Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Bis (1,3-Dithiole) Electron Donors by Oxidative Intramolecular Cyclization of 2,2′-Bis(1,4-Dithiafulven-6-yl)-3,3′-Bithienyls

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To cite this article: Akira Ohta & Yoshiro Yamashita (1997): Novel Bis (1,3-Dithiole) Electron Donors by Oxidative Intramolecular Cyclization of 2,2′-Bis(1,4-Dithiafulven-6-yl)-3,3′-Bithienyls, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 296:1, 1-18

To link to this article: http://dx.doi.org/10.1080/10587259708032309

Mol. Cryst. Liq. Cryst., 1997, Vol. 296, pp. 1–18
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NOVEL BIS(1,3-DITHIOLE) ELECTRON DONORS BY OXIDATIVE INTRAMOLECULAR CYCLIZATION OF 2,2'-BIS(1,4-DITHIAFULVEN-6-YL)-3,3'-BITHIENYLS

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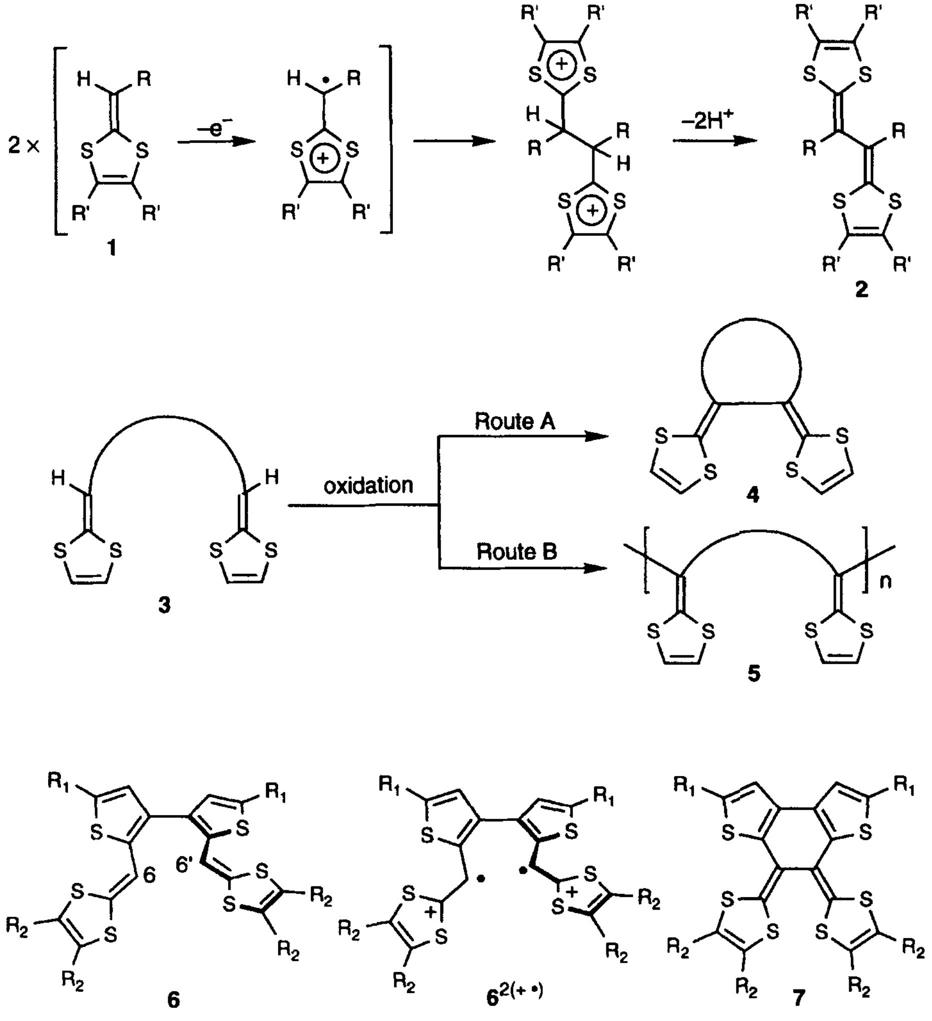
(Received 24 June 1996; In final form 2 September 1996)

Abstract 2,2'-Bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls **6** were prepared by using either a Wittig or a Wittig–Horner reaction. The cyclic voltammograms of **6** revealed that they undergo an intramolecular cyclization by electrochemical oxidation. Chemical oxidation of **6** with tris(4-bromophenyl)aminium hexachloroantimonate gave intramolecular cyclization products **16** as dication salts. The hexachloroantimonate ion was found to act as an oxidizing agent in the reaction. Chemical reduction of the dication salts with zinc afforded the corresponding neutral bis(1,3-dithiole) donors **7** in high yields. The cyclic voltammograms of **7** showed reversible one-stage two-electron oxidation waves, and the potentials are fairly low. A conductive TCNQ 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.

Keywords: bis(1,3-dithiole) donor, oxidation, electrochemistry, intramolecular cyclization

INTRODUCTION

1,3-Dithiole donors with extended π-conjugation play an important role in the field of organic conductors[1] or superconductors.[2] On the design of such donors, the high stability of their oxidized states is one of the most important requirements. On the other hand, 1,3-dithiole compounds which can be converted into other systems by oxidation are of synthetic interest.[3–5] Recently, Benahmed-Gasmi *et al.*[6] and Lorcy *et al.*[7] pointed out the synthetic utility of the oxidative intermolecular coupling of 1,4-dithiafulvene



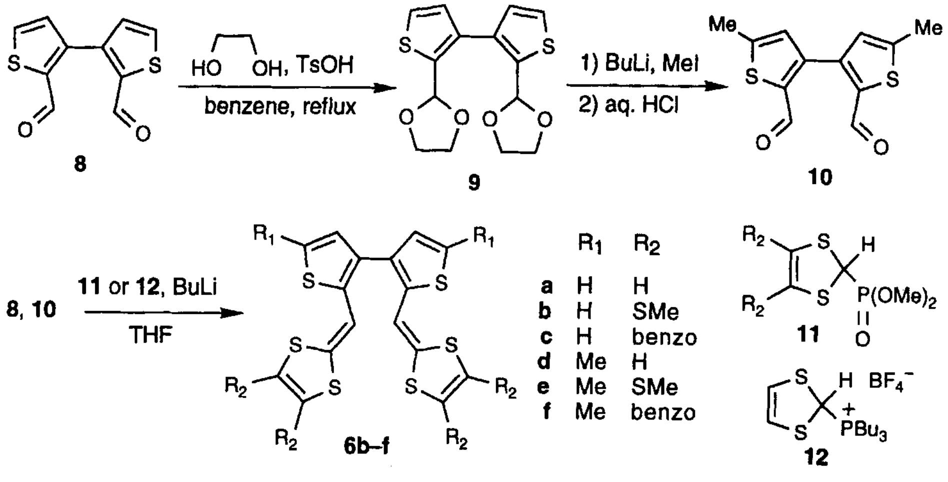
SCHEME 1

derivatives **1** to give TTF vinylogs **2**.[8–10] In contrast to such intermolecular reactions, the corresponding intramolecular cyclization is unknown so far. If compound **3** possessing two dithiafulvenyl groups at 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 when the spacer unit of **3** has an appropriate length (Scheme 1, Route A). Such an electron donor is little known except for radialene derivatives.[11] On the other hand, since the molecule **3** has two reactive groups, an intermolecular coupling reaction giving a polymer **5** is also possible (Route

B). Indeed, some bis(1,3-dithiole) compounds were reported to afford oligomers or polymers upon oxidation.[5,10,12] 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 will be suitable for such a spacer if two 1,4-dithiafulven-6-yl groups are introduced into its 2- and 2'-positions as represented by compound **6**. Since the 3,3'-bithienyl unit twists around the central C–C bond due to the steric interactions between the atoms on the 2,4- and 2',4'-positions, conjugation interactions between the two halves of **6** are considered to be small.[13] 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, we decided to prepare the bis(1,3-dithiole) compounds **6** containing the 3,3'-bithienyl unit.[14] The compounds **6** are expected to afford novel bis(1,3-dithiole) donors **7** upon oxidation. We report here the preparation and electrochemical properties of the compounds **6** and the successful formation of the corresponding cyclization products.

RESULTS AND DISCUSSION

The new bis(1,3-dithiole) compounds **6** were synthesized according to Scheme 2.



SCHEME 2

Although the parent compound **6a** could not be isolated in pure form, **6b** and **6c** were prepared by a Wittig–Horner reaction of aldehyde **8**[15] with the corresponding carbanions derived from phosphonate esters **11**[16] in 85 and 82% yields, respectively. For **6b** and **6c**, an oxidative intermolecular coupling at the α-positions of the thiophene rings is also possible, as seen in the synthesis of polythiophenes by oxidation of thiophene derivatives. Therefore, in order to examine the influence of α-substituents (R_1) upon the redox properties, dimethyl derivatives **6d–f** were also prepared. Thus the formyl groups of **8** were protected as dioxolane groups to give compound **9** in 96% yield. Lithiation of **9** with butyllithium followed by treatment with methyl iodide gave **10** in 84% yield. A Wittig reaction of a phosphonium salt **12**[17] (for **6d**) or a Wittig–Horner reaction of **11** with **10** afforded **6d–f** in 69, 90, and 93% yields, respectively. Attempts to prepare **6d** by a Wittig–Horner reaction gave only an unidentified insoluble solid.

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

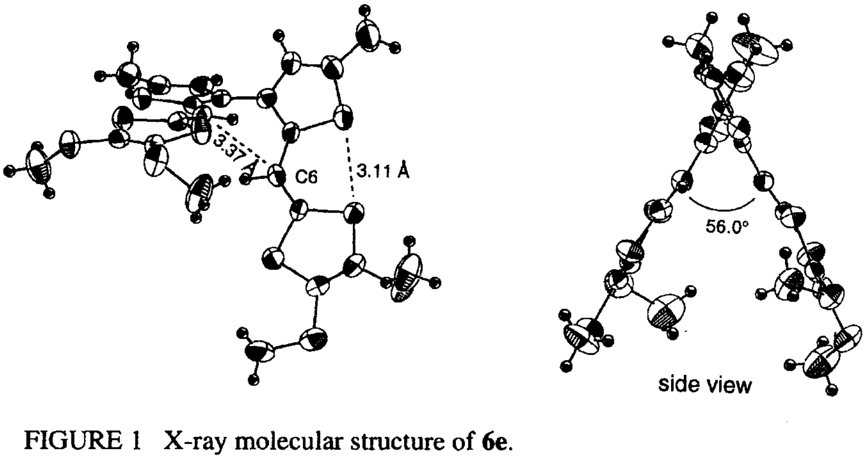
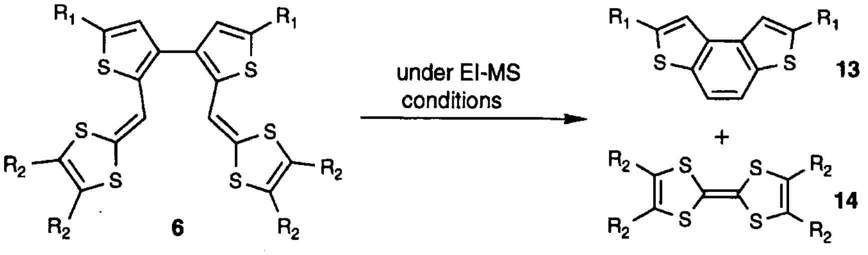


FIGURE 1 X-ray molecular structure of **6e**.

In order to investigate the electronic structure of **6**, MNDO-PM3 calculations[18] were carried out on **6a**. The geometry of the molecule was based on the structure solved by the X-ray analysis. The results indicated that the carbon atoms at the 6-positions of the dithiafulvenyl groups have larger atomic-orbital coefficients in the HOMO than the α-carbons of the thiophene ring do. Therefore, if the oxidative coupling reaction is governed by the HOMO, it may occur selectively at the 6-positions to give a cyclization product. The HOMO energy level of –8.11 eV is lower than that of TTF (–7.99 eV) and comparable to that of 2-(1,4-dithiafulven-6-yl)thiophene (–8.15 eV), indicating that the conjugation interaction of the two halves of **6** is small due to the twisted structure.

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. These observations are attributed to a metathesis-like fragmentation of the molecular ion (Scheme 3). This fact suggests that there exist some interactions between the two dithiafulvenyl groups in the cation radical state.



SCHEME 3

The electrochemical properties of **6** in solution were studied by cyclic voltammetry. The cyclic voltammogram (CV) of **6b** in benzonitrile is shown in Figure 2, and the redox potentials of **6** are summarized in Table I. The CVs of **6** are typical for

TABLE I Redox potentials of compounds **6**.[a]

Compound	R_1	R_2	E_{pa}	$E(\text{new})_{1/2}$
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).

compounds in which electron transfer is accompanied by chemical reactions.[19] 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 correlated with the first oxidation peaks (E_{pa}) 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_1) 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,[6] suggesting that the molecules consist of the two almost independent dithiafulvenylthiophene units due to the twisted structure.

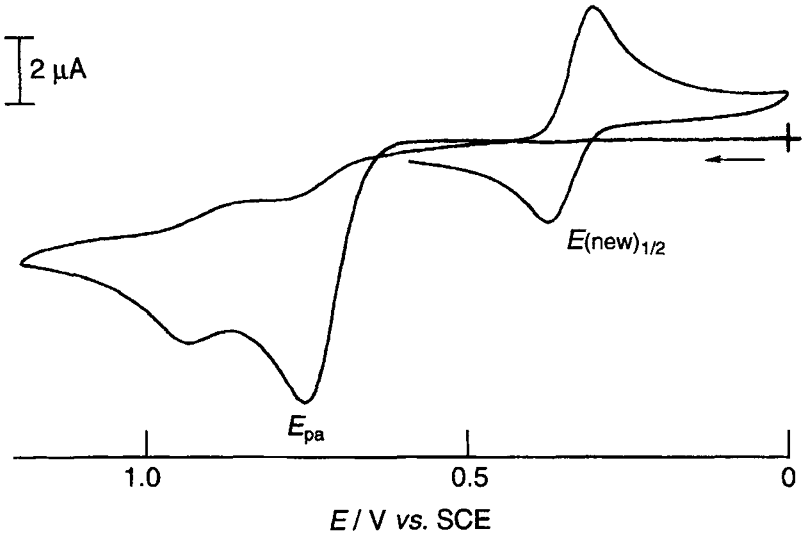
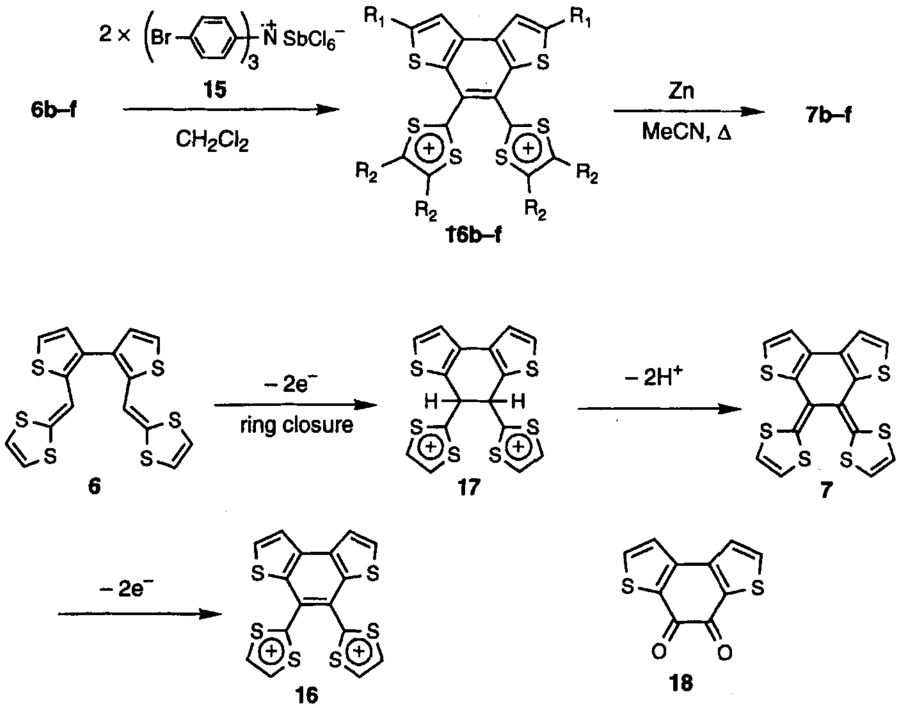


FIGURE 2 Cyclic voltammogram of **6b** in PhCN at a scan rate of 100 mV s^{-1}.

Chemical oxidation of the compounds **6b–f** with 2 equivalents of tris(4-bromophenyl)aminium hexachloroantimonate **15** in dichloromethane at room temperature gave cyclization products **16b–f** as dication salts in high yields (Scheme 4). No products arising from intermolecular reactions were detected. Although the elemental analyses data of the dication salts did not agree with the formula **16**·$2SbCl_6^-$, the structures of the dications were determined on the basis of 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 benzodithiophene unit.



SCHEME 4

X-ray structural analyses of the salts of **16e** were carried out in order to confirm the structure. Prism-like single 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 3). The structure of the dication will be discussed later in this paper. The presence of trivalent chloroantimonate ions ($SbCl_5^{2-}$ and $Sb_2Cl_8^{2-}$) suggests that hexachloroantimonate ion acts as an oxidant in the reaction. The oxidizing ability of $SbCl_6^-$ for organic compounds was reported previously.[20] 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 4).[21]

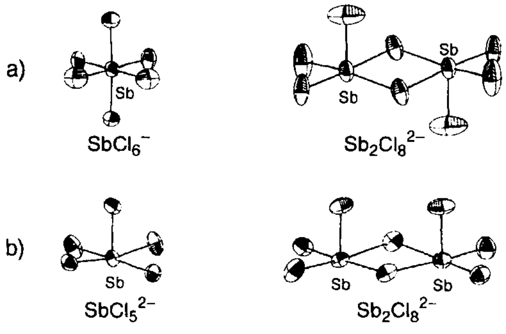


FIGURE 3 X-ray molecular structures of the chloroantimonate ions found in (a) the prism-like and (b) the needle-like single crystals of the dication salt **16e**.

The dications **16** showed reversible redox waves, and the potentials are in complete agreement with $E(\mathrm{new})_{1/2}$ 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. 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 **11** (R_2,R_2 = benzo) with the corresponding quinone **18**[15] resulted in recovery of the starting quinone. This result indicates the usefulness of the cyclization reaction described here to prepare such bis(1,3-dithiole) donors.

The donors **7b–f** are air-stable reddish orange crystals. The UV–VIS spectrum of **7b** in dichloromethane showed the longest absorption maximum at 471 nm, which is red-shifted by 93 nm compared with that of the bithienyl **6b** due to the extension of π-conjugation. The donors showed reversible one-stage two-electron redox waves, and the CVs are nearly identical with those of the dications. The peak widths (40 mV) are a little larger than those for indentical two-electron transfer (28.25 mV), suggesting that a one-electron transfer occurs in two step. The coalescence of the two one-electron processes indicates that the cation radical states are thermodynamically unstable. 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 × 10^{-5} S cm^{-1} on a compressed pellet. The IR absorption of cyano group of the complex observed at 2170 cm^{-1}, indicatig complete charge transfer.

In order to compare the molecular structure of the neutral donor **7e** with that of the dication, the X-ray structural analysis of the donor **7e** was carried out. The single crystal was obtained by recrystallization from chloroform–hexane. Figure 4(a) 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 found in the crystal. The X-ray molecular structure of the dication **16e** found in the prism-like crystal is shown in

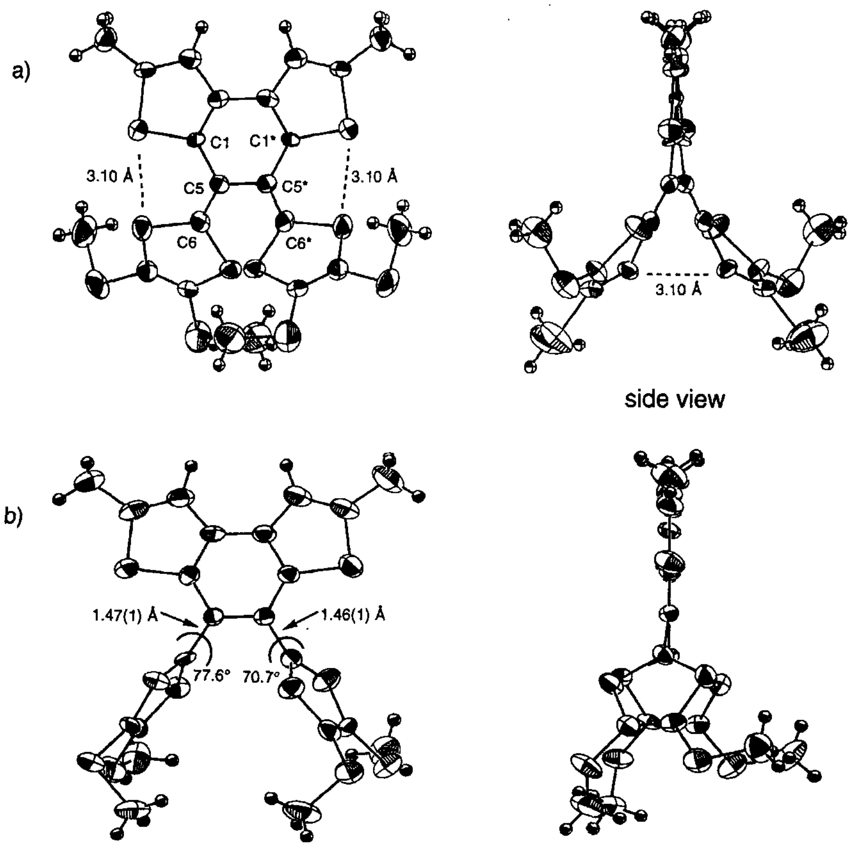


FIGURE 4 X-ray molecular structure of (a) the neutral donor **7e** and (b) the dication **16e**.

Figure 4(b). The π-skeleton of the molecule has an approximate C_2 symmetry. In contrast to the neutral molecule, in the dication the two 1,3-dithiole rings are almost orthogonal to the completely planar tricyclic system. The dihedral angles formed by the dithiole rings and the benzodithiophene moiety are 77.6 and 70.7°. 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. 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.

CONCLUSION

The oxidative intramolecular cyclization of 2,2'-bis(1,4-dithiafulven-6-yl)-3,3'-bithienyls **6** has been investigated. The compounds **6** gave the corresponding cyclization products by both electrochemical and chemical oxidation with high efficiency. The result shows that this cyclization reaction is useful to afford bis(1,3-dithiole)electron donors containg a 1,2-bis(1,3-dithiol-2-ylidene)ethano moiety. The X-ray analyses revealed that new donors **7** undergo a large conformational change upon oxidation.

EXPRERIMENTAL

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 (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were measured on a JEOL-JNM-EX270 spectrometer. EI (70 eV) and high resolution 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. 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. All solutions were purged with argon and retained under the inert atmosphere during the experiment. MNDO-PM3 calculations were performed by using the MOPAC version 6.10 program. 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**[15] (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 an 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, and then with 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, Th-H), 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-bis(methylthio)-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 **11** (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}; ^{1}H NMR (DMSO-d_6) δ = 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) δ = 17.79, 18.01, 107.59, 123.25, 124.12, 127.32, 129.17, 130.37, 131.56, 135.17; UV (CH_2Cl_2) λ_{max} (log ε) 250 (4.35), 378 (4.41) nm; MS *m/z* (rel intensity) 388 (TMTTTF$^+$, 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 a similar procedure. In the case of **6d**, the phosphonium salt **12** was used instead of the 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}; ^{1}H NMR (DMSO-d_6) δ = 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) δ = 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) λ_{max} (log ε) 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}; ^{1}H NMR (DMSO-d_6) δ = 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) δ = 15.06, 105.23, 118.78, 119.23, 127.98, 130.53, 134.14, 134.40, 136.66; UV (CH_2Cl_2) λ_{max} (log ε) 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) λ_{max} (log ε) 255 (4.33), 367 (4.37) nm; MS *m/z* (rel intensity) 388 ($TMTTTF^+$, 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) λ_{max} (log ε) 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 salt **16b** (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) λ_{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 same 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) λ_{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) λ_{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}; ^{1}H NMR (CD_3CN) $\delta = 2.74$ (6H, s, Me), 2.85 (12H, s, SMe), 7.68 (2H, s, Th-H) ; UV (CH_2Cl_2) λ_{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}; ^{1}H 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) λ_{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}; ^{1}H 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) λ_{max} (log ε) 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 same 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}; ^{1}H 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) λ_{max} (log ε) 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) λ_{max} (log ε) 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}; ^1H 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) λ_{max} (log ε) 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}; ^1H NMR (DMSO-d_6) $\delta = 2.56$ (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) λ_{max} (log ε) 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. The mixture was concentrated to *ca.* 1 ml under reduced pressure. The resulting solid was collected by filtration and 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}. Found: C, 58.78; H, 2.90; N, 11.82%. These values correspond to composition of 2 : 3 for **7d** : TCNQ (C, 59.48; H, 2.50; N, 11.56%).

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 **11** (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**[15] (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[22]

The single crystals of the compounds **6e** and **7e** were prepared by recystallization from

TABLE II Details of X-ray structural analyses.

	6e	**7e**	2(**16e**)· $2SbCl_6 \cdot Sb_2Cl_8$	2(**16e**)· $SbCl_5 \cdot Sb_2Cl_8$
formula	$C_{22}H_{22}S_{10}$	$C_{22}H_{20}S_{10}$	$C_{44}H_{40}Cl_{20}$ $S_{20}Sb_4$	$C_{44}H_{40}Cl_{13}$ $S_{20}Sb_3$
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)
α (deg)	90	90	90	99.127(8)
β (deg)	93.45(1)	90	109.91(2)	101.839(7)
γ (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 (g cm^{-1})	1.46	1.53	1.93	1.82
cryst size (mm)	0.40 × 0.15 × 0.10	0.25 × 0.15 × 0.10	0.20 × 0.20 × 0.20	0.45 × 0.10 × 0.02
abs coeff (cm^{-1})	7.78 (Mo-Kα)	8.18 (Mo-Kα)	216.2 (Cu-Kα)	187.6 (Cu-Kα)
$2\theta_{max}$ (deg)	55	55	148.6	148.6
total data measd (3σ)	7095	1687	9065	16155
obsd unique data	1872	697	4755	5535
R	0.048	0.048	0.064	0.067

chloroform–hexane. The single crystals of the dication salts 2(**16e**)·$2SbCl_6$·Sb_2Cl_8 and 2(**16e**)·$SbCl_5$·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. Absorption corrections (Ψ-scan-method) were applied for all cases. Details are summarized in Table II. The structures were solved by the direct method using the SHELXS86 program [for **6e**, **7e**, and 2(**16e**)·$2SbCl_6$·Sb_2Cl_8] or heavy-atom Patterson method using the PATTY program [for 2(**16e**)·$SbCl_5$·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.

DEDICATION

It is our pleasure to dedicate this paper to Professor Fumio Ogura and Professor Yusei Maruyama on the occasion of their retirement celebration.

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21. In the preliminary communication[14], we explained the formation of the dication **16** by dehydogenation from the intermediates **17**. However, taking into accoant the oxidizing ability of $SbCl_6^-$, the mechanism shown in Scheme 4 seems more reasonable.
22. We have deposited atomic coordinates for **6e** and **7e** with the Cambridge Crystallographic Data Centre.