SYNTHESIS AND PROPERTIES OF (4-HYDROXY-5-METHOXYCARBONYLTHIENO)-TETRATHIAFULVALENES

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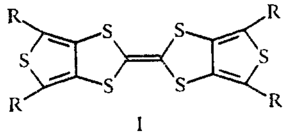
6-Hydroxy-5-methoxycarbonylthieno[2,3-d]-1,3-dithiol-2-thione, -2-one, and 2-selenone were prepared by intramolecular cyclocondensation of 4-methoxycarbonylmethylthio-1,3-dithiol-2-thione-, 2-one-, and 2-selenone-5-carboxylic acid methyl ester. 2,6(7)-Di(methoxycarbonylmethylthio)-3,7(6)-di(methoxycarbonyl)tetra-thiafulvalene, 2-methoxycarbonylmethylthio-3-methoxycarbonyl-6,7-ethylenedithiotetrathiafulvalene, and the corresponding thieno-condensed tetrafulvalene derivatives were synthesized from them. The electrochemical oxidation potentials of the new tetrafulvalene derivatives were determined.

Tetrathiafulvalene derivatives are compounds with strong electron-donor properties and are easily oxidized into radical cation salts. Tetrathiafulvalenes can form stable charge transfer complexes and radical ion salts having elevated electrical conductivity with electron-acceptor compounds.

There are published data on synthesis of 3,4-thieno-condensed derivatives of tetrathiafulvalene I [1-4].

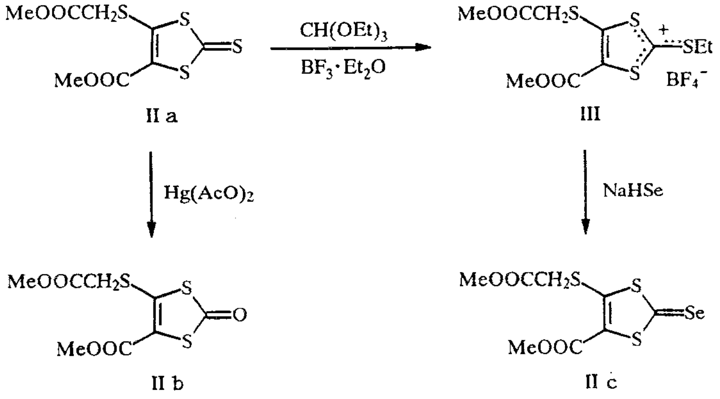


I

R = H, Me

In the present study, the synthesis and properties of 2,3-thieno-condensed tetrathiafulvalene derivatives [5] were investigated by closure of the thiophene ring in the corresponding 1,3-dithiol or tetrafulvalene derivatives. The starting compounds were 4-methoxycarbonylmethylthio-1,3-dithiol-2-thione-5-carboxylic acid methyl ester (IIa), 4-methoxycarbonylmethylthio-1,3-dithiol-2-one-5-carboxylic acid methyl ester (IIb), and 4-methoxycarbonylmethylthio-1,3-dithiol-2-selenone-5-carboxylic acid methyl ester (IIc).

Compound IIa was prepared by condensation of O-methyl(S-methoxycarbonylmethyl)dithiocarbonate with carbon disulfide in the presence of sodium *tert*-butoxide [6] and subsequent alkylation with bromoacetic acid methyl ester. 1,3-Dithiol-2-thione IIa was converted into 1,3-dithiol-2-one IIb in boiling with mercury acetate [7] in chloroform–glacial acetic acid mixture. 1,3-Dithiol-2-selenone IIc was prepared with a solution of sodium hydrogen selenide prepared by the reaction of selenium and sodium borohydride and 2-ethylthio-1,3-dithiolium tetrafluoroborate (III) [8].



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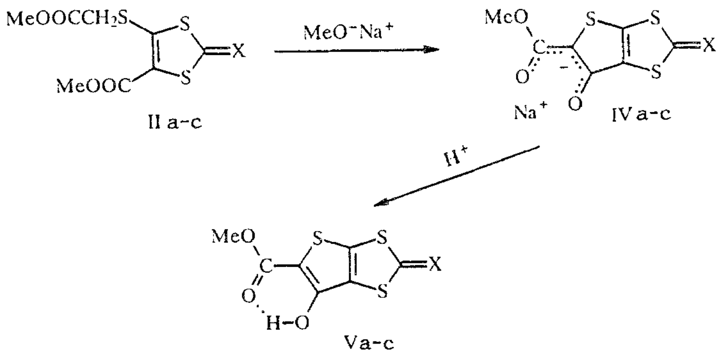
0009-3122/93/2906-0652$12.50

The latter is formed in the reaction of 1,3-dithiol-2-thione IIa with a mixture of boron tetrafluoride etherate and *o*-formic acid triethyl ester [9].

Intramolecular condensation with formation of thieno[2,3-*d*]-1,3-dithiol-2-thione derivative IVa takes place in the reaction of thione IIa with sodium methoxide [5], which we also demonstrated in [10].

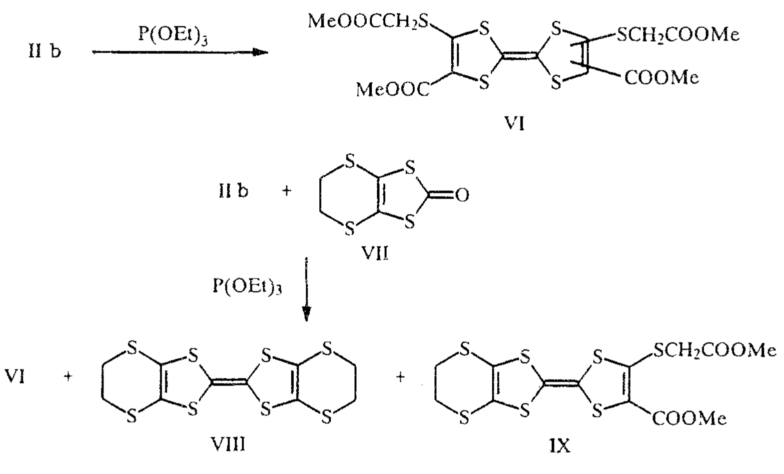
In investigating the possible cyclization of compounds IIa-c, we found that intramolecular cyclocondensation in the reaction of these compounds with sodium methoxide takes place not only in the case of thione IIa but also for compounds IIb and IIc. In all cases, 6-hydroxy-5-methoxycarbonylthieno[2,3-*d*]-1,3-dithiol-2-thione (IVa), -2-one (IVb), and -2-selenone (IVc) sodium salts are initially formed, and the corresponding thieno derivatives Va-c are obtained when solutions of these salts are acidified with hydrochloric acid.



II, IV, V a X = S, b X = O, c X = Se

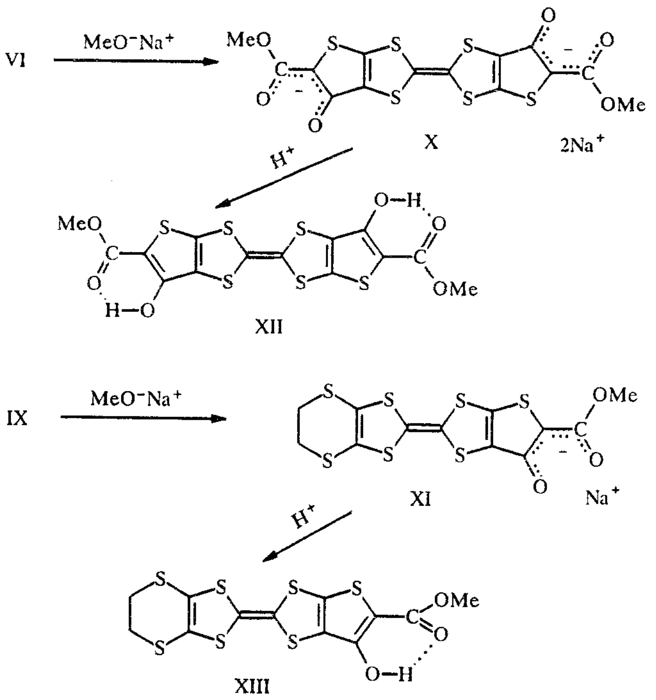
To obtain the corresponding tetrathiafulvalene derivatives, we investigated the reaction of compounds IIa-c and Va-c with triethyl phosphite in heating to 100°C [11]. We found that compounds IIa, c and Va-c do not form the desired products in the reaction with triethyl phosphite, while heating of 1,3-dithiol-2-one IIb with triethyl phosphite in toluene at 100°C yields 2,6(7)-di(methoxycarbonylmethylthio)-3,7(6)-di(methoxycarbonyl)tetrathiafulvalene[2,2-bi-(4-methoxycarbonylmethylthio-5-methoxycarbonyl-1,3-dithiolylidene)] (VI) with a yield of 60-70%, probably in the form of a mixture of two geometric isomers.

Heating a mixture of dithiolone IIb and 4,5-ethylenedithio-1,3-dithiol-2-one (VII) with triethyl phosphite in toluene at 110°C yields a mixture of a symmetric derivative of tetrathiafulvalene VI, bis(ethylenedithio)tetrathiafulvalene (VIII), and asymmetric 2-methoxycarbonylmethylthio-3-methoxycarbonyl-6,7-ethylenedithiotetrathiafulvalene (IX).

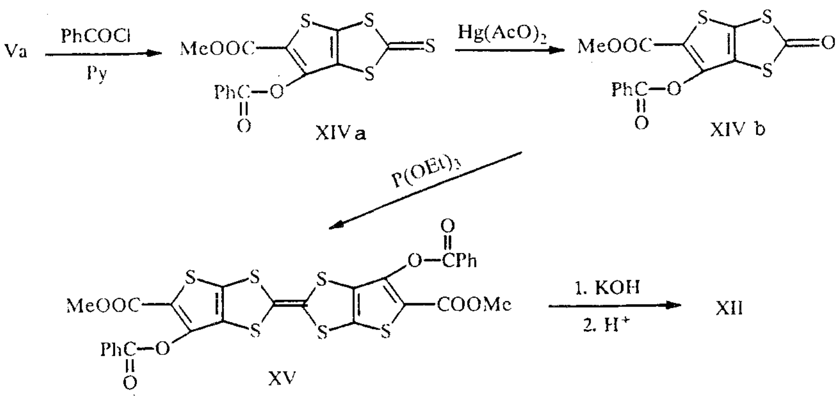


Intramolecular condensation of tetrathiafulvalene VI and IX with sodium methoxide passes through formation of the corresponding sodium salts X and XI, and when they were acidified with hydrochloric acid, bis(4-hydroxy-5-methoxycarbonylthieno)tetrathiafulvalene (XII) was separated in a mixture of isomers and 2,3-(4-hydroxy-5-methoxycarbonylthieno)-6,7-ethylenedithiotetrathiafulvalene (XIII). (See scheme at the top of the next page.)

Because of the low solubility of compounds VI and IX, it is difficult to obtain thieno-condensed tetrathiafulvalene XII. It was found that ultrasound accelerates the cyclization reaction.



Thieno-condensed derivatives Va-c do not react with triethyl phosphite, and we thus attempted to obtain tetrathiafulvalene XII from thieno-condensed 1,3-dithiol-2-thione Va according to the following scheme:



Thione XIVa, obtained by benzoylation of compound Va, is converted into the corresponding dithiolone XIVb by boiling with mercury acetate, which yields bis(4-benzoyloxy-5-methoxycarbonylthieno)tetrathiafulvalene (XV) with a yield of 87% when heated to 100°C with triethyl phosphite in toluene. Elimination of the benzoyl group yields tetrathiafulvalene XII.

The composition and structure of the compounds obtained were confirmed by the data from elemental analysis, IR, and PMR spectroscopy (Table 1).

The IR spectra of compounds IIa-c and tetrathiafulvalene derivatives VI and IX contain two absorption bands characteristic of an alkoxycarbonyl group in the 1690-1735 cm^{-1} region. Significant changes in the region of absorption of the C=O group are observed after cyclization. The absorption spectra of compounds Va-c, XII, and XIII contain one absorption band in the 1645-1670 cm^{-1} region (C=O) and a broad absorption band characteristic of an intramolecular hydrogen bond at 2900-3296 cm^{-1}. There is an additional absorption band at 1655-1680 cm^{-1} characterizing a carbonyl group (S−CO−S) in the spectra of 1,3-dithiol-2-ones IIb, Vb, and XIVb. A characteristic absorption band of a trithiocarbonate group appears in the region of 1020-1095 cm^{-1} in the spectra of 1,3-dithiol-2-thiones IIa, Va, and XIVa.

TABLE 1. Physicochemical Properties of the Synthesized Compounds

Compound	T_{mp}, °C	IR spectrum, ν, см$^{-1}$	UV spectrum		PMR spectrum, δ, ppm	Yield, %
			solvent	λ_{max}, nm (lg ε)		
IIa	106...107	1730, 1690, 1300, 1095, 1070, 1030	$CHCl_3$ C_2H_5OH	280 (3,99), 383 (4,22) 280 (3,96), 380 (4,19)	3,79 (2H, s, SCH_2); 3,81 (3H, s, OCH_3), 3,87 (3H, s, OCH_3)	71
IIb	103...104	1732, 1695, 1655, 1260	$CHCl_3$	287 (3,75), 324 (3,93)	3,71 (2H, s, SCH_2), 3,73 (3H, s, OCH_3); 3,80 (3H, s, OCH_3)	79
IIc	104...105	1730, 1705, 1309, 1257, 960	C_2H_5OH	295 (3,81), 413 (4,23)	3,75 (5H, s, SCH_2, OCH_3), 3,81 (3H, s, OCH_3)	27
Va	217...218	3250...2900, 1670, 1535, 1080, 1060, 1020	$CHCl_3$	295 (4,12), 340 (3,72), 386 (4,48)	2,88 (3H, s, OCH_3); 9,75 (1H, s, OH)	61
Vb	181...182	3270...2910, 1730, 1680, 1530, 1315, 1176, 1130	$CHCl_3$	295 (4,26), 334 sh (3,97)	3,85 (3H, s, OCH_3), 9,78 (1H, s, OH)	85
Vc	245...246	3270...3005, 1670, 1535, 1408, 1330, 1205	$CHCl_3$	295 (4,23), 320 sh (3,98), 413 (4,49)	3,79 (3H, s, OCH_3); 9,73 (1H, s, OH)	63
VI	230 decomp.	1734, 1689, 1500, 1260, 1252, 1085	1,4-dioxane	295 (4,38), 307 sh (4,36), 330 sh (4,18), 440 (3,60)	3,54 (2H, s, SCH_2), 3,69 (3H, s, OCH_3); 3,74 (3H, s, CH_3)**	36
IX	173...174	1728, 1684, 1668, 1652, 1306, 1254, 1168	$CHCl_3$	315 (4,16), 343 sh (4,06), 440 (3,34)	3,23 (4H, s, CH_2S); 3,73 (3H, s, OCH_3); 3,74 (5H, s, SCH_2, OCH_3)**	20
XII	234 decomp.	3245...2940, 1645, 1530, 1415, 1330, 1130	1,4-dioxane	307 (4,60), 322 sh (4,15), 402 (3,92)	3,94 (6H, s, OCH_3), 9,62 (2H, s, OH)**	40 94***
XIII	194...195 decomp.	3296...2900, 1650, 1533, 1414, 1331, 1240, 1127	$CHCl_3$	307 (4,38), 335 sh (4,12), 404 (3,59)	3,25 (4H, s, CH_2S), 3,81 (3H, s, OCH_3), 9,58 (1H, s, OH)**	42
XIVa	120...121	1742, 1532, 1080, 1050, 1020	$CHCl_3$	274 (3,08), 315 (3,55), 384 (3,41)	3,73 (3H, s, OCH_3), 7,55...8,13 (5H, м, C_6H_5)	80
XIVb	115...116	1740, 1706, 1655, 1533, 1300	$CHCl_3$	278 (4,29), 315 (4,16), 340 sh (4,06)	3,74 (3H, s, OCH_3), 7,68...8,16 (5H, м, C_6H_5)	82
XV	223 decomp.	1742, 1712, 1527, 1297, 1262, 1182, 1125, 1087, 1059	$CHCl_3$	290 (4,51), 3,25 sh (4,25), 410 (3,90)	3,75 (6H, s, $2OCH_3$), 7,58...8,17 (10H, м, $2C_6H_5$)**	45

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*$CDCl_3$.

**$CDCl_3$-DMSO

***From XIV.

TABLE 2. Electrochemical Oxidation Potentials of Tetrathiafulvalene Derivatives (PhCN), TVAR, Ag/AgCl Reference Electrode

Compound	E_1^{ox} / E_1^{red}	E_2^{ox} / E_2^{red}	Compound	E_1^{ox} / E_1^{red}	E_2^{ox} / E_2^{red}
VI	0,79 / 0,67	1,09 / 0,91	XIII	0,71 / 0,56	1,03 / 0,86
IX	0,68 / 0,54	0,98 / 0,84	XV	0,85 / 0,73	1,12 / 1,00
XII	0,59 / 0,49	0,87 / 0,75	VIII	0,60 / 0,46	0,94 / 0,78

There is a characteristic absorption band at 380 nm in the UV spectrum of thione IIa, and it can be interpreted as the corresponding $\pi-\pi^*$-transition of a $S_2C=S$ group. There is no significant change in the electronic structure during cyclization, but the intensity of the long-wave absorption band increases slightly and a new band appears at 340 nm.

The UV spectra of tetrathiafulvalenes VI and IX contain a characteristic absorption band at 440 nm, as for tetrathiafulvalene carboxylic acid esters [12], corresponding to a $\pi-\pi^*$-transition with the participation of an ester group. The second broad intense absorption band characteristic of the tetrathiafulvalene system itself is located in the 295-345 nm region and has several inflections.

In comparison to carboxylic acid esters II and IX, the first long-wave absorption band for thieno-condensed tetrathiafulvalene derivatives XII and XIII has a strong hypsochromic shift and is located in the 402-404 nm region, and the intensity of absorption increases slightly.

The oxidation potentials (E^{ox}) (Table 2) were determined by cyclic voltammetry to characterize the electron-donor properties of the synthesized tetrathiafulvalenes.

The new tetrathiafulvalenes are oxidized with more difficulty than compound VIII because of the electron-acceptor effect of the methoxycarbonyl group. The effect of the 4-hydroxy-5-methoxycarbonylthieno group is weaker than the total effect of the methoxycarbonyl and methoxycarbonylmethylthio groups. Compound XII is of interest for preparation of radical ion salt derivatives, since its oxidation potential is closest to the oxidation potential of well-studied compound VIII [13].

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 (suspension in paraffin oil for the 600-2000 cm^{-1} region and suspensions in hexachlorobutadiene for the 2000-3600 cm^{-1} region). The PMR spectra were made on Bruker WH-90/DS and Tesla BS 487C instruments with TMS as the internal standard. The UV spectra were recorded on a Specord UV-vis spectrophotometer. The electrochemical oxidation potentials were determined on a NI-50-1 potentiostat on a glass–graphite electrode (0.28 cm^2) relative to a silver–silver chloride electrode in benzonitrile. The measurements were performed at room temperature. Tetrabutylammonium perchlorate in 0.1 M concentration was used as the supporting electrolyte, and the concentration of depolarizer was 10^{-4} M. The potential scanning rate was 200 mV/sec.

4-Methoxycarbonylmethylthio-1,3-dithiol-2-thione-5-carboxylic Acid Methyl Ester (IIa, $C_8H_8O_4S_4$). Here 5 g (28 mmole) of O-methyl(S-methoxycarbonylmethyl) dithiocarbonate was dissolved in 30 ml of DMF and 2 ml (34 mmole) of carbon disulfide was added. While cooling to 0°C and stirring, 4.05 g (42 mmole) of sodium *tert*-butoxide was gradually added. The mixture was stirred at room temperature for 1 h, then 2.6 ml (4.32 g, 28 mmole) of bromoacetic acid methyl ester was added and stirred for 0.5 h, and 100 ml of water was added. The precipitated yellow crystals were filtered off and washed with methanol. They were recrystallized from methanol or acetic acid, yielding 5.8 g of needle-shaped yellow crystals.

4-Methoxycarbonylmethylthio-1,3-dithiol-2-one-5-carboxylic Acid Methyl Ester (IIb, $C_8H_8O_5S_3$). A solution of 3.2 g (10 mmole) of mercury acetate in 5 ml of acetic acid was added to a hot solution of 2 g (6.7 mmole) of thione IIa in 15 ml of chloroform and boiled for 2 h. It was filtered through a layer of silica gel and the silica gel was washed with hot chloroform. The filtrate was washed with a solution of $NaHCO_3$, dried with $CaCl_2$, and the chloroform was then evaporated. The sediment was recrystallized from acetic acid, yielding 1.58 g of colorless needle-shaped crystals.

4-Methoxycarbonylmethylthio-1,3-dithiol-2-selenone-5-carboxylic Acid Methyl Ester (IIc, $C_8H_8O_4S_3Se$). Here 1 g (3.4 mmole) of thione IIa was dissolved in 15 ml of chloroform and 2 ml of $HC(OC_2H_5)_3$ and 2 ml of $BF_3 \cdot O(C_2H_5)_2$ were added while heating at 60°C. After 0.5 h, 100 ml of diethyl ether was added. The 2-ethylthio-1,3-dithiolium salt III obtained was decanted after 2 h, washed with 50 ml of diethyl ether, dissolved in 10 ml of acetonitrile, and added to a solution of sodium hydrogen selenide prepared from 0.54 g (6.8 mmole) of selenium and 1.08 g (28 mmole) of sodium borohydride in

20 ml of water. Then 20 ml of benzene was added and stirred under argon for 2 h. The benzene layer was separated and the aqueous layer was extracted with benzene (3 × 10 ml). The extract was washed with water, dried with $CaCl_2$, and filtered through a layer of silica gel. The solvent was distilled off and the sediment was recrystallized from methanol, yielding 0.31 g of needle-shaped orange crystals.

6-Hydroxy-5-methoxycarbonylthieno[2,3-*d*]-1,3-dithiol-2-thione (Va, $C_7H_4O_3S_4$). Here 7.8 ml (3.4 mmole) of a solution of sodium methoxide ($4.34 \cdot 10^{-4}$ mole/ml) in methanol was added to a suspension of 1 g (3.4 mmole) of thione IIa in 10 ml of methanol and stirred for 1.5 h. Light yellow crystals precipitated. Then 30 ml of water was added and it was acidified with conc. hydrochloric acid to pH 3. It was stirred for another 1 h. The precipitated crystals were filtered off and recrystallized from acetic acid, yielding 0.54 g of needle-shaped yellow crystals.

6-Hydroxy-5-methoxycarbonylthieno[2,3-*d*]-1,3-dithiol-2-one (Vb, $C_7H_4O_4S_3$). Here 94 g (1.74 mmole) of sodium methoxide was added to a suspension of 0.5 g (1.74 mmole) of dithiolone IIb in 5 ml of methanol. The reaction was conducted similar to the method for preparation of thione Va. Recrystallization from acetic acid yielded 0.35 g of colorless needle-shaped crystals.

6-Hydroxy-5-methoxycarbonylthieno[2,3-*d*]-1,3-dithiol-2-selenone (Vc, $C_7H_4O_3S_3Se$). Here 0.15 g of needle-shaped dark orange crystals was obtained from 0.15 g (0.44 mmole) of selenone IIc after recrystallization from acetic acid, similar to synthesis of thione Va.

2,6(7)-Di(methoxycarbonylmethylthio-2,7(6)-di(methoxycarbonyl)tetrathiafulvalene (VI, $C_{16}H_{16}O_8S_6$). Here 1.3 g (4.6 mmole) of dithiolone IIb was heated with 5 ml of triethyl phosphite in 12 ml of toluene at 100°C for 1 h. It was cooled, 20 ml of methanol was added, and it was filtered. The sediment was washed with methanol. Recrystallization from diglyme yielded 0.44 g of a dark red substance.

2-Methoxycarbonylmethylthio-3-methoxycarbonyl-6,7-ethylenedithiotetrathiafulvalene (IX, $C_{13}H_{12}O_4S_7$). Here 1.07 g (3.82 mmole) of dithiolone IIb and 1.2 g (5.72 mmole) of dithiolone VII were heated with 5 ml of triethyl phosphite at 110°C for 1 h. The reaction mixture was cooled, 30 ml of methanol was added, and the precipitated sediment was filtered off, yielding 1.2 g (69%) of a mixture of tetrathiafulvalene derivatives VI, VIII, and IX. A fraction with R_f 0.55 was separated by chromatography on silica gel (chloroform eluent). The solvent was evaporated and the sediment was recrystallized from acetonitrile, yielding 0.35 g of needle-shaped red crystals.

Bis(4-hydroxy-5-methoxycarbonylthieno)tetrathiafulvalene (XII, $C_{14}H_8O_6S_6$). A. Here 18.9 mmole of sodium methoxide in methanol was added to 1 g (1.89 mmole) of tetrathiafulvalene VI and stirred for 2 h in an ultrasound setup, then boiled for 4 h. Then 100 ml of water was added and the mixture was acidified to pH 3 with HCl. The sediment was filtered and washed with methanol. Recrystallization from dioxane yielded 0.7 g of orange compound XII.

B. Here 1 g (1.49 mmole) of compound XV was dissolved in 10 ml of dioxane and a solution of 14.9 mmole of KOH in 10 ml of water was added. It was stirred for 15 min in an ultrasound setup. HCl was added to pH 3 and it was filtered, yielding 0.45 g of compound XII.

6-Benzoyloxy-5-methoxycarbonylthieno[2,3-*d*]-1,3-dithiol-2-thione (XIVa, $C_{14}H_8O_4S_4$). While heating, 0.5 g (0.55 mmole) of thione Va was dissolved in 3 ml of pyridine and 0.22 ml (0.93 mmole) of benzoyl chloride was added to the hot solution; the sediment precipitated after 3 h was suspended in 15 ml of hexane and filtered off. It was washed on the filter with water. Recrystallization from benzene–hexane mixture yielded 0.56 g of needle-shaped yellow crystals.

6-Benzoyloxy-5-methoxycarbonylthieno[2,3-*d*]-1,3-dithiol-2-one (XIVb, $C_{14}H_8O_5S_3$). Here 0.5 g (1.35 mmole) of thione XIVa was dissolved in 10 ml of chloroform and 0.52 g (1.62 mmole) of mercury acetate in 5 ml of acetic acid was added. The reaction mixture was boiled for 5 h. It was separated similar to compound IIb. It was recrystallized from benzene–hexane mixture, yielding 4 g of colorless needle-shaped crystals.

Bis(4-benzoyloxy-5-methoxycarbonylthieno)tetrathiafulvalene (XV, $C_{28}H_{16}O_8S_6$). Here 0.3 g (0.85 mmole) of dithiolone XIVb was heated with 2 ml of triethyl phosphite in 5 ml of toluene at 100°C for 3 h. It was separated similar to compound VI and recrystallized from benzene–hexane mixture, yielding 0.12 g (87%) of orange compound XV.

2,3-(4-Hydroxy-5-methoxycarbonylthieno)-6,7-ethylenedithiotetrathiafulvalene (XIII, $C_{12}H_8O_3S_7$). Here 0.2 g (2.19 mmole) of compound IX was mixed with 5 ml (10.95 mmole) of a solution of sodium methoxide in 5 ml of methanol in an ultrasound setup. The precipitated yellow salt XI was filtered off, yielding 0.19 g (99%). Sodium salt XI was suspended in 15 ml of water and acidified to pH 3 with HCl. It was stirred in the ultrasound setup for 2 h. The sediment of XIII was filtered off and recrystallized from chloroform–ethanol mixture, yielding 0.08 g of brown substance.

REFERENCES

1. L. Y. Chiang, P. Shu, D. Holt, and D. O. Cowan, J. Org. Chem., **4**, 4713 (1983).
2. K. Lerstrup, M. Lee, D. O. Cowan, and T. J. Kistenmacher, Mol. Cryst. Liq. Cryst., **120**, 295 (1985).
3. P. Shu, L. Chiang, T. J. Emge, D. Holt, T. J. Kistenmacher, M. Lee, J. Stokes, T. O. Poehler, A. N. Bloch, and D. O. Cowan, J. Chem. Soc. Chem. Commun., No. 7, 920 (1981).
4. K. Kobayashi, Chem. Lett., No. 9, 1423 (1985).
5. I. V. Sudmale and V. Yu. Khodorkovskii, Proceedings of the III Conference of Young Scientists from the Chemical Technology Factory of Riga Polytechnical Institute [in Russian], Riga (1989), p. 43; Ref. Zh. Khim., 23Zh347 (1989).
6. M. Augustin, W. Dölling, and A. Vogt, Z. Chem., **23**, No. 9, 333 (1983).
7. K. Hartke, T. Kissel, J. Quante, and R. Matusch, Chem. Ber., **113**, 1898 (1980).
8. V. Yu. Khodorkovskii, Ya. N. Kreitsberga, K. A. Balodis, and O. Ya. Neiland, Izv. Akad. Nauk LatvSSR, Ser. Khim., No. 1, 120 (1988).
9. V. Yu. Khodorkovskii, D. V. Bite, M. V. Petrova, and O. Ya. Neiland, Khim. Geterotsikl. Soedin., No. 5, 705 (1984).
10. W. Dölling, A. Vogt, and M. Augustin, Z. Naturforsch., **46b**, No. 2, 133 (1991).
11. A. Krief, Tetrahedron, **42**, 1209 (1986).
12. Ya. N. Kreitsberga, R. B. Kampare, and O. Ya. Neiland, Khim. Geterotsikl. Soedin., No. 12, 1630 (1984).
13. V. Khodorkovsky, A. Edžina, and O. Neilands, J. Molec. Electr., **5**, 33 (1989).