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Effect of Methyl Substitution on Conformation and Molecular Arrangement of BEDT-TTF Derivatives in the Crystalline Environment

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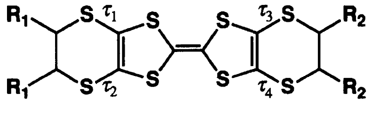
Two methylated bis(ethylenedithio)tetrathiafulvalene (ET) derivatives, $\mathrm{Me_2ET}$ and $\mathrm{Me_4ET}$ were stereoselectively synthesized to examine the effect of methylation on conformations of dihydrodithiin rings and molecular arrangements in the crystalline state. Since the donating ability of $\mathrm{Me_2ET}$ and $\mathrm{Me_4ET}$ are similar to that of ET, the methylated ET derivatives are considered to be appropriate to investigate the "lattice pressure" effect on ET radical salts by changing the volume of donor molecules. The upper limit of an activation energy for the ring inversion of the dimethylated dihydrodithiin in solution was estimated to be $32\ \mathrm{kJ\,mol^{-1}}$ by $^{13}\mathrm{C}$ NMR spectroscopy. The X-ray structure analyses revealed that orientations of methyl groups are fixed to axial in $\mathrm{Me_2ET}$ and to equatorial in $\mathrm{Me_4ET}$, accompanied by the change of molecular stacking. The "volume of a methyl group" was evaluated by comparing the molecular volumes of $\mathrm{Me_2ET}$ and $\mathrm{Me_4ET}$ with that of ET, and the effective volume for the axial methyl group turns out to be 15% larger than that of the equatorial. The solid state $^{13}\mathrm{C}$ NMR (CP/MAS) spectra of ET and its derivatives showed that the chemical shifts of resonance lines reflect the conformations of dihydrodithiin rings in crystals.

A large number of organic metals and superconductors have been synthesized based on cation radical salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (**1**, abbreviated to ET, hereafter).[1] One of the interesting features of ET salts is a "lattice pressure" effect, which is recognized in a series of superconducting ET salts with linear trihalide-like anions ($\mathrm{X^-}$).[2] This concept was proposed to explain influence of the lattice volume on the superconducting transition temperature (T_c) in reference to the density of states at the Fermi level. When an external pressure is applied to the β-type salts of $\mathrm{(ET)_2X}$, the lattice volume shrinks, resulting in the decrease of the T_c. The same tendency is observed when linear anions of different lengths are used as counter anions. Shorter anions leads to shrinkage of the lattice volume, accompanied by the decrease of T_c, while swelling of the lattice volume by replacing with larger anions raises T_c. This tendency can be explained as follows: When the lattice volume is enlarged, the intermolecular distance between ET molecules becomes larger, leading to decrease of intermolecular interaction between donor molecules. A weaker interaction makes the band width narrower, leading to the higher density of states. As a result, the larger lattice volume is considered to increase T_c.[2] Recent success in increasing T_c of ET salts by using large polymeric anions is based on this concept.[3] Therefore it is considered to be reasonable that a larger donor also increases T_c, provided that the larger donor forms a β-type salts with larger intermolecular distance.

We have attempted to increase the volume of ET by introducing substituent groups, instead of changing the size of counter anions. The substituent should satisfy following two conditions: (a) A size of the substituent should be moderate to avoid a drastic change in the packing pattern of ET molecules in crystals. (b) Polarity of the substituent should be small to keep the donating ability of ET similar. A methyl group was chosen as the substituent from the above aspects and two kinds of methylated ET derivatives, *trans*-5,6-dimethyl-ET ($\mathrm{Me_2ET}$, **2**) and *trans*-5,6:*trans*-5'6'-tetramethyl-ET ($\mathrm{Me_4ET}$, **3**) were synthesized (Chart 1).[4] Substitution by methyl groups also introduces asymmetric methine carbons to the donor molecules,[5] which makes preparation of optically active ET donors inevitable. In this paper, we report detailed synthesis of optically pure $\mathrm{Me_2ET}$ and $\mathrm{Me_4ET}$ and influence of methylation on the donating ability and on the crystal structure. The effective size of methylated ET donors is discussed based on the conformation of the donor molecules determined by X-ray crystallographic data. The conformation of dihydrodithiin rings of ET donors is also analyzed in terms of solid state $^{13}\mathrm{C}$ NMR (CP/MAS) spectroscopy. The methodology may be applicable to elucidate conformations of other ET donors whose crystal structures are not available. Besides it is interesting to compare the conformation of the donor in the solid state with that in solution.

Results and Discussion

Synthetic Routes for Methylated ETs. Optically active methyl-substituted ET derivatives, (5*R*, 6*R*)-$\mathrm{Me_2ET}$ ($\mathbf{2}_{\boldsymbol{R}}$) and (5*R*,6*R*,5'*R*,6'*R*)-$\mathrm{Me_4ET}$ ($\mathbf{3}_{\boldsymbol{RR}}$)

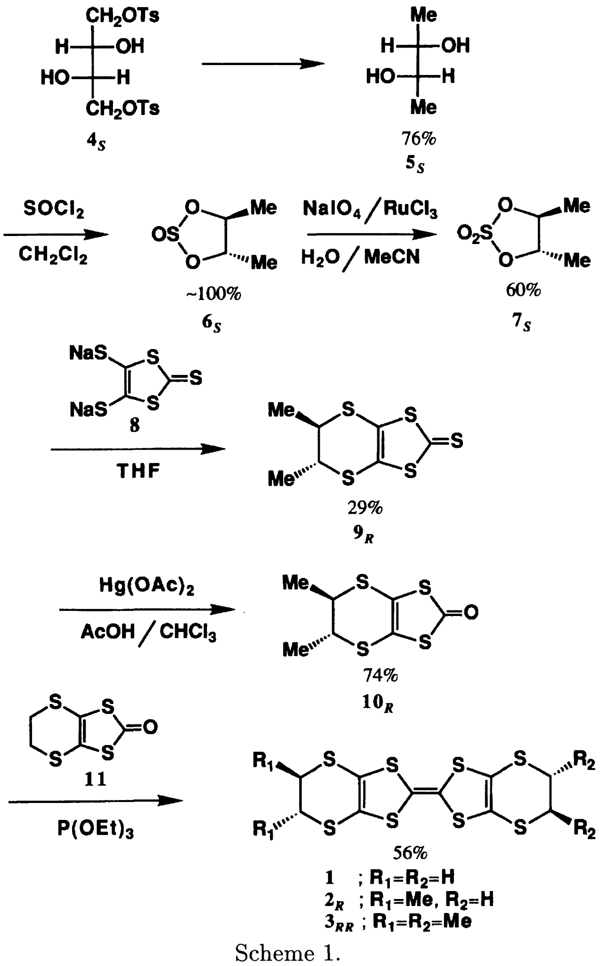


ET (**1**); $\mathrm{R_1=R_2=H}$
$\mathrm{Me_2ET}$ (**2**); $\mathrm{R_1=Me,\ R_2=H}$
$\mathrm{Me_4ET}$ (**3**); $\mathrm{R_1=R_2=Me}$

Chart 1. Structure **1**—**3**.

were synthesized as shown in Scheme 1. The key compound in this synthetic route is L-threitol 1,4-ditosylate ($\mathbf{4}_S$) which is available by hydrolysis of (4*S*,5*S*)-2,2-dimethyl-4,5-bis(*p*-tolylsulfonyloxymethyl)-1,3-dioxolane.[6] The ditosylate was reduced to give optically pure (2*S*,3*S*)-2,3-butanediol ($\mathbf{5}_S$). Chiral cyclic sulfite ($\mathbf{6}_S$) was prepared from the diol $\mathbf{5}_S$ and $SOCl_2$[7] and was oxidized to give sulfate ($\mathbf{7}_S$),[8] which was coupled with disodium 2-thioxo-1,3-dithiole-4,5-dithiolate (**8**)[9] in THF to give dimethylated bicyclic thione ($\mathbf{9}_R$). The thione $\mathbf{9}_R$ was converted to the corresponding ketone ($\mathbf{10}_R$) by mercury(II) acetate. The methylated ketone $\mathbf{10}_R$ and an unsubstituted counterpart **11**[10] were cross-coupled in triethyl phosphite to form a mixture of **1**, $\mathbf{2}_R$, and $\mathbf{3}_{RR}$ in a molar ratio of 1 : 2 : 1. The mixture was separated by gel permeation chromatography. Homocoupling of $\mathbf{10}_R$ also gave $\mathbf{3}_{RR}$ selectively. The racemic mixtures of di- and tetramethylated ETs (**2** and **3**) were synthesized in the same procedure, using a mixture of $\mathbf{9}_R$ and $\mathbf{9}_S$.

Donating Ability of Methylated ET Derivatives Estimated by Cyclic Voltammetry. In an attempt to compare the donating ability of Me_2ET and Me_4ET with that of ET, the redox potentials of ET, Me_2ET, Me_4ET were measured by cyclic voltammetry in CH_2Cl_2 in the presence of n-Bu_4NClO_4 as a supporting electrolyte (Table 1). Comparison of the first half-wave potentials reveals that oxidation potentials of Me_2ET and Me_4ET are similar to that of ET. This result suggests that methyl substitution causes little change on the donating ability of ET.



Scheme 1.

Although the second oxidation waves of ET and Me_2ET are irreversible, Me_4ET gives a reversible second oxidation wave. This difference may be understood in the following way: High solubility of Me_4ET is supposed to increase the solubility of dication, and besides four methyl groups of Me_4ET may sterically retard the rate of the chemical deposition on the surface of the electrode after the second oxidation takes place.

Conformational Inversion of Methylated ET Derivatives in Solution. The methylated ET donors carry 2,3-dihydro-1,4-dithiin rings in the periphery of TTF skeleton. In order to estimate the effective volume of methylated ETs in crystals, it is crucial to analyze conformation of dihydrodithiin rings and orientation of methyl groups. Unfortunately, detailed information on the stable conformation and an activation energy of ring inversion of dihydrodithiins have not been available.[11] Therefore it may be helpful to resort to stable conformations of 2,3-dihydro-1,4-dioxin, the oxa analogue of dihydrodithiin, which has been extensively studied by various means.[12] The stable conformation of dihydrodioxin is known to be a half-chair form and the conformation at the transition state of the ring inversion is a boat form (Fig. 1) with an activation energy of ca. 32 $kJ\,mol^{-1}$ (7.6 $kcal\,mol^{-1}$). It is likely that dihydrodithiins also have a low inversion barrier.

We tried to determine activation energy of the ring inversion of the *trans*-5,6-dihydro-5,6-dimethyl-1,4-dithiin ring of $\mathbf{9}_R$ by means of variable temperature ^{13}C NMR spectroscopy. The NMR spectra of $\mathbf{9}_R$ were measured in CD_2Cl_2 with a temperature range of 25°C to −85°C. Only a slight line broadening was observed on the resonance signals of methyl (δ=22.2) or methine (δ=41.4) carbons caused by the increase of viscosity of the solution, but no sign of coalescence or line splitting was detected even at −85°C. As described later, the orientations of methyl groups are fixed to be diaxial in the crystals of Me_2ET $\mathbf{2}_R$ and diequatorial in the crystals of Me_4ET **3** (Figs. 3, 4, 5, and 6). By adopting the chemi-

Table 1. Redox Potentials of ET (**1**) and Methylated Derivatives (**2** and **3**)[a]

Compound	Potentials/V[b]					
	E_1^{ox}	E_1^{red}	$E_1^{1/2}$	E_2^{ox}	E_2^{red}	$E_2^{1/2}$
ET **1**	0.55	0.46	0.51	0.85	Irr.	—
Me_2ET **2**[c]	0.55	0.39	0.47	0.87	Irr.	—
Me_4ET **3**[c]	0.60	0.44	0.52	0.94	0.78	0.86

a) Measured in CH_2Cl_2 containing 0.1 $mol\,dm^{-3}$ n-Bu_4NClO_4. b) V vs. Ag/AgCl. c) A racemic mixture was used as a sample.

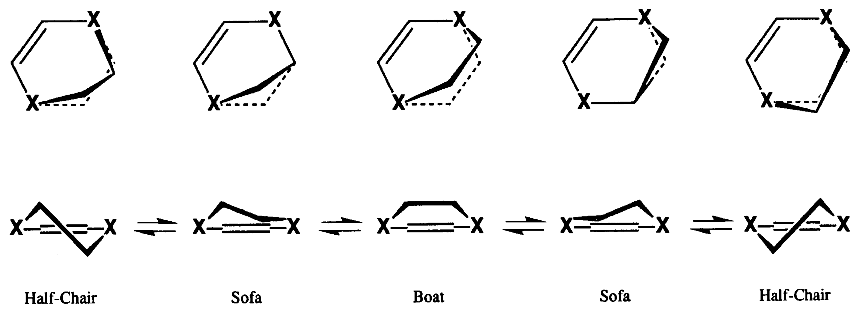


Fig. 1. Schematic representation of conformational inversion of 2,3-dihydro-1,4-dioxin (X=O) and 2,3-dihydro-1,4-dithiin (X=S).

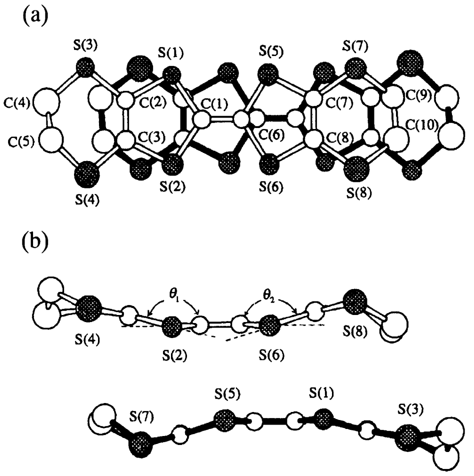


Fig. 2. Dimeric molecular structure of ET **1** in crystal.[13] (a) The mode of molecular overlapping within a dimer. (b) Bent angles of the TTF skeleton and conformations of dihydrodithiin rings.

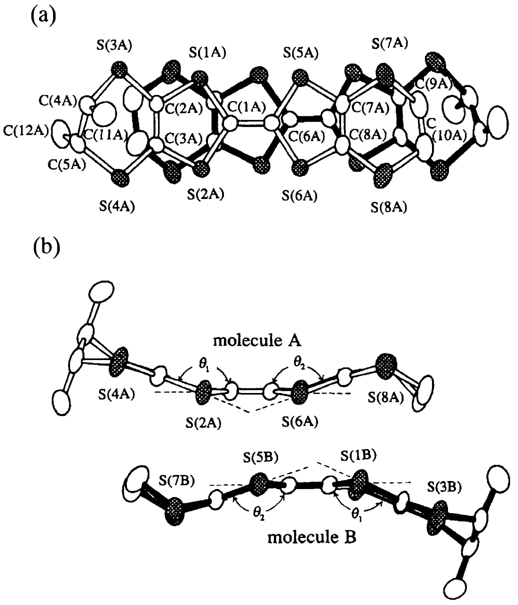


Fig. 3. Dimeric molecular structure of Me$_2$ET $\mathbf{2}_R$ in crystal. (a) The mode of molecular overlapping within a dimer. (b) Bent angles of the TTF skeletons and conformations of dihydrodithiin rings.

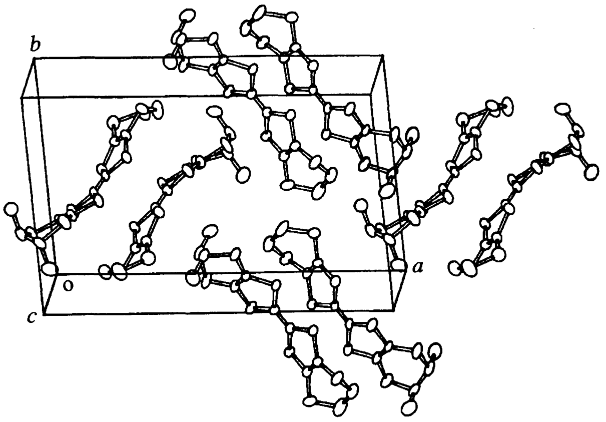


Fig. 4. Molecular packing of Me$_2$ET $\mathbf{2}_R$.

cal shifts of these methyl carbons (δ=25.0 for axial and δ=20.4 for equatorial), the free energy of activation for the ring inversion of $\mathbf{9}_R$ in solution was estimated to be lower than 32 kJ mol^{-1} (7.7 kcal mol^{-1}), assuming that the upper limit of coalescence temperature is −100°C. Thus it is confirmed that dihydrodithiin ring is very flexible in solution.

Molecular and Crystal Structure of ET, Me$_2$ET, and Me$_4$ET. NMR measurement of $\mathbf{9}_R$ in solution revealed that the diaxial and diequatorial isomers are rapidly interconverting each other. The conformational inversion of the dihydrodithiin ring, however, may be suppressed in the crystalline environment to afford one particular conformer predominantly. In this section, we discuss the effect of the methyl substitution on the molecular arrangement in crystals in relation to the conformation of dihydro-1,4-dithiin rings. The conformation of the dihydrodithiin ring is defined by τ, the torsional angle around the bond between sp^2 carbon and sulfur atoms at the ring fusion site (the sign is + for a clockwise torsion and − for a counterclockwise torsion: see Table 5). The three conformations of the dihydrodithiin ring are defined as follows: half-chair; $\tau_1 \cdot \tau_2 > 0$, both $|\tau_1|$ and $|\tau_2|$ exceed 7.5°, sofa; either $|\tau_1|$ or $|\tau_2|$ is below 7.5°, boat; $\tau_1 \cdot \tau_2 < 0$, both $|\tau_1|$ and $|\tau_2|$ exceed 7.5°.

In crystals of ET, two molecules which are correlated

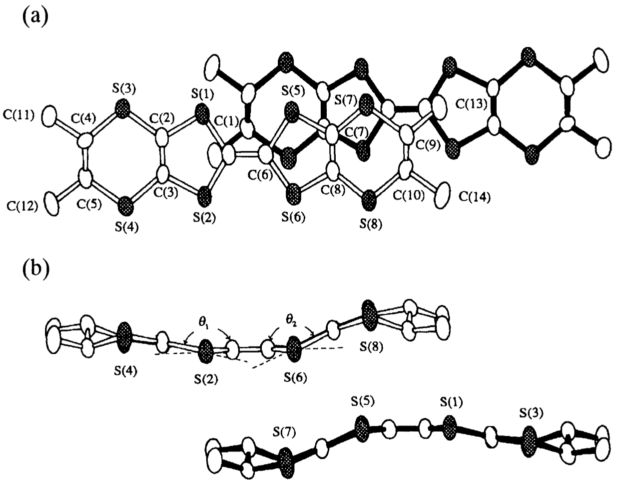


Fig. 5. Dimeric molecular structure of Me_4ET **3** in crystal. (a) The mode of molecular overlapping within a dimer. (b) Bent angles of the TTF skeleton and conformations of dihydrodithiin rings. In (a) and (b), only the rings of 70% occupancy are drawn.

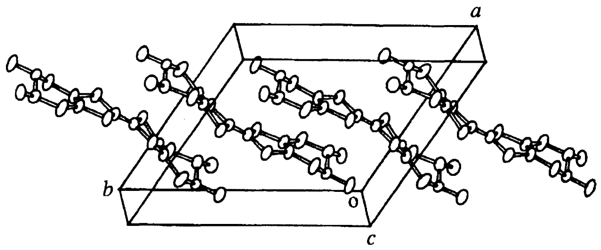


Fig. 6. Molecular packing of Me_4ET **3**. Only the major form of 70% occupancy are drawn.

Table 2. Crystal Data of ET and Methylated Derivatives **1**—**3**

	ET[a] **1**	Me_2ET $\mathbf{2}_R$	Me_4ET **3**
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1$	$P\bar{1}$
a/Å	6.614(11)	20.624(4)	11.604(4)
b/Å	13.985(2)	12.745(3)	14.152(7)
c/Å	16.646(3)	6.473(3)	6.950(1)
α/°	90.00(0)	90.00(0)	94.48(3)
β/°	109.55(2)	97.65(2)	92.77(3)
γ/°	90.00(0)	90.00(0)	125.05(2)
V/Å^3	1449.6	1686.33(8)	925.27(7)

a) Cited from Ref. 13.

by the center of symmetry form a dimer.[13] The overlapping mode within the dimer is a ring-over-bond type (Fig. 2a). The TTF skeleton of ET is bent backward against the counterpart (Fig. 2b). The interplane distance within a dimer is 3.432(3) Å, between the best planes made of the $S_2C{=}CS_2$ group at the center of the TTF skeleton. The dimers are arranged in a herringbone style, being parallel to the *bc* plane. The inside-dihydrodithiin ring (facing to the 1,3-dithiole ring of the counterpart) is of a boat form, which is considered to be energetically disadvantageous in solution (Fig. 2b and Table 5). Although the reason for taking a boat form is not clear,[14] it may be due to preference of a closer packing of dimers, by avoiding repulsion between hydrogen atoms of the inside dihydrodithiin ring and the neighboring dimer. Here we define a molecular volume of the donor by dividing the unit cell volume by the number of molecules within the unit cell. The molecular volume of ET was estimated to be 362.4 Å^3 (1449.6 Å^3/4 molecules).

The crystal structure of Me_2ET $\mathbf{2}_R$ is very similar to that of ET. Namely, two symmetrically independent Me_2ET molecules within the asymmetric unit form a dimer (Fig. 3), and dimers are packed in a herringbone manner (Fig. 4). The overlapping of donors within the dimer is a ring-over-bond type (Fig. 3a), as seen in the case of ET. The unsubstituted dihydrodithiin ring of Me_2ET is located inward of the dimer and is boat-formed (Fig. 3b and Table 5). The methyl-substituted dihydrodithiin ring is located outside and take a half-chair form (Table 5). The methyl groups are fixed in diaxial orientation to fill the space among dimers (Figs. 3 and 4).

The TTF skeleton of Me_2ET is more severely bent than that of ET (Fig. 3b). The averaged angles made of an $S_2C{=}CS_2$ plane at the ring fusion site and a central $S_2C{=}CS_2$ plane of the molecule are $\theta_1=159°$ (outside) and $\theta_2=163°$ (inside), respectively. They are smaller than corresponding angles of ET ($\theta_1=168°$ and $\theta_2=165°$; see Table 6 and Fig. 2b). The intradimer distance between the central $S_2C{=}CS_2$ planes of Me_2ET molecules is 3.416(3) Å. This value is slightly shorter than that of ET, though the size of Me_2ET is larger than ET. The tendency that the bent angle outside is smaller than the inside may be caused by the steric repulsion between the methyl group of the outside dihydrodithiin ring and the unsubstituted ethylene bridge of the counterpart molecule. The smaller intradimer distance may be caused by the severe bending of TTF skeleton in Me_2ET. The "volume of a methyl group" is estimated to be 29.6 Å^3, by subtracting a molecular volume of ET from a molecular volume of Me_2ET (421.6 Å^3; 1686.3 Å^3/4 molecules) and dividing the remainder by the number of methyl groups per molecule.

The structure of Me_4ET **3** is in a sharp contrast to the above two cases. The donors are almost uniformly stacked along the *b* axis, although a slight dimerization is recognized through the bending of TTF skeleton (Figs. 5 and 6). The overlapping mode of donors is different from those of ET and Me_2ET: The upper Me_4ET molecule is shifted not only to the long axis of the molecule, but also to the perpendicular direction (Fig. 5a). In the crystals of ET and Me_2ET, the intradimer overlapping of $S_2C{=}CS_2$ planes is observed at the center of TTF moieties. Whereas, intermolecular

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors of $\mathbf{2}_{\boldsymbol{R}}$

Atom	x	y	z	$B_{\mathrm{eq}}{}^{\mathrm{a)}}/\mathrm{Å}^2$
Molecule A				
S(1A)	6416(1)	176(0)	5726(2)	2.91(3)
S(2A)	5873(1)	−27(1)	1312(2)	3.13(3)
S(3A)	5321(1)	1410(1)	6966(2)	3.19(3)
S(4A)	4667(1)	1195(1)	1665(2)	4.21(4)
S(5A)	7348(1)	−1876(1)	5274(2)	2.80(3)
S(6A)	6822(1)	−2006(1)	825(2)	2.80(3)
S(7A)	7919(1)	−4066(1)	5293(2)	4.03(4)
S(8A)	7286(1)	−4205(1)	383(2)	4.56(4)
C(1A)	6407(2)	−542(3)	3404(6)	2.3(1)
C(2A)	5650(2)	767(3)	4956(6)	2.3(1)
C(3A)	5402(2)	687(4)	2936(6)	2.7(1)
C(4A)	4480(2)	1586(4)	5752(7)	3.4(1)
C(5A)	4453(2)	2109(5)	3616(7)	3.6(1)
C(6A)	6794(2)	−1372(4)	3217(6)	2.4(1)
C(7A)	7444(2)	−3073(4)	3998(7)	2.7(1)
C(8A)	7205(2)	−3142(4)	1968(7)	2.9(1)
C(9A)	8440(3)	−4291(5)	3254(10)	4.8(2)
C(10A)	8119(3)	−4633(6)	1236(11)	5.9(2)
C(11A)	4093(3)	570(6)	5780(10)	4.8(2)
C(12A)	4832(3)	3112(5)	3623(10)	5.2(2)
Molecule B				
S(1B)	8595(1)	−1692(1)	−468(2)	3.26(3)
S(2B)	9173(1)	−1360(1)	3874(2)	3.65(3)
S(3B)	9695(1)	−2888(1)	−1712(2)	4.40(4)
S(4B)	10404(1)	−2501(1)	3515(2)	4.37(4)
S(5B)	7646(1)	352(1)	−155(2)	2.86(3)
S(6B)	8188(1)	590(1)	4266(2)	3.04(3)
S(7B)	7065(1)	2539(1)	−349(2)	3.92(4)
S(8B)	7712(1)	2804(1)	4503(2)	4.36(4)
C(1B)	8608(2)	−932(4)	1773(7)	2.7(1)
C(2B)	9386(2)	−2218(4)	296(7)	2.9(1)
C(3B)	9651(2)	−2062(4)	2259(7)	2.8(1)
C(4B)	10382(3)	−3582(5)	−217(9)	4.1(1)
C(5B)	10806(2)	−2872(5)	1280(8)	3.9(1)
C(6B)	8216(2)	−100(3)	1926(6)	2.3(1)
C(7B)	7541(2)	1579(4)	1005(7)	2.8(1)
C(8B)	7795(2)	1678(4)	3030(7)	2.8(1)
C(9B)	6548(3)	2874(6)	1612(10)	5.4(2)
C(10B)	6866(3)	3175(7)	3723(11)	5.9(2)
C(11B)	10158(4)	−4568(6)	772(14)	6.8(3)
C(12B)	11057(3)	−1926(6)	225(10)	5.2(2)

a) $B_{\mathrm{eq}}=(4/3)\cdot(B_{11}\boldsymbol{a}\cdot\boldsymbol{a}+B_{12}\boldsymbol{a}\cdot\boldsymbol{b}+B_{13}\boldsymbol{a}\cdot\boldsymbol{c}+\cdots)$.

overlapping of $\mathrm{Me_4ET}$ is recognized between $\mathrm{S_2C{=}CS_2}$ planes at the ring fusion site (Figs. 5a and 6). The intradimer distance between $\mathrm{S_2C{=}CS_2}$ planes of ring-fusion site is 3.734(6) Å, which is 0.3 Å longer than intradimer distances of ET and $\mathrm{Me_2ET}$. The interdimer distance of 3.820(5) Å is a little longer than that of the intradimer. Thus the mode of packing and the intermolecular distance suggest that the degree of dimerization of $\mathrm{Me_4ET}$ is much smaller than ET and $\mathrm{Me_2ET}$. The methyl groups of $\mathrm{Me_4ET}$ are fixed to the diequatorial orientation on both sides. From the molecular volume of 462.7 Å^3 (925.3 Å^3/2 molecules), the volume of the methyl group is estimated to be 25.1 Å^3, which is 15% smaller than that for $\mathrm{Me_2ET}$. This tendency means that the effective volume of diequatorial methyl groups is smaller than that of diaxial.

In the racemic crystals of $\mathrm{Me_4ET}$, (*S*,*S*)-form of dihydrodithiin rings is disordered with (*R*,*R*)-form at the outside of the dimer, vice versa on the other side (Fig. 7). When the conformation of one of the molecules in the unit cell (the molecule which atomic parameters are shown in Table 4) is examined closely, the occupation ratio of dihydrodithiin ring outside of the dimer is 70:30 for (*S*,*S*)- and (*R*,*R*)-forms, the ratio being reversed on the other side. The outside dihydrodithiin ring takes a half-chair for (*S*,*S*)- and a sofa for (*R*,*R*)-form, while the inside ring takes a boat conformation regardless of the configuration (Table 5).

The difference of the crystal structure of $\mathrm{Me_4ET}$ compared to those of ET and $\mathrm{Me_2ET}$ can be explained by the following way: $\mathrm{Me_2ET}$ molecules dimerize with methyl groups directing outside in order to avoid steric repulsion, so that two molecules overlap in the same manner as ET. On the other hand, $\mathrm{Me_4ET}$, having methyl groups on both sides, cannot avoid repulsion between the inside methyl groups and the counterpart molecule. The situation makes the ET-like packing unfavorable, and the donor arranges in a quasi-uniform stacking.

The intermolecular sulfur-sulfur contacts, which are commonly found in the crystals of neutral and radical salts of ET,[1,13)] are also observed in the crystals of $\mathrm{Me_2ET}$ and $\mathrm{Me_4ET}$. The short contacts (S–S distance <3.7 Å) exist within the dimer of $\mathrm{Me_2ET}$ (3.689(2) Å

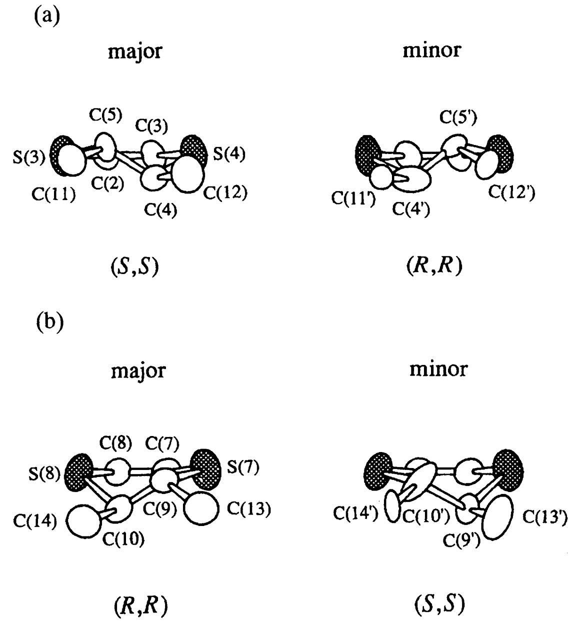


Fig. 7. Dihydrodithiin rings of disordered conformation. (a) The major and minor form of the outside dihydrodithiin ring. (b) The major and minor form of the inside dihydrodithiin ring.

Table 4. Atomic Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors of **3**

Atom	x	y	z	$B_{eq}$$^{a)}$/Å^2
S(1)	5937(2)	3612(2)	7916(3)	4.2(1)
S(2)	6460(2)	4162(1)	3901(3)	4.0(1)
S(3)	6897(3)	5968(2)	9568(3)	5.0(1)
S(4)	7433(3)	6600(2)	4792(3)	4.2(1)
S(5)	4171(1)	839(1)	6314(3)	4.0(1)
S(6)	4780(2)	1417(2)	2340(3)	4.3(1)
S(7)	1698(3)	−1582(2)	5066(3)	5.5(1)
S(8)	2385(3)	−926(2)	421(3)	4.8(1)
C(1)	5675(8)	3082(6)	5460(11)	3.6(3)
C(2)	6555(8)	5030(5)	7468(11)	3.6(3)
C(3)	6786(8)	5284(5)	5679(10)	3.5(3)
C(6)	4968(8)	1947(6)	4786(11)	3.4(3)
C(7)	3021(8)	−251(6)	4384(11)	3.5(3)
C(8)	3272(7)	10(5)	2597(11)	3.4(3)
Major (population 0.70)				
C(4)	7384(11)	7285(8)	8638(13)	3.4(4)
C(5)	8358(11)	7622(8)	6979(16)	3.5(4)
C(9)	933(10)	−2625(8)	2824(16)	3.3(4)
C(10)	1944(11)	−2264(8)	1328(15)	3.7(4)
C(11)	8014(14)	8220(9)	10498(17)	4.3(5)
C(12)	8891(15)	8832(9)	6299(20)	5.5(6)
C(13)	475(15)	−3793(10)	3617(21)	5.3(6)
C(14)	1339(14)	−3194(10)	−628(20)	5.3(6)
Minor (population 0.30)				
C(4′)	8176(27)	7409(20)	8720(48)	4.8(1)
C(5′)	7567(22)	7539(18)	7019(32)	2.7(8)
C(9′)	1656(29)	−2557(20)	3024(30)	3.7(11)
C(10′)	1201(35)	−2390(20)	1115(44)	5.8(13)
C(11′)	8447(24)	8257(17)	10309(38)	3.4(9)
C(12′)	8594(26)	8707(19)	6419(35)	3.6(9)
C(13′)	729(36)	−3724(22)	3493(48)	6.4(13)
C(14′)	981(30)	−3208(17)	−316(29)	3.5(11)

a) $B_{eq}=(4/3)\cdot(B_{11}\boldsymbol{a}\cdot\boldsymbol{a}+B_{12}\boldsymbol{a}\cdot\boldsymbol{b}+B_{13}\boldsymbol{a}\cdot\boldsymbol{c}+\cdots)$.

for S(5A)–S(6B) and 3.552(2) Å for S(5B)–S(6B)) like in the case of ET (3.686(2) Å for S(5)–S(6)), but this kind of contact is not found in Me$_4$ET. While the side-by-side type contacts exist in all three ET derivatives, the number of contacts differ in each case. In the crystal of ET, three short contacts (3.482(2) Å for S(2)–S(3), 3.545(2) Å for S(3)–S(4), and 3.692(2) Å for S(7)–S(8)) are found. Me$_2$ET has four side-by-side contacts (two for each independent molecule; 3.422(2) Å for S(2A)–S(3A), 3.499 Å for S(3A)–S(4A), 3.506(2) Å for S(2B)–S(3B) and 3.624(2) Å for S(3B)–S(4B)). On the other hand, Me$_4$ET has only two contacts (3.600(4) Å for S-(3)–S(4) and 3.691(4) Å for S(7)–S(8)). In addition, "diagonal" type contacts (contacts between molecule A of a dimer and molecule B of the neighboring dimer) are found in ET (3.629(2) Å for S(1)–S(5)) and Me$_2$ET (3.435(2) Å for S(1A)–S(5B) and 3.518(2) Å for S(1B)–S(5A)), this type of contact being absent in Me$_4$ET. Thus a clear relation can be recognized between the volume of the donor molecule and the number of short intermolecular S–S contacts. The larger the donor, the smaller the number of short contacts.

It is concluded that the orientation of methyl groups are fixed in Me$_2$ET or Me$_4$ET and the conformational inversion of the dihydrodithiin rings cannot occur in crystals. The effective volume of methyl groups turns out to depend on the orientation in crystals.

Conformational Analysis of ETs in the Crystalline State. ^{13}C NMR spectra of ET and methylated ET derivatives afford single resonance lines for methyl (δ=21.3—21.4), methylene (δ=29.4), and methine (δ=43.2) carbons in solution, due to a rapid inversion of the dihydrodithiin ring. In crystals, however, the conformation of dihydrodithiin rings and methyl groups are fixed uniquely for each compound, thus the resonance lines inherent for each conformer should be detected.

The solid state ^{13}C NMR spectrum of Me$_2$ET is shown in Fig. 8, and the chemical shift data for ET and its methylated derivatives are summarized in Table 7 together with the data obtained in solution. The methyl groups of Me$_2$ET take a diaxial orientation and the resonance lines of methyl carbons shift to the lower magnetic field of δ=24.2—25.9 compared with the value observed in solution (δ=21.4). In the crystal of Me$_4$ET **3**, the equatorial methyl groups resonate in the similar fields (δ=18.7—22.2) as in solution. The shifts and the site splittings of resonance lines can also be seen for other carbons. For example, methylene carbons of ET resonate at four different positions (δ=29.3, 31.7, 34.1, and 35.5). The chemical shifts of the former two resonance lines are similar to that of the corresponding signal of ET in solution (δ=29.4), while the latter two resonate at lower magnetic fields. The difference may

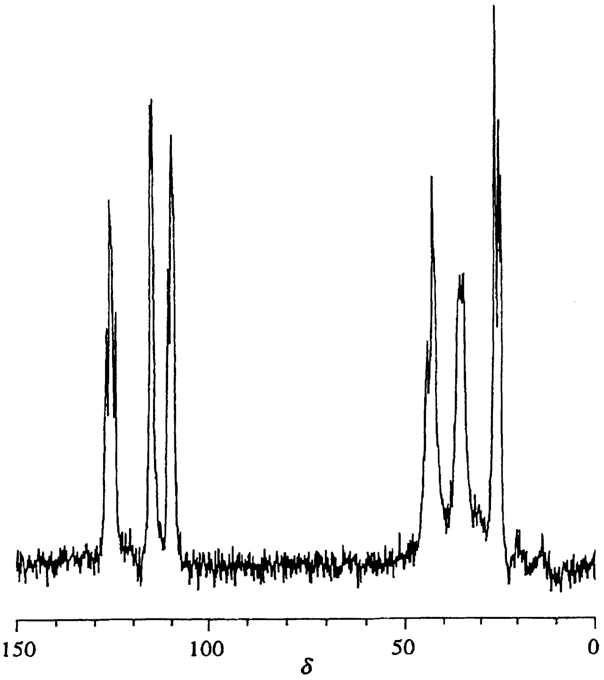


Fig. 8. ^{13}C NMR spectrum of Me$_2$ET **2$_R$** in crystal (CP/MAS, 25°C).

Table 5. Conformations of the Dihydrodithiin Rings of ET (**1**) and Methylated Derivatives ($\mathbf{2}_R$ and **3**)

		Dihedral angles/°[a]					
Compound		τ_1	τ_2	Conformation[b]	τ_3	τ_4	Conformation
ET[c] **1**		13.4(7)	12.1(7)	Half-chair	36.7(6)	−40.6(6)	Boat
Me_2ET $\mathbf{2}_R$	Molecule A	13.9(6)	15.6(5)	Half-chair	44.4(5)	−39.4(6)	Boat
	Molecule B	15.7(6)	13.4(6)	Half-chair	−43.4(5)	41.9(6)	Boat
Me_4ET **3**	Ring A (70%)	8.2(11)	22.5(11)	Half-chair	10.4(10)	−31.0(10)	Boat
	Ring B (30%)	−18.1(14)	−4.7(13)	Sofa	34.3(14)	−7.6(16)	Boat

a) Definition of dihedral angles τ_1—τ_4; τ_1, C(3)–C(2)–S(3)–C(5): τ_2, C(2)–C(3)–S(4)–C(4): τ_3, C(8)–C(7)–S(7)–C(9): τ_4, C(7)–C(8)–S(8)–C(10). b) Definition of conformation: Half-chair; $\tau_1 \cdot \tau_2 > 0$, both $|\tau_1|$ and $|\tau_2|$ exceed 7.5°: Sofa; either $|\tau_1|$ or $|\tau_2|$ is below 7.5°: Boat; $\tau_1 \cdot \tau_2 < 0$, both $|\tau_1|$ and $|\tau_2|$ exceed 7.5°. c) Recalculated using the atomic coordinates from Ref. 13.

come from the different conformation of inside or outside dihydrodithiin rings of the dimeric pair in crystals. Since the outside dihydrodithiin ring takes the half-chair conformation like in solution, the former two lines may be assigned to these methylene carbons. The latter two resonance lines may be assignable to methylene carbons of the boat-formed dihydrodithiin ring, which is located inside of the dimer. This assignment seems to be consistent with the result of Me_2ET, which has the similar conformation of dihydrodithiin rings. The unsubstituted dihydrodithiin ring is placed inside of the dimer and boat-formed. Its methylene carbons resonate at $\delta = 34.5$—36.1, whose chemical shifts are nearly identical to the corresponding inside methylene carbons of ET.

Whereas the methine carbons in the crystal of Me_2ET resonate at $\delta = 42.0$—44.1, almost the same value as in solution. Assuming that the chemical shifts of the methine carbons reflect the conformation of the dihydrodithiin ring as well, the conformation of *trans*-dimethylated dihydrodithiin ring in solution may be concluded to exist as a half-chair form predominantly. In the case of Me_4ET, the methine carbons show several overlapped resonance lines in the range of $\delta = 43$—51 (δ values for only two prominent lines are shown in Table 7). The wide range of the chemical shifts of methine carbons suggests that the dihydrodithiin rings of Me_4ET exist as a variety of conformations in crystals. The interpretation is consistent with the presence of disordered conformation revealed by the X-ray structure analysis.

The olefinic carbons at the center of TTF moiety show little change of chemical shifts ($\delta = 108.9$—111.0) in the crystalline environment compared to those in solution ($\delta = 109.7$). On the other hand, olefinic carbons at the ring fusion sites ($\delta = 111.0$ at the methylated side and 113.2 at the unsubstituted side in solution) resonate at the lower field and split into two groups ($\delta = 112.9$—115.2 and 121.2—126.8) in crystals. These two groups can be assigned to the inside and outside olefinic carbons, respectively. Nevertheless, the assignment of these resonance lines is not unambiguous yet.

Table 6. The Angles Made of $S_2C{=}CS_2$ Planes in ET (**1**) and Methylated Derivatives ($\mathbf{2}_R$ and **3**)

		Bent angles/°[a]	
Compound		θ_1	θ_2
ET[b] **1**		167.74(4)	165.38(4)
Me_2ET $\mathbf{2}_R$	Molecule A	159.91(5)	163.47(5)
	Molecule B	158.69(5)	162.50(5)
Me_4ET **3**		167.76(7)	159.09(7)

a) For definition of θ_1 and θ_2, see Figs. 2b, 3b, and 5b.
b) Cited from Ref. 13.

Conclusion

The synthetic route for some of the optically pure and racemic methyl-substituted ET derivatives has been established. The electrochemical and structural studies proved that introduction of methyl groups to ET makes the molecular volume larger without perturbing its donating ability. The comparison of crystal structures of ET, Me_2ET, and Me_4ET revealed that the orientation of methyl groups is fixed in the crystal. The methyl groups of Me_2ET take the diaxial orientation, which has not yet been reported for similar *trans*-methylated ET derivatives and for their radical ion salts. Chemical shifts of ethylene carbons in solid state ^{13}C NMR (CP/MAS) spectra of ET derivatives reflect the conformations of dihydrodithiin rings. Thus the solid state NMR analysis may be useful in determining the conformation of ET derivatives, of which crystal structures are not available from X-ray crystallographic analyses.

Experimental

General. All the starting materials were commercially available and used without further purificaiton. Ether and THF were distilled over sodium/benzophenone. Dichloromethane and carbon disulfide were distilled over P_2O_5. Pyridine was distilled over KOH. Triethyl phosphite was distilled over sodium under a nitrogen atmosphere. Preparative liquid chromatography was performed by Japan Analytical Industry (JAI) LC-08 with two JAIGEL-1H gel permeation columns connected in series with chloroform as solvent. All the melting points were measured on Laboratory Devices Mel-Temp apparatus and uncorrected. Elementary analyses were performed at the Ibaraki University Instrumental Anal-

Table 7. ^{13}C NMR Resonance Lines of ET (**1**) and Methylated Derivatives (**2**$_R$ and **3**)

Compound		CH$_3$		CH$_2$		CH	
		Inside	Outside	Inside	Outside	Inside	Outside
ET **1**	In soln.			29.4			
	In cryst.			34.1	29.3		
				35.5	31.7		
Me$_2$ET **2**$_R$	In soln.	21.4		29.4		43.2	
	In cryst.	—	24.2	34.5	—	—	42.0
		—	24.8	35.0	—	—	42.6
		—	25.9	35.4	—	—	44.1
				36.1	—		
Me$_4$ET **3**	In soln.	21.4				43.2	
	In cryst.	20.2	18.7			50.3	46.1
		22.2	19.6				

ysis Center and at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. ^{1}H NMR spectra were obtained with JEOL GSH-270 (270 MHz), GSX-400 (400 MHz), and Varian EM390 (90 MHz) spectrometers. ^{13}C NMR spectra were obtained with JEOL GSH-270 (67.8 MHz) and GSX-400 (100.5MHz) spectrometers. Infrared spectra were recorded on Perkin-Elmer 1640 and Hitachi 295 spectrometers. Optical rotations were measured with a JASCO DIP-140 polarimeter.

(*R*,*R*)-Diethyl Tartrate. (*R*,*R*)-Diethyl tartrate was prepared from (*R*,*R*)-tartaric acid according to the method of Seebach et al.,[6a] using Amberlyst 15E (Japan Organo Co. Ltd.) as cation-exchange resin. From 750 g (5.00 mol) of (*R*,*R*)-tartaric acid, 974 g (4.72 mol, 95%) of (*R*,*R*)-diethyl tartrate was obtained; bp 93—95°C/0.3 mmHg (1 mmHg= 133.322 Pa, lit,[6a] 107°C/0.7 mmHg).

(4*S*, 5*S*)-2, 2-Dimethyl-4, 5-bis(*p*-tolylsulfonyloxymethyl)-1,3-dioxolane. The synthesis of this compound was performed referring to the method of Carmack and Kelley.[6b] The yield from (*R*,*R*)-diethyl tartrate was 88%. IR (KBr) 1600 m, 1355 s, 1177 s, 1100 m, 1076 m, 976 s, 862 s, 820 s, 662 m, and 559 m; ^{1}H NMR (CDCl$_3$) δ=1.30 (6H, s, -CH$_3$), 2.46 (6H, s, Ar-CH$_3$), 4.0—4.2 (6H, m, -CH- and -CH$_2$-), 7.37 (4H, d, J=8.4 Hz, Ar-H), and 7.79 (4H, d, J=8.4 Hz, Ar-H).

L-Threitol 1,4-Ditosylate (4$_S$). The dioxolane ring of the above compound was hydrolyzed according to the method of Seebach et al.[6a] The reaction temperature was lowered to 60°C to improve the yield from 70% to 87%. IR (KBr) 1600 m, 1358 s, 1177 s, 1100 m, 1076 m, 961 s, 808 m, 662 m, and 557 m; ^{1}H NMR (CDCl$_3$) δ=1.7 (2H, br, -OH), 2.45 (6H, s, Ar-CH$_3$), 4.08 (4H, d, -CH$_2$-), 4.89 (2H, t, -CH-), 7.38 (4H, d, J=8.4 Hz, Ar-H), and 7.79 (4H, d, J=8.4 Hz, Ar-H).

(2*S*,3*S*)-2,3-Butanediol (5$_S$). In a 1000-ml three-necked flask, 8.90 g (235 mmol) of LiAlH$_4$ was suspended in 500 ml of anhydrous ether and magnetically stirred. To this suspension, 50.0 g (116 mmol) of the ditosylate **4**$_S$ was slowly added. The addition rate was controlled to keep the suspension reflux gently. If necessary, the suspension was cooled to control the reaction temperature. After the addition, the reaction mixture was refluxed for 4 h and kept stirring at room temperature for another 4 h. The excess LiAlH$_4$ was decomposed by adding 9 ml of water, 28 ml of 10% aqueous NaOH, and 23 ml of water successively. The white precipitates were filtered with suction. The filtrate was dried over Na$_2$SO$_4$ and the solvent was distilled off to give crude butanediol **5**$_S$. The precipitate was extracted with ether using a Soxhlet apparatus for 24 h to give a second batch of **5**$_S$. The crude product was combined and distilled under a reduced pressure to give 7.95 g (88.2 mmol, 76%) of colorless diol **5**$_S$: bp 86°C/16 mmHg (lit,[15] 86—87°C/16 mmHg), $[\alpha]_D^{25}$=+13.41° (neat) (lit,[15] $[\alpha]_D^{20}$=+12.85° (neat)).

(4*S*,5*S*)-4,5-Dimethyl-1,3,2-dioxathiolane 2-Oxide (6$_S$). This compound was prepared by the method of Garner and Lucas.[7] From 16.6 g (184 mmol) of butanediol **5**$_S$, 25.1 g (184 mmol, 100%) of sulfite **6**$_S$ was obtained. **6**$_S$; IR (NaCl) 1207 s, 1038 s, 908 s, 838 s, 749 s, 693 s, and 668 s; ^{1}H NMR (CDCl$_3$) δ=1.45 (3H, d, J=6.2 Hz, -CH$_3$), 1.54 (3H, d, J=6.2 Hz, -CH$_3$), 4.09 (1H, dq, J=8.9 and 6.2 Hz, -CH-), and 4.65 (1H, dq, J=8.9 and 6.2 Hz, -CH-).

The racemic mixture of **6**$_S$ and its enantiomer **6**$_R$ were prepared from commercially available 2,3-butanediol (1 : 1 mixture of *erythro* and *threo* isomers) and separation from *cis* isomer of **6** was performed by a fractional distillation under a reduced pressure.

(4*S*,5*S*)-4,5-Dimethyl-1,3,2-dioxathiolane 2,2-Dioxide (7$_S$). The synthesis of this compound was performed referring to the method of Gao and Sharpless.[8] A mixed solvent of 130 ml of water and 90 ml of acetonitrile was placed in a 300-ml flask and 27.7 g (130 mmol) of NaIO$_4$ and 20 mg (ca. 0.1 mmol) of RuCl$_3$ hydrate were dissolved. To this solution 13.6 g (100 mmol) of sulfite **6**$_S$ was slowly added and the solution was stirred at room temperature for 24 h. The reaction mixture was extracted with 800 ml of ether. The extract was washed twice with 200 ml of aqueous NaHCO$_3$ and once with 200 ml of saturated aqueous NaCl, and dried over MgSO$_4$. Ether was evaporated to give 12.0 g of crude **7**$_S$. The crude product was distilled under a reduced pressure (bp 46°C/0.05 mmHg) to give 9.07 g (59.6 mmol, 60%) of colorless sulfate **7**$_S$; bp 46°C/0.05 mmHg (lit, for **7**$_R$; 123.8—124.0°C/10 mmHg[7]); IR (NaCl) 1377 s, 1208 s, 1033 s, 918 s, 824 s; ^{1}H NMR (CDCl$_3$) δ=1.55 (6H, m, -CH$_3$) and 4.71 (2H, m, -CH-).

(5*R*,6*R*)-5,6-Dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione (9$_R$). Under N$_2$ atmosphere, 7.46 g (30.9 mmol) of disodium 2-thioxo-1,3-dithiole-4,5-dithiolate (**8**) (prepared by the method of Varma et al.[10]) was dissolved in 350 ml of anhydrous THF. To this solution, 4.69

g (30.8 mmol) of sulfate $\mathbf{7}_S$ was added and stirred overnight at 40—50°C. The reaction mixture was evaporated and the residue was extracted with $CHCl_3$ using a Soxhlet apparatus. The extract was evaporated to give 2.23 g (8.83 mmol, 29%) of thione $\mathbf{9}_R$ as orange needles. $\mathbf{9}_R$; IR (NaCl) 1701 m, 1490 m, 1457 m, 1437 m, 1378 m, 1063 s, 1036 m, 1008 m, and 903 m; ^{1}H NMR ($CDCl_3$) δ=1.49 (6H, m, $-CH_3$) and 3.29 (2H, m, –CH–).

(5*R*,6*R*)-5,6-Dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-one ($\mathbf{10}_R$). In a mixture of $CHCl_3$ (100 ml) and acetic acid (100 ml), 3.45 g (13.7 mmol) of thione $\mathbf{9}_R$ was dissolved. To this solution, 10.9 g (34.2 mmol) of mercury(II) acetate was added and the solution was stirred for 4 h at room temperature. The precipitate was removed by filtering with suction and the filtrate was successively washed with water (200 ml, twice), 5% aqueous NaOH (200 ml), and water (200 ml, twice). The solution was dried with $MgSO_4$ and $CHCl_3$ was evaporated to give 2.38 g (10.1 mmol, 74%) of pale yellow plates of ketone $\mathbf{10}_R$; $[\alpha]_D^{25}$= +257.2° (*c* 11.82, $CHCl_3$); IR (KBr) 1687 s, 1634 s, 1503 m, 1446 m, 1337 m, 891 s, and 774 s; ^{1}H NMR ($CDCl_3$) δ=1.51 (6H, m, $-CH_3$) and 3.31 (2H, m, –CH–).

Ketone $\mathbf{10}_S$, the enantiomer of $\mathbf{10}_R$, prepared from (2*R*, 3*R*)-2,3-butanediol was shown to have the specific rotation of $[\alpha]_D^{25}$=−245.3° (*c* 11.82, $CHCl_3$). Therefore the reaction of **7** and **8** is found to be stereospecific.

2-(5,6-Dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (ET, 1), (5*R*,6*R*)-2-(5,6-Dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5,6-dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin ((*R*,*R*)-Me_2ET, $\mathbf{2}_R$), and (5*R*,6*R*)-2-[(5*R*,6*R*)-Dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene]-5,6-dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin ((*R*,*R*,*R*,*R*)-Me_4ET, $\mathbf{3}_{RR}$). In a 30-ml round-bottomed flask, 417 mg (2.00 mmol) of 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-one (**11**) (prepared by the method of Varma et al.[10]), 473 mg (2.00 mmol) of $\mathbf{10}_R$ and 1 ml of triethyl phosphite were added. The mixture was heated at 120°C for 2.5 h under a N_2 atmosphere. The red precipitate was filtered and washed with methanol to give 462 mg (1.12 mmol, 56%) of mixture of **1**, $\mathbf{2}_R$, and $\mathbf{3}_{RR}$ (1 : 2 : 1 product ratio). The mixture was separated using GPC and recrystallized from $CHCl_3$. The retention volumes for **1**, $\mathbf{2}_R$, and $\mathbf{3}_{RR}$ were 194 ml, 169 ml, and 153 ml, respectively.

1: Red needles, mp 238—240°C (decomp) (lit, 246—248°C (decomp)[10]); IR (KBr) 1408 s, 1285 s, 1260 m, 1126 m, 998 m, 918 s, 906 s, 890 m, 875 m, and 772 s; ^{1}H NMR ($CDCl_3$) δ=3.30 (8H, s, $-CH_2-$).

$\mathbf{2}_R$: Orange needles, mp 196—200°C (decomp) (lit, for enantiomer of $\mathbf{2}_R$; 212°C (decomp)[5f]); MS (70 eV) *m*/*z* 412 (M^+); Calcd for $C_{12}H_{12}S_8$: C, 34.92; H, 2.93%. Found: C, 35.11; H, 3.03%. IR (KBr) 1438 s, 1376 s, 1293 s, 1202 m, 1124 m, 999 m, 977 m, 910 s, 876 s, 772 s, and 679 m; ^{1}H NMR ($CDCl_3$) δ=1.42 (6H, m, $-CH_3$), 3.20 (2H, m, –CH–), and 3.27 (4H, s, $-CH_2-$).

$\mathbf{3}_{RR}$: Red needles, mp 200—203°C (decomp); MS (70 eV) *m*/*z* 440 (M^+). Calcd for $C_{14}H_{16}S_8$: C, 38.15; H, 3.66%. Found: C, 38.40; H, 3.74%. IR (KBr) 1449 s, 1371 m, 1331 m, 1235 s, 1192 m, 1068 m, 1002 m, 950 m. 889 s, and 770 s; ^{1}H NMR ($CDCl_3$) δ=1.43 (12H, m, $-CH_3$) and 3.17 (4H, m, –CH–).

Cyclic Voltammetry. Cyclic voltammograms were obtained by a three-electrode method with a Hokuto Denko HAB-151 function generator and a Riken Denshi F-35 X-Y plotter. A BAS PTE platinum electrode (1.6 mm diameter) was employed as a working electrode, and a BAS RE-1B Ag/AgCl electrode was employed as a reference electrode. The counter electrode was a platinum wire (0.5 mm diameter). The voltammetric measurements were performed in CH_2Cl_2 in the presence of 0.1 mol dm^{-3} *n*-Bu_4NClO_4. The sweeping rate was 200 mV s^{-1}.

X-Ray Structure Analysis. Orange needles of $\mathbf{2}_R$ were obtained by a slow evaporation of a solution of $\mathbf{2}_R$ in CH_2Cl_2. Single crystals of **3** (prepared from racemic mixture of $\mathbf{14}_R$ and $\mathbf{14}_S$) were obtained as orange needles by a slow evaporation from a solution of **3** in 1,1,2-trichloroethane solution, but for the case of $\mathbf{3}_{RR}$ the same procedure has not been successful in obtaining single crystals of $\mathbf{3}_{RR}$ with an appropriate size and quality. The X-ray diffraction data were collected by a ω-2θ scan on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo *K*α radiation (λ=0.71073 Å) at room temperature and used for structure analyses with no absorbance correction. The structures were solved by a direct method with SAPI-85.[16] Structures were refined for all non-hydrogen atoms with anisotropic temperature factors by a block-diagonal least-squares method using a UNICS-III[17] system. The coordinates of hydrogen atoms were recalculated with the isotropic temperature factor of 4.0 Å^2 at the end of each refinement cycle. In the case of $\mathbf{2}_R$, the *y* coordinate of S(1A) was fixed throughout the refinements. The coordinates of sulfur atoms in the two symmetry-independent molecules of $\mathbf{2}_R$ have a false centrosymmetrical relationship, $x,y,z \rightarrow 0.75-x, 0.07-y, 0.25-z$, and this false symmetry led the lengths of the "symmetrically related" bonds to give unacceptable values. This kind of behavior also appeared in the case of the enantiomer of $\mathbf{13}_R$.[18] The atoms within the unsymmetrical unit were divided into two groups which form two independent molecules, and the coordinates of the atoms belonging to these groups were alternately fixed and refined to give acceptable results. The lattice parameters of $\mathbf{2}_R$ and **3** are shown in Table 2 with the crystal data of **1** by Kobayashi et al.[13] The crystal data are as follows.

$\mathbf{2}_R$: Chemical formula $C_{12}H_{12}S_8$; molecular weight $M=412.76$; $Z=4$; $D_c=1.63$ g cm^{-3}; μ (Mo$K\alpha$)=10.05 cm^{-1}; crystal size 0.40×0.35×0.30 mm; 2θ range 3.0°—55.0°; scan width $\Delta\omega=(1.40+0.14\tan\theta)°$; 3367 independent $|F_o|>3\sigma|F_o|$ reflections were used for refinement; weighting scheme $w=0.8|F_o|$ ($|F_o|<10.0$), $1.0|F_o|$ ($10.0\leqq|F_o|<40.0$), and $1600.0/|F_o|$ ($40.0\leqq|F_o|$); final $R=0.038$ and $R_w=0.040$.

3: Chemical formula $C_{14}H_{16}S_8$; molecular weight $M=440.81$; $Z=2$; $D_c=1.58$ g cm^{-3}; μ (Mo$K\alpha$)=9.21 cm^{-1}; crystal size 0.40×0.25×0.10 mm; 2θ range 3.0 — 45.0°; scan width $\Delta\omega=(1.20+0.50\tan\theta)°$; 2412 independent $|F_o|>3\sigma|F_o|$ reflections were used for refinement; weighting scheme $w=1.0|F_o|$ ($|F_o|<25.0$) and $625.0/|F_o|$ ($25.0\leqq|F_o|$); final $R=0.070$ and $R_w=0.096$. The atomic parameters of $\mathbf{2}_R$ and **3** are shown in Tables 3 and 4.[19]

Solid State NMR Spectroscopy. The ^{13}C solid state NMR spectra were obtained by a CP/MAS method on a JEOL GSH-270 spectrometer (67.8 MHz) at room temperature and were externally referenced to methyl carbons of hexamethylbenzene (δ=17.4). The contact time and the repetition time applied were 1 ms and 10 s, respectively.

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