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4,5-Amino and Thioether Derivatives of 1,8-Dihydroxyanthraquinone

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SUMMARY

The synthesis of a series of N-*alkyl and* N-*aryl-1,8-dihydroxy-4,5-diaminoanthraquinones is described. These compounds dye synthetic-polymer fibres in blue to bluish-green hues of good fastness properties.* N,N′-*bis-substituted derivatives are less satisfactory colourants but, in admixture with the* N-*substituted derivatives, good colouration can be achieved. The effect of replacing the amino group in these dyes by the thioether substituent is reported and the effect of substituent changes on the colour of the dyes evaluated.*

1 INTRODUCTION

4,5-Dinitro-1,8-dihydroxyanthraquinone (4,5-dinitrochrysazin, DNCZ), 4,8-dinitro-1,5-dihydroxyanthraquinone (4,8-dinitroanthrarufin, DNAR) and their reduction products, 4,5-diaminochrysazin (DACZ) and 4,8-diaminoanthrarufin (DAAR) are widely utilised in the synthesis of blue disperse dyes. Thus, condensation of DNAR and DNCZ with arylamines affords[1] fast dyes, typified by 4-nitro-5-(4-β-hydroxyethyl)anilino-CZ (C.I. Disperse Blue 27, C.I. 60727).

DACZ has been used as a disperse dye (C.I. 63600), but more satisfactory dyes are obtained by *N*-alkylation. Thus, reaction with methanol–sulphuric acid mixtures, arylsulphonic acid diesters, hydroxylalkyl halides or alkylene oxides gives[2] blue dyes for cellulose secondary acetate, and similar dyes result[3] from alkylation of leuco-DACZ with formaldehyde. More selective

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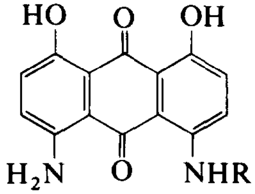
monoalkylation can be effected[4] by acylation of one amino group, alkylation and hydrolysis. Fast blue dyes for polyester result from the methylation of DACZ with formaldehyde in presence of mineral acids[5] and polyalkylated derivatives have also been claimed[6] to be satisfactory dyes.

We have previously reported the synthesis and properties of brominated derivatives of DAAR and DACZ,[7] of *N*-alkylated derivatives of DAAR,[8] and of *N*-alkylated-4-anilino-8-amino-AR and 4-anilino-5-amino-CZ.[9]

The synthesis and properties of a series of *N*-substituted (I) and *N*,*N*′-substituted (II) derivatives of DACZ are now reported, together with comparative data for some thioether analogues of **I** and **II**.



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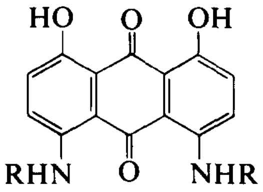


II

2 EXPERIMENTAL

2.1 4-Amino-5-nitro-1,8-dihydroxyanthraquinone (III)

This was prepared by partial reduction of DNCZ with D-glucose using the procedure previously described[8] for DNAR. Compound **III** was obtained as dark brownish-violet prisms. M.p. (nitrobenzene) 314–316°C (sublimes); 97%; λ_{max}(log ε) in chlorobenzene, 551 nm (4·05) and 593 nm (4·02).

2.2 4,5-Dibromochrysazin

DACZ (2·7 g) was added over 30 min at 20°C to nitrosylsulphuric acid (prepared from 0·7 g sodium nitrite and 10 ml conc. sulphuric acid). After stirring for 4 h the mixture was added over 30 min to a stirred suspension of cuprous bromide (3 g) in conc. hydrobromic acid (30 ml). After stirring for 2 h at 20°C and standing overnight at room temperature, the liquor was warmed to 70°C for 1 h, cooled and filtered to give 3·5 g (87%) of a dark orange solid. TLC indicated the presence of a small amount of violet impurity, removed on recrystallisation from 20% aq. DMF (Norit) to give dark orange prisms, m.p. 248–250°C. $C_{14}H_6O_4Br_2$ requires: C, 42·2; H, 1·5; Br, 45·2. Found: C, 42·0; H, 1·4; Br, 44·9%.

2.3 4-Bromo-5-nitro-CZ

4-Amino-5-nitro-CZ (3 g) was diazotised as above and similarly treated with cuprous bromide to give an orange solid (3·3 g, 91%) which was recrystallised from 2-methoxyethanol (Norit) in orange needles, m.p. 295–297°C, of 4-bromo-5-nitro-CZ. $C_{14}H_6NO_6Br$ requires: C, 46·15; H, 1·65; N, 3·85; Br, 22·0. Found: C, 46·0; H, 1·5; N, 3·7; Br, 21·8%.

2.4 4-Amino-5-bromo-CZ

A mixture of 4-bromo-5-nitro-CZ (2 g), 35% sodium hydrogen sulphide (12 ml) and water (50 ml) was stirred at 90–95°C for 90 min. The liquor was diluted with water (50 ml), stirred while cooling and filtered to give a reddish-blue solid (1·63 g, 89%) which recrystallised from 2-methoxyethanol (Norit) in dark violet prisms, m.p. 279–280°C, of 4-amino-5-bromo-CZ. $C_{14}H_8NO_4Br$ requires: C, 50·3; H, 2·4; N, 4·2; Br, 23·95. Found: C, 50·0; H, 2·2; N, 4·1; Br, 23·7%. λ_{max} (log ε) in chlorobenzene, 547 nm (4·07) and 588 (3·99).

2.5 4-*N*-Methylamino-5-amino-CZ (I.1) and 4,5-bis-*N*-methylamino-CZ (II.1)

DACZ (6 g) was stirred into a cooled mixture of methanol (16 ml) and conc. sulphuric acid (16 ml) and the mixture heated at 150–155°C for 6 h. It was cooled, added to ice-water (500 ml) and filtered to give a blue solid (6·2 g) which was separated by chromatography (see below) to give, in increasing order of R_f value, 18% of DACZ, 47% of the monomethyl derivative **I.1** and 26% of the bismethylated derivative **II.1**.

DACZ (5 g) was stirred into a mixture of conc. sulphuric acid (30 ml) and dimethyl sulphate (7 ml) and the mixture stirred at 155°C for 4 h. The liquor was cooled, added to ice-water and the reddish-blue solid (4·8 g) separated as above to give, as the main constituent, 67% of **II.1**.

2.6 4-*N*-Ethylamino-5-amino-CZ (I.2) and 4,5-bis-*N*-ethylamino-CZ (II.2)

Similar reaction to the above, replacing the methanol by ethanol, afforded a mixture which was separated into 20% DACZ, 50% of **I.2** and 20% of **II.2**.

2.7 General synthesis of I and II

Method A. Reaction of DNCZ with alkylamines

To a refluxing solution of DNCZ (3·3 g, 0·01 mol) in *o*-dichlorobenzene (30 ml) was added over 1 h a solution of alkylamine (0.12 mol) in *o*-

dichlorobenzene (10 ml). The mixture was refluxed for 2 h, solvent removed by steam distillation and the reddish-blue product collected. TLC indicated the products to contain, in increasing order of R_f value, **III**, DACZ, **I** and **II**. Variation in reaction times, amount of alkylamine, etc., produced similar mixtures with varying percentages of the above four components. Under the reaction conditions above, mixtures of the approximate composition shown in Table 1 were obtained.

*Method B. Reaction of 4-amino-5-nitro-CZ (**III**) with alkylamines*

A solution of alkylamine (0·05 mol) in *o*-dichlorobenzene (30 ml) was added over 1 h to a refluxing solution of **III** (3 g, 0·01 mol) in *o*-dichlorobenzene (30 ml). The mixture was refluxed a further 5 h, steam-distilled and the product filtered. TLC indicated the formation of **I** and DACZ in ratios dependent on the alkylamine used. Column chromatography afforded the following mono-alkylated derivatives **I**: propylamine, 24%; isopropylamine, 22%; butylamine, 20%; isobutylamine, 18%; 3-methoxypropylamine, 14%; 2-aminoethanol, 9%; cyclohexylamine, 15%; benzylamine, 18%. The residual balance in all cases was predominantly DACZ.

Method C. Reaction of DACZ with alkyl halides

A solution of DACZ (2·7 g, 0·01 mol) in *o*-dichlorobenzene (20 ml) was refluxed in presence of anhydrous potassium carbonate (2 g) and a solution of alkyl halide (0·06 mol) in *o*-dichlorobenzene (30 ml) was added in three portions (each portion added over 30 min and the mixture refluxed a further 30 min prior to the next addition). After refluxing a further 8 h, the liquor was steam-distilled and the product filtered. TLC indicated them to contain

TABLE 1
Reaction of DNCZ with Alkylamines

Amine	*Product* (%)			
	DACZ	*III*	*I*	*II*
Ethylamine	30	30	20	10
Propylamine	30	25	30	15
Isopropylamine	50	20	10	20
Butylamine	30	30	30	10
Isobutylamine	55	10	20	15
sec-Butylamine	35	20	25	20
3-Methoxypropylamine	70	—	15	15
2-Aminoethanol	65	—	20	15
Cyclohexylamine	50	20	20	10
Benzylamine	90	—	10	—

I and **II**, with smaller amounts of DACZ and of polyalkylated derivatives. Chromatographic separation gave the following percentages of **I** and **II** respectively: 1-iodopropane, 25%, 55%; 2-iodopropane, 30%, 45%; 1-iodobutane, 25%, 50%; 1-iodo-2-methylpropane, 20%, 40%; 2-bromobutane, 25%, 40%; 2-bromoethanol, 15%, 15%; 2-bromocyclohexane, 15%, 20%; benzyl bromide, 25%, 35%.

Method D. Reaction of 4-amino-5-nitro-CZ (III) with alkyl halides, and reduction
To a refluxing solution of **III** (3 g, 0·01 mol) in *o*-dichlorobenzene (20 ml) was added over 2 h a solution of alkyl halide (0·04 mol) in *o*-dichlorobenzene (20 ml). The mixture was refluxed 10 h, steam-distilled and the resultant blue solid (2 g used) reduced by stirring at 90–95°C for 1 h in water (30 ml) and 30% aq. sodium hydrogen sulphide (10 ml). TLC of the products indicated the major component to be **I**, separated by chromatography to give, from 1-iodopropane, 64%; 2-iodopropane, 60%; 1-iodobutane, 66%; 1-iodo-2-methylpropane, 45%; 2-bromobutane, 55%; 2-bromoethanol, 40%; benzyl bromide, 40% and 2-bromocyclohexane, 35% of the respective **I**. The residual balance comprised DACZ mainly, with some **II**.

2.8 4-Arylamino-5-amino-CZ (I.12–I.14)

DNCZ (3 g) was refluxed for 4 h with the arylamine (5 g) in 2-methoxyethanol (75 ml). The liquor was cooled, added to 20% aq. hydrochloric acid (250 ml) and the resultant blue solid filtered, washed neutral and the wet cake reduced by heating for 2 h at 95°C in water (50 ml) and 35% sodium hydrogen sulphide (15 ml). After cooling to 60°C, the liquor was diluted with water (50 ml) and the 4-arylamino-5-amino-CZ (**I.12–I.14**, Table 2) collected (85–95% yield) and purified by recrystallising from 2-methoxyethanol.

2.9 4,5-Bis-anilino-CZ (II.12)

DNCZ (2·5 g) was refluxed for 16 h in aniline (30 ml), the liquor cooled, filtered and the residue (2·1 g, 66%) washed with dilute HCl, then water and finally recrystallised from 2-methoxyethanol (Norit) in dark blue needles, m.p. 241–243°C.

2.10 4,5-Bis-4-methylanilino-CZ (II.13)

DNCZ (2·5 g) was refluxed for 60 h with 4-toluidine (2 g) in *o*-dichlorobenzene (30 ml). TLC of the reaction liquor indicated it to contain **II.13**, 4-nitro-5-(4-methylanilino)-CZ and 4-amino-5-(4-methylanilino)-CZ (**I.13**) in

TABLE 2
Characterisation Data for Monosubstituted Dyes I

Compd	*R*	*M.p. (°C)*	λ_{max} *(nm) (log ε) in monochlorobenzene*		*Fastness on polyester*			
					Lightfastness			*Sublimation (°C)*
					0·1%	*0·5%*	*2·5%*	
I.1	CH_3	247–248	611 (4·21)	656 (4·25)	4–5	4–5	5	130
I.2	CH_2CH_3	181–182	612 (4·21)	658 (4·25)	4–5	4–5	4–5	130
I.3	$CH_2CH_2CH_3$	170–171	614 (4·15)	659 (4·22)	4	4	4–5	130
I.4	$CH(CH_3)_2$	233–234	614 (4·16)	660 (4·25)	4–5	5	5	140
I.5	$CH_2CH_2CH_2CH_3$	156–157	616 (4·08)	659 (4·18)	4	4	4	140
I.6	$CH_2CH(CH_3)_2$	148–149	620 (4·08)	658 (4·16)	4	4	4	140
I.7	$CH(CH_3)CH_2CH_3$	165–166	620 (4·16)	662 (4·25)	4–5	5	5	140
I.8	C_2H_4OH	207–209	610 (4·17)	656 (4·24)	4	4	4	140
I.9	$C_3H_6OCH_3$	151–152	620 (4·10)	657 (4·16)	5	5	5	140
I.10	C_6H_{11}	187–188	622 (4·14)	664 (4·22)	5	5–6	5–6	140
I.11	$CH_2C_6H_5$	216–218	606 (4·06)	648 (4·16)	5	5	5	150
I.12[a]	C_6H_5	243–244	610 (4·22)	650 (4·31)	6	6	6	160
I.13	$C_6H_4CH_3$-*p*	250–251	610 (4·21)	649 (4·32)	6	6	6	160
I.14	$C_6H_4OCH_3$-*p*	232–233	612 (4·24)	649 (4·34)	6	6	6	160

[a] Data from Ref. 9.

an approximate ratio 50:35:15. The crude product was collected after removal of solvent by steam distillation and **II.13** separated from it by column chromatography (see below).

II.3 was also obtained by refluxing a mixture of DACZ (2 g), anhydrous potassium carbonate (2 g), cuprous bromide (0·5 g) and 4-bromotoluene (6 g) in nitrobenzene (30 ml) for 50 h. The liquor was cooled and filtered to give 1·8 g (54%) of a dark blue solid which crystallised from 10% aq. DMF in dark blue needles of **II.13**, m.p. 261–262°C. $C_{28}H_{22}N_2O_4$ requires: C, 74·7; H, 4·9; N, 6·2%. Found: C, 74·5; H, 4·8; N, 6·0%.

2.11 4,5-Bis-4-methoxyanilino-CZ (II.14)

Similar reaction of DNCZ with 4-methoxyaniline (90 h) gave a crude product from which was isolated by column chromatography 62% of **II.14** (as highest-R_f component), m.p. 208–211°C. $C_{28}H_{22}N_2O_6$ requires: C, 69·7; H, 4·6; N, 5·8. Found: C, 69·4; H, 4·3; N, 5·6%. The principal by-product was 4-amino-5-(4-methoxyanilino)-CZ (**I.14**) (18%).

2.12 4-Amino-5-phenylthio-CZ

To a solution of DNCZ (3·3 g, 0·01 mol) in DMF (20 ml) containing anhydrous sodium acetate (0·6 g) was added dropwise over 40 min at −20°C a solution of thiophenol (1·21 g, 0·011 mol) in DMF (10 ml). The solution was stirred for 4 h at −20°C, the temperature then allowed to rise to ambient and after stirring a further 1 h the liquor was stirred into 5% aq. hydrochloric acid (400 ml) and filtered to give 4·1 g of a reddish-orange solid. TLC indicates this to contain three main components, separation of which was effected by column chromatography. From 1 g crude reaction product was obtained, in decreasing order of R_f value:

(a) Orange zone, 0·46 g, showing P^+ at m/e 438 on its mass spectrum, i.e. corresponding to a β-phenylthio-DNCZ.
(b) Red zone, 0·22 g of 4-nitro-5-phenylthio-CZ, m.p. 210–211°C. $C_{20}H_{11}NO_6S$ requires: C, 61·1; H, 2·8; N, 3·6; S, 8·1. Found: C, 60·8; H, 2·7; N, 3·4; S, 7·8%. λ_{max} (log ε) in chlorobenzene, 535 nm (3·95) and 560 nm (3·91).
(c) Mauve zone, 0·08 g of 4,5-bisphenylthio-CZ, identical to the product prepared below.

Reduction of the first two components in 30% sodium hydrogen sulphide afforded, from (a), 2-phenylthio-4,5-diamino-CZ, m.p. 241–243°C

($C_{20}H_{14}N_2O_4S$ requires: C, 63·5; H, 3·7; N, 7·4; S, 8·5. Found: C, 63·2; H, 3·5; N, 7·1; S, 8·3%); P^+ at *m/e* 378; λ_{max} (log ε) in chlorobenzene, 592 nm (4·33) and 629 nm (4·37); and from (b) 4-amino-5-phenylthio-CZ, m.p. 229–231°C. $C_{20}H_{13}NO_4S$ requires: C, 66·1; H, 3·6; N, 3·9; S, 8·8. Found: C, 65·8, H, 3·3; N, 3·6; S, 8·6%. P^+ at *m/e* 363; λ_{max} (log ε) in chlorobenzene, 564 nm (4·22) and 603 nm (4·22).

Alternatively, 4-amino-5-nitro-CZ (**III**) (3g) was stirred in DMF (20 ml) at room temperature and thiophenol (1·5 g) in DMF (10 ml) run in over 30 min. After stirring 2 h at room temperature and then at 80–85°C for 1 h, the mixture was added to ice-cold 20% aq. HCl and filtered. The product, after two recrystallisations from 2-methoxyethanol (Norit), gave 2·2 g (61%) of 4-amino-5-phenylthio-CZ, m.p. 227–229°C. Similarly, a mixture of 4-amino-5-bromo-CZ (3 g), thiophenol (4 g) and anhydrous potassium carbonate (2 g) in DMF (20 ml) was stirred for 8 h at 120°C. The cooled liquor, on dilution with methanol (10 ml) and water (25 ml) gave, on filtration, 2·4 g (74%) of 4-amino-5-phenylthio-CZ.

2.13 4,5-Bis-phenylthio-CZ

To a solution of thiophenol (3·3 g, 0·03 mol) in DMF (15 ml) containing anhydrous potassium carbonate (0·2 g) at 100–110°C was added 4,5-dibromo-CZ (3·98 g, 0·01 mol). The mixture was then stirred at 125–130°C for 8 h, cooled, diluted with methanol (10 ml) and ice-water (20 ml) and the brownish-red precipitate (4·1 g, 90%) collected. This was recrystallised twice from 2-methoxyethanol in dark red prisms, m.p. 251–253°C. $C_{26}H_{16}S_2O_4$ requires: C, 68·4; H, 3·5; S, 14·0. Found: C, 68·2; H, 3·1; S, 13·7%. λ_{max} (log ε) in chlorobenzene, 544 nm (4·18) and 576 (4·22).

2.14 4-Amino-5-(2-benzothiazolyl)thio-CZ

DNCZ (3·3 g) was stirred at 145–150°C for 6 h with 2-mercaptobenzothiazole (2·5 g) in DMF (25 ml) in presence of anhydrous sodium acetate (1 g). The liquor was cooled, diluted with a little ice-water and filtered to give 2·6 g of a dark red solid which was recrystallised from 2-methoxyethanol in deep red plates of 4-nitro-5-(2-benzothiazolyl)thio-CZ, m.p. 246–247°C. $C_{21}H_{10}N_2O_6S_2$ requires: C, 56·0; H, 2·2; N, 6·2; S, 14·2. Found: C, 55·8; H, 2·1; N, 6·0; S, 13·9%. λ_{max} (log ε) in chlorobenzene, 516 nm (4·16).

Reduction of the above with sodium hydrogen sulphide (as above) afforded 4-amino-5-(2-benzothiazolyl)thio-CZ, bright purple needles, m.p. 245–246°C (2-methoxyethanol). $C_{21}H_{12}N_2O_4S_2$ requires: C, 60·0; H, 2·9; N, 6·7; S, 15·2. Found: C, 59·7; H, 2·8; N, 6·5; S, 15·1%. λ_{max} (log ε) in monochlorobenzene, 557 nm (4·16) and 599 nm (4·13).

TABLE 3
Characterisation Data for Bis-substituted Dyes **II**

Compd	*R*	*M.p. (°C)*	λ_{max} *(nm) (log ε) in monochlorobenzene*		*Fastness on polyester*			
					Lightfastness			*Sublimation (°C)*
					0·1%	*0·5%*	*2·5%*	
II.1	CH_3	279–281	635 (4·19)	685 (4·26)	4	4	4	150
II.2	CH_2CH_3	238–239	637 (4·20)	685 (4·26)	4	4	4	150
II.3	$CH_2CH_2CH_3$	212–213	640 (4·19)	688 (4·27)	4	4	4	150
II.4	$CH(CH_3)_2$	241–242	640 (4·20)	688 (4·27)	5	5	5	150
II.5	$CH_2CH_2CH_2CH_3$	175–176	642 (4·18)	689 (4·25)	4	4	4	150
II.6	$CH_2CH(CH_3)_2$	187–188	642 (4·18)	691 (4·26)	4	4	4	150
II.7	$CH(CH_3)CH_2CH_3$	143–144	644 (4·15)	691 (4·23)	5	5	5	150
II.8	C_2H_4OH	258–260	631 (4·14)	681 (4·20)	4	4	4	160
II.9	$C_3H_6OCH_3$	167–168	640 (4·16)	685 (4·22)	5	5	5	150
II.10	C_6H_{11}	225–226	643 (4·18)	692 (4·22)	5	5–6	5–6	160
II.11	$CH_2C_6H_5$	240–241	630 (4·21)	680 (4·29)	4–5	4–5	4–5	170
II.12[a]	C_6H_5	241–243	642 (4·26)	684 (4·31)	6–7	6–7	6–7	180
II.13	$C_6H_4CH_3$-*p*	261–262	645 (4·22)	684 (4·29)	6–7	6–7	6–7	180
II.14	$C_6H_4OCH_3$-*p*	208–211	646 (4·20)	686 (4·27)	6–7	6–7	6–7	180

[a] Data from Ref. 9.

2.15 Due purification and properties

All dyes were purified, where necessary, by column chromatography on Kieselgel 60 (Merck). Dyes were applied from solution on *o*-dichlorobenzene and eluting solvent was toluene containing up to 5% ethyl acetate as appropriate. Requisite zones were extracted with boiling ethanol and the products further recrystallised where necessary. Purity was confirmed by mass spectrometry and elemental analyses. Electronic spectra were recorded on a Unicam SP800 from dye solutions in monochlorobenzene. Dyeings on polyester and fastness assessments were carried out as previously described.[7,10] Relevant data for **I** and **II** are shown in Tables 2 and 3 respectively.

3 RESULTS AND DISCUSSION

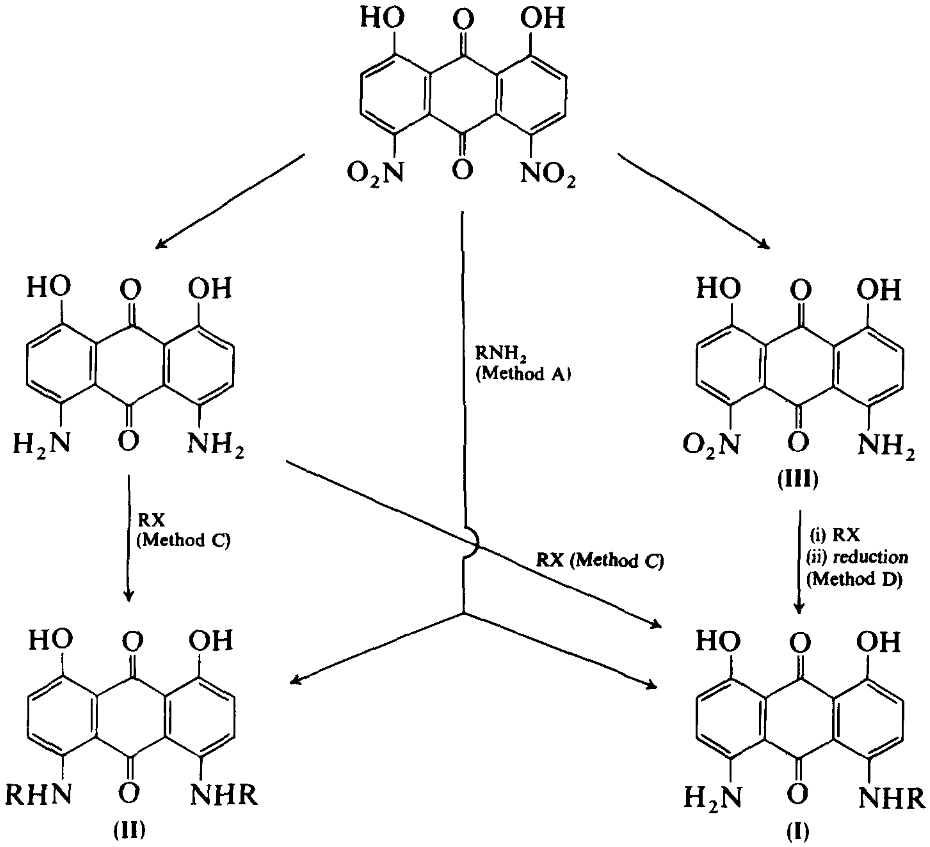
3.1 Syntheses

The mono-(**I**) and bis-alkylated derivatives (**II**) were obtained as shown in Scheme 1. Condensation of DNCZ with alkylamines (Method A) was generally unsatisfactory, the principal reaction being reduction, with the formation of large amounts of fully (DACZ) and partially reduced (**III**) products. This tendency for reduction was considerably greater than in analogous reactions with DAAR.[8] Low yields of **I** and **II** could be isolated by chromatography and the method was useful in obtaining derivatives not readily available via other routes, e.g. **II.9**.

Reduction occurred during the synthesis of **I** by reaction of alkylamines with the partially reduced DNCZ derivative **III** (Method B). Yields of condensed product were again low, the reduction process being especially dominant in reactions with 2-aminoethanol, 3-methoxypropylamine, benzylamine and cyclohexylamine. In both Methods A and B, gradual addition of the alkylamine facilitated the formation of **I** and/or **II**; when the reactant ratios given in Section 2 were mixed and refluxed, reduction side-reactions were enhanced.

A gradual addition of alkyl halides to a refluxing solution of DACZ in *o*-dichlorobenzene was also more advantageous in Method C. Selective alkylation was not possible, the initially formed **I** undergoing alkylation to **II** as readily as alkylation of unreacted DACZ. Whilst good conversion to **II** might have been anticipated on prolonged alkylation, this was found not to occur, polyalkylation proceeding readily.

A more selective synthesis of the monoalkylated derivatives (Method D) was by alkylation of **III**, followed by reduction, the major by-product being

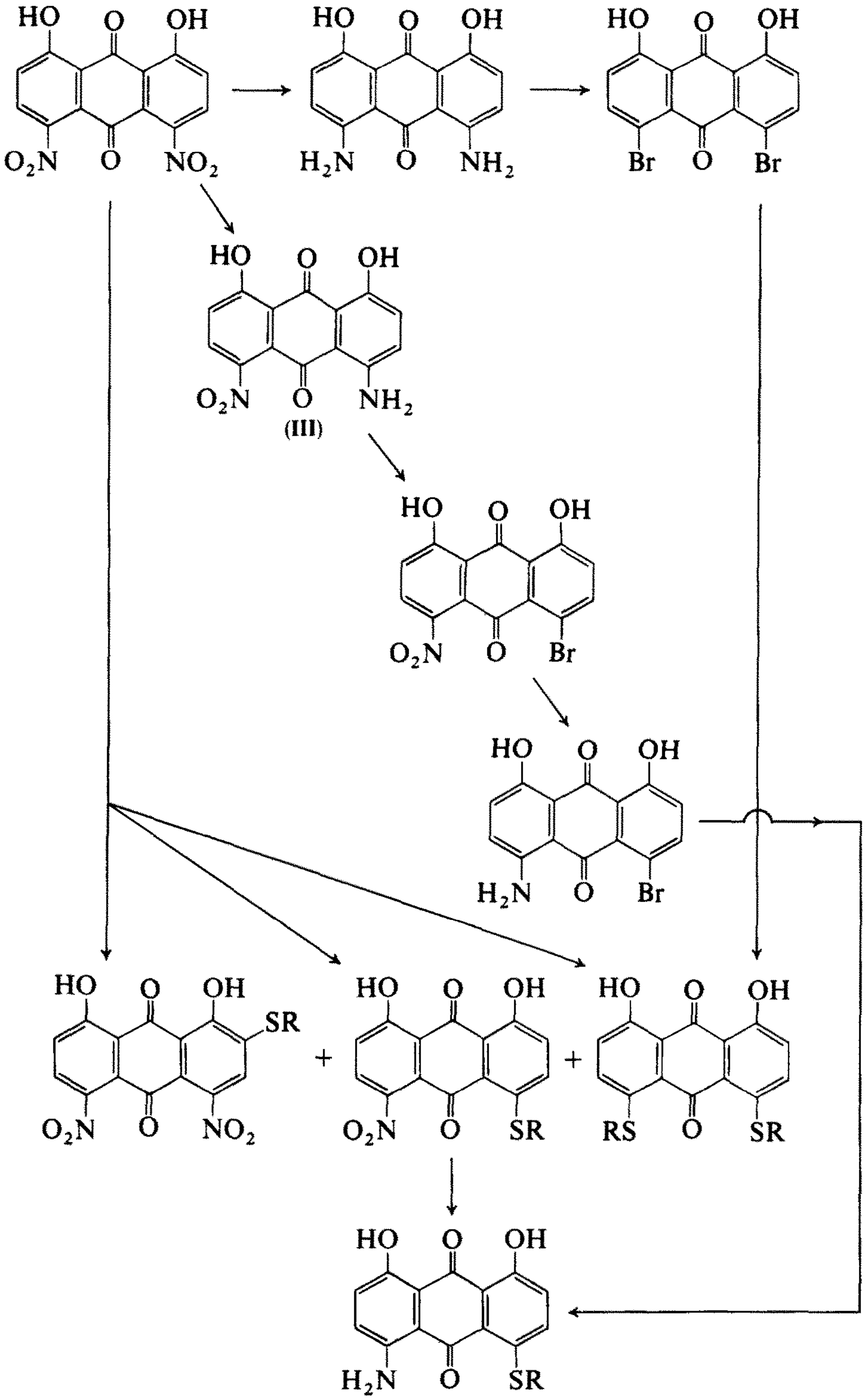


Scheme 1. General methods of synthesis used for dyes **I** and **II**.

N,N-bis-alkylated derivatives formed in the first stage. Compound **III** used in this and other methods is itself a useful violet dye for polyester and was obtained by reduction of DNCZ with alkaline D-glucose. In addition to glucose,[11] other reducing agents useful in the partial reduction include glucose–diethanolamine mixtures,[12] ammonium hydroxide–sodium sulphohydrate mixtures,[12] phenolic compounds in presence of alkali,[13–15] and hydrazine hydrate either alone[16] or in admixture with phenols[17] or with *N,N*-dimethylaniline.[18]

Reaction of 4-amino-5-bromo-CZ with alkylamines did not proceed well at atmospheric pressure, only limited replacement of the bromo substituent occurring. In view of the additional stages involved, i.e. diazotisation of **III**, Sandmeyer reaction and reduction, the method appears to offer no advantages.

Thioether analogues of the above were obtained as outlined in Scheme 2. Condensation of DNCZ with thiophenols gave a mixture of products. Using



Scheme 2. General methods of synthesis used for 1,8-dihydroxyanthraquinone-α-thioethers.

1 mol of thiophenol and a temperature range from −30°C to reflux in DMF gave, in varying proportions, unreacted DNCZ, 4-nitro-5-phenylthio-CZ, 4,5-bis-phenylthio-CZ and a β-substituted derivative. The latter on reduction gave an identical product to that obtained[19] by condensation of 2-bromo-CZ with thiophenol, i.e. 2-phenylthio-CZ. The general tendency was for the formation of higher percentages of the bis-phenylthio derivative at temperatures above 100°C and the β-phenylthio derivative at below 0°C. The β-substituted derivatives have been prepared from the corresponding β-sulphonic acids or β-bromo derivatives,[20–23] by reaction of thiols on anthraquinone quinone-imines followed by oxidation[24,25] and by direct β-substitution into DNCZ followed by reduction, e.g. reaction with 2-mercaptoethanol,[26] or with thiophenols in pyridine below 0°C.[27–29]

4-Amino-5-phenylthio-CZ and 4,5-bis-phenylthio-CZ were prepared by generally lower- and higher-temperature condensations respectively (see Section 2) of DNCZ with thiophenol, although similar reactions using 4,5-dibromo-CZ and 4-amino-5-bromo-CZ were more satisfactory, the use of the halogeno intermediates obviating formation of the reduction by products observed in reactions of the nitro compounds. The reduction side-reactions can be minimised by reaction of DNCZ with arylthiols in presence of bases such as triethanolamine, triethylamine or dimethylaniline,[30] whilst replacement of α-halogeno substituents with thiols has been extensively utilised in the synthesis of pleochroic anthraquinone thioethers, e.g. Refs 31–38.

Condensation of DNCZ with 2-mercaptobenzothiazole gave mainly the monocondensed derivative and little of the reductive side-reactions apparent with thiophenol. The blue and violet dyes resulting from the condensation of various α-nitroanthraquinones with 2-mercaptobenzothiazole[39] have been stated to be more readily obtained by the use of di-2-benzothiazolyl disulphide as a source of the thiol.[40]

3.2 Electronic spectra

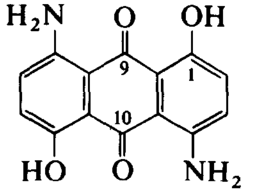
N-Alkylation of DACZ results in significant bathochromic shifts in both of the principal visible absorption bands. Methylation, for example, results in a displacement of the 582 nm and 619 nm absorptions in DACZ to 611 nm and 656 nm for the monomethylated derivative and to 635 nm and 685 nm for the bismethylated compound. The shifts are larger than those resultant from bromination of DACZ,[7] and with bisalkylation, λ_{max} values similar to those of 4-alkylamino-5-arylamino-CZ derivatives[9] are observed. The presence of longer alkyl chains gives further slight shifts in λ_{max}, of similar order to those resultant from *N*-alkyl substitution in 1-aminoanthraquinone[31] and DAAR.[8]

The bathochromic shifts are relatable both to the electron-donating character of the *N*-alkylamino substituent and to intramolecular H-bonding between the NH and CO groups. Typical delocalisation structures for 1,4,5,8-tetra-(donor)-substituted anthraquinones have been outlined,[42] and such compounds can, in simple terms, be regarded as two 1,4-bis-substituted anthraquinones. On such a basis, the absorption maxima of DACZ and of DAAR may be expected to be similar, since both contain what may be regarded as two residues of 1-amino-4-hydroxyanthraquinone. However, studies[43] on a range of bis-substituted anthraquinones have indicated that the conjugation between substituents in different rings is not totally interrupted by the anthraquinone C═O groups, and the splitting of the long-wavelength bands of 1,5- and 1,8-diaminoanthraquinones and their *N*-alkyl derivatives in non-polar solvents has been related[44] to the interaction of two partially conjugated amino groups with each other, in addition to their interaction with the π-cloud of the anthraquinone ring system. The spectra of 1,8-diaminoanthraquinone, in which both amino groups conjugate with the same C═O group (crossed conjugation), show a more complex structure than the spectra of the 1,5-isomer,[43] and the spectrum of 1,8-dihydroxyanthraquinone shows similar crossed conjugation, leading to a non-equivalence of the C═O groups.[45]

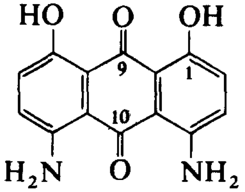
The contribution of the donor substituent–acceptor carbonyl resonance structures has additionally been concluded to be of more significance to the ground state than to the first excited state.[46] Thus, the increase in π-electron density in the first excited state of 1-substituted derivatives has been shown to be greater at the C═O (10) oxygen atom than at the C═O (9) oxygen, in contrast to simple resonance theory. Hence the changes in π-electron density resultant from excitation to the first excited state are not confined solely to the donor atom and the adjacent C═O residue.

One could however argue that in terms of simple resonance theory, an increased electron density at the C═O (10) moiety might be concluded on the basis of the more extended conjugation at this position with a 1-donor substituent. Additionally, hydrogen-bonding factors are also operative, and differences in the nature of such bonding in 1-hydroxy- and 1-aminoanthraquinones has been extensively studied.[45,47,48] Whilst in the 1-amino derivatives the H-bond between the amino and carbonyl functions may weaken and break on photoexcitation, that between the hydroxy and carbonyl function is more stable.[45]

In general terms, if the hydroxy–carbonyl H-bond, in the form of a relatively stable quasi-aromatic ring, can be regarded as being more stable than that of the amino–carbonyl H-bond formed by dipole and acceptor–donor interactions, then in DAAR one might expect the H-bonds between the 1-hydroxy and 9-carbonyl residues and between the 5-hydroxy



(DAAR)



(DACZ)

and 10-carbonyl residues to be the more dominant. In DACZ however, additional resonance structures involving H-bonds between the 1- and 8-hydroxy groups and the 9-carbonyl group may be envisaged (and also between the 10-carbonyl group and the adjacent amino groups). Such additional resonance would be expected to result in bathochromic shifts in the absorption maxima of DACZ and its derivatives relative to DAAR and this is in fact observed, e.g., DAAR 574 nm and 612 nm,[7] DACZ 582 nm and 619 nm; *N*-methyl-DAAR 605 nm and 655 nm,[8] *N*-methyl-DACZ (**I.1**), 611 nm and 656 nm; *N,N'*-dimethyl-DAAR 627 nm and 680 nm,[8] *N,N'*-dimethyl-DACZ (**II.1**) 635 nm and 685 nm (all in monochlorobenzene).

The *N*-aryl derivatives (**I.12–I.14**; **II.12–II.14**) absorb in a similar region to the analogous *N*-alkyl derivatives. In monosubstituted anthraquinones, phenylation results in slight bathochromic shifts or no change in absorption maxima relative to methylation, depending on the solvent. For example, λ_{max} are as follows: 1-amino, 463 nm; 1-*N*-methylamino, 500 nm; 1-anilino, 504 nm, in toluene;[49] and 1-*N*-methylamino and 1-anilino, 508 nm for each in chloromethane.[50] These colour shifts can be reversed slightly in the tetra-substituted dyes, viz.

4,5-$(NH_2)_2$-CZ	582 and 619 nm
4-NH_2-5-NHMe-CZ (**I.1**)	611 and 656 nm
4-NH_2-5-NHPh-CZ	610 and 650 nm
4,5-$(NHMe)_2$-CZ (**II.1**)	635 and 685 nm
4-NHMe-5-NHPh-CZ[9]	635 and 683 nm
4,5-$(NHPh)_2$-CZ	642 and 684 nm

The position of substitution also appears to affect the relative shifts from *N*-phenylation and *N*-methylation, since in 1,5-bis-substituted derivatives, the bisanilino derivative (λ_{max} 533 nm) is significantly more bathochromic than the bis-*N*-methylamino analogue (λ_{max} 514 nm) (in benzene[43]), whilst in the 1,4-analogues a reverse effect is observed (bis-*N*-methylamino λ_{max} 593 nm and 650 nm, bisanilino λ_{max} 603 nm and 645 nm, in benzene).[51]

The significance of H-bonding to the colour of these dyes is further apparent in the marked hypsochromic shifts resultant from replacing the amino groups by thiol substituents. In azobenzene derivatives, the lower electron-donating character of the thiol group is shown in the decrease in both absorption maximum and extinction coefficient of 4-methylthioazobenzene (λ_{max} 362 nm, log ε 4·38) relative to 4-*N*-methylaminoazobenzene (λ_{max} 402 nm, log ε 4·41)[52] (in 95% ethanol), viz. a hypsochromic shift of 40 nm, unrelatable to intramolecular H-bonding factors. Much larger differences are apparent in the anthraquinone analogues, e.g. 1-*N*-methylamino, λ_{max} 508 nm; 1-methylthio, λ_{max} 438 nm[50] (in dichloromethane), viz. a hypsochromic shift of 70 nm. Introduction of additional donor residues into the thiol substituent, whilst giving bathochromic shifts, does not develop the colour of the amino derivatives. Thus values of λ_{max} of 455 nm (in chloroform)[53] and 450 nm (in ethanol)[54] have been reported for 1-methoxythioanthraquinone and of 460 nm[53] and 470 nm[54] for 1-hydroxythioanthraquinone.

In bis-substituted derivatives, differences between alkylthio and alkylamino derivatives are of an order double those of the monosubstituted compounds. Thus, λ_{max} 500–509 nm, for 1,4-bismethylthioanthraquinone[55] and 593 nm and 650 nm for 1,4-bis-*N*-methylaminoanthraquinone[51] have been reported (in benzene) and similar differences are apparent in aryl analogues, e.g. λ_{max} 489–495·5 nm for 1,4-bisphenylthioanthraquinone[55] and λ_{max} 595 nm and 632 nm for 1,4-bisanilinoanthraquinone[51,56–58] (both in ethanol).

Whilst these differences in $\Delta\lambda$ values between the amino and thiol derivatives in the azobenzene derivatives, in which no intramolecular H-bonding is possible, and in the anthraquinone derivatives, in which it is, may not totally reflect the shifts in absorption maxima directly relatable to H-bonding, the overall bathochromic effect of such bonding is apparent.

In the dyes synthesised in this present study, differences in the order of 50 nm for each replacement of phenylamino substituents by phenylthio are observed, viz.

4-NH$_2$-5-NHPh-CZ (**I.12**)	λ_{max} 610 and 650 nm
4-NH$_2$-5-SPh-CZ	λ_{max} 564 and 603 nm

4,5-(NHPh)$_2$-CZ (**II.12**)	λ_{max} 642 and 684 nm
4,5-(SPh)$_2$-CZ	λ_{max} 544 and 576 nm

Replacement of the phenyl residue in the thiol substituent by the electron-attracting 2-benzothiazolyl (2BT) residue results in significant hypsochromic shifts in the case of the additionally nitro-substituted compounds, but when the nitro group is replaced by the donor amino group, the differences are almost eliminated, viz.

4-NO$_2$-5-SPh-CZ	λ_{max} 535 and 560 (sh) nm
4-NO$_2$-5-S(2BT)-CZ	λ_{max} 516 nm

4-NH$_2$-5-SPh-CZ	λ_{max} 564 and 603 nm
4-NH$_2$-5-S(2BT)-CZ	λ_{max} 557 and 599 nm

A similar effect is seen in other aminated derivatives, in which the influence of an amino group in the system tends to negate the differences in λ_{max} apparent in analogous nitro compounds, thus demonstrating the influence of additional donor–acceptor interaction on the colour of these dyes, e.g.

4-NO$_2$-5-NHMe-CZ[17]	λ_{max} 589 and 633 nm
4-NO$_2$-5-NHPh-CZ[9]	λ_{max} 598 and 622 nm
4-NH$_2$-5-NHMe-CZ (**I.1**)	λ_{max} 611 and 656 nm
4-NH$_2$-5-NHPh-CZ[9]	λ_{max} 610 and 650 nm

3.3 Dyeing and fastness properties

All the monoalkylated derivatives **I** coloured polyester in deep blue shades, considerably greener in hue than DACZ. Differences in build-up with variation of the *N*-substituent were slight, the cyclohexyl (**I.10**) and benzyl (**I.11**) derivatives being the weakest and the 3-methoxypropyl (**I.9**) and 2-hydroxyethyl (**I.8**) derivatives the strongest. The bisalkylated dyes **II** were much greener in hue than **I**, but of more limited build-up and could not be regarded as satisfactory dyes. Even with those of relatively better build-up, i.e. the 3-methoxypropyl (**II.9**) and 2-hydroxyethyl (**II.8**) derivatives, visual differences between 0·5% and 2·5% dyeings were very small.

Mixtures of **I** and **II** gave generally very good colouration of polyester, as did the mixtures of DACZ, **I** and **II** obtained as crude reaction products in the various preparative routes used. Compared with analogous mixture dyeings from DAAR analogues,[8] the DACZ-based mixtures tended to give better build-up, probably relatable to the much better dyeing properties of DACZ compared with DAAR. Thus, mixtures of DACZ and the monomethylated derivative **I.1**, in ratios varying from 1:4 to 4:1, all gave very strong dyeings, and although the bismethylated derivative **II.1** was a poor dye, mixtures of DACZ, **I.1** and **II.1** in 1:1:1, 1:2:1 and 1:3:1 ratios all gave dyeings of similar build-up to those obtained from **I.1** alone.

The *N*-phenylated derivatives **I.12–I.14** also gave good colouration of polyester, dyeings being slightly greener than those of the *N*-alkylated analogues and not significantly weaker in colour strength. The dyeing properties of the anilino derivative **I.12** and its derivatives have been previously described.[9] The *N*,*N'*-bisphenylated compounds **II.12–II.14** were poor dyes, having very limited build-up on polyester, but mixtures of them with the monophenylated derivatives showed improved dyeing properties. Thus, dyeings of **I.12** and **II.12** in 3:1 ratio were very similar to those of **I.12** alone, and in 1:1 ratio build-up was lower but still very good.

All compounds **I** had acceptably good lightfastness of an order similar to those of analogous DAAR derivatives.[8] As with the latter, sublimation fastness was moderate only and the two series of dyes thus have similar colouration and fastness properties, the CZ isomers being slightly greener.

The thiol derivatives also gave very good colouration of polyester, although in much redder hues than the amino derivatives, viz. 4-nitro-5-(2-benzothiazolyl)thio-, dark red; 4-amino-5-(2-benzothiazolyl)thio-, dark violet; 4-nitro-5-phenylthio-, deep magenta; 4-amino-5-phenylthio-, reddish-blue, and 4,5-bis-phenylthio-, dark purple. Light fastness of all the above, except for the 4-amino-5-phenylthio derivative (5–6) was 6–7 at all depths of shade and the general area of initial mark-off on the sublimation list was 180–200°C. All these thiol derivatives are thus excellent dyes for polyester. Hue, build-up and fastness were also of a similar order to those observed for 4-amino-5-nitro-CZ (dark violet) and 4-amino-5-bromo-CZ (deep violet). Anthraquinone-α-thioethers have been the subject of patent specifications in the context of disperse dyes for synthetic-polymer fibres, e.g. 1,4-dihydroxy-5-amino-8-thioethers,[59,60] and 1,8-dihydroxy-4-amino- and 4-nitro-5-thioethers,[61,62] in addition to their use as pleochroic dyes as previously noted.

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