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Monoazo Disperse Dyes Derived from Nitro-2-Aminobenzothiazoles

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ABSTRACT

The synthesis of a series of monoazo disperse dyes derived from 4-, 5-, 6- and 7-nitro-2-aminobenzothiazoles is reported and the colour of the dyes evaluated with respect to the orientation of the nitro group. Similar data are reported for dyes derived from 4,6-, 5,6- and 5,7-dinitro-2-aminobenzothiazoles.

1 INTRODUCTION

The use of substituted 2-aminobenzothiazoles as diazo components in the generation of disperse dyes having essentially red hues is well established. Of the various substituents which have been described in the patent literature, the nitro group is particularly advantageous in inducing bathochromic shifts in the derived dyes.

Whilst 6-nitro-2-aminobenzothiazole is the most widely recognised diazo component, many patent specifications pertain to the 4-nitro isomer, although this isomer is probably less cost effective to synthesise on an industrial scale. The 6-nitro derivative is commercially utilised in dyes such as CI Disperse Red 177 and CI Disperse Violet 52.[1]

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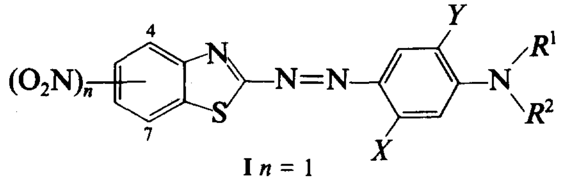
Some comparative data on dyes derived from these two isomers, using *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline as coupling component, have been reported.[2] The most widely described dinitro-2-aminobenzothiazole is the 4,6-dinitro isomer. This can be obtained by nitration of 2-aminobenzothiazole or of 4-nitro-2-aminobenzothiazole;[3] whilst affording colourants showing extended long wavelength absorption, difficulties in attaining consistently high yield diazotisation–coupling processes appear to have precluded any extensive commercial utilisation.

5-Nitro-2-aminobenzothiazole is readily obtainable by nucleophilic displacement of the labile chlorine substituent in 2,4-dinitrochlorobenzene by the thiocyanate anion and subsequent reductive-ring closure.[4] Dyes derived from this intermediate have been described in patent specifications.[5–7] Related dyes from 5-nitro-2-aminobenzothiazole containing other substituents in the 6- and/or 4-positions have also been described, e.g. from 5,6-dinitro-, 5-nitro-6-bromo-, and 5-nitro-4,6-dichloro-2-aminobenzothiazoles.[8] Few data are available with respect to comparative colour shifts in azo disperse dyes derived from the use of isomeric nitro-2-aminobenzothiazoles as diazo components, and, in particular, on the orientation of the nitro group(s).

We report here the syntheses of a series of dyes **I** and **II** and an evaluation of their visible absorption spectra with respect to the influence of the nitro group(s).



I $n = 1$
II $n = 2$

2 EXPERIMENTAL

2.1 5-Nitro-2-aminobenzothiazole

2,4-Dinitrochlorobenzene (10 g, 0·05 mole) and potassium thiocyanate (8·1 g, 0·1 mole) were refluxed for 4 h in ethanol (60 ml). The liquor was then added to ice-water (300 ml) and the resultant precipitate filtered, washed with cold water, and recrystallised from 10% aq. ethanol to give 8·2 g (74%) of pale cream prisms of 2,4-dinitrophenylthiocyanate, m.p. 136–138°C (lit.[9] m.p. 138–139°C); *m*/*z* (EI) 225, M^+, 100%; IR, ν SCN 2130 cm^{-1}.

Reductive cyclisation of the above was effected following the previously described procedure;[4] 22·5 g (0·1 mole) of the product was refluxed in glacial acetic acid (200 ml), the stirred liquor cooled to 60°C and iron powder (22 g) added over 30 min at 60–80°C. After a further 30 min, the liquor was added to ice-water (1 l) and the precipitate filtered. The press-cake was stirred for 30 min in glacial acetic acid (500 ml), filtered, the cake washed with hot acetic acid (100 ml), and the filtrate added to ice-water (2 l), neutralised with aq. sodium hydroxide and the product filtered and washed neutral. Recrystallisation from ethanol gave 15·2 g (67%) of 5-nitro-2-aminobenzothiazole, yellow needles, m.p. 320–322°C (lit.[4] m.p. 310°C). ^{1}H NMR (d$_6$-DMSO): δ 8·05, 1H, d, J = 2·14 Hz, H-4; δ 7·99, 2H, s, NH_2 (D_2O exchangeable); δ 7·94, 1H, d, J = 8·16 Hz, H-7; δ 7·88, 1H, dd, J = 8·42 Hz and 2·14 Hz, H-6.

2.2 4-Nitro-2-aminobenzothiazole

α-Benzoyl-β-(2-nitrophenyl)thiourea was prepared by reaction of 2-nitroaniline (13·8 g, 0·1 mole) and benzoyl isothiocyanate, following the procedure previously reported for halogenoanilines.[10] Hydrolysis was effected by heating the product at 120°C in 50% H_2SO_4 (100 ml) for 5 min and then stirring the liquor into ice-cold water (1 l). The product was filtered, washed with water and recrystallised from ethanol, giving bright yellow needles (13·6 g, 70%) of 2-nitrophenylthiourea, m.p. 135–137°C. (cf. Ref. 2).

Ring closure in concentrated sulphuric acid in the presence of ammonium bromide[10] gave 76% of 4-nitro-2-aminobenzothiazole, m.p. 263–265°C (cf. Ref. 2).

2.3 7-Nitro-2-aminobenzothiazole

Following a similar procedure, 3-nitroaniline afforded 76% of 3-nitrophenylthiourea, m.p. 160–162°C (lit.[11] m.p. 156–158°C), and thence 68% of 7-nitro-2-aminobenzothiazole, m.p. 258–260°C (lit.[11] m.p. 278°C); *m/z* (EI), 195, M$^+$, 100%; ^{1}H NMR (d$_6$-DMSO): δ 7·98, 1H, dd, J = 8·42 Hz and 1·10 Hz, H-4; δ 7·94, 2H, s, NH_2 (D_2O exchangeable); δ 7·73, 1H, dd, J = 8·06 Hz and 1·10 Hz, H-6; δ 7·48, 1H, dd, J = 8·06 Hz, H-5.

2.4 5,6-Dinitro-2-aminobenzothiazole

5-Nitro-2-aminobenzothiazole (3·9 g) was stirred into concentrated sulphuric acid (25 ml) at 0–5°C and a mixture of fuming nitric acid (d. 1·52, 6 ml) and concentrated sulphuric acid (6 ml) was run in over 30 min. Stirring was continued at 0–5°C for 1 h, then at ambient temperature for 12 h, and finally at 90–95°C for 2 h. The cooled liquor was added to ice-water (250 ml) and the product filtered and washed neutral. Crude material (4·9 g) was recrystallised from ethanol in bright yellow needles, m.p. >300°C; *m/z* (EI), 240, M^+, 100%; 1H NMR (d_6-DMSO): δ 8·73, 1H, s, H-7; δ 8·60, 2H, s, NH_2 (D_2O exchangeable); δ 7·94, 1H, s, H-4.

2.5 5,7-Dinitro-2-aminobenzothiazole

3,5-Dinitroaniline (3·7 g, 0·02 mole) was reacted with ammonium thiocyanate and benzoyl chloride, as for 2-nitroaniline (Section 2.2). The resultant α-benzoyl-β-(3,5-dinitrophenyl)thiourea was then stirred into 50% H_2SO_4 (40 ml) at 80–85°C for 1 h, and the cooled liquor was added to ice-water (200 ml) and the product filtered and washed neutral (3·2 g, 66%). Recrystallisation from ethanol gave yellow prisms of 3,5-dinitrophenylthiourea, m.p. 196–198°C; *m/z* (EI), 242, M^+, 100%. Calculated for $C_7H_6N_4O_4S$: C, 34·7; H, 2·5; N, 23·1; S, 13·2. Found: C, 34·2; H, 2·2; N, 22·7; S, 13·8%.

Ring closure (as in Section 2.2) gave, after recrystallisation from ethanol, yellow needles of 5,7-dinitro-2-aminobenzothiazole (59%), m.p. >300°C; *m/z* (EI) 240, M^+, 100%; ^{1}H MNR (in d_6-DMSO): δ 8·56; 1H, d, J = 1·71 Hz, H-4; δ 8·42, 2H, s, NH_2 (D_2O exchangeable); δ 8·34, 1H, d, J = 1·71 Hz, H-6.

2.6 Dye synthesis

Mononitro-2-aminobenzothiazoles were diazotised and coupled using nitrosylsulphuric acid and an acetic acid–propionic acid medium, as previously reported.[2] For dinitro-2-aminobenzothiazoles, the amine (4·8 g, 0·02 mole) was stirred into 85% H_3PO_4 (50 ml) using an external ice-salt

TABLE 1
Characterisation Data for 4-Nitro-2-Aminobenzothiazole Based Dyes (**I**)

Dye	R^1	R^2	*X*	*Y*	*Yield*	*M.p. (°C)*	*Absorption in ethanol*		*Light fastness for dyeings on polyester*		
							λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{4}$	*0·1%*	*0·5%*	*2·5%*
I.1	C_2H_4CN	C_2H_4CN	H	H	79	224–226	502	4·1	5	5–6	5–6
I.2	C_2H_5	C_2H_4CN	H	H	75	202–204	523	4·6	5	5	5–6
I.3	C_2H_5	C_2H_4OH	H	H	71	242–244	542	4·5	5	5	5
I.4	C_2H_4CN	C_2H_4OH	H	H	68	223–224	522	4·1	5	5	5–6
I.5	C_2H_4OH	C_2H_4OH	H	H	73	188–190	540	3·8	4	4–5	4–5
I.6	C_2H_5	C_2H_5	H	NHAc	75	216–218	553	5·5	5–6	5–6	6
I.7	C_2H_5	C_2H_5	OMe	NHAc	63	196–198	580(sh) 599	3·8 4·2	5	5–6	5–6

TABLE 2

Characterisation Data for 5-Nitro-2-Aminobenzothiazole Based Dyes (**II**)

Dye	R^1	R^2	*X*	*Y*	*Yield*	*M.p. (°C)*	*Absorption in ethanol*		*Light fastness for dyeings on polyester*		
							λ_{max} *(nm)*	$\varepsilon_{max} \times 10^4$	*0·1%*	*0·5%*	*2·5%*
II.1	C_2H_4CN	C_2H_4CN	H	H	76	242–244	491	3·8	5	5–6	5–6
II.2	C_2H_5	C_2H_4CN	H	H	74	200–202	512	4·4	5	5	5
II.3	C_2H_5	C_2H_4OH	H	H	78	238–240	529	4·8	5	5	5
II.4	C_2H_4CN	C_2H_4OH	H	H	68	224–226	511	4·4	5	5	5–6
II.5	C_2H_4OH	C_2H_4OH	H	H	70	222–224	527	3·9	4–5	4–5	4–5
II.6	C_2H_5	C_2H_5	H	NHAc	75	230–232	542	5·5	5–6	6	6
II.7	C_2H_5	C_2H_5	OMe	NHAc	65	198–200	562(sh)	3·6	5	5–6	5–6
							588	4·4			

bath with addition, as required, of 'dry-ice' to maintain a temperature of *c.* −10°C. Nitrosylsulphuric acid (from 1·5 g $NaNO_2$ and 10 ml conc. H_2SO_4) was added over 20 min and diazotisation continued at −10°C for 2 h. Excess nitrite was eliminated by addition of sulphamic acid and the diazo liquor was added over 30 min to a solution of the appropriate coupling component (0·02 mole) in ice-water (100 ml) and conc. HCl (20 ml). After stirring for 90 min, the liquor was neutralised with sodium acetate, stirred for 30 min, filtered and the product washed neutral.

TABLE 3

Characterisation Data for 6-Nitro-2-Aminobenzothiazole Based Dyes (**III**)

Dye	R^1	R^2	*X*	*Y*	*Yield*	*M.p. (°C)*	*Absorption in ethanol*		*Light fastness for dyeings on polyester*		
							λ_{max} *(nm)*	$\varepsilon_{max} \times 10^4$	*0·1%*	*0·5%*	*2·5%*
III.1	C_2H_4CN	C_2H_4CN	H	H	77	240–242	507	3·9	5–6	6	6
III.2	C_2H_5	C_2H_4CN	H	H	76	196–198	530	4·6	6	6	6
III.3	C_2H_5	C_2H_4OH	H	H	74	200–202	548	4·4	5	5–6	5–6
III.4	C_2H_4CN	C_2H_4OH	H	H	72	197–199	527	4·5	5	5	5–6
III.5	C_2H_4OH	C_2H_4OH	H	H	68	220–222	545	4·0	4–5	5	5
III.6	C_2H_5	C_2H_5	H	NHAc	71	222–224	559	5·3	5–6	5–6	6
III.7	C_2H_5	C_2H_5	OMe	NHAc	61	212–214	585(sh)	3·6	5–6	5–6	6
							606	4·2			

TABLE 4
Characterisation Data for 7-Nitro-2-Aminobenzothiazole Based Dyes (**IV**)

Dye	*R^1*	*R^2*	*X*	*Y*	*Yield*	*M.p. (°C)*	*Absorption in ethanol*		*Light fastness for dyeings on polyester*		
							λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{4}$	*0·1%*	*0·5%*	*2·5%*
IV.1	C_2H_4CN	C_2H_4CN	H	H	70	243–245	493	4·0	5–6	5–6	5–6
IV.2	C_2H_5	C_2H_4CN	H	H	71	238–240	514	4·5	5	5	5–6
IV.3	C_2H_5	C_2H_4OH	H	H	74	248–250	528	4·8	5	5	5
IV.4	C_2H_4CN	C_2H_4OH	H	H	68	226–228	512	4·4	5	5	5–6
IV.6	C_2H_5	C_2H_5	H	NHAc	66	233–235	545	5·3	5–6	5–6	6
IV.7	C_2H_5	C_2H_5	OMe	NHAc	61	206–208	560(sh)	3·4	5–6	5–6	5–6
							590	4·5			

All dyes were purified by column chromatography (Section 2.7); yields shown in Tables 1–7 are based on recovery of pure dye from 0·5 g crude material applied to the column.

2.7 General

6-Nitro- and 4,6-dinitro-2-aminobenzothiazole, and all coupling components, were kindly supplied by Yorkshire Chemicals plc (Leeds), and were used without further purification.

TABLE 5
Characterisation Data for 4,6-Dinitro-2-Aminobenzothiazole Based Dyes (**V**)

Dye	*R^1*	*R^2*	*X*	*Y*	*Yield*	*M.p. (°C)*	*Absorption in ethanol*		*Light fastness for dyeings on polyester*		
							λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{4}$	*0·1%*	*0·5%*	*2·5%*
V.1	C_2H_4CN	C_2H_4CN	H	H	54	232–234	536	3·6	5	5	5–6
V.2	C_2H_5	C_2H_4CN	H	H	59	186–188	563	4·0	5	5	5
V.3	C_2H_5	C_2H_4OH	H	H	52	236–238	585	4·3	4–5	4–5	5
V.4	C_2H_4CN	C_2H_4OH	H	H	45	226–228	560	4·4	4–5	5	5
V.5	C_2H_4OH	C_2H_4OH	H	H	56	217–219	581	4·6	4	4–5	4–5
V.6	C_2H_5	C_2H_5	H	NHAc	46	248–250	579	4·9	5	5–6	5–6
V.7	C_2H_5	C_2H_5	OMe	NHAc	39	245–247	560(sh)	3·0	4–5	5	5
							630	4·5			

TABLE 6
Characterisation Data for 5,6-Dinitro-2-Aminobenzothiazole Based Dyes (**VI**)

Dye	*R^1*	*R^2*	*X*	*Y*	*Yield*	*M.p. (°C)*	*Absorption in ethanol*		*Light fastness for dyeings on polyester*		
							λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{4}$	*0·1%*	*0·5%*	*2·5%*
VI.1	C_2H_4CN	C_2H_4CN	H	H	70	258–260	516	3·5	6	6	6–7
VI.2	C_2H_5	C_2H_4CN	H	H	72	250–252	538	4·4	6	6	6
VI.3	C_2H_5	C_2H_4OH	H	H	76	239–241	557	4·8	5	5–6	5–6
VI.4	C_2H_4CN	C_2H_4OH	H	H	68	236–238	537	4·3	5–6	6	6
VI.5	C_2H_4OH	C_2H_4OH	H	H	67	231–233	554	4·0	4–5	5	5
VI.6	C_2H_5	C_2H_5	H	NHAc	68	252–254	560	5·0	6	6	6
VI.7	C_2H_5	C_2H_5	OMe	NHAc	60	254–256	596(sh) 610	3·3 4·6	5	5–6	5–6

Electronic spectra were recorded on a Philips PU8730 UV-Vis spectrophotometer, mass spectra on an AEI MS 902 (EI ionisation, 70 eV, 8 kV accelerator voltage, source plot temperature 230°C), and ^1H NMR spectra on a JEOL GX270 FT spectrometer (using d_6-DMSO as solvent and TMS as internal reference).

Column chromatography was effected on silica gel (Janssen Chimica), applying the dyes from solution in toluene or chlorobenzene and eluting with toluene containing up to 50% ethyl acetate, as appropriate.

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

TABLE 7
Characterisation Data for 5,7-Dinitro-2-Aminobenzothiazole Based Dyes (**VII**)

Dye	*R^1*	*R^2*	*X*	*Y*	*Yield*	*M.p. (°C)*	*Absorption in ethanol*		*Light fastness for dyeings on polyester*		
							λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{4}$	*0·1%*	*0·5%*	*2·5%*
VII.1	C_2H_4CN	C_2H_4CN	H	H	74	258–260	510	3·9	5–6	6	6
VII.2	C_2H_5	C_2H_4CN	H	H	76	218–220	533	4·3	5	6	6
VII.3	C_2H_5	C_2H_4OH	H	H	68	241–243	551	4·4	5	5–6	5–6
VII.4	C_2H_4CN	C_2H_4OH	H	H	70	239–241	531	4·8	5–6	5–6	5–6
VII.6	C_2H_5	C_2H_5	H	NHAc	58	238–240	553	5·0	5–6	6	6

3 RESULTS AND DISCUSSION

3.1 Synthesis

4- and 6-Substituted 2-aminobenzothiazoles can be obtained unambiguously from the appropriate 2- and 4-substituted anilines respectively, using well established procedures. The product obtained from the direct thiocyanation–ring closure of 2-nitroaniline, initially stated[12] to be 4-nitro-2-aminobenzothiazole, was later shown[13] to be 4-amino-3-nitro-1-thiocyanatobenzene. 4-Nitro-2-aminobenzothiazole is, however, readily prepared by ring closure of 2-nitrophenylthiourea, the latter resulting from reaction of 2-nitroaniline with thiophosgene, and thence of the resulting 2-nitrophenylisothiocyanate with ammonia.[13,14] Arylthioureas can also be obtained[15] by hydrolysis of α-benzoyl-β-arylthioureas[16] with aq. NaOH, a method recently utilised in the synthesis of a series of dichlorophenylthioureas.[10] This hydrolysis has been reported to be unsatisfactory with α-benzoyl-β-(mononitrophenyl)thioureas,[15] and observations in the present investigation confirmed this. Hydrolysis using 50% H_2SO_4 was, however, more facile, satisfactory yields of 2-nitrophenylthiourea being obtained. Ring closure to 4-nitro-2-aminobenzothiazole proceeded readily in concentrated sulphuric acid, following a similar procedure to that described for 6-nitro-2-aminobenzothiazole.[17]

The use of 3-substituted anilines as precursor intermediates can give 5-and/or 7-substituted 2-aminobenzothiazoles, depending on the substituent. Thus, ring closure of 3-substituted phenylthioureas gives predominantly the 5-substituted 2-aminobenzothiazole where the substituent is an electron donor, e.g. the 5-methyl[18,19] and 5-methoxy derivatives.[11,20] Where the substituent is an electron acceptor, 7-substituted 2-aminobenzothiazoles result, e.g. 7-nitro, 7-carboethoxy.[11] In other cases, e.g. 3-chlorophenylthioureas, ring closure affords isomer mixtures.[21]

Alternatively, the 5- and 7-substituted derivatives can be selectively obtained by reductive-cylisation of the appropriately substituted 2-nitrophenylthiocyanates, e.g. 5-chloro-,[22] 7-chloro-,[22] and 5-methoxy-2-aminobenzothiazoles,[11] or by amination at the 2-position of substituted benzothiazoles with hydroxylamine, e.g. for 5-methyl-,[23] 5-carboxy-,[23] 4-nitro-,[24] 6-nitro-[24] and 5-nitro-2-aminobenzothiazoles.

In this present investigation, 5-nitro-2-aminobenzothiazole was obtained by reduction–cyclisation of 2,4-dinitrophenylisocyanate with iron and acetic acid.[4] The method uses as starting material the readily available 2,4-dinitrochlorobenzene, and proceeds via nucleophilic replacement of the labile chloro group with potassium thiocyanate, i.e. a more convenient process than introduction of the thiocyanato group via the diazo reaction.[22]

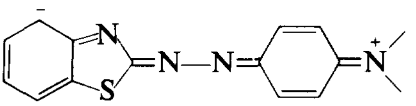
A similar reaction with 2,6-dinitrochlorobenzene did not proceed satisfactorily despite numerous modifications of the reaction conditions, and 7-nitro-2-aminobenzothiazole was preferably obtained by ring closure of 3-nitrophenylthiourea. As noted above for 2-nitrophenylthiourea, alkaline hydrolysis of α-benzoyl-β-(3-nitrophenyl)thiourea did not proceed readily, but the use of 50% H_2SO_4 was satisfactory. In accord with previous observations,[11] cyclisation of the electron-acceptor substituted phenylthiourea occurred *ortho* to the substituent, the crude reaction product after recrystallisation showing ^{1}H NMR data fully in accord with 7-substitution.

Whereas 2,4-dinitroaniline has been shown not to react with benzoylisothiocyanate,[15] 3,5-dinitroaniline afforded 3,5-dinitrophenylthiourea by this route, and thence 5,7-dinitro-2-aminobenzothiazole, although in relatively low overall yield. Nitration of 5-nitro-2-aminobenzothiazole, following modification of previously described procedures,[3,8] gave 5,6-dinitro-2-aminobenzothiazole; ^{1}H NMR data confirmed this orientation, the spectrum showing singlets for the 4- and 7-protons, compared with the two doublets with appropriate coupling constants for *meta*-substitution apparent in the spectrum of the 5,7-isomer. Introduction of a nitro group *ortho* to an existing nitro group is unusual in aromatic electrophilic substitution, and nitration of the 5-nitro derivative might have been expected to yield the 5,7-dinitro compound. Charge delocalisation in 2-aminobenzothiazole is well documented, with the resultant electrophilic substitution occurring predominantly at the 6- and 4-positions, and presumably such delocalisation overrides the polar effect of the 5-nitro group.

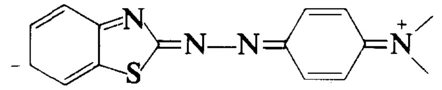
Mononitro-2-aminobenzothiazoles were diazotised by addition of nitrosylsulphuric acid to a suspension of the amine in a mixture of glacial acetic and propionic acids;[25] good yields of resulting dyes were obtained, the orientation of the nitro group having little significant effect on dye yield. Use of this method with 4,6-dinitro-2-aminobenzothiazole gave erratic results, typical dye yields varying from 20% to 60% in consecutive synthesis of any one specific dye. Phosphoric acid medium (cf. Ref. 1) gave more consistent results, and whilst the 5,6- and 5,7-dinitro isomers gave very satisfactory dye yield using acetic acid–propionic acid as diazotisation medium, these isomers were also diazotised using phosphoric acid for comparative purposes. For all the coupling components used, dye yields from the 4,6-dinitro isomer were consistently lower than those from the other two isomers. All products required chromatographic purification to eliminate contaminants arising from diazo decomposition and/or by-products present in the industrially sourced coupling components used. In addition, removal of undiazotised amine was necessary in several dyes; prolonged diazotisation periods in some instances failed to effect 100% diazotisation, resulting in carry-through of the amine into the end-product, necessitating repeated chromatography to ensure its total elimination (and consequent diminution of recovery yields of pure dyes).

3.2 Dye characteristics

On the basis of conventional donor–acceptor interactions in benzothiazolylazo dyes, the principal delocalisation structures (**III**, **IV**) are in accord with enhanced bathochromicity arising from the presence of strongly electron acceptor substituents, e.g. nitro, at the 4- and/or 6-positions in the precursor diazo component. The absorption maxima data in Tables 1–7 show that the 6-nitro derived dyes are the most bathochromic of the mono-nitro derivatives.



(III)



(IV)

Taking the dyes from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline as illustrative (data on ranges of other dyes from this coupling component being available in the literature), the 4- and 6-nitro based dyes show $\Delta\ \lambda$ 27 nm (Dye **I.4**, Table 1) and $\Delta\ \lambda$ 32 nm (Dye **III.4**, Table 3) with respect to the parent dye from 2-aminobenzothiazole (λ_{max} 495 nm, Ref. 2). Comparative shifts in 4-*N*-β-hydroxyethyl-*N*-β-cyanoethylaminoazobenzenes are 27 nm and 54 nm for 2'- and 4'-nitro substitution respectively,[26,27] although in the 2'-nitro isomer, polar effects of the nitro group are not the sole operative factor.[2] Comparison of dyes in which polar effects can be considered as predominantly operative, e.g. the 4'-nitro derivative in 4-aminoazobenzenes and the hetaryl analogue from 6-nitro-2-aminobenzothiazole, show that the $\Delta\ \lambda$ value in the latter is roughly half that in the carbocyclic system, despite its more extended donor–acceptor conjugation. This would imply that donor–acceptor interactions within the overall dye system also involve, in the hetarylazo dyes, the hetero nitrogen atom or the hetero moiety as a whole, as additional electron acceptor centres.

Where the nitro group is not in a position directly conjugated with the donor nitrogen atom of the coupler residue, colour shifts are diminished.

Only minimal differences between the dyes derived from 5-nitro and 7-nitro-2-aminobenzothiazoles are observed, $\Delta\ \lambda$ values being 16 nm (Dye **II.4**, Table 2) and 17 nm (Dye **IV.4**, Table 4) respectively, i.e. approximately half those for the 4-nitro and 6-nitro based dyes.

For dinitro-substituted dyes in the 4-aminoazobenzene series, the 2',4'-dinitro derivative shows an enhanced 'additive' effect of 16 nm relative to summation of the individual effects of the 2'-nitro and 4'-nitro derivatives; the influence of factors not directly relatable solely to the polar effects of the nitro group[2] are shown by the lower 'additive' effect of 2 nm in the 2',6'-dinitro isomer.[26,27]

In the nitro-2-aminobenzothiazole based dyes, only polar factors need to be considered. The $\Delta\ \lambda$ values noted above for the 4-nitro and 6-nitro based dyes afford a 'calculated' $\Delta\ \lambda$ value of 59 nm for the 4,6-dinitro based dye (**V.4**), namely a value of 554 nm. The observed value (Table 5) is 560 nm, i.e. an 'additive' value of 6 nm; the lower 'additive' effects in benzothiazolylazo dyes compared with carbocyclic analogues have been previously noted.[2] In the 5,7-dinitro-2-aminobenzothiazole derived dye (**VII.4**, Table 7), relative to the unsubstituted dye,[2] $\Delta\ \lambda$ values for the 5-nitro (**II.4**, Table 2) and 7-nitro based dyes (**IV.4**, Table 4) are 16 nm and 17 nm, giving a 'calculated' value for **VII.4** of 528 nm. The observed value (Table 7) is 531 nm, a small 'additive' shift. Similarly, for the 5,6-dinitro-2-aminobenzothiazole derived dye (**VI.4**, Table 6), $\Delta\ \lambda$ values of the individual nitro groups (16 nm and 32 nm) afford a 'calculated' λ_{max} of 543 nm; the observed value is 537 nm, i.e. a 'subtractive' effect, presumably relatable to the adjacent nitro group.

Overall, λ_{max} of the nitro-2-aminobenzothiazole based dyes, using *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline as coupling component, follow the order

$$4,5 > 5,6 > 5,7 > 6 > 4 > 7 > 5.$$

This order is generally followed for other coupling components (Tables 1–7).

Nitro derivatives of 2-aminobenzothiazole thus offer potential for the attainment of a diverse colour range in derived monoazo dyes. For the range of coupling components used in this investigation, absorption maxima of the dyes synthesised were within the range 491 nm (**II.1**, Table 2) to 630 nm (**V.7**, Table 5), an overall range of 139 nm. For a specific coupling component, the $\Delta\ \lambda$ range for variation in the nature of the diazo component varied from 37 nm (3-acetylamino-*N*,*N*-diethylaniline) to 57 nm (*N*-ethyl-*N*-β-hydroxyethylaniline). No structural variations studies could equate to the extended colour shifts resulting from the use of 4,6-dinitro-2-aminobenzothiazole as diazo component. However, within certain colour parameters, other dinitro derivatives offer potential for the generation of dyes of similar colour without recourse to the unpredictable diazotisation–coupling reactions of the 4,6-dinitro derivative.

For example, for a dye absorbing at *c.* 560 nm, dye **V.4** (4,6-dinitro-2-aminobenzothiazole → *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline) could be simulated by dye **VI.3** (5,6-dinitro-2-aminobenzothiazole → *N*-ethyl-*N*-β-hydroxyethylaniline), with improved yield in the dye synthesis. Similarly, dyes **VI.2** and **VI.4** (5,6-dinitro-2-aminobenzothiazole → *N*-ethyl-*N*-β-cyanoethylaniline and *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline respectively, λ_{max} 538 nm) and dye **VII.2** (5,7-dinitro-2-aminobenzothiazole → *N*-ethyl-*N*-β-cyanoethylaniline, λ_{max} 532 nm) are equatable with dye **V.I** (4,6-dinitro-2-aminobenzothiazole → *N*,*N*-bis-β-cyanoethylaniline, λ_{max} 536 nm). However, the longest wavelength absorbing dye synthesised, **V.7** (4,6-dinitro-2-aminobenzothiazole → 2-acetylamino-5-methoxy-*N*,*N*-diethylaniline) had λ_{max} 630 nm); no other dye synthesised approached this λ_{max}, the closest being **VI.7** from 5,6-dinitro-2-aminobenzothiazole and the same coupling component (610 nm).

It can be concluded that, within a more limited colour range, the 5,6- and 5,7-dinitro isomers have potential interest as possible replacements for 4,6-dinitro-2-aminobenzothiazole. Whilst the 5,7-isomer is only available via the relatively unavailable (industrially) and expensive 3,5-dinitroaniline precursor, the synthesis of the 5,6-dinitro isomer utilises the readily available 2,4-dinitrochlorobenzene.

It seems doubtful whether the 5- and 7-nitro isomers offer any significant advantage, the colour range attainable from them being readily available from the widely used 6-nitro derivative.

Build-up of dyeings on polyester was of similar order for all the mono and dinitro based dyes. Light fastness of the dyeings from isomeric mononitro derived dyes was also of similar order, but dyeings from both 5,6- and 5,7-dinitro-2-aminobenzothiazole derived dyes tended to have higher fastness than those of the 4,6-dinitro based isomers.

4 CONCLUSIONS

Whilst both 5- and 7-nitro-2-aminobenzothiazoles afford excellent dyes for polyester, the colour range attainable from them is not as extensive as that from the industrially utilised 6-nitro isomer. Both 5,6- and 5,7-dinitro-2-aminobenzothiazoles offer potential for more facile generation of dyes than the 4,6-dinitro isomer. Whilst both the 5,6- and 5,7-isomers afford dyes having hypsochromic colour shifts with respect to the 4,6-dinitro derivative, within certain colour parameters, dyes of similar hue to those from the latter can be obtained with more consistent and acceptable dye yield. The 5,6-isomer is the more readily attainable, source materials being widely available.

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