GALLAZANES AND RELATED COMPOUNDS

by

ALLEN DAVID PENLAND

B.Sc. (Hons.) University of British Columbia 1969

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

In The Department of Chemistry

We accept this thesis as conforming to the

required standard

The University of British Columbia

July 1971

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of CHEMISTRY

The University of British Columbia
Vancouver 8, Canada

Date Aug. 1. 1971.

ABSTRACT

This work involved preparation of cyclical dimeric or trimeric gallazanes of general formula: $(RNHGaH_2)_n$ where n= 2 or 3 and R = Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, or Bu^t. The effect of larger R group on ring size (n value) was determined. Some deuterated analogues of these compounds were also prepared. These were $(EtNHGaD_2)_3$, $(Bu^tNHGaD_2)_2$, and $(Pr^iNHGaD_2)_2$.

Attempted preparation of $\emptyset NHGaH_2$ resulted in isolation of $\emptyset NH.GaH_2.NMe_3$. Reactions were undertaken with $\emptyset NH.GaH_2.NMe_3$ and it partially deuterated analogue $\emptyset NHGaD_2.NMe_3$, and shown to involve proton transfer through a 4-centre transition state.

Additional work on the effects of R group on the nitrogen within the gallazanes involved preparation of dimeric gallazanes of general formula $((CH_2)_xN.GaH_2)_2$ where x = 2,3,4 or 5.

Additional work on double ring systems involved preparation of analogous alazanes of general formula $((CH_2)_xN.AlH_2)_n$ where x = 2,3,4,5 and n = 2 or 3. Similar borazanes were likewise prepared and were of general formula: $((CH_2)_xN.BH_2)_n$ where x = 2,3,4,5 and n = 2 or 3.

Adducts of general formula: $(CH_2)_2NH.EMe_3$ where E = B, Al, Ga, In, were also prepared. Upon pyrolysis these adducts yield methane plus materials of the general formula: $((CH_2)_2N.EMe_2)_3$ where E = Al,Ga, In.

Characterization of these materials as well as gaseous reaction products was accomplished by infrared spectroscopy. Additional data was obtained by 60MHz and 100MHz ^1H nmr as well as mass spectrometry. Molecular weights were determined cryoscopically in benzene and analyses for galluim, aluminum or hydrolysable hydrogen carried out by standard means.

Table of Contents:

LIST OF TABLES:

List of Figures

Page

ACKNOWLEDGEMENT

I would like to express my sincerest thanks to my research director Dr. Alan Storr, for his invaluable advice, guidance, and enlightening discussions throughout the course of this work.

I would also like to thank Dr. B. S. Thomas for his help with some of the more difficult preparative procedures encountered during the course of this work.

INTRODUCTION

The chemistry of gallium hydride has developed quickly since the discovery of the stable adduct, $Me_3N.GaH_3$, trimethylamine gallane (1). Previous to this there had been a long search for uncoordinated gallium hydride and its derivatives.

Free gallium hydride, although originally believed to be a temperature stable dimer digallane, Ga_2H_6 (2), has recently been shown to be a viscous polymeric liquid which disproportionates at -15°C into gallium and hydrogen (3). On the basis that this material was benzene insoluble, these workers suggested that it was not dimeric, but rather, polymeric like aluminum hydride. IR spectroscopy showed the characteristic strong υ Ga-H at 1980 cm^{-1} and δ Ga-H at ca. 700 cm^{-1} for this compound. In addition, analysis showed a gallium to hydrogen ratio of one to three, proving that this was the long sought after (4) hydride of gallium.

By a procedure analogous to that used for the preparation of gallium hydride, monochloro gallium hydride $(GaH_2Cl)_x$ was prepared and characterized as polymeric (5). Subsequently dichloro gallium hydride $(GaHCl_2)_2$ was prepared (6) by a different route and shown to be dimeric rather than polymeric.

Lithium gallium hydride, $LiGaH_4$, was first isolated by Finholt, Bond and Schlesinger (7) by the reaction:

$$4LiH(s) + GaCl_3(s) \xrightarrow{Et_2O} LiGaH_4 + 3LiCl(s) \quad .$$

This compound is the only complex metal gallium hydride which is stable

at room temperature, and then only as an ether solution. Two other unstable analogues, both disproportinating at below -15°C, are $AgGaH_4$ (8) and $Tl(GaH_4)_3$ (9). The reaction of $LiGaH_4$ with water causes vigorous evolution of four moles of hydrogen. Hence anhydrous conditions are necessary for preparation and storage of this compound.

The GaH_3 moeity forms complexes with a number of organo compounds of the group V and group VI elements, in addition to adducts formed with the hydride ion (H^-), as found in $LiGaH_4$. The preparation of these compounds is summarized in a recent review on gallium hydride and derivatives (10).

Trimethylamine gallane, $Me_3N.GaH_3$, is, in comparison with other gallium hydrides, fairly temperature stable and can readily be sublimed at room temperature. It can be prepared easily by the reaction of excess Lithium gallium hydride with timethylamine hydrochloride in the following manner:

$$LiGaH_4(s) + Me_3NHCl(s) \longrightarrow Me_3N.GaH_3(s) + LiCl(s) + H_2(g).$$

This compound was the first metal hydride to have sufficient vapor pressure to enable the gas phase IR spectrum to be recorded (11). The gas phase IR spectrum exhibited strong absorptions due to ν Ga-H at 1853 cm^{-1} and δ Ga-H at 758 cm^{-1}. These assignments were confirmed by deuteration of the protons on the gallium atom. The shift of the Ga-H stretching and deformation vibrations to lower frequency was by a factor of $1/\sqrt{2}$, as expected.

Trimethylamine gallane has been shown by tensiometric titration to add a molar equivalent of trimethylamine gas and form a

2:1 adduct (11). Upon warming to room temperature this material reverted back to the starting material with evolution of trimethylamine gas.

Dimethylamine gallane was prepared recently by transamination of trimethylamine gallane with dimethylamine gas (12).

$$Me_2NH(g) + Me_3N.GaH_3(s) = Me_3N(g) + Me_2NH.GaH_3(s)$$

$$2Me_2NH{\cdot}GaH_3(s) \longrightarrow 2H_2 + Me_2N - GaH_2$$

$$\downarrow \quad \uparrow$$

$$H_2Ga - NMe_2$$

Over a period of a few weeks Me_2NHGaH_3 evolved one molar equivalent of hydrogen to give the gallazane shown in the second equation (above). It was shown that this adduct was dimeric in benzene solution. From consideration of the gas phase IR spectrum, it was concluded, however, that this compound was monomeric in the gas phase, having C_{2V} symmetry (12).

The transamination reaction with gaseous ammonia has recently been shown to proceed via hydrogen elimination to give a quantitative yield of the polymeric solid $(NH_2GaH_2)_x$ (13) according to the following reaction:

$$Me_3N.GaH_3(s) + NH_3(g) \longrightarrow H_2N.GaH_2(s) + Me_3N(g) + H_2(g).$$

A similar reaction with methylamine gas gave a mixture of two isomers of trimeric $(MeNH.GaH_2)_3$ according to the overall equation:

$$Me_3N.GaH_3(s) + MeNH_2(g) \longrightarrow MeNH.GaH_2(s) + Me_3N(g) + H_2(g).$$

The present study involved an extension of this series of gallazanes, $(RNH.GaH_2)_n$, in an attempt to elucidate the various factors

which govern the value of n, the degree of association. In addition to the use of primary alkylamines [R = Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t], the transamination reaction using aniline was also investigated.

The second part of this work was concerned with a study of the reaction of cyclic imines, $[(CH_2)_xNH$ where x = 2, 3, 4 or 5] with trimethylamine gallane. The imino gallane products $[(CH_2)_xNGaH_2]_n$, were expected to involve some double ring strain and an investigation of this effect was undertaken. A further extension of this latter study involved the preparation and characterization of similar boron $[CH_2)_xNBH_2]_n$ and aluminum $[(CH_2)_xAlH_2]_n$ compounds.

The reaction of imine bases with diborane to yield adducts with the general formula, $[CH_2]_xNH.BH_3$, where x = 2, 3, 4, 5 was studied in 1956 by Burg and Good (14). Three of these adducts gave, on hydrogen elimination, materials of composition: $(CH_2)_xN.BH_2$ [where x = 3, 4, 5]. However, the aziridine compound, x = 2, appeared to give ring-opened, polymeric products, and was not isolated. In 1969 S. Akerfeldt et al (15) prepared the adduct aziridine borane, as well as aziridino borazane. The latter compound was until then believed unpreparable. Simultaneously, a crystal structure of the adduct $(CH_2)_2NH.BH_3$ was reported (16), in addition to a ^1H nmr and infrared study of both the adduct and the aziridino borazane (17). This latter study rejected the previous formulation of a ring opened product, $\left[\begin{smallmatrix}NH_2\\ \downarrow\\ BH_2\end{smallmatrix}\right]$, in the preparation of the adduct. (18)

The preparation of aziridino alazane and related cyclic imino alazanes has received some recent attention. The first preparation of the cyclic compounds dates back to 1962, when some Italian workers

isolated the piperidino and pyrolidino alazanes (19). Their preparation of aziridino alazane was hampered by the fact that this material decomposed with some violence at room temperature in the absence of solvent. More recently, Ehrlich (20) discussed in detail the preparation and subsequent ring opening of this material; which he suggests is polymeric. The present study on cyclic imino borazanes and alazanes has a twofold purpose. Firstly, as indicated previously, to compare these compounds with the gallium derivatives; and secondly to reinvestigate and extend the previous studies.

The final part of this work involved preparing the aziridino metal dimethyl derivatives, $[(CH_2)_2NMMe_2]_n$ where M = B, Al, Ga, In, in order to investigate the effect, on the degree of association, of replacing the hydrogens on the group III atom with methyl groups.

EXPERIMENTAL

A. Experimental Techniques

(a) Desiccation

All gases were dried first by fractionating under high vacuum through a trap at -20°C, to remove large amounts of water, and then condensed at -196°C into one limb of a drying pistol, see Figure 1, packed with a mixture of glass-wool and phosphorus pentoxide. The gas is passed through the phosphorus pentoxide by alternately cooling one limb and then the other limb. The dried gases are then stored at less than one atmosphere in large glass bulbs attached to the vacuum line.

All solvents were dried and redistilled before use; diethyl ether over lithium aluminum hydride, benzene and cyclohexane over molten potassium. The amine ligands which were commercially available were dried by refluxing over CaH_2 followed by distillation.

Solid components were purified by sublimation, either by vacuum bulb-to-bulb sublimation or as with trimethylamine hydrochloride, sublimed to the cooled central finger of the apparatus shown in Figure 2. Trimethylamine gallane was sublimed under dynamic vacuum from the flask to the large vertical tube, marked as A, of the apparatus, which was cooled to -80°C, shown in Figure 3.

All glassware was washed with acetone, oven dried, evacuated and filled with nitrogen before use. All nitrogen used was Canada Liquid Air "L" grade, purified nitrogen.

The hydride and alkyl derivatives, because of their relative instability and extreme reactivity with oxygen or water vapour were

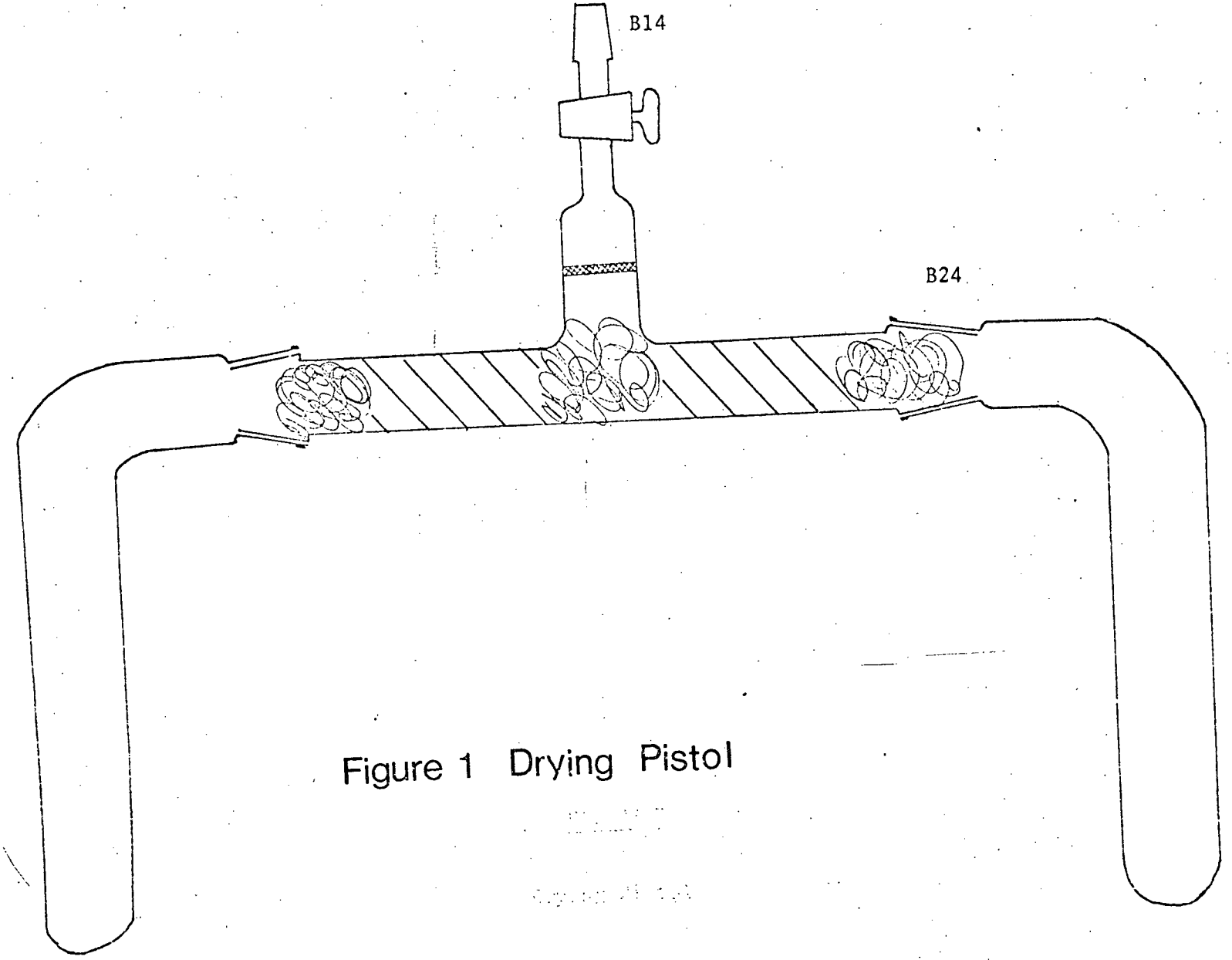


Figure 1 Drying Pistol

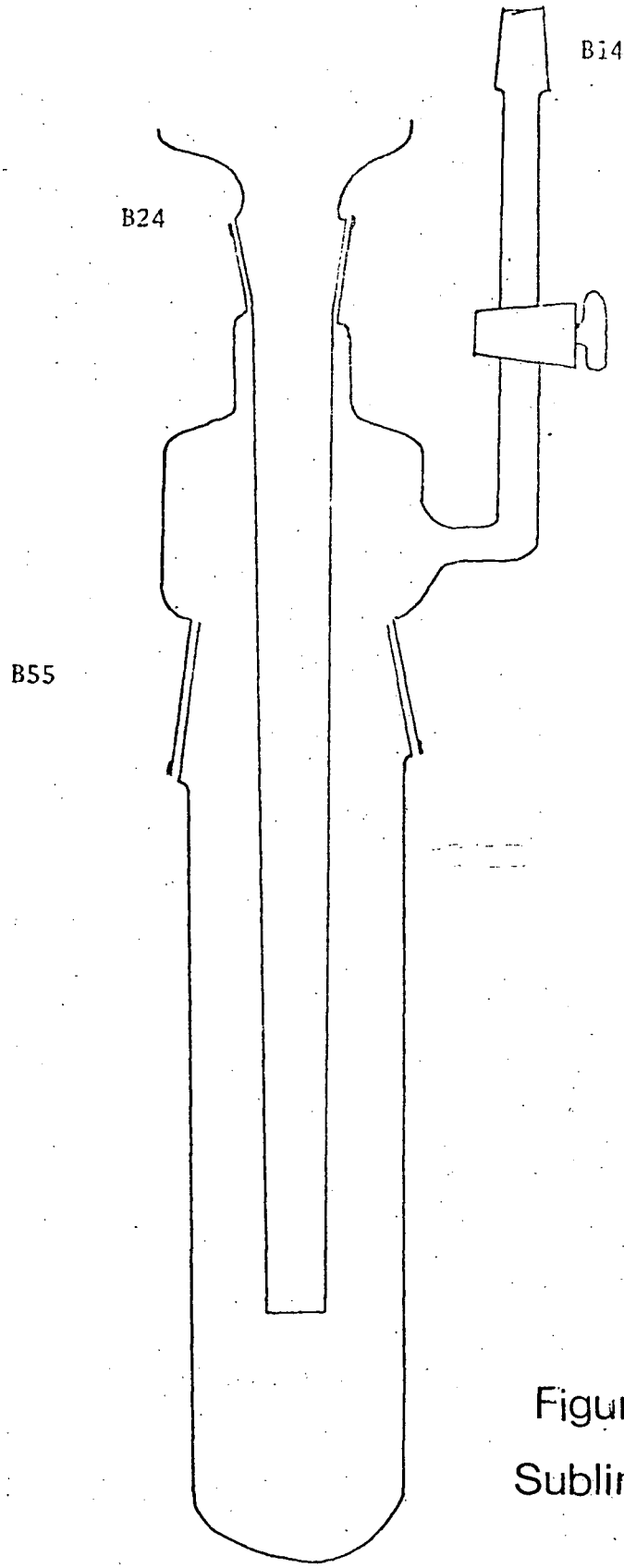
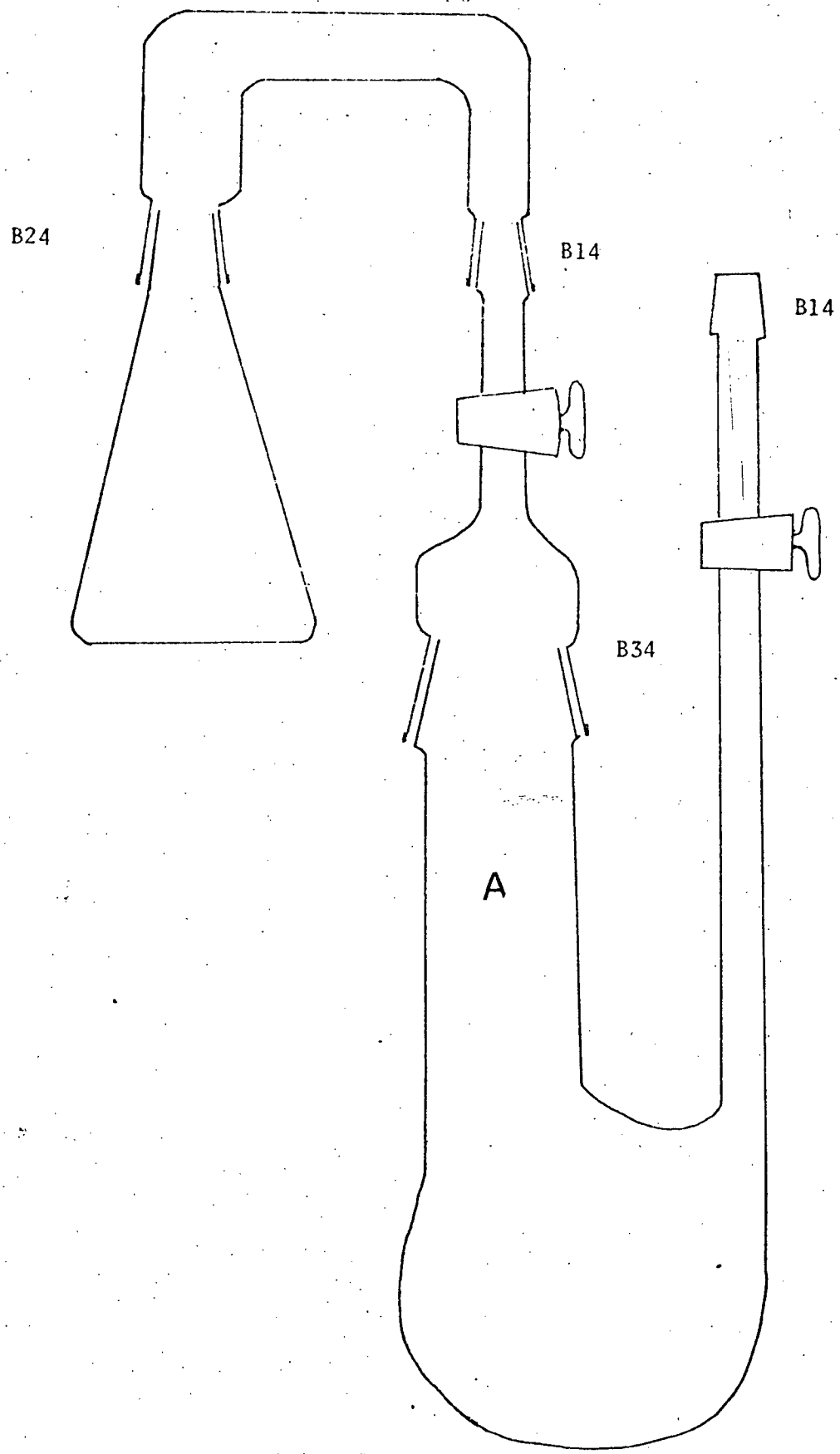


Figure 2
Sublimer



Me_3NGaH_3 Sublimer

Figure 3

all prepared and handled in either a high-vacuum system or a nitrogen filled dry box. The high vacuum system developed for the work is shown in Figure 4. A double-stage rotary oil pump (Welch Scientific Co.) and an electrically heated single stage mercury diffusion pump were used to obtain a vacuum of greater than 10^{-4} mm of Hg.

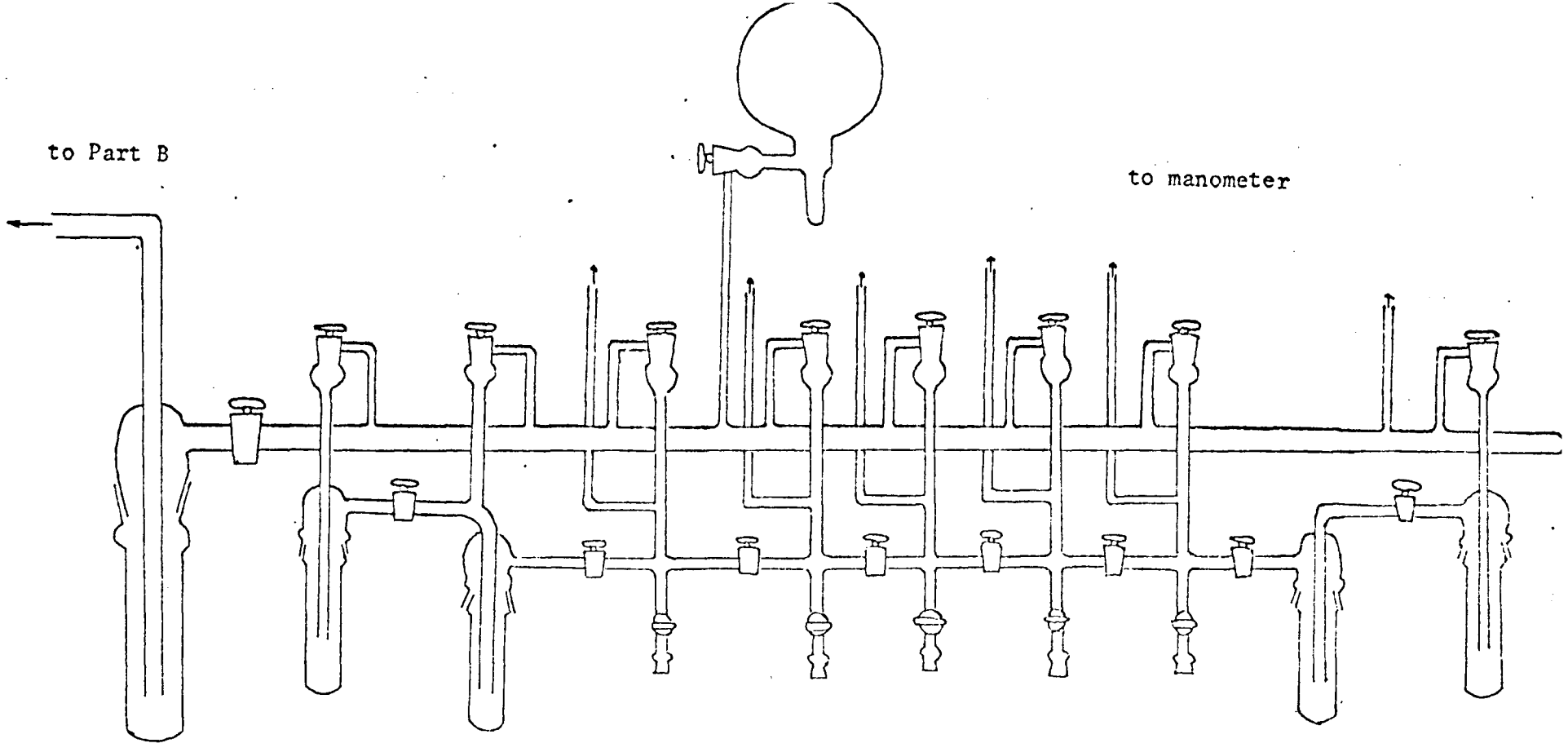
The dry box (Kewaunee Scientific Equipment) had a special fore-chamber that could be evacuated by a double-stage rotary oil pump and then filled with dry nitrogen to ensure the purity of the atmosphere in the box. The dry box is also connected to a circulating pump which circulates the box's atmosphere through a drying train containing molecular sieve (Fisher type 5A) and a copper furnace to remove any oxygen.

(b) Reaction-Filtration Apparatus

The apparatus shown in Figure 5 found extensive use in our wor The apparatus is evacuated, filled with dry nitrogen, and the reactants are placed in flask A. Additional reagents may be added during the cour of a reaction by rotating the dumper tube B, the reaction mixture is stirred by a magnetic bar C. The products, if gaseous may be removed b a Topler pump through one of the stopcocks, or if in solution can be filtered through the sintered disc D (medium porosity) by cooling or evacuating the receiver flask E.

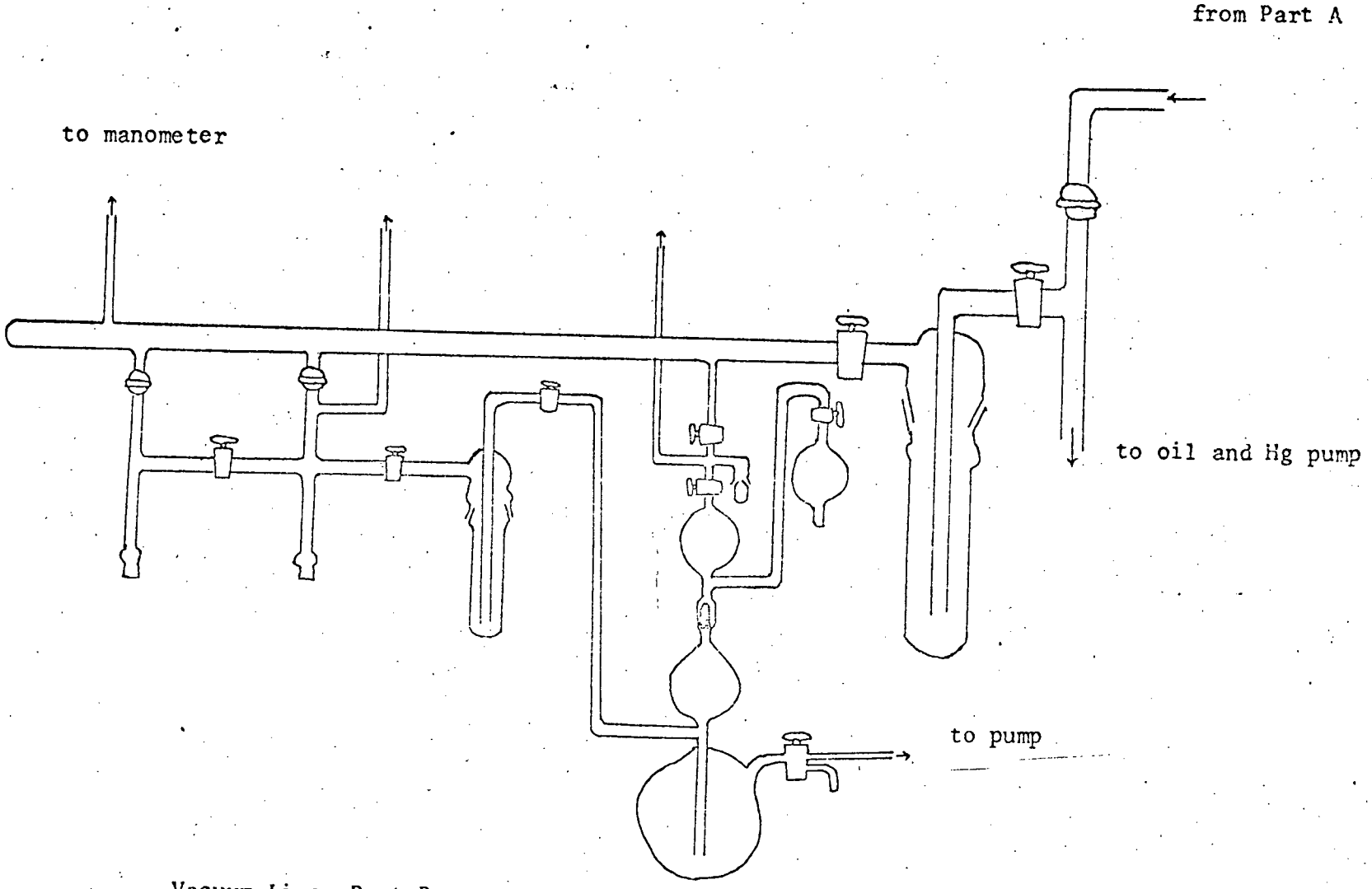
(c) Molecular Weights

Molecular weights were determined by the cryoscopic method. I the dry box an accurately known weight of pure compound was dissolved ir a weighed sample of pure benzene (about 10 ml). The benzene solution was poured into the molecular weight apparatus, see Figure 6, and remov



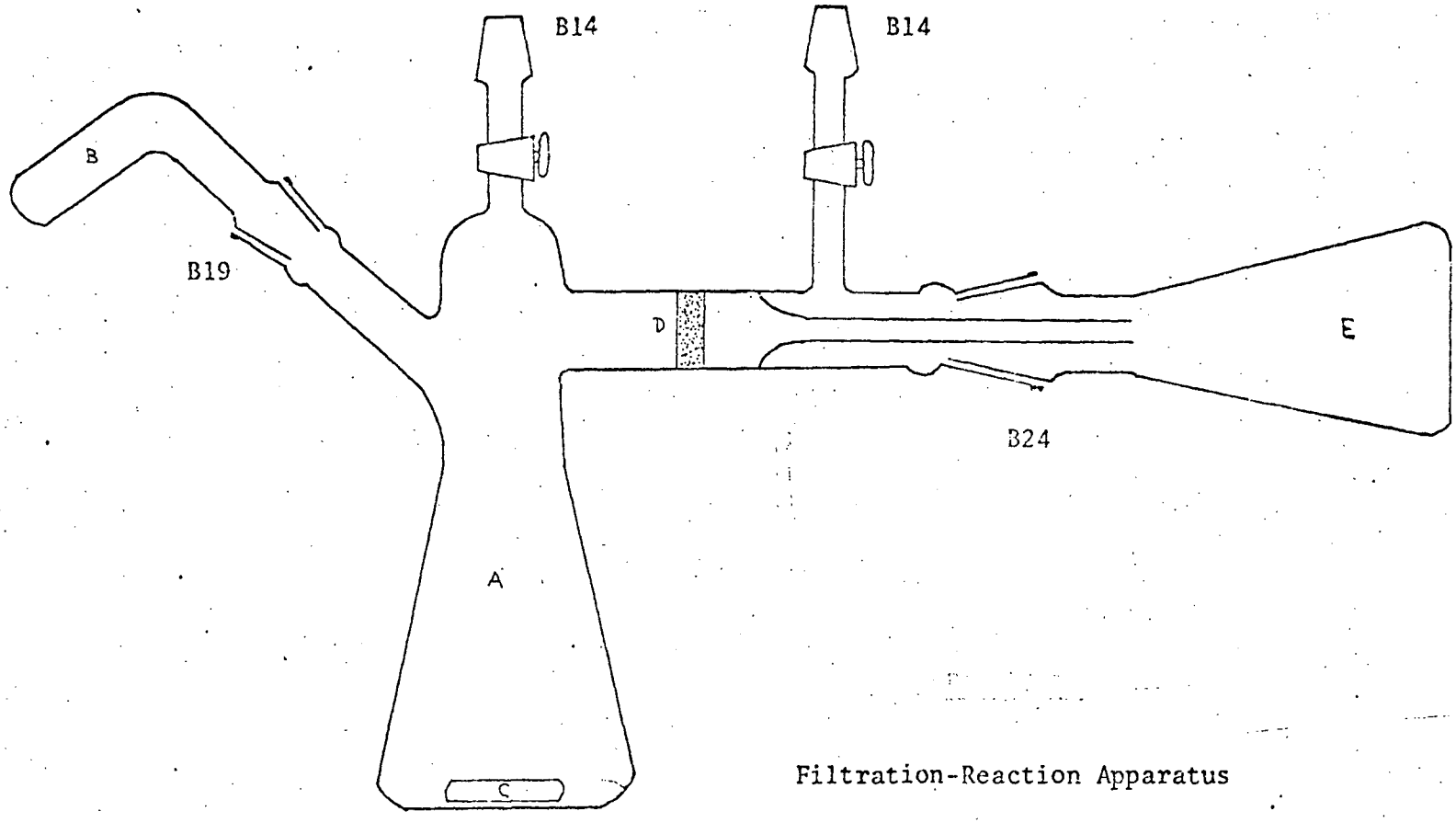
Vacuum Line, Part A

Figure 4



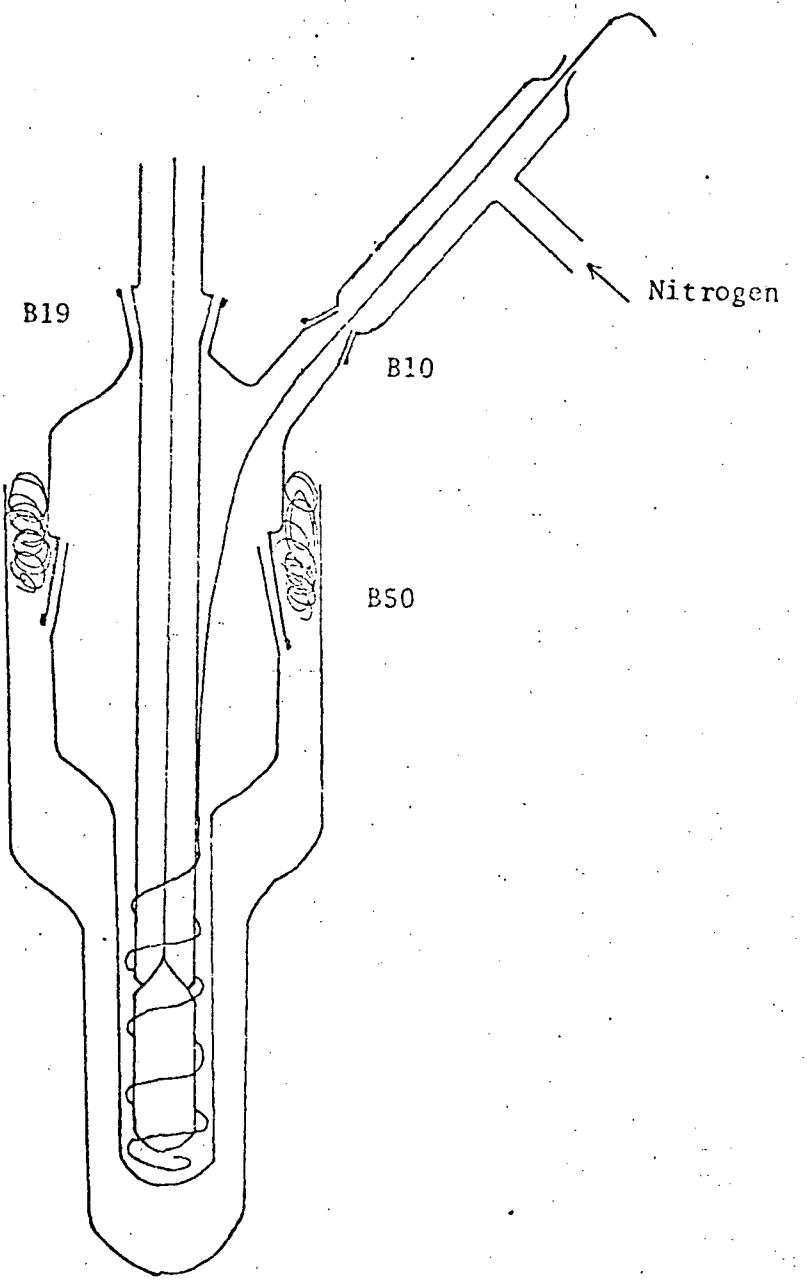
Vacuum Line, Part B

Figure 4



Filtration-Reaction Apparatus

Figure 5



Molecular Weight Apparatus

Figure 6

from the dry box. A slow stream of pure nitrogen was flushed through the apparatus as it was cooled in an ice bath. The freezing point of the solution was recorded and compared with that of pure benzene solvent and with standard solutions of biphenyl in benzene solvent. The following empirical formula was used to calculate the molecular weights.

$$\text{molecular weight} = \frac{[K_f]X[\text{weight of sample (gms)}]}{[\text{weights of benzene solvent (gms)}]X\ [\text{change in temperature } (^{o}C)]}$$

K_f = freezing point depression constant 5.20°C per molal.

(d) Spectroscopy

Infrared spectroscopy was used throughout this work for semi-quantitative analysis and for structural determination of compounds. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer (4000 - 250 cm^{-1}). The observable range for both liquid and gas samples was between 4000 and 400 cm^{-1} because KBr windows were used.

For gaseous or volatile samples a 10 cm gas cell was used with KBr windows. For liquid or solution samples a 0.05 cm fixed path length solution cell with KBr windows was used and a variable-thickness cell filled with pure solvents (usually benzene) was placed in the reference beam to compensate for solvent absorption. Because of the instability of most of the hydride adducts prepared, all infrared solution cells were loaded in the dry box and a spectrum run as rapidly as possible.

As with infrared spectroscopy, nuclear magnetic resonance spectroscopy, NMR, was used as a tool to investigate reactions and for structural determination. The instruments used were a Varian A-60 and Varian T-60 both operating with a radiofrequency of 60 megacycles per

second and a Varian HA-100 which operates at a radiofrequency of 100 megacycles per second. Most samples were run in benzene solution with a concentration of about 0.1 M to 1 M. The benzene proton signal was used as an internal standard and was defined as τ = 2.840 p.p.m. Tetramethylsilane, TMS, was used as an external standard on several samples and is defined as τ_{TMS} = 10.000 p.p.m.

The NMR sample tubes were specially fitted with a flame-seal constriction and a B-10 quick-fit cone so that the samples could be loaded and sealed under an atmosphere of nitrogen. As with the infrared samples, the NMR spectra were run as rapidly as possible since steady decomposition at room temperature often impeded prolonged investigation.

(e) Elemental Analysis

(i) Active Hydrogen:

Active hydrogen was measured by placing a small weighed amount of compound in a round bottom flask in the dry box, attaching a stopcock adaptor and evacuating on the vacuum line. A small volume of degassed, dilute aqueous HNO_3 solution was then condensed onto the solid at -196°C. The mixture was allowed to reach room temperature and left to react for about one hour with stirring.

$$Me_3NGaH_3 + 3H^+ \longrightarrow Me_3N + Ga^{+3} + 3H_2$$

The volume of hydrogen gas, non-condensable at -196°C, was then measured using a Topler pump. The amount of active hydrogen in the compound was then calculated.

This aqueous solution was made up to a known volume and an aliquot was used in the determination of gallium as indicated below.

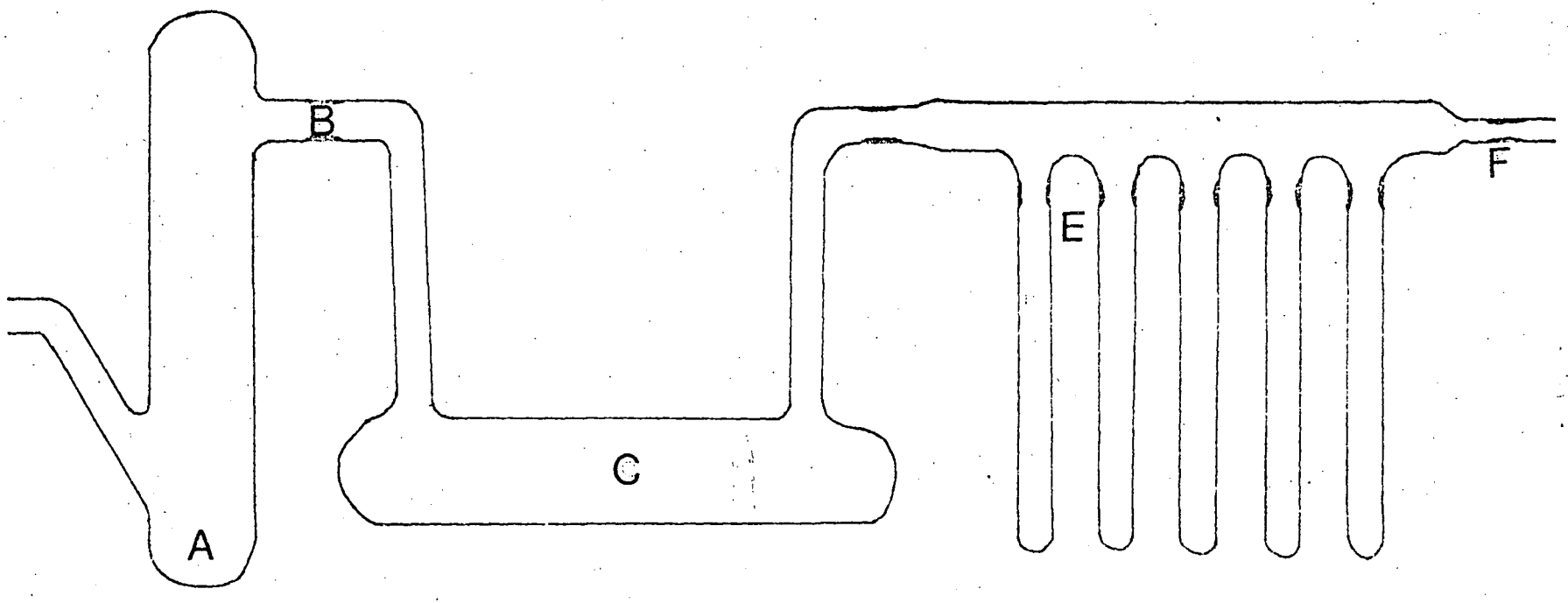
(ii) Gallium (Aluminum):

A measured aliquot of the solution prepared in section (i) was measured out into a beaker. The solution was first made neutral with dilute ammonia solution, then was made slightly acidic, pH 5-7, with dilute aqueous HCl. The solution was then heated to 80°C and a slight excess of a 5% solution of 8-hydroxyquinoline in glacial acetic acid was added followed by an aqueous solution of saturated ammonium acetate until precipitation of $Ga(C_9H_6NO)_3$ is complete. After digestion at 80°C for one hour, the yellow precipitate was collected in a filtration crucible and the precipitate washed, first with hot, then cold water. The precipitate was then dried at 120°C, weighed and its gallium content calculated from the formula $Ga(C_9H_6NO)_3$ which is 13.89% gallium by weight. This method has been found to give accurate determinations for a minimum concentration of 10 mg of gallium in 50 ml of solution. Aluminum was determined similarly as its 8-hydroxyquinolate.

B. Preparative

(a) Preparation of Gallium Trichloride (23) $GaCl_3$

Gallium trichloride was prepared by direct combination of the elements. Pure chlorine gas (Matheson Ltd.) was dried by passing through concentrated sulphuric acid in a bubbler and was then passed into the all glass apparatus shown in Figure 7. The gallium metal, about 15 gms, (Alfa Inorganics Inc.) placed in A soon melted on warming with a bunsen burner, and reacted with the chlorine, first to give a colourless liquid, gallium tetrachlorogallate (21), Ga_2Cl_4 (melting point 170.5°C (22)). On adding more chlorine this liquid Ga_2Cl_4 disappeared and the liquid gallium



Gallium Trichloride Apparatus

Figure 7

burned with a grey-white flame giving a volatile white solid, gallium trichloride $GaCl_3$, (melting point 79°C).

$$2Ga(l) + 2Cl_2(g) \longrightarrow (Ga^+)(GaCl_4^-)$$

$$(Ga^+)(GaCl_4^-)(l) + Cl_2(g) \longrightarrow Ga_2Cl_6$$

The rate of flow of chlorine gas and rate of heating the molten gallium were adjusted so that most of the volatile $GaCl_3$ was deposited in the cooled receiver boat C. After all the gallium had reacted (essentially 100%), any sublimate in A was driven into C by warming and then flame sealing the constriction at B. The apparatus was then evacuated and flame sealed at F. The crude halide was then resublimed into the ampoules E and then these were sealed at their constrictions. The gallium trichloride was found to remain stable indefinitely when stored this way.

(b) Preparation of Lithium Gallium Hydride (7), $LiGaH_4$

$$4LiH + GaCl_3 \xrightarrow[\text{room Temp.}]{Et_2O} LiGaH_4 + 3LiCl$$

An ampoule of $GaCl_3$, was weighed and broken open in the dry box and placed in a conical flask. The gallium trichloride was then dissolved in diethyl ether and the ampoule washed several times to ensure quantitative removal of $GaCl_3$. The empty ampoule was reweighed and the weight of $GaCl_3$ determined. The ethereal solution of $GaCl_3$ and all the washings were now added to the nitrogen filled reaction-filtration apparatus (see Figure 5) and the solution brought up to about 150 ml.

From the weight of $GaCl_3$ calculated, (8.59 gms; 48.8 mmoles)

the weight of about 16 molar equivalents of finely ground lithium hydride (7.45 gms; 938 mmoles) (Alfa Inorganics Inc.), enough for a four-fold excess, was weighed out under nitrogen into the dumper tube.

The reaction flask was cooled to -50°C in an acetone-solid CO_2 bath and the dumper tube rotated upwards to permit the slow addition of LiH to the reaction flask over a period of about thirty minutes. A bubbler was attached to the apparatus so that the reaction could be carried out under a constant pressure of one atmosphere of nitrogen. The coolant was allowed to warm up to room temperature and the mixture was stirred for about fifty hours to ensure complete reaction.

The resulting reaction mixture was filtered through the glass sintered disc and a clear colourless filtrate resulted. This filtrate was then transferred, in the dry box, to a conical flask fitted with a break seal and an extended neck which was flame sealed for storage. The $LiGaH_4$ ether solution was observed to be indefinitely stable if stored in all glass ampoules under a nitrogen atmosphere and cooled below 0°C.

Lithium gallium deuteride, $LiGaD_4$, was prepared and stored in exactly the same manner as $LiGaH_4$, only lithium deuteride, LiD, (Alfa Inorganics Inc.) was substituted in the preparation for lithium hydride.

(c) Preparation of Trimethylamine Gallane (1), Me_3NGaH_3

$$LiGaH_4 + Me_3NHCl \xrightarrow[\text{room temp.}]{Et_2O} Me_3NGaH_3 + LiCl + H_2$$

A known amount of lithium gallium hydride (2.38 gms; 29.4 mmoles) in ether solution was placed in the reaction-filtration apparatus, see Figure 5. Slightly less than the stoichiometric amount of trimethylamine hydrochloride, Me_3NHCl, (2.644 gms; 27.6 mmoles) (Alfa Inorganics Inc.)

dried and purified by sublimation, was placed in the dumper tube of the reaction vessel which contained a nitrogen atmosphere.

The ether solution of $LiGaH_4$ was first cooled to $-50^{\circ}C$ in a dry-ice cooled acetone bath, as the trimethylamine hydrochloride was added over a period of about 10 minutes. Then the solution was allowed to warm up to room temperature and stirred for about four hours to ensure complete reaction.

The solution was next filtered through the glass sinter and the receiver flask containing the clear ether solution was attached to the sublimation apparatus, see Figure 5. This apparatus was attached to the vacuum line and the ether was pumped off at $-50^{\circ}C$. When most of the ether was removed, the residue was allowed to warm up to room temperature while the large bulb part of the sublimation apparatus was immersed in an acetone-solid CO_2 slush bath. The pure trimethylamine gallane was vacuum sublimed as long needle like crystals into the cooled receiver. The overall yield in going from gallium trichloride to trimethylamine gallane was about 60%.

The deuterated compound, trimethylamine trideuterogallane, Me_3NGaD_3 was prepared in the same manner only lithium gallium deuteride was substituted for lithium gallium hydride. Trimethylamine alane, Me_3NAlH_3, was also obtained similarly from commercially available $LiAlH_4$ and trimethylamine hydrochloride.

(d) Preparation of Alkylamino Gallazanes $(RNHGaH_2)_n$

As the procedures are similar for preparation of all the gallazane compounds, only the procedure for the ethylamino compound will be given as an example.

benzene. A weighed quantity of this solution was removed from the cryoscopic molecular weight apparatus and hydrolysed. The volume of hydrogen evolved on hydrolysis was then determined. The gallium content was determined gravimetrically by standard procedures. The deuterio derivative, $(EtNHGaD_2)_3$, was obtained by an exactly similar procedure to the above, but using Me_3NGaD_3 as the starting material. Experimental details for the other alkylamino gallazanes are summarized in table 1.

(e) Reaction of Me_3NGaH_3 with aniline $(C_6H_5NH_2)$

Aniline (.405 g, 4.352 mmoles) was condensed onto trimethylamine gallane (.573 g, 4.351 mmoles) at -196°C and allowed to warm to room temperature After complete reaction (about two days) the flask was cooled to -196°C and the volume of evolved hydrogen measured (Found: 92.5 ml; Calc. 97.8 ml). The mixture was then allowed to warm to room temperature and a trace of Me_3N was gas detected. The white solid product, Me_3NGaH_2NH , was monomeric in benzene (Found: 224, Calc. 223) and gave the following analysis: Ga: Found: 31.9%, Calc: 31.2%. H active: Found: 1.12%, Calc: 1.12%. Reaction of a two molal quantity of aniline led to an insoluble polymeric material. It evolved a 2 molal quantity of hydrogen as well as a molal quantity of Me_3N.

Reaction of $\phi NHGaH_2NMe_3$ with Methylamine

A measured amount of methylamine gas (42.8 ml) was condensed onto a weighed quantity of $\phi NHGaH_2NMe_3$ (.426 g, 1.878 mmoles) at -196°C and this mixture was then permitted to warm to room temperature. No hydrogen was evolved. The volume of trimethylamine gas was measured (Found: 92.4 ml, Calc: 91.8 ml) and its purity was checked by gas phase infrared spectroscopy. This product, as well as the products resulting

Table 1

Analytical data for cyclogallazane compounds prepared by the reaction:-

$$Me_3NGaH_3 + RNH_2 \rightleftharpoons (RNHGaH_2)_n + H_2 + Me_3N$$

Compound	Phase at 25°C	Moles H_2 per mole RNH_2	Moles Me_3N per mole RNH_2	Degree of association, n	Analysis			
					Found %		$(RNHGaH_2)$ requires %	
					Ga	Hydrolysable hydrogen	Ga	Hydrolysable hydrogen
$EtNHGaH_2$	Viscous liquid	1.01	1.01	2.92	60.1	1.73	60.2	1.73
Pr^nNHGaH_2	Viscous liquid	0.98	1.02	2.64	53.5	1.53	53.7	1.54
Bu^nNHGaH_2	Viscous liquid	1.00	1.09	2.57	48.4	1.37	48.5	1.39
Pr^iNHGaH_2	Mobile liquid	0.92	0.98	1.91	53.6	1.55	53.7	1.54
Bu^iNHGaH_2	Viscous liquid	0.95	1.03	2.15	48.4	1.38	48.5	1.39
Bu^sNHGaH_2	Mobile liquid	0.92	1.02	1.83	48.5	1.40	48.5	1.39
Bu^tNHGaH_2	White solid	0.97	1.02	1.83	48.4	1.37	48.5	1.39

from the reactions: aniline plus Me_3NGaD_3, aniline plus Me_3NGaH_3, methylamine plus $\phi NHGaD_2NMe_3$, and methylamine plus $\phi NHGaH_2NMe_3$ were characterized by infrared and ^1H nmr spectroscopy.

(f) Preparation of Cyclic Imino Gallazanes

Since the procedure for the preparation of these "double ring strain" gallazanes is standard throughout the series, and since the technique and apparatus are essentially the same as those used in preparation of the simple gallazanes, only a short procedure for aziridino gallazane will be given as an example.

Preparation of Aziridino Gallazane

Aziridino gallazane was prepared by condensing aziridine gas (23.8 ml; 1.50 mmoles) onto trimethylamine gallane (0.140 g; 1.60 mmoles) at -196°C, and allowing the mixture to warm slowly to room temperature. After complete reaction (about 1 h) the flask was cooled to -196°C, and the volume of evolved hydrogen measured (Found: 23.6 ml, Calc: 23.8 ml). The mixture was again brought to room temperature and the volume of trimethylamine gas was measured (Found: 24.4 ml, Calc: 23.8 ml). The purity of the Me_3N was checked by its gas phase i.r. spectrum. The white, crystalline solid product was analysed for hydrolysable hydrogen and for gallium by the previously discussed methods. The analytical data for the compounds prepared in this series are given in table 2.

(g) Preparation of Cyclic Imino Alazanes

The procedure for the preparation of this series of alazane compounds is standard throughout the series. Hence the pyrrolidino alazane preparation, only is given as an illustrative example.

Table 2

Analytical data for imine cyclogallazane compounds prepared by the reaction:-

$$Me_3NGaH_3 + (CH_2)_xNH \rightleftharpoons ((CH_2)_xNGaH_2)_n + H_2 + Me_3N$$

Compound	Phase at 25°C	Moles H_2 per mole imine	Moles Me_3N per mole imine	Degree of association, n.	Analysis			
					Found %		Theory %	
					Ga	Hydrol. hydrogen	Ga	Hydrol. hydrogen
$(CH_2)_2NGaH_2$	White solid	1.01	1.00	2.00 (2.56)*	62.1	1.76	61.4	1.76
$(CH_2)_3NGaH_2$	White solid	0.99	1.01	2.00	54.1	1.55	54.5	1.56
$(CH_2)_4NGaH_2$	White solid	0.99	0.99	2.02	49.0	1.38	49.2	1.41
$(CH_2)_5NGaH_2$	White solid	0.99	0.98	1.89	43.9	1.26	44.7	1.28

* Degree of association immedtately after dissolving imine cyclogallazane in benzene.

Preparation of Pyrrolidino Alazane $(CH_2)_4NAlH_2$

The bis trimethylamine alane used in the reaction was prepared by condensing excess Me_3N gas onto trimethylamine alane at -196°C. After equilibration of this system at room temperature, the excess trimethylamine was removed at -20°C, leaving the bis adduct.

Pyrrolidine (35.0 ml, 1.559 mmoles) was condensed onto bis trimethylamine alane (0.228 g; 1.542 mmoles) dissolved in 5 ml of dry benzene. This mixture was permitted to warm to room temperature. After the evolution of hydrogen had ceased, the flask was cooled to -196°C and the volume of hydrogen measured (Found: 35.2 ml; Calc: 35.0 ml). The benzene solvent and trimethylamine gas from the reaction were then removed at -20°C to leave a white crystalline solid in the reaction vessel. Analyses for aluminum and hydrolysable hydrogen were performed only on the aziridino alazane since most of these compounds had been previously prepared and analysed (23). Experimental data for this series of compounds is summarized in table 3.

(h) Preparation of Cyclic Imino Borazanes

The procedure for the preparation of these borazane compounds is standard for three of the derivatives, $(CH_2)_xNBH_2$ where x = 3, 4, 5 and therefore the preparation of pyrrolidino borazane only will be given. The preparation of aziridino borazane differs slightly and will be described later.

Preparation of Pyrrolidino Borazane

Pyrrolidino borazane was prepared by condensing pyrrolidine (100 ml, 4.45 mmoles) on a previously condensed sample of diborane (50 ml, 2.22 mmoles) in a 500 ml break-seal flask. The mixture was

Table 3

Analytical data for imino cycloalazane compounds prepared by the reaction:-

$$(Me_3N)_2AlH_3 + (CH_2)_xNH \longrightarrow ((CH_2)_xNAlH_2)_n + H_2 + 2Me_3N$$

Compound	Phase at 25° C	Moles H_2 per mole imine	Molecular weight	Degree of association n
$(CH_2)_2NAlH_2$	White solid	1.02	298	4.20 (3.14*)
$(CH_2)_3NAlH_2$	White solid	1.00	263*	3.06*
$(CH_2)_4NAlH_2$	White solid	1.01	308	3.10
$(CH_2)_5NAlH_2$	White solid	0.98	243	2.17

Analytical data for imino cycloborazane compounds prepared by the reaction:-

$$\tfrac{1}{2} B_2H_6 + (CH_2)_xNH \longrightarrow ((CH_2)_xNBH_2)_n + H_2$$

Compound	Phase at 25° C	Moles H_2 per mole imine	Molecular weight	Degree of association, n
$(CH_2)_2NBH_2$	White solid	----	165	3.00
$(CH_2)_3NBH_2$*	White solid	0.97	134	1.94
$(CH_2)_4NBH_2$	White solid	1.03	166	2.00
$(CH_2)_5NBH_2$	White solid	1.08	196	2.02

* Private communication Dr. B. S. Thomas.

allowed to warm to room temperature to form the liquid adduct. The bulb was then cooled and sealed off under vacuum. It was then placed in an oven at 128°C for 3 1/2 hours to pyrolyse the adduct. After pyrolysis was complete, the flask was attached to the vacuum line, cooled to -196°C and the fragile break-seal ruptured with a bar magnet. The evolved hydrogen was measured (Found: 103 ml, Calc: 100 ml). The product was then warmed to room temperature and checked for non-condensibles. Experimental data for these compounds is given in the lower part of table 3.

(i) Preparation of Aziridino Borazane

This compound was prepared by condensing aziridine (100 ml, 4.45 mmoles) onto a sample of diborane (50 ml, 2.22 mmoles) at -196°C. About 5 ml of strictly dry diethyl ether was condensed onto this mixture and the mixture warmed to -130°C. At this point the mixture was permitted, by means of a propane slush bath, to warm slowly to -78°C. The ether was removed giving a product, which when solvent free was a white crystalline solid. The infrared and ^{1}H nmr spectra of this adduct agreed with those found in the literature (18). The adduct was dissolved in benzene and refluxed under an atmosphere of dry nitrogen for three to four hours. The aziridino borazane product was separated by removing the benzene solvent at -20°C. The IR and ^{1}H nmr spectra recorded for the aziridino borane obtained by this method, agreed with those found in the literature (18).

Attempts to prepare this complex by a pyrolysis method using the reaction of aziridine with either $Me_3N.BH_3$ or diborane failed to give the desired product. These reactions were non-stoichiometric, yielding 40% of the theoretical hydrogen and 77% of the Me_3N in the first case and only 54% of hydrogen in the last. The products in each of these cases

gave liquid plus solid but were not soluble in benzene to any significant extent.

(j) Preparation of Aziridine Gallium trimethyl and Aziridino Gallium dimethyl

The adduct aziridine gallium trimethyl was prepared by condensing aziridine (75.5 ml, 3.36 mmoles) onto gallium trimethyl (75.5 ml, 3.36 mmo at -196°C and warming to room temperature. The adduct was a clear mobile liquid which was stable to methane elimination at room temperature.

The aziridino gallium dimethyl was prepared by pyrolysing a 0.413 g sample of the previously prepared adduct at 110°C for 5 hours in a break-seal bulb. After the five hour reaction time the bulb, now containing a white solid (mp 184°C) was connected to the high vacuum line, cooled to -196°C, the glass break seal ruptured and the methane measured (Found: 56.8 ml, Calc: 58.8 ml). The product was then warmed to room temperature and checked for the presence of condensibles.

The analytical data for the other compounds of this series is given in table 4.

(k) Preparation of Aziridine, 

Since commercial samples of aziridine were not available the preparation of this material was undertaken using the following route. The methods of Wenker (24) Leighton (25) and Reeves (26) were all tried but gave lower yields than the following method.

96% H_2SO_4 (109.9 g, 1.04 moles) was added directly to a stirred sample of ethanolamine (65.7 g, 1.07 moles). This mixture was then heated to 100°C under water aspirator vacuum to give a quantitative yield of ethonolamine sulfate according to the following scheme:

Table 4

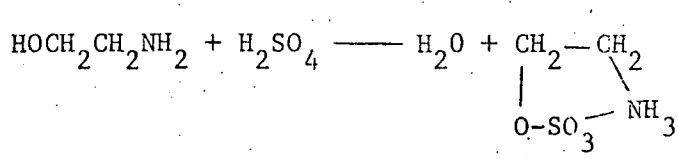
Analytical data for imine metal trimethyl and imino metal dimethyl compounds prepared by the following:

$$Me_3M + (CH_2)_2NH \longrightarrow Me_3M.NH(CH_2)_2$$

$$Me_3M.NH(CH_2)_2 \longrightarrow (Me_2M.N(CH_2)_2)_n + CH_4$$

Compound	Phase at 25°C	Moles methane per mole imine	Pyrolysis temperature	Degree of association n
$Me_3GaNH(CH_2)_2$	mobile liquid	----	110°C,5h	----
$Me_2GaN(CH_2)_2$	white solid	0.97	----	2.88
$Me_3BNH(CH_2)_2$	mobile liquid	----	180°C,12h	----
$Me_2BN(CH_2)_2$	white solid	0.68	----	polymeric solids and liquids
$Me_3AlNH(CH_2)_2$	mobile liquid	evolves CH_4 at r.t.	60°,4h	----
$Me_2AlN(CH_2)_2$	white solid	0.88	----	2.96
$Me_3InNH(CH_2)_2$	mobile liquid	evolves CH_4 at r.t.	80°C,12h	----
$Me_2InN(CH_2)_2$	white solid	0.70	----	3.00*

*Private communication Dr. R. S. Thomas.



The white solid product was ground with 95% EtOH, suction filtered and dried in a vacuum descicator over P_2O_5.

The ethonolamine sulfate was then placed in a 1000 ml round bottomed flask surmounted by a still head and water condenser set for downward distillation and overlaid with a 40% NaOH solution (95 g NaOH, 143 g H_2O). The flask was heated with an open flame and the distillate collected rapidly in a well cooled 500 ml receiver. Once distillation was complete, enough KOH to obtain a saturated solution was added and the flask stored in the fridge overnite. The upper organic layer was then removed and dried over CaH_2/KOH. The product, when water and ethanol free was stored over CaH_2 at $+5^{\circ}$ until required. (Yield $\sim$15%).

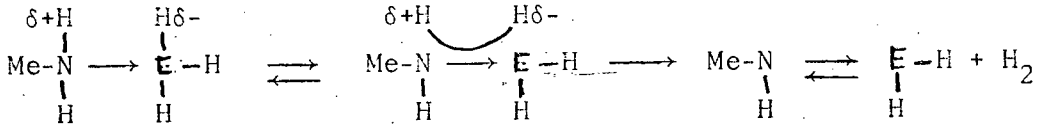
Azetidine (27),  .

Azetidine was prepared by the same procedure as above but starting with propanolamine instead of ethanolamine. The yield was about 1%.

DISCUSSION

Part 1

The ease of intramolecular hydrogen elimination from adducts of the type $MeNH_2$, EH_3, where E is B, Al or Ga follows the sequence B < Ga < Al as illustrated in figure 8. Note that 90° (28) is required for hydrogen elimination with boron; $MeNH_2GaH_3$ eliminates hydrogen at room temperature (13), while $MeNH_2AlH_3$ eliminates two molar equivalents of hydrogen at -20° (29). Stone (30) explains this sequence in terms of the relative electro-negativity values of the atoms involved.



In the above scheme the hydrogen attached directly to the nitrogen atom is considered to lose electron density on formation of an electron donor bond by the donor moeity. Hydrogen attached to the acceptor atom, E, simultaneously increases in electron density and an electrical strain is thus created in the adduct. The strain is relieved when hydrogen elimination occurs. On the basis that the differences between the Allred-Rochow (31) electro-negativities of the E atoms and that of hydrogen (at 2.1) increase in the order B, Ga, Al, the hydridic character in EH_3, and hence the ease of hydrogen elimination should decrease in the order Al through Ga to B, as observed.

The factors affecting the association of the products from hydrogen elimination are believed to be the following (32).

(i) Steric Effect - With the same donor and acceptor atoms

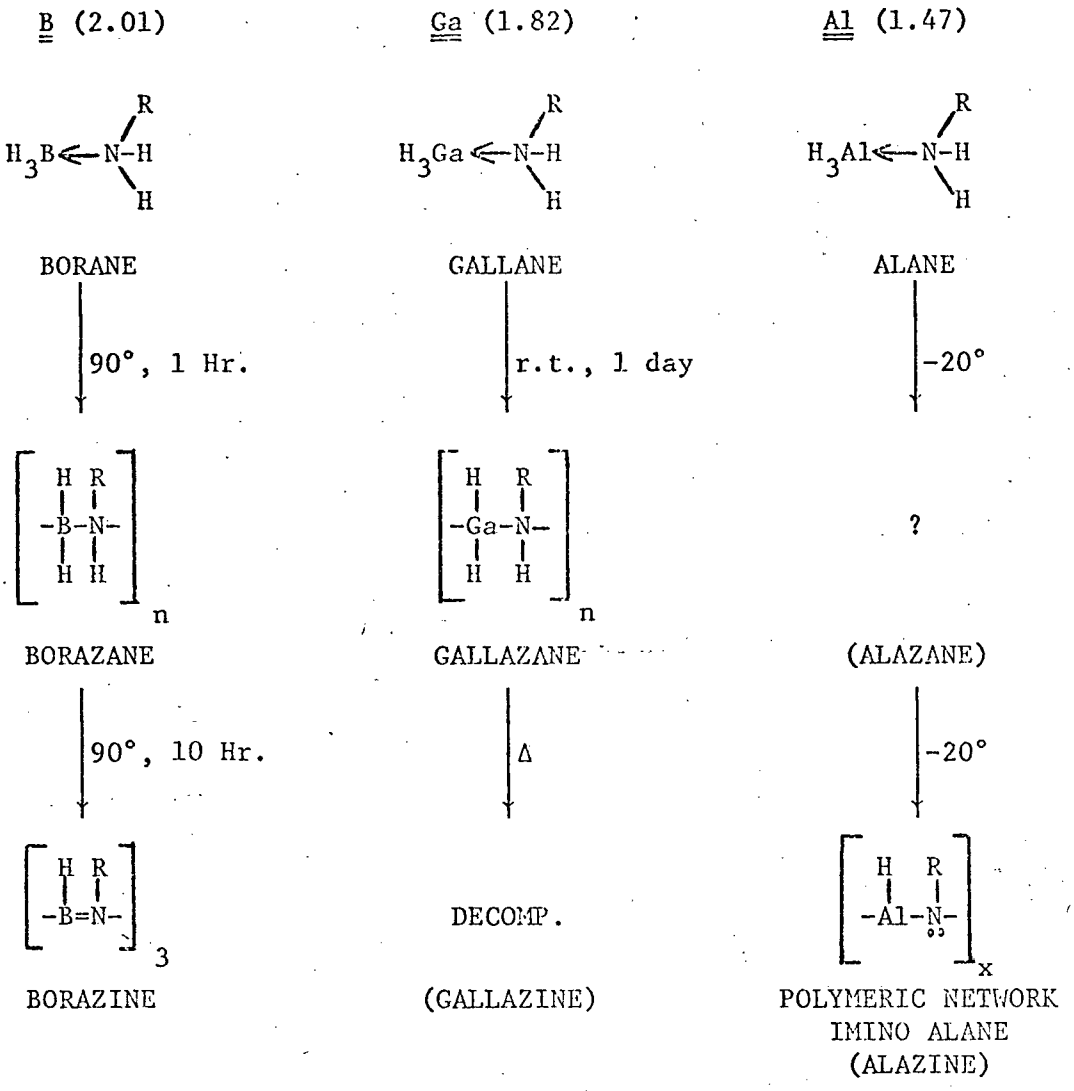

B (2.01)
Ga (1.82)
Al (1.47)
BORANE
GALLANE
ALANE
90°, 1 Hr.
r.t., 1 day
-20°
BORAZANE
GALLAZANE
(ALAZANE)
?
90°, 10 Hr.
Δ
-20°
DECOMP.
BORAZINE
(GALLAZINE)
POLYMERIC NETWORK
IMINO ALANE
(ALAZINE)

Figure 8

increased size of R groups on the E atom cause a shift to lower oligomers.

(ii) Valency angle strain - Dimers contain more strain than trimers, but this is easier to tolerate with larger donor and acceptor atoms.

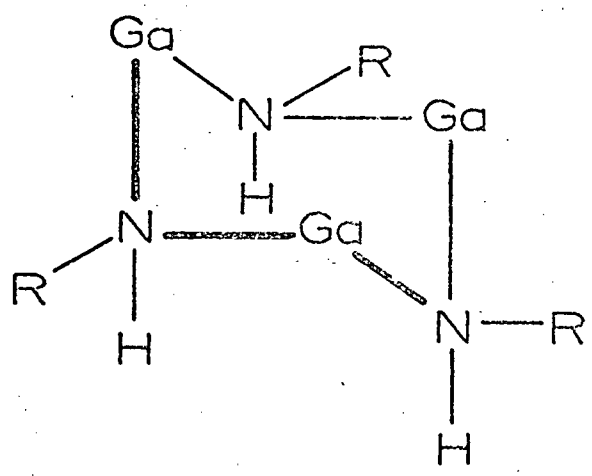
(iii) Entropy - Prefers monomer over dimer and dimer over trimer.

(iv) Nature of reaction intermediates.

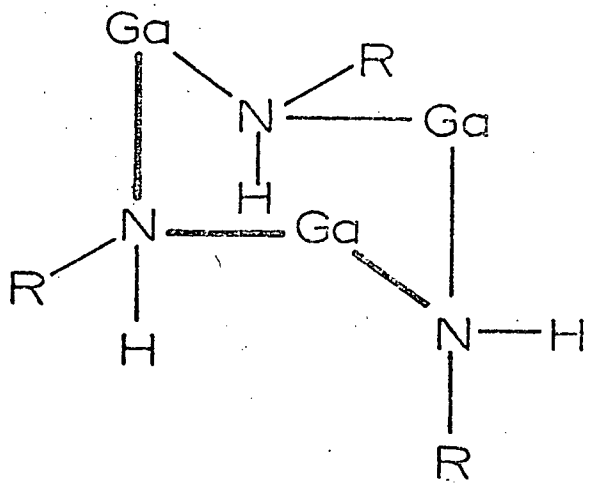
The cyclogallazanes prepared in this study ranged from white solids to mobile liquids and all had satisfactory analyses for gallium and hydrolysable hydrogen; all were soluble in common organic solvents. As is evident from Table 1, increasing the size of the R group coincides with the formation of lower oligomers. Thus, steric interactions in cyclohexane-type trimers become too large and a preference for the angularly-strained dimers, with lower steric requirements, becomes apparent. With both the trimeric and dimeric species the physical data (i.r. and ^1H nmr spectra) indicate the presence of at least two configurational isomers in benzene solution.

Trimeric Cyclogallazanes $(RNHGaH_2)_3$

A cyclohexane-type ring structure for trimeric cyclogallazanes, $(RNHGaH_2)_3$, is proposed on evidence collected from ^1H nmr data and from supplementary evidence from i.r. spectroscopy measurements. As observed with the methyl derivative, (13) at least two configurational isomers are present in benzene solutions of the new trimers. Figure 9. The most stable isomer, on steric grounds, is the one in which all three N-alkyl groups occupy equatorial positions on the ring. The next most stable isomer, sterically, is one in which one N-alkyl group is axial and the remaining two N-alkyl groups equatorial to the $(Ga-N)_3$ ring.



CIS



TRANS

Conformations of Trimeric Gallane Species

Figure 9

These isomers will be termed cis and trans respectively.

$(EtNHGaH_2)_3$ - 1,3,5-Triethylcyclogallazane, a viscous liquid at room temperature, is trimeric in benzene solution. The partial ^1H nmr spectrum of the benzene solution at 100 MHz (Figure 10) shows clearly the presence of a number of non-equivalent β-CH_3 groups. The signals from these groups consist of three well-defined triplets (J_{HCCH} ca. 7 Hz). The pattern of signals suggests that the triplets A and B arise from β-CH_3 groups in similar environments whereas the triplet C, at higher field, appears unique. It is therefore tempting to assign triplets A and C to the trans-isomer (ca. 2:1 ratio), and the triplet B to the cis-isomer. The triplets A and B, both assigned to equatorial β-CH_3 groups, occur very close together which is to be expected since little change in equatorial β-CH_3 environment will occur between the two isomers. These assignments would indicate that the trans-isomer is in greater abundance, which is somewhat surprising for a cyclohexane-type ring on purely steric arguments. Similar trimeric borazanes, (33) however, show this same preference for trans-isomer formation. An alternate explanation is to assign the triplet A to the cis-isomer and the triplets B and C (ca. 1:2 ratio) to a twist conformation similar to the one recently reported for the ethyleniminodimethylaluminium trimer (34). In the twist conformation one could again obtain β-CH_3 groups in different environments in a 1:2 ratio, the unique β-CH_3 group being attached to the nitrogen on the two-fold axis of the molecule. This alternate explanation would then indicate the sterically favoured cis-isomer in greater abundance. If the chair-type model is accepted for the trimeric gallazanes, it is interesting to note the appearance of the axial β-CH_3 signal in $(EtNHGaH_2)_3$ at higher field than the equatorial

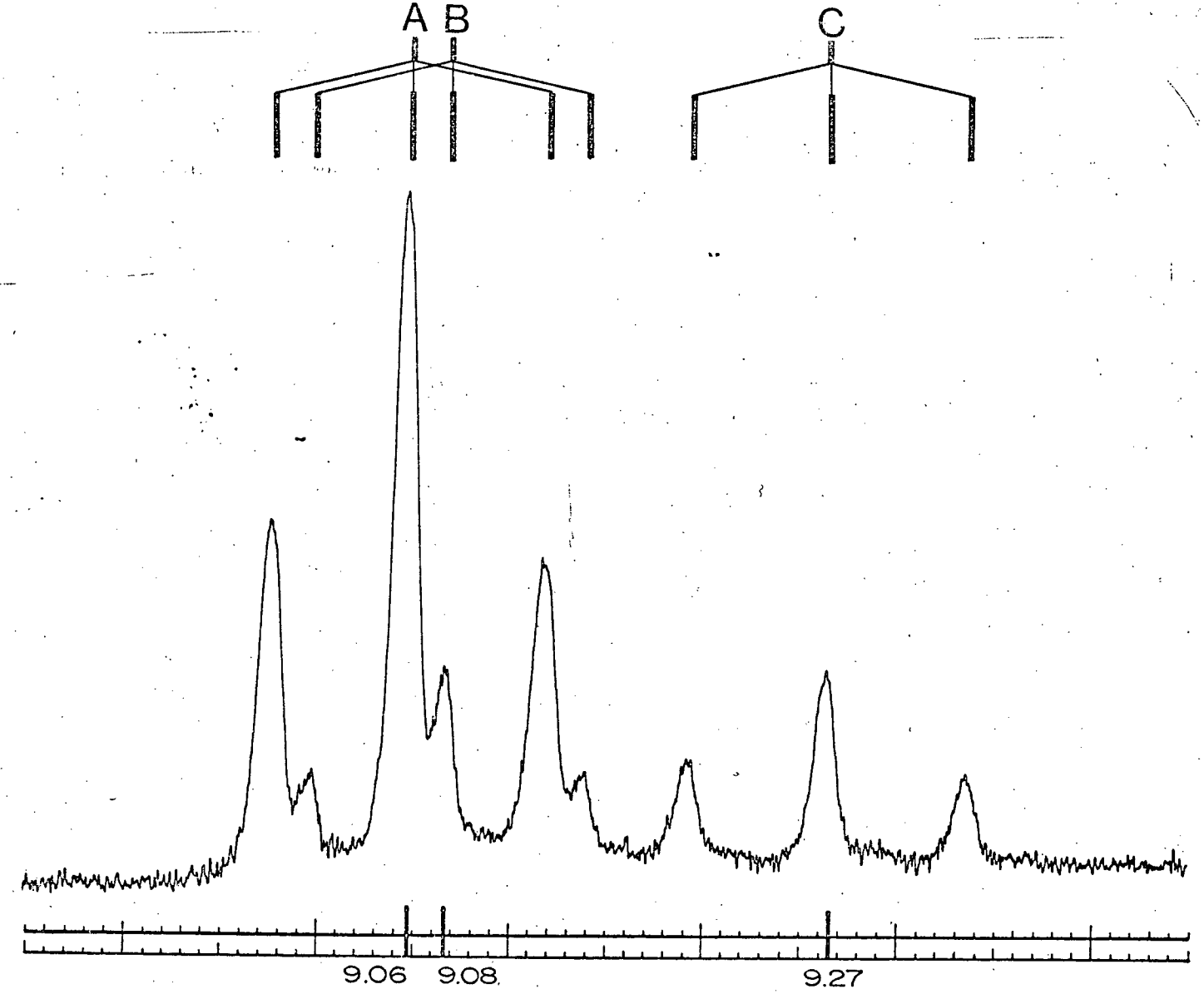
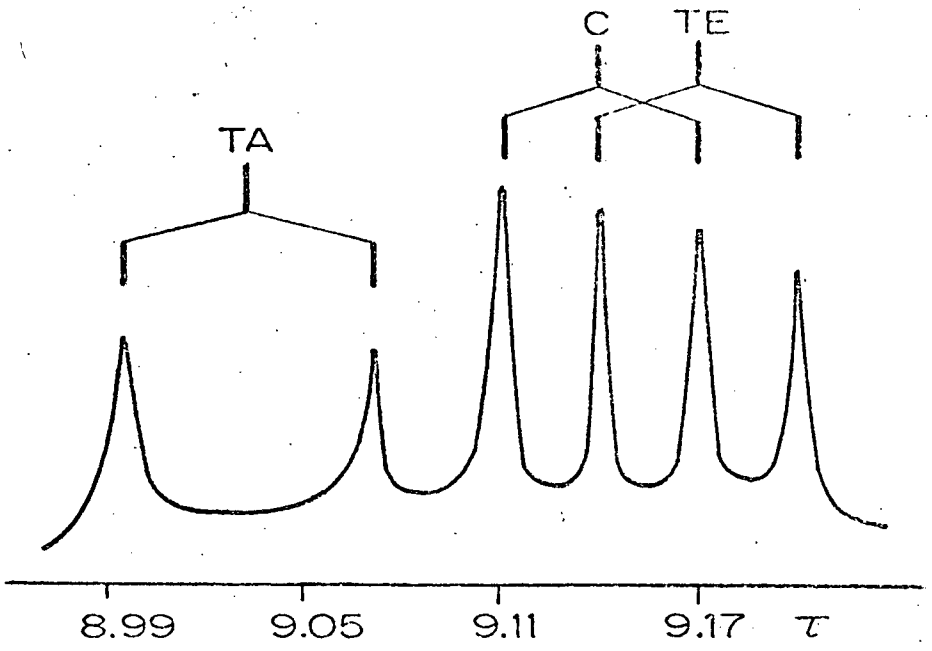
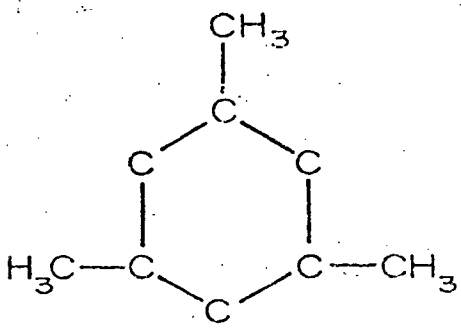


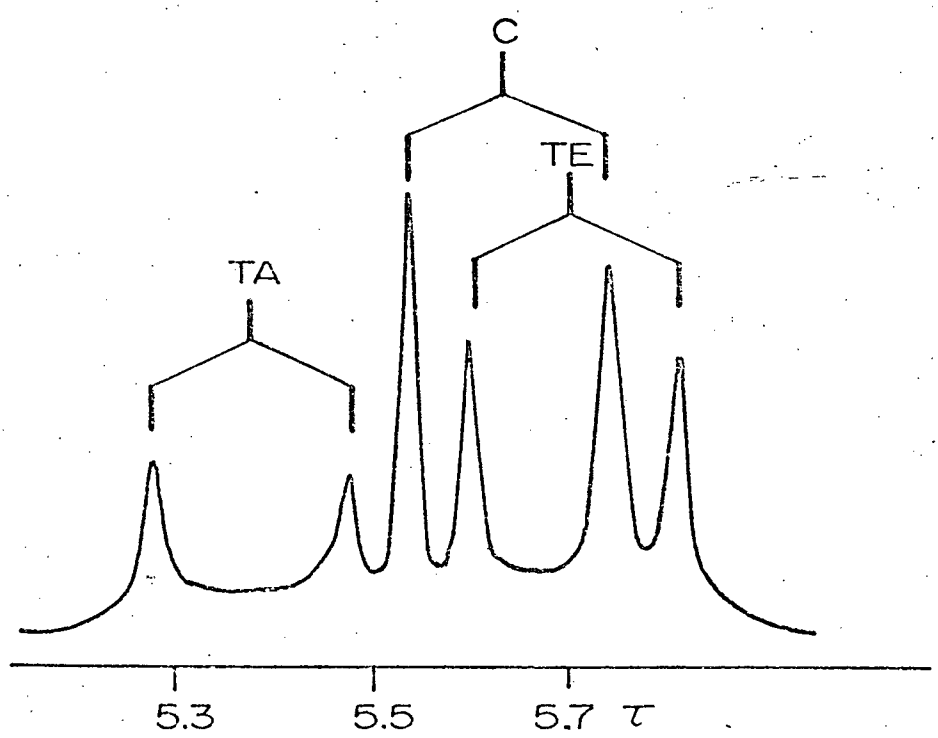
Fig. 10 100 Mc/s ^1H n.m.r. spectrum of $EtNHGaH_2$ in benzene solution

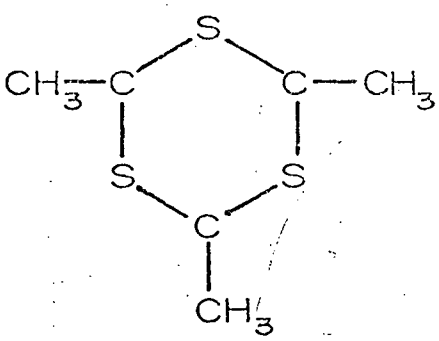
β-CH_3 signals. This is in contrast to the axial NMe signal in the trans-$(MeNHGaH_2)_3$ trimer, which appears at lower field than the equatorial signals (13). It seems that this downfield shift for methyl groups axial to cyclohexane-type rings is quite common, occurring in a variety of inorganic ring systems, $(MeNHBH_2)_3$, (35) $(MeCH.S)_3$, (36) $(MeCH.CH_2)_3$, (37) and $(MeCH.O)_3$, (38) two of which are shown in Figure 11. Perhaps this phenomenon can be accounted for by invoking van der Waals deshielding due to 1,3-axial interactions. With the β-CH_3 groups of $(EtNHGaH_2)_3$ the proximity to axial hydrogens on the nitrogen atoms is evidently not sufficient to give this type of deshielding. The methylene protons in $(EtNHGaH_2)_3$ do not give well resolved signals but overlapping quintets are apparent in the ^1H nmr spectra ($J_{HCCH} \cong J_{HNCH}$) (Figure 12), presumably arising from the axial and equatorial environments in the different isomers. The NH resonance is partly 'hidden' under the β-CH_3 signals in the hydride compound occurring at ca τ 9.3, but it appears as a broad triplet (J_{HNCH} ~7 Hz) at higher field (τ 9.52) in the spectrum of the deuterioderivative, $(EtNHGaD_2)_3$, at 100 MHz (Figure 13). Signals due to GaH protons were not observed principally because of low concentrations but also perhaps because of nuclear quadrupole broadening (39, 40).

The ^1H nmr spectra of the remaining trimeric gallazanes (R = Pr^n and Bu^n) are less clearly resolved, even at 100 MHz. The γ-CH_3 proton signals in $(Pr^nNHGaH_2)_3$ appear as a series of triplets (J_{HCCH} ca. 7.2 Hz) centred at τ 9.43, 9.44, and 9.46 again indicating the presence of at least two isomers. These triplets are tentatively assigned to cis- and trans-isomers, the triplet at higher field being









^{1}H n.m.r. of some cis and trans trimers.

Figure 11

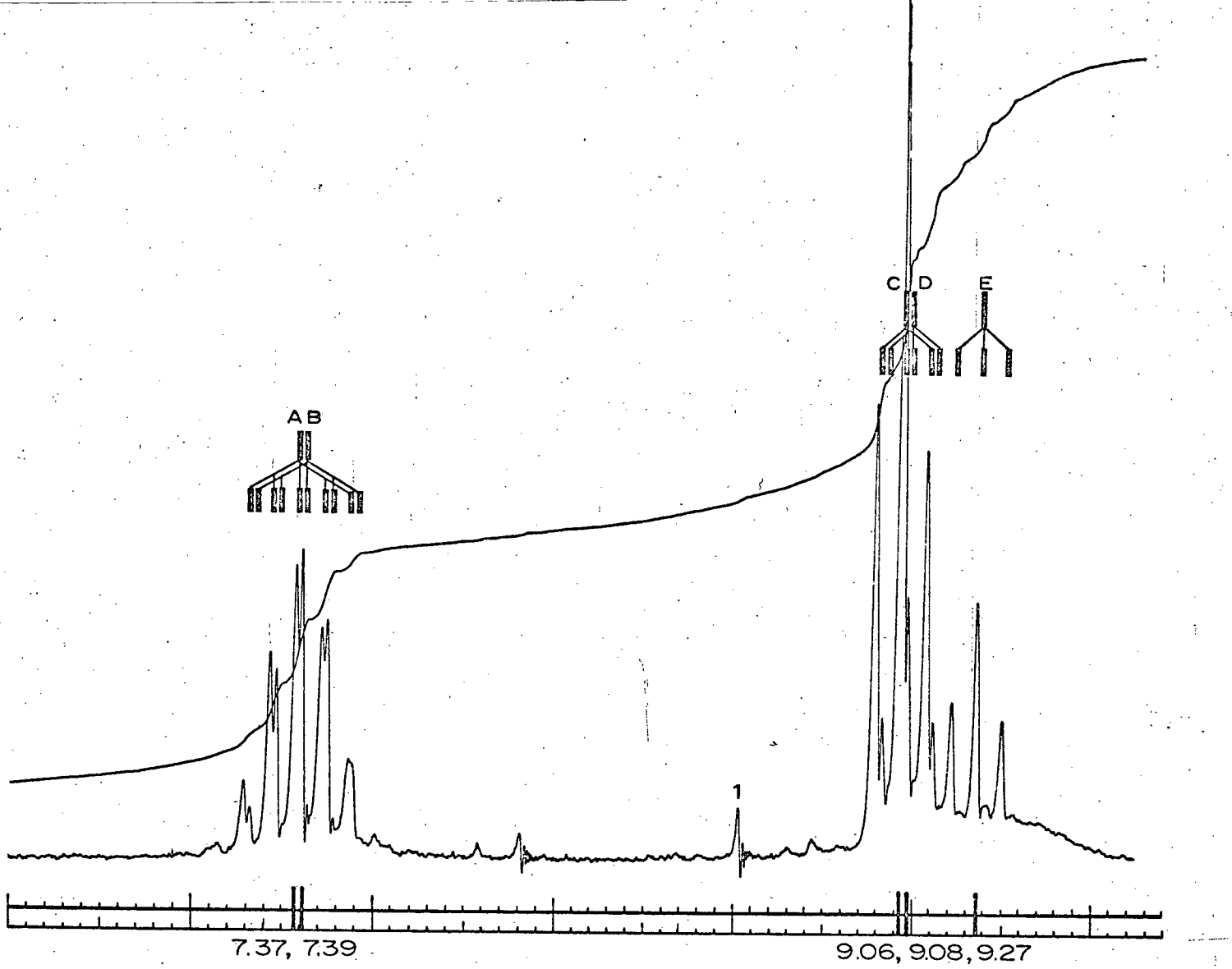


Fig.12 100 Mc/s ^1H n.m.r. spectrum of $EtNHGaH_2$ in benzene solution.

assigned to the axial γ-CH_3 group of the trans-isomer. The ^1H nmr spectra of the n-butyl derivative are very complex, even at 100 MHz, and no assignment is attempted.

Dimeric Cyclogallazanes, $(RNHGaH_2)_2$

Dimeric cyclogallazanes, $(RNHGaH_2)_2$ may exist as configurational isomers with the N-alkyl groups cis or trans on the ring [(IIa) and (IIb) respectively]. A number of additional variations are possible if the $(Ga\text{-}N)_2$ ring is nonplanar, which has been shown to be the case for numerous analogous substituted cyclobutane derivatives (41, 42). Non-planar configurations may be expected more especially in the cis-isomer, to relieve steric interactions between adjacent, bulky, R groups.

$(Pr^iNHGaH_2)_2$ - 1,3-Di-isopropylcyclogallazane is a mobile liquid at room temperature and is readily sublimed. In benzene solution its molecular weight corresponds to a dimer. The ^1H nmr spectrum in benzene solution consists of a series of doublets in the γ-CH_3 region of the spectrum (Figure 14). The major doublets, D and E (J_{HCCH} 6.3 Hz) at τ 9.14 and 9.15 are assigned to the cis- and trans-isomers of the dimer. The remaining small doublets in this region may be due partly to NH signals (J_{HNCH} 6.3 Hz) or to the presence of small amounts of other oligomers. Attempted fractional distillation, however, failed to separate any components and all fractions when dissolved in benzene gave similar spectra to that shown in Figure 14. The possibility of restricted rotation of the isopropyl groups in one isomer leading to both the major doublets A and B in the spectrum was investigated by obtaining spectra at a series of temperatures (0 - 60°). Although the separation between the two doublets decreased slightly at higher temperatures there was no

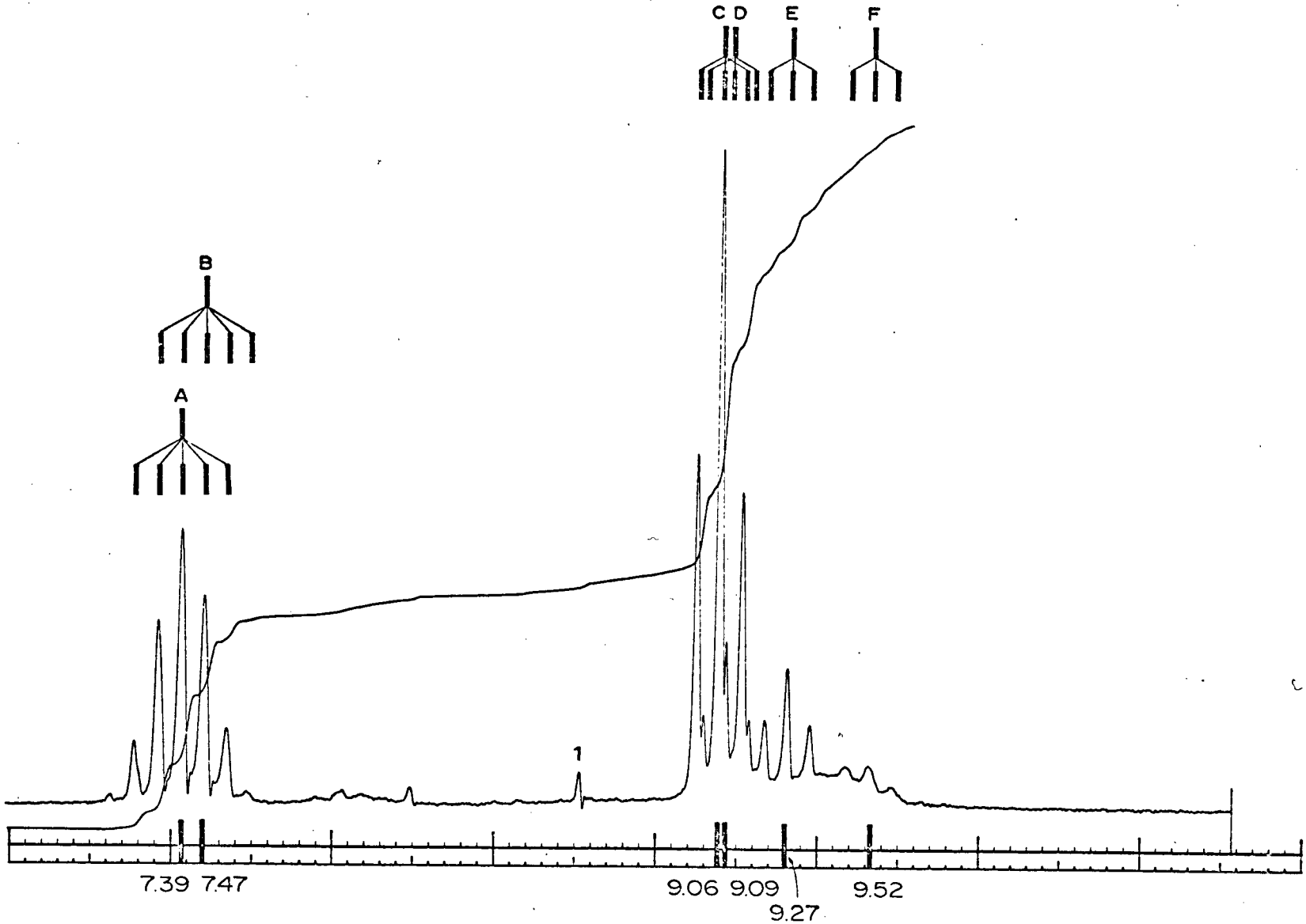


Fig. 13 100 Mc/s ^1H n.m.r. spectrum of $EtNHGaD_2$ in benzene solution.

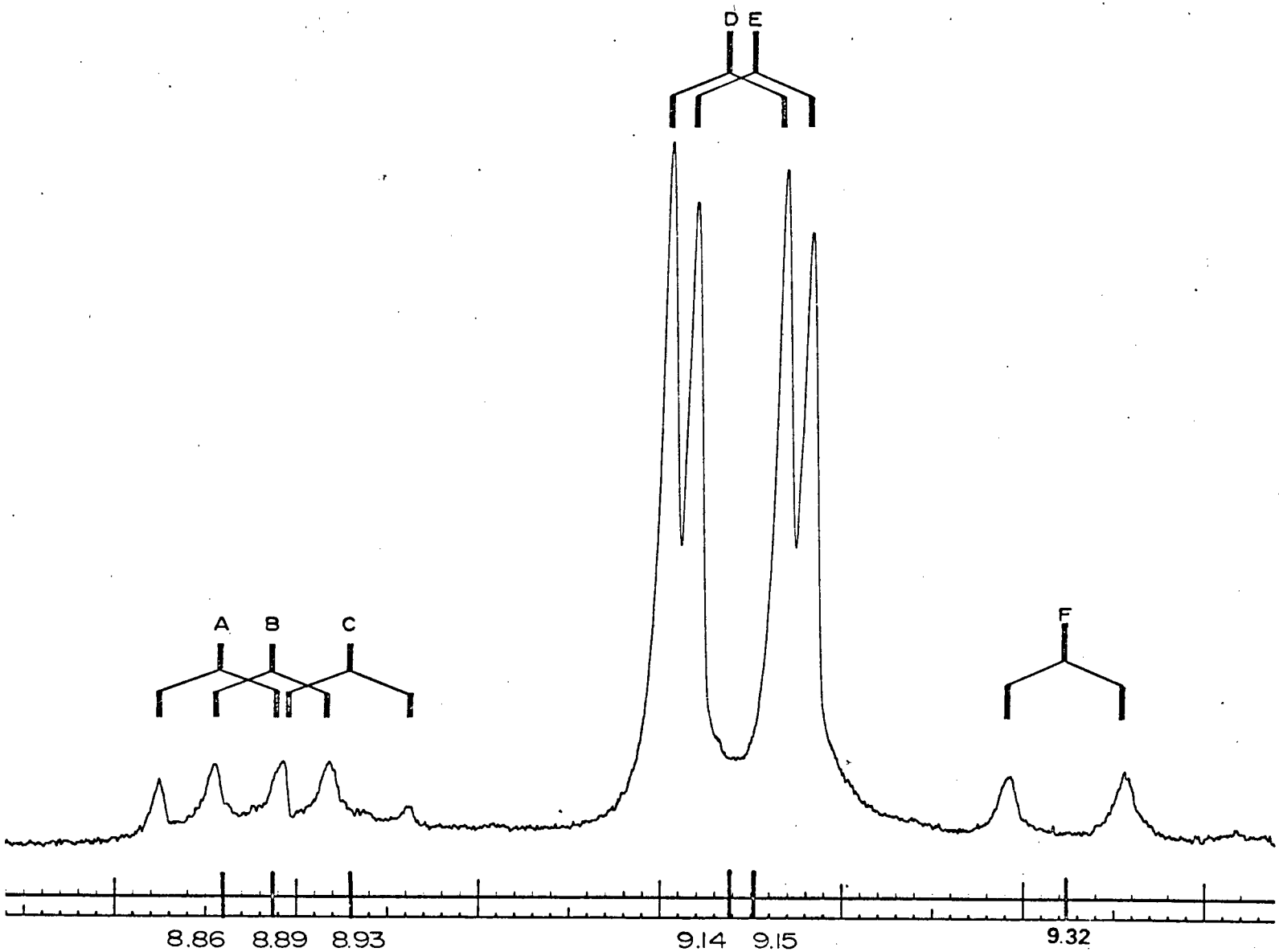


Fig. 14 100 Mc/s ^1H n.m.r. spectrum of i-$PrNHGaH_2$ in benzene solution.

indication of a collapse to just one doublet and therefore the assignment of A and B to cis- and trans-isomers is preferred.

The neat liquid $(Pr^{i}NHGaH_2)_2$ and its deuterio analogue gave the novel ^{1}H nmr spectra shown in Figure 15. Here, for the first time, the GaH signals are clearly seen as broad resonances at τ 4.71 and 4.88. The signals are field dependent and indicate the presence of different environments for hydrogens on gallium atoms. These signals are, of course, absent in the spectrum of the deuterio-derivative, thus confirming the assignment. In addition, the CH multiplet ($J_{HCCH} \cong J_{HNCH}$), centred at τ 6.34, and the broad NH resonance at τ 7.94 are clearly distinguished. The remaining doublets, A and B, (J_{HCCH} 6.4 Hz) due to β -CH_3 groups are centred at τ 8.15 and 8.32. Again a mixture of cis- and trans-dimers (Figure 16) is postulated and it is seen as fortuitous that the ratio of the β-CH_3 doublets is approximately 1:2. The presence of the trimer in the liquid form, which could give rise to this ratio, is discounted on the mass spectra data obtained for the deuterio-compound, $(Pr^{i}NHGaD_2)_2$. The ions of high m/e values are listed in Table 5 and correspond to the pattern expected from the dimer $(Pr^{i}NHGaD_2)_2$ taking into account the isotopic distribution of gallium atoms in the molecules [^{69}Ga(60%), ^{71}Ga(40%)]. Molecular-ion peaks, although weak, occur in the mass spectrum in addition to peaks due to the more abundant ions which have lost deuterium from gallium. The most intense peak in the spectrum occurs at m/e = 44 and may correspond to the propane ion $C_3H_8^{+}$. The spectrum gave no indication of the presence of trimeric units, and since it is unlikely for the dimer to be converted into trimer in going from vapour to liquid, a dimeric constitution for the neat compounds is

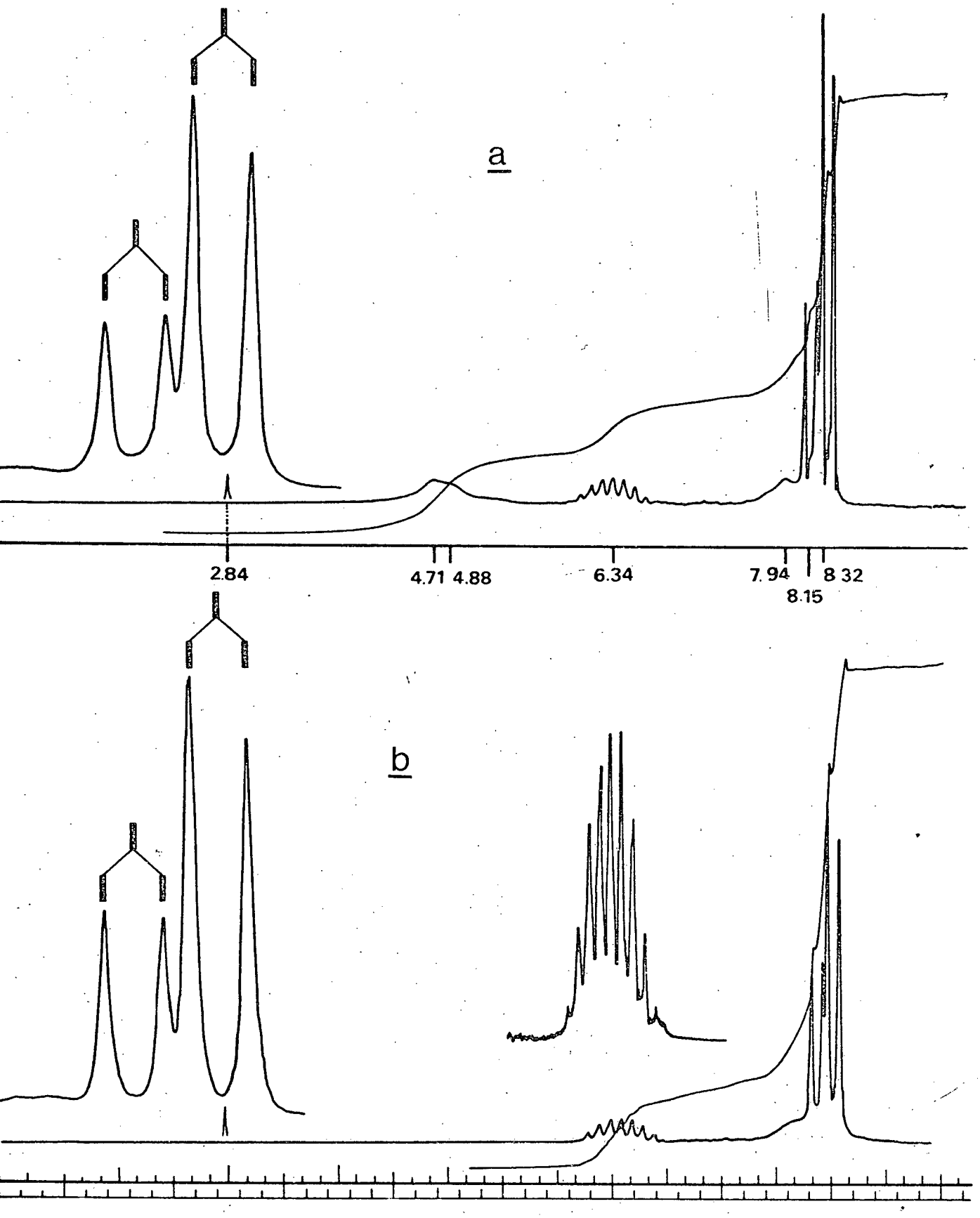
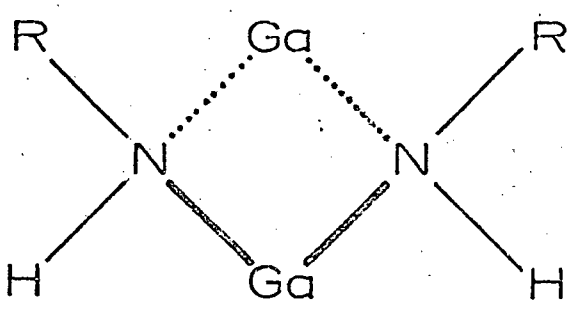
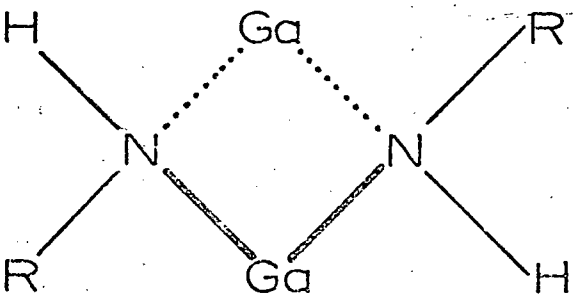


Fig.15 60 MHz ^{1}H n.m.r. spectrum of neat a Pr^iNHGaH_2 and b Pr^iNHGaD_2



IIa

CIS



IIb

TRANS

Conformations of Dimeric Gallane Species.

Figure 16

predicted.

$(Bu^{s}NHGaH_2)_2$ - 1,3-Di-s-butylcyclogallazane is a mobile liquid at room temperature. It is dimeric in benzene solution and in this solvent it has a ^1H nmr spectrum which exhibits two strong doublets (J_{HCCH} ca. 6.6 Hz) at τ 9.13 and 9.16 which are assigned to the β-CH_3 groups in the cis- and trans-dimers. Signals due to the γ-CH_3 protons appear at higher field but the triplets expected on a first-order basis are poorly resolved. The ^1H nmr spectrum of the neat liquid showed essentially the same pattern as the solution spectrum but once again, in addition, the GaH signals are clearly visible at τ 4.64 and 4.81 (Figure 17).

$(Bu^{i}NHGaH_2)_2$ - 1,3-Di-isobutylcyclogallazane is a viscous liquid at room temperature and in solution probably exists as a mixture of dimers and trimers. Branching of the hydrocarbon chain of the R group at the β-carbon atom possibly reduces the steric interaction sufficiently to lead to both dimer and trimer formation. Four well-defined doublets (J_{HCCH} ca. 6.6 Hz) at τ 9.27, 9.30, 9.31, and 9.38 appear in the high field region of the ^1H nmr spectrum in benzene solution at 100 MHz. These are assigned to β-CH_3 groups but no further assignment is attempted.

$(Bu^{t}NHGaH_2)_2$ - 1,3-Di-t-butylcyclogallazane is a white solid at room temperature, dimeric in benzene solution, and displaying three β-CH_3 signals in its ^1H nmr spectrum in this solvent. Two of these signals are close together at τ 8.96 and 8.97, and a third, much weaker signal, occurs at higher field (τ 9.15). The signals are all field dependent and therefore not due to coupling. The major signals are assigned to the cis- and trans-dimers, the third weaker signal, accounting for ca. 5% of the total integral, is possibly due to monomer in solution.

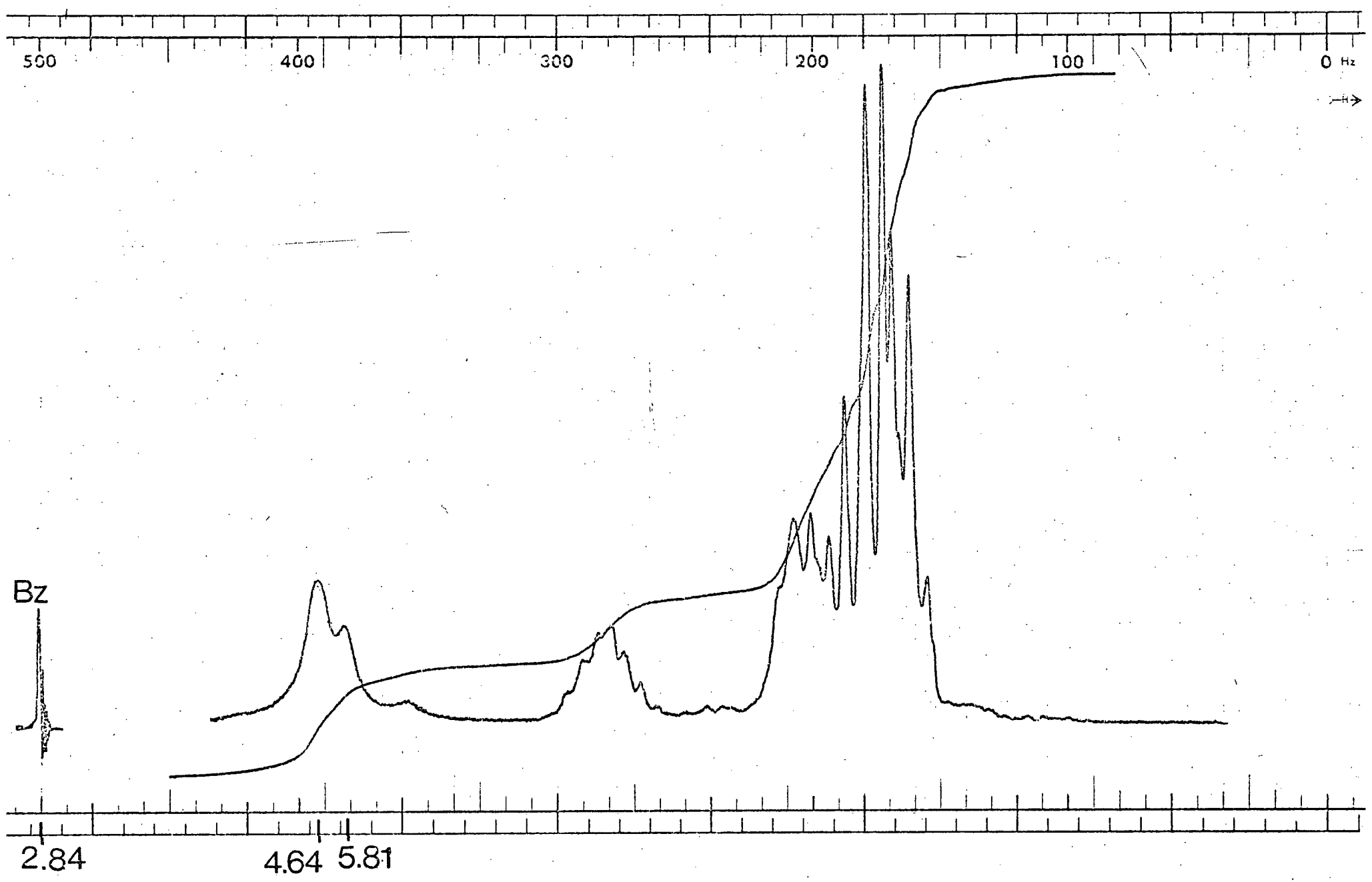


Fig.17 60Mc/s ^1H n.m.r. spectrum of neat sec-$BuNHGaH_2$.

Table 5

Ions of high m/e in mass spectrum of $(Pr^{i}NHGaD_2)_2$.

	m/e	Relative Abundance	
	266	0.5	
	265	0.5	
	264	5.0	
	263	2.5	
	262	17.5	
	261	3.7	
	260	27.7	
	259	12.5	
	258	16.0	
	257	0.5	
	.		
	.		
	.		
	44	100.0	

I.r. Spectra of Cyclogallazanes $(RNHGaH_2)_n$

I.r. spectra of the cyclogallazanes $(RNHGaH_2)_n$, and their deuterio-derivatives $(RNHGaD_2)_n$ in some cases, in benzene solution were recorded in the range 4000 - 250 cm^{-1}. As observed previously with gallane derivatives (5, 11), the strongest absorptions were attributable to the Ga-H and Ga-D stretching and deformation modes. Selected absorption bands are listed and assigned in Table 6 for the ethyl and isopropyl derivatives which are representative of the trimeric and dimeric cyclogallazanes respectively. As expected on a mass effect the ratio ν(Ga-H)/ν(Ga-D) is close to 1.4. The NH stretching abosrptions are interesting in that three bands occur in this region for trimeric species but two bands only, for dimeric species. Presumably the different possible environments for the NH unit in the various cis- and trans-isomers lead to the observed vibrations but is is noteworthy that the band at 3280 cm^{-1} in the ethyl derivatives is concentration dependent, decreasing in relative intensity on dilution. Perhaps hydrogen bonding of the type invoked recently by Brown et al (43), to explain the i.r. spectra of similar cycloborazanes at various concentrations, could be operative, also, in these gallium systems.

The i.r. spectra of neat $(Pr^iNHGaH_2)_2$ and its deuterio-analogue were also recorded. In each spectrum the NH stretching vibration occurred as a broad band at 3270 cm^{-1}. Similarly, Ga-H(D) stretching vibrations appeared as broad bands at 1875 and 1825 (1350) cm^{-1}. The Ga-H(D) deformation modes occurred at 725 and 690 (510, 493) cm^{-1} and absorptions attributable to ring vibrations came in the region 540 - 590 cm^{-1}.

Table 6

Infrared spectra of some cyclogallazane derivatives in benzene solution.

$EtNH.GaH_2$	$EtNH.GaD_2$	$\frac{GaH}{GaD}$	Assignment
3338 w 3318 m 3280 s	3338 w 3316 m 3280 s		N-H stretch
1875 vs 1825 vs	1350 vs 1335 vs	1.374	Ga-H(D) stretch
745 vs	502 vs 496 vs	1.404	Ga-H(D) defn.
580 s 550 s 510 m	542 s 522 s		Ring modes

Pr^iNHGaH_2	Pr^iNHGaD_2	$\frac{GaH}{GaD}$	Assignment
3320 m 3283 s	3320 w 3283 m		N-H stretch
1875 vs 1820 vs	1355 vs 1330 s	1.364	Ga-H(D) stretch
745 vs	508 vs 497 vs	1.465	Ga-H(D) defn.
586 s 560 m 490 m	596 s 552 s 536 m		Ring modes

Bu^tNHGaH_2	Bu^tNHGaD_2	$\frac{GaH}{GaD}$	Assignment
3307 w 3208 vs	3312 s 3264 s		N-H stretch
1890 vs 1820 m	1318 vs	1.408	Ga-H(D) stretch
745 s	538 vs 521 vs	1.402	Ga-H(D) stretch
598 s	554 s		Ring modes

Part 2

The reaction of aniline with trimethylamine gallane proceeded as indicated in the following equation:

$$Me_3N.GaH_3(s) + \phi NH_2(g) \longrightarrow \phi NH.GaH_2.NMe_3(s) + H_2(g)$$

The monomeric material, $\phi NH.GaH_2.NMe_3$, giving the ^1H nmr shown in Figure 18, was somewhat unexpected since with the primary alkylamine reactions discussed in part 1, complete elimination of trimethylamine occurred with the production of a gallazane $(Ga-N)_n$ ring species. In the present case it appears that due to some electron withdrawing effect of the phenyl ring a cyclic gallazane was not formed. This effect seems to have reduced the donor properties of the lone pair on the aniline nitrogen atom, and hence prevents coordination to a second gallium and consequent ring formation.

It was believed that introduction of a strong acceptor would remove the trimethylamine from the complex, $\phi NH.GaH_2.NMe_3$, since a strong donor such as nitrogen always prefers a strong acceptor over a weak acceptor.

The acceptor of choice was diborane since it is both a strong acceptor and would not undergo any unwanted side reactions such as might occur if the boron trifluoride, BF_3, acceptor were used. However, the reaction of diborane with $\phi NH.GaH_2.NMe_3$ resulted, not in production of the desired gallazane, $\phi NH.GaH_2$, but in decomposition into gallium, hydrogen, aniline as well as the expected trimethylamine borane. The following sequence of reactions summarizes these experimental observations:

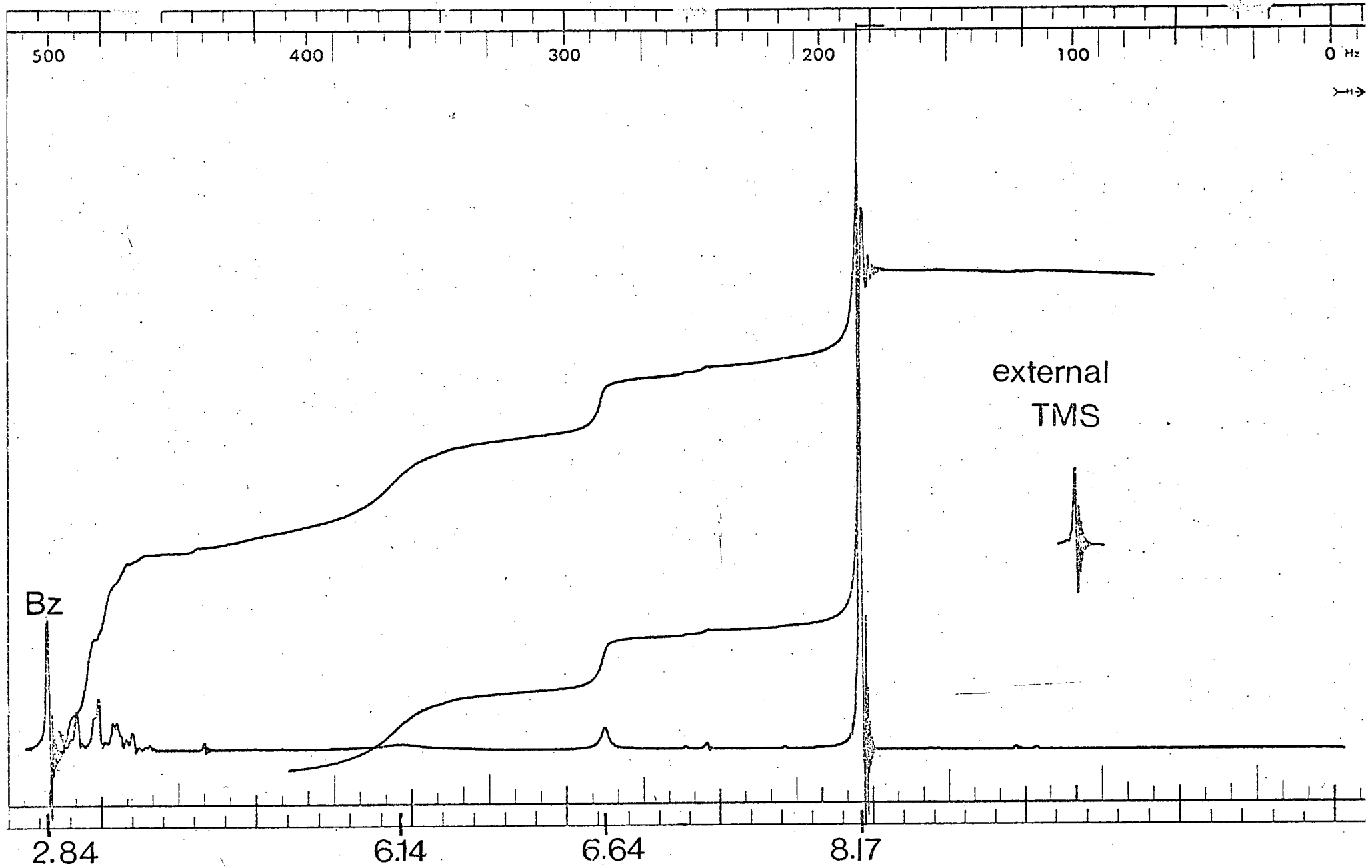


Fig. 18 60 Mc/s ^1H n.m.r. spectrum of $\phi NHGaH_2 \cdot NMe_3$ in benzene solution

$$Me_3N.GaH_2.NH\phi + 1/2B_2H_6 \longrightarrow Me_3N.BH_3 + \phi NHGaH_2$$

$$\phi NHGaH_2 \longrightarrow \phi NH_2 + Ga + 1/2H_2$$

It seems likely that when the ' $\phi NH.GaH_2$ ' is formed in the reaction, the donor strength of the nitrogen connected to the phenyl ring is so reduced that formation of a stable cyclic gallazane does not occur. The monomeric unit is evidently unstable, when formed and decomposes to its components even below 0^oC.

It was of further interest to react $\phi NH.GaH_2.NMe_3$ with methylamine in the hope that displacement of trimethylamine would occur and yield a novel cyclic gallazane on hydrogen elimination according to the following sequence of reactions:

$$\phi NH.GaH_2.NMe_3 + MeNH_2 \longrightarrow Me_3N + \phi NH.GaH_2.NH_2Me$$

$$\phi NH.GaH_2.NH_2Me \longrightarrow \text{' } \phi NH.GaH.NHMe \text{' } + H_2$$

The actual mixture of products obtained was identified by nmr and infrared spectroscopy. Figure 19 shows the N-H stretching region for each of aniline and methyl-gallazane as well as the reaction mixture. It should be noted that the two upper spectra combine to give the lower spectrum. Hence, although trimethylamine was displaced as expected, the elimination of aniline and production of the familiar $(MeNH.GaH_2)_3$ trimer occur as follows:

$$Me_3N.GaH_2.NH\phi + MeNH_2 \longrightarrow \phi NH_2 + 1/3[MeNH.GaH_2]_3$$

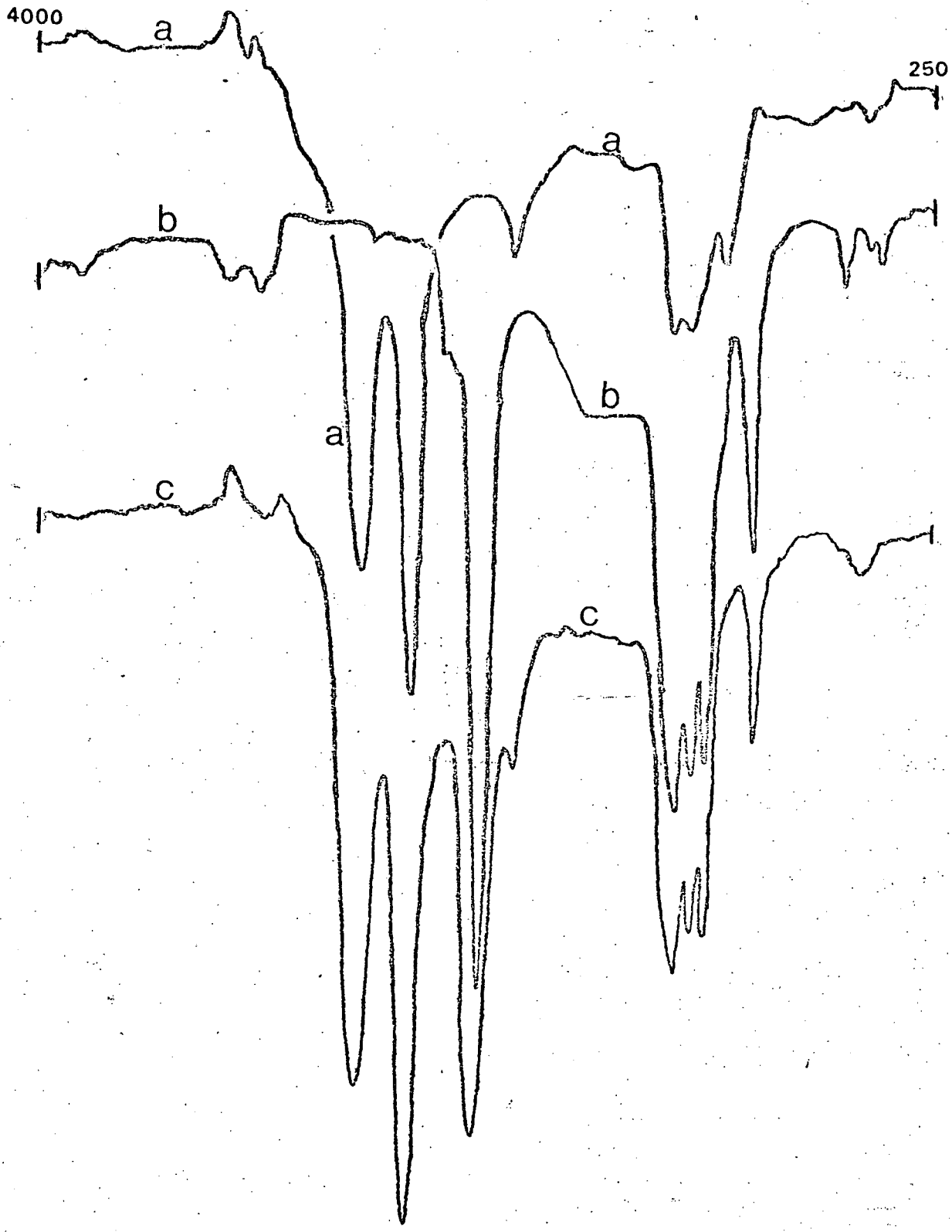
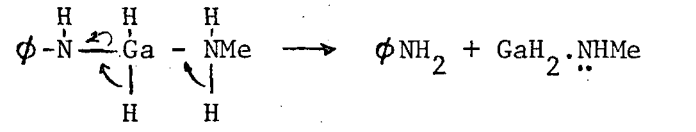
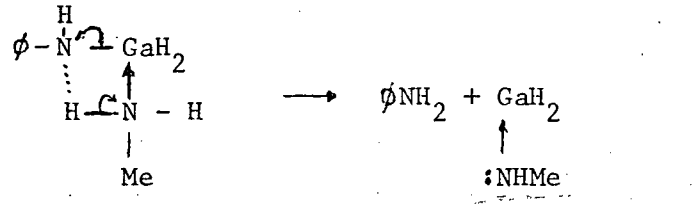


Fig. 19 Infrared spectra of: a aniline; b $MeNHGaH_2$; c aniline & $MeNHGaH_2$

The products were identified also by means of their characteristic ^1H nmr spectra.

It was of interest to then establish the mechanism of hydrogen transfer. The two most probable mechanisms for this transfer are illustrated below:

A. 

B. 

In the first mechanism, the proton which transfers to the aniline comes from the gallium. In the second mechanism a four centre intermediate is formed with the hydrogen atom for aniline production coming from the methylamine nitrogen. The deuterated compound, $\phi NH.GaD_2.NMe_3$ was therefore prepared and reacted with methylamine. The infrared spectrum of the products did not display either a N-D stretch for aniline or a Ga-H stretch for the gallazane, thus eliminating mechanism A as a possible route to the products. It therefore seems likely that mechanism B is the actual mode of proton transfer.

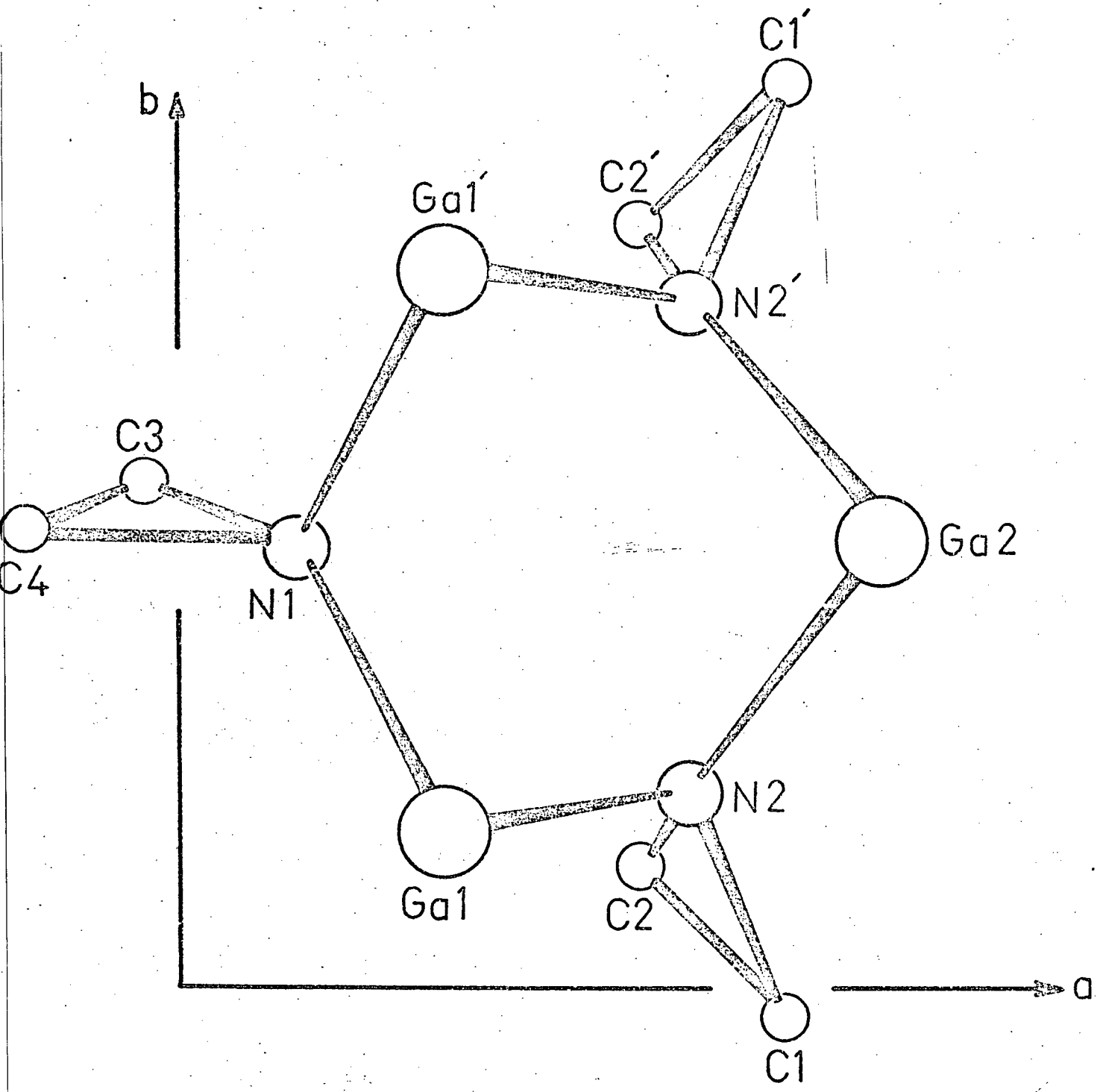
Part 3 Imino Gallazanes

The reaction of aziridine, azetidine, pyrrolidine and piperidine with trimethylamine gallane yields compounds of the type $[(CH_2)_xNGaH_2]_n$ where x = 2, 3, 4 or 5; following elimination of molar equivalents of hydrogen and trimethylamine. Cryoscopic measurements on centrifuged benzene solutions indicate that all these materials are dimeric (Table 2) in benzene.

Recently, however, an x-ray crystallographic study (45) on a single crystal of aziridino gallazane produced by sublimation under about 5 - 7 cm of nitrogen pressure, resulted in the characterization of this compound as a trimer in which the $(Ga-N)_3$ ring is in the chair conformation (Figure 20). The mean dimensions found were Ga-N 1.97, N-C 1.54, C-C 1.55Å; N-Ga-N = 100°, Ga-N-Ga = 121, Ga-N-C = 116°; while the angles in the three membered rings were close to 60°.

This structure, although confirming the predictions in part 1 concerning the configuration of the $(Ga-N)_3$ ring, is somewhat unexpected in view of the cryoscopic molecular weight in benzene solution. The resolution of this apparent dilemma could be the following.

It has been found that freshly dissolved samples of aziridino gallane, whether freshly prepared or not, give degrees of association of 2.55 to 2.65. Samples dissolved in benzene and stored for a few days give a degree of association of 2.00. Since the solid is trimeric, it would seem that the cryoscopic results indicate the gradual formation of dimer in the benzene solvent. It was also observed that a significant amount of insoluble material was formed on dissolving the solid. The following mechanism seems plausible:



Structure of Aziridino Gallazane

Figure 20

$$(\text{Azir GaH}_2)_3 \longrightarrow (\text{Azir GaH}_2)_2 + (\text{Azir GaH}_2)$$

$$(\text{Azir GaH}_2)_x$$

Thus the trimer gives unstable monomer which polymerizes, leaving the dimer in solution. Another possible mechanism appears to be the following:

$$(\text{Azir GaH}_2)_3 \rightarrow (\text{Azir GaH}_2)_2$$

$$(\text{Azir GaH}_2)_3 \rightarrow (\text{Azir GaH}_2)_x$$

where two competing rearrangements occur, one giving polymer, the other dimer.

If the degree of association of gallazanes in benzene is not necessarily an indication of the association in the solid or neat liquid phase, possibly the neat nmr spectrum of isopropylamino gallazane (Figure 15) could be also rationalized in terms of a trans trimer configuration, in agreement with the observed intensity ratio of 2:1 for the β-CH_3 proton signals.

The nmr spectrum of aziridino gallazane (Figure 21) shows only a sharp singlet, indicating a single isomeric constitution which is expected on the basis of a planar $(GaN)_2$ ring with all hydrogens equivalent.

Figure 22 shows the ^1H nmr spectrum of dimeric azetidino gallazane, with integrals of the two areas of resonance in the ratio of 2:1. The splitting observed is that expected on the basis of a planar $(GaN)_2$ ring, a triplet for the four α protons and a quintet for the two β protons.

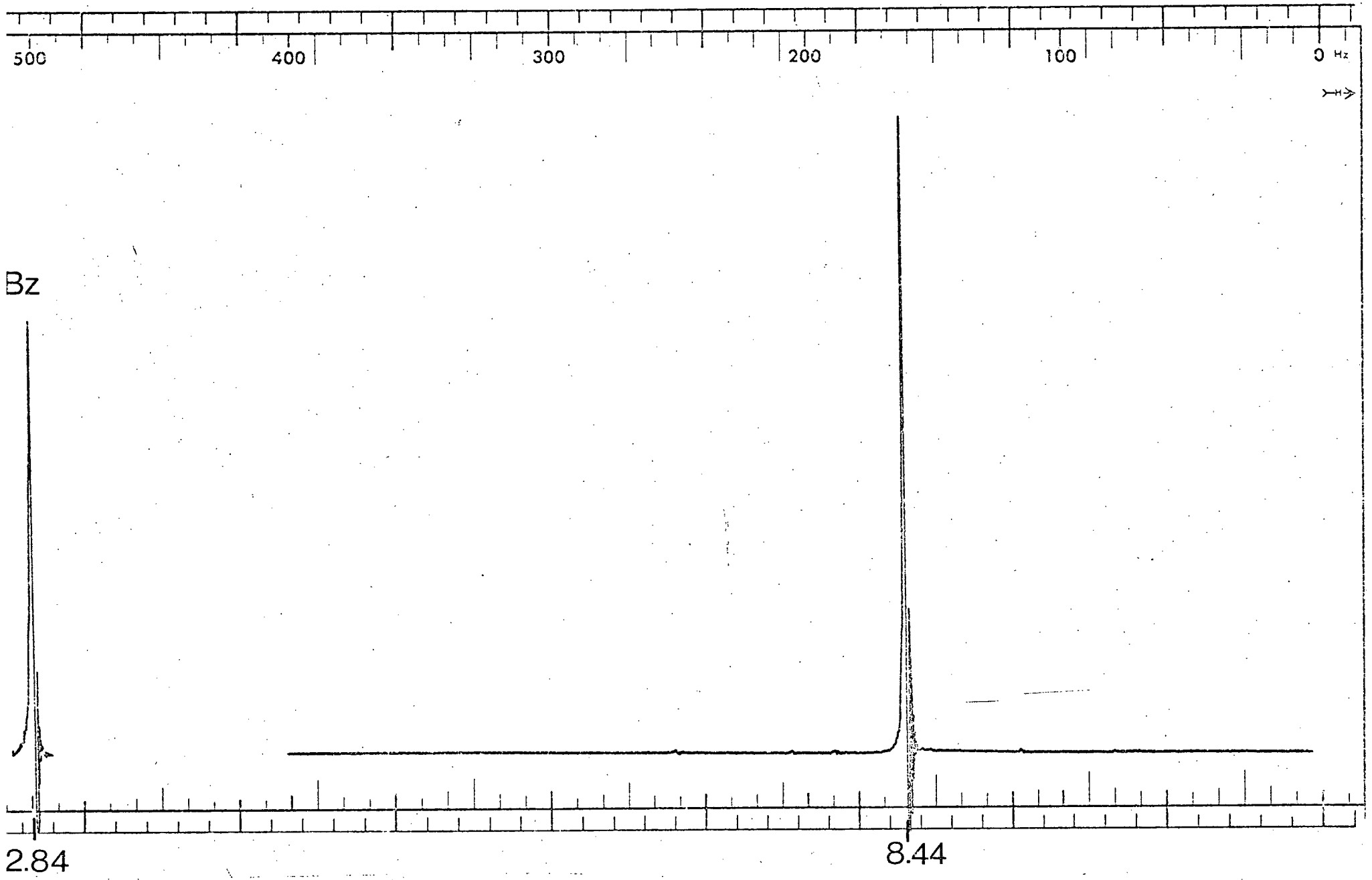


Fig.21 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_2NGaH_2$ in benzene solution

Figures 23 and 24 show the ^{1}H nmr spectra of pyrrolidino gallazane (integration of 1:1 as expected for the four α and four β protons) and piperidino gallazane (integration of 4:6 for α : $\beta + \gamma$ proton multiplets). The latter two spectra are no longer simple, with evidence of complicated spin-spin interaction.

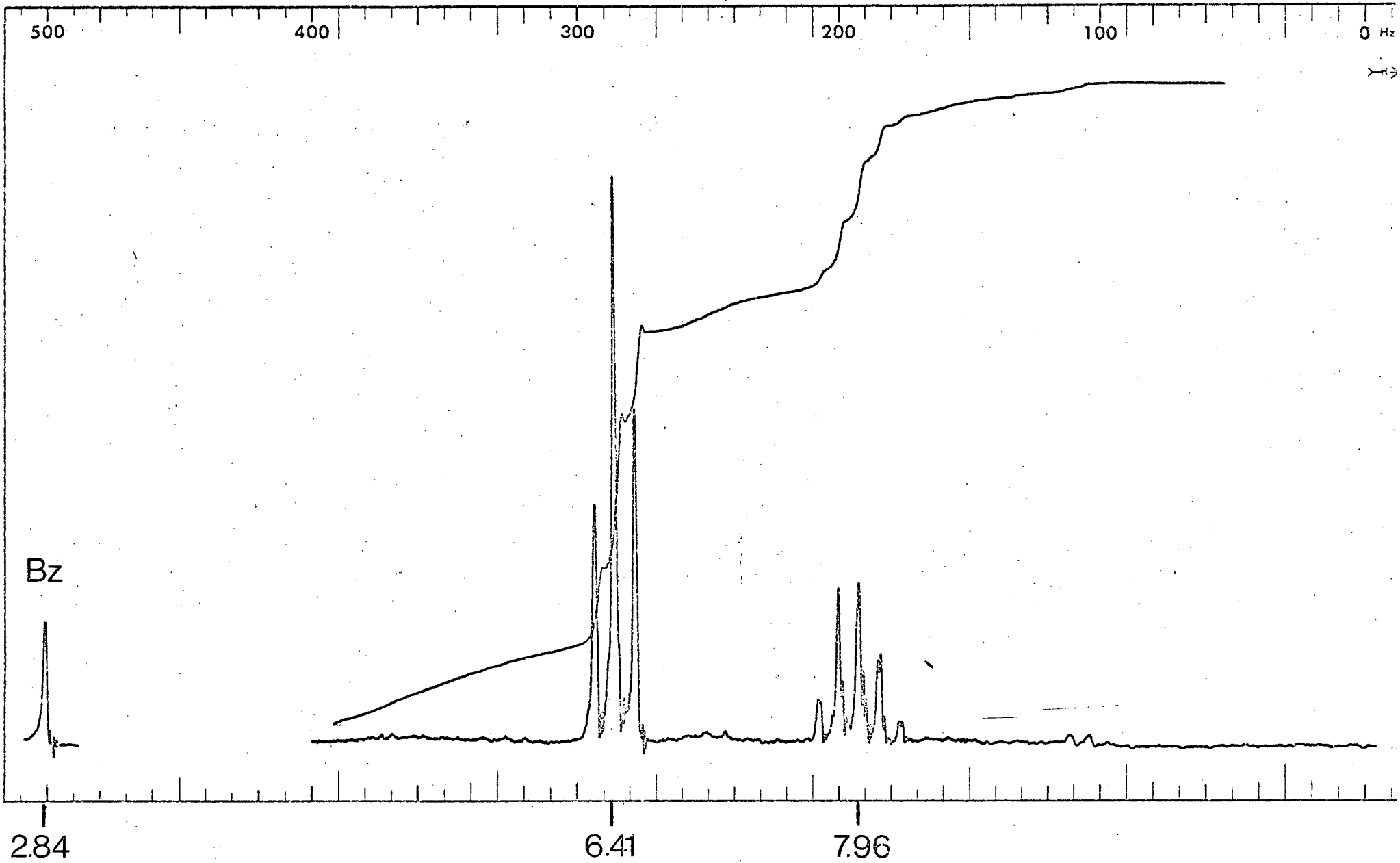


Fig.22 60 Mc/s ^{1}H n.m.r. spectrum of $(CH_2)_3NGaH_2$ in benzene solution

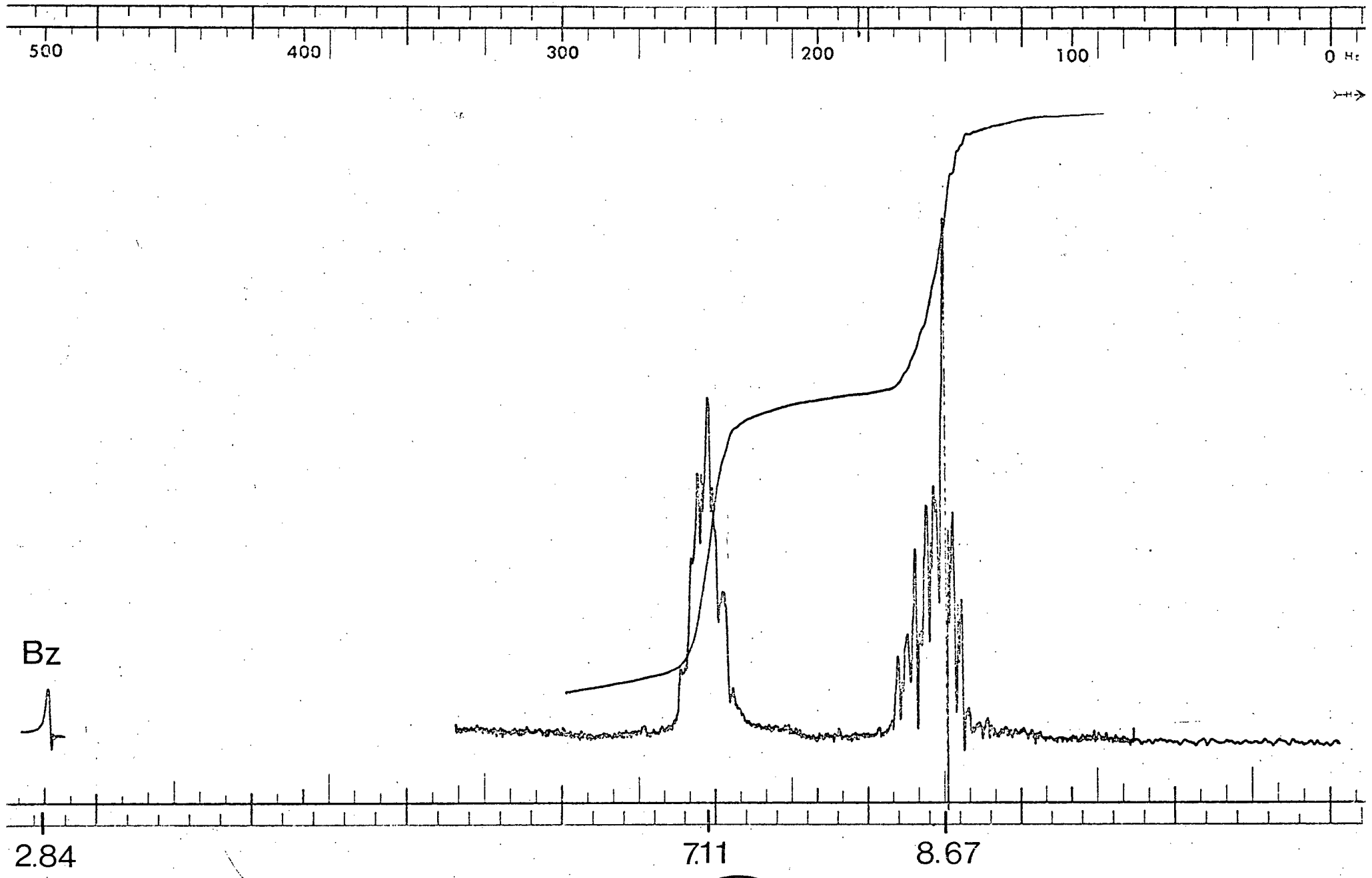


Fig.23 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_4NGaH_2$ in benzene solution

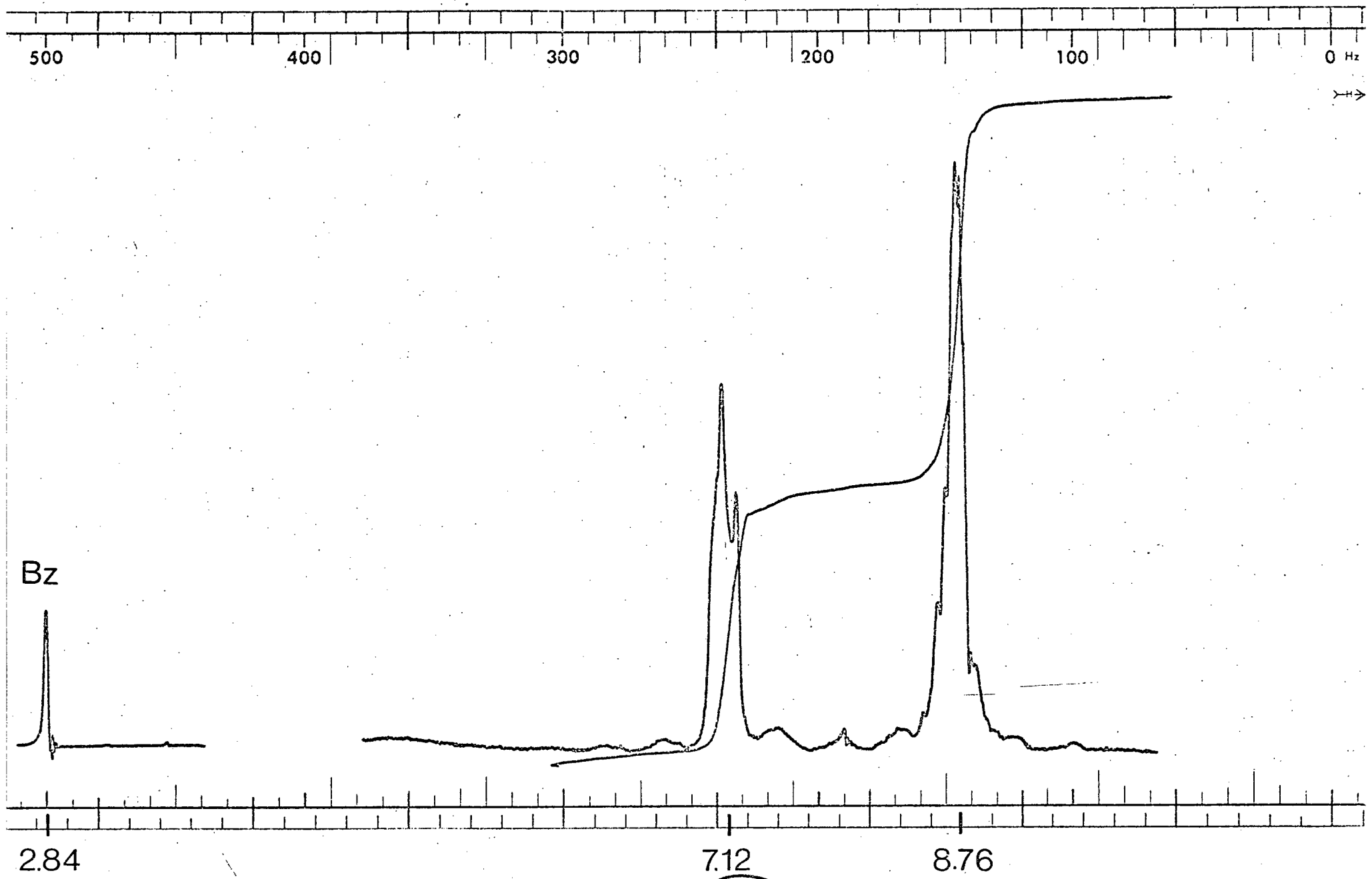


Fig.24 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_5NGaH_2$ in benzene solution

Part 4 Imino Alazanes

The reaction between ethylenimine (aziridine) and bis trimethylamine alane was first attempted in 1962 by Marconi (19). These workers did not isolate the aziridino alazane product.

A more recent discussion of this reaction product (20) suggests that ring opening of the aziridine ring occurs on solvent removal yielding an average degree of association of n = 10.

The product prepared in this study gave initially the nmr spectrum of figure 25.

Since this spectrum contains a high field triplet and evidence of a lower field quartet the previous formulation (20) of ring opening to give ethyl groups seems fairly conclusive. However, the spectrum a few hours later (Figure 26) showed an increased intensity of the high field triplet with respect to the broad singlet for the aziridine rings. The following day, after storage at +5°C, the nmr spectrum showed the high field triplet to be even more intense than previously. These results indicate that ring opening occurs at a fairly steady rate at 5° - 25°C. The initial aluminum to active hydrogen ratio was found to be $Al_{1.00}H_{2.02}$ while the analysis of the same product left at room temperature for three days under dry nitrogen was found to be $Al_{1.00}H_{1.05}$. These results indicate that in the limit, complete aziridine ring opening could occur to give all N-ethyl groups in an insoluble polymeric product.

It was of interest to see what the degree of association would be if ring opening could be held to a minimum. Thus the degree of association of freshly prepared aziridino alazane was determined in

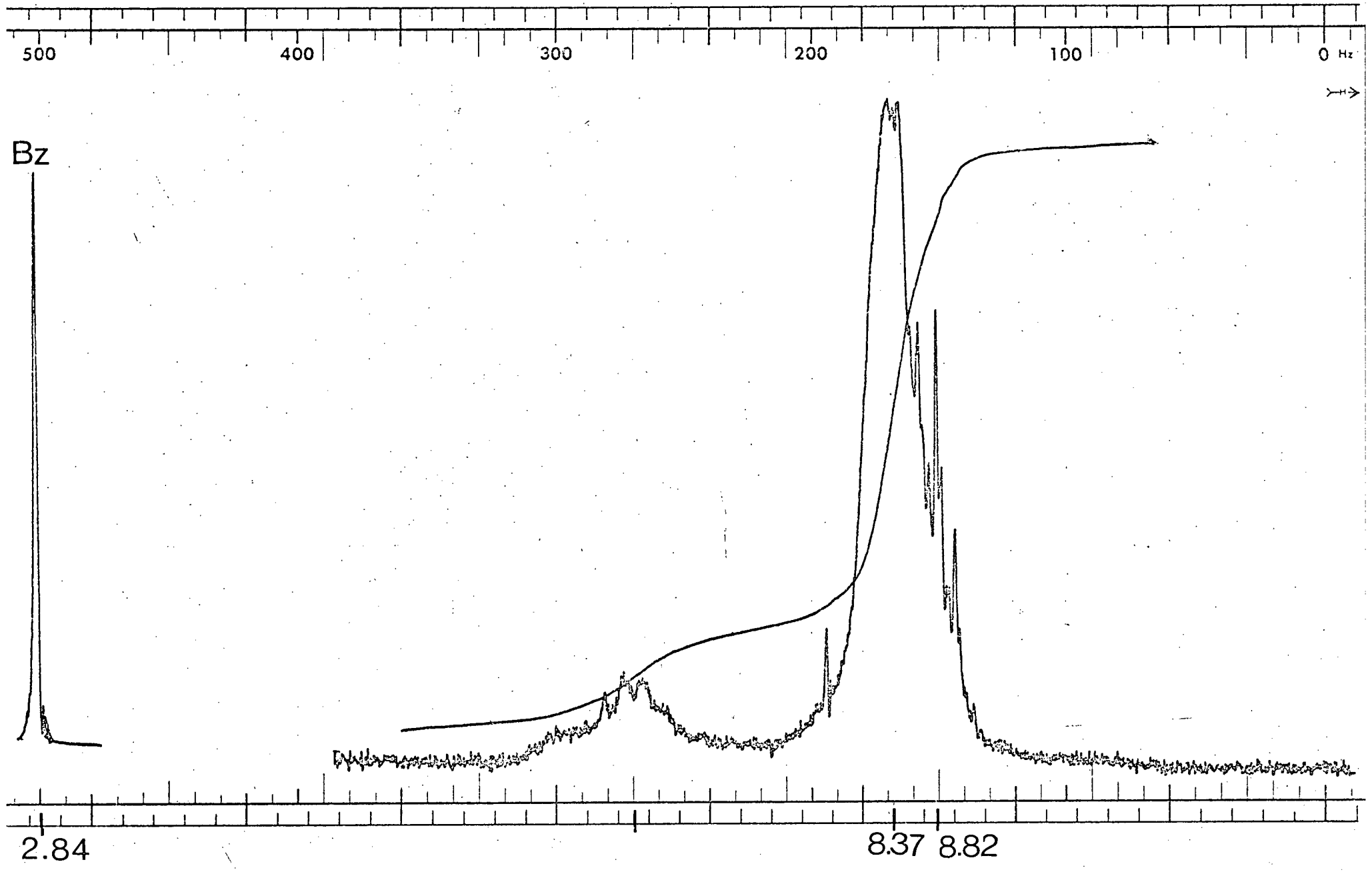


Fig. 25 60 Mc/s ^1H n.m.r. spectrum of $(CH_2)_2NAlH_2$ in benzene solution

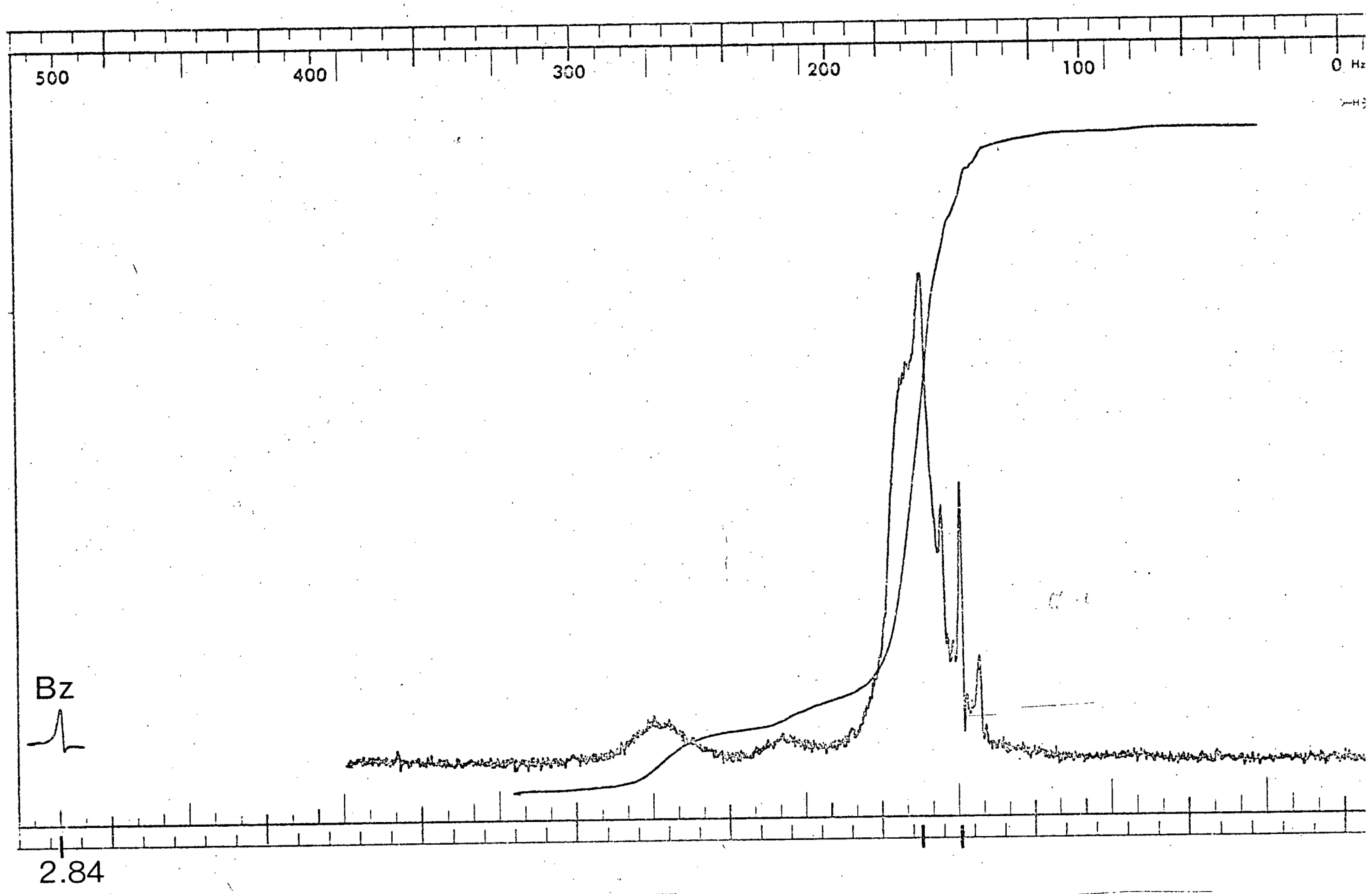


Fig.26 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_2NAlH_2$ in benzene solution

benzene solution with a minimum of delay. This worker was able to obtain a minimum value of n = 4.2 whilst a co-worker was able to obtain n = 3.14.

These results suggest that the degree of association before ring opening sets in, is likely n = 3. This is the expected degree of association in view of the results for the other alazanes of table 3.

The product from the reaction of the bis trimethylamine alane with azetidine did not give up all its trimethylamine, some of which remained coordinated to it (Figure 27). Pumping at $0^{o}C$ removed most of this trimethylamine to give the spectrum of Figure 28. The integration ratio is 2:1 for the $\alpha:\beta$ protons. The molecular weight is consistent with the formulation of this compound as a trimer.

Similarly the ^{1}H nmr spectrum of trimeric pyrrolidino alazane shows two areas of resonance in the ratio of 1:1. One resonance is centred at τ = 7.10 and the other at τ = 8.50. The piperidino alazane appears to be mainly dimer in benzene solution (n = 2.17) possibly resulting from the larger steric requirements of the piperidino ring. The nmr spectrum for this compound shows two resonances in the ratio of 6:4 at τ = 8.61 and at τ = 7.18 respectively. These correspond to $\beta+\gamma$ and α proton resonances.

It appears that trimeric species are common with the imino alazanes and in this respect they differ from the dimeric imino gallazanes. Since the bond lengths of Al-N and Ga-N are known to be almost identical, the reason for this difference probably lies more in the nature of the reaction intermediate leading to these species than in steric or other effects. Possibly this difference is due to the relative ease with which aluminum can go 5-coordinate in the intermediate, but this is highly speculative as no mechanism utilizing a 5-coordinate aluminum has actually been demonstrated.

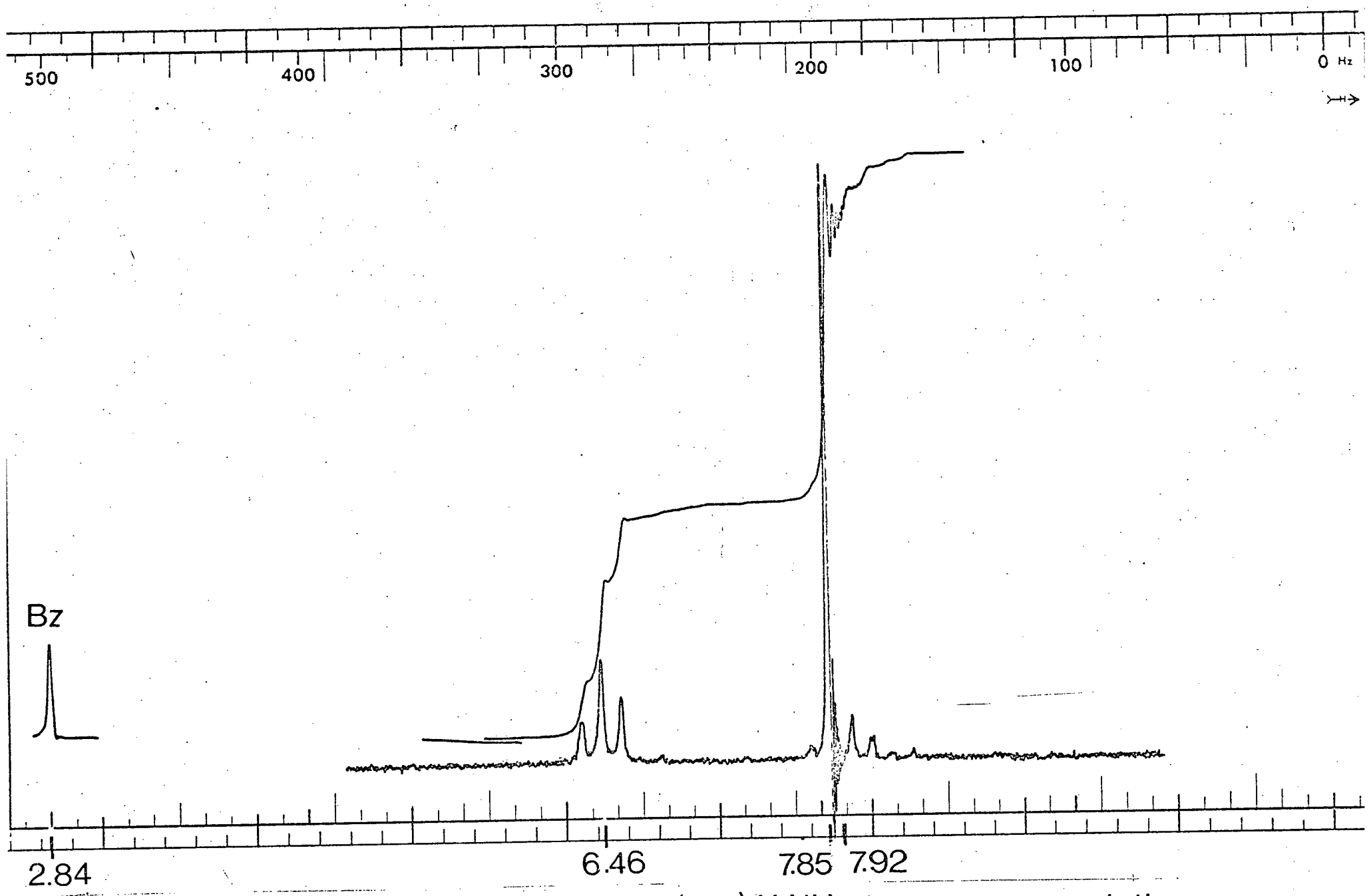


Fig.27 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_3NAlH_2$ in benzene solution

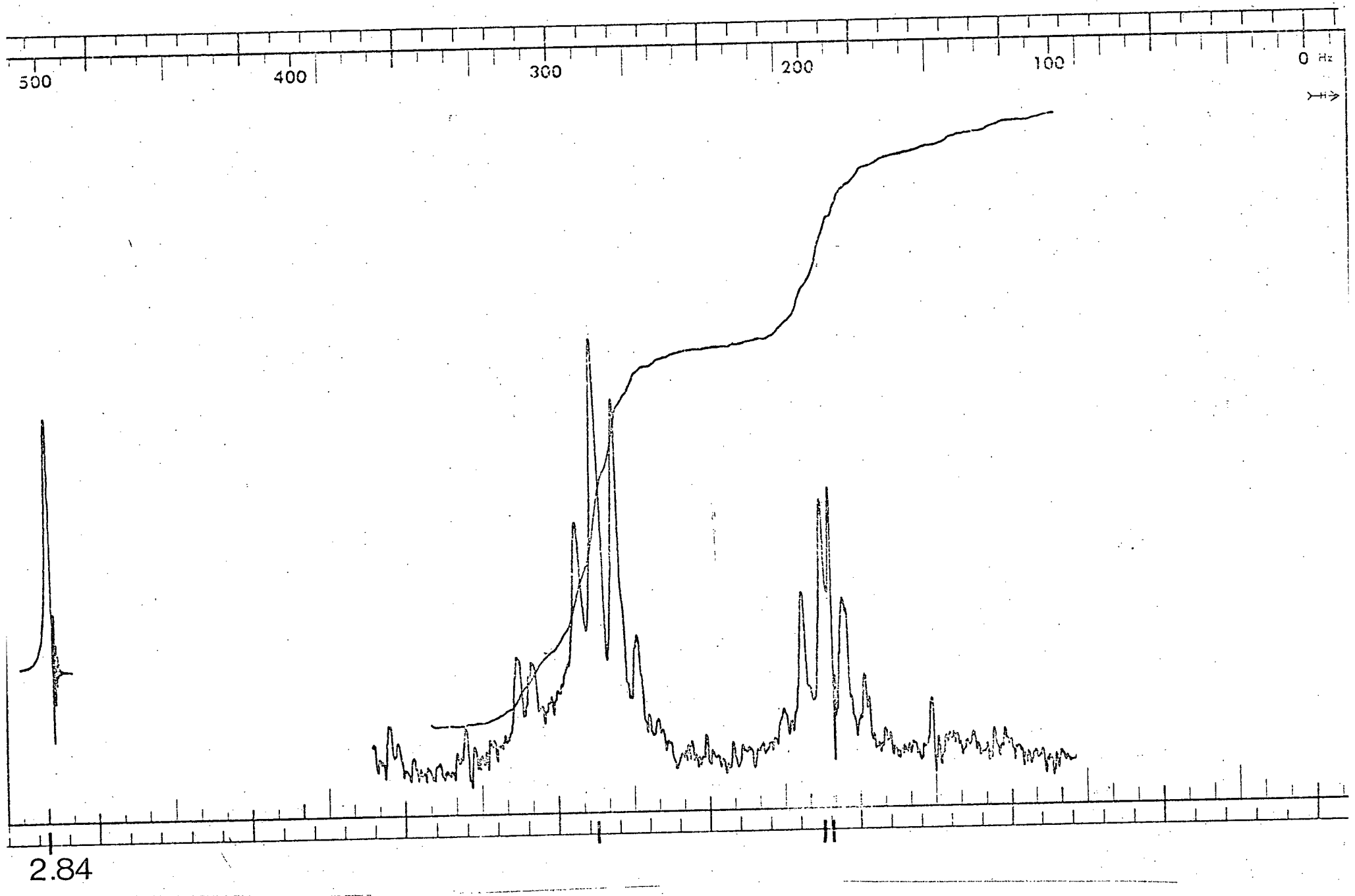


Fig.28 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_3NAlH_2$ in benzene solution

Part 5 Imino Borazanes

The fact that azetidino, piperidino and pyrrolidino borazane are dimeric in benzene is not surprising since boron-nitrogen systems generally prefer a monomeric or dimeric state to that of trimer.

The nmr spectra of these three compounds are given in Figures 29, 30 and 31 and are all in agreement with the formulation of these compounds as having planar $(B-N)_2$ rings and containing each a single isomeric form.

The aziridino borazane prepared by the method of Akerfeldt (17) gave a singlet for the aziridino ring hydrogen in agreement with the literature (18) (Figure 32). The adduct, prepared by the Burg method (14) gave the nmr spectrum of figure 33 in agreement with the literature (18). The aziridino borazane has a trimeric constitution in contrast to the remaining members of this series. The reasons for this different constitution may be a result of the preparative route used to obtain the compound.

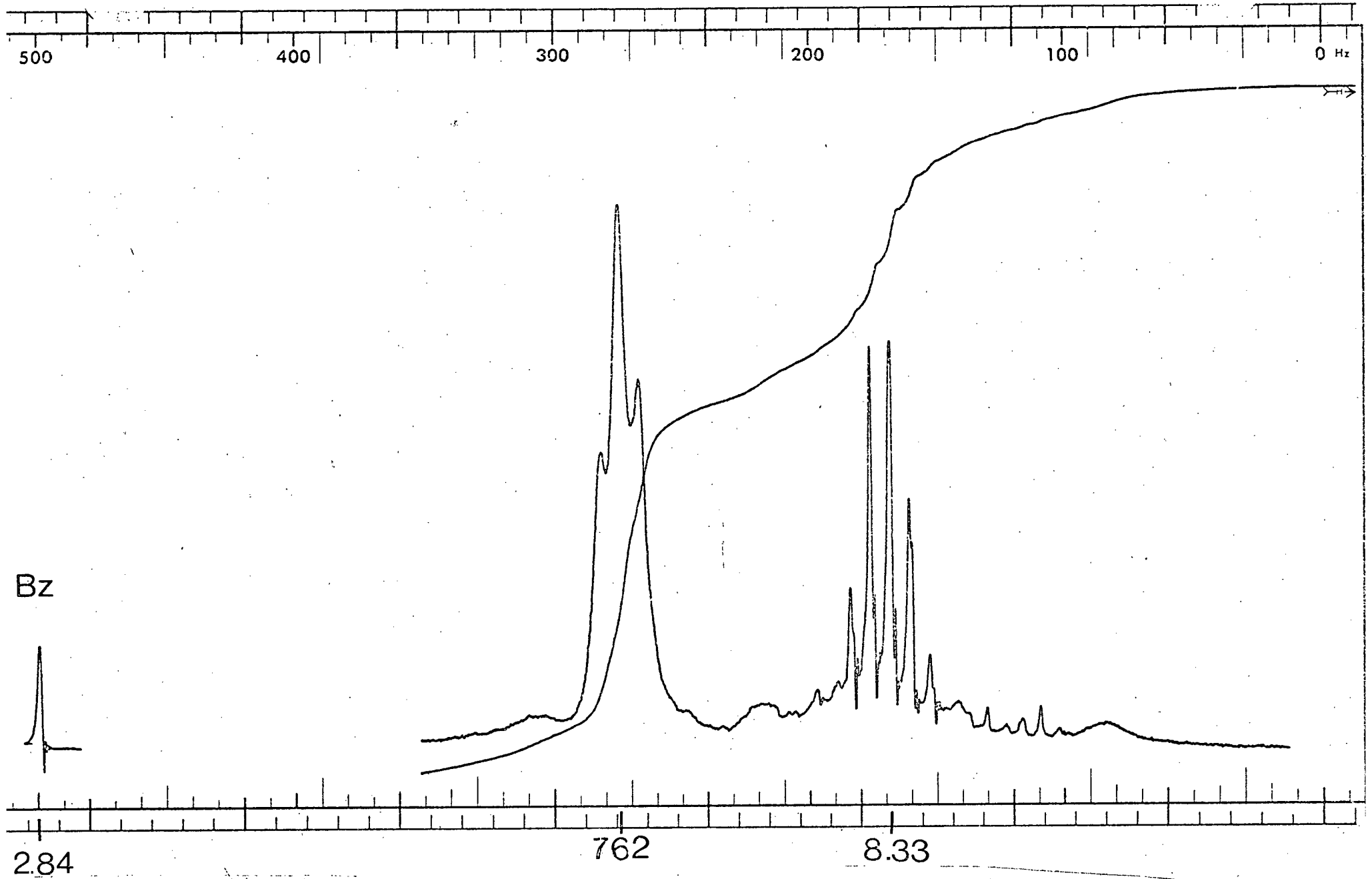


Fig. 29 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_3NBH_2$ in benzene solution

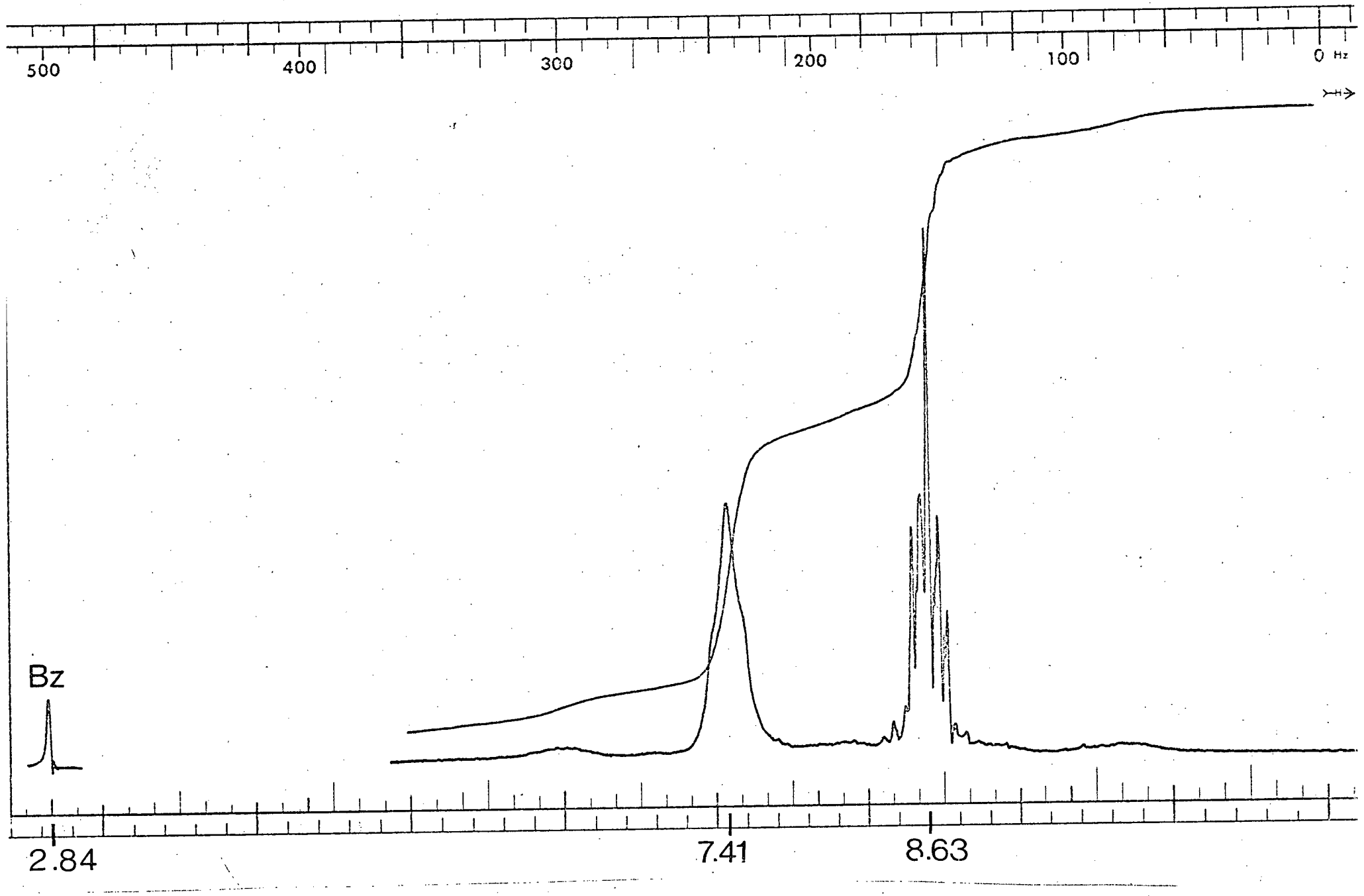


Fig.30 60 Mc/s ^1H n.m.r. spectrum of $(CH_2)_4NBH_2$ in benzene solution

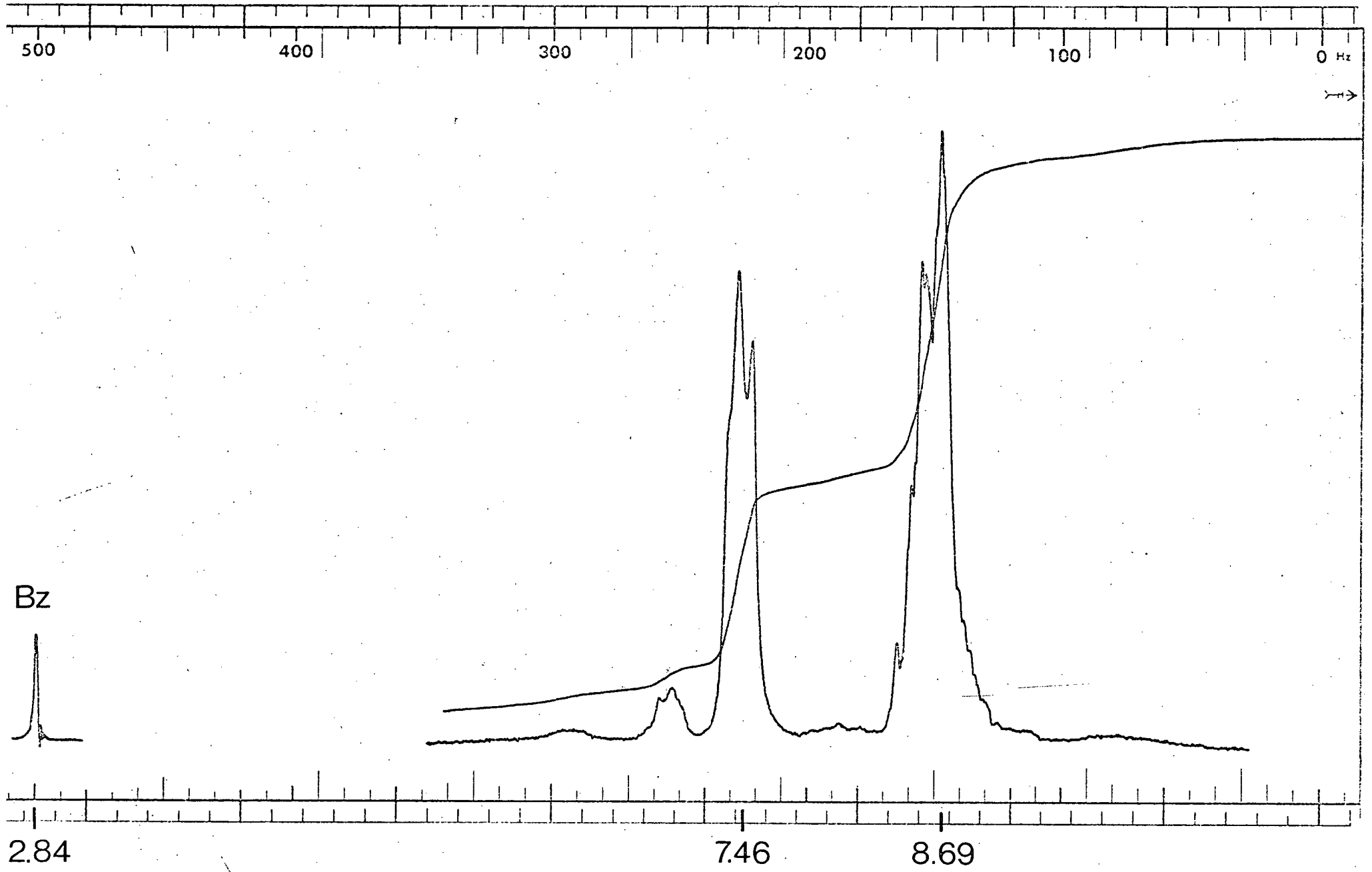


Fig. 31 60 Mc/s ^1H n.m.r. spectrum of $(CH_2)_5NBH_2$ in benzene solution

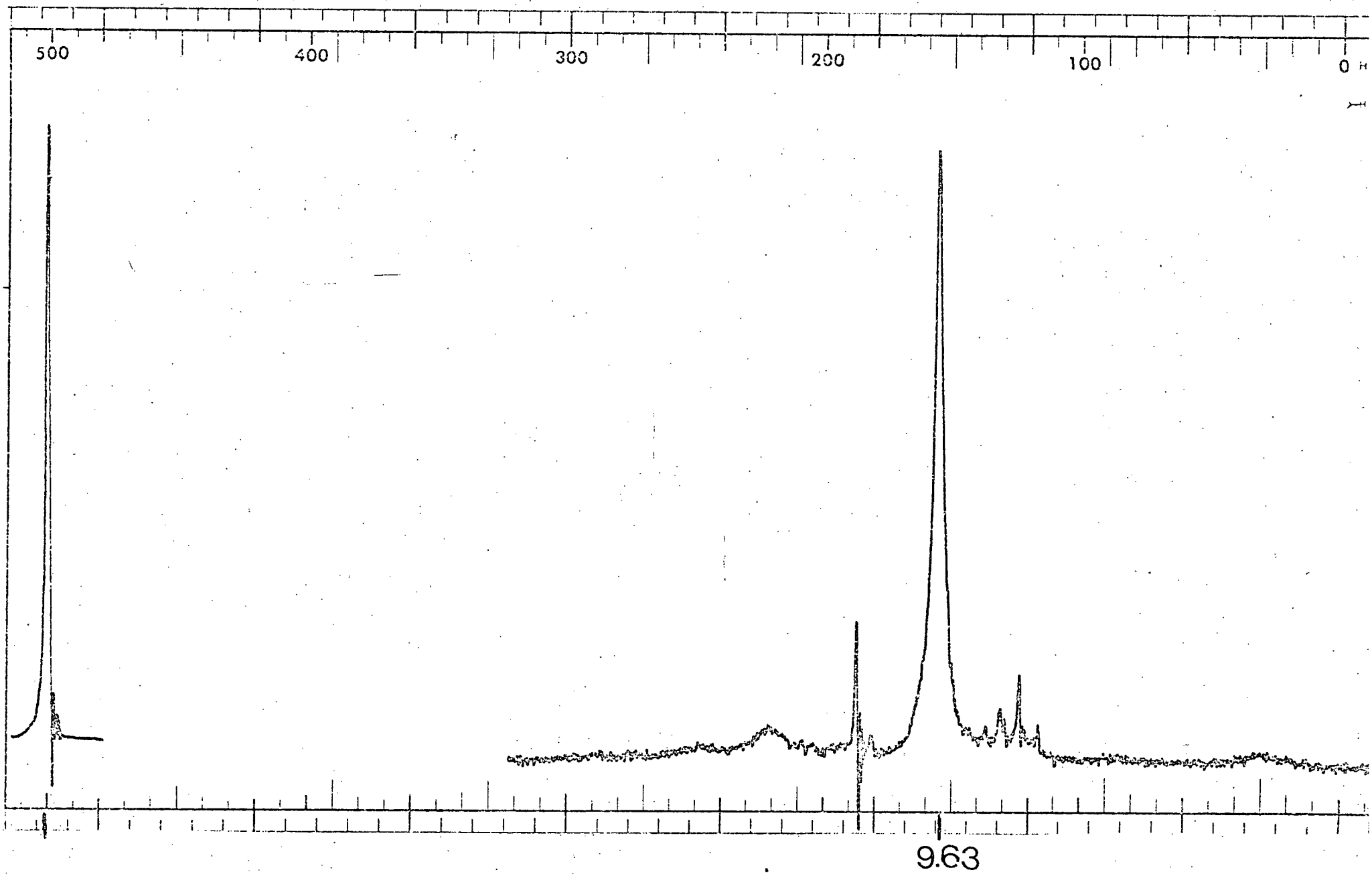


Fig.32 60Mc/s ^1H n.m.r. spectrum of $(CH_2)_2N \cdot BH_2$ in benzene solution

Part 6 Reactions of Imine Bases with EMe_3 E = B, Al, Ga, In

Reaction of EMe_3 with aziridine gave, on methane elimination, compounds which were trimeric in benzene solution. Since the hydrido analogues previously prepared were trimeric as well, this result suggests that the groups about the E atom have little effect in determining the final degree of association of the complexes studied here.

The compound $Me_2BN(CH_2)_2$ was not isolated, as the high temperatures necessary to achieve methane elimination from the adduct also cause polymerization.

The nmr spectra of the two stable adducts $Me_3BNH(CH_2)_2$ (Figure 34) and $Me_3GaNH(CH_2)_2$ (Figure 35) are characteristic but very different. The aziridine ring protons of the boron compound give rise to a singlet at low field - probably the result of nitrogen inversion or fast exchange reactions in solution. The higher field singlet is the resonance of the boron methyl protons. The aziridine ring protons of the gallium adduct, on the other hand, appear to be split into a multiplet. This complex splitting is believed to be the result of not only primary but also second order magnetic coupling of the hydrogen nuclei on the aziridine ring.

The three methane elimination products had simple and very similar nmr spectra. These spectra consisted of a lower field singlet for the aziridino protons and a high field singlet for the methyl groups of the E atoms.

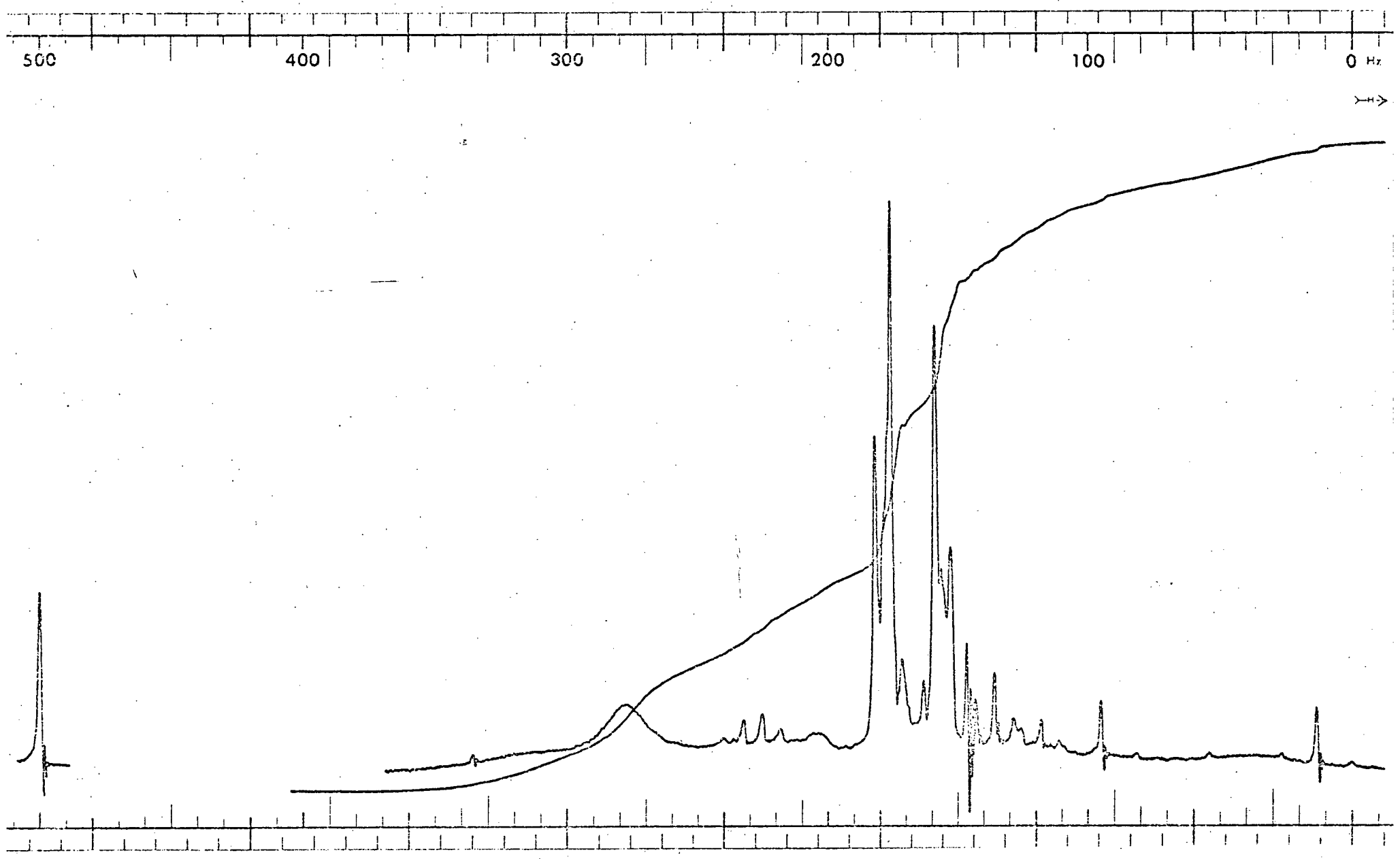


Fig.33 60 Mc/s ^1H n.m.r. spectrum of $H_3B{\cdot}NH(CH_2)_2$ in benzene solution

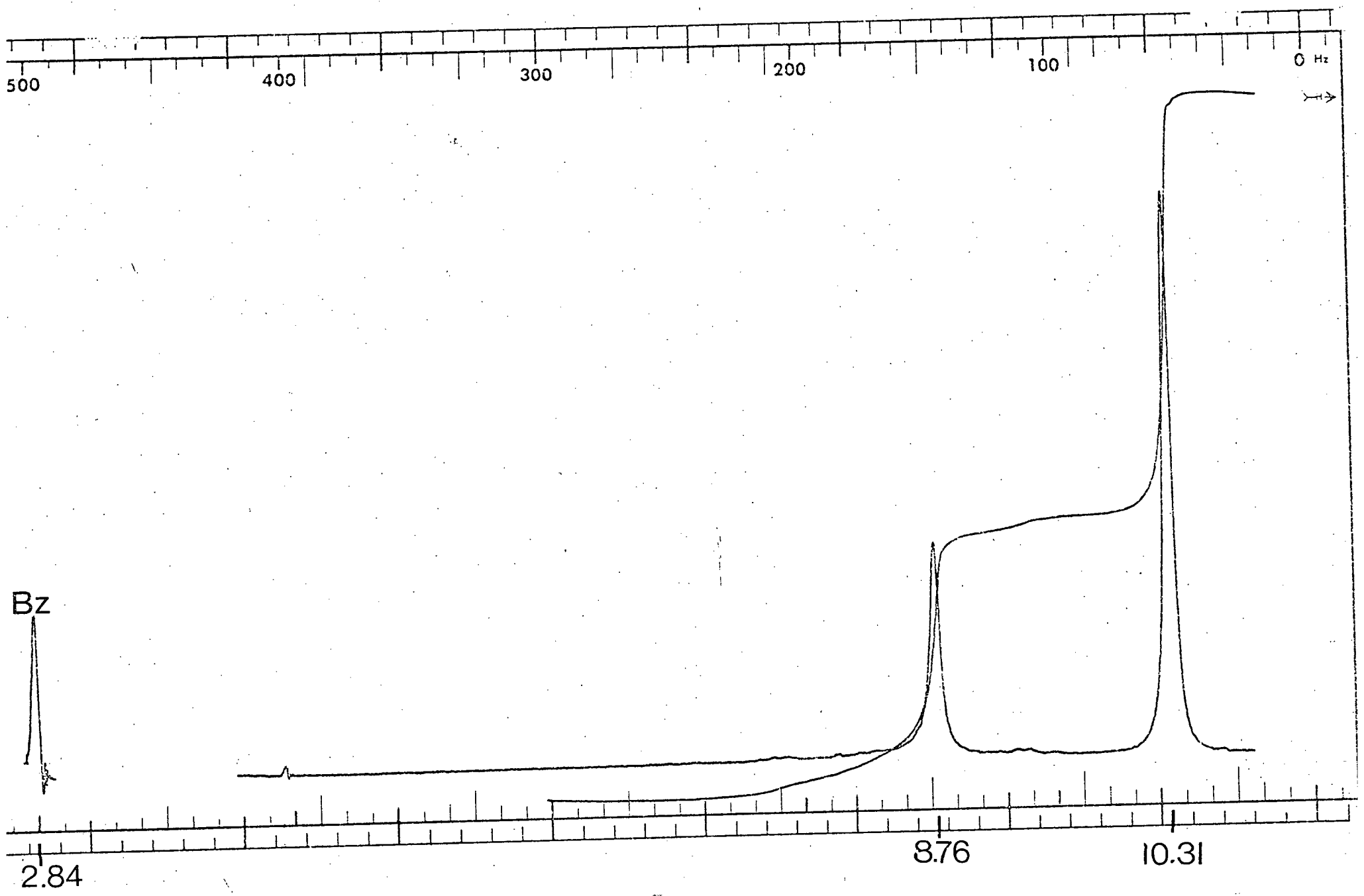


Fig.34 60Mc/s ^1H n.m.r. spectrum of $Me_3B{\cdot}NH(CH_2)_2$ in benzene solution

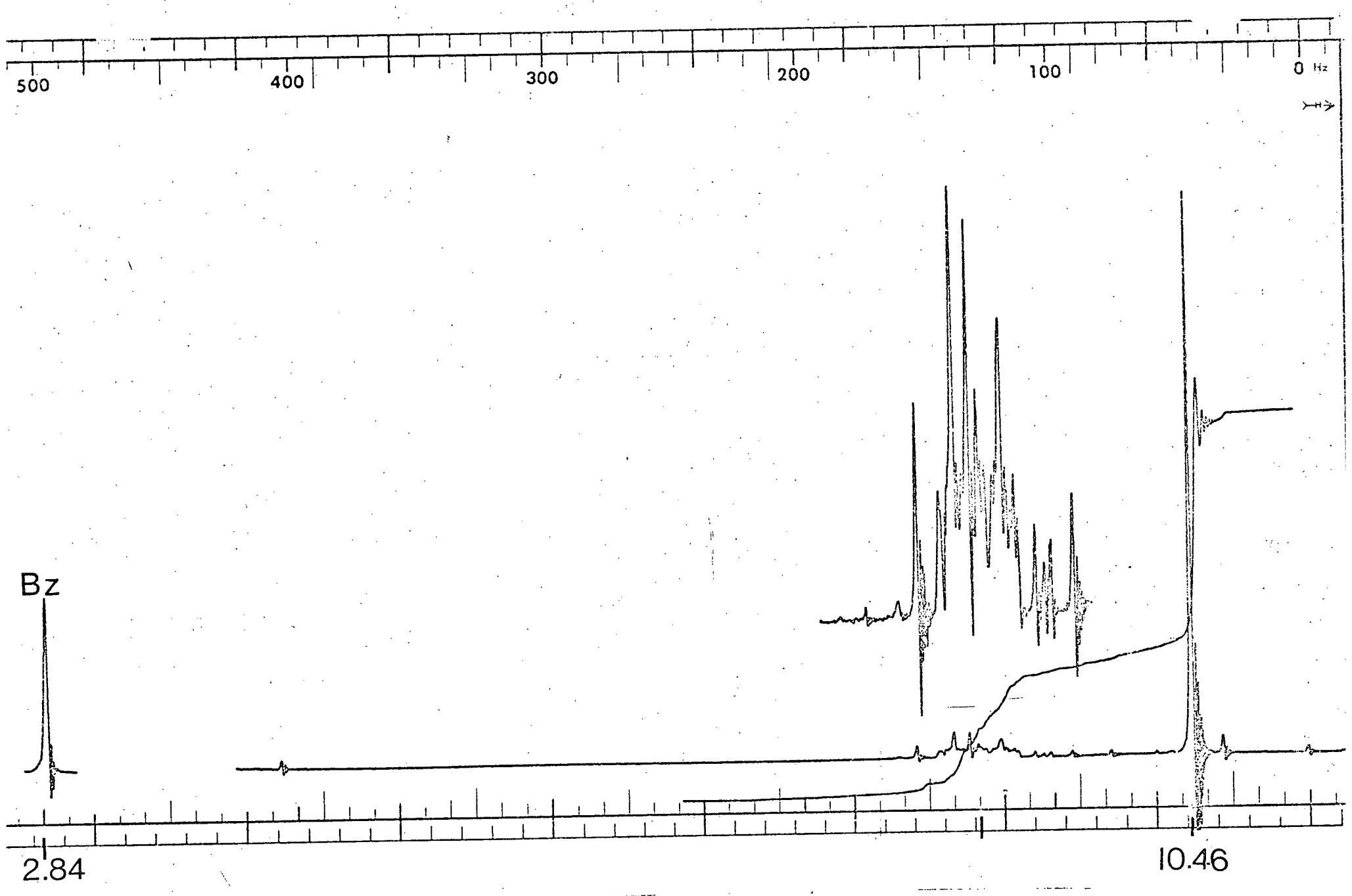


Fig.35 60Mc/s ^1H n.m.r. spectrum of $Me_3Ga{\cdot}NH(CH_2)_2$ in benzene solution

REFERENCES

1. N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, J. Chem. Soc., 249 (1962)
2. E. Wiberg et. al., Z. Anorg. Chem., 251, 114 (1943).
3. B. Siegel, J. Chem. Ed., 38, 496 (1961).
4. N. N. Greenwood, and M. G. H. Wallbridge, J. Chem. Soc., 3912 (1963).
5. N. N. Greenwood and A. Storr, J. Chem. Soc., 3426 (1965).
6. H. Bretsacher and B. Siegel. JACS, 87, 4255 (1967).
7. A. E. Finholt, A. C. Bond, and H. I. Schlesinger, JACS, 69, 1199 (1947)
8. E. Wiberg and H. Noth, F. Naturforsch, 63 (1957)
9. E. Wiberg and H. Heule, ibid, 126, 576 (1952).
10. N. N. Greenwood, New Pathways in Inorganic Chemistry, Camb. U. Press, 1968, P37.
11. N. N. Greenwood, A. Storr and M. G. H. Wallbridge, Inorg. Chem., 2, 1036 (1963)
12. N. N. Greenwood, E. J. F. Ross, and A. Storr, J. Chem. Soc.(A), 706 (1966).
13. A. Storr, J. Chem. Soc.(A), 2605 (1968)
14. A. B. Burg and C. D. Good, J. Inorg. Nucl. Chem., 2, 237 (1956)
15. S. Akerfeldt et. al., Acta Chem. Scand., 23, 115 (1969)
16. H. Ringertz, Acta Chem. Scand., 23, 137 (1969)
17. S. Akerfeldt and M. Hellstrom, Acta Chem. Scand., 20, 1418 (1966)
18. R. L. Williams, Acta Chem. Scand., 23, 149 (1969)
19. W. Marconi et. al., Gazz. Chim.Ital., 92, 1062 (1962)
20. R. Ehrlich et. al., Inorg. Chem., 628 (1964)
21. E. J. F. Ross.,Ph. D. Thesis, 1965, University of Newcastle-Upon-Tyne
22. "Handbook of Chemistry and Physics" 49 th ed. Chemical Rubber Co., Cleveland, 1968.

23. N. N. Greenwood and K. Wade., J. Chem. Soc., 1527 (1956)

24. H. Wenker, JACS, 57, 2328 (1935)

25. P. Leighton et. al., JACS, 69, 1540 (1947)

26. W. Reves et. al.,JACS 73, 3522 (1951)

27. P. Leighton et. al., JACS, 75, 2505 (1953)

28. D. G. Gains and L. Schaeffer, JACS, 85, 395 (1963)

29. J. K. Ruff and M. F. hawthorne, JACS, 82, 2141 (1960)

30. F. G. A. Stone, Chem. Rev., 58, 101 (1958)

31. B. Allred and F. Rochow, J. Inorg. Nucl. Chem., 5, 264 (1958)

32. O. T. Beachley and G. E. Coates, JCS, 591 (1965)

33. M. P. Brown, R. W. Heseltine and L. H. Sutcliffe, J. Chem. Soc. (A),612 (1968)

34. J. L. Atwood and G. D. Stucky, JACS, 92, 285 (1970)

35. G. E. Coates and K. Wade Organometallic Compounds: Methuen, London 1967
vol. 1., p 307

36. E. Campaigne, N. F. Chamberlain, and B. E. Edwards, JOC, 27, 135 (1962)

37. A. Segre and J. Musher, JACS, 89, 706 (1962)

38. J. L. Jungnickel and C. A. Rielly, Nuclear Magnetic Resonance in Chemistry,
ed. B. Pesce, Acad. Press, 1965, P 83

39. N. N. Greenwood, E. J. F. Ross and A. Storr, JCS (A), 706 (1966)

40. N. N. Greenwood, E. J. F. Ross and A. Storr, JCS, 1400 (1965).

41. T. N. Marfulis and M. Fisher, JACS, 89, 223 (1967)

42. E. Adman and T. N. Margulis, JACS, 90, 4517 (1968)

43. M. P. Brown, R. W. Heseltine, P. A. Smith, and P, J. Walker, JCS (A), 410 (1970)

44. P. L. Corio, J. Chem. Ed., 46, 345 (1969)

45. W. Harrison, A. Storr and J. Trotter, Chem. Comm., submitted for publication.