# Preparation of Some Monophenyltetrathiafulvalenes and (*p*-Vinylphenyl)tetrathiafulvalene and Its Polymerization

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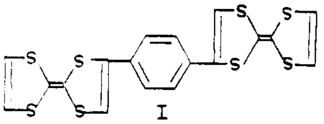
A method for the synthesis of phenyltetrathiafulvalene (PhTTF) and some substituted PhTTF's is reported. (*p*-Vinylphenyl)tetrathiafulvalene(III) was prepared and its thermal, bulk polymerization accomplished. Standard techniques for anionic and free-radical polymerizations failed in the case of III, and the anionic polymerization of styrene was shown to be inhibited by TTF. The poly[(*p*-vinylphenyl)tetrathiafulvalene] readily incorporated varying amounts of elemental bromine with a concomitant increase in the compressed pellet semiconductor behavior of the material.

## I. Introduction

It is becoming more apparent that the electrical conductivity of organic systems will probably not be improved substantially until a material can be designed that will get away from the donor–acceptor compounds which invariably depend on a one-dimensional or pseudo-one-dimensional structure for their properties.[1] One approach to this problem of achieving higher dimensionality in conducting compounds is to take known systems with high 1d conductivity, and attach more than one donor or acceptor unit to the same molecule. Thus, a network of a multidimensional nature might be built up. This method has been attempted with the synthesis of *p*-phenylenebis(tetrathiafulvalene) (I).[2] That species was found to form a 1:1 complex with TCNQ which had a room temperature compressed pellet conductivity about an order of magnitude worse than TTF–TCNQ. Although with I a highly conducting material was not achieved it may yet be possible with such an approach to design a highly conducting organic system with higher than unit dimensionality.

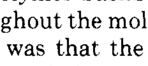


I

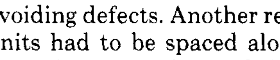
Another possible mode of attack on the problem of building molecules with advantageous electrical properties lies within the realm of organic polymer chemistry. The study of conductivity in polymers is not new, and a large body of information already exists.[3] Among the myriad of polymeric conductors known the most familiar to the organic solid state chemist are those based on anion-radical TCNQ salts of polymeric cations.[4,5] The highest conductivities in this series are about $10^{-2}$ ohm$^{-1}$ cm$^{-1}$. For comparison, the conductivity of the 1d compound TTF–TCNQ is about $10^{3}$ ohm$^{-1}$ cm$^{-1}$ ($\sim$2 ohm$^{-1}$ cm$^{-1}$ in the compressed pellet).

Radical cations have also been incorporated into polymers without a great deal of success toward the goal of improving electrical conduction.[6]

The purpose of this work was to attempt to incorporate TTF (II) into a polymer in such a way that its attachment to the polymer backbone was regular, uniform, and complete throughout the molecule, avoiding defects. Another requirement was that the TTF units had to be spaced along the polymer chain so as to permit close $\pi$ overlap and thus the formation of a band-type conductor. Further, a polymer backbone was chosen whose solubility characteristics were good in general, thereby providing the opportunity to fabricate cast films and prepare the desired oxidation state of the polymer by reaction with appropriate acceptors.



II

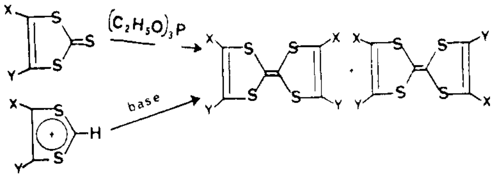


VIII

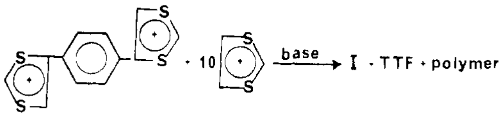
Polystyrene was chosen as the polymer backbone because it fulfilled all the criteria mentioned above, and in addition, the polymerization of styrene is one of the most studied reactions in polymer chemistry and that store of knowledge could apparently be used to good advantage. This paper reports the synthesis and properties of some monophenyltetrathiafulvalenes including (*p*-vinylphenyl)tetrathiafulvalene (VIII) and its polymerization.

## II. Results and Discussion

The methods used to synthesize substituted TTF molecules have, until recently, resulted in symmetrical molecules. That is, by necessity, two dithiole type starting materials were joined together by a suitable technique,[7] e.g.,



Recently, a synthetic method based on the low-temperature lithiation of TTF has been shown to give monosubstituted TTF's.[8] The first monophenyl-substituted TTF, however, was I.[2] That preparation relied upon the simultaneous deprotonation of a mixture of two different dithiolium cations and the subsequent physical separation of the products formed.



In the present case a similar scheme was relied upon for the synthesis of monoaryl-substituted TTF's (Scheme I). Phenyltetrathiafulvalene was made by this series of reactions in order to work out the appropriate conditions for each step. Thus, when sodium dimethylaminodithiocarbamate was refluxed with $\alpha$-bromoacetophenone in ethanol/acetone a 67.6% yield of once recrystallized product (mp 109.0–109.5 °C) was obtained. Dithio acids have been previously shown to produce $\beta$-keto dithio esters (IIIb) by condensation with $\alpha$-halo ketones.[9] The NMR spectrum of IIIb in $CDCl_3$ exhibited two multiplets at $\delta$ 8.25 and $\delta$ 7.20 (with a total area of 5.0 H) assigned to the methylene group, and a broad singlet at $\delta$ 3.55 (6.2 H) assigned to the methyl groups. Cyclization of IIIb was accomplished in 72% yield by strong acid.[9] The salt IVa exhibited an NMR spectrum with a doublet absorption at $\delta$ 3.55 (6.0 H) assigned to the methyl groups and a multiplet at $\delta$ 7.67

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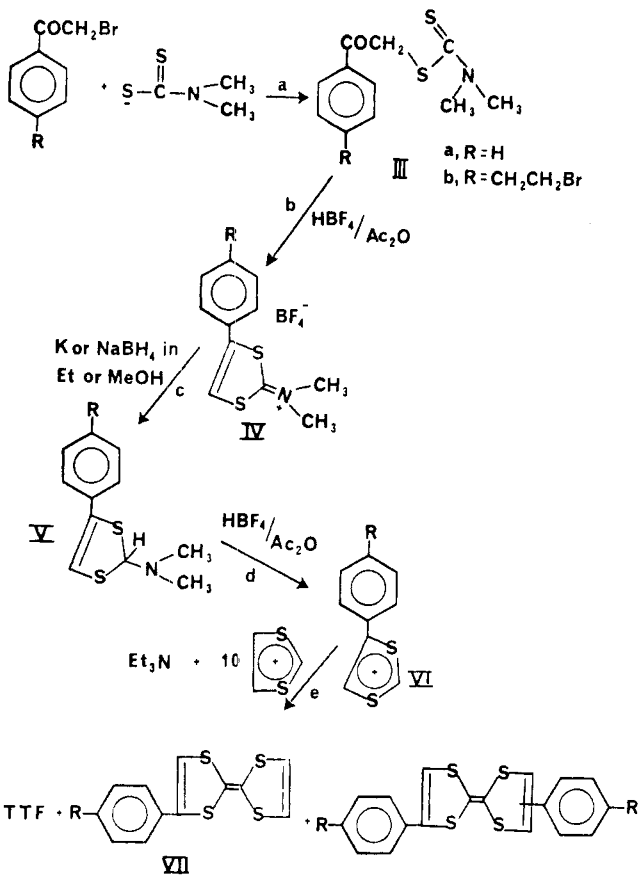
Scheme I



(6.0 H) assigned to the phenyl and dithiolium ring hydrogens.

Reduction of IVa to Va was performed with $KBH_4$ in ethanol and occurred in 89% yield. The product melted at 68.5–70 °C and had an NMR spectrum consisting of a multiplet at δ 7.53 (5.0 H) corresponding to the phenyl protons and singlets at δ 6.57 (1 H), 6.42 (1 H), and 2.32 (6.0 H) assigned to the olefinic, methine, and methyl protons, respectively.

The deamination was carried out in 74% yield by treatment of amine Va with fluoboric acid. The synthesis of 4-para-substituted phenyl-1,3-dithiolium salts by the reduction of immonium salts followed by acid deamination has been reported previously.[10] The thiomethyl group has been cleaved in the same manner in the preparation of unsubstituted 1,3-dithiolium tetrafluoborate[11] and of methyl-substituted 1,3-dithiolium salts.[12] It would be expected for 1,3-dithiolium compounds that the NMR chemical shifts for the five-membered ring hydrogens would exhibit a dramatic deshielding effect and appear far downfield. What was observed was an aromatic multiplet absorption at δ 7.90 and doublets at δ 9.40 and 11.33 assigned to H-5 and H-2, respectively. This is entirely analogous to the assignments in the 1,3-dithiolium cation.[11]

The coupling reaction to produce VIIa was accomplished by using a 10:1 molar ratio of 1,3-dithiolium cation to 4-phenyl-1,3-dithiolium cation. The large excess of TTF thus formed can be effectively removed by fractional crystallization and vacuum sublimation. The residue in the sublimer (crude yield 64%) was then purified by recrystallization to give a canary yellow solid melting at 78–81 °C. The NMR spectrum was characteristic of substituted TTF's and compares well with chemical shifts observed for symmetrical diphenyltetrathiafulvalene.[13] The aromatic proton resonances of diphenyltetrathialfulvalene occurred at δ 7.29 while in VIIa they appeared at δ 7.20. The olefinic protons in diphenyltetrathiafulvalene were found at δ 6.39 and in VIIa (olefinic adjacent to phenyl) at δ 6.30. The olefinic protons on the TTF ring away from the phenyl substituent absorb at δ 6.16 which is close to the δ 6.25 measured for unsubstituted TTF.[12] The strong IR band at 748 cm$^{-1}$ indicated the presence of a monosubstituted benzene.[14]

The UV–vis spectrum of VIIa exhibited the characteristics of a substituted TTF. The three-band fine structure at 297, 302, and 322 nm with extinction coefficients of from 12 000 to 14 000 seems to occur regularly at about the same wavelengths in substituted TTF's.[12] The long wavelength band at 400 nm with an extinction coefficient of about 2800 corresponds well with the 403-nm absorption ($\epsilon$ 2700) observed for diphenyltetrathiafulvalene.[13]

The ESR spectrum of VIIa radical cation is somewhat surprising in that it appeared as a simple quartet ($g = 2.0078$, $a_H$ 1.25 G). This implied that there was almost no spin density on the phenyl ring and that the three hydrogens on the TTF were equivalent. The $g$ value was normal for a sulfur-based radical and the hyperfine coupling constant the same as that reported for TTF itself.[12]

The radical cation $BF_4^-$ salt of VIIa was prepared in the same manner as the tetrafluoborate salt of TTF,[15] i.e., with $HBF_4$ and $H_2O_2$ in acetonitrile. The dark green crystals had a measurable melting point (mp 176 °C) unlike the decompositions noted for the fluoborate salts of TTF and methylated TTF's.[16] The elemental analysis of the salt showed it to have the composition $(Ph\ TTF)_3(BF_4)_2$, identical to that for TTF,[15] but different than the composition found for the fluoborate salts of methylated TTF's.[16] Also, where $(TTF)_3(BF_4)_2$ was found to be an electrical insulator in compressed pellet measurements,[15] $(Ph\ TTF)_3(BF_4)_2$ was a semiconductor with a resistance of 400 Ω.

Once the steps in the synthesis of VIIa were developed it became a relatively simple matter to extend these procedures to prepare VIIb. In step a of Scheme I we started with *p*-(2-bromoethyl)chloroacetylbenzene which was made by a straightforward Friedel-Crafts acylation of (2-bromoethyl)benzene with chloroacetyl chloride. The condensation of the acylated product with sodium dimethyldithiocarbamate proceeded normally, although purification of carbodithioate IIIb was difficult. The NMR spectrum was very similar to that of IIIa except for the multiplets at δ 3.57 and 3.20 attributable to the bromoethyl group.

Subsequent treatment of IIIb with fluoboric acid effects cyclization in theoretical yield to the cation IVb which was much like the compound IVa. The only difference in the NMR spectrum from that of IVa again was due to the bromoethyl group multiplets at δ 3.67 and 3.17.

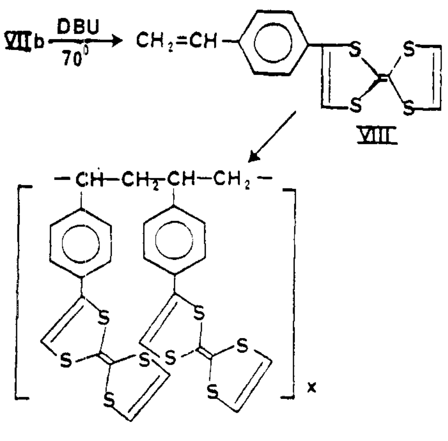
Reduction to Vb was carried out with $KBH_4$ in 96% yield in the mixed solvent ethanol/$CH_3CN$. The only differences in the NMR spectrum from that of Va were the two multiplets at δ 3.50 and 3.08 due to the bromoethyl group.

The deamination (step d) to VIb did not proceed smoothly as in the case of VIa. Isolation and purification of the product were complicated by the presence of some deep red impurity. Several recrystallizations resulted in only a 20% yield of a pink solid whose NMR spectrum was directly analogous to VIa except for the multiplets at δ 3.75 and 3.22 due to the bromoethyl group.

Finally, the TTF VIIb was prepared and isolated in 56% yield as before for VIIa. Its properties were clearly those of a *p*-(2-bromoethyl)phenyltetrathiafulvalene. The NMR spectrum consisted of an AB quartet for the aromatic hydrogens at δ 7.23, two singlets in the ratio of 2:1 for the olefinic hydrogens at δ 6.25 and 6.37, and the two multiplets of the $A_2B_2$ system of the bromoethyl group at δ 3.47 and 3.12.

Dehydrohalogenation of VIIb proceeded in excellent yield (99%) merely upon heating the bromoethyl compound at 70 °C with DBU in dimethyl sulfoxide (Scheme II). The progress

Scheme II



of the reaction was followed by NMR and the appearance of the vinylic hydrogens was complete in 2 h. The (*p*-vinylphenyl)tetrathiafulvalene (VIII) had an NMR spectrum which, in addition to the aromatic and TTF hydrogen absorptions, had the typical ABC styrene vinyl resonance pattern.[17] The infrared spectrum of VIII also was characteristic. The lines at 738, 775, and 800 cm$^{-1}$ appear in all TTF molecules which are not completely substituted. The strong band at 840 cm$^{-1}$ is diagnostic of para-disubstituted benzenes.[18] The 915- and 987-cm$^{-1}$ bands result from the out-of-plane deformation modes of the monosubstituted ethylene.[19]

Having the (*p*-vinylphenyl)tetrathiafulvalene in hand, we proceeded to attempt an anionic polymerization. This mode of polymerization was chosen because it was felt that the donor nature of the pendant TTF's would not interfere with the reactive chain-propagating species, which was a benzyl anion.[20] Also, the preparation of highly tactic vinyl polymers is usually accomplished by means of ionic polymerizations.[21]

Examination of molecular models of isotactic polystyrene with pendant TTF groups revealed that the polymer could exist in a helical configuration, and that the TTF's could be on the outside of the helix in a spatial relationship permitting significant close $\pi$ overlap. In one-dimensional organic conductors this condition of close $\pi$ overlap (or stacking) is a necessary prerequisite for the formation of a conduction band[3,22,23] and leads to the anisotropic transport properties observed for these compounds. In the isotactic poly(styrenetetrathiafulvalene) polymer direct one above one stacking would not be possible although strong interactions between TTF's could occur.

However, when we attempted typical anionic polymerizations of VIII with sodium benzophenone ketyl, sodium naphthalenide, or butyllithium no polymerization was detected and starting material was recovered unchanged. In order to determine if, in fact, TTF was an inhibitor of anionic polymerizations, we ran side by side polymerization of (1) styrene and (2) styrene + TTF. Unsubstituted TTF did inhibit the polymerization of styrene while the styrene itself underwent normal, rapid polymerization under the same conditions. While it may be possible to ascribe the inhibitory effect of TTF to the presence of small amounts of radical-cation impurities there is no spectroscopic evidence to bear this thesis out. In the case of some of the initiators, e.g., sodium naphthalenide and butyllithium, inhibition might be due simply to proton transfer from the TTF unit.[8]

Next, a simple bulk polymerization of VIII initiated with AIBN was attempted. This, too, failed. The last attempt at a polymerization of VIII was carried out in a sealed tube in vacuo at 130 °C for 3 days. Indeed a polymer was isolated, evidently in theoretical yield. The carbon–hydrogen analysis was correct for a polymer that had retained the integrity of the (*p*-vinylphenyl)tetrathiafulvalene unit ($C_{14}H_{10}S_4$). The shiny, hard, brown, brittle polymer was found to be insoluble in all the usual organic solvents. Gel permeation chromatography with 1,2,4-trichlorobenzene at 135 °C was attempted in order to get a feeling for the molecular weight. Although almost none of the polymer dissolved the small amount that was soluble appeared to give a very broad elution pattern, the center of which occurred at about mol wt 50 000 (compared to polystyrene standard samples).

The infrared spectrum of the polymer also confirmed the existence of the TTF unit by virtue of the presence of strong bands at 730, 780, and 800 cm$^{-1}$. The aliphatic absorption band at 2920 cm$^{-1}$ was also apparent, indicating that polymerization had indeed occurred.

Other workers have reported polymers with TTF structures.[24-26] Two of these groups attempted to prepare charge-transfer complexes with TCNQ and DDQ. In the case of the polyamide-containing TTF polymer[24] no complexes were formed. The polymer-containing TTF units joined by tri- and tetramethylene groups[25] did form complexes, and in the case of TCNQ these were 6 TTF's to each TCNQ. In neither case were conductivities reported.

Compressed pellet conductivity measurements of poly(styrenetetrathiafulvalene) itself and in combination with varying amounts of bromine are reported in Table I. The trend is obvious and it is clear that the presence of a good donor such as TTF raises the conductivity of a styrene-like polymer orders of magnitude. This is probably due to some small amount of air oxidation to the radical cation. The electrical conductivity of (TTF)$Br_{0.75}$ is about 500 ohm$^{-1}$ cm$^{-1}$.[27] [Poly(styrene-TTF)]$Br_{0.6}$ has a conductivity of only $10^{-8}$ ohm$^{-1}$ cm$^{-1}$. The explanation for this gross difference is probably not due to any single factor. The greatest share of responsibility for the relatively poor conductivity in the polymer can, no doubt, be attributed to its low tacticity. The low tacticity prevents a continuous donor-unit overlap structure to develop, thereby causing many large defect domains in the potential conduction band. To overcome this severe problem a polymeric system with 100% stereoregularity will need to be synthesized, perhaps an impossible task.

**Table I. Conductivity and Composition of Poly(styrene-TTF bromides)**

| compd | composition | conductivity, $\Omega^{-1}$ cm$^{-1}$ |
|---|---|---|
| polystyrene | $[C_8H_8]_x$ | $10^{-18}$ (ref 3) |
| poly(styrene-TTF) | $[C_{14}H_{10}S_4]_x$ | $5 \times 10^{-10}$ |
| poly(styrene-TTF-Br) | $[C_{14}H_{10}S_4Br_{0.6}]_x$ | $10^{-8}$ |
| poly(styrene-TTF-Br) | $[C_{14}H_{10}S_4Br_4]_x$ | $5 \times 10^{-7}$ |

## III. Experimental Section

Spectroscopic data were taken on the following instruments: NMR, Jeolco C-60 HL; IR, Perkin-Elmer 137 Infracord; UV-vis, Cary 14, EPR, Varian E15. Melting points were determined on a binocular microscope fitted with a Mettler FP-52 hot stage and were corrected.

Cyclic voltammetry was carried out in acetonitrile with 0.1 M ($n$-$C_4H_9)_4NBF_4$ as supporting electrolyte, with a platinum working electrode and silver|silver chloride reference electrode. A Model 2011 ESA polarograph was used in these experiments. Elemental analyses were performed on a Perkin-Elmer 240 CHN analyzer.

**Preparation of Phenacyl Dimethylaminocarbodithioate (IIIa).** To a hot solution of the sodium salt of dimethylaminodithiocarbamate (19.7g, 0.11 mol, Aldrich) in 200 mL of ethanol was added a solution of $\alpha$-bromoacetophenone (19.9 g, 0.1 mol, E.K.) in 200 mL of acetone. The mixture was refluxed ca. 2 h and then permitted to stand overnight (16 h) at room temperature. It was concentrated to dryness and then extracted several times with $CH_2Cl_2$ (400 mL total). The $CH_2Cl_2$ solution was concentrated to dryness and the product was recrystallized from $CH_3CN$. A white, crystalline solid was isolated with mp 109.0–109.5 °C, yield 16.13 g (67.6%).

Anal. Calcd for $C_{11}H_{13}NOS_2$: C, 55.19; H. 5.47. Found: C, 55.47; H, 5.43.

The NMR spectrum ($CDCl_3$, $Me_4Si$) showed the following absorptions: δ 8.25 and 7.20 (multiplets, total 5.0 H), 4.95 (s, 1.9 H), and 3.55 (broad s, 6.2 (H) ($C_{11}H_{13}O_2N$).

**Preparation of 4-Phenyl-2-dimethylamino-1,3-dithiolium Tetrafluoborate (IVa).** To a solution of $HBF_4$ (40% aqueous) (20 g, 0.1 mol, Baker and Adamson) in acetic anhydride (100 mL) (this reagent must be prepared cautiously, with external cooling!) was added phenacyl dimethylaminocarbodithioate (11.95 g, 0.05 mol). The mixture was stirred under $N_2$ and heated to the boiling point. After a few moments the reaction mixture became homogeneous and pale green. At this point it was stoppered and permitted to stand overnight at room temperature (16 h). The white needles which had formed were collected, washed with acetic anhydride, and dried under $N_2$; yield 12.28 g (72%).

The NMR spectrum of the product in ($CD_3CN$, $Me_4Si$) consisted of a doublet (δ 3.55, 6.0 H) and multiplet (7.67, 6.0 H).

Anal. Calcd for $C_{11}H_{12}S_2NBF_4$: C, 42.73; H, 3.91. Found: C, 42.64; H, 4.03.

**Preparation of 4-Phenyl-2-dimethylamino-1,3-dithiole (Va).** To a slurry of 4-phenyl-2-dimethylamino-1,3-dithiolium tetrafluoborate (6.18 g, 0.02 mol) in 200 mL of ethanol at 0 °C was added $KBH_4$ (10.8 g, 0.2 mol) in two batches. The mixture was stirred under $N_2$ for 45 min. Water (500 mL) was added and after stirring for 15 min (slight foaming) the white solid which formed was collected, washed with water, and dried under $N_2$. The solid was taken up in $CH_2Cl_2$ and filtered. The pale yellow solution was concentrated to dryness under reduced pressure; yield 3.96 g (89%).

The mp of the product was 68.5–70 °C. Its NMR spectrum exhibited absorptions ($CDCl_3$, $Me_4Si$) at δ 7.53 (m, 5 H), 6.57 (s, 1 H), 6.42 (s, 1 H), and 2.32 (s, 6 H).

Anal. Calcd for $C_{11}H_{13}S_2N$: C, 59.15; H, 5.87. Found: C, 59.17; H, 5.82.

**Preparation of 4-Phenyl-1,3-dithiolium Tetrafluoborate (VIa).** To a solution of 4-phenyl-2-dimethylamino-1,3-dithiole (2.23 g, 0.01 mol) in 50 mL of acetic anhydride at 0 °C under $N_2$ was added dropwise (rapidly) a solution of $HBF_4$ (40% aqueous) (8.8 g, 0.04 mol) in acetic anhydride (caution when preparing this reagent, vide supra). When the addition was complete the solution was stirred 10 min at 0 °C then permitted to warm to room temperature at which point stirring was continued for an additional hour. The solution was then cherry red, and 300 mL of ether was added to precipitate the product. The white needles which resulted were collected, washed with ether, and dried under $N_2$: yield 1.96 g (74%); mp > 140 °C dec. The NMR spectrum in ($CD_3CN$, $Me_4Si$) showed three absorption lines at δ 7.90 (m, 5.0 H), 9.40 (d, 1.1 H, $J$ = 2.2 Hz), and 11.33 (d, 1.0 H, $J$ = 2.2 Hz).

Anal. Calcd $C_9H_7S_2BF_4$: C, 40.62; H, 2.65. Found: C, 40.79; H, 2.92.

**Preparation of 2-(4-Phenyl-1,3-dithiol-2-ylidene)-1,3-dithiole (Phenyltetrathiafulvalene) (VIIa).** A solution, under $N_2$, containing 4-phenyl-1,3-dithiolium tetrafluoborate (1.33 g, 0.005 mol) and 1,3-dithiolium tetrafluoborate (9.55 g, 0.05 mol) in 50 mL of $CH_3CN$ was cooled to 0 °C and treated with excess triethylamine (13 mL, 9.3 g, 0.092 mol). After stirring at ice temperature for ca. 1 h, water was added to precipitate the products. The orange solid which formed was collected, washed with water, and dried under $N_2$. The solid was dissolved in ca. 750 mL of hot hexane, filtered, and allowed to cool. The first crop of crystals to form was collected and shown to be relatively pure TTF by NMR; yield of TTF 2.75 g (60%). The mother liquors were concentrated to dryness and vacuum sublimed at 70 °C and ca. 0.05 torr of pressure yielding TTF, 0.96 g (21%). The brownish-orange solid remaining in the bottom of the sublimer, 0.90 g (64%), proved to be crude phenyltetrathiafulvalene by NMR. It was recrystallized twice, first from methanol and then from hexane, to give a canary yellow solid with mp 78–81 °C. The NMR spectrum ($CS_2$, $Me_4Si$) showed three singlets at δ 7.20 (5.0 H), 6.30 (1.0 H), and 6.16 (1.9 H).

Anal. Calcd for $C_{12}H_8S_4$: C, 51.39; H, 2.87. Found: C, 51.38; H, 3.05.

The UV–vis spectrum $\lambda_{max}$ ($\epsilon$) was: 228 nm (11 400), 277 (13 900), 302 (14 100), 322 (12 500), and 400 (2820). The IR spectrum (KBr) was: 3080 (w) $cm^{-1}$, 1480 (w), 1430 (w), 1245 (w), 1200 (w), 1090 (w), 1070 (w), 1030 (w), 927 (m), 913 (m), 830 (w), 800 (m), 780 (m), 748 (s), 735 (shoulder, m), 690 (m).

**Preparation of Phenyltetrathiafulvalene Tetrafluoborate.** To a solution of phenyltetrathiafulvalene (140 mg, 0.0005 mol) in 10 mL of $CH_3CN$ was added a solution of $H_2O_2$ (30%) (19 mg, 0.00017 mol) and $HBF_4$ (40%) (110 mg, 0.0005 mol) in 1 mL of $CH_3CN$. The mixture turned dark green immediately and after standing 1 h at room temperature it was refrigerated for 1 h. The green crystalline mass which formed was collected, washed with cold $CH_3CN$ followed by ether, and then dried under $N_2$: yield 110 mg; mp 176 °C. The compressed pellet resistance of the product was 400 ohms.

Anal. Calcd for 3:2 salt, $C_{36}H_{24}S_{12}B_2F_8$: C, 42.60; H, 2.38. Found: C, 42.80; H, 2.44. The ESR spectrum of the salt in propylene carbonate was a quartet, $g$ = 2.0078; $a_H$ = 1.25 G.

**Preparation of *p*-(2-Bromoethyl)chloroacetylbenzene.** In a 500 mL, three-necked, round-bottom flask with stirrer, dropping funnel, and drying tube was placed a mixture of $AlCl_3$ (Fisher, 16.0 g, 0.12 mol) and 1,2-dichloroethane (150 mL). The mixture was cooled to 0 °C and chloroacetyl chloride (Aldrich 11.9 g, 0.105 mol) was added dropwise with stirring. The cooling bath was changed to a water bath at ca. 15 °C and 2-(bromoethyl)benzene (Aldrich, 18.5 g, 0.10 mol) was added dropwise. When the addition was complete stirring was continued for another hour. The reaction mixture was added to 200 mL of ice and water and stirred until the organic layer became pale yellow. Concentrated HCl (ca. 10 mL) was added to dissolve the aluminum salts. The organic layer was separated and the aqueous layer extracted with two 50-mL portions of 1,2-dichloroethane and the extracts combined with the organic layer. After three washings with 100-mL portions of water the solution was dried over anhydrous $Na_2SO_4$. The mixture was filtered and the filtrate concentrated to dryness. The crystalline mass was collected, washed with hexane, and dried under $N_2$; yield 20 g (77%).

The NMR spectrum ($CDCl_3$, $Me_4Si$) was δ 7.45 (q, 4.1), 4.60 (s, 1.9), 3.17 (m, 2.0), and 3.53 (m, 2.0).

**Preparation of *p*-(2-Bromoethyl)phenacyl Dimethylaminocarbodithioate (IIIb).** To a stirred solution of *p*-(2-bromoethyl)-chloroacetylbenzene (19.0 g, 0.073 mol) in 100 mL of acetone was added, dropwise over 1 h, a solution of sodium dimethyldithiocarbamate (13.0 g, 0.073 mol, Aldrich) in 200 mL of ethanol. After the addition, stirring was continued for 3 h at room temperature. The mixture was filtered (to remove NaCl), the filtrate concentrated to dryness, and the solid taken up in ca. 200 mL of $CH_2Cl_2$. The solution was dried over $Na_2SO_4$, filtered, and concentrated to dryness. The solid was recrystallized twice from 1,2-dichloroethane/hexane: yield 11.77 g (47%); mp 103–110 °C.

The NMR spectrum ($CDCl_3$, $Me_4Si$) exhibited five absorptions at δ 7.65 (q, 4.0 H), 4.80 (s, 2.0 H), 3.57 (m, 2.2 H), 3.47 (br s, 5.6 H), and 3.20 (m, 2.2 H).

**Preparation of 4-[*p*-(2-Bromoethylphenyl)]-2-dimethylaminodithiolium Tetrafluoborate (IVb).** To a solution of $HBF_4$ (40%) (14.6 g, 0.0667 mol) in 75 mL of acetic anhydride (Caution: vide supra) was added *p*-(2-bromoethyl)phenacyl dimethylaminocarbodithioate (11.42 g, 0.033 mol). The reaction mixture was stirred under argon, heated to boiling, and permitted to stand overnight at room temperature. Ether was added and the oil which separated was washed several times, by decantation, with ether and dried in a $N_2$ stream; yield 14.0 g (100%). No further purification of the oil was attempted. The NMR of the oil ($CD_3CN$, $Me_4Si$) showed absorptions at δ 7.43 (m, 5.0 H), 3.43 (d, 6.6), 3.67 (m, 1.9), and 3.17 (m, 1.4) (Vb).

**Preparation of 4-[*p*-(2-Bromoethyl)phenyl]-2-dimethylamino-1,3-dithiole.** To a stirred solution, under argon, of 4-[*p*-(2-bromoethylphenyl)]-2-dimethylaminodithiolium tetrafluoborate (14.0 g, 0.033 mol) in 300 mL of ethanol/$CH_3$ CN (5:1) at 0 °C was added, in portions, $KHB_4$ (18.0 g, 0.33 mol). The solution was stirred at 0 °C for an additional 2 h. Water and ice (400 mL) were added and the tacky yellow solid product which formed was collected and washed with water. The NMR spectrum ($CDCl_3$, $Me_4Si$) of the product showed six absorptions. These occurred at δ 7.27 (q, $J_{AB}$ = 18 Hz), 6.37 (s), 6.23 (s), 3.50 (m), 3.08 (m), and 2.25 (s). The product was taken up in $CH_2Cl_2$, dried over $Na_2SO_4$, filtered, and concentrated to dryness. The yield of viscous yellow oil was 10.45 g (96%).

**Preparation of 4-(*p*-2-Bromoethylphenyl)-1,3-dithiolium Tetrafluoborate (VIb).** To a chilled (0 °C) solution of 4-[*p*-(2-bromoethylphenyl)]-2-dimethylamino-1,3-dithiole (10.45 g, 0.032 mol) in 50 mL of acetic anhydride was added a solution of $HBF_4$ (48%) (23.5 g, 0.128 mol) in 50 mL of acetic anhydride. The addition was carried out in small portions under argon. The mixture became deep red and was allowed to stand overnight at room temperature. The mixture was added to 500 mL of ether and the partially solidified deep red oil which separated was collected by decantation. After washing several times with ether, the product was recrystallized twice from 1,2-dichloroethane to give a pink solid; yield 2.44 g (20%).

The NMR spectrum of ($CD_3CN$, $Me_4Si$) of this material appeared as the following: δ 11.01 (d, 1.0 H, $J$ = 2.5 Hz), 9.05 (d, 0.94 H, $J$ = 2.5 Hz), 7.58 (q, 4.0 H, $J$ = 20 Hz), 3.75 (m, 2.0 H), and 3.22 (m, 2.2 H).

**Preparation of 2-[4-(*p*-2-Bromoethylphenyl)-1,3-dithiol-2-**

**ylidene]-1,3-dithiole [*p*-(2-Bromoethyl)phenyltetrathiafulvalene] (VIIb).** To a solution containing *p*-(2-bromoethyl)phenyl-1,3-dithiolium tetrafluoborate (0.746 g, 0.002 mol) and 1,3-dithiolium tetrafluoborate (3.80 g, 0.02 mol) in 50 mL of deaerated $CH_3CN$ at 0 °C was added triethylamine (3.14 mL, 0.026 mol). After the addition, stirring was continued for 15 min. Deaerated water (140 mL) was then added and the yellow solid that formed was collected by filtration, washed with water, and then dried in a $N_2$ stream. The yield of total crude product (i.e., TTF + *p*-(2-bromoethyl)phenyltetrathiafulvalene) was 2.56 g (98%). The components were first separated by vacuum sublimation at 70–90 °C (0.01 torr). The TTF recovered from the cold finger was 1.35 g (73%). The residue in the sublimer was extracted several times with hot cyclohexane (total of 100 mL) and the orange solution was filtered. It was concentrated to 75 mL and refrigerated. The orange crystals which formed were collected and dried in a $N_2$ stream: yield 0.43 g (56%); mp 126–131 °C. After one recrystallization from cyclohexane the mp became 128–133 °C.

Anal. Calcd for $C_{14}H_{11}S_4Br$: C, 43.39; H, 2.87. Found: C, 43.64; H, 2.69.

The NMR spectrum ($CS_2$, $Me_4Si$) showed lines at $\delta$ 7.23 ($q_{AB}$, 4.0 H), 6.37 (s, 0.91 H), 6.25 (s, 2.1 H), 3.47 (m, 2.0 H), and 3.12 (m, 2.2 H).

**Preparation of 2-(4-Vinylphenyl)-1,3-dithiol-2-ylidene-1,3-dithiol [(4-Vinylphenyl)tetrathiafulvalene] (VIII).** A solution of *p*-(2-bromoethyl)phenyltetrathiafulvalene (194 mg, 0.5 mmol) and (DBU) 1,5-diazabicyclo[5.4.0]undec-5-ene (76 mg, 0.5 mmol) in 2 mL of dimethyl sulfoxide was heated, under $N_2$, for 2 h at 80 °C. The reaction mixture was quenched in ca. 10 mL of water. The yellow solid which formed was collected, washed with water, and dried under $N_2$. The yield of crude product was 151 mg (99%). Recrystallization from cyclohexane afforded orange microcrystals, mp 100–104 °C. The NMR spectrum ($CS_2$, $Me_4Si$) consisted of absorptions at $\delta$ 7.20 (s, 3.7 H), 6.60 (doublet of doublets, 1.0 H, $J_{AB}$ = 18 Hz, $J_{AC}$ = −11 Hz), 6.33 (s, 1.1 H), 6.20 (s, 2.0 H), 5.63 (doublet of doublets, 1.1 H, $J_{AB}$ = 18 Hz, $J_{BC}$ = 1.5 Hz), and 5.17 (doublet of doublets, 1.1 H, $J_{AC}$ = 11 Hz, $J_{BC}$ = 1.5 Hz).

Anal. Calcd for $C_{14}H_{10}S_4$: C, 54.86; H, 3.29. Found: C, 54.08, H. 3.33.

The infrared spectrum (KBr) had the following lines: 3080 $cm^{-1}$ (w), 1630 (m), 1550 (w), 1520 (m), 1480 (w), 1190 (w), 1110 (w), 987 (s), 915 (s), 840 (s), 800 (s), 780 (shoulder, m), 775 (s), and 738 (s).

**Polymerization of (*p*-Vinylphenyl)tetrathiafulvalene.** A Pyrex ampule containing 30 mg of (*p*-vinylphenyl)tetrathiafulvalene was sealed in vacuo and heated at 130 °C for 65 h. The ampule was cooled to room temperature and then opened. The rust colored, shiny, brittle solid was removed by scraping it out with a stainless steel spatula. After washing several times with $CS_2$ the polymer was dried under $N_2$. The infrared spectrum (KBr) was as follows: 3050 $cm^{-1}$ (m), 2920 (m), 1650 (w), 1630 (w), 1600 (w), 1570 (m), 1540 (m), 1490 (m), 1440 (w), 1400 (m), 1275 (m), 1230 (w), 1200 (m), 1120 (m), 1085 (m), 1020 (m), 990 (m), 924 (s), 834 (s), 800 (s), 780 (s), 763 (s), and 730 (s).

Anal. Calcd for $C_{14}H_{10}S_4$: C, 54.86; H, 3.29. Found: C, 54.87; H, 3.27.

The polymer appeared to be virtually insoluble in halogenated hydrocarbons, tetrahydrofuran, halobenzenes, and other common solvents. It did not appear to soften up to 300 °C.

Anionic polymerization of the (4-vinylphenyl)tetrathiafulvalene was attempted with sodium benzophenone ketyl and with 1,1-diphenylhexyllithium as initiators in dried and degassed solvents. The 1,1-diphenylhexyl anion is a deep red color, and the styryl anion a pale red. These colors were used to determine qualitatively the stability of anions in the polymerization apparatus. Neither electron transfer from the ketyl nor direct anionic initiation produced detectable polymer in preliminary investigations.

Anionic polymerization of styrene in the presence of TTF was also attempted. Three milliliters of styrene (2.6 × $10^{-2}$ mol) and an equimolar amount of TTF (5.35 g) were dissolved in dried THF. The solution was sealed in a septum capped bottled and chilled to −78 °C while a steady stream of argon was bubbled through the solution. To a small amount of THF containing 0.14 mL of 1,1-diphenylethylene (7.8 × $10^{-4}$ mol) was added 0.34 mL of butyllithium in hexane (2.2 M, 7.5 × $10^{-4}$ mol). Half of this red solution of 1,1-diphenylhexyllithium was added by syringe to the chilled styrene/TTF solution. The color of the initiator was quenched within seconds of the addition. The other half of the initiator was added to a control solution to which no TTF had been added. The red color expected from the polystyrene anion persisted until the reaction was quenched with methanol. A quantitative yield of polystyrene was formed.

In a separate pair of experiments TTF (87.5 mg, 4.3 × $10^{-4}$ mol) in slight molar excess of the initiator was used. Once again, polystyrene polymerization was quenched in the TTF-containing reaction, whereas polystyrene was formed quantitatively in the control reaction.

**Treatment of Poly[(4-vinylphenyl)tetrathiafulvalene] with Bromine.** Small amounts of polymer in glass vials were treated at room temperature with bromine vapor. After standing for a few minutes at room temperature the excess bromine vapor (if there was any) was removed by a nitrogen purge. The polymer became black in color and seemed to soften somewhat during bromine treatment. Compressed pellet conductivities were measured (Table I) and elemental analyses were performed.

Anal. Calcd for $C_{14}H_{10}S_4Br_{0.62}$: C, 47.24; H, 2.81. Found: C, 47.26; H, 3.17.

Anal. Calcd for $C_{14}H_{10}S_4Br_{4.6}$: C, 24.95; H, 1.50. Found: C, 24.84; H, 1.94.

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**Registry No.**—IIIa, 23839-34-1; IIIb, 67745-76-0; IVa, 67745-78-2; IVb, 67745-80-6; Va, 24372-79-0; Vb, 67745-81-7; VIa, 67745-82-8; VIb, 67745-84-0; VIIa, 67745-85-1; VIIb, 67745-86-2; VIII, 67745-87-3; phenyltetrathiafulvalene tetrafluoborate, 67760-69-4; poly(styrene-tetrathiafulvalene), 67784-48-9; *p*-(2-bromoethyl)chloroacetylbenzene, 14396-60-2; sodium dimethylaminodithiocarbamate, 128-04-1; α-bromoacetophenone, 70-11-1; 1,3-dithiolum tetrafluoborate, 53059-75-9; chloroacetyl chloride, 79-04-9; (2-bromoethyl)benzene, 103-63-9.

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