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Ring-Closure of Halogenonaphthoquinones with Potassium 2-Aminobenzenethiolate: Tautomerism and Substituent Effects†

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SUMMARY

Ring-closure of halogenonaphthoquinones by reaction with potassium 2-aminobenzenethiolate gave a series of naphthoquinoid infrared dyes which were useful as optical information recording media for semiconductor lasers. The ring-closure reaction was influenced mainly by the ring-substituents, by the quinone–quinoneimine tautomerism of the intermediates and also by the reaction conditions. Some of the tautomers were isolated and tautomerism in solution was also observed.

1. INTRODUCTION

The synthesis of deep-coloured functional dyes for use in optical information recording media for semiconductor lasers is an area of current technological interest.[1,2] We have recently reported the synthesis of some

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aminonaphthoquinone[3,4] and of some phenothiazinequinone and phenoselenazinequinone infrared dyes[5] for use in optical recording media. These dyes absorbed infrared light at about 750–800 nm, which is the most suitable wavelength region for the gallium–arsenic semiconductor laser which emits the laser light at 800–830 nm. Monolayer recording media can be made by means of sublimation using these dyes and the media showed good properties for optical recording and long-term stability.

In this paper, we report the syntheses of new deep-coloured aminonaphthoquinone dyes obtained by the ring-closure reaction of halogenonaphthoquinones with potassium 2-aminobenzenethiolate, and we discuss the structures of the products on the basis of their visible absorption and ^{1}H-NMR spectra.

2. RESULTS AND DISCUSSION

2.1. Reaction of 2,3-dihalogeno-1,4-naphthoquinones 1 with potassium 2-aminobenzenethiolate 3

We have reported that the reaction of 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone **1a** with potassium 2-aminobenzenethiolate **3** gave **4a**, 10,11-dithia-5*H*,16*H*-5,16-diazadinaphtho[3,2-*a*][2,3-*c*]-1,4-naphthoquinone, in 86% yield together with a trace amount of **5a**, 1,4-dihydroxy-6-chloro-7-thia-12-azanaphtho[3,2-*a*]naphthalen-5-one. In the reaction, the main product **4a** was isolated in the quinone form, but tautomerism between the quinoneimine **6a** and the quinone form **4a** in solution was observed.[6] On the other hand, **5a** was isolated in the quinoneimine form and tautomerism was not observed with this compound.

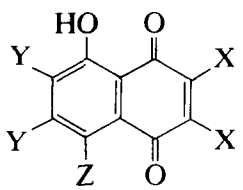
The reaction of 2,3-dichloro-5-hydroxy-8-amino-1,4-naphthoquinone **1b** with **3** gave the quinoneimine **6b** in 67% yield and a trace amount of its tautomer **7**, 4-amino-10,11-dithia-16*H*-5,16-diazadinaphtho[3,2-*a*][2,3-*c*]-naphthalen-1-one. Typical substituent effects were observed in these reactions. Thus, replacement of the 8-hydroxy group in **1a** by the 8-amino group in **1b** affected both the reaction products and also the tautomeric structures of the products. It is concluded that the amino group at the 4-position stabilizes structure **6b**, which was tautomerized to **7** in small amount, but further tautomerism to **4b** was not observed. Separation of both the tautomers **6b** and **7** by column chromatography was effected and the structures of these products were confirmed by their visible, ^{1}H-NMR and mass spectra.

The reaction of 2,3,6,7-tetrabromo-5,8-dihydroxy-1,4-naphthoquinone

1c with **3** gave two types of ring-closure products, i.e. **4c**, 2,3-dibromo-10,11-dithia-5*H*,16*H*-5,16-diazadinaphtho[3,2-*a*][2,3-*c*]-1,4-naphthoquinone, and **8b**, 2,10-dibromo-3,11-dithia-8*H*,16*H*-8,16-diazadinaphtho[3,2-*a*][3,2-*f*]-1,9-naphthoquinone, depending on the reaction conditions. A typical solvent effect was observed. In a basic solvent such a pyridine or dimethylformamide, **4c** was obtained preferentially, but **8b** was obtained when ethanol was used as solvent. Dye **5c** was obtained mainly under mild conditions. The structures of **4c** and **8b** were confirmed by their mass and visible absorption spectra as described below.

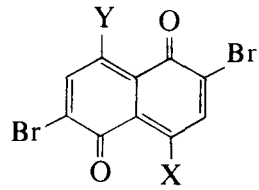
2.2. Reaction of 2,6-dibromo-1,5-naphthoquinones 2 with potassium 2-aminobenzenethiolate 3

Dyes **8** absorbed at much longer wavelengths than the structural isomer **4** and were thus of interest as functional infrared dyes. The 2,6-dibromo-1,5-naphthoquinone derivatives **2** were prepared and reacted with **3** to give dyes **8**. The reaction of 2,6-dibromo-4,8-dihydroxy-1,5-naphthoquinone **2a** with **3** gave **8a** in 63% yield; this compound absorbed at 750 nm. The initially formed 1,5-quinoneimine **9a** subsequently tautomerized to **8a**



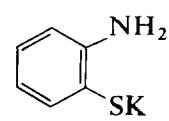
1

a: X = Cl, Y = H, Z = OH
b: X = Cl, Y = H, Z = NH_2
c: X = Y = Br, Z = OH



2

a: X = Y = OH
b: X = OH, Y = NH_2
c: X = Y = NH_2



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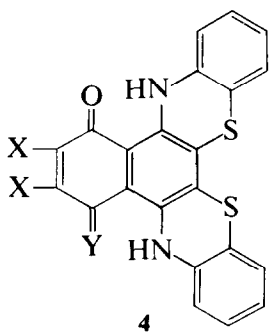
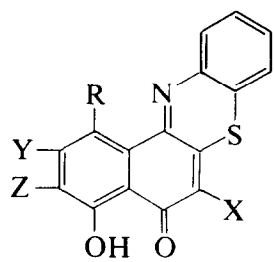


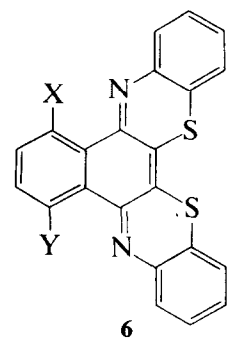
4

a: X = H, Y = O
b: X = H, Y = NH
c: X = Br, Y = O



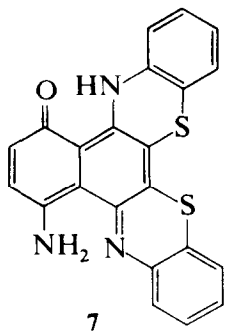
5

a: X = Cl, Y = Z = H, R = OH
b: X = Y = H, Z = Br, R = NH_2
c: X = Y = Z = Br, R = OH

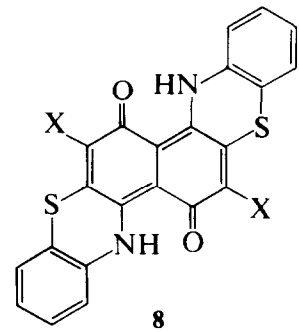


6

a: X = Y = OH
b: X = OH, Y = NH_2

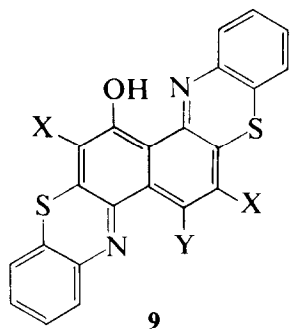


7



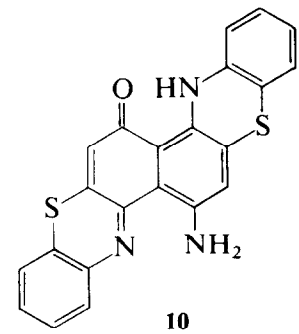
8

a: X = H
b: X = Br



9

a: X = H, Y = OH
b: X = H, Y = NH_2



10

under the reaction conditons. Tautomerism between **8a** and **9a** in solution was not observed. The structure of the previously obtained **8b** was confirmed by the analogy of its visible absorption spectra with that of **8a** (Fig. 1). On the other hand, reaction of 2,6-dibromo-4-hydroxy-8-amino-1,5-naphthoquinone **2b** with **3** gave **8a** in 12·2% yield together with **10**, 9-amino-3,11-dithia-16*H*-8,16-diazadinaphtho[3,2-*a*][3,2-*f*]-naphthalen-1-one, in 9·9% yield, after separation of the reaction product by column chromatography. Dye **5b**, 1-amino-3-bromo-4-hydroxy-7-thia-12-aza-naphtho[3,2-*a*]naphthalen-5-one, was also isolated in trace amounts. The yield of **8a** decreased from 63% in the reaction of **2a** to 12·2% in the reaction of **2b**, which contains an amino group at the 8-position. Thus, compound **2a** was much more reactive than **2b**, and tautomerism of the amino group in **10**, followed by the hydrolysis of the imino group to the carbonyl group to give compound **8a**, did not proceed well. Reaction of 2,6-dibromo-4,8-diamino-1,5-naphthoquinone (**2c**) with **3** gave **8a** in 4·5% yield as the only identified product after colum chromatography. Many other products were detected during the column chromatography but these could not be identified. The yield of **8a** thus decreased depending on

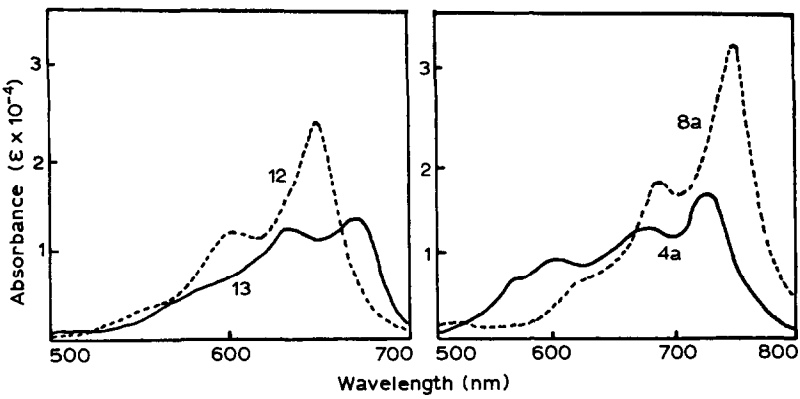


Fig. 1. Comparison of the absorption spectra of isomeric dyes **13** and **12**, or **4a** and **8a**.

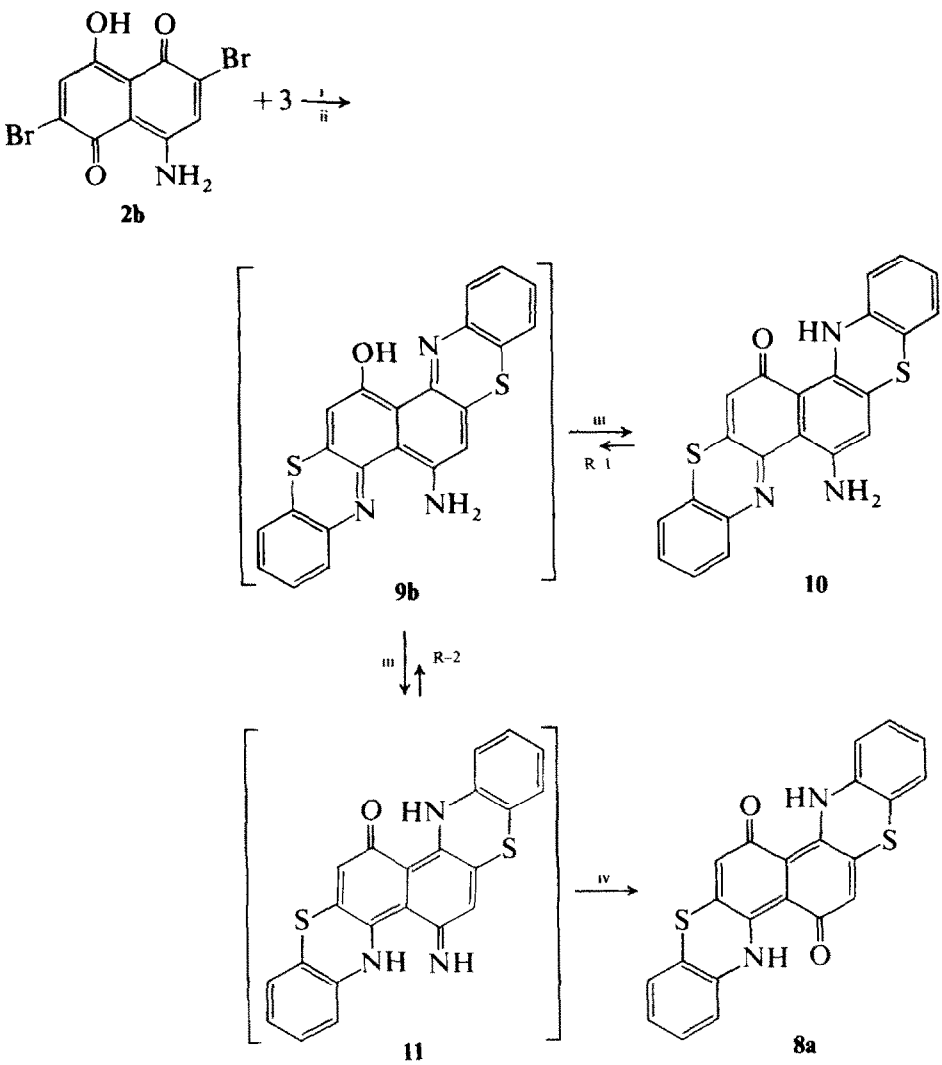
the number of amino groups in the derivatives **2** in the following order: **2a** (63%) > **2b** (12·2%) > **2c** (4·5%).

The proposed reaction pathways between **2b** and **3** are shown in Scheme 1. Nucleophilic substitution of the bromine atom by the thiolate anion, followed by dehydration, gives **9b**. A proton shift from the 1-hydroxy group to the 16-aza group of **9b** gives the tautomeric product **10** via route 1 (R–1). On the other hand, **9b** tautomerizes via route 2 (R–2) to **11**, then hydrolysis of the 9-imino group, to give **8a**.

Similar reaction of **1b** with **3** gave **6b** and **7**, but not **4b**, as shown in Scheme 2. Tautomerism of **6b** to **7** by proton transfer from the 1-hydroxy group to the 16-aza group occurred, but not that from the 4-amino group to the 5-aza group. The amino groups in **1** and **2** thus significantly affect the tautomerism of the intermediates and the nature of the products. The structures of products were confirmed by their ^{1}H-NMR and visible absorption spectra.

2.3. Structure assignments of the products

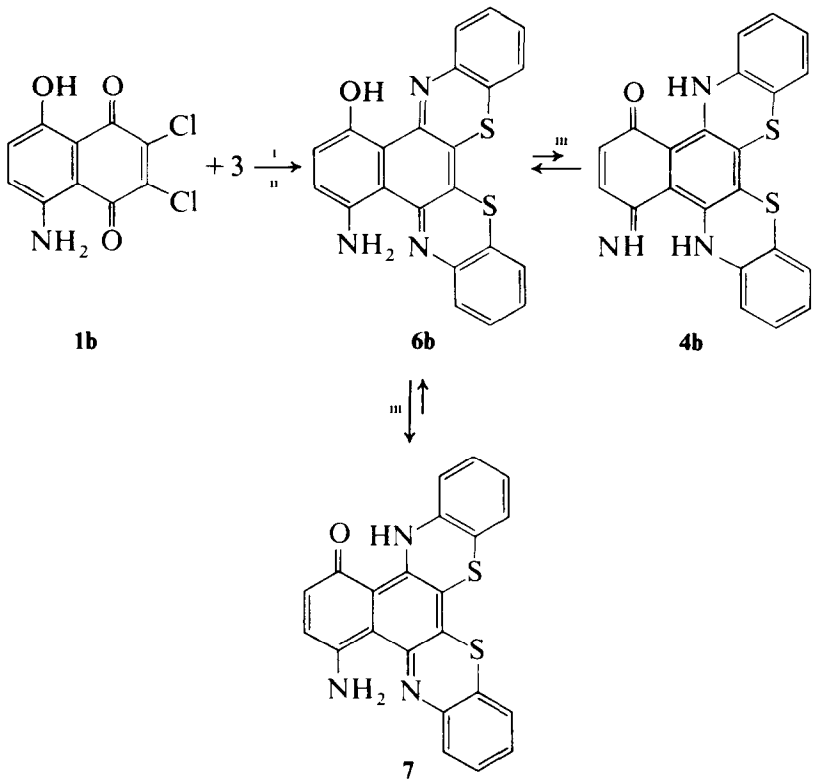
The visible absorption spectra of the products are shown in Table 1. It is generally known that 5,8-bis(alkylamino)-1,4-naphthoquinones and 4,8-bis(alkylamino)-1,5-naphthoquinones show quite different shapes in their absorption spectra,[8] and this enables the isomers to be readily distinguished, as shown in Fig. 1. The three absorption maxima (λ_1–λ_3) are attributed to the vibrational level of the first transition in the visible region. The value $\varepsilon_1/\varepsilon_2$, which is the ratio of the apparent absorbance at λ_1 and λ_2, is also useful in distinguishing between 1,4-naphthoquinones and 1,5-naphthoquinones. The values for 1,4-naphthoquinones are about 1·2 but



Scheme 1. i, $-2KBr$; ii, $-2H_2O$; iii, tautomerism; iv, $+H_3^+O$.

those for 1,5-naphthoquinones are 2·0 (see Table 1). The $\varepsilon_1/\varepsilon_2$ values of the 1,4-naphthoquinone dyes **4a** and **4c** are about 1·2 and those of the 1,5-naphthoquinone dyes **8a** and **8b** are 1·8–2·1.

Dyes **5c** and **6b** showed typical tautomerism in chloroform–dimethylformamide mixture as shown in Fig. 2. This quinone–quinoneimine tautomerism has been observed in dye **4a** and its analogues.[6,7] Dye **7**, which is the tautomer of **6b**, was isolated by column chromatography. Dyes **6b** and **7** showed the same parent peak in the mass spectrum at $M^+ = 399$ but their visible absorption spectra were different. The ^{1}H-NMR spectrum of **7**



Scheme 2. i, $-2HCl$; ii, $-2H_2O$; iii, tautomerism.

TABLE 1
Visible Absorption Spectra of the Ring-Closure Products in Chloroform

Dye	λ_1 (*nm*)	$(\varepsilon_1 \times 10^{-4})$	λ_2 (*nm*)	$(\varepsilon_2 \times 10^{-4})$	λ_3 (*nm*)	$(\varepsilon_3 \times 10^{-4})$	λ_4 (*nm*)	$(\varepsilon_4 \times 10^{-4})$	$\varepsilon_1/\varepsilon_2$
4a	725	(1·52)	666	(1·22)	606	(0·97)	570[s]	(0·78)	1·25
4c	756	(1·63)	685	(1·55)	625	(1·17)	580[s]	(0·87)	1·05
5c	768	(0·55)	676	(0·89)	621[s]	(1·48)	579	(1·91)	—[a]
6b	728[s]	(0·28)	665[s]	(0·65)	578	(1·90)	545[s]	(1·80)	—[a]
7	693	(1·43)	636	(0·94)	588[s]	(0·60)	542[s]	(0·37)	1·52
8a	750	(3·20)	685	(1·83)	623[s]	(0·82)	—		1·75
8b	785	(2·43)	716	(1·17)	660	(0·41)	—		2·08
10	682	(2·10)	632	(1·70)	580[s]	(0·97)	—		1·24
12[b]	657	(2·19)	606	(1·07)	550[s]	(0·38)	—		2·05
13[c]	686	(1·32)	628	(1·14)	583[s]	(0·63)	—		1·16

[a] Small amount of quinone tautomer which absorbs at $\lambda_1 - \lambda_3$ was mixed.
[b] 4,8-Bis(methylamino)-1,5-naphthoquinone.[8]
[c] 5,8-Bis(methylamino)-1,4-naphthoquinone.[8]

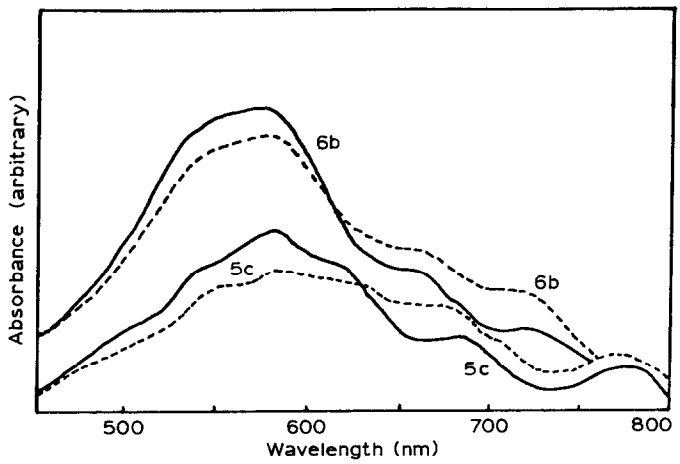


Fig. 2. Quinone–quinoneimine tautomerism of **5c** and **6b** in chloroform (——) and dimethylformamide (– – –) solutions.

in perdeuterodimethyl sulphoxide solution showed the 4-amino protons at 8·68 ppm as a broad peak of 2H, and the quinoid 2- and 3-protons at 6·52 and 6·78 as an AB quartet ($J = 8$ Hz) of 2H; the structure of **7** is thus confirmed. In the case of dye **10**, the ^{1}H-NMR spectrum in perdeuterodimethyl sulphoxide solution showed the 9-amino protons at 8·73 as a broad peak of 2H, the 2-quinoid proton at 6·23 as a singlet of 1H and the 10-benzenoid proton at 6·71 as a singlet of 1H. The $\varepsilon_1/\varepsilon_2$ value of **10** was 1·2 and consequently the structure of **10** is confirmed.

3. EXPERIMENTAL

Melting points are uncorrected. UV–visible and mass spectra were obtained with a Hitachi EPS-3T spectrophotometer and a Shimadzu LKB-9000 spectrometer, respectively. Chloroform was used as solvent for UV–visible spectra. The ^{1}H-NMR spectra were obtained with a Nihon Denshi JNM-FX60Q FT NMR spectrometer using $SiMe_4$ as internal standard. Unless otherwise stated, perdeuterodimethyl sulphoxide [$(CD_3)_2SO$] was used as solvent. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. Column chromatography was carried out on a silica gel (Wakogel C-300) using chloroform as eluent.

3.1. Starting materials

The starting materials **1a**,[9] **1b**,[10,11] **1c**,[12] **2b** and **2c**[10,11] were prepared using previously described procedures. Compound **2a** was prepared by hydrolysis

of **2c** and was purified by column chromatography and recrystallization. Structures were confirmed from data described in the literature and from the data shown below. All the other compounds and solvents were commercially available and were used without further purification.

2,3-Dichloro-5,8-dihydroxy-1,4-naphthoquinone, **1a**[9]
M.p. 193–194°C; NMR ($CDCl_3$): $\delta = 7{\cdot}32$ (2H, s), 12·32 (2H, s).

2,3-Dichloro-5-hydroxy-8-amino-1,4-naphthoquinone, **1b**[10,11]
M.p. 260°C (dec.); NMR [$(CD_3)_2SO$]: 7·30 (1H, s), 7·33 (1H, s), 8·66 (2H, broad), 13·38 (1H, s).

2,3,6,7-Tetrabromo-5,8-dihydroxy-1,4-naphthoquinone, **1c**[12]
M.p. 300°C; NMR ($CDCl_3$): 13·12 (2H, s); mass (rel. intensity): 502 (M^+, 17%), 504 (M^+, 66%), 506 (M^+, 100%), 508 (M^+, 66%), 510 (M^+, 17%).

2,6-Dibromo-4,8-dihydroxy-1,5-naphthoquinone, **2a**
M.p. 184–185°C (chloroform); UV λ_{max} (nm) (chloroform) ($\varepsilon \times 10^{-4}$): 500[s] (0·74), 533 (0·84), 575 (0·54); mass: 350 (M^+, 53%), 348 (M^+, 100%), 346 (M^+, 57%), 269 (58%), 267 (60%), 241 (47%); NMR ($CDCl_3$): 7·60 (2H, s), 12·55 (2H, s).

2,6-Dibromo-4-hydroxy-8-amino-1,5-naphthoquinone, **2b**[10,11]
M.p. >300°C; NMR [$(CD_3)_2SO$]: 7·67 (1H, s), 7·81 (1H, s), 8·29 (2H, broad), 12·8 (1H, s).

2,6-Dibromo-4,8-diamino-1,5-naphthoquinone, **2c**[10,11]
M.p. >300°C; NMR [$(CD_3)_2SO$]: 7·45 (2H, s), 8·30 (2H, broad), 11·8 (2H, broad).

Reaction of halogenoquinones 1 (or 2) with potassium 2-aminobenzenethiolate 3

General procedure
An ethanol solution (100 ml) of **1** (1 mmol) was added to a solution of 2-aminobenzenethiol (2·2 mmol) and potassium hydroxide (2·2 mmol) in ethanol (20 ml) and the mixture was stirred for 5–6 h at 40–50°C, poured on to water and acidified to pH 1 with aqueous hydrochloric acid. The product was filtered, washed with water, dried and separated by column chromatography [silica gel (Wakogel C-300); chloroform]. The isolated products were purified by recrystallization. In the reaction of **1c** with **3**, a typical solvent effect was observed An addition of pyridine (6 mmol) to the reaction mixture afforded **5c** in 34·2% yield, together with a trace amount

of **4c**. When the reaction was carried out in dimethylformamide as solvent, **5c** and **4c** were obtained in 30% and 4·5% yield, respectively. After prolonged reaction times (24 h), **4c** was the predominant product (50% yield). However, when the reaction was carried out in ethanol, **8b** was obtained in 49% yield. The structures of the products obtained were confirmed from the data shown below.

*10,11-Dithia-5*H,*16*H-*5,16-diazadinaphtho*[*3,2*-a][*2,3*-c]-*1,4-naphthoquinone*, **4a**
M.p. >310°C (chloroform); analysis—found: C, 65·60; H, 2·53; N, 6·48; $C_{22}H_{12}N_2O_2S_2$ requires: C, 65·98; H, 3·02; N, 7·00%; UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 570^s (0·78), 606 (0·97), 666 (1·22), 725 (1·52); mass: 400 (M^+, 100%), 336 (22%).

*2,3-Dibromo-10,11-dithia-5*H,*16*H-*5,16-diazadinaphtho*[*3,2*-a][*2,3*-c]-*1,4-naphthoquinone*, **4c**
M.p. >310°C (chloroform); UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 580^s (0·87), 625 (1·17), 685 (1·55), 756 (1·63); mass: 560 (M^+, 67%), 558 (M^+, 100%), 556 (M^+, 52%), 479 (23%), 477 (22%), 398 (25%).

1,4-Dihydroxy-6-chloro-7-thia-12-azanaphtho[*3,2*-a]*naphthalene-5-one*, **5a**
M.p. >300°C (chloroform); analysis—found: C, 58·39; H, 2·03; N, 4·15; $C_{16}H_8ClNO_3S$ requires: C, 58·28; H, 2·45; N, 4·25%; UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 456^s (0·48), 490^s (0·64), 545^s (0·92), 571 (1·00), 616 (0·68), 642^s (0·46); mass: 331 (M^+, 44%), 329 (M^+, 100%), 296 (18%), 294 (18%).

1-Amino-3-bromo-4-hydroxy-7-thia-12-azanaphtho[*3,2*-a]*naphthalen-5-one*, **5b**
M.p. >300°C (chloroform); analysis—found: C, 52·03; H, 2·60; N, 7·83; $C_{16}H_9N_2O_2BrS$ requires: C, 51·61; H, 2·42; N, 7·53%; UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 582^s (1·04), 628 (1·46), 686 (1·39); mass: 374 (M^+, 100%), 372 (M^+, 98%), 294 (24%).

1,4-Dihydroxy-2,3,6-tribromo-7-thia-12-azanaphtho[*3,2*-a]*naphthalen-5-one*, **5c**
M.p. >300°C (chloroform); analysis—found: C, 36·27; H, 1·37; N, 2·83; $C_{16}H_6NO_3SBr_3$ requires: C, 36·09; H, 1·13; N, 2·65%; UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 540^s (1·57), 579 (1·91), 621^s (1·48), 676 (0·89), 768 (0·55); mass: 535 (M^+, 37%), 533 (M^+, 100%), 531 (M^+, 96%), 529 (M^+, 33%).

10,11-Dithia-5,16-diazadinaphtho[*3,2*-a][*2,3*-c]-*1-hydroxy-4-aminonaphthalene*, **6b**
M.p. 289–291°C (chloroform); analysis—found: C, 65·40; H, 2·98; N, 9·94;

$C_{22}H_{13}N_3OS_2$ requires: C, 66·15; H, 3·26; N, 10·52%; UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 545^s (1·80), 578 (1·90), 665^s (0·65), 728^s (0·28); mass: 399 (M^+, 100%), 367 (21%).

*10,11-Dithia-16*H*-5,16-diazadinaphtho*[*3,2*-a][*2,3*-c]*-4-aminonaphthalen-1-one*, **7**

M.p. 261–263°C (chloroform); UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 542^s (0·37), 588^s (0·60), 636 (0·94), 693 (1·43); NMR [$(CD_3)_2SO$]: 6·52 (1H, d, $J = 8$ Hz), 6·78 (1H, d, $J = 8$ Hz), 8·69 (2H, broad), 7·04–7·41 (8H, m), 16·08 (1H, s); mass: 399 (M^+, 100%), 367 (19%).

*3,11-Dithia-8*H*,16*H*-8,16-diazadinaphtho*[*3,2*-a][*3,2*-f]*-1,9-naphthoquinone*, **8a**

M.p. >300°C (chloroform); analysis—found: C, 64·87; H, 2·93; N, 6·97; $C_{22}H_{12}N_2O_2S_2$ requires: C, 66·00; H, 3·00; N, 7·00%; UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 623^s (0·82), 685 (1·83), 750 (3·20); mass: 400 (M^+, 100%), 346 (54%), 281 (79%).

*2,10-Dibromo-3,11-dithia-8*H*,16*H*-8,16-diazadinaphtho*[*3,2*-a][*3,2*-f]*-1,9-naphthoquinone*, **8b**

M.p. >300°C (chloroform); UV λ_{max} (chloroform) ($\varepsilon \times 10^{-4}$): 660 (0·41), 716 (1·17), 785 (2·43); mass: 560 (M^+, 56%), 558 (M^+, 100%), 556 (M^+, 47%).

*3,11-Dithia-16*H*-8,16-diazadinaphtho*[*3,2*-a][*3,2*-f]*-9-aminonaphthalen-1-one*, **10**

M.p. >300°C (chloroform): UV (chloroform): 580^s (0·97), 632 (1·70), 682 (2·10); NMR [$(CD_3)_2SO$]: 6·32 (1H, s), 6·71 (1H, s), 7·11–7·41 (8H, m), 8·73 (2H, broad), 15·69 (1H, s); mass: 399 (M^+, 100%), 367 (10%).

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