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A Simple Synthesis of Angular Anthrathiophenediones via Acetylenic Derivatives of Anthraquinone

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Abstract: Condensation of 2-alkynyl-1-chloro- and 1-alkynyl-2-chloroanthraquinones with Na_2S under mild conditions afforded anthra[1,2-*b*]thiophene-6,11-diones and anthra[2,1-*b*]thiophene-6,11-diones, respectively. A variety of angular anthrathiophenediones was synthesized by this method. The acetylenic precursors were prepared by a modified procedure of the Sonogashira reaction.

Key words: quinones, alkynes, cross-coupling, ring closure, sulfur

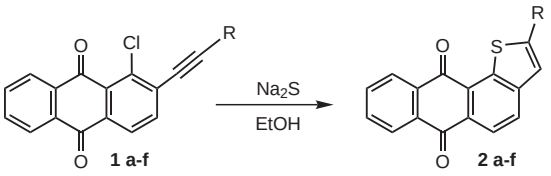
Heterocyclic derivatives of quinones are of importance as biologically active substances and technical materials. Many condensed quinoid compounds including nitrogen- and oxygen-containing rings are known. There is less information about such compounds with a sulfur-containing heterocycle.

At the same time, introduction of an S-heterocyclic fragment can determine the character of biological activity of a quinoid compound,[1] reduce side-effects of a drug preserving its basic action,[2] impart new properties to technical materials or improve their quality.[3,4] Also, the presence of a sulfur-containing substructure in compounds which do not belong to quinones often determine their pharmacological properties.[5,6] The above reasons prompted us to develop a method for the annulation of anthraquinone by a thiophene ring. To our knowledge, general methods for the synthesis of anthrathiophenediones have not yet been described.

Earlier, we reported the synthesis of condensed quinoid structures including pyrrole, furan, pyridine, pyridazine, pyrazole, pyran and diazepin rings, which was based on acetylenic derivatives of anthraquinone and naphthoquinone as key intermediates.[7–12] In this work we used the same approach for the synthesis of an anthrathiophenedione system. Recently, a method for the synthesis of substituted benzo[*b*]thiophenes by cyclization of *ortho*-(methylthio)alkynyl- and *ortho*-(benzylthio)alkynylbenzenes under the action of electrophilic agents was elaborated.[6,13] However, its extension to derivatives of anthraquinone is complicated by the limited availability of corresponding sulfides. Other methods for formation of benzothiophenes from acetylenic precursors are not sufficiently general.[14–17]

We supposed that *vic*-alkynylchloroanthraquinones could be appropriate acetylenic precursors of anthrathiophenediones. In anthraquinone, a chlorine atom irrespective of its position possesses a high nucleofugal lability.[18] In *vic*-alkynylchloroanthraquinones it is additionally activated by an acetylenic substituent and readily substituted by nucleophiles.[19] On the other hand, the triple bond in these compounds has an enhanced electrophilicity and is capable of interacting with a nucleophile as well.[7,19] One would expect that these particular properties of alkynylchloroanthraquinones would allow us to annulate the anthraquinone nucleus by a thiophene ring using Na_2S as the simplest heterocyclizing agent.

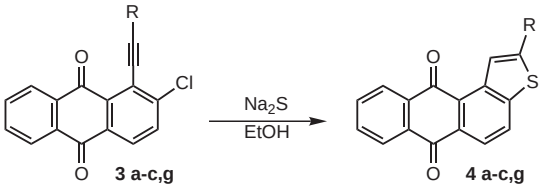
Indeed, we have found that acetylenes **1a–f** bearing a chlorine atom in position 1 react easily with an excess of Na_2S in 95% ethanol at 80 within 10–20 min to give anthra[1,2-*b*]thiophene-6,11-diones **2a–f** in 57–90% yields (Scheme 1).



a: R = H
b: R = Ph
c: R = CMe_2OH
d: R = CH(OH)(*i*-Pr)
e: R = CH_2OH
f: R =

Scheme 1

1-Alkynyl-2-chloroanthraquinones **3a–c,g** having the halogen atom in position 2, have also been shown to condense similarly to **1** with Na_2S and under the same condi-



a: R = H
b: R = Ph
c: R = CMe_2OH
g: R = Bu

Scheme 2

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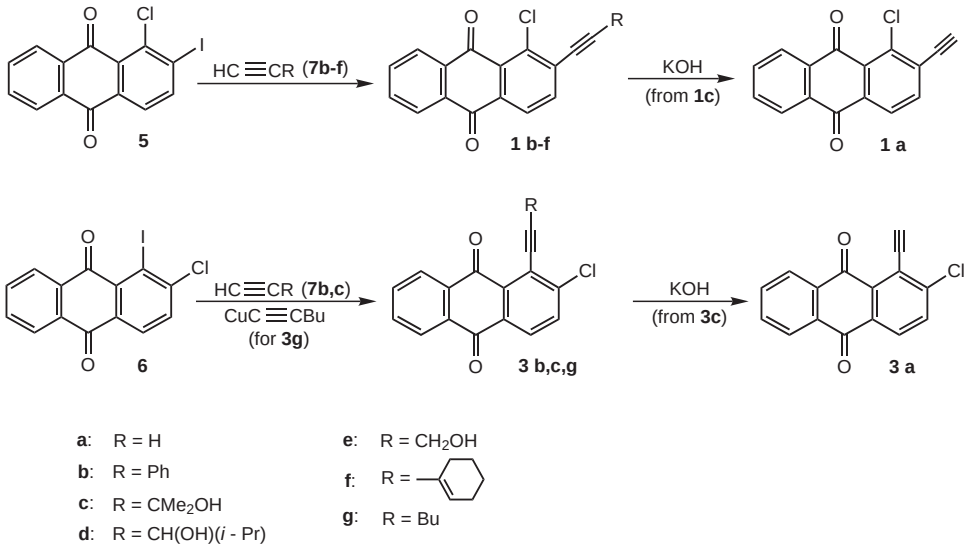

Scheme 3

tions. The yields of anthra[2,1-*b*]thiophene-6,11-diones **4a**–**c**,**g** are 64–97% (Scheme 2).

It is noteworthy, that in the ^{1}H NMR spectra of anthrathiophenediones **4** the signal of H in the β-position of the thiophene ring, which is brought together spatially with the carbonyl group, is shifted to lower field with respect to that of the similar H in spectra of compounds **2** ($\Delta\delta$ = 1.3–1.4).

The key acetylenes **1b**–**f** and **3b**,**c** were synthesized by cross-coupling of 1-chloro-2-iodo- (**5**) and 2-chloro-1-iodoanthraquinone (**6**) with corresponding terminal acetylenes **7b**–**f** in aqueous dioxane in the presence of Na_2CO_3, $Pd(PPh_3)_2Cl_2$ and CuI[9,20] (Scheme 3).

In our opinion, this modified procedure of the Sonogashira reaction is the best method for the introduction of acetylenic substituents into quinones. Acetylene **3g** was prepared by condensing the iodide **6** with cuprous butylacetylide in pyridine. Chloroethynylanthraquinones **1a** and **3a** were obtained from tertiary alcohols **1c** and **3c** by the Favorsky retro-reaction.[20]

Thus, the cyclocondensation of available *vic*-alkynylchloroanthraquinones with Na_2S is a convenient method for the synthesis of angular anthrathiophenediones.

^{1}H NMR spectra were recorded on a Bruker DPX-200 (200 MHz) spectrometer in $CDCl_3$ at 25 °C using TMS as an internal standard. IR spectra were determined with an UR-20 spectrometer in $CHCl_3$. Mps were measured on a Boetius micro mp hot stage apparatus and were uncorrected. The course of the reactions was monitored by TLC on Silufol UV 254 plates.

1-Chloro-2-iodoanthraquinone (5)

To a solution of 1-amino-2-iodoanthraquinone[21] (8.00 g, 22.9 mmol) in H_2SO_4 (96%; 56 mL) at 20 °C was slowly added a suspension of $NaNO_2$ (7.90 g, 114.5 mmol) in H_2SO_4 (34.5 mL) cooled to 10 °C. The mixture was stirred for 20 min at r.t., poured onto ice (250 g), and then urea (5.70 g, 95.0 mmol) in H_2O (32 mL) was carefully added. The obtained suspension of the diazonium salt was added stepwise into a solution of CuCl (2.32 g, 23.3 mmol) in concd HCl (80 mL) and stirred at 20 °C for 40 min and at 70 °C for 40 min. The resulting mixture was stored overnight at r.t. The product was filtered off, washed with H_2O, dried and chromatographed on SiO_2 in toluene.

Yield of chloroiodoanthraquinone **5**: 6.80 g (80.5%); mp 188–189 °C (benzene).[22]

2-Chloro-1-iodoanthraquinone (6)

1-Amino-2-chloroanthraquinone (7.75 g, 30.0 mmol) was diazotized by $NaNO_2$ (8.20 g, 120.0 mmol) in H_2SO_4 (96%; 50 mL) at 20 °C. The resulting solution was slowly added with agitation to a solution of KI (16.60 g, 100.0 mmol) in H_2O (400 mL) at 0–5 °C and then heated to 90–100 °C. After cooling, the formed precipitate was filtered off, washed with H_2O and dried. The product was purified by flash chromatography on Al_2O_3 in benzene.

Yield of chloroiodoanthraquinone **6**: 8.85 g (79.7%); mp 167–168 °C (benzene).[22]

***vic*-Alkynylchloroanthraquinones 1b–f, 3b,c; General Procedure**

To a stirring solution of *vic*-chloroiodoanthraquinone **5** or **6** (5 mmol) in dioxane (60 mL) at 60 °C under Ar were added successively terminal acetylene **7** (7.5 mmol), $Pd(PPh_3)_2Cl_2$ (40 mg, 0.06 mmol), CuI (20 mg, 0.10 mmol) and aq Na_2CO_3 (7.5 mmol; 30 mL) preheated to 70–80 °C. The mixture was refluxed with stirring for 5–20 min, cooled, diluted with $CHCl_3$ (200 mL), washed with H_2O (3 × 200 mL) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel; toluene or $CHCl_3$) and recrystallized (toluene–hexane mixture) to give **1** or **3**.

1-Chloro-2-phenylethynylanthraquinone (1b)

Yield: 85%, mp 193.5–194 °C.[19]

1-Chloro-2-(3-hydroxy-3-methylbutynyl)anthraquinone (1c)

Yield: 84%, mp 168–168.5 °C.

IR: 1690 (C=O), 2240 (C≡C), 3605 (OH) cm^{-1}.

^{1}H NMR: δ = 1.70 (s, 6 H, Me), 7.83 (d, 1 H, *J* = 8.1 Hz, H-3), 7.75–7.90 (m, 2 H, H-6,7), 8.26 (d, 1 H, *J* = 8.1 Hz, H-4), 8.20–8.35 (m, 2 H, H-5,8).

Anal.Calcd for $C_{19}H_{13}O_3Cl$: C, 70.27; H, 4.03; Cl, 10.91. Found: C, 70.40; H, 3.95; Cl, 10.78.

1-Chloro-2-(3-hydroxy-4-methylpentynyl)anthraquinone (1d)
Yield: 47%, mp 160–161.5 °C.

IR: 1690 (C=O), 2235 (C≡C), 3400 br, 3615 (OH) cm^{-1}.

^1H NMR: δ = 1.10 (d, 3 H, *J* = 6.7 Hz, Me), 1.13 (d, 3 H, *J* = 6.7 Hz, Me), 1.95–2.10 (m, 2 H, $CHMe_2$, OH), 4.45–4.55 (m, 1 H, CHO), 7.75–7.85 (m, 2 H, H-6,7), 7.83 (d, 1 H, *J* = 8.0 Hz, H-3), 8.25 (d, 1 H, *J* = 8.0 Hz, H-4), 8.25–8.35 (m, 2 H, H-5,8).

Anal. Calcd for $C_{20}H_{15}O_3Cl$: C, 70.90; H, 4.46; Cl, 10.46. Found: C, 70.78; H, 4.46; Cl, 10.40.

1-Chloro-2-(3-hydroxypropynyl)anthraquinone (1e)
Yield: 47%; mp 197.5–199 °C.

IR: 1690 (C=O), 2240 (C≡C), 3400 br, 3620 (OH) cm^{-1}.

^1H NMR: δ = 4.67 (s, 2 H, CH_2), 7.75–7.90 (m, 3 H, H-3,6,7), 8.20–8.30 (m, 3 H, H-4,5,8).

Anal. Calcd for $C_{17}H_9O_3Cl$: C, 68.82; H, 3.06; Cl, 11.95. Found: C, 68.66; H, 3.02; Cl, 11.79.

1-Chloro-2-(1-cyclohexenylethynyl)anthraquinone (1f)
Yield: 73%, mp 194–195 °C.

IR: 1690 (C=O), 2210 (C≡C) cm^{-1}.

^1H NMR: δ = 1.55–1.80 (m, 4 H, 4′, 5′-CH_2), 2.10–2.40 (m, 4 H, 3′, 6′-CH_2), 6.35–6.45 (m, 1 H, 2′-CH), 7.75–7.85 (m, 2 H, H-6,7), 7.99 (d, 1 H, *J* = 8.3 Hz, H-3), 8.20–8.30 (m, 2 H, H-5,8), 8.35 (d, 1 H, *J* = 8.3 Hz, H-4).

Anal. Calcd for $C_{22}H_{15}O_2Cl$: C, 76.19; H, 4.36; Cl, 10.22. Found: C, 75.94; H, 4.30; Cl, 9.86.

2-Chloro-1-phenylethynylanthraquinone (3b)
Yield: 78%, mp 196.5–197 °C.[19]

2-Chloro-1-(3-hydroxy-3-methylbutynyl)anthraquinone (3c)
Yield: 79%, mp 183.5–184.5 °C.

IR: 1690 (C=O), 2240 (C≡C), 3400 br, 3615 (OH) cm^{-1}.

^1H NMR: δ = 1.76 (s, 6 H, Me), 2.97 (br s, 1 H, OH), 7.70–7.80 (m, 2 H, H-6,7), 7.80 (d, 1 H, *J* = 8.5 Hz, H-3), 8.20–8.30 (m, 2 H, H-5,8), 8.20 (d, 1 H, *J* = 8.5 Hz, H-4).

Anal. Calcd for $C_{19}H_{13}O_3Cl$: C, 70.27; H, 4.03; Cl, 10.92. Found: C, 70.20; H, 4.04; Cl, 11.03.

2-Chloro-1-(hex-1-ynyl)anthraquinone (3g)
A mixture of 2-chloro-1-iodoanthraquinone (**6**) (0.74 g, 2 mmol) and cuprous butylacetylide (0.45 g, 3 mmol) in pyridine (50 mL) was stirred at 60 °C under Ar for 1 h, diluted with $CHCl_3$ (150 mL), washed with aq HCl (18%; 100 mL) and H_2O up to pH 7 and dried ($MgSO_4$). After evaporation of the solvent in vacuo the residue was chromatographed (silica gel; toluene). The product was crystallized (toluene–hexane mixture).

Yield of **3g**: 0.51 g (78%); mp 123–124 °C.

IR: 1680 (C=O), 2230 (C≡C) cm^{-1}.

^1H NMR: δ = 0.99 (t, 3 H, *J* = 7.0 Hz, Me), 1.50–1.85 (m, 4 H, β-, γ-CH_2), 2.68 (t, 2 H, *J* = 7.0 Hz, α-CH_2), 7.70–7.85 (m, 2 H, H-6,7), 7.81 (d, 1 H, *J* = 8.5 Hz, H-3), 8.17 (d, 1 H, *J* = 8.5 Hz, H-4), 8.20–8.35 (m, 2 H, H-5,8).

Anal. Calcd for $C_{20}H_{15}O_2Cl$: C, 74.42; H, 4.68; Cl, 10.98. Found: C, 74.43; H, 4.79; Cl, 10.91.

1-Chloro-2-ethynylanthraquinone (1a)
1-Chloro-2-(3-hydroxy-3-methylbutynyl)anthraquinone (**1c**) (1.45 g, 4.5 mmol) and powdered KOH (1.00 g, 17.9 mmol) in absolute benzene (100 mL) were refluxed with stirring for 45 min. The mixture was filtered, benzene was removed under reduced pressure. 1-Chloro-2-ethynylanthraquinone (**1a**) was purified by flash chromatography (alumina; toluene) and by crystallization (toluene–hexane mixture).

Yield: 0.90 g (73%); mp 211–212 °C.

IR: 1690 (C=O), 2130 (C≡C), 3310 (C≡CH) cm^{-1}.

^1H NMR: δ = 3.67 (s, 1 H, HC≡C), 7.75–7.90 (m, 2 H, H-6,7), 7.91 (d, 1 H, *J* = 8.1 Hz, H-3), 8.20–8.35 (m, 2 H, H-5,8), 8.28 (d, 1 H, *J* = 8.1 Hz, H-4).

Anal. Calcd for $C_{16}H_7O_2Cl$: C, 72.06; H, 2.65; Cl, 13.29. Found: C, 71.98; H, 2.84; Cl, 13.09.

2-Chloro-1-ethynylanthraquinone (3a)
Compound **3a** was prepared under the same conditions as 1-chloro-2-ethynylanthraquinone (**1a**), but from 2-chloro-1-(3-hydroxy-3-methylbutynyl)anthraquinone (**3c**).

Yield: 31%; mp 244–245 °C.

IR: 1690 (C=O), 2120 (C≡C), 3320 (C≡CH) cm^{-1}.

^1H NMR: δ = 3.97 (s, 1 H, HC≡C), 7.70–7.90 (m, 2 H, H-6,7), 7.87 (d, 1 H, *J* = 8.4 Hz, H-3), 8.25–8.45 (m, 2 H, H-5,8), 8.27 (d, 1 H, *J* = 8.4 Hz, H-4).

Anal. Calcd for $C_{16}H_7O_2Cl$: C, 72.06; H, 2.65; Cl, 13.29. Found: C, 72.18; H, 2.59; Cl, 13.26.

Angular Anthrathiophene-6,11-diones 2a–f and 4a–c,g; General Procedure
To a stirring suspension of anhyd Na_2S (3.5 mmol) in 95% EtOH (35 mL) at 60–70 °C was added *vic*-alkynylchloroanthraquinone **1** or **3** (1.0 mmol). The reaction mixture was refluxed and stirred for 10–20 min and poured into H_2O (300 mL). The product was extracted with $CHCl_3$ (3 × 100 mL), the combined organic extracts were washed with H_2O (2 × 100 mL), dried ($MgSO_4$) and evaporated in vacuo. The resulting residue was purified by flash chromatography (silica gel or alumina; toluene or $CHCl_3$) and crystallized (toluene–hexane mixture).

Anthra[1,2-*b*]thiophene-6,11-dione (2a)
Yield 67%; mp 216–217 °C.

^1H NMR: δ = 7.48 (d, 1 H, *J* = 5.5 Hz, H-3), 7.90 (d, 1 H, *J* = 5.5 Hz, H-2), 7.75–7.85 (m, 2 H, H-8,9), 8.18 [d, 1 H, *J* = 8.2 Hz, H-4(5)], 8.30–8.35 [m, 3 H, H-5(4),7,10].

Anal. Calcd for $C_{16}H_8O_2S$: C, 72.71; H, 3.05; S, 12.13. Found: C, 72.52; H, 2.94; S, 11.86.

2-Phenylanthra[1,2-*b*]thiophene-6,11-dione (2b)
Yield: 90%; mp 287–288 °C.

^1H NMR: δ = 7.40–7.55 (m, 3 H, 3 HPh), 7.65 (s, 1 H, H-3), 7.80–7.90 (m, 4 H, 2 HPh, H-8,9), 8.12 [d, 1 H, *J* = 8.2 Hz, H-4(5)], 8.30–8.40 [m, 3 H, H-5(4),7,10].

Anal. Calcd for $C_{22}H_{12}O_2S$: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.60; H, 3.69; S, 9.40.

2-(1-Hydroxy-1-methylethyl)anthra[1,2-*b*]thiophene-6,11-dione (2c)
Yield 83%; mp 184–184.5 °C.

^1H NMR: δ = 1.78 (s, 6 H, Me), 2.30 (br s, 1 H, OH), 7.28 (s, 1 H, H-3), 7.75–7.85 (m, 2 H, H-8,9), 8.01 [d, 1 H, *J* = 8.2 Hz, H-4(5)], 8.20–8.35 [m, 3 H, H-5(4),7,10].

Anal. Calcd for $C_{19}H_{14}O_3S$: C, 70.79; H, 4.38; S, 9.95. Found: C, 70.90; H, 4.54; S, 9.91.

2-(1-Hydroxy-2-methylpropyl)anthra[1,2-*b*]thiophene-6,11-dione (2d)
Yield: 72%; mp 162–163 °C.

^{1}H NMR: δ = 0.99 (d, 3 H, *J* = 6.7 Hz, Me), 1.07 (d, 3 H, *J* = 6.7 Hz, Me), 2.10–2.25 (m, 1 H, $CHMe_2$), 2.30 (br s, 1 H, OH), 4.82 (d, 1 H, *J* = 4.7 Hz, CHO), 7.28 (s, 1 H, H-3), 7.75–7.85 (m, 2 H, H-8,9), 8.03 [d, 1 H, *J* = 8.2 Hz, H-4(5)], 8.25–8.35 [m, 3 H, H-5(4),7,10].

Anal. Calcd for $C_{20}H_{16}O_3S$: C, 71.41; H, 4.79; S, 9.53. Found: C, 71.27; H, 4.71; S, 9.38.

2-Hydroxymethylanthra[1,2-*b*]thiophene-6,11-dione (2e)
Yield: 87%; mp 212–213 °C.

^{1}H NMR: δ = 2.23 (br s, 1 H, OH), 5.00 (s, 2 H, CH_2), 7.33 (s, 1 H, H-3), 7.75–7.85 (m, 2 H, H-8,9), 8.05 [d, 1 H, *J* = 8.2 Hz, H-4(5)], 8.25–8.35 [m, 3 H, H-5(4),7,10].

Anal. Calcd for $C_{17}H_{10}O_3S$: C, 69.37; H, 3.42; S, 10.89. Found: C, 69.26; H, 3.65; S, 10.81.

2-(1-Cyclohexenyl)anthra[1,2-*b*]thiophene-6,11-dione (2f)
Yield: 76%; mp 207–208 °C.

^{1}H NMR: δ = 1.60–1.90 (m, 4 H, 4′, 5′-CH_2), 2.10–2.60 (m, 4 H, 3′, 6′-CH_2), 6.55–6.65 (m, 1 H, 2′-CH), 7.19 (s, 1 H, H-3), 7.75–7.85 (m, 2 H, H-8,9), 7.98 [d, 1 H, *J* = 8.2 Hz, H-4(5)], 8.24 [d, 1 H, *J* = 8.2 Hz, H-5(4)], 8.20–8.35 (m, 3 H, H-7,10).

Anal. Calcd for $C_{22}H_{16}O_2S$: C, 76.72; H, 4.68; S, 9.31. Found: C, 76.47; H, 4.63; S, 9.35.

Anthra[2,1-*b*]thiophene-6,11-dione (4a)
Yield: 66%; mp 182.5–183.5 °C.

^{1}H NMR: δ = 7.75–7.85 (m, 2 H, H-8,9), 7.81 [d, 1 H, *J* = 5.5 Hz, H-2(1)], 8.20–8.35 (m, 4 H, H-4,5,7,10), 8.81 [d, 1 H, *J* = 5.5 Hz, H-1(2)].

Anal. Calcd for $C_{16}H_8O_2S$: C, 72.71; H, 3.05; S, 12.13. Found: C, 72.54; H, 3.01; S, 11.93.

2-Phenylanthra[2,1-*b*]thiophene-6,11-dione (4b)
Yield: 84%; mp 246.5–247.5 °C.

^{1}H NMR: δ = 7.40–7.55 (m, 3 H, 3 HPh), 7.75–7.90 (m, 4 H, 2 HPh, H-8,9), 8.19 [d, 1 H, *J* = 8.4 Hz, H-4(5)], 8.25–8.35 [m, 3 H, H-5(4),7,10], 9.08 (s, 1 H, H-1).

Anal. Calcd for $C_{22}H_{12}O_2S$: C, 77.63; H, 3.55; S, 9.42. Found: C, 77.67; H, 3.61; S, 9.50.

2-(1-Hydroxy-1-methylethyl)anthra[2,1-*b*]thiophene-6,11-dione (4c)
Yield: 97%; mp 171–172 °C.

^{1}H NMR: δ = 1.77 (s, 6 H, Me), 2.32 (br s, 1 H, OH), 7.75–7.85 (m, 2 H, H-8,9), 8.14 [d, 1 H, *J* = 8.4 Hz, H-4(5)], 8.24 [d, 1 H, *J* = 8.4 Hz, H-5(4)], 8.25–8.30 (m, 2 H, H-7,10), 8.59 (s, 1 H, H-1).

Anal. Calcd for $C_{19}H_{14}O_3S$: C, 70.79; H, 4.38; S, 9.95. Found: C, 70.80; H, 4.20; S, 9.81.

2-Butylanthra[2,1-*b*]thiophene-6,11-dione (4g)
Yield: 64%; mp 83.5–84.5 °C.

^{1}H NMR: δ = 0.98 (t, 3 H, *J* = 7.4 Hz, Me), 1.46 (sext, 2 H, *J* = 7.4 Hz, γ-CH_2), 1.81 (quint, 2 H, *J* = 7.4 Hz, β-CH_2), 3.02 (t, 2 H, *J* = 7.4 Hz, α-CH_2), 7.75–7.80 (m, 2 H, H-8,9), 8.13 [d, 1 H, *J* = 8.4 Hz, H-4(5)], 8.23 [d, 1 H, *J* = 8.4 Hz, H-5(4)], 8.25–8.30 (m, 2 H, H-7,10), 8.50 (s, 1 H, H-1).

Anal. Calcd for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03; S, 10.01. Found: C, 74.78; H, 5.27; S, 10.00.

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