

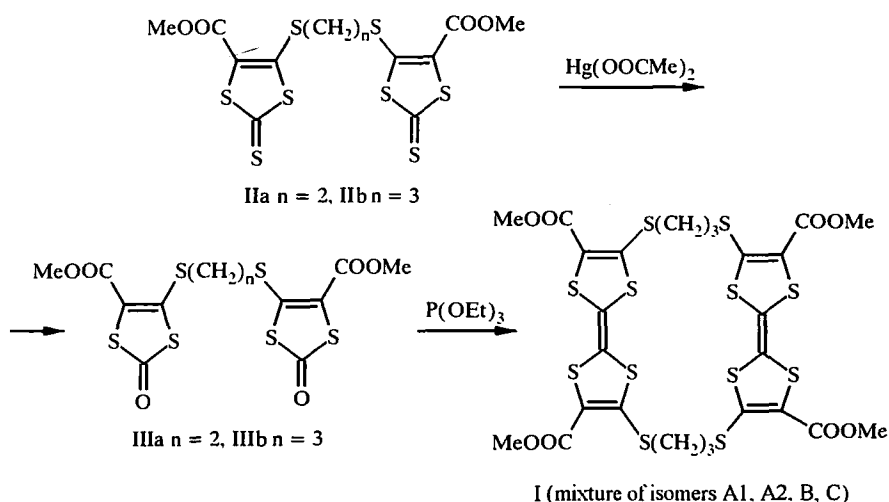
PREPARATION OF TWO STEREOISOMERS OF THE MACROCYCLIC ELECTRON DONOR TETRAMETHOXYCARBONYL[5.5]- TETRATHIAFULVALENOPHANE WITH BRIDGES CONTAINING TWO SULFUR ATOMS

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Isomers of a macrocycle containing two tetrathiafulvalene structural units joined by propylenedithio bridges are prepared. The electrochemical oxidation potentials are determined. Possible conformations of tetramethoxycarbonyl[5.5]tetrathiafulvalenophane are analyzed using the AM1 method.

The unusual electron-donating properties of tetrathiafulvalenes that enable them to undergo redox reactions have stimulated during the last 20 years research on organic conductors and superconductors [1-6]. The electronic properties of charge-transfer complexes of tetrathiafulvalenes with electron-acceptors have also been extensively studied. Investigations of macrocycles containing tetrathiafulvalenes [7] were started in 1980 with the publication of the synthesis of the first tetrathiafulvalenoparacyclophanes and tetrathiafulvalenophanes [8, 9]. Recently several new derivatives of tetrathiafulvalenoparacyclophanes and tetrathiafulvalenophanes containing two and more tetrathiafulvalene structural units [10-17], catenanes [17, 18], crown ethers [19], oligomeric macrocyclic tetrathiafulvalenes [20], and tetrathiafulvalenes with a cage structure [21, 22] have been prepared.

We used readily available derivatives of a 1,3-dithiol-2-thione, namely 4-mercapto-5-methoxycarbonyl-1,3-dithiol-2-thione [23], to prepare the macrocyclic tetrathiafulvalenes I according to the following scheme:



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TABLE 1. Physicochemical Characteristics of Synthesized Compounds

Compound	mp, °C	IR spectrum, v, cm ⁻¹	UV spectrum, λ_{max} , nm (log ϵ) (CHCl ₃)	PMR spectrum, δ , ppm (CDCl ₃)	Yield, %
IIIa	105-106	1698, 1650 1241, 1183 1097, 1004	280 sh (2.94) 330 (3.23)	3.24 (4H, t, SCH ₂) 3.80 (6H, s, OCH ₃)	57
IIIb	100-101	1696, 1658 1610, 1258 1090	280 sh (3.00) 323 (3.28)	2.1 (2H, q, CH ₂) 3.08 (4H, t, SCH ₂) 3.80 (6H, s, OCH ₃)	62
I (<i>R_f</i> 0.58)	112-117	1703, 1665 1487, 1261 1193, 1089	309 (4.55) 439 (3.58)	2.15 (4H, q, CH ₂) 3.08 (8H, t, SCH ₂) 3.74 (6H, s, OCH ₃) 3.76 (6H, s, OCH ₃)	13.8
I (<i>R_f</i> 0.18)	125-127	1705, 1659 1489, 1433 1259, 1089	285 (4.24) 323 (4.49) 435 (2.02)	2.15 (4H, q, CH ₂) 3.08 (8H, t, SCH ₂) 3.76 (12H, s, OCH ₃)	24.6

Boiling 4,4'-(alkylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-thiones) (IIa,b) with mercury acetate in a mixture of CHCl₃ and glacial acetic acid produce 4,4'-(alkylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-ones) (IIIa,b). Heating dione IIIb with triethylphosphite at 100°C in toluene gives the cyclic tetrathiafulvalenes I as a mixture of several stereoisomers A1, A2, B, and C (Fig. 1) and oligomeric products. The mixture is difficult to separate owing to photochemical activity. We isolated two fractions with *R_f* 0.58 and 0.18 using column chromatography on silica gel (CHCl₃ eluent). The fractions contain isomers of I with different physical and chemical properties.

The spectral properties and physical constants of the prepared compounds are given in Table 1.

The isomers have similar IR spectra. However, the PMR spectra are different. The PMR spectra of the isomer with *R_f* 0.18 has one singlet for the methoxycarbonyl protons whereas those of the isomer with *R_f* 0.58 has two singlets corresponding to protons of the different methoxycarbonyl groups.

The electronic spectra of the isolated compounds I are quite similar. However the extinction coefficients of the long-wavelength absorption bands differ significantly. Quantum-chemical calculations for the two *cis-cis* (A1 and A2), *cis-trans* (B), and *trans-trans* isomers (C) were performed by ZINDO method in order to study the nature

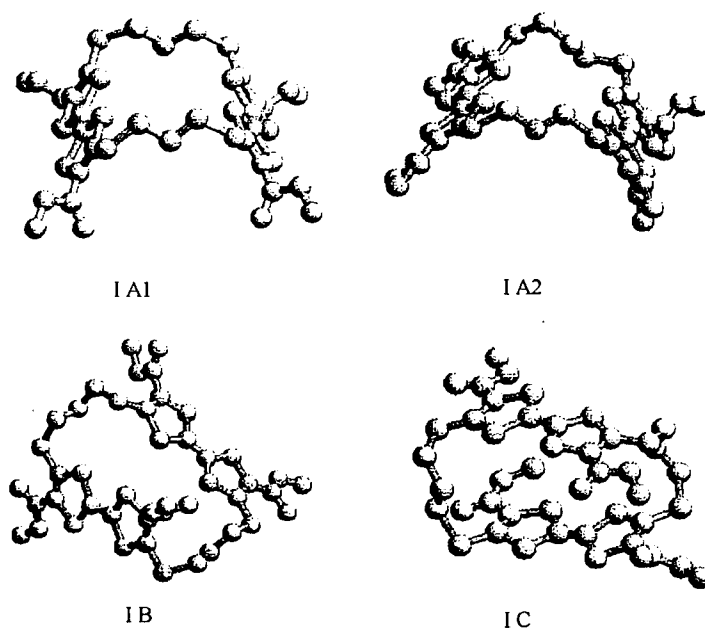


Fig. 1. Calculated possible conformations of tetramethoxycarbonyl[5.5]tetrathiafulvalenophane I.

of the UV absorption (Fig. 1). The calculated energies of these compounds are relatively close. However, it is energetically improbable that one isomer converts into another (with the exception of the $A1 \rightarrow A2$ and $A1 \leftarrow A2$ conversions). The calculated UV spectra reproduce well the observed second absorption band at 310-325 nm, which contains several electronic transitions, including HOMO \rightarrow LUMO. All orbitals involved in these transitions are localized mainly on the fulvalene moieties. A comparatively weak absorption band at 435 nm ($\epsilon \sim 3,800$) is observed in the experimental spectra of isomers I. Orbitals partially localized on the ester moieties are involved in these long-wavelength transitions (near 435 nm). Such a weak absorption band at ~ 430 nm is characteristic of a tetrathiafulvalene-acceptor system (in particular, of alkoxy carbonyl tetrathiafulvalenes) [24].

Cyclic voltammetry was used to determine the electrochemical oxidation potentials of the prepared tetrathiafulvalenes. Two reversible one-electron oxidation waves at $E^1 = 0.77$ and $E^2 = 1.1$ V are observed in the cyclic voltammogram of the mixture of isomers with R_f 0.58; at $E^1 = 0.78$ and $E^2 = 1.09$ V, for the isomer with R_f 0.18. The new tetrathiafulvalenes I are oxidized much more difficultly than analogous decarboxylated tetrathiafulvalenes [25].

The isomers have different photochemical properties. Red crystals of the isomer with R_f 0.18 turn colorless upon prolonged storage or solar illumination. Photodimerization to the corresponding photodimers probably occurs under these conditions [26, 27]. Solutions of the isomers of compound I in CHCl_3 also undergo photochemical conversions.

Attempts to prepare an ion-radical salt or a charge-transfer complex of tetrathiafulvalene I (R_f 0.58) with I_2 and tetracyanoquinodimethane were unsuccessful.

We believe that the isomer of I with R_f 0.58 is the *cis-trans* conformer (IB) and that the isomer with R_f 0.18 is most probably the *cis-cis* (IA2 or IA2) or the *trans-trans* (IC) conformer based on the differences in the PMR and electronic spectra and the comparison of the quantum-chemical calculations for dimethylmercaptodimethoxycarbonyltetrathiafulvalenes.

EXPERIMENTAL

IR spectra were measured on a Specord IR-75 (paraffin oil suspension for the range 600-2000 cm^{-1} and hexachlorobutadiene suspension for the range 2000-3600 cm^{-1}). PMR spectra were recorded on Bruker WH-90/DS and Tesla BS-487C instruments with working frequency 80 MHz and TMS internal standard. UV spectra were recorded on a Specord UV-Vis spectrophotometer. Electrochemical oxidation potentials were determined in CH_3CN using a NI-50 potentiostat with a glassy-carbon electrode (0.28 cm^2) versus a AgCl electrode in CH_3CN . The measurements were made at room temperature. The supporting electrolyte was tetrabutylammonium perchlorate (0.1 M). The potential scan rate was 200 mV/sec.

Quantum-chemical calculations were performed using the HYPERCHEM 4.0 programs. The molecular geometry was optimized using the AM1 method [28]. Electronic spectra were calculated using the ZINDO/S method taking into account CI (6 occupied and 6 vacant orbitals).

4,4'-(Alkylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-ones) (IIIa,b). A hot solution of II (0.99 mmol) in CHCl_3 (50 ml) is treated with a solution of $\text{Hg}(\text{OAc})_2$ (2.38 mmol) in glacial acetic acid (15 ml) and boiled for 5-10 h. The hot solution is filtered and washed on the filter with hot CHCl_3 . The CHCl_3 is evaporated. The solid is recrystallized from acetic acid. White needlelike crystals of IIIa,b are obtained. Compound IIIa. Found, %: C 32.45; H 2.24; S 43.39. $\text{C}_{12}\text{H}_{10}\text{O}_6\text{S}_6$. Calculated, %: C 32.57; H 2.28; S 43.46. Compound IIIb. Found, %: C 34.31; H 2.58; S 42.25. $\text{C}_{13}\text{H}_{12}\text{O}_6\text{S}_6$. Calculated, %: C 34.70; H 2.65; S 42.13.

Tetramethoxycarbonyl[5.5]tetrathiafulvalenophanes (I). Dithiolone IIIb (0.7 g, 1.5 mmol) is heated at 110°C for 30 min with triethylphosphite (3 ml) and cooled. Methanol (20 ml) is added. The solid is filtered off. Yield 0.35 g (54%) of a mixture of isomers of I, which is separated on a silica-gel column (CHCl_3 eluent). Fraction with R_f 0.58 and 0.18 are collected. An orange finely crystalline compound (0.09 g, R_f 0.58) and reddish-orange needlelike crystals (0.16 g, R_f 0.18) are obtained after evaporation and recrystallization from CH_3CN . Compound with R_f 0.58: found, %: S 45.22. $\text{C}_{26}\text{H}_{24}\text{O}_8\text{S}_{12}$. Calculated, %: S 45.30. Compound with R_f 0.18: found, %: S 45.20. $\text{C}_{26}\text{H}_{24}\text{O}_8\text{S}_{12}$. Calculated, %: S 45.30.

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