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LETTERS

Synthesis and Redox Properties of Tetraethynyl Tetrathiafulvalenes

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Abstract: The synthesis and characterization of protected tetraethynyltetrathiafulvalenes (**1a** and **1b**) is reported. The cation radical of **1a** has a slightly more positive oxidation potential ($E_{\mathrm{ox}0/1}$ = 0.63 V *vs* Ag/AgCl) than TTF. Stable CT solids can be prepared with iodine and TCNQF$_4$. These compounds are the first members of a series of highly unsaturated TTF derivatives having in-plane π-orbitals.

Highly unsaturated tetrathiafulvalenes (TTFs) such as **1c** and **2** (Chart 1) have the potential to form conductive charge transfer (CT) salts with enhanced dimensionality because their overall π-rich surface could enhance lateral and π-stacking interactions between individual units.[1] Lateral σ,π/π,π-interactions, in particular, would be a new type of contact due to the presence of *in-plane* alkyne π-orbitals, interacting through-bond with σ-orbitals on sulfur atoms as shown by PM3 calculations (Figure 1). The inherent nature of the many extended TTF systems having sp^2-hybridized frameworks does not lend to this type of interaction.[2,3] A recent approach addressing the issue of increased dimensionality in organic CT conductors has resulted in the synthesis of 3-dimensional cyclophane systems linking TTF units with saturated bridges.[4]

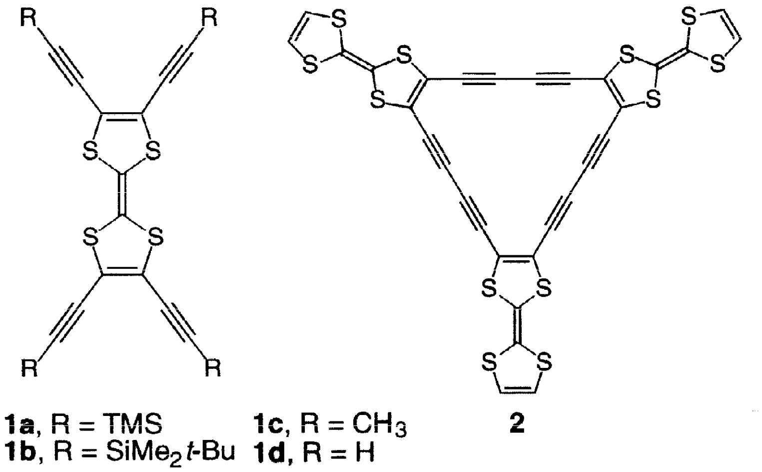

Chart 1.

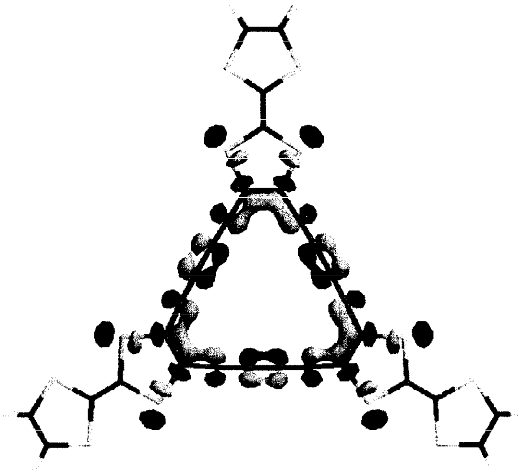

Figure 1. PM3 calculated LUMO(+1) orbital of **2** (0.64 eV above LUMO) showing significant overlap of in-plane π and σ-orbitals.

Although a large body of work describes the preparation of a host of TTF derivatives and similar electron-rich systems,[5] we are not aware of reports on conjugated acetylenic TTFs other than two dithiole-linked alkynyl systems (alkynylogous TTFs).[6,7] In our initial attempts to prepare **1a-c**, alkynylation reactions of several halogenated TTFs under Stephens-Castro or Stille conditions were unsuccessful.[8,9] It is known that oxidative insertion of Pd° into electron-rich vinyl halides is difficult, which simply fails in the case of the TTF halides.[10]

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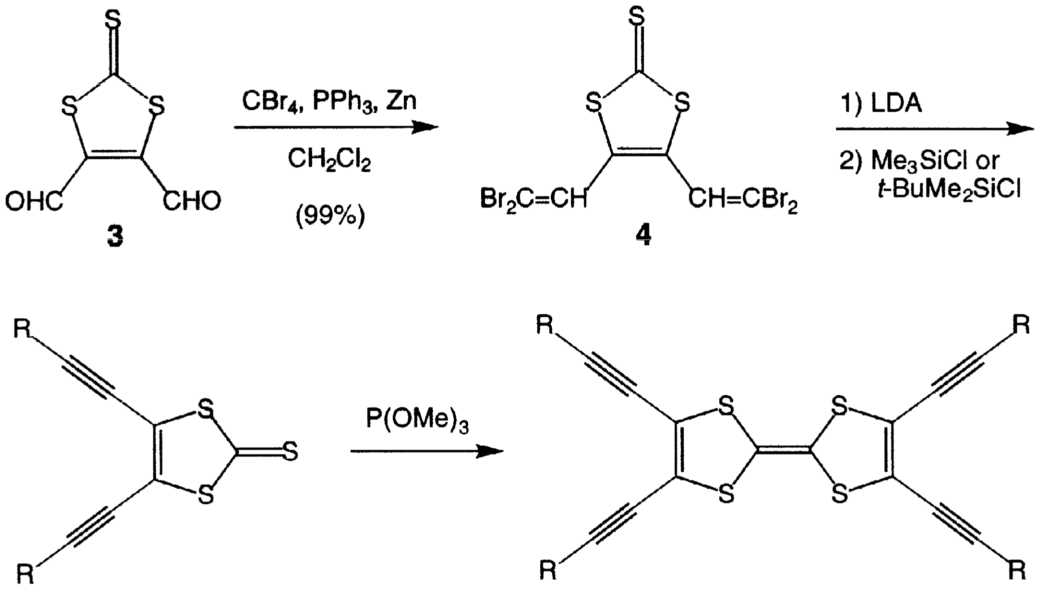
We have prepared the first members of this series by employing a generally reliable alkynylation strategy: Corey-Fuchs dibromoolefination[11] of aldehyde 3[12] led to the 1,3-dithiole-2-thione **4**, which afforded the silylated alkynes **5a** and **5b** after treatment with LDA and quenching with a silyl chloride. Coupling of the 1,3-dithiole-2-thiones **5a** and **5b** with $P(OMe)_3$ proceeded cleanly to give the deep red tetraethynyl TTFs **1a** and **1b**.[13] Deprotection of either the trimethylsilyl dithiole thione **5a** or the TTF **1a** (K_2CO_3, MeOH/THF) gave the parent compounds **5c** and **1d** as very unstable crystalline materials, showing not surprisingly that terminal groups are needed to protect these enediynes. It is noteworthy that direct access to tetraethynyl TTFs **1a** and **1b** from the TTF-tetraaldehyde[12] using this methodology was unsuccessful due to the insolubility of the corresponding tetrakis(dibromoolefin).



5a, R = $SiMe_3$ (86%)
5b, R = $SiMe_2t$-Bu (25%)
5c, R = H

1a, R = $SiMe_3$ (45%)
1b, R = $SiMe_2t$-Bu (50%)
1d, R = H

X-ray characterization was carried out on the *t*-butyldimethylsilyl (TBS) derivative **1b** since trimethysilyl derivative **1a** crystallized only in very thin needles (Figure 2a). Not unexpectedly, the sterically demanding TBS groups hinder efficient stacking of the TTF moieties. Although the plane-to-plane distance along the stacking axis (*b*) is short (2.795 Å), the overlap between TTFs is practically nonexistent owing to the large tilt angle (75.7°, Figure 2b) between the planes of the molecules.

Because of the very sensitive nature of the enediyne moieties in these molecules, it was unclear whether oxidation of these TTFs would lead to stable cations. Promising data from cyclic voltammetry of the less sterically hindered TMS derivative **1a** show two clean reversible oxidation waves at $E_{ox0/1} = 0.63$ and $E_{ox1/2} = 1.13$ V (*vs* Ag/AgCl in CH_2Cl_2, Figure 2c). On the other hand, the alkynylogous systems reported in the literature show poor oxidation behavior with irreversible redox waves.[6,7] The tetraethynyl TTFs **1a** and **1b** have higher redox potentials than TTF ($E_{ox0/1} = 0.34$ and $E_{ox1/2} = 0.71$ V *vs* Ag/AgCl in MeCN)[5b] due to the mild electron-withdrawing nature of the alkynyl substituents. The high stability of the radical cation of **1a** was confirmed by preparative oxidation with iodine or $TCNQF_4$, giving air-stable dark green solutions. Formation of a waxy solid resulted upon evaporation of these solutions, showing that the greasy nature of the silyl group hampers formation of well-behaved crystalline materials. We are currently pursuing the synthesis of several alkynyl TTFs with smaller end-groups (Br, I, CH_3 = **1c**) that will be suitable for the collection of meaningful powder and crystal conductivity data.

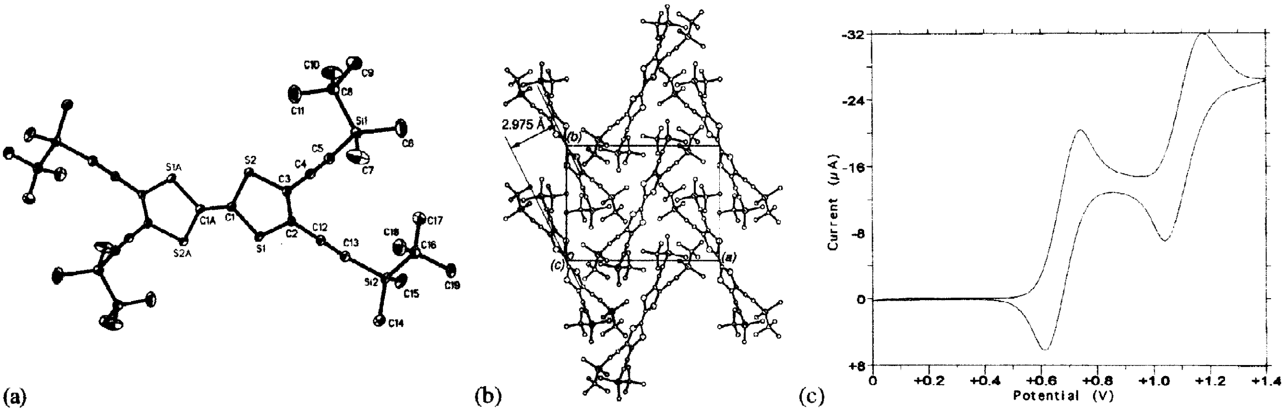


Figure 2. (a) X-ray structure of compound **1b**. (b) Crystal packing structure of compound **1b**. (c) Cyclic voltammogram of TMS derivative **1a** (CH_2Cl_2, 0.1 M TBAP, 10 mV·s^{-1}, 25 °C, *vs* Ag/AgCl).

Although the donating properties of the tetraethynyl TTFs are somewhat diminished compared to the parent system, the ability to rapidly modify their electronic structure by changing the substitution on the alkyne appendages or on one of the dithiole rings should give great versatility to this approach. Preliminary results indicate that the diethynyl tetrathiafulvalene required for cyclization to the trimer **2** can be formed in a manner similar to compounds **1a** and **1b**, and we are actively pursuing the synthesis of this interesting system.

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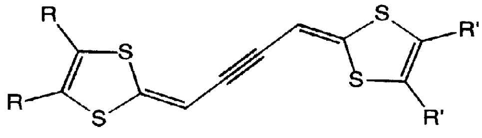
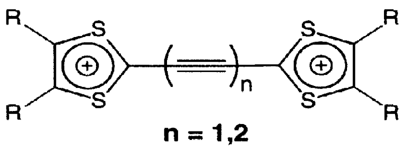
(7) Papers in ref. 6 describe the systems shown below. Those of the latter type have been isolated only as the dications; the cumulenic neutral forms are unstable.



(R = H, Me, CO_2Me, $(HC{=}CH)_2$)



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(13) Characterization data for compound **1a**: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.23 (s); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) –0.32, 94.45, 106.03, 110.24, 121.60; HR-MS (EI): Calcd for $C_{26}H_{36}S_4Si_4$ (M^+): 588.0777; found: 588.0770. For compound **1b**: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.13 (s, 24H), 0.94 (s, 36H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) –4.88, 16.61, 26.11, 94.94, 104.67, 110.54, 121.21; IR (CCl_4) ν (cm^{-1}) 2146 (w); HR-MS (FAB): Calcd for $C_{38}H_{60}S_4Si_4$ (M^+): 756.2655; found: 756.2631.