Syntheses and Structures of Novel Fused-Ring Systems Containing Six or Seven Sulfur Atoms: 2,3:5,6-Bis(ethylenedithio)thieno[3,2-*b*]thiophene and 3,4:6,7-Bis(ethylenedithio)thieno[3,2-*c*][1,2]dithiin

Motoko Tanaka, Takayuki Ishida, Takashi Nogami,* Hajime Yoshikawa, Masanori Yasui, and Fujiko Iwasaki

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofugaoka, Chofu, Tokyo 182

(Received September 26, 1994)

Novel fused-ring molecules, 2,3:5,6-bis(ethylenedithio)thieno[3,2-*b*]thiophene and 3,4:6,7-bis(ethylenedithio)thieno[3,2-*c*][1,2]dithiin, were synthesized for the development of new conducting organic salts. They have six and seven sulfur atoms, respectively. Their molecular and crystal structures were determined by X-ray crystallographic analyses. Their oxidation potentials were measured, compared with those of the related donor molecules, and analyzed by a molecular-orbital calculation.

Electron-donor molecules possessing multi-chalcogen atoms such as tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF), and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have attracted much attention because they have given conducting and/or superconducting organic salts.[1] BEDT-TTF has afforded several ambient-pressure superconducting salts with two-dimensional electrical properties, which are caused by intermolecular sulfur–sulfur contacts.[2] This intermolecular interaction is crucial for suppressing a metal-insulator transition often observed in a number of organic salts.[3] All of the studies on conducting organic salts containing TTF and its derivatives have been made for 1,3,1′,3′-tetrathiafulvalene (TTF) and its derivatives.[1—3] Although the synthesis of the derivatives of 1,2,1′,2′-tetrathiafulvalene (1,2-TTF) has been reported previously,[4] no systematic study has been made concerning the synthesis of charge-transfer complexes and ion-radical salts containing these 1,2-TTF derivatives. We thought that 3,4:3′,4′-bis(ethylenedithio)-1,2,1′,2′-tetrathiafulvalene (abbreviated as BEDT-1,2-TTF) is an attracting target molecule because it is a derivative of 1,2-TTF and is the isomer of BEDT-TTF. Although the synthesis of BEDT-1,2-TTF has already been reported,[5] we could not reproduce the synthesis. During a trial of the synthesis of BEDT-1,2-TTF we obtained two multi-sulfur fused-ring molecules, 2,3:5,6-bis(ethylenedithio)thieno[3,2-*b*]thiophene (BEDT-TT) and 3,4:6,7-bis(ethylenedithio)thieno[3,2-*c*][1,2]dithiin (BEDT-TDT), which have six and seven sulfur atoms, respectively, and are attracting donor molecules for the development of organic conducting salts (Chart 1).[6] Their molecular and crystal structures were determined by X-ray crystallographic analyses. Their oxidation potentials were measured, and compared with those of the related donor molecules.

Experimental

Synthesis of Multi-Sulfur Fused-Ring Molecules. Two multi-sulfur fused-ring molecules (BEDT-TT and BEDT-TDT) were prepared by the following procedures (Scheme 1).

2,3:5,6-Bis(ethylenedithio)thieno[3,2-*b*]thiophene (BEDT-TT) : 4,5-Ethylenedithio-1,2-dithiol-3-one (**2**) was synthesized by a reaction of the corresponding thione (**1**)[7] with mercury(II) acetate.[8] The dispersion of **2** (332 mg, 1.548 mmol) in trimethyl phosphite (5.5 ml), which had been freshly distilled, was heated at 110 °C for 2 h under a nitrogen atmosphere. After cooling to room temperature, precipitated powders were eliminated by filtration. After methanol (5 ml) was added to the filtrate, the solution was kept overnight at −15 °C. The precipitate was collected and washed with methanol. The crude product was purified by silica-gel column chromatography by using chloroform as an eluent; the first colorless fraction gave BEDT-TT as white powders. It was recrystallized from the mixed solvent of chloroform and methanol (49.5 mg, 20% yield). Mp 188 °C. MS *m/z* 320 (M^+). Found: C, 37.36; H, 2.52; S, 60.15%. Calcd for $C_{10}H_8S_6$: C, 37.46; H, 2.51; S, 60.01%. ^{1}H NMR (270 MHz, $CDCl_3$) δ=3.30—3.43 (AA′BB′). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ=27.9, 28.9, 116.8, 122.2, 132.9.

3,4:6,7-Bis(ethylenedithio)thieno[3,2-*c*][1,2]dithiin (BEDT-TDT) : 4,5-Ethylenedithio-3-methylthio-1,2-dithiol-3-ylium iodide (**3**) was synthesized by the reaction of 4,5-ethylenedithio-1,2-dithiole-3-thione (**1**) with methyl iodide, as reported previously.[9] A mixture of acetonitrile (10

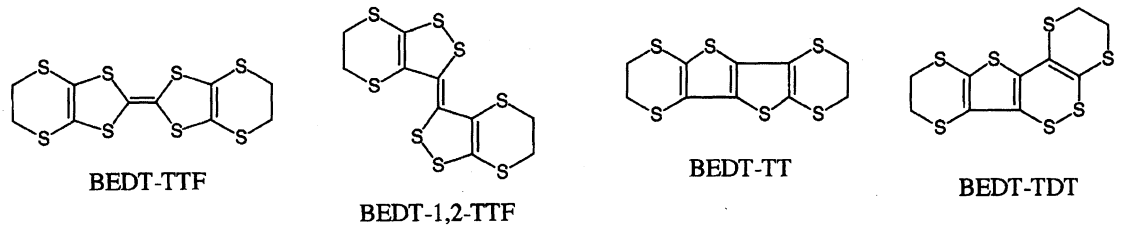
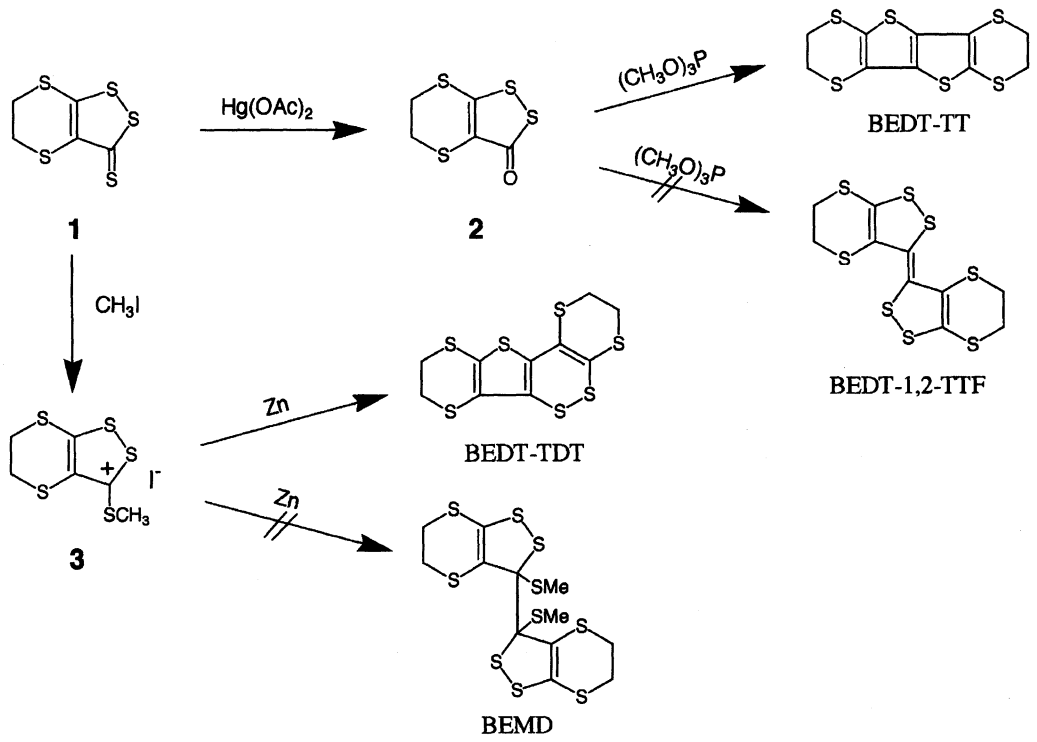


Chart 1.



Scheme 1.

ml), *N*,*N*-dimethylformamide (4 ml), activated zinc powder (95 mg, 1.45 mmol),[10] and **3** (1.023 g, 2.79 mmol) was refluxed for 15 h under a nitrogen atmosphere. After eliminating inorganic materials and slight amounts of unidentified precipitates by filtration, the solvent was evaporated to dryness. The residue was dissolved in toluene, the solution was washed with water, and toluene was evaporated to dryness. The crude mixture of the reaction products was chromatographed on a silica-gel column by using the mixed solvent of hexane and carbon disulfide as eluents. Red and orange fractions gave BEDT-TDT (74.4 mg, 15%) and **1** (422.8 mg, 68%) respectively. BEDT-TDT was recrystallized from a mixed solvent of chloroform and methanol. Mp 198—200 °C. MS *m*/*z* 352 (M^+). UV ($CHCl_3$) λ_{max} 321.5 ($\log\varepsilon$=4.0), 472.1 nm (3.7). ^{1}H NMR (270 MHz, $CDCl_3$) δ=3.14—3.46 (m). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ=27.8, 28.8, 31.2, 33.9, 116.6, 122.1, 123.1, 123.3, 123.9, 136.0.

X-Ray Crystallographic Analysis. Crystal data, details of data collection and the structure refinement of BEDT-TT and BEDT-TDT are listed in Table 1. Intensity data were collected using Rigaku AFC-5R and AFC-4 diffractometers for BEDT-TT and BEDT-TDT, respectively, with a graphite monochromator. Absorption corrections were applied numerically. The structure was solved by a direct method with the program MULTAN78,[11] and was refined using block-diagonal least squares with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms. $\sum w(|F_o|-k|F_c|)^2$ was minimized, where $w=1/(\sigma^2(F_o)+0.0007|F_o|^2)$ for BEDT-TT and $w=1/(\sigma^2(F_o)+0.004|F_o|^2)$ for BEDT-TDT respectively. All of the hydrogen atoms could be found by Difference Fourier Synthesis for both crystals. Atomic-scattering factors were used from International Tables for X-Ray Crystallography.[12] The final atomic parameters of BEDT-TT and BEDT-TDT are listed in Tables 2 and 3, respectively.[13] Computations were performed on an IBM 3090-180S Computer of the Information Processing Center of the University of Electro-Communications with the programs, UNICS III,[14] MULTAN 78, and ORTEP II[15].

Measurements. ^{1}H and ^{13}C NMR spectra of BEDT-TT and BEDT-TDT were measured at room temperature on GX-270 (JEOL) and UNITY plus-500LS (Varian). Cyclic voltammetries of BEDT-TT and BEDT-TDT were made for acetonitrile solutions, which had been bubbled by nitrogen gas beforehand, by using platinum plate electrodes, Ag/Ag^+ reference electrode, and tetrabutylammonium perchlorate as a supporting electrolyte. A Function Generator (HB-104, Hokuto Denko) and a Potentiostat (HA-501, Hokuto Denko) were used for the measurement.

Table 1. Crystal Data, and Details and Data Collection and Structure Refinement.

	BEDT-TT	BEDT-TDT
Color	Colorless	Wine red
Crystal shape	Plate	Plate
Molecular formula	$C_{10}H_8S_6$	$C_{10}H_8S_7$
Formula weight	320.57	352.64
Crystal size/mm	0.37×0.37×0.39	0.50×0.70×0.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	6.800(1)	9.727(4)
b/Å	11.647(2)	15.752(4)
c/Å	8.319(2)	9.005(3)
β/°	107.11(2)	104.32(4)
V/Å^3	629.6(2)	1336.8(9)
Z	2	4
D_c/Mg m^{-3}	1.700	1.752
Radiation	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71069	0.71069
μ/mm^{-1}	1.017	1.107
For cell parameters		
2θ range/°	26.90—34.70	25.01—36.40
No. of reflections	25	25
Scan range 2θ/°	3—55	3—55
Scan width $\Delta\omega$/°	1.5+0.5 tan θ	1.3+0.5 tan θ
Scan speed 2θ/min^{-1}	8	4
Scan mode	2θ–ω	2θ–ω
Monitored reflections	3 3 −1, 1 −7 −2,	0 13 1, 7 3 −5
(every 100 reflections)	1 1 6	3 0 4
Variation of intensities	0.995—1.004	0.977—1.047
Range of h, k, l	0—8, 0—15, −10—10	0—12, 0—20, −11—11
Time for back-ground/s	10	10
No. of reflections		
Measured	1663	3451
Unique	1446	3077
Observed ($\|F_o\|>3\sigma(F_o)$)	1331	2739
R	0.0218	0.0425
wR	0.0360	0.0725
$\Delta\rho_{max}-\Delta\rho_{min}$/eÅ^{-3}	0.284—−0.199	0.646—−0.373

Table 2. Fractional Coordinates and Equivalent Isotropic Temperature Factors of Non-Hydrogen Atoms in BEDT-TT

Atom	x	y	z	B_{eq}[a)]/Å^2
S(1)	0.75265(5)	0.05787(3)	0.43111(4)	2.56(1)
S(2)	0.09967(5)	0.09854(3)	0.18672(4)	2.86(1)
S(3)	0.55756(6)	0.18459(4)	0.10592(5)	3.43(1)
C(1)	0.5321(2)	0.1058(1)	0.2771(2)	2.43(3)
C(2)	0.3537(2)	0.0718(1)	0.3075(2)	2.25(3)
C(3)	0.1314(2)	0.1786(1)	0.0094(2)	3.15(4)
C(4)	0.3165(3)	0.1426(1)	−0.0437(2)	3.24(4)
C(5)	0.6028(2)	−0.0067(1)	0.5407(2)	2.20(3)

a) B_{eq} is defined using anisotropic temperature factors, β_{ij}, as, $B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Results and Discussion

Synthesis of Multi-Sulfur Fused-Ring Molecules. The synthetic routes in the present study are summarized in Scheme 1. 4,5-Ethylenedithio-1,2-dithiole-3-thione (**1**)[7] was converted to the corresponding carbonyl compound **2**, 4,5-ethylenedithio-1,2-dithiol-3-one, by treating **1** with $Hg(OAc)_2$. The synthesis of BEDT-1,2-TTF was attempted by the coupling reaction of **2** by using trimethyl phosphite, because the molecule was reported to be obtained by this reaction.[5] We tried this reaction under various reaction conditions by changing the reaction time, temperature, and molar ratios of the reactants. However, we obtained 2,3:5,6-bis(ethylenedithio)thieno[3,2-*b*]thiophene (BEDT-TT) as only one characterizable product among several unidentified by-products. Although several possibilities are conceivable for the reaction product, its molecular structure was identified conclusively by an X-ray crystallographic analysis (vide infra). Thus, the reaction of **2** with trimethyl phosphite involves bimolecular coupling-reaction at the carbonyl group, a sulfur-elimination reaction by trimethyl phosphite at the disulfide portion,[16] and an isomerization reaction.

Table 3. Fractional Coordinates and Equivalent Isotropic Temperature Factors of Non-Hydrogen Atoms in BEDT-TDT

Atom	x	y	z	B_{eq}[a)]/Å^2
S(1)	−0.05478(7)	0.09605(5)	0.16468(7)	2.86(2)
S(2)	0.10032(8)	0.09750(5)	0.36741(7)	3.20(2)
S(3)	0.37138(7)	−0.03741(4)	0.14429(7)	2.85(2)
S(4)	−0.04835(7)	0.19137(5)	−0.11058(7)	3.00(2)
S(5)	0.29309(7)	0.12554(6)	−0.06941(9)	3.86(2)
S(6)	0.27486(8)	−0.05753(5)	0.58477(8)	3.41(2)
S(7)	0.50406(8)	−0.16076(5)	0.39479(9)	3.53(2)
C(1)	0.2178(2)	0.0275(2)	0.3088(3)	2.46(6)
C(2)	0.2461(3)	0.0364(2)	0.1673(3)	2.45(6)
C(3)	0.1813(3)	0.0982(2)	0.0500(3)	2.38(6)
C(4)	0.0489(3)	0.1279(2)	0.0376(3)	2.36(5)
C(5)	0.2989(3)	−0.0368(2)	0.4019(3)	2.46(6)
C(6)	0.3884(3)	−0.0766(2)	0.3287(3)	2.59(6)
C(7)	0.4090(4)	−0.2061(2)	0.5231(4)	4.50(10)
C(8)	0.3933(4)	−0.1452(2)	0.6497(4)	4.51(9)
C(9)	0.0268(3)	0.1555(2)	−0.2638(3)	3.34(7)
C(10)	0.1815(3)	0.1763(2)	−0.2361(4)	3.84(8)

a) See Table 2 for the definition of B_{eq}.

We tried another route to obtain BEDT-1,2-TTF. The reaction of **1** with methyl iodide gave 4,5-ethylenedithio-3-methylthio-1,2-dithiol-3-ylium iodide (**3**). The reduction of **3** with activated zinc powder did not give 3,3′-bi(4,5-ethylenedithio-3-methylthio-1,2-dithiol-3-yl) (BEMD, a precursor molecule to BEDT-1,2-TTF) through bimolecular radical-coupling reaction,[17] but did give 3,4:6,7-bis(ethylenedithio)thieno[3,2-*c*][1,2]-dithiin (BEDT-TDT). Thus, the reaction is considered to involve a radical-coupling reaction, followed by elimination reactions of both the dimethyl disulfide and sulfur atom, and an isomerization reaction. Although several possibilities are conceivable for the reaction product, the molecular structure was also identified by an X-ray crystallographic analysis (vide infra). The reaction of **3** with Zn also gave **1** by an elimination reaction of methyl iodide. The reaction mechanism is not clear.

X-Ray Crystallographic Analysis of Multi-Sulfur Fused-Ring Molecules. Figure 1 shows the molecular structures of BEDT-TT with the atomic numbering. Since the molecule lies on a crystallographic center of symmetry, half of the molecule occupies an asymmetric unit. The bond distances and angles are listed in Table 4. An X-ray study has revealed that this molecule has a thienothiophene skeleton at the central part. Two sulfur atoms are located at the opposite sides of the thienothiophene moiety. The bond distances and angles of the thienothiophene moiety were essentially identical to those of the thienothiophene derivatives determined by Cox et al.[18] The non-hydrogen atoms are planar, except for C(4). The maximum deviations from the best plane, defined by S(1), C(1), C(2), S(3), C(5), and S(2), is 0.016(1) Å. The deviation of C(4) from this plane is 0.824(2) Å. The six-membered ring has a half-chair conformation.

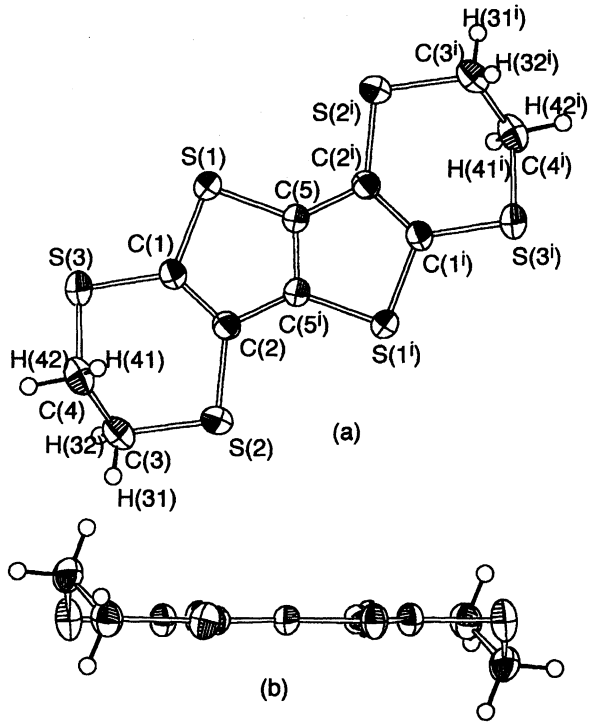


Fig. 1. ORTEP II drawing of BEDT-TT with thermal ellipsoids at 50% probability. (a) Viewed on the molecular plane, (b) viewed along the C(5^i)–C(5) vector. Symmetry code i: $1-x$, $-y$, $1-z$.

Table 4. Bond Lengths (l) and Angles (θ) of Non-Hydrogen Atoms of BEDT-TT

Length	l/Å	Length	l/Å
S(1)–C(1)	1.752(1)	S(3)–C(4)	1.809(2)
S(1)–C(5)	1.727(1)	C(1)–C(2)	1.369(2)
S(2)–C(2)	1.751(1)	C(2)–C(5^i)	1.427(2)
S(2)–C(3)	1.811(2)	C(3)–C(4)	1.511(2)
S(3)–C(1)	1.745(1)	C(5)–C(5^i)	1.372(3)

Angle	θ/°	Angle	θ/°
C(1)–S(1)–C(5)	90.79(7)	S(2)–C(2)–C(5^i)	121.0(1)
C(2)–S(2)–C(3)	103.01(7)	C(1)–C(2)–C(5^i)	111.6(1)
C(1)–S(3)–C(4)	97.59(7)	S(2)–C(3)–C(4)	113.9(1)
S(1)–C(1)–S(3)	119.67(8)	S(3)–C(4)–C(3)	112.9(1)
S(1)–C(1)–C(2)	112.8(1)	S(1)–C(5)–C(5^i)	111.3(1)
S(3)–C(1)–C(2)	127.5(1)	S(1)–C(5)–C(2^i)	134.2(1)
S(2)–C(2)–C(1)	128.4(1)	C(2)–C(5^i)–C(5)	114.4(1)

Symmetry code i: $1-x$, $-y$, $1-z$.

Figure 2 shows the molecular structures of BEDT-TDT along with the atomic numbering. The bond distances and angles are listed in Table 5. The structure turned out to be a fused ring of three six-membered rings and one five-membered ring. One sulfur atom in the thiophene ring and two sulfur atoms in the dithiin ring are located at the opposite sides of the fused ring. The bond distances, angles, and planarity of the moiety in common with BEDT-TT were very similar to each other. The thiophene-ring and four atoms bonded

to the thiophene-ring are planar. The maximum deviation of the best plane, defined by S(2), S(3), S(6), S(7), C(1), C(2), C(3), C(5), and C(6), is 0.039(2) Å. The conformations of three six-membered rings are half-chair, distorted-boat, and half-chair for C(5)–C(6)–S-(7)–C(7)–C(8)–S(6), C(1)–C(2)–C(3)–C(4)–S(1)–S(2), and C(3)–C(4)–S(4)–C(9)–C(10)–S(5), respectively.

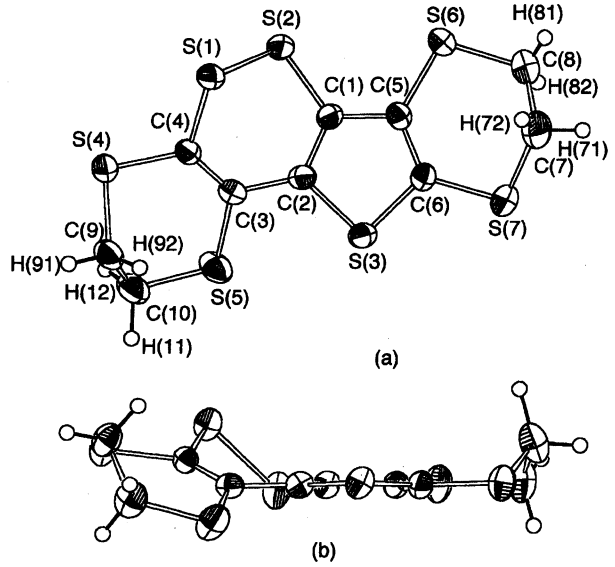


Fig. 2. ORTEP II drawing of BEDT-TDT with thermal ellipsoids at 50% probability. (a) Viewed on the thiophene plane, (b) side view of (a).

Table 5. Bond Lengths (l) and Angles (θ) of Non-Hydrogen Atoms of BEDT-TDT

Length	l/Å	Length	l/Å
S(1)–S(2)	2.0608(8)	S(6)–C(8)	1.801(4)
S(1)–C(4)	1.775(3)	S(7)–C(6)	1.746(3)
S(2)–C(1)	1.760(3)	S(7)–C(7)	1.797(4)
S(3)–C(2)	1.733(3)	C(1)–C(2)	1.376(4)
S(3)–C(6)	1.740(3)	C(1)–C(5)	1.423(4)
S(4)–C(4)	1.746(3)	C(2)–C(3)	1.460(4)
S(4)–C(9)	1.804(3)	C(3)–C(4)	1.349(4)
S(5)–C(3)	1.761(3)	C(5)–C(6)	1.367(4)
S(5)–C(10)	1.806(4)	C(7)–C(8)	1.526(6)
S(6)–C(5)	1.750(3)	C(9)–C(10)	1.499(5)

Angle	θ/°	Angle	θ/°
S(2)–S(1)–C(4)	99.21(9)	C(2)–C(3)–C(4)	121.6(2)
S(1)–S(2)–C(1)	96.59(9)	S(1)–C(4)–S(4)	111.6(1)
C(2)–S(3)–C(6)	91.6(1)	S(1)–C(4)–C(3)	122.1(2)
C(4)–S(4)–C(9)	99.2(1)	S(4)–C(4)–C(3)	126.0(2)
C(3)–S(5)–C(10)	106.3(1)	S(6)–C(5)–C(1)	120.2(2)
C(5)–S(6)–C(8)	103.0(2)	S(6)–C(5)–C(6)	128.2(2)
C(6)–S(7)–C(7)	97.5(2)	C(1)–C(5)–C(6)	111.6(2)
S(2)–C(1)–C(2)	120.5(2)	S(3)–C(6)–S(7)	119.7(2)
S(2)–C(1)–C(5)	125.2(2)	S(3)–C(6)–C(5)	112.1(2)
C(2)–C(1)–C(5)	114.2(2)	S(7)–C(6)–C(5)	128.1(2)
S(3)–C(2)–C(1)	110.5(2)	S(7)–C(7)–C(8)	113.1(3)
S(3)–C(2)–C(3)	123.5(2)	S(6)–C(8)–C(7)	114.4(3)
C(1)–C(2)–C(3)	126.1(2)	S(4)–C(9)–C(10)	112.6(2)
S(5)–C(3)–C(2)	112.6(2)	S(5)–C(10)–C(9)	114.5(2)
S(5)–C(3)–C(4)	125.8(2)		

Figure 3 shows the crystal structures of BEDT-TT and BEDT-TDT. Molecules are stacked along the c-axis in BEDT-TT. The shortest intermolecular distances between the sulfur atoms are 3.571 Å of S(1)–S-(2^{i}) (i: $1+x$, y, z) and 3.525(1) Å of S(1)–S(6^{ii}) (ii: $-x$, $-y$, $1-z$) in BEDT-TT and BEDT-TDT respectively. Another significant contact shorter than the sum of van der Waals radii is not found in both crystals.

Cyclic Voltammetry of BEDT-TT and BEDT-TDT. Table 6 summarizes the half-wave oxidation potentials of BEDT-TT and BEDT-TDT. This table also shows the oxidation potentials of BEDT-TTF and perylene for the sake of a comparison. BEDT-TT and BEDT-TDT have similar $E_{1/2}(1)$ values. This is consistent with the molecular-orbital (MO) calculation based on MOPAC ver. 6;[19] the calculated first ionization po-

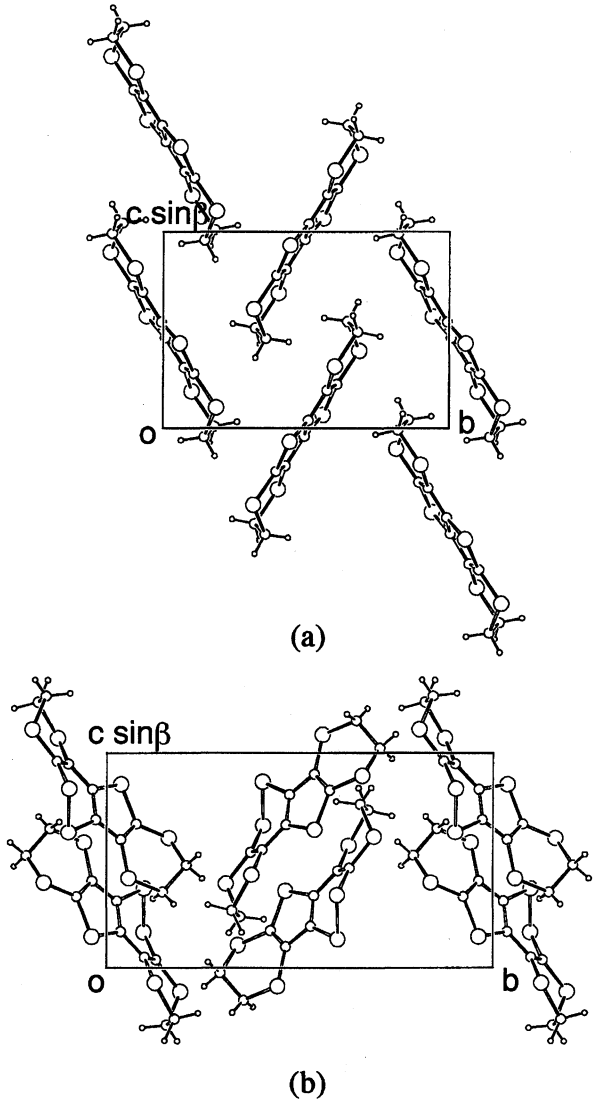


Fig. 3. Projections of the crystal structures of (a) BEDT-TT, and (b) BEDT-TDT, viewed along the a-axis.

Table 6. Half-Wave Oxidation Potentials ($E_{1/2}(i)$, i=1—3),[a] and Values $E_{1/2}(2)-E_{1/2}(1)$ of BEDT-TT, BEDT-TDT, BEDT-TTF, and Perylene

Materials	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_{1/2}(2)-E_{1/2}(1)$
	V vs. Ag/Ag^+	V vs. Ag/Ag^+	V vs. Ag/Ag^+	V
BEDT-TT	0.57	0.85		0.28
BEDT-TDT	0.58	0.78	0.93	0.20
BEDT-TTF	0.18	0.42		0.24
Perylene	0.58	0.90		0.32

a) Measured in an acetonitrile solution by using platinum plate electrodes and tetrabutylammonium perchlorate as an electrolyte.

tentials are close to each other (8.78 eV for BEDT-TT and 8.90 eV for BEDT-TDT). The $E_{1/2}(1)$ values of BEDT-TT and BEDT-TDT were by 0.4 V larger than that of BEDT-TTF, and almost similar to that of perylene. The on-site Coulomb repulsion energies, deduced from the values $E_{1/2}(2)-E_{1/2}(1)$, were not very different for BEDT-TT, BEDT-TDT, and BEDT-TTF. Although two redox waves have often been observed for organic donor molecules, BEDT-TDT exhibited three redox waves. This fact suggests that the orbital energy of the next-highest occupied MO (NHOMO) might be close to that of the highest occupied MO (HOMO) in BEDT-TDT. However, an MO calculation showed that the orbital energies of NHOMO are −9.30 eV for both BEDT-TT and BEDT-TDT. Since BEDT-TDT has a much more flexible molecular structure than does BEDT-TT, the mono- and di-cations of the former molecule are assumed to have molecular structures that are fairly deviated from its neutral form to which the MO calculation was made. Thus, a quantitative discussion concerning the values of $E_{1/2}(2)$ and $E_{1/2}(3)$ of BEDT-TDT by an MO calculation is difficult at present.

BEDT-TT and BEDT-TDT have multi-sulfur atoms, which is believed to be important for realizing two-dimensional conductors; since they have donor abilities comparable to perylene (typical donor molecule for the conducting organic salts),[20] these molecules are attractive for the development of new conducting organic salts. Although BEDT-TDT has a distorted molecular structure in its neutral form, the planarity of the oxidized form in the ion-radical salt may be improved, because improvements of the planarity of the multi-sulfur donor molecules on going from the neutral form to the cation-radical form are found in several molecules.[21] The synthesis of ion-radical salts by electrochemical crystallizations of BEDT-TT and BEDT-TDT has been unsuccessful up to now.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Molecular Conductors" (Area No. 253/06243213), from the Ministry of Education, Science and Culture.

References

1) *Synth. Met.*, **55**, Nos. 1—3 (1993); *Synth. Met.*, **56**, Nos. 1—3 (1993); *Synth. Met.*, **57**, Nos. 1—3 (1993). "Proceedings of the International Conference on Science and Technology of Synthetic Metals (ICSM'92)," Göteborg, Sweden (1992).

2) J. M. Williams, M. A. Beno, H. H. Wang, P. C. W. Leung, T. J. Emge, U. Geiser, and K. D. Carlson, *Acc. Chem. Res.*, **18**, 261 (1985).

3) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. H. Whangbo, "Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory," Prentice-Hall, NJ (1992).

4) H. Behringer and E. Meinetsberger, *Tetrahedron Lett.*, **1975**, 3473; H. Behringer and E. Meinetsberger, *Liebigs Ann. Chem.*, **1981**, 1928.

5) G. C. Papavassiliou, *Chem. Scr.*, **25**, 167 (1985).

6) T. Nogami, T. Ishida, H. Yoshikawa, M. Tanaka, T. Naito, H. Kobayashi, and A. Kobayashi, *Synth. Met.*, **55—57**, 2039 (1993).

7) G. Steimecke, H. Sieler, R. Kirmse, W. Dietzsch, and E. Hoyer, *Phosphorus and Sulfur*, **12**, 237 (1982).

8) T. Nakamura, S. Iwasaka, H. Nakano, K. Inoue, T. Nogami, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **60**, 365 (1987).

9) M. Bryce, G. R. Davison, A. J. Moore, M. B. Hursthouse, and K. M. Malik, *Tetrahedron*, **48**, 8143 (1992).

10) Commercially available zinc powder was treated with dilute hydrochloric acid, and then washed successively with water, methanol, diethyl ether, and DMF, just before the reaction.

11) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. -P. Declercq, and M. M. Woolfson, "MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univ. of York, England and Louvain, Belgium (1978).

12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV, p. 71.

13) Tables of anisotropic thermal parameters of nonhydrogen atoms, atomic parameters of hydrogen atoms, calculated bond distances and angles, and observed and calculated structure factors are deposited as Document No. 68015 both for BEDT-TT and BEDT-TDT at the Office of the Editor of Bull. Chem. Soc. Jpn.

14) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

15) C. K. Johnson, "ORTEP II. Report ORNL-5138," Oak Ridge National Laboratory, Tennessee (1976).
16) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).
17) E. Fanghanel, L. V. Hinh, and G. Schukat, *Z. Chem.*, **16**, 317 (1976); R. R. Moses and J. Q. Chambers, *J. Am. Chem. Soc.*, **96**, 945 (1974).
18) E. G. Cox, R. J. J. H. Gillot, and G. A. Jeffrey, *Acta Crystallogr.*, **2**, 356 (1949).
19) Calculated for the molecular structures determined in the present study. "MOPAC ver. 6," J. J. P. Stewart, *QCPE Bull.*, **9**, 10 (1989).
20) M. J. Matos, R. T. Henriques, and L. J. Alcacer, *Synth. Met.*, **19**, 389 (1987); J. Wieland, U. Haeberlen, D. Schweitzer, and H. J. Keller, *Synth. Met.*, **19**, 393 (1987).
21) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 301 (1986); H. Kobayashi, A. Kobayashi, T. Nakamura, T. Nogami, and Y. Shirota, *Chem. Lett.*, **1987**, 559; H. Nakano, K. Miyawaki, T. Nogami, Y. Shirota, S. Harada, and N. Kasai, *Bull. Chem. Soc. Jpn.*, **62**, 2604 (1989); H. Nakano, K. Miyawaki, T. Nogami, Y. Shirota, S. Harada, N. Kasai, A. Kobayashi, R. Kato, and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **63**, 2281 (1990).