Preparation of New Tetrathiafulvalene (TTF) Derivatives with Two Functional Groups at Symmetrical Positions: 2,6-Diiodo-3,7-diphenyl-TTF, 2,6-Bis[2-(trimethylsilyl)ethynyl]-3,7-diphenyl-TTF, and 2,6-Diethynyl-3,7-diphenyl-TTF

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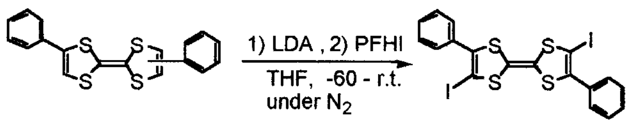
Received 18 June 1997; revised 9 September 1997

Abstract: Lithiation of diphenyltetrathiafulvalene (diphenyl-TTF) followed by treatment with perfluorohexyl iodide selectively gives a symmetrically diiodized product, 2,6-diiodo-3,7-diphenyl-TTF, from which 2,6-bis[2-(trimethylsilyl)ethynyl]-3,7-diphenyl-TTF and 2,6-diethynyl-3,7-diphenyl-TTF are derived.

Key words: tetrathiafulvalene, symmetrical diiodide, diacetylenic compounds, bis(trimethylsilyl)ethynyl, diethynyl

Tetrathiafulvalene (TTF) and its derivatives are the subject of recent interest. They have highly electron-donating properties[1] and form electrically conducting adducts with electron acceptors. In order to develop the chemistry of TTF and its derivatives, introduction of various reactive functional group(s) is desirable. Especially, introduction of two functional groups (preferably at symmetrical positions and with a functional group in each 5-membered ring) is desirable to obtain starting materials for various purposes (e.g., for polycondensation and molecular architecture[2]). However, examples of introduction of two functional groups to TTF at symmetrical positions have been limited.[3] For example, although Bernstein, Becker, and their co-workers as well as Kato and his co-workers have reported diiodization of TTF,[3a, 3d, 3e] isolation (e. g., by column chromatography) of isomers of the diiodized TTF with iodine in each five-membered ring is difficult. Here we report preparation and isolation of new TTF derivatives with two iodo and acetylenic groups at the symmetrical positions.

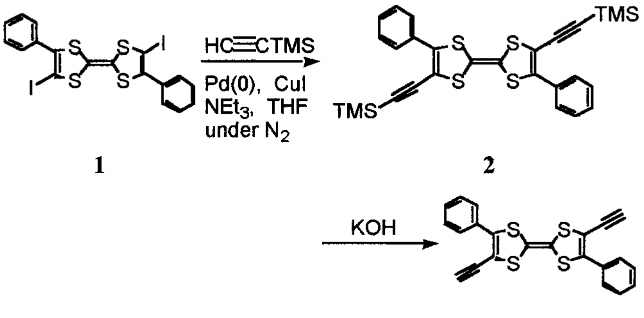
Treatment of diphenyltetrathiafulvalene[4] (diphenyl-TTF) with LDA (2.7 mol/diphenyl-TTF) followed by addition of perfluorohexyl iodide (PFHI; 3.5 mol/diphenyl-TTF) and work-up including recrystallization from toluene gives *trans*-2,6-diiodo-3,7-diphenyltetrathiafulvalene **1** in 62% yield. The HPLC trace of the product **1** obtained after the recrystallization gives only one peak, whereas the filtrate obtained in the recrystallization gives an additional one peak (relative peak area to that of **1** = about 1/3) assigned to a *cis*-isomer of **1**. The diphenyl- TTF used are considered to be a mixture of *cis*- and *trans*-isomers,[4] and the *trans* product **1** is formed as the major product and isolated as crystal. ^{1}H- and ^{13}C-NMR spectra of a product (product **1**′) obtained by drying up the filtrate show no observable difference from those of isolated **1**, indicating that **1** and the *cis*-isomer give rise to essentially the same NMR data. NMR spectra of the product **1**′ exhibit no peaks assignable to other products like a mono-iodized product. The *trans*-product **1** gives a melting point of 220–222°C, whereas the product **1**′ shows a melting point of 212–215 °C. The *trans* structure of **1** is unequivocally established by X-ray crystallography as shown in Figure 1.



Scheme 1 **1**

We have tried similar diiodization of 2,6-dimethyltetrathiafulvalene under various conditions. However, the attempts have so far not been successful (presumably due to competitive lithiation of the methyl group).

The reaction of **1** with trimethylsilylacetylene (3.4 mol/**1**) in the presence of $Pd(PPh_3)_4$ (5 mol%/**1**), CuI (5 mol%/**1**), and NEt_3 (excess) in THF gives symmetrical 2,6-bis[2-(trimethylsilyl)ethynyl]-3,7-diphenyltetrathiafulvalene (**2**) in 70% yield. Treatment of **2** with 1 M aqueous KOH easily generates **3**. The molecular structure of **2** determined by X-ray crystallography is shown in Figure 2.



Scheme 1 **3**

Compounds **2** and **3** are not so stable in solutions, and their isolation requires rapid treatment of the solution (cf. experimental part).

Thus, new symmetrical TTF derivatives **1–3** with the functional groups and the well-defined *trans* structure have been obtained. Since iodo and the –C≡CH group have high reactivity in organic reactions, **1** and **3**, which contain these two functional groups, are expected to serve as starting materials to prepare various TTF derivatives.

For example, it is known that polycondensation based on C–C coupling[6, 7] between ArX and Ar′C–CH can be carried out by using Pd-catalyst and bifunctional aromatic compounds to yield $(\text{Ar–C≡C-Ar}'\text{-C≡C})_n$ type polymers; n X–Ar–X + n HC≡C–Ar′ C≡CH → $(\text{Ar–C–C-Ar}'\text{–C≡C})_n$.[8] For obtaining such polymers with the TTF unit, TTF derivatives with the two functional groups are necessitated, and our preliminary investigation indicates that such polycondensation proceeds smoothly between **1** and **3**; the results will be reported elsewhere. Although intro-

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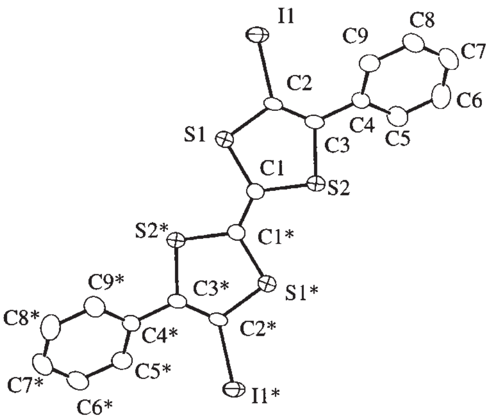

Figure 1. Molecular structure of **1**. Selected structural parameters (Å, °): I1-C2 2.076(5), S1-C1 1.746(6), S1-C2 1.752(6), S2-C1 1.775(6), S2-C3 1.782(6), C1-C1 1.32(1), C2-C3 1.310(7), C3-C4 l.472(7), C1-S1-C2 95.3(3), C1-S2-C3 95.7(3), S1-C1-S2 113.7(3), S1-C1-C1 124.8(6), S2-C1-C1 121.5(6), I1-C2-S1 113.2(3), I1-C2-C3 126.9(4), S1-C2-C3 119.9(4), S2-C3-C2 115.4(4), S2-C3-C4 113.9(4), C2-C3-C4 130.6(5).

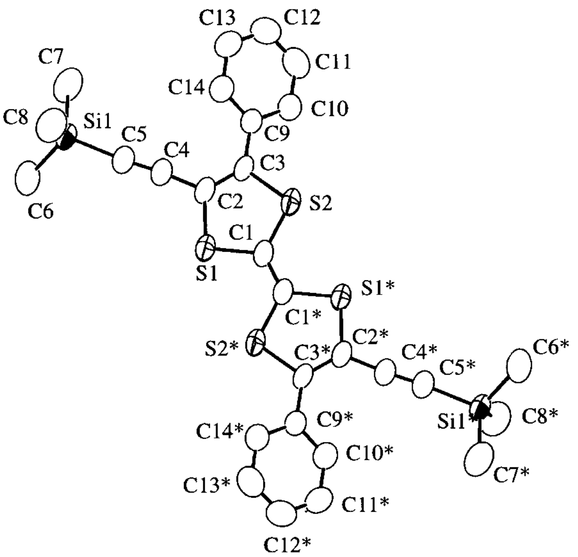

Figure 2. Molecular structure of **2**. Selected structural parameters (Å, °): S1-C1 1.767(4), S1-C2 1.758(4), S2-C1 1.750(4), S2-C3 1.767(4), Si1-C5 1.832(4), C1-C1 1.307(7), C2-C31.349(5), C2-C4 1.423(5), C4-C5 1.203(5), C1-S1-C295.3(2), C1-S2-C397.3(2), S1-C1-S2 113.1(2), S1-C1-C1 122.2(4), S2-C1-C1 124.7(4), S1-C2-C3 118.9(3), S1-C2-C4 114.0(3), C3-C2-C4 127.1(4), S2-C3-C2 114.6(3), S2-C3-C9 117.0(3), C2-C3-C9 128.4(3), C2-C4-C5 174.7(4), Sil-C5-C4 173.7(4).

duction of one –C–CSiMe$_3$ or –C≡CH group to TTF has been reported,[9] preparation of the TTF derivative with the –C–CSiMe$_3$ or –C≡CH group in each 5-membered ring has no precedent to our knowledge.

2,6-Diiodo-3,7-diphenyltetrathiafulvaleue (1):

2,6(7)-Diphenyltetrathiafulvalene (diphenyl-TTF purchased from Aldrich Chemical Co. Inc.[4]; 0.700 g, 1.96 mmol) in anhyd THF (25 mL) was lithiated at –78 °C with LDA (2.7 mol/diphenyl-TTF). After stirring for 1 h, perfluorohexyl iodide (PFHI; 3.5 mol/diphenyl-TTF) was added dropwise to the suspension. The mixture was stirred at –60°C for 1 h and at r.t. for 1 h. After quenching with water, the powder formed was washed with water (3 ×) and Et$_2$O (3 ×). Crystallization from toluene gave red needles of **1**; yield: 0.743 g (62%).

^{1}H NMR: δ = 7.40–7.50 (m, 10H, -Ph)

MS: m/z = 608 (M$^+$).

Anal. Found: C, 35.45; H, 1.70. Calcd.: C, 35.54; H, 1.66.

2,6-Bis[2-(trimethylsilyl)ethynyl]-3,7-diphenyltetrathiafulvalene (2):

1 (0.600 g, 0.986 mmol) was dissolved in anhyd THF (20 mL). CuI (5 mol%; 9.37 mg, 0.0494 mmol), Pd(PPh$_3$)$_4$ (5 mol%; 57.0 mg, 0.0494 mmol) and NEt$_3$ (20 mL) were added, and then the mixture was stirred for a few minutes. Trimethylsilylacetylene (0.331 g, 3.35 mmol) was added dropwise to the mixture. The mixture was stirred for 12 h at 60 °C. Flash column chromatography (silica gel, toluene) and crystallization (toluene) gave red plates of **2**; yield: 0.142 g (27%).

^{1}H NMR: δ = 7.31–7.80 (m, 10H, -Ph), 0.18 (s, 18H, Si–CH_3).

IR: ν = 2136 (C≡C), 1248, 844 cm^{-1} (Si–CH_3).

Anal. Found: C, 60.87; H, 4.95. Calcd.: C, 61.26; H, 5.14.

2,6-Diethynyl-3,7-diphenyltetrathiafulvalene (3):

2 (0.142 g, 0.259 mmol) was dissolved in Et$_2$O (45 mL) and MeOH (30 mL). 1 M aq KOH (15 mL) was added to the solution. The mixture was stirred for 1 h and washed with water repeatedly. Purification on a silica gel column (hexane/toluene 3:1) gave an orange powder of **3**; yield: 0.221 g (47.5%).

^{1}H NMR: δ = 7.35–7.70 (m, 10H, –Ph), 3.34 (s, 2H, C≡C–H).

IR: ν = 3282 (C≡C–H), 2090 cm^{-1} (C≡C).

MS: m/z = 404 (M$^+$), isotope pattern agreed.

HPLC Analysis:

A recycle-type preparative HPLC Type LC-908 made by Japan Analytic Industry Co. Ltd. was used with two columns (JAI GEL H-1 and H-2) set in series; eluent was CHCl$_3$.

Crystal Structure Determination of 1:

Crystal of **1** suitable for crystallography was obtained by recrystallization from toluene. The crystal was mounted in a glass capillary tube. The unit cell parameters were obtained by least-squares refinement of 2 θ values of 20 reflections with 5≤2 θ<55°. Intensities were collected on Rigaku AFC-5R automated fourcycle diffractometer by using Mo-Kα radiation (λ = 0.71069 Å) and the ω-2θ method.

Calculations were carried out by using a program package TEXSAN on a DEC Micro VAX-II computer. Atomic scattering factors were obtained from the literature. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. The hydrogens were located by assuming ideal positions (d (C–H) = 0.95 Å) and included in the structure calculation without further refinement of the parameters.

The compound crystallizes in monoclinic space group P2$_1$/c (14) a = 4.137 (4), b = 12.99 (1), c = 17.937 (9) Å. V = 961 (1) Å$_3$, Z = 4, and β = 93.96 (7)°. The calculated density and the total number of electrons in the cell amount to 2.10 g cm^{-3} and F(000) = 576. R = 3.2%. Rw = 3.2%.

Crystal Structure Determination of 2:

Crystal of **2** suitable for crystallography was obtained by recrystallization from toluene. The crystals was mounted in a glass capillary tube. The unit cell parameters were obtained by least-squares refinement of 2 θ values of 20 reflections with 5≤2 θ<55°. Intensities were collected on Rigaku AFC-5R automated fourcycle diffractometer by using Mo-Kα radiation (λ = 0.71069 A) and the ω-2θ method.

Calculations were carried out in a manner similar to those applied for the crystal structure determination of **1**.

The compound crystallizes in monoclinic space group P2$_1$/n (14) a = 14.308 (6), b = 6.051 (2), c = 17.100 (6) Å. V = 1480.4 (9) Å^3, Z = 4, and β = 90.55 (3)°. The calculated density and the total number of electrons in the cell amount to 1.231 g cm^{-3} and F(000) = 576. R = 5.7%. Rw = 5.5%.

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(4) Purchased from Aldrich Chemical Co. Inc. The figure in the catalogue shows a *cis* structure for diphenyl-TTF. However, the response from Aldrich Chemical Co. Inc. says that it may be a mixture of *cis*- and *trans*-diphenyl-TTF and their separation has not been carried out.

(5) With a recycle-type preparative HPLC Type LC-908 made by Japan Analytical Industry Co. Ltd.; two columns (JAI GEL-H1 and JAI GEL-H29) were used in series; eluent: $CHCl_3$

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