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## CYCLOTHIOMETHYLATION OF FUNCTIONAL SUBSTITUTED ANILINES BY CH<sub>2</sub>O AND H<sub>2</sub>S

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**Abstract** – *N*-Aryl substituted 1,3,5-dithiazinanes have been synthesized (20–60 °C) in 32–95% yield by cyclocondensation of *o*-, *p*-aminobenzoic, 4-, 5-aminosalicylic acids, *p*-aminobenzoic acid ethyl or ( $\beta$ -diethylamino)ethyl esters and *p*-aniline sulfamide with CH<sub>2</sub>O and H<sub>2</sub>S (1:3:2 ratio). At ambient temperature *p*-aminobenzoic acid, 5-aminosalicylic acid and *p*-aminobenzoic acid ethyl ester together with 1,3,5-dithiazinanes form appropriate *N*-aryl substituted 1,3-thiazetidines. Cyclothiomethylation of *p*-aminobenzoic acid ethyl ester (0 °C) results in *N,N*-diaryl-1,3,5-thiadiazinane. Heterocyclization of *p*-aniline sulfamide with CH<sub>2</sub>O and H<sub>2</sub>S at a molar ratio of 1:6:4 (pH 1.3–1.5) was found to afford *bis*-1,3,5-dithiazinanes involving two amino groups. Condensation of *p*-aniline sulfacetamide with 37% formalin (CH<sub>2</sub>O) and H<sub>2</sub>S (pH 2.5) led to the compound, which was built as macroheterocycle from two fragments of *p*-aniline sulfacetamide molecule bound to each other by *sym*-dimethyl sulfide chain (CH<sub>2</sub>SCH<sub>2</sub>).

## INTRODUCTION

In organic chemistry there is an original method for the synthesis of 1,3,5-dithiazinane<sup>la-e</sup> based on Wohl reaction namely multimolecular cyclocondensation of methyl amine, 37% formalin (CH<sub>2</sub>O) and H<sub>2</sub>S. Compounds, which contain dithiazinane ring, are used as insecticides and fungicides<sup>2a,b</sup> as well as

additives modified and intensified product taste,<sup>2c,d,e,f,g</sup> inhibitors, ferments,<sup>2h</sup> complexons,<sup>3a,b,c,d,e,f,g</sup> sorbents for gold and silver.<sup>4a,b</sup>

For the last 5 years we systematically investigated the Wohl reaction using cyclothiomethylation of aliphatic<sup>5a</sup> and aromatic<sup>5b</sup> amines, amino acids,<sup>5c</sup> aminoalcohols<sup>5d</sup> aminophenols<sup>5e</sup> as an example to obtain the corresponding *N*-substituted 1,3,5-dithiazinanes,<sup>5a,b,c,d,e</sup> 1,3-thiazetidines<sup>5a,b,c</sup> and 1,3,5-thiadiazinanes.<sup>5b</sup> The direction of the cyclothiomethylation reaction depends on the structure of initial amines and reaction conditions (ratio and order of reagent mixing,<sup>5a,c</sup> temperature,<sup>5a,b,c,d,e</sup> medium pH), under which cyclocondensation is conducted. Thus, it was shown that in the cyclothiomethylation reaction of aliphatic<sup>5a</sup> and aromatic<sup>5b</sup> amines with CH<sub>2</sub>O and H<sub>2</sub>S (amine:CH<sub>2</sub>O:H<sub>2</sub>S = 1:3:2) the decrease in basicity of amines causes the increase in the yield of target 1,3,5-dithiazinanes. Further more thorough and deep analysis of cyclocondensation of functionally-substituted anilines, namely *o*-, *m*- and *p*-aminophenols, with CH<sub>2</sub>O and H<sub>2</sub>S has shown, that the direction of the cyclothiomethylation reaction of aminophenols depends on the position of functional amino group.<sup>5e</sup> Aminophenols, *o*- and *p*-isomers, were established to interact with CH<sub>2</sub>O and H<sub>2</sub>S as a reactant mixture (3:2 ratio) to form 1,3,5-dithiazinanes. *m*-Aminophenol under analogous conditions undergoes intermolecular condensation with CH<sub>2</sub>O and H<sub>2</sub>S simultaneously involving OH and NH<sub>2</sub> groups to form macroheterocycle, which contains the fragments of *m*-aminophenol molecules. Different reactivity of isomeric aminophenols under interaction with CH<sub>2</sub>O and H<sub>2</sub>S is caused by a change of NH<sub>2</sub> group basicity and OH group acidity according to their arrangement in aromatic ring.

Herein we report on the results of our further investigations in the field of cyclothiomethylation of functionally substituted aromatic amines in order to develop novel procedures for a synthesis of new *N*-aryl substituted 1,3,5-dithiazinanes, 1,3,5-thiadiazinanes and macroheterocycles.

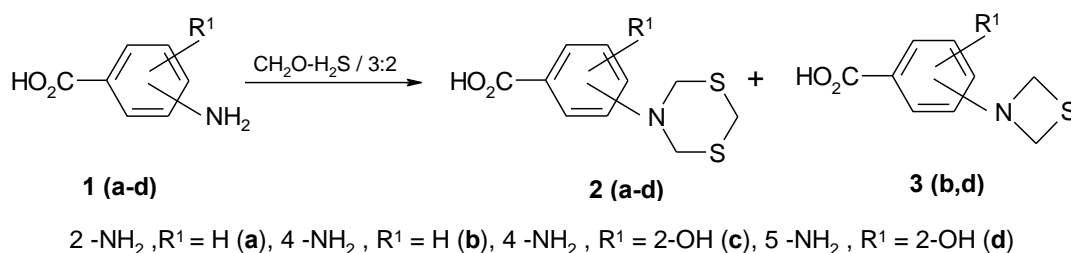
## RESULTS AND DISCUSSION

### CYCLOTHIOMETHYLATION OF AROMATIC AMINO ACIDS AND *p*-AMINOBENZOIC ACID ESTERS

In cyclocondensation with CH<sub>2</sub>O and H<sub>2</sub>S there have been involved aromatic amino acids and their derivatives namely *o*- (**1a**) and *p*-aminobenzoic **1b** acids, 4-(**1c**) and 5-aminosalicylic **1d** acids, and also *p*-aminobenzoic acid ethyl **1e** and ( $\beta$ -diethylamino)ethyl **1f** esters. Using *o*- (**1a**), *p*-aminobenzoic **1b** and 4- (**1c**), 5-aminosalicylic **1d** acids as an example we have studied the influence of COOH group position in aromatic ring on the activity of NH<sub>2</sub> and OH groups in the cyclothiomethylation reaction.

Thus, condensation of aminobenzoic acid **1a** with CH<sub>2</sub>O and H<sub>2</sub>S (1:3:2 ratio) at 20 °C led exclusively to *o*-(1,3,5-dithiazinan-5-yl)benzoic acid **2a** in 61% yield, whereas *p*-aminobenzoic acid **1b** gave a mixture of *p*-(1,3,5-dithiazinan-5-yl)- (**2b**) and *p*-(1,3-thiazetididin-3-yl)benzoic (**3b**) acids with good yields (51 and

34%, respectively) (Scheme 1). Dithiazinane **2b** has been selectively obtained at 60 °C in 95% yield.



Scheme 1 Cyclothiomethylation of *o*- and *p*-aminobenzoic acids, 4- and 5-aminosalicylic acids

4-Aminosalicylic acid **1c**, similar to acid **1a**, reacts with CH<sub>2</sub>O and H<sub>2</sub>S to form exclusively 4-(1,3,5-dithiazinan-5-yl)-2-hydroxybenzoic acid **2c** in 89% yield, and 5-aminosalicylic acid **1d**, similar to acid **1b**, gave a mixture of 5-(1,3,5-dithiazinan-5-yl)-2-hydroxybenzoic acid **2d** and 5-(1,3-thiazetididin-3-yl)-2-hydroxybenzoic acid **3d** in the yields of 32 and 22%, respectively.

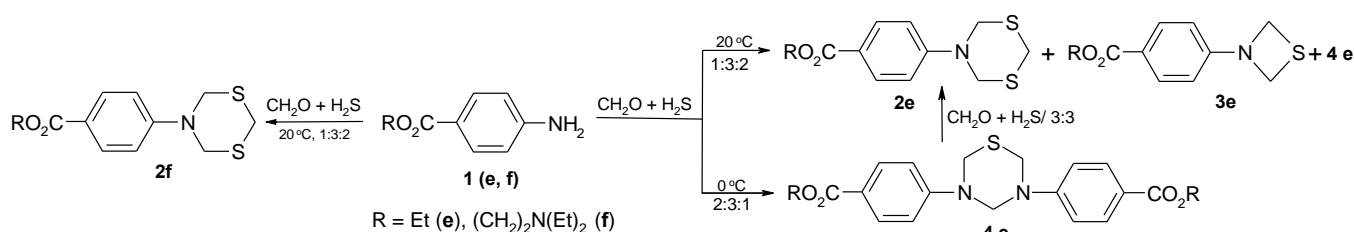
4-Aminosalicylic acid **1c**, in which OH and NH<sub>2</sub> groups occupy *meta*- position, in contrast to *m*-aminophenol, reacts with CH<sub>2</sub>O and H<sub>2</sub>S exclusively at the amino group, probably, as a result of the intramolecular hydrogen bonding between OH and COOH groups (OH... O the *ortho*-effect).<sup>6</sup> As is evident, the direction of cyclothiomethylation of isomeric aromatic amino acids with the aid of CH<sub>2</sub>O and H<sub>2</sub>S depends on the arrangement of functional groups in aromatic ring and their mutual influence.

Individual compounds **2a-d** and **3b,d** have been isolated by means of fractional crystallization. The structures of dithiazinanes **2a-d** and thiazetidines **3b,d** are proven by spectral methods: <sup>1</sup>H NMR and <sup>13</sup>C NMR, GC/MS, and also by the data of element analysis. Molecular weight was determined by Rast cryoscopic method.<sup>7</sup> Heterocycle **2a** was obtained earlier<sup>4a</sup> with 81% yield by cyclocondensation of **1a** with NaHS and CH<sub>2</sub>O, for which any spectral characteristics were absent.

Thus, aromatic amino acids were condensed with CH<sub>2</sub>O and H<sub>2</sub>S only at NH<sub>2</sub> group with the formation of *N,S*-containing heterocycles (1,3,5-dithiazinanes and 1,3-thiazetidines). One should notice that *para*-position of COOH group contributes to an increase of NH<sub>2</sub> group activity in the condensation reaction with CH<sub>2</sub>O and H<sub>2</sub>S. The greatest yield of target dithiazinanes **2a-d** was reached in temperature range from 20 to 60 °C. An increase in reaction temperature up to 80 °C led to a decrease in selectivity with formation of by-product of the reaction – 1,2,4-trithiolane.<sup>8</sup>

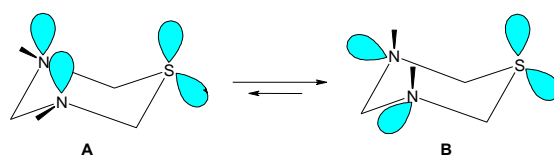
By the reaction of *p*-aminobenzoic acid ethyl **1e** or ( $\beta$ -diethylamino)ethyl **1f** esters with CH<sub>2</sub>O and H<sub>2</sub>S (1:3:2 ratio) at 20 °C the compounds of dithiazinane row **2e,f** has been obtained. Amino ester **1e** in this reaction together with ethyl-4-(1,3,5-dithiazinan-5-yl) benzoate **2e** gave ethyl-4-(1,3-thiazetididin-3-yl) benzoate **3e** and 3,5-di(4-ethylcarboxyphenyl)-1,3,5-thiadiazinane **4e** in 56, 18% and 15% yields, respectively (Scheme 2). At 60 and 80 °C the reaction resulted in a mixture of products **2e-4e**. The latter compounds were isolated by column chromatography.

The regioselective synthesis of thiadiazinane **4e** was carried out at 0 °C by cyclocondensation of *p*-aminobenzoic acid ethyl ester **1e** with CH<sub>2</sub>O and H<sub>2</sub>S (2:3:1 ratio) in 93% yield. Heterocyclic **4e** in the presence of three-molar excess of a thiomethylation mixture CH<sub>2</sub>O-H<sub>2</sub>S at ambient temperature was completely converted into the appropriate dithiazinane **2e**.



Scheme 2. Cyclothiomethylation of *p*-amino benzoic acid ethyl and ( $\beta$ -diethylamino)ethyl esters

According to X-ray diffraction analysis the molecule of **4e** has local plane of symmetry passing through C(2) and S(1) atoms (Figure 2a). The thiadiazinane ring has a chair conformation with axial *cis* position of (4-ethoxycarbonyl)phenylic substituent at the nitrogen atoms. In this orientation the lone pairs at the nitrogen atoms occupy *cis* equatorial position and are antiperiplanar to the lone pairs of the sulfur atom (conformer B).



The orbital repulsion of lone electron-pairs of the nitrogen and sulfur atoms stabilizes an axial *cis* position of (4-ethoxycarbonyl)phenylic substituent (anomeric effect).<sup>9a,b</sup>

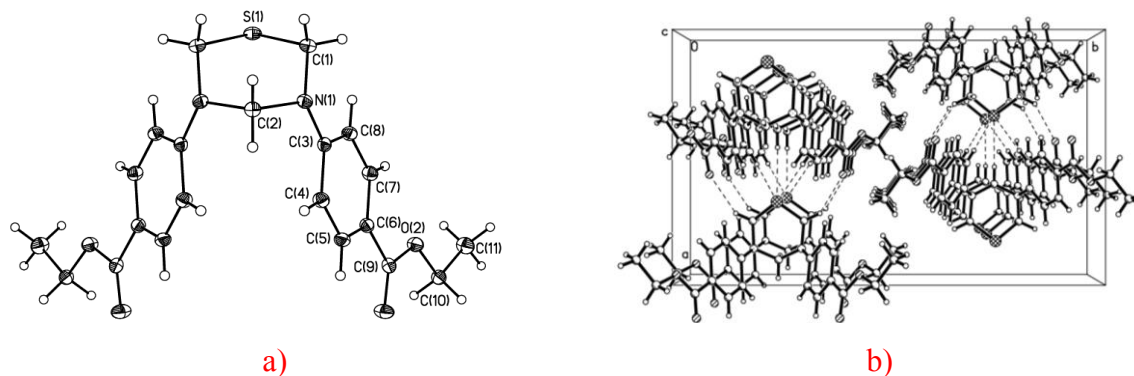


Figure. General view (a) and fragment of crystal packing (b) of compound **4e** in the crystal

In crystal structure above there are two types of intermolecular hydrogenous bonds (Figure 2b). The sulfur atom of one thiadiazinane molecule forms hydrogenous bonds with protons on the two aromatic

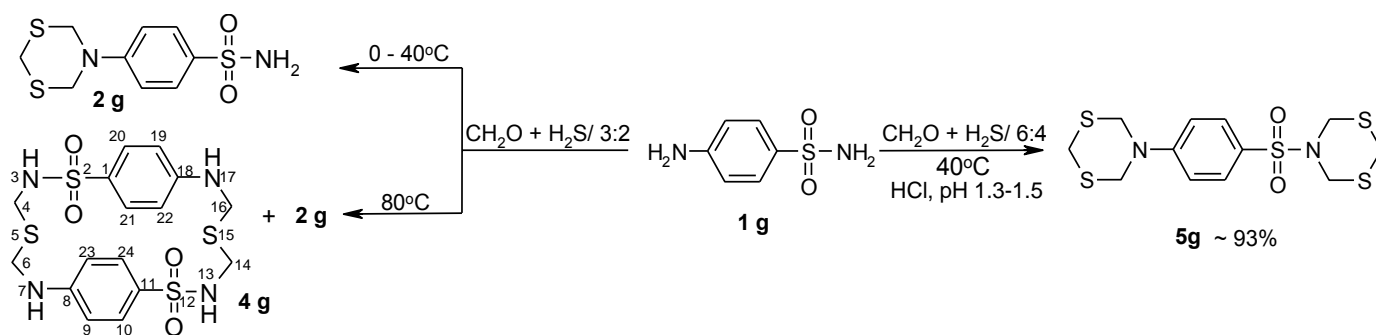
rings at C(4) and with methylene protons of another thiadiazinane molecule at C(2): HC(4)...S(1)...HC(4') и HC(2)...S(1) (where H...S distances are equal to 2.83Å (x 2) and 2.78Å, respectively). At the same time, the ester carbonyl groups of the first thiadiazinane molecule are connected with methylene protons of two other thiadiazinane molecules: O(1)...HC(1A) and O(1')...HC(1B) (distances O...H 2.54Å (x 2)).

In the  $^1\text{H}$  NMR spectra of dithiazinane cycles **2a-f** one could observe two singlets of methylene protons at  $\delta_{\text{H}}$  3.40-4.22 (SCH<sub>2</sub>S) and 4.15-5.20 ppm (NCH<sub>2</sub>S) with integrated intensities ratio of 1:2. The  $^{13}\text{C}$  NMR spectra contain signals at  $\delta_{\text{C}}$  30.61-34.80 (SCH<sub>2</sub>S) and 44.51-56.89 ppm (NCH<sub>2</sub>S) belonging to the carbon atoms. The  $^1\text{H}$  NMR spectrum of thiazetidine cycle (compounds **3b,d,e**) exhibits singlets of methylene protons (NCH<sub>2</sub>S) at  $\delta_{\text{H}}$  4.30-5.15 ppm, while the  $^{13}\text{C}$  NMR spectra contain peaks at  $\delta_{\text{C}}$  51.97-54.60 ppm. In the  $^1\text{H}$  NMR spectra of thiadiazinane **4e** the signals for CH<sub>2</sub>SCH<sub>2</sub> and NCH<sub>2</sub>N methylene protons are observed at  $\delta_{\text{H}}$  4.94 and 5.32 ppm (2:1 ratio), while the  $^{13}\text{C}$  NMR spectrum contains signals at  $\delta_{\text{C}}$  53.13 and 68.23 ppm assigned to the carbon atoms located between two nitrogen atoms and the sulfur and nitrogen atoms, respectively.

#### CYCLOMETHYLATION OF *p*-ANILINE SULFAMIDE AND ITS DERIVATIVES

We investigated cyclothiomethylation of *p*-aminosulfanyl acid amides, namely, *p*-aniline sulfamide **1g**, *p*-aminobenzene sulfacetamide **1h**, 2-(*p*-aminobenzenesulfamido)-3-methoxypyrazine and 4-(*p*-aminobenzenesulfamido)-2,6-dimethoxypyrimidine with the aid of CH<sub>2</sub>O and H<sub>2</sub>S.

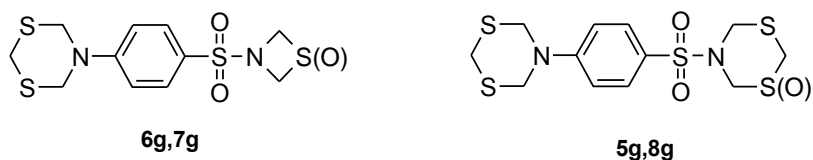
Condensation of *p*-aniline sulfamide **1g** was carried out (**1g**: CH<sub>2</sub>O: H<sub>2</sub>S = 1:3:2) under different temperature conditions (0-80 °C). It was stated that cyclothiomethylation of *p*-aniline sulfamide **1g** within the temperature range from 0 to 40 °C gave rise to the dithiazinane cycle formation exclusively involving the amino group of the aromatic ring to obtain 4-(1,3,5-dithiazinane-5-yl)aniline sulfamide **2g** in 35-73% yield (Scheme 3, Table 1). The increase the temperature to 80 °C facilitates the involvement of less reactive SO<sub>2</sub>NH<sub>2</sub> into the cyclocondensation reaction. So, in these experiments together with **2g** cyclodimer **4g**. The obtained mixture of compounds **2g** and **4g** (3:1 ratio) was divided by fractional crystallization (Scheme 3).



Scheme 3. Cyclothiomethylation of *p*-aniline sulfamide

Cryoscopic determinations<sup>7</sup> with a value of  $285 \pm 10$  correspond to the molecular weight (mass) of compound **2g**, and a value of  $493 \pm 10$  corresponds to the molecular weight of macroheterocycle **4g**. The element analysis of compound **2g** confirms the molecular formula  $C_9H_{12}N_2O_2S_3$  and the molecular formula  $C_{16}H_{20}N_4O_4S_4$  for compound **4g** as well.

To obtain 1,3,5-dithiazinanes simultaneously involving of both amino groups of *p*-aniline sulfamide **1g** into the reaction with  $CH_2O$  and  $H_2S$ , we have increased a quantity of a thiomethylation mixture: **1g**:  $CH_2O$ :  $H_2S$  = 1:6:4 (0, 20, 40, and 80 °C). As a result, cyclocondensation proceeded via both  $NH_2$  groups to give the four-component mixture, GC/MS spectrum of which contains peaks of molecular ions of the characteristic residual fragments with  $m/z$  318 (**7g**), 334 (**6g**), 364 (**8g**) and 380 (**5g**), apparently corresponding to compounds with the (oxy)thiazethidine **6g,7g** and (oxy)dithiazinane **5g,8g** cycles.



Cyclocondensation of **1g** by a mixture of  $CH_2O$  and  $H_2S$  (**1g**:  $CH_2O$ :  $H_2S$  = 1:6:4) in acid medium ( $pH$  1.3-1.5) at 40 °C led to the formation of 5-[4-(1,3,5-dithiazinane-5-sulfonyl)phenyl]-1,3,5-dithiazinane **5g** in 93% yield and with 100% selectivity (Scheme 3, Table).

Table. The influence of  $pH$  medium and initial reagent ratio on the yield and product content of *p*-aniline sulfamide **1g** cyclomethylation

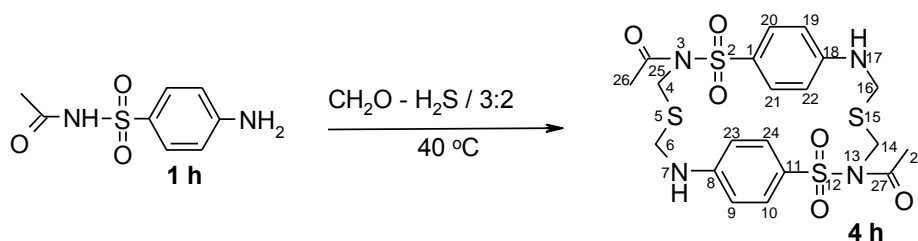
Reagent ratio <b>1g</b> : $CH_2O$ : $H_2S$	$pH$	T, °C	Yield (%)		
			<b>2g</b>	<b>4g</b>	<b>5g</b>
1 : 3 : 2	7.3-7.4	0	35	-	-
	7.3-7.4	20	58	-	-
	7.3-7.4	40	73	-	-
	7.3-7.4	80	52	14	-
1 : 6 : 4	1.3-1.5	40	-	-	93

The  $^1H$  NMR spectrum of heterocycle **2g** exhibits proton signals of aromatic ring at  $\delta_H$  6.80-7.67 ppm. Singlet signals at  $\delta_H$  3.82 and 4.32 ppm correspond to methylene protons located between the sulfur atoms and atoms of N and S, respectively, with integrated intensity of 1:2. The  $^{13}C$  NMR spectrum for **2g** contains signals of the carbon atoms in aromatic rings at  $\delta_C$  116.48, 127.12, 133.99, and 147.86 ppm. The signals at  $\delta_C$  32.96 and 53.30 ppm evidences the presence of the dithiazinane ring methylene groups in compound **2g**.

The  $^1\text{H}$  NMR spectrum of heterocycle **4g** exhibits proton signals of aromatic ring at  $\delta_{\text{H}}$  6.73-7.11 ppm. The singlet signals, which correspond to the methylene protons between the nitrogen and sulfur atoms, appeared at 3.98 and 4.52 ppm at a ratio of 1:1. The proton signals at  $\delta_{\text{H}}$  7.54 and 7.63 ppm belong to NH group. The  $^{13}\text{C}$  NMR spectrum of compound **4g** contains the carbon atom signals of aromatic rings at  $\delta_{\text{C}}$  112.73, 127.35, 131.91, and 149.39 ppm. The presence of signals at  $\delta_{\text{C}}$  44.74 and 63.49 ppm for **4g** characterizes the presence of  $\text{CH}_2$  groups between N and S atoms.

In  $^1\text{H}$  NMR spectrum of compound **5g** the protons of aromatic ring are observed at  $\delta_{\text{H}}$  6.73-8.02, the methylene protons of  $\text{SCH}_2\text{S}$  and  $\text{SCH}_2\text{N}$  groups of the dithiazinane ring, linked with aromatic ring, are observed at  $\delta_{\text{H}}$  3.93 and 4.72 ppm (1:2 ratio), and of sulfo group at  $\delta_{\text{H}}$  4.26 and 5.14 ppm, respectively. The  $^{13}\text{C}$  NMR spectrum of compound **5g** exhibits the signals of dithiazinane cycle carbon atoms, bound with aromatic ring, at  $\delta_{\text{C}}$  31.48 and 56.05 ppm, and with sulfo group at  $\delta_{\text{C}}$  33.10 and 63.40 ppm.

Cyclothiomethylation of *p*-aniline sulfacetamide **1h** was found to proceed simultaneously via  $\text{NH}_2$  and  $\text{SO}_2(\text{Ac})\text{NH}$  groups in acid medium (*pH* 2,5). Under these conditions cyclodimer **4h** has been obtained in 50% yield as a result of intermolecular condensation of two molecules of **1h** with a thiomethylation reagent  $\text{CH}_2\text{O}-\text{H}_2\text{S}$  (Scheme 5) with 70% conversion. In neutral and alkaline medium, *p*-aniline sulfacetamide **1h** did not react with  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{S}$  and 1,2,4-trithiolane was predominantly formed.<sup>8</sup>



Scheme 4. Cyclothiomethylation of *p*-aniline sulfo acetamide

The molecular weight of  $543.53 \pm 10$  (calc.  $M_{\text{cr}}$  544) determined by Rast cryoscopy method<sup>7</sup> and the data of element analysis correspond to molecular formula  $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_6\text{S}_4$  that proved the formation of macroheterocycle **4h**. The  $^1\text{H}$  NMR spectrum shows signals of methylene sulfide protons connected with amino group at  $\delta_{\text{H}}$  4.50 ppm, and connected with the sulfo acetamide group at  $\delta_{\text{H}}$  5.11 ppm. The  $^{13}\text{C}$  NMR spectrum contains signals at  $\delta_{\text{C}}$  43.61 and 44.28 ppm assigned to carbon atoms of  $\text{CH}_2\text{NH}$  and  $\text{CH}_2\text{NSO}$  groups, respectively.

Cyclocondensation of [(*p*-aniline)sulfamido]-3-methoxypyrazine and [4-(*p*-aniline)sulfamido]-2,6-dimethoxypyrimidine containing pyrimidine rings under conditions described above does not proceed with  $\text{CH}_2\text{O}$  or  $\text{H}_2\text{S}$ . The low activity of  $\text{NH}_2$  group in compounds **1i** and **1k** is, apparently, connected with the formation of the intermolecular hydrogenous bonds between  $\text{NH}_2$  group and the nitrogen atoms of pyrimidine ring.

In conclusion, cyclocondensation of *o*- (**1a**), *p*- (**1b**) aminobenzoic, 4- (**1c**), 5- (**1d**) aminosalicyclic acids, ethyl- (**1e**), ( $\beta$ -diethylamino)ethyl esters- (**1f**) of *p*- (**1b**) and *p*-aniline sulfamide **1g** with CH<sub>2</sub>O and H<sub>2</sub>S under optimized conditions leads to the formation of the corresponding dithiazinanes **2a-g**, whereas *p*-aminobenzoic **1b**, 5-aminosalicylic acid **1d** and *p*-aminobenzoic acid ethyl ester **1e** together with dithiazinanes give rise to thiazetidines. Cyclothiomethylation of *p*-aminobenzoic acid ethyl ester by the CH<sub>2</sub>O-H<sub>2</sub>S reagent at 0 °C was found to afford *N,N*-diaryl-1,3,5-thiadiazinane **4e** in quantitative yield (93%). The reaction for obtaining *bis*-1,3,5-dithiazinanes **5g** (93%) from *p*-aniline sulfamide **1g** are more effective in acid medium (pH 1.3-1.5) at 40 °C. It was shown that in the cyclothiomethylation at 80 °C together with the formation of dithiazinane (56%) *p*-aniline sulfamide **1g** undergoes intermolecular condensation to give cyclodimer **4g** (14%). The analogous intermolecular cyclocondensation of *p*-aniline sulfacetamide in acid medium (pH 2,5) leads to cyclodimer **4h** (50%) built from two fragments of *p*-aniline sulfacetamide linked by *sym* dimethyl sulfide chain (CH<sub>2</sub>SCH<sub>2</sub>).

## EXPERIMENTAL

All solvents were freshly distilled. The <sup>1</sup>H NMR spectra of compounds **2a-g**, **3b,d,e** and **4g**, **5g** were measured on spectrometer "Tesla BS-487", <sup>13</sup>C NMR - on spectrometer Jeol FX 90Q (22.50 MHz), internal standard - Me<sub>4</sub>Si. NMR experiments of compounds **4e** and **4h** were recorded on a Bruker AVANCE-400 spectrometer. The GLC-mass spectrometry was carried out on Finigan 4021 instrument. The IR-spectra were recorded on Specord 75 IR in spectrophotometer in Nujol mulls. Elemental analysis of C, H, N, S samples was determined on element analyser of Karlo Erba, model 1106. The pH values of solutions were determined on a pH meter (pH – 340). Melting points were determined on Kofler unit. Column chromatography was performed with the use of silica gel.

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo-K $\alpha$  radiation at 100 K. All calculations were performed on an IBM PC/AT using the SHELXTL software [G. M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI-53719, USA]. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC), deposition numbers 679451 (**4e**).

**Cyclothiomethylation of functional substituted anilines (1a-1h).** The calculated amount of 37% formalin (1.1 mL, 0.015 mol) or (2.2 mL, 0.030 mol) were charged to a three-neck flask equipped with a stirrer and barbotager thermostated at the chosen temperature. Hydrogen sulfide (prepared in excess amount from Na<sub>2</sub>S and HCl) was barbotaged to give CH<sub>2</sub>O-H<sub>2</sub>S mixture at a ratio of 3:2 or 6:4. Then calculated amount of anilines (**1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g** or **1h**; 0.005 mol) was added to the reaction mixture. The mixture was stirred for 2-3 h at a chosen temperature. Compounds **2e**, **3e**, **4e** were isolated

by column chromatography with C<sub>6</sub>H<sub>6</sub>/EtOAc (10:1) as the eluent. The products **2a–d**, **3b**, **3d**, **2g**, **4g** were selected by fractional crystallization from CHCl<sub>3</sub>. Compounds **5g** and **4h** were filtered.

**7-(1,3,5-Dithiazinane-5-yl)-2-benzoic acid (2a)**. White powder (61%). mp 159-160 °C. *m/z* (%): 241 (5) [*M*]<sup>+</sup>, 197 (47), 163 (5), 150 (30), 120 (53), 105 (5), 92 (44), 77 (12), 61 (100). <sup>1</sup>H NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 3.75 (s, 2H, 2H-2), 4.66 (s, 4H, 2H-4, 2H-6), 6.64-7.00 (m, 2H, H-10, H-12), 7.28-7.53 (m, 2H, H-9, H-11), 8.00 (s, H, H-15). <sup>13</sup>C NMR (22.5 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 32.2 (C-2), 44.5 (C-6, C-4), 109.9 (C-8), 114.9 (C-10), 116.6 (C-12), 131.5 (C-9), 134.0 (C-11), 151.7 (C-7), 169.9 (C-13). IR (KBr): 750, 1230, 1600, 1660, 2900, 3320 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>NS<sub>2</sub>: C 49.79, H 4.56, N 5.80, S 26.55. Found: C 50.11, H 4.60, N 5.79, S 26.46.

**7-(1,3,5-Dithiazinane-5-yl)-4-benzoic acid (2b)**. White powder (95%). mp 227-229 °C. *m/z* (%): 241 (9) [*M*]<sup>+</sup>, 207 (12), 91 (15); 44 (100). <sup>1</sup>H NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 4.00 (d, *J*=8.0 Hz, 2H, 2H-2), 4.64 (br. s, 4H, 2H-4, 2H-6), 6.72 (d, *J*=8.0 Hz, 2H, H-8, H-12), 7.17 (d, *J*=8.0 Hz, 2H, H-9, H-11), 7.83 (s, H, H-13). <sup>13</sup>C NMR (22.5 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 33.7 (C-2), 56.3 (C-6, C-4), 113.8 (C-8, C-12), 121.0 (C-10), 131.0 (C-9, C-11), 149.1 (C-7), 167.7 (C-13). IR (KBr): 780, 1200, 1600, 1680, 2900, 3300 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>NS<sub>2</sub>: C 49.79, H 4.56, N 5.80, S 26.55. Found: C 49.79, H 4.56, N 5.80, S 26.63.

**5-(1,3-Thiazetidine-3-yl)-4-benzoic acid (3b)**. White powder (51%). mp 209-210 °C. *m/z* (%): 195 (52) [*M*]<sup>+</sup>, 150 (33); 120 (57); 92 (48); 61 (100). <sup>1</sup>H NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 4.36 (br. s, 4 H, 2H-2, 2H-4), 6.72 (d, *J*=8.0 Hz, 2 H, H-6, H-10), 7.17 (d, *J*=8.0 Hz, 2 H, H-7, H-9), 7.75 (s, H, H-11). <sup>13</sup>C NMR (22.5 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 53.3 (C-2, C-4), 116.4 (C-6, C-10), 120.0 (C-8), 131.0 (C-7, C-9), 147.2 (C-5), 167.7 (C-11). IR (KBr): 780, 1200, 1600, 3300 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>NS: C 55.38, H 4.61, N 7.17, S 16.41. Found: C 55.53, H 4.59, N 7.29, S 16.92.

**4-(1,3,5-Dithiazinane-5-yl)-2-hydroxybenzoic acid (2c)**. White powder (89%). mp 258-260 °C. <sup>1</sup>H NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 4.06 (s, 2 H, 2H-2), 5.20 (s, 4 H, 2H-4 and 2H-6), 6.23 (s, H, H-12), 6.70 (s, H, H-8), 7.85 (s, H, H-11), 8.50 (br. s, 2 H, H-13, H-14). <sup>13</sup>C NMR (22.5 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 33.6 (C-2), 53.2 (C-4, C-6), 103.7 (C-10), 106.4 (C-8), 108.4 (C-12), 131.4 (C-11), 151.5 (C-7), 163.1 (C-9), 172.3 (C-13). IR (KBr): 720, 1170, 1450, 1600, 2900, 3360 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>NS<sub>2</sub>: C 46.69, H 4.28, N 5.44, S 24.90. Found: C 47.21, H 4.33, N 5.48, S 25.16.

**5-(1,3,5-Dithiazinane-5-yl)-2-hydroxybenzoic acid (2d)**. White powder (32%). mp 194-196 °C. <sup>1</sup>H NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 4.00 (s, 2 H, 2H-2), 5.20 (s, 4 H, 2H-4 and 2H-6), 6.80-7.50 (m, 3 H, H-8, H-11 and H-12), 8.45 (br. s, 2 H, H-13, H-14). <sup>13</sup>C NMR (22.5 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 33.5 (C-2), 56.9 (C-4, C-6), 113.0 (C-9), 114.7 (C-11), 117.9 (C-8), 123.0 (C-12), 137.7 (C-7), 155.0 (C-10), 171.8 (C-14). IR (KBr): 800, 1190, 1440, 1600, 1660, 2900 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>NS<sub>2</sub>: C 46.69, H 4.28, N 5.44, S 24.90. Found: C 46.73, H 4.27, N 5.54, S 25.00.

**5-(1,3-Thiazetidine-3-yl)-2-hydroxybenzoic acid (3d).** White powder (22%). mp 164-166 °C. <sup>1</sup>H NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 4.35 (s, 4 H, 2H-2, 2H-4), 6.80-7.50 (m, 3 H, H-6, H-9, H-10) 8.47 (br. s, 2 H, H-11, H-12). <sup>13</sup>C NMR (22.5 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 54.5 (C-2, C-4), 113.0 (C-7), 115.1 (C-9), 119.2 (C-6), 126.3 (C-10), 138.1 (C-5), 158.8 (C-8), 172.2 (C-12). IR (KBr): 800, 1190, 1440, 1600, 1660, 2900 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>9</sub>H<sub>9</sub>O<sub>3</sub>NS: C 51.17, H 4.29, N 6.63, S 15.18. Found: C 51.53, H 4.36, N 6.42, S 15.03.

**Ethyl-4-(1,3,5-dithiazinan-5-yl)benzoate (2e).** White powder (56%). mp 136-138 °C. *m/z* (%) = 269 (40) [*M*]<sup>+</sup>, 191 (21), 177 (70), 163 (24), 149 (33), 132 (100), 77 (36) 45 (52). <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ (ppm) 1.38 (t, *J*=7.2 Hz, 3 H, H<sub>3</sub>C-16), 3.92 (s, 2 H, 2H-2), 4.30 (s, 4 H, 2H-4, 2H-6), 5.10 (br. s, 2 H, 2H-15), 7.05 (d, *J*=9.0 Hz, 2 H, H-8, H-12), 8.05 (d, *J*=9.0 Hz, 2 H, H-9, H-11). <sup>13</sup>C NMR (22.5 MHz, CDCl<sub>3</sub>): δ (ppm) 14.3 (C-16), 34.8 (C-2), 54.5 (C-4, C-6), 60.4 (C-15), 116.2 (C-8, C-12), 121.9 (C-10), 131.0 (C-9, C-11), 148.5 (C-7), 164.6 (C-13). IR (KBr): 750, 1230, 1450, 1660, 3320 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>12</sub>H<sub>15</sub>O<sub>2</sub>NS<sub>2</sub>: C 53.53, H 5.58, N 5.20, S 23.79. Found: C 54.19, H 5.48, N 5.11, S 23.77.

**Ethyl-4-(1,3-thiazetidin-3-yl)benzoate (3e).** White powder (18%). mp 175-177 °C. *m/z* (%) = 225 (0.4) 223 (9) [*M*]<sup>+</sup>, 177 (9), 150 (15), 149 (100), 132 (15), 44 (42), 46 (1.7). <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ (ppm) 1.34 (t, *J*=7.2 Hz, 3H, H<sub>3</sub>C-14), 4.25 (k, *J*= 9.0 Hz, 2 H, H<sub>2</sub>C-13), 5.10 (br. s, 4H, 2H-2, 2H-4), 6.98 (d, *J*=6.3 Hz, 2 H, H-6, H-10), 7.68 (d, *J*=6.3 Hz, 2 H, H-7, H-9). <sup>13</sup>C NMR (22.5 MHz, CDCl<sub>3</sub>): δ (ppm) 14.4 (C-14), 53.2 (C-2, C-4), 60.6 (C-13), 116.4 (C-10, C-6), 125.5 (C-8), 131.2 (C-7, C-9), 155.0 (C-5), 165.6 (C-11). IR (KBr): 750, 1230, 1450, 1660, 3320. *Anal.* Calcd for C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>NS: C 59.19, H 5.83, N 6.28, S 14.35. Found: C 57.20, H 5.42, N 6.11, S 15.77.

**3,5-Di-(4-ethylcarboxyphenyl)-1,3,5-thiadiazinane (4e).** Compound **4e** was isolated by column chromatography (yield 15%). And also the compound **4e** has selectively been received at 0 °C, the starting reagents were taken in the ratio **1e**:CH<sub>2</sub>O:H<sub>2</sub>S = 2:3:1 (yield 93%). White powder, mp 184-186 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 1.32 (t, *J*=6.5 Hz, 6 H, H<sub>3</sub>C-22, H<sub>3</sub>C-26), 4.24 (d, *J*= 6.8 Hz, 4 H, 2H-21, 2H-25), 4.94 (s, 4 H, 2H-2, 2H-6), 5.32 (s, 2 H, 2H-4), 6.91 (d, *J*=8.1 Hz, 4 H, H-8, H-12, H-14, H-18), 7.79 (d, *J*=8.1 Hz, 4 H, H-9, H-11, H-15, H-17). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 14.4 (C-22, C-26), 53.1 (C-2, C-6), 60.57 (C-25, C-21), 68.2 (C-4), 116.3 (C-12, C-8, C-18, C14), 122.1 (C-16, C-10), 131.2 (C-11, C-9, C-17, C-15), 150.5 (C-7, C-13), 166.4 (C-23, C-19). IR (KBr): 750, 1230, 1450, 1660, 3320. *Anal.* Calcd for C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>NS: C 62.98, H 5.04, N 6.99, S 8.01. Found: C 63.25, H 5.32, N 7.11, S 8.65.

**4-(1,3,5-Dithiazinane-5-yl)-2-(diethylamino)ethylbenzoate (2f).** White powder (79%). mp 51-52 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ (ppm) 0.45 (t, *J*=6.3 Hz, 6 H, H<sub>3</sub>C-19, H<sub>3</sub>C-22), 1.30 (t, *J*=9.0Hz, 2 H, 2H-16), 3.12 (k, *J*=10.1 Hz, 4 H, 2H-18, 2H-21), 3.80 (t, *J*=9.0 Hz, 2 H, 2H-15), 4.22 (s, 2 H, 2H-2), 4.68 (s, 4 H, 2H-4, 2H-6), 7.3 (br. s, 2H, H-8, H-12), 7.87 (s, 2 H, H-9, H-11). <sup>13</sup>C NMR (22.5 MHz, CDCl<sub>3</sub>): δ (ppm)

8.5 (C-19, C-22), 32.4 (C-2), 47.1 (C-18, C-21), 49.5 (C-4, C-6), 53.8 (C-16), 58.2 (C-15), 116.9 (C-8, C-12), 131.1 (C-9, C-11), 150.5 (C-7), 164.5 (C-13). IR (KBr): 770, 1100, 1380-1450, 1600, 1680, 2900  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{16}\text{H}_{24}\text{O}_2\text{N}_2\text{S}_2$ : C 56.47, H 8.24, N 8.24, S 18.82. Found: C 51.97, H 7.46, N 7.70, S 19.50.

**4-(1,3,5-Dithiazinane-5-yl)benzenesulfonamid (2g).** White powder (73%). mp 135-137 °C.  $^1\text{H}$  NMR (80 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 3.90 (s, 2 H, 2H-2), 4.56 (s, 4 H, 2H-4, 2H-6), 5.16 (s, 2 H, 2H-14), 6.80 (d,  $J=8.3$  Hz, 2H, H-8, H-12), 7.67 (d,  $J=8.3$  Hz, 2 H, H-9, H-11).  $^{13}\text{C}$  NMR (22.5 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 33.0 (C-2), 53.3 (C-4, C-6), 116.5 (C-8, C-12), 127.1 (C-9, C-11), 134.0 (C-7), 147.9 (C-10). IR (KBr): 685, 820, 1090, 1140, 1305, 1450, 1600, 2905, 3365  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_9\text{H}_{12}\text{N}_2\text{S}_3\text{O}_2$ : C 39.11, H 4.38, N 10.14, S 34.80. Found: C 39.47, H 4.84, N 11.84, S 35.67.

**2,2,12,12-Tetraon-2 $\lambda^6$ ,5,12 $\lambda^6$ ,15-tetrathia-3,7,13,17-tetraazatricyclo[16.2.2.2 $^{8,11}$ ]-tetracos-1(20),8,10,18,21,23-hexaene (4g).** White powder (14%). mp 146-148 °C.  $^1\text{H}$  NMR (80 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 3.98 (s, 4 H, 2H-6, 2H-16), 4.52 (s, 4 H, 2H-4, 2H-14), 6.73 (d,  $J=8.44$  Hz, 4 H, H-9, H-22, H-19, H-23), 7.11 (d,  $J=8.44$  Hz, 4 H, H-10, H-20, H-22, H-24), 7.54 (m, 2 H, NH-7, NH-17), 7.63 (s, 2 H, NH-3, NH-13).  $^{13}\text{C}$  NMR (22.5 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 44.7 (C-6, C-16), 63.5 (C-4, 14), 112.7 (C-9, C-19, C-21, C-24), 127.4 (C-10, C-20, C-22, C-23), 131.9 (C-8, C-18), 149.4 (C-1, C-11). IR (KBr): 560, 815, 1095, 1150, 1305, 1460, 1600, 2910, 3370  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_4\text{S}_4\text{O}_4$ : C 41.72, H 4.38, N 12.16, S 27.85. Found: C 39.35, H 4.54, N 11.82, S 33.73.

**5-[4-(1,3,5-Dithiazinan-5-ylsulfonyl)phenyl]-1,3,5-dithiazinane (5g).** Analogously to the above-described procedure compound (5g) was prepared with accompaniment of the 0.01 mol HCl. After 2 h the reaction mixture was neutralized with an aqueous KOH solution. White powder (93%). mp 154-156 °C.  $^1\text{H}$  NMR (80 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 3.93 (s, 2 H, 2H-2), 4.26 (s, 2 H, 2H-17), 4.72 (s, 4 H, 2H-4, 2H-6), 5.14 (s, 4 H, 2H-15, 2H-19), 6.73 (d,  $J=7.98$ , 2 H, H-8, H-12), 8.02 (d,  $J=7.98$ , 2 H, H-9, H-11).  $^{13}\text{C}$  NMR (22.5 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 31.5 (C-2), 33.1 (C-17), 56.1 (C-4, C-6), 63.4 (C-15, C-19), 114.0 (C-8, C-12), 127.0 (C-9, C-11), 128.0 (C-10), 146.6 (C-7). IR (KBr): 645-695, 1005, 1090, 1140, 1300, 1445, 1595, 2900  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{S}_5\text{O}_2$ : C 37.87, H 4.24, N 7.36, S 42.13. Found: C 37.71, H 4.53, N 8.18, S 43.91.

**5-[4-(1,3-Thiazetan-3-ylsulfonyl)phenyl]-1,3,5-dithiazinane (6g).** White powder (20%).  $m/z$  (%): 334 (5)  $[M]^+$ , 156 (15), 108 (35), 43 (50). IR (KBr): 550, 1005, 1090, 1140, 1300, 1445, 1595, 2900  $\text{cm}^{-1}$ .

**5-[4-(1,3-Oxazetan-3-ylsulfonyl)phenyl]-1,3,5-dithiazinane (7g).** White powder (20%).  $m/z$  (%): 318 (5)  $[M]^+$ , 156 (12), 108 (40), 76 (24), 43 (95). IR (KBr): 550, 1005, 1140, 1300, 1445, 1595, 2900  $\text{cm}^{-1}$ .

**5-[4-(1,3,5-Oxathiazinan-5-ylsulfonyl)phenyl]-1,3,5-dithiazinane (8g).** White powder (20%).  $m/z$  (%): 364 (2)  $[M]^+$ , 200 (20), 136 (60), 78 (30), 43 (100). IR (KBr): 550, 810, 1090, 1300, 1445, 2900  $\text{cm}^{-1}$ .

**2,2,12,12-Tetraon-2 $\lambda^6$ ,5,12 $\lambda^6$ ,15-tetrathia-(3,13-diacyl)-3,7,13,17-tetraazatricyclo[16.2.2.2 $^{8,11}$ ]-**

**tetracos-1(20),8,10,18,21,23-hexaene (4h)**. Analogously to the above-described procedure compound (4h) was prepared with accompaniment of the 0.01 mol HCl. After 3h the reaction mixture was neutralized with an aqueous KOH solution. White powder (51%). mp 126-127 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.88 (s, 6 H, H<sub>3</sub>C-26, H<sub>3</sub>C-28), 4.5 (s, 4 H, 2H-6, 2H-16); 5.11 (s, 4 H, 2H-4, 2H-14); 6.73 (d, *J* = 6.85, 4 H, H-9, H-23, H-19, H-22); 7.63 (d, *J* = 6.85, 4 H, H-10, H-24, H-20, H-21); 21 (m, 2 H, NH-7, NH-17). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 23.4 (C-26, C-28), 43.6 (C-6, C-16); 44.3 (C-4, C-14); 116.3 (C-9, C-19, C-22, C-24); 129.6 (C-20, C-21, C-10, C-24), 147.4 (C-1, C-11), 153.8 (C-8, C-18), 169.0 (C-25, C-27). IR (KBr): 770, 1100, 1400-1450, 1570, 1620, 2900 cm<sup>-1</sup>. *Anal.* Calcd for C<sub>20</sub>H<sub>24</sub>N<sub>4</sub>S<sub>4</sub>O<sub>6</sub>: C 44.10, H 4.48, N 10.09, S 23.55. Found: C 42.78, H 5.07, N 9.88, S 23.65.

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