Bull Soc Chim Fr (1996) 133, 301-308

A new synthesis of polyenic analogues of tetrathiafulvalene

Thi-Thao Nguyen[1], Yvon Gouriou[1], Marc Sallé[1], Pierre Frère[1],
Michel Jubault[1], Alain Gorgues[1]*, Loïc Toupet[2], Amédée Riou[1]

[1] *Ingénierie moléculaire et matériaux organiques, CNRS EP 66, Université d'Angers,*
2, boulevard Lavoisier, 49045 Angers cedex;
[2] *Groupe matière condensée et matériaux, URA 804, Bat 11B, Faculté des sciences de Rennes,*
35042 Rennes cedex, France

(Received 2 January 1996; accepted 5 March 1996)

Summary — Wittig(-Horner) olefination of the mono(dimethylacetal) of fumaraldehyde with phosphorane or phosphonate anions bearing a 1,3-dithiol-2-ylidene moiety, produces the corresponding (2*E*) 4-(1,3-dithiol-2-ylidene)but-2-enals after acidolysis. Via a second analogous olefination or a McMurry coupling reaction, these powerful synthetic intermediates allow easy access to various polyenic analogues of tetrathiafulvalene, in which the two dithiole moieties are separated by three, four or five conjugated double bonds. The UV-vis spectra of these extended π-donors, as well as their electrochemical behavior, underline the marked influence of the length of the polyenic chain on their effective conjugation and π-donating ability.

fumaraldehyde / tetrathiafulvalene / extended analogue of TTF / Wittig(-Horner) reaction

Résumé — Une nouvelle synthèse d'analogues polyéniques du tétrathiafulvalène. *Divers* (2E) *4-(1,3-dithiol-2-ylidène)but-2-énals sont isolés par oléfination de Wittig(-Horner) du mono(diméthylacétal) du fumaraldéhyde à l'aide de phosphoranes porteurs de groupements 1,3-dithiol-2-ylidene, suivie d'une acidolyse. Grâce à une seconde oléfination analogue ou un couplage de type McMurry, ces intermédiaires permettent un accès facile à différents analogues polyéniques du tétrathiafulvalène dans lesquels les deux hétérocycles dithioles sont séparés par trois, quatre ou cinq doubles liaisons. Les spectres UV-vis de ces analogues, ainsi que leurs propriétés électrochimiques, mettent en évidence l'importance de la longueur de la jonction polyénique, à la fois sur la conjugaison effective et sur le pouvoir donneur-π.*

fumaraldéhyde / tétrathiafulvalène / analogue du TTF / réaction de Wittig(-Horner)

Extended tetrathiafulvalene (TTF) derivatives **1**–**3** (fig 1), incorporating a conjugating spacer between the two 1,3-dithiole heterocycles, are subject to intense work in the fields of i) molecular conductors [1, 2] and ii) non linear optics (NLO) [3].

In the first area, the spatial extension of the molecules with respect to the parent TTF strengthens their π-donating ability, as evidenced by the lowering of both oxidation potentials E_1 and E_2, and also reduces on-site coulombic repulsions in the dicationic species, as exhibited by the decreasing of $E_2 - E_1$. Therefore in the solid state the corresponding cation radical salts are expected to possess an enhanced dimensionality (greater than 1) thanks to the weakening of the intermolecular coulombic repulsions between the cationic species, resulting from a lowering of their charge density as well as to enhanced π-bonding interactions between the donors.

In the second area, in addition to the well-known electron-donating character of the 1,3-dithiole moiety, useful for the designing of second order NLO-active chromophores incorporating the donor–linker–acceptor (D-π-A) system [4], some of these polyenic analogues of TTF have been shown to possess interesting third order NLO properties [3b, c].

Based on these considerations, we were interested in a new synthesis of compounds **1** to **3** (fig 1), using, as key precursors, the diolefinic aldehydes **4** which are also promising intermediates for the preparation of D-π-A systems. We report here our synthetic strategy, and in addition present some electrochemical features of our target compounds which, as expected, are endowed with strong π-donating ability, a prerequisite for reaching organic metals.

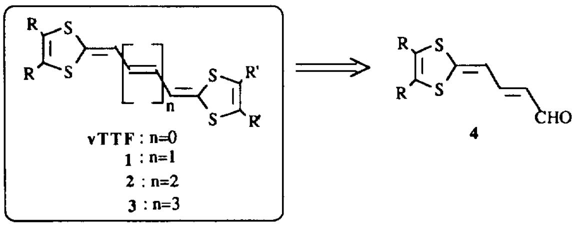
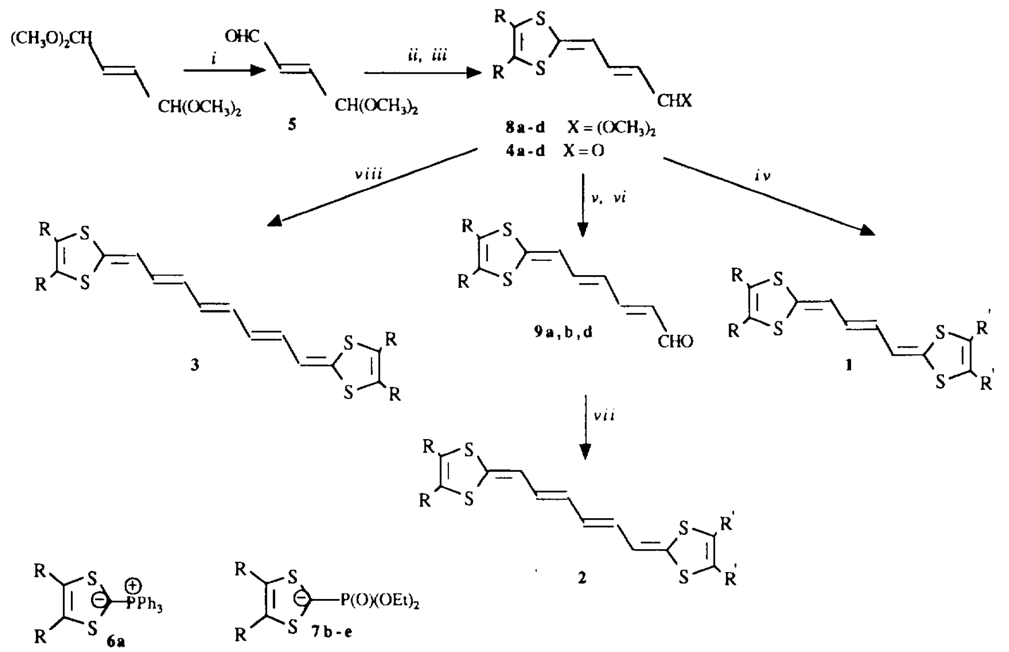


Fig 1

---

[*] Correspondence and reprints



a : R = CO_2CH_3 ; b : R-R = $(CH{=}CH)_2$; c : R-R = $(SCH_2\text{-}CH_2\text{-}S)$; d : R = CH_3 ; e : R = H.

Fig 2. General synthetic pathway: i) $HCO_2H/CHCl_3$; ii) **6** or **7**; iii) H^+; iv) **6** or **7**; v) (1,3-dioxan-2-ylmethyl)tributylphosphonium bromide, BuLi; vi) SiO_2; vii) **6**; viii) $TiCl_3/LiAlH_4$.

Synthesis

Previous syntheses of compounds **1** have involved the building of the central ethylenic spacer in the final step, either by a thermal dimerization-desulfurization of a thial [5, 6a], or through a titanium-mediated coupling of an aldehyde [6]. However, both methodologies are restricted to the building of symmetrically substituted derivatives (R = R').

In our approach, the central *trans* ethylenic linkage is introduced with the starting material, ie, the mono(dimethylacetal) of fumaraldehyde **5**. Aldehydes **4** allow a more flexible access to asymmetrical as well as symmetrical compounds **1**, and also, after further steps, to the other new extended molecules **2** and **3** (fig 2).

Compound **5** could be prepared according to Grée et al by hemihydrolysis of fumaraldehyde bis(dimethylacetal) either with perchloric acid [7], or in the presence of Amberlyst-15 [8]. However, we observed that it could also be conveniently produced in similar yields by hemiacidolysis with HCO_2H in the presence of $CHCl_3$ [9]. Compound **5** was then subjected to Wittig(-Horner) olefination with the Akiba's reagents [10], ie, the P-ylids **6** or the phosphonate anions **7** bearing the 1,3-dithiolylidene moiety adequately 4,5-disubstituted. The raw acetals **8** thus produced were then directly hydrolyzed in aldehydic derivatives **4** either in the presence of Amberlyst-15 or during chromatographic purification on an SiO_2 column; overall yields from compound **5** ranged from 55–85% [11].

The structure of aldehydes **4**, and in particular their (*E*) configuration as well as *δ-trans* conformation, were fully ascertained by ^1H NMR and IR spectroscopy, and also by X-ray diffraction in the case of **4d**. Thus, the Ortep view of **4d** (fig 3) confirms that the *trans*-substituted olefinic system lies in the same plane as the heterocycle, thus providing optimized π-electron delocalization.

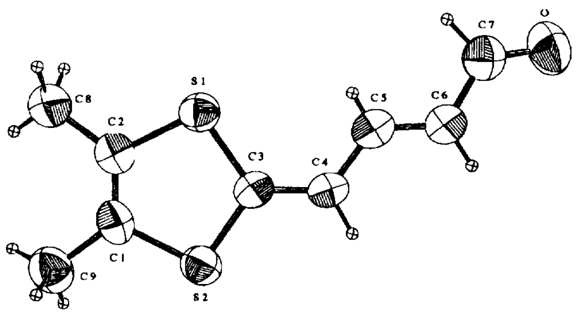


Fig 3. Ortep view of **4d**.

As indicated in figure 2, these aldehydes **4** can serve as starting materials for reaching our target donors. Hence, a second Wittig(-Horner) olefination with the Akiba's reagents **6** or **7** affords the conjugated analogues of TTF **1**, the only difficulties lying in the lack of electrophilicity of the CHO functional group resulting from the strong electron-releasing effect of the conjugated heterocyclic moiety. This drawback could be prevented by achieving the reaction with **7** at 0 °C [12]. Symmetrical as well as asymmetrical derivatives **1** could be isolated in fair to good yields (table I) after silica-gel column chromatography or, for the less soluble derivatives, precipitation with chloroform. Of course, symmetrical derivatives could also be obtained through a direct bis-olefination of fumaraldehyde as demonstrated for **1aa** and **1bb**, but the step-by-step methodology was still preferred taking into account the difficulty in isolating fumaraldehyde [13].

Table I. Yields of olefination to compounds 1.

Compound	**1aa**	**1ab**	**1ae**	**1bb**	**1be**	**1cc**	**1cd**	**1dd**
Yield (%)	57	47	46	81	70	60	86	75

In a similar manner, compounds **2** with an additional C=C bond could also be prepared starting from the same precursor **4**. Thus, a Wittig olefination of **4** with (1,3-dioxan-2-ylmethylene)tributylphosphorane [14] directly afforded the trienic aldehydes **9a**, **9b** and **9d** in approximately 60% yield after SiO_2 column chromatography, the dioxolane protecting group being removed during the purification step. As expected, the rate of this olefination was dependent on the electronic effects of the R substituents. With the R = CO_2Me electron-withdrawing substituent, the CHO group of **4a** was electrophilic enough that compound **9a** formed rapidly (unseparable mixture of *Z* and *E* isomers on the last double bond formed), whereas with the R-R = $(CH{=}CH)_2$ and R = Me electron-releasing groups, **9b** and **9d** respectively required a longer reaction time (*E*-isomers only). In the final step, aldehyde **9b** was subjected to a Wittig olefination with **6a** (rt, 6 h), which afforded the asymmetrical π-donor **2ab** in a yield of 50%.

In contrast, our most conjugated systems **3** were also produced from compound **4** via a McMurry coupling [15]. However, only compound **3aa** (30% yield) could be fully characterized, **3bb** being poorly soluble in most usual solvents, and **3dd** being very unstable.

UV-vis spectroscopic and electrochemical properties

UV-vis spectra of the new extended π-donors, and those of the corresponding vinylogues of tetrathiafulvalene **vTTF** ($n = 0$) [6, 16], have been recorded in methylene chloride and maximum absorption wavelengths are given in table II. As expected, increasing the length of the conjugating linker leads to a redshift in λmax from 393 to 444 nm (for **vTTFab** ($n = 0$) to **2ab** ($n = 2$)) in the asymmetrical **ab** series and from 389 to 462 nm (for **vTTFaa** ($n = 0$) to **3aa** ($n = 3$)) in the symmetrical **aa** series. Consequently, the redshift values observed when one compares **2ab** and **1ab** (21 nm) or **3aa** and **1aa** (42 nm), associated with the maintenance of the fine vibronic structure (fig 4), are indicative of the absence of any important conformational distorsions when the π-system is lengthened [17].

The electrochemical properties of compounds **1–3** were studied by cyclic voltammetry; $E\text{pa}_1$ and $E\text{pa}_2$ values, as well as $\Delta E = E\text{pa}_2 - E\text{pa}_1$, are collated in table II (along with those of **vTTFaa,ab** and **TTFaa** [tetrakis(methoxycarbonyl)TTF] for comparison). Representative cyclovoltammograms relating to the **aa** series (including the corresponding **vTTFaa**) are shown in figure 5. The ΔE values are linked to the $D^{+\cdot}$ formation constant $K = (D^{+\cdot})_2/(D)(D^{2+})$ by the classical equation $\Delta E = 0.059 \text{ Log K}$, where D, $D^{+\cdot}$ and D^{2+} represent respectively the neutral, the monocation radical and the dication states of the π-donor.

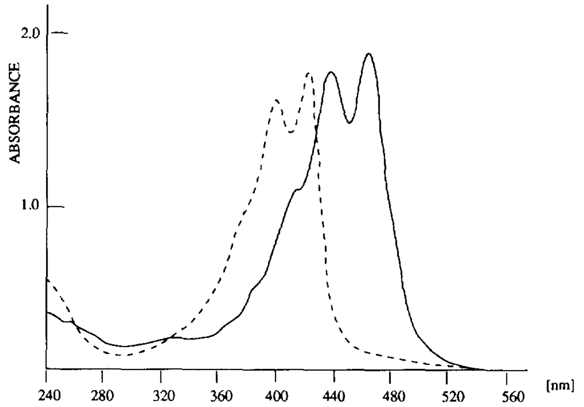


Fig 4. Electronic spectra of compounds **1aa** (---) and **3aa** (—), 4×10^{-5} mol L^{-1} in dichloromethane.

Table II. Cyclovoltammetric and UV-vis data of compounds **1–3**: oxidation peaks (*E*pa1) and (*E*pa2) are determined (V/SCE) with n-Bu_4NPF_6 (0.1 mol L^{-1}) in CH_2Cl_2 as supporting electrolyte, scan rate: 100 mV sec^{-1}; electronic spectra are recorded in CH_2Cl_2.

Compound	E*pa1* *(V/SCE)*	E*pa2* *(V/SCE)*	ΔE *(V)*	λ*max* *(nm)*
TTFaa	0.94	1.34	0.40	–
vTTFaa	0.71	0.94	0.23	389
1aa	0.64	0.76	0.12	420
3aa	0.56		0.00	462
vTTFab	0.62	0.90	0.28	393
1ab	0.54	0.69	0.15	423
2ab	0.52(sh)	0.55	0.03	444
1ae	0.45	0.61	0.16	428
1bb	0.47	0.61	0.14	424
1be	0.37	0.49	0.12	430
1cc	0.44	0.52	0.12	453
1cd	0.31	0.43	0.12	449
1dd	0.17	0.30	0.13	445

Using acetonitrile as a solvent, Yoshida et al [6b] observed only one $2e^-$ reversible oxidation peak during their electrochemical study of compounds **1**, resulting from the coalescence of both oxidation peaks. Using dichloromethane, which allows a better separation of the oxidation potentials [18], we observed two fairly well separated $1e^-$ reversible oxidation peaks with, of course, very weak values of ΔE, indicative of low on-site coulombic repulsions. Looking at both the **aa** and **ab** series, one observes a strong decrease in ΔE with a lengthening of the conjugated linker [19] (from **vTTF** to **2**) till coalescence ($\Delta E = 0$) in the case of **3**, in accordance with a $2e^-$ process ($E\text{pc} - E\text{pa} = 30$ mV [20]). In agreement with previous results by the Japanese group [6b], such a decrease in ΔE leads to a parallel lowering of the thermodynamic stability of $D^{+\cdot}$, the extent of the decrease being most favored in the case of the most extended **3**.

Another classical feature of all these compounds is the dependence of their π-donor ability on the length of the conjugation, as demonstrated by the values of $E\mathrm{pa}_1$ which decrease from 0.62 (**vTTFab**, $n = 0$) to 0.52 V (**2ab**, $n = 2$) in the **ab** series, and from 0.71 (**vTTFaa**, $n = 0$) to 0.56 V (**3aa**, $n = 2$) in the **aa** series. On the other hand, as expected, the nature of the R and R′ substituents have a marked influence on the oxidation potential ($E\mathrm{pa}_1 = 0.64$ and 0.17 V/SCE for **1aa** and **1dd** respectively), in accordance with the electronic effects of the substituents on the HOMO [19].

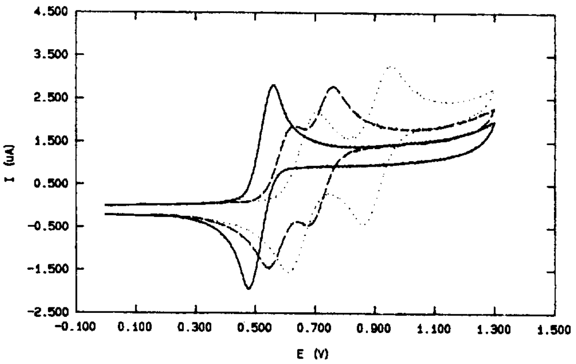


Fig 5. Cyclovoltammograms of **vTTFaa** (...), **1aa** (---) and **3aa** (—) (10^{-3} mol L^{-1}) in CH_2Cl_2, n-Bu_4NPF_6 (10^{-1} mol L^{-1}), 100 mV sec^{-1}, V/SCE.

Conclusion

The main results of this paper deal with a new synthetic methodology to reach asymmetrical compounds **1**, as well as unprecedented derivatives **2** and **3**, from the diacetal of fumaraldehyde. As expected, study of their electrochemical behavior confirms their strong π-donor ability.

Considering the superconducting state recently observed for the first time in a cation radical salt of an extended analog of TTF [2a], π-donors **1**–**3** constitute promising candidates for obtaining electroconducting materials. Attempts to reach the corresponding electrogenerated materials are underway. Thus, electrooxidation of **1cc**, an ethylenic analog of the famous BEDT-TTF, in the presence of ClO_4^- or ReO_4^- anions, has already produced shiny copper-like microcrystals. These materials exhibit a $(\mathbf{1cc})_1/(\mathrm{anion})_1$ stoichiometry as determined by X-ray energy dispersion, and efforts are still underway to produce mixed valence salts.

In addition, it should be emphasized that several aldehydic intermediates are of much interest in the preparation of D-π-A materials prone to generating second order hyperpolarizabilities [21].

Experimental section

High resolution mass spectra were recorded by J Orduna and J Garin (University of Zaragoza) [22] and by P Guénot (Centre de mesures physiques de l'Ouest, Rennes). The chemical shifts are expressed in ppm relative to tetramethylsilane as internal reference, and the coupling constants are in Hz. IR absorption wavenumbers are expressed in cm^{-1}. Elemental analysis results were obtained from the CNRS (Centre d'analyse, Vernaison).

Fumaraldehyde mono(dimethylacetal) 5

A solution of the bis(dimethylacetal) of fumaraldehyde (19.7 g, 0.1 mol) in 350 mL chloroform was treated at room temperature overnight with 24 mL formic acid. The solution was washed four times with water and dried over $MgSO_4$. Compound **5** was purified by distillation ($\mathrm{Bp}_{(10\ \mathrm{mBar})}$ = 88–94 °C) and was obtained as a pale yellow liquid (12.85 g, 68% yield).

^1H NMR ($CDCl_3$): 9.63 (d, $^3J = 8$ Hz, 1H); 6.76 (dd, $^3J = 16$ Hz, $^3J = 4$ Hz, 1H); 6.31 (dd, $^3J = 16$ Hz, $^3J = 8$ Hz, 1H); 5,03 (d, $^3J = 4$ Hz, 1H); 3.33 (s, 6H).

IR (Nujol): 1 680 cm^{-1}.

4-(4,5-Disubstituted-1,3-dithiol-2-ylidene)but-2-enals 4

Depending on the nature of R, two different procedures were used, involving either a phosphonium salt (4,5-dimethoxycarbonyl-1,3-dithiol-2-yl) tributylphosphonium fluoroborate **6a** [23] or a phosphonate ester anion **7b,c,d**.

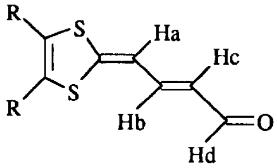


Fig 6. Indexation of H atoms for NMR spectra of **4**.

- *Case of* **4a**

A mixture of **5** (5 mmol) and **6a** (1 equiv) in 20 mL dry THF was treated at 0 °C with excess Et_3N (5 mL). After 1 h of stirring, the THF was evaporated and the residue was extracted by CH_2Cl_2 and washed with water. The solid residue obtained after evaporation was treated with 0.4 g of Amberlyst-15 in 40 mL acetone containing two drops of water. The reaction time was controlled by TLC (CH_2Cl_2). Acetone was evaporated after filtration of the solid, and the residue was purified by chromatography over silica gel (CH_2Cl_2). Compound **4a** was obtained as a yellow solid, fairly stable on standing in air.

4a: Yield: 53%. Mp: 133–137 °C.

^1H NMR ($CDCl_3$): 9.52 (d, $J_{dc} = 9$ Hz, Hd); 6.93 (dd, $J_{bc} = 17$ Hz, $J_{ba} = 12$ Hz, Hb); 6.30 (d, $J_{ab} = 12$ Hz, Ha); 6.22 (dd, $J_{cb} = 17$ Hz, $J_{cd} = 9$ Hz, Hc).

^{13}C NMR ($CDCl_3$): 192.8 (*C*HO); 159.2 and 159.0 (*C*O_2Me); 146.4 (S*C*S); 145.4 (*C*-Hb); 132.1 and 130.8 (S*C*=*C*S); 127.4 (*C*-Ha); 111.8 (*C*-Hc); 53.6 (2 × CH_3).

IR (KBr): 1 740 cm^{-1} ($C(OCH_3)=O$); 1 664 cm^{-1} ($C(H)=O$).

MS (EI), m/e: calc for $C_{11}H_{10}O_5S_2$ 285.99696, found 285.9969.

- *Case of* **4b–d**

Phosphonate anions **7b–d** (5 mmol) were generated with one equivalent of n-BuLi (1.6 M in hexane) in 20 mL dry THF at −80 °C. A stoichiometric amount of aldehyde **5** in dry THF was then added dropwise and the reaction allowed to warm to room temperature. The reaction mixture was then treated according to the same procedure as for **4a**.

4b: Yield: 71%. Mp: 114–117 °C.

IR (KBr): 1 711 cm^{-1} (C=O).

^{1}H NMR (CDCl$_3$): 9.52 (d, J_{dc} = 8 Hz, Hd); 7.45 (m, 4H); 7.28 (dd, J_{bc} = 14.5 Hz, J_{ba} = 11.5 Hz, Hb); 6.71 (d, J_{ab} = 11.5 Hz, Ha); 5.97 (dd, J_{cb} = 14.5 Hz, J_{cd} =8 Hz, Hc).

^{13}C NMR (CDCl$_3$): 193.4 (*C*-Hd); 148.9 (S*C*S); 147.1 (*C*-Hb); 134.6 (S*C*=*C*S); 126.9 and 122.6 (4 × aromatic *C*); 126.6 (*C*-Ha); 112 (*C*-Hc).

Anal calc for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; O, 7.26; S, 29.10. Found: C, 59.79; H, 3.80; O, 7.56; S, 28.87.

MS (EI), *m/e*: calc for $C_{11}H_8OS_2$: 220.00166, found 220.0010.

4c: Yield: 79%. Mp: 161–162 °C.

IR (KBr): 1 649 cm^{-1} (CO).

^{1}H NMR (CDCl$_3$): 9.51 (d, J_{dc} = 8 Hz, Hd); 6.97 (dd, J_{bc} = 14.6 Hz, J_{ba} = 11.5 Hz, Hb); 6.31 (d, J_{ab} = 8 Hz, Ha); 5.92 (dd, J_{cb} = 14.6 Hz, J_{cd} = 11.5 Hz, Hc); 3.34 (s, 4H).

^{13}C NMR (CDCl$_3$): 192.8 (CO); 148.1 (S*C*S); 146.3 (*C*-Hb); 126.1 (*C*-Ha); 113.2 and 112.9 (S*C*=*C*S); 110.8 (*C*-Hc); 29.4 (S*C*H$_2$*C*H$_2$S).

Anal calc for $C_9H_8OS_4$: C, 41.54; H, 3.07. Found: C, 41.73; H, 3.01.

4d: Yield: 72%. Mp: 104 °C.

IR (KBr): 1 658 cm^{-1} (CO).

^{1}H NMR (CDCl$_3$): 9.44 (d, J_{dc} = 8 Hz, Hd); 7.03 (dd, J_{bc} = 14.5 Hz, J_{ba} = 11.5 Hz, Hb); 6,23 (d, J_{ab} = 8 Hz, Ha); 5.85 (dd, J_{cb} = 14.5 Hz, J_{cd} = 11.5 Hz, Hc); 1.99 and 1.90 (2s, 6H).

^{13}C NMR (CDCl$_3$): 192.9 (*C*-Hd); 153.4 (S*C*S); 147.4 (*C*-Hb); 124.4 (*C*-Ha); 123.7 and 123.6 (S*C*=*C*S); 108.7 (*C*-Hc); 13.6 and 13.2 (2 × CH$_3$).

Anal calc for $C_9H_{10}OS_2$: C, 54.51; H, 5.08; S, 32.34. Found: C, 54.47; H, 4.80; S, 32.72.

MS (EI), *m/e*: calc for $C_9H_{10}OS_2$: 198.01731, found 198.0176.

6-(4,5-Disubstituted-1,3-dithiol-2-ylidene) hexa-2,4-dienals 9

A solution of aldehyde **4a**, **4b** or **4d** (2 mmol) and (1,3-dioxan-2-ylmethyl)tributylphosphonium bromide (2 equiv) in 10 mL dry THF was treated with 2 equiv *n*-BuLi (1.6 M in hexane) at room temperature. After stirring for 1 h (for **4a**) or 3 h (for **4b** and **4d**), THF was removed in vacuo and the residue was dissolved in methylene chloride, washed with water and dried over MgSO$_4$. After removing the solvent, **9a**, **9b** and **9d** were purified by chromatography over silica gel (CH$_2$Cl$_2$) and obtained as yellow powders.

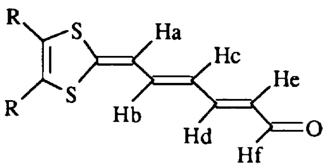


Fig 7. Indexation of H atoms for NMR spectra of **9**.

9a (*E*): Yield: 45%.

IR (KBr): 1 730 cm^{-1} (C(OCH$_3$)=O); 1 665 cm^{-1} (C(H)=O).

^{1}H NMR (CDCl$_3$): 9.54 (d, J_{fe} = 8.0 Hz, Hf); 7.12 (dd, J_{de} = 15.2 Hz, J_{dc} = 10.8 Hz, Hd); 6.45 (dd, J_{bc} = 14.3 Hz, J_{ba} = 11.3 Hz, Hb); 6.25 (dd, J_{cb} = 14.3 Hz, J_{cd} = 11.3 Hz, Hc); 6.15 (d, J_{ab} = 11 Hz, Ha); 6.12 (dd, J_{ed} = 15.2 Hz, J_{ef} = 8.0 Hz, He); 3.86 and 3.85 (2s, 6H).

Anal calc for $C_{13}H_{12}O_5S_2$: C, 49.98; H, 3.87. Found: C, 50.19; H, 4.30.

9b: Yield: 60%. Mp 130–134 °C.

IR (KBr): 1 665 cm^{-1} (CO).

^{1}H NMR (CDCl$_3$): 9.61 (d, J_{fe} = 8 Hz, Hf); 7.39–7.20 (m, aromatic H and Hd); 6.73 (dd, J_{bc} = 14.3 Hz, J_{ba} = 11 Hz, Hb); 6.35 (dd, J_{cb} = 14.3 Hz, J_{cd} = 11 Hz, Hc); 6.36 (J_{ab} = 11.5 Hz, Ha); 6.22 (dd, J_{ed} = 15 Hz, J_{ef} = 8 Hz, He).

^{13}C NMR (CDCl$_3$): 197.4 (*C*-Hf); 152.3 (*C*-Hd); 143.5 (S*C*S); 138.2 (*C*-Hb); 135.5 (S*C*=*C*S); 129.7 (*C*-He); 126.2 and 121.8 (4 × aromatic C); 125.5 (*C*-Ha); 113.2 (*C*-Hc).

Anal calc for $C_{13}H_{10}OS$: C, 63.38; H, 4.10; S, 26.03. Found: C, 63.14; H, 4.25; S, 25.84.

9d: Yield: 23%. Mp 90–91 °C.

IR (KBr): 1 664 cm^{-1} (CO).

^{1}H NMR (CDCl$_3$): 9.49 (d, J_{fe} = 8 Hz, Hf); 7.13 (dd, J_{de} = 14.8 Hz, J_{dc} = 11.3 Hz, Hd); 6.56 (dd, J_{bc} = 14.3 Hz, J_{ba} = 12 Hz, Hb); 6.20–6.02 (m, Ha, Hc, He); 1.99 and 1.96 (2s, 6H).

^{13}C NMR (CDCl$_3$): 193.4 (*C*-Hf); 153 (*C*-Hd); 146.6 (S*C*S); 138.9 (*C*-Hb); 128.5 (*C*-He); 123.6 (*C*-Ha); 123 (S*C*=*C*S); 110.5 (*C*-Hc); 13.6 and 13.2 (2 × CH$_3$).

2,2'-(But-2-ene-1,4-diylidene)bis(4,5-disubstituted-1,3-dithioles) 1

- **1aa** *and* **1ab**

A large excess of triethylamine was added dropwise at room temperature to a mixture of **4a** (or **4b**) (5 mmol) and **6a** (5 mmol). The resulting precipitate was filtered off and rinsed with methanol and diethyl ether to produce **1aa** (or **1ab**) as an orange powder.

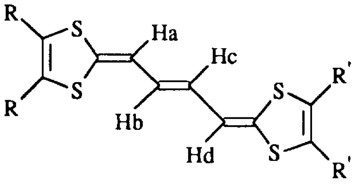


Fig 8. Indexation of H atoms for NMR spectra of **1**.

- *Tetramethyl 2,2'-(but-2-ene-1,4-diylidene)bis (1,3-dithiole-4,5-dicarboxylate)* **1aa**

Yield: 57%. Mp: 254–256 °C. Spectroscopic measurements are in agreement with those obtained by McKinnon and Buchshriber [5].

- *Dimethyl 2-[4-(1,3-benzodithiol-2-ylidene)but-2-enylidene]-1,3-dithiole-4,5-dicarboxylate* **1ab**

Yield: 47%. Mp: 160–162 °C.

^{1}H NMR (CDCl$_3$): 7.24–7.08 (m, 4H); 6.13 (d, J_{ab} = 11 Hz, Ha); 6.06 (d, J_{dc} = 11 Hz, Hd); 5.96 (dd, J_{bc} = 13.6 Hz, J_{ba} = 11 Hz, Hc); 5.75 (dd, J_{cb} = 13.6 Hz, J_{cd} = 11 Hz, Hd); 3.84 (s, 6H).

^{13}C NMR (CDCl$_3$): 160 (2 × CO); 135.9 and 135.8 (MeOOC*C*=*C*COOMe); 133.6 (*C*=C-Hd); 131.5 and 130.1 (S*C*=*C*S); 128.9 (*C*=C-Ha); 126.7 (*C*-Hd); 125.9 and 125.7 (2 × aromatic *C*); 124.4 (*C*-Hb); 121.6 and 121.4 (2 × aromatic *C*); 115.7 (*C*-Ha); 114.4 (*C*-Hc); 53.3 (2 × COOCH$_3$).

Anal calc for $C_{18}H_{14}O_4S_4$: C, 51.16; H, 3.34; O, 15.14; S, 30.35. Found: C, 51.08; H, 3.35; O, 15.09; S, 30.16.

MS (EI), m/e: calc for $C_{18}H_{14}O_4S_4$: 421.97749, found 421.9753.

• **1ae**, **1bb**, **1be** *and* **1cc**

These π-donors were synthesized using a procedure similar to that for the preparation of **4b** [**1ae** (from aldehyde **4a** and phosphonate anion **7e**), **1bb** (from **4b** and **7b**), **1be** (from **4b** and **7e**), and **1cc** (**4c** and **7c**)].

■ *Dimethyl 2-[4-(1,3-dithiol-2-ylidene)but-2-enylidene]-1,3-dithiole-4,5-dicarboxylate* **1ae**

Yield: 46%. Mp: 138 °C.

^{1}H NMR ($CDCl_3$): 6.62 (s, 2H); 6.33 (d, J_{ab} = 11 Hz, Ha); 6.27 (d, J_{dc} = 11 Hz, Hd); 5.96 (dd, J_{bc} = 14.2 Hz, J_{ba} = 11 Hz, Hb); 5.76 (dd, J_{cb} = 14.2 Hz, J_{cd} = 11 Hz, Hc); 3.80 (s, 6H).

Anal calc for $C_{14}H_{12}O_4S_4$: C, 45.14; H, 3.25; O, 17.18; S, 34.42. Found: C, 45.63; H, 3.16; O, 17.30; S, 33.78.

MS (EI), m/e: calc for $C_{14}H_{12}O_4S_4$: 371.96184, found 371.9615.

■ *2,2′-(But-2-ene-1,4-diylidene)bis-(1,3-benzodithiole)* **1bb**

Yield: 81%. Mp: 254–256 °C.

^{1}H NMR ($CDCl_3$): 7.14 (m, 8H); 6.17 (dd, Ha and Hd); 5.97 (dd, Hb and Hc).

Anal calc for $C_{18}H_{12}S_4$: C, 60.64; H, 3.39; S, 35.97. Found: C, 60.40; H, 3.41; S, 35.94.

MS (EI), m/e: calc for $C_{18}H_{12}S_4$: 355.98219, found 355.9825.

■ *2-[4-(1,3-Dithiol-2-ylidene)but-2-enylidene]-1,3-benzodithiole* **1be**

Yield: 70%. Mp: 158–160 °C.

^{1}H NMR ($CDCl_3$): 7.01–6.92 (m, 4H); 6.05 (s, 2H); 5.93 (m, Ha and Hd); 5.74 (m, Hb and Hc).

Anal calc for $C_{14}H_{10}S_4$: C, 54.86; H, 3.29. Found: C, 54.55; H, 3.64.

MS (EI), m/e: calc for $C_{14}H_{10}S_4$: 305.96654, found 305.9665.

■ *2,2′-(But-2-ene-1,4-diylidene)bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiine)* **1cc**

Yield: 60%. Mp: 228–231 °C (dec).

^{1}H NMR ($CDCl_3$): 5.85 (dd, Ha and Hd); 5.66 (dd, Hb and Hc); 3.08 (s, 8H).

MS (EI), m/e: calc for $C_{14}H_{12}S_8$: 435.87048, found 435.8687.

• **1cd** *and* **1dd**

Compounds **1cd** and **1dd** were synthesized from aldehyde **4d** (5 mmol) and the phosphonate anion **7c** or **7d** respectively (5 mmol), generated with 1.1 equiv of n-BuLi (1.6 M in hexane) at 0 °C. The resulting precipitate was filtered off, washed with methanol and then purified by chromatography over silica gel with CH_2Cl_2/hexane (50:50) as eluent, to produce the desired π-donors as orange powders.

■ *2-[4-(4,5-Dimethyl-1,3-dithiol-2-ylidene)but-2-enylidene]-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiine* **1cd**

Yield: 86%. Mp: 183 °C.

^{1}H NMR ($CDCl_3$): 5.86–5.52 (m, Ha, Hd, Hb and Hc); 3.09 (s, 4H); 1.83 and 1.81 (2s, 6H).

Anal calc for $C_{14}H_{14}S_6$: C, 44.88; H, 3.77; S, 51.35. Found: C, 44.66; H, 3.77; S, 51.22.

MS (EI), m/e: calc for $C_{14}H_{14}S_6$: 373.94198, found 373.9422.

■ *2,2′-(But-2-ene-1,4-diylidene)bis(4,5-dimethyl-1,3-dithiole)* **1dd**

Yield: 75%. Mp: 183 °C.

^{1}H NMR ($CDCl_3$): 5.85 (dd, Ha and Hd); 5.63 (dd, Hb and Hc); 1.94 and 1.92 (12 H).

Anal calc for $C_{14}H_{16}S_4$: C,53.80; H, 5.16. Found: C, 54.07; H, 5.39.

MS (EI), m/e: calc for $C_{14}H_{16}S_4$: 312.01348, found 312.0135.

Dimethyl 2-[6-(1,3-benzodithiol-2-ylidene)hexa-2,4-dienylidene]-1,3-dithiole-4,5-dicarboxylate **2ab**

Compound **2ab** was obtained from aldehyde **9** (2 mmol) and **6a** (2 mmol) using a procedure similar to the preparation of **1aa**.

2ab: Yield: 60%. Mp: 179–181 °C.

IR (KBr): 1 763-1 730-1 691 (CO).

^{1}H NMR ($CDCl_3$): 7.15 (m, 4 × aromatic H); 6.04 (m, 6H ethylenic); 3.85 (s, 6H, CO_2Me).

Anal calc for $C_{20}H_{16}O_4S_4$: C, 53.53; H, 3.59; O, 14.27; S, 28.60. Found: C, 52.83; H, 3.57; O, 13.87; S, 28.16.

Tetramethyl 2,2′-(octa-2,4,6-triene-1,8-diylidene)bis-(1,3-dithiole-4,5-dicarboxylate) **3aa**

A mixture of aldehyde **4a** and 1 mL pyridine in 15 mL dry THF, was added slowly to a suspension of the McMurry's reagent $LiAlH_4(TiCl_3)$ [24] in 20 mL dry THF. The mixture was refluxed for 2 h and was filtered off after cooling. The solvent was evaporated and the solid residue dissolved in 30 mL CH_2Cl_2, washed with water and dried over $MgSO_4$. Compound **3aa** was then purified on a short column of silica gel (CH_2Cl_2) and obtained as a brown powder.

3aa: Yield: 20%. Mp: 218–220 °C.

IR (KBr): 1 747, 1 721, 1 695 (CO).

^{1}H NMR ($CDCl_3$): 6.3–5.9 (m, 8H); 3.84 (s, $COOCH_3$, 12H).

MS (EI), m/e: calc for $C_{22}H_{20}O_8S_4$: 540.00410, found 540.0045.

Crystallographic data for 4-(4,5-dimethyl-1,3-dithiol-2-ylidene)but-2-enal **4d**

The sample (0.12 × 0.45 × 0.50 mm) was studied on an automatic diffractometer CAD4 Enraf-Nonius with graphite-monochromatized Mo$K\alpha$ radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The data collection parameters ($2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range hkl: h 0.7, k 0.14, l 0.26, intensity controls without appreciable decay (0.2%)) gave 1 995 reflections, of which 801 were independent, with $I > 5\sigma(I)$ (table III). After Lorentz and polarization corrections, the structure was solved with direct methods which reveal all the non hydrogen atoms. After isotropic ($R = 0.09$), then anisotropic refinement ($R = 0.075$), the hydrogen atoms were found with a Fourier difference (between 0.39 and 0.19 eÅ^{-3}). The whole structure was refined by the full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for S, C and O atoms and x, y, z for H atoms; 140 variables and 801 observations; $w = 1/\sigma(Fo)^2 = [\sigma^2(I)+(0.04Fo^2)^2]^{-1/2})$ with the resulting $R = 0.045$, $R_w = 0.043$ and $S_w = 1.54$ (residual $\Delta p \leqslant 0.27$ eÅ^{-3}). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a Digital Micro VAX 3100 computer with the Molen package (Enraf-Nonius, 1990).

Table III. Crystallographic data for compound **4d**.

Formula	$C_9H_{10}OS_2$
Mol wt	198.3
Cryst system	Orthorhombic
Space group	*Pbca*
a	7.124(5)
b	12.266(10)
c	22.658(12)
α	–
β	–
γ	–
V	1 980(4)
Z	8
ρ calc g cm^{-3}	1.33
F(000)	832
$\mu(\mathrm{Mo}K\alpha)$ cm^{-1}	4.68
T (K)	294
Crystal size (mm)	0.12 × 0.45 × 0.50
Radiation	Mo$K\alpha$
Max 2θ (°)	50
Scan	$w/2\theta = 1$
$t_{\max}$ (for one measure), s	60
Variance of standards	0.2%
Range of *hkl*	0.7; 0.14; 0.26
Reflections measured	1995
Reflections observed ($I > \sigma(I)$)	801 (5σ)
R_{int} (from merging equiv refl)	–
R (isotropic)	0.09
R (anisotropic)	0.075
Fourier difference	0.39-0.19
N(obs)/N(var)	801/140
Final R	0.045
Rw	0.043
$w = 1/\sigma(Fo)^2 = [\sigma^2(I) + (0.04Fo^2)^2]^{-1/2}$	
Sw	1.54
Max residual e.Å^{-3}, Δ/σ	0.27, 0.8

Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° = SUP 90411 and are available on request from the Document Supply Centre.

Acknowledgments

We are indebted to the CNRS and the Direction de la recherche et des études doctorales (DRED) for their financial support, and the Centre national d'études des télécommunications (CNET) de Bagneux for a grant to TT Nguyen.

References

1 For reviews on TTF chemistry and physical properties, see: a) Garìn J, *Adv Heterocyclic Chem* (1995) 62, 249-304
b) Schukat G, Fanghanel E, *Sulfur Rep* (1993) 14, 245-390
c) Special issue on Molecular Conductors, *J Mater Chem* (1995) 5, 1469-1760
d) Williams JM, Ferraro JR, Thorn RJ, Carlson KD, Geiser U, Wang HH, Kini AM, Wangbo MH, *Organic Superconductors (Including Fullerenes)*, Simon-Schuster, Englewood Cliffs, NJ, 1992

2 A superconducting state has recently been observed for the first time in a conjugated TTF system:
a) Misaki Y, Higuchi N, Fujiwara H, Yamabe T, Mori T, Mori H, Tanaka S, *Angew Chem Int Ed Engl* (1995) 34, 1222-1225
For other exemples of highly extended TTF derivatives, see:
b) Frère P, Belyasmine A, Gouriou Y, Jubault M, Gorgues A, Duguay G, Wood S, Reynolds CD, Bryce MR, *Bull Soc Chim Fr* (1995) 132, 975-984
c) Sallé M, Belyasmine A, Gorgues A, Jubault M, Soyer N, *Tetrahedron Lett* (1991) 32, 2897-2900
d) Bryce MR, Moore AJ, Hason M, Ashwell GJ, Fraser AT, Clegg T, Hursthouse MB, Karoulov AI, *Angew Chem Int Ed Engl* (1990) 29, 1450- 1452
e) Adams M, Buhnen A, Enkelmann V, Müllen K, *Adv Mater* (1991), 3, 600-602
f) Hansen TK, Lakshmikantham MV, Cava MP, Niziurski-Mann RE, Jensen FE, Becher J, *J Am Chem Soc* (1992), 114, 5035-5039

3 a) Khanous A, Gorgues A, Sylla M, Zaremba J, Chevalier R, Rivoire G, *Synth Metals* (1993) 59, 111-121
b) Sahraoui B, Sylla M, Bourdin JP, Rivoire G, Zaremba J, Nguyen TT Sallé M, *J Modern Optics* (1995) 42, 2095-2107
c) Simonsen KB, Bjornholm T, Becher J, Geiser T, Petersen JC, *NATO Advanced Research Workshop*, Hindsgavl, Denmark, May 7-11, 1994

4 Barzoukas M, Blanchard-Desce M, Josse D, Lehn JM, Zyss J, *Chem Phys* (1989) 133, 323

5 McKinnon DM, Buchshriber JM, *Can J Chem* (1971) 49, 3299-3304

6 a) Yoshida ZI, Kawase T, Awaji H, Yoneda S, *Tetrahedron Lett* (1983) 24 3473-3476
b) Sugimoto T, Awaji H, Sugimoto I, Misaki Y, Kawase T, Yoneda S, Yoshida ZI, *Chem Mater* (1989) 1, 535-547

7 Grée R, Tourbah H, Carrié R, *Tetrahedron Lett* (1986) 27, 4983-4986

8 Coppola GM, *Synthesis* (1984) 1021-1023

9 Formolysis has already been used for the obtention of acetylenedicarbaldehyde:
a) Gorgues A, Simon A, Le Coq A, Hercouet A, Corre F, *Tetrahedron* (1986) 42, 351-370
b) Gorgues A, Stephan D, Belyasmine A, Khanous A, Le Coq A, idem (1990) 46, 2817-2826

10 a) Ishikawa K, Akiba K, Inamoto N, *Tetrahedron Lett* (1976) 17, 3695-3698
b) Akiba K, Ishikawa K, Inamoto N, *Synthesis* (1977) 861-862
c) idem, *Bull Chem Soc Jpn* (1978) 51, 2674-2683

11 Compounds **4** have to be isolated rapidly otherwise yields become lower

12 a) Benhamed-Gasmi A, Frère P, Garrigues B, Gorgues A, Jubault M, Carlier R, Texier F, *Tetrahedron Lett* (1992) 33, 6457-6460
b) For a detailed study of the Wittig reaction involving **6**, see: Fabre JM, Giral L, Gouasmia A, Cristau HJ, Ribeill Y, *Bull Soc Chim Fr* (1987) 5, 823-826

13 Cherkaoui H, Martelli J, Grée R, *Tetrahedron Lett* (1991) 32, 7259-7260 and ref cited

14 a) Spangler CW, Mc Coy RK, *Synth Commun* (1988) 18, 51-59
b) Van Eyk SJ, Naarmann H, *Synth Metals* (1993) 58,233-242

15 Mc Murry JE, *Chem Rev* (1989) 89, 1513-1524

16 For the synthesis of vinylogues of TTF ($n = 0$), see ref [6] and the following papers:
a) Khodorkovsky VY, Veselova LN, Neiland OY, *Khim Getero Soedin*, (1990) 1, 130-131
b) Moore AJ, Bryce MR, Ando DJ, Hursthouse MB, *J Chem Soc, Chem Commun* (1991)320-321
c) Hansen TK, Lakshmikantham MV, Cava MP, Becher

J, *J Chem Soc, Perkin Trans I* (1991) 2873-2875
d) Hansen TK, Lakshmikantham MV, Cava MP, Metzger RM, Becher J, *J Org Chem* (1991) 56, 2720-2722
e) Bryce MR, Coffin MA, Clegg W, *J Org Chem* (1992) 57, 1696-1699

17 Jaffé HH, Orchin M, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962

18 Lichtenberger DL, Johnston RL, Hinkelmann K, Suzuki T, Wudl F, *J Am Chem Soc* (1990) 112, 3302-3307

19 Deuchert K, Hünig S, *Angew Chem, Int Ed Engl* (1978) 17, 875-886

20 Bard AJ, Faulkner LR, *Electrochimie, Principes, Méthodes et Applications*, Masson, Paris, 1983, pp 259-263

21 Nguyen TT, Sallé M, Gorgues A, Ledoux I, in preparation

22 Orduna J, Garin J, Frère P, Nguyen TT, Gorgues A, Sanchez A, Martin N, Seoane C, *Rapid Commun Mass Spectrom* (1995) 9, 856

23 Sato M, Gonnella NC, Cava MP, *J Org Chem* (1979) 44, 930

24 Dang Y, Geise HJ, *Janssen Chim Act* (1988) 6, 3