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Vinylogs of Tetrathiafulvalene (TTF) Bearing Four 1,4-Dithiafulven-6-yl Substituents : Novel Highly Extended and Sulfur-rich π-Donors

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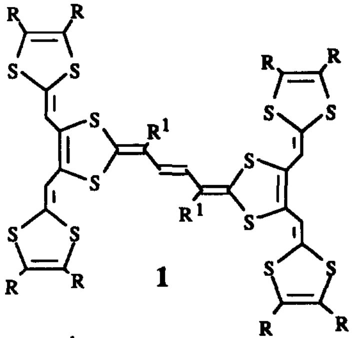
Abstract : The title compounds **1** were synthesized from the mono-diEt-acetal of acetylenedicarbaldehyde and 2-thioxo-1,3-dithioles through three key steps: cycloaddition, dimerization-desulphurization of the resulting thials, and after deketalization, fourfold Wittig olefination of the tetraformyl TTF-vinylogs **4** with the P-ylids Wα–γ bearing the 1,3-dithiol-2-ylidene moiety. Cyclic voltammetry shows that these compounds are very strong π-donors and good precursors of conducting cation-radical salts.

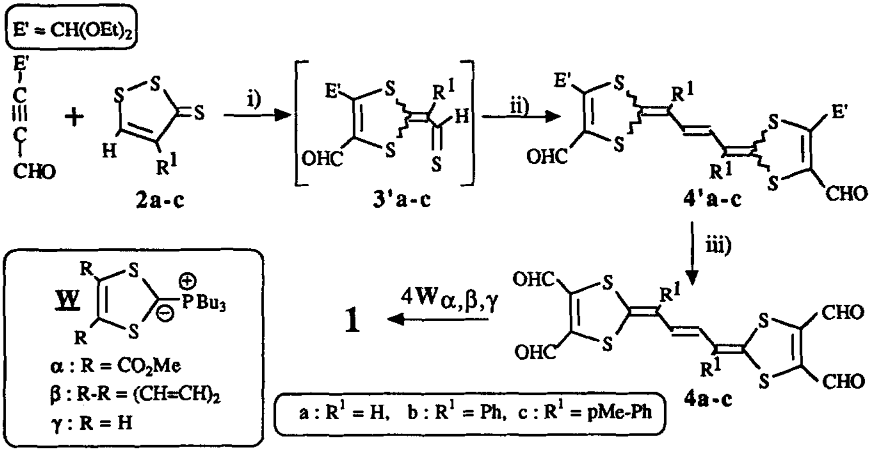
When endowed with an excessive monodimensionality, the organic metals of the tetrathiafulvalene (TTF) series[1] suffer a breakdown of their electroconductive properties below a given temperature, mainly due to the arising of subtle crystalline transitions (Peierls distortions). A suitable way to overcome Peierls' instability consists in enhancing the dimensionality of these materials, which can be chemically achieved *via* suitable structural modifications to the TTF framework.[2] Examples of the more successful modifications are *i)* replacing S by Se atoms, which possess more diffuse orbitals, has led to the famous tetramethyltetraselenafulvalene (TMTSF) based superconductors,[3] and *ii)* the substitution of H-atoms by sulfur-rich groups in order to increase the number of S...S interchain contacts, such as in bis-(ethylenedithio)-TTF (BEDT-TTF), has given rise to the highest Tc organic superconductors of this series achieved so far.[4]

Another recent trend involves the building of highly extended analogs of TTF in which the central olefinic linkage is replaced by larger conjugated spacers.[5] In this way, one can anticipate an increase in the number of contacts, due to a lowering of the molecular charge density and to an enhancement of the π-bonding interactions. Moreover, such planar extensions may result in weaker coulombic repulsions in the di- (or poly-) cationic states. Based on these considerations which are supported by recent results,[6a] we have focused on the giant analogs of TTF **1** in which the vinylog core of TTF bears four S-rich 1,4-dithiafulven-6-yl side arms. In this Letter, we describe their synthesis and their unusual redox properties.[6b]



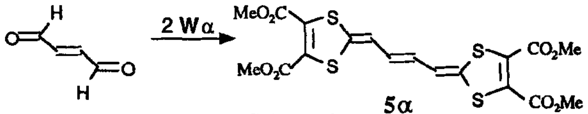
R^1= H (a), Ph (b), pMe-Ph (c)
R or R-R = CO_2Me (α), $(CH{=}CH)_2$ (β), H (γ)

As outlined in Scheme 1, our general synthetic strategy involves three main steps. The first uses the well known cycloaddition of 3-thioxo-1,2-dithioles **2a-c** onto electrophilic alkynes[7] bearing, in this case, two aldehyde functions for the generation of the thials **3'**. The second lies in the dimerization with loss of sulphur of the latter, on simple refluxing in an inert high boiling point solvent.[7] After deketalization of **4'**, the final step consists of a fourfold Wittig olefination of the tetraaldehydes **4a-c** with the P-ylids **W**α-γ[8] bearing the 1,3-dithiol-2-ylidene moiety adequately R-substituted (*).



Scheme 1 : *i)* xylene 20 min., r.t., *ii)* xylene reflux, 3 h, *iii)* Amberlyst-15, acetone/water, r.t.

The starting material for this sequence is the monoacetal of acetylenedicarbaldehyde (ADCA)[9] which, despite its reduced electrophilicity with respect to ADCA itself, is more easily handled, and results in better overall yields. Using a 10 % molar excess of **2** in xylene or dichloromethane avoids any further [4+2] cycloaddition of the alkyne onto the vinylthial **3'** produced.[7] Refluxing the xylene solution in the dark under inert atmosphere affords the hexatrienes **4'a-c**, isolated in 75-80% yield after silicagel column chromatography (CH_2Cl_2 eluent). These compounds are obtained as a mixture of two or three diastereoisomers depending on the R-substituent, all of them containing the (E)-configuration for the central linkage (see below). These purple solid mixtures of **4'** are deketalized into the corresponding **4** on treatment with Amberlyst-15 in acetone/water[10] (% yields, **4a** 30, **4b** 78, **4c** 77). The (E)-configuration of the central CH=CH bond of **4a** (further for **4b** and **4c**, and then for **1**) was determined by comparison of its UV-visible spectrum with that of the unequivocal-trans tetraester analog 5α,[11] which we prepared by double Wittig olefination of fumaric dialdehyde with **W**α (Scheme 2), $\lambda_1$max and $\lambda_2$max (nm) with ($\varepsilon[\times 10^3]$) being respectively 4.13 (4.0), 3.91 (4.1) for **4a** and 4.18 (4.15), 3.96 (3.68) for 5α.



Scheme 2

The fourfold olefinations of the last step have been accomplished by addition of tetraaldehydes **4**, either as a THF solution (**4b,c**) or directly as a solid (**4a**) at -80°C, to a solution of the P-ylids **W**α–γ, freshly generated by treatment of the corresponding phosphonium salts[8d] with *n*-BuLi in THF at -80°C. After their precipitation by dilution with ethanol, target compounds **1** [yield: 50% (**1aα**), 80% (**1bα**), 79% (**1cα**), 51% (**1aβ**), 55% (**1bβ**), 73% (**1cβ**), 50% (**1aγ**), 51% (**1bγ**), 63% (**1cγ**)] were purified by washing with EtOH, then acetonitrile, and again EtOH. Recrystallization from EtOH/dimethylformamide (DMF) could only be carried out for the most soluble CO_2Me substituted derivatives **1aα**, **1bα** and **1cα**.

As exhibited by their cyclovoltammograms (Table), the π-donor ability of compounds **1** appears exceptionally strong, since for all of them, the first oxidation potential (Ep_{a1}) is markedly lower than that of the parent TTF (0.38V in DMF), even in the cases of **1a-cα**, despite their eight electron withdrawing methoxycarbonyl substituents. In CH_2Cl_2 as the solvent, one observes two very close $1e^-$ reversible oxidation processes (likewise for **5α** in the same solvent), followed by a single $2e^-$ reversible oxidation peak. For the strongest donors **1a-cγ** (with R=H), the use of CH_2Cl_2 induces their rapid intramolecular cyclization.[6b,c,12] On the other hand, in DMF, two $2e^-$ reversible oxidation processes are observed corresponding to the formation of stable dicationic ($Ep_{a1} = Ep_{a2}$) and tetracationic ($Ep_{a3} = Ep_{a4}$) species. In all the cases reported in the Table, the extremely low values of Ep_a as well as their differences ΔEp_a are particularly noticeable and obviously indicative of the marked weakening of the coulombic repulsions in the polyoxidized states of the donors.

TABLE Oxidation peaks of **1**
(V/SCE, v = 0.2 $V.s^{-1}$; $^a Bu_4NPF_6$ 0.1 $mol.l^{-1}$; $^b Bu_4NClO_4$ 0.1 $mol.l^{-1}$)

Products	Solvent	Ep_{a1}	Ep_{a2}	$Ep_{a3} = Ep_{a4}$
1aα	CH_2Cl_2[a]	0.22	0.40	0.89
1bα	DMF[b]	0.35	0.55	0.81
1cα	CH_2Cl_2[a]	0.25	0.35	0.84
	DMF[b]	0.30	0.56	0.81
1aγ	DMF[b]	0.12		0.47
1bγ	DMF[b]	0.25		0.56
1cγ	DMF[b]	0.20		0.42

Compounds **1aβ** and **1bβ** are too poorly soluble to allow any accurate determination of the Ep_a values; however, for **1cβ**, fairly soluble in DMF, one observes a wide, poorly reversible oxidation wave from 0.20 to 0.55 V/SCE.

As expected from these results, all new compounds **1** behave as good precursors for organic metals: they react very quickly with tetracyanoquinodimethane to afford electroconductive black-green charge transfer salts, and they give rise to black microcrystalline electroconductive cation radical salts upon anodic oxidation with different anions, efforts still being devoted in order to obtaining single crystals.

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(*) All new compounds gave satisfactory spectral data and/or elemental analyses; ^{1}H and^{13}C high field nmr. as well as h.r.m.s. were recorded by the CRMPO (Rennes) and analyses by the CNRS (Vernaison). Selected examples:

4'c Red powder, m.p. 83-85°C; m.s. calcd (found) 668.0868 (668.0888) ; analysis, C 61.05 (61.31), H 5.42 (5.41), O 14.35 (14.19), S 19.17 (18.56); mixture of two isomers as shown by 300 MHz ^{1}H nmr ($CDCl_3$): δ (major/minor given) at 1.13/1.22 (t, 12H, 4 CH_3), 2.42/2.41(s, 6H, 2 p$\underline{\mathrm{Me}}$-Ph), 3.60/3.60 (m, 8H, 4 OCH_2), 5.56/5.60 (s, 2H, 2 $C\underline{H}(OEt)_2$), 5.80/5.81 (s, 2H, CH=CH), 7.24/7.06 (m, 8H, 2 pMe-$\underline{\mathrm{Ph}}$), 9.78/9.78 (s, 1H, 1 CHO), 9.95/9.95 (s, 1H, 1 CHO) ; 75 MHz ^{13}C nmr for the major isomer 180.0 (CHO), 96.8 and 96.5 ($\underline{C}H(OEt)_2$), 62.2 and 61.8 (OCH_2), 14.9 ($OCH_2\underline{C}H_3$), 21.5 (p$\underline{\mathrm{Me}}$-Ph), 138.1, 130.4, 130.1, 135.3 (pMe-$\underline{\mathrm{Ph}}$), 127.5 (CH=CH), 130.0 (S=C=$\underline{C}$), 154.5 ($(EtO)_2CH\text{-}\underline{C}=$), 134.4 (OCH-$\underline{C}$=), 125.2 ($S_2C=$).

4c Black crystals, m.p. (CH_2Cl_2) 272°C; m.s., calcd (found) 548.0244 (548.0223); analysis C 61.28 (61.32), H 3.67 (3.53), O 11.66 (11.85), S 23.37 (23.08); 300 MHz ^{1}H nmr ($CDCl_3$), 10.09 and 10.14 (2s, 2H, 2 CHO), 7.13 (m AA'BB', 8H, 2 pMe-$\underline{\mathrm{Ph}}$), 5.82 (s, 2H, CH=CH), 2.43 (s, 6H, 2 Me); 75 MHz ^{13}C nmr ($CDCl_3$) 178.3 and 178.2 (2 CHO), 127.9 ($S_2C=$), 129.6 ($S_2C=\underline{C}$), 127.6 (CH=CH), 149.3 and 148.6 (OCH-$\underline{C}$=$\underline{C}$-CHO), 134.6, 128.73, 130.4, 138.9 (pMe-$\underline{\mathrm{Ph}}$), 21.4 (Me).

1cγ Purple solid, m.p. (decompn) 180-183°C (DMF-EtOH), m.s. (FAB) 892; 300 MHz ^{1}H nmr (CS_2) 7.10 (m, 8H, 2 pMe-$\underline{\mathrm{Ph}}$), 6.20 and 6.13 (s and s, 4H and 4H, 4 S-CH=CH-S), 5.95 (s, 6H, CH=CH and 2 $CH=CS_2$), 5.73 (s, 2 $CH=CS_2$), 2.36 (s, 6H, 2 Me); 75 MHz ^{13}C nmr (CS_2 + acetone-d_6) 141.6 and 141.2 (2 t, $^3J=8$, $\underline{C}H=CS_2$), 137.9, 137.5, 130.0 and 22.6 (p$\underline{\mathrm{Me}}$-$\underline{\mathrm{Ph}}$), 133.4 (s, pMe-Ph-C=$\underline{C}S_2$), 127.8 (d, $^1J=153$, CH=CH), 126.5 and 126.1 (2s, SC=CS and pMe-Ph-$\underline{C}=CS_2$), 120.5 and 119.3 (2 dd, $^1J=186$, $^2J=5$, S-CH=CH-S), 105.2 and 105.0 (2 d, $^1J=161$, $\underline{C}H=CS_2$).

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