Halogenated Bis(methylthio)tetrathiafulvalenes as a Unique Donor System

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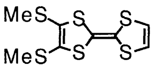
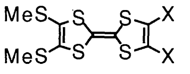
Chlorination, bromination and iodination of bis(methylthio)tetrathiafulvalene (BMT-TTF) produced mainly the dihalogenated products (BMT-TTFX$_2$) with small amounts of the monohalogenated derivatives (BMT-TTFX). The molecular structures of BMT-TTFBr$_2$ and BMT-TTFBr$_2$•I$_3$ have been determined, and the conductivities of CT-complexes and radical salts derived from BMT-TTFX$_2$ have been measured.

Weak intermolecular interactions have been recognized to play an important part in determination of crystal structures.[1] In particular, the Cl•••Cl interaction in molecular crystals has been investigated extensively to utilize the weak intermolecular interactions in crystal engineering.[2] We are interested in the halogenated tetrathiafulvalene and its derivatives, because these halogenated donors may show a unique crystal structure and an unusual electric conductivity behavior.[3,4] We report here the synthesis of BMT-TTFX$_2$ and the electric conductivities of their CT-complexes and radical salts with the X-ray structures of BMT-TTFBr$_2$ and BMT-TTFBr$_2$•I$_3$.

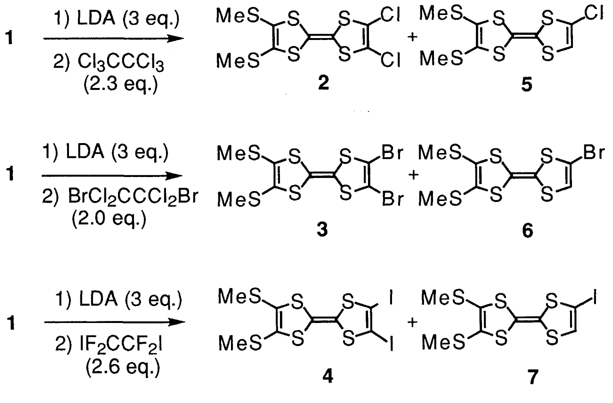


1 (BMT-TTF)



2: X = Cl (BMT-TTFCl$_2$)
3: X = Br (BMT-TTFBr$_2$)
4: X = I (BMT-TTFI$_2$)

Synthesis of the halogenated BMT-TTF derivatives was carried out by using lithiation of **1** with 3 equiv. of lithium diisopropylamide (LDA), followed by treatment with 2.0-2.6 equiv. of the halogenating reagents (Scheme 1). Although the reaction of ethylenedithiotetrathiafulvalene (EDT-TTF) with 2 equiv. of LDA led to the cleavage of the ethylenedithio ring,[5] the treatment of BMT-TTF **1** with 3 equiv. of LDA produced the corresponding lithio derivative without decomposition. Thus, the reaction of **1** with 3 equiv. of LDA in THF at -78 °C, followed by treatment with 2.3 equiv. of hexachloroethane at -78 °C to room temperature produced the dichloride **2** in 49% yield together with a small amount of the monochloride **5** (1%).[6] A similar reaction of **1** with 3 equiv. of LDA in THF at -78 °C, followed by treatment with 2 equiv. of 1,2-dibromotetrachloroethane at -78 °C to room temperature gave the dibromide **3** in 50% yield together with small amounts of the monobromide **6** (1%). In addition, iodination of **1** smoothly produced the diiodide **4** in contrast to the result of EDT-TTF.[3] Thus, the reaction of **1** with 3 equiv. of LDA in THF at -78 °C, followed by treatment with 2.6 equiv. of CF$_2$ICF$_2$I at -78 °C to room temperature gave **6** in 73% yield with the monoiodide **7** (5%).



Scheme 1.

The oxidation potentials of TTF, BMT-TTF, BEDT-TTF, and **2**-**4** measured by cyclic voltammetry are shown in Table 1. Although the halogenated BMT-TTF derivatives (**2**-**4**) show lower donor ability as compared with TTF and BMT-TTF, the oxidation potentials are only a little larger than BEDT-TTF which is a well-known donor.

Table 1. Cyclic voltammetric[a] and melting point data of BMT-TTFX$_2$ and related compounds

Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V	Mp/°C
TTF	0.36	0.74	—
BMT-TTF **1**	0.44	0.77	—
BEDT-TTF	0.52	0.83	—
2	0.69	0.94	111-111.5
3	0.66	0.91	121.5-122
4	0.59	0.87	115-115.5

[a]Conditions: n-Bu$_4$NClO$_4$ (0.1 mol dm^{-3}), benzonitrile, 20 °C, Pt working and counter electrodes. Potentials were measured against a Ag/Ag$^+$ electrode and converted to the value vs SCE (Fc/Fc+ = 0.31 V).

The molecular structure and packing diagram of **3** are shown in Figure 1.[7] The introduction of two bromine atoms into the BMT-TTF framework leads to a slight change in the C=C bonds of TTF core. The TTF core, two sulfur substituents and two bromine atoms in **3** show high coplanarity, the maximum atomic deviation from the least-squares plane being 0.153(1) Å. The packing mode is a centrosymmetric P2$_1$/c. There is no intermolecular S•••S distance less than the sum of the van der Waals radii, presumably due to the protrusive methyl groups which prevent the tight stacking of the molecule [Figure 1(c)].

Although compounds (**2**-**4**) formed no CT-complexes with TCNQ, solid complexes were isolated from acetonitrile-chloroform solutions of **2** and **3** with TCNQF$_4$ or from a benzene-chloroform solution of **4** with DDQ. The CT-complexes of **2** and **3** with TCNQF$_4$ showed electric conductivities of 1.2 x 10^{-2} and 8.5 x 10^{-3} S cm^{-1}, respectively, at room temperature, and the CT-complex of **4** with DDQ showed conductivity of 3.2

x 10^{-1} S cm^{-1}. Electrocrystallization of **2** and **4** gave fine crystals of the corresponding radical-cation salts. A compressed pellet of **2**•ClO_4 showed conductivity of 3.5 x 10^{-5} S cm^{-1}, whereas a compressed pellet of **4**•I_3 showed conductivity of 1.7 x 10^{-2} S cm^{-1}. On the other hand, single crystals of **3**•I_3 were obtained from electrocrystallization of **3**.

As shown in Figure 2, the crystal packing of **3**•I_3 indicates a very interesting structure.[8] The Br•••I and S•••I intermolecular interactions control the packing mode of **3**•I_3 in the crystal. Thus, the Br(1)•••I(1), Br(1)•••I(2), S(3)•••I(1), and S(3)•••I(2) distances are 3.896(2), 3.635(1), 3.803(3), and 3.746(3) Å, respectively, which are much shorter than the Br•••I and S•••I van der Waals distances (Br: 1.95 Å; S: 1.85 Å; I: 2.15 Å) [Figure 2(a)]. The donor molecule has a crystallographic C_{2v} symmetry, and the two-fold axis passes through the central C(1)=C(2) double bond [Figure 2(a)]. The central double bond C(1)=C(2) [1.42(2) Å] is fairly elongated as compared with that of the neutral **3** [1.334(5) Å]. Although **3**•I_3 forms as a 1:1 radical cation salt with a completely mixed-stacking structure, the room temperature conductivity of **3**•I_3 is found to be 2.1 x 10^{-2} S cm^{-1}. It is curious that there are no intermolecular short S•••S distances less than the sum of van der Waals radii. In order to estimate the conducting interaction, the overlap integrals of the conductive orbitals have been calculated [a1 in Figure 2(c) and c1 in Figure 2(b)]. The largest interaction is a head-to-head, donor-donor interaction a1 along the a axis. Along the c axis, the side-by-side interaction c1 is large, but other side-by-side interactions are zero. Our results reported here disclose that halogen-bonded TTF derivatives may produce a new type of synthetic metals using the X•••S and X•••X interactions in the crystals.

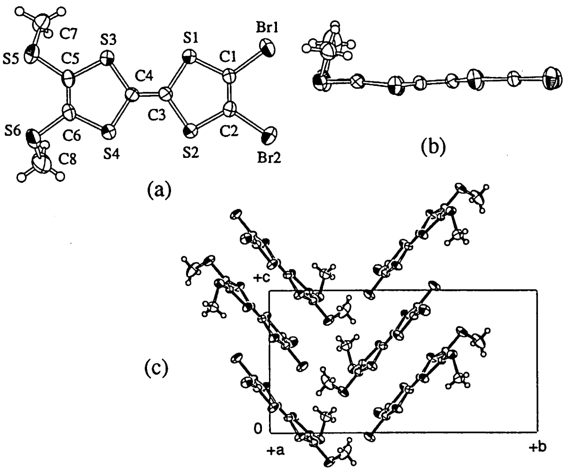


Figure 1. Crystal structure of 3. (a) Top view. (b) Side view. (c) Packing diagram. Selected bond distances [Å] and angles [°]: C1-Br1 = 1.861(4), C1-S1 = 1.742(4), C1-C2 = 1.316(5), S1-C3 = 1.756(4), C3-C4 = 1.334(5), C4-S3 = 1.763(4), S3-C5 = 1.756(4), C5-C6 1.340(5), Br1-C1-S1 = 115.9(2), Br1-C1-C2 126.1(3).

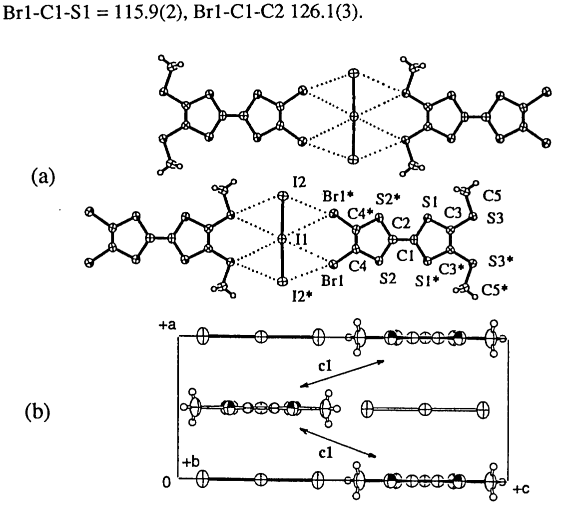


Figure 2. Crystal packing of 3•I_3. (a) Packing diagram along the a axis. (b) Packing diagram along the b axis. (c) Packing diagram along the c axis. Selected bond distances [Å]: Br1-C4 = 1.873(9); C1-C2 = 1.42(2), C3-C3* = 1.34(2), C4-C4* = 1.30(2). Overlap integrals (x10^{-3}) of the conduction orbitals in 3•I_3 are: a1 = -2.45; c1 = 0.86.

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6 The structures of all new compounds reported here were fully characterized by spectroscopic analyses. The selected data are as follows. **2**: MS (m/z) 366, 364 (M^+); ^1H NMR ($CDCl_3$) δ 2.43 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 127.8, 114.3, 114.1, 105.5, 19.2. **3**: MS (m/z) 458, 456, 454 (M^+); ^1H NMR ($CDCl_3$) δ 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 127.7, 113.3, 109.9, 101.5, 19.3. **4**: MS (m/z) 546 (M^+); ^1H NMR ($CDCl_3$) δ 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 127.6, 118.0, 111.1, 76.8, 19.3.
7 Crystal data for **3**: $C_8H_6S_6Br_2$, FW = 454.30, monoclinic, space group $P2_1/c$ (#14); a = 7.735(2) Å, b = 18.681(1) Å, c = 9.922(2) Å, β = 93.32(2) °, V = 1431.4(4) $Å^3$, Z = 4, d_{calcd} = 2.108 g cm^{-3}. The structure was solved by direct method using SIR92. Full matrix least-squares refinement yielded the final R value of 0.030 (R_W = 0.027) for 2043 independent reflections [$2\theta \leq 55.0$ °, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and ω-2θ scan.
8 Crystal data for **3**•I_3: $C_8H_6S_6Br_2I_3$, FW = 835.02, orthorhombic, space group $Cmcm$ (#63); a = 7.200(1) Å, b = 16.294(1) Å, c = 16.623(2) Å, V = 1950.2(4) $Å^3$, Z = 4, d_{calcd} = 2.844 g cm^{-3}. The structure was solved by direct method using SIR92, full matrix least-squares refinement yielding the final R value of 0.033 (R_W = 0.034) for 828 independent reflections [$2\theta \leq 55.0$ °, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and ω-2θ scan.