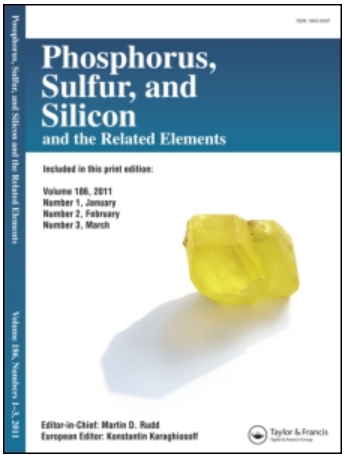


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# NEW PERHYDRODITHIAZINES, NMR AND X-RAY DIFFRACTION STUDIES

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# NEW PERHYDRODITHIAZINES, NMR AND X-RAY DIFFRACTION STUDIES

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A series of new perhydro-1,3,5-dithiazines have been prepared: 1,1′-*bis*-[5-(perhydro-1,3,5-dithiazinyl)]dimethylsulfide **2**, *bis*-[5-(perhydro-1,3,5-dithiazinyl)]methane **3**, 1,2-*bis*-[5-(perhydro-1,3,5-dithiazinyl)]ethane **4**, 1,3-*bis*-[5-(perhydro-1,3,5-dithiazinyl)]propane **5**, 1,4-*bis*-[5-(perhydro-1,3,5-dithiazinyl)]butane **6**, 1-[5-perhydro-1,3,5-dithiazinyl)]-3-[4-morpholinyl]propane **7**, and 1,1′-[5-(perhydro-1,3,5-dithiazinyl)]-3,3′-[1,4-piperazinyl]propane **8**. The structure of all compounds was studied by $^{1}H$ and $^{13}C$ NMR and molecular mechanics calculations. An X-ray diffraction study was performed on compounds 5-methyl-perhydro-1,3,5-dithiazine **1a** and 5-*tert*-butyl-perhydro-1,3,5-dithiazine **1b** and **5–7**. In the X-ray diffraction studies and in the molecular mechanics calculation it was found that all the six-membered rings were in a chair conformation and that in all the studied perhydro-1,3,5-dithiazines the substituent at the nitrogen atom was in the axial position, even in spite of a strong steric hindrance as in compound **1b**. The structure of dithiazines obtained by molecular mechanics calculations agrees quite well with those obtained by X-ray diffraction studies.

*Key words:* Perhydrodithiazines; NMR; X-ray diffraction.

## INTRODUCTION

We have synthesized molecules with one perhydrodithiazine ring joined by a chain of differing size with another perhydrodithiazine or another six-membered nitrogen heterocycle (**3–8**) (Figure 1). We are interested in these molecules because they are rich in lone electron pairs and possible ligand models for coordination complexes. Also, we wished to establish the conformational behaviour of the ring and of the nitrogen atom in these new compounds since the lone pairs of electrons can be either in the equatorial or axial positions.

The syntheses of the dithiazine heterocycles were difficult; they did not give good yields because there are many other compounds in the reaction mixture. It was also necessary to carefully separate the dithiazines from the different products because they are fragile structures and easily hydrolyzed. The structures of all new

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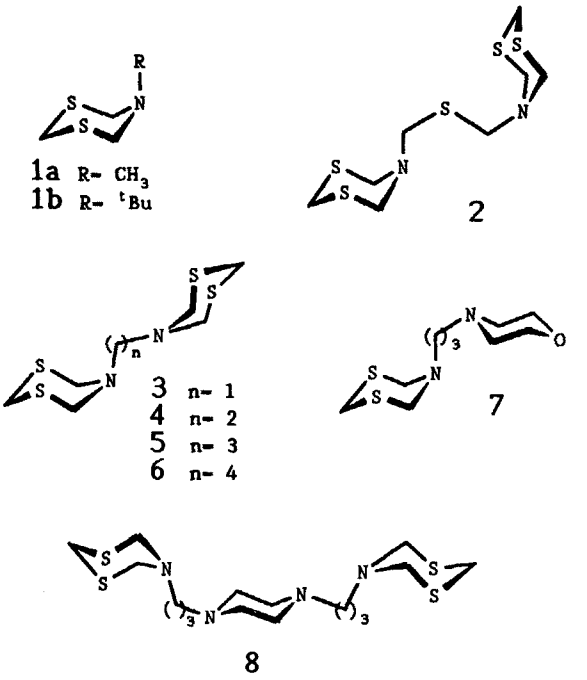



FIGURE 1 Structure of compounds **1–8**.

compounds (**2–8**) has been studied by $^{1}H$ and $^{13}C$ NMR and molecular mechanics calculations (MM).[1] An X-ray diffraction study was performed on compounds **1** and **5–7** (Tables I–III).

## RESULTS AND DISCUSSION

### *Compound 1a*

The N-methyl dihydrodithiazine **1a** was submitted to an X-ray diffraction study in order to unambiguously establish its ring and nitrogen conformation. This molecule has been studied by Katritzky *et al.*[2] They found that the NMR spectra of **1a** at room temperature shows a ring conformational equilibrium with the nitrogen atom conformation anchored and the methyl group in the unusual axial position. Their proposition was based on $^{1}H$ NMR data. The phenomenon has been explained by repulsion between the axial nitrogen lone pair with those of the sulfur atoms. We have also deduced by $^{13}C$ NMR that in solution the methyl group of **1a** is in an axial position.[3,4] To our knowledge, no structural characterization in the solid state has been reported. Therefore, we decided to carry out an X-ray diffraction study with several dithiazine derivatives in order to obtain more information about the ring and nitrogen conformations.

In the X-ray diffraction study, the structure of compound **1a** (Figure 2) has been found to have a chair conformation, with the methyl group in an axial position. The angles around the nitrogen atom are very open indicating a 50% $sp^2$ character.

TABLE I

Crystal data

| | **Compound 1a** | **Compound 1b** | **Compound 5** | **Compound 6** | **Compound 7** |
|---|---|---|---|---|---|
| formula | $C_4H_9NS_2$ | $C_7H_{15}NS_2$ | $C_9H_{18}N_2S_4$ | $C_{10}H_{20}N_2S_4$ | $C_{10}H_{20}ON_2S_2$ |
| fw | 135.24 | 177.33 | 282.50 | 296.52 | 248.41 |
| system | monoclinic | monoclinic | orthorhombic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ | P bca | $P2_1/n$ | C2/c |
| a, Å | 7.855(1) | 6.131(1) | 8.042(2) | 7.255(2) | 25.196(1) |
| b, Å | 7.389(1) | 14.708(2) | 13.338(6) | 7.606(2) | 5.068(1) |
| c, Å | 11.629(2) | 10.769(1) | 21.548(4) | 13.029(3) | 23.381(1) |
| β, ° | 107.51(2) | 103.12(9) | | 104.99(2) | 118.61(4) |
| V, Å | 644(3) | 945.7(2) | 2599(1) | 694(3) | 2508.7 |
| Z | 4 | 4 | 8 | 2 | 8 |
| $\mu$(MoK$\alpha$), $cm^{-1}$ | 6.78 | 4.8 | 6.75 | 6.35 | 3.9 |
| dcalc., g $cm^{-3}$ | 1.395 | 1.25 | 1.44 | 1.418 | 1.32 |
| 2θ range, ° | 3<2θ<56 | 2<2θ<38 | 3<2θ<50 | 3<2θ<56 | 4<2θ<42 |
| scan type | ω/2θ | ω/2θ | ω/2θ | ω/2θ | ω/2θ |
| scan width, ° | 0.8 + 0.34 tgθ | 0.7 + 1.030 tgθ | 0.8 + 0.34 tgθ | 0.8 + 0.35 tgθ | 0.5 + 1.5 tgθ |
| scan speed, ° $min^{-1}$ | 1.65<sp<16.48 | 2.0<sp<20.0 | 1.65<sp<16.48 | 1.50<sp<16.48 | 2<sp<20.4 |
| Diffractometer | CAD4F | CAD4F | CAD4F | CAD4F | CAD4F |
| no. of reflections collected | 1600 | 884 | 2623 | 1870 | 1183 |
| no. of unique reflections | 1415 | 884 | 2274 | 1666 | 843 |
| merging R factor | 0.072 | | | 0.026 | |
| abs coeff. corr. | 0.67<coeff.<1.27 | 6.25<coeff.<0.999 | 0.87<coeff.<1.16 | 0.71<coeff.<1.30 | 0.903<coeff.<0.999 |
| no. of reflections with I>3σI) | 1119 | 666 | 647 | 1290 | 843 |
| R | 0.041 | 0.054 | 0.044 | 0.034 | 0.047 |
| Rw | 0.044 | 0.052 | 0.047 | 0.034 | 0.045 |
| weighting scheme | unity | unity | unity | unity | unity |
| no. of variables | 94 | 151 | 82 | 106 | 196 |

TABLE II

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

**Compound 1a.**

| Atom | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| S(1) | 0.9480(1) | 0.1981(1) | 0.83176(8) | 0.0551 |
| S(3) | 0.6931(1) | 0.0181(1) | 0.94443(8) | 0.0509 |
| N(5) | 0.6477(3) | 0.3703(4) | 0.8587(2) | 0.0447 |
| C(2) | 0.8259(5) | -0.0030(5) | 0.8428(3) | 0.0523 |
| C(4) | 0.5540(4) | 0.2081(5) | 0.8680(3) | 0.0480 |
| C(6) | 0.7570(5) | 0.3525(6) | 0.7805(3) | 0.0536 |
| C(7) | 0.7369(6) | 0.4579(7) | 0.9743(4) | 0.0636 |

**Compound 1b.**

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 0.9401(3) | 0.2049(1) | 1.0160(1) | 0.05370 |
| S(3) | 1.2258(3) | 0.2957(1) | 0.8592(2) | 0.05585 |
| N(5) | 0.9263(7) | 0.1561(3) | 0.7612(3) | 0.3039 |
| C(2) | 1.043(1) | 0.3078(3) | 0.9657(5) | 0.0595 |
| C(4) | 1.014(1) | 0.2401(4) | 0.7313(5) | 0.4432 |
| C(6) | 0.7961(9) | 0.1648(4) | 0.8542(5) | 0.4179 |
| C(7) | 1.0471(9) | 0.0702(4) | 0.7562(5) | 0.3546 |
| C(8) | 1.177(1) | 0.0739(4) | 0.6528(5) | 0.5319 |
| C(9) | 0.879(1) | -0.0070(4) | 0.7256(5) | 0.5572 |
| C(10) | 1.217(1) | 0.0457(4) | 0.8818(5) | 0.5066 |

**Compound 6.**

| Atom | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| S(1) | 0.2555(1) | -0.49398(9) | 0.06908(5) | 0.0441 |
| S(3) | 0.63453(9) | -0.3110(1) | 0.15624(6) | 0.0488 |
| N(5) | 0.2835(3) | -0.1510(3) | 0.1451(1) | 0.0322 |
| C(2) | 0.4977(4) | -0.5110(4) | 0.1494(2) | 0.0472 |
| C(4) | 0.4785(4) | -0.1635(4) | 0.2078(2) | 0.0409 |
| C(6) | 0.1825(4) | -0.3144(3) | 0.1432(2) | 0.0370 |
| C(7) | 0.2673(4) | -0.0693(4) | 0.0408(2) | 0.0377 |
| C(8) | 0.0650(4) | -0.0521(4) | -0.0260(2) | 0.0362 |

**Compound 5.**

| Atom | x/a | y/b | z/c | U(1so) | U(eq) |
|---|---|---|---|---|---|
| S(1) | 0.2741(3) | 0.9877(2) | 0.4257(1) | | 0.0389 |
| S(3) | 0.0863(3) | 0.9121(2) | 0.3203(1) | | 0.0369 |
| S(10) | 0.2486(4) | 1.3571(2) | 0.1015(1) | | 0.0396 |
| S(12) | 0.5015(3) | 1.2267(2) | 0.0588(1) | | 0.0388 |
| N(5) | 0.3401(8) | 1.0267(6) | 0.3014(3) | 0.025(2) | |
| N(14) | 0.260(1) | 1.1508(6) | 0.1240(3) | 0.026(2) | |
| C(2) | 0.172(1) | 0.8832(7) | 0.3932(4) | 0.033(3) | |
| C(4) | 0.259(1) | 0.9430(7) | 0.2778(4) | 0.036(2) | |
| C(6) | 0.406(1) | 1.0034(9) | 0.3610(5) | 0.042(3) | |
| C(7) | 0.266(1) | 1.1236(7) | 0.3001(4) | 0.034(3) | |
| C(8) | 0.204(1) | 1.1513(8) | 0.2355(4) | 0.030(3) | |
| C(9) | 0.325(1) | 1.1551(7) | 0.1868(4) | 0.028(2) | |
| C(11) | 0.372(1) | 1.3258(8) | 0.0376(5) | 0.039(3) | |
| C(13) | 0.365(1) | 1.1280(7) | 0.0759(4) | 0.032(3) | |
| C(15) | 0.164(1) | 1.2345(8) | 0.1090(4) | 0.035(3) | |

**Compound 7.**

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 0.05013(5) | 0.1355(3) | 0.71286(6) | 0.0489 |
| S(3) | 0.16251(5) | 0.1445(3) | 0.69827(6) | 0.0564 |
| O(13) | 0.4688(1) | -0.0102(7) | 1.0583(1) | 0.0507 |
| N(5) | 0.1612(1) | -0.0472(7) | 0.8144(2) | 0.0347 |
| N(10) | 0.3417(1) | 0.0888(7) | 0.9924(2) | 0.0329 |
| C(2) | 0.0824(2) | 0.074(1) | 0.6585(2) | 0.0545 |
| C(4) | 0.1865(2) | -0.086(1) | 0.7701(2) | 0.0507 |
| C(6) | 0.0973(2) | -0.096(1) | 0.7814(2) | 0.0494 |
| C(7) | 0.1783(2) | 0.1969(9) | 0.8547(2) | 0.0393 |
| C(8) | 0.2458(2) | 0.2435(9) | 0.8947(2) | 0.0418 |
| C(9) | 0.2793(2) | 0.0223(9) | 0.9439(2) | 0.0380 |
| C(11) | 0.3691(2) | -0.1246(9) | 1.0412(2) | 0.0418 |
| C(12) | 0.4340(2) | -0.062(1) | 1.0914(2) | 0.0494 |
| C(14) | 0.4428(2) | 0.200(1) | 1.0108(2) | 0.0507 |
| C(15) | 0.3783(2) | 0.140(1) | 0.9594(2) | 0.0455 |

TABLE III

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

**Compound 1a.**

| | | | |
|---|---|---|---|
| S(1) - C(2) | 1.794(4) | S(1) - C(6) | 1.836(4) |
| S(3) - C(2) | 1.803(4) | S(3) - C(4) | 1.836(3) |
| N(5) - C(4) | 1.428(4) | N(5) - C(6) | 1.433(4) |
| N(5) - C(7) | 1.466(5) | | |

| | | | |
|---|---|---|---|
| C(6)-S(1)-C(2) | 97.8(2) | C(4)-S(3)-C(2) | 97.3(2) |
| C(6)-N(5)-C(4) | 113.1(3) | C(7)-N(5)-C(4) | 114.6(3) |
| C(7)-N(5)-C(6) | 114.2(3) | S(3)-C(2)-S(1) | 113.7(2) |
| N(5)-C(4)-S(3) | 115.7(2) | N(5)-C(6)-S(1) | 116.0(2) |

**Compound 1b.**

| | | | |
|---|---|---|---|
| S(1) -C(2) | 1.771(6) | N(5) -C(6) | 1.421(7) |
| S(1) -C(6) | 1.861(5) | N(5) -C(7) | 1.472(7) |
| S(3) -C(2) | 1.784(7) | C(7) -C(8) | 1.509(8) |
| S(3) -C(4) | 1.855(5) | C(7) -C(9) | 1.519(8) |
| N(5) -C(4) | 1.413(7) | C(7) -C(10) | 1.551(7) |

| | | | |
|---|---|---|---|
| C(2) -S(1) -C(6) | 96.4(3) | S(1) -C(6) -N(5) | 117.7(4) |
| C(2) -S(3) -C(4) | 94.9(3) | N(5) -C(7) -C(8) | 110.5(4) |
| C(4) -N(5) -C(6) | 112.6(4) | N(5) -C(7) -C(9) | 109.1(4) |
| C(4) -N(5) -C(7) | 121.5(4) | N(5) -C(7) -C(10) | 114.3(4) |
| C(6) -N(5) -C(7) | 118.1(4) | C(8) -C(7) -C(9) | 108.2(4) |
| S(1) -C(2) -S(3) | 115.5(3) | C(8) -C(7) -C(10) | 106.9(4) |
| S(3) -C(4) -N(5) | 117.0(3) | C(9) -C(7) -C(10) | 107.7(4) |

**Compound 6[a].**

| | | | |
|---|---|---|---|
| S(1) - C(2) | 1.802(3) | S(1) - C(6) | 1.829(3) |
| S(3) - C(2) | 1.806(3) | S(3) - C(4) | 1.839(3) |
| N(5) - C(4) | 1.442(3) | N(5) - C(6) | 1.440(3) |
| N(5) - C(7) | 1.471(3) | C(7) - C(8) | 1.506(3) |
| C(8) - C(8)' | 1.519(5) | | |

| | | | |
|---|---|---|---|
| C(6)-S(1)-C(2) | 96.8(1) | C(4) -S(3)-C(2) | 98.6(1) |
| C(6)-N(5)-C(4) | 111.9(2) | C(7) -N(5)-C(4) | 112.5(2) |
| C(7)-N(5)-C(6) | 115.5(2) | S(3) -C(2)-S(1) | 114.2(2) |
| N(5)-C(4)-S(3) | 116.1(2) | N(5) -C(6)-S(1) | 116.0(2) |
| C(8)-C(7)-N(5) | 113.8(2) | C(8)'-C(8)-C(7) | 114.4(3) |

**Compound 5.**

| | | | |
|---|---|---|---|
| S(1) -C(2) | 1.82(1) | S(1) -C(6) | 1.85(1) |
| S(3) -C(2) | 1.79(1) | S(3) -C(4) | 1.86(1) |
| S(10)-C(11) | 1.82(1) | S(10)-C(15) | 1.81(1) |
| S(12)-C(11) | 1.82(1) | S(12)-C(13) | 1.84(1) |
| N(5) -C(4) | 1.43(1) | N(5) -C(6) | 1.45(1) |
| N(5) -C(7) | 1.46(1) | N(14)-C(9) | 1.48(1) |
| N(14)-C(13) | 1.44(1) | N(14)-C(15) | 1.45(1) |
| C(7) -C(8) | 1.54(1) | C(8) -C(9) | 1.52(1) |

| | | | |
|---|---|---|---|
| C(6) -S(1) -C(2) | 97.1(5) | C(4) -S(3) -C(2) | 96.8(4) |
| C(15)-S(10)-C(11) | 96.7(5) | C(13)-S(12)-C(11) | 98.0(5) |
| C(6) -N(5) -C(4) | 111.0(8) | C(7) -N(5) -C(4) | 116.8(8) |
| C(7) -N(5) -C(6) | 113.4(8) | C(13)-N(14)-C(9) | 114.0(8) |
| C(15)-N(14)-C(9) | 114.3(7) | C(15)-N(14)-C(13) | 113.4(7) |
| S(3) -C(2) -S(1) | 113.2(5) | N(5) -C(4) -S(3) | 115.5(7) |
| N(5) -C(6) -S(1) | 115.3(7) | C(8) -C(7) -N(5) | 113.3(8) |
| C(9) -C(8) -C(7) | 111.7(8) | C(8) -C(9) -N(14) | 110.4(8) |
| S(12)-C(11)-S(10) | 111.7(6) | N(14)-C(13)-S(12) | 115.8(7) |
| N(14)-C(15)-S(10) | 117.7(7) | | |

**Compound 7.**

| | | | |
|---|---|---|---|
| N(5) -C(4) | 1.420(7) | C(2) -S(3) | 1.804(5) |
| N(5) -C(6) | 1.431(5) | C(2) -S(1) | 1.786(5) |
| N(5) -C(7) | 1.466(5) | C(6) -S(1) | 1.842(4) |
| C(4) -S(3) | 1.839(5) | C(9) -C(8) | 1.512(6) |
| C(12)-C(11) | 1.513(5) | C(9) -N(10) | 1.459(4) |
| C(12)-O(13) | 1.413(7) | C(11)-N(10) | 1.454(5) |
| C(15)-C(14) | 1.500(5) | C(14)-O(13) | 1.423(6) |
| C(15)-N(10) | 1.453(7) | C(7) -C(8) | 1.510(5) |

| | | | |
|---|---|---|---|
| C(4) -N(5) C(6) | 113.0(3) | C(15)-C(14)-O(13) | 111.5(4) |
| C(4) -N(5) -C(7) | 116.1(4) | C(12)-O(13)-C(14) | 110.8(3) |
| C(6) -N(5) -C(7) | 112.8(4) | C(4) -S(3) -C(2) | 97.6(2) |
| N(5) -C(4) -S(3) | 117.1(3) | N(5) -C(7) -C(8) | 114.4(4) |
| C(11)-C(12)-O(13) | 111.9(3) | C(2) -S(1) -C(6) | 97.9(2) |
| C(14)-C(15)-N(10) | 111.6(4) | C(9) -C(8) -C(7) | 113.0(4) |
| S(3) -C(2) -S(1) | 113.5(2) | C(15)-N(10)-C(9) | 112.8(3) |
| N(5) -C(6) -S(1) | 116.1(3) | C(15)-N(10)-C(11) | 109.2(3) |
| C(8) -C(9) -N(10) | 113.5(4) | C(9) -N(10)-C(11) | 110.0(3) |
| C(12)-C(11)-N(10) | 111.2(4) | | |

[a]Symmetry operations: ' = -x+1/2,y+1/2,1/2-z.

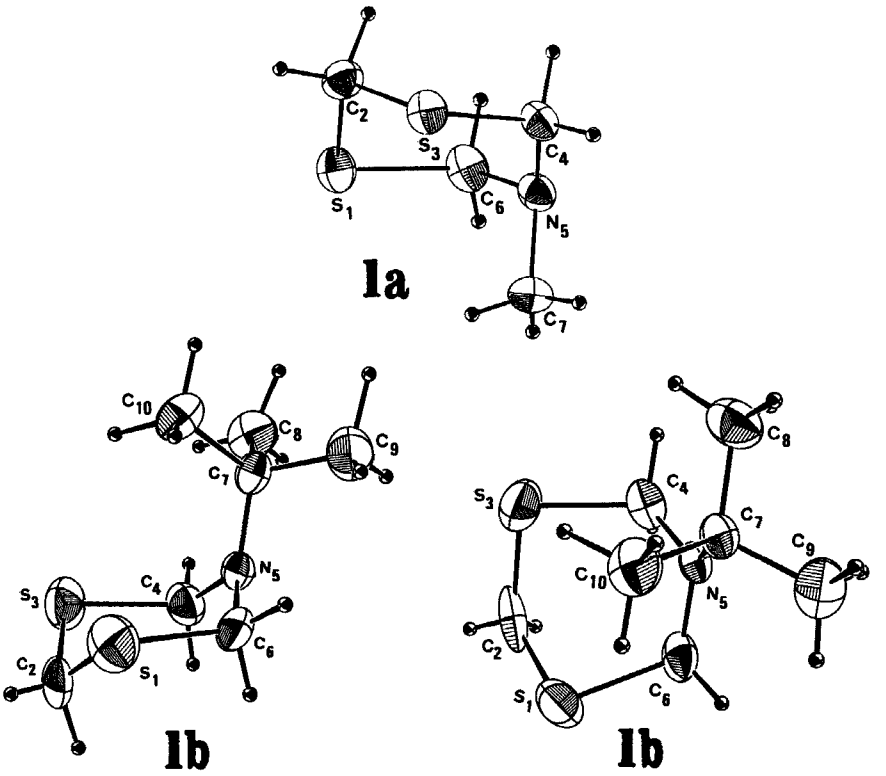



FIGURE 2 X-ray structure of compound **1a**, and two different views of the X-ray structure of **1b**.

This is a consequence of the repulsion effect between the methyl group and the axial sulfur lone pairs. This effect was also observed from the value of the torsional angle S(3)—C(4)—N(5)—C(7) = 65.71° and S(1)—C(6)—N(5)—C(7) = 66.88°. One of the hydrogen atoms (Ha) on the methyl group is directed towards C(2) through the axial sulfur lone pairs due to the staggered conformation of the C(7)—N(5) bond. The intracyclic nitrogen-carbon atom distances are slightly shorter than normal CN single bonds and this is also the case for the bond distance between the S atoms and C(2). The sulfur atoms have similar conformations and their axial lone pairs are parallel. The small C—S—C angle 97.3[2] and 97.8°[2] produced by the repulsion of the lone pairs of each sulfur atom is similar to that found for dimethyl sulfide (99.1°)[5a] and dihydrosulfide (92.1°).[5b] These small angles are compensated by the more open angles of the other atoms of the ring: S(1)—C(2)—S(3) (113.7°[2]); S(3)—C(4)—N(5) (115.7°[2]) and S(1)—C(6)—N(5) (116.0°[2]).

*Compound 1b*

5-*tert*-butyl-perhydro-1,3,5-dithiazine **1b** was also studied by Katritzky[2] and it was proposed that the N-substituent was in an axial position. But due to the strong steric effect produced by the *tert*-butyl it was interesting to investigate if the proposition was correct and if the chair conformation was maintained in spite of the strong steric strain. The X-ray diffraction study showed that as in **1a**, the molecule

was in a chair conformation (Figure 2). It is interesting that the molecule presents the same relationships of angles and bond lengths as in **1a**, the only difference between the two molecules being the nitrogen atom structure that is more planar in **1b**, the sum of the nitrogen angles values is 352° (75% of $sp^2$ hydridation). The bond lengths around nitrogen are similar to those of compound **1a**, N(5)—C(7) (1.472 [7] Å) is a longer bond than N(5)—C(4) (1.413 [7] Å) and N(5)—C(6) (1.421 [7] Å). The X-ray diffraction structure corresponds to the lowest energy conformer for the N(5)—C(4) bond that has a methyl group directed towards C(2). Two hydrogen atoms of this *endo* methyl are directed to the axial lone pair of the sulfur atoms and separated by a distance equal to the sum of their van der Waals radius (3.0 Å). The distance H(10b)—S(1) being 2.889 Å and H(10c)—S(2) 2.943 Å.

*Compound 2*

Compound **2** has been prepared in low yield (7%) from reaction of two equivalents of $NH_4OH$ with formaldehyde and sodium hydrosulfide hydrate in water. The structure of compound **2** was deduced from the elemental analysis, mass spectrum and from NMR studies. The exocyclic methylene group, C(7), presents a $^{13}C$ chemical shift characteristic of a carbon neighboring to a nitrogen and a sulfur atoms ($\delta_{observed}$ = 50.79 and $\delta_{calculated}$ = 48.6 ppm[6]). It is assumed by comparison with the other systems that the methylene carbon is in an axial position. In the mass spectrum the parent ion ($M^{+\cdot}$135, 100%) correspond to the exocyclic carbon sulfur bond fragmentation.

*Compound 3*

Compound **3** was formed from the reaction of one equivalent of $Na_4OH$ with formaldehyde and sodium hydrosulfide hydrate in water with a 10% yield. This molecule presents a methylene group between two nitrogen atoms, as can be deduced from its $^{13}C$ NMR chemical shift of $\delta$ = 64.76 ppm. This value is lower than expected (around 89 ppm[6]) and can be attributed to a double axial position. The structure was also established by comparison with the NMR data and the X-ray diffraction studies of compounds **1**, **4–6**. From the MM calculations it is observed that each exocyclic N—C bond presents a staggered conformation and that the rings are in perpendicular planes as shown in Figure 3.

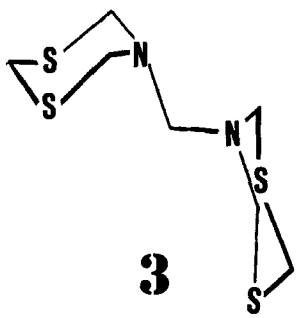
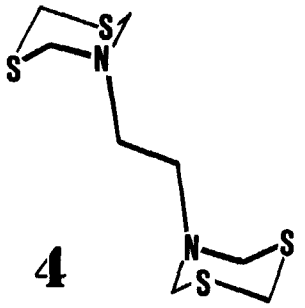
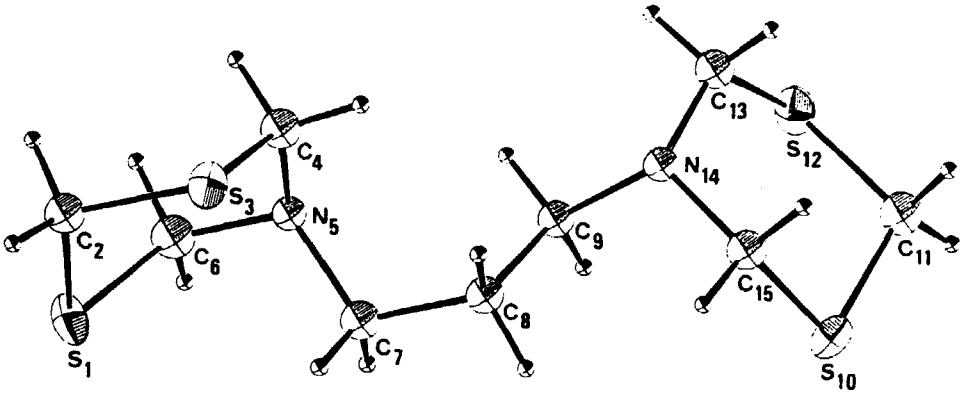



FIGURE 3 View of the more stable conformer of compound **3** obtained by molecular mechanics.




4

FIGURE 4 View of the more stable conformer of compound **4** obtained by molecular mechanics.




5

FIGURE 5 View of the X-ray structure of compound **5**.



*Compound 4*

Compound **4** has been prepared from the reaction of ethylenediamine, formaldehyde and sodium hydrosulfide hydrate in water in 20% yield. The lowest energy conformation (15.92 Kcal/mol) has the ethylenic chain in a staggered conformation, the Newman projections between the two ethylenic carbons showing the N—C—C—N bonds a dihedral angle of 180 degrees (Figure 4).

*Compound 5*

Compound **5** is formed in a similar reaction to the synthesis of **4** but using 1,3-propylenediamine, with a yield of 10%. The molecule has two heterocycles joined by a propylene group. The X-ray diffraction study shows a similar ring conformation as in compound **1** with the methylene groups attached to the nitrogen in an axial position (Figure 5). The bonds of the exocyclic chain have a staggered conformation. In the Newman projection of the N(5) and C(7) bond, C(8) is found between the nitrogen lone pair and C(4). The methylene groups at C(4) and C(8) have a steric interaction (the distance C(4) and C(8) is 2.968 [15] Å) stronger than that found between C(6) and C(8) (3.806) [15] Å), this interaction explains the more open

angle (116.8°[8]) between C(4)—N(5)—C(7) compared with that formed between C(6)—N(5)—C(7) (113.4°[8]). The effect of the proximity of the lone pair to C(8) is observed in its $^{13}C$ NMR chemical shift (28.86 ppm) which is shifted to low field compared with the equivalent carbon atom in compounds **6**, **7** or **8** (24.55 ppm).

*Compound 6*

Compound **6** was prepared from butylenediamine by the same method as **4** and **5**. The X-ray diffraction study gives similar results to those in compounds **1** and **5** (Figure 6). Only half of the molecule is present in the asymmetric unit. Molecule **6** presents a steric interaction between the methylene groups at C(6) and C(8) (their distance being 2.931 [3] Å while C(4) and C(8) have 3.777 [3] Å) which is also reflected in a more open angle for C(6)—N(5)—C(7) (115.5°[2]), when compared with C(4)—N(5)—C(7) (112.5°[2]). The difference between the X-ray diffraction study of compounds **5** and **6** and the MM calculations is that the nitrogn atoms in the crystalline structure have a greater $sp^2$ character than in the calculated one. Other features from the crystalline structure are also found in the MM calculations.



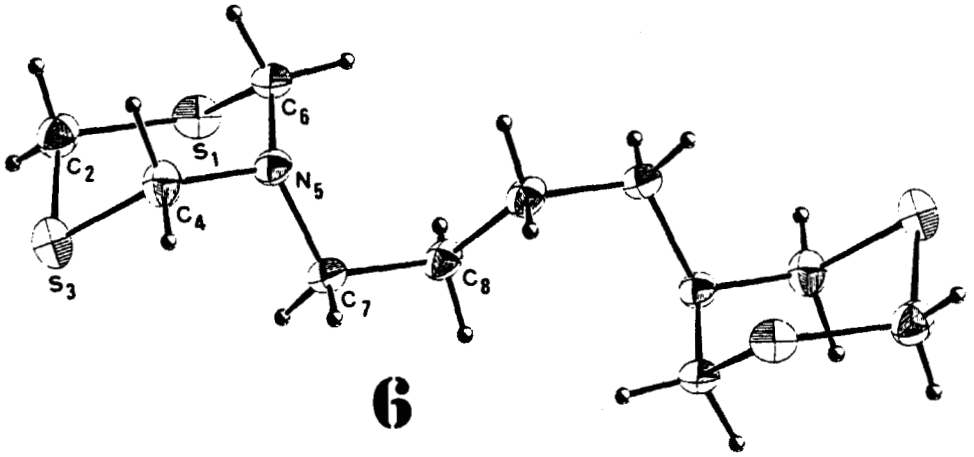



FIGURE 6 View of the X-ray structure of compound **6**.

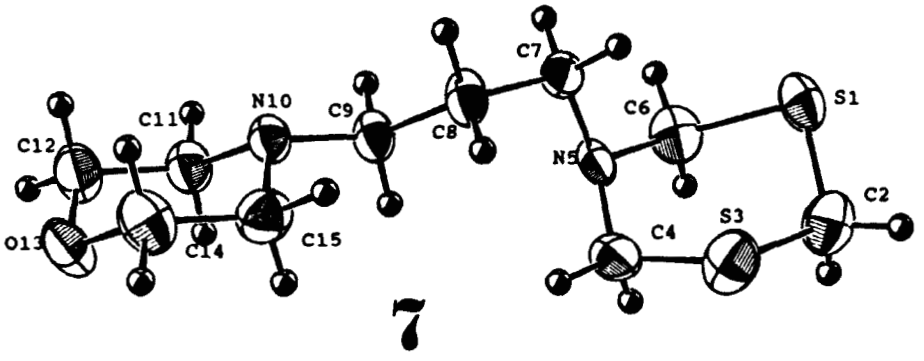



FIGURE 7 View of the X-ray structure of compound **7**.

*Compound 7*

Compound **7** was formed from the reaction of 3-aminopropylmorpholine, formaldehyde and sodium hydrosulfide hydrate in water in 15% yield. The methylene attached to the nitrogen of the dithiazine is in an axial position whereas the methylene attached to the morpholine is in an equatorial position, as has been found from the $^{13}C$ spectroscopic data and the X-ray diffraction study (Figure 7). The conformation of both rings is chair.

*Compound 8*

Compound **8** was prepared from 1,4-*bis*-(3-aminopropyl)piperazine in 15% yield. The axial position of the exocyclic methylene groups in the dihydrodithiazine and the equatorial position of the methylene groups attached to the piperidine ring are corroborated with $^{13}C$ NMR data.

In general it was found that the axial methylene groups bonded to dithiazine appear, in $^{13}C$ NMR, at $\delta$ = 45.2 ppm whereas the methylene groups bonded to the nitrogen atoms of the morpholine (**7**) or piperazine (**8**) are in an equatorial position (54.6 ppm).[6] In the $^1H$ NMR it is also possible to establish the nitrogen methylenic substituent position as equatorial as it appears at 2.4 ppm whereas in axial the chemical shift is 3.0 ppm. In general the structure of dithiazine agrees quite well with those obtained by molecular mechanics calculations.

These particular structures **3–8** could be very interesting for metal coordination because the relative position of the nitrogen lone pairs (axial or equatorial) will determine the way in which the heterocycles can coordinate. Studies on the coordination capabilities of these ligands towards several metals ions are presently being carried out.



## EXPERIMENTAL

I.R. spectra were measured as KBr pellets, on a Perkin Elmer 16F PC FT-IR spectrometer. NMR spectra were recorded by using the frequency of 270 or 90 for $^1H$ and 67.8 MHz for $^{13}C$, respectively. Chemical shifts are reported in $\delta$ units. Mass spectra were recorded on a Hewlett Packard 5989 mass spectrometer. Melting points are uncorrected.

N-Alkylperhydro-1,3,5-dithiazines **1a** and **1b** were prepared as described in Reference 7.

*N-Methylperhydrodithiazine* **1a**. M.p. 61–62°C (lit.[7] 65–66°C). I.R. (KBr) 2900, 1442, 1400, 1330, 1302, 1290, 1200, 1150 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 90.05 MHz, at 27°C) $\delta$ 4.39 (sbr, 4H, 2H-4 and 2H-6), 4.05 (sbr, 2H, 2H-2), 2.61 (sbr, 3H, 3H-7). $^{13}C$ NMR ($CDCl_3$, 67.8 MHz, at 27°C) $\delta$ 34.28 (C-2), 59.89 (C-4, C-6), 37.49 (C-7). MS (70 eV) m/z (%) $M^+$ 135(59), 89(31), 57(67), 42(100), 15(83).

*N-tert-butylperhydrodithiazine* **1b**. M.p. 44–45°C (lit.[2] 44–46°C). I.R (KBr) 3000, 2964, 1346, 1288, 1270, 1198, 1146, 1118, 1060 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 90.05 MHz, at 27°C) $\delta$ 4.68 (sbr, 4H, 2H-4 and 2H-6), 4.28 (sbr, 2H, 2H-2), 1.32 (sbr, 9H, 3H-8, 3H-9 and 3H-10). $^{13}C$ NMR ($CDCl_3$, 67.8 MHz, at 27°C) $\delta$ 35.06 (C-2), 54.26 (C-4, C-6), 55.60 (C-7), 29.77 (C-8, C-9 and C-10). MS (70eV) m/z (%) $M^+$ 177(100), 162(25), 98(52), 75(55), 57(87), 43(84), 42(78).

*General procedure for the synthesis of the bis-dithiazines.* One equivalent of the corresponding primary amine was added to 14 equivalents of aqueous formaldehyde (37%), and the mixture was stirred for 5 min. Another solution of 5 equivalents of $NaSH$-$H_2O$ in water was added, and the mixture was stirred 12 h at room temperature. Then, the solids were discarded by filtration and the remaining aqueous solution was extracted with $CH_2Cl_2$. The organic phase was dried with $Na_2SO_4$ and evaporated to give

the crude product. The new compounds were isolated and purified by chromatography or by crystallization as is indicated below.

*1,1'-Bis-[5-(Perhydro-1,3,5-dithiazinyl)]dimethylsulfide* **2** was prepared by the reaction of two equivalents of $NH_4OH$ following the general procedure. The crude product, a white solid, was recrystallized from $CH_2Cl_2$/hexane (30:70). Compound **2** was obtained in a 10% yield. M.p. 113–117°C. I.R (KBr) 3018, 2922, 1710, 1422, 1210, 1156 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 270.05 MHz, at 27°C) $\delta$ 4.16 (sbr, 2H, H-2), 4.52 (sbr, 4H, H-4 and H-6), 4.09 (sbr, 2H, H-7). $^{13}C$ NMR ($CDCl_3$, 67.8 Mhz, at 27°C) $\delta$ 33.78 (C-2), 56.71 (C-4, C-6), 50.79 (C-7). MS (70 ev) m/z 135(100). Anal. Calcd. for $C_8H_{16}N_2S_5$: C, 31.97; H, 5.36; N, 9.32. Found: C, 31.97; H, 5.27; N, 8.74.

*Bis-[5-(Perhydro-1,3,5-dithiazinyl)]methane* **3** was obtained from one equivalent of $NH_4OH$ following the general procedure. A gum was obtained, that was purified by a silica gel column chromatography with $CH_2Cl_2$/hexane (40:60). Compound **3** was obtained as a white solid in a 7% yield. M.p. 135–138°C. I.R (KBr) 3018, 2922, 1424, 1388, 1222, 1092 $cm^{-1}$. $^1H$ NMR (THF-$d_8$, 270.05 MHz, at 27°C) $\delta$ 4.10 (sbr, 2H, H-2), 4.45 (sbr, 4H, H-4 and H-6), 4.35 (s, 1H, $CH_2$); (THF-$d_8$, 270.05 MHz, at −40°C) $\delta$ 4.62 (d, 1H, $J$ = 13.9, H-2ax), 3.64 (dbr, 1H, $J$ = 13.9, H-2eq), 4.83 (d, 2H, $J$ = 13.0, H-4ax and H-6ax), 4.11 (dbr, 2H, $J$ = 13.0, H-4eq and H-6eq), 4.30 (s, 1H, H-7). $^{13}C$ NMR (THF-$d_8$, 67.8 MHz, at −40°C) $\delta$ 33.72 (C-2), 56.15 (C-4 and C-6), 64.76 (C-7). MS (70 eV) m/z (%) 134 (1), 121 (1), 85 (80), 83 (100). Anal. Calcd. for $C_7H_{14}N_2S_4$: C, 33.04; H, 5.54; N, 11.01. Found: C, 33.83; H, 5.58; N, 10.26.

*1,2-Bis-[5-(Perhydro-1,3,5-dithiazinyl)]ethane* **4** was obtained from the reaction of $(H_2N—CH_2)_2/CH_2O$/NaSH, following the general procedure. The crude product, a yellow solid, was washed with $CH_2Cl_2$ in order to eliminate the impurities. Compound **4** was obtained as a white solid in 20% yield. M.p. 182–184°C. I.R (KBr) 3000, 2886, 2880, 1458, 1435, 1414, 1382, 1344, 1269, 1190, 1090 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$, 90 MHz, at 27°C) $\delta$ 4.10 (sbr, 2H, H-2), 4.45 (sbr, 4H, H-4 and H-6), 3.20 (s, 2H, H-7). $^{13}C$ NMR (DMSO-$d_6$, 67.8 MHz, at 27°C) $\delta$ 32.45 (C-2), 57.17 (C-4 and C-6), 45.12 (C-7). MS (70 eV) m/z (%) 268 ($M^+$, 5), 189 (70), 134 (100), 42 (70). Anal. Calcd. for $C_8H_{16}N_2S_4(1/3\ H_2O)$: C, 33.76; H, 5.74; N, 9.85. Found: C, 33.96; H, 5.71; N, 10.08.

*1,3-Bis-[5-(Perhydro-1,3,5-dithiazinyl)]propane* **5** was obtained from $(H_2N—CH_2)_2CH_2/CH_2O$/NaSH, following the general procedure. After evaporation of the $CH_2Cl_2$, a gum was obtained. Compound **5** was recrystallized from a mixture of $CH_2Cl_2$/hexane (50:50) and obtained as colorless crystals in a 16% yield. M.p. (116–118°C. I.R (KBr) 2976, 2890, 1432, 1336, 1280, 1194, 1108, 1064 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 270.05 MHz, at 27°C) $\delta$ 4.10 (sbr, 2H, H-2), 4.43 (sbr, 4H, H-4 and H-6), 3.04 (dd, 2H, $J$ = 7.2, 7.5, H-7), 1.56 (td, 1H, $J$ = 7.2, 7.5, H-8); (THF-$d_8$, 270.05 MHz, at −55°C) $\delta$ 4.58 (d, 1H, $J$ = 13.2, H-2ax), 3.61 (dbr, 1H, $J$ = 13.2, H-2eq), 4.87 (d, 2H, $J$ = 13.2, H-4ax and H-6ax), 4.05 (d, 2H, $J$ = 13.2, H-4eq and H-6eq), 3.02 (dd, 2H, $J$ = 7.26, 6.6, H-7), 1.55 (td, 1H, $J$ = 6.6, 7.26, H-8). $^{13}C$ NMR ($CDCl_3$, 67.8 MHz, at 27°C) $\delta$ 33.91 (C-2), 58.22 (C-4 and C-6), 46.39 (C-7), 28.86 (C-8). MS (70 eV) m/z (%) 282 ($M^+$, 10), 235 (71), 42 (100). Anal. Calcd. for $C_9H_{18}N_2S_4$: C, 38.29; H, 6.38; N, 9.93. Found: C, 38.13; H, 6.34; N, 10.00.

*1,4-Bis-[5-(Perhydro-1,3,5-dithiazinyl)]butane* **6** was obtained from the reaction of $(H_2N—CH_2—CH_2)_2/CH_2O$/NaSH, following the general procedure. The solid yellow product obtained was washed with acetone (3 × 50 ml) and recrystallized from $CH_2Cl_2/CH_3OH$ (9:1). The compound **6** was obtained as colorless crystals in an 80% yield. M.p. 139–141°C. I.R (KBr) 2890, 2844, 1440, 1380, 1330, 1280, 1250, 1200, 1195 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 270.05 MHz, at 27°C) $\delta$ 4.10 (sbr, 2H, H-2), 4.43 (sbr, 4H, H-4 and H-6), 3.04 (m, 2H, H-7), 1.49 (m, 2H, H-8). $^{13}C$ NMR ($CDCl_3$, 67.8 MHz, at 27°C) $\delta$ 33.97 (C-2), 58.24 (C-4 and C-6), 48.51 (C-7), 24.55 (C-8). MS (70 eV) m/z (%) 296 ($M^+$, 24), 249 (75), 217 (98), 42 (100). Anal. Calcd. for $C_{10}H_{20}N_2S_4$: C, 40.54; H, 6.75; N, 9.46. Found: C, 40.37; H, 6.82; N, 9.48.

*1-[5-Perhydro-1,3,5-dithiazinyl)]-3-[5-(morpholinyl)]propane* **7** was formed with 4-(3-aminopropyl)morpholine/$CH_2O$/NaSH, following the general procedure. A white solid was obtained after evaporation of $CH_2Cl_2$. A slow recrystallization from $CH_2Cl_2$/hexane (1:3), gave compound **7** as a white solid in a 22% yield. M.p. 84–85°C. I.R (KBr) 3001, 2964, 2939, 2913, 2854, 2812, 1448, 1431, 1416, 1335, 1282, 1240, 1194, 1115, 1080, 1006, 962 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 270.05 MHz, at 27°C) $\delta$ 4.10 (sbr, 1H, H-2), 4.42 (sbr, 2H, H-4 and H-6), 3.06 (t, 1H, $J$ = 7.2, H-7), 1.63 (m, 1H, H-8), 2.40 (dd, 1H, $J$ = 7.26, 14.5, H-9), 3.71 (t, 2H, $J$ = 4.6, H-11 and H-15), 2.43 (t, 2H, $J$ = 4.6, H-12 and H-14); (THF-$d_8$, 270.05 MHz, at −90°C) $\delta$ 4.62 (d, 1H, $J$ = 12.9, H-2ax), 3.65 (dt, 1H, $J$ = 12.9, 2.4, H-2eq), 4.82 (d, 2H, $J$ = 12.9, H-4ax and H-6ax), 4.07 (dd, 2H, $J$ = 12.9, 2.4, H-4eq and H-6eq), 3.01 (t, 2H, $J$ = 7.08, H-7), 1.57 (quint, 2H, $J$ = 7.08, H-8), 2.28 (t, 2H, $J$ = 7.08, H-9), 2.70 (dbr,

2H, $J$ = 11.5, H-11eq and H-15eq), 1.94 (ddd, 2H, $J$ = 11.5, 11.0, 2.3, H-11ax and H-15ax), 3.69 (dbr, 2H, $J$ = 11.0, H-12eq and H-14eq), 3.44 (t, 2H, $J$ = 11.0, H-12ax), and H-14ax). $^{13}$C NMR (THF-$d_8$, 67.8 MHz, at −90°C) $\delta$ 33.82 (C-2), 58.19 (C-4, C-6), 46.81 (C-7), 24.55 (C-8), 57.35 (C-9), 54.68 (C-11, C-15), 67.42 (C-12, C-14). MS (70 eV) m/z (%) 248 ($M^+$, 11), 201 (97), 169 (88), 100 (100), 42 (75). Anal. Calcd. for $C_{10}H_{20}N_2OS_2$: C, 48.38; H, 8.06; N, 11.17. Found: C, 47.97; H, 8.04, N, 11.17.

*1,1'-[5-(Perhydro-1,3,5-dithiazinyl)]-3,3'-[N,N'-(piperazinyl)]propane* **8** was obtained from the reaction of 1,4-*bis*-(3-aminopropyl)piperazine/$CH_2O$/NaSH, following the general procedure. The green oil obtained from the reaction was recrystallized from a mixture of $CH_2Cl_2$/hexane (1:4). A crystalline colorless solid was obtained in 15% yield. M.p. 163–164°C. I.R (KBr) 2946, 2921, 2815, 1465, 1433, 1416, 1374, 1356, 1282, 1193, 1161, 1099 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 270.05 MHz, at 27°C) $\delta$ 4.10 (sbr, 2H, H-2), 4.42 (sbr, 4H, H-4 and H-6), 3.04 (t, 2H, $J$ = 7.2, H-7), 1.63 (quint, 2H, $J$ = 7.2, H-8), 2.38 (t, 2H, $J$ = 7.3, H-9), 2.48 (sbr, 4H, H-11, H-15). $^{13}$C NMR ($CDCl_3$, 67.8 MHz, at 27°C) $\delta$ 33.97 (C-2), 58.32 (C-4 and C-6), 46.99 (C-7), 24.55 (C-8), 56.13 (C-9), 53.24 (C-11 and C-15). MS (70 eV) m/z (%) 408 ($M^+$, 6), 58 (88), 44 (65), 42 (100). Anal. Calcd. for $C_{16}H_{32}N_4S_4$: C, 47.07; H, 7.84; N, 13.72. Found: C, 47.33; H, 7.90; N, 13.81.

*Crystal data.* Selected crystals were set up on an automatic diffractometer and 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[8] for **1a**, **5** and **6**, and PSISCAN for **1b** and **7**) were applied.

Computations for compounds **1a**, **5** and **6** were performed by using CRYSTALS[9] adapted on a Micro Vax II while those for **1b** and **7** were carried out using MOLEN.[10] Atomic form factors for neutral S, C, N, O and H were taken from Reference 11. Anomalous dispersion was taken into account (not in the case of compounds **1b** and **7**). Structures **1a**, **5** and **6** were solved by direct methods using the SHELX86 program.[12] **1a** and **7** was also solved by direct methods using MOLEN. Anisotropic temperature factors were introduced for all non-hydrogen atoms for all compounds but compound **5**. In that case the low number of data did not allow anisotropic refinement for C atoms. Hydrogen atoms were found on difference electron density maps. Their atomic coordinates were refined with an overall isotropic temperature factor except for compound **5** and **7**, in which 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 $\Sigma\, w(|F_0| - |F_c|)^2$, where $F_0$ and $F_c$ are observed and calculated structure factors, respectively. Unit weights were used. Models reached convergence with $R = \Sigma\, (||F_0| - |F_c||)/\Sigma\, |F_0|$ and $R_w = [\Sigma\, w(|F_0| - |F_c|)^2/\Sigma\, w(F_0)^2)^{1/2}$ having values listed in Table I. Critieria 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.

Atomic coordinates are given in Table II, and Table III contains interatomic distances and bond angles.

## ACKNOWLEDGEMENT

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