Anal. Calcd for $C_9H_5N_3O_2$: C, 57.72; H, 2.69; N, 22.46. Found: C, 57.52; H, 2.47; N, 22.18.

4,5-Dihydro-4-methylsydno[3,4-*a*]quinoxaline (12) and 4-Methylsydno[3,4-*a*]quinoxaline (13).—A solution of methyllithium (5 ml, 2.1 *M* in ether) was slowly added to a suspension of **7a** (0.3 g, 1.7 mmol) and anhydrous ether (5 ml) at −20° under a dry nitrogen atmosphere. The mixture was stirred for 1 hr and added to a solution of ethyl formate (0.5 g, 6.7 mmol) in ether (20 ml). After stirring for 1 hr, the mixture was extracted with aqueous ammonium chloride solution. The ether solution was dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. The residue was taken up in methylene chloride and placed on a 15-g column of silica gel (Woelm). Elution with methylene chloride–ethyl acetate (95:5) yielded 26 mg of **13**, recrystallized from benzene–hexane: mp 160–162° (sublimes); ir (KBr) 1800 cm^{-1} (C=O); uv max (H_2O) 346 nm (ϵ 7320); nmr ($CDCl_3$) δ 2.9 (s, 3, CH_3), 7.8 (m, 4, aryl); mass spectrum (70 ev) *m/e* (rel intensity) 201 (16), 173 (9), 171 (25), 145 (23), 144 (56), 143 (100), 132 (11), 117 (42), 103 (10), 102 (44), 81 (10), 78 (22), 77 (21), 76 (34), 75 (21), 69 (20), 50 (25).

Anal. Calcd for $C_{10}H_7N_3O_2$: C, 59.70; H, 3.51; N, 20.89. Found: C, 59.20; H, 3.33; N, 20.44.

Further elution gave 20 mg of **12** which was recrystallized from benzene: mp 166–167°; ir (KBr) 1735 cm^{-1} (C=O); uv max (EtOH) 325 nm (ϵ 4580), 242 (25,700); nmr ($CDCl_3$) δ 1.54 (d, 3, CH_3), 4.5 (broad, 1, NH), 4.75 (q, 1, C_4 H), 6.6–7.9 (m, 4, aryl). This compound when exposed to air was slowly transformed to a substance identical in melting point and ir and nmr spectra with **13**. In solution this transformation was facile and **12** could be converted to **13** by shaking a solution of **12** in chloroform in a separatory funnel. The mass spectrum of **12** was identical with that of **13** when introduced *via* the glass inlet system.

Kinetic Procedures.—For alkaline hydrolsyes, a few drops of a master solution of the compound in ethanol were added to a cuvette containing aqueous KOH which had been brought to 39 ± 0.1° in the sample holder of a Gilford Model 2400 uv spectrophotometer by means of a circulating constant-temperature bath. Readings of optical density of the longest wavelength maximum were recorded until no perceptible change could be detected. Base concentrations ranged from 0.02 to 0.8 *N* with a minimum of three different values being used for each compound. Concentrations of sydnone were *ca.* 10^{-4} *M*. The apparent first-order rate constants were calculated by the method of least squares. For acid hydrolyses, 20 ml of a 10^{-3} *M* master solution of sydnone was added to 80 ml of 1.0 *M* hydrochloric acid solution maintained at 80°. Aliquots, which were quickly cooled, were taken over a period of 7 days to observe the decrease in optical density of the longest wavelength ultraviolet maximum.

Semiempirical SCF–MO Calculations.—The semiempirical self-consistent field π molecular orbital calculations were performed using QCPE program 167 which was modified to include the variable electronegativity procedure[9] and a Givens method of obtaining eigenvalues and eigenvectors. Repulsion integrals were obtained by the Mataga method and penetration integrals were neglected. Resonance integrals were evaluated by $B_{ij}^{SCF} = KS_{ij}(I_i + I_j)$ where S_{ij} is the overlap integral between atoms i and j and *I* is the ionization potential. The value of *K* was adjusted to reproduce the spectrum of 3-phenylsydnone (including CI) and was given the value 0.65.

The semiempirical all valence electron calculation was performed using the CNINDO program of Dobosh (QCPE 142). Only a limited number of geometries were investigated.

Registry No.—**6b** (R = Br), 14715-65-2; **7a**, 34315-02-3; **7b**, 34315-04-3; **7c**, 34315-05-4; **8a**, 11094-23-8; **8b**, 11094-25-0; **8c**, 11094-28-3; **9**, 11094-26-1; **11**, 11094-22-7; **12**, 11094-27-2; **13**, 11094-24-9.

Acknowledgment.—The authors are grateful to the SUNY/Buffalo Computing Center for their donation of computing services of a CDC 6400 computer. This investigation was supported by a training grant (5-Tl-GM-55-08) from the Division of Medical Sciences, U. S. Public Health Services, Bethesda, Md.

Thiophene Analogs of Anthraquinone

D. W. H. MacDowell* and James C. Wisowaty[1]

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

Received July 26, 1971

Six possible isomers resulting from the replacement of one or both benzene rings in 9,10-anthraquinone with thiophene rings have been synthesized: 4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione (**1**), 4,9-dihydronaphtho-[2,3-*c*]thiophene-4,9-dione (**2**), 4,8-dihydrobenzo[1,2-*b*:5,4-*b′*]dithiophene-4,8-dione (**3**), 4,8-dihydrobenzo[1,2-*b*:4,5-*b′*]dithiophene-4,8-dione (**4**), 4,8-dihydrobenzo[1,2-*b*:4,5-*c′*]dithiophene-4,8-dione (**5**), and 4,8-dihydrobenzo[1,2-*c*:4,5-*c′*]dithiophene-4,8-dione (**6**). Compound **6** was prepared by dechlorination of 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c′*]dithiophene-4,8-dione (**15**). The compounds **1**, **2**, **3**, **4**, **5**, and **15** were subjected to reduction by means of an equimolar mixture of aluminum chloride–lithium aluminum hydride. Compounds **3** and **4** show only reduction to the hydroquinone stage. Compounds **2** and **15** provide good yields of the corresponding dihydroaromatic systems, while **1** and **5** afford only moderate yields of the dihydroaromatic systems. These results are explained in terms of the position of keto–enol tautomerism in the corresponding anthrone–anthrol systems and the stability of the parent aromatic systems.

Two previous papers[2] report the synthesis of a series of thiophene analogs of anthrone which possess significantly different enolizabilities. It was found that substitution of a *b*-fused thiophene ring for one of the benzene portions of anthrone leads to an increase in the stability of the enol form, while a similar substitution of a *c*-fused thiophene ring promotes a decrease in the stability of the enol tautomer.

Replacement of one or both of the benzene rings in 9,-10-anthraquinone by a thiophene ring gives rise to two isomeric naphthothiophenediones **1** and **2** and four isomeric benzodithiophenediones **3**–**6**. Of these, **1** has been known for some time,[3] while a brief, recent report[4] refers to a synthesis of **4**.

Synthesis of the Six Diones.—The known quinone 4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione (**1**) was prepared in 75% yield by the cyclization of *o*-(2-thenoyl)benzoic acid under the influence of aluminum chloride in nitrobenzene following the method of Weinmayr.[3c] A direct pathway to 4,9-dihydronaptho-[2,3-*c*]thiophene-4,9-dione (**2**) can be envisioned as

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[1] NDEA Fellow, 1967–1970.

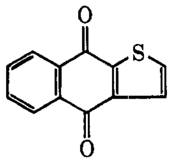
[2] D. W. H. MacDowell and J. C. Wisowaty, *J. Org. Chem.*, **36**, 3999, 4004 (1971).

[3] (a) W. Steinkopf and W. Butkiewicz, *Justus Liebigs Ann. Chem.*, **407**, 94 (1914); (b) R. Goncalves and E. V. Brown, *J. Org. Chem.*, **17**, 698 (1952); (c) V. Weinmayr, *J. Amer. Chem. Soc.*, **74**, 4353 (1952).

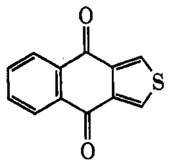
[4] D. W. Slocum and P. L. Gierer, *Chem. Commun.*, 305 (1971).

TABLE I

Dione	Color	Recrystn solvent	Mp, °C	$\nu_{C=O}$, cm^{-1} (KBr)	Uv (95% EtOH), λ_{max} (ϵ_{max})
1	Yellow	CH_3CO_2H	227–228	1660	248 (23,300), 253 (24,500), 283 (10,070), 334 (3060)
2	Yellow	CH_3CO_2H	277	1665	256 (43,900), 327 (2420)
3	Yellow	CH_3CO_2H	235–237	1640	236 (18,800), 293 (15,400), 334 (5400)
4	Yellow	CH_3CO_2H	258–260	1640	240 (15,300), 291 (13,280), 343 (4600)
5	Yellow	CH_3CO_2H	296–297	1640	258 (34,400), 280 (10,240), 329 (3960)
6	Yellow-orange	$C_2H_5CO_2H$	340	1655	259 (61,800)
15	Yellow	$CHCl_3$–CCl_4	208–209°	1670	261 (52,100), 327 (2840)



1



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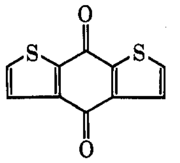

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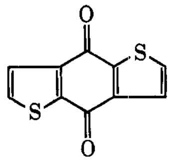

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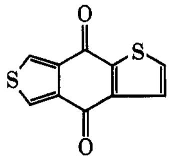

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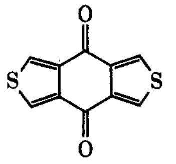


6

utilizing thiophene-3,4-dicarboxylic acid as an intermediate as shown in Scheme I.

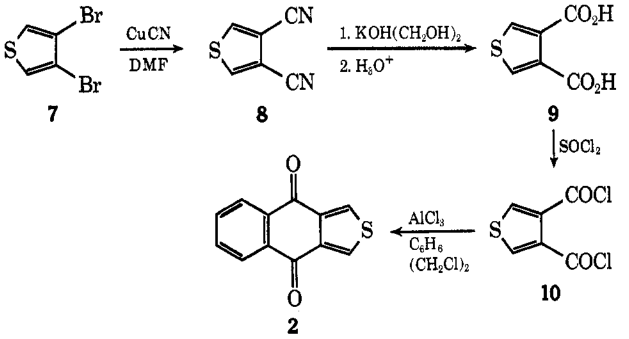
The transformation of 3,4-dibromothiophene (**7**) to the dinitrile **8** was accomplished by a modification of a method reported in the literature.[5] Hydrolysis of the dinitrile to the diacid **9** was best accomplished using potassium hydroxide in ethylene glycol in yields of 69–88%. The cyclic diacylation of benzene by means of **10** and aluminum chloride afforded the dione **2** in 42% yield accompanied by small amounts of other materials, the structures of which are under investigation at present.

Reaction of the diacid chloride **10** with thiophene (**12**) and aluminum chloride under similar conditions gave 4,8-dihydrobenzo[1,2-*b*:4,5-*c*′]dithiophene-4,8-dione (**5**) in 37% yield along with a small amount of a white solid which was shown to be 3,4-bis(2-thenoyl)thiophene (**13**) (Scheme II). This method was also applied to the synthesis of **6**. When the acid chloride **10** was treated with 2,5-dichlorothiophene (**14**) in 1,2-dichloroethane, a 50% yield of 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (**15**) was obtained. The dichlorodione **15** was dechlorinated by a suspension of copper metal in refluxing propionic acid[6] to give a 72% yield of 4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (**6**). The diketone is a high-melting orange-yellow solid, very slightly soluble in most organic solvents.

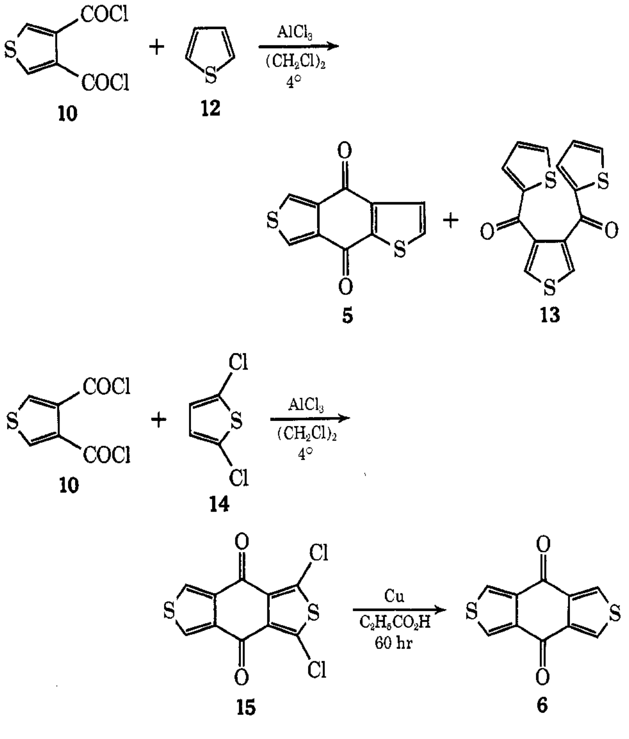
The remaining isomers, 4,8-dihydrobenzo[1,2-*b*:5,4-*b*′]dithiophene-4,8-dione (**3**) and 4,8-dihydrobenzo-[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (**4**) were prepared from the known[2] acetoxy compounds 8-acetoxybenzo-[1,2-*b*:5,4-*b*′]dithiophene (**16**) and 4-acetoxybenzo[1,2-*b*:4,5-*b*′]dithiophene (**17**) by oxidation with chromium trioxide in acetic acid. The yields of **3** and **4** were 79 and 54%, respectively (Scheme III).

The properties of the aforementioned diones are collected in Table I.

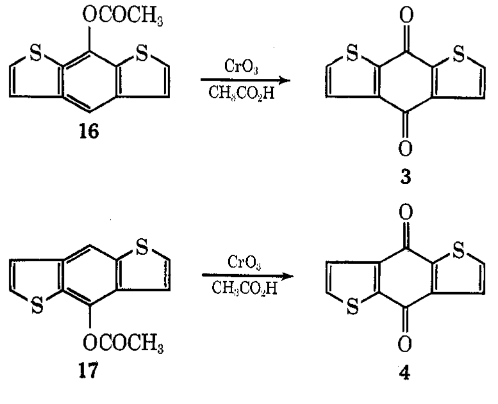
SCHEME I



SCHEME II



SCHEME III



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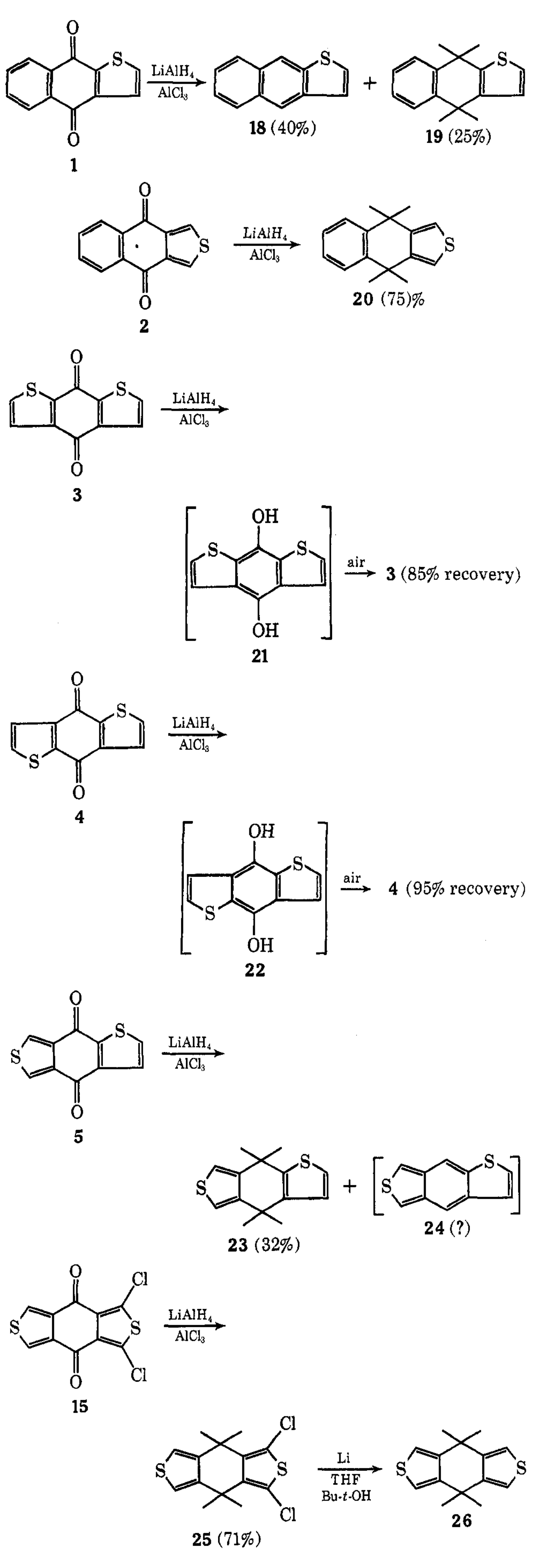
[5] J. Morel, C. Paulmier, and P. Pastour, *C. R. Acad. Sci., Ser. C*, **266**, 1300 (1968).

[6] J. Skramstad, *Acta Chem. Scand.*, **23**, 703 (1969).

SCHEME IV



Hydride Reduction of the Diones.—When ethereal suspensions of diones **1–5** and **15** were treated with an excess of an equimolar mixture of aluminum chloride and lithium aluminum hydride, reaction took place at the carbonyl functions. The products of reaction in each case were separated by chromatography on alumina using hexane as eluent and are shown in Scheme IV.

An examination of the reduction products seemed to place the diones into three separate classes: **3** and **4** show only reduction to the hydroquinone stage, **2** and **15** provide good yields of the respective dihydro compounds **20** and **25**, while **1** and **5** afford only moderate yields of the dihydro compounds **19** and **23**. A 40% yield of naptho[2,3-*b*]thiophene was also obtained from the reduction of **1**. The insolubility of **6** in ether necessitated the use of its dichloro derivative **15** in this study. As an additional structural proof, **25** was dechlorinated using lithium metal and *tert*-butyl alcohol in tetrahydrofuran solution[7] to 4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene (**26**) in 53% yield.

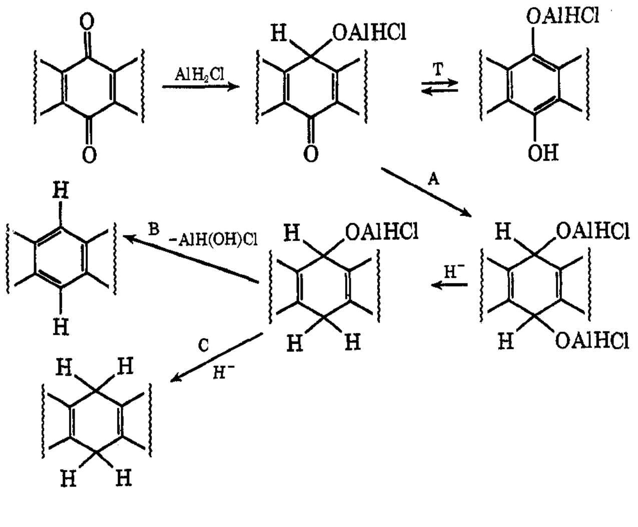
Discussion

When equimolar quantities of aluminum chloride and lithium chloride are mixed in ether, an acid–base reaction takes place, resulting in the formation of dihydridoaluminum chloride and lithium chloride.[8] The reaction

$$\mathrm{LiAlH_4 + AlCl_3 \longrightarrow LiCl + 2AlH_2Cl}$$

of a quinone with this reducing mixture can be postulated to follow the general steps which are outlined in Scheme V.

SCHEME V



The four steps which determine product formation are designated A, B, C, and T. Step T involves the isomerization of the partially reduced quinone to a salt of the hydroquinone. Isomerization takes place only if step T is faster than the rate of attack at the second carbonyl function (step A). Since this transformation is in effect related to keto–enol tautomerism, the formation of the hydroquinone indicates a fast step T and also suggests a stable enol form in the corresponding keto–enol analogs. Therefore, the termination of the

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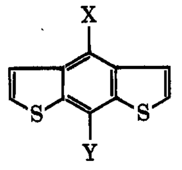
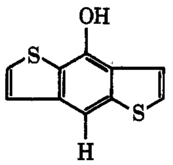
[7] P. Bruck, *Tetrahedron Lett.*, 449 (1962).

[8] M. N. Rerick in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, p 3.

reduction of diones **3** and **4** at the respective hydroquinone stage is in agreement with the lack of ketone character in the benzodithiophene derivatives **27a,b** and **28**.[2]



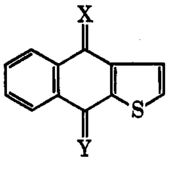
27a, X = OH; Y = H
b, X = H; Y = OH



28

The formation of an aromatic system is a result of step T and also step B. The isolation of only the product resulting from step C indicates a lack of driving force toward the formation of an aromatic system. Thus, the reduction of diones **2** and **15** to the corresponding dihydroaromatic compounds in good yield is not surprising, since it has been recently shown that naphtho[2,3-*c*]thiophene is a very unstable substance and could not be isolated.[9]

The reduction of dione **1** provides the products of both step B and step C, since the formation of naphtho[2,3-*b*]thiophene is a favorable process. Unlike the enol systems **27a,b** and **28**, the naphtho[2,3-*b*]thiophenones **29a,b** show considerable keto character,[2] hence an absence of the corresponding hydroquinone in the reaction mixture.



29a, X = O; Y = H_2
b, X = H_2; Y = O

The isolation of only the dihydro compound **23** from the reaction of dione **5** seems to indicate its similarity to diones **2** and **15**. However, a similarity to dione **1** can also be postulated by assuming the formation of benzo[1,2-*b*:4,5-*c*′]dithiophene (**24**). In order to resolve this ambiguity the preparation of **24** has been undertaken and will be the subject of a future publication.

Experimental Section[10]

Synthesis of 4,9-Dihydronaphtho[2,3-*b*]thiophene-4,9-dione (1).—A solution of *o*-(2-thenoyl)benzoic acid[11] (5.0 g, 22 mmol) and aluminum chloride (6.65 g, 50 mmol) in nitrobenzene (33 ml) was maintained at 130° for 18 hr and then allowed to cool. The nitrobenzene was removed by steam distillation and the black gummy residue was dissolved in hot benzene and run onto a column packed with neutral alumina. Elution with benzene (1000 ml) provided 3.85 g of yellow solid. Recrystallization from acetic acid afforded 3.45 g (75%) of the quinone: mp 227–228° (lit.[3c] 229–230°); uv max (95% C_2H_5OH) 248 mμ (ϵ 23,300), 253 (24,500), 283 (10,070), 334 (3060); ir (KBr) 1660 cm^{-1} (C=O); nmr (CF_3COOH) τ 1.63–2.44 (m).

Synthesis of 4,9-Dihydronaphtho[2,3-*c*]thiophene-4,9-dione (2). A. 3,4-Dicyanothiophene (8).—A stirred solution of 3,4-dibromothiophene (**7**) (242 g, 1 mol) and cuprous cyanide (260 g, 2.9 mol) in dry dimethylformamide (250 ml) was maintained at reflux for 4 hr. The dark mixture was then poured into a solution of hydrated ferric chloride (1000 g) in hydrochloric acid (1750 ml, 1.7 *M*) and maintained at 60–70° for 30 min. After the mixture had sufficiently cooled, methylene chloride (1250 ml) was added and the layers were separated. The aqueous phase was extracted four times with 1250-ml portions of methylene chloride. Each organic extract was washed successively with two 100-ml portions of hydrochloric acid (6 *M*), water, saturated sodium bicarbonate solution, and again with water. The individual portions were combined, dried ($MgSO_4$), and evaporated. The resulting slightly yellow solid was sublimed at 110° (0.1 mm) to give 100.6 g (75%) of white solid. Recrystallization from acetonitrile provided an analytical sample: mp 169–170° (lit.[5] 171°); ir (KBr) 2235 and 2240 cm^{-1} (CN); nmr (acetone-d_6) τ 1.50 (s).

Anal. Calcd for $C_6H_2N_2S$: C, 53.71; H, 1.50; N, 20.89; S, 23.90. Found: C, 53.65; H, 1.43; N, 20.76; S, 24.09.

B. Thiophene-3,4-dicarboxylic Acid (9).—A stirred solution of 3,4-dicyanothiophene (27.6 g, 0.21 mol) and potassium hydroxide (76.2 g, 1.36 mol) in ethylene glycol (300 ml) was refluxed for 4 hr and then allowed to cool, forming a yellow precipitate. The mixture was poured into water. The resulting solution was washed with ether (200 ml) and the aqueous phase was cooled in an ice bath and acidified with excess hydrochloric acid (12 *M*). The white precipitate was filtered and taken up in ether. The aqueous filtrate was extracted three times with 500-ml portions of ether. The ethereal solutions were combined, dried ($MgSO_4$), and evaporated, leaving a faintly yellow solid which was recrystallized from water to give 28 g (79%) of white needles, mp 227–229 (lit.[12] 230–231°), ir (KBr) 1690 cm^{-1} (acid C=O).

C. Thiophene-3,4-dicarbonyl Chloride (10).—A stirred suspension of thiophene-3,4-dicarboxylic acid (8.6 g, 50 mmol) in thionyl chloride (20 ml) was maintained at reflux for 1 hr. The dark solution was allowed to cool and the excess thionyl chloride was removed under reduced pressure. The residue was treated with two 10-ml portions of dry benzene, followed by the evaporation of each portion. The tan solid was dried in vacuum for 1 hr, and used without further purification.

D. 4,9-Dihydronaphtho[2,3-*c*]thiophene-4,9-dione (2).—A solution of the acid chloride **10** obtained above in dry 1,2-dichloroethane (50 ml) was added dropwise to a stirred suspension of aluminum chloride (15.0 g, 0.11 mol) in dry 1,2-dichloroethane (50 ml) maintained at 4°. The mixture was allowed to stir at 4° for 10 min and a solution of dry benzene (4 g, 51 mmol) in 1,2-dichloroethane (25 ml) was slowly added. The yellow suspension was allowed to stir at room temperature for 18 hr and was then poured into ice and hydrochloric acid (50 ml, 2 *M*). Chloroform (300 ml) was added and the mixture was shaken vigorously. The layers were separated and the aqueous layer was extracted with chloroform. The combined organic portions were washed with saturated sodium bicarbonate solution and with water, then dried ($MgSO_4$) and concentrated to 200 ml. The chloroform solution was run onto a column of neutral alumina followed by an additional 1500 ml of chloroform. The yellow residue, which remained after the solvent was evaporated, was recrystallized from acetic acid to give 4.5 g (42%) of the cyclic dione. An analytical sample was obtained by means of repeated recrystallization from acetic acid: mp 277°; uv max (95% C_2H_5OH) 256 mμ (ϵ 43,900) and 327 (2420); ir (KBr) 1665 cm^{-1} (C=O); nmr (CF_3COOH) τ 1.55 (s, 2 H, C_1 and C_3 protons) 1.63–1.96 (m, 2 H, C_5 and C_8 protons), 2.03–2.33 (m, 2 H, C_6 and C_7 protons).

Anal. Calcd for $C_{12}H_6O_2S$: C, 67.28; H, 2.82; S, 14.96. Found: C, 67.39; H, 2.81; S, 15.05.

Synthesis of 4,8-Dihydrobenzo[1,2-*b*:5,4-*b*′]dithiophene-4,8-dione (3).—A suspension of 8-acetoxybenzo[1,2-*b*:5,4-*b*′]dithiophene[2b] (10.45 g, 0.043 mol) and chromium(VI) oxide (~0.1 g) in glacial acetic acid was heated to 80° with stirring. The remainder of the chromium(VI) oxide (11.05 g, 0.11 mol) was added portionwise over a 5-min period. The dark solution began to reflux vigorously. Reflux was maintained for 5 min after the addition was completed and then hydrochloric acid (12 *M*,

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[9] D. W. H. MacDowell, A. T. Jeffries, and M. B. Meyers, *J. Org. Chem.*, **36**, 1416 (1971).

[10] All temperatures are uncorrected. All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian HA-60 high resolution spectrometer as approximately 10% (weight–volume) solutions in solvents as specified using tetramethylsilane as an internal standard (τ 10). The ultraviolet spectra were determined in 95% ethanol on a Bausch and Lomb Spectronic 505 spectrometer.

[11] M. Rajsner, J. Metysova, and M. Protiva, *Collect. Czech. Chem. Commun.*, **34**, 468 (1969).

[12] J. Sice, *J. Org. Chem.*, **19**, 70 (1954).

20 ml) was added and the mixture was boiled for another 5-min period. The dark solution was diluted with water (200 ml) and cooled to 0°. The resulting precipitate was filtered, washed with water, and taken up in chloroform. The organic solution was washed with saturated sodium bicarbonate solution and with water, then dried ($MgSO_4$) and concentrated to give a yellow-green solid. This impure material was dissolved in benzene and chromatographed on neutral alumina using benzene as the eluent. Following concentration of the benzene solution, a yellow solid was obtained and subsequently recrystallized from acetic acid to give 7.45 g (79%) of the quinone. An additional recrystallization from acetic acid provided an analytical sample: mp 235–237°; uv max (95% C_2H_5OH) 236 mμ (ϵ 18,800), 293 (15,400), 334 (5400); ir (KBr) 1640 cm^{-1} (C=O); nmr (CF_3COOH) τ 2.13 (d, 2 H, $J_{2,3} = 5$ Hz, C_2 and C_6 protons), 2.36 (d, 2 H, $J_{2,3} = 5$ Hz, C_3 and C_5 protons).

Anal. Calcd for $C_{10}H_4O_2S_2$: C, 54.53; H, 1.83; S, 29.12. Found: C, 54.68; H, 1.95; S, 29.27.

Synthesis of 4,8-Dihydrobenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (4).—A small quantity of chromium(VI) oxide (0.1 g) was added to a stirred suspension of 4-acetoxybenzo[1,2-*b*:4,5-*b*′]dithiophene (12.4 g, 0.05 mol) in glacial acetic acid (200 ml). The mixture was heated to 80° and the remainder of the chromium(VI) oxide (13.8 g, 0.14 mol) was added portionwise over a 3-min period, thus causing a vigorous reflux. The dark green solution was maintained at reflux for 10 min and then hydrochloric acid (12 *M*, 25 ml) was cautiously added. Work-up as for **3** yielded a granular yellow solid. Recrystallization from acetic acid provided 5.9 g (54%) of the quinone. Recrystallization from acetic acid afforded an analytical sample: mp 259–260°; uv max (95% C_2H_5OH) 240 mμ (ϵ 15,300), 291 (13,280), 343 (4600); ir (KBr) 1640 cm^{-1} (C=O); nmr (CF_3COOH) τ 2.08 (d, 2 H, $J_{2,3} = 5$ Hz, C_2 and C_6 protons), 2.28 (d, 2 H, $J_{2,3} = 5$ Hz, C_3 and C_7 protons).

Anal. Calcd for $C_{10}H_4O_2S_2$: C, 54.53; H, 1.83; S, 29.12. Found: C, 54.75; H, 1.88; S, 28.99.

Synthesis of 4,8-Dihydrobenzo[1,2-*b*:4,5-*c*′]dithiophene-4,8-dione (5).—The acid chloride **10**, which is described above, was dissolved in dry 1,2-dichloroethane (75 ml) and the resulting solution was added dropwise to a stirred suspension of aluminum chloride (14.6 g, 0.11 mol) in 1,2-dichloroethane (50 ml) which was maintained at 4°. The mixture was allowed to stir at 4° for 10 min after the addition had been completed. A solution of thiophene (5 g, 60 mmol) in 1,2-dichloroethane (25 ml) was slowly added to the cold mixture. The ice bath was removed and stirring was continued for 18 hr. The reaction mixture was then poured into ice and 2 *M* hydrochloric acid and shaken vigorously. Extraction with chloroform gave a red-brown solid, which was dissolved in chloroform and chromatographed on neutral alumina using chloroform as the eluent to give a yellow solid. Recrystallization from acetic acid gave 4.1 g (37%) of yellow plates. An additional recrystallization from acetic acid provided an analytical sample: mp 296–297°; uv max (95% C_2H_5OH) 258 mμ (ϵ 34,400), 280 (10,240), 329 (3960); ir (KBr) 1640 cm^{-1} (C=O); nmr (CF_3COOH) τ 1.50 (s, 2 H, C_5 and C_7 protons), 2.05 (d, 1 H, $J_{2,3} = 5$ Hz, C_2 proton), 2.23 (d, 1 H, $J_{2,3} = 5$ Hz, C_3 proton).

Anal. Calcd for $C_{10}H_4O_2S_2$: C, 54.53; H, 1.83; S, 29.12. Found: C, 54.46; H, 1.78; S, 29.05.

A similar experiment, in which the thiophene solution was more rapidly added to the acid chloride–aluminum chloride mixture, resulted in the formation and subsequent isolation of a small quantity of 3,4-bis(2′-thenoyl)thiophene (**13**) from the mother liquor of **5**. Recrystallization from benzene–hexane provided an analytical sample: mp 143–144°; ir (KBr) 1635 cm^{-1} (ketone C=O); nmr (acetone-d_6) τ 1.79 (s, 2 H, C_2 and C_5 protons), 2.06 (m, 2 H, $J_{4,5} = 5$ Hz, $J_{3,5} = 1.3$ Hz, C_5' protons), 2.23 (m, 2 H, $J_{3,4} = 3.6$ Hz, $J_{3,5} = 1.3$ Hz, C_3' protons), 2.79 (m, 2 H, $J_{4,5} = 5$ Hz, $J_{3,4} = 3.6$ Hz, C_4' protons).

Anal. Calcd for $C_{14}H_8O_2S_3$: C, 55.24; H, 2.65; S, 31.60. Found: C, 55.38; H, 2.58; S, 31.35.

Synthesis of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (6). A. 1,3-Dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]-dithiophene-4,8-dione (15).—A solution of the acid chloride **10**, prepared as previously described from thiophene-3,4-dicarboxylic acid (20.6 g, 0.125 mol) and thionyl chloride (30 ml), in dry 1,2-dichloroethane (75 ml) was added dropwise to a stirred suspension of aluminum chloride (34 g, 26 mmol) in dry 1,2-dichloroethane (200 ml), which was maintained at 4°. The mixture was allowed to stir at 4° for 10 min and then a solution of 2,5-dichlorothiophene (19.0 g, 0.125 mol) in 1,2-dichloroethane (50 ml) was slowly added. The reaction mixture was stirred at room temperature for 18 hr and then poured into ice and 2 *M* hydrochloric acid (200 ml). Chloroform (300 ml) was added and the mixture was shaken vigorously. The layers were separated and the aqueous phase was extracted with chloroform (150 ml). The combined organic portions were washed with saturated sodium bicarbonate solution and with water, then dried ($MgSO_4$) and evaporated. The impure diketone was dissolved in a minimum amount of chloroform and run onto a column (25 × 6 cm) of neutral alumina. Elution with chloroform provided an initial dark red fraction which was discarded, followed by a slightly yellow fraction, which contained 17.25 g (50%) of the diketone. Repeated recrystallization from chloroform–carbon tetrachloride afforded an analytical sample: mp 208–209°; uv max (95% C_2H_5OH) 261 mμ (ϵ 52,100) and 327 (ϵ 2840); ir (KBr) 1670 cm^{-1} (C=O); nmr (CF_3COOH) τ 1.39 (s).

Anal. Calcd for $C_{10}H_2Cl_2O_2S_2$: C, 41.53; H, 0.70; S, 22.18; Cl, 24.52. Found: C, 41.35; H, 0.71; S, 21.95; Cl, 24.62.

B. 4,8-Dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (6).—A stirred suspension of 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (**12**) (3.2 g, 11 mmol) and copper powder (2.55 g, 0.04 g-atom) in propionic acid (100 ml) was maintained at reflux for 60 hr.[6] The hot solution was quickly filtered and allowed to cool. The crude product was filtered, washed with water, and recrystallized from propionic acid to give 1.75 g (72%) of yellow-orange plates. An additional recrystallization from chloroform provided an analytical sample: mp 340°; uv max (C_2H_5OH) 259 mμ (ϵ 61,800); ir (KBr) 1655 cm^{-1} (ketone C=O); nmr (CF_3COOH) τ 1.38 (s).

Anal. Calcd for $C_{10}H_4O_2S_2$: C, 54.53; H, 1.83; S, 29.12. Found: C, 54.71; H, 1.73; S, 28.97.

Reduction of 4,9-Dihydronaphtho[2,3-*b*]thiophene-4,9-dione (1).—A solution of aluminum chloride (10.0 g, 75 mmol) in absolute ether (50 ml) was added to a stirred suspension of lithium hydride (2.84 g, 75 mmol) in absolute ether (30 ml). The mixture was stirred for 15 min and then 4,9-dihydronaphtho[2,3-*b*]-thiophene-4,9-dione (4.0 g, 18.7 mmol) was added portionwise by means of Gooch tubing. The gray ethereal suspension was maintained at reflux for 2 hr. Ethyl acetate (30 ml) was added dropwise in order to decompose the excess hydride reagent. The reaction mixture was poured into ice and 2 *M* hydrochloric acid. The layers were separated and the aqueous phase was extracted with 50 ml of ether. The combined ethereal solution was washed with saturated sodium bicarbonate solution and with water, then dried ($MgSO_4$) and concentrated. The dark, gummy solid was dissolved in hot benzene and chromatographed on neutral silica gel. Elution with benzene–hexane (1:1) followed by concentration provided 2.3 g of white, solid material. The white solid was chromatographically separated on neutral alumina using hexane as the eluent. Two fractions were obtained: 4,9-dihydronaphtho[2,3-*b*]thiophene (0.84 g, 25%) [mp 105.5–106.5° (lit.[13] 104–105°); nmr ($CDCl_3$) τ 2.81 (s, 4 H, benzene), 2.88 (d, 1 H, $J_{2,3} = 5$ Hz, C_2 proton), 3.10 (s, 1 H, $J_{2,3} = 5$ Hz, C_3 proton), 5.78–6.17 (m, 4 H, $-CH_2-$)], followed by 1.36 g (40%) of naphtho[2,3-*b*]-thiophene [mp 192.5–194° (lit.[14] 192–193°); uv max (95% C_2H_5OH) 230 mμ (ϵ 32,600), 251 (57,400), 256 (57,700), 315 (3690), 327 (4910), 335 (5400), 351 (6440); nmr (CCl_4) τ 1.68 (s, 1 H, C_9 proton), 1.76 (s, 1 H, C_4 proton), 2.00–2.28 (m, 2 H, C_5 and C_8 protons), 2.45–2.73 (m, 4 H, C_2, C_3, C_6, and C_7 protons)].

Reduction of 4,9-Dihydronaphtho[2,3-*c*]thiophene-4,9-dione (2).—A solution of aluminum chloride (5.0 g, 37 mmol) in absolute ether (50 ml) was added to a stirred suspension of lithium aluminum hydride (1.42 g, 37 mmol) in absolute ether (50 ml). The mixture was stirred for 10 min and 4,9-dihydronaphtho-[2,3-*c*]thiophene-4,9-dione (2.0 g, 9.3 mmol) was added portionwise by means of a Gooch tube. The gray ethereal suspension was maintained at reflux for 2 hr. Ethyl acetate (20 ml) was dropwise added in order to decompose the excess reagent. Work-up was carried out as described in the reduction of **1**. The sticky yellow solid thus obtained was dissolved in hot hexane and chromatographed on neutral alumina. Hexane was employed as the eluent. Evaporation of the solvent left 1.3 g (75%) of 4,9-dihydronaphtho[2,3-*c*]thiophene as a white solid. Two recrystallizations from ethanol–water afforded an analytical

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(13) W. Carruthers, *J. Chem. Soc.*, 4477 (1963).

(14) W. Carruthers, A. G. Douglas, and J. Hill, *ibid.*, 704 (1962).

sample: mp 74.5–75.5°; nmr (CCl_4) τ 2.92 (s, 4 H, benzene), 3.12 (s, 2 H, thiophene), 6.11 (s, 4 H, $-CH_2$).

Anal. Calcd for $C_{12}H_{10}S$: C, 77.37; H, 5.41; S, 17.22. Found: C, 77.53; H, 5.24; S, 17.35.

Reduction of 4,8-Dihydrobenzo[1,2-*b*:5,4-*b'*]dithiophene-4,8-dione (3).—A solution of aluminum chloride (10.0 g, 75 mmol) in absolute ether (50 ml) was added to a stirred suspension of lithium aluminum hydride (2.84 g, 75 mmol) in absolute ether (100 ml). The mixture was stirred for 5 min and then 4,8-dihydrobenzo-[1,2-*b*:5,4-*b'*]dithiophene-4,8-dione (4.0 g, 18.2 mmol) was added portionwise by means of Gooch tubing. The gray ethereal suspension was maintained at reflux for 2 hr, during which time all the quinone dissolved, forming a slightly green ethereal solution. Ethyl acetate (30 ml) was added dropwise in order to decompose the excess hydride reagent. The reaction mixture was poured into ice and 3 *M* sulfuric acid. The layers were separated and the aqueous phase was extracted with three 200-ml portions of ether. The combined ethereal solution was washed with saturated sodium bicarbonate solution and with water, then dried ($MgSO_4$) and allowed to stand for 18 hr. The solvent was removed to give 3.4 g (85% recovery) of starting quinone, identical melting point and mixture melting point with those of authentic material.

Reduction of 4,8-Dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (4).—A solution of aluminum chloride (5.0 g, 38 mmol) in absolute ether (100 ml) was added to a stirred suspension of lithium aluminum hydride (1.41 g, 38 mmol) in absolute ether (50 ml). The mixture was stirred for 5 min and the 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (2.0 g, 9.1 mmol) was added portionwise by means of Gooch tubing. The gray ethereal suspension was maintained at reflux for 18 hr. A yellow-green ethereal solution resulted after all the quinone had dissolved. The excess hydride was decomposed by dropwise addition of ethyl acetate (35 ml). Work-up was achieved as described in the reduction of **3**. The solvent was removed to give 1.8 g (90% recovery) of the starting quinone, identical melting point and mixture melting point with those of authentic material.

Reduction of 4,8-Dihydrobenzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (5).—A solution of aluminum chloride (10.0 g, 75 mmol) in absolute ether (55 ml) was briskly run into a stirred suspension of lithium aluminum hydride (2.83 g, 75 mmol) in absolute ether (140 ml). Stirring was continued for 5 min and then 4,8-dihydrobenzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (4 g, 18 mmol) was added portionwise by means of Gooch tubing. The reaction mixture was maintained at reflux for 18 hr and then cooled. Ethyl acetate (50 ml) was added dropwise in order to decompose the excess reagent. Work-up was carried out as described in the reduction of **1**. The yellow, gummy solid thus obtained was washed six times with hot hexane (50 ml). The hexane fractions were combined, concentrated to 50 ml, and run onto a chromatography column which was packed with neutral alumina. Elution with hexane (500 ml) followed by evaporation of the solvent provided 1.1 g (32%) of 4,8-dihydrobenzo[1,2-*b*:4,5-*c'*]dithiophene as white flakes. Sublimation at 70° (0.1 mm) followed by several recrystallizations from pentane afforded an analytical sample: mp 106–107°; nmr (CCl_4) τ 3.0 (d, 1 H, $J_{2,3}$ = 5 Hz, C_2 proton), 3.12 (s, 2 H, C_5 and C_7 protons), 3.28 (d, 1 H, $J_{2,3}$ = 5 Hz, C_3 proton), 5.92–6.25 (m, 4 H, $-CH_2-$).

Anal. Calcd for $C_{10}H_8S_2$: C, 62.46; H, 4.19; S, 33.35. Found: C, 62.38; H, 4.16; S, 33.16.

Reduction of 1,3-Dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (15).—A solution of aluminum chloride (18.5 g, 139 mmol) in absolute ether (75 ml) was briskly run into a stirred suspension of lithium aluminum hydride (5.30 g, 139 mmol) in absolute ether (50 ml). The reducing mixture was stirred for 10 min and then 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (10.0 g, 34.6 mmol) was added portionwise by means of Gooch tubing. The gray suspension was maintained at reflux for 2 hr. Sulfuric acid (3 *M*) was added dropwise in order to decompose the excess reagent. Work-up was carried out as described in the reduction of **1**. The impure product thus obtained was dissolved in hexane and chromatographed on neutral alumina. Hexane served as the eluent. Evaporation of the solvent left a white, crystalline solid, which was recrystallized from pentane to give 6.4 g (71%) of 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene (**25**) as white needles. An additional recrystallization from pentane provided an analytical sample: mp 100–101°; nmr (CCl_4) τ 3.02 (s, 2 H, thiophene), 6.24 (s, 4 H, $-CH_2-$).

Anal. Calcd for $C_{10}H_6Cl_2S_2$: C, 45.98; H, 2.32; Cl, 27.15; S, 24.55. Found: C, 46.05; H, 2.34; Cl, 26.99; S, 24.77.

4,8-Dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene (26).—A stirred suspension of 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene (**25**) (4.47 g, 17 mmol), *tert*-butyl alcohol (4 g, 54 mmol), and finely chopped lithium ribbon (0.7 g, 0.1 g-atom) was maintained at reflux under nitrogen for 2 hr. The mixture was allowed to cool and 95% ethanol was cautiously added in order to destroy the excess lithium metal. Water (100 ml) and ether (100 ml) were added and the mixture was shaken vigorously. The layers were separated and the aqueous phase was extracted with two 50-ml portions of ether. The combined ethereal solution was washed twice with water and dried ($MgSO_4$). The solution was evaporated and the residue was dissolved in hot hexane and chromatographed on neutral alumina using hexane as the eluent. The resulting solution was concentrated to 50 ml and allowed to cool. The white solid (1.75 g, 53%) thus obtained was recrystallized from hexane as long white needles: mp 143–144°; nmr (CCl_4) τ 3.12 (s, 4 H, thiophene), 6.12 (s, 4 H, $-CH_2-$).

Anal. Calcd for $C_{10}H_8S_2$: C, 62.46; H, 4.19; S, 33.35. Found: C, 62.55; H, 4.26; S, 33.55.

Registry No.—**1,** 4968-81-4; **2,** 33527-20-7; **3,** 33527-21-8; **4,** 32281-36-0; **5,** 33527-22-9; **6,** 33527-23-0; **8,** 18853-32-2; **9,** 4282-29-5; **10,** 33527-26-3; **13,** 33527-27-4; **15,** 33527-28-5; **25,** 33527-29-6; **26,** 33527-30-9; 4,9-dihydronaphtho[2,3-*b*]thiophene, 33608-30-9; naptho[2,3-*b*]thiophene, 269-77-9; 4,9-dihydronaphtho[2,3-*c*]thiophene, 33608-31-0; 4,8-dihydrobenzo[1,2-*b*:4,5-*c'*]dithiophene, 33527-31-0.

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