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Two Isomeric Triple-Layered Tetrathiafulvalenophanes: Syntheses, Structures, and Electrochemical Properties

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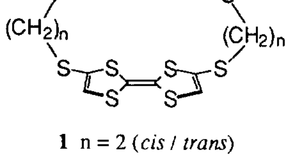
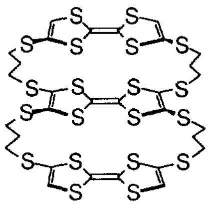
Abstract: The first triple-layered tetrathiafulvalenophanes of two different stacking types have been synthesized and characterized with cyclic voltammetry. In addition, the structure of an isomer of the parallel-oriented type was elucidated by an X-ray crystal analysis. © 1997 Elsevier Science Ltd.

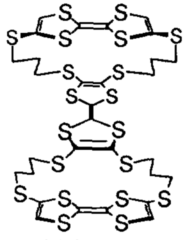
Much effort in the field of recent organic conductors has been devoted to the development of novel tetrathiafulvalenophanes in which the two TTF units are stacked by two or more bridges.[1-5] Such dimeric TTF phanes with different linkage modes have the advantage of controlling the stoichiometry and dimensionality of their conductive molecular complexes.[6] Among them, the simple double-bridged TTF phanes **1**[1] and **2**[2] have turned out to be the best electron donors forming highly conductive molecular complexes, though these compounds consist of a mixture of the *cis* and *trans* isomers as well as the *syn* and *anti* flexible conformers concerning the mutual positions of the TTF units. Thus, multi-layered TTF phanes are probably a more interesting system, because all the TTF units might take an interactive conformation. However, more than double-layered TTF phanes have been so far unknown, though macrocyclic cage molecules surrounded by three TTF bridges were recently reported.[7] Here we describe the syntheses, structures, and electrochemical properties of two isomeric triple-layered TTF phanes **3** and **4**.



1 n = 2 (*cis* / *trans*)
2 n = 3 (*cis* / *trans*)

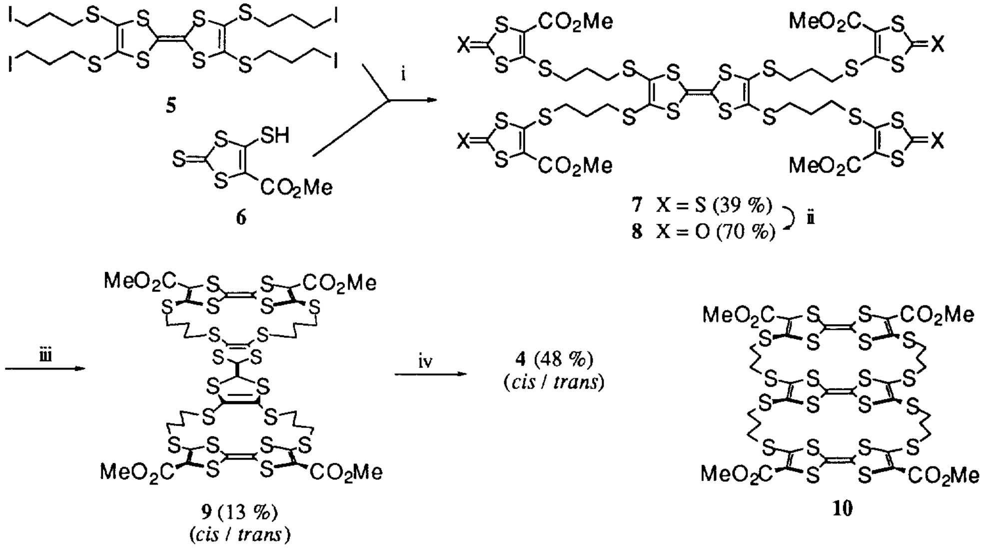


3 (*cis* / *trans*)

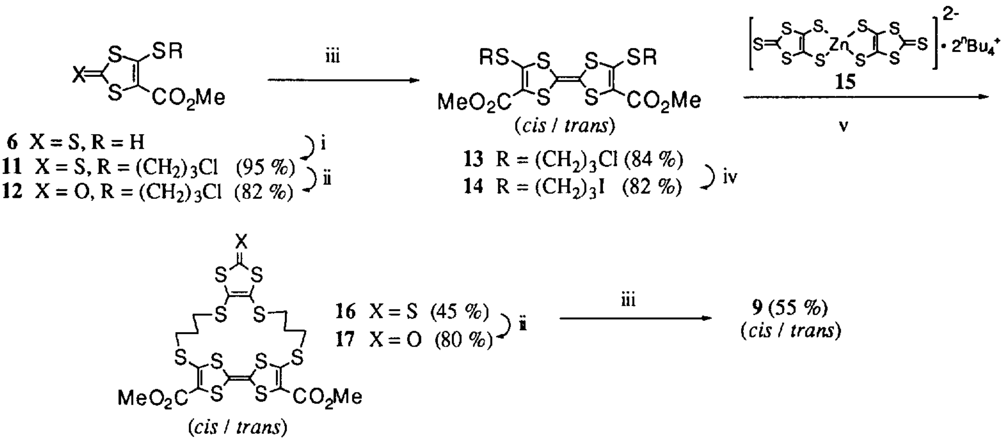


4 (*cis* / *trans*)

Some synthetic strategies of **3** and **4** may be proposed. As the simplest one, we first of all studied an approach via simultaneous construction of the two outer TTF units from the tetra-substituted TTF, as shown in Scheme 1. Thus reaction of 2,3,6,7-tetrakis(3-iodopropylthio)tetrathiafulvalene **5**[4] and 4-mercapto-5-methoxycarbonyl-1,3-dithiole-2-thione **6**[8] gave the TTF derivative **7**, which was then converted to the ketone **8** and subjected to the intramolecular double-coupling reaction induced by triethyl phosphite. Only one of the desired coupling products was obtained in 13% yield, which corresponded to the precursor **9** of the cross-oriented type. Another precursor **10** of the parallel-oriented type was not detected. The structural assignment of **9** was very difficult, because usual spectroscopic analyses were useless for distinguishing these two isomers. Eventually the structure of **9** was confirmed by its alternative synthesis, which involves the construction of the outer TTF units in the first stage and the inner TTF unit in the last stage, as shown in Scheme 2. Compound **9** thus obtained was decarboxylated with lithium bromide hydrate in dimethyl acetamide (DMA) to give **4** in 48 % yield.[9]

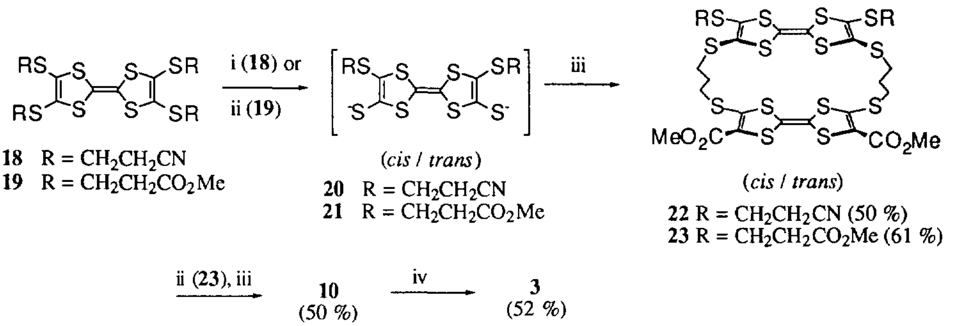


Scheme 1. Reagents and conditions: i, MeONa, MeOH-THF, reflux, overnight; ii, $Hg(OAc)_2$, $AcOH-CHCl_3$, rt, 2h; iii, $P(OEt)_3$, toluene, reflux, overnight; iv, $LiBr \cdot H_2O$, DMA, 160-165 °C, 10-15 min.



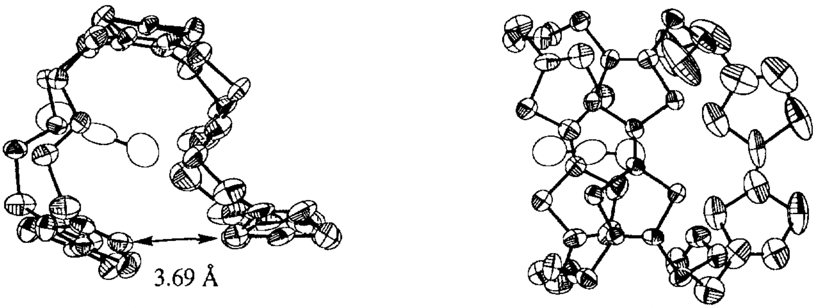
Scheme 2. Reagents and conditions: i, MeONa, MeOH-THF, $Br(CH_2)_3Cl$, reflux, overnight; ii, $Hg(OAc)_2$, $AcOH-CHCl_3$, rt, 2h; iii, $P(OEt)_3$, toluene, reflux, overnight; iv, NaI, acetone-dioxane, reflux, overnight; v, THF, reflux, 1 day.

The synthesis of the parallel-oriented TTF phane **3** was more complicated, because the three TTF units must have been stepwise constructed as shown in Scheme 3. This approach was attempted by using the strategy of a selective deprotection sequence of the protected TTF tetrathiolate developed recently by Becher.[10] Thus treatment of 2,3,6,7-tetrakis(2-cyanoethylthio) TTF **18**[11] with 2 equivalent cesium hydroxide monohydrate selectively generated the bisthiolate **20**, which was *in situ* coupled with the diiodide **14** to give the double-layered TTF phane **22** in 50 % yield. Because of its relatively low solubility, however, **22** was very hard to isolate from oligomeric byproducts and to use in the following reaction on a large scale preparation. Then, we examined another precursor with different protective groups, tetrakis(2-methoxycarbonylethylthio) TTF **19**:[12] the bisthiolate **21**, produced by selective treatment of **19** with 2 equivalent potassium t-butoxide, was similarly coupled with **14** to give the TTF phane **23** in 61 % yield. The better solubility of **23** than **22** allowed not only its ready purification but also the smooth second coupling reaction using the same technique to give **10** in 50% yield. Decarboxylation of **10** was accomplished by treatment of lithium bromide monohydrate in DMA to give **3** in 52 % yield.



Scheme 3. Reagents and conditions: i, $CsOH{\cdot}H_2O$ (2.1 equiv.), MeOH, DMF, rt, 1h; ii, t-BuOK (2.1 equiv.), DMF, rt, 1h; iii, **14**, DMF, rt, overnight; iv, $LiBr{\cdot}H_2O$, DMA, 160-165 °C, 10-15 min.

As indicated by multiplet peaks (δ 6.3-6.5) for the tetrathiafulvalenyl protons in the ^1H NMR spectra, **3** and **4** exist as an isomeric mixture of the *cis* and *trans* forms. However, recrystallization of **3** from carbon disulfide afforded orange prisms, whose NMR spectrum indicated a single isomer with high symmetry.[13] An X-ray crystal analysis clearly revealed that it is the isomer of all-*cis* form (Fig. 1).[14] The molecular structure consists of three relatively planar TTF moieties; one of the outer TTFs overlaps with the inner one, and between them is encapsulated a crystal solvent, carbon disulfide. The other outer TTF is located on the side of the overlap as if it makes a metacyclophane-like *anti*-conformation with the inner TTF. The closest non bonded S-S distance between the two outer TTFs is 3.69 Å, suggesting the presence of a weak interaction.



(a) (b)

Figure 1. Molecular structure of the prismatic isomer of **3**. (a) side view. (b) top view.

Compounds **3** and **4**, though both have the same redox components, demonstrated different electrochemical behavior: the cyclic voltammogram of **3** contains three redox waves ($E_{1/2}$: +0.50 (2e), +0.63 (1e), and +0.80 (3e) V), whereas that of **4** two redox waves ($E_{1/2}$: +0.56 (2e) and 0.70 (4e) V) (Fig. 2). Considering the redox potentials ($E_{1/2}$: +0.49 and +0.62 V) of 2,7(6)-bis(methylthio)TTF and ($E_{1/2}$: +0.57 and +0.68 V) of 2,3,6,7-tetrakis(methylthio)TTF for reference, it is reasonable to assign that the first two-electron wave of **3** comes from the oxidation of the two outer TTF units, the second one-electron wave from the oxidation of the inner TTF, and the third three-electron wave from the simultaneous second oxidations of all the TTFs. The much higher potential of the third wave than the second oxidation potentials of the reference compounds indicates large coulombic repulsion between the TTF units in the oxidation states. On the other hand, the first wave of **4** similarly comes from the oxidation of the outer TTF units, but unlike the case of **3**, the second wave remains unresolved and appears as coalescence of the remaining oxidations. This means that coulombic repulsion between the TTF units of **4** are very small.

The two triple-layered TTF phanes **3** and **4** with different electronic interactions are expected to form unique molecular complexes with distinct solid properties. Further study along this line is now under way.

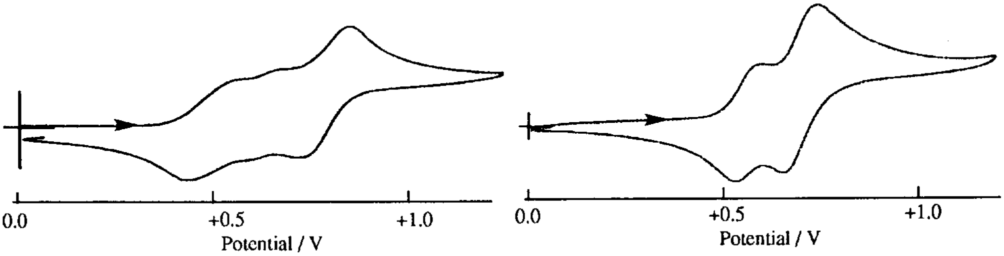


Figure 2. Cyclic voltammograms of **3** (left) and **4** (right) in DMF using an Ag/AgCl reference electrode.

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12. 2,3,6,7-Tetrakis(2-methoxycarbonylethylthio)tetrathiafulvalene **19** was prepared by reaction of the zincate **15** and methyl 3-bromopropionate followed by oxidation with mercury (II) diacetate and finally self-coupling reaction of the resulting 4,5-bis(2-methoxycarbonylethylthio)-1,3-dithiole-2-one promoted by triethyl phosphite. Use of the same protecting group for tetrathiafulvalenethiolate was described in the 13th Symposium on Fundamental Organic Chemistry (November 1996, Nagoya): Tanabe, J.; Izuoka, A.; Sugawara, T., Saito, T.; Y. Kawada. *Abstr.* p. 318 (3P61).
13. Analytical data of orange prismatic crystals of **3**: mp. 92.0-93.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (q, J=7.36 Hz, 8H, CH_2), 2.83 (t, J=7.36 Hz, 8H, CH_2), 2.91 (t, J=7.36 Hz, 8H, CH_2), 6.40 (s, 4H, CH); MS (EI, 70 eV) m/z 1024 (M^+); Anal. Calcd. for $C_{33}H_{28}S_{26}$ (including three carbon disulfides per one molecule as a crystal solvent): C, 31.50; H, 2.24 %. Found: C, 31.38; H, 2.35 %.
14. Crystal data for **3** including three carbon disulfide per molecule: $C_{33}H_{28}S_{26}$, F.W = 1258.14, monoclinic, $P2_1/n$, a = 15.299 (4), b = 20.711 (4), c = 16.881(1) Å, β = 98.499 (1) °, V = 5290 (1) Å^3, Z = 4, Dc = 1.58 gcm^{-3}, graphite-monochromated Cu-$K\alpha$ (1.5418 Å) radiation, crystal dimensions 0.62 x 0.23 x 0.20 mm, 2847 unique reflections, R = 0.069 (Rw 0.070).

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