Double-Bridged Tetrathiafulvalenophanes as Novel Electron Donors: Syntheses, Structures, and Properties of Three Structural Isomers

Kazuo Takimiya, Yoshio Aso, Fumio Ogura, and Tetsuo Otsubo*
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739

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Novel three isomeric tetrathiafulvalenophanes, of which the two TTF units are connected with double ethylenedithio spacers, have been synthesized and separated from one another. Their structures were determined by X-ray crystallographic analyses as well as ^{1}H-NMR analyses.

Multi-tetrathiafulvalene (TTF) compounds containing more than one TTF units have been perceived as an attractive system in view of their potential of providing conductive charge-transfer complexes not only with multi-dimensionality but also in partially ionized states.[1-4] Of a number of such compounds ever designed, tetrathiafulvalenophanes are of particular interest because of their layered structures showing through-space interactions. Staab *et al.* reported [2.2]- and [3.3]-tetrathiafulvalenophanes as the first TTF phanes,[3] and Robert *et al.* recently reported another TTF phanes with double trimethylenedithio spacers.[4] For such doubly bridged TTF phanes, there might be some structural and stereo-isomers, which provide different transannular electronic interaction. Staab *et al.* indicated the *cis-cis* configuration for the [2.2]tetrathiafulvalenophane on the basis of an X-ray structural analysis,[3] but its detailed structure as well as the existence of the other isomers has not been reported. We have studied the structural chemistry of novel tetrathiafulvalenophane (**1**), of which the two TTF units are connected with double ethylenedithio spacers, and found that it consists of a mixture of three structural isomers. In this paper we report the syntheses, characterizations and some properties of three isomers **1a-c**.

The syntheses of **1a-c** were carried out as shown in Scheme. The key starting material **2** was prepared according to the method reported by Cava *et al.*[2] and was converted into the corresponding ketone **3** on treatment with mercuric acetate in acetic acid-chloroform at room temperature. Intermolecular coupling reaction of **3** was promoted by trimethylphosphite in refluxing toluene to afford an isomeric mixture of tetramethoxycarbonyl TTF phanes **4** as well as higher oligomers. However, it was troublesome to separate each isomer at this stage. Thus **4** was decarboxylated to **1** without precise purification. The decarboxylation products (**1**) were first purified by column chromatography with carbon disulfide and then subjected to elaborate fractional crystallization. Treatment with carbon disulfide afforded the following three fractions: sparingly soluble yellow solid, orange prisms, and fairly soluble orange solid. The first yellow solid was further recrystallized from chlorobenzene to give yellow plates, which were characterized as the *cis-cis* structural isomer (**1a**) by an X-ray crystallographic analysis (Figure 1).[5] The TTF moieties are almost planar and take a typical step-by-step *anti*-conformation reminiscent of [2.2]metacyclophane. The second orange prisms were also determined on the basis of an X-ray structural analysis to be the *trans-trans* isomer (**1c**) (Figure 2).[6] The two TTF axes cross each other, and the transannular distance between the planar TTF moieties is approximately 3.9 Å. In agreement with this structure, the ^{1}H-NMR spectrum of **1c** showed only two singlets assigned to fulvalenic protons and methylene protons. The third fairly soluble solid upon further recrystallization from carbon disulfide-hexane gave orange fine needles, which were, however, not suitable for an X-ray analysis. The structure of **1b** was then determined by its ^{1}H-NMR spectrum, which showed two fulvalenic singlets and an AA'BB' multiplet of ethylenedithio parts, clearly indicating the *cis-trans* configuration.[7]

Despite of the successful separation and purification of **1a-c**, gradual isomerization was observed to occur in solution. A ^{1}H-NMR study demonstrated that pure **1b** or **1c** in carbon disulfide-acetone-d_6 turned into a complete mixture of **1b** and **1c** together

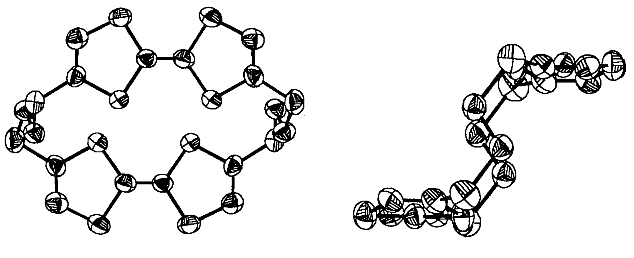
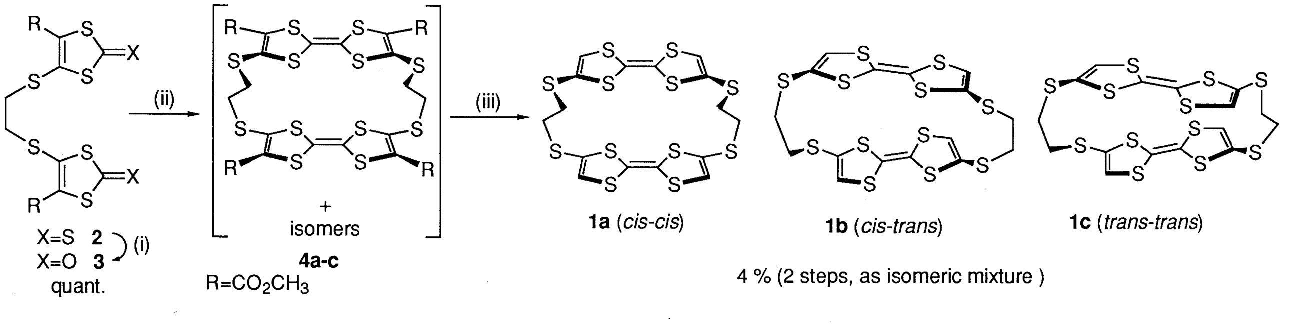


Figure 1. ORTEP drawing of **1a**.



(i) Hg(OAc)$_2$, CHCl$_3$/AcOH, rt, overnight. (ii) P(OCH$_3$), toluene, 110 °C, 18 h. (iii) LiBr•H$_2$O, HMPA, 130 °C, 5 min.

Scheme.

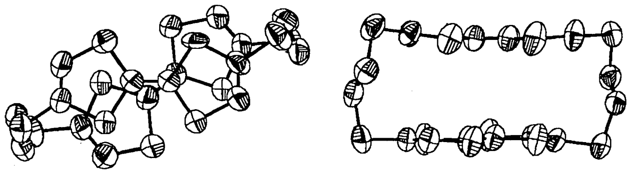


Figure 2. ORTEP drawing of **1c**.

with deposition of the insoluble **1a** in the period of one week. The isomerization is speculated to be promoted by the presence of trace amounts of acidic media as mentioned previously.[8] In fact, ^{1}H-NMR spectra of **1b** and **1c** measured in the presence of pyridine or triethylamine showed no isomerization.

The transannular electronic interactions of **1b** and **1c** were studied by cyclic voltammetry, though the limited solubility of **1a** prevented a study of its accurate electrochemical behaviors. The cyclic voltammogram of **1b** measured in freshly purified benzonitrile[9] showed two reversible one-electron redox waves ($E_{1/2}$: +0.41 and +0.56 V vs. Ag/AgCl) and one quasi-reversible two-electron redox wave ($E_{1/2}$: +0.83 V). On comparing these values with those ($E_{1/2}$: +0.45 and +0.80 V) of 4,4'(5')-bis(methylthio)tetrathiafulvalene as a reference, it is reasonable to conclude that the split of the first redox process indicates the existence of a marked transannular electronic interaction between two TTF moieties. The cyclic voltammogram of **1c** was identical to that of **1b**, indicating no marked difference in transannular interaction between the structural isomers **1b** and **1c**.

Preliminary electrochemical crystallization with **1b** in chlorobenzene containing tetrabutylammonium perchlorate at 80 °C afforded a radical cation salt as black thin plates, which had a conductivity of 0.16 Scm^{-1} at room temperature. This result proved that the present tetrathiafulvalenophanes have a potential as electron donors forming conductive charge-transfer salts. The X-ray crystallographic analysis of the radical cation salt as well as further investigation to obtain other CT salts are now under way.

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References and Notes

1 For a recent review, see M. Adam and K. Müllen, *Adv. Mater.*, **6**, 439 (1994).

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5 Crystal data for **1a**: $C_{16}H_{12}S_{12}$, FW=589.04, orthorhombic *Pbca*, a=22.446(3), b=12.290(2), c=8.310(2) Å, V=2292.5(6) Å^3 , Z=4, D_c=1.707, graphite-monochromated Cu-$K\alpha$ radiation, crystal dimensions 0.30 × 0.28 × 0.05 mm, unique reflections 1587 ($|Fo| \geq 1.0\sigma(|Fo|)$). The final R factor was 7.29%.

6 Crystal data for **1c**: $C_{16}H_{12}S_{12}$, FW=589.04, monoclinic $P2/m$, a=17.173(2), b=7.977(1), c=17.719(3) Å, β= 106.21(1) °, V=2330.8(6) Å^3, Z=4, D_c=1.679, graphite-monochromated Cu-$K\alpha$ radiation, crystal dimensions 0.44 × 0.33 × 0.07 mm, unique reflections 2716 ($|Fo| \geq 3.0\sigma(|Fo|)$). The final R factor was 7.13%.

7 All new compounds gave satisfactory elemental analyses. Selective spectral data of **3**: colorless needles from chloroform-hexane; mp 168 °C; MS *m/z* 442 (M$^+$); IR (KBr) 1698 (esteric C=O), 1651 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 3.29 (s, 4H, CH_2) and 3.85 (s, 6H, CH_3). **1a**: yellow plates from chlorobenzene; mp 258-260 °C (decomp.); MS *m/z* 588 (M$^+$); IR (KBr) 3071 and 769 cm^{-1}. **1b**: orange fine needles from carbon disulfide-hexane; mp 223-224 °C ; MS *m/z* 588 (M$^+$); ^{1}H-NMR (CS_2-acetone-d_6) δ 2.87-3.01 (AA'BB' multiplet, 8H, CH_2), 6.45 (s, 2H, CH) and 6.50 (s, 2H, CH). **1c**: orange prisms from carbon disulfide; mp 245-255 °C (decomp.); MS *m/z* 588 (M$^+$); ^{1}H-NMR (CS_2-acetone-d_6) δ 2.92 (s, 8H, CH_2) and 6.55 (s, 4H, CH).

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9 A separate study confirmed that freshly purified benzonitrile did not promote the isomerization.