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# Disazo Disperse Dyes Derived from 5,6(6,7)-Dichloro-2-Aminobenzothiazole

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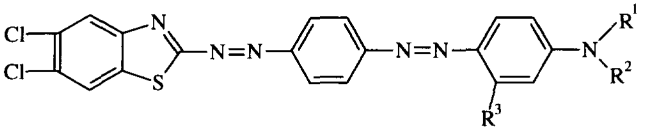
## ABSTRACT

*The isomer mixture of 5,6- and 6,7-dichloro-2-amino-benzothiazole was used as first component in the synthesis of a series of disazo disperse dyes. The influence of structural variations in the end and middle components on the colour of the dyes is evaluated. Copyright © 1996 Elsevier Science Ltd*

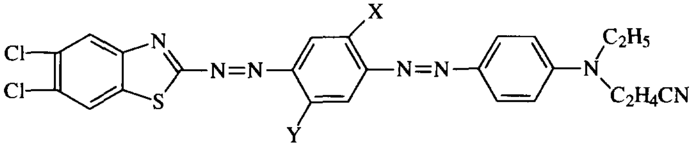
## INTRODUCTION

Dichloro-2-aminobenzothiazoles are useful diazo components in the generation of disperse dyes, particularly those in the orange–red to violet colour range. Structure–property relationships in monoazo dyes derived from various dichloro-[1,2] and mononitro- dichloro-2-aminobenzothiazoles[3] have been reported. Disazo analogues have not been extensively described, but typically the use of 5,6-disubstituted-2-aminobenothiazoles, e.g. 5,6-dimethyl-, as first component in disazo and polyazo dyes affords useful dichroic dyes absorbing above 600 nm, particularly when appropriate naphthalene, perimidine or julolidine based derivatives are used as end-components.[4]

We report here the synthesis of some disazo dyes of general formulae **I** and **II** and an evaluation of substituent effects on the colour of the dyes. The formulae shown represent only the component in the dye mixtures which is derived from 5,6-dichloro-2-aminobenzothiazole. All data reported below pertain to the isomer mixtures resultant from a commercial 5,6(6,7)-dichloro-2-aminobenzothiazole sample. Previous studies of monoazo dyes have shown



I



II

that there is negligible difference in the electronic spectra parameters of dyes based on the isomer mixture or on individual isomers.[5]

## EXPERIMENTAL

### General

Electronic spectra were recorded on a Philips PU8730 UV/VIS spectrometer, and mass spectra (EI) on an AEI MS 902. Column chromatography was effected on Silica Gel (Acros), applying the dyes from solution in chlorobenzene (with up to 10% ethyl acetate as necessary) and eluting with toluene:ethyl acetate 95:5 to 5:95, as appropriate.

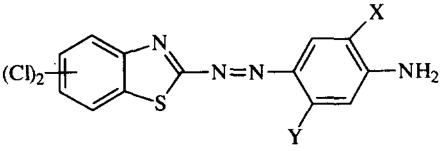
5,6(6,7)-Dichloro-2-aminobenzothiazole and all coupling components were industrial samples kindly supplied by Yorkshire Chemicals plc. and were used without further purification.

### Dye Synthesis

*Stage 1. 2-(4′-Aminophenylazo)-5,6(6,7)-dichlorobenzothiazoles III*

The appropriate arylamine (0.1 mol) was added portionwise over 20 min to a stirred solution of formaldehyde sodium bisulphite addition compound (40 g, 0.3 mol) (Aldrich) in water (100 ml) at 70°C. Stirring was then continued at 75–80°C for 30 min during addition of ethanol (75 ml), and the mixture finally refluxed for 10 min. After standing overnight (refrigerator), the resultant *N*-sulphomethylanilines were filtered, air dried (yields 80–95%) and used directly in subsequent dye synthesis.

5,6(6,7)-Dichloro-2-aminobenzothiazole (4.38 g, 0.02 mol) was diazotised with nitrosylsulphuric acid in glacial acetic acid – propionic acid following the previously described procedure.[1] The diazonium liquor was run into a solution of the appropriate *N*-sulphomethylaniline (0.02 mol) in ice-water (75 ml). The pH was adjusted to 4–5 by addition of sodium acetate and the liquor stirred for 3 h at 0–5°C. The products were filtered and the (moist) presscake stirred in a solution of NaOH (10 g) in ethanol (50 ml) and water (100 ml) at 55–60°C, maintaining pH > 12, until hydrolysis was complete (3–5 h). The cooled liquor was filtered and the monoazo dyes **III** filtered and washed with warm water. Recrystallisation from ethanol (Norit) gave 75–85% yield of the following **III**; given - X, Y, m.p. (°C), $\lambda_{max}$ ($\epsilon_{max} \times 10^{-3}$):- H, H, 278–280, 506 (34.4); OMe, H, 199–202, 520 (34.1); H, OMe, 231–235, 518 (33.8); Me, H, 236–239, 504 (35.4); H, Me, 239–242, 511 (36.9); Cl, H, 260–264, 492 (32.7); H, Cl, 280–283, 503 (33.2); Cl, Cl, 169–172, 484 (33.2); OMe, OMe, 220–224, 540 (37.3).



**III**

*Stage 2. Disazo dyes I and II*

The monoazo Precursor **III** (0.01 mol) was stirred into glacial acetic (30 ml), with warming where necessary to dissolve. Concentrated HCl (5 ml) was added, the liquor stirred whilst cooling to 5°C and diazotised by addition of nitrosylsulphuric acid (prepared from 0.011 mol $NaNO_2$ and 5 ml $H_2SO_4$, followed by dilution with 10 ml glacial acetic acid: propionic acid 3:1). After stirring at 5°C for 3 h, excess nitrite was removed by addition of sulphamic acid and the diazonium liquor added portionwise to a solution of the appropriate coupling component (0.01 mol) in glacial acetic acid (50 ml) and ice-water (20 ml). After 2 h, the liquor was neutralised with sodium acetate and the products filtered and washed neutral. Yields of crude dyes were in the 80–90% region and all dyes were purified (0.5 g scale) as noted in the *General* section. Relevant data is given in Table 1 (yields shown are for % recovery of pure material by chromatography, and pertain to the dichloro-2-aminobenzothiazole used as initial diazo component).

**TABLE 1**
Data for Disazo Dyes I and II

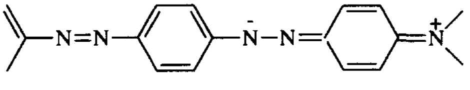
| *Dye* | *R*$^1$ | *R*$^2$ | *R*$^3$ | *X* | *Y* | *Yield (%)* | *M.p.* (°C) | *Absorption in ethanol* | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $\lambda_{max}$(*nm*) | $\epsilon_{max} \times 10^{-3}$ |
| I.1 | $C_2H_4$ | $C_2H_4CN$ | H | — | — | 58 | 202–205 | 509 | 31.2 |
| I.2 | $C_2H_5$ | $C_2H_4CN$ | H | — | — | 64 | 186–189 | 535 | 33.4 |
| I.3 | $C_2H_4OH$ | $C_2H_4CN$ | H | — | — | 53 | 198–202 | 534 | 32.6 |
| I.4 | $C_2H_5$ | $C_2H_4OH$ | H | — | — | 60 | 271–274 | 556 | 33.7 |
| I.5 | $C_2H_5$ | $C_2H_5$ | $NHCOCH_3$ | — | — | 51 | 244–248 | 575 | 37.9 |
| II.1(I.2) | — | — | — | H | H | 64 | 186–189 | 535 | 33.4 |
| II.2 | — | — | — | $CH_3$ | H | 59 | 227–230 | 537 | 32.1 |
| II.3 | — | — | — | H | $CH_3$ | 61 | 238–241 | 536 | 30.7 |
| II.4 | — | — | — | $OCH_3$ | H | 53 | 243–247 | 551 | 31.5 |
| II.5 | — | — | — | H | $OCH_3$ | 58 | 203–207 | 547 | 33.2 |
| II.6 | — | — | — | $OCH_3$ | $OCH_3$ | 62 | 269–272 | 592 | 35.1 |
| II.7 | — | — | — | Cl | H | 51 | 241–244 | 551 | 31.5 |
| II.8 | — | — | — | H | Cl | 56 | 267–270 | 550 | 33.4 |
| II.9 | — | — | — | Cl | Cl | 49 | 286–290 | 576 | 32.8 |

## RESULTS AND DISCUSSION

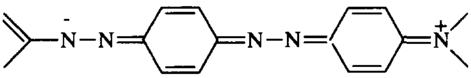
The disazo dyes **I** and **II** were obtained by standard procedures, involving initial monoazo precursor synthesis via the pertinent *N*-sulphomethylaniline. Colour shifts in the monoazo dyes (*Dye Synthesis* section, Stage 1) are in general accord with established substituent effects in 4-aminoazobenzenes, *viz.* $\lambda_{max}$ are shifted bathochromically by donor methyl and methoxy groups, and hypsochromically by the chloro substituent. $\epsilon_{max}$ values are not significantly altered, indicative of the diminished steric interactions for substituents ortho to a primary amino group compared to similar substitution in 4-*N*, *N*-dialkylaminoazobenzenes, cf.[6]

Diazotisation – coupling processes of the monoazo intermediates employing the essentially aqueous phase systems satisfactory for 4-aminoazobenzene based disazo dyes[7–10] were unsatisfactory, significant contamination with undiazotised monoazo dye occurring. The use of relatively non-aqueous media, using nitrosylsulphuric acid as nitrosating agent, was more viable (cf.[4]) although chromatographic separation was necessary to isolate the pure disazo dyes. Principal contaminant, even after prolonged diazotisation, was undiazotised start material; similar problems have been noted in the diazotisation of various nitro -2-aminobenzothiazoles.[3,11]

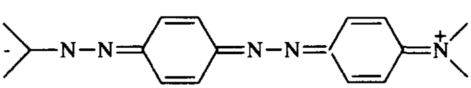
In the disazo dyes, progressive electron delocalisation from the terminal amino group will result in structures typified by **IV** – **VI**.



**IV**



**V**



**VI**

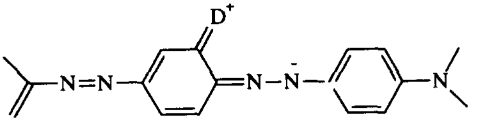
In dyes **I**, with constant first and middle components, the delocalisation will depend on the relative electron donor characteristics of the end component.

Table 1 illustrates the effect of different end components, the *N*, *N*-bis-cyanoethylated dye **I.1** showing $\lambda_{max}$ at the lowest wavelength in the series. Relative to the monoazo dye 5,6(6,7)-dichloro-2-aminobenzothiazole → *N*, *N*-bis-$\beta$-cyanoethylaniline, $\lambda_{max}$ 489 nm,[1] introduction of the central phenylazo moiety gives a bathochromic shift of 20 nm. Slightly higher $\Delta\lambda$ values pertain to dyes **I.2** – **I.4** when compared to the corresponding monoazo dyes derived from the same coupling component, *viz.* *N*-ethyl-*N*-cyanoethylaniline 25 nm, *N*-$\beta$-hydroxyethyl-*N*-$\beta$-cyanoethylaniline 24 nm, and *N*-ethyl-*N*-$\beta$-hydroxyethylaniline 28 nm. These values are similar to those in 4-aminoazobenzenes, e.g. 4-nitroaniline → *N*, *N*-dimethylaniline $\lambda_{max}$ 475 nm; 4-nitroaniline → aniline → *N*, *N*-dimethylaniline $\lambda_{max}$ 500 nm.[12] With the enhanced donor properties and additional intramolecular H-bonding in the 2-acetylamino-4, *N*, *N*-diethylaniline derived dye **I.5**, the $\Delta\lambda$ value increases to 35 nm. In general therefore, extension of the azo chromogen system by one azophenyl unit results in shifts of 20–35 nm, depending on the nature of the end component.

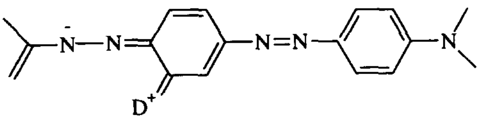
Where the first and end components are constant, substituents in the middle ring will induce additional charge delocalisations. Little data has been published on specific effects of such substitution, although it has been noted[13] that donor substitution in the middle ring has a bathochromic influence. From the data for dyes **II** (Table 1), it is evident that the presence of the relatively weakly-donating methyl group in either the 2′-(Y) or 5′- (X) position has only minimal effect on $\lambda_{max}$, whereas the more strongly-donating methoxy group produces significant shifts, with substitution in the 5′- position being the more bathochromic. The most likely additional charge transfer structures (**VIII** and **IX**), however, both pertain to 2′-substitution. Mesomeric effects for 5′-substitution can only result in **VII** and would not be expected to give notable colour shifts. Inductive factors are also possible, but the methoxy group has an electron acceptor nature in this respect.

Interestingly, the presence of methoxy groups in both the 2′- and 5′- positions (dye **II.6**) results in a bathocromic shift of 57 nm, double that of the additive effect of individual 5′- (dye **II.4**, 16 nm) and 2′- substitution (dye **II.5**, 12 nm). The advantageous use in disazo dyes of middle components such as cresidines and 2,5-dimethoxyaniline is well established and is often considered to result in enhanced colour value in resultant dyeings. This may, however, not necessarily be related to greater dye uptake, but to a displacement of $\lambda_{max}$ to longer wavelengths, with a consequent apparently greater visual impact of the dyeings.

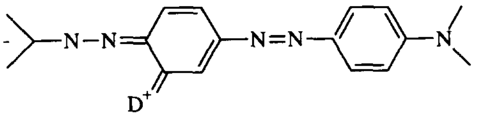
Substitution by electron acceptor substituents in the middle ring results in only a limited number of additional charge transfer structures (e.g. **X**) when considering only mesomeric interactions, and for 5′-substitution only. The



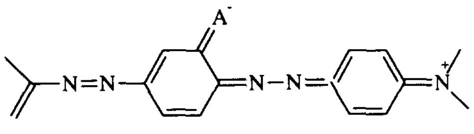
**VII**



**VIII**



**IX**



**X**

chloro substituents in dyes **II.7** and **II.8** are, however, electron attracting only in an inductive capacity. In monoazo dyes, inductive influences are well documented, e.g. in 4′-nitro-4-*N*, *N*-diethylaminoazobenzene, substitution in the 2-position by chloro, cyano and nitro groups results in shifts of a similar order, indicating that the stabilising effect is inductive in origin.[14] Such shifts are hypsochromic since the substitution is in the donor ring system. Introduction of cyano groups into the acceptor ring, e.g. the diazo component of 4-*N*, *N*-diethylaminoazobenzene, gives large bathochromic shifts in the conjugated 2′- and 4′- positions (47 nm and 51 nm, respectively), ascribed mainly to mesomeric factors.[15] However, in the non-conjugated 3′- position, a shift of 31 nm occurs and an additive shift of 63 nm results from 3′, 5′- disubstitution; these shifts are relatable to inductive factors.

In dyes **II**, chloro substitution produces bathochromic shifts of a very similar order in both the 2′- (dye **II.8**, 15 nm) and 5′- positions (dye **II.7**, 16 nm), and these shifts are equatable to those arising from substitution by the donor methoxy group. As with the latter, conjoint substitution in both the 2′- and 5′- positions (dye **II.9**) gives a shift (41 nm) greater than the additive effect of the individual substituents.

The effect on colour resulting from substitution in the middle ring by groups having a + M or –I influence is thus of a similar order, irrespective of their orientation. An oversimplified viewpoint could be to treat the system in terms of a monoazo dye, and to regard the diazo moiety in conjunction with electron attractor-substituted middle components, or the end-component coupler moiety in conjunction with electron donor substituted middle components, as 'complex' acceptor or donor residues respectively.

The disazo dyes **II** are based on a typical 'hypsochromic' type coupler, *viz.* *N*-ethyl-*N*-$\beta$-cyanoethylaniline, which in analogous monoazo dyes gives a dye having $\lambda_{max}$ 510 nm[2]. The di-methoxy substituted disazo dye **II.6** has $\lambda_{max}$ 590 nm, a value not attainable in monoazo dyes, even with typical 'bathochromic' couplers such as 2-methoxy-5-acetylamino-*N*, *N*-diethylaniline ($\lambda_{max}$ 577 nm[1]). However, whilst synthesis of the monoazo dyes is relatively straightforward, that of the disazo dyes is not so facile, the generation of pure dyes requiring, under the synthetic conditions used in this present investigation, more exhaustive purification procedures. Such problems could, however, possibly be obviated by more detailed evaluations of the pertinent diazotisation and coupling conditions.

## ACKNOWLEDGEMENT

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