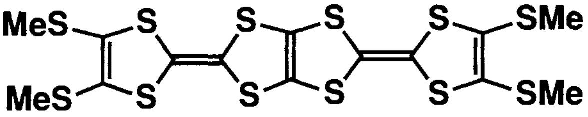
CHEMISTRY LETTERS, pp. 729-732, 1993.

# Bis(methylthio) Substituted Unsymmetrical 2,5-Bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalenes

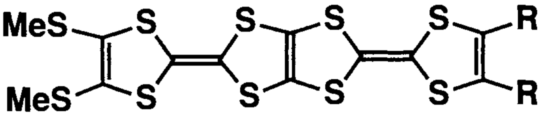
Yohji MISAKI, Hiroyuki NISHIKAWA, Tokio YAMABE,* Takehiko MORI, †* Hiroo INOKUCHI,†
Hatsumi MORI,†† and Shoji TANAKA††
Department of Hydrocarbon Chemistry and Division of Molecular Engineering,
Kyoto University, Yoshida, Kyoto 606
†Institute for Molecular Science, Okazaki 444
††International Superconductivity Technology Center, Mutsuno, Nagoya 456

The title compounds (**2**) were synthesized as the donor components for organic conductors, and preparation and electrical properties of their cation radical salts were investigated. Among various cation radical salts obtained so far, $AsF_6$ salt of ethylenedithio-**2** and $SbF_6$ salt of ethylenedioxy-**2** showed metallic temperature dependence of conductivities down to 0.6 K.

Development of the extended π-electron systems derived from tetrathiafulvalene (TTF) is one of the most important strategies for preparation of new organic conductors.1) Among such donors the bis-fused TTF, 2,5-bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP), is of considerable interests as a promising donor realizing the two-dimensional molecular arrangement in the cation radical salts as well as a higher homologue of TTF.2) Very recently we have succeeded in the synthesis of tetrakis(methylthio) derivative of BDT-TTP (**1**), which gave highly conducting $I_3$ salt showing metallic temperature dependence of conductivity.3) In order to elucidate electrical properties of conducting salts based on BDT-TTP donors, synthesis of various derivatives of BDT-TTP is needed in addition to prepare the other conducting salts of **1**. In particular unsymmetrical derivatives of **1** have the advantages that they have a half unit of **1** producing a metallic cation radical salt, and that the common precursors with **1** can be utilized in their synthesis. Herein we report the synthesis of bis(methylthio) substituted unsymmetrical BDT-TTP derivatives (**2**) and electrical properties of their conducting salts.

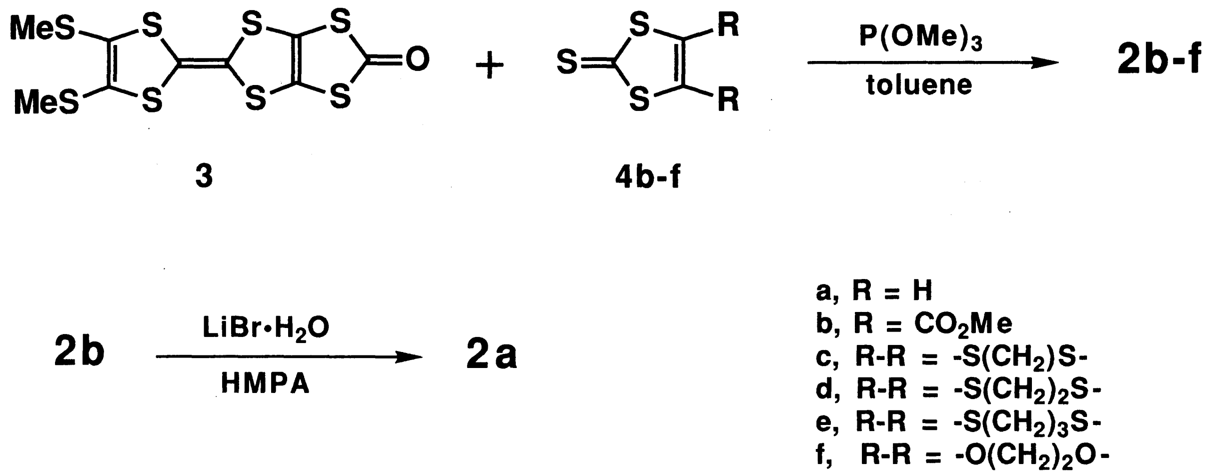


**1**



**2a**, R = H
**2b**, R = $CO_2Me$
**2c**, R-R = $-SCH_2S-$
**2d**, R-R = $-S(CH_2)_2S-$
**2e**, R-R = $-S(CH_2)_3S-$
**2f**, R-R = $-O(CH_2)_2O-$

The synthesis of the new unsymmetrical donors was achieved as shown in Scheme 1. A 1,3-dithiol-2-one fused with bis(methylthio)-TTF (**3**) and 2 equimolar amounts of the appropriate 1,3-dithiole-2-thiones (**4b**-**f**) were allowed to react with a large excess of trimethylphosphite in toluene at 100 °C. The precipitates were filtered off and then were column chromatographed on silica-gel with $CS_2$ as the eluent to afford the target **2b**-**f** in 17-78% yields. The bis(methoxycarbonyl) derivative **2b** was treated with an excess of LiBr·$H_2O$ in hexamethylphosphoramide (HMPA) at 90-110 °C to give bis(methylthio)-BDT-TTP (**2a**) in 54% yield.[4)] The cyclic voltammograms of these donors consisted of four pairs of redox waves corresponding to one-electron transfer processes similarly to that of **1**, although the third and fourth oxidation processes of **2c** could not be clearly observed (see Table 1).



Scheme 1.

Table 1. Redox Potentials of Unsymmetrical BDT-TTP Derivatives (**2**)[a)]

| Compound | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $E_2$-$E_1$ |
|---|---|---|---|---|---|
| **2a** | +0.49 | +0.71 | +0.99 | +1.13[b)] | 0.22 |
| **2b** | +0.58 | +0.81 | +1.12 | +1.31[b)] | 0.23 |
| **2c** | +0.51 | +0.70 | -[c)] | -[c)] | 0.19 |
| **2d** | +0.53 | +0.74 | +1.00 | +1.18[b)] | 0.21 |
| **2e** | +0.51 | +0.73 | +1.02 | +1.20[b)] | 0.23 |
| **2f** | +0.51 | +0.72 | +0.97 | +1.12 | 0.21 |
| **1** | +0.53 | +0.71 | +0.99 | +1.11 | 0.18 |

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 potential. c) The redox wave could not be clearly observed.

Various conducting salts based on the donors newly synthesized were prepared by use of electrochemical crystallization or diffusion method. The electrical conductivities of these salts were measured using four-probe technique on single crystals, and the results are summarized in Table 2. Most of salts showed high electrical conductivities in the order of $10^0$-$10^2$ S $cm^{-1}$. Although many of them showed semiconducting behavior, several salts showed metallic temperature dependence. Among them $AsF_6$ and $HgBr_3$ (needle-like crystal) salts of **2d**, and $SbF_6$ salt of **2f** exhibited typical metallic temperature dependence of resistivities as shown in Fig. 1. Especially it is noted that **2d**•$(AsF_6)_{0.34}$ and **2f**•$(SbF_6)_{0.25}$ revealed metallic conductive behavior down to 0.6 K. The crystal and electronic structures of several cation radical salts of **2d** are to be reported.5)

Table 2. Electrical Properties of Cation Radical Salts and CT Complex of **2** (**2**•$A_x$)

| Donor | Anion | Solvent a) | Form b) | $x$ c) | $\sigma_{rt}$/S $cm^{-1}$ d) | $E_a$ / eV |
|---|---|---|---|---|---|---|
| **2a** | $SbF_6$ | THF | P | 1.0 | 0.1 | 0.06 |
| **2d** | $ClO_4$ | TCE, THF | N | - e) | 13 | 0.06 f) ($T_{MI}$ = 170 K) |
| | $IO_4$ | THF | P | 0.13-0.22(I) g) | 9 | 0.06 |
| | $ReO_4$ | THF | P | 0.35(Re), 0.34(X) | 31 | 0.07 f) |
| | $BF_4$ | TCE | P | - e) | 18 | 0.08 f) |
| | $PF_6$ | TCE, THF | N | 0.27(X) | 45 | 0.10 f) |
| | $SbF_6$ | TCE | P | 0.37(Sb) h) | 25 | 0.008 |
| | $AsF_6$ | DCE | N | 0.34(As) | 18 | metallic down to 0.6 K |
| | $I_3$ | TCE | N | 0.25(I) | 6 i) | 0.04 f) |
| | $AuI_2$ | THF | N | 0.20(Au), 0.23(I), 0.25(X) | 23 | 0.08 f) |
| | $AuBr_2$ | THF | P | 0.20(Au), 0.20(Br) | 45 | 0.03 f) |
| | $AuCl_2$ | THF | P | 0.20(Au) | 23 | 0.05 f) ($T_{MI}$ = 170 K) |
| | $Au(CN)_2$ | TCE | N | 0.38(Au) | 18 | 0.07 |
| | Cl | PhCN | P | - e) | 13 | 0.05 f) ($T_{MI}$ = 260 K) |
| | Br | PhCN | P | 0.34(Br) | 170 | 0.04 f) |
| | $HgBr_3$ | PhCN | P | 0.25(Hg), 0.25(Br) | 5 | 0.10 f) |
| | $HgBr_3$ | PhCN | N | 0.42(Hg), 0.43(Br) | 300 | $T_{MI}$ = 80 K |
| | TCNQ | THF | P | - e) | 52 | 0.06 f) |
| **2f** | $ClO_4$ | THF | N | - e) | 0.2 | 0.09 |
| | $SbF_6$ | THF | P | 0.25(Sb) | 170 | metallic down to 0.6 K |

a) TCE = 1,1,2-trichloroethane; DCE = 1,2-dichloroethane. b) P = plates; N = needles. c) Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. X represents the value determined from the single crystal X-ray structure analysis. d) Room temperature conductivity on a single crystal. e) The contents of light elements such as B, N, and Cl were not reliably determined by EDS. f) Conductivity of these salts shows very weak temperature dependence around room temperature. The activation energy was determined below 150 K. g) Microscopically large scatter was observed in $x$. h) This salt contains the solvent, TCE. i) Measured on a compressed pellet.

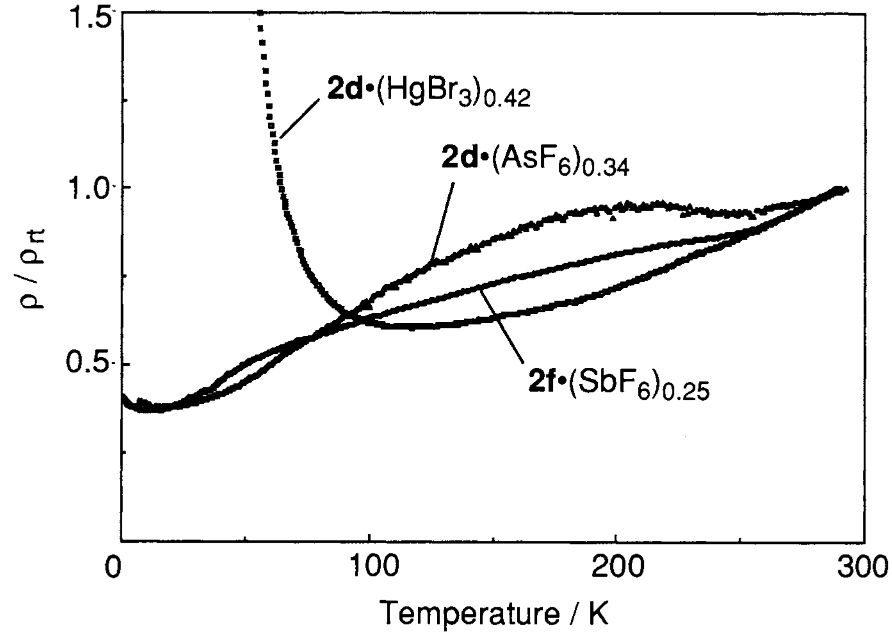


Fig. 1. Temperature dependence of the resistivities of **2d**•$(AsF_6)_{0.34}$, **2d**•$(HgBr_3)_{0.42}$, and **2f**•$(SbF_6)_{0.25}$ (normalized to those at room temperature).

One of the authors (Y. M.) is indebted to the Yazaki Memorial Foundation for Science and Technology for support of this work.

References

1) P. Wolf, H. Naarmann, and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, **27**, 288 (1988); Y. Yamashita, K. Kobayashi, and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, **28**, 1052 (1989); K. Takahashi, T. Nihira, K. Takase, and K. Shibata, *Tetrahedron. Lett.*, **30**, 2091 (1989); Y. Misaki, Y. Matsumura, T. Sugimoto, and Z. Yoshida, *ibid.*, **30**, 5289 (1989); K. Bechgaard, K. Lerstrup, M. Jørgensen, I. Johannsen, J. Christensen, and J. Larsen, *Mol. Cryst. Liq. Cryst.*, **181**, 161 (1990); T. Tachikawa, A. Izuoka, R. Kumai, T. Sugawara, and Y. Sugawara, *Solid State Commun.*, **82**, 19 (1992).

2) R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, **102**, 6652 (1980).

3) Y. Misaki, H. Nishikawa, K. Kawakami, S. Koyanagi, T. Yamabe, and M. Shiro, *Chem. Lett.*, **1992**, 2321.

4) **2a**: brown powder; Mp 163-164.5 °C (dec.); $^1H$ NMR ($\delta$ in $CS_2$-$C_6D_6$) 2.32 (s, 6H), 6.15 (s, 2H); *m/z* 472 ($M^+$). **2b**: 78% yield; reddish brown microcrystals; Mp 202.5-203.5 °C (dec); $^1H$ NMR ($\delta$ in $CS_2$-$C_6D_6$) 2.41 (s, 6H), 3.83 (s, 6H); Mass *m/z* 588 ($M^+$). **2c**: 58% yield; brown powder; Mp 193-194 °C (dec); $^1H$ NMR ($\delta$ in $CS_2$-$C_6D_6$) 2.29 (s, 6H), 4.70 (s, 2H); Mass *m/z* 548 ($M^+$). **2d**: 26% yield; orange microcrystals; Mp 200.5-202 °C (dec.); $^1H$ NMR ($\delta$ in $CS_2$-$C_6D_6$) 2.31 (s, 6H), 3.10 (s, 4H); Mass *m/z* 562 ($M^+$). **2e**: 25% yield; orange powder; Mp 212-213 °C (dec.); $^1H$ NMR ($\delta$ in $CS_2$-$C_6D_6$) 2.24 (m, 2H), 2.30 (s, 6H), 2.52 (t, 4H); Mass *m/z* 576 ($M^+$). **2f**: 17% yield; red microcrystals; Mp 187.5-189 °C (dec.); $^1H$ NMR ($\delta$ in $CS_2$-$C_6D_6$) 2.31 (s, 6H), 4.02 (s, 4H); Mass *m/z* 530 ($M^+$).

5) T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori, and S. Tanaka, *Chem. Lett.*, **1993**, the following paper.

(Received January 29, 1993)