# *Studies on Novel 1,3-Dithiole Compounds Containing Thiophene-Related Systems*

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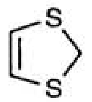
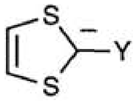
# *Chapter 1 General Introduction*

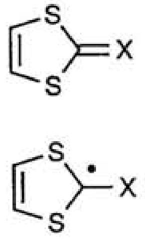
## Introduction

In the field of materials chemistry, the 1,3-dithiole ring system **1**[1,2] is one of the most widely investigated and attractive heterocycles due to its unique redox properties as shown below. On the development of new organic materials, the 1,3-dithiole unit has the following advantages. First, the 1,3-dithiole unit is a strong electron-releasing group which is useful to enhance the electron-donating ability of molecules and the stability of cationic species. Second, intermolecular interactions in the solid state may be strengthened by interactions between sulfur atoms of the 1,3-dithiole ring. Third, substituents can be easily introduced to the 1,3-dithiole ring to modify the molecular structure and the properties. Finally, starting materials giving 1,3-dithiole compounds are generally cheap, and synthetic methodologies are almost established.[1-3] From these viewpoints, a large number of new 1,3-dithiole electron donors affording organic conductors or superconductors have been developed.[4-7] The most important example is tetrathiafulvalene (TTF) **2**.[8] On the other hand, a new application of the 1,3-dithiole unit as a building-block of supramolecules has been also pointed out recently.[9]

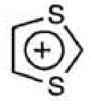

**1**



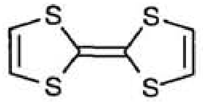
8π-anion



neutral

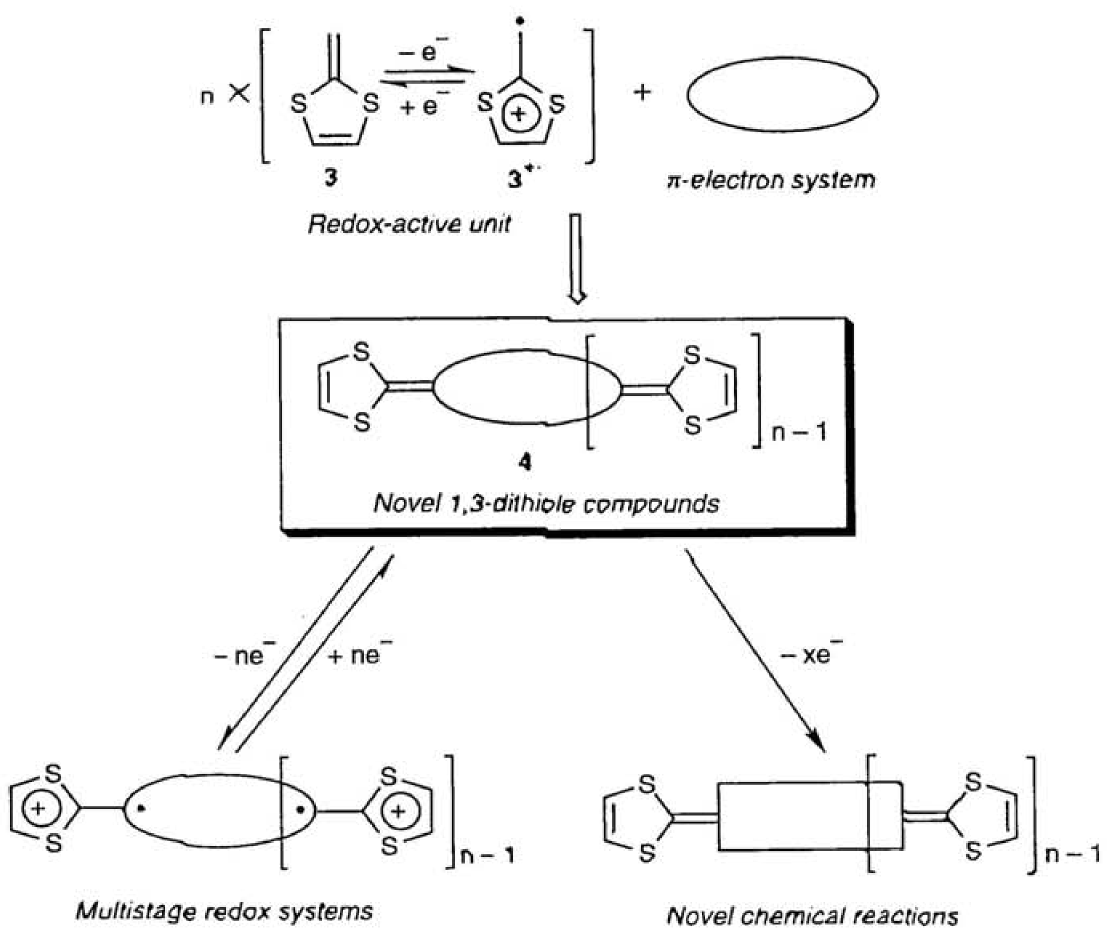


6π-cation



**2** TTF

Here the author wishes to propose the following idea as a new use of the 1,3-dithiole unit. 2-Methylene-1,3-dithiole **3**, which is a component of TTF, is considered to give the corresponding cation radical $3^{+\cdot}$ upon one-electron oxidation. In other words, it can be regarded as a source of cation radical species. Thus, introduction of this unit into an appropriate π-electron system is expected to produce various novel redox systems **4** showing interesting properties and reactivities inherent to the configuration and the number of the 1,3-dithiole units as well as to the nature of the π-electron system (Scheme 1). Therefore, on the development of novel organic functional materials as well as organic conductors, it is worthwhile to prepare such redox systems and study their properties.

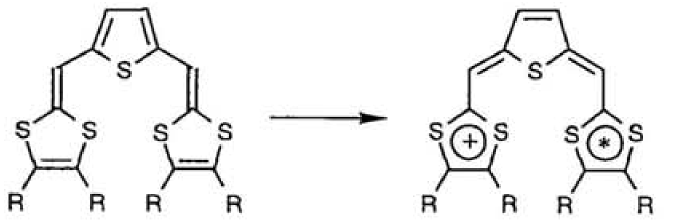


**Scheme 1**

With this in mind, in this research work the author designed several 1,3-dithiole compounds containing thiophene-related systems and investigated their electrochemical properties, reactivities, and crystal structures to explore new applications of the 1,3-

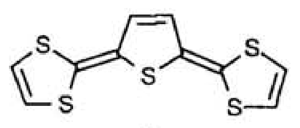
dithiole unit. The thiophene derivatives were chosen as spacer units for following reasons. (i) The electron-releasing thiophene ring is expected to enhance the electron-donating ability of the molecules and to stabilize the cationic species formed by oxidation.[10] (ii) The expansion of π-conjugation caused by insertion of the thiophene units may reduce intramolecular Coulombic repulsion. (iii) The structural modification is generally easy. The following paragraphs describe the recent studies on the 1,3-dithiole electron donors related to this research work.

The thiophene ring system is also an actively investigated heterocycle as seen in the field of conducting polymers.[11] Recently, several 1,3-dithiole electron donors containing thiophene-related units have been reported. In these donors, the thiophene units are used as spacer groups, fused rings, and end groups. The usefulness of the thiophene units has been pointed out in these reports. The typical examples of each use are as follows. 2,5-Bis(1,4-dithiafulven-6-yl)thiophenes **5**, in which the thiophene units are used as a spacer group, were independently synthesized by three research groups at

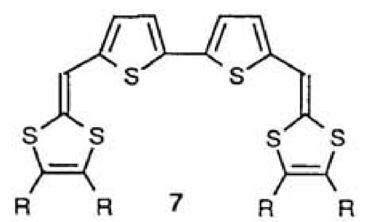


**5**

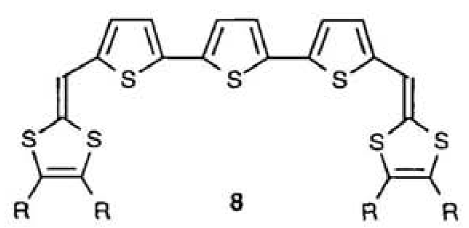
$5^{+\cdot}$ or $5^{2+}$ $* = \bullet$ or $+$



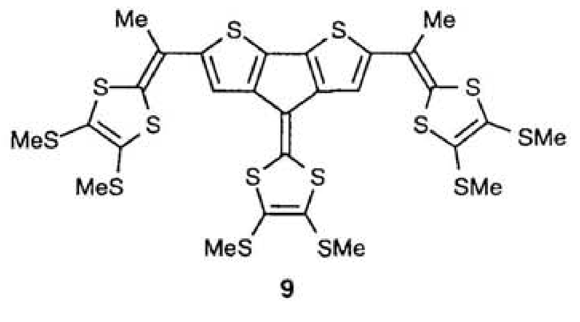
**6**



**7**



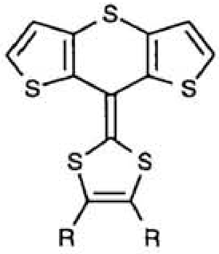
**8**



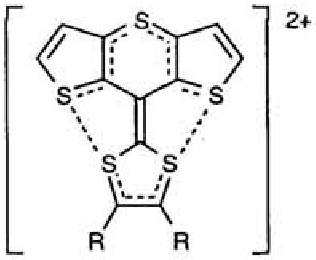
**9**

the almost same time.[12-14] The cyclic voltammetry indicated that the insertion of the thiophene unit effectively reduces the on-site Coulombic repulsion in the dication state. In spite of extension of π-conjugation, the electron donating ability of the donors is not so high. The first oxidation potential of the parent donor **5** (R = H) is comparable to that of TTF. This fact is attributed to the loss of aromaticity of the thiophene ring in the oxidized states $\mathbf{5}^{+\cdot}$ or $\mathbf{5}^{2+}$. In contrast, the first oxidation potential of **6** containing a quinoid thiophene unit, which generates an aromatic thiophene ring upon oxidation, is lower by 0.25 V than that of TTF.[15] Furthermore, bis(1,3-dithiole) donors **7** and **8** containing 2,2'-bithienyl and terthienyl units, respectively, were synthesized as a model of the small bandgap thiophene oligomers.[16-18] Their spectroscopic and electrochemical data indicated that the combination of thiophene oligomer and 1,3-dithiole units decreases the oxidation potentials and HOMO–LUMO gaps of the molecules. A rigidified molecule **9** was also prepared.[19] This donor showed both oxidation and reduction waves in the cyclic voltammogram and the first oxidation potential is fairly low (0.18 V *vs.* SCE). The decrease in HOMO–LUMO gap is attributed to its rigid structure which dissolves the unfavorable bond rotation between the thiophene rings found in **7**.

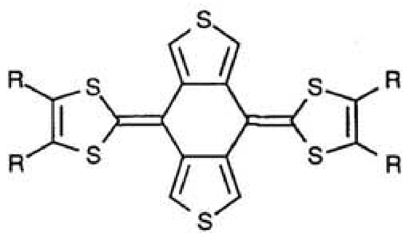
An interesting example of 1,3-dithiole donors containing fused thiophene rings is 2-(thiopyran-4-ylidene)-1,3-dithioles **10**.[20] The cyclic voltammograms of **10** revealed that the molecules are strong electron donors like TTF and intramolecular Coulombic repulsion in the dication states is reduced. The most striking feature of the donors is intramolecular S···S interaction affecting the redox properties and molecular geometries. In the neutral state, the molecule takes a nonplanar conformation with short S···S contacts (3.03–3.09 Å). On the other hand, the molecular geometry of the cation radical formed from **10** is planar and the intramolecular distances between the sulfur atoms are shortened (2.86 and 2.87 Å). *Ab initio* calculations suggests that the positive charge in the cation radical and dication states are delocalized over the π-electron system through the short S···S contacts. Another thiophene-fused donor **11** was also reported. The donor gave conductive complex with iodine ($\rho = 3.5 \times 10\ \Omega$ cm).



**10**

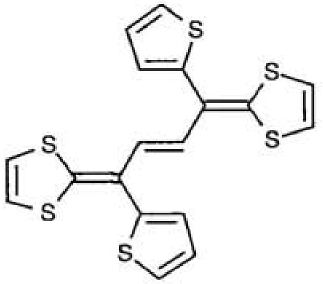


**10**$^{2+}$

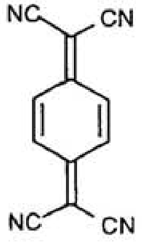


**11** R, R = benzo

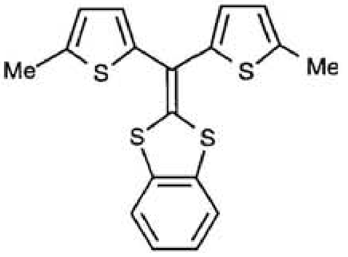
In an extended bis (1,3-dithiole) donor **12**, thiophene rings are used as end groups. This compound was reported by the author previously.[21] According to MO calculations, the molecule has a nonplanar structure. This donor showed one-stage two-electron redox wave in the cyclic voltammogram, indicating the reduced Coulombic repulsion in the dication state. The donor gave conductive charge-transfer complexes with iodine or tetracyanoquinodimathane **13** ($\sigma = ca.\ 10^{-2}$ S cm$^{-1}$). It is noted that such a nonplanar donor **12** gave the conductive complexes. Moreover, it was suggested that the thiophene groups stabilize the cation state of **12**. Another compound **14** showed a smaller difference in the first and second oxidation potential ($\Delta E$ = 0.12 V in acetonitrile) than that of TTF **2** ($\Delta E$ = 0.37 V), indicating the small Coulombic repulsion in the dication state.[22] In a similar way to **10**, this fact was explained by the intramolecular S···S interactions stabilizing the cationic states.



**12**



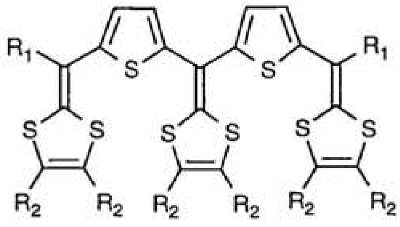
**13**



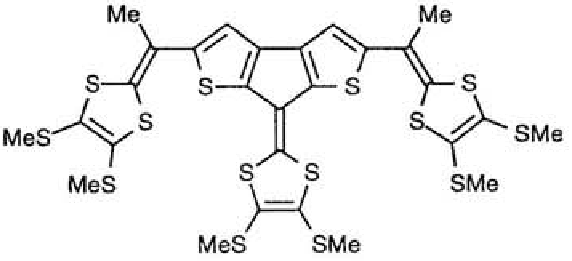
**14**

## Constitution of Present Thesis

The present thesis consists of the following three chapters in addition to this one. The abstract of each chapter is as follows. In *Chapter 2*, 6,6-bis[5-(1,4-dithiafulven-6-yl)-2-thienyl]-1,4-dithiafulvene **15** and its derivatives have been prepared as novel cross-conjugated tris(1,3-dithiole) donors, and their properties are discussed. According to MNDO-PM3 calculations on a parent compound, the molecule takes a nonplanar conformation, in which one dithiafulvenyl unit is orthogonal to the plane of the 2,5-bis(dithiafulvenyl)thiophene skeleton. The cyclic voltammograms (CV) showed that the donors are oxidized to trication radicals or tetracations. The first oxidation waves correspond to two-electron processes, indicating the reduced on-site Coulombic repulsion in the dication states. The electron-donating ability of the donors is estimated to be comparable to that of TTF. The donors gave conducting iodine complexes. A redox active polymer was formed from a certain derivative by electrochemical oxidation. Furthermore, the synthesis and redox properties of a tris(1,3-dithiole) donor **16** containing a cyclopentadithiophene moiety were also discussed.



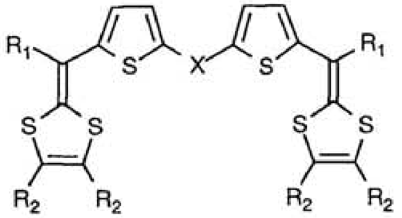
**15**



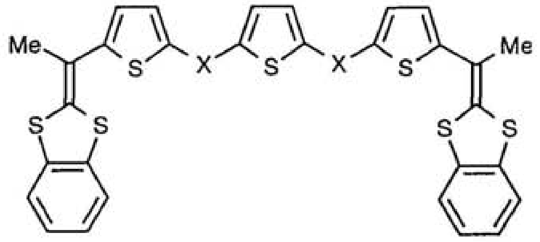
**16**

*Chapter 3* deals with the preparation and properties of bis(1,3-dithiole) compounds containing thienylmethylene units affording novel cations by oxidation. Molecules possessing a methylene group adjacent to electron-donating moieties seem to undergo deprotonation by oxidation to give the corresponding methyl cations. In order to show the generality of this type of reaction and to prepare interesting cations, bis(1,3-dithiole) compounds **17a** containing a dithienylmethane skeleton have been prepared.

The CV of **17a** suggested that redox active products were formed through electrochemical oxidation followed by chemical reactions and the reactions were dependent on the substituents R on the C6-carbons of the dithiafulvenyl groups. When R was methyl group, chemical oxidation of the compounds with $NOBF_4$ gave the corresponding dithienylmethyl cations **17b** in moderate yields. They were also prepared by hydride abstraction with $Ph_3CBF_4$. The cations were characterized by intense absorptions in the near-infrared region (900–980 nm in MeCN). The absorption band was blue-shifted to *ca.* 820 nm in a thin film, indicating that they are interesting as near-infrared absorbing dyes. The polymethine cyanine like structure of the cation was revealed by the X-ray analysis. On the other hand, in the case of R = H, a redox active oligomer was formed by oxidation. Furthermore, isolation of the dication salt **18b** derived from 2,5-bis[5-(6-methyl-1,4-dithiafulven-6-yl)-2-thienylmethyl]thiophene **18a**, which has two methylene groups, was also attempted.

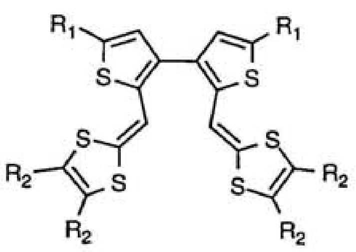


**17a** X = $CH_2$
**17b** X = $CH^+$

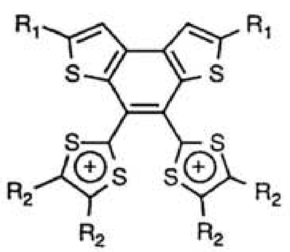


**18a** X = $CH_2$
**18b** X = $CH^+$

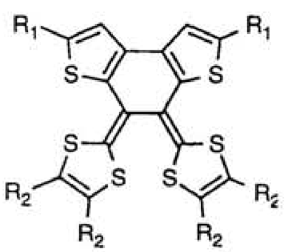
Although it has been reported that 1,4-dithiafulvene derivatives undergo oxidative intermolecular coupling reactions at the 6-position, the corresponding intramolecular reaction is unknown. *Chapter 4* describes the oxidative intramolecular cyclization of 2,2'-bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls **19**. The CVs of the compounds showed that they are irreversibly oxidized to afford redox active products. Chemical oxidation with tris(4-bromophenyl)aminium hexachloroantimonate gave cyclization products **20** as dication salts in high yields. The X-ray structural analyses of the dication salts revealed that they contain trivalent chloroantimonate ions ($Sb_2Cl_8^{2-}$ and $SbCl_5^{2-}$), suggesting that



**19**



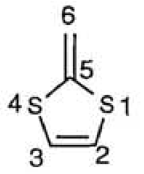
**20**



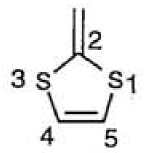
**21**

$SbCl_6^-$ ion acts as an oxidizing agent in the reaction. Chemical reduction of the dication salts with zinc gave the corresponding neutral donors **21** in high yields. According to the X-ray analysis, the molecule adopts a nonplanar structure with short intramolecular S···S contacts. The CVs of the donors showed reversible one-stage two-electron oxidation waves, and the potentials are fairly low compared with TTF. A tetracyano-quinodimethane complex was formed from one of them.

In this thesis, a term "1,4-dithiafulvene," which means 2-methylene-1,3-dithiole, is used according to circumstances.



1,4-dithiafulvene



2-methylene-1,3-dithiole

## References

(1) N. Lozac'h and M. Stavaux, *Adv. Heterocycl. Chem.*, **27**, 151 (1980).

(2) H. Gotthardt, "1,3-Dithioles," in "Comprehensive Heterocyclic Chemistry," ed by A.R. Katritzky, Pergamon Press, Oxford (1984), Vol. 6, pp. 813.

(3) A. Krief, *Tetrahedron*, **1986**, 1209.

(4) M. R. Bryce, *J. Mater. Chem.*, **5**, 1481 (1995).

(5) T. K. Hansen and J. Becher, *Adv. Mater.*, **5**, 288 (1993).

(6) F. Ogura, T. Otsubo, and Y. Aso, *Sulfur Rep.*, **11**, 439 (1992).

(7) M. R. Bryce, *Chem. Soc. Rev.*, **1991**, 355.

(8) F. Wudl, G. M. Smith, and E. J. Hufnagel, *J. Chem. Soc., Chem. Commun.*, **1970**, 1453.

(9) T. Jørgensen, T. K. Hansen, and J. Becher, *Chem. Soc. Rev.*, **1994**, 41.

(10) B. Abarca, G. Asensio, R. Ballesteros, and T. Varea, *J. Org. Chem.*, **56**, 3224 (1991).

(11) J. Roncali, *Chem. Rev.*, **92**, 711 (1992).

(12) T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. E. Niziurski-Mann, F. Jensen, and J. Becher, *J. Am. Chem. Soc.*, **114**, 5035 (1992).

(13) A. S. Benahmed-Gasmi, P. Frère, B. Garrigues, A. Gorgues, M. Jubault, R. Carlier, and F. Texier, *Tetrahedron Lett.*, **43**, 6457 (1992).

(14) K. Takahashi, T. Nihira, M. Yoshifuji, and K. Tomitani, *Bull. Chem. Soc. Jpn.*, **66**, 2330 (1993).

(15) K. Takahshi, T. Nihara, and K. Tomitani, *J. Chem. Soc., Chem. Commun.*, **1993**, 1617.

(16) J. Roncali, M. Giffard, P. Frère, M. Jubault, and A. Gorgues, *J. Chem. Soc., Chem. Commun.*, **1993**, 689.

(17) J. Roncali, M. Giffard, M. Jubault, and A. Gorgues, *Synth. Met.*, **60**, 163 (1993).

(18) J. Roncali, L. Rasmussen, C. Thobie-Gautier, P. Frère, H. Brisset, M. Sallé, J. Becher, O. Simonsen, T. K. Hansen, A. Benahmed-Gasmi, J. Orduna, J. Garin, M. Jubault, and A. Gorgues, *Adv. Mater.*, **6**, 841 (1994).

(19) H. Brisset, C. Thobie-Gautier, M. Jubault, A. Gorgues, and J. Roncali, *J. Chem. Soc., Chem. Commun.*, **1994**, 1765.

(20) T. Suzuki, T. Sakimura, S. Tanaka, Y. Yamashita, H. Shiohara, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, **1994**, 1431.

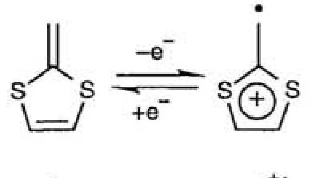
(21) A. Ohta, T. Kobayashi, and H. Kato, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 905.

(22) T. Sakimura, Master's Thesis, Tohoku University, Sendai, Japan, 1990.

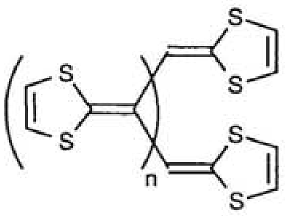
# *Chapter 2 Preparation and Properties of Novel Tris(1,3-dithiole) Donors Containing Thiophene Spacer Units*

## Introduction

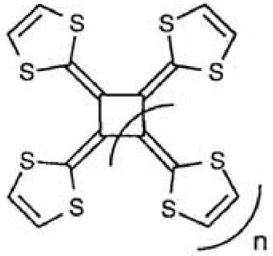
As described in chapter 1, the 2-methylene-1,3-dithiole unit **1** is considered to function as a source of cation radical species $\mathbf{1}^{+\bullet}$. Molecules in which the 1,3-dithiole units **1** are included in a cross-conjugated system are expected to show interesting electronic and magnetic properties in the oxidized states.[1] In this connection, simple 1,3-dithiole compounds containing a cross-conjugated system, *e.g.*, dendralenes **2**[1,2] and radialenes **3**,[3-6] have been synthesized and their physical properties have been investigated. It was reported that the dication state of [5]-radialene **3** (n = 2) is a ground state triplet in the charge-transfer complex of **3** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[4]



**1** $\mathbf{1}^{+\bullet}$

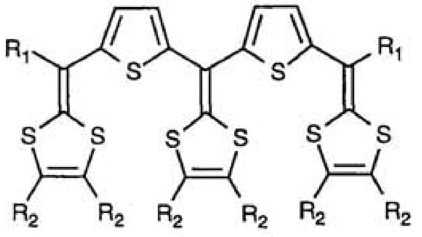


**2** n = 1,2



**3** n = 1–3

In this research work, the author designed novel cross-conjugated tris(1,3-dithiole) donors **4** and **5** containing thiophene spacer units. This donors can be regarded as vinylogues of the [3]-dendralene **2** (n = 1) extended by the thiophene units and are expected to show multistage redox behavior. Recently electron donors containing many 1,3-dithiole units attract much attention because they are expected to have enhanced dimensionality of electrical conduction.[7-14] The donors **4** and **5** are also of interest from this viewpoint. In this chapter, preparation and electrochemical properties of **4**, **5**, and a related tris(1,3-dithiole) donor are described.



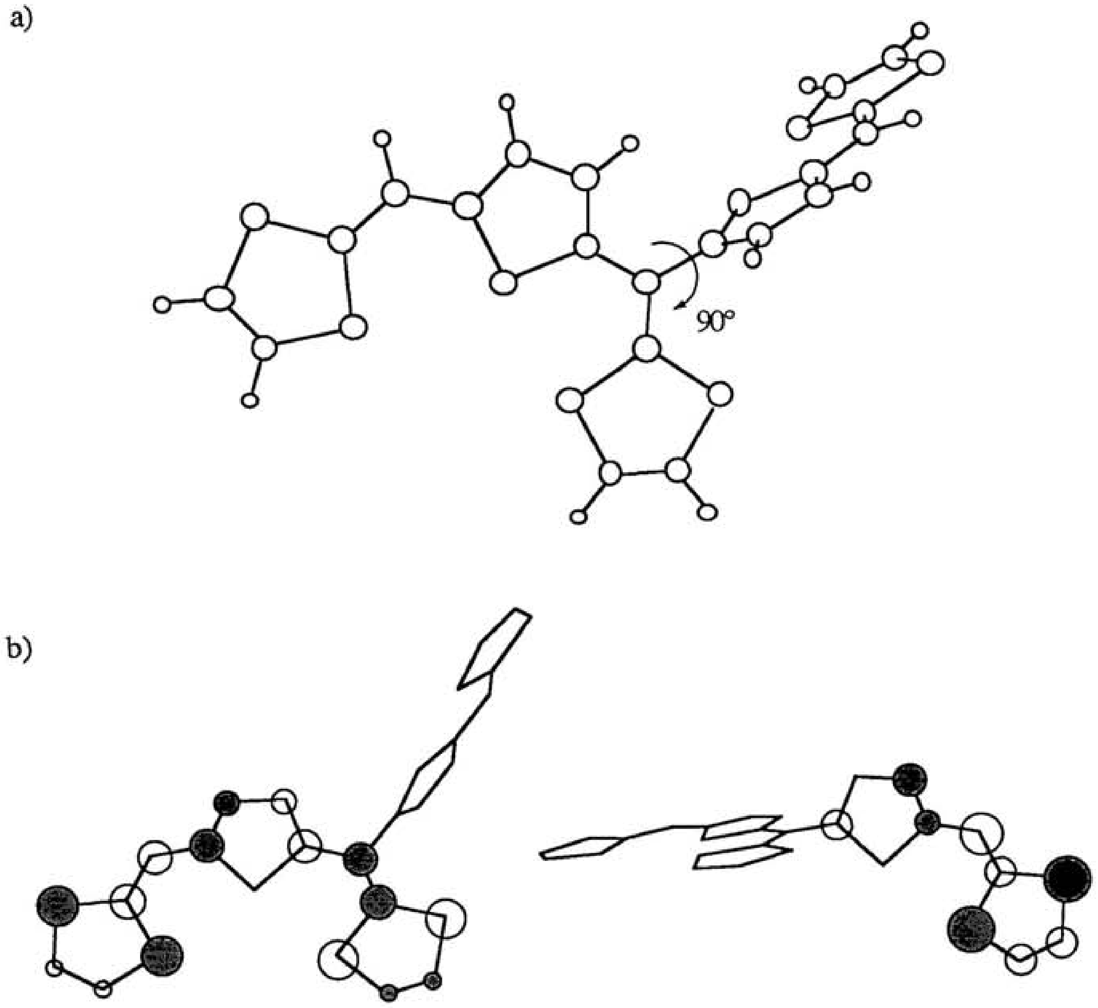
**4a–d** $R_1$ = H **5a–d** $R_1$ = Me

$R_2$, $R_2$
**a** H
**b** SMe
**c** $SCH_2CH_2S$
**d** benzo

## Results and Discussion

### Molecular Orbital Calculations

First of all, it is important to determine the molecular structures for understanding physical properties of the donors **4** and **5**. Unfortunately, since single crystals suitable for X-ray analysis could not be obtained, no crystallographic data are available. Thus, MNDO-PM3[15] molecular orbital calculations were performed on **4a** to optimize the structure. Because of the conformational flexibility of the molecule, the calculations started from several possible conformations. According to the calculations, the most stable conformer takes a nonplanar conformation, in which one dithiafulvenyl unit is orthogonal to a plane formed by 2,5-bis(dithiafulvenyl)thiophene moiety [Figure 1 (a)]. The atomic orbital coefficients in the HOMO and next-HOMO are shown in Figure 1 (b). While the HOMO is restricted within the 2,5-bis(dithiafulvenyl)thiophene skeleton, the next-HOMO is localized on the dithiafulvenyl unit. These results suggest that each unit acts as an independent system. The HOMO energy level (–7.86 eV) of **4** is close to that of TTF (–7.99). Thus the donor is expected to show the electron-donating ability comparable to TTF.



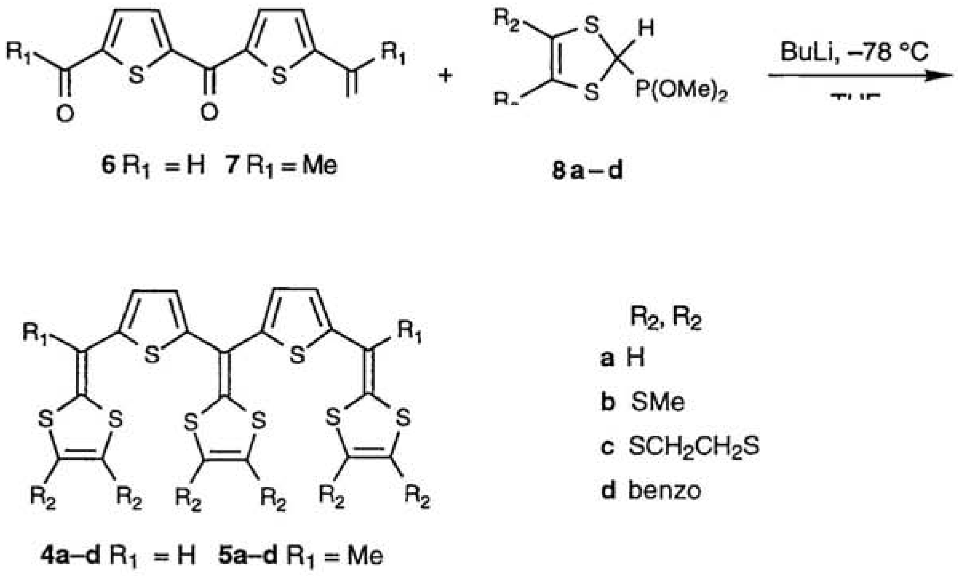
HOMO: –7.86 eV

next-HOMO: –8.17 eV

**Figure 1**. Results of MNDO-PM3 calculations. (a) Optimized structure of the donor **4a**. (b) Atomic orbital coefficients in the HOMO and next-HOMO.

## Preparation and Characterization of Donors

Carbonyl compounds **6** and **7**[16] and phosphonium esters **8a–d**[17] were prepared by reported methods. The donors **4a–d** and **5a–d** were synthesized by a Wittig–Horner reaction of the corresponding carbanions derived from **8** with aldehyde **6** or ketone **7** in 27–72% yields, as shown in Scheme 1. The donors are air-stable yellow or orange crystals. The structures of the new compounds were determined on the basis of the $^1$H and $^{13}$C NMR spectra, mass spectra, and elemental analyses. The solubility of the donors in common solvents is slightly low except for the methylthio derivatives.



**6** R₁ = H **7** R₁ = Me

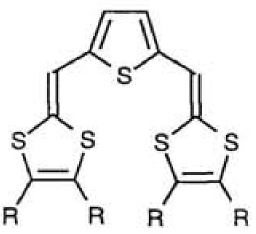
**8a–d**

**4a–d** R₁ = H **5a–d** R₁ = Me

R₂, R₂
**a** H
**b** SMe
**c** SCH₂CH₂S
**d** benzo

**Scheme 1**

The absorption maxima of the donors **4** and **5** in dichloromethane are summarized in Table 1, and the spectrum of **4a** is shown in Figure 2. These values are comparable to those of the related donors **9**[18-20] which are components of **4** and **5**. This fact suggests that the conformation of the molecules in solution are similar to the structure predicted by the MO calculations. The methyl substituents on the C6-carbons of the dithiafulvenyl groups make the absorption slightly blue-shifted. Observation of vibronic fine structures in the spectra of **4a,d** and **5a,d** suggests the rigid structures of the donors in the solution state.[21]



R, R = H, benzo

**9**

**Table 1.** Absorption maxima of the donors **4** and **5**.[a]

| Donor | $R_2$ | $\lambda_{max}$ / nm | Donor | $R_2$ | $\lambda_{max}$ / nm |
|---|---|---|---|---|---|
| **4a** | H | 425, 448 | **5a** | H | 399, 421 |
| **4b** | SMe | 432 | **5b** | SMe | 424 |
| **4c** | $SCH_2CH_2S$ | 439, 464 | **5c** | $SCH_2CH_2S$ | 432 |
| **4d** | benzo | 399, 420, 442 | **5d** | benzo | 393, 415 |

[a] In dichloromethane.

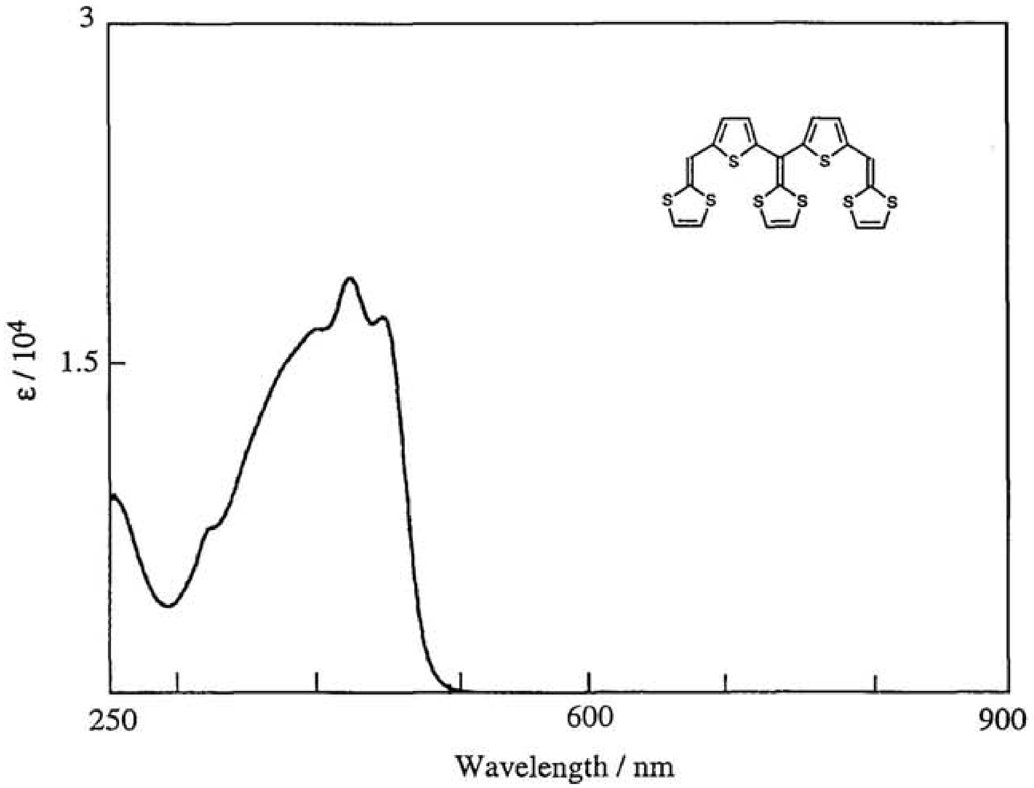


**Figure 2.** Absorption spectrum of the donor **4a** in dichloromethane.

**Electrochemical Properties**

In order to investigate the electrochemical properties of the new donors, cyclic voltammograms (CV) were measured at a Pt disk as a working electrode, in benzonitrile containing 0.1 mol $dm^{-3}$ of tetrabutylammonium tetrafluorobrate as a supporting electrolyte, and with a scan rate of 100 mV $s^{-1}$. The data are summarized in Table 2. The donors **4** and **5** showed two and three pairs of redox waves, respectively, as shown in Figure 3. For both cases, the last steps are irreversible processes. Since the first waves were resolved into nearly overlapped two waves in dichloromethane for **4c,d** and **5c,d**, they can be assigned to two-electron oxidation processes. Thus, the donors **4** and **5** are oxidized to trication radicals and tetracations, respectively. The presence of the third waves in the CVs of **5** indicates that the methyl substituents on the C6-carbons of the dithiafulvenyl groups stabilize the trication radical states.

**Table 2.** Oxidation potentials of the donors **4** and **5**.[a]

| Donor | $R_1$ | $R_2$ | $E_1{}^b$ | $E_2$ | $E_3$ |
|---|---|---|---|---|---|
| **4a** | H | H | 0.48 | $0.82^c$ | – |
| **4b** | H | SMe | 0.58 | $0.92^c$ | – |
| **4c** | H | $SCH_2CH_2S$ | 0.58 | $0.91^c$ | – |
| **4d** | H | benzo | 0.66 | $1.02^c$ | – |
| **5a** | Me | H | 0.50 | 0.88 | $1.22^c$ |
| **5b** | Me | SMe | 0.59 | 0.90 | $1.18^c$ |
| **5c** | Me | $SCH_2CH_2S$ | 0.59 | 0.92 | $1.22^c$ |
| **5d** | Me | benzo | 0.68 | 1.04 | $1.30^c$ |

[a] $Bu_4NBF_4$ (0.1 mol $dm^{-3}$) in PhCN, Pt electrode, scan rate 100 mV $s^{-1}$, *E*/V *vs.* saturated calomel electrode (SCE). [b] Two-electron process. [c] Irreversible wave.

The first oxidation potential of the parent donor **4a** is comparable to that of TTF ($E_{1/2}{}^1 = 0.45$, $E_{1/2}{}^2 = 0.86$ V *vs.* SCE in PhCN). This fact is consistent with the results of the MO calculations. The coalescence of the two one-electron processes indicates the

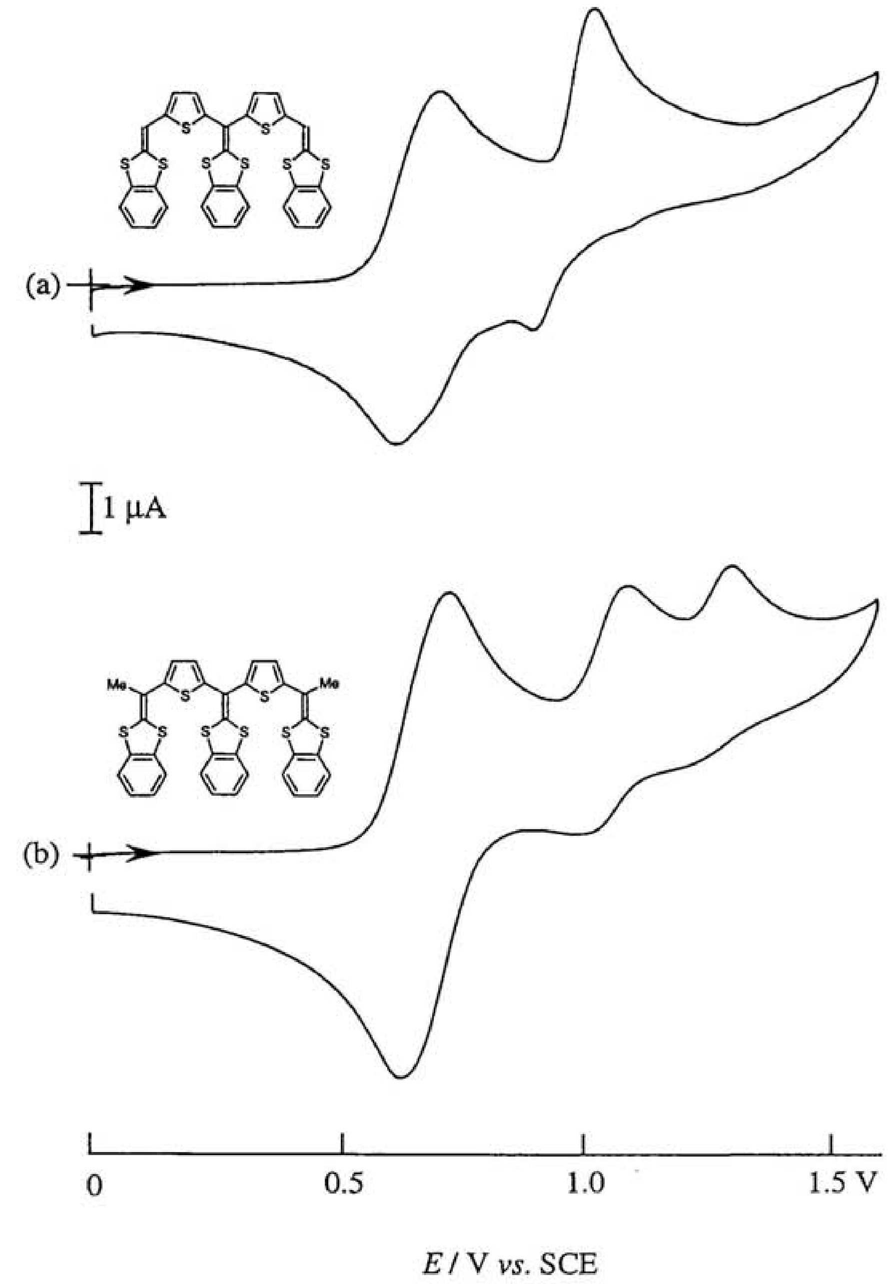
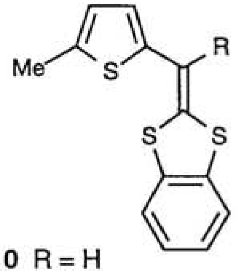


**Figure 3**. Cyclic voltammograms of the donors (a) **4d** and (b) **5d** in benzonitrile.

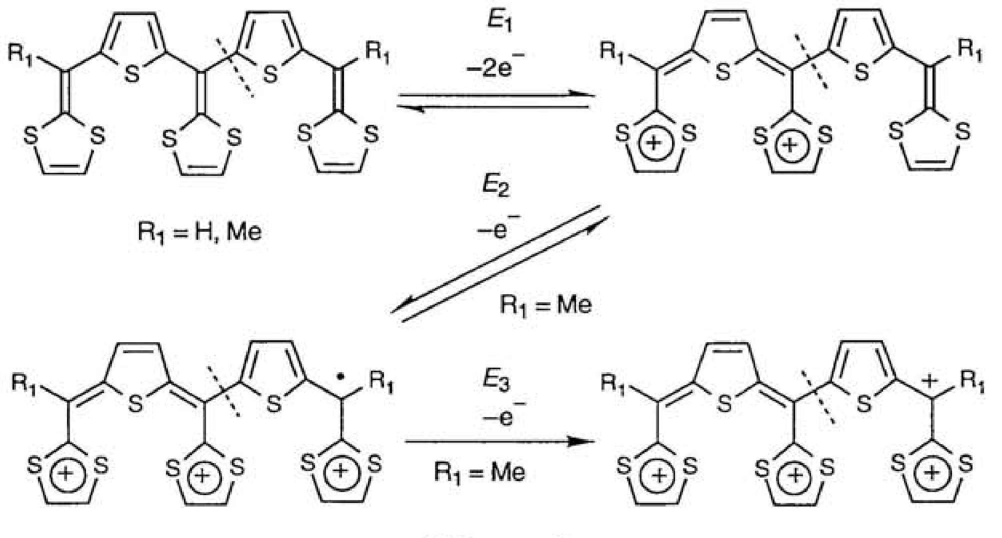
reduced intramolecular Coulombic repulsion in the dication states. These features of the first waves are similar to the redox behavior of the 2,5-bis(1,4-dithiafulven-6-yl)thiophene **9** (R = H), which shows a one-stage two-electron wave at the half-wave potential of 0.40 V *vs.* SCE in MeCN.[20] These facts suggest that the first redox waves for **4** and **5** are due to the 2,5-bis(dithiafulvenyl)thiophene moiety. The other waves can be attributed to the redox reaction of the thienyldithiafulvenyl subunit.

In order to confirm the above interpretation, the redox behavior of thienyldithiafulvene derivatives **10**[22] and **11** was examined. The methyl group was introduced to protect the reactive α-position of the thiophene ring. The CVs of **10** and **11** are shown in Figure 4. The shapes of the redox waves of **10** and **11** closely resemble those of the second and third (for **5**) waves of the corresponding donors **4** and **5**, although the oxidation potentials are negatively shifted. Therefore, it is concluded that the redox behavior of the donors **4** and **5** is explained by the combination of the independent 2,5-bis(dithiafulvenyl)thiophene and thienyldithiafulvene moieties. Scheme 2 shows a summary of the redox behavior of the donors **4** and **5**.



**10** R = H

**11** R = Me



**Scheme 2**

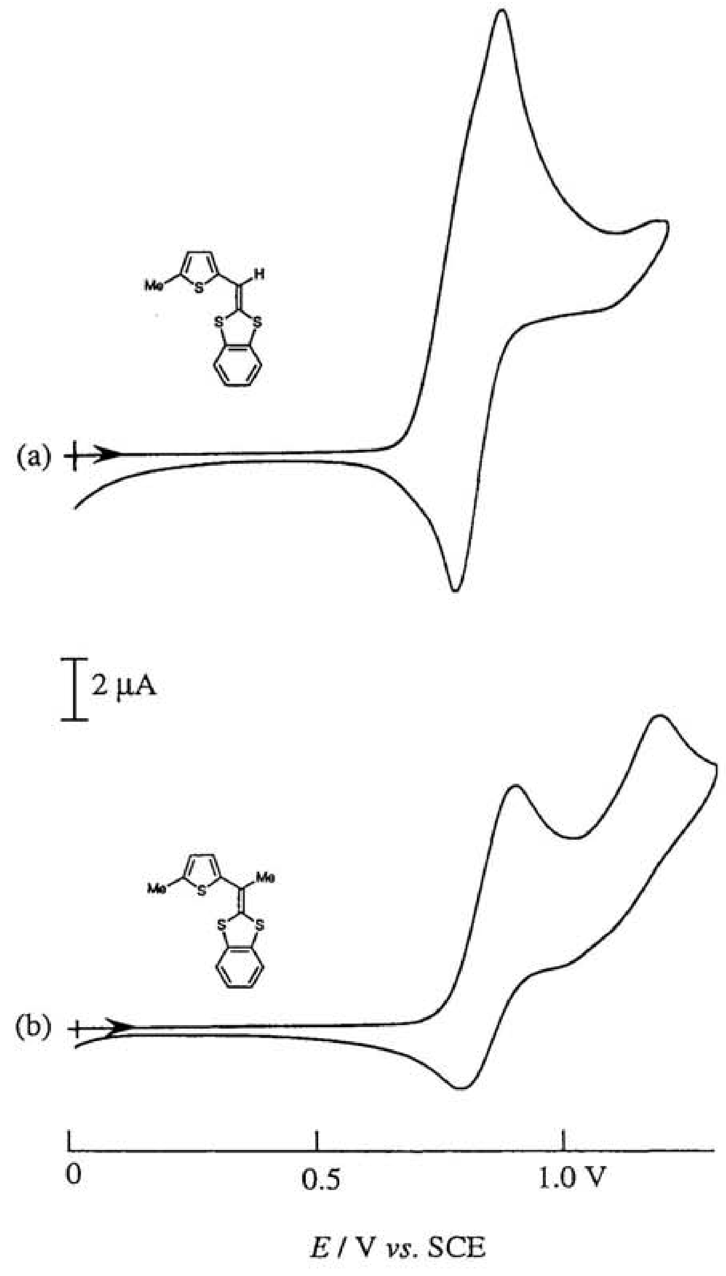
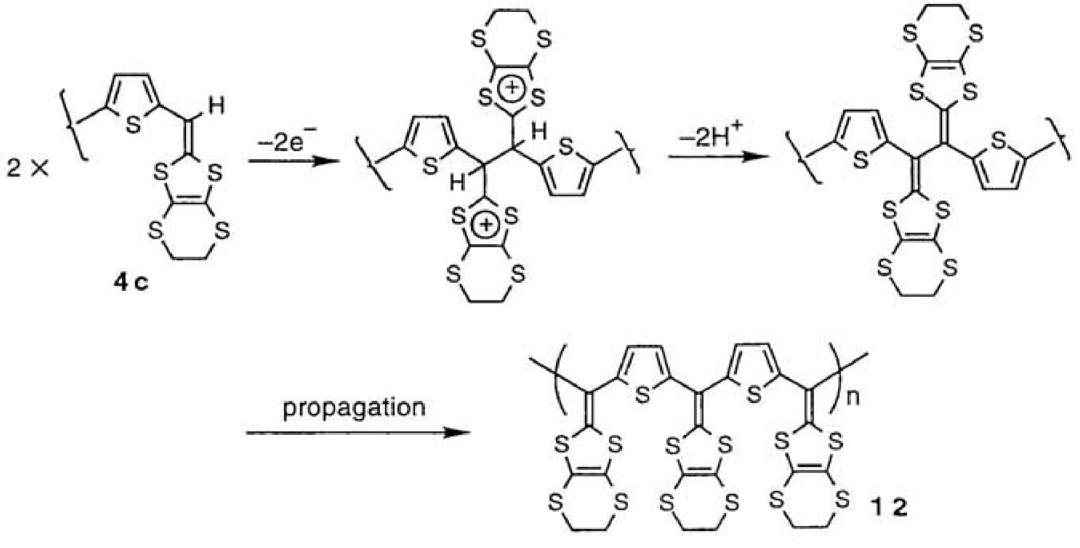


**Figure 4**. Cyclic voltammograms of the compounds (a) **10** and (b) **11** in benzonitrile.

## Formation of Polymer

In the case of **4c**, when dichloromethane was used as a solvent on the CV measurement, the peak current increased steadily with the repetition of scans as shown in Figure 5 (a). This observation indicates that an electroactive polymer was formed on the surface of the electrode. The possible structure **12** and a mechanism for the formation of the polymer is shown in Scheme 3. The other donors did not give any polymers under the same conditions. A similar electrochemical behavior of an extended 1,3-dithiole donor was reported recently.[23] Since the peak current of the polymer is proportional to the scan rate [figure 5 (b)], the electrode reactions of the films are phenomenologically equivalent to that of a surface-attached redox species.[24] The oxidation peak potential (0.85 V *vs.* SCE in $CH_2Cl_2$, at Pt) of the polymer is higher than that of the monomer **4c** ($E_1$: 0.58 V). This fact indicates that π-conjugation dose not extend efficiently along the polymer chain probably due to steric interactions. The neutral polymer film grown on an indium-tin oxide (ITO) glass electrode showed a broad absorption, which is almost superimposable with that of the monomer **4c** on ITO (Figure 6). This fact indicates that interactions between the monomer units in the polymer chain are small. An additional broad peak was observed at 786 nm in the doped state. This spectral change was reversible.



Scheme 3

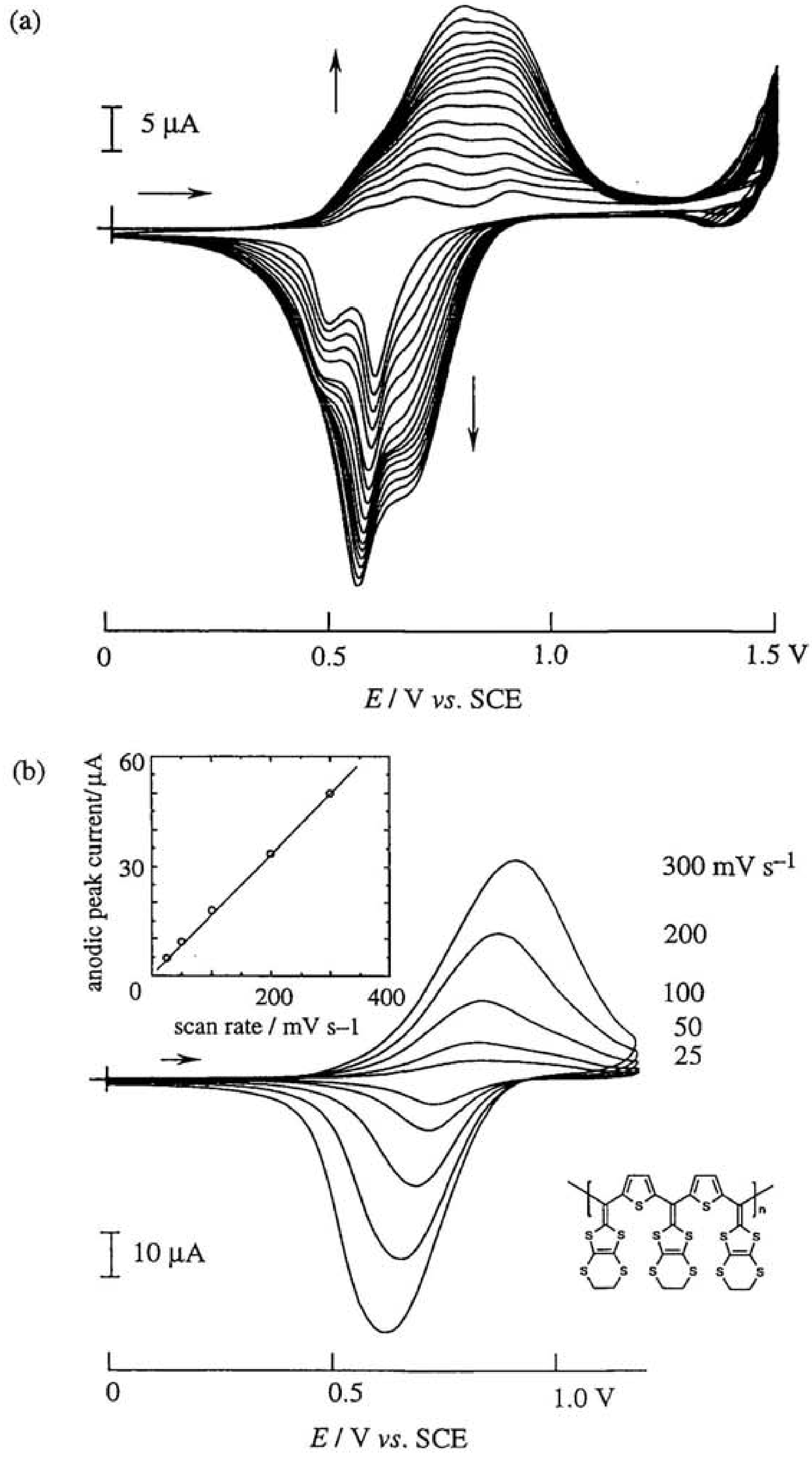


**Figure 5**. (a) Successive cyclic voltammograms of **4c** in dichloromethane. (b) Cyclic voltammograms of the polymer **12** at various scan rates in dichloromethane. The insert shows the dependence of $i_{pa}$ on scan rate.

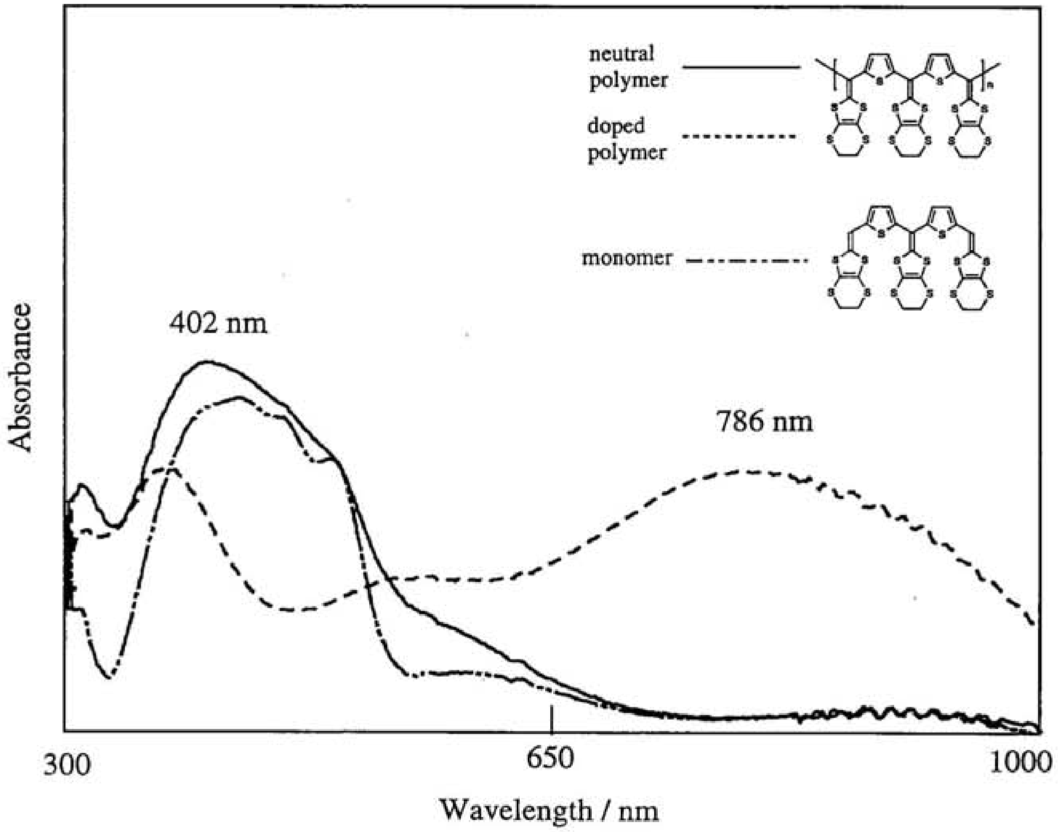


**Figure 6**. Absorption spectra of the neutral polymer **12** (—), doped polymer (---), and monomer **4c** (–··) on ITO glass.

## Charge-Transfer Complexes

The donors afforded conductive charge-transfer complexes with iodine except for **4b**. The conductivities measured on compressed pellets by a two-probe method and the component ratios determined by elemental analyses are summarized in Table 3. The complexes show moderate conductivities of *ca.* $10^{-2}$ S $cm^{-1}$ except for the complex of **5b**. It should be noted that the nonplanar donors such as **4** and **5** afford conducting complexes. On the other hand, no tetracyanoquinodimethane complex was obtained probably due to the unfavorable nonplanarity for molecular packing and the high oxidation potentials of the donors.

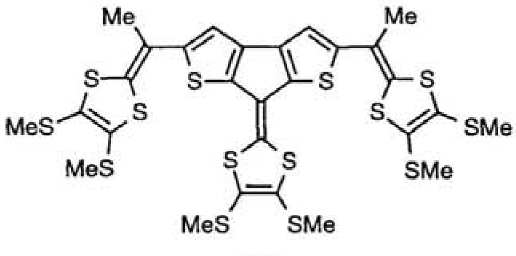
**Table 3**. Conductivities and component ratios of the iodine complexes.

| Donor | $R_1$ | $R_2$ | I / Donor[a] | $\sigma$ / S $cm^{-1}$[b] |
|---|---|---|---|---|
| **4a** | H | H | 3.5 | $2.9 \times 10^{-2}$ |
| **4b** | H | SMe | – | – |
| **4c** | H | $SCH_2CH_2S$ | 2.7 | $7.2 \times 10^{-2}$ |
| **4d** | H | benzo | 3.4 | $1.1 \times 10^{-2}$ |
| **5a** | Me | H | 3.2 | $5.1 \times 10^{-2}$ |
| **5b** | Me | SMe | 5.6 | $8.3 \times 10^{-5}$ |
| **5c** | Me | $SCH_2CH_2S$ | 4.2 | $2.9 \times 10^{-2}$ |
| **5d** | Me | benzo | 3.3 | $1.9 \times 10^{-2}$ |

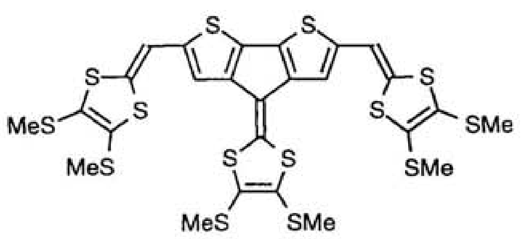
[a] Determined on the basis of elemental analyses. [b] Measured on compressed pellets by a two-probe technique at room temperature.

## Structural Modification of Donors

Next, the author investigated the redox properties of another tris(1,3-dithiole) donor **13** containing a cyclopentadithiophene moiety since the molecule is considered to have a planar structure which seems to reflect in the electron-donating ability. Very recently a closely related donor **14** has been reported as a model of thiophene oligomer with small bandgap.[25] The donor **14** showed both oxidation and reduction waves in the cyclic voltammogram, and the difference between the oxidation and reduction potentials was 1.08 V in dichloromethane.

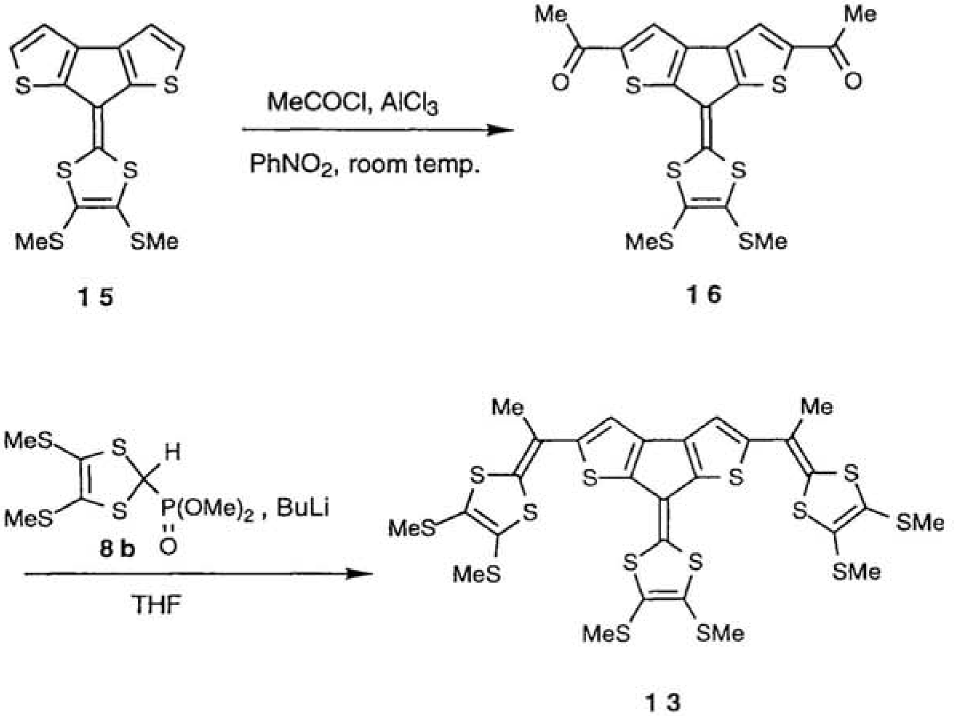


**13**



**14**

The donor **13** was synthesized according to Scheme 4. A diketone **16** was prepared by Friedel–Crafts acetylation of a 1,3-dithiole compound **15**[26] with acetyl chloride and aluminium chloride in nitrobenzene (96%). A Wittig–Horner reaction of **16** with the phosphonate ester **8b** afforded the tris(1,3-dithiole) donor **13** as a deep red solid in 42% yield. The structure of the donor **13** was determined on the basis of the $^1$H NMR and FAB-mass spectra.



**Scheme 4**

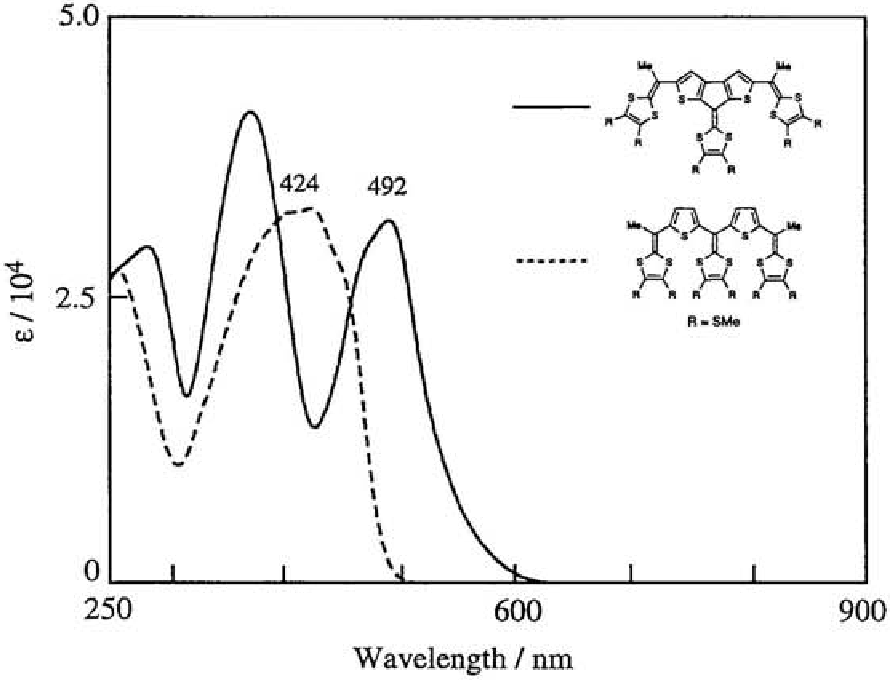


**Figure 7.** Absorption spectra of the donors **13** (—) and **5b** (---) in dichloromethane.

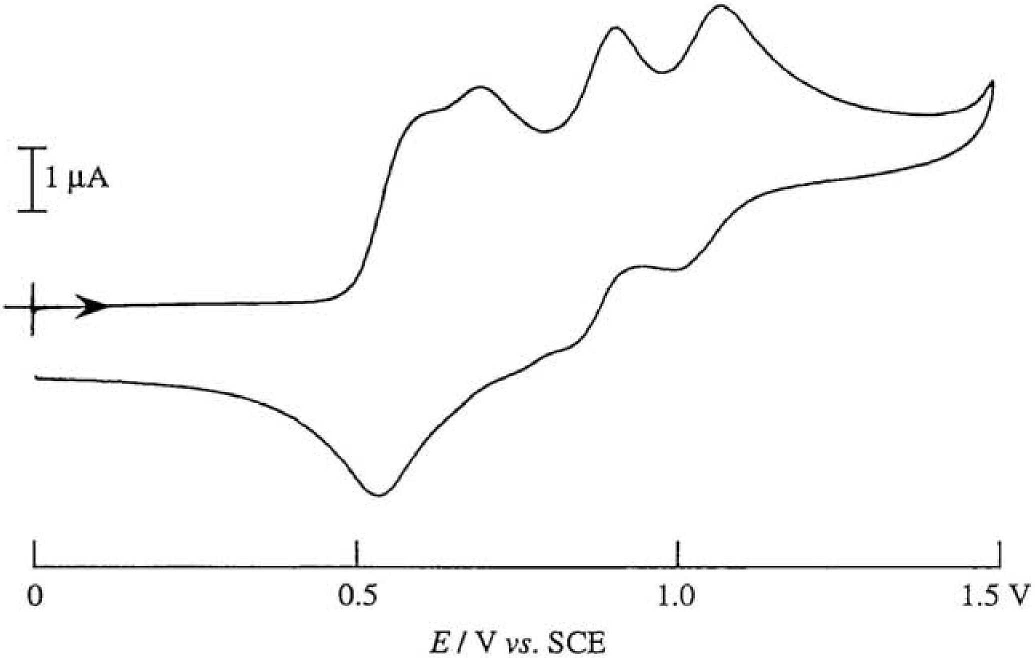


**Figure 8.** Cyclic voltammogram of the donor **13** in benzonitrile.

Figure 7 shows the absorption spectra of the donors **13** and **5b** in dichloromethane. The longest absorption maxima (492 nm) is red-shifted by *ca.* 70 nm compared with that of **5b** ($\lambda_{max} = 424$ nm), indicating a polarized structure of **13**. The CV of the donor showed four oxidation waves at peak potentials of $E_1$, 0.59; $E_2$, 0.69; $E_3$, 0.88; and $E_4$, 1.05 V *vs.* SCE (Figure 8). Taking into account the $i_{pa}$ value for $E_1$, the first wave seems to correspond to a two-electron process. The first oxidation potential of **13** is comparable to that of the donor **5b** in spite of the improvement of planarity. This fact can be attributed to the electron-accepting property of the cyclopentadienylidene moiety.

## Conclusion

Novel tris(1,3-dithiole) donors **4** and **5** containing thiophene spacer units were synthesized by using a Wittig–Horner reaction. MNDO-PM3 calculations indicated nonplanar structures of the donors. The cyclic voltammograms of the donors reveal that they undergo multistage redox reactions to yield trication radical or tetracation species and on-site Coulombic repulsion in the dication state is reduced. The cyclic voltammetric behavior of the donors were explained by the combination of the isolated 2,5-bis(1,4-dithiafulvenyl)thiophene and thienyldithiafulvene moieties. The electron-donating ability of the donors are comparable to that of TTF. The donors gave conductive charge-transfer complexes with iodine. A novel type of redox active polymer **12** was formed from the ethylenedithio derivative **4c** and its redox and optical properties were discussed. Moreover, a tris(1,3-dithiole) donor **13** containing a cyclopentadithiophene moiety was also prepared. The donor **13** showed multistage redox behavior in the CV.

## Experimental

**General**. Melting points were measured on a Yanaco MP-500D melting point apparatus and are uncorrected. IR and UV spectra were recorded on a Perkin-Elmer FTIR 1600 and a Shimadzu UV-3101PC spectrometer, respectively. Unless otherwise stated, $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were measured on a JEOL JNM-GX400 spectrometer. 270 MHz $^1$H and 67.8 MHz $^{13}$C NMR spectra were measured on a JEOL JNM-EX270 spectrometer. EI (70 eV) and FAB (Xe, 7kV) mass spectra were measured on a Shimadzu GCMS-QP1000EX and a Shimadzu Kratos CONCEPT 1S spectrometer, respectively. Elemental analyses were performed on a Yanaco MT-3 CHN CORDER. Chromatographic separations were performed with Merk aluminium oxide 90 (activity II to III). Yields are based on isolated products with sufficient purity. Tetrahydrofuran was distilled over lithium aluminium hydride prior to use.

**Electrochemical Measurements**. Cyclic voltammetry experiments were performed in a three-compartment cell with a Pt disc working electrode, Pt wire counter electrode, and saturated calomel reference electrode. Measurements were made with a Toho Technical Research Polarization Unit PS-07 potentiostat / galvanostat with a scan rate of 100 mV $s^{-1}$. The cell contained a solution of a substrate (*ca.* 1 mmol $dm^{-3}$) and tetrabutylammonium tetrafluoroborate (0.1 mol $dm^{-3}$) as supporting electrolyte in benzonitrile or dichloromethane. All solutions were purged with argon and retained under the inert atmosphere during the experiment.

**Computational Studies**. MNDO-PM3 calculations were performed by using the MOPAC version 6.10 program.[15] The calculations were carried out using the Sony-Tektronix CAChe system.

**6,6-Bis[5-(1,4-dithiafulven-6-yl)-2-thienyl]-1,4-dithiafulvene (4a)**. A solution of butyllithium in hexane (1.6 mol $dm^{-3}$, 1.3 ml, 2.1 mmol) was added to a solution of phosphonate ester **8a**[17] (403 mg, 1.9 mmol) in THF (10 ml) at –78 °C under argon. After stirring for 15 min, the aldehyde **6**[16] (100 mg, 0.4 mmol) was added to the mixture. The mixture was stirred for 2 h at –78 °C and allowed to warm to room temperature. To the reaction mixture was added water (50 ml), and the product was extracted with dichloromethane. The extract was washed with water and dried over $Na_2SO_4$, and concentrated under reduced pressure to give the donor **4a** (55 mg, 27%) as yellow plates (from $CS_2$–hexane): mp 206–207 °C; IR (KBr) 3065, 1066, 1052, 812, 646 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 6.36$ (4H, s, dithiole-H), 6.41 (2H, s, dithiole-H), 6.73 (2H, s, =CH), 6.81 (2H, d, $J = 3.7$ Hz, Th-H), 6.90 (2H, d, $J = 3.7$ Hz, Th-H); $^{13}C$ NMR (DMSO-$d_6$) $\delta = 106.07$, 119.06, 119.49, 119.99, 120.00, 123.65, 126.53, 135.20, 139.21, 140.60, 140.83; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 425 (4.28), 448 (4.23) nm; FAB–MS *m/z* 508 ($M^+$); Found: C, 47.04; H, 2.49%. Calcd for $C_{20}H_{12}S_8$: C, 47.21; H, 2.38%.

The other donors were synthesized by the similar method. In the cases of **4c,d** and **5c,d** the products were isolated by addition of water to the reaction mixture. The data are as follows.

**4b**: 69%; yellow needles (from $CHCl_3$–hexane); mp 147–148 °C; IR (KBr) 2916, 1563, 1498, 1418, 798, 770 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.42$ (6H, s, SMe), 2.43 (6H, s, SMe), 2.44 (6H, s, SMe), 6.64 (2H, s, =CH), 6.80 (2H, d, $J = 4.0$ Hz, Th-H), 6.89 (2H, d, $J = 4.0$ Hz, Th-H); $^{13}C$ NMR ($CDCl_3$) $\delta = 18.96$, 19.09, 108.16, 112.72, 123.99, 125.30, 127.20, 127.47, 127.87, 130.81, 134.27, 140.57, 141.00; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 432 (4.56), 455 (4.51, sh) nm; FAB–MS *m/z* 784 ($M^+$); Found: C, 39.64; H, 3.06%. Calcd for $C_{26}H_{24}S_{14}$: C, 39.76; H, 3.08%.

**4c**: 54%; orange needles (from toluene); mp 206–208 °C (decomp.); IR (KBr) 2916, 1561, 1516, 1286, 919, 815 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 3.31$ (4H, s, $SCH_2CH_2S$), 3.32 (8H, s, $SCH_2CH_2S$), 6.67 (2H, s, =CH), 6.78 (2H, d, $J = 3.8$ Hz, Th-H), 6.87 (2H, d, $J = 3.8$ Hz, Th-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 439 (4.53), 464

(4.51) nm; FAB–MS *m/z* 778 ($M^+$); Found: C, 40.39; H, 2.51%. Calcd for $C_{26}H_{18}S_{14}$: C, 40.26; H, 2.33%.

**4d**: 72%; yellow needles (from $CS_2$–hexane); mp 272–273 °C IR (KBr) 3051, 1573, 1553, 1448, 1434, 1290, 1122, 739 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 6.75$ (2H, s, =CH), 6.91 (2H, d, $J = 4.0$ Hz, Th-H), 7.00 (2H, d, $J = 4.0$ Hz, Th-H), 7.12–7.16 (6H, m, benzo-H), 7.24–7.32 (6H, m, benzo-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 399 (4.59), 420 (4.63), 442 (4.57) nm; FAB–MS *m/z* 658 ($M^+$); Found: C, 58.21; H, 2.99%. Calcd for $C_{32}H_{18}S_8$: C, 58.32; H, 2.75%.

**5a**: 26%; yellow solid (from $CHCl_3$–hexane); mp 164–165 °C; IR (KBr) 3059, 1552, 1514, 1430, 792, 650 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta = 2.20$ (6H, s, Me), 6.38–6.43 (4H, AB system, dithiole-H), 6.39 (2H, s, dithiole-H), 6.92 (2H, d, $J = 4.0$ Hz, Th-H), 6.98 (2H, d, $J = 4.0$ Hz, Th-H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) $\delta = 23.69$, 111.43, 112.67, 117.93, 118.83, 119.03, 122.88, 126.45, 131.52, 138.65, 140.99, 144.10; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 399 (4.37), 421 (4.40) nm; MS *m/z* (rel intensity) 536 ($M^+$, 76), 217 (32), 166 (29), 103 (97), 58 (100); Found: C, 49.10; H, 3.07%. Calcd for $C_{22}H_{16}S_8$: C, 49.21; H, 3.00%.

**5b**: 54%; yellow needles (from $CHCl_3$–hexane); mp 145–147 °C; IR (KBr) 2917, 1546, 1498, 1426, 898, 794, 769 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.16$ (6H, s, Me), 2.42 (6H, s, SMe), 2.43 (6H, s, SMe), 6.90 (2H, d $J = 4.0$ Hz, Th-H), 6.94 (2H, d $J =$ 4.0 Hz, Th-H); $^{13}C$ NMR ($CDCl_3$) $\delta = 18.96$, 19.00, 22.52, 112.60, 114.36, 123.60, 126.80, 126.92, 127.00, 127.14, 124.47, 134.29, 140.33, 143.80; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 424 (4.53) nm; FAB–MS *m/z* 812 ($M^+$); Found: C, 41.27; H, 3.43%. Calcd for $C_{28}H_{28}S_{14}$: C, 41.34; H, 3.47%.

**5c**: 52%; orange solid (from $CS_2$–hexane); mp 245–246 °C (decomp.); IR (KBr) 1548, 1509, 1286, 776 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.18$ (6H, s, Me), 3.30 (4H, s,

$SCH_2CH_2S$), 3.32 (8H, s, $SCH_2CH_2S$), 6.88 (2H, d, $J$ = 4.0 Hz, Th-H), 6.92 (2H, d, $J$ = 4.0 Hz, Th-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 432 (4.14) nm; FAB–MS *m/z* 806 ($M^+$); Found: C, 41.44; H, 2.90%. Calcd for $C_{28}H_{22}S_{14}$: C, 41.65; H, 2.75%.

**5d**: 47%; yellow needles (from THF); mp 233–234 °C; IR (KBr) 1568, 1538, 1448, 1433, 1289, 1124, 741 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ = 2.28 (6H, s, Me), 7.01 (2H, d, $J$ = 4.0 Hz, Th-H), 7.09 (2H, d, $J$ = 4.0 Hz, Th-H), 7.11–7.14 (6H, m, benzo-H), 7.26–7.30 (6H, m, benzo-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 393 (4.56), 415 (4.56) nm; MS *m/z* (rel intensity) 686 ($M^+$, 100); Found: C, 59.65; H, 3.45%. Calcd for $C_{34}H_{22}S_8$: C, 59.43; H, 3.23%.

**2-[1-(5-methyl-2-thienyl)ethylidene]-1,3-benzodithiole (11).** A solution of butyllithium in hexane (1.6 mol $dm^{-3}$, 0.3 ml, 0.5 mmol) was added to a solution of 2-[1-(2-thienyl)ethylidene]-1,3-benzodithiole[22] (100 mg, 0.38 mmol) in THF (10 ml) at –78 °C under argon. After stirring for 30 min, methyl iodide (0.5 ml, 8.0 mmol) was added to the solution. The mixture was stirred at –78 °C for 30 min and allowed to warm to room temperature. The solvent was removed under reduced pressure. To the residue was added water, and the product was extracted with dichloromethane. The extract was concentrated, and the residue was triturated with hexane to give the compound **11** (81 mg, 77%) as pale yellow plates (from hexane): mp 66–67 °C; IR (KBr) 3056, 1568, 1537, 1448, 1432, 1290, 1262, 1126, 1029, 784, 736, 696 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ = 2.20 (3H, s, =CMe), 2.49 (3H, d, $J$ = 1.0 Hz, Th-Me), 6.71 (1H, dd, $J$ = 3.6 and 1.0 Hz, Th-H), 6.89 (1H, d, $J$ = 3.6 Hz, Th-H), 7.07–7.12 (2H, m, benzo-H), 7.21–7.27 (2H, m, benzo-H); MS *m/z* (rel intensity) 276 ($M^+$, 100), 153 (27).

**Iodine complex of 4a**: A solution of iodine (13 mg, 0.051 mmol) in dichloromethane (10 ml) was added to a solution of the donor **4a** (25 mg, 0.049 mmol) in dichloromethane (20 ml). The resulting solid was collected by filtration and washed with dichloromethane to give the complex (18 mg): black solid; mp >300 °C; Found: C, 25.22; H, 1.39%. Calcd for $C_{20}H_{12}S_8I_{3.5}$: C, 25.21; H, 1.27%.

The other iodine complexes of **4c,d** and **5a–d** were prepared by the similar procedure. The data are as follows.

**Iodine complex of 4c**: black solid; mp >300 °C; Found: C, 27.77; H, 1.61%. Calcd for $C_{26}H_{18}S_{14}I_{2.7}$: C, 27.83; H, 1.62%.

**Iodine complex of 4d**: black solid; mp 195–200 °C; Found: C, 35.09; H, 1.89%. Calcd for $C_{32}H_{18}S_8I_{3.4}$: C, 35.24; H, 1.66%.

**Iodine complex of 5a**: black solid; mp >300 °C; Found: C, 28.18; H, 1.82%. Calcd for $C_{22}H_{16}S_8I_{3.2}$: C, 28.02; H, 1.71%.

**Iodine complex of 5b**: black solid; mp 124–126 °C; Found: C, 22.08; H, 1.82%. Calcd for $C_{28}H_{28}S_{14}I_{5.6}$: C, 22.06; H, 1.85%.

**Iodine complex of 5c**: black solid; mp >300 °C; Found: C, 25.06; H, 1.70%. Calcd for $C_{28}H_{22}S_{14}I_{4.2}$: C, 25.09; H, 1.65%.

**Iodine complex of 5d**: black solid; mp 203–205 °C; Found: C, 36.75; H, 2.13%. Calcd for $C_{34}H_{22}S_8I_{3.3}$: C, 36.93; H, 2.00%.

**2,5-Diacetyl-7-(4,5-dimethylthio-1,3-dithiol-2-ylidene)-7*H*-cyclopenta[1,2-b;4,3-b']dithiophene (16)**. Acetyl chloride (0.10 ml, 1.41 mmol) was added to a suspension of aluminium chloride (160 mg, 1.20 mmol) in nitrobenzene (10 ml) at room temperature. After stirring for 5 min, the 1,3-dithiole compound **15**[26] in nitrobenzene (5 ml) was added to the mixture over a period of 10 min. The mixture was stirred for 5 h at room temperature and poured into ice-water (50 ml). The product was extracted with dichloromethane, and the extract was washed with water, dried over $Na_2SO_4$, and concentrated under reduced pressure. To the residue was added hexane, and the resulting solid was collected by filtration to give the ketone **16** (176 mg, 96%): dark orange needles (from $CHCl_3$/MeCN); mp 291–293 °C; IR (KBr) 1645 (C=O), 1525, 1461, 1421, 1346, 1313, 1265 cm$^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) $\delta = 2.59$ (6H, s, SMe), 2.60 (6H, s, COMe), 7.69 (2H, s, Th-H); MS *m/z* (rel intensity) 454 ($M^+$, 100), 439 (26), 406 (26), 304 (22), 289 (41), 261 (25), 217 (22), 175 (16), 135 (27), 91 (38).

**2,5-bis(6-methyl-2,3-dimethylthio-1,4-dithiafulven-6-yl)-7-(4,5-dimethylthio-1,3-dithiol-2-ylidene)-7*H*-cyclopenta[1,2-b;4,3-b']-dithiophene (13).** A solution of butyllithium in hexane (1.65 mol $dm^{-1}$, 0.18 ml, 0.30 mmol) was added to a solution of phosphonate ester **8b** (80 mg, 0.26 mmol), in THF (5 ml) at –78 °C under argon. After stirring for 10 min, the ketone **16** (50 mg, 0.11 mmol) was added to the solution. The solution was stirred for 20 min at –78 °C and allowed to warm to room temperature. The solvent was removed under reduced pressure. To the residue was added water, and the product was extracted with dichloromethane. The extract was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (alumina / dichloromethane) to give the tris(1,3-dithiole) donor **13** (38 mg, 42%) as a dark red solid: decomp.p. 190–200 °C; IR (KBr) 2915, 1561, 1484, 1370, 1310, 967, 894, 820 $cm^{-1}$; $^1H$ NMR (270 MHz, DMSO-$d_6$) $\delta = 2.19$ (6H, s, Me), 2.46, 2.49, and 2,59 (each 6H, s, SMe), 7.28 (2H, s, Th-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$ ) 283 (4.48), 372 (4.62), 492 (4.51) nm; FAB–MS *m/z* 810 ($M^+$).

## References

(1) M. A. Coffin, M. R. Bryce, A. S. Batsanov, and J. A. K. Howard, *J. Chem. Soc., Chem. Commun.*, **1993**, 552.

(2) Y. Misaki, Y. Matsumura, T. Sugimoto, and Z. Yoshida, *Tetrahedron Lett.*, **30**, 5289 (1989).

(3) T. Sugimoto, H. Awaji, Y. Misaki, Z. Yoshida, Y. Kai, H. Nakagawa, and N. Kasai, *J. Am. Chem. Soc.*, **107**, 5729 (1985).

(4) T. Sugimoto, Y. Misaki, Y. Arai, Y. Yamamoto, Z. Yoshida, Y. Kai, and N. Kasai, *J. Am. Chem. Soc.*, **110**, 628 (1988).

(5) T. Sugimoto, Y. Misaki, T. Kajita, Z. Yoshida, Y. Kai, and N. Kasai, *J. Am. Chem. Soc.*, **109**, 4106 (1987).

(6) Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.*, **27**, 1573 (1988).

(7) M. Sallé, A. Belyasmine, A. Gorgues, M. Jubault, and N. Soyer, *Tetrahedron Lett.*, **32**, 2897 (1991).

(8) M. Sallé, M. Jubault, A. Gorgues, K. Boubekeur, M. Fourmigué, P. Batail, and E. Canadell, *Chem. Mater.*, **5**, 1196 (1993).

(9) M. Sallé, A. J. Moore, M. R. Bryce, and M. Jubault, *Tetrahedron Lett.*, **34**, 7475 (1993).

(10) M. Adam, E. Fanghänel, K. Müllen, Y.-J. Shen, and R. Wegner, *Synth. Met.*, **66**, 275 (1994).

(11) M. Adam and K. Müllen, *Adv. Mater.*, **6**, 439 (1994).

(12) E. Aqad, J. Y. Becker, J. Bernstein, A. Ellern, V. Khodorkovsky, and L. Shapiro, *J. Chem. Soc., Chem. Commun.*, **1994**, 2775.

(13) Y. Misaki, K. Kawakami, T. Matsui, T. Yamabe, and M. Shiro, *J. Chem. Soc., Chem. Commun.*, **1994**, 459.

(14) Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, and S. Tanaka, *Angew. Chem., Int. Ed. Engl.*, **34**, 1222 (1995).

(15) J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209, 221 (1989).

(16) M. Ahmed and O. Meth-Cohn, *J. Chem. Soc. (C)*, **1971**, 2104.

(17) K. Akiba, K. Ishikawa, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2674 (1978).

(18) T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. E. Niziurski-Mann, F. Jensen, and J. Becher, *J. Am. Chem. Soc.*, **114**, 5035 (1992).

(19) A. S. Benahmed-Gasmi, P. Frère, B. Garrigues, A. Gorgues, M. Jubault, R. Carlier, and F. Texier, *Tetrahedron Lett.*, **43**, 6457 (1992).

(20) K. Takahashi, T. Nihira, M. Yoshifuji, and K. Tomitani, *Bull. Chem. Soc. Jpn.*, **66**, 2330 (1993).

(21) J. Roncali, L. Rasmussen, C. Thobie-Gautier, P. Frère, H. Brisset, M. Sallé, J. Becher, O. Simonsen, T. K. Hansen, A. Benahmed-Gasmi, J. Orduna, J. Garin, M. Jubault, and A. Gorgues, *Adv. Mater.*, **6**, 841 (1994).

(22) A. Benahmed-Gasmi, P. Frère, J. Roncali, E. Elandaloussi, J. Orduna, J. Garin, M. Jubault, and A. Gorgues, *Tetrahedron Lett.*, **36**, 2983 (1995).

(23) M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson, and P. Batail, *J. Am. Chem. Soc.*, **115**, 3752 (1993).

(24) N. Oyama, T. Ohsaka, and H. Miyamoto, *Synth. Met.*, **28**, C193 (1989).

(25) H. Brisset, C. Thobie-Gautier, M. Jubault, A. Gorgues, and J. Roncali, *J. Chem. Soc., Chem. Commun.*, **1994**, 1765.

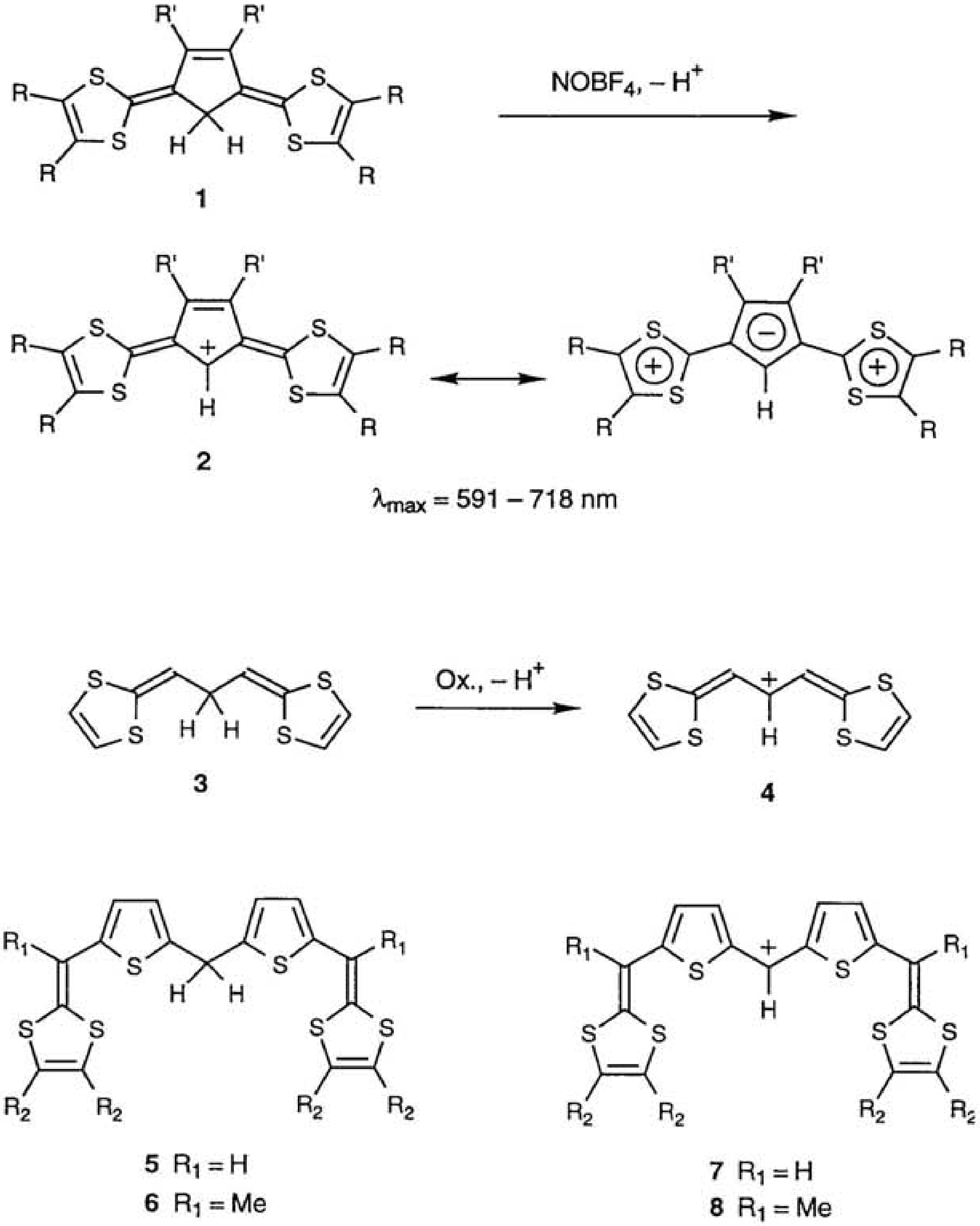
(26) M. Kozaki, S. Tanaka, and Y. Yamashita, *J. Org. Chem.*, **59**, 442 (1994).

# *Chapter 3 Preparation and Properties of Bis(1,3-dithiole) Compounds Containing Thienylmethylene Units*

## Introduction

On the development of organic conducting charge-transfer complexes or ion radical salts, the high stability of the ion radical species formed from their components is one of the most important requirements.[1] From this point of view, electron-donors or acceptors in which electron transfer is accompanied by chemical reactions have been considered quite useless. However, if the reaction processes and the resulting products can be identified properly, these compounds will be useful to explore the novel type of chemical reactions induced by electron transfer. In this connection, the author's research group reported that extended bis(1,3-dithiole) donors **1**, which showed irreversible redox waves in the cyclic voltammograms, underwent deprotonation by oxidation to give novel deeply-colored cations **2** (Scheme 1).[2]

A molecule **3** containing a methylene group adjacent to electron-donating moieties such as a 1,3-dithiole unit seems to undergo a similar reaction to give the corresponding methyl cation **4**. In order to prove the generality of this type of reaction and to apply it to the preparation of novel cations, the author designed bis(1,3-dithiole) compounds **5** and **6** containing a dithienylmethane unit. These systems are considered as vinylogues of the molecule **3** extended by two thiophene units. The resulting cations **7** and **8** are expected to be stabilized by electron-donating groups and to show interesting properties owing to their extended $\pi$-conjugation caused by the insertion of the thiophene units. In this chapter, the author describes the preparation, redox properties, and oxidation of **5** and **6**, and isolation and characterization of their oxidation products.

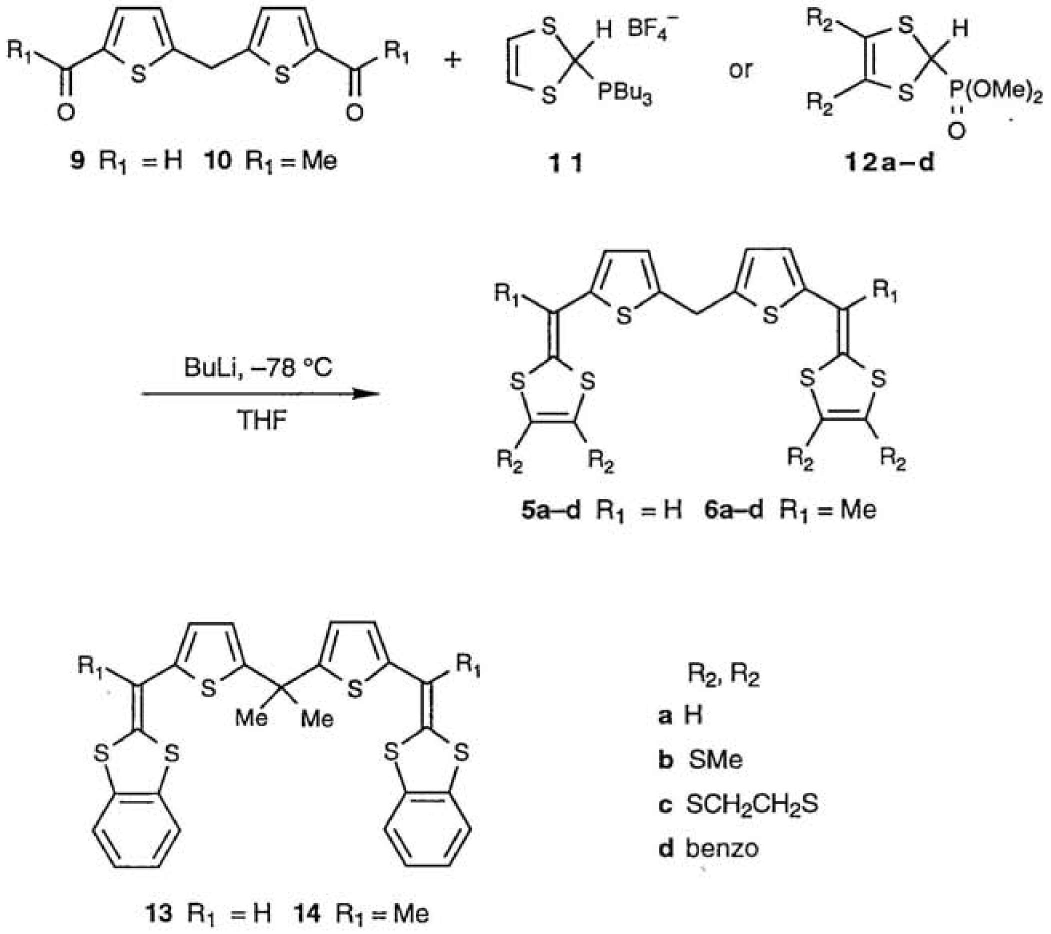


Scheme 1

## Results and Discussion

### Preparation of Bis[5-(1,4-dithiafulven-6-yl)-2-thienyl]methanes

Aldehyde **9** and ketone **10** were synthesized by reported methods.[3] The new 1,3-dithiole compounds **5** and **6** were prepared by either a Witttig reaction of phosphonium salt **11**[4] (for **5a**) or a Wittig-Horner reaction of phosphonate esters **12a–d**[5] with aldehyde **9** or ketone **10** in 47 to 94% yields (Scheme 2). For comparison, dimethyl derivatives **13** and **14** were synthesized by the similar method from the corresponding carbonyl compounds[3] in 65 and 69% yields, respectively. The structures of the new compounds were determined on the basis of the $^{1}$H and $^{13}$C NMR spectra, mass spectra, and elemental analyses.



**Scheme 2**

The X-ray molecular structure of the ethylenedithio derivative **6c** is shown in Figure 1. The two thiophene rings are orthogonal, while the thienyldithiafulvenyl subunits are nearly planar with the largest deviations of 0.39 and 0.63 Å from the mean planes. The interatomic distances between the sulfur atoms of the thiophene and the dithiole (3.01 and 3.02 Å) are shorter than the sum of the van der Waals radii (3.70 Å), indicating that there exist attractive interactions between them.[6]

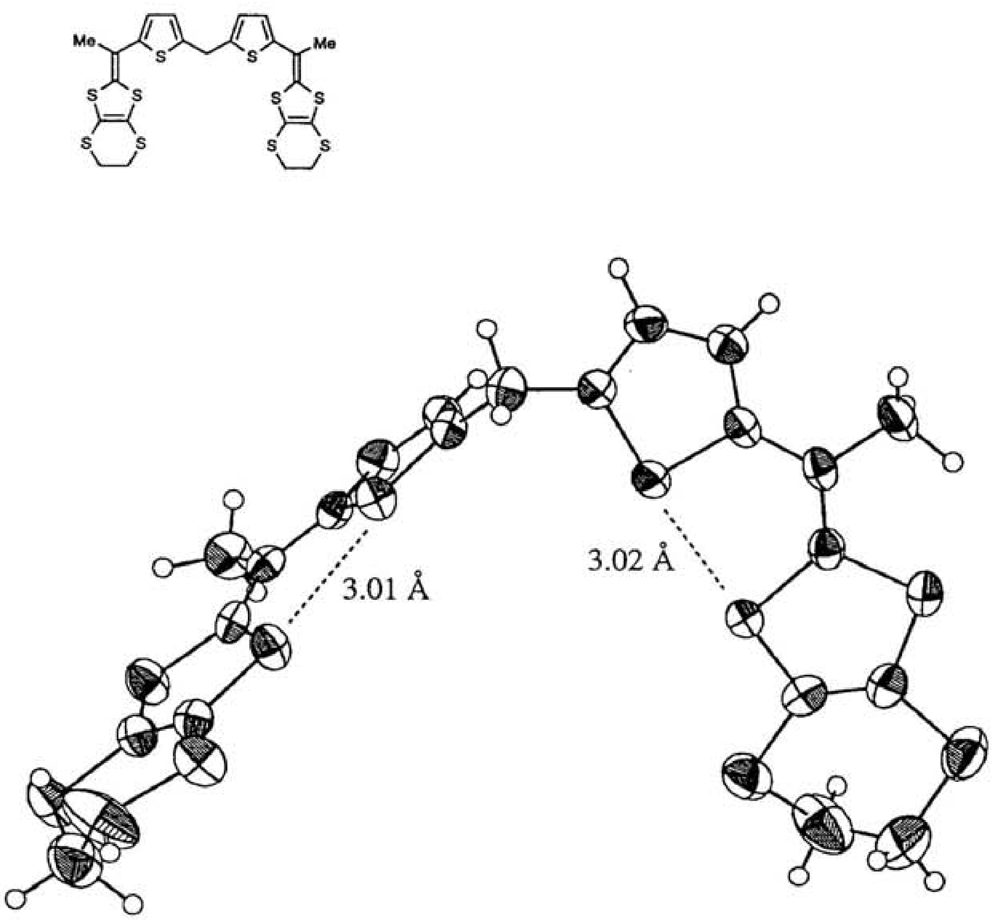


Figure 1. X-ray molecular structure of **6c**.

## Electrochemical Properties

In order to investigate the solution electrochemical behavior of the compounds **5** and **6**, cyclic voltammetry experiments were carried out. The redox potentials are summarized in Table 1. The typical examples of the cyclic voltammograms (CV) of **5d** and **6d** are shown in Figures 2 and 3 along with the corresponding dimethyl derivatives **13** and **14** for comparison. Both CVs of **5** and **6** showed irreversible oxidation waves at $E_{pa}$. In the reverse scan new reduction waves due to the oxidation products caused by subsequent chemical reactions were observed at lower potentials of $E_{pc}$(new). However, the shapes of the CVs were strongly dependent upon the substituents $R_1$ on the C6-carbons of the dithiafulvenyl groups. In the case of $R_1$ = H, both **5** and **13** exhibit almost the same cyclic voltammetric behavior. This means that the methyl groups on the central carbon atom don't affect the subsequent reaction. This result indicates that **5** do not undergo deprotonation by oxidation, but another reaction takes place. The details will be discussed later in this chapter (p. 49, *Formation of Oligomer*). On the other hand, the dimethyl derivative **14** showed a reversible redox wave in the potential rage of –0.5 to 1.10 V. Thus, it can be concluded that the new reduction peaks [$E_{pc}$(new)] observed in the CV of **6** correspond to the reduction of the cations **8** which arose from deprotonation subsequent to electrochemical oxidation of **5**.

**Table 1**. Redox potentials of the compounds **5** and **6**.[a]

| Compound | $E_{pa}$ | $E_{pc}$(new) | Compound | $E_{pa}$ | $E_{pc}$(new) |
|---|---|---|---|---|---|
| **5a** | 0.69 | –0.10 | **6a** | 0.82 | –0.13 |
| **5b** | 0.72 | –0.30 | **6b** | 0.82 | –0.04 |
| **5c** | 0.72 | –0.30 | **6c** | 0.82 | –0.05 |
| **5d** | 0.83 | –0.23 | **6d** | 0.93 | –0.08 |

[a] measured in benzonitrile.

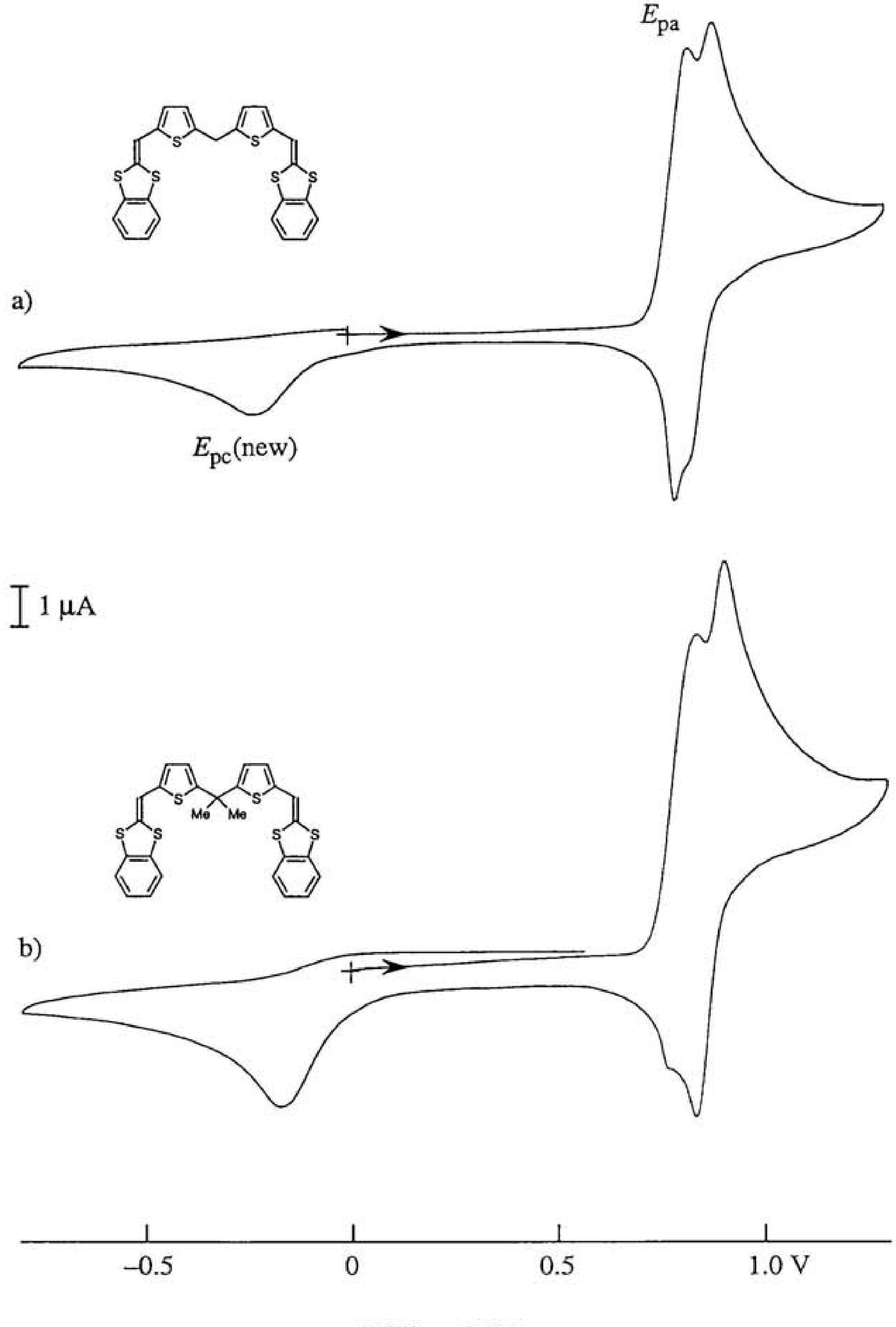


**Figure 2**. Cyclic voltammograms of (a) **5d** and (b) **13** in benzonitrile.

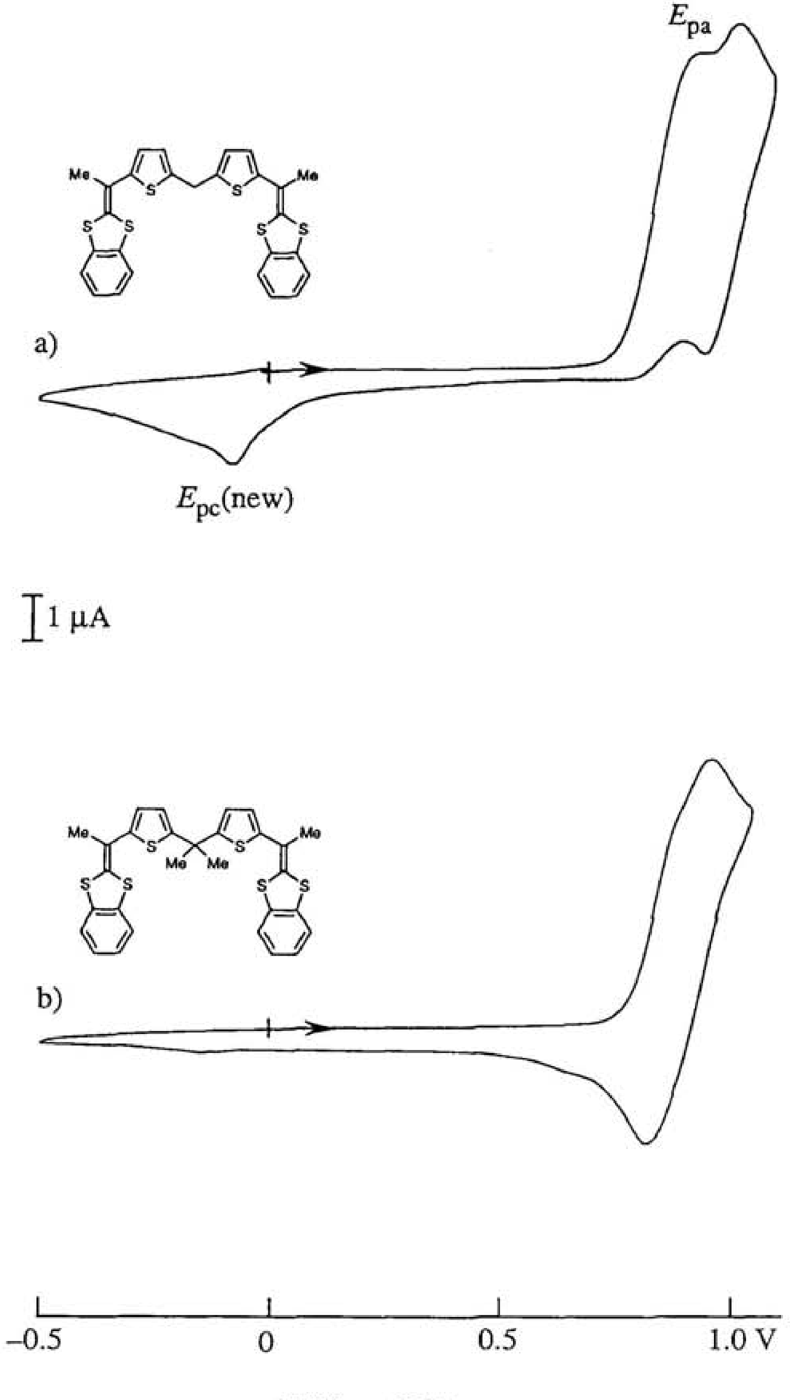
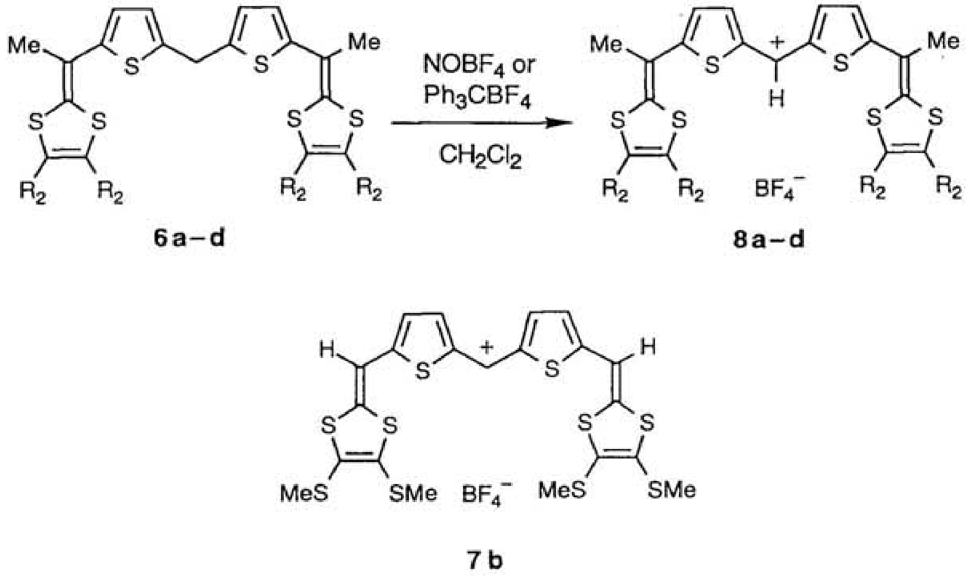


**Figure 3**. Cyclic voltammograms of (a) **6d** and (b) **14** in benzonitrile.

## Isolation and Characterization of Cations

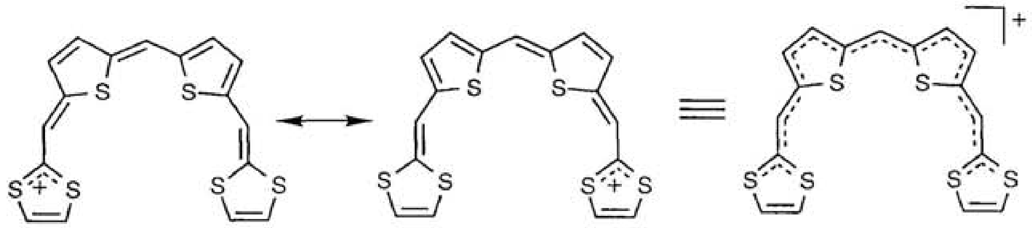
*Isolation.*— As described above, the cyclic voltammetry experiments implied that the bis(1,3-dithiole) compounds **6** would afford the cations **8** by electrochemical oxidation. Next, isolation of the cations by chemical oxidation was attempted. Oxidation of **6a–d** with one equivalent of nitrosyl tetrafluoroborate ($NOBF_4$) in dichloromethane at room temperature gave the corresponding cation salts **8a–d**·$BF_4$ in 32 to 48% yields (Scheme 3). Although only $^1H$ NMR spectrum of **8b**·$BF_4$ was obtained because of the low solubilities of the other cations, the structure of **8b** is supported by the presence of the signals of the methine proton at $\delta$ 7.50 (s, 1H) and the thienyl protons at $\delta$ 6.91 (d, 2H) and 7.27 (d, 2H). The structures of other cations are determined solely by elemental analyses data. Attempted preparation of the cation salts **7a–d**·$BF_4$ by oxidation of **5a–d** gave only a small amount of unidentified products. The cations **8a–d** were also obtained by hydride abstraction of **6a–d** with an equimolecular amount of trityl tetrafluoroborate ($Ph_3CBF_4$) in dichloromethane in 50 to 87% yields. The successful preparation of the cation salt **7b**·$BF_4$ was achieved by using this method in 88% yield. The cations are fairly stable in both solid and solution states, and the $^1H$ NMR spectrum of **8b**·$BF_4$ in $CD_3CN$ did not change after storage at room temperature under air for several months.



Scheme 3

*Electrochemical properties.*— The cyclic voltammograms of the cations **8a–c** in benzonitrile showed both oxidation and reduction waves. The reduction potentials are in complete agreement with $E_{\mathrm{pc}}$(new) for the compounds **6a–c**, although the CV of **8d** could not be obtained due to its low solubility. Figure 4 shows the CV of **8b** along with that of **6b** for comparison. The three-stage one-electron oxidation waves corresponding to the formation of the dication radical, trication, and tetracation radical were observed at 0.91, 1.15, and 1.39 V, respectively.

*X-ray structure.*—In order to investigate the structure of the cations, an X-ray structural analysis was carried out on the cation salt **7b**$\cdot BF_4$. A single crystal was obtained by slow recrystallization from acetonitrile. There exist two crystallographically independent molecules (molecule I and molecule II) in the crystal. Although there are differences in the conformations of the methylthio groups, the geometries of the π-skeleton of the molecule I and II are similar to each other. Figure 5 (a) shows the molecular structure of molecule I. The thienyldithiafulvene moieties are almost planar. The two thiophene rings form a dihedral angle of 9.7°. The molecule has an approximate $C_2$ symmetry. The molecular structure of molecule II with bond lengths is shown in Figure 5 (b). The decrease in bond alternations is found in the carbon-framework of the molecule. Namely, while the C23–C24, C25–C26, C27–C28, C33–C34, C35–C36, and C37–C38 bonds are lengthened, the C24–C25, C26–C27, C34–C35, and C36–C37 ones are shortened compared with the corresponding bond lengths of the molecule **6c**. Furthermore, the average bond length of C28–S12, C28–S13, C38–S17, and C38–S18 bonds (1.73 Å) is slightly shorter than that of neutral molecule **6c** (1.76 Å). These observations show the polymethine cyanine like structure of the cation as shown in Scheme 4.[7-11]



**Scheme 4**

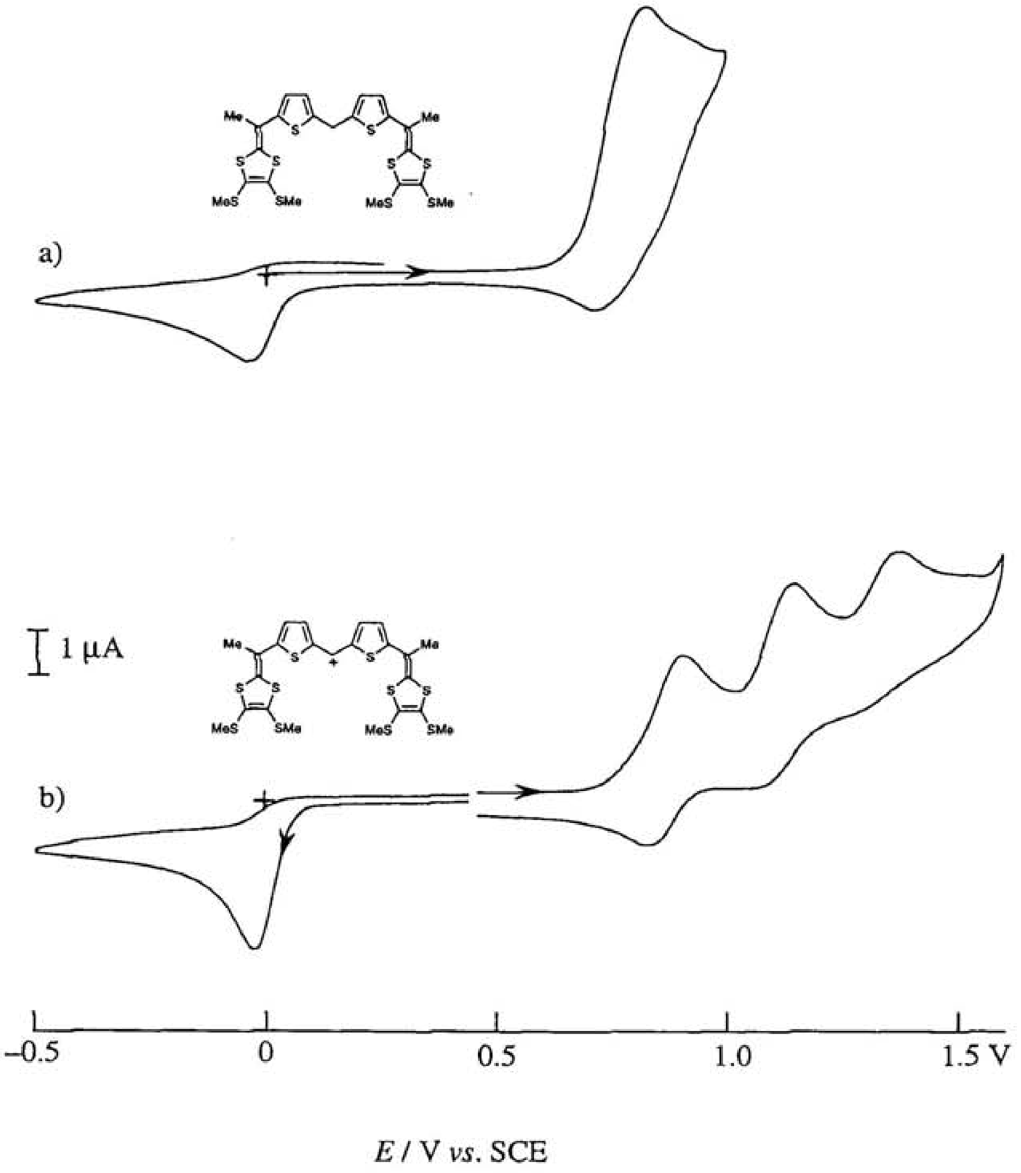


**Figure 4**. Cyclic voltammograms of (a) **6b** and (b) **8b** in benzonitrile.

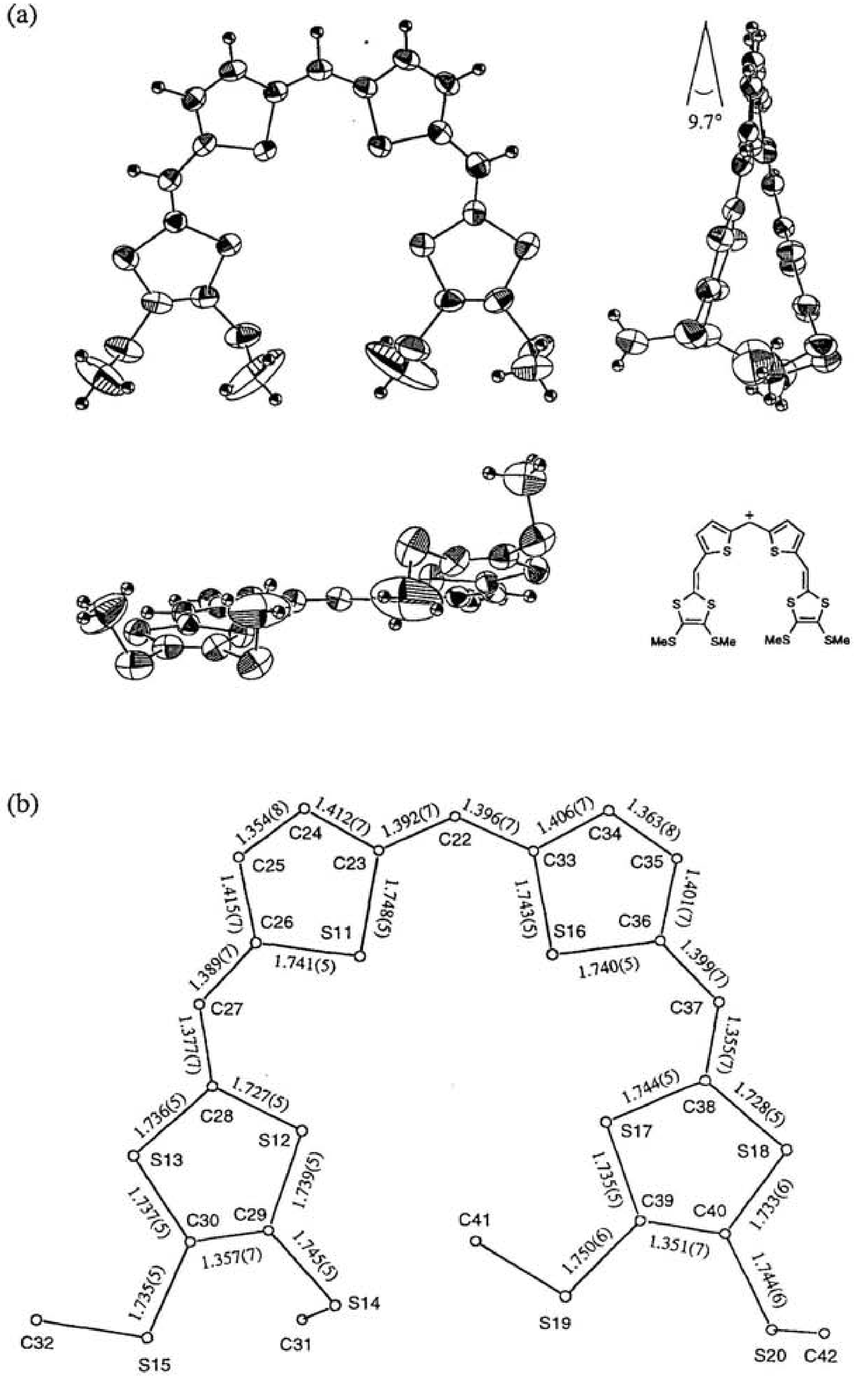


**Figure 5**. X-ray molecular structure of the cation **7b**. (a) Molecule I. (b) Molecule II with bond lengths (Å). Hydrogen atoms are omitted.

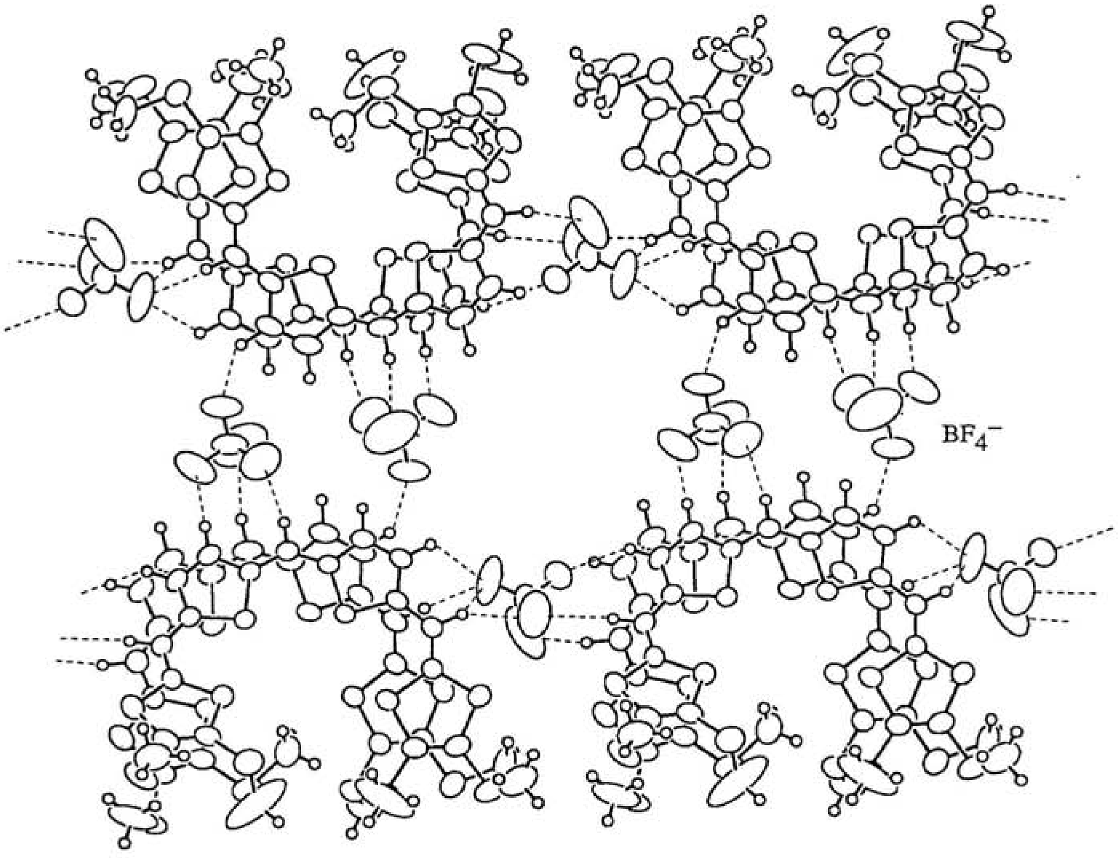


**Figure 6**. Crystal structure of the cation salt **7b**·BF$_4$. Broken lines indicate short F···H contacts.

The molecule I and molecule II form a dimer as shown in Figure 6. Each dimer is connected by the counteranion $BF_4^-$ with short F···H contacts (< 2.67 Å) to form a ladder-like network.

*Optical properties.*— The cations **7b** and **8a–d** show intense absorptions in the near-infrared region (*ca.* 900–980 nm in acetonitrile) due to their polymethine cyanine type structure.[12] The spectrum of **8b** in acetonitrile is shown in Figure 7, and the longest absorption maxima are summarized in Table 2. These values are considerably longer than that of some di(2-thienyl)methyl cation derivatives[11,13,14] and 1,3-dithiolium dyes[15] owing to the expansion of π-conjugation. The alkylthio groups on the 1,3-dithiole rings make the absorptions much red-shifted. The absorption maxima observed in solution are over the absorption region for the Ga-As laser diode (780–840 nm). However, the absorptions are blue-shifted in thin films, and **8b** showed the maximum at 824 nm in a thin film (Figure 7, broken line). This finding indicates that they are interesting as near-infrared absorbing dyes. Recently much attention has been focused on the near-infrared absorbing dyes for optical memory media.[16-18]

**Table 2.** Longest absorption maxima of the cations.[a]

| Cation | $R_1$ | $R_2$ | $\lambda_{max}$ / nm (log ε) |
|---|---|---|---|
| **7b** | H | SMe | 938 (4.76) |
| **8a** | Me | H | 921 (4.85) |
| **8b** | Me | SMe | 950 (4.69) |
| **8c** | Me | $SCH_2CH_2S$ | 976 (4.38) |
| **8d** | Me | benzo | 906 (4.56) |

[a] Measured in acetonitrile.

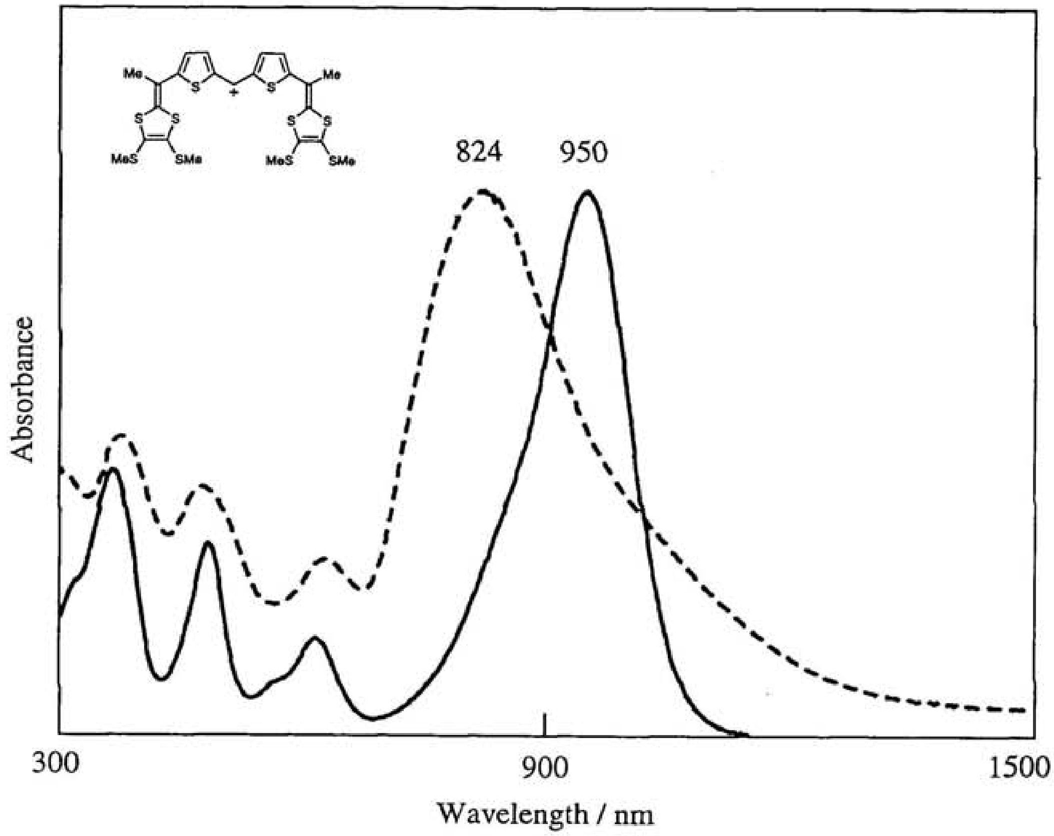


**Figure 7.** Absorption spectra of the cation **8b** in acetonitrile (—) and as a thin film (---).

## Formation of Oligomer

As described above (p. 39, *Electrochemical Properties*), the cyclic voltammetric behavior of the compounds **5** was different from that of **6**. In a similar way to the case of the tris(1,3-dithiole) compound **15**, which gave a polymer by oxidation as described in chapter 2, the compounds **5** seem to undergo an intermolecular coupling, since **5** have eliminable hydrogen atoms on the C6-carbons of dithiafulvenyl groups.[19-23] Taking into account this hypothesis, the new reduction peaks [$E(\text{new})_{\text{pc}}$] observed in the CVs of **5** can be attributed to the reduction of an intermediate **16**. This interpretation is supported by the fact that 1,3-benzodithiolium cation **17**[24] is reduced at a peak potential of –0.24 V *vs*. SCE in benzonitrile. Next, isolation of the oxidation product of **5b** was attempted. When **5b** was oxidized with tris(4-bromophenyl)aminium hexachloroantimonate as an oxidizing agent, a sparingly soluble black solid was obtained as an oxidized form. Treatment of the product with hydrazine hydrate gave a neutral product as a brown solid. The gel-permeation chromatography (GPC) analysis of the product showed a weight-average molecular weight of 6177 (polystylene standard) with a polydispersity of 1.5. These data indicate that the product is an oligomer **18** composed of about ten monomer units.

The absorption maximum (372 nm) of the oligomer **18** in dichloromethane is red-shifted by only 8 nm compared with that of the monomer **5b** (Figure 8). A similar relationship was observed between the absorption wavelengths of closely related compound **19** ($\lambda_{\text{max}}$ 352 nm) and its dimer **20** ($\lambda_{\text{max}}$ 362 nm).[23] These facts support the structure of the oligomer **18**. Figure 9 shows the cyclic voltammogram of **18** in benzonitrile. The oligomer showed only one redox wave, and the oxidation peak potential (0.69 V) is slightly lower than that of **5b** ($E_{\text{pa}}$ = 0.72 V), indicating that the degree of intramolecular interaction between the monomer units seems small probably due to steric interactions. When the working electrode was soaked in a solution of oligomer for *ca*. 30 minutes, a new symmetrical redox wave with a large peak current was observed. These phenomena are typical for a redox active species adsorbed on the surface of the electrode.[25] Since the oligomer **18** can be regarded as an assembly of the

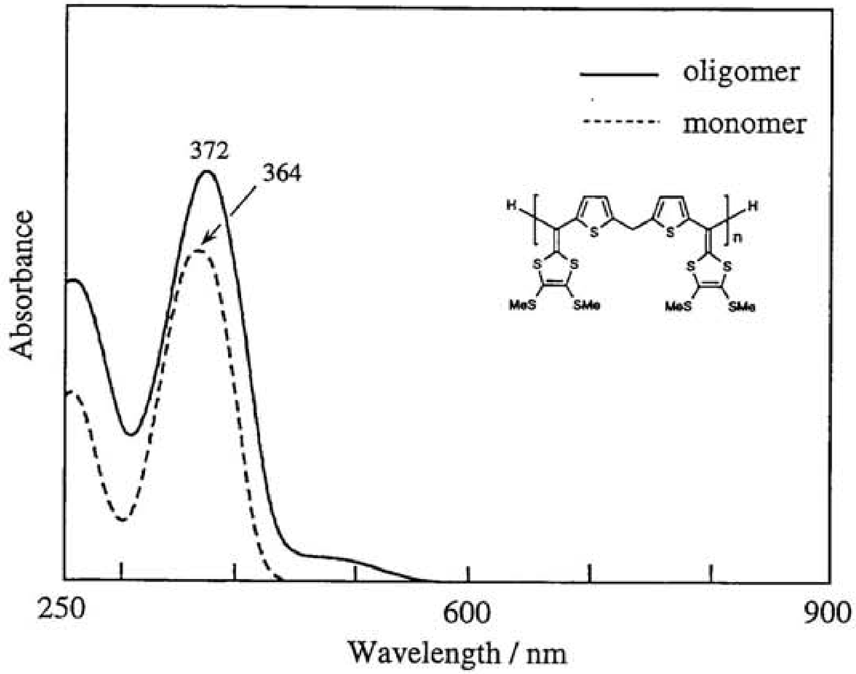


**Figure 8**. Absorption spectra of the oligomer **18** (—) and the monomer **5b** (---).

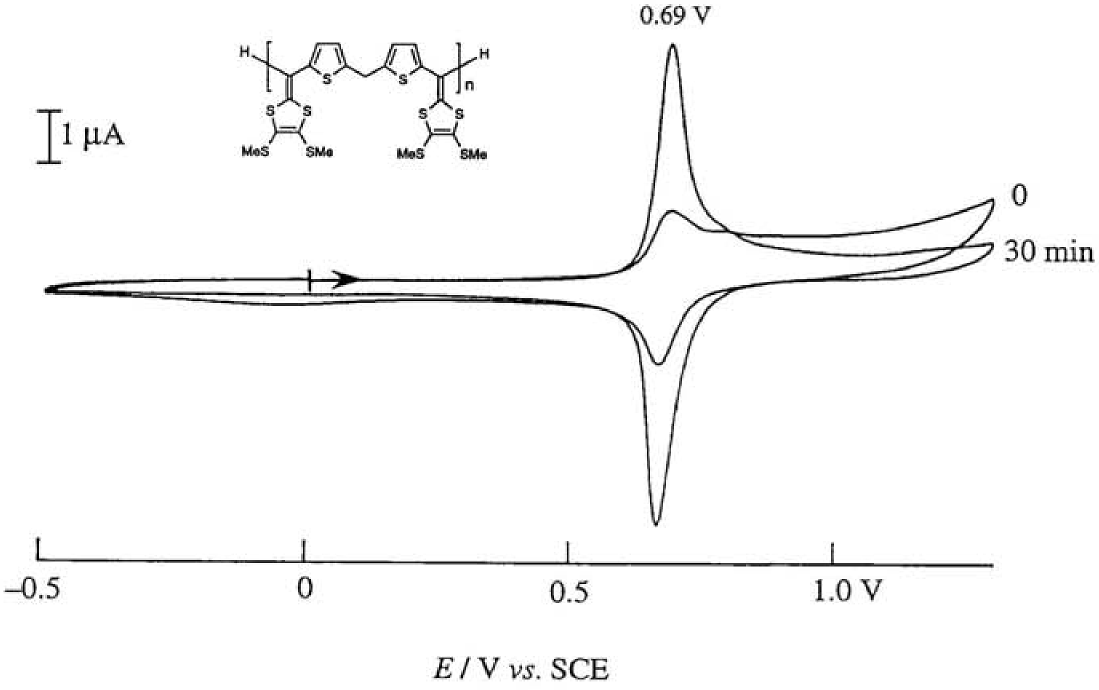
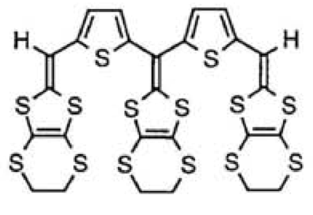
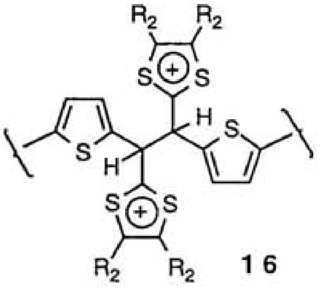


**Figure 9**. Cyclic voltammograms of the oligomer **18** in benzonitrile.

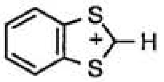
extended TTF **20**, it seems interesting as a novel redox active oligomer presented by a general structure, ···D-σ-D-σ-D-σ···, in which electronically isolated donor units are connected by σ-linkage.[26]



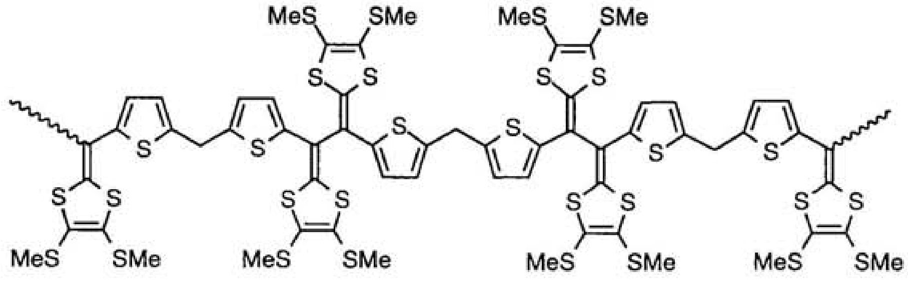
**15**



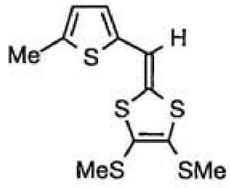
**16**



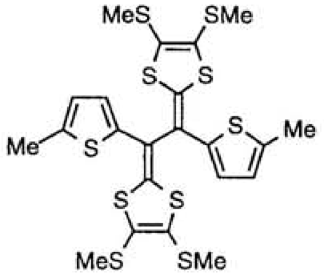
**17**



**18**



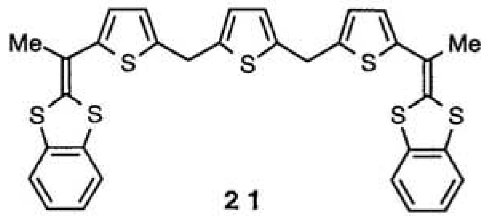
**19**

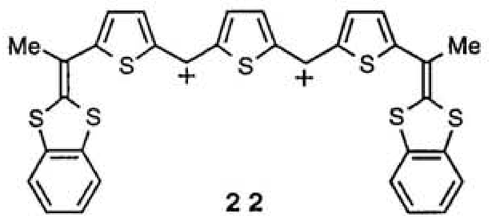


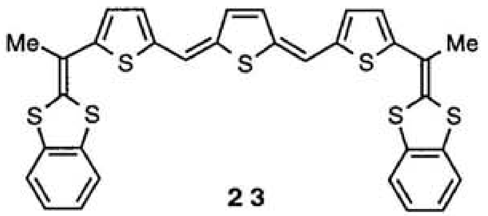
**20**

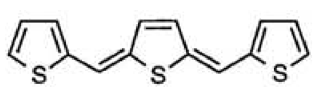
### Preparation and Properties of 2,5-bis[5-(6-methyl-1,4-dithiafulven-6-yl)-2-thienylmethyl]thiophene

Next, the author attempted oxidation of a bis(1,3-dithiole) compound **21** containing two methylene groups as an application of the oxidation–deprotonation reaction. The compound **21** is expected to give the corresponding dication **22**, which is considered as the dicaion state of a highly extended bis(1,3-dithiole) donor **23**. Since the donor **23** contains a 2,5-dihydro-2,5-bis(2-thienylmethylene)thiophene skeleton **24**, which has been actively investigated by Hanack *et al.* as a model of narrow bandgap polymer,[27-29] the electronic properties of the donor **23** is particularly interesting.

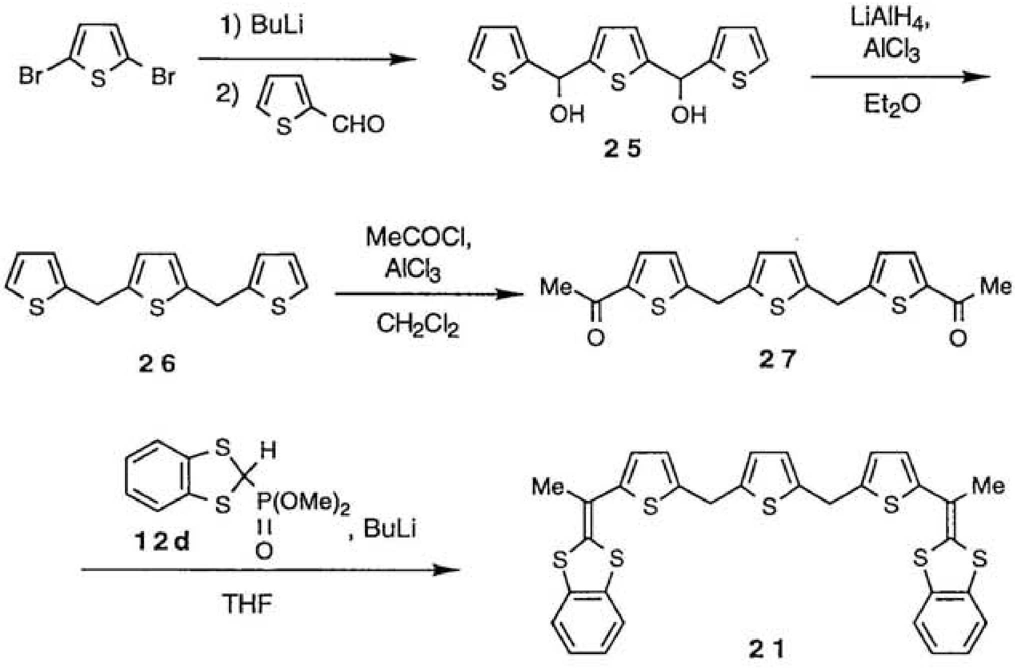

**21**


**22**


**23**


**24**

The synthetic route of **21** is summarized in Scheme 5. A reaction of 2,5-dilithiothiophene derived from 2,5-dibromothiophene with 2-thiophenecarbaldehyde gave a dialcohol **25**, which was reduced by $LiAlH_4$–$AlCl_3$ to give 2,5-bis(2-thienylmethyl)-



**Scheme 5**

thiophene **26**[3] (52% yield from 2,5-dibromothiophene). Diketone **27** was obtained by Friedel–Crafts acetylation of **26** (77%). A Wittig–Horner reaction of the phosphonate ester **12d** with **27** afforded the compound **21** in 96% yield. The structure of **21** was determined on the basis of the spectral and elemental analysis data.

The cyclic voltammogram of the compound **21** is shown in Figure 10 (a). The electrochemical behavior of **21** was completely different from that of the compounds **6**. When the switching potential was 1.0 V, one reversible redox wave was observed (broken line). On the other hand, after rising the potential to 1.3 V, a new redox couple appeared at *ca.* 0.45 V. These observations suggest that a product possessing the redox potential of 0.45 V generated after the electrochemical oxidation of **21**.

Isolation of the product was attempted by chemical oxidation of **21** with $NOBF_4$. Treatment of **21** with excess $NOBF_4$ in dichloromethane gave the dication salt **22**·$2BF_4$ as a black solid in 87% yield. The redox potential of **22** is in complete agreement with that of the new redox wave observed in the CV of **21** [Figure 10 (b)]. An irreversible oxidation wave with large $i_{pa}$ was observed at 1.48 V. As shown in Figure 11 (a), the dication **22** showed a broad absorption band around 780–1080 nm with a maximum at 936 nm in acetonitrile. An intense absorption was observed at 553 nm.

Chemical reduction of the dication salt **22**·$2BF_4$ with zinc afforded a neutral donor **23** as a dark violet solid. Since the donor **23** is not so stable in the solution state and tends to decompose to insoluble brown substances during concentration, a pure sample for elemental analysis could not be obtained. Furthermore, the low solubility of the donor prevented the measurements of NMR spectra. Therefore, the structural assignment of **23** was based solely on the FAB-mass spectrum, in which the peaks corresponding to the molecular ion $M^+$ and protonated species $[M+H]^+$ were observed. The structure of **23** is also supported by the fact that the CV of the donor **23** is essentially identical with that of the dication **22** [Figure 10 (c)]. Because the first wave of **23** consists of nearly overlapped two waves, it is considered as a two-electron process. This fact indicates that on-site Coulombic repulsion is small in the dication

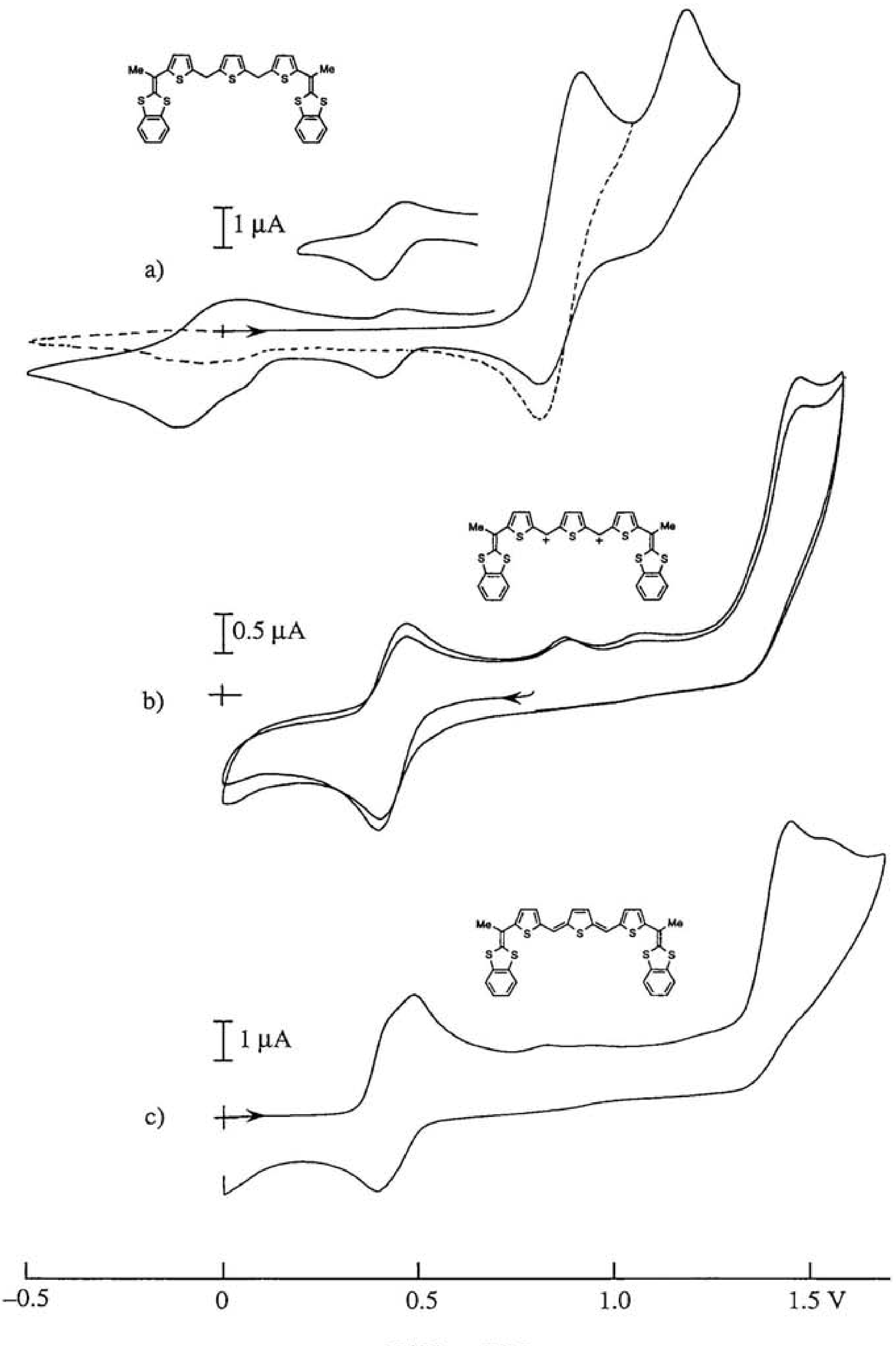
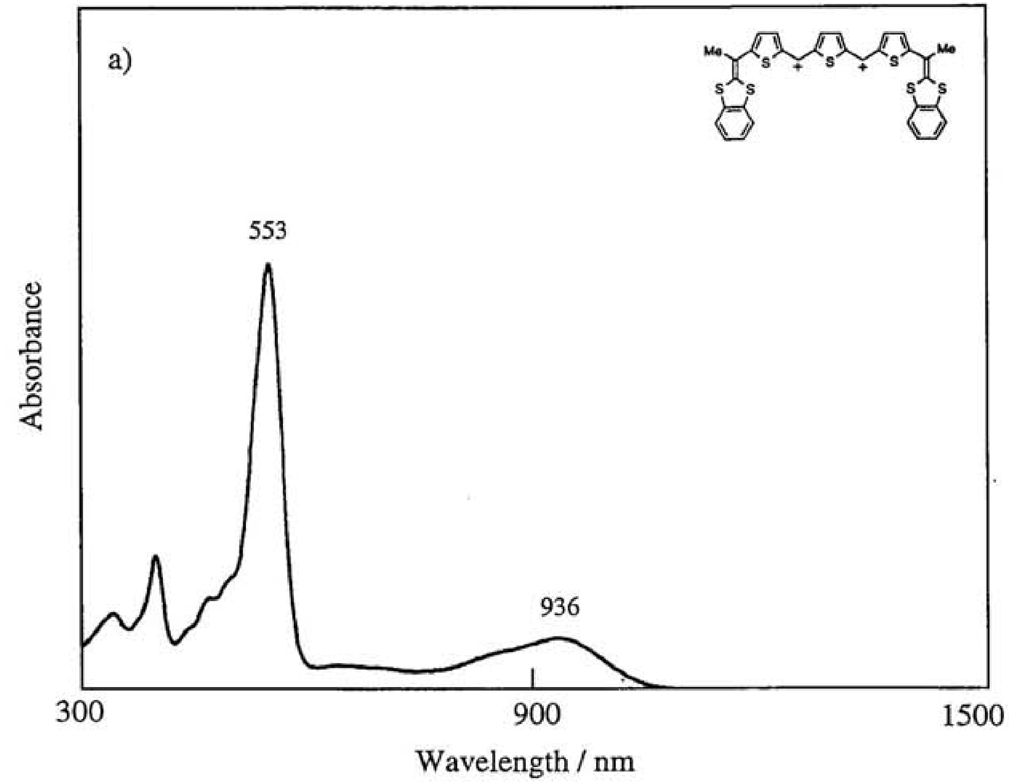


**Figure 10**. Cyclic voltammograms of (a) **21**, (b) **22**, and (c) **23** in benzonitrile.



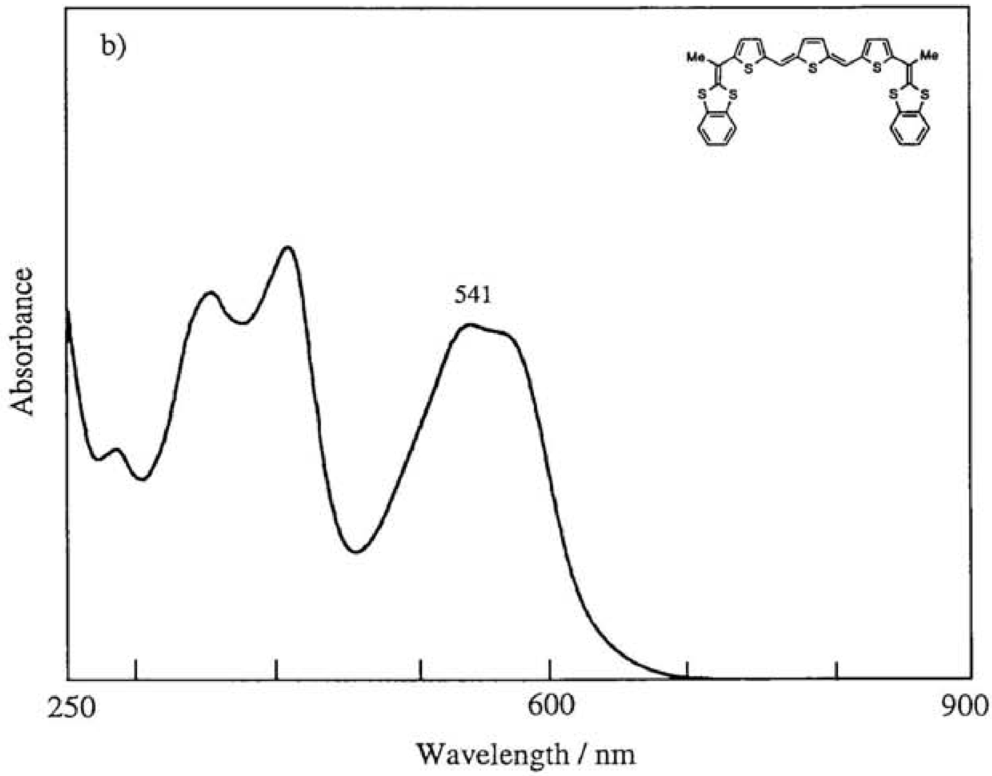
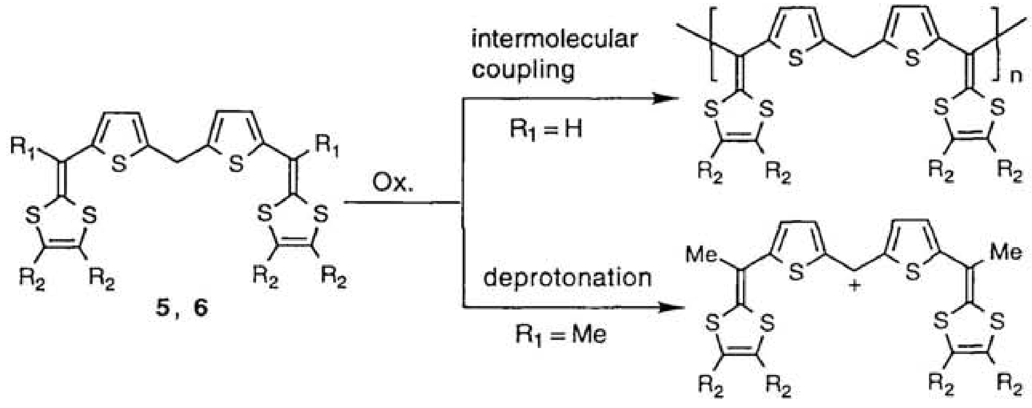


**Figure 11**. Absorption spectra of (a) the dication **22** in acetonitrile and (b) the neutral donor **23** in dichloromethane.

state. Figure 11 (b) shows the absorption spectrum of the donor **23** in dichloromethane. The absorption maxima (541 nm) is much red-shifted compared with that of TTF due to the expansion of π-conjugation. For further discussion, it is necessary to improve the stability and solubility of the donor **23**. This is a problem to be solved.

## Conclusion

In order to explore novel chemical reactions induced by electron transfer, oxidation of bis(1,3-dithiole) compounds **5** and **6** containing a dithienylmethane unit was investigated. Their cyclic voltammograms showed irreversible oxidation waves, and new redox waves due to the oxidation products were observed. Isolation of the products was attempted by chemical oxidation. The reactions were strongly dependent on the substituents ($R_1$) on the C6-carbons of the dithiafulvenyl groups (Scheme 6). In the case of $R_1$ = H (**5**), intermolecular coupling giving an oligomer selectively occurred. The properties of the oligomer were investigated by GPC analysis, cyclic voltammetry, and UV–VIS spectroscopy. On the other hand, when $R_1$ was Me, oxidation of **6** gave the corresponding dithienylmethyl cations which show intense absorptions in the near-infrared region. An X-ray analysis revealed the polymethine cyanine like structure of the cation.



Scheme 6

Furthermore, oxidation of the bis(1,3-dithiole) compound **21** containing two methylene groups was also examined, and the corresponding dication **22** was obtained. The dication shows an absorption at 936 nm. Reduction of the dication gave a neutral bis(1,3-dithiole) donor **23** with low purity. Electrochemical properties of **21–23** were studied by cyclic voltammetry.

## Experimental

**General.** Melting points were measured on a Yanaco MP-500D melting point apparatus and are uncorrected. IR and UV spectra were recorded on a Perkin-Elmer FTIR 1600 and a Shimadzu UV-3101PC spectrometer, respectively. Unless otherwise stated, $^1H$ (400 MHz) and $^{13}C$ (100 MHz) NMR spectra were measured on a JEOL JNM-GX400 spectrometer. 270 MHz $^1H$ NMR spectra were measured on a JEOL JNM-EX270 spectrometer. EI (70 eV) and FAB (Xe, 7kV) mass spectra were measured on a Shimadzu GCMS-QP1000EX and a Shimadzu Kratos CONCEPT 1S spectrometer, respectively. Elemental analyses were performed on a Yanaco MT-3 CHN CORDER. GPC analysis were performed by using a Shimadzu LC-9A liquid chromatograph with a Tosoh TSK–GEL G3000HHR column (7.8 nm × 30 cm) and tetrahydrofuran as a solvent. Chromatographic separations were performed with Merk aluminium oxide 90 (activity II to III). Yields are based on isolated products with sufficient purity. Tetrahydrofuran was distilled over lithium aluminium hydride prior to use.

**Electrochemical Measurements.** Cyclic voltammetry experiments were performed in a three-compartment cell with a Pt disc working electrode, Pt wire counter electrode, and saturated calomel reference electrode. Measurements were made with a Toho Technical Research Polarization Unit PS-07 potentiostat / galvanostat with a scan rate of 100 mV $s^{-1}$. The cell contained a solution of a substrate (*ca.* 1 mmol $dm^{-3}$) and tetrabutylammonium tetrafluoroborate (0.1 mol $dm^{-3}$) as supporting electrolyte in benzonitrile or dichloromethane. All solutions were purged with argon and retained under the inert atmosphere during the experiment.

**Bis[5-(1,4-dithiafulven-6-yl)-2-thienyl]methane (5a).** Aq NaOH (10%, 5 ml) was added to a solution of the aldehyde **9**[3] (300 mg, 1.27 mmol) and the phosphonium salt **11**[4] (1.05 g, 2.68 mmol) in dichloromethane (5 ml), and the mixture was vigorously stirred for 10 min at room temperature. The resulting solid was washed with water, followed by ethanol to give the compound **5a** (486 mg, 94%) as colorless needles (from $ClCH_2CH_2Cl$): mp 190–191 °C (decomp.); IR (KBr) 3056, 1567, 1303, 1046, 821, 801, 650, 502 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 4.31$ (2H, s, $CH_2$), 6.32 (2H, d, $J = 6.7$ Hz, dithiole-H), 6.34 (2H, d, $J = 6.7$ Hz, dithiole-H), 6.67 (2H, s, =CH), 6.70 (2H, d, $J = 3.7$ Hz, Th-H), 6.80 (2H, d, $J = 3.7$ Hz, Th-H); $^{13}C$ NMR ($CDCl_3$) $\delta$ = 30.80, 106.68, 117.89, 122.81, 125.69, 134.06, 140.25, 140.90; UV-VIS ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 246 (3.99), 362 (4.42), 375 (4.40, sh) nm; MS *m/z* (rel intensity) 408 ($M^+$, 100), 306 (60), 153 (49), 95 (21), 69 (30); Found: C, 49.87; H, 3.05%. Calcd for $C_{17}H_{12}S_6$: C, 49.97; H, 2.96%.

**5b**: A solution of BuLi in hexane (1.63 mol $dm^{-3}$, 0.91 ml, 1.48 mmol) was added to a solution of phosphonate ester **12b**$^5$ (510 mg, 1.68 mmol) in THF at –78 °C under argon. After stirring for 10 min, the aldehyde **9** (160 mg, 0.68 mmol) was added to the solution. The mixture was stirred for 30 min at –78 °C and allowed to warm to room temperature. To the solution was added water (30 ml), and the product was extracted with dichloromethane. The extract was washed with water, dried over $Na_2SO_4$, and concentrated. The residue was separated by column chromatography (alumina / toluene) to give the compound **5b** (299 mg, 75%) as yellow needles (from acetone). mp 82–83 °C; IR (KBr) 2914, 1570, 1498, 1426, 1298, 800, 504 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ = 4.43 (6H, s, SMe), 4.40 (6H, s, SMe), 4.30 (2H, s, $CH_2$), 6.59 (2H, s, =CH), 6.69 (2H, d, $J = 3.5$ Hz, Th-H), 6.80 (2H, d, $J = 3.5$ Hz, Th-H); $^{13}C$ NMR ($CDCl_3$) $\delta$ = 18.85, 19.00, 30.75, 108.44, 123.68, 124.86, 125.71, 127.65, 129.54, 139.34, 141.63; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 256 (4.04), 364 (4.28) nm; MS *m/z* (rel intensity) 592 ($M^+$, 100), 153 (52), 91 (74); Found: C, 42.56; H, 3.43%. Calcd for $C_{21}H_{20}S_{10}$: C, 42.54; H, 3.40%.

The other compounds **5c,d**, **6a–d**, **13**, and **14** were synthesized from the corresponding carbonyl compounds by using the similar method (Wittig–Horner reaction). In the cases of the compounds **5c,d** and **6c,d**, the products were isolated directly by addition of water and ethanol to the reaction mixture without extraction. The data are as follows.

**5c**: 92%; yellow needles (from $ClCH_2CH_2Cl$); mp 207–209 °C (decomp.); IR (KBr) 1561, 1518, 1284, 820, 796, 509 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 3.32$ (8H, s, $SCH_2CH_2S$), 4.29 (2H, s, $CH_2$), 6.63 (2H, s, =CH), 6.69 (2H, d, $J = 3.7$ Hz, Th-H), 6.80 (2H, d, $J = 3.7$ Hz, Th-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 257 (4.06), 371 (4.26), 396 (4.08, sh) nm; FAB–MS $m/z$ 588 ($M^+$); Found: C, 42.60; H, 2.83%. Calcd for $C_{21}H_{16}S_{10}$: C, 42.83; H, 2.74%.

**5d**: 71%; colorless plates (from toluene); mp 226–228 °C (decomp.); IR (KBr) 3051, 1577, 1557, 1448, 1432, 1124, 826, 743 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 4.34$ (2H, s, $CH_2$), 6.68 (2H, s, =CH), 6.78 (2H, d, $J = 3.7$ Hz, Th-H), 6.84 (2H, d, $J = 3.7$ Hz, Th-H), 7.11–7.13 (4H, m, benzo-H), 7.22–7.24 (4H, m, benzo-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 247 (4.20), 354 (4.44), 369 (4.39, sh) nm; MS $m/z$ (rel intensity) 508($M^+$, 100), 356 (42), 261 (27), 209 (22), 203 (30), 190 (24), 178 (32), 153 (38) 108 (24); Found: C, 59.21; H, 3.36%. Calcd for $C_{25}H_{16}S_6$: C, 59.02; H, 3.17%.

**6a**: 47%; colorless needles (from acetone); mp 74–75 °C; IR (KBr) 3059, 1556, 1519, 1420, 1236, 986, 803, 786, 643, 594 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.14$ (6H, s, Me), 4.29 (2H, s, $CH_2$), 6.35 (2H, d, $J = 6.7$ Hz, dithiole-H), 6.37 (2H, d, $J = 6.7$ Hz, dithiole-H), 6.82 (2H, d, $J = 3.7$ Hz, Th-H), 6.85 (2H, d, $J = 3.7$ Hz, Th-H); $^{13}C$ NMR ($CDCl_3$) $\delta = 23.77$, 30.63, 112.78, 117.79, 118.76, 122.70, 125.50, 130.80, 140.33, 143.58; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 247 (4.17), 359 (4.50), 367 (4.44, sh) nm; MS $m/z$ (rel intensity) 436 ($M^+$, 100), 334 (33), 225 (13), 167 (13), 103 (10); Found: C, 52.29; H, 3.78%. Calcd for $C_{19}H_{16}S_6$: C, 52.26; H, 3.69%.

**6b**: 70%; yellow needles (from $CHCl_3$–EtOH); mp 90–91 °C; IR (KBr) 2915, 1553, 1499, 1424, 969, 897, 792, 786 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.11$ (6H, s, Me), 2.42 (6H, s, SMe), 2.45 (6H, s, SMe), 4.29 (2H, s, $CH_2$), 6.82 (4H, s, Th-H); $^{13}C$ NMR ($CDCl_3$) $\delta = 18.86$, 18.93, 22.51, 30.55, 114.60, 123.43, 125.48, 126.03, 126.42, 126.82, 140.90, 142.68; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 256 (4.05), 360 (4.22) nm;

MS *m/z* (rel intensity) 620 ($M^+$, 100), 558 (13), 470 (16), 320 (14), 249 (18), 167 (36), 135 (26), 91 (66); Found: C, 44.50; H, 3.88%. Calcd for $C_{23}H_{24}S_{10}$: C, 44.48; H, 3.90%.

**6c**: 93%; yellow prisms (from $CHCl_3$–hexane); mp 167–168 °C; IR (KBr) 1557, 1527, 1516, 1409, 1286, 801, 791 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.13$ (6H, s, Me), 3.31 (8H, s, $SCH_2CH_2S$), 4.28 (2H, s, $CH_2$), 6.81 (4H, s, Th-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 257 (4.06), 367 (4.18) nm; FAB–MS *m/z* 616 ($M^+$); Found: C, 44.57; H, 3.38%. Calcd for $C_{23}H_{20}S_{10}$: C, 44.77; H, 3.27%.

**6d**: 86%; colorless needles (from $CHCl_3$–hexane); mp 159–160 °C; IR (KBr) 3057, 2908, 1571, 1547, 1448, 784, 735 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.21$ (6H, s, Me), 4.32 (2H, s, $CH_2$), 6.85 (2H, d, $J = 3.7$ Hz, Th-H), 6.94 (2H, d, $J = 3.7$ Hz, Th-H), 7.08–7.11 (4H, m, benzo-H), 7.23–7.27 (4H, m, benzo-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 246 (4.04), 352 (4.14), 364 (4.09) nm; MS *m/z* (rel intensity) 536 ($M^+$, 100), 153 (63), 69 (42); Found: C, 60.25; H, 3.84%. Calcd for $C_{27}H_{20}S_6$: C, 60.41; H, 3.76%.

**2,2-Bis[5-(1,4-beznodithiafulven-6-yl)-2-thienyl]propane (13).** 65%; pale yellow solid; mp 130–138 °C; IR (KBr) 2966, 1573, 1552, 1447, 1432, 801, 741 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 1.88$ (6H, s, Me), 6.66 (2H, s, =CH), 6.75 (2H, d, $J = 3.7$ Hz, Th-H), 6.81 (2H, d, $J = 3.7$ Hz, Th-H), 7.08–7.13 (4H, m, benzo-H), 7.20–7.23 (2H, m, benzo-H), 7.25–7.29 (2H, m, benzo-H); MS *m/z* (rel intensity) 536 ($M^+$, 14), 521 (100); Found: *m/z* 535.99069. Calcd for $C_{27}H_{20}S_6$: 535.98894.

**2,2-Bis[5-(6-methyl-1,4-benzodithiafulven-6-yl)-2-thienyl]propane (14).** 69%; pale yellow needles (from acetone), mp 115 – 120 °C; IR (KBr) 2967, 1571, 1547, 1449, 1434, 1123, 792, 739 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta = 1.88$ (6H, s, Me), 2.21 (6H, s, =CMe), 6.83 (2H, d, $J = 3.7$ Hz, Th-H), 6.93 (2H, d, $J =$

3.7 Hz, Th-H), 7.08–7.12 (4H, m, benzo-H), 7.22–7.27 (4H, m, benzo-H); MS *m/z* (rel intensity) 564 ($M^+$, 49), 549 (100), 302 (25), 275 (37), 153 (47); Found: C, 61.47; H, 4.27%. Calcd for $C_{29}H_{24}S_6$: C, 61.65; H, 4.28%.

**Isolation of cation salt 8a·BF$_4$ (General procedure). Method A**: Argon was bubbled into a stirred solution of the compound **6a** (100 mg, 0.23 mmol) in dichloromethane (10 ml). To this solution was added $NOBF_4$ (28 mg, 0.24 mmol) in acetonitrile (1 ml) at room temperature. After addition, argon bubbling was continued for 10 min. The mixture was stirred for further 20 min, and the resulting solid was collected by filtration and washed with dichloromethane to give the cation salt **8a·BF$_4$** (50 mg, 42%). **Method B**: Trityl tetrafluoroborate (80 mg, 0.24 mmol) was added to a solution of **6a** (100 mg, 0.23 mmol) in dichloromethane (5 ml) at room temperature under argon. The mixture was stirred for 1 h, and the resulting solid was collected by filtration and washed with dichloromethane to give the cation salt **8a·BF$_4$** (104 mg, 87%): black solid (from AcOH); mp *ca.* 250 °C (decomp.); IR (KBr) 1557, 1348, 1193, 1151, 1086, 1053, 986, 742 cm$^{-1}$; UV (MeCN) $\lambda_{max}$ (log ε) 324 (4.21), 362 (4.18), 458 (4.70), 547 (3.85), 590 (3.86), 921 (4.85) nm; Found: C, 43.06; H, 2.93%. Calcd for $C_{19}H_{15}S_6BF_4$: C, 43.68; H, 2.89%.

The other cation salts were prepared by the similar method. The data are as follows.

**8b·BF$_4$**: Method A: 32%; Method B: 83%; black solid (from AcOH); mp 177–179 °C (decomp); IR (KBr) 1555, 1353, 1149, 1088, 1052, 986, 736 cm$^{-1}$; $^1$H NMR ($CD_3CN$) δ = 2.11 (6H, s, Me), 2.53 (12H, broad s, SMe), 6.91 (2H, d, *J* = 4.9 Hz, Th-H), 7.27 (2H, d, *J* = 4.9 Hz, Th-H), 7.50 (1H, s, CH); UV (MeCN) $\lambda_{max}$ (log ε) 254 (4.25), 367 (4.38), 484 (4.24), 617 (3.95), 950 (4.69) nm; Found: C, 38.80; H, 3.33%. Calcd for $C_{23}H_{23}S_{10}BF_4$: C, 39.08; H, 3.28%.

**8c·BF$_4$**: Method A: 38%; Method B: 50%; black solid (from AcOH); mp > 300 °C; IR (KBr) 1557, 1451, 1424, 1344, 1194, 1152, 1091, 1052, 985, 737 cm$^{-1}$; UV (MeCN) $\lambda_{max}$ (log ε) 377 (4.16), 501 (4.00), 645 (3.86), 976 (4.38) nm; Found: C, 38.39; H, 2.74%. Calcd for $C_{23}H_{19}S_{10}BF_4$: C, 39.31; H, 2.72%.

**8d·BF$_4$**: Method A: 48%; Method B: 64%; black fine needles; mp 281–283 °C (decomp.); IR (KBr) 1557, 1364, 1197, 1155, 1094, 1057, 986, 738 cm$^{-1}$; UV (MeCN) $\lambda_{max}$ (log ε) 352 (4.37), 463 (4.26), 583 (3.78), 906 (4.56) nm; Found: C, 51.80; H, 3.27%. Calcd for $C_{27}H_{19}S_6BF_4$: C, 52.09; H, 3.08%.

**7b·BF$_4$**: Trityl tetrafluoroborate (56 mg, 0.17 mmol) was added to a solution of **5b** (100 mg, 0.17 mmol) in dichloromethane (2 ml) at room temperature under argon. The mixture was stirred for 1 h, and the resulting solid was collected by filtration and washed with a small amount of dichloromethane to give the cation salt **7b·BF$_4$** (101 mg, 88%) as a dark green solid (from AcOH): mp 228 – 236 °C (decomp.); IR (KBr) 1518, 1459, 1386, 1293, 1171, 1139, 1064, 711 cm$^{-1}$; UV (MeCN) $\lambda_{max}$ (log ε) 369 (4.49), 480 (4.40), 604 (4.02), 938 (4.76) nm; Found: C, 36.76; H, 2.84%. Calcd for $C_{21}H_{19}S_{10}BF_4$: C, 37.16; H, 2.82%.

**Oxidative oligomerization of 5b**. Tris(4-bromophenyl)aminium hexachloroantimonate (140 mg, 0.17 mmol) was added to a solution of **5b** (100 mg, 0.17 mmol) in dichloromethane (10 ml) at room temperature. The mixture was stirred for 2 h, and the resulting solid was collected by filtration and washed with dichloromethane to give a dark blue solid (94 mg). To a suspension of this solid (59 mg) in dichloromethane was added hydrazine hydrate (0.05 ml), and the mixture was stirred for 5 min. An insoluble solid was removed by filtration, and the filtrate was washed with water, dried over $Na_2SO_4$, and concentrated *in vacuo* to give the oligomer **18** (10 mg) as a brown solid: UV ($CH_2Cl_2$) $\lambda_{max}$ 372 nm. GPC analysis indicated weight- and number-average molecular weights of 6177 and 4241 (polystylene standard), respectively.

**2,5-bis[hydroxy(2-thienyl)methyl]thiophene (25).** A solution of BuLi in hexane (1.60 mol dm$^{-3}$, 57 ml, 91.2 mmol) was added over a period of 5 min to a solution of 2,5-dibromothiophene (10 g, 41.0 mmol) in THF (200 ml) at –55 to –50 °C under argon. The mixture was stirred for 1 h at this temperature. To the mixture was added a solution of 2-thiophenecarbaldehyde (10.2 g, 90.9 mmol) in THF (20 ml). The mixture was stirred for 30 min at –60 °C, allowed to warm to room temperature, and concentrated to 100 ml. To the residue were added water (200 ml) and aq. $NH_4Cl$ (1 mol dm$^{-3}$, 200 ml), and the product was extracted with dichloromethane. The extract was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was separated by column chromatography (silica gel / $CH_2Cl_2$ followed by 10% MeOH in $CH_2Cl_2$) to give dialcohol **25** (9.25 g, 73%) as a pale yellow oil: MS *m/z* (rel intensity) 308 ($M^+$, 14), 111 (100). This product was used to the next step without further purification.

**2,5-bis(2-thienylmethyl)thiophene (26).**[3] Aluminium chloride (24.2 g, 181.5 mmol) and lithium aluminium hydride (2.3 g, 60.5 mmol) were carefully added successively by portions to diethyl ether (100 ml) in an ice bath. After addition, the ice bath was removed and the mixture was stirred for 1 h at room temperature. A solution of the crude dialcohol **25** (9.25 g) in ether (50 ml) was added to the mixture over a period of 20 min with ice-cooling. After addition, the mixture was stirred for 1 h at room temperature. The unreacted lithium aluminium hydride was destroyed by addition of ethyl acetate (30 ml). Water was added to the mixture, and the product was extracted with dichloromethane. The extract was dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was distilled at 210 °C under 0.05 torr by using Kugelrohr apparatus to give the title compound **26** (5.89 g, 52% from dibromothiophene) as a pale yellow oil: $^1$H NMR ($CDCl_3$) $\delta = 4.26$ (4H, s, $CH_2$), 6.68 (2H, s, central Th-H), 6.86 (2H, d, $J$ = 3.4 Hz, Th-3-H), 6.92 (2H, dd, $J$ = 5.2 and 3.4 Hz, Th-4-H), 7.15 (2H, dd, $J$ = 3.4 and 1.2 Hz, Th-5-H); MS *m/z* (rel intensity) 276 ($M^+$, 53), 179 (100).

**2,5-Bis(5-acetyl-2-thienylmethyl)thiophene (27).** Aluminum chloride (2.13 g, 16 mmol) was added over a period of 10 min to a solution of 2,5-bis(2-thienylmethyl)thiophene **26** (2.2 g, 8.0 mmol) and acetyl chloride (1.13 ml, 16 mmol) at 0 °C, and the mixture was stirred for 30 min at 0 °C. The mixture was poured into ice-water (50 ml). The organic phase was separated and washed with sat. aq $Na_2CO_3$ followed by water, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was washed with ethanol to give the diketone **27** (2.21 g, 77%) as colorless needles (from EtOH): mp 117–118 °C; IR (KBr) 1661 (C=O), 1458, 1361, 1274, 1036, 820 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.51$ (6H, s, Me), 4.28 (4H, s, $CH_2$), 6.73 (2H, s, Th-H), 6.89 (2H, d, $J = 3.7$ Hz, Th-3), 7.53 (2H, d, $J = 3.7$ Hz, Th-3); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) $\delta = 26.49$, 31.04, 125.68, 126.45, 132.65, 140.77, 143.22, 152.54, 190.40; MS *m/z* (rel intensity) 360 ($M^+$, 73), 317 (38), 221 (100); Found: C, 59.84; H, 4.50%. Calcd for $C_{18}H_{16}O_2S_3$: C, 59.97; H, 4.47%.

**2,5-bis[5-(6-methyl-1,4-benzodithiafulven-6-yl)-2-thienylmethyl]-thiophene (21).** A solution of BuLi in hexane (1.64 mol $dm^{-3}$, 3.6 ml, 5.9 mmol) was added to a solution of the corresponding phosphonate ester **12d** (1.53 g, 5.8 mmol) in THF at –78 °C under argon. After stirring for 20 min, the diketone **27** (1.0 g, 2.8 mmol) was added to the mixture. The mixture was stirred for 30 min at –78 °C and allowed to warm to room temperature. Water (20 ml) and ethanol (20 ml) were added to the mixture. The resulting solid was collected by filtration and washed with water followed by ethanol to give the title compound **21** (1.68 g, 96%) as colorless needles (from toluene): mp 185–186 °C; IR (KBr) 3061, 2897, 1572, 1551, 1449, 1432, 801, 740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.20$ (6H, s, Me), 4.26 (4H, s, $CH_2$), 6.72 (2H, s, Th-H), 6.82 (2H, d, $J = 3.7$ Hz, Th-H), 6.92 (2H, d, $J = 3.7$ Hz, Th-H), 7.06–7.11 (4H, m, benzo-H), 7.21–7.27 (4H, m, benzo-H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) $\delta =$ 23.34, 30.73, 114.68, 121.15, 121.58, 123.94, 125.01, 125.39, 125.57, 127.19, 135.62, 137.11, 141.40, 141.85, 143.20; MS *m/z* (rel intensity) 632 ($M^+$, 100), 316

(17), 275 (34), 153 (55); Found: C, 61.02; H, 3.98%. Calcd for $C_{32}H_{24}S_7$: C, 60.72; H, 3.82%.

**Isolation of dication salt 22·2BF$_4$.** Argon was bubbled into a stirred solution of the compound **21** (300 mg, 0.47 mmol) in dichloromethane (60 ml) To the solution was added $NOBF_4$ (330 mg, 2.8 mmol) in acetonitrile (5 ml) at room temperature. Argon bubbling was continued for 1 h. The mixture was stirred for further 1 h, and the resulting solid was collected by filtration and washed with dichloromethane to give the dication salt **22·2BF$_4$** (373 mg, 98%) as a black solid: mp 243–248 °C (decomp.); IR (KBr) 1553, 1458, 1424, 1315, 1110, 1064, 1047, 992, 745, 726 cm$^{-1}$; UV (MeCN) $\lambda_{max}$ 341, 399, 470, 553, 936 nm; Found: C, 46.47; H, 2.88%. Calcd for $C_{32}H_{24}S_7B_2F_8$: C, 47.77; H, 2.76%.

**Attempted preparation of neutral donor 23.** A mixture of dication salt **22·2BF$_4$** (200 mg, 0.25 mmol) and zinc dust (500 mg) in acetonitrile (20 ml) was heated under reflux for 30 min under argon. The precipitate was collected by filtration and washed with acetonitrile. The product was extracted with refluxing toluene (4 × 50 ml), and the extract was concentrated under reduced pressure. The residue was washed with ethanol to give the crude donor **23** (112 mg) as a black solid: mp 155–170 °C (decomp.); IR (KBr) 1570, 1534, 1448, 1433, 1288, 1260, 1123, 1029, 739 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 284, 354, 408, 541 nm; FAB-MS *m/z* 630 (M$^+$), 631 {[M+H]$^+$}.

**X-ray structural analyses.** All of the data collections were performed on an Enraf-Nonius CAD4 diffractometer (40 kV, 30 mA) with graphite-monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.541 Å); $\omega$–2$\theta$ scan technique. Details are summarized in Table 3. The atomic and thermal parameters, bond lengths, and angles are presented in appendix as the end of this thesis.

**Table 3**. Details of X-ray structural analyses.

| | **6c** | **7b**·BF$_4$ |
|---|---|---|
| formula | $C_{23}H_{20}S_{10}$ | $C_{21}H_{19}S_{10}BF_4$ |
| fw | 617.09 | 678.78 |
| space group | $P2_1/a$ | $P\bar{1}$ |
| $a$ (Å) | 10.551(2) | 14.7572(6) |
| $b$ (Å) | 24.797(3) | 14.9204(8) |
| $c$ (Å) | 9.907(2) | 15.4377(6) |
| $\alpha$ (deg) | 90 | 96.523(4) |
| $\beta$ (deg) | 94.30(1) | 110.719(3) |
| $\gamma$ (deg) | 90 | 111.367(4) |
| $V$ (Å$^3$) | 2584.8(8) | 2843.7(3) |
| $Z$ | 4 | 4 |
| $D_c$ | 1.59 | 1.59 |
| cryst. size (nm) | 0.30 × 0.30 × 0.10 | 0.50 × 0.25 × 0.10 |
| radiation | Cu-K$\alpha$ | Cu-K$\alpha$ |
| $2\theta_{max}$ (deg) | 140 | 148.6 |
| total data measd. ($3\sigma$) | 5395 | 12055 |
| obsd. unique data | 3944 | 7973 |
| $R$ | 0.0728 | 0.053 |

**6c**: The single crystal was prepared by recrystallization from 1,2-dichloroethane. The structure was solved by the direct method using the SHELX86 program and refined by the block-diagonal least squares analysis based on F values using the UNICS III program package. The positions of all hydrogen atoms were calculated using the HYCO80 program. All the non-hydrogen atoms were refined with anisotropic temperature factors. At the final stage, all hydrogen atoms were included in the refinement with isotropic factors. These calculations were carried out in the Computer Center of Institute for Molecular Science.

**$7b \cdot BF_4$**: The single crystal was obtained by recrystallization from acetonitrile. The structure was solved by the direct methods using the SHELXS86 program and expanded by Fourier techniques using the DIRDIF92 program. The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were included at calculated positions but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

## References

(1) V. Khodorkovsky and J. Y. Becker, "Molecular Design of Organic Conductors," in "Organic Conductors: Fundermentals and Applications," ed by J.-P. Farges, Marcel Dekker, New York (1994), Chap. 3, pp. 75.

(2) Y. Yamashita, S. Tanaka, and M. Tomura, *J. Chem. Soc., Chem. Commun.*, **1993**, 652.

(3) M. Ahmed and O. Meth-Cohn, *J. Chem. Soc. (C)*, **1971**, 2104.

(4) K. Takahashi, T. Nihira, M. Yoshifuji, and K. Tomitani, *Bull. Chem. Soc. Jpn.*, **66**, 2330 (1993).

(5) K. Akiba, K. Ishikawa, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2674 (1978).

(6) T. Suzuki, T. Sakimura, S. Tanaka, Y. Yamashita, H. Shiohara, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, **1994**, 1431.

(7) K. Elbl, C. Krieger, and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, **25**, 1023 (1986).

(8) H. Bock, A. Rauschenbach, K. Ruppert, and Z. Havlas, *Angew. Chem., Int. Ed. Engl.*, **30**, 714 (1991).

(9) H. A. Staab, J. Hofmeister, and C. Krieger, *Angew. Chem., Int. Ed. Engl.*, **30**, 1030 (1991).

(10) H. Bock, K. Ruppert, C. Näther, and Z. Havlas, *Angew. Chem., Int. Ed. Engl.*, **30**, 1180 (1991).

(11) T. Suzuki, H. Shiohara, M. Monobe, T. Sakimura, S. Tanaka, Y. Yamashita, and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, **31**, 455 (1992).

(12) S. Dähne and D. Leupord, *Angew. Chem., Int. Ed. Engl.*, **5**, 984 (1966).

(13) H. Hartmann and S. Scheithauer, *J. Prakt. Chem.*, **311**, 827 (1969).

(14) F. A. Mikhailenko and L. I. Shevchuk, *Synthesis*, **1973**, 621.

(15) R. Wizinger-Aust, *Q. Rep. Sulfur Chem.*, **5**, 191 (1970).

(16) M. Emmelius, G. Pawlowski, and H. W. Vollmann, *Angew. Chem., Int. Ed. Engl.*, **28**, 1445 (1989).

(17) J. Fabian and R. Zahradník, *Angew. Chem., Int. Ed. Engl.*, **28**, 677 (1989).

(18) J. Fabian, H. Nakazumi, and M. Matsuoka, *Chem. Rev.*, **92**, 1197 (1992).

(19) V. R. Mayer and H. Kröber, *J. Prakt. Chem.*, **316**, 907 (1974).

(20) U. Schöberl, J. Salbeck, and J. Daub, *Adv. Mater.*, **4**, 41 (1992).

(21) M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson, and P. Batail, *J. Am. Chem. Soc.*, **115**, 3752 (1993).

(22) D. Lorcy, R. Carlier, A. Robert, A. Tallec, P. L. Maguerès, and L. Ouahab, *J. Org. Chem.*, **60**, 2443 (1995).

(23) A. Benahmed-Gasmi, P. Frère, J. Roncali, E. Elandaloussi, J. Orduna, J. Garin, M. Jubault, and A. Gorgues, *Tetrahedron Lett.*, **36**, 2983 (1995).

(24) J. Nakayama, K. Fujiwara, and M. Hoshino, *Chem. Lett.*, **1975**, 1099.

(25) E. Laviron, *J. Electroanal. Chem.*, **100**, 269 (1979).

(26) G. J. Marshallsay and M. R. Bryce, *J. Org. Chem.*, **59**, 6847 (1994).

(27) M. Hanack, U. Schmid, S. Echinger, F. Teichert, and J. Hieber, *Synthesis*, **1993**, 634.

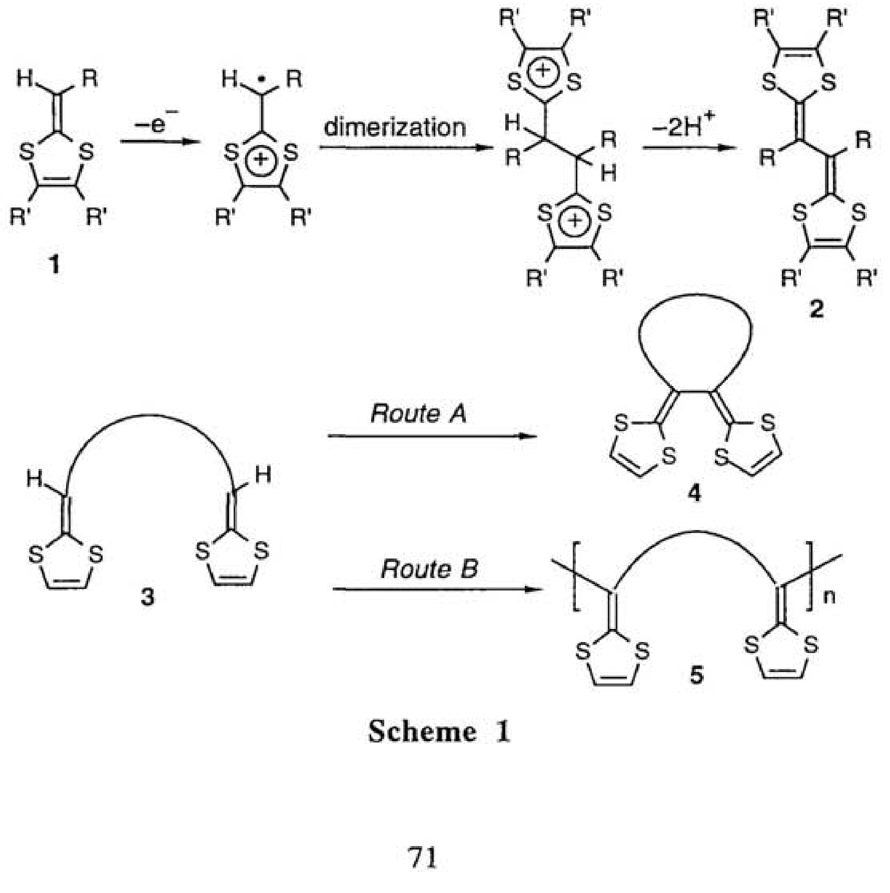
(28) M. Hanack, U. Schmid, U. Röhrig, J.-M. Toussaint, C. Adant, and J.-L. Bredas, *Chem. Ber.*, **126**, 1487 (1993).

(29) G. Hieber, M. Hanack, K. Wurst, and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, **124**, 1597 (1991).

# *Chapter 4 Oxidative Intramolecular Cyclization of 2,2'-Bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls*

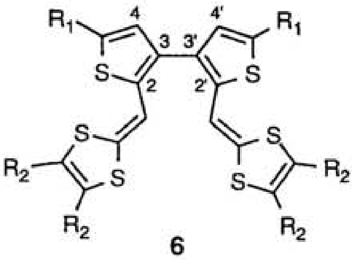
## Introduction

It is known that 1,4-dithiafulvene derivatives **1** undergo intermolecular coupling reactions at the 6-position by oxidation to give 1,2-bis(1,3-dithiol-2-ylidene)ethane derivatives **2**.[1-5] Very recently, Benahmed-Gasmi *et al.*[4] and Lorcy *et al.*[5] pointed out the synthetic utility of such reactions. However, the corresponding intramolecular cyclization is unknown so far. If a compound **3** possessing two dithiafulvenyl groups in the terminal positions undergoes this type of reaction, it should give a novel bis(1,3-dithiole) donor **4** containing a 1,2-bis(1,3-dithiol-2-ylidene)ethano moiety with *cis* configuration (Scheme 1, *Route A*). Such an electron donor is little known except for radialene derivatives.[6] On the other hand, since the molecule **3** has two reactive groups,

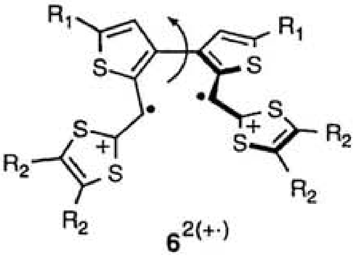


**Scheme 1**

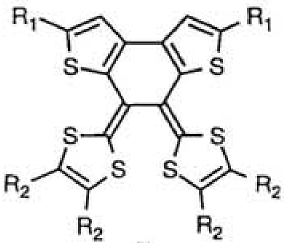
an intermolecular coupling reaction giving a polymer **5** is also possible (*Route B*). Actually, a certain bis(1,3-dithiole) compound afforded a polymer as described in chapter 2 and chapter 3. To avoid such an intermolecular reaction, it is necessary to choose an appropriate spacer unit that makes two terminal dithiafulvenyl groups close to each other. From this viewpoint, a 3,3'-bithienyl unit seems suitable for such a spacer when two 1,4-dithiafulven-6-yl groups are attached to the 2- and 2'-positions. Moreover, since the 3,3'-bithienyl unit twists around the central C–C bond due to the steric interactions between the atoms on the 2-, 2'-, 4-, and 4'-positions, conjugation interactions between the two halves of **6** are considered to be small.[7] Therefore, the corresponding dication species is expected to show a dication diradical character $\mathbf{6}^{2(+\cdot)}$, which seems favorable for the radical ring closure. Taking this hypothesis into account, the author decided to prepare the bis(1,3-dithiole) compounds **6** containing a 3,3'-bithienyl unit. The compounds **6** are expected to afford novel bis(1,3-dithiole) donors **7**. In this chapter, the preparation and electrochemical properties of the compounds **6** and the successful formation of the corresponding cyclization products are described.



**6**



$\mathbf{6}^{2(+\cdot)}$

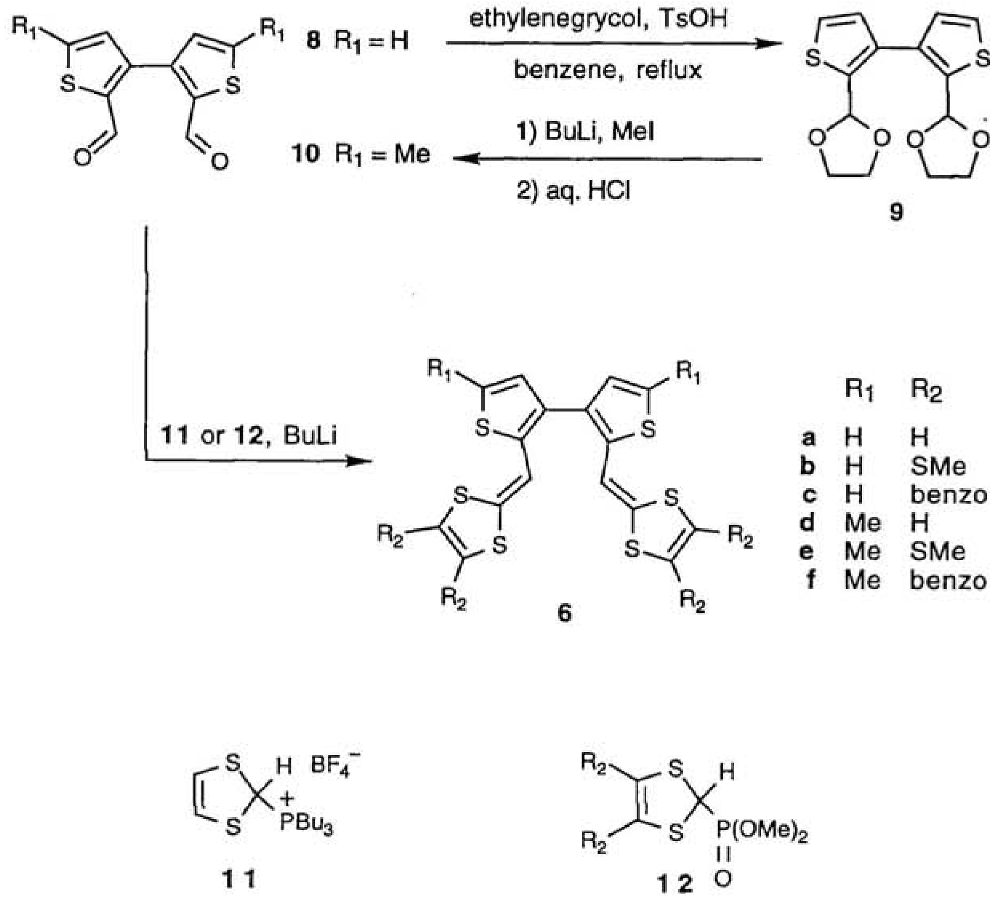


**7**

## Results and Discussion

### Preparation and Characterization of 2,2'-Bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls

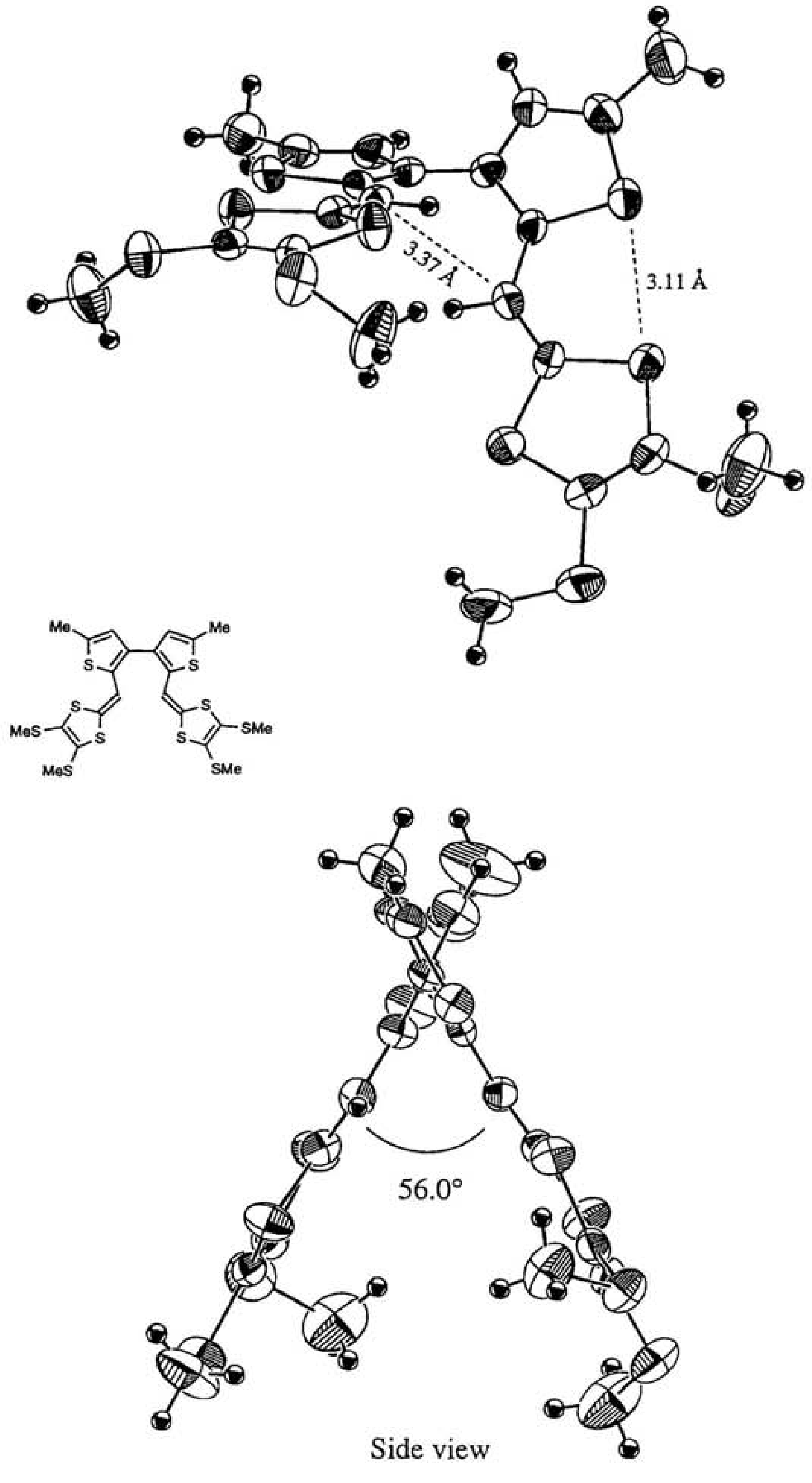
The new bis(1,3-dithiole) compounds **6** were synthesized according to Scheme 2. The formyl groups of aldehyde **8**[8] were protected as dioxolane groups to give a compound **9** in 96% yield. Methylation of **9** with butyllithium and methyl iodide gave a dimethyl derivative **10** in 84% yield. Although the parent compound **6a** could not be isolated in pure form, the compounds **6b–f** were prepared by either a Wittig reaction of a phosphonium salt **11**[9] (for **6a**) or a Wittig–Horner reaction of phosphonate esters **12**[10] with the corresponding aldehydes **8** and **10** in 69–93% yields.



| | R1 | R2 |
|---|---|---|
| **a** | H | H |
| **b** | H | SMe |
| **c** | H | benzo |
| **d** | Me | H |
| **e** | Me | SMe |
| **f** | Me | benzo |

**Scheme 2**

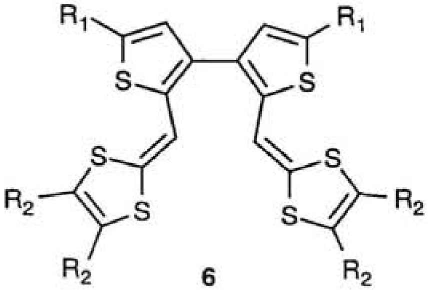
The X-ray structural analysis of **6e** reveals that the molecule twists around the central C–C bond and the two dithiafulvenylthiophene subunits are almost planar as shown in Figure 1. The dihedral angle formed by two thiophene rings is 56.0°. The short S···S contacts between the sulfur atoms of the thiophene and the dithiole (3.11 and 3.23 Å) are observed. The interatomic distance between C6- and C6'-carbons of the dithiafulvenyl groups is 3.37 Å.



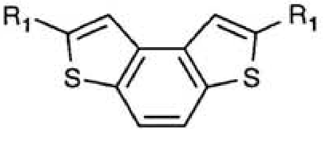
Side view

Figure 1. X-ray molecular strucure of **6e**.

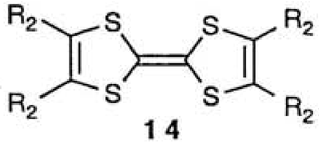
In the electron impact mass spectra of **6**, the molecular ion peaks were rarely observed. Instead, fragment ion peaks corresponding to benzodithiophene derivatives **13** and tetrasubstituted tetrathiafulvalenes **14** were observed with sufficient intensities. The data are listed in Table 1. These observations are attributed to a metathesis-like fragmentation of the molecular ion. This fact suggests that there exist some interactions between the two dithiafulvenyl groups in the cation radical state.



**6**



**13**



**14**

**Table 1**. Selected peaks in the mass spectra of the compounds **6**.[a]

| Compound | | | *m* / *z* (relative intensity, %) | | |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $M^+$ | $13^{+\cdot}$ | $14^{+\cdot}$ |
| **6b** | H | SMe | 578 (0) | 190 (74) | 388 (100) |
| **6c** | H | benzo | 494 (2) | 190 (37) | 304 (100) |
| **6d** | Me | H | 422 (5) | 218 (33) | 204 (100) |
| **6e** | Me | SMe | 606 (0) | 218 (38) | 388 (100) |
| **6f** | Me | benzo | 522 (6) | 218 (27) | 304 (100) |

[a] Electron impact ionization, 70 eV.

According to the MNDO-PM3 calculations[11] on **6a**, the carbon atoms at the 6-positions of the dithiafulvenyl groups have larger atomic orbital coefficients in the HOMO than the α-carbons of thiophene ring (Figure 2). If the oxidative coupling reaction is governed by the HOMO, it may occur selectively at these positions to give a cyclization product.

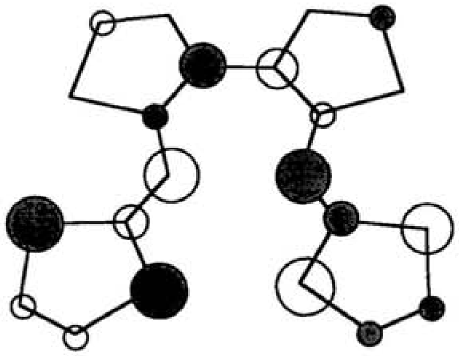


**Figure 2.** Atomic orbital coefficients in the HOMO of **6a** calculated by the MNDO-PM3 method.

### Electrochemical Properties

The solution electrochemical properties of the bis(1,3-dithiole) compounds **6** were studied by cyclic voltammetry. The cyclic voltammogram (CV) of **6b** in benzonitrile is shown in Figure 3 and the redox potentials are summarized in Table 2. The CVs of **6** are typical for compounds in which electron transfer is accompanied by chemical reactions.[12] Namely, they are irreversibly oxidized at peak potentials of $E_{pa}$ to give new redox active products which show reversible waves at half-wave potentials of $E(\mathrm{new})_{1/2}$ by subsequent chemical reactions. The re-reduction peaks corresponding to the first

**Table 2.** Redox potentials of the compounds **6**.[a]

| Compound | $R_1$ | $R_2$ | $E_{pa}$ | $E(\mathrm{new})_{1/2}$ |
|---|---|---|---|---|
| **6b** | H | SMe | 0.75 | 0.34 |
| **6c** | H | benzo | 0.88 | 0.41 |
| **6d** | Me | H | 0.58 | 0.18 |
| **6e** | Me | SMe | 0.69 | 0.29 |
| **6f** | Me | benzo | 0.83 | 0.35 |

[a] $Bu_4NBF_4$ (0.1 mol dm$^{-3}$) in PhCN, Pt electrode, scan rate 100 mV s$^{-1}$, $E$ / V *vs.* saturated calomel electrode (SCE).

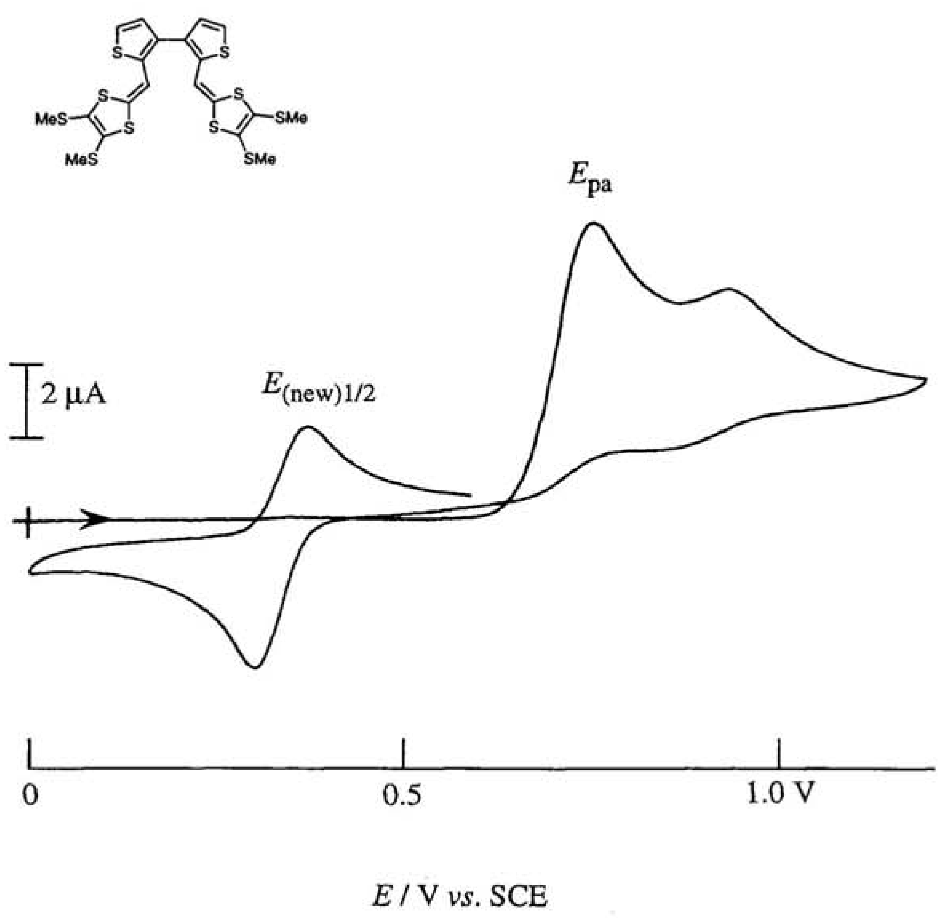
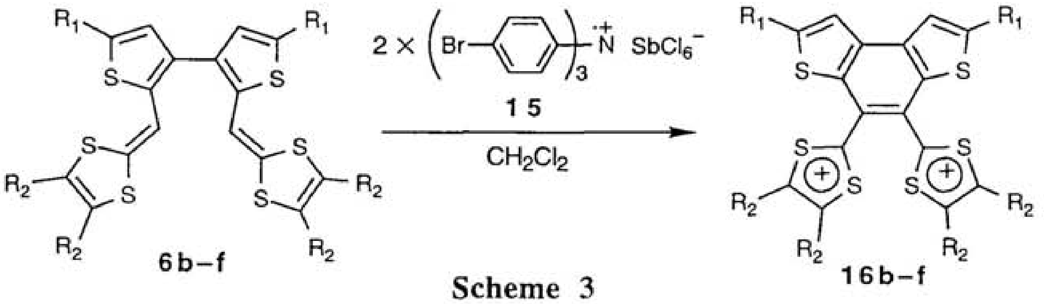


**Figure 3**. Cyclic voltammogram of **6b** in benzonitrile.

oxidation peaks could be observed only at the high scan rate (> 5 V $s^{-1}$), indicating that the subsequent chemical reactions are very fast. Since such electrochemical behaviors were independent of α-substituents ($R_2$) on the thiophene rings, the reactions seem to take place at the C6-carbons of the dithiafulvenyl groups as predicted by the PM3 calculations. The $E_{pa}$ values of **6** are close to those of the corresponding 2-(1,4-dithiafulven-6-yl)thiophenes,[4] suggesting that the molecules consist of the two almost independent dithiafulvenylthiophene units due to the twisted structure.

## Oxidative Intramolecular Cyclization

Isolation of oxidation products was attempted by using tris(4-bromophenyl)aminium hexachloroantimonate **15** as a one-electron oxidizing agent. Treatment of the compounds **6b–f** with 2 equivalents of **15** in dichloromethane at room temperature gave cyclization products **16b–f** as dication salts in high yields (Scheme 3). Any products arising from intermolecular reactions were not detected. The structure assignments of the dications were based on the $^1H$ NMR spectra. For example, the dication **16d** showed the $^1H$ NMR signals of methyl protons at δ 2.75 (s, 6H), thienyl protons at δ 7.72 (s, 2H), and deshielded dithiole ring protons at δ 9.21 (s, 4H). Observation of the singlet for the four dithiole ring protons indicates the single bond character of the C–C bonds between the dithiole rings and the tricyclic system. These dications can be regarded as the first example of 2,2'-(*o*-phenylene)bis(1,3-dithiolium) cation derivative, which has been considered unstable due to Coulombic repulsion between the positive charges.[13]

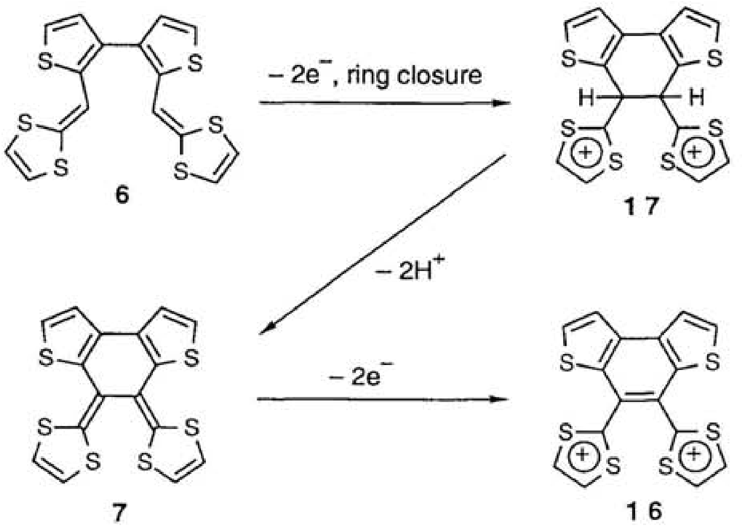


Scheme 3

In order to confirm the structure of inorganic conteranions as well as the dication, X-ray structural analyses were carried out on the salt of **16e**. Prism-like crystals were obtained by slow evaporation of dichloromethane. On the other hand, vapor diffusion of ether to a solution of the salt of **16e** in dichloromethane gave needle-like single crystals. The analysis for each crystal revealed that they are different in their counteranion. Namely, while the prism-like crystal contains $SbCl_6^-$ and $Sb_2Cl_8^{2-}$, the needle-like one includes $SbCl_5^{2-}$ and $Sb_2Cl_8^{2-}$ (Figure 4). The presence of trivalent chloroantimonate ions such as $SbCl_5^{2-}$ and $Sb_2Cl_8^{2-}$ suggests that hexachloroantimonate ion ($SbCl_6^-$) acts as an oxidant in the reaction (Scheme 4). The oxidizing ability of $SbCl_6^-$ for organic compounds was reported previously.[14] The structure of the dication will be discussed later in this chapter (p. 83, *X-ray Structural Analyses*). The formation of dication **16** can be explained by deprotonation from an intermediate **17**, followed by two-electron oxidation of the resulting neutral donor **7** (Scheme 5).

$$\begin{tikzcd} & {\left[\mathrm{Sb^{III}Cl_4^-}\right]} \arrow[r, "\text{dimerization}"] & \mathrm{Sb_2{}^{III}Cl_8^{2-}} \\ \mathrm{Sb^{V}Cl_6^-} \arrow[ur, "+2e^-,\ -2Cl^-"] \arrow[dr, "+2e^-,\ -Cl^-"'] & & \\ & \mathrm{Sb^{III}Cl_5^{2-}} & \end{tikzcd}$$

Scheme 4



Scheme 5

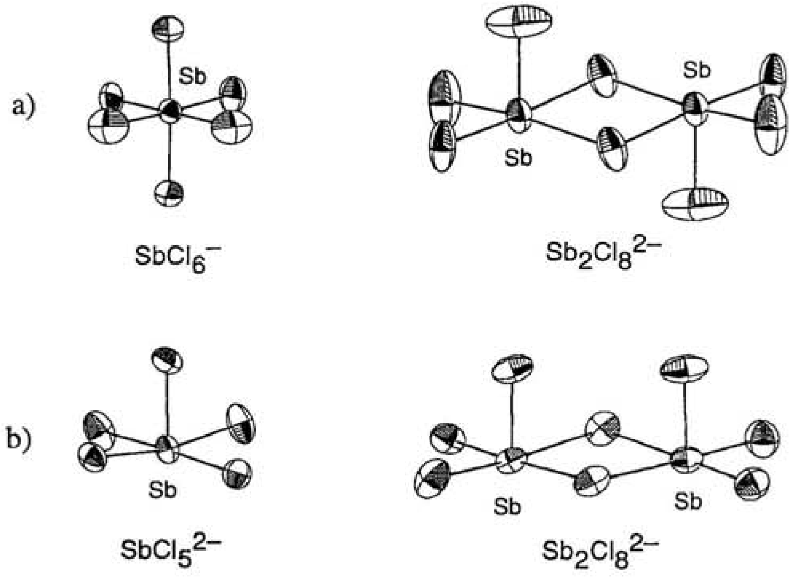


**Figure 4**. X-ray molecular structures of the chloroantimonate ions found in (a) the prism-like and (b) the needle-like crystals of the dication salt **16e**.

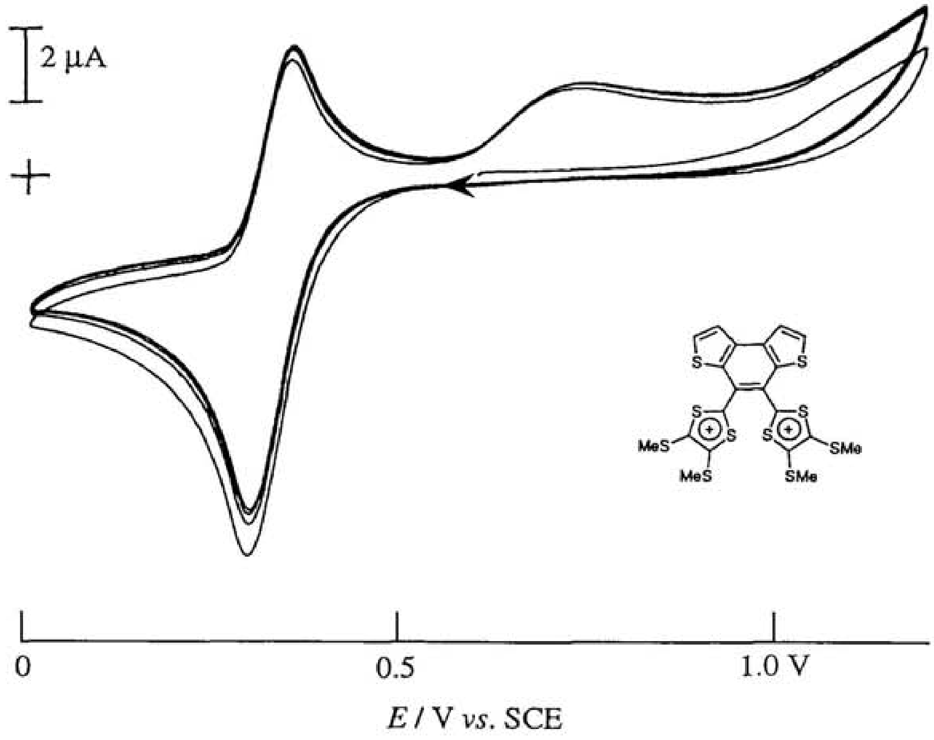
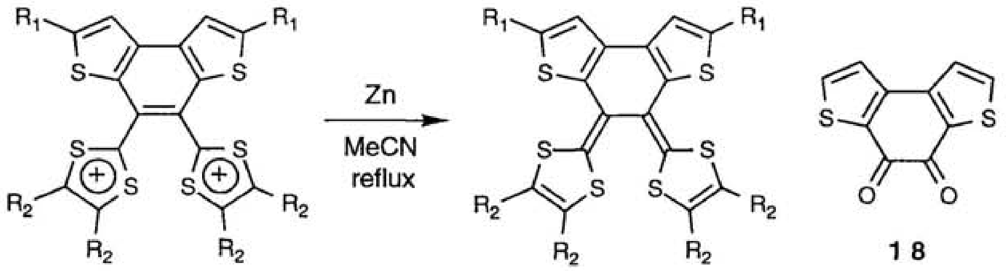


**Figure 5**. Cyclic voltammogram of the dication salt **16b** in benzonitrile.

The CV of **16b** is shown in Figure 5. The redox potentials of the dications **16** are in complete agreement of $E(\text{new})_{1/2}$ for the starting compounds **6**. This fact shows that the new reversible waves observed in the CVs of **6** correspond to the redox reactions of the electrochemically generated dications **16**. Chemical reduction of the dication salts **16b–f** with zinc in refluxing acetonitrile afforded the corresponding neutral donors **7b–f** in good yields (Scheme 6). The structures of **7** were established on the basis of the $^1$H and $^{13}$C NMR spectra, elemental analyses, and high resolution mass spectra. On the other hand, attempted preparation of **7c** using a Wittig–Horner reaction of **12** ($R_2$,$R_2$ = benzo) with the corresponding quinone **18** resulted in recovery of **18**. This result indicates the usefulness of the cyclization reaction described here to prepare such bis(1,3-dithiole) donors.



16b–c

7b–c

18

Scheme 6

The donors **7b–f** are air-stable reddish orange crystals. The UV–VIS spectrum of **7b** in dichloromethane showed absorption maxima at 266, 278, 342, and 471 nm, and the longest wavelength absorption band is red-shifted by 93 nm compared with that of the bithienyl **6b** due to the extension of π-conjugation (Figure 6). The donors showed reversible one-stage two-electron redox waves, and the CVs are nearly identical with those of the dications. The typical example of the CV of **7b** is shown in Figure 7. Although the donors have fairly low oxidation potentials (**7b**, 0.34; **7c**, 0.41; **7d**, 0.18; **7e**, 0.29; **7f**, 0.35 V *vs.* SCE), their ability to form charge-transfer (CT) complexes is poor. Among them the donor **7d** gave a CT complex with tetracyanoquinodimethane which showed a conductivity of $1.7 \times 10^{-5}$ S cm$^{-1}$ as a compressed pellet.

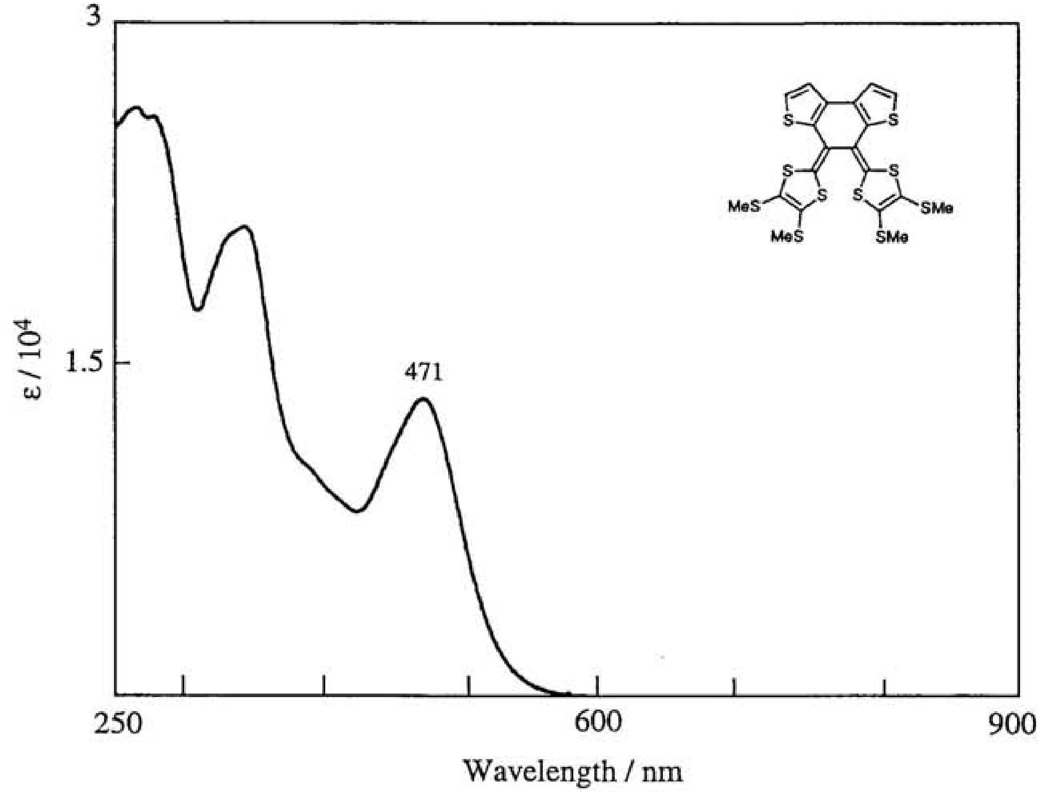


**Figure 6**. Absorption spectrum of the donor **7b** in dichloromethane.

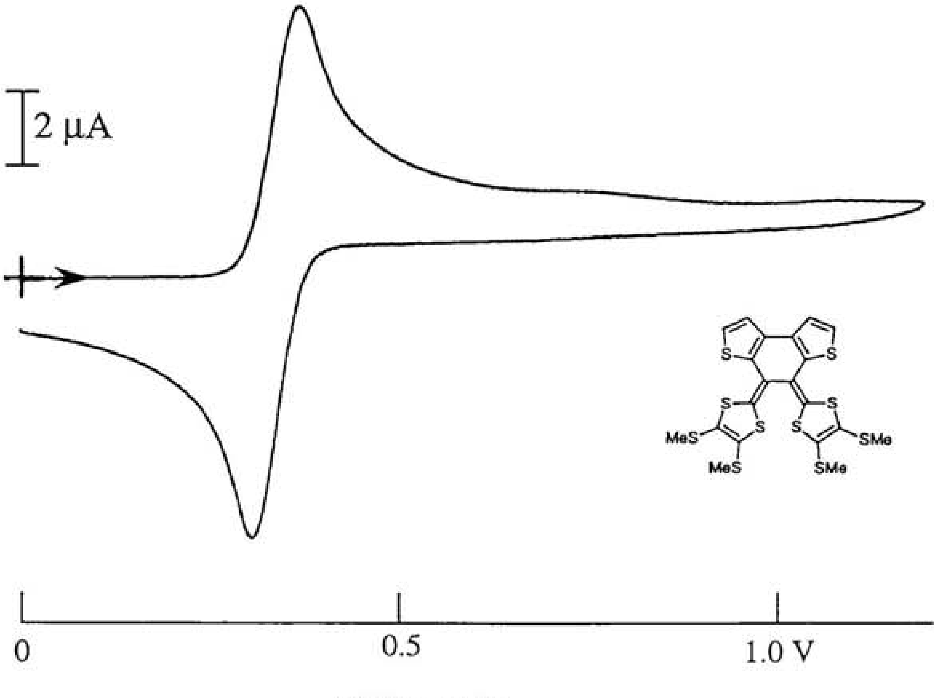
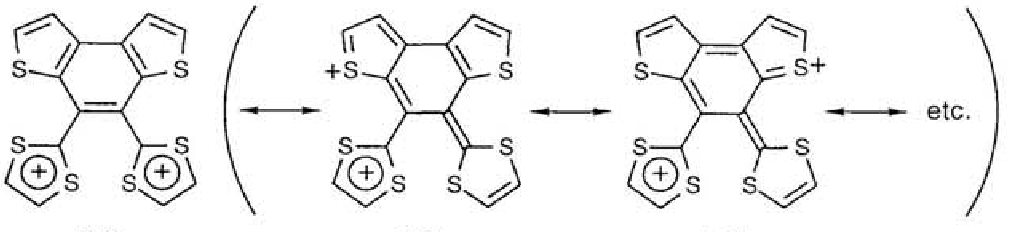


**Figure 7**. Cyclic voltammogram of the donor **7b** in benzonitrile.

## X-ray Structural Analyses

In order to investigate the molecular structure of the neutral donor, the X-ray structural analysis was carried out on the donor **7e**. The single crystal was obtained by recrystallization from chloroform–hexane. Figure 8 shows the X-ray molecular structure of the neutral donor **7e**. The molecule has a $C_2$ symmetry and takes a nonplanar structure. The two 1,3-dithiole rings deviate largely from the plane of the tricyclic system to avoid the steric interaction between the sulfur atoms of the dithiole rings. Short intramolecular S···S contacts (3.01 Å) are observed. The central six-membered ring adopts a slightly twisted conformation. The torsion angles formed by C1–C5–C5*–C1* and C6–C5–C5*–C6* atoms are 29(2) and 38(2)°, respectively. No significant intermolecular interaction is observed.

The X-ray molecular structure of the dication **16e** found in the prism-like crystal is shown in Figure 9. The molecule has an approximate two-fold symmetry. In contrast to the neutral molecule, in the dication the two 1,3-dithiole rings are attached to the completely planar tricyclic system with the dihedral angles of 77.6 and 70.7°. The average bond length of the C–C bonds in the central six-membered ring is 1.41 Å which is comparable to that of benzene (1.399 Å). The C–C bond lengths between the 1,3-dithiole rings and the tricyclic system are 1.47(1) and 1.46(1) Å, indicating the single bond character of these bonds. Thus, the contribution of canonical forms **16'** and **16"**, in which the positive charges are delocalized over the whole molecule, is negligible. There are no significant intramolecular interactions between the sulfur atoms. It appears that the steric interactions between the sulfur atoms found in the neutral molecule are reduced by the rotation of 1,3-dithiole rings.



**16** **16'** **16"**

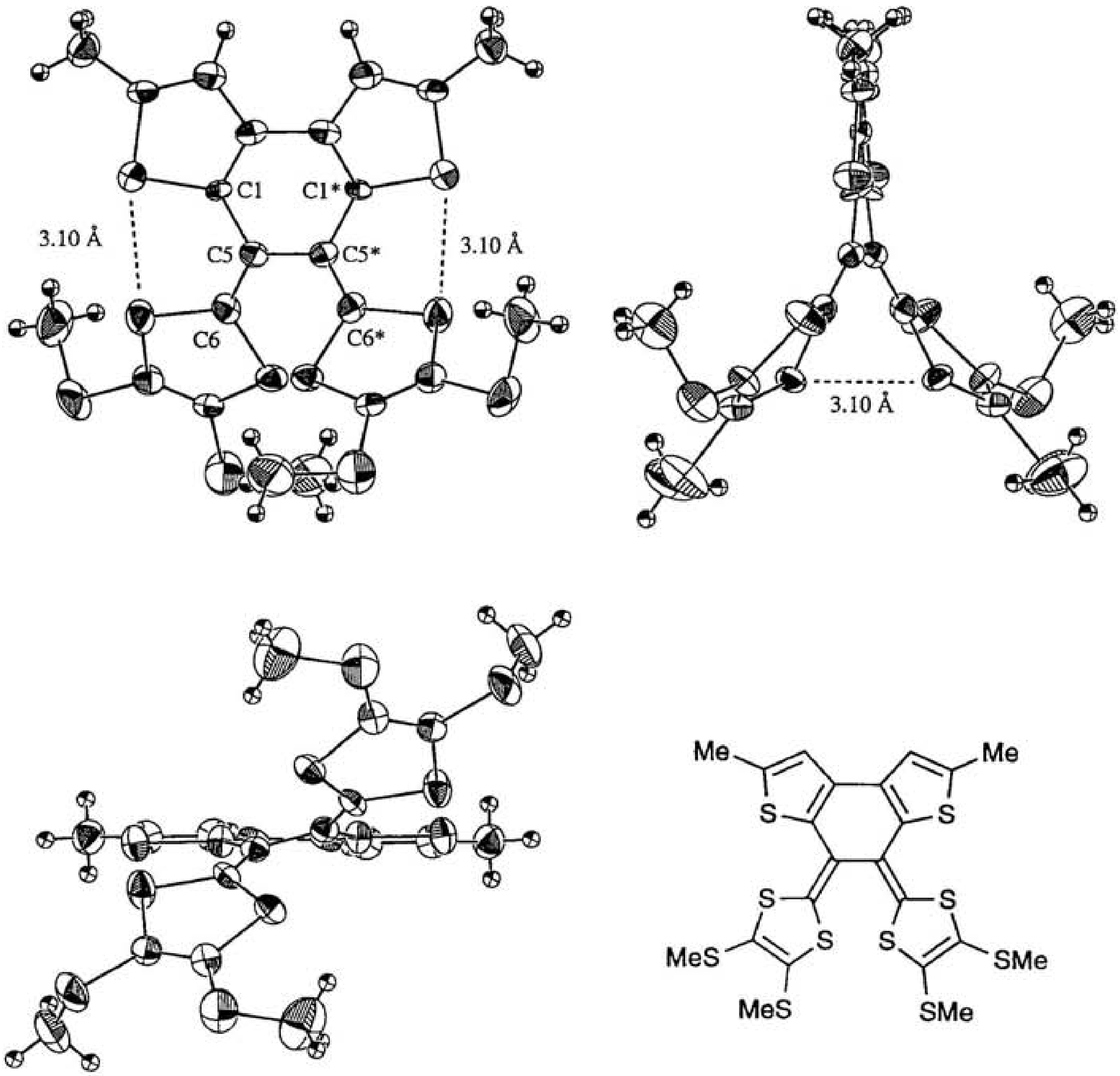


**Figure 8**. X-ray molecular structure of the donor **7e**.

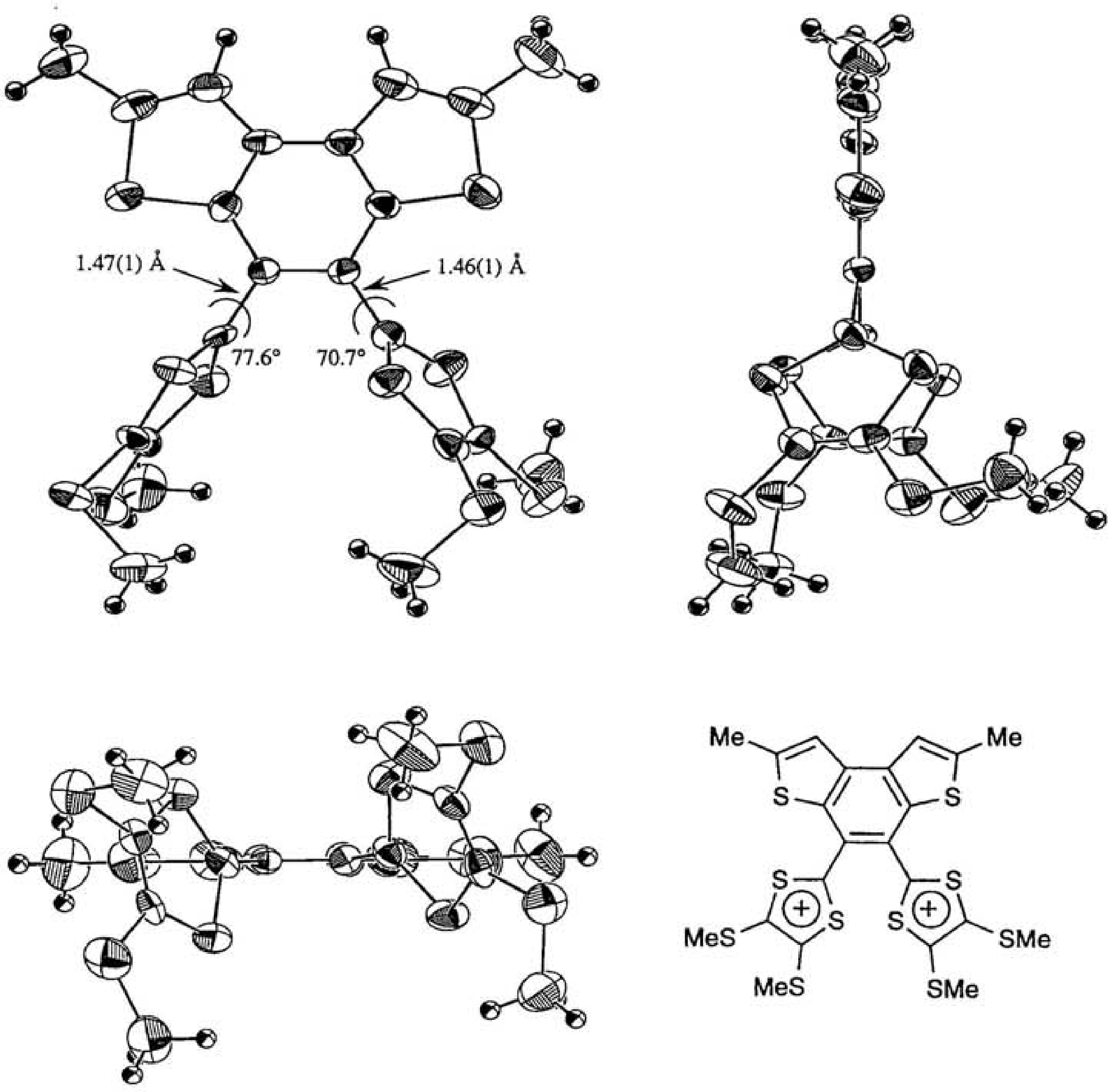


**Figure 9**. X-ray molecular structure of the dication **16e**.

## Conclusion

Oxidative intramolecular cyclization of 2,2'-bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls **6** was investigated, and the usefulness of this reaction on the syntheses of the novel bis(1,3-dithiole) donor was proved. The cyclic voltammograms of the compounds reveal that they undergo intramolecular cyclization by electrochemical oxidation. Chemical oxidation of **6** with tris(4-bromophenyl)aminium hexachloroantimonate gave dication **16**. It was found that the hexachloroantimonate ion acts as an oxidizing agent in the reaction. The neutral donors were obtained by chemical reduction of the dication salts with zinc in high yields. The CVs of the donors showed reversible one-stage two-electron oxidation waves, and the potentials are fairly low compared with TTF. A conductive tetracyanoquinodimethane complex was formed from one of them. X-ray analyses of the neutral and dication states of the donor show that there is a large conformational change between them.

## Experimental

**General**. Melting points were measured on a Yanaco MP-500D melting point apparatus and are uncorrected. IR and UV spectra were recorded on a Perkin-Elmer FTIR 1600 and a Shimadzu UV-3101PC spectrometer, respectively. $^1$H (200 MHz) and $^{13}$C (67.8 MHz) NMR spectra were measured on a JEOL-JNM-EX270 spectrometer. EI (70 eV) and FAB (Xe, 7kV) mass spectra were measured on a Shimadzu GCMS-QP1000EX and a Shimadzu Kratos CONCEPT 1S spectrometer, respectively. Elemental analyses were performed on a Yanaco MT-3 CHN CORDER. Chromatographic separations were performed with Merk aluminium oxide 90 (activity II to III). Yields are based on isolated products with sufficient purity. Tetrahydrofuran (THF) was distilled over lithium aluminium hydride prior to use.

**Electrochemical Measurements**. Cyclic voltammetry experiments were performed in a three-compartment cell with a Pt disc working electrode, Pt wire counter electrode, and saturated calomel reference electrode. Measurements were made with a Toho Technical Research Polarization Unit PS-07 potentiostat / galvanostat with a scan rate of 100 mV s$^{-1}$. The cell contained a solution of a substrate (*ca.* 1 mmol dm$^{-3}$) and tetrabutylammonium tetrafluoroborate (0.1 mol dm$^{-3}$) as supporting electrolyte in benzonitrile or dichloromethane. All solutions were purged with argon and retained under the inert atmosphere during the experiment.

**Computational Studies**. MNDO-PM3 calculations were performed by using the MOPAC version 6.10 program.[11] The calculations were carried out using the Sony-Tektronix CAChe system.

**2,2'-Bis(1,3-dioxolan-2-yl)-3,3'-bithienyl (9)**. A mixture of aldehyde **8**[8] (4.0 g, 18 mmol), ethyleneglycol (3.0 g, 48 mmol), and *p*-toluenesulfonic acid (50 mg, 0.26 mmol) in benzene (50 ml) was heated under reflux for 4 h with removal of the resulting water as azeotropic mixture by using a Dean–Stark apparatus. The solution was washed with sat. aq. $NaHCO_3$, dried over $Na_2SO_4$, and concentrated under reduced pressure. The resulting solid was washed with hexane to give the dioxolane **9** (5.4 g, 96%) as pale yellow prisms (from $Et_2O$): mp 117–118 °C; IR (KBr) 3104, 2892, 1445, 1394, 1192, 1067, 952, 863, 726, 659 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 3.90–4.02$ (4H, AA'BB', dioxolane-H), 4.10–4.22 (4H, AA'BB', dioxolane-H), 5.91 (2H, s, CH), 7.10 (2H, d, $J = 5.3$ Hz, Th-H), 7.35 (2H, d, $J = 5.3$ Hz, Th-H); $^{13}C$ NMR ($CDCl_3$) $\delta = 65.21$, 98.87, 125.28, 129.81, 135.00, 137.30; MS *m/z* (rel intensity) 310 ($M^+$, 9), 265 (18), 237 (76), 193 (61), 177 (13), 166 (10), 155 (14), 121 (22), 91 (27), 73 ($C_3H_5O_2^+$, 100); Found: C, 54.11; H, 4.54%. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.17; H, 4.55%.

**2,2'-Diformyl-5,5'-dimethyl-3,3'-bithienyl (10).** A solution of BuLi in hexane (1.64 mol $dm^{-3}$, 22.0 ml, 36.1 mmol) was added to a solution of the dioxolane **9** (5.0 g, 16.1 mmol) in THF (50 ml) over a period of 10 min at –60 to –50 °C under argon. After stirring for 20 min, methyl iodide (5 ml, 80 mmol) was added to the mixture. The mixture was stirred for 20 min at –60 °C and allowed to warm to room temperature. To the mixture aq HCl (1 mol $dm^{-1}$, 50 ml) was added, and the mixture was stirred for 1 h at room temperature. The resulting solid was collected by filtration and washed with water, followed by ethanol to give the aldehyde **10** (3.36 g, 84%) as colorless needles (from EtOH): mp 203–204 °C; IR (KBr) 2924, 1656, 1643, 1442, 1356, 1225, 848, 675, 502 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta = 2.60$ (6H, d, $J = 1.0$ Hz, Me), 6.90 (2H, d, $J = 1.0$ Hz, Me), 9.70 (2H, s, CHO); $^{13}C$ NMR ($CDCl_3$) $\delta = 16.16$, 130.10, 138.80, 142.35, 150.57, 182.26; MS *m/z* (rel intensity) 250 ($M^+$, 4), 235 (6), 221 (M–CHO, 100); Found: C, 57.56; H, 4.05%. Calcd for $C_{12}H_{10}O_2S_2$: C, 57.58; H, 4.03%.

**2,2'-Bis(2,3-dimethylthio-1,4-dithiafulven-6-yl)-3,3'-bithienyl (6b).** A solution of BuLi in hexane (1.64 mol $dm^{-3}$, 3.0 ml, 4.9 mmol) was added to a solution of the phosphonate ester **12**[10] ($R_2$ = SMe, 1.5 g, 4.9 mmol) in THF (20 ml) at –78 °C under argon. After stirring for 10 min, a solution of the aldehyde **8** (520 mg, 2.3

mmol) in THF (5 ml) was added to the mixture. The mixture was stirred for 15 min at −78 °C and allowed to warm to room temperature. The solvent was removed under reduced pressure, water was added to the residue, and the product was extracted with dichloromethane. The extract was washed with water, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography (alumina / toluene) to give the compound **6b** (1.15 g, 85%) as yellow prisms (from $CHCl_3$–hexane): mp 179–180 °C; IR (KBr) 2917, 1567, 1498, 1481, 1428, 970, 890, 850, 730, 694, 654, 595 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta = 2.42$ (6H, s, SMe), 2.44 (6H, s, SMe), 6.42 (2H, s, =CH), 7.03 (2H, d, $J$ = 5.3 Hz, Th-H), 7.62 (2H, d, $J$ = 5.3 Hz, Th-H); $^{13}C$ NMR (DMSO-$d_6$) $\delta = 17.79$, 18.01, 107.59, 123.25, 124.12, 127.32, 129.17, 130.37, 131.56, 135.17; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 250 (4.35), 378 (4.41) nm; MS *m/z* (rel intensity) 388 (TMTTF$^+$, 100), 233 (31), 190 (74); Found: C, 41.18; H, 3.08%. Calcd for $C_{20}H_{18}S_{10}$: C, 41.48; H, 3.13%.

The other compounds **6c–f** were prepared by the similar procedure. In the case of **6d**, the phosphonium salt **11**[9] was used instead of a phosphonate ester.

**6c**: 82%; yellow needles (from $CHCl_3$–EtOH); mp 193–194 °C; IR (KBr) 1572, 1556, 1481, 1448, 1434, 737, 687 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta = 6.55$ (2H, s, =CH), 7.12 (2H, d, $J$ = 5.3 Hz, Th-H), 7.19–7.24 (4H, m, benzo-H), 7.41–7.44 (2H, m, benzo-H), 7.58–7.62 (2H, m, benzo-H), 7.73 (2H, d, $J$ = 5.3 Hz, Th-H); $^{13}C$ NMR (DMSO-$d_6$) $\delta = 107.32$, 121.64, 122.48, 124.64, 126.11, 126.60, 129.74, 131.11, 131.90, 134.43, 135.37, 135.67; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 245 (4.49), 353 (4.49), 379 (4.48) nm; MS *m/z* (rel intensity) 494 (M$^+$, 2), 341 (11), 304 (DBTTF$^+$, 100), 190 (37); Found: C, 58.00; H, 3.08%. Calcd for $C_{24}H_{14}S_6$: C, 58.27; H, 2.85%.

**6d**: 69%; yellow prisms (from $CHCl_3$–hexane); mp 186–188 °C; IR (KBr) 3069, 2912, 1565, 1522, 805, 638, 507 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta = 2.49$ (6H, s, Me), 6.42 (2H, s, =CH), 6.70 (2H, s, Th-H), 6.73 (2H, d, $J$ = 6.6 Hz, dithiole-H), 6.77 (2H, d, $J$ = 6.6 Hz, dithiole-H); $^{13}C$ NMR (DMSO-$d_6$) $\delta = 15.06$, 105.23, 118.78, 119.23, 127.98, 130.53, 134.14, 134.40, 136.66; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 253 (4.26), 362 (4.41), 388 (4.41) nm; MS *m/z* (rel intensity) 422 ($M^+$, 5), 319 (11), 287 (16), 231 (36), 218 (33), 204 ($TTF^+$, 100); Found: C, 51.35; H, 3.39%. Calcd for $C_{18}H_{14}S_6$: C, 51.15; H, 3.34%.

**6e**: 90%; yellow prisms (from $CHCl_3$–hexane); mp 159–160 °C; IR (KBr) 2916, 1567, 1428, 969, 892, 509 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta = 2.41$ (6H, s, SMe), 2.44 (6H, s, SMe), 2.48 (6H, s, Me), 6.38 (2H, s, =CH), 6.72 (2H, s, Th-H); $^{13}C$ NMR (DMSO-$d_6$) $\delta = 15.06$, 18.10, 18.37, 108.21, 122.81, 127.59, 127.94, 128.50, 131.72, 133.30, 138.17; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 255 (4.33), 367 (4.37) nm; MS *m/z* (rel intensity) 388 ($TMTTF^+$, 100), 373 (20), 262 (15), 218 (38); Found: C, 43.48; H, 3.75%. Calcd for $C_{22}H_{22}S_{10}$: C, 43.53; H, 3.65%.

**6f**: 93%; yellow powder (from $CHCl_3$–hexane); mp 278–280 °C; IR (KBr) 2996, 2911, 1578, 1446, 1435, 1122, 813, 739 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 249 (4.45), 350 (4.47), 378 (4.43, sh) nm; MS *m/z* (rel intensity) 522 ($M^+$, 6), 382 (10), 369 (13), 337 (10), 304 ($DBTTF^+$, 100), 218 (27), 153 (10); Found: C, 59.56; H, 3.56%. Calcd for $C_{26}H_{18}S_6$: C, 59.73; H, 3.47%. NMR spectra could not be measured because of its low solubility.

**Chemical oxidation of the compound 6b**. A solution of the compound **6b** (100 mg, 0.17 mmol) in dichloromethane (10 ml) was added to a suspension of tris(4-bromophenyl)aminium hexachloroantimonate (285 mg, 0.35 mmol) in dichloromethane (50 ml) at room temperature under argon. The mixture was stirred for 2 h and concentrated to *ca.* 30 ml under reduced pressure. To the residue was added dry diethyl ether (30 ml), and the precipitate was collected by filtration and washed with ether to give dication **16b** salt (200 mg) as a violet solid: decomp.p. 115–125 °C; IR (KBr) 1466, 1418, 1368, 1315, 1243, 1060, 847, 748 $cm^{-1}$; $^1H$ NMR ($CD_3CN$) $\delta = 2.87$ (12H, s, SMe), 8.10 (2H, d, $J = 5.6$ Hz, Th-H), 8.19 (2H, d, $J = 5.6$ Hz, Th-H); UV ($CH_2Cl_2$)

$\lambda_{max}$ 256, 306 (sh), 499 nm; Found: C, 24.33; H, 1.67%. These values correspond to a formula, 2(**16b**)·$SbCl_5^{2-}$·$Sb_2Cl_8^{2-}$ (C, 24.26; H, 1.63%).

The other compounds **6c–f** were oxidized by the similar procedure to give the corresponding dication salts **16c–f**. These salts were used to the next step without further purification. The data are as follows.

**16c**: violet solid; decomp.p. 160–170 °C; IR (KBr) 1544, 1460, 1309, 1239, 1113, 1020, 846, 747 $cm^{-1}$; $^1H$ NMR ($CD_3CN$) $\delta = 8.06–8.12$ (4H, AA'BB', benzo-H), 8.18 (2H, d, $J$ = 5.6 Hz, Th-H), 8.26 (2H, d, $J$ = 5.6 Hz, Th-H), 8.63–8.65 (4H, AA'BB', benzo-H); UV ($CH_2Cl_2$) $\lambda_{max}$ 259, 321, 503 nm.

**16d**: violet solid; decomp.p. 150–160 °C; IR (KBr) 1558, 1488, 1447, 1298, 1243, 1174, 721 $cm^{-1}$; $^1H$ NMR ($CD_3CN$) $\delta = 2.75$ (6H, s, Me), 7.72 (2H, s, Th-H), 9.21 (4H, s, dithiole-H) ; UV ($CH_2Cl_2$) $\lambda_{max}$ 258, 321, 500 nm.

**16e**: violet solid; decomp.p. 208–213 °C; IR (KBr) 1558, 1484, 1419, 1374, 1294, 1240, 1174, 1059, 971, 832 $cm^{-1}$; $^1H$ NMR ($CD_3CN$) $\delta = 2.74$ (6H, s, Me), 2.85 (12H, s, SMe), 7.68 (2H, s, Th-H) ; UV ($CH_2Cl_2$) $\lambda_{max}$ 258, 321, 508 nm; Found: C, 25.91; H, 2.10% These values correspond to a formula, 2(**16e**)·$SbCl_5^{2-}$ ·$Sb_2Cl_8^{2-}$ (C, 25.96; H, 1.98%).

**16f**: violet solid; decomp.p. 165–170 °C; IR (KBr) 1550, 1479, 1436, 1293, 1239, 1174, 1110, 1021, 750 $cm^{-1}$; $^1H$ NMR ($CD_3CN$) $\delta = 2.77$ (6H, d, $J$ = 1.1 Hz, Me), 7.76 (2H, d, $J$ = 1.1 Hz, Th-H), 8.04–8.11 (4H, AA'BB', benzo-H), 8.60–8.67 (4H, AA'BB', benzo-H); UV ($CH_2Cl_2$) $\lambda_{max}$ 259, 325, 364 (sh), 503 nm; Found: C, 27.86; H, 1.56%. These values correspond to a formula, 2(**16f**)·2$SbCl_6^-$·$Sb_2Cl_8^{2-}$ (C, 27.91; H, 1.44%).

**Chemical reduction of the dication salt 16b.** To a solution of the dication salt **16b** (285 mg) in acetonitrile (20 ml) was added zinc dust (500 mg), and the mixture was heated under reflux for 30 min. The precipitate was collected by filtration, washed with acetonitrile, and dissolved in dichloromethane (30 ml). Remaining unchanged zinc dust was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was separated by column chromatography (alumina / toluene) to give the donor **7b** (63 mg, 63% from **6b**) as orange needles (from $CHCl_3$–hexane): mp 213–214 °C; IR (KBr) 3095, 2916, 1484, 1472, 1428, 1338, 972, 854, 846, 706, 603 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta = 2.45$ (6H, s, SMe), 2.50 (6H, s, SMe), 7.63 (2H, d, $J = 5.3$ Hz, Th-H), 7.75 (2H, d, $J = 5.3$ Hz, Th-H); $^{13}C$ NMR (DMSO-$d_6$) $\delta = 18.78$, 118.10, 122.93, 125.45, 125.57, 127.12, 129.06, 130.48, 131.20; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 266 (4.37), 278 (4.37), 342 (4.28), 471 (4.08) nm; MS *m/z* (rel intensity) 576 ($M^+$, 40), 458 (21), 323 (100), 232 (73), 188 (49), 150 (80), 118 (70), 103 (75), 91 (77); Found: C, 41.47; H, 2.79%. Calcd for $C_{20}H_{16}S_{10}$: C, 41.64; H, 2.80%.

The other salts of **16c–f** were reduced by the similar method to give the corresponding neutral donors **7c–f**. The data are as follows.

**7c**: 59%; orange prisms (from $CHCl_3$–hexane); mp 280–281 °C; IR (KBr) 1568, 1528, 1493, 1447, 1434, 1337, 1122, 856, 846, 737, 709, 606 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta = 7.26$–7.33 (4H, m, benzo-H), 7.60 (2H, d, $J = 5.3$ Hz, Th-H), 7.65–7.72 (4H, m, benzo-H), 7.75 (2H, d, $J = 5.3$ Hz, Th-H); $^{13}C$ NMR (DMSO-$d_6$) $\delta =$ 117.47, 122.12, 122.32, 122.93, 125.05, 126.31, 126.56, 130.19, 131.00, 131.74, 134.16, 135.71; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 261 (4.45), 331 (4.40), 452 (4.13) nm; MS *m/z* (rel intensity) 492 ($M^+$, 100), 383 (11), 352 (20), 339 (27), 246 (12); Found: *m/z* 491.92552. Calcd for $C_{24}H_{12}S_6$: 491.92634.

**7d**: 21%; red powder (from $CHCl_3$–hexane); mp 220–230 °C (decomp.); IR (KBr) 3060, 2911, 1537, 1495, 1456, 1229, 854, 832, 805, 744, 650 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta = 2.54$ (6H, s, Me), 6.97 (2H, d, $J = 6.6$ Hz, dithiole-H), 7.18 (2H, d, *J*

= 6.6 Hz, dithiole-H), 7.18 (2H, s, Th-H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 14.97, 116.16, 118.53, 120.88, 121.62, 129.60, 130.33, 130.50, 137.34; UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 271 (4.32), 342 (4.35), 469 (3.98) nm; MS *m/z* (rel intensity) 420 ($M^+$, 100), 318 (50), 260 (34), 210 (35); Found: *m/z* 419.92670. Calcd for $C_{18}H_{12}S_6$: 419.92633.

**7e**: 77%; red prisms (from $CHCl_3$–hexane); mp 229–232 °C (decomp.); IR (KBr) 2917, 1428, 970, 890, 852, 834, 742 cm$^{-1}$; $^1$H NMR (THF-$d_8$) $\delta$ = 2.41 (6H, s, SMe), 2.45 (6H, s, SMe), 2.49 (6H, s, Me), 7.06 (2H, s, Th-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 269 (4.45), 279 (4.45), 325 (4.27), 477 (3.97) nm; MS *m/z* (rel intensity) 604 ($M^+$, 17), 486 (31), 351 (74), 336 (49), 304 (24), 260 (74), 150 (61), 135 (30), 118 (54), 103 (72), 91 (100), 88 (74); Found: C, 43.73; H, 3.33%. Calcd for $C_{22}H_{20}S_{10}$: C, 43.68; H, 3.33%.

**7f**: 90%; red prisms (from $CHCl_3$–hexane); mp 280–282 °C; IR (KBr) 3054, 2915, 2851, 1567, 1501, 1440, 1122, 853, 830, 740, 680, 618 cm$^{-1}$; $^1$H NMR $\delta$ = 2.56 (6H, d, *J* = 1.0 Hz, Me), 7.21 (2H, d, *J* = 1.0 Hz, Th-H), 7.25–7.31 (4H, m, benzo-H), 7.63–7.74 (4H, m, benzo-H); UV ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 267 (4.44), 328 (4.35), 459 (4.03) nm; MS *m/z* (rel intensity) 520 ($M^+$, 100), 380 (13), 367 (11), 353 (17), 260 (26); Found: *m/z* 519.95850. Calcd for $C_{26}H_{16}S_6$: 519.95764.

**Tetracyanoquinodimethane (TCNQ) complex of 7d**. A solution of the donor **7d** (10 mg) in dichloromethane (20 ml) was added to a solution of TCNQ (6 mg) in dichloromethane (10 ml) at room temperature. After addition, the mixture was concentrated to *ca.* 1 ml under reduced pressure. The resulting solid was collected by filtration, washed with a small amount of dichloromethane to give the complex (5 mg) as a dark green solid: mp 190–200 °C (decomp.), IR (KBr) 2170 (CN), 1574, 1505, 1357, 1178, 832, 717 cm$^{-1}$.

**Attempted preparation of the donor 7c by Wittig–Horner reaction.** A solution of BuLi in hexane (1.64 mol $dm^{-3}$, 0.3 ml, 0.49 mmol) was added to a solution of the phosphonate ester **12** ($R_2$, $R_2$ = benzo, 110 mg, 0.42 mmol) in THF (5 ml) at –78 °C under argon. After stirring for 10 min, the quinone **18** (30 mg, 0.14 mmol) was added to the mixture. The mixture was stirred for 30 min at –78 °C and allowed to warm to room temperature. Water was added to the solution, and the product was extracted with dichloromethane. The extract was dried over $Na_2SO_4$ and concentrated. The residue was washed with methanol to afford the starting quinone **18** (15 mg, 50% recovery), identical with an authentic sample.

**X-ray structural analyses.** The single crystals of the compounds **6e** and **7e** were prepared by recystallization from chloroform–hexane. The single crystals of the dication salts 2(**16e**)·$2SbCl_6 \cdot Sb_2Cl_8$ and 2(**16e**)·$SbCl_5 \cdot Sb_2Cl_8$ were prepared by slow evaporation of dichloromethane and vapor diffusion of diethyl ether to a dichloromethane solution, respectively. The data collections were performed on a Rigaku AFC-5S (for **6e** and **7e**) and an Enraf-Nonius CAD4 (for the dication salts **16e**) diffractometers. Details are summarized in Table 3. The structures were solved by the direct method using the SHELXS86 program [for **6e**, **7e**, and 2(**16e**)·$2SbCl_6 \cdot Sb_2Cl_8$] or heavy-atom Patterson method using the PATTY program [for 2(**16e**)·$SbCl_5 \cdot Sb_2Cl_8$] and expanded using Fourier techniques using the DIRDIF92 program. The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were included at calculated positions but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The atomic and thermal parameters and bond lengths and angles are presented in appendix as the end of this thesis.

**Table 3**. Details of X-ray structural analyses.

| | **6e** | **7e** | 2(**16e**)<br>$\cdot 2SbCl_6 \cdot Sb_2Cl_8$ | 2(**16e**)<br>$\cdot SbCl_5 \cdot Sb_2Cl_8$ |
|---|---|---|---|---|
| formula | $C_{22}H_{22}S_{10}$ | $C_{22}H_{20}S_{10}$ | $C_{44}H_{40}S_{20}$<br>$Sb_4Cl_{20}$ | $C_{44}H_{40}S_{20}$<br>$Sb_3Cl_{13}$ |
| fw | 607.02 | 605.00 | 2406.06 | 2036.14 |
| space group | $P2_1/n$ | $Fdd2$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 13.179(3) | 15.104(6) | 11.090(3) | 18.916(2) |
| $b$ (Å) | 7.864(5) | 36.944(7) | 26.408(8) | 22.885(3) |
| $c$ (Å) | 26.690(3) | 9.416(6) | 15.002(4) | 9.1392(7) |
| $\alpha$ (deg) | 90 | 90 | 90 | 99.127(8) |
| $\beta$ (deg) | 93.45(1) | 90 | 109.91(2) | 101.839(7) |
| $\gamma$ (deg) | 90 | 90 | 90 | 74.318(8) |
| $V$ (Å$^3$) | 2761(1) | 5254(3) | 4130(1) | 3705(1) |
| $Z$ | 4 | 8 | 2 | 2 |
| $D_C$ | 1.46 | 1.53 | 1.93 | 1.82 |
| cryst. size (nm) | 0.40 × 0.15 × 0.10 | 0.25 × 0.15 × 0.10 | 0.20 × 0.20 × 0.20 | 0.45 × 0.10 × 0.02 |
| radiation | Mo-K$\alpha$ | Mo-K$\alpha$ | Cu-K$\alpha$ | Cu-K$\alpha$ |
| $2\theta_{max}$ (deg) | 55 | 55 | 148.6 | 148.6 |
| total data measd. ($3\sigma$) | 7095 | 1687 | 9065 | 16155 |
| obsd. unique data | 1872 | 697 | 4755 | 5535 |
| $R$ | 0.048 | 0.048 | 0.064 | 0.067 |

## References

(1) V. R. Mayer and H. Kröber, *J. Prakt. Chem.*, **316**, 907 (1974).

(2) U. Schöberl, J. Salbeck, and J. Daub, *Adv. Mater.*, **4**, 41 (1992).

(3) M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson, and P. Batail, *J. Am. Chem. Soc.*, **115**, 3752 (1993).

(4) A. Benahmed-Gasmi, P. Frère, J. Roncali, E. Elandaloussi, J. Orduna, J. Garin, M. Jubault, and A. Gorgues, *Tetrahedron Lett.*, **36**, 2983 (1995).

(5) D. Lorcy, R. Carlier, A. Robert, A. Tallec, P. L. Maguerès, and L. Ouahab, *J. Org. Chem.*, **60**, 2443 (1995).

(6) Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.*, **27**, 1573 (1988).

(7) G. N. Jean and F. F. Nord, *J. Org. Chem.*, **20**, 1370 (1955).

(8) H. Wynberg and H. J. M. Sinnige, *Rec. Trav. Chim. Pays-Bas*, **88**, 1244 (1969).

(9) K. Takahashi, T. Nihira, M. Yoshifuji, and K. Tomitani, *Bull. Chem. Soc. Jpn.*, **66**, 2330 (1993).

(10) K. Akiba, K. Ishikawa, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2674 (1978).

(11) J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209, 221 (1989).

(12) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(13) J. Nakayama, K. Ueno, and M. Hoshino, *Synthesis*, **1977**, 770.

(14) G. W. Cowell, A. Ledwith, A. C. White, and H. J. Woods, *J. Chem. Soc. (B)*, **1970**, 227.

# *Conclusion*

In this research work, the author has proposed a strategy for the molecular design of new 1,3-dithiole compounds and developed some novel chemical reactions giving interesting compounds. Several novel 1,3-dithiole compounds containing thiophene-related systems were designed and synthesized, and their redox properties, reactivities, and structures were elucidated. From the studies, the following results were obtained.

In chapter 2, 6,6'-bis[5-(1,4-dithiafulven-6-yl)-2-thienyl]-1,4-dithiafulvene and its derivatives were synthesized as novel cross-conjugated tris(1,3-dithiole) donors. Some physical properties of the donors were explained on the basis of the molecular structures optimized by the MNDO-PM3 calculations. The details of the multistage redox behavior of the donors were elucidated by the cyclic voltammetry. The electron-donating ability of the donors was estimated to be comparable to that of TTF. It was proved that the introduction of thiophene units effectively reduced the intramolecular Coulombic repulsion in the dication states. The donors afforded conductive iodine complexes. A novel redox active polymer was formed from one of them by electrochemical oxidation .

In chapter 3, oxidation of bis(1,3-dithiole) compounds containing a dithienylmethane unit was investigated to explore novel chemical reactions induced by electron transfer. Interesting near-infrared absorbing cations and a redox active oligomer were obtained. The X-ray analysis revealed the polymethine cyanine like structure of the cation. The electrochemical and optical properties of the oligomer were investigated by the cyclic voltammetry and UV–VIS spectroscopy, respectively. Moreover, a bis(1,3-dithiole) compound containing two methylene groups also afforded the corresponding dication by oxidation.

In chapter 4, the oxidative intramolecular cyclization of 2,2'-bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls was investigated, and a new synthetic method for the preparation of a novel bis(1,3-dithiole) donor was proposed. The cyclic voltammetry indicated that the compounds undergo intramolecular cyclization by electrochemical oxidation. The cyclization products were easily obtained preparatively by chemical oxidation of the compounds with $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{+\cdot}\text{SbCl}_6^-$, followed by reduction with zinc. The novel electron donors obtained by the above reactions showed fairly low oxidation potentials. The X-ray structural analyses of the neutral and dication states of the donor showed that there exists a large conformational change between them.

Finally, the author is convinced that these results will provide useful hints for the development of novel organic electronic and optical materials.

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Akira Ohta
The Graduate university for Advanced Studies
November 1995

## *List of Publications*

1) "Preparation and properties of tris(1,3-dithiole) donors containing thiophene spacer units," A. Ohta and Y. Yamashita, *Heterocycles*, **41**, 123 (1995).

2) "Preparation and properties of bis[5-(6-methyl-1,4-dithiafulven-6-yl)-2-thienyl]-methanes affording near-infrared absorbing cations by oxidation," A. Ohta and Y. Yamashita, *J. Chem. Soc., Chem. Commun.*, 557 (1995).

3) "Oxidative intramolecular cyclization of 2,2'-bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls affording novel bis(1,3-dithiole) electron donors," A. Ohta and Y. Yamashita, *J. Chem. Soc., Chem. Commun.*, **1995**, 1761.

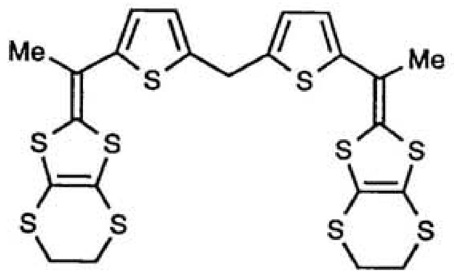
## *Other Publications*

1) "Preparation of thienyl-substituted fulvalene and tetrathiafulvalene vinylogues as electron donors and conductive complexes derived from one of them," A. Ohta, T. Kobayashi, and H. Kato, *J. Chem. Soc., Chem. Commun.*, 431 (1993).

2) "Hetero-analogues of Hückel degenerate systems and related compounds: preparation of thienyl-substituted fulvalene and electron-donating tetrathiafulvalene vinylogues and conductive complexes," A. Ohta, T. Kobayashi, and H. Kato, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 905.

# *Appendix X-ray Diffraction Data*

## *Chapter 3* Compound **6c**



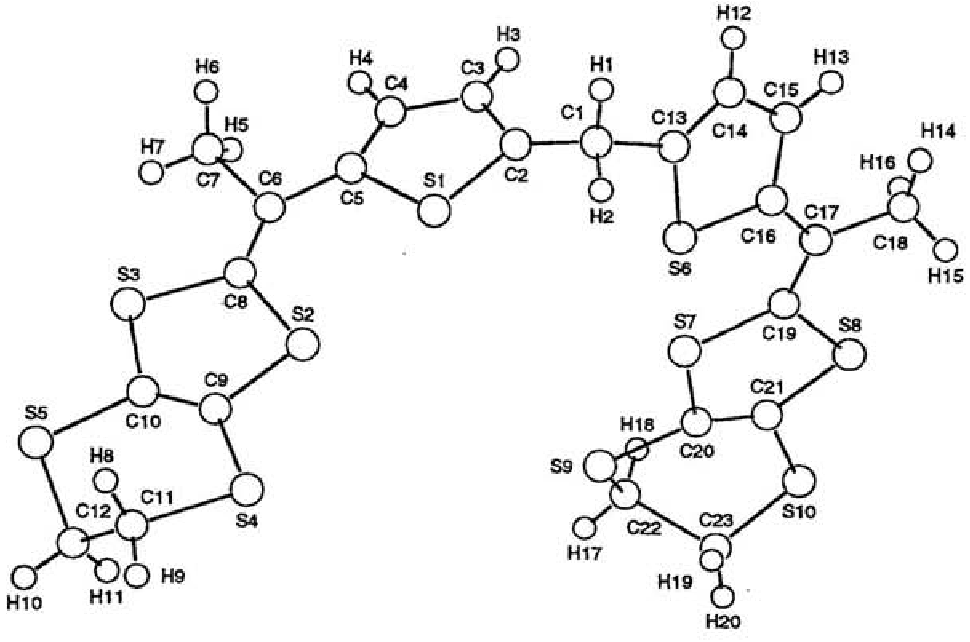


**Figure 1**. Atomic numbering system.

**Table 1.** Fractional atomic coordinates and equivalent isotropic thermal parameters (Å$^2$).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| S1 | 0.4903(1) | 0.3309(1) | 0.4406(1) | 3.33 |
| S2 | 0.6058(1) | 0.4419(1) | 0.4409(1) | 3.71 |
| S3 | 0.5125(2) | 0.5098(1) | 0.2122(1) | 4.18 |
| S4 | 0.8190(1) | 0.5126(1) | 0.5307(2) | 4.73 |
| S5 | 0.7072(2) | 0.5932(1) | 0.2544(2) | 5.27 |
| S6 | 0.2837(1) | 0.2513(1) | 0.7606(1) | 3.48 |
| S7 | 0.1077(2) | 0.3205(1) | 0.9132(1) | 4.02 |
| S8 | –0.0255(1) | 0.2612(1) | 1.1151(1) | 4.13 |
| S9 | –0.0144(2) | 0.4252(1) | 0.9600(2) | 5.61 |
| S10 | –0.1545(2) | 0.3555(1) | 1.2204(2) | 5.63 |
| C1 | 0.4412(5) | 0.2299(2) | 0.5498(5) | 3.74 |
| C2 | 0.3962(5) | 0.2756(2) | 0.4567(5) | 3.10 |
| C3 | 0.2870(5) | 0.2793(2) | 0.3735(5) | 3.36 |
| C4 | 0.2802(5) | 0.3272(2) | 0.2959(5) | 3.57 |
| C5 | 0.3837(4) | 0.3607(2) | 0.3198(5) | 2.86 |
| C6 | 0.4053(5) | 0.4125(2) | 0.2580(5) | 3.04 |
| C7 | 0.3131(6) | 0.4277(3) | 0.1382(6) | 4.50 |
| C8 | 0.4967(5) | 0.4487(2) | 0.2983(5) | 3.05 |
| C9 | 0.6875(5) | 0.5021(2) | 0.4156(5) | 3.36 |
| C10 | 0.6457(5) | 0.5331(2) | 0.3114(5) | 3.50 |
| C11 | 0.8902(7) | 0.5707(3) | 0.452 (1) | 8.05 |
| C12 | 0.8065(8) | 0.6112(3) | 0.3925(7) | 6.72 |
| C13 | 0.3426(5) | 0.2099(2) | 0.6401(5) | 3.11 |
| C14 | 0.2906(6) | 0.1604(2) | 0.6450(5) | 3.90 |
| C15 | 0.2016(5) | 0.1552(2) | 0.7432(6) | 3.99 |
| C16 | 0.1854(5) | 0.2007(2) | 0.8169(5) | 3.12 |
| C17 | 0.1024(5) | 0.2083(2) | 0.9265(5) | 3.32 |
| C18 | 0.0483(6) | 0.1591(2) | 0.9871(6) | 4.65 |
| C19 | 0.0690(5) | 0.2570(2) | 0.9756(5) | 3.27 |
| C20 | 0.0037(5) | 0.3571(2) | 1.0070(6) | 4.09 |
| C21 | –0.0539(5) | 0.3303(2) | 1.1026(5) | 3.99 |
| C22 | –0.1533(7) | 0.4418(3) | 1.039 (1) | 7.76 |
| C23 | –0.148 (1) | 0.4264(4) | 1.1858(9) | 8.87 |
| H1 | 0.5227(5) | 0.2390(2) | 0.6051(6) | 5.13 |
| H2 | 0.4678(5) | 0.1973(2) | 0.4881(5) | 5.02 |
| H3 | 0.2237(5) | 0.2526(2) | 0.3687(5) | 4.40 |
| H4 | 0.2077(5) | 0.3337(2) | 0.2327(5) | 3.78 |
| H5 | 0.2891(6) | 0.3950(3) | 0.0919(7) | 7.69 |
| H6 | 0.2306(6) | 0.4476(3) | 0.1623(7) | 6.81 |
| H7 | 0.3561(6) | 0.4516(3) | 0.0652(6) | 6.56 |
| H8 | 0.9435(9) | 0.5834(4) | 0.522 (1) | 13.95 |
| H9 | 0.9236(9) | 0.5628(4) | 0.3448(9) | 12.32 |
| H10 | 0.7560(9) | 0.6242(4) | 0.4876(9) | 13.28 |
| H11 | 0.8745(7) | 0.6467(3) | 0.3623(8) | 9.97 |
| H12 | 0.3159(6) | 0.1338(2) | 0.5741(6) | 6.23 |
| H13 | 0.1505(5) | 0.1222(2) | 0.7520(5) | 4.61 |
| H14 | 0.0984(7) | 0.1301(3) | 0.9872(7) | 8.84 |
| H15 | –0.0305(7) | 0.1560(3) | 0.9451(7) | 10.56 |
| H16 | 0.0203(7) | 0.1701(3) | 1.0932(7) | 9.31 |

**Table 1**. (Continued).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| H17 | –0.2299(8) | 0.4220(3) | 0.9902(9) | 11.80 |
| H18 | –0.1499(9) | 0.4801(4) | 1.0372(9) | 13.13 |
| H19 | –0.0606(8) | 0.4374(4) | 1.2063(9) | 11.55 |
| H20 | –0.2136(7) | 0.4458(3) | 1.2282(7) | 9.02 |

**Table 2**. Bond lengths (Å).

| atom | length / Å | atom | length / Å |
|---|---|---|---|
| S1 – C2 | 1.708(5) | S1 – C5 | 1.744(5) |
| S2 – C8 | 1.763(5) | S2 – C9 | 1.752(5) |
| S3 – C8 | 1.752(5) | S3 – C10 | 1.751(5) |
| S4 – C9 | 1.748(5) | S4 – C11 | 1.826(9) |
| S5 – C10 | 1.739(6) | S5 – C12 | 1.718(8) |
| S6 – C13 | 1.726(5) | S6 – C16 | 1.746(5) |
| S7 – C19 | 1.751(5) | S7 – C20 | 1.745(6) |
| S8 – C19 | 1.768(5) | S8 – C21 | 1.742(6) |
| S9 – C20 | 1.757(6) | S9 – C22 | 1.759(9) |
| S10 – C21 | 1.751(6) | S10 – C23 | 1.792(9) |
| C1 – C2 | 1.515(7) | C1 – C13 | 1.506(8) |
| C2 – C3 | 1.368(7) | C3 – C4 | 1.413(8) |
| C4 – C5 | 1.378(7) | C5 – C6 | 1.449(7) |
| C6 – C7 | 1.524(7) | C6 – C8 | 1.356(7) |
| C9 – C10 | 1.334(7) | C11 – C12 | 1.44(1) |
| C13 – C14 | 1.346(8) | C14 – C15 | 1.409(8) |
| C15 – C16 | 1.362(8) | C16 – C17 | 1.457(7) |
| C17 – C18 | 1.492(8) | C17 – C19 | 1.358(7) |
| C20 – C21 | 1.340(8) | C22 – C23 | 1.51(1) |

**Table 3**. Bond angles (degree).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| C2 – S1 – C5 | 93.1(2) | C8 – S2 – C9 | 95.9(2) |
| C8 – S3 – C10 | 96.5(2) | C9 – S4 – C11 | 99.8(3) |
| C10 – S5 – C12 | 100.6(3) | C13 – S6 – C16 | 92.7(2) |
| C19 – S7 – C20 | 96.2(3) | C19 – S8 – C21 | 96.1(3) |
| C20 – S9 – C22 | 100.7(3) | C21 – S10 – C23 | 100.9(4) |
| C2 – C1 – C13 | 114.2(4) | S1 – C2 – C1 | 120.0(4) |
| S1 – C2 – C3 | 111.0(4) | C1 – C2 – C3 | 129.0(5) |

**Table 3**. (Continued).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| C2 – C3 – C4 | 113.0(5) | C3 – C4 – C5 | 113.9(4) |
| S1 – C5 – C4 | 108.9(4) | S1 – C5 – C6 | 123.5(4) |
| C4 – C5 – C6 | 127.6(4) | C5 – C6 – C7 | 115.9(4) |
| C5 – C6 – C8 | 126.4(4) | C7 – C6 – C8 | 117.6(5) |
| S2 – C8 – S3 | 113.1(3) | S2 – C8 – C6 | 125.5(4) |
| S3 – C8 – C6 | 121.4(4) | S2 – C9 – S4 | 114.1(3) |
| S2 – C9 – C10 | 117.6(4) | S4 – C9 – C10 | 128.3(4) |
| S3 – C10 – S5 | 113.8(3) | S3 – C10 – C9 | 116.7(4) |
| S5 – C10 – C9 | 129.4(4) | S4 – C11 – C12 | 117.9(6) |
| S5 – C12 – C11 | 117.8(6) | S6 – C13 – C1 | 121.0(4) |
| S6 – C13 – C14 | 110.4(4) | C1 – C13 – C14 | 128.6(5) |
| C13 – C14 – C15 | 113.8(5) | C14 – C15 – C16 | 114.3(5) |
| S6 – C16 – C15 | 108.8(4) | S6 – C16 – C17 | 123.4(4) |
| C15 – C16 – C17 | 127.8(5) | C16 – C17 – C18 | 117.7(5) |
| C16 – C17 – C19 | 124.6(5) | C18 – C17 – C19 | 117.8(5) |
| S7 – C19 – S8 | 112.5(3) | S7 – C19 – C17 | 126.9(4) |
| S8 – C19 – C17 | 120.6(4) | S7 – C20 – S9 | 114.8(3) |
| S7 – C20 – C21 | 117.0(5) | S9 – C20 – C21 | 128.1(5) |
| S8 – C21 – S10 | 114.4(3) | S8 – C21 – C20 | 117.0(5) |
| S10 – C21 – C20 | 128.6(5) | S9 – C22 – C23 | 113.5(6) |
| S10 – C23 – C22 | 115.8(6) | | |

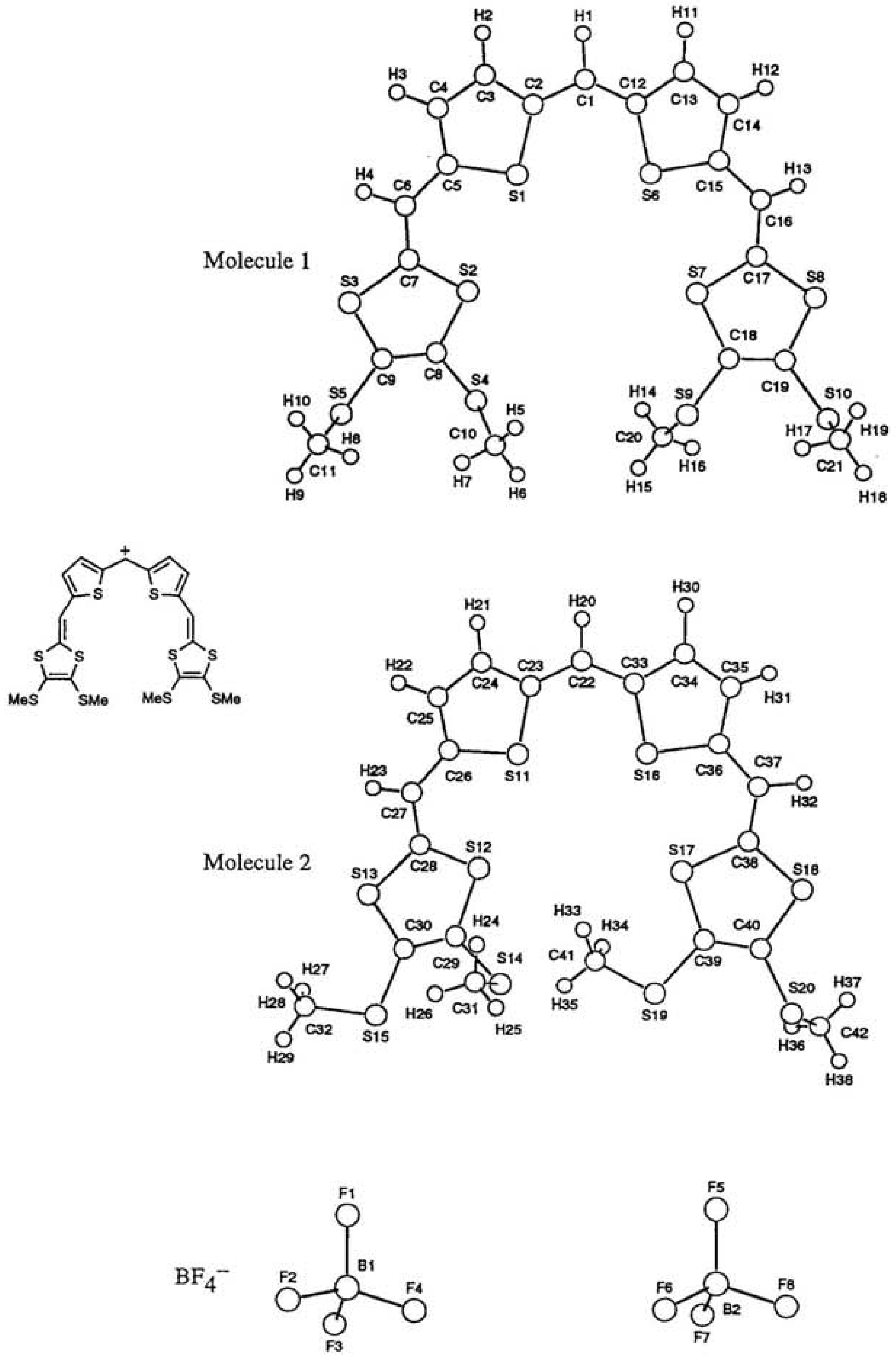


**Figure 2.** Atomic numbering system.

**Table 4**. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å$^2$).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| S1 | 0.8884(1) | 1.03627(8) | 0.43625(8) | 3.37(2) |
| S2 | 0.7835(1) | 0.8193(1) | 0.4530(1) | 4.34(3) |
| S3 | 0.7990(1) | 0.8146(1) | 0.6451(1) | 4.40(3) |
| S4 | 0.6585(1) | 0.5968(1) | 0.3685(1) | 6.36(4) |
| S5 | 0.6691(1) | 0.5911(1) | 0.5877(1) | 6.50(5) |
| S6 | 0.8947(1) | 1.03102(9) | 0.22805(9) | 3.46(3) |
| S7 | 0.8735(1) | 0.8258(1) | 0.1344(1) | 4.66(3) |
| S8 | 0.8732(1) | 0.8085(1) | −0.0544(1) | 4.74(3) |
| S9 | 0.8923(2) | 0.6358(1) | 0.1531(1) | 7.55(5) |
| S10 | 0.8853(2) | 0.6136(1) | −0.0738(1) | 7.14(5) |
| S11 | 0.6451(1) | 1.1132(1) | 0.3133(1) | 4.13(3) |
| S12 | 0.5207(1) | 0.9065(1) | 0.3310(1) | 4.63(3) |
| S13 | 0.5812(1) | 0.8969(1) | 0.5286(1) | 4.56(3) |
| S14 | 0.3782(1) | 0.6861(1) | 0.2460(1) | 5.71(4) |
| S15 | 0.4503(1) | 0.6717(1) | 0.4688(1) | 5.83(4) |
| S16 | 0.6492(1) | 1.08680(9) | 0.1110(1) | 3.88(3) |
| S17 | 0.5965(1) | 0.8701(1) | 0.0396(1) | 4.27(3) |
| S18 | 0.5722(1) | 0.8099(1) | −0.1554(1) | 5.32(4) |
| S19 | 0.5321(2) | 0.6608(1) | 0.0609(1) | 7.23(5) |
| S20 | 0.4922(1) | 0.5912(1) | −0.1655(1) | 7.65(5) |
| F1 | −0.0382(5) | 0.4444(4) | 0.2300(4) | 13.8(2) |
| F2 | 0.0143(5) | 0.4381(4) | 0.3756(4) | 12.7(2) |
| F3 | −0.0836(5) | 0.5147(5) | 0.3234(6) | 16.0(3) |
| F4 | 0.0760(4) | 0.5820(3) | 0.3419(4) | 12.8(2) |
| F5 | 0.1797(4) | 0.8653(3) | 0.1205(3) | 11.4(2) |
| F6 | 0.1711(6) | 0.8733(4) | 0.2620(4) | 13.7(2) |
| F7 | 0.1480(5) | 0.9798(5) | 0.1848(4) | 12.9(2) |
| F8 | 0.3017(5) | 0.9864(7) | 0.2457(4) | 19.3(3) |
| C1 | 0.9444(4) | 1.2032(3) | 0.3647(4) | 3.7(1) |
| C2 | 0.9362(4) | 1.1632(3) | 0.4406(3) | 3.4(1) |
| C3 | 0.9638(4) | 1.2212(4) | 0.5327(4) | 3.9(1) |
| C4 | 0.9486(4) | 1.1666(4) | 0.5955(3) | 3.7(1) |
| C5 | 0.9054(4) | 1.0622(3) | 0.5550(3) | 3.2(1) |
| C6 | 0.8789(4) | 0.9901(4) | 0.6047(3) | 3.5(1) |
| C7 | 0.8281(4) | 0.8885(3) | 0.5706(3) | 3.3(1) |
| C8 | 0.7246(4) | 0.7011(4) | 0.4690(4) | 4.5(1) |
| C9 | 0.7315(4) | 0.6991(4) | 0.5581(4) | 4.5(1) |
| C10 | 0.7577(7) | 0.5563(8) | 0.3850(8) | 16.3(4) |
| C11 | 0.7782(7) | 0.5825(7) | 0.6718(6) | 11.3(3) |
| C12 | 0.9243(4) | 1.1556(3) | 0.2715(3) | 3.4(1) |
| C13 | 0.9297(4) | 1.2063(4) | 0.2004(4) | 3.8(1) |
| C14 | 0.9094(4) | 1.1457(4) | 0.1160(4) | 3.8(1) |
| C15 | 0.8915(4) | 1.0468(4) | 0.1178(3) | 3.4(1) |
| C16 | 0.8780(4) | 0.9744(4) | 0.0417(4) | 3.8(1) |
| C17 | 0.8731(4) | 0.8804(4) | 0.0415(3) | 3.6(1) |
| C18 | 0.8786(5) | 0.7178(4) | 0.0830(4) | 4.9(1) |
| C19 | 0.8807(4) | 0.7117(4) | −0.0041(4) | 4.6(1) |
| C20 | 0.762(1) | 0.555(1) | 0.118(1) | 21.6(7) |

**Table 4.** (Continued).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| C21 | 1.0186(6) | 0.6278(5) | −0.0121(6) | 7.8(2) |
| C22 | 0.7239(4) | 1.2708(4) | 0.2393(5) | 4.7(1) |
| C23 | 0.7151(4) | 1.2381(4) | 0.3181(4) | 4.2(1) |
| C24 | 0.7641(4) | 1.2988(4) | 0.4140(4) | 4.8(1) |
| C25 | 0.7483(4) | 1.2471(4) | 0.4780(4) | 4.6(1) |
| C26 | 0.6844(4) | 1.1425(4) | 0.4373(4) | 4.1(1) |
| C27 | 0.6594(4) | 1.0733(4) | 0.4881(4) | 4.2(1) |
| C28 | 0.5950(4) | 0.9717(4) | 0.4516(3) | 3.7(1) |
| C29 | 0.4645(4) | 0.7888(4) | 0.3474(4) | 4.2(1) |
| C30 | 0.4941(4) | 0.7840(4) | 0.4400(4) | 4.2(1) |
| C31 | 0.2503(5) | 0.6745(5) | 0.2357(5) | 7.5(2) |
| C32 | 0.4924(5) | 0.7091(6) | 0.5955(5) | 6.6(2) |
| C33 | 0.6956(4) | 1.2164(4) | 0.1466(4) | 4.2(1) |
| C34 | 0.7095(5) | 1.2569(4) | 0.0718(5) | 5.0(1) |
| C35 | 0.6847(5) | 1.1863(4) | −0.0078(4) | 5.0(1) |
| C36 | 0.6519(4) | 1.0878(4) | −0.0007(4) | 4.2(1) |
| C37 | 0.6269(4) | 1.0023(4) | −0.0692(4) | 4.2(1) |
| C38 | 0.6022(4) | 0.9074(4) | −0.0621(3) | 3.9(1) |
| C39 | 0.5577(4) | 0.7441(4) | −0.0080(4) | 4.6(1) |
| C40 | 0.5449(4) | 0.7155(4) | −0.0994(4) | 5.2(1) |
| C41 | 0.6041(6) | 0.7403(6) | 0.1802(5) | 7.8(2) |
| C42 | 0.6024(6) | 0.5787(5) | −0.1720(7) | 10.5(2) |
| B1 | −0.0036(7) | 0.4958(5) | 0.3198(8) | 6.7(2) |
| B2 | 0.2003(8) | 0.9219(7) | 0.2034(6) | 6.2(2) |
| H1 | 0.954 | 1.281 | 0.377 | 7.7 |
| H2 | 0.998 | 1.299 | 0.556 | 7.7 |
| H3 | 0.961 | 1.198 | 0.666 | 7.7 |
| H4 | 0.892 | 1.019 | 0.676 | 7.7 |
| H5 | 0.823 | 0.607 | 0.388 | 16.1 |
| H6 | 0.735 | 0.497 | 0.336 | 16.1 |
| H7 | 0.779 | 0.539 | 0.446 | 16.1 |
| H8 | 0.826 | 0.576 | 0.643 | 11.7 |
| H9 | 0.756 | 0.524 | 0.695 | 11.7 |
| H10 | 0.821 | 0.640 | 0.726 | 11.7 |
| H11 | 0.952 | 1.281 | 0.213 | 7.7 |
| H12 | 0.916 | 1.172 | 0.062 | 7.7 |
| H13 | 0.869 | 0.993 | −0.023 | 7.7 |
| H14 | 0.721 | 0.588 | 0.130 | 22.7 |
| H15 | 0.755 | 0.503 | 0.151 | 22.7 |
| H16 | 0.727 | 0.521 | 0.050 | 22.7 |
| H17 | 1.034 | 0.623 | 0.055 | 8.6 |
| H18 | 1.033 | 0.577 | −0.041 | 8.6 |
| H19 | 1.073 | 0.692 | −0.005 | 8.6 |
| H20 | 0.762 | 1.349 | 0.252 | 7.7 |
| H21 | 0.817 | 1.378 | 0.439 | 7.7 |
| H22 | 0.781 | 1.286 | 0.553 | 7.7 |
| H23 | 0.691 | 1.096 | 0.562 | 7.7 |
| H24 | 0.241 | 0.733 | 0.228 | 8.4 |
| H25 | 0.192 | 0.619 | 0.182 | 8.4 |

**Table 4**. (Continued).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| H26 | 0.240 | 0.662 | 0.293 | 8.4 |
| H27 | 0.569 | 0.748 | 0.630 | 7.4 |
| H28 | 0.460 | 0.751 | 0.612 | 5.8 |
| H29 | 0.472 | 0.653 | 0.621 | 7.4 |
| H30 | 0.735 | 1.343 | 0.078 | 7.7 |
| H31 | 0.690 | 1.203 | −0.066 | 5.8 |
| H32 | 0.621 | 0.999 | −0.143 | 7.7 |
| H33 | 0.582 | 0.792 | 0.190 | 8.6 |
| H34 | 0.682 | 0.775 | 0.197 | 8.6 |
| H35 | 0.599 | 0.704 | 0.228 | 8.6 |
| H36 | 0.659 | 0.592 | −0.110 | 11.0 |
| H37 | 0.636 | 0.625 | −0.204 | 11.0 |
| H38 | 0.584 | 0.512 | −0.208 | 11.0 |

**Table 5**. Bond lengths (Å).

| atoms | length / Å | atoms | length / Å |
|---|---|---|---|
| S1 – C2 | 1.747(5) | S1 – C5 | 1.737(5) |
| S2 – C7 | 1.741(5) | S2 – C8 | 1.749(5) |
| S3 – C7 | 1.736(5) | S3 – C9 | 1.744(6) |
| S4 – C8 | 1.749(5) | S4 – C10 | 1.728(9) |
| S5 – C9 | 1.743(5) | S5 – C11 | 1.732(8) |
| S6 – C12 | 1.735(5) | S6 – C15 | 1.730(5) |
| S7 – C17 | 1.727(5) | S7 – C18 | 1.753(5) |
| S8 – C17 | 1.728(5) | S8 – C19 | 1.736(6) |
| S9 – C18 | 1.743(6) | S9 – C20 | 1.69(1) |
| S10 – C19 | 1.753(5) | S10 – C21 | 1.775(7) |
| S11 – C23 | 1.748(5) | S11 – C26 | 1.741(5) |
| S12 – C28 | 1.727(5) | S12 – C29 | 1.739(5) |
| S13 – C28 | 1.736(5) | S13 – C30 | 1.737(5) |
| S14 – C29 | 1.745(5) | S14 – C31 | 1.779(7) |
| S15 – C30 | 1.735(5) | S15 – C32 | 1.779(6) |
| S16 – C33 | 1.743(5) | S16 – C36 | 1.740(5) |
| S17 – C38 | 1.744(5) | S17 – C39 | 1.735(5) |
| S18 – C38 | 1.728(5) | S18 – C40 | 1.733(6) |
| S19 – C39 | 1.750(6) | S19 – C41 | 1.769(8) |
| S20 – C40 | 1.744(6) | S20 – C42 | 1.739(8) |
| C1 – C2 | 1.396(6) | C1 – C12 | 1.406(6) |
| C2 – C3 | 1.410(6) | C3 – C4 | 1.362(7) |
| C4 – C5 | 1.413(6) | C5 – C6 | 1.412(6) |
| C6 – C7 | 1.360(6) | C8 – C9 | 1.347(7) |
| C12 – C13 | 1.410(6) | C13 – C14 | 1.366(7) |
| C14 – C15 | 1.407(6) | C15 – C16 | 1.407(7) |

**Table 5**. (Continued).

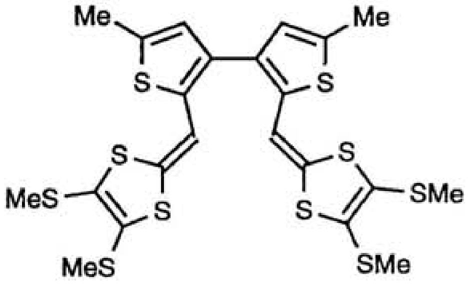
| atoms | length / Å | atoms | length / Å |
|---|---|---|---|
| C16 – C17 | 1.378(7) | C18 – C19 | 1.348(7) |
| C22 – C23 | 1.392(7) | C22 – C33 | 1.396(7) |
| C23 – C24 | 1.412(7) | C24 – C25 | 1.354(8) |
| C25 – C26 | 1.415(7) | C26 – C27 | 1.389(7) |
| C27 – C28 | 1.377(7) | C29 – C30 | 1.357(7) |
| C33 – C34 | 1.406(7) | C34 – C35 | 1.363(8) |
| C35 – C36 | 1.401(7) | C36 – C37 | 1.399(7) |
| C37 – C38 | 1.355(7) | C39 – C40 | 1.351(7) |
| F1 – B1 | 1.32(1) | F2 – B1 | 1.31(1) |
| F3 – B1 | 1.327(9) | F4 – B1 | 1.291(8) |
| F5 – B2 | 1.318(8) | F6 – B2 | 1.314(9) |
| F7 – B2 | 1.344(9) | F8 – B2 | 1.31(1) |

**Table 6**. Bond angles (degree).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| C2 – S1 – C5 | 91.9(2) | C7 – S2 – C8 | 96.8(2) |
| C7 – S3 – C9 | 97.1(2) | C8 – S4 – C10 | 100.8(3) |
| C9 – S5 – C11 | 102.0(3) | C12 – S6 – C15 | 92.1(2) |
| C17 – S7 – C18 | 96.7(3) | C17 – S8 – C19 | 96.7(2) |
| C18 – S9 – C20 | 101.3(4) | C19 – S10 – C21 | 104.0(3) |
| C23 – S11 – C26 | 92.4(3) | C28 – S12 – C29 | 96.9(2) |
| C28 – S13 – C30 | 96.9(2) | C29 – S14 – C31 | 101.2(3) |
| C30 – S15 – C32 | 103.8(3) | C33 – S16 – C36 | 92.6(3) |
| C38 – S17 – C39 | 96.7(3) | C38 – S18 – C40 | 97.4(3) |
| C39 – S19 – C41 | 102.9(3) | C40 – S20 – C42 | 104.2(3) |
| C2 – C1 – C12 | 130.1(4) | S1 – C2 – C1 | 126.1(4) |
| S1 – C2 – C3 | 110.0(4) | C1 – C2 – C3 | 123.9(4) |
| C2 – C3 – C4 | 114.1(4) | C3 – C4 – C5 | 113.6(4) |
| S1 – C5 – C4 | 110.4(4) | S1 – C5 – C6 | 125.5(3) |
| C4 – C5 – C6 | 124.1(4) | C5 – C6 – C7 | 129.0(4) |
| S2 – C7 – S3 | 113.3(3) | S2 – C7 – C6 | 126.0(4) |
| S3 – C7 – C6 | 120.7(4) | S2 – C8 – S4 | 117.9(3) |
| S2 – C8 – C9 | 116.5(4) | S4 – C8 – C9 | 125.6(4) |
| S3 – C9 – S5 | 119.2(3) | S3 – C9 – C8 | 116.4(4) |
| S5 – C9 – C8 | 124.2(4) | S6 – C12 – C1 | 126.4(4) |
| S6 – C12 – C13 | 110.5(4) | C1 – C12 – C13 | 123.0(4) |
| C12 – C13 – C14 | 112.9(4) | C13 – C14 – C15 | 114.4(4) |
| S6 – C15 – C14 | 110.0(4) | S6 – C15 – C16 | 126.2(4) |
| C14 – C15 – C16 | 123.8(5) | C15 – C16 – C17 | 127.7(5) |
| S7 – C17 – S8 | 113.9(3) | S7 – C17 – C16 | 125.6(4) |
| S8 – C17 – C16 | 120.4(4) | S7 – C18 – S9 | 117.1(3) |
| S7 – C18 – C19 | 115.8(4) | S9 – C18 – C19 | 126.8(4) |
| S8 – C19 – S10 | 116.5(3) | S8 – C19 – C18 | 116.9(4) |

**Table 6**. (Continued).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| S10 – C19 – C18 | 126.6(5) | C23 – C22 – C33 | 130.3(5) |
| S11 – C23 – C22 | 124.5(4) | S11 – C23 – C24 | 109.8(4) |
| C22 – C23 – C24 | 125.7(5) | C23 – C24 – C25 | 113.8(5) |
| C24 – C25 – C26 | 114.8(5) | S11 – C26 – C25 | 109.3(4) |
| S11 – C26 – C27 | 125.0(4) | C25 – C26 – C27 | 125.7(5) |
| C26 – C27 – C28 | 127.8(5) | S12 – C28 – S13 | 113.6(3) |
| S12 – C28 – C27 | 126.0(4) | S13 – C28 – C27 | 120.4(4) |
| S12 – C29 – S14 | 118.8(3) | S12 – C29 – C30 | 116.4(4) |
| S14 – C29 – C30 | 124.8(4) | S13 – C30 – S15 | 121.5(3) |
| S13 – C30 – C29 | 116.2(4) | S15 – C30 – C29 | 122.2(4) |
| S16 – C33 – C22 | 123.8(4) | S16 – C33 – C34 | 109.9(4) |
| C22 – C33 – C34 | 126.0(5) | C33 – C34 – C35 | 113.1(5) |
| C34 – C35 – C36 | 115.4(5) | S16 – C36 – C35 | 108.9(4) |
| S16 – C36 – C37 | 123.7(4) | C35 – C36 – C37 | 127.3(5) |
| C36 – C37 – C38 | 128.9(5) | S17 – C38 – S18 | 113.0(3) |
| S17 – C38 – C37 | 124.5(4) | S18 – C38 – C37 | 122.5(4) |
| S17 – C39 – S19 | 119.5(3) | S17 – C39 – C40 | 116.9(5) |
| S19 – C39 – C40 | 123.6(5) | S18 – C40 – S20 | 119.5(3) |
| S18 – C40 – C39 | 116.0(4) | S20 – C40 – C39 | 124.2(5) |
| F1 – B1 – F2 | 107.9(6) | F1 – B1 – F3 | 106.2(8) |
| F1 – B1 – F4 | 111.3(9) | F2 – B1 – F3 | 109.1(8) |
| F2 – B1 – F4 | 115.9(9) | F3 – B1 – F4 | 106.0(7) |
| F5 – B2 – F6 | 115.4(8) | F5 – B2 – F7 | 108.1(8) |
| F5 – B2 – F8 | 109.8(7) | F6 – B2 – F7 | 107.6(7) |
| F6 – B2 – F8 | 111.5(8) | F7 – B2 – F8 | 103.7(8) |



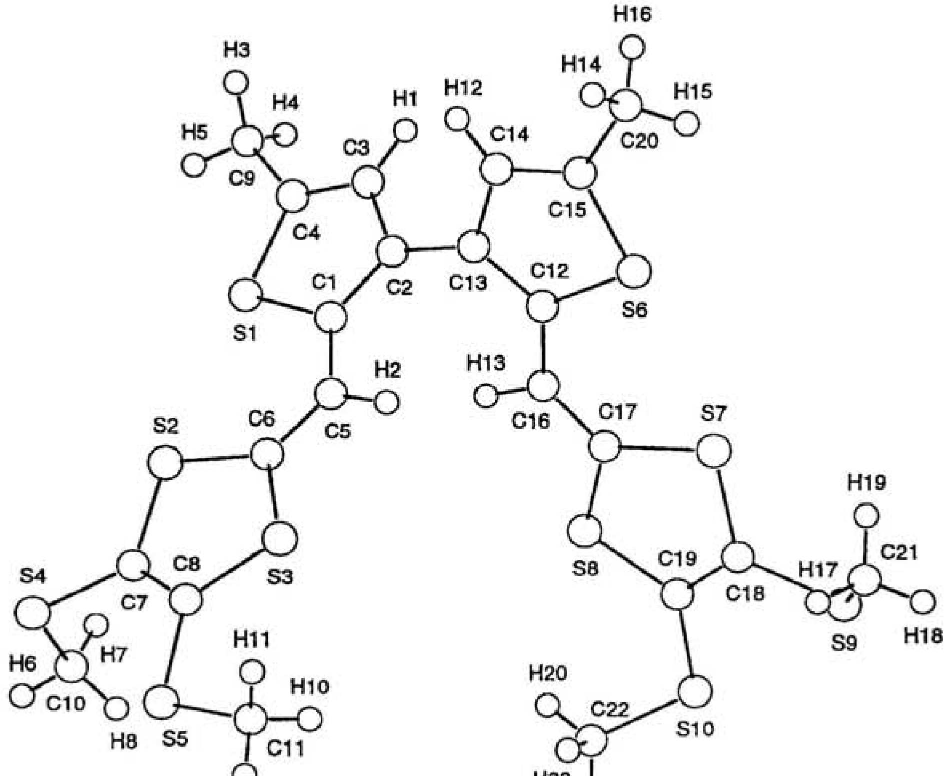


**Figure 3.** Atomic numbering system.

**Table 7**. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å$^2$).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| S1 | 1.1749(2) | 0.7630(4) | 0.23243(9) | 5.00(7) |
| S2 | 0.9917(2) | 0.7983(3) | 0.29976(9) | 4.52(6) |
| S3 | 0.8216(2) | 0.5729(3) | 0.26886(9) | 4.70(7) |
| S4 | 0.8751(2) | 0.9715(4) | 0.3788(1) | 5.90(8) |
| S5 | 0.6836(2) | 0.7293(4) | 0.3435(1) | 5.42(7) |
| S6 | 0.9945(2) | 0.2453(3) | 0.06010(8) | 3.72(5) |
| S7 | 0.8198(2) | 0.4936(3) | 0.01154(8) | 3.94(6) |
| S8 | 0.8297(2) | 0.8298(3) | 0.0592(1) | 4.49(6) |
| S9 | 0.6259(2) | 0.5852(3) | −0.05039(9) | 4.46(6) |
| S10 | 0.6329(2) | 0.9479(3) | 0.0057(1) | 5.20(7) |
| C1 | 1.0925(6) | 0.618(1) | 0.2020(3) | 3.3(2) |
| C2 | 1.1419(6) | 0.533(1) | 0.1650(3) | 3.2(2) |
| C3 | 1.2446(6) | 0.584(1) | 0.1632(3) | 4.6(3) |
| C4 | 1.2737(6) | 0.703(1) | 0.1964(3) | 5.1(3) |
| C5 | 0.9907(6) | 0.585(1) | 0.2168(3) | 3.4(2) |
| C6 | 0.9440(6) | 0.647(1) | 0.2559(3) | 3.4(2) |
| C7 | 0.8783(7) | 0.824(1) | 0.3302(3) | 4.1(2) |
| C8 | 0.8011(6) | 0.722(1) | 0.3159(3) | 3.6(2) |
| C9 | 1.3754(8) | 0.793(2) | 0.2048(5) | 9.7(4) |
| C10 | 0.846(1) | 1.159(1) | 0.3458(4) | 8.5(4) |
| C11 | 0.6091(7) | 0.573(2) | 0.3117(4) | 8.0(4) |
| C12 | 1.0156(5) | 0.428(1) | 0.0969(3) | 2.8(2) |
| C13 | 1.0980(6) | 0.402(1) | 0.1309(3) | 3.1(2) |
| C14 | 1.1440(6) | 0.239(1) | 0.1252(3) | 4.1(2) |
| C15 | 1.0965(6) | 0.140(1) | 0.0892(3) | 3.9(2) |
| C16 | 0.9566(6) | 0.580(1) | 0.0908(3) | 3.1(2) |
| C17 | 0.8795(6) | 0.623(1) | 0.0590(3) | 3.1(2) |
| C18 | 0.7185(6) | 0.634(1) | −0.0029(3) | 3.5(2) |
| C19 | 0.7207(6) | 0.787(1) | 0.0198(3) | 3.3(2) |
| C20 | 1.1239(7) | −0.037(1) | 0.0738(3) | 5.2(3) |
| C21 | 0.6026(8) | 0.368(1) | −0.0389(4) | 6.4(3) |
| C22 | 0.6172(9) | 1.047(1) | 0.0634(4) | 8.1(4) |
| H1 | 1.2900 | 0.5408 | 0.1380 | 5.4 |
| H2 | 0.9489 | 0.5055 | 0.1943 | 4.0 |
| H3 | 1.4315 | 0.7147 | 0.2115 | 10.5 |
| H4 | 1.3939 | 0.8573 | 0.1748 | 10.5 |
| H5 | 1.3773 | 0.8737 | 0.2316 | 10.5 |
| H6 | 0.8426 | 1.2575 | 0.3684 | 9.0 |
| H7 | 0.8982 | 1.1886 | 0.3230 | 9.0 |
| H8 | 0.7829 | 1.1549 | 0.3266 | 9.0 |
| H9 | 0.5418 | 0.5649 | 0.3238 | 8.5 |
| H10 | 0.6015 | 0.5932 | 0.2761 | 8.5 |
| H11 | 0.6393 | 0.4602 | 0.3159 | 8.5 |
| H12 | 1.2029 | 0.2013 | 0.1450 | 4.8 |
| H13 | 0.9782 | 0.6714 | 0.1155 | 3.7 |
| H14 | 1.1213 | −0.1184 | 0.1013 | 5.5 |
| H15 | 1.0781 | −0.0811 | 0.0471 | 5.5 |
| H16 | 1.1916 | −0.0450 | 0.0620 | 5.5 |

**Table 7.** (Continued).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| H17 | 0.5798 | 0.3462 | −0.0055 | 7.0 |
| H18 | 0.5520 | 0.3183 | −0.0622 | 7.0 |
| H19 | 0.6636 | 0.2971 | −0.0413 | 7.0 |
| H20 | 0.6801 | 1.0898 | 0.0786 | 8.5 |
| H21 | 0.5690 | 1.1369 | 0.0616 | 8.5 |
| H22 | 0.5924 | 0.9646 | 0.0881 | 8.5 |

**Table 8.** Bond lengths (Å).

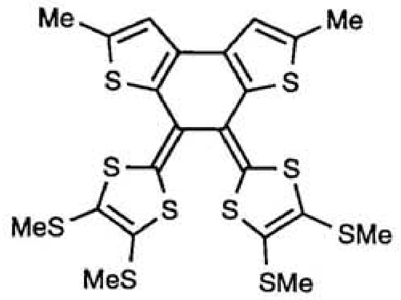
| atoms | length / Å | atoms | length / Å |
|---|---|---|---|
| S1 – C1 | 1.744(8) | S1 – C4 | 1.731(9) |
| S2 – C6 | 1.761(8) | S2 – C7 | 1.755(8) |
| S3 – C6 | 1.768(8) | S3 – C8 | 1.748(8) |
| S4 – C7 | 1.746(9) | S4 – C10 | 1.75(1) |
| S5 – C8 | 1.757(8) | S5 – C11 | 1.76(1) |
| S6 – C12 | 1.750(8) | S6 – C15 | 1.723(9) |
| S7 – C17 | 1.773(8) | S7 – C18 | 1.758(8) |
| S8 – C17 | 1.752(8) | S8 – C19 | 1.761(8) |
| S9 – C18 | 1.748(8) | S9 – C21 | 1.763(9) |
| S10 – C19 | 1.739(8) | S10 – C22 | 1.75(1) |
| C1 – C2 | 1.39(1) | C1 – C5 | 1.44(1) |
| C2 – C3 | 1.42(1) | C2 – C13 | 1.47(1) |
| C3 – C4 | 1.33(1) | C4 – C9 | 1.52(1) |
| C5 – C6 | 1.331(9) | C7 – C8 | 1.33(1) |
| C12 – C13 | 1.39(1) | C12 – C16 | 1.43(1) |
| C13 – C14 | 1.44(1) | C14 – C15 | 1.36(1) |
| C15 – C20 | 1.50(1) | C16 – C17 | 1.33(1) |
| C18 – C19 | 1.35(1) | | |

**Table 9.** Bond angles (degree).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| C1 – S1 – C4 | 91.8(4) | C6 – S2 – C7 | 96.0(4) |
| C6 – S3 – C8 | 95.9(4) | C7 – S4 – C10 | 101.6(4) |
| C8 – S5 – C11 | 104.7(4) | C12 – S6 – C15 | 92.7(4) |
| C17 – S7 – C18 | 95.4(4) | C17 – S8 – C19 | 96.6(4) |
| C18 – S9 – C21 | 102.0(4) | C19 – S10 – C22 | 104.1(4) |
| S1 – C1 – C2 | 109.9(6) | S1 – C1 – C5 | 123.4(6) |

**Table 9**. (Continued).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| C2 – C1 – C5 | 126.6(8) | C1 – C2 – C3 | 112.4(7) |
| C1 – C2 – C13 | 126.4(7) | C3 – C2 – C13 | 121.3(7) |
| C2 – C3 – C4 | 114.5(8) | S1 – C4 – C3 | 111.4(7) |
| S1 – C4 – C9 | 118.5(7) | C3 – C4 – C9 | 130.1(9) |
| C1 – C5 – C6 | 129.2(7) | S2 – C6 – S3 | 112.7(4) |
| S2 – C6 – C5 | 127.0(6) | S3 – C6 – C5 | 120.3(6) |
| S2 – C7 – S4 | 118.7(5) | S2 – C7 – C8 | 117.1(7) |
| S4 – C7 – C8 | 124.2(7) | S3 – C8 – S5 | 120.2(5) |
| S3 – C8 – C7 | 117.4(6) | S5 – C8 – C7 | 122.4(7) |
| S6 – C12 – C13 | 110.0(6) | S6 – C12 – C16 | 123.6(6) |
| C13 – C12 – C16 | 126.3(7) | C2 – C13 – C12 | 124.8(8) |
| C2 – C13 – C14 | 122.6(7) | C12 – C13 – C14 | 112.2(8) |
| C13 – C14 – C15 | 114.0(8) | S6 – C15 – C14 | 111.1(7) |
| S6 – C15 – C20 | 121.1(7) | C14 – C15 – C20 | 127.9(9) |
| C12 – C16 – C17 | 132.6(8) | S7 – C17 – S8 | 112.6(4) |
| S7 – C17 – C16 | 126.8(7) | S8 – C17 – C16 | 120.6(7) |
| S7 – C18 – S9 | 120.6(5) | S7 – C18 – C19 | 117.8(6) |
| S9 – C18 – C19 | 121.2(6) | S8 – C19 – S10 | 120.0(5) |
| S8 – C19 – C18 | 115.7(6) | S10 – C19 – C18 | 123.7(6) |



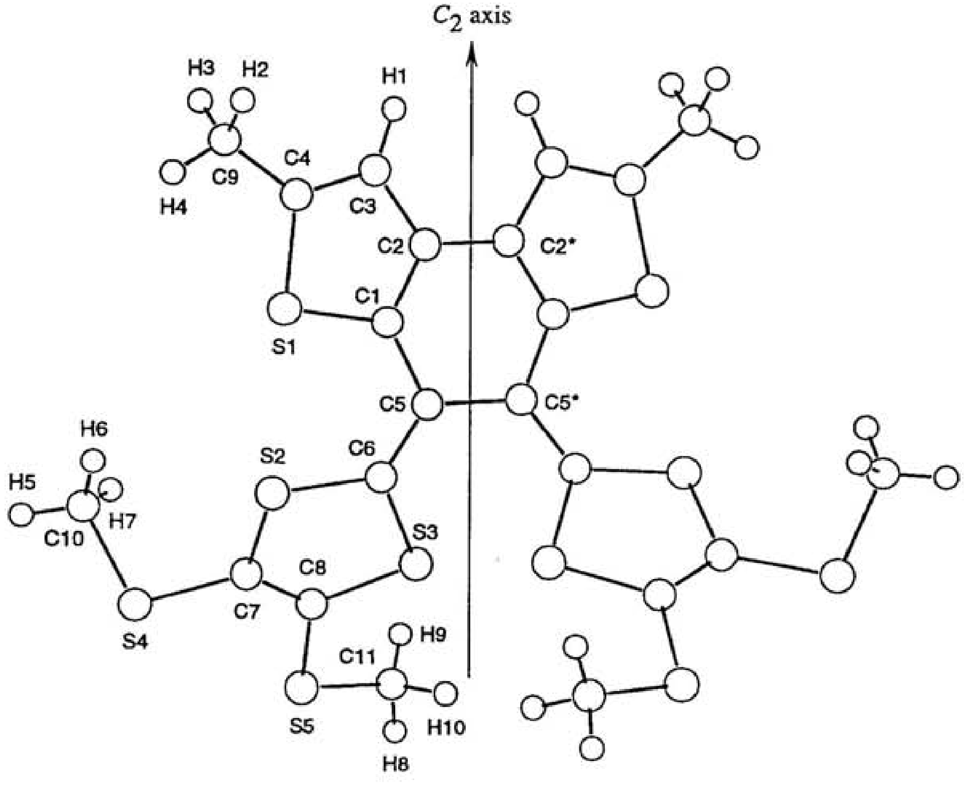


**Figure 4**. Atomic numbering system.

**Table 10**. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å$^2$).

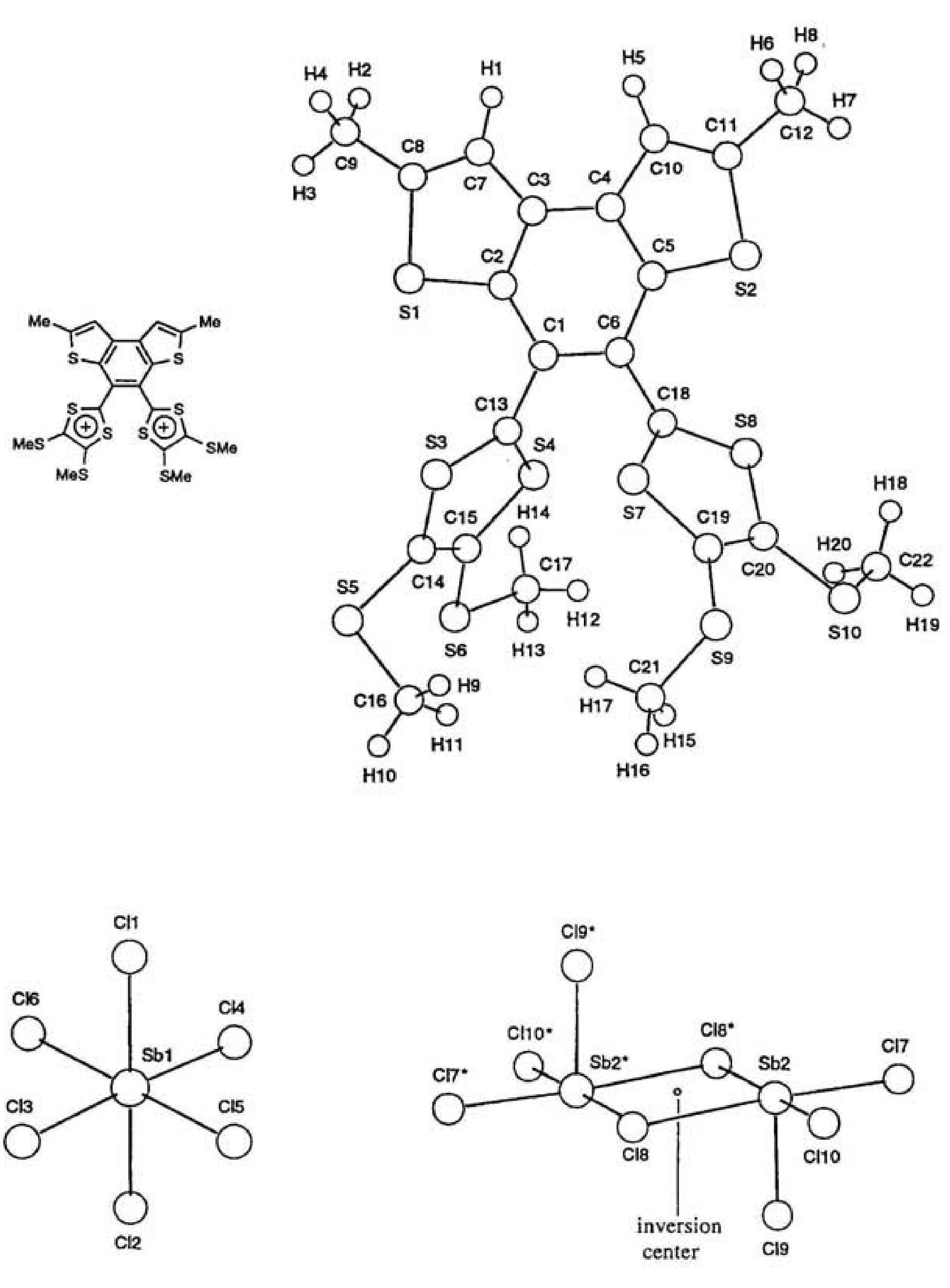
| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| S1 | −0.1858(2) | 0.4632(1) | 0.0125 | 3.34(8) |
| S2 | −0.1528(2) | 0.4407(1) | 0.3149(5) | 4.01(9) |
| S3 | 0.0152(2) | 0.45980(8) | 0.4447(5) | 2.92(7) |
| S4 | −0.1780(3) | 0.3734(1) | 0.4881(6) | 4.9(1) |
| S5 | 0.0097(3) | 0.3966(1) | 0.6484(6) | 6.1(1) |
| C1 | −0.0836(7) | 0.4831(3) | 0.043(1) | 2.5(3) |
| C2 | −0.0449(7) | 0.4924(3) | −0.080(1) | 2.4(3) |
| C3 | −0.0969(8) | 0.4845(3) | −0.202(1) | 3.4(3) |
| C4 | −0.1759(8) | 0.4690(3) | −0.169(1) | 2.9(3) |
| C5 | −0.0373(7) | 0.4871(3) | 0.181(1) | 2.5(3) |
| C6 | −0.0566(8) | 0.4668(3) | 0.298(1) | 2.7(3) |
| C7 | −0.1121(8) | 0.4111(3) | 0.446(1) | 3.0(3) |
| C8 | −0.0350(8) | 0.4194(3) | 0.503(1) | 3.0(3) |
| C9 | −0.2457(9) | 0.4560(3) | −0.263(1) | 3.9(3) |
| C10 | −0.180(1) | 0.3489(4) | 0.326(2) | 5.8(4) |
| C11 | 0.119(1) | 0.4091(5) | 0.654(2) | 7.9(6) |
| H1 | −0.0790 | 0.4903 | −0.3010 | 4.3 |
| H2 | −0.2701 | 0.4746 | −0.3232 | 4.8 |
| H3 | −0.2248 | 0.4369 | −0.3278 | 4.8 |
| H4 | −0.2960 | 0.4451 | −0.2134 | 4.0 |
| H5 | −0.2096 | 0.3265 | 0.3362 | 7.0 |
| H6 | −0.1989 | 0.3622 | 0.2510 | 7.0 |
| H7 | −0.1158 | 0.3415 | 0.3040 | 7.0 |
| H8 | 0.1518 | 0.3986 | 0.7358 | 8.5 |
| H9 | 0.1527 | 0.4040 | 0.5725 | 8.5 |
| H10 | 0.1266 | 0.4359 | 0.6715 | 8.5 |

**Table 11**. Bond lengths (Å).

| atoms | length / Å | atoms | length / Å |
|---|---|---|---|
| S1 – C1 | 1.73(1) | S1 – C4 | 1.73(1) |
| S2 – C6 | 1.75(1) | S2 – C7 | 1.76(1) |
| S3 – C6 | 1.78(1) | S3 – C8 | 1.76(1) |
| S4 – C7 | 1.75(1) | S4 – C10 | 1.78(2) |
| S5 – C8 | 1.74(1) | S5 – C11 | 1.72(2) |
| C1 – C2 | 1.34(2) | C1 – C5 | 1.49(2) |
| C2 – C2* | 1.47(2) | C2 – C3 | 1.42(2) |
| C3 – C4 | 1.36(2) | C4 – C9 | 1.46(2) |
| C5 – C5* | 1.48(2) | C5 – C6 | 1.36(2) |
| C7 – C8 | 1.32(1) | | |

**Table 12**. Bond angles (degree).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| C1 – S1 – C4 | 91.9(6) | C6 – S2 – C7 | 96.8(6) |
| C6 – S3 – C8 | 96.0(6) | C7 – S4 – C10 | 102.7(6) |
| C8 – S5 – C11 | 105.5(7) | S1 – C1 – C2 | 110.8(8) |
| S1 – C1 – C5 | 127.2(8) | C2 – C1 – C5 | 122(1) |
| C1 – C2 – C2 | 120.0(7) | C1 – C2 – C3 | 114(1) |
| C2 – C2 – C3 | 126.0(7) | C2 – C3 – C4 | 112(1) |
| S1 – C4 – C3 | 111(1) | S1 – C4 – C9 | 120(1) |
| C3 – C4 – C9 | 129(1) | C1 – C5 – C5 | 115.0(7) |
| C1 – C5 – C6 | 124(1) | C5 – C5 – C6 | 121.3(8) |
| S2 – C6 – S3 | 110.7(7) | S2 – C6 – C5 | 124(1) |
| S3 – C6 – C5 | 125.3(9) | S2 – C7 – S4 | 116.8(7) |
| S2 – C7 – C8 | 116.6(9) | S4 – C7 – C8 | 127(1) |
| S3 – C8 – S5 | 119.3(7) | S3 – C8 – C7 | 116.7(9) |
| S5 – C8 – C7 | 123.3(9) | | |



$SbCl_6^{-}$

$Sb_2Cl_8^{2-}$

**Figure 5**. Atomic numbering system.

**Table 13**. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å$^2$).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| Sb1 | 0.10495(9) | 0.28106(3) | 0.62984(6) | 3.65(2) |
| Sb2 | 0.51123(9) | 0.47779(3) | 0.12789(6) | 3.83(2) |
| Cl1 | 0.2244(4) | 0.3519(2) | 0.7087(3) | 5.8(1) |
| Cl2 | -0.0217(4) | 0.2130(2) | 0.5436(4) | 7.5(1) |
| Cl3 | 0.0753(5) | 0.2541(2) | 0.7698(3) | 8.5(2) |
| Cl4 | 0.1375(4) | 0.3043(2) | 0.4902(3) | 6.0(1) |
| Cl5 | 0.2953(4) | 0.2324(2) | 0.6699(3) | 6.5(1) |
| Cl6 | -0.0817(4) | 0.3315(2) | 0.5949(3) | 5.7(1) |
| Cl7 | 0.4605(4) | 0.5201(1) | 0.2555(2) | 6.5(1) |
| Cl8 | 0.5823(4) | 0.4263(1) | -0.0115(2) | 5.3(1) |
| Cl9 | 0.7160(4) | 0.5130(2) | 0.1814(4) | 10.0(2) |
| Cl10 | 0.5626(6) | 0.4009(2) | 0.2155(3) | 8.7(2) |
| S1 | 0.5446(3) | 0.8542(1) | 0.9588(2) | 3.76(8) |
| S2 | 0.0688(4) | 0.9945(1) | 0.8299(2) | 4.42(9) |
| S3 | 0.4534(3) | 0.8519(1) | 0.7004(2) | 3.26(7) |
| S4 | 0.2643(3) | 0.7907(1) | 0.7349(2) | 3.36(7) |
| S5 | 0.5286(4) | 0.7741(1) | 0.5835(2) | 4.44(9) |
| S6 | 0.3199(4) | 0.7012(1) | 0.6284(3) | 5.1(1) |
| S7 | 0.1742(3) | 0.9395(1) | 0.5997(2) | 3.72(8) |
| S8 | -0.0269(3) | 0.8974(1) | 0.6514(2) | 3.86(8) |
| S9 | 0.0169(4) | 0.9521(2) | 0.3937(2) | 5.1(1) |
| S10 | -0.2146(3) | 0.8993(2) | 0.4500(2) | 4.8(1) |
| C1 | 0.321(1) | 0.8847(4) | 0.8163(7) | 2.2(2) |
| C2 | 0.406(1) | 0.8893(4) | 0.9084(8) | 2.7(3) |
| C3 | 0.390(1) | 0.9246(4) | 0.9738(8) | 2.9(3) |
| C4 | 0.280(1) | 0.9566(5) | 0.9420(8) | 3.0(3) |
| C5 | 0.194(1) | 0.9515(4) | 0.8508(8) | 2.8(3) |
| C6 | 0.212(1) | 0.9162(4) | 0.7853(7) | 2.4(2) |
| C7 | 0.491(1) | 0.9220(5) | 1.0621(9) | 4.0(3) |
| C8 | 0.579(1) | 0.8867(5) | 1.0664(8) | 4.0(3) |
| C9 | 0.694(1) | 0.8731(6) | 1.148(1) | 5.8(4) |
| C10 | 0.243(1) | 0.9964(5) | 0.9949(9) | 4.1(4) |
| C11 | 0.132(1) | 1.0188(5) | 0.943(1) | 4.4(4) |
| C12 | 0.066(2) | 1.0607(6) | 0.974(1) | 6.4(5) |
| C13 | 0.345(1) | 0.8462(4) | 0.7535(7) | 2.4(2) |
| C14 | 0.433(1) | 0.7935(4) | 0.6504(7) | 2.8(3) |
| C15 | 0.346(1) | 0.7634(4) | 0.6690(8) | 2.8(3) |
| C16 | 0.413(2) | 0.7820(6) | 0.466(1) | 5.5(4) |
| C17 | 0.197(1) | 0.6820(5) | 0.669(1) | 6.3(4) |
| C18 | 0.127(1) | 0.9165(4) | 0.6868(8) | 2.9(3) |
| C19 | 0.034(1) | 0.9302(4) | 0.5080(8) | 3.3(3) |
| C20 | -0.064(1) | 0.9106(4) | 0.5314(8) | 3.1(3) |
| C21 | 0.081(2) | 0.9021(6) | 0.347(1) | 7.0(5) |
| C22 | -0.283(1) | 0.8610(6) | 0.516(1) | 5.8(4) |
| H1 | 0.494 | 0.945 | 1.115 | 4.6 |
| H2 | 0.675 | 0.862 | 1.201 | 6.7 |
| H3 | 0.742 | 0.846 | 1.131 | 6.7 |
| H4 | 0.753 | 0.902 | 1.167 | 6.7 |

**Table 13.** (Continued).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| H5 | 0.294 | 1.006 | 1.060 | 4.9 |
| H6 | 0.118 | 1.091 | 0.990 | 7.3 |
| H7 | -0.013 | 1.070 | 0.924 | 7.3 |
| H8 | 0.043 | 1.052 | 1.028 | 7.3 |
| H9 | 0.384 | 0.817 | 0.455 | 6.3 |
| H10 | 0.448 | 0.773 | 0.418 | 6.3 |
| H11 | 0.338 | 0.761 | 0.457 | 6.3 |
| H12 | 0.121 | 0.703 | 0.644 | 6.9 |
| H13 | 0.170 | 0.648 | 0.652 | 6.9 |
| H14 | 0.222 | 0.684 | 0.738 | 6.9 |
| H15 | 0.037 | 0.871 | 0.346 | 7.9 |
| H16 | 0.081 | 0.909 | 0.284 | 7.9 |
| H17 | 0.171 | 0.896 | 0.386 | 7.9 |
| H18 | -0.285 | 0.878 | 0.572 | 6.6 |
| H19 | -0.369 | 0.851 | 0.480 | 6.6 |
| H20 | -0.234 | 0.830 | 0.536 | 6.6 |

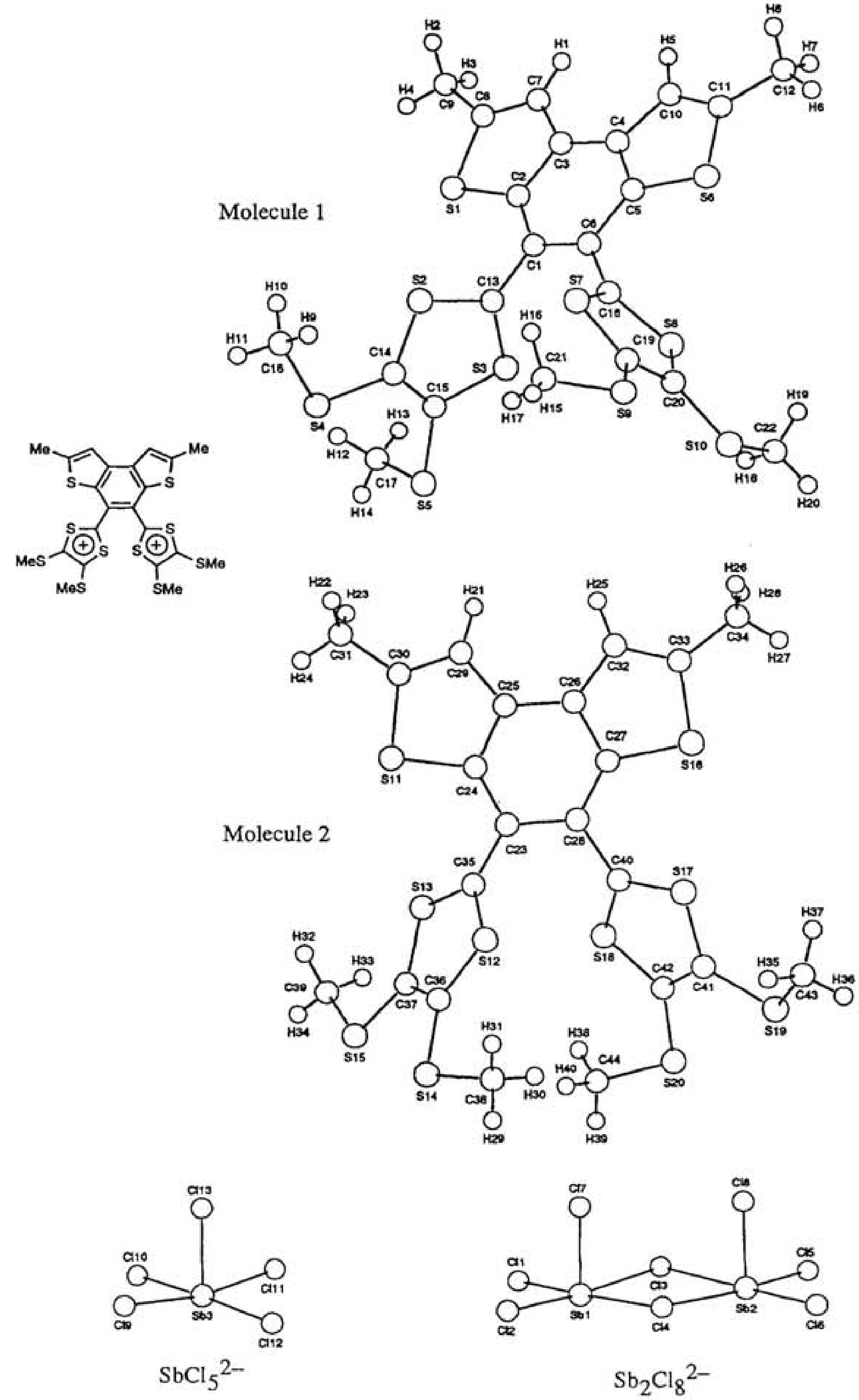
**Table 14.** Bond lengths (Å).

| atoms | length / Å | atoms | length / Å |
|---|---|---|---|
| Sb1 – Cl1 | 2.364(4) | Sb1 – Cl2 | 2.374(4) |
| Sb1 – Cl3 | 2.344(4) | Sb1 – Cl4 | 2.326(4) |
| Sb1 – Cl5 | 2.368(4) | Sb1 – Cl6 | 2.366(4) |
| Sb2 – Cl7 | 2.442(3) | Sb2 – Cl8 | 2.823(3) |
| Sb2 – Cl8* | 3.051(4) | Sb2 – Cl9 | 2.330(5) |
| Sb2 – Cl10 | 2.379(4) | S1 – C2 | 1.73(1) |
| S1 – C8 | 1.75(1) | S2 – C5 | 1.73(1) |
| S2 – C11 | 1.73(1) | S3 – C13 | 1.66(1) |
| S3 – C14 | 1.70(1) | S4 – C13 | 1.69(1) |
| S4 – C15 | 1.71(1) | S5 – C14 | 1.76(1) |
| S5 – C16 | 1.81(1) | S6 – C15 | 1.74(1) |
| S6 – C17 | 1.75(2) | S7 – C18 | 1.68(1) |
| S7 – C19 | 1.71(1) | S8 – C18 | 1.68(1) |
| S8 – C20 | 1.74(1) | S9 – C19 | 1.76(1) |
| S9 – C21 | 1.76(2) | S10 – C20 | 1.73(1) |
| S10 – C22 | 1.75(2) | C1 – C2 | 1.39(1) |
| C1 – C6 | 1.41(1) | C1 – C13 | 1.47(1) |
| C2 – C3 | 1.41(1) | C3 – C4 | 1.43(2) |
| C3 – C7 | 1.41(2) | C4 – C5 | 1.38(1) |
| C4 – C10 | 1.45(2) | C5 – C6 | 1.42(1) |
| C6 – C18 | 1.46(1) | C7 – C8 | 1.34(2) |
| C8 – C9 | 1.49(2) | C10 – C11 | 1.35(2) |
| C11 – C12 | 1.48(2) | C14 – C15 | 1.35(2) |
| C19 – C20 | 1.35(2) | | |

**Table 15**. Bond angles (degree).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| Cl1 – Sb1 – Cl2 | 176.7(2) | Cl1 – Sb1 – Cl3 | 91.0(2) |
| Cl1 – Sb1 – Cl4 | 90.6(1) | Cl1 – Sb1 – Cl5 | 90.2(2) |
| Cl1 – Sb1 – Cl6 | 87.9(1) | Cl2 – Sb1 – Cl3 | 91.2(2) |
| Cl2 – Sb1 – Cl4 | 87.3(2) | Cl2 – Sb1 – Cl5 | 92.2(2) |
| Cl2 – Sb1 – Cl6 | 89.7(1) | Cl3 – Sb1 – Cl4 | 177.5(2) |
| Cl3 – Sb1 – Cl5 | 89.6(2) | Cl3 – Sb1 – Cl6 | 89.5(2) |
| Cl4 – Sb1 – Cl5 | 88.5(2) | Cl4 – Sb1 – Cl6 | 92.6(1) |
| Cl5 – Sb1 – Cl6 | 177.9(1) | Cl7 – Sb2 – Cl8 | 176.6(1) |
| Cl7 – Sb2 – Cl9 | 90.3(2) | Cl7 – Sb2 – Cl10 | 91.9(1) |
| Cl8 – Sb2 – Cl9 | 87.8(2) | Cl8 – Sb2 – Cl10 | 85.6(1) |
| Cl9 – Sb2 – Cl10 | 97.4(2) | C2 – S1 – C8 | 91.1(6) |
| C5 – S2 – C11 | 92.0(6) | C13 – S3 – C14 | 97.0(6) |
| C13 – S4 – C15 | 96.2(6) | C14 – S5 – C16 | 99.3(6) |
| C15 – S6 – C17 | 101.8(7) | C18 – S7 – C19 | 97.6(6) |
| C18 – S8 – C20 | 97.1(6) | C19 – S9 – C21 | 102.8(6) |
| C20 – S10 – C22 | 101.5(7) | C2 – C1 – C6 | 119(1) |
| C2 – C1 – C13 | 119(1) | C6 – C1 – C13 | 121.3(9) |
| S1 – C2 – C1 | 125.9(9) | S1 – C2 – C3 | 110.6(9) |
| C1 – C2 – C3 | 123(1) | C2 – C3 – C4 | 117(1) |
| C2 – C3 – C7 | 112(1) | C4 – C3 – C7 | 131(1) |
| C3 – C4 – C5 | 120(1) | C3 – C4 – C10 | 128(1) |
| C5 – C4 – C10 | 113(1) | S2 – C5 – C4 | 110.7(9) |
| S2 – C5 – C6 | 126.9(9) | C4 – C5 – C6 | 122(1) |
| C1 – C6 – C5 | 118(1) | C1 – C6 – C18 | 122(1) |
| C5 – C6 – C18 | 120(1) | C3 – C7 – C8 | 114(1) |
| S1 – C8 – C7 | 112(1) | S1 – C8 – C9 | 120(1) |
| C7 – C8 – C9 | 128(1) | C4 – C10 – C11 | 112(1) |
| S2 – C11 – C10 | 113(1) | S2 – C11 – C12 | 120(1) |
| C10 – C11 – C12 | 127(1) | S3 – C13 – S4 | 115.4(6) |
| S3 – C13 – C1 | 124.2(8) | S4 – C13 – C1 | 120.3(8) |
| S3 – C14 – S5 | 120.0(7) | S3 – C14 – C15 | 115.9(8) |
| S5 – C14 – C15 | 123.9(9) | S4 – C15 – S6) | 123.0(7) |
| S4 – C15 – C14 | 115.4(8) | S6 – C15 – C14 | 121.6(9) |
| S7 – C18 – S8 | 114.5(6) | S7 – C18 – C6 | 121.5(9) |
| S8 – C18 – C6 | 123.9(8) | S7 – C19 – S9 | 120.1(8) |
| S7 – C19 – C20 | 116.0(9) | S9 – C19 – C20 | 124(1) |
| S8 – C20 – S10 | 122.0(8) | S8 – C20 – C19 | 114.7(9) |
| S10 – C20 – C19 | 123(1) | | |

*Chapter 4* Dication salt $2(\mathbf{16e})\cdot SbCl_5^{2-}\cdot Sb_2Cl_8^{2-}$ (needle-like crystal)



$SbCl_5^{2-}$

$Sb_2Cl_8^{2-}$

**Figure 6**. Atomic numbering system.

**Table 16**. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å$^2$).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| Sb1 | 0.75604(8) | 0.22308(7) | 0.5074(2) | 3.85(4) |
| Sb2 | 0.75646(8) | 0.40769(7) | 0.5008(2) | 4.16(4) |
| Sb3 | 0.79548(8) | 0.81316(7) | 0.9189(1) | 3.54(3) |
| Cl1 | 0.6791(3) | 0.1592(3) | 0.3463(6) | 5.1(2) |
| Cl2 | 0.8232(4) | 0.1389(3) | 0.6614(7) | 6.4(2) |
| Cl3 | 0.6691(3) | 0.3249(3) | 0.3520(6) | 5.1(2) |
| Cl4 | 0.8359(3) | 0.3058(3) | 0.6833(6) | 4.9(2) |
| Cl5 | 0.6846(4) | 0.4882(3) | 0.3440(7) | 6.1(2) |
| Cl6 | 0.8371(3) | 0.4718(3) | 0.6617(7) | 5.4(2) |
| Cl7 | 0.6702(3) | 0.2576(3) | 0.6781(6) | 5.5(2) |
| Cl8 | 0.6704(4) | 0.4382(3) | 0.6677(6) | 6.6(2) |
| Cl9 | 0.6635(3) | 0.8360(2) | 0.9907(6) | 4.6(1) |
| Cl10 | 0.8466(4) | 0.7462(3) | 1.1377(6) | 6.2(2) |
| Cl11 | 0.9233(3) | 0.7720(3) | 0.8239(7) | 6.4(2) |
| Cl12 | 0.7428(3) | 0.8885(3) | 0.7021(6) | 4.9(2) |
| Cl13 | 0.7609(3) | 0.7279(2) | 0.7608(6) | 4.8(1) |
| S1 | 0.9033(3) | 0.1279(3) | 0.2907(6) | 4.6(2) |
| S2 | 0.9905(3) | 0.1730(3) | 0.6783(6) | 5.0(2) |
| S3 | 1.1030(3) | 0.1595(3) | 0.5067(7) | 5.3(2) |
| S4 | 1.0882(4) | 0.0847(3) | 0.8960(7) | 5.9(2) |
| S5 | 1.2208(4) | 0.0762(4) | 0.7058(9) | 7.8(2) |
| S6 | 0.8999(3) | 0.3987(3) | 0.2820(6) | 4.0(1) |
| S7 | 0.9915(3) | 0.3490(3) | 0.7031(6) | 4.5(1) |
| S8 | 1.0822(3) | 0.3394(3) | 0.4855(6) | 4.6(2) |
| S9 | 1.0729(4) | 0.4299(4) | 0.9300(7) | 7.1(2) |
| S10 | 1.1801(4) | 0.4150(4) | 0.6864(8) | 7.3(2) |
| S11 | 0.4126(3) | 0.8429(2) | 1.1844(6) | 3.9(1) |
| S12 | 0.5913(3) | 0.7145(2) | 0.9367(6) | 3.6(1) |
| S13 | 0.4441(3) | 0.7145(2) | 0.9633(6) | 3.7(1) |
| S14 | 0.6471(4) | 0.5786(3) | 0.9419(9) | 6.7(2) |
| S15 | 0.4837(4) | 0.5774(3) | 0.9758(7) | 5.6(2) |
| S16 | 0.4873(3) | 0.9472(2) | 0.6662(6) | 3.7(1) |
| S17 | 0.5891(3) | 0.8142(3) | 0.5957(6) | 3.9(1) |
| S18 | 0.4859(3) | 0.7444(3) | 0.5962(6) | 3.9(1) |
| S19 | 0.6465(4) | 0.7365(4) | 0.3238(7) | 7.2(2) |
| S20 | 0.5412(4) | 0.6508(3) | 0.3470(7) | 6.3(2) |
| C1 | 0.961(1) | 0.229(1) | 0.420(2) | 3.2(5) |
| C2 | 0.913(1) | 0.2017(9) | 0.312(2) | 3.3(5) |
| C3 | 0.863(1) | 0.236(1) | 0.198(2) | 3.1(5) |
| C4 | 0.864(1) | 0.2958(9) | 0.197(2) | 3.0(5) |
| C5 | 0.911(1) | 0.323(1) | 0.304(2) | 3.4(5) |
| C6 | 0.961(1) | 0.289(1) | 0.420(2) | 3.4(5) |
| C7 | 0.821(1) | 0.200(1) | 0.098(3) | 4.9(6) |
| C8 | 0.834(1) | 0.143(1) | 0.129(2) | 5.5(7) |
| C9 | 0.803(1) | 0.091(1) | 0.048(3) | 6.4(8) |
| C10 | 0.821(1) | 0.338(1) | 0.088(2) | 4.5(6) |
| C11 | 0.835(1) | 0.393(1) | 0.116(2) | 4.1(6) |
| C12 | 0.802(2) | 0.448(1) | 0.034(2) | 6.3(8) |

**Table 16.** (Continued).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| C13 | 1.015(1) | 0.192(1) | 0.526(2) | 3.7(5) |
| C14 | 1.073(1) | 0.124(1) | 0.737(2) | 4.1(5) |
| C15 | 1.129(1) | 0.116(1) | 0.656(3) | 5.0(6) |
| C16 | 0.999(1) | 0.109(1) | 0.958(3) | 7.9(9) |
| C17 | 1.201(2) | 0.007(1) | 0.622(3) | 11(1) |
| C18 | 1.008(1) | 0.3208(8) | 0.526(2) | 2.8(4) |
| C19 | 1.059(1) | 0.386(1) | 0.753(2) | 4.1(5) |
| C20 | 1.105(1) | 0.382(1) | 0.651(2) | 4.5(6) |
| C21 | 1.037(2) | 0.398(2) | 1.043(3) | 11(1) |
| C22 | 1.215(2) | 0.395(1) | 0.520(3) | 6.8(8) |
| C23 | 0.479(1) | 0.8190(9) | 0.929(2) | 2.7(5) |
| C24 | 0.440(1) | 0.8606(9) | 1.028(2) | 2.9(5) |
| C25 | 0.416(1) | 0.9239(9) | 1.021(2) | 3.1(5) |
| C26 | 0.433(1) | 0.9482(9) | 0.902(2) | 2.8(5) |
| C27 | 0.474(1) | 0.907(1) | 0.801(2) | 3.1(5) |
| C28 | 0.494(1) | 0.8446(9) | 0.806(2) | 2.8(5) |
| C29 | 0.375(1) | 0.957(1) | 1.138(2) | 3.6(5) |
| C30 | 0.369(1) | 0.919(1) | 1.232(2) | 3.5(5) |
| C31 | 0.328(1) | 0.937(1) | 1.362(2) | 4.8(6) |
| C32 | 0.414(1) | 1.0102(8) | 0.872(2) | 3.2(5) |
| C33 | 0.437(1) | 1.016(1) | 0.744(2) | 3.4(5) |
| C34 | 0.429(1) | 1.073(1) | 0.676(2) | 4.5(6) |
| C35 | 0.504(1) | 0.7551(8) | 0.944(2) | 2.8(4) |
| C36 | 0.578(1) | 0.6445(9) | 0.943(2) | 3.5(5) |
| C37 | 0.509(1) | 0.6434(9) | 0.961(2) | 3.3(5) |
| C38 | 0.713(1) | 0.600(1) | 0.870(4) | 9(1) |
| C39 | 0.391(2) | 0.602(1) | 1.000(3) | 6.7(8) |
| C40 | 0.522(1) | 0.8028(8) | 0.673(2) | 2.7(4) |
| C41 | 0.591(1) | 0.7516(9) | 0.462(2) | 3.5(5) |
| C42 | 0.546(1) | 0.717(1) | 0.470(2) | 3.7(5) |
| C43 | 0.712(1) | 0.780(1) | 0.385(2) | 6.2(7) |
| C44 | 0.510(2) | 0.607(1) | 0.447(3) | 7.6(9) |
| H1 | 0.784 | 0.216 | 0.011 | 5.8 |
| H2 | 0.749 | 0.100 | 0.042 | 6.9 |
| H3 | 0.812 | 0.080 | -0.054 | 6.9 |
| H4 | 0.823 | 0.054 | 0.098 | 6.9 |
| H5 | 0.785 | 0.326 | 0.000 | 5.6 |
| H6 | 0.822 | 0.482 | 0.082 | 7.1 |
| H7 | 0.809 | 0.442 | -0.069 | 7.1 |
| H8 | 0.748 | 0.463 | 0.032 | 7.1 |
| H9 | 0.985 | 0.153 | 0.983 | 8.3 |
| H10 | 0.960 | 0.099 | 0.882 | 8.3 |
| H11 | 1.000 | 0.091 | 1.046 | 8.3 |
| H12 | 1.165 | -0.004 | 0.666 | 11.9 |
| H13 | 1.182 | 0.007 | 0.515 | 11.9 |
| H14 | 1.245 | -0.027 | 0.632 | 11.9 |
| H15 | 1.040 | 0.416 | 1.143 | 11.9 |
| H16 | 0.985 | 0.397 | 1.004 | 11.9 |

**Table 16**. (Continued).

| atom | X | Y | Z | Beq |
|---|---|---|---|---|
| H17 | 1.063 | 0.354 | 1.047 | 11.9 |
| H18 | 1.230 | 0.351 | 0.496 | 7.6 |
| H19 | 1.178 | 0.411 | 0.435 | 7.6 |
| H20 | 1.258 | 0.411 | 0.523 | 7.6 |
| H21 | 0.356 | 1.002 | 1.149 | 4.5 |
| H22 | 0.348 | 0.965 | 1.436 | 5.4 |
| H23 | 0.276 | 0.955 | 1.330 | 5.4 |
| H24 | 0.331 | 0.901 | 1.410 | 5.4 |
| H25 | 0.388 | 1.045 | 0.936 | 4.0 |
| H26 | 0.453 | 1.101 | 0.744 | 5.0 |
| H27 | 0.451 | 1.064 | 0.586 | 5.0 |
| H28 | 0.378 | 1.094 | 0.648 | 5.0 |
| H29 | 0.756 | 0.566 | 0.861 | 9.6 |
| H30 | 0.694 | 0.612 | 0.769 | 9.6 |
| H31 | 0.729 | 0.633 | 0.930 | 9.6 |
| H32 | 0.384 | 0.632 | 1.089 | 6.9 |
| H33 | 0.359 | 0.623 | 0.916 | 6.9 |
| H34 | 0.369 | 0.570 | 1.010 | 6.9 |
| H35 | 0.743 | 0.769 | 0.480 | 6.8 |
| H36 | 0.745 | 0.774 | 0.315 | 6.8 |
| H37 | 0.689 | 0.823 | 0.399 | 6.8 |
| H38 | 0.463 | 0.627 | 0.475 | 8.2 |
| H39 | 0.506 | 0.568 | 0.391 | 8.2 |
| H40 | 0.545 | 0.597 | 0.540 | 8.2 |

**Table 17**. Bond lengths (Å).

| atoms | length / Å | atoms | length / Å |
|---|---|---|---|
| Sb1 – Cl1 | 2.452(6) | Sb1 – Cl2 | 2.472(6) |
| Sb1 – Cl3 | 2.859(6) | Sb1 – Cl4 | 2.834(5) |
| Sb1 – Cl7 | 2.376(6) | Sb2 – Cl3 | 2.850(6) |
| Sb2 – Cl5 | 2.446(6) | Sb2 – Cl6 | 2.500(6) |
| Sb2 – Cl8 | 2.352(6) | Sb3 – Cl9 | 2.607(5) |
| Sb3 – Cl10 | 2.581(6) | Sb3 – Cl11 | 2.620(6) |
| Sb3 – Cl12 | 2.690(6) | Sb3 – Cl13 | 2.394(5) |
| S1 – C2 | 1.72(2) | S1 – C8 | 1.77(2) |
| S2 – C13 | 1.71(2) | S2 – C14 | 1.70(2) |
| S3 – C13 | 1.66(2) | S3 – C15 | 1.73(2) |
| S4 – C14 | 1.76(2) | S4 – C16 | 1.80(3) |
| S5 – C15 | 1.73(2) | S5 – C17 | 1.74(3) |
| S6 – C5 | 1.73(2) | S6 – C11 | 1.76(2) |
| S7 – C18 | 1.70(2) | S7 – C19 | 1.67(2) |
| S8 – C18 | 1.69(2) | S8 – C20 | 1.70(2) |

**Table 17**. (Continued).

| atoms | length / Å | atoms | length / Å |
|---|---|---|---|
| S9 – C19 | 1.78(2) | S9 – C21 | 1.68(3) |
| S10 – C20 | 1.75(2) | S10 – C22 | 1.74(2) |
| S11 – C24 | 1.75(2) | S11 – C30 | 1.75(2) |
| S12 – C35 | 1.68(2) | S12 – C36 | 1.70(2) |
| S13 – C35 | 1.69(2) | S13 – C37 | 1.75(2) |
| S14 – C36 | 1.70(2) | S14 – C38 | 1.72(2) |
| S15 – C37 | 1.73(2) | S15 – C39 | 1.74(3) |
| S16 – C27 | 1.74(2) | S16 – C33 | 1.73(2) |
| S17 – C40 | 1.68(2) | S17 – C41 | 1.73(2) |
| S18 – C40 | 1.65(2) | S18 – C42 | 1.72(2) |
| S19 – C41 | 1.74(2) | S19 – C43 | 1.74(2) |
| S20 – C42 | 1.74(2) | S20 – C44 | 1.74(2) |
| C1 – C2 | 1.40(2) | C1 – C6 | 1.36(2) |
| C1 – C13 | 1.45(2) | C2 – C3 | 1.43(3) |
| C3 – C4 | 1.38(2) | C3 – C7 | 1.39(3) |
| C4 – C5 | 1.37(2) | C4 – C10 | 1.46(3) |
| C5 – C6 | 1.45(3) | C6 – C18 | 1.43(2) |
| C7 – C8 | 1.34(3) | C8 – C9 | 1.49(3) |
| C10 – C11 | 1.32(3) | C11 – C12 | 1.51(3) |
| C14 – C15 | 1.37(3) | C19 – C20 | 1.37(3) |
| C23 – C24 | 1.38(2) | C23 – C28 | 1.45(2) |
| C23 – C35 | 1.43(2) | C24 – C25 | 1.40(2) |
| C25 – C26 | 1.42(2) | C25 – C29 | 1.45(2) |
| C26 – C27 | 1.41(2) | C26 – C32 | 1.42(2) |
| C27 – C28 | 1.38(2) | C28 – C40 | 1.51(2) |
| C29 – C30 | 1.35(2) | C30 – C31 | 1.49(3) |
| C32 – C33 | 1.36(2) | C33 – C34 | 1.48(2) |
| C36 – C37 | 1.36(2) | C41 – C42 | 1.33(2) |

**Table 18**. Bond angles (degree).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| Cl1 – Sb1 – Cl2 | 91.6(2) | Cl1 – Sb1 – Cl3 | 89.1(2) |
| Cl1 – Sb1 – Cl4 | 175.0(2) | Cl1 – Sb1 – Cl7 | 92.3(2) |
| Cl2 – Sb1 – Cl3 | 174.2(2) | Cl2 – Sb1 – Cl4 | 93.2(2) |
| Cl2 – Sb1 – Cl7 | 89.1(2) | Cl3 – Sb1 – Cl4 | 86.0(2) |
| Cl3 – Sb1 – Cl7 | 85.2(2) | Cl4 – Sb1 – Cl7 | 86.4(2) |
| Cl3 – Sb2 – Cl5 | 92.6(2) | Cl3 – Sb2 – Cl6 | 172.0(2) |
| Cl3 – Sb2 – Cl8 | 85.8(2) | Cl5 – Sb2 – Cl6 | 94.6(2) |
| Cl5 – Sb2 – Cl8 | 90.9(2) | Cl6 – Sb2 – Cl8 | 90.8(2) |
| Cl9 – Sb3 – Cl10 | 88.7(2) | Cl9 – Sb3 – Cl11 | 170.0(2) |
| Cl9 – Sb3 – Cl12 | 90.9(2) | Cl9 – Sb3 – Cl13 | 84.9(2) |
| Cl10 – Sb3 – Cl11 | 89.4(2 | Cl10 – Sb3 – Cl12 | 176.8(2) |

**Table 18**. (Continued).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| Cl10 – Sb3 – Cl13 | 89.5(2) | Cl11 – Sb3 – Cl12 | 91.5(2) |
| Cl11 – Sb3 – Cl13 | 85.3(2) | Cl12 – Sb3 – Cl13 | 93.6(2) |
| Sb1 – Cl3 – Sb2 | 95.8(2) | C2 – S1 – C8 | 91(1) |
| C13 – S2 – C14 | 97(1) | C13 – S3 – C15 | 99(1) |
| C14 – S4 – C16 | 103(1) | C15 – S5 – C17 | 92(2) |
| C5 – S6 – C11 | 91(1) | C18 – S7 – C19 | 97.7(9) |
| C18 – S8 – C20 | 98(1) | C19 – S9 – C21 | 104(1) |
| C20 – S10 – C22 | 103(1) | C24 – S11 – C30 | 91.9(9) |
| C35 – S12 – C36 | 97.8(9) | C35 – S13 – C37 | 96.0(9) |
| C36 – S14 – C38 | 102(1) | C37 – S15 – C39 | 105(1) |
| C27 – S16 – C33 | 92.7(9) | C40 – S17 – C41 | 95.0(9) |
| C40 – S18 – C42 | 95.8(9) | C41 – S19 – C43 | 106(1) |
| C42 – S20 – C44 | 104(1) | C2 – C1 – C6 | 121(2) |
| C2 – C1 – C13 | 118(2) | C6 – C1 – C13 | 120(2) |
| S1 – C2 – C1 | 129(2) | S1 – C2 – C3 | 111(1) |
| C1 – C2 – C3 | 120(2) | C2 – C3 – C4 | 119(2) |
| C2 – C3 – C7 | 112(2) | C4 – C3 – C7 | 129(2) |
| C3 – C4 – C5 | 121(2) | C3 – C4 – C10 | 129(2) |
| C5 – C4 – C10 | 111(2) | S6 – C5 – C4 | 112(2) |
| S6 – C5 – C6 | 127(2) | C4 – C5 – C6 | 121(2) |
| C1 – C6 – C5 | 118(2) | C1 – C6 – C18 | 125(2) |
| C5 – C6 – C18 | 116(2) | C3 – C7 – C8 | 115(2) |
| S1 – C8 – C7 | 112(2) | S1 – C8 – C9 | 118(2) |
| C7 – C8 – C9 | 131(2) | C4 – C10 – C11 | 114(2) |
| S6 – C11 – C10 | 112(2) | S6 – C11 – C12 | 118(2) |
| C10 – C11 – C12 | 130(2) | S2 – C13 – S3 | 114(1) |
| S2 – C13 – C1 | 121(1) | S3 – C13 – C1 | 125(1) |
| S2 – C14 – S4 | 122(1) | S2 – C14 – C15 | 117(2) |
| S4 – C14 – C15 | 120(2) | S3 – C15 – S5 | 121(1) |
| S3 – C15 – C14 | 113(2) | S5 – C15 – C14 | 126(2) |
| S7 – C18 – S8 | 113(1) | S7 – C18 – C6 | 123(1) |
| S8 – C18 – C6 | 124(1) | S7 – C19 – S9 | 123(1) |
| S7 – C19 – C20 | 117(2) | S9 – C19 – C20 | 120(2) |
| S8 – C20 – S10 | 122(1) | S8 – C20 – C19 | 114(2) |
| S10 – C20 – C19 | 124(2) | C24 – C23 – C28 | 115(2) |
| C24 – C23 – C35 | 123(2) | C28 – C23 – C35 | 122(2) |
| S11 – C24 – C23 | 125(1) | 11 – C24 – C25 | 109(1) |
| C23 – C24 – C25 | 125(2) | 24 – C25 – C26 | 118(2) |
| C24 – C25 – C29 | 115(2) | 26 – C25 – C29 | 127(2) |
| C25 – C26 – C27 | 117(2) | 25 – C26 – C32 | 128(2) |
| C27 – C26 – C32 | 114(2) | 16 – C27 – C26 | 109(1) |
| S16 – C27 – C28 | 128(1) | C26 – C27 – C28 | 123(2) |
| C23 – C28 – C27 | 120(2) | C23 – C28 – C40 | 120(2) |
| C27 – C28 – C40 | 119(2) | C25 – C29 – C30 | 111(2) |
| S11 – C30 – C29 | 113(1) | S11 – C30 – C31 | 120(2) |
| C29 – C30 – C31 | 127(2) | C26 – C32 – C33 | 112(2) |
| S16 – C33 – C32 | 112(1) | S16 – C33 – C34 | 120(1) |
| C32 – C33 – C34 | 128(2) | S12 – C35 – S13 | 115(1) |
| S12 – C35 – C23 | 123(1) | S13 – C35 – C23 | 122(1) |

**Table 18**. (Continued).

| atoms | angle / ° | atoms | angle / ° |
|---|---|---|---|
| S12 – C36 – S14 | 124(1) | S12 – C36 – C37 | 116(2) |
| S14 – C36 – C37 | 120(2) | S13 – C37 – S15 | 121(1) |
| S13 – C37 – C36 | 115(1) | S15 – C37 – C36 | 124(2) |
| S17 – C40 – S18 | 117(1) | S17 – C40 – C28 | 121(1) |
| S18 – C40 – C28 | 122(1) | S17 – C41 – S19 | 122(1) |
| S17 – C41 – C42 | 116(1) | S19 – C41 – C42 | 122(2) |
| S18 – C42 – S20 | 121(1) | S18 – C42 – C41 | 116(2) |
| S20 – C42 – C41 | 123(2) | | |