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Preparation, Crystal Structure and Electrical Properties of 2-Cyclopentanylidene-1,3-dithiolo[4,5-*d*]tetrathiafulvalene Derivatives

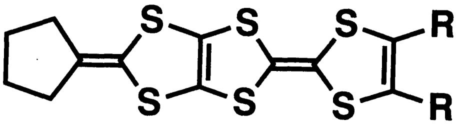
Yohji MISAKI, Kazuya KAWAKAMI, Hiroyuki NISHIKAWA, Hideki FUJIWARA,
Tokio YAMABE,* and Motoo SHIRO†
Department of Hydrocarbon Chemistry and Division of Molecular Engineering,
Kyoto University, Yoshida, Kyoto 606
†Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima 196

The title compounds (**1**) were prepared as the donor components for organic conductors. The molecular and crystal structures of bis(methylthio) derivative were determined by X-ray diffractional analysis. Among charge-transfer complexes and cation radical salts of **1** prepared so far, I_3^- salt of unsubstituted-**1** and IBr_2^- salt of methylenedithio-**1** showed metallic temperature dependence of conductivities.

Since discovery of organic superconductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), the multi-dimensional intermolecular interaction in charge-transfer (CT) complexes and cation radical salts has been regarded as one of the most important factors for design and preparation of organic superconductors.[1)] 1,3-Dithiol-2-ylidene group is one of the most promising substituents to achieve two-dimensional arrangement of donor molecules in the conducting solids.[2)] Very recently we have succeeded in the synthesis of several TTF derivatives condensed with one or two 1,3-dithiol-2-ylidenes, bis(2-methylidene-1,3-dithiolo[4,5-*d*])-TTF and 2-isopropylidene-1,3-dithiolo[4,5-*d*]-TTF (MeDT-TTF).[3),4)] Among them ClO_4^- and IBr_2^- salts of ethylenedithio derivative of MeDT-TTF showed metallic conductive behavior down to 88 K.[4)] In this context modification of alkyl groups at the terminal 1,3-dithiol-2-ylidene in MeDT-TTF is of interest in addition to that of substituents on 4,5-positions of 1,3-dithiole ring in order to search new organic metals based on 1,3-dithiolo[4,5-*d*]-TTF derivatives. In this communication we report preparation, crystal structure of 2-cyclopentanylidene-1,3-dithiolo[4,5-*d*]-TTF (CpDT-TTF, **1**) derivatives, and electrical properties of their CT complexes and cation radical salts.

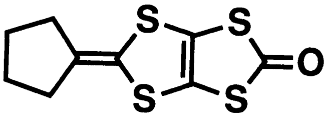
CpDT-TTFs were prepared by the similar method of that of MeDT-TTFs.[4)] The cross coupling reactions of cyclopentanylidene-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one (**2**) and 2 equimolar amount of the appropriate 1,3-dithiole-2-thiones (**3b**-**e**) in neat triethylphosphite gave the target CpDT-TTFs (**1b**-**e**) in 55-64% yields. The unsubstituted derivative of **1** (**1a**) was prepared by heating of **1b** with an excess of $LiBr \cdot H_2O$ in HMPA at 90-100 °C.[5)] All of the cyclic voltammograms of **1** exhibited two pairs of reversible redox waves and one pair of irreversible waves (see Table 1), and their redox potentials were almost equal to those of the corresponding MeDT-TTFs.

Among the donors newly synthesized, a single crystal of **1c** was obtained, and the molecular and crystal structures were determined by X-ray diffractional analysis.[6)] Figure 1 shows the molecular structure of **1c**. The



1a-e

Symbol
a, R = H
b, R = CO_2Me
c, R = SMe
d, R-R = $-SCH_2S-$
e, R-R = $-S(CH_2)_2S-$



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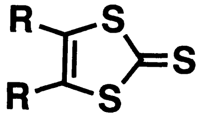

3b-e

Table 1. Redox Potentials of CpDT-TTF Derivatives (**1a-e**)[a)]

Compound	E_1	E_2	E_3[b)]	E_2-E_1
1a	+0.43	+0.74	+1.43	0.31
1b	+0.60	+0.89	+1.47	0.29
1c	+0.50	+0.75	+1.37	0.25
1d	+0.51	+0.74	+1.37	0.23
1e	+0.51	+0.77	+1.38	0.26

a) 0.1 mol dm^{-3} Bu_4NClO_4 in PhCN, Pt electrode, 25 °C, scan rate 50 mV s^{-1}, V vs. SCE.
b) Irreversible step. Anodic peak potentials.

TTF skeleton and 1,3-dithiol-2-ylidene moiety in the **1c** molecule were almost coplanar, but cyclopentane ring had a non-planar half chair conformation. Two methylthio groups were bent nearly perpendicular from the molecular plane toward the same direction. The crystal consists of both stacking columns and sheet-like networks as shown in Fig. 2. The molecules were stacking in a head-to-head manner, and the dihedral angle between adjacent columns was ca. 128°. Several intermolecular S•••S contacts less than the sum of van der Waals radii (3.70 Å) were observed between adjacent molecules in a sheet, whereas there were no short S•••S contacts less than 3.70 Å in the columns.

Several CT complexes with tetracyano-*p*-quinodimethane (TCNQ) and cation radical salts of CpDT-TTFs were prepared.[7)] The electrical properties of them are summarized in Table 2. The electrical conductivities of TCNQ complexes were not so high values of 10^{-2} - 10^{-6} S cm^{-1}. On the other hand, room

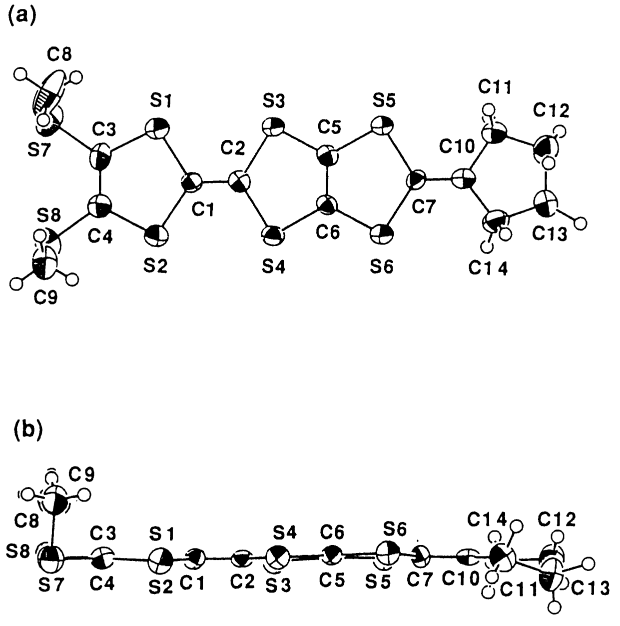

Fig. 1. Molecular structure of **1c** (a) and the side view (b).

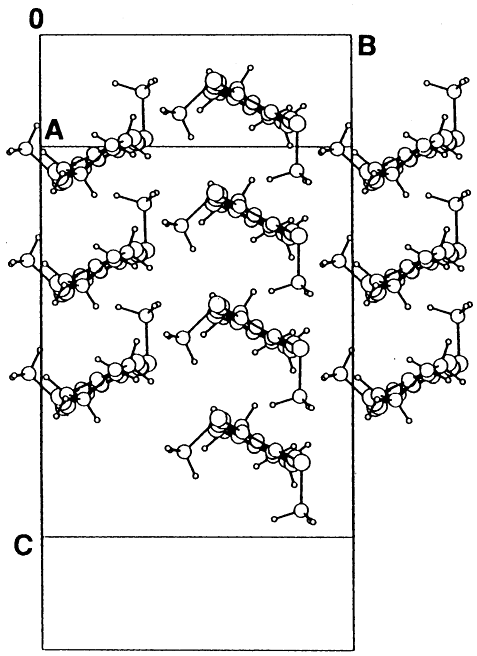

Fig. 2. Crystal structure of **1c**.

Table 2. Electrical Properties of TCNQ Complexes and Cation Radical Salts of **1**

Donor	Acceptor	D : A a)	σ_{rt} / S cm^{-1}	
1a	TCNQ	5 : 2	1.3x10^{-4} b,d)	
1a	I_3^-	7 : 2	8.1 c,e)	metallic down to 89 K
1c	TCNQ	2 : 1	2.9x10^{-6} b,d)	
1c	I_3^-	1 : 1	1.4x10^{-5} b,c)	
1d	IBr_2^-	5 : 3	1.3 c,d)	metallic down to 120 K f)
1e	TCNQ	3 : 2	2.8x10^{-2} b,e)	
1e	I_3^-	5 : 2	2.3x10^{-7} c,e)	

a) Determined based on elemental analyses. b) Measured by two-probe method. c) Measured by four-probe method. d) Measured on a single crystal. e) Measured on a compressed pellet.
f) Cracked at this temperature.

temperature conductivities of $(\mathbf{1a})_7(I_3)_2$ on a compressed pellet and $(\mathbf{1d})_5(IBr_2)_3$ on a single crystal were relatively high values of 8.1 and 1.3 S cm^{-1}, respectively, both of which exhibited metallic temperature dependence of conductivities down to 120 K, and 89 K, respectively. It is noteworthy that $(\mathbf{1a})_7(I_3)_2$ showed such metallic conductive behavior in spite of the measurement was carried out on a compressed pellet. While the room temperature conductivity of the corresponding salt of ethylenedithio-**1** (**1e**) was very low value of 10^{-7} S cm^{-1}. We are currently investigating preparation of the higher quality single crystals suitable for X-ray diffractional analysis.

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5) **1a**: 89% yield; brown microcrystals; Mp 161-162 °C (dec.); ^{1}H NMR (δ in CS_2-$CDCl_3$) 1.66-1.90 (m, 4H), 1.90-2.27 (m, 4H), 6.29 (s, 2H); *m/z* 346 (M$^+$). **1b**: 64% yield; black microcrystals; Mp 214.5 °C (dec); ^{1}H NMR (δ in CS_2-C_6D_6) 1.40-1.71 (m, 4H), 1.80-2.10 (m, 4H), 3.41 (s, 6H); Mass *m/z* 516 (M$^+$). **1c**: 57% yield; orange plates; Mp 172-173 °C (dec); ^{1}H NMR (δ in CS_2-acetone d_6) 1.68–1.92 (m, 4H), 1.98-2.25 (m, 4H), 2.42 (s, 6H); Mass *m/z* 438 (M$^+$). **1d**: 55% yield; reddish brown microcrystals; Mp 215-215.5 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 1.52–1.79 (m, 4H), 1.94-2.14 (m, 4H), 4.50 (s, 2H); Mass *m/z* 422 (M$^+$). **1e**: 58% yield; red crystals; Mp 213-214 °C (dec), ^{1}H NMR (δ in CS_2-C_6D_6) 1.52–1.74 (m, 4H), 1.87-2.10 (m, 4H), 2.73 (s, 4H); Mass *m/z* 436 (M$^+$).
6) Crystal data for **1c**: $C_{14}H_{14}S_8$, F_w, 438.74, monoclinic, space group $P2_1/n$, a =5.1 (1), b = 11.1(2), c = 31.6 (1) Å, β = 92 (2)°, V = 1787 Å^3, Z = 4, D_{calcd} = 1.631 g cm^{-3}, R = 0.059 for 1304 observed reflections.
7) TCNQ complexes and triiodide salts were prepared by mixing donors and TCNQ or tetra-*n*-butylammonium triiodide or iodine in chlorobenzene. On the other hand single crystals of dibromoiodide salt of **1d** were obtained by diffusion method with tetra-*n*-butylammonium dibromoiodide in chlorobenzene-EtOH (10%, v/v). The preparation of the other cation radical salts by the electrochemical methods were also attempted, however, single crystals suitable for measurements of electrical conductivities and X-ray diffractional analysis could not be obtained so far.

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