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Cyclothiomethylation of Aliphatic Polyamines with Formaldehyde and Hydrogen Sulfide

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Abstract—Cyclothiomethylation of the terminal amino groups in *N*-(2-aminoethyl)ethane-1,2-diamine, *N*,*N*′-bis(2-aminoethyl)ethane-1,2-diamine, and *N*,*N*′-bis(2-aminoethyl)ethane-1,1-diamine with formaldehyde and hydrogen sulfide gave the corresponding bis-1,3,5-dithiazinane derivatives. The reaction in aqueous butanol at 0°C was accompanied by intermolecular thiomethylation at the secondary amino groups with formation of previously unknown polyheterocyclic compounds containing nitrogen and sulfur atoms.

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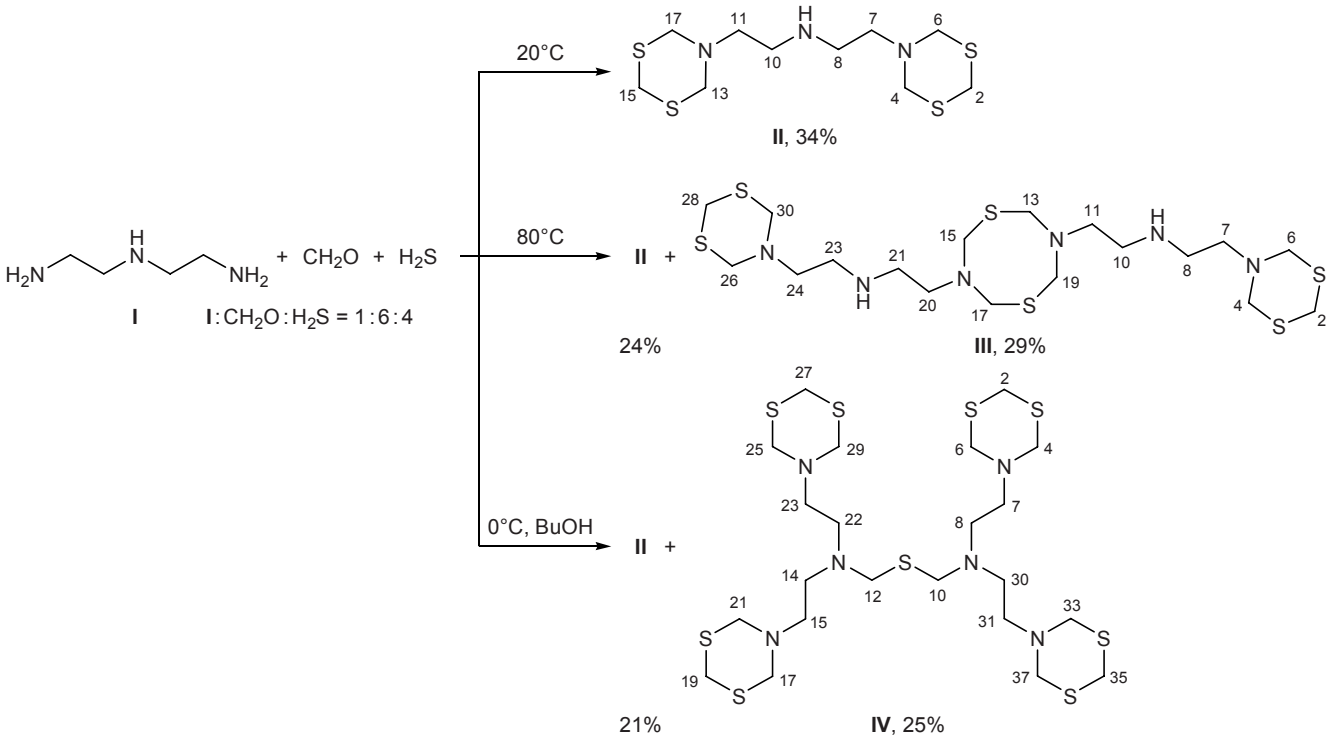
In the recent years, one-pot syntheses of heterocyclic compounds via cascade heterocyclizations attract growing interest [1, 2]. Among these, multicomponent condensations of primary amines with hydrogen sulfide and formaldehyde, leading to 1,3,5-dithiazinane derivatives [3–6] and polycyclic systems containing thiadiazinane fragments [7, 8], have been reported. N,S-Containing heterocycles are used as extractants, flotation agents, selective sorbents, and complexing agents toward noble metals [9, 10]; in addition, they exhibit biological activity [11].

In continuation of our studies on the cyclothiomethylation of amines with the system formaldehyde–hydrogen sulfide in the present work we examined reactions of *N*-(2-aminoethyl)ethane-1,2-diamine (**I**), *N*,*N*′-bis(2-aminoethyl)ethane-1,2-diamine (**V**), and *N*,*N*′-bis(2-aminoethyl)ethane-1,1-diamine (**VI**) with CH_2O and H_2S with a view to develop effective procedures for the synthesis of N,S-heterocycles of practical interest and compare the reactivities of primary and secondary amino groups in the polyamine molecule. The reactions were carried out in different solvents at different temperatures using different reactant concentrations to estimate the effect of these factors on the yield and composition of the cyclothiomethylation products.

N-(2-Aminoethyl)ethane-1,2-diamine (**I**) reacted with formaldehyde and hydrogen sulfide at molar ratios of 1:3:2 and 1:6:4) at 0 and 20°C in aqueous medium to give 2-(1,3,5-dithiazinan-5-yl)-*N*-[2-(1,3,5-dithiazinan-5-yl)ethyl]ethanamine (**II**) whose yield varied from 20 to 34% (calculated on the initial polyamine **I**). The conversion of amine **I** was 50–60%, depending on the conditions. Bis-1,3,5-dithiazinane **II** was isolated from the reaction mixture by extraction with chloroform. In the IR spectrum of **II**, stretching vibrations of the C–S bonds appeared in the region 590–720 cm^{-1}, absorption band at 1090 cm^{-1} was assigned to stretching vibrations of the C–N bonds, and the band at 1640 cm^{-1} corresponded to bending vibrations of the secondary amino group [12]. The ^1H NMR spectrum of **II** contained singlets at δ 3.91 and 4.23 ppm with an intensity ratio of 1:2 due to methylene protons in the dithiazinane ring at C^2/C^{15} and $C^4/C^6/C^{13}/C^{17}$, respectively. In the ^{13}C NMR spectrum of **II** we observed a triplet at δ_C 33.40 ppm, belonging to the methylene carbon atom located between sulfur atoms, and the signal at δ_C 57.92 ppm corresponds to the methylene carbon atoms located between nitrogen and sulfur atoms in the dithiazinane ring [13].

Raising the temperature to 80°C resulted in the formation of dimer **III** as a poorly soluble solid together with bis-1,3,5-dithiazinane **II**. In the ^1H NMR spectrum of compound **III**, broadened singlets at δ 4.7 and 5.2 ppm correspond to methylene protons in the dithiazinane rings, and two signals at δ 4.13 and

Scheme 1.



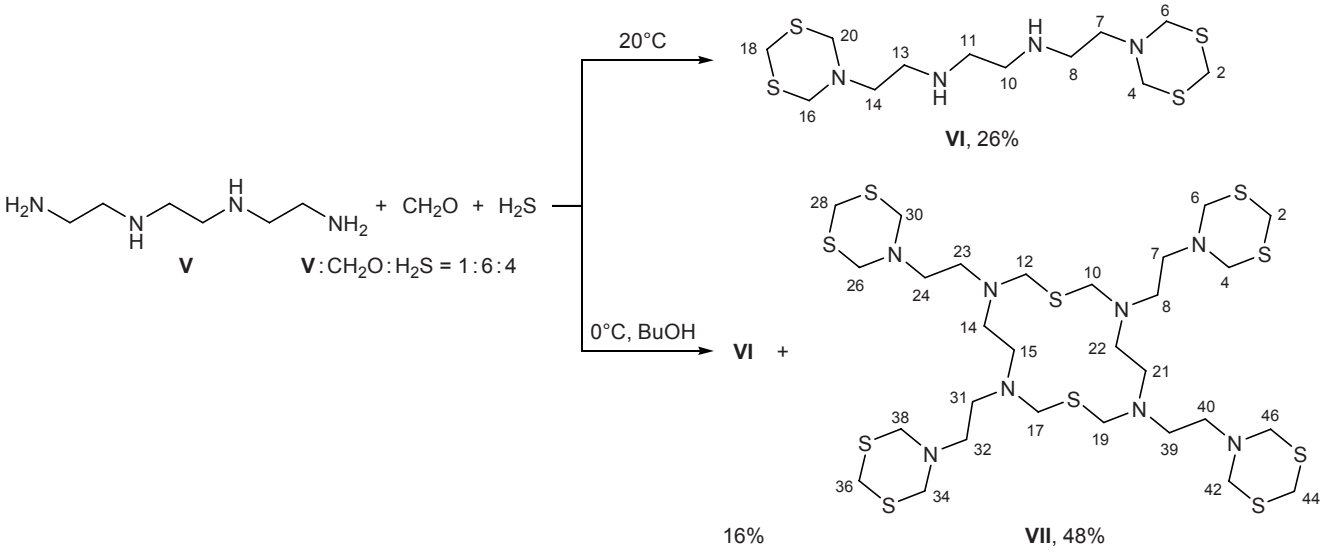
4.27 ppm belong to equatorial and axial protons in the eight-membered dithiadiazocane ring. An analogous eight-membered heterocycle was obtained by us previously from arylhydrazines [14], and its structure was confirmed by X-ray analysis. Compound **III** melted at 172–175°C. Its molecular weight determined by cryoscopy was 520 (M_{calc} 530), and the elemental composition was consistent with the formula $C_{18}H_{38}N_6S_6$; therefore, compound **III** was assigned the structure of *N*-[2-(1,3,5-dithiazinan-5-yl)ethyl]-2-(7-{2-[2-(1,3,5-dithiazinan-5-yl)ethylamino]ethyl}-1,5,3,7-dithiadiazocan-3-yl)ethanamine.

When the reaction of polyamine **I** with CH_2O and H_2S at a molar ratio of 1:6:4 was performed in butan-1-ol (**I**–BuOH ratio 1:5) at 0°C, a mixture of bis-1,3,5-dithiazinane **II** (21%) and dimeric product **IV** (25%) was obtained. Obviously, compound **IV** was formed by intermolecular thiomethylation of two molecules **II** at the secondary amino groups. Dimer **IV** was isolated from the reaction mixture by extraction with chloroform and subsequent precipitation from the extract with methanol. Its structure was confirmed by the ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of **IV** contained a broadened singlet at δ 3.3 ppm due to methylene protons in the thiodimethylene bridge ($C^{10}H_2$ and $C^{12}H_2$). The corresponding carbon atoms gave one triplet signal at δ_C 52.4 ppm in the ^{13}C NMR spectrum. These data indicate symmetric structure of molecule **IV**. Carbon signals at δ_C 33.2 and 57.4 ppm belong to the methylene carbon atoms between two sulfur atoms and between nitrogen and sulfur atoms, respectively, in the dithiazinane rings.

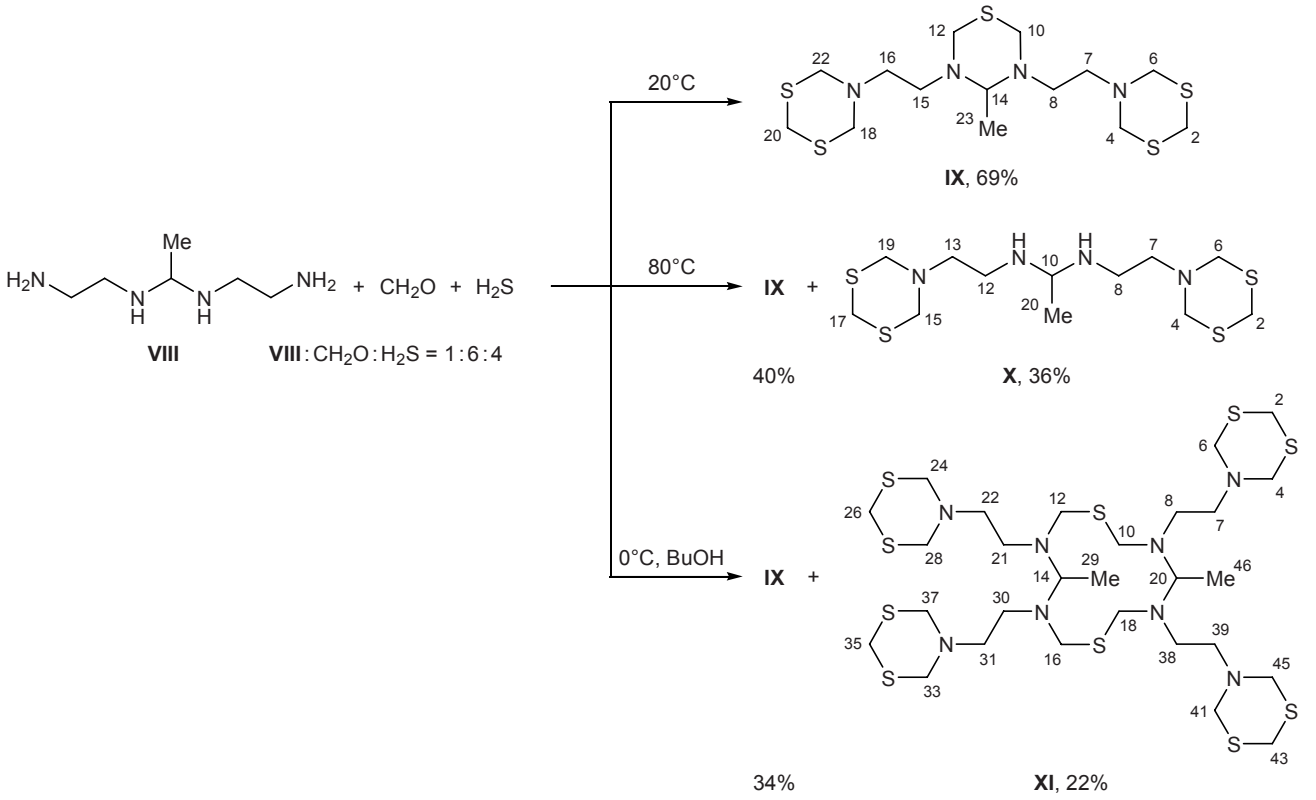
The reaction of *N*,*N*′-bis(2-aminoethyl)ethane-1,2-diamine (**V**) with formaldehyde and hydrogen sulfide (molar ratios 1:3:2 and 1:6:4) in aqueous medium at 0 and 20°C gave *N*,*N*′-bis[2-(1,3,5-dithiazinan-5-yl)-ethyl]ethane-1,2-diamine (**VI**) (Scheme 2). Compound **VI** in the ^1H NMR spectrum displayed singlets at δ 4.09 and 4.50 ppm from the methylene protons on C^2/C^{18} and $C^4/C^6/C^{16}/C^{20}$, respectively. The corresponding carbon atoms resonated in the ^{13}C NMR spectrum at δ_C 33.63 and 58.60 ppm.

Polyamine **V** reacted with CH_2O and H_2S (ratio 1:6:4) in butan-1-ol (1:5) at 0°C to give a mixture of bis-dithiazinane **VI** and macroheterocycle **VII**, the latter being formed via subsequent intermolecular thiomethylation of compound **VI**. Compound **VII** separated from the reaction mixture during the process. Its ^1H NMR spectrum contained a broadened singlet at δ 3.8 ppm from protons in the bridging methylene groups ($C^{10}H_2SC^{12}H_2$ and $C^{17}H_2SC^{19}H_2$). The C^{10}, C^{12}, C^{17}, and C^{19} atoms resonated in the ^{13}C NMR spectrum at δ_C 61.5 ppm; their equivalence suggests symmetric structure of molecule **VII**. The signals at δ_C 32.7 and

Scheme 2.



Scheme 3.



57.9 ppm correspond to the methylene carbon atoms in the dithiazinane rings located, respectively, between two sulfur atoms and between sulfur and nitrogen atoms. Cryoscopic determination of the molecular weight of compound **VII** gave a value of 821 (M_{calc} 824), and the elemental composition of **VII** conformed to the formula $C_{28}H_{56}N_8S_{10}$. These data allowed us to assign compound **VII** the structure of 3,6,10,13-tetrakis[2-(1,3,5-dithiazinan-5-yl)ethyl]-1,8-dithia-3,6,10,13-tetraazacyclotetradecane.

Likewise, heterocyclization of *N*,*N*′-bis(2-aminoethyl)ethane-1,1-diamine (**VIII**) with formaldehyde and hydrogen sulfide in aqueous medium at 20°C resulted in the formation of 3,5-bis[2-(1,3,5-dithiazinan-

5-yl)ethyl]-4-methyl-1,3,5-thiadiazinane (**IX**) as the only product (yield 69%; Scheme 3). When the reaction was performed at elevated temperature (80°C), bis-1,3,5-dithiazinane **X** was formed together with compound **IX**. Compounds **IX** and **X** were isolated from the reaction mixture by extraction with chloroform, followed by precipitation of **IX** with methanol. In the IR spectrum of **IX**, stretching vibrations of the C–S bonds had a frequency of 690–720 cm^{-1}. The band at 1100 cm^{-1} was attributed to stretching vibrations of the C–N bonds, and C–H stretching vibrations of the methylene groups gave rise to absorption at 2900 cm^{-1}. In the ^1H NMR spectrum of **IX** we observed broadened singlets at δ 4.14 and 4.50 ppm with an intensity ratio of 1:2 due to methylene protons on C^2 (C^{20}) and C^4/C^6 (C^{18}/C^{22}), respectively. The corresponding carbon atoms resonated in the ^{13}C NMR spectrum at δ_C 33.59 and 58.50 ppm. The signal from the methylene carbon atoms in the thiadiazinane ring (C^{10}/C^{12}) was located at δ_C 53.06 ppm. No such signal was present in the ^{13}C NMR spectrum of **X**, for its molecule lacked thiadiazinane fragment, and the CH signal was observed in a stronger field, at δ_C 62.0 ppm.

The reaction of polyamine **VIII** with CH_2O and H_2S (molar ratio 1:6:4) in BuOH (1:5) at 0°C gave a mixture of compound **IX** and poorly soluble macroheterocycle **XI** (~22%). By analogy with compound **VII**, the ^1H NMR spectrum of **XI** contained a broadened singlet at δ 3.9 ppm from the methylene protons in the twelve-membered heteroring. Compound **XI** had mp 153–155°C and a molecular weight of 834 (determined by cryoscopy; M_{calc} 824); its elemental composition was estimated as $C_{28}H_{56}N_8S_{10}$. The above data led us to assign the structure of 3,5,9,11-tetrakis[2-(1,3,5-dithiazinan-5-yl)ethyl]-4,10-dimethyl-1,7-dithia-3,5,9,11-tetraazacyclododecane to compound **XI**.

Thus, the results of our study showed that the reactions of polyethylenepolyamines with formaldehyde and hydrogen sulfide initially involve the terminal primary amino groups in the polyamine with formation of symmetric α,ω-bis-dithiazinane derivatives. The optimal conditions for the preparation of the latter are polyamine–CH_2O–H_2S ratio 1:6:4, temperature 20°C, and aqueous medium. Heterocyclization of polyamines with the system CH_2O–H_2S at 0°C in the presence of BuOH, apart from the above bis-1,3,5-dithiazinane derivatives, gives intermolecular thiomethylation products as a result of reaction at the secondary amino groups. These transformations provide simple and efficient synthetic routes to N,S-containing bi-, tri-, tetra-, and pentacyclic compounds with a unique structure.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Tesla BS-487 spectrometer at 80 MHz, and the ^{13}C NMR spectra were measured on a Jeol FX 90Q instrument at 22.50 MHz; tetramethylsilane was used as internal reference, and $CDCl_3$ and DMSO-d_6, as solvents. The IR spectra were obtained on a Specord 75IR spectrophotometer from samples dispersed in mineral oil. The elemental compositions were determined on a Carlo Erba 1106 analyzer. The molecular weights were determined according to Rast [15]. The melting points were measured using an RNMK 80/2617 melting point apparatus. The refractive indices (n_D^{20}) were determined on an IRF-22 refractometer. The purity of the products was checked by TLC on Silufol UV-254 plates using hexane–ethyl acetate (4:3) as eluent (development with iodine vapor), as well as by NMR spectroscopy.

The solvents used were purified and dehydrated according to standard procedures [16]. Hydrogen sulfide was bubbled using an ANP-10 peristaltic pump.

General procedure for the reactions of polyamines with hydrogen sulfide and formaldehyde. Hydrogen sulfide prepared from required amounts of sodium sulfide and hydrochloric acid was bubbled over a period of 30 min through a required amount of a 37% formaldehyde solution. Polyamine **I**, **V**, or **VIII** was added to the resulting CH_2O–H_2S mixture (3:2 or 6:4) in water or butan-1-ol (**I**:BuOH = 1:5) to a ratio of 1:3:2 or 1:6:4. and the mixture was stirred for 3 h at 0, 20, or 80°C. Poorly soluble products **III**, **VII**, and **XI** separated during the process and were filtered off, washed with chloroform, and dried. The filtrate was extracted with chloroform (2 × 30 ml) to isolate compounds **II**, **VI**, **IX**, and **X**. The extract was dried over $CaCl_2$ and evaporated to leave a tarry substance. Compounds **IV** and **X** were isolated from the chloroform extract by precipitation with methanol on cooling to 0–2°C.

2-(1,3,5-Dithiazinan-5-yl)-*N*-[2-(1,3,5-dithiazinan-5-yl)ethyl]ethanamine (II). Yield 20–34%, n_D^{20} = 1.6392, R_f 0.52 (hexane–ethyl acetate, 4:3). IR spectrum, ν, cm^{-1}: 590–720, 1090, 1280, 1420, 1600, 2900, 3200. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.68 s (1H, 9-H), 2.51 d (4H, 8-H, 10-H, J = 6.1 Hz), 2.97 d (4H, 7-H, 11-H, J = 6.1 Hz), 3.91 br.s (4H, 2-H, 15-H), 4.23 br.s (8H, 4-H, 6-H, 13-H, 17-H). ^{13}C NMR spectrum, δ_C, ppm: 33.40 t (C^2, C^{15}), 46.10 t (C^8, C^{10}), 48.18 t (C^7, C^{11}), 57.92 t (C^4, C^6, C^{13}, C^{17}). Found, %: C 37.60; H 5.82; N 12.88; S 40.35. $C_{10}H_{21}N_3S_4$. Calculated, %: C 38.55; H 6.79; N 13.49; S 41.17.

***N*-[2-(1,3,5-Dithiazinan-5-yl)ethyl]-2-(7-{2-[2-(1,3,5-dithiazinan-5-yl)ethylamino]ethyl}-1,5,3,7-dithiadiazocan-3-yl)ethanamine (III).** The reaction was carried out at 80°C. Yield 3 g (28%), mp 172–175°C. IR spectrum, ν, cm^{-1}: 590–640, 1090, 1270, 1380, 1430, 1600, 2900, 3200. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.85–3.35 m (16H, 7-H, 8-H, 10-H, 11-H, 20-H, 21-H, 23-H, 24-H), 4.13 s and 4.27 s (4H each, 13-H, 15-H, 17-H, 19-H), 4.7 br.s (4H, 2-H, 28-H), 5.2 br.s (8H, 4-H, 6-H, 26-H, 30-H). Found, %: C 39.6; H 7.08; N 13.10; S 38.30. *M* 520. $C_{18}H_{38}N_6S_6$. Calculated, %: C 40.72; H 7.21; N 15.83; S 36.24. *M* 530.

Thiobis{*N*,*N*-bis[2-(1,3,5-dithiazinan-5-yl)ethyl]-methanamine} (IV). Yield 1.7 g (25%) (0°C, BuOH), n_D^{20} = 1.6009, R_f 0.20 (hexane–ethyl acetate, 4 : 3). IR spectrum, ν, cm^{-1}: 650–720, 1090, 1280, 1320, 1430, 2900. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.5–3.0 m (16H, 7-H, 8-H, 14-H, 15-H, 22-H, 23-H, 30-H, 31-H), 3.3 br.s (4H, 10-H, 12-H), 3.9 br.s (8H, 2-H, 19-H, 27-H, 35-H), 4.3 br.s (16H, 4-H, 16-H, 17-H, 21-H, 25-H, 29-H, 33-H, 37-H). ^{13}C NMR spectrum, δ_C, ppm: 33.2 t (C^2, C^{19}, C^{27}, C^{35}), 45.8 t (C^8, C^{14}, C^{22}, C^{30}), 49.7 t (C^7, C^{15}, C^{23}, C^{31}), 52.4 t (C^{10}, C^{12}), 57.9 t (C^4, C^6, C^{17}, C^{21}, C^{25}, C^{29}, C^{33}, C^{37}). Found, %: C 38.28; H 6.17; N 11.53; S 42.26. $C_{22}H_{44}N_6S_9$. Calculated, %: C 38.79; H 6.51; N 12.34; S 42.36.

***N*,*N*′-Bis[2-(1,3,5-dithiazinan-5-yl)ethyl]ethane-1,2-diamine (VI).** Yield 16–26%, n_D^{20} = 1.5716, R_f 0.65 (hexane–ethyl acetate, 4:3). IR spectrum, ν, cm^{-1}: 680–720, 1090, 1280, 1420, 1600, 2900, 3200. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.56 s (4H, 10-H, 11-H), 2.75 s (4H, 8-H, 13-H), 3.50 s (4H, 7-H, 14-H), 4.09 br.s (4H, 2-H, 18-H), 4.50 br.s (8H, 4-H, 6-H, 16-H, 20-H). ^{13}C NMR spectrum, δ_C, ppm: 33.63 t (C^2, C^{18}), 47.72 t (C^{10}, C^{11}), 53.10 t (C^8, C^{13}), 56.29 t (C^7, C^{14}), 58.60 t (C^4, C^6, C^{16}, C^{20}). Found, %: C 39.22; H 6.71; N 14.88; S 37.85. $C_{12}H_{26}N_4S_4$. Calculated, %: C 40.64; H 7.39; N 15.80; S 36.17.

3,6,10,13-Tetrakis[2-(1,3,5-dithiazinan-5-yl)-ethyl]-1,8-dithia-3,6,10,13-tetraazacyclotetradecane (VII). Yield 3.93 g (48%), mp 147–149°C. IR spectrum, ν, cm^{-1}: 650–720, 1090, 1380, 1450, 2900. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.7 br.s (8H, 14-H, 15-H, 21-H, 22-H), 3.8 br.s (8H, 10-H, 12-H, 17-H, 19-H), 4.4 br.s (16H, 7-H, 8-H, 23-H, 24-H, 31-H, 32-H, 39-H, 40-H). ^{13}C NMR spectrum, δ_C, ppm: 33.7 t (C^2, C^{28}, C^{36}, C^{44}), 48.3 t (C^{14}, C^{15}, C^{21}, C^{22}), 52.4 t (C^8, C^{23}, C^{31}, C^{39}), 52.9 t (C^7, C^{24}, C^{32}, C^{40}), 57.9 t (C^4, C^6, C^{26}, C^{30}, C^{34}, C^{38}, C^{42}, C^{46}), 61.5 t (C^{10}, C^{12}, C^{17}, C^{19}). Found, %: C 40.81; H 7.15; N 12.81; S 37.96. *M* 821. $C_{28}H_{56}N_8S_{10}$. Calculated, %: C 40.74; H 6.84; N 13.57; S 38.85. *M* 824.

3,5-Bis[2-(1,3,5-dithiazinan-5-yl)ethyl]-4-methyl-1,3,5-thiadiazinane (IX). Yield 34–69%, n_D^{20} = 1.5951, R_f 0.80 (hexane–ethyl acetate, 4:3). IR spectrum, ν, cm^{-1}: 690–750, 1100, 1380, 1420, 2900. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 d (3H, 23-H), 2.30–3.40 m (12H, 7-H, 8-H, 10-H, 12-H, 15-H, 16-H), 3.92 s (1H, 14-H), 4.14 br.s (4H, 2-H, 20-H), 4.50 br.s (8H, 4-H, 6-H, 18-H, 22-H). ^{13}C NMR spectrum, δ_C, ppm: 18.22 d (C^{23}), 33.59 t (C^2, C^{20}), 47.50 t (C^8, C^{15}), 51.27 t (C^7, C^{16}), 53.06 t (C^{10}, C^{12}), 58.50 t (C^4, C^6, C^{18}, C^{22}), 75.66 s (C^{14}). Found, %: C 40.47; H 6.88; N 13.51; S 38.12. $C_{14}H_{28}N_4S_5$. Calculated, %: C 40.74; H 6.84; N 13.57; S 38.85.

***N*,*N*′-Bis[2-(1,3,5-dithiazinan-5-yl)ethyl]ethane-1,1-diamine (X).** Yield 2.5 g (36%), n_D^{20} = 1.5325, R_f 0.72 (hexane–ethyl acetate, 4:3). IR spectrum, ν, cm^{-1}: 680–720, 1100, 1280, 1370, 1600, 2900, 3200. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 br.s (3H, 20-H), 2.19 br.s (2H, 9-H, 11-H), 2.8–3.3 m (8H, 7-H, 8-H, 12-H, 13-H), 3.9 br.s (1H, 10-H), 4.12 br.s (4H, 2-H, 17-H), 4.50 br.s (8H, 4-H, 6-H, 15-H, 19-H). ^{13}C NMR spectrum, δ_C, ppm: 18.6 d (C^{20}), 33.5 t (C^2, C^{17}), 47.5 t (C^8, C^{12}), 52.8 s (C^7, C^{13}), 58.4 t (C^4, C^6, C^{15}, C^{19}), 62.0 s (C^{10}). Found, %: C 39.30; H 6.33; N 14.85; S 36.90. $C_{12}H_{26}N_4S_4$. Calculated, %: C 40.64; H 7.39; N 15.80; S 36.17.

3,5,9,11-Tetrakis[2-(1,3,5-dithiazinan-5-yl)ethyl]-4,10-dimethyl-1,7-dithia-3,5,9,11-tetraazacyclododecane (XI). Yield 1.41 g (35%), mp 153–155°C. IR spectrum, ν, cm^{-1}: 670–720, 1090, 1380, 1460, 2900. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.33 br.s (6H, 29-H, 46-H), 2.8–3.2 m (16H, 7-H, 8-H, 21-H, 22-H, 30-H, 31-H, 38-H, 39-H), 3.3 br.s (2H, 14-H, 20-H), 3.9 br.s (8H, 10-H, 12-H, 16-H, 18-H), 4.09 br.s (8H, 2-H, 26-H, 35-H, 43-H), 4.43 br.s (16H, 4-H, 6-H, 24-H, 28-H, 33-H, 37-H, 41-H, 45-H). Found, %: C 40.44; H 6.82; N 13.07; S 38.30. *M* 834. $C_{28}H_{56}N_8S_{10}$. Calculated, %: C 40.78; H 6.84; N 13.57; S 38.85. *M* 824.

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