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BADANIE BOROPOCHODNYCH 3,3′-DWUAMINODWUPROPYLAMINY I ZWIĄZKÓW POKREWNYCH

Komorowski Ludwik

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mgr Ludwik Komorowski

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Ludwik Komorowski

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Promotor: Prof. Dr Kurt Niedenzu
Uniwersytet Kentucky
Lexington, Kentucky, USA

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A STUDY ON BORON DERIVATIVES OF 3,3′-DIAMINODIPROPYLAMINE AND SOME RELATED SPECIES

THESIS

by

Ludwik Komorowski

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Professor of Chemistry
at The University of Kentucky
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1978

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PREFACE

The chemistry of boron-nitrogen-carbon heterocycles has attained considerable attention within the last two decades. The saturated ring systems are nowadays readily available by transamination of various aminoboranes with appropriate aliphatic amines and 3,3'-diaminodipropylamine is a suitable reactant leading to the formation of 1,8,10,9-triazaboradecalin.

The major preparative goal of this work was to perform a detailed study of the interaction of 3,3'-diaminodipropylamine with various boron derivatives in order to elucidate the factors governing the cyclization process and to establish whether or not chain-like species may also result from such reactions. Furthermore, physicochemical properties of the resultant products were to be investigated in order to gain a better understanding of the intermolecular interactions and the structure of products, and to correlate spectral data of chemically related molecules.

AN INTRODUCTION INTO SOME ASPECTS OF BORON-NITROGEN-CARBON HETEROCYCLES

2.1 Historical Aspects

Since 1955 several preparative routes have been reported in the literature that lead to saturated sigma-bonded boron-nitrogen-carbon heterocycles. In contrast to the borazaromatics, such systems do not contain any formal multiple bonds (ref. 1).

Heterocyclic systems containing one annular boron incorporated between two nitrogen atoms that are, in turn, linked by an alkyl chain are known as 1,3,2-diazaboracycloalkanes ; such analogs of cyclopentane, cyclohexane, and cycloheptane are known. On the basis of an examination of molecular models it has been suggested that 8- and 9-membered heterocycles of this type do not exist (ref. 2), whereas the analogs of cyclodecane and higher cycloalkanes can be built without noticeable ring strain. Also, decalin has a boron-nitrogen-carbon analog, i.e., 1,8,10,9-triazaboradecalin, a compound that has been most extensively studied (refs. 2, 3). The first compound of this group of B-N-C heterocycles ever obtained, 2-methyl-1,3,2-diazaboracyclopentane was prepared by Goubeau and Zappel (ref. 4), but species of this type received little attention until the middle sixties, when a convenient method for their syntheses was developed by Niedenzu and coworkers (ref. 5). A wide variety of 1,3,2-diazaboracycloalkanes have since become available. Considerable effort has been devoted to study the B-N bond character of the species. Initially this was done by IR spectroscopy utilizing ν_{BN} stretching frequencies as a rough measure of the bond order (ref. 2). The subsequent decade brought a rapid development of nuclear magnetic resonance techniques for various nuclei and boron-11 NMR chemical shift data of many representatives of the 1,3,2-diazaboracycloalkanes have since been reported (refs. 6, 7) and provided additional informations on bond orders. Most recently, carbon-13 and nitrogen-14 NMR data are being collected for that same purpose (refs. 8, 9). The constantly growing number of experimental data should permit some correlation and, hence, some generalization concerning the molecular properties.

1,3,2-Diazaboracycloalkanes are structurally related to aminoboranes as well as to borazines ; this is reflected by a variety of their physical properties (ref. 10). The hydrolitic instability of 1,3,2-diazaboracycloalkanes - that, in fact, is typical for the great majority of boron-nitrogen compounds - has so far impaired their practical applications. Recent findings show, however, an increased stability upon nitrogen alkylation (ref. 11), that may perhaps stimulate future research in this area. The boron analogs of purine systems, i.e., 8-borapurine and others, are structurally related to 1,3,2-diazaboracycloalkanes but are - in contrast to the latter - hydrolitically quite stable, and have recently been tested as antimetabolites in cancer therapy (refs. 12, 13, 14, 15).

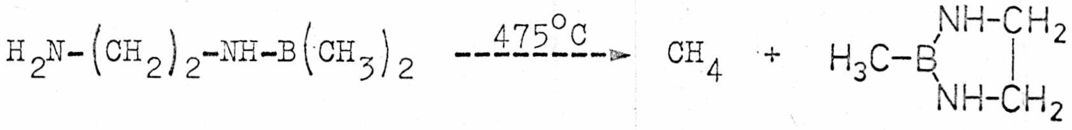
2.2 1,3,2-Diazaboracycloalkanes

Preparative procedures that are commonly used for the synthesis of 1,3,2-diazaboracycloalkanes involve aliphatic α,ω-diamines as starting materials, that are reacted with either trimethylborane (ref. 4), bisaminoboranes (ref. 11), or haloboranes (refs. 16, 17). The first synthesis by Goubeau and Zappel (ref. 4) involved the condensation of trimethylborane with ethylenediamine according to the scheme as depicted in Equation 1.

$$B(CH_3)_3 + H_2N-(CH_2)_2-NH_2 \xrightarrow{\text{room temp.}} H_2N-(CH_2)_2-NH_2 \cdot B(CH_3)_3$$

Compound 1

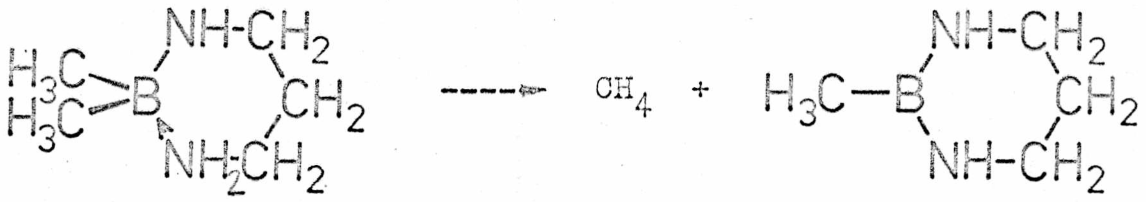
$$\text{Compound 1} \xrightarrow{250^\circ C} H_2N-(CH_2)_2-NH-B(CH_3)_2 + CH_4$$



Compound 2

Equation 1

Pyrolitic decomposition was necessary in order to obtain the final product from the intermediate amine-borane type adduct, Compound 1. When 1,3-diaminopropane was employed, the initially formed intermediate had a cyclic structure, Compound 3, and decomposed at 350°C to give 2-methyl-1,3,2-diazaboracyclohexane, Equation 2.

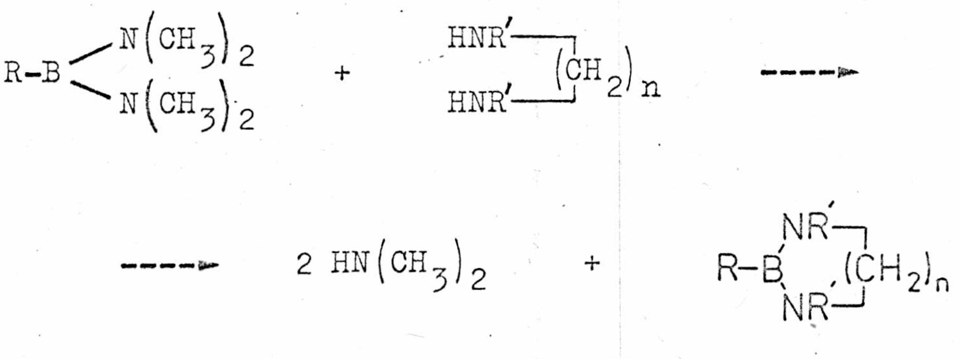


Compound 3

Equation 2

The use of pyrolysis processes to yield the heterocyclic B-N-C systems is only of historical value, since more efficient methods of synthesis have been developed. However, this principal reaction contributed to the elucidation of the mechanism of cyclization by evidencing the amine-borane type intermediates, e.g., Compounds 1 and 3.

The transamination of α,ω-diamines with bisaminoboranes has become the most convenient route for the synthesis of 1,3,2-diazaboracycloalkanes ; it proceeds under mild conditions and with high yields (refs. 3, 5). The general scheme is illustrated by Equation 3 :

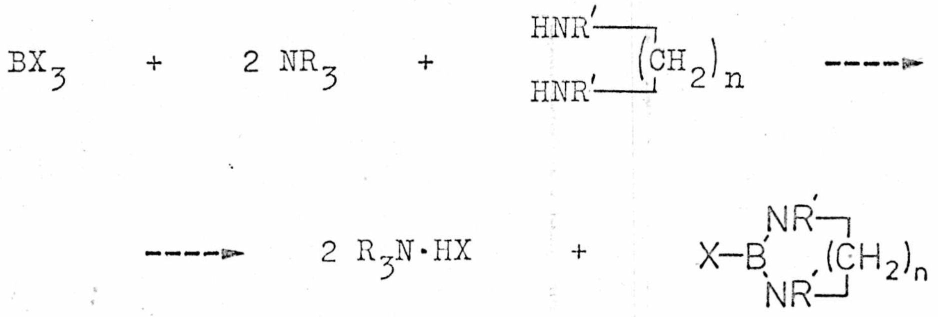


Compound 4

Equation 3

Intermediates of the process have not been isolated, but they are expected to be similar to Compound 3.

Another synthetic route employs the reaction illustrated by Equation 4, where X = halogen.



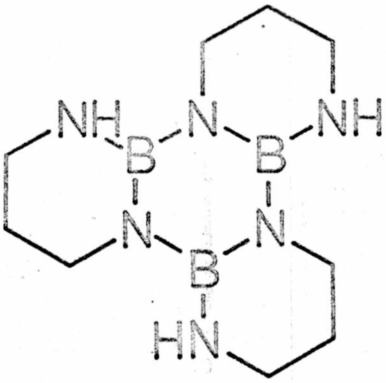
Equation 4

This latter reaction is a dehydrohalogenation process (ref. 16) ; it was used primarily in the synthesis of B-halogen substituted heterocycles. Analogous processes may occur in a pyrolytic dehydrohalogenation, provided that dihaloboranes are used (ref. 17).

This listing of methods does not exhaust all possible reactions leading to 1,3,2-diazaboracycloalkanes ; other processes, however, have not been developed as a general preperative method, <u>e.g.</u>, the replacement of silicon by boron within a heterocycle (ref. 18).

Among the 1,3,2-diazaboracycloalkanes, derivatives are known that are either symmetrically or unsymmetrically substituted at the nitrogen sites. By using appropriate amines, it is also possible to obtain derivatives that are substituted at annular carbon atoms (ref. 1).

The known nitrogen substituents are alkyl or aryl groups or hydrogen. A wider spectrum of boron substituents can be found : alkyl, aryl, halogen, alkyloxy and alkylthio groups, dialkylamino groups, and various others. The dimethylamino substituent is most noteworthy since it exhibits a pronounced tendency to promote intermolecular condensation of three molecules, unless the annular nitrogen atoms are protected by organic substituents (ref. 2). For example, the condensation of three molecules of 2-dimethylamino-1,3,2-diazaboracyclohexane yields a symmetrically substituted borazine, Compound 5.



Compound 5

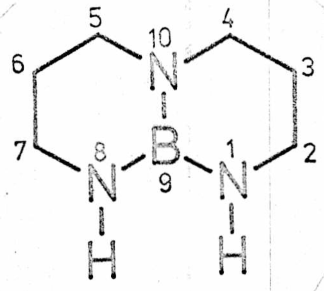
The chemistry of 1,3,2-diazaboracycloalkanes has not been explored as well as their syntheses. However, under aprotic conditions the ring does not cleave and substituents on the boron may be interchanged, *e.g.*, halogen may be replaced by an alkyl group *via* reaction with a Grignard reagent (ref. 1). The dehydrogenation at endocyclic carbon sites has also been possible (ref. 19) and leads to an unsaturated ring system which, for n=2, is isoelectronic with the cyclopentadienide anion. The B-N bond does not resist, however, the action of protic reagents such as hydrogen chloride, alkohols or water (ref. 1).

The molecular structure of 1,3,2-diazaboracyclopentanes and -hexanes is reasonably well established ; it has been studied in details by electron diffraction (refs. 20, 21) and, most extensively, by proton NMR spectroscopy (ref. 22). The annular CNBNC grouping forms a planar moiety and the five-membered ring system is completely coplanar. In 1,3,2-diazaboracyclohexanes, the central annular carbon atom is slightly out-of-plane, and in the seven-membered system supposedly two carbon atoms must be out-of-plane ; NMR data conform with these assumptions. The coplanarity of the annular CNBNC moiety supports the particular character of the B-N bond within the ring. Early work by IR spectroscopy already suggested a rather high B-N bond order (refs. 23, 24), based on force constants data of the bond. However, more detailed analyses of the nature of the B-N bond in the heterocycles under consideration here have not yet been performed.

2.3 The Synthesis and Properties of 1,8,10,9-Triazaboradecalin

1,8,10,9-Triazaboradecalin, Compound 6, was the first polycyclic 1,3,2-diazaboracycloalkane ever synthesized (refs. 2, 3). Utilizing a standard procedure to form boron-nitrogen compounds, *i.e.*, by a transamination reaction, 3,3′-diaminodipropylamine was reacted with tris(dimethylamino)borane in 1:1 molar ratio. The reaction was conducted in benzene solution and yielded the colorless, crystalline solid, m.p. 38 - 41°C, that is readily distilled under reduced pressure. The overall reaction is shown in Equation 5.

$$B\left[N(CH_3)_2\right]_3 \quad + \quad HN\left[(CH_2)_3NH_2\right]_2 \quad \dashrightarrow \quad 3\ (CH_3)_2NH \quad +$$

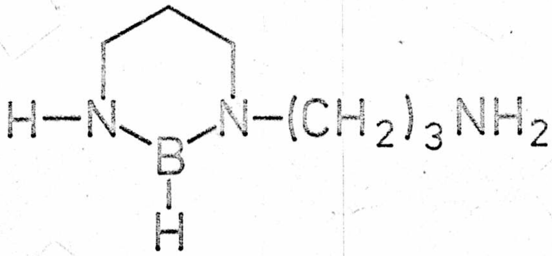


Compound 6

Equation 5

An alternate preparation to obtain Compound 6 involves the reaction of 3,3′-diaminodipropylamine with BH_3, which is generated *in situ* from $NaBH_4$ in THF solution (refs. 25, 26); the overall processes are illustrated in Equations 6 and 7.

$$NaBH_4 + I_2 + HN\left[(CH_2)_3NH_2\right]_2 \dashrightarrow HI + H_2 + NaI +$$



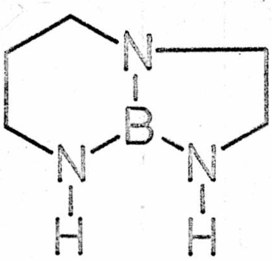
Compound 7

Equation 6

$$\text{Compound 7} \xrightarrow{150^{\circ}C} \text{Compound 6} + H_2$$

Equation 7

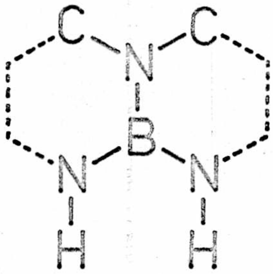
An analogous reaction was described for 3-aminopropyl-2-aminoethyl-amine (ref. 27), which yielded Compound 8.



Compound 8

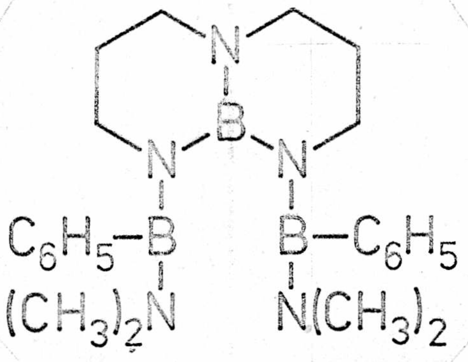
The intermediate - corresponding to the Compound 7 - was found to be the six-membered heterocycle with the shorter aminoalkyl side chain (ref. 27). The system with both rings being five-membered, i.e., 1,6,8,7-triazaboracyclooctane, has not yet been synthesized. Presumably, steric factors are playing an important role in the cyclization process and the six-membered ring appears to be the most favorable arrangement.

The molecular structure of Compound 6 and its spectroscopic properties were studied in considerable detail in order to elucidate the character of the B-N bond, which is supposedly similar to that in borazines, $(-BR-NR-)_3$. X-Ray diffraction studies on the crystalline material provided a picture of the atomic arrangement in the molecule (refs. 28, 29), which is not paralleling that of decalin but rather resembles the naphthalene molecule. The arrangement



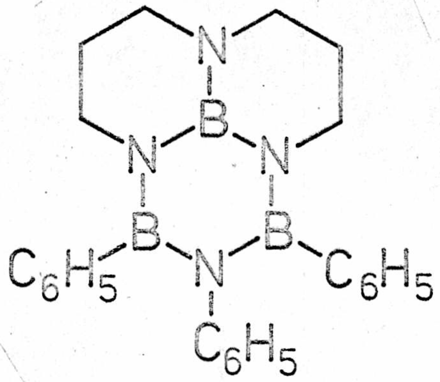
was found to be coplanar, whereas the remaining carbon atoms are out-of-plane by -0.47 Å and +0.20 Å. This is in contrast to the 1,3,2-diazaboracyclohexanes, where only one endocyclic carbon was found to be out of the ring plane ; see section 2.2. The symmetry of Compound 6 is C_{1V} with bond lengths d_{BN}= 1.424 Å, whereas for borazine d_{BN} is 1.44 Å (ref. 10). The boron atom is found to be in almost exactly trigonal environment and sp^2-hybridization may be assumed. A thorough discussion of the vibrational spectrum of 1,8,10,9-triazaboradecalin resulted in a value of 1510 cm^{-1} for the antisymmetrical B-N stretching frequency. This assignment is substantially higher than in acyclic trisaminoboranes. For $B(NHCH_3)_3$ - with a similar planar arrangement of the BN_3 moiety - ν_{as}BN is observed at 1440 cm^{-1} (ref. 30). In $B[N(CH_3)_2]_3$, the BN_3 unit is also coplanar but the NC_2 groups are twisted ; therefore the overlap of p_z-orbitals is smaller and the B-N bond order is expected to be smaller for this latter compound. Consequently, the absorption at 1380 cm^{-1} was assigned to the antisymmetric B-N stretching mode. The borazines exhibit B-N stretching frequencies in the range of about 1430 to 1530 cm^{-1} (ref. 31). These data suggest a relatively high bond order for the B-N bond in Compound 6, since the ν_{as}BN value has been recognized as a convenient guideline to estimate the B-N bond order in aminoboranes. The empirical Gordy's rule (refs. 32, 33) was applied for a comparison of the formal bond orders in Compound 6 and borazine ; this event led to the conclusion that the B-N bond order in Compound 6 is about 8% greater than in borazine, $(-BH-NH-)_3$.

The chemistry of 1,8,10,9-triazaboradecalin has been studied with the specific goal of building condensed heterocyclic B-N systems <u>via</u> substitution of the N-bonded hydrogens. The nitrogen sites can be lithiated (ref. 34) and subsequent reaction, with (dimethylamino)phenylchloroborane provides Compound 9.



Compound 9

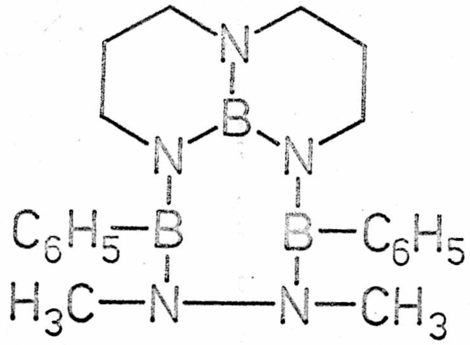
This latter compound shows an unusual close packing of substituents on the N^1 and N^8 sites in an overcrowded situation. Compound 9 also readily reacts with aniline to yield Compound 10.



Compound 10

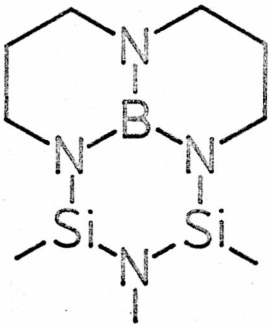
This latter species can be viewed as an unsymmetrically substituted borazine.

Another novel boron-nitrogen heterocycle is produced in a transamination reaction of Compound 9 with symmetrical dimethylhydrazine to yield Compound 11, which contains an unusual seven-membered B-N ring system.

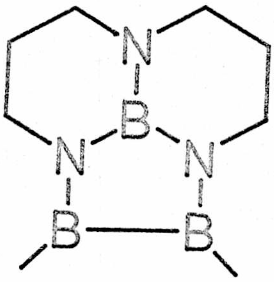


Compound 11

There are several more examples of heterocyclic systems that were built utilizing 1,8,10,9-triazaboradecalin as a starting material, e.g.:



(ref. 35)



(ref. 36)

Compound 6 seems to be suitable for a large variety of syntheses of additional heterocyclic systems that are fused onto its planar and rigid boron-nitrogen skeleton, where actually the hydrogen atoms in the 1 and 8 positions are the only ready reactive sites of the molecule. However, the most symmetrical trigonal boron compound of this type, <u>i.e.</u>,

has not yet been prepared.

Cleavage of the B-N bonds of 1,8,10,9-triazaboradecalin hardly occurs and few reactions occuring with ring opening have been reported, although addition of isocyanates or isothiocyanates leads to the formation of an unusual eight-membered ring. Hydrolytically Compound 6 is rather unstable, as is to be expected for molecules of this particular type.

3

NUCLEAR MAGNETIC RESONANCE STUDIES ON 1,3,2-DIAZABORACYCLOALKANES AND RELATED COMPOUNDS

3.1 Introduction

Nuclear magnetic resonace studies have been recognized very early as a valuable tool in the undertaking of structural studies of boron compounds. In fact, a considerable part of Lipscomb's fundamental work on boron hydrides was accomplished by means of NMR techniques (ref. 37). These have been further developed ever since and all nuclei that are components of the boron compounds under consideration here have nowadays become accessible to resonance investigations of high accuracy, TABLE 1.

There is a considerable number of boron-11 NMR data scattered throughout the literature for the various classes of boron compounds, but studies of nitrogen-14 and carbon-13 NMR spectra of organoboron derivatives are considerably less abundant. Due to experimental difficulties, there exist only few reliable data on coupling constants between boron and nuclei other than proton. One of the objectives of the present work is aimed to obtain detailed insight into the electronic structure of a molecule, e.g., electron densities and bond orders, but also to detect possible correlations between chemical shift data of various nuclei. This latter objective appears to be a tempting and ambitious task that - if achieved - would tend to assist in

TABLE 1

SELECTED MAGNETIC PROPERTIES OF NUCLEI FREQUENTLY EMPLOYED IN NMR STUDIES IN BORON CHEMISTRY

Nucleus	Natural abundance %	Spin	Magnetic moment [Bohr magnetons]	Electric quadrupole moment $[10^{-24} e\ cm^2]$	Commonly employed NMR frequency [MHz]	Chemical shift range [ppm]	Commonly used standard
^1H	99.98	1/2	2.79	-	60	10	$Si(CH_3)_4$
^{11}B	80.4	3/2	2.69	0.04	32.9	150	$B(OCH_3)_3$; $(C_2H_5)_2O\cdot BF_3$
^{13}C	1.11	1/2	0.70	-	20	200	$Si(CH_3)_4$; CS_2
^{14}N	99.68	1	0.40	0.70	7.226	1000	NO_3^-

the ready structural elucidation of new compounds.

3.2 General Remarks on the Nuclear Shielding in Organoboron Compounds.

The general theory of nuclear resonance as elaborated by Ramsay (ref. 38) formulates the nuclear shielding constants σ as a sum of diamagnetic and paramagnetic contributions

$$\sigma = \sigma^{d} + \sigma^{p} ,$$

the chemical shift being a difference of the shielding constants of the given nucleus and of the reference. σ^{d} is dependent on the eigenfunction of the ground state of the molecule only ; σ^{p}, in contrast, is contributed to by the eigenfunctions of all excited states as well as their relative energies. In order to utilize the theory, several approximate approaches have been proposed that aim to interpret the terms σ^{d} and σ^{p}. The most noted approach is that of Karplus and Pople (ref. 39), who used a concept of average excitation energy and developed the following relationship for aromatic systems :

$$\sigma_{A} = \sigma^{d}_{AA} + \sigma^{p}_{AA} + \sum_{B \neq A} \sigma_{AB} + \sigma_{A,ring}$$

σ^{d}_{AA} and σ^{p}_{AA} are local dia- and paramagnetic contributions, σ_{AB} denotes the contributions from other atoms, and $\sigma_{A,ring}$ is an additional increment for the ring system.

Formulas to calculete each particular contribution were derived but only qualitative results were anticipated by the authors. It was suggested that for a series of chemically related compounds the last two terms may be omitted and from the remaining two terms σ^{d}_{AA} and σ^{p}_{AA}, only the paramagnetic term changes appreciably, the diamagnetic remaining roughly constant. Moreover, a linear dependence of σ^{p}_{AA} on the π-charge density was predicted. A test of this approximation came firstly from Bloor and Breen (refs. 40, 41) for carbon-13 chemical shifts. A rough linear dependence of experimental $\delta^{13}C$ values on calculated π-electron densities was found, the correlation being even more exact when total charge densities were employed. Similarily, σ^{p} and σ^{d} were calculated for a variety of nitrogen compounds and were found to change within the range of 1000 ppm and 200 ppm, respectively (ref. 42). An approximate linear relationship between the chemical shift data and electron densities was then reported for a great number of compounds, <u>e.g.</u>,

$\delta^{14}N$ in borazines	(ref. 43)
in azoles	(ref. 44)
$\delta^{11}B$ in substituted boranes	(refs. 45, 46, 47)
$\delta^{35}Cl$ in chloroboranes	(ref. 48)

A different phenomenological approach to evaluate chemical shift data was forwarded by Good and Ritter (ref. 46), who assumed that σ-and π-electrons contribute separately to the chemical shift :

$$\delta = \delta_{\sigma} + \delta_{\pi}$$

By comparing $\delta^{11}B$ of purely σ-bonded trimethylborane with $\delta^{11}B$ of vinylboranes (where some π-contribution to the B-C bond is expected) they calculated standard additive σ- and π-contributions for methyl, vinyl, and halogen substituents to the boron chemical shift. This approach resulted in negative $\delta_{\sigma}{}^{11}B$ values that increas in the order

$$CH_3 < C_2H_3 = C_6H_5 < Br < Cl < F$$

which corresponds to increasing electron donation from the boron (- deshielding). π-Contributions were found to be positive, since boron acts as π-acceptor with these sustituents. Moreover, a reasonable linear relationship of δ_{π}- and π-charge density was demonstrated. Although the authors were cautious in extending the approach to other compounds than the ones discussed, the method was widely accepted (refs. 45, 49, 50, 51, 52).

Nöth and Vahrenkamp (ref. 52) reviewed boron-11 chemical shift data of more than one hundred boron compounds and found it possible to divide the $\delta^{11}B$ into following contributions

$$\delta = \delta_{\sigma} + \delta_{\pi} + \delta_{N} ,$$

where the new term δ_N denotes contributions from neighbors. The importance of δ_N term was further established by Jameson and Gutowsky (ref. 53) and a linear relationship of δ_{σ} and the alectronegativity En of the atom directly bonded to the boron was also illustrated :

$$\delta_{\sigma} = A - B \cdot En$$

A and B are positive constants, depending solely on the coordination number of the boron atom. When there are two or more different substituents bonded to the same boron atom, each substituent was attributed its own $\delta_{\sigma}(En)$ contribution. δ_{π}-Values were found to be proportional to the bond order between a specific substituent and the boron atom. The influence of the electronegativity of the substituent on the chemical shift of the atom to which it is bonded was first analysed in detail for simple organic compounds. The electronegativity of the atom bonded to a carbon atom has been shown to cause a proportional change in the proton chemical shift of hydrogen atoms bonded to the same carbon (ref. 54). An excellent linearity was demonstrated by Dailey and Shoolery (ref. 55) for the dependency

$$\Delta = \delta^{1}H_{CH_3} - \delta^{1}H_{CH_2}$$

in CH_3CH_2X on the electronegativity of X ; a specific NMR electronegativity scale was proposed on the basis of this work.

Similar studies on boron derivatives has led to evaluate the electron distribution around boron in relation to various ligands (refs. 56, 57). Nöth and

Vahrenkamp (ref. 56) studied the electronegativity of the boron by the method of Dailey and Shoolery and found it to be changing by as much as 0.7 units upon the change of substituents on the boron. Values larger than 2.5 (in trialkylboranes) and smaller than 1.9 (in tetracoordinated boron derivatives) were found, whereas the electronegativity value of boron is 2.0 on Pauling's scale and 2.01 on the Mulliken's scale. Three factors were proposed to account for this behavior :

1. The inductive effect ; the power to withdraw electrons from the boron increases with the electronegativity of a substituent and, hence, decreases within groups in the periodic table.

2. π-Back bonding effect (resonance effect) ; substituents capable to form a dative π-bond with the boron cause additional shielding of the boron by π-electron donation.

3. Neighbor magnetic anisotropy effect ; the magnetic interaction of free electron pairs of the substituents atom cause additional shielding of the atom directly bonded (α-atom) and deshielding of the next atom within the chain (β-atom). The effect insreases in periods along with the electronegativity and also increases within groups of the periodic table along with an increase of the principal quantum number of the free electron pair. Therefore, the effect is negligible for the elements of the second period ; it is strongest for iodine.

Besides the forementioned, two additional features of great importance are claimed to influence the chemical shift of the central boron atom, e.g., its hybridization state as well as steric factors that may impair the overlap of boron p_z-orbitals with others and therefore may cause a decrease of the resonance interaction (refs. 52, 56, 59).

In a survey of the various analyses of the chemical shifts, the work by Dewar et al. (ref. 60) should also be mentioned. They proposed a formula for the chemical shift value

$$\delta_i = Aq_i + \sum_{j \neq i} Bq_j / r_{ij}^3$$

where q_i - π-charge at the atom "i"

q_j - total net charge at the atom "j"

r_{ij} - interatomic distance

This formula properly accounts for the effect of an unshared electron pair of the atom adjacent to the boron.

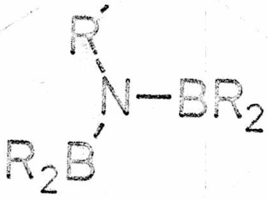
There are also examples of purely phenomenological analyses of the chemical shifts (refs. 61, 62). Some additive increments have been introduced to reproduce the carbon-13 chemical shifts data in hydrocarbons. Specific increments for carbons in any position within a chain (α-, β-, γ-atoms) as well as contributions for branched systems, double bonds etc. were proposed. Although this treatment provides an excellent agreement of calculated values with the experimental data, it is arrived at by statistical methods and does not involve any model of intramolecular interactions.

In the NMR studies of the boron-nitrogen compounds a considerable effort is placed on discovering possible correlations of the boron-11 chemical shift data with that of other nuclei, e.g., nitrogen-14 and carbon-13, and correlations involving proton chemical shift data have also been described (usually involving proton bonded to the atom next to the boron). One method directly relates δ^1H to the electronegativity of a second substituent on the boron (ref. 63). A less pronounced influence on the Hammett's (or Taft's) constant of the second substituent was also proposed (ref. 64), yet its validity remains questionable (ref. 65).

Establishment of $\delta^{13}C$ - $\delta^{11}B$ correlations has been impaired by the difficulty in the direct observation of the chemical shift of a boron-bonded carbon atom. Nöth and coworkers obtained $\delta^{13}C$ values and $\delta^{13}C$ - $\delta^{11}B$ coupling constants in methylaminoboranes by double resonance methods (ref. 66), and found $\delta^{13}C$ to be proportional to $\delta^{11}B$; however, since they did not isolate σ and π shares in δ, the meaning of such a correlation is still questionable (ref.67).

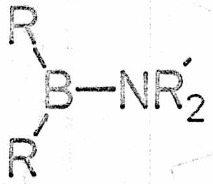
Data for $\delta^{14}N$ and $\delta^{11}B$ correlations are more abundant ; most of them were suggested by Nöth and coworkers, too (refs. 51, 68). For two series of boron-nitrogen compounds an upfield shift of $\delta^{14}N$ in the sequence A to D (see next page) is accompanied with an upfield shift in $\delta^{11}B$, although it is not necessarily a linear relationship as shown in Figure 1.

A



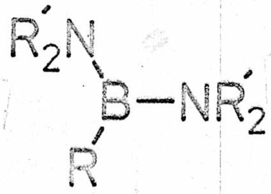
Bis(dialkylboryl)alkylamine

B



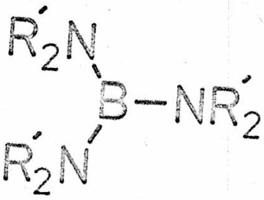
(dialkylamino)Dialkylborane

C



Bis(dialkylamino)alkylborane

D



Tris(dialkylamino)borane

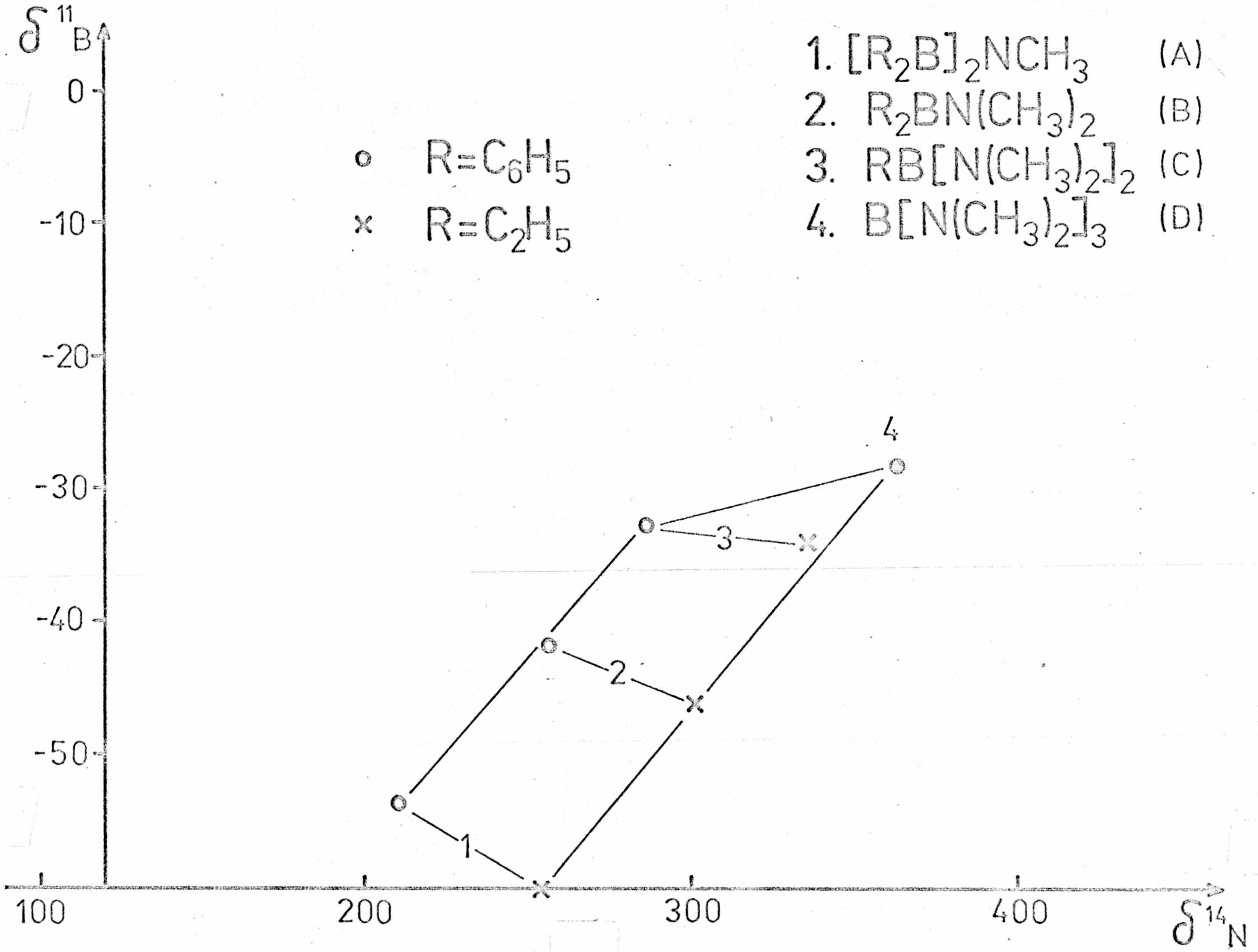


Figure 1

δ^{11}B *versus* δ^{14}N Plot for the Series of (dimethylamino)Alkylboranes

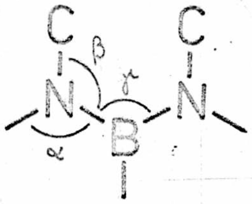
That behavior reflects a simple fact that the shielding of both nuclei originates primarily from free electron pairs of nitrogen. On the other hand, the variation of a boron substituents in bisaminoboranes and monoaminoboranes does not result in a meaningful variation for $\delta^{11}B$ and $\delta^{14}N$ that could be attributed to the electronegativity of the substituent (ref. 68). In a study on amine-boranes deshielding effects of alkyl groups were investigated (ref. 69). Also, boron-11 chemical shifts in aminoboranes were compared to carbon-13 chemical shifts in alkenes (ref. 70),amine-boranes were plotted against alkanes (ref. 71), and boranes against carbonium ions (ref. 71). The chemical shifts of both cited nuclei are closely parallel for all these isoelectronic and isosteric systems. Spielvogel and Purser (ref. 72) proposed a rationalization for the slope of the resulting straight line of the linear relationship, which they viewed as the ratio of the nuclear shielding constants for both nuclei.

To complete the survey, coupling constants of boron-11 with nuclei other than proton should be mentioned. The available data are very limited (refs. 7, 8, 66, 73, 74, 75) and have not yet been subject of a thorough analysis ; no general conclusion can be found in the literature except for a justification of neglecting spin-spin and spin-dipolar interaction and that only Fermi contact shift is effective (ref. 76). On the other hand, the value of a coupling constant J_{AB} is proportional to the density of sigma-electrons in the site of both nuclei A and B ;

therefore, its knowledge may aid to estimate the σ-bond character in the bond.

3.3 Boron-11 and Nitrogen-14 Chemical Shifts in 1,3,2-Diazaboracycloalkanes

The annular boron, two nitrogen and two carbon atoms form a planar entity in 1,3,2-diazaboracycloalkanes, that is independent of the ring size :



The bond angles within this skeleton depend on the ring size as is evidenced by the structural data compiled in TABLE 2.

TABLE 2

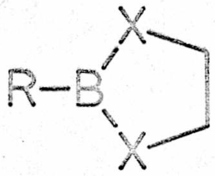
BOND ANGLE DATA FOR 1,3,2-DIAZABORACYCLOALKANES

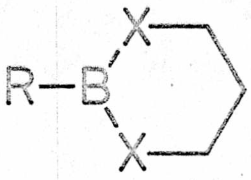
Angle	$ClB(-NCH_3-CH_2-)_2$ (ref. 20)	$ClB(-NCH_3-CH_2-)_2CH_2$ (ref. 21)
α	128.0	124.1
β	108.6	121.6
γ	110.8	120.8

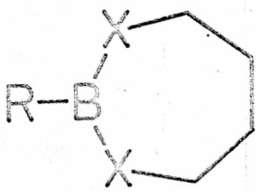
There are no structural data for 1,3,2-diazaboracycloheptanes available. Simple consideration of molecular models indicates, however, that the environment of the nitrogen might be slightly distorted from planarity toward the sp^3 configuration.

Two features seem to be of primary importance in a consideration of mutual boron-nitrogen interaction in 1,3,2-diazaboracycloalkanes, i.e., firstly the influence of the ring size, and secondly substituent effects, since there are three principal sites of substitution in the molecules.

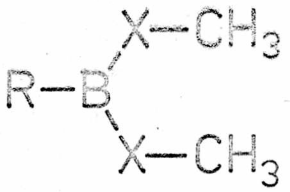
The boron-11 and nitrogen-14 chemical shifts data of selected 1,3,2-diazaboracycloalkanes and some related systems are collected in the TABLE 3. The aim of this compilation is to compare compounds within the following set :

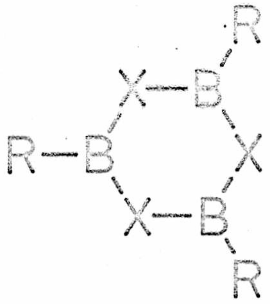






and to correlate them with the following species, which serve as reference compounds :





X = NR , O, S.

A comparison of boron-11 chemical shift data within one ring type has not been pursued here, since they will depend on electronegativity of the B-substituents (ref. 14) and, to a lesser degree, on the N-substituents (ref. 6). In order to obtain a usuful comparison, a Δ value with respect to the reference is introduced. This procedure is likely to involve primarily steric factors, since the chemical environment in both 1,3,2-diazaboracycloalkanes and related bisaminoboranes is virtually identical. TABLE 3 contains only these heterocycles for which data of at least one reference material are available ; hence, the five-membered ring system is reasonably well represented whereas the data for seven-membered rings are rather limited. The collected data are not completely satisfying ; <u>e.g.</u>, they originated from various laboratories and spectra were recorded under various conditions and with different instruments. Therefore, discrepancies of less than 1 ppm should not be viewed as significant.

TABLE 3

BORON-11 AND NITROGEN-14 CHEMICAL SHIFTS OF 1,3,2-DIAZABORACYCLOALKANES AND RELATED SYSTEMS

1	2	3	4	5	6	7	8	9	10	11
R	X	$\delta^{11}B$	$\delta^{14}N$	ref.[a]	Δ_1B	Δ_1N	ref.[b]	Δ_2B	Δ_2N	ref.[c]
1,3,2-Diazaboracyclopentanes										
C_6H_5	NCH_3	-32.2		19	0.3		51			
		-31.1		7	1.4		51			
C_6H_5	NC_2H_5	-31.5		7	2.6^{d}		51			
CH_3	NCH_3	-32.4	313	9	1.1	-23	51	3.4	38	43
		-31.6		6	1.9		51	4.2		43
$N(CH_3)_2$	NCH_3	-26.5	326 361^{e}	9	0.8	-39 -5^{e}	51	2.3		43
		-26.1		6	1.2		51	2.7		43
OCH_3	NCH_3	-24.1	326	9	1.0		52			

TABLE 3 (continued)

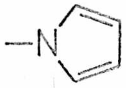
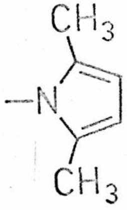
1	2	3	4	5	6	7	8	9	10	11
SCH_3	NCH_3	-31.2	322	9				6.1	44	43
$C\equiv C-CH_3$	NCH_3	-24.9	310	96	-1.1	-13	96			
I	NCH_3	-21.3		6	3.7		52			
Br	NCH_3	-26.0		6	1.6		52	2.7		43
Cl	NCH_3	-27.0		6	0.9		52	4.2		52
H	NCH_3	-28.3		6	0.3		52	3.3		43
	NCH_3	-26.4	335	9	0	5	9			
	NCH_3	-27.6	314 218^e	9	-0.9	-6 13^e	9			

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11
C_6H_5	O	-31.2	-	78	-1.0	-	7	-2.2	-	7
$N(CH_3)_2$	O	-24.7	346^e	9	-3.4	-	52	-3.7	10^e	9
C_6H_5	S	-66.0	-	7	-1.3	-	7		-	
$N(CH_3)_2$	S	-46.2	304^e	9		-		-7.8	9^e	9
1,3,2-Diazaboracyclohexanes										
H	NH	-28.7		3				0.4		43
		-21.8		3				7.3		43
CH_3	NH	-27.0		3	4.7		51	7.5		43
C_2H_5	NH	-30.1		3	2.1^f		51	5.4		43
C_6H_5	NH	-28.7		7	1.7		51	4.6		43
		-27.1		3	3.3		51	6.7		43
C_6H_5	NCH_3	-29.0		8	3.5		51			
		-29.5		78	3.0		51			
		-32.5		7	0		51			

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11
C_6H_5	NC_2H_5	-29.4		7	4.7[d]		51			
H	$N(CH_2)_3NH_2$[g]	-23.7		84	4.9[h]		52	7.9[i]		52
$N(CH_3)_2$	NCH_3	-25.2		6	2.1		52			
CH_3	NCH_3	-29.2		6	4.6		51	7.6		52
H	NCH_3	-26.0		6	2.6		52	5.6		43
C_6H_5	O	-27.0	-	7	3.2	-	7	2.0	-	7
		-27.8	-	78	2.4	-	7	1.2	-	7
C_6H_5	S	-58.7	-	7	6.0	-	7		-	
I	NCH_3	-21.4		6	3.6		52			
Br	NCH_3	-24.8		6	2.8		52	3.9		43
Cl	NCH_3	-25.1		6	2.8		52	6.1		52

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11
				1,3,2-Diazaboracycloheptanes						
C_6H_5	NCH_3	-32.5		7	0		51			
C_6H_5	NC_2H_5	-31.9		7	2.2[d]		51			
CH_3	NH	-29.9		3	1.8		51	4.6		43
n-C_4H_9	NH	-30.7		3	1.5		51	4.8[j]		43
C_6H_5	NH	-28.5		3	1.9		51	5.3		42

REMARKS TO TABLE 3

$\Delta_1 B = \delta^{11}B - \delta^{11}B$(standard bisaminoborane) see p. 30.

$\Delta_2 B = \delta^{11}B - \delta^{11}B$(standard borazine) see p. 30.

The definitions for $\Delta_1 N$ and $\Delta_2 N$ are analogous.

Notes : [a] Reference for chemical shifts data ;

[b] Reference for chemical shift of standard bisaminoborane ;

[c] Reference for chemical shift of standard borazine ;

[d] Relative to $C_6H_5B[N(C_2H_5)_2]_2$;

[e] Datum for the nitrogen atom within R ;

[f] Relative to $n\text{-}C_4H_9B(NHCH_3)_2$;

[g] Compound 7, unsymmetrically substituted ;

[h] Relative to $HB[N(CH_3)_2]_2$;

[i] Relative to $(\text{-}BH\text{-}NCH_3\text{-})_3$;

[j] Relative to $(\text{-}BC_2H_5\text{-}NH\text{-})_3$;

Some qualitative conclusions can be made on the basis of these data, the fundamental one being that the ring size contributions to the shielding of the boron nucleus are largely of steric nature ; the ring structure does not promote a specific aromatic type delocalization of electron density but the annular CNBNC moiety always is in planar conformation, which is most favorable for B-N interaction.

Findings :

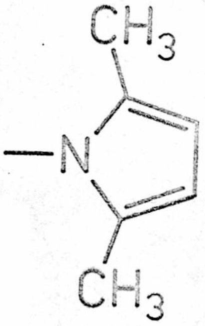
1. The boron-11 resonance signal of 1,3,2-diazaboracyclohexanes occurs usually at higher field than for any other species (relative to the standard bisaminoboranes), i.e., the shielding of the boron nucleus is most effective. This observation is readily understood, since there are no strains affecting the sp^2-hybridization on the B or N atoms and the overlap of their p_z-orbitals is best. The range of $\delta^{11}B$ is distinctly upfield from that of related borazines by about 6 ppm ; less effective shielding in the latter may be caused by the B:N ratio which is 1:1 in borazines but is 1:2 in 1,3,2-diazaboracycloalkanes.

2. The boron-11 NMR signals for 1,3,2-diazaboracyclopentanes are downfield from those of the analogous six-membered heterocycles by roughly 2 ppm. This observation can be accounted for by a change in the ring angles which disturbs planar sp^2-hybridization and thus somewhat reduces the B-N interaction. The exocyclic B-substituent seems to have virtually no influence on this effect.

3. The boron-11 chemical shift of 1,3,2-diazaboracyclopentanes is at still higher field than in related bisaminoboranes, though with some characteristic exceptions.

Bisaminoboranes do not have completely planar configuration but the NBN and CNC planes are twisted in an averaged position ; also, sterical hindrance of rotation disturbs the π-interaction (ref. 77), which disappears upon the ring closure. The resultant increase in boron shielding when going from bisaminoboranes to 1,3,2-diazaboracyclopentanes is , therefore, to be expected. The effect of a B-substituent on the Δ value appears to be minor with some exceptions which are worth of individual discussion. These exceptions are observed for the boron substituents

R^1 =



$R^2 = -C \equiv C-CH_3$

For both species, the boron-11 chemical shift of the diazaboracyclopentane is found at unusually low field as compared to the respective bisaminoborane. In the case of R^1 the effect of steric hindrance is evident : The NBN heterocycle and the pyrole ring can hardly be coplanar in a 1,3,2-diazaboracyclopentane derivative, due to the hindrance by the methyl groups which lowers the (R)N-B interaction. In fact, the nitrogen atoms within the B-N heterocycle appear to be deshielded whereas the shielding of the (R)N-nitrogen increases as is evidenced by the nitrogen-14 NMR data. In other words, the (R)N-B interaction is weakened in favor of the B-N(CH_3) interaction. The case of the alkinyl group R^2 can be interpreted by the strong mesomeric (M_-) effect of the alkinyl group, which causes deshielding of both the boron and the nitrogen nuclei, as evidenced by Δ_1N value. This interaction is apparently more effective within the planar arrangement of the heterocycle than it is in the bisaminoborane.

4. 1,3,2-Dioxaboracyclopentanes and 1,3,2-dithiaboracyclopentanes do not conform with the observations stated under 3. There is no steric hindrance whatsoever in comparable borates or thiolates and the five-membered ring formation diminishes only the B-X interaction, and the boron-11 NMR signals are observed downfield for the cyclic compound. It is worthnoting that the 1,3,2-dioxa- and 1,3,2-dithiaboracyclohexanes exhibit, in contrast, the boron-11 signal upfield from the corresponding borate or thiolate and upfield - but close to - the boroxine or borthiine, respectively.

5. The data on 1,3,2-diazaboracyloheptanes are rather limited in number. However, their boron-11 chemical shifts are upfield from the related bisaminoboranes by about 2 ppm and downfield from 1,3,2-diazaboracyclohexanes, close to the range of 1,3,2-diazaboracyclopentanes. Ring deformation _via_ changes in the B-N-C angles is supposedly responsible for this effect, although this type of ring enables a more effective B-N interaction than is encountered in bisaminoboranes.

Finally, the chemical shifts of 1,8,10,9-triazaboradecalin are considered on the basis of the following data (ref. 51) :

	$\delta^{11}B$	$\delta^{14}N$
1,8,10,9-triazaboradecalin	-22.0	335
tris(dimethylamino)borane	-27.3	365

Here, the planar, trigonal environment of the boron atom provides for a very effective π-electron donation to the boron from all three adjacent nitrogen atoms. Hence, the shielding of the boron atom increases, whereas the nitrogen becomes deshielded as compared to tris(dimethylamino)borane. Again, the great importance of the planarity of the boron environment is illustrated.

Very few NMR studies of 1,3,2-diazaboracycloalkanes substituted at endocyclic carbon atoms have been reported. Davis et al. (ref. 78) measured the boron-11 chemical shifts of 1,3-dimethyl-2-phenyl-1,3,2-diazaboracyclohexanes and 2-phenyl-1,3,2-dioxaboracyclohexanes substituted by methyl groups at the central endocyclic carbon site. The chemical shifts were found to be identical with these of the parent nonsubstituted compounds within error limits.

The system :

appears quite insensitive to the γ (and farther) substituents (relatively to the boron), provided this does not involve a change of bonding character within the NBN moiety.

The preceding discussion indicates that the steric arrangement in 1,3,2-diazaboracycloalkanes is largely responsible for the difference in boron-11 and nitrogen-14 chemical shifts as compared to corresponding bisaminoboranes. In contrast to previous efforts of a semiquantitative evaluation of the boron-11 chemical shift values by means of additive contributions depending solely on the electronegativity of the substituent, the present data show that the boron-11 chemical shift also clearly reflects the geometry of the boron coordination sphere.

3.4 Carbon-13 NMR Studies on 1,3,2-Diazaboracycloalkanes

Until most recently, aminoboranes and 1,3,2-diazaboracycloalkanes have not been subject of carbon-13 NMR investigations. Although the carbon-13 NMR technique is increasingly common (refs. 78, 79) and the precision of chemical shift determination by means of Fourier spectrometer is very high, application of carbon-13 NMR spectroscopy in boron chemistry has not yet been developed in detail, due to specific experimental difficulties. Due to its quadrupole magnetic moment the ^{11}B nucleus couples with the spin of ^{13}C nuclei and causes the longitudinal relaxation time T_1 to be long ; thus, the carbon-13 signal broadens and frequently cannot be observed at all. Two principal methods have been developed to overcome this difficulty. Double resonance techniques were successfully applied by Nöth et al. to aminoboranes (ref. 66), whereas Niedenzu and coworkers (ref. 8) have found, that the $^{13}C(B)$ NMR signal is temperature dependent. In some instances as in the case of $B(C_2H_5)_3$, it appears as a sharp single line at -50°C, broadens at about room temperature, then splits into a quartet near 130°C. A pulse delay in the Fourier spectroscopy may also be required for recording boron-bonded carbon-13 signals (ref. 8). Figures 2 to 7 illustrate the thermal decoupling of boron-bonded carbon atoms. The latter method has been used in an extensive study of 1,3,2-diazaboracycloalkanes (ref. 7).

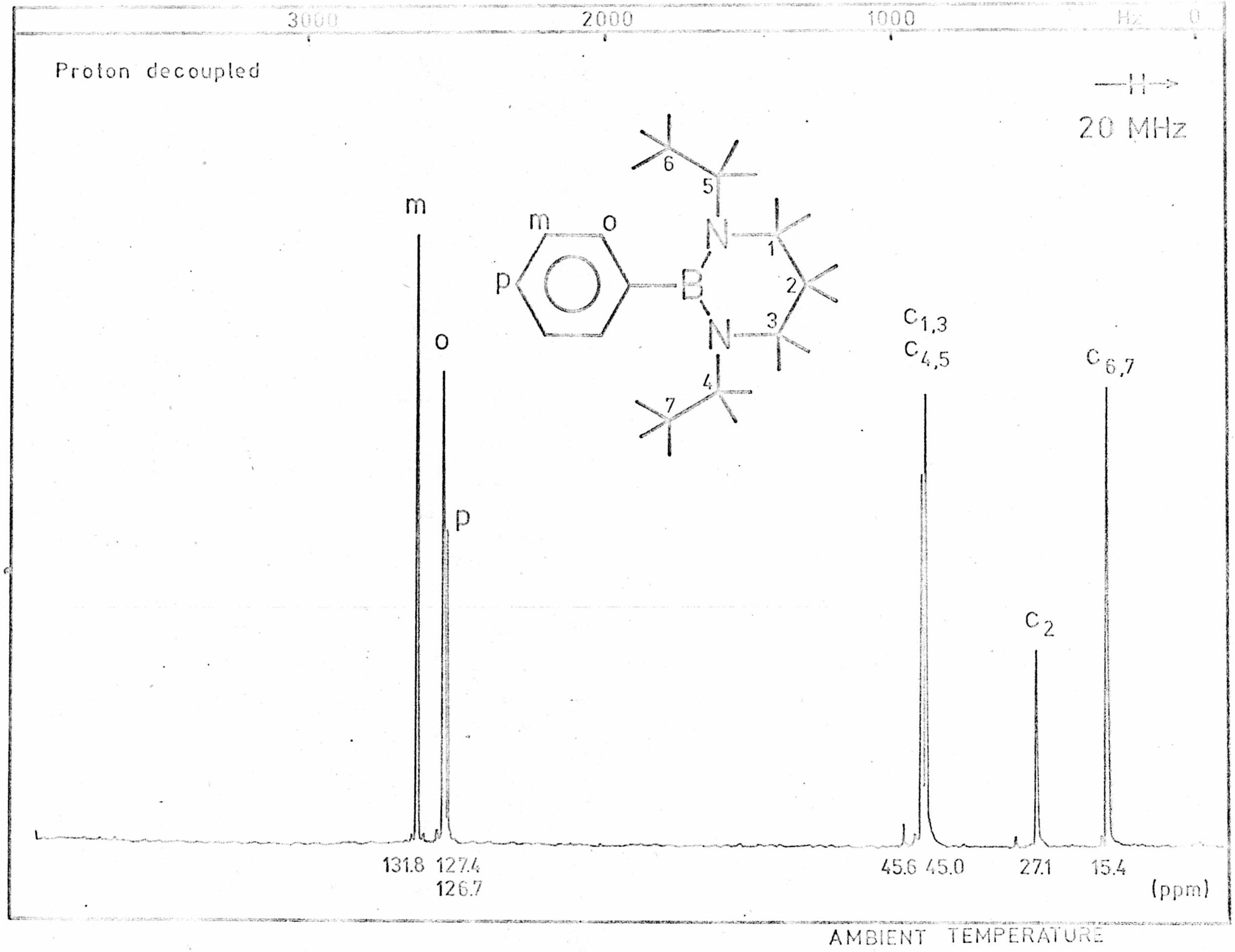


Figure 2

Proton-Decoupled Carbon-13 NMR Spectrum of
1,3-Diethyl-2-Phenyl-1,3,2-Diazaboracyclohexane

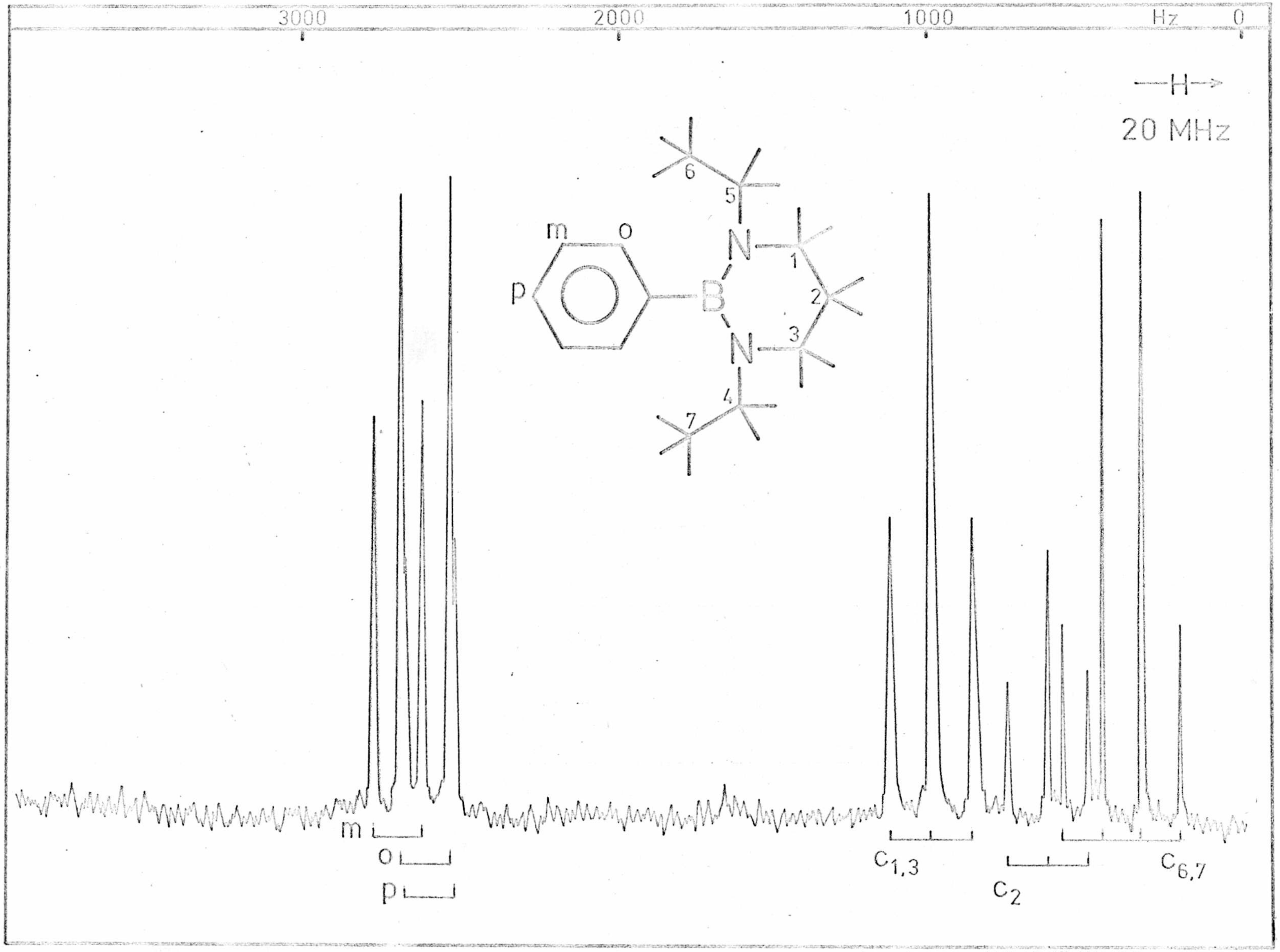


Figure 3

Proton-Coupled Carbon-13 NMR Spectrum of 1,3-Diethyl-2-Phenyl-1,3,2-Diazaboracyclohexane

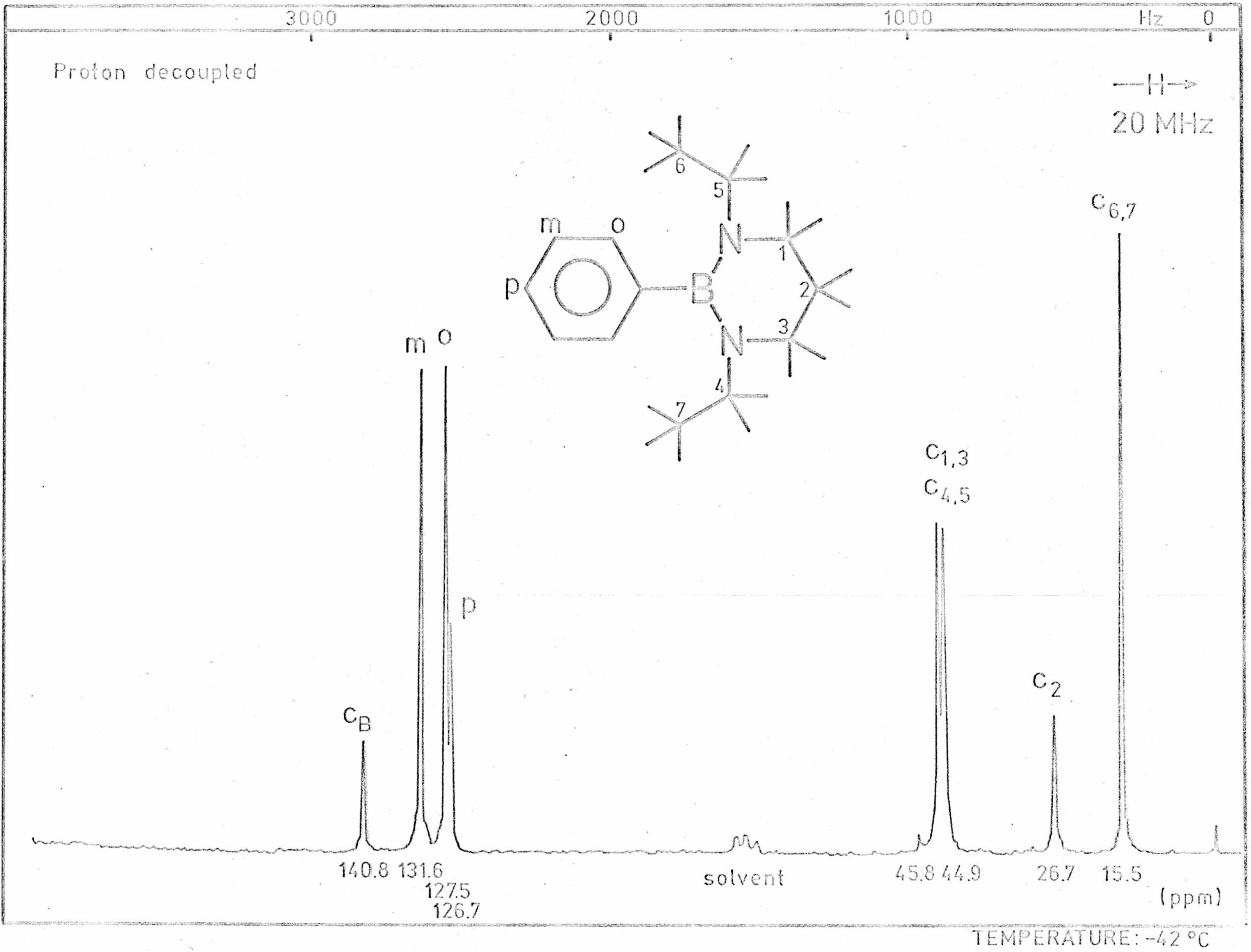


Figure 4

Carbon-13 NMR Spectrum of 1,3-Diethyl-2-Phenyl-1,3,2-Diazaboracyclohexane Recorded at -42°C

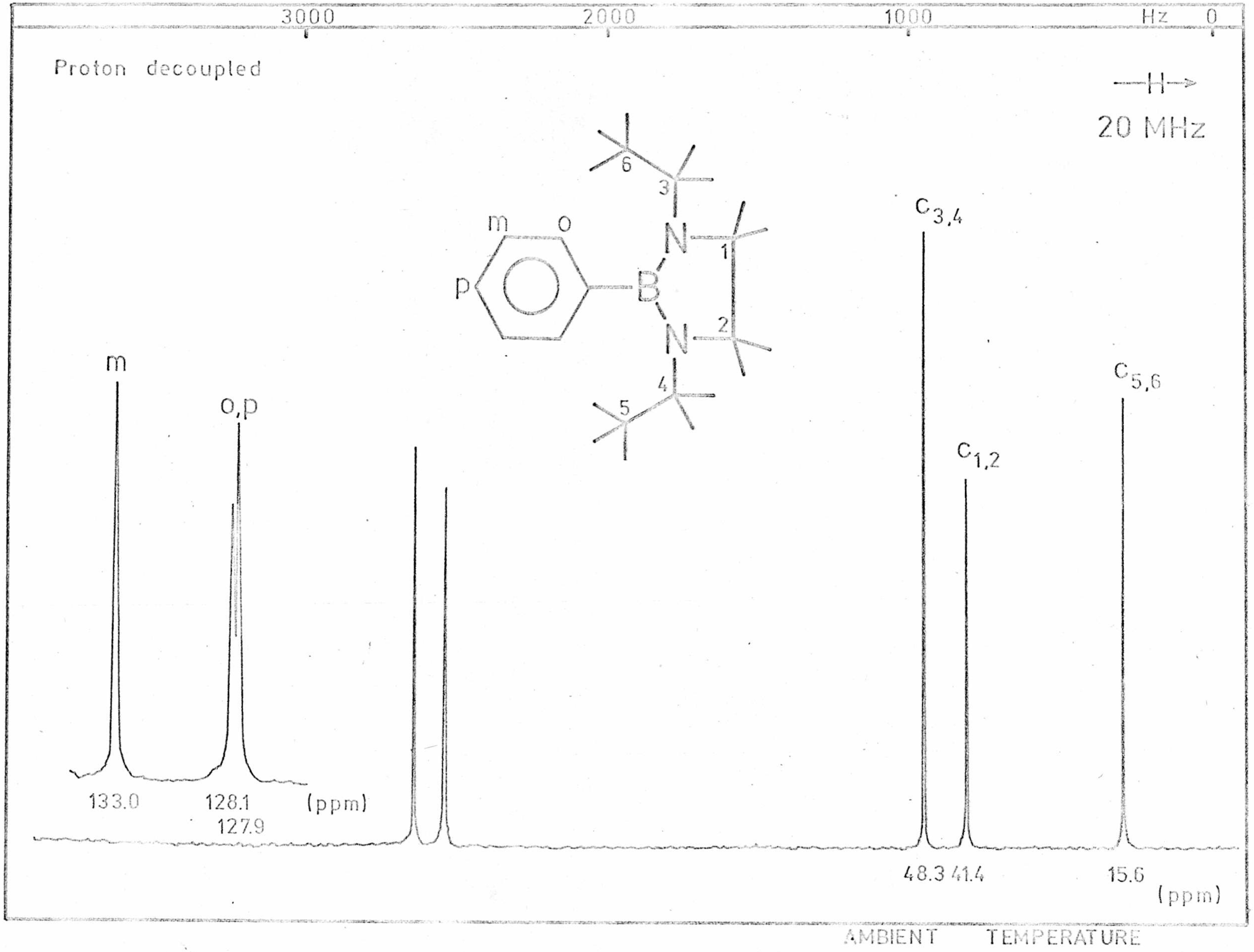


Figure 5

Proton-Decoupled Carbon-13 NMR Spectrum of
1,3-Diethyl-2-Phenyl-1,3,2-Diazaboracyclopentane

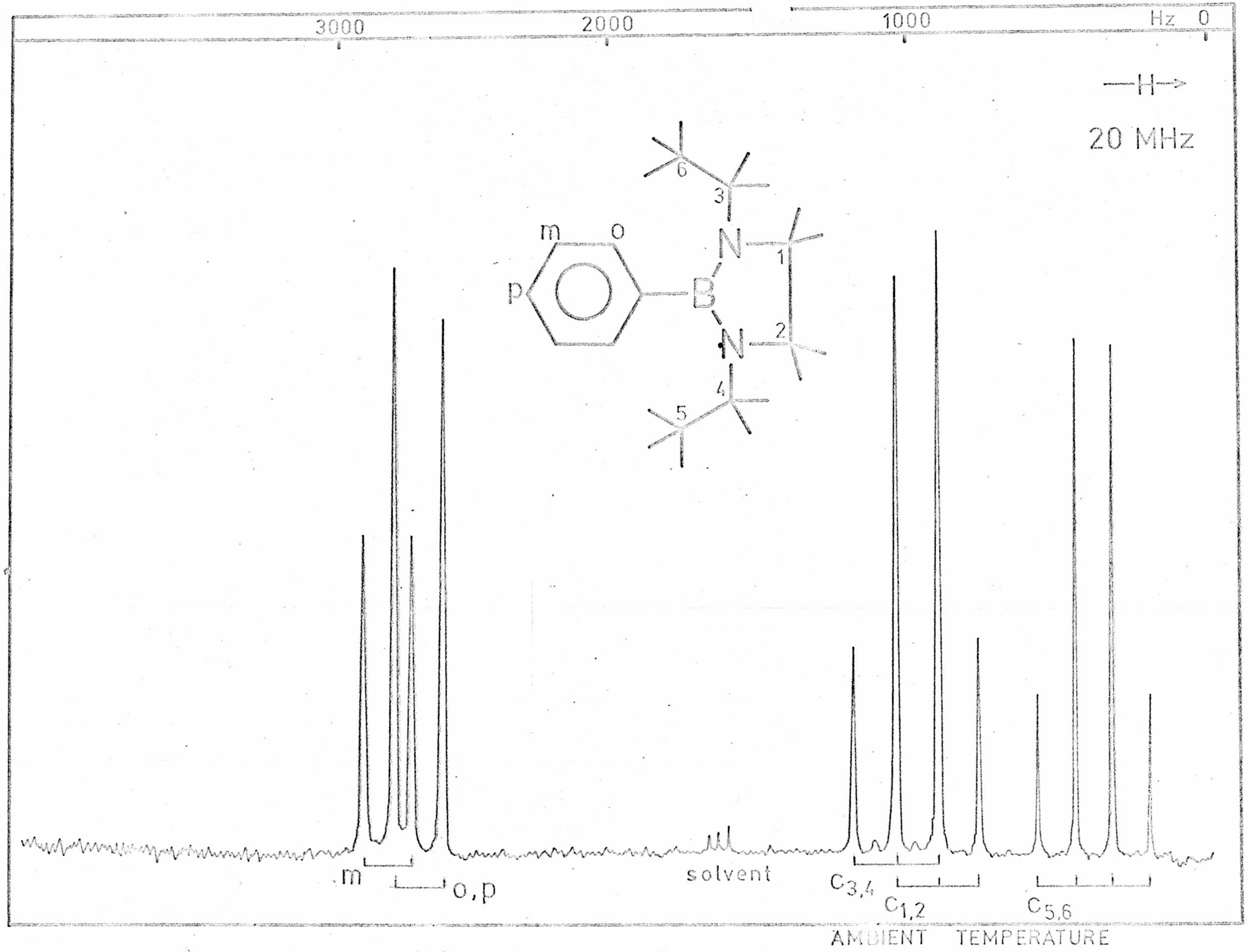


Figure 6

Proton-Coupled Carbon-13 NMR Spectrum of
1,3-Diethyl-2-Phenyl-1,3,2-Diazaboracyclopentane

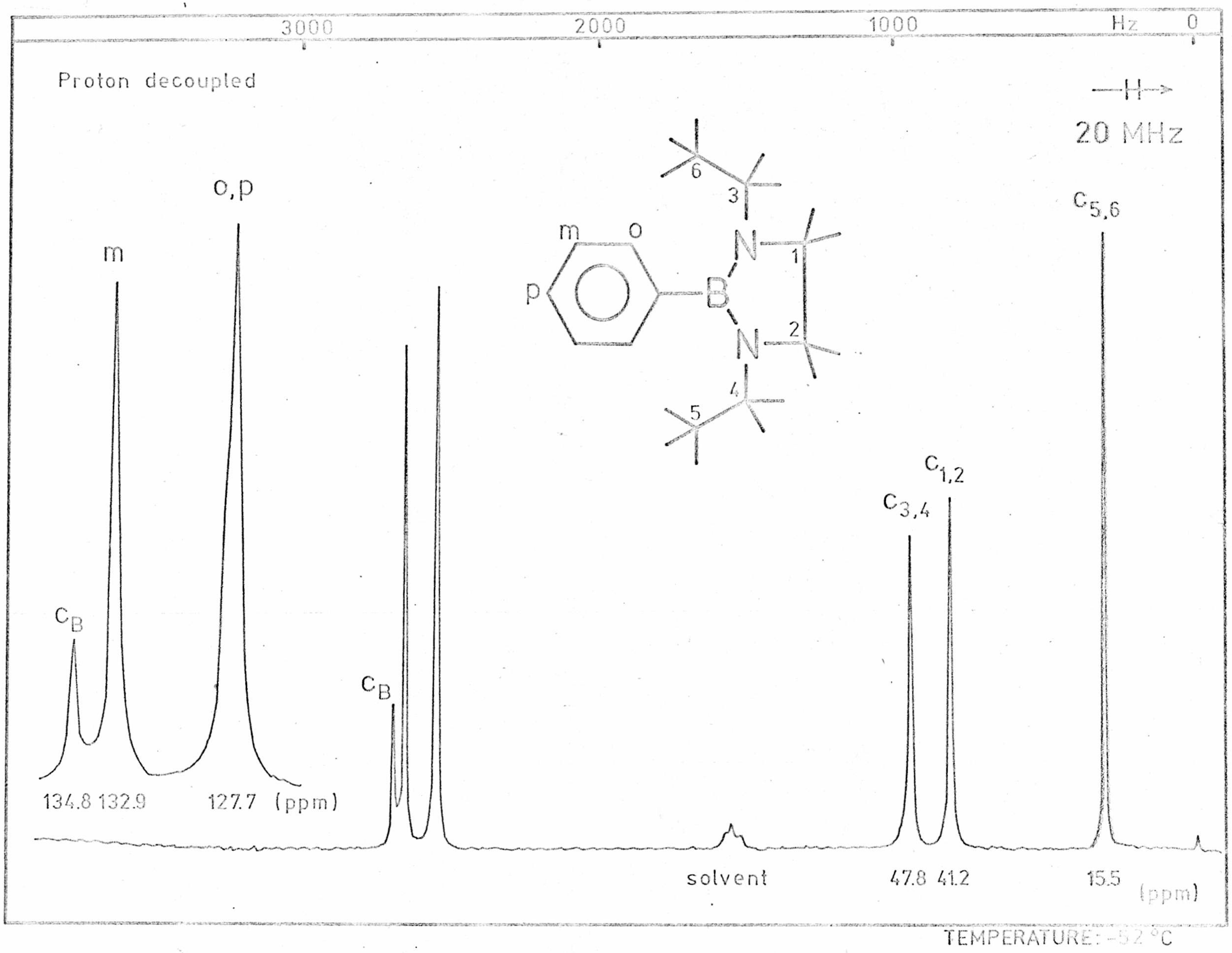
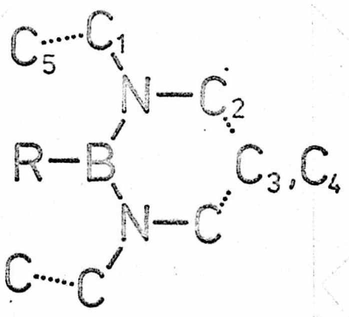


Figure 7

Carbon-13 NMR Spectrum of 1,3-Diethyl-2-Phenyl-1,3,2-Diazaboracyclopentane Recorded at -52°C

There are two points of interest in this present undertaking, e.g., the effect of boron substituents on $\delta^{13}C$ of endo- and exocyclic carbon atoms and the effect of the ring size on $\delta^{13}C$ of boron-attached phenyl carbon atoms.

An attempt to find a quantitative rationalization of the first problem failed, although some meaningful differences between the 1,3,2-diazaboracyclohexane and -pentane systems were eleborated. It is interesting, however, to point out some other regularities. For that purpose the data from the ref. 7, which were largely gathered within the framework of this thesis will be used with the numbering of carbon atoms as follows :



According to data (ref. 7), the value

$$\Delta = \delta^{13}C^{2} - \delta^{13}C^{1}$$

is independent on the type of the substituent R in 1,3,2-diazaboracyclopentanes with a value of 17.3 ± 0.4 ppm.

This constancy must result from the ring structure that makes Δ insensitive to the influence of the exocyclic boron substituent ; this does not occur in 1,3,2-diazaboracyclohexanes, where Δ values range between 6.1 ppm for R = H and 13.3 ppm for R = OCH_3 . Also, individual values of $\delta^{13}C^2$ and $\delta^{13}C^1$ vary by as much as 4 ppm and no regularity for this change was found. The data substantiate a statement, however, that the $^{13}C^2$ signal occurs at lower field in five-membered than in six-membered heterocycles, whereas the $^{13}C^1$ value is, in contrast lower in the 1,3,2-diazaboracyclohexanes. The data reported are for N,N′-dimethyl derivatives; it should be noted that the comparison between the methyl carbon C^1 and the methylene carbon C^2 is not completely satisfactory : ideally two methylene carbons should be compared, e.g., the N,N′-diethyl derivative should be employed. The data available are compiled in the TABLE 4.

TABLE 4

CARBON-13 CHEMICAL SHIFTS
OF 1,3-DIETHYL-2-PHENYL-1,3,2-DIAZABORACYCLOALKANES

n	C^1	C^2	C^3	C^5
2	41.4	48.2	-	15.5
3	45.0	45.6	27.1	15.4
4	46.5	47.6	27.4	16.4

n denotes a number of carbons within the ring

The chemical shift values of both endo- and exocyclic carbon atoms bonded to nitrogen are almost identical in 1,3,2-diazaboracyclohexanes and -heptanes. This observation indicates that the ring system does not exert any strain on the endocyclic C^2 carbon, which interacts with the nitrogen atom almost identically to the C^1 atom. For the five-membered ring the differences in chemical shifts are as large as 6.8 ppm and may be accounted for by the distortion in the nitrogen's sp^2-hybridization which probably increases the s-character in the $N-C^1$ bond and reduces the s-contribution to the $N-C^2$ bond. Consequently, the C^1 atom is better shielded, since the sigma-electrons provide a more efficient shielding. The $\delta^{13}C$ values of C^1 do not seem to depend on other factors such as the side chain length and/or the nature of the boron substituent, e.g., $\delta^{13}C^1 = 45.1$ for Compound 7 (see p. 66). The datum for an open-chain system, Compound 13 (see p. 100) with $\delta^{13}C_{CNC} = 46.0$ ppm indicates that this value corresponds to that of a free borylated configuration

where the nitrogen atom is in sp^2 state. This conclusion may be of considerable value, since it suggests an analogy between chain and ring systems.

TABLE 5

CARBON-13 CHEMICAL SHIFTS OF THE CENTRAL ANNULAR CARBON ATOM WITHIN THE RING OF 1,3,2-DIAZABORACYCLOALKANES AND OTHER BORYLATED SPECIES

Compound	$\delta^{13}C$ in ppm
$HB\left(-NCH_3-CH_2-\right)_2CH_2$	26.9
$C_6H_5B\left(-NCH_3-CH_2-\right)_2CH_2$	26.6
$CH_3B\left(-NCH_3-CH_2-\right)_2CH_2$	27.0
$CH_3OB\left(-NCH_3-CH_2-\right)_2CH_2$	27.1
$C_6H_5B\left(-NC_2H_5-CH_2-\right)_2CH_2$	27.1
$C_6H_5B\left(-NC_2H_5-CH_2-CH_2-\right)_2$	27.4
1,8,10,9-Triazaboradecalin (Compound 6)	27.4
Compound 17	27.7, 28.4
Compound 7	28.6
$C_6H_5B\left(-O-CH_2-\right)_2CH_2$	28.8
Chain Species	
Compound 20	34.0
Compound 13	34.5
3,3'-Diaminodipropylamine	33.9

The data for C^3 chemical shifts are compiled in TABLE 5 ; neither the ring size nor the nature of boron or nitrogen substituents affect the values by more than 0.5 ppm. The ring opening, however, is accompanied by a remarkable deshielding of the C^3 carbon, which is likely due to the increase of rotational freedom. Analogous aspects would hold true for the C^5 carbon atom, $\delta^{13}C$ = 15.5 ppm, which is also fairly independent on the system.

Analysis of the chemical shifts of phenyl carbon atoms was to provide information on the mutual interaction of the phenyl ring with the heterocyclic B-N-C system. The first detailed study of the carbon-13 chemical shifts of substituted benzenes was reported by Spiesecke and Schneider (ref. 62), who presented a basic consideration of mesomeric and inductive effects on the $\delta^{13}C$ of ortho, meta, and para carbons, and also discussed the magnetic anisotropy effect that frequently overshadows inductive or mesomeric interaction. This latter aspect may be omitted in the present study - except for sulfur derivatives - since it is negligible for the elements of the first period. It would be useful to know whether or not the phenyl ring is coplanar with the NBN arrangement of 1,3,2-diazaboracycloalkanes, since the coplanarity would enhance mesomeric interaction. There are indications (refs. 81, 82) that in B-phenylated borazines the rings are not coplanar but rather are perpendicular to each other. The rotational barrier is unknown ; it may be relatively low, since it is about 4.2 kcal/mol for vinyl-substituted boron species (ref. 67).

In Figure 8 the carbon-13 chemical shifts of B-bonded phenyl carbon atoms of various boron derivatives relative to benzene are plotted. If one assumes a pure mesomeric M₋ effect as being responsible for $\delta^{13}C$ of the para carbon atom of the phenyl ring, one finds it to be most pronounced in the case of BS_2 species, then decreasing in the order $BS_2 > BO_2 > BN_2$(pentanes) $> BN_2$(hexanes, heptanes). This sequence can be attributed to the increase of π-electron density on the boron. Here, again, the poorer shielding of the boron in five-membered ring is apparent.

The boron-bonded phenyl carbon atom is exposed to both inductive and resonance interaction, both acting in the same (-) direction ; therefore, its chemical shift is very much downfield from benzene. The inductive interaction of the substituent with ortho carbon atom is weaker than with C(B) , but the resonance effect should lower its chemical shift remarkably (ref. 62). In contrast, the meta position is least sensitive to any of the two effects ; the chemical shift of the meta carbon atoms of phenyl derivatives has been found virtually constant by ±2 ppm for large variety of substituents including NO_2 , NR_2 , and halogenes and being close to $\delta^{13}C$ of benzene. The present study on 1,3,2-diazaboracycloalkanes has led to the reverse conclusion - the most invariable signal was assigned to the ortho carbon as shown in Figure 8. However, the assignement was made solely by comparative methods whereas the better way would be to assign the

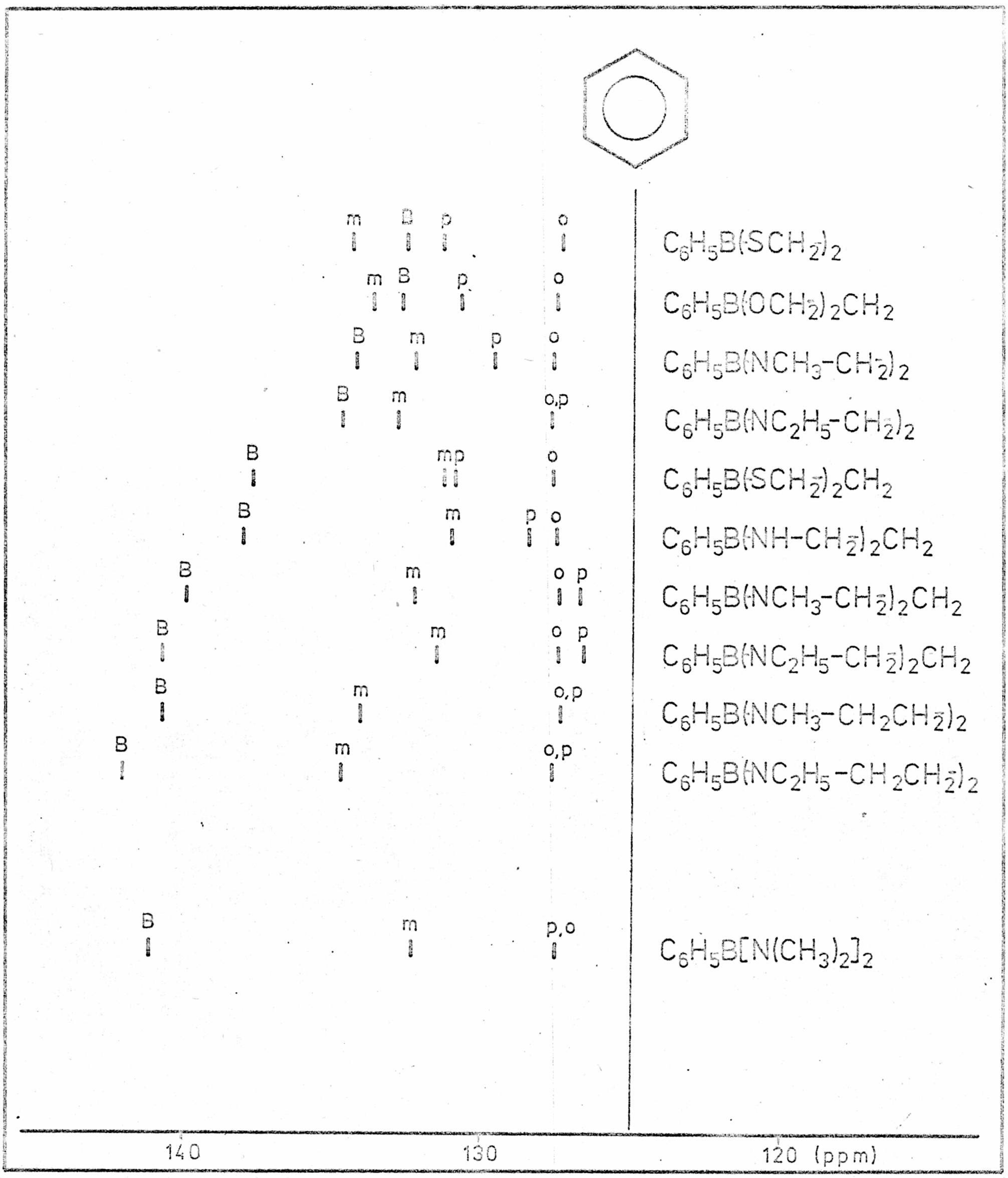


Figure 8

Carbon-13 Chemical Shifts of the Carbon Atoms within the Phenyl Ring of B-phenylated 1,3,2-Diazaboracycloalkanes and Related Species signals by substitution studies (ref. 62). Thus, it is not impossible that signals of ortho and meta carbons have to be interchanged.

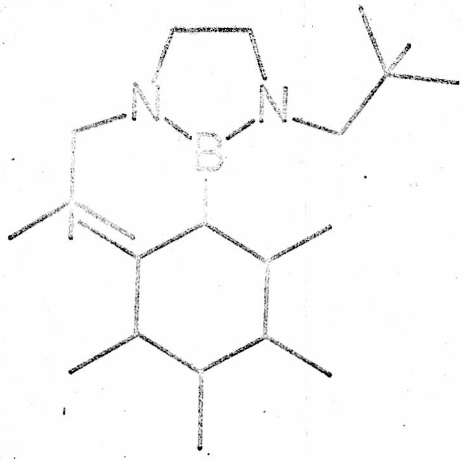
An additional interesting aspect of the carbon-13 chemical shift studies of the phenylborane derivatives is encountered when the appropriate bisaminoboranes are utilized as reference compounds (compare p.30). The value corresponding to those in TABLE 3 but based on $\delta^{13}C$ are collected in the TABLE 6. The $\delta^{13}C(B)$ value is fairly sensitive on going from open-chain bisaminoboranes to the ring systems ; the difference is quite pronounced for diazaboracycloalkyl _versus_ bisaminoboryl substituents, which again demonstrates the special nature of the five-membered heterocycle.

A significant aspect in the discussion of the mutual interaction of the phenyl ring and the heterocycle seems to be the case of 1,3-diethyl-2-phenyl-1,3,2-diazaboracyclopentane (see Figure 8). Its p-carbon chemical shift is in the range that is typical for the six-membered heterocycles ; in other words, the M_- resonance effect is as weak as it is in case of 1,3,2-diazaboracyclohexyl substituent. There is a reasonable explanation of this feature which provides a basis for the discussion of other systems. The structure for this latter compound is illustrated in the following scheme that shows the steric hindrance upon the rotation of methyl groups.

TABLE 6

CARBON-13 CHEMICAL SHIFTS OF THE CARBON ATOMS WITHIN THE PHENYL RING OF B-PHENYLATED 1,3,2-DIAZA-, -OXA-, AND -THIABORACYCLOALKANES RELATED TO THE CORRESPONDING BISAMINOBORANES

Compound	$\delta^{13}C_B$	$\delta^{13}C_o$	$\delta^{13}C_m$	$\delta^{13}C_p$	$\delta^{11}B$	Reference Compound
$C_6H_5B(-NCH_3-CH_2-)_2$	-6.9	0.3	-1.7	2.3	1.3, 0.3	$C_6H_5B[N(CH_3)_2]_2$
$C_6H_5B(-NC_2H_5-CH_2-)_2$	-6.4	0.3	-1.1	0.3	1.0	$C_6H_5B[N(CH_3)_2]_2$
$C_6H_5B(-S-CH_2-)_2$	-5.5	-0.4	2.9	2.0	-1.3	$C_6H_5B(SCH_3)_2$
$C_6H_5B(-NCH_3-CH_2-)_2CH_2$	-1.2	0.1	-1.7	-0.6	3.5, 0	$C_6H_5B[N(CH_3)_2]_2$
$C_6H_5B(-NC_2H_5-CH_2-)_2CH_2$	-0.4	0.1	-2.4	-0.7	3.1	$C_6H_5B[N(CH_3)_2]_2$
$C_6H_5B(-NH-CH_2-)_2CH_2$	-1.9	-0.1	-1.7	0.8	3.3, 1.7	$C_6H_5B(NHCH_3)_2$
$C_6H_5B(-O-CH_2-)_2CH_2$	1.0	0.6	-0.2	1.7	3.2, 2.5	$C_6H_5B(OCH_3)_2$
$C_6H_5B(-S-CH_2-)_2CH_2$	-0.2	-0.1	-0.2	0.6	6.0	$C_6H_5B(SCH_3)_2$
$C_6H_5B(-NCH_3-CH_2-CH_2-)_2$	-0.4	0	0.2	0	0	$C_6H_5B[N(CH_3)_2]_2$
$C_6H_5B(-NC_2H_5-CH_2-CH_2-)_2$	0.9	-0.1	-1.2	-0.1	0.6	$C_6H_5B[N(CH_3)_2]_2$



Here, the average position of the phenyl ring is likely to be perpendicular to the NBN plane, due to steric interaction with the terminal methyl groups ; the corresponding compounds with BS_2 , BO_2 , or $B(NH)_2$ arrangements do not exhibit this feature. The lack of coplanarity should weaken the mesomeric effect, exactly as it is reflected by the p-carbon chemical shift. This argument also accounts for those six-membered systems which - with a relatively free rotating phenyl ring - show substantially lower p-carbon chemical shifts, due to the enhanced mesomeric effect. This event is not reflected by the boron-11 chemical shift data, probably since contributions from the neighbors within the ring and from the ring size mask it effectively. The C(B) chemical shift, however, demonstrates the same tendency as the p-carbon, although in the opposite direction.

The NMR investigations of the 1,3,2-diazaboracycloalkanes that have been presented here tend to suggest the lack of any specific "ring contributions" that would differ these compounds from their counterparts, the aminoboranes. The most important features that determine their electronic structure are :

1. The exact planarity of BN_2 entity ;

2. Geometrically induced distortion of the sp^2-hybridization of the boron ;

3. Steric hindrance ;

not to mention the B-N interactions that are, however, equally important as in aminoboranes. On this basis, but a quantitative discussion is not yet feasible.

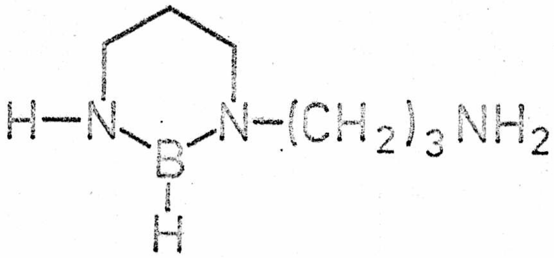
4

BORON DERIVATIVES OF 3,3′-DIAMINODIPROPYLAMINE

As mentioned in section 2.3, 3,3′-diaminodipropylamine is ready starting material for the synthesis of the decalin- or cyclohexane-like diazaboracycloalkanes. The present chapter is concerned with an investigation of interaction of 3,3′-diaminodipropylamine with BH_3, $B[N(CH_3)_2]_3$, or $(CH_3)_2N{-}B(C_2H_5)_2$ in various molar ratios.

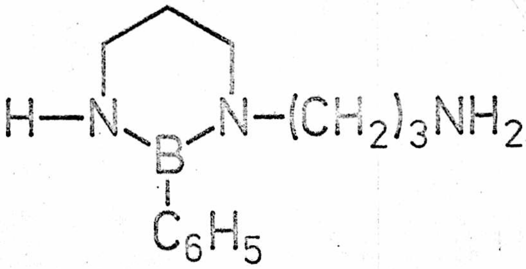
4.1 Survey of Previously Known Boron Derivatives of 3,3′-Diaminodipropylamine

The 1:1 molar interaction of BH_3 - generated *in situ* from $NaBH_4$ - with 3,3′-diaminodipropylamine has been studied previously (ref. 25). It was possible to isolate the intermediate (Compound 7) which, on heating to 150°C, eliminated hydrogen to yield Compound 6 (see [illegible] Compound 7 may be considered as the parent of an entire group of materials that includes the product of the transamination reaction of 3,3′-diaminodipropylamine with bis(dimethylamino)phenylborane in 1:1 molar ratio, Compound 12 (ref. 2).



Compound 7

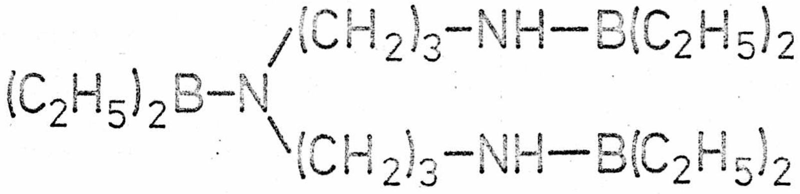
1-(ω-aminopropyl)-1,3,2-diazaboracyclohexane



Compound 12

1-(ω-aminopropyl)-2-phenyl-1,3,2-diazaboracyclohexane

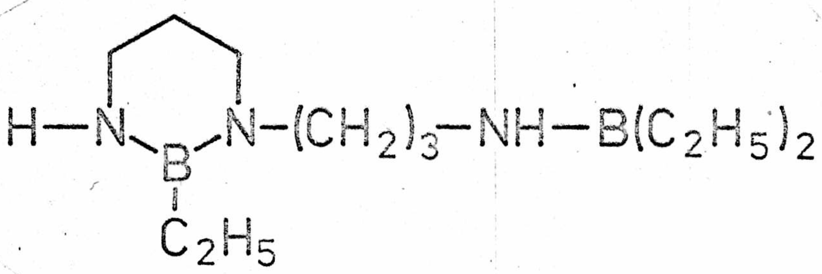
Another representative of this type was obtained in the reaction of 3,3'-diaminodipropylamine with an excess of (diethylamino)diethylborane, $(C_2H_5)_2N-B(C_2H_5)_2$. This reaction was reported to yield Compound 13 ; however, it could not be isolated in pure form. Rather, on attempts to purify the material by distillation, intramolecular condensation occured with the formation of Compound 14.



$$(C_2H_5)_2B-N\begin{array}{l}\diagup (CH_2)_3-NH-B(C_2H_5)_2\\ \diagdown (CH_2)_3-NH-B(C_2H_5)_2\end{array}$$

Compound 13

N,N′,N″-tris(diethylboryl)-3,3′-diaminodipropylamine

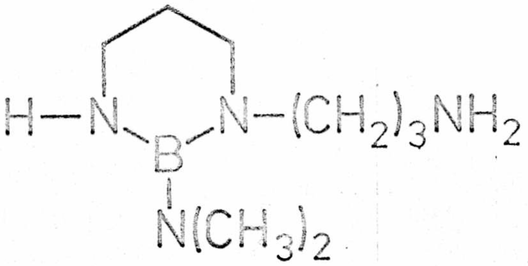


Compound 14

1-(ω-diethylborylaminopropyl)-2-ethyl-1,3,2-diazaboracyclohexane

Compounds 12 and 14 are of reasonable chemical stability although their pyrolysis might produce the 1,8,10,9-triazaboradecalin (Compound 6) and an appropriate hydrocarbon ; this event, however, has not yet been reported. In contrast, Compound 7 readily splits off one hydrogen molecule to give Compound 6. This process is slow at room temperature, but the sample cannot be stored for a prolonged period of time, unless confined into a close system.

In analogy to the compounds discussed above, the intermediate in the reaction of 3,3′-diaminodipropylamine with tris(dimethylamino)borane, Compound 15, was proposed but was never found (ref. 2).



Compound 15

1-(ω-aminopropyl)-2-dimethylamino-1,3,2-diazaboracyclohexane

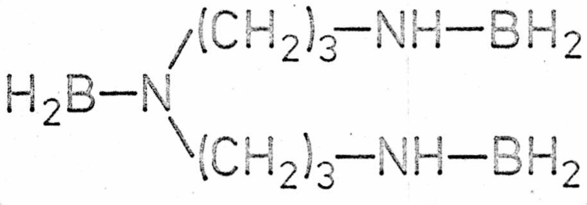
The instability of Compound 15 is belived to be due to the high tendency of boron to undergo transamination reactions, which seems to be an intrinsic property of species containing an exocyclic NR_2 group bonded to a boron which is adjacent to an annular NH group.

The assignement of the structures of Compounds 7, 13, 14 was based primarily on the results of the elemental analyses and infrared spectroscopic evidence. It was not established whether or not the boron in these compounds is truly in trigonal environment or is tetracoordinated by either intra- or intermolecular coordination. Furthermore, no attempt has been reported to obtain additional species which might be formed either as precursors to the heterocycles or from interaction of the latter with any of the starting materials.

4.2 The Interaction of 3,3′-Diaminodipropylamine with Trimethylamine-Borane

Trimethylamine-borane, $(CH_3)_3NBH_3$, is a ready and convenient source for the generation of borane(3), BH_3 . On refluxing of a 1:1 molar mixture of trimethylamine-borane with 3,3′-diaminodipropylamine, Compound 7 is formed in approximately 72 % yield. No intermediate of the amine-borane type resulting from a simple base displacement could be obtained under these conditions. As expected, pyrolysis of Compound 7 at 150°C under atmospheric pressure results in essentially quantitative conversion to 1,8,10,9-triazaboradecalin.

Reaction of a 3:1 molar ratio of trimethylamine-borane and 3,3′-diaminodipropylamine in benzene at reflux temperature was found to result in the formation of Compound 16.



Compound 16

N,N′,N″-tris(dihydroboryl)-3,3′-diaminodipropylamine

Compound 16 is a colorless solid which decomposes on heating evolving a gas.

On utilization of a 2:1 molar ratio of trimethylamine-borane and 3,3'-diaminodipropylamine in analogous reaction, a mixture of Compounds 7 and 16 is obtained ; no pure product containing two BH_2 moieties bonded to one molecule of the amine can be isolated. Furthermore, Compound 16 readily reacts with additional 3,3'-diaminodipropylamine to yield Compound 7.

The physicochemical properties of Compound 7 are essentially identical to the literature data (ref. 25), minor deviations being due to the inherent instability of the compound. Although the material does not readily decompose at temperatures up to 100°C, slow decomposition occurs even at room temperature and leads to formation of Compound 6. The observed boiling point of 54 - 55°C/1 Torr is lower than the literature value of 66 - 68°C/0.5 Torr ; this discrepancy may result from the inaccuracy of pressure measurements. The mass spectrum of this compound is identical with the mass spectrum of Compound 6, which observation can be explained by decomposition of the material under the operating conditions of the spectrometer. The NH stretching mode of Compound 7 could not be resolved but appeared as a relatively broad absorption centered at 3418 cm^{-1}. However, the BH stretching mode assigned at 2486 cm^{-1} corresponds closely with the literature value. The proton NMR spectrum of Compound 7 consist of two overlapping quintuplets centered at δ = 1.80 ppm and two triplets at δ = 2.98 and 2.68 ppm, respectively, as shown in Figure 9. The boron-11 NMR spectrum of the compound shows a single and reasonably sharp resonance line with a chemical shift δ = -23.7 ppm which is close to that of other 1,3,2-diazaboracycloalkanes , see Figure 10.

The carbon-13 NMR spectrum of Compound 7 is complex (see Figures 11, 12) and is difficult to be assigned, since the sample contains byproducts due to partial decomposition. However, based upon the data available for the 1,3,2-diazaboracyclohexane system (see chapter 2), an interpretation of the proton-decoupled spectrum of Compound 7, containing a total of twelve lines can be attempted. Besides the signal assigned to Compound 7 two sets of peaks are present corresponding to the signals in the proton-decoupled spectrum of pure 1,8,10,9-triazaboradecalin (D) and pure 3,3'-diaminodipropylamine (A), compare Figures 13 - 16. Moreover, the proton-coupled spectrum as shown in Figure 12 may be interpreted, provided one assumes some 3,3'-diaminodipropylamine to be present in the sample. There is no supporting evidences for this latter assumption ; the results of the elemental analysis are in good agreement with the data calculated for Compound 7. Also, the observation of only one sharp signal in the boron-11 NMR spectrum as shown in Figure 10 does not substantiate the presence of admixtures as suggested by carbon-13 NMR spectral data. It may be worth mentionning that the samples for the boron-11 NMR spectrum and the elemental analysis were sealed in glass tubes. Hence, conversion Compound 7 ---> Compound 6 may have been impaired since it is accompanied by gas evolution. On the

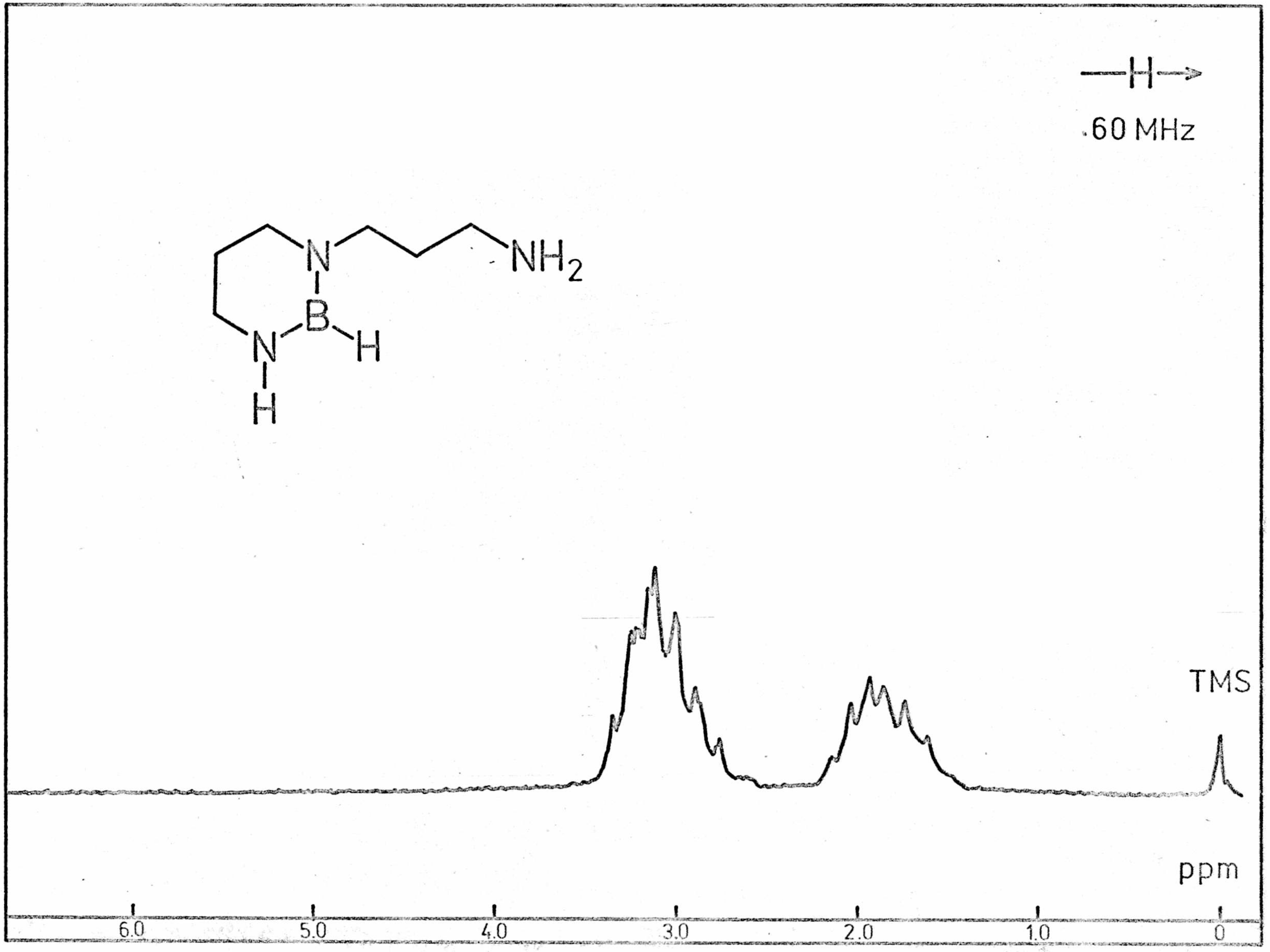


Figure 9

Proton NMR Spectrum of Compound 7

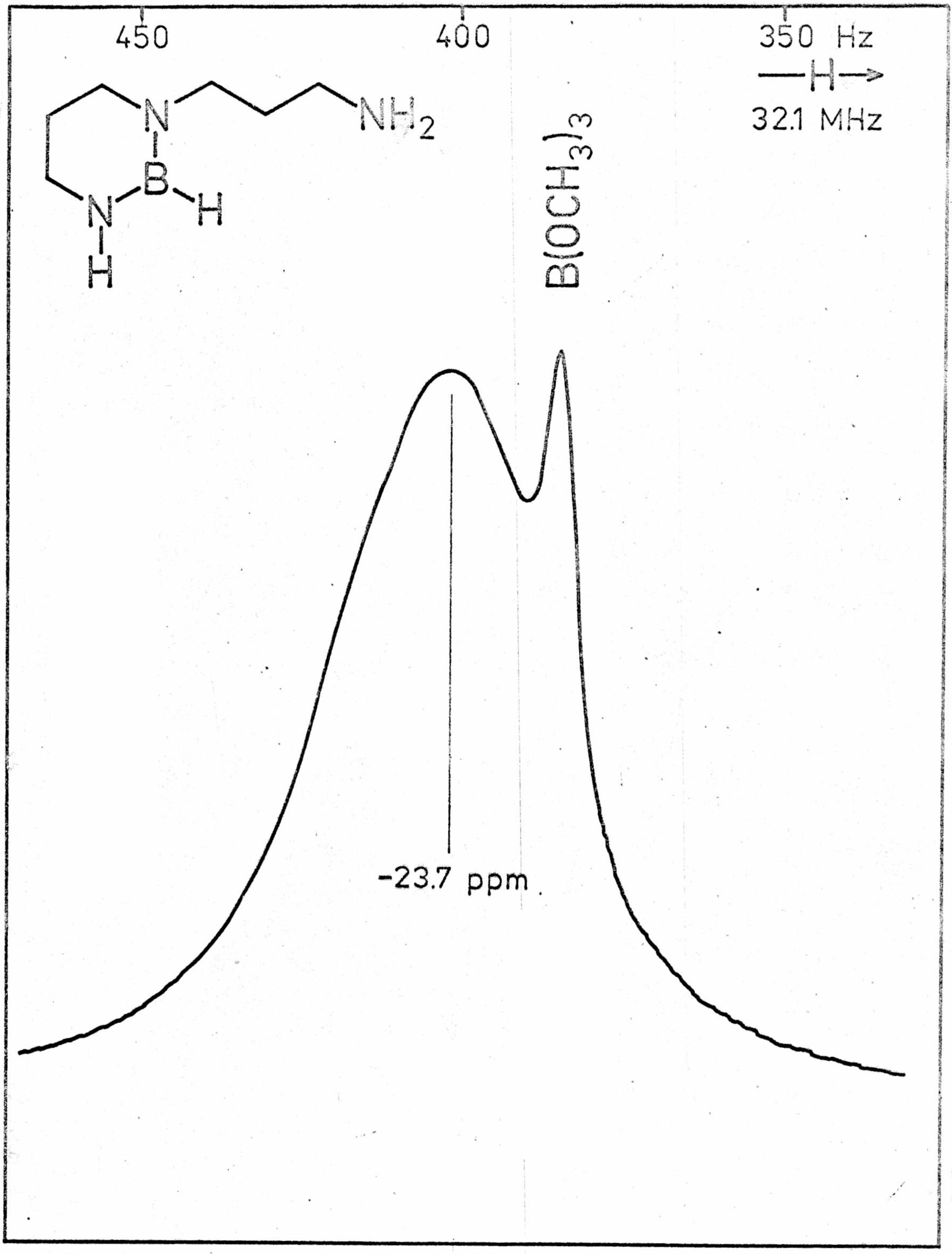


Figure 10

Boron-11 NMR Spectrum of Compound 7

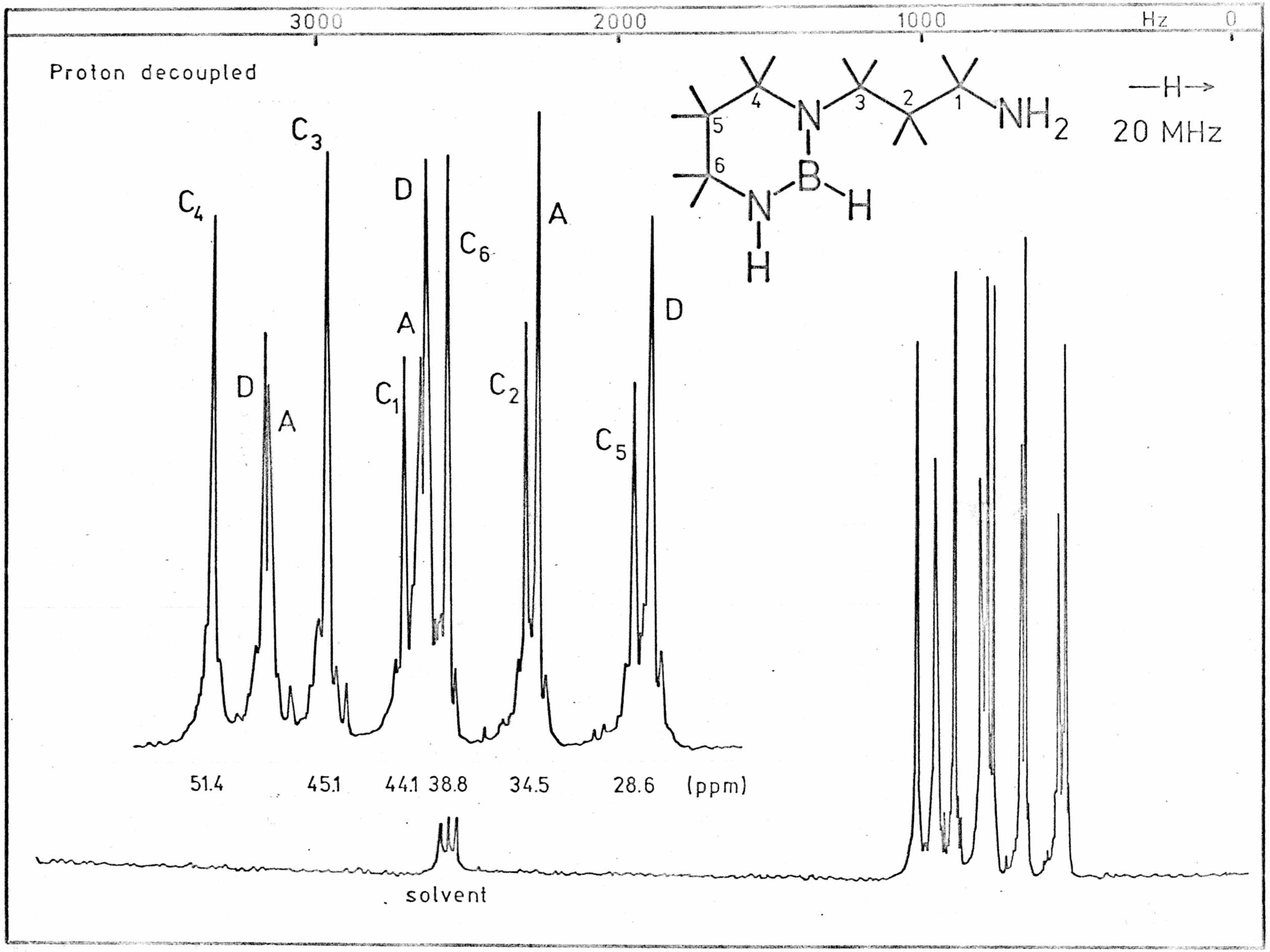


Figure 11

Proton-Decoupled Carbon-13 NMR Spectrum of Compound 7

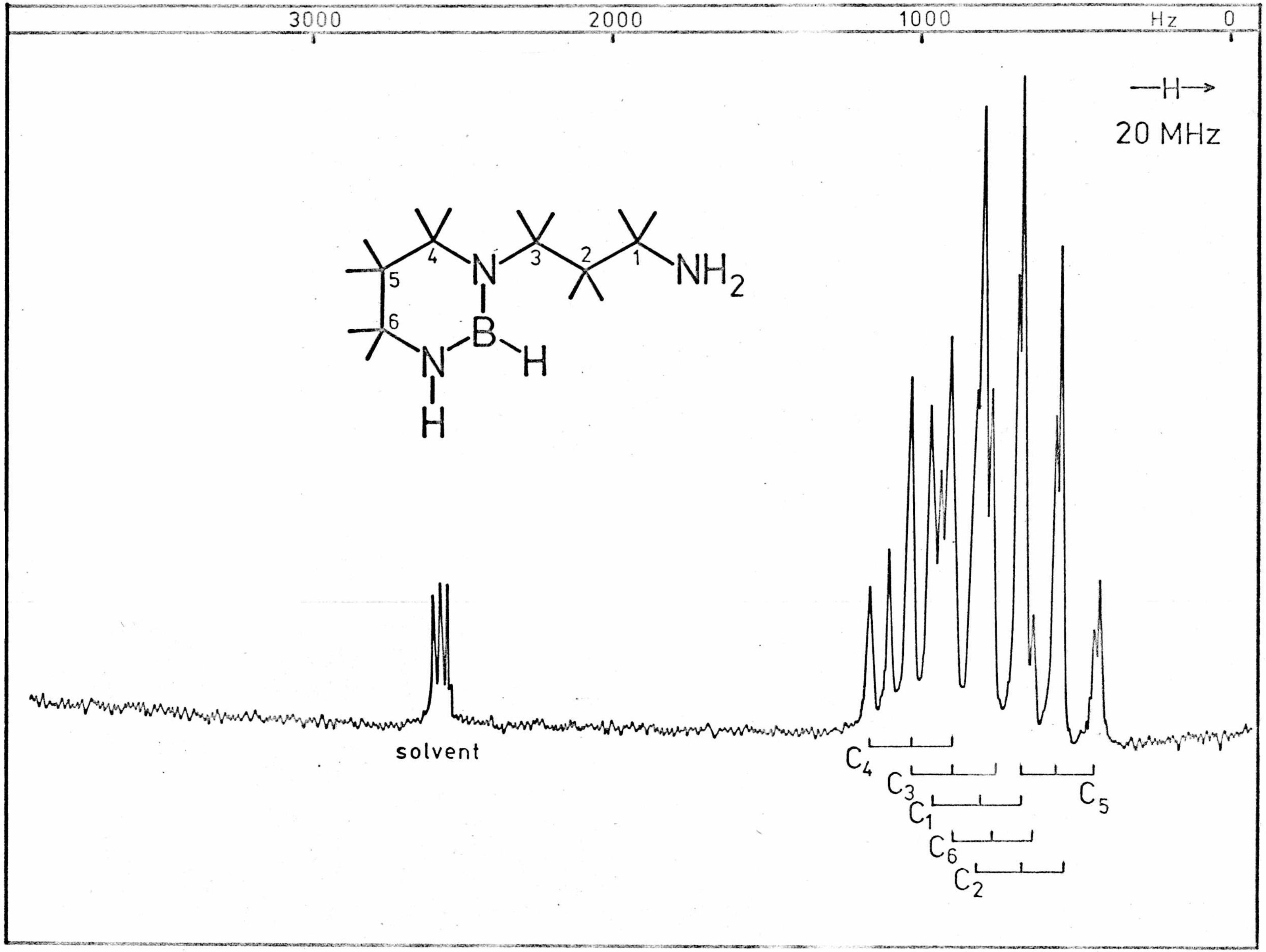


Figure 12

Proton-Coupled Carbon-13 NMR Spectrum of Compound 7

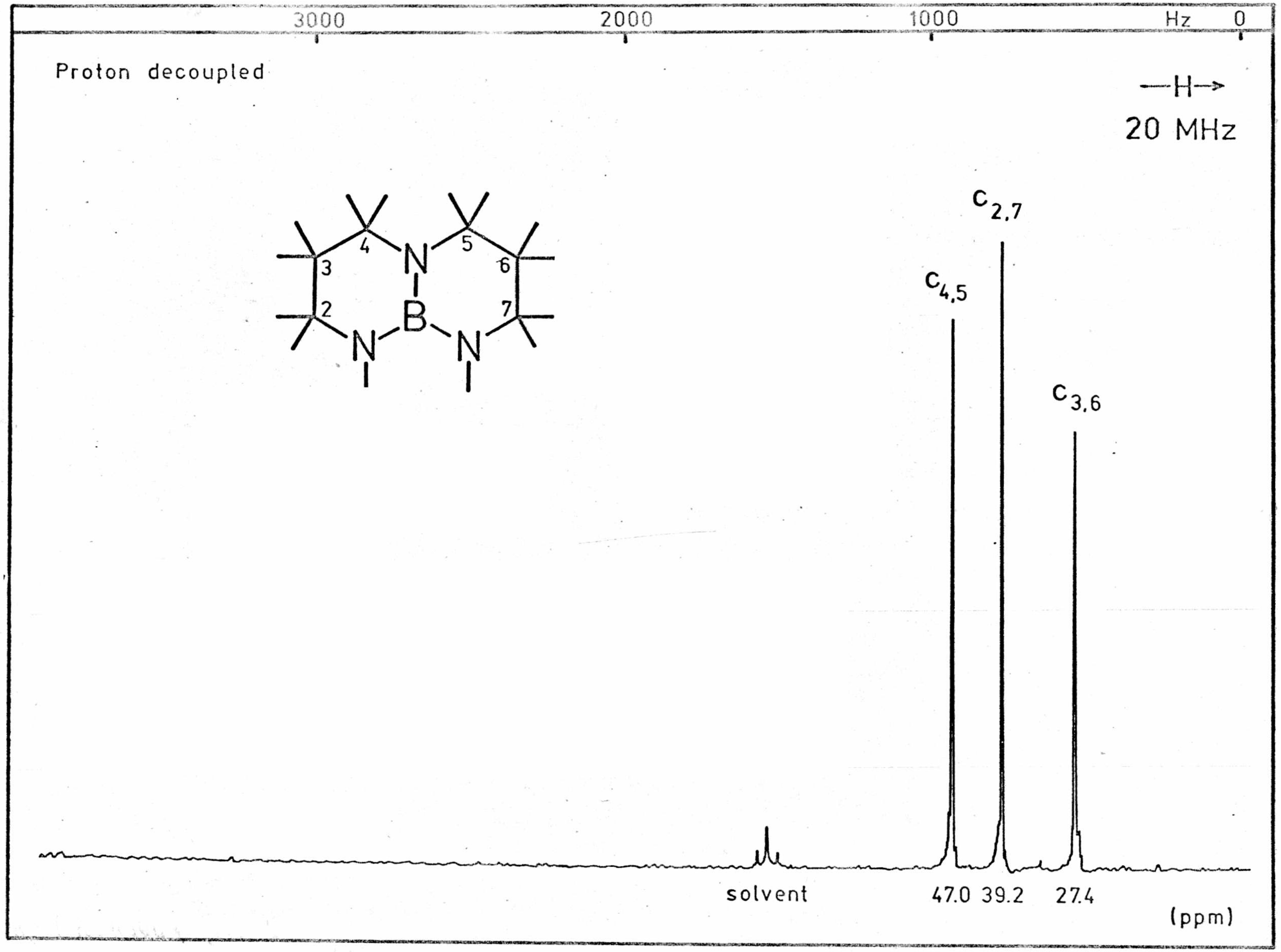


Figure 13

Proton-Decoupled Carbon-13 NMR Spectrum of 1,8,10,9-Triazaboradecalin

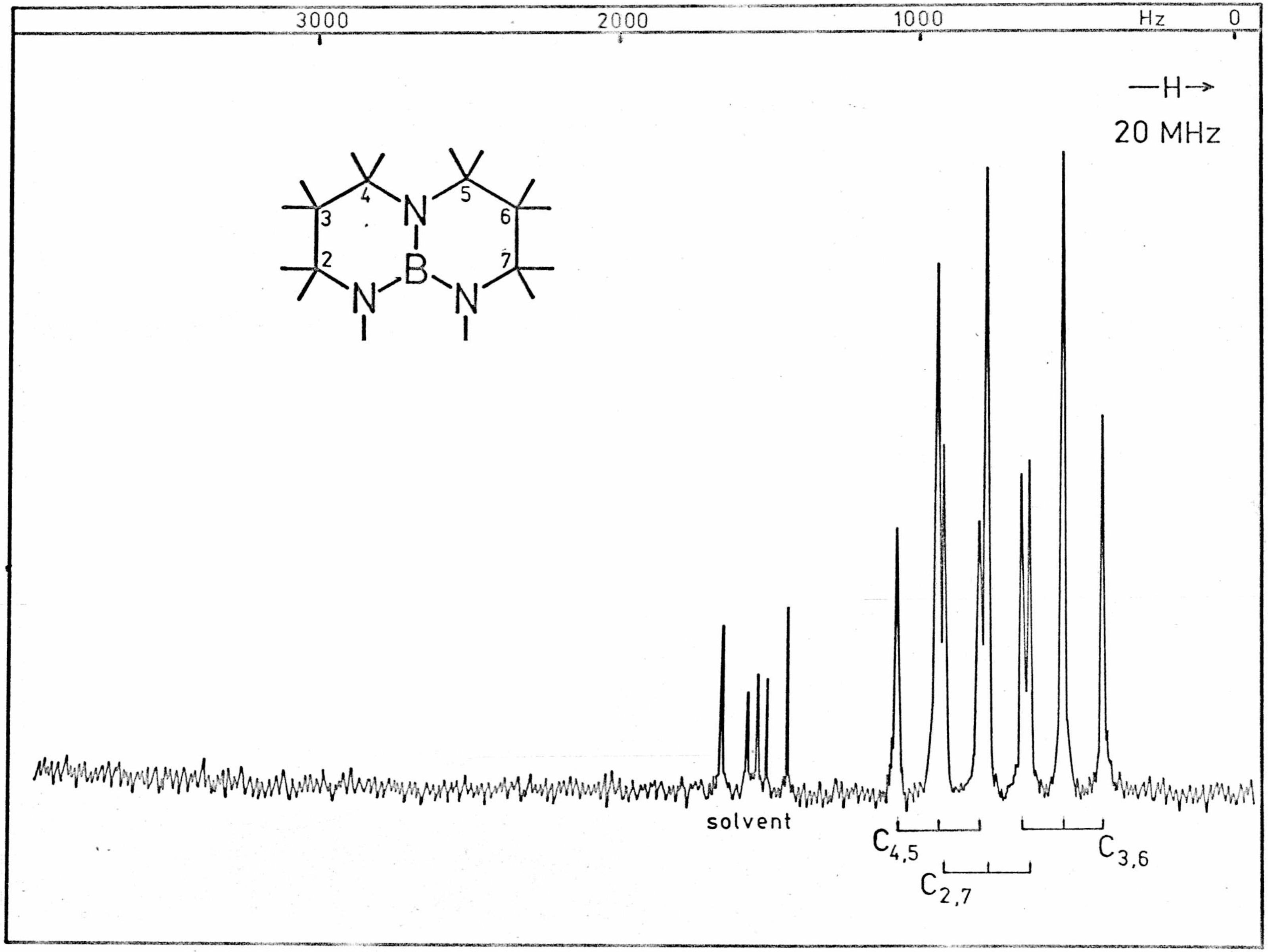


Figure 14

Proton-Coupled Carbon-13 NMR Spectrum of 1,8,10,9-Triazaboradecalin

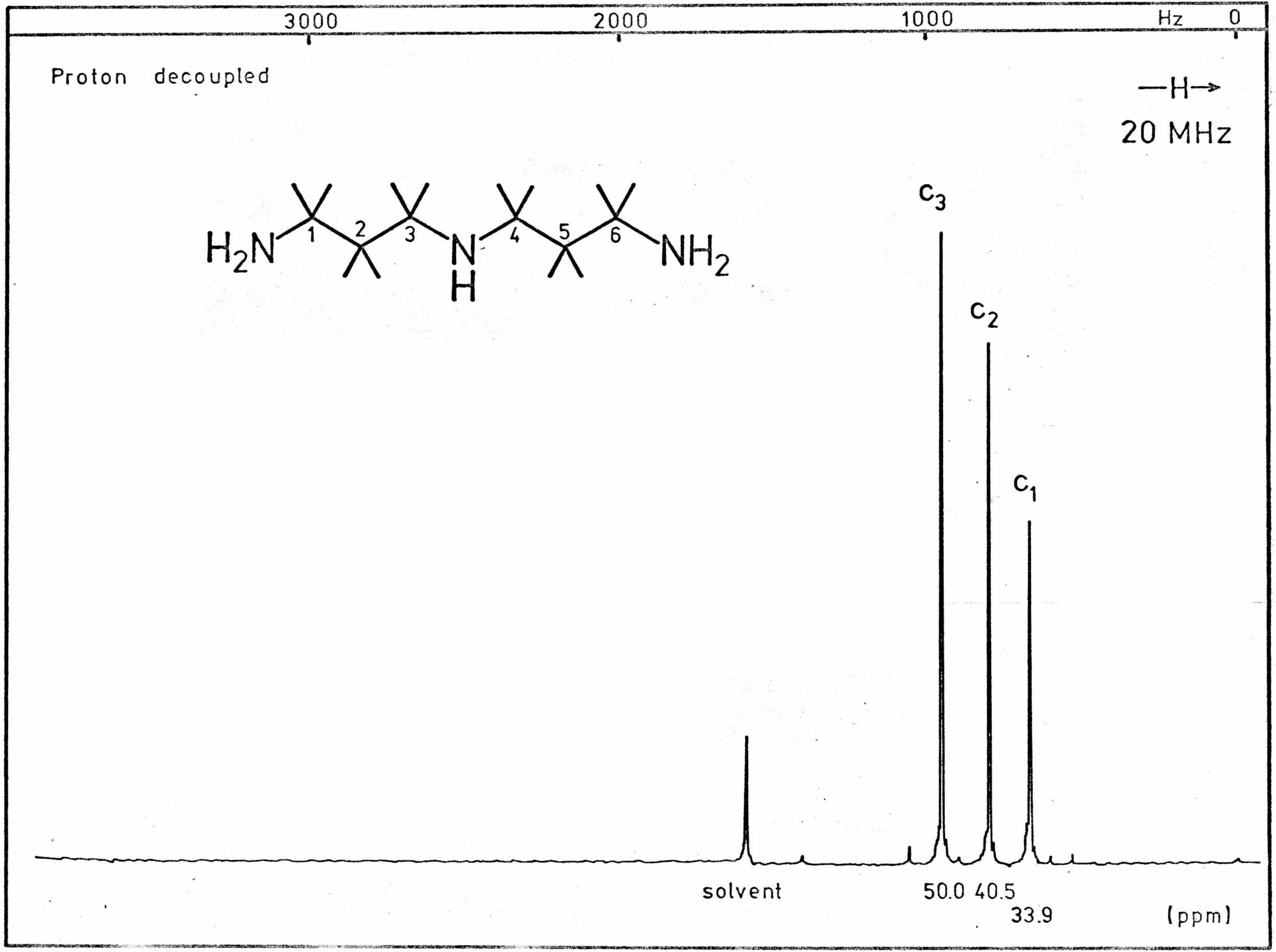


Figure 15

Proton-Decoupled Carbon-13 NMR Spectrum of 3,3′-Diaminodipropylamine

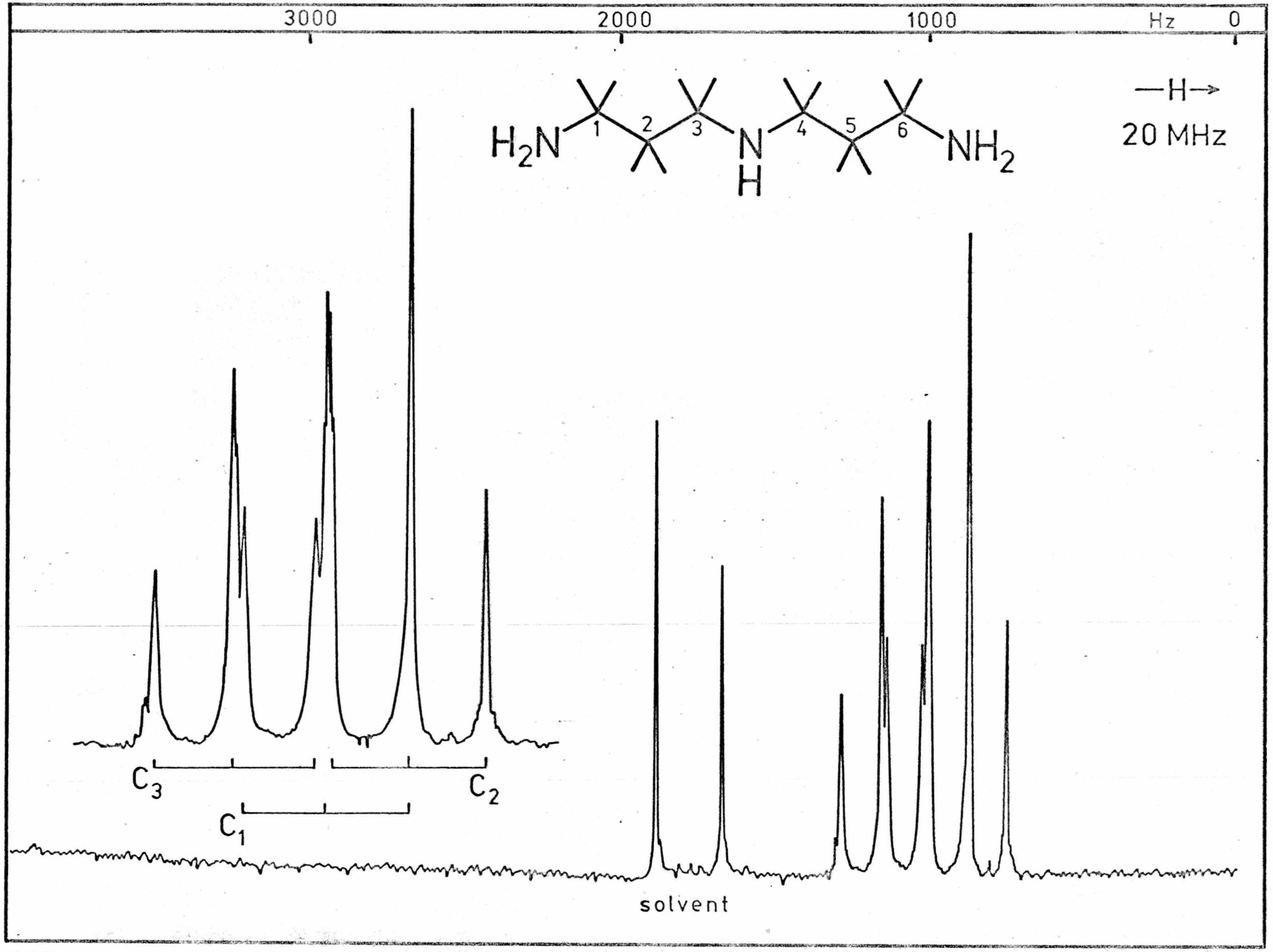
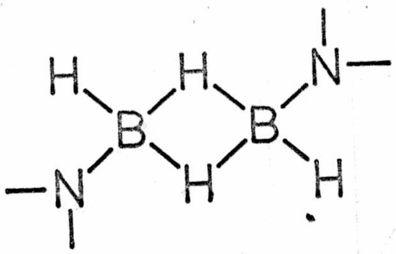


Figure 16

Proton-Coupled Carbon-13 NMR Spectrum of 3,3'-Diaminodipropylamine other hand, the carbon-13 spectrum was obtained on an unsealed sample ; therefore it may be possible that both Compound 6 and another species, preasumably 3,3′-diaminodipropylamine, is formed in the decomposition of Compound 7.

The complex carbon-13 NMR spectrum of Compound 16 cannot be assigned with a reasonable degree of certainity. Also, no mass spectrum of Compound 16 could be obtained since, under the available operating conditions, the compound decomposes with formation of Compound 6. The elemental analysis is in good agreement with the data calculated for Compound 16. The infrared spectrum of the material exhibits two broad absorptions in the NH stretching region centered near 3410 and 3250 cm^{-1}, respectively, as shown in Figure 17. An unresolved broad and intense absorption ranging from 2260 to 2440 cm^{-1} with maxima near 2360 and 2295 cm^{-1} is indicative of BH stretching. However, both values are at quite low frequency and, hence, seem to suggest terminal BH modes rather than terminal BH_2 modes, since the latter are normally observed near 2600 cm^{-1} (ref.85). If this interpretation is correct, then a relatively broad absorption at 1575 cm^{-1} is readily explained as a BH_2B bridges bond :



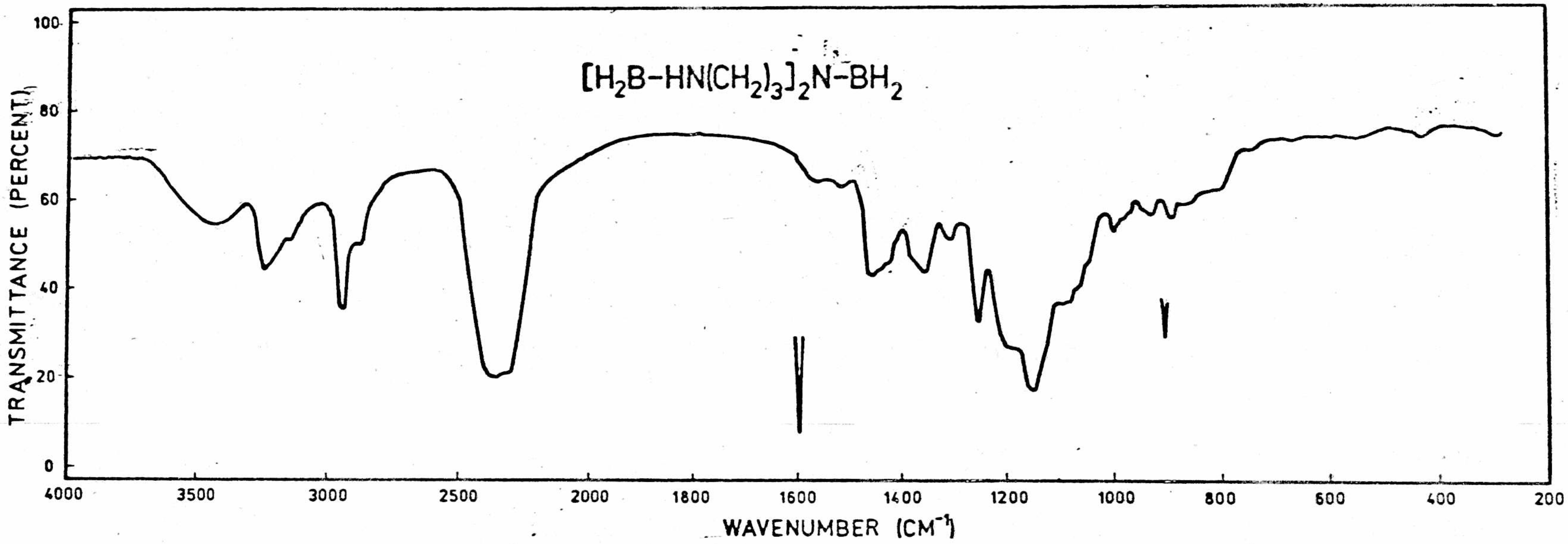


Figure 17

Infrared Spectrum of Compound 16

The existence of such bonding is supported by the fact that neither of the starting materials of the synthesis of Compound 16 nor the ultimate product of the reaction, i.e., Compound 6, show absorbances in this particular frequency region. Additional evidence for the tetracoordinate nature of boron in Compound 16 is obtained by boron-11 NMR data as shown in Figure 18. Two relatively broad resonance signals are observed in the boron-11 NMR spectrum of the compound (solution in benzene with $\delta = 5.1$ and 15.5 ppm, respectively, indicative of tetracoordinate boron. The latter peak is of lower intensity and thus should be assigned to the boron atom that is bonded to the secondary nitrogen atom of the molecule.

Under these aspects it is not surprising that Compound 16 is a solid and its true structure is more likely to be oligomeric or polymeric by inter- or intramolecular BH_2B bridge bonding of individual species. This assumption is in agreement with the cryoscopic weight determination in benzene that yields values between 196 and 279. An additional interesting datum is provided by calorimetric studies of Compound 16. The thermal decomposition was studied in the temerature range of 315 K to 420 K. No definite melting point was found ; rather a constant endothermic effect was recorded (see Figure 19) that resembles the melting of a polymer. Decomposition was observed to occur at temperature above 374 K. The final product of this pyrolysis was a colorless glassy solid of rather high hardness. The loss of weight during the pyrolysis was about 3.8 %. Assuming the BH_2B bonding

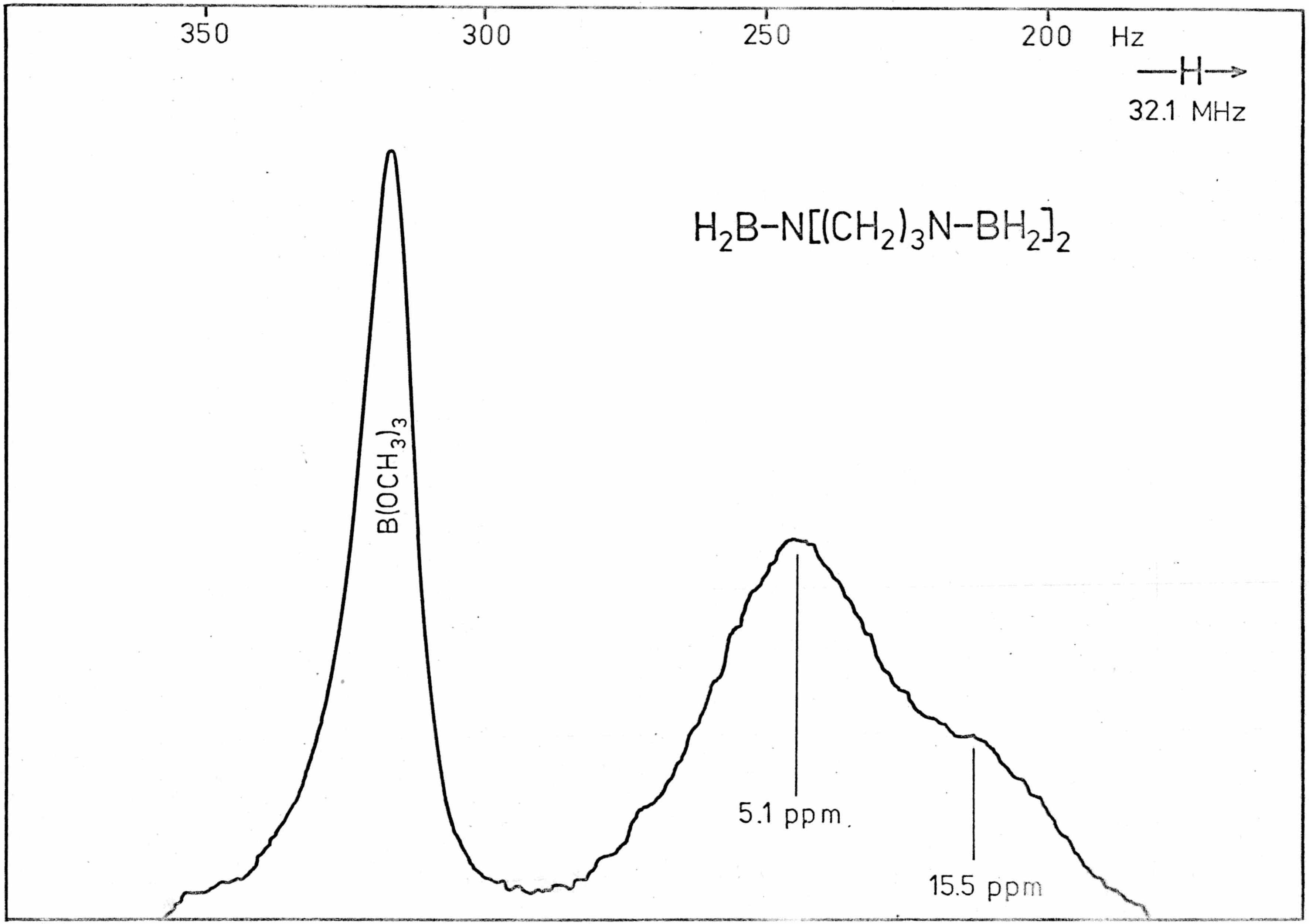


Figure 18

Boron-11 NMR Spectrum of Compound 16

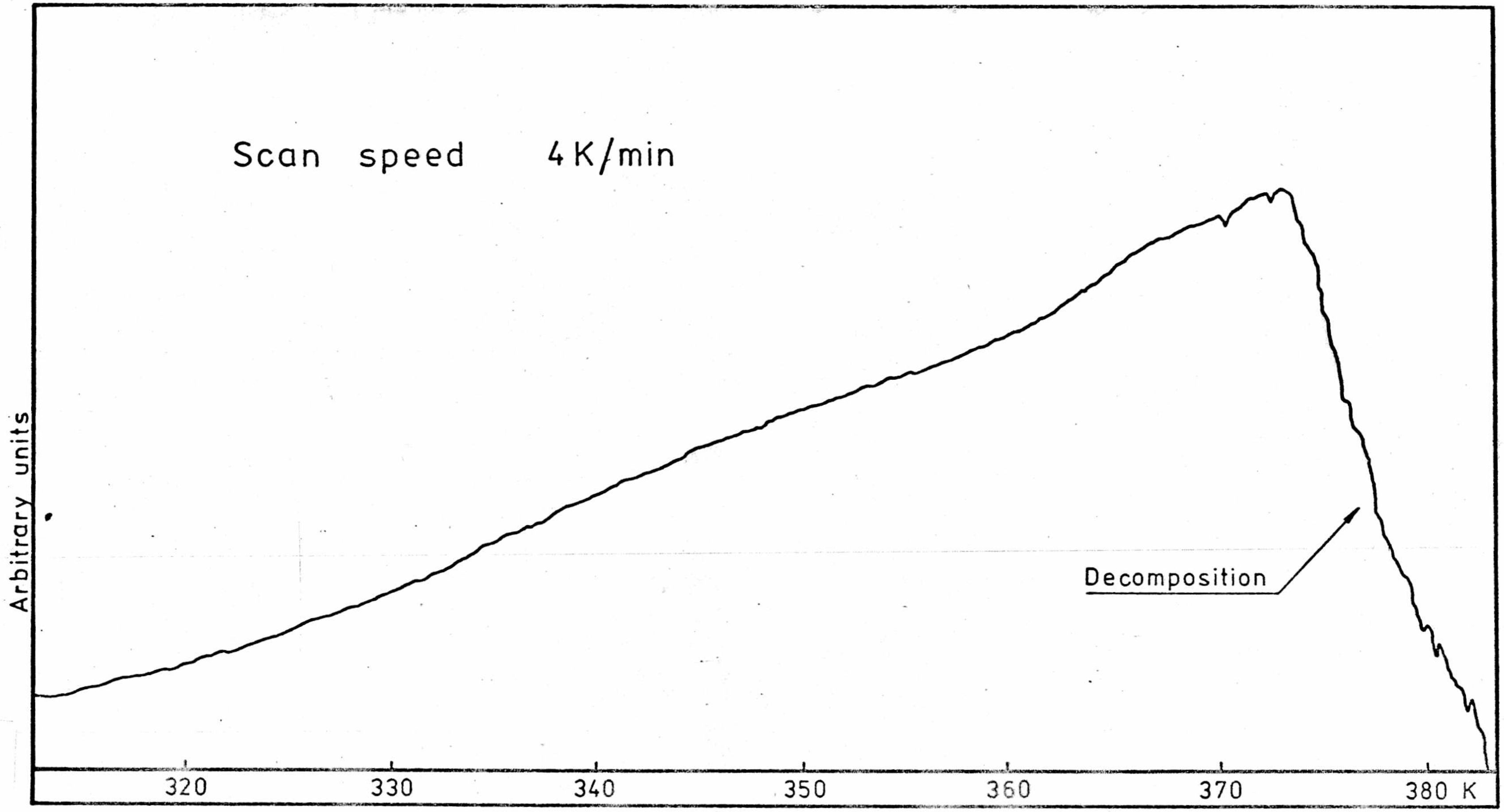
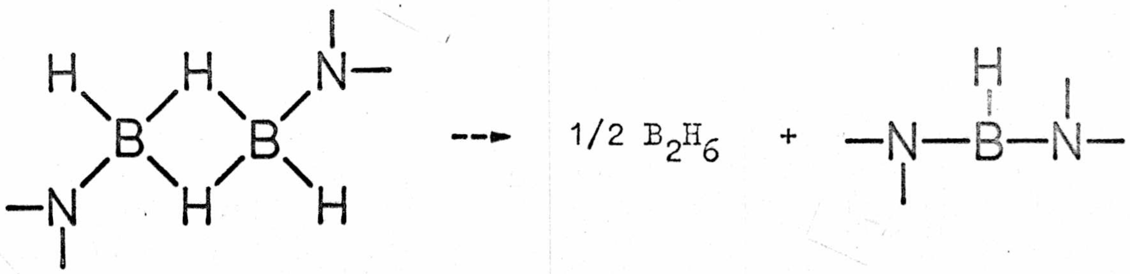


Figure 19

Heat Absorption Curve (DSC run) of Compound 16 in Compound 16 to be intermolecular, one can speculate on the possible structure of this pyrolysis product. A reasonable assumption appears to be the generation of B_2H_6 , resulting in the formation of a polymer containing covalent intermolecular bonds as illustrated by Equation 8.

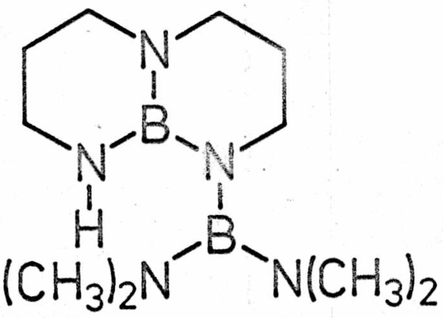


Equation 8

The observed weight loss would indicate the release of about one molecule of B_2H_6 for four molecules of the monomer.

4.3 The Reaction of 3,3′-Diaminodipropylamine with Tris(dimethylamino)borane

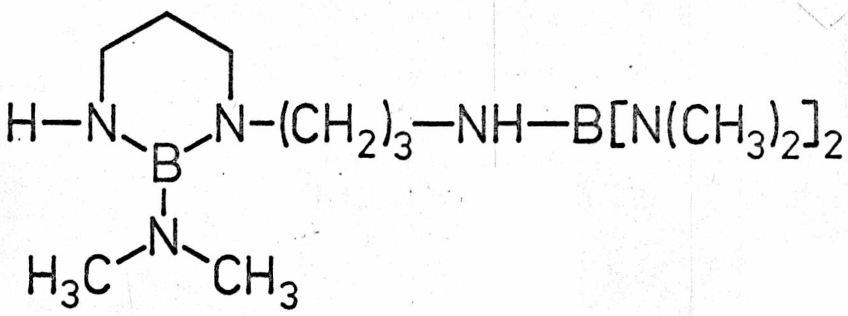
In previous studies (refs. 2, 3) only equimolar amounts of tris(dimethylamino)borane and 3,3′-diaminodipropylamine were reacted to yield Compound 6. However, utilizing an excess of tris(dimethylamino)borane, Compound 17 is obtained in essentially quantitative yield, calculated for the 3,3′-diaminodipropylamine. Compound 17 is a liquid material that can be distilled under reduced pressure without noticeable decomposition.



Compound 17

1-dimethylaminoboryl-1,8,10,9-triazaboradecalin

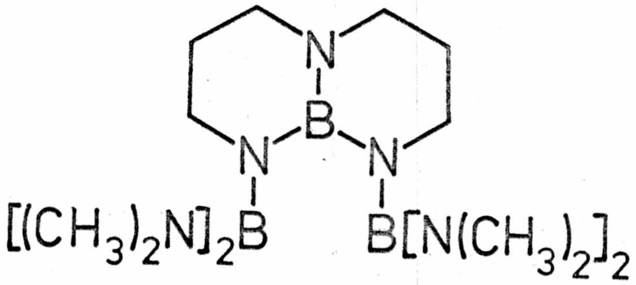
Although the product obtained in this fashion is analytically pure, mass spectral data suggest contamination of the material with traces of a second compound, most likely corresponding to the structure of Compound 18.



Compound 18

1-(ω-dimethylaminoborylaminopropyl)-2-dimethylamino-1,3,2-diazaboracyclohexane

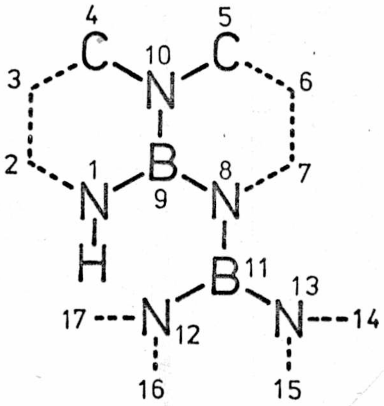
Even when a large excess of tris(dimethylamino)-borane is utilized in the reaction, the desired diborylated 1,8,10,9-triazaboradecalin, Compound 19, could not be obtained.



Compound 19

1,8-bis(dimethylaminoboryl)-1,8,10,9-triazaboradecalin

Hence, it is not surprising that only Compound 17 is obtained, even on prolonged reflux of a mixture of Compound 6 and an excess of tris(dimethylamino)borane. This observation tends to suggest that steric factors prevent the displacement of the second N-bonded hydrogen of 1,8,10,9-triazaboradecalin by a bis(dimethylamino-boryl)group. This is somewhat surprising, since both NH groups of Compound 6 can be lithiated and even bulky substituents can subsequently be bonded to the N^1 and N^8 atoms of Compound 6 (ref. 34). The observation of a sharp infrared absorption band for the NH stretching mode of Compound 17 at 3460 cm^{-1} disputes any intramolecular hydrogen bonding, which could render the NH site of the molecule inert. Hence, one must assume that the bis(dimethylamino)boryl substituent at N^1 of Compound 17 is indeed protecting the N^8 site from further attack by steric factors only. The relatively high π-contributions to the B-N bond are well known (refs. 86, 87) ; they cause a conjugate B-N bond system to stay planar. The possible rotation around B-N bond is hindered in the order of about 20 kcal/mol (refs. 86, 88, 89, 90). Therefore, a planarity might be anticipated for the large part of the molecule of the Compound 17 that would account for the inert character of the N^1 site. The following scheme illustrates the arrangement of atoms in Compound 17 ; the entity which is probably planar is marked by a solid line.



The analytical data of Compound 17 are consistent with its proposed structure. The mass spectrum as shown in Figure 20 exhibits the parent peak - disregarding a minor impurity at m/e = 281 - at m/e = 237, which corresponds to the molecular ion. The base peak of the spectrum is observed at m/e = 193 ; it is readily interpreted by

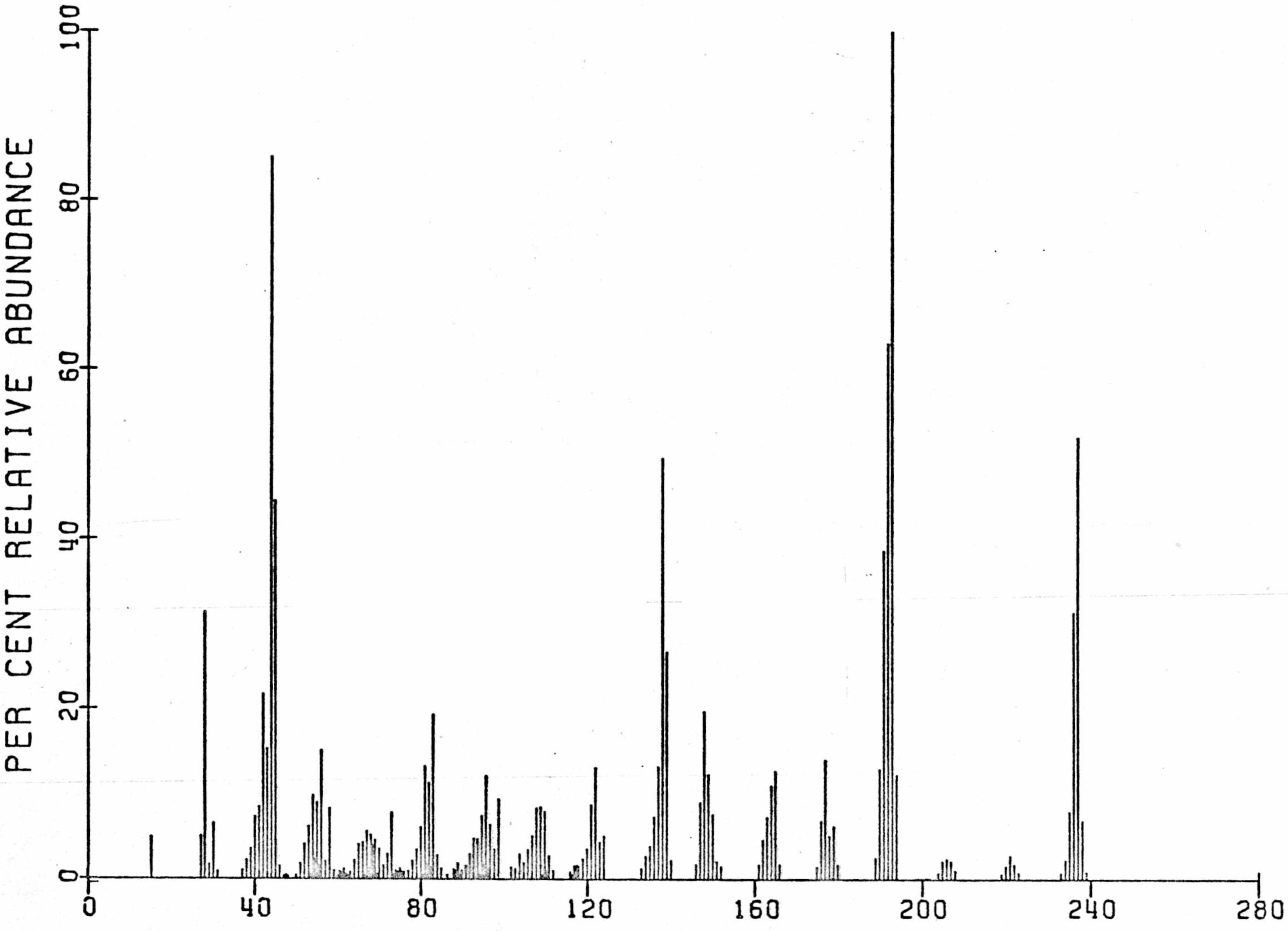


Figure 20

70 eV Mass Spectrum of Compound 17

the loss of a dimethylamino group from the parent species. It is worth noting that the low-voltage mass spectrum shows only four peaks : the molecular ion - which is also the base peak - and peaks at m/e = 193, 139, 45 (see Figure 21).

The infrared spectrum of Compound 17 shows a single sharp absorption at 3460 cm^{-1} assigned to a NH stretching mode (see Figure 22). A BN stretching mode may be tentatively assigned to an intense absorption near 1498 cm^{-1} , exhibiting a shoulder on the high frequency side. Any further interpretation of the multi-line spectrum cannot be attempted.

The proton NMR spectrum of Compound 17 exhibits a singlet with a chemical shift $\delta = 2.37$ ppm attributable to the N-methyl protons. The annular methylene group protons are evidenced by a triplet with $\delta = 2.68$ ppm and a quintuplet with $\delta = 1.62$ ppm in the calculated intensity ratio (see Figure 23).

As expected, two resonance signals are observed in the boron-11 NMR spectrum of the compound with chemical shift $\delta = -23.5$ and $\delta = -27.2$ ppm, respectively (Figure 24) ; the signal at the higher field is assigned to the annular boron atom by comparison to Compound 6. The carbon-13 NMR spectrum of the compound (Figures 25, 26) is readily interpreted in conjunction with the spectra of Compound 6 (Figures 13, 14) and of 3,3'-diaminodipropylamine (Figures 15, 16). For the assignment of the spectrum see TABLE 7.

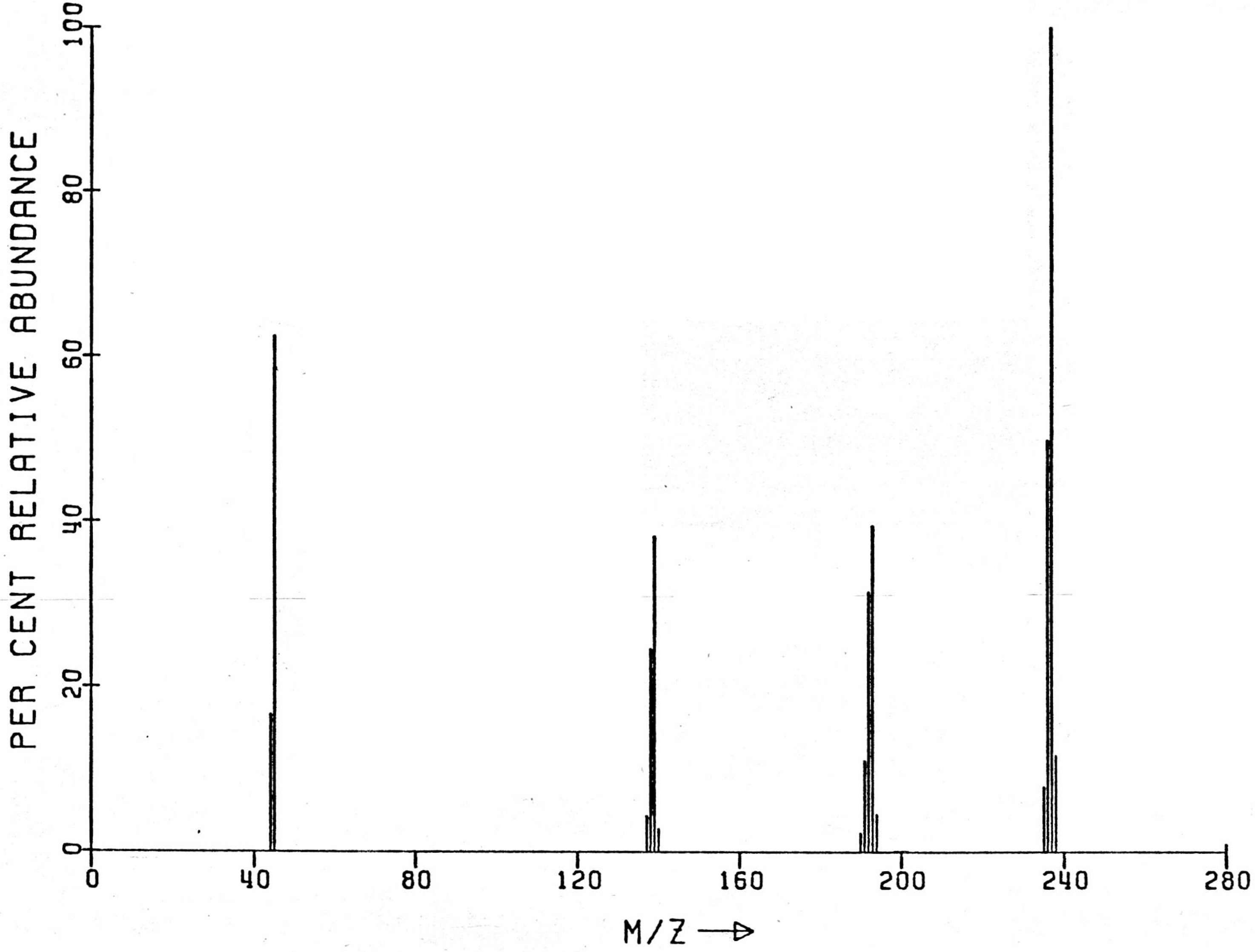


Figure 21

12 eV Mass Spectrum of Compound 17

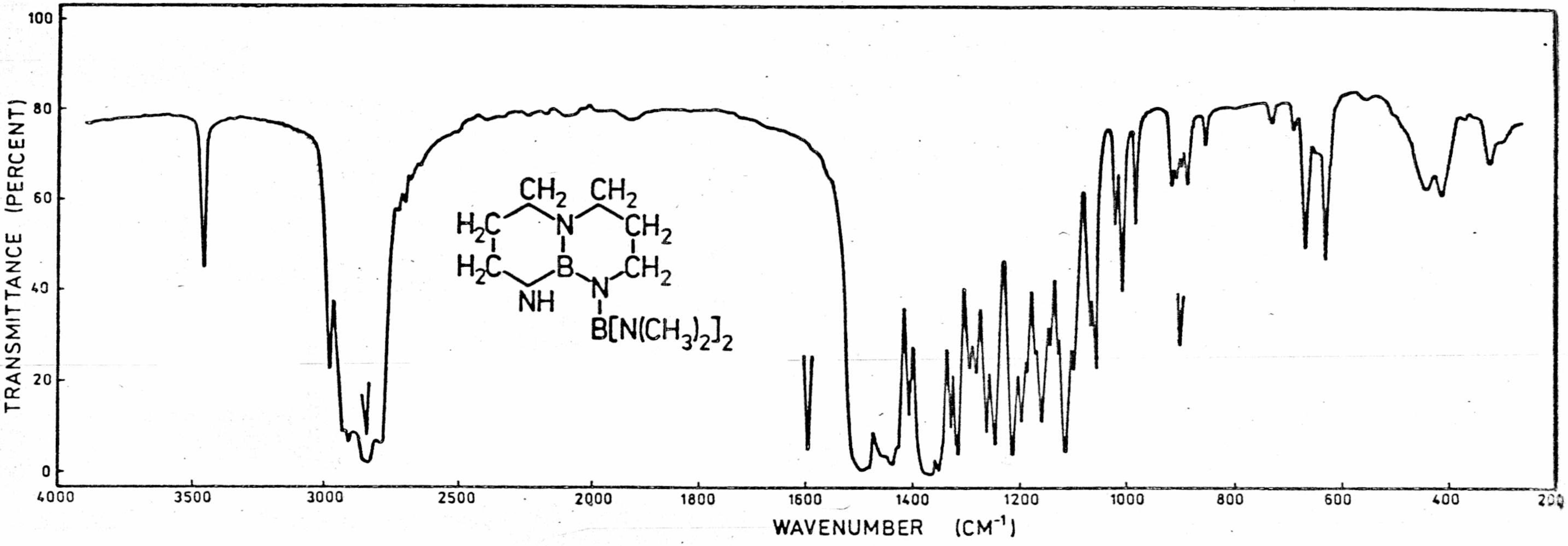


Figure 22

Infrared Spectrum of Compound 17

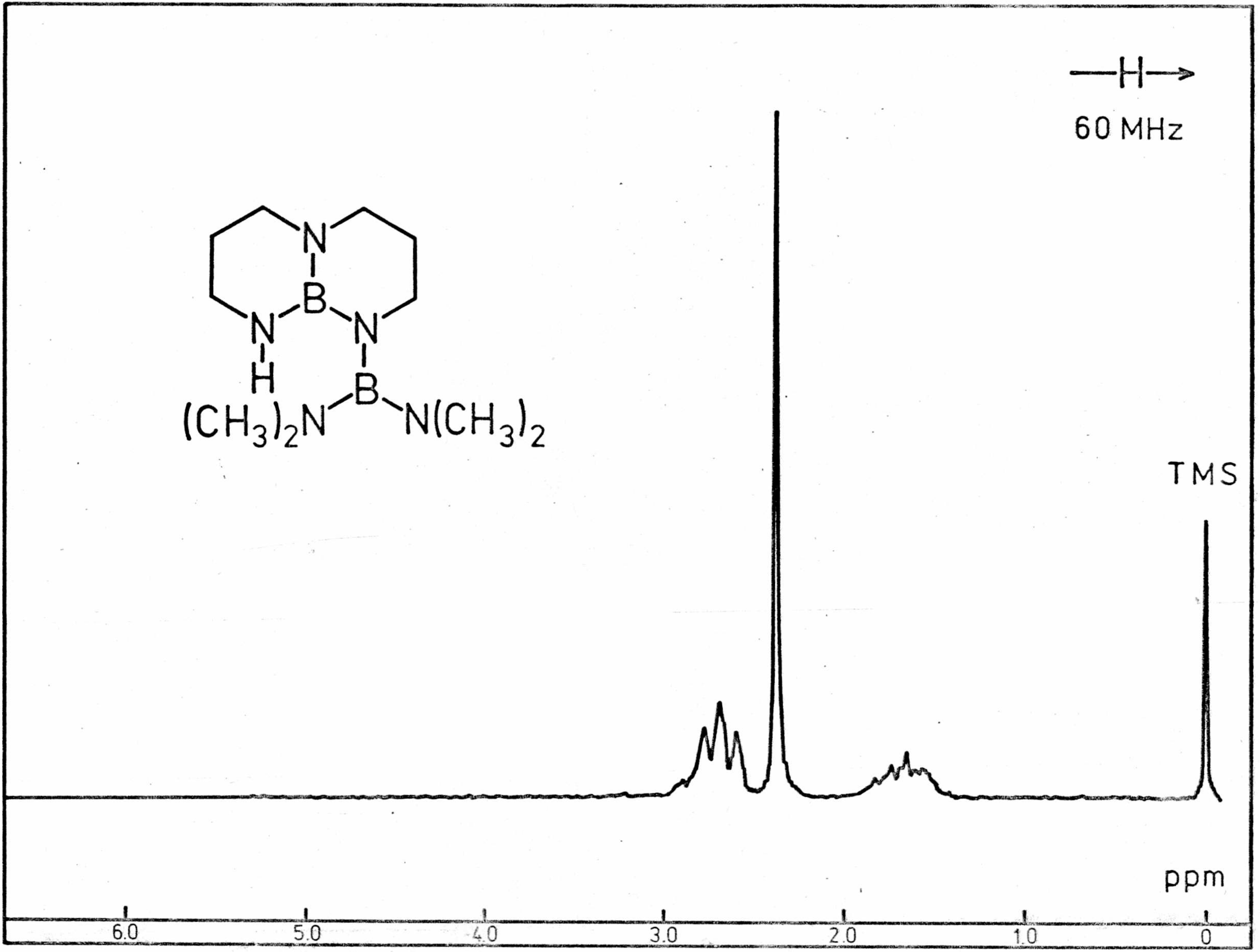


Figure 23

Proton NMR Spectrum of Compound 17

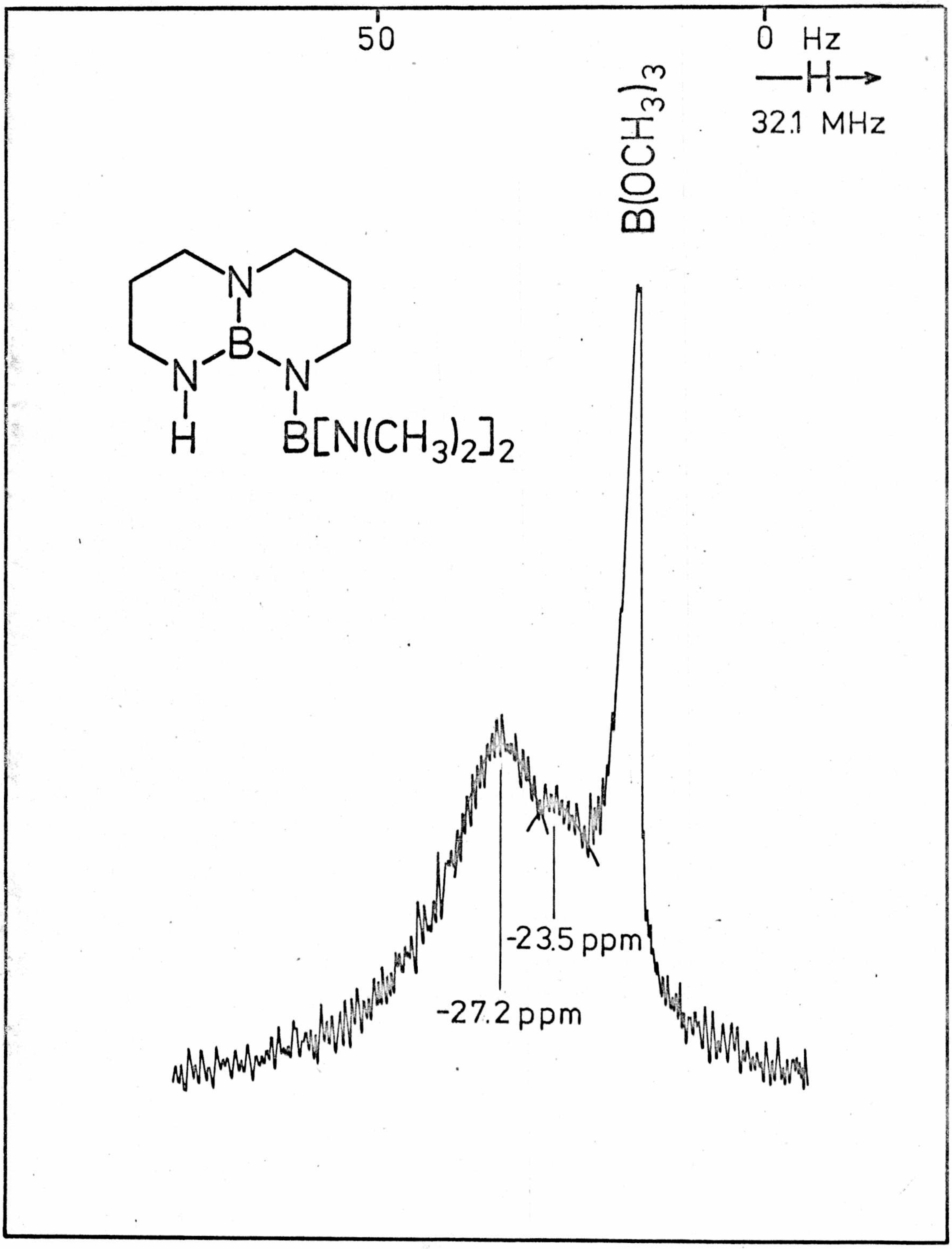


Figure 24

Boron-11 NMR Spectrum of Compound 17

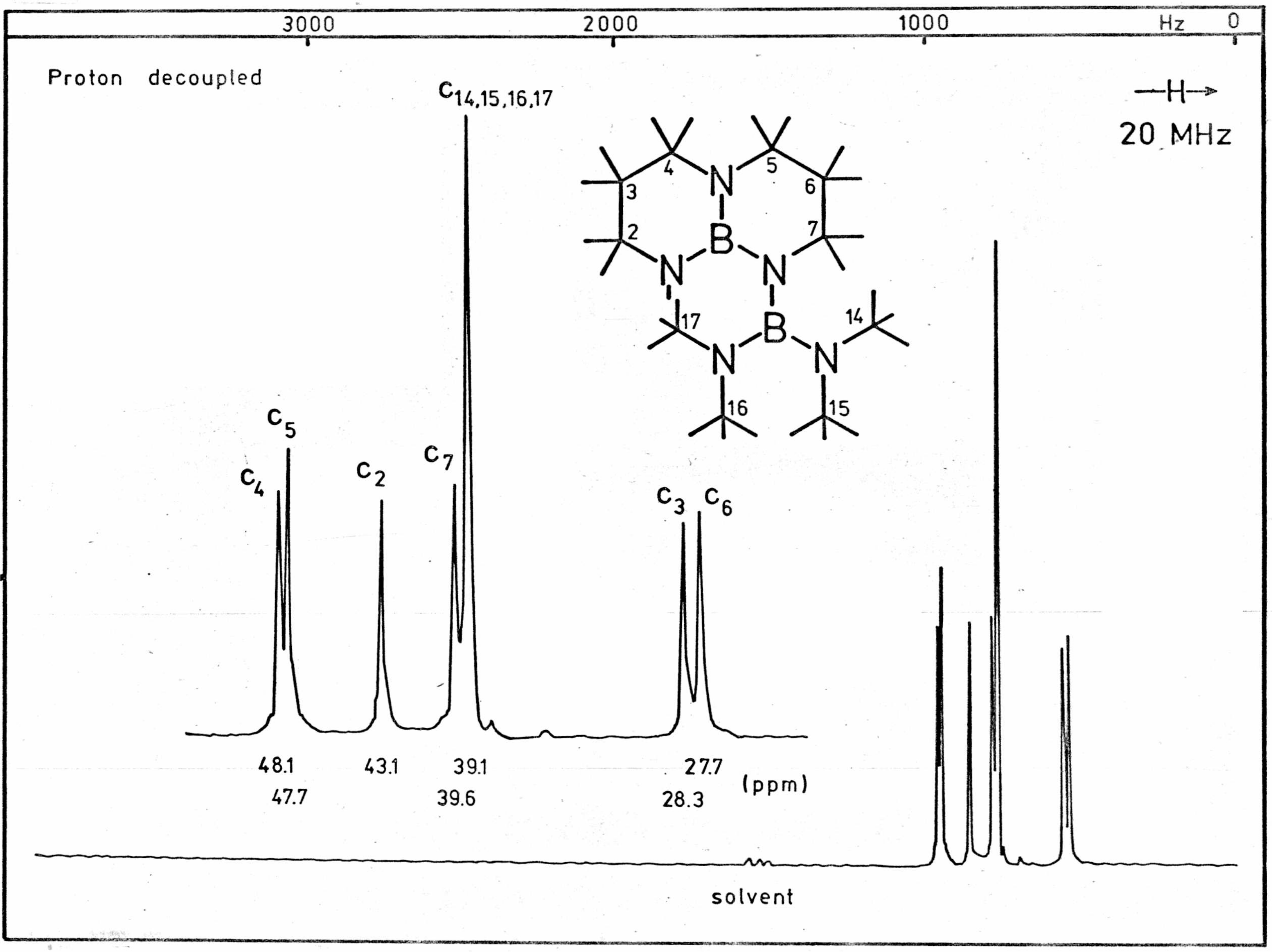


Figure 25

Proton-Decoupled Carbon-13 NMR Spectrum of Compound 17

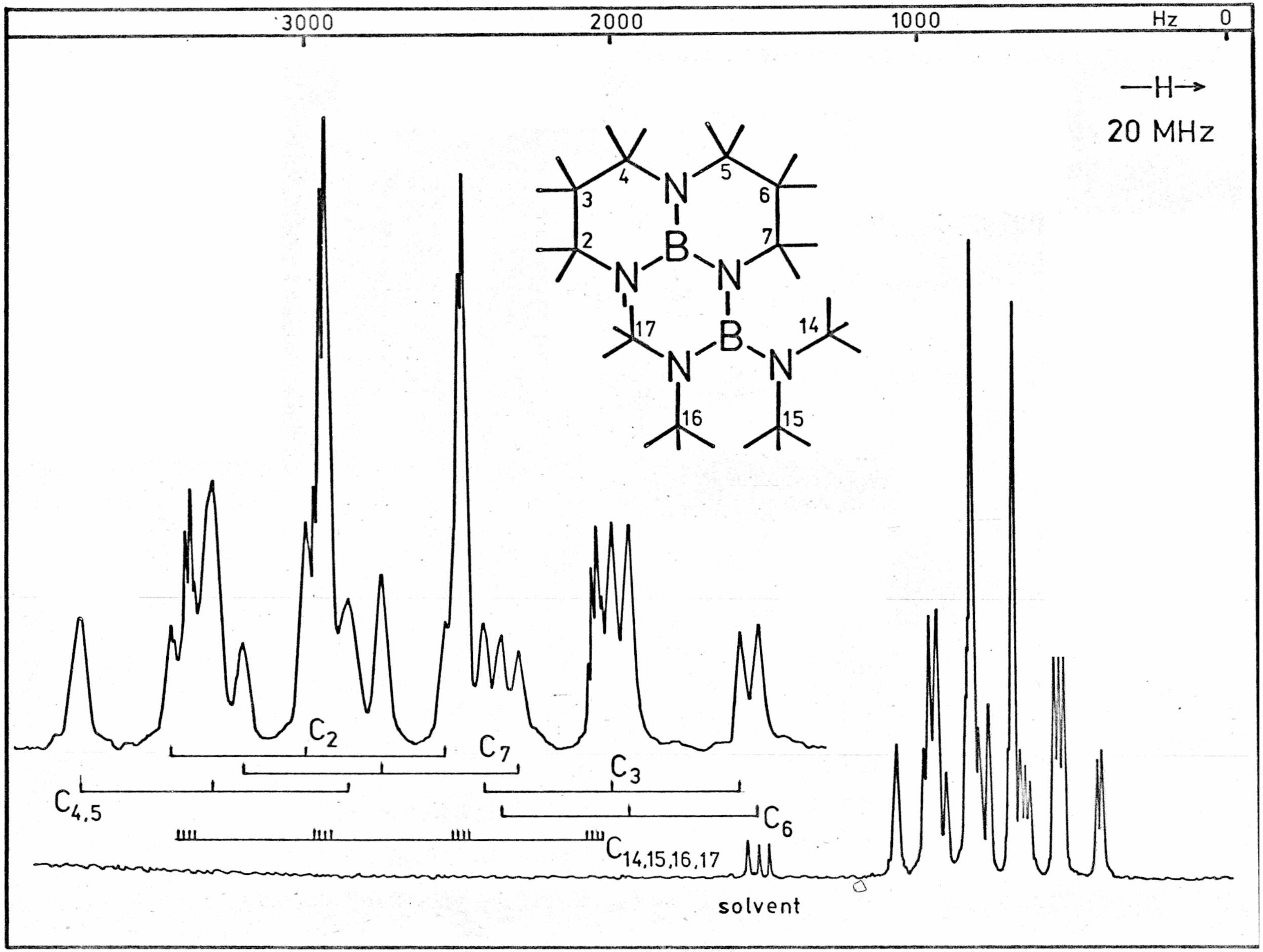


Figure 26

Proton-Coupled Carbon-13 NMR Spectrum of Compound 17

TABLE 7

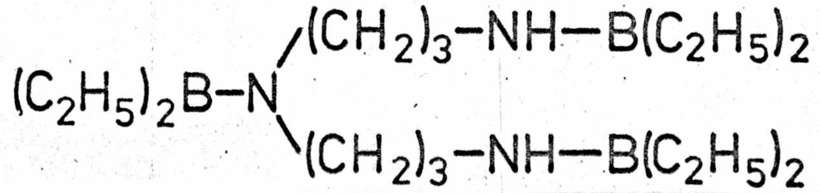
REFINEMENT OF THE CARBON-13 NMR SPECTRUM OF COMPOUND 17

Carbon Atom	$\delta^{13}C$ in ppm	Coupling Constants in Hz	
		J_{CH}	J_{CNCH}
14 - 16	39.1	133	4
2	43.1	134	
3	28.3	125	
4	48.1	132	
5	47.7	132	
6	27.7	126	
7	39.6	134	

For the numbering of carbon atoms see p. 83.

4.4 The Reaction of the 3,3'-Diaminodipropylamine with (dimethylamino)Diethylborane

The reaction of excess (diethylamino)diethylborane with 3,3'-diaminodipropylamine has previously been reported (ref. 2) to yield Compound 13.



Compound 13

N,N',N''-tris(diethylboryl)-3,3'-diaminodipropylamine

However, the compound was not characterized since, on attempt to purify it by distillation, elimination of triethylborane was observed with the formation of Compound 14, see p. 62. If (dimethylamino)diethylborane is used in an analogous reaction and the reagents are employed in nearly stoichiometric quantities, it is possible to isolate the desired Compound 13 as colorless liquid with a sharp boiling point of 123°C/0.05 Torr (ref. 2 : 130 to 150°C/1 Torr) and to determine characteristic data on the species. Besides Compound 13, another species i.e., Compound 20 (see p. 101) was simultaneously produced in course of the reaction in 3:1 molar ratio.

A weak parent peak is observed at m/e = 335 in the mass spectrum of the Compound 13. The first group of peaks of major intensity is centered at m/e = 306, indicating the ready loss of one ethyl fragment from the parent. The base peak of the mass spectrum is observed at m/e = 125. The infrared spectrum of the compound features one strong and relatively broad absorption in the NH stretching region at 3407 cm^{-1} (Figure 27). The proton NMR spectrum of Compound 13 exhibits a broad singlet with a chemical shift of 0.98 ppm which is assigned to the protons of the boron-bonded ethyl groups (see Figure 28). In addition, a quintet with $\delta = 1.45$ ppm and a quartet centered at $\delta = 2.78$ ppm are observed which are closely paralleling the chemical shift values of the carbon-bonded protons of the starting material, 3,3′-diaminodipropylamine, recorded at 1.53 and 2.65 ppm, respectively. The boron-11 NMR spectrum of Compound 13 exhibits an extremely broad signal with $h_{1/2} = 280$ Hz and containing a shoulder on the low field side (Figure 29). Carbon-13 NMR resonance signals of the boron-bonded ethyl groups of Compound 13 are evidenced by three sharp singlets and two broad bands (Figures 30, 31). The sharp signals are assigned to the methyl carbons of the diethylboryl units of which the one with lowest chemical shift is due probably to the diethylboryl group bonded to the central nitrogen of the amine moiety, see TABLE 8.

The carbon-13 chemical shift data clearly suggest steric nonequivalence of the terminal methyl groups in the molecule of Compound 13. This is not surprising in view of the structure of the compound. The nonequivalence of the boron attached methylene groups is also quite apparent,

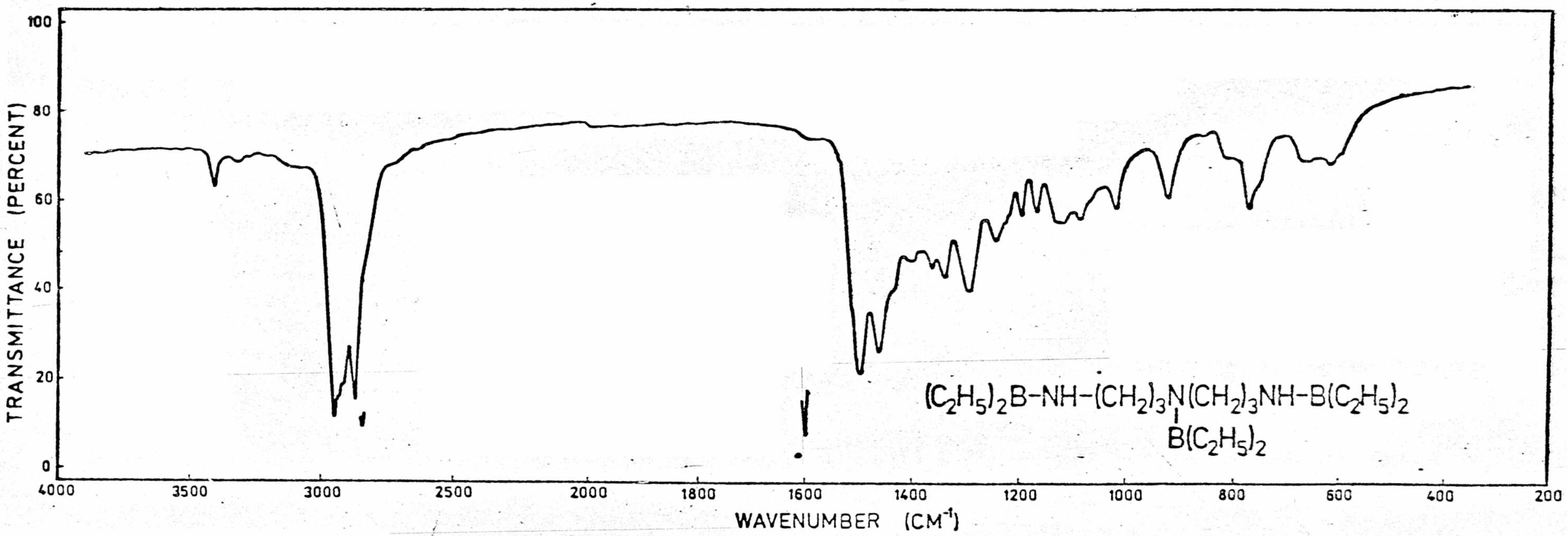


Figure 27

Infrared Spectrum of Compound 13

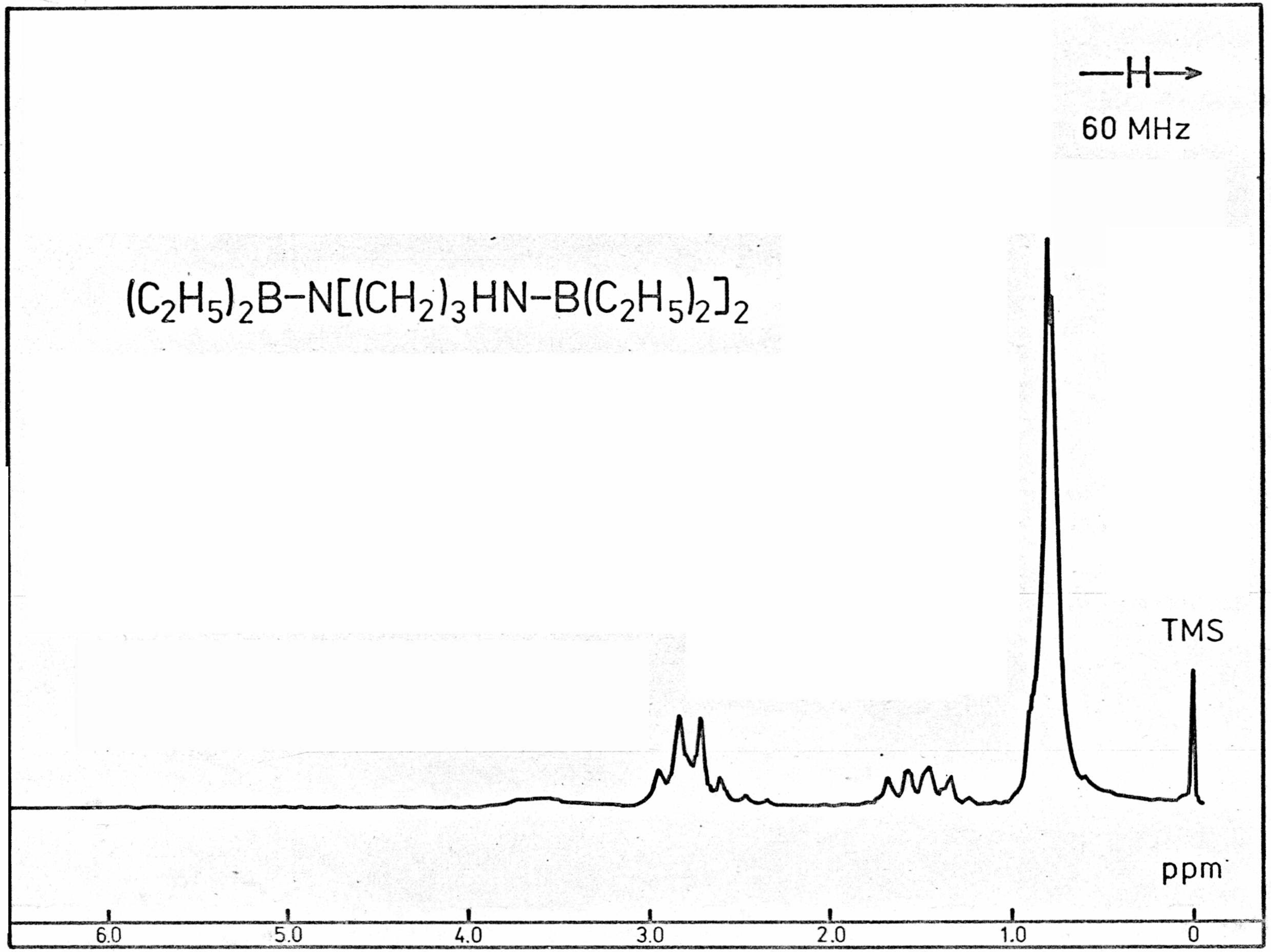


Figure 28

Proton NMR Spectrum of Compound 13

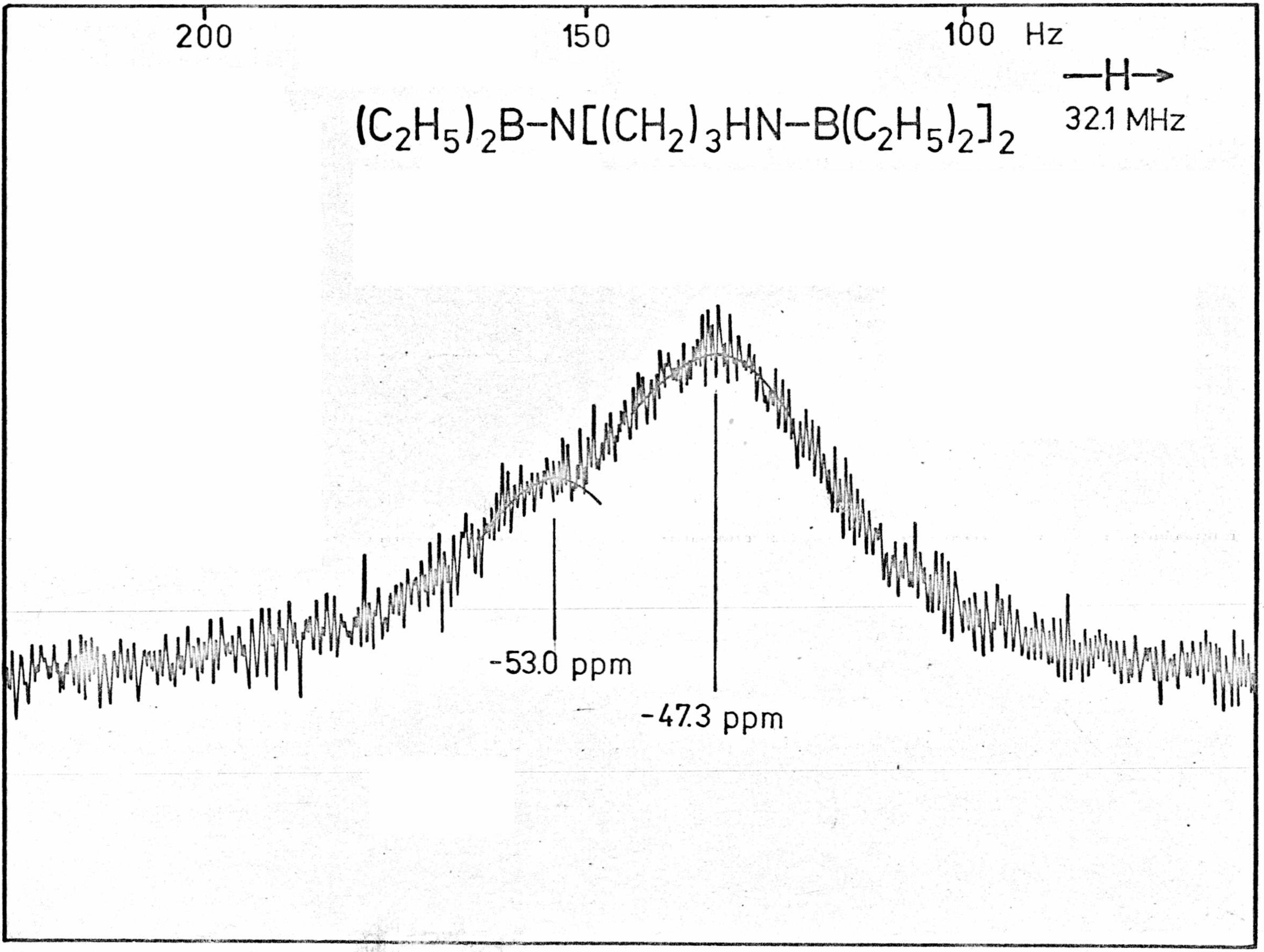


Figure 29

Boron-11 NMR Spectrum of Compound 13

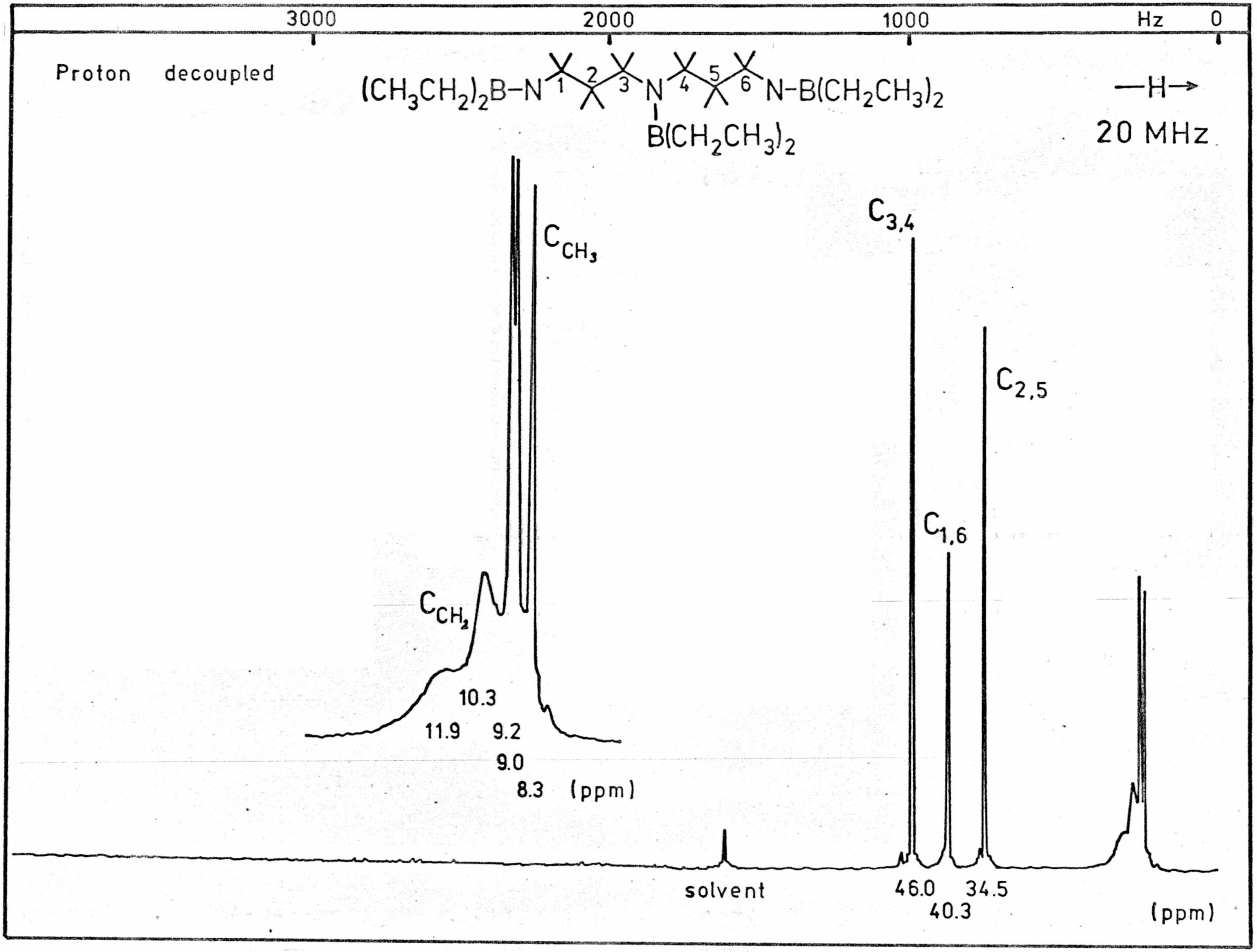


Figure 30

Proton-Decoupled Carbon-13 NMR Spectrum of Compound 13

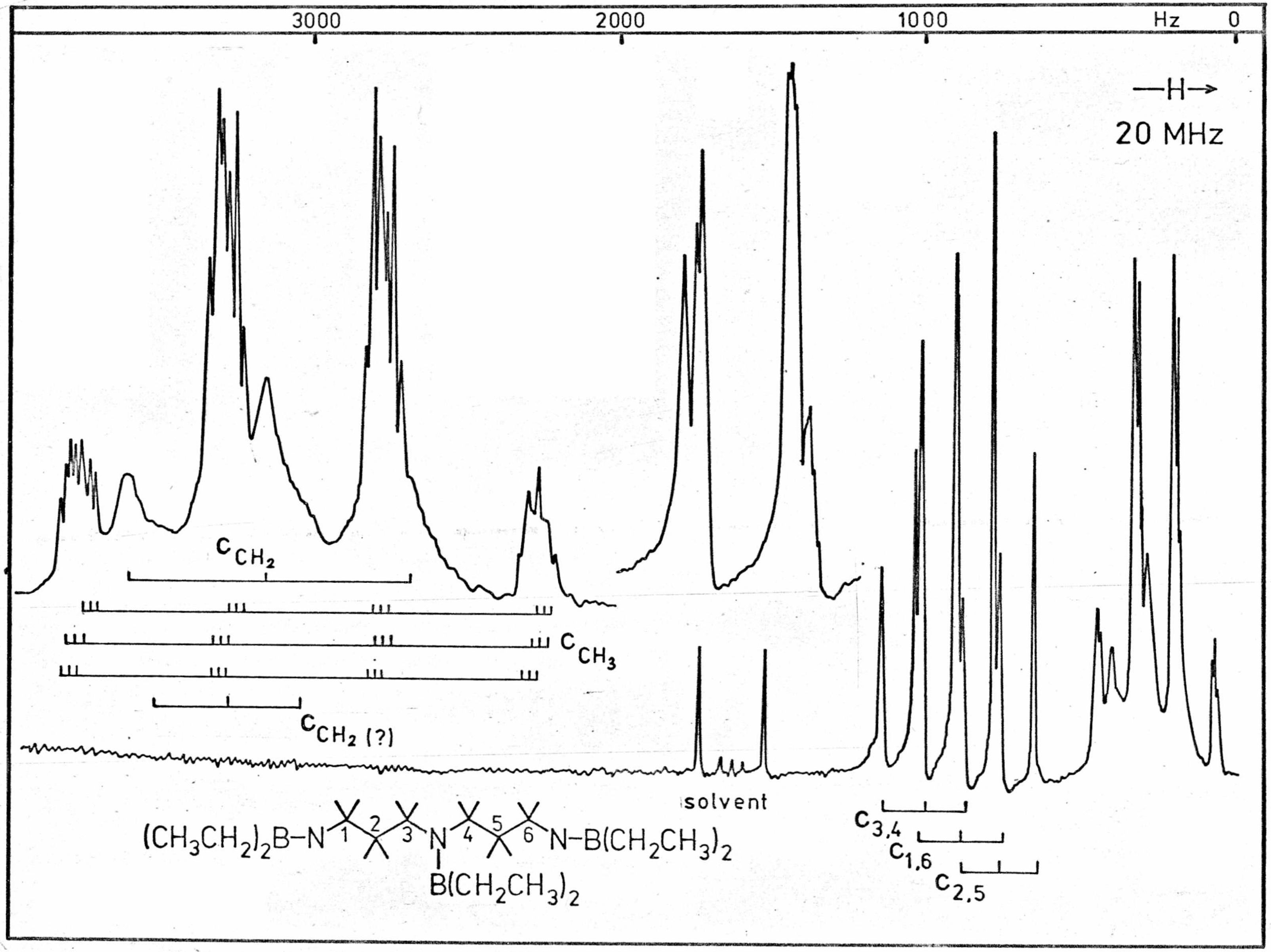


Figure 31

Proton-Coupled Carbon-13 NMR Spectrum of Compound 13

TABLE 8

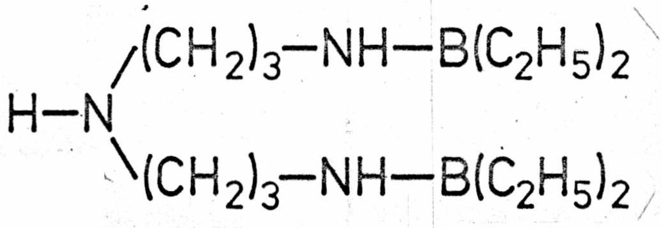
CHEMICAL SHIFT AND COUPLING CONSTANT DATA FOR COMPOUND 13

Carbon atom	$\delta^{13}C$ in ppm	Coupling Constants in Hz J_{CH}	J_{CCH}
1, 6	40.3	134	
2, 5	34.5	126	
3, 4	46.0	133	4
(B)$\underline{C}H_2$	10.3, 11.9	115, 70 ?	
$\underline{C}H_3$	8.9, 9.0, 9.2	126	6

since the difference in chemical shift values is pronounced with Δ = 1.6 ppm.

Based on the data of the elemental analysis, the second product of the cited reaction, i.e., Compound 20, b.p. 94 - 95°C, is a bis(diethylboryl)derivative of 3,3'-diaminodipropylamine. Subsequently, this same compound was obtained in good yield by reacting (dimethylamino)diethylborane and 3,3'-diaminodipropylamine in a 2:1 molar ratio.

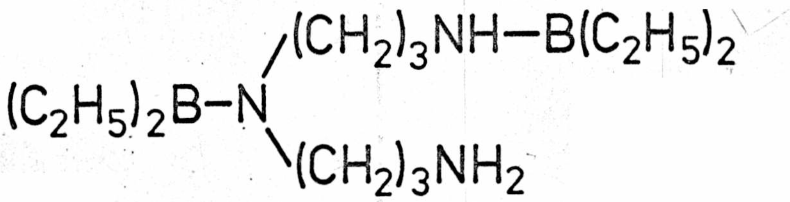
Two structures are possible, i.e.:



Compound 20

3,3'-bis(diethylborylamino)-dipropylamine

And unsymmetrical structure :



The mass spectrum of the material shows a very weak parent peak at m/e = 267 ; a significant peak is observed at m/e = 238, which corresponds to the loss of ethyl from the parent ion. In the infrared spectrum of the compound two bands are observed in the NH stretching region at 3408 (sharp) and 3340 (broad) cm^{-1}, respectively (see Figure 32). The proton NMR spectrum exhibits a broad resonance signal with δ = 0.83 ppm which is assigned to the proton of the boron bonded ethyl groups, two triplets of equal intensity centered at δ = 2.63 and 3.03 ppm respectively (N-methylene groups), and a quintet with δ = 1.57 ppm

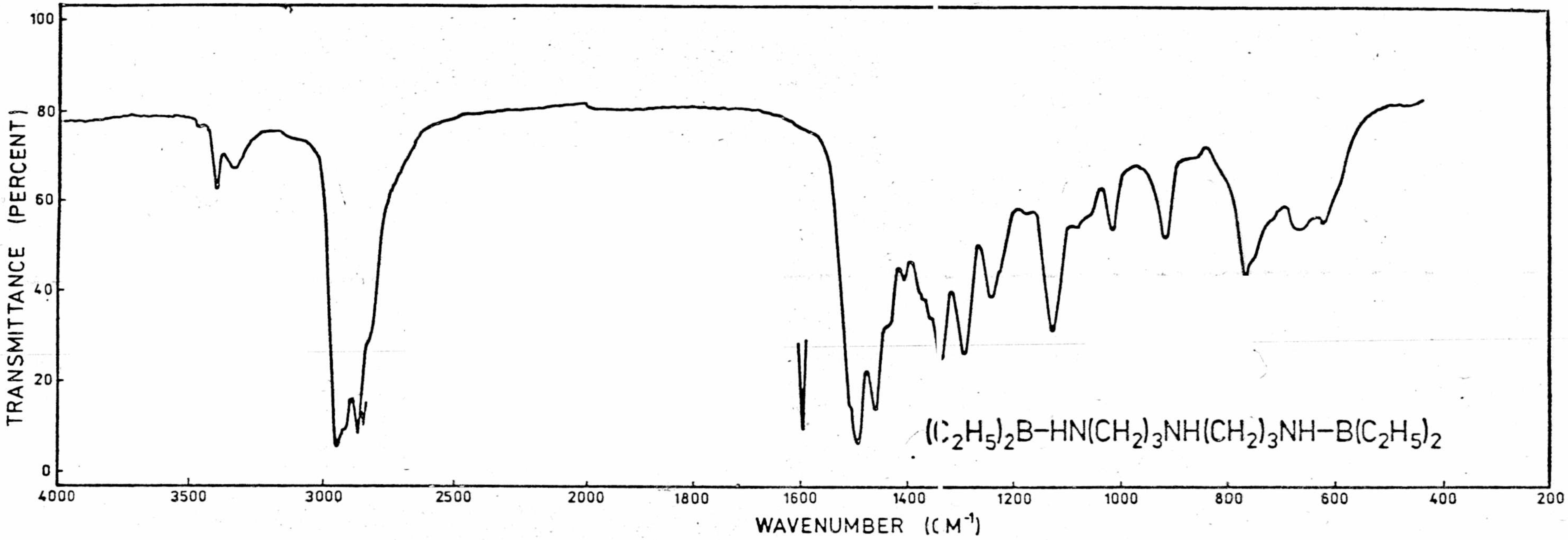


Figure 32

Infrared Spectrum of Compound 20

assigned to the two central methylene groups protons of the amine moiety.

The proton-decoupled carbon-13 NMR spectrum exhibits a singlet with δ = 9.1 ppm, assigned to the carbon of the boron bonded ethyl groups, and three sharp singlets with δ = 34.0, 41.3, and 48.2 ppm, respectively, assigned to the carbon atoms of the amine moiety. These data seem to support the symmetrical structure of Compound 20. This latter is further substantiated by the observation of only one boron-11 signal with a chemical shift δ = -41.1 ppm, see Figure 33.

The formation of Compound 20 appears to be unusual in view of the findings on the interaction of triethylamine-borane as a source of borane(3) with 3,3'-diaminodipropylamine. In this latter reaction only the trihydroboryl analog of Compound 13 was obtained and all attempts to prepare an analog of Compound 20 were in vain. On the other hand, employing a 1:1 molar ratio of (dimethylamino)-diethylborane and 3,3'-diaminodipropylamine it was not possible to obtain a monoborylated species. Rather, exclusive formation of Compound 20 occured and the excess of 3,3'-diaminodipropylamine was recovered.

It is of considerable interest to note, that 1,8,10,9-triazaboradecalin does not react with (dimethylamino)diethylborane. Even on prolonged reflux of a mixture of the two compounds at temperatures up to 120°C no reaction occurred and the two reactants were recovered unchanged in essentially quantitative yield.

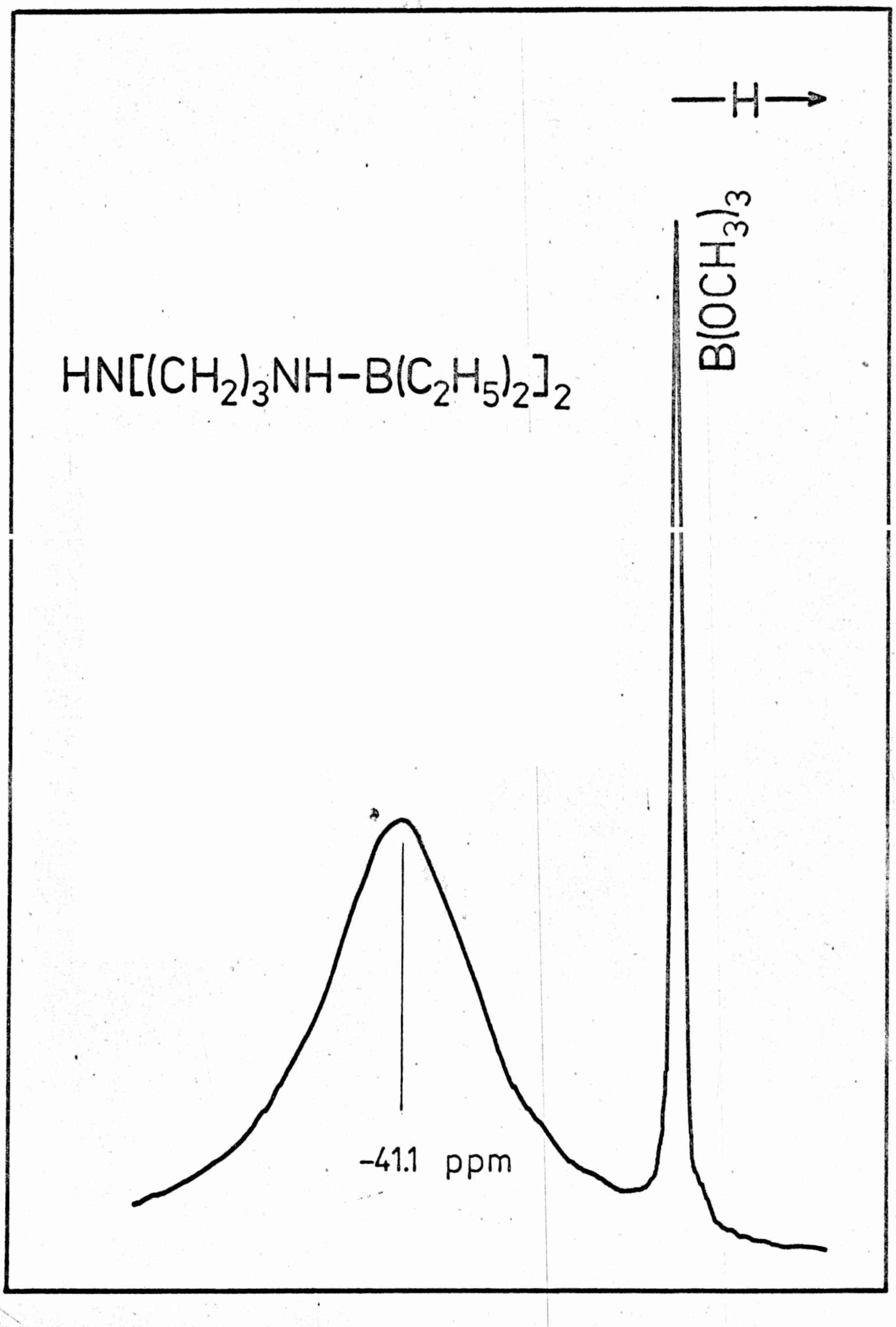


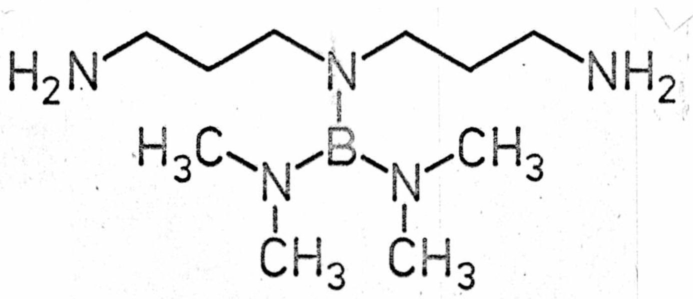
Figure 33

Boron-11 NMR Spectrum of Compound 20

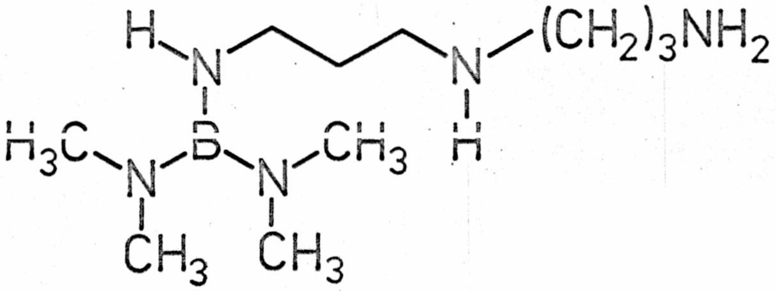
4.5 Discussion

The objective of the work as described in the preceding sections was to study boron derivatives of 3,3′-diaminodipropylamine. Two important mechanistic features of the compound under consideration were established. Firstly, the tendency of boron to achieve four-coordination leads to the formation of various inter- or intramolecular coordinated species and secondly, some geometrical factors - among which the planarity of a X_2BN moiety seems to be most significant - play an important role in governing the overall processes.

Intermolecular interactions lead to the stabilization of linear species, e.g., Compound 16. If the intermolecular interaction is diminished by appropriate substitution on boron, e.g., ethyl groups, triborylated species exist but cyclize readily. The lack of formation of a tris(bisdimethylaminoboryl) derivative of 3,3′-diaminodipropylamine is readily explained by the great tendency of a boron-attached dimethylamino group to undergo a transamination and it appears reasonable to view the reaction of 3,3′-diaminodipropylamine with tris(dimethylamino)borane as a stepwise process. After one $B[N(CH_3)_2]_2$ group is bonded to a nitrogen atom of the amine, the molecular arrangement may be illustrated by the following two possibilities :



or



Both arrangements show equally close proximity of the bis(dimethylamino)boryl moiety to either a C_2NH or CNH_2 entity, promoted by the planarity of the CNBNC unit that is caused by the multiple bond character of the BN unit. This occurrence provides for an extremely favorable situation to undergo an intramolecular transamination reaction, *i.e.*, elimination of $HN(CH_3)_2$, which leads then to the formation of a 1,3,2-diazaboracyclohexane ring. This type of intramolecular transamination seems to take precedence over an intermolecular reaction with a new $B[N(CH_3)_2]_3$ molecule. After the first ring is closed, the geometrical arrangement of the remaining boron attached dimethylamino group seems to favor another transamination process and the overall reaction yields 1,8,10,9-triazaboradecalin as the only isolable product of such a reaction. The existence of diborylated intermediate is an requirement for intramolecular interaction that either promotes close B-N proximity and elimination of H_2 or of trialkylborane, or this latter process is hindered by substitution on boron.

Monoborylated linear 3,3'-diaminodipropylamine derivatives remain unknown. Their existence as isolable species may be excluded in case of amino- or hydroborylated molecules, since they so readily cyclize.

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Monoborylated linear 3,3'-diaminodipropylamine derivatives remain unknown. Their existence as isolable species may be excluded in case of amino- or hydroborylated molecules, since they so readily cyclize.

TABLE 9

MOLECULAR PARAMETERS OF COMPOUNDS 6 AND 7

Interatomic Distances in Å		Bond Angles in degree	
	Compound 6		
C-H	1.060	HCH	109.5
H-H	0.885	NBN internal	119.5
N-B	1.424	NBN external	121.5
(B)N-C(C)	1.453	BNC	121.4
(N)C-C(C)	1.520		
	Compound 7		
C-H	1.115	NBN	120.0
C-C	1.534	BNC	121.6
N-C	1.454	CCC	113.4
N-B	1.417	NCC	110.4

For Compound 6 the molecular parameters were taken from crystallographic data (ref. 29) as listed in TABLE 9. The parameters for Compound 7 were based on the electron diffraction data reported for some 1,3,2-diazaboracycloalkanes (ref. 20, 21).

Calculation of the molecular parameters was performed by the INDO semiempirical method; its parametrisation has been described in detail (ref. 91). It is based on the general LCAO MO model and an accurate fit of the calculated electronic spectra with experimental data that has been demonstrated for many simple organic compounds. According to the authors, properties of an isolated molecule in either ground or excited state are better reproduced than in any other semiempirical approach.

5.2 Ionization Energy, Electron Affinity, Dipole Moments

Selected LCAO coefficients that are indicative of the participation of a given atomic orbital in the molecular orbital are illustrated in Figures 34 and 35 for the highest occupied and the lowest empty orbitals for both molecules under consideration.

The common feature of both species is the relatively high participation of p_z-orbitals of nitrogen in the MO of the molecule and the high share of boron p_z-orbitals in the MO of the negative ion. The vertical ionization energy in Koopmans approximation was calculated for each molecule. The results of such calculations are known to be

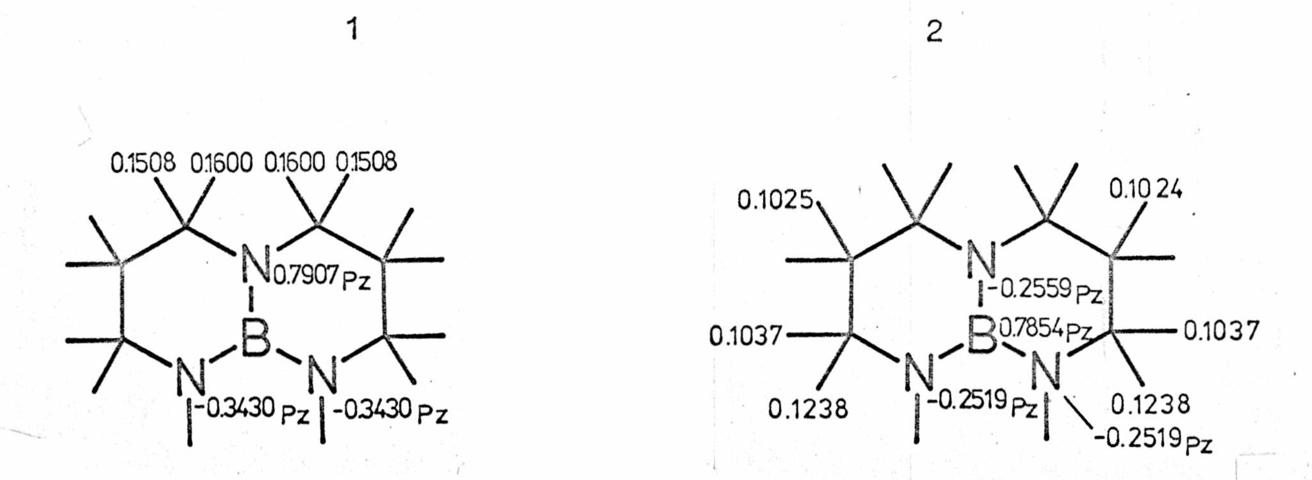


Figure 34

LCAO Coefficients of the Highest Occupied (1) and the Lowest Empty MO (2) for the Molecule Compound 6

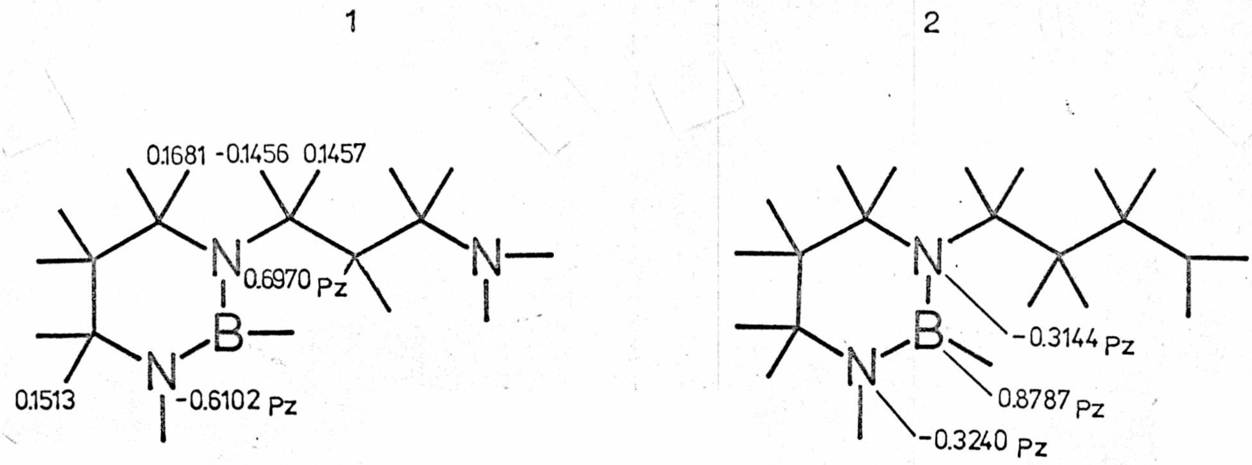


Figure 35

LCAO Coefficients of the Highest Occupied (1) and the Lowest Empty MO (2) for the Molecule Compound 7 high by about 10 %. Also, the electron affinity and the dipole moments for the neutral molecule were calculated. The data are summarized in TABLE 10.

TABLE 10

PARAMETERS CALCULATED BY THE INDO METHOD FOR THE MOLECULES OF COMPOUNDS 6 AND 7 IN THEIR ELECTRONIC GROUND STATES

Parameter	Units	Compound 6	Compound 7
Ionization Energy	eV	10.20	10.78
Electron Affinity	eV	-1.76	-0.904
Dipole Moment	D	0.24	3.32

5.3 Net Atomic Charges and Bond Orders

The excess charges on selected atoms within the molecules were calculated ; only the atoms involved in a planar configuration were considered. The charge is then divided into σ- and π-contributions according to the π-electron approximation. The net charge on the atom has been defined as

$$q_A = n_A - \sum_{i \in A} P_{ii}$$

where n_A is a number of valence electrons of the particular atom and P_{ii} is the matrix of the bond order. A negative sign of q_A denotes that the effective charge on the atom is greater than n_A , *i.e.*, the atom gained some extra charge as shown in TABLE 11. In both cases the boron appears to be σ-electron donor, although it gains relatively high extra π-charge into its p_z-orbital. There is a charge deficiency on the boron by as much as 0.35e, whereas all nitrogens atoms accumulate extra charge. The electron donation from nitrogen to boron occurs only in the π-electron sphere and is compensated by σ-electron drift toward the nitrogen. The bond orders are calculated as π-bond indices and as bond orders according to the Wiberg's definition (ref.92) for all atoms in the planar moiety ; they are given in TABLE 12.

TABLE 11

NET ATOMIC CHARGES CALCULATED BY THE INDO METHOD

Atom	q_A(total)	$q_A(\sigma)$	$q_A(\pi)$
	Compound 6		
H(NH)	0.1187	0.1187	-
N(CNC)	-0.2937	-0.4733	0.1996
N(NH)	-0.3463	-0.5376	0.1913
B	0.3501	0.8619	-0.5118
	Compound 7		
H(NH)	0.1268	0.1268	-
H(BH)	-0.1506	-0.1506	-
N(CNC)	-0.2150	-0.4650	0.2500
N(NH)	-0.2796	-0.5190	0.2394
B	0.2285	0.6700	-0.4419

TABLE 12

π-BOND INDICES AND WIBERG'S BOND ORDERS FOR THE BONDS WITHIN THE PLANAR PART OF THE MOLECULES OF COMPOUNDS 6 AND 7

Compound	Bond	π-Bond index	W_{AB}
6	B-N(CNC)	0.4918	1.1340
6	B-N(NH)	0.5024	1.1430
6	C-N(CNC)	0.1343	0.9733
7	B-N(CNC)	0.5740	1.2440
7	B-N(NH)	0.5837	1.2522

$$W_{AB} = \sum_{i \in A} \sum_{j \in B} (P_{ij})^2$$

The B-N bond order in Compound 7 appears to be greater than in Compound 6. This somewhat surprising result may be caused by the bond distance data, which are smaller for Compound 7. The bond indices for the B-N bond are in the same range as reported for borazines (ref. 87). Although their relatively high values suggest the overall bond order to be high, a value of 1.25 was the largest obtained. Unfortunately, no reliable assignments of the B-N stretching modes of Compound 7 have been reported and, hence, no comparison of calculated bond orders with the antisymmetric B-N stretching mode can be made.

5.4 The UV Spectrum of 1,8,10,9-Triazaboradecalin

Altough there are some theoretical as well as experimental studies on UV spectra of borazines (ref. 43), very little attention has been paid to the 1,3,2-diazaboracycloalkanes (ref. 19).

The UV spectrum of Compound 6 was recorded on saturated solutions of the species in cyclohexane and n-hexane. The concentration was less than 10^{-5} mol/l and the extinction coefficient could not be determined due to the lack of exact concentration data. The spectrum does not exhibit any absorption beyond λ = 210 nm, but there appears to be at least one absorption band at about 200 nm; however, this is below the solvent cut-off limit and thus could not be completely recorded. The calculated data do not contradict the experimental spectrum, at least with respect to not showing transitions at wavelength longer than 210 nm (see Figure 36). The calculation also reveals that all transitions of reasonably large oscillator strength are in the range 170 - 200 nm (see TABLE 13).

It was also possible to compare the bond orders and excess charges of atoms in various excited states; the data are compiled in TABLE 14. Inspection of this listing indicates that in the first three electronic transisions the σ-charge density on all atoms remains unchanged and, hence, they may be classified as π-transitions. The first one, $S_0 - S_1$, effects the most dramatic change: electrons are shifted from the nitrogen toward boron that becomes

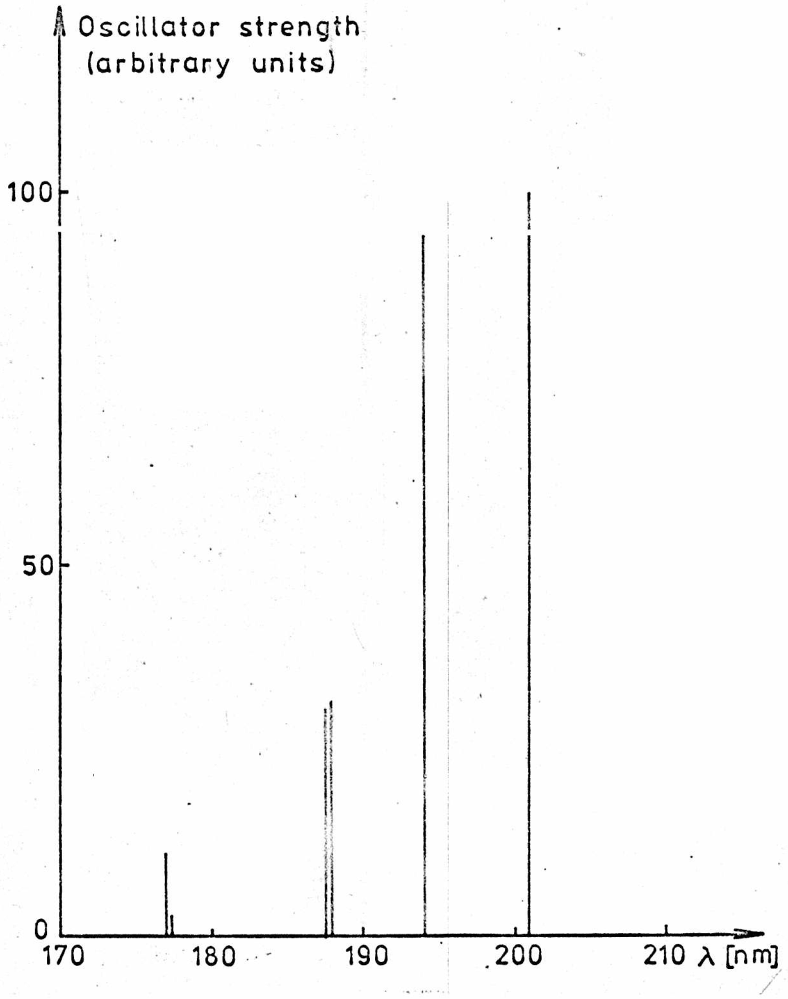


Figure 36

First Six Electronic Transitions, S-S$_0$, Calculated by the INDO Method for 1,8,10,9-Triazaboradecalin

TABLE 13

FIRST EXCITED STATES (SINGLETS) OF 1,8,10,9-TRIAZABORADECALIN AS RESULTING FROM INDO CALCULATIONS

Electronic state	Energy [eV]	Oscillator strength	Wave length [nm]	Polarization
S_1	6.14	0.233	201	yz
S_2	6.40	0.221	194	x
S_3	6.58	0.074	188	yz
S_4	6.61	0.071	187	x
S_5	7.00	0.006	177	x
S_6	7.02	0.026	176	yz

Energies are related to the electronic ground state

In the employed coordinate system the xy plane was the plane of the BN_3 moiety with the y axis going along the annular B-N bond.

TABLE 14

NET ATOMIC CHARGES AND BOND INDICES OF 1,8,10,9-TRIAZABORADECALIN IN EXCITED STATES (SINGLETS) RELATED TO THE GROUND STATE

Electronic State	Net Atomic Charges						Bond Indices		Dipole Moment in [D]
	B		(C)N(C)		N(H)		B-N (CNC)	B-N (NH)	
	σ	π	σ	π	σ	π			
S_0	0.8619	-0.5118	-0.4933	0.1996	-0.5376	0.1913	0.4918	0.5024	0.24
S_1	0.8617	-1.1707	-0.4935	0.6935	-0.5392	0.2740	0.2669	0.2904	3.99
S_2	0.8613	-1.0509	-0.4937	0.1716	-0.5390	0.5654	0.3232	0.3195	2.65
S_3	0.8599	-0.5768	-0.4950	0.4010	-0.5363	0.5010	0.4894	0.4465	1.05

a center of a negative charge in the molecule. The B-N π-bond order diminishes distinctly. This observation may indicate that in its first excited state, S_1 , 1,8,10,9-triazaboradecalin could be subject of electrophilic attack to the boron ; this interpretation implies the possibility of interesting photochemical reactions of this compound.

5.5 Heat of Dehydrogenation

The preceding calculations provided the total energy values for Compound 6 and 7. These two compounds are related to each other by a simple dehydrogenation - condensation process. It is possible to estimate the heat of such a thermal intramolecular condensation on the basis of the employed method. Total energies as obtained from the INDO calculation are :

Compound 6 $E_d = -1768.246$ eV

Compound 7 $E_c = -1736.191$ eV

H_2 $E_h = -37.025$ eV

The heat of the following reaction is considered:

$$\text{Compound 7} \longrightarrow \text{Compound 6} + H_2 \qquad -\Delta E$$

Energy conservation principle requires that

$$E_c = E_d + E_h - \Delta E$$

and thus

$$\Delta E = E_c - E_d - E_h = 4.97 \text{ eV} = 114.1 \text{ kcal/mol}$$

The sign of this latter value meets the expectation for the endothermic reaction, but the numerical value is quite high. Since the datum is obtained by the same method as the parameters of the UV spectrum and other data as outlined above, it should be viewed with considerable caution. It is known that the INDO method does not provide sufficiently accurate results when it is utilized in this type of calculation.

6

EXPERIMENTAL

The general high sensitivity of boron-nitrogen compounds toward moisture and oxygen requires special preparative techniques, in order to assure sufficient purity of compounds to be synthesized. Hence, all reactions ans transfers were carried out in inert atmosphere under argon cover.

Solvents were dried by conventional methods employing appropriate drying agents and were subsequently rectified under argon.

6.1 Analyses

Eelemental analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., USA. The following data were obtained in the Department of Chemistry of the University of Kentucky, Lexington, Ky., USA:
IR spectra were recorded using a Perkin-Elmer Model 621 spectrometer employing standard operating condition. Proton NMR spectra were recorded on a Varian T-60 spectrometer using TMS as external reference. Carbon-13 spectra were obtained on the Varian CFT-20 spectrometer; lock signals were provided from a deutereted solvent or a sealed capillary tube filled with acetone-d_6. TMS is used as a reference, positive values of the chemical shift denote downfield shift from standard. Mass spectral data were obtained on a Perkin-Elmer-Hitachi RMU-7 instrument.

Boron-11 spectra were recorded on a Varian HA-100 spectrometer at 32.1 MHz, using external $B(OCH_3)_3$ as a reference ; chemical shifts were recalculated and are given versus $(C_2H_5)_2O \cdot BF_3$ as a reference, negative sign denoting downfield shift from standard. The spectra were provided by Professor S. G. Shore of the Ohio State University, Columbus, Ohio, USA. One spectrum (Figure 33) was recorded on a Bruker HX8 instrument ; it was supplied by Professor A. Meller of the University of Göttingen, Göttingen, Germany.

The following analytical data were obtained at the Institute of the Organic and Physical Chemistry of the Technical University of Wrocław, Wrocław, Poland : The UV spectrum was recorded on the UNICAM SP-1800 spectrometer in the Analytical Laboratory. Calorimetric studies employed the Perkin-Elmer DSC-1b differential scanning calorimeter. The molecular weight determination was performed by the cryoscopic method in benzene using naphthalene as a standard.

Computer calculations were performed at the Computer Center of the Technical University of Wrocław on the ODRA 1300 computer ; the employed program was kindly provided by Dr J. Lipiński of the Technical University of Wrocław.

6.2 Starting Materials and Known Compounds

1. 3,3′-Diaminodipropylamine

3,3′-Diaminodipropylamine (Ames Laboratory, Milford, Connecticut, USA) was stored over KOH pellets and freshly distilled under vacuum before use.

2. Trimethylamine-Borane

Trimethylamine-borane was a commercial product (Columbia Organic Chemical Co., Inc., Columbia, South Carolina, USA).

3. Tris(dimethylamino)borane

Tris(dimethylamino)borane was prepared following the procedure described in ref. 93, using BCl_3 (Matheson Gas Company, East Rutherford, New Jersey, USA) and dimethylamine (Fisher Scientific Co., Cincinnati, Ohio, USA) as starting materials. The product was distilled twice under reduced pressure using a 20 cm silver-mantle column to yield up to 86% of tris(dimethylamino)borane, b.p. 38°C/ 9 Torr. Proton NMR and IR spectra of the compound were compared with those of authentic samples of the material.

4. (dimethylamino)Diethylborane

(dimethylamino)Diethylborane was prepared by prolonged reflux of a 1:2 molar mixture of tris(dimethylamino)borane and triethylborane (Callery Chemical Co., Callery, Pensylvania, USA) in benzene. The solvent was then stripped off and the product was distilled under normal pressure, b.p. 119°C (Lit. 118°C, ref. 94).

5. Compound 7 - Reaction of trimethylamine-borane with 3,3′-diaminodipropylamine in 1:1 molar ratio.

A solution of 22.50 g (0.308 mol) of trimethylamine-borane in 150 ml of benzene is warmed to approximately 75°C and 40.7 g (0.310 mol) of 3,3′-diaminodipropylamine are added very slowly with stirring and continued heating. After heating for another hour, benzene is distilled off and the residue is distilled under reduced pressure over a 20 cm silver-mantle column to yield approximately 33 g of Compound 7 as a colorless liquid, b.p. 54 - 55°C/1 Torr. Analysis: Found: C,51.28; H, 11.68; N, 29.67; B, 7.74. $C_6H_{16}N_3B$ calcd.: C,51.08; H, 11.44; N, 29.81; B, 7.67%.

The material does not readily decompose on heating to 100°C ; however, on prolonged storing at room temperature, slow gas evolution is observed. Ready decomposition occurs within several hours at 170°C and under athmospheric pressure ; it leads to the quantitative formation of Compound 6. The nature of the latter was verified by comparison with an authentic sample of the compound (ref. 2).

The vast majority of additional compounds needed for this work as described in Chapter 3 was also prepared by the author in the framework of this thesis. Details can be found in ref. 7 and need not to be repeated here.

6.3 Preparation of New Compounds

1. Compound 16 - Reaction of trimethylamine-borane with 3,3′-diaminodipropylamine in 3:1 molar ratio.

A mixture of 12.40 g (0.170 mol) of trimethylamine-borane, 7.55 g (0.058 mol) of 3,3′-diaminodipropylamine, and 100 ml benzene is refluxed for approximately 15 h. After approximately 3 h some inhomogeneity of the mixture is observed which disappears after relatively short period of additional heating. Benzene is stripped off at athmospheric pressure and remaining volatiles are removed at room temperature under vacuum to leave Compound 16 as a colorless glassy material.

Analysis: Found: C, 42.47; H, 12.18; N, 25.06; B, 19.63.
$C_6H_{20}N_3B_3$ calcd.: C, 43.11; H, 11.98; N, 25.15; B, 19.76%.

The product does not have a sharp melting point (see section 4.2, p. 75). The mass spectrum of the material does not show the expected parent peak at m/e = 167. Rather, the highest peak is observed at m/e = 139, corresponding to Compound 6, thus indicating decomposition of Compound 16 under the operating conditions..

2. Compounds 7 and 16 - Simultaneous formation of the species in the reaction of trimethylamine-borane with 3,3′-diaminodipropylamine in 2:1 molar ratio.

A mixture of 3.99 g (0.055 mol) of trimethylamine-borane, 3.59 g (0.027 mol) of 3,3′-diaminodipropylamine, and 75 ml of benzene is heated to gentle reflux. After a period of about 3 h, the mixture separates into two layers ; a small sample of the lower layer was removed (see below).

The mixture is further heated and homogenous solution is quickly obtained. After a total heating time of 9 h, benzene is removed and a liquid fraction is distilled off the residue under vacuum to yield a material, b.p. 55°C/1 Torr, identical to Compound 7 (see above) as evidenced by the spectroscopic properties. The remaining solid is identified as Compound 16 (see above).

The small sample taken from the preceding reaction was stored under vacuum for 15 h. Continous gas evolution was observed and no consistent elemental analysis data could be obtained. However, the data as well as infrared spectral evidence would tend to suggest that this intermediate is impure 1-(ω-dihydroborylaminopropyl)-1,3,2-diazaboracyclohexane. However, no bis(dihydroboryl) derivative of 3,3′-diaminodipropylamine is formed. In order to confirm this assumption, the following experiment was prformed : A quantity, 3.34 g (0.020 mol) of Compound 16 is dissolved in a minimal amount of benzene and 1.34 g (0.010 mol) of 3,3′-diaminodipropylamine is added. The mixture is refluxed overnight, benzene is stripped off, and the residue is distilled over a 20 cm silver-mantle column to yield Compound 7 and a very minor amount of Compound 6. Hence, this reaction can be described by the equation :

$$\left[H_2B\text{-}NH\text{-}\left(CH_2\right)_3\right]_2N\text{-}BH_2 \; + \; 2\left[H_2N\text{-}\left(CH_2\right)_3\right]_2NH \longrightarrow 3\ \text{Compound 7}$$

3. Compound 17 - Reaction of tris(dimethylamino)borane with 3,3′-diaminodipropylamine in 3:1 molar ratio.

A mixture of 6.0 g (0.045 mol) of 3,3′-diaminodipropylamine and 20.0 g (0.140 mol) of tris(dimethylamino)borane (ref. 95) is stirred vigorously and slowly warmed in a reflux system. At 40°C homogeneity of the mixture is achieved and slow evolution of gas is observed. Note : Reaction at 50°C is quite vigorous ! The mixture is maintained at 45°C for a period of 8 h and then heated to 100°C for 2 h. Excess tris(dimethylamino)borane is distilled off under reduced pressure and the residue is distilled under high vacuum. Redistillation of the latter product using a 20 cm silver-mantle column yields 6.2 g (58.6 %) of pure Compound 17, b.p. 83 - 84°C/0.05 Torr.

Analysis: Found: C, 50.77; H, 10.52; N, 29.31; B, 9.12.

$C_{10}H_{25}N_5B_2$ calcd.: C, 50.68; H, 10.63; N, 29.56; B, 9.12%.

4. Compound 17 - Alternate procedure

A solution of 9.7 g (0.69 mol) of 1,8,10,9-triazaboradecalin in 50 ml of benzene is warmed to approximately 75°C and 20.0 g (0.140 mol) of tris(dimethylamino)borane is added dropwise. The mixture is refluxed overnight and benzene is stripped off. The excess of tris(dimethylamino-borane is removed and the residue is distilled. Redistillation of the product employing a 20 cm silver-mantle column yields 9.8 g (59.0%) of Compound 17, identical to the material described above.

5. Compound 13 and 20 - Reaction of excess (dimethylamino)diethylborane with 3,3′-diaminodipropylamine.

A 50 ml flask equipped with reflux condenser and dropping funnel is charged with 23.0 g (0.204 mol) of (dimethylamino)diethylborane and 8.7 g (0.066 mol) of 3,3′-diaminodipropylamine is added with vigorous stirring. Evolution of gas is observed and the mixture is stored at ambient temperature overnight. Subsequently, it is heated slowly to 130°C until gas evolution ceases (approximately 4 h). Unreacted (dimethylamino)diethylborane and traces of dimethylamine are removed under reduced pressure and the residue is distilled under vacuum to give 5.9 g of Compound 20, b.p. 95 - 99°C/0.05 Torr (after redistillation), and 9.5 g of Compound 13, b.p. 123°C/0.05 Torr (after redistillation).

Analyses:

Compound 13 : Found: C, 64.31; H, 13.06; N, 12.57; B, 9.72.
$C_{18}H_{43}N_3B_3$ calcd.: C, 64.54; H, 13.24; N, 12.54; B, 9.68%.
Compound 20 : Found: C, 62.67; H, 13.04; N, 15.45; B, 7.97.
$C_{14}H_{34}N_3B_2$ calcd.: C, 62.96; H, 13.21; N, 15.73; B, 8.10%.

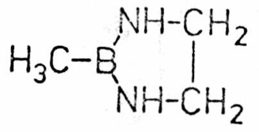
7

APPENDIX

List of Structural Drawings for Compounds Under Consideration Here

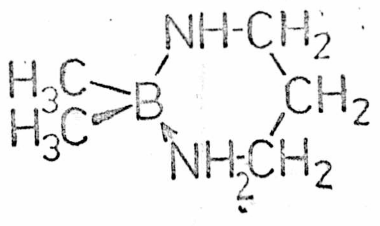
$H_2N-(CH_2)_2-NH_2\cdot B(CH_3)_3$

Compound 1

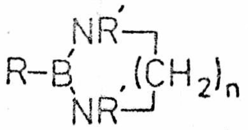


Compound 2

2-Methyl-1,3,2-diazaboracyclopentane

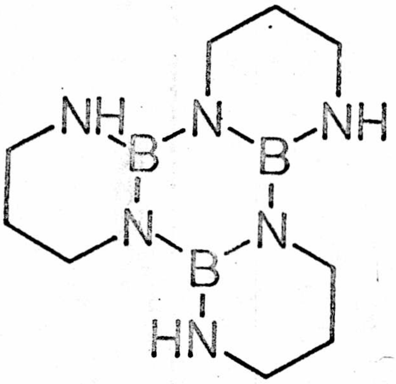


Compound 3

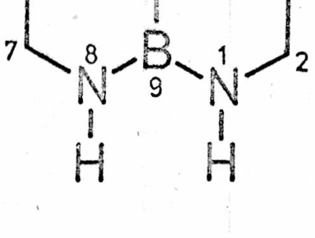


Compound 4

General formula for 1,3,2-diazaboracycloalkanes

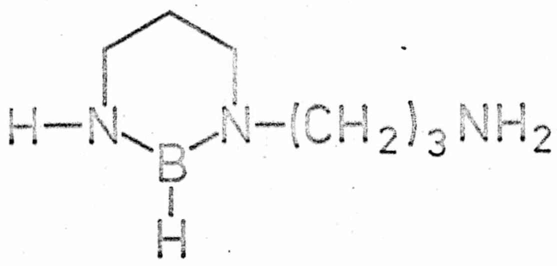


Compound 5



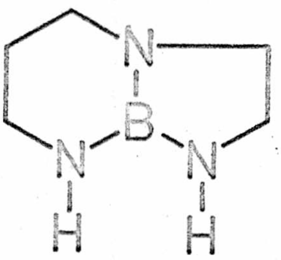
Compound 6

1,8,10,9-Triazaboradecalin

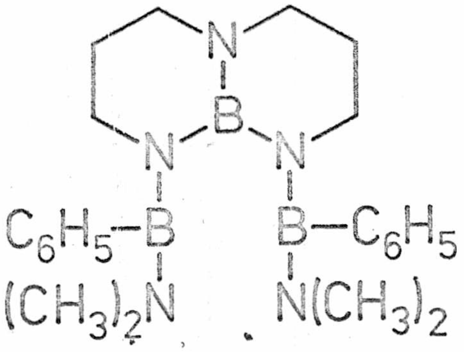


Compound 7

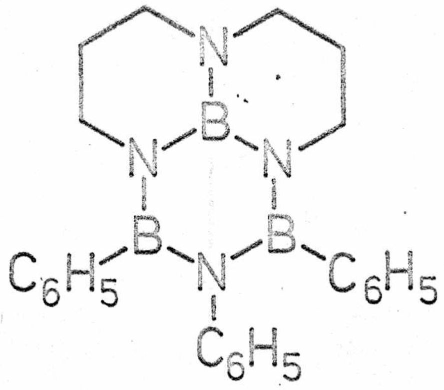
1-(ω-aminopropyl)-1,3,2-Diazaboracyclohexane



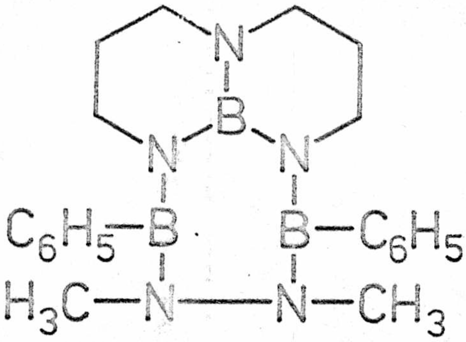
Compound 8



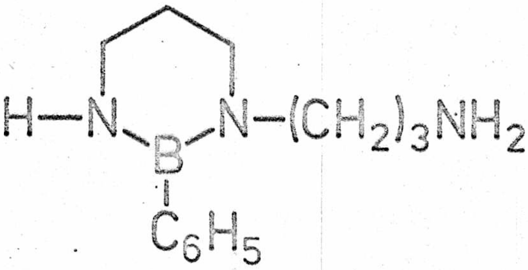
Compound 9



Compound 10

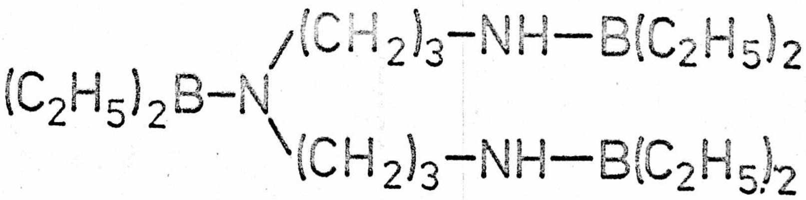


Compound 11



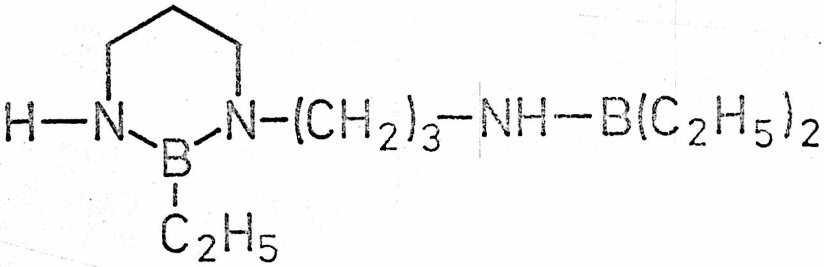
Compound 12

1-(ω-aminopropyl)-2-Phenyl-1,3,2-diazaboracyclohexane



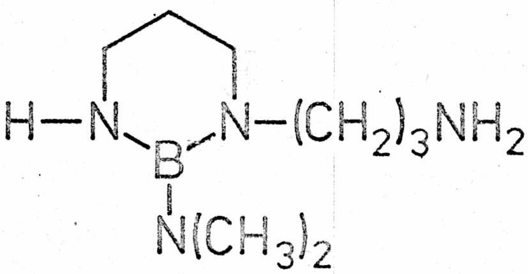
Compound 13

N,N',N''-Tris(diethylboryl)-3,3'-diaminodipropylamine



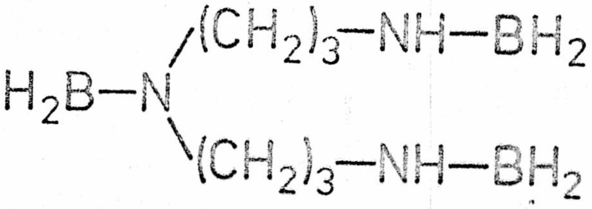
Compound 14

1-(ω-diethylborylaminopropyl)-2-Ethyl-
-1,3,2-diazaboracyclohexane



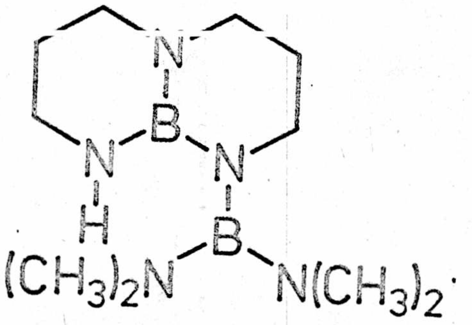
Compound 15

1-(ω-aminopropyl)-2-Dimethylamino-1,3,2-diazaboracyclohexane



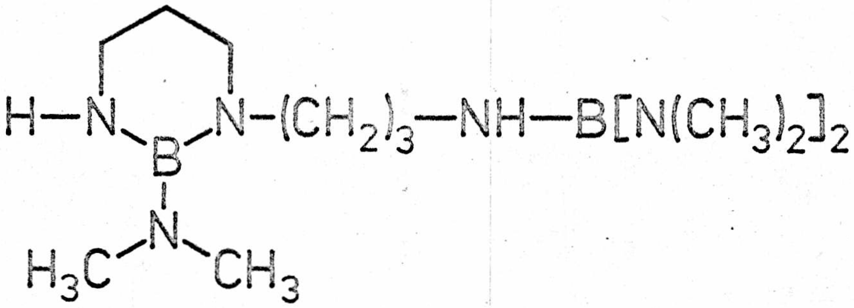
Compound 16

N,N',N''-Tris(dihydroboryl)-3,3'-diaminodipropylamine



Compound 17

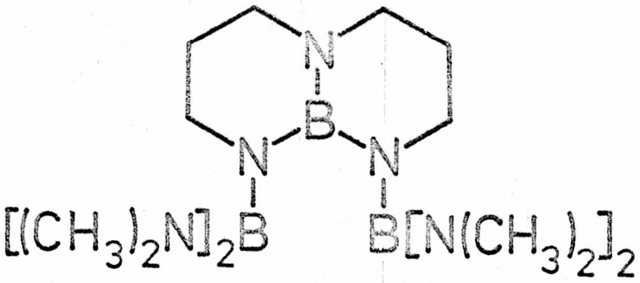
1-Dimethylaminoboryl-1,8,10,9-triazaboradecalin



Compound 18

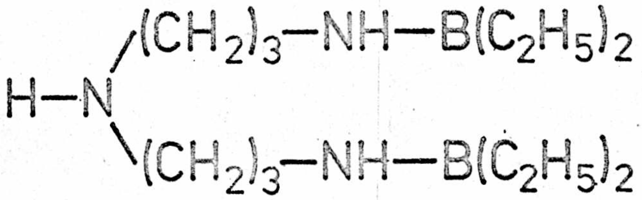
1-(ω-dimethylaminoborylaminopropyl)-2-Dimethylamino-

-1,3,2-diazaboracyclohexane



Compound 19

1,8-Bis(dimethylaminoboryl)-1,8,10,9-triazaboradecalin



$$H{-}N\begin{cases}(CH_2)_3{-}NH{-}B(C_2H_5)_2\\(CH_2)_3{-}NH{-}B(C_2H_5)_2\end{cases}$$

Compound 20

3,3'-Bis(diethylborylamine)-dipropylamine

8

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ABSTRACT

Reactions of 3,3′-diaminodipropylamine with tris-dimethylamino borane, (dimethylamino)diethylborane, and borane(3)were studied. They lead to the formation of either 1,3,2-diazaboracycloalkanes or N-borylated chain derivatives of 3,3′-diaminodipropylamine. The tendency of the boron to achieve four-coordination leads to stabilization of chain species by inter- or intramolecular coordination. Analytical and spectroscopic data for the prepared compounds are presented. Also, carbon-13 and boron-11 NMR spectra were recorded and discussed. The carbon-13, boron-11, and nitrogen-14 chemical shifts data for a large group of 1,3,2-diazaboracycloalkanes and some other structurally related systems were collected. They were found to depend significantly on the geometry of a molecule. Additionally, quantum chemical calculations of the electronic states of 1,8,10,9-triazaboradecalin molecule are presented.

STRESZCZENIE

W pracy opisano cykl reakcji 3,3′-dwuaminodwupropyloaminy z $B\left[N(CH_3)_2\right]_3$, $(CH_3)_2NB(C_2H_5)_2$ i BH_3 wiodących ku układom pierścieniowym z grupy 1,3,2-dwuazaboracykloalkanów, $XB(-NY-CH_2-)_2(CH_2)_n$. Stwierdzono możliwość podstawienia azotu w 3,3′-dwuaminodwupropyloaminie grupami BX_2. Połączenia takie są trwałe gdy istnieje możliwość wewnątrz- lub międzycząsteczkowej koordynacji między azotem i borem nie związanymi ze sobą bezpośrednio. Oprócz wyników standardowych badań analitycznych i spektroskopowych przedstawiono widma NMR ^{13}C oraz ^{11}B zsyntetyzowanych substancji. Przeprowadzono porównawczą dyskusję przesunięć chemicznych ^{13}C, ^{11}B, ^{14}N dla szerokiej grupy 1,3,2-dwuazaboracykloalkanów oraz substancji strukturalnie pokrewnych na podstawie zebranych wyników własnych i danych literaturowych. Wykazano poważny wpływ czynników geometrycznych na przesunięcia chemiczne. Dla cząsteczki 1,8,10,9-trójazaboradekaliny przedstawiono wyniki kwantowochemicznych obliczeń stanów elektronowych.

Egzemplarze niniejszej pracy otrzymują:

1.	Prof. Dr Przemysław Mastalerz (recenzent) Politechnika Wrocławska	1
2.	Prof. Dr Kurt Niedenzu (promotor) Uniwersytet Kentucky	1
3.	Prof. Dr Krzysztof Pigoń Politechnika Wrocławska	1
4.	Prof. Dr Józef W. Rohleder Politechnika Wrocławska	1
5.	Prof. Dr Barbara Serafin (recenzent) Politechnika Warszawska	1
6.	Doc. Dr Michał Witanowski (recenzent) Instytut Chemii Organicznej PAN	1
7.	Biblioteka Instytutu Chemii Organicznej i Fizycznej Politechniki Wrocławskiej	1
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9.	Autor	2

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Praca własna

Charakter pracy: podstawowa
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Analiza dokumentacyjna

<D W pracy opisano cykl reakcji 3,3'-dwuaminodwupropyloaminy z trój/dwumetyloamino/borem, /dwumetyloamino/-dwuetyloborem i borowodorem/3/, wiodących ku układom pierścieniowym z grupy 1,3,2-dwuazaboracykloalkanów lub ku systemom łańcuchowym, dwu- lub trój-N-podstawionym grupami BX2. Oprócz wyników standardowych badań analitycznych i spektroskopowych przedstawiono widma NMR C13 oraz B11 zsyntetyzowanych substancji. Przeprowadzono porównawczą dyskusję przesunięć chemicznych C13, B11 i N14 dla szerokiej grupy dwuazaboracykloalkanów oraz substancji strukturalnie pokrewnych, na podstawie zebranych danych literaturowych i wyników własnych. Dla cząsteczki 1,8,10,9-trójazaboradekaliny przedstawiono wyniki kwantowochemicznych obliczeń stanów elektronowych. Dyskutowano wpływ czynników geometrycznych na charakter wiązania B-N w omawianej grupie związków.

Imię i Nazwisko autora analizy

Ludwik Komorowski

Słowa kluczowe

<S aminoborany, 1,3,2-dwuazaboracykloalkany, synteza, spektroskopia NMR, obliczenia kwantowochemiczne

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Tylko PRL	CINTE	APW	Podpis red.	Podpis asyst. d/s badań	Potwierdzenie przyjęcia poprawki	Potwierdzenie przyjęcia karty w Oddziale Dokumentacji
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