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Synthesis of thiadiazabicyclane and bis-1,3,5-dithiazinane by cyclothiomethylation of aliphatic diamines with CH_2O and H_2S

Vnira R. Akhmetova,[a] Ruslan A. Vagapov,[c] Guzel R. Nadyrgulova,[a,*] Tat'yana V. Tyumkina,[a] Zoya A. Starikova,[b] Mikhail Yu. Antipin,[b] Raikhana V. Kunakova[a,c] and Usein M. Dzhemilev[a]

[a]*Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 Prospekt Oktyabrya, 450075 Ufa, Russian Federation*
[b]*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov str., 119991 Moscow, Russian Federation*
[c]*Ufa State Academy of Economics and Service, 145 Chernyshevskii str., 450077 Ufa, Russian Federation*

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Abstract—Cyclocondensation of aliphatic diamines with CH_2O and H_2S (1:3:2 ratio, 0 °C) was carried out to give thiadiazabicyclanes and dithiadiazabicyclanes (1:6:4 ratio), which were previously difficult to synthesize. Symmetric α,ω-bis-1,3,5-dithiazinanes were synthesized at 80 °C by this reaction. The stereochemistry of thiadiazabicyclanes was assigned by ^1H and ^{13}C NMR spectroscopy and by theoretical DFT calculations, and of bis-dithiazinanes by X-ray diffraction study in the solid state.

1. Introduction

An aliphatic diamine cyclothiomethylation with CH_2O and NaHS to give symmetric bis-1,3,5-dithiazinane has been described.[1,2] The selective synthesis of 1,3,5-dithiazinanes and 1,3-thiazetidines based on ethylendiamine, CH_2O, and H_2S was carried out later.[3] The chemoselectivity of the reaction depends on the concentration and sequence of introduction of initial reagents to the reaction mixture.

To continue a study on aliphatic diamine cyclothiomethylation and design *N*,*S*-containing heterocycles of new types and practical interest[1,4] we have studied the influence of the structure of the initial aliphatic 1,2-diamines (**1a**,**b**) on the direction of its heterocyclization with CH_2O and H_2S. Ethylene- (**1a**), 1,2-propane- (**1b**), 1,3-propane- (**1c**), 1,4-butane- (**1d**), 1,5-pentane- (**1e**), and 1,6-hexane-(**1f**) diamines were used for the study. The reactions of diamines with H_2S and CH_2O were carried out at various temperatures because the reaction temperature sufficiently effected the direction of amine and hydrazine[5] cyclothiomethylation.

2. Results and discussion

The reaction of ethylenediamine[3] (**1a**) and 1,2-propanediamine (**1b**) with CH_2O and H_2S at 0 °C was stated to afford selectively 3-thia-1,5-diazabicyclo[3.2.1]octane (**2a**) and 6-methyl-3-thia-1,5-diazabicyclo[3.2.1]octane (**2b**) in 85 and 87% yields, respectively (Scheme 1, Table 1), while at 80 °C **1a** gave symmetric bis-1,3,5-dithiazinane **3a** in 65% yield, and **1b**—5-[2-(1,3,5-dithiazinane-5-yl)-1-methylethyl]-1,3,5-dithiazinane **3b** in 73% yield.

The observed chemoselectivity of the diamine cyclothiomethylation reaction versus reaction temperature is probably an effect of the conformational equilibrium shift of the initial 1,2-diamines (and related intermediates). According to literature data, ethylenediamine **1a** exists as mixture of conformers **1a′** and **1a″** with a predominance of synclinal (*sc*) type **1a′** (n=0.77) toward C–C bond in both gaseous phase[6] and aqueous solution,[7] from which *cis*-rotamer with NH···N type hydrogen bond is found to be more stable (Fig. 1).

The predomination of **1a′** was confirmed by means of both ab initio[8] and DFT B3LYP/6-31G(d,p) calculations, where $\Delta;E_{sc-ap}$=1.2 kcal mol^{-1}, $\varphi(N–C–C–N)$=57.7°. Substitution of the hydrogen atom at C(2) by a methyl group does not change conformational composition in 2-methylethylenediamine **1b** (ΔE_{sc-ap}=1.8 kcal mol^{-1}, $\varphi(N–C–C–N)$= 57.3°). Thereby, the shift of the equilibrium to synclinal

Keywords: Thiadiazabicyclane; bis-1,3,5-Dithiazinane; Cyclothiomethylation; Aliphatic diamines; *N*,*S*-Containing heterocycles; Formaldehyde; Hydrogen sulfide; X-ray crystal analysis.
* Corresponding author. Tel./fax: +7 3472 312750; e-mail: ink@anrb.ru

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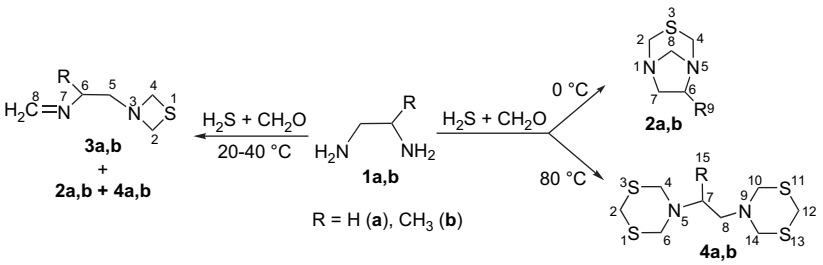


Scheme 1.

(*sc*) conformation with the hydrogen bond of NH–N type **1a′** at 0 °C suggests that the formation of the only product of 3-thia-1,5-diazabicyclo[3.2.1]octane (**2a**) proceeds according to the known principle of the least movement, i.e., the conformation of the product is defined by the conformation of the reacting isomer.[9]

Compounds **2a**,**b** were identified by means of (1D and 2D) ^{1}H and ^{13}C NMR spectroscopy. In 3-thia-1,5-diazabicyclo[3.2.1]octane (**2a**), carbon atoms C-2,4 and C-6,7 were shown to be magnetically equivalent in pairs. Therefore, the ^{13}C NMR spectrum of **2a** contains only three signals at 76.4, 58.0, and 51.1 ppm, which were assigned to C-8, C-2,4, and C-6,7, respectively. The configuration of the methyl group in **2b** was established by a comparison of chemical shifts of the bridge carbon atoms in nonsubstituted **2a** and methyl substituted **2b**. The upfield signal shift of bridge C-8 by 3.0 ppm in nonsubstituted bicyclane **2a** compared with the appropriate signal of **2b** may serve as a criterion for determining the structure of **2b** as *exo*-isomer on the basis of the similar effect of the 1,3-interaction in norbornane systems.[10] Compound **2b** was not described previously. Moreover, the signals of four carbon atoms are located in a narrow field at 57.0–59.0 ppm. Therefore, we carried out two-dimensional NMR experiments of homo- and heteronuclear correlation.

Table 1. Effect of temperature, initial reagent ratios, solvent on yield and composition of reaction products of cyclomethylation of **1a–f** diamines with CH_2O and H_2S

Diamine **1a–f**	T (°C)	Ratio	Solvent	Reaction products and yield (%)				
		Diamine: CH_2O:H_2S		**2**	**3**	**4**	**5**	**6**
1a	0	1:3:2	H_2O	54	—	—	—	—
		1:6:4		85	—	—	—	—
	20			21	7	42	—	—
	40			8	6	44	—	—
	80			—	5	50	—	—
1b	0	1:3:2	H_2O	70	—	—	—	—
		1:6:4		87	—	—	—	—
	20			46	5	3	—	—
	40			33	3	30	—	—
	80			—	—	73	—	—
1c	0	1:3:2	H_2O	49	—	—	—	—
			BuOH–H_2O	36	—	8	2	—
	80	1:6:4	H_2O	32	—	24	10	—
			H_2O	—	—	61	—	—
			BuOH–H_2O	—	—	74	—	—
1d	0	1:3:2	H_2O	37	—	5	—	—
			BuOH–H_2O	35	—	8	—	—
		1:6:4	H_2O	24	8	17	13	9
			BuOH–H_2O	28	2	25	—	2
	20		H_2O	27	12	34	—	8
			BuOH–H_2O	8	—	71	—	—
	40		H_2O	12	5	48	—	11
	80		H_2O	—	—	20	—	—
			BuOH–H_2O	—	—	82	—	—
1e	0	1:3:2	H_2O	21	—	8	2	—
			BuOH–H_2O	18	—	10	4	—
		1:6:4	H_2O	17	4	22	15	—
	20		H_2O	15	14	23	—	—
			MeOH–H_2O	25	10	10	5	—
			EtOH–H_2O	5	7	48	—	15
			BuOH–H_2O	—	—	72	—	7
	40		H_2O	9	12	31	—	—
	80		H_2O	—	—	42	—	—
			BuOH–H_2O	—	—	75	—	—
1f	0	1:3:2	H_2O	17	—	15	4	—
		1:6:4	H_2O	14	—	32	14	—
	80		H_2O	—	—	42	—	—
			BuOH–H_2O	—	—	64	—	—

The ^{1}H NMR spectrum exhibits the downfield doublets at 4.80 and 4.81 ppm, which are assigned to axial protons at the C-2 and C-4 carbon atoms. The insignificant difference of their chemical shifts is caused by the loss of symmetry due to the *exo*-methyl group at C-7. Equatorial protons at 3.50 ppm interact with geminal proton H_a (^{2}J=12.5 Hz) and, moreover, have long-range spin–spin interaction with bridge proton H_b (^{4}J=1.4 Hz). The analogous interactions are observed in nonsubstituted 3-thia-1,5-diazabicyclo[3.2.1]octane **2a** (Fig. 2).

The presence of long-range coupling between hydrogen atoms H_e-4,6 and H_b-8 in **2a** and **2b** points to their W-position. Therefore, the thiadiazine fragment exists preferably in a *chair* conformation in solution. Assignments of axial and equatorial protons were made on the basis of $^{4}J_{H4,6–H8}$ constant. In contrast with cyclohexanes with $\delta H_a < \delta H_e$ regularity, in **2a**,**b** systems we observed an inverse order of proton chemical shifts at C-2 and C-4, i.e., $\delta H_e < \delta H_a$ analogously to six-membered dithiazines.[11] Furthermore, a value of vicinal ^{3}J=4.8 Hz between the *endo*-oriented H-6 and H-7 protons evidences for the *exo*-configuration of the methyl group in **2b**, whereas ^{3}J (H-6_{exo}-H-7_{exo}) should be 9 Hz.[12]

Thus, the obtained spectral characteristics evidence a formation of 6-*exo*-methyl-3-thia-1,5-diazabicyclo[3.2.1]octane **2b**. This fact may be additionally explained by DFT-calculation B3LYP/6-31G(d,p), which showed that the *endo*-isomer is less energetically stable by 2.0 kcal mol^{-1}.

Cyclothiomethylation of **1a**,**b** at 20–40 °C gives a mixture of **2a**,**b** and **3a**,**b** together with 3-(2-methylideneaminoethyl)-1,3-thiazetidines (**4a**,**b**) (Scheme 1). The latter were

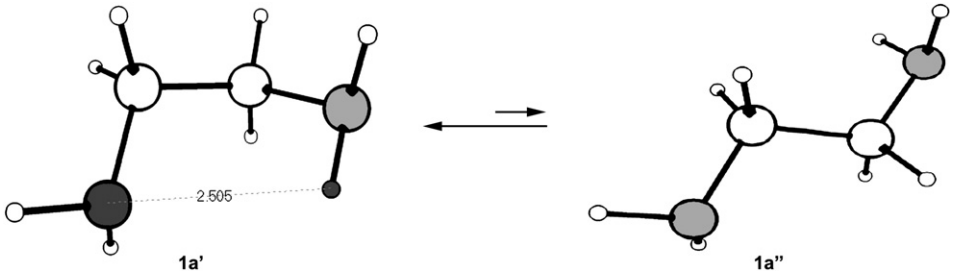


Figure 1. Conformation equilibrium in **1a**.

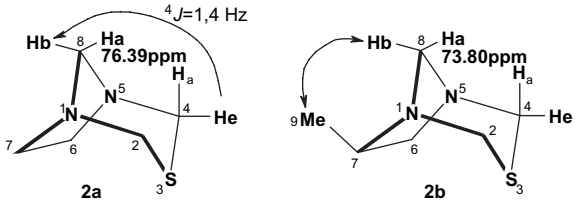


Figure 2. Criteria of determination of configuration Me-group in **2b** and *chair* conformation thiadiazine cycle in compounds of **2a** and **2b**.

observed by GC–MS. Mass spectra of **4a**,**b** contain peaks of molecular ions $[M]^+$ with *m*/*z* 130 **4a** and 144 **4b**.

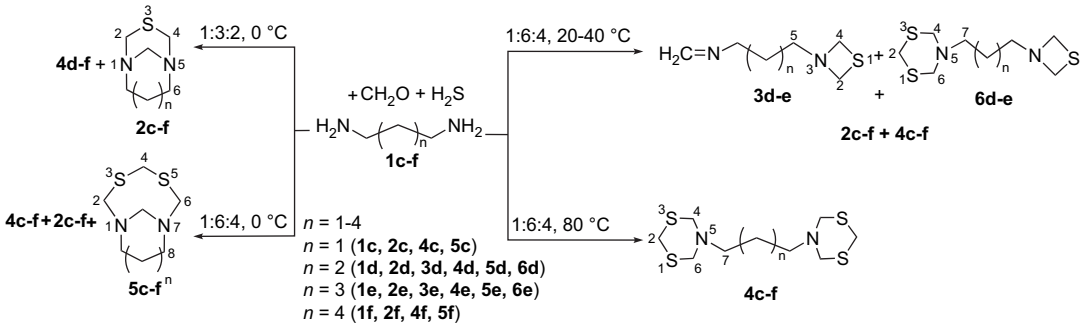
The analogous regularity was observed in cyclothiomethylation of 1,3-propane- (**1c**), 1,4-butane- (**1d**), 1,5-pentane- (**1e**), and 1,6-hexane-(**1f**) diamines. Under the chosen conditions at 0 °C (**1c–f**:CH_2O:H_2S, 1:3:2) 3-thia-1,5-diazabicyclo[3.3.1]nonane (**2c**), 3-thia-1,5-diazabicyclo[4.3.1]decane (**2d**), 3-thia-1,5-diazabicyclo[5.3.1]undecane (**2e**) and 3-thia-1,5-diazabicyclo[6.3.1]dodecane (**2f**) were produced (Scheme 2, Table 1). The structure and stereochemistry of the latter were identified by ^{1}H and ^{13}C NMR spectroscopy.

At 0 °C and ratio **1c–f**:CH_2O:H_2S=1:6:4, a formation of thiadiazabicyclanes **2c–f** and dithiadiazabicyclanes **5c–f** (~2–14%) was observed, the latter were identified by GC–MS. Reaction of **1e–f** with H_2S and CH_2O at 1:6:4 ratio at 80 °C temperature gave 5-[3-(1,3,5-dithiazinane-5-yl)-propyl]-1,3,5-dithiazinane (**3c**), 5-[4-(1,3,5-dithiazinane-5-yl)butyl]-1,3,5-dithiazinane (**3f**), 5-[5-(1,3,5-dithiazinane-5-yl)pentyl]-1,3,5-dithiazinane (**3e**), and 5-[6-(1,3,5-dithiazinane-5-yl)hexyl]-1,3,5-dithiazinane (**3f**), respectively (Scheme 2, Table 1).

At 20–40 °C a thiomethylation of **1e–f** diamines proceeds nonselectively. Thus, 1,4-butanediamine (**1d**) along with **2d** and **3d** forms bis-adducts 3-(4-methylenaminobutyl)-1,3-thiazetidine (**4d**) and 5-[4-(1,3-thiazetidine-3-yl)butyl]-1,3,5-dithiazinane (**6d**) (Table 1). In all thiomethylation reactions of aliphatic diamines, the formation of trace amounts of trithiolane and tetrathiepane (<5%) was observed together with major products **2a–f** and **3a–f**.

The ^{1}H NMR spectrum of **2c** showed two doublets with ^2J=13.0 Hz of an AB-system of the bridge protons analogously to those of **2a** and **2b**. However, these resonances are overlapped with the signals of magnetically equivalent equatorial protons at C-2 and C-4 of thiadiazine fragment with loss of information about NMR parameters. We used the double resonance method with irradiating the downfield doublet at δ_H=5.21 ppm of axial protons H_a-2 and H_a-4. By the NMR experiment the chemical shifts of H_a-9 at δ=4.18 ppm and H_b-9 at δ 4.08 ppm protons and W-coupling constant between H_e-2–H_b-9 of ^4J=1.8 Hz as in **2a** and **2b** structures were established (Fig. 3). Therefore, a *chair* conformation of thiadiazine cycle of 3-thia-1,5-diazabicyclo[3.3.1]nonane **2c** has been adopted. The *chair–chair* conformation of bicyclic system in solution was determined on the basis of interaction between H_a-6 and H_a-7 with large axial–axial coupling constant ($^3J_{aa}$=12.7 Hz). This is the preferred comformation for 1,5-dithia-3,7-diazabicyclo[3.3.1]nonane in solution and in the solid state.[13] The configuration of double *chair* was confirmed by DFT-calculations also. The *chair–chair* conformation **A** (Fig. 3) is more energetically favorable than **B** with boat disposition of the second ring (relative energies of conformers in kcal mol^{-1} are given in the brackets).

The *double chair* type conformation in derivatives of 3-azabicyclo[3.3.1]nonane was established on the basis of a difference of chemical shifts $\Delta\delta_{He-Ha} \approx 1.2$ ppm at C-7.[14,15] It was shown that a $\Delta\delta_{He-Ha}$ criterion is not used for the identification of bicyclic configuration of 3-thia-1,5-



Scheme 2.

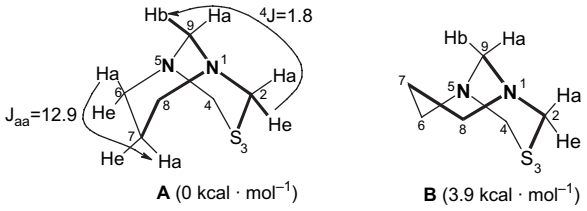


Figure 3. Criteria of determination *double chair* based on NMR coupling constants. Relative energies of found stable conformations of compound **2c**, calculated by B3LYP-method.

diazabicyclo[3.3.1]nonane system (**2c**), because the protons in ^{1}H NMR spectrum provide the only multiplet. Probably, it deals with a distance between heteroatom and H_a-7 in bicyclic systems. In optimized by DFT calculations structure conformation **A** S···H_a-7 of 2.75 Å is more than distance N···H_a(7) (2.57 Å) in the derivatives of 3-azabicyclo[3.3.1]-nonane.[16]

The constant ^4J=1.8 Hz between bridge and equatorial protons H-2 and H-4 was observed in the molecular system of 3-thia-1,5-diazabicyclo[4.3.1]decane **2d**. Therefore, a thiadiazine fragment exists as a *chair* conformation. We showed by B3LYP/6-31G(d,p) method that the second cycle can exist in three possible stable conformations, namely **C**, **D**, and **E** (Fig. 4). The results of DFT calculations of energy showed a relative energetic predominance of 2.7 kcal mol^{-1} for conformations **C** over **D**, and of 3.0 kcal mol^{-1} over **E**.

In the case of symmetric structures **D** and **E** the magnetic equivalence in a pair of axial and equatorial H-2 and H-4 protons must take place. However, the ^{1}H NMR spectrum of **2d** contains magnetically nonequivalent ($\Delta\delta$=0.01 ppm) signals of these protons. Therefore, on the basis of DFT calculations and ^{1}H NMR data the conformation **C** of 3-thia-1,5-diazabicyclo[4.3.1]decane is preferred in the solution. Assignments of signals were carried out on the basis of spectrum of COSY HH.

For all compounds synthesized the corresponding molecular ions are observed in mass spectra, besides the presence of sulfur atoms containing 4% of ^{34}S isotope and its amount in a molecule is correlated with the intensity of $[M+2]^+$ peaks with respect to the corresponding peak of molecular ion $[M]^+$.[17]

The peaks of molecular ions $[M]^+$ with *m*/*z* 190 (**5c**), 204 $[M]^+$ (**5d**), 218 (**5e**), 232 (**5f**) and characteristic fragments $[M-SH]^+$ 157 (**5c**), 171 (**5d**), 185 (**5e**), 199 (**5f**); $[M-SCH_2S]^+$ 111 (**5c**), 125 (**5d**), 139 (**5e**), 153 (**5f**) were observed in mass spectra of compounds **5c–f**. Mass spectra of **4e**,**d** contain peaks of molecular ions $[M]^+$ with *m*/*z* 158 (**4e**), 171 $[M-H]^+$ (**4d**) and fragments $[M-SH]^+$ 125 (**4e**), 139 (**4f**); $[M-NCH_2SCH_2]^+$ 84 (**4e**), 98 (**4f**). Mass spectra of **6d**,**e** contain peaks of molecular ions $[M]^+$ with *m*/*z* 250, 264 and fragments $[M-SH]^+$ 217 (**6d**), 231 (**6e**), $[M-SCH_2SH]^+$ 171 (**6d**), 185 (**6e**).

The bis-1,3,5-dithiazinanes **3a–f** were identified by ^{1}H and ^{13}C NMR spectroscopy methods by a comparison with previously synthesized derivatives,[3–6] and with a calculation of the known heteroatom increments.[18] The broad singlet of methylene protons N–CH_2–S in ^{1}H NMR spectrum in solution at room temperature evidences for the free inversion of dithiazine cycle.

X-ray diffraction study of compounds **3c**,**d** was carried out to establish the compound structure in the solid state (Figs. 5 and 6). In a crystal **3c** the molecule has two 1,3,5-dithiazinane cycles of *chair* type conformation in *trans*-position with respect to the lone electron pairs of nitrogen atoms with an axial position (Fig. 5). A conformation of six-membered cycles was shown to be c*hair* with an axial position of trimethylene chain. An anomeric effect was caused by the interaction between the nitrogen atom lone electron pair and σ-loosening orbitals of C–S bond,[19,20] and by unfavorable dipole–dipole interactions between nitrogen and sulfur atoms.[21,22] Molecule **3c** form crystallohydrate due to a hydrogen bond N1···HOH···N1B.

Analogously, the monomolecule of **3d** has two 1,3,5-dithiazinane cycles of *chair* type conformation in *trans*-position with respect to the lone electron pairs of nitrogen atoms with an axial position (Fig. 6). Molecules of compound **3d** are joined in chains due to attractive dipole–dipole interactions: S···S with a distance equal to 3.5077(4)Å, a value of the latter is less than a sum of Van-der-Waals radii (3.68Å).[23] In the crystal, the chains are packed in layers.

The study on the cyclomethylation reaction of aliphatic diamines with CH_2O and H_2S showed an increase in the length of hydrocarbon chain between amine groups that causes a decrease of selectivity of the formation of thiadiazabicyclanes **2a–f** and bis-dithiazinanes **4a–f**. It should be noted that at 80 °C in aqueous solution butane- (**1d**), pentane- (**1e**), hexane-(**1f**) diamines with H_2S and CH_2O gave hardly soluble cyclooligomers together with **3d–f**. The selective synthesis of bis-dithiazinanes **3d–f** was found to proceed in butanol at 80 °C.

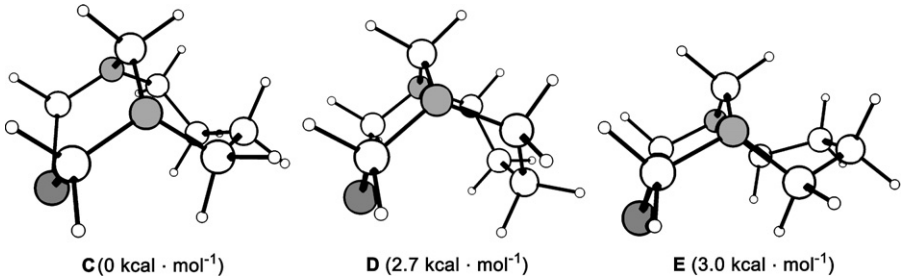


Figure 4. Optimized geometries of stable conformations of compound **2d** and their relative energy calculated at the DFT-level (B3LYP).

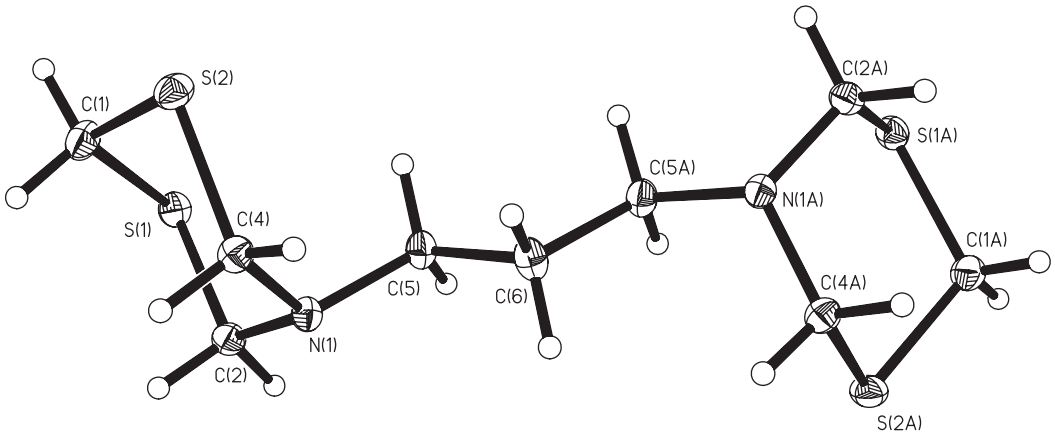


Figure 5. Molecular structure of **4c** in crystal.

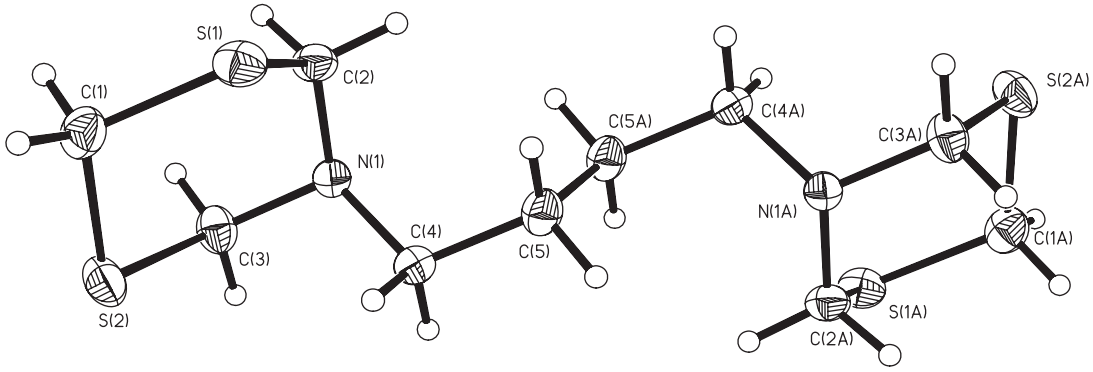


Figure 6. Molecular structure of **4d** in crystal.

3. Conclusion

Thus, cyclothiomethylation of aliphatic diamines with CH_2O and H_2S at 0 °C leads to thiadiazabicyclanes **2a–f** in 27–87% yields, and at 80 °C to bis-1,3,5-dithiazinanes **3a–f** in 50–82% yields (for **1d–f** in BuOH).

The product 6-*exo*-methyl-3-thia-1,5-diazabicyclo[3.2.1]octane (**2b**) was formed stereoselectively under the reaction conditions by the interaction between 1,2-propanediamine, CH_2O, and H_2S (1:3:2 ratio, 0 °C). The stereochemistry of thiazabicyclanes was determined by ^1H and ^{13}C NMR spectroscopy: the thiadiazine cycle of **2a–d** has a *chair*-shape conformation, and 3-thia-1,5-diazabicyclo[3.3.1]nonane (**2c**)—the conformation of *chair–chair*. These results were confirmed by theoretical DFT calculations by B3LYP/6-31G(d,p) method. X-ray difraction studies of 5-[3-(1,3,5-dithiazinane-5-yl)propyl]-1,3,5-dithiazinane (**3c**) and 5-[4-(1,3,5-dithiazinane-5-yl)butyl]-1,3,5-dithiazinane (**3d**) showed that the six-membered rings have *chair* conformations with axial positions of the tri(tetra)methylene chain.

4. Experimental

4.1. General

The ^1H NMR spectra of compounds **2a**,**b**,**c**,**d** and **3c**,**d**,**e** were recorded on spectrometer Bruker AH-300.47 (300 MHz), ^{13}C NMR—on spectrometer Jeol FX 90Q (22.50 MHz), internal standard—Me_4Si, solvent—$CDC1_3$ and DMSO-d_6. The IR-spectra were recorded on Specord 75IR in suspension in vaseline oil. The GC–mass spectra were obtained on Finigan 4021 (70 eV). Elemental analysis of C, H, N, S samples was determined on element analysator of Karlo Erba, model 1106. A barbotage of hydrogen sulfide was carried out with the use of peristaltic pump ANP-10. Melting points were determined on Kofler unit. An individuality and a purity of synthesized compounds were controlled with the use of TLC on Silufol UV-254 plates, I_2 was used as developer.

Quantum-chemical calculations were carried out with Gaussian 98 program by DFT method with three-parameter inverse-correlation potential B3LYP. Basis set 6-31 G was used. A total optimization of geometry was carried out and energetic characteristics including normal vibration frequencies were determined. The calculated vibration frequencies characterize optimized frequencies as minimum (a number of negative eigen values of gessian in the point N_{imag}=0).

4.2. Total procedure for cyclothiomethylation of aliphatic diamines

The calculated amount of 37% formaline (2.21 mL, 30 mmol) or (4.42 mL, 60 mmol) were charged to a three-neck flask equipped with stirrer and barbotager thermostated

at the chosen temperature, hydrogen sulfide (prepared in excess amount from Na_2S and HCl) was barbotaged to give CH_2O–H_2S mixture in 3:2 or 6:4 ratio. Then 10 mmol of diamine (1,2-ethylene- **1a**, 1,2-propane- **1b**, 1,3-propane- **1c**, 1,4-butane- **1d**, 1,5-pentane- **1e**, and 1,6-hexane-**1f** diamines) was added into the reaction mixture. When the reaction proceeded in a solvent, diamine was dissolved in 1:5 ratio and a solution was added at room temperature. The mixture was stirred for 3 h at chosen temperature (0, 20, 40, 80 °C). The product mixture was extracted with chloroform, dried ($CaCl_2$), concentrated. The solid product was filtered.

4.2.1. 3-Thia-1,5-diazabicyclo[3.2.1]octane (2a). Yellow oil, yield 1.1 g, 85%, R_f 0.24 (eluent hexane–ethylacetate, 4:3); IR ν_{max} 750 (C–S), 1140 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.70–2.81 (m, 2H, H-6$_{endo}$, H-7$_{endo}$), 3.21–3.35 (m, 2H, H-6$_{exo}$, H-7$_{exo}$), 3.52 (dd, 2H, H_e-2, H_e-4, ^2J=11.2, ^4J=1.4 Hz), 4.08 (dt, 1H, H_b-8, ^2J=10.9, ^4J=1.4 Hz), 4.65 (d, 2H, H_a-2, H_a-4, ^2J=12.5 Hz); ^{13}C NMR ($CDCl_3$): δ 50.1 (H-6,7), 57.2 (H-2,4), 75.8 (H-8). MS *m/z* (rel int.): 130 $[M]^+$ (100), 97 $[M-SH]^+$ (95), 56 $[(CH_2)_2NCH_2]^+$ (77), 42 $[CH_2CH_2N]^+$ (80). Anal. Calcd for $C_5H_{10}N_2S$: S, 24.63; H, 7.74; C, 46.10; N, 21.51. Found S, 25.29; H, 7.59; C, 45.57; N, 20.47.

4.2.2. *exo*-6-Methyl-3-thia-1,5-diazabicyclo[3.2.1]octane (2b). Deep-yellow oil, yield 1.25 g, 87%, R_f 0.17 (eluent hexane–ethylacetate, 2:5); IR ν_{max} 750 (C–S), 1150 (C–N) 1470 (CH_3) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91 (d, 3H-9), ^3J=6.8 Hz), 2.38 (dd, 1H, H-7$_{endo}$, ^2J=12.0, ^3J=4.8 Hz), 3.34–3.44 (m, 2H, H_a-8, H-7$_{exo}$), 3.48 (dd, 1H, H_e-2, ^2J=12.5, ^4J=1.4 Hz), 3.52 (dd, 1H, H_e-4, ^2J=12.5, ^4J=1.4 Hz), 3.62 (m, 1H, H-6$_{endo}$), 3.90 (dt, H_b-8, ^2J=11.1, ^4J=1.4 Hz), 4.59, 4.60 (d, 2H, H_a-2, H_a-4, ^2J=12.5 Hz); ^{13}C NMR ($CDCl_3$): δ 19.6 (C-9), 57.2 (C-6), 57.4 (C-4), 57.7 (C-2), 59.0 (C-7), 74.0 (C-8). MS *m/z* (rel int.): 144 (64) $[M]^+$, 111 (100) $[M-SH]^+$, 69 (36) $[CH_2CHNCH_2N]^+$, 56 (60) $[CH_2CHN(CH_2)]^+$, 42 (90) $[CH_2CHCH_3]^+$. Anal. Calcd for $C_6H_{13}N_2S$: S, 22.23; H, 8.39; C, 49.96; N, 19.42. Found: S, 23.17; H, 8.07; C, 50.31; N, 18.11.

4.2.3. 3-Thia-1,5-diazabicyclo[3.3.1]nonane (2c). Colourless oil, yield 0.7 g, 49%, R_f 0.25 (eluent hexane–ethylacetate, 1:4); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.10–1.40 (m, 2H, H-7), 3.32 (ddd, 2H, H_e-6, H_e-8, ^2J=12.9, ^3J=6.3, $^3J_{e-e}$=2.0 Hz), 3.45 (td, 2H, H_a-6, H_a-8, $^2J \approx {}^3J_{a-a}$=12.9, $^3J_{a-e}$=5.3 Hz), 4.09 (dt, 1H, H_b-9, ^2J=13.0, ^4J=1.8 Hz), 4.17 (dd, 2H, H_e-2, H_e-4, ^2J=12.7, ^4J=1.8 Hz), 4.18 (d, 1H, H_a-9, ^2J=13.0 Hz), 5.21 (d, 2H, H_a-2, H_a-4, ^2J=12.7 Hz); ^{13}C NMR ($CDCl_3$): δ 22.1 (C-7), 51.0 (C-6,8), 55.9 (C-2,4), 69.5 (C-9). MS *m/z* (rel int.): 144 $[M]^+$ (76), 111 $[M-SH]^+$ (100), 97 $[M-CH_2SH]^+$ (71), 82 $[M-(CH_2)_3SH]^+$ (11), 70 $[N(CH_2)_3N]^+$ (33), 56 $[N(CH_2)_3]^+$ (19), 42 $[(CH_2)_3]^+$ (44). Anal. Calcd for $C_5H_{10}N_2S$: S, 22.29; H, 7.54; C, 48.59; N, 18.45. Found: S, 22.23; H, 8.39; C, 49.96; N, 19.42.

4.2.4. 3-Thia-1,5-diazabicyclo[4.3.1]decane (2d). Colorless oil, yield 0.58 g, 37%, R_f 0.27 (eluent hexane–ethylacetate, 2:1); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.68–1.71 (m, 2H, H_a-7, H_a-8), 2.22–2.39 (m, 2H, H_b-7, H_b-8), 2.92–3.10 (m, 4H, H-6, H-9), 3.94 (dd, 2H, H_e-2, H_e-4, ^2J=13.0, ^4J=1.8 Hz), 4.01 (dm, 1H, H_b-10, ^2J=14.4, ^4J=1.8 Hz), 4.18 (d, 1H, H_a-10, ^2J=14.4 Hz), 4.97 (d, 2H, H_a-2, H_a-4, ^2J=13.0 Hz); ^{13}C NMR ($CDCl_3$): δ 28.7 (C-8,7), 49.3 (C-9,6), 59.0 (C-2,4), 67.8 (C-10). MS, *m/z* (rel int.):158 (98) $[M]^+$, 125 (100) $[M-SH]^+$, 97 (89) $[M-(CH_2)_2SH]^+$, 84 (90) $[M-CH_2SCH_2N]^+$, 70 (81) $[(CH_2)_4N]^+$, 42 (92) $[(CH_2)_3]^+$. Anal. Calcd for $C_7H_{14}N_2S$: S, 20.26; H, 8.92; C, 53.12; N, 17.70. Found: S, 21.3; H, 8.54; C, 50.95; N, 16.95.

4.2.5. 3-Thia-1,5-diazabicyclo[5.3.1]undecane (2e). Deep-brown oil, yield 0.43 g, 25%, R_f 0.32 (eluent hexane–ethylacetate, 3:1); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.20 (m, 5H, H-7,8,9), 2.88 (m, 4H, H-6,10), 3.80–4.50 (m, 6H, H-2,4,11);[†] ^{13}C NMR ($CDCl_3$): δ 25.1 (C-8), 28.3 (C-7,9), 51.9 (C-6,10), 56.0 (C-2,4), 73.5 (C-11); MS *m/z* (rel int.):172 (20) $[M]^+$, 139 (24) $[M-SH]^+$, 111 (96) $[M-NCH_2SH]^+$, 98 (44) $[M-CH_2SCH_2N]^+$, 84 (43) $[(CH_2)_5N]^+$, 70 (45) $[(CH_2)_5]^+$, 56 (30) $[(CH_2)_4]^+$, 42 (100) $[(CH_2)_3]^+$. Anal. Calcd for $C_8H_{16}N_2S$: S, 18.61; H, 9.36; C, 55.77; N, 16.26. Found: S, 19.63; H, 8.89; C, 53.84; N, 15.43.

4.2.6. 3-Thia-1,5-diazabicyclo[6.3.1]dodecane (2f). Colorless oil, yield 0.32 g, 17%, R_f 0.37 (eluent hexane–ethylacetate, 4:1); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.10 (br s, 8H, H-7–10), 2.43 (br s, 4H, H-6,11), 3.85–4.17 (m, 6H, H-2,4,6);[†] ^{13}C NMR ($CDCl_3$): δ 28.0 (C-9,10), 33.5 (C-8,11), 52.6 (C-7,12), 56.4 (C-2,6), 78.5 (C-4); MS *m/z* (rel int.):186 (15) $[M]^+$, 153 (26) $[M-SH]^+$, 125 (81) $[M-NCH_2SH]^+$, 111 (32) $[M-CH_2NCH_2SH]^+$, 84 (54) $[(CH_2)_5N]^+$, 70 (41) $[(CH_2)_5]^+$, 56 (25) $[(CH_2)_4]^+$, 42 (100) $[(CH_2)_3]^+$. Anal. Calcd for $C_9H_{18}N_2S$: S, 17.21; H, 9.74; C, 58.02; N, 15.04. Found: S, 17.35; H, 8.97; C, 57.74; N, 14.79.

4.2.7. 5-(1,3,5-Dithiazinane-5-yl)ethyl-1,3,5-dithiazinane (3a).[1,3] White crystal, yield 1.34 g, 50%, mp 179–180 °C.[3]

4.2.8. 5-[2-(1,3,5-Dithiazinane-5-yl)-1-methylethyl-1,3,5-dithiazinane (3b). White crystal, yield 2.45 g, 87%, mp 94–95 °C, R_f 0.78 (eluent hexane–ethylacetate, 2:5); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.30 (d, 3H, H-15, ^3J=6.4 Hz), 2.91 (dd, 1H, H_a-8, ^2J=13.5, ^3J=6.3 Hz), 3.28 (dd, 1H, H_b-8, ^2J=13.5, ^3J=6.3 Hz), 3.74 (m, 1H, H-7), 4.15 (br s, 4H, H-2,12), 4.58 (br s, 8H, H-4,6,10,14); ^{13}C NMR ($CDCl_3$): δ 17.0 (C-15), 33.8 (C-2), 33.8 (C-12), 48.7 (C-7), 53.2 (C-8), 56.7 (C-4,6), 59.4 (C-10,14); MS *m/z* (rel int.): 282 $[M]^+$ (6), 235 $[M-CH_2-SH]^+$ (36), 203 $[M-SCH_2SH]^+$ (6), 148 $[M-CH_2-NCH_2SCH_2SCH_2]^+$ (100), 134 $[CH_2NCH_2SCH_2SCH_2]^+$ (8), 102 $[CH_2SCH_2N(CH_2)_2]^+$ (13), 70 $[NCH_2CHNCH_3]^+$ (12), 56 $[N(CH_2)_3]^+$ (29), 42 $[(CH_2)_3]^+$ (24). Anal. Calcd for $C_9H_{18}N_2S_4$: S, 45.4; H, 6.42; C, 38.26; N, 9.92. Found: S, 45.37; H, 6.23; C, 37.91; N, 9.62.

4.2.9. 5-[2-(1,3,5-Dithiazinane-5-yl)propyl]-1,3,5-dithiazinane (3c).[2] White crystal, yield 2.08 g, 74%, mp 132–133 °C, R_f 0.74 (eluent hexane–ethylacetate, 1:4); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.53

[†] This signals of compounds **2e**,**f** and **4e**,**f** is overlapped.

(q, 2H, H-8, ^3J=6.3 Hz), 3.07 (t, 4H, H-7,9, ^3J=6.3 Hz), 4.05 (s, 4H, H-2,13), 4.41 (s, 8H, H-2,4,11,15); ^{13}C NMR ($CDCl_3$): δ 24.5 (C-8), 34.0 (C-2,13), 46.6 (C-7,9), 58.3 (C-4,6,11,15); MS *m/z* (rel int.): 282 $[M]^+$ (7), 235 $[M-SH]^+$ (100), 203 $[M-SCH_2SH]^+$ (39), 125 $[CHCH_2N(CH_2)_3N(CH_2)_2]^+$ (28), 111 $[CHN(CH_2)_3N(CH_2)_2]^+$ (18), 70 $[N(CH_2)_3N]^+$ (17), 42 $[(CH_2)_3]^+$ (20). Anal. Calcd for $C_9H_{18}N_2S_4$: S, 45.4; H, 6.42; C, 38.26; N, 9.92. Found: S, 45.43; H, 6.34; C, 38.11; N, 9.89.

4.2.10. 5-[4-(1,3,5-Dithiazinane-5-yl)butyl]1,3,5-dithiazinane (3d).[2] White crystal, yield 2.43 g, 82%, mp 134–135 °C, R_f 0.75 (eluent hexane–ethylacetate, 2:1); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.45 (m, 4H, H-8,9), 3.01 (t, 4H, H-7,10, ^3J=6.3 Hz), 4.17 (s, 4H, H-2,14), 4.47 (s, 8H, H-4,6,12,16); ^{13}C NMR ($CDCl_3$): δ 24.4 (C-8,9), 33.9 (C-2,14), 48.4 (C-7,10), 58.2 (C-4,6,12,16); MS *m/z* (rel int.): 296 $[M]^+$ (12), 263 $[M-SH]^+$ (29), 249 $[M-CH_2SH]^+$ (53), 217 $[M-SCH_2SH]^+$ (75), 139 $[(CH_2)_2N(CH_2)_4NCH_2CH]^+$ (43), 125 $[CHN(CH_2)_4N(CH_2)_2]^+$ (30), 98 $[CH_2N(CH_2)_4N]^+$ (30), 84$[N(CH_2)_4N]^+$ (100), 70 $[N(CH_2)_4]^+$ (17), 42 $[N(CH_2)_2]^+$ (53). Anal. Calcd for $C_{10}H_{20}N_2S_4$: S, 43.25; H, 6.80; C, 40.50; N, 9.45. Found: S, 44.09; H, 6.52; C, 38.44; N, 9.09.

4.2.11. 5-[5-(1,3,5-Dithiazinane-5-yl)pentyl]-1,3,5-dithiazinane (3e). White crystal, yield 2.32 g, 75%, mp 115–117 °C, R_f 0.72 (eluent hexane–ethylacetate, 3:1); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.47 (m, 6H, H-8,9,10), 2.97 (m, 4H, H-7,11, J=8 Hz), 4.09 (s, 4H, H-2,15), 4.40 (s, 8H, H-4,6,13,17); ^{13}C NMR ($CDCl_3$): δ 24.7 (C-9), 26.8 (C-8,10), 34.0 (C-2,15), 48.7 (C-7,11), 58.3 (C-4,6,13,17); MS *m/z* (rel int.): 310 (7) $[M]^+$, 277 (23) $[M-SH]^+$, 263 (40) $[M-CH_2SH]^+$, 231 (32) $[M-SCH_2SH]^+$, 185 (67) $[M-CHN(CH_2)_5N]^+$, 98 (100) $[N(CH_2)_5N]^+$, 70 (22) $[(CH_2)_5]^+$, 56 (28) $[(CH_2)_4]$, 42 (25) $[(CH_2)_3]^+$. Anal. Calcd for $C_{11}H_{22}N_2S_4$: S, 41.30; H, 7.14; C, 42.54; N, 9.02. Found: S, 40.47; H, 7.42; C, 41.09; N, 9.31.

4.2.12. 5-[6-(1,3,5-Dithiazinane-5-yl)hexyl]-1,3,5-dithiazinane (3f). White crystal, yield 2.07 g, 64%, mp 96–97 °C. R_f 0.64 (eluent hexane–ethylacetate, 4:1); IR ν_{max} 750 (C–S), 1150 (C–N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.3 (br s, 8H, H-8,9,10,11), 2.92 (m, 4H, H-7,12), 4.05 (s, 4H, H-2,16), 4.40 (s, 8H, H-4,6,14,18); ^{13}C NMR ($CDCl_3$): δ 27.1 (C-8,9,10,11), 34.1 (C-2,16), 48.8 (C-7,12), 58.4 (C-4,6,14,18); MS, *m/z* (rel int.): 324 (10) $[M]^+$, 291 (13) $[M-SH]^+$, 277 (24) $[M-CH_2SH]^+$, 245 (42) $[M-SCH_2SH]^+$, 98 (100) $[N(CH_2)_6]^+$, 84 (30) $[(CH_2)_6]^+$, 70 (32) $[(CH_2)_5]^+$, 56 (38) $[(CH_2)_4]$, 42 (45) $[(CH_2)_3]^+$. Anal. Calcd for $C_{12}H_{24}N_2S_4$: S, 39.51; H, 7.45; C, 44.40; N, 8.63. Found: S, 38.74; H, 7.65; C, 43.38; N, 7.54.

4.2.13. 3-(2-Methylidenaminoethyl)-1,3-thiazetidine (4a).[3] Yield 5%. MS *m/z* (rel int.): 130 $[M]^+$ (56), 98 $[M-S]^+$ (8), 84 $[M-SCH_2]^+$ (8), 56 $[M-S(CH_2)_2N]^+$ (45).

4.2.14. 3-(2-Methyl-2-methylidenaminoethyl)-1,3-thiazetidine (4b). Yield 7%. MS *m/z* (rel int.):144 $[M]^+$ (27), 111 $[M-SH]^+$ (67), 97 $[M-CH_2SH]^+$ (27), 69 $[CH_2NCHCH_3]^+$ (51), 61 $[(CH_2)_2SH]^+$ (28), 56 $[CH_2NCHCH_3)]^+$ (93), 42 $[CH_2NCH_2]^+$ (100).

4.2.15. 3-(4-Methylidenaminobutyl)-1,3-thiazetidine (4d). Yield 12%. MS *m/z* (rel int.): 158 $[M]^+$ (89), 125 $[M-SH]^+$ (100), 111 $[M-CH_2SH]^+$ (15), 97 $[M-(CH_2)_2SH]^+$ (70), 84 $[M-NCH_2SCH_2]^+$ (33), 70 $[(CH_2)_3NCH_2]^+$ (42), 42 $[(CH_2)_3]^+$ (49).

4.2.16. 3-(5-Methylidenaminopentyl)-1,3-thiazetidine (4e). Yield 14%. MS *m/z* (rel int.):171 $[M-H]^+$ (67), 157 $[M-CH_3]^+$ (8), 139 $[M-SH]^+$ (42), 111 $[M-NCH_2SH]^+$ (25), 98 $[M-CH_2SCH_2N]^+$ (70), 96 $[M-CHN(CH_2)_5]^+$ (100), 84 $[N(CH_2)_5]^+$ (41), 70 $[(CH_2)_3NCH_2]^+$ (35), 57 $[CH_3NCH_2CH_3]^+$ (27), 42 $[(CH_2)_3]^+$ (85).

4.2.17. 3,5-Dithia-1,7-diazabicyclo[5.3.1]undecane (5c). Yield 10%. MS *m/z* (rel int.): 190 $[M]^+$ (5), 157 $[M-SH]^+$ (7), 143 $[M-CH_2SH]^+$ (31), 111 $[M-SCH_2SH]^+$ (100), 97 $[M-CH_2SCH_2SH]^+$ (10), 70 $[N(CH_2)_3N]^+$ (28), 42 $[(CH_2)_3]^+$ (51).

4.2.18. 3,5-Dithia-1,7-diazabicyclo[5.4.1]dodecane (5d). Yield 13%. MS *m/z* (rel int.): 204 $[M]^+$ (7), 171 $[M-SH]^+$ (15), 157 $[M-CH_2SH]^+$ (71), 125 $[M-SCH_2SH]^+$ (34), 97 $[M-CHSCH_2SCH_2]^+$ (25), 84 $[N(CH_2)_4N]^+$ (100), 70 $[N(CH_2)_4]^+$ (27), 42 $[(CH_2)_3]^+$ (71).

4.2.19. 3,5-Dithia-1,7-diazabicyclo[5.5.1]tridecane (5e). Yield 15%. MS *m/z* (rel int.): 218 $[M]^+$ (31), 185 $[M-SH]^+$ (100), 171 $[M-CH_2SH]^+$ (12), 139 $[M-SCH_2SH]^+$ (21), 112 $[M-CH_2SCH_2SCH_2]^+$ (54), 110 $[M-CHSCH_2SCH]^+$ (65), 98 $[N(CH_2)_5N]^+$ (21), 89 $[(CH_2)_2NCH_2SH]^+$ (41), 42 $[(CH_2)_3]^+$ (74).

4.2.20. 3,5-Dithia-1,7-diazabicyclo[6.5.1]tetradecane (5f). Yield 15%. MS *m/z* (rel int.): 232 $[M]^+$ (4), 199 $[M-SH]^+$ (8), 185 $[M-CH_2SH]^+$ (47), 171 $[M-NCH_2SH]^+$ (17), 153 $[M-SCH_2SH]^+$ (52), 110 $[M-CHSCH_2SCH]^+$ (100), 70 $[(CH_2)_5]^+$ (14), 42 $[(CH_2)_3]^+$ (45).

4.2.21. 5-[4-(1,3-Thiazetidine-3-yl)butyl]-1,3,5-dithiazinane (6d). Yield 17%. MS *m/z* (rel int.): 250 $[M]^+$ (12), 217 $[M-SH]^+$ (100), 171 $[M-SCH_2SH]^+$ (27), 139 $[(CH_2)_2N(CH_2)_4NCH_2CH]^+$ (40), 130 $[(CH)_4N(CH)_2S]^+$ (17), 125 $[(CH)_2N(CH)_4NCH]^+$ (41), 98 $[CH_2N(CH_2)_4N]^+$ (32), 83 $[(CH_2)_4NCH]^+$ (54), 70 $[(CH_2)_4N]^+$ (25), 55 $[(CH_2)_2NCH]^+$ (23), 42 $[(CH_2)_3]^+$ (92).

4.2.22. 5-[5-(1,3-Thiazetidine-3-yl)pentyl]1,3,5-dithiazinane (6e). Yield 15%. MS *m/z* (rel int.): 264 (30) $[M]^+$, 231 (100) $[M-SH]^+$, 217 (27) $[M-CH_2SH]^+$, 185 (90) $[M-SCH_2SH]^+$, 153 (44) $[M-NCH_2SCH]^+$, 139 (61) $[M-CH_2N(CH_2)_5NCH]^+$, 97 (88) $[(CH_2)_5NCH]^+$, 84 (61) $[(CH_2)_5N]^+$, 70 (41) $[(CH_2)_5]^+$, 56 (34) $[(CH_2)_4]^+$, 42 (54) $[(CH_2)_3]^+$.

5. X-ray analyses

5.1. Crystal data for 4c

Atoms with A symbol were formed by a transformation: −X, −Y, −Z, with B symbol: 1−X, 1−Y, −Z. Ortho-rhombic crystals of **4c** compound were formed by a crystallization from hexane–ethylacetate (4:3). Parameters of elemental

cell and intensities 10,733 of reflections (1975 idependent, R_{int}=0.0171) were measured on a difractometer CAD 4 Enraf-Nonius at 100(2) K (Mo Kα-isolation, graphite monochromater, $\theta/2\theta$ scanning, $2\theta_{max}$=54 °C) from a crystal of size 0.60×0.45×0.30 mm ($C_9H_{21}N_2S_4$): a=22.1163(13), b=6.4481(4), c=9.6267(6), α=90°, β=90°, γ=90°, V=1372.85(15), d_{calcd}=1.459 g cm^{-3}, Z=4, a spatial group $P2(1)/n$. A structure was decoded by a direct method and précised in anizotropic approach by F^2_{hkl}. The final divergence factors: wR_2=0.0535 (calculated by F^2_{hkl} for all 5376 reflections), R_1=0.0218 (calculated by F_{hkl} for 1893 reflections with $I>2\sigma(I)$), GOF=1.008, 78 of precised parameters.

5.2. Crystal data for 4d

Atoms with A symbols were formed by a transformation: −X, −Y, −Z, with symbols B: 1−X, 1−Y, −Z. Monocrystals of compound **4d** were formed by a slow crystallization from chloroform. Parameters of elemental cell and intensity 8541 of reflections (1978 independent, R_{int}=0.0364) were measured on difractometer CAD 4 Enraf-Nonius at 100 K (Mo Kα-isolation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max}$=54 °C) from monoclinic crystal of 0.50×0.35×0.25 mm ($C_{10}H_{20}N_2S_4$): a=7.2485(3), b=7.5592(3), c=12.9148(5), α=90°, β=104.8180(10)°, γ=90°, V=684.10(5), d_{calcd}=1.439 g cm^{-3}, Z=2, size, a spatial group $P2(1)/n$. A structure was decoded by a direct method and precised in anisotropic approach by F^2_{hkl} Hydrogen atoms were localized in different syntheses of electron density and precised in a model 'rider'. The final divergence factors: wR_2=0.0579 (calculated by F^2_{hkl} for all 5376 reflections), R=0.0219 (calculated by F for 1738 reflections with $I>2\sigma(I)$), GOF=1.008, 73 precised parameters. All calculations were carried out according to a complex of SHELXTL-PLUS 5[23] program.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-643791 (**4c**), CCDC-643790 (**4d**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax:+44-1223-336033 or e-mail: deposit@ccdc.ac.uk).

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