The Synthesis of Benzo[*b*]phenanthro[*d*]thiophenes and Anthra[*b*]benzo[*d*]thiophenes

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The synthesis of benzo[*b*]phenanthro[2,3-*d*]thiophene (**5**), benzo[*b*]phenanthro[4,3-*d*]thiophene (**6**), benzo[*b*]phenanthro[2,1-*d*]thiophene (**9**), benzo[*b*]phenanthro[3,2-*d*]thiophene (**14a**), anthra[1,2-*b*]benzo[*d*]thiophene (**24**), anthra[2,3-*b*]benzo[*d*]thiophene (**29**) and anthra[2,1-*b*]benzo[*d*]thiophene (**30**) is described as well as the preparation of 13-methylbenzo[*b*]phenanthro[3,2-*d*]thiophene (**14b**).

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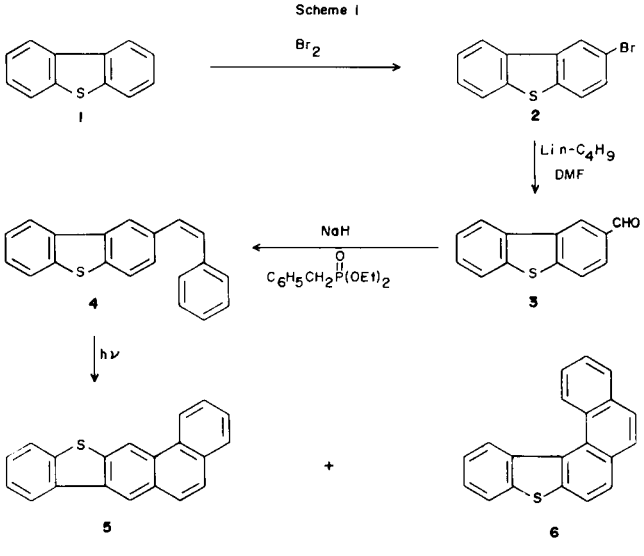
In continuation of our program [3-14] directed toward the synthesis of all of the unsubstituted polycyclic thiophenes and their monomethyl-, dimethyl- and monoethyl derivatives which occur or are suspected of occurring in coal liquids and related coal-derived products, we now report the synthesis of all of the unsubstituted benzo[*b*]phenanthro[*d*]thiophenes and anthra[*b*]benzo[*d*]thiophenes together with 13-methylbenzo[*b*]phenanthro[3,2-*d*]thiophene (**14b**).

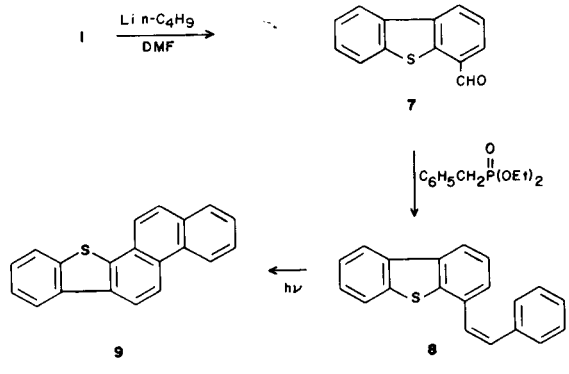
Benzo[*b*]phenanthro[2,3-*d*]thiophene (**5**) and benzo[*b*]phenanthro[4,3-*d*]thiophene (**6**) were obtained in a chromatographically separable mixture (neutral alumina) in four steps. Compounds **5** and **6** were both previously prepared *via* a different method by Pillai, Murthy and Tilak [15] and also by Pratap, Lee and Castle [16], respectively. Bromination of dibenzothiophene (**1**) gave 2-bromodibenzothiophene (**2**) (89% yield) which was lithiated (*n*-butyllithium, DMF, using the conditions outlined by Campaigne and Ashby [17]) to give dibenzothiophene-2-carboxaldehyde (**3**) (85% yield) which upon treatment with diethyl benzylphosphonate (Wadsworth-Emmons conditions) gave 2-styryldibenzothiophene (**4**) (86% yield) which upon photocyclization and separation gave benzo[*b*]phenanthro[2,3-*d*]thiophene (**5**) (37% yield) and benzo[*b*]phenanthro[4,3-*d*]thiophene (**6**) (50% yield). These transformations are illustrated in Scheme 1.

Scheme 1



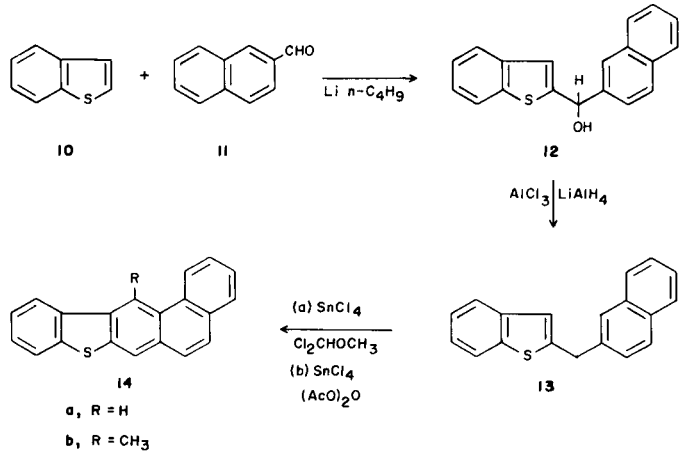
Benzo[*b*]phenanthro[2,1-*d*]thiophene (**9**), previously synthesized by Croisy, Jacquignon and Perin [18] by a different route, was obtained in three steps in this investigation. Reaction of dibenzothiophene (**1**) with *n*-butyllithium, which has been shown to metallate predominantly at the 4-position [19], followed by treatment with DMF gave dibenzothiophene-4-carboxaldehyde (**7**) (86% yield) which upon treatment with diethyl benzylphosphonate gave 4-styryldibenzothiophene (**8**) (85% yield) which upon photocyclization gave benzo[*b*]phenanthro[2,1-*d*]thiophene (**9**) in 83% yield (Scheme 2).

Scheme 2



Benzo[*b*]phenanthro[3,2-*d*]thiophene (**14a**), which was previously prepared *via* different methods by F. Mayer [20], Badger and Christie [21] and also by Pillai, Murthy and Tilak [16], and 13-methylbenzo[*b*]phenanthro[3,2-*d*]thiophene (**14b**) were both prepared in three steps, however, all intermediates were common until the last step.

Scheme 3

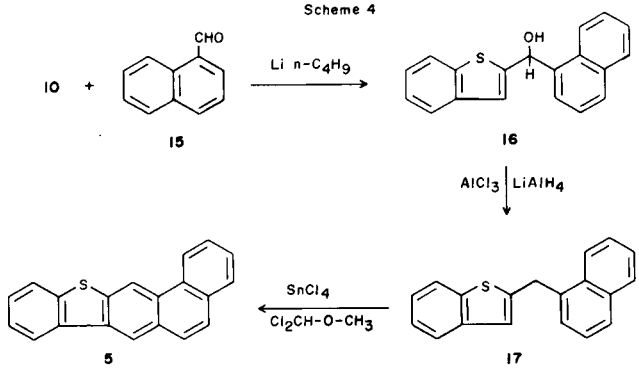


Benzo[*b*]thiophene (**10**) was lithiated (*n*-butyllithium) and allowed to react with naphthalene-2-carboxaldehyde (**11**) to give 2-benzo[*b*]thienyl-2-naphthylmethanol (**12**) (67% yield) which was then reduced with lithium aluminum hydride and aluminum chloride to give 2-(2-naphthylmethyl)benzo[*b*]thiophene (**13**) (88% yield).

The Bradsher reaction [22] has been widely applied to the synthesis of specially substituted anthracenes and related hydrocarbons. This was later adopted to polycyclic thiophenes by Ahmed, Ashby, Ayad and Meth-Cohn [23]. When **13** was heated with dichloromethyl ether and stannic chloride in dichloromethane according to Meth-Cohn's procedure [23], the product was benzo[*b*]phenanthro[3,2-*d*]thiophene (**14a**) (63% yield). The mp obtained (185°) did not agree with those reported in the literature: 173° [20], 142° [21] and 115° [15]. Therefore, the synthetic pathway was repeated by both co-authors of this paper (M. L. T. and Y. T.) and the same results were obtained. The spectral data confirms that **14a** has the structure proposed. When **13** was allowed to react with acetic anhydride, stannic chloride and dichloromethane as the solvent, the cyclized product was 13-methylbenzo[*b*]phenanthro[3,2-*d*]-thiophene (**14b**) in 35% yield (Scheme 3).

Compound **5** was also prepared unambiguously in four steps from benzo[*b*]thiophene (**10**). Compound **10** was allowed to react with *n*-butyllithium and the lithio derivative was treated with naphthalene-1-carboxaldehyde (**15**). The product, 2-benzo[*b*]thienyl-1-naphthylmethanol (**16**), was obtained in 83% yield. Reduction of **16** (LAH and aluminum chloride) gave 2-(1-naphthylmethyl)benzo[*b*]-thiophene (**17**) (86% yield) which upon treatment with dichloromethyl methyl ether and stannic chloride gave benzo[*b*]phenanthro[2,3-*d*]thiophene (**5**) in 60% yield (Scheme 4). The nmr spectra and melting point of compound **5** made *via* this route, was a further proof of the correct structural assignment of the products of the photocyclization of compound **4**.

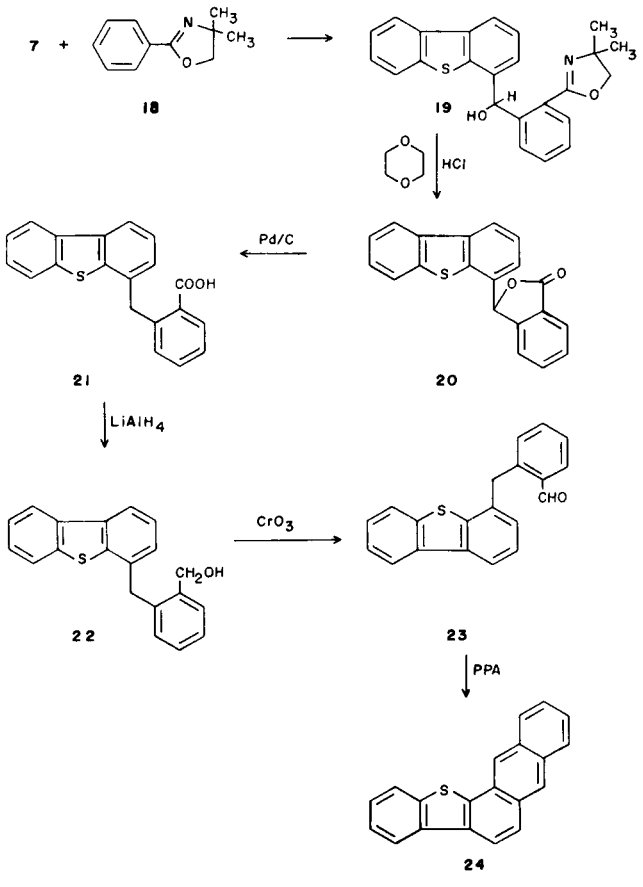
Scheme 4



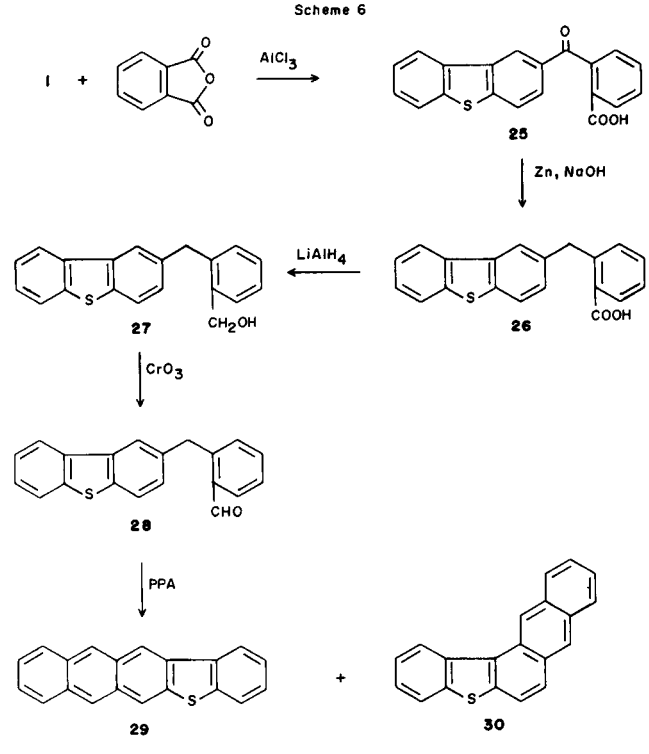
Anthra[1,2-*b*]benzo[*d*]thiophene (**24**), previously prepared by a different route by Sastry and Tilak [24], was obtained in this program in six steps. 4,4-Dimethyl-2-phenyl-2-oxazoline (**18**) [25] was lithiated (*n*-butyllithium) and allowed to react with dibenzothiophene-4-carboxaldehyde (**7**) to give 4-dibenzothienyl-2-(4,4-dimethyl-2-oxazolin-2-yl)phenylmethanol (**19**) in 77% yield. Ring-opening of the oxazoline ring with hydrochloric acid in 1,4-dioxane gave the intermediate carboxylic acid which was not isolated, but which spontaneously lactonized to give 3-(benzo[*b*]thien-4-yl)isobenzofuran-1-one (**20**) in 81% yield. The lactone **20** was reduced (Pd/C and acetic acid) to give 4-(*o*-carboxybenzyl)dibenzothiophene (**21**) (94% yield) which was reduced (LAH) to the alcohol **22** (85% yield) which was oxidized (chromium trioxide-pyridine complex) to the aldehyde **23** (71% yield) which was then cyclized (PPA) to anthra[1,2-*b*]benzo[*d*]thiophene (**24**) in 83% yield (Scheme 5).

Anthra[2,3-*b*]benzo[*d*]thiophene (**29**), which was prepared previously by Mayer [20] and also by Gverdtsiteli and Litvinov [26], and anthra[2,1-*b*]benzo[*d*]thiophene (**30**) were synthesized as a chromatographically separable mixture in five steps. When dibenzothiophene (**1**) was allowed to undergo a Friedel-Crafts reaction with phthalic anhydride, 2-(*o*-carboxybenzoyl)dibenzothiophene (**25**) was ob-

Scheme 5



Scheme 6



tained in 83% yield. This reaction was previously carried out by Gilman and Jacoby [19], however, only crude product was isolated and no spectral data of this compound was reported. Reduction of the ketone (zinc and sodium hydroxide) gave 2-(2-carboxybenzyl)dibenzothiophene (**26**) (80% yield) which was reduced (LAH) to the alcohol **27** (85% yield). Compound **27** was oxidized (chromium trioxide-pyridine complex) to the aldehyde **28** (78% yield) which upon cyclization with PPA gave after chromatography (neutral alumina, hexane) anthra[2,1-*b*]benzo[*d*]thiophene (**30**) (31% yield) and (elution with benzene) anthra-[2,3-*b*]benzo[*d*]thiophene (**29**) (55% yield) (Scheme 6). Compound **29** exists in two different crystalline forms: mp 280° [20,26] and 250° [27].

Some of the pentacyclic thiophenes are being screened against TA-98 and TA-100 in the Ames test (S9 liver homogenate activation) and these results will be published elsewhere.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. The ir spectra were obtained on a Beckmann Acculab 2 spectrometer. The ^{1}H-nmr spectra were obtained on a Varian EM-360A spectrometer and JEOL FX-90Q spectrometer in deuteriochloroform. Chemical shifts are reported in δ units. Mass spectra were obtained on a Hewlett-Packard model 5980A mass spectrometer. The uv spectra were obtained on a Cary Model 14 spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

2-Styryldibenzothiophene (**4**).

Sodium hydride (50% dispersion in mineral oil, 0.3 g, 12.5 mmoles) was washed twice with 10 ml of petroleum ether and suspended in 35 ml of 1,2-dimethoxyethane. The slurry was cooled to 20° and 1.0 g (4.4 mmoles) of diethyl benzylphosphonate was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 30 minutes. To this solution maintained below 25° and under a nitrogen atmosphere, dibenzothiophene-2-carboxaldehyde (**3**) [17] (0.65 g, 3.1 mmoles) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 2 ½ hours and then heated to 50° for 20 minutes. A large excess of water was added and the resulting white precipitate was collected by filtration. This product was recrystallized from benzene to give 0.75 g (86%) of white crystals, mp 175-176°; ir (potassium bromide): 1630 cm^{-1} (C=C); nmr (deuteriochloroform): δ 7.2-7.9 (m, 3-H, 4-H, 6-H, 7-H, 8-H, Ar*H*, phenyl-H and ethenyl-2H, 12H), 8.2 (bs, 1-H, 9-H, 2H, Ar*H*); ms: m/e 288 (M$^+$ +2, 6.8), 287 (M$^+$ +1, 23) 286 (M$^+$, 100), 285 (50), 284 (35), 282 (11), 252 (12).

Anal. Calcd. for $C_{20}H_{14}S$: C, 83.88; H, 4.93; S, 11.20. Found: C, 83.99; H, 5.06; S, 11.07.

Benzo[*b*]phenanthro[2,3-*d*]thiophene (**5**).

Stannic chloride (1.5 ml, 13 mmoles) was added to a stirred solution of 2-(1-naphthylmethyl)benzo[*b*]thiophene (**17**) (1.37 g, 5 mmoles) in 30 ml of methylene chloride at 0°. To this solution was added dichloromethyl methyl ether (2 g, 13 mmoles). The mixture was maintained at 0° for one hour and then at room temperature overnight. The reaction mixture was poured into ice and water. The organic phase was washed with water, dried with sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on an alumina column using hexane-benzene (4:1) as the eluent to give 0.85 g (60%) of pale yellow crystals, mp 327°, lit 327-328° [15]; nmr (deuteriobenzene): δ 6.90-7.35 (m, H-2, H-3, H-5, H-7, H-9, H-10, 6H, Ar*H*), 7.50-7.95 (m, H-4, H-6, H-8, 3H, Ar*H*), 8.50-9.05 (m, H-1, H-11,

2H, Ar*H*), 9.75 (bs, H-13, 1H, ArH); uv (hexane): λ max (log ε) 220 (3.78), 240 (3.82), 264 (sh) (3.59), 294 (3.56); ms: m/e 285 ($M^+ + 1$, 24), 284 (M^+, 100), 283 (97), 281 (11).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.67; H, 4.27; S, 11.19.

Benzo[*b*]phenanthro[4,3-*d*]thiophene (**6**) and Benzo[*b*]phenanthro[2,3-*d*]thiophene (**5**).

A solution of 1.50 g (5.2 mmoles) of 2-styryldibenzothiophene (**4**) and 0.1 g of iodine in 360 ml of benzene was irradiated for 5 hours with a 450 watt Hanovia medium pressure mercury lamp. 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 chromatographed on a silica gel column using hexane as the eluent giving 0.75 g (50%) of colorless crystals of **6**, mp 133°, lit 132-133 [16] and 0.55 g (37%) of colorless crystals of **5**.

The physical properties of compound **5** obtained by separation of this mixture were identical to those obtained for **5** prepared from **17** as described above. For compound **6** the physical properties are; nmr (deuteriochloroform): δ 7.15-7.60 (m, H-2, H-3, H-11, H-12, 4H, Ar*H*), 7.65-8.10 (m, H-4, H-5, H-6, H-10, 4H, Ar*H*), 7.75 (s, H-7, H-8, 2H, Ar*H*), 8.61-8.80 (m, H-13, 1H, Ar*H*), 8.90-9.15 (m, H-1, 1H, Ar*H*); uv (hexane): λ max (log ε) 218 (3.92), 237 (3.80), 281 (3.64), 298 (3.69); ms: m/e 286 ($M^+ + 2$, 6), 285 ($M^+ + 1$, 23), 284 (M^+, 100), 283 (94), 282 (82).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.35; H, 4.23; S, 11.28.

4-Styryldibenzothiophene (**8**).

This compound was prepared from 4-dibenzothiophenecarboxaldehyde (**7**) [19] (2.0 g, 9.4 mmoles) in a manner similar to the preparation of 2-styryldibenzothiophene (**4**) and 2.3 g (85%) was obtained as colorless crystals, mp 121-122°; nmr (deuteriochloroform): δ 7.15-7.65 (m, H-2, H-3, H-6, H-7, H-8, Ar*H*, phenyl-H and ethenyl-2H, 12H), 7.85-8.15 (m, H-1, H-9, 2H, Ar*H*); ir (potassium bromide): 1615 cm^{-1} (C=C); ms: m/e 287 ($M^+ + 1$, 24), 286 (M^+, 100), 285 (67), 284 (38), 282 (11), 271 (11), 252 (15).

Anal. Calcd. for $C_{20}H_{14}S$: C, 83.88; H, 4.93; S, 11.20. Found: C, 84.02; H, 5.06; S, 11.11.

Benzo[*b*]phenanthro[2,1-*d*]thiophene (**9**).

This compound was prepared from 4-styryldibenzothiophene (**8**) (1.0 g, 3.49 mmoles) in a manner similar to the preparation of benzo[*b*]-phenanthro[4,3-*d*]thiophene (**6**). Colorless crystals were obtained in 83% yield (0.82 g), mp 330°, lit 331° [18]; nmr (deuteriochloroform): δ 7.25-7.65 (m, H-2, H-3, H-8, H-9, 4H, Ar*H*), 7.75-8.00 (m, H-1, H-6, H-7, H-13, 4H, Ar*H*), 8.05-8.20 (m, H-4, H-5, 2H, Ar*H*), 8.25-8.55 (m, H-10, 1H, Ar*H*), 8.60-8.90 (m, H-12, 1H, Ar*H*); uv (hexane): λ max (log ε) 258 (3.59), 266 (sh) (3.52), 276 (3.49), 283 (sh) (3.51), 292 (3.60); ms: m/e 286 ($M^+ + 2$, 6), 285 ($M^+ + 1$, 20), 284 (M^+, 100), 283 (5), 280 (2).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.29; H, 4.18; S, 11.29.

2-Benzo[*b*]thienyl-2-naphthylmethanol (**12**).

Benzo[*b*]thiophene (**10**) (6.4 g, 48 mmoles) in 100 ml of dry ether was placed in a 500 ml three necked flask with an addition funnel, thermometer and a drying tube as an inlet for dry nitrogen. This solution was then cooled to −70° in a dry-ice acetone bath. *n*-Butyllithium solution (1.6 *M* in hexane, 35 ml, 56 mmoles) was added dropwise. After the addition, the mixture was stirred for one hour at −20° to −10° and for an additional two hours at room temperature. The mixture was then cooled to −70° and naphthalene-2-carboxaldehyde (7.8 g, 50 mmoles) in 50 ml of dry ether was added dropwise. After the addition, the solution was allowed to warm to 25° and was stirred for an additional 20 hours. The reaction mixture was poured into 300 ml of 10% hydrochloric acid solution and the mixture was extracted with 2 × 200 ml portions of chloroform. The chloroform layer was dried over anhydrous sodium sulfate and evaporated *in vacuo* giving a tan solid. The product was recrystallized from cyclohexane-benzene to give 9.3 g (67%) of tan crystals, mp 102°; ir (potassium bromide): 3550 cm^{-1} (OH); nmr (deuteriochloroform): δ 5.64 (s, C-H, 1H), 7.07 (s, H-3, benzo[*b*]thiophene, 1H, Ar*H*), 7.11-7.90 (m, naphthalene and benzo[*b*]thiophene rings, 11H).

Anal. Calcd. for $C_{19}H_{14}OS$: C, 78.59; H, 4.86; S, 11.04. Found: C, 78.47; H, 4.63; S, 11.23.

2-(2-Naphthylmethyl)benzo[*b*]thiophene (**13**).

To a suspension of lithium aluminum hydride (0.8 g, 21 mmoles) in 100 ml of dry ether was added aluminum chloride (2.66 g, 20 mmoles) in 50 ml of dry ether. To this solution was added 2-benzo[*b*]thienyl-2-naphthylmethanol (**12**) (5.8 g, 20 mmoles) in ether. The mixture was refluxed for 2 hours. After cooling, the reaction mixture was poured into 10% hydrochloric acid solution. The ether phase was washed successively with water, dilute aqueous alkali and water and then dried over anhydrous magnesium sulfate. The ether was evaporated *in vacuo* giving a tan solid which was recrystallized from methanol to give 4.8 g (88%) of pale yellow crystals, mp 147°; nmr (deuteriochloroform): δ 4.33 (s, CH_2, 2H), 6.95 (s, 3-position of benzo[*b*]thiophene ring, 1H), 7.13-7.83 (m, naphthalene and benzo[*b*]thiophene rings, 11H); ms: m/e 275 (M^+, + 1, 22), 274 (M^+, 100), 273 (89), 272 (12), 271 (28), 147 (33).

Anal. Calcd. for $C_{19}H_{14}S$: C, 83.17; H, 5.14; S, 11.69. Found: C, 83.18; H, 5.11; S, 11.75.

Benzo[*b*]phenanthro[3,2-*d*]thiophene (**14a**).

Compound **14a** was prepared from 2-(2-naphthylmethyl)benzo[*b*]thiophene (**13**) (1.50 g, 5.5 mmoles) in a manner similar to the preparation of benzo[*b*]phenanthro[2,3-*d*]thiophene (**5**) and 0.98 g (63%) of **14a** was obtained as a white solid. An analytical sample was recrystallized from hexane to give colorless needles, mp 185°, lit 173° [20], 142° [21] and 115° [15]; nmr (deuteriochloroform): δ 7.34-7.91 (m, H-2, H-3, H-4, H-9, H-10, H-11, 6H, Ar*H*), 7.66 (s, H-5, H-6, 2H, Ar*H*), 8.18 (s, H-7, 1H, Ar*H*), 8.70-8.93 (m, H-1, 1H, Ar*H*), 9.31 (s, H-13, 1H, Ar*H*); uv (hexane): λ max (log ε), 250 (3.51), 273 (sh) (3.52), 284 (3.66), 294 (3.82), 304 (3.68); ms: m/e 286 ($M^+ + 2$, 7), 285 ($M^+ + 1$, 23), 284 (M^+, 100).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.83; H, 4.11; S, 10.93.

13-Methylbenzo[*b*]phenanthro[3,2-*d*]thiophene (**14b**).

Stannic chloride (1 ml, 13 mmoles) was added to a stirred solution of 2-(2-naphthylmethyl)benzo[*b*]thiophene (**13**) (0.55 g, 2 mmoles) in 20 ml of methylene chloride at 0°. Acetic anhydride (1 ml) was added to the above solution. The mixture was maintained at 0° for 1 hour and then at room temperature for 20 hours. The reaction mixture was poured into ice-water and extracted with chloroform (100 ml). The organic layer was dried with sodium sulfate and evaporated *in vacuo*. The residue was mixed with 20 g of polyphosphoric acid. The mixture was heated at 100° for one hour. The reaction mixture was poured into 200 ml of ice water and extracted with benzene. The benzene layer was dried with anhydrous sodium sulfate to give a brown solid. This compound was purified on an alumina column using hexane as the eluent giving 0.21 g (35%) of product as colorless crystals. An analytical sample was recrystallized from hexane to give colorless needles, mp 163°; nmr (deuteriochloroform): δ 3.47 (s, CH_3, 3H), 7.20-7.55 (m, H-2, H-3, 10-H, 11-H, 4H, Ar*H*), 7.61 (s, H-5, H-6, 2H, Ar*H*), 7.77-7.92 (m, H-4, H-9, 2H, Ar*H*), 8.06 (s, H-7, 1H, Ar*H*), 8.42-8.69 (m, H-1, H-12, 2H, Ar*H*).

Anal. Calcd. for $C_{21}H_{14}S$: C, 84.53; H, 4.73; S, 10.74. Found: C, 84.78; H, 4.83; S, 10.68.

2-Benzo[*b*]thienyl-1-naphthylmethanol (**16**).

This compound was prepared from benzo[*b*]thiophene (**10**) (6.4 g, 48 mmoles) and 1-naphthaldehyde (**15**) (7.8 g, 50 mmoles), in a manner similar to the preparation of 2-benzo[*b*]thienyl-2-naphthylmethanol (**12**) and was obtained as tan crystals in 83% yield (11.6 g), mp 122°; ir (potassium bromide): 3600 cm^{-1} (OH); nmr (deuteriochloroform): δ 2.43 (bs, OH, 1H), 6.71 (s, C(OH)-*H*, 1H), 7.01 (s, 3-H, of thiophene ring, 1H, Ar*H*), 7.11-8.15 (m, aromatic protons, 11H, AR*H*).

Anal. Calcd. for $C_{19}H_{14}OS$: C, 78.59; H, 4.86; S, 11.04. Found: C, 78.41; H, 4.71; S, 11.01.

2-(1-Naphthylmethyl)benzo[*b*]thiophene (**17**).

This compound was prepared from 2-benzo[*b*]thienyl-1-naphthylmethanol (**16**) (5.8 g, 20 mmoles) in a manner similar to the preparation of 2-(2-naphthylmethyl)benzo[*b*]thiophene (**13**) and was obtained as tan needles in 86% yield (4.7 g), mp 103°. An analytical sample was recrystallized from methanol to give tan needles; nmr (deuteriochloroform): δ 4.62 (s, CH_2, 2H), 6.87 (s, 3-H of thiophene ring, 1H, Ar*H*), 7.10-8.12 (m, aromatic-H, 11H, Ar*H*); ms: m/e 275 ($M^+ + 1$, 23), 274 (M^+, 100), 273 (81), 272 (12), 271 (30).

Anal. Calcd. for $C_{19}H_{14}S$: C, 83.17; H, 5.14; S, 11.69. Found: C, 83.30: H, 5.22; S, 11.55.

4-Dibenzothienyl-2-(4,4-dimethyl-2-oxazolin-2-yl)phenylmethanol (**19**).

n-Butyllithium (32 ml of 1.7 *M* solution in hexane) was added *via* a syringe over a period of 30 minutes to a dry solution of the oxazoline **18** [25] (5.0 g, 28.5 mmoles) and 300 ml of dry ether under nitrogen at −78° whereupon a yellow precipitate separated from the solution. The mixture was allowed to warm to −5° and cooled back to −78°, after which dibenzothiophene-4-carboxaldehyde (**7**) [19] (5.5 g, 25.9 mmoles) was added slowly with a spatula. The mixture was allowed to warm slowly and was then stirred overnight at room temperature. It was then poured into ice and the layers separated and extracted twice with 100 ml of ethyl ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo* giving 7.7 g (77%) of a pale yellow oil; ir (potassium bromide): 3400 (OH), 1645 cm^{-1} (C=N); nmr (deuteriochloroform): δ 1.35 (s, 2-CH_3, 6H), 4.05 (AB-quartet, J = 6 Hz, -CH_2-of oxazoline, 2H), 4.90 (bs, -C(O*H*)-H, 1H), 2.20 (s, -C(OH)-*H*, 1H), 7.20-7.60 (m, H-2, H-3, H-7, H-8 of dibenzothiophene, H-5′, H-6′ of benzene, 6H, Ar*H*), 7.75-8.40 (m, H-1, H-6, H-9 of dibenzothiophene, 2′-H, 4′-H of benzene, 5H, Ar*H*); ms: m/e 388 ($M^+ + 1$, 17), 387 (M^+, 63), 315 (68), 184 (100).

Anal. Calcd. for $C_{24}H_{21}NO_2S$: C, 74.39; H, 5.46; S, 8.26. Found: C, 74.52; H, 5.58; S, 8.03.

3-(4-Dibenzothienyl)benzo[*c*]furan-1(3*H*)-one (**20**).

A solution of **19** (1.7 g, 4.4 mmoles), 40 ml of 50% hydrochloric acid and 60 ml of 1,4-dioxane was refluxed for 20 hours. The solution was allowed to cool slowly to give light brown needles. The solution was filtered and washed twice with 50 ml of hexane to give 1.1 g (81%) of product. An analytical sample was recrystallized from hexane-benzene to give colorless needles, mp 206°; ir (potassium bromide): 1760 (C=O) 1280 cm^{-1} (C-O-C); nmr (deuteriochloroform): δ 6.65 (s, C-H, 1H), 7.30-7.67 (m, H-2, H-3, H-7, 8-H of dibenzothiophene, H-4′, H-5′ and H-6′ of benzene 7H, Ar*H*), 7.90-8.25 (m, H-1, H-6, H-9 of dibenzothiophene and H-7′ of benzene, 4H, Ar*H*); ms: m/e 317 ($M^+ + 1$, 35), 316 (M^+, 100), 271 (67), 183 (36).

Anal. Calcd. for $C_{20}H_{12}O_2S$: C, 75.93; H, 3.82; S, 10.13. Found: C, 76.11; H, 3.98; S, 9.95.

4-(*o*-Carboxybenzyl)dibenzothiophene (**21**).

A mixture of **20** (1.5 g, 4.7 mmoles), 0.5 g of 5% palladium on carbon and 250 ml of acetic acid was hydrogenated overnight at 80-90° at atmospheric pressure. The solution was then boiled and filtered after cooling to remove the catalyst. The acetic acid solution was dissolved in 600 ml of water and white crystals, 1.4 g (94%), appeared. An analytical sample was recrystallized from benzene to give colorless needles, mp 179°; ir (potassium bromide): 1690 (C=O), 3550 cm^{-1} (OH); nmr (deuteriochloroform): δ 4.65 (s, CH_2, 2H), 7.0-7.60 (m, H-2, H-3, H-7, H-8 of dibenzothiophene, H-3′, H-4′ and H-5′ of benzene, 7H, Ar*H*); 7.70-8.30 (m, H-1, H-6, H-9 of dibenzothiophene and H-6′ of benzene, 4H, Ar*H*); ms: m/e 319 ($M^+ + 1$, 19), 318 (M^+, 80), 300 (100), 271 (64).

Anal. Calcd. for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; S, 10.07. Found: C, 75.54; H, 4.46; S, 9.88.

4-(2-Hydroxymethylbenzyl)dibenzothiophene (**22**).

Compound **21** (0.7 g, 2.2 mmoles) was dissolved in 200 ml of dry ether and lithium aluminum hydride (0.2 g, 5.3 mmoles) was added slowly portionwise. This mixture was refluxed for 2.5 hours. After cooling, the mixture was poured into 200 ml of ice water and acidified with 50 ml of 10% sulfuric acid. The mixture was extracted with 3 × 75 ml portions of chloroform, and the chloroform layer was dried over anhydrous sodium sulfate and evaporated *in vacuo* giving 0.57 g (85%) of white crystals. An analytical sample was recrystallized from hexane-benzene to give colorless needles, mp 115°; ir (potassium bromide): 3400 cm^{-1} (OH); nmr (deuteriochloroform): δ 4.50 (s, C(H_2)-OH, 2H), 4.15 (s, CH_2, 2H), 6.90-7.50 (m, H-2, H-3, H-7, H-8 of dibenzothiophene, H-3′, H-4′ and H-5′ of benzene, 7H, Ar*H*); ms: m/e 305 ($M^+ + 1$, 6), 304 (M^+, 28), 286 (72), 285 (100).

Anal. Calcd. for $C_{20}H_{16}OS$: C, 78.91; H, 5.30; S, 10.53. Found: C, 79.00; H, 5.25; S, 10.55.

4-(2-Formylbenzyl)dibenzothiophene (**23**).

Chromium trioxide (0.8 g, 8 mmoles) was carefully added in small portions to 11 ml of dry pyridine. After all of the chromium trioxide had dissolved, compound **22** (0.5 g, 1.64 mmoles) dissolved in 10 ml of pyridine was added to the suspension of chromium trioxide. After stirring at room temperature for two hours, the reaction mixture was filtered to remove the chromium trioxide which was washed twice with chloroform. The filtrate was washed with 10% hydrochloric acid and then 10% aqueous sodium carbonate solution. The chloroform layer was dried over sodium sulfate and evaporated *in vacuo* giving 0.35 g (71%) of a pale brown oil. An analytical sample was prepared by chromatography on an alumina column using hexane as the eluent, giving a pale yellow oil; ir (potassium bromide): 1670 cm^{-1} (C=O); nmr (deuteriochloroform): δ 4.67 (s, CH_2, 2H), 6.90-7.50 (m, H-2, H-3, H-7, H-8 of dibenzothiophene, H-3′, H-4′, and H-5′ of benzene, 7H, Ar*H*), 7.60-8.25 (m, H-1, H-6, H-9 of dibenzothiophene and H-6′ of benzene, 4H, Ar*H*), 10.15 (s, C*H*O, 1H).

Anal. Calcd. for $C_{20}H_{14}OS$: C, 79.44; H, 4.67; S, 10.60. Found: C, 79.67; H, 4.75; S, 10.31.

Anthra[1,2-*b*]benzo[*d*]thiophene (**24**).

Compound **23** (0.3 g, 1.05 mmoles) was mixed with polyphosphoric acid (8 g) and heated to 100° for one hour. After cooling, an additional 100 ml of water was added and the mixture was stirred until all of the polyphosphoric acid had dissolved. The mixture was extracted with 2 × 50 ml portions of benzene and the benzene layer was dried over sodium sulfate and evaporated *in vacuo* giving 0.23 g (83%) of pale yellow leaves. An analytical sample was recrystallized from benzene, mp 226° lit mp 228° [24]; nmr (deuteriochloroform): δ 7.30-7.66 (m, H-2, H-3, H-9 and H-10, 4H, Ar*H*), 7.75-8.33 (m, H-1, H-4, H-8 and H-11, 4H, Ar*H*), 7.96 (s, H-6 and H-7, 2H, Ar*H*), 8.44 (s, H-5, 1H, Ar*H*), 8.59 (s, 13-H, 1H, Ar*H*); uv (hexane): λ max (log ε) 252 (3.45), 251 (3.44), 283 (3.66), 294 (3.91).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.39; H, 4.26; S, 11.20.

2-(*o*-Carboxybenzoyl)dibenzothiophene (**25**).

To a solution of 33 g (0.25 mole) of aluminum chloride in 1,2-dichloroethane (180 ml) was added a suspension of 12 g (0.081 mole) of phthalic anhydride in 120 ml of 1,2-dichloroethane. The resulting yellow suspension was stirred for 30 minutes and then a solution of dibenzothiophene (20 g, 0.11 mole) in 100 ml of 1,2-dichloroethane was added dropwise with stirring over a one hour period, such that the temperature of the reaction remained below 30°. The reaction mixture was then allowed to stir for 4 hours at ambient temperature, and then was poured into a solution of 500 ml of water and 200 ml of concentrated hydrochloric acid. The layers were separated and the combined organic layers were extracted with 10% sodium hydroxide solution. The basic extracts were treated with decolorizing carbon, filtered and acidified to afford 29.9 g (83%) of yellow crystals. Recrystallization from hexane-benzene gave **25**, mp 183°, lit mp of the crude product was 120-125° [19]; ir (potassium bromide): 1645 (C=O), 1675 (C(OH)=O), 3500 cm^{-1} (OH); nmr (deuteriochloroform): δ 7.25-7.80 (m, H-4, H-6, H-7, H-8 of dibenzothiophene, H-4′ and H-5′ of benzene, 6H, Ar*H*), 7.91-8.32 (m, H-9 of dibenzothiophene H-3′ and H-6′ of benzene, 3H, Ar*H*), 8.48 (bs, H-1, 1H, Ar*H*); ms: m/e 288 (11), 287 (17), 211 (100).

Anal. Calcd. for $C_{20}H_{12}O_3S$: C, 72.27; H, 3.64; S, 9.65. Found: C, 71.98; H, 3.86; S, 9.83.

2-(2-Carboxybenzyl)dibenzothiophene (**26**).

A stirred mixture of **25** (20 g, 0.06 mole), zinc dust (30.5 g, 0.47 g-atom), sodium hydroxide (32 g, 0.8 mole) and 400 ml of water was maintained at reflux temperature for 48 hours. After cooling, the mixture was filtered and acidified with concentrated hydrochloric acid to afford 15.3 g (80%) of white crystals. An analytical sample was recrystallized from hexane-benzene (1:1) to give colorless needles, mp 165°; ir (potassium bromide): 1585 (C=O), 3550 cm^{-1} (OH); nmr (deuteriochloroform): δ 4.58 (s, CH_2, 2H), 7.06-7.49 (m, H-3, H-7, H-8 of dibenzothiophene, H-3′, H-4′ and H-5′ of benzene, 6H, Ar*H*), 7.55-8.18 (m, H-1, H-4, H-6, H-9 of dibenzothiophene H-6′ of benzene, 5H, Ar*H*), 10.91 (bs, OH, 1H); ms: m/e 319 ($M^+ + 1$, 14), 318 (M^+, 63), 300 (100), 271 (75).

Anal. Calcd. for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; S, 10.07. Found: C, 75.78; H, 4.51; S, 9.83.

2-(2-Hydroxymethylbenzyl)dibenzothiophene (**27**).

This compound was prepared from 2-(2-carboxybenzyl)dibenzothiophene (**26**) (3 g, 9.4 mmoles) in a manner similar to the preparation of 4-(2-hydroxymethylbenzyl)dibenzothiophene (**22**) and was obtained as white crystals in 85% yield (2.4 g). An analytical sample was prepared by alumina column chromatography using hexane as the eluent giving colorless crystals, mp 92°; ir (potassium bromide): 3390 cm^{-1} (OH); nmr (deuteriochloroform): δ 4.10 (s, CH_2, 2H), 4.56 (s, CH_2OH, 2H), 7.05-7.53 (m, H-3, H-7, H-8 of dibenzothiophene H-3′, H-4′ and H-5′ of benzene, 6H, Ar*H*), 7.60-8.13 (m, H-1, H-4, H-6, H-9 of dibenzothiophene and H-6′ of benzene, 5H, Ar*H*); ms: m/e 305 ($M^+ + 1$, 6), 304 (M^+, 27), 286 (72), 285 (100), 284 (36).

Anal. Calcd. for $C_{20}H_{16}OS$: C, 78.91; H, 5.30; S, 10.53. Found: C, 78.91; H, 5.22; S, 10.45.

2-(2-Formylbenzyl)dibenzothiophene (**28**).

This compound was prepared from 2-(2-hydroxymethylbenzyl)dibenzothiophene (**27**) (2.4 g, 7.94 mmoles) in a manner similar to the preparation of 4-(2-formylbenzo)dibenzothiophene (**23**) and was obtained as a brown oil in 78% yield (1.85 g). An analytical sample was prepared by alumina column chromatography using hexane as the eluent giving a pale yellow oil; ir (potassium bromide): 1660 cm^{-1} (C=O); nmr (deuteriochloroform): δ 4.50 (s, CH_2, 2H), 6.9-7.50 (m, H-3, H-7, H-8 of dibenzothiophene H-3′, H-4′ an H-5′ of benzene, 6H, Ar*H*), 7.55-8.18 (m, H-1, H-4, H-6, H-9 of dibenzothiophene and H-6′ of benzene, 5H, Ar*H*), 10.24 (s, C*H*O, 1H); ms: m/e 302 (M^+, 100), 301 (63), 285 (71), 284 (83).

Anal. Calcd. for $C_{20}H_{14}OS$: C, 79.44; H, 4.67; S, 10.60. Found: C, 79.58; H, 4.82; S, 10.67.

Anthra[2,3-*b*]benzo[*d*]thiophene (**29**) and Anthra[2,1-*b*]benzo[*d*]thiophene (**30**).

These compounds were prepared from 2-(2-formylbenzyl)dibenzothiophene (**28**) (3.0 g, 9.92 mmoles) in a manner similar to the preparation of anthra[1,2-*b*]benzo[*d*]thiophene (**24**) and compounds **29** and **30** were obtained. The mixture was separated by column chromatography (basic alumina) using hexane as the eluent to obtain 1.55 g (55%) of **29**. When the basic alumina column was eluted with benzene, 0.87 g (31%) of **30** was obtained.

Compound **30** was obtained as yellow leaves, mp 168-169°; nmr (deuteriochloroform): δ 7.16-7.57 (m, H-2, H-3, H-10 and H-11, 4H, Ar*H*), 7.60-8.23 (m, H-1, H-4, H-6, H-7 and H-9, 5H, Ar*H*), 8.40 (s, H-5, 1H, Ar*H*), 8.68-9.03 (m, H-12, 1H, Ar*H*), 9.33 (s, H-13, 1H, Ar*H*); uv (hexane): λ max (log ϵ) 221 (3.59), 249 (sh) (3.64), 256 (3.73), 284 (3.76), 294 (sh), (3.68); ms: m/e 285 ($M^+ + 1$, 22), 284 (M^+, 100), 282 (13), 142 (14).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.29; H, 4.38; S, 11.30.

Compound **29** was obtained as fluorescent yellow leaves, mp 280°, lit 278-280° [20,26] and 250° [22]; nmr (deuteriochloroform): δ 7.26-7.61 (m, H-2, H-3, H-8, H-9 and H-10, 5H, Ar*H*), 7.79-7.93 (m, H-4, 1H, Ar*H*), 8.00-8.26 (m, H-1 and H-11, 2H, Ar*H*), 8.40 (s, H-6, 1H, Ar*H*), 8.48 (s, H-13, 1H, Ar*H*); uv (hexane): λ max (log ϵ) 248 (3.54), 281 (sh) (3.66), 292 (3.88); ms: m/e 285 ($M^+ + 1$, 22), 284 (M^+, 100), 142 (22), 141 (7).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.63; H, 4.39; S, 11.40.

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