# A new promising π-donor of the tetrathiafulvalene series: bis(2,3-dithiabutane-1,4-diyl)tetrathiafulvalene, the symmetrical outer S-position isomer of BEDT-TTF

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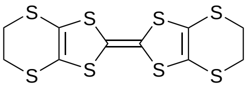
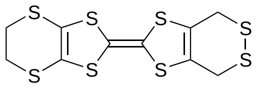
**New functionalities are introduced into the 2-(thi)oxo-1,3-dithiole system and applied to the synthesis of the title compound.**

Among the organic donors of the tetrathiafulvalene (TTF) family,[1] bis(ethylenedithio)tetrathiafulvalene **1** (BEDT-TTF or ET) is still regarded as the best precursor for superconducting organic metals[2] endowed with the highest $T_c$ in that series.[3] In their solid state structure, the related radical cation salts exhibit bidimensional character mainly originating from strong peripheral S···S intermolecular interactions. Therefore, modifications of ET are of interest to establish relationships between the solid state structure and the transport properties of the corresponding salts, particularly by varying the position and the nature (S, Se, Te) of the chalcogen.[2b,4]

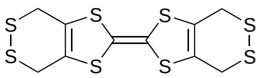
In this context, we have become interested in the unsymmetrical and symmetrical S-position isomers of ET, **2** and **3** respectively, with the aim of understanding the possible role of the position of the peripheral sulfur atoms on the dimensionality of the related materials.[5] After our previous study devoted to the unsymmetrical ET isomer **2** and some of its charge transfer salts,[6] we have extended this work to the symmetrical ET isomer **3**. We report here on the synthesis of the latter, based on the introduction of new functionalities on the 2-(thi)oxo-1,3-dithiolic precursors,[7] and also describe some preliminary electrochemical results emphasizing its promising π-donor ability for molecular conductors.



**1** (BEDT-TTF or ET)



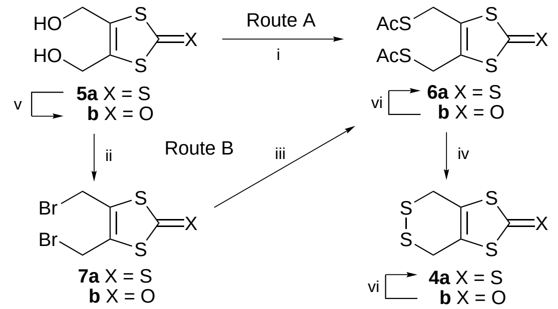
**2**



**3**

In our synthetic approach, we first studied a pathway involving the standard symmetrical or cross-coupling of the corresponding 2-(thi)oxo-1,3-dithioles **4a** and **4b**. These were synthesized according to Scheme 1 *via* two possible routes, A and B.

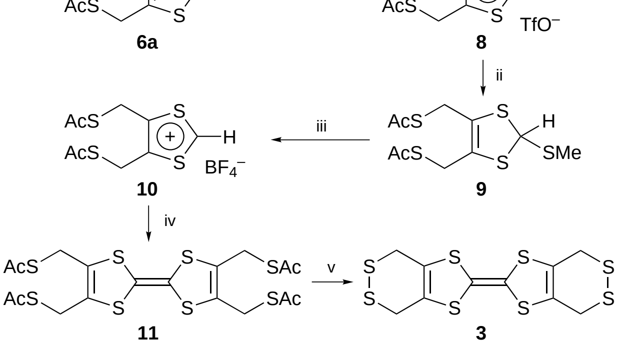
In route A, we used our standard procedure[6] allowing the conversion of the 4,5-bis(hydroxymethyl)-2-(thi)oxo-1,3-dithiole **5a**[8] or **5b** to **6a** or **6b** with thioacetic acid, either *via* the Mitsunobu reaction[9] (32% yield for **6a**) or after activation of the alcoholic groups with *N,N*-dimethylformamide diethyl acetal[10] (52% yield for **6b**). In route B, diol **5a** was easily dibrominated with $PBr_3$ in 94% yield,[11] similar results being also obtained for **5b**. Upon treatment of **7a** and **7b**[12] with thioacetic acid and pyridine or its potassium salt, the corresponding thioesters were formed in good yield (*ca.* 90%), even on a large scale. To achieve the S–S intramolecular closure, best results were obtained by cleaving[13] the thioester groups with CsOH in MeOH and by oxidizing the corresponding generated dithiolate with iodine in $Et_2O$. Note that the $NaBH_4$–LiCl mediated cleavage successfully used in the corresponding TTF series[6] affords **4a** or **4b** in poorer yields.§



**Scheme 1** *Reagents and conditions*: i, (for **6a**) DEAD, $PPh_3$, AcSH, THF (32%); (for **6b**) $Me_2NCH(OEt)_2$, $CH_2Cl_2$, 40 °C (52%); ii, $PBr_3$, THF–$CCl_4$ (1 : 2, v/v) (**7a** = 94%, **7b** = 62%); iii, AcSH, THF, Py or $ACS^-K^+$, THF (**6a** = 94%, **6b** = 89%); iv, CsOH, MeOH, then $I_2$, $Et_2O$ (**4a** = 85%, **4b** = 46%); v, $Hg(OAc)_2$, AcOH–$CHCl_3$ (44%); vi, $P_4S_{10}$, toluene, 100 °C (**6a** = 28%, **4a** = 37%)

Whereas the trialkyl phosphite induced self- or cross-coupling reaction of 2-(thi)oxo-1,3-dithioles is a classical method for TTF core building,[14] all attempts from **4a** and **4b** were inefficient, as they were when using octacarbonyl dicobalt.[15] A similar failure was observed of **6a** and $P(OMe)_3$, the expected derivative **11** being formed only as a side product (5% yield), besides the main product, the oxo derivative **6b** (70% yield).[16]

Given these results, we investigated the other pathway depicted in Scheme 2. Methylation of **6a** with MeOTf in dry



**Scheme 2** *Reagents and conditions*: i, MeOTf, $CH_2Cl_2$ (98%); ii, $NaBH_4$, $Pr^iOH$–MeCN (1 : 8, v/v) (82%); iii, $HBF_4$, $Ac_2O$ (83%); iv, $Et_3N$, MeCN (61%); v, $MeO^-Na^+$, MeOH–DMF (10 : 1, v/v) (63%)

**Table 1** Oxidation peak potentials[a] $E\text{pa}_1$ and $E\text{pa}_2$

| Compound | $E$/V *vs.* SCE[b] $E\text{pa}_1$ | $E\text{pa}_2$ | $\Delta E\text{p}$ |
|---|---|---|---|
| BEDT-TTF **1** | 0.51 | 0.92 | 0.41 |
| **2** | 0.49 | 0.93 | 0.44 |
| **3** | 0.54 | 0.99 | 0.45 |

[a] Pt electrode, 20 °C, under nitrogen atmosphere, $Bu_4N^+PF_6^-$ 0.1 M in $CH_2Cl_2$, scan rate 0.1 V s$^{-1}$, [compound] ≈ $10^{-3}$ M. [b] Saturated calomel electrode.

$CH_2Cl_2$ afforded the corresponding salt **8** quantitatively. Reduction of the latter with $NaBH_4$ in $Pr^iOH$–MeCN at 0 °C produced **9** in 82% yield. Subsequent conversion to the 1,3-dithiolium tetrafluoroborate **10** was performed under classical conditions ($HBF_4$–$Ac_2O$) (83% yield).[17] Upon immediate treatment of **10** with an excess of $Et_3N$ in MeCN, the TTF derivative **11** was obtained in fairly good yield (61%). Finally, transformation of **11** to the required target compound **3** could also be carried out as indicated above for the analogous conversion of **6** to **4**, but the yields were improved (63%) by treatment of **11** with $MeO^-$ in MeOH–DMF, without isolation of the dithiolate intermediate.¶

The cyclovoltammogram of **3** resembles that of TTF derivatives, with two reversible oxidation peaks indicative of the successive generation of stable radical cation $\mathbf{3}^{\cdot+}$ and dication $\mathbf{3}^{2+}$, at potential values ($E\text{pa}_1$ and $E\text{pa}_2$) close to those of their isomeric counterparts **1** (ET) and **2** (Table 1). This π-donor behaviour is also confirmed by the ready formation of black charge transfer salts upon oxidation with $Br_2$, $I_2$ and TCNQ, and also upon electrooxidations in the presence of various anions, structural studies of the resulting materials being currently underway.

## Notes and References

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§ Transformations of **5a** into the corresponding 2-oxo-1,3-dithiole **5b** using $Hg(OAc)_2$ in AcOH–$CHCl_3$, and **4b** and **6b** into 2-thioxo-1,3-dithioles **4a** and **6a** using $P_4S_{10}$ in toluene at reflux, were carried out but yields were not as good as expected.

¶ All new compounds gave satisfactory analytical and spectral data. *Selected data* for **3**: pink powder, mp 220 °C (decomp.); $\delta_H$ ($CS_2$ + $CDCl_3$) 3.45 (s, $SCH_2CH_2S$); *m/z* 384 ($M^{\cdot+}$, 39%), 320 (67), 256 (100), 172 (25), 128 (18); Raman/cm$^{-1}$ 511 (S–S), 1542 (C=C); Calc. for $C_{10}H_8S_8$ (384.655): C, 31.22; H, 2.10; S, 66.68. Found: C, 31.25; H, 2.06; S, 66.59%.

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