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Properties of some novel monoazo disperse dyes derived from ester-substituted tetrahydroquinoline and indoline coupling components

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Dedicated to Dr. A.T. Peters in recognition of his contribution to dye chemistry

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Abstract

Two series of dyes have been prepared by coupling conventional carbocyclic and heterocyclic diazo components to *N*-β-methoxycarbonylethyl-1,2,3,4-tetrahydroquinoline and *N*-β-methoxycarbonylethylindoline. The spectroscopic characteristics of the dyes were consistent with theoretical expectations as well as literature data for analogous structures derived from tetrahydroquinoline and indoline couplers. No clear-cut structure–light fastness relationships were identified within either series, although a general correlation between ratings for these and previously-reported sets of related dyes was observed. Since alkoxycarbonylalkyl functions have been exploited as a means of conferring alkali-clearability on commercial colorants, several members of the synthesised range of dyes were examined for signs of this behaviour; comparison with isomeric *N*-acetoxyethyl analogues indicated that the presence of a single *N*-β-methoxycarbonylethyl residue was not sufficient to bring about a significant effect. © 2000 Elsevier Science Ltd. All rights reserved.

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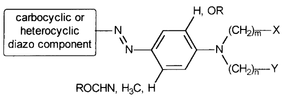
1. Introduction

It is well known that most disperse dyes for polyester, both in terms of the number of commercialised structures and volume of industrial production, are based on azo chromophores. A large proportion take the form of monoazo structures of type **1** derived from benzenoid coupling components. Many of these couplers are *N*,*N*-dialkylaniline derivatives, which typically bear short acyclic alkyl chains that have been selected to confer desirable performance on the dye, such as build-up or fastness, rather than to determine the general hue since they usually exert only a relatively small influence over the position of absorption bands [1,2].



m, n = usually 2 ; R = CH_3, C_2H_5 ;
X, Y = H, CN, OH, $OCOCH_3$, CO_2CH_3, etc.

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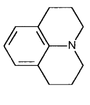

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In certain cases, however, it is possible to design dyes in which the terminal alkyl chains have a pronounced effect on colour, for example, monoazo structures containing cyclic bridging groups

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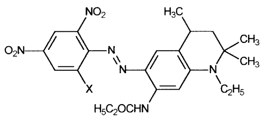
at the amino function [3], such as those based on coupling components like julolidine (**2**) and 1,2,3,4-tetrahydroquinoline (**3**; R = H). The geometry of the two bridging groups of julolidinylazo dyes favours effective overlap between the lone pair orbital of the amino function and the rest of the chromophoric π-system, resulting in increased absorption intensity and marked bathochromism [4]; unfortunately, these effects are accompanied by a propensity for low light fastness. Monoazo dyes derived from tetrahydroquinoline coupling components possess just one cyclic bridging alkyl group and offer a compromise in that they are more bathochromic than analogous dialkylaniline-based colorants [5], but do not suffer from the low levels of photostability associated with related dyes produced from julolidine [6]. Consequently, tetrahydroquinolinylazo derivatives, such as CI Disperse Blue 335 (**4**; X = Br) and CI Disperse Blue 338 (**4**; X = CN) [7], have been exploited commercially for the coloration of polyester.



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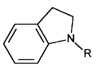

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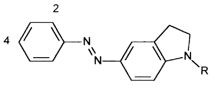
Bridging in coupling components based on indoline (**5**; R = H) has also been found to confer bathochromism on dyes of type **6** relative to non-bridged analogues, but to a lesser degree compared to their tetrahydroquinolinylazo counterparts **7**, which was ascribed to the five-membered ring in the indoline skeleton being more strained than six-membered bridging residues and so less efficient in enforcing planarity and conjugation [8].



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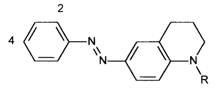

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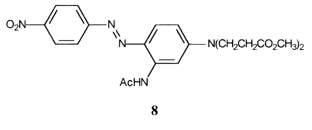
The effects of introducing various alkyl [9,10], cyanoalkyl [11,12] and haloalkyl [9] groups into the substituent R of tetrahydroquinolinylazo dyes **7** have been reported previously. For example, increasing inductive electron-withdrawal by R was found to lead, as expected, to hypsochromism and slightly higher photostability. Since the methoxycarbonyl function acts as an electron acceptor, similar behaviour would be expected from derivatives where R = $CH_2CH_2CO_2CH_3$, but, in addition, colorants of this type may possess the advantage of being alkali-clearable. Such a property obviates the need for reduction clearing, which is the conventional procedure that must be employed after dyeing polyester in order to remove any colorant that is loosely attached to the fibre surface and which could be readily removed on subsequent washing leading to poor wash fastness; the operation involves heating the dyed material in an alkaline solution of a reducing agent to destroy any dye which has not diffused into the polyester. However, the process increases effluent loading and damages natural fibres which precludes its use with blends such as polyester-cotton. For some time, colorants have been marketed which may be cleared in alkali, without the need for reducing agent, avoiding the aforementioned difficulties. One approach has been to utilise chromophores that are destroyed by alkali, as in the case of certain hetarylazo and benzodifuranone dyes. An alternative strategy relies on attaching carboxylic acid ester groups to a dye, typically methoxycarbonylethyl functions on the coupling component, which are hydrolysed in alkali to solubilising carboxylic acids residues [13,14]; dyes such as CI Disperse Red 278 (**8**) are therefore more readily removed by alkaline wash-offs, and exhibit lower staining in alkaline wash tests, than isomers possessing acetoxyethyl groups [2]



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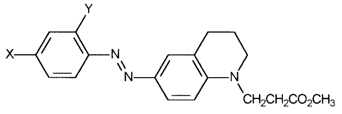
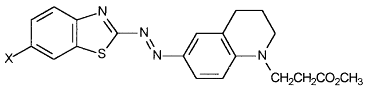
We now describe the synthesis of a range of methoxycarbonylethyl derivatives **9–13** and a comparison of their spectroscopic properties with data reported for other tetrahydroquinolinyl- and indolinyl-azo dye series. The light fastness of exhaustion-dyed polyester, as well as transfer-printed nylon and triacetate, has been investigated. In addition, the alkali-clearability of

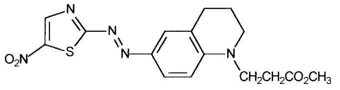


	X	Y
9a	OCH_3	H
9b	CH_3	H
9c	H	H
9d	Br	H
9e	CF_3	H

	X	Y
9f	$COCH_3$	H
9g	CN	H
9h	NO_2	H
9i	NO_2	CN



	X
10a	SO_2CH_3
10b	NO_2



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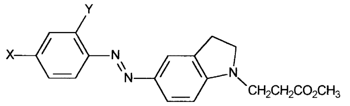
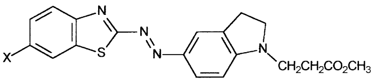
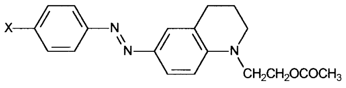


	X	Y
12a	OCH_3	H
12b	CH_3	H
12c	H	H
12d	Br	H
12e	CF_3	H

	X	Y
12f	$COCH_3$	H
12g	CN	H
12h	NO_2	H
12i	NO_2	CN



	X
13a	SO_2CH_3
13b	NO_2



	X
14a	CH_3
14b	NO_2

selected dyes was examined and their behaviour compared with that of the acetoxyethyl analogues **14**, which were synthesised expressly for this purpose.

2. Experimental

Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Microanalyses were carried out in the School of Chemistry, University of Leeds. Mass spectroscopic analysis was performed by the EPSRC National Mass Spectrometry Service Centre at the University of Wales, Swansea. UV/visible spectra were obtained with Unicam SP800 or JASCO V-530 spectrophotometers. Ethanolic hydrogen chloride was prepared by bubbling dry hydrogen chloride gas through ethanol and its molarity determined by titration against standard aqueous sodium hydroxide with phenolphthalein as indicator. For each of the dyes **9–13**, a series of solutions containing known equivalents of hydrogen chloride to dye were prepared from stock solutions of ethanolic hydrogen chloride and of dye in ethanol, so that the optimum concentration of acid required for maximisation of peak height of the monoprotonated forms of the dyes could be found. For dyes **9a–h** and **12a–h**, 100–200 equivalents were required while the other derivatives demanded 200–600 equivalents.

2.1. Synthesis of coupling components

Two approaches were used to prepare **3** ($R = CH_2CH_2CO_2CH_3$): esterification of the requisite carboxylic acid [15] or addition of methyl acrylate to 1,2,3,4-tetrahydroquinoline in acetic acid. The former methodology was also successfully applied to the synthesis of **5** (R = $CH_2CH_2CO_2CH_3$), although the latter route failed, furnishing only *N*-acetylindoline; however, addition of copper(I) chloride as a catalyst led to the formation of the desired product.

2.1.1. N-β-*Methoxycarbonylethyl-1,2,3,4-tetrahydro-quinoline (**3**; R = $CH_2CH_2CO_2CH_3$)*

2.1.1.1. From esterification of N-β-*carboxyethyl-1,2,3,4-tetrahydroquinoline.* *N*-β-carboxyethyl-1,2,3,4-tetrahydroquinoline [15] (20.0 g, 0.10 mol) was dissolved in anhydrous methanol (60 cm^3) and the solution saturated with dry hydrogen chloride. After refluxing for 5 h, the cooled mixture was neutralised (aqueous K_2CO_3) and extracted with dichloromethane. A quantitative yield of dark brown oil was obtained on removal of the solvent; vacuum-distillation furnished pure *N-β*-methoxycarbonylethyl-1,2,3,4-tetrahydroquinoline (17.1 g, 80%) as a pale yellow liquid, b.p. 145–148°C at 1.8 mmHg. FTIR 1731 cm^{-1} (ester C=O). Found: C, 71.5; H, 7.9; N, 6.3%; M^+ 219. $C_{13}H_{17}NO_2$ requires: C, 71.2; H, 7.8; N, 6.4%; M 219.

2.1.1.2. From 1,2,3,4-tetrahydroquinoline and methyl acrylate. Methyl acrylate (98%, 29.0 g, 0.33 mol) was added dropwise over 90 min to a stirred mixture of 1,2,3,4-tetrahydroquinoline (99%, 33.6 g, 0.25 mol) and acetic acid (42 g) at 90°C. After stirring at 100°C for 18 h, the dark orange liquid was cooled to room temperature and neutralised (aqueous K_2CO_3), before extracting four times with dichloromethane. The combined organic phases were water-washed (3 × 50 cm^3), dried over $MgSO_4$ and rotary evaporated free of solvent to give a brownish oil (54.2 g, 99%). Pure *N-β*-methoxycarbonylethyl-1,2,3,4-tetrahydroquinoline, of identical properties to that isolated in (a), was obtained by vacuum distillation as a very pale yellow oil (44.6 g, 81%), b.p. 142–144°C at 0.6 mBar.

2.1.2. N-β-*Methoxycarbonylethylindoline (**5**; R = $CH_2CH_2CO_2CH_3$)*

2.1.2.1. From esterification of N-β-*carboxyethylindoline.* The same procedure as in 2.1.1 a applied to *N-β*-carboxyethylindoline [16] (10.0 g, 0.05 mol) furnished a light brown oil (7.95g, 81%), which when vacuum-distilled gave pure *N-β*-methoxycarbonylethylindoline (7.80 g, 76%) as a pale yellow liquid, b.p. 145–146°C at 1.4 mmHg. Found: C, 70.3; H, 7.3; N, 6.9%. $C_{12}H_{15}NO_2$ requires: C, 70.2; H, 7.3; N, 6.8%.

2.1.2.2. From indoline and methyl acrylate. Indoline (20.0 g, 0.17 mol), methyl acrylate (25.9 g, 0.30 mol), acetic acid (6 cm^3) and freshly-prepared copper (I) chloride (1.6 g) were refluxed for 7 h under nitrogen after which more methyl acrylate (19.8 g, 0.23 mol) was added and then refluxed for a further 5 h. Following cooling and basification (conc. aqueous ammonia), the mixture was extracted with dichloromethane, dried and rotary evaporated to give crude product (32.8 g, 95%), which was vacuum-distilled, furnishing pure *N-β*-methoxycarbonylethylindoline (28.2 g, 81%) as a pale yellow liquid of b.p. 139–140°C at 1.0 mmHg. Found: C, 70.8; H, 7.6; N, 6.7%. $C_{12}H_{15}NO_2$ requires: C, 70.2; H, 7.3; N, 6.8%.

2.1.3. N-β-*Acetoxyethyl-1,2,3,4-tetrahydroquinoline (**3**; R = $CH_2CH_2OCOCH_3$)*

A mixture of 1,2,3,4-tetrahydroquinoline (40.3 g, 0.30 mol) and 2-chloroethanol (50.7 g, 0.63 mol) was stirred and heated for 24 h at 110°C, when more 2-chloroethanol (10.0 g, 0.12 mol) was added to the orange-brown mixture and the whole stirred at 120°C for a further 18 h. After cooling, addition of water (200 cm^3) and raising the pH to 9 (20% aqueous NaOH), the brown organic layer was separated and the aqueous layer extracted with toluene (4 × 100 cm^3). The combined organic material was washed with water (2 × 250 cm^3) and dried with $MgSO_4$. Upon removal of solvent under vacuum, crude *N-β*-hydroxyethyl-1,2,3,4-tetrahydroquinoline was obtained as a yellow-brown oil (48.7 g, 92%) which was then refluxed with acetic anhydride (250 cm^3) for 45 min. Excess anhydride was destroyed by stirring with water (500 cm^3) at 70°C and the mixture neutralised (aqueous NaOH) before separating the aqueous layer, extracting with toluene (4 × 100 cm^3) and combining the extracts with the organic layer. Following water-washing (2 × 300 cm^3), drying ($MgSO_4$) and rotary evaporation, the obtained yellow-brown oil (57.8 g, 88% crude yield based on tetrahydro-quinoline) was

Table 1
Purification methods, yields and melting points of the dyes **9**–**14**

Dye	Purification method[a]	Pure yield (%)	Melting point (°C)	Appearance
9a	αβ	45	73–74	Fine yellow needles
9b	αβ	43	72	Fine yellow needles
9c	α	19	70	Yellow solid
9d	αβ	28	76	Fine yellow needles
9e	αγ	36	60	Red solid
9f	αβ	55	110–111	Fine red needles
9g	ββ	65	103–104	Fine red needles
9h	ββ	81	111–112	Dark red leaflets
9i	αγ	34	134	Fine greenish needles
10a	αγ	14	120–122	Dark brown crystals
10b	αβ	11	155	Dark blue needles
11	αααβ	15	167–168	Fine greenish needles
12a	αβ	23	65–65.5	Fine yellow needles
12b	αβ	49	82	Fine yellow needles
12c	α	–	–	Viscous liquid
12d	αγ	40	80	Fine yellow needles
12e	αγ	15	105	Red solid
12f	αβ	55	103	Fine red needles
12g	ββ	70	108	Red solid
12h	δ	58	152	Dark brown needles
12i	αβ	28	149	Fine green needles
13a	αβ	13	166–167	Fine brownish crystals
13b	αβ	11	182	Blue-black crystals
14a	ϵβ	59	85	Bright orange solid
14b	ϵβ	71	121–122	Shiny green platelets

[a] Purification methods — α, ϵ = column chromatography on silica using dichloromethane and 9:1 toluene:ethyl acetate, respectively; β, γ, δ = recrystallisation from ethanol, methanol and acetone/petroleum ether (b.p. 40–60°C), respectively.

vacuum distilled to give *N*-β-acetoxy-ethyl-1,2,3,4-tetrahydroquinoline as a very pale yellow oil (41.4 g, 63%), b.p. 133–136°C at 0.5 mbar. FTIR 1736 cm^{-1} (ester C=O); *m*/*z* 219 (M$^+$).

2.2. Dye synthesis

Derivatives **9**–**14** were prepared by diazotising commercially available carbocyclic and heterocyclic amines on a 0.01–0.02 mol scale by conventional methods and coupling the diazonium ions to the corresponding derivative **3** or **5** dispersed in a vigorously stirred 1:2–3:3 mixture of acetic acid (99%), sodium acetate and water at 0°C. Purification was effected by column chromatography and/or recrystallisation as shown in Table 1 and purity confirmed by microanalysis ($\leqslant \pm 0.3\%$ C, H, N and, where appropriate, S, F and Br).

2.3. Dye application

2.3.1. Vapour-phase transfer printing

Transfer papers were prepared by soaking filter paper strips (10 cm by 4 cm) in dichloromethane solutions of dye (0.5% w/v) for 2 min, removing excess dye solution by means of glass rods, and drying at room temperature for 1 h. Prints were then made by placing dye-impregnated filter paper on top of the substrate (nylon 6,6 or cellulose triacetate, 12 cm × 5 cm) and heating the assembly to 200°C for 30 s in a Badische hot press.

2.3.2. High temperature exhaustion dyeing

Powdered dye samples (1.000 g), Ufoxane 2 (0.50 g), zirconium oxide beads (80.0 g) and distilled water (20 cm^3) were sealed in 60 cm^3 capacity jars, treated with ultrasound for 10 min and then roll-milled for 72 h. The beads were removed and the dispersions diluted to a total volume of 200 cm^3 with distilled water. Dyebaths were prepared from each of the dispersions (40 cm^3; 0.2 g dye), Ufoxane 2 (15 cm^3 of 1% solution) and distilled water (85 cm^3), which were then adjusted to pH 4.5 with acetic acid (2%) and made up to 150 cm^3. Polyester (10.0 g) was immersed and dyebath temperature was raised from room temperature to 130°C over 15min with a Zeltex Polycolor machine, maintained at 130°C for 75 min and then lowered to 85°C, before the dyed polyester was removed and thoroughly rinsed in running cold water. The air-dried fabric was either reduction cleared (aqueous solution of 1 g dm^{-3} Na$_2$S$_2$O$_4$ and 1 g dm^{-3} NaOH; 80°C, 10 min), alkali cleared (aqueous solution of 20 g dm^{-3} Na$_2$CO$_3$; 80°C, 15 min), or received no aftertreatment. A proportion of the reduction- and alkali-cleared samples was stentered at 180°C for 30 s.

2.4. Fastness testing

Light fastness of the dyed or printed samples was assessed using ISO 105 B02 [17]. Wash fastness of the dyed polyester was evaluated by means

Table 2
Spectroscopic properties of dyes **9**–**14** in neutral and acidic solution

Dye	Ethanol		Ethanolic HCl		
	λ_{max} (nm)	ϵ_{max} (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	ϵ_{max} (dm^3 mol^{-1} cm^{-1})	$\Delta\lambda_{max}$[a] (nm)
9a	413	25 700	570	49 300	157
9b	414	31 300	550	58 900	136
9c	415	25 400	550	63 100	135
9d	428	31 300	528	67 300	100
9e	438	39 800	512	62 600	74
9f	460	34 600	530	60 000	70
9g	464	39 900	518	66 500	54
9h	492	41 800	520	69 300	28
9i	542	47 000	522	27 000	-20
10a	544	52 800	590	51 800	46
10b	558	50 500	570	46 300	12
11	590	55 600	592	41 400	2
12a	408	25 700	560	48 000	152
12b	410	24 800	540	48 900	130
12c	412	23 200	538	45 900	126
12d	425	27 100	528	65 000	93
12e	437	24 400	506	48 100	69
12f	456	28 700	523	56 200	67
12g	464	20 500	512	36 000	48
12h	490	26 500	514	55 600	24
12i	546	32 900	499	26 600	-47
13a	550	56 000	568	52 400	18
13b	561	67 600	564	65 900	3
14a	416	28 500	–	–	–
14b	491	33 200	–	–	–

[a] $\Delta\lambda_{max} = \lambda_{max}$ (acid)$-\lambda_{max}$ (neutral).

of ISO 105 C06:B2S, employing ECE reference detergent and steel balls, but without souring [17].

3. Results and discussion

3.1. Spectroscopic properties of the dyes

As anticipated, increasing the electron-withdrawing strength of the substituents on the diazo component of the carbocyclic dyes **9** and **12** resulted in bathochromism and increases in ϵ_{max} (Table 2).

In accord with a previous comparison between *N*-methylindolinylazo dyes and analogous *N*-methyl-1,2,3,4-tetrahydroquinoline-derived colorants [8], dyes **12** were typically found to be hypsochromic and hypochromic relative to the corresponding derivatives **9** (Table 2), presumably as a result of more ring strain and reduced conjugation in the former series.

The effects of the *N*-ester functions on absorption maxima and halochromism are in line with theory. As can be seen in Table 3, increasing the electron withdrawing strength of the *N*-alkyl substituent causes hypsochromism, the absorption maxima of the methoxycarbonylethyl- and acetoxyethyl-based tetrahydroquinoline dyes falling between those of analogues derived from *N*-β-cyanoethyl and *N*-alkyl groups as expected. According to the data for the series **6**/**7**

Table 3
Absorption maxima (in nm) and extinction coefficients (in 10^{-4} dm^3 mol^{-1} cm^{-1}) of some dyes **6** and **7** in ethanol

Dye	4-H	4-Br	4-NO$_2$	Ref.
7 ($R = CH_3$)	419 (3.02)	432 (3.22)	498 (3.16)	[11]
7 ($R = CH_2CF_3$)	398 (2.26)	409 (2.38)	450 (2.59)	[9]
7 ($R = CH_2CN$)	390 (2.22)	402 (2.36)	440 (2.81)	[12]
7 ($R = CH_2CH_3$)	424 (2.36)	440 (3.38)	503 (3.56)	[9]
7 ($R = CH_2CH_2CN$)	410 (2.40)	420 (2.66)	476 (2.56)	[11]
7 ($R = CH_2CH_2CO_2CH_3$)	415 (2.54)	428 (3.13)	492 (4.18)	[b]
7 ($R = CH_2CH_2OCOCH_3$)	416 (2.85)[a]	–	491 (3.32)	[c]
7 ($R = CH_2CH_2CH_3$)	425 (2.71)	446 (2.13)	502 (3.33)	[10]
6 ($R = CH_3$)	412 (2.23)	428 (2.76)	495 (2.76)	[8]
6 ($R = CH_2CH_2CO_2CH_3$)	412 (2.32)	425 (2.71)	490 (2.65)	[d]

[a] 4-CH_3 derivative.

[b] Dyes **9c**, **9d**, **9h.**

[c] Dyes **14a**, **14b**.

[d] Dyes **12c**, **12d**, **12h.**

Table 4
Halochromic shifts (in nm) of some tetrahydroquinolinyl- and indolinyl-azo dyes

Dye	4-H	4-Br	4-CF_3	4-$COCH_3$	4-CN	4-NO_2	Ref.
7 (R = CH_3)	103	91	60	48	33	12	[11]
7 (R = CH_2CF_3)	147	142	123	125	115	96	[9]
7 (R = CH_2CN)	149	147	128	131	118	103	[12]
7 (R = CH_2CH_3)	99	87	47	50	36	14	[9]
7 (R = CH_2CH_2CN)	120	110	81	74	64	40	[11]
7 (R = $CH_2CH_2CO_2CH_3$)	135	100	74	70	54	28	
6 (R = CH_3)	104	92	58	55	37	12	[8]
6 (R = $CH_2CH_2CO_2CH_3$)	126	93	69	67	48	24	

(R = $CH_2CH_2CO_2CH_3$) and **6**/**7** (R = CH_3), the terminal amino nitrogen atom experiences slightly weaker electron donation from a methoxycarbonylethyl function compared to a methyl group as indicated by the hypsochromism of the former type of dye.

Whilst a reduction in the donor strength of the terminal nitrogen atom leads to hypsochromism in the neutral azo species, bathochromic shifts in azonium species, arising from protonation at the azo group in ethanolic HCl, also result. Consequently, the absorption maxima of the neutral and azonium forms diverge as the acceptor strengths of *N*-substituents are increased, which is reflected in the more marked positive halochromism exhibited on moving from methyl to trifluoroethyl and to cyanomethyl derivatives (Table 4). The observation that the halochromic shifts of dyes **7** (R = $CH_2CH_2CO_2CH_3$) lie between those of **7** (R = CH_2CH_3) and **7** (R = CH_2CH_2CN) conforms to this pattern. The greater electron withdrawal of *N*-methoxycarbonylethyl functions compared to *N*-methyl groups ensures that, as in the tetrahydroquinoline series, the indolinyl dyes **6** (R = $CH_2CH_2CO_2CH_3$) give more marked positive halochromic shifts than their analogues **6** (R = CH_3).

In parallel with previously reported data concerning the halochromism of *N*-methylindoline and *N*-methyl-1,2,3,4-tetrahydroquinoline dyes [8] (Table 4), the azonium forms of the indolinyl dyes were found to be bathochromic relative to those of the analogous tetrahydroquinolinyl derivatives (Table 2). As expected, in both the tetrahydro-quinolinyl- and indolinyl-based series **9** and **12**, positive halochromic shifts ($\Delta\lambda_{max}$) became smaller and then negative as the electron-accepting strength of substituents on the diazo ring was raised (see Table 2). Like many other azobenzene-derived chromophores, good linear correlations between halochromic shifts in terms of frequency difference and the appropriate Hammett σ-constants were observed for series **9** and **12** (Fig. 1).

The similarity in the gradients of the best-fit lines for the azotetrahydroquinoline and azoindoline series indicates that the difference in bridging at the terminal amino nitrogen atom has little influence over the sensitivity of the halochromism towards substituent effects. This finding is in contrast to an analogous comparison between azojulolidine and azolilolidine series [18]: a bigger difference in slope ($3950\ \sigma - 3380\ cm^{-1}$ and $5500\ \sigma - 4320\ cm^{-1}$, respectively) was revealed, implying that the change in bridging has a greater impact on halochromism.

The small positive halochromic shifts of the hetarylazo dyes **10**, **11** and **13** (see Table 2) can be attributed to the creation of diazahemicyanine species by protonation at the nitrogen atom of the (benzo)thiazole ring.

3.2. Fastness properties of the dyes applied to hydrophobic fabrics

Light fastness ratings of dyed polyester, as well as those of transfer-printed nylon and triacetate samples, are shown in Table 5. Photostability was

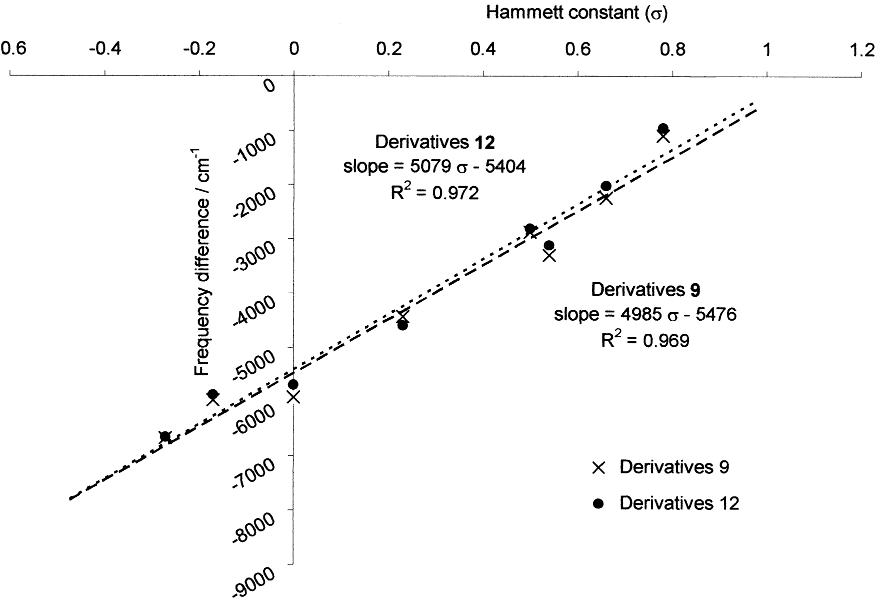


Fig. 1. Relationship between Hammett constants σ and halochromic shifts exhibited by 4-substituted derivatives **9** and **12**.

found to be only poor to moderate for both the tetrahydroquinolinyl- and indolinyl-azo dye series on each substrate, fastness tending to be poorest on triacetate. Ratings of 2–3 to 4 were noted for dyes **9–11** on polyester and nylon, while derivatives **12** and **13** yielded corresponding figures of 3 to 4 with one exception.

Table 5
Light fastness of some dyes **9–13** on polyester, nylon and triacetate

Dye	Polyester	Nylon	Triacetate
9a	2–3	4	3
9b	4	4	3–4
9c	3–4	3	2–3
9d	4	4	2–3
9e	4	3–4	3
9f	3	3–4	2–3
9g	3–4	3–4	2–3
9h	2–3	3	1–2
9i	3–4	2–3	2
10b	4	–	–
11	4	–	–
12a	3	3–4	3
12b	3	4	3
12d	3–4	4	2–3
12e	4	4	3
12f	3–4	3–4	3
12g	3	3–4	3
12h	3	3	1–2
12i	3	1–2	2
13b	3	–	–

No clear correlation between dye structure and photostability on polyester was evident within either the methoxycarbonylethyl-tetrahydroquinoline or -indoline series. This has also generally been found to be the case with *N*-alkyl and *N*-cyano-ethyl derivatives, whereas definite trends were observed within *N*-trifluoroethyl and *N*-cyanomethyl series (Table 6).

It has been known for some time that increasing the electron withdrawing strength of *N*-alkyl substituents in 4-aminoazobenzenes can lead to improved light fastness on polyester [1,2]. Despite complicating factors such as differing depths of shade and application methods between individual series, the data presented in Table 6 shows that this course of action also improves photostability in the case of dyes of type **6** and **7**. Amongst the tetrahydroquinoline-derived series, the strongest acceptor (*N*-trifluoroethyl) generally yields the highest figures, while the best donors (*N*-ethyl, -propyl and -butyl) produce the most fugitive colorants (Table 6). Placing a methoxycarbonyl

Table 6
Light fastness ratings of some *N*-substituted tetrahydroquinolinyl- and indolinyl-azo derivatives on polyester (P) and nylon (N)

Dye	Substitution										Ref.
	4-Br		4-COCH$_3$		4-CN		4-NO$_2$		2-CN-4-NO$_2$		
	P	N	P	N	P	N	P	N	P	N	
7 (R = CH$_3$)	4–5	4	4–5	4	4–5	4	4–5	4–5	3–4	3–4	[11]
7 (R = C$_2$H$_5$-C$_4$H$_9$)[a]	3	2	3	2–3	3	3	3	3	3	3	[9,10]
7 (R = CH$_2$CF$_3$)	4–5	2	5	4	6	6	6–7	6	7	6–7	[9]
7 (R = CH$_2$CN)	4	3	3	2–3	3–4	2–3	5	2	5–6	1	[12]
7 (R = CH$_2$CH$_2$CN)	4–5	4	4–5	4	4–5	4	4	4	4	3	[11]
7 (R = CH$_2$CH$_2$CO$_2$CH$_3$)	4	4	3	3–4	3–4	3–4	2–3	3	3–4	2–3	
6 (R = CH$_3$)	2–3	3–4	2–3	2–3	3	1–2	3	1	–	–	[8]
6 (R = CH$_2$CH$_2$CO$_2$CH$_3$)	3–4	4	3–4	3–4	3	3–4	3	3	3	1–2	

[a] Values on nylon for ethyl derivatives only.

Table 7
Wash fastness ratings (ISO 105 C06:B2S; D = staining of diacetate; N = staining of nylon) of some uncleared (NC), reduction-cleared (RC) and alkali-cleared (AC) polyester dyeings (2% o.m.f.) with and without heat setting (180°C, 30 s) after clearing

Dye	No heat setting						Heat setting			
	NC		RC		AC		RC		AC	
	D	N	D	N	D	N	D	N	D	N
9b	2	2–3	4	4	3	3–4	3	3–4	3	3–4
9h	2	2	5	5	4	4	3	3–4	3	3–4
9i	2	2–3	5	5	4	4–5	3	3–4	3	3–4
11	2	2–3	5	5	5	5	3	3–4	3	3–4
14a	2	2–3	4–5	4–5	4	4	4	4	4	4
14b	2	2	5	5	4	4	3–4	3–4	3–4	3–4

function onto **7** (R = CH$_2$CH$_3$) to give **7** (R = CH$_2$CH$_2$CO$_2$CH$_3$) tends to produce an increase in photostability, but not as effectively as the more strongly withdrawing cyano group as indicated by the higher ratings for dyes **7** (R = CH$_2$CH$_2$CN). Curiously, while members of the indoline series **6** (R = CH$_3$) consistently have lower fastness compared to their counterparts in **6** (R = CH$_2$CH$_2$CO$_2$CH$_3$) in line with the above findings, the analogous comparison between tetrahydroquinolinylazo dyes reveals the methyl derivatives to be more photostable. However, the higher alkyl derivatives (**7**; R = C$_2$H$_5$–C$_4$H$_9$) are more fugitive than their analogues in series **7** (R = CH$_2$CH$_2$CO$_2$CH$_3$).

The wash fastness of polyester dyeings of selected dyes from series **7** (R = CH$_2$CH$_2$CO$_2$CH$_3$) was examined in attempt to assess whether the presence of the methoxycarbonyl function conferred the property of alkali-clearability. Dyeings from the acetoxy dyes **14a** and **14b** were also investigated for comparative purposes because, although being isomeric with **9b** and **9h**, the first two derivatives were not expected to be alkali-clearable since their ester functions cannot give carboxy-substituted dyes upon hydrolysis. As both isomer pairs gave dyeings of very similar depth at 2% o.m.f., it was considered that direct comparisons between wash fastness ratings would be valid. The diacetate and nylon components of multifibre adjacent fabric are particularly prone to staining during washing of disperse dyed polyester: figures for the staining of these fibres are shown in Table 7 for dyeings which have been conventionally reduction cleared or received no treatment at all. In addition, ratings were obtained for another set of dyeings which were treated only with aqueous sodium carbonate to establish the effectiveness of attempting to clear using just alkali. Finally, a proportion of the reduction- and alkali-cleared dyeings were heat set prior to washing to reveal the extent to which thermomigration undermines the effects of either type of clearing.

Predictably, reduction clearing produced a marked improvement in levels of staining in the cases of the methoxycarbonyl derivatives **9** and **11**: while non-cleared samples gave heavy staining, that of the reduction-cleared dyeings was good to excellent. Alkali clearing also raised fastness levels but to a lesser extent, except in the case of **11**, for which either clearing operation eliminated any staining. Unexpectedly, staining by alkali-cleared dyeings from **14a** and **14b** was similar or even better than that of **9b** and **9h**, respectively, which suggests that ester hydrolysis is not the primary mechanism behind the increase in fastness over non-cleared material associated with alkali-clearing. The excellent alkali-clearability of **11** may be a result of this colorant, like other nitrothiazole dyes, being susceptible to alkali-induced decolorisation through destruction of the chromophore.

In all cases, heat setting lowered fastness owing to thermomigration as anticipated, although, surprisingly, while ratings did not fall as low as those without clearing, the same values were obtained irrespective of whether reduction clearing or alkali clearing had been employed prior to the heat treatment.

4. Conclusions

Monoazo dyes can be prepared from *N*-β-methoxycarbonylethyl-1,2,3,4-tetrahydroquinoline and *N*-β-methoxycarbonylethylindoline using conventional methods. The spectroscopic properties of these colorants in neutral and acidic solution are consistent with theoretical expectations as well as published data for analogous azotetrahydroquinoline and azoindoline derivatives. The light fastness of the dyes in synthetic fibre substrates ranged from very poor to moderate; for a particular derivative, photostability on polyester and nylon was superior to that on triacetate. However, no clear trends between structure and fastness were evident, although general correlations could be found between the ratings of the ester substituted series as a whole and those reported for ranges of other tetrahydroquinoline- and indoline-based dyes.

Alkali clearing of the dyeings produced from the methoxycarbonylethyl derivatives did generally improve wash fastness relative to non-cleared samples, although the treatment was less effective than reduction clearing. Comparison of the performance of *N*-methoxycarbonyl derivatives with isomeric acetoxy dyes which would not be expected to be alkali-clearable suggested that, while there may be several complicating factors, hydrolysis of ester functions does not appear to play an important role in the improvement in fastness. One possible explanation is that the presence of just a single ester function on each dye molecule which can be hydrolysed to a *N*-carboxy group is insufficient for solubilisation: it is noteworthy that commercially successful alkali-clearable dyes that rely on the solubilisation approach generally bear two such residues, for example, CI Disperse Brown 19 and CI Disperse Red 278, which are based on *N*,*N*-di(β-methoxycarbonylethyl)-substituted couplers. In the one instance of alkali clearing being equally efficient as reduction clearing in raising fastness, which was observed with a 5-nitrothiazole derivative, it is likely that the cause stems from destruction of the chromophore rather than solubilisation.

Thermomigration of dye brought about by heat setting of the cleared samples increased staining but not to the levels of uncleared material; curiously, fastness ratings were the same irrespective of the type of clearing treatment employed which indicates that, under these circumstances, alkali clearing can used instead of reduction clearing just as effectively.

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