Synthesis of Dimethyl-substituted BDH-TTP Derivative DMDH-TTP as a Diastereomeric Mixture, and the Formation of Metallic Salts Involving Only *meso*-DMDH-TTP

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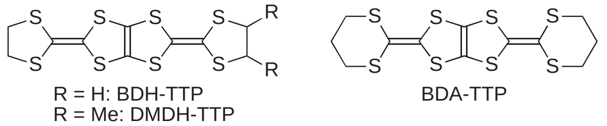
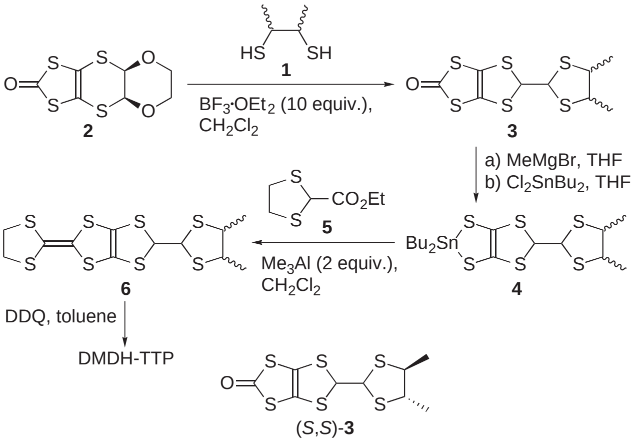
The synthesis of DMDH-TTP [2-(4,5-dimethyl-1,3-dithiolan-2-ylidene)-5-(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene] as a mixture of meso- and trans-forms has been accomplished, electrocrystallization of which with *n*-Bu_4NX ($X = AsF_6$ and BF_4) provides single crystals of the metallic AsF_6 and BF_4 salts incorporating only *meso*-DMDH-TTP as donor components.

We have reported that a series of organic superconductors are obtainable from the π-electron donor BDA-TTP [2,5-bis-(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene] (Scheme 1).[1] The mo-lecular design of BDA-TTP is based on the destabilization of the stable metallic state that occurs with the use of BDH-TTP [2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene] by extending the σ-framework.[1] Indeed, compared to rigid outer dithiolane rings of BDH-TTP, BDA-TTP has more expanded outer dithiane rings capable of adopting chair conformations. Accordingly, the replacement of the outer rings in BDH-TTP with dithiane rings would be regarded as an increase of steric bulk on the periphery of BDH-TTP. An alternative synthetic strategy in this regard is the attachment of alkyl substituents to the outer dithiolane ring of BDH-TTP. This strategy coupled with the reports that *meso*-DMBEDT-TTF [1,2-dimethylethylenedithio(ethylenedithio)tetrathiafulvalene] as well as (*S*,*S*)-DMBEDT-TTF give rise to superconducting salts under pressure[2] encouraged the study of the dimethyl-substitued BDH-TTP donor DMDH-TTP. We report here on the synthesis of DMDH-TTP as a diastereomeric mixture of a meso-form and a trans-form (which comprises an enantiomeric pair) and also on the conducting and structural properties of the AsF_6 and BF_4 salts containing only *meso*-DMDH-TTP as donor components.



Scheme 1.

The synthetic route to DMDH-TTP (Scheme 2) is essentially the same as that to BDH-TTP except for the use of commercially available 2,3-butanedithiol **1** as a mixture of meso-, (*R*,*R*)-, and (*S*,*S*)-forms instead of 1,2-ethanedithiol.[1a,1c] Thus, the $BF_3 \cdot OEt_2$-mediated reaction of the dioxane-fused oxone **2** with **1** gave oxone **3** with a dimethyl-substituted dithiolane ring in 94% yield as a 3.4:1 mixture of cis- and trans-dimethyl isomers. The ratio was determined by ^1H NMR integration for the methyl methine proton, and we were able to ascertain that the minor product corresponds to the trans-isomer by comparing with the ^1H NMR spectrum of (*S*,*S*)-**3** (Scheme 2) obtained via a similar $BF_3 \cdot OEt_2$-meadiated reaction of **2** with (*S*,*S*)-**1**.[3] Conversion of **3** into tin dithiolate **4** followed by the Me_3Al-promoted reaction with ester **5** led to the coupling product **6** (40% overall yield). Finally, DDQ oxidation of **6** in refluxing toluene furnished, after purification by silica gel chromatography followed by recrystallization, DMDH-TTP in 63–70% yields. The ^1H NMR spectrum showed two sets of signals to the methyl and methine protons,[4] and the intensity ratios for the two methine protons were 3.7:1–4.7:1. Taking into account the cis-to-trans ratio of **3**, it is most likely that the major isomer is *meso*-DMDH-TTP. A comparison of the oxidation potentials of the resulting DMDH-TTP [$E_1 = 0.54$, $E_2 = 0.81$, $E_3 = 1.36$, and ΔE $(E_2 - E_1) = 0.27$ V (vs SCE)] with those of BDH-TTP [$E_1 = 0.56$, $E_2 = 0.85$, $E_3 = 1.24$, E_4 (irreversible) $= 1.44$, and ΔE $(E_2 - E_1) = 0.29$ V], measured by cyclic voltammetry under identical conditions,[1c] indicates that the attachment of two methyl groups, acting as electron-donating substituents, causes a slight enhancement in the donor ability and a slight decrease in the on-site Coulombic repulsion.



Scheme 2.

The controlled-current electrocrystallization[5] of a diastereomeric mixture of DMDH-TTP in 1,1,2-trichloroethane with *n*-Bu_4NX ($X = AsF_6$ and BF_4) gave single crystals with the composition $(DMDH\text{-}TTP)_2X$ ($X = AsF_6$ and BF_4), as determined by X-ray diffraction studies (see below), along with other crystals of unsuitable quality or size for an X-ray structure determination. Single crystals of the AsF_6 and BF_4 salts exhibited room-temperature conductivities of 31 and 54 $S\,cm^{-1}$, respectively. The temperature dependence of their resistivities revealed that both salts are metallic down to 4.2 K.

By X-ray analysis,[6] the AsF_6 salt was found to consist of two

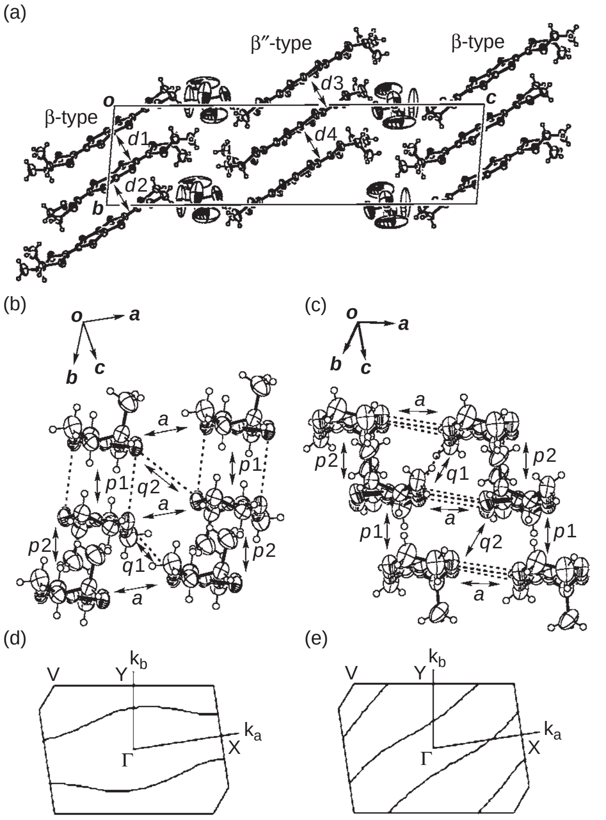


Figure 1. (a) Crystal structure of (*meso*-DMDH-TTP)$_2$AsF$_6$. Interplanar distances *d*1 and *d*2 in the β-type donor layer are 3.61 and 3.78 Å, respectively, and interplanar distances *d*3 and *d*4 in the β''-type donor layer are 3.739 and 3.737 Å, respectively. (b) β-Type donor arrangement. Short S···S contacts [3.643(3)–3.710(2) Å] are shown by broken lines. Intermolecular overlap integrals *p*1, *p*2, *a*, *q*1 and *q*2 ($\times 10^{-3}$) are 17.4, 11.4, −2.87, 12.0, and 4.43, respectively. (c) β''-Type donor arrangement. Short S···S contacts [3.549(4)–3.708(3) Å] are drawn by broken lines. Intermolecular overlap integrals *p*1, *p*2, *a*, *q*1 and *q*2 ($\times 10^{-3}$) are 4.66, 1.69, 3.80, 17.6, and 17.0, respectively. (d) Fermi surface of the β-type donor layer. (e) Fermi surface of the β''-type donor layer.

distinct types of donor layers interleaved by an anion layer (Figure 1a): a donor layer of the β-type (Figure 1b) and a donor layer of the β''-type (Figure 1c).[7] The asymmetric unit includes two crystallographically independent DMDH-TTP molecules, both of which are the meso-form. Each donor layer contains only one independent *meso*-DMDH-TTP molecule, and *meso*-DMDH-TTP donor molecules are stacked in a head-to-tail manner. In the β-type donor layer, parallel stacks of somewhat dimerized donor molecules occur along the *b*-axis, and intermolecular S···S contacts close to or shorter than the van der Waals distance (3.70 Å) exist within and between donor stacks. Large values of the intermolecular overlap integrals are calculated for the intrastack interactions *p*1 and *p*2 and the interstack interaction *q*1,[8] whereas the absolute value of the interstack overlap integral *a* along the crystallographic *a*-axis is smallest. These anisotropic interactions in the donor layer result in a one-dimensional (1D) Fermi surface being open along the interstacking *a*-direction (Figure 1d). Meanwhile, the β''-type layer contains donor stacks aligned along the [101] direction, and the stack has *meso*-DMDH-TTP donor molecules alternating at almost the same separation of ca. 3.74 Å. Short S···S contacts occur between donor stacks rather than within a donor stack. Also, the values of the interstack overlap integrals *q*1 and *q*2 are larger than those of the intrastack overlap integrals *p*1 and *p*2, leading to an open Fermi surface along the intrastaking [101] direction (Figure 1e). Fortunately, the respective opening directions of two 1D Fermi surfaces differ, so that this salt would exhibit metallic behavior down to a low temperature. According to structural information on the BF$_4$ salt, the salt consists of alternating layers containing only *meso*-DMDH-TTP donor molecule and only BF$_4^-$ anion. The donor molecule arrangement belongs to the λ-type category. Further structural details will be reported separately.

In conclusion, it has been found that despite the use of a mixture of *meso*- and *trans*-DMDH-TTP donors in electrocrystallization, single crystals of CT salts derived from only *meso*-DMDH-TTP are obtained,[9] which retain the metallic state down to low temperatures. In contrast to the tendency for BDH-TTP to give κ-type salts,[1a,1c] *meso*-DMDH-TTP seems to have the ability to form relatively rare packing motifs, as supported by the structural and electronic features of its AsF$_6$ salt described herein. Therefore, the construction of new molecular packing patterns conductive to metallic conductivity and superconductivity may become feasible by using *meso*-DMDH-TTP. To settle this issue, we are currently carrying out the preparation of other *meso*-DMDH-TTP salts.

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References and Notes

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6 Crystal data for (*meso*-DMDH-TTP)$_2$AsF$_6$: C$_{24}$H$_{24}$AsF$_6$S$_{16}$, fw = 1014.42, triclinic, space group $P\bar{1}$, $a = 6.4485(10)$, $b = 8.8750(9)$, $c = 32.482(4)$ Å, $\alpha = 94.362(4)°$, $\beta = 93.5360(9)°$, $\gamma = 97.9906(11)°$, $V = 1830.6(4)$ Å^3, $T = 295$ K, $Z = 2$, $D_{\text{calcd}} = 1.84$ g cm^{-3}, μ(Mo Kα) = 1.894 mm^{-1}, $R = 0.098$ and $R_w = 0.095$ for 5271 observed reflections with $I > 3\sigma(I)$ from 7261 unique reflections.

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8 For the parameters used for calculation, see: T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **57**, 627 (1984).

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