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Phenylenediamine and 4,4'-Diaminodiphenyls in Cyclothiomethylation with CH_2O and H_2S

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Abstract—Cyclothiomethylation of *o*-phenylenediamine with CH_2O and H_2S gives rise to 1,2,4,5-tetrahydrobenzo[*d*][1,3,6]thiadiazepine and 1,2,6,7-tetrahydrobenzo[*f*][1,3,5,8]dithiadiazonine, whereas *m*-phenylenediamine forms benzothiaza macroheterocycles of various structure, comprising 4–8 molecules of the starting diamine, formaldehyde, and hydrogen sulfide. 4,4'-Diaminodiphenyls give bis(1,3,5-dithiazinanes), along with oligomeric hetero(N,S,O)atomic compounds.

Keywords: benzothiaza macroheterocycles, phenylenediamines, multicomponent condensation, thiomethylation, bisdithiazinanes

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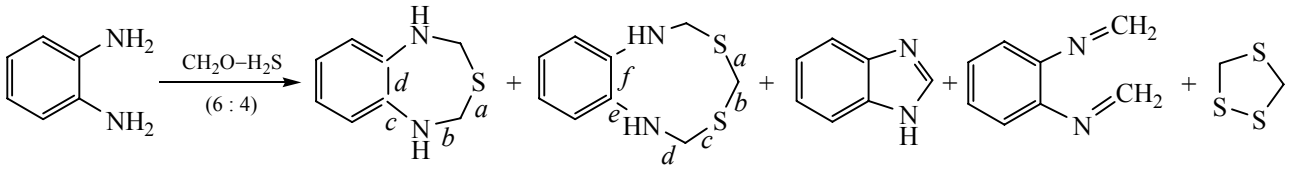
According to [1–4], cyclothiomethylation of aliphatic and aromatic primary amines, as well as amides of carboxylic acids [5, 6] with CH_2O and H_2S gives rise to the corresponding 1,3,5-dithiazinanes; but with functionally substituted anilines, benzothiaza macroheterocycles were obtained [3, 4]. Hydrazines [7, 8] and aliphatic α,ω-diamines [9, 10] form condensed bicycles or bis(1,3,5-dithiazinanes), depending on cyclothiomethylation conditions. As known, aryl-containing hetero(N,S,O)atomic compounds, including macrocycles, hold promise as photochromic molecular sensors for metal analysis [11, 12].

Before our research, cyclothiomethylation of isomeric phenylenediamines and 4,4'-diaminodiphenyls and their derivatives with CH_2O and H_2S has never been reported.

With the aim to synthesize a new class of nitrogen- and sulfur-containing heterocycles and explore the possibility to involve in cyclothiomethylation the above-mentioned aromatic amines, we have studied intra- and intermolecular reactions of the latter with CH_2O and H_2S.

It was found that *o*-phenylenediamine (**I**) enters multicomponent intramolecular condensation with CH_2O and H_2S to form a complex mixture of heteroatomic compounds, including 1,2,4,5-tetrahydrobenzo[*d*][1,3,6]thiadiazepine (**II**), 1,2,6,7-tetrahydrobenzo[*f*][1,3,5,8]dithiadiazonine (**III**), 1*H*-1,3-benzimidazole (**IV**), *N,N*'-dimethylene-1,2-phenylenediamine (**V**), and 1,2,4-trithiolane (**VI**) (Scheme 1). The mixture of compounds **II–V** was separated by column chromatography on SiO_2. The structure of heterocycles **II** and **III** was established by spectral methods.

Scheme 1.



I **II** **III** **IV** **V** **VI**

Cyclothiomethylation of *o*-phenylenediamine with CH_2O and H_2S.

Effect of reaction temperature and starting reagent ratio on the yield and composition of *o*-phenylenediamine (**I**) cyclothiomethylation products

T, °C	**I** : CH_2O : H_2S ratio	Yield of reaction products (wt %)				
		II	**III**	**IV**	**V**	**VI**
0	1 : 2 : 1	35	4	10	16	3
20	1 : 2 : 1	32	4	13	18	3
40	1 : 2 : 1	40	3	19	10	7
0	1 : 3 : 2	18	16	27	10	2
20	1 : 3 : 2	26	12	23	8	2
40	1 : 3 : 2	41	16	11	11	1
20	1 : 6 : 4	35	10	13	15	6
70	1 : 6 : 4	42	7	14	18	6

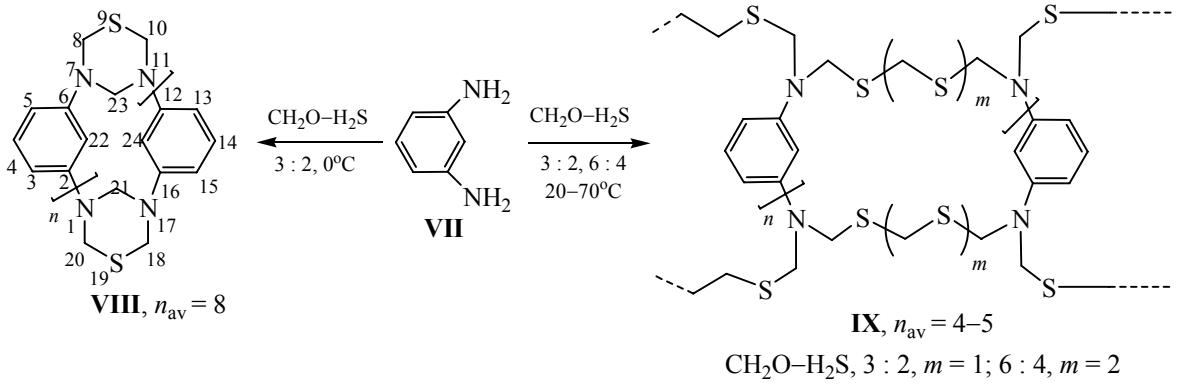
The mass spectra of compounds **II** and **III** contain strong molecular ion peaks $[M]^+$ at *m*/*z* 166 and 212, respectively. The ^1H and ^{13}C NMR spectra of compound **II** show, in view of the symmetric molecular structure, by three aromatic proton and carbon signals, as well as by one upfield signal at δ_H 4.40 и δ_C 55.16 ppm, characteristic of the methylene groups bridging the N and S atoms. The ^1H and ^{13}C NMR spectra of compound **III** contains, along with aromatic proton and carbon signals, by two methylene signals at δ_H 3.95 and δ_C 36.92 ppm (SCH_2S) and δ_H 4.63 and δ_C 54.93 ppm (NCH_2S). The IR spectra of products **II** and **III** show an NH deformation vibration band at 1618 cm^{-1}.

Aiming at developing a selective cyclothiomethylation procedure for *o*-phenylenediamine (**I**), we have studied the effect of temperature and starting reagent ratio on the yield and composition of this compound with CH_2O and H_2S. The cyclothiomethylation reaction of compound **I** involves both its NH_2 groups. As seen from the table, in our experimental conditions the main reaction was, as a rule, heterocycle **II**, and, therewith, its yield increased to 40% as the reaction temperature was increased (40–70°C). At higher temperatures, along with compounds **II** and **III**, we observed formation of poorly soluble oligomeric heteroatomic compounds. The nine-membered N,S-heterocycle **III** could be prepared in low yield, and the best yield (16%) was obtained at a 1 : 3 : 2 reagent ratio (see table).

Cyclothiomethylation of *m*-phenylenediamine (**VII**) with CH_2O and H_2S at a 1 : 3 : 2 reagent ratio and 0°C gave macroheterocycle **VIII** (yield 99%) as the result of intermolecular heterocyclization with the oligomerization degree $n_{av} = 8$. As the temperature was increased (20–70°C), an exclusive reaction product was three-membered oligomer **IX** with n_{av} = 4–5 (yield 91–99%) (Scheme 2).

The ^1H NMR spectra of suspensions of poorly soluble cyclic oligomers **VIII** and **IX** in DMSO-d_6 display aromatic proton signals at δ_H 6.60–8.05 ppm, as well as proton signals of the SCH_2N and NCH_2N groups at δ_H 4.39 and 4.63 ppm, respectively, in a 2 : 1 ratio (for compound **VIII**). The SCH_2S and NCH_2S methylene proton signals in the spectrum of compound **IX** are observed at δ_H 3.84 and 4.40 ppm, respectively (integral intensity ration 1 : 2). It should be noted that the oligomer **IX** produced by the reaction of *m*-phenylenediamine with excess CH_2O–H_2S (6 : 4) at temperatures above 20°C contains more $–CH_2S–$ units (*m* = 2), and, as a result, the signal at δ_H 3.84 ppm in its ^1H NMR spectrum has a higher intensity. The absorption band at 720 cm^{-1} in the IR spectra of

Scheme 2.



compounds **VIII** and **IX** provides evidence for the presence of a C–S bond. The band at 1460 cm^{-1} relates to the C_{Ar}–N bond and that at 1600 cm^{-1} is assignable to the aromatic ring (C_{Ar}–N, C=C_{Ar}). The IR and ^1H NMR spectra contain no terminal NH_2, OH, or SH signals, which is obviously explained by the formation of cyclic oligomers. The cryoscopic molecular weights M_{cr} [13] of benzothiaza macrocycle **VIII** and cross-linked cyclic oligomer **IX** are 1598 ± 10 (n_{av} 8) and 1570–2207 ± 10 (n_{av} 4–5), respectively. The mass spectra of compounds **VIII** and **IX** have low information content because of the instability of these products. A low-intensity peak of the $[CH_2NC_6H_4NCH_2S]^+$ ion at *m*/*z* 164 is present, and the most intense peaks belong to the $[C_6H_6]^+$ and $[CH_2S]^+$ ions (*m*/*z* 78 and 46, respectively).

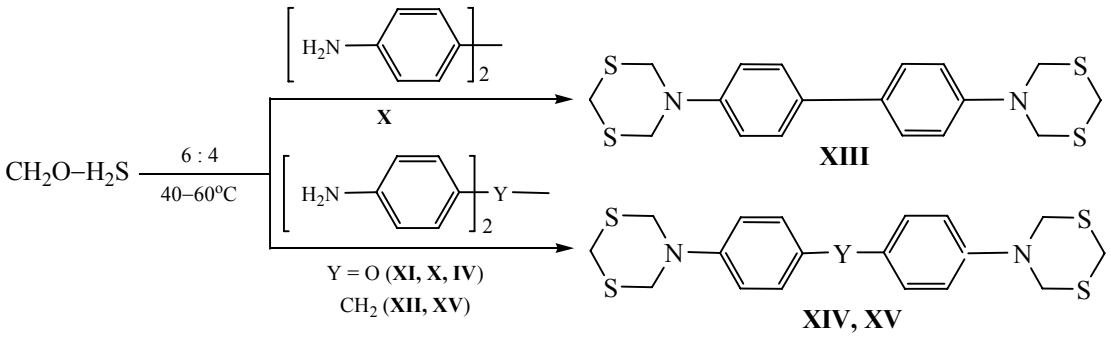
The obtained evidence allowed compounds **VIII** and **IX** to be assigned cyclic oligomeric structures built of units containing *m*-phenylenediamine fragments linked by methylene sulfide CH_2SCH_2 groups. The reaction at 0°C involves initial formation of an NCH_2N bonds followed by cyclization under the action of CH_2O–H_2S to form a 1,3,5-thiadiazine cycle. The same products are also formed at 0°C from anilines [14–16] and aliphatic diamines [9, 10]. In should be mentioned that cyclothiomethylation of *m*-aminophenol [4] with CH_2O and H_2S, too, involves intermolecular cyclocondensation to form macroheterocycles, whereas *o*- and *p*-aminophenols undergo intramolecular heterocyclization to form the corresponding 1,3,5-dithiazinanes. Furthermore, the intermolecular thiomethylation by two functional groups of the substrates, yielding benzothiaza macrocycles is also characteristic of *m*-aminothiophenol [3].

p-Phenylenediamine fails to enter the thiomethylation reaction at any reagent ratios and temperature conditions, probably, because of the high basicity of one the NH_2 groups (K_b 110 × 10^{-10} and 0.035 × 10^{-10}) [17, 18]. *p*-Phenylenediamine hydrochloride, too, could not be involved in thiomethylation. As a result, *p*-phenylenediamine catalyzes polycondensation of formaldehyde with H_2S to form poly(methylene sulfide) [19]. At the same time, *o*- and *m*-phenylenediamines, the basicities of the amino groups in which are 3.3 × 10^{-10} and 7.6 × 10^{-10}, undergo cyclothiomethylation. Thus, the 1,3,5-dithiazinane cycles we previously prepared by cyclothiomethylation of aliphatic and aromatic amines, and aliphatic α,ω-diamines could not be prepared from *o*-, *m*-, and *p*-phenylenediamines. At the same time, 4-(1,3,5-dithiazinan-5-yl)aniline was selectively synthesized by the transamination of 5-methyl-1,3,5-dithiazinane with *p*-phenylenediamine in the presence of a $FeCl_3·6H_2O$ catalyst in 60% [20], and *o*-phenylenediamine under the same conditions formed 1,2,6,7-tetrahydrobenzo[*f*]-[1,3,5,8]dithiadiazonine (**III**) in 67% yield.

Cyclothiomethylation of 4,4'-diaminodiphenyl (**X**), 4,4'-diamonidiphenyl oxide (**XI**), and 4,4'-diaminodiphenylmethane (**XII**) with CH_2O and H_2S (1 : 6 : 4, 40–80°C) in chloroform gives rise to bis-(1,3,5-dithiazinanes) **XIII**–**XV** in yields of 62–99%. The highest yields of compounds **XIII**–**XV** is observed at 40–45°C. Along with bis(1,3,5-dithiazinane) **XV**, the reaction with 4,4'-diaminodiphenylmethane (**XII**) forms oligomeric products. The yield of compounds **XIII**–**XV** decreases in the order: **XIV** (99%) > **XIII** (69%) > **XV** (62%) (Scheme 3).

Cyclothiomethylation of 4,4'-diaminodiphenyls at 0–30°C or above 80°C gives poorly soluble oligomeric products as the result of thee-component condensation of diamines **X**–**XII** with CH_2O and H_2S. The reaction products contain –CH_2S– (**XVI**) and –CH_2O– fragments (**XVII**). Bisdithiazinanes **XIII**–**XV** were extracted with chloroform. In the reaction with

Scheme 3.



diamine **XII**, we made use of fractional crystallization to isolate cyclic oligomers **XVI** and **XVII** is a total yield of about 30%; therewith, oligomer **XVII** precipitated immediately upon formation (Scheme 4).

The MALDI-TOF mass spectra of bisdithiazianes **XIII** and **XIV** show molecular ion peaks $[M]^+$ at *m*/*z* 392 and 408, and the spectrum of compound **XV** contains an $[M - H]^+$ ion peak at *m*/*z* 405. In the spectra of oligomers **XVI** and **XVII**, molecular ion peaks at *m*/*z* 549 $[M - H]^+$ and 583 $[M + H + Na]^+$ are observed. The ^1H and ^{13}C NMR spectra of bisdithiazianes **XIII**–**XV** contain, along with aromatic proton and carbon signals, signals at δ_H 4.98–5.11 and δ_C 53.53–55.37 ppm, corresponding to two magnetically equivalent NCH_2S methylene carbons in the dithiazine ring, and the SCH_2S methylene signals are observed at δ_H 4.29–4.36 and δ_c 34.04–34.94 ppm. The ^1H and ^{13}C NMR signals of compound **XV** also contain signals at δ_H 3.92 and δ_C 46.78 ppm, which can be assigned to the methylene bridge between the two benzene rings.

It should be noted that the cyclothiomethylation of diphenyldiamines **X**–**XI** in ethanol results in preferential formation of various cyclic dimers formed by two-component intermolecular condensation of diamines **X**–**XI** with CH_2O and three-component intermolecular condensation of **X**–**XII** with CH_2O and H_2S.

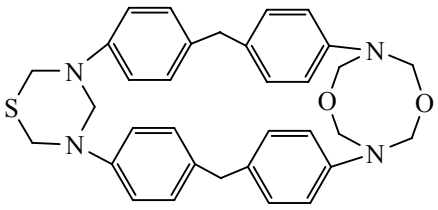
Thus, aromatic diamines in the cyclothiomethylation reaction with formaldehyde and H_2S tend to form benzothiaza macroheterocycles. 1,3,5-Dithiazinanes can only be synthesized from diamines with the amino groups separated by a diphenyl bridge, whereas in phenylenediamines, where the NH_2 groups mutually influence each other, the cyclothiomethylation results are not so definite. The *p*-isomer fails to react, whereas the *o*- and *m*-isomers undergo cyclothiomethylation by the two NH_2 groups simultaneous. With the *o*-isomer, the reaction involves intramolecular cyclization, while with *m*-isomer, intermolecular cyclization takes place.

EXPERIMENTAL

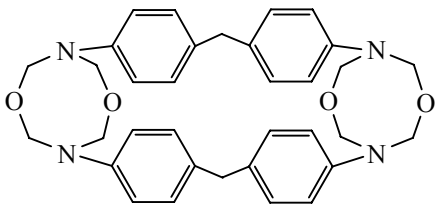
The purity of the starting compounds was no less than 95%. The ^1H and ^{13}C NMR spectra of compounds **II**–**VI**, **VIII**, **IX**, and **XIII** were registered on a Jeol FX-90Q spectrometer [22.5 (^{13}C), 90 MHz (^1H)] and those of compounds **XIV**–**XV**, on a Bruker Avance 400 spectrometer [100.62 (^{13}C), 400.13 MHz (^1H)], solvents $CDCl_3$ and DMSO-d_6, internal standard TMS. The IR spectra were measured on a Specord 75 IR spectrometer for suspensions in mineral oil. The mass spectra of compounds **II**–**IX** were registered on a Finnigan 4021 GCMS system (glass capillary column 50000×0.25 mm, stationary phase HP-5, carrier gas helium, temperature programming from 50 to 300°C at a rate of 5 deg/min, injector temperature 280°C, ion source temperature 250°C, 70 eV). The mass spectra of compounds **XIII**–**XVII** were obtained on a Bruker Autoflex **III** MALDI TOF/TOF instrument (dried droplet sample preparation technique, matrices α-cyano-4-hydroxycinnamic and 2,5-dihydrobenzoic acids). The elemental compositions were determined on a Carlo Erba instrument. The melting points were measured on an RNMK 80/2617 apparatus. Thin-layer chromatography was performed on Silufol W-254 plates, development in an iodine chamber. Column chromatography was performed on a KSK silica (100–200 μm).

Thiomethylation of *o*-, *m*-, and *p*-phenylenediamines *(general procedure)*. A solution of 37% formaldehyde (2.2 mL, 0.03 mol) was saturated with H_2S (0.02 mol, prepared from $Na_2S·9H_2O$ and HCl) for 30 min at 20°C. A solution of 1.08 g (0.01mol) of *o*-phenylenediamine (**I**) in 50 mL of $CHCl_3$ [*m*- and *p*-phenylenediamines were dissolved in 50 mL of EtOH (95%)] was added dropwise to the resulting solution. The mixture was stirred for 3 h at a preset temperature (0–70°C) and then extracted with chloroform. The extract was dried over $CaCl_2$, the solvent was evaporated, and the residue was subjected to column

Scheme 4.



XVI



XVII

chromatography on SiO_2 (eluent hexane–ethyl acetate, 3 : 1) to obtain a mixture of compounds **II–VI**. The product obtained from *p*-phenylenediamine was filtered off and washed with EtOH.

1,2,4,5-Tetrahydrobenzo[*d*][1,3,6]thiadiazepine (II). Yield 0.55 g (26% at 20°C), mp 137–139°C, R_f 0.52 (hexane–ethyl acetate, 3 : 1). IR spectrum, ν, cm^{-1}: 750 (C–S), 1480 (Ar), 1600 (Ar), 1618 (NH), 2900 (CH_2), 3300 (N–H). 1H NMR spectrum (DMF-d_6), δ, ppm: 4.27 br.s (2H, NH), 4.40 br.s (2H, $H_2C^{2,7}$), 6.90–7.30 m (4H, HC^{8-11}). 13C NMR spectrum (DMF-d_6), δ_C, ppm: 55.16 ($C^{2,7}$), 114.46 ($C^{8,11}$), 122.92 ($C^{9,10}$), 135.23 ($C^{4,5}$). Mass spectrum, *m*/*z* (I_{rel}, %): 166 (28) $[M]^+$, 120 (100) $[M - CH_2S]^+$, 105 (45) $[M - CH_2SCH_3]^+$, 92 (55) $[C_6H_4NH_2]^+$, 77 (79) $[M - C_6H_5]^+$. Found, %: C 57.88; H 6.64; N 16.53; S 20.30. $C_8H_{10}N_2S$. Calculated, %: C 57.80; H 6.06; N 16.85; S 19.29.

1,2,6,7-Tetrahydrobenzo[f][1,3,5,8]dithiadiazonine (III). Yield 0.25 g (12% at 20°C), mp 147–148°C, R_f 0.65 (hexane–ethyl acetate, 3 : 1). IR spectrum, ν, cm^{-1}: 750 (C–S), 1500 (Ar), 1600 (Ar), 1618 (NH), 2900 (CH_2), 3300 (N–H). 1H NMR spectrum ($CDCl_3$), δ, ppm: 3.95 br.s (2H, H_2C^2), 4.25 br.s (2H, NH), 4.63 br.s (4H, $H_2C^{4,9}$), 7.00–7.30 m (4H, HC^{10-13}). ^{13}C NMR spec-trum ($CDCl_3$), δ_C, ppm: 36.92 (C^2), 54.93 ($C^{4,9}$), 115.39 ($C^{10,13}$), 129.39 ($C^{11,12}$), 133.37 ($C^{6,7}$). Mass spectrum, *m*/*z* (I_{rel}, %): 212 (20) $[M]^+$, 149 (100) $[M - NH_2SCH_3]^+$, 133 (20) $[M - SCH_2SH]^+$, 120 (33) $[M - CH_2SCH_2SH]^+$, 105 (27) $[CHSCH_2SCH_2]^+$, 92 (40) $[CH_2SCH_2S]^+$, 77 (20) $[C_6H_5]^+$. Found, %: C 50.82; H 5.67; N 13.20; S 30.71. $C_9H_{12}N_2S_2$. Calculated, %: C 50.91; H 5.70; N 13.19; S 30.20.

1*H*-1,3-Benzimidazole (IV). Yield 0.27 g (23% at 20°C), mp 164–166°C, R_f 0.34 (hexane–ethyl acetate, 3 : 1). Mass spectrum, *m*/*z* (I_{rel}, %): 118 (100) $[M]^+$, 91 (33) $[C_6H_4NH]^+$. The NMR spectra are identical to those in [21].

***N,N*'-Dimethylene-1,2-phenylenediamine (V).** Yield 0.11 g (8% at 20°C), mp 154–156°C, R_f 0.30 (hexane–ethyl acetate, 3 : 1). Mass spectrum, *m*/*z* (I_{rel}, %): 132 (100) $[M]^+$, 104 (27) $[C_6H_5NN]^+$, 77 (17) $[C_6H_5]^+$. The NMR spectra are identical to those in [20].

1,3,4-Trithiolane (VI). The physicochemical characteristics are identical to those in [15].

1,7,11,17-Tetraaza-9,19-dithiapenta-cyclo-[15,3,1,$1^{2,6}$,$1^{7,11}$,$1^{12,16}$]tetracosa-2(22),3(4),5(6),-12(13),14(15),16(24)-hexaene (VIII) was synthesize by the above-described procedure at 0°C from 0.18 g (0.001 mol) of *m*-phe-nylenediamine dihydrochloride, 0.22 mL (0.003 mol) of 37% formaldehyde, and 0.02 mol of H_2S under stirring for 3 h. The reaction mixture was neutralized with 50% KOH, the precipitate that formed was filtered off, washed with distilled water, and dried. Yield 0.18 g (99%), mp 290°C (decomp.), M_{cr} 1598 ± 10 (n_{av} = 9). IR spectrum, ν, cm^{-1}: 720 (C–S), 1370, 1450 (Ar), 1600 (Ar), 2900 (CH_2). 1H NMR spectrum (DMSO-d_6), δ, ppm: 4.39 br.s (4H, $NC\underline{H}_2S$), 4.63 br.s (2H, $NC\underline{H}_2N$), 6.75 s (1H, HC_{Ar}), 7.40 br.s (2H, HC_{Ar}), 8.05 s (1H, HC_{Ar}). UV spectrum (DMSO), λ_{max}, nm (ε): 311.7 (0.75). Mass spectrum, *m*/*z* (I_{rel}, %):164 (6) $[CH_2NC_6H_4NCH_2S]^+$, 78 (59) $[C_6H_6]^+$, 46 (100) $[CHS]^+$. Found, %: C 60.68; H 5.46; N 15.18; S 18.43. $C_9H_{10}N_2S$. Calculated, %: C 60.64; H 5.65; N 15.72; S 17.99.

In a similar way, from 0.18 g of *m*-phenylene-diamine dihydrochloride at 20°C we obtained 0.20 g of compound **IX** [63%, M_{cr} 1570 ± 10 (n_{av} = 5, *m* = 1)]; at 40°C: 0.28 g [89%, M_{cr} 2207 ± 10 (n_{av} = 6, *m* = 1)].

Polymer IX. mp 290–320°C (decomp.). IR spectrum, ν, cm^{-1}: 730 (C–S), 1460 (Ar), 1620 (Ar), 2930 (CH_2). UV spectrum (DMSO), λ_{max}, nm (ε): 311.7 (0.75). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.84 s (4H, $SC\underline{H}_2S$), 4.40 s (8H, $NC\underline{H}_2S$), 6.62 s (2H, HC_{Ar}), 7.27 s (4H, HC_{Ar}), 7.93 s (2H, HC_{Ar}). Found, %: C 46.35; H 5.05; N 8.68; S 40.50. $C_{12}H_{16}N_2S_4$. Calculated, %: C 45.53; H 5.09; N 8.85; S 40.52.

Thiomethylation of 4,4'-diaminodiphenyls *(general procedure).* A solution of 0.184 g (0.001 mol) of 4,4'-diaminodiphenyl (**X**) in 10 mL of $CHCl_3$ was added dropwise at 40°C to a solution of 37% formaldehyde (0.5 mL, 0.006 mol) saturated with H_2S (0.01 mol) for 30 min at 20°C. Before adding 4,4'-diaminodiphenyl the H_2S-saturated formaldehyde solution was heated to 40°C, and H_2S was further bubbled at that temperature under stirring for 1 h. After bubbling was stopped, the reaction mixture was stirred for an additional 2 h and then extracted with chloroform, dried over $CaCl_2$, and evaporated in a vacuum to obtain bis-4-(1,3,5-dithiazinan-5-yl)phenyl (**XIII**).

Bis[4-(1,3,5-dithiazinan-5-yl)phenyl] (XIII). Yield 0.27 g (69%), light yellow crystals, mp 170–171°C. IR spectrum, ν, cm^{-1}: 700 (C–S), 1200 (C–N), 1480 (CH_2), 1600 (Ar), 2900 (CH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.36 br.s (2H, $H_2C^{2,2'}$), 5.11 br.s (4H, $H_2C^{4,6,4',6'}$), 6.65–6.80 br.s (4H, $HC^{8,12,8',12'}$), 7.41

br.s (4H, $HC^{9,11,9',11'}$). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 33.41 ($C^{2,2'}$), 53.53 ($C^{4,6,4',6'}$), 117.41 ($C^{8,12,8',12'}$), 126.53 ($C^{9,11,9',11'}$), 130.86 ($C^{10,10'}$), 143.76 ($C^{7,7'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 392 (28) $[M]^+$, 315 (100) [*M* – CH_2S_2 + H], 301 (45) [*M* – $(CH_2)_2S_2$ + H], 288 (55) [*M* – $(CH_2)_3S_2$ + 2H], 255 (79) [*M* – $(CH_2S)_3$ + H], 223 (79) [$Ph_2N_2(CH_2)_3$ + H], 209 (79) [$Ph_2N_2(CH_2)_2$ + H]. Found, %: C 55.45; H 5.40; N 7.62; S 32.82. $C_{18}H_{20}N_2S_4$. Calculated, %: C 55.06; H 5.13; N 7.14; S 32.67.

Cyclothiomethylation of 4,4'-diaminodiphenyl oxide (**XI**) (0.1 g, 0.0005 mol) with CH_2O and H_2S by the above-described procedure gave bis[4-(1,3,5-dithiazinan-5-yl)phenyl] oxide (**XIV**) (0.202 g, 99%), and from 4,4'-diaminodiphenylmethane (**XII**) (0.1 g, 0.0005 mol) we obtained a mixture of compounds **XV**–**XVII**. Oligomer **XVII** insoluble in organic solvents was filtered off from the reaction mixture, and the filtrate was evaporated. Chloroform, 50 mL, was added to the residue, and the precipitate that formed was filtered off (oligomer **XVI**). The chloroform filtrate was evaporated to obtain product **XV**.

Bis[4-(1,3,5-dithiazinan-5-yl)phenyl] oxide (XIV). Yield 0.2 g (99%), light yellow crystals, mp 186–190°C. IR spectrum, ν, cm^{-1}: 750 (C–S), 1050 (C–O–C), 1600 (Ar), 2900 (CH_2). 1H NMR spectrum (DMSO-d_6), δ, ppm: 4.33 s (4H, $H_2C^{2,2'}$), 5.06 s (8H, $H_2C^{4,6,4',6'}$), 7.01 d. d (8H, $HC^{8,9,11,12,8',9',11',12'}$, J^1 9.0, J^2 21.7 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 34.04 ($C^{2,2'}$), 54.46 ($C^{4,6,4',6'}$), 118.86 ($C^{8,12,8',12'}$), 119.46 ($C^{9,11,9',11'}$), 141.19 ($C^{7,7'}$), 150.67 ($C^{10,10'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 408 (28) [*M*], 331 (26) [*M* – SCH_2S + H], 239 (10) [*M* – $(CH_2S)_3CH_2N$ + 3H], 163 (100) [*M*– $CH_2S(CH_2)$ NPh]. Found, %: C 52.93; H 4.55; N 6.67; S 31.30. $C_{18}H_{20}N_2S_4O$. Calculated, %: C52.91; H 4.93; N 6.86; S 31.39.

Bis[4-(1,3,5-dithiazinan-5-yl)phenyl]methane (XV). Yield 0.13 g (62%), light yellow crystals, mp 167–170°C. IR spectrum, ν, cm^{-1}: 800 (C–S), 1250 (C–N), 1600 (Ar), 2900 (CH_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.92 s (2H, H_2C^{13}), 4.29 s (4H, $H_2C^{2,2'}$), 4.98 s (8H, $H_2C^{4,6,4',6'}$), 7.01 d (4H, $HC^{8,12,8',12'}$, *J* 8.6 Hz), 7.19 d (4H, $HC^{9,11,9',11'}$, *J* 8.6 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 34.94 ($C^{2,2'}$), 46.78 (C^{13}), 55.37 ($C^{4,6,4',6'}$), 117.65 ($C^{8,12,8',12'}$), 129.95 ($C^{9,11,9',11'}$), 133.54 ($C^{10,10'}$), 142.97 ($C^{7,7'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 405 (100) [$\bar{M}$ H], 381 (82) [*M* – NC + H], 329 (59) [*M* – SCH_2S + H], 315 (36) [*M* – $(CH_2S)_2CH_2N$ + H]. Found, %: C 55.98; H 5.45; N 6.74; S 31.32. $C_{19}H_{22}N_2S_4$. Calculated %: C 56.12; H 5.45; N 6.89; S 31.54.

Oligomer XVI. Yield 15%. Mass spectrum, *m*/*z* (I_{rel}, %): 549 (100) [*M* – H], 457 (4) [*M* – $PhNH_2$]. $C_{33}H_{34}N_4SO_2$.

Oligomer XVII. Yield 15% Mass spectrum, *m*/*z* (I_{rel}, %): 583 (19) [*M* + H + Na], 381 (100) [*M* – NCH_2OH]. $C_{34}H_{36}N_4O_4$.

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