Novel highly extended and sulfur rich tetrathiafulvalene (TTF) derivatives through an unprecedented TTF core building process

C. Boulle,[a,b] **O. Desmars,**[b] **N. Gautier,**[b] **P. Hudhomme,***[a,b]† **M. Cariou**[a] **and A. Gorgues***[a]

[a] *Ingénierie Moléculaire et Matériaux Organiques, UMR-CNRS 6501, 2 Boulevard Lavoisier, 49045 Angers Cedex, France*
[b] *Laboratoire de Synthèse Organique, UMR-CNRS 6513, 2 rue de la Houssinière, 44322 Nantes Cedex 03, France*

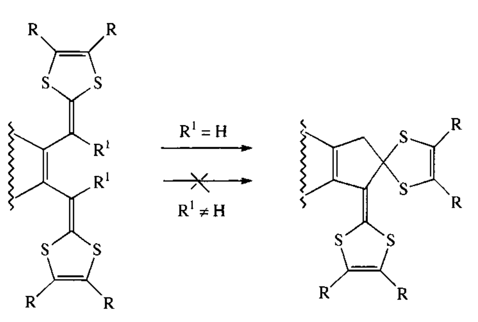
A new and unexpected tetrathiafulvalene (TTF) core building process is observed *via* reaction of a 1,3-dithiole phosphonate anion with a 2-oxo-1,3-dithiole functionality.

Since their discovery, the transport properties of the charge-transfer salts related to the TTF series have been improved.[1] In particular, chemical modifications[2] of the donor have allowed enhancement of the dimensionality of the related materials, thus preventing metal-to-insulator transitions (Peierls distorsions). With this aim, space extended and sulfur-rich analogs of TTF as the donors constitute very good candidates.[3] Thus, bis(1,4-dithiafulven-6-yl)TTFs were found able to afford interesting 2D electroconductive materials thanks to intermolecular intra- and inter-chain S···S contacts. Unfortunately, under acidic or oxidative conditions, these donors may undergo unwanted internal cyclization reactions when R^1 = H (Scheme 1).[4]

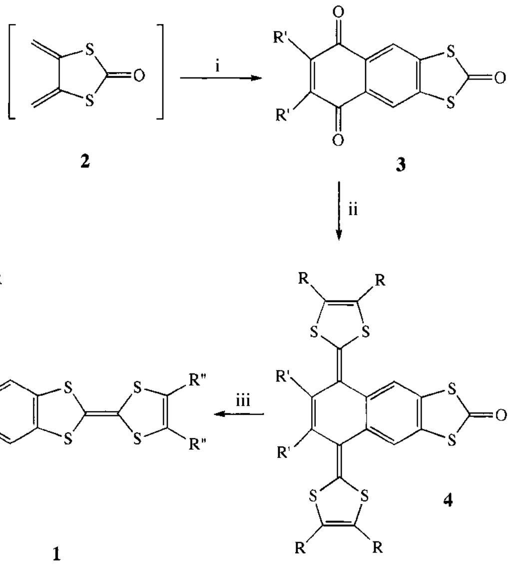
Following our efforts to suppress such side reactions, which have a spoiling effect during the slow electrooxidation process,[3c,d] we have designed new donors **1** related to benzoTTF, bearing no hydrogen atom in the R^1 position, in which the 1,3-dithiol-2-ylidene moieties are connected *via* the R^1–R^1 vinylene substituent. We report here on their straightforward synthesis and on their electrochemical properties.

As outlined in Scheme 2, our synthetic strategy was based on three main steps: (i) a Diels–Alder cycloaddition between 2-oxo-4,5-bis(methylene)-1,3-dithiole **2** and paraquinonic dienophiles with further aromatization of the cycloadduct, (ii) a bis-Horner–Wadsworth–Emmons olefination of the quinonic carbonyl functionalities of **3** with Akiba's reagents,[5] and (iii) a final coupling reaction of the resulting compound **4** with 2-(thi)oxo-1,3-dithioles.

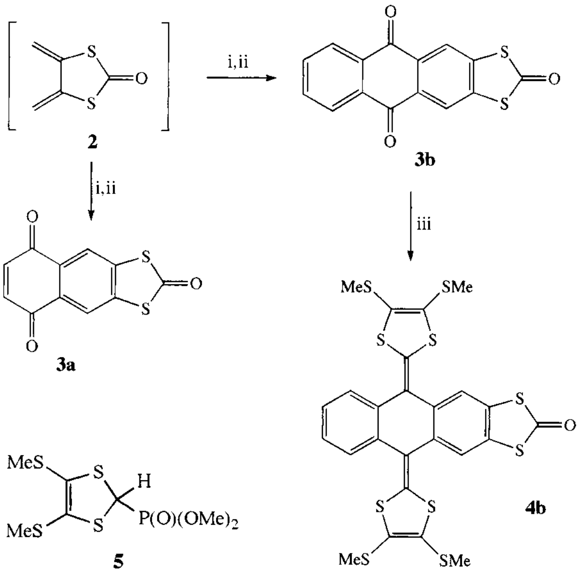
Thus, in the first step, diene **2** was generated *via* two independent routes,[6] either by an annulating reaction involving the thermal decomposition of *S*-propargyl xanthate[7] (Route **A**), or by an iodide induced reductive elimination on 2-oxo-4,5-bis(bromomethyl)-1,3-dithiole[8] (Route **B**). This diene was trapped with a quinone (*p*-benzoquinone or 1,4-naphthoquinone) and further addition of DDQ[9] to perform the aromatization, furnished the corresponding target compounds **3a** and **3b** (Scheme 3).



Scheme 1

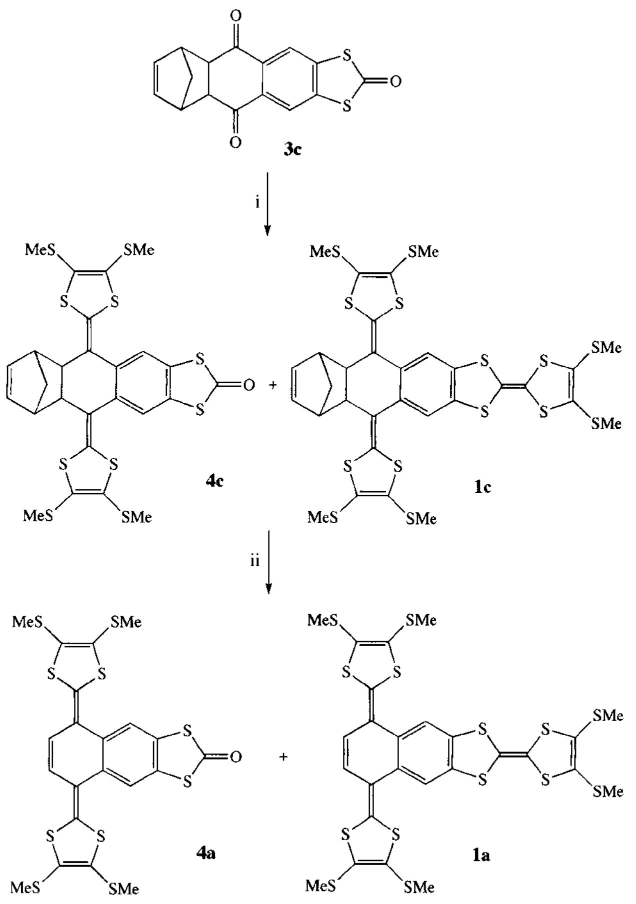


Scheme 2 *Reagents and conditions*: i, Diels–Alder cycloaddition with further aromatization; ii, bis-Horner–Wadsworth–Emmons olefination; iii, coupling reaction



Scheme 3 *Reagents and conditions*: (Route **A**): i, reflux, chlorobenzene, *p*-benzoquinone or 1,4-naphthoquinone; ii, DDQ (**3a**: 30%, **3b**: 46%); (Route **B**): i, $Et_4N^+I^-$, MeCN, *p*-benzoquinone or 1,4-naphthoquinone; ii, DDQ (**3a**: 83%, **3b**: 54%); iii, **5**, BuLi, THF, −78 °C

For the second step, we checked the behaviour of **3a** and **3b** with the anion of **5** generated upon treatment of the corresponding phosphonate with BuLi in THF at −78 °C. From **3a**, the olefination was unsuccessful, this failure being interpreted as resulting from an electron transfer between the quinonic compound acting as the π-acceptor (Ep^1_{red} = −0.56 V *vs.* SCE)[10] and the phosphonate anion acting as the donor.[3d] From



Scheme 4 *Reagents and conditions*: i, **5**, BuLi, THF, −78 °C; ii, thermal treatment

the less oxidizing compound **3b** (Ep^1_{red} = −0.84 V *vs.* SCE), upon treatment with a large excess of the anion of **5**, the bis-olefinated product **4b** could be isolated in 28% yield after silica gel column chromatography (hexane–CH_2Cl_2 1 : 1).

In order to perform the required olefination of **3a**, we decided to suppress the accepting quinonic character thanks to a prior Diels–Alder cycloaddition of cyclopentadiene, this latter being possibly subsequently removed (Yamashita's methodology[11]). Thus, cyclic voltammetry confirmed that the corresponding cycloadduct **3c** is a poor π-acceptor (Ep^1_{red} = −1.42 V *vs.* SCE). Unexpectedly, after reaction of **3c** (0.33 mmol) with a large excess of the anion of **5** (1.98 mmol) in THF (35 ml) and silica gel column chromatography (CS_2–CH_2Cl_2 8 : 1), we observed that the bis-olefinated compound **4c** appearing as the main product (50% yield) was accompanied by the tris-olefinated compound **1c** (25% yield), this latter corresponding to a TTF core building through an unprecedented Horner–Wadsworth–Emmons olefination of the 2-oxo-1,3-dithiole functionality with Akiba's reagent (Scheme 4). We also noted the partial decomposition of the phosphonate anion of **5** to tetrakis(methylsulfanyl)TTF and elimination of dimethyl phosphite.[12] The yield of **1c** was increased to 43% by using 10 equiv. of Akiba's reagent and BuLi. Cyclic voltammetry of **1c** exhibited an irreversible process, suggesting the possible loss of cyclopentadiene which obviously could be induced electrochemically. Nevertheless, this reaction was more readily performed by classical thermal treatment of **1c** in *o*-dichlorobenzene or, directly, in the dry state, in a Kugelrohr apparatus[13] in quantitative yield.

Cyclic voltammetry of **1a** exhibited three reversible oxidation peaks (Table 1), the first one corresponding to a $2e^-$ process arising from the π-extended *p*-quinodimethane analog of TTF (by analogy with the voltammogram of **4a** and similar observations on such conjugated quinonic systems[3g,11a]) followed by two $1e^-$ oxidation peaks related to the TTF moiety. These features are in agreement with the sequence: $\mathbf{1a} \rightleftharpoons \mathbf{1a}^{2+} \rightleftharpoons \mathbf{1a}^{3+\cdot} \rightleftharpoons \mathbf{1a}^{4+}$.

Table 1 Cyclic voltammetry of compounds **1a** and **4a**[a]

	E/V *vs.* SCE					
	In CH_2Cl_2			In *o*-dichlorobenze		
	E_{ox}^1	E_{ox}^2	E_{ox}^3	E_{ox}^1	E_{ox}^2	E_{ox}^3
1a	0.27	0.71	1.12	0.39	0.76	1.15
4a	0.28			0.49		

[a] 1.5 mM in solvent–Bu_4NPF_6 (0.1 M), v = 100 mV s^{-1}.

Given the good π-donor ability of **1a**, efforts are now in progress to generalize this methodology to the synthesis of varied compounds **1** and formation of their corresponding cation radical salts.

Notes and References

† E-mail: pietrick.hudhomme@univ-angers.fr

‡ All new compounds gave satisfactory spectroscopic data. *Selected data* for **1a**: δ_H(o-$C_6D_4Cl_2$) 2.51 (s, 18H, SMe), 7.14 (s, 2H, CH quinone), 7.40 (s, 2H, CH arom) (Calc: C, 39.86; H, 2.83. Found: C, 39.05; H, 2.85%). For **4a**: δ_H($CDCl_3$) 2.45 (s, 12H, SMe). 6.32 (br s, 2H, CH quinone), 7.71 (s, 2H, CH arom); *m/z* (EI) 604 (M^+, 1%), 94 (100). For **1c**: δ_H($CDCl_3$) 1.54 (s, 2H, CH_2), 2.36 (s, 6H, SMe), 2.44 (s, 6H, SMe), 2.45 (s, 6H, SMe), 3.03 (br s, 2H, CH), 3.35 (br s, 2H, CH), 5.43 (t, *J* 1.7, 2H, HC=CH), 7.09 (s, 2H, CH arom); *m/z* [FAB (+, m-NBA)] 848 (M^+, 36%), 782 (100), 632 (28).

1 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M. H. Whangbo, *Organic Superconductors (including fullerenes)*, Prentice Hall, Englewood Cliffs, New Jersey, 1992; *Organic conductors. Fundamentals and Applications*, ed. J. P. Farges, Marcel Dekker, New York, 1994; M. R. Bryce, *J. Mater. Chem.*, 1995, **5**, 1481.

2 G. Schukat and E. Fanghänel, *Sulfur Rep.*, 1993, **14**, 245; J. Garín, *Adv. Heterocycl. Chem.*, 1995, **62**, 249 and references cited therein.

3 (*a*) M. Sallé, M. Jubault, A. Gorgues, K. Boubekeur, M. Fourmigué, P. Batail and E. Canadell, *Chem. Mater.*, 1993, **5**, 1196; (*b*) A. Gorgues, M. Jubault, A. Belyasmine, M. Sallé, P. Frère, V. Morisson and Y. Gouriou, *Phosphorus Sulfur Silicon*, 1994, **95–96**, 235; (*c*) P. Leriche, A. Belyasmine, M. Sallé, A. Gorgues, M. Jubault, J. Garín and J. Orduna, *Tetrahedron Lett.*, 1997, **38**, 1399; (*d*) A. Gorgues, M. Sallé, P. Hudhomme, P. Leriche, C. Boulle, C. Durand, F. Le Derf, M. Cariou, M. Jubault and P. Blanchard, *Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets*, ed. J. Veciana and C. Rovira, NATO ASI Series, Kluwer, Dordrecht, 1998, in the press. For other highly extended and sulfur rich π-donors see, for example: (*e*) T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki, T. Kawase, S. Yoneda and Z. I. Yoshida, *Chem. Mater.*, 1989, **1**, 535; (*f*) Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1222; (*g*) N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela and R. Viruela, *J. Org. Chem.*, 1998, **63**, 1268.

4 A. Benhamed-Gasmi, P. Frère, A. Belyasmine, K. M. A. Malik, M. B. Hursthouse, A. J. Moore, M. R. Bryce, M. Jubault and A. Gorgues, *Tetrahedron Lett.*, 1993, **34**, 2131.

5 K. Akiba, K. Ishikawa and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2674; A. J. Moore and M. R. Bryce, *Synthesis*, 1991, **26.**

6 C. Boulle, M. Cariou, M. Bainville, A. Gorgues, P. Hudhomme, J. Orduna and J. Garín, *Tetrahedron Lett.*, 1997, **38**, 81.

7 J. Boivin, C. Tailhan and S. Z. Zard, *Tetrahedron Lett.*, 1992, **33**, 7853.

8 R. M. Renner and G. R. Burns, *Tetrahedron Lett.*, 1994, **35**, 269.

9 D. Walker and R. G. Harvey, *Chem. Rev.*, 1967, 153; P. P. Fu and R. G. Harvey, *Chem. Rev.*, 1978, 317.

10 Conditions of cyclic voltammetry: 1.5 mM in CH_2Cl_2–$Bu^n_4NPF_6$ (0.1 M), v = 100 mV s^{-1}, Ep_{red} in V *vs.* SCE.

11 (*a*) Y. Yamashita, T. Suzuki and T. Miyashi, *Chem. Lett.*, 1989, 1607; (*b*) K. Saito, C. Sugiura, E. Tanimoto, K. Saito and Y. Yamashita, *Heterocycles*, 1994, **38**, 2153.

12 E. D. Bergmann and A. Solomonovici, *Synthesis*, 1970, 183.

13 A. Merz and M. Rauschel, *Synthesis*, 1993, 797.

Received in Liverpool, UK, 20th July 1998; 8/05653F