

# A simple route to novel functionalized tetrathiafulvalene vinyllogues

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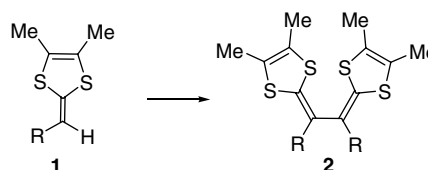
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**Abstract**—The synthesis and X-ray structural determination of vinylogous tetrathiafulvalenes (TTFV) bearing functional groups on the central conjugation are reported. An unexpected evolution of the bis hydroxymethyl TTFV leading to a derivative, which acts simultaneously as a diene and a dienophile in a Diels–Alder reaction is also described.  
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Several molecular devices (switches, motors, sensors, etc.) can be envisioned with molecules exhibiting molecular movements powered by various energies: chemical, electrochemical, light, etc.<sup>1</sup> In that respect, vinylogous tetrathiafulvalenes (TTFV) **2**, especially those bearing various substituents (R) on the central conjugation, are of particular interest due to their ability to exhibit important structural changes upon electron transfer.<sup>2–5</sup> Interestingly, the donor ability of the TTFV is not modified by the presence of bulky R substituents even if, due to steric interactions, the donor is not planar.<sup>6</sup> The presence of methyl groups is also sufficient to prevent the donor to be planar.<sup>3</sup> Upon electron transfer, a stretch movement is observed inducing the formation of a planar oxidized TTFV core with the R substituents now located in perpendicular planes.<sup>2–4,6,7</sup> The oxidative chemical or electrochemical coupling of 1,4-dithiafulvenes **1** allows for an easy access to TTFV with various substituents (R) on the central conjugation.<sup>2–8</sup> Most of the TTFV prepared so far via this route are substituted on the central conjugation by bulky substituents such as aromatic ones. Having in mind to bring functional groups closer to the redox active core, we investigated the synthesis of substituted 1,4-dithiafulvenes **1** with R = CO<sub>2</sub>Et, CN and COMe and studied the oxidative coupling of these derivatives in the presence of various oxidizing agents, opening an access to a series of new TTFV **2** containing functional groups on the central

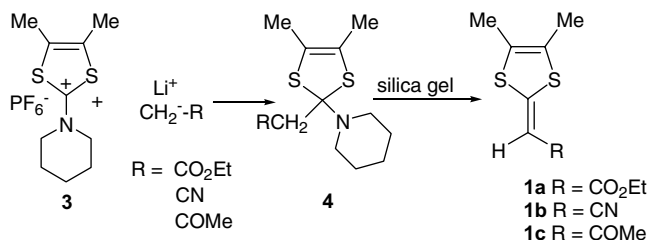
unsaturation. Their electrochemical properties and structural characterizations are also presented. Moreover, we report an original Diels–Alder reaction, which occurred unexpectedly starting from the bis(hydroxymethyl)TTFV (R = CH<sub>2</sub>OH).



The principal pathway used for the synthesis of 1,4-dithiafulvenes **1** consists into a Wittig or Horner–Emmons reaction involving the reaction of a dithiole phosphonium salt or dithiole phosphonate in basic medium with various aldehydes. Using this methodology, mainly aromatic substituted 1,4-dithiafulvenes **1** have been prepared.<sup>2–8</sup> Herein, we present a simple and rapid synthesis of functionalized dithiafulvenes **1**, starting from 1,3-dithiolium cation as outlined in Scheme 1. Indeed, 1,3-dithiolium cations with a leaving group linked to the C-2 atom are known to react with various nucleophiles such as amines or carbanions.<sup>9</sup> The carbanions generated from acetonitrile, ethyl acetate or acetone in the presence of LDA react with the 4,5-dimethyl-2-piperidin-1-yl-1,3-dithiol-2-ylum hexafluorophosphate **3** to afford the adducts **4a–c**. These intermediates can be either isolated or directly transformed into dithiafulvenes **1a–c** in acidic medium. The piperidino leaving group can also be simply removed by chromatography of the reaction mixture on silica gel, which is acidic enough to convert the intermediate **4** into **1**.

**Keywords:** Dithiafulvene; Tetrathiafulvalene; Oxidative coupling; Diels–Alder.

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Scheme 1.

Using this procedure, molecules **1a–c** bearing, respectively, an ester, nitrile or acetyl moiety have been prepared. The redox behaviour of the dithiafulvenes **1** has been studied by cyclic voltammetry. On the first anodic scan, one irreversible oxidation peak is observed corresponding to the oxidation of the dithiafulvene into the cation radical and upon recurrent scans, a reversible ox-

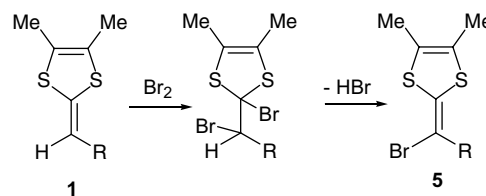
idation peak appears at a lower potential. This reversible system is attributed to the vinylogous TTF **2** formed in the medium by oxidative coupling.<sup>10</sup> All the dithiafulvenes **1** and the corresponding TTFV **2** exhibit high oxidation potentials due to the functionalization of the redox active core with electron withdrawing substituents (Table 1). For instance, a positive shift of 470 mV is observed when going from **2a** ( $\text{R} = \text{CO}_2\text{Et}$ ) to **2e** ( $\text{R} = \text{Me}$ ). The observation of one single two-electrons oxidation wave in **2a** and **2c** indicates the occurrence of potentials inversion, a phenomenon already observed in similar hindered TTFV and attributed to important molecular rearrangements upon oxidation.<sup>5</sup> On the other hand, the less distorted structure of the neutral **2b** ( $\text{R} = \text{CN}$ , see below) is coherent with two one-electron oxidation waves.

In order to prepare quantitatively the TTFV, we realized a comparative study of the chemical oxidative

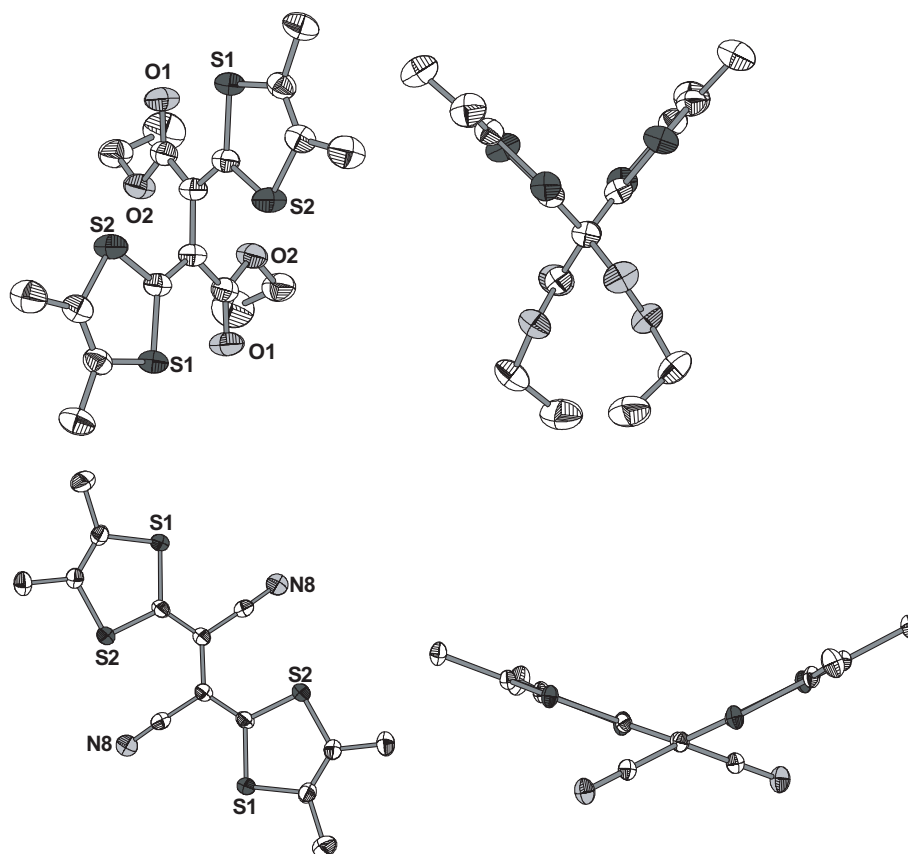
**Table 1.** Cyclic voltammetry data,  $E$  in  $V$  versus SCE, Pt working electrode with 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  scanning rate 100 mV/s in  $\text{CH}_2\text{Cl}_2$

	R	1: $E_{\text{pa}}$	2: $E$ ( $E_{\text{pa}} - E_{\text{pc}}$ )mV
<b>a</b>	$\text{CO}_2\text{Et}$	1.06 <sup>a</sup>	0.78 (60)
<b>b</b>	CN	1.22 <sup>a</sup>	0.85 (60) 0.98 (70)
<b>c</b>	COMe	1.04 <sup>a</sup>	0.97 <sup>a</sup>
<b>d</b>	$\text{CH}_2\text{OH}$	—	0.36 <sup>a</sup>
<b>e</b>	Me	—	0.31 (70)

<sup>a</sup> Irreversible.



Scheme 2.



**Figure 1.** Crystal structure of **2a** (top) and **2b** (bottom), showing the atom labelling (left) viewed along the central C–C axis (right).

coupling in the presence of various oxidizing agents. For that purpose, we chose iodine,<sup>11</sup> tris(4-bromophenyl)aminium hexachloroantimonate,  $(\text{BrC}_6\text{H}_4)_3\text{N-SbCl}_6$ ,<sup>3,6c,7b,c</sup>  $\text{AgBF}_4$ <sup>12</sup> and bromine.<sup>13</sup> The dithiafulvene **1** is first reacted with the oxidizing agent in a 1:1 mixture and then the highly coloured solution of the dicationic species is reduced either with zinc powder or with  $\text{Na}_2\text{S}_2\text{O}_4$ . Work up of the reaction leads to the neutral TTFV **2a–c**.<sup>14</sup> The efficiency of the reactants towards the oxidation of **1a–b** and the formation the TTFV **2a–b** is as follows:  $\text{AgBF}_4 > \text{I}_2 > (\text{BrC}_6\text{H}_4)_3\text{NSbCl}_6 > \text{Br}_2$ . The use of  $\text{AgBF}_4$  allowed us to isolate **2a–b** in the highest yields (50%) while the oxidation of the dithiafulvenes **1a–c** with bromine affords **2a–c** in lower yield (10%) together with another product **5**. Indeed, despite a reduction potential for  $\text{Br}_2$  higher than for  $\text{I}_2$ , this reagent gives rise to the corresponding electrophilic addition over the double bond (Scheme 2), in competition with the oxidative coupling. In the case of **1c**, the formation of **2c** was not observed using either  $\text{AgBF}_4$  or  $\text{I}_2$  as the oxidizing agent.

Single crystals of TTFV **2a** ( $\text{R} = \text{CO}_2\text{Et}$ )<sup>15</sup> and **2b** ( $\text{R} = \text{CN}$ )<sup>15</sup> have been isolated by slow evaporation of dichloromethane solutions. As shown in Figure 1, X-ray structure analyses reveal that both donors adopt a non-planar geometry similar to other substituted TTFV analogues.<sup>3–6</sup> The steric influence of the substituent can be viewed in Figure 1 where the molecules **2a** and **2b** are shown along the central C–C axis. The TTFV **2b**, with the cyano groups, presents the less constrained geometry. The acute dihedral angles based on this central C–C bond and the two dithiole rings amount to  $77^\circ$  and  $134^\circ$  for **2a** and **2b**, respectively.

We also investigated the formation of the bis(hydroxymethyl) substituted TTFV **2d**. Reduction of the ester groups in **2a** with  $\text{LiAlH}_4$  (Scheme 3) afforded **2d** quantitatively.<sup>16</sup> Recrystallization of **2d** in acetonitrile affords a novel compound **6** presenting a different and complex  $^1\text{H}$  NMR spectrum.<sup>16</sup> The structure of **6** has been established thanks to a X-ray diffraction study and results from the association of two starting molecules (Fig. 2). A rationale for this transformation was unexpectedly obtained from the identification of another intermediate. Indeed, we observed that **2d** upon standing slowly

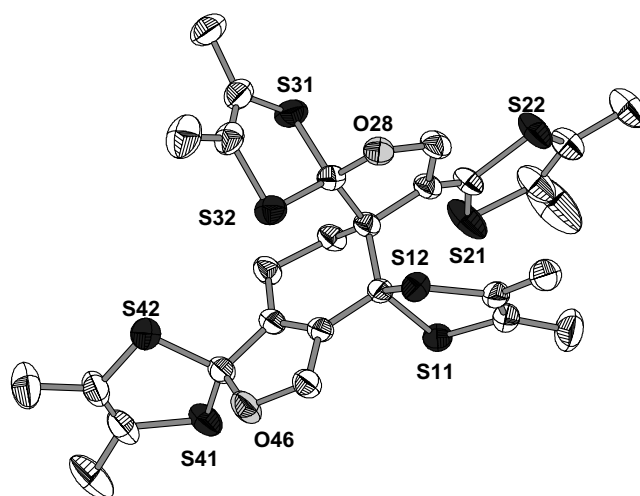
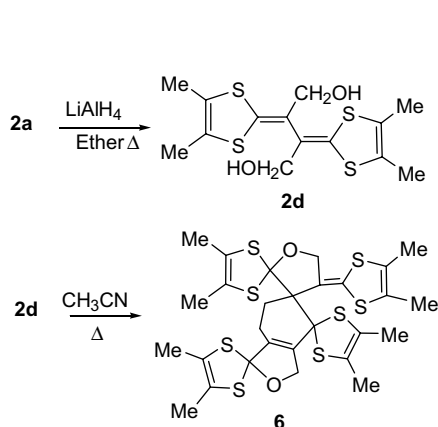


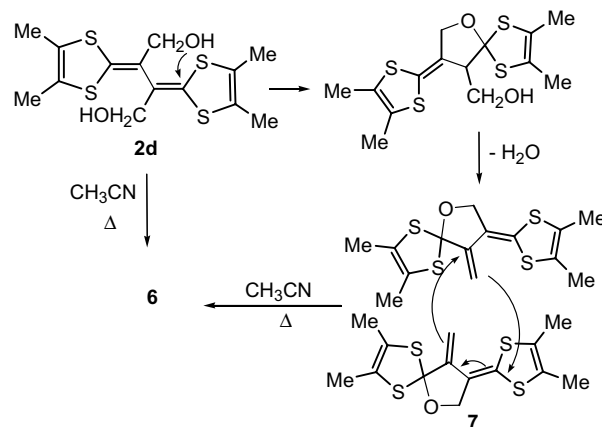
Figure 2. Molecular structure view of **6** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

evolves in the solid state into **7**. The  $^1\text{H}$  NMR spectrum of TTFV **2d** exhibits indeed four signals, including those of the hydroxymethyl moiety with the OH at 3.06 ppm and the  $\text{CH}_2$  at 4.16 ppm. These two signals have disappeared in **7** and are replaced by three new signals at 4.43, 5.11 and 5.87 ppm, with 2H:1H:1H intensity ratio. Recrystallization of this derivative **7** in acetonitrile also affords compound **6**. We can then postulate that the formation of **6** results from the Diels–Alder reaction of **7** generated from TTFV **2d** as depicted in Scheme 4. The nucleophilic addition of one hydroxy group on the C-2 of one dithiole ring leading to a tetrahydrofuran ring followed by dehydration can explain the formation of **7** (Scheme 4). Interestingly, the derivative **7** in the cycloaddition acts simultaneously as the diene and the dienophile to afford the Diels–Alder adduct **6**.

In summary, we have demonstrated that the oxidative coupling of functionalized 1,4-dithiafulvenes with electron withdrawing groups affords TTFV bearing reactive groups on the central conjugation. Our approach for the synthesis of the dithiafulvenes avoids the Wittig or



Scheme 3.



Scheme 4.

Horner–Emmons chemistry, which is not compatible with the reactive functions linked here to the dithiafulvene. The synthetic strategy described here has significant potential to access a variety of other substituted TTFV, which can serve as precursors for the construction of molecular devices.

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- Selected data for **2a** (R = CO<sub>2</sub>Et): diethyl bis(4,5-dimethyl-1,3-dithiol-2-ylidene)succinate: orange crystals; mp 176 °C; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 1.19 (t, 6H), 2.00 (s, 6H), 2.06 (s, 6H), 4.15 (m, 4H); <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>) δ 13.0, 13.5, 14.6, 60.15, 106.4, 122.9, 128.1, 162.4, 165.4; IR ν<sub>CO</sub> = 1648 cm<sup>-1</sup>; HRMS calcd for C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>S<sub>4</sub>: 430.0401. Found: 430.0396. Anal. Calcd for C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>S<sub>4</sub>: C, 50.21; H, 5.15; S, 29.78. Found: C, 50.72; H, 5.19; S, 29.79. Selected data for **2b** (R = CN): bis(4,5-dimethyl-1,3-dithiol-2-ylidene)succinonitrile: yellow crystals; mp 228 °C; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 2.01 (s, 6H), 2.03 (s, 6H); <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>) δ 13.6, 13.7, 82.4, 115.6, 125.8, 126.3, 164.3; IR ν<sub>CN</sub> = 2186 cm<sup>-1</sup>; HRMS calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>S<sub>4</sub>: 335.9883. Found: 335.9873. Selected data for **2c**: 3,4-bis(4,5-dimethyl-1,3-dithiol-2-ylidene)hexane-2,5-dione (R = COMe): orange powder; mp 245 °C; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 2.08 (s, 6H), 2.10 (s, 6H), 2.15 (s, 6H); <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>) 12.9, 13.6, 25.5, 116.8, 123.5, 130.3, 164.9, 191.1; IR ν<sub>CO</sub> = 1710 cm<sup>-1</sup>; HRMS calcd for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>S<sub>4</sub>: 370.0190. Found: 370.0197.
- The X-ray crystallographic data of **2a** (R = CO<sub>2</sub>Et), **2b** (R = CN) and **6** have been deposited, as supplementary publication number CCDC 268605, CCDC 268606 and CCDC 268607, respectively, at the Cambridge Crystallographic Data. Copies of the data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).
- Selected data for **2d** (R = CH<sub>2</sub>OH): 2,3-bis(4,5-dimethyl-1,3-dithiol-2-ylidene)butane-1,4-diol: yellow crystals; mp 162 °C; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 1.92 (s, 6H), 1.94 (s, 6H), 3.06 (s, 2H) 4.16 (s, 4H); <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>) 13.4, 13.7, 62.6, 119.9, 121.7, 122.0, 137.6; IR ν<sub>OH</sub> = 3273 cm<sup>-1</sup>; HRMS calcd for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>S<sub>4</sub>: 346.0189. Found: 346.0180. Selected data for **6** colourless crystals; mp > 260 °C; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 1.78 (s, 3H), 1.82 (s, 3H), 1.92 (s, 6H), 1.95 (s, 6H), 1.97 (s, 6H), 2.21 (m, 1H), 2.42 (m, 1H), 2.71 (m, 1H), 3.02 (m, 1H), 4.15–4.4 (m, 2H), 4.97–5.17 (m, 2H); <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>) 12.9, 13.3, 13.7, 13.8, 13.9, 14.0, 14.1, 14.2, 21.4, 29.3, 62.3, 70.8, 74.2, 77.2, 113.9, 114.1, 117.3, 118.2, 118.3, 118.7, 119.4, 120.2, 121.2, 122.3, 122.8, 128.5, 133.4, 136.5.