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The Synthesis of 4,5-Ethylenedithio-4′,5′-vinylenedithiotetrathiafulvalene (EVT) and Its Methyl and Dimethyl Derivatives (EMVT, EDMVT), and the Molecular and Crystal Structures of EVT

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New donor molecules, 4,5-ethylenedithio-4′,5′-vinylenedithiotetrathiafulvalene (EVT) and its methyl and dimethyl derivatives (EMVT and EDMVT), were synthesized for the study of conducting organic salts. They are unsymmetrical TTF derivatives possessing moieties of both BEDT-TTF and bis(vinylenedithio)tetrathiafulvalene (VT) or its methyl and dimethyl derivatives. Their oxidation potentials were measured and then compared with those of the related donor molecules. The X-ray crystal structure analysis of EVT revealed that its molecular and crystal structures are very close to that of BEDT-TTF.

BEDT-TTF salts have given a variety of organic superconductors, and the superconducting transition temperature has now been raised to 10.4 K or 11.1 K in (BEDT-TTF)$_2$Cu(SCN)$_2$.[1] The crystal structures of the BEDT-TTF salts exhibit sulfur–sulfur networks shorter than the van der Waals distance among donor sites.[2] This crystal structure is believed to be effective for suppressing the Peierls transition inherent in a one-dimensional system. The donor molecules possessing molecular structures similar to BEDT-TTF are interesting, because they can be expected to give highly conducting organic complexes even at low temperatures. The replacement of the ethylene group of BEDT-TTF with vinylene group is one of the most attractive strategies in this regard. Thus, we synthesized bis(vinylenedithio)tetrathiafulvalene (VT) and its dimethyl and tetramethyl derivatives (DMVT and TMVT respectively).[3] Detailed electrical and structural studies of VT$_2$PF$_6$ revealed that this salt exhibits a quasi-one-dimensional electrical property and that a metal–insulator (M-I) transition occurs around 180 K.[4] Several VT-salts also showed an M-I transition,[5] probably due to the one-dimensional nature. Therefore, we have synthesized new unsymmetrical TTF-derivatives, EVT, EMVT, and EDMVT, which possess moieties of both BEDT-TTF and VT or its methyl and dimethyl derivatives, in the hope that they might give two-dimensional conducting salts. Here, EVT, EMVT, and EDMVT stand for 4,5-ethylenedithio-4′,5′-vinylenedithiotetrathiafulvalene, 4,5-ethylenedithio-4′,5′-(methylvinylenedithio)tetrathiafulvalene, and 4,5-ethylenedithio-4′,5′-(dimethylvinylenedithio)tetrathiafulvalene respectively.[6] The molecular and crystal structures of EVT are also reported.

Experimental

4,5-Ethylenedithio-4′,5′-vinylenedithiotetrathiafulvalene (EVT). To a mixture of 4,5-ethylenedithio-1,3-dithiole-2-thione (1.0 g, 4.45 mmol)[7] and 4,5-vinylenedithio-1,3-dithiol-2-one (0.92 g, 4.45 mmol),[3] we added triethyl phosphite (20 ml), which had been distilled freshly. The temperature of the solution was gradually elevated to 110 °C with stirring under a nitrogen atmosphere; thereafter, it was stirred for another 2 h at 110 °C. After cooling to room temperature, the precipitate was collected, washed with methyl alcohol, and dried under a vacuum. The crude product was chromatographed on a silica-gel column, using carbon disulflde as an eluent; the second main fraction gave almost pure EVT (0.75 g, 44%). Recrystallization from benzene gave reddish orange needle crystals. Mp 218°C (decomp). MS m/z 382 (M$^+$). Calcd for $C_{10}H_6S_8$: C, 31.39; H, 1.58; S, 67.03%. Found: C, 31.74; H, 1.57; S, 66.74%. ^{1}H NMR (CS$_2$) δ=3.25 (4H, s), 6.47 (2H, s). UV $\lambda_{\max}^{\mathrm{THF}}$ (log ε) 318.4 nm (4.33), 344.4 nm (4.24).

4,5-Ethylenedithio-4′,5′-(methylvinylenedithio)tetrathiafulvalene (EMVT) and 4,5-Ethylenedithio-4′,5′-(dimethylvinylenedithio)tetrathiafulvalene (EDMVT). EMVT and EDMVT were synthesized under reaction conditions similar as those described for EVT. 4,5-Methylvinylenedithio-1,3-dithiol-2-one[3] and 4,5-dimethylvinylenedithio-1,3-dithiol-2-one[3] were, therefore, used instead of 4,5-vinylenedithio-1,3-dithiol-2-one for the synthesis of EMVT and EDMVT respectively. EMVT: yield, 61%. orange needles. Mp 210 °C (decomp). MS m/z 396 (M$^+$). Calcd for $C_{11}H_8S_8$: C, 33.30; H, 2.03; S, 64.66%. Found: C, 33.40; H, 1.89; S, 64.39%. ^{1}H NMR (CS$_2$) δ=2.12 (3H, s), 3.26 (4H, s), 6.02 (1H, s). UV $\lambda_{\max}^{\mathrm{THF}}$ (log ε) 318.0 nm (4.12), 346.0 nm (4.02).

EDMVT: yield, 49%. yellow needles. Mp 217 °C (decomp). MS m/z 410 (M$^+$). Calcd for $C_{12}H_{10}S_8$: C, 35.09; H, 2.45; S, 62.45%. Found: C, 35.08; H, 2.30; S, 62.35%. ^{1}H NMR (CS$_2$) δ=2.30 (6H, s), 3.28 (4H, s). UV $\lambda_{\max}^{\mathrm{THF}}$ (log ε) 318.4 nm (4.15), 346.8 nm (4.06).

Determination of Molecular and Crystal Structures of EVT. $C_{10}H_6S_8$, M=382.68, monoclinic, space group $P2_1/n$, a=6.563(1), b=13.507(8), c=15.866(8) Å, β=93.47(2)°, V=1404(1) Å^3, D_c=1.80 g cm^{-3} for Z=4. The crystal used had a needle shape with approximate dimensions of 0.19×0.60×0.18 mm^3. The reflection intensities were measured by the θ-2θ scan technique up to 2θ=55° on a Rigaku AFC-4 four-circle diffractometer, using Mo $K\alpha$ radiation (λ=0.70926 Å). The scan rate was 4° min^{-1}, and the scan width, $\Delta\theta$=(1.20+0.5 tanθ)°. Backgrounds were counted for 3 s at both ends of a scan. No significant intensity decay of the standard reflections, which were measured after every 100 reflections, was detected. Of the 3513 reflections mea-

Table 1. Atomic Parameters of Nonhydrogen Atoms of EVT Molecule, with Equivalent Isotropic Temperature Factors[11)]

Atom	x	y	z	$B_{eq}/\text{Å}^2$
C(1)	0.1049(8)	0.0455(5)	0.3656(4)	2.4
C(2)	0.0823(9)	−0.0236(5)	0.2143(4)	3.2
C(3)	0.278(1)	−0.0347(6)	0.2432(4)	3.6
C(4)	0.168(1)	−0.1268(7)	0.0728(5)	5.7
C(5)	0.375(1)	−0.0816(8)	0.0835(6)	6.1
C(6)	0.0677(8)	0.0970(5)	0.4362(4)	2.5
C(7)	−0.0831(9)	0.2199(5)	0.5374(4)	2.9
C(8)	0.1120(9)	0.2114(5)	0.5652(4)	2.6
C(9)	−0.175(1)	0.2847(6)	0.6917(5)	4.6
C(10)	0.024(1)	0.2773(6)	0.7200(5)	4.4
S(1)	−0.0877(3)	0.0184(1)	0.2877(1)	3.2
S(2)	0.3430(3)	−0.0045(1)	0.3478(1)	3.3
S(3)	−0.0278(3)	−0.0524(2)	0.1143(1)	4.3
S(4)	0.4806(3)	−0.0800(3)	0.1877(1)	6.3
S(5)	−0.1765(3)	0.1414(1)	0.4571(1)	3.0
S(6)	0.2558(3)	0.1195(1)	0.5175(9)	2.9
S(7)	−0.2554(3)	0.2992(1)	0.5839(1)	3.9
S(8)	0.2262(3)	0.2771(1)	0.6501(1)	3.9

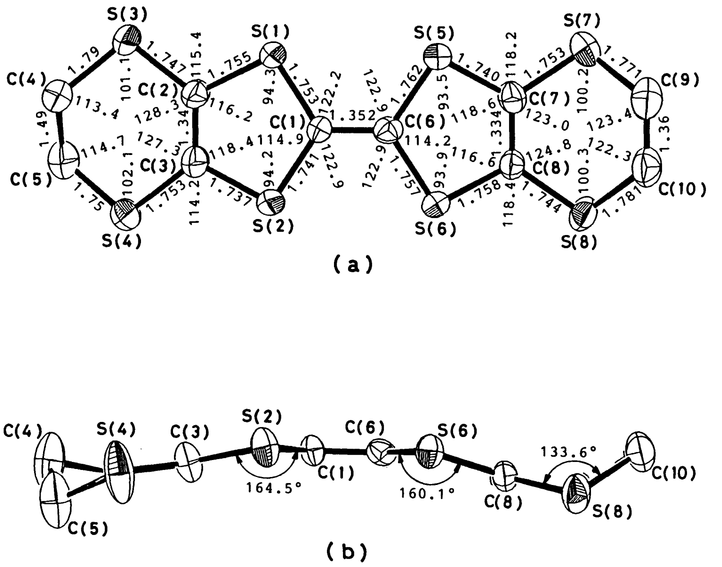


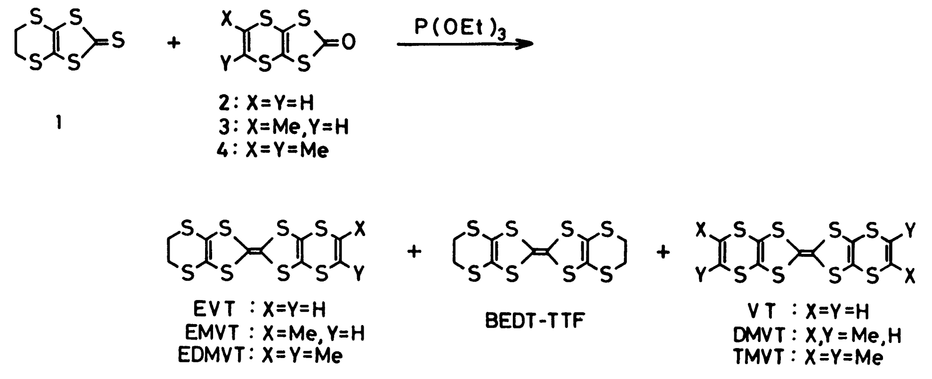
Fig. 1. Molecular structure of EVT.[14)] (a) Over view, (b) side view. Nonhydrogen atoms are drawn as thermal ellipsoids with 50% probability level. Estimated standard deviations of the bond lengths and angles are 0.006—0.02 Å and 0.3—0.7° respectively.

sured, the number of reflections observed was 2517 ($|F_o|>2\sigma(F_o)$). The usual Lorentz and polarization corrections were applied, but no absorption correction was made [$\mu(\text{Mo}\,K\alpha)=11.9\ \text{cm}^{-1}$].

The structure was solved by the direct method (*MULTAN* 78)[8)] and was refined anisotropically by a block-diagonal least-squares procedure (*HBLS* V).[9)] The hydrogen atoms could not be found on a D-map, probably because of their large thermal motion. Therefore, the hydrogen atoms were omitted in the final refinement. The function minimized was $\sum\omega(\Delta F)^2$. The weighting function used in the final stage of the refinement was $\omega=[\sigma^2(F_o)+0.0654|F_o|+0.0005|F_o|^2]^{-1}$. The atomic scattering factors were taken from those of the International Tables for X-Ray Crystallography.[10)] The final R index was 0.070. The atomic coordinates of nonhydrogen atoms with equivalent isotropic temperature factors[11)] are given in Table 1.[12)] The bond lengths and bond angles are shown in Fig. 1.

Results and Discussion

Synthesis and Oxidation Potentials of EVT, EMVT, and EDMVT. The cross-coupling reaction of 4,5-ethylenedithio-1,3-dithiole-2-thione (**1**)[7)] and 4,5-vinylenedithio-1,3-dithiol-2-one (**2**)[3)] or its methyl (**3**) or dimethyl derivatives (**4**)[3)] gave EVT, EMVT, or



Scheme 1.

Table 2. Half-Wave Oxidation Potentials of Donor Molecules in a THF Solution

Donor	$E_{1/2}(1)$ V vs. SCE	$E_{1/2}(2)$ V vs. SCE
EVT	0.75	
EMVT	0.76	
EDMVT	0.76	
BEDT-TTF[a)]	0.69	0.82
VT[a)]	0.83	
DMVT[a)]	0.80	
TMVT[a)]	0.80	

a) Ref 3.

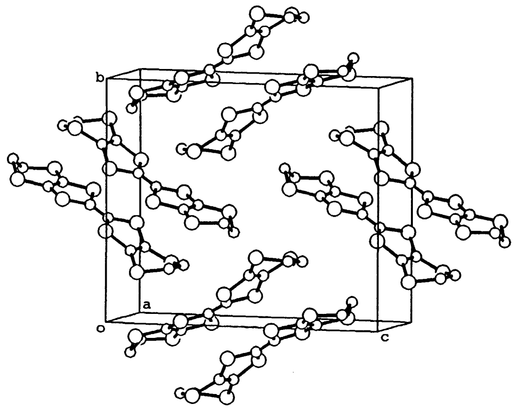


Fig. 2. Crystal structure of EVT.[15)]

EDMVT as the main product (Scheme 1). Self-coupling products (BEDT-TTF and VT or DMVT or TMVT) were always found as minor products. The amount of the cross-coupling product was usually more than 70% of the total coupling products. It is fortunate that, although the reaction products have similar molecular structures, the cross-coupling product can easily be separated from the self-coupling products by means of silica-gel chromatography, using carbon disulfide as the eluent. The absence of the self-coupling products in the purified EVT, EMVT, and EDMVT was confirmed by a study of the mass spectra. The coupling reaction of a mixture of **1** and 4,5-vinylenedithio-1,3-dithiole-2-thione[3)] in triethyl phosphite gave BEDT-TTF as the main product. Thus, **2** should be used instead of its thiocarbonyl derivative in order to obtain EVT.

The cyclic voltammetries of EVT, EMVT, and EDMVT were measured for THF solutions by using tetrabutylammonium perchlorate as the electrolyte and platinum plates as electrodes. Table 2 summarizes their half-wave oxidation potentials (vs. SCE), together with those of BEDT-TTF, VT, DMVT, and TMVT for the sake of comparison.[3)] EVT, EMVT, and EDMVT gave only one redox wave. Since the oxidation potentials of BEDT-TTF, VT, DMVT, and TMVT have been found to be in the order of BEDT-TTF<DMVT≈TMVT<VT,[3)] the following order of the oxidation potentials is predicted: BEDT-TTF<EVT<VT, BEDT-TTF<EMVT<DMVT, BEDT-TTF<EDMVT<TMVT. Table 2 shows that the prediction is satisfied for these new donor molecules.

The electrochemical crystallization of EVT was made for I_3^-, PF_6^-, AsF_6^-, and IBr_2^--salts. Their electrical conductivities at 0 °C were 184 $S\,cm^{-1}$ (I_3-salt), 0.76 $S\,cm^{-1}$ (PF_6-salt), 0.17 $S\,cm^{-1}$ (AsF_6-salt), and 4.2 $S\,cm^{-1}$ (IBr_2-salt). The temperature dependence of their electrical conductivities showed semiconducting behavior.

Molecular and Crystal Structures of EVT. The EVT molecule is not planar (Fig. 1(b)). The central portion of tetrathio-substituted ethylene is almost planar, but the outer parts are all bent in the same direction. This molecular structure is much closer to that of BEDT-TTF[13)] than to that of VT; the outer parts of VT are bent in the opposite directions.[4)] The pair-by-pair arrangement of EVT molecules, related by a center of symmetry, is shown in Fig. 2. The molecular arrangement is very close to that found in the BEDT-TTF crystal.[13)] The mode of overlapping of the paired molecules is shown in Fig. 3. The mode of the overlapping of the two molecules is also very close to that of BEDT-TTF.[13)] Several intermolecular S····S distances [$S(5)(x,y,z)\cdots S(6)(-x,-y,1-z)$ (=3.588(3) Å), $S(1)(x,y,z)\cdots S(4)(-1+x,y,z)$(=3.431(4) Å), $S(3)(x,y,z)\cdots S(4)(-1+x,y,z)$(=3.516(4) Å), and S(7)

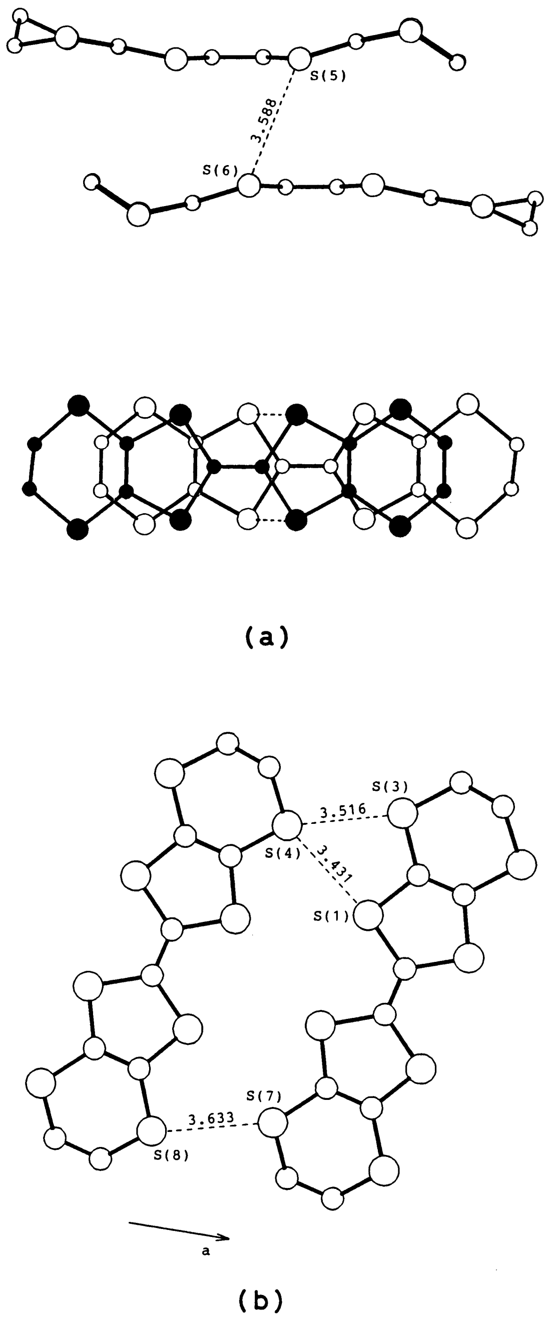


Fig. 3. (a) The mode of overlapping of the paired EVT molecules.[15] The dotted lines indicate the S···S contacts shorter than van der Waals distance (3.7 Å). (b) Molecular arrangememt along the *a* axis.[15]

(x,y,z)···S(8) $(-1+x,y,z)$(=3.633(3) Å)] are shorter than the van der Waals distance (3.7 Å) (Figs. 3(a) and 3(b)).

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