Syntheses and Properties of Halogenated EDT-TTF Derivatives

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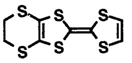
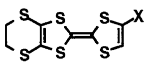
Chlorination and bromination of EDT-TTF produced mainly the dihalogenated products (EDT-TTFCl$_2$ and EDT-TTFBr$_2$) with small amounts of the monohalogenated derivatives. In contrast, iodination of EDT-TTF afforded the monoiodinated derivative as the major product, together with the diiodinated compound. The molecular structures of EDT-TTFCl$_2$ and EDT-TTFBr$_2$ have been determined, and the conductivities of CT-complexes and radical salts of new donors reported here have been measured.

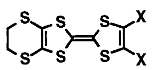
Ethylenedithiotetrathiafulvalene (EDT-TTF, **1**) has attracted considerable attention because this molecule affords high conducting cation-radical salts with various anions.[1] Furthermore, the two unsubstituted positions of EDT-TTF **1** enable the introduction of a variety of functional groups to this molecule to be utilized for the design of new donor systems. We report here the halogenation of EDT-TTF **1** and the X-ray analysis of two halogenated EDT-TTF's together with the data on the conductivities of their CT-complexes and radical salts.



1 (EDT-TTF)

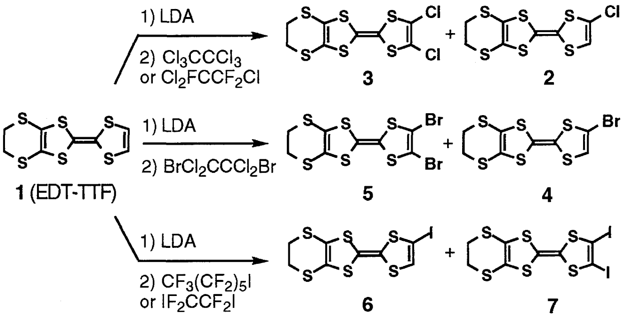


2: X = Cl (EDT-TTFCl)
4: X = Br (EDT-TTFBr)
6: X = I (EDT-TTFI)



3: X = Cl (EDT-TTFCl$_2$)
5: X = Br (EDT-TTFBr$_2$)
7: X = I (EDT-TTFI$_2$)

Synthesis of the halogenated EDT-TTF derivatives was carried out by using lithiation of **1** with lithium diisopropylamide (LDA), followed by treatment with halogenating reagents (Scheme 1).[2] Thus, the reaction of **1** with 1 equiv. of LDA in THF at -80 °C, followed by treatment with 2 equiv. of hexachloroethane at -80 °C to room temperature produced the dichloride **3** (82 % based on the consumed **1**) and the monochloride **2** (17% based on the consumed **1**) with the recovered starting **1** (58%).[3] 1,1,2-Trichloro-1,2,2-trifluoroethane can be used for the chlorinating reagent; more amounts of the monochloride **2** was obtained, but the yields of **2** and **3** were low (16-24%). A similar reaction of **1** with 1 equiv. of LDA at -80 °C, followed by treatment with 1,2-dibromotetrachloroethane ($BrCCl_2$-CCl_2Br, 2 equiv.) at -80 °C to room temperature gave the dibromide **5** in 92% yield (based on the consumed **1**) with the recovered **1** (36%). In this reaction, a small amount of the monobromide **4** was obtained in some cases.[4] In contrast to chlorination and bromination, iodination of **1** resulted in the preferred formation of the monoiodide **6**.[5] Thus, the reaction of **1** with 1 equiv. of LDA in THF at -80 °C, followed by treatment with $CF_3(CF_2)_5I$ at -80 °C to room temperature gave **6** in 94% yield without the recovered **1**. Interestingly, a similar iodination with 1,2-diiodotetrafluoroethane (ICF_2-CF_2I, 2 equiv.) afforded **6** and **7** in 80 and 3% yields (based on the consumed **1**), respectively, with the recovered **1** (19%).



Scheme 1.

The molecular structure and packing diagram of **5** are shown in Figure 1.[6] The introduction of two bromine atoms into the EDT-TTF framework leads to a slight change of the C=C bonds of TTF core. The TTF core and two bromine atoms in **5** shows the high coplanarity, the maximum atomic deviation from the least-squares plane being 0.146(5) Å. The packing mode is a centrosymmetric P2$_1$/n. There is only one intermolecular S•••S distance less than the sum of the van der Waals radii [S(5)•••S(6) 3.63(1) Å]. In contrast, the Br(1)•••S(6), Br(1)•••C(6), and Br(1)•••Br(2) intermolecular contacts are 3.360(7), 3.57(1), and 3.72(1) Å, which are much less than the Br-S and Br-C van der Waals distances.

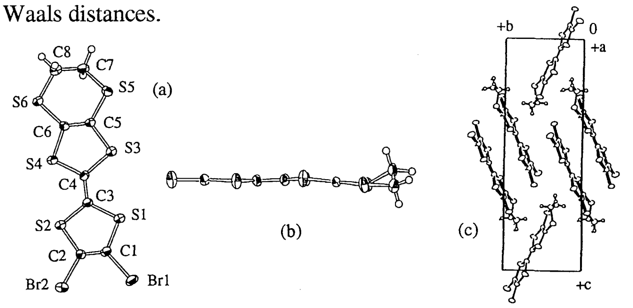


Figure 1. Crystal structure of **5**. (a) Top view. (b) Side view. (c) Packing diagram. Selected bond distances [Å] and angles [°]: C1-Br1 = 1.889(6), C1-S1 = 1.756(7), S1-C3 = 1.762(6), C3-C4 = 1.334(7). C4-S3 = 1.758(8), S3-C5 = 1.764(6), C5-C6 1.316(8), Br1-C1-S1 = 115.4(4), Br1-C1-C2 125.6(5).

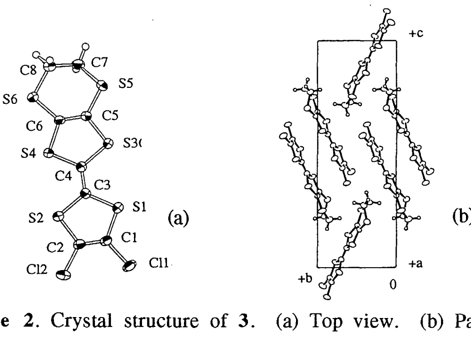


Figure 2. Crystal structure of **3**. (a) Top view. (b) Packing diagram.

Table 1. Cyclic Voltammetric[a] and Melting Point Data of EDT-TTF Derivatives

Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V	Mp/°C
TTF	0.36	0.74	–
1	0.34	0.70	–
2	0.57	0.88	174-176
3	0.68	0.94	119-120
4	0.56	0.88	113-114
5	0.66	0.93	167-168
6	0.53	0.85	119-120
7	0.60	0.89	146-147

[a] Conditions: n-Bu_4NClO_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).

Crystal data indicate that the crystals of **3** are isostructural to those of **5**.[7] As shown in Figure 2, the molecular structure and packing diagram of **3** closely resemble those of **5**. Thus, the S(5)•••S(6) and Cl(1)•••S(6) intermolecular contacts are 3.544(1) and 3.397(1) Å. However, there are no intermolecular Cl•••Cl and Cl•••C distances less than the sum of the van der Waals radii, presumably due to the smaller van der Waals radii of chlorine atom.

The oxidation potentials of TTF and **1**-**7** measured by cyclic voltammetry are shown in Table 1. Although the halogenated EDT-TTF derivatives (**2**-**7**) show lower donor ability, the oxidation potentials are comparable or a little larger than BEDT-TTF which is an well-known donor.

Although compounds (**3**, **5** and **6**) formed no CT-complexes with tetracyano-p-quinodimethane (TCNQ), solid complexes were isolated from benzene/acetonitrile solutions of **3**, **5** and **6** with 2,3,5,6-tetrafluoro-p-tetracyanoquinodimethane ($TCNQF_4$). The CT-complexes of **3**, **4** and **5** with $TCNQF_4$ showed electric conductivities in the range of 0.34-9.8 x 10^{-1} S cm^{-1} at room temperature. Electrocrystallization of **3**, **5** and **6** gave the corresponding radical-cation salts. Interestingly, a compressed powder of **5**•ClO_4 showed a conductivity of 7.3 S cm^{-1}, whereas a crystal of **3**•ClO_4 was an insulator. Experiments to obtain the single crystals of the CT-complexes and radical-cation salts are underway.

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References and Notes

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3 The structures of all new compounds reported here were fully characterized by the spectroscopic analysis. The selected data are as follows. **2**: MS (m/z) 328, 326 (M^+); ^1H NMR ($CDCl_3$-CS_2) δ 6.11 (s, 1H), 3.28 (s, 4H); ^{13}C NMR ($CDCl_3$-CS_2) δ 117.8, 114.8, 114.5, 113.8, 108.4, 30.1. **3**: MS (m/z) 366, 364, 362 (M^+); ^1H NMR ($CDCl_3$-CS_2) δ 3.29 (s, 4H); ^{13}C NMR ($CDCl_3$-CS_2) δ 113.9, 112.4, 109.9, 107.7, 30.2. **4**: MS (m/z) 374, 372 (M^+); ^1H NMR ($CDCl_3$-CS_2) δ 6.23 (s, 1H), 3.28 (s, 4H); ^{13}C NMR ($CDCl_3$-CS_2) δ 117.8, 116.0, 113.9, 113.8, 107.8, 100.7, 30.2. **5**: MS (m/z) 454, 452, 450 (M^+); ^1H NMR ($CDCl_3$-CS_2) δ 3.29 (s, 4H); ^{13}C NMR ($CDCl_3$-CS_2) δ 113.9, 112.1, 111.3, 101.6, 30.3. **6**: MS (m/z) 420 (M^+); ^1H NMR ($CDCl_3$-CS_2) δ 6.38 (s, 1H), 3.27 (s, 4H); ^{13}C NMR ($CDCl_3$-CS_2) δ 124.0, 118.7, 113.9, 106.6, 64.1, 30.3. **7**: MS (m/z) 546 (M^+); ^1H NMR (CD_2Cl_2-CS_2) δ 3.28 (s, 4H); ^{13}C NMR (CD_2Cl_2-CS_2) δ 120.4, 114.4, 109.6, 77.8, 31.0.

4 After the chromatographic separation of the reaction mixture on silica gel, the products were usually separated by gel-permeation chromatography (two JAIGEL-1H columns, $CHCl_3$).

5 A similar iodination of **1** with ICl was reported recently: T. Imakubo, H. Sawa, and R. Kato, International Symposium on Novel Electronic States in Molecular Conductors (Tokyo), Abstracts PS 12, Aug. 1-3, 1994.

6 Crystal data for **5**: $C_8H_4S_6Br_2$, FW = 452.29, monoclinic, space group $P2_1/n$; a = 6.68(3) Å, b = 8.20(8) Å, c = 23.98(3) Å, β = 96.4(3)°, V = 1306(9) $Å^3$, Z = 4, d_{calcd} = 2.300 g cm^{-1}. The structure was solved by direct method using SAPI91.[8] Full matrix least-squares refinement yielded the final R value of 0.036 (R_W = 0.029) for 2245 independent reflections [$2\theta \leq 55.1°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and ω-2θ scan.

7 Crystal data for **3**: $C_8H_4S_6Cl_2$, FW = 363.39, monoclinic, space group $P2_1/n$; a = 6.5563(9) Å, b = 8.1265(4) Å, c = 23.725(1) Å, β = 96.233(8)°, V = 1256.6(2) $Å^3$, Z = 4, d_{calcd} = 1.921 g cm^{-1}. The structure was solved by direct method using SAPI91, full matrix least-squares refinement yielding the final R value of 0.035 (R_W = 0.030) for 2377 independent reflections [$2\theta \leq 55.1°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and ω-2θ scan.

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