

Monoxygen-containing Analogue of BDH-TTP, DHOT-TTP [2-(1,3-Dithiolan-2-ylidene)-5-(1,3-oxathiolan-2-ylidene)-1,3,4,6-tetrathiapentalene], and Its Metallic AuI₂ Salt

Jun-ichi Yamada,* Ken-ichi Kunigita, Hiroki Akutsu, Shin'ichi Nakatsuji, and Koichi Kikuchi[†]
 Department of Material Science, Graduate School of Material Science, University of Hyogo,
 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297

[†]Department of Chemistry Graduate School of Science, Tokyo Metropolitan University,
 Hachioji, Tokyo 192-0397

(Received September 16, 2004; CL-041091)

The synthesis of DHOT-TTP, in which one sulfur atom of BDH-TTP [2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene] is substituted by oxygen, has been accomplished. The DHOT-TTP donor possesses a less planar molecular structure than BDH-TTP, and gives a metallic AuI₂ salt stable down to 1.4 K, the crystal structure of which is elucidated.

We have found that BDH-TTP with various anions forms stable metallic salts,^{1,2} and that BDA-TTP [2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene] yields superconductors β -(BDA-TTP)₂X (X = SbF₆, AsF₆, and PF₆) and β -(BDA-TTP)₂MCl₄ (M = Ga and Fe) at ambient pressure and under pressure, respectively.^{1,2} An important structural change, leading to the realization of superconductivity, from BDH-TTP to BDA-TTP is an increase of nonplanarity by replacement of the ethylene end groups of BDH-TTP with the trimethylene groups,¹ because such a structural modification is thought to weaken intermolecular interaction, and, consequently, to cause the destabilization of the stable metallic state, which would be required for achieving superconductivity.^{2,3} Another structural modification in this regard might be the substitution of only one sulfur atom in the outer ring of BDH-TTP by oxygen (which leads to DHOT-TTP). That is, this substitution means the introduction of two C–O bonds instead of two C–S bonds into the rigid five-membered ring of BDH-TTP, which is expected to result in the deformation of the entire molecular structure due to the difference between the C–O and C–S bond lengths. Meanwhile, it has been reported that the same substitution in the flexible six-membered outer ring of ET [bis(ethylenedithio)tetrathiafulvalene] has little influence on the conformational change of the

prototype ET molecule.⁴ Thus, to probe whether this subtle modification to BDH-TTP gives rise to an appreciable structural change and also to reveal what difference is found in the conducting behaviors of the BDH-TTP and DHOT-TTP salts, we undertook the synthesis and study of DHOT-TTP.

We planned the synthesis of DHOT-TTP beginning with the oxathiolane-attached oxone **1a**. However, as previously reported by us,⁵ formation of **1a** from its dioxolane analogue **1b** results in a mixture of **1a**, **1b**, and the dithiolane-attached oxone **1c**. The exclusive formation of **1a** was thus examined. Treatment of **1b** with conc. H₂SO₄ in refluxing MeOH gave dimethyl acetal **2** (72% yield), which upon heating with 2-mercaptoethanol in benzene containing a catalytic amount of *p*-TsOH led successfully to **1a** in 74% yield. Subsequently, treatment of **1a** with MeMgBr and Cl₂SnBu₂ in THF afforded tin dithiolate **3**, which was immediately reacted with 2-ethoxycarbonyl-1,3-dithiolane in the presence of Me₃Al (2 equiv.) in CH₂Cl₂ to give the coupling product **4** in 39% overall yield. Oxidation of **4** with DDQ in refluxing toluene furnished DHOT-TTP in 88% yield.⁶ By X-ray analysis it was revealed that the DHOT-TTP molecules crystallize in an orientationally disordered fashion with respect to the oxygen atom (O4 or O4' in the atomic numbering scheme of Figure 1a) and the sulfur atom (S4 or S4').⁷ In the molecular structure of DHOT-TTP, the dihedral angle between the planes formed by the central tetrathioethylene moiety and the external one is 152.2° (Figure 1b), which is smaller than that in the BDH-TTP molecule (173°). Therefore, it is obvious that DHOT-TTP has a nonplanar structure compared to BDH-TTP.¹

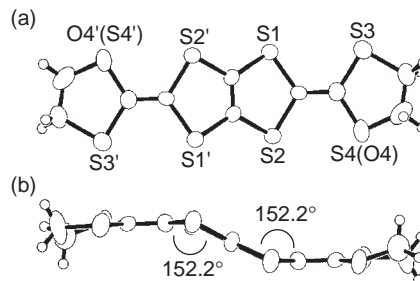
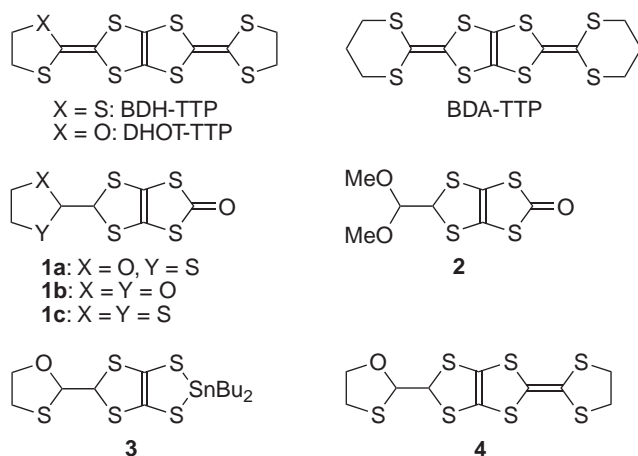


Figure 1. (a) Top and (b) side views of the molecular structure of DHOT-TTP.

A comparison of the oxidation potentials for DHOT-TTP [$E_1 = 0.52$, $E_2 = 0.80$, $E_3 = 1.16$, $\Delta E (E_2 - E_1) = 0.28$ V (vs SCE)] with those for BDH-TTP [$E_1 = 0.56$, $E_2 = 0.85$, $E_3 = 1.24$, E_4 (irreversible) = 1.44, $\Delta E (E_2 - E_1) = 0.29$ V], measured by cyclic voltammetry under identical conditions (0.1 M *n*-Bu₄NClO₄ in PhCN, Pt electrode, scan rate 50 mV s⁻¹), indicates that the displacement of the sulfur atom with oxygen

slightly enhances the donating ability, but does not remarkably affect the on-site Coulombic repulsion. Electrocrystallization of DHOT-TTP with $n\text{-Bu}_4\text{NX}$ ($X = \text{I}_3$, AuI_2 , and BF_4) in 1,1,2-trichloroethane by the controlled-current technique⁸ gave single crystals of the corresponding DHOT-TTP salts. The I_3 (donor:anion = 2:1, $\sigma_{\text{IT}} = 7.0 \text{ S cm}^{-1}$, $E_a = 17 \text{ meV}$) and BF_4 (donor:anion = 3:2, $\sigma_{\text{IT}} = 0.60 \text{ S cm}^{-1}$, $E_a = 45 \text{ meV}$) salts exhibited semiconducting behavior, which is in contrast to the fact that the same salts of BDH-TTP are metallic down to 2.0 K.¹ On the other hand, the AuI_2^- anion, providing a stable metallic 2:1 salt of BDH-TTP (>2.0 K),¹ also formed a metallic salt ($\sigma_{\text{IT}} = 32 \text{ S cm}^{-1}$) with DHOT-TTP, which retained the metallic state down to 1.4 K.

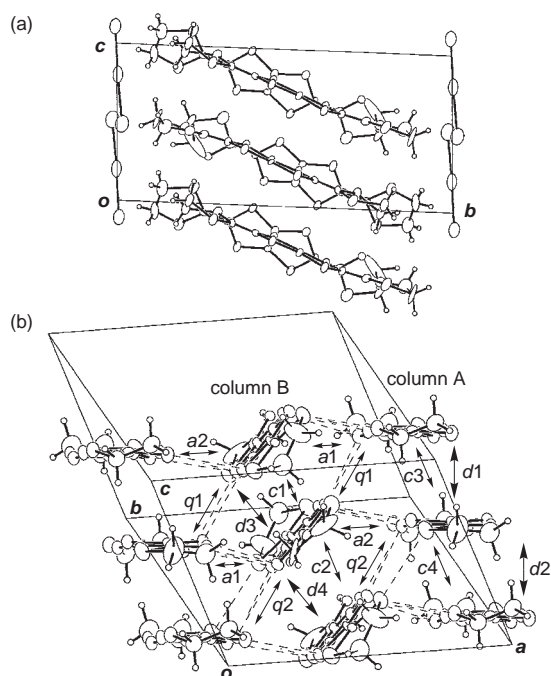


Figure 2. (a) Crystal structure of $(\text{DHOT-TTP})_2(\text{AuI}_2)_{0.87}$. (b) Donor arrangement in $(\text{DHOT-TTP})_2(\text{AuI}_2)_{0.87}$. Interplanar distances in column A are 3.66 (d_1) and 3.61 (d_2) Å, whereas those in column B are 3.57 (d_3) and 3.66 (d_4) Å. Short S...S contacts (<3.70 Å) are drawn by broken lines. Intermolecular overlap integrals ($\times 10^{-3}$) c_1 , c_2 , c_3 , c_4 , a_1 , a_2 , q_1 , and q_2 are -2.96 , -0.26 , -2.72 , -1.86 , -5.61 , -7.56 , 6.10 , and 9.07 , respectively.

The stoichiometry and crystal structure of the AuI_2 salt of DHOT-TTP was determined by X-ray analysis.⁹ The salt has a 2:0.87 donor-to-anion ratio and consists of alternate layers of DHOT-TTP donor molecules arranged in the α -packing motif and layers of AuI_2^- anions (Figure 2a). In the donor layer, there are two crystallographically independent DHOT-TTP molecules, in one of which no orientational disorder was discerned, whereas population analysis of the other resulted in a 0.63 occupancy for the oxygen atom. The structures of both independent DHOT-TTP molecules have considerable planarity: the respective dihedral angles between the planes formed by the central and external tetrathioethylene moieties in one DHOT-TTP molecule, which has no disorder, are 175.2° and 169.8° , and the corresponding angles in the other are 174.5° and 177.1° . DHOT-TTP donor molecules are stacked with some dimerization along

the c axis to form two columns (columns A and B in Figure 2b). The molecular plane of DHOT-TTP on column B is tilted by 50.1° from that on column A. Instead of no S...S contact shorter than the van der Waals distance (3.70 Å) in each DHOT-TTP column, there are many short S...S contacts between columns. Also, the values of the overlap integrals between columns are larger than those within each column,¹⁰ which would lead to a two-dimensional electronic structure responsible for the metallic conductivity down to 1.4 K. Since one independent DHOT-TTP molecule is free from disorder, its HOMO (highest occupied molecular orbital) could be investigated by the extended Hückel method (Figure 3). It should be noted that the oxygen atom has an extremely small HOMO coefficient compared to the sulfur atoms.

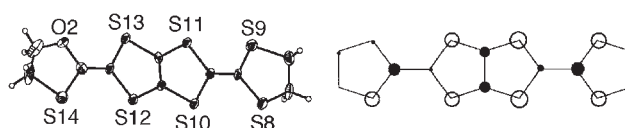


Figure 3. ORTEP drawing (left) and HOMO (right) of one independent DHOT-TTP molecule in $(\text{DHOT-TTP})_2(\text{AuI}_2)_{0.87}$.

In conclusion, the structural modification described herein failed to increase nonplanarity in the charged state. However, it is possible that the introduced oxygen atom plays a key role in the destabilization of the stable metallic state owing to its electron density of HOMO insufficient to participate in the formation of intermolecular interaction. Further pursuit of this possibility is ongoing in our laboratories.

This work was supported by grants from MEXT (No. 15073102) and JSPS (14540539).

References and Notes

- J. Yamada, H. Nishikawa, and K. Kikuchi, in "TTF Chemistry—Fundamentals and Applications of Tetrathiafulvalene," ed. by J. Yamada and T. Sugimoto, Kodansha & Springer, Tokyo (2004), Chap. 11, p 261.
- J. Yamada, *J. Mater. Chem.*, **14**, 2951 (2004).
- For another example, see: H. Nishikawa, A. Machida, T. Morimoto, K. Kikuchi, T. Kodama, I. Ikemoto, J. Yamada, H. Yoshino, and K. Murata, *Chem. Commun.*, **2003**, 494.
- M. Moge, J. Hellberg, K. W. Törnroos, and J.-U. von Schütz, *Adv. Mater.*, **8**, 807 (1996).
- J. Yamada, R. Oka, T. Mangetsu, H. Akutsu, S. Nakatsui, H. Nishikawa, I. Ikemoto, and K. Kikuchi, *Chem. Mater.*, **13**, 1770 (2001).
- DHOT-TTP: mp 215°C (decomp.); $^1\text{H NMR}$ (600 MHz, $\text{CDCl}_3\text{-CS}_2$); δ 3.32–3.37 (m, 2H), 3.44–3.49 (m, 4H), 4.35–4.40 (m, 2H). Anal. Found: C, 32.36; H, 2.16%. Calcd for $\text{C}_{10}\text{H}_8\text{OS}_7$: C, 32.58; H, 2.19%.
- Crystal data for DHOT-TTP: $\text{C}_{10}\text{H}_8\text{OS}_7$, $M = 368.59$, monoclinic, space group $P2_1/n$, $a = 6.353(3)$, $b = 8.962(2)$, $c = 12.420(4)$ Å, $\beta = 90.85(4)^\circ$, $V = 707.0(4)$ Å³, $T = 298$ K, $Z = 2$, $\mu(\text{Mo K}\alpha) = 10.96 \text{ cm}^{-1}$, $D_{\text{calcd}} = 1.731 \text{ g cm}^{-3}$, $R = 0.057$ and $R_w = 0.064$ for 824 observed reflections with $I > 3\sigma(I)$ from 1734 unique reflections.
- H. Anzai, J. M. Delrieu, S. Takasaki, S. Nakatsui, and J. Yamada, *J. Cryst. Growth*, **154**, 145 (1995); H. Nishikawa, T. Sato, T. Kodama, I. Ikemoto, K. Kikuchi, H. Anzai, and J. Yamada, *J. Mater. Chem.*, **9**, 693 (1999).
- Crystal data for $(\text{DHOT-TTP})_2(\text{AuI}_2)_{0.87} \cdot \text{C}_{20}\text{H}_{16}\text{O}_2\text{S}_{14}\text{Au}_{0.87}\text{I}_{1.73}$, $M = 1128.09$, triclinic, space group $P1$, $a = 11.247(2)$, $b = 17.547(5)$, $c = 8.587(2)$ Å, $\alpha = 90.23(2)^\circ$, $\beta = 109.41(2)^\circ$, $\gamma = 95.69(2)^\circ$, $V = 1589.2(7)$ Å³, $T = 301$ K, $Z = 2$, $\mu(\text{Mo K}\alpha) = 66.70 \text{ cm}^{-1}$, $D_{\text{calcd}} = 2.357 \text{ g cm}^{-3}$, $R = 0.069$ and $R_w = 0.069$ for 2929 observed reflections with $I > 3\sigma(I)$ from 7288 unique reflections.
- 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).