

Some Methyl Substituted Benzo[*b*]naphtho[2,3-*d*]thiophenes (1)*E. Campaigne, John Ashby, and S. W. Osborn (2)*

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Seven benzo[*b*]naphtho[2,3-*d*]thiophenes have been prepared with methyl groups substituted in the 6,7, and 8-positions. These compounds are structurally related to the sulfur analogs of cholanthrene and methylcholanthrene.

Recently attention has been focussed on the antitumor properties of the indole alkaloids, ellipticine (1), olivacine (II) and related compounds (3). Swan has suggested that the activity of these alkaloids is due to absorption onto either adenine-thymine or guanine-cytosine pairs at the end of DNA molecules (4). The sulfur isosteres of I and II, namely thiaellipticine (III) (5) and thiaolivacine (6), have been prepared and are at present being biologically evaluated.

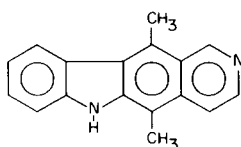
Evaluation of antitumor properties has also prompted the synthesis of IV (7) and V (8), the sulfur isosteres of the carcinogenic hydrocarbons, methylcholanthrene and 7,12-dimethyl-1,2-benzanthracene. The close structural similarity between III, the sulfur isostere of ellipticine and V, the sulfur isostere of 7,12-dimethyl-1,2-benzanthracene (VI) suggests that the carcinogenic properties of the 1,2-benzanthracenes (including cholanthrene) can be explained using similar arguments to those used by Swan for the activity of the ellipticine class of compounds. The sulfur compound IV and its desmethyl parent compound were also synthesized in these laboratories by a different route (9). We now report the synthesis of the related series of methyl substituted benzonaphthothiophenes (VII, a-g) which will be evaluated for antitumor activity.

The general approach to the synthesis of these compounds was the acylation of dibenzothiophene or 4-methyldibenzothiophene (10) with either succinic anhydride or methylsuccinic anhydride. Succinylation of 4-methyldibenzothiophene has been shown to occur in the 2-position of the dibenzothiophene nucleus (10). Wolff-Kishner reduction of this keto-acid followed by intramolecular cyclization yielded 6-methyl-7-keto-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (VIIIa). Cyclization was shown to have occurred at the 3-position by reference to the nmr of the product, in which the methyl resonance occurred at δ 2.84, consistent with an *ortho*-related carbonyl group (11). A singlet at δ 7.65 was assigned to H-11. Had cyclization occurred at the 1-position the singlet for H-3 (numbering based on dibenzothiophene) would have occurred at δ 7.3 or below (11). Grignard methylation of the known 7-keto-7,8,9,10-

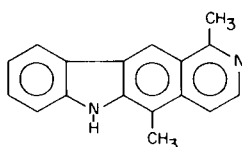
tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (VIIIb) (12) followed by dehydration and aromatization yielded 7-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIIb). Grignard methylation of VIIIa followed by dehydration and aromatization yielded 6,7-dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIe). Alternatively reduction and dehydrogenation of VIIIa yielded 6-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIc).

Acylation of aromatic nuclei with substituted succinic anhydrides, including methylsuccinic anhydride, has been studied with a wide variety of aromatic compounds and the subject has been reviewed by Berliner (13). With methylsuccinic anhydride the product isolated was invariably an α -methyl- β -aroylpropionic acid, and such has been assumed to be the case in the following compounds. Acylation of dibenzothiophene with methylsuccinic anhydride occurred in the 2-position as shown by the nmr spectrum of the product which was characteristic of a 2-substituted dibenzothiophene (11). Wolff-Kishner reduction followed by cyclization gave a product formulated as 8-methyl-7-keto-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (VIIIc) by analogy with VIIIb. A similar sequence of reactions involving Grignard methylation or reduction of the ketone function of VIIIc yielded 7,8-dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIId) and 8-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIa). The linearity of the latter two compounds was confirmed by comparison of their ultraviolet spectra with the recently published spectra of the isomeric benzonaphthothiophenes (14) (Table I).

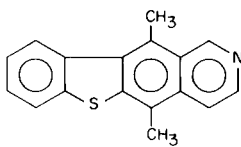
Reaction of 4-methyldibenzothiophene with methylsuccinic anhydride gave a poorly defined keto-acid which could not be crystallized, Wolff-Kishner reduction of which gave an oily acid which likewise could not be purified. Cyclization of this crude acid gave a crystalline ketone whose nmr spectrum was almost identical to that of VIIIa showing a singlet for H-11 at δ 7.75 and a deshielded C-6 methyl resonance at δ 2.88. The product was therefore formulated as 6,8-dimethyl-7-keto-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (VIIId). A similar sequence of reactions, involving either Grignard methylation or reduction of the ketone function of VIIId yielded



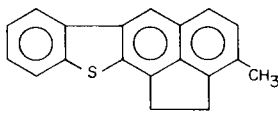
I



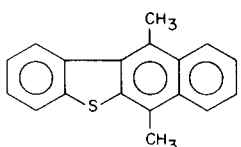
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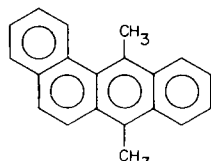
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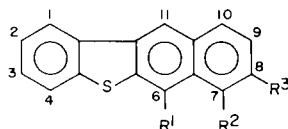
IV



V

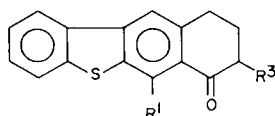


VI



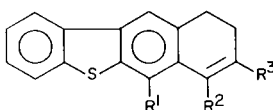
VII

- a, $R^1 = R^2 = H, R^3 = CH_3$
 b, $R^1 = R^3 = H, R^2 = CH_3$
 c, $R^2 = R^3 = H, R^1 = CH_3$
 d, $R^1 = H, R^2 = R^3 = CH_3$
 e, $R^3 = H, R^1 = R^2 = CH_3$
 f, $R^2 = H, R^1 = R^3 = CH_3$
 g, $R^1 = R^2 = R^3 = CH_3$
 h, $R^1 = R^2 = R^3 = H$



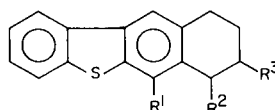
VIII

- a, $R^1 = CH_3, R^3 = H$
 b, $R^1 = R^3 = H$
 c, $R^1 = H, R^3 = CH_3$
 d, $R^1 = R^3 = CH_3$



IX

- a, $R^1 = H, R^2 = R^3 = CH_3$
 b, $R^1 = R^2 = R^3 = CH_3$
 c, $R^1 = R^2 = CH_3, R^3 = H$
 d, $R^1 = R^3 = H, R^2 = CH_3$



X

- a, $R^1 = R^2 = H, R^3 = CH_3$
 b, $R^1 = R^3 = CH_3, R^2 = H$
 c, $R^1 = CH_3, R^2 = R^3 = H$

6,7,8-trimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIg) and 6,8-dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIf).

The ultraviolet spectra of the seven benzonaphthothiophenes prepared here are recorded in Table I. These

spectra are in all cases virtually superimposable upon the spectrum of the unsubstituted ring, benzo[*b*]naphtho[2,3-*d*]thiophene (VIIh) (14). This fact along with the presence of a peak at $\lambda_{\text{max}} \text{ ca. } 370 \text{ m}\mu$ (14) confirms the linearity of the compounds prepared. The 100 MHz nmr spectra of compounds VIIa, c, d, and f, have been recorded. The infrared and mass spectra of compounds of type VII with the exception of VIIg and VIIe have been recorded elsewhere (15).

EXPERIMENTAL

Melting points were measured on a Meltemp apparatus and are corrected. Infrared spectra were determined as potassium bromide mulls on a Perkin Elmer Model 21 Spectrometer. Ultraviolet spectra were measured in 95% ethanol on a Beckman DK-1 spectrometer. 2,4-Dinitrophenylhydrazones were prepared by the method of Johnson (16) and sulfones by the method of Bordwell (17). NMR spectra were measured on a Varian HA-100 spectrometer, solvents and standard are specified in each case. In reporting the nmr spectra the following abbreviations have been used: s = singlet, d = doublet, m = multiplet, values for the latter representing the center of the resonance.

2-(β -Carboxybutanoyl)dibenzothiophene.

The method used was similar to that of Gilman and Jacoby (18). Dibenzothiophene (92 g., 0.51 mole), methylsuccinic anhydride (58 g., 0.51 mole) and 400 ml. of *sym*-tetrachloroethane were combined in a 1 l. round-bottom flask, heated to boiling and 20 ml. of the solvent allowed to distill in order to remove traces of water from the system. The reaction mixture was cooled to -5° with an ice-salt bath, and solution of anhydrous aluminum chloride (140 g., 1.05 mole) in dry nitrobenzene (200 ml.) added dropwise over one hour without allowing the temperature to rise above 0° , and stirring was continued for four hours. The mixture was kept at 0° for 24 hours (if the temperature was allowed to rise above 2° even for short periods of time the yield was decreased appreciably) and then hydrolyzed by pouring it with stirring into a mixture of ice (2 kg.) and concentrated hydrochloric acid. After allowing the hydrolysis mixture to stand overnight, the upper, aqueous, acid layer was decanted and the lower layer was steam distilled for 3-4 hours to remove the solvents. The aqueous layer was again decanted and an excess of sodium carbonate solution (100 g. of sodium carbonate in 1 l. of water) added. Steam distillation was continued for 2 hours (caution, frothing). Then the alkaline solution was cooled, filtered with the aid of filter cel, and carefully acidified to litmus with concentrated hydrochloric acid. The keto-acid precipitated as a sticky, cream-colored mass which hardened upon standing. It was collected by filtration, and crystallized from ethyl acetate (103 g., 69%) m.p. 182° (softens 145°). Two further recrystallizations from a large volume of benzene raised the melting point to $185\text{-}187^\circ$; nmr δ (DMSO, TMS external standard) 1.3 (d, J 7Hz, CH_3), 3.25 (m, aliphatic), 7.5 (m, H-7,8), 8.0 (m, H-6), 8.04 (s, H-3,4), 8.46 (m, H-9) and 8.92 (s, H-1).
Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{S}$: C, 68.4; H, 4.7; S, 10.7. Found: C, 68.0; H, 4.9; S, 10.4.

The product was converted to its 2,4-dinitrophenylhydrazone which was crystallized from ethanol-ethyl acetate, m.p. 233° dec.

Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_6\text{S}$: C, 57.7; H, 3.8. Found: C, 57.8; H, 3.8.

2-(β -carboxybutanoyl)-4-methyldibenzothiophene.

TABLE I

The Ultraviolet Absorption of the Methyl-substituted Benzo[*b*]naphtho[2,3-*d*]thiophenes (VII).

R ¹	R ²	R ³	λ max (ethanol) (log ₁₀ ε)								
H	H	H	226 (4.31)	244 (4.62)	263 (4.56)	275 (4.59)	283 (4.49)	315 (3.78)	330 (3.78)	355 (3.5)	377 (3.47)
H	H	CH ₃	228 (4.37)	245 (4.62)	265 (4.59)	275 (4.9)	282 (4.46)	318 (3.7)	332 (3.68)	347 (3.44)	367 (3.25)
H	CH ₃	H	227 (4.38)	246 (4.54)	265 (4.56)	275 (4.92)	283 (4.34)	314 (3.66)	330 (3.53)	353 (3.25)	370 (3.37)
CH ₃	H	H	226 (4.37)	243 (4.54)	265 (4.56)	275 (4.78)	283 (4.13)	315 (3.69)	330 (3.65)	353 (3.33)	376 (3.44)
H	CH ₃	CH ₃	228 (4.37)	247 (4.56)	267 (4.62)	278 (5.0)	283 (4.44)	321 (3.69)	335 (3.68)	352 (3.49)	373 (3.4)
CH ₃	CH ₃	H	228 (4.37)	248 (4.53)	267 (4.62)	275 (4.88)	283 (4.34)	314 (3.65)	328 (3.62)	353 (3.34)	370 (3.35)
CH ₃	H	CH ₃	231 (4.37)	243 (4.51)	267 (4.62)	276 (4.90)	283 (4.37)	317 (3.65)	334 (3.72)	350 (3.49)	368 (3.38)
CH ₃	CH ₃	CH ₃	230 (4.40)	243 (4.60)	265 (4.60)	276 (5.03)	283 (4.38)	318 (3.71)	333 (3.67)	350 (3.31)	367 (3.25)

This was prepared from 4-methyldibenzothiophene (10) by the above method in similar yield, m.p. 155-164°. The product was a sticky solid which was not further purified.

2-(γ-Carboxybutyl)dibenzothiophene.

The Huang-Minlon modification of the Wolff-Kishner reduction was used (19). A mixture of 2-(β-carboxybutanoyl)dibenzothiophene (28.4 g., 0.095 mole), sodium hydroxide (15 g.) hydrazine hydrate (85%, 15 ml.) and diethylene glycol (210 ml.) was heated under reflux for 1 hour. The condenser was removed and vapors allowed to distill until the temperature of the solution reached 200°, where it was maintained for 3 hours, when the mixture was poured onto ice (500 g.). After 1 hour the aqueous solution was clarified by filtration through filter cel and neutralized with dilute hydrochloric acid. The organic acid precipitated as a tarry mass which hardened after standing at room temperature. It was collected and recrystallized three times from 80% methanol, yielding 25 g. (92%) of colorless crystals, m.p. 111-112°.

Anal. Calcd. for C₁₇H₁₆O₂S: S, 11.28. Found: S, 10.98.

The product was converted to an amide *via* the acid chloride and ammonia, collected by filtration, washed with water, and recrystallized from ethanol to give colorless plates, m.p. 153-154°.

Anal. Calcd. for C₁₇H₁₇NOS: C, 72.05; H, 6.05. Found: C, 71.8; H, 5.9.

2-(γ-Carboxybutyl)-4-methyldibenzothiophene.

This was formed from crude 2-(β-carboxybutanoyl)-4-methyldibenzothiophene by the above procedure as an oil (57%) which was not further purified.

2-(γ-Carboxypropyl)-4-methyldibenzothiophene.

The product, prepared as above from 2-(β-carboxypropanoyl)-4-methyldibenzothiophene, crystallized from 80% methanol (86%), m.p. 141-142°.

Anal. Calcd. for C₁₇H₁₆O₂S: S, 11.28. Found: S, 11.21.

The acid was converted to its amide by the method described above. After recrystallization from ethanol, the colorless product

has m.p. 150-150.5°.

Anal. Calcd. for C₁₇H₁₇NOS: C, 72.0; H, 6.05. Found: C, 71.9; H, 5.85.

8-Methyl-7-keto-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (VIIIc).

The method used was essentially that of Bachmann and Wilds (20). 2-(γ-Carboxybutyl)dibenzothiophene (7.5 g., 0.026 mole) was treated with phosphorus pentachloride (6.25 g., 0.030 mole) in 30 ml. of dry benzene. The mixture was swirled gently at room temperature and after 10 minutes the reactants had dissolved. The solution was cooled in a dry ice-acetone bath until the benzene began to solidify when a solution of freshly distilled anhydrous stannic chloride (6.5 ml., 14.3 g., 0.055 mole) in an equal volume of benzene was added in one portion. A red complex formed immediately. The mixture was swirled for 10 minutes in an ice bath, then was hydrolyzed with ice (250 g.) and hydrochloric acid (38%, 50 ml.). The mixture was allowed to stand for several hours to complete the hydrolysis, and was then heated for 2 hours on the steam bath to evaporate the benzene. Upon cooling, the solidified organic phase was collected and washed with 10% sodium carbonate solution and with water. The product was recrystallized from ethanol-ethyl acetate (80:20) as colorless needles (6.6 g., 94%), m.p. 175.5-176°; ir 1680 cm⁻¹ (C=O).

Anal. Calcd. for C₁₇H₁₄OS: C, 76.7; H, 5.3. Found: C, 76.5; H, 5.4.

6,8-Dimethyl-7-keto-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (VIIIId).

This was prepared from crude 2-(γ-carboxybutyl)-4-methyldibenzothiophene by the above method. The tarry product was dissolved in ether and washed with 10% sodium bicarbonate solution and water. The ether layer was dried and reduced in volume (*ca.* 75 ml.) when the product crystallized (10.5 g., 66%), m.p. 118-119°; ir 1660 cm⁻¹ (C=O); nmr δ (deuteriochloroform, TMS internal standard) 1.3 (d, J 7 Hz, 8-CH₃), 2.88 (s, 6-CH₃), 2.35

(m, aliphatic) 7.4 (m, H-2,3), 7.75 (s, H-11), 8.0 and 8.06 (m, H-1 and H-4).

Anal. Calcd. for $C_{18}H_{16}OS$: C, 77.1; H, 5.8. Found: C, 77.0; H, 5.9.

6-Methyl-7-keto-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (VIIIa).

The product, prepared as above from 2-(γ -carboxypropyl)-4-methylthiophene (10), had m.p. 116-117.5° from ethanol (79%); ν 1680 cm^{-1} (C=O); nmr δ (deuteriochloroform, TMS internal standard) 2.1 and 2.8-3.0 (m, aliphatic CH_2), 2.84 (s, 6- CH_3), 7.38 (m, H-2,3), 7.65 (s, H-11), 7.7 (m, H-4) and 7.97 (m, H-1).

Anal. Calcd. for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.30; H, 5.33.

The ketone was converted to its 2,3-dinitrophenylhydrazone which recrystallized from dimethylformamide, m.p. 293-296°.

Anal. Calcd. for $C_{23}H_{18}N_4O_4S$: C, 61.9; H, 4.1. Found: C, 61.9; H, 4.1.

9,10-Dihydro-7,8-dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (IXa).

The method used was essentially that of Bachmann and Wilds (21). A Grignard reagent, prepared from 0.02 mole of methyl bromide, was cooled to -5° in an ice salt bath and a solution of VIIIc (5 g., 0.019 mole) in 50 ml. of dry benzene was added in one portion. The mixture was allowed to stand overnight at 0° and then hydrolyzed by pouring it carefully with stirring into 400 ml. of an ice cold saturated solution of ammonium chloride. The benzene layer was separated and the aqueous phase extracted with benzene (3 x 50 ml.). The benzene solutions were combined, washed with water, dried with anhydrous sodium sulfate, and the benzene evaporated in an air stream. The oily residue crystallized on standing to yield 4.47 g. (85%) of crude carbinol which was used without further purification. The crude methyl carbinol (4.00 g., 0.0142 mole) was heated in a sublimation apparatus at atmospheric pressure to 200° until bubbling ceased (15 minutes). The oil was then collected at 0.3 mm. (approximately 170° bath temperature) and the colorless product recrystallized from ethanol to yield 3.09 g. (83%), m.p. 130-132°.

Anal. Calcd. for $C_{18}H_{16}S$: C, 81.78; H, 6.10. Found: C, 81.54; H, 6.08.

9,10-Dihydro-6,7,8-trimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (IXb).

The product was prepared as above from VIIIc yielding an oil which did not distill at temperatures up to 290°/0.3 mm. and was therefore recrystallized directly from ethanol yielding, after two recrystallizations, 1.22 g. (41%) of colorless plates, m.p. 79.5-80°.

Anal. Calcd. for $C_{19}H_{18}S$: C, 82.0; H, 6.5. Found: C, 81.8; H, 6.6.

9,10-Dihydro-6,7-dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (IXc).

The product, prepared as above from VIIIa, was crystallized from ethanol to yield 1.98 g. (90%) of colorless plates, m.p. 84-86°.

Anal. Calcd. for $C_{18}H_{16}S$: C, 81.78; H, 6.10. Found: C, 81.45; H, 6.15.

9,10-Dihydro-7-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (IXd).

The product, prepared as above from VIIIb, sublimed (65%), m.p. 118-119°.

Anal. Calcd. for $C_{17}H_{14}S$: C, 81.6; H, 5.6. Found: C, 81.3; H, 5.7.

8-Methyl-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (Xa).

A solution of VIIIc (8.0 g., 0.030 mole), sodium hydroxide (5 g.) and 85% hydrazine hydrate (5 ml.) in diethylene glycol (80 ml.) was heated under reflux for one hour. The condenser was inverted and solvent distilled from the mixture until the temperature of the boiling solution reached 200°. Refluxing was then maintained at 200° for 3 hours. The mixture was cooled, diluted with 250 ml. of water and clarified by filtration through filter cel. The solution was acidified to litmus with dilute hydrochloric acid and the brownish fluorescent product collected by filtration, washed with water, and recrystallized from 80% ethanol. The ethanolic solution was treated with carbon, which removed the fluorescence. After two recrystallizations 4.5 g. (59%) of colorless crystals were obtained, m.p. 78-78.5°.

Anal. Calcd. for $C_{17}H_{16}S$: C, 80.9; H, 6.4. Found: C, 80.6; H, 6.4.

6,8-Dimethyl-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (Xb).

This compound prepared as above from VIIIc crystallized from ethanol, m.p. 140-141° (67%).

Anal. Calcd. for $C_{18}H_{18}S$: C, 81.1; H, 6.8. Found: C, 80.8; H, 6.5.

6-Methyl-7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (Xc).

The product, prepared as above from VIIIa, had m.p. 125-126.5° from ethanol (74%).

Anal. Calcd. for $C_{17}H_{16}S$: C, 80.9; H, 6.4. Found: C, 80.8; H, 6.4.

8-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIa).

A mixture of Xa (2.04 g., 0.008 mole) and powdered selenium (1.58 g., 0.020 mole) was heated in a small round bottomed flask equipped with a condenser, using a Wood's metal bath. A rubber tube connected to the top of the condenser was fitted to the bottom of a glass tower filled with 50 g. of calcium hypochlorite. Hydrogen selenide was evolved at 360° and heating was continued until evolution ceased. The mixture was cooled and extracted thoroughly with boiling ethanol. The hot extracts were treated with carbon, filtered and concentrated to 50 ml. Upon cooling the product was collected by filtration and recrystallized from ethanol to yield 1.56 g. (78%), m.p. 178-180°; nmr (deuteriochloroform, TMS internal standard) δ 8.5 (s, H-11), 8.1 (m, H-1), 8.12 (s, H-6), 7.88 (d, $J_{10,9}$ 8 Hz, H-10), 7.76 (m, H-4), 7.62 (d, $J_{7,9}$ 1 Hz, H-7), 7.4 (m, H-2,3), 7.3 (dd, $J_{9,10}$ 8 Hz, $J_{9,7}$ 1 Hz, H-9), 2.54 (s, 8- CH_3).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.2; H, 4.9. Found: C, 82.1; H, 4.9.

The sulfone was recrystallized from ethanol as yellow needles, m.p. 266-267° dec. The color was not removed by treatment with carbon.

Anal. Calcd. for $C_{17}H_{12}O_2S$: C, 72.8; H, 4.3. Found: C, 72.6; H, 4.3.

7-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIb).

This product, prepared as above from IXd, crystallized from ethanol, m.p. 175.5-176° (86%).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.2; H, 4.9. Found: C, 82.4; H, 4.9.

The sulfone was recrystallized from ethanol, m.p. 285-286°.

Anal. Calcd. for $C_{17}H_{12}O_2S$: C, 72.8; H, 4.3. Found: C, 72.4; H, 4.4.

6-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIc).

This compound prepared from Xc by selenium dehydrogenation crystallized from ethanol, m.p. 95.5-96° (70%); nmr (deuteriochloroform, TMS internal standard) δ 8.35 (s, H-11), 8.0, 7.75 and 7.4 multiplets, 2,83 (s, 6-CH₃). Due to lack of material a sulfone was not prepared.

Anal. Calcd. for C₁₇H₁₂S: C, 82.2; H, 4.9. Found: C, 81.8; H, 5.0.

7,8-Dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIId).

This compound, prepared from IXa by selenium dehydrogenation crystallized from ethanol, m.p. 193-194° (79%); nmr (deuteriochloroform, TMS internal standard) δ 8.45 and 8.38 (s, H-11,6), 8.15 (m, H-1), 7.74 (m, H-4), 7.74 (d, J_{10,9} 8 Hz, H-10), 7.39 (m, H-2,3), 7.6 (d, J_{9,10} 8 Hz, H-9), 2.61 and 2.49 (s, 7,8-CH₃).

Anal. Calcd. for C₁₈H₁₄S: C, 82.4; H, 5.4. Found: C, 82.15; H, 5.5.

The sulfone was recrystallized from ethanol, m.p. 274° dec.

Anal. Calcd. for C₁₈H₁₄O₂S: C, 73.4; H, 4.8. Found: C, 73.0; H, 4.8.

6,7-Dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIe).

This compound was prepared as above from IXc and crystallized from ethanol, m.p. 150-152° (79%).

Anal. Calcd. for C₁₈H₁₄S: C, 82.4; H, 5.4. Found: C, 82.6; H, 5.1.

The sulfone crystallized from ethanol, m.p. 262° dec.

Anal. Calcd. for C₁₈H₁₄O₂S: C, 73.4; H, 4.8. Found: C, 73.0; H, 4.6.

6,8-Dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIf).

This compound was prepared as above from Xb and crystallized from ethanol, m.p. 113.5-115° (77%); nmr (deuteriochloroform, TMS internal standard) δ 8.35 (s, H-11), 8.14 (m, H-1), 7.86 (d, J_{10,9} 8 Hz, H-10), 7.8 (d, J_{7,9} 1 Hz, H-7), 7.78 (m, H-4), 7.4 (m, H-2,3), 7.3 (dd, J_{9,10} 8 Hz, J_{9,7} 1 Hz, H-9), 2.85 (s, 6-CH₃), and 2.6 (s, 8-CH₃).

Anal. Calcd. for C₁₈H₁₄S: C, 82.4; H, 5.4. Found: C, 82.4; H, 5.4.

The sulfone formed pale yellow needles from ethanol, m.p. 242° dec.

Anal. Calcd. for C₁₈H₁₄O₂S: C, 73.4; H, 4.8. Found: C, 73.8; H, 4.6.

6,7,8-Trimethylbenzo[*b*]naphtho[2,3-*d*]thiophene (VIIg).

This compound, prepared as above from IXb, crystallized from ethanol, m.p. 110-112° (73%).

Anal. Calcd. for C₁₉H₁₆S: C, 82.5; H, 5.8. Found: C, 82.3; H, 5.5.

The sulfone crystallized from ethanol, m.p. 208° dec.

Anal. Calcd. for C₁₉H₁₆O₂S: C, 74.0; H, 5.2. Found: C, 74.3; H, 5.1.

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