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Reaction of Thiourea with Formaldehyde and Simplest Aliphatic Diamines

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Abstract—*N*,*N*′-Bis(hydroxymethyl)thiourea reacted with propane-1,3-diamine at a molar ratio of 2 : 1 to give 5,5′-propane-1,3-diylbis(1,3,5-triazinane-2-thione), whereas 1,3,5,7,11,13,15,17-octaazatricyclo[$15.3.1.1^{7,11}$]-docosane-4,14-dithione was obtained in the reaction with equimolar amounts of the reactants. Tricyclic product was also formed in the three-component condensation of thiourea with formaldehyde and propane-1,3-diamine at a ratio of 1 : 3 : 1. The reactions of *N*,*N*′-bis(hydroxymethyl)thiourea with ethane-1,2-diamine (2 : 1) and of thiourea with formaldehyde and butane-1,4-diamine (1 : 2 : 1) afforded 5,5′-(ethane-1,2-diyl)bis(1,3,5-triazinane-2-thione) and 5,5′-(butane-1,4-diyl)bis(1,3,5-triazinane-2-thione), respectively.

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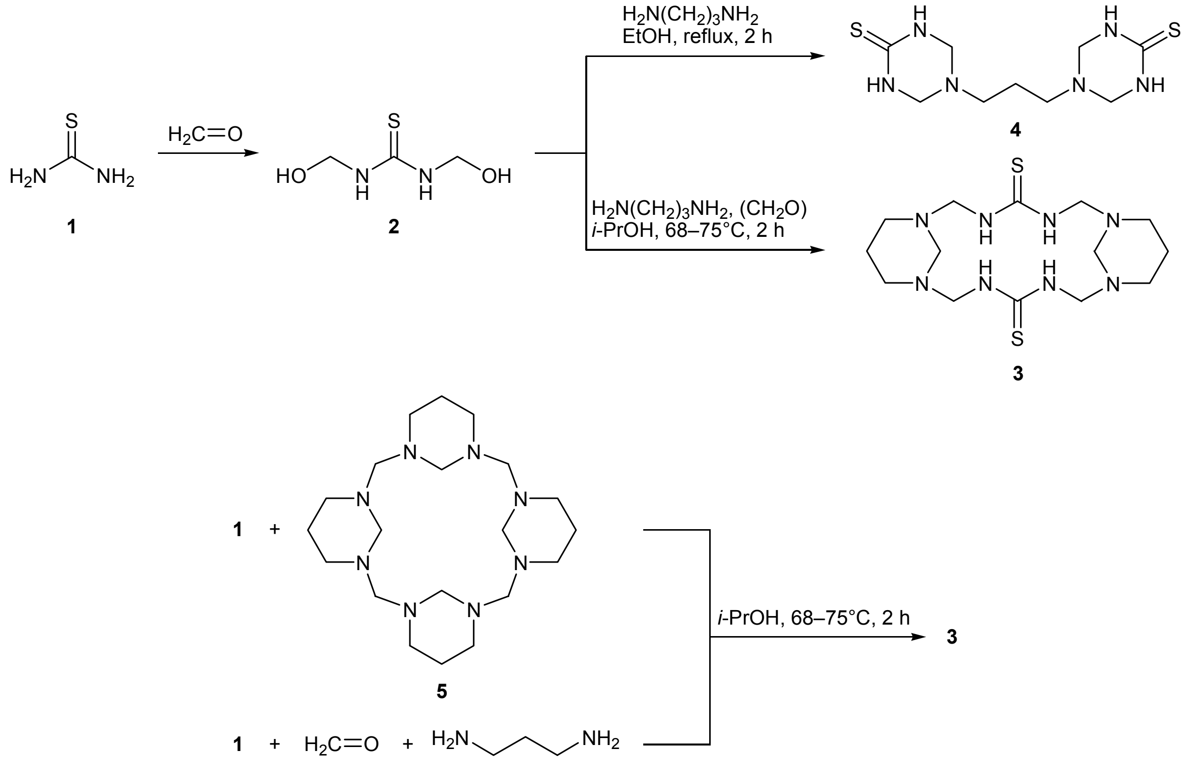
Aminomethylation of thiourea (**1**) with formaldehyde and primary amines, leading to the formation of 5-substituted 1,3,5-triazinane-2-thiones, is well known (see, e.g., [1, 2] and references therein). However, only a few data are available on three-component condensations of thiourea (**1**) with formaldehyde and simplest aliphatic diamines. Paquin [3, 4] reported on the reactions of thiourea with formaldehyde and ethylenediamine at molar ratios of 1 : 2 : 1 and 2 : 4 : 1, which afforded 5-(2-aminoethyl)-1,3,5-triazinane-2-thione and 5,5′-(ethane-1,2-diyl)bis(1,3,5-triazinane-2-thione), respectively. Neither three-component condensations of thiourea (**1**) with formaldehyde and propane-1,3-diamine or butane-1,4-diamine nor two-component condensations of *N*,*N*′-bis(hydroxymethyl)thiourea (**2**) with ethane-1,2-, propane-1,3-, and butane-1,4-diamines were studied previously. By reaction of *N*,*N*′-bis(hydroxymethyl)urea with propane-1,3-diamine we previously obtained tricyclic 1,3,5,7,11,13,-15,17-octaazatricyclo[$15.3.1.1^{7,11}$]docosane-4,14-dione instead of expected 5-substituted 1,3,5-triazinan-2-one [5]. The present work was aimed at synthesizing a thioxo analog of the above tricyclic product starting from both thiourea (**1**) (i.e., via three-component condensation of thiourea with formaldehyde and propane-1,3-diamine) and from *N*,*N*′-bis(hydroxymethyl)thiourea (**2**) (by condensation with propane-1,3-diamine). In addition, attempts were made to obtain homologous tricyclic thiones using butane-1,4-diamine instead of propane-1,3-diamine in the three-component condensation and ethane-1,2-diamine in the two-component condensation.

Under the conditions reported in [5] for the formation of tricyclic docosane-4,14-dione [molar ratio *N*,*N*′-bis(hydroxymethyl)urea–propane-1,3-diamine 2 : 1, ethanol, reflux, 2 h], the reaction of **2** with propane-1,3-diamine afforded 94% of 5,5′-(propane-1,3-diyl)bis(1,3,5-triazinane-2-thione) (**4**) instead of expected tricyclic product **3**. 1,3,5,7,11,13,15,17-Octaazatricyclo[$15.3.1.1^{7,11}$]docosane-4,14-dithione (**3**) was obtained in a poor yield (16%) when the condensation of **2** with propane-1,3-diamine was carried out with equimolar amounts of the reactants in isopropyl alcohol (Scheme 1). The yield of **3** was improved to 39% by adding 1 equiv of formaldehyde solution to an equimolar mixture of **2** and propane-1,3-diamine.

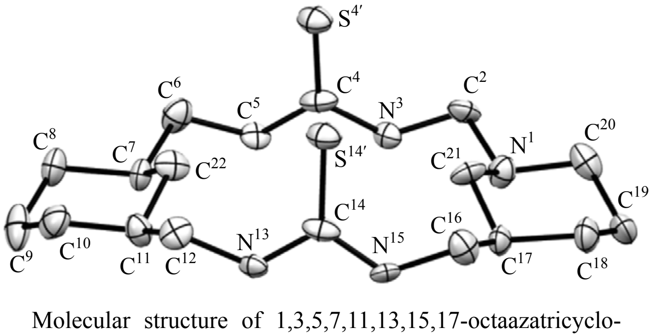
Compound **3** was also synthesized, though with a low yield (27%), by three-component condensation of thiourea (**1**) with formaldehyde and propane-1,3-diamine (1 : 3 : 1) under the same conditions as for the two-component condensation of **2** with propane-1,3-diamine (isopropyl alcohol, 68–75°C, 2 h). Furthermore,

Scheme 1.



tricyclic compound **3** was formed in the 2 : 1 reaction of **1** with 1,3,7,9,13,15,19,21-octaazapentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane (**5**) (macrocyclic product of the reaction of propane-1,3-diamine with formaldehyde [6]); however, the yield of **3** was as low as 8%.

Like the oxo analog [5], tricyclic dithione **3** may be regarded as macrocyclic Mannich base formed as a result of a multistep process with the difference that the substrate is thiourea rather than urea. The structure of **3** was determined on the basis of its NMR and mass spectra and X-ray diffraction data (see figure). The single crystal of **3** subjected to X-ray analysis was a solvate with the composition $3 \cdot H_2O \cdot 0.3CHCl_3$. The tricyclic molecule is composed of two identical fragments related to each other through a twofold symmetry axis. It is a 20-membered macrocycle with two methylene bridges. The molecule has 1*R*,7*S*,11*R*,17*S* configuration and C_{2v} symmetry. Two macrocycles **3** in a unit cell are related to each other through a fourfold inversion axis and are almost parallel, but their longitudinal axes are mutually orthogonal. The tricycles are linked to each other by symmetry-independent hydrogen bonds with lengths of 2.984 and 2.956Å; with account taken of the crystal symmetry, there are total of eight N–H···N hydrogen bonds (see table).

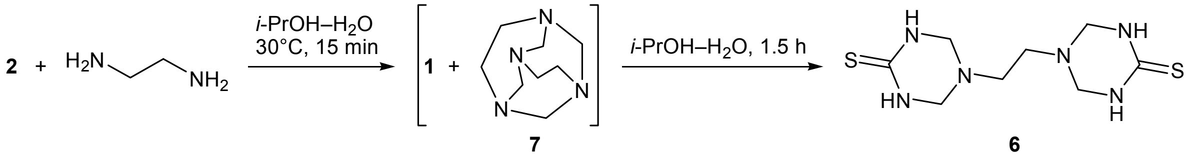


Molecular structure of 1,3,5,7,11,13,15,17-octaazatricyclo-[15.3.1.1^{7,11}]docosane-4,14-dithione (**3**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%. Hydrogen atoms are not shown. The X-ray diffraction data are available from the authors upon request by e-mail.

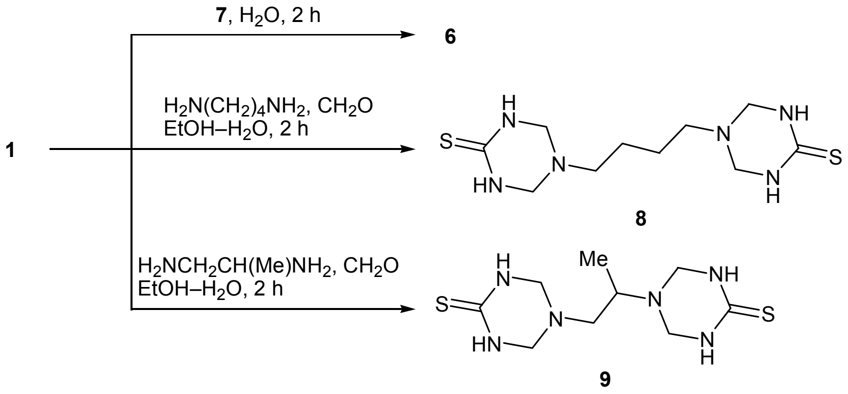
The ^{1}H NMR spectrum of **3** is similar to the spectrum of its oxo analog [5] and is represented by a characteristic set of multiplets. The signals were assigned, and the coupling constants ^2J and ^3J were determined, using ^{1}H–^{1}H COSY and ^{1}H–^{13}C{^{1}H} HMQC techniques.

With the goal of obtaining a smaller tricyclic compound homologous to **3** (with ethylene bridges), compound **2** was brought into condensation with ethylenediamine at a molar ratio of 2 : 1 in 75% isopropyl alcohol. However, the product was not the expected tricycle but 5,5′-(ethane-1,2-diyl)bis(1,3,5-triazinane-

Scheme 2.



Scheme 3.



2-thione) (**6**) which was isolated in 70% yield (Scheme 2). In the first step, 1,3,6,8-tetraazatricyclo-[4.4.1.1^{3,8}]dodecane (**7**) was formed by reaction of ethylenediamine with formaldehyde [7], and the subsequent reaction of **7** with thiourea afforded final product **6**. In fact, by condensation of **1** with **7** in water we obtained 40% of **6** (Scheme 3).

In order to obtain a higher homolog of **3**, the reaction of thiourea (**1**) with butane-1,4-diamine (putrescine) and formaldehyde was carried out at a reactant ratio of 1 : 2 : 1 in 50% aqueous ethanol. As in the preceding case, no tricyclic product was formed, but 5,5′-(butane-1,4-diyl)bis(1,3,5-triazinane-2-thione) (**8**) was isolated in 75% yield (Scheme 3). Likewise, thiourea reacted with propane-1,2-diamine and formaldehyde in 50% ethanol to afford 78% of 5,5′-(propane-1,2-diyl)bis(1,3,5-triazinane-2-thione) (**9**) (Scheme 3). Signals in the ^{1}H NMR spectrum of **9** were assigned using 2D ^{1}H–^{1}H COSY experiment.

Thus, among the examined diamines, the activation and/or thermodynamic parameters of the condensation of thiourea with formaldehyde and alkanediamine favor formation of tricyclic product rather than bistriazinane derivative only in the reaction with propane-1,3-diamine.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Shimadzu FTIR-8400S spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III-400 spectrometer at 400 and 100 MHz, respectively, relative to the residual proton and carbon signals of the deuterated solvents (DMSO-d_5, δ 2.51 ppm; $CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.0 ppm). Two-dimensional ^{1}H–^{13}C{^{1}H} HMQC and ^{1}H–^{1}H COSY experiments were carried out in $CDCl_3$ (**3**) and DMSO-d_6 (**9**) on the same instrument. The mass spectra were obtained at the Center for Chemical Analysis and Materials Research (St. Petersburg State University) on a Bruker MaXis 62 instrument [electrospray ionization, quadrupole time-of-flight mass analyzer (ESI-QTOF); positive ion detection; solvent methanol; capillary voltage 4.5 kV]; isotope distributions for the molecular ions coincided with the calculated values.

The X-ray diffraction data for compound **3** were obtained on an Agilent Technologies SuperNova Atlas

Hydrogen bond parameters in the crystal structure of 1,3,5,7,11,13,15,17-octaazatricyclo[15.3.1.1^{7,11}]docosane-4,14-dithione (**3**)

D–H···A	d(D···A), Å	d – vdW, Å
$N^{3'}\cdots N^{1}$	2.984	–0.116
$N^{5'}\cdots N^{17}$	2.956	–0.144
$N^{13'}\cdots N^{11}$	2.984	–0.116
$N^{15'}\cdots N^{7}$	2.956	–0.144
$N^{3}\cdots N^{1'}$	2.956	–0.144
$N^{5}\cdots N^{17'}$	2.984	–0.116
$N^{13}\cdots N^{11'}$	2.956	–0.144
$N^{15}\cdots N^{7'}$	2.984	–0.116

diffractometer (Research Center for X-ray Diffraction Studies, St. Petersburg State University) using CrysAlisPro software package [8]. The structure was initially solved by the direct method using SIR2011 [9]. Hydrogen atoms in molecule **3** were placed into calculated positions which were refined in the rigid body approximation. However, at this step solvent atoms were not revealed by the Fourier difference syntheses, and the *R*-factor was too large (12–13%). Therefore, the structure was solved by the SQUEEZE procedure [10] included in SHELXL [11], and then chloroform and water molecules were detected by the Fourier difference syntheses; nevertheless, refinement of the coordinates of atoms therein and their thermal parameters was not reliable. For that reason, the coordinates of atoms in the solvent molecules and their populations were not included in the deposited crystallographic information file (CIF) but are available from the authors.

Compound **3** crystallized in tetragonal crystal system, space group $I4_1/a$. $C_{14}H_{28}N_8S_2$. Unit cell parameters: $a = 17.7648(7)$, $c = 20.0444(13)$ Å; $V = 6325.8(6)$ Å^3; $d_{\mathrm{calc}} = 0.787$ g/cm^3 (without solvent molecules); $Z = 8$; $F(000) = 1600$. Final divergence factors $R = 0.071$ $[F^2 > 2\sigma(F^2)]$, $wR = 0.196$ (F^2); goodness of fit 1.01; number of variables 109; absorption coefficient 1.59 mm^{-1}. Intensities of 7093 reflections, including 2763 independent nonequivalent reflections, were measured at 100 K (micro-focused monochromatized CuK_α radiation, λ 1.54184Å; $\theta_{\min} = 3.3°$, $\theta_{\max} = 67.5°$) from a 0.15×0.13×0.17-mm single crystal of **3**, which was grown at room temperature by slow evaporation of the mother liquor obtained by recrystallization of a crude sample of **3** from chloroform–isopropyl alcohol (2 : 1). The molecular structure of **3** was plotted using Mercury 3.5.1 [12]. The crystallographic data were deposited to the Cambridge crystallographic Data Centre (entry no. CCDC 1433826).

The melting points were determined on a PTP-M melting point apparatus and are uncorrected. Commercial solvents used for the recrystallization of **3** were preliminarily purified by distillation, the first 5% and the last 10% of the distillate being discarded.

***N*,*N'*-Bis(hydroxymethyl)thiourea (2)** was synthesized according to a simplified procedure [13]. Thiourea (**1**), 32.7 g (0.43 mol), was dissolved on heating in 74.5 g (0.87 mol) of a 35% formaldehyde solution, and the mixture was stirred for 15 min at 45–50°C and kept for 10–12 h in a crystallizer (according to [13], water was distilled off). The syrupy liquid was kept for 1 h at 0°C, and the solidified material was ground to obtain a white powder which was dried under reduced pressure. Yield 50.0 g (85%), mp 90–92°C; published data [13]: mp 86–88°C. IR spectrum, ν, cm^{-1}: 3280 (NH), 2996, 2960 (CH_2), 1567 (C–N, δN–H), 1340 (C–N), 1301 (C=S), 1014 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.83 s (4H, CH_2), 5.48 s (2H, OH), 8.03 s (2H, NH). Found: *m*/*z* 159.0199 $[M + \mathrm{Na}]^+$. $C_3H_8N_2NaO_2S$. Calculated: $M + \mathrm{Na}$ 159.0198.

1,3,5,7,11,13,15,17-Octaazatricyclo[15.3.1.1^{7,11}]-docosane-4,14-dithione (3). *a*. Modified procedure [5]. A suspension of 5.45 g (40 mmol) of compound **2** in 22 mL of isopropyl alcohol was cooled to 3°C, 3.35 mL (2.96 g, 40 mmol) of propane-1,3-diamine was added under vigorous stirring, and the mixture was stirred for 10 min at 3°C, heated for 2 h at 68–75°C, and left overnight at room temperature. The precipitate was filtered off, washed with 10 mL of isopropyl alcohol, and dried under reduced pressure. Yield 0.795 g (16%), mp 203–204°C (from $CHCl_3$–*i*-PrOH, 2 : 1). IR spectrum, ν, cm^{-1}: 3443 (OH), 3238, 3160 (NH), 3007, 2969, 2937, 2925, 2857, 2826, 2801, 2757 (CH_2), 1578, 1574 (C–N, δNH), 1300 (C=S). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.75 d.m (2H, 9-H_B, 19-H_B,* $^2J = 12.9$ Hz), 1.85 pseudo-q.t (2H, 9-H_A, 19-H_A, $^2J = 12.9$, $^3J_{AB} = 12.6$, $^3J_{AA} = 4.3$ Hz), 2.32 pseudo-t.d (4H, 8-H_B, 10-H_B, 18-H_B, 20-H_B, $^2J = 11.8$, $^3J_{BA} = 11.8$, $^3J_{BB} = 2.6$ Hz), 2.86 d (2H, 21-H_B, 22-H_B, $^2J = 10.3$ Hz), 2.90 d.m (4H, 8-H_A, 10-H_A, 18-H_A, 20-H_A, $^2J = 11.2$ Hz), 3.62 d.d (4H, 2-H_B, 6-H_B, 12-H_B, 16-H_B, $^2J = 11.9$, $^3J_{\mathrm{NH},B} = 2.7$ Hz), 4.23 d (2H, 21-H_A, 22-H_A, $^2J = 10.0$ Hz), 5.29 d.d (4H, 2-H_A, 6-H_A, 12-H_A, 16-H_A, $^2J = 11.6$, $^3J_{\mathrm{NH},A} = 9.8$ Hz), 9.85 d.d (4H, NH, $^3J_{\mathrm{NH},A} = 9.8$, $^3J_{\mathrm{NH},B} = 2.7$ Hz); the spectrum also contained signals of water (δ 1.64 ppm) and weak signals of solvate propan-2-ol. ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 185.01 (C^4, C^{14}), 70.72 (C^{21}, C^{22}), 63.08 (C^2, C^6, C^{12}, C^{16}), 50.46 (C^8, C^{10}, C^{18}, C^{20}), 24.33 (C^9, C^{19}); the spectrum also contained a weak signal of solvate propan-2-ol (δ_C 25.37 ppm). Found: *m*/*z* 373.1951 $[M + \mathrm{H}]^+$. $C_{14}H_{29}N_8S_2$. Calculated: $M + \mathrm{H}$ 373.1951.

b. A solution of 2.96 g (40 mmol, 3.35 mL) of propane-1,3-diamine in 7 mL of isopropyl alcohol was cooled to 5°C, a mixture of 3.25 g (40 mmol) of 37% formaldehyde solution and 8 mL of isopropyl alcohol was added dropwise over a period of 10 min under vigorous stirring, and 5.45 g (40 mmol) of compound **2**

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* Hereinafter, H_A stands for pseudoequatorial, and H_B, for pseudoaxial protons.

was added in one portion under stirring. The mixture was allowed to warm up to 20°C, heated to 65°C over a period of 1.5 h, and kept for 30 min at that temperature, and a crystalline solid separated. The mixture was transferred to a beaker and left overnight. The resulting transparent jelly material with some embedded crystals was treated in succession with 25 mL of ethanol and 25 mL of acetone, and the precipitate was filtered off and dried under reduced pressure. Yield 2.90 g (39%), mp 204–205°C (from $CHCl_3$–*i*-PrOH, 2:1). A single crystal separated from the mother liquor on the next day after recrystallization was taken for X-ray analysis. The recrystallized product rapidly grew dim and effloresced on exposure to air.

c. A solution of 2.96 g (40 mmol, 3.35 mL) of propane-1,3-diamine in 7 mL of isopropyl alcohol was cooled to 3°C, a mixture of 9.75 g (120 mmol) of a 37% formaldehyde solution and 7 mL of isopropyl alcohol was added dropwise over a period of 15 min under vigorous stirring, and 3.00 g (40 mmol) of thiourea (**1**) was then added in one portion under stirring. The mixture was allowed to warm up to 10°C, heated to 65°C over a period of 1.5 h, and kept for 30 min at that temperature, and a crystalline solid separated. The mixture was transferred into a beaker and left overnight. The resulting transparent jelly material with embedded crystals was treated with 50 mL of chloroform–isopropyl alcohol (4:1), and the mixture was heated for 5 min under reflux. The mixture was allowed to settle down, and the upper transparent solution was separated from the bottom yellow oily material. The solution was filtered through a filter paper and evaporated in a stream of warm air to dryness, and the residue was dried under reduced pressure. Yield 2.01 g (27%), mp 202–203°C (from $CHCl_3$–*i*-PrOH, 2:1).

d. Compound **5**, 3.93 g (10 mmol), was added in one portion under vigorous stirring to a suspension of 1.52 g (20 mmol) of thiourea (**1**) in 15 mL of isopropyl alcohol. The mixture was heated over a period of 1 h to 68–75°C and stirred for 1 h at that temperature; when the temperature attained 60°C, the mixture became homogeneous, and it turned turbid by the end of the process. The mixture was left overnight, and the crystals were filtered off and dried under reduced pressure. Yield 0.30 g (8%), mp 202–204°C (from $CHCl_3$–*i*-PrOH, 2:1).

5,5′-(Propane-1,3-diyl)bis(1,3,5-triazinane-2-thione) (4). A suspension of 10.9 g (80 mmol) of compound **2** in 15 mL of 96% ethanol was cooled to 5°C, 3.36 mL (2.97 g, 40 mmol) of propane-1,3-diamine was added under vigorous stirring, and the mixture was stirred for 10 min. The mixture was then heated for 2 h under reflux with stirring and cooled to room temperature while continuing stirring. The precipitate was filtered off, washed with cold (5°C) 96% ethanol, and dried in air. Yield 10.2 g (93%), mp 183–185°C (from H_2O). IR spectrum, ν, cm^{-1}: 3204 (NH), 2930, 2863 (CH_2), 1546 (C–N, δN–H), 1370 (C–N), 1298 (C=S). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.02 br.s (4H, NH), 4.00 s (8H, NCH_2N), 2.56 t (4H, $NC\mathbf{H}_2CH_2C\mathbf{H}_2N$, $J = 6.7$ Hz), 1.60 quint (2H, $NCH_2C\mathbf{H}_2CH_2N$, $J = 7.0$ Hz). Found: *m*/*z* 275.1107 $[M + H]^+$. $C_9H_{19}N_6S_2$. Calculated: $M + H$ 275.1107.

1,3,7,9,13,15,19,21-Octaazapentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane (5) was synthesized according to modified procedure [6]. Paraformaldehyde, 12.0 g (0.40 mol), was added in portions over a period of 45 min under vigorous stirring to a solution of 14.8 g (0.20 mol, 16.7 mL) of propane-1,3-diamine in 25 mL of 96% ethanol. The mixture was stirred for 1 h at 50°C, the heating bath was removed, and the mixture was stirred for 1 h more, kept for 3 days at room temperature, and evaporated to 1/3 of the initial volume in a stream of warm air. The thick white residue was treated with 100 mL of water, and the precipitate was filtered off and dried under reduced pressure. Yield 11.6 g (59%), mp 160–170°C; published data [6]: mp 161–168°C. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 75.18 and 72.30 (NCH_2N), 51.62 ($N\mathbf{C}H_2CH_2\mathbf{C}H_2N$), 23.90 ($NCH_2\mathbf{C}H_2CH_2N$).

5,5′-(Ethane-1,2-diyl)bis(1,3,5-triazinane-2-thione) (6). *a.* A suspension of 11.0 g (81 mmol) of compound **2** in 15 mL of 75% isopropyl alcohol was cooled to 5°C, 2.40 g (2.67 mL, 40 mmol) of ethane-1,2-diamine was added under stirring, and the mixture was heated while continuing stirring. After 15 min, compounds **1** and **7** (identified by special experiment) separated from the mixture at 30°C, and the precipitate dissolved at 60°C. The mixture was then heated for 1.5 h under reflux, and the precipitate was filtered off from the hot mixture and dried under reduced pressure. Yield 7.21 g (69%), mp 195–200°C (from H_2O); published data: mp 208–210°C [3], 209–210°C [4, 14].

b. Compound **7**, 5.05 g (30 mmol), was added in one portion under vigorous stirring to a solution of 4.57 g (60 mmol) of thiourea (**1**) in 15 mL of water, and the mixture was heated for 2 h under reflux. The mixture was then cooled to 4°C and kept for 1 h at that temperature, and the precipitate was filtered off and dried under reduced pressure. Yield 3.12 g (40%), mp 197–200°C (from H_2O).

1,3,6,8-Tetraazatricyclo[4.4.1.1^{3,8}]dodecane (7) was synthesized according to [7]. Yield 56%, mp 195–197°C (from *i*-PrOH); published data: mp 190–210°C [6], 183–184°C [7].

5,5′-(Butane-1,4-diyl)bis(1,3,5-triazinane-2-thione) (8). A mixture of 1.67 g (22 mmol) of thiourea (**1**), 3.56 g (44 mmol) of a 37% formaldehyde solution, and 15 mL of water was added dropwise under stirring to a solution of 0.969 g (11 mmol) of butane-1,4-diamine in 15 mL of 96% ethanol. The mixture was heated for 2 h under reflux and was then left to stand for 24 h at room temperature. The precipitate was filtered off, washed with cold (5°C) 96% ethanol, and dried under reduced pressure. Yield 2.38 g (75%), mp 205–206°C (from H_2O). IR spectrum, ν, cm^{-1}: 3224 (NH), 2930, 2907, 2861, 2837 (CH_2), 1547 (C–N, δN–H), 1373 (C–N), 1303 (C=S). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.47 m (4H, $NCH_2C\mathbf{H}_2$), 2.53 m (4H, $NC\mathbf{H}_2CH_2$),** 4.00 d (8H, NCH_2N, J = 1.4 Hz), 8.00 br.s (4H, NH). Found: *m*/*z* 289.1264 $[M + H]^+$. $C_{10}H_{21}N_6S_2$. Calculated: *m*/*z* 289.1264.

5,5′-(Propane-1,2-diyl)bis(1,3,5-triazinane-2-thione) (9) was synthesized in a similar way from 0.740 g (0.833 mL, 10 mmol) of propane-1,2-diamine, 1.52 g (20 mmol) of thiourea, and 3.25 g (40 mol) of a 37% formaldehyde solution. After heating under reflux, the mixture was evaporated to 1/3 of the initial volume in a stream of warm air. Yield 2.15 g (78%), mp 198–199°C (from H_2O). IR spectrum, ν, cm^{-1}: 1298 (C=S), 1374 (C–N), 1547 (C–N, δN–H), 2880, 2930, 2947 (CH_2), 3211 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.11 d (3H, $CHC\mathbf{H}_3$, ^3J = 6.5 Hz], 2.46 d.d [1H, $C\mathbf{H}_AH_BCH(CH_3)$, ^3J = 6.2, ^2J = 13.2 Hz], 2.61 d.d [1H, $CH_A\mathbf{H}_BCH(CH_3)$, ^3J = 5.3, ^2J = 13.2 Hz], 2.86 m (1H, $C\mathbf{H}CH_3$), 4.00 pseudotriplet and 4.10 pseudotriplet (4H each, NCH_2N), 8.02 br.s and 8.03 br.s (2H each, NH). Found: *m*/*z* 297.0927 $[M + Na]^+$. $C_9H_{18}N_6NaS_2$. Calculated: M + Na 297.0926.

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** Overlapped by the residual proton signal of the solvent.