*Dyes and Pigments* **20** (1992) 291–305

# 2,3-Dihydroanthra(1,2-*b*)(1,4)oxazine-7,12-diones. Dyes for Synthetic Polymer Fibres

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(Received 12 August 1992; accepted 28 September 1992)

*ABSTRACT*

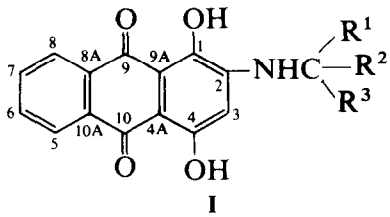
*Condensation of 2-bromo-1,4-dihydroxyanthraquinone with 2-amino-2-methyl-1,3-propanediol affords, initially, 2-(1,1-bis-hydroxymethyl)ethylamino-1,4-dihydroxyanthraquinone, which is then converted under more stringent reaction conditions into the ring closed 2,3-dihydro(1,2-b)(1,4)oxazine-7,12-dione analogue. This compound has two resolved long wavelength maxima at 20 and 60 nm longer wavelength than the uncyclised precursor and gives deep violet–red colorations of excellent fastness to light on polyester. Similar reactions with analogous aminoalcohols are also reported.*

## 1 INTRODUCTION

The condensation of 2-bromo-1,4-dihydroxyanthraquinone with various primary and secondary amines generally results[1] in the formation of the corresponding 2-aminated derivatives, which colour synthetic polymer fibres in red hues of good light fastness properties. With 2-amino-2-methyl-1,3-propanediol, the formation of either a red (**I**) or violet–red (**II**) product occurs, depending on the reaction conditions.



*Dyes and Pigments* 0143-7208/93/$06.00 

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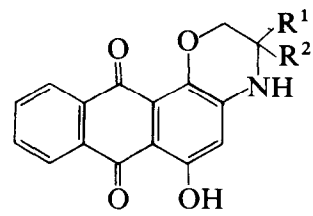



II

We report here the isolation and characterisation of these products, an evaluation of their coloration properties on polyester, and similar reactions with other aminoalcohols.

## 2 EXPERIMENTAL

### 2.1 Reaction of 2-bromo-1,4-dihydroxyanthraquinone with 2-amino-2-methyl-1,3-propanediol

2-Bromo-1,4-dihydroxyanthraquinone (0·64 g, 0·002 mol) and 2-amino-2-methyl-1,3-propanediol (1·05 g, 0·01 mol) were stirred under reflux in 2-methoxyethanol (30 ml) for 10 h. The cooled liquor was added to ice-cold 5% hydrochloric acid (120 ml) and the brownish-red precipitate (0·66 g) was filtered and washed neutral with warm water. Column chromatography (see Section 2.8) (of 0·5 g) gave, from a lower $R_f$ red zone, 2-(1,1-bis-hydroxymethyl)ethylamino-1,4-dihydroxyanthraquinone (**I.1**, $R^1$ = $R^2$ = $CH_2OH$, $R^3$ = Me), (0·32 g), m.p. 226–227°C, and from a higher $R_f$ reddish-violet zone, 6-hydroxy-3-methyl-3-hydroxymethyl-2,3-dihydroanthra(1,2-*b*)(1,4)oxazine-7,12-dione (**II.1**, $R^1$ = $CH_2OH$, $R^2$ = Me), (0·14 g), m.p. 210–211°C.

A similar reaction, but replacing the 2-methoxyethanol by dimethylsulphoxide (DMSO), gave after 8 h at 150 to 155°C, a deep purple material (0·62 g). Chromatographic purification (of 0·5 g) gave 0·46 g of **II.1**. In *N*-methylpyrrolidone at 180 to 185°C conversion to **II.1** was quantitative in 90 min.

**I.1** HRMS: 343.1067, 14·7%, $M^+$, Calc. for $C_{18}H_{17}NO_6$ 343.1056; 312.0865, 100%, M—$CH_2OH$, Calc. for $C_{17}H_{14}NO_5$ 312.0860; 282.0769, 5·7%, M—$CH_2OH$, CHO, Calc. for $C_{16}H_{12}NO_4$ 282.0766; 255.0546, 82·7%, Calc. for $C_{14}H_9NO_4$ 255.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 15·03, 1H, s, Ar-OH; $\delta$ 8·49–8·36, 2H, m, H-5,8; $\delta$ 7·76–7·63, 2H, m, H-6,7; $\delta$ 6·93, 1H, s, H-3; $\delta$ 4·26, 2H, d,

J = 10·6 Hz, $\underline{CH_2}OH$; δ 4·13, 2H, d, J = 10·6 Hz, $\underline{CH_2}OH$; δ 1·63, 3H, s, $CH_3$.

$^1$H-NMR ($d_6$-DMSO): δ 14·39, 1H, s, Ar-OH; δ 14·06, 1H, s, Ar-OH; δ 8·28–8·23, 2H, m, H-5,8; δ 7·97–7·84, 2H, m, H-6,7; δ 3·62, 2H, d, J = 11·0 Hz, $\underline{CH_2}OH$; δ 3·50, 2H, d, J = 11·0 Hz, $\underline{CH_2}OH$; δ 1·31, 3H, s, $CH_3$.

$^{13}$C-NMR ($d_6$-DMSO): δ 181·87 (C-9,10); 176·26 (C-9,10); 165·71 (C-1); 154·56 (C-4); 146·38 (C-2); 134·50 (C-6,7); 133·72 (C-8A, 10A); 132·85 (C-6,7); 131·29 (C18A,10A); 126·16 (C-5,8); 125·69 (C-5,8); 109·49 (C-9A); 101·68 (C-4A); 101·52 (C-3); 63·44 ($\underline{C}H_2OH$); 58·34, ($\underline{C}$—$CH_3$); 17·48, (C—$\underline{C}H_3$).

**II.1** HRMS: 325.0940, 16%, $M^+$, Calc. for $C_{18}H_{15}NO_5$ 325.0950; 295.0830, 19·2%, M—HCHO, Calc. for $C_{17}H_{13}NO_4$ 295.0845; 294.0777, 100%, M—$CH_2OH$, Calc. for $C_{17}H_{12}NO_4$ 294.0766; 280.0603, 6·7%, M—HCHO, $CH_3$, Calc. for $C_{16}H_{10}NO_4$ 280.0610; 279.0527, 8·5%, M—$CH_2OH$, $CH_3$, Calc. for $C_{16}H_9NO_4$ 279.0532.

$^1$H-NMR ($d_5$-pyridine): δ 14·69, 1H, s, 4-OH; δ 10·58, 1H, s, N$\underline{H}$; δ 8·52–8·44, 2H, m, H-6,7; δ 7·77–7·65, 2H, m, H-5,8; δ 6·92, 1H, s, H-3; δ 4·52, 1H, dd, J = 10·8 Hz and 1·1 Hz, cyclic $CH_2$; δ 4·07, 1H, d, J = 10·8 Hz, cyclic $CH_2$; δ 3·93, 1H, d, J = 10·6 Hz, $\underline{CH_2}OH$; δ 3·81, 1H, d, J = 10·6 Hz, $\underline{CH_2}OH$; δ 1·45 3H, s, $CH_3$.

$^1$H-NMR ($d_6$-DMSO): δ 14·16, 1H, s, 4-OH; δ 10·15, 1H, s, NH; δ 8·22–8·29, 2H, m, H-6,7; δ 7·92–7·82, 2H, m, H-5,8; δ 6·75, 1H, s, H-3; δ 4·30, 1H, d, J = 10·6 Hz, cyclic $CH_2$; δ 4·06, 1H, d, J = 10·6 Hz, cyclic $CH_2$; δ 3·50, 1H, d, J = 10·6 Hz, $\underline{CH_2}OH$; δ 3·40, 1H, d, J = 10·6 Hz, $\underline{CH_2}OH$; δ 1·29, 3H, s, $CH_3$.

$^{13}$C-NMR ($d_6$-DMSO): δ 183·99 (C-9,10); 181·34 (C-9,10); 159·19 (C-1); 152·88 (C-4); 135·65 (C-2); 134·18 (C-8A,10A); 134·01 (C-6,7); 133·08 (C-6,7); 132·35 (C-8A,10A); 126·12 (C-5,8); 125·80 (C-5,8); 109·90 (C-3); 107·64 (C-4A,9A); 107·42 (C-4A,9A); 69·6 (cyclic $\underline{C}H_2$); 64·38, ($\underline{C}H_2OH$); 51·71, (cyclic $\underline{C}$-$R^1R^2$); 20·42 (—$\underline{C}H_3$).

## 2.2 Reaction of 2-bromo-1,4-dihydroxyanthraquinone with 2-amino-2-ethyl-1,3-propanediol

Replacing the 2-amino-2-methyl-1,3-propanediol in Section 2.1 by 2-amino-2-ethyl-1,3-propanediol (1·2 g) gave, after 10 h in 2-methoxyethanol, 0·68 g of a dark red material. Chromatography (of 0·5 g) gave,

from a higher $R_f$ violet zone, 0·06 g of **II.2** (see below) and from a lower $R_f$ cherry-red zone, 2-(1,1-bis-hydroxymethyl)propylamino-1,4-dihydroxyanthraquinone (0·28 g) (**I.2**, $R^1 = R^2 = CH_2OH$, $R^3 = Et$), m.p. 170–171°C.

In DMSO, for 4 h at 150 to 155°C, a violet–red solid (0·64 g) resulted. Chromatography (of 0·5 g) gave, from the principal violet zone, 0·42 g of 6-hydroxy-3-ethyl-3-hydroxymethyl-2,3-dihydroanthra(1,2-*b*)(1,4)oxazine-7,12-dione (**II.2**, $R^1 = CH_2OH$, $R^2 = Et$), m.p. 209–210°C.

**I.2** HRMS: 357.1206, 16·2%, $M^+$, Calc. for $C_{19}H_{19}NO_6$ 357.1212; 327.1100, 26%, M—HCHO, Calc. for $C_{18}H_{17}NO_5$ 327.1107; 326.1035, 100%, M—$CH_2OH$, Calc. for $C_{18}H_{16}NO_5$ 326.1028; 296.0927, 47·5%, M—$CH_2OH$, HCHO, Calc. for $C_{17}H_{14}NO_4$ 296.0923; 255.0538, 58·6%, Calc. for $C_{14}H_9NO_4$ 255.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 15·03, 1H, s, Ar-OH; $\delta$ 8·50–8·37, 2H, m, H-6,7; 8·50–8·37, 2H, m, H-6,7; $\delta$ 7·77–7·64, 2H, m, H-5,8; $\delta$ 6·96, 1H, s, H-3; $\delta$ 5·89, 1H, bd, NH; $\delta$ 4·26, 2H, d, J = 11·0 Hz, $CH_2OH$; $\delta$ 4·20, 2H, d, J = 11·0 Hz, $\underline{CH_2}OH$; $\delta$ 2·11, 2H, q, J = 7·3 Hz, $\underline{CH_2}CH_3$; $\delta$ 1·02, 3H, t, J = 7·3 Hz, $CH_2\underline{CH_3}$.

**II.2** HRMS: 339.1098, 12·4%, $M^+$, Calc. for $C_{19}H_{17}NO_5$ 339.1107; 308.0934, 100%, M—$CH_2OH$, Calc. for $C_{18}H_{14}NO_4$ 308.0923; 280.0603, 8·9%, M—HCHO, $C_2H_5$, Calc. for $C_{16}H_{10}NO_4$ 280.0610; 279.0518, 21·2%, M—$CH_2OH$, $C_2H_5$, Calc. for $C_{16}H_9NO_4$ 279.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 14·73, 1H, s, 4-OH; $\delta$ 10·71, 1H, s, NH; $\delta$ 8·56–8·45, 2H, m, H-6,7; $\delta$ 7·74–7·58, 2H, m, H-5,8; $\delta$ 6·92, 1H, s, H-3; $\delta$ 4·54, 1H, d, J = 10·6 Hz, cyclic $CH_2$; $\delta$ 4·17, 1H, d, J = 10·6 Hz, cyclic $CH_2$; $\delta$ 3·96, 1H, d, J = 11·0 Hz, $\underline{CH_2}OH$; $\delta$ 3·86, 1H, d, J = 11·0 Hz, $\underline{CH_2}OH$; $\delta$ 1·95, 2H, q, J = 7·7 Hz, $\underline{CH_2}CH_3$; $\delta$ 1·07, 3H, t, J = 7·7 Hz, $CH_2\underline{CH_3}$.

### 2.3 Reaction of 2-bromo-1,4-dihydroxyanthraquinone with 2-amino-2-methyl-1-propanol

A similar reaction with 2-amino-2-methyl-1-propanol (0·9 g), for 4 h in 2-methoxyethanol, gave a dark red product (0·63 g). Chromatography (of 0·5 g), after elution of minor high $R_f$ yellow (unreacted starting material) and violet (**II.3**) zones, gave, from a principal deep red lower $R_f$ zone, 2-(1-methyl-1-hydroxymethyl)ethylamino-1,4-dihydroxyanthraquinone (0·41 g) (**I.3**, $R^1 = CH_2OH$, $R^2 = R^3 = Me$), m.p. 212–213°C.

In DMSO, the major product after 45 min was **I.3**, showing gradual conversion over 7 h to a reddish-violet material (0·59 g). Chromatography of this yielded, from 0·5 g of crude material, 0·46 g of 6-hydroxy-3,3-dimethyl-2,3-dihydroanthra(1,2-*b*)(1,4)oxazine-7,12-dione (**II.3**, $R^1$ = $R^2$ = Me), m.p. 201–202°C.

**I.3** HRMS: 327.1100, 11·6%, $M^+$, Calc. for $C_{18}H_{17}NO_5$ 327.1108; 296.0915, 100%, M—$CH_2OH$, Calc. for $C_{17}H_{14}NO_4$ 296.0923; 255.0524, 11·4%, Calc. for $C_{14}H_9NO_4$ 255.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 15·06, 1H, s, Ar-OH; $\delta$ 8·57–8·33, 2H, m, H-5,8; $\delta$ 7·72–7·62, 2H, m, H-6,7; $\delta$ 3·88, 2H, d, $\underline{CH_2}OH$; $\delta$ 1·46, 6H, s, $CH_3$.

**II.3** HRMS: 309.1008, 63·8%, $M^+$, Calc. for $C_{18}H_{15}NO_4$ 309.1001; 294.0755, 100%, M—$CH_3$, Calc. for $C_{17}H_{12}NO_4$ 294.0766; 279.0521, 11·5%, M—$CH_3$, $CH_3$, Calc. for $C_{16}H_9NO_4$ 279.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 14·70, 1H, s, 4-OH; $\delta$ 10·32, 1H, s, NH; $\delta$ 8·51–8·42, 2H, m, H-6,7; $\delta$ 7·76–7·68, 2H, m, $\delta$ 6·92, 1H, s, H-3; $\delta$ 4·61, 4·55, 2H, J = 11·0 Hz, cyclic $CH_2$; $\delta$ 4·25, 2H, d, J = 10·8 Hz, $\underline{CH_2}OH$; $\delta$ 4·13, 2H, d, J = 10·8 Hz, $\underline{CH_2}OH$).

### 2.4 Reaction of 2-bromo-1,4-dihydroxyanthraquinone with tris(hydroxymethyl) aminomethane

The reaction is as in Section 2.1, but with tris-(hydroxymethyl)-aminomethane (1·2 g) in 2-methoxyethanol at 115 to 120°C for 40 min, which gave an orange-red material (0·67 g), chromatography of which (0·5 g) afforded, after elution of unreacted starting material (0·12 g), from a mid $R_f$ violet zone, 0·19 g of **II.4** (see below), and from a lower $R_f$ red zone, 0·14 g of 2-(1,1-bis-hydroxymethyl-2-hydroxyethylamino)-1,4-dihydroxyanthraquinone (**I.4**, $R^1$ = $R^2$ = $R^3$ = $CH_2OH$), m.p. 223–225°C.

Reaction in DMSO at 150 to 155°C for 90 min gave 0·65 g of a deep violet material, which was recrystallised from 2-methoxyethanol in dark violet prisms of 6-hydroxy-3,3-bis-hydroxymethyl-2,3-dihydroanthra(1,2-*b*)(1,4)oxazine-7,12-dione (**II.4**, $R^1$ = $R^2$ = $CH_2OH$), m.p. 251–253°C.

**I.4** HRMS: 359.0996, 15·6%, $M^+$, Calc. for $C_{18}H_{17}NO_7$ 359.1005; 329.0882, 28·1%, M—HCHO, Calc. for $C_{17}H_{15}NO_6$ 329.0899; 328.0813, 100%, M—$CH_2OH$, Calc. for $C_{17}H_{14}NO_6$ 328.0821; 297.0654, 10·8%, M—$CH_2OH$, $CH_2OH$, Calc. for $C_{16}H_{11}NO_5$ 297.0637; 255.0523, 38·9%, Calc. for $C_{14}H_9NO_4$ 255.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 15·02, 1H, s, Ar-OH; $\delta$ 8·58–8·36, 2H, m, H-5,8; $\delta$ 7·76–7·58, 2H, m, H-6,7; $\delta$ 6·93, 1H, s, H-3; $\delta$ 4·49, 6H, bd, s, $\underline{CH_2}OH$.

**II.4** HRMS: 341.0886, 23·6%, $M^+$, Calc. for $C_{18}H_{15}NO_6$ 341.0899; 310.0714, 100%, M—$CH_2OH$, Calc. for $C_{17}H_{12}NO_5$ 310.0715; 280.0626, 31·6%, M—$CH_2OH$, HCHO, Calc. for $C_{16}H_{10}NO_4$ 280.0610; 279.0520, 40·3%, M—$CH_2OH$, $CH_2OH$, Calc. for $C_{16}H_9NO_4$ 279.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 14·72, 1H, s, 4-OH; $\delta$ 8·57–8·36, 2H, m, H-6,7; $\delta$ 7·75–7·67, 2H, m, H-5,8; $\delta$ 6·92, 1H, s, H-3; $\delta$ 4·61, 4·55, 2H, J = 11·0 Hz, cyclic $CH_2$; $\delta$ 4·25, 2H, d, J = 10·8 Hz, $\underline{CH_2}OH$; $\delta$ 4·13, 2H, d, J = 10·8 Hz, $\underline{CH_2}OH$).

## 2.5 2-(1,1-Dimethyl-4-hydroxy)propylamino-1,4-dihydroxyanthraquinone (I.5)

2-Bromo-1,4-dihydroxyanthraquinone (0·6 g) was refluxed for 5 h with 3-amino-3-methyl-1-butanol (1 g) in 2-methoxyethanol (25 ml). Addition of the cooled liquor to 10% aq. HCl (60 ml) gave a pink–red solid (0·58 g), chromatography of which gave, from the principal cherry-red zone, 0·5 g of **I.5** ($R^1 = R^2 = Me$, $R^3 = C_2H_4OH$), m.p. 170–172°C.

HRMS: 341.1269, 42·5%, $M^+$, Calc. for $C_{19}H_{19}NO_5$ 341.1263; 296.0932, 64·63%, M—$C_2H_4OH$, Calc. for $C_{17}H_{14}NO_4$ 296.0923; 255.0526, 100%, Calc. for $C_{14}H_{19}NO_5$ 255.0532.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 15·25, 1H, s, Ar-OH; $\delta$ 8·50–8·35, 2H, m, H-5,8; $\delta$ 7·76–7·61, 2H, m, H-6,7; $\delta$ 6·63, 1H, s, H-3; $\delta$ 4·07, 2H, t, J = 5·9 Hz, $CH_2\underline{CH_2}OH$; $\delta$ 2·04, 2H, t, J = 5·9 Hz, $\underline{CH_2}CH_2OH$; $\delta$ 1·46, 6H, s, $CH_3$.

A similar product was obtained in DMSO after 2 h; continued reaction for 40 h resulted only in the gradual decomposition of **I.5**, no formation of any ring closed material being apparent.

## 2.6 2-(*tert*-Butylamino)-1,4-dihydroxyanthraquinone (I.6)

A similar reaction to that of Section 2.5, but using *tert*-butylamine, gave 0·52 g of a red material, which yielded, from the principal cherry-red zone, on chromatography, 0·49 g of **I.6** ($R^1 = R^2 = R^3 = Me$), m.p. 208–209°C.

HRMS: 311.1143, 27·9%, $M^+$, Calc. for $C_{18}H_{17}NO_4$ 311.1157;

296.0911, 27·6%, M—$CH_3$, Calc. for $C_{17}H_{14}NO_4$ 296.0923; 255.0519, 100%, Calc. for $C_{14}H_9NO_4$ 255.0531.

$^1$H-NMR ($d_5$-pyridine): $\delta$ 15·04, 1H, s, OH; $\delta$ 8·51–8·35, 2H, m, H-5,8; $\delta$ 7·78–7·64, 2H, m, H-6,7; $\delta$ 6·60, 1H, s, H-3; $\delta$ 6·16, 1H, bd, s, NH; $\delta$ 1·33, 9H, s, $CH_3$.

$^1$H-NMR (DMSO): $\delta$ 14·48, 1H, s, OH; $\delta$ 13·49, 1H, s, OH; $\delta$ 8·31–8·26, 2H, m, H-5,8; $\delta$ 7·99–7·89, 2H, m, H-6,7; $\delta$ 6·38, 1H, s, H-3; $\delta$ 6·29, 1H, s, NH; $\delta$ 1·45, 9H, s, $CH_3$.

### 2.7 2-Amino-1,4-dihydroxyanthraquinone

Prepared as previously described.[1]

$^1$H-NMR ($d_5$-pyridine): $\delta$ 14·72, 1H, s, Ar-OH; $\delta$ 8·48–8·36, 2H, m, H-5,8; $\delta$ 7·76–7·62, 2H, m, H-6,7; $\delta$ 6·7, 1H, s, H-3.

$^1$H-NMR (DMSO): $\delta$ 14·08, 1H, s, OH; $\delta$ 13·65, 1H, s, OH; $\delta$ 8·27–8·22, 2H, m, H-5,8; $\delta$ 7·97–7·84, 2H, m, H-6,7; $\delta$ 7·17, 2H, s, $NH_2$; $\delta$ 6·31, 1H, s, H-3.

### 2.8 General

Reaction products were purified on silica gel (for column chromatography, 0·060–0·200 nm, pore diameter *c.* 4 nm) (Janssen Chimica), applying from solution in chlorobenzene or toluene, and eluting with toluene containing up to 35% of ethyl acetate as appropriate.

Electronic spectra were recorded on a Philips PU8730 from dye solutions in absolute ethanol or chlorobenzene. Mass measurements were performed on an AEI MS902, EI ionisation at 70 eV; HRMS by dynamic scanning (dynamic resolution 6600); $^1$H-NMR spectra were recorded on a JEOL GX270 FT NMR spectrometer, chemical shifts being referenced to TMS as internal standard. Carbon atom types were determined using $^{13}$C($^1$H) and DEPT (distortionless enhancement by polarisation transfer) 135 pulse sequencies;[2–4] the assignments for **II**, are, for comparative purposes, based on the conventional ring numbering for anthraquinone, i.e. as in **I**.

Dyeings on polyester and light fastness assessments (Xenotest 450) were carried out by standard procedures.

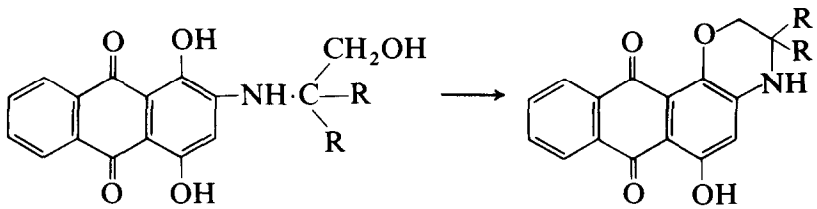
2-Bromo-1,4-dihydroxyanthraquinone was prepared as previously noted.[1] The amines were all of commercial origin and were used without further purification.

## 3 RESULTS AND DISCUSSION

In the course of previous investigations[1] of some 2-aminated derivatives of 1,4-dihydroxyanthraquinone, the condensation of 2-bromo-1,4-dihydroxyanthraquinone, with 2-amino-2-methyl-1,3-propanediol was found to afford a product which had visible absorption characteristics significantly different from typical 2-amino derivatives. This product was the ultimate component of the reaction, which proceeded via initial formation of a red product (**I**) having a colour compatible with that anticipated for a 2-amino derivative, followed by its conversion to a violet–red material (**II**). The formation of the latter compound was time/temperature dependent. Thus, in 1-butanol, no appreciable reaction was evident after 12 h at reflux, with only minimal formation of **I**. In 2-methoxyethanol, the reaction proceeded more rapidly, with initial formation of **I**, followed by **II**. After 4 h, the reaction liquor contained *c.* 40% starting material, 40% **I** and 20% **II**; after 10 h, *c.* 60% **I** and 30% **II**; and after 24 h, only **II**. The use of higher boiling solvents gave more rapid formation of **II**, e.g. in DMSO at 150 to 155°C, total conversion to **II** occurred in 6 h, and in *N*-methyl-2-pyrrolidone at 180 to 185°C reaction was complete in 1·5 h. In dimethylformamide (DMF), at reflux, all starting product had reacted after 90 min; column chromatography indicated the formation of *c.* 25% **I**, 45% **II** and 30% of 2-*N*,*N*-dimethylamino-1,4-dihydroxyanthraquinone. Formation of the latter compound has been previously observed[1] in the condensation of 2-bromo-1,4-dihydroxyanthraquinones and amines in DMF.

This initial formation of the 2-amino derivatives (**I**), followed by their conversion to **II**, was also observed with other alkylamines containing a hydroxymethyl group as one of the substituents in a *tert*-alkyl moiety. With 2-amino-2-ethyl-1,3-propanediol or 2-amino-2-methyl-1-propanol, **I** were readily isolated from reactions in 2-methoxyethanol, although chromatography was necessary to effect, depending on the duration of the reaction, separation of **I** from the starting product or of **I** from **II**. Compounds **II** could be obtained relatively free from contaminants by reaction in DMSO at more elevated temperature. Thus, with 2-amino-2-methyl-1-propanol, **I** was the major product in 2-methoxyethanol after 3 to 4 h, and in DMSO after 1 h; conversion to **II** was complete in 24 and 4 h, respectively.

With tris-(hydroxymethyl)aminomethane, formation of **II** was particularly facile, e.g. in DMSO after 90 min. In 2-methoxyethanol at reflux, **I** was rapidly converted to **II**, and for isolation of **I** the use of lower reaction temperatures and incomplete reaction of starting material was necessary; when the reaction was continued until all the 2-bromo derivative had reacted, **II** was the major reaction component. No formation of



III IV

compounds of type **II** was observed with 3-amino-3-methyl-1-butanol; after 48 h in DMSO, only **I** was formed. The ring closure thus appears to be specific to **I** in which one of $R^1$–$R^3$ is a hydroxymethyl substituent, viz. as in the conversion **III** → **IV**, in which R may be an alkyl or substituted alkyl moiety.

The mass spectra (EI) of **I** showed molecular ions at relatively low intensity, the base peak in the spectra of dyes containing a hydroxymethyl group in the amino residue tending to appear at *m/z* corresponding to M—$CH_2OH$. Initial loss of HCHO was also evident for some dyes. Where the dyes contained added hydroxymethyl groups, further fragment ions resulted from loss of HCHO from the M—$CH_2OH$ ion, or of —$CH_2OH$ from the M—HCHO ion; the tris-hydroxymethylated derivative (**I.4**) showed progressive loss of two —$CH_2OH$ groups. In no instance was a fragment corresponding to the loss of all three side chain substituents (viz. *m/z* 266) apparent, but all dyes showed a major ion at *m/z* 255, corresponding to 2-amino-1,4-dihydroxyanthraquinone, varying from relatively low intensity (**I.3**) to the base peak (**I.4** and **I.5**) of the spectrum.

The principal fragment ions of **II** corresponded to M—$CH_2OH$, or to M—$CH_3$ where no hydroxymethyl group was present, followed by further loss of the second side chain substituent in the heterocyclic ring (viz. —$CH_2OH$, Me or Et). The mass spectra of all **II** were thus compatible with the assigned structures, i.e. relative to **I**, the absence of one hydroxymethyl side chain, and also of the 1-hydroxy group (no *m/z* 255 peak appearing in any spectrum).

NMR data were also compatible with the structural assignments for **II**. Taking analogous dyes **I.1** and **II.1** as typical representatives, the $^1$H-NMR spectrum of **I.1**, in $d_5$-pyridine shows the presence of two hydroxymethyl groups (four proton integration) at $\delta$ 4·26 and $\delta$ 4·13. Spectrum integration at $\delta$ 15·03 (aromatic OH) was for one proton only. This phenomenon was evident in the spectra of all **I**, which showed in $d_5$-pyridine, integration for only one aromatic hydroxy group, but in $d_6$-DMSO integration for both the 1- and 4-hydroxy groups. Similar results were obtained with 2-amino- and 2-*tert*-butylamino-1,4-dihydroxyan-

thraquinone, but with 1,4-dihydroxyanthraquinone the spectrum in $d_5$-pyridine showed a two-proton singlet at $\delta$ 13·17. Representative samples of 1,4-dihydroxyanthraquinone-2-ethers and 2-thioethers also showed only one aromatic OH signal in $d_5$-pyridine, and with 2-sulphone derivatives, no signal was apparent; all these compounds showed both hydroxy protons in $d_6$-DMSO, and the absence of some signals in $d_5$-pyridine is presumably relatable to the basic solvent promoting ionisation, and hence exchange with traces of HOD.

The ring closed analogue **II.1** showed only one aromatic OH signal in both solvents; signals for only one hydroxymethyl substituent (two proton integration) were apparent at $\delta$ 3·93 and 3·81, and the signals at $\delta$ 4·52 and 4·07 were assigned to the cyclic methylene group after spin decoupling. The larger chemical shift differential between the signals of the pair of protons in the cyclic methylene group reflects their different environment relative to side chain hydroxymethyl substituents. They are closer to the deshielding effect of the aromatic ring than in the uncyclised analogues and the signals are shifted downfield. Additionally, the hydroxymethyl group in **II.1** is more separated, and held in a more rigid conformation than in **I.1**, and thus show upfield shifts. The cyclic methylene group in **II.1** also shows an additional long range through-space coupling ($J$ = 1·1 Hz) to the cyclic imino group (removed on $D_2O$ exchange) (although this was not observed in all dyes).

$^{13}$C-NMR data were also comparable with the ring closed configuration of **II** (DEPT data[2–4] being used to differentiate the various carbon atom types), The presence of two different methylene moieties in **II.1** was shown by signals at $\delta$ 69·60 for the cyclic methylene carbon and at $\delta$ 64·38 for the side chain hydroxymethyl carbon atom; the uncyclised derivative **I.1** showed only the signal for the side chain substituent ($\delta$ 63·64). Other carbon atom assignments listed (see Section 2) were made following DEPT analysis and are essentially in accord with previous assignments for 1,4-dihydroxyanthraquinone and related compounds.[5,6]

Visible absorption maxima, in chlorobenzene, of **I** are similar to those of previously reported 2-amino derivatives of 1,4-dihydroxyanthraquinone.[1] The presence of hydroxymethyl substituents results in small hypsochromic shifts due to the -I effect of the aliphatic hydroxy group, these shifts increasing with the number of hydroxymethyl groups, as exemplified by the $\lambda_{max}$ values for **I.6** 516 nm, **I.3** 515 nm, **I.1** 512 nm and **I.4** 511 nm.

The ring closure in dyes **II** induces a significant change in the spectral characteristics, with general displacement of the absorptions to longer wavelength, the spectra also showing full resolution of the two longer

wavelength bands. The shifts broadly equate to the lower wavelength inflexion of **II** being in a similar region to the principal resolved maxima of **I**, the lower wavelength resolved band of **II** being in a similar region to the longer wavelength inflexion of **I**, and an additional absorption in **II** in the 570 to 575 nm region. For comparative purposes, representative spectra of **I.1** and **II.1** (qualitative) are shown in Fig. 1. The small hypsochromic influence of the hydroxymethyl group is also apparent in these dyes, e.g. **II.3**, $\lambda_{max}$, 540 and 580 nm; **II.1** 536 and 575 nm; **II.4** 533 and 572 nm (Table 1).

The shifts in **II** are unusual, in that the ring closure of **I** to **II** involves loss of one of the colour imparting moieties, viz. the 1-hydroxy group. Alkylation of 1-hydroxyanthraquinones results in loss of intramolecular H-bonding with the adjacent carbonyl group, with significant hypsochromic shifts, cf. 1-hydroxy-, $\lambda_{max}$ 406 nm and 1-methoxyanthraquinone, $\lambda_{max}$ 374 nm (in carbon tetrachloride[7]). The ether group in **II** is part of a saturated cyclic system in which significant enhancement of polar effects relative to **I** would not be anticipated.

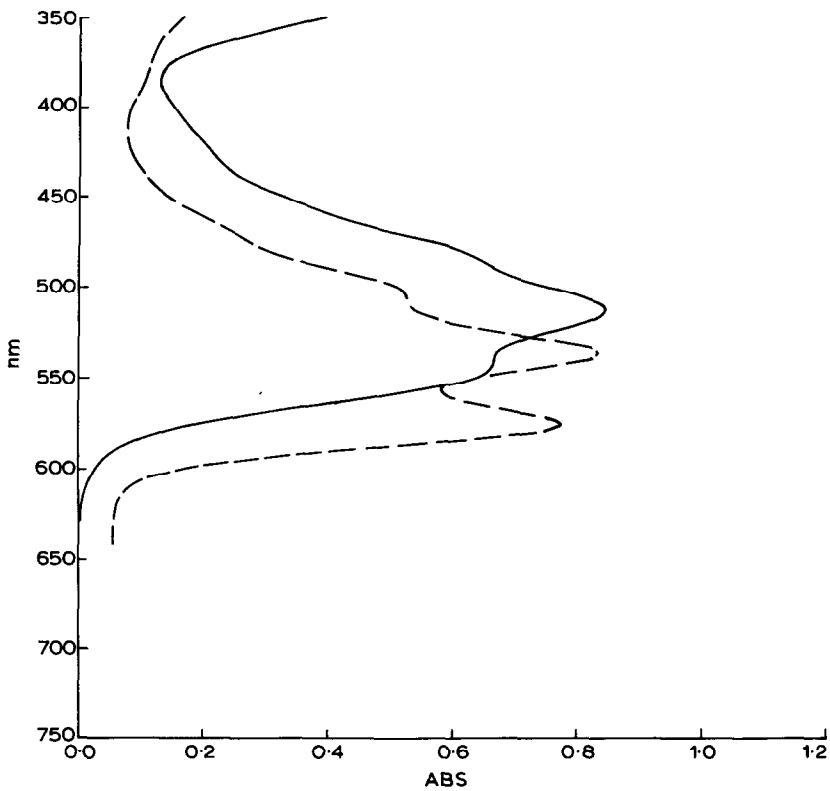



**Fig. 1.** Representative spectra of **I.1** (—) and **II.1** (- - -) in chlorobenzene.

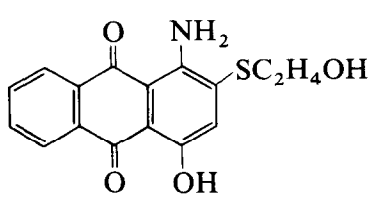
**TABLE 1**
Visible Absorption Maxima from **I** and **II** ($\lambda_{max}$, $\log_e$)

| *Compound* | $R^1$ | $R^2$ | $R^3$ | *Chlorobenzene* | | | | | | *Ethanol* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **I.1** | $CH_2OH$ | $CH_3$ | $CH_2OH$ | 492[a] | (3·89) | 512 | (3·99) | 539[a] | (3·89) | 513 | (4·06) | 534 | (3·98) | | |
| **I.2** | $CH_2OH$ | $CH_2CH_3$ | $CH_2OH$ | 492[a] | (3·89) | 513 | (3·97) | 540[a] | (3·86) | 514 | (4·07) | 534[a] | (4·01) | | |
| **I.3** | $CH_3$ | $CH_2OH$ | $CH_3$ | 493[a] | (3·94) | 515 | (4·03) | 539[a] | (3·94) | 512 | (4·02) | 532[a] | (3·95) | | |
| **I.4** | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | | | 511 | | 537 | | 515 | (4·09) | | | | |
| **I.5** | $CH_3$ | $CH_2CH_2OH$ | $CH_3$ | 494[a] | (3·94) | 517 | (4·02) | 549[a] | (3·89) | 515 | (4·11) | 534[a] | (4·06) | | |
| **I.6** | $CH_3$ | $CH_3$ | $CH_3$ | 492[a] | (3·96) | 516 | (4·05) | 540[a] | (3·92) | 509 | (4·05) | 534[a] | (3·95) | | |
| **II.1** | $CH_3$ | $CH_2OH$ | — | 507[a] | (3·85) | 536 | (4·07) | 575 | (4·04) | 506[a] | (3·89) | 534 | (4·12) | 573 | (4·10) |
| **II.2** | $CH_2CH_3$ | $CH_2OH$ | — | 508[a] | (3·86) | 537 | (4·08) | 575 | (4·06) | 506[a] | (3·84) | 535 | (4·06) | 574 | (4·03) |
| **II.3** | $CH_3$ | $CH_3$ | — | 514[a] | (3·85) | 540 | (4·09) | 580 | (4·07) | 509[a] | (3·86) | 536 | (4·10) | 575 | (4·08) |
| **II.4**[b] | $CH_2OH$ | $CH_2OH$ | — | 506[a] | (3·95) | 533 | (4·13) | 572 | (4·06) | 504[a] | (3·88) | 534 | (4·07) | 572 | (4·02) |

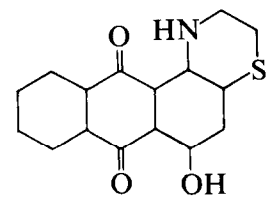
[a] Incompletely resolved band.
[b] **I.4** not sufficiently soluble in chlorobenzene for $\varepsilon$ max evaluation.

Ring closure in anthraquinone derivatives across the 1,2-positions usually results in bathochromic shifts. Thus, whilst 1-amino-2-(2-hydroxyethyl) thio-4-hydroxyanthraquinone (**III**) has $\lambda_{max}$ at 533 and 565 nm,[8] the analogous ring closed 1*H*,2,3-dihydro-6-hydroxyanthra(2,1-*b*)(1,4)thiazine-7,12-dione (**IV**) absorbs at 564 and 605 nm.[9] Similar shifts (*c.* 25 nm) occur on ring closure of 1-amino-2-dialkylaminomethylanthraquinones to the corresponding naphtho(2,3-*h*)quinazolines (**V**).[10] Where the ring closed moiety contains a condensed carbocyclic ring, e.g. as in derivatives of 14*H*-naphtho(2,3-*a*)phenothiazine-8,13-dione,[9] and in 3,4-phthaloyl-acridones[11,12] relative to analogous $\alpha$-anilinoanthraquinones,[13,14] the bathochromic effect of ring closure tends to be enhanced. In all these derivatives, the retention of both polar and H-bonding interactions between the 1-amino moiety and the 9-carbonyl substituent is retained, the latter probably being enhanced due to the more fixed conformation of the dye structure. In **II**, one of the major contributing colour imparting interactions, i.e. H-bonding involving the 1-substituent, is absent, and bathochromic shifts relative to **I** would not be anticipated.

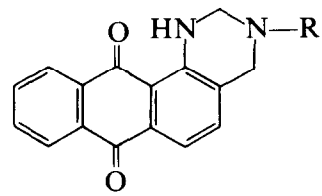
Solvent effects, with respect to chlorobenzene and ethanol, are of a generally low order for both **I** and **II** and are in accord with the diminishing effects which occur in anthraquinone derivatives as the degree of $\alpha$-hydroxy and/or $\alpha$-amino substitution increases and the absorption maxima are displaced to longer wavelengths. In previously reported 2-amino-1,4-dihydroxyanthraquinones,[1] $\lambda_{max}$ in chlorobenzene are at longer wavelengths than in ethanol. Dyes **I** exhibit a similar behaviour, although as the number of hydroxymethyl groups in the amine side chain increases,




**III**




**IV**




**V**

the solvent effect reverses and $\lambda_{max}$ in ethanol are at longer wavelengths, presumably due to enhancement of solvent–solute interactions. Thus, $\Delta\lambda$ values between chlorobenzene and ethanol are +7 nm for **I.6**, +4 nm for **I.3**, −1 nm for **I.1** and −4 nm for **I.4**. Similar effects are apparent in dyes **II**, cf. $\Delta\lambda$ +4 nm for **II.3**, +2 nm for **II.1** and −1 nm for **II.4**.

The 2-aminated derivatives **I** gave bright bluish-red dyeings of good build-up on polyester, with light fastness of a similar order to those of related 2-hydroxyalkylamino derivatives,[1] viz. **I.1**, 4–5, 4–5, 4–5; **I.2**, 4, 4, 4–5; **I.3**, 4, 4–4–5; **I.4**, 3–4, 4, 4; **I.5**, 4, 4, 4–5 and **I.6**, 4, 4, 4. The ring closed dyes **II** gave brilliant violet hues of good build-up, the dyeings showing higher light fastness than analogous **I**, viz. **II.1**, 5–6, 5–6, 5–6; **II.2**, 5–6, 5–6, 5–6; **II.3**, 5–6, 5–6, 6; **II.4**, 5, 5, 5. The colour, dyeing and light fastness parameters of **II** are of a similar order to those of 1-amino-4-hydroxyanthraquine-2-arylthioethers.[8]

The formation of **II** thus gives potential for the synthesis of long wavelength and near-IR absorbing anthraquinone derivatives having very good light stability. The application of the reaction to other polyfunctional $\alpha$-hydroxy anthraquinones containing labile substituents in the $\beta$-position is being investigated and will be reported later.

## ACKNOWLEDGEMENTS

We thank the Teachers' University of Huhhot, and the Government of The People's Republic of China, for leave of absence and financial assistance to enable M.X. to participate in this investigation, also Dr D. J. Maitland (Bradford) for the NMR spectra and discussions thereon.

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