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Bis and Tetrakis(6-methyl-1,4-dithiafulven-6-yl) Substituted Tetrathiafulvalenes (TTF) and their Vinylogs as Novel π-Donors

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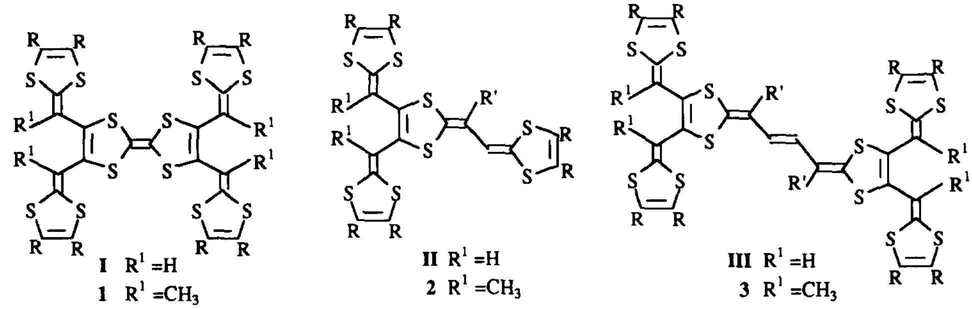
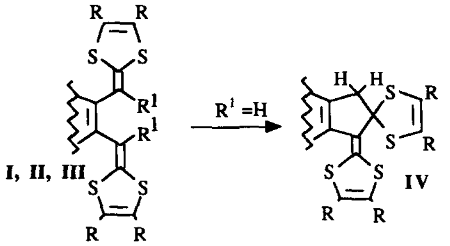
Abstract The synthesis of highly extended and sulfur rich tetrathiafulvalene derivatives, designed to avoid any internal cyclisation during their subsequent electrooxidation, is described. Their π-donating ability is confirmed by cyclic voltammetry, as well as the good stability of each of their oxidized species (up to an hexacationic state in one case).

The design of new π-donors able to afford electroconductive materials possessing a structural dimensionality greater than one is still of actuality, main goal being to improve their transport properties at low temperature. Thus in some 2D materials, suppression of Peierls distorsions has allowed to reach metal-like conducting and even superconducting cation radical salts in the TTF series.[1]


I R^1 =H
1 R^1 =CH_3
II R^1 =H
2 R^1 =CH_3
III R^1 =H
3 R^1 =CH_3

Scheme 1

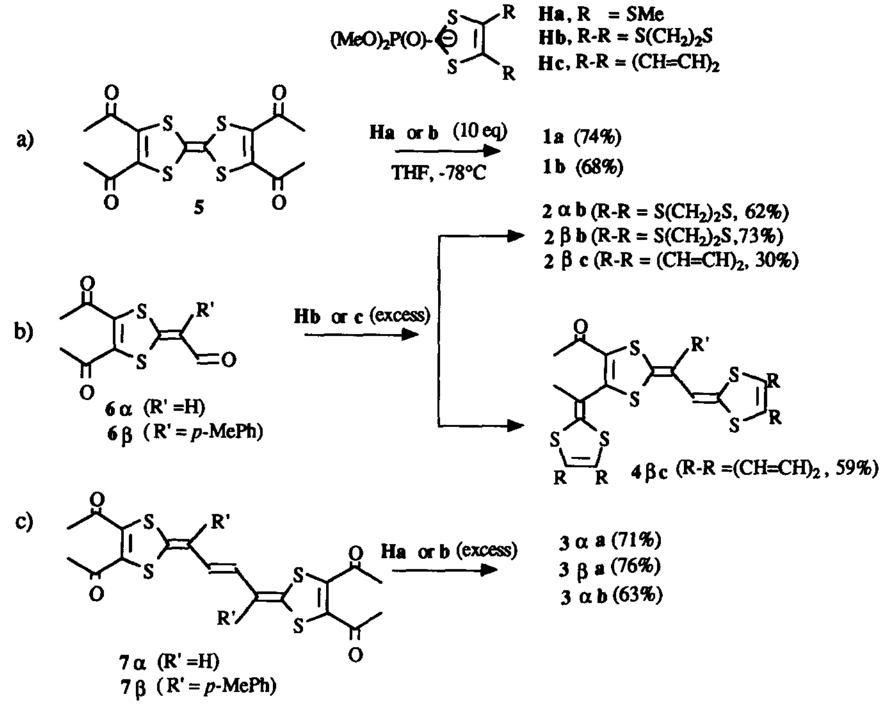
To date, besides the famous BEDT-TTF salts, most interesting materials belong to highly space-extended and S-enriched TTF derivatives[2] and in our quest in this field, significant results have been recently obtained upon electrooxidation of bis and tetrakis (1,4-dithiafulvene-6-yl) substituted TTF derivatives **I-III**[3] (R^1=H in scheme 1). However, despite many attempts of electrocrystallization under varied experimental conditions, suitable materials for structural and physical studies could be harvested in few cases only. A putative reason for such difficulties lies in the possible arising during the electooxidative process, of an internal cyclization to compounds **IV**[4] (scheme 2), resulting from


I, II, III
IV

Scheme 2

prototropy (R^1=H) involving two vicinal dithiafulvenyl side arms. Therefore, in order to avoid any spoiling trace of by-product **IV** possibly formed during electrolyses of **I-III**, we have focused on the preparation of the corresponding dithiafulvenyl TTF derivatives **1-3** with R^1=Me (schemes 1 and 3).

We report here on their synthesis and present some preliminary results emphasizing their unusual and very good π-donor ability.



Scheme 3

Tetrakis(6-methyl-1,4-dithiafulven-6-yl)TTFs **1a**[7] (R = SMe) and **1b** (R-R = $S(CH_2)_2S$) (scheme 3a) could be prepared in good yields (respectively 74 and 68% after precipitation with MeOH) by tetraolefination of tetraacetyl-TTF **5**[5]. In order to bring the four successive olefinations to completion, the phosphonate anions **H**[6] (THF, BuLi, -78°C) were used rather than the less nucleophilic corresponding P-ylids, and additionally, a very large excess of these reagents (10 eq. instead of 4 per mol of tetraketone) needed to be engaged.[7]

Olefinations of compounds **6**[5] were found to be mainly dependent on the R substituents in anions **H** (scheme 3b). Thus, the reaction of **6β** (R'=*p*-MePh) with a large excess of **Hc** (R-R= $(CH=CH)_2$), produced the di and triolefination products, **4βc** (59%) and **2βc** (30%) respectively. By contrast, when **Hb** (R-R = $S(CH_2)_2S$)) was used, the triolefinated compounds **2αb** and **2βb** were directly obtained from **6α** and **6β** respectively (**2αb** : 62% and **2βb** : 73%).[7]

Finally, the tetrasubstituted TTF vinylogs **3α** and **3β** (scheme 3c) could be obtained in fairly good yields (63-76%) in one step only, thanks to the good enough reactivity of the corresponding tetraketonic starting materials **7α**[5] and **7β**[5] towards the phosphonate anions **Ha** and **Hb**.[7]

Cyclic voltammetric studies (see table) reveal the uncommon and very good π-donor ability of the new compounds produced, with the occurence of multi (*up to five*) reversible oxidation peaks.

	1a$^{(a)}$	**2αb**$^{(b)}$	**2βb**$^{(b)}$	**2βc**$^{(a)}$	**3αa**$^{(b)}$	**3αb**$^{(b)}$	**3βa**$^{(b)}$	**Ia**$^{(a)}$	**IIβb**$^{(a)}$	**TMSTTF**
Epa_1	0.42	0.35	0.30	0.34	0.29	0.31	0.28	0.08	0.17	0.55
Epa_2	0.72*	0.55	0.52	0.63	0.37	0.38	0.40	0.17	0.33	0.83
Epa_3	-	0.88	0.95	1.17*	0.83$^{(c)}$	0.80	0.81	0.51*	0.92	-
Epa_4	-	1.16	1.08	-	1.24*	1.12$^{(c)}$	0.97	-	1.12	-
Epa_5	-	-	-	-	-	-	1.21*	-	-	-

*Table : Oxidation potentials (Epa_i/SCE) of compounds **1-3**, Bu_4NPF_6 (0.1 mol/L) in (a) CH_2Cl_2 or (b) CH_2Cl_2/CH_3CN 1/1; 100 mV/s, 20°C; (c) irreversible redox process. All of the reversible redox processes involve 1e-, with the exception of those indicated by (*) for which 2e- are exchanged (Epa - Epc = 30 mV).*

Study of compounds **1** has been restricted to the most soluble derivative **1a**, this latter being compared with its unsubstituted analog **Ia** (R^1=H) and with tetra(methylsulfanyl)-TTF (TMSTTF). As expected from the substitution of the TTF core by four electrodonating dithiolylidene moieties, **1a** (Epa_1=0.42V) is better a donor molecule than TMSTTF (Epa_1=0.55V), but not as good as **Ia** (Epa_1=0.08V). Such a behaviour is also in agreement with the UV-vis spectra (**1a**: λ_{max} = 349 nm, and **Ia**: λ_{max} = 500 nm); these data suggest a lower conjugation in **1** compared to **I**, due to a difference in flatness, the former being distorted by steric hindrance between both close 6-Me substituents.

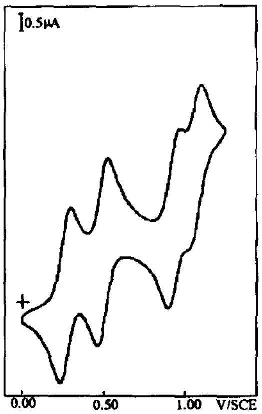


Figure : Cyclic voltammetry of compound 2βb, 1mM.L^{-1}, Bu_4NPF_6 (0.1 mol/L) in CH_2Cl_2/CH_3CN 1/1; 100 mV/s, 20°C.

Similar steric hindrance between Me groups may also explain the lower π-donating ability of **2b-c**, when considering Epa_1 and Epa_2 values, relative to their corresponding compounds **II** (R^1=H). On the other hand, the good reversibility of any of the four redox processes in compounds **2αb** and **2βb** (Epa_i-Epc_i=60mV) clearly demonstrates the stability of each oxidized species which are reached upon the following oxidative sequence (Figure) :

$$\mathbf{2b} \overset{-\,1e-}{\rightleftharpoons} \mathbf{2b}^{\bullet+} \overset{-\,1e-}{\rightleftharpoons} \mathbf{2b}^{2+} \overset{-\,1e-}{\rightleftharpoons} \mathbf{2b}^{\bullet 3+} \overset{-\,1e-}{\rightleftharpoons} \mathbf{2b}^{4+}$$

Moreover, the close identity of Epa_3 and Epa_4 values between compounds of both **2** and **II** series would suggest the occurence of a S···S stabilizing internal 1,5-bonding interaction in the polycationic states, forcing the peripheral dithiafulvenyl groups to tend to a coplanarity with the TTF vinylog central core whatever R^1= H or Me.

Similarly, compounds **3** behave as very good π-donors. For example, the CV of compound **3βa** displays up to five reversible redox peaks, the fifth one corresponding to a 2e- process (Epa_5-Epc_5=30mV) allowing to reach an hexacationic state, according to the following oxidative sequence :

$$3\beta a \overset{-\,1e^-}{\rightleftharpoons} 3\beta a^{\cdot+} \overset{-\,1e^-}{\rightleftharpoons} 3\beta a^{2+} \overset{-\,1e^-}{\rightleftharpoons} 3\beta a^{\cdot3+} \overset{-\,1e^-}{\rightleftharpoons} 3\beta a^{4+} \overset{-\,2e^-}{\rightleftharpoons} 3\beta a^{6+}$$

In conclusion, the synthesis of new extended tetrathiafulvalenes **1-3** designed to avoid any occurence of undesirable intramolecular cyclisation as encountered in systems **I-III**, has been accomplished. Compounds **1-3** exhibit good π-donating abilities and good stabilities for each of the cationic species reached upon electrooxidation (up to an hexacationic state in the case of **3βa**). These features are very promising for the preparation of new materials involving highly extended and S-enriched TTF derivatives, upon preparative electrooxidation.

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7 All new compounds gave satisfactory spectroscopic data. Selected examples :

Compound **1a** : m.p. = 110°C; ^1H nmr ($CDCl_3$): 2.42 (s, 24H, SCH_3), 1.88(s, 12H, CH_3); ^{13}C nmr ($CDCl_3$): 134.6, 131.5, 129.2, 124.9, 112.4, 21.5, 19.2, 19.1; MS (FAB+) 1084 ($M^{+\cdot}$); UV (CH_2Cl_2) λmax = 500nm.

Compound **2αb** : m.p. = 129°C; ^1H nmr ($CDCl_3$): 5.83 (d, 1H, ^3J = 11Hz), 5.69 (d,1H, ^3J = 11Hz), 3.32 (s, 4H, SCH_2), 1.91 (s, 3H, CH_3), 1.90 (s, 3H, CH_3); ^{13}C nmr ($CDCl_3$): 133.2, 131.6, 130.9, 126.2, 114.5, 113.4, 113.1, 112.9, 112.5, 110.8, 30.4, 30.3, 22.2, 22.1; MS (FAB+) 756 ($M^{+\cdot}$); UV (CH_2Cl_2) λmax = 404nm.

Compound **3αa** : m.p. = 130°C; ^1H nmr ($CDCl_3$): 6.02 (d, 2H, ^3J = 11Hz), 5.81(d,1H, ^3J = 11Hz), 2.42 (s, 12H, SCH_3), 1.87 (s, 6H, CH_3), 1.85 (s, 6H, CH_3); ^{13}C nmr ($CDCl_3$): 134.9, 132.7, 130.8, 130.6, 129.7, 125.5, 125.2, 114.4, 112.7, 112.5, 22.0, 21.9, 19.64, 19.57; Calcd(Found): C 40.11 (39.66), H 3.54 (3.69).

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