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

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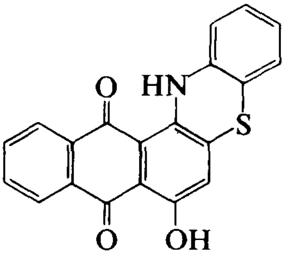
ABSTRACT

*Condensation of 2-substituted-1,4-dihydroxyanthraquinones with 2-aminobenzenethiol generally results in the elimination of the 2-substituent and formation of 7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**I**). In addition to the anticipated replacement of labile 2-substituents such as halogeno, sulphone, carboxamido and* t*-amino, the elimination of ether, thioether, 1° and 2°-amino and hydroxy groups also occurs. 2-Alkyl substituents are retained, affording the 6-alkyl derivatives (**II**). 1,4-Dihydroxyanthraquinone undergoes direct thiolation and ring closure to **I** and similar reaction of 1-hydroxy-4-amino- and 1-hydroxy-4-arylamino-anthraquinones also gives **I**, with preferential reaction* ortho *to the amino group. The use of 1-hydroxy(or amino)-2-bromo-4-aminated anthraquinones, however, yields 7-aminated analogues (**III**). With both the 2- and 3-bromo-derivatives of 1-hydroxy-4-aminoanthraquinone, the reaction proceeds via debromination and subsequent reaction as with 1-hydroxy-4-aminoanthraquinone, giving **I**. The isomeric 6-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione was obtained via 1,3-dihydroxyanthraquinone.*

1 INTRODUCTION

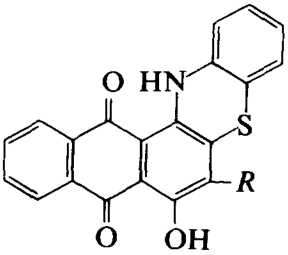
7-Hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**I**) is readily obtained by reaction of 2-bromo-1,4-dihydroxyanthraquinone with 2-aminobenzenethiol. Derivatives of this type were initially described by Eastman Kodak[1] as blue dyes for synthetic polymer fibres. Subsequent patent specifications pertained to *N*-substituted derivatives[2] and 7-aminated analogues.[3]



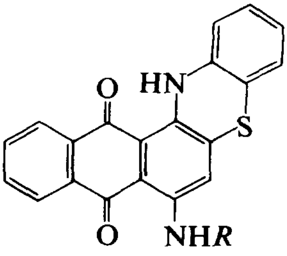
I

Colour–structure relationships, together with dyeing and fastness properties on synthetic-polymer fibres, have been reported for some dyes of this type.[4] In view of the large colour shifts resulting from the cyclisation of 2-thioethers of 1,4-dihydroxyanthraquinone (e.g. cf. the 2-(2'-aminophenyl)thio derivative, λ_{max} 482 sh, 503 and 522 sh,[5] with **I**, λ_{max} 635 nm and 685 nm, in chlorobenzene),[4] these compounds have also received attention as near-IR absorbing dyes. Thus, condensation of 2,3-dibromo-1,4-dihydroxyanthraquinone with 2-aminobenzenethiol gives 11,12-dithia-6H, 17H, 6,7-diazadinaphtho[3,2-*a*][2,3-*c*]-5, 18-anthraquinone, which absorbs at 655 nm and 712 nm (in chloroform); the presence of appropriate substituents in the unsubstituted ring of the anthraquinone moiety results in compounds absorbing up to 810 nm.[6]

The formation of **I** proceeds via the intermediate 2-thioether,[5] and whilst such thioethers are most usually prepared by replacement of the labile 2-bromo substituent,[5,7,8] other leaving groups such as nitro or sulphonic acid can be utilised.[5,9] Alternatively, 1,4-dihydroxyanthraquinone can be directly thiolated.[4,5,10] Whilst reaction of alkyl- and arylthiols with 2-bromo-1,4-dihydroxyanthraquinone proceeds readily in low b.p. solvents such as propanols, the use of higher b.p. media, e.g. DMF or *N*-methylpyrrolidine, facilitates the thiolation/ring-closure reaction with 2-aminobenzenethiol to give **I**.[4,5]



II



III.1 R=H
III.2 R=C_6H_5
III.3 R=$C_6H_4CH_3$-*p*

We report here some further reactions in DMF of a series of 2-substituted-1,4-dihydroxyanthraquinones with 2-aminobenzenethiol, to compare the relative ease of replacement of, or retention of, the 2-substituent and hence to evaluate the feasibility of the formation of the 6-substituted derivatives **II**. Similar reactions of other 2-substituted-1,4-(amino)(hydroxy) anthraquinones are also reported, giving **I** or **III** depending on the precursor material used.

2 EXPERIMENTAL

2.1 General

2-Bromo-,[5] and 2,3-dibromoanthraquinone,[6] 2-amino-1,4-dihydroxyanthraquinones,[11] 1,4-dihydroxyanthraquinone-2-ethers,[12] thioethers,[5] sulphones,[12] and carboxamides[13] were prepared as previously described. Other intermediates used were of industrial origin (1-amino-2-bromo-4-hydroxyanthraquinone; 1-amino-2-phenoxy-4-hydroxyanthraquinone; 1,4-diaminoanthraquinone; 1-amino-4-hydroxyanthraquinone; Yorkshire Chemicals plc) or commercial origin (1,2-dihydroxy- and 1,2,4-trihydroxyanthraquinones, Aldrich Chemical Co.) or were samples originating from previous investigations in these laboratories.

Column chromatography was effected on Silica Gel (for column chromatography, Janssen Chimica), eluting with toluene containing up to 10% ethyl acetate as appropriate.

Electronic spectra were recorded on a Philips PU 8730 spectrophotometer, mass spectra on an AEI MS 902, and IR (KBr) on a Nicolet 205 FT-IR.

2.2 General reaction conditions

The appropriate anthraquinone derivative (0·01 mol) was stirred into DMF (10 ml) at 50°C, and 2-aminobenzenethiol (1·25 g, 0·1 mol) was added. The mixture was then heated to 140–145°C and stirring continued until all starting material had reacted (TLC monitoring), or, in cases where the reaction was not very facile, until reaction had proceeded to an extent which enabled sufficient product to be isolated for characterisation purposes. After cooling the mixture, methanol (50 ml) was added and the liquor stirred for 1 h prior to filtration (in the case of reactions in which starting material had fully reacted). The residue was washed initially with cold methanol, and finally with warm methanol to remove residual thiol. Mass spectrometry confirmed removal of all 2-aminobenzenethiol (*m*/*z* 125)

TABLE 1
Reactions of 2-Substituted-1,4-Dihydroxyanthraquinones

2-Substituent	*Reaction time*	*Conversion*[a] *(%)*	*Isolation method*	*Isolation*[b] *(%)*	*Reaction product*
SO_2CH_3	45 min	100	A	90	**I**
$SO_2C_6H_5$	30 min	100	A	90	**I**
SCH_3	30 min	100	A	85	**I**
SC_4H_9	30 min	100	A	95	**I**
SC_6H_5	30 min	100	A	90	**I**
OC_2H_4OH	45 min	100	A	75	**I**
$OC_2H_4OCH_3$	45 min	100	A	75	**I**
OC_6H_5	30 min	100	A	80	**I**
$OC_6H_4OCH_3$-p	30 min	100	A	80	**I**
OH	4 h	100	A	75	**I**
NH_2	20 h	80	B	50	**I**
$NHCH_3$	20 h	70	B	40	**I**
$N(CH_3)_2$	1 h	100	A	75	**I**
Morpholino	75 min	100	A	70	**I**
Piperidino	90 min	100	A	75	**I**
Pyrrolidino	5 h	100	A	80	**I**
NHC_2H_4OH	20 h	60	B	40	**I**
$NHC_3H_6OCH_3$	20 h	70	B	45	**I**
NHC_6H_5	12 h	100	A	70	**I**
$NHC_6H_4CH_3$-p	12 h	100	A	70	**I**
$CONHC_6H_5$	5 h	100	A	80	**I**
$CONHC_6H_4CH_3$-p	5 h	100	A	80	**I**
CH_3	10 h	100	A	75	**II.1**
C_3H_7	10 h	100	A	65	**II.2**
C_8H_{17}	12 h	100	A	65	**II.3**
$CH_2C_6H_5$	8 h	100	A	80	**II.4**

[a] Estimated (by TLC) conversion of starting material.

[b] Recovery (%) of pure product using denoted isolation procedure.

and its oxidation product 2,2'-diaminodiphenyldisulphide (*m/z* 248). This isolation procedure (Method A, Tables 1 and 2) was used in the majority of the reactions. Yields shown in Tables 1 and 2 pertain to product isolated in this way; no attempt was made to work-up mother liquors.

Where a more incomplete reaction occurred, the reaction liquor was stirred into 10% aq. HCl at 60–65°C for 30 min (Method B). The residue, after filtration, was washed with warm water and finally with cold methanol, prior to separation by column chromatography. Compounds **I** and **III.2-III.3** were equivalent to those previously described.[4] New compounds isolated during this investigation were:

TABLE 2
Reactions of Other Substituted Anthraquinones

Substituents in anthraquinone ring				*Reaction time*	*Conversion (%)*	*Isolation method*	*Recovery (%)*	*Product*
1	2	3	4					
OH				18 h	100	A	55	**V**[a]
OH	OH			72 h	0			
OH		OH		4 h	100	A	65	**IV**
OH			OH	3 h	100	A	80	**I**
OH	OH		OH	3 h	100	A	80	**I**
OH			NH_2	20 h	60	B	45	**I**
OH	Br		NH_2	5 h	100	A	85	**I**
OH		Br	NH_2	20 h	60	B	45	**I**
OH		OC_6H_5	NH_2	20 h	60	B	45	**I**
OH			NHC_6H_5	4 h	100	A	70	**I**
OH			$NHC_6H_4CH_3$-p	3 h	100	A	75	**I**
OH	Br		NHC_6H_5	3 h	100	A	75	**III.2**
OH	Br		$NHC_6H_4CH_3$-p	3 h	100	A	75	**III.3**
NH_2			NH_2	72 h	0			
NH_2			NHC_6H_5	72 h	0			
NH_2	Br		NH_2	8 h	100	A	70	**III.1**
NH_2	Br		NHC_6H_5	3 h	100	A	75	**III.2**
NH_2	Br		$NHC_6H_4CH_3$-p	3 h	100	A	75	**III.3**

[a] V is 14H-naphtho[2,3-*a*]phenothiazine-8,13-dione.

*6-Methyl-7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**II.1**)*
M.p. 210–211°C ($C_{21}H_{13}NO_3S$ requires: C, 70·2; H, 3·6; N, 3·9; S, 8·9. Found: C, 69·9; H, 3·5; N, 3·6; S, 8·5%); *M/z* (EI) 359, M^+, 100%.
λ_{max}, nm, (log e) in chlorobenzene: 580 (sh), (3·73), 620 (3·82) and 678 (3·98).

*6-Propyl-7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**II.2**)*
M.p. 183–184°C ($C_{23}H_{17}NO_3S$ requires: C, 71·3; H, 4·4; N, 3·6; S, 8·3. Found: C, 71·0; H, 4·1; N, 3·2; S, 7·9%); *M/z* (EI) 387, M^+, 100%.
λ_{max}, nm, (log e) in chlorobenzene: 586 (sh), (4·03), 631 (4·14) and 684 (4·22).

*6-Octyl-7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**II.3**)*
M.p. 159–161°C ($C_{28}H_{27}NO_3S$ requires: C, 73·5; H, 5·9; N, 3·1; S, 7·0. Found: C, 73·1; H, 5·5; N, 2·9; S, 6·5%); *M/z* (EI) 457, M^+, 100%.
λ_{max}, nm, (log e) in chlorobenzene: 577 (sh), (3·85), 632 (4·05) and 688 (3·97).

6-Benzyl-7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (II.4)
M.p. 239–240°C ($C_{27}H_{17}NO_3S$ requires: C, 74·5; H, 3·9; N, 3·2; S, 7·4. Found: C, 74·0; H, 3·6; N, 2·9; S, 7·0%); *M/z* (EI) 435, M^+, 100%.
λ_{max}, nm, (log e) in chlorobenzene: 592 (sh), (3·89), 636 (4·05) and 690 (3·95).

6-Hydroxy-14H-naphtho[2,3-a]phenothiazine-8,13-dione (IV)
M.p. 262–264°C ($C_{20}H_{11}NO_3S$ requires: C, 69·6; H, 3·2; N, 4·1; S, 9·3. Found: C, 69·3; H, 3·0; N, 3·8; S, 9·0%); *M/z* (EI) 345, M^+, 100%.
λ_{max}, nm, (log e) in chlorobenzene: 560 (sh), (3·34), 603 (4·07) and 641 (4·01).

2.3 6-Bromo-7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione

2,3-Dibromo-1,4-dihydroxyanthraquinone was reacted with 2-aminobenzenethiol in ethanol following the previously described procedure;[6] the reaction liquor was worked-up after 7 h reaction time (cf. 12 h for complete reaction). Column chromatography of the resultant product, using toluene as eluant, gave, from the initial fraction 6-bromo-7-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (0·06 g from 0·2 g); m.p. 295–296°C; *M/z* (EI) 423/425, M^+, 100%; λ_{max}, nm, (log e) in chlorobenzene 595 (3·85), 639 (4·08) and 695 (4·04); later fractions contained the previously reported bis-condensate.[6]

3 RESULTS AND DISCUSSION

3.1 Syntheses

7-Hydroxy-14H-[2,3-*a*] phenothiazine-8,13-dione (**I**) is readily obtained by interaction of 2-bromo-1,4-dihydroxyanthraquinone and 2-aminobenzenethiol. Whilst the reaction proceeds satisfactorily in propan-2-ol, more rapid ring closure of the intermediate 2-(2'-aminophenylthio)-1,4-dihydroxyanthraquinone occurs in higher b.p. media such as DMF.[5] 1,4-Dihydroxyanthraquinone also affords **I** in propan-2-ol over a prolonged reaction time, but the use of higher reaction temperatures again enhances the facility of the thiolation ring closure process.[4]

In the present investigation, reaction of 1,4-dihydroxyanthraquinone with 3, 10 and 20 mol of 2-aminobenzenethiol in DMF at 140–145°C resulted in total conversion to **I** in 8 h, 3 h and 45 min, respectively. With leuco-1,4-dihydroxyanthraquinone and 10 mol excess of thiol, reaction was complete in 1 h. Prolonged reaction times (up to 80 h) and increased molar ratios of thiol (up to 50 mol) failed to initiate any second thiolation–

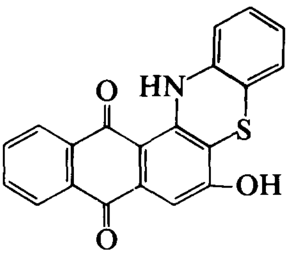
ring closure involving the 7-hydroxy group in **I**. The formation[6] of 11,12-dithia-6H,17H,6,17-diazadinaphthol[3,2-*a*][2,3-*c*]-5,18-anthraquinone thus appears to require 2,3-dibromo-1,4-dihydroxyanthraquinone as precursor intermediate.

For comparative purposes, reactions in this present investigation were arbitrarily standardised using a 10 mol excess of 2-aminobenzenethiol in DMF at 140–145°C, conditions under which 1,4-dihydroxyanthraquinone and 2-bromo-1,4-dihydroxyanthraquinone were fully reacted in 3 h and 1·5 h respectively.

The 2-sulphone group was a very effective leaving group, **I** being formed quantitatively in a very short reaction time (Table 1). An equally facile elimination of 2-ether and 2-thioether substituents occurred irrespective of the presence of an alkyl or aryl substituent in the side chain. Exchange of 2-aryloxy substituents by 2-alkoxy is well established, the preferred synthesis, for example, of 1-amino-2-alkoxy-4-hydroxyanthraquinones being via the 2-phenoxy derivative, either as starting material or prepared *in situ.*[14] The replacement of e.g. the 2-phenylthio substituent by the 2-(2'-aminophenyl)thio substituent, and hence ring closure to **I** was not anticipated, particularly in the short reaction time observed.

2-Aminoanthraquinones could be considered as relatively stable compounds, but replacement of amino, alkylamino and arylamino substituents occurred over more prolonged reaction times (Table 1). *t*-Amino substituents were the more readily replaced and whilst the 2-piperidino, 2-morpholino and 2-*N*,*N*-dimethylamino derivatives gave rapid formation of **I**, the 2-pyrrolidino derivative was much less reactive, showing a similar reaction time to 2-carboxamido derivatives (5 h). Complete replacement of 2-arylamino substituents occurred over 12 h, but 2-alkylamino substituents were only partially replaced over more prolonged reaction.

A relatively facile elimination of the 2-hydroxy group also occurred, with only **I** being obtained from 1,2,4-trihydroxyanthraquinone (purpurin). However, 1,2-dihydroxyanthraquinone (alizarin) did not react even over very prolonged reaction times, but 1-hydroxyanthraquinone was completely converted to 14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**V**, Table 2) over 18 h. 1,3-Dihydroxyanthraquinone afforded 6-hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**IV**). Small amounts of **I** were also formed due to trace impurities in the starting material; these were removed by digesting the reaction product in chlorobenzene, in which **I** was the more soluble component. Retention of the 2-substituent was only observed in reactions from 2-alkyl-1,4-dihydroxyanthraquinones, relatively prolonged reaction times affording the 6-alkyl derivatives **II.1**-**II.4**. The stability of the alkyl substituents was further indicated in the non-reactivity of 2,3-dimethyl-1,4-dihydroxyanthraquinone (100 h reaction time).



IV

With 1-amino-4-hydroxyanthraquinone, thiolation–ring closure occurred *ortho* to the amino group, giving **I**; the same product also resulted from 1-arylamino-4-hydroxyanthraquinones. This preferential thiolation adjacent to the arylamino group, with subsequent elimination of arylamine during the ring closure, is unusual compared with what could be considered a more facile reaction *ortho* to the hydroxy group, and elimination of water.

The presence of a bromo substituent *ortho* to the hydroxy or amino group reverses the reaction, both 1-hydroxy-2-bromo-4-arylamino- and 1-amino-2-bromo-4-arylaminoanthraquinones giving the 7-arylamino derivatives **III.2** and **III.3**. The facile formation of the phenothiazine derivatives from 1-amino-2-bromoanthraquinones using 2-aminobenzenethiol instead of the previously utilised 2-nitrobenzenethiol[3,4] is further exemplified in the formation of 7-amino-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**III.1**) from 2-bromo-1,4-diaminoanthraquinone and of **I** from 1-amino-2-bromo-4-hydroxyanthraquinone. **I** was also formed readily from 1-amino-2-phenoxy-4-hydroxyanthraquinone, and was also, surprisingly, the principal reaction product from 1-amino-3-bromo-4-hydroxyanthraquinone, despite the presence of the potentially more reactive α-hydroxy-β-bromo system. TLC of the reaction liquor showed that whilst 1-amino-3-bromo-4-hydroxyanthraquinone gave *c*. 75% conversion to **I** after 1 h, 1-amino-4-hydroxyanthraquinone, 1-amino-2-phenoxy-4-hydroxyanthraquinone and 1-amino-2-bromo-4-hydroxyanthraquinone showed only *c*. 30% conversion. In all four reactions, the only component present after 1 h, apart from **I**, was 1-amino-4-hydroxyanthraquinone (confirmed by chromatographic separation and comparison with an authentic sample). Whilst neither of the two bromo isomers showed any debromination when stirred in DMF at 140°C for 10 h, in the presence of 2-aminobenzenethiol both isomers were fully debrominated within 15 min. During this initial period, the 3-bromo isomer gave the more rapid formation of **I**, further formation of **I** then being governed by the reactivity of 1-amino-4-hydroxyanthraquinone. Similar debrominations have been previously observed in analogous reactions with alkyl- and arylthiols.[14]

TABLE 3
λ_{max}, nm, (log ε) and PPP-MO Calculated Data

	Chlorobenzene	*Absolute ethanol*	*Cyclohexane*	*DMSO*	*Acetone*	*PPP-MO calculated* λ_{max} *(F)*
V	584 (3·88)	598	578	587	574	574 (0·57)
IV	560 (sh) (3·34); 603 (4·07); 641 (4·01)	616; 659	581 (sh); 626; 674	628; 671 (sh)	609; 653 (sh)	576 (0·41)
I	584 (sh) (3·95); 625 (4·15); 682 (4·07)	578 (sh); 629; 678	582; 626; 682	596 (sh); 641; 692	588 (sh); 631; 681	580 (0·71)

3.2 Electronic spectra

Electronic spectra for 14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**V**) and of the 6-hydroxy (**IV**) and 7-hydroxy derivatives (**I**) are shown in Table 3. In chlorobenzene, data for **I** and **V** are of a similar order to that previously reported.[4] The 6-hydroxy derivative shows a significant hypsochromic shift relative to the 7-hydroxy analogue, in accord with the presence of the hydroxy group in a position in which neither charge transfer interaction nor intramolecular H-bonding with the 8-carbonyl group can occur. The 6-alkyl derivatives (**II**) show similar absorption parameters to **I** (see Section 2.2), λ_{max} tending to marginally longer wavelengths with an increase in the length of the alkyl chain.

Solvent effects in hydroxy- and aminoanthraquinones are well documented, these being most pronounced where no intramolecular H-bonding in the dye molecule occurs (and, conversely, least apparent where strong H-bonding is present). In 14H-naphthol[2,3-*a*]phenothiazine-8,13-dione (**V**), λ_{max} is at 20 nm longer wavelength in ethanol relative to cyclohexane (Table 3), a $\Delta\lambda$ value of similar order to that in 1-*N*-methylaminoanthraquinone (15 nm, methanol–cyclohexane).[15] Shifts in λ_{max} are, however, not fully in accord with solvent polarity (on the basis of the pertinent dielectric constant). For example, in the lowest polarity solvent used (cyclohexane, ε 2·02), λ_{max} was at 4 nm longer wavelength than in acetone (ε 20·7); also, in chlorobenzene (ε 5·7), λ_{max} was at similar wavelength to that in DMSO (ε 46·7). Solute–solvent interactions were most apparent in ethanol (ε 24·3), in which λ_{max} was at 12 nm longer wavelength than in the most polar solvent used (DMSO).

Both of the hydroxy substituted derivatives **I** and **IV** show similar λ_{max}–solvent polarity deviations. In simpler substituted hydroxyanthraquinones, solute–solvent interactions are evident in comparing[16] 2-hydroxyanthraquinone (e.g. λ_{max} 340 nm in chlorobenzene, 373–380 nm in ethanol) with 1-hydroxyanthraquinone (e.g. λ_{max} 407 in chlorobenzene, 402–406 nm in ethanol). In the β-hydroxy substituted **IV**, λ_{max} in ethanol is at longer wavelength than in chlorobenzene, but this is reversed in the α-hydroxy derivative **I**. For **I**, in the more highly polar DMSO, λ_{max} is at the longest wavelength (692 nm), but not significantly so with respect to that in chlorobenzene (682 nm) and in the more weakly polar cyclohexane (682 nm); in both of the latter solvents, λ_{max} is of a similar order to that in the more highly polar acetone (681 nm). In **IV** also, the absence of normal solvent polarity effects is evident when comparing data in cyclohexane, the latter (most weakly polar medium) giving λ_{max} at longer wavelengths than in either DMSO or ethanol.

Since both **I** and **IV** show multiple-band absorptions due to vibronic transitions, comparison of solvent effects based solely on the longest wavelength absorption band is not fully valid. However, on ‘smoothing’ the composite absorption bands into a ‘single’ curve, variations are still apparent. ‘Smoothed’ values, in order of increasing ε value of the solvent (cyclohexane, chlorobenzene, acetone, ethanol, DMSO), were (in nm) 645, 650, 635 and 650 for **I** and 635, 620, 625, 630 and 640 for **IV**.

A conventional PPP SCF-CI programme[17] was used for the calculations of the electronic transitions in **I**, **IV** and **V** (Table 3). Standard parameters[18] were used, except for the C—S bond, for which values recommended for phenothiazines (namely VSIP 21.00) were used;[19] (use of the C—S values given in Ref. 18 (VSIP 24.00) gave calculated λ_{max} of 558 nm, 559 nm and 570 nm for **V**, **VI**, and **I** respectively). For 14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**V**), the calculated λ_{max} was in excellent agreement with the observed value in cyclohexane. With introduction of a hydroxy group, the lower wavelength absorption is not significantly changed (Table 3, cyclohexane), the very small observed bathochromic shifts in **V** → **IV** → **I** being similarly shown in the calculated values. Whilst such principal electronic transition values are in good agreement, they are not fully indicative of the visually perceived colour of **I** and **IV**, which is more relatable to the longer wavelength vibronic bands not calculated within the PPP-MO framework used.

Several previous studies of correlations between experimental and PPP-MO calculated λ_{max} of anthraquinone dyes have been reported. Typically,[20] such data, whilst giving satisfactory results, do so only in respect of the principal transition, i.e the lower wavelength absorption band in dyes which exhibit multiple absorptions. The PPP-MO computations also give an indication of the electron density changes within the dye molecule. The introduction of substituents, particularly of an electronacceptor nature, into the unsubstituted phenyl ring of the anthraquinone moiety, is predicted to induce bathochromic shifts of λ_{max}. Results of such studies will be reported later.

4 CONCLUSIONS

7-Hydroxy-14H-naphtho[2,3-*a*]phenothiazine-8,13-dione (**I**) results by interaction of a variety of 2-substituted 1,4-dihydroxyanthraquinones with 2-aminothiophenol in DMF at elevated temperature. Established 'leaving' groups, such as halogeno, sulphone, ether and *t*-amino are replaced readily, but 1° and 2° amino substituents, thioether and hydroxy groups are also eliminated on more prolonged reaction. The presence of a labile substituent in the 2-position is not essential, **I** being formed readily from 1,4-dihydroxyanthraquinone. Where an amino and a hydroxy group are present in the 1,4-positions, the thiolation ring closure surprisingly proceeds via the amino substituent; 7-aminated derivatives, however, do result in reactions from 1-hydroxy(or amino)-2-bromo-4-substituted aminoanthraquinones. Whilst 1,2-dihydroxyanthraquinone did not react with 2-aminobenzenethiol, 1,2,4-trihydroxyanthraquinone reacted readily, with elimination of the 2-hydroxy group, giving **I**. 1,3-Dihydroxyanthraquinone afforded the isomeric 6-hydroxy derivative, λ_{max} of which is at considerably lower wavelength than **I**. The presence of 6-alkyl substituents in **I** results in only minor colour shifts.

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