

Synthesis, X-Ray Crystal Structure and Coupling Reactions of 4,5-(1',2'-diphenylethylenedithio)-1,3-dithiole-2-thione (dPhEDT-DTT)

Ha-Jin Lee and Dong-Youn Noh*

Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea

Received November 24, 1997

A facile synthesis of 4,5-(1',2'-diphenylethylenedithio)-1,3-dithiole-2-thione (dPhEDT-DTT) is carried out via a Diels-Alder type [2+4] cycloaddition reaction of 1,3-dithiol-2,4,5-trithione oligomer and *t*-stilbene. Molecular structure of dPhEDT-DTT is determined by x-ray crystallography: space group P1, $a=11.694(3)$ Å, $b=12.117(3)$ Å, $c=14.688(3)$ Å, $\alpha=113.12(2)^\circ$, $\beta=102.23(2)^\circ$, $\gamma=107.02(2)^\circ$, $V=1699.1(7)$ Å³, $Z=2$. It turns out that dPhEDT-DTT crystallizes as a racemic compound consisting of (*R,R*) and (*S,S*) enantiomers. Coupling reaction of dPhEDT-DTO undergone in neat P(OEt)₃ yields TTF(SEt)₄ instead of ET derivative. When PR₃ (R=OEt, OPh, Ph) is used in benzene, toluene or xylene, however, dPhEDT-DTO is decomposed.

Introduction

A number of π -electron donors have been intensively developed during the last several decades because of their potential applications in material science¹ such as molecular magnet, nonlinear optics, molecular superconductor, LB film and redox active molecular sensor, among which BEDT-TTF (or ET: bis(ethylenedithio)tetrathiafulvalene; Scheme 1) is one of the most important donor used for superconducting complexes.^{1c} The most predominantly employed method for the synthesis of ET derivatives involves coupling reaction of EDT-DTT(4,5-ethylenedithio-1,3-dithiole-2-thione) or EDT-DTO (4,5-ethylenedithio-1,3-dithiole-2-one) derivatives^{1b} utilizing trivalent phosphorous reagents such as trialkyl phosphites and triphenyl phosphines. In this aspect, a number of EDT-DTT derivatives containing functional groups on C(sp³) have been synthesized and utilized in the preparation of new functional ET compounds.^{2,3}

Oligomeric 1,3-dithiole-2,4,5-trithione(abbreviated as trithione, hereafter) was prepared and characterized by Neilands *et al.*,^{3a,3b} and employed thereafter as an efficient diene in many [2+4] cycloaddition reactions with appropriate dienophiles such as TTF,^{3c,3g} 1,4-dioxene,^{3d} dimethyl acetylenecarboxylate^{3f} and 2,3-dihydro-1,4-oxathiine.^{3e} This

reaction has been considered to open up new facile ways of preparing various EDT-DTT derivatives.

In this paper, we report the preparation of dPhEDT-DTT via a Diels-Alder type [2+4] cycloaddition reaction and its coupling reaction along with x-ray single crystal structure.

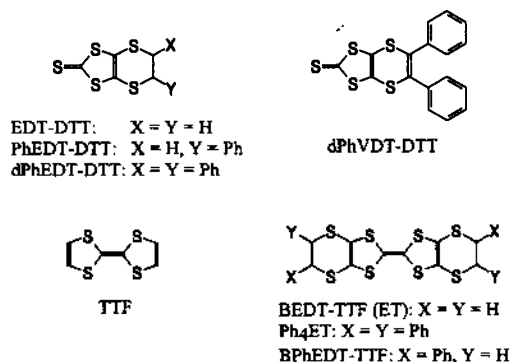
Experimental

General Methods. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AC-250 spectrometer, infrared spectra by KBr method on MIDAC FT-IR spectrometer and UV-vis spectra in acetonitrile on HP 8452A diod array spectrometer. High- and low-resolution electron impact(HREI/LREI) mass spectra were obtained on a double focusing mass spectrometry (JMS-SX-102A, JEOL, Akishima) operating with a resolving power of 10000. The ionization energy was set at 70 eV, acceleration voltage 10 kV and the ion source temperature 200 °C. Cyclic voltametry was measured at room temperature with EG&G VersaStat model Potentiostat/Galvanostat in an acetonitrile solution (20 mL) containing 0.1 M *n*-Bu₄N-ClO₄ as electrolyte, Ag/AgCl as reference electrode, Pt-button working electrode, platinum wire as a counter electrode.

X-ray Analysis of dPhEDT-DTT. X-ray crystallographic data of dPhEDT-DTT were collected on an Enraf-Nonius CAD-4 automatic diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å) at 293(2) K. Intensities of 5963 [R(int)=0.0191] independent reflections within θ range 1.62-25.01° were measured using $\omega/2\theta$ scan mode for the range $0 \leq h \leq 13$, $-14 \leq k \leq 13$, $-17 \leq l \leq 17$. 5963 reflections were considered [$I > 2\sigma(I)$] and used in calculations performed on IBM PC 486 computer using SHELXS-86 and SHELXL-93 (Sheldrick, 1986, 1993)⁴ and atomic scattering factors for all nonhydrogen atoms were supplied by the SHELXS-86 system. Crystal parameters and procedural information corresponding to data collection are given in Table 1.

Chemical Synthesis

Oligo(1,3-dithiole-2,4,5-trithione). It was synthesized according to the reported procedure^{3c} at room temperature: yield 97%; FT-IR (KBr, cm⁻¹) 1642 (C=C) 1065



Scheme 1.

*To whom correspondence should be addressed.

(C=S); UV (CH₃CN, nm) 214 (st) 246 (st) 366 (w).

4,5-(1',2'-Diphenylethylenedithio)-1,3-dithiole-2-thione: dPhEDT-DTT

Method A. To a 30 mL benzene solution of oligomeric trithione (3.9 g, 20 mmol) was added *t*-stilbene (3.6 g, 20 mmol), which was refluxed for 2 h and cooled down to room temperature. Orange-coloured reaction mixture was filtered and organic solvent was evaporated under reduced pressure. To obtain an analytical sample, crude product was decolourized by refluxing over activated carbon for 20 min. and recrystallized from CH₂Cl₂/CH₃OH (1:1): yield 48%; mp >180 °C (dec.); ¹H NMR (CDCl₃, δ) 7.2 (10H, m), 4.85 (2H, m); ¹³C NMR (CDCl₃, δ), 208.6, 135.9, 128.9, 128.7, 128.3, 125.9, 54.5; FT-IR (KBr, cm⁻¹), 1636 (C=C), 1489, 1453, 1069 (C=S), 714, 693; UV (CH₃CN, nm), 218 (st), 276 (w), 408 (m); HR-EIMS calc. for C₁₇H₁₂S₅ 375.9543 found 375.9550; LR-EIMS (m/z, %), 376 (M⁺, 18), 180 (M⁺-C₃S₅, 100).

Method B. To a 5 mL benzene solution of oligomeric trithione (196 mg, 1 mmol) in 20 mL quartz tube was added *t*-stilbene (180 mg, 1 mmol), which was irradiated by UV light (254 nm) with stirring for 5 h. Orange-coloured reaction mixture was filtered and organic solvent was evaporated under reduced pressure. Crude product was recrystallized from CHCl₃/C₂H₅OH (1:5): yield 39%.

4,5-(1',2'-Diphenylethylenedithio)-1,3-dithiole-2-one: dPhEDT-DTO. Glacial acetic acid (80 mL) and Hg(OAc)₂ (3.3 g, 10.4 mmol) were dissolved in a chloroform solution (90 mL) of dPhEDT-DTT (1.96 g, 5.2 mmol). The mixture was stirred at room temperature for 30 min. and filtered. The organic phase was washed several times with saturated NaHCO₃ aqueous solution, and finally with water. Drying over Na₂SO₄ and evaporation of solvent gave the product as pale yellow crystal, which was recrystallized from CH₂Cl₂/CH₃OH (1:1): yield 85%; mp >190 °C (dec.); ¹H NMR (CDCl₃, δ) 7.2 (10H, m), 4.8 (2H, m); ¹³C NMR (CDCl₃, δ) 136.4, 128.8, 128.6, 128.2, 116.4, 56.0; FT-IR (KBr, cm⁻¹), 1671 (C=C), 1632 (C=O), 1505, 1454, 716, 694; UV (CH₃CN, nm), 224 (st), 294 (w); HR-EIMS calc. for C₁₇H₁₂OS₄ 359.9771 found 359.9764; LR-EIMS (m/z, %), 360 (M⁺, 24) 180 (M⁺-C₃OS₄, 100).

Tetrathioethoxytetrathiafulvalene: TTF(SEt)₄. dPhEDT-DTO (720 mg, 2 mmol) was dissolved in freshly distilled triethylphosphite (8 mL, 46 mmol) and refluxed for 0.5–3 h. The reaction mixture was allowed to cool down to room temperature and left overnight at 4 °C after adding MeOH (10 mL). The resultant orange crystal was collected by filtration and washed with MeOH (5 mL): yield 35%; mp >190 °C (dec.); ¹H NMR (CDCl₃, δ), 2.9 (8H, qr), 1.35 (12H, t); FT-IR (KBr, cm⁻¹), 1442, 1370, 1257, 1052, 963, 886, 755, 502; UV (CH₃CN, nm) 220, 268, 308, 330; HR-EIMS calc. for C₁₄H₂₀S₈, 443.9331 found 443.9337; LR-EIMS (m/z, %), 444 (M⁺, 100), 415 (M⁺-C₂H₅, 18), 382 (M⁺-SC₂H₅, 36).

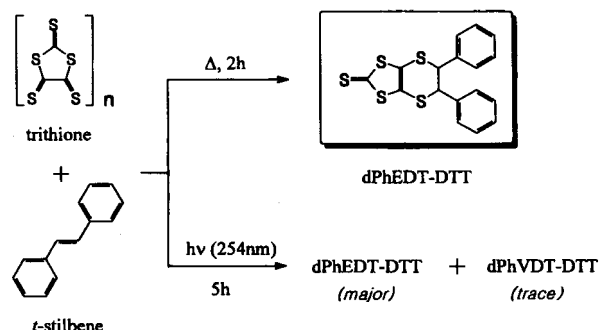
The combined filtrate was evaporated under vacuum and left overnight at 4 °C again. Some white crystals were obtained and identified as *t*-stilbene by FT-IR.

Triphenylphosphine sulfide: S=PPh₃. A mixture of dPhEDT-DTO (360 mg, 1 mmol) and PPh₃ (530 mg, 2.02 mol) dissolved in solvent (benzene, toluene or xylene) was refluxed for 0.5–10 h and then cooled to room temperature.

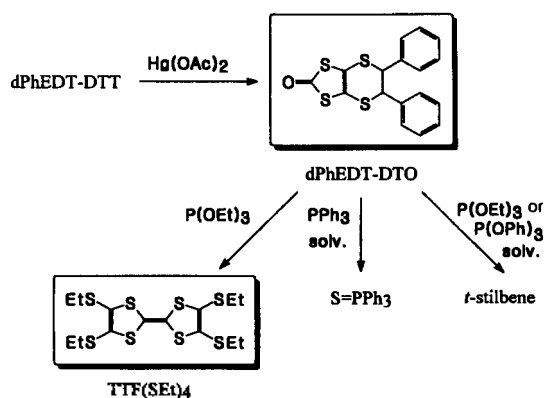
Black precipitate was filtered off and filtrate was evaporated under vacuum. The brown product was purified by column chromatography on silica gel eluting with chloroform. The second light-brown band was collected and crystallized as white needle-shape crystals: yield 53% (solvent: Bz), 82% (solvent: Tol), 62% (solvent: Xyl); mp 162–163 °C; Elemental analysis (%) calc. for C₁₈H₁₅SP C 73.45, H 5.14, S 10.87 found C 73.08, H 5.66, S 11.49; ¹H NMR (CDCl₃, δ), 7.6 (m), 7.8 (m); ¹³C NMR (CDCl₃, δ), 133.6, 132.3, 132.2, 131.6, 131.5, 128.6, 128.4; FT-IR (KBr, cm⁻¹), 1480, 1473, 1103, 752, 714, 691, 639, 515; UV (CH₃CN, nm), 222, 256; LR-EIMS (m/z, %), 294 (S=PPh₃⁺, 100), 262 (PPh₃⁺, 15), 217 (S=PPh₂⁺, 6), 185 (PPh₂⁺, 43); FAB-MS (m/z, %), 588.0 (M²⁺, 1), 294.9 (M+H⁺, 100).

Results and Discussion

Synthesis and Chemical Properties. dPhEDT-DTT was easily obtained via a Diels-Alder type [2+4] cycloaddition of oligomeric trithione with *t*-stilbene: refluxing in benzene (direct thermal reaction) for 2 h. (Scheme 2) Orange crystals of plate-shape were isolated after recrystallization from CH₂Cl₂/CH₃OH (1:1) in 48% yield. The product was identified by spectroscopic methods and high-/low-resolution electron impact mass spectra (HR-/LR-EIMS). This compound can be obtained by photoreaction as well: the reaction mixture in 20 mL quartz tube was irradiated by UV light of 254 nm. The major product obtained in 39% yield was confirmed as dPhEDT-DTT. We tried to prepare a totally conjugate system, dPhVDT-DTT (Scheme 1), by the deprotonation of dPhEDT-DTT using



Scheme 2. Two synthetic pathways to dPhEDT-DTT.



Scheme 3. Coupling reactions of dPhEDT-DTO.

DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), which is expected to be a potential precursor to electronic materials. This attempt turned out to be unsuccessful. However, trace amount of dPhVDT-DTT was occasionally separated as needle-shaped crystal in the photoreaction described above and identified by x-ray single crystal analysis method.

Coupling Reaction. dPhEDT-DTT was subsequently converted to its oxo-derivative (dPhEDT-DTO) according to a standard method^{2b} using Hg(OAc)₂ in chloroform (Scheme 3). Reaction of dPhEDT-DTO in neat refluxing P(OEt)₃ affords TTF(SEt)₄ in 35% yield with the elimination of *t*-stilbene moiety, which was identified by high-resolution electron impact mass spectroscopy as well as other spectroscopic methods such as ¹H NMR, FT-IR and UV-vis. This type of unusual coupling behavior can be found in a few cases,^{3f} where the reaction was suggested to proceed via an Arbusov rearrangement following the attack of the phosphorus at the *sp*³ carbon. In this unusual coupling reaction, it is not surprising for S-C(*sp*³) bond to be broken by the attack of phosphorous considering the MS results of dPhEDT-DTO: Peak at *m/z*=180 with 100% abundance corresponds to stilbene produced by the decomposition process while mother peak with 24% abundance only. It can be seen in the MS result of dPhEDT-DTT, too, indicating that S-C(*sp*³) bond is the most susceptible to bond breakage among any others in the molecule.

Redox potentials of TTF(SEt)₄ were measured with cyclic voltammetry (0.626 mM of CH₃CN containing *n*-Bu₄N·ClO₄ (0.1 M) as electrolyte; Pt-button electrode; potential vs Ag/AgCl; scan rate 0.05 V/sec). It shows two reversible oxidation potentials at E₁=0.61 V and E₂=0.83 V (ΔE=0.22 V), which is similar to TTF. This potential difference (ΔE) is smaller than that of TTF itself (ΔE=0.36 V; E₁=0.35 V and E₂=0.71 V)⁵ indicating the smaller on-site Coulomb potential of TTF(SEt)₄.

The same coupling reaction was carried out using P(OEt)₃

or P(OPh)₃ in solvents such as benzene, toluene or xylene. It led to *t*-stilbene and unidentified yellow residue which might be the decomposition products of dPhEDT-DTO. PPh₃ was also employed as a coupling reagent in the same solvents used before, but white needle-shape crystals were obtained in 53-82% yield depending on the solvent used. Unidentified mixtures were also obtained probably coming from the decomposition of dPhEDT-DTO. This white crystal was identified as triphenylphosphine sulfide (S=PPh₃) according to the elemental analysis, NMR and MS data:

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for dPhEDT-DTT

	x	y	z	U(eq) ^a
S(1)	-931(1)	4117(1)	2378(1)	62(1)
S(2)	-2501(1)	1521(1)	2131(1)	50(1)
S(3)	-3783(1)	3034(1)	1636(1)	46(1)
S(4)	-6414(1)	1146(1)	1041(1)	62(1)
S(5)	-4885(1)	-750(1)	1572(1)	54(1)
S(21)	311(1)	3372(1)	4556(1)	65(1)
S(22)	2097(1)	3588(1)	3417(1)	52(1)
S(23)	2669(1)	5844(1)	5403(1)	53(1)
S(24)	5192(1)	7481(1)	5478(1)	59(1)
S(25)	4460(1)	4713(1)	3091(1)	59(1)
C(1)	-2320(4)	2955(4)	2065(3)	46(1)
C(2)	-4178(4)	796(4)	1670(3)	46(1)
C(3)	-4775(4)	1511(4)	1455(3)	47(1)
C(4)	-7172(4)	-496(4)	885(4)	53(1)
C(5)	-6407(4)	-751(4)	1691(4)	54(1)
C(6)	-8492(4)	-645(4)	903(3)	45(1)
C(7)	-8682(5)	97(5)	1799(4)	61(1)
C(8)	-9895(5)	-64(5)	1786(4)	65(1)
C(9)	-10943(4)	-962(5)	870(4)	58(1)
C(10)	-10774(4)	-1698(4)	-26(4)	61(1)
C(11)	-9559(5)	-1549(4)	-22(3)	55(1)
C(12)	-7133(4)	-2075(4)	1597(3)	46(1)
C(13)	-7615(5)	-3266(5)	662(4)	58(1)
C(14)	-8273(5)	-4441(5)	623(4)	64(1)
C(15)	-8450(5)	-4465(5)	1497(5)	70(1)
C(16)	-7964(6)	-3287(6)	2438(5)	73(2)
C(17)	-7320(5)	-2108(5)	2478(4)	62(1)
C(21)	1618(4)	4223(4)	4480(3)	46(1)
C(22)	3557(4)	4922(4)	3899(3)	43(1)
C(23)	3833(4)	5981(4)	4835(3)	47(1)
C(24)	5554(5)	7485(4)	4339(3)	56(1)
C(25)	5791(5)	6328(4)	3697(4)	58(1)
C(26)	6679(4)	8795(4)	4749(3)	47(1)
C(27)	7895(5)	9112(5)	5387(4)	62(1)
C(28)	8906(5)	10271(6)	5710(4)	71(1)
C(29)	8707(6)	11130(6)	5396(4)	82(2)
C(30)	7529(7)	10876(6)	4775(5)	88(2)
C(31)	6475(5)	9666(5)	4442(4)	68(1)
C(32)	6182(4)	6407(4)	2789(3)	47(1)
C(33)	7398(5)	6508(5)	2836(4)	64(1)
C(34)	7797(6)	6590(6)	2041(6)	89(2)
C(35)	6969(9)	6541(6)	1187(6)	93(2)
C(36)	5751(8)	6424(6)	1145(4)	87(2)
C(37)	5377(6)	6368(5)	1959(4)	69(1)

^aU(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 1. Crystal Data and Structure Refinement for dPhEDT-DTT

formula	C ₃₄ H ₂₄ S ₁₀
formula weight	753.13
crystal system	triclinic
space group	P1(No.2)
a, Å	11.694(3)
b, Å	12.117(3)
c, Å	14.688(3)
α, deg.	113.12(2)
β, deg.	102.23(2)
γ, deg.	107.02(2)
V, Å ³	1699.1(7)
Z	2
D _{calc} , Mg/m ³	1.472
μ(Mo-Kα), mm ⁻¹	0.674
F(000)	776
reflections collected	6283
independent reflections	5963 [R(int)=0.0191]
data / restraints / parameters	5963 / 0 / 397
goodness-of-fit on F ²	1.070
final R indices [I>2σ(I)]	R ₁ =0.0664, wR ₂ =0.1696

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2 \}^{1/2}$$

mother ion ($SPPH_3^+$) was observed at $m/z=294$ (100%) along with the dimer ion peak at $m/z=588.0$ (1%). Consequently, tetraphenyl-substituted ET (Ph_4ET) was not synthesized in the coupling reaction of dPhEDT-DTO or dPhEDT-DTT using phosphite or phosphine coupling reagents. The TTF derivative was obtained only when neat P(OPh)₃ was used as a coupling reagent. These results are compared to those of the coupling reactions of (Ph)EDT-DTT: Synthesis of BPhEDT-TTF as well as BEDT-TTF by the standard coupling reaction of (Ph)EDT-DTT is very well known and carried out under the mild conditions. (100–130 °C, 30 min. in P(OEt)₃ for BPhEDT-TTF^{2b} and 110–120 °C, 45 min. in P(OEt)₃ for BEDT-TTF^{1b}).

Crystal Structure of dPhEDT-DTT. As expected in a Diels-Alder type [2+4] cycloaddition reaction, an enantiomer mixture of dPhEDT-DTT was obtained: In the cycloaddition reaction of oligomeric trithione with planar *t*-stilbene, two distinct products denoted as (*R,R*) and (*S,S*) are expected with equal probability depending on the orientation of the approach (*exo* and *endo* approaches).⁵ Single crystals of dPhEDT-DTT (prepared by thermal reaction) suitable for an x-ray diffraction study were grown in $CH_2Cl_2/MeOH$. Crystal data and structure refinement parameters of this compound are collected in Table 1. Atomic coordinates

Table 3. Selected Bond Lengths [Å] and Angles[deg] for dPhEDT-DTT

S(1)-C(1)	1.634(4)	S(21)-C(21)	1.628(4)
S(2)-C(2)	1.742(4)	S(22)-C(22)	1.733(4)
S(2)-C(1)	1.732(4)	S(22)-C(21)	1.739(4)
S(3)-C(1)	1.737(4)	S(23)-C(21)	1.731(4)
S(3)-C(3)	1.747(4)	S(23)-C(23)	1.742(4)
S(4)-C(3)	1.743(4)	S(24)-C(23)	1.745(4)
S(4)-C(4)	1.821(4)	S(24)-C(24)	1.811(4)
S(5)-C(2)	1.744(4)	S(25)-C(22)	1.742(4)
S(5)-C(5)	1.823(5)	S(25)-C(25)	1.819(4)
C(2)-C(3)	1.347(6)	C(22)-C(23)	1.351(5)
C(4)-C(6)	1.508(6)	C(24)-C(25)	1.494(6)
C(4)-C(5)	1.517(6)	C(24)-C(26)	1.518(6)
C(5)-C(12)	1.514(6)	C(25)-C(32)	1.527(6)
C(2)-S(2)-C(1)	97.7(2)	C(22)-S(22)-C(21)	97.9(2)
C(1)-S(3)-C(3)	97.3(2)	C(21)-S(23)-C(23)	97.7(2)
C(3)-S(4)-C(4)	104.0(2)	C(23)-S(24)-C(24)	99.9(2)
C(2)-S(5)-C(5)	100.5(2)	C(22)-S(25)-C(25)	104.5(2)
S(1)-C(1)-S(3)	123.3(3)	S(21)-C(21)-S(23)	125.3(3)
S(1)-C(1)-S(2)	124.1(3)	S(21)-C(21)-S(22)	122.7(3)
S(3)-C(1)-S(2)	112.6(2)	S(23)-C(21)-S(22)	112.0(2)
C(3)-C(2)-S(2)	116.0(3)	C(23)-C(22)-S(22)	116.0(3)
C(3)-C(2)-S(5)	127.6(3)	C(23)-C(22)-S(25)	129.0(3)
S(2)-C(2)-S(5)	116.4(2)	S(22)-C(22)-S(25)	115.0(2)
C(2)-C(3)-S(4)	129.0(3)	C(22)-C(23)-S(23)	116.0(3)
C(2)-C(3)-S(3)	116.3(3)	C(22)-C(23)-S(24)	126.1(3)
S(4)-C(3)-S(3)	114.7(2)	S(23)-C(23)-S(24)	117.8(2)
C(6)-C(4)-C(5)	113.7(4)	C(25)-C(24)-C(26)	112.6(4)
C(6)-C(4)-S(4)	105.0(3)	C(25)-C(24)-S(24)	114.6(3)
C(5)-C(4)-S(4)	114.7(3)	C(26)-C(24)-S(24)	107.2(3)
C(12)-C(5)-C(4)	112.7(4)	C(24)-C(25)-C(32)	113.3(4)
C(12)-C(5)-S(5)	105.6(3)	C(24)-C(25)-S(25)	116.2(3)
C(4)-C(5)-S(5)	113.7(3)	C(32)-C(25)-S(25)	105.7(3)

are given in Table 2, and selected bond lengths and angles in Table 3. dPhEDT-DTT crystallizes in a triclinic system with two crystallographic unit ($Z=2$) in a unit cell. It means that equal number of enantiomers, (*R,R*)- and (*S,S*)-dPhEDT-DTT, crystallizes together in a crystal. Molecular structure of the racemic compound is shown in Figure 1, where a couple of dPhEDT-DTT with different stereospecificity are depicted. The close-packing of molecules is shown in Figure 2. The average S-C(sp^3) bond length in six-

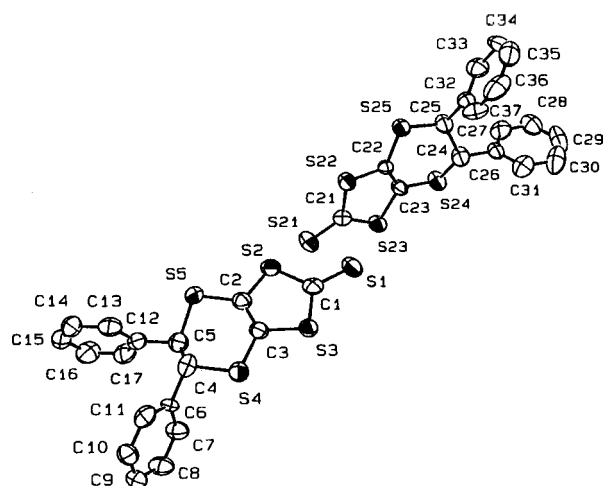


Figure 1. ORTEP Drawing of the dPhEDT-DTT Single Crystal Structure.

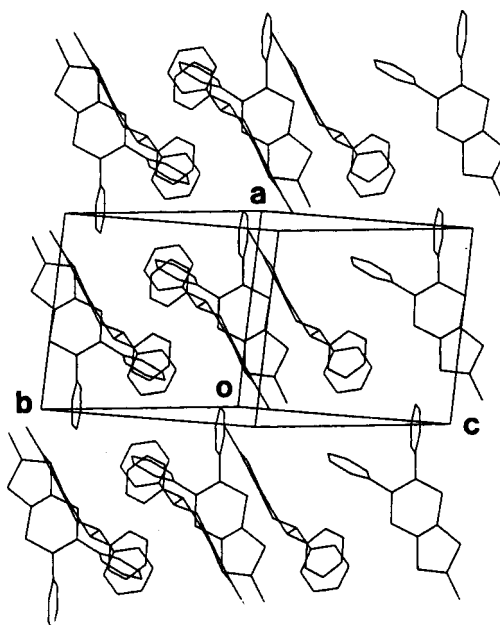


Figure 2. Packing Diagram of the dPhEDT-DTT Unit Cell.

Table 4. Intermolecular S...S Distances for dPhEDT-DTT

Atoms	Dist. (Å)	Atoms	Dist. (Å)
S(1)···S(21) ^a	3.772	S(3)···S(23) ^b	3.792
S(1)···S(22) ^a	3.884	S(2)···S(21) ^a	3.602
S(4)···S(25) ^c	3.832	S(2)···S(23) ^b	3.864
S(3)···S(23) ^c	3.718		

^a(x, y, z), ^b(-x, -y, 1-z), ^c(-1+x, y, z).

membered rings (1.819 Å) is longer than that of S-C(sp^2) (1.744 Å) which is consistent with the result that S-C(sp^3) bond is more susceptible to bond breakage than S-C(sp^2) bond in the reaction with phosphite. Some intermolecular S...S contact distances in the crystal structure are collected in Table 4, where S(2)...S(21) distance (3.602 Å) is close to the sum of their van der Waals radii (3.6 Å).⁷ High thermal stability of this crystal (decomposition above 180 °C) could be attributed to the close intermolecular contact.

Conclusions

As a potential precursor to electronic material, dPhEDT-DTT is successfully synthesized via a Diels-Alder type [2+4] cycloaddition based on thermal reaction as well as photoreaction. It crystallizes as a racemic compound consisting of (*R,R*) and (*S,S*) enantiomers. In this crystal, intermolecular S(2)...S(21) distance (3.602 Å) is close to the sum of their van der Waals radii (3.6 Å). Reaction of dPhEDT-DTO in neat refluxing P(OEt)₃ yields TTF(SET)₄ via an Arbuzov rearrangement. Treatment of dPhEDT-DTT(O) with PR₃ (R=OEt, OPh, Ph) in benzene, toluene or xylene, however, leads to the decomposition process affording stilbene and/or S=PPh₃. Metal complexes in which dPhEDT-DTT is used as a ligand precursor are expected to exhibit optical property such as strong near-IR absorption, and therefore applicable to laser material.

Acknowledgment. The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1997.

Supplementary Material Available. Tables of atomic coordinates, bond lengths, bond angles and anisotropic thermal parameters for non-hydrogen atoms of dPhEDT-DTT are available.

References

- (a) Khodorkovsky, V. Y.; Becker, J. Y. In *Organic Conductors*; Ed. Farges, J. P.; Marcel Dekker: NY, 1994; pp 75-114. (b) Montgomery, L. K. In *Organic Conductors* Ed. Farges, J. P.; Marcel Dekker: NY, 1994; pp 115-145. (c) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory*; Prentice Hall; Englewood Cliffs, NJ, 1992. (d) Ishiguro, T.; Yamaji, K. *Organic Superconductors*; Springer-Verlag: Berlin, 1990. (e) Saito, G.; Kagoshima, S. *The Physics and Chemistry of Organic Superconductor*; Springer-Verlag: Berlin, 1990. (f) Becher, I.; Schaumburg, K. Ed. *Molecular Engineering for Advanced Materials*; Kluwer; Netherlands, 1995. (g) Petty, M. C.; Bryce, M. R.; Bloor, D. Ed. *Introduction to Molecular Electronics*; 1995.
- (a) Noh, D.-Y.; Lee, H.-J.; Hong, J.; Underhill, A. E. *Tetrahedron Lett.* 1996, 37, 7603. (b) Varma, K. S.; Evans, J.; Edge, S.; Underhill, A. E.; Bojesen, G.; Becher, J. *J. Chem. Soc., Chem. Commun.* 1989, 257. (c) Wallis, J. D.; Karrer, A.; Dunitz, J. D. *Helv. Chim. Acta* 1986, 69, 69. (d) Ozturk, T.; Povey, D. C.; Wallis, J. D. *Tetrahedron* 1994, 50, 11205. (e) Nogami, T.; Inoue, K.; Nakamura, T.; Iwasaka, S.; Nakano, H.; Mikawa, H. *Synth. Metals* 1987, 19, 539. (f) Ozturk, T. *Tetrahedron Lett.* 1996, 37, 2821. (g) Ozturk, T.; Rice, C. R.; Wallis, J. D. *J. Mater. Chem.* 1995, 5, 1553.
- (a) Neilands, O. Ya.; Katsens, Ya. Ya.; Kreitsberga, Ya. N. *Zh. Org. Khim.* 1989, 25, 658. (b) Neilands, O. Ya.; Katsens, Ya. Ya.; Kreitsberga, Ya. N. Russian Patent #SU 1428753, 1988; *Chem. Abstr.* 1989, 110, 95252. (c) Khodorkovsky, V. Y.; Becker, J. Y.; Bernstein, J. *Synthesis* 1992, 1071. (d) Kotov, A. I.; Faulmann, C.; Cas-soux, P.; Yagubskii, E. B. *J. Org. Chem.* 1994, 59, 2626. (e) Hellberg, J.; Balodis, K.; Moge, M.; Korall, P.; von Schutz, J.-U. *J. Mater. Chem.* 1997, 7, 31. (f) Yang, X.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* 1990, 34. (g) Khodorkovsky, V. Y.; Becker, J. Y.; Bernstein, J. *Synth. Metals* 1993, 55-57, 1931.
- (a) Sheldrick, G. M. SHELXS-86: A Program for Structure Determination; University of Gottingen, Germany, 1986. (b) Sheldrick, G. M. SHELXS-93: A Program for Structure Refinement; University of Gottingen, Germany, 1993.
- It is obtained from the measurement in this work.
- McMurry, J. *Organic Chemistry*, 4th. Ed.; Brooks/Cole; Pacific Grove, CA., 1995.
- Bondi, A. *J. Phys. Chem.* 1964, 68, 441.