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Synthesis and Electrochemical Properties of Fused [3,4]Furano-Tetrathiafulvalenes

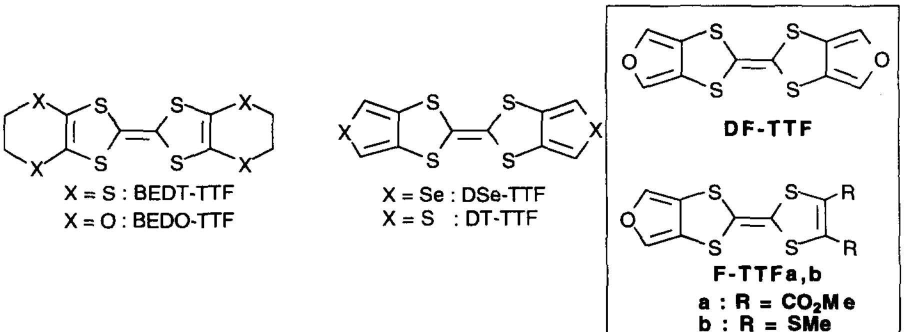
Yann Siquot,[a] Pierre Frère,[a]* Tomasz Nozdryn,[a] Jack Cousseau,[a] Marc Sallé,[a] Michel Jubault,[a] Jesus Orduna,[b] Javier Garín[b] and Alain Gorgues[a]*

[a]Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, associé au CNRS, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France.
[b]Departamento de Química Orgánica, ICMA, Universidad de Zaragoza - CSIC, E- 50009 Zaragoza, Spain

Abstract : The synthesis of the first fused [3,4]furano-TTFs has been accomplished starting from the 4-formyl-5-diethoxymethyl-2-thioxo-1,3-dithiole. Two routes have been explored involving either the furan ring or the TTF core. In particular, the first proceeds via the new [3,4]furano-2-thioxo-1,3-dithiole .

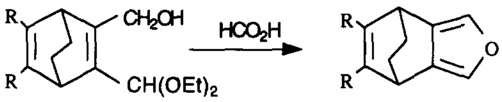
Owing to their high electrical conductivity, mixed valence radical cation salts of the tetrathiafulvalene (TTF) series constitute an important class of "organic metals".[1] However, when they are endowed with an excessive monodimensional character, they lose their transport properties on cooling, due to crystalline transitions (Peirls distorsions) resulting from electron-phonon couplings. In order to improve the electroconduction of these materials at low temperature, an increase of their dimensionality is required.[2] Among the possible structures available, the prominent role of peripheral chalcogen atoms branched on the TTF core is now well recognized since these atoms are responsible for additional intermolecular contacts. For instance bis(ethylenedioxy) and mainly bis(ethylenedithio) TTFs (BEDO-TTF[3] and BEDT-TTF[4] in scheme 1) are the most representative examples, the latter donor in particular furnishing truly 2D superconducting κ-phases below 12K.[5] Similarly, recent reports[6,7] emphasize the role of the peripheral S atoms in the 2D solid state organization of the donors and of their related salts.

On these grounds, we have been interested in the synthesis of the mono and di-[3,4]furano TTFs **F-TTF** and **DF-TTF**[8], which are still unknown, contrary to their S and Se elementologs **DT-TTF**[9] and **DSe-TTF**[10] respectively (scheme 1). We report here on their preparation and on their electrochemical properties.



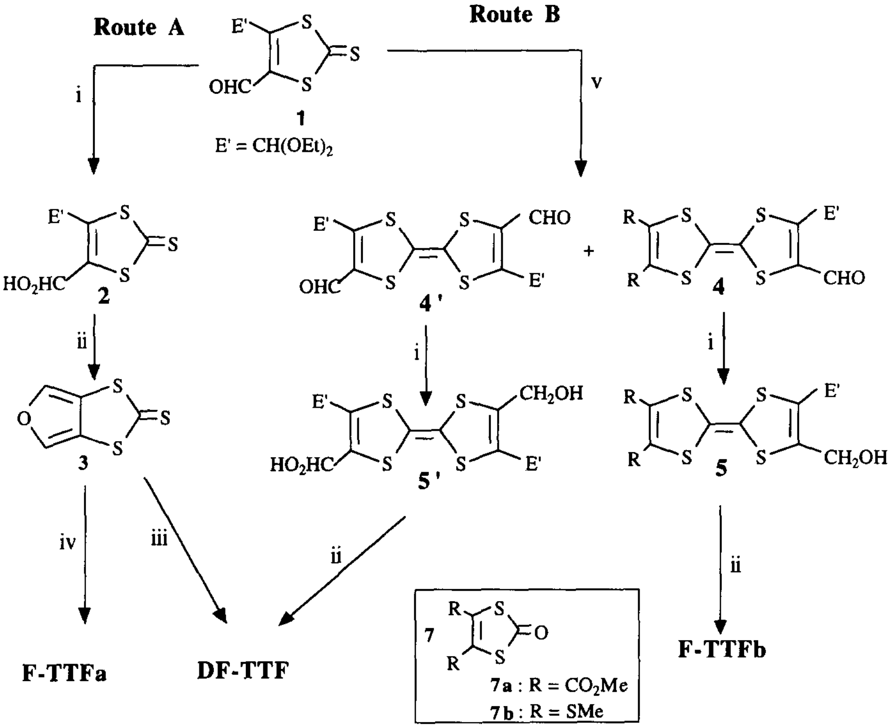
Scheme 1

The key step in our synthetic strategy lies in the formation of the fused [3,4]furano group. This could be efficiently carried out by using a HCO_2H mediated bis 1,4-elimination of ethanol according to Stephan *et* *al.*[11] who performed the 3,4-furan ring closure from a but-2-ene fragment substituted, in the terminal positions, by an OH and two OEt groups respectively (scheme 2).



Scheme 2

Two approaches starting from 4-formyl-5-diethoxymethyl-2-thioxo-1,3-dithiole **1**[12] have been explored (Scheme 3). In route A, the furan cycle is first formed with the synthesis of fused [3,4]furano-2-thioxo-1,3-dithiole **3**, followed by a usual coupling reaction. On the contrary, route B proceeds via the coupling of thione **1** in the first step, the furan core being formed in the last one.



Scheme 3 : i) $NaBH_4$, CH_2Cl_2 - CH_3OH; ii) HCO_2H (30% v/v in $CHCl_3$); iii) $P(OMe)_3$; iv) **7a** (3eq) $P(OMe)_3$; v) **7b** (3eq), $Co_2(CO)_8$, $PhCH_3$.

Route A: via the synthesis of thione 3.

The aldehyde group of **1** was reduced by $NaBH_4$ in CH_2Cl_2-MeOH (50/50 v/v) at room temperature to yield alcohol **2** (90% yield) which was converted into **3** (62% yield) by treatment with a solution of 30% formic acid in $CHCl_3$. Attempts at self-coupling reactions of thione **3** in the presence of trimethylphosphite were disappointing, **DF-TTF** being isolated in a 5% yield only. This low yield has to be compared with previous results of self-coupling reactions in the corresponding [3,4]thieno series.[9] On the other hand, thione **3** was cross-coupled with 4,5-bis(methyloxycarbonyl)-2-thioxo-1,3-dithiole **7a**, best yield (13%) of **F-TTFa** being obtained by using an excess (3 eq.) of **7a**. In this process, tetrakis(methyloxycarbonyl)-TTF was also formed, but no **DF-TTF**. Under the same conditions, our efforts to isolate **F-TTFb** by using **7b** have been so far unsuccessful. Attempts of decarbomethoxylation of compound **F-TTFa** by action of LiBr / HMPA allowed to isolate a product of monodecarbomethoxylation only and in very poor yield (< 5%).

Route B: Formation of the furan ring from the TTF core.

Since thione **3** could be self- (or cross-)coupled only in poor yields, we decided to build the TTF core in the first step by cross-coupling of thione **1** with 4,5-bis(methylsulfanyl)-2-oxo-1,3-dithiole **7b** in the presence of $Co_2(CO)_8$ under standard conditions.[12,13] The resulting TTFs **4** and **4'** were separated by SiO_2 column chromatography, and the corresponding alcohols **5** and **5'** were obtained after reduction of the aldehyde groups with $NaBH_4$. Due to their instability, the subsequent formolysis had to be carried out very rapidly in order to allow the isolation of **F-TTFb** and **DF-TTF** in 17% and 13% yields from aldehyde **4** and **4'** respectively.

Electrochemical properties

As expected, the cyclovoltammograms of the new donors exhibit two 1 e^- reversible oxidation peaks corresponding to the successive generation of the radical cation and the dication (Table I). Comparison of Epa$_1$ and Epa$_2$ between **DF-TTF** and its related S analog **DT-TTF** or dibenzo-TTF (**DB-TTF**)[14] shows that in this series, the nature of the aromatic cycle[15] fused to the TTF core does not seem to play an important role on their -donor ability.

Compounds	Solvent	Epa$_1$ (V)	Epa$_2$ (V)
F-TTFa	CH_3CN	0,72	1,04
F-TTFb	CH_3CN	0,66	1,06
DF-TTF	CH_3CN	0,72	1,03
DT-TTF[9b]	DMF	0,78	0,96
DB-TTF[14]	CH_3CN	0,72	1,06

Table I : Electrochemical data for **DF-TTF** and **F-TTFa,b** : 10^{-3} mol.L^{-1} in 0.1 mol.L^{-1} Bu_4NPF_6, scan rate 100 mV.s^{-1}, Reference SCE.

Conclusion

Main results of this paper concern the synthesis and the evaluation of -donating character of the [3,4]furano-TTFs **DF-TTF** and **F-TTF**. These compounds appear to be interesting in the field of TTF chemistry since the furano groups may allow subsequent functionalizations by [4+2] cycloaddition,[11,16] or by formylation.[17] Our main efforts are currently devoted to the preparation of their radical cation salts by chemical and electrochemical oxidation, in order to examine the possible role of the furan heterocycle on the solid state structural organization.

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8 All compounds show spectroscopic data in accordance with the proposed structures. Selected data :

3 : yellow crystals, m.p. 90°C ; $M^{+\cdot}C_5H_2O_1S_3$ calc. 173.92678, found 173.9262;

^1H n.m.r.($CDCl_3$) 7.47 (s, 2H, =CH).

DF-TTF : yellow powder, m.p. 130°C dec.; $M^{+\cdot}C_{10}H_4O_2S_4$ calc. 283.90942, found 283.9093 ;

^1H n.m.r.(DMSO d_6) 7.69 (s, 4H).

F-TTFa : brown powder, m.p. 173°C, $M^{+\cdot}$ $C_{12}H_8O_5S_4$ calc. 359.92546, found 359.9248 ;

^1H n.m.r.($CDCl_3$) 7.36 (s, 2H, =CH), 3.85 (s, 6H, CO_2Me).

F-TTFb : orange powder; m.p.136°C , $C_{10}H_8O_1S_6$ calc. 335.88995, found 335.8891

^1H n.m.r. ($CDCl_3$) 7.31 (s, 2H, =CH) ; 2.48 (s, 6H, SMe)

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