Synthesis of Benzo[4,5]phenaleno[1,9-*bc*]thiophene and Benzo[4,5]phenaleno[9,1-*bc*]thiophene

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Two pentacyclic thiophenes, benzo[4,5]phenaleno[1,9-*bc*]thiophene (**1**) and benzo[4,5]phenaleno[9,1-*bc*]-thiophene (**2**) were synthesized *via* the corresponding 3-methylphenanthro[2,1-*b*]thiophene (**7**) and 1-methylanthra[2,1-*b*]thiphene (**19**).

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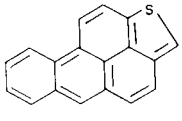
It is known that benzo[*a*]pyrene has been the most extensively investigated among the large number of polycyclic hydrocarbons (2). Many heterocyclic analogues of these carcinogenic hydrocarbons, such as acridine, carbazole, and thiophene derivatives, have been prepared and the relationship between their chemical structure and biological activity has been studied (3). However, the report of heterocyclic analogues of benzo[*a*]pyrene occurs much less frequently. Further, little research concerning the carcinogenicity of these compounds appears in the literature. The synthesis and carcinogenic evaluation of pyreno[1,2-*b*]-thiophene, a benzo[*a*]pyrene analog, was reported by Tilak, who published a review concerning the synthesis and carcinogenesis of thiophene isosters of several polycyclic hydrocarbons (4). Recently, we have synthesized tricyclic and tetracyclic thiophene derivatives and have tested these compounds for mutagenic activity (5). Karcher, *et al.*, reported the separation and determination of structure for two isomers of pentacyclic thiophenes, benzo[2,3]phenanthro[4,5-*bcd*]thiophene and chyrseno[4,5-*bcd*]thiophene, which have been found in coal tar (6). At this time, the preparation of these two compounds had already been accomplished by our group (7). We now wish to report the synthesis of the remaining two thia analogues of benzo[*a*]-pyrene, benzo[4,5]phenaleno[1,9-*bc*]thiophene (**1**) and benzo[4,5]phenaleno[9,1-*bc*]thiophene (**2**).



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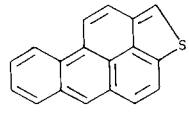

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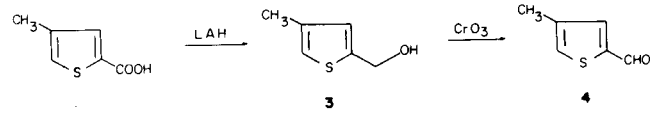
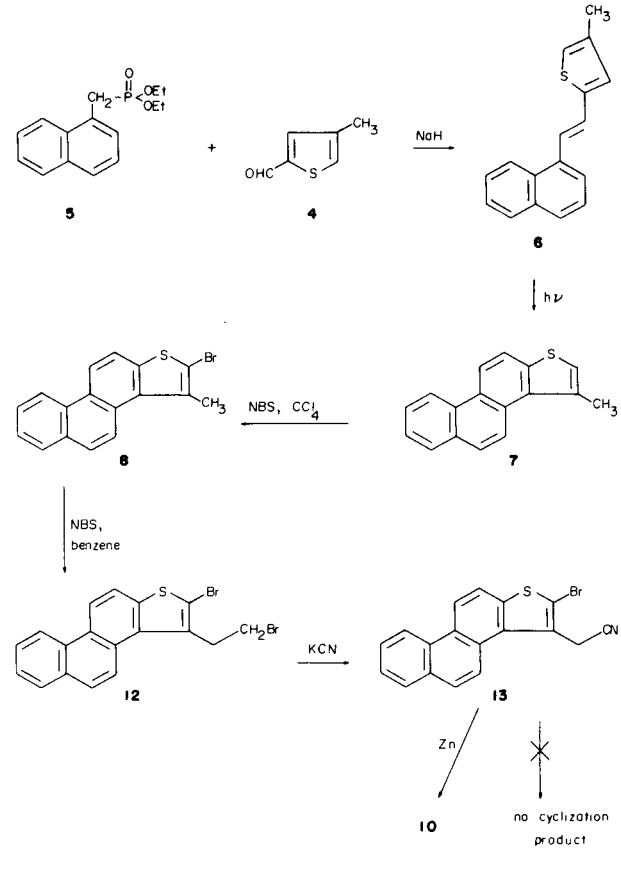
The key intermediates in this study were the corresponding methyl compounds, 3-methylphenanthro[2,1-*b*]-thiophene (**7**) and 1-methylanthra[2,1-*b*]thiophene (**19**), respectively. Recently, Iwao, *et al.*, reported a convenient synthesis of phenanthro[*b*]thiophenes by a combination of the Wadsworth-Emmons procedure and photocyclization (5). We applied the above reaction to the preparation of the methyl compound **7**.

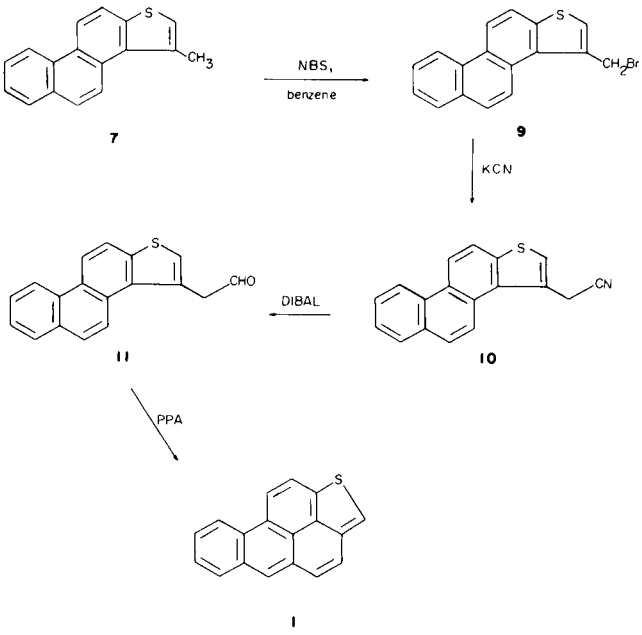


The reaction of 4-methyl-2-thiophenecarboxaldehyde (**4**), which was prepared by the oxidation of 4-methylthiophene-2-methanol (**3**) with chrominum trioxide, with diethyl naphthylmethylphosphonate (**5**) in the presence of sodium hydride in dimethoxyethane gave 4-methyl-2-(1-



naphthyl)ethenylthiophene (**6**) in 68% yield. Compound **6** was irradiated with a 450 Watt Hanovia medium pressure mercury lamp in the presence of iodine to give 3-methylphenanthro[2,1-*b*]thiophene (**7**) in 86% yield. The bromination of **7** with *N*-bromosuccinimide in carbon tetrachloride was unsuccessful. This reaction gave only the 2-bromo compound **8** in 50% yield. However, by using dry benzene as the solvent instead of carbon tetrachloride, the desired 3-bromomethylphenanthro[2,1-*b*]thiophene (**9**) was obtained in 62% yield. The same phenomenon was also observed in the bromination of 1-methylnaphtho-[2,1-*b*]thiophene with *N*-bromosuccinimide (**8**). Campaigne and Neiss (9) have also reported a similar reaction in the case of the bromination of 3-methylbenzo[*b*]thiophene.

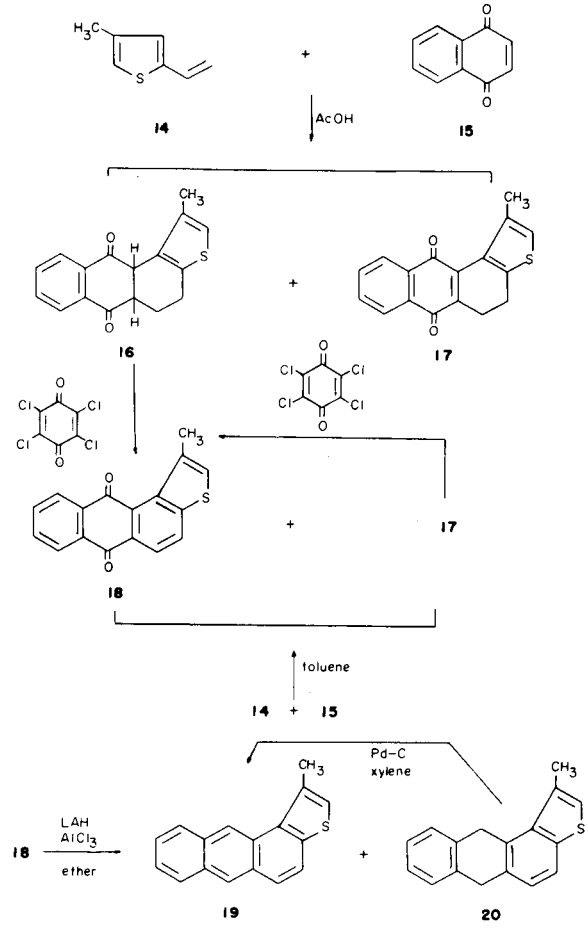
Recently, Newman and Kannan (10) reported a convenient cyanation of bromomethyl compounds with potassium cyanide in the presence of methyl tricaprylammonium chloride (**11**). Thus, treatment of **9** with potassium cyanide in the presence of Aliquat 336 in benzene/water gave **10** in 71% yield. Compound **10** was reduced with diisobutylaluminum hydride to give the corresponding aldehyde, which was cyclized with polyphosphoric acid to the final product, benzo[4,5]phenaleno[1,9-*bc*]thiophene (**1**), in 23% overall yield from **10**. Conversely, cyclization of 2-bromo-



3-cyanomethylnaphtho[2,1-*b*]thiophene (**13**) under conditions similar to those employed in the preparation of **1**, did not afford the desired product. Compound **13** was prepared in good yield by the bromination of **7** with *N*-bromosuccinimide in dry benzene followed by cyanation with potassium cyanide. Treatment of **13** with zinc dust in acetic acid under reflux for 1.5 hours gave the debrominated product, **10**, in 45% yield.

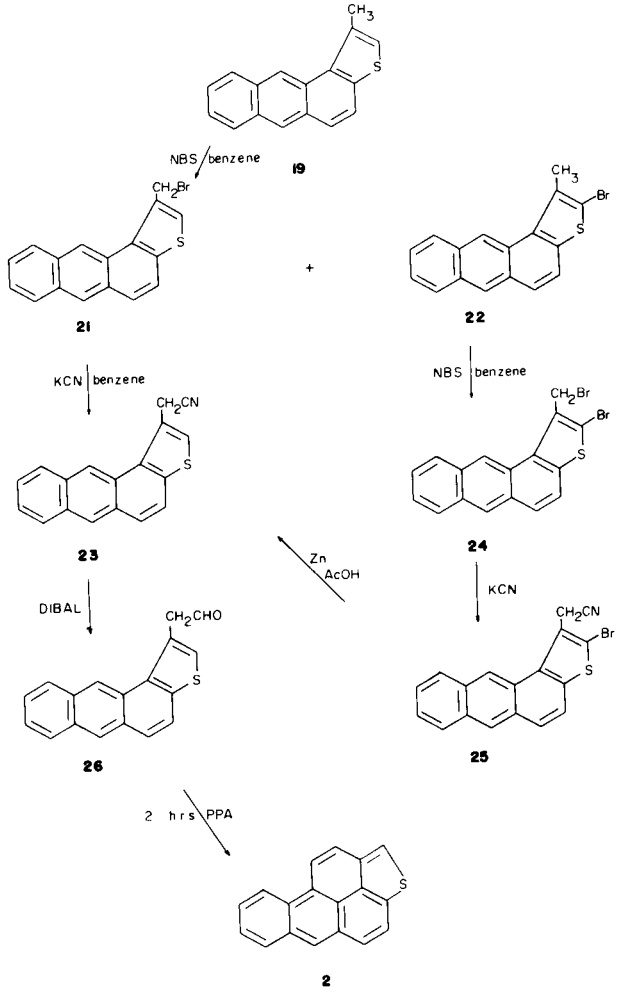
The synthesis of benzo[4,5]phenaleno[9,1-*bc*]thiophene (**2**) is described using a combination of the Diels-Alder reaction and Newman's procedure (10).

The reaction of 4-methyl-2-vinylthiophene (**14**) with 1,4-naphthoquinone (**15**) in acetic acid gave two compounds, 4,5,5a,6,11,11a-hexahydro-1-methyl-6,11-dioxoanthra[2,1-*b*]thiophene (**16**) and 4,5,6,11-tetrahydro-1-methyl-6,11-dioxoanthra[2,1-*b*]thiophene (**17**), in 11% and 6% yields, respectively. When either compound **16** or **17** was treated with chloranil in toluene the corresponding dehydro compound **18** was obtained in good yield. When the cyclo-addition reacton of **14** with **15** was carried out in toluene as the solvent instead of acetic acid, two products, **17** and **18** were obtained in 5% and 10% yields, respectively. These structures were determined by elemental analysis, ir, nmr and mass spectral data (see Experi-



mental). Reduction of **16** with lithium aluminum hydride in the presence of aluminium chloride in ether gave a mixture of 1-methylanthra[2,1-*b*]thiophene (**19**) and 6,11-dihydro-1-methylanthra[2,1-*b*]thiophene (**20**). The mixture was treated with palladium-charcoal in toluene under reflux to give only **19** as pale greenish yellow needles, mp 101° in 66% overall yield from **18**. Bromination of **19** with *N*-bromosuccinimide in a manner similar to the prepara-

tion of **9** gave a mixture of two compounds, 1-bromomethylanthra[2,1-*b*]thiophene (**21**) and 2-bromo-1-methylanthra[2,1-*b*]thiophene (**22**). Attempts to separate these compounds by column chromatography and fractional crystallization failed. This mixture was treated with potassium cyanide to give 1-cyanomethylanthra[2,1-*b*]thiophene (**23**) and **22** which were easily separable. However, this preparation from **19** gave **23** in poor yield.



Compound **22** was treated with *N*-bromosuccinimide to give 2-bromo-1-bromomethylanthra[2,1-*b*]thiophene (**24**) which was converted to 2-bromo-1-cyanomethylanthra-[2,1-*b*]thiophene (**25**) by treatment with potassium cyanide. In the preparation of **23**, compound **25** was treated with zinc dust in a manner similar to that of compound **10** from **13**. The overall yield was 18% from **22**. The desired compound **2** was obtained from **23** in 8% yield in a manner similar to the preparation of **1**. The compound **2**, mp 136°, yellow needles, was not stable and became dark green at room temperature after one week and about 3 hours in deuteriochloroform.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The ir spectra were obtained on a Perkin Elmer model 457 spectrophotometer and a Beckman Acculab 2 spectrophotometer. The ^{1}H nmr spectra were obtained on a Varian EM 390 spectrometer and JEOL FX 90Q spectrometer in the solvents indicated. Chemical shifts are reported in ppm from TMS as an internal standard and are given in δ units. Mass spectra were obtained on a Hewlett-Packard model 5980 A mass spectrometer. The uv spectra were recorded for solutions in cyclohexane with a Perkin Elmer 320 spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

4-Methylthiophene-2-methanol (3).

Into a stirred solution of 5.2 g (137 mmoles) of lithium aluminium hydride in 400 ml of absolute ether, 14.22 g (100 mmoles) of 4-methyl-2-thiophenecarboxylic acid was slowly added dropwise. When the addition was complete, the ether was brought to reflux for 5 hours, quenched cautiously by adding 80 ml of water, and enough 10% hydrochloric acid to dissolve the inorganic salts. The ether phase was separated and the aqueous phase was extracted with 300 ml of ether. The combined ether layers were washed successively with 100 ml of 5% sodium hydroxide and water and were dried over sodium sulfate. Evaporation of the ether yielded a colorless oil which was distilled at 78-80°/1.5 mm to give 11.0 g (86%) of a colorless oil; ir (neat): 3400 (OH broad); nmr (deuteriochloroform): δ 2.18 (s, CH_3, 3H), 2.52 (t, J = 6 Hz, OH, 1H), 4.64 (d, J = 6 Hz, -CH_2-O, 2H), 6.76 (s, H-3, H-5, 2H).

Anal. Calcd. for C_6H_8OS: C, 56.22; H, 6.30; S, 25.01. Found: C, 56.41; H, 6.09; S, 24.82.

4-Methyl-2-thiophenecarboxaldehyde (4).

A solution of 12.8 g (100 mmoles) of 4-methylthiophene-2-methanol (**3**) in 180 ml of dry pyridine was added slowly to a suspension of chromium trioxide-pyridine complex made from 22 g of chromium trioxide and 220 ml of dry pyridine. After stirring 2 hours at room temperature, the reaction mixture was filtered and washed with chloroform. The filtrate was washed successively with 10% hydrochloric acid and saturated sodium carbonate and was then dried over sodium sulfate. Evaporation of the chloroform yielded a brown oil which was distilled at 65-68°/0.75 mm to give 9.05 g (72%) colorless oil. This aldehyde had the odor of an aromatic aldehyde, such as benzaldehyde, and changed to a yellow oil on standing at room temperature for about 2 days; ir (neat): 1660 (C=O); nmr (deuteriochloroform): δ 2.28 (s, CH_3, 3H), 7.35 (s, H-5, 1H), 7.53 (s, H-3, 1H), 9.85 (s, -CH=O, 1H).

Anal. Calcd. for C_6H_6OS: C, 57.11; H, 4.79; S, 25.41. Found: C, 57.23; H, 4.81; S, 25.22.

4-Methyl-2-(1-naphthyl)ethenylthiophene (6).

Sodium hydride (50%, 1.92 g, 40 moles) was placed in 200 ml of 1,2-dimethoxyethane. Sodium hydride was used after washing twice with 20 ml of petroleum ether. The slurry was cooled to 20° and 5.56 g (20 mmoles) of diethyl 1-naphthylmethylphosphonate (**12**) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 30 minutes until the gas evolution had ceased. To the pale yellow solution, maintained below 25°, was added dropwise 2.52 g (20 mmoles) of 4-methylthiophene-2-carboxaldehyde (**4**). During the addition, a gummy precipitate appeared. The solution was stirred at room temperature for 2 hours and heated at 50° for 20 minutes. After cooling, a large excess of water was added and the resulting precipitate was collected by filtration. The crude product was purified by chromatography on a silica gel column using hexane as the eluent giving 8.41 g (68%) of product as pale yellow crystals, mp 74-75°. An analytical sample was recrystallized from hexane; nmr (deuteriochloroform): δ 2.25 (s, CH_3, 3H), 6.82 (s, H'-5 or H'-3, 1H), 6.93 (s, H'-5 or H'-3, 1H), 7.20 (d, J = 15 Hz, ethenyl proton, 1H), 7.42-7.92 (m, naphthyl and ethenyl protons, 7H), 8.17 (m, H-8, 1H); ms: m/e 250 (M^+, 100), 249 (M − 1, 35), 235 (M − 15, 20).

Anal. Calcd. for $C_{17}H_{14}S$: C, 81.56; H, 5.64; S, 12.81. Found: C, 81.80; H, 5.66; S, 12.68.

3-Methylphenanthro[2,1-*b*]thiophene (**7**).

A solution of 2 g (8 mmoles) of 4-methyl-2-(1-naphthyl)ethenylthiophene (**6**) and 0.1 g of iodine in 750 ml of cyclohexane was irradiated for 4 hours with a 450 watt Hanovia medium pressure mercury lamp through a corex filter. During the course of the reaction a slow stream of air was passed through the solution. The solvent was evaporated *in vacuo* and the residue was washed with a small amount of ethanol giving 1.67 g (84%) of colorless crystals, mp 153-154°; ir (potassium bromide): 3040 (w), 860, 810, 745; nmr (deuteriochloroform): δ 2.96 (s, C*H*$_3$, 3H), 7.23 (s, H-2, 1H), 7.59-7.75 (m, H-7, H-8, 2H), 7.86-8.10 (m, H-5, H-6, H-11, 3H), 8.60-8.83 (m, H-4, H-9, H-10, 3H), ms: m/e 248 (M^+, 100).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.22; H, 4.87; S, 12.91. Found: C, 81.99; H, 4.89; S, 13.17.

Reaction of 3-Methylphenanthro[2,1-*b*]thiophene (**7**) with NBS in Carbon Tetrachloride.

A mixture of 1.24 g (5 mmoles) of 3-methylphenanthro[2,1-*b*]thiophene (**7**), 0.88 g (5 mmoles) of *N*-bromosuccinimide, 5 mg of benzoyl peroxide, and 30 ml of carbon tetrachloride was shaken vigorously and then heated. During the first ten minutes an additional 5 mg of benzoyl peroxide was added. The reaction mixture was shaken frequently during the first hour, and the mixture was refluxed for an additional 2 hours. The mixture was then cooled in an ice bath. The succinimide was removed by filtration and washed with an additional 10 ml of carbon tetrachloride. The carbon tetrachloride was removed under reduced pressure and the residue was chromatographed on a silica gel column using hexane as an eluent to give pale brown crystals, mp 138-139°. An analytical sample was recrystallized from hexane giving 0.82 g (50%) of colorless prisms (**8**), mp 139°; nmr (deuteriochloroform): δ 2.88 (s, C*H*$_3$, 3H), 7.57-7.72 (m, H-7, H-8, 2H), 7.79-7.98 (m, H-5, H-6, H-11, 3H), 8.58-8.75 (m, H-4, H-9, H-10, 3H); ms: m/e 328 (M + 2, 98), 326 (M^+, 100), 247 (M − 79, 40).

Anal. Calcd. for $C_{17}H_{11}BrS$: C, 62.40; H, 3.39; S, 9.80. Found: C, 62.80; H, 3.36; S, 9.90.

3-Bromomethylphenanthro[2,1-*b*]thiophene (**9**).

A mixture of 0.89 g (5 mmoles) of *N*-bromosuccinimide, 1.24 g (5 mmoles) of 3-methylphenanthro[2,1-*b*]thiophene (**7**), 0.005 g of benzoyl peroxide and 50 ml of dry benzene was gently refluxed. Boiling was continued for 2.5 hours; the mixture was cooled in an ice-water bath and the crystals of succinimide were removed by filtration. The filtrate was washed with 10% sodium hydroxide solution and water. The benzene layer was dried over sodium sulfate and evaporated. The residue was recrystallized from hexane giving 1.0 g (62%) of colorless needles (**9**), mp 181°. The mother liquor was evaporated *in vacuo* and the residue was chromatographed on a silica gel column using hexane as an eluent to give 0.11 g (7%) of additional 2-bromo-3-methylphenanthro[2,1-*b*]thiophene (**8**), mp 137°; nmr (deuteriochloroform): δ 5.15 (s, C*H*$_2$, 2H), 7.22 (s, H-2, 1H), 7.56-7.77 (m, H-7, H-8, 2H), 7.87-8.09 (m, H-5, H-6, H-11, 3H), 8.58-8.81 (m, H-4, H-9, H-10, 3H); ms: m/e 328 (M + 2, 17), 326 (M^+, 16), 247 (100).

Anal. Calcd. for $C_{17}H_{11}BrS$: C, 62.40; H, 3.39; S, 9.80. Found: C, 62.35; H, 3.51; S, 9.28.

3-Cyanomethylphenanthro[2,1-*b*]thiophene (**10**).

A mixture of 1.13 g (5 mmoles) of 3-bromoethylphenanthro[2,1-*b*]thiophene (**9**), 2.5 g of potassium cyanide, 100 ml of benzene, 15 ml of water, and 10 drops of Aliquat 336 was refluxed for 2.5 hours. After the addition of 100 ml of benzene, the benzene layer was washed successively with water, 10% hydrochloric acid and water. After drying with sodium sulfate, the benzene was evaporated. The residue was recrystallized from benzene/hexane (1:1) giving 0.97 g (71%) of pale brown needles, mp 148-150°; ir (potassium bromide): 2460 (CN); nmr (deuteriochloroform): δ 4.34 (s, C*H*$_2$, 2H), 7.60-8.17 (m, H-2, H-4, H-5, H-6, H-7, H-9, H-11, 7H), 8.59-8.79 (m, H-9, 1H), 8.66 (d, J = 9 Hz, H-10, 1H); ms: m/e 258 (M^+, 100), 234 (M − 24, 7).

Anal. Calcd. for $C_{18}H_{11}NS$: C, 79.09; H, 4.06; N, 5.13; S, 11.73. Found: C, 78.69; H, 4.28; N, 5.02; S, 11.39.

2-Bromo-3-bromoethylphenanthro[2,1-*b*]thiophene (**12**).

A mixture of 0.65 g (2 mmoles) of 2-bromo-3-methylphenanthro[2,1-*b*]thiophene (**8**), 0.35 g (2 mmoles) of *N*-bromosuccinimide, 0.005 g of benzoyl peroxide and 50 ml of dry benzene was refluxed for 2 hours. The reaction mixture was cooled in an ice-bath and the precipitate was removed by filtration. the filtrate was washed with 10% sodium hydroxide solution and water. The benzene layer was dried with sodium sulfate and evaporated to yield white crystals which were recrystallized from benzene giving 0.71 g (88%) of colorless needles, mp 188-189°; nmr (deuteriochloroform): δ 5.11 (s, C*H*$_2$, 2H), 7.57-7.75 (m, H-7, H-8, 2H), 7.82-8.03 (m, H-5, H-6, H-11, 3H), 8.56-8.77 (m, H-4, H-9, H-10, 3H); ms: m/e 408 (M + 2, 12), 406 (M^+, 23), 327 (53), 325 (52), 246 (100).

Anal. Calcd. for $C_{17}H_{10}Br_2S$: C, 50.28; H, 2.48; S, 7.89. Found: C, 50.02; H, 2.76; S, 7.66.

2-Bromo-3-cyanomethylphenanthro[2,1-*b*]thiophene (**13**).

A mixture of 0.81 g (2 mmoles) of 2-bromo-3-bromoethylphenanthro-[2,1-*b*]thiophene (**12**), 1.5 g of potassium cyanide, 5 drops of Aliquat 336, 50 ml of benzene, and 10 ml of water was refluxed for 2 hours. After addition of 50 ml of benzene, the benzene layer was washed successively with water. After drying, the benzene was evaporated. The residue was recrystallized from benzene to give 0.33 g (47%) of pale brown needles, mp 223°; ir (potassium bromide): 2250 (CN); ms: m/e 353 (M + 2, 100), 351 (M^+, 96).

Anal. Calcd. for $C_{18}H_{10}BrNS$: C, 61.38; H, 2.86; N, 3.98; S, 9.10. Found: C, 61.70; H, 3.03; N, 3.91; S, 9.22.

Debromination of 2-Bromo-3-cyanomethylphenanthro[2,1-*b*]thiophene (**13**).

A mixture of 0.5 g (1.66 mmoles) of 2-bromo-3-cyanomethylphenanthro[2,1-*b*]thiophene (**13**), 1 g of zinc dust, and 30 ml of acetic acid was refluxed for 1.5 hours. After cooling, the reaction mixture was poured into 200 ml of ice-water and extracted with benzene. The benzene layer was dried with sodium sulfate and evaporated under reduced pressure. The residue was recrystallized from ethanol to give 0.21 g (45%) of 3-cyanomethylphenanthro[2,1-*b*]thiophene (**10**), mp 150°.

Benzo[4,5]phenaleno[1,9-*bc*]thiophene (**1**).

Diisobutylaluminum hydride (25% solution in toluene, 2 ml, 8 mmoles) was added with a syringe to a solution of 0.5 g (1.83 mmoles) of 3-cyanomethylphenanthro[2,1-*b*]thiophene (**10**) in 15 ml of dry benzene. The mixture was stirred at room temperature for 2 hours. Dilute hydrochloric acid was added and the product was extracted with chloroform. Evaporation of the dried extract gave the aldehyde as an oil which slowly crystallized; ir (neat): 1700 (C=O).

A mixture of the above crude aldehyde and 10 g of polyphosphoric acid was heated on a steam-bath for 1 hour. The reaction mixture was poured into ice-water and extracted with chloroform. The chloroform solution was washed successively with water and sodium carbonate solution, dried over sodium sulfate, and evaporated. The residue was chromatographed on a silica gel column using hexane as the eluent giving 0.11 g (23%) of pale yellow crystals. An analytical sample was recrystallized from hexane giving pale yellow leaflets, mp 154°; ir (potassium bromide): 3040 (w), 2930 (w), 1720 (w), 875, 825, 790, 750; uv (cyclohexane): λ max nm (log ε) 264 (4.82), 285 (4.42), 297 (4.37), 311 (4.38), 338 (4.35), 354 (4.59), 373 (4.78), 395 (3.95); nmr (deuteriochloroform): δ 7.49 (d, J = 1 Hz, H-3, H-4, 2H), 7.67 (s, H-2, 1H), 7.64-7.79 (m, H-7, H-8, 2H), 8.08-8.18 (m, H-6, 1H), 8.11 (s, H-5, 1H), 8.25 (d, J = 9 Hz, H-11, 1H), 8.79 (d, J = 9 Hz, H-10, 1H), 8.82 (near dd, H-9, 1H); ms: m/e 258 (M^+, 100), 234 (7), 213 (15).

Anal. Calcd. for $C_{18}H_{10}S$: C, 83.69; H, 3.90; S, 12.41. Found: C, 83.74; H, 4.04; S, 12.50.

The picrate was obtained as brown needles, mp 184-185°, from ethanol.

Anal. Calcd. for $C_{24}H_{13}N_3O_7S$: C, 59.14; H, 2.68; N, 8.62; S, 6.58. Found: C, 58.58; H, 2.88; N, 8.49; S, 6.46.

Reaction of 4-Methyl-2-vinylthiophene (**14**) with 1,4-Naphthoquinone (**15**).

(a) A solution of 38 g (241 mmoles) of 1,4-naphthoquinone (**15**) and 10 g (8 mmoles) of 4-methyl-2-vinylthiophene (**14**) in 20 ml of acetic acid was heated on a steam bath for 48 hours. After cooling, the precipitate was removed by decantation. The acetic acid layer was poured into 200 ml of water. The mixture was extracted with 300 ml of benzene. The benzene was removed at reduced pressure. The residue was chromatographed on silica gel using hexane/benzene (3:1) as eluent giving 1.24 g (6%) of orange red crystals. An analytical sample was recrystallized from ethanol to give orange red prisms (**17**), mp 196°; ir (potassium bromide): 1660, 1640 (C=O); nmr (deuteriochloroform): δ 2.28 (s, CH_3, 3H), 2.88 (s, -CH_2-CH_2-, 4H), 6.80 (s, H-2, 1H), 7.67-7.83 (m, H-8, H-9, 2H), 8.05-8.26 (m, H-7, H-10, 2H); ms: m/e 280 (M^+, 100).

Anal. Calcd. for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.31; S, 11.44. Found: C, 72.74; H, 4.43; S, 11.18.

Subsequent elution using benzene/hexane (1:1) afforded an orange red substance which recrystallized from ethanol to give 2.61 g (11%) of orange prisms (16), mp 126°; ir (potassium bromide): 1675, 1660 (C=O); nmr (deuteriochloroform): δ 1.67-2.30 (m, H-5, 5', 2H), 2.15 (s, C$H_{3'}$, 3H), 2.92 (q, J = 4, 9 Hz, H-4, 4', 2H), 3.32 (dq, J = 3, 5, 12 Hz, H-5a, 1H), 4.25 (d, J = 5 Hz, H-11a, 1H), 6.82 (s, H-2, 1H), 7.70-7.88 (m, H-8, H-9, 2H), 8.00-8.20 (m, H-7, H-10, 2H); ms: m/e 282 (M^+, 71), 104 (100).

Anal. Calcd. for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00; S, 11.36. Found: C, 72.39; H, 4.69; S, 10.58.

(b) A solution of 9.6 g (60.8 mmoles) of 1,4-naphthoquinone (**15**) and 5 g (40.3 mmoles) of 4-methyl-2-vinylthiophene (**14**) in 300 ml of dry toluene was refluxed for 48 hours. After cooling, the precipitate which formed was removed by filtration. The product gave brown needles, mp 187°, and was identified as 1,4-dihydroxynaphthalene. The toluene layer was washed with 300 ml of 10% sodium hydroxide solution and dried with sodium sulfate. The toluene was removed at reduced pressure. The residue was chromatographed on silica gel using hexane followed by hexane/benzene (3:1) as the eluents giving 0.56 g (5%) of 4,5,6,11-tetrahydro-1-methyl-6,11-dioxoanthra[2,1-*b*]thiophene (**17**) as red orange prisms, mp 195°.

Subsequent elution using hexane/benzene (1:1) afforded yellow crystals which were recrystallized from ethanol-benzene (1:1) to give 1.1 g (10%) of yellow needles, (**18**), mp 211°; ir (potassium bromide): 1665 (C=O); nmr (deuteriochloroform): δ 2.63 (s, CH_3, 3H), 7.36 (s, H-2, 1H), 7.66-7.83 (m, H-8, H-9, 2H), 8.06-8.33 (m, H-4, H-5, H-7, H-10, 4H); ms: m/e 278 (M^+, 100).

Anal. Calcd. for $C_{17}H_{10}O_2S$: C, 73.62; H, 3.62; S, 11.52. Found: C, 73.47; H, 3.53; S, 11.42.

Dehydration of **16** and **17** with Chloranil.

(a) A solution of 1.0 g (3.55 mmoles) of 4,5,6,11-tetrahydro-1-methyl-6,11-dioxoanthra[2,1-*b*]thiophene (**17**), 1.0 g (4.1 mmoles) of chloranil in 50 ml of toluene was refluxed 15 hours. After cooling, the precipitate was removed by filtration and the toluene solution was added to 30 ml of 10% sodium hydroxide solution. The mixture was then extracted with 100 ml of benzene. The organic layer was dried over anhydrous sodium sulfate. The benzene and toluene were removed by evaporation to yield yellow crystals which were chromatographed on a silica gel column using hexane/benzene (1:1) as the eluent giving 0.82 g (83%) of **18** as yellow needles, mp 211°.

(b) The dehydration of 1 g (3.5 mmoles) of 4,5,5a,6,11,11a-hexahydro-6,11-dioxoanthra[2,1-*b*]thiophene (**16**) with chloranil (2 g, 8.2 mmoles) gave also the desired product **18** in 62% yield in a manner similar to the dehydration above.

1-Methylanthra[2,1-*b*]thiophene (**19**).

A solution of 6 g (45 mmoles) of aluminum chloride in 40 ml of absolute ether was added to a stirred suspension of 2 g (53 mmoles) of lithium aluminum hydride in 80 ml of absolute ether. The mixture was stirred for 15 minutes and then 2 g (7 mmoles) of 6,11-dihydro-1-methyl-6,11-dioxoanthra[2,1-*b*]thiophene (**18**) was added portionwise. The gray ethereal suspension was maintained at reflux for 2 hours. Ethyl acetate (40 ml) was added dropwise in order to decompose the excess hydride reagent. The reaction mixture was poured into ice and 5% hydrochloric acid. The ether layer was separated and the aqueous phase was extracted with 3 × 50 ml portions of ether. The combined ethereal solution was successively washed with saturated sodium bicarbonate solution and water, and was then dried over sodium sulfate and concentrated *in vacuo*. The pale yellow gummy solid was chromatographed on a silica gel column using hexane as an eluent to yield a pale yellow substance, mp 75-81°. This product was a mixture of two compounds, 1-methylanthra-[2,1-*b*]thiophene (**19**) and 6,11-dihydro-1-methylanthra[2,1-*b*]thiophene (**20**). The tlc showed two spots at Rf 0.17 and 0.29 [hexane as the solvent on pre-coated tlc sheets (Silica Gel 60F-254, Merck)]. The mass spectrum of this mixture showed an ion peak at 250 (M^+, 100) and 248 (M^+, 88) due to **19** and **20**. A mixture of these reduction products, 0.3 g of 10% palladium on charcoal, and 50 ml of dry *m*-xylene was refluxed for 30 hours under stirring. The reaction mixture was cooled to below 20° and the catalyst removed by filtration. The *m*-xylene was removed under reduced pressure. The residue was chromatographed on silica gel using hexane as an eluent giving 1.16 g (66%) of pale yellow crystals. An analytical sample was recrystallized from ethanol to give pale yellow needles, mp 101°; nmr (deuteriochloroform): δ 2.98 (s, CH_3, 3H), 7.20 (s, H-2, 1H), 7.41-7.59 (m, H-8, H-9, 2H), 7.73 (s, H-4, H-5, 2H), 8.01 (near dd, H-7, H-10, 2H), 8.18 (s, H-6, 1H), 9.26 (s, H-11, 1H); ms: m/e 248 (M^+, 100), 202 (M − 46, 27).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.43; H, 5.01; S, 12.75.

1-Cyanomethylanthra[2,1-*b*]thiophene (**23**).

(a) A mixture of 0.72 g (4 mmoles) of *N*-bromosuccinimide, 1 g (4 mmoles) of 1-methylanthra[2,1-*b*]thiophene (**19**) 0.005 g of benzoyl peroxide, and 100 ml of dry benzene was gently refluxed. Boiling was continued for 2 hours, the mixture was cooled in an ice-water bath and the crystals of succinimide were removed by filtration. The filtrate was washed successively with 10% sodium hydroxide solution and water. The benzene layer was dried over sodium sulfate and evaporated to give crystals. The product was a mixture of 1-bromomethylanthra[2,1-*b*]thiophene (**21**) and 2-bromo-1-methylanthra[2,1-*b*]thiophene (**22**). A mixture of the above products was treated with potassium cyanide in a manner similar to the synthesis of **10**. The residue was chromatographed on a silica gel column using hexane as the eluent giving 0.8 g (62%) of greenish pale yellow leaflets (**22**), mp 168°; nmr (deuteriochloroform): δ 2.68 (s, CH_3, 3H), 7.42-7.80 (m, H-4, H-5, H-8, H-9, 4H), 7.90-8.10 (m, H-7, H-10, 2H), 8.36 (s, H-6, 1H), 8.99 (s, H-11, 1H); ms: m/e 326 (M^+, 100), 328 (M + 2, 100).

Anal. Calcd. for $C_{17}H_{11}BrS$: C, 62.40; H, 3.39; S, 9.80; Found: C, 62.63; H, 3.42; S, 9.59.

Subsequent elution using hexane/benzene (3:2) as the eluent gave 50 mg (5%) of 1-cyanomethylanthra[2,1-*b*]thiophene (**23**). An analytical sample was recrystallized from ethanol to give pale yellow needles, mp 172-174°; ir (potassium bromide): 2250 (CN); nmr (deuteriochloroform): δ 4.50 (s, CH_2CN, 2H), 7.50-7.88 (m, H-2, H-4, H-5, H-8, H-9, 5H), 7.98-8.10 (m, H-7, H-10, 2H), 8.50 (s, H-6, 1H), 8.69 (s, H-11, 1H).

Anal. Calcd. for $C_{18}H_{11}NS$: C, 79.09; H, 4.06; N, 5.13; S, 11.73. Found: C, 78.84; H, 4.26; N, 4.87; S, 12.33.

(b) 1-Cyanomethylanthra[2,1-*b*]thiophene (**23**) was also synthesized by the debromination of 2-bromo-1-cyanomethylanthra[2,1-*b*]thiophene (**25**) with zinc dust in acetic acid in 24% overall yield from **22**. The compound **25** was prepared from **22** in a manner similar to the synthesis of **10** from **8**. The mass spectrum of **25** showed an ion peak at 351 (M^+, 96), 353 (M + 2, 96), and 245 (100) and the ir (potassium bromide) absorbed at 2240 cm^{-1} due to the cyano group. The intermediate compound 2-bromo-1-bromomethylanthra[2,1-*b*]thiophene (**24**) was also identified by mass spectrum (m/e 406 (M^+, 100)).

Benzo[4,5]phenaleno[9,1-*bc*]thiophene (**2**).

Compound **2** was prepared from **23** *via* the intermediate aldehyde **26**

[ir neat): 1720 cm^{-1} (C=O)] and was obtained as yellow needles in 8% yield, mp 136°; ir (potassium bromide): 3040 (w), 2930, 2850 (w), 1375 (w), 1160 (w), 1150 (w), 875, 830, 795, 740, 655; uv (cyclohexane): λ max nm (log ε) 242 (4.52), 275 (4.60), 286 (4.67), 298 (4.80), 383 (3.95), 4.05 (4.32), 432 (4.49); nmr (deuteriochloroform): δ 7.18 (bs, H-1, 1H), 7.62-7.77 (m, H-7, H-8, 2H), 7.90 (d, J = 7 Hz, H-11, 1H), 8.05 (s, H-3, H-4, 2H), 8.23 (near dd, H-6, 1H), 8.54 (s, H-5, 1H), 8.59 (d, J = 7 Hz, H-10, 1H), 8.82 (near dd, H-9, 1H); ms: m/e 258 (M^+, 100), 256 (20), 248 (7), 213 (15).

Anal. Calcd. for $C_{16}H_{10}S$: C, 83.69; H, 3.90; S, 12.41. Found: C, 83.49; H, 4.07; S, 12.29.

The picrate was obtained as dark green needles, mp 165° dec from ethanol.

Anal. Calcd. for $C_{24}H_{13}N_3O_7S$: C, 59.14; H, 2.68; N, 8.62; S, 6.58. Found: C, 58.61; H, 2.92; N, 8.39; S, 6.46.

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