Journal of Molecular Structure 1047 (2013) 149–159

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Mono- and di-alkyl-[1,3,5]-dithiazinanes and their N–borane adducts revisited. Structural and theoretical study

Angelina Flores-Parra [a,*], Carlos Guadarrama-Pérez [a], Juan Carlos Gálvez Ruiz [b], Sonia A. Sánchez Ruiz [a], Galdina V. Suarez-Moreno [a], Rosalinda Contreras [a]

[a] Departamento de Química, Centro de Investigación y de Estudios Avanzados (Cinvestav), A.P. 14-740, México, DF 07000, Mexico
[b] Departamento de Ciencias Químico-Biológicas, Universidad de Sonora, Hermosillo, Sonora, Mexico

HIGHLIGHTS

- A series of 2,5-dialkyl-[1,3,5]-dithiazinanes derivatives is reported.
- Structures were determined by ^{11}B, ^{13}C and ^{1}H NMR and the X-ray diffraction analyses.
- Optimization of chair conformers were performed by ab-initio methods and their minimum energy is compared.
- 2-R or N-BH_3 anchor the ring conformation allowing the analyses of steric and electronic interactions and the lone pairs effect.

ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form 9 April 2013
Accepted 10 April 2013
Available online 18 April 2013

Keywords:
2,5-Dialkyl-[1,3,5]-dithiazinanes
N–BH_3-5-alkyl-[1,3,5]-dithiazinanes
X-ray diffraction analyses
Theoretical analysis of conformers

ABSTRACT

Structural analyses of a series of 5-alkyl-[1,3,5]-dithiazinanes [R = Me (**1**), *i*Pr (**2**), *t*Bu (**3**)], their N–BH_3 adducts (**1**BH_3–**3**BH_3) and their 2-alkyl (R′) derivatives are reported: R = Me, R′ = Me (**7**); R = Me, R′ *i*Pr (**8**); R = *i*Pr, R′ = Me (**10**); R = *t*Bu, R′ = Me (**11**); and R = Me, R′ = *n*Bu (**12**). The reaction of 2-lithium-5-methyl-[1,3,5]-dithiazinane (**4**) with I_2 affords the *bis*-(5-methyl-[1,3,5]-dithiazinan-2-yl) (**13**). Isostructural compounds: [2,5,5]-trimethyl-[1,3,5]-dithiazinan-5-ium iodide (**14**), 5-borane-2,5-dimethyl-[1,3,5]-dithiazinane (**15**) and 2,5,5-trimethyl-[1,3,5,6]-dithiazaborata (**16**) are compared. Structures of **7**, **8** and **10**–**13** were determined by ^{11}B, ^{13}C and ^{1}H NMR and the X-ray diffraction analyses of **2**, **1**BH_3, **13** and **14** are reported. Optimization of two chair conformers of heterocycles **1**–**3**, **1**BH_3–**3**BH_3, **7**, **9** (R = Me, R′ = *t*Bu), **13**–**16** were performed by HF/6-31++G and B3LYP/6-31G(d,p) methods and their minimum energy is compared. 2-Alkyl substituents or N–BH_3 anchor the [1,3,5]-dithiazinane ring conformation allowing the analyses of steric and electronic interactions as well as the lone pairs effect in these molecules.

1. Introduction

We are currently working on the chemistry of [1,3,5]-heterocyclohexanes [1,2] such as [1,3,5]-dithiazinanes **1**–**3** [3,4], Scheme 1. These compounds can act as ligands for metal atoms by coordination of the heteroatoms lone pairs [5–7]. They react with borane to give N–BH_3 adducts [8] and can also be used as building blocks in tripodal derivatives [9] or in branched chains [10].

In continuation of our studies, here we firstly report the revised structural analysis of compounds **1**–**3** [3,4] and of their N–borane adducts (**1**BH_3–**3**BH_3) [8], Scheme 1. These compounds are known, however the X-ray diffraction analyses of these N–BH_3 adducts have not been reported. Crystalline compounds **2** and **1**BH_3 were analyzed by X-ray diffraction. *Ab initio* theoretical studies [HF/6-31++G] in compounds **1**–**3** and **1**BH_3–**3**BH_3 reported here afforded useful information for better understanding the structure and reactivity of 5-alkyl-[1,3,5]-dithiazinanes and their adducts. Secondly, we report a series of [1,3,5]-dithiazinanes where one of the SCH_2S protons was substituted by an alkyl group (**7**, [11] **8**, **10**–**14**), Schemes 2 and 3. A motivation for the structural analysis of these 2,5-dialkyl-[1,3,5]-dithiazinanes is their anchored rings, which allow to investigate the effect of sulfur lone pairs in the ^{1}H NMR spectra and sulfur weak interactions in conformational equilibrium [5,6,12–17]. Our attempts to synthesize the C-2 *tert*butyl derivatives were unsuccessful, however the minimum energy structure of 2-*tert*butyl-5-methyl-[1,3,5]-dithiazinane (**9**) was calculated and compared with that of compounds **7**, **8**, **10** and **11**, Scheme 2. In the third part of this paper we review the isostructural compounds: [2,5,5]-trimethyl-[1,3,5]-dithiazinan-5-ium iodide (**14**), 5-BH_3-2,5-dimethyl-[1,3,5]-dithiazinane (**15**) and 2,5,5-trimethyl-[1,3,5,6]-dithiazaborata (**16**), and report the X-ray diffraction

* Corresponding author.
E-mail address: aflores@cinvestav.mx (A. Flores-Parra).

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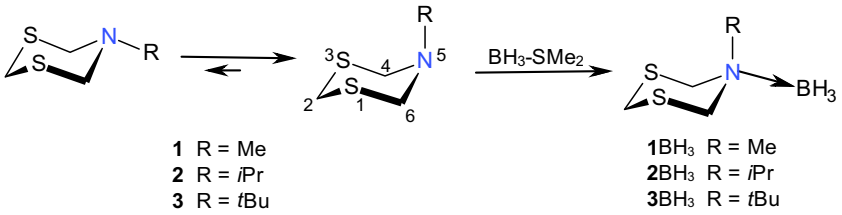
http://dx.doi.org/10.1016/j.molstruc.2013.04.021



Scheme 1. Nitrogen conformers of 5-R-[1,3,5]-dithiazinanes **1**–**3** and their adducts **1**BH_3–**3**BH_3.

analyses of **14**, Schemes 3 and 4. Calculations of compounds **14**–**16** are discussed and compared with those of [1,3,5]-dithiazinanes having a free nitrogen lone pair, in order to acquire information about the electronic density and charge distribution in the ring.

2. Experimental

2.1. General

Reagents were purchased from Sigma–Aldrich Chemical, Fluka Chemika and Strem Chemical, and were used without purification. Vacuum line techniques were employed for all manipulations with air and moisture sensitive compounds. THF was dried by distillation from sodium–benzophenone under a nitrogen atmosphere prior to use. Dry $CDCl_3$, and THF-d_8, were purchased from Aldrich and used without further purification. Compounds **1**–**3** [3], **1**BH_3 [8], **4**, **7** and **14**–**16** [11] were synthesized according to the literature.

Melting points were obtained on a Mel-Temp II apparatus and are uncorrected. Mass spectra in the EI mode were recorded at 20 eV on a Hewlett–Packard HP 5989A spectrometer. High resolution mass spectra were obtained by LC/MSD TOF on an Agilent Technologies instrument with ESI as ionization source. Elemental analyses were performed on Flash (EA) 1112 series, equipment. NMR spectra were obtained on a Jeol GSX-270, Jeol Eclipse 400 MHz and Bruker Avance 300 MHz. ^{7}Li [Ξ 10.3976, LiCl], ^{1}H, ^{13}C [Ξ 25.145020].

2.2. X-ray crystallography

Crystallographic data were measured on a Nonius Kappa CCD instrument with a CCD area detector using graphite-monochromated Mo Kα radiation. Intensities were measured using $\varphi + \omega$ scans. Crystal data and selected bond lengths and angles are presented in Tables 2, 3 and 5. The structures were solved using direct methods with SHELX-97 [18], Sir 2002 and Sir 2004 [19]. The refinement for all structures (based on F^2 of all data) was performed by full matrix least-squares techniques with crystals 12.84 [20]. All non-hydrogen atoms were refined anisotropically. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with numbers: **1**BH_3 (921690), **2** (921691), **13** (921692), **14** (921693). Copies can be obtained, free of charge, on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 336033 or www.ccdc.cam.ac.uk/products/csd/request/].

2.3. Calculation analysis

Calculations were performed in order to obtain the molecular geometries using the Gaussian 98 package [21]. Geometries were checked to be the minimal by the frequency analysis.

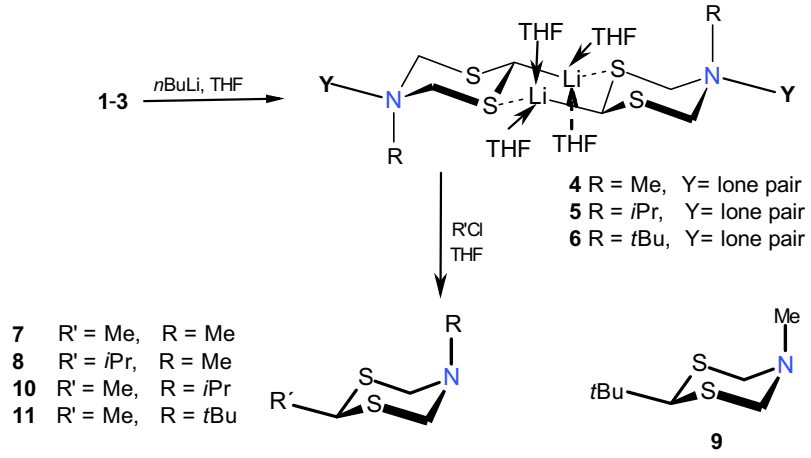
2.4. Synthesis of the compounds

2.4.1. 5-*iso*Propyl-[1,3,5]-dithiazinane ***2***

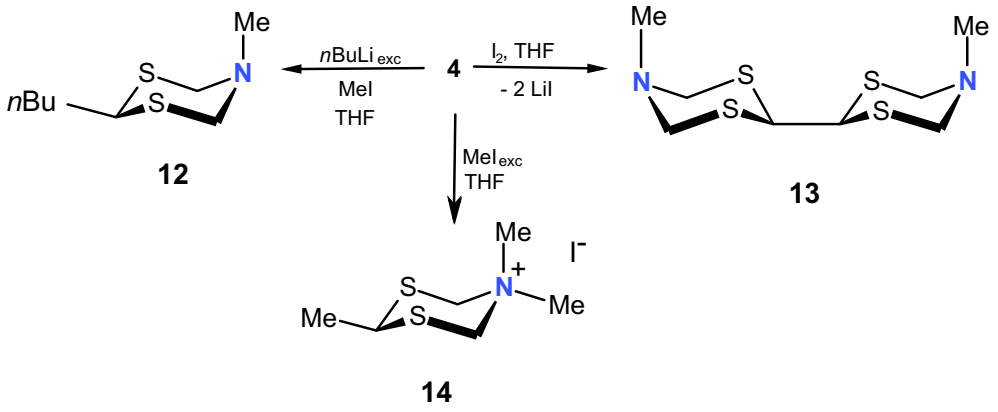
To *iso*propylamine (7.3 mL, 84.6 mmol), water (50 mL) was added and cooled at 0 °C, then a mixture of NaSH 95% (15.0 g, 253 mmol) and 37% aq. H_2CO (31.5 mL, 423 mmol) was slowly added. The reaction mixture was stirred for 24 h at rt. The solids formed were filtered, washed with distilled water, and dissolved in CH_2Cl_2. The CH_2Cl_2 solution was dried with Na_2SO_4, filtered, and the solvent evaporated. Compound **2** is a crystalline colorless solid (9.71 g, 70%). Mp 40 °C. NMR ($CDCl_3$, 25 °C, δ ppm) ^{1}H, *i*Pr group: 3.78 (hept, ^{3}J 6.5 Hz, 1H, CH), 1.14 (d, 6H, ^{3}J 6.5 Hz, CH_3). NMR (THF-d_8, −95 °C, δ ppm) ^{13}C: 34.0 (C2), 56.4 (C4/C6), *i*Pr group: 45.3 (CH), 20.7 (CH_3). (+)TOF calcd. for $(C_6H_{14}NS_2)^+$, *m/z* (uma): 164.0567; found 164.0563.

2.4.2. 2-Lithium-5-isopropyl-[1,3,5]-dithiazinane (***5***)

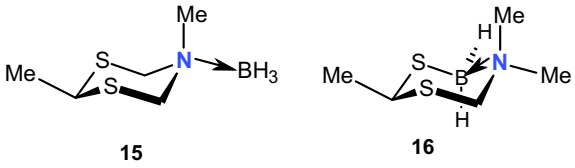
Compound **2** (0.3 g, 1.85 mmol) was dissolved in THF (50 mL) and cooled at −78 °C, then 1 M *t*BuLi solution in hexane (1.85 mL, 1.85 mmol) was added at −78 °C. The mixture was



Scheme 2. Synthesis of compounds **4**–**8**, **10**, **11**. Compound **9** was calculated.



Scheme 3. Synthesis of compounds **12**–**13** from organolithium **4**.



Scheme 4. Compounds **15** and **16**.

stirred for 30 min. The lithium compound **5** was formed quantitatively and used *in situ*. NMR (THF-d_8, 25 °C, δ ppm) ^{1}H, *i*Pr group: 3.53 (hept, ^{3}J 6.4, 1H, CH), 1.10 (d, ^{3}J 6.4, 6H, CH_3). ^{13}C: 44.6 (C2), 57.3 (C4/C6), *i*Pr group: 45.1 (CH), 21.1 ($2CH_3$). δ^7Li: −1.71.

*2.4.3. 5-tertButyl-2-lithium-[1,3,5]-dithiazinane (**6**)*

Compound **6** was prepared following the same procedure as **5** from compound **3** (0.33 g, 1.85 mmol) and 1 M *t*BuLi solution in hexane (1.86 mL, 1,86 mmol). NMR (THF-d_8, 25 °C, δ ppm) ^{1}H, *t*Bu group: 1.29 (s, 9H, CH_3). ^{13}C: 34.9 (C2), 56.8 (C4/C6), *t*Bu group: 55.0 (C), 29.5 ($3CH_3$). δ^7Li: −1.93.

*2.4.4. 2-isoPropyl-5-methyl-[1,3,5]-dithiazinane (**8**)*

Following the procedure described in **5**, to a solution of compound **1** (0.5 g, 3.7 mmol)], 2-iodo-propane (0.4 mL, 3.7 mmol) was slowly added and the mixture stirred for 15 min. Water (10 mL) was added to the reaction mixture and the product extracted with CH_2Cl_2 (3 × 15 mL). The CH_2Cl_2 solution was dried with Na_2SO_4 the solvent evaporated. Compound **8** is a viscous liquid (0.6 g, 90%). NMR ($CDCl_3$, 27 °C, δ ppm) ^{1}H, Me group: 2.65 (s, 3H, CH_3). ^{13}C: 34.7 (C2), 60.6 (C4/C6), 37.4 (C7), *i*Pr group: 59.2 (CH), 19.5 ($2CH_3$). (+)TOF calcd. for $(C_7H_{16}NS_2)^+$, *m/z* (amu): 178.0724; found 178.0725. Anal. calcd. for ($C_7H_{15}NS_2$): C, 47.44; H, 8.54; N, 7.91. Found: C, 47.08; H, 8.69; N, 7.61.

*2.4.5. 5-isoPropyl-2-methyl-[1,3,5]-dithiazinane (**10**)*

Compound **10** was prepared from a solution compound **2** (0.12 g, 0.74 mmol] and MeI (4.3 mL, 1.5 mmol) following the procedure for **8**. Compound **10** is a yellow viscous liquid (0.11 g, 80%). NMR ($CDCl_3$, 25 °C, δ ppm) ^{1}H, Me group: 1.44 (d, ^{3}J 6.9, 3H, CH_3), *i*Pr group: 3.53 (hept, ^{3}J 6.4, 1H, CH), 1.10 (d, ^{3}J 6.4, 6H, CH_3). ^{13}C: 44.6 (C2), 57.3 (C4/C6), 30.0 (CH_3), *i*Pr group: 45.1 (CH), 21.1 ($2CH_3$). Anal. calcd. for ($C_7H_{15}NS_2$): C, 47.41; H, 8.53; N, 7.90. Found: C, 47.23; H, 8.48; N, 7.65.

*2.4.6. 5-tertButyl-2-methyl-[1,3,5]-dithiazinane (**11**)*

Compound **11** *was* prepared following the general procedure for **9** from a solution of compound **3** (0.13 g, 0.74 mmol)] and MeI (5.8 mL, 1.5 mmol). Compound **11** is a viscous liquid (0.11 g, 75%). NMR ($CDCl_3$, 25 °C, δ ppm) ^{1}H, Me group: 1.55 (d, ^{3}J 6.9, 3H, CH_3), *t*Bu group: 1.32 (s, 9H, CH_3). ^{13}C: 45.9 (C2), 55.2 (C4/C6), 30.2 (CH_3), *t*Bu group: 55.9 (C), 20.6 ($3CH_3$). MS (20 eV) *m/z* (%) 57.00(100), 75.00(79), 98.15(67), 135.05(36), 191.20(75). (+)TOF calcd. for $(C_8H_{18}NS_2)^+$, *m/z* (amu): 192.0880; found 192.0886. Anal. calcd. for ($C_8H_{17}NS_2{\cdot}1/2CH_2Cl_2$): C, 43.68; H, 7.77; N, 6.00. Found: C, 44.03; H, 8.02; N, 5.92.

*2.4.7. 2-nButyl-5-methyl-[1,3,5]-dithiazinane (**12**)*

A solution of compound **1** (0.2 g, 1.5 mmol) in dried THF (100 mL) was cooled at −78 °C, then a 1 M solution of *n*BuLi in hexane (3.1 mL, 3.1 mmol) was slowly added. After 30 min stirring at −78 °C, MeI (8.5 mL, 1.5 mmol) was added and left for 1 h at 0 °C. The solvent was evaporated under vacuum and the product dissolved in CH_2Cl_2 (20 mL), washed with water (3 × 10 mL). The organic phase was dried with anhydrous Na_2SO_4, filtered and the solvent evaporated under vacuum to give an extremely stink viscous liquid. It was distilled (0.25 mmHg, 75 °C) and compound **12** was obtained (0.23 g, 80%). NMR ($CDCl_3$, 25 °C, δ ppm) ^{1}H, Me group: 2.57 (s, 3H, CH3), *n*Bu group: 1.75 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 0.90 (t, ^{3}J 6.7, 3H, CH_3). ^{13}C: 36.8 (C2), 60.5 (C4/C6), 37.4 (C7), *n*Bu group: 50.7 (CH_2), 27.7 (CH_2), 22.4 ($2CH_2$), 14.0 (CH_3). (+)TOF calcd. for $(C_8H_{18}NS_2)^+$, *m/z* (amu): 192.0875; found 192.0875. Anal. calcd. for ($C_8H_{17}NS_2$): C, 50.21; H, 8.95; N, 7.32. Found: C, 49.72; H, 8.51; N, 7.18.

*2.4.8. Bis[5-methyl-[1,3,5]-dithiazin-2-yl] (**13**)*

To a solution of compound **1** (0.2 g, 1.5 mmol)] in THF (20 mL), 1 M *t*BuLi solution in hexane (1.6 mmol, 1.6 mL) at −78 °C a solution of I_2 (1.6 mmol) in THF (20 mL) was added. The resulting mixture was stirred for 15 min at rt, then water was added (2 mL) and the solvent evaporated in vacuum. The residue was dissolved in CH_2Cl_2 (20 mL), washed with water (3 × 10 mL). The organic phase was dried with anhydrous Na_2SO_4, filtered and the solvent evaporated in vacuum. Beige crystals of **13** were obtained (0.14 g, 72%). Mp 120 °C. NMR ($CDCl_3$, 25 °C, δ ppm) ^{1}H, Me group: 2.68 (s, 3H, CH_3). ^{13}C: 55.8 (C2), 61.2 (C4/C6), 37.6 (C7). (+)TOF calcd. for $(C_8H_{17}N_2S_4)^+$, *m/z* (uma): 269.027; found 269.0263. Anal. calcd. for ($C_8H_{16}N_2S_4$): C, 35.82; H, 6.02; N, 10.45. Found: C, 35.96; H, 5.83; N, 10.68.

3. Results and discussion

*3.1. Heterocycles **1**–**3** and their N–BH_3 adducts **1**BH_3–**3**BH_3*

3.1.1. Theoretical studies

The ring of compounds **1**–**3** is in conformational equilibrium in solution at room temperature, whereas the N-alkyl group is

maintained in axial position. The preferred nitrogen conformation is attributed to the electronic repulsion between the sulfur and nitrogen lone pairs. Our HF/6-31++G calculations indicate that conformers with alkyl group in axial position are more stable than those with the alkyl in equatorial position by 37.0 (**1**), 34.3 (**2**) and 55.0 (**3**) kJ/mol, Scheme 1.

As we will discuss later, the C–S–C angles determined by X-ray diffraction analyses in compounds **1**–**3** indicate that sulfur atoms are partially sp^3 hybridized [~40% (**1**) [3], ~36% (**2**), ~33% (**3**) [3]]. It means that sulfur lone pairs occupy orbitals with sp^3 partial hybridization with incipient lobes in equatorial and axial positions. The calculated electrostatic potential surface calculated for compounds **1**, **1**BH_3, **7**, **14**–**16** by B3LYP/6-31++G(d,p) (mesh value 0.0004), is found as Supplementary material.

Reactions of compounds **1**–**3** with BH_3–SMe_2 give the corresponding N-adducts (**1**BH_3–**3**BH_3) [4]. Compound **1**BH_3 is stable in the solid state under anhydrous conditions at low temperature, and in solution of THF for a few days. Compound **2**BH_3, when standing in dry THF solution and at low temperature, is transformed in a few hours into the borata heterocycle and then, into other reduced fragments, Scheme 5. **3**BH_3 is so unstable that in cool dry THF is reduced in a few minutes [4]. The different stability of compounds **1**BH_3–**3**BH_3 is attributed to the growing steric hindrance of the N-substituent.

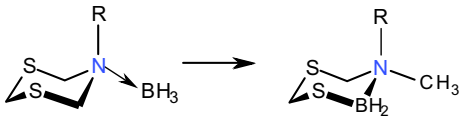
According to NMR spectra, the adduct **1**BH_3 is in a preferred conformation, in solution at room temperature, with the methyl group in axial position and the BH_3 in equatorial position [4]. The *ab initio* calculations (HF 6-31++G) of the energy difference between the two chair conformers of compounds **1**BH_3–**3**BH_3 confirm that the preferred conformation of the molecules with the borane in equatorial is the most stable [ΔE = 42.3 (**1**BH_3); 49.2 (**2**BH_3) and 26.8 (**3**BH_3) kJ/mol], Scheme 6. The superposition of the structure found by X-ray diffraction analysis of compound **1**BH_3 with the calculated structure is shown in Fig. 1.

Calculated energy also means that methyl and *iso*propyl groups have similar steric effects, due to the fact that the *iso*propyl group in **2**BH_3eq is oriented with the C–H pointing towards the sulfur atoms diminishing the steric effect between the *iso*propyl group and the sulfur atoms, Fig. 2a. As expected **3**BH_3 with a *tert*butyl group shows a smaller energy difference between both chair conformers due to an increased energy of conformer **3**BH_3eq by the steric repulsion between the axial *t*Bu group and the ring, Fig. 2b. Additional stabilization for these conformations are provide by the hydride–proton contacts [22,23].

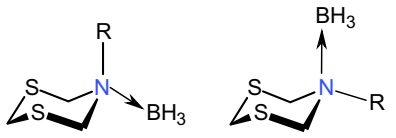
The calculated dipole moment of **1**BH_3eq is 2.9 D, whereas for **1**BH_3ax is 6.4 D, which is in agreement with the highest stability of the first one. Also, calculations indicate that the dipole moments in N–BH_3 adducts are inverted with respect of the free dithiazinanes, Scheme 7. The calculated NBO charges [6-31++G] for dithiazinanes **1** and **1**BH_3 are in Table 1. The charges indicate that C2 is more negative than C4 and C6. Sulfur atoms have partial positive charges, whereas the nitrogen atom is partially negative.

3.1.2. NMR analysis

The spectroscopic behavior in [1,3,5]-dithiazinanes is different from that of cyclohexane. The ^{1}H NMR spectra of deuterated cyclohexane-D_{11} recorded at low temperature let recognize the equatorial (1.65 ppm) and the axial (1.20 ppm) protons chemical shifts. The difference between equatorial and axial signal has been attributed to hyperconjugative interactions between antiperiplanar C–H bonds [24,25], which also provokes the enlargement of C–Hax bonds [26]. The ^{1}H NMR chemical shifts of axial and equatorial protons in 5-methyl-[1,3,5]-dithiazinane (**1**) (270 MHz, $CDCl_3$, −80 °C) show an anchored conformation. The equatorial sulfur and nitrogen lone pairs produce a notorious gauche effect over the axial and equatorial methylene protons, shifting them to higher frequencies with respect to those of cyclohexane [27,28], Table 2. In addition, the antiperiplanar effect of the axial sulfur lone pairs shifts the axial methylene protons ~1 ppm to higher frequencies with respect to the equatorial ones [8].



Scheme 5. Isomerization of **1**BH_3–**3**BH_3 adducts [**1** R = Me; **2** R = *i*Pr, **3** R = *t*Bu] into borata heterocycles.



Scheme 6. Chair conformers of compounds **1**BH_3 to **3**BH_3.

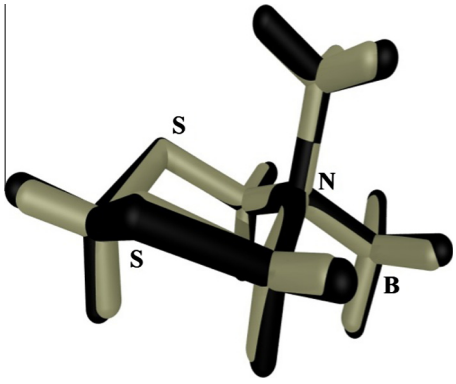


Fig. 1. Superposition of the structure of compound 2 obtained by X-ray diffraction analyses (gray), with its modeled structure (black).

The nitrogen lone pair effect on the chemical shifts of the methylene protons in [1,3,5]-dithiazinanes can be deduced when they are compared with the low temperature ^{1}H NMR spectrum of dithiane, where the methylene protons appear overlapped [29], Table 2. The ^{1}H NMR spectrum of **1**BH_3 indicates that the N–BH_3 coordination diminishes the N-lone pair effect over the axial protons which are shifted ~0.5 ppm to lower frequencies with respect to those of the free heterocycle **1**.

3.1.3. X-ray diffraction analysis of compounds *2* and *1*BH_3

Compound **2** crystallized from $CHCl_3$. Its X-ray diffraction structure depicts a heterocycle in a chair conformation with the N-*iso*propyl group in axial position, Fig. 3, Tables 3–5. The nitrogen is almost planar, due to the steric repulsion between the isopropyl group and the ring. The nitrogen sp^2 character (~75%) is deduced from angles around the nitrogen atom: C4–N–C7 (115.9°), C6–N–C7 (115.4°) and C4–N–C6 (110.2°). The value of the C–S–C angle (97°) corresponds to sulfur atoms with ~36% of sp^3 character. The C7–H proton distances to the sulfur atoms (2.96 and 2.94 Å) are shorter than the reported distance of the highest incidence for C–H···S contacts 3.21 Å [30], these contacts could contribute to stabilize the N-alkyl preferred axial position.

The bond lengths of [1,3,5]-dithiazinane **2** merit some discussion. Equatorial C–H bonds are shorter than axial ones, C2–H [0.902(3) *vs* 0.935(3) Å], C4–H [0.852(2) *vs* 0.952(2) Å] and C6–H [0.881(2) *vs* 0.971(2) Å], due to the strong electronic effect of

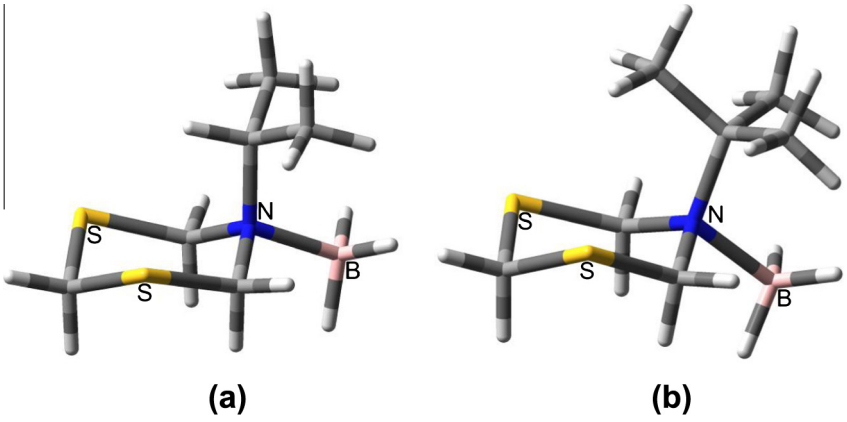
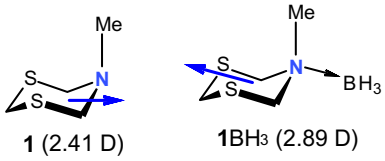


Fig. 2. Calculated structures of minimum energy for compounds **2**BH_3 (a) and **3**BH_3 (b).



Scheme 7. Calculated [HF/6-31++G] dipole moments for compounds **1** and **1**BH_3.

equatorial sulfur and nitrogen lone pairs, Table 4. Interactions $n \rightarrow \sigma^*$ between equatorial lone pairs on the sulfur atoms and C4–N5 or C6–N5 bonds explain that S–C4 [1.826(3) Å] and S–C6 [1.828(3) Å] bonds are longer than S–C2 bonds [1.785(2) and 1.793(3) Å], and C4–N [1.434(4) Å] and C6–N [1.438(2) Å] are shorter than axial exocyclic N–C bond [1.482(4) Å] [11], Table 3.

Compound **1**BH_3 crystallized in anhydrous conditions from $CDCl_3$. The X-ray diffraction analysis shows the BH_3 group in equatorial position, Fig. 4, Tables 3–5. The value of C–S–C angles (97.69° and 98.76°) indicates ~35–46% of sp^3 hybridization of the sulfur atoms. N–borane coordination diminishes the nitrogen lone pair effect whereas that of the antiperiplanar sulfur lone pairs persists. In compound **1**BH_3, the intracyclic C–N bonds are elongated with respect to those of the free dithiazinane **1** [from 1.433(4) Å in **1** to 1.494(2) Å in **1**BH_3], due to the suppression of the nitrogen lone pair, Table 3. The cooperative proton–hydride interactions, contribute to the anchored conformation of **1**BH_3 in solution, as can be deduced from the short proton–hydride contacts [22,23]. These distances are in the range of 2.33–2.52 Å shorter than the sum of the van der Waals radii for a proton and a hydride (Σ_{vdW} = 2.65 Å), Fig. 4.

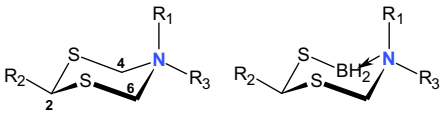
3.2. Alkylation reactions

The interest of the substitution of a C2-proton by an alkyl group was based on the ring anchorage effect which facilitates the study of electronic and steric interactions. Also, it was relevant to analyze if the carbon bound to C2 could have an interaction with the vicinal sulfur atoms. The alkylation of compounds **1**–**3** was performed through the reactions of the 2-lithium compounds **4**–**6** with alkyl chlorides in THF, Scheme 2.

3.2.1. Lithium compounds

Compound **4** has been previously reported by us [11], whereas **5** and **6** are new. It is assumed that lithium derivative **4**–**6** form dimers by two cooperative S → Li coordination bonds, as it was established in the mass spectrum of compound **4** [11]. The organolithium compounds **4**–**6** were directly characterized from the reaction mixtures after solvent evaporation by lithium NMR spectra ^{7}Li [δ = −2.4 (**4**), −1.9 (**5** and **6**) ppm, THF-d_8], Table 2. ^{1}H and ^{13}C NMR

Table 1
Calculated NBO charges [6-31++G].

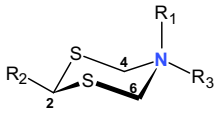


1, **1**BH_3, **14**, **15** **16**

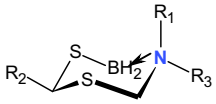
	R_1	R_2	R_3
1	Me	H	lone pair
1BH_3	Me	H	BH_3
14	Me	Me	Me
15	Me	Me	BH_3
16	Me	Me	Me

	C_2	S_1,S_2	C_4,C_6	N	R_2(H/C)	H_{2ax}	H_{4ax},H_{6ax}	H_{4eq},H_{6eq}	R_1	R_3
1	−0.73	+0.11	−0.31	−0.60	+0.27	+0.25	+0.25	+0.24	−0.40	–
1BH_3	−0.74	+0.18	−0.34	−0.58	+0.28	+0.25	+0.26	+0.27	−0.40	−0.03
14	−0.53	+0.27	−0.38	−0.44	−0.66	+0.27	+0.26	+0.28	−0.40	−0.40
15	−0.53	+0.18	−0.34	−0.58	−0.65	+0.26	+0.26	+0.27	−0.40	−0.03
16	−0.51	+0.17S(B) −0.07	−0.36B + 0.06	−0.60	−0.65	+0.25	+0.26H(B) −0.05	+0.25H(B) −0.05	−0.40	−0.40

Table 2
^{1}H and ^{13}C NMR ($CDCl_3$) data for **1**BH_3, **1–8**, **10–16**: δ in ppm and ($^{n}J(^{1}H\text{-}^{1}H)$) in Hz.



1BH_3, **1-8**, **10-15**



16

Cpd	R_1	R_2	R_3	H_{2eq}	H_{2ax}	H_{4eq}, H_{6eq}	H_{4ax},H_{6ax}
Dithiane[a]	–	–	–	3.81(m)	3.81(m)	2.86(m)	2.86(m)
1[b,c]	Me	H	L pair	3.56 (dt, ^{2}J 13.3, ^{4}J 2.6)	4.60 (d, ^{2}J 13.3)	3.93 (dt, ^{2}J 12.6, ^{4}J 2.6)	4.95 (d, ^{2}J 12.6)
1BH_3	Me	H	BH_3	3.40 (dt, ^{2}J 13.9, ^{4}J 2.0)	4.05 (d, ^{2}J 13.9)	3.85 (dt, ^{2}J 13.2, ^{4}J 2.0)	4.37 (d, ^{2}J 13.2)
2[b,d]	iPr	H	L pair	3.64 (br d, ^{2}J 13.9)	4.65 (d, ^{2}J 13.9)	4.29 (d, ^{2}J 13.0)	4.80 (d, ^{2}J 13.0)
3[b,d]	tBu	H	L pair	3.68(br s) **R**′(^{7}Li)	4.72(br s)	4.78(br s)	4.55(br s)
4	Me	Li	I pair	-2.4(s)	3.31(s)	3.22(d)	4.53(d)
5	iPr	Li	I pair	-1.9(s)	3.44(s)	4.39(d, ^{2}J 13.2)	4.55(d, ^{2}J 13.2)
6	tBu	Li	I pair	-1.9(s) **R**′(^{13}C)	3.62(s)	3.90(d, ^{2}J 12.6)	4.25(d, ^{2}J 12.6)
7	Me	Me	I pair	22.8	4.11(q, ^{3}J 6.7)	3.96(d, ^{2}J 12.2)	4.69(d, ^{2}J 12.2)
8	Me	iPr	I pair	59.2	4.21(d, ^{3}J 5.5)	4.07(d, ^{2}J 13.3)c	4.65(d, ^{2}J 13.3)
10	iPr	Me	I pair	21.1	4.28(q, ^{3}J 6.9)	4.39(d, ^{2}J 13.0)	4.49(d, ^{2}J 13.0)
11	tBu	Me	I pair	20.6	4.33(q, ^{3}J 6.9)	4.59(d, ^{2}J 13.3)	4.65(d, ^{2}J 13.3)
12	Me	nBu	I pair	50.7	4.41 (br s)	4.08(d, ^{2}J 13.5)	4.67(d, ^{2}J 13.5)
13	Me	$C_4H_3NS_2$	I pair	55.8	4.61(s)	4.18(d, ^{2}J 13.9)	4.68(d, ^{2}J 13.9)
14	Me	Me	Me	18.5	5.30(br s)	4.79(br s)	4.79(br s)
15[e]	Me	Me	BH_3	22.1	4.10(q, ^{3}J 6.8)	3.58(d, ^{2}J 12.4)	4.47(d, ^{2}J 12.4)
16[b]	Me	Me	Me	19.8	4.05(q, ^{3}J 6.5)	3.60(d, ^{2}J 13.9)	4.22(d, ^{2}J 13.9)

[a] Ref. [1].
[b] In THF-d_8.
[c] At −80 °C.
[d] At −95 °C.
[e] Ref. [25].

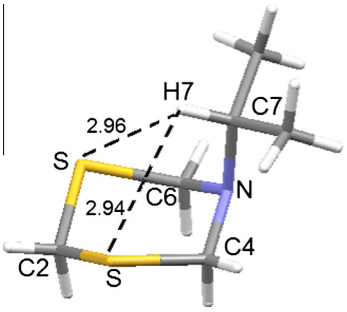


Fig. 3. Solid state structure of compound **2** determined by X-ray diffraction analyses. Intramolecular H7···S short distances are shown.

spectra showed that two THF molecules complete the coordination sphere at the lithium [11]. ^{1}H NMR spectra at room temperature showed the disappearance of the C2–H proton signal. The ^{1}H coupling patterns indicate that in solution compounds **5–6** are in an anchored conformation attributed to their dimeric structure, as it was determined for **4** [11,31]. Calculations of axial and equatorial carbanions of compound **1** show that the equatorial carbanion is more stable than the axial one by 14.1 kJ/mol. The calculated minimum energy structure for compound **5** is in Fig. 5.

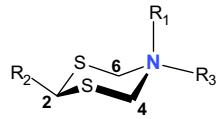
3.2.2. 2-Alkyl derivatives

Reactions of compound **4** with methyl iodide and *iso*propyl chloride give compounds **7** [11] and **8**, respectively whereas reactions of **5** and **6** with methyl iodide afforded compounds **10** and **11**, Scheme 2. Compound **9** with a *tert*butyl group at C2 was calculated, Fig. 6. Its synthesis, in our hands, was unsuccessful, probably due to steric hindrance. When lithium compound **4** was treated with 3 equivalents of *n*BuLi followed by one of methyl iodide in THF, a liquid compound **12**, with an *n*Bu group at C2, was obtained in 80%, Scheme 3. The formation of **12** results from the exchange reaction between MeI and *n*BuLi which affords *n*BuI and MeLi [32]. Then, reaction of *n*BuI with lithium compound **4** gives **12**. This compound has an extremely unpleasant odor. Compounds **7**, **8**, **10–12** are liquids. The calculated structure of **7** is in Fig. 6.

Reaction of the lithium compound **4** with one equivalent of I_2 in THF produces a coupling reaction, leading compound **13** in 72%. A crystal of compound **13** was submitted to X-ray diffraction analysis. The new compound has two coupled dithiazinanes through the C2 atoms. Its central ethylene group bears four sulfur atoms, as described in Scheme 3.

3.2.2.1. ^{1}H NMR. The ^{1}H NMR spectra at room temperature of compounds **7** [11], **8**, **10–13** indicate that they have a preferred chair conformation with the 2-alkyl substituent in equatorial and the N-alkyl group in axial position. The 2-alkyl group shifts (~0.2 ppm) the C4, C6 methylene protons to higher frequencies with respect of the parent dithiazinanes **1–3**, Table 2. This effect is similar to that produced by the N–BH_3 coordination and could be explained by the isolobal relationship of C–C and N–B bonds.

Table 3
Selected bond lengths (Å) and angles (°) from X-ray diffraction analysis of **1**, **1**BH_3, **2**, **13** and **14**.

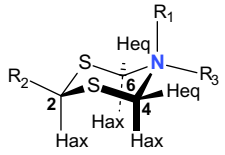


	R_1	R_2	R_3
1	Me	H	lone pair
1BH_3	Me	H	BH_3
2	*i*Pr	H	lone pair
13	Me	Dtz	lone pair
14	Me	Me	Me

	C2–R_2	S1–C2	S3–C2	S1–C6	S3–C4	C4–N5	C6–N5
1[3]	–	1.803(4)	1.794(4)	1.836(4)	1.836(4)	1.428(4)	1.433(4)
1BH_3	–	1.800(2)	1.798(2)	1.802(2)	1.795(2)	1.494(2)	1.494(2)
2	–	1.793(3)	1.785(2)	1.828(3)	1.826(3)	1.434(4)	1.438(2)
13*syn*	1.526(4)	1.823(3)	1.801(3)	1.852(4)	1.847(4)	1.433(5)	1.438(5)
13*anti*	1.516(4)	1.817(3)	1.812(3)	1.835(4)	1.845(4)	1.435(4)	1.435(5)
14	1.521(9)	1.812(5)	1.806(7)	1.781(5)	1.777(4)	1.511(5)	1.506(7)

	S–C2–S	S1–C2–R_2	S3–C2–R_2	C2–S3–C4	C2–S1–C6
1	113.7(2)	–	–	97.3(2)	97.8(2)
1BH_3	112.3(1)	–	–	97.7(2)	98.8(9)
2	113.9(1)	–	–	97.0(1)	97.0(1)
13*syn*	111.7(1)	109.2(2)	109.2(2)	97.1(2)	97.1(2)
13*anti*	111.6(1)	109.7(2)	109.2(2)	98.4(1)	97.5(2)
14	111.2(3)	109.3(5)	108.3(5)	99.3(3)	99.8(3)

Table 4
C–H Selected bond lengths (Å) from X-ray diffraction analyses of **1**BH_3, **2** and **14**.



1BH_3 R_1= Me, R_2= H, R_3= BH_3
2 R_1= *i*Pr, R_2= H, R_3= lone pair
14 R_1= Me, R_2= Me, R_3= Me

	H_{2ax}	H_{2eq}	H_{4ax}	H_{4eq}	H_{6ax}	H_{6eq}
1BH_3	0.96(2)	1.00(2)	0.97(2)	0.93(2)	0.98(2)	0.91(2)
2	0.935(3)	0.902(3)	0.952(2)	0.852(2)	0.971(2)	0.881(2)
14	0.992(8)	–	0.967(7)	0.970(6)	0.981(6)	0.964(6)

3.2.3. X-ray diffraction analysis of compound *13*

The X-ray diffraction analysis of compound **13** shows that there are two molecules in the asymmetric unit, each one in a different conformation. In one (**13***syn*) the C2–C2′ bond has an alternated conformation with the four sulfur atoms and the two hydrogen atoms in a gauche relationship, (dihedral angle H–C2–C2–H is 57.3°). The distances between the sulfur atoms of different rings are short (3.30 and 3.36 Å) compared to the sum of the van der Waals radii (Σ_{vdWr} S···S is 3.6 Å [33]), Fig. 7 and Tables 3–5.

In the second conformer **13***anti*, the C2–C2′ bond has also an alternated arrangement with the sulfur and hydrogen atoms in *anti* position, Fig. 8. The distances between the sulfur atoms of the different rings are even shorter (3.18 Å) than **13***syn*, and it may be considered as a result of stabilizing interactions [5,6,12–17]. Figs. 7 and 8 show the intramolecular sulfur–sulfur contacts in both conformers. The four sulfur atoms shift the C2 resonance by ~20 ppm towards higher frequencies (^{13}C δ = 55.8 ppm). This effect is calculated by comparison with 2-*iso*propyl-dithiazinane **10** where C2 appears at 37.4 ppm.

3.3. 2-Methyl compounds

The treatment of the lithium compound **4** with an excess of methyl iodide gave the ammonium derivative **14**, by methylation of C2 and quaternization of the tertiary amine, Scheme 3. The reaction of compound **7** with BH_3–DMS afforded the N–BH_3 adduct **15**. This adduct in $CDCl_3$ at 40 °C is transformed into its isomer, the borata heterocycle **16** by the exchange of CH_2 by BH_2, Scheme 4. The transformation was established by ^1H, ^{13}C and ^{11}B NMR. Compounds **14**–**16** are isostructural with a quaternary nitrogen atom. Therefore, comparison of all these compounds is interesting. Only the ionic molecule **14** crystallized from $CHCl_3$, and its X-ray diffraction analysis could be performed.

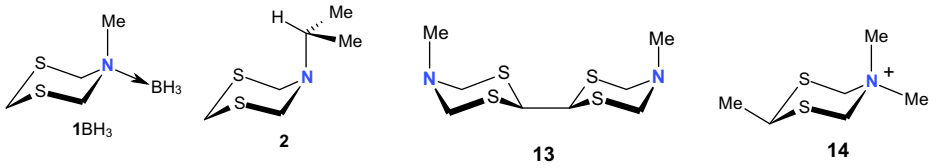
3.3.1. NMR analysis

The ^1H NMR spectrum of 2-methyldithiazinane **7** indicates a preferred chair conformation at room temperature, contrastingly with methyl cyclohexane and 2-methyl-1,3-dithiane which are fluxional under the same conditions, Table 2. This result means that the equatorial methyl group increases the already high ring inversion energy (46 kJ/mol) of the 5-methyl-[1,3,5]-dithiazinane (**1**).

Upon borane coordination of **7**, methylene protons close to borane are shifted to lower frequencies due to the suppression of the electroattracting effect of the N-lone pair. The neutral compounds **15** and **16** have similar chemical shifts, whereas the protons of the cation **14** are considerably shifted to higher frequencies by the positive charge effect, Scheme 8.

Methylation of compound **1** (C2–H δ = 4.60 ppm) to give **7** (C2–H δ = 4.11 ppm) shifts the C2-axial proton to lower frequencies. The latter indicates that interactions between the C2–Me and the sulfur lone pairs could occur, Table 2. This is contrasting with the methylation of cyclohexane which shifts the C1–H axial proton to higher frequency (δ = 1.33 ppm [34]) with respect of cyclohexane C–H axial protons (δ = 1.20 ppm [24]).

Table 5
Crystal data of compounds **1**BH_3, **2**, **13** and **14**.



Compd.	**2**	**1**BH_3	**13**	**14**
Empirical formula	$C_6H_{13}NS_2$	$C_4H_{12}BNS_2$	$C_{16}H_{32}N_4S_8$	$C_6H_{14}INS_2$
Molecular mass	163.31	149.08	268.47	291.22
Crystal size (mm)	0.5 × 0.25 × 0.15	0.35 × 0.3 × 0.17	0.2 × 0.18 × 0.1	0.3 × 0.25 × 0.1
	Prism	Prism	Prism	
Crystal color	Colorless	Colorless	Colorless	yellow
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P21/n	P21/c	Pbcn	Cc
a (Å)	6.2474 (1)	7.52	18.947	12.77
b (Å)	22.6589 (5)	9.052	9.407	7.46
c (Å)	6.8158 (2)	11.77	13.895	13.38
β (°)	114.343 (1)	94.6		117.63
V (Å^3)	879.06 (4)	798.6	2476.6	1128.72 (1)
Z	4	4	8	4
ρ (calcd.) (mg/m^3)	1.234	1.24	1.44	1.714
μ (mm^{-1})	0.53	0.57	0.73	3.15
F (000)	352	320	1136	568
Temperature (K)	293	293	293	293
2*θ* Range for data collection	27.5–1.8	26.4–3.4	2.9–27.5	3.3–27.5
Index ranges	$-7 \leqslant h \leqslant 7$	$-9 \leqslant h \leqslant 9$	$-20 \leqslant h \leqslant 24$	$-10 \leqslant h \leqslant 9$
	$-29 \leqslant k \leqslant 23$	$-11 \leqslant k \leqslant 11$	$-11 \leqslant k \leqslant 12$	$-13 \leqslant k \leqslant 13$
	$-8 \leqslant l \leqslant 8$	$-14 \leqslant l \leqslant 12$	$-16 \leqslant l \leqslant 18$	$-16 \leqslant l \leqslant 16$
Reflections collected	3120	6490	27,520	5405
Reflections unique	1888	1615	2816	2103
Reflections observed (4*σ*)	1347	1347	1623	2029
R (int)	0.03	0.031	0.122	0.059
Number of variable	82	121	143	91
Weighting scheme $^{[a]}x/Y$	0.0/0.01	0.0313/0.1557	0.0275/1.9263	
GOOF	1.09	1.02	1.02	1.66
Final *R* (4*σ*)	0.044	0.029	0.053	0.036
Final *R* wR^2	0.051	0.074	0.108	0.061
Largest residual peak (e/Å^3)	0.19	0.16	0.37	0.33

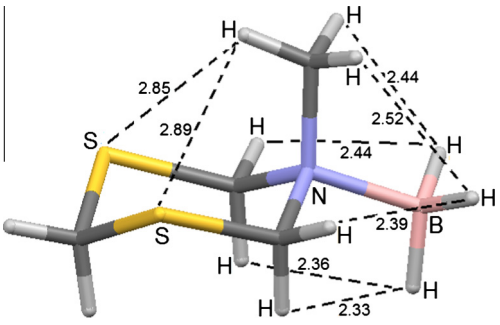


Fig. 4. X-ray diffraction structure of compound **1**BH_3. The [$H^{\delta+}$–$H^{\delta-}$] and [$H^{\delta+}$–$S^{\delta-}$] distances are shown.

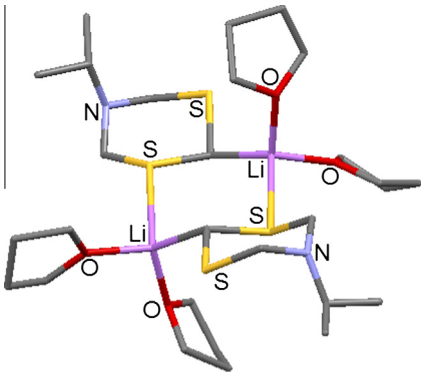


Fig. 5. Calculated minimum energy structure for lithium compound **5**. Hydrogen atoms were deleted for clarity of the figure.

3.3.2. *Ab initio* calculations

Ab initio calculations [HF/6-31++G] of compounds **7** and **14**–**16** were performed. The dipole moments are in Scheme 9, and their electrostatic potential in Supplementary material. Calculated NBO charges [6-31++G] are in Table 1. The cation **14** has the more positive sulfur atoms and lesser negative nitrogen atom. In compound **16**, the boron and B–H hydrogen atoms are almost neutral whereas the nitrogen atom has almost a negative charge unity. The difference in the free enthalpy energy between the two isomers **15** and **16** is 119.1 kJ/mol, borata **16** is the most stable.

3.3.3. X-ray diffraction analyses of compound *14*

The solid state structure of **14** is in Fig. 9 and data is in Tables 3–5. Compound **14** it has the C2-methyl group in equatorial position. The compound has two short contacts between the sulfur atoms and the exocyclic carbon atom C9 [2.72 and 2.70 Å (Σ_{vWr} C,S 3.5 Å [33])]. Examination of S–C2–C9 angles indicates that they have the expected values (109.5(6) and 109.3(6)°) and that there is no steric repulsion between the sulfur atoms and the methyl

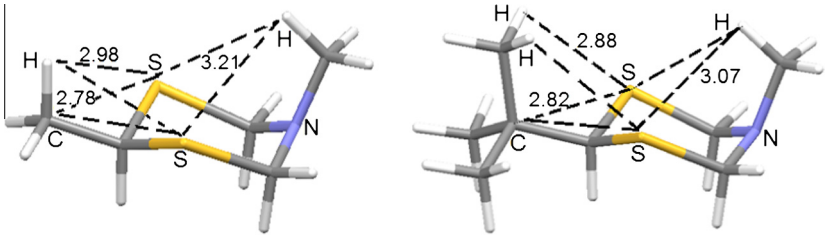


Fig. 6. Calculated structures of compounds **7** (left) and **9** (right). The distances of C–H to sulfur atoms are depicted.

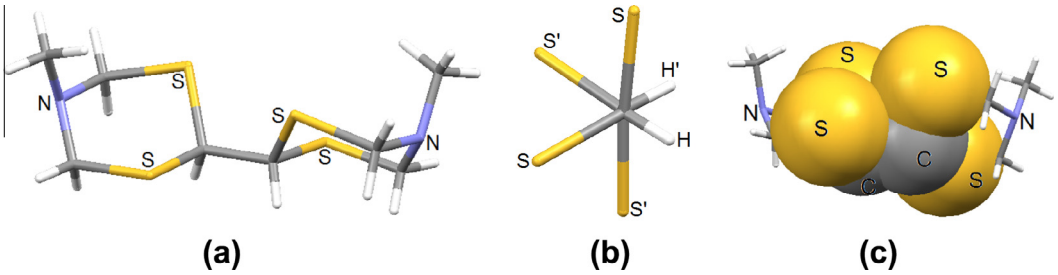


Fig. 7. (a) Conformer **13***syn* found in the crystal of compound **13**. (b) Newman projection of C2–C2′ bond conformation. (c) Representations showing the van der Waals radii of sulfur and C2 atoms.

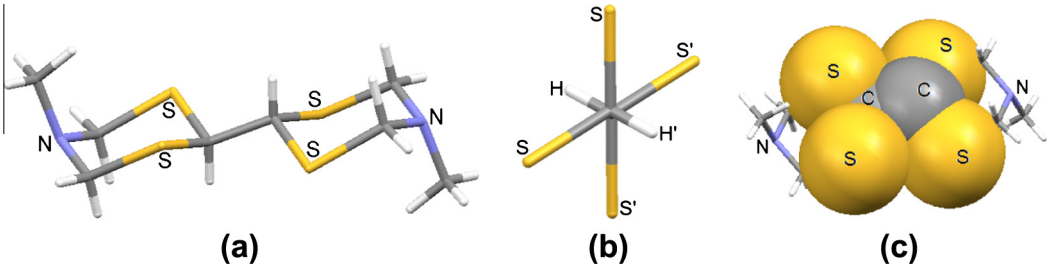
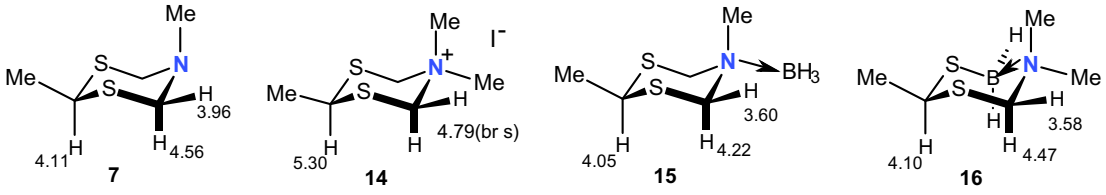


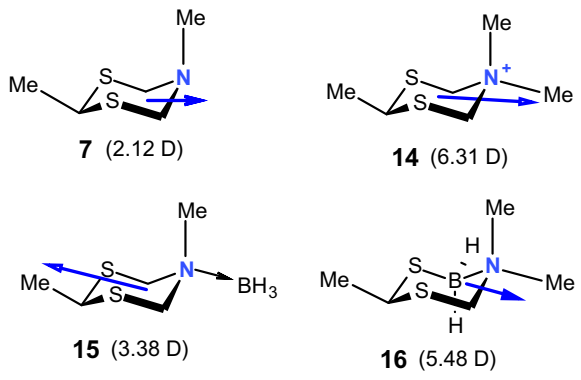
Fig. 8. (a) Conformer **13***anti* found in the crystal of compound **13**. (b) Newman projection of C2–C2′ bond conformation. (c) Representations showing the van der Waals radii of sulfur and C2 atoms.



Scheme 8. δ(^{1}H) of H-2$_{ax}$ and H-6 protons of compounds **7**, **14**–**16** is shown. Compound **14** is in conformational equilibrium, data is for both equatorial and axial protons.

group and therefore a stabilizing interaction between the methyl group and the two sulfur atoms may exist through S···H and C···S short weak interactions. Interionic (I···H) hydrogen bonds stabilize the crystal [H4ax···I (3.04 Å) and H6ax···I (2.99 Å)] (Σ_{vWr} I,H 3.3 Å [33]). Comparison of the C2–H axial bond lengths in compounds **2** [0.935(3)] and **14** [0.992(8)] shows that in **14**, the C2-methyl effect on sulfur atoms elongates the axial C–H bond.

Also the difference between free dithiazinane **2**, coordinated amine **1**BH_3, bis[dithiazinanyl] **13**, and the dithiazinanium cation **14**, is reflected in the bond length values of the ring atoms, Table 3. S–C2 bonds are longer in compounds **14** [1.812(5) 1.806(7)], **13**syn [1.823(3) 1.801(3)], **13**anti [1.817(3) and 1.812(3)] compared to **2** [1.793(3), 1.785(2)]. The S–C4 and S–C6 bonds are shorter in **1**BH_3 [1.802(2); 1.795(2)] and **14** [1.781(5); 1.777(4)] compared to **1** [1.836(4)], **2** [1.828(3) 1.826(3)] and **13**syn [1.852(4);



Scheme 9. Calculated [HF/6-31++G] dipole moments for compounds **7**, **14**, **15** and **16**.

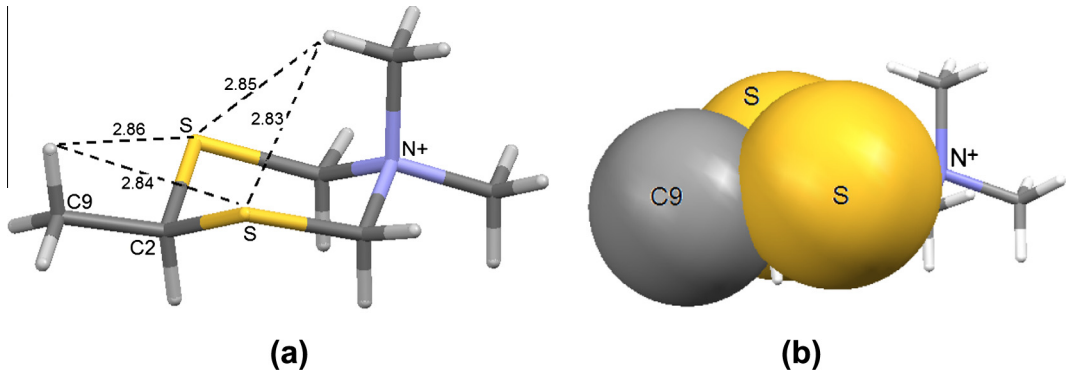


Fig. 9. X-ray diffraction structure of compound **14**. (a) C–7H, C–9H and sulfur atoms intramolecular hydrogen bonds. (b) Representation of the *van* der Walls radii of C9 and sulfur atoms.

1.847(4)], **13**anti [1.835(4); 1.845(4)]. C4–N and C6–N bonds are longer in **1**BH_3 [1.494(2)] and **14** [1.511(5); 1.506(7)] compare to **1** [1.428(4) 1.433(4)] and **2** [1.434(4) 1.438(2)]. The S–C2–S angles are slightly closer in all C2 substituted compounds with respect to non-substituted dithiazinanes.

4. Conclusions

NMR data, X-ray diffraction analyses and calculations of a series of 5-alkyl-[1,3,5]-dithiazinanes [R = Me (**1**), *i*Pr (**2**), *t*Bu (**3**)] and their N–BH_3 adducts (**1**BH_3–**3**BH_3) were analyzed. Agreement between the calculations and the experimental results was found.

^{1}H NMR spectra show, that the ring CH_2 protons are affected by sulfur and nitrogen lone pairs, shifting their resonances to higher frequencies. In addition the axial C–H protons are also shifted to higher frequencies by the antiperiplanar effect of axial sulfur lone pair. The latter explains why the axial protons in dithiazinanes are found ~1 ppm to higher frequencies with respect to equatorial ones. Calculations confirmed the lone pairs effect on the electronic density distribution and explained the ^{1}H NMR trends.

X-ray diffraction and calculations confirmed that the more stable compounds have a chair conformation with the N-R group (R = methyl, isopropyl or *tert*butyl) in axial position and that this conformation is also retained in the N–BH_3 adducts which have the borane in equatorial.

A series of 2-alkyl-1,3,5-dithiazinanes and 2-alkyl-5-borane-1,3,5-dithiazinanes were obtained. The structure in solution was deduced from the ^{1}H and ^{13}C NMR chemical shifts. The C-2 substitution anchors the ring inversion allowing a valuable collection of NMR data about the conformational and stereoelectronic behavior of 2-alkyl-[1,3,5]-dithiazinanes **7**, **8** **10**–**13**.

Calculations provided the energy difference between the conformers, data is in accord with the ring fluxionality and nitrogen configuration.

Bis[N-methyl-1,3,5-dithiazinane] **13** obtained by coupling reaction of the lithium derivative with iodine has a central ethylene group bearing four sulfur atoms. The crystal of **13** contained the *syn* and *anti* C2–C2 bond conformations. The solid state structures showed that the carbon bound to C-2 presents through the space C···S distances shorter than the sum of the van der Waals radii, allowed by weak stabilizing interactions.

Isostructural compounds: 2,5,5-trimethyl-[1,3,5]-dithiazinan-5-ium iodide (**14**), 5-borane-2,5-dimethyl-[1,3,5]-dithiazinane (**15**) and 2,5,5-trimethyl-[1,3,5,6]-dithiazaborata (**16**) were compared. N–borane coordination and N-methyl quaternization give evidence of the nitrogen lone pair effect on S–C and N–C bond lengths. This effect was confirmed by comparison with 1,3-dithiane. The bond lengths determined by X-ray diffraction analyses showed that the antiperiplanar effect of axial sulfur lone pairs elongate the axial C–H protons. The calculated atomic charges and the electrostatic potential explain the NMR spectra trends.

Acknowledgements

We are grateful to Cinvestav for the facilities using of the supercomputer HPC-cluster Xiuhcoatl. We thank Prof. Angeles Paz-Sandoval for helpful discussions.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.04.021.

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