A New Lithium 5-Methyl-1,3-dithia-5-azacyclohex-2-ylborate–5-Borane and Two Dimeric 5-Methyl-1,3-dithia-5-azacyclohex-2-yllithium Compounds – Stereochemistry and Reactivity

Carlos Guadarrama-Pérez, Gregorio Cadenas-Pliego, Luz Maria R. Martínez-Aguilera, and Angelina Flores-Parra*

Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional,
Apartado Postal 14-740, México D.F. 07000, México

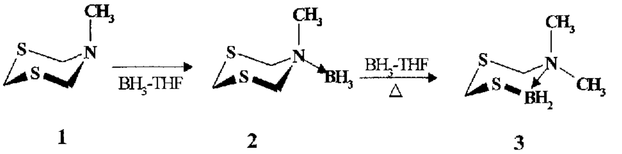
Received November 7, 1996

Keywords: Lithium 5-methyl-1,3-dithia-5-azacyclohex-2-ylborate–5-borane / 5-Methyl-1,3-dithia-5-azacyclohex-2-yllithium / Nitrogen heterocycles / Sulfur heterocycles / Lithium

Syntheses of the dimers of axial 5-methyl-2-dithiazinyllithium (**4**) and equatorial 5-methyl-2-dithiazinyllithium–5-borane (**5**), and lithium 5-methyl-2-dithiazinanylborate–5-borane (**6**) are reported. Compounds **4**, **5**, and **6** are configurationally and conformationally stable. The ^{1}H-, ^{13}C-, ^{11}B-, and ^{7}Li-NMR study of the reactions of **4** and **5** with $BH_3-S(CH_3)_2$, BH_3–THF, and CH_3I is presented.

We have previously reported that dithiazine **1**, which is a molecule with five lone pairs available for coordination, reacts with borane–THF to give a stable N–BH_3 adduct **2** which has a preferred conformation with the BH_3 group equatorial; the sulfur atoms do not coordinate to BH_3[1–3]. Heating transforms the heterocycle **2** into the boradithiazine **3**[2] (Scheme 1). We have decided to add a new lone pair to dithiazines **1** and **2**, through the synthesis of a carbanion at C-2, and to explore the competition for coordination to Lewis acids. Herein, two 2-dithiazinyllithium compounds (**4** and **5**) are reported, and their reactions with borane and methyl iodide are investigated.

Scheme 1

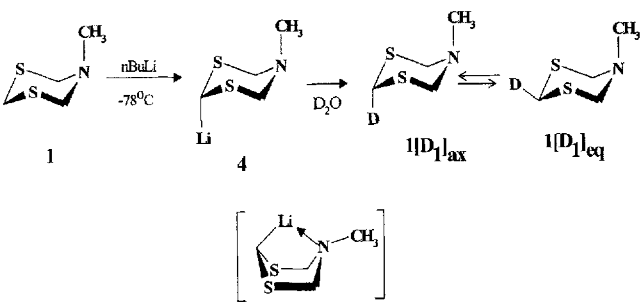


Results and Discussion

Synthesis of 2-Dithiazinyllithium Heterocycles 4 and 5

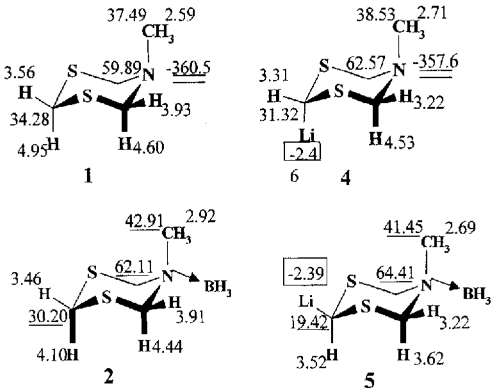
A) *5-Methyl-1,3-dithia-5-azacyclohex-2-yllithium* (**4**): One of us has earlier reported on the synthesis of **4**[4]. It was prepared from the reaction of heterocycle **1** with butyllithium in THF. The carbanion is stable enough to allow determination of its structure by NMR; its resists solvent evaporation and dissolution in dry [D$_8$]THF. The ^{1}H-NMR spectrum showed the presence of a pure compound. Evidence of the covalent lithium–carbon atom bond is provided in the ^{1}H-coupled ^{13}C-NMR spectrum, by the shift of the C-2 resonance to lower frequencies ($\Delta\delta = 3.0$ ppm) which appears as a doublet ($\delta = 31.3$, $J_{CH} = 130$ Hz; in the parent compound C-2 is a triplet, $J_{C-H} = 151$), the smaller coupling constant C–H for C-2 in compound **4** is a consequence of the donor character of the lithium ion. In the ^{1}H-NMR spectrum 2-H gives rise to a singlet ($\delta = 3.36$). The ^{1}H-, ^{13}C-, and ^{15}N-chemical shift data for NCH_3 in **4** are similar to those of **1**, this indicates the axial position of the methyl group and the absence of a lithium coordination to the nitrogen atom, for example, in a boat conformation (Scheme 2). The ^{7}Li-NMR spectrum ($\delta = -0.16$, $w_{1/2} = 8.4$ Hz, [D$_8$]THF) is characteristic of alkyllithium compound (δ^7Li of BuLi is 0.63, [D$_8$]THF, sharp line)[5]. Methylation and deuteration at C-2 give additional evidence of the lithium bonding. Addition of D_2O provides the monodeuterated compounds at C-2 (**1[D$_1$]$_{ax}$** and **1[D$_1$]$_{eq}$**).

Scheme 2



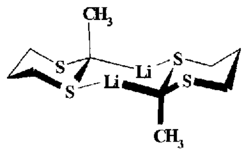
Compound **4** was found in a preferred chair conformation as denoted by the different resonances of equatorial and axial hydrogen atoms in its ^{1}H-NMR spectrum at room temperature. The configuration of C-2 was deduced by comparison of the NMR data of **4** with those of the frozen dithiazine **1** (−90°C, 270 MHz, [D$_8$]THF)[1,3] and compound **5** (Figure 1). The lithium ion principally affects the chemical shifts of the C-2 and 2-H signals; in the equatorial position its electronic donor effect is stronger than in axial position (compound 5[6]). The NMR spectra of the isolated compound **4** show the presence of tetrahydrofuran coordinated to the lithium ion, OCH_2 and OCD_2 (from the deuterated solvent) groups are slightly shifted to high field (^{13}C $\Delta\delta = 0.2$).

Figure 1. ^1H-, ^{13}C- (−), ^7Li- (□) and ^{15}N- (=)-NMR data of compounds **1**, **2**, **4** and **5**



A peak at 281.30 in the mass spectrum shows the presence of a dimer [$M^+ - H$], the monomeric compound is also observed ($C_4NS_2LiH_8$: 141.15). The dimeric structure is supported by the report of an X-ray diffraction study of a similar dimeric lithium compound[7] (Figure 2).

Figure 2. Reported structure of the dimer of 5-methyl-1,3-dithiocyclohexane found by an X-ray diffraction study; the lithium ions are also coordinated to *N,N,N′,N′*-tetramethylethylenediamine[7]



An explanation of the stability of the axial lithium group in compound **4** is that it forms a stable dimer as demonstrated by the molecular mechanic calcualtions[8] [$E = 10.7$ kcal]. The isomeric dimer, with the lithium ion in equatorial position, has a similar calculated energy [$E = 11.9$ kcal] (Figure 3).

In order to check the structure of compound **4** we decided to synthesize the 1,3-dithiocyclohex-2-yllithium from butyllithium and 1,3-dithiocyclohexane. It was earlier reported that this compound is in a preferred conformation with the lithium ion in the equatorial position, its dimeric nature was not mentioned[9,10]. The ^1H-NMR spectrum was uncorrectly assigned in ref.[10]. We have performed 2D-$^{13}C/^1H$-HETCOR and $^1H/^1H$-COSY experiments in order to unequivocally assign the spectra. The shifts of the axial and equatorial 4-H and 6-H signals in 1,3-dithiocyclohex-2-yllithium were compared with those of an anchored 2-substituted 1,3-dithiocyclohexane[11]. We have found the same trends as in compound **5** indicating the equatorial preference of the lithium ion in both compounds (Figure 4).

B) *5-Methyl-1,3-dithia-5-azacyclohex-2-yllithium−5-Borane* (**5**): The reaction of the BH_3 adduct **2** with *n*BuLi proceeds cleanly to give the corresponding carbanion without affecting the N−borane group. The stereochemistry of **5** was deduced from the ^1H- and ^{13}C-NMR data (Figure 1). The C-2 signal is a doublet in the ^1H-coupled ^{13}C spectrum ($\delta = 19.4$, $J = 133$), the 2-H gives rise to a singlet ($\delta = 3.52$). The reaction afforded only one isomer in a fixed conformation with the lithium ion in the equatorial position, coordinated THF is detected in the NMR spectra. Compound **5** shows a signal at $\delta = -2.39$ in the ^7Li-NMR spectrum ($w_{1/2} = 8.4$ Hz, [D8]THF). The mass spectrum presents a peak at 284.50 for the dimer [$M^+ - B_2H_4$], another peak at 155.45 is attributed to the monomer $C_4NS_2BLiH_{11}$. Addition of D_2O provides two compounds monodeuterated at C-2 (**2[D1]eq**, **2[D1]ax**) with anchored conformation in a ratio 60:40 (Scheme 3).

Reactions of 2-Dithiazinyllithium Compounds with Borane and Methyl Iodide

A) *2-Dithiazinyllithium* **4**: The reaction of compound **4** with one equivalent of $BH_3-S(CH_3)_2$ gave regioselectively the $N-BH_3$ adduct **5**, under these conditions the borane adduct does not react with the anionic position C-2 (Scheme 3), while reaction of compound **4** with two equivalents of BH_3−THF afforded a mixture of dithiazinyllithium−5-borane **5**, lithium 2-dithiazinylborate−5-borane **6** and lithium 2-dithiazinylborate **7** (Scheme 4). Compound **4** reacts with one equivalent of CH_3I to give the product 2,5-dimethyl-1,3-dithia-5-azacyclohexane (**8**) which, by reaction with borane−THF, afforded the 2,5-dimethyl-1,3-dithia-5-azacyclohexane−5-borane (**9**). The reaction of **4** with an excess of methyl iodide produced the 2,5,5-trimethyl-1,3,5-dithiazinium iodide **10**.

B) *2-Dithiazinyllithium−5-Borane* **5**: The reaction of **5** with CH_3I at 40°C leads to an exchange of an endocyclic carbon versus an exocyclic boron atom to yield 2,5,5-trimethyldithia-5-azonia-4-boratacyclohexane (**11**). It has a stereogenic center at C-2 and prefers the conformation shown in Scheme 5. The reaction of compound **5** with one equivalent of $BH_3-S(CH_3)_2$ produces, as the main product, the lithium 2-dithiazinylborate **6**, which presents in the ^{11}B-NMR spectrum a quadruplet at $\delta = -29.7$ ($J_{B-H} = 80$ Hz, $CDCl_3$) of the 2-BH_3 group, and a broad signal at $\delta = -8.0$ of the $N-BH_3$ group. The ^7Li-NMR shows a signal at $\delta = -1.35$ ($w_{1/2} = 33.6$ Hz). In this reaction some trimethylamine−borane is produced by reductive cleavage of the ring.

Conclusions

Two stable dimeric covalent organolithium compounds, 5-methyl-1,3,5-dithiazinyllithium **4** and 5-methyl-1,3,5-dithiazinyllithium−5-borane **5**, were prepared which showed a preferred chair conformation with two different configurations at the carbanion center. Compounds **4** and **5** have the lithium ion in axial and equatorial positions, respectively. The lithium 5-methyl-1,3,5-dithiazinylborate−5-borane **6** was obtained which is also in a fixed conformation with both borane groups in equatorial positions. Reaction of **4** with one equivalent of $BH_3-S(CH_3)_2$ afforded

Figure 3. a) Stable structures of the dimer of **4** and b) its equatorial lithium isomer, found by molecular-mechanics calculations[8]

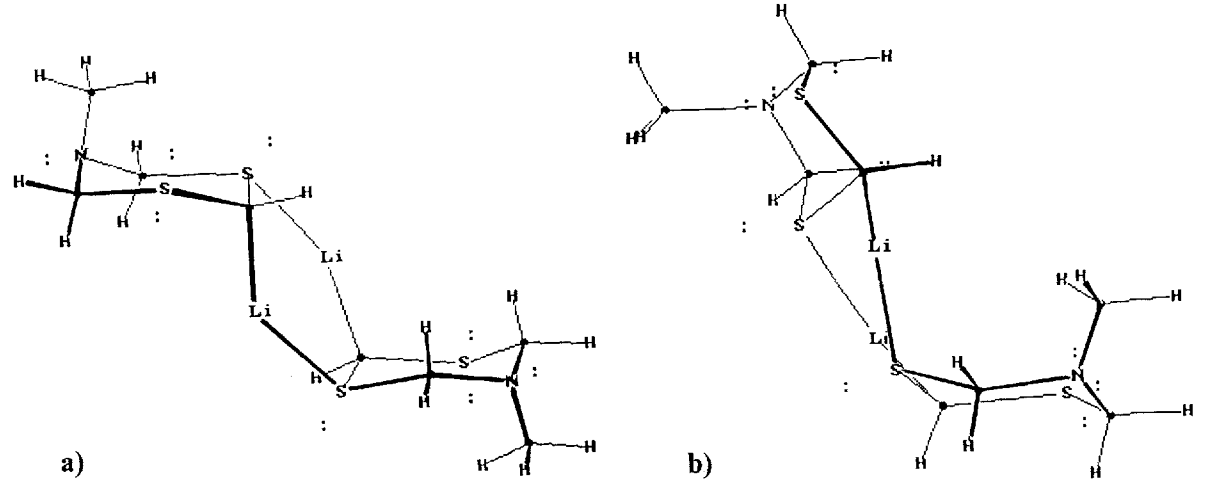
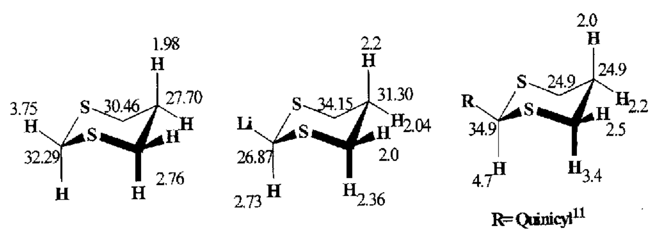
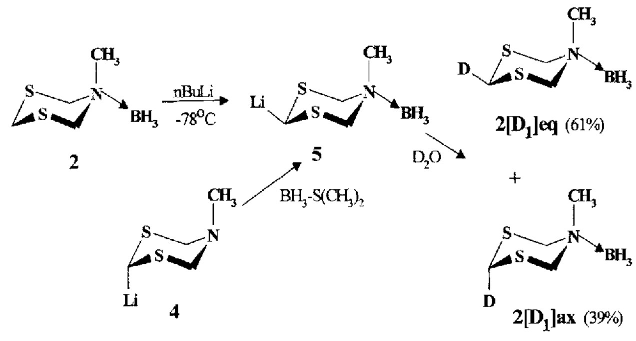


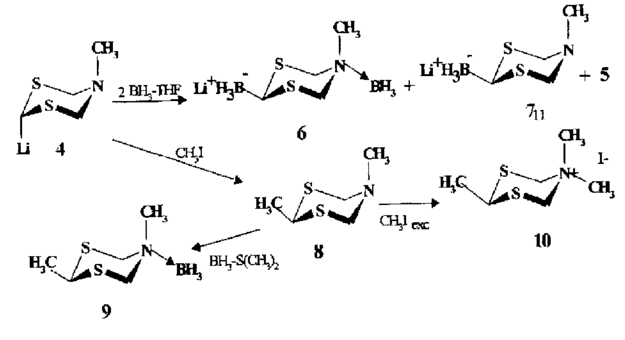
Figure 4. ^1H- and ^{13}C-NMR data of 1,3-dizhiocyclohexane, its lithium and 2-alkyl derivative



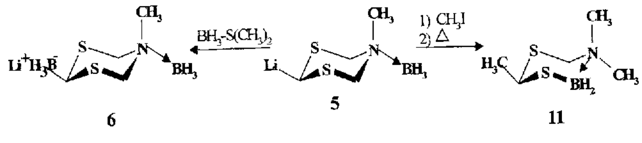
Scheme 3



Scheme 4



Scheme 5



exclusively compound **5**. With an excess of borane, compound **6** was also observed. The reported compounds may be classified in two isolobal groups, one including **1**–**4** and **5**, and another **6**, **9**, **7**, and **11**.

Experimental Section

General: ^1H, ^7Li, ^{11}B, ^{13}C, and ^{15}N NMR: Jeol 270 GXS spectrometer at 270, 104.88, 86.55, 67.80, and 27.25 MHz, respectively; ^1H- and ^{13}C-NMR chemical shifts were referenced to TMS, δ^7Li to $LiClO_4$ (D_2O infinited dilution), $\delta^{11}B$ to Et_2O-BF_3 and $\delta^{15}N$ to neat CH_3NO_2. – Anhydrous solvents were prepared according to the usual laboratory methods. All reactions were carried out in an inert atmosphere in oven-dried glassware. – Mass spectra were recorded with a Hewlett-Packard 5989 mass spectrometer. – Melting points are uncorrected.

5-Methyl-1,3,5-dithiazine **1**: Compound **1** was prepared as described in ref.[12]. – ^1H NMR (90.05 MHz, $CDCl_3$): δ = 4.39 (br. s, 4H, 2 × 4-H and 2 × 6-H), 4.05 (br. s, 2H, 2-H), 2.61 (br. s, 3H, 7-H). – ^1H NMR (90.05 MHz, −80°C, $[D_8]THF$): δ = 2.59 (s, 3H, 7-H), 3.56 (dt, J = 13.3 and 2.6, 1H, 2-H_{eq}), 3.93 (dt, J = 12.7 and 2.6, 2H, 4-H_{eq} and 6-H_{ax}), 4.60 (d, J = 13.3, 1H, 2-H_{ax}), 4.95 (d, J = 12.7, 2H, 4-H_{ax} and 6-H_{ax}). – ^{13}C NMR (67.80 MHz, $CDCl_3$): δ = 34.28 (d, J = 151.0, C-2), 59.89 (d, J = 152.1, C-4 and C-6), 37.49 (q, J = 135.5, C-7). – ^{15}N NMR (27.25 MHz, $CDCl_3$): δ = −360.5 (s).

5-Methyl-1,3,5-dithiazin-2-yllithium **4**[4]: A solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled at −78°C under dry nitrogen, and 0.81 ml of a solution of *n*BuLi/hexane (1.0 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for 30 min and then the solvent was evaporated in vacuo to −5°C to leave compound **4** as a white solid. – ^1H NMR (270 MHz, $[D_8]THF$): δ = 2.71 (s, 3H, $N[CH_3]_{ax}$), 3.22 (d, J = 12.1, 2H, 4-H_{eq} and 6-H_{eq}), 3.31 (s, 1H, 2-H_{eq}), 4.53 (d, J = 12.1, 2H, 4-H_{ax} and 6-H_{ax}). – ^{13}C NMR (68.80 MHz, $[D_8]THF$): δ = 31.32 (d, J = 130, C-2), 38.43 (q, J = 133.3, $N[CH_3]_{ax}$), 62.57 (t,

$J = 145.3$, C-4 and C-6). – ^{7}Li NMR (104.88 MHz, [D$_8$]THF): $\delta = -2.46$ (s). – ^{15}N NMR (27.25 MHz, [D$_8$]THF): $\delta = -357.6$ (s). – MS (15 eV); *m/z* (%): 141.15 (1) [1/2 M$^+$], 281.30 (8) [M$^+$ – H].

2-Deuterio-5-methyl-1,3,5-dithiazine **1[D$_1$]**: To a solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) 0.5 ml of D_2O were added. The reaction mixture was stirred for 5 min and then the solvent was evaporated in vacuo. Compound **1[D$_1$]** is a yellow liquid (0.1 g, 100%). – $C_4H_8DNS_2[C_4H_8O]_{1/8}$ (145.27): calcd. C 37.20, H 7.63, N 9.64, S 44.14; found C 37.47, H 6.92, N 10.24, S 45.20. – ^{1}H NMR (270 MHz, [D$_8$]THF): $\delta = 2.61$ (s, 3H, N[CH$_3$]$_{ax}$), 4.04 (s, 1H, 2-H), 4.40 (s, 4H, 2 × 4-H and 2 × 6-H). – ^{13}C NMR (68.80 MHz, [D$_8$]THF): $\delta = 34.02$ (t, $J_{CD} = 22.0$, C-2), 37.53 ([CH$_3$]$_{ax}$), 59.81 (C-4 and C-6). – MS (20 eV) *m/z* (%): 44.00 (100), 42.00 (84), 57.15 (81), 135.15 (55), 136.15 (27).

Equatorial Isomer **1[D$_1$]$_{eq}$**: ^{1}H NMR (270 MHz, –80°C, [D$_8$]THF): $\delta = 2.59$ (s, 3H, N[CH$_3$]$_{ax}$), 3.96 (d, $J = 12.5$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.57 (s, 1H, 2-H$_{ax}$), 4.94 (d, $J = 12.5$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

Axial Isomer **1[D$_1$]$_{ax}$**: ^{1}H NMR (270 MHz, –80°C, [D$_8$]THF): $\delta = 2.59$ (s, 3H, N[CH$_3$]$_{ax}$), 3.60 (s, 1H, 2-H$_{ax}$), 3.96 (d, $J = 12.5$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.94 (d, $J = 12.5$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

5-Methyl-1,3,5-dithiazine–5-Borane **2**[3]: A solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled at –78°C under dry nitrogen and 0.24 ml of a solution of BH_3–THF (3.03 M, 0.74 mmol) was added. The reaction mixture was stirred for 30 min and then the solvent was evaporated in vacuo at –5°C to give compound **2**. – ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 2.92$ (s, 3H, CH$_{3\ ax}$), 3.46 (dt, $J = 13.9$, 2.0; 1H, 2-H$_{eq}$), 3.91 (dd, $J = 13.9$, 2.0; 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.10 (d, $J = 13.9$, 1H, 2-H$_{ax}$), 4.44 (d, $J = 139$, 1H, 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): $\delta = 30.20$ (ddt, $J = 155.3$, 147.6, 6.6, C-2), 42.91 (qt, $J = 141.1$, 5.5, N[CH$_3$]$_{ax}$), 62.11 (t, $J = 154.6$, C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): $\delta = -8.0$ (q, $J = 98$).

5-Methyl-1,3,5-dithiazin-2-yllithium–5-Borane **5** was prepared by two methods: a) the same procedure as applied to the synthesis of **4**, using compound **2**, b) same procedure as applied to the synthesis of **2**, using compound **4**. – ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 2.69$ (s, 3H, N[CH$_3$]$_{ax}$), 3.22 (d, $J = 13.0$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 3.52 (s, 1H, 2-H$_{ax}$), 3.62 (d, $J = 13.0$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): $\delta = 19.42$ (d, $J = 133.0$, C-2), 41.45 (q, $J = 140.0$, N[CH$_3$]$_{ax}$), 64.41 (t, $J = 152.6$, C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): $\delta = -8.45$ (br. s). – ^{7}Li NMR (104.88 MHz, CDCl$_3$): $\delta = -2.39$ (s). – MS (15 eV) *m/z* (%): 155.45 (2) [1/2 M$^+$], 285.50 (1) [M$^+$ – B$_2$H$_4$].

2-Deuterio-5-methyl-1,3-dithia-5-azacyclohexane–5-Borane **2[D$_1$]**: To a solution of compound **5** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) 0.5 ml of D_2O was added. The reaction mixture was stirred for 5 min and then the solvent was evaporated in vacuo. A mixture of compounds **2[D$_1$]** with 10% of dithiazine **1** was obtained. – ^{13}C NMR (68.80 MHz, CDCl$_3$): $\delta = 29.85$ (t, $J_{CD} = 24.3$, C-2), 42.86 (N[CH$_3$]$_{ax}$), 62.05 (C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): $\delta = -8.18$ (q, $J = 100$). – MS (20 eV) *m/z* (%): 44.15 (40), 57.15 (100), 89.20 (72), 136.30 (79), 137.30 (87), 150.30 (2).

Equatorial Isomer **2[D$_1$]$_{eq}$**: ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 2.92$ (s, 3H, N[CH$_3$]$_{ax}$), 3.92 (d, $J = 13.7$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.08 (s, 1H, 2-H$_{eq}$), 4.44 (d, $J = 13.7$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

Axial Isomer **2[D$_1$]$_{ax}$**: ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 2.92$ (s, 3H, N[CH$_3$]$_{ax}$), 3.92 (d, $J = 13.7$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 3.45 (s, 1H, 2-H$_{ax}$), 4.44 (d, $J = 13.7$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

2,5-Dimethyl-1,3,5-dithiazine–5-Borane **9**: Compound **9** was obtained by two methods: a) from anion **5** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) at –78°C, by treatment with CH_3I (0.23 ml, 3.7 mmol); or b) from compound **8** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) by adding 0.24 ml (3.03 M BH_3–THF, 0.74 mmol) at –78°C. The reaction mixture was stirred for 5 min, and the solvent was evaporated in vacuo. Compound **9** was obtained as a white solid; m.p. 190°C (dec.). – $C_5H_{14}BNS_2$ (163.11): calcd. C 36.81, H 8.65, N 8.59; found C 36.65, H 7.00, N 8.46. – ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 1.52$ (d, $J = 6.8$, 3H, C[CH$_3$]$_{eq}$), 2.86 (s, 3H, N[CH$_3$]$_{ax}$), 3.93 (d, $J = 41.1$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.22 (q, $J = 6.8$, 1H, 2-H$_{ax}$), 4.47 (d, $J = 14.1$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): $\delta = 19.54$ (q, $J = 134.4$, C[*C*H$_3$]$_{eq}$), 41.09 (d, $J = 157.5$, C-2), 42.55 (q, $J = 140.0$, N[CH$_3$]$_{ax}$), 63.02 (t, $J = 154.2$, C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): $\delta = -8.5$ (q, $J = 94.7$).

2,5,5-Trimethyl-1,3-dithia-5-azonia-4-boratacyclohexane **11**: A solution of compound **9** (0.12 g, 0.74 mmol) in anhydrous THF (20 ml) was heated (40°C). The reaction mixture was stirred for 20 min and the solvent was evaporated in vacuo. Compound **11** was obtained as a white solid; m.p. 190°C (dec.). – $C_5H_{14}BNS_2$ (163.11): calcd. C 36.81, H 8.65, N 8.59; found C 36.52, H 6.91, N 8.79. – ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 2.65$ (d, $J = 6.8$, 3H, C[CH$_3$]$_{eq}$), 2.71 (s, 3H, N[CH$_3$]$_{eq}$), 2.80 (s, 3H, N[CH$_3$]$_{ax}$), 3.93 (d, $J = 12.7$, 1H, 4-H$_{eq}$), 4.05 (q, $J = 6.8$, 1H, 2-H$_{ax}$), 4.30 (d, $J = 12.7$, 1H, 4-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): $\delta = 23.17$ (q, $J = 127.8$, C[CH$_3$]$_{eq}$), 41.77 (d, $J = 142.1$, C-2), 44.92 (q, $J = 140.0$, N[CH$_3$]$_{ax}$), 51.07 (q, $J = 139.9$, N[CH$_3$]$_{eq}$), 63.70 (t, $J = 152.6$, C-4). – ^{11}B NMR (86.55 MHz, CDCl$_3$): $\delta = -3.60$ (t, $J = 113.7$).

Lithium 5-Methyl-1,3,5-dithiazin-2-ylborate–5-Borane **6**: A solution of compound **5** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled to –78°C under dry nitrogen and 0.6 ml of a solution of BH_3–S(CH$_3$)$_2$ (1.33 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for 15 min, and the solvent was evaporated in vacuo at –5°C, to give compound **6** as a white solid. – ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 2.84$ (s, 3H, N[CH$_3$]$_{ax}$), 3.46 (br. s, 1H, 2-H$_{ax}$), 3.75 (d, $J = 13.8$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.32 (d, $J = 13.8$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): $\delta = 36.20$ (br. s, C-2), 42.12 (q, $J = 139.0$, N[CH$_3$]$_{ax}$). – ^{11}B NMR (86.55 MHz, CDCl$_3$): $\delta = -8.0$ (br. s), –29.7 (q, $J = 82.1$). – ^{7}Li NMR (104.88 MHz, CDCl$_3$): $\delta = -2.87$ (s).

2,5-Dimethyl-1,3,5-dithiazine **8**: A solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled to –78°C under dry nitrogen, 0.81 ml of *n*BuLi/hexane (1.0 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for 30 min, and CH_3I (0.23 ml, 3.7 mmol) was added. The reaction was stirred and quenched after 20 min with 10 ml of water. Compound **8** was extracted from the reaction mixture with CH_2Cl_2 to give a yellow liquid (0.11 g, 100%). – $C_5H_{11}NS_2[H_2O]_2$ (185.31): calcd. C 32.41, H 8.15, N 7.55, S 34.60; found C 33.19, H 5.94, N 7.25, S 31.01. – ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 1.46$ (d, $J = 4.2$, 3H, C[CH$_3$]$_{eq}$), 2.56 (s, 3H, N[CH$_3$]$_{ax}$), 4.09 (d, $J = 12.6$, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.24 (q, $J = 4.2$, 1H, 2-H$_{ax}$), 4.67 (d, $J = 12.6$, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): $\delta = 22.64$ (q, $J = 129.4$, C[CH$_3$]$_{eq}$), 37.02 (q, $J = 135.2$, N[CH$_3$]$_{ax}$), 44.43 (d, $J = 153.1$, C-2), 60.30 (t, $J = 153.1$, C-4 and C-6). – MS (20 eV) *m/z* (%): 44.05 (100), 42.00 (92), 57.05 (64), 149.20 (53).

2,5,5-Trimethyl-1,3,5-dithiazinium Iodide **10**: A solution of compound **4** (0.10, 0.74 mmol) in anhydrous THF (20 ml) was cooled to –78°C under dry nitrogen, 0.8 ml of *n*BuLi/hexane (1.0 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for

30 min and CH_3I (3.7 ml, 0.23 mmol) was added. The reaction was quenched with water (5 ml) and extracted with CH_2Cl_2. Compound **10** is a yellow liquid (0.17 g, 80%). – ^1H NMR (270 MHz, $[D_6]$DMSO): δ = 1.52 (br. s, 3H, $C[CH_3]$), 3.32 (s, 3H, $N[CH_3]$), 3.31 (s, 3H, $N[CH_3]$), 4.79 (br. s, 2H, 4-H_{eq} and 6-H_{eq}), 5.30 (br. s, 3H, 2-H_{ax}, 4-H_{ax} and 6-H_{ax}). – ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 19.03 (br. s, $C[CH_3]$), 39.40 (br. s, C-2), 44.01 (s, $N[CH_3]_{ax}$), 54.21 (br. s, $N[NCH_3]_{eq}$), 64.24 (br. s, C-4 and C-6).

---

[1] A. Flores-Parra, A. I. Hernández-Bautista, L. Hernández-Sánchez, R. Contreras, *Tetrahedron* **1991**, *47*, 6903–6914.

[2] G. Cadenas-Pliego, M. J. Rosales-Hoz, R. Contreras, A. Flores-Parra, *Tetrahedron Asymm.* **1994**, *5*, 633–640.

[3] A. Flores-Parra, G. Cadenas-Pliego, L. M. R. Martinez Aguilera, M. L. Garcia-Nares, R. Contreras, *Chem. Ber.* **1993**, *126*, 863–867.

[4] A. Flores-Parra, F. Khuong-Huu, *Tetrahedron* **1986**, 5925–5930.

[5] F. W. Wehrli in *Annual Reports on NMR Spectroscopy* (Ed.: G. A. Webb), Academic Press Inc., New York, **1979**, *9*, p. 149 153.

[6] J.-M. Lehn, G. Wipff, *J. Am. Chem. Soc.* **1976**, *98*, 7498 7505.

[7] R. Amstutz, D. Seebach, P. Seiler, B. Schweizer, J. D. Dunitz, *Angew. Chem.* **1979**, *92*, 59–60; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 53–53.

[8] U. Burkert, N. L. Allinger, *Molecular Mechanics, A.C.S.* Monograph 177, Am. Chem. Soc., Washington D. C. **1982**.

[9] A. G. Abatjoglou, E. L. Eliel, L. F. Kuyper, *J. Am. Chem. Soc.* **1977**, 8262–8269.

[10] S. A. Vinogradov, A. E. Mistrukov, I. P. Beletskaya, *J. Chem. Soc., Dalton Trans.* **1995**, 2679–2687.

[11] A. Flores-Parra, D. M. Gutiérrez-Avella, R. Contreras, F. Khuong-Huu, *Magn. Reson. Chem.* **1989**, *27*, 544–555.

[12] French Patent, 1,341,792/1963 (*Chem. Abstr.* **1964**, *60* 5528).

[96249]