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Novel Syntheses of Anthraquinonoid Near-Infrared Absorbing Dyes

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SUMMARY

New series of anthraquinonoid near-infrared absorbing dyes (hereinafter referred to as infrared dyes) for optical recording media were synthesised by the ring-closure reaction between 2,3-dibromoquinizarins and potassium 2-aminobenzenethiolate. These dyes absorb near-infrared light at 700–810 nm. It was found that substitution of electron-accepting groups, such as tetrahalogeno or the dicarboximide residue, on the quinizarin residue produces a large bathochromic shift of 40–100 nm, and that of the electron-donating alkoxy group at the 5-position of the thiol also produces a bathochromic shift of 25–40 nm.

1. INTRODUCTION

Infrared quinonoid dyes have been developed as functional dyes for optical information-recording media. A new organic medium incorporating infrared dyes, having a single-layer structure, can be recorded and played back by a laser diode through a substrate, and shows excellent long-term stability properties. As the gallium–aluminium–arsenic (GaAlAs) diode laser emits infrared light at 800–830 nm, the dyes have to absorb light in the range 700–830 nm. Recently some infrared dyes such as the squarylium and pentamethine cyanine dyes have been reported as suitable for an optical information-recording medium for semiconductor

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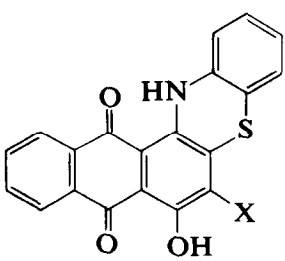
lasers.[1] We have also reported, in connection with these subjects, the syntheses[2] and some characteristics[3] of 5-amino-8-arylamino-2,3-dicyano-1,4-naphthoquinones, and the syntheses of deep coloured aminonaphthoquinonoid dyes.[4]

In this paper, we wish to report the syntheses of new types of anthraquinonoid infrared dyes obtained by the reaction of 2,3-dibromoquinizarins with potassium 2-aminobenzenethiolate and to correlate the colour–structure properties of these dyes.

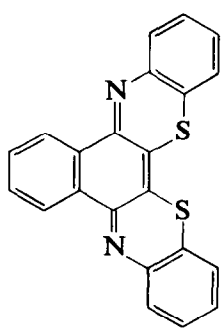
2. RESULTS AND DISCUSSION

2.1 Reaction of 2,3-dibromoquinizarins with potassium 2-aminobenzenethiolate

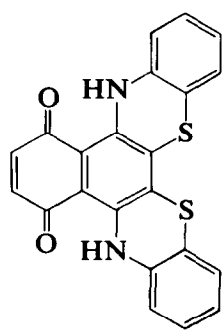
It has been shown that the reaction of 2-bromoquinizarin with 2-aminobenzenethiol gives 7-hydroxy-14*H*-naphtho[2,3-*a*]phenothiazine-8,13-dione, **1a**, which has been evaluated as a deep coloured disperse dye for polyester.[5] On the other hand, the reaction of 2,3-dichloro-1,4-naphthoquinone with 2-aminobenzenethiol in pyridine gives the bis-ring-closure product, 10,11-dithia-5,16-diazadinaphtho[3,2-*a*], [2,3-*c*]-naphthalene **2**.[6] We have also reported that the reaction of 2,3-dibromonaphthazarin with potassium 2-aminobenzenethiolate gives the bis-ring-closure product, 10,11-dithia-5*H*,16*H*-5,16-diazadinaphtho-[3,2-*a*], [2,3-*c*]-1,4-naphthoquinone, **3**, which absorbs near-infrared light at 725 nm.[4] The characteristics of dye **3** as an infrared dye for optical



1
a, X = H 685 nm[5]
b, X = Br



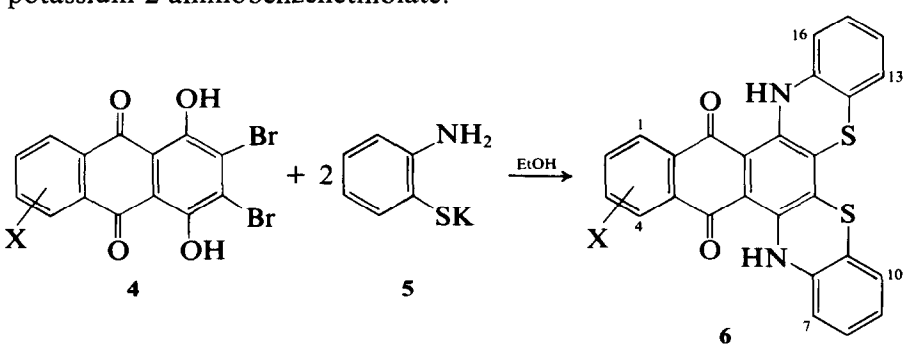
2
538 nm[6]



3
725 nm[4]

recording media are under investigation and the syntheses of anthraquinone analogues of dye **3** is of interest in respect of their characteristics as functional dyes and in their colour-structure relationship.

Reaction of 2,3-dibromoquinizarin **4a** with potassium 2-aminobenzenethiolate, **5**, gave the bis-ring-closure product **6a**, 11,12-dithia-6*H*,17*H*-6,17-diazadinaphtho[3,2-*a*], [2,3-*c*]-5,18-anthraquinone, in 74% yield, and none of the corresponding mono-ring-closure product **1b** was obtained. Dye **6a** absorbs infrared light at 712 nm in chloroform and produces a hypsochromic shift of 13 nm in comparison to the corresponding naphthoquinone analogue **3**. As the first visible absorption of anthraquinonoid dyes is caused by the intramolecular charge-transfer character of the transition,[7] the introduction of an electron-acceptor group into the quinone residue and/or that of an electron-donor group into the phenothiazine residue of dye **6** may produce a bathochromic shift of the first band. A series of anthraquinonoid infrared dyes **6** were synthesised by the reaction of substituted 2,3-dibromoquinizarins with potassium 2-aminobenzenethiolate.

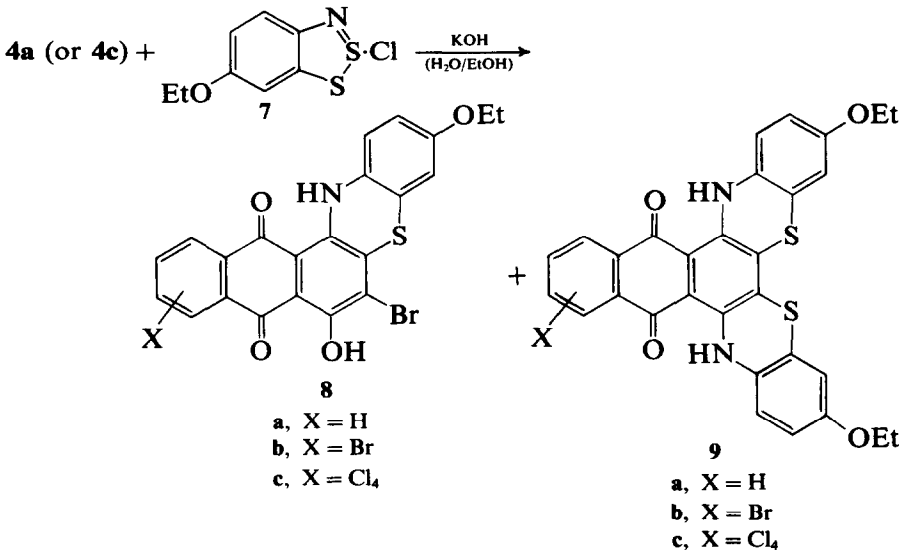


4 **5** **6**

a, X = H; **b**, X = Br; **c**, X = Cl_4; **d**, X = 2—CO_2H; **e**, X = CO_2Et; **f**, X = 2, 3—$(CO_2H)_2$; **g**, X = 2, 3—$(CO)_2O$; **h**, X = 2, 3—$(CO)_2NPh$; **i**, X = 2, 3—$(CO)_2NC_6H_4CN$ (*p*)

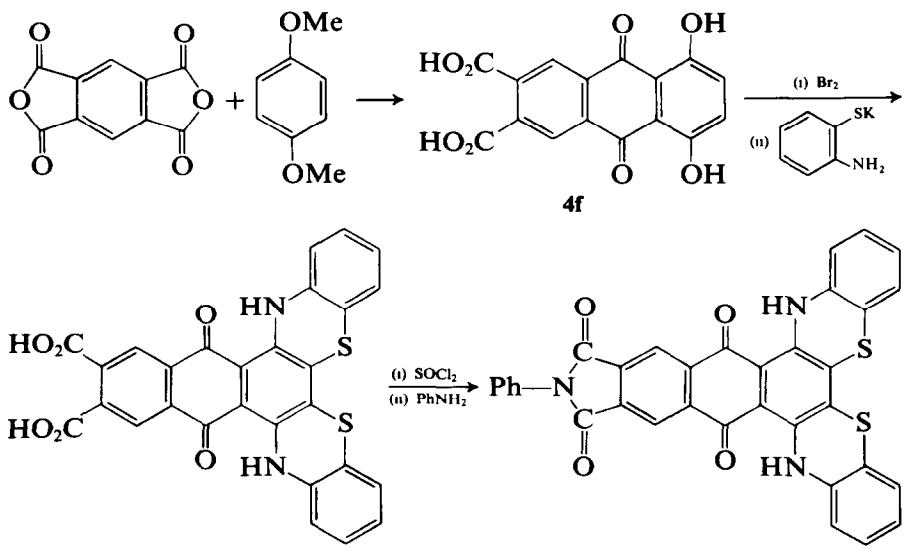
Ethoxy substituted dyes **8** and **9** were synthesised by the reaction of 2,3-dibromoquinizarins (**4a** or **4c**) with 6-ethoxy-1,3,2-benzothiazathiolium chloride, **7**, which is the precursor of 5-ethoxy-2-aminobenzenethiol. In the reaction, the mono-ring-closure (**8**) and the bis-ring-closure (**9**) products were obtained.

Quinizarin derivatives (**4c**, **4d** and **4f**) were synthesised by the Friedel–Crafts reaction of substituted phthalic anhydride with 1,4-dimethoxybenzene. Bromination of quinizarin was carried out in sulphuric acid with excess of bromine. Dibromoquinizarin, **4a**, was obtained mainly at 100 °C and tribromoquinizarin, **4b**, was mainly



produced at 120 °C. Dye **6e** was obtained by the esterification of **6d** with ethanol. Dehydration of **6f** with thionyl chloride gave **6g**. Dyes **6h** and **6i** were synthesised by the reaction of **6g** with substituted anilines. Reaction pathways are shown in Scheme 1.

Results of the reaction between **4** and **5** or **7** are summarised in Table 1.



Scheme 1

TABLE 1
Reaction of Dibromoquinizarins **4** with 2-Aminobenzenethiols **5** or **7**

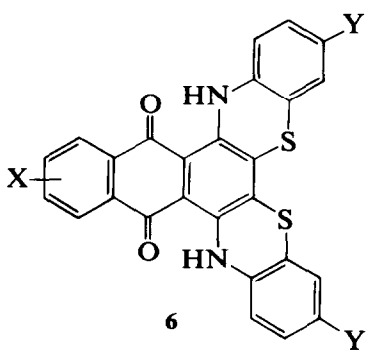
Run	*Reactant*	*Reagent*	*Solvent*	*Temp.* (°C)	*Time* (*h*)	*Product* (*yield* %)[a]
1	**4a**	5	EtOH	50	7	**6a** (74)
2	**4c**	5	EtOH	80	5	**6c** (78)
3	**4d**	5	EtOH	70	5	**6d** (85)
4	**4f**	5	EtOH	50	6	**6f** (85)
5	**4a**	7	H_2O + EtOH (1:1)	50	5	**8** (7·2)[b], **9** (6·1)[b]

[a] Isolated yield based on reactant used.
[b] Isolated yield after chromatography.

The ring-closure reactions between **4** and **5** proceeded easily and the corresponding bis-ring-closure product **6** was obtained as the only product in 75–85 % yield. The reactivity of **7** against **5** was very poor, and **8** was obtained together with **9** in a low yield. The formation of 5-ethoxy-2-aminobenzenethiol by alkaline hydrolysis of **7** failed.

2.2. Visible absorption spectra

We have quantitatively evaluated the colour–structure relationship of anthraquinonoid dyes by means of the PPP MO method.[7] In the case of dye **6** (Scheme 2), introduction of an electron-accepting group X and/or of an electron-donating group Y may produce a bathochromic shift of the first visible absorption band.



6

X = Acceptor
Y = Donor

Scheme 2

The substituent effects of the visible absorption spectra of anthraquinonoid infrared dyes are shown in Table 2. Introduction of the ethoxy group as Y into **1a** produced a 42 nm red shift (dye **8a**) and into **6a** produced a 23 nm red shift in dye **9a**. Substitution by the ethoxy group as electron donor and the tetrachloro group as electron acceptor into **8c** produced an additive large bathochromic shift of 88 nm compared to **1a**. However, substitution by strong electron-accepting groups such as tetrachloro (**6c**) and dicarboxyl groups (**6f**) produced a large bathochromic shift of about 100 nm, but substitution by the bromo (**6b**) and

TABLE 2
Visible Absorption Spectra of Anthraquinonoid Infrared Dyes[a]

Dye No.	*X*	*Absorption maxima*				$\Delta\lambda_2$	$\Delta\lambda_1$
		$\lambda_{2\,max}$ (*nm*)	$\varepsilon \times 10^{-4}$	$\lambda_{1\,max}$ (*nm*)	$\varepsilon \times 10^{-4}$		
1a	H	635	1·10	690	0·86	—	—
8a	H	672	—[b]	732	—[b]	37	42
8c	Cl_4	708	1·44	778	1·21	73	88
6a	H	655	1·77	712	1·50	—	—
9a	H	683	—[c]	735	—[c]	28	23
6b	Br	660	2·31	717	1·99	5	5
6c	Cl_4	748	1·45	805	1·36	93	93
6d	2-CO_2H	655	—[d]	715	—[d]	0	3
		646	1·14[e]	702	0·97[e]		
6e	2-CO_2Et	650	—[d]	708	—[d]	−5	−4
		645	0·97[e]	700	0·89[e]		
6f	2,3-$(CO_2H)_2$	725	—[d]	800	—[d]	70	88
		695	1·68[e]	755	1·49[e]		
6g	2,3-$(CO)_2O$	750	—[d]	810	—[d]	95	98
		690	1·38[e]	760	0·92[e]		
6h	2,3-$(CO)_2NPh$	685	—[d]	750	—[d]	30	38
		650	1·28[e]	705	1·21[e]		
6i	2,3-$(CO)_2NC_6H_4CN$-(P)	690	—[d]	750	—[d]	35	38
		680	1·36[e]	740	1·28[e]		

[a] Measured in chloroform in a concentration of 1×10^{-4} mol litre^{-1}.
[b] Mass spectra showed traces of **8b** present.
[c] Mass spectra showed traces of **9b** present.
[d] Solubility was too low to determine molar extinction coefficients accurately.
[e] Measured in dimethylformamide.

ethoxycarbonyl groups (**6e**) was less effective. Almost all of these dyes absorbed infrared light over 700 nm, and dyes **6c** and **6f** absorbed infrared light over 800 nm. It is known that some types of ionic dye such as cyanine and squarylium absorb infrared light over 800 nm, but few of these dyes are of the disperse type. The characteristics of these dyes for optical information-recording media are under investigation and will be reported separately.

3. EXPERIMENTAL

All melting points are uncorrected. The visible spectra were measured using a Shimadzu UV-240 spectrophotometer. The mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 80 eV. Elemental analysis were recorded on a Yanako CHN recorder MT-2. Column chromatography was carried out on silica gel (Wakogel C-300) using chloroform or benzene as eluent.

3.1. Materials

Quinizarin was commercial grade and was used after recrystallisation from benzene. Tetrachloroquinizarin and 6-carboxyquinizarin were synthesised by the usual methods. Quinizarin-6,7-dicarboxylic acid was synthesised by the Friedel–Crafts reaction of pyromellitic acid anhydride with 1,4-dimethoxybenzene at 200 °C for 1 h.

> Yield 90%, m.p. >300 °C. UV(DMF) 540, 620, 675 nm. Analysis, Found: C, 58·79; H, 2·68; $C_{16}H_8O_8$ requires: C, 58·53; H, 2·44%.

2-Aminobenzenethiol was reagent grade and used without further purification.

3.2. 2,3-Dibromoquinizarin 4a: general procedures

Quinizarin (0·1 mol) and iodine (50 mg) were dissolved in conc. sulphuric acid (400 ml), and bromine (11 ml; 0·22 mol) was added dropwise to the solution at 100 °C. The reaction mixture was stirred at 140 °C for 6 h, then poured into water. The separated product was collected by filtration, washed with water and recrystallised from benzene to give **4a** in 83% yield. Other 2,3-dibromoquinizarins were prepared by similar procedures. Results are summarised in Table 3.

TABLE 3
Preparation of 2,3-dibromoquinizarins

Dye	*M.p.* (°C)	*Yield* (%)	*Temp.* (°C)	*Mol. formula*	*MS* M^{+a}	*Analysis* (%)	
						Calcd	*Found*
4a	239–240	83	100	$C_{14}H_6O_4Br_2$	396	C: 42·42 H: 1·51	42·85 1·37
4b	260–263	70	140	$C_{14}H_5O_4Br_3$	475	C: 35·29 H: 1·06	36·00 1·00
4c	281–282	60	130	$C_{14}H_2O_4Cl_4Br_2$	—	C: 31·34 H: 0·37	30·88 0·42
4d	> 300	65	140	$C_{15}H_6O_6Br_2$	440	C: 40·72 H: 1·36	41·27 0·92
4f	> 300	56	180	$C_{16}H_6O_8Br_2$	—	C: 39·51 H: 1·23	40·02 1·57

[a] Fragments caused by the chlorine and bromine isotopes were observed.

3.3. Reaction of 2,3-dibromoquinizarin 4a with potassium 2-aminobenzenethiolate: general procedures

A mixture of 2-aminobenzenethiol (11·1 mmol) and potassium hydroxide (11·1 mmol) in ethanol (100 ml) was added dropwise to a suspension of 2,3-dibromoquinizarin **4a** (5·05 mmol) in ethanol (300 ml) at 50 °C. The reaction mixture was stirred at 50 °C for 7 h, poured into water and neutralised with aqueous hydrochloric acid. The separated product was collected by filtration, washed with water and recrystallised from chloroform to give **6a** in 74 % yield. Other bis-ring-closure products were prepared by similar procedures. Characterisation data of the products thus obtained are as follows:

6a M.p. 246–247 °C. Mass: 450(M^+), 418(M^+ −32). Analysis, Found: C, 69·28; H, 3·27; N, 6·16; $C_{26}H_{14}N_2O_2S_2$ requires: C, 69·33; H, 3·11; N, 6·22 %.

6b M.P. > 300 °C. Mass: 529(M^+). Analysis, Found: C, 59·46; H, 2·58; N, 5·28; $C_{26}H_{13}N_2O_2BrS_2$ requires: C, 59·09; H, 2·46; N, 5·28 %.

6c M.p. > 300 °C. Analysis, Found: C, 53·65; H, 2·00; N, 3·90; $C_{26}H_{10}N_2O_2Cl_4S_2$ requires: C, 53·08; H, 1·71; N, 4·76 %.

6d M.p. >300°C. Analysis, Found: C, 66·02; H, 2·71; N, 3·26; $C_{27}H_{14}N_2O_4S_2$ requires: C, 65·59; H, 2·83; N, 5·67%.

6e M.p. >300°C. Analysis, Found: C, 66·74; H, 3·92; N, 4·21; $C_{29}H_{18}N_2O_4S_2$ requires: C, 66·66; H, 3·44; N, 5·36%.

6f M.p. >300°C. Analysis, Found: C, 62·38; H, 2·23; N, 4·73; $C_{28}H_{14}N_2O_6S_2$ requires: C, 62·45; H, 2·60; N, 5·20%.

6g M.p. >300°C. Analysis, Found: C, 62·68; H, 2·24; N, 6·18; $C_{28}H_{12}N_2O_5S_2$ requires: C, 64·61; H, 2·31; N, 5·38%.

6h M.p. >300°C. Analysis, Found: C, 68·38; H, 2·23; N, 7·22; $C_{34}H_{17}N_3O_4S_2$ requires: C, 68·57; H, 2·85; N, 7·06%.

6i M.p. >300°C. Analysis, Found: C, 69·36; H, 3·30; N, 9·16; $C_{35}H_{16}N_4O_4S_2$ requires: C, 67·74; H, 2·58; N, 9·03%.

8a Mass: 469($M^+ + 2$), 467(M^+), 438($M^+ - 29$).

8c Mass: 609($M^+ + 6$), 607($M^+ + 4$), 605($M^+ + 2$), 603(M^+), 574($M^+ - 29$). Analysis, Found: C, 45·30; H, 1·79; N, 2·79; $C_{22}H_{10}NO_4BrCl_4S$ requires; C, 43·60; H, 1·66; N, 2·31%.

9a Mass: 538(M^+), 509($M^+ - 29$), 480($M^+ - 58$).

3.4. Preparation of 6g from 6f

A mixture of dye **6f** (20·5g; 38 mmol) and thionyl chloride (9 g; 76 mmol) in *o*-dichlorobenzene (170 ml) was stirred under reflux for 2 h, then solvent was distilled off under reduced pressure to give dye **6g**, which was used without further purification.

3.5. Preparation of 6i from 6g

A mixture of dye **6g** (3g; 5·7 mmol) and 4-aminobenzonitrile (28 mmol) in *o*-dichlorobenzene (50 ml) was stirred under reflux for 6h. Solvent was evaporated under reduced pressure and the resulting solid was recrystallised from DMF/H_2O (5:1) to give **6i** in 79% yield. Dye **6h** was prepared similarly by the reaction of **6g** with aniline.

3.6. 6-Ethoxy-[1,3,2]benzothiazathiolium chloride,7

To a solution of *p*-ethoxyaniline (3 g; 22 mmol) in chlorobenzene (45 ml), sulphur monochloride (7 g; 52 mmol) was added dropwise over 30 min at

60 °C, and the mixture stirred at 90 °C for 2 h. The separated product was collected by filtration and washed with chlorobenzene to give **7** in quantitative yield

M.p. 189–190 °C. NMR($CDCl_3$): $\delta = 1{\cdot}64$(t,3H), 4·97(q,2H), 7·8–8·6(m,3H). Analysis: C, 41·09; H, 3·71; N, 6·07; $C_8H_8NOS_2Cl$ requires: C, 41·11; H, 3·45; N, 5·99%.

3.7. Reaction of 4a with 7

To an ethanol solution (250 ml) of **4a** (500 mg) and potassium hydroxide (200 mg), **7** (650 mg) in water (250 ml) was added and the mixture stirred at 50 °C for 5h. The mixture was then added to water and the product was collected by filtration, washed with water, dried and chromatographed on silica gel to give **8a** (7·2%) and **9a** (6·1%). Dye **8c** was obtained from the reaction of **4c** with 7 in 3·6% yield after chromatography, but **9c** was not obtained.

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