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Ethylenedioxy Substituted 2,5-Bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalenes and Their Conducting Salts

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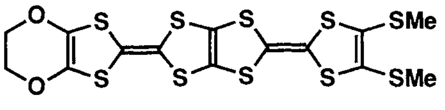
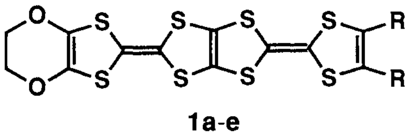
The title compounds were prepared and their electrochemical properties were investigated. Several cation radical salts composed of them showed metallic conductive behavior down to 0.6 K. The X-ray crystal structure of AsF_6 salt of ethylenedithio derivative, $(EOET\text{-}TTP)_3AsF_6$, revealed that the donors have "κ-type" arrangement in the conducting sheet.

2,5-Bis(1',3'-dithiol-2'-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) and its derivatives are of interest as donor components of organic metals, because several BDT-TTPs known so far gave highly conducting cation radical salts showing metallic temperature dependence of conductivities.[1-3] In particular, TMEO-TTP (depicted as below) gave many metallic cation radical salts which are stable down to 0.6 K.[2,4] In this context, preparation and properties of conducting salts based on ethylenedioxy substituted BDT-TTPs are attractive. In this communication we report the preparation of a series of ethylenedioxy substituted BDT-TTP derivatives (**1a**-**e**). Furthermore electrical properties of their conducting salts and crystal structure of AsF_6 salt of ethylenedithio derivative (EOET-TTP, **1c**) are described.

A similar synthetic methodology to that of BDT-TTPs described previously was applied to the synthesis of **1a**-**e**. Thus, the $P(OEt)_3$-mediated cross-coupling reaction of 4,5-ethylenedioxy-1,3-dithiole-2-thione (**2a**) and 4,5-bis(*p*-acetoxy-benzylthio)-1,3-dithiol-2-one (**3**) at 110 °C gave the corresponding unsymmetrical TTF (**4**) in 51% yield. The acetoxybenzyl groups of **4** were removed by treatment with an excess of NaOMe in CH_2Cl_2-

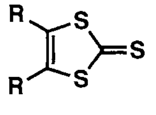


TMEO-TTP

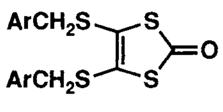


1a-**e**

a, R-R = $-O(CH_2)_2O-$
b, R-R = $-SCH_2S-$
c, R-R = $-S(CH_2)_2S-$
d, R = CO_2Me
e, R = H
Ar = C_6H_4OAc-*p*



2a-**d**



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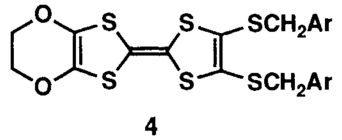

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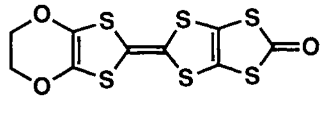

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MeOH (1 : 3, v/v) and then with $ZnCl_2$ at room temperature. After addition of Bu_4NBr, the reaction mixture was treated with excess triphosgen in THF at -78 °C to afford sparingly soluble ethylenedioxy-TTF fused with 1,3-dithiol-2-one (**5**, 66% yield). The compounds **5** and **2a-d** were cross-coupled with a large excess of $P(OMe)_3$ in toluene at 100 °C to give the target molecules **1a-d** in 20-65% yields. On the other hand, **1e** was obtained in 55% yield by heating of **1d** with an excess of $LiBr{\cdot}H_2O$ in HMPA at 90-120 °C.[5)] All compounds are much less soluble than BEDT-TTF. So satisfactory cyclic voltammograms were obtained only for **1a** and **b**, and their redox potentials in benzonitrile are as follows; **1a**: +0.47, +0.62, +0.99 and +1.14 (V vs. SCE), **1b**: +0.54, +0.79, +1.12, +1.13V.[6)] The E_1 value of **1e** is slightly higher than that of the parent BDT-TTP (+0.44 V).

Preparation of the tetracyano-*p*-quinodimethane (TCNQ) complexes and the I_3 salts were carried out by mixing of the donors and TCNQ or Bu_4NI_3 in hot chlorobenzene. The other cation radical salts were prepared by electrochemical oxidation with Bu_4NX ($X = ClO_4$, PF_6, SbF_6 and AsF_6) at a constant current of 0.4-1 μA in 1,1,2-trichloroethane (TCE) or THF. The electrical properties are summarized in Table 1. The ClO_4, PF_6 and AsF_6 salts of EOET-TTP (**1c**) were obtained as single crystals, and show high electrical conductivity at room temperature: 50 S cm^{-1} for the ClO_4 salt, 400 S cm^{-1} for the PF_6 salt and 600 S cm^{-1} for the AsF_6 salt.[7)] They exhibit metallic conducting behavior down to 0.6 K. No superconductivity was observed for all cases. Electrical conductivity of other salts was measured on compressed pellets. Their room temperature conductivity is 0.4 - 15 S cm^{-1}. Most of them shows semiconducting behavior with small activation energy (0.010 - 0.045 eV), whereas $(\mathbf{2e})_3I_3$ is metallic down to 4.2 K.[7)]

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	3 : 1	4	0.025
	I_3	3 : 1	9	0.029
1b	TCNQ	3 : 2	0.6	0.045
	I_3	5 : 2	0.4	0.040
1c	TCNQ	3 : 1	0.5	0.038
(EOET-TTP)	I_3	5 : 2	0.5	0.027
	ClO_4	-[c)]	50[d)]	metallic down to 0.6 K
	PF_6	-[c)]	400[d)]	metallic down to 0.6 K
	AsF_6	3 : 1[e)]	600[d)]	metallic down to 0.6 K
1e	TCNQ	3 : 2	15	0.010
	I_3	3 : 1	8	metallic down to 4.2 K
	PF_6	-[c)]	1.5	0.026
	SbF_6	3 : 2	0.4	0.034

a) The ratio of donor and acceptor was determined based on elemental analyses for TCNQ complexes, and on the energy dispersion spectroscopy (EDS) from the ratio of S and I (Sb) for I_3 (SbF_6) salts. b) Room temperature conductivity measured by a four-probe technique on a compressed pellet. c) The contents of light elements such as P and Cl were not reliably determined by EDS. d) Measured on a single crystal. e) Determined by X-ray structure analysis.

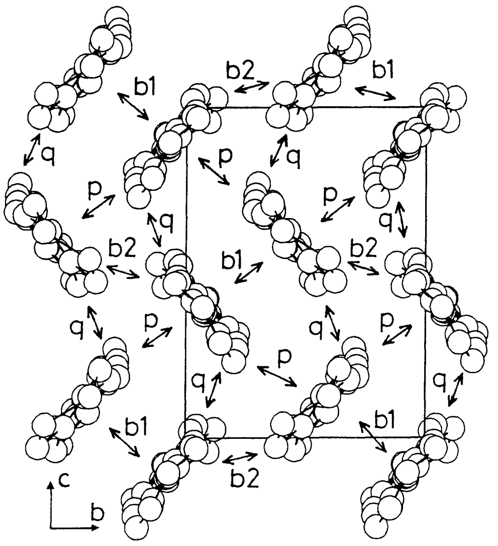
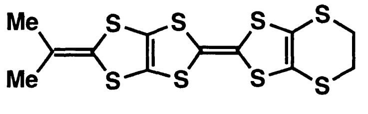


Fig. 1. Donor arrangement of $(EOET\text{-}TTP)_3AsF_6$ viewed along the molecular long axis.

Table 2. Ratio of the lattice constants, *c*/*b* in the κ-salts

$(BEDT\text{-}TTF)_2I_3$	1.516
$(BEDT\text{-}TTF)_2Cu(NCS)_2$	1.555
$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$	1.516
$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$	1.530
$(MeDTET)_3PF_6TCE_x$	1.406
$(EOET\text{-}TTP)_3AsF_6$	1.401



MeDTET

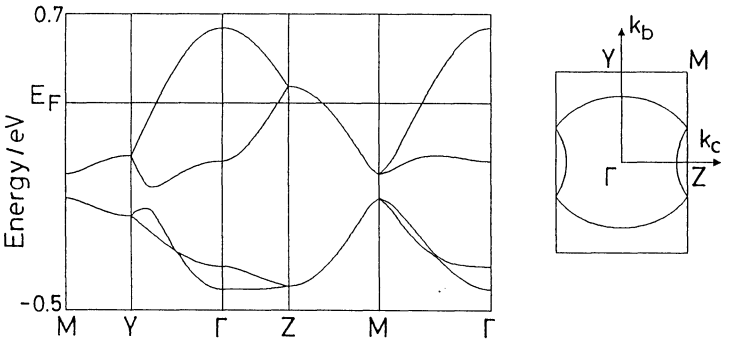


Fig. 2. Energy band structure and Fermi surface of $(EOET\text{-}TTP)_3AsF_6$. The intermolecular integrals are b1=21.0, b2=16.1, p=7.9, q=-6.6 x 10^{-3}.

The crystal structure of the AsF_6 salt is depicted in Fig. 1.[8,9] The donors form conducting sheet along the bc plane. Population analysis shows the composition to be nearly 3:1. The donor arrangement is so called "κ-type";[10,11] this is the first κ-type structure in the BDT-TTP series. The donor molecules dimerize in a head-to-tail manner. It is noteworthy that the present salt has a composition 3:1; all other already known κ-type salts have 2:1 composition, but $(MeDTET)_3PF_6$ (MeDTET = 2-isopropylidene-1,3-dithiolo[4,5-*d*]ethylenedithio-TTF), which we have reported very recently,[11] has an exceptional 3:1 composition. The present salt is the second example of the κ salt having a composition other than 2:1. As shown in Table 2, the ratio of the lattice constants *c*/*b* in the conducting plane is 1.5 - 1.55 in the BEDT-TTF salts, but about 1.4 in the MeDTET and the present EOET-TTP salts. This ratio is probably related to the difference of the composition. The dimer (two donors connected by the b1 interaction in Fig. 1) has ring-over-bond type overlap. The oxygen atoms are disordered on both sides of the donor. The energy band structure and the Fermi surface (Fig. 2) are similar to those of the other κ salts. The Fermi surface is degenerated on the ZM zone boundary.

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5) **1a**: reddish brown powder; Mp 214 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 4.03 (s); Mass *m/z* 496 (M^+) (M^+). **1b**: 40% yield; geenish brown powder; Mp 188.5-189 °C (dec); ^{1}H NMR (δ in CS_2-C_6D_6) 3.99 (s, 4H), 4.69 (s, 2H); Mass *m/z* 514 (M^+). **1c**: 50% yield; reddish brown powder; Mp 188-190 °C (dec); ^{1}H NMR (δ in CS_2-C_6D_6) 3.14 (s, 4H), 4.08 (s, 4H); Mass *m/z* 528 (M^+). **1d**: 65% yield; dark brown powder; Mp 200-202 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 3.67 (s, 6H), 4.04 (s, 4H); Mass *m/z* 554 (M^+). **1e**: 55% yield; dark red plates; Mp 234.5-237 °C (dec.); ^{1}H NMR (δ in CS_2-C_6D_6) 4.08 (s, 4H), 6.17 (s, 2H); Mass *m/z* 438 (M^+).

6) The cyclic voltammetry was performed in benzonitrile containing 0.1 M 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, 50 mV/s). The E_3 and E_4 values are anodic peak potentials, since cathodic peak potentials could not be observed owing to electrochemical irreversibility.

7) The resistivity of AsF_6 salt increases below 20 K. This increase is, however, not large, and the resistivity seems to go to a finite value at 0 K. In addition the temperature where the resistance increases changed from sample to sample. Therefore we do not think that this resistance increase is related to some intrinsic phase transition, but possibly due to crystal perfection. The other metallic salts are also metallic at room temperature, but their resistances start to increase at higher temperature. We again think this increase to be poorer quality of samples.

8) Crystal data of $(EOET\text{-}TTP)_3AsF_6$: monoclinic, space group C2/c, a = 46.74(2), b = 8.013(3), c = 11.225(7) Å, β = 98.96(4)°, V = 4153(3) Å^3. Since the quality of the crystals was very poor, only preliminary structure analysis was attempted. Intensities were measured by the ω scan technique on a Rigaku automated four-circle diffractometer AFC-5R with graphite monochromatized Mo$K\alpha$ radiation ($2\theta<55°$). Though the quality of the data is very poor (R = 0.168 for independent 934 reflections), the final difference Fourier synthesis shows that the structure is essentially correct.

9) X-ray photography suggested that the PF_6 and the AsF_6 salts have the same structure.

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