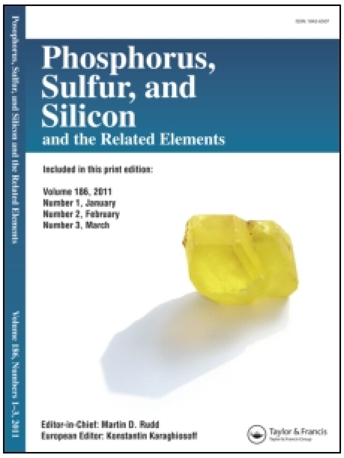

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SYNTHESIS AND X-RAY DIFFRACTION STUDY OF 1,5-DITHIA-3,7-DIAZABICYCLO[3.3.1]NONANE AND ITS N-BORANE ADDUCTS[1]

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We report herein the synthesis of 1,5-dithia-3,7-diazabicyclo[3.3.1]nonane. Its structural study in solution made by NMR, and its X-ray diffraction structure. Compound **1** forms *mono-* or *di*-adduct N—BH_3 in the presence of 1.3 or 2.3 equivalents of BH_3-THF, respectively.

Key words: NMR; conformational study; X-ray diffraction; N—BH_3 adducts; 1,5-dithia-3,7-diazabicyclo[3.3.1]nonane.

INTRODUCTION

We are working in the synthesis of heterocycles rich in lone pairs of electrons. Some related compounds previously reported are the dithiazine derivatives.[2-4] We are interested in to know how the presence of nitrogen and sulfur atoms bonded through methylene groups determine the reactivity of heterocycles. The synthesis of 1,5-dithia-3,7-diazabicyclo[3.3.1]nonane **1** from ammonium sulfide and formaldehyde is found in the literature,[5] but its structure has not been determined by spectroscopy.

We have prepared **1** in order to obtain information about its structure in solution and in the solid state, thus we have undertaken a careful NMR and X-ray diffraction study. Also, we have explored the reactivity with borane of the different basic sites of **1**: nitrogen and sulfur atoms in order to study if more than two borane molecules could be added to **1**. The geometry of the molecule and the proximity of the sulfur atoms could be a factor to allow S—BH_3 coordination in addition to the expected N—BH_3 adducts. The results of this study are reported herein.

SYNTHESIS

Compound **1**, $C_5H_{10}N_2S_2$, was obtained from the reaction between ammonium hydroxide, sodium hydrosulfide hydrate and formaldehyde in water, purified by recrystallization from CH_2Cl_2/hexane (30:70) and obtained in a 20% yield.

NMR STUDY

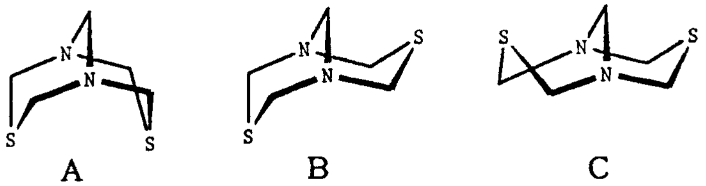
A study by NMR of the bicyclic compound **1** afforded information about the conformation of the molecule. In principle, it was possible to find it in a conformational equilibrium between three conformers: chair-chair (saddle conformation) **A**, chair-boat **B** and boat-boat **C** or in a preferred conformation that could be one of these conformers (Figure 1). The ^1H NMR spectrum of **1** in $CDCl_3$ at room temperature showed an anchored conformation. Two different hydrogen atoms: axial and equatorial were observed for the methylene S—CH_2—N ($\delta = 4.29$ and 5.25 ppm, $J = 13.2$ Hz). By comparison with the dihydrodithiazine systems[2,3] the signal at 5.25 was assigned to the axial hydrogen atoms. The solution was heated until 80°C but the same pattern remains, indicating a very stable preferred conformation. The other methylene group appears as a singlet at $\delta = 4.31$ ppm. The proton-coupled ^{13}C NMR spectrum presents two triplets, one at 55.33 (for four carbons, ^1J(C—H) = 153.0 Hz) and another at 69.90 ppm (^1J(C—H) = 149.2 Hz).

The symmetry of the NMR spectra allows to reject the presence of the conformer chair-boat **B** but we were unable to eliminate one of the two possibilities **A** or **C** only by the NMR information. So, we decided to do a molecular mechanics calculation.[6] The study revealed that the chair-chair **A** conformation was more stable by 22.88 Kcal/mol than the chair-boat **B** and 24.46 Kcal/mol than the boat-boat **C**. The latter information allows to assume that the preferred conformation of **1** in solution is the chair-chair **A**. As we will discuss later, this is also the most stable conformation in the solid state.

REACTIVITY WITH BH_3-THF

We have tested the reactivity of **1** with borane-THF, the reaction with 1.3 equivalents afforded the N—BH_3 *mono*-adduct **2**, as a pure compound as was deduced from the ^{11}B chemical shift (^{11}B NMR, $\delta = -9.6$ ppm, q, J(B—H) = 97 Hz) that is similar to that found for the N-methyl dihydrodithiazine N—BH_3[2,3] (Figure 2).

Compound **2** loses a symmetry plane and the C_2 axis by coordination with borane, but a plane that contains N—CH_2—N—B remains. In the ^1H NMR, the adduct presents one singlet at 4.29 ppm and two AB systems. The equatorial protons were



A B C

FIGURE 1

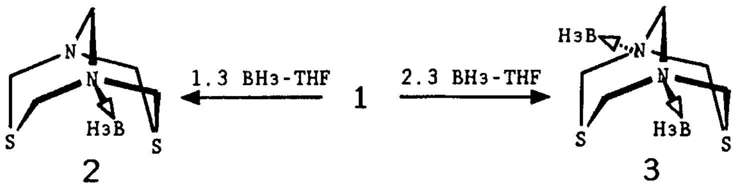


FIGURE 2

identified by their ω coupling constants. The equatorial protons vicinals to borane appears at $\delta = 4.33$, the axial at 4.77 ppm, these methylene groups have the biggest AB coupling constant owing to the electroattractive effect of N-borane group ($^2J_{AB} = 13.2$ Hz). The other AB system appears at $\delta = 4.16$ (equatorial) and 4.83 ppm (axial, $^2J_{AB} = 12.5$ Hz). The changes of the chemical shifts of hydrogen atoms produced by the presence of borane are remarkable. It was noted before for the dithiazine, that the N—BH$_3$ coordination to dihydrodithiazine does not have any effect on equatorial bonds but shifts to high frequency the nearest axial protons in C-2 and C-5 by $\Delta\delta = 0.48$ ppm and the remote axial protons by 0.42 ppm. This fact is attributed to the lone pairs of the sulfur when the nitrogen lone pair effect is suppressed by coordination. In the ^{13}C NMR spectrum three different carbon atoms are observed, the C-4 ($\Delta\delta = 5.7$ ppm, ^1J(C—H) of 157.5), two S—CH$_2$—N—B (C-7 and C-9, $\Delta\delta = 3.1$ ppm, ^1J(C—H) of 156.7 Hz) shifted to high frequency by the electronic effect of borane and both S—CH$_2$—N shifted at low frequency (C-2 and C-5, $\Delta\delta = 2.8$ ppm, ^1J(C—H) of 153.5) probably by the same effect of sulfur lone pairs mentioned above. The presence of borane group is clearly indicated by the ^1J(C—H) coupling constants that are bigger for the carbon atoms near the borane that have reduced their electronic density. This assignment was verified by a HETCOR ^{13}C/^{1}H NMR spectrum.

The reaction of 2.3 equivalents of BH$_3$—THF afforded compound **3**, in which the molecule recovers its symmetry (Figure 2). The *di*-adduct N—BH$_3$ presents at the ^{11}B NMR spectrum a quartet at $\delta = -9.42$ ppm, J(B—H) = 97 Hz. At the ^{1}H NMR spectrum an AB system for eight protons (4.35 and 4.28 ppm, $J_{AB} = 12.7$ Hz) and a singlet at $\delta = 4.25$ ppm for C-4. The electronic effect of a second coordination is observed in the axial protons that move to low frequency by $\Delta\delta = 0.58$ ppm. The equatorial hydrogen does not suffer any important change. The spectrum of ^{13}C NMR presents only two signals, one for C-4 (74.1) and the second for the rest of the methylene groups (S—CH$_2$—N) at 57.1 ppm, $\Delta\delta = 1.8$ ppm both chemical shifts reflects the electronic attraction of borane coordination. It was interesting to contrast the weakness of the B—N bonding in compounds **2** and **3**, with the B—N adducts of the dihydrodithiazines.[3] When we evaporated the solvent (THF or CH$_2$Cl$_2$) from the reaction mixtures of compounds **2** or **3** the N—BH$_3$ coordination is lost in part. This fact can be attributed to the very open angles around the nitrogen atoms that do not favor a strong coordination. The N—B bond is weaker in **3** when compared with **2**, the electroattractive effect of the borane makes an important electronic withdrawing effect over the second nitrogen weakening the second coordination. This was also observed in 1,3-diazolidines N—BH$_3$ adducts.[7] We have never observed coordination of the borane with the sulfur atoms of compound **1** even in an excess of borane.

When the THF was evaporated and compound **2** dissolved in DMSO, the heterocycle was opened and protonated to give bis(dimethylamine)methylene.[8] Two singlets appear in ^{13}C NMR spectrum, one at 54.82 (N—$\underline{C}H_2$—N) and the other at 43.93 (N—$\underline{C}H_3$). The same feature is observed in the ^{1}H NMR spectrum, two singlets appear at 5.75 (1H) and 2.76 (6H) ppm. The anion of this protonated compound is the $B(OH)_4^-$ (^{11}B NMR, $\delta = +1.2$ (s) ppm). This fragmentation was observed before for the dihydrodithiazines.[3] The sulfur part of the molecule forms a precipitate that contains a boron, carbon and sulfur derivative which has not been completely identified.

X-RAY STUDY

The X-ray diffraction study of compound **1** shows a bicyclic structure, with two six membered rings each in a chair conformation (Figure 3). Only half the molecule is present in the asymmetric unit. The eight membered ring has a saddle conformation with two nitrogens bonded by a methylene and its free lone pairs directed to the outside. Each of the two sulfur atoms at the stirrups possess one lone pair in an *endo* position and another in an *exo* position. In Table I the crystal data are given. Atomic coordinates are in Table II. Table III and IV contain interatomic

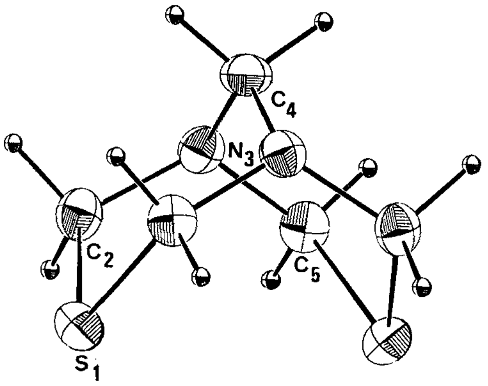


FIGURE 3

TABLE I

Crystal data

formula	$C_5H_{10}N_2S_2$	scan type	ω/2θ
fw	162.27	scan width, °	1.0
system	monoclinic	scan speed, °min^{-1}	1.80<sp<16.48
space group	C2/c	Diffractometer	CADF4
a, Å	10.486(3)	no. of reflections collected	2347
b, Å	8.911(2)	no. of unique reflections	1109
c, Å	7.587(1)	merging R factor	0.035
β, Å	93.69(2)	abs. coeff. corr.	0.85<coeff.<1.28
V, Å	708(1)	no. of reflections with I>3σI	936
Z	4	R	0.029
μ(MoKα), cm^{-1}	6.33	R_w	0.029
dcalc., g cm^{-3}	1.521	weighting scheme	unity
2θ range, °	3<2θ<60	no. of variables	58

distances and bond and torsion angles. The stereoscopic view of the crystal packing is presented in Figure 4.

Compound **1** is a symmetric molecule that has a C_2 axis that passes through C-(4) and between the two nitrogen atoms. In addition, it possesses two symmetry planes, one that passes through the two nitrogen atoms and C-(4) that the second through C-(4) and the two sulfur atoms. The nonbonding distance between nitrogen atoms is 2.433(3) Å and between two sulfur atoms is 3.360(1) Å. The nitrogen atoms are not completely pyramidal and have 63% sp^3 character calculated from the angles around them. The C—S—C angle 96.52(8)° and the S—C—N 116.0(1)° are similar to that found in N-methyl dithiazine[4] 97.8(2)° and 115.7(2), respectively.

TABLE II

Fractional atomic coordinates with e.s.d.'s in parentheses, and equivalent isotropic thermal parameter U(eq)(A^2) U(eq) = [U(11)*U(22)*U(33)]**$^{1/3}$

Atom	x/a)	y/b	z/c	U(eq)
S(1)	-0.13539(4)	0.10789(5)	0.11912(6)	0.0428
N(3)	0.0624(1)	0.3184(2)	0.1204(2)	0.0385
C(2)	-0.0296(2)	0.2371(2)	0.0075(2)	0.0421
C(4)	0.0000	0.4076(3)	0.2500	0.0423
C(5)	0.1693(2)	0.2350(2)	0.1985(2)	0.0418

TABLE III

Interatomic distances (Å) and bond angles (deg.)

S(1)-C(2)	1.843(2)	S(1)-C(5)	1.842(2)
N(3)-C(2)	1.444(2)	N(3)-C(4)	1.453(2)
N(3)-C(4)	1.453(2)	N(3)-C(5)	1.441(2)
C(5)-S(1)-C(2)	96.52(8)	C(4)-N(3)-C(2)	111.4(1)
C(4)-N(3)-C(2)	111.4(1)	C(5)-N(3)-C(2)	117.2(1)
C(5)-N(3)-C(4)	112.1(1)	C(5)-N(3)-C(4)	112.1(1)
N(3)-C(2)-S(1)	116.0(1)	N(3)'-C(4)-N(3)	113.7(2)
N(3)-C(5)-S(1)	116.3(1)		

symmetry operation: ' = -x,y,1/2-z.

TABLE IV

Torsion angles (deg.)

S(1) -C(2) -N(3) -C(4)	-58.21
S(1) -C(2) -N(3) -C(5)	72.75
C(2) -N(3) -C(4) -N(3)'	67.15
N(3) -C(4) -N(3)'-C(5)'	-66.40
C(4) -N(3)'-C(5)'-S(1)	56.54
N(3)'-C(5)'-S(1) -C(2)	-42.24
C(5)'-S(1) -C(2) -N(3)	43.14

symmetry operation ' = -x,y,1/2-z.

A positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

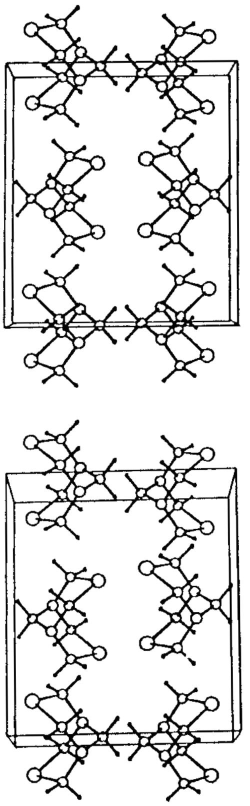


FIGURE 4

EXPERIMENTAL

^1H, ^{13}C and ^{11}B NMR spectra were recorded by using the frequency of 270, 67.8 and 86.55 MHz, respectively. ^1H and ^{13}C NMR spectra were recorded with TMS as internal reference and ^{11}B NMR spectra with BF_3—OEt_2 as external reference. Mass spectra were recorded on a Hewlett Packard 5989 mass spectrometer. Melting points are uncorrected.

Synthesis of 1,5-dithia-3,7-diazabicyclo[3.3.1]nonane **1**. Sixteen ml of ammonium hydroxide (25%, 0.114 mol) were added to 35.1 ml (0.4 mol) of aqueous formaldehyde (37%) and the mixture was stirred for 5 min. Another solution of 8 g NaSH (0.14 mol) in 15 ml of water was added and the mixture was stirred 12 h at room temperature. The reaction mixture was then extracted with CH_2Cl_2, dried with Na_2SO_4 and evaporated to give the crude product. Compound **1** was purified by recrystallization from CH_2Cl_2/hexane (30:70), to give 1.85 g yield 20%. M.p. 193–195°C. Anal. for $C_5H_{10}N_2S_2$, Calcd. C 37.02, H 6.17, N 17.28; Found C 37.05, H 6.19, N 17.29. ^1H NMR ($CDCl_3$, 270.05 MHz, at 27°C) δ 4.28 (d, J_{AB} = 13.2 Hz, 4H, N—$\underline{H}$eq—S), 4.29 (sbr, 2H, 2H-4), 5.25 (d, J_{AB} = 13.2 Hz, 4H, N—$\underline{H}$ax—S). ^{13}C NMR ($CDCl_3$, 67.8 MHz, at 27°C) δ 55.33 (4C, t, J(C—H)= 153.0 Hz, C-2, C-5, C-7 and C-9), 69.90 (C-4). MS(70 eV) m/z 162 ($[M-S]^{+\cdot}$).

Reactivity of 1,5-dithia-3,7-diazabicyclo[3.3.1]nonane **1** *with* BH_3*—THF. General procedure. Preparation of N—*BH_3 *mono-adduct* **2**. To compound **1** (0.2 g, 1.23 mmol) in 20 ml of dry CH_2Cl_2 at −78°C was added 1.3 equivalent of a solution 2.4 M of BH_3—THF (0.67 ml). The mixture was stirred for 5 min, the solvent was removed and the crude product, a white solid, was analyzed by NMR spectroscopy, ^1H, ^{13}C and ^{11}B. Compound **3** was obtained when an excess of BH_3 was added, 2.3 equivalents.

N-Borane-1,5-dithia-3,7-diazabicyclo[3.3.1]nonane, **2**. ^1H NMR ($CDCl_3$, 270.05 MHz, at 27°C) δ 4.16 (d, J_{AB} = 12.5 Hz, 2H, H-7eq and H-9eq), 4.33 (d, J_{AB} = 13.2 Hz, 2H, H-2eq and H-5eq), 4.29 (s, 2H, 2H-4), 4.77 (d, J_{AB} = 13.2 Hz, 2H, H-2ax and H-5ax), 4.83 (d, J = 12.5 Hz, 2H, H-7ax and H-9ax). ^{13}C NMR ($CDCl_3$, 67.8 MHz, at 27°C) δ 52.48 (2C, t, 153.5 Hz, C-7 and C-9), 58.46 (2C, t, 156.7 Hz, C-2 and C-5), 74.74 (C-4, t, 157.5 Hz). ^{11}B NMR ($CDCl_3$, 86.55 MHz, at 27°C) δ −9.6 (q, J(B—H)= 97 Hz).

N,N'-Diborane-1,5-dithia-3,7-diazabicyclo[*3.3.1*]*nonane*, **3**. ^1H NMR ($CDCl_3$, 270.05 MHz, at 27°C) δ 4.25 (s, 2H, 2H-4), 4.28 (d, J_{AB} = 12.7 Hz, 4H, N-$\underline{H}$eq-S), 4.35 (d, 4H, N-$\underline{H}$ax-S). ^{13}C NMR ($CDCl_3$, 67.8 MHz, at 27°C) δ 57.10 (4C, N-$\underline{C}H_2$—S), $\underline{74.09}$ (C-4). ^{11}B NMR ($CDCl_3$, 86.55 MHz, at 27°C) δ − 9.42 (q, J(B—H)= 96.8 Hz).

Crystal data. Selected crystals were mounted on an automatic diffractometer and diffraction data collected using Molybdenum radiation. Unit cell dimensions with estimated standard derivations were obtained from least-squares refinements of the setting angles of 25 well centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table I. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs[9]) were applied.

Computations for compound **1** were performed by using CRYSTALS[10] adapted for a Micro Vax II. Atomic form factors for neutral S, C, N, O and H were taken from Reference 11. Anomalous dispersion was taken into account. The structure was solved by direct methods using the SHELX86 program.[12] Anisotropic temperature factors were introduced for all non-hydrogen atoms for compound **1**. Hydrogen atoms were found on difference electron density maps. They were placed in calculated positions (C—H: 0.96 Å) with an isotropic thermal parameter 1.20 × that of their supporting carbon atom and refined riding on that carbon atom. Least-squares refinements with approximation in three blocks to the normal matrix were carried out by minimizing the function Σ w(|Fo| − |Fc|)^2, where Fo and Fc are observed and calculated structure factors, respectively. Unit weights were used. Models reached convergence with R = Σ(||Fo| − |Fc||)/Σ|Fo| and Rw = [Σ w(|Fo| − |Fc|)^2/Σ w(Fo)^2]$^{1/2}$ having values listed in Table I. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in the final difference maps.

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