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N-BH₃ ADDUCTS OF TRIALKYL-1,3,5-TRIAZACYCLOHEXANES WITH STABLE STEREOGENIC NITROGEN ATOMS, STEREOCHEMICAL STUDY

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Abstract: The syntheses and stereochemical studies of N-BH₃ adducts of trialkyl-1,3,5-triazacyclohexanes [**1**, R= CH₃; **2**, R= *iso*-C₃H₇; **3**, R= CH(CH₃)(C₆H₅)(R); **4**, R= *tert*-C₄H₉] are reported. Different reagent ratios were used in order to obtain *mono*- and *di*-N-borane adducts. Tri-N-borane adducts were never observed; *di*-N-borane adducts were formed with triazine **1** and **2** whereas **3** and **4** afforded only the *mono*-boranes. It appears that low steric strain is an important factor in the synthesis of these compounds. Borane addition produced in all cases ring and nitrogen conformationally stable compounds which were studied by NMR. All the reactions were 100% stereoselective affording one isomer in each reaction.

We have been interested in using borane as a steric probe and as an anchor in conformational studies of nitrogen in six membered ring heterocycles such as piperidines^{1a,c,e}, piperazine^{1a,b}, morpholine^{1a}, dithiazines^{1a,c,e}, 1,5-dithia-3,7-diazabicyclo[3,3,1]nonane^{1d} and 1,5-dithia-3,7-diazacyclooctane^{1e}. N-Borane adduct formation in these heterocycles freezes the ring conformation as has been observed through NMR studies at room temperature and gives a stable nitrogen configuration. In many cases only one stereoisomer was isolated. The axial or equatorial positions of borane have been already established, based on steric and electronic effects of borane over the neighbouring groups¹.

Herein, we report our results in the study of the reaction of borane with trialkyl-1,3,5- triazacyclohexane [**1**, R= CH₃; **2**, R= *iso*-C₃H₇; **3**, R= CH(CH₃)(C₆H₅)(R); **4**, R= *tert*-C₄H₉], Figure 1. Conformational analyses of compounds **1**, **2** and **4** have been reported². At room temperature the ring and the nitrogen atoms of **1-4** are in conformational equilibrium, two of the N-substituents are in an equatorial position whereas one always remains in an axial position. This behaviour has been attributed to non-bonded electronic interactions which preclude three parallel axial lone pairs^{2b}. The nitrogen inversion is still fast at low temperature (-100°C, THF-*d*₈, ¹H NMR at 270 MHz). Thus, we decided to add BH₃ to the systems **1-4** in order to study the addition of BH₃ molecules, to check the influence of BH₃ on the conformational equilibrium of six membered heterocycles with three nitrogen atoms and to analyse the stereochemistry of the reaction products.

The triazacyclohexanes **1-4** were prepared following reported procedures³, purified and then reacted with BH₃-THF at -78°C. The reaction mixtures were warmed to room temperature and immediately evaporated in vacuum. The reactions were quantitative and pure products were isolated by solvent evaporation. Then, they were dissolved in CDCl₃ and observed by NMR. Different reagents ratios were used in order to try to obtain *mono*- *di*- and *tri*-N-borane adducts. The latter were never observed, *di*-N-borane adducts were formed for triazines **1** and **2**. When

bulky N-substituents are present, such as in **3** and **4**, only the *mono*-boranes were prepared. It appears that low steric strain is required for the multiple addition of BH_3 in these substrates.

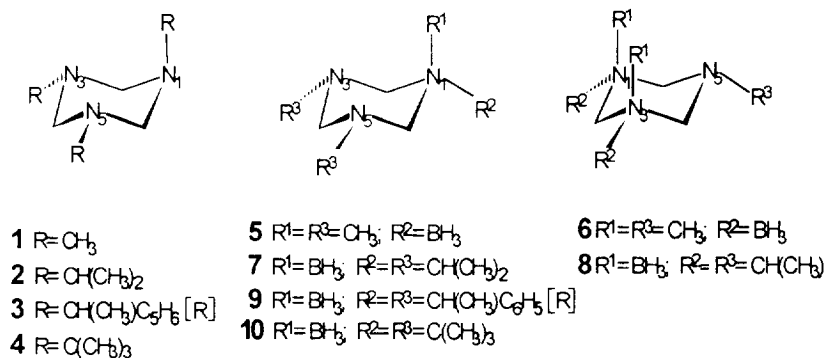


Figure 1

Reaction of Compound **1** with BH_3 -THF.

Triazacyclohexane **1** is observed to be in a ring preferred conformation at -90°C in $\text{THF}-d_8$ (^1H NMR, 270 MHz). The methylene protons are an AB system but there is still only one signal for the methyl groups indicating a fast nitrogen inversion. But in the ^{13}C NMR, the methyl groups present one signal even at -90°C . The reaction of **1** with one equivalent of BH_3 -THF afforded compound **5**. Its NMR data were compared with those of the frozen molecules trimethyltriazacyclohexane **1**^{2a} and dithiazine **11**^{1a}, Figure 2.

At room temperature in the ^1H NMR spectrum, adduct **5** was observed as a preferred conformer with frozen nitrogen conformations, two different methyl groups and four different methylene protons were distinguished. The methyl group in an axial and in equatorial position are shifted to high frequencies in the coordinated heterocycle, compared with frozen heterocycle **1** ($\Delta\delta$ 0.21 and 0.36 ppm respectively). In compound **5**, the N- BH_3 in an equatorial position neutralizes the dipole effect of the equatorial lone pair of the triazine **1**, the stronger effects produced by borane complexation to this lone pair are observed at the axial proton at C-4 and at the methyl group of the free nitrogen atoms, Figure 2. The analysis of the chemical shifts clearly established that only one BH_3 is introduced; the assignment of the stereochemistry was based on a comparison with the chemical shifts of similar systems such as N-borane dithiazine **12**^{1a,b} or piperazine^{1a}. In their ^{13}C NMR spectra, the axial N-methyl group bonded to borane presents a signal at 44.0 ppm whereas in an equatorial position it appears at 55 ppm^{1a,c}. The axial position of the CH_3 group in compound **5** was deduced from the shift of ^{13}C of the methyl group (45.35 ppm). Similarly it was deduced that the other two N- CH_3 groups of **5** ($\delta=39.21$ ppm) were preferentially in an equatorial position. The BH_3 preference for the equatorial position shows that BH_3 is larger than CH_3 and this is in analogy with the N-configuration observed for other six membered NCH_3 - BH_3 heterocycles, piperazines and dithiazines and contrasts with the finding that in the N- BH_3 adduct of N-methyl morpholine the ring does not have a preferred conformation^{1a}. Therefore the explanation for the anchorage of adduct **5** is attributed to the presence of heteroatoms in position 3 and 5 and to the equatorial free methyl groups of N-3 and N-5.

Significantly, borane coordination produces opposite effects in triazine and in dithiazine. In the latter the methylene groups are shifted to lower frequencies by borane coordination. This could be explained based on the fact that in dithiazine the orbitals of sulfur atoms are not hybrids and that they have a lone pair in a p and another in an s orbital⁴. In triazine the nitrogen atoms have a sp^3 hybridisation and the proton atoms are affected by the two sp^3

lone pairs on each nitrogen atom.

The stereochemical analysis of compound **5** shows that it is a *meso* compound with a plane of symmetry passing through N-BH₃ and C-4, the anchored conformation makes tricoordinated nitrogen N-3 and N-5 stereogenic centers of opposite chirality.

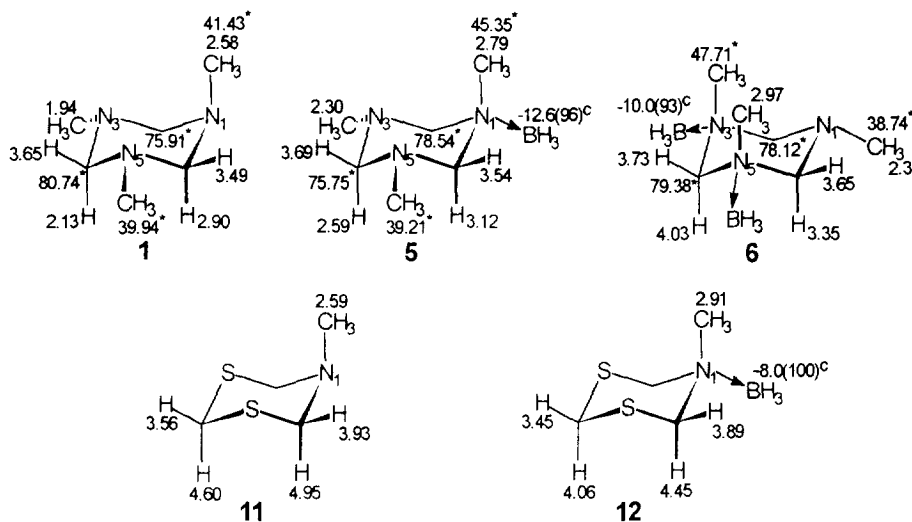


Figure 2. ¹H, ¹³C (*) and ¹¹B (°) NMR chemical shifts (δ, ppm) of trimethyltriazacyclohexanes **1** (-90°C), **5** and **6** (27°C), N-methyldihydroditiazines **11** (at 80°C) and **12** (27°C)^{1a}.

Addition of two or three equivalents of BH₃ gives only one compound: borane diadduct **6**, Figure 2. We do not have evidence for the introduction of three molecules of BH₃ on **1**. Compound **6** is also an anchored molecule, the two BH₃ groups were found to be in an equatorial position (δ ¹¹B = -10.0 ppm), the methylene groups between a N-BH₃ and a free nitrogen atom suffer small shifts to high frequencies, the axial proton between the two N-BH₃ groups is shifted *ca.* 1.9 ppm compared with the anchored triazine **1**, Figure 2. The deshielding effect on the axial protons could not be explained based on the proximity of BH₃ because the equatorial protons are also near to a BH₃ group and they have a small effect. A better explanation is again that borane adduct formation neutralize the shielding antiperiplanar effect of the equatorial lone pair of compound **1**. The change on ¹³C chemical shifts is not as important as in other examples; the coordinated N-CH₃ is shifted about 6 ppm to high frequency when compared with the free molecule, the chemical shift indicates an axial position (47.71 ppm) while the free N-CH₃ group remains in an equatorial position (δ = 38.74 ppm). ¹¹B NMR data is in agreement with the configuration of the nitrogen atoms. From these NMR data, it is deduced that triazines (δ = -12.6 (**5**) and -9.9 (**6**)) produce a stronger N-B bond with borane than ditiazines (δ = -8.0 ppm (**12**)).

An important question about the stereochemistry of diborane **6** is the following. Does the *cis* configuration correspond on the kinetic isomer produced by an attack of two borane molecules on the two axial lone pairs with inversion of configuration, or does the thermodynamic product arise from isomerization of a *trans* isomer which comes from a two step reaction, the first step produces adduct **5** and the second involves a borane addition to **5** which has two axial lone pairs giving the *trans* some after isomerization. We have performed two experiments addition of two equivalents of BH₃ to the triazine or addition of one equivalent and then another one. In both

cases we have only obtained the *cis* isomer, which is consistent with a thermodynamic product.

Compound **6** is also a *meso* molecule with a plane of symmetry through N-5 and C-2. The quaternary nitrogen atoms are stereogenic centers of stable configuration. A ring-chair conformation for compounds **5** and **6** is supported by the ^1H NMR data, specially from W coupling constants $^4\text{J}(\text{H-H})$ [1.7 and 1.8 Hz, respectively].

Reactions of compound **2** with $\text{BH}_3\text{-THF}$.

Compound **2**, in spite of the bulky N-substituents, is in a conformational equilibrium with an *iso*-propyl group in axial position^{2b}. Reactions of one or two BH_3 equivalents with compound **2** afford the *mono*-borane adduct **7** indicating there is steric hindrance for the second borane addition. With three equivalents of $\text{BH}_3\text{-THF}$ only 10% of the diadduct **8** is observed, enough to obtain its NMR data and to deduce its structure. The stereochemistry of the *mono*-adduct **7** is different from the previously discussed compounds because in **7** the borane is found in an axial position owing to the larger *iso*-propyl group which remains in an equatorial position. The conformational preference of the N-*iso*-propyl coordinated group was established from the shift of ^{11}B (-18.5 ppm) which corresponds to the expected value calculated from the steric effect of the nitrogen substituent and the axial position of BH_3 . All three *iso*-propyl groups in **7** are equatorial owing to their steric hindrance and to the fact that coordination of one nitrogen atom eliminates the electronic repulsion between the three lone pairs. In this frozen molecule, the *iso*-propyl groups of N-3 and N-5 have diastereotopic methyl groups because the free nitrogen atoms are stereogenic centers with a slow inversion rate. The methyne proton in the *iso*-propyl group which neighbours the N-borane group is strongly shifted to high frequencies ($\delta = 4.19$ ppm). This fact is attributed to its proximity with BH_3 , indicating a preferred conformation of the N-C bond in which the proton is in a *gauche* position to the BH_3 group^{1e,1f}, Figure 3.

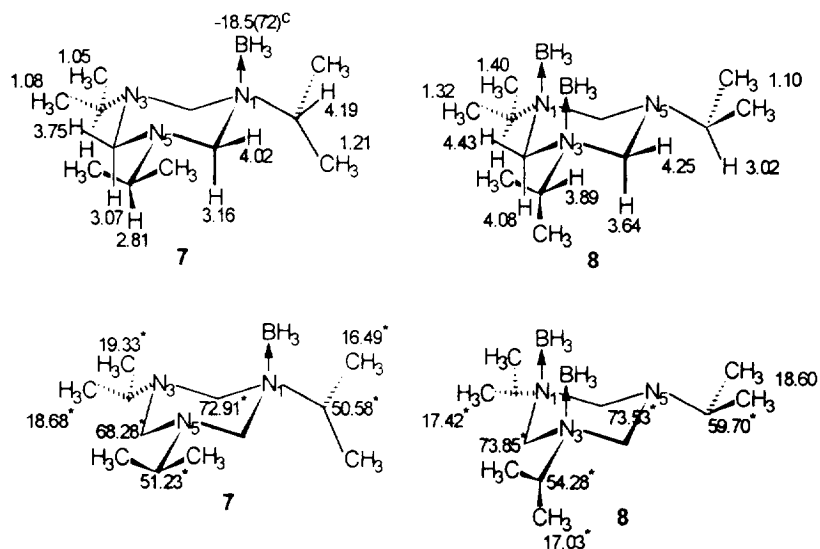


Figure 3. ^1H , ^{13}C (*) and ^{11}B (°) NMR chemical shifts (δ , ppm) of trimethyltriazacyclohexanes **7** and **8**.

The analysis of the NMR data of diborane compound **8** shows that all the proton signals in this compound were shifted to high frequency. The N_1 and N_3 *iso*-propyl groups have diastereotopic methyl groups because the quaternary stereogenic nitrogen atoms have a stable configuration. The assignment of the NMR data is shown in Figure 3.

Reactions of compound **3** with $\text{BH}_3\text{-THF}$.

The optically active heterocycle **3** is also in a conformational equilibrium at room temperature; by lowering the temperature the ring conformation is frozen $\Delta G = 12.33 \pm 1.2$ KJ/mol [coalescence temperature 273°K], but the nitrogen inversion is very fast even at -105° . By addition of $\text{BH}_3\text{-THF}$ (1 equivalent), the *mono*-borane adduct **9** is obtained with the BH_3 in an axial position ($\delta = -17.5$ ppm). In **9** the three nitrogen atoms are stereogenic centers. From eight possible isomers only one is obtained owing to the fact that the N-substituents are preferentially in an equatorial position. The large difference between the ^1H chemical shifts of the ring protons indicates that the *exo* N-C bond conformation is not the same for each nitrogen atom, a strong shift of the methyne of N-1 ($\delta = 5.42$ ppm) means that in the quaternary amine the preferred conformation is the one with the C-H *gauche* to the N-B bond^{1c}, Figure 4. This N-C conformation makes a strong difference to the chemical shift of the neighbouring methylene protons. The ^1H NMR chemical shifts were assigned taking into account the preferred conformations and the shielding effects of the methyl and phenyl groups^{1c}, Figure 4. The reaction of **3** in an excess of BH_3 did not afford the *di*-adduct.

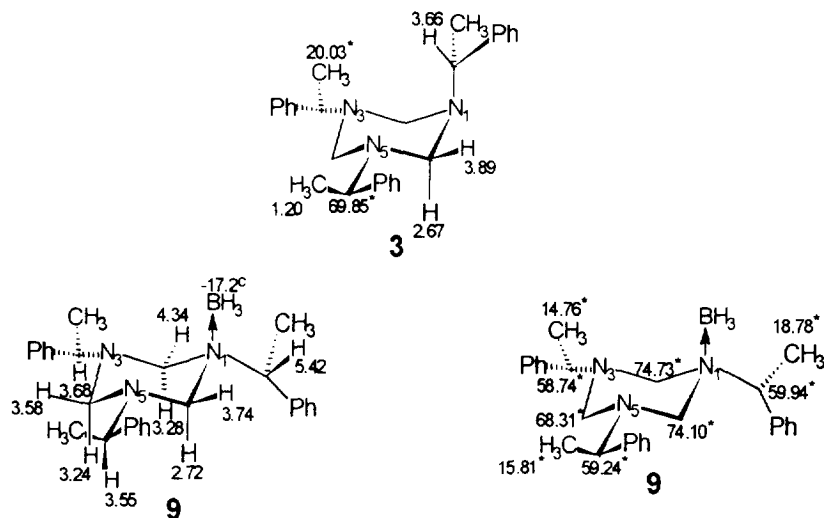


Figure 4. ^1H , ^{13}C (*) and ^{11}B (°) NMR chemical shifts (δ , ppm) of trimethyltriazacyclohexanes **3** and **9**.

Reactions of compound **4** with $\text{BH}_3\text{-THF}$.

Reaction of compound **4** with two or three $\text{BH}_3\text{-THF}$ equivalents affords the borane *mono*-adduct **10** as the main product which is stable enough to be observed by NMR. It decomposes on standing; its low stability was attributed to the large steric hindrance of the *tert*-butyl groups. The ^1H and ^{13}C NMR data are described in Figure 5. The quaternary nitrogen atom of compound **10** has also the alkyl group in an equatorial and the BH_3 in an axial position.

CONCLUSIONS

The triazines reacted stereoselectively with borane affording N- BH_3 adducts. For N-methyl triazine species the equatorial position of borane was preferred. Other examples, **2-4**, with bulky substituents, give borane in an axial position. From the different adducts it was possible to know the electronic and steric effects of equatorial or axial

BH₃ groups. The chiral borane derivative **9** could be a good reagent for asymmetric reduction reactions.

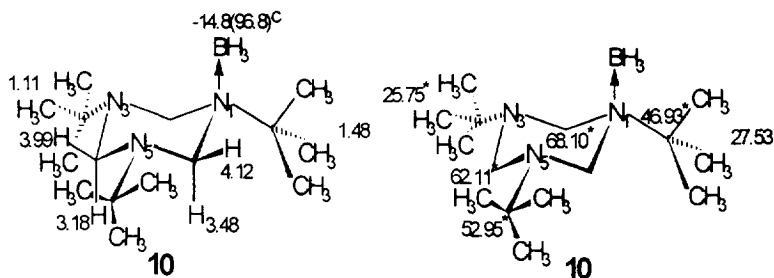


Figure 5. ¹H, ¹³C (*) and ¹¹B (°) NMR chemical shifts (δ, ppm) of trimethyltriazacyclohexane **10**.

EXPERIMENTAL

¹H (270 MHz) and ¹³C (67.8 MHz) NMR spectra were recorded with TMS as internal reference and ¹¹B (86.55 MHz) NMR spectra with BF₃·OEt₂ as external reference. Melting points are uncorrected. The [α]_D²⁰ values were obtained on a Perkin-Elmer 241 Polarimeter. IR spectra were recorded with a Perkin Elmer 16F PC infrared spectrometer. Tetrahydrofuran was distilled under dry nitrogen from sodium using benzophenone and BH₃-THF complex was prepared using a published procedure⁵.

General Procedure of 1,3,5-tris-alkylhexahydrotriazine synthesis. The *tris*-alkyltriazines were prepared by treatment of the alkylamines with 37% aqueous solution of formaldehyde in a 1:1.3 ratio, by 12 h at 0°C³. The mixture reaction was extracted with CH₂Cl₂ and the organic layer was separated, dried over NaOH, and concentrated under vacuum. The hexahydrotriazines **1**, **2** and **4** were purified by distillation and **3** by recrystallization from CH₂Cl₂:CH₃OH (1:1).

1,3,5-tris-methylhexahydrotriazine, 1 (74% yield). B. p. 52-54°C/1.5 mm [lit.^{3a} 166°C/760 mm]. ¹H NMR [CDCl₃, 27°C] δ 3.09 (sb, 2H₂, 2H₄, 2H₆), 2.19 (s, 3CH₃) ppm. ¹H NMR [C₄D₈O, -90°C] δ 2.57 (d, ²J_{AB}= 9.9, H_{2ax}, H_{4ax} and H_{6ax}), 3.57 (d, ²J_{AB}= 9.9, H_{2eq}, H_{4eq} and H_{6eq}), 2.17 (s, 3CH₃) ppm. ¹³C NMR [CDCl₃, 27°C] δ 76.27 (t, ²J_{CH}= 143.2, C-2, C-4 and C-6), 39.31 (q, ²J_{CH}= 133.3, 3CH₃) ppm. ¹³C NMR [C₄D₈O, -90°C] δ 77.66 (t sb, ²J_{CH}= 143.0, C-2, C-4 and C-6), 40.17 (q, ²J_{CH}= 134.0, 3CH₃) ppm.

1,3,5-tris-iso-propylhexahydrotriazine, 2 (66% yield). B. p. 94-97°C/0.25 mm [lit.^{3b} 104-106 /16 mm]. ¹H NMR [CDCl₃, 27°C] δ 3.52 (sb, 2H₂, 2H₄, 2H₆), 2.83 (sb, 3CH), 1.06 (s, 6CH₃) ppm. ¹³C NMR [CDCl₃, 27°C] δ 68.13 (t, ²J_{CH}= 141.5, C-2, C-4 and C-6), 49.38 (d, ²J_{CH}= 134.5, 3CH), 19.49 (q, ²J_{CH}= 125.6, 6CH₃) ppm.

1,3,5-tris[(R)-(+)-phenylethyl]hexahydrotriazine, 3 (78% yield, M.p. 63-64) [lit.^{3d} M.p. 52-54°C, [α]_D²⁰= -70.3 (c= 2, CHCl₃) for the S isomer] [α]_D²⁰= +77 (c= 2, CHCl₃). ¹H NMR [CDCl₃, 27°C] δ 3.34 (sb, 2H₂, 2H₄, 2H₆), 3.68 (q, ²J= 6.9, 3CH), 1.24 (d, ²J= 6.9, 3CH₃), 7.12-7.27 (m, 3C₆H₅) ppm. ¹H NMR [C₄D₈O, -90°C] δ 2.67 (d, ²J_{AB}= 9.2, H_{2ax}, H_{4ax} and H_{6ax}), 3.89 (d, J_{AB}= 9.2, H_{2eq}, H_{4eq} and H_{6eq}), 3.66 (q, ²J= 6.9, 3CH), 1.20 (d, ²J= 6.9, 3CH₃), 7.10-7.30 (m, 3C₆H₅) ppm. ¹³C NMR [CDCl₃, 27°C] δ 69.85 (tquint, J_{CH}= 143.2 and 2.2, C-2, C-4 and C-6), 59.32 (dd, J_{CH}= 134.4 and 2.2, 3CH), 20.03 (qd, J_{CH}= 126.7 and 3.3, 3CH₃), 144.09 (ddd, J_{CH}= 14.3, 6.6 and 4.4, 3C_i), 128.02 (dd, J_{CH}= 158.6 and 6.6, 6C_o), 127.26 (dq, J_{CH}= 157.5 and 5.5, 6C_m), 126.67 (dt, J_{CH}= 160.9 and 6.6, 3C_p) ppm.

1,3,5-tris-*tert*-butylhexahydrotriazine, 4 (76% yield). B.p. 124°C 1.5 mm [lit.^{3c} 125-130°C/20 mm]. ¹H NMR [C₄D₈O, 27°C] δ 3.68 (sb, 2H₂, 2H₄, 2H₆), 1.10 (s, 9CH₃) ppm. ¹H NMR [C₄D₈O, -90°C] δ 3.05 (d, J_{AB}= 9.9, H_{2ax}, H_{4ax} and H_{6ax}), 4.24 (d, J_{AB}= 9.9, H_{2eq}, H_{4eq} and H_{6eq}), 1.10 (s, 9CH₃) ppm. ¹³C NMR [C₄D₈O, 27°C] δ 64.36 (tqint, J_{CH}= 139.9 and 4.4, C-2, C-4 and C-6), 53.43 (s, 3C quaternary), 27.89 (qsept, J_{CH}= 124.5 and 4.5, 9CH₃) ppm. ¹³C NMR [C₄D₈O, -90°C] δ 64.12 (tb, J_{CH}= 139.9, C-2, C-4 and C-6), 53.24 (s, 3C quaternary), 27.73 (q, J_{CH}= 126.0, 9CH₃) ppm.

General Procedure for the Borane Adducts Preparation. To a stirred solution cooled at -78°C, containing 1 mmol of the hexahydrotriazine **1-3** or **4** in 25 ml of THF, was added dropwise 0.5 ml or 1.0 ml of a solution of BH₃-THF in THF (2.0 M, 1 mmol). The mixture reaction was warmed at room temperature, and the solvent was evaporated in vacuum to afford almost quantitatively the *mono*- or *di*-adducts as moisture sensitive white solids. Formation of compound **8** (10%) required three equivalents of BH₃-THF.

1-Borane-1,3,5-tris-methylhexahydrotriazine, 5. M.p. 113.3°C decomp. IR (CHCl₃) 2395, 2332 and 2273 (B-H), 1174 (B-N). ¹H NMR [CDCl₃, 27°C] δ 3.12 (d, ²J_{AB}= 11.0, H_{2ax} and H_{6ax}), 3.54 (dd, J_{AB}= 11.0 and ⁴J_{2eq-4eq}= 1.70, H_{2eq} and H_{6eq}), 2.59 (d, J_{AB}= 9.15, H_{4ax}), 3.69 (dt, J_{AB}= 9.15 and ⁴J_{2eq-4eq}= ⁴J_{4eq-6eq}= 1.70, H_{4eq}), 2.79 (s, CH₃ ax), 2.30 (s, 2CH₃ eq) ppm. ¹³C NMR [CDCl₃, 27°C] δ 78.54 (tb, J_{CH}= 149.0, C-2 and C-6), 75.75 (tb, J_{CH}= 142.7, C-4), 45.35 (q, J_{CH}= 140.0, CH₃ ax), 39.21 (q, J_{CH}= 134.4, 2CH₃ eq) ppm. ¹¹B NMR [CDCl₃, 27°C] δ -12.6 (q, J_{BH}= 96) ppm.

1-Borane-1,3,5-tris-*iso*-propylhexahydrotriazine, 7. M.p. 98°C decomp. IR (CHCl₃) 2400 and 2362 (B-H), 1222 (B-N). ¹H NMR [CDCl₃, 27°C] δ 3.16 (d, J_{AB}= 11.0, H_{2ax} and H_{6ax}), 4.02 (dd, J_{AB}= 11.0 and ⁴J_{2eq-4eq}= ⁴J_{4eq-6eq}= 1.72, H_{2eq} and H_{6eq}), 3.07 (d, J_{AB}= 7.8, H_{4ax}), 3.75 (dt, J_{AB}= 7.8 and ⁴J_{4eq-2eq}= ⁴J_{4eq-6eq}= 1.72, H_{4eq}), *iso*-propyl group of N-1: 4.19 (hept, J= 6.84, 1CH), 1.21 (d, J= 6.65, 2CH₃), *iso*-propyl groups of N-3 and N-5: 2.81 (hept, J= 6.65, 2CH), 1.08 (d, J= 6.84, 2CH₃), 1.05 (d, J= 6.65, 2CH₃) ppm. ¹³C NMR [CDCl₃, 27°C] δ 72.91 (t, J_{CH}= 149.8, C-2 and C-6), 68.28 (t, J_{CH}= 141.1, C-4), *iso*-propyl group of N-1: 50.58 (d, J_{CH}= 144.3, 1CH), 16.49 (qqint, J_{CH}= 126.7 and 3.8, 2CH₃), *iso*-propyl group of N-2: 51.23 (d, J_{CH}= 134.4, 2CH), 18.66 (qqint, J_{CH}= 125.6 and 4.0, 2CH₃), 19.33 (qqint, J_{CH}= 125.6 and 3.8, 2CH₃) ppm. NMR [CDCl₃, 27°C] δ 1-18.5 (q, J_{BH}= 72) ppm.

1-Borane-1,3,5-tris-*tert*-butylhexahydrotriazine, 10. Viscous liquid. IR (CHCl₃) 2400 and 2283 (B-H), 1270 (B-N). ¹H NMR [CDCl₃, 27°C] δ 3.18 (db, J_{AB}= 6.55, H_{4ax}), 3.99 (d, J_{AB}= 6.55, H_{4eq}), 3.48 (d, J_{AB}= 10.92, H_{2ax} and H_{6ax}), 4.12 (d, J_{AB}= 10.92, H_{2eq} and H_{6eq}), 1.11 (s, 9CH₃, *tert*-butyl groups of N-3 and N-5), 1.48 (s, 3CH₃, *tert*-butyl group of N-1) ppm. ¹³C NMR [CDCl₃, 27°C] δ 62.11 (t, J_{CH}= 144.1, C-2), 68.10 (t, J_{CH}= 150.0, C-4 and C-6), *tert*-butyl groups of N-3 and N-5: 52.95 (s, 2C quaternary), 25.75 (q, J_{CH}= 126.2, 6CH₃), *tert*-butyl group of N-1: 46.93 (s, 1C quaternary), 27.53 (q, J_{CH}= 126.0, 3CH₃) ppm. ¹¹B NMR [CDCl₃, 27°C] δ -14.8 (q, J_{BH}= 96.8) ppm.

1-Borane-1,3,5-tris-[(*R*)-(+)-phenylethyl]hexahydrotriazine, 9. Viscous liquid. [α]_D²⁰= +63.2 (c= 1.72, CHCl₃). IR (CHCl₃) 2360 (B-H), 1180 (B-N). ¹H NMR [CDCl₃, 27°C] δ 2.72 (d, J_{AB}= 10.05, H_{2ax}), 3.74 (db, J_{AB}= 10.05, H_{2eq}), 3.24 (d, J_{AB}= 10.58, H_{4ax}), 3.58 (d, J_{AB}= 10.58, H_{4eq}), 3.28 (d, J_{AB}= 11.2, H_{6ax}), 4.34 (d, J_{AB}= 11.2, H_{6eq}), ethyl group of N-1: 5.42 (q, J= 7.16, CH), 1.54 (d, J= 7.16, CH₃); ethyl group of N-3: 3.55 (q, J= 6.53, 1CH), 1.37 (d, J= 6.53, CH₃); ethyl group of N-5: 3.68 (q, J= 6.84, 1CH), 1.20 (d, J= 6.84, CH₃); phenyl groups: 7.1-7.7 (m, 15H, 3C₆H₅) ppm. ¹³C NMR [CDCl₃, 27°C] δ 74.10 (t, J_{CH}= 143.2, C-2), 68.31 (t, J_{CH}= 144.7, C-4), 74.73 (t, J_{CH}= 146.6, C-6); phenylethyl group of N-1: 59.94 (d, J_{CH}= 136.7, 1CH), 18.78 (qd, J_{CH}= 126.7 and 3.3, 1CH₃), 142.49 (s, 1C_i), 131.56 (d, 1C_p); phenylethyl group of N-3: 58.74 (d, J_{CH}= 133.3, 1CH), 14.76 (qd, J_{CH}= 126.4 and 3.3, 1CH₃), 137.67 (s, 1C_i), 131.56 (1C_p); phenylethyl group of N-5: 59.24 (dd, J_{CH}= 128.9, 1CH),

15.81 (qd, $J_{\text{CH}} = 128.9$ and 3.3 , 1CH_3), 140.24 (s, 1C_i), 131.56 (s, 1C_p); signals of *Co* and *Cm* are not assigned: 127.44, 127.28, 127.13, 128.48, 128.33, 129.15 ppm. ^{11}B NMR [CDCl_3 , 27°C] δ -17.2 (sb) ppm.

3,5-Di-borane-1,3,5-tris-methylhexahydrotriazine, 6. M.p. 103.9°C decomp. IR (CHCl_3) 2389, 2332 and 2274 (B-H), 1171 (B-N). ^1H NMR [CDCl_3 , 27°C] δ 3.35 (d, $J_{\text{AB}} = 11.60$, $\text{H}_{2\text{ax}}$ and $\text{H}_{6\text{ax}}$), 3.65 (dd, $J_{\text{AB}} = 11.60$ and $^4J_{2\text{eq}-4\text{eq}} = 1.83$, $\text{H}_{4\text{eq}}$ and $\text{H}_{6\text{eq}}$), 4.03 (d, $^2J_{\text{AB}} = 13.84$, $\text{H}_{2\text{ax}}$), 3.73 (dt, $J_{\text{AB}} = 13.84$ and $^4J_{4\text{eq}-2\text{eq}} = ^4J_{4\text{eq}-6\text{eq}} = 1.83$, $\text{H}_{2\text{eq}}$), 2.97 (s, N(1)- CH_3 and N(3)- CH_3), 2.39 (s, N(5)- CH_3) ppm. ^{13}C NMR [CDCl_3 , 27°C] δ 79.38 (t, $J_{\text{CH}} = 162.5$, C-2), 78.12 (t, $J_{\text{CH}} = 151.5$, C-4 and C-6), 47.71 (q, $J_{\text{CH}} = 141.1$, N(1)- CH_3 and N(3)- CH_3), 38.74 (q, $J_{\text{CH}} = 136.6$, N(5)- CH_3) ppm. ^{11}B NMR [CDCl_3 , 27°C] δ -10.0 (q, $J_{\text{BH}} = 93$) ppm.

3,5-Di-borane-1,3,5-tris-*iso*-propylhexahydrotriazine, 8. ^1H NMR [CDCl_3 , 27°C] δ 4.08 (d, $J_{\text{AB}} = 14.70$, $\text{H}_{2\text{ax}}$), 4.43 (dt, $J_{\text{AB}} = 14.70$ and $^4J_{2\text{eq}-4\text{eq}} = 1.62$, $\text{H}_{2\text{eq}}$), 3.64 (d, $J_{\text{AB}} = 12.83$, $\text{H}_{4\text{ax}}$ and $\text{H}_{6\text{ax}}$), 4.25 (dd, $J_{\text{AB}} = 12.83$ and $^4J_{4\text{eq}-2\text{eq}} = ^4J_{4\text{eq}-6\text{eq}} = 1.62$, $\text{H}_{4\text{eq}}$ and $\text{H}_{6\text{eq}}$), *iso*-propyl groups of N-1 and N-3: 3.89 (hept, $J = 6.45$, 2CH), 1.4 (db, $J = 6.81$, 2CH_3), 1.37 (db, $J = 5.91$, 2CH_3), *iso*-propyl group of N-5: 3.03 (hept, $J = 6.80$, 1CH), 1.05 (d, $J = 6.80$, 2CH_3) ppm. ^{13}C NMR [CDCl_3 , 27°C] δ 73.85 (t, $J_{\text{CH}} = 152.1$, C-2), 73.53 (t, $J_{\text{CH}} = 154.2$, C-4 and C-6), *iso*-propyl groups of N-1 and N-3: 54.28 (d, $J_{\text{CH}} = 146.6$, 2CH), 52.09 (qb, $J_{\text{CH}} = 146.6$, 2CH_3), *iso*-propyl group of N-5: 59.70 (d, $J_{\text{CH}} = 144.3$, 1CH), 52.28 (qb, $J_{\text{CH}} = 144.4$, 1CH_3 eq), 18.60 (quint, 1CH_3), 17.42 (quint, 1CH_3), 17.03 (quint, 1CH_3). The ^{11}B signal of compound **8** was not observed it was probably under the signal of compound **7**.

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