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LETTERS

New extended analogues of TTF via triethylphosphite-mediated reaction

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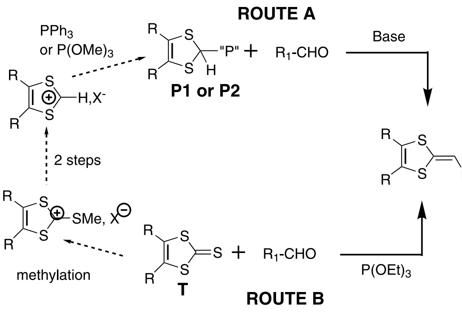
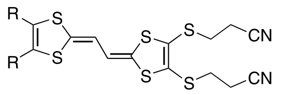
Abstract—New extended derivatives of TTF bearing cyanoethylsulfanyl or furan groups which cannot be obtained by Wittig-type reaction with Akiba's reagent have been synthesized using a clean, cheap-step and rapid methodology; their electrochemical and optical behavior are studied. © 2003 Elsevier Science Ltd. All rights reserved.

Linearly extended tetrathiafulvalene analogs, built by insertion of a π-conjugated system between two 1,3-dithiole cycles represent a topic of great interest in the field of molecular conductors, small band gap molecular semi-conductors and nonlinear optics.[1]

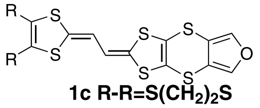
These compounds are generally obtained by Wittig or Wittig–Horner olefinations (Route A) of a conjugated core end capped by aldehyde groups with phosphonium salts **P1** or phosphonates **P2** bearing the 4,5-disubstituted-1,3-dithiol-2-ylidene moiety (Akiba's reagent). However, despite its efficiency, this strategy presents some inherent limitations as the functional groups grafted on the dithiole cycle do not allow either the basic conditions necessary for the condensations or the formation of the Akiba's reagents. The phosphorus reagents are classically obtained in four steps starting from corresponding 2-thioxo-1,3-dithioles **T** following the methodology described in Scheme 1 (dotted arrows). Indeed, cyanoethylsulfanyl groups grafted on dithiole rings can be rapidly removed in mild basic conditions leading to thiolate anion and acrylonitrile.[2] This protecting thiolato group has largely been used in TTF chemistry for developing macrocycles or crown ether TTF.[3] Thus, phosphonium salt bearing cyanoethylsulfanyl groups was recently described.[4] As already known in literature for other functionalized salts,[5] this one was condensed onto dithiolium salts in presence of weak base as triethylamine. Nevertheless, its reactivity in presence of strong base prevented the formation of extended TTFs by Wittig reaction. On the other hand, 2-thioxo-1,3-dithiole **T** bearing a furan core did not allow the obtention of corresponding phosphorus reagents due to their instability in presence of strong methylating reagents.[6]



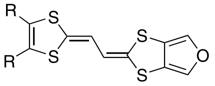
Scheme 1. Synthesis of extended TTFs.



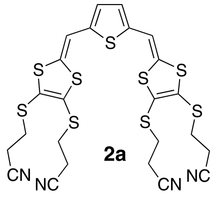
1a R-R=S(CH$_2$)$_2$S
1b R=SMe



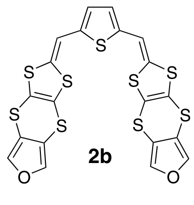
1c R-R=S(CH$_2$)$_2$S
1d R=SMe
1e R-R=(CH=CH)$_2$



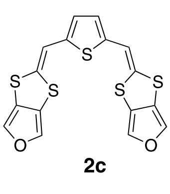
1f R-R=(CH=CH)$_2$



2a



2b



2c

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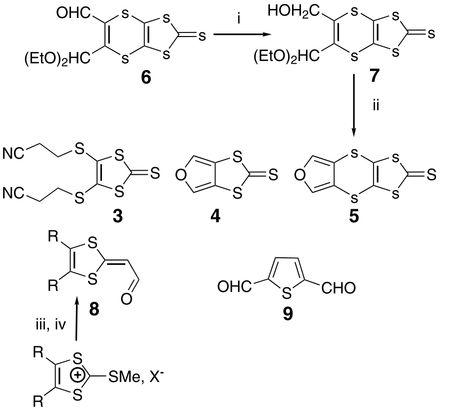
A possible alternative could consist in a direct $P(OEt)_3$ mediated coupling between **T** and aldehyde groups (route B),[7] thus avoiding the use of Akiba's reagents. In the frame of our current interest on extended TTFs, we have considered the synthesis of TTF vinylogues **1** and hybrid thiophene-TTF **2** substituted by cyanoethylsulfanyl groups or furan cores by coupling of 2-thioxo-1,3-dithiole **3**, **4** and **5** with aldehyde **8** or 2,5-thiophenedicarbaldehyde **9**.

Starting 2-thioxo-1,3-dithioles are synthesized as described in the literature[6,8] except **5** (Scheme 2) which is obtained as follows. The reduction by $NaBH_4$ of derivative **6**,[9] obtained by cycloaddition of oligo (2,4,5-trithioxo-1,3-dithiole)[10] onto monoacetal of ADCA,[11] led to alcohol **7**. Treatment of **7** by acid amberlyst resin in methylenechloride afforded the dithiolethione **5** in 81% yield for the two steps. The synthesis of aldehydes **8** is generally achieved by Wittig–Horner reaction between an Akiba's reagent and the monoacetal of glyoxal followed by an hydrolysis.[12] A more rapid methodology, flabbergastedly very poorly used involves the successive addition of iodine and triethylamine onto a dithiolium salt dissolved in acetonitrile (Scheme 2).[13] Hydrolysis of the diethylimmonium salt obtained led to aldehyde **8** in good to quantitative yields.

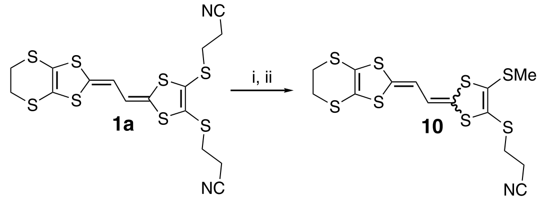
Finally, reagents 2-thioxo-1,3-dithioles **3–5** in one part, aldehydes **8** and **9** on the other part, introduced in stoichiometric amount were refluxed in toluene in the presence of $P(OEt)_3$ until disappearance of starting materials.† The reactions were never conducted longer than two hours after which decomposition of derivatives was observed. The symmetrical coupling of 2-thioxo-1,3-dithiole was never observed, hence demonstrating the great electrophilic reactivity of aldehydes. Derivatives **1a–f** and **2a–c** were stored without particular precaution and gave satisfactory spectroscopic data.[14]

The generation of a thiolate anion of **1a** has been achieved by treatment with 1 equivalent of $CsOH,H_2O$ in degassed DMF followed by addition of iodomethane (Scheme 3). Compound **10** was isolated as a 1/1 mixture of isomers. Additionally, successive additions of an excess of base and methylating agent onto **1a** or **2a** led to the corresponding methylsulfanyl derivatives in quantitative yields.[15]

Electrochemical and optical properties of new extended TTFs are gathered in Table 1.



Scheme 2. *Reagents*: (i) $NaBH_4$, CH_2Cl_2, MeOH; (ii) amberlyst ion exchange resin, CH_2Cl_2; (iii) I_2, NEt_3, CH_3CN; (iv) H_2O.



Scheme 3. *Reagents*: (i): CsOH, H_2O, DMF, MeOH; (ii): MeI.

Table 1. Electrochemical[a] and UV-visible spectroscopic[b] data

Entry	Yield	E°_1	E°_2	ΔE	λ_{max}	λ_{0-0}
1a	70	0.40	0.62	0.22	403	423
1b	75	0.40	0.58	0.18	400	413
1c[c]	65	0.37	0.59	0.22	408	430
1d[c]	60	0.39	0.58	0.19	403	422
1e	50	0.43	0.66	0.23	397	414
1f	20	0.54	0.80	0.26	368	387
2a	60	0.50	0.62	0.12	433	452
2b	65	0.46	0.61	0.15	443	459
2c	35	0.58	0.72	0.14	407	429
10	85	0.37	0.56	0.19	404	422
BEDTTTF	–	0.51	0.92	0.41	–	–

[a] 10^{-3} mol L^{-1} in t-Bu_4NPF_6 (0.1 mol L^{-1}) CH_2Cl_2, scan rate 200 $mV \cdot s^{-1}$ versus Ag, AgCl (0.1 mol L^{-1}), determinate from deconvoluted voltammogram.

[b] 10^{-5} $mol \cdot L^{-1}$ in CH_2Cl_2.

[c] CV experiments were recorded with saturated solutions.

All electronic spectra of compounds **1** and **2** present two main absorption bands namely λ_{max} and λ_{0-0}. These well-resolved fine structures are characteristic of rigid extended systems. The rigidification of compounds **2** is enhanced by intramolecular S---S interactions between the central thiophene rings and the end-capped 1,3-dithiole cycles.[16]

The cyclic voltammograms (CV) of compounds **1** and **2** exhibit two reversible one-electron oxidation waves corresponding to the successive generation of the cation radical and the dication. Values of redox potentials

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† Typical procedure for coupling reactions involved 0.1 mmol of each derivative, **3–5** on one part, **8–9** on the other part. The mixture was refluxed in 1 mL of toluene until dissolution and 2 mL of triethylphosphite were then added. Extended TTFs **1** and **2** were generally isolated by filtration after addition of petroleum ether. Flash chromatography on florisil was necessary in some cases. All derivatives were isolated in yields varying from 20 to 85% as indicated in Table 1. It can be noted that the yields for derivatives **1f** and **2c** are lower due to the low reactivity of **4**.

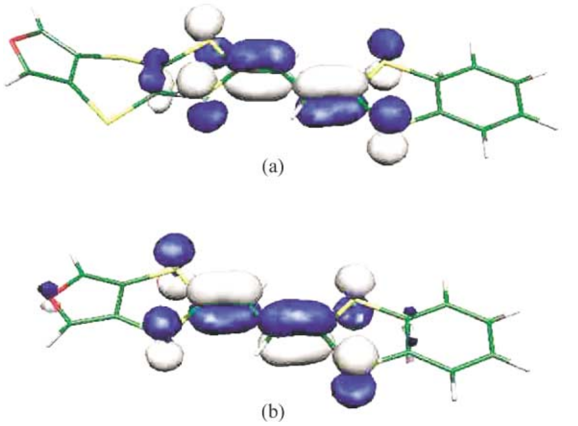

Figure 1. Optimised geometric structures and HOMO orbitals for **1e** (a) and **1f** (b).

show a marked dependence on the nature of the spacer and of the substituents R grafted on the dithiole cycles. Compounds **1a**–**d** and **2a**–**b**, substituted by four S–R groups, present both lower values of the first oxidation potentials E_1° and smaller difference $\Delta E = E_2^\circ - E_1^\circ$ than those of parent TTFs such as bisethylenedithio–TTF (BEDT–TTF). As expected for extended TTF, the enhancement of the π-donor ability is indicative of the best stability of the cation radical due to the delocalization of the charge along the conjugated chain. On the other hand, the formation of the dication is facilitated by the possible migration of the two charges away from each other. Thus, the lengthening of the conjugated system allows to decrease the Coulombic repulsion leading to the strong reduction of ΔE.

Comparison of the data of **1e** and **1f** or **2b** and **2c** shows that the insertion of sulfur atoms between the furan and dithiole rings provokes the decrease of the values of oxidation potential E_1° of about 100 mV. In order to investigate the influence of the external sulfur atom on the electronic properties of extended TTF, theoretical calculations at the ab initio density of functional level with the Gaussian 98 package[17] were performed on **1e** and **1f**. The optimized geometric structures[18] and the HOMO orbitals of **1e** and **1f** are presented in Figure 1. Although compound **1f** is fully planar, the furan ring of **1e** is not in the plane described by the dithiole rings. For both molecules, the biggest HOMO coefficients are mainly located on the central extended (S2C=C–C=CS2) fragment, hence showing the strong influence of the conjugated spacer on the electronic properties of extended TTFs. As shown in Figure 1, the more noticeable difference between the two compounds concerns the coefficients of the outer carbons of the dithiole ring on which the furan cores are grafted (directly or via the sulfur atoms). Although no contribution of these atoms undergoes for **1f**, a significant contribution of those appeared in the HOMO for **1e**. The role of the outer sulfur atoms is to provide an additional energy rising up the HOMO, hence leading to the enhancement of the π-donors ability.

In summary, several new extended analogues of TTF have been isolated using a phosphite-mediated coupling methodology. Due to the high versatility of the cyanoethylsulfanyl group, derivatives **1a**–**b** and **2a** are key intermediates for the syntheses of new original extended TTF. Moreover, with respect to TTF analogues which recently led to metallic salts in $[Ni(tmdt)_2]$,[19] the extended dithiolato TTF could be used as ligand with a large variety of metals.

Acknowledgements

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14. Selected data for derivative:
1a: brown solid, m.p. (decomp) 140°C; ^{1}H NMR (CDCl$_3$): 5.82 (d, 2H, $^3J = 11$ Hz); 5.75 (d, 2H, $^3J = 11$ Hz); 3.30 (s, 4H); 3.06 (m, 4H); 2.77 (m, 4H); MALDI-TOF: M$^+$ calcd. 489.9 found 489.9 for $C_{16}H_{14}S_8N_2$;
1e: green solid, m.p. 209°C; ^{1}H NMR (DMSO): 7.3 (s, 2H); 7.20 (m, 2H); 7.08 (m, 2H); 5.94 (d, 1H, $^3J = 11$ Hz); 5.91 (d, 1H, $^3J = 11$ Hz); MALDI-TOF: M$^+$ calcd. 407.9, found 407.8 for $C_{16}H_8S_6O$;
1f: grey solid, m.p. 248°C; ^{1}H NMR (CS$_2$, CDCl$_3$): 7.2–7.1 (m, 3H); 7.1–7.05 (m, 3H); 5.99 (d, 1H, $^3J = 11$ Hz); 5.96 (d, 1H, $^3J = 11$ Hz); HRMS (EI+): Calcd. 319.9458; found 319.9451 for $C_{14}H_8S_4O$;
2a: yellow solid, ^{1}H NMR (CDCl$_3$): 6.82 (s, 2H); 6.67 (s, 2H); 3.11 (3, 8H); 2.78 (m, 8H); HRMS (EI+): Calcd. 651.9174; found 651.9178 for $C_{24}H_{20}N_4S_9$;
2b: brown solid, m.p. (decomp) 198°C; ^{1}H NMR (DMSO, 313K): 7.90 (s, 4H); 7.10 (s, 2H); 6.96 (s, 2H); MALDI-TOF: M$^+$ calcd. 567.8, found 567.6 for $C_{20}H_8S_9O_2$;
2c: brown solid, m.p. 205°C; ^{1}H NMR (DMSO, 313K): 7.75 (s, 2H); 7.65 (s, 2H); 7.08 (s, 2H); 7.02 (s, 2H); MALDI-TOF: M$^{+\bullet}$ calcd. 391.9, found 391.9 for $C_{16}H_8S_5O_2$.

15. (a) for derivatives **1**, see Moore, A. J.; Bryce, M. R. *Tetrahedron Lett.* **1992**, *33*, 1783–1786; (b) for derivatives **2**, see Benahmed-Gasmi, A.; Frère, P.; Garrigues, B.; Gorgues, A.; Jubault, M.; Carlier, R.; Texier, F. *Tetrahedron Lett.* **1992**, *33*, 6457-6460.
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