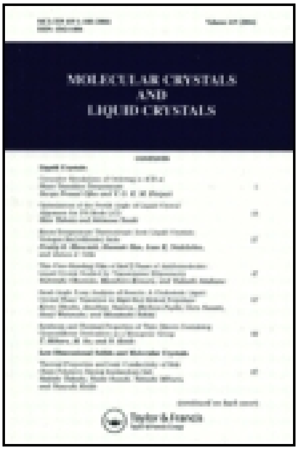

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New Organic Conductors and Superconductors Based on Dihydro-TTF (DHTTF) Donors

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The synthesis of dihydrotetrathiafulvalene (DHTTF) donors and the preparation of their charge-transfer (CT) salts have been undertaken to develop new organic metals and superconductors. The molecular structures of methylenedithio-DHTTF (MDHT), 1,4-dioxane-2,3-diyldithio-DHTTF (DODHT), and methylmethylidenedithio-DHTTF (Me-MDHT) are secured by X-ray crystallographic analyses. These DHTTF donors provide CT salts characterized by a wide range of conducting behavior from semiconducting to metallic and superconducting. The crystal structures of CT salts from each category are described.

Keywords: crystal structures; dihydro-TTF donors; molecular structures; organic conductors; organic superconductors

INTRODUCTION

Since the discovery of superconductivity in a series of CT (charge-transfer) salts of TMTSF (tetramethyltetraselenafulvalene, Fig. 1) [1], the development of new organic superconductors continues to be

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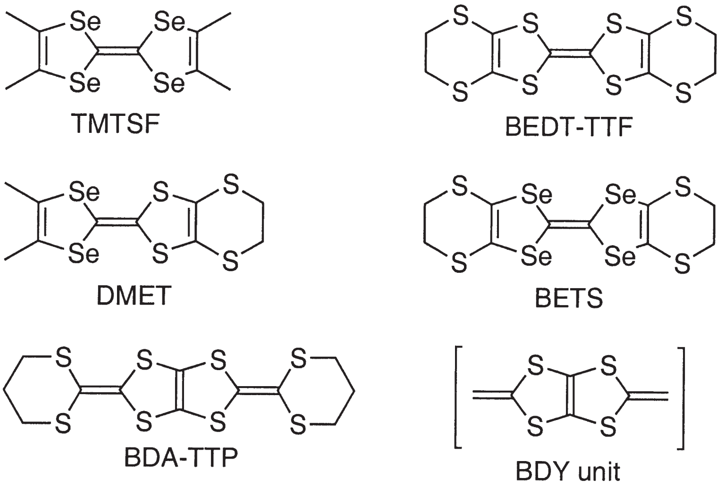
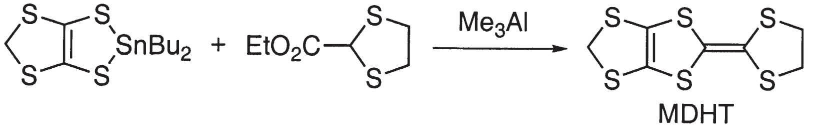


FIGURE 1 TCF donors and BDA-TTP.

a major topic in the field of molecular conductors [2]. Most organic superconductors have so far been derived from TCF (tetrachalcogenafulvalene) derivatives, such as BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene], DMET [dimethyl(ethylenedithio)diselenadithia fulvalene], and BETS [bis(ethylenedithio)tetraselenafulvalene] [3], whereas we have found that BDA-TTP [2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene], which comprises the BDY (bis-fused 1,3-dithiol-2-ylidene) unit instead of the TTF (tetrathiafulvalene) unit as a π-electron system, produces the superconducting β-(BDA-TTP)$_2$X (X = SbF$_6$, AsF$_6$, PF$_6$, GaCl$_4$) salts [4]. Additionally, we revealed that the β-(BDA-TTP)$_2$SbF$_6$ superconductor [5] has the largest value of the effective cyclotron mass ($m_c^* = 12.4 \pm 1.1\, m_e$) yet found in an organic superconductor [6]. Further production of such organic superconductors as to exhibit notable physical properties that cannot be observed in the TCF-containing superconductors is considered to be of importance in the development of this field. Our next attention was thus focused on the achievement of superconductivity in CT salts of DHTTF (dihydro-TTF) donors in which the π-system is less extended than that of TCF donors. In this paper, we describe our continued research to explore organic metals and superconductors based on DHTTF donors [7].

STRUCTURES OF MDHT AND ITS METALLIC SALT

As reported previously by us [8,9], the synthesis of MDHT can be attained by the Me$_3$Al-promoted reaction of the corresponding tin



SCHEME 1 Synthesis of MDHT.

dithiolate with 2-ethoxycarbonyl-1,3-dithiolane (Scheme 1). The molecular structure of MDHT was determined by X-ray analysis [10]. The MDHT molecule contains two tetrathioethylene medium units in an approximately common plane, and both the ethylene and methylene end groups are somewhat distorted from that plane (Fig. 2).

Single crystals of the AuX$_2$ (X = Cl and I) salts of MDHT were prepared by the controlled-current electrocrystallization method [8,11]. The (MDHT)$_2$AuCl$_2$ salt was found to be a small gap semiconductor [E_a (activation energy) = 6 meV, σ_{rt} (room-temperature conductivity) = 250 S cm^{-1}] with a β-type donor arrangement [11]. On the other hand, the (MDHT)$_2$AuI$_2$ salt exhibited metallic conducting behavior (σ_{rt} = 60 S cm^{-1}) down to 1.4 K [8], the crystal structure of which was determined by X-ray analysis [12]. This salt consists of alternating layers containing only MDHT donor molecule and only AuI$_2^-$ anion (Fig. 3a). In the anion layer, two independent positions are observed for the Au site, the occupancies of which are distributed to 0.670(3) and 0.1651(15), respectively. There is neither diffuse line nor additional reflection in the X-ray data, indicating that the Au atoms are randomly situated in these two positions. The donor molecules are stacked in the θ-type arrangement (Fig. 3b), and the dihedral angle between the planes formed by donor molecules on adjacent stacks is 78.2°. Several intermolecular S···S contacts shorter than the sum of the van der Waals radii (3.70 Å) are observed between stacks, whereas there is no S···S contact within a stack: a similar

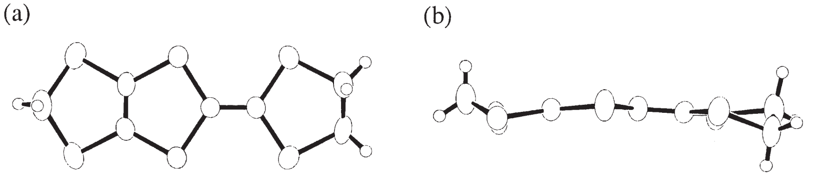


FIGURE 2 Top (a) and side (b) views of the molecular structure of MDHT.

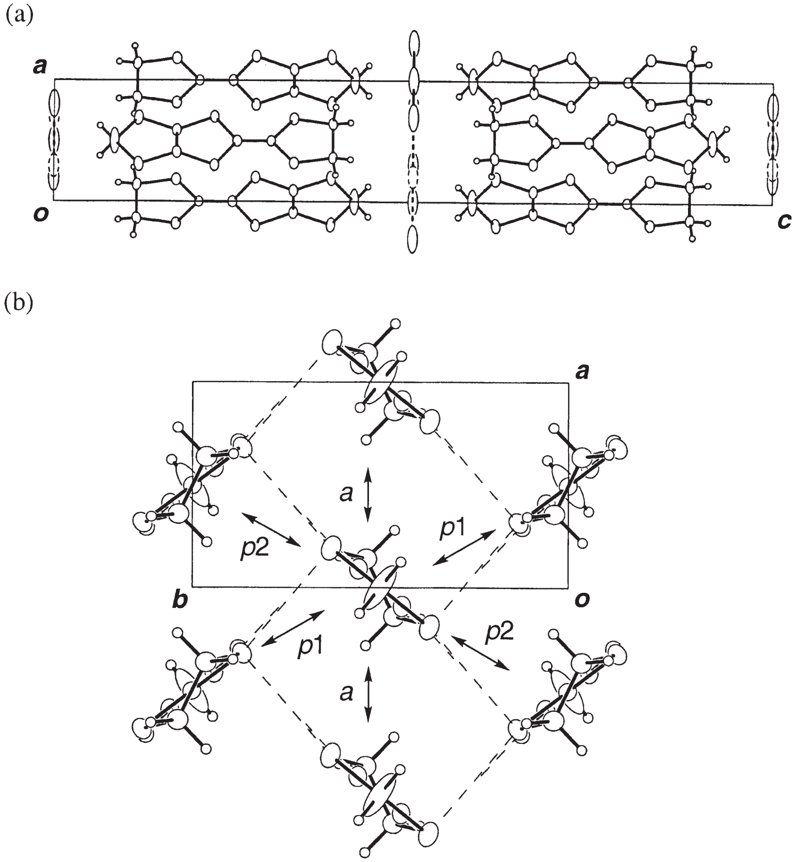


FIGURE 3 (a) Crystal structure of $(MDHT)_2AuI_2$ viewed along the *b*-axis. The Au atoms are mainly situated in positions depicted by open circles, and broken circles indicate the other positions of the Au atoms (see text). (b) Donor arrangement of $(MDHT)_2AuI_2$. Intermolecular S···S contacts (<3.70 Å) are drawn by dashed lines. Intermolecular overlap integrals a, $p1$, and $p2$ are -1.46, -14.5, and -14.3×10^{-3}, respectively.

S···S contact pattern can be found in θ-(BEDT-TTF)$_2$I$_3$ [13]. The large intermolecular overlap integrals are also calculated between stacks, which cause two-dimensional (2D) interaction in the *ab*-plane. The tight-binding band calculation results in the 2D band dispersion relation and closed Fermi surface (Fig. 4), although the Fermi surface is less round than that of θ-(BEDT-TTF)$_2$I$_3$. This band structure is responsible for the metallic behavior down to the observed low temperature.

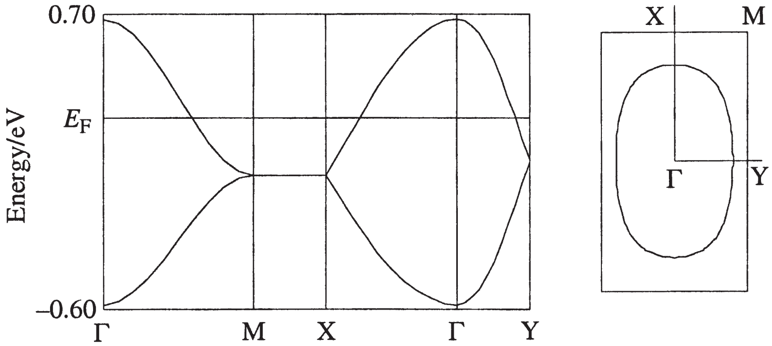


FIGURE 4 Energy band structure and Fermi surface of $(MDHT)_2AuI_2$.

DODHT-BASED SUPERCONDUCTORS

We succeeded in obtaining the stable metallic salt $(MDHT)_2AuI_2$ from the DHTTF donor family, but this salt failed to develop superconductivity. Therefore, further structural modification to the DHTTF donors we synthesized would be required to achieve superconductivity. We thus designed a derivative of the ethylenedithio-substituted DHTTF donor with a dioxane ring appended by cis fusion, *viz.*, DODHT (Fig. 5), because we have revealed that the cis-fused dioxane ring, though bulky, on TTF derivatives does not necessarily break metallic electronic structures, as can be found in $(DOET)_2BF_4$ [DOET = (1,4-dioxane-2,3-diyldithio)ethylenedithiotetrathiafulvalene], $(DOES)_2(AuI_2)_{0.75}$ [DOES = (1,4-dioxane-2,3-diyldithio)ethylenediselenotetrathiafulvalene], and $(DOEO)_2BF_4$ [DOEO = (1,4-dioxane-2,3-diyldithio) ethylenedioxotetrathiafulvalene] [14]. Such a bulky donor molecule with a reduced π-system does not appear to adhere to the conventional line of molecular design for π-donors capable of providing superconductors; hence, the successful production of DODHT-based superconductors would lead to a new angle in the design of organic superconductors.

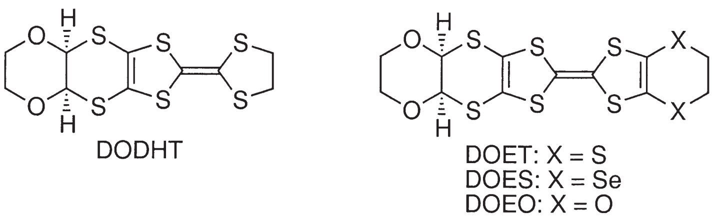
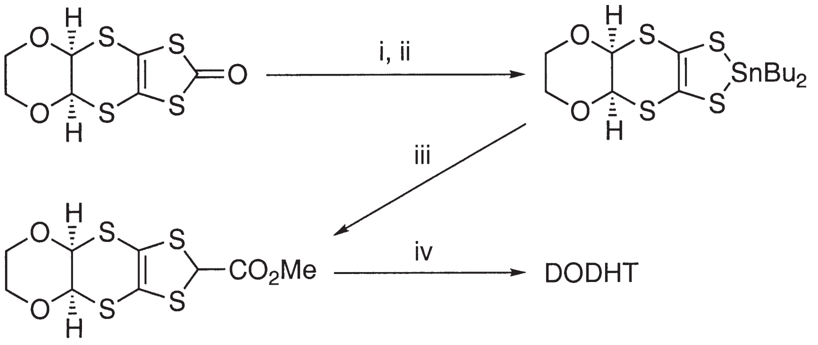


FIGURE 5 Dioxane-fused DHTTF and TTF donors.



Reagents and conditions: (i) MeONa, MeOH, 0 °C, 1 h; (ii) Cl_2SnBu_2, THF, –78 °C → room temperature; (iii) *n*-BuLi, Cl_2CHCO_2Me, THF –78 °C → room temperature, overnight (74% overall yield); (iv) bis(dimethylaluminum) 1,2-ethanedithiolate, CH_2Cl_2,–78 °C → room temperature, overnight (46% yield).

SCHEME 2 Synthesis of DODHT.

Our synthetic route to DODHT is outlined in Scheme 2 [15]. X-ray analysis of the resulting DODHT confirmed the cis stereochemistry for the fusion pattern of the dioxane ring (Fig. 6) [16]. Two tetrathioethylene medium units in DODHT fail to form a common plane, in contrast to those in MDHT.

In addition to the $(DODHT)_2X$ ($X = AsF_6$ and PF_6) salts, which exhibit superconductivity under pressure [$(DODHT)_2AsF_6$, T_c (superconducting transition temperature) $= 3.3\,K$ (16.5 kbar); $(DODHT)_2PF_6$, $T_c = 3.1\,K$ (16.5 kbar)] [15,16], the $(DODHT)_2BF_4{\cdot}H_2O$ hydrate was found to undergo a superconducting transition at 3.2 K under a hydrostatic pressure of 15.5 kbar [17]. Figure 7a shows the crystal structure of this hydrate, which consists of alternating layers

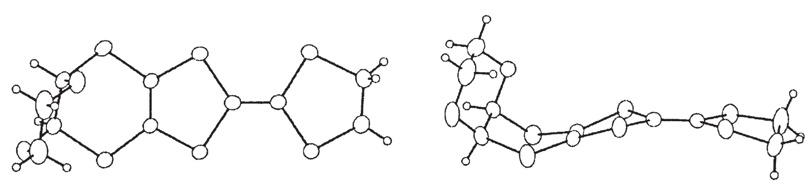


FIGURE 6 Top (a) and side (b) views of the molecular structure of DODHT.

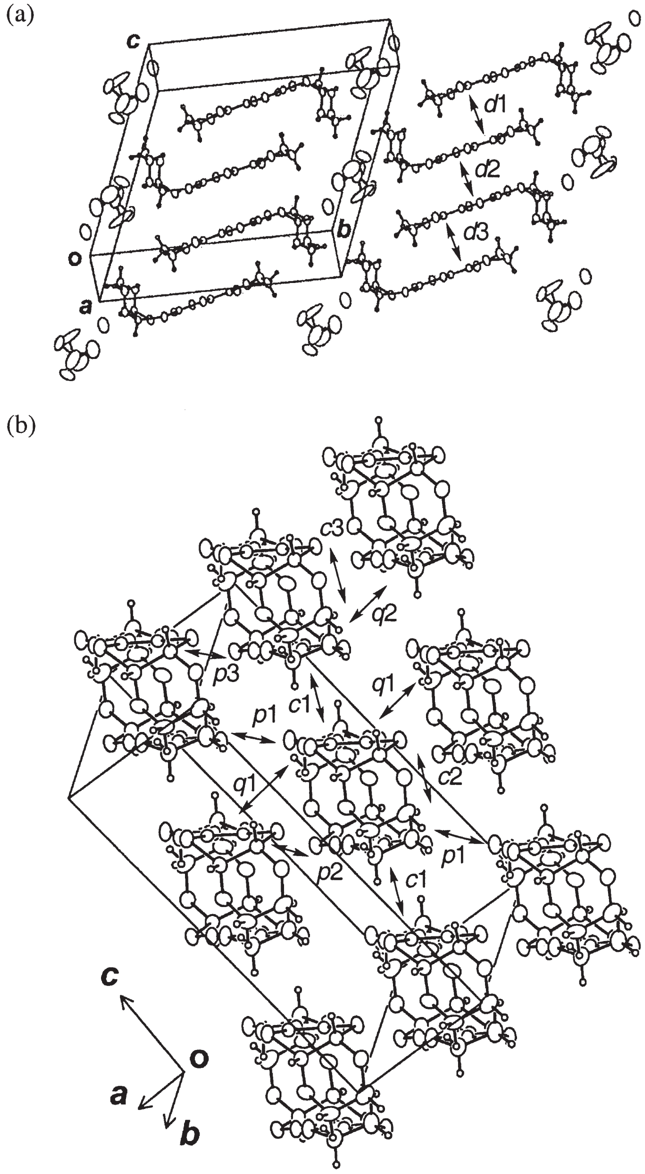


FIGURE 7 (a) Crystal structure of $(DODHT)_2BF_4{\cdot}H_2O$. Interplanar distances in the DODHT stack are 3.85 (*d*1), 3.57 (*d*2), and 3.81 (*d*3) Å. (b) Donor arrangement of $(DODHT)_2BF_4 \cdot H_2O$. Intermolecular overlap integrals *c*1, *c*2, *c*3, *p*1, *p*2, *p*3, *q*1, and *q*2 are 0.77, −1.99, −1.89, 11.04, −9.81, −8.54, −10.84, and -12.35×10^{-3}, respectively.

of DODHT donor molecules and layers containing BF_4^- and H_2O. Although the donor arrangement belongs to the β"-type category similar to those of the isostructural superconductors $(DODHT)_2X$ ($X = AsF_6$ and PF_6), the crystal structure is by no means isostructural to those of the AsF_6 and PF_6 salts. There exist two crystallographically independent donor molecules, which are stacked with a four-folded period to form two types of cyclic-like pairs with interplanar distances of 3.85, 3.57, and 3.81 Å. The intermolecular overlap integrals indicate that the interaction within a stack is much weaker than that between stacks (Fig. 7b): the same can be said for the AsF_6 and PF_6 salts. However, unlike these salts, the respective absolute values of the overlap integrals within the two cyclic-like donor pairs ($c2 = 1.99$ and $c3 = 1.89 \times 10^{-3}$) are larger than that between these pairs ($c1 = 0.77 \times 10^{-3}$). This is probably due to an only slight difference in the deviation of overlap of donor molecules, which causes an appreciable change in the effective area of the π-system of DODHT that is capable of overlapping. Thus, in the DODHT superconductors, such a subtle variation in the donor packing motifs has a marked influence on the intermolecular interaction.

It is noted that all the three DODHT superconductors exhibit various aspects of the pressure-induced conducting behavior, including semiconducting, metallic, and superconducting phases [15–17]. Therefore, it is an important subject of continued interest to reveal how structure change is brought about by applied pressures.

MONO-ALKYLATED MDHT DONORS

As mentioned above, the extension of a derivative of DHTTF by appending the cis-fused dioxane ring is a useful approach in the design of organic superconductors. Another attractive strategy for constructing DHTTF donors extended by a σ-bond framework is the introduction of a simple alkyl group, because we have found that the ethylated MET [methylenedithio(ethylenedithio)tetrathiafulvalene] donor (Et-MET, Fig. 8) produces the metallic ClO_4 and PF_6 salts [18], although the

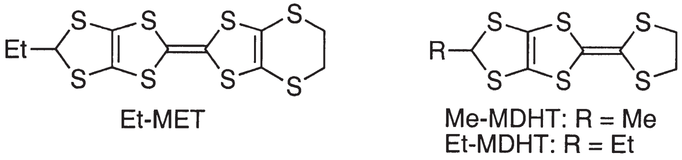
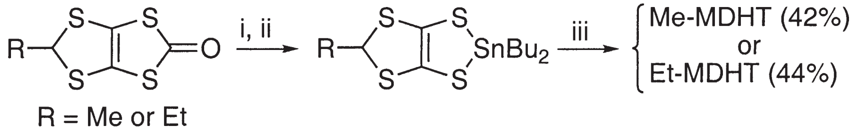


FIGURE 8 Mono-alkylated MET and MDHT donors.



Reagents and conditions: (i) MeMgBr, THF, room temperature, 2 h; (ii) Cl_2SnBu_2, THF, –78 °C → room temperature; (iii) Me_3Al 2-ethoxycarbonyl-1,3-dithiolane, –78 °C → room temperature.

SCHEME 3 Synthesis of Me-MDHT and Et-MDHT.

parent MET donor has been reported to give the semiconducting ClO_4, PF_6, and ReO_4 salts [19]. Thus, we investigated the synthesis of the methylated and ethylated MDHT donors Me-MDHT and Et-MDHT.

Conversion of the Me- and Et-attached 1,3-dithiol-2-ones [18] into the corresponding tin dithiolates, followed by the Me_3Al-promoted reaction with 2-ethoxycarbonyl-1,3-dithiolane gave Me-MDHT and Et-MDHT in 42% and 44% overall yields, respectively (Scheme 3). Needle-like and prismatic single crystals of Me-MDHT could be obtained by recrystallization from $CHCl_3$-EtOH. X-ray analysis of a needle-like crystal revealed that the methyl group is almost perpendicularly attached to the MDHT skeleton (Fig. 9) [20], but no significant difference between the structures of the MDHT moiety and the parent MDHT molecule was discerned. On the other hand, the MDHT moiety of Me-MDHT in a prismatic crystal was found to be curved toward the opposite side of the methyl group by X-ray analysis (Fig. 10) [21]. A similar curved MDHT moiety was observed in the molecular structure of Et-MDHT confirmed by X-ray analysis (Fig. 11) [22]. Another feature of this molecular structure is that the ethyl group and the MDHT moiety overlap each other.

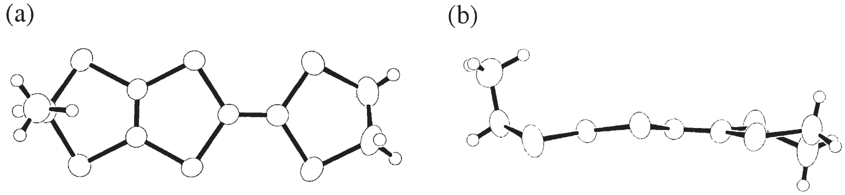


FIGURE 9 Top (a) and side (b) views of the molecular structure of Me-MDHT in a needle-like crystal.

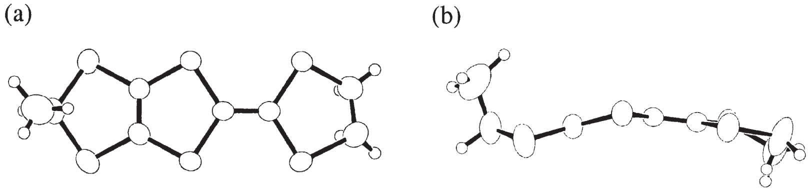


FIGURE 10 Top (a) and side (b) views of the molecular structure of Me-MDHT in a prismatic crystal.

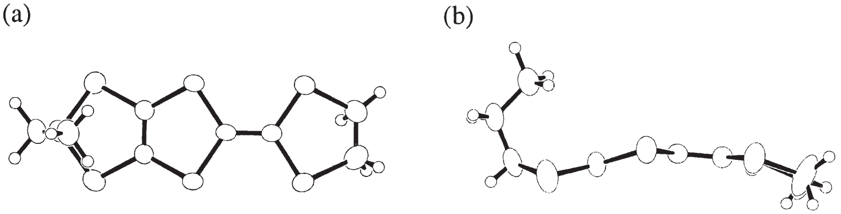


FIGURE 11 Top (a) and side (b) views of the molecular structure of Et-MDHT.

Cyclic voltammetry measurements of Me-MDHT and Et-MDHT indicated that introduction of the methyl and ethyl groups does not remarkably affect either the electron-donating ability or the on-site Coulombic repulsion of the parent MDHT molecule (Table 1). Nevertheless, our attempt to prepare the Et-MDHT salts with I_3^-, AuI_2^-, BF_4^-, ClO_4^-, PF_6^-, and AsF_6^- anions by controlled-current electrocrystallization in TCE (1,1,2-trichloroethane), PhCl, or CH_3CN was unsuccessful. On the other hand, single crystals of the AuI_2 salt of Me-MDHT could be obtained in CH_3CN, although Me-MDHT with I_3^-, BF_4^-, ClO_4^-, PF_6^-, and AsF_6^- anions formed no or only a trace of CT salt in TCE, PhCl, THF, or CH_3CN.

TABLE 1 Oxidation Potentials of MDHT and its Mono-Alkylated Derivatives[†]

Compound	E_1	E_2	ΔE (E_2–E_1)
MDHT	0.57	1.00	0.43
Me-MDHT	0.59	0.99	0.40
Et-MDHT	0.57	0.98	0.41

[†] V *vs*. saturated calomel electrode (SCE), 0.1 M n-Bu_4NClO_4 in PhCN, Pt electrode, at room temperature, under nitrogen, scan rate 50 mV s^{-1}.

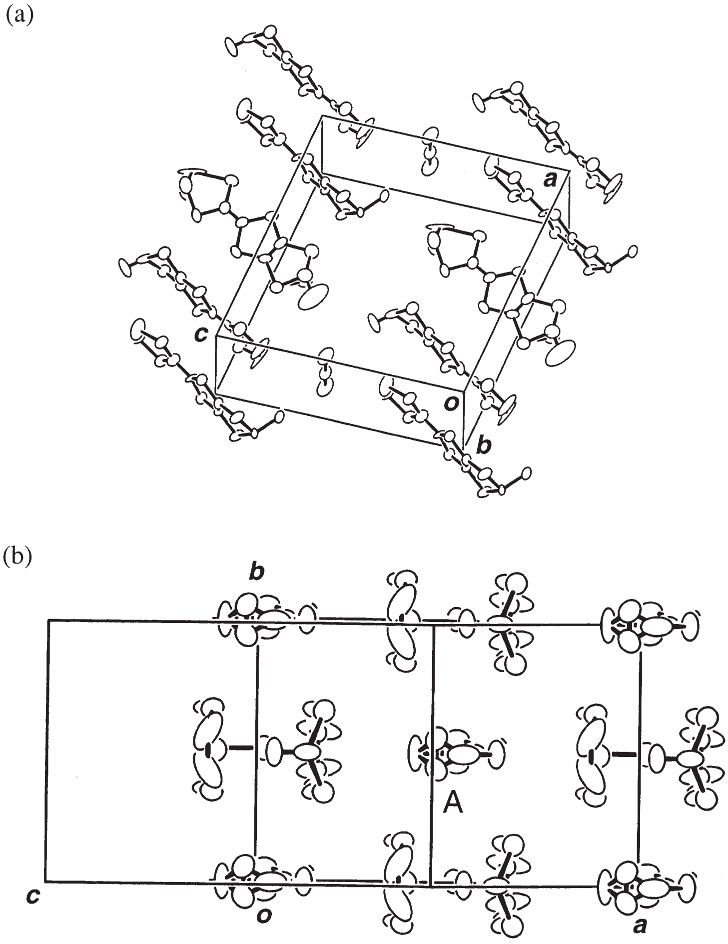


FIGURE 12 (a) Crystal structure of (Me-MDHT)$_3$AuI$_2$. Hydrogen atoms are omitted for clarify. (b) Donor arrangement of (Me-MDHT)$_3$AuI$_2$.

The stoichiometry and crystal structure of the resulting AuI$_2$ salt of MDHT was determined by X-ray analysis [23]. This salt has a 3:1 donor to anion ratio, represented as (Me-MDHT)$_3$AuI$_2$, and consists of donor layers alternating with anion layers [Fig. 12a]. In the donor layer, there is a monomer [corresponding to molecule A in Fig. 12b] surrounded by four dimers, which has considerable positional disorder in the carbon atom linking the methyl group. It is expected that charge separation among donor molecules may occur in such a donor arrangement containing monomers and dimers [24]. However, an accurate estimate of the bond lengths of donor molecules could not be carried out due to the observed disorder. The temperature dependence of the resistivity of (Me-MDHT)$_3$AuI$_2$ showed semiconducting behavior ($E_a = 28\,\text{meV}$, $\sigma_{rt} = 8.5\,\text{S cm}^{-1}$), and a significant change in the conducting behavior of this salt has not yet been found at pressures of up to 5 kbar.

CONCLUSION

The use of DHTTF derivatives as donor components of organic conductors has hitherto received little attention [25], in striking contrast to the broad study of the TTF-based organic conductors. This is presumably due to the prediction that the partial reduction of the π-system of the TTF core would adversely affect the electron-donating ability and the on-site Coulombic repulsion and, consequently, would be deemed crucial in forming the segregated stacking of donor molecules in CT materials. Nevertheless, we could demonstrate that the fusion of a 1,3-dithiolane ring on the DHTTF core generates tight intermolecular cohesion to retain the stable metallic state, and that further attachment of a dioxane ring by cis fusion results in moderately loose donor packing motifs which are required for achieving superconductivity [4]. On the other hand, the introduction of an alkyl group, which is less bulky than a dioxane ring, into the MDHT molecule prevented a facile formation of crystalline CT salts, although mono-alkylated MDHT donors have the donating ability somewhat superior to that of DODHT ($E_1 = 0.64\,\text{V}$ *vs.* SCE in PhCN) [15]. This result suggests that the cis-fused dioxane ring plays an important role in crystallization of CT materials, which cannot be expected from only the donating ability. Further work on the design and synthesis of new DHTTF donors capable of providing CT materials with more interesting and exiting solid-state properties is ongoing in our laboratories.

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[10] Crystal data for MDHT: $C_7H_6S_6$, $M = 282.52$, monoclinic, $P2_1/a$, $a = 8.478(5)\,\text{Å}$, $b = 11.474(4)\,\text{Å}$, $c = 12.155(4)\,\text{Å}$, $\beta = 109.96(3)^\circ$, $V = 1111.4(8)\,\text{Å}^3$, $Z = 4$, $D_c = 1.69\,\text{g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.179\ \text{mm}^{-1}$, $R = 0.046$, $R_w = 0.049$.

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[20] Crystal data for Me-MDHT in a needle crystal: $C_8H_8S_6$, $M = 296.55$, monoclinic, $P2_1/n$, $a = 9.560(1)\,\text{Å}$, $b = 11.277(1)\,\text{Å}$, $c = 12.252(1)\,\text{Å}$, $\beta = 111.36(1)^\circ$, $V = 1230.1(2)\,\text{Å}^3$, $Z = 4$, $D_c = 1.60\,\text{g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.070\,\text{mm}^{-1}$, $R = 0.041$, $R_w = 0.048$.

[21] Crystal data for Me-MDHT in a prismatic crystal: $C_8H_8S_6$, $M = 296.55$, monoclinic, $P2_1/n$, $a = 12.4391(9)\,\text{Å}$, $b = 9.1352(16)\,\text{Å}$, $c = 12.5948(3)\,\text{Å}$, $\beta = 120.6858(7)^\circ$, $V = 1230.8(2)\,\text{Å}^3$, $Z = 4$, $D_c = 1.60\,\text{g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.069\,\text{mm}^{-1}$, $R = 0.049$, $R_w = 0.048$.

[22] Crystal data for Et-MDHT: $C_9H_{10}S_6$, $M = 310.54$, monoclinic, $P2_1/c$, $a = 12.526(3)\,\text{Å}$, $b = 9.577(4)\,\text{Å}$, $c = 12.309(3)\,\text{Å}$, $\beta = 119.31(1)^\circ$, $V = 1287.7(6)\,\text{Å}^3$, $Z = 8$, $D_c = 3.203\,\text{g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 2.0504\,\text{mm}^{-1}$, $R = 0.041$, $R_w = 0.042$.

[23] Crystal data for $(\text{Me-MDHT})_3\text{AuI}_2$: $C_{32}H_{32}S_{24}AuI_2$, $M = 1636.82$, monoclinic, Cm, $a = 14.633(2)\,\text{Å}$, $b = 9.602(3)\,\text{Å}$, $c = 14.657(2)\,\text{Å}$, $\beta = 101.26(1)^\circ$, $V = 2019.8(7)\,\text{Å}^3$, $Z = 2$, $D_c = 2.691\,\text{g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 6.4607\,\text{mm}^{-1}$, $R = 0.036$, $R_w = 0.035$.

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