# Pyrazine-Fused Bis(tetrathiafulvalenes)

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*Received August 30, 1994*®

The TTF-like bidentate sulfur nucleophiles **13a,b** have been prepared from the corresponding 4,5-dialkyl-1,3-dithiole *S*-oxides **11a,b**, obtained by the oxidation of the parent 1,3-dithioles **10a,b.** The aromatic nucleophilic substitutions of tetrachloropyrazine by these nucleophiles **13a,b** yield, in a single step, the unsymmetrically substituted pyrazino-TTF **8** or the pyrazine-fused bis-TTF **9a,b** depending on the stoeichiometries of the reactions. The electrochemical properties of these new donors, obtained by cyclic voltammetry, are also reported.

## Introduction

The tetrathiafulvalene (TTF) skeleton has been shown to exhibit a high versatility toward structural modifications during the last two decades, and a growing number of new modified TTFs are still being currently designed and synthesized.[1] Three skeletal variations have been mainly investigated: (a) the *extension* of the $\pi$-conjugation between the 1,3-dithiole rings, by the incorporation of i.e. olefinic,[2] heterocyclic,[3] as well as quinonoid spacers (**1**)[4] (Chart 1), (b) the covalent *bridging* of two or more TTF units by a variety of single atoms (**2**) (X = S) (Chart 1), or longer, either saturated **2** (X = $S(CH_2)_nS$) or unsaturated **2** (X = $SCH_2C_6H_4CH_2S$) links;[5] in a formally similar approach, involving the linkage of peripheral TTF carbons, highly out-of-plane distorted TTF,[6] as well as a range of macrocycles containing planar and/or bent TTF building-blocks, have been prepared;[7] (c) the *condensation* to fused TTF through the sharing of a common double bond[8] (Chart 1) or aromatic ring (**7**).[9]

From the synthesis point of view, which has been comprehensively reviewed,[10] two main methods have been employed for the preparation of this family of compounds: (i) the coupling methods involving preformed 1,3-dithiole rings for a and c, and (ii) the derivatizations through the lithiation of the appropriate parent TTF for b.

**Chart 1**

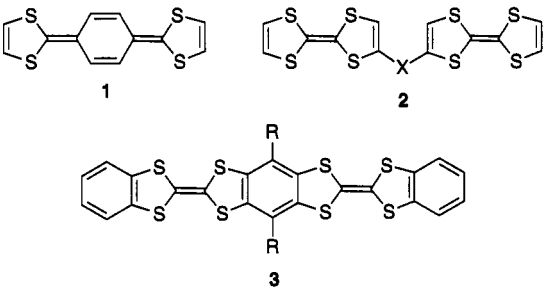
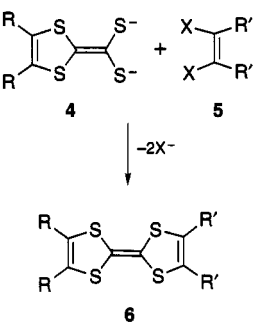


**Chart 2**



We were interested in the preparation of new fused TTFs and decided to investigate a new synthetic approach aimed at a general access to the TTF nucleus, via the TTF-like synthon **4** (Chart 2). This approach involves the nucleophilic substitution-reaction of an appropriate substrate **5** by this bidentate nucleophile and eventually yields the unsymmetrical TTF **6** (R ≠ R′).

We have previously investigated[11,12] the possibility of obtaining such TTF-like nucleophiles starting from the easily available 1,3-dithioles, through the reactions of the corresponding 2-lithio derivatives with carbon disulfide. However, for the 4,5-dialkyl-substituted 1,3-dithioles, an unexpected process[13] hindered the formation of the nucleophiles **4**. We have now found a more controlled route and wish to report the preparation of these syn-

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® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

(1) See for example: Williams, J. W.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. M.; Kini, A. M.; Wangbo, M.-H. *Organic Supraconductors, Synthesis, Structure, Properties and Theory*; Prentice Hall, Englewood Cliffs, NJ, 1992; and references therein.
(2) Moore, A. J.; Bryce, M. R. *Tetrahedron Lett.* **1992**, *33*, 1373 and references cited therein.
(3) Takahashi, K.; Nihira, T.; Takase, K.; Shibata, K.; *Tetrahedron Lett.*, **1989**, *30*, 2091; see also: Hansen, T. K.; Lakshmikantham, M. V.; Cava, M. P.; Niziurski-Mann, R. E.; Jensen, F.; Becher, J. *J. Am. Chem. Soc.* **1992**, *114*, 5035.
(4) Yamashita, Y.; Kobayashi, Y.; Miyashi, T. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1052.
(5) (a) Bryce, M. R.; Marshallsoy, G. J.; Moore, A. J. *J. Org. Chem.* **1992**, *57*, 4859. (b) Sudmale, I. V.; Tormos, G. V.; Khodorkovsky, V. Y.; Edzina, A. S.; Neilands, O. J.; Cava, M. P. *J. Org. Chem.* **1993**, *58*, 1355. (c) Jorgensen, M.; Lerstrup, K. A. Bechgaard, K. *J. Org. Chem.* **1991**, *56*, 5684, and references cited therein.
(6) Röhrich, J.; Wolf, P.; Enkelmann, V.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1377.
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(9) Wegner, R.; Beye, N.; Fanghänel, E.; Scherer, U.; Wirschem, R.; Müllen, K.; *Synth. Met.* **1993**, *53*, 353, and references cited therein.
(10) Reference 1, chapter 2.
(11) Moradpour, A.; Bittner, S. *Tetrahedron Lett.* **1987**, *28*, 3805.
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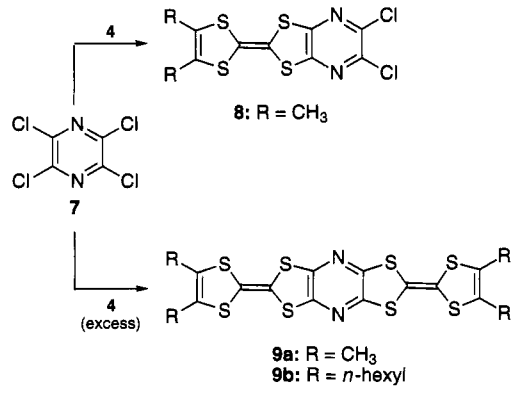
**Chart 3**




thons. We have first applied this methodology to the substitution reactions of tetrachloropyrazine **7**, which yielded, following this method, the unsymmetrically substituted TTF **8** and ultimately the new pyrazine-fused bis-TTF **9** (Chart 3). Since such ring-fused TTFs are expected to exhibit, in relation to the interactions of two conjugated redox centers, interesting electrochemical behavior in solution, the cyclic-voltammetry results of these new TTFs are also reported.

## Experimental Section

**General**. Details of instrumentation have been reported recently.[14] Cyclic voltammetry was carried out using a homemade potentiostat;[15] measurements were effected in anhydrous dichloromethane (with molecular sieves added into the cell), with platinum electrodes and a saturated calomel electrode (separated from the solution by a bridge-compartment) as a reference electrode.

Compounds **7**[16] and **10a**[17,18] were prepared according to the literature methods; the detailed procedures for the preparation of **10b** are included in the supplementary material.

**4,5-Dimethyl-1,3-dithiole 1-Oxide (11a).** Into a stirred solution of **10a** (2 g, 15.15 mmol) in acetic acid (20 mL) at 0 °C was added hydrogen peroxide (35% solution, 1.35 mL, 15.7 mmol) and the stirring maintained at room temperature overnight. The solution was poured into water (100 mL) and unreacted 1,3-dithiole **10a** (0.2 g) was extracted with ether (30 mL); the aqueous phase was then extracted with $CH_2Cl_2$ (3 × 30 mL), the organic phase washed with saturated sodium bicarbonate solution (20 mL) and water (10 mL) and dried over $MgSO_4$. The solvent was evaporated and recrystallization from ether provided the compound **11a** (1.35 g, 60%) as a very hygroscopic, air-stable, pink solid; mp = 38−38.5 °C. NMR: ($\delta_H$, $CDCl_3$) 2.05 (s, 3H), 2.09 (s, 3H), 3.97 (s, 2H). Anal. Calcd for $C_5H_8OS_2$: C, 40.54; H, 5.40; O, 10.81; S, 43.24. Found: C, 40.32; H, 5.20; O, 10.90; S, 42.96. MS (EI), *m/e*: 148($M^+$).

**4,5-Dihexyl-1,3-dithiole 1-Oxide (11b).** Hydrogen peroxide (35% solution, 1.05 mL, 12.25 mmol) was added, at 0 °C, to a solution of **10b** (3.27 g, 12 mmol) in acetic acid (25 mL) and the mixture stirred at room temperature overnight. The solution was poured into water (150 mL) and extracted with ether (3 × 25 mL). The extracts were washed with water (20 mL) and dried over $M_gSO_4$. The ether was evaporated and the residue purified by chromatography on a silica gel column eluting with acetone/cyclohexane (40:60 v/v), yielding **11b** (2 g, 60%) as a colorless liquid. NMR: ($\delta_H$, $CDCl_3$) 0.80 (m, 6H), 1.22 (br s, 12H), 1.51 (m, 4H), 2.33−2.46 (m, 4H), 2.86, 3.98 (2d, $J$ = 13.5 Hz, 2H). Anal. Calcd for $C_{15}H_{28}OS_2$: C, 62.50; H, 9.72; O, 5.55; S, 22.22. Found: C, 62.63; H, 10.2; O, 5.72; S, 22.42. MS (CI), *m/e*: 289 ($MH^+$).

**Dilithium (4,5-Dialkyl-1,3-dithiole-2-ylidene)methanedithiolate Salts 13a,b. General Procedure. (A) Preparation of the Sulfoxide Salts 12a,b**. Into a stirred solution of 4,5-dialkyl-1,3-dithiole 1-oxide (**11a,b**) (4 mmol) in anhydrous THF (25 mL), at −80 °C, a solution of butyllithium (1.6 M in hexane, 2,5 mL, 4 mmol) was added by syringe, under an argon atmosphere. The mixture was stirred for 0.5 h, $CS_2$ (0.3 g, 0,24 mL, 4 mmol) was added, and after 10 min a second equivalent of butyllithium was syringed into the mixture; after an additional 0.5 h stirring at −80 °C, the mixture was allowed to warm to room temperature overnight. The salt **12a**, a yellow air-sensitive solid was filtered, washed with oxygen-free ether (10 ml), and stored under argon (0.77 g, 82%); the salt **12b** remained in solution at this stage, and was used subsequently without purification: the required volume of this solution was syringed in the next reduction step. The actually available amount of **12b** may be estimated based on the yield of the methylated derivative **14b** obtained therefrom (vide infra).

**(B) Preparation of the salts 13a,b**. The salts **12a,b** (2 mmol) were placed (or syringed for **12b** ) in anhydrous THF (25 mL) under inert atmosphere, and $LiAlH_4$ (0.076 g, 2 mmol) was added. The suspension was stirred and after reflux (5 min) was stirred at room temperature overnight. The resulting suspension (greenish for **13a** and brownish for **13b**) was decanted from the excess $LiAlH_4$ and subsequently syringed in the next nucleophilic substitutions steps. These solutions were also reacted with an excess methyl iodide, in order to characterize the salts **13a,b**, by the following methylated derivatives **14a,b**.

**4,5-dimethyl-2-[bis(methylthio)methylene]-1,3-dithiole (14a):**[11] isolated by flash chromatography eluting with toluene/cyclohexane (25:75 v/v) (60% from **12a**). NMR: ($\delta_H$, $CDCl_3$) 1.95 (s, 6H), 2.23 (s, 6H). MS (EI), *m/e*: 236 ($M^+$).

**4,5-Dihexyl-2-[bis(methylthio)methylene]-1,3-dithiole (14b):** isolated by flash chromatography eluting with toluene/cyclohexane (10:90 v/v) as a yellow oil (51% from **11b**). NMR: ($\delta_H$, $CDCl_3$) 0.85 (br t., 6H), 1.26 (m, 12H), 1.46 (m, 4H), 2.26 (s, 6H), 2.28 (t, 4H). Anal. Calcd for $C_{18}H_{32}S_4$: C, 57.45; H, 8.51; S, 34.04. Found: C, 57.74; H, 8.32; S, 34.34. MS-(CI), *m/e*: 377 ($MH^+$).

**Nucleophilic Substitutions of Tetrachloropyrazine 7 by the Dilithium Salts 13a,b. General procedure.** The appropriate volume of the THF solution containing the salts **13a,b** was syringed, under argon, into a vessel and the THF evaporated under a rapid stream of argon. The residue was dissolved in oxygen-free DMF, and the required amount of **7** was added as a solid. The mixture was stirred overnight at room temperature, and, if specified, an excess methyl iodide was added and stirring continued for an additional 1 hour. The mixture was poured into water and filtered. The compounds were purified by recrystallization, soxhlet extraction, or flash-chromatography. The following were obtained:

**2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-5,6-dichloro-(1,3)-dithiolo[4,5-*b*] pyrazine (8)**: from an excess of **7** (1.65 equiv) as compared to **13a**, a red-violet solid (35%) based on **12a**); mp = 100 °C dec (from cyclohexane). Anal. Calcd for $C_{10}H_6Cl_2N_2S_4$: C, 33.99; H, 1.69; Cl, 20.08; N, 7.93; S, 36.26. Found: C, 34.25; H, 2.20; Cl, 20.03; N, 7.60; S,35.85. MS (CI), *m/e*: 352($M - 1$)$^+$.

**2,6-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)bis-1,3-dithiolo[4,5-*b*:4′,5′-*e*] pyrazine (9a)**: from an excess of **13a** (1.7 equiv) as compared to **7** was isolated a dark-red sparingly soluble solid (17% based on **7**) after soxhlet extraction in pyridine. Anal. Calcd for $C_{16}H_{12}N_2S_8$: C, 39.34; H, 2.46; N, 5.73; S, 52.46. Found: C, 39.74; H, 2.58; N, 5.56; S, 51.97. MS(CI), *m/e*: 489 ($MH^+$).

**2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-5-chloro-6-(methylthio)-(1,3)-dithiolo[4,5-*b*] pyrazine (15)**: obtained after addition of an excess of methyl iodide to the reaction mixture leading to compound **9a**. The mother liquors were evaporated, and the residue extracted by $CH_2Cl_2$ and purified by flash-chromatography eluting with toluene/cyclohexane (30:70 v/v): a red-violet solid (20% from **7**), mp = 242−243 °C (from

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(15) Tomasino, J.-B.; Polarede, B.; Medus, D.; de Montauzon, D.; Cassoux, P.; Fabre, P.-L. *Mol. Cryst. Liq. Cryst.* **1993**, *237*, 445.
(16) Allison, C. G.; Chambers, R. D.; Mac Bride, J. A. H.; Musgrave, W. K. R. *J. Chem. Soc.* (C) **1970**, 1023.
(17) Grunwell, J. R.; Willett, J. D. *Int. J. Sulfur Chem.* **1971**, *1*, 60.
(18) Krief, A. *Tetrahedron* **1986**, *42*, 1209.

**Scheme 1**

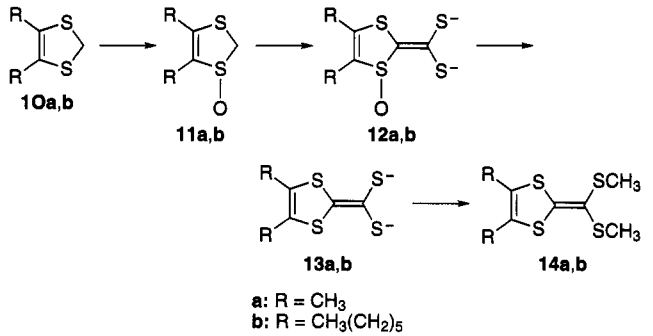
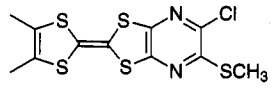



**Chart 4**




cyclohexane). NMR: ($\delta_H$, $CDCl_3$) 1.96 (s, 6H), 2.47(s, 3H). Anal. Calcd for $C_{11}H_9ClN_2S_5$: C, 36.21; H, 2.46; N, 7.68; S, 43.89. Found: C, 36.06; H, 2.49; N, 7.38; S, 43.71. MS (EI), *m/e*: 364 ($M^+$).

Compound **15** was not detected after addition of methyl iodide to the reaction mixture which led to **8**.

**2,6-Bis(4,5-dihexyl-1,3-dithiole-2-ylidene)bis-1,3-dithiolo-[4,5-*b*:4′,5′-*e*] pyrazine (9b)**: from an excess **13b** (2.5 equiv) as compared to **7**. A red solid (25% from **7**), mp = 239–240 °C (from cyclohexane). NMR: ($\delta_C$, $CDCl_3$) 16–33 (n-hexyl), 98.27, 119.08, 129.75, 153.18. Anal. Calcd for $C_{36}H_{52}N_2S_8$: C, 56.25; H, 6.71; N, 3.65; S, 33.33. Found: C, 55.68; H, 6.40; N, 3.50; S, 33.34.

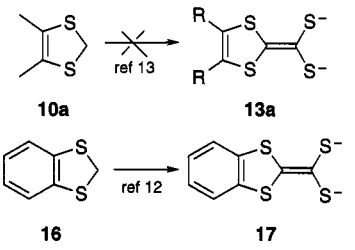
## Results

The air sensitive 1,3-dithiole **10a** was first oxidized, by hydrogen peroxide, to the monosulfoxide **11a** (60% yield) (Scheme 1). The corresponding 2-lithio derivative was generated from the latter with BuLi, at −80 °C, and reacted with $CS_2$; after a second equivalent of BuLi was added, the dilithium salt **12a** precipitated and was isolated. This solid was stored under argon, as the precursor to the nucleophile **13a**; the latter is easily prepared from **12a** by reduction with $LiAlH_4$ in THF. The same reaction sequence, starting from the more lipophilic 1,3-dithiole **10b** led to the nucleophile **13b** (Scheme 1); the greater solubility of the sulfoxide **12b** in the reaction medium precluded its isolation, and therefore its purification, by filtration. Both nucleophiles **13a,b** were first characterized by preparing the corresponding methylated derivatives **14a** (60% yield from **12a**) and **14b** (52% from **12b**). The substitution reactions of tetrachloropyrazine **7** by these nucleophiles were carried out in oxygen-free DMF at room temperature. When an excess of tetrachloropyrazine was first allowed to react with **13a**, the unsymmetrically substituted TTF **8** (Chart 3) was obtained (31% yield). Alternatively, if an excess of nucleophile **13a** is reacted with the substrate **7**, the very sparingly soluble bis-TTF **9a** was formed (18%); in this case, the occurrence of another, more polar compound was also detected (TLC) in the reaction mixture; the addition of an excess of methyl iodide led to the isolation of a significant amount (20%) of the unexpected TTF **15** (Chart 4). This compound was not detected when a similar alkylation reaction was effected on the reaction mixture which led to the previous monosubstituted compound **8**. Similarly, using an excess of the more lipophilic nucleophile **13b**, the soluble pyrazine-fused bis-TTF **9b** was easily prepared (25%), in a single step. The half-wave oxidation potentials of **8** and **9b** were determined by cyclic voltammetry and the results are collected in Table 1.

**Table 1. Cyclic Voltammetry of Compounds 8 and 9b vs SCE in $CH_2Cl_2$ with 0.1 M n-$Bu_4NPF_6$ (scan speed = 100 mV/s)**

| compound no. | $E^1_{1/2}$ | $E^2_{1/2}$ | $E^3_{1/2}$ | $E^4_{1/2}$ (V) |
|---|---|---|---|---|
| **8** | +0.66 | +1.12 | – | – |
| **9b** | +0.49 | +0.71 | +1.24 | +1.50 |

**Scheme 2**




Both compounds showed quasireversible waves: the oxidations are one-electron processes for the TTF **8** (two waves) and also for the bis-TTF **9b** (four waves), each TTF moiety being oxidized sequentially at different potentials.

## Discussion

We have previously found[12] that the reaction of 2-lithio-1,3-benzodithiole **16** with $CS_2$ leads to the expected salt **17** (Scheme 2), while starting with the similar 4,5-dimethyl-1,3-dithiole **10a** and following the same reaction sequence, the corresponding salt **13a** is not formed.[12]

Two possible reactions of carbanions with $CS_2$, mediated by carbophilic or thiophilic attacks, have been reported, both in solution,[19,20] as well as in gas-phase studies.[21] The proportion of attack at sulfur, compared with attack at carbon was observed, in both sets of studies,[20,21] to increase markedly with an increase in the base-strength of the reagents involved.

The presently available data[22] do not allow us to an unambigously assign this dramatic difference in reactions, of an otherwise similar carbanion formed from **10a** and **16**, to such carbophilic vs thiophilic attacks to $CS_2$. However, considering the possible influence of the p*K* values of these carbanions on their reactivity with $CS_2$, we aimed at the modification of their base-strength and investigated the corresponding mono-sulfoxides **11**[23] (Scheme 1). In fact, the reactions of *S*-oxides **11a,b** with $CS_2$ led to the expected salts **13a,b** with acceptable yields

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(20) Verkruijsse, H. D.; Brandsma, L. *J. Organomet. Chem.* **1987**, *332*, 95.

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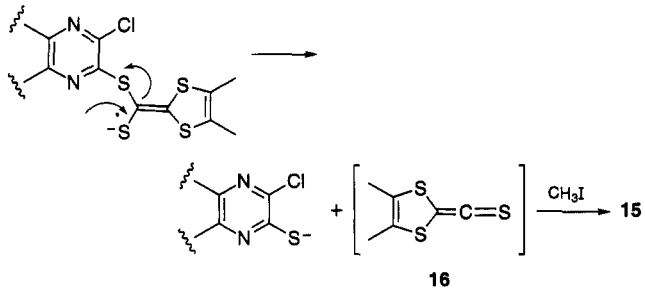
(22) Gas-phase generations of anions from various 1,3-dithioles and the subsequent reaction with $CS_2$ have been studied by tandem mass spectrometry and gave an interesting mechanistic insight to the presently studied reactions; our first results concerned 1,3-benzodithiole and will appear in a forthcoming paper: Gimbert, Y.; de Hoffmann, E.; Dive, G.; Tabet, J. C; Moradpour, A., manuscript in preparation.

(23) Modification of the reactivities in the 2-lithio-1,3-dithiane field by the use of the anions from the corresponding mono-*S*-oxides have been observed, i.e. for 1,2 vs 1,4 additions to unsaturated ketones; see: Gröbel, B.-T.; Seebach, D.; *Synthesis* **1977**, 357 and references cited therein.

**Chart 5**



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for a four-step process (**13a,b** are formed with, respectively, 49 and 51% yield from **11a,b**).

The bidendate TTF-like nucleophile **13a** reacted smoothly with tetrachloropyrazine **7** to give the unsymmetrically substituted TTF **8** or the pyrazine-fused bis-TTF **9a,b** (Chart 3), depending on the stoeichiometries of the substitution reactions. For the latter reactions, the modest yields (25%) for these doubly substituted pyrazines may be accounted for by considering the interesting byproduct **15** (Chart 4) isolated in almost comparable yield (20%). The formation of this unexpected compound may involve a rearrangement of the nucleophile **13a** to the thioketene **16** (Chart 5). Although neither the isolation of this possibly unstable compound nor of the side-products resulting from its reaction in the medium have been attempted, the formation of the methylated derivative **15** is evidence for such a process.[24]

The bis-TTF obtained so far[25] by the present approach exhibits an interesting redox behavior. This bis-TTF **9b** is a fairly good donor, with a first oxidation potential (Table 1) very close to that of BEDT-TTF ($E^1_{1/2}$ = +0.43 V vs SCE in $CH_2Cl_2$)[5c] while the oxidation potentials of the TTF **8** are in the range of similar pyrazinotetrathiafulvalenes.[26] The interaction of the two equivalent TTFs through a conjugative link in **9b** leads to four sequential quasireversible one-electron oxidations, ultimately yielding the fully oxidized tetracation. This redox behavior is typical of two *interacting* redox centers, which exhibit, as already observed[27] in other systems such as **3** (Chart 1), containing TTF units coupled via a $\pi$-conjugated ring, four-wave voltammograms. In the case of nonconjugated links, such as in **2** (X = $S(CH_2)_3S$),[5c] the two coupled TTFs behave independently: no coulombic repulsion exists between the two positively charged moieties formed in the second oxidation step, and consequently the two TTFs are oxidized at the same potential resulting in two two-electron waves.[5c] Interestingly, the shortening of such bridges, as in **2** (X = S(CH2)S),[5c] restores some "interaction" of the two TTF units: the corresponding three-wave voltammogram involves a splitting of the first previously two-electron wave into two one-electron waves. The actual structure of the links mediating such interacting redox centers, as well as other interesting molecular or cooperative solid state properties of these systems, are under study.

**Acknowledgment.** C.B. acknowledges EEC (Human Capital and Mobility) for a fellowship.

**Supplementary Material Available:** Full experimental procedure for the preparation of compound **10b** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(24) In an attempted synthesis of *tert*-butylcyanothioketene the same kind of rearrangement has been considered; see: Schaumann, E. *Tetrahedron* **1988**, *44*, 1827.

(25) Other fused TTFs are also easily obtained by our procedure; those arising from the substitution reactions of hexafluorobenzene will be discussed in a subsequent article: Lahlil, K.; Moradpour, A.; de Hoffmann E., manuscript in preparation.

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