Synthesis and Properties of Bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalenes, a Class of Annelated Tetrathiafulvalene Derivatives with Excellent Electron Donor Properties

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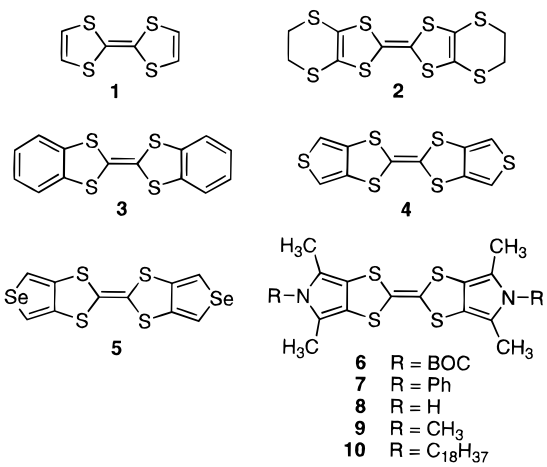
Received July 8, 1996[⊗]

The synthesis of the first derivatives of bis(pyrrolo[3,4-*d*])tetrathiafulvalene has been studied in detail. Starting from the readily available 2,5-dimethylpyrrole (**11**) and *N*-phenyl-2,5-dimethylpyrrole, bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (**8**) and the *N*,*N*′-disubstituted derivatives **6**, **7**, **9**, and **10** were prepared in good yields by practical procedures. In contrast to the other types of aromatic annelated tetrathiafulvalenes (TTFs), which have appreciably higher oxidation potentials than TTF, the redox behavior of the pyrrolo tetrathiafulvalenes (TTFs) is very close to that of TTF itself. The potential of pyrrolotetrathiafulvalenes as a new series of organic metal building blocks is shown by the two-probe conductivities of the tetracyanoquinodimethane (TCNQ) complexes of the *N*-phenyl compound **7** and the *N*-methyl compound **9**, which give higher values than TTF−TCNQ under similar conditions.

Introduction

The chemistry of tetrathiafulvalene (TTF, **1**) and its derivatives has been intensively studied for more than 20 years because of the ability of these compounds to form radical cation salts which have great potential as molecular conductors and even as superconductors.[1] In the latter category, one salt of ET [bis(ethylenedithiolene)-tetrathiafulvalene, **2**], namely $(ET)_2Cu(SCN)_2$, superconducts below $T_c = 10.4$ K;[2] a number of other TTF-related salts have also been reported to show superconductivity under various conditions.[1d]

Many donor molecules have been synthesized in which the TTF core is annelated to two benzenoid, thiophene, or selenophene units (i.e., **3**, **4**, and **5**);[3−6] all of these compounds have oxidation potentials appreciably higher than that of TTF itself. On the other hand, annelation of TTF to two electron-rich pyrrole rings should produce a donor system with a much lower oxidation potential; this has indeed been verified as we reported very briefly some time ago in a preliminary communication.[7] We now present a detailed study of the synthesis of the first bis(pyrrolo[3,4-*d*])tetrathiafulvalenes (**6**−**10**), including a greatly improved route to synthesize these compounds. We also report some electrochemical results and the preparation of some new tetracyanoquinodimethane (TCNQ) complexes having excellent conductivity properties.



Results and Discussion

Synthesis of Pyrrolo-3,4-trithiocarbonates. Our target molecules in this study were pyrrole-annelated TTF derivatives which would be linear molecules free from the complication of *cis*, *trans* isomers. For this purpose, precursors were required bearing sulfur functions only in the β-positions. An excellent starting material proved to be the readily prepared and commercially available 2,5-dimethylpyrrole (**11**). Reaction of **11** with freshly generated thiocyanogen in methanol[8] smoothly (82%) afforded the known 2,5-dimethyl-3,4-dithiocyanopyrrole (**12**),[9] which reacted with BOC anhydride to give (90%) the corresponding *N*-BOC derivative **13**, as shown in Scheme 1.

Several methods were explored to convert **13** into the corresponding trithiocarbonate **15**. In the first of these, we employed the Ueno procedure for the conversion of a

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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(8) Matteson, D. S.; Snyder, H. R. *J. Am. Chem. Soc.* **1957**, *79*, 3610.

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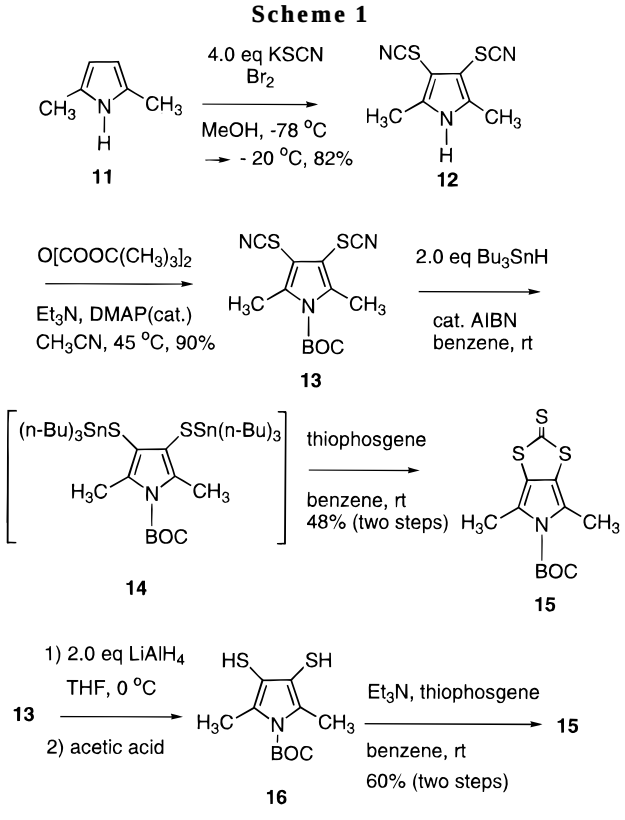
S0022-3263(96)01282-0 CCC: $12.00

Table 1. Crystal Data and Structure Refinement for 18[a]

color/shape	colorless/plate
empirical formula	$C_{22}H_{30}N_2O_4S_4$
formula weight	514.72
temperature	173(2) K
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions (1826 reflections in full ø range)	$a = 6.8845(8)$ Å $\alpha = 89.012(2)°$; $b = 9.0553(10)$ Å $\beta = 78.752(2)°$; $c = 10.9633(12)$ Å $\gamma = 72.068(2)°$
volume	637.10(12) Å^3
Z	1
density (calculated)	1.342 mg/m^3
absorption coefficient	0.403 mm^{-1}
diffractometer/scan	Siemens SMART/CCD area detector
radiation/wavelength	Mo Kα (graphite monochrom.)/0.710 73 Å
F (000)	272
crystal size	0.35 × 0.35 × 0.05 mm
ø range for data collection	1.90 to 23.30°
index ranges	$-5 \le h \le 7$, $-5 \le k \le 10$, $-11 \le l \le 12$
reflections collected	2548
independent/observed refls.	1779 ($R_{int} = 0.0835$)/1654 ([$I > 2\sigma(I)$])
refinement method	Full-matrix least-squares on F^2
computing	SHELXTL, Ver. 5
data/restraints/parameters	1769/0/150
goodness-of-fit on F^2	1.300
SHELX-93 weight parameters	0.0000, 2.7945
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0757$, w$R2 = 0.1587$
R indices (all data)	$R1 = 0.0931$, w$R2 = 0.1707$
largest diff peak and hole	0.339 and −0.452 eÅ^{-3}

[a] The authors have deposited atomic coordinates for **18** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Scheme 1



thiocyanate to a thioester.[10] Thus, the radical-initiated reaction of **13** with tributyltin hydride afforded, after careful chromatography, the oily bis(tributylstannyl) compound **14**, which reacted with thiophosgene to give the desired crystalline trithiocarbonate **15** (48% overall). A simpler route to **15** involved the direct lithium aluminum hydride (LAH) reduction of dithiocyanate **13** to give the air-sensitive dithiol **16**, which reacted with thiophosgene in the presence of triethylamine to give **15** (60% overall).[11] It is noteworthy that the *N*-BOC group of **13** survived the conditions of the LAH reduction.

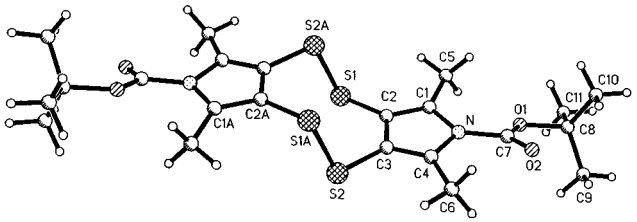


Figure 1. Compound18.

Attempts to reduce **13** to dithiol **16** using $NaBH_4$ led to an unexpected result. Instead of **16**, a virtually quantitative yield of a sparingly soluble yellow product was obtained which proved to be the eight-membered ring **18** (Scheme 2). The same compound was formed in high yield when dithiocyanate **13** was reacted with sodium methoxide or with hydrazine.[12] The conversion of a thiocyanate to a disulfide by an appropriate nucleophile is well documented;[13] however, the use of $NaBH_4$ in such a reaction is, to our knowledge, unprecedented.

When the reaction mixture was heated to 180 °C, **18** cleanly underwent facile loss of its BOC protecting groups[14] to give the unsubstituted **22**. The latter reacted with sodium hydride in DMF to give a dianion which reacted with iodomethane or 1-iodopentane to give the corresponding dialkylated **23** and **24** in high yields.

Although **18** was resistant to reduction by $NaBH_4$, it underwent reductive cleavage by LAH to form dithiol **16**,

(10) Ueno, Y.; Nozomi, M.; Okawara, M. *Chem. Lett.* **1982**, 1119.

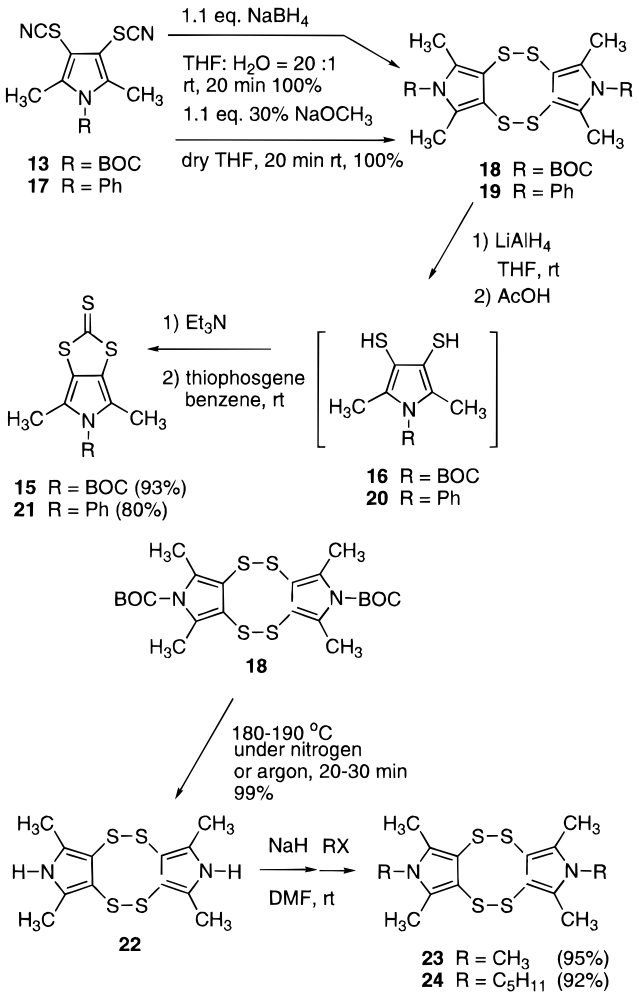
(11) (a) *The Chemistry of the Thiol Group*; Patai, S., Ed.; Chemistry of Functional Groups 31; John Wiley & Sons: London, 1974. (b) Schoberl, A.; Wagner, A. *Methoden Der Organischen Chemie;* Georg Thieme Verlag: Stuttgart, 1955; Chapter IX, p 23. (c) Ookawa, A.; Yokoyama, S.; Soai, K. *Synth. Commun.* **1986**, *22*, 1500.

(12) Maiti, S. N.; Spevak, P.; Singh, M. P.; Reddy, N. *Synth. Commun.* **1988**, *18*, 575.

(13) Tarbell, D. S.; Harnish, D. P. *Chem. Rev.* **1951**, *49*, 79.

(14) Rawal, V. H.; Cava, M. P. *Tetrahedron Lett.* **1985**, *26*, 6141.

Scheme 2



which was directly reacted with thiophosgene to give trithiocarbonate **15** in 93% yield. The route to **15** *via* **18** thus proved to be the best one for the preparation of multigram amounts of **15**.

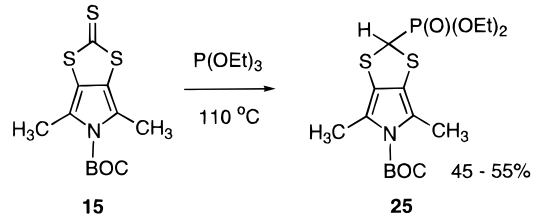
The *N*-phenyl analog (**21**) of **15** was conveniently prepared by a similar procedure. Thus, 2,5-dimethyl-*N*-phenylpyrrole[15] was converted to **21** by way of its 3,4-dithiocyano derivative **17** and **19**.

The structure of **18** was confirmed by X-ray crystallography, as shown in Figure 1. The two dithiopyrrole units lie in parallel planes and in a transoid configuration, an arrangement which minimizes the lone pair repulsions of the four sulfur atoms. The crystal data and structure refinement for **18** are given in Table 1.

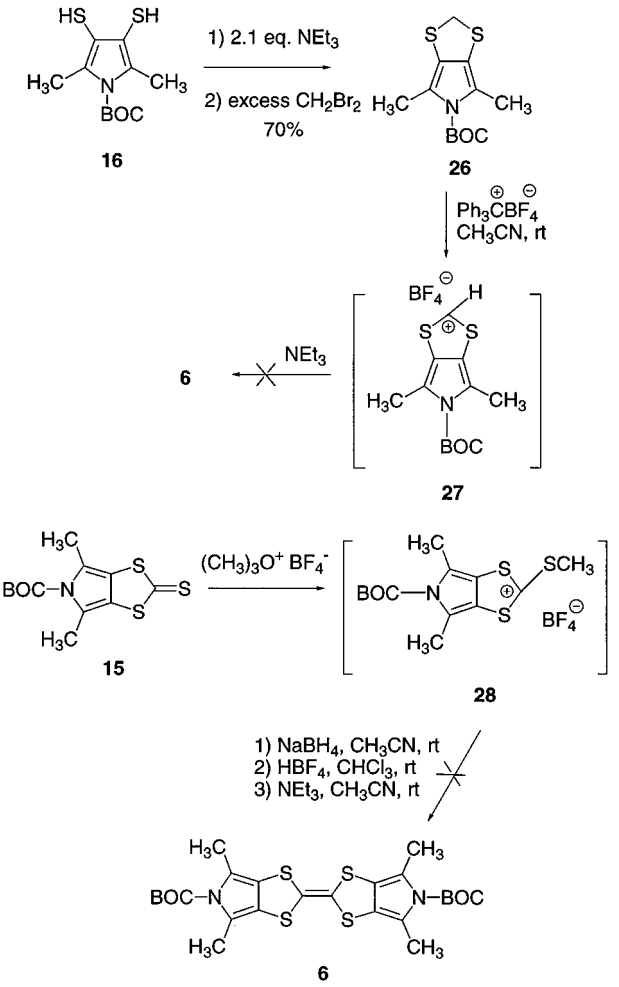
Synthesis of Bis(pyrrolo[3,4-*d*])tetrathiafulvalenes. A number of procedures were explored with the objective of converting either trithiocarbonate **15** or dithiol **16** into the corresponding TTF **6**. In the first of these, the well-known coupling reaction of a thione by a trivalent phosphorus reagent was attempted.[1b] When thione **15** was heated overnight with triethyl phosphite, however, TTF **6** was not obtained but the phosphonate ester **25** was isolated in 45−55% yield as shown in Scheme 3. Formation of this type of product, initiated by a carbophilic rather than a thiophilic attack of phosphorus at the thione function, has been described in other cases.[16]

We also envisioned the possibility of forming **6** by the basic-induced coupling of the appropriate dithiolium salt

Scheme 3



Scheme 4



precursor.[17,18] Thus, dithiol **16** was reacted with triethylamine followed by dibromomethane to give (70%) the crystalline 1,3-dithiole **26** (Scheme 4). Reaction of **26** with triphenylcarbenium fluoroborate gave a dark green solution, presumably containing salt **27**, which was treated with triethylamine. No coupling product **6** was produced. In a variation of this approach, thione **15** was reacted sequentially with trimethyloxonium fluoroborate, $NaBH_4$, HBF_4, and triethylamine;[19] the TTF derivative **6** was not obtained.

The reaction of tetrachloroethylene with the dianion of *o*-benzenedithiol to give dibenzotetrathiafulvalene has been known since 1926.[20] More recently, analogous reactions have been used to prepare related systems,

(15) Al-awar, R.; Wahl, G. H., Jr. *J. Chem. Educ.* **1990**, *67*, 265.
(16) Parg, P. R.; Kilburn, J. D.; Ryan, T. G. *Synthesis* **1994,** 195.
(17) (a) Klingsberg, E. *J. Am. Chem. Soc.* **1962**, *84*, 3410. (b) *Ibid.* **1964**, *86*, 5290.
(18) Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Canfield, N. D. *J. Am. Chem. Soc.* **1971**, *93*, 2258.
(19) (a) Rondestvedt, C. *Org. React.* **1976**, *24*, 225. (b) *Ibid.* **1960**, *11*, 198.
(20) Hurtly, W. R. H.; Smiles, S. *J. Chem. Soc.* **1926**, 2263.

Scheme 5

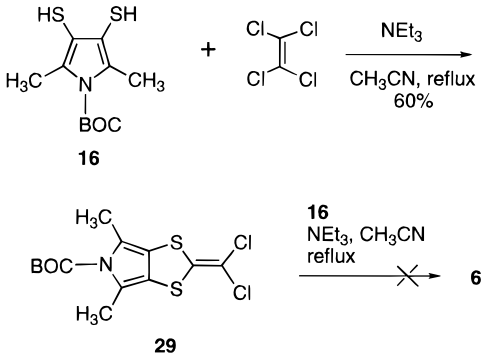
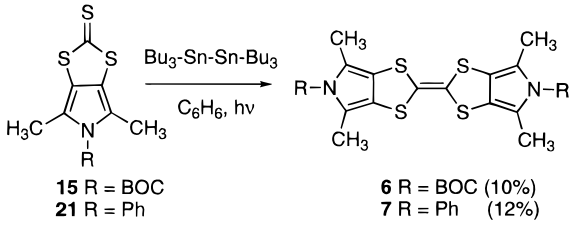


Table 2. Cyclic Voltammetry of Compounds 6, 7, 8, 9, and 10 vs SCE[a]

compound	$E_{1/2}^1$	$E_{1/2}^2$
6	0.613	1.081
7	0.289	0.838
8	0.298	0.863
9	0.289	0.833
10	0.275	0.805
1 (TTF)	0.390	0.765
2 (ET)	0.510	0.921

[a] Cyclic voltammetry was carried out in a 0.1 M solution of Bu_4NPF_6 in dichloromethane at rt; scan speed 100 mV/s.

Scheme 6



including tetratellurafulvalenes.[21,22] In the case of our dithiol **16**, the crystalline dichlorofulvene intermediate **29** was formed in 60% yield as shown in Scheme 5. However, attempts to react **29** with a further molecule of **16** were unsuccessful.

Our first successful synthesis of **6** employed the Ueno methodology, in which a thione is coupled photochemically using hexabutyldistannane as the desulfurizing agent.[23] Unfortunately, yields were variable and low, averaging only 10−12%. A similar reaction using the *N*-phenyl thione **21** gave the corresponding TTF **7** in 15% yield, as shown in Scheme 6.

The phosphite coupling of dithiocarbonates to TTF derivatives often is more successful than trithiocarbonate couplings. Thiones **15**, **21**, and **30** were all converted in high yields (90−92%) by mercuric acetate into the dithiocarbonates **31**, **32**, and **33** (Scheme 7).[24]

When the dithiocarbonates were heated with triethyl phosphite at 110 °C for 12 h, the corresponding TTF derivatives **6**, **7**, and **9** were formed in good yields (73, 53, and 55%, respectively), and the pure products were easily recovered directly from the reaction mixtures. The *N*-BOC **31** was also an excellent precursor to its *N*-alkyl analogs. When the reaction mixture was heated to 180−190 °C, **31** gave the unprotected **34** (92%), which could be alkylated under standard conditions (NaH, DMF) to give the *N*-methyl and *N*-pentyl compounds (**33** and **35**) in almost quantitative yields.

Removal of the *N*-BOC protecting groups of **6** was best carried out by treatment of **6** with sodium methoxide. The resulting TTF, **8**, could be cleanly dialkylated to give the *N*,*N*′-dialkyl derivatives **9** and **10**, as shown in Scheme 8.

Scheme 7

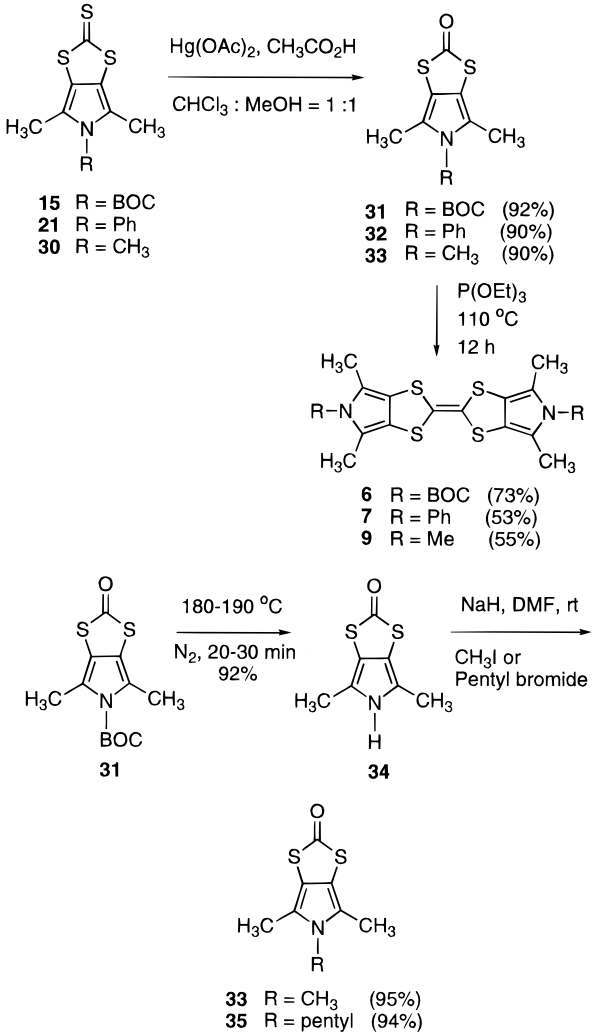


Table 3. Room Temperature 2-Probe Conductivities of TCNQ Complexes of 1, 7, 8, and 9

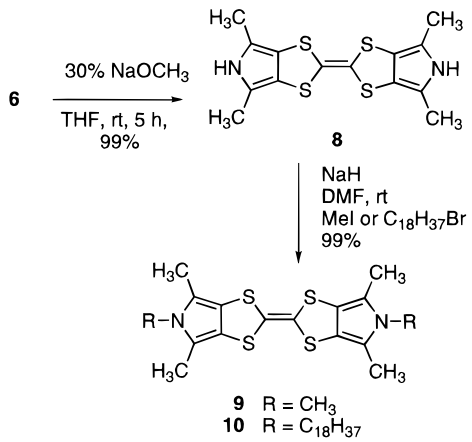
donors	acceptor	ratio	conductivities[a] σ, S cm^{-1}
1	TCNQ	1:1	0.89
7	TCNQ	1:1	0.58
8	TCNQ	1:1	1.2×10^{-7}
9	TCNQ	1:1	1.50

[a] The values represent the averages of five measurements of each complex.

Bis(pyrrolo[3,4-*d*])tetrathiafulvalenes as Electron Donors. Compounds **7, 8, 9**, and **10** proved to be excellent donors and showed two quasi-reversible oxidation waves, while the oxidation potentials for **6** were relatively higher due to the electron-withdrawing BOC groups (Table 2). For comparison with the well-known donors TTF (**1**) and ET (**2**), the oxidation potentials for these compounds were determined under the same conditions and in the same equipment.

(21) Bajwa, G. S.; Berlin, K. D.; Pohl, H. A. *J. Org. Chem.* **1976**, *41*, 145.
(22) Mizuno, M.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 416.
(23) Ueno, Y.; Nakayama, A.; Okawara, M. *J. Am. Chem. Soc.* **1976**, *98*, 7440.
(24) Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Sythesis* **1994**, 809.

Scheme 8



Compounds **7, 8, 9,** and **10** all showed lower first half-wave oxidation potentials than TTF (0.390 V) and ET (0.510 V). It may be noted that the pyrrolotetrathiafulvalene (**10**) with long *N*-alkyl chains showed the lowest oxidation potential, presumably due to the electron donating effect of the long alkyl groups.

With donors **7**, **8**, and **9** in hand, complex formation with TCNQ was investigated. As expected, all three formed crystalline charge-transfer complexes in acetonitrile, which were shown to be 1:1 complexes by elemental analysis. Two-probe conductivity measurements on compressed powders[25] and those compared to TTF−TCNQ as a standard were determined in the same equipment. The results are shown in Table 3. In comparison with TTF−TCNQ (entry 1), the *N*-phenyl derived annelated TTF−TCNQ complex showed comparable conductivity (entry 2, 0.58) as a conductor. However, the pyrrolo-annelated TTF−TCNQ complex (entry 3) showed poor conductivity (around 1.2×10^{-7}) in the semiconductor range. Most strikingly, the *N*-methyl derived annelated TTF−TCNQ complex showed excellent conductivity (entry 4, 1.50), even higher than that of TTF−TCNQ.

Conclusions

Practical syntheses have been developed for several bis(pyrrolo[*d*])tetrathiafulvalenes. The *N*-unsubstituted (**8**), *N*-phenyl (**7**), and *N*-alkyl (**9** and **10**) derivatives all show excellent donor properties, and **7** and **9** form 1:1 TCNQ complexes, which are good conductors. Further work that is in progress in our laboratory is aimed at additional studies of this new annelated TTF family, including the synthesis of unsymmetrical analogs and the growth of single-crystal conducting salts.

Experimental Section

General. All of the reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. THF was distilled from sodium benzophenone ketyl. Conductivities were measured using an instrument made in our laboratory according to ref 25.

2,5-Dimethyl-3,4-dithiocyanopyrrole (12). To a solution of potassium thiocyanate (204 g, 2.05 mol) in MeOH (250 mL) at −78 °C was added slowly a precooled solution of Br_2 (160 g, 1.00 mol) in MeOH (250 mL). The reaction mixture was stirred at −40 °C for 45 min, followed by the addition of a precooled solution of 2,5-dimethylpyrrole (50.0 g, 0.526 mol) in MeOH (175 mL). The reaction mixture was stirred at −25 °C for 45 min, and then it was poured into a mixture of ice (260 g) and NaCl (40 g). After the ice melted, the resulting precipitate was collected by filtration, washed with water, and air-dried. The crude material was purified by recrystallization in dichloromethane/hexane (1:4) to give the pure product (90.1 g, 82%) as a white solid: mp 134−136 °C (lit.[8,9] mp 132 °C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 9.00 (s, 1H), 2.39 (s, 6H).

2,5-Dimethyl-3,4-dithiocyano-*N*-*tert*-butoxycarbonylpyrrole (13). To a solution of 2,5-dimethyl-3,4-dithiocyanopyrrole (**12**) (6.00 g, 28.70 mmol) in acetonitrile (30 mL) were added di-*tert*-butyl dicarbonate (6.27 g, 28.7 mmol), a catalytic amount of DMAP (50 mg), and triethylamine (4.0 mL, 28.7 mmol) at rt. The reaction mixture was heated to 45 °C and stirred for 45 min. The reaction was cooled to rt and the solvent was removed under reduced pressure. The residue was purified by recrystallization in CH_2Cl_2/hexane (1:4) to afford the product (8.00 g, 90%) as pale yellow crystals: mp 165−167 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.60 (s, 6H), 1.64 (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 148.06, 138.97, 109.86, 104.85, 87.05, 27.86, 14.61; MS (*m/e*, M^+) 309 (15), 209 (100), 151 (31), 93 (21). Anal. Calcd for $C_{13}H_{15}N_3S_2O_2$: C, 50.48; H, 4.85; N, 13.59; S, 20.71. Found: C, 49.95; H, 4.62; N, 13.51; S, 20.96.

2,7-Bis(*tert*-butoxycarbonyl)-1,3,6,8-tetramethyl-[1,2,5,6]-tetrathiocino[4,5-*c*]pyrrole (18). To a solution of dithiocyanate **13** (14.78 g, 47.85 mmol) in aqueous THF (180 mL, 20:1 THF/H_2O) was added $NaBH_4$ (1.99 g, 52.63 mmol) at rt. While the mixture was stirred for 2.25 h the reaction became exothermic (H_2 evolution) and a considerable amount of precipitate was formed. The reaction mixture was diluted with water (100 mL), and the solid was collected by filtration and washed with water (20 mL). The air-dried product was purified by treatment with hot acetone to afford the product (12.3 g, 100%) as a pale yellow powder. Recrystallization from $CHCl_3$/hexane (1:2) gave pale yellow crystals: mp > 250 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.56 (s, 6H), 1.59 (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 218.60, 149.25, 137.01, 120.42, 85.09, 46.78, 27.96, 14.65; MS (*m/e*) 314 (M^+, 68), 250 (100), 156 (47), 125 (39), 100 (57), 81 (90); IR (KBr) 3400 (s), 1510 (m), 1395 (m), 640 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_2O_4S_4$: C, 51.36; H, 5.83; N, 5.44; S, 24.90. Found: C, 51.52; H, 5.96; N, 5.41; S, 24.56.

5-*tert*-Butoxycarbonyl-4,6-dimethyl-2-thioxo-1,3-dithiolo[4,5-*c*]pyrrole (15). Method 1. To a solution of **13** (5.00 g, 16.2 mmol) in benzene (45 mL) were added 2.0 equiv of tributyltin hydride (9.30 g, 32.3 mmol) and a catalytic amount of 2,2′-azobis(isobutyronitrile) (AIBN) under nitrogen at rt. The stirred reaction mixture was heated to 75 °C for 5 h and then cooled to rt. After removal of the solvent, the crude product was purified by chromatography (silica gel) using ethyl acetate/hexane (1:10) as the eluent to afford 2,5-dimethyl-3,4-bis(tributylthiostannyl)-*N*-*tert*-butoxycarbonylpyrrole (**14**, 8.10 g) as a pale yellow, light-sensitive oil: ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 6H), 1.63−0.89 (m, 63H). To a solution of the stannyl compound (8.10 g) in benzene (60 mL) was added dropwise a solution of thiophosgene (1.10 g, 9.6 mmol) in benzene (40 mL) under nitrogen at rt. After the mixture was stirred for 2 h, the reaction mixture was poured into water (200 mL). The organic layer was separated, dried over Na_2SO_4, and concd under reduced pressure. The resulting precipitate was filtered, washed with diethyl ether, and recrystallized from CH_2Cl_2/hexane (1:3) to give **15** (2.5 g, 48% overall) as yellow needles.

Method 2. To a solution of lithium aluminum hydride (1.20 g, 32.4 mmol) in dry THF (25 mL) was slowly added 2,5-dimethyl-3,4-dithiocyano-*N*-*tert*-butoxycarbonylpyrrole (**13**) (5.10 g, 16.1 mmol) in dry THF (50 mL) under nitrogen. The reaction mixture was stirred for 5 h at rt, and then acetic acid in diethyl ether was slowly added until the color of the solution changed from pink to yellow. The reaction mixture was added to ice water (200 mL), extracted with diethyl ether (100 mL × 2), and washed with brine (50 mL). The organic layer was dried over sodium sulfate and concd to afford dithiol **16** (2.90 g, 70%) as orange crystals: ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.64 (s, 2H), 2.45 (s, 6H), 1.59 (s, 9H); MS (*m/e*) 259 (M^+, 15), 159 (100), 126 (51), 94 (14). Into neat dithiol **16** (1.05 g, 3.89 mmol) was added triethylamine (1.2 mL, 8.56 mmol) under nitrogen at rt. Benzene (15 mL) was then added, and the reaction mixture was stirred for 10 min. A solution of thiophosgene

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(492 mg, 4.28 mmol) in benzene (20 mL) was then introduced dropwise, and the reaction mixture was stirred for a further 30 min, then concd under reduced pressure, diluted with water (30 mL), and extracted with CH_2Cl_2 (20 mL × 3). The combined extracts were dried over sodium sulfate and concd under reduced pressure to afford the crude product, which was passed through a short column of silica gel. Purification by recrystallization in dichloromethane/hexane (1:5) gave **15** (1.00 g, 85.4%, 60% overall) as yellow needles: mp 165−167 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.39 (s, 6H), 1.62 (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 218.60, 149.45, 124.06, 120.53, 85.15, 28.05, 16.24; MS (*m*/*e*) 301 (M^+, 32), 303 (6), 245 (31), 201 (13), 57 (100); IR (KBr) 1720 (s), 1600 (m), 1350 (m), 1300 (m), 1150 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_2S_3$: C, 47.82; H, 5.06; N, 4.62; S, 31.84. Found: C, 47.82; H, 5.02; N, 4.65; S, 31.91.

Method 3. To a solution of **18** (7.35 g, 14.30 mmol) in dry THF (250 mL) was added $LiAlH_4$ (1.19 g, 31.46 mmol) in portions under nitrogen at rt. The reaction mixture was stirred for 3 h, and a slight excess of acetic acid in diethyl ether was then added carefully. The reaction mixture was concd under reduced pressure, followed by the addition of water (20 mL) and diethyl ether (150 mL). The mixture was shaken vigorously and allowed to stand for 10−15 min. The clear ether layer was carefully decanted, and this procedure was repeated three times. The combined ether layers were dried over Na_2SO_4 and concd under reduced pressure. The crude product, dithiol, **16** was dried under high vacuum (0.5 mmHg) for 5 h, then dissolved in degassed benzene (50 mL) and triethylamine (5.89 mL, 42.22 mmol) that were added with vigorous stirring under nitrogen at rt. To the solution was added dropwise thiophosgene (3.29 g, 28.60 mmol) in benzene (150 mL) under nitrogen. The reaction mixture was stirred for 1 h, the benzene was removed under reduced pressure, water (180 mL) was added, and the mixture was extracted with CH_2Cl_2 (150 mL × 3). The combined extract was dried over Na_2SO_4, concd, and purified by short column chromatography (silica gel) using dichloromethane/hexane (3:1) as the eluent to afford **15** (8.05 g, 93%) as yellow needles.

2,5-Dimethyl-3,4-dithiocyano-*N*-phenylpyrrole (17). This compound was prepared from 2,5-dimethyl-*N*-phenylpyrrole[15] by the procedure used for the preparation of **12**; 75% yield, pale yellow crystals: mp 112−114 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.65−7.43 (m, 2H), 7.26−7.12 (m, 3H), 2.16 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 137.64, 136.57, 129.95, 129.70, 127.47, 110.67, 100.37, 11.77; IR ($CDCl_3$) 3040 (m), 2420 (m), 1610 (m), 1520 (s), 1420 (s), 1250 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{11}N_3S_2$: C, 58.94; H, 3.85; N, 14.73; S, 22.45. Found: C, 58.87; H, 3.87; N, 14.65; S, 22.39.

1,3,6,8-Tetramethyl-2,7-bis(phenyl)-[1,2,5,6]tetrathiocino[3,4-*c*:8,7-*c*′]dipyrrole (19). This was prepared from **17** in 100% yield as a pale yellow powder: mp > 250 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.61−7.29 (m, 8H), 7.15−7.09 (m, 2H), 2.14 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 138.09, 135.69, 129.45, 128.62, 127.95, 116, 65, 11.91; IR ($CDCl_3$) 3400 (s), 3000 (s), 1550 (s), 1520 (s), 1420 cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_2S_4$: C, 61.74; H, 4.72; N, 6.00; S, 27.46. Found: C, 61.57; H, 4.70; N, 5.95; S, 26.95.

4,6-Dimethyl-5-phenyl-2-thioxo-1,3-dithiolo[4,5-*c*]pyrrole (21). This was prepared from **19** by the LAH reduction procedure as yellow crystals in 80% yield: mp 138−140 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.66−7.42 (m, 2H), 7.26−7.12 (m, 3H), 2.04 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 198.45, 136.95, 129.40, 128.15, 127.45, 121.89, 108.95, 12.72; IR (KBr) 1720 (s), 1600 (m), 1350 (m), 1300 (m), 1150 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{11}NS_3$: C, 56.28; H, 3.97; N, 5.05; S, 34.67. Found: C, 56.23; H, 4.00; N, 4.99; S, 34.60

1,3,6,8-Tetramethyl-2*H*,7*H*-[1,2,5,6]tetrathiocino[3,4-*c*:8,7-*c*′]pyrrole (22). 18 (1.00 g, 1.94 mmol) was placed in a 25 mL round-bottom flask and heated to 190−195 °C under nitrogen for 30−40 min. The material was cooled to room temperature and recrystallized from DMF to afford **22** (608 mg, 99%) as pale yellow needles: mp > 250 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.95 (s, 2H), 2.26 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 118.67, 109.23, 12.73; IR ($CDCl_3$) 3400 (m), 3040 (s), 1680 (s), 1380 (m), 1260 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{28}N_4O_2S_4$ (two molecular DMFs): C, 46.95; H, 6.08; N, 12.17; S, 27.82. Found: C, 46.98; H, 6.06; N, 12.12; S, 27.94.

General Procedure for *N*-Alkylation. 1,2,3,6,7,8-Hexamethyl-[1,2,5,6]tetrathiocino[3,4-*c*:8,7-*c*′]dipyrrole (23). To a solution of **22** (2.13 g, 6.78 mmol) in dry DMF (30 mL) was added hexane-washed NaH (650 mg, 27.12 mmol) in portions under nitrogen at rt. The mixture was stirred for 5 min, followed by the addition of iodomethane (568 mg, 23.66 mmol). The solution was stirred for 20 min and water (20 mL) was added carefully. The precipitate was washed with methanol (10 mL) and then acetonitrile (20 mL) to give the product (2.2 g, 95%) as a white solid: mp > 250 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.40 (s, 6H), 2.34 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 116.70, 116.07, 31.35, 11.55; IR ($CDCl_3$) 3040 (s), 1550 (m), 1260 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_2S_4$: C, 49.12; H, 5.26; N, 8.18; S, 37.42. Found: C, 49.03; H, 5.24; N, 8.70; S, 36.97.

2,7-Dicyclopentyl-1,3,6,8-tetramethyl-[1,2,5,6]tetrathiocino[3,4-*c*:8,7-*c*′]dipyrrole (24). Alkylation using 1-iodopentane gave (92%) pale yellow crystals: mp 229−232 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.72 (t, J = 7.86 Hz, 4H), 2.36 (s, 12H), 1.62 (m, 4H), 1.34 (m, 8H), 0.92 (t, J = 6.73 Hz, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 134.34, 116.21, 45.27, 30.11, 28.98, 22.27, 13.86, 11.03; IR ($CDCl_3$) 3040 (s), 1560 (s), 1450 (m), 1395 (m), 1260 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{34}N_2S_4$: C, 58.14; H, 7.48; N, 6.16; S, 28.19. Found: C, 57.61; H, 7.58; N, 6.13; S, 28.01.

5-tert-Butoxycarbonyl-4,6-dimethyl-2(*O*,*O*-diethylphosphonyl)-1,3-dithiolo[4,5-*c*]pyrrole (25). To **15** (2.10 g, 6.6 mmol) was added triethyl phosphite (8 mL) in one portion under nitrogen at rt. The reaction mixture was heated at 110 °C for 5 h. Excess triethyl phosphite was removed under vacuum (1 mmHg) at 80 °C, and the residue was purified by silica chromatography (100 g) using ethyl acetate/hexane (2:1) to afford the product (1.20 g, 45%) as a pale yellow oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.08 (d, J = 6.6 Hz, 1H), 4.32 (m, 4H), 2.30 (s, 6H), 1.56 (s, 9H), 1.29 (t, J = 7.5 Hz, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 149.19, 123.09, 122.04, 83.58, 64.17, 64.09, 53.44, 51.69, 28.07, 16.48, 16.37, 16.31; MS (*m*/*e*) 407 (M^+, 69), 351 (17), 307 (37), 169 (100), 57 (84); IR (neat) 3000 (s), 1760 (s), 1350 (m), 1310 (s), 1270 (s), 980 (m), 870 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{26}NO_5S_2P$: C, 47.17; H, 6.38; N, 3.43; S, 15.72; P, 7.61. Found: C, 47.43; H, 6.33; N, 3.01; S, 15.65; P, 7.90.

Distannane Coupling Reactions. (a) Bis(2,5-dimethyl-*N*-*tert*-butoxycarbonylpyrrolo[3,4-*d*])tetrathiafulvalene (6). To a solution of **15** (0.50 g, 1.60 mmol) in benzene (500 mL) was added hexabutyldistannane (1.40 g, 2.4 mmol). The reaction mixture was irradiated with a 250-W medium pressure mercury immersion lamp for 5 h under nitrogen. After the solvent was removed under reduced pressure, the residue was treated with hexane to give a pale yellow solid. Purification by silica chromatography using ethyl acetate/hexane (1:10) as the eluent, followed by recrystallization from acetonitrile, gave **6** (44.0 mg, 10%) as pale yellow crystals: mp > 250 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.32 (s, 12H), 1.58 (s, 18H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 149.42, 121.36, 120.70, 119.81, 83.91, 28.12, 16.31; MS (*m*/*e*) 538 (M^+, 14), 438 (39), 426 (93), 382 (76), 338 (100), 57 (41); IR (KBr) 2960 (m), 1730 (s), 1310 (s), 1280 (m), 1170 (m), 1130 (s) cm^{-1}.

(b) Bis(2,5-dimethyl-*N*-phenylpyrrolo[3,4-*d*])tetrathiafulvalene (7). Obtained from **21** in 15% yield, yellow crystals: mp > 250 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.52−7.38 (m, 6H), 7.22−7.15 (m, 4H), 1.97 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 138.27, 129.26, 128.25, 128.09, 120.37, 119.48, 116.15, 12.49; IR (KBr) 3215 (s), 3050 (m), 1645 (m), 1450 (m), 1105 (m), 970 (m), 860 (m) cm^{-1}; MS (*m*/*e*) 490 (M^+, 100), 289 (4), 261 (39), 246 (76), 233 (66), 200 (39). Anal. Calcd for $C_{26}H_{22}N_2S_4$: C, 63.64; H, 4.52; N, 5.71; S, 26.13. Found: C, 63.50; H, 4.31; N, 5.45; S, 26.45.

5-*tert*-Butoxycarbonyl-4,6-dimethyl-1,3-dithiolo[4,5-*c*]-pyrrole (26). Into neat dithiol **16** (4.10 g, 15.4 mmol) was added triethylamine (3.40 g, 33.0 mmol) under nitrogen at rt. To the deep red solution was added excess methylene bromide (ca. 10 mL) in one portion. After 10 min, 30 mL of methylene chloride was added, and the resulting mixture was refluxed at 35 °C for 5 h under nitrogen. The white precipitate was filtered off, and the filtrate was washed twice with water (100

mL). The organic layer was dried over Na_2SO_4 and concd under reduced pressure. Purification by chromatography on silica gel using ethyl acetate/hexane (1:8) as the eluent, followed by recrystallization from CH_2Cl_2−hexane (1:5), afforded **26** as white crystals (2.0 g, 60%): mp 110−112 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.75 (s, 2H), 2.32 (s, 6H), 1.56 (s, 9H); MS (*m*/*e*) 271 (M^+, 80), 216 (35), 171 (47), 170 (100), 138 (30), 57 (50); IR (KBr) 3000 (m), 2930 (m), 1740 (s), 1350 (s), 1310 (s), 1150 (s), 870 (s), 780 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{17}NS_2O_2$: C, 53.13; H, 6.27; N, 5.16; S, 23.61. Found: C, 53.17; H, 6.31; N, 5.14; S, 23.70.

5-*tert*-Butoxycarbonyl-4,6-dimethyl-2-dichloromethylene-1,3-dithiolo[4,5-*c*]pyrrole (29). Into neat dithiol **16** (2.90 g, 11.1 mmol) were added tetrachloroethylene (ca. 15 mL) and triethylamine (3.20 g, 31.0 mmol). The reaction mixture was refluxed with stirring under nitrogen for 2 h and then cooled to rt. Water (200 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (70.0 mL × 3). The combined organic extract was dried over Na_2SO_4 and concd under reduced pressure. Purification by chromatography on silica gel using ethyl acetate/hexane (1:8) as the eluent, followed by recrystallization from CH_2Cl_2/hexane (1:5), afforded **29** as white crystals (2.2 g, 50%): mp 170−172 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.23 (s, 6H), 1.61 (s, 9H); MS (*m*/*e*) 352 (M^+, 35), 252 (100), 216 (73); IR (KBr) 3400 (s), 2990 (m), 1540 (m), 1380 (m), 1310 (m), 1120 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{15}NS_2Cl_2O_2$: N, 3.97; S, 18.18; Cl, 20.17. Found: N, 3.66; S, 18.45; Cl, 19.85.

4,5,6-Trimethyl-2-thioxo-1,3-dithiolo[4,5-*c*]pyrrole (30). This was prepared from **23** by the LAH reduction procedure as a yellow solid in 65% yield: mp 142−144 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.48 (s, 3H), 2.23 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 218.63, 118.68, 118.39, 31.32, 12.12; IR ($CDCl_3$) 3020 (s), 2910 (m), 1560 (m), 1480 (m), 1060 (s) cm^{-1}. Anal. Calcd for $C_8H_9NS_3$: C, 44.65; H, 4.18; N, 6.51; S, 44.65. Found: C, 44.49; H, 4.23; N, 6.44; S, 44.51.

General Procedure for Dethionation by Mercuric Diacetate. (a) 5-*tert*-Butoxycarbonyl-4,6-dimethyl-2-oxo-1,3-dithiolo[4,5-*c*]pyrrole (31). To a solution of (**15**) (1.59 g, 4.98 mmol) in $CHCl_3$ (8 mL) was added mercuric diacetate (2.38 g, 7.47 mmol) in aqueous methanol (8 mL) and acetic acid (1.5 mL) at rt. The reaction mixture was stirred for 3 h, and the precipitate was then filtered off through a Celite-packed funnel under aspirator suction, the Celite being then washed with chloroform (30 mL). The filtrate was washed with saturated sodium bicarbonate, water, and brine and dried over sodium sulfate. Upon concentration under reduced pressure, the residue was purified by chromatography on silica gel (30.0 g) using CH_2Cl_2/hexane (3:1) as the eluent to afford the product (1.30 g, 92%) as a colorless solid. The crude product was purified by crystallization from methanol: mp 185−187 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.41 (s, 6H), 1.61 (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 220.43, 149.32, 122.78, 114.67, 84.72, 28.07, 16.52; IR (KBr) 3215 (s), 3050 (m), 1645 (m), 1450 (m), 1105 (m), 970 (m), 860 (m) cm^{-1}; MS (*m*/*e*) 285 (M^+, 28), 257 (36), 185 (100), 157 (45), 156 (58), 112 (19), 93 (24). Anal. Calcd for $C_{12}H_{15}NO_3S_2$: N, 4.91; S, 22.45. Found: N, 4.86; S, 22.72.

(b) 4,6-Dimethyl-5-phenyl-2-oxo-1,3-dithiolo[4,5-*c*]pyrrole (32). This was obtained in 90% yield as pale yellow crystals: mp 185−187 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.61−7.48 (m, 3H), 7.32−7.16 (m, 2H), 2.10 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 195.77, 137.54, 129.45, 128.61, 128.15, 121.15, 109.32, 12.72; IR ($CDCl_3$) 3040 (s), 2045 (m), 1730 (s), 1660 (s), 1520 (s), 1400 (s), 1250 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{11}NOS_2$: C, 59.77; H, 4.21; N, 5.36; S, 24.52. Found: C, 59.75; H, 4.25; N, 5.41; S, 24.61.

(c) 4,5,6-Trimethyl-2-oxo-1,3-dithiolo[4,5-*c*]pyrrole (33). This was obtained in 90% yield as pale yellow crystals: mp 96−98 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.46 (s, 3H), 2.23 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 196.15, 120.31, 107.87, 30.91, 12.31; IR ($CDCl_3$) 3030 (s), 1680 (s), 1650 (m), 1450 (m), 1380 (m), 1050 (m) cm^{-1}. Anal. Calcd for $C_8H_9NOS_2$: C, 48.24; H, 4.52; N, 7.03; S, 32.16. Found: C, 48.32; H, 4.55; N, 6.97; S, 32.26.

4,6-Dimethyl-2-oxo-5*H*-1,3-dithiolo[4,5-*c*]pyrrole (34). This was prepared by pyrolysis of the BOC derivative **31** (see synthesis of **22** from **18** for conditions). It formed white crystals (92%): mp 183−184 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.93 (s, 1H), 2.28 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 196.55, 118.66, 109.30, 12.75; IR ($CDCl_3$) 3400 (s), 2995 (m), 1780 (s), 1540 (m) cm^{-1}. Anal. Calcd for $C_7H_7NS_2O$: C, 45.40; H, 3.78; N, 7.56; S, 34.59. Found: C, 45.48; H, 3.86; N, 7.55; S, 34.61.

Alkylation of 34. 4,6-Dimethyl-5-pentyl-2-oxo-1,3-dithiolo[4,5-*c*]pyrrole (35). For the procedure used, see general *N*-alkylation (preparation of **24**). Purification by chromatography (silica gel) and using CH_2Cl_2/hexane (3:1) as the eluent afforded a colorless oil (94%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.80 (t, J = 7.6 Hz, 2H), 2.25 (s, 6H), 1.65 (m, 2H), 1.32 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 196.20, 119.28, 108.20, 44.50, 30.77, 28.88, 22.36, 13.90, 12.31; IR ($CDCl_3$) 2980 (s), 2045 (m), 1760 (s), 1660 (s), 1520 (s), 1400 (s), 1250 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{17}NOS_2$: C, 56.47; H, 6.66; N, 5.49; S, 25.09. Found: C, 56.55; H, 6.71; N, 5.54; S, 25.12.

General Procedure for Triethyl Phosphite Coupling. A solution of the dithiocarbonate in triethyl phosphite (1:6 mol ratio) was heated to 105−110 °C under nitrogen for 12 h. The product usually separated out during the course of the reaction. The reaction mixture was cooled to rt, double the volume of methanol was added, and the product was collected by filtration and washed with methanol. Purification was effected by washing with hot acetonitrile or recrystallization from DMF to give the following tetrathiafulvalenes:

(a) Bis(2,5-dimethyl-*N*-*tert*-butoxycarbonylpyrrolo-[3,4-*d*])tetrathiafulvalene (6). 73% yield. The physical and spectroscopic data were identical to those of the material formed by the distannane method.

(b) Bis(2,5-dimethyl-*N*-phenylpyrrolo[3,4-*d*])tetrathiafulvalene (7). 53% yield. The physical and spectroscopic data were identical to those of the material formed by the distannane method.

(c) Bis(2,5-dimethyl-*N*-methylpyrrolo[3,4-*d*])tetrathiafulvalene (9). 55% yield, yellow microcrystals: mp > 250 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.34 (s, 6H), 2.13 (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 120.15, 118.63, 114.42, 30.98, 11.99; IR ($CDCl_3$) 3040 (s), 2995 (m), 1760 (m), 1540 (m), 1440 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{18}N_2S_4$: C, 52,46; H, 4.91; N, 7.65; S, 34.97. Found: C, 52.49; H, 4.98; N, 7.65; S, 34.90.

Bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (8). A solution of BOC−TTF **6** (1.62 g, 3.01 mmol) in dry DMF (120 mL) was degassed by a nitrogen stream for 15−20 min. To this solution was added 30% sodium methoxide in methanol (2.87 mL, 15.05 mmol) at rt, and the mixture was stirred under nitrogen for 12 h. Water (10 mL) was added, and the solvents were partially removed under reduced pressure. An additional 10 mL of water was added, and the resulting precipitate was collected by filtration and washed with methanol (15 mL) to give the product (1.05 g, 99%) as yellow crystals: mp > 250 °C; ^{1}H NMR (360 MHz, DMSO-d_6) δ 10.60 (s, 2H), 2.08 (s, 12H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 124.51, 122.16, 118.44, 17.22; IR (KBr) 3230 (s), 2930 (s), 1620 (m), 1460 (m), 1375 (m), 1159 (s), 870 (s), 785 (m) cm^{-1}; MS (*m*/*e*) 338 (M^+, 100), 314 (12), 213 (53), 169 (13). Anal. Calcd for $C_{14}H_{14}N_2S_4$: C, 49.70; H, 4.28; N, 8.28; S, 37.86. Found: C, 49.61; H, 4.35; N, 8.10; S, 37.62.

Bis(2,5-dimethyl-*N*-methylpyrrolo[3,4-*d*])tetrathiafulvalene (9). This compound was obtained from **8** by the general procedure for *N*-alkylation (99% yield). All of the physical and spectroscopic data were identical to those of the compound obtained by the coupling reaction in triethyl phosphite.

Bis(2,5-dimethyl-*N*-octadecanylpyrrolo[3,4-*d*])tetrathiafulvalene (10). This compound was obtained from **8** by the general procedure for *N*-alkylation (99% yield) as yellow crystals: mp 126−128 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.65 (m, 4H), 2.15 (s, 12H), 1.60−1.15 (m, 64H), 0.90 (t, J = 6.58 Hz, 6H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 117.82, 115.00, 114.68, 44.47, 31.91, 31.50−27.00 (13C), 26.77, 22.68, 14.10, 11.99; IR ($CDCl_3$) 2980 (s), 2270 (m), 1470 (s), 1420 (s), 1390

(s), 1100 (m) cm^{-1}. Anal. Calcd for $C_{50}H_{86}N_2S_4$: C, 71.25; H, 10.21; N, 3.32; S, 15.20. Found: C, 71.16; H, 10.27; N, 3.25; S, 15.29.

General Procedure for the Preparation of Charge-Transfer Complexes. A degassed hot solution of the donor (1.0 equiv) in acetonitrile was treated with a hot acetonitrile solution of TCNQ (1.0 equiv). The resulting green solution was allowed to cool to rt very slowly (which was accomplished by wrapping the flask with cotton or glass wool). After 3−4 h, the green charge-transfer complex crystals were collected by vacuum filtration.

Complex of Donor 7 with TCNQ. Anal. Calcd for $C_{38}H_{26}N_6S_4$: C, 65.68; H, 3.77; N, 12.09; S, 18.45. Found: C, 65.69; H, 3.83; N, 12.01; S, 18.44.

Complex of Donor 8 with TCNQ. Anal. Calcd for $C_{26}H_{18}N_6S_4$: C, 57.54; H, 3.34; N, 15.48; S, 23.63. Found: C, 57.66; H, 3.39; N, 15.37; S, 23.52.

Complex of Donor 9 with TCNQ. Anal. Calcd for $C_{26}H_{18}N_6S_4$: C, 58.92; H, 3.89; N, 14.72; S, 22.47. Found: C, 58.67; H, 3.96; N, 14.53; S, 22.67.

Acknowledgment. We thank the National Science Foundation (Grant CHE9224899) for support of this work.

JO961282H