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Derivatives of 14H-Naphtho[2,3-*a*]Phenothiazine-8,13-Dione. Part 2: Syntheses from 1,4-Dihydroxy-5-(6-,7-,8-)Substituted Anthraquinones

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ABSTRACT

*The synthesis of some 7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-diones containing electron donor and acceptor substituents in the unhydroxylated anthraquinone ring affords colorants of near-infrared absorbing potential. The relative influence of electron donor and acceptor substituents on the absorption maxima of the dyes is reviewed.*

1 INTRODUCTION

The reaction between 1,4-dihydroxyanthraquinone and various 2-substituted derivatives with 2-aminobenzenethiol has been shown to give, in the majority of cases, 7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**I**, X = H).[1] Only with 2-alkylquinizarins were 6-substituted analogues obtained, the λ_{max} values of which were similar to that of **I** (X = H). In the bis-ring closed analogue, viz. 11,12-dithia-6H,17H-6,7-diazanaphtho[3,2-*a*][2,3-*c*]-5,18-anthraquinone (**II**), PPP-MO data indicate[2] that introduction of electron acceptor substituents into the unsubstituted phenyl ring of the anthraquinone moiety should result in bathochromic shifts of the first visible absorption band. Several derivatives of this type were reported. The results[2] showed that when one electron acceptor carboxylic acid or ester group was present in the β-position, colour shifts were small. Introduction of an electron acceptor substituent in both β-positions, exemplified

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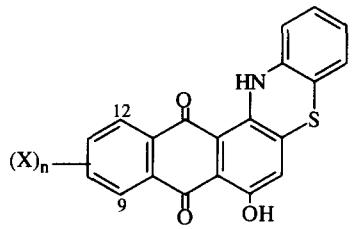
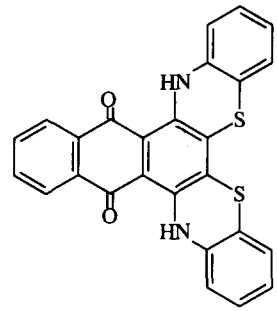


I



II

by the bis-carboxylic acid or anhydride, gave extensive bathochromic shifts of 90–100 nm. Less significant shifts (*c.* 40 nm) resulted from the presence of a dicarboximide moiety across the two β-positions. One halogeno substituent (bromo, presumably in the α-position) gave very small shifts in λ_{max} (5 nm), but substitution at all four α- and β-positions by chloro gave a similar shift to that from the bis-β-carboxy derivatives.

PPP-MO calculations for **I** (X = H), using previously reported parameters,[1] indicated that the presence of electron acceptor substituents should also result in bathochromic shifts, particularly at the β-positions. We report here the synthesis of some colorants **I** in which X is either an electron donor or acceptor, and an evaluation of the colour shifts resulting from such substitutions.

2 EXPERIMENTAL

2.1 General

The substituted 1,4-dihydroxyanthraquinones used were of commercial origin (6,7-dichloro- and 5,8-dichloroquinizarin, 1,2,5,8-tetrahydroxyanthraquinone; Aldrich), industrial origin (1,4,5,8-tetrahydroxyanthraquinone; Yorkshire Chemicals plc), or were samples originating in these laboratories (1,4,5-trihydroxyanthraquinone and 5,6,7,8-tetrachloroquinizarin). Commercial and industrial samples were purified by column chromatography prior to use. Column chromatography was effected on Silica gel (Janssen Chimica), applying the dyes from solution in chlorobenzene and eluting with toluene containing up to 10% ethyl acetate as appropriate.

Electronic spectra were recorded on a Philips PU 8730 and mass spectra (EI) on an AEI MS 902.

2.2 6,9-Dihydroxybenzo[*g*]quinoline-5,10-quinone (5-azaquinizarin) and 6,9-dihydroxybenzo[*g*]isoquinoline-5,10-quinone (6-azaquinizarin)

These compounds were prepared by Friedel–Craft type interaction of quinolinic anhydride or of cinchomeronic anhydride, respectively, with 1,4-dimethoxybenzene following the reported procedure.[3] 5-Azaquinizarin was obtained in 45% yield, m.p. 237–238°C (lit.[3] 237–240°C); *M/z* (EI) 241, M^+, 100%, and 6-azaquinizarin in 37% yield, m.p. 208–210°C (lit.[3] 210–212°C); *M/z* (EI) 241, M^+, 100%).

2.3 6,7-Bisthiophenoxyquinizarin

Thiophenol (5 g) was added to a stirred solution of 6,7-dichloroquinizarin (1 g) in 2-methoxyethanol (30 ml) and the mixture refluxed for 6 h. The cooled liquor, after dilution with methanol (10 ml), was filtered and the residue washed with a little cold methanol and then with water. Yield 0·93 g (63%), dark orange needles, m.p. 191–192°C; *M/z* (EI) 456, M^+, 100%.

2.4 6,7-Bisphenylsulphonylquinizarin

6,7-Bisthiophenoxyquinizarin (0·5 g) was refluxed in glacial acetic acid (20 ml) and H_2O_2 (30% wt aq. solution, 5 ml) added dropwise over 30 min. After refluxing for 2 h, the solution was cooled, stirred into ice-water (200 ml) and the precipitate collected; yield 0·48 g (84%). Recrystallisation from toluene gave reddish-orange needles, m.p. 271–272°C; *M/z* (EI) 520, M^+, 100%.

2.5 Synthesis of 7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-diones (I)

Unless otherwise indicated, reactions of the substituted quinizarins (0·5 g) with 2-aminobenzenthiol (10 mole equivalents) were carried out in DMF (15 ml) following a similar procedure to that previously reported,[1] viz. with dilution of the final reaction liquor with methanol (50 ml), filtering and washing the product with hot methanol until all soluble contaminants had been removed. All reactions were monitored by TLC, the reaction product appearing as high R_f blue to green material (Kodak Chromagram Sheets, Type 13181 Silica Gel; test sample applied from solution in DMF and developed with toluene : ethyl acetate : glacial acetic acid 7 : 2 : 1). Products thus obtained were generally of high purity, **I** being relatively insoluble during the methanol washing.

7,9-(and/or 7,12-)Dihydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.1**)
From 1,4,5-trihydroxyanthraquinone; reaction at 140–145°C for 1 h; yield after methanol washing, 80%; m.p. 284–286°C; *M/z* (EI) 361, M^+, 100%.

7,9,12-Trihydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.2**)
From 1,4,5,8-tetrahydroxyanthraquinone; reaction at 135–140°C for 2 h; yield after methanol washing, 75%; m.p. 311–313°C; *M/z* (EI) 377, M^+, 100%.

7,9,10-(and/or 7,11,12-)Trihydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.3**)
From 1,2,5,8-tetrahydroxyanthraquinone (quinalizarin); reaction at 140–145°C for 1 h; yield after methanol washing, 85%; m.p. 324–326°C; *M/z* (EI) 377, M^+, 100%.

10,11-Dichloro-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.4**)
From 6,7-dichloroquinizarin; reaction at 80°C for 1 h; yield after methanol washing, 68%; m.p. 320–322°C; *M/z* (EI) 414, M^+, 100%.

9,12-Dichloro-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.5**)
5,8-Dichloroquinizarin (0·25 g), 2-aminobenzenethiol (5 ml), DMF (15 ml) and cupric chloride (0·3 g) were stirred at room temperature for 48 h; the liquor was diluted with methanol (15 ml), stirred for 1 h, filtered and the residue washed with warm methanol until all the cherry-red coloured contaminant was removed. The resultant steel-blue product was extracted with dichloromethane, giving, after removal of solvent, 55% of a dark blue product; m.p. 275–277°C; *M/z* (EI) 414, M^+, 100%.

9,10,11,12-Tetrachloro-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.6**)
From 5,6,7,8-tetrachloroquinizarin; reaction at 80°C for 1 h; yield after methanol washing, 85%; m.p. >340°C; *M/z* (EI) 483, M^+, 100%.

9-(and/or 12-)Aza-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.7**)
5-Azaquinizarin (0·3 g) and 2-aminobenzenethiol (1·5 g) were refluxed in ethanol (20 ml) for 1 h. The liquor was stirred into ice-water (30 ml), the product (0·27 g) filtered and washed with cold methanol. Column chromatography gave 0·23 g (85%) of the title compound(s); m.p. 272–275°C; *M/z* (EI) 346, M^+, 100%.

10-(and/or 11-)Aza-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.8**)
From 6-azaquinizarin, following the same procedure as for **1.7** above. Yield 75%; m.p. 256–258°C; *M/z* (EI) 346, M^+, 100%.

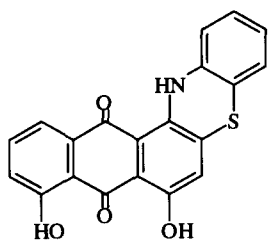
10,11-Bisthiophenoxy-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.9**)
From 6,7-bisthiophenoxyquinizarin; reaction at 140–145°C for 30 min. Yield after methanol washing, 80%; m.p. 280–282°C; *M/z* (EI) 561, M^+, 100%.

10,11-Bisphenylsulphonyl-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (**I.10**)
6,7-Bisphenylsulphonylquinizarin (0·5 g) was stirred at 80–85°C for 40 min in 2-methoxyethanol (20 ml) with addition of boric acid (1 g). 2-Aminothiophenol (2·5 g) was added and the mixture refluxed for 2 h, before cooling and diluting with methanol (50 ml). The product was filtered and washed with methanol to give 0·41 g (85%) of **I.10**; m.p. 335–337°C; *M/z* (EI) 625, M^+, 100%.

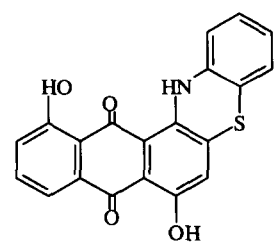
3 RESULTS AND DISCUSSION

3.1 Synthesis of dyes

Using the conditions previously reported[1] for the reaction of quinizarin derivatives with 2-aminobenzenethiol, viz. in DMF at 140–145°C, a similar reaction proceeded with 1,4,5-trihydroxyanthraquinone, 1,4,5,8-tetrahydroxy- and 1,2,5,8-tetrahydroxyanthraquinones, and with 6,7-bisthiophenoxyquinizarin. Good yields of high purity material resulted after methanol washing of the product filtered from the reaction liquor. With the 1,4,5-trihydroxy and 1,2,5,8-tetrahydroxy derivatives, isomer formation is possible, e.g. **I.1(a)** and **I.1(b)**; all data reported pertain to such possible mixtures. Similar reactions, under the conditions used for **I.1**, with 1,5- and 1,8-dihydroxyanthraquinones (A. T. Peters, unpublished data) showed that whilst reaction of the 1,5-isomer proceeded (but with considerably less facility than with quinizarin, and over a reaction time relatable to



I.1(a)



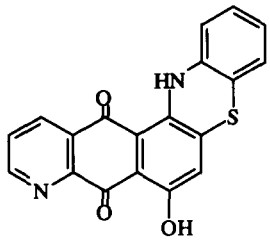
I.1(b)

that for 1-hydroxyanthraquinone[1]), reaction with the 1,8-isomer was more inhibited. By analogy, it is possible therefore that the major reaction product is **I.1(a)**; similar conclusions may be pertinent in other cases where isomer formation is possible.

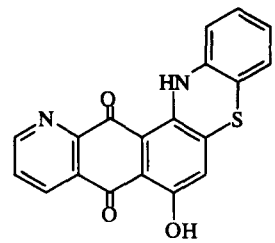
With 6,7-dichloroquinizarin, reaction at higher temperature resulted, in addition to the anticipated product at *m/z* 414, in components at *m/z* 466 and 591; formation of the latter was inhibited by carrying out the reaction at 80°C, at which temperature only **I.4** was formed. The by-products presumably arise by interaction of 2-aminobenzenethiol with the chloro substituents, giving the bis-2'-aminophenylthio derivative (**I**, X = 10,11-$SC_6H_4NH_2$-2) (*m/z* 591) and the ring-closed 5,10-dithia-15H,18H-15,18-diazadinaphtho[2,3-*a*][2,3-*e*]-8,17-anthraquinone (and/or isomeric product) (**I**, X = 10,11- and/or 11,10-SC_6H_4NH-) (*m/z* 466). Mixtures of these two products, formed on further condensation of **I.4** with 2-aminobenzenethiol, could not be fully resolved due to their very similar R_f values and solubilities in a range of recrystallisation solvents.

Similar reactions with 5,8-dichloroquinizarin were unsatisfactory; at 80°C, and after 2 h, only an estimated 5–10% of blue product was evident on TLC, the major component appearing as a deep cherry-red zone. Upward adjustment of reaction time and/or temperature gave no improvement. No attempt was made to isolate the red compound, which presumably arose by reaction of the α-chloro substituent(s) with the thiol. Reaction at ambient temperature, however, showed *c.* 30% formation of the required blue product after 8 h, not significantly changing with more prolonged reaction. Addition of cupric chloride gave a significant improvement, *c.* 75% of blue product being apparent after 48 h (ambient temperature); the red by-product was the major contaminant, but with the usual 'methanol' work-up, this was fully eliminated during the washing process. The reaction parallels that reported for the copper catalysed direct amination of, for example, quinizarin.[4,5]

No red component was evident in reactions from 5,6,7,8-tetrachloroquinizarin, despite the two α-chloro substituents. However, at high temperatures dehalogenation side-reactions occurred, but facile reaction proceeded at 80°C in both DMF and *N*-methylpyrrolidone. Using high temperature reaction in DMF for 6,7-bisphenylsulphonylquinizarin was also unsatisfactory, replacement of the phenylsulphonyl groups occurring, with formation of the *m/z* 466 and *m/z* 591 products noted above. The preferred reaction conditions involved the use of 2-methoxyethanol as reaction medium, in the presence of boric acid. Excellent yields of **I.10** resulted, and the method was found to have wide applicability in the synthesis of derivatives of 14H-naphtho[2,3-*a*]phenothiazine-8,13 diones. Details for this will be reported separately.



I.7(a)

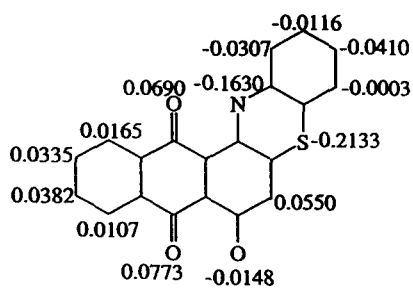


I.7(b)

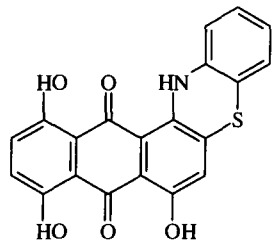
Modified reaction conditions were also necessary with 5- and 6-aza-quinizarins, high temperature reaction in DMF resulting in the formation of dark coloured material, with very low recovery yield of **I** following a chromatography work-up. Reaction was, however, found to proceed readily in ethanol at reflux. As with reactions from 1,4,5-trihydroxy- and 1,2,5,8-tetrahydroxyanthraquinone, isomer formation is possible in both cases, e.g. **I.7(a)** and **I.7(b)**. The isomer content was not evaluated.

3.2 Electronic spectra

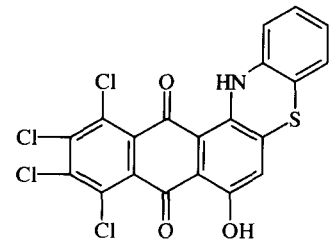
Using the input parameters previously noted for 7-hydroxy-14H-naphtho-[2,3-*a*]phenothiazine-8,13-dione,[1] the PPP SCF-CI programme used gave the electron density changes in the molecule as shown in **III**. The λ_{max} calculations were in good accord with experimental values for the principal electron transition, viz. the lower wavelength visible absorption (calculated λ_{max} 580 nm, observed λ_{max} in cyclohexane 582 nm). Additional vibronic transitions at 625 nm and 682 nm, responsible for the potential NIR-absorption of **I** (X = H) and its derivatives, are not calculated within the programme framework used. The charge density changes shown in **III** indicate the possibility of further bathochromic shifts arising from appropriate substitution of electron donor substituents in the phenyl ring of the heterocyclic moiety and of electron acceptor substituents in the un-



III



I.2
λ max 623 (sh), 674, 734 nm



I.6
λ max 622 (sh), 676, 740 nm

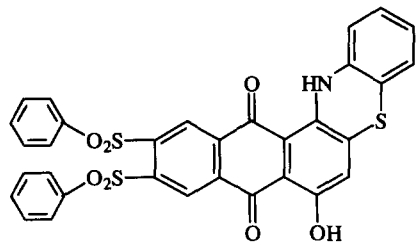
substituted phenyl ring of the anthraquinone moiety. PPP-MO calculations for the bis-condensed derivative **II** afforded similar indications, and pertinent substitution was found to result in shifts in accord with the predictions.[2]

This present investigation was concerned only with substituent effects in the anthraquinone ring system. In contrast to the electron density changes shown in **III**, the presence of electron donor substituents gave significant bathochromic shifts, particularly for α-hydroxy substitution. The extent of the shift increases as the degree of α-hydroxy substitution increases (cf. **I.1**, **I.2**) although additional β-hydroxy substitution is not as effective (**I.3**).

The presence of the strongly donating phenylthio group in both β-positions (**I.9**) also results in bathochromic shifts, λ_{max} being of a similar order to that of the α,β-dihydroxy derivative **I.3**.

Chloro-substitution is also bathochromic; comparison between the α- and β-substituted isomers **I.4** and **I.5** shows the α-substitution pattern to be the more effective, but the conjoint α- and β-substitution in the tetrachloro derivative **I.6** results in extensive displacement of λ_{max} to longer wavelength. It is of interest to note that although the PPP-MO data imply a preferred substitution by electron acceptor substituents, absorption parameters of the tetrachloro-derivative **I.6** are almost identical with those of the donor substituted dihydroxy derivative **I.2**.

Replacement of one of the ring carbon atoms in the unhydroxylated ring of **I** by the electron withdrawing —N= also results in bathochromic shifts (**I.7** and **I.8**), the effect being stronger in a β-orientation. Data in Table 1 for **I.7** and **I.8** are for spectra in dichloromethane, these compounds being relatively insoluble in chlorobenzene. Values of λ_{max} for **I** are broadly relatable in the two solvents, although both bathochromic (e.g. **I** (X = H), λ_{max} 593 sh, 635 and 687 nm) and hypsochromic effects (e.g. **I.4**, λ_{max} 599 sh, 648 and 703 nm) can occur in dichloromethane.



I.10

λ max 647 (sh), 705 and 774 nm

The effect of electron withdrawing substituents is most apparent in the phenylsulphone derivative **I.10**; particularly when compared with the analogous phenythio derivative **I.9**. The longest wavelength absorption occurs at 774 nm, a value approaching that of many derivatives of the bis-condensed **II**.

CONCLUSIONS

The development of potential NIR absorbing dyes is possible by introduction of both electron donor and electron acceptor substituents into the unhydroxylated ring of 7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-

TABLE 1
Electronic Spectral Data for **1**

	X	λ_{max}, *log e* *(in chlorobenzene)*[a]		
I	H	584 (sh) (3·95)	625 (4·15)	682 (4·07)
I.1	9-(10-)-OH	620 (sh) (4·08)	644 (4·27)	720 (4·18)
I.2	9,12-$(OH)_2$	623 (sh) (4·12)	674 (4·33)	734 (4·29)
I.3	9,10-(11,12-)-$(OH)_2$	601 (sh) (3·86)	649 (4·02)	704 (3·94)
I.4	10,11-Cl_2	604 (sh) (3·94)	652 (4·13)	710 (4·06)
I.5	9,12-Cl_2	610 (sh) (3·85)	659 (4·09)	718 (3·92)
I.6	9,10,11,12-Cl_4	622 (sh) (4·01)	676 (4·22)	740 (4·26)
I.7	9-(12)C-X is —N=	604 (sh) (3·81)	647 (3·98)	703 (3·89)
I.8	10-(11)C-X is —N=	606 (sh) (4·13)	658 (4·19)	716 (4·15)
I.9	10,11-$(SPh)_2$	600 (sh) (3·72)	649 (3·90)	702 (3·81)
I.10	10,11-$(SO_2Ph)_2$	647 (sh) (4·10)	705 (4·31)	774 (4·25)

[a] All data are for spectra in chlorobenzene, except for **I.7** and **I.8** for which dichloromethane was used.

8,13-dione. The shifts resultant from tetrachloro substitution are similar to those from α,α-dihydroxy substitution, but the presence of the strongly electron accepting sulphone group in the β-positions is especially effective.

ACKNOWLEDGEMENT

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