# SYNTHESIS AND PROPERTIES OF BIS(VINYLENEDITHIO)- AND BIS(DIMETHYLVINYLENEDITHIO)TETRATHIAFULVALENES

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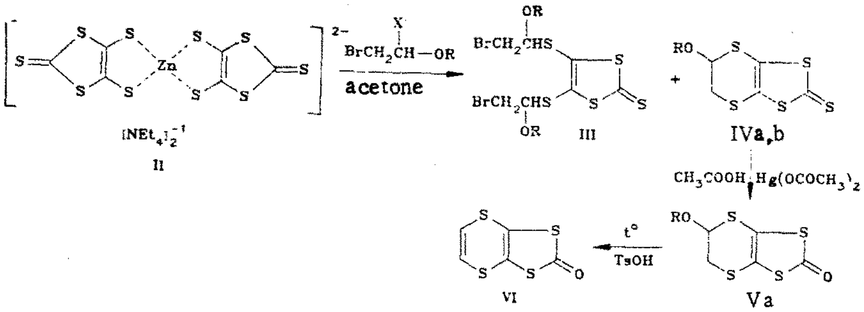
A method was developed for the preparation of bis(vinylenedithio)- and bis(dimethylvinylenedithio)tetrathiafulvalenes from 1,3-dithiole-2-thione-4,5-dithiolate.

As a result of the discovery of superconductivity in bis(ethylenedithio)tetrathiafulvalene triiodide [1], it was desirable to synthesize its unsaturated analog, bis(vinylenedithio)tetrathiafulvalene (Ia) and its tetramethyl derivative (Ib). The zinc complex of 1,3-dithiole-2-thione-4,5-dithiolate (II) was used as the starting compound, obtained by the reduction of carbon disulfide by sodium [2]. In acetone solution, complex II is alkylated by α,β-dibromoethyl ester of acetic acid and α-chloro-β-bromoethyl ethyl ether to form acetoxy- or ethoxy-ethylenedithio-1,3-dithiole-2-thione (IVa, b), respectively. Compound III was isolated as a byproduct.

When thiones IVa,b are heated in inert solvents (in toluene, xylene) with p-toluenesulfonic acid, $P_2O_5$, or in the presence of boron trifluoride etherate, the reaction mixture strongly resinifies, and vinylenedithio-1,3-dithiole-2-thione is isolated from it in a yield of 5-10% only. To increase the yield, thione IVa is converted into dithiolone Va using mercuric acetate. Heating Va with p-toluenesulfonic acid in toluene gave vinylenedithio-1,3-dithiol-2-one (VI) in a yield of 40%.



a $R=CH_3CO$, $X=Br$; b $R=C_2H_5$, $X=Cl$;

To obtain the starting compound XI for the synthesis of tetrathiafulvalene Ib, we studied the reaction of the zinc complex II with 3-chloro(bromo)-2-butanone. It was found that the reaction proceeds only on heating in a DMFA solution, and only acyclic compound VIII is formed. In contrast to complex II, the disodium salt of 1,3-dithiole-2-thione-4,5-dithiolate, synthesized by splitting dibenzoylthio-1,3-dithiole-2-thione (VII) by sodium methylate [3], undergoes this reaction at 20°C. After acidification of the reaction mixture, compound IX was obtained in a yield of 70%.

When heated in toluene with an equimolar amount of p-toluenesulfonic acid, compound IX forms thione X, which is converted into dithiolone XI by mercuric acetate.

The structures of all the thiones and dithiolones III-XI obtained were confirmed by IR and PMR spectra data (see Table 1).

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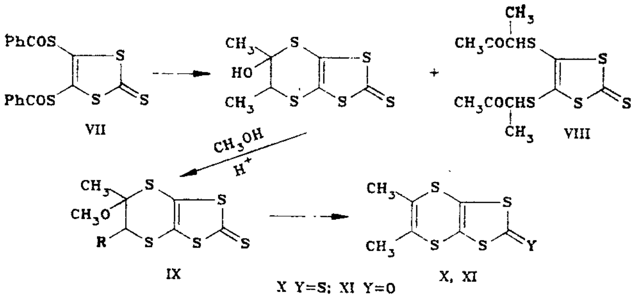
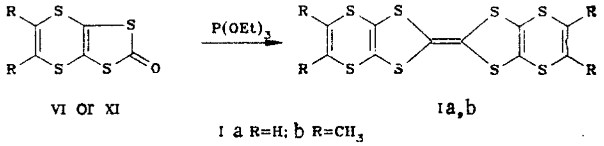


The desired tetrathiafulvalenes Ia,b were obtained by brief heating of compound VI or XI with triethyl phosphite at 120-130°C, in analogy to [4]. Compounds IVa, Va, X do not form derivatives Ia,b under these conditions.



The characteristics of tetrathiafulvalenes Ia,b obtained for the first time, and the known bis(ethylenedithio)tetrathiafulvalene (XII) are given in Table 2.

The anode oxidation potentials ($E_{OX}$) were evaluated by the method of cyclic voltamperometry. The value of $E_{OX}$ of compounds Ia,b is higher by 0.12-0.15 V, compared with that of compound XII, i.e., introduction of double bonds into a molecule hinders its oxidation.

## EXPERIMENTAL

The IR spectra were run on a Specord 75 IR spectrophotometer, in mineral oil, the UV spectra on a Specord UV-Vis spectrophotometer. The PMR spectra were obtained on a Perkin-Elmer R-12A spectrometer with a working frequency of 80 MHz, using HMDS as internal standard. The polarographic studies were carried out on a PAR-170 electrochemical system by a three-electron scheme, relative to a saturated calomel electrode, using a glass-graphite working electrode with surface area of 0.28 cm$^2$, temperature 20°C, tetrabutyl ammonium perchlorate (0.1 mole/liter) as a polarographic background, and scanning velocity of 100 mV/sec.

α-Chloro-β-bromoethyl ethyl ether was obtained by bromination of vinyl acetate by the method described in [6], followed by reaction with thionyl chloride according to [7]. α,β-Dibromoethyl ethyl ester of acetic acid was obtained according to [8], and 3-chloro-2-butanone, according to [9].

Acetoxyethylenedithio-1,3-dithiole-2-thione (IVa). A mixture of 8 g (10 mmole) of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolate) zincate (II) and 3 ml (25 mmoles) of α,β-dibromoethyl ester of acetic acid in 25 ml of acetone is boiled for 4 h. The acetone is evaporated, and the residue is dissolved with boiling in ~300 ml of benzene, and 4.3 g (69%) of compound IVa are precipitated by hexane, mp 120-121°C. Found, %: S 56.2. $C_7H_6O_2S_5$. Calculated, %: S 56.7.

Ethoxyethylenedithio-1,3-dithiole-2-thione (IVb) and 4,5-bis[(1-Ethoxy-2-bromo)ethylthio]-1,3-dithiole-2-thione (III). A 2.6 g portion (14 mmoles) of α-chloro-β-bromoethyl ethyl ether is added at 0°C in the course of 30 min to a solution of 5 g (7 mmoles) of compound II in 10 ml of acetone. The mixture is stirred for 2 h at 20°C and 1 h at 50°C. Acetone is evaporated, the residue is dissolved in 10-15 ml of benzene (at 60°C) and the benzene solution is chromatographed on a column with $SiO_2$. The first fraction contains 0.4 g (6%) of compound III, yellow crystals, mp 74-75°C (from hexane). Found, %: C 26.1, H 3.1, Br 31.4, S 3.0. $C_{22}H_{16}Br_2O_2S_5$. Calculated, %: C 26.4, H 3.2, Br 32.0, S 32.1. The second fraction contains 2 g (56%) of compound IVb, light-yellow crystals, mp 106-107°C (from hexane). Found, %: C 31.8, H 3.1, S 59.0. $C_7H_8OS_5$. Calculated, %: C 31.5, H 2.6, S 59.2.

TABLE 1. Spectral Characteristics of Compounds III-VI, VIII-XI

| Compound | IR spectrum, $cm^{-1}$ | PMR spectrum ($CDCl_3$), ppm |
|---|---|---|
| III | | 1,26 t (3H); 3,60 d (2H); 3,90 q (2H); 4,74 t (1H) |
| IVa | 1742 | 2,13 s (3H); 3,28 t (2H); 6,45 t (1H) |
| IVb | | 1,24 t (3H); 3,34 d (2H); 4,04 q (2H); 5,39 t (1H) |
| Va | 1739, 1678,<br>1635, 1604 | 2,15 s (3H); 3,30 t (2H); 6,48 t (1H) |
| VI | 1652, 1624 | 6,55 s |
| VIII | 1707 | 1,45 d (3H); 2,30 s (3H); 3,80 q (1H) |
| IX | | 1,34 d (3H); 1,65 s (3H); 3,36 s (3H); 3,78 q (1H) |
| X | | 2,03 s |
| XI | 1677 | 2,03 s |

TABLE 2. Characteristics of Compounds Ia,b, XII

| Compound | UV spectrum, $\lambda_{max}$, nm (log ε) in dioxane | Electrochemical oxidation potentials in benzonitrile, V | |
|---|---|---|---|
| | | $E_{ox1}$ | $E_{ox2}$ |
| Ia | 313 (4,15), 340 (4,16), 480 (2,55) | 0,73 | 0,99 |
| Ib | 312 (4,12), 344 (4,15), 490 (2,63) | 0,70 | 0,96 |
| XII | 321 (4,22), 346 (4,06), 490 (2,60) | 0,58* | 0,89 |

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*According to data in [10], $E_{ox1}$ = 0.532, $E_{ox2}$ = 0.773 V in acetonitrile, relative to SCE.

Acetoxyethylenedithio-1,3-dithiol-2-one (V). A mixture of 3 g (0.01 mole) of compound IVa, 3.6 g (12 mmoles) of mercuric acetate, 90 ml of chloroform, and 60 ml of acetic acid is boiled for 3 h; then HgS is filtered, the filtrate is diluted with water, and the chloroform layer is washed with water and evaporated. Yield, 1.9 g (70%), colorless crystals, mp 97-98°C. Found, %: S 47.9. $C_7H_6O_3S_4$. Calculated, %: S 48.1.

Vinylenedithio-1,3-dithiol-2-one (VI). A mixture of 2 g (7.5 mmoles) of compound (Va) and 0.6 g of p-toluenesulfonic acid in 100 ml of toluene is boiled for 15 h. It is then filtered, the filtrate is washed with water and a $NaHCO_3$ solution, and evaporated. The residue is purified by column chromatographs ($SiO_2$, eluent benzene). The first fraction is collected. Yield, 0.6 g (40%). Found, %: S 61.4. $C_5H_2OS_4$. Calculated, %: S 62.2.

bis(Vinylenedithio)tetrathiafulvalene (Ia). A 1 g portion (5 mmoles) of compound VI in 3.7 ml (25 mmoles) of thiethyl phosphate is heated at 120-130°C for 1 h. When cool, 0.7 g of red crystals are obtained, which are recrystallized from 110 ml of pyridine. Yield, 0.4 g (43%), dec. > 200°C. Found, %: C 31.2, H 7.0, S 67.0. $C_{10}H_4S_8$. Calculated, %: C 31.5, H 1.0, S 67.4.

4,5-(1,2-Dimethyl-1-methoxyethylenedithio)-1,3-dithiole-2-thione (IX) and 4,5-bis(1-Methyl-2-oxopropylthio)-1,3-dithiole-2-thione (VIII). A 12 ml portion of 0.01 N sodium methylate is added in an argon atmosphere in the course of 1 h to 4.45 g (12 mmoles) of compound VII in 80 ml of methanol. A 1.3 ml portion (12 mmoles) of 3-chloro-2-butanone is added, and the mixture is stirred for another 2 h and then acidified by HCl. Yield 0.3 g of yellow crystals of compound VIII, mp 86-87°C (from hexane). Found, %: S 51.8. $C_{11}H_{14}S_5$. Calculated, %: S 52.2. After the separation of compound VIII, the filtrate is diluted with water and the mixture is extracted by ether. The ether solution is washed with a $NaHCO_3$ solution and water, evaporated, and the residue is recrystallized from methanol. Yield, 2.4 g (71%) of compound IX, mp 108-110°C. Found, %: S 56.5. $C_8H_{10}S_5$. Calculated, %: S 56.7.

Dimethylvinylenedithio-1,3-dithiole-2-thione (X). A mixture of 2.4 g (8.5 mmoles) of compound IX and 1.4 g (8.5 mmoles) of p-toluenesulfonic acid in 50 ml of toluene is boiled for 3 h. Compound X was isolated from the reaction mixture in a similar way as compound VI. Yield, 0.74 g (35%), mp 124-125°C (from methanol). Found, %: S 63.5. $C_7H_6S_5$. Calculated, %: S 64.0.

Dimethylvinylenedithio-1,3-dithiol-2-one (XI) was obtained in a yield of 80% in a similar way as compound Va. Colorless crystals, mp 120-122°C. Found, %: S 54.3. $C_7H_6OS_4$. Calculated, %: S 54.7.

bis(Dimethylvinylenedithio)tetrathiafulvalene (Ib) was obtained in a similar way as Ia. Yield 75%, yellow crystals (from pyridine), mp > 230°C (dec). Found, %: C 38.3, H 2.6, H 58.9. $C_{14}H_{12}S_8$. Calculated, %: C 38.5, H 2.8, S 58.7.

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# 5-SUBSTITUTED 2-METHYL- AND 2-METHYLENEINDOLINES

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A method for the synthesis of 5-substituted 1,3,3-trimethyl-2-methyleneindolines has been developed, in which the substituents are introduced into the benzene ring of 1,2,3,3-tetramethylindolines, followed by oxidation.

1,3,3-Trimethyl-2-methyleneindoline (the "Fischer base") and its quaternary salts are starting materials for the synthesis of dyes [1-4]. Therefore derivatives of this compound, including substituted derivatives in the benzene ring, are also of considerable interest. The latter compounds are usually obtained from the corresponding hydrazones by the Fischer reaction [2, 3], or by exhaustive methylation of substituted indoles [3, 4]. It appeared to us desirable to use a method which is employed primarily for the synthesis of substituted indoles, i.e., to carry out the reaction in the benzene ring of indoline, followed by oxidation [5, 6].

1,2,3,3-Tetramethylindoline (I) was obtained by catalytic hydrogenation of a technical grade Fischer base. For the synthesis of 5-bromo-, 5-formyl-, 5-dichlorophosphinyltetramethylindolines (II-IV) from compound I, we used electrophilic substitution reactions described for N,N-dimethylaniline [7-9].

In the thiocyanation of indoline I, instead of the expected 5-thiocyanato-1,2,3,3-tetramethylindoline, disulfide V was obtained, which possibly formed as the result of thermal decomposition of the expected thiocyanate during distillation. We should note that not all electrophilic substitution reactions which proceed smoothly with dimethylaniline, proceed so successfully with indoline I. Thus, we were unable to carry out the benzoylation of compound I, although a similar reaction with dimethylaniline is classical [10].

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