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Syntheses of Deep Coloured Aminonaphthoquinonoid Dyes. Reaction of Dichloronaphthazarins with 2-Aminobenzenethiol and Related Compounds

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SUMMARY

The reaction of 2,3-dichloronaphthazarin **1a** *with potassium 2-aminobenzenethiolate gives the ring-closure product 10,11-dithia-5H,16H-5,16-diazadinaphtho[2,3a],[2,3c]-1,4-naphthoquinone* **9** *in 86·2% yield together with small amounts of 5-hydroxy-6-chloro-7-thia-12H-12-azanaphtho[2,3a]-1,4-naphthoquinone* **8**. *Dye* **9** *is green in colour and absorbs infrared light at 727 nm. Oxidation of* **9** *by hydrogen peroxide gives 10,11-dithia-5H,16H-5,16-diazadinaphtho[2,3a],[2,3c]-1,4-naphthoquinone-10,11-dioxide* **14** *which absorbs infrared light at 827 nm. The reaction of* **1a** *with 2-aminoethanethiol gives 5-hydroxy-6-chloro-7-thia-10-aza-8,9,10-trihydrobenzo[2,3a]-1,4-naphthoquinone* **4** *and 2,3-dichloro-5-hydroxy-7-thia-10-aza-8,9,10-trihydrobenzo[2,3a]-1,4-naphthoquinone* **5** *in yields of 14·2% and 3·2%, respectively.*

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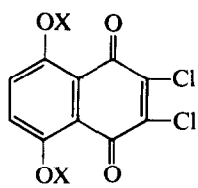
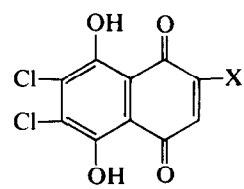
1. INTRODUCTION

Deep coloured naphthoquinonoid dyes have been anticipated as functional dyes for guest–host liquid crystal display[1] or optical information recording medium. Recently, some infrared dyes such as squarylium and pentamethine derivatives have been reported as dyes for optical information recording medium for semiconductor lasers.[2] It is known that some naphthoquinonoid dyes can be synthesized by the direct 8-arylamination of 5-amino-2,3-dicyano-1,4-naphthoquinone. These dyes absorb infrared light at about 780 to 800 nm.[3] Additionally, it is well known that the reaction of 2,3-dichloro-1,4-naphthoquinone with 1,2-diaminobenzene, 2-aminobenzenethiol and 2-aminophenol gives the corresponding ring-closed heterocyclic compounds.[4] In this paper, we report the synthesis of deep coloured aminonaphthoquinonoid dyes formed by the reaction of 2,3-dichloronaphthazarins **1** with 2-aminobenzenethiol and related compounds, and comment on the visible absorption spectra of these dyes.



1a, X = H
1e, X = Me



1b, X = OMe
1c, X = NHBu
1d, X = NHBz

Scheme 1

2. RESULTS AND DISCUSSIONS

2.1. Reaction of 1a with sodium benzenethiolate

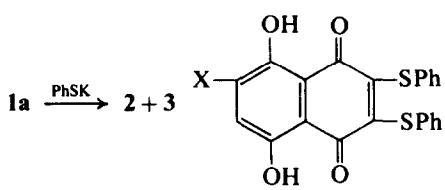
The reaction of 1,4-naphthoquinones, such as juglone, with thiols has been shown to give the Michael adduct which may be oxidized to give substitution products;[5] the reaction of 2,3-dichloro-1,4-naphthoquinone with benzenethiol gives 2,3-bis(phenylthio)-1,4-naphthoquinone.[6] In this present work reaction of 2,3-dichloronaphthazarin **1a** with sodium benzenethiolate gave 2,3-bis(phenylthio)naphthazarin **2** (Table 1, Run 1),

TABLE 1
Reaction of Dichloronaphthazarins with Thiols[a]

Run	*Reactant*	*Thiol*	*(mol)*[b]	*Time (h)*	*Product (Yield, %)*[c]
1	**1a**	PhSNa	(1·1)	40	**2**(51·5)[d]
2	**1a**	PhSNa	(30)	5	**3**(49)
3	**1a**	$ClH_3N(CH_2)_2SH$	(2·1)	44	**4**(14·2), **5**(3·2)[e]
4	**1a**	$2\text{-}H_2NC_6H_4SK$	(2·5)	24	**8**(1·5), **9**(86·3)
5	**1a**	$2\text{-}H_2NC_6H_4SH$	(2·5)	24	**8**(30·4), **9**(43·1)
6	**1b**	$2\text{-}H_2NC_6H_4SK$	(2·5)	24	**10**(65·4)
7	**1c**	$2\text{-}H_2NC_6H_4SK$	(2·5)	24	**11**(63·4)
8	**1d**	$2\text{-}H_2NC_6H_4SK$	(2·5)	24	**12**(66·2)
9	**1e**	$2\text{-}H_2NC_6H_4SK$	(2·5)	24	**13**(51·4)

[a] Reactions were carried out under room temperature.
[b] Molar ratio, [thiol]/[reactant].
[c] Isolated yield based on **1** reacted.
[d] Reactant **1a** was recovered in 8%.
[e] Reactant **1a** was recovered in 0·8%.

but with excess of thiolate, 2,3,6(or 7)-tris(phenylthio)naphthazarin **3** was the principal product (Run 2). Thiolate anion predominantly reacts with the chlorine atoms on the quinonoid ring but also reacts with the quinonoid hydrogen.



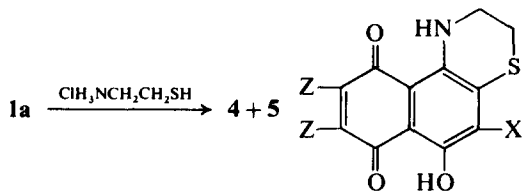
2, X = H
3, X = SPh

Scheme 2

2.2. Reaction of 1a with 2-aminoethanethiol hydrochloride

The reaction of **1a** with 2-aminoethanethiol hydrochloride gave two ring-closed products. One of these was 5-hydroxy-6-chloro-7-thia-10-aza-8,9,10-trihydrobenzo[2,3*a*]-1,4-naphthoquinone **4** which can be formed by the initial substitution of chlorine atoms followed by a ring-closure

reaction between the 2-amino group and the quinonoid carbonyl group. The other product was 2,3-dichloro-5-hydroxy-7-thia-10-aza-8,9,10-trihydrobenzo[2,3*a*]-1,4-naphthoquinone **5** which is formed by the initial Michael addition of thiol followed by ring-closure and then by oxidation of the leuco compound (Run 3). Similar ring-closure reactions between 2,3-dichloronaphthoquinone and potassium 2-aminobenzenethiolate have been reported.[4]

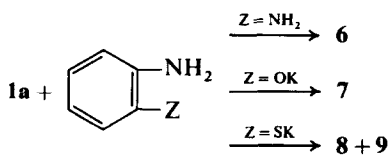


4, X = Cl, Z = H
5, X = H, Z = Cl

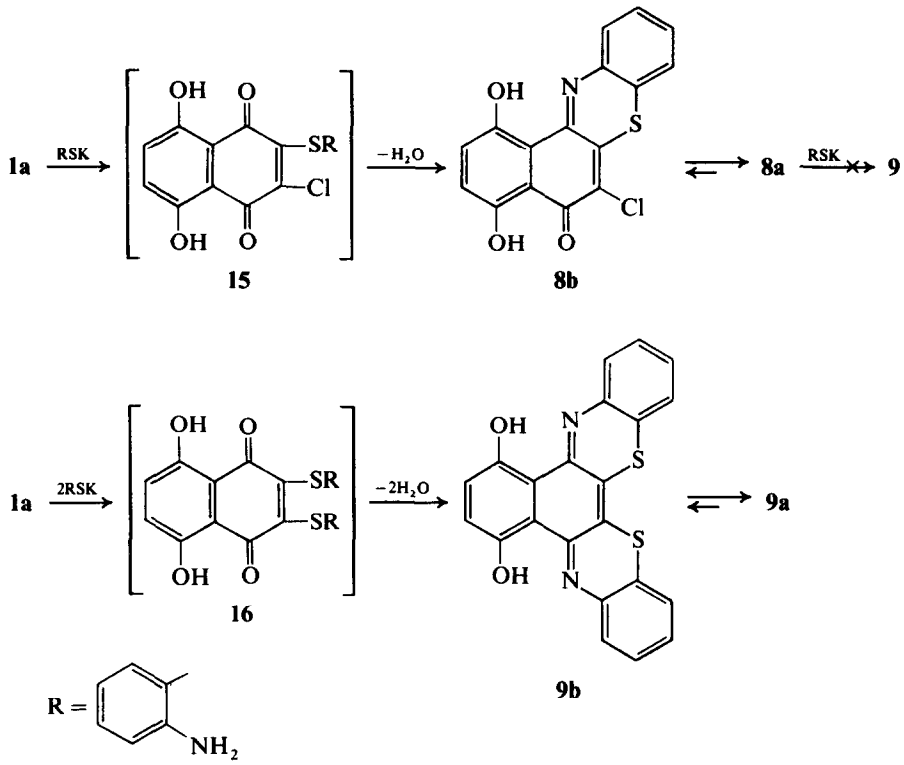
Scheme 3

2.3. Reaction of 1a with 2-substituted anilines

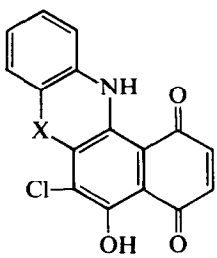
Reaction of **1a** with 1,2-diaminobenzene gave the mono-ring-closure product **6**, 5-hydroxy-6-chloro-7,12-dihydro-7,12-diazanaphtho[2,3*a*]-1,4-naphthoquinone in 83% yield. Reaction of **1a** with potassium 2-aminophenolate also gave the corresponding mono-ring-closure product **7** in 9% yield. However, reaction of **1a** with potassium 2-aminobenzenethiolate gave the bis-ring-closure product **9**, 10,11,-dithia-5*H*,16*H*-5,16-diaza-dinaphtho[2,3*a*],[2,3*c*]-1,4-naphthoquinone in 86·3% yield together with small amounts of the mono-ring-closure product **8**, 5-hydroxy-7-thia-12-azanaphtho[2,3*a*]-1,4-naphthoquinone (Run 4). When 2-aminobenzenethiol was used, the yield of **8** was increased and that of **9** was decreased (Run 5). Further reaction of **8** with potassium 2-aminobenzenethiolate no longer gave **9**, and **8** was recovered. Neither **6** nor **7** reacted with potassium 2-aminobenzenethiolate. It is proposed that



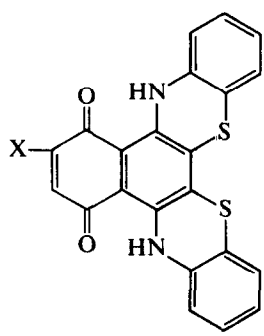
Scheme 4



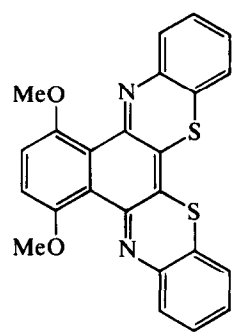
Scheme 5



6, X = NH
7, X = O
8, X = S



9, X = H
10, X = OMe
11, X = NHBu
12, X = NHBz



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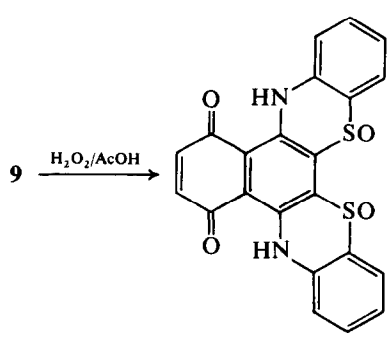
the initial substitution of chlorine atoms by the thiol plays an important role in these reactions. Reaction pathways to **9** and **8** are proposed in Scheme 5. Initial substitution of chlorine atoms at the 2- and 3-positions of **1a** by thiolate anion gives the intermediate **16**, which is subsequently dehydrated to give the ring-closure product **9b**. Quinone–quinoneimine tautomerism between **9a** and **9b** was observed in solution and **9a** was the predominant tautomer in solid state and solution. The mono-substitution product **15** was also dehydrated to give **8b** which was subsequently tautomerized to **8a**, and consequently the benzenoid chlorine atom at the 6-position of **8a** no longer reacted with excess of thiolate to give **9**. Reaction of 2-(donor substituted)-6,7-dichloronaphthazarins (**1b–1d**) with potassium 2-aminobenzenethiolate also gave the corresponding bis-ring-closure products (**10–12**) in 63–66% yield (Runs 6–8). Reaction of 5,8-dimethoxy-2,3-dichloro-1,4-naphthoquinone **1e** with potassium 2-aminobenzenethiolate gave the bis-ring-closure product **13**, 1,4-dimethoxy-10,11-dithia-5,16-diazadinaphtho[2,3*a*],[2,3*c*]naphthalene, in 51% yield (Run 9). In dye **13** tautomerism is not possible and this compound exists only in the quinoneimine form.

2.4. Oxidation of 9 with hydrogen peroxide

Oxidation of **9** with hydrogen peroxide in acetic acid gave the new type of dye **14**, 10,11-dithia-5*H*,16*H*-5,16-diazadinaphtho[2,3*a*],[2,3*c*]-1,4-naphthoquinone-10,11-dioxide, in 11% yield. Some other products also formed in small amounts were detected on column chromatography but these could not be identified. Dye **14** absorbed infrared light at 827 nm and was yellowish brown in colour.



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Scheme 6

2.5. Visible absorption spectra

The colour and constitution of naphthoquinonoid dyes has been well correlated by means of the PPP MO method by Griffiths.[7] We have also reported the substituent effects[8] and the quinone–quinoneimine tautomerism[9] of some aminonaphthoquinonoid dyes. On the basis of these results, deep coloured aminonaphthoquinonoid dyes should result from syntheses designed to introduce strong donor substituents at the 5- and 8-positions together with strong acceptor substituents at the 2-, 3-, 6- and 7-positions. Whilst arylamination of naphthazarin or leuco naphthazarin to 5,8-bis(anilino)naphthoquinone **17** (λ_{max} 665 nm in $CHCl_3$) did not proceed well, the analogous arylamination of **1a** to give **9** readily occurred by the method described in this paper. Dye **9** absorbed infrared light of much longer wavelength than **17** ($\Delta\lambda = 60$ nm). Ring formation through the thio bridge in **9** produced a large bathochromic shift. Dye **8** also absorbed longer wavelength visible light than the imino analogue (dye **6**, $\Delta\lambda = 58$ nm) and the oxo analogue (dye **7**, $\Delta\lambda = 54$ nm). Oxidation of **9** to give **14** should be an ideal structural modification to obtain a deep coloured dye and a large bathochromic shift of 102 nm between **9** and **14** was in fact observed. Dye **14** absorbed infrared light at 827 nm. The structural modifications of **1** to **9** and **14** are thus shown to be a useful method in obtaining deep coloured aminonaphthoquinonoid infrared dyes. Quinone–quinoneimine tautomerism of aminonaphthoquinonoid dyes was observed in **8**, **9** and **14**, but not in **6**, **7** and **10**–**12**. Studies of substituents effects on the quinone–quinoneimine tautomerism of these dyes will be reported separately.[10]

3. EXPERIMENTAL

All melting points are uncorrected. Visible spectra in chloroform solution were recorded on a Hitachi EPS-3T spectrophotometer. The nmr spectra were recorded on a Nihon Denshi JNM-FX60Q FT NMR spectrometer, unless otherwise stated in $CDCl_3$ solution with tetramethylsilane as internal standard. Mass spectra were recorded on a Hitachi RMU-6E spectrometer operating at 80 eV. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. Column chromatography was carried out on silica gel (Wakogel C-300) using chloroform as eluent.

3.1. Materials

2,3-Dichloronaphthazarin **1a**,[11] 2,3-dichloro-5,8-dimethoxy-1,4-naphthoquinone **1e**[11] and 2-(donor substituted)-6,7-dichloronaphthazarins **1b–1d** were synthesized by the methods described[12] and purified by column chromatography followed by recrystallization from benzene. Thiols were reagent grade and were used without further purification.

3.2. Reaction of 2,3-dichloronaphthazarin 1a with sodium benzenethiolate

An ethanol solution (80 ml) of **1a** (1 mmol) was added to a solution of sodium benzenethiolate (1 mmol) in ethanol (10 ml) at room temperature and the mixture stirred for 4 h. The reaction mixture was poured into water and neutralized with aqueous HCl; the product was extracted with chloroform, solvent evaporated and the residue chromatographed. Compound **2** was isolated in 51·5% yield.

3.3. Reaction of 1a with 2-aminoethanethiol hydrochloride

A solution of **1a** (1 mmol) in ethanol (200 ml) was added to an ethanol solution (20 ml) of 2-aminoethanethiol hydrochloride (2·1 mmol) at room temperature. After 4 h, the product was isolated as above. From column chromatography, **5** was isolated in 3·2% yield as the first fraction and **4** was then isolated in 14·2% yield. Starting material **1a** was recovered in 8% yield.

3.4. Reaction of 1a with 1,2-diaminobenzene or 2-aminophenol

An ethanol solution (40 ml) of **1a** (1 mmol) and 1,2-diaminobenzene (1·5 mmol) was stirred under reflux for 3 h. The reaction mixture was poured into water and the separated product filtered. Dye **6** was obtained in 73% yield. Reaction of **1a** (1 mmol) with 2-aminophenol was carried out in pyridine under reflux for 3 h. The mixture was poured into water, neutralized and the separated product filtered, washed, dried and chromatographed. Dye **7** was isolated in 9% yield.

3.5. Reaction of 1a with 2-aminobenzenethiol (general procedures)

An ethanol solution (100 ml) of **1a** (1 mmol) was added to a solution of 2-aminobenzenethiol (2·2 mmol) and potassium hydroxide (2·2 mmol) in

ethanol (20 ml) at room temperature and the mixture stirred for 12 h. The reaction mixture was poured into water and the solution neutralized with aqueous HCl. The product was filtered, washed with water, dried and chromatographed. Dyes **8** and **9** were obtained in 1·5% and 86·3% yield respectively. The reactions of **1b–1e** with 2-aminobenzenethiol were carried out in a similar manner.

3.6. Oxidation of 9 with hydrogen peroxide

To a suspension of **9** (1 mmol) in acetic acid (100 ml), 30% aqueous hydrogen peroxide (4 mmol) was added and the mixture stirred for 2 h under reflux. The reaction liquor was poured into water and the product isolated by extracting with chloroform. On chromatography, **14** was obtained in 10·8% yield.

3.7. Characterization and identification of products

Compounds **1a**,[11] **1b–1d**,[12] and **1e**[11] are known compounds and were characterized by data described in the literature and the following.

1a: m.p. 197–198 °C; nmr: $\delta = 7{\cdot}32$(2H, s), 12·32(2H, s)
1b: m.p. 187–188 °C; nmr: 1·0–1·6(7H, m), 3·2(2H, q), 5·6(1H, s), 6·0(1H, broad), 12·1(1H, s), 13·9(1H, s)
1c: m.p. 204–205 °C; nmr: 4·42(2H, d), 5·77(1H, s), 6·46(1H, broad), 7·36(5H, s), 12·37(1H, s), 14·13(1H, s)
1d: m.p. 218–219 °C; nmr: 3·95(3H, s), 6·25(1H, s), 12·7(1H, s), 13·22(1H, s)
1e: m.p. 235–236 °C; nmr: 3·97(6H, s), 7·36(2H, s)

2,3-Bis(phenylthio)naphthazarin, **2**
M.p. 171–172 °C; uv λ_{max}(nm), ($\varepsilon \times 10^{-4}$): 475 (0·88), 512(1·1), 528^s(1·1), 580^s(0·71); mass: 406(M^+), 297($M^+ - 109$); nmr: 7·20(2H, s), 7·30(10H, s), 12·27(2H, s); Analysis, Found: C, 65·4; H, 3·7; $C_{22}H_{14}O_4S_2$ requires: C, 65·0; H, 3·5%.

2,3,6(or 7)-Tris(phenylthio)naphthazarin, **3**
M.p. 211–212 °C; uv: 412(0·56), 525^s(1·1), 561(1·2), 606^s (0·79); mass: 514(M^+), 405($M^+ - 109$), 296($M^+ - 218$); nmr: 6·24(1H, s); 7·27(10H, s), 7·51(5H, s), 12·88(1H, s), 12·99(1H, s); Analysis, Found: C, 64·8; H, 4·0; $C_{28}H_{18}O_4S_3$ requires: C, 65·35; H, 3·5%.

5-Hydroxy-6-chloro-7-thia-10-aza-8,9,10-trihydrobenzo[2,3a]-1,4-naphthoquinone, **4**
M.p. >300 °C; uv: 520^{s}(0·34), 562^{s}(0·82), 605(1·4), 655(1·3); mass: 283($M^+ + 2$), 281(M^+), 247($M^+ - 34$); nmr: 3·07–3·24(2H, m), 3·8–4·0(2H, m), 7·00(2H, s), 11·98(1H, broad), 14·39(1H, s); Analysis, Found: C, 50·55; H, 2·6; N, 5·0; $C_{12}H_8ClNO_3S$ requires: C, 51·2; H, 2·9; N, 5·0%.

2,3-Dichloro-5-hydroxy-7-thia-10-aza-8,9,10-trihydrobenzo[2,3a]-1,4-naphthoquinone, **5**
M.p. >320 °C; uv: 472(0·29), 580(0·40), 621(0·92), 672(1·2); mass: 317($M^+ + 2$), 315(M^+), 302($M^+ - 13$), 300($M^+ - 15$); nmr: 3·02–3·22(2H, m), 3·87–4·03(2H, m), 7·02(1H, s), 11·30(1H, broad), 13·73(1H, s).

5-Hydroxy-6-chloro-7,12-dihydro-7,12-diazanaphtho[2,3a]-1,4-naphthoquinone, **6**
M.p. >300 °C; uv: 480^{s}(0·25), 507^{s}(0·37), 551(0·61), 584(0·58); mass: 314($M^+ + 2$), 312(M^+), 278($M^+ - 34$), 262($M^+ - 50$); Analysis, Found: C, 61·2; H, 2·3; N, 8·1; $C_{16}H_9ClN_2O_3$ requires: C, 61·4; H, 2·9; N, 9·0%.

5-Hydroxy-6-chloro-7-oxo-12H-12-azanaphtho[2,3a]-1,4-naphthoquinone, **7**
M.p. 278–280 °C; uv: 434(0·76), 460(0·85), 516^{s}(1·3); 545(1·4); 588^{s}(0·81); mass: 313(M^+); nmr(d_6-DMSO): 6·75(4H, m), 7·27(2H, s), 11·71(1H, broad), 12·69(1H, s).

5-Hydroxy-6-chloro-7-thia-12H,12-azanaphtho[2,3a]-1,4-naphthoquinone, **8**
M.p. >300 °C; uv: 456^{s}(0·48), 490^{s}(0·64), 545^{s}(0·92), 571(1·0), 616(0·68), 642(0·46); mass: 331($M^+ + 2$), 329(M^+), 297($M^+ - 32$), 294($M^+ - 35$); Analysis, Found: C, 58·4; H, 2·0; N, 4·15; $C_{16}H_8ClNO_3S$ requires: C, 59·3; H, 2·45; N, 4·25%.

10,11-Dithia-5H,16H-5,16-diazadinaphtho[2,3a],[2,3c]-1,4-naphthoquinone, **9**
M.p. >310 °C; uv: 563^{s}(0·78), 608(0·97), 665(1·2), 725(1·5); mass: 400(M^+), 336($M^+ - 64$); Analysis, Found: C, 65·6; H, 2·5; N, 6·5; $C_{22}H_{12}N_2O_2S_2$ requires: C, 66·0; H, 3·0; N, 7·0%.

2-Methoxy-10,11-dithia-5H,16H-5,16-diazadinaphtho[*2,3a*],[*2,3c*]-*1,4-naphthoquinone*, **10**
M.p. >300 °C; uv: 570s(0·65), 615(1·1), 668(1·6), 732(1·0); mass: 430(M^+), 398($M^+ - 32$).

2-Butylamino-10,11-dithia-5H,16H-5,16-diazadinaphtho[*2,3a*],[*2,3c*]-*1,4-naphthoquinone*, **11**
M.p. 230–231 °C; uv: 568s(0·32), 622(0·85), 673(1·5), 735(1·4); mass: 471(M^+), 456($M^+ - 15$), 428($M^+ - 43$); nmr(d_6-DMSO): 0·91(3H, t), 1·25–1·66(4H, m), 3·03–3·60(2H, m), 5·74(1H, s), 6·50–7·39(8H, m), 7·88(1H, broad), 12·77(1H, s), 16·69(1H, s).

2-Benzylamino-10,11-dithia-5H,16H-5,16-diazadinaphtho[*2,3a*],[*2,3c*]-*1,4-naphthoquinone*, **12**
M.p. >320 °C; uv: 568s(0·22), 619(0·76), 673(1·5), 735(1·3); mass: 505(M^+), 415($M^+ - 90$), 400($M^+ - 105$).

1,4-Dimethoxy-10,11-dithia-5,16-diazadinaphtho[*2,3a*],[*2,3c*]-*naphthalene*, **13**
M.p. 262–263 °C; uv: 496(1·3); mass: 428(M^+), 426($M^+ - 2$), 415($M^+ - 13$), 400($M^+ - 28$); nmr: 3·98(6H, s), 7·23–7·31(8H, m), 7·55–7·78(2H, m); Analysis, Found: C, 68·0; H, 3·5; N, 6·2; $C_{24}H_{16}N_2O_2S_2$ requires: C, 67·3; H, 3·8; N, 6·5%.

10,11-Dithia-5H,16H-5,16-diazadinaphtho[*2,3a*],[*2,3c*]-*1,4-naphthoquinone-10,11-dioxide*, **14**
M.p. 306–307 °C; uv: 410(0·65), 515(0·45), 624s(0·27), 685(0·73), 748(1·6), 827(1·8); mass: 432(M^+).

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