



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



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HIGHLIGHTS

- A series of 2,5-dialkyl-[1,3,5]-dithiazinanes derivatives is reported.
- Structures were determined by ¹¹B, ¹³C and ¹H 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-BH₃ anchor the ring conformation allowing the analyses of steric and electronic interactions and the lone pairs effect.

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ABSTRACT

Structural analyses of a series of 5-alkyl-[1,3,5]-dithiazinanes [R = Me (**1**), *i*Pr (**2**), *t*Bu (**3**)], their N–BH₃ adducts (1BH₃–3BH₃) 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 I₂ affords the *bis*-(5-methyl-[1,3,5]-dithiazinane-2-yl) (**13**). Isostructural compounds: [2,5,5]-trimethyl-[1,3,5]-dithiazinane-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 ¹¹B, ¹³C and ¹H NMR and the X-ray diffraction analyses of **2**, 1BH₃, **13** and **14** are reported. Optimization of two chair conformers of heterocycles **1–3**, 1BH₃–3BH₃, **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–BH₃ 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.

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1. Introduction

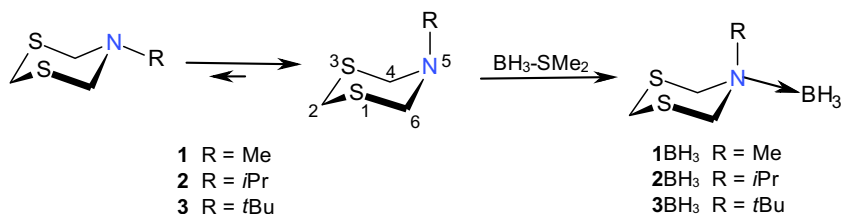
We are currently working on the chemistry of [1,3,5]-heterocyclohexanes [1,2] such as [1,3,5]-dithiazinanes **1–3** [3,4], Scheme 1. These compounds can act as ligands for metal atoms by coordination of the heteroatoms lone pairs [5–7]. They react with borane to give N–BH₃ adducts [8] and can also be 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 (1BH₃–3BH₃) [8], Scheme 1. These compounds are known, however the X-ray diffraction analyses of these N–BH₃ adducts have not been reported. Crystalline compounds **2** and 1BH₃ were analyzed by X-ray diffraction. *Ab initio* theoretical studies [HF/6-

31++G] in compounds **1–3** and 1BH₃–3BH₃ 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 SCH₂S 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 ¹H 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]-dithiazinane-5-ium iodide (**14**), 5-BH₃-2,5-dimethyl-[1,3,5]-dithiazinane (**15**) and 2,5,5-trimethyl-[1,3,5,6]-dithiazaborata (**16**), and report the X-ray diffraction

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Scheme 1. Nitrogen conformers of 5-R-[1,3,5]-dithiazinanes **1–3** and their adducts **1BH₃–3BH₃**.

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 CDCl₃, and THF-*d*₈, were purchased from Aldrich and used without further purification. Compounds **1–3** [3], **1BH₃** [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. ⁷Li [Ξ 10.3976, LiCl], ¹H, ¹³C [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 φ + ω 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: **1BH₃** (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.

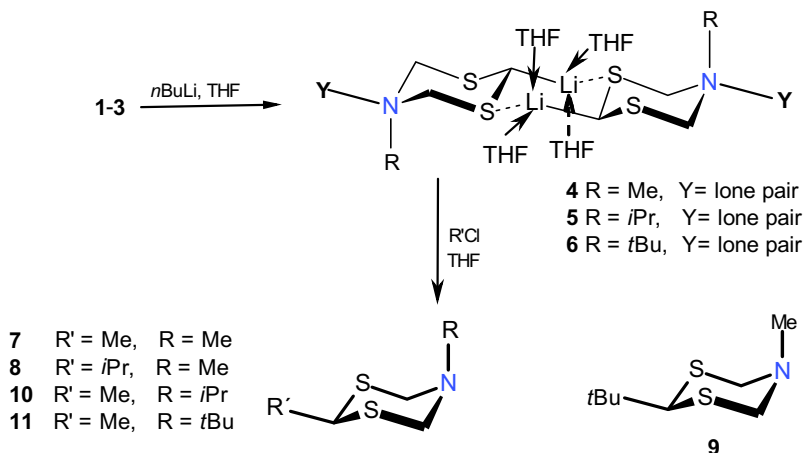
2.4. Synthesis of the compounds

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

To isopropylamine (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. H₂CO (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 CH₂Cl₂. The CH₂Cl₂ solution was dried with Na₂SO₄, filtered, and the solvent evaporated. Compound **2** is a crystalline colorless solid (9.71 g, 70%). Mp 40 °C. NMR (CDCl₃, 25 °C, δ ppm) ¹H, *i*Pr group: 3.78 (hept, ³J 6.5 Hz, 1H, CH), 1.14 (d, 6H, ³J 6.5 Hz, CH₃). NMR (THF-*d*₈, –95 °C, δ ppm) ¹³C: 34.0 (C2), 56.4 (C4/C6), *i*Pr group: 45.3 (CH), 20.7 (CH₃). (+)TOF calcd. for (C₆H₁₄NS₂)⁺, *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.

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