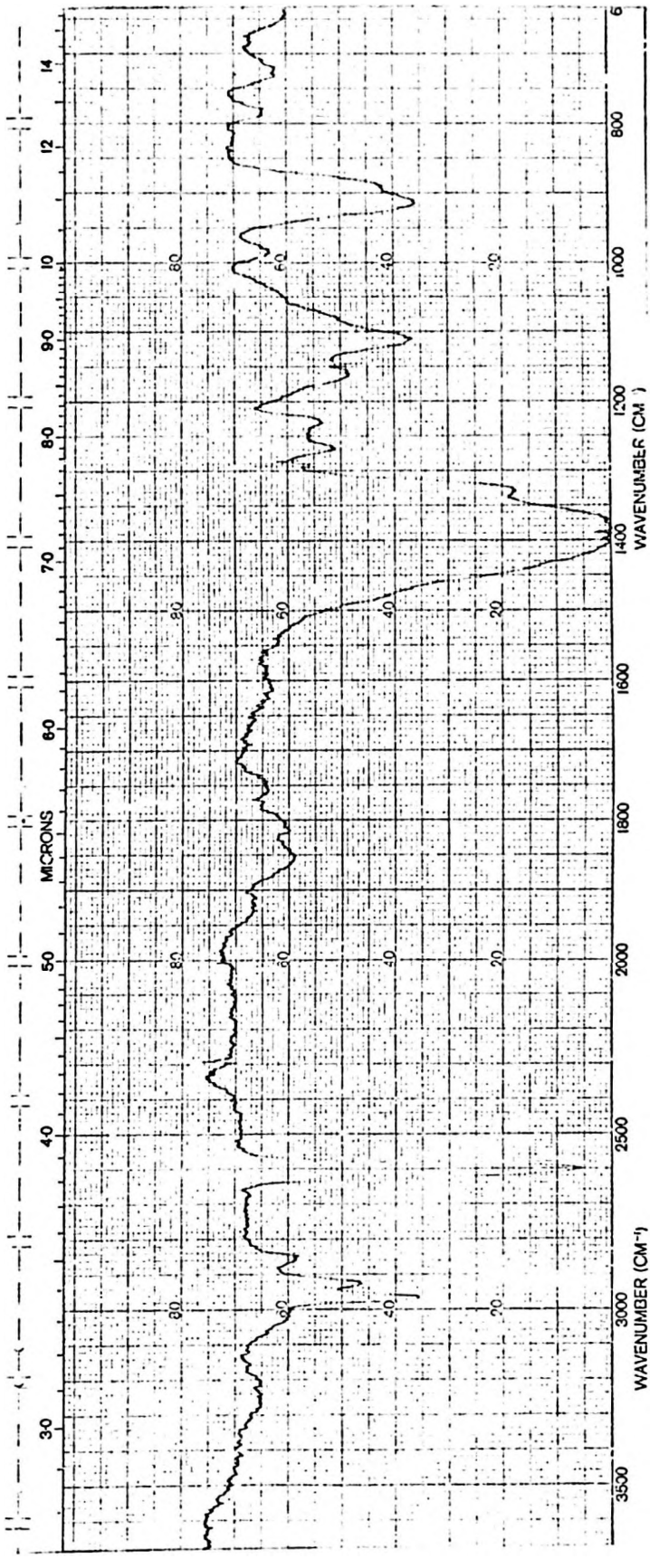


Figure 7. Infrared spectrum of 1,2-dimethylpentaborane(9).

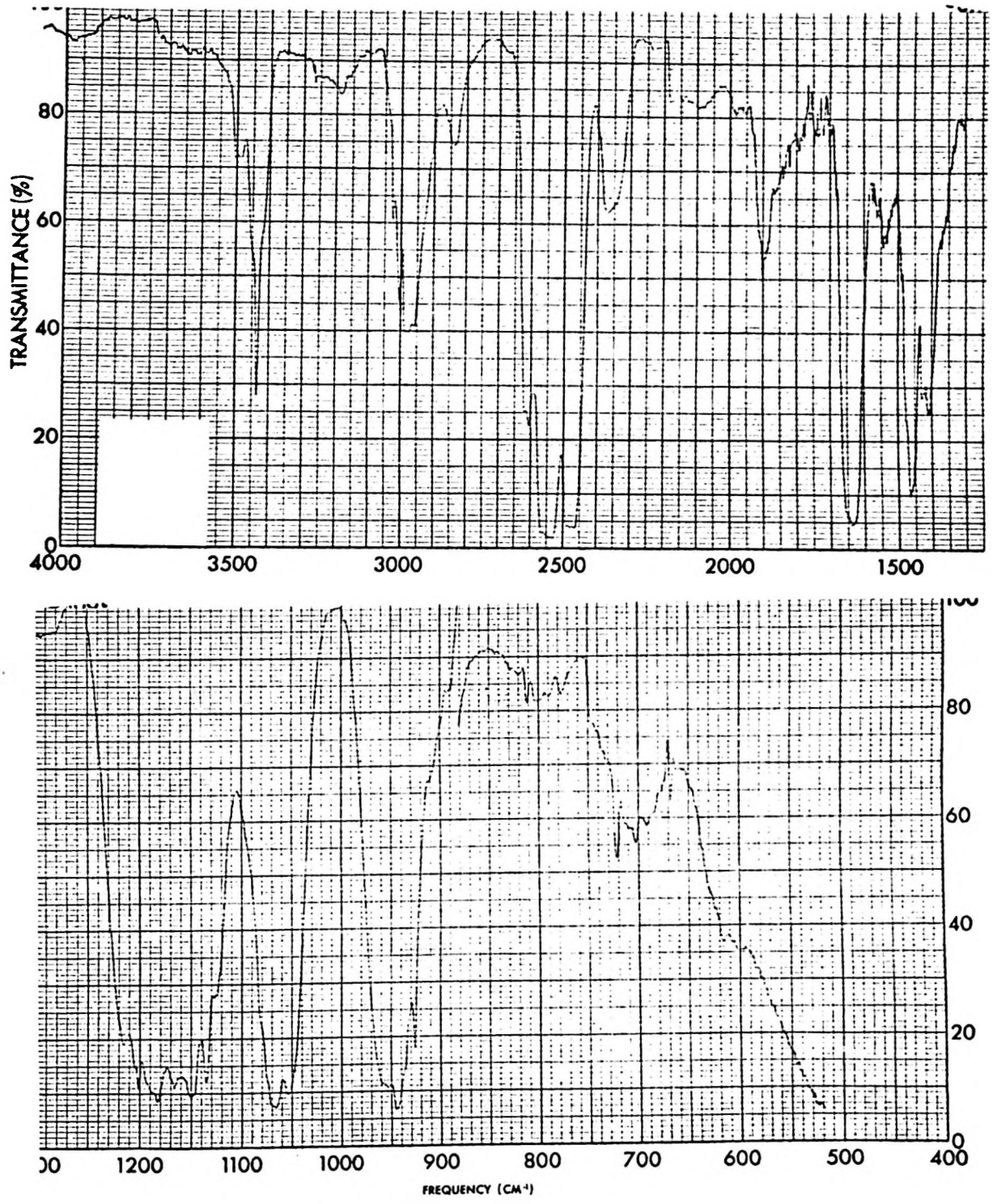


Figure 8. Infrared spectrum of μ-methylaminodiborane.

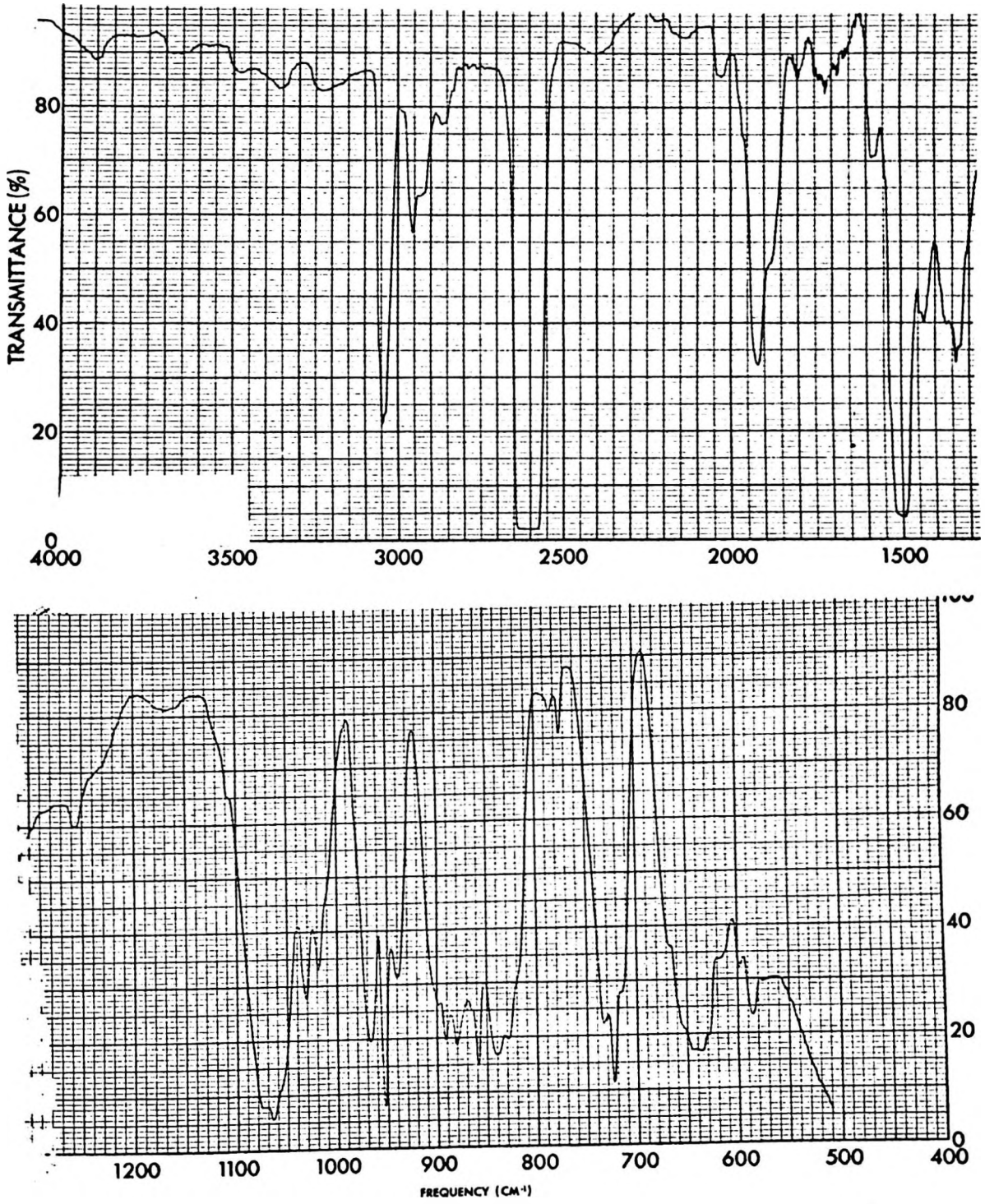


Figure 9. Infrared spectrum of 4,5-dicarba-nido-hexaborane(8).

TABLE 1

Typical Boron Bond Infrared Absorption Frequency Ranges

Type of Vibration	Absorption Region in cm^{-1}
Bridge N-H stretch	3460
Cage C-H stretch	3020
Alkyl C-H stretch	3000-2800
Terminal B-H stretch (BH_2 groups shown doubling in this region)	2600-2500
Terminal BH_2 stretch (u-aminodiboranes)	2550-2450
Bridge B-H symmetric stretch	1900-1800
Amino B-N stretch	1650-1600
Bridge B-H asymmetric stretch	1500
C-Alkyl asymmetric deformation	1500-1400
N-carbon stretch	1450-1400
B-Alkyl symmetric deformation (Asymmetric)	1350-1280 1460-1405
B-H bend	1114-1105
BH_2 scissoring	1205-1140
BH_2 wagging	975-945
Cage vibrations	1100-700

Conversely, the power of negative inference cannot be over-emphasized; if the spectrum does not contain an absorption typical of a certain functional group, the molecule does not contain that functional group. If the spectrum contains no absorption in the 1800-1900 cm^{-1} region, the sample does not contain a bridge hydrogen.

Proton magnetic resonance spectra were obtained using a Varian HA-100 spectrometer (University of Alabama) and a Joelco-60 spectrometer (University of Alabama at Birmingham). ^{11}B NMR spectra were obtained using a HA-40 (Rohm and Haas Company) at 12.8 MHz and a HA-100 (University of Virginia) at 34.6 MHz. A discussion about the magnetic resonance of boron compounds can be divided into proton resonance and ^{11}B resonance.

The NMR spectra of boron compounds are influenced by several factors. There are two boron isotopes and both are NMR active. The ^{11}B (80%) nucleus has a nuclear spin of 3/2 while the ^{10}B (20%) nucleus has a spin of 3. Using the formula 2s+1, any hydrogen atom attached to boron will be split into a quartet, overlapped by very low intensity septets. Fortunately, the ^{10}B septet can be neglected because of its low intensity and all that can usually be seen is the quartet. Furthermore, there is virtually no coupling between boron atoms not directly attached to protons. Both isotopes of boron have quadrupole moments which result in significantly broader spectral line widths than is obtainable in pure carbon hydrogen spectra. If

there were spin-spin coupling between neighboring boron atoms, with the resulting quartet of quartets, proton spectra would be unusually broad. This is observed in the NMR absorption spectra of bridge proton which are bonded to two different boron nuclei. Their chemical shifts are never well defined and usually occur as unresolved multiplets in the region of tetramethylsilane (TMS).

Terminal B-H hydrogen atoms absorb downfield from TMS between 2 and 3 ppm, and protons bonded to cage carbon atoms absorb at around 6 ppm downfield. For comparison, alkyl absorption occurs between 1 and 2 ppm downfield from TMS. Coupling constants for terminal B-H bonds are around 150 to 170 cps (Hz.) and for bridge hydrogens bonds between 30 and 40 cps. It is interesting to note that alkyl groups bonded to cage atoms, either carbon or boron, are generally not resolved into the fine structure that is typical of hydrocarbon NMR spectra.

The position of alkyl substitution can be determined from the NMR spectrum because alkyl substitution eliminates the quartet caused by the substituted proton-boron coupling. Consider pentaborane(9) as an example. The proton spectrum (figure 10) of B_5H_9 shows three types of absorptions of relative intensity 4:4:1. There is a broad band upfield of intensity 4 caused by the bridge protons. The apical proton gives a quartet of intensity 1 in the same general area, and slightly downfield there is another quartet of intensity 4 caused by the terminal basal proton. Alkyl

substitution at the apical boron atom would eliminate the small quartet, whereas basal substitution would eliminate neither set of quartets, only reducing the intensities of the large quartet from 4 to 3.

In general, the ^{11}B spectra are somewhat less complicated than proton spectra, since each boron absorption is only split into a doublet ($s=\frac{1}{2}$ for ^{1}H) by terminal proton. The ^{11}B NMR chemical shifts and coupling constants for the spectrum of B_5H_9 (figure 11) are assigned in Table 2. The ^{11}B spectrum is relatively simple as it consists of two doublets. The low field doublet is due to the resonance of the four borons at the base of the tetragonal pyramid of B_5H_9, coupled to their terminal hydrogens, and the high field doublet is assigned to the apical boron coupled to a terminal hydrogen.

The ^{1}H and ^{11}B NMR spectra of $C_2B_4H_8$ are shown in figures 12 and 13 respectively. The data is summarized in Table 2. The proton spectrum of $C_2B_4H_8$ shows two sets of overlapping quartets with the one of higher intensity slightly downfield from the smaller. The larger quartet results from the basal boron atoms while the smaller upfield quartet is due to the terminal hydrogens being split by its apical boron atom. There is an absorption downfield from the basal proton quartet which is a singlet arising from the protons attached to cage carbon atoms. The multiplet slightly upfield results from bridge proton.

The boron-11 NMR spectrum of $C_2B_4H_8$ (figure 13) exhibits three sets of doublets. The two low field doublets are assigned to the three basal borons at the base. The two basal boron atoms adjacent to the carbon atoms give rise to the stronger of the two low field doublets which is further split into doublets due to their coupling to a terminal hydrogen. The remaining basal boron atom gives rise to a low field doublet which overlaps but is slightly upfield from the larger doublet. The high field doublet is assigned to the terminal hydrogen on the apical boron.

In summary, as in the case of ^{1}H NMR there are several characteristics in ^{11}B NMR which greatly facilitate their interpretation:

1) Spin-spin coupling between boron atoms bonded to other boron atoms and carbon is not generally observable.

2) The effect of bridge protons is either small, resulting in multiplets separated by only about 40 Hz, or is not detected at all.

3) Principal coupling occurs only with boron which is bonded to one or more terminal hydrogens. Bonding to one terminal hydrogen gives rise to a doublet with lines of equal intensity (arising from the spin of ½ for hydrogen), while a second terminal hydrogen on the same boron splits the doublet again resulting, with overlap, in a triplet with line intensity of 1:2:1.

4) Coupling constants of multiplets arising from boron bonded to one terminal hydrogen generally fall in the

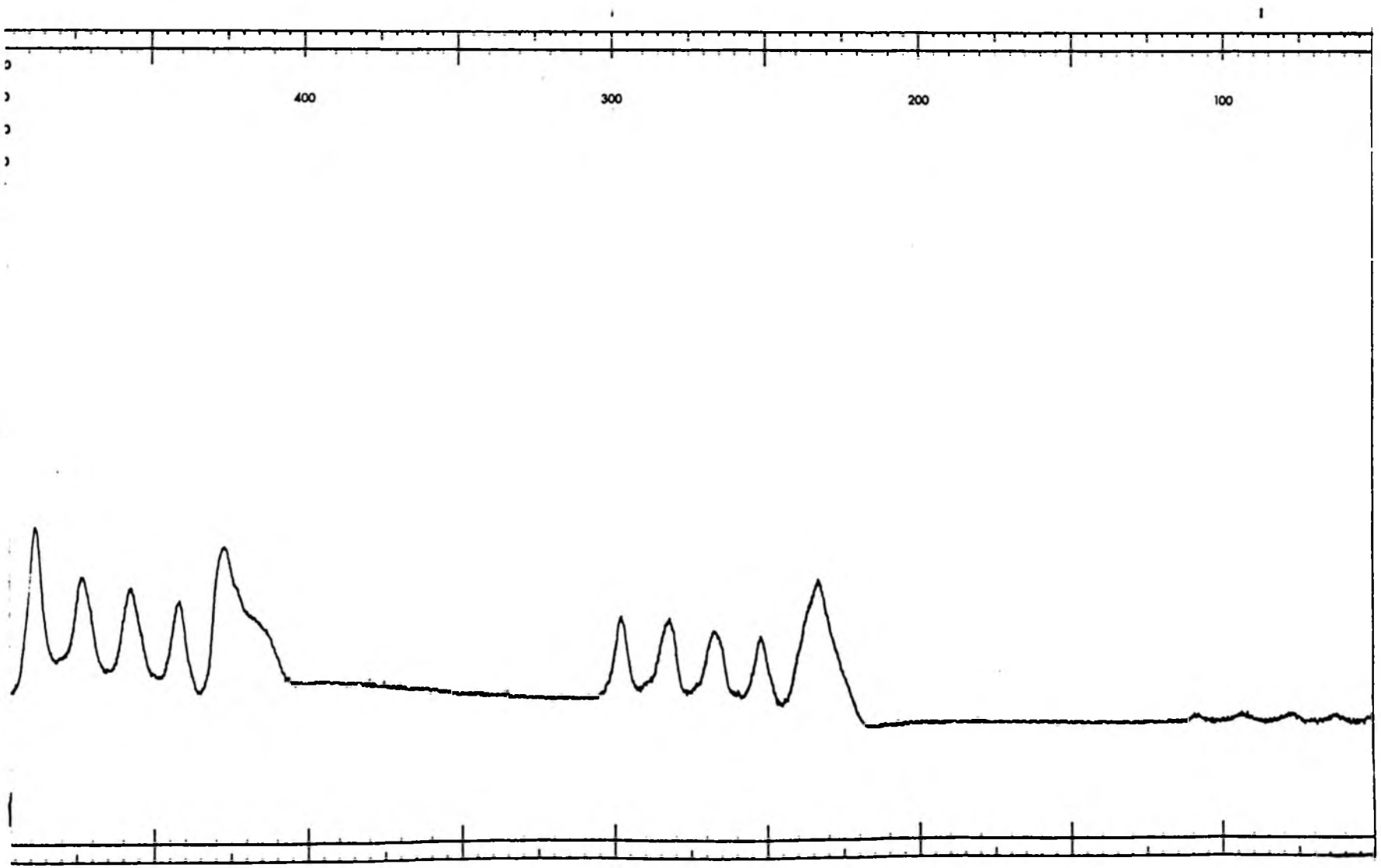


Figure 10. ^{1}H NMR spectrum of pentaborane(9).

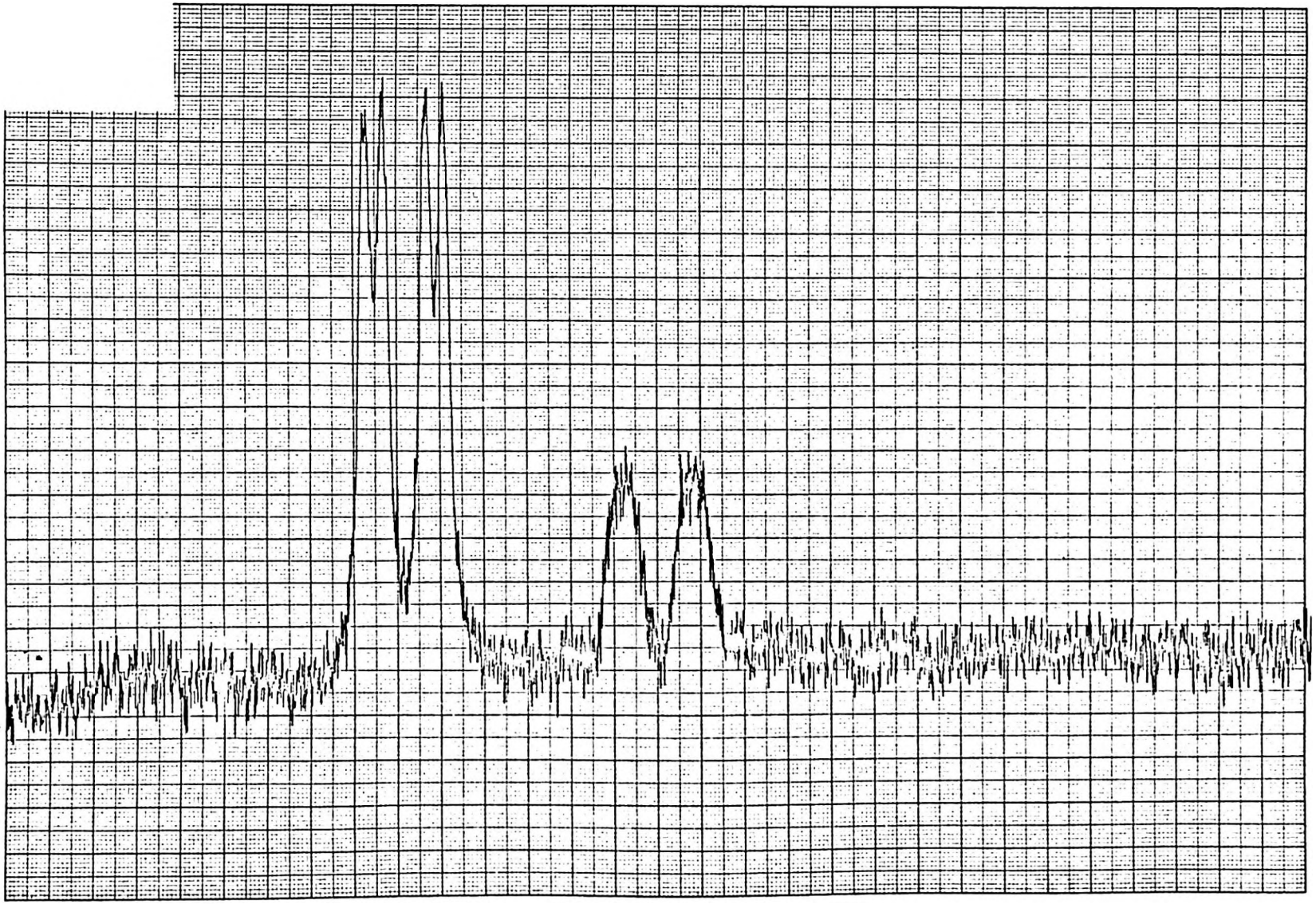


Figure 11. ^{11}B NMR spectrum of pentaborane(9).

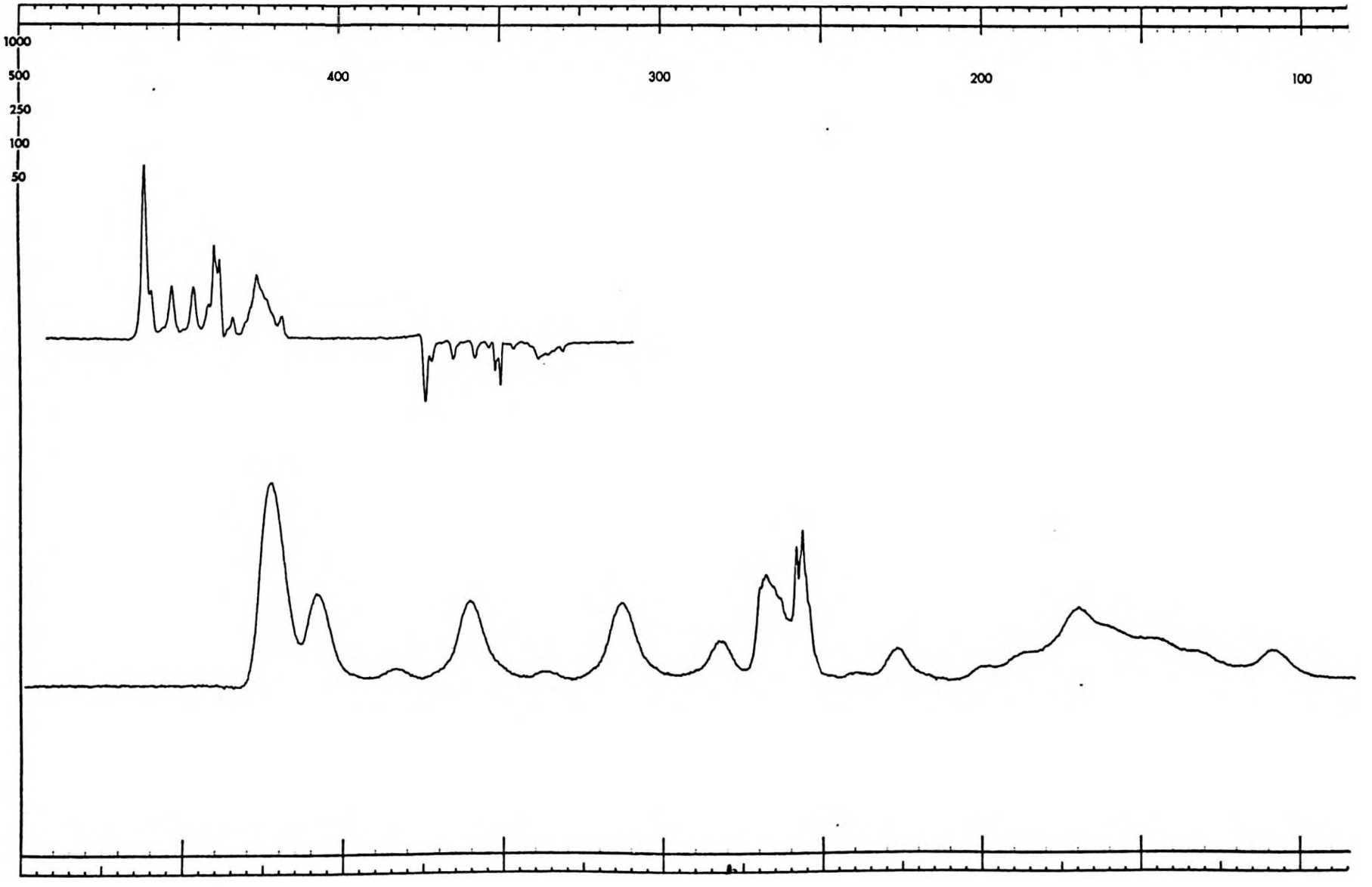


Figure 12. ^{1}H NMR spectrum of 4,5-dicarba-nido-hexaborane(8).

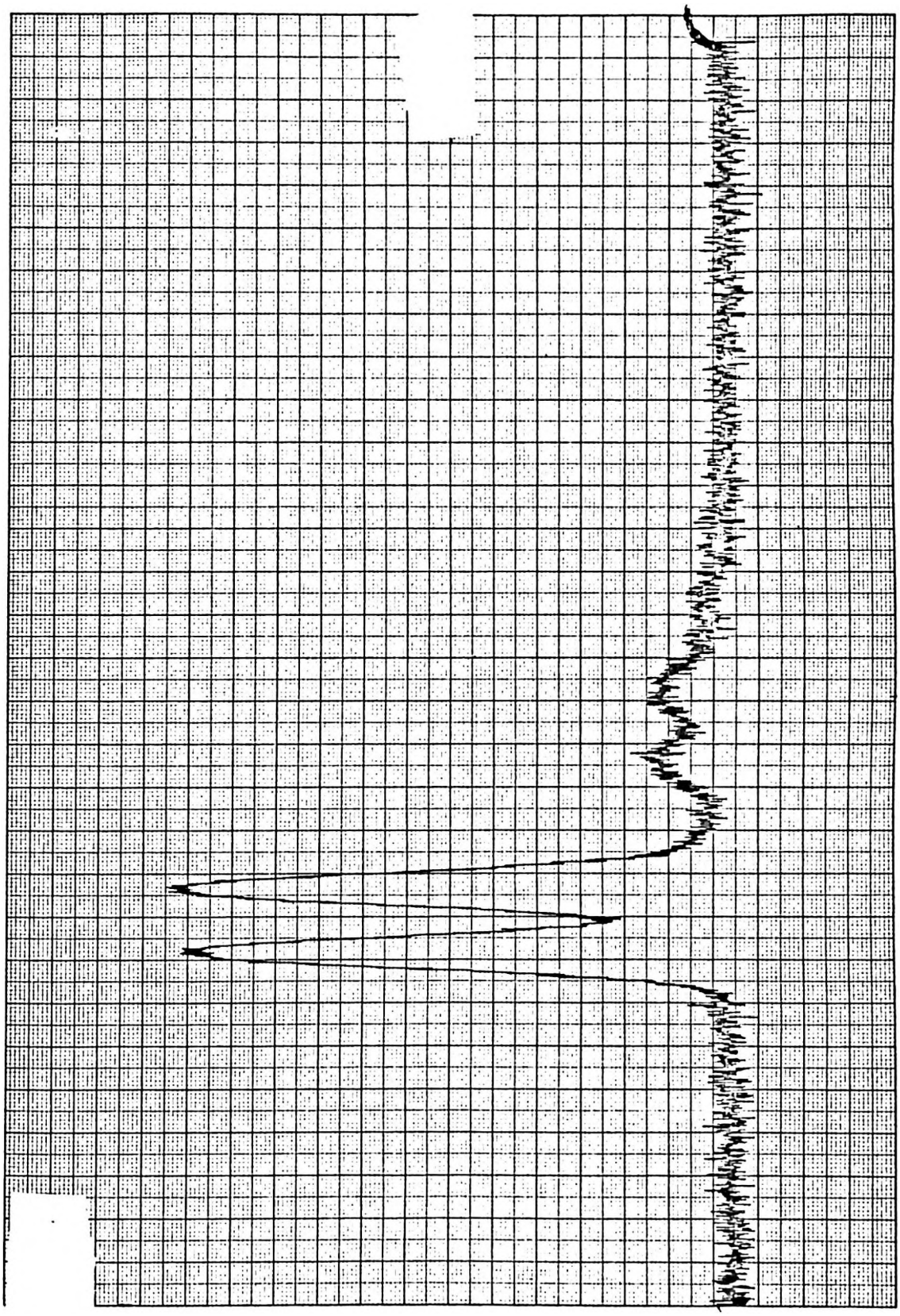


Figure 13. ^{11}B NMR spectrum of 4,5-dicarba-nido-hexaborane(8).

TABLE 2

Typical Chemical Shifts and Coupling Constants for Boranes

	Boron-11 NMR			Proton NMR		
Compound	Atom	Shift(ppm)[a]	J(Hz)	Atom	Shift[b](ppm)	J(Hz)
B_5H_9	B(2,3,4,5)	+12.5	161	H-B(2,3,4,5)	-0.95	165
	B(1)	+51.8	178	H-B(1)	-.255	175
				Bridge H	+2.20	45
$C_2B_4H_8$	B(4,6)	+0.6	154	H-B(4,5,6)	-3.44	158
	B(5)	+3.3	160	H-B(1)	+1.13	181
	B(1)	+50.5	180	H-C	-6.32	
				bridge H	+2.4	

a. relative to methylborate
b. relative to TMS

range 140-190 Hz., while multiplets due to two terminal hydrogens have coupling constants of approximately 120-130 Hz.

Mass spectra were obtained using a CEC 21-104 single focusing mass spectrometer equipped with a metal inlet system for gaseous analysis. The mass spectrum is a very important analytical method used in boron chemistry for several reasons.

Boranes and carboranes each have their own characteristic mass spectral patterns. Boranes under electron impact fragment rather severely, the "unstable" class of compounds, the nido-carboranes, somewhat more so that the "stable". Consequently, they as well as their alkylated derivatives, display broad, rounded mass spectral profiles. Conversely, the stable class of compounds, the closocarboranes (and their alkylated derivatives), are quite resistant to fragmentation, and hence their spectral profiles have sharp cut-off points at their high mass numbers.

Extremely small sample sizes can yield a large amount of information. This is important because of the very low yield of products generally achieved in boron chemistry. Excellent mass spectra were obtained using sample sizes that showed practically no infrared absorptions.

Boron hydrides, carboranes, and their alkylated derivatives exhibit very sharp high mass cut-offs at the parent ion masses. Molecular weights are, therefore, easy to determine. Because of the high intensities of parent ion peaks, and the fact that alkylation does not diminish

these intensities, mass spectral profile are very useful as fingerprints in the identification procedures. Fragmentation patterns of alkylated derivatives are very useful in determining the substituted alkyl group. Consider, for example, 1-methylpentaborane(9) (Table 3) which shows parent ion peaks starting at mass 78. There is another group of ion peaks starting at p-15 or mass 63 which corresponds to the loss of a methyl group. Also, the same general fragmentation patterns hold true for the related alkyl-boranes as the unsubstituted boranes. Adding methyl groups merely shifts the cut-off upward 14 mass numbers, reflecting the addition of CH_2 to the molecular weight. The fact that the parent group profile is changed only slightly suggests that the hydrogen abstraction upon electron impact occurs preferentially on the borane skeleton, not on the alkyl side chains, and this has been verified by mass spectral analysis of compounds with deuterated alkyl groups.[52]

Another feature of the mass spectra of boron hydrides, carboranes and their alkylated derivatives is the fact that there are N + 1 parent ion peaks for compounds containing N boron atoms. This feature is a result of the fact that naturally occuring boron contains two isotopes: ^{10}B and ^{11}B. The ratio of $^{10}B/^{11}B$ is 1/4 or 0.25. This means

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[52]R. E. Williams and F. J. Gerhart, Adv. Chem. Series, 72, 201, (1966).

that a compound containing one boron atom will give two peaks corresponding to the parent ion, one containing two boron atoms will give three parent ion peaks, and so forth. For ion groups containing small numbers of borons (say B_1^+ to B_4^+) the spectral profile is statistically weighted in favor of the higher mass numbers of the group, because of the high concentration (80%) of the ^{11}B; i.e., in the B_3-group, $^{11}B_3^+$ is the most abundant ion, while in the B_4-group, $^{11}B_4^+$ and $^{11}B_3{}^{10}B$, are in equal abundance. As the number of borons increases beyond four, however, the maximum intensity peak (or peaks) begins to shift away from the cut-off peak. In the B_5-group, $^{11}B_4{}^{10}BH_9^+$ would be statistically most probable. Since electron impact also knocks hydrogen off some of the pentaborane molecules, however, the entire spectrum of ions from m/e 50($^{10}B_5^+$) to m/3 64 ($^{11}B_5H_9^+$) shows up. Furthermore, $B_5H_5^+$ is the ion of highest intensity, and varied yields of the various $B_5H_n^+$ ions combined with the statistical distribution of boron isotopes causes the profile to peak at m/e 59 to m/e 60, as shown in Table 4. The effect is even more pronounced for the BH_2-containing "unstable" boranes; B_9H_{15} which has its maximum intensity peak nine mass numbers below its molecular weight of 114, and in the B_{10}-group, it is $^{11}B_8{}^{10}B_2^+$, which is 2.81 times as abundant at $^{11}B_{10}^+$. Thus, due to the statistical distribution of the isotopes, the greater the number of boron atoms in a particular ion group, the

farther removed will be the peak of maximum intensity from the high mass number.

An important factor in determining ion intensities for a particular compound is the ease of hydrogen abstraction. For boron hydrides and nido-carboranes, this hydrogen abstraction occurs relatively easily and it is not affected by alkyl substitution to a great extent. In almost all cases the peak of highest intensity has fewer hydrogen atoms than the parent molecule. For closo-carboranes, abstraction is minimal and the highest intensity peaks are usually those of the parent ions.

The mass spectra of naturally occurring boron compounds are polyisotopic due to their isotopic distribution ($^{11}B/^{10}B=4.0$), and for ordinary analytical purposes the polyisotopic spectrum is sufficient. One can, however, gain considerable information concerning structure changes by simplifying the spectrum by reducing it to its monoisotopic form. This method is particularly useful for alkylated derivatives since intensities for the parent ion are not only affected by the statistical distribution of boron isotopes, but also hydrogen abstraction from the alkyl group. The monoisotopic spectrum for these alkylated compounds is the hydrogen abstraction spectrum for the boron compound influenced by alkyl hydrogen abstraction.

The monoisotopic spectrum is calculated by simply stripping out all species that contain boron-10.[53] This can be done without any previous knowledge of the relative concentrations of the two boron isotopes, because the correct value to use is that which gives the minimum stripping residues. The concentration of any ion containing "X" atom of ^{11}B and "Y" atom of ^{10}B is given by:

$$^{11}B_x\ ^{10}B_y = W\ (.80)^x(.20)^y$$

where W is a binomial coefficient numerically equal to (X+Y)!/x!y!, and represents the number of different ways ^{11}B and ^{10}B can be arranged in a given molecule containing X+Y boron atoms. The monoisotopic spectrum is calculated by assuming that a particular compound contains a certain number of boron atoms; and using the above formula, the abundance of any given combination of ^{11}B and ^{10}B atom can be calculated for a certain mass. The ion abundance for each combination of ions that ^{10}B atoms is substracted from the total ion abundance and this leaves only ^{11}B containing ions.

For example, the monoisotopic spectrum of B_5H_9 (Table 4) is obtained by first measuring $^{11}B_5H_9^+$(m/e 64), then subtracting $^{11}B_4{}^{10}BH_9^+$, $^{11}B_3{}^{10}B_2H_9^+$, etc. from m/e 63 down to m/e 59 ($^{10}B_2H_9^+$). The residual of m/e 63 then is

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[53] I. Sharior, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, Adv. Chem. Series, 32, 127, (1961).

$^{11}B_5H_8^+$, and from this the intensities of $^{11}B_4{}^{10}BH_8^+$, $^{11}B^{10}B_2H_8^+$, etc., and ultimately all ions, $B_5H_9^+$, $B_5H_8^+$, $B_5H_7^+$, ...B_5^+ are determined. If the wrong number of boron atoms is assumed, the monoisotopic spectrum will contain peaks that are either less than zero (negative) or obviously too large. The criterion, therefore, is the largest number of boron atoms that will suitably reduce the data. Thus, the correct number of boron atoms in a molecule can be deduced, and an exact fingerprint spectrum can be obtained.

TABLE 3

The Mass Spectrum of 1-Methylpentaborane(9)

m/e	Relative Peak Height	m/e	Relative Peak Height
78	54.0	64	16.2
77	71.2	63	19.8
76	77.4	62	43.2
75	63.0	61	39.6
74	99.0	60	37.8
73	100.0	59	39.6
72	79.2	58	34.2
71	60.4	57	30.6
70	32.4	56	21.6
69	28.8	55	12.6
68	28.8	54	5.4
67	19.8	53	1.8
66	7.2	52	1.0
65	1.8	51	1.8

TABLE 4

The Polyisotopic and Monoisotopic Spectra of Pentaborane(9)

m/e	Relative Peak Heights		m/e	Relative Peak Heights	
	Poly-	Mono-		Poly-	Mono-
65			48	33.4	29.3
64	47.8	47.8	47	41.2	4.8
63	60.0	0.3	46	30.0	14.0
62	76.0	45.8	45	22.7	5.1
61	67.2	2.4	44	12.0	1.6
60	98.0	65.5	43	6.6	3.2
59	100.0	9.5	42	2.1	0.1
58	67.8	13.8	41		
57	46.7	13.2	40		
56	41.2	13.3	39	1.0	0.4
55	36.9	9.6	38	1.2	0.8
54	25.6	11.3	37	3.0	2.5
53	11.3	5.2	36	9.5	6.9
52	41.0	2.1	35	12.0	6.0
51			34	9.2	2.7
50	4.1	4.1	33	30	0.2
49	11.0	0.0	32	1.0	0.1

EXPERIMENTAL

Procedure

Boron hydrides are spontaneously flammable in air, readily hydrolyzed to boric acid and hydrogen and are highly toxic. Their alkylated derivatives exhibit these same qualities. Small open cage carboranes and their alkyl derivatives are also unstable in the presence of oxygen. For this reason, high vacuum techniques are necessary for chemical investigation.

A conventional type of high vacuum system was designed and built along the lines indicated by Stock[1]. It consisted of a series of four Pyrex glass U-tubes or traps, each one-half inch inside diameter, and sealed with greased high vacuum stopcocks. These traps were connected via Pyrex glass manifolds to the pumping system. One of the U-tubes was equipped with a mercury manometer for measuring pressures up to about one atmosphere. This trap's volume was standardized and therefore, the number of moles of any gas could be calculated using the ideal gas law. The entire vacuum system was connected to a pumping system consisting of a vane-type mechanical pump in series with a two stage mercury diffusion pump. The mechanical pump had a free air capacity of 160 liters per minute. Traps were

located on both sides of the mercury diffusion pump to prevent contamination of the mercury. High vacuum pressures were measured using a single scale McLeod gauge. Using such a pumping combination, a working pressure of 10^{-5} torr was obtainable.

Gas phase reactions were carried out using round-bottom Pyrex flask equipped with a thick-walled capillary neck for easy sealing and a side arm break off seal for removal of volatile products. Reactants were condensed in these flask at liquid nitrogen temperature (-196°), the neck was sealed, and the flask, after returning to room temperature, was placed in a suitable temperature oven. After the reaction was completed, the flask was again immersed in liquid nitrogen and sealed to the vacuum system by its break off side arm. When a suitable vacuum was obtained, the side arm tip was broken and any gases that did not condense at -196° were measured using a mercury manometer. The liquid nitrogen was removed and the volatile reactants were then transferred to a U-tube trap for further analysis.

Both reactants and products were purified by one or both of two methods: vacuum line distillation and preparative scale gas-liquid chromatography. Vacuum line distillation was achieved by passing a mixture of gases through a series of U-tube traps, each trap being held at a successively lower temperature, and collecting that fraction of gases that condensed between a certain temperature interval. Consider, for example, the purification of

methylamine. At a trap temperature of -78°, methylamine has an appreciable vapor pressure which means that it will not condense entirely at this temperature. If a mixture of gases containing methylamine are passed through a series of two traps, the first trap at -78° and second trap at -196°, methylamine will pass through the 78° traps while most of the other gases will condense at this temperature. The methylamine will condense, however, at the next trap, which is held at -196°. By this method, a separation of gaseous mixture was achieved and the methylamine has been purified.

The different temperature traps can be easily made by choosing a solvent that has a melting point (or freezing point) that coincides with the desired temperature and making a slurry using liquid nitrogen. A list of the generally used solvents and their melting temperatures is given in Table 5.

A second method of purification is preparative scale gas-liquid chromatography. This method is more efficient than vacuum line distillation but usable sample size is considerable smaller. Because of the reactivity of the compounds involved, the gas chromatograph is completely enclosed in a high vacuum system and can be evacuated to pressures as low as 10^{-5} -10^{-6} torr. The column and detector are fitted to the vacuum systems by ground glass joints and epoxy cement.

The carrier gas, which is helium, is introduced into the system in such a way that on the injector side of the column, the pressure is approximately atmospheric. There

is a large pressure drop through any one of several U-tube traps before it is pumped out of the system through a needle valve by a small mechanical pump. This flow scheme differs from the conventional gas chromatographs in that helium is pumped through this system as opposed to being forced through other systems by a larger positive pressure.

Samples are condensed into a U-tube injector trap with liquid nitrogen. The helium flow is then diverted through this trap, the liquid nitrogen removed and replaced by hot water. The hot water vaporizes the sample, which is then swept into the column by the helium flow. As the separated components come off the column, they are detected by a thermal conductivity detector and can be separated into different U-tube traps cooled by liquid nitrogen. Several chromatographs are generally necessary to completely purify any component.

Purified components can then be transferred to a gas infrared cell to obtain infrared and mass spectra or condensed into NMR tubes, sealed and used for ^{1}H and ^{11}B magnetic resonance spectroscopy.

Except for the column, the general construction of the unit was of Pyrex glass, and all connections and seals were made with high vacuum stopcocks and ground glass joints. The columns were made of copper tubing, one-fourth inch i.d., and nine to ten feet long. When not in use the entire system including column and detector unit was evacuated down to a pressure of approximately 10^{-5} -10^{-6} torr.

Four liquid phases were used on the solid substrate (Chromosorb W), Apiezon L, Dexsil 300, Kel F and TCP (tricresyl phosphate). The liquid phase made up 30% of the total column packing weight, with the single exception, Dexsil 300, which was 15% by weight. Columns were heated by placing them in a metal can wrapped with nichrome wire or by an infrared lamp, and adjusting the heater current with a standard laboratory variac. The four different columns were easily interchangeable. The thermal conductivity detector was heated in a like manner and insulated by layers of asbestos wrappings. The relative retention times of all components studied during the course of this work as well as other compounds which may be useful as future references are given in Tables 6 and 7. All retention times are given relative to pentaborane(9) unless standard otherwise. Peak areas in square inches were measured and converted to millimoles using a previously determined calibration.

The Reaction of Pentaborane(9) With Ammonia and Monomethylamine

In a typical reaction 1.20 mmoles of B_5H_9 and 1.20 mmoles of ammonia or monomethylamine were condensed into a 100 ml round bottom reaction flask by means of liquid nitrogen. The reactor was sealed by heating the thick-walled capillary neck with an oxygen-methane torch, and the flask, after returning to room temperature, was placed in an oven at the desired temperature.

TABLE 5

Low Temperature Baths

Solvent	Melting Point
Liquid Nitrogen	-196
Pet. Ether (low boiling)	-135
n-Pentane	-128
Toluene	- 95
Solid CO_2 - Isopropyl Alcohol	- 78
Chloroform	- 63
Cyclohexanone	- 45
3-Heptanone	- 39
Carbon Tetrachloride	- 23

TABLE 6

Gas Chromatographic Retention Times of Boron Hydrides

Compound	TCP[a,b]		Apiezon-L[a,b]		Dexsil 300[a,c]	
	70°C	80°C	70°C	85°C	50°C	60°C
B_2H_6	0.15	0.21	0.21	0.23	0.15	0.16
B_4H_{10}	0.51	0.66	0.61	0.60	0.24	0.27
B_5H_9	1.00	1.00	1.00	1.00	1.00	1.00
$1\text{-}CH_3B_5H_8$	1.48	1.95	1.45	1.42	1.76	1.56
$2\text{-}CH_3B_5H_8$	2.42	3.00	2.6	2.28	2.28	2.40
$C_2B_4H_8$					1.27	

a. $B_5H_9 = 1$

b. 30% on Chromosorb W

c. 15% on Chromosorb W

TABLE 7

Gas Chromatographic Retention Times of

Boron-Nitrogen Compounds

Compound	TCP[a,b]		Apiezon-L[a,b]		Dexsil 300[a,c]	
	64°C	80°C	55°C	75°C	25°C	50°C
$(CH_3)_2NBH_3$						0.37
μ-$CH_3NHB_2H_5$	0.35		0.66	0.69	0.60	0.66
Borazine	0.44		0.76	0.82	0.67	0.80
N-Methyl	1.66	1.17	1.90	1.67	2.54	1.63
N,N-Dimethyl	2.41	2.00	3.34	2.57	5.53	3.09
N,N,N-Trimethyl	3.57	3.44	3.97	3.07	7.07	3.81
B-Methyl		4.00			1.77	1.66
B,B,-Dimethyl		9.20			4.61	4.44
B,N,N,N-Tetramethyl		10.88				

[a] B_5H_9= 1

[b] 30% on Chromosorb W

[c] 15% on Chromosorb W

In all of these reactions a small amount of clear viscous liquid appeared to form throughout most of the reaction time. After the appropriate amount of time the flask was again immersed in liquid nitrogen and sealed to the vacuum system by its break-off side arm. When a suitable vacuum was obtained, the side arm tip was broken and the noncondensable gases at -196° were measured using a mercury manometer. The residual volatile products were then transferred to a U-tube trap which serves as an injection port for the gas-liquid chromatograph (glc). The mixture by a glc using different chromatographic columns at various temperatures. The viscous liquid which formed in all reactions turned out to be nonvolatile and did not transfer out of the reactor.

Separation of the volatile products of the B_5H_9 - monomethylamine reaction at 100° gave, in addition to the reactant peak, B_5H_9 four other chromatographic peaks. Upon repeated chromatographing, each component was purified such that it was the only peak obtained on respective individual chromatograms. The reaction of B_5H_9 with ammonia under similar conditions yielded, in addition to the reactant peak, only one other chromatographic peak, and the combined reaction of B_5H_9 with ammonia and monomethylamine produced all the previous indicated chromatographic peaks with similar retention times.

In order to identify each, the purified components were then transferred to a gas infrared cell to obtain

infrared and mass spectra or condensed into NMR tubes, sealed and used for ^{1}H and ^{11}B magnetic resonance spectroscopy. This sometimes required repetition of the same reaction several times until enough of each component was collected in order to obtain NMR spectra.

The results of the reactions of B_5H_9 with ammonia and monomethylamine are shown in Table 8. $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, $H_3B_3N_3H(CH_3)_2$, $H_3B_3N_3(CH_3)_3$, and u-$CH_3NHB_2H_5$ were prepared by allowing B_5H_9 to react with NH_3 and CH_3NH_2 in the gas phase at 100°. Identical products, but significantly lower yields, were reported for the same reactions at room temperature. With the exception of unsubstituted borazine the same products were formed in the reaction between B_5H_9 and CH_3NH_2, however, the yields of unsymmetrical derivatives were lower than in the reaction which included NH_3, while the yield of the trimethyl derivative was higher.

The yield of the compound, μ-methylaminodiborane (ca. 57.8%) was based upon the amount of B_5H_9 that was consumed in each reaction. The presence of such a considerable yield of the compound suggested a possible mechanism for the formation of the borazine ring in which B_5H_9 and the amines react to form μ-methylaminodiborane followed by conversion to the borazine ring system. This would be consistent with the work of Schlesinger, Ritter

TABLE 8

Reaction of B_5H_9 with CH_3NH_2 and NH_3

B_5H_9	NH_3	CH_3NH_2	Temp, ^oC	Time, hr.	B_5H_9	μ-CH_3 NHB_2H_5	H_3B_3-$N_3(CH_3)_3$	H_3B_3-N_3H_3
1.20		1.20	100	1	0.347	0.325	0.028	
1.20		1.20	25	24	0.330	0.090	0.012	
1.273		1.273	-78	24	0.390	0.082	0.005	
1.20	1.20		100	1	0.582			0.066
1.20	1.20		25	24	0.442			0.060
1.20	1.20	1.20	100	1	0.260	0.488	a	0.200
1.20	1.20	1.20	25	24	0.304	0.118		0.065

a. Very small, but easily detectable, amounts.

and Burg[54] who reported obtaining high yields of borazine by heating u-aminodiborane. This led to an investigation of the products formed in the pyrolysis of u-methylamine-diborane.

The B_5H_9-monomethylamine reaction was also carried out at 78° by condensing the reactants into the reactor using liquid nitrogen at -196° and then replacing the liquid nitrogen dewar with a dry ice (CO_2)-isopropyl alcohol slurry. Thus the reactor was thermostated at -78°. After the desired length of time, the volatile materials were slowly passed through traps maintained at -78°, -63° and -33°. Each partition was transferred to the gas chromatograph for complete separation. In the -78° trap there was found 0.390 mmole of B_5H_9 (31% recovery) identified by infrared and mass spectrometry. In a similar manner, 0.022 mmole of $CH_3NHB_2H_5$ and 0.005 mmoles of $H_3B_3N_3(CH_3)_3$ were found in the -63° and -33° traps respectively.

u-Methylaminodiborane(I), was identified on the basis of mass, infrared, ^1H NMR and ^{11}B NMR spectra of the pure compound and by comparison with that of an authentic sample made by the method of Burg and Randolph.[55] In the mass spectrum (Table 9) the product had a m/e cut-off at mass 57 corresponding to $^{12}C^{14}N^{11}B_2H_9^+$, and displayed some

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[54]H. I. Schlesinger, D. M. Ritter and A. B. Burg, J. Am. Chem. Soc., 60, 2297, (1938).

[55]A. B. Burg and C. L. Randolph, Jr., J. Am. Chem. Soc., 71, 345, (1949).

of the characteristic boron isotope spread and minimal hydrogen loss found in boron hydrides. The most abundant species in the spectrum of I corresponds to the parent minus a methyl group, $^{14}N^{11}B_2H_6^+$, (m/e 42). The parent peak (minus a hydrogen) is of greater intensity than the preceding peaks establishing that fewer than four boron atoms are present in the molecule (see section on interpretation of spectra).

The infrared spectrum of I (figure 14) indicates an open-cage boron hydride structure having a doublet absorption at 2530 cm^{-1} due to terminal BH_2 vibrations and absorptions near 1875 and 1500 cm^{-1} due to bridge hydrogen atoms. Moreover, the relative weakness of the latter band is consistent with the presence of only one such bridge. An N-methyl group is strongly indicated due to the presence of C-H absorption at 2988 cm^{-1} and N-methyl deformation bands near 1409 cm^{-1}. The presence of an N-H absorption at 3423 cm^{-1} and a B-N absorption band near 1550 cm^{-1} are consistent with this assignment of I as the u-methylamino derivative of diborane.

The 12.8 MHz ^{11}B NMR spectrum (figure 15) is compatible with the structural assignments made on the basis of mass, infrared, and ^1H NMR spectra and indicates two boron atoms in the molecule. The spectrum shown a 1:2:1 triplet split into doublets at a chemical shift (ppm relative to methyl borate) δ +22.7, J=130Hz assigned to B-H terminal, and J=30 Hz assigned to B-H-B bridging.

TABLE 9

Mass Spectrum of μ-Methylaminodiborane

m/e	Relative Peak Heights	m/e	Relative Peak Heights
57	1	40	68
56	46	39	24
55	36	38	12
54	30	37	6
53	24	36	1
52	20	29	1
51	11	28	7
50	3	27	7
49	1	26	5
44	1	25	2
43	24	24	3
42	100	23	2
41	32	22	1

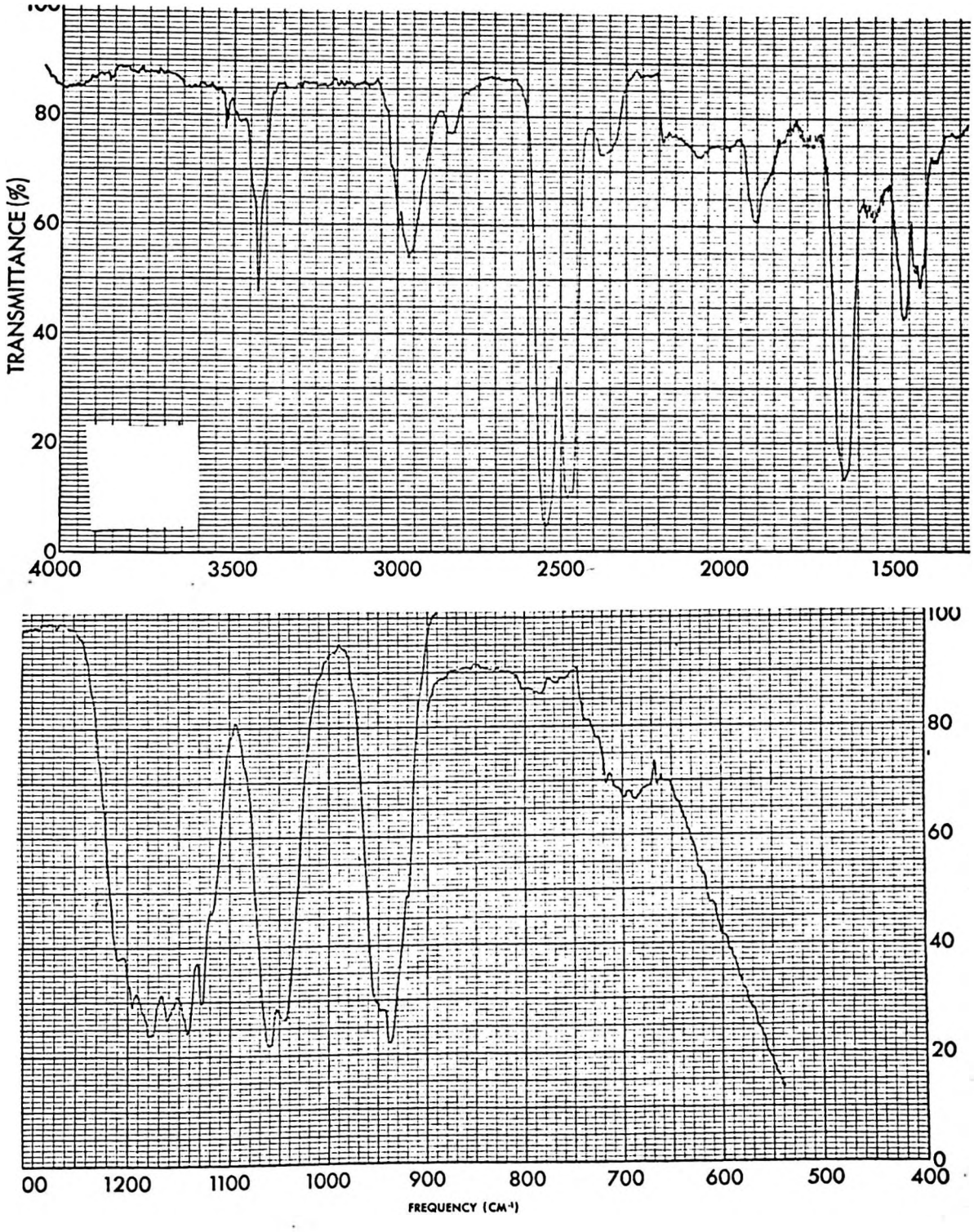


Figure 14. Infrared spectrum of μ-methylaminodiborane.

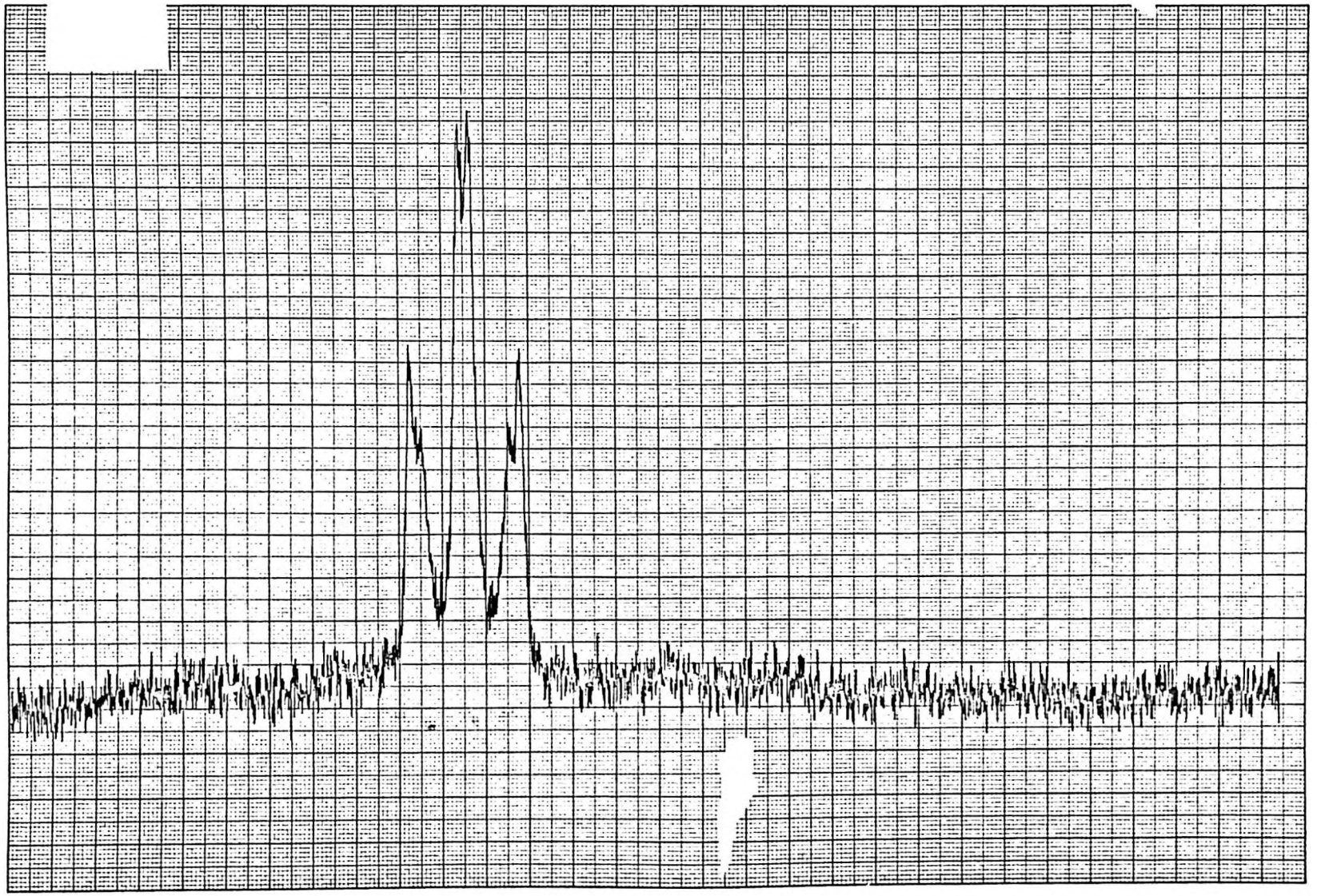


Figure 15. ^{11}B NMR spectrum of μ-methylaminodiborane.

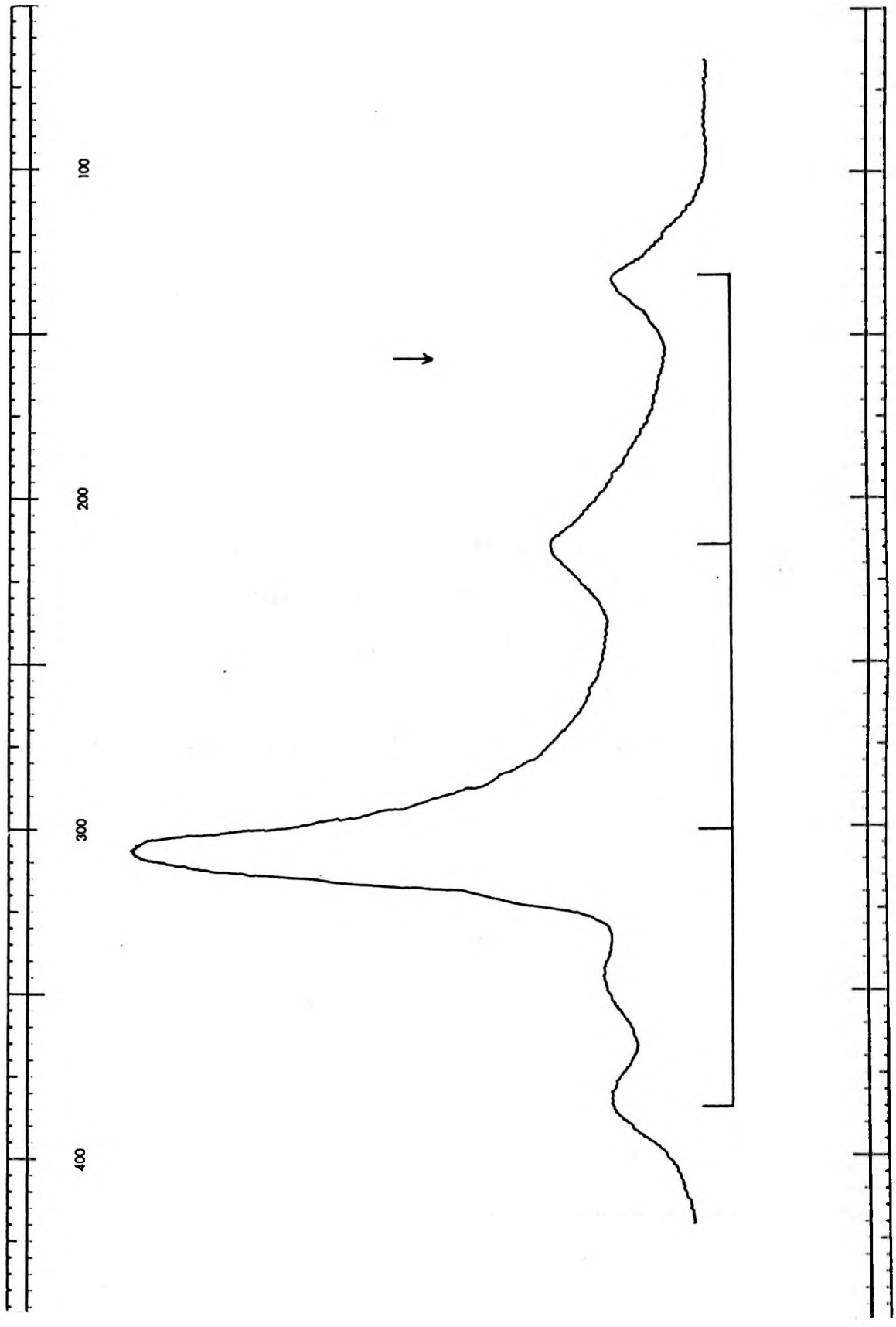


Figure 16. ^{1}H NMR spectrum of μ-methylaminodiborane.

The presence of the triplet split into doublets (see section on interpretation of spectra) demonstrates that each boron atom is bonded directly to two terminal hydrogens, and connected by a bridging hydrogen, verifying that the methyl group is attached at a nitrogen position. This spectrum at 12.8 MHz was in agreement with that reported at 19.3 MHz by Gaines and Schaeffer[56] for u-methylaminodiborane.

The 60 MHz ^1H NMR spectrum (figure 16) of u-methyl-aminodiborane displays a quartet due to the splitting of the terminal hydrogens coupled to a boron atom and a strong absorption peak corresponding to the hydrogen in the methyl group. The chemical shift (ppm relative to TMS) for the quartet is δ - 1.54 (J = 125 Hz), assigned to BH (terminal) and that of the strong singlet is δ - 2.68 assigned to CH (methyl). There was evidence of a bridge hydrogen absorption at δ - 1.50 but as expected this rather broad peak was overlapped by the quartet, making assignment difficult. In like manner, the absorption due to the nitrogen hydrogen was tentively assigned - 3.5.

The compounds $H_3B_3N_3H_3$(II), $H_3B_3N_3H_2CH_3$(III), $H_3B_3N_3H(CH_3)_2$(IV), and $H_3B_3N_3(CH_3)_3$(V), prepared in the $B_5H_9 \cdot NR_3$(R=CH_3, H) reaction were identified using mass, infrared, ^1H NMR and B^{11} NMR spectra. The mass spectra of the N-methyl borazine , II-V (Tables 10 & 11) have

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[56]D. F. Gaines and R. Schaeffer, J. Am. Chem. Soc., 86, 1505, (1964).

parent peaks at m/e = 81, 95, 109, and 123 respectively as indicated by sharp high mass cut-offs. The most abundant species in the spectra of II-V, (mass 80, 94, 108, and 122 respectively) are due to the parent minus a hydrogen, $B_3N_3CH_7^+$, $B_3N_3C_2H_{10}^+$, and $B_3N_3C_3H_{13}^+$. With this loss of hydrogen, the spectra all agree very closely with the expected spectra on the basis of the natural abundance of the boron isotopes; i.e., the parent peak is of greater intensity than the preceding peak establishing that fewer than four boron atoms are present in the molecule. The similarities in the fragmentation patterns of II-V are indicative that they have a similar but more highly substituted structure.

The infrared spectral data are given in figures 17-20. The strong B-N ring vibrations near 1465 cm^{-1} coupled with a change in the frequency of the BH stretching vibrations (to a longer wave number) suggest that probability of amine borane or borazine type compounds. There is present in all except V, an absorption at 3500 cm^{-1} due to NH stretching. Thus, the nitrogens in V are fully substituted by methyl groups indicated by the obvious absences of NH absorption and an increase in the intensity of the CH (alkyl) absorption at 2980 cm^{-1}. In like manner, the absence of the C-H (alkyl) absorption is indicative of an unsubstituted borazine in II. Although the infrared spectra is quite similar for the mono- and disubstituted borazines, they were easily distinguished from one another

TABLE 10

Mass Spectra of $H_3B_3N_3H_3$, $H_3B_3N_3H_2(CH_3)$ and $H_3B_3N_3H(CH_3)_2$

Relative Peak Heights

m/e	$H_3B_3N_3H_3$	$N_3B_3N_3H_2(CH_3)$	$H_3B_3N_3H(CH_3)_2$
110			1
109			33
108			100
107			80
106			22
105			5
104			1
96		2	
95		26	1
94		100	2
93		67	10
92		20	7
91		5	4
90		1	2
82	1	1	1
81	36	2	23
80	100	5	47
79	64	4	26
78	24	2	11

by a comparison of the region from 11-700 cm^{-1}. The difference in the spectra in this region reflects the substituent effect upon the rings vibrations and distortions

The proton NMR spectra for the N-methylborazines are shown in figures 21 and 22. The proton spectra of the N-methylborazines consist of a sharp resonance due to the methyl group, a well defined triplet with the center band more intense than the outer bands due to the protons on nitrogen, and a symmetrical quartet due to the proton on boron. The lowest field BH resonance was clearly recognizable but the others were either partially or completely masked by the NH and CH resonance. The chemical shifts and coupling constants obtained by proton NMR are given in Table 12 for the N-methylborazines.

The ^{11}B NMR were extremely simple; they are shown in figures 23 & 24. The N-methylborazines were symmetrical couplets. This is consistent with the structure of the N-methyl borazines in which each boron atom is bonded directly to a hydrogen atom. The chemical shifts of the proton ^{11}B resonance are given in Table 13. The N-methylborazine are downfield from I reflecting either magnetic effects of change in electron density.

Pyrolysis of μ-Methylaminodiborane

A measured quantity of μ-$CH_3NHB_5H_8$ (1.164 mmole) was condensed into a previously evacuated 20-ml reactor cooled in liquid nitrogen, after which the flask was sealed, the liquid nitrogen removed, and the reactor and its contents

TABLE 11

Mass Spectrum of $H_3B_3N_3(CH_3)_3$

m/e	$H_3B_3N_3(CH_3)_3$	m/e	$H_3B_3N_3(CH_3)_3$
138		118	1
137		117	
136		116	
135		115	
134		114	
133		113	
124	2	112	
123	37	111	2
122	100	110	28
121	66	109	22
120	21	108	9
119	4	107	2

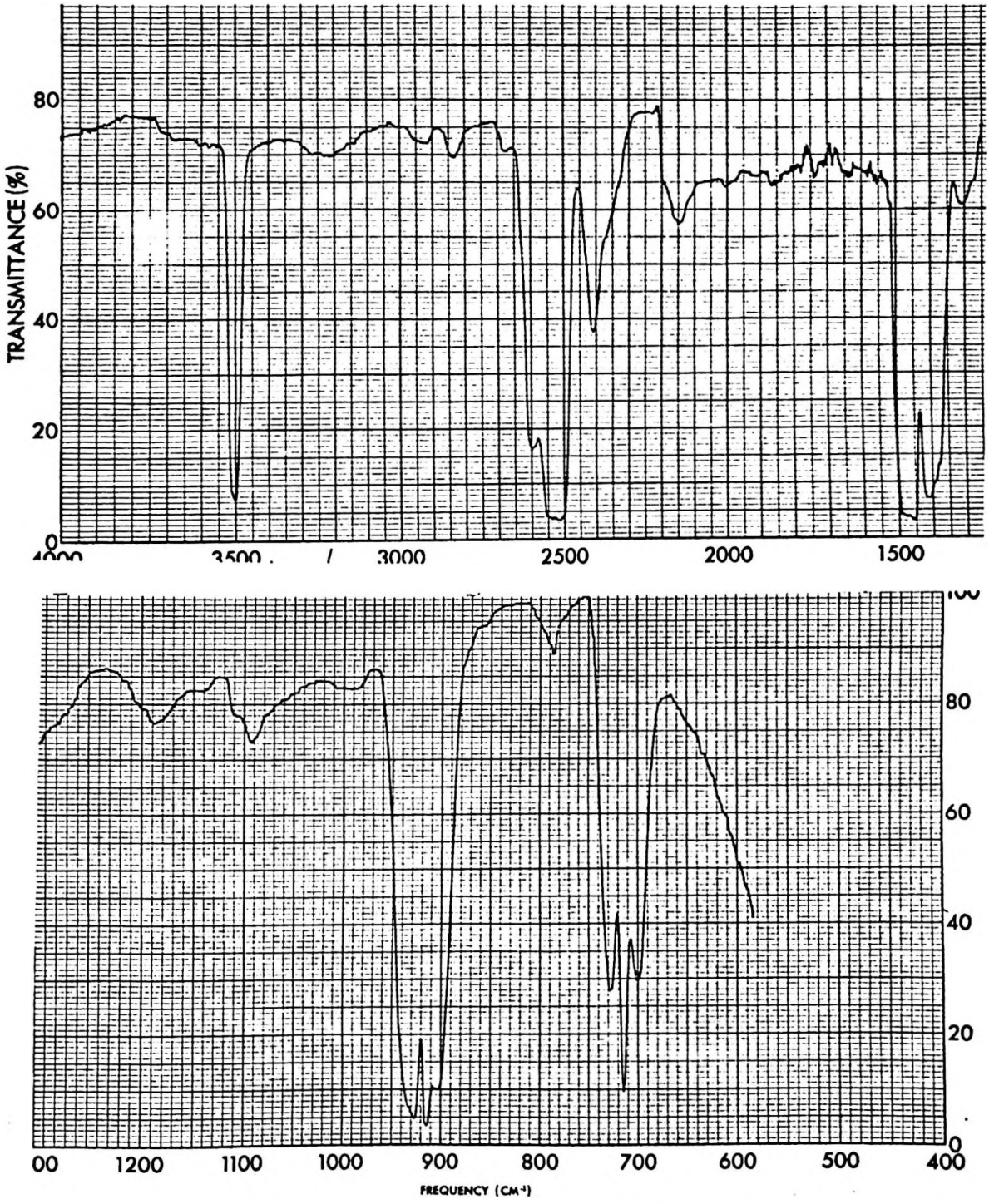


Figure 17. Infrared spectrum of borazine.

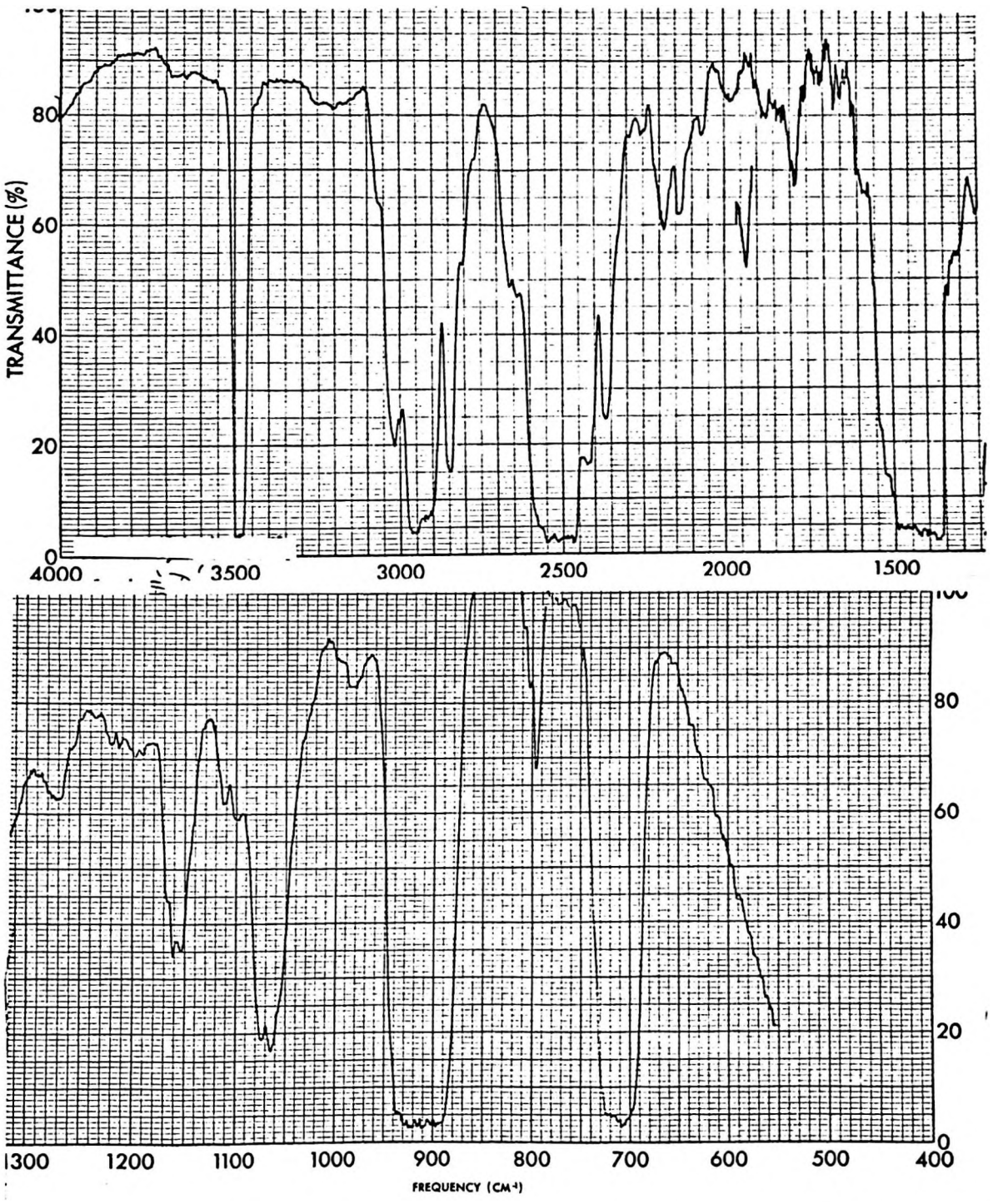


Figure 18. Infrared spectrum of N-methylborazine.

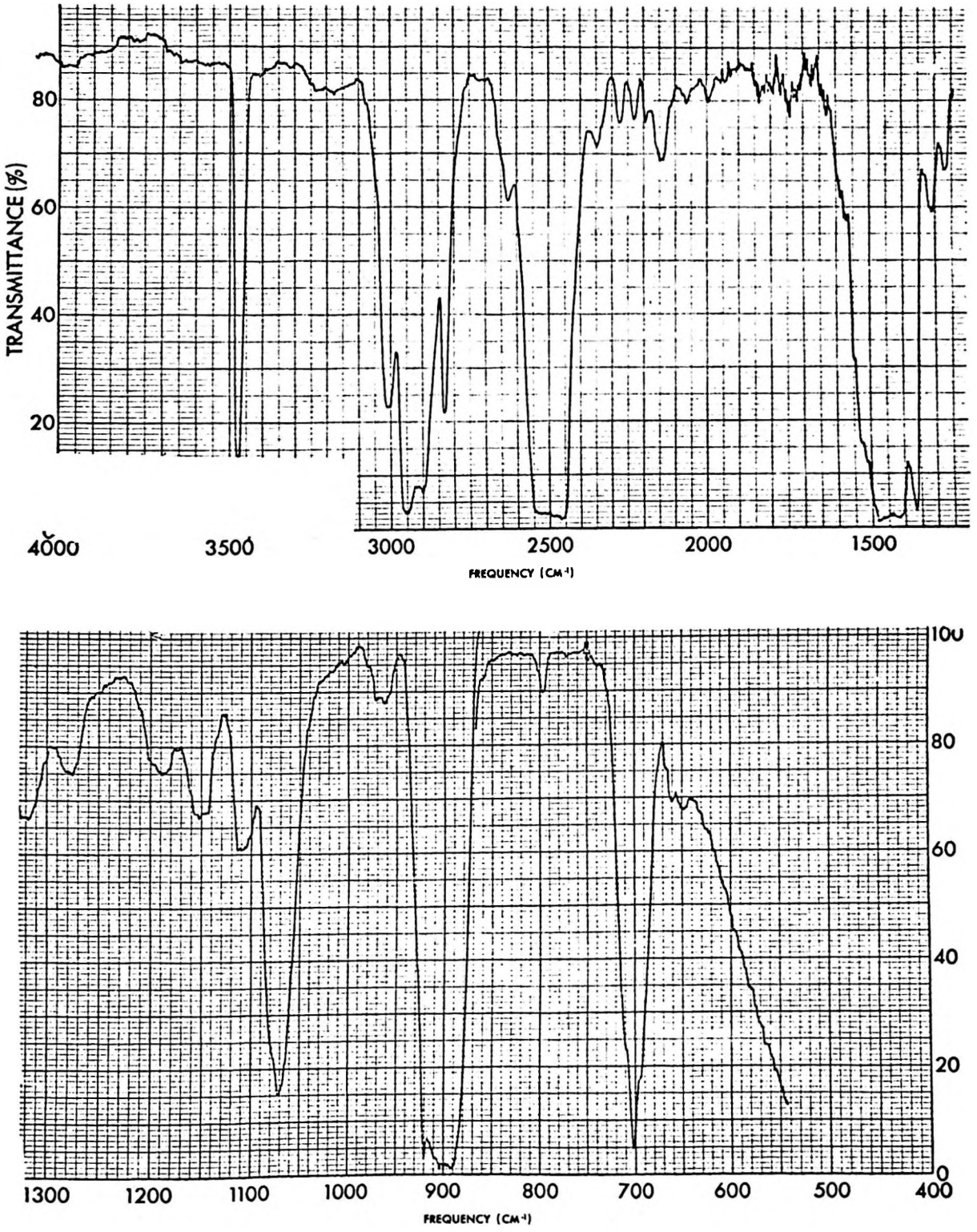


Figure 19. Infrared spectrum of N,N-dimethylborazine.

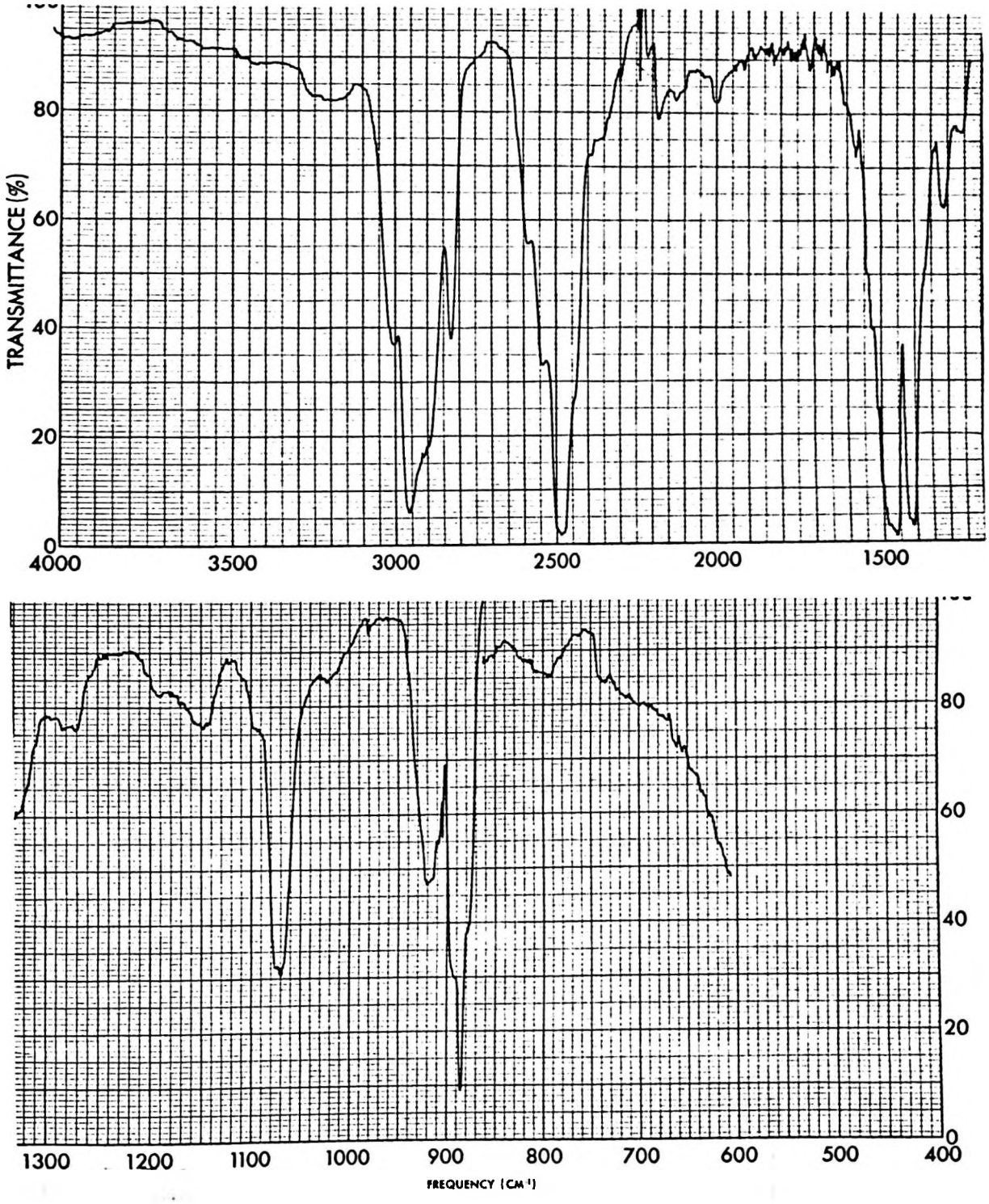


Figure 20. Infrared spectrum of N,N,N-trimethylborazine.

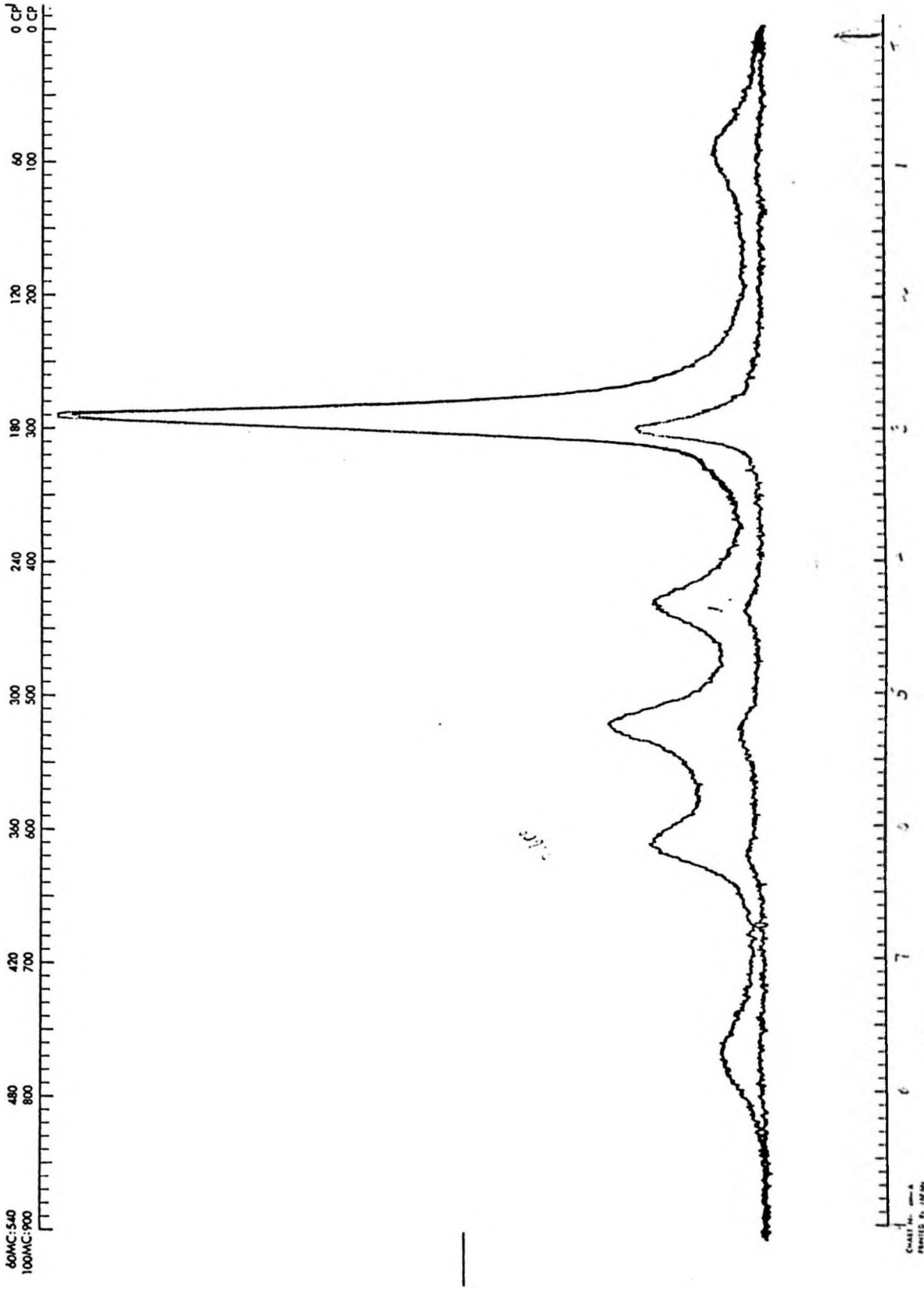


Figure 21. ^{1}H NMR spectrum of N-methylborazine.

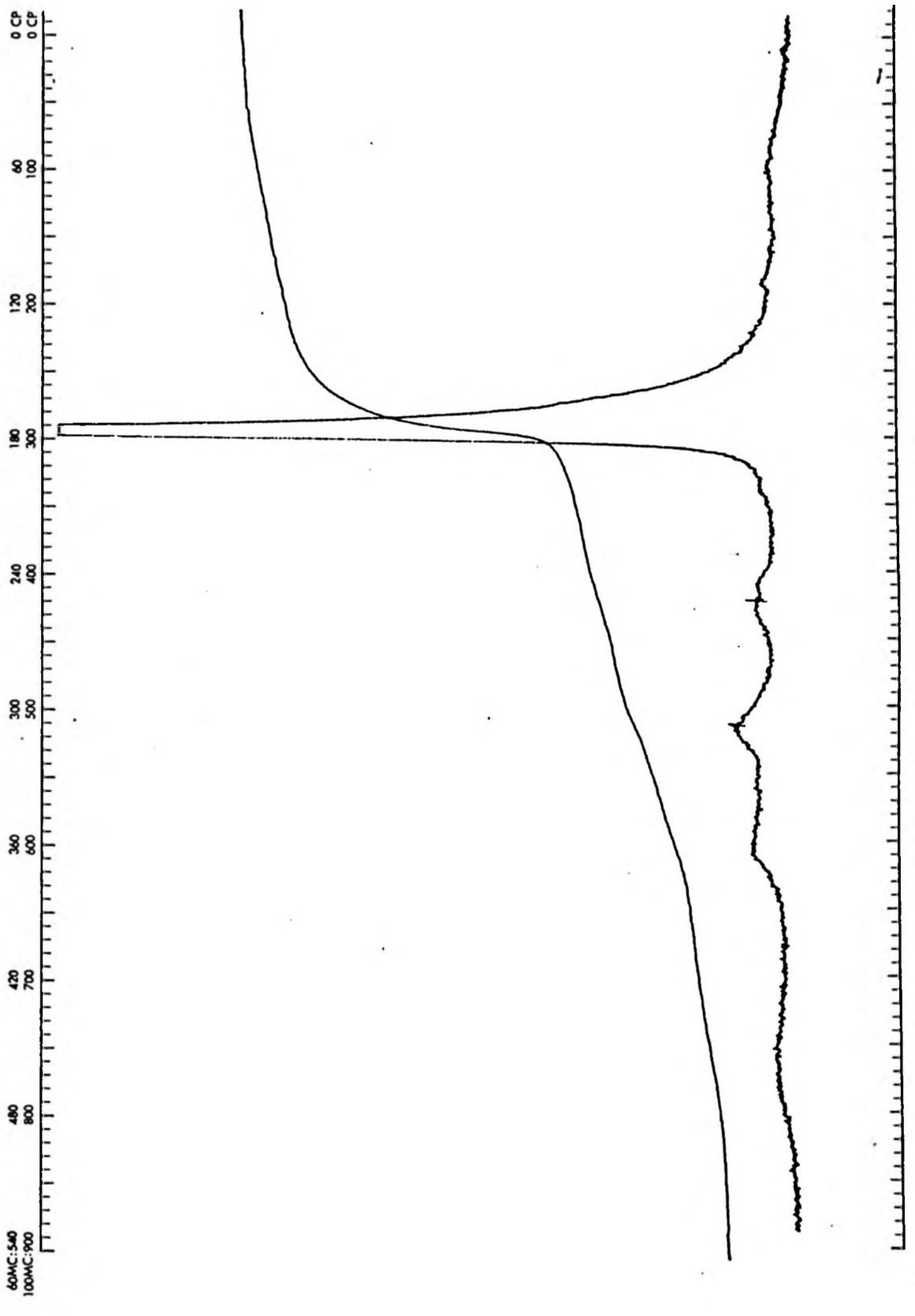


Figure 22. ^{1}H NMR spectrum of N,N-dimethylborazine.

TABLE 12

^{1}H NMR Data for the N-Methylborazines[a]

Compound	NH, (ppm)	J, (Hz)	BH, (ppm)	J, (Hz)	CH, (ppm)
$H_3B_3N_3H_3$[b]	-5.26	50	-4.47	113	
$H_3B_3N_3H_2CH_3$	-5.25	49	-4.41	113	-3.00
$H_3B_3N_3H(CH_3)_2$	-5.28	49	-4.40	113	-2.95
$H_3B_3N_3(CH_3)_3$[b]			-4.45	105	-3.00

[a]relative to TMS

[b]reference 44

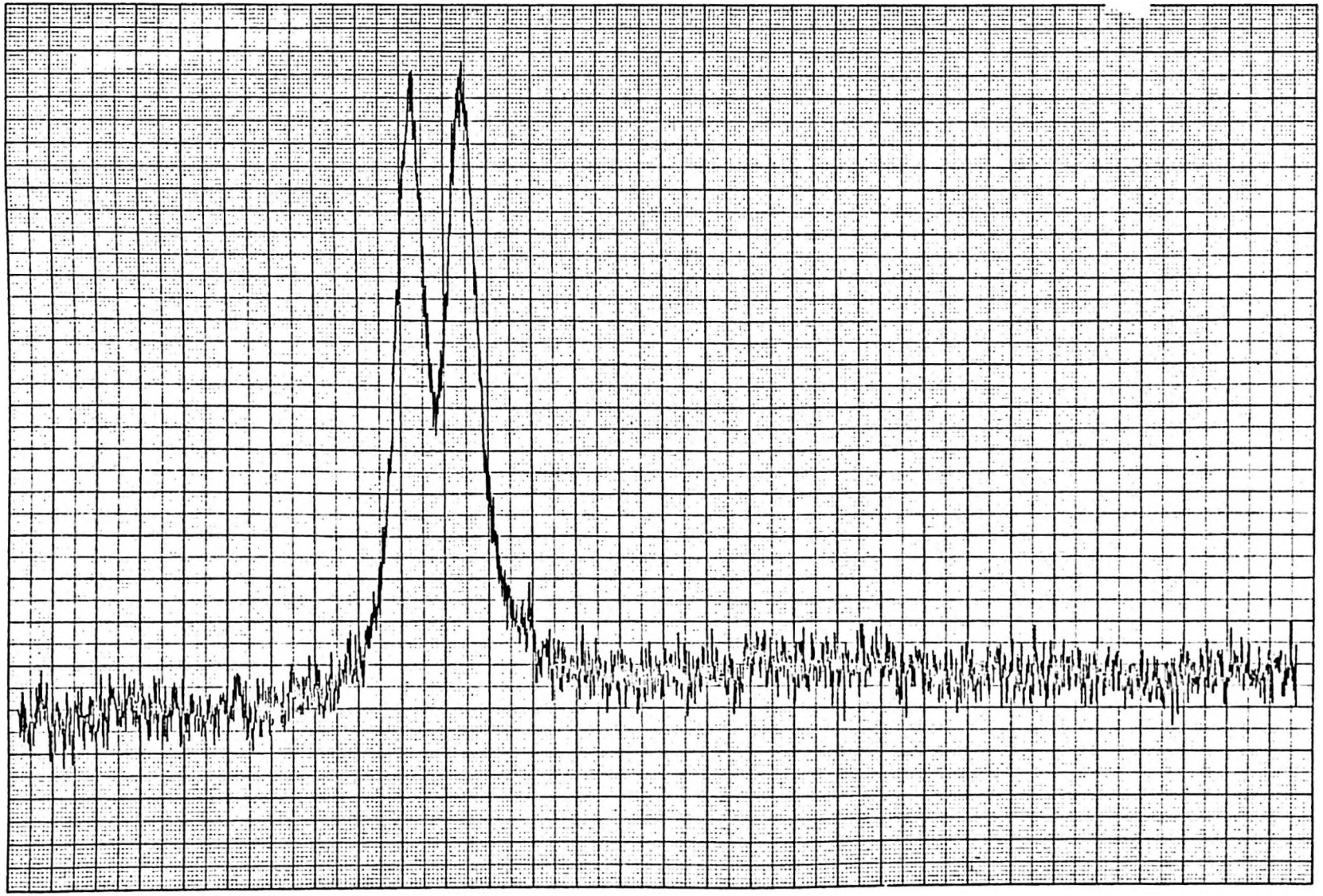


Figure 23. ^{11}B NMR spectrum of N-methylborazine.

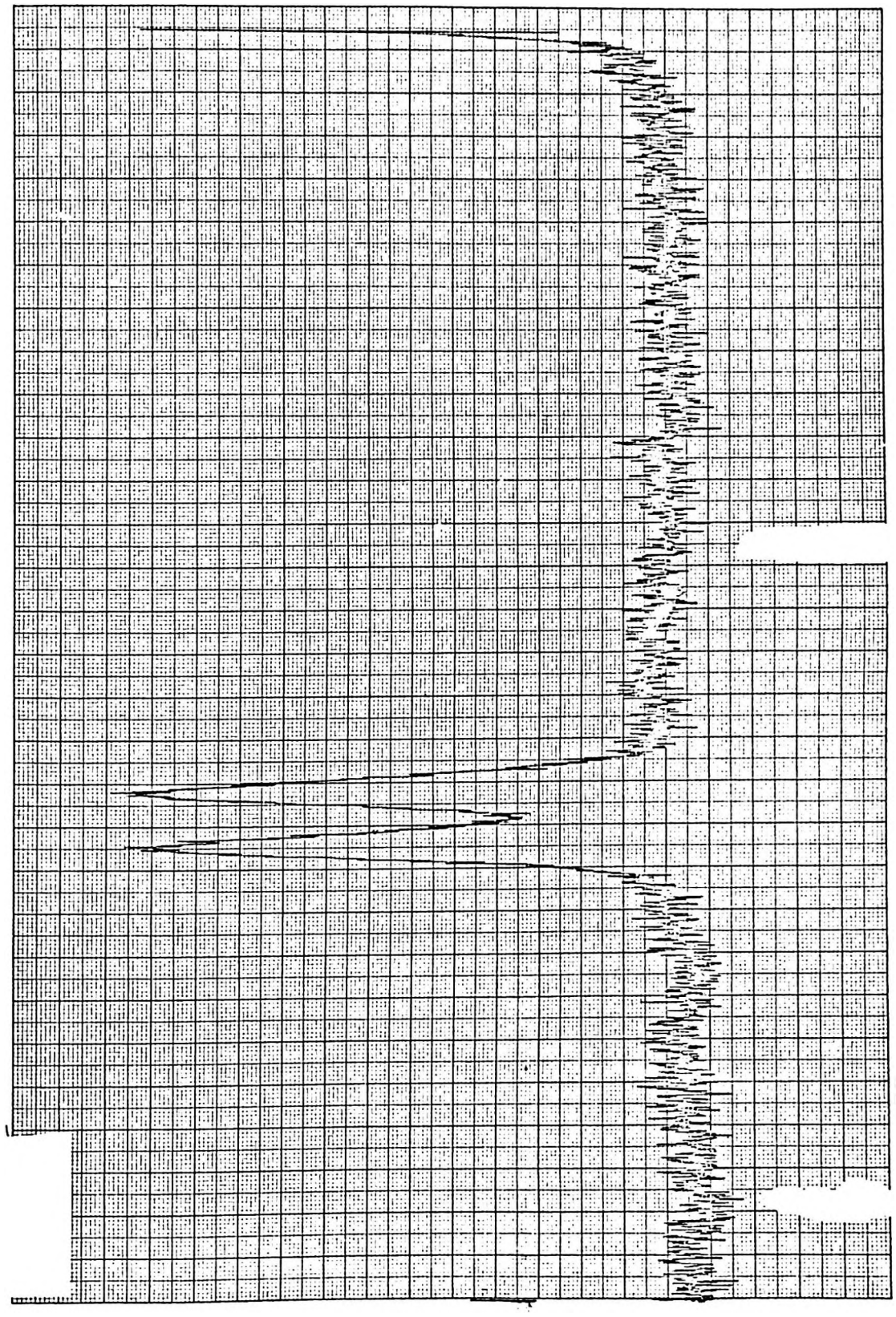


Figure 24. ^{11}B NMR spectrum of N,N,N-trimethylborazine.

TABLE 13

^{11}B NMR Data for the N-Methylborazines[a]

Compound	BH, (PPM)	J, (ppm)
$H_3B_3N_3H_3$[b]	-30	138
$H_3B_3N_3H_2CH_3$	-32	140
$H_3B_3N_3H(CH_3)_2$[b]	-32	140
$H_3B_3N_3(CH_3)_3$	-35.1	124

[a]relative to methylborate

[b]reference 44

allowed to warm to room temperature. After heating in an oven at 110° for 1 hour, the reactor was again cooled in liquid nitrogen and opened into the vacuum line. The contents were separated by gas chromatography (Table 7). The resulting products with yields were B_5H_9 (0.006 mmole), B_2H_6 (0.024 mmole), $H_3B_3N_3(CH_3)_3$ (0.280 mmole), recovered u-$CH_3NHM_2H_5$ (0.330 mmole), and trace amount of $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$ and $H_3B_3N_3H(CH_3)_2$ as shown in Table 14.

The Reaction of 1- and 2-Methylpentaborane(9) with Ammonia and Monomethylamine

The reactions of 1- and 2-methylpentaborane(9) with ammonia and monomethylamine were carried out using essentially the same experimental procedures as those followed in the previously described section involving pentaborane(9).

The results of reactions of 1-CH_3- and 2-$CH_3B_5H_8$ with monomethylamine are given in Tables 15 and 16. Using equimmolar amounts of reactants (0.267 mmole), the reaction of 1-$CH_3B_5H_8$ with CH_3NH_2 at 100° for 1 hour failed to yield any B-methyl compounds but the analoguous reaction involving 2-$CH_3B_5H_8$ produced a small but easily detectable amount of $(CH_3)H_2B_3N_3(CH_3)_3$. Similar reactions conducted at room temperature yielded identical products but in reduced amounts.

As shown in Tables 17 and 18, $H_3B_3N_3H_3$, $(CH_3)H_2B_3N_3H_3$ and $(CH_3)_2HB_3N_3H_3$ were prepared by allowing 1-CH_3- and 2-$CH_3B_5H_8$ to react with ammonia. Varying the relative

TABLE 14

The Pyrolysis of μ-Methylaminodiborane

REACTANT: M Mole			VOLATILE PRODUCT: M Mole			
μ-CH_3NH-B_2H_5	Temp.°C	Time, hr.	μ-CH_3NH-B_2H_5	H_3B_3-$NH_2(CH_3)$	H_3B_3-$NH(CH_3)_2$	H_3B_3-$N(CH_3)_3$
1.164	110	1	0.330	a	a	0.280

a. Trace amounts.

amounts of ammonia to alkylpentaborane from a 1:1 mixture to about 4:1 led to an increased yield of all borazine products regardless of whether 1-CH_3- or 2-$CH_3B_5H_8$ is the reactant. In almost all cases, a small amount of the reciprocal isomer of the reactant was found as a product of the reaction.

No intermediate fragments, for example, alkylaminoborines, were found in any of the reactions involving 1-CH_3 and 2-$CH_3B_5H_8$ with ammonia or monomethylamine.

The compounds $(CH_3)H_2B_3N_3H$ (VI), $(CH_3)_2HB_3N_3H_3$(VII), and $(CH_3)H_2B_3N_3(CH_3)_3$ (VIII), prepared in the reaction 1-CH_3- and 2-$CH_3B_5H_8$ with ammonia and monomethylamine, were identified using mass and infrared spectra. The mass spectra of the B-methyl borazines, VI-VIII (Tables 19 and 20) have parent peaks at m/e = 95, 109, and 137 respectively as indicated by sharp high mass cutoffs. The most abundant species in the spectra of VI-VIII (mass 80, 94, and 122 respectively) are due to the parent minus a methyl group, $B_3N_3H_5^+$, $B_3H_3CH_7^+$, and $B_3N_3C_3H_{14}$. With this loss of a methyl group, the spectra all agree closely with the expected spectra, the parent peak minus a methyl group is of greater intensity than the preceeding peaks, establishing that fewer than four boron atoms are present in the molecule.

The infrared spectral data are given in Figures 25-27. The infrared spectra of VI-VIII exhibit absorptions characteristic of borazines; strong absorption at 3480 cm^{-1} (N-H stretching vibration), strong absorption near 3000 cm^{-1} (C-H stretching vibrations), strong absorption at

TABLE 15

Reaction of 1-$CH_3B_5H_8$ with CH_3NH_2

1-CH_3-B_5H_8	CH_3NH_2	Temp.^oC	Time, hr.	1-CH_3-B_5H_8	H_3B_3-$N_3H_2(CH_3)$	H_3B_3-$N_3(CH_3)_3$	$(CH_3)_2HB_3$-N_3H_3
0.267	0.267	100	1	0.112	0.050	0.024	
0.267	0.267	25	24	0.101	0.030	0.010	
0.267	0.267	100	72	0.092	0.007	0.096	a
0.267	0.569	100	1	0.050	0.005	0.020	
1.200	1.200	100	1	0.465	0.090	0.005	
0.365	0.365	-78	24	0.223	0.002		

a. Very small, but easily detectable, amounts.

TABLE 16

Reaction of $2\text{-}CH_3B_5H_8$ with CH_3NH_2

$2\text{-}CH_3\text{-}B_5H_8$	CH_3NH_2	Temp. °C	Time, hr.	$2\text{-}CH_3\text{-}B_5H_8$	$H_3B_3\text{-}N_3H_2(CH_3)$	$H_3B_3\text{-}N_3(CH_3)_3$	$(CH_3)_2HB_3\text{-}N_3H_3$
0.267	0.267	100	1	0.180	0.001	0.005	0.003
0.267	0.267	25	24	0.068		a	a
0.178	0.178	100	1	0.061	0.007	0.003	0.001
1.273	1.273	100	1	0.760	0.018	0.024	0.010
0.167	0.840	100	1	a		0.010	0.005

a. Very small, but easily detectable, amounts.

TABLE 17

Reaction of $1\text{-}CH_3B_5H_8$ with NH_3

REACTANTS: M Mole				VOLATILE PRODUCTS: M Mole			
$1\text{-}CH_3\text{-}B_5H_8$	NH_3	Temp. °C	Time, hr.	$2\text{-}CH_3\text{-}B_5H_8$	$H_3B_3\text{-}N_3H_3$	$(CH_3)H_2B_3\text{-}N_3H_3$	$(CH_3)_2HB_3\text{-}N_3H_3$
0.457	0.457	100	1	0.005	0.022	0.061	0.012
0.457	0.457	25	24	a	a	a	
0.308	0.572	100	1	0.001	0.006	0.008	0.006
0.926	0.890	100	1	a	0.031	0.014	0.001
0.613	2.247	100	1		0.094	0.245	0.100

a. Very small, but easily detectable amounts.

TABLE 18

Reaction of $2\text{-}CH_3B_5H_8$ with NH_3

REACTANTS: M Mole				VOLATILE PRODUCTS: M Mole			
$2\text{-}CH_3\text{-}B_5H_8$	NH_3	Temp. °C	Time, hr.	$2\text{-}CH_3\text{-}B_5H_8$	$H_3B_3\text{-}N_3H_3$	$(CH_3)H_2B_3\text{-}N_3H_3$	$(CH_3)_2HB_3\text{-}N_3H_3$
0.457	0.457	100	1	0.323	0.016	0.023	0.007
0.457	0.457	25	24	0.195			
0.320	1.655	100	1	0.003	0.002	0.186	0.015
0.158	1.318	50	24	0.002	0.007	0.131	0.043

a. Very small, but easily detectable, amounts.

TABLE 19

Mass Spectra of $(CH_3)H_2B_3N_3H_3$ and $(CH_3)H_2B_3N_3H_3$

m/e	Relative Peak Heights		m/e	Relative Peak Heights	
	$(CH_3)H_2B_3N_3H_3$	$(CH_3)_2HB_3N_3H_3$		$(CH_3)H_2B_3N_3H_3$	$(CH_3)_2HB_3N_3H_3$
110		1	77	14	14
109		37	76	10	11
108		30	75	3	5
107		10	74	3	1
106		2	73	1	
96	2		68	2	2
95	47	3	67	38	55
94	70	100	66	28	43
93	26	75	65	10	16
92	6	21	64	4	2
91	4	6	63	10	3
90	2		62	9	3
82		2	61	4	2
81	1	2	60	2	1
80	100	4			
79	73	4			
78	25	2			

TABLE 20

Mass Spectrum of $(CH_3)H_2B_3N_3(CH_3)_3$

m/e	Relative Peak Height	m/e	Relative Peak Height
138	2	115	11
137	9	114	3
136	29	113	21
135	21	112	1
134	4	111	18
133	3	110	14
132	1	109	7
131	1	108	1
124	1	98	1
123	18	97	4
122	100	96	4
121	65	95	5
120	13	94	5
119	3	93	10
118	1	92	3
117	1	91	3
116	1	90	1

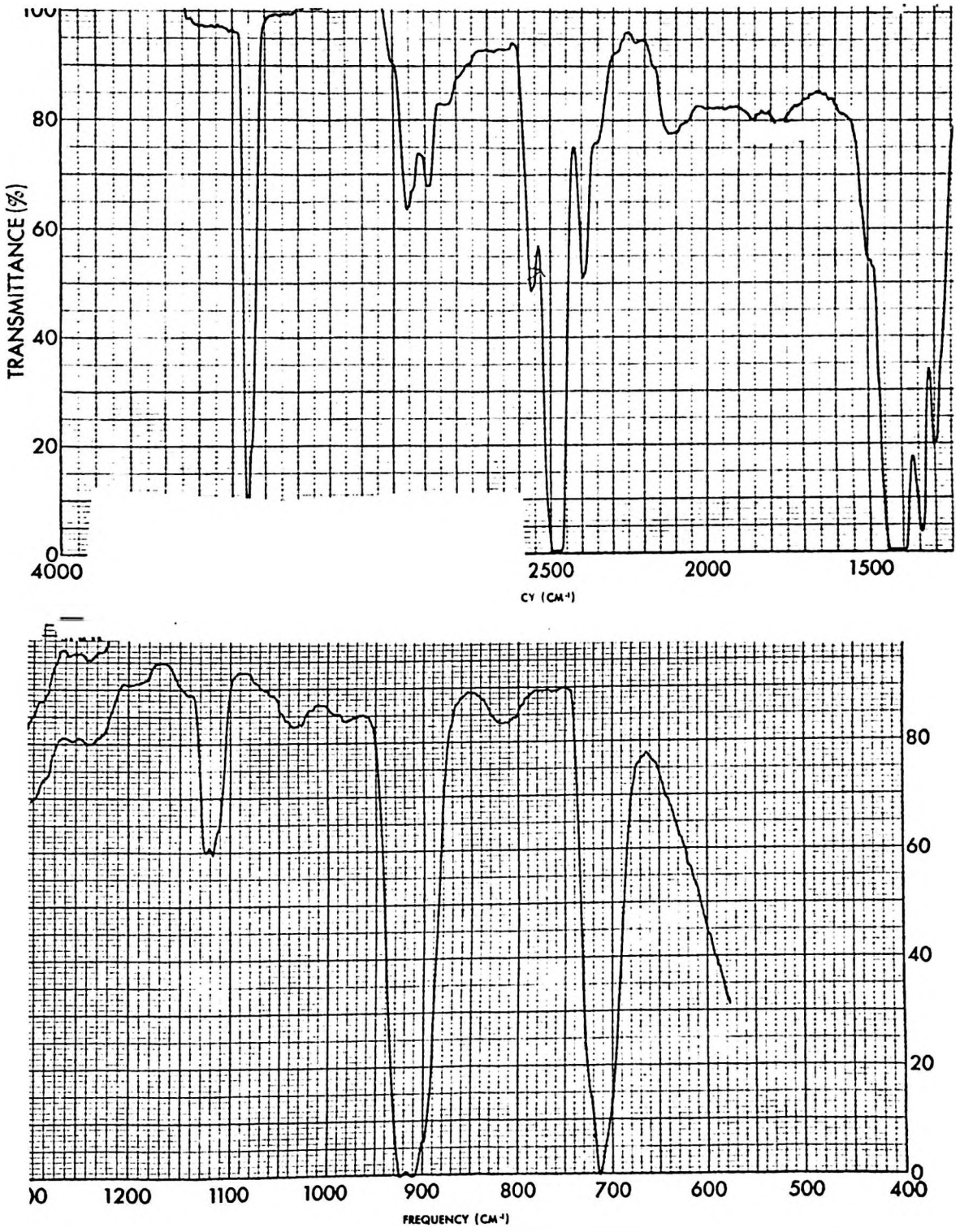


Figure 25. Infrared spectrum of B-methylborazine.

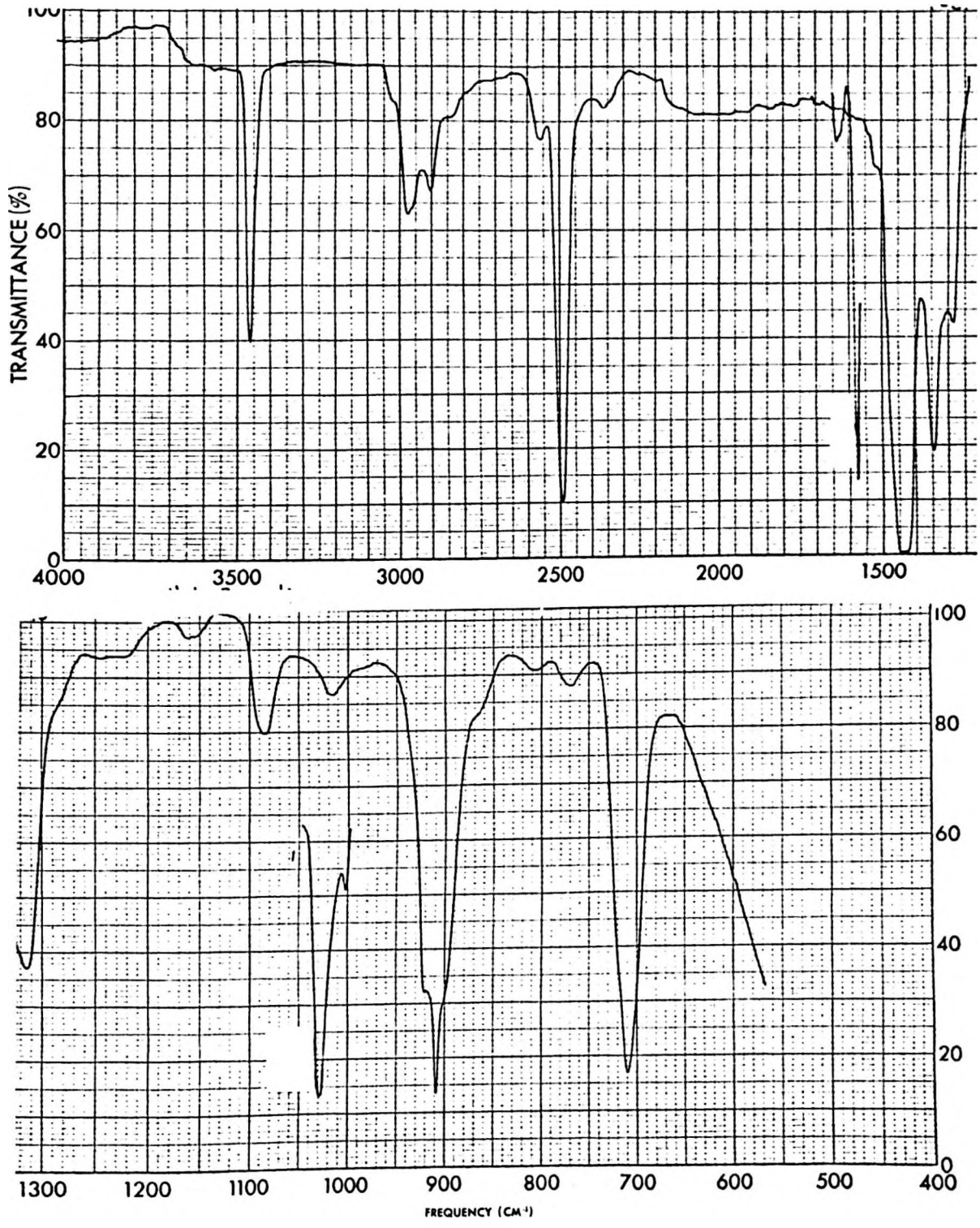


Figure 26. Infrared spectrum of B,B-dimethylborazine.

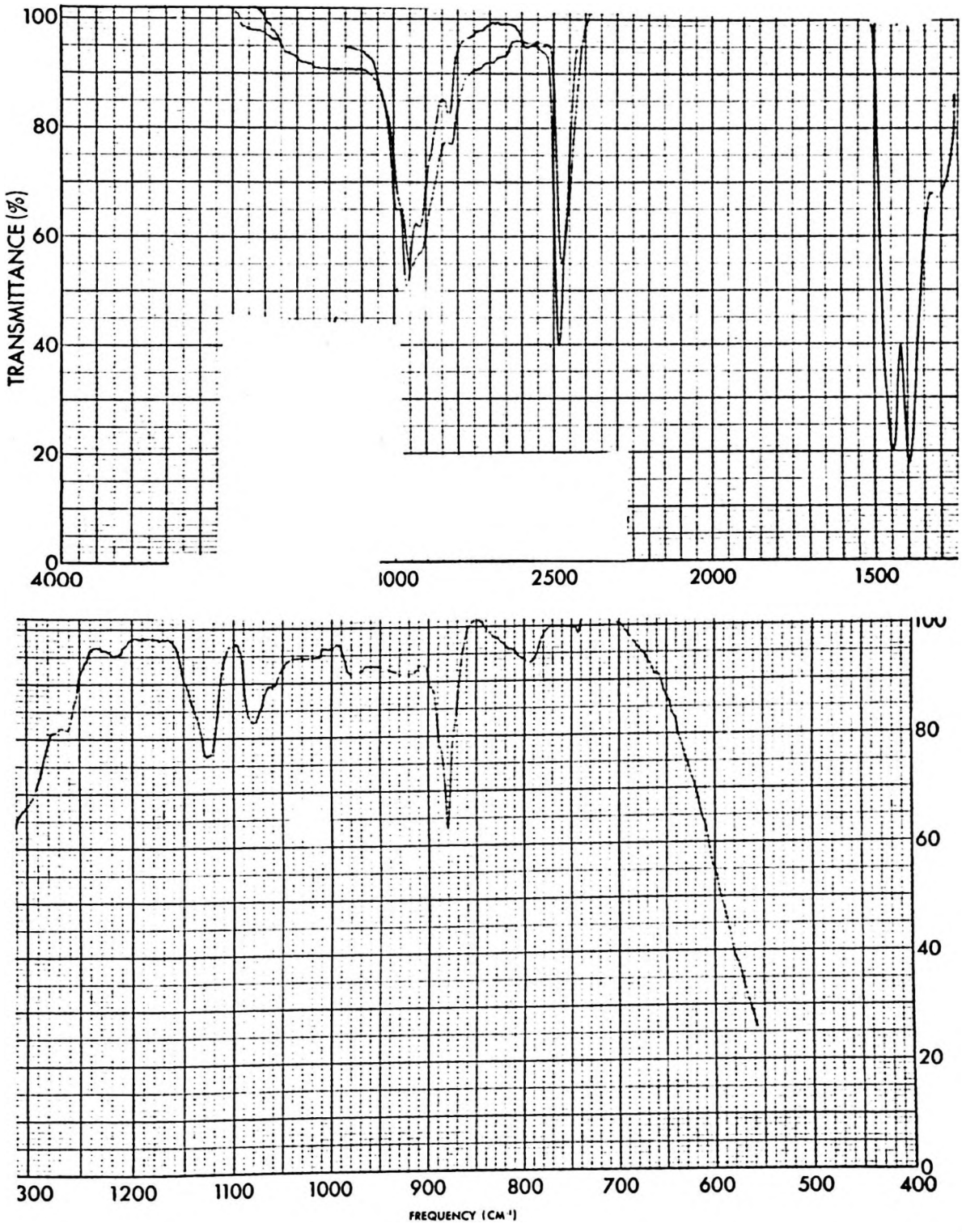


Figure 27. Infrared spectrum of B,N,N,N-tetramethylborazine.

2500 cm^{-1} (B-H stretching vibrations), strong absorption at 1479 cm^{-1} (B-N stretching vibrations), and several absorptions in the region 1100-700 cm^{-1} (representive of the ring vibration and substituent effect on the ring). The absence of a band near 3480 cm^{-1} and a slight broading of the band at 3000 cm^{-1} indicate the nitrogens in VIII are fully substituted. The B-methylborazine are readily distinguished from the N-methylborazine as there is a small change in frequency of the N-H, B-H stretching vibrations, and B-N ring vibraticns. For example, the B-N ring vibrations are at a higher frequency ($\sim$1479 cm^{-1}) for the B-methyl compounds than for the N-methyl derivatives ($\sim$1463 cm^{-1}).

DISCUSSION

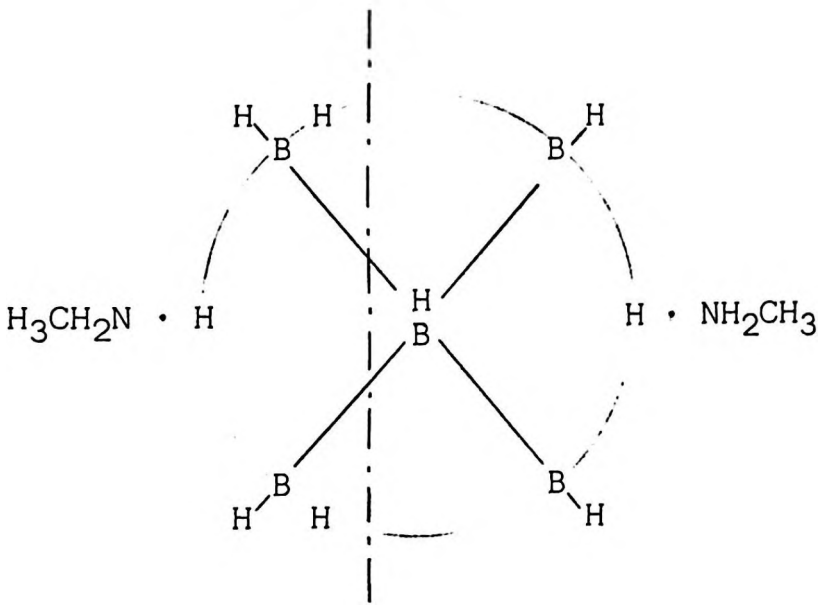
The vapor-phase reaction of pentaborane(9) with monomethylamine at 100° was found to yield the three N-methyl derivatives of borazine; $H_3B_3N_3H_2(CH_3)$, $H_3B_3N_3H(CH_3)_2$ and $H_3B_3N_3(CH_3)_3$. The tri substituted derivative was by far the major borazine product. In addition, μ-methylaminodiborane was recovered as a major reaction product (approx. 50%). The general stoichiometry equation of the reaction is as follows:

$$B_5H_9 + 2CH_3NH_2 \longrightarrow \mu\text{-}CH_3NHB_2H_5 + (CH_3NH_2 \cdot B_3H_3) + H_2$$

When a quantity of $\mu\text{-}CH_3NHB_2H_5$ was heated at 110° for 1 hour in a sealed reactor, good yields of $H_3B_3N_3(CH_3)_3$ were obtained along with trace amounts of $H_3B_3N_3H_3$, $H_3B_3N_3H_2(CH_3)$, and $H_3B_3N_3H(CH_3)_2$. This result strongly supports the above mechanism in which B_5H_9 and the amine react to form the intermediate fragment, $\mu\text{-}CH_3NHB_2H_5$, followed by conversion to the borazine ring system. The formation of unsymmetrical derivatives probably involves some additional interaction between $\mu\text{-}CH_3NHB_2H_5$ and one or more of the original reactants.

The most obvious mechanism of the cleavage of B_5H_9 by monomethylamine to form the reported products is one in which the base first associates with a bridge hydrogen in the structural pattern, The base then removes B_2H_5 leaving the

remaining (B_3H_4) moiety to attach itself to excess base to form the observed thermally stable nonvolatile liquid. The driving force of the reaction would be the extreme Lewis acid strength of the B_2H_5 moiety, beginning to take effect as the B-H-B bridges in B_5H_9 are loosened by thermal vibration.



The implication that the first step of this mechanism involves interaction between the amine and a bridge hydrogen of B_5H_9 rather than abstraction of a BH_3 unit suggests that the predominate factor with respect to the mode of cleavage is the acidic character of the bridge hydrogens. The

absence of other intermediate fragments, for example, $CH_3NH_2BH_3$ supports the proposed mechanism and also helps discredit the probability of BH_3 abstraction by base.

Furthermore, reactions carried out at low temperatures (-78^o to 25^o) provide additional evidence for the proposed mechanism. Pentaborane(9) and methylamine react to form a 1:2 adduct at -78^o which decomposes at 25^o to yield u-methylaminodiborane, (approx. 50%) by vacuum fractionation through a -63^o trap. The only other detectable products were trace amounts of B_2H_6 at -128^o and $(CH_3)_3N_3B_3H_3$ at -33^o. These results obtained under the conditions mentioned eliminate the possibility of BH_3, i.e. $\frac{1}{2}B_2H_6$ first being expelled from the adduct and subsequently reacting with amine to form the major reaction product, u-$CH_3NHB_2H_5$ as in the following reaction scheme;

$$B_5H_9 + 2CH_3NH_2 \longrightarrow \left[B_5H_9 \cdot 2CH_3NH_2\right] \longrightarrow CH_3NH_2 \cdot B_4H_6 + BH_3$$

$$CH_3NH_2 + 2(BH_3) \longrightarrow u\text{-}CH_3NHB_2H_5 + H_2$$

Thus, it is proposed that the reaction of B_5H_9 with monomethylamine proceeds through a reaction mechanism which involves bridge hydrogen association (BHA) by an amine group preceding abstraction of B_2H_5. The remaining B_3H_4 moiety reacts with excess amine to form an amphorous resin.

$$B_5H_9 + CH_3NH_2 \longrightarrow u\text{-}CH_3NHB_2H_5 + CH_3NH_2 \cdot B_3H_4$$

and finally,

$$u\text{-}CH_3NH_2B_2H_5 \longrightarrow (CH_3)_3N_3B_3H_3 + H_2$$

It became apparent early in the study of pentaborane-amine chemistry that it was essential to establish the nature of amine attack, i.e. apical versus basal. One expects that nucleophilic substitution will take place most easily at the boron atom with the greatest positive charge, (basal borons). Similarly, electrophilic substitution is expected to occur at the site of greatest negative charge, (apical boron). The concept of electrophilic substitution at the apex boron has been definitely observed in B_5H_9 by numerous researchers. On the other hand, nucleophilic substitution at the basal borons remains ambiguous. No substantiating evidence in support of nucleophilic attack by amine has been reported.

The reaction of pentaborane(9) with monomethylamine lends experimental support for the plausibility of expecting nucelophilic attack by amines at the base of the B_5H_9 pyramid. Although the first step of the proposed mechanism involves replacement of a bridge hydrogen by an amine, it additionally requires bond formation to two adjacent basal boron atoms.

In an effort to investigate more fully the nature of amine attack, experiments were conducted involving the reactions of 1-CH_3- and 2-$CH_3B_5H_8$ with amines. It was expected that the substituent groups on the borazine derivative would give insight as to the source of specific boron atoms from the alkylated pentaborane cage.

The results of reaction of B_5H_9, 1-CH_3- and 2-$CH_3B_5H_8$ with monomethylamine are shown in Table 21. The percent yield of products is based upon the amount of reactant consumed.

It is noted that the B_5H_9-amine reaction products differ from those obtained from the alkylpentaborane-amine reaction. The emphasis now, however, is focused on the difference between the reaction products of 1-$CH_3B_5H_8$ and 2-$CH_3B_5H_8$. Both reactants yield $H_3B_3N_3(CH_3)_3$ as a reaction product but only 2-$CH_3B_5H_8$ yields the B-methyl derivative, $(CH_3)H_2B_3N_3$-$(CH_3)_3$. The obvious significance of this result is that the apical substituted methyl group including the apical boron are not used in the formation of borazine derivatives. The basal substituted methyl group along with its boron atom are used in the formation of B-methyl derivatives. Thus, the experiment has clearly shown that the amine attack is via a basal boron and not apical, i.e. nucleophilic attack.

One of the most significant mechanistic implications found in these reactions is the complete absence of μ-$CH_3NHB_2H_5$ as a reaction product. The absence of u-$CH_3NH_2B_2H_5$ can possibly be interpreted by steric interactions, changes in Lewis acidity of the boron atoms, the acidity of the bridge hydrogens, or some combination of all of these factors. Regardless of which is the predominating factor, the fact that the alkyl substituent on pentaborane(9) prevents the formation of μ-$CH_3NHB_2H_5$ provides additional support for the previously discussed cleavage mechanism.

TABLE 21

Percent Reactants Recovered and Percent Yield of Products:

Reaction of B_5H_9, 1-$CH_3B_5H_8$ and 2-$CH_3B_5H_8$ with CH_3NH_2

B_5H_9	1-CH_3-B_5H_8	2-CH_3-B_5H_8	μ-CH_3-NHB_2H_5	H_3B_3-$N_3H_2(CH_3)$	H_3B_3-$N_3H(CH_3)_2$	H_3B_3-$N_3(CH_3)_3$	$(CH_3)H_2B_3$ $N_3(CH_3)_3$
28.9			57.8	0.1	0.1	4.9	
	42.0					16.1	
		38.3				2.6	4.4

Speculation as to the specific sequenc of the many possible mechanisms appears presumptive with the data available. Certain mechanisms, however, can be eliminated from consideration due to the power of negative inference.

For example, the fact that no detectable amounts of u-$CH_3NHB_2H_5$ are formed during the thermal vapor-phase reaction of alkylpentaborane with monomethylamine lends further support to exclude the possibility of BH_3 from being split from the structural pattern. Under these reaction conditions, a considerable amount of the missing compound, u-$CH_3NHB_2H_5$ would have been formed as shown;

$$1\text{-}RB_5H_8 + \tfrac{1}{2}CH_3NH_2 \longrightarrow CH_3NH_2 \cdot B_4H_5R + BH_3$$

$$2(BH_3) \longrightarrow B_2H_6$$

$$\tfrac{1}{2}CH_3NH_2 + B_2H_6 \longrightarrow u\text{-}CH_3NHB_2H_5 + H_2$$

Furthermore, the basal substituted pentaborane(9) results in the formation of a B-methylborazine derivative, $(CH_3)_3N_3B_3H_2(CH_3)_3$. The resulting compound might be expected to have been formed from the degradation of an intermediate compound, such as an alkyl substituted u-methylaminodiborane. This compound was not observed, however. In addition, the existence of a methylated derivative of u-methylaminodiborane has never been reported in the literature. The inability to form a B-methylated u-aminodiborane might be related to the electron-releasing effect of the methyl group, permitting resonance-contributions which would add to the stability

of either a B- or N substituted diborane, but would have the opposite effect if both were present on the same molecule. Steric effects, however, may well be more important.

The isomerization of excess 1-methylpentaborane(9) to the more thermodynamically stable 2-alkyl derivative was not observed even after heating at an elevated temperature for 1 hour. In contrast, Onak et al.[7] have reported that when a mixture of 1-ethylpentaborane(9) was raised from -196° to room temperature for a period of 1 hour, fractional condensation gave a 38% yield of the 2-alkyl isomer. This anomalous behavior in the case of monomethylamine can perhaps be attributed to the bridge hydrogen association that is involved in the first step of the proposed mechanism. In such a fashion the bridging amine groups would prevent the wholesale tautomerisation of hydrogens and accompanying skeletal rearrangement that is necessary to accomplish alkyl isomerization.

Furthermore, Onak[14] has shown that the methyl substituent has an effect on the chemical shifts of the bridge hydrogens in alkylpentaboranes as determined by a comparison of the proton nmr. He found that the bridge hydrogens adjacent to a methyl group shift downfield from those in pentaborane about 0.6 ppm while the bridge hydrogens non-adjacent to the methyl group shift 0.1 ppm. Finally, the apical substituted methyl group shifts the bridge hydrogens 0.2 ppm. A similar substituent effect was reported for the ^{11}B chemical shifts of the boron atoms in alkylpentaboranes.

In summary the introduction of methyl substituent on pentaborane(9) changes its chemical reactivity with monomethylamine. This change in reactivity prevents the formation of μ-$CH_3NHB_2H_5$ as a reaction product.

Therefore, the reaction of 1- and 2-methylpentaborane(9) with monomethylamine probably proceeds by a mechanism similar to that proposed for the pentaborane(9)-monomethylamine reaction. The first step involves association of amine group with bridge hydrogen. This phenomenon would account for the fact that no 2-methylpentaborane(9) is recovered. However, in the next step, methylation prevents the formation of the stable intermediate of μ-methylaminodiborane. Thus the only possible intermediate fragments that could lead to the formation of the borazine derivatives are the relatively unstable amineboranes, $CH_3NH_2BH_3$ and $CH_3NH_2BH_2(CH_3)$. Thus the results suggest chemical processes expressed by the following idealized equations;

$$1\text{-}CH_3B_5H_8 + 2CH_3NH_2 \longrightarrow CH_3NH_2BH_3 + CH_3NH_2 \cdot B_4H_5R$$
$$3CH_3NH_2BH_3 \longrightarrow (CH_3)_3N_3B_3H_3 + 6H_2$$

$$2\text{-}CH_3B_5H_8 + 2CH_3NH_2 \longrightarrow CH_3NH_2BH_3(CH_3) + CH_3NH_2 \cdot B_4H_6$$
$$3CH_3NH_2BH_2(CH_3) \longrightarrow (CH_3)_3N_3B_3H_2(CH_3) + 5H_2$$

Pentaborane(9) has been found to react stiochiometrically in a 1:2 ratio with ammonia to yield only one volatile product, $H_3B_3N_3H_3$. No intermediate fragments were

observed which could lead to the formation of this product. A considerable amount of hydrogen was generated during the course of the reaction.

A plausible explanation for these results is a mechanism in which the first step is symmetrical cleavage by the base to form the fragment, H_2BNH_2. Condensation of three of these unstable species[57] with loss of hydrogen would result in the formation of the borazine ring system. The remaining $B_4H_6^-$ moiety reacts with excess amine to form a non-volatile resin.

It can also be argued that the current information relative to stoichiometry and structures of the products produced in these reactions may be accounted for by assuming that attack by the base produces a salt with the more acidic fragment and concurrently displaces a BH_3 group, which either reacts very rapidly with another base molecule or associates with another BH_3 to produce B_2H_6. Thus, a borane split occurs as a consequence of reaction with a base. An example of this type of mechanism is the vapor-phase reaction between dimethyl sulfide and pentaborane(9) that has been recently studied by Burg et al.[49] It was reported that no base as weak as $(CH_3)_2S$ could attack B_5H_9 by first removing BH_3, for the complex $(CH_3)_2S{\cdot}BH_3$ is extensively dissociated in the vapor state, as B_5H_9 itself is not. Therefore it was

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[57]G. W. Schaeffer, M. D. Adams, and F. J. Koenig, J. Am. Chem. Soc., 78, 725, (1956).

proposed that $(CH_3)_2S$ invades B_5H_9 to displace BH_3 and attach itself to the remaining $B_4H_6^-$ moiety, which then undergoes a condensation to resin.

It therefore seems reasonable that stronger bases which require similar temperatures for dismemberment of B_5H_9, also first seize B_4H_6 and displace BH_3, although the order of events is less obvious because the displaced BH_3 is irreversibly captured by these strong bases. The displacement sequence strongly suggest that $B_4H_6^-$ is a stronger Lewis acid than BH_3.

From the results obtained in the course of this work, it is possible that ammonia reacts with pentaborane(9) in a displacement fashion, expressed by the following equations.

$$NH_3 + B_5H_9 \longrightarrow NH_3 \cdot B_4H_6 + BH_3$$

$$NH_3 + BH_3 \longrightarrow (NH_2BH_2) + H_2$$

$$3(NH_2BH_2) \longrightarrow H_3B_3N_3H_3 + 3H_2$$

A full proof of such a mechanism would be very difficult, especially since the process occurs at elevated temperatures in the vapor phase, however, the following results are in agreement with the proposed mechanism.

1) The aminoborane compound, H_2NBH_2 is not known in monomeric form, but has long been thought to be highly associative and unstable. This would account for the absence of intermediate fragments among the reaction products.

2) The $NH_3 \cdot B_4H_6$ units account for the formation of non-volatile polymeric products observed in all reactions.

3) The experimental yield of borazine, 11% is in good agreement with the calculated value, 16% based upon the amount of B_5H_9 consumed. In terms of the suggested mechanism, it would appear that there is expelled one BH_3 unit per B_5H_9 molecule consumed. Each BH_3 unit is captured by ammonia molecules and condensed into the borazine ring system.

The effect of methylation upon B_5H_9 in its reaction with ammonia is evident from Table 22. In contrast to the unmethylated B_5H_9-ammonia reaction both 1-CH_3- and 2-$CH_3B_5H_8$ react with ammonia to give good yields of B-methylborazines ($(CH)_3H_2B_3N_3H_3$ and $(CH_3)_2BH_3N_3H_3$). Of special interest is the fact that both apical and basal isomer gave good yield of the B-methyl derivatives. This implies that the reaction proceeds through an intermediate in which all five boron positions are equal.

A similar observation has been reported by Onak et al.[58] in which he liberated B_5H_9 from its bis-trimethylamine adduct by diborane. When $^{10}B_2H_6$ was used in the reaction a considerable amount of ^{10}B was found to be incorporated in the recovered B_5H_9 as determined by mass spectroscopic analysis.

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[58] T. Onak, R. P. Drake, and I. W. Searcy, Chem. Ind., 7, 1865 (1964).

TABLE 22

Percent Reactants Recovered and Percent Yield of Products:

Reaction of B_5H_9 1-$CH_3B_5H_8$ and 2-$CH_3B_5H_8$ with NH_3

B_5H_9	1-CH_3-B_5H_8	2-CH_3 B_5H_8	H_3B_3 N_3H_3	$(CH_3)H_2B_3$-N_3H_3	$(CH_3)_2HB_3$-N_3H_3
50.0			11.7		
	78.8		23.1	31.6	13.6
		71.0	12.2	17.5	5.3

The relative basal to apical ^{11}B ratio in the ^{10}B enriched pentaborane was nearly identical to that of $^{n}B_5H_9$ as determined by ^{11}B NMR, implying equilibration of all five boron atoms.

This equilibration of all five boron atoms can be explained by the formation of a trigonal bipyramidal transition state as proposed by Lipscomb, et al.[59] The existence of this intermediate was proposed in order to explain the results of the base-catalyzed rearrangement of 1,2- to 2,3-dimethylpentaborane. Only the cis product, $2,3(CH_3)_2B_5H_7$ was obtained from the arrangement, not a mixture of cis and trans isomers as might be expected. Absence of the 2,4 isomer was attributed to H(Methyl)----H(bridge) repulsions in the proposed trigonal bypyramidal intermediate.

The structural and to some extent the mechanistic implications of this intermediate species may also apply in the present work. The formation of this intermediate preceding fragmentation of the pentaborane cage system would account for the results obtained in the reaction of $1\text{-}CH_3$- and $2\text{-}CH_3B_5H_8$ with ammonia..

The proposed mechanism then is as follows; the interaction of ammonia with the methylated isomer of a trigonal bipyramidal transition state followed by the symmetrical cleavage of a BH_3, or BH_2CH_3 unit by ammonia, and finally

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[59]T. Onak, L. Friedman, J. Hartsuck and W. L. Lipscomb, J. Am. Chem. Soc., 88, 3439, (1966).

condensation of several of these fragments into the borazine ring system.

It is unlikely that 1-alkylpentaborane(9) simply isomerized to 2-alkylpentaborane in the presence of the Lewis base, ammonia, and then reacted with the base to give similar results to those obtained in the 2-alkylpentaborane(9)-ammonia reaction. First vacuum fractionation of products of the reaction of 1-$CH_3B_5H_8$ with ammonia at various reaction temperatures, (-78^o to 100^o) failed to yield but trace amounts of 2-$CH_3B_5H_8$. It has been demonstrated that the borane-amine reactions are reversible and that the reactants can be recovered by vacuum fractionation; therefore, it would be expected that considerable quantity of 2-$CH_3B_5H_8$ would be recovered from the reaction products if complete isomerization occurs before cleavage.

Finally, small quantities of 1-$CH_3B_5H_8$ were recovered from each of the reactions of 2-$CH_3B_5H_8$ with ammonia. This result strongly indicates that the 1-CH_3- to 2-$CH_3B_5H_8$ isomerization is not a nonreversible process, but perhaps is best illustrated as an equilibrium involving an intermediate transition state.

The mechanisms by which amines react with pentaborane(9) are exceedingly complex in nature. It has not been the author's intention in the course of this work to prove conclusively that the proposed mechanisms are indeed the actual ones, but rather to propose the best plausible

mechanisms that can fit the experimental results. Therefore, this work represents a new approach which could have meaningful implication for continuing research in the field of boron-nitrogen chemistry.

APPENDIX

List of Chemicals

Pentaborane(9):	Callery; purified by gas chromatography
Ammonia:	fractionated through -63° and -95° trap
Monomethylamine:	Matheson; fractionated through -23° and -95° trap
Aluminum Chloride:	Baker; purified by sublimation
Methylchloride:	Matheson; fractionated through a -80° trap
1-Methylpentaborane:	prepared using previously reported procedures[9]
2-Methylpentaborane:	prepared using previously reported procedures[9]
Helium:	Temerson; purified by passage through a -196° trap