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Hetarylazo Disperse Dyes derived from 5,6-Dichloro- and 6,7-Dichloro-2 Aminobenzothiazoles

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ABSTRACT

The isomer mixtures resulting from the diazotisation of 5,6-(6,7-)dichloro-2-aminobenzothiazole and coupling to N*-substituted anilines were separable by column chromatography. Isomer characterisation was effected by unambiguous dye synthesis from the individual dichloro-2-aminobenzothiazoles, and by* ^1H *NMR. The colour and dyeing parameters of isomers were found to be essentially equivalent, and similar to those of the corresponding isomer mixtures.*

1 INTRODUCTION

Hetarylazo disperse dyes derived from the isomer mixture of 5,6-(6,7)-dichloro-2-aminobenzothiazole are well-established industrial colorants, and have been described[1] in the context of possible alternatives to anthraquinone-based dyes. The colour range obtainable from such isomer mixtures, when diazotised and coupled to *N*-substituted anilines and 1-naphthylamines, has been reported,[2] but despite the long-established interest in these dyes (see, e.g., Refs 3 and 4), no data has been reported with respect to the individual isomers. We describe here the isolation and characterisation of some isomer pairs derived from 5,6-dichloro- and 6,7-dichloro-2-aminobenzothiazoles, viz. dyes **I** and **II**, respectively.

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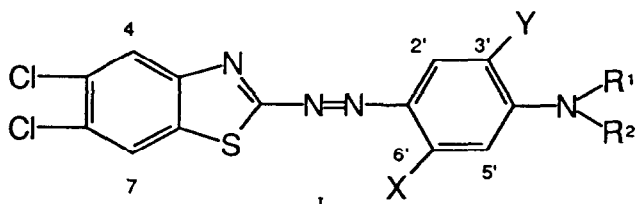
2 EXPERIMENTAL

2.1 Separation of isomer dyes

Isomer mixtures of the hetarylazo dyes were prepared as previously described.[2] Separation of the isomers was effected by column chromatography on silica gel, applying the dyes from solution in either toluene or chlorobenzene, and eluting with toluene containing up to 50% ethyl acetate as appropriate. In some instances, e.g. the dyes from *N*-ethyl-*N*-β-cyanoethylaniline, *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline and *N*-β-acetoxyethyl-*N*-ethylaniline (as illustrative), a relatively clear separation of the isomers occurred with gradual development of the column (5,6-dichloro-based isomer at higher R_f). With several dye mixtures, separation was less defined. In these cases, eluant was collected fractionwise and the major higher and lower R_f fractions thus isolated were rechromatographed to effect total separation. Intermediate fractions in the initial separation, containing mixtures of isomers in ratios between 70:30 and 30:70 were discarded. Yields of isomers, from a 0·5 g isomer mixture, were in the general region of 0·15–0·20 g of the 6,7-dichloro–based product (**II**) and 0·20–0·24 g of the 5,6-dichloro–based product (**I**).

2.2 5,6-Dichloro- and 6,7-dichloro-2-aminobenzothiazoles

The isomer mixture of 5,6(6,7)-dichloro-2-aminobenzothiazole (1·5 g), prepared as previously described,[2] was dissolved in boiling chlorobenzene (400 ml). To the partially cooled solution was added (at 70°C) ethyl acetate (50 ml). After standing overnight, crystallised material (0·3 g) was



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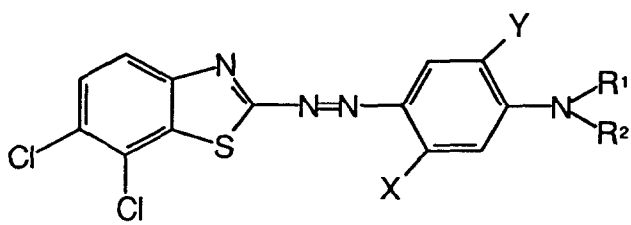

II

TABLE 1
Characterisation and Fastness Data for 5,6-Dichloro-Based Dyes (**I**)

Compound	R^1	R^2	*X*	*Y*	*m.p.* (°C)	*Absorption in ethanol*		*Light fastness on polyester*		
						λ_{max} (nm)	$\epsilon_{max} \times 10^{-4}$	0·1%	0·5%	2·5%
I.1	C_2H_5	C_2H_5	—	—	227–228	527	5·21	5	5	5
I.2	C_2H_5	C_2H_4CN	—	—	219–220	510	5·61	5	5	5–6
I.3	C_2H_4CN	C_2H_4CN	—	—	268–269	489	4·46	5–6	5–6	6
I.4	C_2H_5	C_2H_4OH	—	—	238–239	528	4·84	4	4–5	4–5
I.5	C_2H_5	$C_2H_4OCOCH_3$	—	—	144–145	520	5·08	5–6	5–6	6
I.6	C_2H_2CN	C_2H_4OH	—	—	255–256	510	5·15	4–5	4–5	4–5
I.7	C_2H_4CN	$C_2H_4OCOCH_3$	—	—	157–158	504	4·58	5	5–6	5–6
I.8	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	—	—	159–160	512	4·78	5–6	5–6	5–6
I.9	C_2H_5	C_2H_4OH	CH_3	—	220–221	536	5·16	4–5	5	5
I.10	C_2H_5	$C_2H_4OCOCH_3$	CH_3	—	153–154	529	5·36	5–6	5–6	6
I.11	C_2H_4OH	C_2H_4OH	CH_3	—	193–194	535	5·29	4–5	4–5	5
I.12	$C_2H_4OCOH_3$	$C_2H_4OCOCH_3$	CH_3	—	160–161	520	4·94	5–6	5–6	6
I.13	C_2H_5	C_2H_5	$NHCOCH_3$	—	225–226	538	6·15	5–6	6	6
I.14	C_2H_4CN	C_2H_4OH	$NHCOCH_3$	OCH_3	183–184	554	4·08	4–5	4–5	5
I.15	C_2H_5	C_2H_5	$NHCOCH_3$	OCH_3	231–232	587	4·58	5	5–6	5–6

TABLE 2
Characterisation and Fastness Data for 6,7-Dichloro-Based Dyes (**II**)

Compound	R^1	R^2	X	Y	*m.p.* (°C)	*Absorption in ethanol*		*Light fastness on polyester*		
						λ_{max} (nm)	$\epsilon_{max} \times 10^{-4}$	*0·1%*	*0·5%*	*2·5%*
II.1	C_2H_5	C_2H_5	—	—	211–212	528	5·32	5	5	5–6
II.2	C_2H_5	C_2H_4CN	—	—	181–182	510	5·55	5	5–6	5–6
II.3	C_2H_4CN	C_2H_4CN	—	—	252–253	490	4·65	5–6	6	6
II.4	C_2H_5	C_2H_4OH	—	—	184–185	528	4·91	4	4	4–5
II.5	C_2H_5	$C_2H_4OCOCH_3$	—	—	172–173	520	5·16	5–6	5–6	6
II.6	C_2H_4CN	C_2H_4OH	—	—	196–197	510	4·90	4–5	4–5	5
II.7	C_2H_4CN	$C_2H_4OCOCH_3$	—	—	186–187	504	4·32	5–6	5–6	6
II.8	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	—	—	153–154	512	4·59	5	5–6	5–6
II.9	C_2H_5	C_2H_4OH	CH_3	—	197–198	535	4·92	4–5	4–5	5
II.10	C_2H_5	$C_2H_4OCOCH_3$	CH_3	—	141–142	528	5·14	5–6	5–6	6
II.11	C_2H_4OH	C_2H_4OH	CH_3	—	208–209	535	5·49	4–5	5	5
II.12	$C_2H_4OCOCH_3$	$C_2H_4OCOCH_3$	CH_3	—	168–169	520	5·17	5–6	5–6	6
II.13	C_2H_5	C_2H_5	$NHCOCH_3$	—	206–207	539	5·99	5–6	5–6	6
II.14	C_2H_4CN	C_2H_4OH	$NHCOCH_3$	OCH_3	195–196	554	4·16	4–5	5	5
II.15	C_2H_5	C_2H_5	$NHCOCH_3$	OCH_3	184–185	586	4·67	5	5–6	5–6

filtered and the filtrate applied to a column of silica gel (column height 90 cm, internal diameter 2 cm, silica gel 100 g). Elution was effected with toluene; ethyl acetate 80 : 20; eluant was collected in 250 ml fractions until all material had eluted (*c.* 8 h).

Initial fractions afforded 5,6-dichloro-2-aminobenzothiazole (0·63 g), m.p. 213–214°C (lit.[5] 210°C) (^{1}H NMR, d_6-DMSO: δ 7·98, 1H, s, H-7; δ 7·52, IH, s, H-4) and subsequent fractions gave 6,7-dichloro-2-aminobenzothiazole (0·38 g), m.p. 238–239°C (lit.[5] 222–223°C) (^{1}H NMR, d_6-DMSO: δ 7·44, 1H, d, I = 8·5 Hz, H-5; δ 7·25, 1H, d, I = 8·5 Hz, H-4). Intermediate fractions (0·17 g), containing mixtures of isomers, were not investigated further.

The isomers thus separated were diazotised and coupled to selected coupling components by standard procedures;[2] dyes identical to those isolated as in Section 2.1 above resulted.

2.3 General

3,4-Dichloroaniline was diazotised and coupled to *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline; purification of the product by column chromatography gave 3',4'-dichloro-4-*N*-β-cyanoethyl-*N*-β-hydroxyethylaminoazobenzene, orange needles, m.p. 95–96°C (ethanol); λ_{max} (ethanol) 418 nm, ϵ_{max} 32200).

Electronic spectra were recorded on a Phillips PU (Cambridge, UK) 8730 UV/VIS spectrophotometer from dye solutions in absolute ethanol. Relevant data is shown in Tables 1 and 2. ^{1}H NMR spectra were recorded on a JEOL Ltd (Tokyo, Japan) GX 270 FT NMR spectrometer; values reported in Tables 3 (5,6-isomers) and 4 (6,7-isomers) are for spectra in d_6-DMSO, δ values being relative to TMS (Table 4 lists only data pertinent to the carbocyclic ring of the hetero moiety; signals for the coupling component protons were similar to those for the isomers reported in Table 3).

Column chromatography was effected on Silica Gel for column chromatography, 0·060–0·200 mm, pore diameter *c.* 4 nm (Janssen Chimica, Geel, Belgium).

3 RESULTS AND DISCUSSION

The isomer mixture of 5,6- and 6,7-dichloro-2-aminobenzothiazole is readily accessible using standard procedures for the synthesis of substituted 2-aminobenzothiazoles.[2] However, generation of the individual isomers is not especially facile. A previously reported procedure[5] involves isomer separation based on the differential solubilities of the hydrochloride salts. The process requires large volumes of ether and the use of hydrochloric

TABLE 3

^{1}H NMR Data (d_6-DMSO) for 5,6-Dichloro-Based Dyes (**I**) (δ values relative to TMS)

Compound	*H-7*	*H-4*	*H-2',6'*	*H-3',5'-*				
I.1	8·39 1H s	8·24 1H s	7 86 2H d J = 9 5 Hz	6·95 2H d J = 9 5 Hz	3·58	4H q	J = 7·0 Hz	(NCH_2CH_3)
					1·21	6H t	J = 7 0 Hz	(NCH_2CH_3)
I.2	8 40 1H s	8·27 1H s	7·85 2H d J = 9·3 Hz	7·03 2H d J = 9·3 Hz	3·87	2H t	J = 6·8 Hz	(NCH_2CH_2CN)
					3·63	2H q	J = 7·0 Hz	(NCH_2CH_3)
					2·89	2H t	J = 6 8 Hz	(NCH_2CH_2CN)
					1·20	3H t	J = 7·0 Hz	(NCH_2CH_3)
I.3	8·46 1H s	8·34 1H s	7 91 2H d J = 9·3 Hz	7·17 2H d J = 9·3 Hz	3·93	4H t	J = 7·0 Hz	(NCH_2CH_2CN)
					2·88	4H t	J = 7·0 Hz	(NCH_2CH_2CN)
I.4	8·38 1H s	8 24 1H s	7·85 2H d J = 9·3 Hz	6·98 2H d J = 9 3 Hz	3·61–3·63		6H m	(NCH_2)
					1·19	3H t	J = 7·0 Hz	(NCH_2CH_3)
I.5	8·40 1H s	8·27 1H s	7·88 2H d J = 9·2 Hz	7·03 2H d J = 9·2 Hz	4 27	2H t	J = 5·5 Hz	($NCH_2CH_2OCOCH_3$)
					3·81	2H t	J = 5·5 Hz	($NCH_2CH_2OCOCH_3$)
					3·61	2H q	J = 7·0 Hz	(NCH_2CH_3)
					2·00	3H s		(—$COCH_3$)
					1 19	3H t	J = 7·0 Hz	(NCH_2CH_3)
I.6	8·39 1H s	8·26 1H s	7·86 2H d J = 9 3 Hz	7·08 2H d J = 9 3 Hz	4·98	1H bd s		(OH)
					3·94	2H t	J = 7 0 Hz	(NCH_2CH_2CN)
					3·68	4H s		(NCH_2CH_2OH)
					2·90	2H t	J = 7 0 Hz	(NCH_2CH_2CN)
I.7	8·40 1H s	8 27 1H s	7·89 2H d J = 9·5 Hz	7·11 2H d J = 9 5 Hz	4·28	2H t	J = 5·5 Hz	($NCH_2CH_2OCOCH_3$)
					3·85–3·93	4H m		(NCH_2)
					2·89	2H t	J = 7·0 Hz	(NCH_2CH_2CN)
					2·00	3H s		($COCH_3$)
I.8	8·39 1H s	8·26 1H s	7·87 2H d J = 9·5 Hz	7·08 2H d J = 9·5 Hz	4·27	4H t		($NCH_2CH_2OCOCH_3$)
					3·84	4H t		($NCH_2CH_2OCOCH_2$)
					1·99	6H s		($COCH_3$)

TABLE 3—*contd.*

Compound	*H-7*	*H-4*	*H-2'*	*H-3'*	*H-5'*				
I.9	8·33 1H s	8·18 1H s	7·81 1H d J = 9·5 Hz	6·82 1H d J = 9·5 Hz	6·77 1H s	4·93	1H bd s		(OH)
						3·62	6H bd s		(N$\underline{CH_2}CH_3$)($\underline{CH_2}CH_2$OH)
						2·57	3H s		(6'—CH_3)
						1·18	3H t		(NCH$_2\underline{CH_3}$)
I.10	8·33 1H s	8·19 1H s	7·82 1H d J = 9·2 Hz	6·85 1H d J = 9 2 Hz	6·88 1H s	4 25	2H t	J = 5·5 Hz	(NCH$_2\underline{CH_2}$OCOCH$_3$)
						3·78	2H t	J = 5·5 Hz	(N$\underline{CH_2}$CH$_2$OCOCH$_3$)
						3·60	2H q	J = 7·0 Hz	(N$\underline{CH_2}$CH$_3$)
						2·58	3H s		(6'—CH_3)
						2·00	3H s		(CO$\underline{CH_3}$)
						1·18	3H t		(NCH$_2\underline{CH_3}$)
I.11	8·30 1H s	8·16 1H s	7·78 1H d J = 9·2 Hz	6·85 1H d J = 9·2 Hz	6·80 1H s	4·94	2H s		(OH)
						3·66	8H bd s		(all —CH_2)
						2·55	3 H s		(6'—CH_3)
I.12	8·36 1H s	8·23 1H s	7·81 1H d J = 9·5 Hz	6·94–6·87	2H m	4·26	4H t	J = 5·5 Hz	(NCH$_2\underline{CH_2}$OCOCH$_3$)
						3 83	4H t	J = 5·5 Hz	(N$\underline{CH_2}$CH$_2$OCOCH$_3$)
						2·59	3H s		(6'—CH_3)
						2·00	6H s		(CO$\underline{CH_3}$)
I.13	8·34 1H s	8 16 1H s	7·75 1H d J = 9·5 Hz	6·77 1H d J = 9·5 Hz	7·86 1H s	10·40	1H bd s		(N$\underline{H}$COCH$_3$)
						3 56	4H q	J = 7·0 Hz	(N$\underline{CH_2}$CH$_3$)
						2·22	3H s		(NHCO$\underline{CH_3}$)
						1·22	6H t	J = 7·0 Hz	(NCH$_2\underline{CH_3}$)
I.14	8·37 1H s	8·19 1H s	7 28 1H s	—	7·77 1H s	9·82	1H s		(N$\underline{H}$COCH$_3$)
						4 85	1H bd s		(OH)
						3·91	2H t	J = 7·0 Hz	(N$\underline{CH_2}$CH$_2$CN)
						3·86	3H s		(3'—O$\underline{CH_3}$)
						3·68–3·62	4H m		(N$\underline{CH_2}\underline{CH_2}$OH)
						2·90	2H t	J = 7·0 Hz	(NCH$_2\underline{CH_2}$CN)
						2·20	3H s		(NHCO$\underline{CH_3}$)
I.15	8·35 1H s	8·15 1H s	7·29 1H s	—	7·83 1H s	9·81	1H s		($\underline{NH}$COCH$_3$)
						3·85	3H s		(3'—OCH$_3$)
						3·57	4H q	J = 7·0 Hz	(N$\underline{CH_2}$CH$_3$)
						2·21	3H s		(NHCO$\underline{CH_3}$)
						1·23	6H t	J = 7·0 Hz	(NCH$_2\underline{CH_3}$)

TABLE 4
^{1}H NMR Data (d_6-DMSO) for 6,7-Dichloro-Based Dyes (**II**)

Compound	*H-5*			*H-4*		
II.1	7·94	1H d	J = 8·8 Hz	7·72	1H d	J = 8·8 Hz
II.2	7·92	1H d	J = 8·6 Hz	7·72	1H d	J = 8·6 Hz
II.3	8·01	1H d	J = 8·6 Hz	7·76	1H d	J = 8·8 Hz
II.4	7·92	1H d	J = 8·8 Hz	7·70	1H d	J = 8·8 Hz
II.5	7·93	1H d	J = 8·6 Hz	7·76	1H d	J = 8·8 Hz
II.6	7·98	1H d	J = 8·8 Hz	7·74	1H d	J = 8·8 Hz
II.7	8·01	1H d	J = 8·8 Hz	7·78	1H d	J = 8·8 Hz
II.8	7·99	1H d	J = 8·8 Hz	7·74	1H d	J = 8·8 Hz
II.9	7·87	1H d	J = 8·8 Hz	7·67	1H d	J = 8·8 Hz
II.10	7·92	1H d	J = 8 8 Hz	7·69	1H d	J = 8 8 Hz
II.11	7 83	1H d	J = 8·8 Hz	7·62	1H d	J = 8·8 Hz
II.12	7·95	1H d	J = 8·8 Hz	7·72	1H d	J = 8·8 Hz
II.13	7·89	1H d	J = 8·8 Hz	7·68	1H d	J = 8·8 Hz
II.14	7·90	1H d	J = 8·6 Hz	7·69	1H d	J = 8·6 Hz
II.15	7·90	1H d	J = 8·8 Hz	7·68	1H d	J = 8·8 Hz

acid gas and is stated to afford an overall recovery of 21% of the 6,7-isomer and 10% of the 5,6-isomer. We found the method difficult to fully replicate, generally obtaining fractions relatively rich (70–75%) in one isomer; repeated recrystallisations gave purer material (95%) but recovery rates of these were very low.

Isomer separation in amounts sufficient for the small-scale evaluations required in this investigation were found to be readily attainable by conventional column chromatography techniques using silica gel. The isomer mixture readily crystallised from hot chlorobenzene, but addition of ethyl acetate to the partially cooled liquor obviated this problem to some extent and retained sufficient material in solution for the chromatographic process. The method was relatively simple and yielded good recovery rates of the individual isomers in sufficient quantity for the required laboratory-scale dye syntheses. Whilst the higher R_f 5,6-dichloro isomer was obtained in good yield (relative to its content in the initial isomer mix[2]), recovery of the 6,7-isomer was lower, probably due to the frequency of eluant sampling. Insoluble material filtered from the chlorobenzene/ethyl acetate liquor prior to chromatography also contained a higher ratio of the 6,7-isomer (5,6-, 32·4%; 6,7-, 67·6%).

Dyes **I** and **II** were similarly isolated by column chromatography of the respective isomer mixtures, the higher R_f 5,6-dichloro–based isomer showing, under the conditions used, sufficient R_f differential to allow facile separation from the 6,7-analogues. Characterisation of the products thus isolated was established by ^{1}H NMR in d_6-DMSO. Proton signals

for the carbocyclic ring of the hetero moiety allow structural assignments to be made, viz. in the 5,6-dichloro–based dyes **I**, the H-4 and H-7 protons appear as two singlets, whilst in the 6,7-isomers the H-4 and H-5 protons appear as doublets, with appropriate coupling constants for ortho-substitution. Relevant ^{1}H-NMR data for all **I** and **II** is given in Tables 3 and 4, respectively. Full characterisation data is listed for dyes **I** (Table 3); only the proton assignments for the carbocyclic ring of the hetero moiety are given for dyes **II** (Table 4), all other signals being very similar or identical to those for dyes **I**. Assignments for the aliphatic and aromatic protons of the coupler moiety are generally in accord with data for analogous 4-aminoazobenzene derivatives. Whilst the α- and β-methylene groups of the *N*-β-acetoxyethyl substituents show clearly resolved and distinctive signals (the lower J-values for the latter reflecting vicinal bond angles), those of the *N*-β-hydroxyethyl group tend to overlap, not only for the α- and β-methylene groups (e.g. **I.6**, **I.11**), but also with the α-methylene groups of conjoint *N*-ethyl groups (e.g. **I.4**, **I.9**). The methyl group protons for the *N*-ethyl, *O*-acetoxy, *N*-acetylamino, carbocyclic methyl and methoxy substituents are distinctive, in the general area of δ 1·2, 2·0, 2·2, 2·6 and 3·8, respectively. Aromatic protons in the 3'- and 5'-positions of coupler residues containing a 6'-methyl substituent were in most dyes sufficiently resolved, the 3'-H signal appearing as a doublet (upfield or downfield with respect to the 5'-H signal, differences being of limited significance) with analogous ortho-coupling constants to the 2'-H signal. The diamagnetic anisotropic effect of the carbonyl residue in 6'-acylamino–substituted dyes shifts the 5'-H signal downfield to the δ 8·0 region, allowing characterisation of dyes containing these substituents to be made.

Authentication of dyes **I** and **II** was also established by synthesis of selected isomer pairs from the respective 5,6- and 6,7-dichloro-2-aminobenzothiazoles. Products thus obtained were identical with those isolated from the higher and lower R_f fractions, respectively, on column chromatography of the isomer mixtures.

Electronic spectra data for **I** and **II** are shown in Tables 1 and 2. The influence of a single chloro substituent into the diazo component of benzothiazolylazo dyes results in bathochromic shifts in the order of 10 nm.[2,6] Further chloro substituents have a more limited effect. Thus, for dyes derived from *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline as coupling component, dyes from 4-chloro- and 6-chloro-2-aminobenzothiazole have λ_{max} at 504 and 506 nm, respectively,[7] (i.e. $\Delta\lambda$ 9 nm and 11 nm with respect to the dye from 2-aminobenzothiazole). Analogous dyes (**I.6**, **II.6**) derived from 5,6- and 6,7-dichloro-2-aminobenzothiazoles absorb at 510 nm, i.e. an additional shift of 4–6 nm. A similar effect is apparent in

dyes derived from *N*-β-cyanoethyl-*N*-β-hydroxyethyl-3-toluidine, which gives dyes of λ_{max} 517 nm with 5-, 6- and 7-chloro-2-aminobenzo-thiazoles;[6] the dyes from 5,6- and 6,7-dichloro-2-aminobenzothiazoles both have λ_{max} at 520 nm, viz. $\Delta\lambda$ 3 nm.[8]

The shifts in the monochloro benzothiazolylazo dyes are of a similar order to those for monochloro substitution into the diazo component of 4-aminoazobenzene dyes, e.g. for dyes derived from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline, 3'-chloro- and 4'-chloro-substitution (λ_{max} 409 nm and 408 nm, respectively) gives bathochromic shifts of 12 nm and 11 nm.[9] Introduction of a second chloro group, as in the dye from 3,4-dichloro-aniline, results in a shift of λ_{max} to 418 nm, viz. the second substituent effects a similar shift to that of the first. This further exemplifies the more limited additive colour shifts of substituents in benzothiaolylazo dyes.[7]

Absorption maxima of individual isomers **I** and **II**, and of their mixture,[2] are the same, orientation of the halogeno groups having no influence on the colour of the dyes. Dyeings on polyester of individual isomers showed no apparent visual differences, each isomer giving similar hue, build-up and light fastness to the isomer mixtures.

To confirm these visual assessments, representative isomer pairs were applied at approximately 1/1, 2/1 and 4/1 standard depths for each dye and also for a 50:50 mixture (this ratio being generally equivalent to the isomer ratio in the parent diazo component). Integ measurements[10] were made on each dyeing and the experimentally obtained Integ values for each mixture compared with the calculated (arithmetic) values. Integ 24 is taken as equivalent to a 1/1 standard depth, but in view of the small amounts of dye available, an arbitrary base of 0·2% owf was selected as giving such a depth; experimental values showed this to be a reasonable qualitative approximation for the dye pairs used. Whilst the arithmetic Integ values for the mixtures do not take into account deviations from a straight line Integ *versus* dye concentration relationship, the dyes did show a satisfactory straight-line response up to 2/1 depth, after which levelling-off occurred. Results can therefore be considered as valid relative to predicted values more correctly derived from calibration curves. Typical results were (Integ values given: isomer **I**, isomer **II**, 50:50 mix, calculated values for 50:50 mix, % deviation):

For dyes **I.2** and **II.2**: 0·2% owf, 21·27, 20·84, 20·85, 21·06 (−1%); 0·4% owf, 37·26, 37·18, 35·08, 37·22 (−5·7%); 0·8% owf, 48·56, 52·58, 55·40, 50·57 (+9·6%).

For dyes **I.5** and **II.5**: 0·2% owf, 26·46, 23·37, 24·49, 24·92 (−1·7%); 0·4% owf, 43·50, 41·35, 42·51, 42·43 (+0·2%); 0·8% owf, 53·18, 52·03, 53·50, 52·61 (+1·7%).

The results, although not directly relatable to absolute 1/1, 2/1 and 4/1 depths, show little evidence of any synergistic build-up in the mixtures and confirm the minimal visual differences apparent between the dyed samples.

There appears, therefore, to be little advantage, technically, in the application of individual isomers, particularly when considering the additional processes involved in their synthesis. The patent literature consistently cites the use of the isomer mixture, although one reference[11] appears to claim the 6,7-isomer–based dye, although this may be a generalisation in the pertinent abstracts.[12]

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REFERENCES

1. Annen, O., Egli, R., Hasler, R., Henzi, B., Jakob, H. & Matzinger, P., *Rev. Prog. Colouration*, **17** (1987) 72.
2. Peters, A. T. & Gbadamosi, M. N. A. *Dyes and Pigments*, **18** (1992) 115.
3. Martin Marietta Corp., British Patent 1,256,434 (1968).
4. Yorkshire Chemicals, British Patent 1,351,375 (1971).
5. Alaimo, R. J., *J. Heterocyclic Chem.*, **8** (1971) 309.
6. Peters, A. T., *J. Soc. Dyers Colourists*, **85** (1969) 507.
7. Peters, A. T. and Gbadamosi, M. N. A., *J. Chem. Tech. Biotechnol.*, **53** (1992) 301–8.
8. Peters, A. T., (unpublished).
9. Mehta, H. P. & Peters, A. T., *Dyes and Pigments*, **2** (1981) 259.
10. Derbyshire, A. N. & Marshall, W. J., *J. Soc. Dyers Colourists*, **96** (1980) 166.
11. Mitsui Toatsu, Japanese Patent 61,160,490 (1986).
12. Derwent 86-321388/49 and *Chem. Abs.* **106** 121389.