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2,5-Bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalene and Its Related Unsymmetrical Donors

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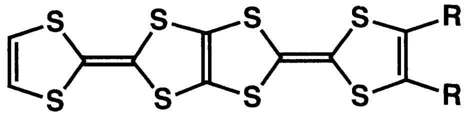
The title compound (**1a**) and its related unsymmetrical derivatives were prepared as new donors for organic conductors, and electrochemical properties and crystal structure of **1a** were investigated. Several charge-transfer complexes and cation radical salts using them showed metallic temperature dependence of conductivity down to ca. 100 K.

Recently considrable attention has been focused on bis- and tris-tetrathiafulvalene (TTF) systems in the search for new organic metals and organic superconductors.1) Such donors have the advantage that on-site Coulombic repulsion in the dicationic states considerably decreases by delocalization of two positive charges over four or six redox-active 1,3-dithioles, while two positive charges must localize in each 1,3-dithiole ring in the case of TTF. On the other hand, the bis-fused TTF, 2,5-bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP, **1a**), has the additional interest that its conducting salts are expected to show two-dimensional conducting property because it has ladder-like array of sulfur atoms suitable for two-dimensional arrangement of the donor molecules. We have recently synthesized its tetrakis(methylthio) derivative (**2**) and a series of bis(methylthio)-substituted unsymmetrical ones, and have obtained several highly conducting cation-radical salts showing metallic temperature dependence of conductivity.2,3) However the parent BDT-TTP (**1a**) still remains as a synthetic target, although it is the most desirable molecule for investigating the nature of BDT-TTP donors. Herein we report the synthesis, structure and electrochemical properties of **1a** and its related unsymmetrical derivatives (**1b**-**e**), and electrical properties of their conducting salts.

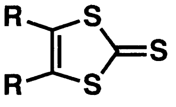
The synthesis of **1a**-**e** was achieved by the similar procedure to **2**. 1,3-Dithiole-2-thione (**3a**) and 4,5-bis(*p*-acetoxybenzylthio)-1,3-dithiol-2-one (**4**) were cross-coupled in neat triethylphosphite at 110 °C to give 4,5-bis(*p*-acetoxybenzylthio)-TTF (**5**) in 47% yield. The reaction of **5** with excess sodium methoxide in dichloromethane-methanol (1 : 3, v/v) at room temperature, followed by treatment with zinc chloride and tetrabutylammonium bromide, and then with an excess of triphosgen in THF at -78 °C afforded TTF fused with 1,3-dithiol-2-one (**6**, 50% yield). By the cross-coupling reaction between **6** and appropriate 1,3-dithiole-2-thiones (**3b**-**e**, 2 equiv.) with a large excess of trimethylphosphite in refluxing toluene were obtained the target **1b**-**e** in 33-82% yields. The parent BDT-TTP (**1a**) was obtained by heating of **1b** with an excess of $LiBr \cdot H_2O$ in hexamethylphosphoramide (HMPA) at 90-120 °C in 87% yield.4)

A single crystal of **1a** was obtained by recrystallization from carbon disulfide - toluene, and its molecular and crystal structures were determined by X-ray diffractional analysis.5) Figure 1 shows its molecular

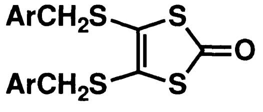


1a-e

a, R = H
b, R = CO_2Me
c, R-R = $-SCH_2S-$
d, R-R = $-S(CH_2)_2S-$
e, R-R = $-S(CH_2)_3S-$
Ar = C_6H_4OAc-*p*



3a-e



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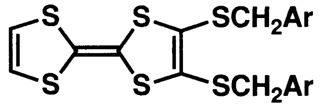

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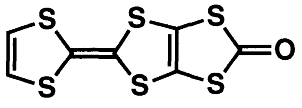

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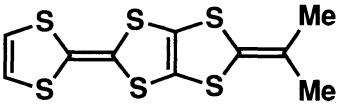

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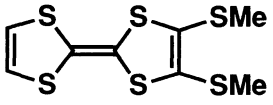

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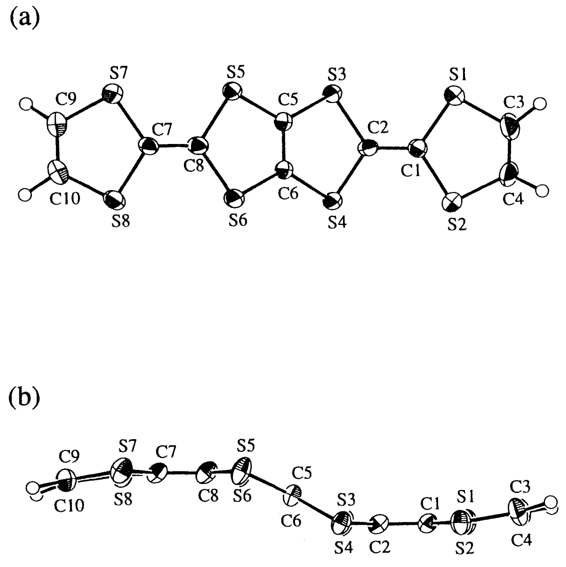

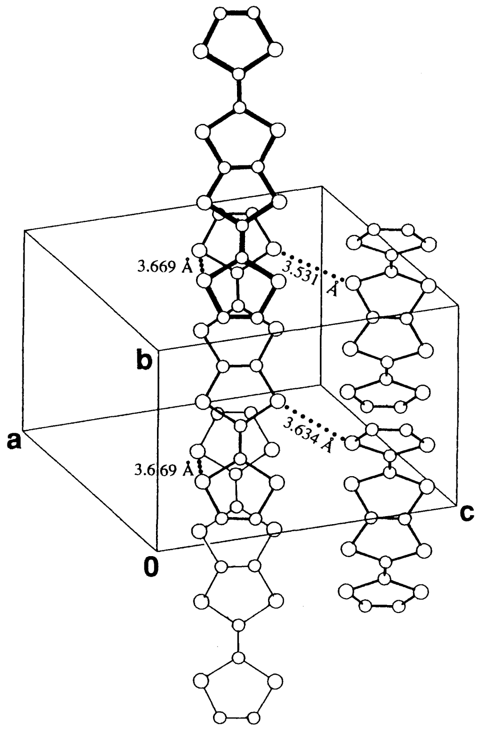

Fig. 1. Molecular structure of **1a** (a) and the side view (b).

Fig. 2. Crystal structure of **1a** showing close intermolecular contacts with dotted lines.

structure. The five-membered rings in the central tetrathiapentalene moiety take an envelope form, C2 and C8 being flapped in the opposite directions to each other. Thus, the molecule adopts a slightly flat chair conformation in contrast with the BDT-TTP skeleton of its tetrakis(methylthio) derivative (**2**) which is almost planar.[2)] The dihedral angle between two planes composed of S1-S2-C1-C2-S3-S4 (S5-S6-C7-C8-S7-S8) and S3-S4-C5-C6-S5-S6 is 27.17° (27.33°). The crystal does not form sheet-like networks as is observed in **2**, but there are several intermolecular S···S contacts less than the sum of the van der Waals radii (3.70 Å) as shown in Fig. 2.

The cyclic voltammogram of **1a** in benzonitrile shows four pairs of redox waves at +0.44, +0.62, +1.05 and +1.13 V (vs. SCE).[6,7)] To be surprisingly the E_1 value of **1a** (+0.44 V) is higher by ca. 0.1 V than that of TTF (+0.35 V), and is comparable to those of 2-isopropylidene-1,3-dithiolo[4,5-*d*]-TTF (**7**, +0.45 V) and 4,5-bis(methylthio)-TTF (**8**, +0.44 V) measured under the similar conditions.[8,9)] This result strongly indicates that fusion of two TTF units is not effective for rise of the donor ability, although π-conjugation mode of **1a** is apparently extended than that of TTF. On the other hand, the $E_2 - E_1$ value (0.18 V) is smaller by 0.15-0.24 V than those of TTF (0.42 V), **7** (0.37 V) and **8** (0.33 V), suggesting significantly decreased on-site Coulombic repulsion in the dicationic state of **1a**.

The tetracyano-*p*-quinodimethane(TCNQ) complexes and cation radical salts using these donors were prepared,[10)] and their electrical conductivities were measured down to ca. 100 K. The results are summarized in Table 1. Most of salts showed high electrical conductivity at room temperature except for $(\mathbf{1c})_2\cdot$TCNQ. Among them single crystals of ClO_4, AsF_6 and I_3 salts of **1a**, and compressed pellets of TCNQ complex and I_3 salt of **1d** revealed metallic temperature dependence of conductivity down to the lowest temperature measured, while **1a**·TCNQ and $(\mathbf{1c})_3\cdot I_3$ showed semiconducting behavior with small activation energy. Further investigations, especially electrical conductivity measurement of these organic metals down to lower temperature and their X-ray diffractional analyses are now in progress.

Table 1. Electrical Properties of TCNQ Complexes and Cation Radical Salts of **1**

Donor	Anion	D : A[a)]	σ_{rt} / S cm^{-1} [b)]	E_a / eV
1a	TCNQ	1 : 1	8[c)]	0.012
	I_3	4 : 1	260[d)]	metallic down to 115 K[e)]
	ClO_4	- [f)]	120[d)]	metallic down to 110 K
	AsF_6	- [f)]	800[d)]	metallic down to 95 K
1c	TCNQ	2 : 1	10^{-8} [c)]	-
	I_3	3 : 1	4[c)]	0.008
1d	TCNQ	1 : 1	66[c)]	metallic down to 100 K
	I_3	3 : 1	77[c)]	metallic down to 100 K

a) Determined based on elemental analyses. b) Room temperature conductivity measured by a four-probe technique. c) Measured on a compressed pellet. d) Measured on a single crystal. e) Cracked at this temperature. f) Not determined because adequate quantity of samples for elemental analyses could not be obtained.

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4) **1a**: reddish brown prism; Mp 179-180 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 6.23 (s); *m/z* 380 (M^+). **1b**: 82% yield; black powder; Mp 191-192 °C (dec); ^{1}H NMR could not be obtained due to insolubility for the common solvents; Mass *m/z* 496 (M^+). **1c**: 61% yield; reddish brown powder; Mp 215-215.5 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 4.70 (s, 2H), 6.10 (s, 2H); Mass *m/z* 456 (M^+). **1d**: 66% yield; reddish brown powder; Mp 210-210.5 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 3.57 (s, 4H), 6.05 (s, 2H); Mass *m/z* 470 (M^+). **1e**: 33% yield; reddish brown needles; Mp 215-215.5 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 2.11 (m, 2H), 2.40 (t, 4H), 5.97 (s, 2H); Mass *m/z* 484 (M^+).

5) Crystal data for **1a**: $C_{10}H_4S_8$, F_w, 380.62, monoclinic, space group $P2_1/c$, a = 12.096 (1), b = 9.026 (1), c = 12.546 (2) Å, β = 96.96 (1)°, V = 1359.6 (3) Å^3, Z = 4, D_{calcd} = 1.859 g cm^{-3}, R = 0.037 for observed 1531 reflections.

6) The E_3 and E_4 values are anodic peak potentials because the third and fourth oxidation processes are electrochemically irreversible.

7) The cyclic voltammetry of **1a** was performed in benzonitrile containing 0.1 mol dm^{-3} Bu_4NClO_4 as an electrolyte by use of Pt working and counter electrodes and a standard SCE reference electrode at 25 °C (scan rate, 1 V s^{-1}). Satisfactory cyclic voltammogams of **1b**-**e** could not be obtained owing to their extreme insolubility for the common solvent.

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9) The compound **8** was prepared by treatment of **5** with an excess of sodium methoxide, followed by the reaction with excess iodemethane in 65% yield.

10) All of TCNQ complexes and I_3 salts of **1c**, **d** were prepared by mixing donors and TCNQ or Bu_4NI_3 in chlorobenzene. On the other hand, single crystals of $(\mathbf{1a})_4 \cdot I_3$ was obtained using diffusion method with Bu_4NI_3 in THF-EtOH (10%, v/v). The preparation of ClO_4 and AsF_6 salts of **1a** was carried out by an electrochemical oxidation at a constant current of 0.5 μA in THF-EtOH.

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