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Pyrrolo Annelated Tetrathiafulvalenes: The Parent Systems

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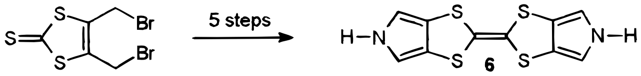
ABSTRACT



The synthesis of the parent bis(pyrrolo[3,4-*d*])tetrathiafulvalene via a nonclassical and simple pyrrole synthesis is reported, together with a detailed study of the fundamental redox behavior of some of this class of heterocycles.

The chemistry of tetrathiafulvalene (TTF, **1**) and its derivatives has been intensively studied since the discovery of the first metallic charge-transfer TTF complex.[1] The TTF skeleton has been extensively modified over the past two decades to favor enhanced dimensionality in the related charge-transfer salts.[2] Among those modifications, the heterocyclic-fused TTF donor, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **2**) has given rise to more superconducting salts than any other TTF derivative, with κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Br as the current record holder.[3]

Many other donor molecules have been synthesized in which the TTF core is annelated to benzenoid (**3**),[4] furan,[5] thiophene,[6] or selenophene[7] units (**4**) (Figure 1); all of these compounds have oxidation potentials appreciably higher than that of TTF itself. Cava and co-workers have recently presented a detailed study of bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (**5**) and its *N*-alkylated derivatives.[8] The synthesis of **5** involves classical pyrrole chemistry, building up the 1,3-dithiole-2-thione moiety from a 2,5-dimethylpyrrole core.[9] Annelation of TTF to two electron rich 2,5-dimethylpyrrole rings produces a donor system with a lower

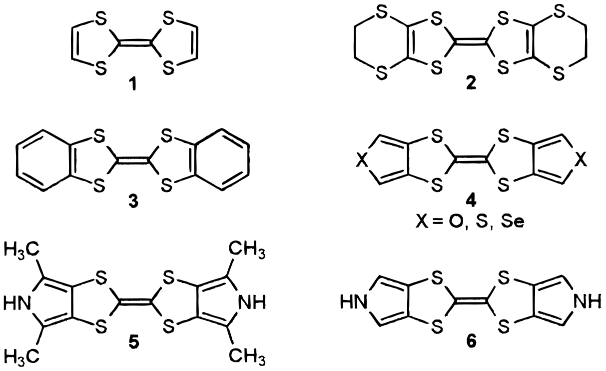


Figure 1.

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(9) The two methyl groups are mandatory in this synthesis because the first step is an electrophile thiocyanation at the β-positions and they serve to block the more reactive α-positions.

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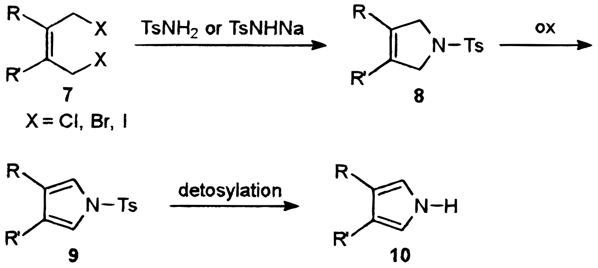
oxidation potential than that of the parent TTF (**1**), and we have found **5** to be a useful building block in supramolecular chemistry, devoid of *cis*/*trans* isomerism as in the simple TTFs.[10] However, the four methyl groups in **5**, acting as protecting groups during synthesis, block the α-positions in the pyrrole units and exclude the possibility for further *C*-functionalization in addition to *N*-alkylations. Furthermore, steric hindrance can be expected from the methyl groups, when **5** is incorporated in macrocyclic systems.

In this context bis(pyrrolo[3,4-*d*])tetrathiafulvalene (**6**) appeared interesting and we present here a straightforward access to **6** and the related monopyrrolo annelated TTF **19**, through a nonclassical pyrrole synthesis.[11]

The construction of α,α′-unsubstituted *N*-tosyl-2,5-dihydropyrrole annelated heterocycles **8** from tosylamide/sodium tosylamide (Scheme 1) and unsaturated 1,2-bishalomethyl precursors **7** has been sporadically described in the literature.[12] However, to the best of our knowledge subsequent oxidations to the corresponding *N*-tosylpyrroles **9** and complete detosylation to give α,α′-unsubstituted pyrroles **10** have apparently not been reported.[13]

Scheme 1 Nonclassical and Novel Pyrrole Synthesis

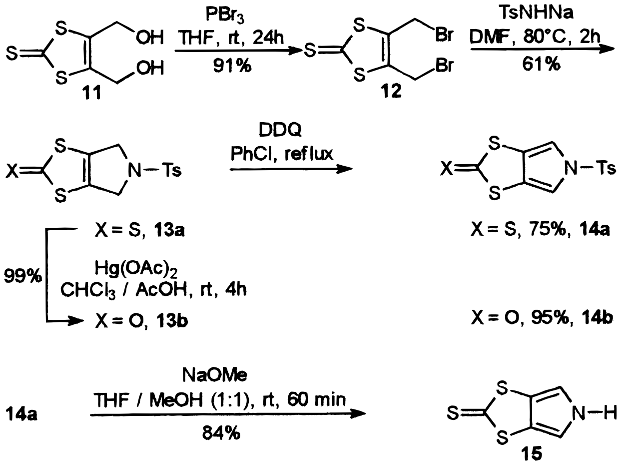


In our approach the pyrrole ring is constructed in two steps from a 1,3-dithiole-2-thione core bearing two vicinal bromomethyl groups, where the first step is a ring closure reaction with sodium tosylamide followed by oxidation of the annelated dihydropyrrole ring to give the *N*-tosyl-protected pyrrole. The tosyl group plays a triple role. First, it activates the nitrogen in the ring closure reaction. Second, it works as an excellent protecting group for the pyrrole nitrogen during the harsh triethyl phosphite coupling reaction. Finally, the tosyl groups can be removed almost quantitatively under mild conditions from the aromatic pyrrole ring.

The π-donor ability of the new systems was investigated by cyclic voltammetry as well as preliminary formation of a tetracyanoquinodimethane (TCNQ) complex.

The starting material in our synthesis is diol **11**,[14] which was dibrominated with phosphorus tribromide (PBr_3) to give dibromide **12** (Scheme 2).[15,16]

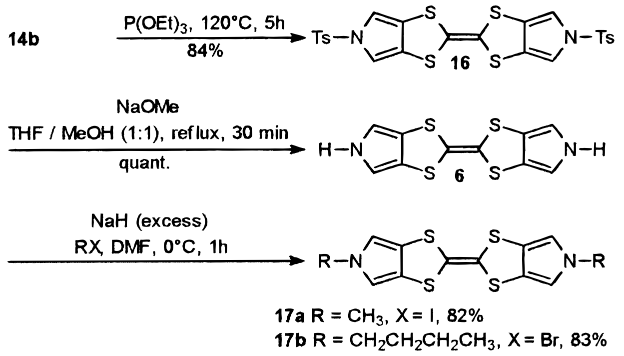
Scheme 2. Synthesis of (1,3)-Dithiolo[4,5-*c*]pyrrole-2-chalcogenones



Cyclization was performed by treatment of **12** with sodium tosylamide, affording the dihydropyrrolo compound **13a** in 61% yield. Transchalcogenation of thione **13a** with mercuric acetate gave ketone **13b** in 99% yield.[17] Dehydrogenation of **13a**,**b** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the *N*-tosylated (1,3)-dithiolo[4,5-*c*]pyrrole-2-chalcogenones **14a**,**b** in 75% and 95% yields, respectively. Detosylation of **14a** was carried out by treatment of **14a** with sodium methoxide, affording the pyrrole **15** in 84% yield.[18]

Self-coupling of the ketone **14b** to the TTF **16** using triethyl phosphite proceeded in 84% yield (Scheme 3).

Scheme 3. Synthesis of Bis(pyrrolo[3,4-*d*])tetrathiafulvalenes



Removal of the tosyl protecting groups of **16** was carried out by treatment of **16** with sodium methoxide to give the

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novel bis(pyrrolo)-TTF **6** in quantitative yield. Finally **6** was dialkylated to give the *N,N′*-dialkyl derivatives **17a**,**b** in 82−83% yields (Scheme 3).

The asymmetrical monopyrrolo-TTF **19** (Scheme 4) was obtained in optimum yield by cross-coupling of **14b** with 4,5-bis(methylthio)-1,3-dithiole-2-thione in neat triethyl phophite followed by detosylation of **18** using sodium methoxide. Likewise, alkylation of **19** proceeded smoothly to give the *N*-alkylated derivatives **20a**,**b**. Single crystals of **20b** were obtained by recrystallization from dichloromethane−hexane, and its structure was confirmed by X-ray crystallography.[19]

Scheme 4. Synthesis of Monopyrrolo[3,4-*d*]tetrathiafulvalenes

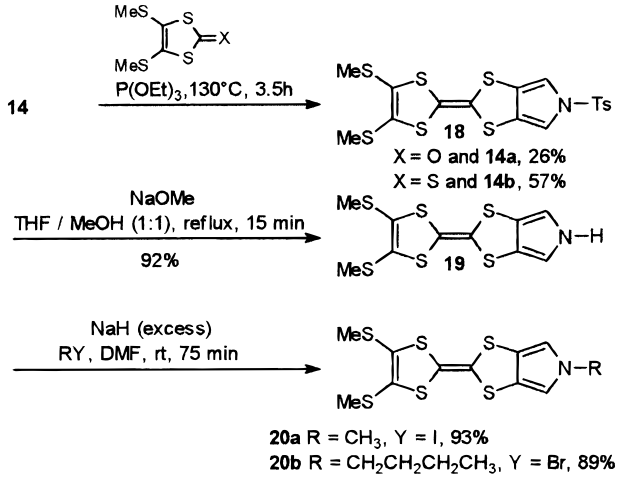

Table 1. Oxidation Potentials $E_{1/2}^1$ and $E_{1/2}^2$ of New TTF Derivatives **6**, **16**, **17a**,**b**, **18**, **19**, and **20a**,**b** Determined by Cyclic Voltammetry[a,b]

compound	$E_{1/2}^1$ [V]	$E_{1/2}^2$ [V]	ΔE_p [V]	E_{ox}^1(DFT) [eV]
TTF (**1**)	0.34	0.73	0.39	4.65
5	0.33	0.74	0.41	4.45
6	0.38	0.72	0.34	4.56
16[c]	0.55	0.96	0.41	4.91
17a	0.36	0.70	0.34	4.49
17b	0.36	0.70	0.34	
18	0.59	0.86	0.27	4.82
19	0.44	0.75	0.31	4.65
20a	0.42	0.74	0.32	4.61
20b	0.42	0.73	0.31	
21	0.42	0.76	0.34	4.59

[a] Conditions: Ag/AgCl electrode, Pt electrode, 20 °C, Bu_4NPF_6 (0.1 M in CH_3CN), scan rate 0.1 Vs^{-1}, [compound] 10^{-3} M. E_{ox}^1(DFT) is the calculated first oxidation potentials using the B3LYP/6-31G(d) method and the PCM solvent model. [b] The oxidation potentials for parent TTF, bis(2,5-dimethylpyrrolo-[3,4-*d*])tetrathiafulvalene (**5**),[8] and 4,6-dimethyl-2-{4,5-bis(methylthio)-1,3-dithiole-2-yliden}-(1,3)-dithiolo[4,5-*c*]pyrrole (**21**) (i.e., α,α′-dimethyl-substituted analogue of **19**)[22] were for comparison measured under identical conditions. [c] [**16**] ≪ 10^{-3} M, due to the low solubility in CH_3CN.

Solution oxidation potentials obtained from cyclic voltammograms (CVs) of pyrrolo-TTF π donors (D) and DFT calculated first oxidation potentials are summarized in Table 1.[20,21]

The CVs of all compounds showed two pairs of reversible redox waves, indicating good stability of the corresponding radical cation ($D^{\bullet+}$) and dication (D^{2+}). Compound **6** showed a higher first half-wave oxidation potential $E_{1/2}^1$ (50 mV) than its α,α′,α″,α‴-tetramethylated analogue **5**. This effect was also observed for **19** and its α,α′-bismethylated analogue **21** (20 mV) due to the electron-donating effect of the α-methyl groups. The first half-wave oxidation potential $E_{1/2}^1$ of **6** is higher (40 mV) than that of TTF (**1**), indicating that annelation of two pyrrolo units to the TTF framework results in a decrease of the electron-donating ability. Both for the bis(pyrrolo)-TTF series and the monopyrrolo-TTF series the *N*-tosylated pyrrolo-TTFs (i.e., **16** and **18**) showed the highest oxidation potentials (both $E_{1/2}^1$ and $E_{1/2}^2$), whereas the *N*-alkylated pyrrolo-TTFs (i.e., **17a**,**b** and **20a**,**b**) showed the lowest oxidation potentials (both $E_{1/2}^1$ and $E_{1/2}^2$), due to the inductive effect exhibited from the tosyl groups and alkyl groups, respectively. As shown in Table 1, the calculated E_{ox}^1(DFT) reproduces the major trends in the experimental first oxidation potentials $E_{1/2}^1$.

An interesting feature of the monopyrrolo-TTFs is found in their ^{13}C chemical shifs, which are summarized in Table 2 together with the ^1H chemical shifts.

As expected, the tosyl group has a strong influence on the chemical shift of the pyrrole protons. The most remarkable fact, however, is that the tosyl group is able to shift most of the ^{13}C resonances in **18**. Especially for the fulvene $C_a{=}C$, which is located six bonds away from the tosyl group, a significant change in the chemical shift is observed, indicating a pronounced extension of the π-surface in monopyrrolo-TTFs.

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(16) The use of PBr_3 has been reported in a communication from Gorgues and co-workers, see: Durand, C.; Hudhomme, P.; Duguay, G.; Jubault, M.; Gorgues, A. *Chem. Commun.* **1998**, 361−362.

(17) Self-coupling of **13b** using triethyl phosphite afforded bis(2,5-dihydro-*N*-tosylpyrrolo[3,4-*d*])tetrathiafulvalene in 35% yield. All attempts to remove the tosyl groups failed due to the chemical stability of the sulfamide bond.

(18) Care must be taken during workup, especially with regard to temperature; otherwise ring opening occurs in the 1,3-dithiole ring and a mixture of **15** and 3,4-bis(methylthio)pyrrole is isolated.

(19) The X-ray data and molecular structure are included as Supporting Information.

(20) The first oxidation potentials were calculated from the energy difference between D and $D^{\bullet+}$ with the B3LYP/6-31G(d) method and the PCM solvent model, using PM3-optimized geometries.

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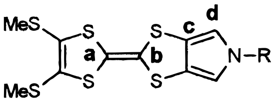
Table 2. ^{1}H NMR Chemical Shifts for Pyrrole α-protons and Selected ^{13}C NMR Chemical Shifts (in ppm) for *N*-Substituted Asymmetrical Monopyrrolo-TTF **18**, **19**, and **20a**[a]



	fulvene	fulvene	dithiole		
R	C_a=C	C=C_b	=C_cC=	pyrrole C_d	H_α
Ts	112.54	117.73	126.14	112.84	7.40
H	107.27	121.95	117.16	110.88	6.81
Me	107.24	121.34	116.77	114.66	6.78

[a] Spectra were recorded in DMSO-d_6 (25 °C) at 300 and 75 MHz for protons and carbons, respectively.

To shed more light on the extension of the π-surface in pyrrolo-TTFs, the characters of the highest occupied molecular orbital (HOMO) of **6** and **19** were calculated using the semiempirical PM3 method.[23] Figure 2 shows the electron distribution of **6**, and it is noteworthy that approximately 20% of the HOMO density is located on the outer two pyrrole rings, similar to that of BEDT-TTF (**2**) where the outer sulfur atoms have relatively large HOMO densities with the same phase as the inner sulfur atoms.[24]

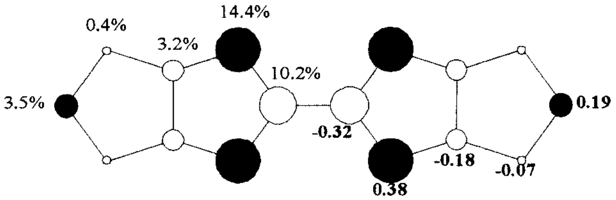


Figure 2. HOMO orbital of **6**: light face numbers = HOMO electron density, bold face numbers = HOMO coefficients.

For the asymmetrical monopyrrolo-TTF **19**, approximately 13% of the HOMO density is located on the outer pyrrole ring, clearly demonstrating an extension of the π-surface in pyrrolo-TTFs.

A combination of equimolar amounts of the new donor **6** and TCNQ gave a 1:1 charge transfer complex, and its conductivity on a single crystal at room temperature was relatively high, 0.02 S cm^{-1}.

In conclusion, we have demonstrated an efficient short route to the potentially useful symmetric bis(pyrrolo)-TTF **6** and the asymmetric monopyrrolo-TTF **19** and proved that the new approach for construction of α,α′-unsubstituted pyrrolo annelated heterocycles is useful for 1,3-dithiole-2-thione. This route can probably be extended to other fused pyrroles as well.

Investigations in the direction of tetrathiafulvalene-containing polypyrroles and porphyrin[25] systems are currently in progress.

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Supporting Information Available: Compound characterization data; X-ray crystal structure, crystal data, data collection details and refinement parameters for **20b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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