

Monoazo Disperse Dyes Derived from Mononitro-Dichloro-2-Aminobenzothiazoles

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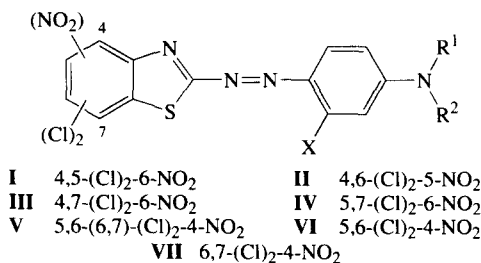
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ABSTRACT

Nitration of dichloro-2-aminobenzothiazoles afforded the corresponding mononitro derivatives. Diazotisation of these and coupling to N-substituted anilines gave red to reddish-blue dyes for polyester. The colour of the dyes is discussed with respect to the relative orientation of the nitro and chloro substituents. Data on dyes from a trichloro- and a nitro-trichloro-2-aminobenzothiazole are also reported.

1 INTRODUCTION

Colour–structure relationships in monoazo disperse dyes derived from dichloro-2-aminobenzothiazoles^{1,2} and nitro-2-aminobenzothiazoles³ have been previously reported. Whilst the orientation of chloro substituents has little influence on the colour of the dyes, that of a nitro substituent is more significant. As an extension of these investigations, we report here the synthesis of some nitro-dichloro-2-aminobenzothiazoles and an evaluation of colour–structure relationships in dyes **I–VII** derived from them.



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2 EXPERIMENTAL

2.1 Nitration of dichloro-2-aminobenzothiazoles

A solution of the appropriate dichloro-2-aminobenzothiazole (5 g) in conc. H_2SO_4 (20 ml) was stirred at 0–5°C and a mixture of fuming nitric acid (d. 1.49) (2 g) and conc. H_2SO_4 (10 ml) added over 30 min. Stirring was continued at 0–5°C for 1 h, and the temperature then allowed to rise to ambient and stirring continued for a further 1 h. After addition of the liquor to ice-water and neutralising with NH_4OH , the precipitate was filtered, washed and recrystallised from ethanol to afford the following:

6-nitro-4,5-dichloro-2-aminobenzothiazole, 84%, m.p. 308–310°C; m/z (EI) 263, M^+ , 100%; ^1H NMR. (d_6 -DMSO): δ 8.63, 2H, s, NH_2 (D_2O exchangeable); 8.55, 1H, s.

5-nitro-4,6-dichloro-2-aminobenzothiazole, 87%, m.p. 283–285°C; m/z (EI) 263, M^+ , 100%; ^1H NMR (d_6 -DMSO): δ 8.46, 2H, s; 7.63, 1H, s.

6-nitro-4,7-dichloro-2-aminobenzothiazole, 78%, m.p. 316–318°C; m/z (EI) 263, M^+ , 100%; ^1H NMR (d_6 -DMSO): δ 8.79, 2H, s; 8.20, 1H, s.

6-nitro-5,7-dichloro-2-aminobenzothiazole, 84%, m.p. 288–290°C; m/z (EI) 263, M^+ , 100%; ^1H NMR (d_6 -DMSO): δ 8.46, 2H, s; 7.83, 1H, s.

4-nitro-5,6(6,7)-dichloro-2-aminobenzothiazole, 79%, m.p. 238–243°C; m/z (EI) 263, M^+ , 100%.

4-nitro-5,6-dichloro-2-aminobenzothiazole, 81%, m.p. 281–283°C; m/z (EI) 263, M^+ , 100%; ^1H NMR (d_6 -DMSO): δ 8.48, 2H, s; 8.25, 1H, s.

4-nitro-6,7-dichloro-2-aminobenzothiazole, 86%, m.p. 295–297°C; m/z (EI) 263, M^+ , 100%; ^1H NMR (d_6 -DMSO): δ 8.31, 2H, s; 7.96, 1H, s.

2.2 4,6,7-trichloro- and 5-nitro-4,6,7-trichloro-2-aminobenzothiazoles

2,4,5-Trichloroaniline (7.8 g, 0.04 mole) was stirred into toluene (75 ml) at 50–60°C; conc. HCl (4 ml) was added, followed by ammonium thiocyanate (3 g). The mixture was heated to 100–110°C, stirred for 2.5 h and then vigorously stirred whilst cooling to room temperature. The cream-coloured granular residue was filtered, washed with cold toluene and then with warm water giving 9.4 g (92%) of 2,4,5-trichlorophenylthiourea, m.p. 173–175°C (ethanol); m/z (EI) 219, $(\text{M}-\text{Cl})^+$, 100%.

Ring closure of the above in conc. H_2SO_4 in the presence of ammonium bromide, following the procedure previously used for dichloro derivatives,²

gave 93% of 4,6,7-trichloro-2-aminobenzothiazole, white needles, m.p. 295–297°C (ethanol); m/z (EI) 252, M^+ , 100%.

Nitration, following the general procedure as in 2.1 above, gave 88% 5-nitro-4,6,7-trichloro-2-aminobenzothiazole, pale yellow needles, m.p. 345–347°C (ethanol); m/z (EI) 297, M^+ , 100%.

2.3 Dye synthesis

The nitro-chloro-2-aminobenzothiazoles were diazotised with nitrosyl sulphuric acid in acetic acid–propionic acid, and coupled with a solution of the appropriate arylamine in glacial acetic acid following a previously reported procedure.⁴ All products were purified by column chromatography on silica gel (for column chromatography, 0.060–0.200 mm, pore diameter *c.* 4 nm, Acros Chimica), applying the dyes from solution in toluene or chlorobenzene and developing with toluene containing up to 35% ethyl acetate as appropriate.

Characterisation data for dyes I–VII is shown in Tables 1–5; in addition 4,6,7-trichloro-2-aminobenzothiazole \rightarrow N- β -cyanoethyl-N- β -hydroxyethylani-line (VIII); m.p. 234–236°C; λ_{\max} ($\epsilon \times 10^{-4}$) 522 nm (4.8), and 5-nitro-4,6,7-trichloro-2-aminobenzothiazole \rightarrow N- β -cyanoethyl-N- β -hydroxyethylaniline (IX); m.p. 268–270°C; λ_{\max} ($\epsilon \times 10^{-4}$) 534 nm (4.4) were prepared.

TABLE 1
Characterisation Data for 6-Nitro-4,5-Dichloro-2-Aminobenzothiazole Based Dyes I

Dye	R^1	R^2	X	m.p. (°C)	λ_{\max} , $\epsilon_{\max} \times 10^{-4}$ (in ethanol)	Light fastness on polyester (0.1%, 0.5%, 2.5% dyeings)			
I.1	C ₂ H ₄ CN	C ₂ H ₄ CN	H	268–270	512	4.4	5–6	6	6
I.2	C ₂ H ₅	C ₂ H ₄ CN	H	218–220	536	4.8	6	6	6–7
I.3	C ₂ H ₅	C ₂ H ₄ OH	H	230–232	556	4.6	4–5	5	5
I.4	C ₂ H ₄ OH	C ₂ H ₄ CN	H	222–224	538	4.6	5–6	5	5
I.5	C ₂ H ₅	C ₂ H ₄ OH	CH ₃	228–230	567	4.4	4–5	5	5
I.6	C ₂ H ₅	C ₂ H ₅	NHCOCH ₃	236–238	562	5.3	6	6	6–7

TABLE 2
Characterisation Data for 5-Nitro-4,6-Dichloro-2-Aminobenzothiazole Based Dyes II

Dye	R^1	R^2	X	m.p. (°C)	λ_{\max} , $\epsilon_{\max} \times 10^{-4}$ (in ethanol)	Light fastness on polyester (0.1%, 0.5%, 2.5% dyeings)			
II.1	C ₂ H ₄ CN	C ₂ H ₄ CN	H	274–276	506	4.4	5	5	5
II.2	C ₂ H ₅	C ₂ H ₄ CN	H	238–240	526	4.6	5	5–6	5–6
II.3	C ₂ H ₅	C ₂ H ₄ OH	H	212–214	544	4.5	4–5	5	5
II.4	C ₂ H ₄ OH	C ₂ H ₄ CN	H	206–208	525	4.7	5	5–6	5–6
II.5	C ₂ H ₅	C ₂ H ₄ OH	CH ₃	236–238	554	4.6	4–5	4–5	5
II.6	C ₂ H ₅	C ₂ H ₅	NHCOCH ₃	216–218	548	5.2	5–6	6	6

TABLE 3
Characterisation Data for 6-Nitro-4,7-Dichloro-2-Aminobenzothiazole Based Dyes **III**

Dye	R^1	R^2	X	$m.p.$ (°C)	$\lambda_{max}, \epsilon_{max} \times 10^{-4}$ (in ethanol)	Light fastness on polyester (0.1%, 0.5%, 2.5% dyeings)		
III.1	C ₂ H ₄ CN	C ₂ H ₄ CN	H	254–256	525	4.6	5–6	6
III.2	C ₂ H ₅	C ₂ H ₄ CN	H	240–242	546	4.9	6	6–7
III.3	C ₂ H ₅	C ₂ H ₄ OH	H	214–216	565	4.7	5	5
III.4	C ₂ H ₄ OH	C ₂ H ₄ CN	H	220–222	546	4.9	5–6	5–6
III.5	C ₂ H ₅	C ₂ H ₄ OH	CH ₃	206–208	576	4.6	5	5
III.6	C ₂ H ₅	C ₂ H ₅	NHCOCH ₃	257–259	571	5.4	6	6–7

TABLE 4
Characterisation Data for 6-Nitro-5,7-Dichloro-2-Aminobenzothiazole Based Dyes **IV**

Dye	R^1	R^2	X	$m.p.$ (°C)	$\lambda_{max}, \epsilon_{max} \times 10^{-4}$ (in ethanol)	Light fastness on polyester (0.1%, 0.5%, 2.5% dyeings)		
IV.1	C ₂ H ₄ CN	C ₂ H ₄ CN	H	222–224	512	4.1	5	5–6
IV.2	C ₂ H ₅	C ₂ H ₄ CN	H	250–252	534	4.6	5	5–6
IV.3	C ₂ H ₅	C ₂ H ₄ OH	H	202–204	550	4.8	4	4–5
IV.4	C ₂ H ₄ OH	C ₂ H ₄ CN	H	191–193	532	4.6	5	5–6
IV.5	C ₂ H ₅	C ₂ H ₄ OH	CH ₃	199–201	561	4.5	4	5
IV.6	C ₂ H ₅	C ₂ H ₅	NHCOCH ₃	184–186	555	5.5	5–6	6

TABLE 5
Characterisation Data for 4-Nitro- (5,6)(6,7)- Dichloro-2-Aminobenzothiazole Based Dyes **V, VI, VII**

Dye	R^1	R^2	X	$m.p.$ (°C)	$\lambda_{max}, \epsilon_{max} \times 10^{-4}$ (in ethanol)	Light fastness on polyester (0.1%, 0.5%, 2.5% dyeings)		
V.1	C ₂ H ₄ CN	C ₂ H ₄ CN	H	220–223	508	4.9	5	5–6
V.2	C ₂ H ₅	C ₂ H ₄ CN	H	243–247	529	5.1	5–6	5–6
V.3	C ₂ H ₅	C ₂ H ₄ OH	H	214–217	546	5.2	4	4–5
V.4	C ₂ H ₄ OH	C ₂ H ₄ CN	H	203–207	528	5.0	5	5
V.5	C ₂ H ₅	C ₂ H ₄ OH	CH ₃	191–195	555	4.9	4–5	4–5
V.6	C ₂ H ₅	C ₂ H ₅	NHCOCH ₃	203–206	550	5.5	6	6–7
VI.2	C ₂ H ₅	C ₂ H ₄ CN	H	258–260	528	5.1	5–6	6
VI.4	C ₂ H ₄ OH	C ₂ H ₄ CN	H	219–221	527	4.9	5	5
VI.6	C ₂ H ₅	C ₂ H ₅	NHCOCH ₃	249–251	548	5.4	6	6–7
VII.2	C ₂ H ₅	C ₂ H ₄ CN	H	246–248	531	5.4	6	6
VII.4	C ₂ H ₄ OH	C ₂ H ₄ CN	H	190–192	529	5.0	5	5
VII.6	C ₂ H ₅	C ₂ H ₅	NHCOCH ₃	228–230	551	5.5	6	6–7

2.4 General

5,6(6,7)-Dichloro-2-aminobenzothiazole was of industrial origin (Yorkshire Chemicals plc) and the isomer mixture was used as received (for dyes V). Small-scale chromatographic separation⁵ afforded the individual isomers used in dyes VI and VII. Other dichloro-2-aminobenzothiazoles were prepared as previously described.²

Mass spectra (EI) were recorded on an AEI MS 902, electronic spectra on a Philips PU 8730 UV/VIS Spectrometer, and ¹H NMR on a JEOL GX 270 FT NMR Spectrometer using TMS as internal reference.

All coupling components were of industrial origin (Yorkshire Chemicals plc) and were used without further purification.

3 RESULTS AND DISCUSSION

The isomeric dichloro-2-aminobenzothiazoles nitrated in excellent yield giving generally homogeneous products. In the majority of cases, nitration proceeded in the available 6- or 4-position, in accord with the established electrophilic substitution patterns in 2-aminobenzothiazoles. The marked tendency for preferred 6-substitution is exemplified in the facile formation of the 5,6-dinitro derivative on nitration of nitro-2-aminobenzothiazole;³ when the 6-position is unavailable, as in 6-nitro-2-aminobenzothiazole, substitution proceeds in the 4-position. Ambiguities could arise in the case of the 4,6-dichloro derivative, in which neither of the preferred sites is available. The ¹H NMR spectrum of the crude reaction product indicated the formation of a small amount of a second component; after two recrystallisations, the spectrum of the product was in accord with that of a homogeneous material and a 5-nitro substitution pattern has been ascribed.⁶

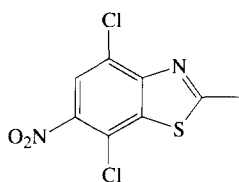
Whilst the readily available 5,6(6,7)-dichloro-2-aminobenzothiazole isomer mixture was nitrated *per se* and the resultant mixture used in general dye synthesis, selected dyes were also obtained *via* nitration of the individual isomers, which were generated on a small scale following the previously noted method.⁵

Diazotisation-coupling reactions proceeded readily by conventional processes, dye formation occurring with similar facility for each nitro-dichloro-2-aminobenzothiazole. Crude yields were in the 85% region, but all dyes required column chromatography to eliminate dye components originating from minor impurities in the coupling components. Additionally, similar problems of incomplete diazotisation noted for nitro-2-aminobenzothiazoles³ were also apparent and repeated chromatography was necessary in several cases (depending on relative *R_f* values) to effect full elimination of residual amines from the dyes.

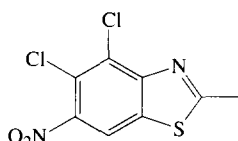
Electronic spectra data (Tables 1–5) show marked differences in λ_{\max} between isomeric dyes. In accord with the enhanced colour-imparting influence of 6-nitro substitution,³ dyes **I**, **III** and **IV** are the most bathochromic, but the orientation of the two chloro substituents results in significant differences between these three series.

As illustrative, the following evaluations pertain to dyes derived from *N*- β -cyanoethyl-*N*- β -hydroxyethylaniline as coupling component, since relevant data on dyes from 2-aminobenzothiazole,⁴ and its nitro³ and dichloro derivatives^{2,5} are available for comparison.

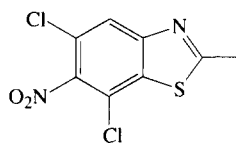
In the 6-nitro-4,7-dichloro-based dye **III.4**, any steric restraints operative will be relatively minimal and λ_{\max} for this isomer occurs at the longest wavelength (546 nm). Based on the additive effect of 6-nitro³ and 4,7-dichloro substitution,² a 'calculated' value of 545 nm results, viz, the observed value is essentially that of the summation of the individual substituent effects. Relative to this isomer, hypsochromic shifts of 8 nm and 14 nm are evident in the 6-nitro-4,5-dichloro- (**I.4**, λ_{\max} 538 nm) and 6-nitro-5,7-dichloro- (**IV.4**, λ_{\max} 532 nm) based isomers respectively. This can be rationalised in terms of steric crowding factors in the latter dye,



(**III.4**) 546 nm



(**I.4**) 538 nm



(**IV.4**) 532 nm

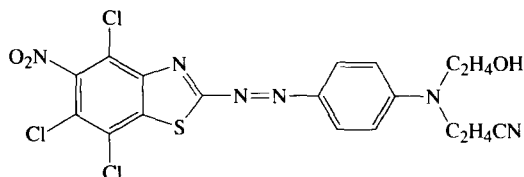
and, relative to the additive effect of the 6-nitro-³ and 5,7-dichloro-² substitution effects, the observed value is at 12 nm lower wavelength, indicative of the diminished electronic influence of the nitro substituent in this environment. In **I.4**, the observed value is at 4 nm lower wavelength than the additive value for 6-nitro and 4,5-dichloro substitution. This effect could be commensurate with a buttressing influence on the nitro group, originating from the two adjacent bulky chloro substituents (Hallas, G., pers. comm.). Such an effect has been previously noted in a comparison of the λ_{\max} values for some 2,3- and 2,5-dimethyl derivatives of Crystal Violet, Malachite Green and Michler's Hydrol Blue.⁷

Dyes derived from 5-nitro-2-aminobenzothiazole absorb at lower wavelength than 6- (and 4-) nitro analogues in view of the relatively decreased conjugation between this position and the terminal amino group of the coupler moiety,³ and dye **II.4** shows (λ_{\max} 525 nm) the lowest wavelength absorption of the dyes derived from *N*- β -cyanoethyl-*N*- β -hydroxyethylaniline. The nitro group is, additionally, in a crowded environment, with chloro substituents in both ortho positions; the observed λ_{\max} is at 3 nm lower

wavelength than that of the additive value from 5-nitro³ and 4,6-dichloro² substitution.

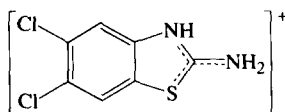
4-Nitro substitution in the benzothiazole system normally results in a colour shift in derived dyes of a similar order to, but slightly hypsochromic to, that from 6-nitro substitution. In dye **V.4**, derived from the nitration product of the 5,6(6,7)-dichloro-2-aminobenzothiazole isomer mixture, λ_{\max} (528 nm) lies between those of the 5-nitro and 6-nitro-dichloro based dyes. In the 4-nitro-6,7-dichloro component of this mixture, the two chlorine substituents have no steric interaction with the nitro group, but in the 4-nitro-5,6-dichloro isomer a possible buttressing effect could be operative. Unambiguous synthesis of the two isomer dyes (**VI.4**, **VII.4**, Table 5) showed only minor differences in the λ_{\max} of the two dyes (2 nm). Similar differences were apparent in isomer pairs derived from other coupling components (Table 5), confirming the minimal buttressing effect for 4-nitro-5,6-dichloro substitution compared to that noted above for 4,5-dichloro-6-nitro substitution.

To further evaluate steric factors, the nitro-trichloro substituted dye **IX** was synthesised. The precursor 2,4,5-trichlorophenylthiourea was obtained by conventional interaction of 2,4,5-trichloroaniline



IX

with ammonium thiocyanate in the presence of HCl. The mass spectrum of the product showed no molecular ion, base peak occurring at $[M-Cl]^+$. On ring closure, the mass spectrum of the product showed the parent ion corresponding to 4,6,7-trichloro-2-aminobenzothiazole. The elimination of a chlorine atom in the phenylthiourea is presumably related to a 'proximity effect', with formation of **X**. Similar elimination of *ortho* substituents



X

(not apparent in the corresponding *para* substituted derivatives) was observed in the mass spectrum of various 2-substituted phenylthioureas, and data pertinent to this will be reported separately.

Dye **VIII** derived from 4,6,7-trichloro-2-aminobenzothiazole and *N*- β -cyanoethyl-*N*- β -hydroxyethylaniline absorbs at 522 nm, viz. at 9–12 nm longer wavelength than the 4,6-, 4,7- and 6,7-dichloro based analogues. Introduction of the third chloro substituent thus results in similar shifts of λ_{\max} to those resulting from mono- and dichloro-substitution.² **VIII** has λ_{\max} at similar wavelength to that of the dye from 4-nitro-2-aminobenzothiazole (λ_{\max} 522 nm³) and not significantly different from that of the 6-nitro-2-aminobenzothiazole derived dye (λ_{\max} 527 nm³).

In **IX**, the presence of the nitro group results in a shift of λ_{\max} to 534 nm, viz. a shift of 12 nm. Thus, although in an orientation in which steric and buttressing effects of the chloro substituents may be operative, and in which the lowest colour shifts for mononitro substitution pertain (i.e. 5-nitro), a significant bathochromic shift occurs. Comparison of the effect of a 5-nitro substituent in dyes derived from *N*- β -cyanoethyl-*N*- β -hydroxyethylaniline shows that $\Delta\lambda$ is 16 nm between dyes from 2-aminobenzothiazole (λ_{\max} 495 nm⁴) and 5-nitro-2-aminobenzothiazole (λ_{\max} 511 nm³); 13 nm between 4,6-dichloro-2-aminobenzothiazole (λ_{\max} 511 nm²) and **II.4**; and 12 nm between **VIII** and **IX**. The limited differences between these values indicate that 5-nitro substitution has a similar influence on colour whether present in an unhindered or sterically crowded environment. Whilst more apparent steric influences are evident with 4-nitro-, and particularly 6-nitro substitution, they are not of a consistently high order and it can be concluded that, in general, electronic factors tend to be the most dominant effects influencing the colour of the dyes.

All the dyes gave good coloration of polyester, building up to bright red to reddish-blue hues. No significant difference was apparent with respect to the build-up or light fastness of individual isomeric dyes within the series.

4 CONCLUSIONS

Nitro derivatives of dichloro-2-aminobenzothiazoles are useful intermediates for monoazo disperse dyes having good coloration properties and light fastness. One of the most bathochromic of substituted 2-aminobenzothiazoles which have been reported for use as a diazo component is the 4,6-dinitro derivative. This is, however, notoriously difficult to diazotise and couple in consistently high dye yield. With *N*- β -cyanoethyl-*N*- β -hydroxyethylaniline, this intermediate gives a dye having λ_{\max} 560 nm,³ compared to the 546 nm for **III.4** (the longest wavelength absorption of the dyes from the same coupling component prepared in this investigation). However, by appropriate selection of coupling component, the nitro-dichloro-2-aminobenzothiazoles can afford dyes absorbing in the 560–575 nm region without the problems inherent with the 4,6-dinitro derivative.

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