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5,6-(6,7-)Dichlorobenzothiazolylazo Dyes for Synthetic-Polymer Fibres

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ABSTRACT

The synthesis and properties of a series of monoazo dyes derived from the isomer mixture of 5,6-dichloro- and 6,7-dichloro-2-aminobenzothiazoles as diazo component are reported. By appropriate selection of substituents in the coupling component, dyes varying in hue from orange–red to deep violet can be obtained. Coloration and light-fastness evaluations of the dyes on polyester fibre indicate that they can be viable alternatives to anthraquinone-based dyes of similar hue.

1 INTRODUCTION

The use of halogeno-2-aminobenzothiazoles as diazo components for azo disperse dyes has long been established, but, in view of the generally moderate properties of derived dyes, the main industrial utilisation of 2-aminobenzothiazoles was with the 6-alkylsulphonyl derivatives,[1] which gave dyes of improved fastness. One of the principal characteristics of these dyes was their brightness and clarity of hue relative to many aminoazobenzene disperse dyes, although their fastness properties tended to be of a lower order than those of anthraquinone-based red dyes.

In recent years, interest in red hetarylazo dyes has developed, particularly with respect to their potential use as replacements, on environmental and economic considerations, for established anthraquinone dyes, e.g. C.I. Disperse Red 60, 1-amino-2-phenoxy-4-hydroxyanthraquinone.[2] One diazo

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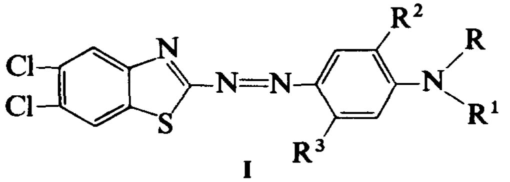
component that has been described[3,4] in this context is 5,6-(6,7-)dichloro-2-aminobenzothiazole, the earlier use of which, in the context of brightness of hue, has more recently been extended into more general investigations into replacement of anthraquinone colorants, i.e. with emphasis on a wider hue range.[5-10]

We report here the synthesis of a series of dyes of general formula **I** and **II**, based on the isomer mixture of 5,6- and 6,7-dichloro-2-aminobenzothiazoles (structures **I** and **II** illustrating the former isomer), and an evaluation of their colour and fastness properties.



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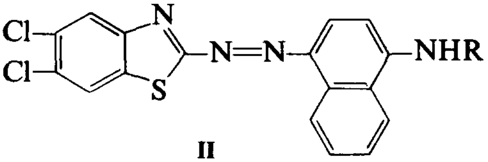


II

2 EXPERIMENTAL

2.1 Synthesis of 5,6-(6,7-)dichloro-2-aminobenzothiazole

2.1.1 Method A

To a well-stirred mixture of 3,4-dichloroaniline (32·4 g, 0·2 mole) and potassium thiocyanate (38·5 g, 0·5 mol) in glacial acetic acid and propionic acid (5:1) (250 ml) at 10°C, bromine (40 g, 0·25 mol) in glacial acetic acid (25 ml) was added dropwise over 90 min. After stirring for 4 h at 10–15°C, the liquor was stirred overnight, allowing the temperature to rise to ambient. The liquor was filtered and the residue stirred in water (2 litre) at 95–100°C for 40 min. After filtering hot, the filtrate was cooled with ice and neutralised with ammonia to give a white precipitate (37·2 g, 85%) of 5,6-(6,7-)dichloro-2-aminobenzothiazole, m.p. 182–193°C.

2.1.2 Method B

α-Benzoyl-β-(3,4-dichlorophenyl)thiourea was prepared[11] by reaction of benzoyl isothiocyanate with 3,4-dichloroaniline; hydrolysis in 10% aq. NaOH[12] afforded 3,4-dichlorophenylthiourea (83%, based on 3,4-dichloroaniline), m.p. 203–204°C (toluene) (lit.[12] m.p. 192–193°C). The thiourea derivative (22·1 g, 0·1 mol) was stirred into conc. sulphuric acid

(45 ml) at room temperature, and Celite (1 g) and activated charcoal (1 g) were added, followed by ammonium bromide (1 g). The mixture was stirred for 3 h at 95–100°C and then slowly run into ice–water (750 ml) at 80°C, the mixture next being heated to 90–95°C and filtered. The filtrate was cooled to 0–5°C and neutralised with 30% aq. NaOH, and the resultant precipitate was filtered and washed with warm water to afford 18·8 g (86%) of product, m.p. 181–190°C.

2.2 Dyestuff synthesis

5,6-(6,7-)Dichloro-2-aminobenzothiazole (4·38 g, 0·02 mol) was stirred into a glacial acetic acid–propionic acid mixture (5:1) (20 ml) at 5–10°C. Nitrosylsulphuric acid, prepared from sodium nitrite (1·4 g, 0·02 mol) and conc. sulphuric acid (8 ml), was added and the mixture stirred for 3 h at 5–10°C. The diazonium liquor was run slowly into a solution of the appropriate coupling component (0·02 mol) in glacial acetic acid (50 ml) with the addition of a little ice. After stirring for 2 h at 0–5°C, the liquor was added to ice–water (500 ml), the mixture stirred for 1 h and filtered, and the presscake washed neutral with cold water (yields 83–94%).

Dyes were purified by column chromatography on Silica Gel 60 (Fluka), applying from solution in toluene or chlorobenzene and eluting with toluene containing, as appropriate, up to 40% ethyl acetate. After elution of minor high-R_f yellow-to-pink contaminants, the principal zone(s) were extracted with ethanol to afford the dyes listed in Table 1. The *O*-acetylated dyes were isolated in some cases as higher-R_f components (up to 10%), arising from the presence of acylated material in the coupling components used and/or acylation occurring during the dye synthesis.

Whereas a composite principal zone of the 5,6- and 6-7-isomers was readily separated from higher- and lower-R_f contaminants, in some dyes an additional separation of the main component into the individual isomers was apparent to some extent. This present investigation pertains to the isomer mixture intrinsically formed in the diazotisation and coupling process of the 2-aminobenzothiazoles derived from 3,4-dichloroaniline. Further studies on individual isomers are being effected and will be reported at a later date.

N-Acetoxyethyl derivatives were more generally obtained by stirring the *N*-β-hydroxyethyl analogue (0·5 g) in acetic anhydride (3 ml) and glacial acetic acid (10 ml) at 80–85°C for 10–40 min (tlc monitor), adding the cooled liquor to ice–water (50 ml), and stirring during the addition of a little ammonia (d. 0·880). The precipitated dyes were filtered, washed neutral, and purified by column chromatography as above. The monoacetyl derivatives I.14 and I.19 shown in Table 1 were isolated as minor zones of slightly lower

TABLE 1
Characterisation and Fastness Data for Dyes I and II

Dye	*R*	*R^1*	*R^2*	*R^3*	*M.p. (°C)*	*Absorption in ethanol*		*Colour*	*Dyeings on polyester fibre light-fastness*		
						λ_{max} (nm)	*$\varepsilon_{max} \times 10^{-4}$*		*0·1%*	*0·5%*	*2·5%*
I.1	C_2H_4OH	H	H	H	175–178	515	5·39	Dark red	4	4	4
I.2	$C_2H_4OCOCH_3$	H	H	H	186–189	508	4·42	Vermilion	5	5	5
I.3	C_2H_4CN	H	H	H	229–231	500	4·64	Orange–red	4–5	4–5	4–5
I.4	C_2H_4CN	C_2H_5	H	H	177–180	510	5·42	Red	5	5	5–6
I.5	C_2H_4OH	C_2H_5	H	H	217–219	528	4·85	Bluish–red	4	4–5	4–5
I.6	$C_2H_4OCOCH_3$	C_2H_5	H	H	146–149	520	5·04	Dark red	5–6	6	6
I.7	C_2H_4OH	C_2H_5	H	CH_3	178–181	536	4·97	Bordeaux	4–5	4–5	5
I.8	$C_2H_4OCOCH_3$	C_2H_5	H	CH_3	144–147	529	5·28	Bluish-red	5–6	6	6
I.9	$C_2H_4COOCH_3$	C_2H_5	H	H	128–132	518	4·64	Dark red	5–6	6	6
I.10	C_2H_4CN	C_2H_4CN	H	H	240–243	489	4·46	Orange-red	5–6	6	6
I.11	C_2H_4OH	C_2H_4CN	H	H	188–191	510	4·85	Red	4–5	4–5	5
I.12	$C_2H_4OCOCH_3$	C_2H_4CN	H	H	148–151	504	4·44	Orange-red	5–6	5–6	6
I.13	C_2H_4OH	C_2H_4OH	H	H	192–195	524	4·54	Bluish-red	4	4	4–5
I.14	C_2H_4OH	$C_2H_4OCOCH_3$	H	H	138–141	518	4·74	Dark red	4–5	4–5	5
I.15	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	H	H	128–131	512	4·65	Red	5	5–6	5–6
I.16	C_2H_4OH	C_2H_4OH	H	CH_3	197–200	535	4·78	Bordeaux	4–5	5	5
I.17	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	H	CH_3	139–141	520	4·67	Crimson	5–6	5–6	6
I.18	C_2H_4OH	C_2H_4OH	H	Cl	197–200	523	3·95	Crimson	4–5	5	5
I.19	C_2H_4OH	$C_2H_4OCOCH_3$	H	Cl	180–183	516	4·07	Dark red	5	5	5–6
I.20	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	H	Cl	149–151	510	4·17	Red	5–6	5–6	6
I.21	C_2H_5	C_2H_5	H	H	191–193	528	5·25	Bluish-red	5	5	5–6
I.22	C_2H_5	C_2H_5	H	$NHCOCH_3$	202–205	540	6·16	Ruby	5–6	5–6	6
I.23	C_2H_5	C_2H_5	OCH_3	$NHCOCH_3$	140–143	577	4·65	Deep violet	5	5	5–6
I.24	C_2H_4OH	C_2H_4CN	OCH_3	$NHCOCH_3$	158–161	554	3·98	Deep magenta	4–5	5	5
I.25	$C_2H_4OCOCH_3$	C_2H_4CN	OCH_3	$NHCOCH_3$	174–177	545	4·09	Ruby	5	5–6	5–6
I.26	C_2H_4OH	C_2H_4OH	OCH_3	$NHCOCH_3$	119–122	562	3·52	Violet	4	4	4–5
I.27	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	OCH_3	$NHCOCH_3$	161–164	550	3·61	Deep magenta	5	5	5–6
I.28	C_2H_4OH	C_2H_4OH	OC_2H_5	$NHCOCH_3$	127–130	563	3·71	Violet	4	4–5	4–5
I.29	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	OC_2H_5	$NHCOCH_3$	191–194	552	3·54	Deep magenta	5	5	5–6
II.1	C_2H_4OH	—	—	—	228–231	571	4·37	Deep violet	3–4	3–4	4
II.2	$C_3H_6OCH_3$	—	—	—	148–151	574	4·24	Deep violet	4	4–5	4–5

R_f value than the principal bis-acetylated materials. All dyes were characterised by satisfactory mass spectra (EI ionisation), molecular ions generally showing 50–85% relative abundance, with major fragments due to typical fission of the *N*-alkyl side chain in the coupler (loss of, e.g. —CH_2OH, —CH_2CN and —CH_2COCH_3), and to cleavage of the C–N bonds of the azo group at the *β*-nitrogen atom.

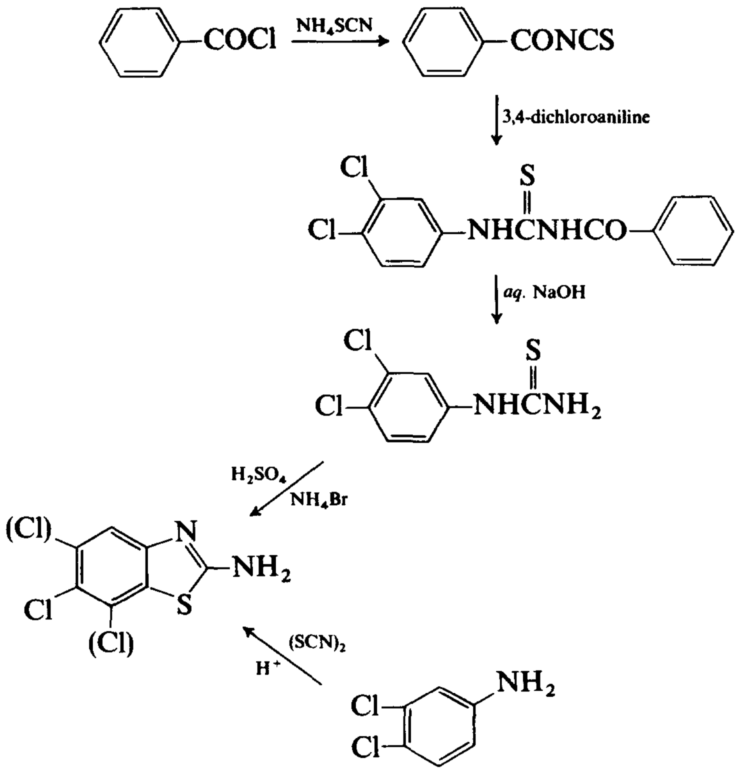
2.3 General

Electronic spectra were recorded on a Pye Unicam PU8800 spectrophotometer from dye solutions in absolute ethanol. Dyeings on polyester fibre and light-fastness assessments were carried out by established procedures. GC analyses were carried out on A.I. Gas Chromatograph 93; 5-ft column packed with 10% OV-17 on Chromosorb W-HP, 85/100 mesh (Phase Sep, Clwyd), N_2 flow rate 50 cm^3/m, injection volume 2 μl in acetone, 255°C, isothermally.

Data reported in Table 1 are for products derived from the diazo component as synthesised in 2.1.2, Method B. Comparative dyes from the product obtained by Method A (2.1.1) provided, after chromatographic purification, similar data; in their crude form, they contained larger amounts of contaminants than those derived from the amine obtained by Method B.

3 RESULTS AND DISCUSSION

The isomer mixture of 5,6-(6,7-)dichloro-2-aminobenzothiazole was readily obtained by one-step thiocyanation–cyclisation of 3,4-dichloroaniline by following generally established procedures,[13,14] and also by ring closure of 3,4-dichlorophenylthiourea (Scheme). The latter compound was obtained by reaction of 3,4-dichloraniline with benzoyl isothiocyanate, followed by hydrolysis of the resultant α-benzoyl-β-(3,4-dichlorophenyl)thiourea.[11,12] The method gave good yields of high-purity material and avoids the use of alternative procedures[15] involving interaction of the arylamine with an alkali-metal thiocyanate in solvents such as monochlorobenzene. The thiourea was obtained in a readily filterable form, compared with the viscous material often resulting from the single-stage procedure. Cyclisation of arylthioureas can be effected by a variety of reagents, typically, bromine,[16] sulphuryl chloride,[17,18] chlorine,[19] sulphur dichloride,[17,18] and antimony pentachloride[20] in chloroform, chlorobenzene, ethylene dichloride, or nitrobenzene. Yields are often low; more recent procedures have utilised thionyl chloride,[21] sulphuric acid,[22] and sulphuryl chloride in an inert solvent in presence of an acid binding agent, such as barium oxide or



Scheme 1. Synthesis of 5,6-(6,7-)Dichloro-2-aminobenzothiazole

magnesium oxide,[23] the presence of which obviates many of the yield and purity problems inherent in previously established sulphuryl chloride procedures. Ring closure with sulphuric acid was used in the present investigation and gave excellent results.

GC of the products showed the one-stage thiocyanation–cyclisation route to give products of 80–85% product content, with a marginally higher 6,7-isomer content; typical results were 41·83% 5,6-isomer and 42·22% 6,7-isomer (the former having the higher retention time). The ring closure of 3,4-dichlorophenylthiourea consistently gave material of 95–97% product content, with a higher 5,6-isomer content, e.g. 43·99% 6,7-isomer and 51·29% 5,6-isomer. Recrystallisation of the latter sample from ethanol removed the *c.* 5% impurities, giving a product containing 48·3% 6,7-isomer and 51·7% 5,6-isomer.

Dyes I and II were obtained in generally excellent yield, principal contaminants being *O*-acetylated material in dyes derived from hydroxyethylated couplers, and arising from a small percentage of acylated product in the coupling components used and/or a slight degree of acylation occurring during the coupling process in the dye synthesis. Both factors are probably pertinent, since diazotisation/coupling reactions in the absence of acetic acid, e.g. by using phosphoric acid in the diazotisation and hydrochloric acid in the coupling, gave products containing somewhat lower contamination with these derivatives. In the series of dyes synthesised, with a representative range of industrially available coupling components used, a colour range from 489 nm (I.3) to 577 nm (I.23) was possible, thus affording orange–red to deep-violet hues. C.I. Disperse Red 60 (1-amino-2-phenoxy-4-hydroxyanthraquinone), a typical brilliant red anthraquinone-based dye, shows in ethanol, λ_{max} 492 sh, 516 and 550 nm.[24] Whereas neither of the dyes I and II showed the typical double absorption maxima characteristic of many anthraquinone colourants, their hue range broadly covers the general area of such dyes. Absorption maxima of I were too close to realise twin absorption peaks when in admixture; thus, the spectrum of mixtures of two dyes having λ_{max} similar to those of Red 60, namely, I.9, λ_{max} 518 nm and I.27. λ_{max} 550 nm showed one composite absorption band with λ_{max} ranging from 529 to 544 nm for mixtures within the 2:1 to 1:2 range (solutions of the same absorbance being used for each dye).

Colour shifts are in accord with variations resultant from changes in substituents in the coupling component observed in 4-aminoazobenzene dyes[25] but of a somewhat lower order. From coupling components containing no ring substituents other than the amino moiety, the *N*,*N*-diethylamino derivative (I.21) absorbs at the longest wavelength, namely, λ_{max} 528 nm. The inductive influence of substituents in the alkyl groups gives hypsochromic shifts relatable to polarisation effects, i.e. relatively small for the hydroxy group (I.5, λ_{max} 528 nm; I.13, λ_{max} 524 nm), larger for carboethoxy (I.9, λ_{max} 518 nm), and greatest for cyano (I.4, λ_{max} 510 nm; I.10, λ_{max} 489 nm).

The introduction of further electron-donor substituents into the coupling component results in additional colour shifts. Whereas the shifts resultant from *m*-toluidine-based couplers (e.g. I.13 and I.16, $\Delta\lambda$, 11 nm; I.6 and I.8, $\Delta\lambda$, 9 nm) are of a similar order to those in 4-aminoazobenzene derivatives derived from 4-nitroaniline, shifts in 3-aminoacetanilide-based dyes (I.21 and I.22, $\Delta\lambda$, 12 nm) are lower than in 4-aminoazobenzenes, cf. 4-nitroaniline → *N*,*N*-diethylaniline, λ_{max} 486 nm and 4-nitroaniline → *N*,*N*-diethyl-3-aminoacetanilide, λ_{max} 511 nm, $\Delta\lambda$, 25 nm;[26] values of 484 and 508 nm (in absolute ethanol) were found for dyes as synthesised by us. The increase in extinction coefficient resulting from 3-acylamino substitution in 4-aminoazobenzenes is, however, apparent in comparing dyes I.21 and I.22.

Lower shifts are also apparent in the dyes derived from alkoxy-acylamino-substituted coupling components. In 4-aminoazobenzenes, the effect of 2-methoxy-5-acetylamino substitution tends to increase with increase in electron-acceptor substitution in the diazo component. Thus, comparing analogous dyes from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline and its 2-methoxy-5-acetylamino derivative, $\Delta\lambda$ values are 32 nm for aniline as diazo component, 55 nm for 4-nitroaniline, 76 nm for 6-chloro-2,4-dinitroaniline, and 83 nm for 6-cyano-2,4-dinitroaniline.[27] The benzothiazolyl moiety has a similar effect to that of 2,4-dinitrophenyl (cf. 2-aminobenzothiazole or 2,4-dinitroaniline → *N*-β-hydroxyethylaniline, both dyes λ_{max} 495 nm in absolute ethanol) (authors' results, unpublished). In 5,6-(6,7-)dichlorobenzothiazole-based dyes, values are lower than those for 4-nitroaniline (cf. I.12 and I.25, 41 nm; I.11 and I.24, 44 nm; I.21 and I.23; 49 nm). The lowering of the extinction coefficient resultant from 2-methoxy substitution in 4-aminoazobenzene dyes[26] is also apparent in dyes I. The more-limited substituent effects in the coupler residue in dyes I are further exemplified for 3-chloro substitution (I.13 and I.18, $\Delta\lambda$, 1 nm; I.15 and I.20, $\Delta\lambda$, 2 nm; cf. 4-nitroaniline → *N*,*N*-diethylaniline and 3-chloro-*N*,*N*-diethylaniline, $\Delta\lambda$, 14 nm[26]).

Acetylation of the terminal hydroxy group in dyes based on hydroxyethylated couplers gives hypsochromic shifts, in accord with the increased polarisation effect, of 6–9 nm for monoacylated derivatives (I.1 and I.2, 7 nm; I.5 and I.6, 8 nm; I.7 and I.8, 7 nm; I.11 and I.12, 6 nm; I.24 and I.25, 9 nm). The shifts are approximately doubled in bisacylated dyes (I.16 and I.17, 15 nm; I.18 and I.20, 13 nm). The progressive effect of the acetylation is apparent in I.13–I.15 and in I.18–I.20, in which each acetyl substituent induces hypochromic shifts of 6–7 nm.

The use of 1-naphthylamine-based couplers (dyes II.1, II.2) allows the synthesis of more longer-wavelength-absorbing dyes without the extensive donor substitution necessary in aniline-based coupling components. Colour shifts are slightly lower than those in 2-methoxy-5-acetylamino-*N*,*N*-diethylaniline (I.23), but higher than those for *N*-hydroxyethyl and *N*-cyanoethyl analogues of the latter (dyes I.24 and I.26).

The over-all colour range in I and II extends over 88 nm (I.10, λ_{max} 489 nm; I.23, λ_{max} 577 nm), a similar order to, but slightly lower than, that in analogous 4-aminoazobenzenes derived from 4-nitroaniline (*N*,*N*-bis-β-cyanoethyl aniline, λ_{max} 432 nm[25]; 2-methoxy-5-acetylamino-*N*,*N*-diethylaniline, λ_{max} 530 nm;[26] i.e. a range of 98 nm).

Dyes I and II gave excellent coloration of polyester fibre, building up to deep, and generally very bright intense hues, ranging from orange–red to deep violet. Light-fastness of the dyeings was of a generally good order, the presence of *N*-acetoxyethyl substituents in the coupling component being particularly advantageous. By appropriate selection of coupling components, it is thus possible to obtain dyes of a range of essentially red hues and having a light-fastness of an order acceptable for industrial utilisation.

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