Synthesis, crystal structure, and interconversions of new *N*-aryl-1,3,5-dithiazinanes, 1,3,5-thiadiazinanes, and 1,5-dithia-3,7-diazacyclooctanes

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Chemoselectivity of multicomponent reaction of anilines with the CH_2O—H_2S thiomethylating mixture in the synthesis of *N*-aryl-substituted 1,3,5-dithiazinanes, 1,3,5-thiadiazinanes, and 1,5-dithia-3,7-diazacyclooctanes has been studied depending on the type and mutual arrangement of substituents in the starting anilines, ratio of reagents, temperature, and reaction time. Conformation of the synthesized heterocycles in crystal has been found by X-ray diffraction. Interconversion of the heterocycles showed stability of *N*-aryl-1,3,5-dithiazinanes.

Key words: multicomponent reaction, thiomethylating mixture, substituted anilines, hydrogen sulfide, formaldehyde, X-ray diffraction study.

Saturated sulfur- and nitrogen-containing heterocycles are involved into formation of transition metal complexes and, therefore, are of interest as potential bidentate ligands.[1,2]

In the last years, we have in detail studied cyclothiomethylation of aliphatic amines with formaldehyde and H_2S in the selective synthesis of 1,3,5-dithiazinanes.[3—5] Heterocyclization of anilines with CH_2O and H_2S proceeded with the formation of different types of heterocyclic compounds:[6] 1,3-thiazetidines, 1,3,5-dithiazinanes, 1,3,5-thiadiazinanes, and 1,3,5-oxathiazinanes and, depending on the nature and position of a substituent in the aromatic ring, predominant formation of one of the listed heterocycles occurred.

The present work deals with the study of chemoselectivity of the multicomponent reaction of anilines **1a—l** with the CH_2O—H_2S thiomethylating mixture (see Ref. 7) in the directed synthesis of *N*-aryl-substituted 1,3,5-dithiazinanes, 1,3,5-thiadiazinanes, and 1,5-dithia-3,7-diazacyclooctanes depending on the type and mutual arrangement of substituents in the starting anilines, ratio of the starting reagents, solvent effect, temperature, and the experiment duration.

Results and Discussion

Regioselective synthesis of 1,3,5-dithiazinanes takes place at stoichiometric ratio of the starting reagents aniline : CH_2O : H_2S equal to 1 : 3 : 2.

Using aniline as an example, it was found that the choice of the solvent (H_2O, C_6H_6, Et_2O, EtOAc, MeOH, EtOH, BuOH) has no effect on the direction of the process, but influences the reaction conversion and selectivity. The use of aqueous ethanol as the solvent in further experiments is due to good solubility of the starting components in this solvent mixture, efficiency of the process, easy isolation of the reaction products, availability, and lower toxicity. It was found that the highest yield is reached in the temperature interval 40—60 °C. *N*-Aryl-substituted 1,3,5-dithiazinanes **2a—l** were selectively synthesized under indicated conditions (the ratio 1 : 3 : 2, 40—60 °C, EtOH—H_2O) (Scheme 1). Note that an increase in the reaction time to 10—12 h leads to an increase in regioselectivity of the process (see Ref. 6), apparently due to the *in situ* transformation of the less stable intermediate heterocycles **3a—l** and **4a—l** to *N*-aryl-1,3,5-dithiazinanes **2a—l**.

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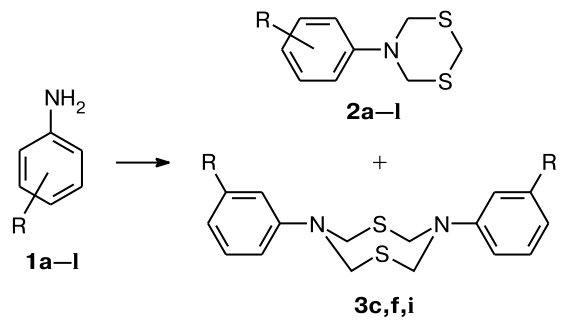
Scheme 1



Reagents and conditions: CH_2O—H_2S (3 : 2), 40—60 °C, EtOH—H_2O

At the same time, *meta*-substituted anilines under these conditions, along with 1,3,5-dithiazinanes, give small amounts (10—20%) of 1,5-dithia-3,7-diazacyclooctanes **3c**, **3f**, and **3i** (Table 1).

Aniline **1a** and *para*-substituted anilines **1d,g,j,l** are more active in the heterocyclization with CH_2O and H_2S. An increase in reactivity was also observed for the sterically hindered *ortho*-substituted anilines with an electron-withdrawing substituent (NO_2, I). To sum up, the heterocyclization of *ortho*- and *para*-substituted anilines **1b,d,e,g,h,j—l** to 1,3,5-dithiazinanes occurs the more readily, the less basic is the NH_2 group. According to the experimental data, the yields of 1,3,5-dithiazinanes increase in the following order: for *para*-substituted anilines, *p*-OMe < *p*-Me < *p*-Br < *p*-NO_2; for *ortho*-substituted anilines, *o*-OMe < *o*-Me < *o*-I < *o*-NO_2.

The structure of compound **2l** was unambiguously established by X-ray diffraction analysis. In the crystal, the 1,3,5-dithiazinane ring is in the *chair* conformation with the axial *p*-bromophenyl substituent (Fig. 1). The lone pair of electrons (further, lp) on the N(1) atom is in conjugation with the aromatic substituent and is involved into stereoelectronic interactions $lp_N \rightarrow \sigma^*_{C-S}$ with the C(1)—S(1) and C(3)—S(2) bonds. The nature of this interaction and its effect on the structure of compounds studied in this work will be more in details considered below.

Table 1. Yields of condensation products of arylamines with CH_2O and H_2S in proportion 1 : 3 : 2 at 40—60 °C

1	R	pK_a[8]	Yield (%)	
			2	3
a	H	4.58	65	—
b	*o*-Me	4.39	40	—
c	*m*-Me	4.69	48	10
d	*p*-Me	5.12	68	—
e	*o*-OMe	4.49	34	—
f	*m*-OMe	4.2	37	10
g	*p*-OMe	5.29	60	—
h	*o*-NO_2	–0.29	64	—
i	*m*-NO_2	2.5	45	20
j	*p*-NO_2	1.02	76	—
k	*o*-I	2.6	56	—
l	*p*-Br	3.91	70	—

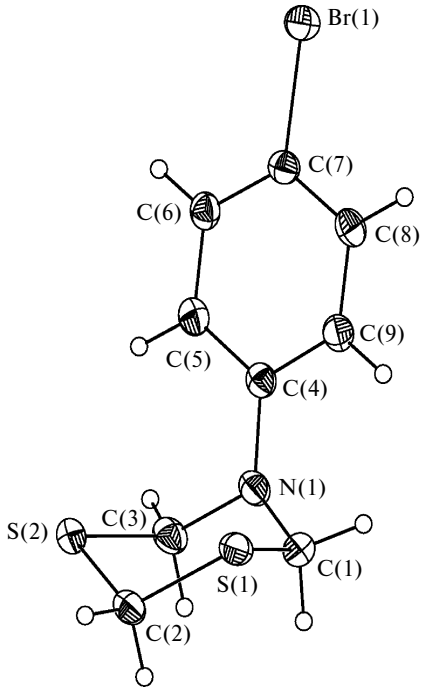


Fig. 1. Molecular structure of **2l** in crystal. Atoms are represented by thermal ellipsoids (p = 50%).

Heterocycles **2a—l** are characterized by free inversion of the dithiazinane ring in solution at room temperature, which was inferred from the singlet signals of the NCH_2S and SCH_2S methylene protons in the ^1H NMR spectra in the region δ 4.70—5.74 and 3.38—4.38, respectively.

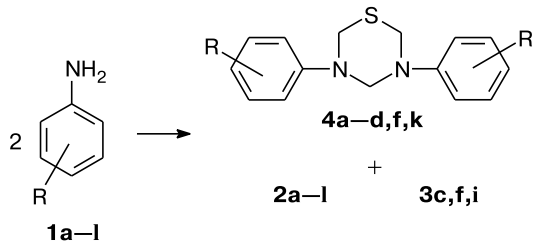
The ^{13}C NMR spectra of dithiazinanes **2a,b,h—l** exhibit the corresponding signals for the methylene groups between two sulfur atoms (δ_C 33.7—43.0) and between nitrogen and sulfur atoms (δ_C 55.1—63.4). In the mass spectra of products **2a**, **2b**, and **2k**, molecular ions $[M]^+$ are observed with m/z 197, 211, and 323, respectively, as well as peaks of characteristic fragment ions with the successive loss of the methylenesulfide units CH_2S.

For the directed synthesis of 1,3,5-thiadiazinanes, the reaction was carried out with the ratio aniline : CH_2O : H_2S = 2 : 3 : 1 at 0°C (see Ref. 9). Regioselectivity of this process is determined by the structure of the starting anilines **1a—l**.

It was found that for all the anilines under these conditions, the corresponding 1,3,5-dithiazinanes **2a—l** are immediately formed (TLC monitoring) together with the target 1,3,5-thiadiazinanes, the amount of which increases with the increase in the reaction time. The complete con-

version is reached after 10 h with the formation of a mixture of heterocycles **2—4** (Scheme 2, Table 2), which were separated by column chromatography on silica gel. Note that weak bases **1h—j** form no 1,3,5-thiadiazinanes, while the stronger base, *p*-bromoaniline **1l**, gives 1,3,5-thiadiazinane **4l** in 83% yield. Earlier,[10] the corresponding 1,3,5-thiadiazinane was synthesized under analogous conditions from ethyl *p*-aminobenzoate in 93% yield. *o*-Substituted anilines **1b,e,h,k** are characterized by low conversion, apparently, due to the "*ortho*-effect",[11] with anilines **1e,k** giving no thiadiazinanes at all. *m*-Isomers **1c,f**, similarly to the preceding experiments (see Scheme 1), form 1,5-dithia-3,7-diazacyclooctanes **3** along with the target **4c,f** (see Scheme 2, Table 2).

Scheme 2



Reagents and conditions: CH_2O—H_2S (3 : 1), 0 °C, EtOH—H_2O

para-Substituted anilines are more reactive in the series of syntheses of 1,3,5-thiadiazinanes, their activity increases with the increase in acidity: *p*-OMe < *p*-Me < < *p*-Br < *p*-COOEt.

The structures of compounds **4a** and **4d** were confirmed by X-ray diffraction. The 1,3,5-thiadiazinane rings in both molecules were in the *chair* conformation with the *syn*-axial arrangement of the substituents (Fig. 2).

The ^1H and ^{13}C NMR spectra of thiadiazinanes **4a,b,l** exhibit the corresponding signals for the methylene groups between two nitrogen atoms (δ_H 5.18—5.27 and δ_C 69.3—71.7) and between the nitrogen and the sulfur atoms (δ_H 4.94—5.01 and δ_C 53.4—53.8).

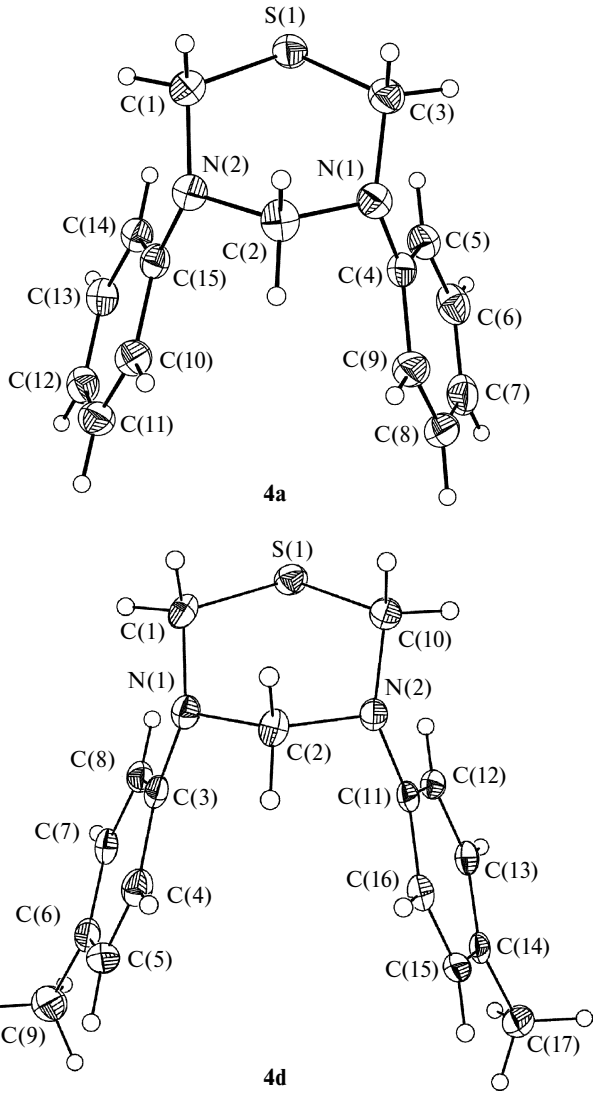


Fig. 2. Molecular structures of **4a** and **4d** in crystal. Atoms are represented by thermal ellipsoids (p = 50%).

Table 2. Yields of condensation products of arylamines with CH_2O and H_2S in proportion 2 : 3 : 1 at 0 °C

1	Yield (%)		
	2	3	4
a	50	—	15
b	15	—	34
c	5	31	45
d	20	—	52
e	20	—	—
f	15	36	30
g	55	—	23
h	21	—	—
i	25	33	—
j	35	—	—
k	37	—	—
l	5	—	83

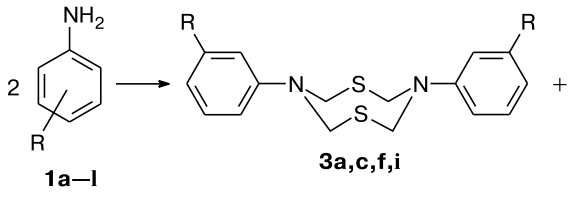
According to the data in Ref. 12, a predominant formation of 1,5-dithia-3,7-diazacyclooctanes **3a,c,d,f** occurs with the ratio aniline—CH_2O—H_2S equal to 1 : 6 : 4 at 0 °C (EtOH—H_2O) (Scheme 3). Heterocycles obtained starting from aniline **1a** and *meta*-substituted anilines **1c,f,i** proved more stable (Table 3), whereas *ortho*-substituted anilines **1b,e,h,k** under these conditions yield only dithiazinanes **2b,e,h,k**. In the ^1H NMR spectra of eight-membered dithiadiazacyclooctanes, the methylene protons, in contrast to dithiazinanes and thiadiazinanes, are found as doublets of doublets (δ_H 4.86—5.29), that indicates decelerated inversion of the cyclooctane ring in solution.[13,14] In the ^{13}C NMR spectra, the singlet methylene signals are found in the region δ 55.9—56.4

Table 3. Yields of condensation products **2—4** of arylamines with CH_2O and H_2S in proportion 1 : 6 : 4 at 0 °C

1	Yield (%)		
	2	**3**	**4**
a	10	70	10
b	31	—	28
c	20	50	—
d	55	5	—
e	25	—	—
f	20	48	—
g	57	10	—
h	28	—	—
i	42	44	—
j	41	8	—
k	40	—	—
l	66	10	—

To sum up, aniline and *m*-substituted anilines only have tendency to the formation of 1,5-dithia-3,7-diazacyclooctanes under indicated conditions. Apparently, 1,3,5-dithiazinanes are the stable form for *o*- and *p*-substituted isomers.

Scheme 3



+ **2a—l** + **4a,b**

Reagents and conditions: CH_2O—H_2S (6 : 4), 0 °C, EtOH—H_2O

The structure of compound **3a** was established by X-ray diffraction. 1,5-Dithia-3,7-diazacyclooctane ring in crystal of **3a** adopts the *chair-chair* (or *crown*) conformation[13] with the axial arrangement of the *N*-aryl substituents (Fig. 3).

In all the compounds considered, the nitrogen atoms could be involved in both the conjugation with the aromatic substituents and stereoelectronic $lp_N \rightarrow \sigma^*_{C-S}$ interactions. The conjugation with the aromatic substituent results in the flattening the nitrogen atom and shortening the $N-C_{arom}$ bond, whereas the $lp_N \rightarrow \sigma^*_{C-S}$ interaction to operate requires antiperiplanar arrangement of the lone pair on the nitrogen atom and polar C—S bond, that corresponds to the value of pseudotorsional angle lp—N—C—S close to 180° (see Ref. 15). The strength of the stereoelectronic interaction can be estimated from the change of the C—S bond distance, which in the $N-CH_2-S$ system is 1.814 Å in the absence of the stereoelectronic interaction and can increase to 1.860 Å if it is present.[16]

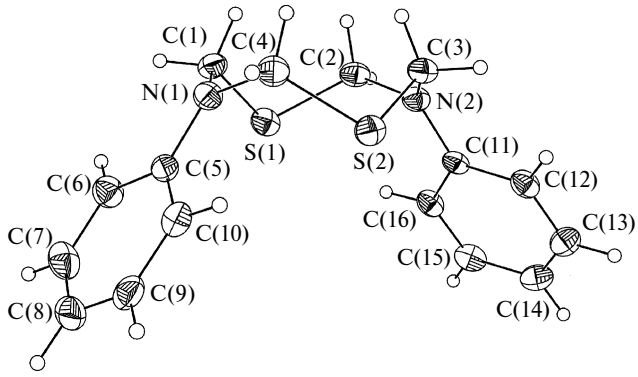


Fig. 3. Molecular structure of **3a** in crystal. Atoms are represented by thermal ellipsoids ($p = 50\%$).

Based on the data given in Table 4, a conclusion can be drawn that the conjugation between the lone pair of electrons on the nitrogen atom and the phenyl ring is present in all the compounds studied (the $N-C_{arom}$ bond is shorter than the value of 1.430 Å characteristic of $(Alk)_2N_{sp^3}-C_{arom}$).[17] At the same time, this conjugation does not lead to a noticeable flattening the nitrogen atom (the nitrogen atom comes out of the plane by 0.15—0.28 Å). The $lp_N > \sigma^*_{C-S}$ interaction operates in all the molecules considered as well, resulting in considerable elongation of the C—S bond as compared to a typical for the $N-CH_2-S$ bond value of 1.814 Å (see Ref. 16). In compounds **4a** and **4d**, this elongation is more pronounced, which is explained by involvement of each nitrogen atom into one lp—N—C—S stereoelectronic interaction, rather than in two as in compounds **2l** and **3a**. It should be noted that the *syn*-diaxial arrangement of substituents in compounds **4a** and **4d** is unfavorable from the point of view of their steric repulsion, but at the same time is optimum for the interaction of the lone pairs on the nitrogen atoms with the σ^*_{C-S} antibonding orbitals of the C—S bonds (**B**, Scheme 4). Thus, a generalized anomeric effect in this case is a determining one for the conformation of

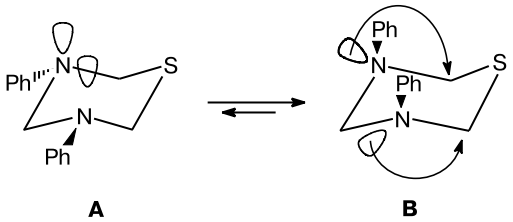
Table 4. Bond lengths (*d*), distances, and pseudotorsional angle lp—N—C—S in molecules **2l**, **3a**, **4a**, and **4d**

Compound	$d(N-C_{ar})$	$d(N-CH_2-S)^a$	ΔN^b	lp—N—C—S /deg
	Å			
2l	1.412(2)	1.837(4)	0.24	177
3a	1.408(2)	1.839(2)	0.15	176
4a	1.418(3)	1.847(2)	0.28	169
4d	1.419(2)	1.846(2)	0.27	167

[a] The average bond distance C—S in the system $N-CH_2-S$.
[b] The distance from the nitrogen atom to the plane of substituents.

1,3,5-thiadiazinane heterocycle. Conformations of compounds **2l** and **3a** also satisfy the maximum possible amount of the $lp_N \rightarrow \sigma^*_{C-S}$ interactions.

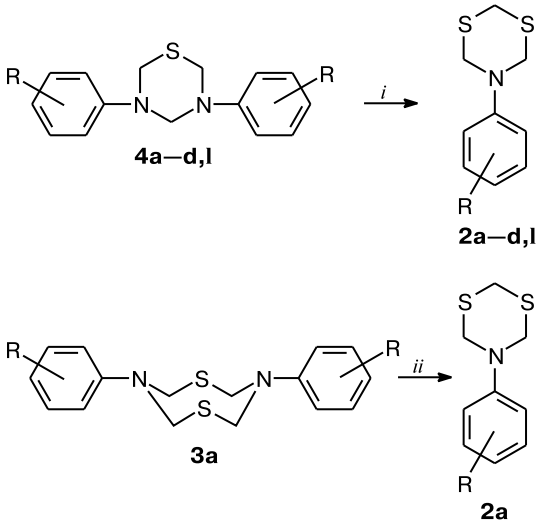
Scheme 4



To sum up, formation of 1,3,5-dithiazinanes **2a—l**, obviously, the final stable products, was observed under any conditions, in which the reaction has been carried out.

To confirm this result, 1,3,5-thiadiazinanes **4a—d,l** and 1,5-dithia-3,7-diazacyclooctane **3a** were treated with CH_2O and H_2S to obtain 1,3,5-dithiazinanes **2a—d,l** (Scheme 5). It should be emphasize that for the formation of dithiazinanes from thiadiazines, a longer time is necessary, since the latter, obviously, are more stable compounds than 1,5-dithia-3,7-diazacyclooctanes.

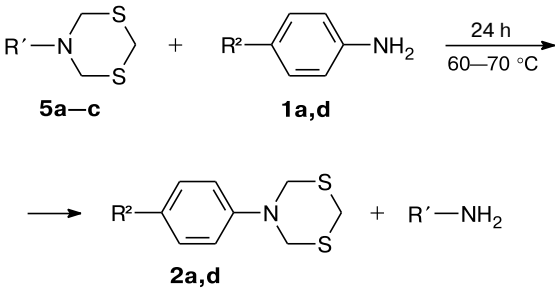
Scheme 5



Reagents and conditions: *i*. $CH_2O—H_2S$ (3 : 3), 20 °C, $CHCl_3$; *ii*. $CH_2O—H_2S$ (2 : 2), 20 °C, $CHCl_3$.

Attempted reverse transformation of **2a—d,l** to **4a—d,l** and **3a** were unsuccessful. However, a number of transformations of 2,4,6-alkyl-substituted dithiazinanes to thiadiazinanes by the reaction of the former with amines and ammonia are known,[18] as well as their transamination reactions.[19] Using the reaction of 5-methyl- (**5a**), 5-*tert*-butyldithiazinanes (**5b**) and 4-(1,3,5-dithiazinan-5-yl)-acetic acid (**5c**) with aniline **1a** and *p*-toluidine **1d**, we showed that more stable *N*-aryl-1,3,5-dithiazinanes **2a,d** are formed (Scheme 6). No transamination takes place upon the action of ammonia, methyl- and *tert*-butylamine, and glycine on aromatic 1,3,5-dithiazinanes **2a,d** and 1,3,5-thiadiazinane **3d**. As it is seen, aryl-substituted 1,3,5-thiadiazinanes are more stable compounds and retain stability upon standing for several years, in contrast to aliphatic analogs, which are decomposing with time.[20,21]

Scheme 6



Rr = Me (**5a**), Bu^t (**5b**), CH_2COOH (**5c**)

In conclusion, the following chemoselectivity can be tracked in the synthesis of saturated *N*-aryl-substituted heterocycles by the multicomponent condensation of anilines with the $CH_2O—H_2S$ thiomethylating mixture: *para*-substituted anilines tend to form 1,3,5-dithiazinanes and 1,3,5-thiadiazinanes, whereas aniline and *meta*-substituted anilines tend to give 1,5-dithia-3,7-diazacyclooctanes. Conformations in crystal of the compounds studied is in the first place determined by the generalized anomeric effect in the lp—N—C—S system: the conformations with the maximum possible amount of the $lp_N \rightarrow \sigma^*_{C-S}$ interactions are present Stability of *N*-aryl-substituted 1,3,5-dithiazinanes was demonstrated by the transamination and interconversion reactions of the heterocycles.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer (80.00 MHz for ^1H, 22.50 MHz for ^{13}C) with Me_4Si as an internal standard and $CDCl_3$ (for compounds **2a,k,e**, **3a**, **4a,b,l**) and DMSO-d_6 (for compounds **2h—j**, **3c,f,i**) as the solvents. The ^1H and ^{13}C NMR spectra of compounds **2c—d**, as well as **4c—d**, are identical to those described earlier.[6] Sorbfil (Sorbpolymer, Krasnodar, Russia) plates were used for TLC in the system benzene—ethanol, 9 : 1 with visualization in I_2 vapors. Silica gel L (KSKG, 50—160 μm) was used for column chromatography. GLC-MS analysis of compounds was performed on a Finnigan 4021 instrument (a 50000×0.25-mm glass capillary column, HP-5 as a stationary phase, helium as a carrier gas, temperature was programmed from 50 to 300 °C at 5 deg min^{-1}, the injector temperature was 280 °C, the temperature of the

source of ions was 250 °C, 70 eV). Elemental analysis was performed on a Carlo Erba 1106 element analyzer; Bromine was determined by burning in a flask with oxygen (the Scheniger method). Compounds obtained are characterized by melting points determined on a PHMK 80/2617 instrument.

X-ray diffraction studies of compounds **2l**, **3a**, **4a**, and **4d** were performed on a SMART APEX 1000 CCD (**2n**) and SMART APEX II CCD diffractometers (**3a**, **4a**, and **4d**) using MoKα irradiation, a graphite monochromator, and ω-scanning. The structures were solved by the direct method and refined by the least-squares method in anisotropic full-matrix approximation on F^2_{hkl}. The basic crystallographic data, refinement parameters, and CCDC are given in Table 5. All the calculations were performed using the SHELXTL 5.10 program package.[22]

***N*-Aryl-1,3,5-dithiazinanes 2a—l.** Aniline (0.005 mol) in EtOH (95%, 5 mL) was added dropwise to 37% aqueous formaline (1.1 mL, 0.015 mol) saturated with hydrogen sulfide over 30 min. The mixture was stirred for 10 h at 40 °C. Compounds **2a,b,e,g,k,l** were extracted with chloroform, isolated, and washed with ethanol; **2c,f,i** were isolated by fractional crystallization; **2d,h,j** were filtered off and washed with chloroform.

5-Phenyl-1,3,5-dithiazinane (2a). The yield was 65%, m.p. 165—167 °C (Ref. 6: 169—170 °C). ^{1}H NMR (80 MHz), δ: 4.27 (s, 2 H, C(2)H_2); 4.96 (s, 4 H, C(4)H_2, C(6)H_2); 7.01—7.41 (m, 5 H, Ar). ^{13}C NMR (22.5 MHz), δ: 34.7 (t, C(2)); 56.4 (t, C(4), C(6)); 117.3 (d, C(12), C(18)); 120.4 (d, C(10)); 129.4 (d, C(11), C(9)); 144.7 (s, C(7)). MS, *m/z* (I_{rel} (%)): 197 $[M]^+$ (55), 151 $[M - CH_2S]^+$ (13), 119 $[M - SCH_2S]^+$ (45), 105 $[M - SCH_2SCH_2]^+$ (100), 91 $[M - SCH_2SCH_2CH_2]^+$ (58), 77 $[C_6H_5]^+$ (15). Found (%): C, 54.64; H, 5.40; N, 7.45; S, 31.98. $C_9H_{11}NS_2$. Calculated (%): C, 54.78; H, 5.62; N, 7.10; S, 32.50.

5-(2-Methylphenyl)-1,3,5-dithiazinane (2b). The yield was 40%, a resin-like compound. ^{1}H NMR (80 MHz), δ: 2.20 (s, 3 H, C(13)H_3); 4.22 (br.s, 2 H, C(2)H_2); 4.70 (br.s, 4 H, C(4)H_2, C(6)H_2); 7.13—7.35 (m, 4 H, Ar). ^{13}C NMR (22.5 MHz), δ: 17.6 (q, C(13)); 33.7 (t, C(2)); 57.0 (t, C(4), C(6)); 122.2 (d, C(12)); 124.4 (d, C(10)); 126.0 (d, C(11)); 130.6 (d, C(9)); 133.4 (s, C(8)); 146.7 (s, C(7)). MS, *m/z* (I_{rel} (%)): 211 $[M]^+$ (47), 133 $[M - SCH_2S]^+$ (38), 132 $[M - SCHS]^+$ (100), 119 $[M - CH_2SCH_2S]^+$ (41), 118 $[M - CH_3SCH_2S]^+$ (90), 91 $[M - NCH_2SCH_2SCH_2]^+$ (31). Found (%): C, 56.50; H, 6.45; N, 6.93; S, 31.00. $C_{10}H_{13}NS_2$. Calculated (%): C, 56.83; H, 6.20; N, 6.63; S, 30.34.

5-(3-Methylphenyl)-1,3,5-dithiazinane (2c). The yield was 48%, m.p. 150—152 °C (Ref. 6: 154—155 °C).

5-(4-Methylphenyl)-1,3,5-dithiazinane (2d). The yield was 68%, m.p. 146—148 °C (Ref. 6: 147—148 °C).

5-(2-Methoxyphenyl)-1,3,5-dithiazinane (2e). The yield was 34%, m.p. 100—102 °C (Ref. 6: 104—105 °C).

5-(3-Methoxyphenyl)-1,3,5-dithiazinane (2f). The yield was 37%, m.p. 115—117 °C (Ref. 6: 119—120 °C).

5-(4-Methoxyphenyl)-1,3,5-dithiazinane (2g). The yield was 60%, m.p. 112—113 °C (Ref. 6: 109—110 °C).

5-(2-Nitrophenyl)-1,3,5-dithiazinane (2h). The yield was 64%, m.p. 260—262 °C. ^{1}H NMR (80 MHz), δ: 3.38 (s, 2 H, C(2)H_2); 4.75 (s, 4 H, C(4)H_2, C(6)H_2); 6.74 (t, 1 H, C(10)H, *J* = 7.4 Hz); 7.13 (d, 1 H, C(12)H, *J* = 7.4 Hz); 7.55 (t, 1 H, C(11)H, *J* = 7.4 Hz); 8.06 (d, 1 H, C(9)H, *J* = 7.4 Hz). ^{13}C NMR (22.5 MHz), δ: 43.0 (t, C(2)); 63.4 (t, C(4), C(6)); 115.6 (d, C(10)); 116.2 (d, C(12)); 126.1 (d, C(9)); 135.9 (d, C(11)); 143.0 (s, C(8)); 143.3 (s, C(7)). Found (%): C, 44.84; H, 4.33; N, 11.05; S, 25.97. $C_9H_{10}N_2O_2S_2$. Calculated (%): C, 44.61; H, 4.16; N, 11.56; S, 26.47.

5-(3-Nitrophenyl)-1,3,5-dithiazinane (2i). The yield was 45%, m.p. 100—102 °C. ^{1}H NMR (80 MHz), δ: 4.36 (s, 2 H, C(2)H_2); 5.18 (s, 4 H, C(4)H_2, C(6)H_2), 7.15—7.86 (m, 4 H, Ar). ^{13}C NMR (22.5 MHz), δ: 33.3 (t, C(2)); 53.4 (t, C(4), C(6)); 111.1 (d, C(12)); 113.5 (d, C(10)); 123.5 (d, C(8)); 130.1 (d, C(9)); 149.0 (s, C(11)); 146.3 (s, C(7)). Found (%): C, 44.56; H, 4.10; N, 11.84; S, 26.45. $C_9H_{10}N_2O_2S_2$. Calculated (%): C, 44.61; H, 4.16; N, 11.56; S, 26.47.

5-(4-Nitrophenyl)-1,3,5-dithiazinane (2j). The yield was 65%, m.p. 198—200 °C. ^{1}H NMR (80 MHz), δ: 4.38 (s, 2 H, C(2)H_2); 5.74 (s, 4 H, C(4)H_2, C(6)H_2); 7.23 (d, 2 H, C(8)H, C(12)H, *J* = 8.0 Hz); 7.96 (d, 2 H, C(9)H, C(11)H, *J* = 8.0 Hz). ^{13}C NMR (22.5 MHz), δ: 33.4 (t, C(2)); 53.0 (t, C(4), C(6)); 116.2 (d, C(8), C(12)); 125.2 (d, C(9), C(11)); 138.8 (s, C(10)); 150.9 (s, C(7)). Found (%): C, 45.00; H, 4.28; N, 11.35; S, 26.50. $C_9H_{10}N_2O_2S_2$. Calculated (%): C, 44.61; H, 4.16; N, 11.56; S, 26.47.

5-(2-Iodophenyl)-1,3,5-dithiazinane (2k). The yield was 56%, 170—172 °C. ^{1}H NMR (80 MHz), δ: 3.68 (br.s, 2 H, C(2)H)); 4.72 (br.s, 4 H, C(4)H_2, C(6)H_2); 6.90—7.81 (m, 4 H, Ar). ^{13}C NMR (22.5 MHz), δ: 34.0 (t, C(2)); 57.9 (t, C(4), C(6)); 99.0 (s, C(8)); 126.8 (d, C(10)); 127.0 (d, C(12)); 128.8 (d, C(11)); 139.8 (d, C(9)); 148.8 (s, C(7)). MS, *m/z* (I_{rel} (%)): 323 $[M]^+$ (25), 245 $[M - SCH_2S]^+$ (25), 231 $[M - SCH_2SCH_2]^+$ (100), 150 $[M - CH_2S - I]^+$ (60), 127 $[I]^+$ (72); 77 $[C_6H_5]^+$ (40). Found (%): C, 33.04; H, 3.46; N, 4.45; S, 20.15. $C_9H_{10}INS_2$. Calculated (%): C, 33.44; H, 3.12; N, 4.33; S, 19.84.

5-(4-Bromophenyl)-1,3,5-dithiazinane (2l). The yield was 70%, m.p. 130—132 °C. ^{1}H NMR (80 MHz), δ: 4.23 (s, 2 H, C(2)H_2); 4.90 (s, 4 H, C(4)H_2, C(6)H_2); 6.90 (d, 2 H, C(8)H, C(12)H, *J* = 8.3 Hz); 7.32 (d, 2 H, C(9)H, C(11)H, *J* = 8.0 Hz). ^{13}C NMR (22.5 MHz), δ: 34.8 (t, C(2)); 55.1 (t, C(4), C(6)); 113.3 (s, C(10)); 119.4 (C(8), C(12)); 132.4 (d, C(9), C(11)); 144.1 (s, C(7)). Found (%): C, 38.44; H, 3.58; N, 4.95; S, 23.15; Br, 29.50. $C_9H_{10}BrNS_2$. Calculated (%): C, 39.13; H, 3.65; N, 5.07; S, 23.22; Br, 28.93.

***N,N*-Diaryl-1,5-dithia-3,7-diazacyclooctanes 3a,c,f,i.** Aniline (0.005 mol) in EtOH (95%, 5 mL) was added dropwise to 37% aq. formaline (2.2 mL, 0.03 mol) saturated with hydrogen sulfide over 30 min. The mixture was stirred for 10 h at 0 °C. Compound **3a** was filtered off, washed with ethanol, **3c,i** were isolated by fractional crystallization, **3f** was isolated by column chromatography (SiO_2, benzene—C_2H_5OH, 9 : 1).

3,7-Diphenyl-1,5-dithia-3,7-diazacyclooctane (3a). The yield was 70%, m.p. 174—175 °C. ^{1}H NMR (80 MHz), δ: 4.86 (br.s, 8 H, C(2)H_2, C(4)H_2, C(6)H_2, C(8)H_2); 6.81—7.40 (m, 10 H, 2 Ar). ^{13}C NMR (22.5 MHz), δ: 56.4 (t, C(2), C(4), C(6), C(8)); 115.0 (d, C(10), C(14); C(16), C(20)); 119.5 (d, C(12), C(18)); 129.6 (d, C(11), C(13), C(17), C(19)); 144.3 (s, C(9), C(15)). Found (%): C, 63.23; H, 5.87; N, 9.13; S, 20.92. $C_{16}H_{18}N_2S_2$. Calculated (%): C, 63.54; H, 6.00; N, 9.26; S, 21.20.

3,7-Bis(3-methylphenyl)-1,5-dithia-3,7-diazacyclooctane (3c). The yield was 50%, m.p. 183—184 °C. ^{1}H NMR (80 MHz), δ: 2.35 (s, 6 H, C(21)H_3, C(22)H_3); 5.29 (br.s, 8 H, C(2)H_2, C(4)H_2, C(6)H_2, C(8)$_2$); 6.62—7.12 (m, 8 H, Ar). ^{13}C NMR (22.5 MHz), δ: 22.0 (s, C(21), C(22)); 55.9 (t, C(2), C(4), C(6), C(8)); 108.1 (d, C(10), C(20)); 112.3 (d, C(14), C(16)); 120.6

(d, C(12), C(18)); 137.5 (d, C(13), C(17)); 130.1 (s, C(11), C(19)); 144.3 (s, C(9), C(15)). Found (%): C, 65.49; H, 6.23; N, 8.61; S, 19.97. $C_{18}H_{22}N_2S_2$. Calculated (%): C, 65.41; H, 6.71; N, 8.48; S, 19.40.

3,7-Bis(3-methoxyphenyl)-1,5-dithia-3,7-diazacyclooctane (3f). The yield was 48%, R_f 0.33. ^{1}H NMR (80 MHz), δ: 3.80 (s, 6 H, C(22)H_2, C(24)H_2); 4.84 and 4.93 (both d, C(2)H_2, C(4)H_2, C(6)H_2, C(8)$_2$, J = 7.2 Hz); 6.44—6.67 (m, 8 H, Ar). ^{13}C NMR (22.5 MHz), δ: 54.8 (q, C(22), C(24)); 56.6 (d, C(2), C(4), C(6), C(8)); 104.5 (d, C(10), C(16)); 105.2 (d, C(12), C(18)); 110.1 (d, C(14), C(20)); 130.3 (d, C(13), C(19)); 146.1 (s, C(9), C(15)); 158.3 (s, C(13), C(19)). Found (%): C, 60.07; H, 6.17; N, 7.56; S, 17.99. $C_{18}H_{22}N_2O_2S_2$. Calculated (%): C, 59.64; H, 6.12; N, 7.73; S, 17.69.

3,7-Bis(3-nitrophenyl)-1,5-dithia-3,7-diazacyclooctane (3i). The yield was 44%, m.p. 210—212 °C. ^{1}H NMR (80 MHz), δ: 5.12 and 5.21 (both d, 8 H, C(2)H_2, C(4)H_2, C(6)H_2, C(8)H_2, J = 7.2 Hz); 7.15—7.52 (m, 8 H, Ar). ^{13}C NMR (22.5 MHz), δ: 55.9 (t, C(2), C(4), C(6), C(8)); 108.1 (d, C(10), C(16)); 112.3 (d, C(12), C(18)); 120.64 (d, C(14), C(20)); 144.3 (s, C(9), C(18)); 148.7 (s, C(11), C(17)). Found (%): C, 49.11; H, 4.26; N. 15.00; S, 15.80. $C_{16}H_{16}N_4S_2O_4$. Calculated (%): C, 48.97; H, 4.11; N, 14.28; S, 16.34.

3,5-Diphenyl-1,3,5-thiadiazinanes 4a—d,f,g,l. Aniline (0.005 mol) in EtOH (95%, 5 mL) was added dropwise to 37% aq. formaline (0.55 mL, 0.0075 mol) saturated with hydrogen sulfide over 30 min. The mixture was stirred for 10 h at 0 °C. Compound **4c** was isolated by fractional crystallization, **4a,b,f,l** by column chromatography (SiO_2, benzene—C_2H_5OH, 9 : 1), **4d,g** were filtered off and washed with ethanol.

3,5-Diphenyl-1,3,5-thiadiazinane (4a). The yield was 20%, R_f 0.21, m.p. 102—104 °C. ^{1}H NMR (80 MHz), δ: 5.01 (s, 4 H, C(2)H_2, C(6)H_2); 5.27 (s, 2 H, C(4)H_2); 7.52—7.69 (m, 10 H, Ar). ^{13}C NMR (22.5 MHz), δ: 53.4 (t, C(2), C(6)); 69.3 (t, C(4)); 117.6 (d, C(18), C(14), C(12), C(8)); 120.3 (d, C(16), C(10)); 128.8 (d, C(17), C(15), C(11), C(9)); 147.4 (s, C(7), C(13)). Found (%): C, 71.12; H, 6.43; N, 10.16; S, 12.45. $C_{15}H_{16}N_2S$. Calculated (%): C, 70.27; H, 6.29; N, 10.93; S, 12.51.

3,5-Di(2-methylphenyl)-1,3,5-thiadiazinane (4b). The yield was 34%, a resin-like compound, R_f 0.21, n_D^{20} 1.5065. ^{1}H NMR (80 MHz), δ: 4.95 (s, 2 H, C(4)H_2); 5.20 (s, 4 H, C(2)H_2, C(6)H_2); 7.11—7.79 (m, 8 H, Ar). ^{13}C NMR (22.5 MHz), δ: 17.9 (q, C(19), C(20)); 55.4 (t, C(2), C(6)); 71.7 (t, C(4)); 122.4 (d, C(12), C(18)); 123.8 (d, C(10), C(16)); 126.8 (d, C(9), C(15)); 130.1 (d, C(11), C(17)); 132.3 (s, C(8), C(14)); 147.7 (s, C(7), C(13)). Found (%): C, 72.23; H, 6.94; N, 9.43; S, 11.64. $C_{17}H_{20}N_2S$. Calculated (%): C, 71.79; H, 7.09; N, 9.85; S, 11.27.

3,5-Di(3-methylphenyl)-1,3,5-thiadiazinane (4c). The yield was 50%, m.p. 195—196 °C (Ref. 6: 196—197 °C).

3,5-Di(4-methylphenyl)-1,3,5-thiadiazinane (4d). The yield was 45%, m.p. 101—103 °C (Ref. 23: 105 °C).

3,5-Di(3-methoxyphenyl)-1,3,5-thiadiazinane (4f). The yield was 30%, m.p. 155—156 °C (Ref. 6: 153—154 °C).

3,5-Di(4-methoxyphenyl)-1,3,5-thiadiazinane (4g). The yield was 23%, m.p. 148—150 °C (Ref. 6: 145—146 °C).

3,5-Di(4-bromophenyl)-1,3,5-thiadiazinane (4l). The yield was 83%, R_f 0.24, m.p. 157—159 °C. ^{1}H NMR (80 MHz), δ: 4.94 (s, 4 H, C(2)H_2, C(6)H_2); 5.18 (s, 2 H, C(4)H_2); 6.90 (d,

Table 5. Principal crystallographic data and parameters of refinement for **2l**, **3a**, **4a**, and **4d**

Compound	**2l**	**3a**	**4a**	**4d**
CCDC number	731758	731759	731761	731762
Molecular formula	$C_9H_{10}BrNS_2$	$C_{16}H_{18}N_2S_2$	$C_{15}H_{16}N_2S$	$C_{17}H_{20}N_2S$
Molecular weight	276.21	302.44	256.36	284.41
T/K	120	100	100	100
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
Z	2	4	4	4
a/Å	4.8446(6)	11.184(2)	8.9325(6)	9.0310(15)
b/Å	9.7580(13)	13.331(3)	14.1147(9)	18.623(3)
c/Å	11.1243(15)	10.324(2)	11.0129(7)	9.1076(15)
α/deg	105.121(4)	90.00	90.00	90.00
β/deg	92.685(2)	103.035(4)	110.0060(10)	103.437(3)
γ/deg	95.425(3)	90.00	90.00	90.00
V/Å^3	504.00(11)	1499.6(5)	1304.71(15)	1489.9(4)
d_{calc}/g cm^{-3}	1.820	1.340	1.305	1.268
μ/cm^{-1}	44.42	3.46	2.31	2.09
F(000)	276	640	544	608
$2\theta_{max}$/deg	59	54	58	56
Numbre of measured reflections	5728	14204	13966	22032
Number of independent reflections	2784	3271	3449	3586
Number of reflections with $I > 2\sigma(I)$	2360	1892	3133	2238
Number of refined parameters	118	181	163	183
R_1	0.0332	0.0549	0.0352	0.0438
wR_2	0.0850	0.0984	0.0945	0.0953
GOOF	1.002	1.000	1.012	1.001
Residual electron density/e Å^{-3}(d_{max}/d_{min})	1.205/−0.523	0.381/−0.389	0.403/−0.289	0.401/−0.377

4 H, C(8)H, C(12)H, C(14)H, H(18), J = 6.5 Hz); 7.31 (d, 4 H, C(9)H, C(11)H, C(15)H, C(17)H, J = 6.5 Hz). ^{13}C NMR (22.5 MHz), δ: 53.8 (t, C(2), C(6)); 69.7 (t, C(4)); 113.4 (s, C(10), C(16)); 119.7 (d, C(8), C(12), C(14), C(18)); 132.3 (d, C(9), C(11), C(15), C(17)); 147.9 (s, C(7), C(13)). Found (%): C, 44.08; H, 3.56; N, 6.50; S, 7.80; Br, 38.62. $C_{15}H_{14}Br_2N_2S$. Calculated (%): C, 43.50; H, 3.41; N, 6.76; S, 7.74; Br, 38.59.

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