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TTF 주게분자의 전구체로서 두 가지 다른 1,3-Dithiole-2-thione 화합물의 합성 및 특성화

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Synthesis and Characterization of Two Different 1,3-Dithiole-2-thiones as the Precursors of TTF Donor Molecule

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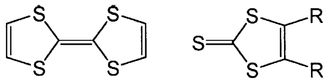
요 약. TTF (tetrathiafulvalene) 유도체의 전구체로서 5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione (화합물 **3**)을 로손반응에 의하여 합성하였다. 치환기의 종류에 따라 1,4-dithiin이나 티오펜이 포함된 두 가지의 서로 다른 생성물이 얻어졌고, 이들은 ^{13}C NMR과 고 분해능 전자충돌(HREI) 질량분석 분광학으로 특성화하였다. 화합물 **3**의 합성은 X-선 구조분석으로도 확인되었다. 결정학적 자료: 삼사정계, 공간군 $P\bar{1}$, a=4.145(2)Å, b=10.600(2)Å, c=12.279(2)Å, α=71.440(10)°, β=84.30(2)°, γ=87.31(2)°, Z=2, $R(wR_2)$=0.0559 (0.1416). 두 가지 생성물의 생성 기구를 비교하여 설명하였다.

ABSTRACT. As a precursor of tetrathiafulvalene (TTF) derivative, 5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4] dithiin-2-thione (compound **3**) was synthesized by the unusual Lawesson's reaction. Depending upon the substituents such as dimethyl and diphenyl groups, two different products containing 1,4-dithiin and thiophene moieties, respectively, were obtained and characterized by ^{13}C NMR and high-resolution electron impact (HREI) mass spectroscopy. The formation of **3** was further characterized by X-ray structure analysis. Crystallographic data for **3**: triclinic, space group $P\bar{1}$, a=4.145(2)Å, b=10.600(2)Å, c=12.279(2)Å, α=71.440(10)°, β=84.30(2)°, γ=87.31(2)°, Z=2 and $R(wR_2)$=0.0559(0.1416). The formation mechanism of two products was suggested and compared each other.

INTRODUCTION

Tetrathiafulvalene (TTF: $C_6H_4S_4$) is one of the versatile electron-donor molecules used for the synthesis of organic metals and new molecular building blocks in the field of molecular engineering.[1-3] With these purposes, many TTF derivatives have been synthesized by several ways[2,3] among which phosphite-based coupling method with 2-thioxo-1,3-dithiole derivatives is fairly common. 2-Thioxo-1,3-dithioles have been prepared by diverse ways,[2-6] one of which is the unusual reaction of Lawesson's reagent (L.R) with 1,8-diketones.[6] We previously reported the synthesis of a thiophene fused 2-thioxo-1,3-dithiole applying this method and its cross-coupled products.[5c] In this paper, we report the synthesis, characterization and X-ray structure analysis of 5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione (compound **3**) and compare them with those of 4,5-diphenylthieno[2,3-*d*]-1,3-dithiole-2-thione (compound **4**). We also suggest the mechanism for the formation of two different products according to the variation of the substituents, phenyl and methyl.



TTF 2-thioxo-1,3-dithiole

EXPERIMENTAL SECTION

^1H and ^{13}C NMR spectra were recorded with a Bruker AMX-500 NMR spectrometer at Korea Basic Science Institute (KBSI). Infrared spectra were obtained by the KBr pellet method on a MIDAC FT-IR spectrometer and UV-vis spectra in acetonitrile on HP 8452A diode array spectrometer. High-resolution electron impact (HREI) mass spectra were obtained on a double focusing mass spectrometer (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.

Synthesis of compound 1. To a 30 mL ethanol suspension of BTDT (1.01 g, 2.5 mmol) was added Na lump (0.12 g, 5 mmol) under nitrogen, and the mixture was stirred for 30 min. 3-Chloro-2-butanone (0.51 mL, 5 mmol) was added to the mixture and stirred overnight at room temperature. The red solution was evaporated under reduced pressure, and the residue was purified by column chromatography on a silica gel support with chloroform/*n*-hexane (1:2) as an eluent. The first band was collected and recrystallized as a light yellow crystal. Yield 58%; HR-EIMS(m/z) calc. for $C_{11}H_{14}O_2S_5$ 337.9597 obs. 337.9614; ^1H NMR (500 MHz, $CDCl_3$) δ 3.84 (2H, -CO-C*H*-, q, *J*=7.15 Hz) 2.35 (6H, -CO-CH_3, s), 1.53 (6H, -CO-CH-CH_3, d, *J* 7.16 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 210.0 (*C*=O) 203.2 (*C*=S) 137.1 (*C*=*C*) 54.02 (-S-*C*H-) 26.83 (-CO-*C*H_3) 16.61 (*C*H_3-CH-); FT-IR (KBr, cm^{-1}) 2982w (CH_3 sym. str.) 2930w (CH_3 sym. str.) 1704s (C=O) 1449m (CH_3 asym. def.) 1354m (CH_3 sym. def.) 1160m (C=C) 1058s (C=S), 1039m (C=S) 968m (C-S) 561m 521m (ring oop); UV (CH_3CN, nm) 196(st) 270(w) 376(st).

Synthesis of compound 3. A toluene solution (30 mL) containing Lawesson's reagent (1.66 mmol, 670 mg) and compound **1** (1.27 mmol, 430 mg) was refluxed for 24 h under nitrogen. After filtration at room temperature, the filtrate was decolorized with activated charcoal. Concentrated under reduced pressure, the orange product was purified by column chromatography on a silica gel eluting with chloroform/*n*-hexane (1:2). The first band was collected and crystallized as an orange needle. Yield 10%; HR-EIMS(m/z) calc. for $C_7H_6S_5$ 249.9066 obs. 249.9073; ^1H NMR (500 MHz, $CDCl_3$) δ 2.11 (6H, -CH_3, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 208.0 (*C*=S) 129.7 (-S_2*C*=*C*S_2-) 128.5 (CH_3-*C*=*C*-CH_3) 20.67 (-*C*H_3); FT-IR (KBr, cm^{-1}) 2923w (CH_3 asym. str.) 2852w (CH_3 sym. str.) 1492w (CH_3 asym. def.) 1434w (CH_3 sym. def.) 1070s (C=S) 909m (C-S) 506m (ring oop); UV (CH_3CN, nm) 202(st) 222(sh) 314(w) 392(m).

Synthesis of compounds 2 and 4. Syntheses and characterization of compound **2** and **4** were achieved by following the same procedures for compounds **1** and **3**, respectively, and described in the previous report in detail.[5c]

X-ray structural analysis. X-ray crystallographic data of compound **3** were collected on an Enraf-Noius CAD-4 automatic diffractometer with graphite-monochromated Mo-K_α radiation (λ=0.71073Å) at 293(2) K.

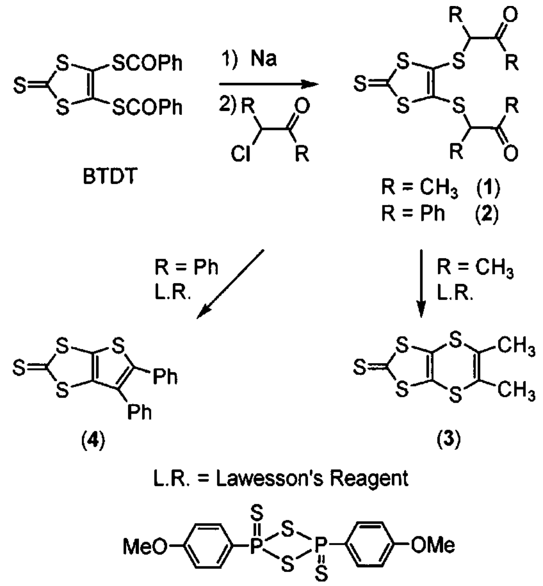
Table 1. Crystal data and structure refinement for compound **3**

Empirical formula	$C_7H_6S_5$
Formula weight	250.42
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	4.145(2)
b (Å)	10.600(2)
c (Å)	12.279(2)
α(°)	71.44(1)
β(°)	84.30(2)
γ(°)	87.31(2)
Volume ($Å^3$)	508.8(3)
Z	2
Calc. density (Mg/m^3)	1.634
Absorption coeff. (mm^{-1})	1.079
F(000)	256
Crystal size (mm^3)	0.13×0.13×0.30
Index ranges	0≤*h*≤4, -12≤*k*≤12, -14≤*l*≤14
Reflections collected/unique	1374/1201 [R(int)=0.0278]
Completeness to 2θ=24.96	67.6%
Data/restraints/parameters	1201/0/109
Goodness-of-fit on F^2	1.085
Final *R* [I>2sigma(*I*)]	R_1=0.0559, wR_2=0.1416
R indices (all data)	R_1=0.0593, wR_2=0.1449
Largest diff. peak and hole	0.495 and -0.460 e.$Å^{-3}$

Intensities of independent reflections within θ range 1.76-24.96° were measured by ω/2θ scan methods. All calculations were performed on an IBM PC using SHELXS-86 and SHELXS-93 programs,[7] and atomic scattering factors for all non-hydrogen atoms were supplied by the SHELXS-86 system.[7a] Crystal parameters and information for data collection are given in *Table* 1.

RESULTS AND DISCUSSION

The synthetic pathway to compounds **3** and **4** is shown in *Scheme* 1. Compounds **1** and **2** were obtained from BTDT according to the known procedure.[5c] The reaction of the compounds **1** and **2** with a Lawesson's reagent (L.R) provides two different types of products depending on the nature of the substituent. Treatment of precursor **1** containing methyl groups with L.R produces a six-membered 1,4-dithiin ring derivative **3**, whereas the reaction of precursor **2** with L.R unexpectedly gives a thiophene derivative **4**. These results were confirmed by $^{1}H/^{13}C$-NMR and HREI mass spectroscopic measurements: HREI mass spectroscopic data (*m/z*=249.9073 for M$^+$) and the equivalent chemical shift for the two sp^2 carbons linked to the methyl group (δ=128.5 ppm) indicate the formation of a 1,4-dithiin ring in compound **3**, which was further confirmed by X-ray structure analysis as will be discussed below. On the contrary, the EI mass data (*m/z*=342 for M$^+$) and the different chemical shifts for the two sp^2 carbons linked to the phenyl group (δ=132.633 and 133.895 ppm)[5b] strongly indicate the formation of a thiophene moiety in compound **4**.



Scheme 1. Synthesis of compounds **3** and **4**.

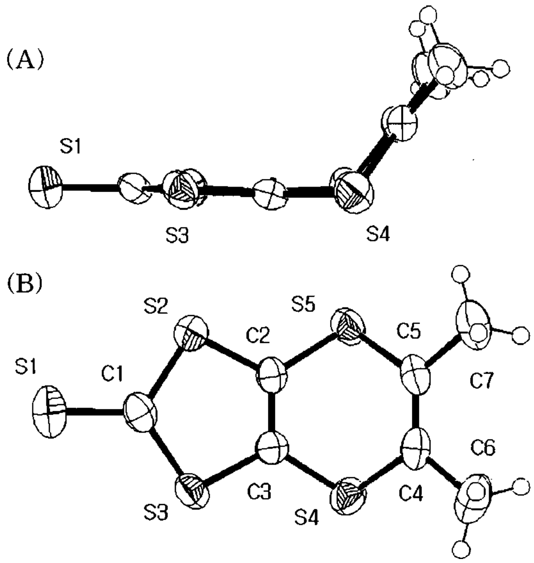


Fig. 1. Molecular structure of compound **3** with atomic numbering scheme: Side (A) and top (B) views. Selected bond lengths (Å) and angles (°): S1-C1 1.636(6), S2-C2 1.726(6), S2-C1 1.728(6), S3-C1 1.729(6), S3-C3 1.740(6), S4-C3 1.738(6), S4-C4 1.777(6), S5-C2 1.746(6), S5-C5 1.777(6), C2-C3 1.342(8), C4-C5 1.339(9), C4-C6 1.495(8), C5-C7 1.498(9), S1-C1-S2 123.1(4), S1-C1-S3 124.1(4), S2-C1-S3 112.8(3).

Molecular structure of compound **3** is demonstrated in *Fig.* 1. All sulfur atoms in compound **3** are almost in a plane (plane A). The atoms (S4, S5, C4 and C5) also form a plane B. These two planes are folded up with the dihedral angle of 126.55°. It is well-known from the molecular orbital calculation of the 1,4-dithiin ring[8] that the nonoxidized 1,4-dithiin ring has a folded-up conformation with a folding angle of 137° whereas the oxidized ring is nearly planar. The bond lengths and angles of compound **3** are very close to those observed in the molecules of this type such as 4,5-(1',2'-diphenylethylenedithio)-1,3-dithiole-2-thione (dPhEDT-DTT).[5b] For example, the distances of S1-C1 (1.636(6)Å) and C2-C3 (1.342(8)Å) in compound **3** are very similar to the corresponding bond distances (1.634(4)Å and 1.347(6)Å, respectively)

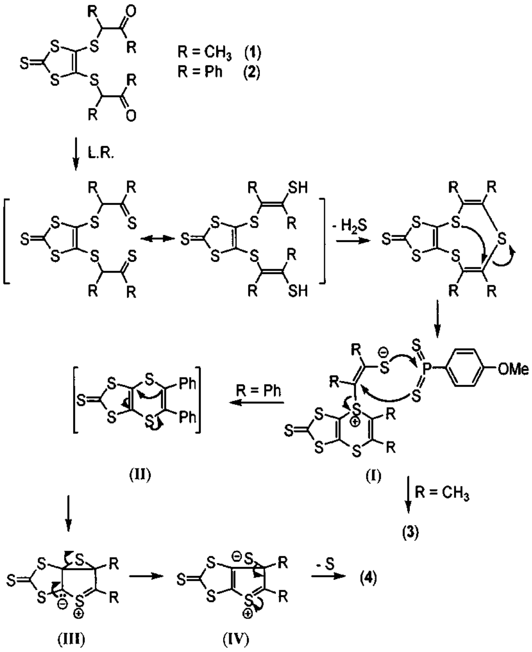
Table 2. Selected S···S and S···H bond distances(Å) for compound **3**

Atoms	Distance	Atoms	Distance
S(1)···S(3)#	3.659	S(2)···S(5)†	3.630
S(3)···S(3)#	3.380	S(5)···S(5)†	3.646
S(1)···H(6C)‡	2.735	S(4)···H(6A)	2.622
S(5)···H(7A)	2.616		

symmetry transformations: #, 1-*x*, 2-*y*, 1-*z*; †, -*x*, 2-*y*, 2-*z*; ‡, *x*+1, *y*-1, *z*

of dPhEDT-DTT. The selected SS and S···H bond distances for compound **3** are collected in *Table* 2. Intermolecular S···S interaction shorter than the sum of van der Waals radii of sulfur atoms (3.7Å)[9] has been regarded as one of the requirements for a facile electrical conduction in this type of molecules.[10] Several intermolecular S···S interactions lie in the range 3.380-3.659Å. Some inter- and intra-molecular S···H bonds are also observed and less than the sum of their van der Waals radii (3.0Å).[11]

The synthetic results showed a similar trend to Ozturk's experimental data in his recent report.[6] However, the mechanism for ring contraction and following desulfurization of an intermediate was ambiguously described in terms of electrocyclic reaction. Therefore, we suggest the detailed formation mechanism of products **3** and **4** in *Scheme* 2. As Ozturk explained, it is expected that the starting materials (compounds **1** and **2**) are converted into six-membered ring derivatives **I** by Lawesson's reaction through several transformations. Interaction of the intermediate **I** (R=CH_3) with L.R gives product **3** resulting in loss of a side chain. The proposed mechanism for the ring contraction of the intermediate **II** (R=Ph) presumably begins with the migration of any polarizable electron pair on the six-membered ring sulfide, generating three- and five-membered rings fused dipolar intermediate **III** such as the Favorskii reaction intermediate.[12] This dipolar intermediate is stabilized by the two phenyl groups and vacant *d*-orbital of the sulfur atom. The anion of the intermediate moves to form carbon-carbon double bond, and it gives rise to ring-opening. The subsequent desulfurization in the intermediate **IV** followed by thiophene formation leads to the product **4**. The reason for the exclusive formation of product **4** from the reaction of L.R with reactant **2** does not seem to be so simple. It may attribute production of compound



Scheme 2. A proposed mechanism for the formation of compounds **3** and **4**.

4 to combination of several factors, such as charge distribution of the dipolar intermediate **III** and thermodynamic stability of compound **4** by electronic delocalization between thiophene and two phenyl groups. We suppose that these effects in formation of compound **3** can be much weaker than those in formation of compound **4**.

Supplementary material available. Tables of anisotropic displacement parameters for non-hydrogen atoms, full bond lengths and angles, and hydrogen coordinates and isotropic displacement parameters are available on request.

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