Synthesis of 7,10-Disubstituted Benzo[*b*]phenazine-6,11-quinones

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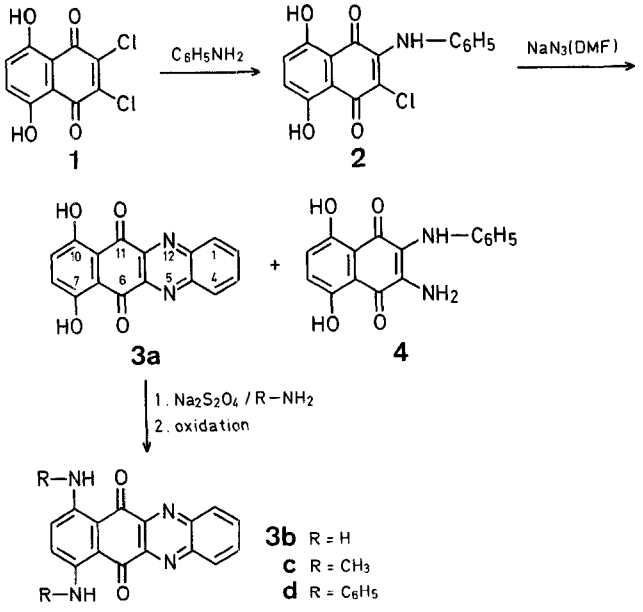
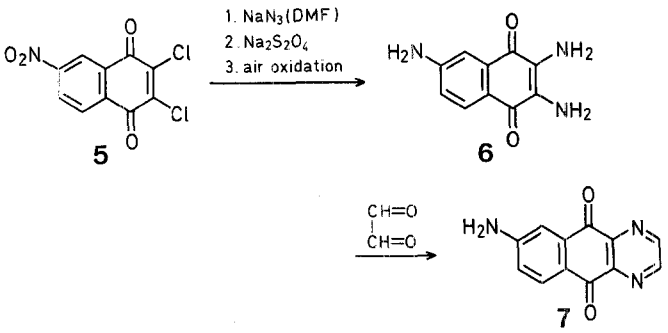
Anthraquinone dyes are of great value as synthetic coloring matter. We have attempted to prepare aza analogues of anthraquinone for use as dyes[1,2]. A bathochromic displacement of the absorption in the visible range has been observed when the benzene moiety of 1-amino-9,10-anthraquinone is replaced by a pyrazine ring[1]. 6-Amino-1,4-diaza-9,10-anthraquinones and 7,10-disubstituted benzo[*b*]phenazine-6,11-quinones are key compounds, corresponding to 2-amino- and 1,4-disubstituted 9,10-anthraquinones, respectively, which can efficiently be converted into other useful dyes. 1,4-Diaza-9,10-anthraquinones have been generally prepared by reaction of appropriate 2,3-diamino-1,4-naphthoquinones with glyoxal or 1,2-quinones[3]. However, the title compound **3** could not be obtained by the same reaction or by reaction of **1** with *o*-phenylenediamine.

In this paper, we report the preparation of new 7,10-disubstituted derivatives of benzo[*b*]phenazine-6,11-quinones **3** and 6-amino-1,4-diazaanthraquinone **(7)** from easily available substrates by an adaption of standard procedures[4].



2-Anilino-3-chloro-5,8-dihydroxy-1,4-naphthoquinone **(2)** is obtained in a simple manner and in good yield by the reaction of **1** with aniline. The reaction of **2** with sodium azide gives 7,10-dihydroxy-benzo[*b*]phenazine-6,11-quinone **(3a)** and 2-anilino-3-amino-5,8-dihydroxy-1,4-naphthoquinone **(4)**. Reduction of **3a** with sodium dithionite gives a leuco-compound which is reacted without purification with aqueous ammonia, methylamine, or aniline to give after subsequent oxidation the 7,10-disubstituted amino derivatives **3b–d**. Thus, the described method provides a useful route to the difficultly accessible 7,10-diamino derivatives of **3**.

The crude diazide from 6-nitro-2,3-dichloro-1,4-naphthoquinone **(5)** when subjected to reduction with sodium dithionite followed by air oxidation yields 2,3,6-triamino-1,4-naphthoquinone **(6)**. Reaction of **6** with glyoxal gives 6-amino-1,4-diazaanthraquinone **(7)** in 72%.



2-Anilino-3-chloro-5,8-dihydroxy-1,4-naphthoquinone (2):
To a solution of 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone[3] (**1**; 2.0 g) in ethanol (100 ml), a solution of aniline (1.4 g) in ethanol (4 ml) is added. The mixture is refluxed for 3 h, then cooled, and filtered by suction. The product is recrystallized from ethanol; yield: 1.7 g (70%); m.p. 205–207 °C.

$C_{16}H_{10}ClNO_4$	calc.	C 60.87	H 3.19	N 4.44
(315.7)	found	60.21	3.11	4.36

M.S.: $m/e = 317$ (39%); 315 (M^+, 100%); 297 (13%); 281 (36%); 280 (57%).

I.R. (KBr): $\nu = 3400, 3200, 1640, 1610\ cm^{-1}$.

7,10-Dihydroxy-benzo[*b*]phenazine-6,11-quinone (3a):
To a solution of **2** (2.3 g) in dimethylformamide (18 ml) sodium azide (0.71 g) dissolved in water (2.1 ml) is added. The mixture is heated for 3 h at 80 °C, then cooled, filtered, and washed with ethanol. The residue is extracted with hot benzene (6 × 100 ml). The extracts are evaporated and the residue is chromatographed on silica gel using benzene/acetone (9 : 1) as an eluent to give **3a** and **4**. These compounds are recrystallized from benzene.

Compound **3a**; yield: 0.61 g (29%); m.p. > 300 °C.

$C_{16}H_8N_2O_4$	calc.	C 65.75	H 2.76	N 9.58
(292.3)	found	65.71	2.77	9.20

M.S.: $m/e = 292$ (M^+, 100%); 264 (14%).

I.R. (KBr): $\nu = 3400, 1630\ cm^{-1}$.

U.V. (benzene): $\lambda_{max} = 465$ (log $\varepsilon = 3.92$); 482 nm (3.95).

Compound **4**; yield: 0.9 g (42%); m.p. 214–215 °C.

$C_{16}H_{12}N_2O_4$	calc.	C 64.86	H 4.08	N 9.45
(296.3)	found	64.98	3.98	9.67

M.S.: $m/e = 296$ (M^+, 100%); 295 (53%).

I.R. (KBr): $\nu = 3480, 3370, 1640, 1625\ cm^{-1}$.

7,10-Bis[methylamino]-benzo[*b*]phenazine-6,11-quinone (3c):
Compound **3a** (0.30 g) and sodium dithionite (0.21 g) are added to 40% aqueous methylamine (10 ml). The mixture is stirred for 18 h at 90 °C in a sealed tube (100 ml), then cooled, and oxidized by bubbling air. The mixture is poured into ice/water (50 ml), acidified with dilute hydrochloric acid (15 ml), and filtered by suction. The product is washed with water and recrystallized from toluene to give **3c**; yield: 0.19 g (58%); m.p. 273–274 °C.

$C_{18}H_{14}N_4O_2$	calc.	C 67.92	H 4.43	N 17.60
(318.3)	found	68.25	4.53	17.05

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M.S.: $m/e = 318$ (M^+, 100%); 301 (73%); 290 (21%); 273 (28%).

I.R. (KBr): $\nu = 3400$, 1640 cm^{-1}.

U.V. (benzene): $\lambda_{max} = 600$ ($\log\varepsilon = 4.12$); 646 nm (4.14).

7,10-Diamino-benzo[*b*]phenazine-6,11-quinone (3b):
The leuco-compound of **3a**, which is obtained *in situ* by reduction of **3a** (0.37 g) with sodium dithionite (0.7 g), and 28% aqueous ammonia (10 ml), is stirred in a sealed tube (100 ml) for 15 h at 100 °C. After cooling and filtration, the residue is dissolved in nitrobenzene (5 ml) including piperidine (5 drops) and then the mixture is heated at 150 °C for 1.5 h. After cooling, the mixture is filtered and washed with ligroin. The residue is chromatographed on silica gel using chlorobenzene/acetone (10:1) as eluent to give **3b**; yield: 0.1 g (27%); m.p. > 300 °C.

$C_{16}H_{10}N_4O_2$	calc.	C 66.20	H 3.47	N 19.30
(290.3)	found	65.81	3.34	18.86

M.S.: $m/e = 290$ (M^+, 100%); 255 (12%); 240 (12%).

I.R. (KBr): $\nu = 3360$, 3230, 1640 cm^{-1}.

U.V. (chlorobenzene): $\lambda_{max} = 540$ ($\log\varepsilon = 3.95$); 574 nm (3.95).

7,10-Bis[phenylamino]-benzo[*b*]phenazine-6,11-quinone (3d):
The leuco-compound of **3a** (0.7 g), boric acid (0.24 g), and aniline (10 ml) are treated under same conditions as described for **3b**. After cooling, the mixture is filtered and washed with methanol. The product is recrystallized from toluene to give **3d**; yield: 0.61 g (58%); m.p. > 300 °C.

$C_{28}H_{18}N_4O_2$	calc.	C 76.00	H 4.10	N 12.66
(442.5)	found	76.18	3.84	12.49

M.S.: $m/e = 442$ (M^+).

I.R. (KBr): $\nu = 3400$, 1620 cm^{-1}.

U.V. (toluene): $\lambda_{max} = 605$ ($\log\varepsilon = 4.18$); 641 nm (4.20).

6-Amino-1,4-diazaanthraquinone (7):
6-Nitro-2,3-dichloro-1,4-naphthoquinone[6] (**5**; m.p. 161–163.5 °C) is obtained as by-product in the nitration of 2,3-dichloro-1,4-naphthoquinone with nitric acid. A diazide compound of **5** is prepared from **5** (15 g) and sodium azide (8.0 g) under the same conditions as for 5-nitro-2,3-diazido-1,4-naphthoquinone[7]. Then, without purification, it is reduced with sodium dithionite (38 g) in water (200 ml) under nitrogen at 70 °C for 3 h. After oxidation by bubbling air for 1 h and filtration, the product is recrystallized from nitromethane to give 2,3,6-triamino-1,4-naphthoquinone **(6)**; yield: 1.7 g (15%); m.p. 231–234 °C.

$C_{10}H_9N_3O_2$	calc.	C 59.11	H 4.46	N 20.68
(203.2)	found	58.84	4.33	20.46

M.S.: $m/e = 203$ (M^+, 100%); 176 (28%); 175 (13%).

I.R. (KBr): $\nu = 3350$, 3200, 1640 cm^{-1}.

To a suspension of **6** (1.41 g) in water (42 ml), 40% aqueous glyoxal (2.0 g) is added dropwise at 40 °C. The mixture is heated for 4 h at 90 °C, then cooled and filtered. The product is recrystallized from dimethylformamide to give **7**; yield: 1.13 g (72%); m.p. > 300 °C.

$C_{12}H_7N_3O_2$	calc.	C 64.00	H 3.39	N 18.50
(225.2)	found	64.45	3.13	18.66

M.S.: $m/e = 225$ (M^+, 100%); 224 (15%); 197 (31%).

I.R. (KBr): $\nu = 3320$, 3230, 1690 cm^{-1}.

U.V. (ethanol): $\lambda_{max} = 470$ nm ($\log\varepsilon = 3.62$).

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