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Bis(1,3-Dithiole-2-chalcogenones) and Tetrathiafulvalenes in the Synthesis of Bridged Tetrathiafulvalene-Containing Structures

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Abstract—Bis(1,3-dithiole-2-chalcogenones) in which the 1,3-dithiole fragments are linked through various bridging groups were synthesized by different methods. Some of these compounds were converted into substituted tetrathiafulvalenes with bridged 1,3-dithiole rings. The same structures were synthesized from preliminarily prepared symmetric tetrathiafulvalenes containing 2-cyanoethylsulfanyl groups in both 1,3-dithiole rings. Similar spacers were used to bridge two tetrathiafulvalene fragments. Syntheses of the involved initial compounds were described.

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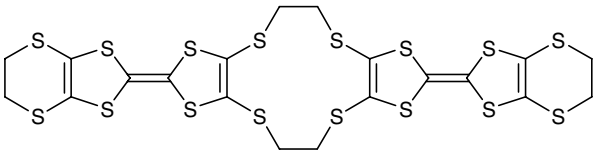
Methods of synthesis of tetrathiafulvalene and its derivatives have been extensively developed over the past three decades. These compounds are unique π-electron donors which give rise to electroconductive organic systems. In fact, radical cation salts and charge-transfer complexes based on tetrathiafulvalenes were meant by the term *organic metals*. Traditionally, electron-donor properties and crystal structures of substituted tetrathiafulvalenes themselves were studied. However, in the recent time, the scope of application and investigation of tetrathiafulvalene-containing systems has become much broader; in particular, these compounds were used as materials for building up macrocyclic and supramolecular structures [1, 2]. From this viewpoint, an interesting group of tetrathiafulvalenes includes structures containing various bridging moieties (linkers) which differ in both chemical nature and size; such linkers could connect either



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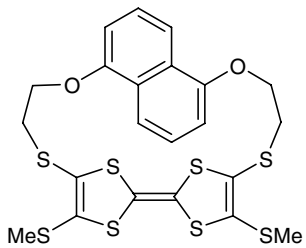

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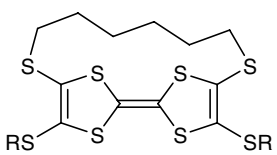

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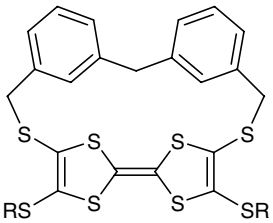

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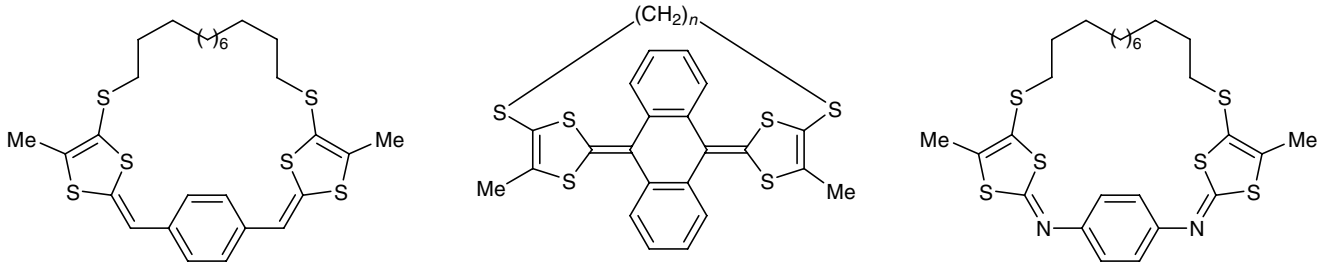
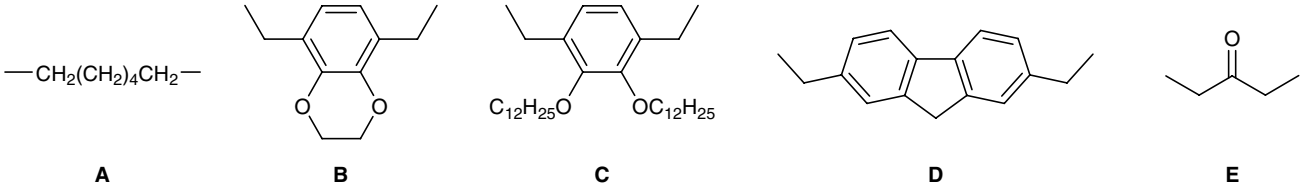
R = *p*-MeC_6H_4.

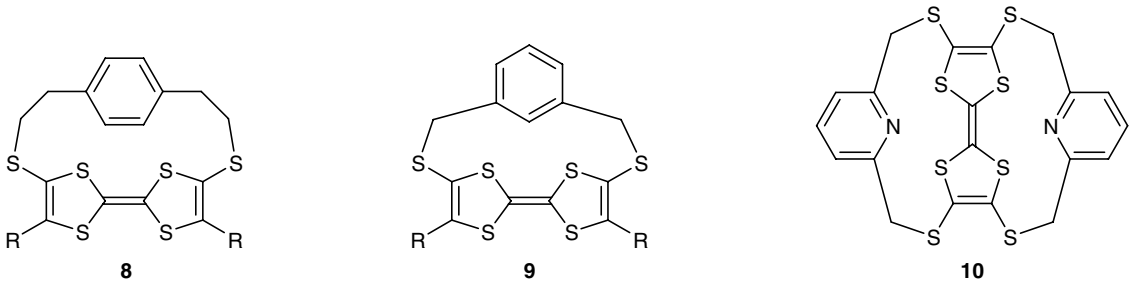


5 **6** **7**

n = 5, 6.



A **B** **C** **D** **E**



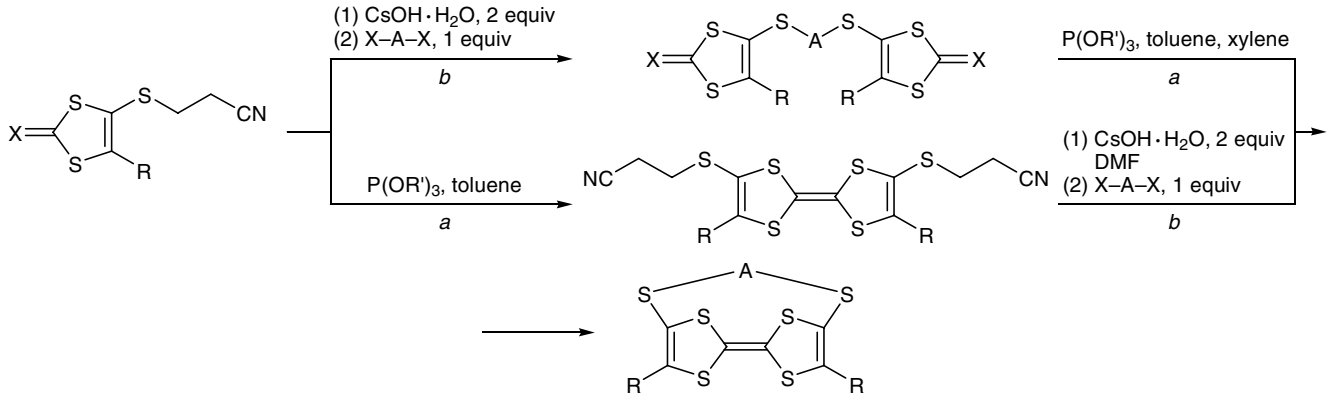
8 **9** **10**

8, R = *p*-MeC_6H_4, MeOCO, H; **9**, R = MeOCO.

several tetrathiafulvalene molecules (having both similar and different structures, e.g., structure **1** [2]) or fragments of a single tetrathiafulvalene molecule to form cavities (e.g., structures **2** [2], **3**, and **4** [3]. In some cases, bridged are fragments of so-called "extended" tetrathiafulvalene molecule, i.e., a molecule in which two 1,3-dithiole fragments of the tetrathiafulvalene core are linked through an unsaturated spacer (e.g., structures **5–7**) [3].

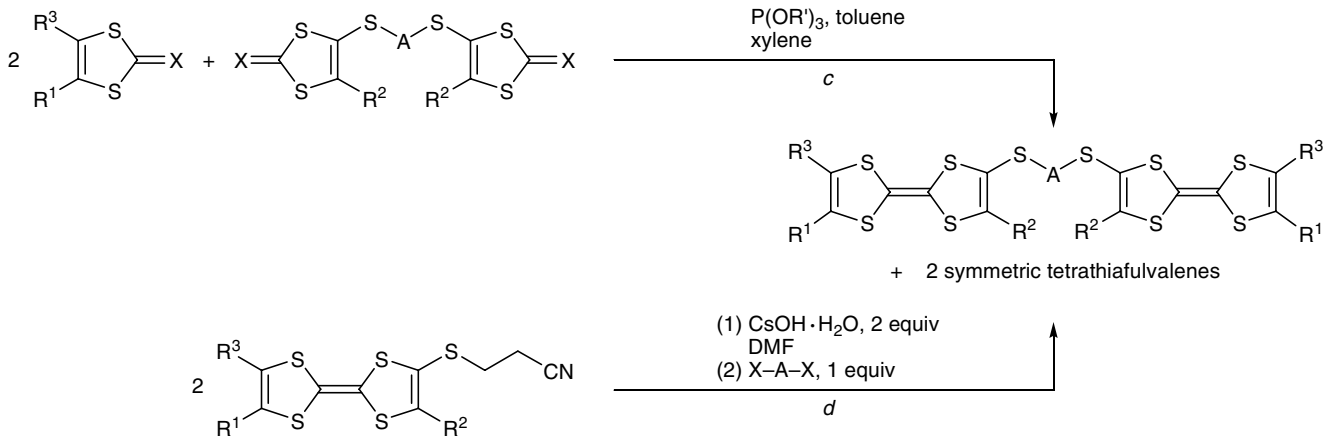
With the goal of extending the series of available tetrathiafulvalene structures for subsequent introduction into conjugated polymers we synthesized a number of intermediate products with various bridging groups (fragments **A–E**). It may appear that fragments **B** and **C** could give rise to strained structures, for the tetrathiafulvalene and aromatic moieties in the resulting compounds are separated by only two atoms (C and S). Nevertheless, such structures have been

Scheme 1.



X = S, O, Se.

Scheme 2.

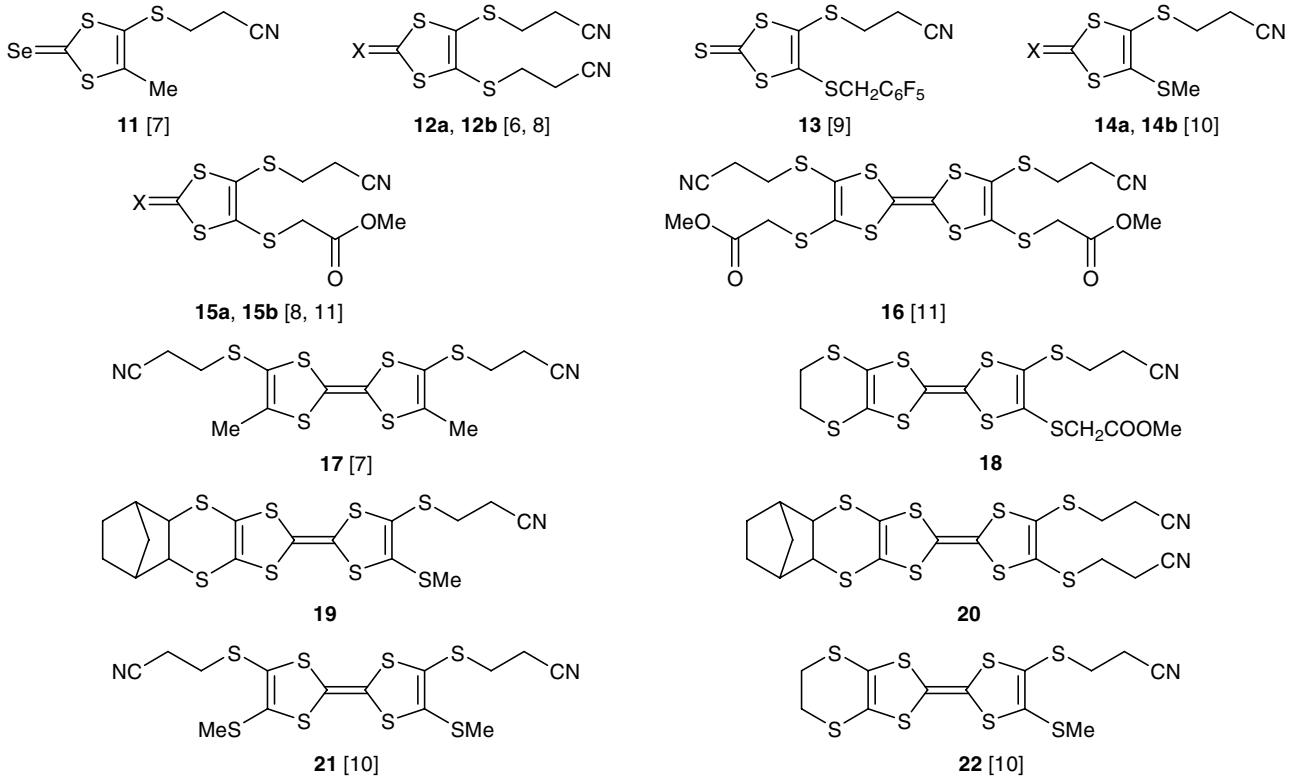


X = S, O, Se.

synthesized (compounds **8**, **9** [4], and **10** [5]), and their electrochemical properties have been described. Tetrathiafulvalene derivatives including linkers **C** and **D** have not been reported so far.

Two methods are used most frequently for the synthesis of tetrathiafulvalene structures like **3**, **4**, and **8–10**: trialkyl phosphite-mediated coupling of bis(1,3-dithiole-2-chalcogenones) under strong dilution (path *a*) [4, 5] and Becher's method [6] employing cesium thiolates obtained from β-cyanoethyl derivatives (path *b*; Scheme 1). To synthesize tetrathiafulvalene structures related to compound **1**, two paths *c* and *d* may be proposed (Scheme 2).

For this purpose, we have synthesized four groups of initial compounds: (1) 1,3-dithiole-2-chalcogenones **11–15** containing a β-cyanoethylsulfanyl group; (2) tetrathiafulvalenes **16** and **17** containing at least two such groups in different 1,3-dithiole rings of the tetrathiafulvalene core; (3) tetrathiafulvalenes **18–22** having one or two β-$NCCH_2CH_2S$ groups in only one



11 [7] **12a**, **12b** [6, 8] **13** [9] **14a**, **14b** [10]

15a, **15b** [8, 11] **16** [11]

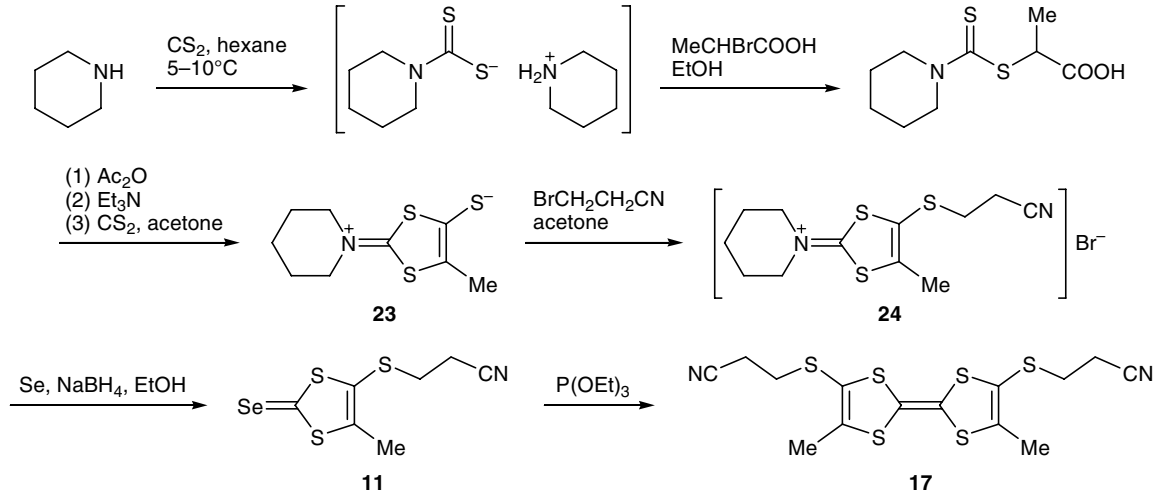
17 [7] **18**

19 **20**

21 [10] **22** [10]

12, **14**, **15**, X = S (**a**), O (**b**).

Scheme 3.



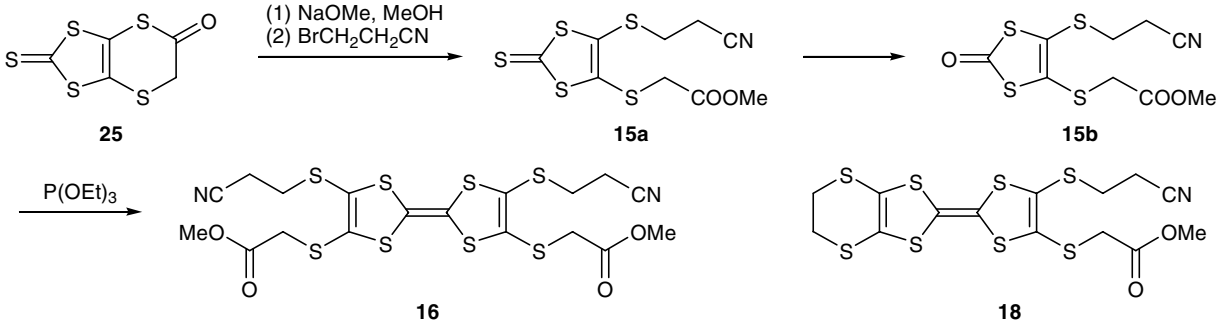
1,3-dithiole ring; and (4) bis(halomethyl)arenes as bridging fragments **B**–**D**. Some of these compounds were reported previously, while compounds **18**–**22** and **33**–**36** were synthesized for the first time.

Tetrathiafulvalene **17** was synthesized in a good yield (72%) from selone **11** which was prepared from mesoionic salt **24** [12] (Scheme 3). Tetrathiafulvalene **16** was synthesized according to Scheme 4 [11] starting from 1,3-dithiole-2-thione **15a** [8, 11]; the latter was obtained by methanolysis of 2-thioxodihydro[1,3]-dithiolo[4,5-*b*][1,4]dithiin-5(6*H*)-one (**25**) which was prepared in turn by reaction of zinc dithiolate complex with chloroacetyl chloride [13, 14]. 1,3-Dithiol-2-one **15b** was used in the synthesis of unsymmetrical tetrathiafulvalene **18**; here, the second component was 4,5-ethylenedisulfanyl-1,3-dithiole-2-thione (-2-one) [15].

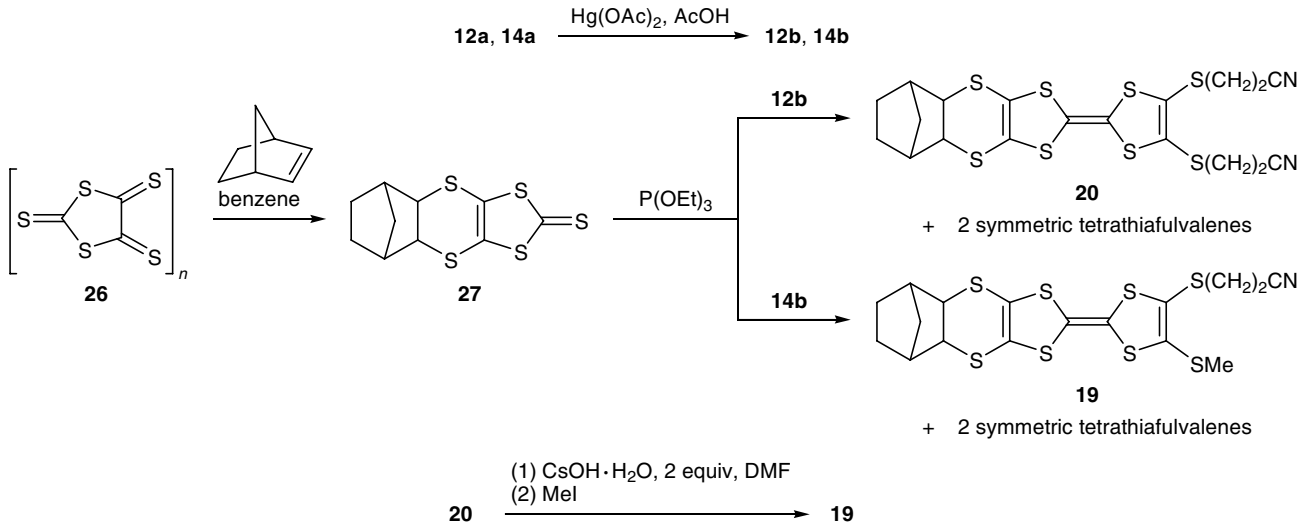
Tetrathiafulvalenes **19** and **21** were obtained by cross-coupling of 1,3-dithiole-2-thione **27** having a fused bicyclo[2.2.1]heptane fragment {it was prepared by [4+2]-cycloaddition of oligo(1,3-dithiole-2,4,5-trithione) (**26**) to norbornene [16]} with oxygen analogs **14b** and **12b** of 1,3-dithiole-2-thiones **14a** and **12a**, respectively. The reactions were carried out using triethyl phosphite as reaction medium (Scheme 5). In each case, a mixture of three products was formed: one of these was the desired unsymmetrically substituted tetrathiafulvalene, while the tho others were symmetric compounds resulting from self-coupling of 1,3-dhitiol-2-ones **14b** and **12b**. The mixtures were separated by either fractional crystallization or column chromatography, and the purity of the products was checked by thin-layer chromatography. Unsymmetrical compound **19** was also synthesized in a different way, via deprotection (removal of the $NCCH_2CH_2$ group) of compound **20**. In both cases, the overall yields of **19** were approximately similar (about 30%). The main difficulty in the first method was to isolate and purify 1,3-dithiole-2-tione **14a** (precursor of **14b**), but separation of the final product from two concomitant symmetric structures was more facile, as compared to the isolation of tetrathiafulvalene **20** which was the starting compound in the second procedure.

Bis(chloromethyl)arenes **32a**, **32b**, **36a**, and **36b** that are necessary for the introduction of bridging

Scheme 4.

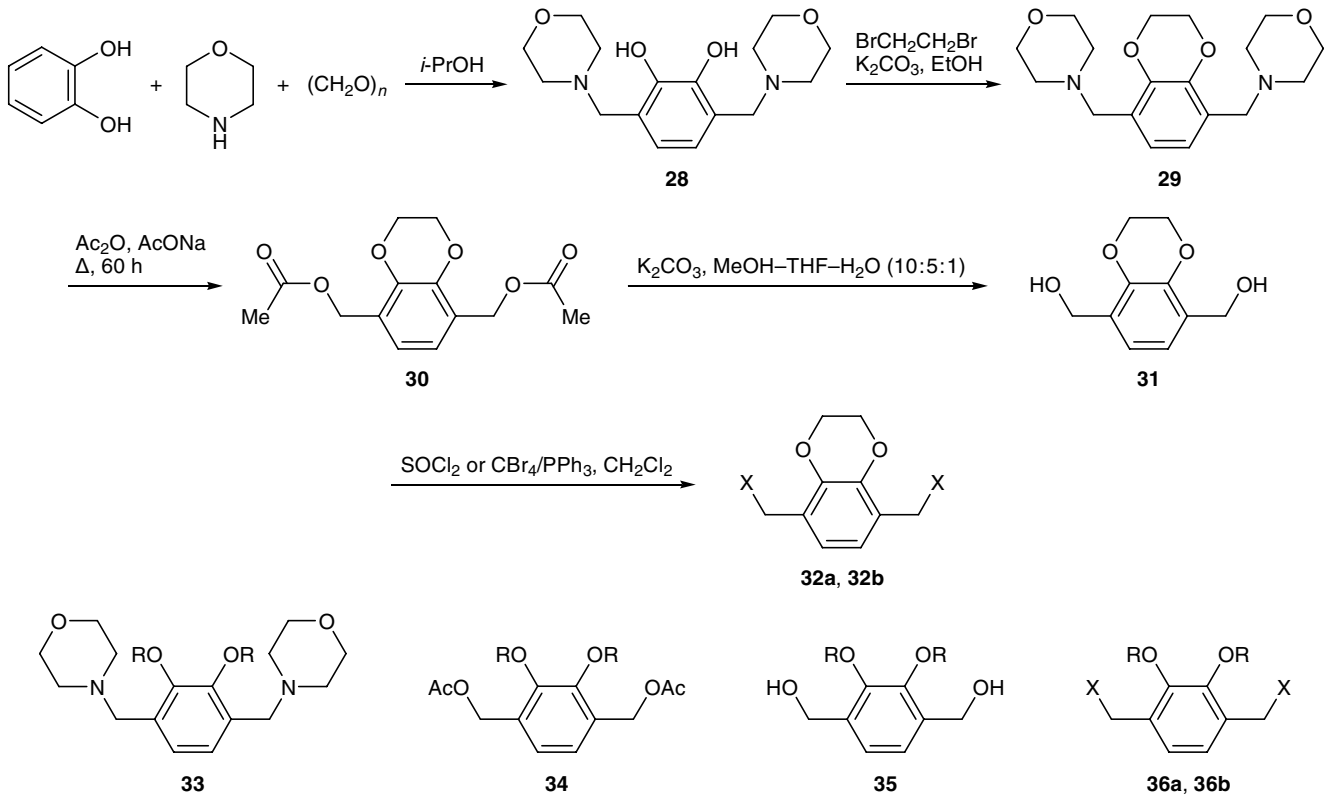


Scheme 5.



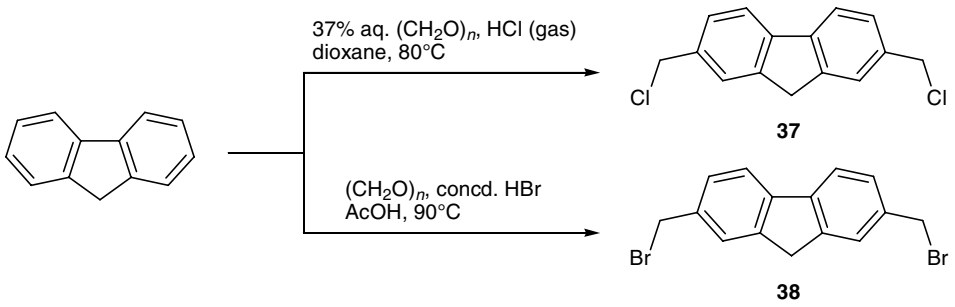
groups **B** and **C** were synthesized according to Scheme 6. By heating a mixture of paraformaldehyde, morpholine, and benzene-1,2-diol in isopropyl alcohol we obtained compound **28** [17] which was treated with methylene bromide in boiling ethanol. 5,8-Bis(morpholinomethyl)-2,3-dihydro-1,4-benzodioxin (**29**) [18] thus formed was converted into diester **30** by the action of acetic anhydride in the presence of sodium acetate [18]. Hydrolysis of **30** in a mixture of methanol with tetrahydrofuran and water gave diol **31** [5,8-bis-(hydroxymethyl)-2,3-dihydro-1,4-benzodioxin]. Treatment of the latter with thionyl chloride in anhydrous methylene chloride led to the formation of 5,8-bis-(chloromethyl)-2,3-dihydro-1,4-benzodioxin (**32a**).

Scheme 6.

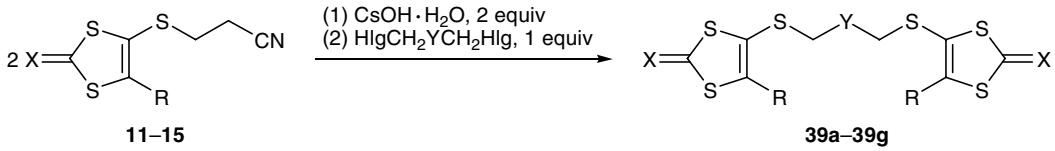


R = $C_{12}H_{25}$; X = Cl (**a**), Br (**b**).

Scheme 7.



Scheme 8.



Bis(1,3-dithiole-2-chalcogenones)

Initial compound no.	X	R	Bridge (Y)	Product no.	Hlg
11	Se	Me	$CH_2CH_2CH_2CH_2$ (**A**)	**39a**	Br
11	Se	Me	1,4-Benzodioxin-5,8-diyl (**B**)	**39b**	Cl, Br
14a	S	SMe		**39c**	Cl
13	S	$SCH_2C_6F_5$	9*H*-Fluorene-2,7-diyl (**D**)	**39d**	Br
15a	S	SCH_2COOMe	9*H*-Fluorene-2,7-diyl (**D**)	**39e**	Br
12	S	SCH_2CH_2CN	9*H*-Fluorene-2,7-diyl (**D**)	**39f**	Br
12	S	SMe	CO (**E**)	**39g**	Cl

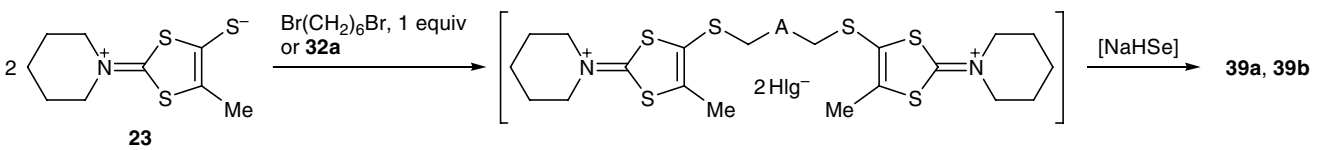
The corresponding bis(bromomethyl) derivative **32b** was obtained from diol **31** by the Appel reaction, i.e., by treatment with carbon tetrabromide in the presence of triphenylphosphine in anhydrous methylene chloride. Compounds **36a** and **36b** were synthesized following an analogous scheme.

In order to introduce a fluorene bridging moiety we used either 2,7-bis(chloromethyl)fluorene (**37**) prepared by chloromethylation of fluorene with 39% aqueous formaldehyde in dioxane in the presence of gaseous hydrogen chloride [19] or 2,7-bis(bromomethyl)fluorene (**38**) which was synthesized by heating fluorene with concentrated hydrobromic acid and paraformaldehyde in acetic acid (Scheme 7) [20].

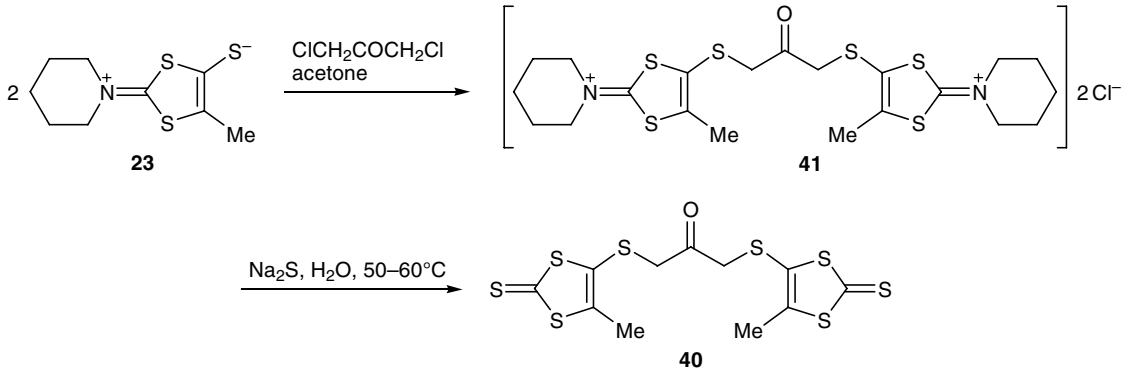
Using compounds **11**–**15** we synthesized bis(1,3-dithiole-2-chalcogenones) **39a–39g** having **A**–**D** linkers (Scheme 8; see table). In the synthesis of selones **39a** and **39b** according to a scheme analogous to the preparation of selone **11**, i.e., through mesoionic salts (Scheme 3) and their subsequent reaction with NaHSe *in situ*, the final products were heavily contaminated, and their yields were poor (Scheme 9).

Bis(1,3-dithiole-2-thione) **40** having bridging group **E** (CH_2COCH_2) was synthesized in a way similar to the synthesis of selone **11**. Heating of 2 equiv of salt **23** with 1 equiv of 1,3-dichloropropan-2-one in acetone gave salt **41** which was converted into compound **40** by treatment with aqueous sodium sulfide at 60°C

Scheme 9.

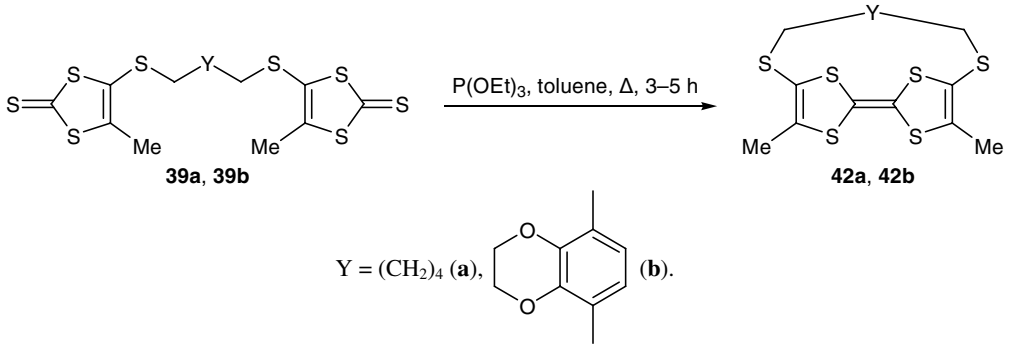


Scheme 10.



23 **41** **40**

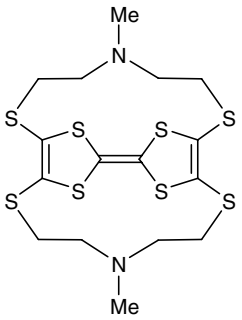
Scheme 11.



39a, **39b** **42a**, **42b**

(Scheme 10). However, unlike the preceding steps which occurred almost quantitatively, the yield at the final step was very poor (~12%).

Some initial bridged bis(1,3-dithiole-2-chalcogenones) were successfully converted into the corresponding bridged tetrathiafulvalenes. Diselones **39a** and **39b** were heated with triethyl phosphite in toluene to obtain tetrathiafulvalenes **42a** and **42b**, respectively. This process occurs as if diselone **39** were turned inside out with formation of the tetrathiafulvalene core (Scheme 11). The reactions were performed under strong dilution using a large amount of trialkyl phosphite: about 5 ml of $P(OEt)_3$ and 70–80 ml of anhydrous toluene per 0.001 mol of bis-chalcogenone were taken [4]. The possibility for formation of such tetrathiafulvalenes via the above procedure was demonstrated by the synthesis of tetrathiafulvalenes **8**–**10**, **43**, and **44** [4, 5], which were obtained by coupling of analogous bis(1,3-dithiol-2-ones) (**8**, **9**) or bis(1,3-dithiole-2-thiones) (**10**, **43**, **44**).



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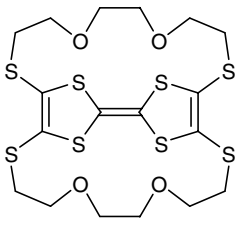

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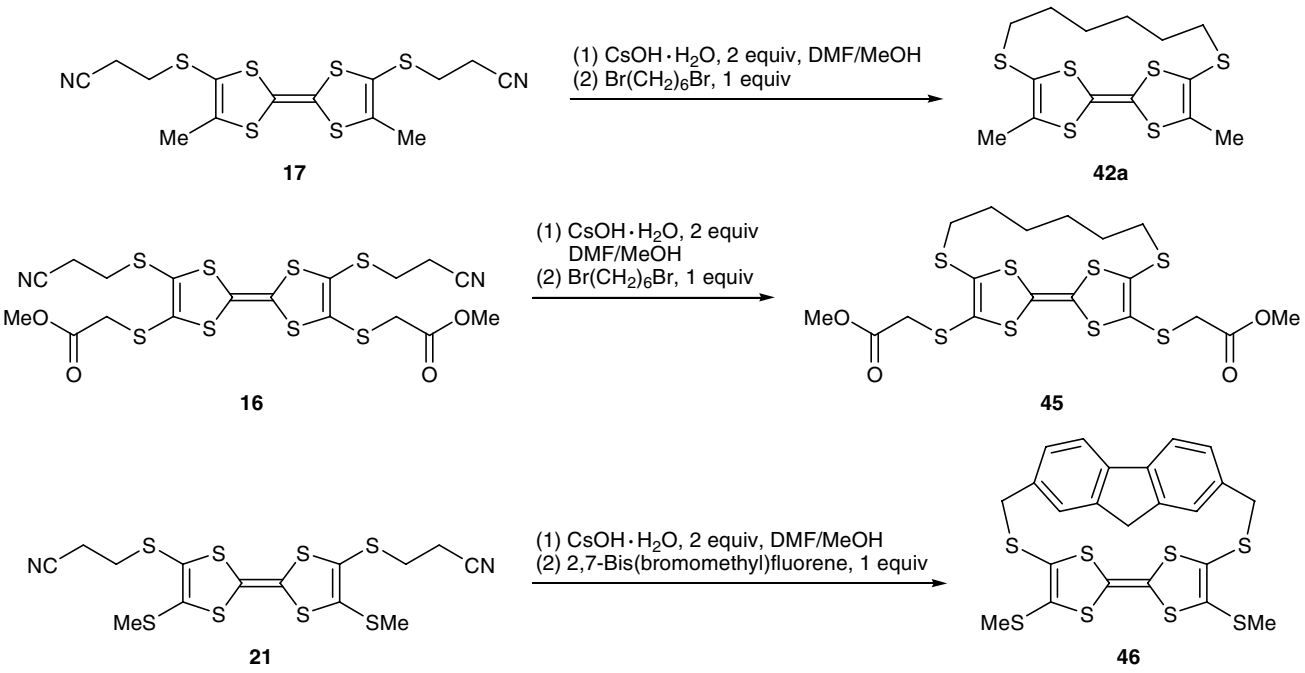
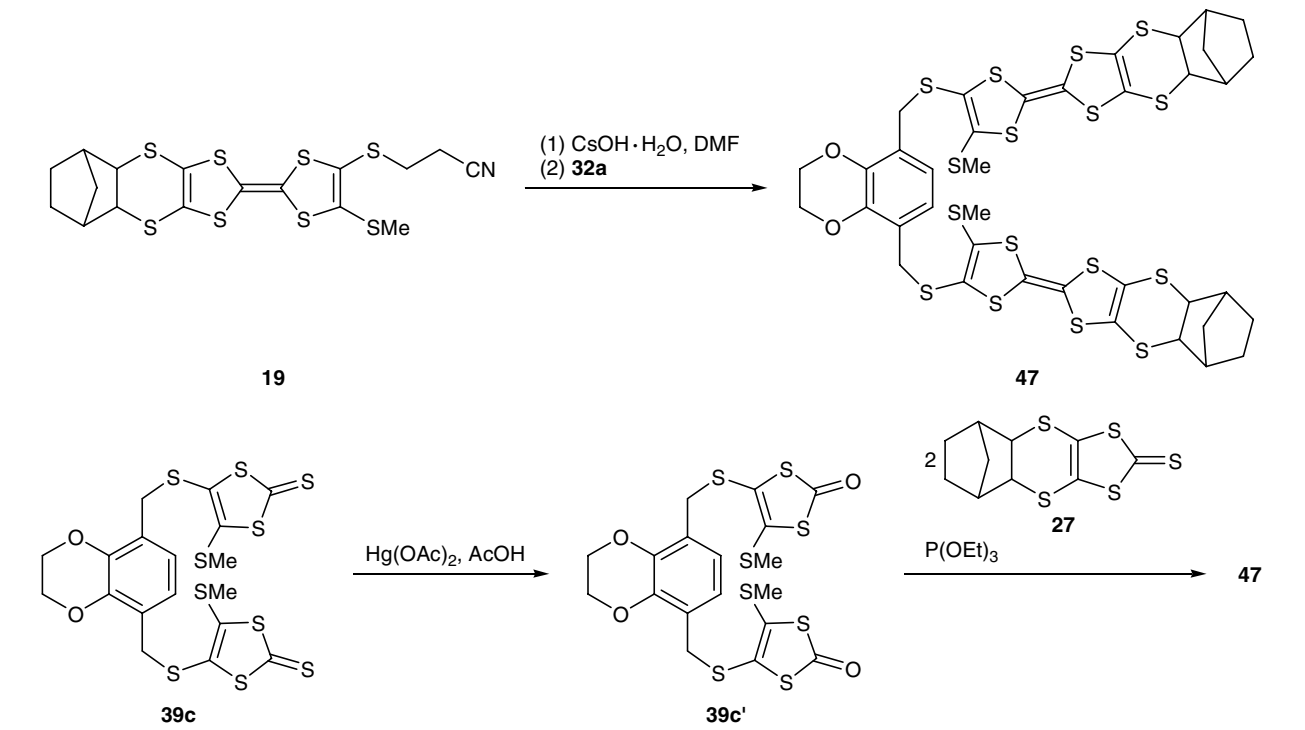
Tetrathiafulvalene **42a** is a red viscous oily substance; it was also synthesized from compound **17** containing β-SCH_2CH_2CN groups in different dithiole rings of the tetrathiafulvalene core (Scheme 12). The reaction was performed under conditions of very strong dilution [4]: equal volumes of solutions of intermediate cesium thiolate and 1,6-dibromohexane in DMF were added simultaneously at a low rate to the same volume of pure DMF under argon over a long time. Likewise, by reactions of tetrathiafulvalenes **16** and **21** with 1,6-dibromohexane and 2,7-bis(bromomethyl)fluorene, respectively, in strongly dilute solution we obtained previously unknown bridged tetrathiafulvalenes **45** and **46** (Scheme 12).

Some dihalogen derivatives (**32a** and **38**) were used to link fragments of unsymmetric (**19**, **22**) and symmetric compounds (**21**). As a result, we obtained in a good yield compound **47**, which was isolated as a yellow crystalline substance (Scheme 13). Compound

Scheme 12.

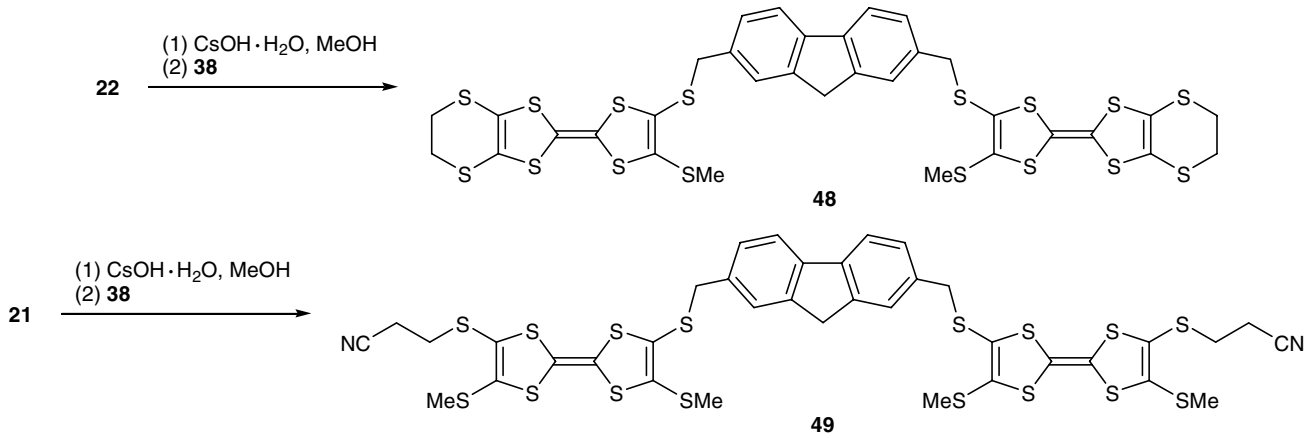


Scheme 13.



47 can also be obtained by coupling of chalcogenones **27** and **39c** in the presence of triethyl phosphite (for this purpose, bis-thione **39c** was preliminarily converted into oxygen analog **39c'**). However, this way was less effective: the reaction was accompanied by formation of a large amount of tarry products, presumably via self-coupling of bis(1,3-dithiol-2-one) **39'c**. Moreover, the latter scheme includes two additional steps, preparation of the oxygen derivative and separation of the target product from the symmetric coupling product containing norbornane fragments, though the latter is soluble very poorly [16].

Scheme 14.



By reaction of 2 mol of tetrathiafulvalene **22** with 1 mol of 2,7-bis(bromomethyl)fluorene (**38**) we obtained in a good yield bridged bis-tetrathiafulvalene **48** (an orange crystalline substance). The same fluorene derivative was used to synthesize molecular ensemble **49** in which two molecules of tetrathiafulvalene **21** are bridged through a 2,7-bis(methylene)fluorene fragment (Scheme 14).

We are now trying to find conditions to obtain crystals suitable for X-ray crystallographic analysis. When a solution of tetrathiafulvalene **18** in acetonitrile was slowly cooled over a period of 10 days, well shaped yellow needles precipitated.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Mercury Plus-300 instrument relative to HMDS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol plates (Kavalier). Silica gel 60 (0.060–0.2 mm, Lancaster) was used for column chromatography.

3-(5-Methylsulfanyl-2-thioxo-1,3-dithiol-4-ylsulfanyl)propanenitrile (14a) [10]**.** A solution of 3.04 g (0.01 mol) of 3,3'-(2-thioxo-1,3-dithiole-4,5-diyldisulfanyl)di(propanenitrile) [6, 8] in 30 ml of anhydrous dimethylformamide was deaerated by purging with argon over a period of 10 min, and a solution of 1.68 g (0.01 mol) of cesium monohydrate $CsOH\cdot H_2O$ in 10 ml of methanol was added. When the formation of cesium thiolate was complete (the solution turned dark red; ~10 min), 0.62 ml (0.01 mol) of methyl iodide was added, and the mixture was heated for 10–15 min at 60°C, cooled, and diluted with water. The precipitate was filtered off, dried in air, and recrystallized from acetic acid. Yield 61%, mp 89–90°C. IR spectrum, ν, cm^{-1}: 1060 (C=S), 2240 (C≡N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 s (3H, SCH_3), 2.76 t (2H, CH_2CN), 3.09 t (2H, SCH_2).

3-(5-Methylsulfanyl-2-oxo-1,3-dithiol-4-ylsulfanyl)propanenitrile (14b) [10]**.** Compound **14a**, 1.62 g (0.006 mol), was dissolved in 60 ml of acetic acid, 1.9 g (0.006 mol) of $Hg(OAc)_2$ was added, and the mixture was heated until the reaction was complete [the mixture turned black due to separation of mercury(II) sulfide]. The mixture was filtered while hot through a fine filter to remove HgS, the filtrate was cooled and diluted with water, and the precipitate was filtered off, dried in air, and recrystallized from ethanol. Yield 57%, mp 60–62°C.

2,3-Dihydro-1,4-benzodioxine-5,8-diyldimethanol (31). A suspension of 6.0 g (0.021 mol) of 2,3-dihydro-1,4-benzodioxine-5,8-diyldimethyl diacetate (**30**) and 7.3 g (0.0525 mol) of K_2CO_3 in 100 ml of a MeOH–THF–H_2O solvent mixture (10:5:1) was stirred for 48 h, excess K_2CO_3 was filtered off and washed with methanol (50 ml) on a filter, the filtrate was evaporated, and the residue was recrystallized from ethanol. Yield 83%, colorless crystals, with mp 148–150°C. IR spectrum, ν, cm^{-1}: 3270 br (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.27 s (4H, OCH_2CH_2O), 4.47 s (4H, CH_2OH), 7.01 s (2H, H_{arom}).

5,8-Bis(chloromethyl)-2,3-dihydro-1,4-benzodioxine (32a). A mixture of 3.4 g (0.017 mol) of compound **31a** and 20.2 g (12.2 ml, 0.17 mol) of thionyl chloride in 300 ml of anhydrous methylene chloride was heated for 3.5 h. The resulting solution was washed with water, a solution of sodium hydrogen carbonate, and water again until neutral reaction, dried

over $CaCl_2$, and evaporated. The reaction completion was checked by IR spectroscopy, following disappearance of the OH absorption band. Yield 59%, colorless crystals, mp 147–149°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.28 s (4H, OCH_2CH_2O), 4.52 s (4H, CH_2Cl), 6.85 s (2H, H_{arom}). Found, %: Cl 30.31. $C_{10}H_{10}Cl_2O_2$. Calculated, %: Cl 30.42.

5,8-Bis(bromomethyl)-2,3-dihydro-1,4-benzodioxine (32b). Triphenylphosphine, 0.03 mol, was added in small portions under vigorous stirring to a suspension of 0.01 mol of compound **31** and 0.025 mol of carbon tetrabromide in 150 ml of anhydrous methylene chloride, cooled to 0°C. The mixture was stirred for 2–3 h at room temperature, poured into water, and extracted with methylene chloride, and the organic phase was separated, washed with water, and dried over $MgSO_4$. The solvent was removed, and the crystalline residue was extracted with boiling methanol. The extract was cooled, and the precipitate was filtered off. Yield 44%, mp 183°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.33 t (4H, CH_2O), 4.43 t (4H, CH_2Br), 6.82 s and 7.20 s (1H each, H_{arom}). Found, %: Br 49.51. $C_{10}H_{10}Br_2O_2$. Calculated, %: Br 49.63.

4,4'-[2,3-Bis(dodecyloxy)benzene-1,4-diyldimethyl]dimorpholine (33) was synthesized as described in [18] for compound **29**. The product was recrystallized from methanol. Yield 50–60%, colorless crystals, mp 42–43°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 t (6H, CH_3), 1.29–2.4 m (40H, CH_2), 3.45 t (8H, CH_2), 3.62 m (12H, CH_2O), 3.93 s (4H, CH_2N), 7.05 m (2H, H_{arom}).

2,3-Bis(dodecyloxy)benzene-1,4-diyldimethyl diacetate (34) was synthesized as described in [18] for compound **30**. Yield 53%, mp 30–31°C. IR spectrum, ν, cm^{-1}: 1740 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.9 t (6H, C**H**$_3$CH$_2$), 1.30 m (40H, CH_2), 2.13 s (6H, CH_3CO), 4.06 t (4H, OC**H**$_2$CH$_2$), 5.18 s (4H, CH_2OCO), 7.05 m (2H, H_{arom}).

2,3-Bis(dodecyloxy)benzene-1,4-diyldimethanol (35) was synthesized as described above for compound **31**. After removal of the solvent, the residue was purified by recrystallization from ethanol. Yield 84%, colorless crystals, mp 65–66°C. IR spectrum, ν, cm^{-1}: 3380 br, 3350 sh. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.83 t (6H, CH_3), 1.23 m (40H, CH_2), 2.25 s (2H, OH), 4.05 t (4H, CH_2C**H**$_2$O), 4.71 s (4H, C**H**$_2$OH), 7.18 m (2H, H_{arom}). Found, %: C 75.72. $C_{32}H_{58}O_4$. Calculated, %: C 75.84.

1,4-Bis(chloromethyl)-2,3-bis(dodecyloxy)benzene (36a) was synthesized as described above for compound **32a**. The solvent was distilled off, and the residue was recrystallized from methanol. Yield 43%, colorless crystals, mp 40–41°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 m (6H, CH_3), 1.29 m (40H, CH_2), 4.34 t (4H, CH_2O), 4.51 s (4H, CH_2Cl), 7.14 m (2H, H_{arom}). Found, %: Cl 12.87. $C_{32}H_{56}Cl_2O_2$. Calculated, %: Cl 13.04.

1,4-Bis(bromomethyl)-2,3-bis(dodecyloxy)benzene (36b) was synthesized as described for compound **32b**. Yield 47%, mp 61–62°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 q (6H, CH_3), 1.27 m (40H, CH_2), 4.15 t (4H, CH_2O), 4.57 s (4H, CH_2Br), 7.2 d (2H, H_{arom}). Found, %: Br 25.17. $C_{32}H_{56}Br_2O_2$. Calculated, %: Br 25.26.

1-[4-(2-Cyanoethylsulfanyl)-5-methyl-1,3-dithiol-2-ylidene]piperidinium bromide (24) [6, 7]. A mixture of 2.3 g (0.01 mol) of salt **23** and 1.3 g (0.9 ml, 0.01 mol) of 3-bromopropanenitrile in 100 ml of acetone was heated for 1 h (until the red color intrinsic to the initial salt disappeared). The light yellow solution was evaporated, and the residue (a red transparent oily substance) was brought into further synthesis without additional purification. Yield ~100%.

3-(5-Methyl-2-selenoxo-1,3-dithiol-4-ylsulfanyl)-propanenitrile (11) [7]**.** A suspension of 0.79 g (0.01 mol) of amorphous selenium in 50 ml of ethanol was deaerated by purging with argon over a period of 15 min, excess sodium tetrahydridoborate, 0.76 g, was added in small portions under stirring until selenium dissolved almost completely, and an equivalent amount of an aqueous solution of salt **24** was added in one portion. A red–brown crystalline product precipitated and was filtered off, washed with water, and recrystallized from acetic acid. Yield 70%, red lustrous crystals, mp 98°C.

Bis(1,3-dithiole-2-selones) 39a and 39b (*general procedure***).** A solution of 0.003 mol of compound **11** in 65 ml of anhydrous methanol was deaerated by purging with argon over a period of 10 min, a solution of 0.003 mol of cesium monohydrate in 10 ml of methanol was added dropwise, and the mixture was heated until it became homogeneous (for about 10 min). The resulting cesium thiolate solution was cooled to room temperature, 1.5 mmol of 1,6-dibromohexane (**39a**) or 5,8-bis(chloromethyl)-2,3-dihydro-1,4-benzodioxine (**39b**) was added, and the precipitate was filtered off and dried in air.

4,4'-(Hexamethylenedisulfanyl)bis(5-methyl-1,3-dithiole-2-selone) (39a). Yield 48%, orange–brown crystals, mp 111–112°C. ^{1}H NMR spectrum ($CDCl_3$),

δ, ppm: 1.2–1.6 m (8H, CH_2), 2.30 s (6H, CH_3), 2.72 t (4H, SCH_2). Found, %: S 35.99. $C_{14}H_{18}S_6Se_2$. Calculated, %: S 35.86.

4,4'-[2,3-Dihydro-1,4-benzodioxine-5,8-diylbis(methylenesulfanyl)]bis(5-methyl-1,3-dithiole-2-selone) (39b). Yield 76%, orange crystals, mp 121–122°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.99 s (6H, CH_3), 3.83 s (4H, SCH_2), 4.18 s (4H, OCH_2CH_2O), 6.58 s (2H, H_{arom}). Found, %: S 31.40. $C_{18}H_{16}S_6Se_2$. Calculated, %: S 31.30.

Bis(1,3-dithiole-2-thiones) 39c–39g (*general procedure*)**.** A solution of 0.003 mol of 1,3-dithiole-2-thione **12–15** in 50–70 ml of anhydrous methanol was deaerated by purging with argon, a solution of 0.003 mol of $CsOH\cdot H_2O$ in 10 ml of methanol was added dropwise, and the mixture was heated for 10 min until it became homogeneous. The resulting cesium thiolate solution was cooled to room temperature, and 0.0015 mol of the corresponding dihalogen derivative [5,8-bis(chloromethyl)-2,3-dihydro-1,4-benzodioxine, 2,7-bis(bromomethyl)fluorene, or 1,3-dichloropropan-2-one] was added. When the reaction was complete (TLC; the mixture turned yellow–brown), the solvent was removed, and the residue was recrystallized from appropriate solvent.

4,4'-[2,3-Dihydro-1,4-benzodioxine-5,8-diylbis(methylenesulfanyl)]bis(5-methylsulfanyl-1,3-dithiole-2-thione) (39c). Yield 58%, mp 69–70°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (6H, SCH_3), 3.92 s (4H, SCH_2), 4.23 s (4H, OCH_2CH_2O), 6.64 s (2H, H_{arom}). Found, %: S 54.66. $C_{18}H_{16}O_2S_{10}$. Calculated, %: S 54.81.

4,4'-[9*H*-Fluorene-2,7-diylbis(methylenesulfanyl)]bis(5-pentafluorophenylmethylsulfanyl-1,3-dithiole-2-thione) (39d). mp 120–125°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.78 s (2H, CH_2), 3.72–3.82 m (4H, CH_2S), 4.01–4.06 m (4H, $SCH_2C_6F_5$), 7.17–7.69 m (6H, fluorene). Found, %: S 33.74. $C_{35}H_{16}F_{10}S_{10}$. Calculated, %: S 33.85.

Dimethyl 5,5'-[9*H*-fluorene-2,7-diylbis(methylenesulfanyl)]bis[(2-thioxo-1,3-dithiol-4-ylsulfanyl)-acetate] (39e). mp 147–150°C. IR spectrum, ν, cm^{-1}: 1710 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.73–3.83 m (10H, OCH_3, CH_2CO), 4.03–4.06 m (4H, CH_2S), 4.05 s (2H, C^9H_2, fluorene), 7.19–7.66 m (6H, H_{arom}, fluorene). Found, %: S 43.77. $C_{27}H_{22}O_4S_{10}$. Calculated, %: S 43.85.

5,5'-[9*H*-Fluorene-2,7-diylbis(methylenesulfanyl)]bis[3-(2-thioxo-1,3-dithiol-4-ylsulfanyl)propanenitrile] (39f). mp 62–65°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.82 t (4H, CH_2CN), 3.10 t (4H, SCH_2), 3.32 s and 3.46 s (2H each, SCH_2), 3.83 m (2H, CH_2), 7.0–7.7 m (6H, fluorene). Found, %: S 46.13. $C_{27}H_{20}N_2S_{10}$. Calculated, %: S 46.26.

1,3-Bis(5-methylsulfanyl-2-thioxo-1,3-dithiol-4-ylsulfanyl)propan-2-one (39g). Yield 95%, mp 139–140°C (from AcOH). IR spectrum, ν, cm^{-1}: 1705 (C=O), 1060 (C=S), 2230 (C≡N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.92 t (4H, CH_2CN), 3.24 t (4H, SCH_2), 4.25 s (4H, SCH_2CO). Found, %: S 66.70. $C_{11}H_{10}OS_{10}$. Calculated, %: S 66.96.

1,3-Bis(5-methyl-2-piperidinio-1,3-dithiol-4-ylsulfanyl)propan-2-one dichloride (41). A solution of 0.63 g (0.005 mol) of 1,3-dichloropropan-2-one in 100 ml of acetone was slowly added under stirring to a suspension of 2.31 g (0.01 mol) of mesoionic salt **23** in 125 ml of acetone. The resulting light yellow solution was evaporated, and the residue was brought into further transformations without purification. Yield 100%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.6–1.8 m (4H, γ-CH_2, piperidine), 2.05 s (6H, CH_3), 3.01–3.4 m (8H, β-CH_2, piperidine), 3.7 s (SCH_2CO), 4.5–4.7 m (8H, CH_2N).

1,3-Bis(5-methyl-2-thioxo-1,3-dithiol-4-ylsulfanyl)propan-2-one (40). A solution of 2.51 g (0.03 mol) of Na_2S in 70 ml of water was slowly added to a solution of 2.9 g (0.005 mol) of salt **41** in 150 ml of water. During the addition, a bright yellow solid separated. After 15 min, the mixture was placed into a bath heated to 50–60°C for 20 min and cooled, and the precipitate was filtered off, dried in air, and purified by recrystallization from ethanol. Yield 21%, decomposition point 54–55°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 s (6H, CH_3), 3.7 s (4H, SCH_2CO). Found, %: S 61.76. $C_{11}H_{10}OS_8$. Calculated, %: S 61.85.

4,4'-(1,6-Hexamethylenedisulfanyl)-5,5'-dimethyl-2,2'-bi(1,3-dithiol-2-ylidene) (42a). *a*. A mixture of 0.33 g (0.6 mmol) of compound **39a** and 8 ml of triethyl phosphite in 70 ml of anhydrous toluene was heated under argon until the reaction was complete (initial selone **39a** disappeared according to the TLC data). The solvent was removed under reduced pressure, and the residue was subjected to column chromatography using hexane–methylene chloride (1:1) as eluent. Yield 48%, red–orange oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.0–1.7 m (8H, CH_2), 2.42 s and 2.7 s (3H each, CH_3), 4.17 m (4H, SCH_2). Found, %: S 50.65. $C_{14}H_{18}S_6$. Calculated, %: S 50.80.

b. A solution of cesium dithiolate prepared from 0.001 mol of compound **17** and 0.002 mol of $CsOH\cdot$

H_2O in 40 ml of DMF (argon atmosphere, 1 h at room temperature) and a solution of 0.001 mol of 1,6-dibromohexane in 40 ml of DMF were slowly (over a period of 2–3 h) and simultaneously added to 70 ml of preliminarily deaerated DMF under vigorous stirring. The mixture was left overnight at room temperature, the solvent was removed under reduced pressure, and the residue was treated as described above in *a*.

1^5,2^5-Dimethyl-$5^2$$5^3$-dihydro-$1^2$*H*,$2^2$*H*-3,7-dithia-1(4,2),2(2,4)-di(1,3-dithiola)-5(5,8)-(1,4-benzodioxina)cycloheptaphan-1^2(2^2)-ene (42b). A suspension of 0.66 g (0.001 mol) of compound **39b** and 2 ml of $P(OEt)_3$ in 150 ml of anhydrous xylene was deaerated by purging with argon over a period of 15 min and was then heated for 3 h under reflux. The mixture turned dark orange. The solvent was distilled off under reduced pressure, and the brown crystalline residue was purified by chromatography using methylene chloride as eluent. Yield 65%, mp 67–69°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.67 s and 2.02 s (3H each, CH_3), 3.77 s (4H, SCH_2), 4.21 s (4H, OCH_2CH_2O), 6.60 br.s (2H, H_{arom}). Found, %: S 42.18. $C_{18}H_{16}O_2S_6$. Calculated, %: S 42.12.

Tetrathiafulvalenes **45** and **46** were synthesized as described for compound **42a** (method *b*).

Dimethyl 5,5'-(1,6-hexamethylenedisulfanyl)-2,2'-bi[(1,3-dithiol-4-ylsulfanyl)acetate] (45). Yield 35%, red thick oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38–1.40 m (4H, $SCH_2CH_2C\mathbf{H}_2$), 1.58–1.61 m (4H, $SCH_2C\mathbf{H}_2CH_2$), 2.8 m (4H, $SC\mathbf{H}_2CH_2CH_2$), 3.47 s (4H, SCH_2CO), 3.69 s (6H, OCH_3). Found, %: S 45.76. $C_{18}H_{22}O_4S_8$. Calculated, %: S 45.89.

1^5,2^5-Bis(methylsulfanyl)-1^2*H*,2^2*H*,5^9*H*-3,7-dithia-1(4,2),2(2,4)-di(1,3-dithiola)-5(2,7)-fluorenacycloheptaphan-1^2(2^2)-ene (46). Yield 32%, orange crystalline substance, mp 119–120°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.88 s and 2.92 s (3H each, SCH_3); 3.79 s (2H, 9-H, fluorene); 4.06 m (4H, SCH_2); 7.19 m, 7.28 m, 7.43 m, and 7.65 m (6H, fluorene). Found, %: S 46.49. $C_{23}H_{18}S_8$. Calculated, %: S 46.56.

Unsymmetrical tetrathiafulvalenes 18–20 and 22 (*general procedure*). A suspension of equimolar amounts of the corresponding 1,3-dithiole-2-chalcogenones [4,5-ethylenedisulfanyl-1,3-dithiole-2-thione and **15a** (**18**) or **14a** (**22**), **27** and **12a** (**20**), or **27** and **14a** (**19**)] in triethyl phosphite [8–10 ml of $P(OEt)_3$ per 0.002 mol of 1,3-dithiole-2-thione] was deaerated by purging with argon over a period of 10 min and was then heated for 30 min at 110–130°C. After 5 min, the mixture turned cherry due to formation of tetrathiafulvalene system. When the reaction was complete, the mixture was cooled to room temperature, the precipitate was filtered off and washed with diethyl ether on a filter, and the product was purified by fractional crystallization.

3-(5-Methylsulfanyl-2-{3,5,7,9-tetrathiatetracyclo[9.2.1.$0^{2,10}$.$0^{4,8}$]tetradec-4(8)-en-6-ylidene}-1,3-dithiol-4-ylsulfanyl)propanenitrile (19). Yield 43%, orange crystals, mp 148–149°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 m (4H, CH_2CH_2, norbornane), 1.65 t (2H, CH_2, norbornane), 2.35 s (3H, SCH_3), 2.60 m (2H, CH, norbornane), 3.00 t (4H, SCH_2-CH_2CN), 3.30 s (2H, SCHCHS). Found, %: S 52.00. $C_{17}H_{17}NS_8$. Calculated, %: S 52.15.

3,3'-(2-{3,5,7,9-Tetrathiatetracyclo[9.2.1.$0^{2,10}$.$0^{4,8}$]-tetradec-4(8)-en-6-ylidene}-1,3-dithiol-4,5-diyldisulfanyl)bis(propanenitrile) (20). Yield 56%, orange crystals, mp 180–182°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 m (4H, CH_2CH_2, norbornane), 1.65 t (2H, CH_2, norbornane), 2.32 t (4H, CH_2CN), 2.69 m (2H, CH, norbornane), 3.05 m (4H, SCH_2), 3.33 s (2H, SCHCHS). Found, %: S 48.22. $C_{19}H_{18}N_2S_8$. Calculated, %: S 48.32.

3-[2-(4,5-Ethylenedisulfanyl-1,3-dithiol-2-ylidene)-5-methylsulfanyl-1,3-dithiol-4-ylsulfanyl]-propanenitrile (22). Yield 35%, yellow–orange crystals, mp 97–98°C (from MeOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.62 t (2H, CH_2CN), 2.95 t (2H, SCH_2), 3.22 s (4H, SCH_2CH_2S), 3.53 s (2H, SCH_2CO), 3.7 s (3H, OCH_3). Found, %: S 52.89. $C_{14}H_{13}NO_2S_8$. Calculated, %: S 53.02.

5,8-Bis{2-(3,5,7,9-tetrathiatetracyclo-[9.2.1.$0^{2,10}$.$0^{4,8}$]tetradec-4(8)-en-6-ylidene)-5-methylsulfanyl-1,3-dithiol-4-ylsulfanylmethyl}-2,3-dihydro-1,4-benzodioxine (47). A flask equipped with a reflux condenser was charged with 0.08 g (1.6 mmol) of tetrathiafulvalene **18** in 10 ml of DMF, the mixture was purged with argon over a period of 10 min, a solution of 0.03 g (1.6 mmol) of $CsOH\cdot H_2O$ in 3–4 ml of anhydrous methanol was added (the mixture turned dark red), and the mixture was heated for 30 min at 60°C. The resulting cesium bis-thiolate solution was cooled to room temperature, and a solution of 0.02 g (0.8 mmol) of 5,8-bis(chloromethyl)-2,3-dihydro-1,4-benzodioxine in a minimal amount of anhydrous DMF was added. After a few minutes, an orange solid separated and was filtered off and washed with diethyl ether. Yield 50%, mp 148–149°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.2 t (8H, CH_2CH_2, norbornane), 1.6 t (4H, CH_2, norbornane), 2.2 s (6H, SCH_3), 3.3 s

(4H, SCH_2), 3.9 m (4H, CH, norbornane), 4.2 s (4H, OCH_2CH_2O), 6.7 s (2H, H_{arom}). Found, %: S 49.25. $C_{38}H_{36}O_2S_{16}$. Calculated, %: S 49.43.

Compounds **48** and **49** were synthesized in a similar way from tetrathiafulvalenes **22** and **21** and 2,7-bis-(dibromomethyl)-9*H*-fluorene.

2,7-Bis[2-(4,5-ethylenedisulfanyl-1,3-dithiol-2-ylidene)-5-methylsulfanyl-1,3-dithiol-4-ylsulfanylmethyl]-9*H*-fluorene (48). Yield 42%, mp 115°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.81 s and 2.88 s (3H each, SCH_3), 3.19 s and 3.22 s (4H each, SCH_2CH_2S), 3.78 s (2H, 9-H, fluorene), 3.97 s and 4.05 s (2H each, SCH_2). Found, %: S 54.70. $C_{33}H_{26}S_{16}$. Calculated, %: S 54.83.

2,7-Bis{2-[4-(2-cyanoethylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-5-methylsulfanyl-1,3-dithiol-4-ylsulfanylmethyl}-9*H*-fluorene (49). Yield 35%, slowly crystallizing dark red oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.23–2.49 m (12H, SCH_3), 2.48 t (4H, CH_2CN), 2.79 t (4H, SCH_2CH_2), 3.63 s (2H, 9-H, fluorene), 3.84–3.90 m (4H, SCH_2), 7.04–7.55 m (6H, fluorene). Found, %: S 50.26. $C_{37}H_{32}N_2S_{16}$. Calculated %: S 50.41.

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