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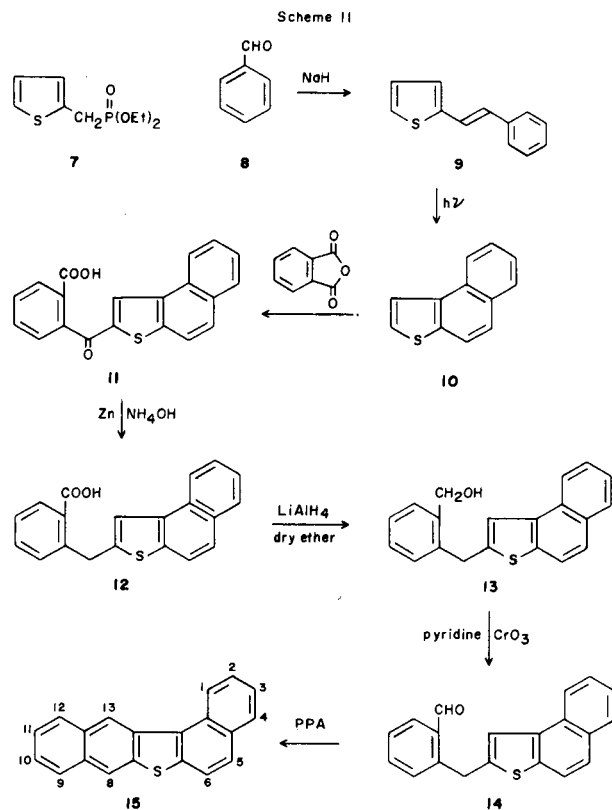
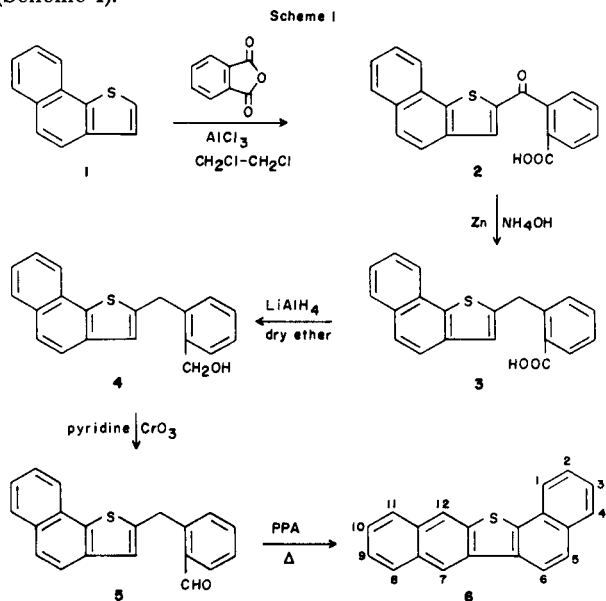
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The synthesis of dinaphtho[1,2-*b*:2',3'-*d*]thiophene (**6**), dinaphtho[2,1-*b*:2',3'-*d*]thiophene (**15**), dinaphtho[1,2-*b*:1',2'-*d*]thiophene (**20**), dinaphtho[2,1-*b*:1',2'-*d*]thiophene (**26**), dinaphtho[2,3-*b*:2',3'-*d*]thiophene (**37**) and dinaphtho[1,2-*b*:2',1'-*d*]thiophene (**45**) has been accomplished.

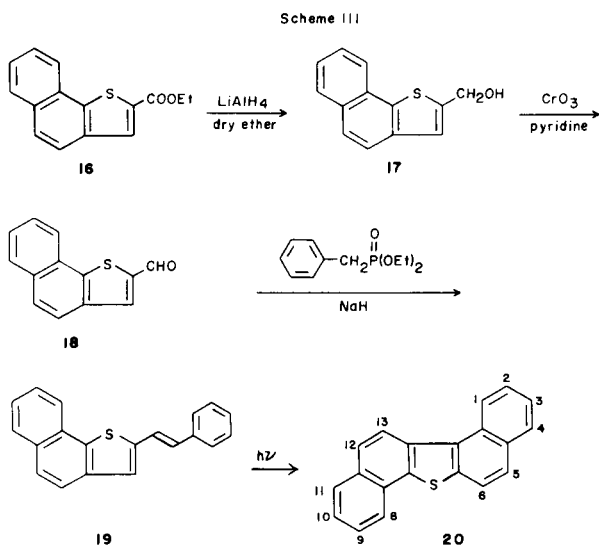
J. Heterocyclic Chem., **20**, 1143 (1983).

In this paper we report the synthesis of all six of the [*b,d*] fused dinaphthothiophenes as a part of our continuing study [3-16] directed toward providing all of the possible polycyclic thiophenes suspected of occurring in coal liquids or related coal-derived products.

The synthesis of dinaphtho[1,2-*b*:2',3'-*d*]thiophene (**6**) previously prepared *via* a different method by Armarego [17] has been accomplished in five steps. Naphtho[1,2-*b*]thiophene (**1**) [18] was allowed to undergo a Friedel-Crafts reaction with phthalic anhydride to give 2-naphtho[1,2-*b*]thiophene (**3**) with zinc and ammonium hydroxide in 71% yield. The ketone **2** was reduced to the corresponding 2-(*o*-carboxybenzyl)naphtho[1,2-*b*]thiophene (**3**) with zinc and ammonium hydroxide in 70% yield. Reduction of the carboxylic acid **3** with lithium aluminum hydride (LAH) gave the primary alcohol **4** in 70% yield which in turn gave the corresponding aldehyde **5** in 80% yield upon oxidation with the chromium trioxide-pyridine complex. Cyclization of the aldehyde **5** with polyphosphoric acid (PPA) gave dinaphtho[1,2-*b*:2',3'-*d*]thiophene (**6**) in 72% yield (Scheme I).



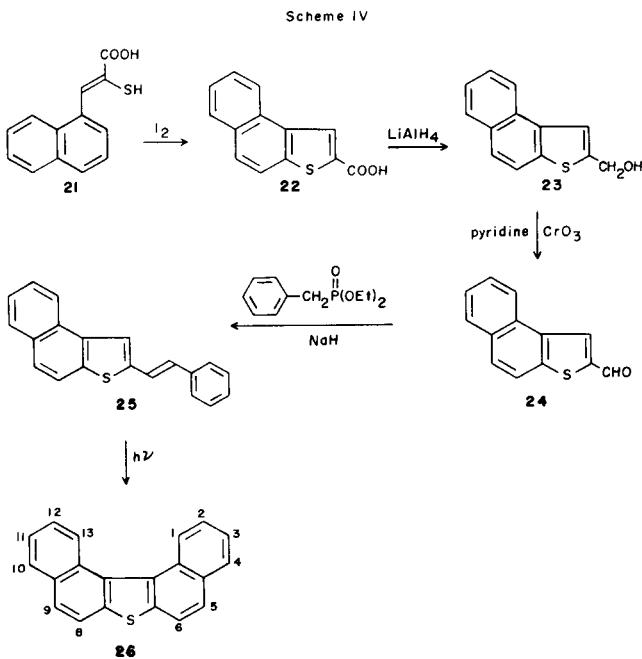
Diethyl 2-phenylphosphonate (**7**) [3] when treated with benzaldehyde (**8**) under Wadsworth-Emmons conditions gave 2-styrylthiophene (**9**) in 78% yield. Photocyclization of **9** produced naphtho[2,1-*b*]thiophene (**10**) [19] in 75% yield. A Friedel-Crafts reaction of **10** and phthalic anhydride gave 2-(*o*-carboxybenzyl)naphtho[2,1-*b*]thiophene (**11**) (70% yield) which when allowed to react with zinc and ammonium hydroxide gave 2-(*o*-carboxybenzyl)naphtho[2,1-*b*]thiophene (**12**) in 83% yield. Lithium aluminum hydride reduction of the acid **12** gave the primary alcohol **13** (79% yield) which upon oxidation with the chromium trioxide-pyridine complex produced the aldehyde **14** (79% yield) which was only characterized spectrally. The crude aldehyde was cyclized with PPA to



give dinaphtho[2,1-*b*:2',3'-*d*]thiophene (**15**) in 69% yield (Scheme II). Compound **15** was previously prepared *via* a different route by Wilputte and Martin [20].

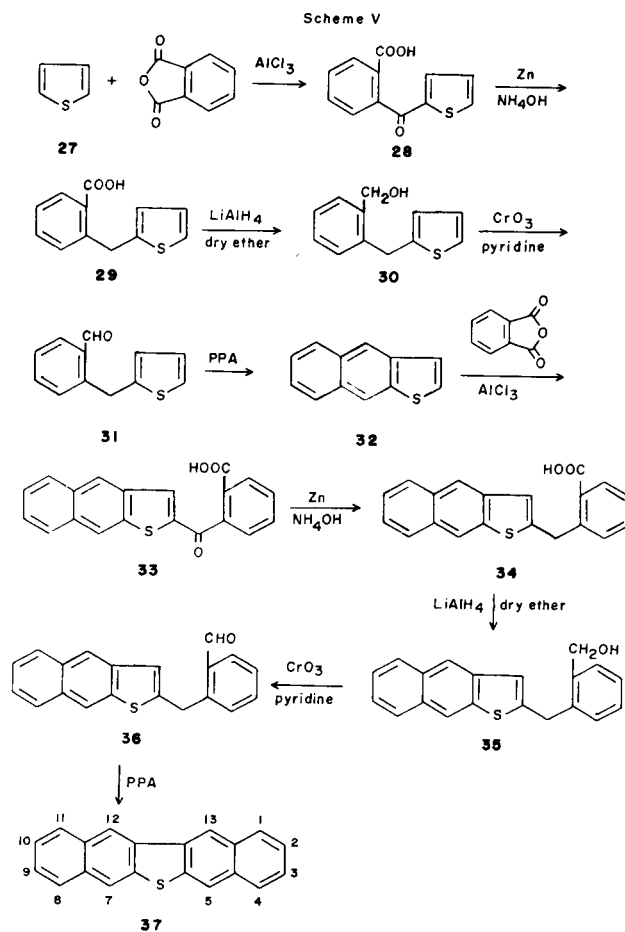
Dinaphtho[1,2-*b*:1',2'-*d*]thiophene (**20**) previously prepared by a different approach by Rabindram and Tilak [21] was synthesized in four steps from ethyl naphtho[1,2-*b*]thiophene-2-carboxylate (**16**) [18]. 2-Naphtho[1,2-*b*]thienylmethanol (**17**) was obtained by LAH reduction of **16** in 90% yield. The alcohol **17** was oxidized to the aldehyde **18** which was used without purification to react with diethyl benzylphosphonate and sodium hydride to give 2-styrylnaphtho[1,2-*b*]thiophene (**19**) in 75% yield which upon photocyclization gave dinaphtho[1,2-*b*:1',2'-*d*]thiophene (**20**) in 72% yield (Scheme III).

For the synthesis of dinaphtho[2,1-*b*:1',2'-*d*]thiophene

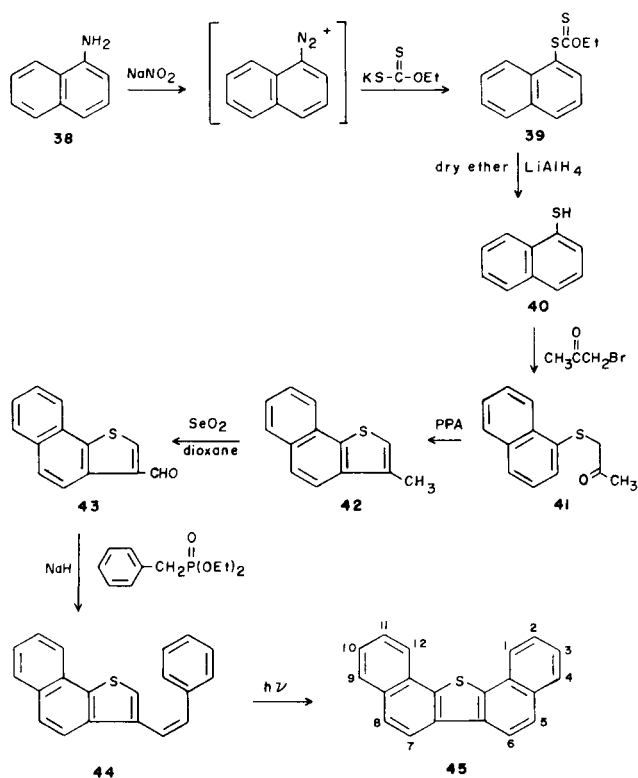


(**26**), 3-(1'-naphthyl)-2-thiopropanoic acid (**21**) [22] was cyclized into naphtho[2,1-*b*]thiophene-2-carboxylic acid (**22**) (82% yield) which upon reduction (LAH) gave 2-naphtho[2,1-*b*]thienylmethanol (**23**) in 89% yield. The alcohol **23** was oxidized to the aldehyde **24** in 78% yield with the chromium trioxide-pyridine complex. Diethyl benzylphosphonate when allowed to react with the aldehyde **24** under Wadsworth-Emmons conditions gave 2-styrylnaphtho[2,1-*b*]thiophene (**25**) in 72% yield. Photocyclization of **25** gave dinaphtho[2,1-*b*:1',2'-*d*]thiophene (**26**) in 45% yield (Scheme IV). This compound was also previously synthesized by Rabindram and Tilak [21] by a different method.

The preparation of dinaphtho[2,3-*b*:2',3'-*d*]thiophene (**37**) was accomplished in ten steps. A Friedel-Crafts reaction between thiophene (**27**) and phthalic anhydride gave the crude ketoacid **28** (82% yield) which upon reduction with zinc and ammonium hydroxide gave 2-(*o*-carboxybenzyl)thiophene (**29**) in 88% yield. Reduction of **29** (LAH) gave the alcohol **30** (83% yield) as a light brown oil which without further purification was oxidized with the chromium trioxide-pyridine complex to give *o*-(2-thenyl)benzaldehyde (**31**) (82% yield). The aldehyde **31** was cyclized (PPA) into naphtho[2,3-*b*]thiophene (**32**) in 73% yield. A Friedel-Crafts reaction between **32** and phthalic



Scheme VI



anhydride gave 2-naphtho[2,3-*b*]thienyl *o*-carboxyphenyl ketone (**33**) (80% yield) which was reduced (zinc and ammonium hydroxide) to 2-(*o*-carboxybenzyl)naphtho[2,3-*b*]thiophene (**34**) in 84% yield. Reduction of the carboxylic acid **34** (LAH) gave the primary alcohol **35** (84% yield) which was oxidized (chromium trioxide-pyridine complex) to give the aldehyde **36** as a dark oil (82% yield) which upon cyclization (PPA) gave dinaphtho[2,3-*b*:2',3'-*d*]thiophene (**37**) in a yield of 75% (Scheme V).

Dinaphtho[1,2-*b*:2',1'-*d*]thiophene (**45**) previously prepared *via* a different method by Clarke, Gregory and Scrowston [18], was prepared in seven steps starting with 1-naphthalenamine (**38**). Diazotization of **38** followed by treatment with potassium ethyl xanthate gave 1-naphthyl ethyl xanthate (**39**) as a dark oil (86% yield) which when allowed to react with LAH gave naphthalene-1-thiol (**40**) (71% yield) as a pale yellow oil. Reaction of **40** with bromoacetone gave 1-(1'-naphthyl)-2-propanone (**41**) which was cyclized (PPA) into 3-methylnaphtho[1,2-*b*]thiophene (**42**) (70% yield). Oxidation of **42** with selenium dioxide gave naphtho[1,2-*b*]thiophene-3-carboxaldehyde (**43**) in 75% yield. The aldehyde **43** was converted into 3-styrylnaphtho[1,2-*b*]thiophene (**44**) *via* the Wadsworth-Emmons reaction in 74% yield. Photocyclization of **44** gave dinaphtho[1,2-*b*:2',1'-*d*]thiophene (**45**) in 76% yield (Scheme VI).

These dinaphthothiophenes 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 ¹H-nmr spectra were obtained on a Varian EM360A spectrometer and a JEOL FX-90Q spectrometer in the solvent indicated. Chemical shifts are reported in δ units. The ir spectra were obtained on a Beckman Acculab 2 spectrometer. Mass spectra were obtained on a Hewlett-Packard model 5980A mass spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

2-Naphtho[1,2-*b*]thienyl *o*-Carboxyphenyl Ketone (**2**).

A solution of 9.4 g of aluminum chloride and 4.9 g (33 mmoles) of phthalic anhydride in 180 ml of 1,2-dichloroethane was prepared at room temperature. To this solution, 6.1 g (33 mmoles) of naphtho[1,2-*b*]thiophene (**1**) was added uniformly over a period of 30 minutes while maintaining the reaction temperature below 30°. The reaction was allowed to stir at room temperature for 4 hours and then poured into 300 ml of ice-water and 150 ml of hydrochloric acid (15%). The mixture was extracted with 2 × 250 ml of chloroform. The chloroform layer was washed several times with sodium hydroxide solution (10%), dried over sodium sulfate and evaporated to give 7.8 g (71%) of yellow crystals. An analytical sample was recrystallized from ethanol to give pale yellow leaves, mp 209°; ir (potassium bromide): 1645 (C=O), 1675 (COOH), 3400 cm⁻¹ (OH); nmr (DMSO-*d*₆): δ 7.28 (s, H-3, 1H, *ArH*), 7.32-8.38 (m, 10H, *ArH*); ms: *m/e* 334 (M⁺ + 2, 5), 333 (M⁺ + 1, 12), 332 (M⁺, 63), 288 (9), 211 (100), 139 (56).

Anal. Calcd. for C₂₀H₁₂O₃S: C, 72.27; H, 3.64; S, 9.65. Found: C, 72.17; H, 3.59; S, 9.76.

2-(*o*-Carboxybenzyl)naphtho[1,2-*b*]thiophene (**3**).

Compound **2** (7.5 g, 23 mmoles) was dissolved in 250 ml of concentrated ammonium hydroxide and 16 g of zinc dust was added. The resulting solution was refluxed with stirring for 24 hours with an additional 40 ml of concentrated ammonium hydroxide added every 4 hours. The cooled reaction mixture was filtered to remove excess zinc and the filtrate was acidified with hydrochloric acid whereupon white crystals appeared. The solid was washed with water, dried and recrystallized from benzene giving 5.0 g (70%) of colorless crystals, mp 159°; ir (potassium bromide): 3425 (OH), 1680 cm⁻¹ (C=O); nmr (DMSO-*d*₆): δ 4.72 (s, CH₂, 2H), 7.18 (s, H-3, 1H, *ArH*), 7.40-7.78 (m, H-5, H-6, H-7, H-8 and *ArH* of substituted benzene, 8H, *ArH*), 7.80-8.14 (m, H-4, H-9, 2H, *ArH*); ms: *m/e* 320 (M⁺ + 2, 12), 319 (M⁺ + 1, 21), 318 (M⁺, 89), 300 (100), 271 (94), 272 (44).

Anal. Calcd. for C₂₀H₁₄O₂S: C, 75.45; H, 4.43; S, 10.07. Found: C, 75.49; H, 4.50; S, 10.23.

2-(*o*-Hydroxymethylbenzyl)naphtho[1,2-*b*]thiophene (**4**).

Into a stirred solution of 2.0 g of lithium aluminum hydride in 200 ml of dry ether, compound **3** (4.6 g, 14 mmoles) was added slowly. When the addition was complete, the mixture was stirred at room temperature for 3.5 hours. It was then quenched by cautiously adding 25 ml of water and enough 10% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice water and extracted with 2 × 150 ml of chloroform. The extract was washed successively with water and saturated sodium bicarbonate solution, dried with sodium sulfate and evaporated.

The residue was chromatographed on a column of neutral alumina using benzene as an eluent giving white crystals which were recrystallized from ethanol giving 3.3 g (76%) of colorless crystals, mp 105°; ir (potassium bromide): 3350 cm⁻¹ (OH); nmr (deuteriochloroform): δ 1.70 (bs, OH, 1H), 4.35 (s, CH₂-OH, 2H), 4.70 (s, CH₂, 2H), 7.08 (s, H-3, 1H, *ArH*), 7.20-7.76 (m, H-5, H-6, H-7, H-8 and *ArH* of substituted benzene, 8H, *ArH*), 7.80-8.10 (m, H-4, H-9, 2H, *ArH*); ms: *m/e* 306 (M⁺ + 2, 1), 305 (M⁺ + 1, 5), 305 (M⁺, 7), 285 (100), 268 (76).

Anal. Calcd. for C₂₀H₁₆OS: C, 78.91; H, 5.30; S, 10.53. Found: C, 78.80; H, 5.21; S, 10.24.

Dinaphtho[1,2-*b*:2',3'-*d*]thiophene (**6**).

A solution (3.0 g, 10 mmoles) of 2-(*o*-hydroxymethylbenzyl)naphtho[1,2-*b*]thiophene (**4**) in 15 ml of dry pyridine was added slowly to a suspen-

sion of chromium trioxide-pyridine complex made from 4.8 g of chromium trioxide and 75 ml of dry pyridine. After stirring for 2.5 hours at room temperature, the reaction mixture was filtered and washed with chloroform. The filtrate was washed with 10% hydrochloric acid and 10% sodium carbonate solution successively. After drying over anhydrous sodium sulfate, the chloroform was evaporated to leave the crude aldehyde (2.4 g, 80%) as a dark oil; ir (neat): 1665 cm^{-1} (C=O); nmr (deuteriochloroform): δ 4.71 (s, CH_2 , 2H), 7.04 (s, H-3, 1H, *ArH*), 7.16-8.06 (m, 10H, *ArH*), 10.22 (s, *CHO*, 1H).

A mixture of the crude *o*-(2-naphtho[1,2-*b*]thenyl)benzaldehyde (**5**) (2.4 g, 8 mmoles) and 30 g of polyphosphoric acid was heated to 80-85° for 30 minutes. After cooling, ice water was added to the reaction mixture and the precipitated brown solid was collected by filtration. After drying, the product was chromatographed on a column of alumina using hexane as the eluent giving 1.6 g (72%) of pale yellow flakes, mp 321° (lit 316-317° [17]); nmr (deuteriochloroform): δ 7.09-7.48 (m, H-2, H-3, H-8, and H-10, 4H, *ArH*), 7.50-8.10 (m, H-1 or H-6, H-4, H-9 and H-11, 4H, *ArH*), 7.81 (d, J = 6 Hz, H-5, 1H, *ArH*), 8.30 (d, J = 6 Hz, H-1 or H-6, 1H, *ArH*), 8.42 (s, H-7 or H-12, 1H, *ArH*), 8.68 (s, H-12 or H-7, 1H, *ArH*); ms: m/e 286 ($\text{M}^+ + 2$), 285 ($\text{M}^+ + 1$, 22), 284 (M^+ , 100), 282 (11).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{S}$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.35; H, 4.17; S, 11.40.

2-Styrylthiophene (**9**).

Sodium hydride (50%, 7.6 g, 158 mmoles) was placed in 200 ml of dry dimethyl sulfoxide. Sodium hydride was used after washing twice with 40 ml of petroleum ether. The slurry was cooled to 20° and diethyl 2-thenylphosphonate (**7**) [3] (11.7 g, 50 mmoles) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 20 minutes. To the pale yellow solution maintained below 25°, was added benzaldehyde (**8**) (5.3 g, 50 mmoles) dropwise. The solution was stirred at room temperature for 3 hours. A large excess of water was added and the resulting precipitate was collected by filtration. This product was recrystallized from methanol to give 7.3 g (78%) of colorless leaflets, mp 110-111° (lit 112-113° [9]).

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

A solution of 1.5 g (8 mmoles) of compound **9** and 0.1 g of iodine in 360 ml of benzene was irradiated for 6 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 1.04 g (75%) of colorless crystals, mp 113° (lit mp 112-114° [19]).

2-Naphtho[2,1-*b*]thienyl *o*-Carboxyphenyl Ketone (**11**).

This compound was prepared from naphtho[2,1-*b*]thiophene (**10**) (2.6 g, 14 mmoles) in a manner similar to the preparation of compound **2** resulting in 3.3 g (70%) of **11** as pale yellow leaves, mp 201-202°; ir (potassium bromide): 1635 (C=O), 1665 (COOH), 3415 cm^{-1} (OH); nmr (deuteriochloroform): δ 7.20 (s, H-3, 1H, *ArH*), 7.24-8.35 (m, H-4, H-6, H-7, H-8, H-9 and *ArH* of benzene, 10H, *ArH*), 8.50 (s, H-3, 1H, *ArH*); ms: m/e 334 ($\text{M}^+ + 2$), 333 ($\text{M}^+ + 1$, 7), 332 (M^+ , 26), 211 (100), 183 (38), 139 (71).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{O}_3\text{S}$: C, 72.27; H, 3.64; S, 9.65. Found: C, 72.48; H, 3.83; S, 9.40.

2-(*o*-Carboxybenzyl)naphtho[2,1-*b*]thiophene (**12**).

This compound was prepared from compound **11** (3.0 g, 9 mmoles) in a manner similar to the preparation of compound **3** and 2.4 g (83%) was obtained as colorless needles, mp 172°; ir (potassium bromide): 3425 (OH), 1665 (C=O); nmr (deuteriochloroform): δ 4.67 (s, CH_2 , 2H), 7.09-8.26 (m, 11H, *ArH*), 10.91 (bs, *COOH*, 1H); ms: m/e 318 (M^+ , 100), 300 (83), 272 (45), 271 (96).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}$: C, 75.45; H, 4.45; S, 10.07. Found: C, 75.69; H, 4.69; S, 9.89.

2-(*o*-Hydroxymethylbenzyl)naphtho[2,1-*b*]thiophene (**13**).

This compound was prepared from compound **12** (2.1 g, 7 mmoles) in a

manner similar to the preparation of compound **4** and 1.6 g (79%) was obtained as colorless crystals, mp 95-96°; ir (potassium bromide): 3355 cm^{-1} (OH); nmr (deuteriochloroform): δ 1.80 (bs, *OH*, 1H), 4.33 (s, CH_2OH , 2H), 4.67 (s, CH_2 , 2H), 7.25-8.26 (m, 11H, *ArH*); ms: m/e 304 (M^+ , 37), 286 (74), 285 (100), 120 (53).

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{OS}$: C, 78.91; H, 5.30; S, 10.53. Found: C, 78.84; H, 5.25; S, 10.64.

Dinaphtho[2,1-*b*:2',3'-*d*]thiophene (**15**).

o-(2-Naphtho[2,1-*b*]thenyl)benzaldehyde (**14**) was prepared from compound **13** (1.3 g, 4 mmoles) in a manner similar to the preparation of compound **5** giving 1.03 g (79%) of the crude aldehyde; ir (potassium bromide): 1670 cm^{-1} (C=O); nmr (deuteriochloroform): δ 4.57 (s, CH_2 , 2H), 7.10 (s, H-3, 1H, *ArH*), 7.20-8.34 (m, 10H, *ArH*); ms: m/e 302 (M^+ , 100), 284 (41), 269 (58), 118 (83).

A mixture of the crude aldehyde **14** (0.9 g, 3 mmoles) was cyclized in a manner similar to the preparation of compound **6** and 0.58 g (69%) of dinaphtho[2,1-*b*:2',3'-*d*]thiophene was obtained. An analytical sample was chromatographed on a column of alumina using hexane as the eluent giving pale yellow flakes, mp 189° (lit 196° [20]); nmr (deuteriochloroform): δ 7.10-8.18 (m, H-2, H-3, H-4, H-5, H-6, H-9, H-10, H-11, H-12, 9H, *ArH*), 8.0 (s, H-8, 1H, *ArH*), 8.61-8.96 (m, H-1, 1H, *ArH*), 8.87 (s, H-13, 1H, *ArH*); ms: m/e 284 (M^+ , 100), 239 (71), 237 (49).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{S}$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.30; H, 4.18; S, 11.43.

2-Naphtho[1,2-*b*]thienylmethanol (**17**).

A solution of 1.5 g (6 mmoles) of ethyl naphtho[1,2-*b*]thiophene-2-carboxylate (**16**) [17] in 100 ml of dry ether was added dropwise to a suspension of 0.3 g of lithium aluminum hydride in 50 ml of dry ether. After refluxing for 3 hours, the reaction mixture was carefully quenched by cautiously adding 15 ml of water and enough 10% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice water and extracted with 200 ml of ether. The extract was washed successively with water and saturated sodium bicarbonate solution, dried over sodium sulfate and evaporated. The residue was recrystallized from methanol to give 1.12 g (90%) of colorless crystals, mp 88° (lit 89-91° [23]).

Naphtho[1,2-*b*]thiophene-2-carboxaldehyde (**18**).

A solution of the alcohol **17** (1.10 g, 5 mmoles) in 30 ml of dry pyridine was added slowly to a suspension of chromium trioxide-pyridine complex made from 1.5 g of chromium trioxide and 10 ml of dry pyridine. After stirring for 2.5 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 then dried over sodium sulfate. Evaporation of the chloroform yielded a brown solid, mp 96° (lit 98.5-100° [18]); ir (potassium bromide): 1670, 1650 cm^{-1} (C=O).

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

Sodium hydride (50%, 0.6 g, 13 mmoles) was placed in 50 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 1.1 g (5 mmoles) of diethyl benzylphosphonate was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 30 minutes. To the pale yellow solution, maintained below 25°, was added 1 g (5 mmoles) of naphtho[1,2-*b*]thiophene-2-carboxaldehyde (**18**). The solution was stirred at room temperature for 6 hours. A large excess of water was added and extracted with benzene. The benzene layer was dried over sodium sulfate and evaporated at reduced pressure. The residue was chromatographed on a silica gel column using hexane as the eluent giving 1.01 g (75%) of pale yellow needles, mp 143°; nmr (deuteriochloroform): δ 7.10 (s, H-3 thiophene, 1H, *ArH*), 7.15-7.64 (m, H-6, H-7, H-8 and aromatic phenyl, 8H, *ArH*), 7.61 (s, H-4, H-5, 2H, *ArH*), 7.80-8.25 (bs, H-9, 1H, *ArH*); ms: m/e 389 ($\text{M}^+ + 2$, 8), 388 ($\text{M}^+ + 1$, 17), 387 (M^+ , 64), 315 (68), 184 (100).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{S}$: C, 83.88; H, 4.93; S, 11.20. Found: C, 83.69; H, 4.99; S, 11.03.

Dinaphtho[1,2-*b*:1',2'-*d*]thiophene (20).

A solution of 0.7 g (2.5 mmoles) of 2-styrylnaphtho[1,2-*b*]thiophene (19) and 0.05 g of iodine in 500 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 chromatographed on a silica gel column using hexane as the eluent giving 0.5 g (72%) of colorless leaflets, mp 162° (lit 161-162° [21]); nmr (deuteriochloroform): δ 6.92-7.61 (m, H-1 or H-8, H-2, H-3, H-4, H-5, H-9, H-10, H-11, H-12, 9H, *ArH*), 7.70-7.82 (m, H-1 or H-8, 1H, *ArH*), 8.28 (m, H-6, 1H, *ArH*), 8.50 (m, H-13, 1H, *ArH*); ms: *m/e* 286 ($M^+ + 2$, 7), 285 ($M^+ + 1$, 23), 284 (M^+ , 100), 282 (17).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.30; H, 4.32; S, 11.18.

Naphtho[2,1-*b*]thiophene-2-carboxylic Acid (22).

A solution of 10 g (43 mmoles) of 3-(1'-naphthyl)-2-thiopropenoic acid and 40 g of iodine in 400 ml of dioxane was maintained at 45° for 20 hours. The solution was then poured into 2 l of water, decolorized with sodium bisulfite and the brown precipitate was collected. The crude product was dissolved in dilute sodium hydroxide, treated with norit and reprecipitated with dilute hydrochloric acid. The solution was saturated with salt and the gelatinous precipitate was extracted with ether. The extracts were dried and evaporated leaving brown crystals. After decolorizing and recrystallizing from xylene, 6.0 g (82%) of silvery-white needles was obtained, mp 277-278° (lit 277-279° [24]).

2-Naphtho[2,1-*b*]thienylmethanol (23).

This compound was prepared from 2-naphtho[2,1-*b*]thiophene-2-carboxylic acid (5.8 g, 25 mmoles) in a manner similar to the preparation of compound 17 and 4.85 g (89%) was obtained as colorless crystals, mp 106° (lit 107-108° [23]).

2-Naphtho[2,1-*b*]thiophene-2-carboxaldehyde (24).

This compound was prepared from compound 23 (4.6 g, 22 mmoles) in a manner similar to the preparation of compound 18 and 3.5 g (78%) was obtained as white needles, mp 118° (lit 119-121° [24]).

2-Styrylnaphtho[2,1-*b*]thiophene (25).

This compound was prepared from 2-naphtho[2,1-*b*]thiophene-2-carboxaldehyde (24) (3.3 g, 15 mmoles) in a manner similar to the preparation of compound 19 and 2.7 g (9 mmoles) was obtained as the desired product. An analytical sample was recrystallized from ethanol to give pale yellow crystals (72% yield), mp 192°; nmr (deuteriochloroform): δ 6.89 (d, J = 4 Hz, *CH-Ph*, 1H), 7.06 (s, H-1, 1H, *ArH*), 7.12-7.82 (m, H-4, H-5, H-6, H-7, H-8, phenyl-H and $CH=C$, 11H); ms: *m/e* 288 ($M^+ + 2$, 7), 287 ($M^+ + 1$, 24), 286 (M^+ , 100), 287 (24), 285 (38), 284 (25).

Anal. Calcd. for $C_{20}H_{14}S$: C, 83.88; H, 4.93; S, 11.20. Found: C, 84.06; H, 4.96; S, 11.06.

Dinaphtho[2,1-*b*:1',2'-*d*]thiophene (26).

This compound was prepared from 2-styrylnaphtho[2,1-*b*]thiophene (25) (1.0 g, 3.5 mmoles) in a manner similar to the preparation of compound 20 and 0.45 g (45%) was obtained as colorless crystals, mp 205° (lit 206-207° [21]); nmr (deuteriochloroform): δ 6.92 (d, J = 4 Hz, H-5 and H-9, 2H, *ArH*), 7.22-7.40 (m, H-2, H-3, H-11, and H-12, 4H, *ArH*), 7.58 (d, J = 4 Hz, H-6 and H-8, 2H, *ArH*), 7.52-7.73 (m, H-4 and H-10, 2H, *ArH*), 8.21-8.48 (m, H-1, H-13, 2H, *ArH*); ms: *m/e* 286 ($M^+ + 2$, 6), 285 ($M^+ + 1$, 22), 284 (M^+ , 92), 283 (100), 282 (88).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.32; H, 4.35; S, 11.05.

2-(*o*-Carboxybenzyl)thiophene (29).

2-Thienyl *o*-carboxyphenyl ketone (28) was prepared from thiophene 27 (20 g, 0.24 mole) in a manner similar to the preparation of compound 2 and 45.3 g (82%) of brown oil was obtained.

Compound 29 was prepared from the crude keto-acid 28 (40 g, 0.172 mole) in a manner similar to the preparation of compound 3 and 33 g (88%) of colorless crystals was obtained, mp 105-106°; ir (potassium bromide): 1685 (C=O), 3425 cm^{-1} (OH); nmr (deuteriochloroform): δ 4.45 (s, CH_2 , 2H), 6.60-7.64 (m, H-4 and phenyl-H, 6H, *ArH*), 8.00 (dd, J = 2, 8 Hz, H-5, 1H, *ArH*); ms: *m/e* 219 ($M^+ + 1$, 4), 218 (M^+ , 31), 200 (100), 172 (29), 171 (66).

Anal. Calcd. for $C_{20}H_{10}O_2S$: C, 66.03; H, 4.62; S, 14.69. Found: C, 66.19; H, 4.58; S, 14.59.

o-(2-Thienyl)benzaldehyde (31).

2-(*o*-Hydroxymethylbenzyl)thiophene (30) was prepared from compound 29 (32 g, 0.146 mole) in a manner similar to the preparation of compound 4 and 24.9 g (83%) of a light brown oil was obtained; ir (potassium bromide): 3415 cm^{-1} (OH); nmr (deuteriochloroform): δ 2.80 (bs, OH, 1H), 4.08 (s, CH_2-OH , 2H), 4.50 (s, CH_2 , 2H), 6.60 (d, J = 4 Hz, H-3 of thiophene, 1H, *ArH*), 6.66-7.38 (m, H-4 and H-5 of thiophene and phenyl-H, 6H, *ArH*); ms: *m/e* 204 (M^+ , 2), 201 (12), 186 (96), 185 (100), 141 (20).

Compound 31 was prepared from the crude alcohol 30 (23 g, 0.113 mole) in a manner similar to the preparation of compound 5 and 18.7 g (82%) of a pale yellow oil which slowly solidified at room temperature was obtained; ir (potassium bromide): 1670 cm^{-1} (C=O); nmr (deuteriochloroform): δ 4.50 (s, CH_2 , 2H), 6.62 (d, J = 2 Hz, H-2 of thiophene, 1H, *ArH*), 6.73-7.49 (m, H-4 of thiophene and phenyl-H, 5H, *ArH*), 7.73 (dd, J = 2, 8 Hz, H-5 of thiophene, 1H, *ArH*); ms: *m/e* 202 (M^+ , 80), 184 (41), 118 (100).

Anal. Calcd. for $C_{12}H_{10}OS$: C, 71.26; H, 4.98; S, 15.85. Found: C, 71.40; H, 4.73; S, 15.67.

Naphtho[2,3-*b*]thiophene (32).

This compound was prepared from *o*-(2-thienyl)benzaldehyde (31) (10 g, 49 mmoles) in a manner similar to the preparation of compound 6, and 6.65 g (73%) of colorless crystals was obtained, mp 192-193° (lit 192-193° [25]).

2-Naphtho[2,3-*b*]thienyl *o*-Carboxyphenyl Ketone (33).

This compound was prepared from naphtho[2,3-*b*]thiophene (5 g, 27 mmoles) in a manner similar to the preparation of compound 2 and 7.21 g (80%) was obtained as fluorescent yellowish leaves, mp 270°; ir (potassium bromide): 1640 (C=O), 1695 (COOH), 3410 cm^{-1} (OH); nmr (deuteriochloroform): δ 7.00-7.66 (m, H-1, H-6, H-7 and phenyl-H, 7H, *ArH*), 7.78-8.16 (m, H-4, H-5 and H-8, 3H, *ArH*), 8.95 (s, H-9, 1H, *ArH*), 10.75 (bs, COOH, 1H); ms: *m/e* 332 (M^+ , 45), 211 (100).

Anal. Calcd. for $C_{20}H_{12}O_3S$: C, 72.27; H, 3.64; S, 9.65. Found: C, 72.14; H, 3.79; S, 9.83.

2-(*o*-Carboxybenzyl)naphtho[2,3-*b*]thiophene (34).

This compound was prepared from 2-naphtho[2,3-*b*]thienyl *o*-carboxyphenyl ketone (33) (6.9 g, 21 mmoles) in a manner similar to the preparation of compound 3 and 5.6 g (84%) was obtained as colorless crystals; mp 184°, ir (potassium bromide): 1685 (C=O), 3425 cm^{-1} (OH); nmr (deuteriochloroform): δ 5.25 (s, CH_2 , 2H), 6.56 (bs, H-1, 1H, *ArH*), 6.82-7.58 (m, H-6, H-7 and phenyl-H, 6H, *ArH*), 7.66-8.35 (m, H-4, H-5 and H-8, 3H, *ArH*), 8.68 (s, H-9, 1H, *ArH*); ms: *m/e* 320 ($M^+ + 2$, 9), 319 ($M^+ + 1$, 22), 318 (M^+ , 100), 271 (85).

Anal. Calcd. for $C_{20}H_{14}O_3S$: C, 75.45; H, 4.43; S, 10.07. Found: C, 75.51; H, 4.32; S, 10.23.

2-(*o*-Hydroxymethylbenzyl)naphtho[2,3-*b*]thiophene (35).

This compound was prepared from 2-(*o*-carboxybenzyl)naphtho[2,3-*b*]thiophene (34) (5.3 g, 17 mmoles) in a manner similar to the preparation of compound 4 and 4.26 g (84%) was obtained as colorless crystals, mp

120-121°; ir (potassium bromide): 3370 cm^{-1} (OH); nmr (deuteriochloroform): δ 4.73 (s, CH_2-OH , 2H), 4.89 (s, CH_2 , 2H), 6.34 (bs, OH, 1H), 6.72 (s, H-1, 1H, *ArH*), 6.89-7.54 (m, H-6, H-7, and phenyl-H, 6H, *ArH*), 7.64-8.00 (m, H-5, H-8, 2H, *ArH*), 8.13 (m, H-4, 1H, *ArH*), 8.28 (s, H-9, 1H, *ArH*); ms: *m/e* 306 ($M^+ + 2$, 7), 305 ($M^+ + 1$, 16), 304 (M^+ , 72), 285 (78).

Anal. Calcd. for $C_{20}H_{16}OS$: C, 78.91; H, 5.30; S, 10.53. Found: C, 78.75; H, 5.19; S, 10.41.

Dinaphtho[2,3-*b*:2',3'-*d*]thiophene (37).

o-(2-Naphtho[2,3-*b*]thenyl)benzaldehyde (36) was prepared from compound 35 (4.0 g, 13 mmoles) in a manner similar to the preparation of *o*-(2-naphtho[1,2-*b*]thenyl)benzaldehyde (5) and 3.26 g (82%) of dark oil was obtained; ir (potassium bromide): 1665 cm^{-1} (C=O); nmr (deuteriochloroform): δ 5.26 (s, CH_2 , 2H), 6.61 (s, H-1, 1H, *ArH*), 7.13-7.56 (m, H-6, H-7 and phenyl-H, 6H, *ArH*), 7.68-7.93 (m, H-5, H-8, 2H, *ArH*), 8.09-8.31 (m, H-4, 1H, *ArH*), 8.30 (s, H-9, 1H, *ArH*).

Dinaphtho[2,3-*b*:2',3'-*d*]thiophene (37) was prepared from compound 36 (3.1 g, 10 mmoles) in a manner similar to the preparation of compound 6 and 2.19 g (75%) of fluorescent yellow leaves was obtained, mp 265-266°; nmr (deuteriochloroform): δ 7.20-7.75 (m, H-3, H-4, H-10 and H-11, 4H, *ArH*), 7.78-8.56 (m, H-2, H-5, H-9 and H-12, 4H, *ArH*), 8.20 (d, J = 2 Hz, H-7 and H-8, 2H, *ArH*), 8.68 (d, J = 2 Hz, H-1 and H-13, 2H, *ArH*); ms: m/e 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, 84.62; H, 4.17; S, 10.98.

1-Naphthalenethiol (40).

1-Naphthyl ethyl xanthate (39) and 100 g of crushed ice was added to a solution of 1-naphthalenamine (30 g, 210 mmoles) in 46 ml of concentrated hydrochloric acid. The solution was maintained at 0° during the diazotization of the amine by the dropwise addition of a solution of sodium nitrite (18 g, 260 mmoles) in 30 ml of water.

Potassium ethyl xanthate (60 g, 370 mmoles) in 75 ml of water was heated to 40° in a 1 l round-bottomed flask equipped with a double wall-ed condenser, a dropping funnel and an efficient stirrer. The cold diazonium solution was added dropwise with stirring at such a rate that the temperature did not exceed 40°. The cooled mixture was extracted 3 × 150 ml of ether. The combined extracts were washed twice with 50 ml of 10% sodium carbonate solution and twice with water and finally dried over sodium sulfate. The volume was reduced *in vacuo* and a dark oil (44.8 g, 86%) was obtained; nmr (deuteriochloroform): δ 1.05 (t, J = 7 Hz, 2 × CH_3 , 6H), 4.36 (q, OCH_2 , 2H), 7.0-8.3 (m, 7H, *ArH*).

Compound 40 was prepared from 1-naphthyl ethyl xanthate (10 g, 40 mmoles) in a manner similar to the preparation of compound 4 and 4.6 g (71%) of pale yellow oil was obtained.

Naphtho[1,2-*b*]thiophene-3-carboxaldehyde (43).

A solution of 10 g (50 mmoles) of 3-methylnaphtho[1,2-*b*]thiophene (42) [26] and 7 g of selenium dioxide in 200 ml of ethanol was refluxed with stirring for 6 hours. The precipitated selenium was filtered from the hot solution and then the volume reduced giving a brown solid which was chromatographed on a silica gel column using benzene:hexane (1:1) as an eluent, giving 8.0 g (75%) of pale yellow prisms, mp 82-83° (lit 81.5-83° [26]).

3-Styrylnaphtho[1,2-*b*]thiophene (44).

This compound was prepared from naphtho[1,2-*b*]thiophene-3-carboxaldehyde (43) (2.0 g, 9 mmoles) in a manner similar to the preparation of compound 19 and 2.0 g (74%) of pale yellow needles was obtained, mp 150-151°; nmr (deuteriochloroform): δ 7.06 (s, H-2, 1H, *ArH*), 7.15-7.70 (m, H-6, H-7, H-8 and phenyl-H, 8H, *ArH*), 7.59 (s, H-4, H-5, 2H, *ArH*), 7.80-8.10 (bs, H-9, 1H, *ArH*).

Anal. Calcd. for $C_{20}H_{14}S$: C, 83.88; H, 4.93; S, 11.20. Found: C, 83.73; H, 5.03; S, 11.40.

Dinaphtho[1,2-*b*:2',1'-*d*]thiophene (45).

This compound was prepared from 3-styrylnaphtho[1,2-*b*:2',1'-*d*]thio-

phene (45) (1.0 g, 3.5 mmoles) in a manner similar to the preparation of compound 20 and 0.74 g (76%) of colorless leaflets was obtained, mp 255° (lit 255-256° [18]); nmr (deuteriochloroform): δ 7.0 (d, J = 2 Hz, H-5 and H-8, 2H, *ArH*), 7.20-7.43 (m, H-2, H-3, H-10 and H-11, 4H, *ArH*), 7.63 (d, J = 2 Hz, H-6 and H-7, 2H, *ArH*), 8.23-8.52 (m, H-1 and H-13, 2H, *ArH*); ms: m/e 284 (M^+ , 89), 283 (100), 282 (79).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.30; H, 4.41; S, 11.03.

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