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# NMR STUDY OF THE EFFECT OF NITROGEN-BORANE COORDINATION ON THE CONFORMATIONAL EQUILIBRIUM OF SIX MEMBERED RING HETEROCYCLES

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*Summary* The syntheses, conformational and spectroscopic studies of N-borane adducts of 14 nitrogen containing six-membered ring heterocycles are reported It was found that borane can act as a conformational and configurational locking agent In addition, it can be very helpful for the assignment of the chemical shifts of other atoms or groups in the molecule as well as to ascertain the configuration at substituted carbons

## Introduction[1]

The analysis of the NMR data of N-borane adducts of organic heterocycles provides important information that allows the configurational assignment at nitrogen and its neighboring carbon atoms We have shown that $^{1}H$, $^{13}C$ and $^{11}B$ chemical shifts are very sensitive to steric and electronic effects produced by borane interactions through bonds and directly through space, and hence, borane addition can be used as a chiral probe[2-4] In amine-borane adducts, the presence of the borane group fixes the configuration at the quaternized nitrogen atom[2-4]

In this paper attention is focused on the application of $^{13}C$, $^{1}H$ and $^{11}B$ chemical shifts to the identification of the preferred conformation of N-borane adducts of six-membered ring heterocycles **1-14** in solution, figure 1 Borane is capable of fixing the ring conformation at room temperature giving N-borane adducts stable enough to allow detailed study by spectroscopic means In turn these results allow the study of ring conformational equilibrium, the establishment of configurations at ring atoms including nitrogen and the assignment of chemical shifts and coupling constants in the NMR spectra Some N-borane adducts of piperidines and piperazines were reported before but a careful and detailed NMR analysis was not undertaken[5-8] Although ammonium salts present spectra very similar to N-borane adducts[9-11], it is important to notice that the nitrogen atom in the borane adducts has a more stable configuration than in the salts and in consequence, such adducts may become important tools for structural analyses

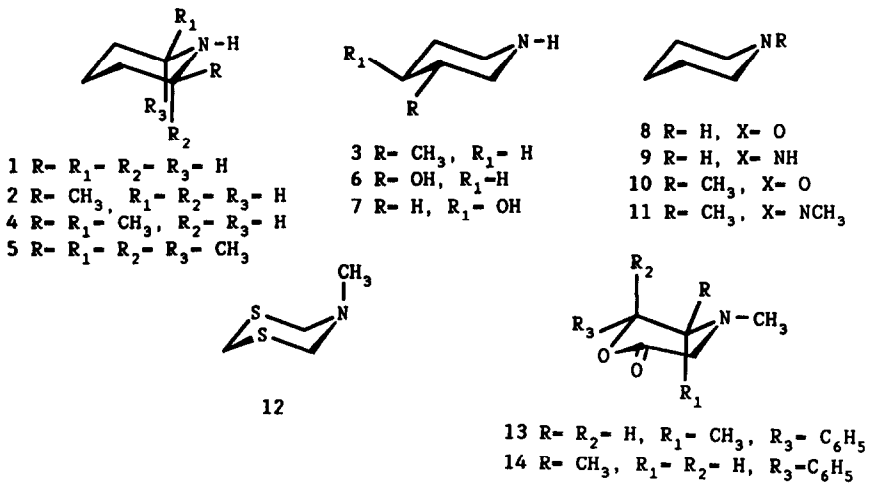



figure 1

**RESULTS AND DISCUSSION.**

**N-H SIX-MEMBERED RING HETEROCYCLES.**

**Piperidine, 1**

Borane addition to piperidine 1 produces an equatorial N-borane adduct (**1Be**, $^{11}B$ chemical shift $\delta$= -15 5 ppm, $J_{B-H}$ = 97 Hz), which shows a predominant chair conformation at room temperature, as established by the $^{1}H$ NMR spectrum The N-*H* appears at $\delta$ = 3 68 ppm coupled to the neighboring protons The equatorial and axial protons of **1Be** appear as separate signals shifted to low field compared to those of the free piperidine 1, the equatorial protons of **1Be** being more shifted than the corresponding axial ones ($\Delta[\delta_{eq}-\delta_{ax}]$ = 0 74 ppm for the C-2 and C-6 protons, 0 25 ppm for those of C-3 and C-5 and 0 18 ppmfor C-4) The $^{13}C$ NMR of **1Be** is similar to that of N-methylpiperidine **15**[9] and even more to its salt **15H**[9] (figure 2) This is explained in terms of the fact that $^{13}C$ NMR is especially sensitive to steric effects and **1Be** is sterically similar to **15H** With the difference that

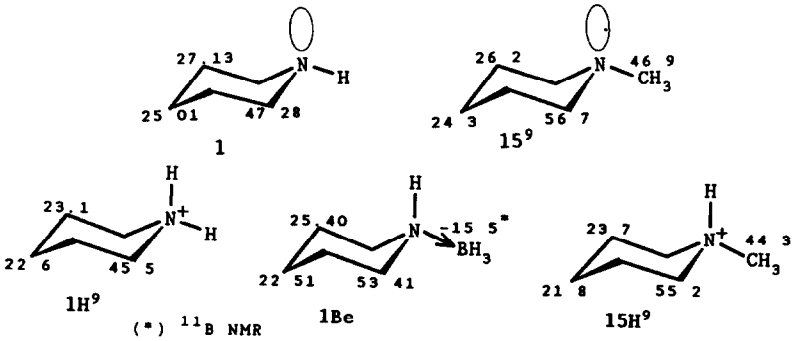
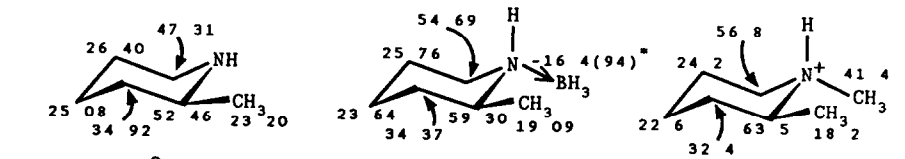



figure 2

the substitution effect of nitrogen at C-2 and C-6 is stronger in the N-methyl derivative (Δδ 9 5 ppm) when compared to compound **1Be** (Δδ 6 1 ppm) This phenomenon can be attributed to the longer bond distance in B-N (1 66 Å)[12] compared to C-N (1 47 Å) Analysis of the $^{13}C$ NMR data indicates that the borane in **1Be** is equatorial since there is no 1,3-diaxial interactions and from the substitution effect on C-2 and C-6 The $^{1}H$ NMR spectrum shows that the equatorial protons are shifted to low field

**2-Methylpiperidine, 2.**

2-Methylpiperidine **2** exists in a preferred chair conformation in chloroform solution at room temperature, with the methyl group in equatorial position Addition of borane gives the kinetic products, N-epimers **2Be** and **2Ba** (figure 3), in a 60-40 ratio Heating the mixture 7 hours at 60°C in an excess of free amine increases the **2Be/2Ba** ratio to 80/20 Compound **2Be** has two equatorial substituents and an evidence that the borane group is largely equatorial is provided by the very small upfield shift at C-3 and C-5 (< 0 7 ppm)

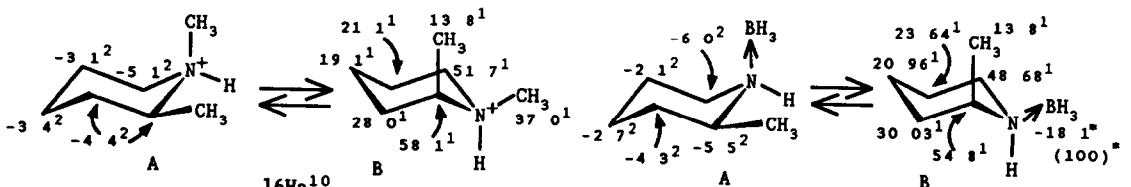


2 2Be 16He[10]

(*) $^{11}B$ NMR ($J_{BH}$, Hz)

figure 3

Compound **2Ba** has an equatorial C-methyl and an axial borane group and may display a conformational equilibrium, figure 4 The latter is supported by the $^{13}C$ NMR 1,3-diaxial effects produced at C-3 and C-5 by the axial-borane in **A** and at C-4 and C-6 by the axial methyl group in **B**[13] Another argument in favor of the equilibrium comes from the chemical shift of borane of δ = - 18 1 ppm (J = 110 Hz), that seems to be an average value between an equatorial (δ = -15 5 ppm, J = 97 Hz) and an axial borane (δ = - 19 5 ppm[15]) A near equal ratio of both conformers may be assumed from comparison between the $^{13}C$ chemical shifts of **2Be** and **2Ba** and between **16Ha** and **16He** (figure 4) that clearly shows the 1,3-diaxial effects produced by the 2-methyl group in the **B** conformers and by N-methyl or



16Ha[10] A B A B 2Ba

(1) $^{13}C$ δ of the equilibrium mixture, (2) Values of 1,3-diaxial interactions, Δδ(2Ba-2Be) or Δδ(16Ha-16He), (*) $^{11}B$ NMR ($J_{BH}$, Hz)

figure 4

N-borane in conformers **A** The existence of an important proportion of the axial borane means that vicinal interactions between an equatorial borane and an equatorial methyl group is destabilizing, favoring the equilibrium The differences in B-H coupling constants indicate a weaker coordination of the nitrogen atom in the axial borane (a larger $J_{B-H}$ value indicates a larger H-B-H angle and a weaker coordination) The similarities between borane adducts and the ammonium salts **16Ha** and **16He**[10] are interesting It is reasonable to assume that **16Ha** is in conformational equilibrium based on comparison of its $^{13}C$ NMR data with those of **2Ba** Analysis of the $^{1}H$ NMR spectrum of **2B**, proved difficult due to the complexity of the mixture which allowed identification of the C-2 and C-6 protons only The C-2 axial proton appears at 2 63 ppm in **2Be** ($\Delta\delta$ = 0 07 ppm to low field with respect to **2**), and at 3 25 ppm in **2Ba** ($\Delta\delta$ = 0 69 ppm to low field with respect to **2**) This effect is observed also at the C-6 axial proton, which evidences a very strong antiperiplanar inductive effect of borane The C-2 methyl is found at 1 36 ppm in **2Be** and at 1 27 ppm in **2Ba**, showing that an equatorial borane has a deshielding effect on the methyl protons

**3-Methylpiperidine, 3.**

The free piperidine **3** exists in a preferred chair conformation, with the 3-methyl group in equatorial position Borane addition produces two N-epimers **3Be** and **3Ba** in an 86 to 14 ratio, as deduced from the NMR spectra, figure 5 This molecule has the advantage to allow comparison between epimers without steric effects near the nitrogen atom In $^{1}H$ NMR, all protons of piperidine **3**, as well as those of the more abundant N-epimer **3Be**, are distinguishable in the spectra Compound **3Be** shows the same trends as those of **1Be**, the molecule is anchored, equatorial protons at C-2 and C-6 are shifted 0 06 ppm to higher field while the corresponding axial protons are shifted 0 10 and 0 31 ppm, respectively, to higher field

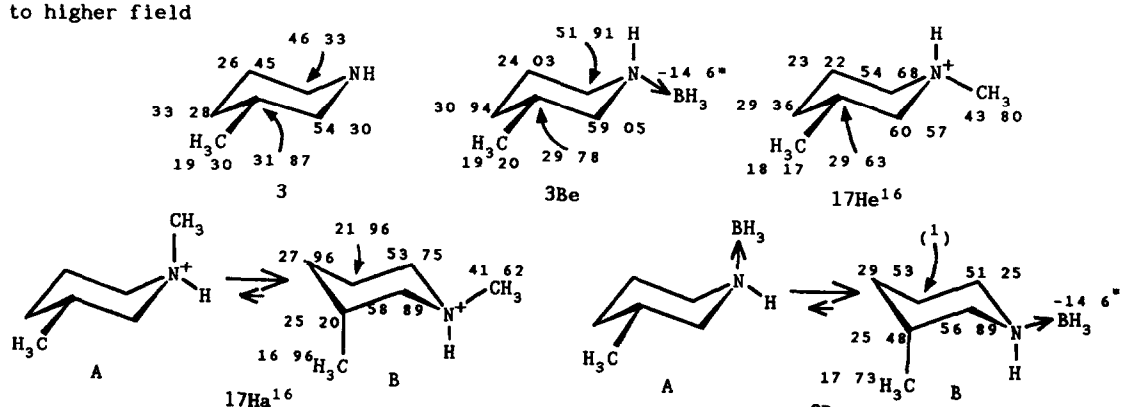
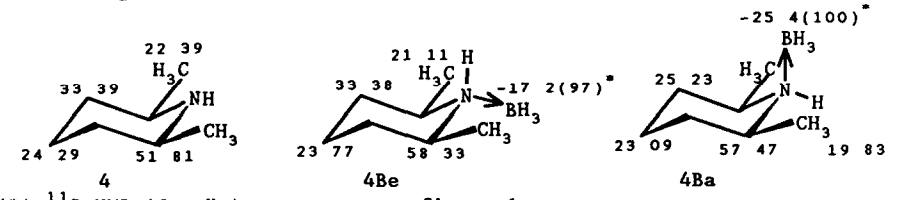



figure 5

Compound **3Ba** seems to be in a conformational equilibrium shifted largely towards **B** This assumption is based on the $^{13}C$ NMR chemical shift of N-$CH_3$ (an axial N-$CH_3$ is expected around 33 ppm) and also the similarity between the C-6 chemical shifts in both compounds **17He** and **17Ha**, that supports an equatorial N-substituent Comparison of the $^{13}C$ chemical shifts[16] of compounds **3Ba** and **17Ha** evidences that the conformational equilibrium of **3Ba** shifted also towards conformer **B** Another important argument in favor of this equilibrium is that the $^{11}B$ NMR spectra shows only a sharp signal at -14 6 ppm which is compatible with two equatorial borane groups from **3Be** and **3Ba**

**Cis-2,6-Dimethylpiperidine, 4.**

Piperidine **4** is in a preferred chair conformation with the methyl groups in equatorial position Borane addition, as in the case of 2-methylpiperidine **2**, gives a mixture of N-epimers (**4Be** and **4Ba**) in a 60 to 40 ratio The presence of two equatorial C-methyl groups produces a steric effect that is evident in the $^{11}B$ chemical shift of the borane groups ($\delta$ = -17 2 ppm for **4Be** and $\delta$ = -25 4 ppm for **4Ba**) The axial protons at C-2 and C-6 show the antiperiplanar effect of borane, the equatorial borane shifts these protons 0 2 ppm to higher field and the axial borane 0 3 ppm to lower field An equatorial N-H appears at 5 8 ppm whereas an axial one is at 4 9 ppm In the $^{13}C$ NMR spectrum the methyl groups are shifted 1 3 ppm to higher field by an equatorial borane and 2 4 ppm to higher field by an axial borane which evidences a larger steric effect of the axial borane over the methyl groups A strong 1,3-diaxial effect is observed in C-3 and C-5 (8 ppm) in **4Ba**



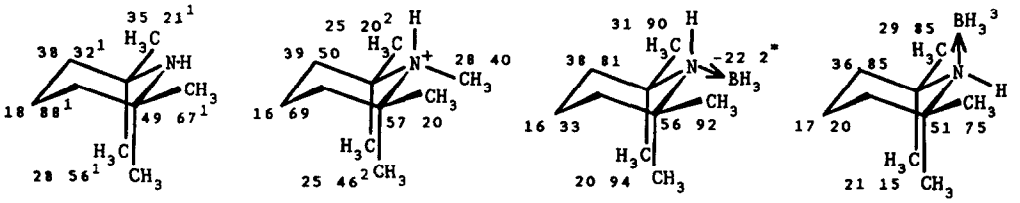

4 4Be 4Ba

(*) $^{11}B$ NMR ($J_{BH}$, Hz)

figure 6

**2,2,6,6-Tetramethylpiperidine, 5**

Piperidine **5** is in conformational equilibrium between the two equivalent chair forms at




5 18 5Be 5Ba

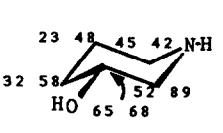
(1) at -105°C, (2) may be interchanged, (3) not observed, (*) $^{11}B$ NMR at -105°C

figure 7

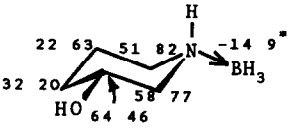
27°C, both methyl groups appear at 31 6 ppm However, for the $^{13}C$ NMR spectrum measured at 67 94 MHz, coalescence of the methyl groups is observed at Tc = -95 ± 0 5° C and the molecule is "frozen" at -105°C with the axial methyl groups at 28 56 ppm and the equatorial ones at 35 21 ppm, the calculated energy for the ring inversion is $\Delta G^{\#}$ = 7 8 ± 0 3 Kcal/mol Borane addition leads to two N-epimers (**5Be** and **5Ba** in a 90 to 10 ratio) Compound **5Be** is in a predominant chair conformation The $^{11}B$ NMR chemical shift of **5Be** is at δ = -22 2 ppm evidencing a very strong steric effect The N-methyl derivative of 5 does not give a borane adduct, presumably due to an extremely strong steric effect However, in the presence of boric acid, a piperidinium salt **18** is obtained with the $B(OH)_4^-$ as anion The protonated salt is an analogue of **5Be**

**3-Hydroxypiperidine, 6.**

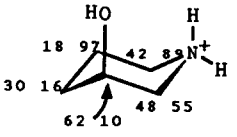
Compound **6** and its hydrochloride **6H** have a preferred chair conformation with the hydroxy group in the equatorial and axial position, respectively, as deduced from the $^{13}C$ NMR data The unexpected OH-axial conformation for **6H** is probably stabilized by hydrogen bonds The $^{1}H$ NMR spectrum (DMSO) of the hydrochloride **6H** shows two N-H signals at 8 99 and 9 35 ppm Reaction with lithium borohydride gives a mixture of epimers of the N-equatorial borane adducts **6Be** and **6Ba** in a 70 to 30 ratio which give only one $^{11}B$ signal at -14 9 ppm Analysis of the NMR data ($^{13}C$ and $^{1}H$) allows one to conclude that the hydroxyl group remains axial in **6Ba** As in compound **3Ba**, a conformational equilibrium largely on the side of conformer **A** appears evident The $^{11}B$ chemical shift, as well as the similarity with the $^{13}C$ data for compound **3Ba** and with calculated values confirm this proposition



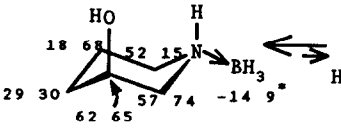

6



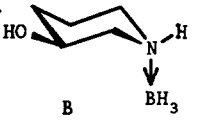

6Be




(*) $^{11}B$ NMR 6H




A




B

figure 8

6Ba

**4-Hydroxypiperidine, 7.**

4-Hydroxypiperidine 7 exists in a preferred chair conformation with the hydroxyl group in the equatorial position The $^{11}B$ NMR spectrum of the reaction product of 7 with borane-THF showed two kinds of boron atoms, a signal at δ -15 1 ppm, expected for an N-borane, and a sharp signal at δ +2 0 ppm which suggests the presence of a N-coordinated borate, similar to a system studied by us in borates of ethanolamine derivatives[15] Since

water addition did not hydrolyze this very stable borate function, we decided to undertake a careful examination of the reaction product We propose that the compound obtained is **7Be(borate)**, after examination of the $^{13}C$ NMR data, since two kinds of rings were recorded, one that was attributed to an N-borane substituted piperidine in a chair conformation and another one to a boat conformation with the piperidine in an intramolecular coordination to boron, figure 9 A similar coordination in a boat conformation was reported for 1,2,2,6,6,-pentamethyl-4-hydroxy-4-phenylpiperidine[17] In order to confirm the structure of this complex we reacted 4-hydroxypiperidine **7** with trimethyl borate to produce **7(borate)** and recorded the $^{11}B$ NMR spectrum which shows a sharp signal at + 1 6 ppm indicative of a nitrogen coordinated borate The molecule presents only one kind of ring signal in $^{13}C$ evidencing a fast exchange between the three rings The same experiment was performed on compound **6**, the resulting N-borate system **6(borate)** shows a $\delta$ $^{11}B$ = + 1 4 ppm Borane addition to **6(borate)** or **7(borate)** gives cleanly compounds **6Be(borate)** and **7Be(borate)** Arguments in favor of an intramolecular coordination complex are based on the fact that 4-hydroxypiperidine gives a $^{11}B$ NMR signal at +18 ppm in the presence of trimethyl borate, characteristic of a borate without N-coordination It was reported that compound **7** was frozen at room temperature using nitrogen coordination to a cobalt reagent[18]

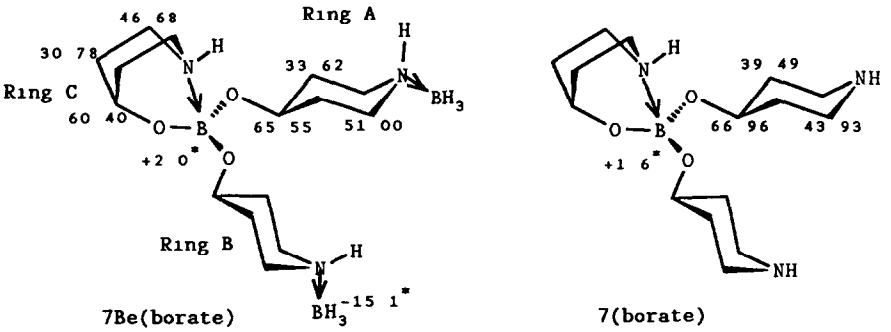
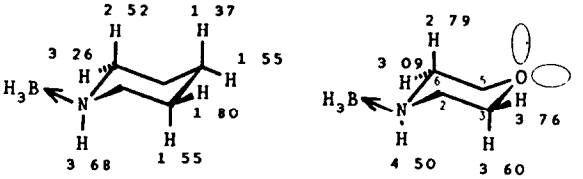



figure 9

**Morpholine, 8.**

Morpholine **8** adds borane to give the equatorial adduct **8Be** in a preferred chair conformation Assignment of all carbon and proton absorptions was done using $^{1}H/^{1}H$ and $^{1}H/^{13}C$ correlation spectra The $^{1}H$ NMR spectrum of compound **8Be** at room temperature is similar to the spectrum of methylmorpholine[19] "frozen" at -60°C The anchored molecule allows one to observe the electronic effect of the oxygen lone pairs on the neighboring protons Comparison of the $^{1}H$ NMR spectra of N-borane substituted piperidine and N-borane substituted morpholine shows that substitution of a methylene group by an oxygen atom has a sizeable deshielding effect on the C-2 and C-6 axial protons and a shielding effect on

the equatorial protons at the same carbons, figure 10

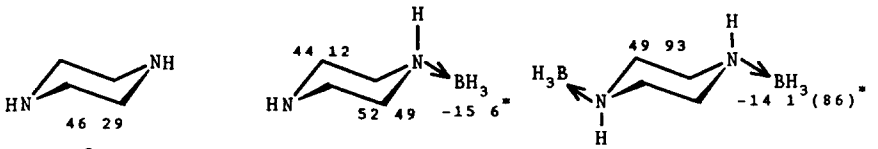



1Be 8Be

figure 10

**Piperazine, 9**

Borane monoaddition to piperazine gives a mixture of compounds, in which monoborane **9Be** can be detected and its $^{13}C$ and $^{11}B$ NMR chemical shifts assigned Borane diaddiation gives in some cases only compound **9BeBe** and in others a mixture with less than 5 % of **9BaBe** ($\delta$ $^{13}C$ = 46 29 ppm) The methylene protons in **9BeBe** display an AB signal, the equatorial hydrogen atoms appearing at 2 90 ppm ($J_{AB}$ = 9 3 Hz) and the axial ones at 2 53 ppm, the latter are coupled with the axial N-H (J = 9 7 Hz) The molecule is in a predominant chair conformation, and $\delta$ $^{11}B$ = -14 1 ppm



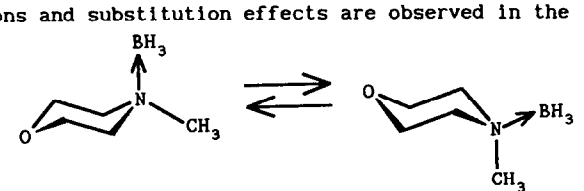

9 9Be 9BeBe

(*) $^{11}B$ NMR ($J_{BH}$, Hz) figure 11

**N-METHYLHETEROCYCLES.**

**N-Methylmorpholine, 10**

This heterocycle is in a conformational equilibrium between the two equivalent chair conformations (in $^{1}H$ NMR its Tc is -31°C in $CD_2Cl_2$ at 100 MHz[19]) Borane addition affords also a complex in conformational equilibrium which shows a $^{11}B$ NMR signal at -10 2 ppm (J = 98 7 Hz) Application of Eliel's equation[20a] using the $\delta$ $B^{11}$ values for an equatorial (-8 0 ppm) or an axial borane (-14 5 ppm)[20b] gives a 40 to 60 ratio of **10Be** to **10Ba** favoring the equatorial methyl over the borane The $^{1}H$ NMR showed four broad multiplets and a singlet for the N-methyl group indicative of an equilibrium, unfortunately insolubility of the complex has precluded variable temperature experiments The 1,3-diaxial interactions and substitution effects are observed in the $^{13}C$ NMR spectrum



10Ba figure 12 10Be

**N,N-Dimethylpiperazine, 11**

Piperazine **11** is in ring conformational equilibrium with the methyl groups in equatorial positions at room temperature, as deduced from the $^{13}C$ NMR data, Tc is reported to be - 8 5 °C in $CD_2Cl_2$[19] Borane diaddition gives two different N-epimers **11BaBa** and **11BaBe** in a 60 to 40 ratio At room temperature, the $^{11}B$ NMR spectrum shows two signals at -13 6 ppm attributed to the axial boranes of **11BaBa** and another one at -11 0 ppm assigned to compound **11BaBe** The latter is in conformational equilibrium since at low temperature the -11 0 ppm signal gives rise to two absorptions, one at δ = -13 6 ppm for an axial borane and the other one at -8 0 ppm for the equatorial one $^{13}C$ NMR low temperature experiments allow one to obtain the chemical shifts of "frozen" **11BaBe**, and $^{11}B$ NMR low temperature experiments to calculate the $\Delta G^*$ for the ring inversion of **11BaBe** ($\Delta G^*$ = 13 4 0 5 Kcal/mol)

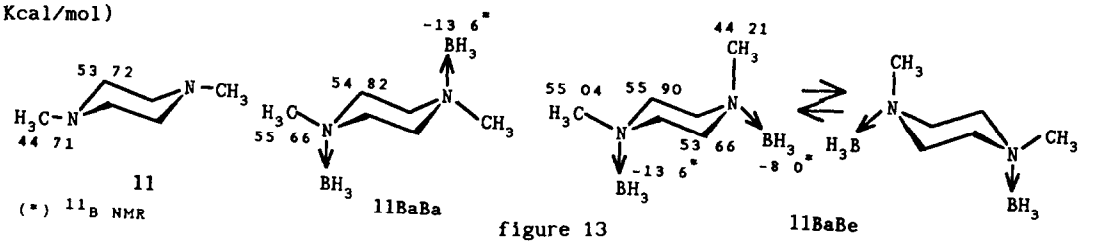
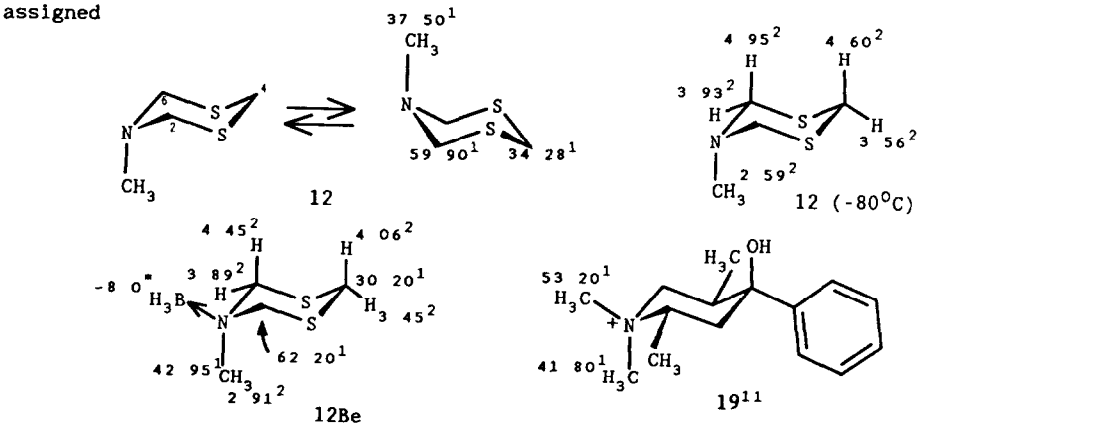



figure 13

**Dihydrodithiazine, 12.**

This molecule was previously studied by Katritzky[21] who found that the ring is in conformational equilibrium between the two chair forms (Tc -41°C in $CDCl_3$ and $CFCl_3$, $\Delta G^*$ 11 Kcal/mol for the ring inversion) with the N-methyl in a preferred axial position, as confirmed by examination of the $^{13}C$ chemical shift of the methyl group (δ = 37 5 ppm) At - 80°C the molecule is "frozen" and all protons in the 90 MHz $^1H$ NMR spectrum can be assigned



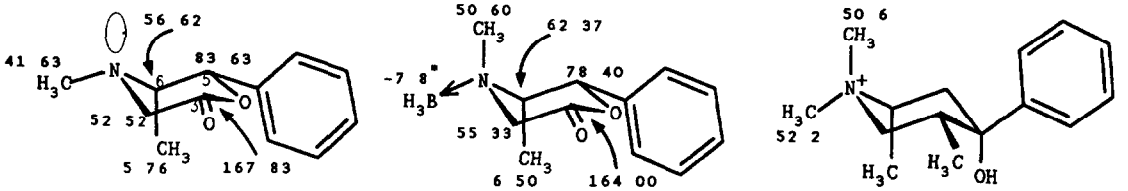

(1) $^{13}C$ NMR, (2) $^1H$ NMR, (*) $^{11}B$ NMR

figure 14

In contrast to morpholine, borane addition gives only **12Be** with the N-methyl group in the axial position ($\delta$ = 42 95 ppm) as established by comparison with $^{13}C$ NMR values of compound **19**[11] where the axial methyl is found at 41 8 ppm The $^{11}B$ NMR value for the equatorial borane ($\delta$ = - 8 ppm) is in agreement with the other values reported here[20b] The conformational homogenicity is supported by the proton NMR spectrum where the C-4 protons give an ABX2 system ($J_{AB}$ = 14 Hz), the equatorial proton showing a W coupling (J = 1 4 Hz) with the C-2 and C-6 equatorial hydrogen atoms, which are observed also as an ABX system The coupling values and pattern allow one to deduce a chair conformation The $^{1}H$ NMR coupling is similar to that of compound **12** at low temperature Comparison between the $^{1}H$ $\delta$ of **12** and **12Be**, figure 13, shows that the axial protons of the borane adduct are shifted to high field (0 54 for C-4 protons and 0 76 ppm for C-2 protons) and the equatorial protons show a very small effect This behavior can be explained by a decrease of electronic density at the axial lone pairs of the sulfur atoms

**N-Methyl-5-methyl-6-phenyl-1,4-oxazin-2-one [derived from (-) ephedrine], 13**

The 270-MHz $^{1}H$ NMR spectrum reveals that at room temperature the morpholone **13** exists solely as a fixed conformer, figure 14, which shows an AB system for the methylene hydrogen atoms Borane addition gives a "frozen" molecule **13Be** with the N-methyl and C-methyl in axial positions The alternative conformation with an syn-axial phenyl and borane groups is very unlikely In both cases the conformation was deduced by comparison of the observed $^{13}C$ NMR chemical shift values with those calculated for both conformers The $^{11}B$ value of -7 8 ppm supports an equatorial borane similar to that of **12Be** The N-methyl group has a downfield shifting effect (50 60 ppm) produced by an anti-axial methyl group *alpha* to it This effect is also found in compound **20**[11] The C-2 and C-6 equatorial protons are shifted to low field ($\Delta\delta$ 0 4 and 0 5 ppm respectively) also indicating the presence of an equatorial borane




(*) $^{11}B$ NMR

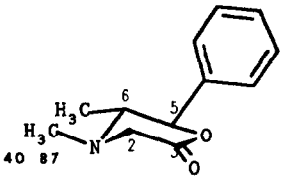
13 13Be 20

figure 15

**N-Methyl-5-methyl-6-phenyl-1,4-oxazin-2-one [derived from (-) *pseudo*ephedrine], 14.**

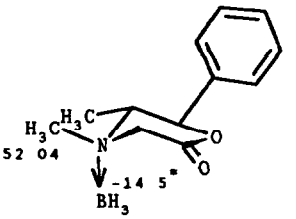
The free morpholone **14** is anchored in a chair conformer with the three substituent groups in equatorial positions, figure 15, as evidenced by the AB system of the methylene protons Borane addition gives two N-epimers **14Ba** and **14Be** in a 90 to 10 ratio The

equatorial N-methyl appears at δ = 52 04 ppm and the axial one at 41 47 ppm $^{11}B$ NMR absorptions are at δ = -14 5 ppm (axial borane) and at -8 0 ppm (equatorial borane) It is important to notice the deshielding effect of the axial borane on the hydrogen at C-6 compared to the other N-epimer (Δδ= 0 5 ppm), which is attributed to a field effect

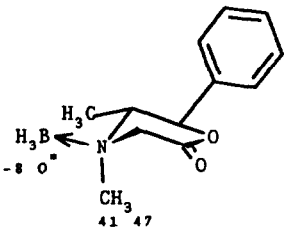



14

(*) $^{11}B$ NMR




14Ba




14Be

figure 16

**Conclusions·**

Borane addition to six membered ring N-heterocycles constitutes an alternative to variable temperature NMR spectroscopy in that borane can be used as a locking group for the observation of preferred conformers Borane addition gives kinetic products favoring axial N-borane adducts It is clear that axial approach of borane is favored somewhat over what would be expected thermodynamically This is related to the observations concerning alkylations of N-substituted piperidines to quarternary salts which involves predominant axial approach[22] The thermodynamic ratio of borane adducts can be approached by heating in the presence of free amine Equatorial boranes are more stable than axial ones

Methyl groups show a systematic steric effect on the $^{11}B$ chemical shifts , the methyl groups in vicinal carbons shifting the $^{11}B$ signal to higher field Axial boranes appear at higher field than equatorial ones

The $^{1}H$ NMR chemical shifts of N-H borane adducts are independent of concentration It is of interest that in **13Be**, **14Ba** and **14Be** the nitrogen atoms become stable chiral centers The locking effect in piperidine analogues bearing another heteroatom allows one to see the effect of anchored lone pairs on the neighboring hydrogen atoms, including antiperiplanar effects The information provided by the study of these model molecules allows one to assign the position of the borane, as well as the configuration of other atoms in more complex heterocycles such as, **13** and **14**, thus pointing to the importance of borane adducts in stereochemical analyses

**EXPERIMENTAL.**

$^{1}H$ and $^{13}C$ NMR spectra were recorded on Varian XL-300GS, Jeol GSX-270 or Jeol FX-90 spectrometers Chemical shifts are reported in parts per million relative to $Me_4Si$ (δ) $^{11}B$ NMR spectra were recorded on a Jeol GSX-270 or a Jeol FX-90 using $BF_3$-etherate as the external standard

Tetrahydrofuran was distilled under dry nitrogen from sodium using benzophenone as indicator, the borane-THF complex was prepared using a published procedure[23] Reactions were carried out under a nitrogen atmosphere The piperidines were commercially available,

tetrahydrodithiazine was prepared as reported[24] and morpholones were prepared by dehydration in dry toluene from the N-(2-hydroxy-1-methyl-2-phenylethyl)-N-methylamino acetic acid derived from (ephedrine **13** and pseudoephedrine **14**)[25]
Preparation of the adducts was carried out by addition of 1 2 or 2 4 equivalents of borane-THF to compounds **1** to **14** to obtain monoborane and diborane addition, respectively, following the general procedure below To a stirred solution containing 10 mmol of the heterocycle in 4 ml of THF was added dropwise a solution of 2 0 M $BH_3$-THF in THF (12 mmol for monoaddition and 24 mmol for diaddition, respectively) The solvent was evaporated immediately and the products were examined by NMR

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