

Synthesis of Dibenzo[*b,i*]thianthrene-5,7,12,14-tetrone

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The reaction of 2,3-dihalogeno-1,4-naphthoquinone with dithiooxamide gave dibenzo[*b,i*]thianthrene-5,7,12,14-tetrone in high yield but not 2,2'-bis(naphtho[2,3-*d*]thiazole-4,9-dione) which was previously reported. A similar reaction of 3,4-dichloro-*N*-phenylmaleimide with dithiooxamide also gave the corresponding sulfur heterocycles but not the reported bithiazole.

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Heterocyclic dye chromophores are currently of interest as functional materials for electronic, opto-electronic and photonic devices [1]. Tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF) or bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have been synthesized as an electron donating molecule and their intermolecular charge-transfer (CT) complexes have been synthesized as synthetic metals [2], organic superconductors [3] and so on. We recently found that 1,4,5,8-tetraamino-9,10-anthraquinone is a new electron donating molecule for CT complexes with high electric conductivity [4]. We intended to synthesize the reported 2,2'-bis(naphtho[2,3-*d*]thiazole-4,9-dione) (**4**) as a component for CT complex by the reported reaction of 2,3-dichloro-1,4-naphthoquinone (**1a**) with dithiooxamide (**2a**) [5]. However the reaction product was not **4** but dibenzo[*b,i*]thianthrene-5,7,12,14-tetrone (**3**), which was previously synthesized by the reaction of 2,3-dichloro-1,4-naphthoquinone with 2,3-dimercapto-1,4-naphthoquinone disodium salt [6]. We carefully followed the reaction conditions reported in the original paper [7] but none of **4** was obtained, but **3** was obtained in high yield. The reaction is shown in Scheme 1 and the results are summarized in Table 1 comparing the reaction product obtained in each reaction. The mp, uv and ir spectra of the product from Entry A and B are almost the same but the values of elemental analysis are different from each other, and the nitrogen content was not observed for **3** (Entry A). The reported analytical CHN values for the product from

Entry B and C are quite different from those of **3**. The ms of **3** support the structure and pmr spectra also confirm the symmetric structure of **3**, but not **4** which will show four different types of ring protons.

The reaction of 2,3-dihalogeno-1,4-naphthoquinones **1** with **2a** was studied in detail and the results are summarized in Table 2. The yield of **3** was not affected so much by the reaction temperature (Runs 1-3), time (Run 4), argon gas atmosphere (Run 5) and the addition of water (Run 6). 2,3-Dibromo-1,4-naphthoquinone (**1b**) also gave **3** in 74% yield (Run 7). None of **4** could be detected from each of the reaction products. The reaction of **1a** with thiourea (**2b**) also gave **3** in 39% yield (Run 8). The reaction is initiated by the nucleophilic attack of sulfur to 2- or 3-position of **1** as reported previously in the reactions of  $\alpha$ -halogenated compounds with thioacetamide [8], which is different from the reported mechanism [7]. The structure of **3** can also be confirmed by oxidation and reduction reactions. The oxidation of **3** with hydrogen peroxide gave dinaphtho[2,3-*b*:2',3'-*d*]thiophene-5,7,12,13-tetrone (**5**) in 87% yield. The reduction of **3** with tin(II) chloride gave 5,7,12,14-tetrahydrodibenzo[*b,i*]thianthrene (**6**) in 70% yield (Scheme 2).

On the other hand, the reaction of 3,4-dichloro-*N*-phenylmaleimide (**7**) with **2a** gave the corresponding sulfur heterocycle, 2,6-diphenyl-2,3,6,7-tetrahydro-1*H*,5*H*-[1,4]dithiino[2,3-*b*:6,5-*b'*]dipyrrole (**8**), in 80% yield, but

Scheme 1

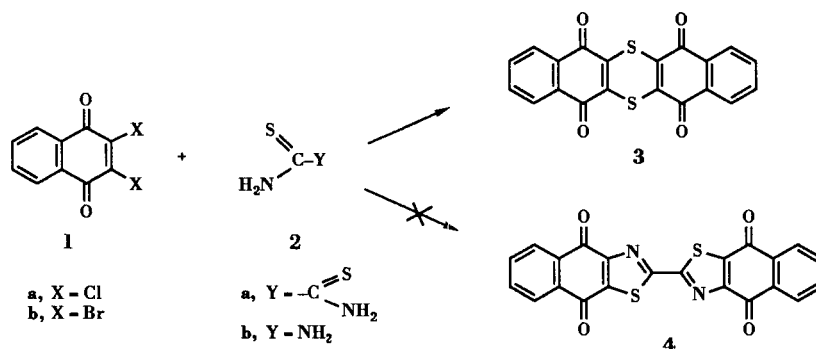


Table 1  
Reaction Product from 2,3-Dichloro-1,4-naphthoquinone and Dithiooxamide

Entry [a]	Product	Mp (°C)	Yield (%)	Ms (m/z)	UV/Vis [b] (DMF) (nm)	IR (KBr) (cm <sup>-1</sup> )	Pmr (CDCl <sub>3</sub> ) (ppm)	C (%)	Calcd. (Found)		S (%)
									H (%)	N (%)	
A	<b>3</b>	308-310	90	376	480	1650, 1580, 1530	7.76 (dd) [c] 8.09 (dd)	63.82 (63.89)	2.14 (1.86)	— [d]	17.04 (16.10)
B	<b>4</b>	>300	57	—	500 480	1650, 1580, 1530	—	61.68 (62.05)	1.88 (2.11)	6.54 [e] (6.80)	—
C	<b>4</b>	304-306	86	—	—	1663, 1645, 1605	—	66.65 (67.24)	2.02 (2.10)	7.07 [f] (7.25)	—

[a] A: This work; B: cited from literature [5]; C: cited from literature [7]. [b] Measured in dimethylformamide. [c] J = 3 and 6 Hz. [d] calcd. for C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>S<sub>2</sub> (376). [e] Calcd. for C<sub>22</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>. [f] Calcd. for C<sub>22</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> in the literature [7] but the formula is wrong.

Table 2  
Synthesis of Dibenzo[*b,i*]thianthrene-5,7,12,14-tetrone (**3**) [a]

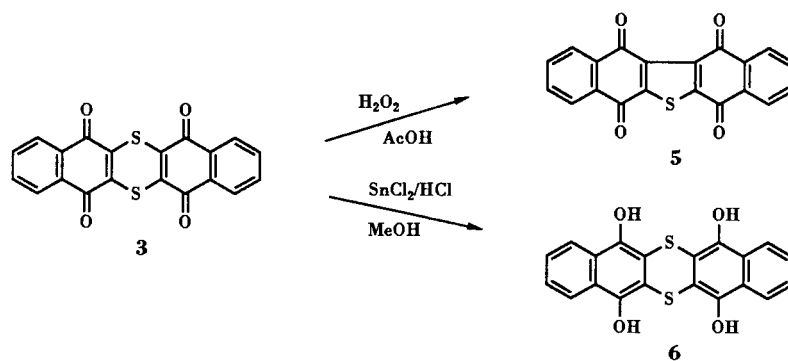
Run	Reactant	Reagent	Molar ratio	Time (hours)	Temperature (°C)	<b>3</b> (%)
1	<b>1a</b>	<b>2a</b>	2:1	10	50	90
2	<b>1a</b>	<b>2a</b>	2:1	4	20	80
3	<b>1a</b>	<b>2a</b>	2:1	4	10	83
4	<b>1a</b>	<b>2a</b>	2:1	2 min	20	80
5	<b>1a</b>	<b>2a</b>	2:1	10 [b]	50	79
6	<b>1a</b>	<b>2a</b> [c]	2:1	10	50	72
7	<b>1b</b>	<b>2a</b>	2:1	10	50	74
8	<b>1a</b>	<b>2b</b>	1:1	5	50	39

[a] The mixtures of **1** (8.8 mmoles) and **2** (4.5 mmoles) in DMF (30 ml) were stirred in the presence of triethylamine (1.8 g). [b] Reaction was carried out under purge of argon gas. [c] Water (10 ml) was added to the reaction mixture.

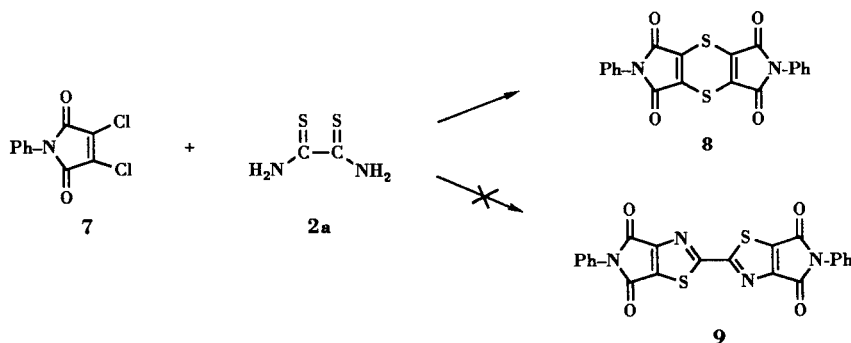
not the reported bisthiazole **9** [5]. The ms and elemental analysis of **8** confirm the structure but **8** is quite different from **9** in mp, ir, uv and analytical values reported in the literature [5] (Scheme 3).

Dithiooxamide (**2a**) is a reagent grade (Tokyo Chemicals) and the structure was confirmed by ms (M<sup>+</sup>, 120). At present, the reason is not known why two pairs of different products, **3/4** and **8/9**, were obtained from each of the same reaction procedures.

Scheme 2



Scheme 3



## EXPERIMENTAL

The pmr spectra were taken on a JEOL JNM-GX270 (270 MHz) spectrometer. The ir spectra were recorded with a Shimadzu IR-420 instrument. The ms spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 70 eV. The visible spectra were measured on a Shimadzu UV-265FS spectrophotometer. Melting points were determined on a Yanaco MP-500D apparatus without correction. Elemental analysis was conducted with a Yanaco CHN MT-3 recorder and sulfur analyses were carried out under the supervision of Mr. H. Nakagawa of Osaka Chemical Analysis Co., Ltd.

2,3-Dichloro-1,4-naphthoquinone (**1a**), dithiooxamide (**2a**) and thiourea (**2b**) are reagent grade and were used without further purification. 2,3-Dibromo-1,4-naphthoquinone (**1b**) and 3,4-dichloro-*N*-phenylmaleimide (**7**) were synthesized and identified by the usual methods.

Dibenzo[*b,i*]thianthrene-5,7,12,14-tetrone (**3**).

2,3-Dichloro-1,4-naphthoquinone (**1a**, 8.8 mmoles) and dithiooxamide (**2a**, 4.4 mmoles) were dissolved in dimethylformamide (30 ml) and triethylamine (1.8 g) was added with stirring and the reaction mixture was heated at 50° for 10 hours (Run 1). The purplish-black product precipitated out during the reaction. After cooling, the product was collected by filtration, washed with water and then ethanol, and recrystallized from dimethylformamide to give **3** (yield 90%).

Dinaphtho[2,3-*b:2',3'-d'*]thiophene-5,7,12,13-tetrone (**5**).

Compound **3** (4 mmoles) was dissolved in acetic acid (50 ml) and 30% aqueous hydrogen peroxide (16 ml) was added and heated for 3 hours under reflux. The orange product precipitated out during the reaction. After cooling, the product was collected by filtration, washed with water and recrystallized from chloroform to give **5**, yield 87%, mp 278-280°; pmr (deuteriochloroform): 7.84 (m, 4H), 8.25 (dd, 2H), 8.35 (dd, 2H); ms: (m/z) 344 (M<sup>+</sup>, 100%), 316 (M<sup>+</sup>-28, 56%); uv/vis (chloroform): λ / max 286 (40000) and 341 nm (ε 8800).

*Anal.* Calcd. for C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>S: C, 69.76; H, 2.34; S, 9.31. Found: C, 69.58; H, 2.30; S, 9.3.

5,7,12,14-Tetrahydroxydibenzo[*b,i*]thianthrene (**6**).

Compound **3** (2.7 mmoles) and tin(II) chloride (2.40 g) was

added to dry-methanol (30 ml) and dry-hydrogen chloride was passed into solution under reflux for 4 hours. After cooling, the reaction mixture was poured into water (300 ml) and the precipitate was collected by filtration, washed with chloroform to give **6**, yield 70%, mp 309-311°; pmr (acetone-d<sub>6</sub>): 8.22 (dd, 4H), 7.55 (dd, 4H), 2.85 (s, 4H); ms: (m/z) 380 (M<sup>+</sup>, 80%), 347 (100%); uv/vis (dimethylformamide): λ / max 359 and 346 nm. Compound **6** was spontaneously oxidized by air and the ε values could not be determined.

*Anal.* Calcd. for C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>S<sub>2</sub>: C, 63.14; H, 3.18; S, 16.89. Found: C, 62.67; H, 2.94; S, 15.9 [9].

2,6-Diphenyl-2,3,6,7-tetrahydro-1*H*,5*H*-[1,4]dithiino[2,3-*b:6,5-b'*]dipyrrole (**8**).

3,4-Dichloro-*N*-phenylmaleimide (**1a**, 8.8 mmoles) and dithiooxamide (**2a**, 4.4 mmoles) was dissolved in dimethylformamide (30 ml) and triethylamine (1.8 g) was added under stirring and the reaction mixture was heated at 50° for 10 hours. The product precipitated out during the reaction. After cooling, the product was collected by filtration, washed with water to give **8**, yield 80%, mp > 330° dec; ms: (m/z) 406 (M<sup>+</sup>, 100%); uv/vis (dimethylformamide): λ / max 355 (2900) and 467 nm (ε 2000).

*Anal.* Calcd. for C<sub>20</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 59.10; H, 2.48; N, 6.89, S, 15.78. Found: C, 58.89; H, 2.52; N, 6.80; S, 15.8.

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- [9] A more satisfactory elemental analysis for sulfur was not obtainable.