Synthesis, Structures, and Properties of a Series of Double-Bridged Tetrathiafulvalenophanes as Novel Electron Donors for Conductive Radical Cation Salts†

Kazuo Takimiya, Akinobu Oharuda, Yoshio Aso,‡ Fumio Ogura,§ and
Tetsuo Otsubo*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 739-8527, Japan

Received March 4, 2000. Revised Manuscript Received May 18, 2000

A series of double-bridged tetrathiafulvalenophanes (TTF phanes) with different alkylenedithio (methylenedithio, ethylenedithio, trimethylenedithio, and tetramethylenedithio) bridges was synthesized as a model of interactive dimeric TTFs. They were found to exist as a mixture of three stereoisomers of cis/cis, cis/trans, and trans/trans (twist) types, which were separated by fractional crystallization, and the unique stacking structures of the three isomers were elucidated by X-ray crystallographic analyses and NMR spectroscopy. Their cyclic voltammograms demonstrated multi-redox waves split by intramolecular through-space electronic interactions depending on the bridge lengths. The principal redox-active species was estimated to be of the trans/trans (eclipse) type in the low oxidation states, which was not detected in the neutral state, and to be of the cis/cis type in the high oxidation states. Electrocrystallization gave various radical cation salts, which were mostly semiconductive and characterized by segregated stacking type of crystal structures exclusively including the cationic species of the trans/trans (eclipse) type. An exception to this was the I_3^- salt of the ethylenedithio-bridged TTF phane, which appeared in dimorphorous shapes of plate and needle, and both included the cationic species of the cis/cis type. The plate crystal showed a very high room-temperature conductivity of 28 S cm^{-1} with metallic temperature behavior, which turned out to be induced by a network of marked intermolecular S···S contacts of the donor species.

Introduction

It has been widely recognized that the conductive properties of molecular complexes deeply depend on their crystal structures and electronic states, i.e., interactive stacking structures and mixed valence states of the component donor or acceptor species.[1] The artificial achievement of these requirements is still accepted to be very formidable and rather serendipitous. It is thus ideal and desirable, if possible, to control the structures and properties of molecular complexes based on the design of the component species. One of such trials in the molecular modifications of tetrathiafulvalene (TTF, Chart 1) has been done with dimeric TTFs, in which two TTF moieties are connected by one or more spacer linkages.[2] This approach is based on the idea that an electronic interaction between the two TTF moieties in a through-space or through-bond manner may afford the chance of controlling the crystal structures and electronic states of the derived complexes. Although a variety of dimeric TTFs have been studied, most of them heretofore studied are of the simple single linkage type (**1**) and double linkage type (**2**), which do not necessarily ensure close interaction between the two TTF moieties. More intriguing but less studied is the cyclophane type, in which a marked through-space interaction is forced by close fixation of the two TTF moieties. As the first example, double-bridged TTF phanes (**3**) were reported by Staab and co-workers in 1980,[3] and since then some related TTF phanes have been developed.[4] We have also studied sophisticated quadruple-bridged TTF phanes (**4**[5] and **5**[6,7]) with different stacking modes. However, neither metallic nor highly conductive complexes from these have been reported. From our study we have considered that the quadruple-bridged TTF phanes are too rigid to adopt a suitable interactive structure between the TTF units and expected that more flexible double-bridged TTF phanes (**6**−**9**) instead could behave

---

† Dedicated to Professor Virgil Boekelheide on the occasion of his 80th birthday.

* Corresponding author. Fax: +81-824-22-7191. E-mail: otsubo@hiroshima-u.ac.jp.

‡ Present address: Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812-8581, Japan.

§ Present address: Department of Industrial Chemistry, Faculty of Engineering, Kinki University, Higashi-Hiroshima 739-2116, Japan.

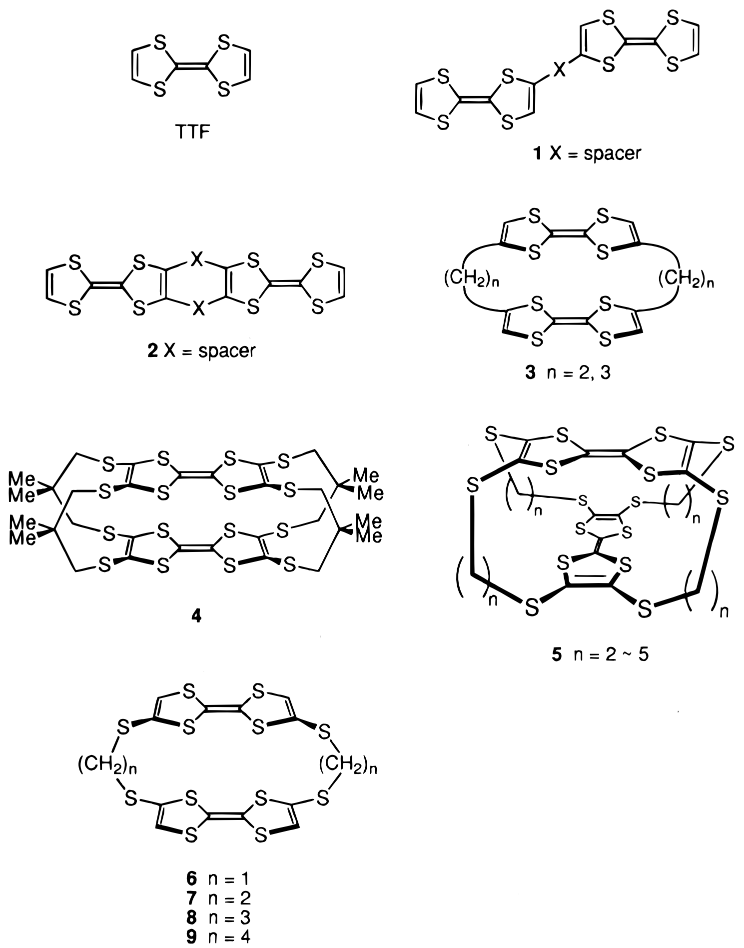
(1) (a) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79−86. (b) Saito, G.; Ferraris, J. P. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2141−2145. (c) Cowan, D. O.; Kini, A.; Chiang, L.-Y.; Lerstrup, K.; Talham, D. R.; Poehler, T. O.; Bloch, A. N. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 1741−1766. (d) Delhaes, P. *Mol. Cryst. Liq. Cryst.* **1983**, *96*, 229−261. (e) Bryce, M. R.; Murphy, L. C. *Nature* **1984**, *309*, 118−126. (f) Yamada, J.; Nishikawa, H.; Kikuchi, K. *J. Mater. Chem.* **1999**, *9*, 617−628.

(2) For recent reviews, see (a) Adam, M.; Müllen, K. *Adv. Mater* **1994**, *6*, 439−459. (b) Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater.* **1996**, *8*, 203-211. (c) Becher, J.; Lau, J.; Mørk, P. In *Electronic Materials: the Oligomer Approach*; Müllen, K.; Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; 198−234.

(3) Ippen, J.; Tao-pen, C.; Starker, B.; Schweitzer, D.; Staab, H. A *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 67−69.

10.1021/cm000117m CCC: $19.00

Chart 1


TTF

1 X = spacer

2 X = spacer

3 n = 2, 3

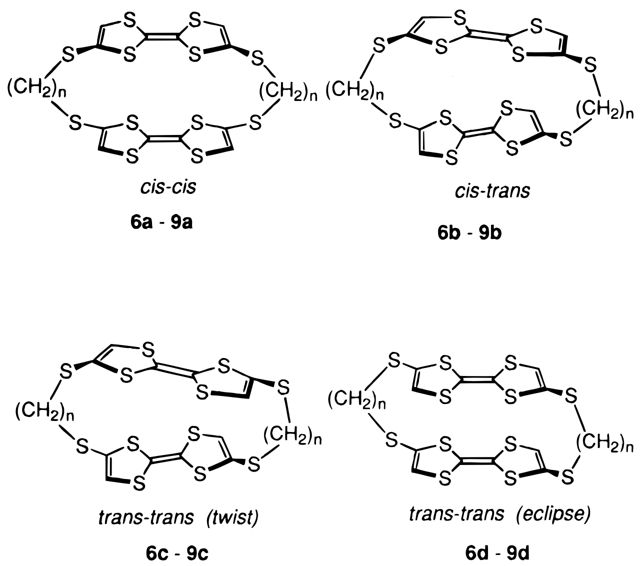
4

5 n = 2 ~ 5

6 n = 1
7 n = 2
8 n = 3
9 n = 4

as an ideal model for interactive TTF dimers. Such double-bridged TTF phanes have a possibility of many stereoisomers, principally resulting from cis and trans substitution modes (Chart 2). This might make the system complicated, but it allows a comprehensive study on the through-space electronic interactions of various stacking types of TTF dimers. Thus main interests in this study are to know (1) whether they can form highly conductive complexes, (2) what type of stereoisomers can exist in the neutral and cationic states or in the conductive complexes, and (3) how the bridge lengths or stacking distances of the TTF phanes can affect the properties of themselves and their complexes. In this paper we would like to describe the detailed synthesis, unique molecular structures, and properties of a series of the double-bridged TTF phanes (**6**−**9**) with different bridging lengths.[8] In addition, the conductive properties and crystal structures of their radical cation salts are also discussed in connection with the molecular structures.

Chart 2


cis-cis
6a - **9a**

cis-trans
6b - **9b**

trans-trans (twist)
6c - **9c**

trans-trans (eclipse)
6d - **9d**

---

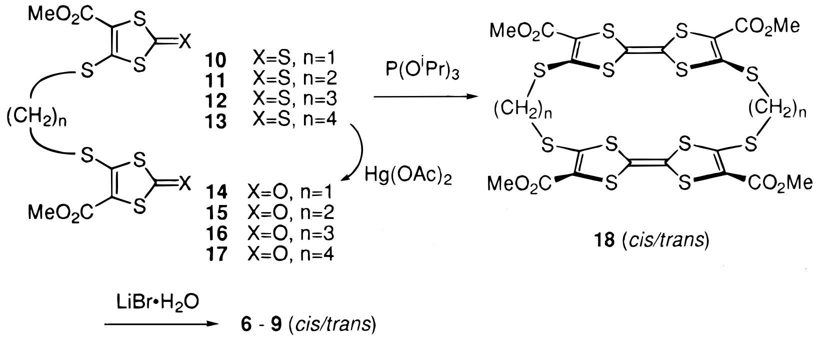
(4) (a) Badri, M.; Majoral, J. P.; Gonce, F.; Caminade, A.-M.; Salle, M.; Gorgues, A. *Tetrahedron Lett.* **1990**, *31*, 6343−6346. (b) Bertho-Thoraval, F.; Robert, A.; Souizi, A.; Boubekeur, K.; Batail, P. *J. Chem. Soc., Chem. Commun.* **1991**, 843−845. (c) Adam, M.; Enkelmann, V.; Räder, H.-J.; Röhrich, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 309−310. (d) Simonsen, K. B.; Thorup, N.; Becher, J. *Synthesis* **1997**, 1399−1404. (e) Nielsen, M. B.; Becher, J. *Liebig Ann. Chem.* **1997**, 2177−2187. (f) Becher, J.; Li, Z.-T.; Blanchard, P.; Svenstrup, N.; Lan, J.; Nielsen, M. B.; Leriche, P. *Pure & Appl. Chem.* **1997**, *69*, 465−470. (g) Batsanov, A. S.; John, D. E.; Bryce, M. R.; Howard, J. A. K. *Adv. Mater.* **1998**, *10*, 1360−1363. (h) Akutagawa, T.; Abe, Y.; Hasegawa, T.; Nakamura, T.; Inabe, T.; Sugiura, K.; Sakata, Y.; Christensen, C. A.; Lau, J.; Becher, J. *J. Mater. Chem.* **1999**, *9*, 2737−2742. (i) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11−23.

(5) Matsuo, K.; Takimiya, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1995**, 523−524.

(6) (a) Takimiya, K.; Shibata, Y.; Imamura, K.; Kashihara, A.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1995**, *36*, 5045−5048. (b) Takimiya, K.; Imamura, K.; Shibata, Y.; Aso, Y.; Ogura, F.; Otsubo, T. *J. Org. Chem.* **1997**, *62*, 5567−5574.

(7) The cross-overlapped TTF phanes (**5**) were independently studied by Sugawara's group: (a) Tanabe, J.; Kudo, T.; Okamoto, M.; Kawada, Y.; Ono, G.; Izuoka, A.; Sugawara, T. *Chem. Lett.* **1995**, 579−580. (b) Tanabe, J.; Ono, G.; Izuoka, A.; Sugawara, T.; Kudo, T.; Saito, T.; Okamoto, M.; Kawada, Y. *Mol. Cryst. Liq. Cryst.* **1997**, *296*, 61−76.

Scheme 1



Results and Discussion

Synthesis and Molecular Structures. The synthesis of a series of double-bridged TTF phanes (**6**−**9**) was carried out as shown in Scheme 1. The starting materials, 4,4-(alkylenedithio)bis(5-methoxycarbonyl-1,3-dithiole-2-thione)s (**10**−**13**), were readily prepared according to Cava's method[9] and converted with mercury acetate into the ketones (**14**−**17**) in almost quantitative yield. The self-coupling reactions of the ketones promoted by triisopropyl phosphite gave the tetrakis(methoxycarbonyl) TTF phanes (**18**), which existed as a mixture of the cis/trans isomers as expected, together with polymeric materials. Because of the low solubility of **18**, complete separation of each isomer at this stage was skipped, and the isomeric mixtures were decarboxylated with LiBr•H_2O to the desired double-bridged TTF phanes (**6**−**9**).

For these double-bridged TTF phanes, four isomers of cis/cis, cis/trans, trans/trans (twist), and trans/trans (eclipse) types are possible. However, in their ^{1}H NMR spectra, the fulvalenyl signals comprised a pair of singlets and two independent singlets, indicating the presence of three isomers. As each isomer has different solubility, they were separated by elaborate fractional crystallization and characterized to be the cis/cis, cis/trans, and trans/trans (twist) isomers by X-ray crystallographic analyses and ^{1}H NMR spectra. A typical separation procedure is as follows: treatment of the mixture of **7** with hot carbon disulfide led to rough separation to the following three fractions, an insoluble yellow solid, orange prisms from the recrystallization, and a fairly soluble orange solid from the mother liquor. The first yellow solid fraction was further recrystallized from chlorobenzene to give yellow plates, which were characterized as the cis/cis isomer (**7a**) by an X-ray crystallographic analysis (Figure 1). The TTF moieties are almost planar and take a step-by-step anti-conformation reminiscent of that of [2.2]metacyclophane. The second orange prismatic fraction was pure in itself and also determined on the basis of an X-ray structural analysis to be the trans/trans (twist) isomer (**7c**) (Figure 2). The two TTF moieties are almost planar and stacked with each other in a twisted manner, and the average through-space distance between them is approximately 3.9 Å. Further recrystallization of the third soluble solid fraction from carbon disulfide−hexane gave fine, orange needles, which were determined to be the cis/trans isomer (**7b**) by taking consideration of two kinds of fulvalenic singlets in its ^{1}H NMR spectrum. These stereoisomers are very stable in the solid state, but isomerize to one another in solution. Monitoring a freshly prepared solution of pure **7b** or **7c** in CS_2−acetone-d_6 on NMR spectroscopy indicated that the isomerization occurred gradually and was completed within 1 week, resulting in a mixture of **7a**, **7b**, and **7c** in the ratio of about 1:2:1. In addition, the isomerization turned out to be retarded by addition of pyridine or triethylamine, indicating that it is promoted by a trace of acidic media contained in solution.[10]

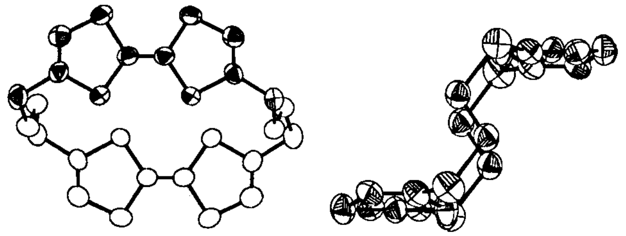


Figure 1. ORTEP drawing of **7a** (cis/cis): (left) top view and (right) side view.

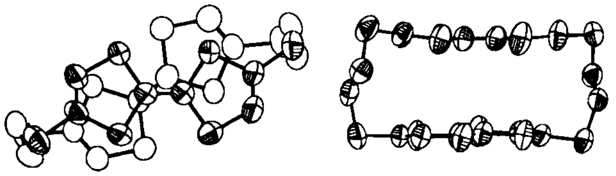


Figure 2. ORTEP drawing of **7c** (trans/trans): (left) top view and (right) side view.

All the three isomers of **8** with the longer bridge chains were also isolated, and only the trans/trans (twist) isomer **8c** gave a good orange crystal for an X-ray analysis. The molecular structure is quite unlike that of **7c**, in that the two TTF moieties are no longer stacked with each other. In the separation of **9** with the longest bridge chains, the cis/cis isomer **9a** and the trans/trans (twist) isomer **9c** were isolated and characterized by X-ray analyses; both structures have a cavity (about 7.0 Å inside distance) between the two TTF moieties large enough to include one carbon disulfide and chloroform, respectively, from the recrystallization solvents.

By recrystallization of **6** with the shortest methylene chains, the cis/cis and cis/trans isomers **6a** and **6b** were

---

(8) A preliminary study of the two TTF phanes (**7** and **8**) as potential electron donors was reported in the following communications: (a) Takimiya, K.; Aso, Y.; Ogura, F.; Otsubo, T. *Chem. Lett.* **1995**, 735−736. (b) Takimiya, K.; Aso, Y.; Otsubo, T. *Synth. Met.* **1997**, *86*, 1891−1892.

(9) Sudmale, I. V.; Tormos, G. V.; Khodorkovsky, V. Y.; Edzina, A. S.; Neilands, O. J.; Cava, M. P. *J. Org. Chem.* **1993**, *58*, 1355−1358.

(10) Souizi, A.; Robert, A.; Batail, P.; Ouahab, L. *J. Org. Chem.* **1987**, *52*, 1610−1611.

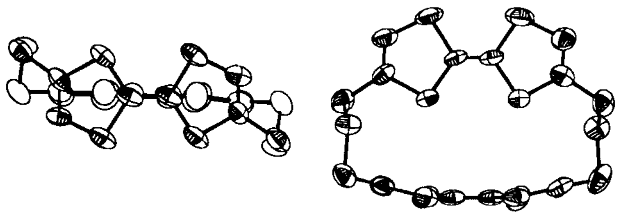


Figure 3. ORTEP drawing of **6b** (cis/trans): (left) top view and (right) side view. Only one of two crystallographically independent molecules is shown.

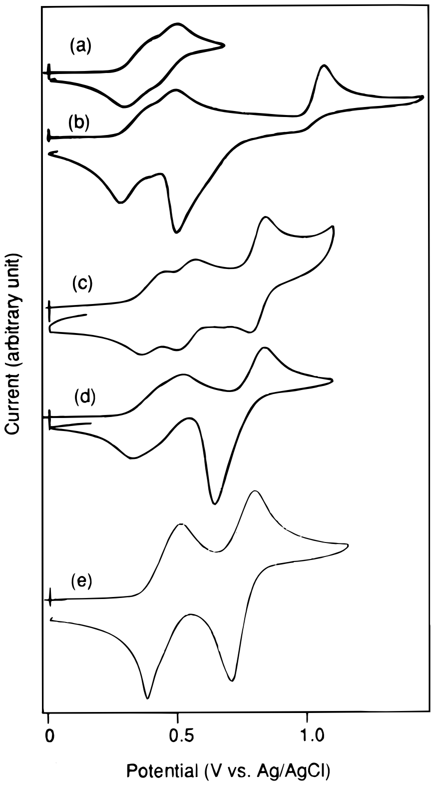


Figure 4. Cyclic voltammograms of (a) **6** (isomer mixture, 0−0.65 V scan), (b) **6** (isomer mixture, 0−1.5 V scan), (c) **7b** (cis/trans), (d) **8c** (trans/trans), and (e) **9c** (trans/trans).

Table 1. Half-Wave Oxidation Potentials of TTF Phanes[a]

compound	$E_{1/2}(1)$/V		$E_{1/2}(2)$/V
6	0.35 (1e)	0.48 (1e)	1.10[b]
7	0.41 (1e)	0.56 (1e)	0.83 (2e)
8	0.40 (1e)	0.50 (1e)	0.78 (2e)
9	0.45 (2e)		0.83 (2e)
bis(methylthio)TTF	0.45 (1e)		0.83 (1e)

[a] Cyclic voltammetry was measured at 100 mV sec^{-1} in benzonitrile containing 0.1 M $^{n}Bu_4NClO_4$ using an Ag/AgCl reference electrode and Pt working and counter electrodes. [b] Irreversible; the indicated value is of the anodic peak.

separated out. An X-ray crystallographic analysis of **6b** revealed that the *cis*-TTF moiety stands perpendicularly over the trans one, as shown in Figure 3. In addition, the *trans*-TTF moiety is deformed into a boat form, owing to the molecular strain.

Cyclic Voltammetry. Cyclic voltammetry affords important information about the electronic interactions of the TTF phanes. Figure 4 demonstrates different electrochemical behaviors of **6**−**9**, and Table 1 summarizes the half-wave oxidation potentials together with those of 2,6(7)-bis(methylthio)tetrathiafulvalene as a reference compound. The cyclic voltammogram of **9** shows only two degenerated two-electron redox waves, whose half-wave oxidation potentials are nearly the same as those of the reference compound. This indicates that, in accordance with the observation of the molecular structure of **9**, the two TTF moieties are too far apart to interact. In contrast, the cyclic voltammograms of **6**−**8** appreciably demonstrate a splitting in the first redox process, meaning that the mono- and dicationic species are differently influenced by the through-space electronic interaction of the two TTF moieties. The interaction is supposed to mainly involve two effects of charge delocalization and Coulombic repulsion: the former especially facilitates the initial oxidation. On the other hand, the latter retards the following oxidation. Thus the splitting is induced by the two opposing effects, and its magnitude depends on the bridge length. The involvement of the isomeric mixture in the splitting may be also conceivable but is excluded because no essential difference in the voltammograms using different isomers was observed. Considering this result as well as the previous report that the isomerization quickly occurs under voltammetric conditions,[11] we can speculate that only one isomer is favorably formed in the oxidation process. If through-space charge delocalization is benefited by large π-overlapping, one may assume that the principal redox active species in the low oxidation state is of the trans/trans (eclipse) type that is never detected in the neutral state. The actual existence of the trans/trans (eclipse) isomer was confirmed by X-ray crystallographic analyses of many radical cations salts of **6**−**8** (vide infra).

In contrast to the first ones, the second redox waves of **6**−**9** demonstrate no splitting, and the half-wave oxidation potentials except that of **6** are normal. This suggests that the redox active species is no longer interactive in the tri- and tetracationic states. A plausible explanation for this is that a conformational change of the initially formed, interactive trans/trans (eclipse) species to a noninteractive one presumably of the cis/cis type occurs to avoid further increasing Coulombic repulsion.[11] The unusual high potential (1.13 V) of **6** indicates that the high oxidation species, even though of the cis/cis type, suffers strong Coulombic repulsion. The disappearance of the corresponding reduction peak and the concomitant appearance of a new reduction peak at a very low potential (0.53 V) supports the instability of the high oxidation species and its ready conversion to a lower oxidation one (Figure 4b).

Radical Cation Salts. Electrocrystallization of **6**−**9** gave single crystals of their radical cation salts, as summarized in Table 2. No matter which donor isomer was used, the same radical cation salt was obtained, again supporting that ready isomerization takes place during electrolysis and the most favorable cation species predominately forms, as above suggested by cyclic voltammetry. The stoichiometry and conductivities of the thus obtained salts are apparently diverse but somewhat dependent on the donor species.

Although the methylenedithio-bridged TTF phane (**6**) complexed with many counterions, such as PF_6^-, AsF_6^-,

---

[11] Boubekeur, K.; Lenoir, C.; Batail, P.; Carlier, R.; Tallec, A.; Le Paillard, M.-P., Lorcy, D.; Robert, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1379−1381.

Table 2. Radical Cation Salts of Dimeric TTF Phanes

salt	appearance	D:A[a]	σ_{RT}/S cm^{-1}	remark	E_{act}/eV
6·PF_6	black plates	1:2[b]	5.3×10^{-4}		
6·AsF_6	black plates	1:2	4.6×10^{-2}	semiconductive	0.09
6·BF_4	brown needles	1:1	8.9×10^{-2} [d]		
6·ClO_4	black plates	2:3	1.1×10^{-2} [d]		
6·I_3	black plates	3:4	6.8×10^{-2}		
7·BF_4	black plates	3:4[b]	1.5	semiconductive	0.077
7·ClO_4	black plates	3:4[b]	2.0×10^{-1}	semiconductive	0.080
7·I_3	black plates	1:1.8 (1:2)[b]	28	metallic (T_{MI} 210 K)	
7·I_3	black needles	1:2[b]	5.8×10^{-7}		
8·PF_6	black plates	1:1[b]	2.1×10^{-2}	semiconductive	0.096
8·I_2Br	black plates	1:1[b]	3.0×10^{-3}	semiconductive	0.072
9·I_3	black plates	1:2	2.0×10^{-4}		

[a] Determined on the basis of elemental analysis unless otherwise stated. **6**·$(AsF_6)_2$: Anal. Calcd for $C_{14}H_8S_{12}As_2F_{12}$: C, 17.91; H, 0.86. Found: C, 18.05; H, 1.05. **6**·BF_4: Anal. Calcd for $C_{14}H_8S_{12}B_1F_4$: C, 25.96; H, 1.24. Found: C, 26.18; H, 1.23. $(\mathbf{6})_2$·$(ClO_4)_3$: Anal. Calcd for $C_{28}H_{16}S_{24}Cl_3O_{12}$: C, 23.86; H, 1.14. Found: C, 23.59; H, 1.31. $(\mathbf{6})_3$·$(I_3)_4$: Anal. Calcd for $C_{42}H_{24}S_{36}I_{12}$: C, 15.74; H, 0.75. Found: C, 16.03; H, 0.77. **7**·$(I_3)_{1.8}$: Anal. Calcd for $C_{16}H_{12}S_{12}I_{5.4}$: C, 15.08; H, 0.95. Found: C, 15.15; H, 0.99. **9**·$(I_3)_2$: Anal. Calcd for $C_{20}H_{20}S_{12}I_6$: C, 17.09; H, 1.43. Found: C, 17.58; H, 1.52. [b] Determined by X-ray crystallographic analysis. [c] Measured on a single crystal with a four-probe method unless otherwise stated. [d] Measured on a compressed pellet with a four-probe method.

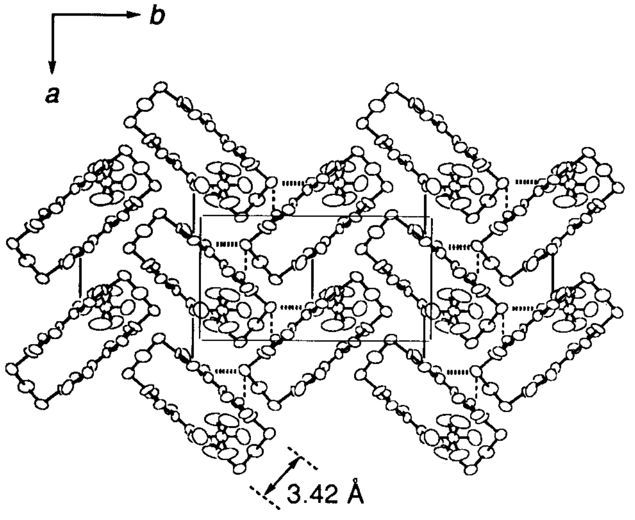


Figure 5. Crystal structure of **6**·PF_6 (*c*-axis projection). Short S···S distances: (solid line) 3.67 Å; (dashed line) 3.79 Å; (bold dashed line) 3.51 Å.

BF_4^-, ClO_4^-, and I_3^-, all the salts formed showed relatively low conductivities on the order of 10^{-2} S cm^{-1} or below at room temperature. Among them, the PF_6^- salt gave a good single crystal for an X-ray analysis, which revealed a herringbone stacking structure of the trans/trans (eclipse) dimeric molecules (Figure 5). The TTF moieties are planar and the stacking distance is 3.42 Å, showing the existence of a strong through-space interaction between the two stacked TTF moieties. In addition, there are intermolecular close S···S contacts advantageous to high conduction, as marked in Figure 6. The stoichiometry of donor to acceptor is, unfortunately, 1:2, indicating a complete charge transfer on each TTF unit. This valence state is of the Mott-insulating type, thus being responsible for the low conductivity of this salt (5.3×10^{-4} S cm^{-1}).

The ethylenedithio-bridged TTF phane (**7**) formed radical cation salts with BF_4^-, ClO_4^-, and I_3^-. The BF_4^- and ClO_4^- salts had similar conductivities of 1.5 and 0.2 S cm^{-1}, respectively, and, on a variable temperature measurement, showed semiconductive behavior with an activation energy of around 0.08 eV. Both salts were found to be crystallographically isostructural with the same stoichiometry of 3:4 (D:A); the representative crystal structure of the **7**·ClO_4^- salt is demonstrated in Figure 6a. The crystal structure unlike that of the **6**·PF_6^- salt consists of segregated stacking columns, as observed for conventional conductive radical cation salts. The donor columns include two independent donor molecules with 2:1 ratio; both are of the trans/trans (eclipse) type, but considerably different in shape. The donor A has a completely overlapped conformation of the two TTF moieties with a separation of 3.39 Å, indicative of stabilization due to large charge delocalization, while the donor B has a sliding conformation with a separation of 3.71 Å, suggestive of the influence of Coulombic repulsion (Figure 6b). The central double bonds of the donors A (1.34−1.35 Å) and B (1.40 Å) lengthen as compared with those (1.32−1.33 Å) of neutral **7a** and **7c**. The much longer bond of the donor B than that of A indicates that the former is in a higher oxidation state than the latter. The 2:1:4 stoichiometry of donor A, donor B, and anion is accommodated by assignments of donor A to a monocationic state and donor B to a dicationic state. Such involvement of cationic species with distinct electronic structures in the same donor column is, however, undesirable for high conduction, because it hinders the formation of a conduction band along the stacking column.

The I_3^- salt of **7** provided two kinds of crystal forms: the plate crystal showed a very high room-temperature conductivity of 28 S cm^{-1} and behaved metallic down to 210 K.[12] On the other hand, the needle crystal was nearly insulating (5.8×10^{-7} S cm^{-1}). The X-ray analyses of both crystals revealed that, in either case, the donor species included is of the cis/cis type, which is very unusual for the cationic double-bridged TTF phane. In the crystal structure of the highly conductive plate sample, there are two kinds of I_3^- anions: those of one kind assemble to form an anionic channel with disordering, while those of the other are individually included in the donor lattice (Figure 7a). The counter I_3^- anions included in the donor lattice stabilize the charged donor species by a Coulombic interaction, and its close approach forces the donor to be of the cis/cis type rather than the normal trans/trans (eclipse) type.

---

(12) Although the X-ray analysis indicated the 1:2 stoichiometry of donor to anion, the microanalysis of the plate crystals of the **7**·I_3^- salt suggests an approximately 10% defect of the I_3^- anion: Calcd for **7**·$(I_3)_{1.8}$: C, 15.08; H, 0.95. Found: C, 15.15; H, 0.99. This holds the donor assembly in the mixed valence state required for high conduction.

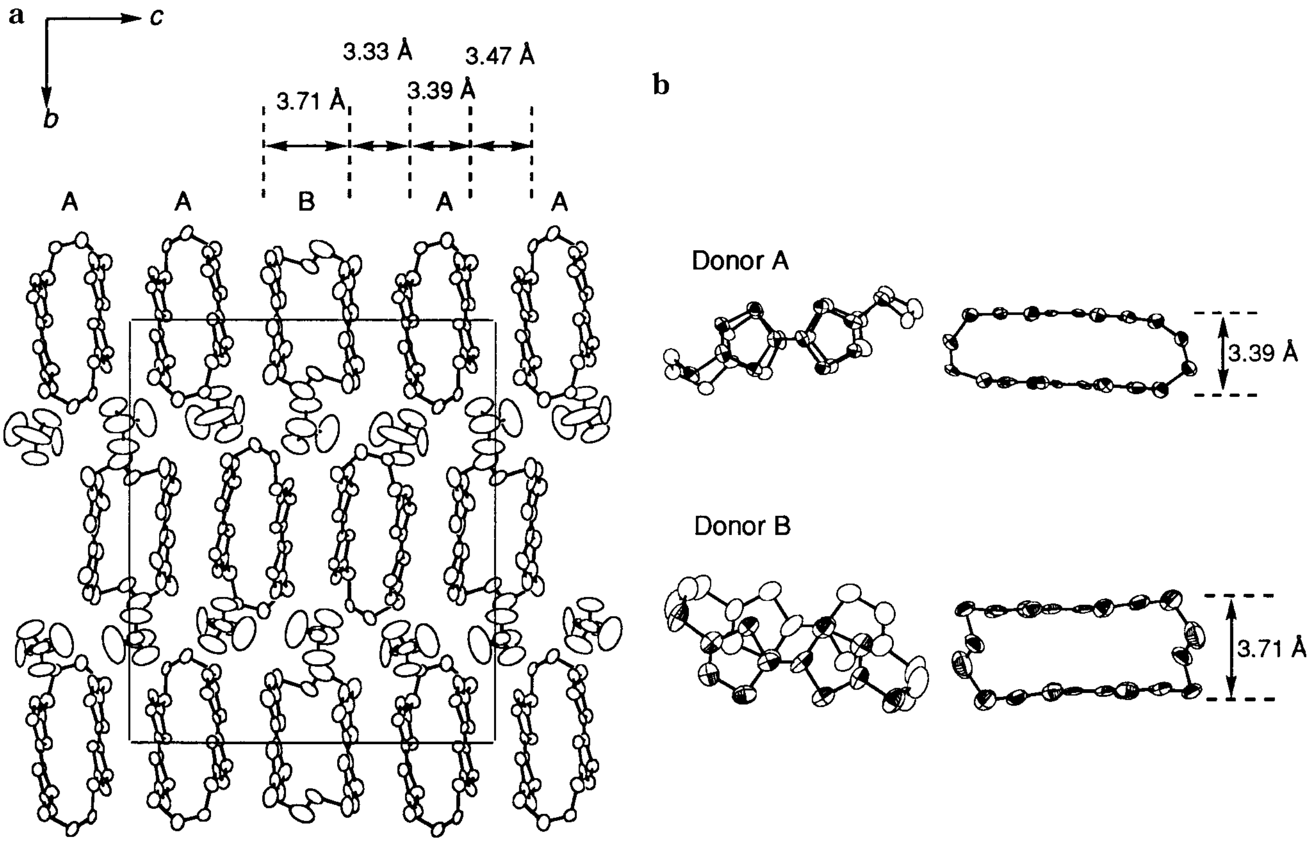


Figure 6. X-ray structure of **7**·ClO_4: (a) packing diagram (*a*-axis projection) (left) and (b) the molecular structures of (top) donor A and (bottom) donor B (right).

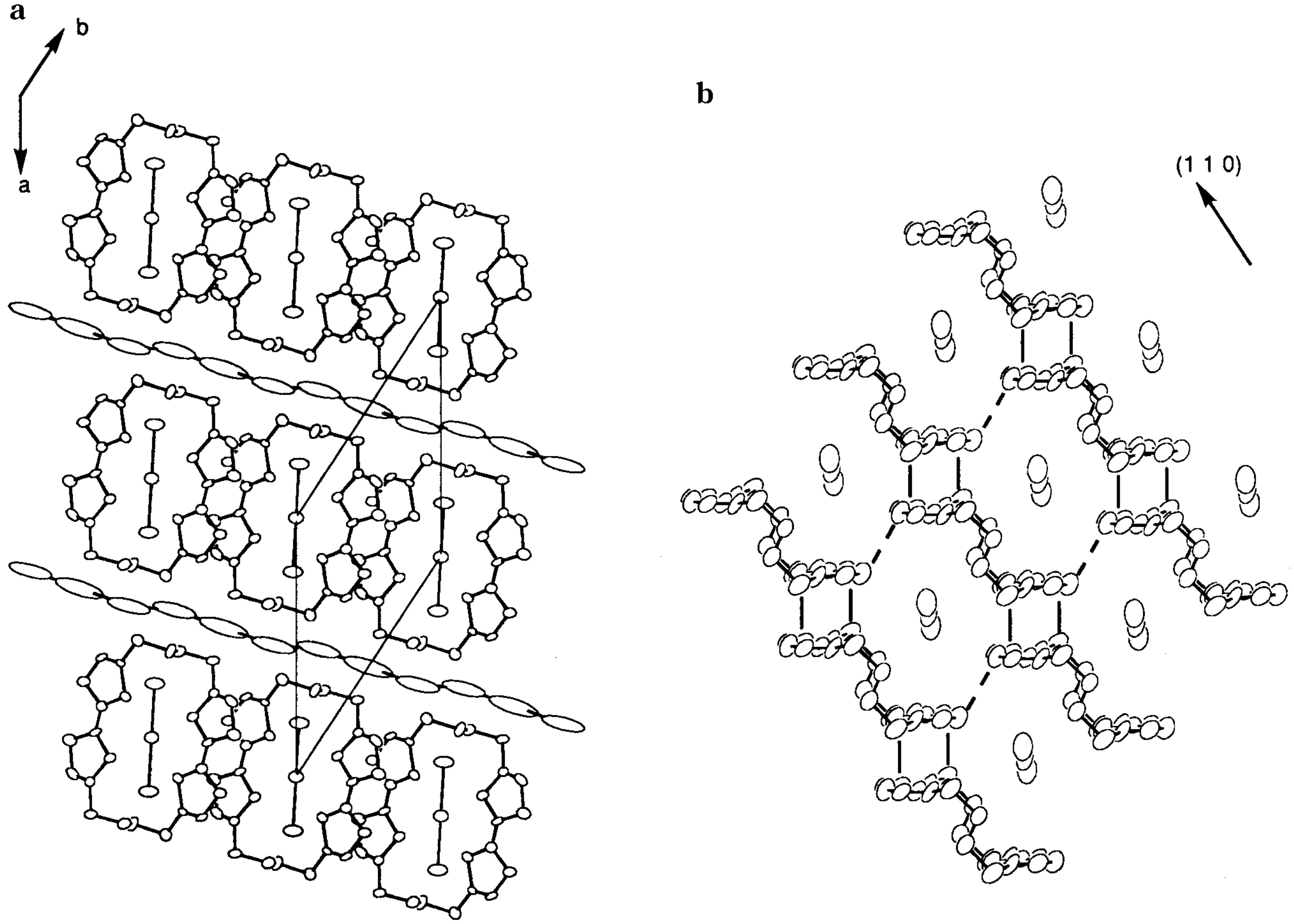


Figure 7. Crystal structure of **7**·I_3 (metallic salt): (a) packing diagram (*c*-axis projection) representing the alternating structure of the donor sheets and I_3^- layers (left) and the (b) side view of the donor sheet; short S···S contacts are (solid line) 3.38−3.40 Å and (dashed line) 3.60 Å (right).

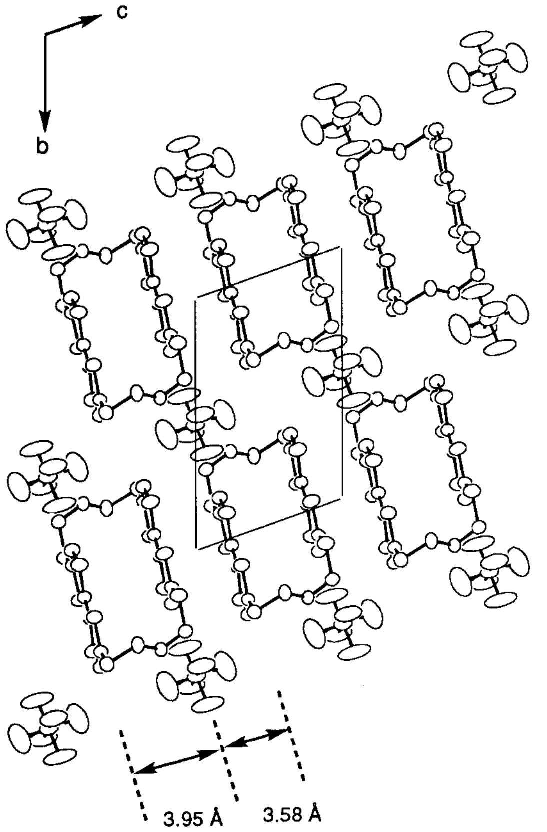


Figure 8. Crystal structure of **8**·PF_6 (*a*-axis projection).

The TTF moiety makes a stack with a TTF moiety of another molecule but no stack with the other TTF of the same molecule (Figure 7b). Very similar crystal structures consisting of alternating stacks of dimerized TTFs and I_3^- anions were previously reported for the I_3^- salts of TTF derivatives, BEDT-TTF[13] and BEDO-TTF.[14]

The alternating stacks of dimerized TTFs and I_3^- anions form no conduction path along the stacking direction. However, the stacked donor pair interacts with two neighboring pairs via close intermolecular S−S contacts to form a diagonal interactive network (Figure 7b). It is thus conceivable that this network corresponds to a conduction path of the sample. Although the nearly insulating needle crystal of the **7**·I_3^- salt also comprises the donor species of the cis/cis type and two I_3^- anions, the packing mode is different from that of the plate crystal. The I_3^- anion included in the donor cavity interferes with the intermolecular interaction between the neighboring donors, thus allowing no formation of the conduction path.

Electrocrystallization of the trimethylenedithio-bridged TTF phane (**8**) gave the PF_6^- and I_2Br^- salts with the conductivities of 2.1×10^{-2} and 3.0×10^{-3} S cm^{-1}, respectively. They have similar crystal structures, and again comprise the stacking columns of the trans/trans (eclipse) isomers, represented by that of the PF_6^- salt in Figure 8. The stacking distance of the trimethylenedithio-bridged TTF phane (**8**) explains their moderate conductivities: the intramolecular stacking distance of the two TTF moieties (ca. 3.95 Å) is much longer than the intermolecular one (ca. 3.58 Å) and beyond van der Waals contacts. Clearly the trimethylenedithio chains are too long to allow close contact between two TTF moieties. Finally electrocrystallization of the tetramethylenedithio-bridged TTF phane (**9**) gave only the I_3^- salt, whose conductivity was 2.0×10^{-4} S cm^{-1}. It is also understandable that the long bridging chains are responsible for the low conduction.

Conclusion

A series of double-bridged TTF phanes (**6**−**9**) with different bridge lengths has been successfully prepared and used as novel electron donors to form various conductive radical cations salts. They existed as a mixture of three stereoisomers of the cis/cis, cis/trans, and trans/trans (twist) types in the neutral state but predominantly as only one isomer of the trans/trans (eclipse) type in the low oxidation state. As a result, the resulting radical cation salts except the dimorphorous I_3^- salts of the ethylenedithio-bridged donor **7** comprised the stacking donors of the trans/trans (eclipse) type, which was stabilized by a marked through-space charge delocalization. A detailed study of the crystal structures as well as electrical conductivities indicated that the double-bridged TTF phanes can serve as an ideal model of interactive dimeric TTFs, but one cannot necessarily control the electronic structure of the donor assembly required for high conduction.

Experimental Section

General. All the chemicals and solvents are of reagent grade. ^1H NMR spectra were recorded on a Hitachi RS 1200 spectrometer (60 MHz) or on a JEOL Lambda 400 spectrometer (400 MHz) in $CDCl_3$ using tetramethylsilane as an internal standard, unless otherwise stated. IR spectra were taken on a Shimadzu FTIR 8100 spectrophotometer with a KBr disk method. MS spectra were measured at 70 eV on a Shimadzu QP 2000 spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV 3200 spectrometer. Cyclic voltammograms were measured in benzonitrile containing tetrabutylammonium perchlorate at room temperature using a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator. The electrical conductivities were measured by the conventional four-probe method, and the electrical contacts were made with gold paint.

4,4-(Alkylenedithio)bis(5-methoxycarbonyl-1,3-dithiole-2-thione) (10−13). Compounds **11**−**13** were prepared according to Cava's method.[9] 4,4-(Methylenedithio)bis(5-methoxycarbonyl-1,3-dithiole-2-thione) (**10**) was similarly obtained as follows: to a solution of sodium methoxide in dry tetrahydrofuran (150 mL), prepared from sodium (2.75 g, 120 mmol) and methanol (110 mL), was added in one portion 4-mercapto-5-methoxycarbonyl-1,3-dithiole-2-thione[9] (26 g, 116 mmol). After the resulting mixture was refluxed for 1 h, dibromomethane (9.08 g, 52.2 mmol) was added. The mixture was further refluxed overnight and cooled to room temperature. Water (500 mL) was added and the resulting precipitate was collected by filtration and dried in vacuo. Recrystallization from benzene−hexane gave orange needles of **10** (yield 66%); mp 185 °C; ^1H NMR δ 3.88 (s, 6H, CH_3) and 4.44 (s, 2H, CH_2); ^{13}C NMR δ 39.36 (CH_2), 53.33 (OCH_3), 125.11 (C=C), 147.09 (C=C), 158.61 (C=O), and 206.69 (C=S); IR 1692 (C=O) and 1065 cm^{-1} (C=S); MS (DI, 70 eV) *m/z* 460 (M^+). Anal. Calcd for $C_{11}H_8O_4S_8$: C, 28.68; H, 1.75. Found: C, 28.84; H, 1.70.

Conversion of Thiones 10−13 into Ketones 14−17 (Typical Procedure). 4,4-(Methylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-one) (14). A mixture of **10** (21.2

---

(13) Shibaeva, R. P.; Kaminskii, V. F.; Yagubskii, E. B. *Mol. Cryst. Liq. Cryst.* **1985**, *119*, 361−373.

(14) Horiuchi, S.; Yamochi, H.; Saito, G.; Matsumoto, K. *Mol. Cryst. Liq. Cryst.* **1996**, *284*, 357−365.

g, 46 mmol) and mercury acetate (70 g, 219 mmol) in chloroform (450 mL) and acetic acid (100 mL) was stirred overnight at room temperature. After evaporation of the solvent, the residue was extracted with dichloromethane and subjected to column chromatography on silica gel eluted with dichloromethane to give the corresponding ketone. Recrystallization from chloroform−hexane gave an analytically pure sample of **10** as colorless needles (16.1 g, 82%); mp 164 °C; ^{1}H NMR δ 3.87 (s, 6H, CH_3) and 4.42 (s, 2H, CH_2); IR 1700 (esteric C=O) and 1655 cm^{-1} (C=O); MS (DI, 70 eV) *m*/*z* 428 (M^+). Anal. Calcd for $C_{11}H_8O_6S_6$: C, 30.83; H, 1.88. Found: C, 30.86; H, 1.96.

4,4-(Ethylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-one) (15). Yield 90%; colorless needles from chloroform−hexane; mp 168 °C; ^{1}H NMR δ 3.29 (s, 4H, CH_2) and 3.85 (s, 6H, CH_3); IR 1698 (esteric C=O) and 1651 (C=O) cm^{-1}; MS *m*/*z* 442 (M^+). Anal. Calcd for $C_{12}H_{10}O_6S_6$: C, 32.57; H, 2.28. Found: C, 32.42; H, 2.23%.

4,4-(Trimethylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-one) (16). Yield: 93%; colorless fine crystals from dichloromethane−hexane; mp 144−145 °C; ^{1}H NMR δ 2.28 (quint., *J* = 6.7 Hz, 2H), 3.22 (t, *J* = 6.7 Hz, 4H, CH_2), and 3.86 (s, 6H, CH_3); IR 1703 (esteric C=O), 1659 (C=O) cm^{-1}; MS *m*/*z* 456 (M^+). Anal. Calcd for $C_{13}H_{12}O_6S_6$: C, 34.20; H, 2.65. Found: C, 34.13; H, 2.63.

4,4-(Tetramethylenedithio)bis(5-methoxycarbonyl-1,3-dithiol-2-one) (17). Yield: 82%; colorless fine crystals from chloroform−hexane; mp 164−165.5 °C; ^{1}H NMR δ 1.89 (m, 4H, CH_2), 3.00 (m, 4H, CH_2), and 3.82 (s, 6H, CH_3); IR 1703 (esteric C=O) and 1651 (C=O) cm^{-1}; MS *m*/*z* 470 (M^+). Anal. Calcd for $C_{14}H_{14}O_6S_6$: C, 35.73; H, 3.00. Found: C, 35.72; H, 3.10.

Double-Bridged TTF Phanes 6−9 (Typical Procedure). Bis(ethylenedithio)-Bridged TTF Phane (7). To a refluxing mixture of **15** (2.21 g, 5 mmol) in dry toluene (120 mL) was added triisopropyl phosphite (8 mL), and then the mixture was refluxed overnight. After the orange precipitate that formed upon cooling was removed by filtration, the filtrate was concentrated to be a pasty oil, which was then treated with methanol (20 mL) to give an orange powder (1.35 g). Purification by column chromatography on silica gel with dichloromethane gave 306 mg (15%) of the dimeric tetraester **18** as an isomeric mixture. A solution of **18** (306 mg, 0.37 mmol) and lithium bromide monohydrate (800 mg, 7.6 mmol) in *N*,*N*-dimethylacetamide (20 mL) was degassed under vacuum and then heated by immersion in an oil bath at 135 °C. After gas evolution ceased in a few minutes, the mixture was further heated for 5 min, cooled rapidly to room temperature, and poured into ice-containing water (50 mL). The resulting precipitate was filtered, washed successively with water and methanol, and dried in the air. Chromatography on silica gel eluted with carbon disulfide gave an isomeric mixture of TTF phanes **7a**−**c** (72 mg, 33%). Treatment from carbon disulfide gave the three components; the insoluble powder was recrystallized from chlorobenzene to give yellow plates, assigned as **7a** (cis/cis) by an X-ray crystallographic analysis. The orange prisms directly formed from the carbon disulfide solution were assigned as 7**c** (trans/trans, twist) by an X-ray crystallographic analysis. The mother liquor contained a soluble **7b** (cis/trans)-rich fraction, which was further purified by recrystallization from carbon disulfide−hexane to give fine, orange needles.

7a: yellow plates; mp 258−260 °C (dec); MS *m*/*z* 588 (M^+); IR (KBr) 3071 and 769 cm^{-1}. Anal. Calcd for $C_{16}H_{12}S_{12}$: C, 32.63; H, 2.05. Found: C, 32.74; H, 2.05. **7b**: fine, orange needles from carbon disulfide−hexane; mp 223−224 °C; ^{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); MS *m*/*z* 588 (M^+). Anal. Calcd for $C_{16}H_{12}S_{12}$: C, 32.63; H, 2.05. Found: C, 32.60; H, 2.05. **7c**: orange prisms from carbon disulfide; mp 245 °C (dec); ^{1}H NMR (CS_2−acetone-*d*$_6$) δ 2.92 (s, 8H, CH_2) and 6.55 (s, 4H, CH); MS *m*/*z* 588 (M^+); Anal. Calcd for $C_{16}H_{12}S_{12}$: C, 32.63; H, 2.05. Found: C, 32.58; H, 2.02.

Bis(methylenedithio)-bridged TTF phane (6): 7% total yield from **14**. **6a**: yellow needles from carbon disulfide; mp 253−254 °C; MS *m*/*z* 560 (M^+); ^{1}H NMR (CS_2−$CDCl_3$) δ 3.99 (s, 4H, CH_2) and 6.46 (s, 4H, CH). **6b**: orange plates from carbon disulfide; mp 245−246 °C; ^{1}H NMR (CS_2−$CDCl_3$) δ 3.92 (d, *J* = 14.2 Hz, 2H, CH_2), 4.28 (d, *J* = 14.2 Hz, 2H, CH_2), 6.38 (s, 2H, CH), and 6.53 (s, 2H, CH). **6c** (not completely isolated): ^{1}H NMR (CS_2−$CDCl_3$) δ 3.41 (d, *J* = 14.8 Hz, 2H, CH_2), 4.64 (d, *J* = 14.8 Hz, 2H, CH_2), and 6.40 (s, 4H, CH). Anal. Calcd for $C_{14}H_8S_{12}$ as an isomeric mixture: C, 29.98; H, 1.44. Found: C, 29.96; H, 1.44.

Table 3. Selected Crystal Data of Neutral Donors

	6b	**7a**	**7c**
formula	$C_{14}H_{16}S_{12}$	$C_{16}H_{12}S_{12}$	$C_{16}H_{12}S_{12}$
formula weight	571.02	589.04	589.04
crystal system	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	Pbca	P2/m
color of crystals	orange	yellow	orange
a/Å	12.145(6)	22.446(3)	17.173(2)
b/Å	16.734(4)	12.290(2)	7.977(1)
c/Å	11.457(6)	8.310(2)	17.719(3)
α/deg	96.83(4)		
β/deg	112.86(3)		106.21(1)
γ/deg	82.71(3)		
V/Å^3	2121(1)	2292.5(6)	2330.8(6)
Z	4	4	4
R	0.065	0.073	0.071

Bis(trimethylenedithio)-bridged TTF phane (8): 8% total yield from **16**. **8a**: mp 84−85 °C; ^{1}H NMR δ 1.95−2.03 (m, 4H, CH_2), 2.68−2.72 (m, 8H, CH_2), and 6.40 (s, 4H, CH); MS *m*/*z* 616 (M^+); IR (KBr) 3063 and 769 cm^{-1}. Anal. Calcd for $C_{18}H_{16}S_{12}$: C, 35.03; H, 2.61. Found: C, 35.13; H, 2.61. **8b**: orange crystals from benzene−ethanol; mp 171−172 °C; ^{1}H NMR δ 2.09 (quintet, *J* = 7.2 Hz, 4H, CH_2), 2.72 (t, *J* = 7.2 Hz, 4H), 2.80 (t, *J* = 7.2 Hz, 4H), 6.41 (s, 2H, CH), and 6.44 (s, 2H, CH). Anal. Calcd for $C_{18}H_{16}S_{12}$: C, 35.03; H, 2.61. Found: C, 35.08; H, 2.56. **8c·CHCl$_3$**: orange prisms from chloroform; mp 204−205 °C; ^{1}H NMR δ 1.95−2.03 (m, 4H, CH_2), 2.75−2.82 (m, 8H, CH_2) and 6.38 (s, 4H, CH); MS *m*/*z* 616 (M^+). Anal. Calcd for $C_{19}H_{17}S_{12}Cl_3$: C, 30.99; H. 2.33. Found C, 30.95; H, 2.26.

Bis(tetramethylenedithio)-bridged TTF phane (9): 9% total yield from **17**. **9a**: yellow prisms from carbon disulfide, which contain two CS_2 molecules per **9a** as solvent of crystallization. Its heating at 80 °C under a reduced pressure for 1 h left the free **9a**; mp 165−166 °C; ^{1}H NMR (CS_2−acetone-*d*$_6$) δ 1.74−1.78 (m, 8H, CH_2), 2.73−2.78 (m, 8H, CH_2), and 6.53 (s, 4H, CH). Anal. Calcd for $C_{20}H_{20}S_{12}$: C, 37.27; H, 3.12. Found: C, 37.09; H, 3.05. **9b** (not isolated): ^{1}H NMR (CS_2−acetone-*d*$_6$) δ 1.74−1.78 (m, 4H, CH_2), 2.73−2.82 (m, 8H, CH_2), 6.51 (s, 2H, CH), and 6.55 (s, 2H, CH). **9c·CS$_2$**: orange prisms from carbon disulfide; mp 154−156 °C; ^{1}H NMR (CS_2−acetone-*d*$_6$) δ 1.74−1.78 (m, 8H, CH_2), 2.73−2.78 (m, 8H, CH_2), and 6.55 (s, 4H, CH). Anal. Calcd for $C_{21}H_{20}S_{14}$: C, 34.97; H, 2.79. Found: C, 34.97; H, 2.76.

Typical Electrocrystallization Procedure. Into a 40 mL H-shaped glass cell with a fine flit dividing the anolyte and catholyte compartments equipped with platinum wire electrodes was placed 20 mL of chlorobenzene and 3 mL of ethanol containing the appropriate tetrabutylammonium salt (100−200 mg). The donor (2−3 mg) was added into the anolyte compartment. The solution was degassed with a dry nitrogen stream and electrolyzed under a constant current of 1−4 μA at 70 °C. Black crystals of radical cation salts gradually grew on the anode electrode during several days. The crystals were collected by filtration, washed with cold dichloromethane, and dried in vacuo.

Crystal Structure Determinations. A Rigaku AFC-6S diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) was used, and data were collected at room temperature for all the crystals except **9a**, the data of which were collected by using or a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Periodic remeasurement of three standard reflections revealed no significant crystal decay. Intensities were measured by continuous ω−2θ scans. All intensities were corrected for Lorenz−polarization effects. The structures were solved by direct methods or Patterson methods followed by subsequent

Table 4. Selected Crystal Data of Radical Cation Salts

	6·PF_6	**7**·ClO_4	**7**·I_3 (plate)	**8**·PF_6
formula	$C_{14}H_8S_{12}P_2F_{12}$	$C_{48}H_{36}S_{36}Cl_4O_{16}$	$C_{16}H_{12}S_{12}I_6$	$C_{18}H_{16}S_{12}PF_6$
formula weight	705.90	2164.83	1350.42	762.01
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
color of crystals	black	black	black	black
a/Å	9.027(8)	7.834(5)	13.529(3)	7.929(1)
b/Å	15.513(3)	23.891(4)	13.540(3)	12.467(3)
c/Å	10.427(2)	20.897(3)	8.177(1)	7.618(3)
α/deg			90.33(2)	109.37(2)
β/deg	109.94(3)	99.08(2)	99.84(2)	90.22(2)
γ/deg			145.21(1)	94.60(1)
V/Å^3	1372(1)	3682(2)	813.0(5)	707.8(3)
Z	2	2	1	1
R	0.064	0.075	0.105	0.0813

Fourier-difference calculation and refined by a full matrix least-squares techniques with anisotropic temperature factors for the non-hydrogen atoms. Structure solution and refinement were carried out using the TEXSAN program package[15] for **6a**, **9a**, **9c**, **6**·PF_6, and all the radical cations salts of **7**. For the refinement of two **7**·I_3 radical salts (both of metallic and insulating ones) the full-matrix least-squares (SHELXL-93)[16] was used.

A summary of crystal data and structural refinement results is given in Tables 3 and 4. The crystallographic data for **7a** and **7c** were deposited in the Cambridge Crystallographic Data Center under reference code ZOVCES and ZOVCIW, respectively, as a part of a previous communication.[8a] The final atomic coordinates and crystallographic data for other crystals have also been deposited.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan. One of the authors (K.T.) is also indebted to a financial support from Yazaki Memorial Foundation for Science and Technology.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **6b**, **7a**, **7c**, **8c**, **9a**, **9c**, **6**·PF_6, **7**·BF_4, **7**·ClO_4, **7**·I_3, and **8**·PF_6; a stereoview of **8c**; ORTEP drawings of **9a** and **9b**; and a packing diagram of **7**·I_3 (needle). This material is available free of charge via the Internet at http://pubs.acs.org.

CM000117M

---

[15] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corp. (1985 and 1992).

[16] Schldric, G. M. SHELEXL-93: Programs for the Refinement of Crystal Structures. University of Goettingen, Germany, 1993.