

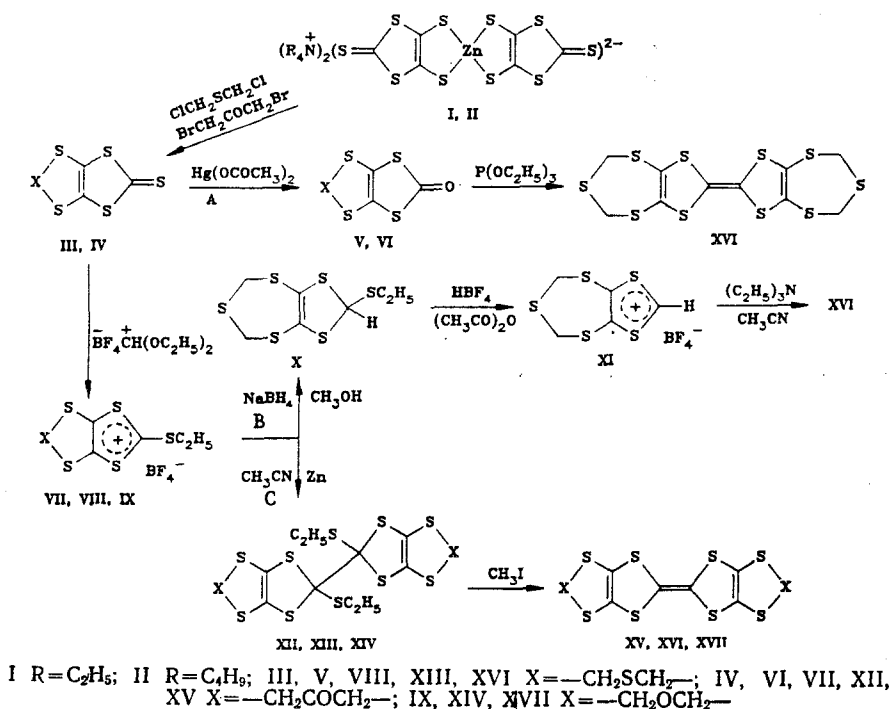
SYNTHESIS OF NEW ELECTRON-DONOR COMPOUNDS: BIS(2-THIA-1,3-PROPYLENEDITHIO)TETRATHIAFULVALENE AND BIS(2-OXO-1,3-PROPYLENE-DITHIO)TETRATHIAFULVALENE

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1,3-Dithiole-2-thione derivatives, which are starting compounds for the synthesis of new electron donors of the tetrathiafulvalene class, viz., bis(2-thia-1,3-propylenedithio)tetrathiafulvalene and bis(2-oxo-1,3-propylenedithio)tetrathiafulvalene, were obtained by the reaction of bis(tetraalkylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)zincates with 1,3-dichlorodimethyl sulfide and 1,3-dibromoacetone.

The vigorous development of the chemistry of tetrathiafulvalene derivatives is associated primarily with their electron-donor properties and the possibility of their extensive use to obtain electricity-conducting organic substances. Organic metals obtained on the basis of bis(ethylenedithio)-tetrathiafulvalene have a number of interesting electrophysical properties, including superconductivity [1-6]. The highest (among known organic semiconductors) temperature of transition to the superconducting state has been achieved for some of them [4, 6].



Continuing our search for new methods for the synthesis of new donor compounds of the tetrathiafulvalene class [7, 8] we studied the reaction of bis(tetraalkylammonium) bis-(1,3-dithiole-2-thione-4,5-dithiolato)zincates I and II with 1,3-dichlorodimethyl sulfide and 1,3-dibromoacetone, as a result of which we obtained the corresponding 1,3-dithiole-2-thiones III and IV. The reactivities of the starting dihalides in this reaction differ.

TABLE 1. Characteristics of the Synthesized Compounds

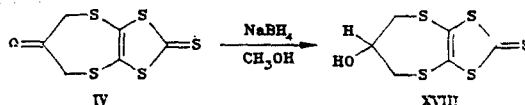
Compound	Empirical formula	mp, °C	IR spectrum, cm <sup>-1</sup>
IV	C <sub>6</sub> H <sub>4</sub> OS <sub>5</sub>	161...162	1705 (C=O); 1030, 1050 (C=S)
VI	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> S <sub>4</sub>	193...194	1705 (C=O); 1665 (C=O)
VII	C <sub>8</sub> H <sub>8</sub> BF <sub>4</sub> OS <sub>5</sub>	Oil	
X*	C <sub>7</sub> H <sub>10</sub> S <sub>6</sub>	79...80	925, 860
XI	C <sub>5</sub> H <sub>5</sub> BF <sub>4</sub> S <sub>5</sub>	180...181	1040
XII	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub> S <sub>10</sub>	139...140	1700 (C=O)
XIII	C <sub>14</sub> C <sub>18</sub> S <sub>12</sub>	135...136	1650, 1070, 890, 860
XIV	C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> S <sub>10</sub>	93...95	1650, 1425, 1310, 1045, 980, 910
XV	C <sub>12</sub> H <sub>8</sub> O <sub>2</sub> S <sub>8</sub>	235...236	1705 (C=O)
XVI	C <sub>10</sub> H <sub>8</sub> S <sub>10</sub>	275...278	1225, 1170, 1130, 860
XVII	C <sub>10</sub> H <sub>8</sub> O <sub>2</sub> S <sub>2</sub>	260...262	1334, 1294, 1230, 998, 915, 698
XVIII	C <sub>6</sub> H <sub>8</sub> OS <sub>5</sub>	180	3450, (O-H); 1060, 1940 (C=S)

\*The PMR spectrum recorded in CDCl<sub>3</sub>.

Whereas heating of the reaction mass is required to obtain thione III, in the case of IV the best result was achieved at 0°C. For the synthesis of thione III it is more convenient to use zincate II as the starting compound. The synthesis of the new tetrathiafulvalene derivatives was accomplished via schemes A-C.

1,3-Dithiole-2-thiones III and IV form 1,3-dithiol-2-ones V and VI when they are refluxed with mercuric acetate in a mixture of chloroform and acetic acid. 1,3-Dithiol-2-one V gives bis(2-thia-1,3-propylendithio)tetrathiafulvalene (XVI) in low yield (5%) when it is heated in triethyl phosphite to 130-140°C (scheme A). This compound is synthesized more conveniently through tetrathiafulvalene VII with its subsequent reduction with sodium borohydride in methanol (scheme B). We have previously synthesized bis(2-oxa-1,3-propylenedithio)tetrathiafulvalene (XVII) by a similar method [8, 9].

Method B proved to be unsuitable for obtaining bis(2-oxo-1,3-propylenedithio)tetrathiafulvalene (XV), since the carbonyl group is reduced in the reduction of tetrathiafulvalene VII with sodium borohydride in methanol. The same reaction also takes place in the action of sodium borohydride on 1,3-dithiole-2-thione IV.



For the synthesis of dicarbonyl-containing tetrathiafulvalene XV we therefore used method C, which includes reduction of tetrafluoroborate VII with zinc dust in acetonitrile [10]. Using this method we also obtained bis(2-thia-1,3-propylendithio)tetrathiafulvalene (XVI) and bis(2-oxo-1,3-propylendithio)tetrathiafulvalene (XVII) in good yields.

The new electron-donor compounds of the tetrathiafulvalene class are high-melting crystalline substances that are only slightly soluble in organic solvents and form electricity-conducting complexes in the form of black powders when they are refluxed in acetonitrile or benzonitrile with 7,7,8,8-tetracyanoquinodimethane.

#### EXPERIMENTAL

The IR spectra of thin layers of suspensions of the compounds in mineral oil were obtained with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. Results of elementary analysis for S that were in agreement with the calculated values were obtained for IV, VI, VII, and X-XVIII. The characteristics of the synthesized compounds are presented in Table 1.

6-Oxo-4,8-dithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiole-2-thione (IV). A solution of 8.64 g (40 mmole) of freshly fractionated 1,3-dibromoacetone was added to a cooled (to 0°C) solution of 14.4 g (20 mmole) of zincate I in 200 ml of acetone, and the mixture was stored for 1 h in a refrigerator. An equal volume of water was then added, and the

PMR spectrum (d <sub>6</sub> -DMSO), δ, ppm	Yield, %
3,65 (4H, s, CH <sub>2</sub> )	91
3,66 (4H, s, CH <sub>2</sub> )	75
	90
1,20 (3H, t, CH <sub>3</sub> ); 2,73 (2H, q, CH <sub>2</sub> ); 3,80 (4H, s, CH <sub>2</sub> ); 5,51 (1H, s, CH)	45
4,33 (4H, s, CH <sub>2</sub> ); 6,60 (1H, s, CH)	87
1,27 (6H, t, CH <sub>3</sub> ); 3,00 (4H, q, CH <sub>2</sub> ); 3,53 (8H, s, CH <sub>2</sub> )	55
1,20 (6H, t, CH <sub>3</sub> ); 2,85 (4H, q, CH <sub>2</sub> ); 4,10 (8H, s, CH <sub>2</sub> )	47
1,25 (6H, t, CH <sub>3</sub> ); 2,80 (4H, q, CH <sub>2</sub> ); 3,75 (8H, s, CH <sub>2</sub> )	43
—	51
—	5 (A), 90 (B), 62 (C)
2,83 (4H, m, CH <sub>2</sub> ); 4,10 (1H, m, CH)	65
	95

crystalline product was removed by filtration, washed with water, dried, and recrystallized from acetic acid to give 9.17 g of yellow-orange crystals.

6-Oxo-4,8-dithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiol-2-one (VI). A boiling solution of 4 g (13 mmole) of mercuric acetate in 50 ml of acetic acid was added to a solution of 2.52 g (10 mmole) of 1,3-dithiole-2-thione IV in 100 ml of acetic acid, during which a white precipitate of a complex of 1,3-dithiole-2-thione IV with mercuric acetate formed. The mixture was refluxed for 8 h in a flask equipped with a reflux condenser. During the refluxing process the color of the precipitate gradually changed to black as a result of the formation of mercuric sulfide. The precipitate was removed by filtration and washed with 20 ml of acetic acid. Chloroform (200 ml) was added to the filtrate, and the organic layer was washed successively with water (three 200-ml portions), 200 ml of 5% sodium carbonate solution, and 200 ml of water and dried with anhydrous sodium sulfate. The solvent was evaporated to give a light-brown crystalline substance, which was purified by recrystallization from acetic acid. The yield was 1.8 g.

2-Ethylthio-6-oxo-4,8-dithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiolium Tetrafluoroborate (VII). A 4.9-g (30 mmole) sample of formic acid ortho ester and 4.3 g (30 mmole) of boron trifluoride etherate were added simultaneously to a refluxing solution of 5 g (20 mmole) of 1,3-dithiole-2-thione IV in 100 ml of dichloroethane, after which the reaction mixture was cooled to 20°C and treated with 200 ml of dry ether. The resulting oily product was washed thoroughly with dry ether. The tetrafluoroborate could not be crystallized, and it was therefore used for the subsequent syntheses without additional purification. The yield was 6.9 g.

2-Ethylthio-4,6,8-trithia-5,5,7,8-tetrahydro-4H-cyclohepta-1,3-dithiole (X). Methanol (100 ml) was added to 3.68 g (10 mmole) of tetrafluoroborate VIII, and 2 g (53 mmole) of NaBH<sub>4</sub> was added in portions with stirring to the reaction mixture. After 1 h, an equal volume of water was added to the reaction mass, and the crystals were removed by filtration and recrystallized from acetic acid. The yield was 1.3 g.

4,6,8-Trithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiolium Tetrafluoroborate (XI). A 1.4g (5 mmole) sample of X was dissolved in 50 ml of acetic anhydride, and the solution was cooled to 0° and treated with 2 ml (65 mmole) of HBF<sub>4</sub>. The mixture was then poured into 200 ml of dry ether, and the precipitated light-brown crystals were removed by filtration and washed with dry ether to give 1.35 g of product, which, because of its low stability, was used without additional purification.

Bis-2-(2-ethylthio-5-oxo-4,6-dithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiole) (XII). A 3.68-g (10 mmole) sample of tetrafluoroborate VII was dissolved in 100 ml of dry acetonitrile, and 3 g of zinc dust was added in portions with stirring in a stream of argon. The color of the reaction mass changed from dark brown to yellow. After 1 h, the zinc dust was removed by filtration and washed on the filter with 10 ml of dry acetonitrile. The solvent was evaporated, and the reaction product was recrystallized from acetone to give 1.55 g of a yellow-crystalline powder.

Bis-2-(2-ethylthio-4,6,8-trithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiole) (XIII and Bis-2-(2-ethylthio-6-oxa-4,8-dithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiole) (XIV). These compounds were similarly obtained.

6-Hydroxy-4,8-dithia-5,6,7,8-tetrahydro-4H-cyclohepta-1,3-dithiole-2-thione (XVIII). A 2.52-g (10 mmole) sample of 1,3-dithiole-2-thione IV was suspended in 50 ml of methanol, and 2 g (53 mmole) of NaBH<sub>4</sub> was added in portions in a stream of argon. After 1 h, equal volume of water was added to the reaction mass, and the crystals were removed by filtration and purified by recrystallization from acetic acid to give 2.4 g of XVIII.

Bis(2-thia-1,3-propylendithio)tetrathiafulvalene (XVI). A) A 2.4-g (10 mmole) sample of 1,3-dithiole-2-thiones V was heated with 5 ml of freshly fractionated triethyl phosphite in a stream of argon at 120-130°C for 1 h, after which the mixture was cooled to 20°C, and a finely crystalline yellow precipitate formed. The crystals were removed by filtration and washed with ether to give 0.11 g of product.

B) A 3.12-g (10 mmole) sample of tetrafluoroborate XI was dissolved in 40 ml of acetonitrile, and 3 ml of triethylamine was added. The resulting finely crystalline yellow precipitate was removed by filtration and washed with acetonitrile and ether to give 2 g of product.

C) A mixture of 2.85 g (5 mmole) of XIII and 30 ml of methyl iodide was refluxed for 3 h, after which the finely crystalline precipitate was removed by filtration and washed with acetone and ether to give 1.4 g of tetrathiofulvalene XVI.

Bis(2-oxo-1,3-propylendithio)tetrathiafulvalene (XV) and Bis(2-oxa-1,3-propylendithio)tetrathiafulvalene (XVII). These compounds were similarly synthesized. Compound XV was purified by recrystallization from pyridine.

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