Heteropolyacene with Thianthrenium Ring Systems Proving π Electron Delocalization over S Atoms

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ABSTRACT

The superacid-induced condensation of *o*-methylsulfinylated thiophenyl(ene) compounds under dilute conditions induces an intramolecular electrophilic ring-closing reaction of a hydroxysulfonium cation onto the adjacent benzene ring to yield the thianthrenium ring systems, which disclose π electron delocalization over sulfonio linkages demonstrating the efficacy of planarization of the benzene rings for the p-π/d-π interaction in arylsulfonium moieties. Crystal structure of the thianthrenium salt reveals that the S^+—C(phenyl) bond is significantly shortened upon the ring closing as a result of the increased bond order by the resonance effect.

Key Words: Conjugated polymer; Condensation; Sulfonium salts.

INTRODUCTION

The thianthrene ring system deserves much attention as a redox active center[1] and a spin coupler[2] due to the stability of the cation radical.[3] The unique reactivity

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of this cation radical is represented by its addition to a variety of alkenes providing monothianthrenium adducts.[4] The product can then be recycled to thianthrene by the reaction with nucleophilic dealkylating reagents such as pyridine.[5,6] A ladder-like polymer containing the thianthrenium repeating units is expected as a multielectron redox center applicable to alkene sensors[4] and high spin polymers.[7,8] We now describe our successful attempt to conveniently synthesize thianthrene ring systems, which can also be applied to the synthesis of the corresponding ladder-like polymer, heteropolyacene.

The synthetic concept consists of the superacid-induced intramolecular condensation of aryl sulfoxides.[9–12] We have already established that the protonation of aryl sulfoxides under strongly acidic conditions produces hydroxysulfonium ions which readily react with suitable aromatic molecules, thus yielding aromatic sulfonium salts at room temperature.[13] This reaction has been exploited for the synthesis of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) from 4-(methylsulfinyl)phenyl phenyl sulfide and triflic acid.[14] The product can be converted into an engineering plastic poly(thio-1,4-phenylene) (PPS) by nucleophilic demethylation using pyridine.[5,6] On the other hand, the superacidification of methylsulfinylbenzene produces only the corresponding dimer, methyl{4-(methylsulfinyl)phenyl}(phenyl)sulfonium triflate; a further propagation reaction is impeded by the decrease in the electron density at the *para* position of the terminal phenyl ring due to the electron withdrawing effect of the sulfonio group.[15] It has also been found that the admixture of methylsulfinylbenzene and triflic acid provides oligo(methylsulfonio-1,4-phenylene triflate) when the reaction is carried out in the presence of an external electron donor such as diphenyl amine to compensate for the inductive effect of the sulfonio group.[16] Herein we report that the protonation of a methylsulfinyl group by triflic acid is, however, not impeded by the sulfonio group at the *para* position of the benzene ring, and hence an admixture of bifunctional 1,4-bis(methylsulfinyl)benzene and electron-rich 1,4-bis(methylthio)benzene having electron-donating methylthio groups successfully provides the prepolymer of the heteropolyacene containing thianthrenium-type repeating units.

EXPERIMENTAL

Materials

Commercial reagents of 4-(methylthio)toluene, methyl phenyl sulfoxide, triflic acid, diethyl ether, pyridine, an aqueous solution of hydrogen peroxide, acetic acid, thianthrene, methyl formate, 1,4-dimethoxybenzene, dimethyl sulfoxide, xylene, aluminum(III) chloride, dimethyl disulfide, and deuterated solvents for NMR experiments were used as received. 1,4-Bis(methylthio)benzene and 1,4-bis(methylsulfinyl)benzene were prepared as previously reported.[17] The other solvents were purified by distillation prior to use.

Synthesis

Methyl(1-Methylthio-4-methylphenyl)(Phenyl)Sulfonium Triflate

To a mixture of 4-methylthiotoluene (10 mmol, 1.4 g) and methyl phenyl sulfoxide (10 mmol, 1.4 g) was slowly added triflic acid (10 mL) at 0°C in the dark. The color of the solution changed from yellow through orange to dark red as the reaction proceeded. The reaction mixture was then stirred at room temperature for 48 h. Pouring the resulting mixture into diethyl ether followed by collecting the white precipitate by filtration gave the desired product, methyl(1-methylthio-4-methylphenyl)(phenyl)sulfonium triflate, in 90% yield which was stored at 0°C in the dark.

^{1}H NMR (CD$_3$OH, TMS, 500 MHz, 0°C, ppm): $\delta = 2.47$ (s, 3H, CH$_3$), 3.31 (s, 3H, SCH$_3$), 3.80 (s, 3H, S$^+$CH$_3$), 7.52–8.32 (m, 8H, ArH).

^{13}C NMR (acetone-d_6, TMS, 500 MHz, 0°C, ppm): $\delta = 21.6$ (CH$_3$), 28.3 (SCH$_3$), 29.0 (S$^+$CH$_3$), 129.4, 130.6, 131.0, 131.6, 131.7, 132.5, 133.1, 133.2, 133.8, 135.8.

IR (KBr pellet, cm^{-1}): 2929 (ν_{CH}), 1257 (ν_{CF}), 812 (δ_{CH}), 639 (ν_{CF}).

1-Methylthio-4-methylphenyl Phenyl Sulfide

Methyl(1-methylthio-4-methylphenyl)(phenyl)sulfonium triflate (9.0 mmol, 3.8 g) was dissolved in pyridine (25 mL). The solution was refluxed for 2 h. Neutralization of the resulting mixture with HCl at 0°C followed by extraction of the product with CHCl$_3$, dehydration, rotary evaporation, and drying under vacuum afforded 1-methylthio-4-methylphenyl phenyl sulfide as an yellow liquid in 86% yield.

^{1}H NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): $\delta = 2.32$ (s, 3H, CH$_3$), 2.44 (s, 3H, SCH$_3$), 7.09–7.24 (m, 8H, ArH).

^{13}C NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): $\delta = 15.9$ (CH$_3$), 21.0 (SCH$_3$), 127.2, 130.0, 131.0, 131.1, 131.3, 131.4, 132.0, 132.9, 137.2, 137.3.

IR (KBr pellet, cm^{-1}): 2918 (ν_{CH}), 807 (δ_{CH}).

1-Methylsulfinyl-4-methylphenyl Phenyl Sulfide (**1a**)

An aqueous solution of hydrogen peroxide (3.7 mL) and acetic acid (0.3 mL) was slowly added to a solution of 1-methylthio-4-methylphenyl phenyl sulfide (3.0 mmol, 0.78 g) in CH$_2$Cl$_2$ (18 mL) and maintained at room temperature. The resulting mixture was stirred at room temperature for 10 h. After the reaction, extraction of the product with CHCl$_3$ followed by dehydration, rotary evaporation, and drying under vacuum afforded a crude product of **1a** which contained a small amount of 1-methylsulfonyl-4-methylphenyl phenyl sulfide as a side product. Purification was accomplished by column chromatography to give a pure product of **1a** in 70% yield.

^{1}H NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): $\delta = 2.38$ (s, 3H, CH$_3$), 2.69 (s, 3H, S(O)CH$_3$), 7.20–7.50 (m, 8H, ArH).

^{13}C NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): $\delta = 21.3$ (CH$_3$), 44.0 (S(O)CH$_3$), 124.1, 128.2, 128.3, 128.5, 130.5, 134.0, 134.1, 139.1, 142.7, 143.0.

IR (KBr pellet, cm^{-1}): 2916 (ν_{CH}), 1056 ($\nu_{S=O}$), 805 (δ_{CH}).

2.5-Dimethylthianthrenium Triflate (**2a**)

A solution of **1a** (0.50 mmol, 0.13 g) in CH$_2$Cl$_2$ (4 mL) with constant stirring in the dark was added very slowly to triflic acid (20 mL) maintained at room temperature. The resulting solution was stirred for 18 h in the dark. After the reaction, pouring the resulting mixture into diethyl ether followed by collecting the white precipitate by filtration in the dark gave **2a** in 78% yield as a gray powder.

^{1}H NMR (acetone-d_6, TMS, 500 MHz, 0°C, ppm): $\delta = 3.53$ (s, 3H, CH$_3$), 3.64 (s, 3H, S$^+$CH$_3$), 7.15–7.69 (m, 7H, ArH).

^{13}C NMR (acetone-d_6, TMS, 500 MHz, 0°C, ppm): $\delta = 22.7$ (CH$_3$), 23.7 (S$^+$CH$_3$), 129.0, 129.5, 130.4, 132.6, 133.6, 133.8, 134.1, 136.4, 136.6, 148.8.

IR (KBr pellet, cm^{-1}): 2920 (ν_{CH}), 1260 (ν_{CF}), 815 (δ_{CH}), 642 (ν_{CF}).

5-Methylthianthrenium Triflate (**2b**)

To a mixture of thianthrene (1.0 mmol, 0.21 g) and methyl formate (2.0 mmol, 0.12 g) maintained at 0°C was very slowly added triflic acid (2.7 mL) with constant stirring in the dark. The resulting purple solution was then stirred at room temperature for 15 h in the dark. After the reaction, pouring the resulting mixture into diethyl ether followed by collecting the light purple precipitate by filtration in the dark afforded **2b** in 72% yield.

^{1}H NMR (acetone-d_6, TMS, 500 MHz, 0°C, ppm): $\delta = 3.50$ (s, 3H, S$^+$CH$_3$), 7.78–8.36 (m, 8H, ArH).

^{13}C NMR (acetone-d_6, TMS, 500 MHz, 0°C, ppm): $\delta = 25.5$ (S$^+$CH$_3$), 120.3, 130.6, 131.1, 134.7, 135.3, 136.5.

IR (KBr pellet, cm^{-1}): 2929 (ν_{CH}), 1267 (ν_{CF}), 887 (δ_{CH}), 765 (ν_{CF}).

Crystal data: C$_{14}$H$_{11}$F$_3$S$_3$O$_3$, $M = 380.41$, colorless prismatic, triclinic, $\bar{P}$T(#2), $a = 10.099(2)$, $b = 12.415(2)$, $c = 6.9170(8)$ Å, $\alpha = 98.33(1)$, $\beta = 94.15(1)$, $\gamma = 69.33(1)°$, $V = 802.6(2)$ Å^3, $Z = 2$, $D_c = 1.574$ g cm^{-3}, μ(Mo K α) = 5.02 cm^{-1}, 3986 reflections measured, 3681 unique ($R_{int} = 0.036$), final $R = 0.043$, $R_w = 0.035$.

Demethylation of **2b** was performed by the treatment of **2b** with refluxing pyridine for 1 h. The product, thianthrene, was isolated in >95% yield which was identified by the conventional spectroscopic methods.

1,4-Dimethoxy-2,5-bis(Methylthio)Benzene

To a mixture of 1,4-dimethoxybenzene (10 mmol, 1.4 g) and dimethylsulfoxide (15 mmol, 1.2 g) maintained at 0°C in the dark was slowly added triflic acid (15 mmol). The resulting mixture was stirred at 100°C in the dark for 16 h. After the reaction, pyridine (10 mL) was slowly added to the resulting solution maintained at 0°C, and then the solution was refluxed for 2 h. Neutralization of the resulting solution with HCl, extraction of

the product with CHCl$_3$, dehydration, rotary evaporation and drying under vacuum afforded 1,4-Dimethoxy-2,5-bis(methylthio)benzene in 90% yield.

^{1}H NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): δ = 2.43 (s, 6H, SCH$_3$), 3.88 (s, 6H, OCH$_3$), 6.76 (s, 2H, ArH).

^{13}C NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): δ = 15.7 (SCH$_3$), 56.7 (OCH$_3$), 111.3, 124.3, 151.6.

IR (KBr pellet, cm^{-1}): 2915 (ν_{CH}), 1207, 1032 (ν_{CO}), 780 (δ_{CH}).

1,4-Dimethyl-2,5-bis(Methylthio)Benzene

To a mixture of aluminum(III) chloride (0.15 mol, 20 g) and *p*-xylene (0.10 mol, 11 g) was slowly added CH$_3$CN (100 mL) maintained at 0°C with constant stirring. To this solution was added dimethyl disulfide (0.15 mol, 14 g), and the resulting solution was refluxed for 48 h. After the reaction, CH$_3$CN was removed by evaporation. The product was extracted with CHCl$_3$ and purified by recrystallization from CH$_3$OH. The purified product was obtained as a colorless crystal in 40% yield.

^{1}H NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): δ = 2.32 (s, 6H, CH$_3$), 2.43 (s, 6H, SCH$_3$), 6.98 (s, 2H, ArH).

^{13}C NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): δ = 16.0 (CH$_3$), 19.6 (SCH$_3$), 127.4, 133.9, 134.5.

IR (KBr pellet, cm^{-1}): 2915 (ν_{CH}), 861 (δ_{CH}).

bis(2,5-Dimethyl-4-Methylthiophenyl) Sulfide

To a mixture of 1,4-dimethyl-2,5-bis(methylthio)benzene (0.50 mmol, 0.099 g) and sodium methanesulfinate (0.50 mmol, 0.043 g) was slowly added triflic acid (2 mL) at 0°C in the dark with constant stirring. The resulting solution was stirred at 100°C for 24 h. After the reaction, the product was collected as a white precipitate by pouring the resulting solution into diethyl ether, which was then dissolved in pyridine (8 mL). The pyridine solution was refluxed for 2 h to accomplish the nucleophilic demethylation of the sulfonium salt. After the reaction, pouring the resulting solution into 5% HCl and extraction of the demethylated product with CHCl$_3$ gave bis(2,5-dimethyl-4-methylthiophenyl) sulfide.

^{1}H NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): δ = 2.21 (s, 6H, CH$_3$), 2.34 (s, 6H, SCH$_3$), 6.85 (s, 2H, ArH), 7.01 (s, 2H, ArH).

^{13}C NMR (CDCl$_3$, TMS, 500 MHz, 25°C, ppm): δ = 15.5 (CH$_3$), 19.4 (CH$_3$), 20.1 (SCH$_3$), 126.7, 130.3, 132.2, 134.2, 136.5, 136.8.

IR (KBr pellet, cm^{-1}): 2919 (ν_{CH}), 811 (δ_{CH}).

Poly(Thio-1,4-phenylenethio-2,5-bis(Methylthio)-1,4-phenylene) (**3**)

The polymer **3** was prepared as previously described[17] with slight modifications as follows. To a mixture of bis(methylsulfinyl)benzene (5.0 mmol, 1.0 g) and

1,4-bis(methylthio)benzene (5.0 mmol, 0.85 g) maintained at $-20°C$ in the dark was slowly added triflic acid (10 mL). The resulting dark blue solution was stirred for 3 h in the dark at $-20°C$ and then for 100 h at room temperature. After the reaction, the solution was poured into diethyl ether to precipitate the product, poly{methylsulfonio-1,4-phenylenemethylsulfonio-2,5-bis(methylthio)-1,4-phenylene bis(triflate)}, as a white powder. The product was then dissolved in pyridine (500 mL) which was refluxed for 10 h. After cooling to room temperature, the resulting solution was poured into methanol containing 5% hydrochloric acid to precipitate the demethylated product, poly(thio-1,4-phenylenethio-2,5-bis(methylthio)-1,4-phenylene) (**3**), which was collected by filtration, washed repeatedly with methanol and water and dried under vacuum. The final product was obtained as a white powder in 96% yield.

^{1}H NMR (CD$_2$Cl$_2$, TMS, 500 MHz, 25°C, ppm): $\delta = 2.37$ (s, 6H, SCH$_3$), 7.12 (s, 4H, ArH), 7.17 (s, 2H, ArH).

^{13}C NMR (CD$_2$Cl$_2$, TMS, 500 MHz, 25°C, ppm): $\delta = 16.1$ (SCH$_3$), 127.8, 130.3, 131.7, 134.4, 143.6.

IR (KBr pellet, cm^{-1}): 2910 (ν_{CH}), 810 (δ_{CH}).

Elemental analysis. C$_7$H$_6$S$_2$ requires: C 54.50, H 3.92, S 41.57. Found: C 55.31, H 4.11, S 40.03%.

GPC (1-chloronaphthalene, 200°C, polystyrene standard): $M_n = 4.4 \times 10^3$, $M_w/M_n = 1.9$.

Poly(Thio-1,4-phenylenethio-2,5-bis(Methylsulfinyl)-1,4-phenylene) (**4**)

To a solution of polymer **3** (0.10 mmol unit, 0.031 g) in CHCl$_2$ (10 mL) was added an aqueous solution of H$_2$O$_2$ (1 mL) and acetic acid (0.2 mL) at room temperature. The resulting solution was stirred at 30°C for 12 h. The color of the solution changed gradually from colorless to light yellow. After the reaction, the solution was poured into CH$_3$OH containing 5% HCl to precipitate the product **4** which was obtained as a white powder in 95% yield.

^{1}H NMR (CD$_2$Cl$_2$, TMS, 500 MHz, 25°C, ppm): $\delta = 2.74$ (s, 6H, SCH$_3$), 7.18 (s, 4H, ArH), 7.91 (s, 2H, ArH).

^{13}C NMR (CD$_2$Cl$_2$, TMS, 500 MHz, 25°C, ppm): $\delta = 41.5$ (SCH$_3$), 130.3, 131.5, 131.8, 138.5, 158.5.

IR (KBr pellet, cm^{-1}): 2914 (ν_{CH}), 1052 ($\nu_{S=O}$), 832 (δ_{CH}).

UV–vis. (CH$_2$Cl$_2$, nm): $\lambda_{max} = 300$.

Elemental analysis: C$_7$H$_6$OS$_2$ requires: C 49.38, H 3.55, S 37.67. Found: C 49.53, H 3.74, S 36.33%.

GPC (1-chloronaphthalene, 200°C, polystyrene standard): $M_n = 2.7 \times 10^3$, $M_w/M_n = 1.8$.

Heteropolyacene (**5**)

To triflic acid (3 mL) was slowly added a solution of **4** (0.030 mmol unit, 0.010 g) in CH$_2$Cl$_2$ (4 mL). The color of the solution gradually changed from yellow to green.

The solution was stirred 80°C for 16 h. After the reaction, the solution was poured into diethyl ether to precipitate the product which was collected by filtration washed with diethyl ether, and dried under vacuum to give **5** as a brown powder in 80% yield.

^{1}H NMR (CD$_3$CN, TMS, 500 MHz, 25°C, ppm): $\delta = 3.16$ (s, 6H, SCH$_3$), 8.11 (s, 4H, ArH).

IR (KBr pellet, cm^{-1}): 1161, 637 (ν_{CF}), 859, 761 (δ_{CH}).

UV–vis. (CH$_3$CN, nm): $\lambda_{max} = 260$, 310, tailing edge 890.

Elemental analysis. C$_3$H$_5$F$_3$O$_3$S$_3$ requires: C 31.78, H 1.67, S 31.82. Found: C 31.97, H 1.98, S 29.99%.

Demethylation of **5** to **10**

Polymer **5** (1.3 g, 2.2 mmol unit) was dispersed in pyridine (100 mL) which was refluxed for 1 week. The resulting pale brown powder was collected by filtration, washed thoroughly with CH$_3$OH, and dried under vacuum to give a ladder polymer **10** having thianthrene-type repeating units in 98% yield (0.29 g).

Elemental analysis. C$_3$HS requires: C 52.14, H 1.46, S 46.40. Found: C 52.19, H 1.53, S 46.50%.

CP/MAS (ppm): $\delta = 131.6$, 135.5.

IR (KBr pellet, cm^{-1}): 849 (δ_{CH}).

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. ^{13}C CP/MAS spectra were obtained using a JEOL GSX-400 spectrometer. Infrared spectra were obtained using a Jasco FT-IR 5300 spectrometer with potassium bromide pellets. UV–vis spectra were recorded using a Shimadzu UV-2100 spectrometer. Thermogravimetry and differential thermal analysis were performed using a Seiko TG-DTA 220 instrument at a heating rate of 10°C/min under nitrogen at a flow rate of 300 mL/min. A 5 mg sample was used for each thermal analysis. Molecular weight measurements were done by gel permeation chromatography (GPC) at 210°C using a Senshu Kagaku VHT-GPC SSC-7000 system equipped with a UV detector set at 365 nm. 1-Chloronaphthalene was used as eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. The intrinsic semiconductivity of the material was determined by the bulk conductivity measurement of a pellet sample using the four-point method.

Crystal structure analysis was performed as follows. Colorless needle-like crystals of **2b** were grown from acetone solutions of the desired compound after layering with diethyl ether. Following microscopic examination in air, a suitable crystal was mounted on a glass fiber at room temperature. All measurements were done on a Rigaku AFC7R diffractometer with a 7.5 kW rotating anode generator and graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å). Unit cell parameters and an orientation matrix for data
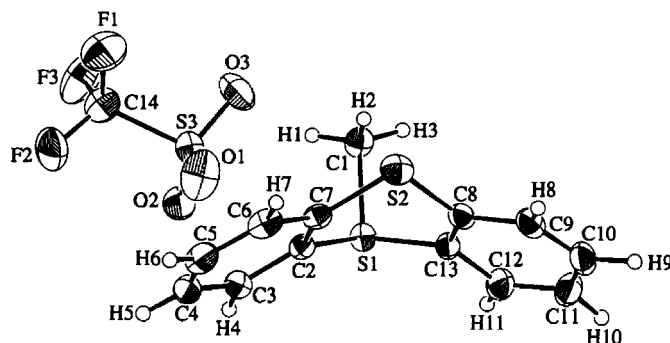
Figure 1. ORTEP view (30% probability ellipsoids) of **2b**. Selected bond length (Å) and angles (deg): S(1)—C(1), 1.798(4); S(1)—C(2), 1.777(3); S(1)—C(13), 1.771(4); S(2)—C(7), 1.753(4); S(2)—C(8), 1.757(4); C(1)—S(1)—C(2), 102.7(2); C(1)—S(1)—C(13), 102.6(2); C(2)—S(1)—C(13), 103.0(2); C(7)—S(2)—C(8), 102.7(2).

collection were determined by least-squares refinements using the setting angles of 25 carefully centered reflections in the range $29.0 < 2\theta < 30.0°$. The data were collected at a temperature of 23°C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 55.0°. Scans were done at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (up to 5 scans). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on the azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.94 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2214 observed reflections ($I > 3.00\sigma(I)$) and 253 variable parameters and converged with unweighted and weighted agreement factors of $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $R_w = (\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2)^{1/2}$ (vide supra). The plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The selected bond lengths and angles are shown in Fig. 1. All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corporation.

RESULTS AND DISCUSSION

Synthesis and Structural Features of Model Compounds

2-(Methylthio)-4-methylphenyl phenyl sulfide, prepared by the condensation of methylsulfinyl benzene and 4-(methylthio)toluene in triflic acid followed by a treatment with pyridine, was oxidized with H_2O_2 in the presence of acetic acid to yield **1a** (Sch. 1). Upon exposure of **1a** to triflic acid at 80°C, a methylsulfonio linkage was formed that
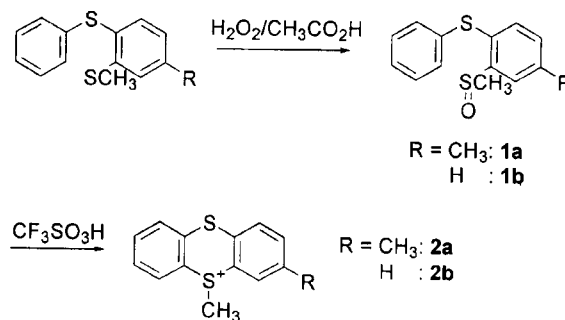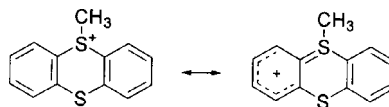
Scheme 1.

forced to decrease the dihedral angle of the two benzene units. The product **2a** was obtained in 90% isolated yield. Triflic acid was found to be the most effective for the quantitative reaction. The products from the intermolecular condensations were not detected when the reaction was carried out under dilute conditions (<0.1 mol/L). An alternative synthetic route to the thianthrenium salt was provided by the superacid-induced transmethylation to thianthrene using methylformate,[5,6] which yielded **2b** (see Experimental section). Conversely, the treatment of **2a** and **2b** with nucleophilic reagents such as pyridine resulted in the conversion of the methylsulfonio linkage to a sulfide bond.

In attempts to deduce the structural features from the bond lengths and angles of the thianthrenium unit,[18,19] the product **2b** was subjected to an X-ray crystallographic analysis. Layering the acetone solution of **2b** with diethyl ether afforded colorless prismatic crystals suitable for an X-ray diffraction study. An important aspect is derived from the comparison of the crystal structure (Fig. 1) with that of diphenyl(methyl)sulfonium hexafluoroantimonate (DPMS),[16] the control of **2b** without the sulfide bond between the two benzene rings. The torsion of the best least-squares plane of the adjacent benzene rings in **2b** (41.06°) is much smaller than that in DPMS (83.12°). Interestingly, the dihedral angle of the benzene rings in **2b** is intermediate between those of thianthrene (50.65°) and its cation radical (6°).[20] The small dihedral angle in **2b** reflects the delocalization of π electrons from the benzene rings into the methylsulfonio moiety through a p-δ/d-δ interaction[20,21] (vide infra). Additional support for this interpretation is provided by three features that warrant attention. In the first place, the S^+—C(phenyl) bond lengths in **2b** (1.777 and 1.771 Å) are shorter than those of DPMS (1.783 and 1.782 Å) as a result of an increased bond order in **2b**. Secondly, a deshielding effect of $\Delta\delta = 0.95$ ppm for the methylsulfonio protons in **2a** ($\delta = 3.64$ ppm) relative to the methylsulfinyl protons in the precursor **1a** ($\delta = 2.69$ ppm) in ^{1}H NMR due to the enhanced electron-withdrawing (inductive) effect of the sulfur atom upon the conversion of the sulfoxide into the sulfonium cation is, however, significantly smaller than that of the analogue without the bridging sulfide bond between the two benzene rings. In fact, a deshielding effect of $\Delta\delta = 1.29$ ppm is observed for the methyl protons in DPMS relative to those in methyl phenyl sulfoxide.[16] These results are rationalized by a significant carbenium ion contribution to the resonance structure of **2b**, the charge delocalization into the aromatic ring causing a decrease in the deshielding effect for the methyl protons

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Scheme 2.

(Sch. 2). Thirdly, the charge delocalization is pronounced when the resulting carbenium ions are stabilized in a strongly acidic medium. While the methylation of thianthrene to **2b** leads to only a small bathochromic shift of λ_{max} in the absorption spectra under neutral conditions indicating that the methylsulfonio and the sulfido linkages act as conjugation barriers, the triflic acid solution of **2b** is green and shows new absorption bands near $\lambda_{max} = 340$ nm ($\varepsilon_{max} = 7 \times 10^3\,M^{-1}\,cm^{-1}$) and 420 nm ($3 \times 10^3\,M^{-1}\,cm^{-1}$) (Fig. 2) due to the resonance structure. The absorption band is not attributable to the intramolecular CT transition because there is no indication of intermolecular donor–acceptor interaction between DPMS and diphenyl sulfide in triflic acid even at very high concentrations. The lack of noticeable changes upon superacidification in the absorption spectra of DPMS demonstrates the efficacy of planarization by the sulfido linkages in **2b** for charge delocalization.

The π electron delocalization over S^+ atoms was enhanced in an oligomer with a polyacene-type framework which was synthesized as follows. In attempts to obtain thiophenylene polymers having methylthio groups on the benzene ring, 1,4-bis(methylsulfinyl)benzene was reacted with a variety of aromatic molecules having methylthio groups (Sch. 3). The reaction with 1,4-dimethoxy-2,5-bis(methylthio)benzene or 1,4-dimethyl-2,5-bis(methylthio)benzene, however, did not give the corresponding polymer because of the concomitant side reactions such as the elimination of the methylthio group during the polymerization. Based on our previous findings that benzene and xylene undergo polymerization with sodium methanesulfinate under strongly acidic conditions to provide the corresponding methylsulfonioarylene polymers (Sch. 4),[16] we
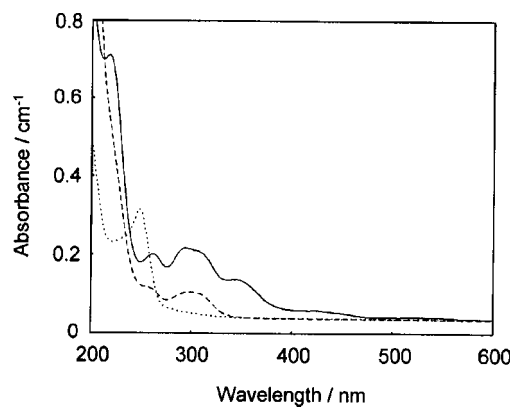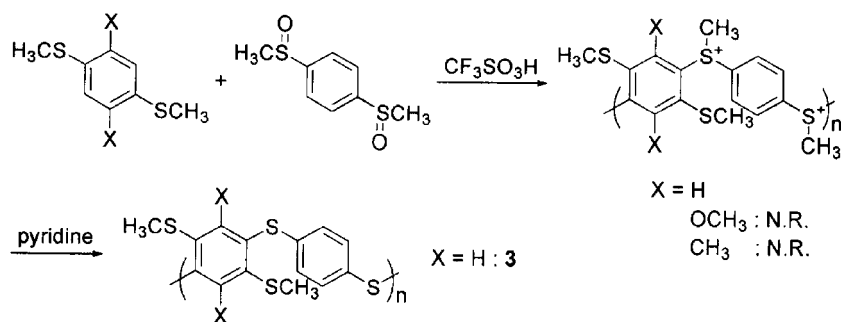

Figure 2. Absorption spectra of **2b** (0.02 mM) in triflic acid (—), **2b** (0.01 mM) in methanol (– – –), and thianthrene (0.01 mM) in methanol (· · ·).
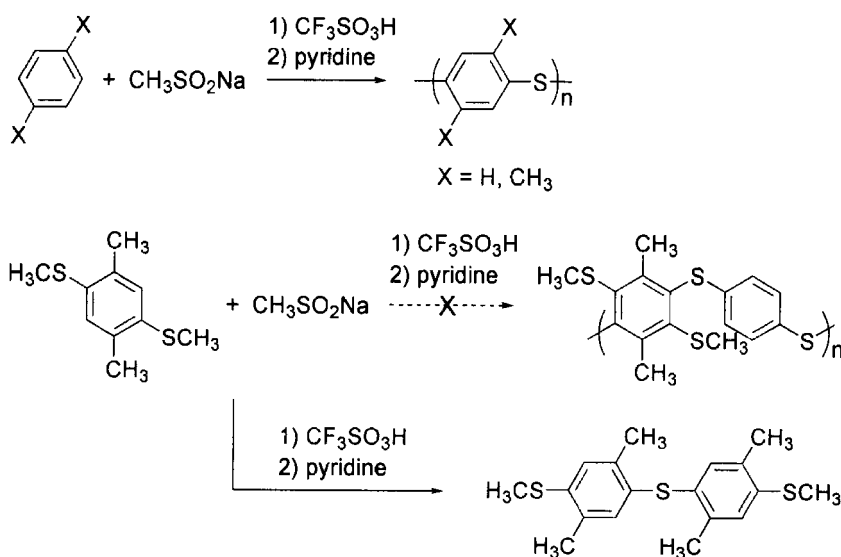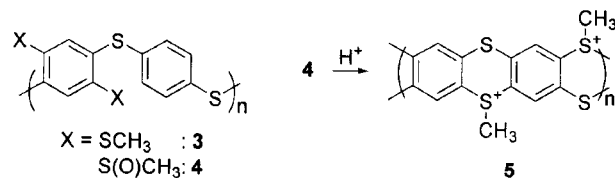
Scheme 3.

also carried out the reaction of 1,4-dimethyl-2,5-bis(methylthio)benzene with sodium methanesulfinate in the presence of triflic acid. However, the product was an undesired dimer, bis(2,5-dimethyl-4-methylthiophenyl) sulfide, due probably to the exchange reaction of the sulfonium ion (Sch. 4). Reasoning that the electrophilic reaction onto the benzene ring might be disfavored by the steric effect, we turned to the polymeriaztion of sterically less crowded monomers. It was found that 1,4-bis(methylthio)benzene was susceptible to polycondensation with 1,4-bis(methylsulfinyl)benzene that produced a precursor **3** on which the synthesis of **5** hinged (Sch. 3). The oxidation of **3** with H_2O_2 in CH_2Cl_2 effected the high yielding conversion of the methylthio groups to methylsulfinyl groups without the formation of undesired methylsulfonyl groups and molecular-weight degradation (see Experimental section). The exposure of **4** to triflic acid at 80°C under
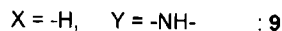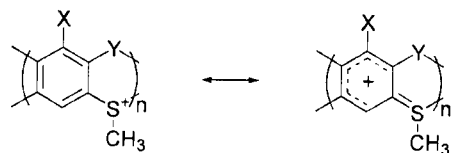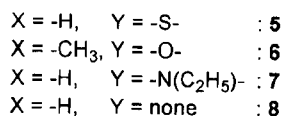

Scheme 4.

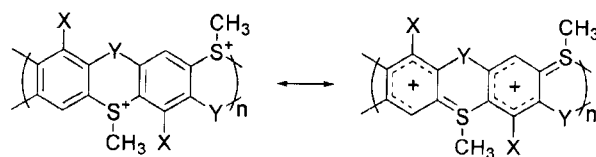666   Oyaizu et al.

Scheme 5.

dilute conditions induced the polymer-analogous ring-closing reaction of the pendant methylsulfinyl groups to yield the planarized oligomer **5** as a dark brown powder (Sch. 5). Because the cyclization at the *ortho*-position to the methylsulfonio group gives a significantly unstable structure in which hydrogen atoms of the two methylsulfonio groups can collide with each other, a linear **5** is exclusively obtained by the regioselective *para*-coupling.

Resonance Structure of Heteropolyacene

The first sulfur-containing heteropolyacene, to our knowledge, is a polycarbenium ion with thioxanthylium-type repeating units reported by Müllen et al., which was claimed to be isoelectronically related to poly[*n*]acenes. However, the characterization was impeded by an insufficient solubility in common solvents. On the other hand, we previously reported the synthesis of several ladder polymers with methylsulfonio linkages by the polymer-analogous Swern condensation of aryl sulfoxides and demonstrated their

X = -H,   Y = -S-   : **5**
X = -CH$_3$, Y = -O-   : **6**
X = -H,   Y = -N(C$_2$H$_5$)- : **7**
X = -H,   Y = none   : **8**

X = -H,   Y = -NH-   : **9**

Scheme 6.

solubility in protonic acids and polar organic solvents.[21–23] First, we reported an oligo(p-phenylene)-type ladder containing sulfide and sulfonio linkages, but the extensive π-conjugation was ascribed rather to the planarization of the benzene rings than to the p-π/d-π interaction between the sulfonium moiety and the benzene ring. Then, ladder polymers **7** and **9** (Sch. 6) containing benzenetetrayl units bridged by imino and methylsulfonio groups, an analogue of **5** containing imino groups in place of the sulfido linkages, were prepared.[22,23] However, the optical band gap estimated from the tailing edge of the absorption spectrum (520 nm, 2.4 eV) indicated that the π-electron conjugation did not extend throughout the polymer chain. The localized intramolecular donor–acceptor interaction between the imino and methylsulfonio moieties was also considered to play a role in the visible absorption.[16,22] A heteropolyacene **6** having phenoxathiinium-type repeating units was also prepared.[21] Taking into account the lack of such donor–acceptor interaction between oxo and methylsulfonio linkages, one could ascribe the smaller band gap in **6** only to the π-electron delocalization through the polymer backbone.[21] The polymer **5** in the present study can serve as an additional example to prove the proposed p-π/d-π interaction in heteropolyacene containing methylsulfonio moieties. In ^{1}H NMR, the methylsulfonio resonance of **5** appeared at a lower magnetic field than the methylsulfinyl resonance of **4**, consistent with the spectral change upon the conversion of **1** to **2**. A small deshielding effect ($\Delta\delta = 0.42$ ppm) for the methylsulfonio protons in **5** relative to the methylsulfinyl protons in **4**, the featureless absorption edge tailing to 890 nm (band gap = 1.2 eV), and the intrinsic semiconductivity of **5** ($\sigma = 1 \times 10^{-5}$ S cm^{-1}) in contrast to **4** ($\sigma < 10^{-11}$ S cm^{-1}) demonstrate that the benzene rings in **5** resonate through the cationic site and develop a π conjugated ladder framework, based on the delocalization of the π electron density into the low-lying vacant 3d orbitals of sulfur. These features are similar to those of other heteropolyacenes (**6**, **7**, and **9** in Sch. 6), but are in striking contrast to those of **8** (Table 1) which shows much lower electric conductivity and much deshielded sulfoniomethyl resonance in ^{1}H NMR due to the lack of the 3d–2p resonance through the methylsulfonio group.

Table 1. Properties of heteropolyacenes.

Molecule[a]	δ (ppm)[b]	σ (S/cm)[c]	Ref.
5	3.16[d]	9×10^{-6}	This work
6	2.89[e]	2×10^{-5}	[21]
7	2.89[f]	8×10^{-6}	[22]
8	3.85[g]	$<10^{-11}$	[16]
9	3.14[e]	8×10^{-6}	[23]

[a] See Sch. 6 for abbreviations.
[b] ^{1}H NMR chemical shifts of methyl groups bound to sulfur atoms.
[c] Intrinsic conductivities of pellet samples.
[d] In CD$_3$CN.
[e] In DMSO-d_6.
[f] In CDCl$_3$.
[g] In D$_2$O.

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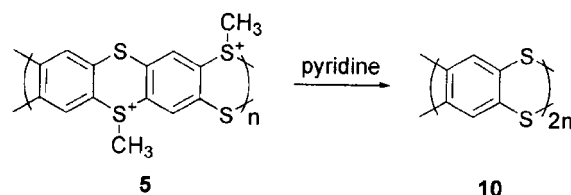
Scheme 7.

Thermal Properties

Poly(phenylene sulfide) (PPS) is a heteroatom-containing polymer with high chemical and thermal stability. PPS is a partly crystalline material ($T_g = 90$, $T_c = 137$ and $T_m = 282°C$) and is slowly decomposed at temperatures above 450°C ($T_{d10\%} = 516°C$).[21] A ladder-like polymer **10** (Sch. 7) with thianthrene-type building blocks should serve as a new material displaying interesting thermal properties. These include a high $T_{d10\%}$ due to the double stranded, rigid and planar structure.

The dealkylation reaction of alkylthianthrenium ions has been reported to take place in CH_3CN at room temperature by nucleophiles such as halide and thiophenoxide ions.[24] The high yielding conversion of **2b** to thianthrene by the treatment with pyridine (see Experimental section) led us to examine the demethylation of **5** (Sch. 7). The efficacy of this reaction for use in polymers has been demonstrated by the successful conversion of poly(methylsulfonio-1,4-phenylene triflate) (**8**) to PPS.[16] Polymer **5** was suspended in pyridine which was refluxed for a sufficiently long time to ensure the completion of the demethylation reaction. The product is obtained as a pale brown powder. The absence of the CH_3S^+-resonance in CP/MAS (see Experimental section) and of the IR signals due to triflate anions indicate the structure of **10** (Sch. 7). A comparison of the $T_{d10\%}$ of the linear analogue, PPS, with that of **10** reveal the enhancement in stability against thermolysis by the ladder framework. Polymer **10** shows the onset of decomposition near 440°C followed by only a slight weight loss; the thermal stability of the polymer **10** ($T_{d10\%} = 533°C$) is slightly higher than that of PPS. On the other hand, Polymer **5** is more easily decomposed upon heating due to the weaker sulfonio linkages. Polymers **5** and **10** both show no X-ray diffraction peak, revealing that they are amorphous. The DSC analysis shows no thermal transition before decomposition indicating the lack of glass transition due to the rigid structure.

CONCLUSIONS

The polymer-analogous condensation of aryl sulfoxides is proposed as a convenient method to prepare a ladder polymer containing sulfonio linkages that forces to decrease the dihedral angles between the consecutive aromatic units. The ladder polymer **5** has bathochromically-shifted absorptions in the electronic spectrum. The bridging methylsulfonio units have a p-π/d-π interaction with the benzene rings, thus allowing for greater electron delocalization between the consecutive benzenetetrayl subunits than

that between the 1,4-phenylene rings in poly(methylsulfonio-1,4-phenylene triflate) and PPS. Based on the delocalization of π-electrons through the sulfonium center, the heteropolyacene can be regarded as a new class of potentially useful π-conjugated polymers.

Supporting Information

Tables giving atomic coordinates, isotropic thermal parameters, anisotropic displacement parameters, bond lengths, bond angles, and torsional angles for **2b** are available from the authors.

ACKNOWLEDGMENTS

REFERENCES

1. Jones, G., II., Yan, D.-X.; Gosztola, D.J.; Greenfield, S.R.; Wasielewski, M.R. J. Am. Chem. Soc. **1999**, *121*, 11016.
2. Izuoka, A.; Hiraishi, M.; Abe, T.; Sugawara, T. J. Am. Chem. Soc. **2000**, *122*, 3234.
3. Doménech, A.; Casades, I.; García, H. J. Org. Chem. **1999**, *64*, 3731.
4. Lee, W.K.; Liu, B.; Park, C.W.; Shine, H.J.; Guzman-Jimenez, I.Y.; Whitmire, K.H. J. Org. Chem. **1999**, *64*, 9206.
5. Miyatake, K.; Yamamoto, K.; Endo, K.; Tsuchida, E. J. Org. Chem. **1998**, *63*, 7522.
6. Miyatake, K.; Endo, K.; Tsuchida, E. Macromolecules **1999**, *32*, 8786.
7. Nishide, H.; Doi, R.; Oyaizu, K.; Tsuchida, E. J. Org. Chem. **2001**, *66*, 1680.
8. Nishide, H.; Maeda, T.; Oyaizu, K.; Tsuchida, E. J. Org. Chem. **1999**, *64*, 7129.
9. Mancuso, A.J.; Swern, D. Synthesis **1981**, 165.
10. Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. J. Am. Chem. Soc. **1993**, *115*, 5819.
11. Wang, L.X.; Soczka-Guth, T.; Havinga, E.; Müllen, K. Angew. Chem. Int. Ed. Engl. **1996**, *35*, 1495.
12. Leuninger, J.; Wang, C.; Soczka-Guth, T.; Enkelmann, V.; Pakula, T.; Müllen, K. Macromolecules **1998**, *31*, 1720.
13. Yamamoto, K.; Kobayashi, S.; Shouji, E.; Tsuchida, E. J. Org. Chem. **1996**, *61*, 1912.
14. Haryono, A.; Yamamoto, K.; Shouji, E.; Tsuchida, E. Macromolecules **1998**, *31*, 1202.
15. Miyatake, K.; Yamamoto, K.; Yokoi, Y.; Tsuchida, E. Macromolecules **1998**, *31*, 403.
16. Miyatake, K.; Oyaizu, K.; Nishimura, Y.; Tsuchida, E. Macromolecules **2001**, *34*, 1172.

17. Oyaizu, K.; Yonemaru, H.; Iwasaki, T.; Matsubara, R.; Tsuchida, E. J. Macromol. Sci. **2003**, *A40*, 415.
18. Houmam, A.; Shukla, D.; Kraatz, H.-B.; Wayner, D.D.M. J. Org. Chem. **1999**, *64*, 3342.
19. Qian, D.-Q.; Shine, H.J.; Guzman-Jimenez, I.Y.; Thurston, J.H.; Whitmire, K.M. J. Org. Chem. **2002**, *67*, 4030.
20. Bock, H.; Rauschenbach, A.; Näther, C.; Kleine, M.; Havlas, Z. Chem. Ber. **1994**, *127*, 2043.
21. Oyaizu, K.; Mikami, T.; Mitsuhashi, F.; Tsuchida, E. Macromolecules **2002**, *35*, 67.
22. Oyaizu, K.; Mitsuhashi, F.; Tsuchida, E. Macromol. Chem. Phys. **2002**, *203*, 1328.
23. Miyatake, K.; Hay, A.S.; Mitsuhashi, F.; Tsuchida, E. Macromolecules **2001**, *34*, 2385.
24. Liu, B.; Shine, H.J. J. Phys. Org. Chem. **2001**, *14*, 81.