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# New Organic Superconductors $\beta$-(BDA-TTP)$_2$X [BDA-TTP = 2,5-Bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene; X$^-$ = SbF$_6{}^-$, AsF$_6{}^-$, and PF$_6{}^-$]

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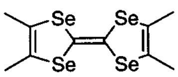
**Abstract:** The synthesis, electrochemical properties, and molecular structure of a new $\pi$-electron donor, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP), is described. In contrast to the hitherto-known tetrachalcogenafulvalene $\pi$-donors providing organic superconductors, this donor contains only the bis-fused 1,3-dithiole-2-ylidene unit as a $\pi$-electron system, yet produces a series of ambient-pressure superconductors $\beta$-(BDA-TTP)$_2$X [X = SbF$_6$ (magnetic $T_c$ = 6.9 K, resistive $T_c$ = 7.5 K), AsF$_6$ (magnetic $T_c$ = 5.9 K, resistive $T_c$ = 5.8 K), and PF$_6$ (magnetic $T_c$ = 5.9 K)], which are isostructural. The values of the intermolecular overlap integrals calculated on the donor layers of these superconductors suggest a two-dimensional (2D) electronic structure with loose donor packing. Tight-binding band calculations also indicate that these superconductors have the 2D band dispersion relations and closed Fermi surfaces.

## Introduction

Following the discovery of superconductivity in organic cation-radical salts (TMTSF)$_2$X (TMTSF = tetramethyltetraselenafulvalene, X = monovalent anions),[1] a good number of molecular-based organic superconductors have been developed over the past two decades.[2] These superconductors, excluding fullerene superconductors, are composed of organic donor components, which are classified into two categories: (i) $\pi$-electron donors such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), dimethyl(ethylenedithio)diselenadithiafulvalene (DMET), and bis(ethylenedithio)tetraselenafulvalene (BETS), which directly contribute to the superconductivity; (ii) organic countercations such as R$_4$N$^+$ in M(dmit)$_2$ (M = Ni and Pd; dimt = isotrithionedithiolate) superconductors, which cannot participate in electrical conduction.[3] However, all the known $\pi$-electron donors belonging to the former category contain the tetrachalcogenafulvalene molecule. Therefore, the very important and challenging question in this field of whether the production of superconductors from a new organic $\pi$-electron donor containing no tetrachalcogenafulvalene molecule was feasible remained unsolved. The settlement of this long-standing issue would change the way of thinking of molecular designers for the design of an organic superconductor.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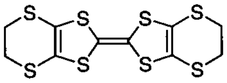
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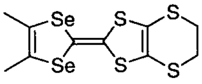
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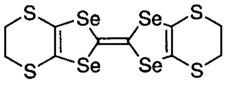
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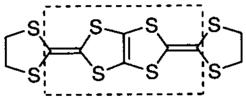
Meanwhile, we have found many metallic 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH-TTP) salts stable down to low temperatures regardless of the counteranions used.[4] This finding indicates that the 2,5-bis(methylene)-1,3,4,6-tetrathiapentalene (BM-TTP) unit alone is a sufficient $\pi$-electron system to form organic metals. The BM-TTP molecule is a structure isomer of tetrathiafulvalene (TTF) *but not TTF*, and, likewise, BDH-TTP is a structure isomer of BEDT-TTF *but not a TTF-containing donor*. In fact, the key structural differ-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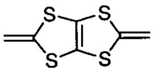
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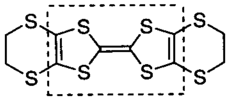
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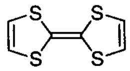
TTF

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[†] Himeji Institute of Technology.

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(1) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2440−2442 and references therein.

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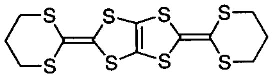
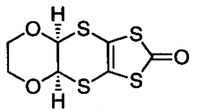
ences when comparing BDH-TTP with BEDT-TTF are the following: (i) the whole molecular structure of BDH-TTP is more planar than that of BEDT-TTF and (ii) the ethylene end groups of BDH-TTP are component parts of the rigid five-membered rings, while those of BEDT-TTF are comprised in the more flexible six-membered rings, which allow the molecule to adopt a variety of different conformations. This structural flexibility is presumably responsible for the fact that BEDT-TTF can produce superconductors, whereas the BDH-TTP salts so far prepared remain metallic all the way down to low temperatures (ca. 2 K) and do not undergo superconducting transitions. Thus, we attempted to synthesize the dithiane analogue of BDH-TTP, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP), with the aim of increasing the structural flexibility of the BDH-TTP molecule. Although the BM-TTP unit or, more generally speaking, the bis-fused 1,3-dithiole-2-ylidene unit has been proposed as a conducting component molecule to classify organic superconductors,[5] there was no practical precedent for the preparation of superconductors from $\pi$-electron donors with only this unit as a $\pi$-system. Therefore, if BDA-TTP could produce superconductors, they would be the first organic superconductors containing no tetrachalcogenafulvalene molecule in a donor component capable of contributing to superconductivity. We now describe the synthesis, molecular structure, and electrochemical properties of BDA-TTP. We also report that BDA-TTP provides a series of superconducting salts β-(BDA-TTP)$_2$X (X = SbF$_6^-$, AsF$_6^-$, and PF$_6^-$ anions).



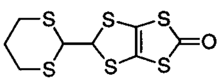
**BDA-TTP**

## Results and Discussion

**Synthesis, Molecular Structure, and Electrochemical Properties of BDA-TTP.** In analogy with the synthetic route to BDH-TTP,[4] the synthesis of BDA-TTP began with the dioxane-fused ketone **1**.[6] Thus, the BF$_3$·OEt$_2$-promoted reaction of **1** with 1,3-propanedithiol gave the dithiane-added ketone **2** via the skeletal rearrangement (70% yield).[7] Treatment of **2** with MeMgBr in THF followed by trapping with Cl$_2$SnBu$_2$ led to the labile tin dithiolate **3**, which was immediately reacted with ethyl 1,3-dithiane-2-carboxylate in the presence of 2 equiv of Me$_3$Al to afford the desired coupling product **4** in 41% overall yield.[8] Subsequent 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation of **4** in refluxing toluene furnished BDA-TTP in 80% yield.



**1**



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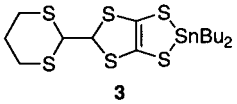

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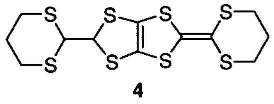

**4**

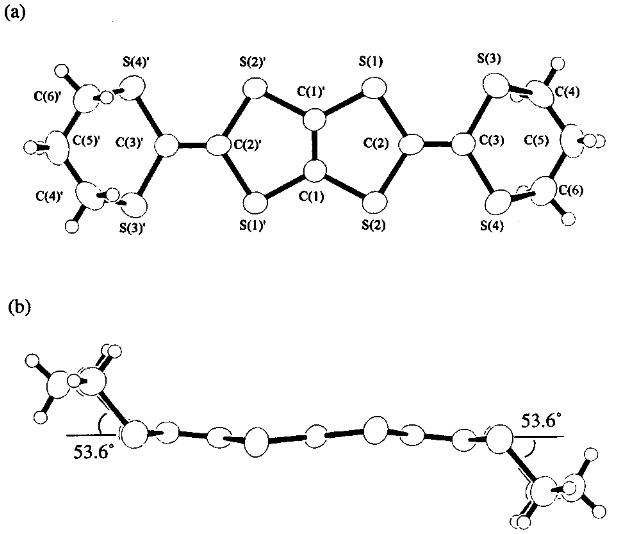

**Figure 1.** Top (a) and side (b) views of the molecular structure of BDA-TTP.

An X-ray diffraction analysis of a single crystal of BDA-TTP obtained by recrystallization from 1,1,2-trichloroethane (TCE) was undertaken for comparison with the molecular structure of BDH-TTP.[4] As depicted in Figure 1, the three tetrathioethylene units of BDA-TTP are found in an almost common plane; the same can be said for BDH-TTP. On the other hand, the two trimethylene end groups are far out of that plane in opposite directions, and the dihedral angle around the intramolecular sulfur-to-sulfur axis in each dithiane ring is 53.6°. Accordingly, the two dithiane rings with an equivalent chair conformation cause the whole molecular structure of BDA-TTP to be less planar than that of BDH-TTP.

For comparison with the oxidation potentials of BDH-TTP by cyclic voltammetry [$E_1 = +0.56$, $E_2 = +0.82$, $E_3 = +1.52$, $\Delta E(E_2 - E_1) = 0.26$ V (vs saturated calomel electrode); 0.1 M $n$-Bu$_4$ClO$_4$ in PhCN/CS$_2$ = 1/1; Pt electrode; at room temperature; under nitrogen; scan rate 50 mV s$^{-1}$],[4] the cyclic voltammetry measurement of BDA-TTP was carried out under the same experimental conditions. Similarly to the redox behavior of BDH-TTP, BDA-TTP showed two reversible oxidation waves [$E_1 = +0.72$, $E_2 = +0.90$, $\Delta E(E_2 - E_1) = 0.18$ V] and an additional irreversible oxidation wave ($E_3 = +1.26$ V). By the replacement of the ethylene end groups of BDH-TTP with the trimethylene end groups, the first oxidation potential ($E_1$) is shifted to a more positive value and the $\Delta E$ value is smaller, suggesting that the electron-donating ability is decreased, but the dicationic state is more easily generated. A similar electrochemical tendency can be observed between the heterocycle-fused DHTTF (dihydro-tetrathiafulvalene) donors and their dithiane analogues.[9] It is assumed that, in these donor systems, the dithiane ring being less planar than the dithiolane ring does not favor the conformational change into the flatter arrangements required to generate the cation-radical

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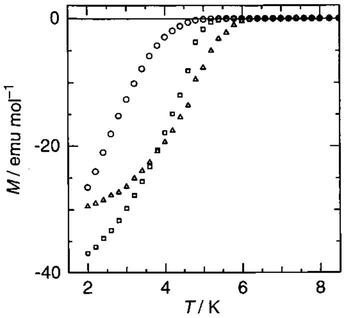

**Figure 2.** Temperature dependence of the ZFC dc magnetization for the $SbF_6$ (triangles), $AsF_6$ (squares), and $PF_6$ (circles) salts of BDA-TTP under an applied magnetic field of 1 Oe.

species ($D^{\bullet +}$), but once these species are formed, the trimethylene group acts as a stronger electron-donating group than the ethylene group to more readily lead to the dication species ($D^{2+}$).

**Preparation of the Charge-Transfer (CT) Materials of BDA-TTP.** The superconducting BDA-TTP salts with the octahedral anions $SbF_6^-$, $AsF_6^-$, and $PF_6^-$ (for superconductivity in these salts, vide infra) were prepared by the controlled-current electrocrystallization method[10] in TCE containing the corresponding tetra-*n*-butylammonium salts as the supporting electrolytes. Preparation of the BDA-TTP salt with the other anions, that is, the tetrahedral anions $ClO_4^-$ and $BF_4^-$, and the linear anion $I_3^-$ was also carried out by the same method. Although we reported that BDH-TTP reacts with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in TCE at room temperature to give the CT complex,[4] our attempt to prepare the crystalline TCNQ complex with BDA-TTP under similar reaction conditions was unsuccessful probably due to the higher $E_1$ value of BDA-TTP relative to that of BDH-TTP. Heating at 80 °C in TCE was thus required to obtain the TCNQ complex with BDA-TTP, while BDA-TTP was found to form the CT complex with a stronger acceptor, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$), in TCE at room temperature.

**Magnetic Properties of the BDA-TTP Superconductors.** The zero-field-cooled (ZFC) temperature dependence of the dc magnetization for the BDA-TTP salts with $SbF_6^-$, $AsF_6^-$, and $PF_6^-$ anions, which was measured using multiple platelike single crystals under an applied magnetic field of 1 Oe, revealed that the onset of diamagnetic transition occurs at temperatures of 6.9 K for the $SbF_6$ salt and of 5.9 K for both the $AsF_6$ and $PF_6$ salts (Figure 2). From their ZFC susceptibility curves at 2 K, we estimated that the diamagnetic shielding effects of the $SbF_6$, $AsF_6$, and $PF_6$ salts are ca. 15%, 20%, and 15% of the perfect diamagnetism ($-1/4\pi$ emu $cm^{-3}$), respectively.[2]

**Electrical Conducting Behavior.** Table 1 summarizes the electrical conducting behavior of the CT salts and complexes based on BDA-TTP. Superconductivity in the $SbF_6$ and $AsF_6$ salts was also recorded by the temperature dependence of their electrical resistivities under ambient pressure, as shown in Figure 3. On the resistive behavior of the $SbF_6$ salt, the resistivity increased as that in a semiconductor on cooling from room temperature to near 150 K, and then exhibited metallic behavior down to 7.5 K. Below this temperature, the resistivity displayed an abrupt drop and became almost zero below 6.5 K. The onset of superconducting transition observed in the subsequent heating process (the inset in Figure 3) was at 7.5 K, which is slightly higher than that in the magnetization measurement. Similar resistive maximum and superconductive behavior were found in the temperature dependence of the resistivity of the $AsF_6$ salt. Below near 160 K, the resistivity of this salt decreased with decreasing temperatures down to a superconducting transition with onset at 5.8 K, which is comparable to that of the magnetic transition, and almost zero resistance was observed below 4.4 K. Although we carried out resistive measurements on numerous single crystals of the $PF_6$ salt, all the crystal specimens were found to disintegrate at temperatures in the range of 110−140 K. In this temperature region, because no anomaly in the magnetic susceptibility of this salt was observed, it appears that there is no marked change in the electronic state. The decomposition of these crystal specimens could therefore be attributed to the stresses of the resistance-measuring probes or some other artifact of the measurements. Owing to the fragile nature of the crystals, superconducting transition of this salt could not be determined by resistive measurements. On the other hand, the temperature dependence of resistivities for the $ClO_4$, $BF_4$, and $I_3$ salts showed semiconductive behavior. Lack of superconductivity in the $ClO_4$ and $I_3$ salts with room-temperature conductivities comparable to those of three BDA-TTP superconductors was confirmed by magnetization measurements from 300 to 2 K. The room-temperature conductivities of the TCNQ and $TCNQF_4$ complexes were lower than those of the obtained BAD-TTP salts, and not superior to those of the corresponding complexes with BDH-TTP.[4]

**Table 1.** Conducting Behavior of the CT Materials Based on BDA-TTP

| acceptor | D:A[a] | $\sigma_{rt}$/S $cm^{-1}$ [b] |
|---|---|---|
| $SbF_6^-$ | 2:1 | 1.5 ($T_c^c = 7.5$ K) |
| $AsF_6^-$ | 2:1 | 2.9 ($T_c = 5.8$ K) |
| $PF_6^-$ | 2:1 | 3.8[d] |
| $ClO_4^-$ | −[e] | 2.4 ($E_a = 3$ meV) |
| $BF_4^-$ | 2:1 | $6.4 \times 10^{-3}$ ($E_a = 200$ meV) |
| $I_3^-$ | 2:1 | 1.3 ($E_a = 110$ meV) |
| TCNQ | 2:1 | $<10^{-6}$ |
| $TCNQF_4$ | 1:1 | $1.2 \times 10^{-5}$ [f] |

[a] Determined by elemental analysis. [b] Room-temperature conductivity measured by a four-probe technique on a single crystal unless otherwise noted. [c] The onset of superconducting transition temperature. [d] See the text. [e] Not determined because this salt may explode during analysis. [f] Measured on a compressed pellet.

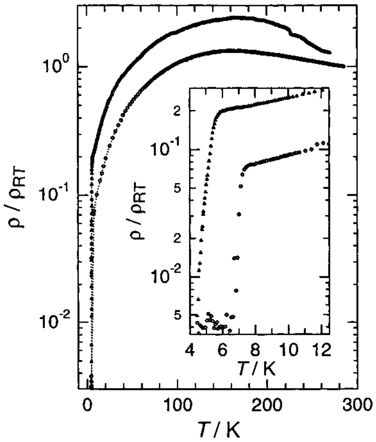

**Figure 3.** Temperature dependence of the relative resistivity for the $SbF_6$ (circles) and $AsF_6$ (triangles) salt of BDA-TTP. The dotted line is a guide for the eye. The inset shows the relative resistivity in the low-temperature region.

**Crystal and Electronic Structures of the BDA-TTP Superconductors.** All new superconductors crystallized in the triclinic space group $P\bar{1}$, which are isostructural. Figure 4 shows the crystal structure of $(BDA\text{-}TTP)_2SbF_6$, in which the molecular

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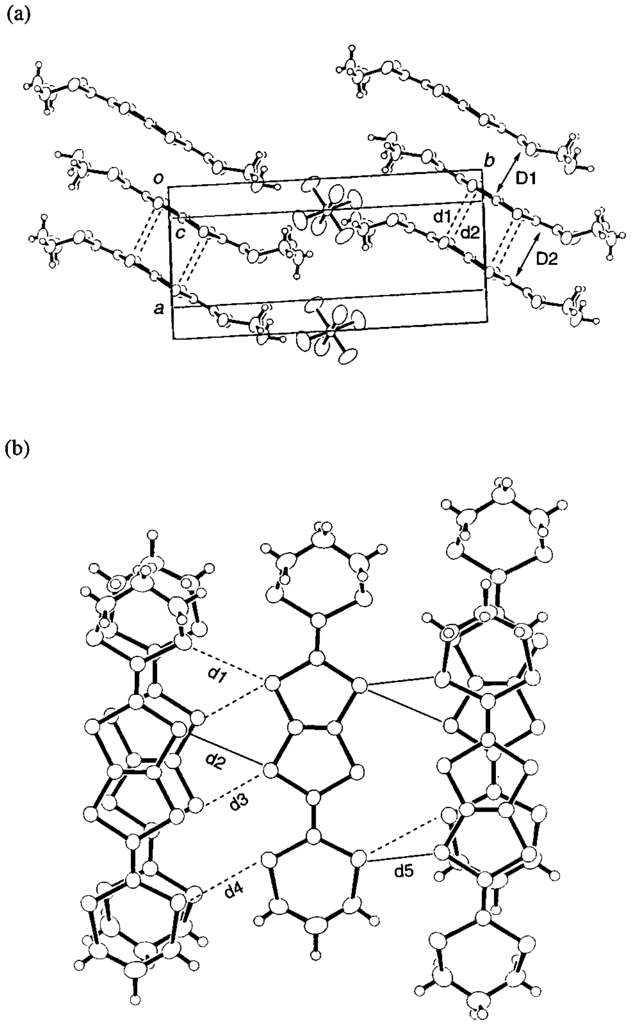

**Figure 4.** Crystal structure of β-(BDA-TTP)$_2$SbF$_6$. (a) Intermolecular S···S contacts (<3.70 Å) are indicated by dotted lines: d1 = 3.694(1) Å, d2 = 3.686(1) Å. Interplanar distances of the BDA-TTP column are 3.52 (D1) and 3.80 (D2) Å. (b) Intermolecular S···S distances close to 3.70 Å are indicated by dotted lines: d1 = 3.722(1) Å, d3 = 3.694(1) Å, d4 = 3.697(1) Å. Short intermolecular S···S contacts are indicated by thin lines: d2 = 3.645(1) Å, d5 = 3.649(1) Å.

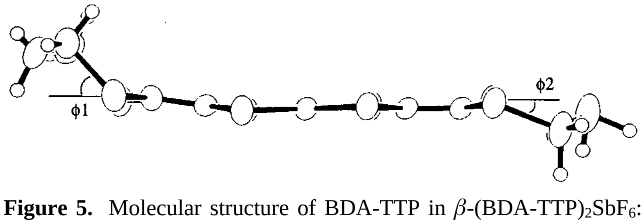

**Figure 5.** Molecular structure of BDA-TTP in β-(BDA-TTP)$_2$SbF$_6$: the dihedral angles $\phi 1$ and $\phi 2$ are 47.9° and 33.2°, respectively.

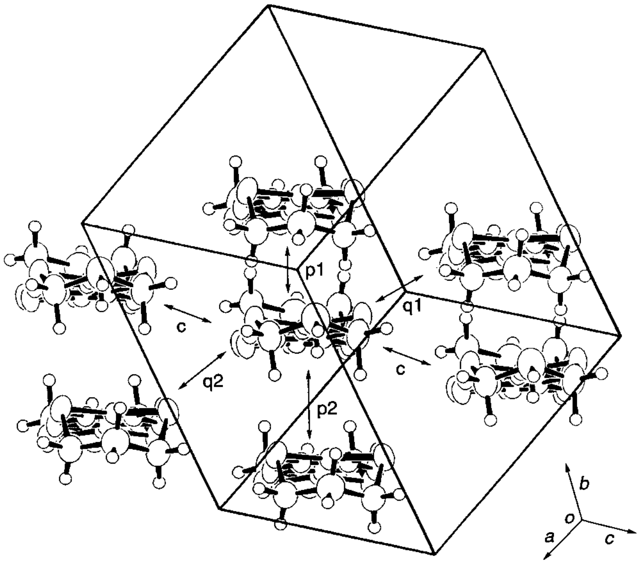

**Figure 6.** The values of intermolecular overlap integrals (× $10^{-3}$): β-(BDA-TTP)$_2$SbF$_6$, c = −0.44, p1 = 14.7, p2 = 6.26, q1 = 8.14, q2 = 8.89; β-(BDA-TTP)$_2$AsF$_6$, c = 0.34, p1 = 14.8, p2 = 5.31, q1 = 7.59, q2 = 9.00; and β-(BDA-TTP)$_2$PF$_6$, c = 0.41, p1 = 13.9, p2 = 9.02, q1 = 6.88, q2 = 8.63.

packing mode is very similar to that in β-(BEDT-TTF)$_2$I$_3$.[11] The whole molecular structure of BDA-TTP in this salt is somewhat flatter than that in the neutral state (Figure 5). Although the chair conformations of two outer dithiane rings remain unchanged, they are nonequivalent and their dihedral angles around the intramolecular sulfur-to-sulfur axis are 47.9° and 33.2°, respectively. The BDA-TTP molecules are stacked along the [101] direction and are somewhat dimerized: the donor molecules alternate at the average interplanar distances of 3.52 and 3.80 Å (Figure 4a). The two donor molecules being 3.52 Å apart are mutually shifted, while one pair with interplanar spacing of 3.80 Å has a nearly eclipsed arrangement, in which there are two intermolecular S···S contacts (3.694 and 3.686 Å) slightly shorter than the sum of van der Waals radii (3.70 Å). As shown in Figure 4b, three intermolecular S···S distances close to 3.70 Å (3.722, 3.694, and 3.697 Å) and two S···S contacts relatively shorter than 3.70 Å (3.645 and 3.649 Å) are observed between stacks. These structural characteristics of β-(BDA-TTP)$_2$SbF$_6$ hold also for the isostructural β-(BDA-TTP)$_2$AsF$_6$ and β-(BDA-TTP)PF$_6$ (see Table 2).

The S···S contact pattern found in intra- and interstacks of each BDA-TTP superconductor reflects the small anisotropy of the intermolecular overlap integrals, calculated on the basis of the extended Hückel method, in the *ac* plane (Figure 6). A tight-binding band calculation based on these overlap integrals also leads to the 2D band dispersion relation and nearly isotropic closed Fermi surface, which are peculiar to the β-structure, for each BDA-TTP superconductor (Figure 7). Furthermore, it is noteworthy that the largest overlap integrals in all three BDA-TTP superconductors (14.7, 14.8, and 13.9 × $10^{-3}$ for the SbF$_6$, AsF$_6$, and PF$_6$ salts, respectively) are roughly half of those in the known organic superconductors such as β-(BEDT-TTF)$_2$I$_3$ (24.5 × $10^{-3}$) [12] and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (25.7 × $10^{-3}$),[13] suggesting that they are characterized as a superconductor system with loose donor packing.

## Conclusion

As a structural modification to the BDH-TTP skeleton, we have succeeded in synthesizing its dithiane analogue, BDA-TTP, and, subsequently, in finding three kinds of superconducting BDA-TTP salts. The occurrence of superconductivity in the BDA-TTP salts demonstrates that tetrachalcogenafulvalene π-donors are not essential to the production of organic superconductors, and also extends the scope of the π-donor component to produce new superconductors. In addition,

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**Table 2.** Selected Structural Characteristics of $\beta$-(BDA-TTP)$_2$AsF$_6$ and $\beta$-(BDA-TTP)$_2$PF$_6$ with Labels Corresponding to Those Given in Figures 4 and 5

| | | | |
|---|---|---|---|
| | Dihedral Angles around the Intermolecular S−S Axis in Two Dithiane Rings | | |
| $\beta$-(BDA-TTP)$_2$AsF$_6$ | $\phi1 = 47.2°$ | $\phi2 = 34.5°$ | |
| $\beta$-(BDA-TTP)$_2$PF$_6$ | $\phi1 = 47.0°$ | $\phi2 = 34.0°$ | |
| | Interplanar Distances between Donors in the Stacking Direction | | |
| $\beta$-(BDA-TTP)$_2$AsF$_6$ | D1 = 3.51 Å | D2 = 3.78 Å | |
| $\beta$-(BDA-TTP)$_2$PF$_6$ | D1 = 3.46 Å | D2 = 3.77 Å | |
| | S···S Contacts within Stacks | | |
| $\beta$-(BDA-TTP)$_2$AsF$_6$ | d1 = 3.683(2) Å | d2 = 3.677(2) Å | |
| $\beta$-(BDA-TTP)$_2$PF$_6$ | d1 = 3.682(2) Å | d2 = 3.677(2) Å | |
| | S···S Distances between Stacks | | |
| $\beta$-(BDA-TTP)$_2$AsF$_6$ | d1 = 3.698(2) Å | d2 = 3.636(2) Å | d3 = 3.702(2) Å |
| | d4 = 3.697(2) Å | d5 = 3.629(2) Å | |
| $\beta$-(BDA-TTP)$_2$PF$_6$ | d1 = 3.689(2) Å | d2 = 3.635(2) Å | d3 = 3.712(2) Å |
| | d4 = 3.705(2) Å | d5 = 3.628(2) Å | |

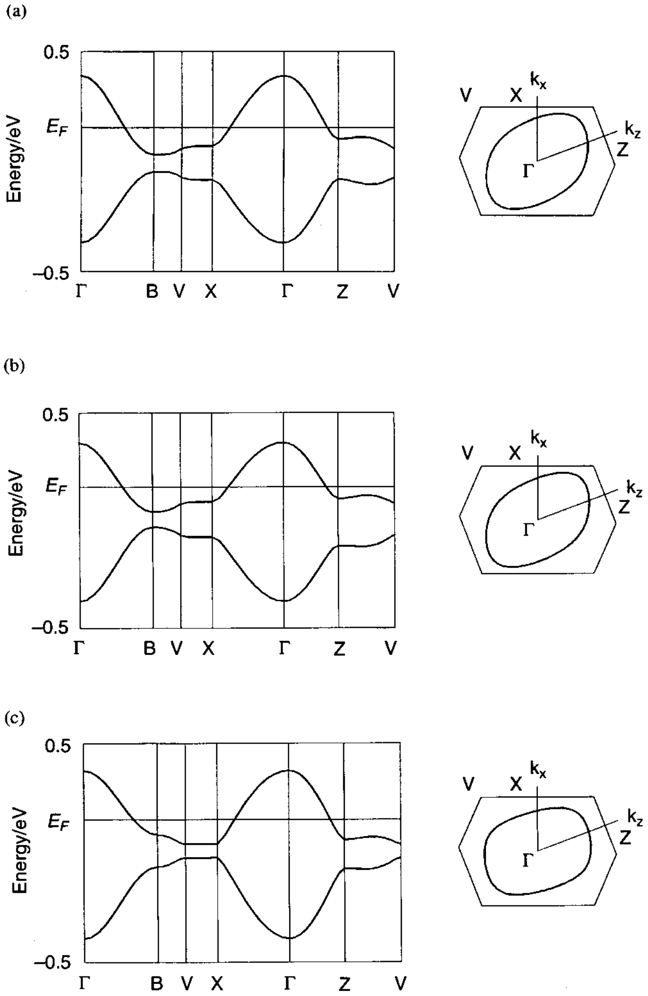

**Figure 7.** Energy band structures and Fermi surfaces of $\beta$-(BDA-TTP)$_2$SbF$_6$ (a), $\beta$-(BDA-TTP)$_2$AsF$_6$ (b), and $\beta$-(BDA-TTP)$_2$PF$_6$ (c).

considering that, among the hitherto-known $\pi$-donors providing superconductors, only BEDT-TTF and BETS produce more than three superconductors with a higher onset temperature of superconducting transition than 5 K under ambient pressure,[14] our finding means we have been able to break into this limited set of donor components.

From a synthetic point of view, our results obtained from investigations of BDH-TTP and BDA-TTP offer the following stepwise access to the achievement of organic superconductivity. First, it would be crucial to construct $\pi$-donor molecules that can generate tight intermolecular cohesion to retain the stable metallic state, irrespective of whether they contain the tetrachalcogenafulvalene molecule. The next step would be to clarify how structural modifications to those $\pi$-donor molecules bring about moderately loose donor packing motifs on the occasion of forming the CT materials. An increase of steric bulk on the periphery of BDH-TTP by introducing trimethylene groups instead of ethylene groups provides a good example of a way to address this issue.

It is expected that useful applications of our synthetic route to the symmetrical donors BDH-TTP and BDA-TTP will be found in the synthesis of other symmetrical analogues with the two same end groups, as well as unsymmetrical analogues with two different end groups. Besides these peripheral modifications, alternative structural modifications will also be applicable to the construction of BDH-TTP derivatives with moderately increased steric bulk. Such modifications of the BDH-TTP molecule are actively in progress in our laboratories, because it is possible that BDH-TTP and a variety of its derivatives, including BDA-TTP, lead to a new $\pi$-donor family that will be the support and driving force of the post-TTF era.

## Experimental Section

**General and Material.** All reactions were carried out in a dry reaction vessel under nitrogen. Column chromatography was performed on Merck Silica gel 60 (70−230 mesh). Melting points were determined on a Yamato Model MP-21 capillary melting point apparatus and are uncorrected. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a JEOL JNM-GX400, and their chemical shifts are expressed in parts per million ($\delta$) relative to CHCl$_3$ ($\delta$ 7.24) for $^1$H NMR and the center peak of CDCl$_3$ ($\delta$ 77.0) for $^{13}$C NMR. Low- and high-resolution mass spectra were obtained on a JEOL JMS-AX505HA. Cyclic voltammogram was registered on a Yanaco polarographic analyzer P-1100 with a Graphtec XY recorder WX2400 under the same conditions as described in our earlier report.[6]

All solvents were reagent grade and distilled prior to use, except CS$_2$ (Wako Pure Chemical Industries, Ltd.) which was used as received. Boron trifluoride diethyl etherate (Kanto Chemical Co., Inc.) was fractionally distilled and stored before use. 1,3-Propanedithiol (Kishida Chemical Co., Ltd.), Cl$_2$SnBu$_2$ (Tokyo Kasei Kogyo Co., Ltd.), ethyl 1,3-dithiane-2-carboxylate (Tokyo Kasei Kogyo Co., Ltd.), and DDQ (Tokyo Kasei Kogyo Co., Ltd.) were used as received. The organometallic reagents MeMgBr/THF and Me$_3$Al/$n$-hexane were purchased from Kanto Chemical Co., Inc., and used without further titration. The organic acceptor TCNQ (Osaka Organic Chemistry Kogyo Co., Ltd.) was purified by recrystallization from CH$_3$CN, whereas TCNQF$_4$ (Tokyo Kasei Kogyo Co., Ltd.) was used as received. The supporting electrolytes $n$-Bu$_4$NBF$_4$, $n$-Bu$_4$ClO$_4$, and $n$-Bu$_4$NPF$_6$ were purchased

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[14] For BEDT-TTF, see ref 2. For BETS, see: Kobayashi, H.; Akutsu, H.; Arai, E.; Tanaka, H.; Kobayashi, A. *Phys. Rev.* **1997**, *B56*, R8526−R8529.

**Table 3.** Crystallographic Data of BDA-TTP and (BDA-TTP)$_2$X (X = SbF$_6$, AsF$_6$, and PF$_6$)

| | BDA-TTP | (BDA-TTP)$_2$SbF$_6$ | (BDA-TTP)$_2$AsF$_6$ | (BDA-TTP)$_2$PF$_6$ |
|---|---|---|---|---|
| formula | $C_{12}H_{12}S_8$ | $C_{24}H_{24}S_{16}Sb_1F_6$ | $C_{24}H_{24}S_{16}As_1F_6$ | $C_{24}H_{24}S_{16}P_1F_6$ |
| temperature/K | 295 | 295 | 295 | 295 |
| formula mass | 412.71 | 1061.15 | 1014.33 | 970.38 |
| crystal system | monoclinic | triclinic | triclinic | triclinic |
| *a*/Å | 6.400(2) | 8.579(1) | 8.523(3) | 8.503(2) |
| *b*/Å | 9.351(1) | 17.636(2) | 17.449(5) | 17.340(5) |
| *c*/Å | 13.9016(8) | 6.514(1) | 6.518(2) | 6.533(1) |
| α/deg | | 93.79(1) | 93.95(2) | 94.07(2) |
| *β*/deg | 90.97(1) | 110.75(1) | 110.74(2) | 110.73(2) |
| *γ*/deg | | 89.00(1) | 89.13(2) | 89.36(2) |
| $V$/Å$^3$ | 831.8(2) | 919.6(2) | 904.4(5) | 898.5(4) |
| space group | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| *Z* | 2 | 1 | 1 | 1 |
| $D_{calcd}$/Mg m$^{-3}$ | 1.648 | 1.92 | 1.86 | 1.79 |
| crystal dimensions/mm$^3$ | 0.3 ×0.2 × 0.1 | 0.5 ×0.35 × 0.2 | 0.5 ×0.3 × 0.25 | 0.3 ×0.3 × 0.1 |
| crystal color | yellow | black | black | black |
| radiation | Mo Kα | Mo Kα | Mo Kα | Mo Kα |
| *F*(000) | 424 | 529 | 511 | 511 |
| $\mu$(Mo Kα)/cm$^{-1}$ | 10.58 | 17.09 | 19.16 | 10.59 |
| diffractometer | Rigaku AFC7R (4-circle) | Rigaku AFC5R (4-circle) | Nonius CAD-4 (4-circle) | Nonius CAD-4 (4-circle) |
| scan type | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ |
| scan rate/deg min$^{-1}$ | 16 | 16 | 5.49 | 4.12 |
| scan width/deg | $1.68 + 0.3 \tan\theta$ | $1.73 + 0.5 \tan\theta$ | $1.70 + 0.35 \tan\theta$ | $1.25 + 0.35 \tan\theta$ |
| total no. of reflcns | 2214 | 5686 | 5682 | 5652 |
| no. of unique reflcns | 2039 | 5353 | 5251 | 5225 |
| 2$\theta$ range/deg | 2−55 | 2−60 | 2−60 | 2−60 |
| corrections | Lorentz−polarization<br>absorption | Lorentz−polarization<br>absorption | Lorentz−polarization<br>absorption | Lorentz−polarization<br>absorption |
| trans. factors | 0.9291−1.0000 | 0.7786−1.0000 | 0.7614−0.99968 | 0.7560−1.0000 |
| solution | direct method (SIR92) | isomorphous replacement from the PF$_6$ salt | isomorphous replacement from the PF$_6$ salt | direct method (SIR92) |
| refinement | full-matrix LS on *F* | full-matrix LS on *F* | full-matrix LS on *F* | full-matrix LS on *F* |
| no. of reflcns obsd ($I > 3.0\sigma(I)$) | 1213 | 3363 | 3489 | 2570 |
| no. of parameters | 109 | 250 | 250 | 250 |
| $R$; $R_W$ | 0.030; 0.017 | 0.038; 0.034 | 0.056; 0.063 | 0.056; 0.054 |
| GOF | 1.96 | 1.97 | 2.05 | 1.98 |
| max shift/error | 0.01 | 0.07 | 0.00 | 0.01 |
| max peak in final diff. map (e/Å$^{-3}$) | 0.23/−0.25 | 0.52/−0.54 | 1.02/−0.73 | 0.89/−0.69 |

from Tokyo Kasei Kogyo Co., Ltd. and purified by recrystallization, whereas *n*-Bu$_4$I$_3$, *n*-Bu$_4$AsF$_6$, and *n*-Bu$_4$SbF$_6$ were prepared by the standard procedures.

**4,5-[(1,3-Dithian-2-yl)methylenedithio]-1,3-dithiol-2-one (2).** To a solution of the dioxane-fused ketone **1** (532 mg, 2.0 mmol) in CHCl$_3$ (20 mL) were successively added 0.26 mL (2.6 mmol) of 1,3-propanedithiol and 3.3 mL (26 mmol) of BF$_3$·OEt$_2$ at room temperature. After the reaction mixture was stirred at 35 °C for 1 day, aqueous saturated NaHCO$_3$ solution was added at 0 °C, and the resulting suspension was filtered through a Celite pad, the Celite then being washed with CHCl$_3$. The aqueous layer was extracted with several portions of CHCl$_3$, and the extracts were combined, dried over MgSO$_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with *n*-hexane−CH$_2$Cl$_2$ as an eluent to give 440 mg (1.4 mmol) of **2** (70% yield): pale yellow powder; mp 136−140 °C dec from EtOH−CH$_2$Cl$_2$; $^1$H NMR (CDCl$_3$) $\delta$ 1.96−2.11 (m, 2 H), 2.71−2.77 (m, 2 H), 2.89−2.96 (m, 2 H), 4.17 (d, $J$ = 9.1 Hz, 1 H), 5.79 (d, $J$ = 9.1 Hz, 1 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 24.7, 27.1, 49.6, 61.9, 112.2, 192.4; MS (EI), *m*/*z* (% relative intensity) 314 (M$^+$ + 2, 5), 312 (M$^+$, 19), 119 (100); HRMS (EI) calcd for $C_8H_8OS_6$ (M$^+$) 311.8899, measured 311.8900. Anal. Calcd for $C_8H_8OS_6$: C, 30.74; H, 2.58. Found: C, 30.78; H, 2.58.

**2-(1,3-Dithian-2-ylidene)-5-(1,3-dithian-2-yl)-1,3,4,6-tetrathiapentalene (4).** To a solution of **2** (313 mg, 1.0 mmol) in THF (15 mL) was added dropwise a THF solution of MeMgBr (0.91 M × 3.6 mL, 3.3 mmol) at 0 °C, and the cooling bath was removed. After being stirred for 2 h, the mixture was cooled to −78 °C, and a solution of Cl$_2$SnBu$_2$ (304 mg, 1.0 mmol) in THF (8 mL) was added dropwise for 30 min. The reaction mixture was allowed to reach 0 °C and was quenched with brine. The resulting suspension was filtered through Celite, and the aqueous layer was extracted with several portions of CHCl$_3$. The organic extracts were combined, dried over MgSO$_4$, and concentrated in vacuo to give the tin dithiolate **3**: $^1$H NMR (CDCl$_3$) $\delta$ 0.93 (t, $J$ = 7.3 Hz, 6 H), 1.38 (sixtet, $J$ = 7.3 Hz, 4 H), 1.68 (m, 4 H), 1.73 (m, 4 H), 1.95−2.08 (m, 2 H), 2.69−2.75 (m, 2 H), 2.86−2.93 (m, 2 H), 4.17 (d, $J$ = 9.3 Hz, 1 H), 5.47 (d, $J$ = 9.3 Hz, 1 H). This compound was immediately subjected to the next reaction without purification, because its decomposition took place through silica gel.

To a solution of the crude **3** in CH$_2$Cl$_2$ (15 mL) at −78 °C were successively added dropwise a *n*-hexane solution of Me$_3$Al (1.01 M × 2.0 mL, 2.0 mmol) and 0.19 mL (1.2 mmol) of ethyl 1,3-dithiane-2-carboxylate via syringes. The reaction mixture was allowed to reach room temperature and was stirred overnight before being carefully quenched with saturated NaHCO$_3$ solution at 0 °C. The fine suspension was removed by filtration through a Celite pad, and the aqueous layer was extracted with several portions of CS$_2$. The organic extracts were combined, dried over MgSO$_4$, and concentrated under vacuum. The residue was purified through silica gel chromatography with hexane and CS$_2$ as eluents, followed by recrystallization from CS$_2$ to give 170 mg (0.41 mmol) of **4** (41% yield): yellow powder; mp 175 °C dec; $^1$H NMR (CDCl$_3$) $\delta$ 1.98−2.06 (m, 2 H), 2.13−2.19 (m, 2 H), 2.69−2.75 (m, 2 H), 2.83−2.86 (m, 4 H), 2.87−2.94 (m, 2 H), 4.23 (d, $J$ = 9.3 Hz, 1 H), 5.92 (d, $J$ = 9.3 Hz, 1 H); MS (EI), *m*/*z* (% relative intensity) 416 (M$^+$ + 2, 20), 414 (M$^+$, 55), 295 (100), 119 (54); HRMS (EI) calcd for $C_{12}H_{14}S_8$ (M$^+$) 413.8861, measured 413.8847. Anal. Calcd for $C_{12}H_{14}S_8$: C, 34.75; H, 3.40. Found: C, 34.77; H, 3.39.

**2,5-(1,3-Dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP).** To a solution of **4** (185 mg, 0.45 mmol) in refluxing toluene (48 mL) over an oil bath at 135 °C was added dropwise a solution of DDQ (126 mg, 97% purity, 0.54 mmol) in toluene (36 mL) for 30 min. After refluxing for an additional 10 min, the cooled reaction mixture was filtered through a Celite pad, and the filtrate was concentrated under vacuum. The residue was purified through silica gel chromatography with hexane−$CS_2$ as an eluent, followed by recrystallization from $CS_2$ to give 147 mg (0.36 mmol) of BDA-TTP (80% yield): mp 243 °C dec; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.15−2.21 (m, 4 H), 2.85−2.88 (m, 8 H); MS (EI), *m/z* (%) 414 ($M^+ + 2$, 37) 412 ($M^+$, 100), 338 (36); HRMS (EI) calcd for $C_{12}H_{12}S_8$ ($M^+$) 411.8705, measured 411.8703. Anal. Calcd for $C_{12}H_{12}S_8$: C, 34.91; H, 2.93. Found: C, 34.96; H, 2.89.

**General Procedure for Preparation of the BDA-TTP Salts.** According to the controlled-current electrocrystallization method described in our earlier papers,[10] all the BDA-TTP salts were prepared from BDA-TTP (0.07 mmol) in the presence of the corresponding tetra-*n*-butylammonium salts (0.28 mmol) in TCE (16 mL) at 20 °C under nitrogen for 35 days. During electrocrystallization, the current was controlled by a personal computer.

**Preparation of the TCNQ Complex.** To a solution of BDA-TTP (20.6 mg, 0.50 mmol) in TCE (10 mL) was added 10.2 mg (0.50 mmol) of TCNQ, and the mixture was heated at 80 °C for 2 h. The solvent evaporated to precipitate a black CT complex, a single crystal of which was obtained by recrystallization from TCE with slow cooling.

**Preparation of the TCNQF$_4$ Complex.** To a solution of BDA-TTP (20.6 mg, 0.50 mmol) in TCE (10 mL) was added 13.8 mg (0.50 mmol) of TCNQF$_4$, and the mixture was stirred overnight. The solvent evaporated to precipitate a dark-green CT complex, which was thoroughly washed with $CS_2$ due to its insufficient solubility in hot TCE.

**X-ray Structural Determination.** The data of X-ray structures were collected on Rigaku AFC7R, Rigaku AFC5R, and Enraf-Nonius CAD-4 diffractiometers. All calculations were performed with the teXsan crystallographic software package of the Molecular Structure Corporation. Detailed crystallographic data are summarized in Table 3.

**Magnetic Susceptibility Measurement.** Measurements were made on nonoriented single crystals held in aluminum foils inside a plastic tube (straw) with a Quantum Design MPMS 2 SQUID magnetometer with a $\mu$-metal shield. In the case of the ZFC measurement for each superconducting $\beta$-(BDA-TTP)$_2$X (X = $SbF_6$, $AsF_6$, or $PF_6$) salt, the sample was first cooled to 2 K under zero magnetic field [<0.3 Oe (the earth field)], and then dc magnetization data were taken in the field of 1 Oe on warming from 2 to 10 K.

**Electrical Conductivity Measurement.** Conductivity was measured by the four-probe technique with use of gold wire contacted to the surface of a single crystal or a compressed pellet with gold paste. It must be noted that the measurements for three BDA-TTP superconductors were made on the freshly cut surfaces of these single crystals.

**Calculation of Band Structures.** See the Experimental Section of ref 10a.

**Supporting Information Available:** Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for BDH-TTP and (BDA-TTP)$_2$X (X = $SbF_6$, $AsF_6$, and $PF_6$) (PDF); geometries of the three-dimensional structure of $\beta$-(BDA-TTP)$_2$X (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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