A Novel Route for the Synthesis of *endo*-Polynuclear Heterocycles

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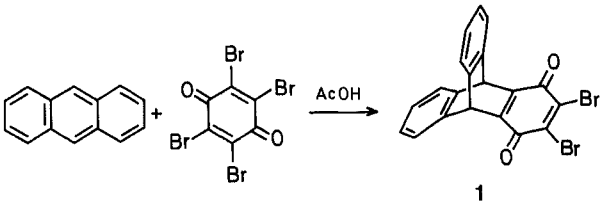
As a continuation of our studies in angular heterocyclic chemistry, we investigated[1-7] the reaction of naphthoquinones with aromatic amines. This aroused our interest to synthesize the analogous, non-coplanar heterocycles for comparative purposes and to examine their colour properties.

This paper describes a novel route for the synthesis of a new class of *endo*-polynuclear heterocycles. The new quinone *endo*-α-9,10-*o*-phenylene-2,3-dibromo-9,10-dihydro-1,4-anthraquinone (**1**) was prepared by the Diels-Alder reaction by heating equimolar amounts of anthracene and bromanil in glacial acetic acid and purified by vacuum sublimation.



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When **1** was condensed with aniline in alcohol it gave only *endo*-9,10-*o*-phenylene-2-anilino-3-bromo-9,10-dihydro-1,4-anthraquinone (**2**), the second bromine atom of **1** not being replaced due to hydrogen bonding. Compound **1** was also reacted with the zinc thiolate of 2-amino-5-chlorothiophenol in alcohol to give only the 3-chloro-*endo*-8,13-*o*-phenylene-8,13-dihydro-6-bromo-7*H*-naphtho[2,3-*a*]phenothiazin-7-one (**3**).

It is interesting to note that when **1** was condensed with the same zinc thiolate in pyridine or dimethylformamide it gave only the 3,8-dichloro-*endo*-12,17-*o*-phenylene-12,17-dihydronaphtho[2,3-*a*][1,4]benzothiazino[3',2'-*c*]phenothiazine (**4**). The phenothiazone (**3**) also reacts with a further molecule of the zinc thiolate or the free thiophenol in pyridine or dimethylformamide to yield the same 3,8-dichloro-*endo*-12,17-*o*-phenylene-12,17-dihydronaphtho[2,3-*a*][1,4]benzothiazino[3',2'-*c*]phenothiazine (**4**).

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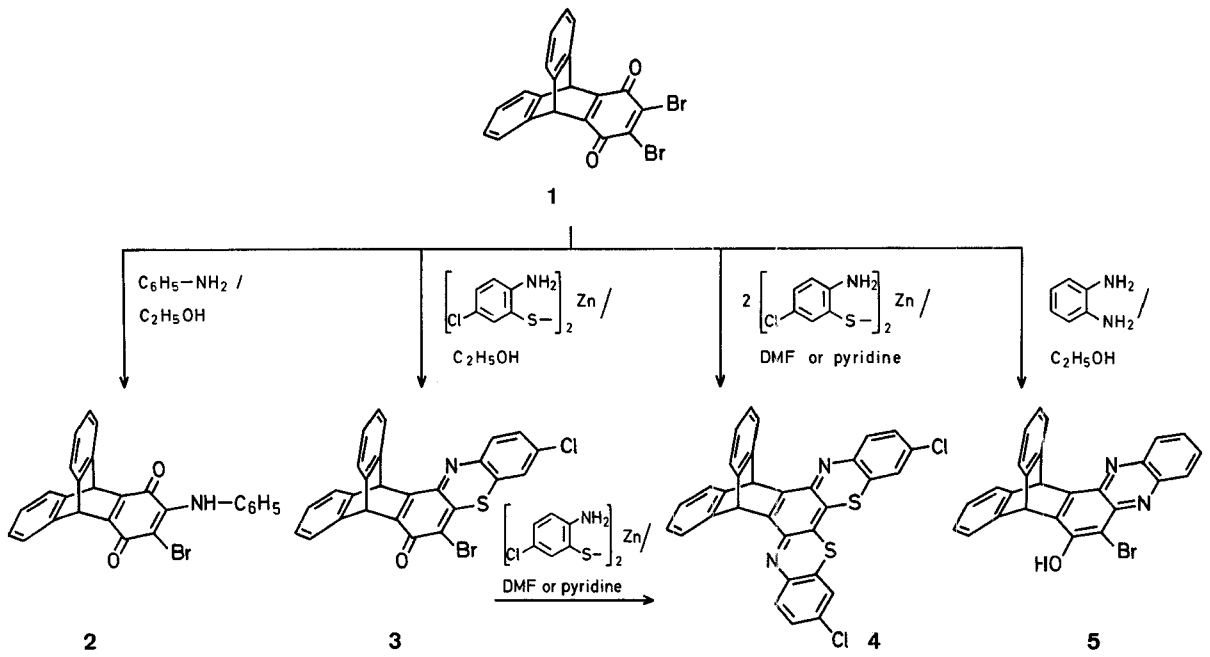

In the reaction (**1**→**3**) zinc thiolate adds once to the quinone system with subsequent loss of water and zinc bromide. The zinc bromide generated may inhibit further condensation by complexation with the product, but the presence of dimethylformamide or pyridine may neutralise this effect.

Continuing interest in phenazine[1] chemistry led us to examine the condensation of **1** with *o*-phenylenediamine in alcohol. This reaction gave the expected *endo*-8,13-*o*-phenylene-8,13-dihydro-6-bromo-7-hydroxynaphtho[2,3-*a*]phenazine (**5**).

The structure of all these *endo*-polynuclear heterocycles were confirmed by microanalyses, I.R., and mass spectral studies, and purity was checked by T.L.C.[5]

Synthesis of *endo*-9,10-*o*-Phenylene-2,3-dibromo-9,10-dihydro-1,4-anthraquinone (1):

To a boiling solution of anthracene (1.78 g, 0.01 mol) in glacial acetic acid (100 ml) is added in one portion bromanil (5.08 g, 0.012 mol). The solution becomes blue-green and a yellow product separates during the course of reaction. Heating under reflux is continued for 8 h. The reaction mixture is filtered while hot and the precipitate washed well with hot acetic acid. It is then crystallised with benzene. Sublimation under reduced pressure provides an analytical pure sample; yield: 1.77 g (40%); m.p. 262° (with partial decomposition).

$C_{20}H_{10}Br_2O_2$	calc.	C 54.33	H 2.27
(442.1)	found	54.54	2.59

Synthesis of *endo*-9,10-*o*-Phenylene-2-anilino-3-bromo-9,10-dihydro-1,4-anthraquinone (2):

To a hot solution of **1** (4.42 g, 0.01 mol) in absolute ethanol (50 ml) is added aniline (0.93 or 1.86 g, 0.01 or 0.02 mol). The solution is heated under reflux for 2 h, cooled, and filtered using a suction pump. The precipitate is washed with water, then with 60% aqueous ethanol, and crystallised from ethanol; yield: 3.18 g (70%); m.p. 270°.

$C_{26}H_{16}BrNO_2$	calc.	C 68.73	H 3.54	N 3.08
(454.3)	found	68.91	3.72	3.49

Synthesis of 6-Bromo-3-chloro-*endo*-8,13-*o*-phenylene-8,13-dihydro-7*H*-naphtho[2,3-*a*]phenothiazin-7-one (3):

A mixture of **1** (4.42 g, 0.01 mol) and the zinc thiolate of 2-amino-5-chloro-thiophenol (1.91 or 4.78 g, 0.005 or 0.0125 mol) in dry ethanol (70 ml) is stirred for 1 h at room temperature. The colour of the solution changes to blue-violet and the mixture is heated under reflux for 2 h. The solid which forms on cooling is filtered and washed with 5% hydrochloric acid (~500 ml) and water. An analytically pure sample is obtained by crystallisation from benzene/chlorobenzene; yield: 4.42 g (84%); m.p. 185°.

$C_{26}H_{13}BrClNOS$	calc.	C 62.10	H 2.60	N 2.78
(502.8)	found	62.30	2.30	2.95

Synthesis of 3,8-Dichloro-*endo*-12,17-*o*-phenylene-12,17-dihydronaphtho[2,3-*a*][1,4]benzothiazino[3',2'-*c*]phenothiazine (4):

Method A: A mixture of **1** (4.42 g, 0.01 mol) and the zinc thiolate of 2-amino-5-chloro-thiophenol (1.91 or 3.82 g, 0.005 or 0.01 mol) in dry pyridine (50 ml) or dimethylformamide (50 ml) is stirred for 0.5 h at room temperature and then heated under reflux for 2 h. An equal volume of methanol is added, the mixture is chilled, filtered, and the precipitate washed with methanol and water to give the desired product. An analytically pure sample is obtained by recrystallisation (three times) from trichlorobenzene; yield: 3.38 g (60%); m.p. >300°.

$C_{32}H_{16}Cl_2N_2S_2$	calc.	C 68.20	H 2.86	N 4.97
(563.4)	found	68.61	2.58	5.15

Method B: A mixture of the **3** (5.02 g, 0.01 mol) and the zinc thiolate of 2-amino-5-chloro-thiophenol (1.91 g, 0.005 mol) or the free thiophenol (1.57 g, 0.01 mol) in dry pyridine or dimethylformamide (25 ml) is heated under reflux for 2 h, then an equal volume of methanol is added, the mixture is chilled, filtered, and the precipitate crystallised from trichlorobenzene; yield: 2.08 g (37%).

Synthesis of *endo*-8,13-*o*-Phenylene-6-bromo-7-hydroxy-8,13-dihydronaphtho[2,3-*a*]phenazine (5):

A mixture of **1** (4.42 g, 0.01 mol), anhydrous potassium acetate (1.56 g, 0.02 mol), and *o*-phenylenediamine (4.42 g, 0.01 mol) in dry ethanol (50 ml) is heated under reflux for 3 h. The resultant solution is cooled to room temperature, filtered, and the precipitate washed well with hot water. An analytically pure sample is obtained by recrystallisation from toluene; yield: 2.57 g (57%); m.p. 210–212° (dec.).

$C_{26}H_{15}BrN_2O$	calc.	C 69.12	H 3.32	N 6.20
(451.3)	found	69.66	3.54	6.01

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