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DYES FOR SYNTHETIC-POLYMER FIBRES: 14H-NAPHTHO[2,3-a]PHENOTHIAZINE-8,13-DIONES AND 1H-2,3-DIHYDROANTHRA[2,1-b][1,4]-THIAZINE-7,12-DIONES

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SUMMARY

Condensation of 1-*amino- or* 1-*hydroxy*-2-*bromoanthraquinones with* 2-*aminobenzenethiol, or of* 1-*amino*-2-*bromoanthraquinones with* 2-*nitrobenzenethiol gives* 14H-*naphtho*[2,3-a]-*phenothiazine*-8,13-*diones. The related* 1H-2,3-*dihydroanthra*[2,1-b][1,4]*thiazine*-7,12-*diones result from interaction of* 1-*amino*-2-*mercaptoanthraquinones with* 1,2-*dibromoethane or of* 1-*hydroxy*-2-*bromoanthraquinones with* 2-*aminoethanethiol. The colour, dyeing and fastness properties of these compounds on synthetic-polymer fibres are described.*

1. INTRODUCTION

In an investigation of the synthesis of derivatives of 2-mercapto-1,4-dihydroxyanthraquinone and their use as disperse dyes,[1] the formation of 7-hydroxy-14H-naphtho[2,3-a]phenothiazine-8, 13-dione from reaction of 2-bromo-1,4-dihydroxyanthraquinone and 2-aminobenzenethiol was noted. We report here the synthesis of other derivatives of this type (I), their 5,5-dioxides (II) and of a series of 1H-2,3-dihydroanthra[2,1-b][1,4]thiazine-7,12-diones (III), together with data on their behaviour as dyes for synthetic-polymer fibres.

2. DISCUSSION

14H-Naphtho[2,3-a]phenothiazine-8,13-diones (I) were obtained by several routes, typified by those for the 7-hydroxy derivative shown in Scheme 1. As in

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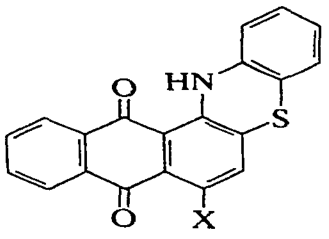

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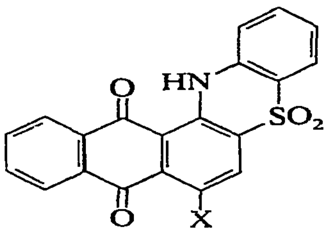

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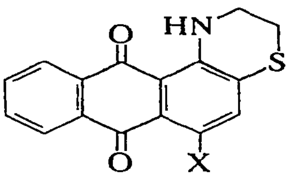

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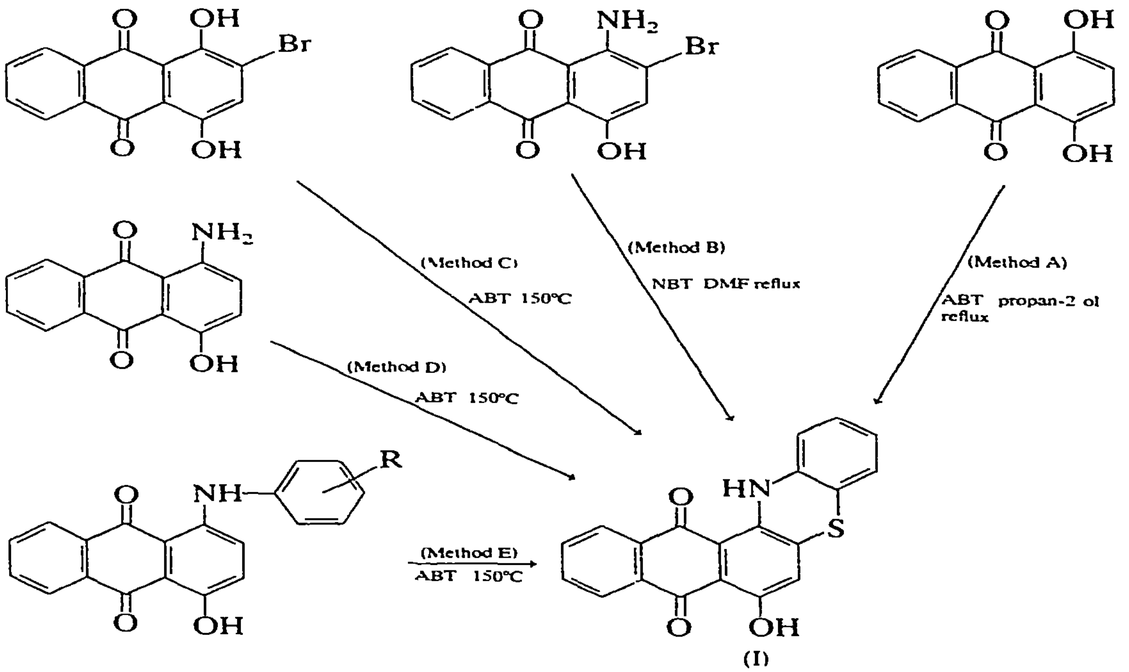


Scheme 1 Synthesis of 7-hydroxy-14H-naphtho[2,3-a] phenothiazine-8,13-dione (Reactions with 2-aminobenzenethiol (ABT) or 2-nitrobenzenethiol (NBT)

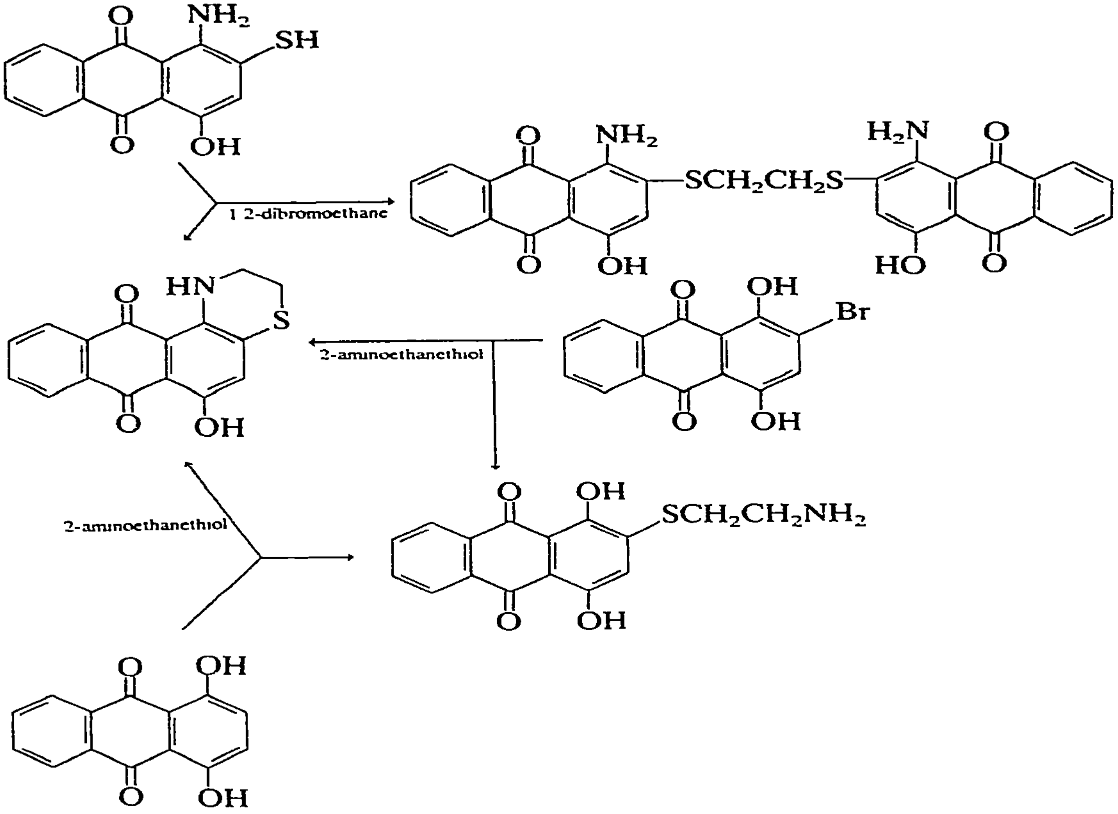
the synthesis of uncyclised 1,4-dihydroxyanthraquinone-2-thiols,[1] thiolation with 2-aminobenzenethiol tended to be the least effective method (Method A), replacement of the 2-bromo substituent (Method C) being more facile, especially in higher boiling solvents. Attempted preparation of the 7-amino-derivative (I, $X = NH_2$) from 1-amino-4-hydroxyanthraquinone and 2-aminobenzenethiol was not successful, the product being the 7-hydroxy compound (Method D) indicating the preferential reactivity of the thiol at positions influenced by the amino group Since the formation of I proceeds through cyclisation of the 2-mercapto compounds,[1] it is unusual that the initial thiolation of 1-amino-4-hydroxyanthraquinone proceeds adjacent to the more strongly electron donating amino group. Even in thiolations of various 1-arylamino-4-hydroxyanthraquinones, no 7-arylamino derivatives [I] resulted, the reaction affording only the 7-hydroxy derivative, i.e., thiolation adjacent to the amino group, with elimination of arylamine during the cyclisation stage (Method E). Reaction of 1-arylamino-4-hydroxyanthraquinone with sulphur monochloride in nitrobenzene also results[2] in the formation of the 7-hydroxy derivatives of I.

The 7-arylamino derivatives of I were obtained[3] from interaction of 1-amino-2-bromo-4-arylaminoanthraquinones with 2-nitrobenzenethiol.

Oxidation of I with hydrogen peroxide in glacial acetic acid gave the corresponding 5,5-dioxides (II).

The 1H-2,3-dihydroanthra[2,1-b][1,4]thiazine-7,12-diones (III) could be synthesised by several routes. Direct thiolation of 1,4-dihydroxyanthraquinone with 2-amino-ethanethiol gave both cyclised and uncyclised products (Scheme 2) together with large amounts of starting product; higher conversion to cyclised material resulted from replacement of the 2-bromo substituent. Alternatively, 2-mercapto-1,4-dihydroxyanthraquinone condensed with 1,2-dibromoethane to give III in admixture with double-linked compounds (Scheme 2).

Dyes were applied to synthetic-polymer fibres as previously described.[4] Compounds of type I, which have been described[2,3] as dyes for hydrophobic fibres, gave only poor colouration of both secondary acetate and triacetate. On polyester, dyeing properties were somewhat better. The unsubstituted dye (I, $X = H$) gave reddish-blue shades of moderate build-up; the 7-amino derivative (greenish-blue) behaved similarly, while the blue 7-hydroxy derivative dyed polyester in deep shades. None of the 7-arylamino derivatives, all bluish-green, built-up well, although dyeings of these in admixture were more effective, e.g. a mixture of the 7-anilino- and 7-*p*-anisidino derivatives in 1:1 ratio gave dyeings very much deeper than those of either individual dye. In comparison with 1,4-bis-anilinoanthraquinone (λ_{max} 598 nm and 636 nm in monochlorobenzene), the 7-arylamino derivatives of I were greener in hue, but the build-up of the bis-anilino dye was much better on polyester, indicating the



Scheme 2 Synthesis of 1H-2 3-dihydro-6-hydroxyanthra[2,1-b][1,4]-thiazine-7,12-dione

poorer substantivity under conventional dyeing procedures resulting from the presence of the cyclised ring system in I. Light fastness of I (Table 1) was of a similar order on polyester to 1,4-bis-anilinoanthraquinone (4–5, 4–5, 5), although the 7-hydroxy derivative was superior. Sublimation fastness of I was, for the stronger dyeing 7-amino- and 7-hydroxy derivatives, good, and of a similar order to 1,4-bis-anilinoanthraquinone (170°C). The high ratings of the 7-arylamino derivatives in Table 1 must be related to the relatively weaker dyeings given by these dyes.

Oxidation of I to the corresponding sulphones II proceeded readily with hydrogen peroxide in glacial acetic acid.[5] Compound II showed the anticipated blue shifts in absorption maxima compared to I, and an improvement in

TABLE 1

COLOUR AND FASTNESS PROPERTIES OF DYES I AND II

	λ_{max}(log ε) *in monochlorobenzene*	*Dyeings on polyester*				
		Colour	*Light fastness* 0·1%	0·5%	2·5%	*Sublimation fastness* (°C) (2·5% *dyeing*)
I, X = H	585 (3·86)	reddish-blue	5	5	5	160
I, X = NH_2	630 (4·19), 682 (4·13)	greenish-blue	5	5	4–5	190
I, X = OH	635 (4·18), 685 (4·07)	bluish-violet	6	6	6	170
I, X = NHC_6H_5	638 (4·15), 688 (4·11)	green	5	5	5	220
I, X = $NHC_6H_4CH_3$-*m*	638 (4·17), 690 (4·10)	green	4–5	4–5	4–5	220
I, X = $NHC_6H_4CH_3$-*p*	638 (4·18), 690 (4·12)	green	4–5	4–5	4–5	220
I, X = $NHC_6H_4OCH_3$-*p*	638 (4·12), 690 (4·10)	green	4–5	4–5	4–5	220
I, X = $NHC_6H_4C_2H_4OH$-*p*	638 (4·15), 690 (4·10)	green	4–5	4–5	4–5	220
II, X = H	480 (3·74)	orange	6	6	6	190
II, X = OH	570 (3·97), 605† (3·79)	violet	6–7	7	7	190
II, X = NHC_6H_5	645 (3·98)	greenish-blue	6–7	6–7	6–7	190
II, X = $NHC_6H_4CH_3$-*p*	650 (3·97)	greenish-blue	6	6–7	6–7	190

† inflexion

TABLE 2

COLOUR AND FASTNESS PROPERTIES OF DYES III

X	λ_{max} (log ε) *in monochlorobenzene*	*Colour of dyeing*	*Light fastness*									*Sublimation fastness*
			Secondary acetate			*Triacetate*			*Polyester*			
			0·1%	0·5%	2·5%	0·1%	0·5%	2·5%	0·1%	0·5%	2·5%	(2·5% *dyeing*)
H	528 (3·86)	bluish red	3–4	3–4	3–4	2–3	2–3	3	4	4	4–5	130
OH	564 (4·11), 605 (4·09)	bluish-violet	4–5	4–5	4–5	4	4	4	4–5	4–5	4–5	140
NH_2	575 (4·08), 620 (4·10)	reddish-blue	4	4	4	3–4	3–4	3–4	2–3	2–3	3	170
NHMe	575 (4·09), 616 (4·07)	greenish-blue	4	4	4	4	4	4	2	2	2	160
NHC_6H_{11}	602 (4·08), 651 (4·14)	greenish-blue	4	4	4	3–4	4	4	2–3	2–3	2–3	170
NHC_6H_5	600 (4·09), 646 (4·12)	green	4	4–5	4–5	4	4	4	4–5	4–5	4–5	160
$NHC_6H_4CH_3$-*p*	602 (4·09), 647 (4·13)	green	5	5	5	5	5	5	4–5	4–5	4–5	160
$NHC_6H_4OCH_3$-*p*	601 (4·07), 645 (4·11)	green	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	160
$NHC_6H_4C_2H_4OH$-*p*	600 (4·08), 645 (4·11)	green	4–5	4–5	4–5	4	4	4	4	4	4	190

colouration properties on polyester, but not of an order to render the 7-arylamino derivatives other than moderately good dyes. The 7-hydroxy derivative again showed the best dyeing properties, building up to deep violet shades. In general, II were considerably faster to light than I.

While some sulphonated derivatives of III have been described for the colouration of wool,[6] their use as dyes for synthetic-polymer fibres has not been previously recorded. Dyeing properties of III were generally extremely good on all fibres investigated. On acetate fibres, the hydroxy, amino and methylamino derivatives built-up to deep shades; the arylamino derivatives were only moderately good. On polyester, dyeing properties were excellent, all III building-up to very deep shades. The arylamino derivatives dyed a similar colour to 1,4-bis-anilinoanthraquinone, but a 2·5% dyeing of the latter had a similar depth to a 0·5% dyeing of the 7-arylamino derivatives III. Sublimation fastness was of a generally high order (Table 2) but the dyeings, especially those from dyes containing amino groups, had a tendency to fade very badly off-tone on light fading.

3. CONCLUSIONS

Both 14H-naphtho[2,3-a]phenothiazine-8,13-diones (I) and their corresponding dioxides (II) are readily synthesised from available anthraquinone intermediates. While the former have generally good fastness properties and give, especially the 7-arylamino derivatives, green disperse dyes not readily available by other routes, colouration properties are not of a high order. In contrast, the 1H-2,3-dihydroanthra[2,1-b][thiazine-7,12-diazones (III) have excellent colouration properties on both acetate and polyester fibres. A marked off-tone fading of some of the dyes is, however, a disadvantage.

4. EXPERIMENTAL

4.1. 14H-*Naphtho*[2,3-a]*phenothiazine*-8,13-*diones* (I)

1-Amino-2-bromoanthraquinone (3·02 g) and 2-nitrobenzenethiol (2 g) were stirred under reflux for 2h in N,N-dimethylformamide (50 ml) in the presence of anhydrous potassium carbonate (1·5 g). The liquor was cooled, added to water (200 ml) and the product (2·5 g, 80%) filtered; recrystallisation from toluene gave violet needles, m.p. 274–275°C of 14H-naphtho[2,3-a]phenothiazine-8,13-dione (I, X = H). ($C_{20}H_{11}NO_2S$ requires: C, 72·9; H, 3·3; N, 4·2; S, 9·7. Found: C, 73·1; H, 3·4; N, 4·2; S, 9·8%.)

2-Bromo-1,4-dihydroxyanthraquinone (2·5 g) and 2-aminobenzenethiol (10 ml) were stirred for 2h at 150°C. After cooling and filtering, the residue was washed with methanol giving 2·3 g (85·1%) of the dark blue 7-hydroxy-14H-naphtho[2.3-a]phenothiazine-8.13-dione (I, X = OH) m.p. 285°C (toluene) (ref. 2, m p. 256°C). ($C_{20}H_{11}NO_3S$ requires: C, 69·6, H, 3·2; N, 4·1; S, 9·3. Found· C, 69·7, H, 3·2; N, 4·1; S, 9·4%.) A similar product was obtained[1] using N,N-dimethylformamide as reaction solvent. 1,4-Dihydroxyanthraquinone (2·4 g) and 2-aminobenzenethiol (2 g) were refluxed for 20h in propan-2-ol (20 ml). After cooling and filtering, the residue was washed with methanol (2 × 100 ml) slurried in 5% aqueous sodium hydroxide (200 ml) and filtered, to give 43·5% of I (X = OH). 1-Amino-4-hydroxyanthraquinone (1 g) and 2-aminobenzenethiol (4 g) were stirred for 2 h at 150°C, the liquor cooled, diluted with methanol (10 ml) and filtered to give 0·9 g (87·8%) of I (X = OH). Similar reaction of 1-amino-4-hydroxyanthraquinone, 1-*p*-anisidino-4-hydroxyanthraquinone, 1-*p*-toluidino-4-hydroxyanthraquinone and 1-*p*-acetamidoanilino-4-hydroxyanthraquinone with 2-aminobenzenethiol gave, in all cases, I (X = OH) in 86–92% yield 1-Amino-2-bromo-4-hydroxyanthraquinone (3·18 g), reacted with 2-nitrobenzenethiol as in the preparation of I (X = H) above, gave 92 8% of I (X = OH). A stirred mixture of 1,4-diaminoanthraquinone (6 g) and 2-methoxyethanol (90 ml) was treated with concentrated hydrochloric acid (4 ml) and zinc dust (1·6 g), the suspension refluxed, 2-aminobenzenethiol (10 g) added and refluxing continued for 4h On cooling, there deposited 7-amino-14H-naphtho[2.3-a]phenothiazine-8,13-dione, bluish-green plates, m p. 283–284°C (toluene) (ref 3 m.p 310–312°C) (3 g, 34·6%) ($C_{20}H_{12}N_2O_2S$ requires. C, 69·8; H, 3·5; N, 8·1; S, 9·3. Found: C, 69·5, H, 3·4, N, 8·2, S, 9·4%)

Using the same procedure as that described above for the preparation of I (X = H), the appropriate 1-amino-2-bromo-4-arylaminoanthraquinones were condensed with 2-nitrobenzenethiol to give the following derivatives of 14H-naphtho[2.3-a]phenothiazine-8,13-dione. (i) 7-anilino-, 92·1%, m p 256–257°C ($C_{26}H_{16}N_2O_2S$ requires: C, 74·3, H, 3·8, N, 6·7, S, 7·6. Found: C, 74·3, H, 3·7 N, 6·8; S, 7·5%.) (ii) 7-*p*-toluidino-, 78·3%, m.p 267–268°C. ($C_{27}H_{18}N_2O_2S$ requires C, 74·65; H, 4·15; N, 6·45, S, 7·4 Found. C, 74·8; H, 4·2, N, 6·3, S, 7 5%.) (iii) 7-*p*-anisidino-, 93 1%, m p. 251–252°C. ($C_{27}H_{18}N_2O_3S$ requires: C, 72·0, H, 4·0; N, 6 2, S, 7 1 Found: C, 72·1; H, 4·1, N, 6·2· S, 7·2%.) (iv) 7-*m*-toluidino-, 82·9%, m p. 262–263°C. (Found. C, 74·7; H, 4·3, N, 6·5; S, 7·3%.) and (v) 7-*p*-(hydroxyethyl)-anilino-, 88·4%, m.p 295–296°C. ($C_{28}H_{20}N_2O_3S$ requires· C, 72·4, H, 4·3; N, 6·0; S, 6·9. Found: C, 72·3; H, 4·4, N, 6·1, S, 6·8%)

4.2. 14H-*Naphtho*[2,3-a]*phenothiazine*-8,13-*dione*-5,5-*dioxides* (II)

14H-Naphtho[2,3-a]phenothiazine-8,13-dione (1 g) was refluxed for 1 h in glacial acetic acid (50 ml) with 30% hydrogen peroxide (6 ml), to give, on cooling and filtering, 63·8% of 14H-naphtho[2,3-a]phenothiazine-8,13-dione-

5,5-dioxide (II, X = H) red needles, m.p. 293°C ($C_{20}H_{11}NO_4S$ requires: C, 66·5; H, 3·05; N, 3·9; S, 8·9. Found: C, 66·6; H, 3·1; N, 3·7; S, 8·7%.) Similarly, from the appropriate I were obtained the following II: (i) 7-hydroxy-, 73·2%, violet needles, m.p. 294–295°C. ($C_{20}H_{11}NO_5S$ requires: C, 63·7; H, 2·9; N, 3·7; S, 8·5. Found: C, 63·8; H, 2·8; N, 3·6; S, 8·5%.) (ii) 7-anilino-, 55·7%, dark blue–green needles, m.p. 283–284°C. ($C_{26}H_{16}N_2O_4S$ requires: C, 69·0; H, 3·5; N, 6·2; S, 7·1. Found: C, 69·1; H, 3·6; N, 6·2; S, 7·2%.) and (iii) 7-*p*-toluidino-, 55·9%, dark blue–green needles, m.p 287–288°C. ($C_{27}H_{18}N_2O_4S$ requires: C, 69·5, H, 3·9, N, 6·0; S, 6·9. Found: C, 69·7: H, 3·7; N, 6·1; S, 6·9%.)

4.3. 1H-2,3-*Dihydroanthra*[2,1-b][1,4]*thiazine*-7,12-*diones* (III)

A solution of 1-amino-2-mercaptoanthraquinone (2·55 g) and sodium hydroxide (0·4 g) in 2-methoxyethanol (50 ml) was added to a solution of 1,2-dibromoethane (10 ml) in 2-methoxyethanol (50 ml). The mixture was refluxed for 8 h, added to water (250 ml) and steam distilled to give a brownish-red residue (2·5 g). Warming in methanol resulted in the isolation, as methanol insoluble fraction, 46%, of 1,2-bis-(1-amino-9,10-dioxo-2-anthrylthio) ethane, m.p. 250–254°C *d* (P^+ at m/e 536). ($C_{30}H_{20}N_2S_2O_4$ requires: C, 67·2; H, 3·7; N, 5·2; S, 11·9. Found: C, 67·0; H, 3·5, N, 5·1, S, 11·7%.) The methanol soluble fraction (54%) yielded 1H-2,3-dihydroanthra[2,1-b][1,4]thiazine-7,12-dione (II, X = H), red needles, m.p. 167–168°C. ($C_{16}H_{11}NO_2S$ requires: C, 68·3, H, 3·8, N, 5·0; S, 11·4%. Found: C, 68·4; H, 3·8, N, 5·1, S, 11·3%.)

1-Amino-4-hydroxy-2-mercaptoanthraquinone (2·71 g) similarly gave 17·5% methanol insoluble 1,2-bis-(1-amino-4-hydroxy-9,10-dioxo-2-anthrylthio)-ethane, m.p 295–296°C *d* (P^+ at m/e 568) ($C_{30}H_{20}N_2S_2O_6$ requires C, 63·4, H, 3·5, N, 4·9; S, 11·3. Found: C, 63·1, H, 3·2; N, 4·7; S, 11·1%) and 82·5% of methanol soluble 1H-2,3-dihydro-6-hydroxy-anthra[2,1-b][1,4]thiazine-7,12-dione, violet needles, m.p. 182°C (II, X = OH). $C_{16}H_{11}NO_3S$ requires: C, 64·65; H, 3·7; N, 4·7; S, 10·8. Found: C, 64·3; H, 3·8; N, 4·9, S, 10·6%.)

Similarly, from 1,4-diamino-2-mercaptoanthraquinone (2·7 g) was obtained, as methanol soluble fraction, 70% of 1H-2,3-dihydro-6-aminoanthra[2,1-b][1,4]thiazine-7,12-dione, dark blue needles, m.p 103°C (II, X = NH_2) $C_{16}H_{12}N_2O_2S$ requires: C, 64·9, H, 4·05, N, 9·5, S, 10·8. Found: C, 64·8; H, 4·1; N, 9·6; S, 10·7%).

From the appropriate 1-amino-2-mercapto-4-arlyaminoanthraquinones were obtained the following 6-substituted-1-,H-2,3-dihydroanthra[2,1-b][1,4]thiazine-7,12-diones: (all II separated by preparative layer chromatography[4] using toluene as eluent), (i) 6-anilino-, 40%, m.p 196–197°C. ($C_{22}H_{16}N_2O_2S$ requires. C, 71·0, H, 4·3; N, 7·5, S, 8·6. Found: C, 71·1; H, 4·4; N, 7·3; S, 8·5%.) (ii) 6-*p*-toluidino-, 51%, m.p. 185–186°C. ($C_{23}H_{18}N_2O_2S$ requires: C, 71·5, H, 4·7; N, 7·25; S, 8·3. Found: C, 71·6; H, 4·8, N, 7·2; S, 8·1%.) (iii) 6-*p*-anisidino-, 72%, m.p. 183–184°C. ($C_{23}H_{18}N_2O_3S$ requires: C, 68·7; H, 4·5; N, 7·0; S, 8·0. Found: C, 68·7; H, 4·6; N, 6·8; S, 7·8%.) (iv) 6-*p*-(hydroxyethyl)anilino-, 83%, m.p. 237–238°C. ($C_{24}H_{20}N_2O_3S$ requires: C, 69·2; H, 4·8; N, 6·7; S, 7·7. Found: C, 69·3; H, 4·7; N, 6·9; S, 7·6%.) (v) 6-cyclohexylamino-, 48%, m.p. 196–197°C. ($C_{22}H_{22}N_2O_2S$ requires: C, 69·8; H, 5·8; N, 7·4; S, 8·5. Found: C, 69·9; H, 5·7; N, 7·3; S, 8·6%) and (iv) 6-methylamino-, 60%, m.p. 100–101°C. ($C_{17}H_{14}N_2O_2S$ requires: C, 65·8; H, 4·5, N, 9·0; S, 10·3. Found: C, 65·7; H, 4·6; N, 9·1; S, 10·4%.)

1,4-Dihydroxyanthraquinone (4·8 g), 2-aminoethanethiol hydrochloride (3·6 g) and anhydrous potassium carbonate (2·1 g) were refluxed for 20 h in propan-1-ol (40 ml). The mixture was cooled, filtered and the residue washed with propan-1-ol (2×50 ml) and water, giving 3·1 g of a dark orange solid, which contained (by t.l.c.) three components Separation by preparative layer chromatography using toluene as eluent yielded, in increasing order of R_f value, 20% of 1,4-dihydroxy-2-(2-aminoethyl thio)anthraquinone, m.p. 201°C. ($C_{16}H_{13}NO_4S$ requires: C, 60·95; H, 4·1; N, 4·4; S, 10·2. found: C, 60·9, H, 4·2; N, 4·3, S, 10·3%), 20% of 1H-2,3-dihydro-6-hydroxyanthra[2,1-b][1,4]thiazine-7,12-dione (III, X = OH) identical to the product prepared as above, and 60% of unreacted starting material.

2-Bromo-1,4-dihydroxyanthraquinone (3·19 g), 2-aminoethanethiol hydrochloride (2·26 g) and anhydrous potassium carbonate (2·8 g) were refluxed for 1·5 h in propan-1-ol (100 ml) and water (10 ml) and water (10 ml). The resultant product, separated by chromatography as above, gave 70% of the cyclised III (X = OH) and 30% of uncyclised material, identical to the products obtained in the reaction above from 1,4-dihydroxyanthraquinone.

Electronic spectra, chromatographic separations, dyeing and fastness testing were all carried out as previously[4] described.

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