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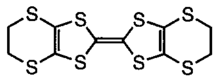
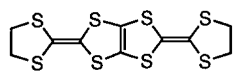
BDH-TTP as a Structural Isomer of BEDT-TTF, and Its Two-Dimensional Hexafluorophosphate Salt

Jun-ichi Yamada,* Maki Watanabe, Hiroyuki Anzai, Hiroyuki Nishikawa,* Isao Ikemoto, and Koichi Kikuchi*

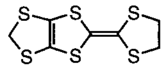
Tetrathiafulvalenes (TTFs) are highly promising π-electron donors for the exploration of new, molecular-based organic metals and superconductors.[1] Of the TTFs synthesized thus far, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is known to yield the largest number of two-dimensional superconducting salts.[2] One structural isomer of BEDT-TTF,[3] the bis-fused dihydrotetrathiafulvalene (DHTTF) compound 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (**1**, BDH-TTP), is very attractive because it contains no TTF moiety, yet it would be expected to produce organic metals that retain the metallic state down to low temperatures. This supposition is based on the results of our recent investigations which showed that a) methylenedithiodihydrotetrathiafulvalene (**2**, MDHT) forms a metallic $(MDHT)_2AuI_2$ salt which is stable down to 1.4 K, although its π-electron system is less extended than that of TTF,[4a] and b) various organic metals are obtained from the fused TTF-DHTTF donors **3a–c** which have more extended π-electron systems than TTF.[4b] Here we report the synthesis, electrochemical properties, and molecular structure of BDH-TTP as well as the conducting behavior of its charge transfer (CT) complexes and salts.



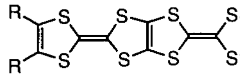
BEDT-TTF



BDH-TTP **1**



MDHT **2**



3a : R = H
3b : R = SMe
3c : R-R = $S(CH_2)_2S$

Our synthetic route to BDH-TTP (**1**) is outlined in Scheme 1. Ketone **5**, a precursor of **6**, was readily available from ketone **4** in 95 % yield.[5] Reaction of **5** with MeMgBr in THF followed by trapping with Cl_2SnBu_2 gave tin dithiolate **6**, which in a key step underwent Me_3Al-promoted coupling[6]

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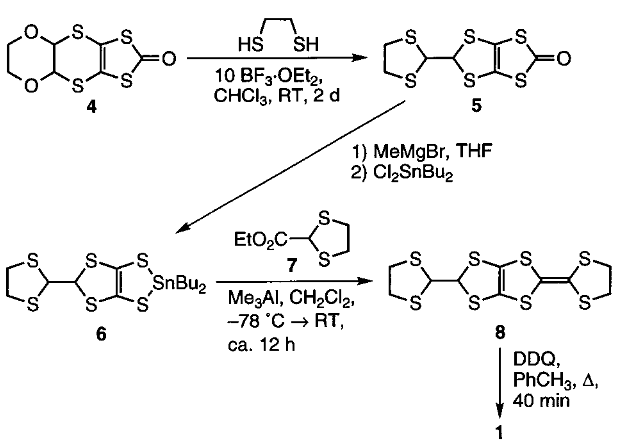

Scheme 1. Synthesis of BDH-TTP (**1**).

with ethyl 1,3-dithiolane-2-carboxylate (**7**; 2 equiv of Me_3Al in CH_2Cl_2) to afford dithiolane-added derivative **8** of MDHT (52% overall yield from ketone **5**). Oxidation of the C–C bond between two dithioacetal groups of **8** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.1 equiv) in refluxing toluene furnished BDH-TTP in 89% yield.

The redox behavior of BDH-TTP was investigated by cyclic voltammetry in $PhCN/CS_2$ (1/1); for comparison, BEDT-TTF was also studied (BDH-TTP: $E_1 = +0.56$, $E_2 = +0.82$, $E_3 = +1.52$, ΔE $(E_2 - E_1) = 0.26$ V (vs. SCE); BEDT-TTF: $E_1 = +0.61$, $E_2 = +0.87$, ΔE $(E_2 - E_1) = 0.26$ V). Two pairs of reversible redox waves and one irreversible oxidation wave (corresponding to E_3) were observed in the cyclic voltammogram of BDH-TTP. The first oxidation potential (E_1) is less positive than that of BEDT-TTF, which suggests that oxidation of BDH-TTP is easier. In contrast, the ΔE value, which reflects the magnitude of the on-site Coulombic repulsion, is equal to that of BEDT-TTF.

The molecular structure of BDH-TTP was determined by X-ray crystallographic analysis of a single crystal obtained by recrystallization from CS_2. As depicted in Figure 1, the BDH-TTP molecule contains three tetrathioethylene units in an approximately common plane, and the two ethylene end groups are distorted from that plane. In contrast to the molecular structure of BEDT-TTF,[7] this structure is approximately planar.

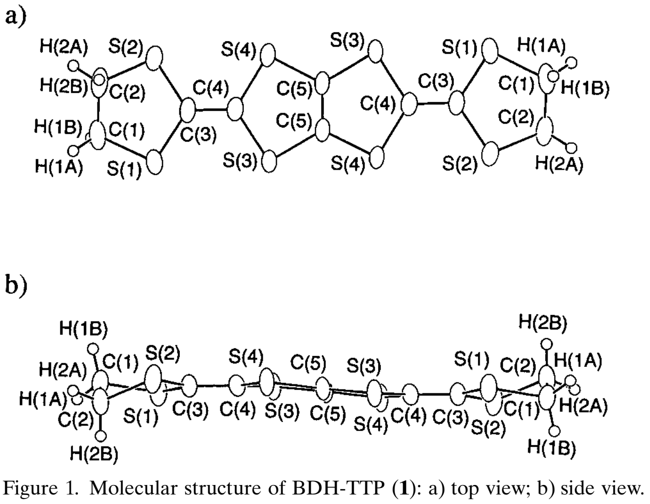

Figure 1. Molecular structure of BDH-TTP (**1**): a) top view; b) side view.

The conducting behavior of the CT complexes and salts of BDH-TTP is summarized in Table 1. As expected from its E_1 value, BDH-TTP reacted with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and the tetrafluoro analogue ($TCNQF_4$) in 1,1,2-trichloroethane (TCE) at room temperature to form CT complexes, but their conductivities at room temperature were fairly low. In contrast, the salts thus far obtained from BDH-TTP and tetrabutylammonium salts with various counter anions in chlorobenzene (PhCl) or TCE by the controlled-current electrocrystallization method[8] remained essentially metallic down to very low temperatures. Moreover, as the temperature decreased, their similar resistive behavior was independent of the structure and volume of the counter anions (Figure 2).

Table 1. Composition and conductive properties of complexes and salts of BDH-TTP (**1**).

Acceptor	Solvent	**1**:A[a]	σ_{RT} [S cm^{-1}][b]
TCNQ	TCE	1:1	2.0×10^{-7} ($E_a = 0.43$ eV)
$TCNQF_4$	TCE	3:2	5.6×10^{-5} ($E_a = 0.42$ eV)[c]
I_3^-	PhCl	2:1	230 (metallic at $T \geq 2.0$ K)
AuI_2^-	TCE	2:1	49 (metallic at $T \geq 2.0$ K)
BF_4^-	TCE	2:1	33 (metallic at $T \geq 2.0$ K)
ClO_4^-	TCE	–[d]	106 (metallic at $T \geq 2.2$ K)
PF_6^-	TCE	2:1	102 (metallic at $T \geq 2.1$ K)
AsF_6^-	TCE	2:1	49 (metallic at $T \geq 2.0$ K)

[a] A = acceptor. Ratio determined by elemental analysis. [b] Room-temperature conductivity measured by a four-probe technique for a single crystal unless otherwise stated. [c] Data for a compressed pellet. [d] Not determined because this complex may explode during analysis.

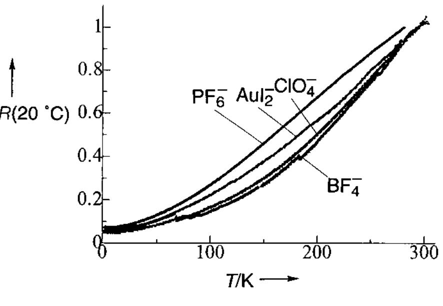

Figure 2. Temperature dependence of the relative electrical resistance, $R(T)/R(20\,^{\circ}C)$, of the metallic BDH-TTP salts with different counter anions.

The crystal structure of $(BDH\text{-}TTP)_2PF_6$ was also determined by X-ray crystallographic analysis. The structure consists of κ-type sheets of BDH-TTP donor molecules and sheets of PF_6^- anions (Figure 3). The interplanar distance between pairs of donor molecules is 3.53 Å, and the dihedral angle of the molecular planes between pairs is 82°. These values are almost identical to those in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[9] In the donor sheet, each molecule is linked by several S···S contacts shorter than the sum of the van der Waals radii (Figure 4). The large intermolecular overlap integrals are also calculated, not only within a pair

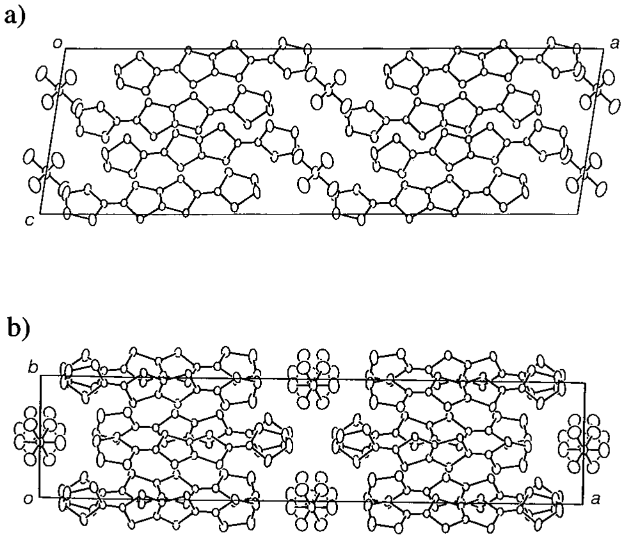

Figure 3. Crystal structure of $(BDH\text{-}TTP)_2PF_6$ viewed along the *b* axis (a) and the *c* axis (b).

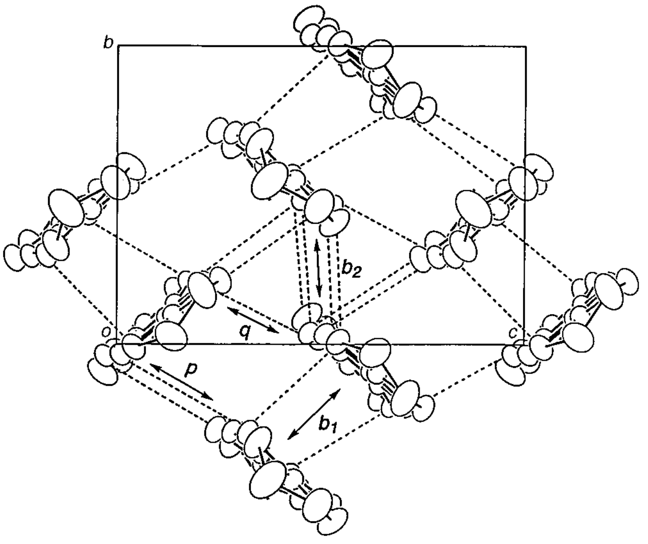

Figure 4. Donor arrangement of $(BDH\text{-}TTP)_2PF_6$. Intermolecular S···S contacts (<3.70 Å) are indicated by the dashed lines. The values of intermolecular overlap integrals are $b_1 = 20.7$, $b_2 = 19.6$, $p = 5.9$, and $q = -7.5 \times 10^{-3}$.

of donor molecules but also between pairs which form the 2D interaction in the *bc* plane. This 2D electronic structure is responsible for the metallic behavior down to low temperatures.

We have also determined the character of the highest occupied molecular orbital of BDH-TTP. Figure 5 shows its distribution as calculated by the extended Hückel method. It is noteworthy that in contrast to other TTP-type donor molecules, the atomic orbital (2pπ) coefficients of two carbon atoms on the central double bond in the DHTTF backbone differ significantly.[10]

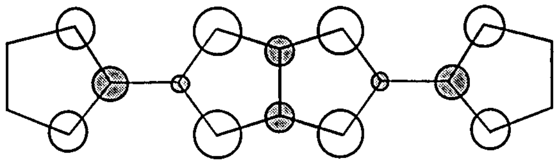

Figure 5. The highest occupied molecular orbital (HOMO) of BDH-TTP (**1**).

In conclusion, the BDH-TTP donor is demonstrated to produce a metallic 2D salt. One synthetic target in this area of chemistry is the construction of a donor which is not based on TTF and which tends to stack with 2D interactions.[11] Our studies on the DHTTF-based donor, described herein, represent a step forward in this direction. Further investigations on X-ray crystallographic analyses of other BDH-TTP salts and crystal growth with complex anions, for example, $[Cu(NCS)_2]^-$ and $[Cu\{N(CN)_2\}X]^-$ (X = Cl and Br), are currently in progress.

Experimental Section

1: M.p. 205 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.47$ (s, 8H): EI-MS: *m*/*z* (%): 386 (35, $[M^{+}+2]$), 384 (100, $[M^{+}]$), 280 (34), 268 (24); HR-MS calcd for $C_{10}H_8S_8$: 383.8392, found: 383.8389; elemental analysis calcd for $C_{10}H_8S_8$: C 31.22, H 2.10; found: C 30.98, H 1.98.

6: M.p. 163 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.14 - 3.25$ (m, 4H), 3.40 – 3.51 (m, 4H), 4.86 (dd, $J = 10.5$, 10.5 Hz, 2H); EI-MS: *m*/*z* (%): 388 (35, $[M^{+}+2]$), 386 (100, $[M^{+}]$), 281 (90); HR-MS calcd for $C_{10}H_{10}S_8$: 385.8548, found: 385.8552; elemental analysis calcd for $C_{10}H_{10}S_8$: C 31.05, H 2.61; found: C 31.06, H 2.51.

Data for X-ray crystallographic analysis were collected at $T = 293$ K on a MacScience MXC18 four-circle diffractometer, and all calculations were performed using CRYSTAN (MacScience, Japan).Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102772 (**1**) and CCDC-102773 ($(\mathbf{1})_2PF_6$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **1**: $C_{10}S_8H_8$, $M_r = 383.84$, monoclinic, space group, $P2_1/n$, $a = 9.583(2)$, $b = 9.593(2)$, $c = 8.106(2)$ Å, $\beta = 106.41(2)°$, $V = 714.8(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.783$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 112.65$ cm^{-1}, crystal dimensions 0.3 × 0.15 × 0.05 mm, min./max. transmission = 0.57. Data were collected with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) with the $\omega - 2\theta$ scan technique to a maximum 2θ of 120° and corrected for absorption by the difabs method. The structure was solved by direct methods and refined by full-matrix least squares (non-hydrogen atoms with anisotropic displacement parameters; all hydrogen atoms refined in isotropic approximation; 86 variables) against F^2 with 994 reflections $[I > 2.00\sigma(I)]$ out of 1175 independent reflection to yield $R = 0.0434$ and $R_w = 0.0579$; max./min. residual electron density 0.29/ – 0.39 e Å^{-3}.

Crystal data for $(\mathbf{1})_2PF_6$: $C_{20}S_{16}H_{16}PF_6$, $M_r = 912.64$, monoclinic, space group $C2/c$, $a = 35.800(9)$, $b = 7.946(3)$, $c = 11.116(4)$ Å, $\beta = 98.75(2)°$, $V = 3125.5(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.939$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 12.029$ cm^{-1}, crystal dimensions 0.35 × 0.3 × 0.1 mm, min./max. transmission = 0.77. Data were collected with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) with the $\omega - 2\theta$ scan technique to a maximum 2θ of 60° and corrected for absorption with the difabs method. The structure was solved by direct method and refined by full-matrix least squares (non-hydrogen atoms with anisotropic displacement parameters; all hydrogen atoms refined in isotropic approximation; 203 variables) against F^2 with 3660 reflections $[I > 2.00\sigma(I)]$ out of 4327 independent reflection to yield $R = 0.0421$ and $R_w = 0.0615$; max./min. residual electron density 0.91/ – 0.67 e Å^{-3}.

Received: September 2, 1998 [Z12366IE]
German version: *Angew. Chem.* **1999**, *111*, 841 – 843

Keywords: charge transfer · conducting materials · Lewis acids · radical ions · sulfur heterocycles

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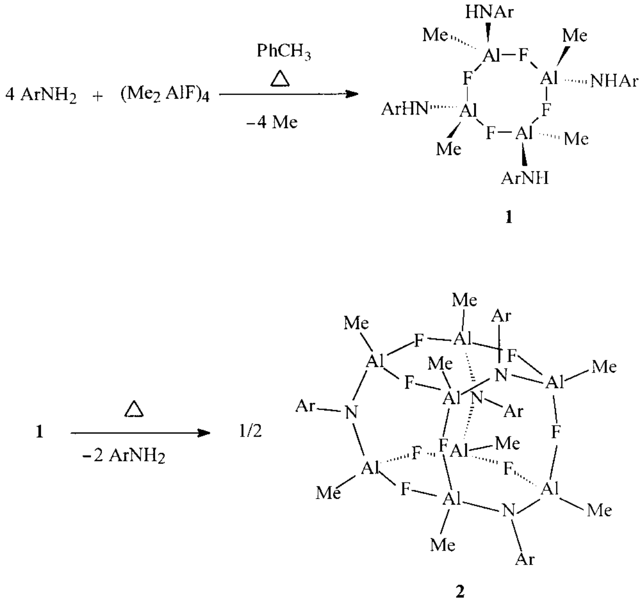
[{MeAl(μ_2-F)}$_2$N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_4$—A Molecular Al-F-N Cage Compound**

Helge Wessel, Hyung-Suh Park, Peter Müller,
Herbert W. Roesky,* and Isabel Usón

AlN and AlF$_3$ are high-melting, temperature-stable solids that are insoluble in organic solvents. In the last years soluble precursors of both compounds have become available which lead to AlN[1] and AlF$_3$[2], respectively, upon elimination under relatively mild conditions. Our goal now was to find out whether it is possible to combine the two systems and to synthesize soluble precursors containing Al, F, and N. Here we describe the synthesis of [(2,6-*i*Pr$_2$C$_6$H$_3$NH)MeAl(μ_2-F)]$_4$ (**1**) and its pyrolysis to the first Al-F-N cage compound **2**, which was characterized by X-ray structure analysis,[3] NMR and IR spectroscopy as well as mass spectrometry. Compound **2** was obtained as colorless crystals after a two-step elimination reaction from Me$_2$AlF and (2,6-*i*Pr$_2$C$_6$H$_3$)NH$_2$ (Scheme 1).



Scheme 1. Synthesis of **1** and **2**. Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

In the first step of the reaction, one methyl group at each Al atom of the eight-membered starting material (Me$_2$AlF)$_4$[4] was replaced by a (2,6-*i*Pr$_2$C$_6$H$_3$)NH residue under methane elimination. Compound **1** was isolated and characterized: In the EI mass spectrum the peak for $[M-3\,\mathrm{Me}]^+$ was detected at m/z 902, the ^{19}F NMR signals ($\delta = -141$ and -140) for the Al-bridging fluorine atoms were in accord with those of known Al-F-Al substructures,[5, 6] and the elemental analysis confirmed the composition. The pyrolysis of **1** then surprisingly took place under (2,6-*i*Pr$_2$C$_6$H$_3$)NH$_2$ elimination. This reaction sequence, which takes place at two very different temperatures, allowed the isolation of **2** in high yields.

Compound **2** crystallizes in the tetragonal space group $P\bar{4}2_1c$ with one-quarter of a molecule in the asymmetric unit; the remaining three-quarters are generated by the $\bar{4}$ axis. The center of the structure is a cubic cage, the six faces of which form four eight-membered Al$_4$N(μ_2-F)$_3$ rings in a half-chair conformation and two likewise eight-membered Al$_4$N$_2$(μ_2-F)$_2$ rings in a boat conformation (Figure 1). All rings consist of alternating metal and nonmetal atoms. To complete the coordination sphere each Al atom carries a methyl group, and each N atom is bound to a 2,6-diisopropylphenyl residue.

The mean Al–N bond length in **2** (1.788(3) Å) lies within the typical range for Al–N bonds,[7] the Al–F bonds (on average 1.785(3) Å) are longer than Al–F single bonds (1.65 Å), but quite typical for μ_2-bridging F atoms.[8] The aluminum atoms are all coordinated in a slightly distorted tetrahedron (angular sum 651.5° (ideal tetrahedron: 657.0°)), in which four groups of angles can be distinguished: F-Al-F (1 ×), C-Al-N (1 ×), N-Al-F (2 ×), and C-Al-F angles (2 ×).

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[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Bundesministerium für Bildung, Forschung und Technologie, the Witco GmbH, Bergkamen, and the Göttinger Akademie der Wissenschaften. H.W. thanks the Fonds der Chemischen Industrie for a doctoral fellowship.