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A new strategy to reach highly extended and quinonoid tetrathiafulvalene (TTF) derivatives

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Abstract

2,3-Bis(bromomethyl)TTFs **4** are used as precursors of 2,3-dimethylene-[2H]-TTFs **5** to reach cycloadducts of high synthetic interest via a [4+2] cycloaddition with quinonic derivatives. Subsequent Horner–Wadsworth–Emmons olefinations with a 1,3-dithiole phosphonate anion afforded highly extended and sulfur-rich analogs of tetrathiafulvalene **1**. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Charge-transfer complexes and cation radical salts of the tetrathiafulvalene (TTF) family exhibit interesting electroconductive properties.[1] Chemical modifications of the TTF core have allowed enhancement of the dimensionality of the corresponding organic materials, thus preventing metal-to-insulator transitions (Peierls distortions).[2] In this topic, highly extended and sulfur enriched analogs of TTF have proved to be efficient.[3,4] For instance, cation radical salts of the 1,4-dithiafulven-6-yl TTF π-donors exhibit a bidimensional character with strong S···S intra- and interchain contacts.[4] Following our efforts[5] to suppress the spoiling effect of a cyclization reaction arising during the slow electropreparative process of these materials,[6] we have decided to synthesize new sulfur-rich and extended *p*-quinodimethane analogs of TTF **1**. Furthermore, such π-extended TTF derivatives of this series show very attractive properties because of their electronic and geometrical particularities as demonstrated by the previously representative π-donors **A**–**C**.[7]

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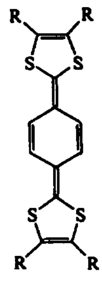

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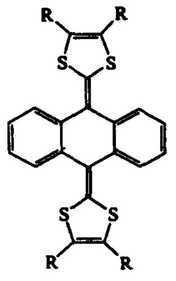

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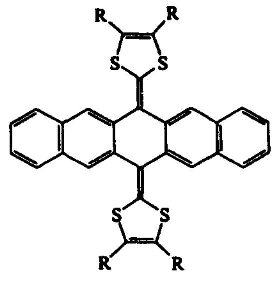

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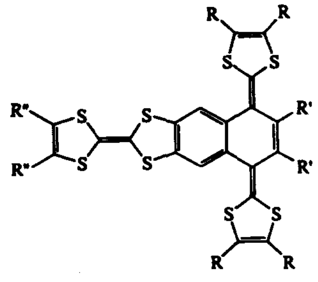

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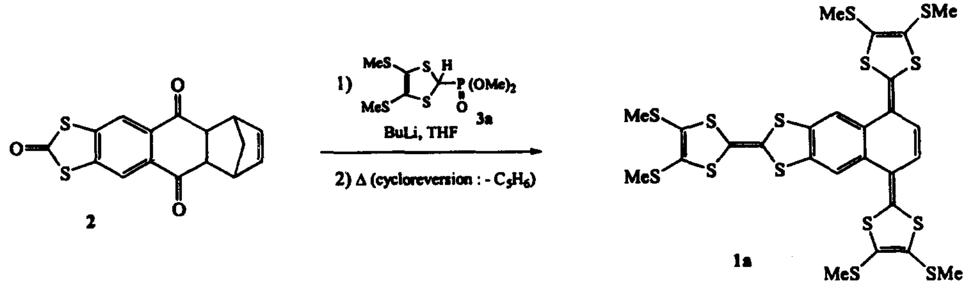
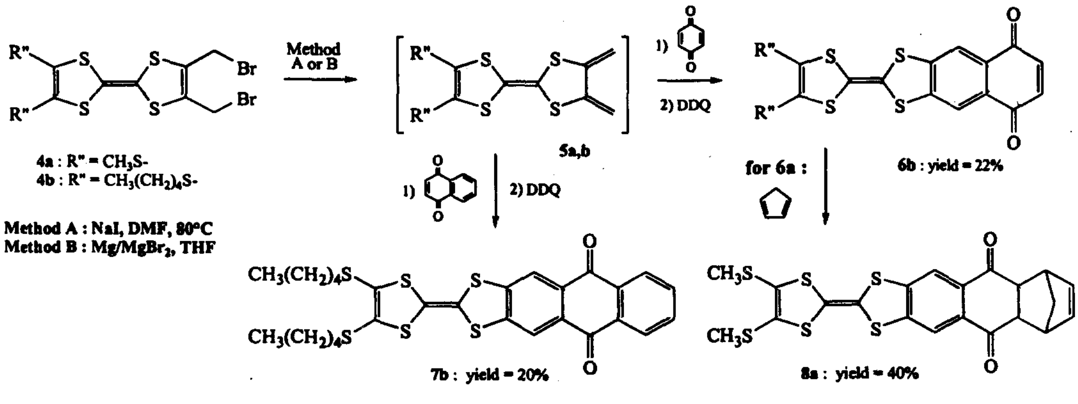
We report here on a new synthetic approach to the related compound **1** for which a strong π-donor character and a multi-redox process have been recently demonstrated.[5] The access to the π-donor **1a** occured via an unprecedented TTF core building from the 2-oxo-1,3-dithiole group of compound **2**, additionally to the bis-olefination of both carbonyl functionalities. The drawbacks of this route are: (i) the impossibility to introduce into compound **1** R and R″ of differing natures; (ii) the difficulty to separate compounds resulting from bis and tris-olefinations.



To solve these problems, we decided to build the TTF core in the first step and to introduce the quinonoid analog of TTF in a second step. Starting materials were the vicinal bis(bromomethyl)TTF derivatives **4**[8] which are prone to generate the 2,3-dimethylene-[2H]-TTFs **5** in situ. As previously illustrated with C_{60} as the dienophile,[9] and considering that C_{60} is a comparable electron acceptor to 1,4-benzoquinone or 1,4-naphthoquinone,[10] we carried out cycloaddition of the latter with diene **5**.

Instead of using KI/[18]crown-6 to generate this transient diene,[9,11] we have applied different procedures to realize the reductive elimination from **4**. Thus, in the case of the condensation with quinonic derivatives, best results were obtained using NaI in anhydrous DMF[12] at 80°C for **4a** (method A) or Mg in the presence of $MgBr_2$ in THF for **4b** (method B).[13] Further aromatization could be performed by subsequent treatment with DDQ to afford intermediate compounds **6a,b** and **7b**.



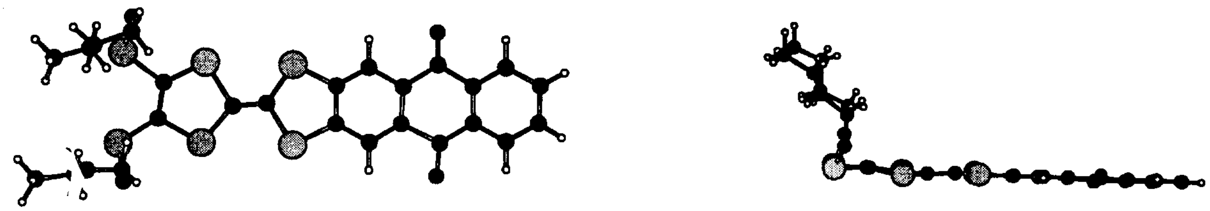
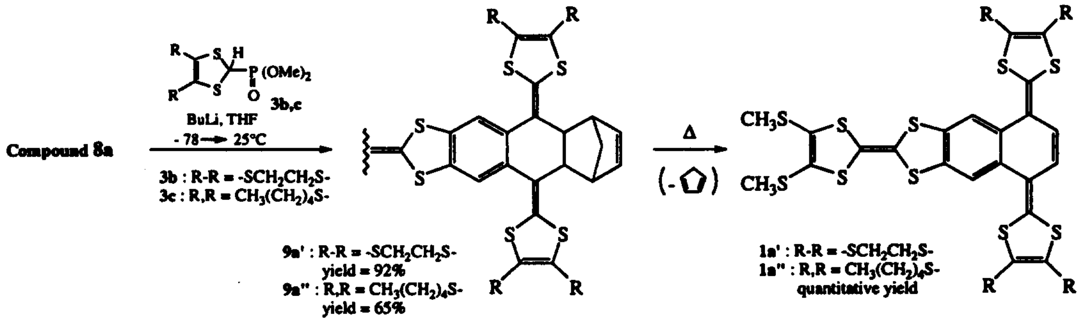


Figure 1. Two views of the molecular structure of **7b**

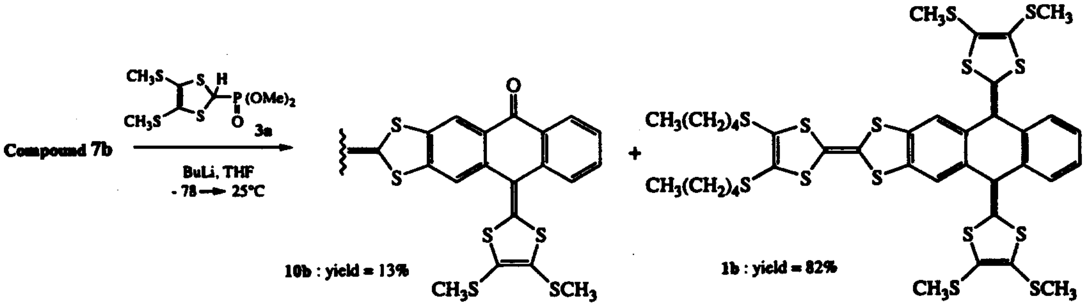
Given the difficulty of purification of the compound **6a** due to its low solubility and also in order to avoid any risk of electron transfer of the phosphonate anion of **3** occuring during the following olefinations step[5] (Ep^1_{red}=−0.65V for **6a**),[14] we submitted the raw material to a [4+2] cycloaddition with cyclopentadiene,[15] the quinonic character being therefore suppressed. Compound **8a** was purified by column chromatography on silica gel (CH_2Cl_2) as well as for **7b** (CS_2/CH_2Cl_2, 4/1).

In addition to the usual analytical data, the structure of **7b** was determined by X-ray diffraction of a single crystal.[16] As shown in Fig. 1, molecule **7b** is essentially planar, with only the pentyl groups deviating from the main molecular plane.

The preparation of our target π-extended donors from **8a** was carried out by using the Horner–Wadsworth–Emmons (HWE) reaction with phosphonate **3b** or **3c**[17] in the presence of *n*-butyllithium at −78°C. Resulting compounds **9a′** and **9a″** were purified by column chromatography on silica gel (CS_2/CH_2Cl_2, 8/1 for **9a′** and petroleum ether/CH_2Cl_2, 3/1 for **9a″**). The required retro Diels–Alder reaction could be cleanly performed from **9a′** upon refluxing in *o*-dichlorobenzene (10 mn) to afford **1a′** and treatment of **9a″** using a Kugelrohr apparatus (2 h at 170°C under 0.5 mmHg) gave the corresponding **1a″**, both in quantitative yield.[18]



When the HWE reaction was carried out on **7b**, we noted that the bis-olefinated compound **1b** was also accompanied by the mono-olefinated **10b**, even when using a large excess (10 equivalents) of phosphonate **3a**, both compounds being separated by column chromatography on silica gel (petroleum ether/CH_2Cl_2, 3/7).



In conclusion, the main results of this work lie in the tuning of a new synthetic strategy allowing the possible introduction of identical or different R and R″ substituents in molecule **1**. Further work is underway to oxidize these strong and multi-stage redox π-donors to get corresponding charge transfer salts.

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16. Crystal structure for **7b**: monoclinic P21/c, Z=4, a=8.003(1) Å, b=33.967(6) Å, c=10.144(2) Å, β=94.32(1)°, V=2749(1) Å^3, calculated density 1.42 g cm^{-3}. X-Ray diffraction data were collected at 293 K on an Enraf Nonius MACH3 four circles diffractometer ($\lambda_{MoK\alpha}$=0.71069). 2964 reflections were measured by the ω scan technique in the 2–23°θ range. The structure was solved by direct methods (SIR program). The full-matrix least-squares refinements of 175 parameters from 961 reflections with $I/\sigma(I)>3$ converged to R=0.094, R_W=0.104 (all non-H atoms refined anisotropically, H atoms fixed (hydro program, use of F magnitude)).
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