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Hetarylazo disperse dyes derived from substituted *N*,*N*-bis-β-hydroxy- and *N*,*N*-bis-β-acetoxy-ethylaniline

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Abstract

The heterocyclic amines 2-amino-6-methoxy- and 2-amino-6-nitro-benzothiazole, 3-amino-5-nitro[2,1]benzisothiazole and 2-amino-3,5-dinitro-thiophene were diazotised and coupled to substituted *N*,*N*-di-β-hydroxyethylaniline and *N*,*N*-di-β-acetoxyethylaniline to give dyes which coloured cellulose acetate in red to greenish-blue hues. The colour of the dyes is discussed with respect to the nature of the heterocyclic ring and to the substituents in the diazo and coupling component and compared to the corresponding dye using aniline as diazo component. Dyeing and fastness properties of the dyes are also reported. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Disperse dyes; Benzothiazolylazo; Benzisothiazolylazo, Thienylazo dyes; Colour–structure relationships; Dyeing and fastness properties

1. Introduction

In previous papers [1–2] we described the synthesis and dyeing properties of a series of dyes obtained by coupling *N*-β-hydroxyethyl-1-naphthylamine with diazotized substituted anilines or heterocyclic amines and discussed the effect of substituents in the diazo component on the colour shifts in these dyes. It is well established that the use of heterocyclic amines, in particular those with sulphur as the π-excessive heteroatom, as diazo components has a marked bathochromic effect compared to analogous dyes derived from benzenoid compounds [3–5].

The use of aniline based coupling components results, in contrast, in lower wavelength absorbing dyes compared to those derived from naphthylamine couplers [6,7].

We report here the synthesis and characterisation of monoazo disperse dyes derived from heterocyclic amines as diazo components and aniline-based coupling components (Scheme 1).

The dyes were applied to cellulose secondary acetate and fastness and dyeing properties were estimated and discussed.

2. Experimental

2.1. Materials and apparatus

The following amines were commercially available and were used without further purification: 2-amino-6-methoxy-benzothiazole (**1**), 2-amino-6-nitro-benzothiazole (**2**) and 3-amino-5-nitro[2,1]-benzisothiazole (**3**), 2-amino-3,5-dinitro-thiophene

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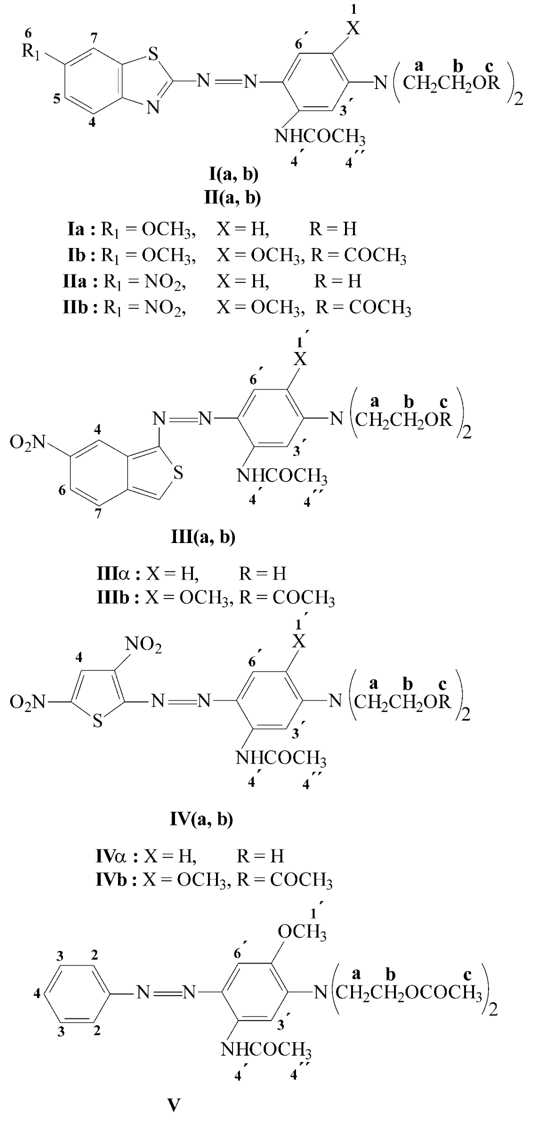

I(a, b)
II(a, b)

Ia : $R_1 = OCH_3$, $X = H$, $R = H$
Ib : $R_1 = OCH_3$, $X = OCH_3$, $R = COCH_3$
IIa : $R_1 = NO_2$, $X = H$, $R = H$
IIb : $R_1 = NO_2$, $X = OCH_3$, $R = COCH_3$

III(a, b)

IIIα : $X = H$, $R = H$
IIIb : $X = OCH_3$, $R = COCH_3$

IV(a, b)

IVα : $X = H$, $R = H$
IVb : $X = OCH_3$, $R = COCH_3$

V

Scheme 1. Structure of dyes **I**–**V**.

(**4**), 3-acetylamino-*N*,*N*-di-β-hydroxyethylaniline (Aldrich and Zhejiang respectively), aniline (**5**) (Fluka).

2-Methoxy-5-acetylamino-*N*,*N*-di-β-acetoxyethylaniline was prepared by acetylation of 2-methoxy-5-acetylamino-*N*,*N*-di-β-hydroxyethylaniline with acetic acid–acetic anhydride.

Melting points were obtained with a Koffler hot stage apparatus and are given uncorrected.

UV–visible spectra were recorded with a Shimadzu UV 2101 spectrometer using methanol as solvent.

^{1}H-NMR data were obtained with a Bruker 300 AM spectrometer using $CDCl_3/d_6$-DMSO as solvent and TMS as internal standard.

Mass spectra were measured with a VG-TS 250 spectrometer.

Elemental analyses were obtained using a Perkin Elmer 2400-II Element Analyzer.

2.2. Synthesis and analytical data of azo dyes **I–V**

These were prepared by diazotisation of amines **1–5** followed by coupling with 3-acetylamino-*N*,*N*-di-β-hydroxyethylaniline and 2-methoxy-5-acetylamino-*N*,*N*-di-β-acetoxyethylaniline. Diazotisation and coupling were carried out by procedures previously reported [2].

Ia: yield of crude product 82%; purified by recrystallisation (ethanol); m.p. 122–125 °C; λ_{max} (nm, CH_3OH): 529.0; ε_{max} ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 57471; ^{1}H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.31 *s* (3H, H-4″), 3.27 *bs* (2H, H-c), 3.79 *t* (4H, H-b), 3.90 *s* (3H, H-6), 4.02 *t* (4H, H-a), 6.54 *d* (1H, H-1′), 7.06 *dd* (1H, H-5), 7.27 *d* (1H, H-7), 7.84 *d* (1H, H-6′), 7.92 *t* (1H, H-4), 8.11 *s* (1H, H-3′), 9.26 *bs* (1H, H-4′); MS (*m*/*e*, %): 355(4), 224(10), 180(10), 165(19), 105(15), 91(100); C (%, calcd, found): 55.54, 55.93; H: 5.49, 5.40; N: 16.07, 16.31.

Ib: yield of crude product 73%; purified by recrystallisation (ethanol); m.p. 148–150 °C; λ_{max} (nm, CH_3OH): 544.5; ε_{max} ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 38910; ^{1}H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.06 *s* (6H, H-c), 2.31 *s* (3H, H-4″), 3.78 *t* (4H, H-a), 3.85 *s* (3H, H-1′), 3.91 *s* (3H, H-6), 4.32 *t* (4H, H-b), 7.09 *dd* (1H, H-5), 7.28 *d* (1H, H-7), 7.43 *s* (1H, H-6′), 7.96 *d* (1H, H-4), 8.26 *s* (1H, H-3′), 9.34 *bs* (1H, H-4′); MS (*m*/*e*, %): 542[$(M-1)^+$(7)], 470(4), 180(57), 165(65), 87(100); C (%, calcd, found): 54.88, 55.24; H: 5.36, 5.38; N: 12.49, 12.88.

IIa: yield of crude product 98%; purified by recrystallisation (ethanol); m.p. 228–230 °C; λ_{max} (nm, CH_3OH): 554.5; ε_{max} ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 60241; ^{1}H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.34 *s* (3H, H-4″), 3.81 *t* (4H, H-b), 3.87 *t* (4H, H-a), 4.95 *bs* (2H, H-c), 6.78 *d* (1H, H-1′), 8.00 *d* (1H, H-6′), 8.02 *d* (1H, H-4), 8.22 *s* (1H, H-3″), 8.29 *dd* (1H, H-5), 8.74 *d* (1H, H-7), 9.18 *bs* (1H, H-4′); MS (*m*/*e*, %): 296(38), 263(29), 91(56), 43(100); C (%, calcd, found): 50.97, 51.34; H: 4.17, 4.54; N: 18.62, 18.91.

IIb: yield of crude product 99%; purified by recrystallisation (ethanol); m.p. 170–171 °C; $\lambda_{\max}$ (nm, CH_3OH): 576.5; $\varepsilon_{\max}$ ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 38219; ^1H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.15 *s* (6H, H-c), 2.30 *s* (3H, H-4″), 3.78 *t* (4H, H-a), 3.85 *s* (3H, H-1′), 3.89 *t* (4H, H-b), 7.13 *s* (1H, H-6″), 7.97 *d* (1H, H-4), 8.25 *dd* (1H, H-5), 8.66 *s* (1H, H-3′), 8.74 *d* (1H, H-7), 9.15 *bs* (1H, H-4′); MS (*m*/*e*, %): 558(23, M^+), 485(20), 367(61), 195(78), 87(100); C (%, calcd, found): 51.27, 51.61; H: 4.39, 4.69; N: 15.22, 15.05.

IIIa: yield of crude product 90%; purified by recrystallisation (ethanol); m.p. 160–163 °C; $\lambda_{\max}$ (nm, CH_3OH): 603.5; $\varepsilon_{\max}$ ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 52083; ^1H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.08 *s* (3H, H-4″), 3.75 *t* (4H, H-b), 4.36 *t* (4H, H-a), 4.78 *bs* (2H, H-c), 6.48 *d* (3H, H-1′), 7.59 *d* (1H, H-7), 7.70 *d* (1H, H-6′), 8.00 *s* (1H, H-3′), 8.09 *dd* (1H, H-6), 8.85 *d* (1H, H-4), 9.40 *bs* (1H, H-4′); MS (*m*/*e*, %): 219(6), 195(6), 91(38), 70(100); C (%, calcd, found): 51.26, 51.34; H: 4.46, 4.54; N: 18.26, 18.91.

IIIb: yield of crude product 71%; purified by recrystallisation (ethanol); m.p. 192–194 °C; $\lambda_{\max}$ (nm, CH_3OH): 623.5; $\varepsilon_{\max}$ ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 22831; ^1H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.08 *s* (6H, H-c), 2.32 *s* (3H, H-4″), 3.00 *t* (4H, H-a), 3.94 *s* (3H, H-1′), 4.36 *t* (4H, H-b), 7.32 *s* (1H, H-6″), 7.68 *d* (1H, H-7), 8.11 *s* (1H, H-3′), 8.16 *d* (1H, H-6), 9.01 *s* (1H, H-4), 9.44 *bs* (1H, H-4′); MS (*m*/*e*, %): 558(29, M^+), 485(14), 367(6), 195(11), 87(100); C (%, calcd, found): 51.35, 51.61; H: 4.50, 4.69; N: 15.00, 15.05.

IVa: yield of crude product 79%; purified by recrystallisation (ethanol); m.p. 105–107 °C; $\lambda_{\max}$ (nm, CH_3OH): 617; $\varepsilon_{\max}$ ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 39217; ^1H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.32 *s* (3H, H-4″), 3.78 *t* (4H, H-b), 4.11 *t* (4H, H-a), 4.87 *bs* (2H, H-c), 6.63 *d* (1H, H-1′), 7.85 *d* (1H, H-6′), 8.11 *s* (1H, H-3′), 12.71 *s* (1H, H-4); MS (*m*/*e*, %): 385(9), 224(12), 154(16), 109(9), 96(14), 58(10), 45(26), 43(100); C (%, calcd, found): 43.70, 43.83; H: 3.88, 4.14; N: 18.77, 19.17.

IVb: yield of crude product 72%; purified by recrystallisation (ethanol); m.p. 175–176 °C; $\lambda_{\max}$ (nm, CH_3OH): 669; $\varepsilon_{\max}$ ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 32895; ^1H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.10 *s* (6H, H-c), 2.31 *s* (3H, H-4″), 3.78 *t* (4H, H-a), 3.90 *s* (3H, H-1′), 4.19 *t* (4H, H-b), 7.29 *s* (1H, H-6′), 8.34 *s* (1H, H-3′), 9.31 *bs* (1H, H-4′), 12.72 *s* (1H, H-4); MS (*m*/*e*, %): 256(30), 174(8), 128(27), 96(20), 64(100); C (%, calcd, found): 45.40, 45.65; H: 3.98, 4.38; N: 14.86, 15.21.

V: purified by column chromatography (silica gel, toluene–ethylacetate); m.p. 175–176 °C; $\lambda_{\max}$ (nm, CH_3OH): 428.3; $\varepsilon_{\max}$ ($l\,mol^{-1}\,cm^{-1}$, CH_3OH): 21540 ^1H-NMR (δ, $CDCl_3/d_6$-DMSO): 2.25 *s* (3H, H-4″), 2.40 *s* (6H, H-c), 3.67 *t* (4H, H a), 3.88 *s* (3H, H-1′), 4.28 *t* (4H, H-b), 7.37 *s* (1H, H-3′), 7.43 *d* (1H, H-4), 7.50 *t* (2H, H-3), 7.79 *d* (2H, H-2), 8.33 *s* (1H, H-6′), 10.02 *s* (1H, H-4′).

*2.3. Aqueous dispersions of dyes **I–IV***

These were obtained using anionic and non-ionic dispersing agents as previously described [2]. These dispersions were applied to cellulose secondary acetate, and dye adsorbed on the fibre, together with fastness and dyeing properties (wash-light and rate of dyeing/temperature range) of the dyeings were assessed by established procedures [2,8–11].

3. Results

3.1. Colour of dyes

$\lambda_{\max}$, $\varepsilon_{\max}$ of compounds **I–V** are given in Table 1.

Dyes (**I–IV**)**b** derived from 2-methoxy-5-acetylamino-*N*,*N*-di-β-acetoxyethylaniline have absorption maxima at longer wavelengths than those of dyes (**I–IV**)**a** derived from 3-acetylamino-*N*,*N*-di-β-hydroxyethylaniline, i.e. acetylation of the *N*,*N*-β-hydroxyethyl groups and introduction of an additional donor methoxy substituent in the coupling component of dyes (**I–IV**)**a** results in bathochromic shifts ranging from 15 nm (**Ia** and **Ib**) to 52 nm (**IVa** and **IVb**). Due to the distance between the acetyl groups and the azo group, their

Table 1
Electronic spectra data of compounds **I**–**V**

Compound	λ_{max} (CH_3OH, nm)	log ε_{max} (CH_3OH)	Colour
Ia	529.0	4.76	Ruby-red
Ib	544.5	4.59	Violet
IIa	554.5	4.78	Deep magenta
IIb	576.5	4.58	Blue
IIIa	603.5	4.72	Deep blue
IIIb	623.5	4.36	Dark blue
IVa	617.0	4.59	Deep blue
IVb	669.0	4.52	Greenish blue
V	428.0	4.33	Deep yellow

positive inductive effect does not affect the bathochromic shift of the molecule. The shifts observed for compounds (**I–IV**)**b** can, therefore, be attributed to the methoxy substituent. Since this substituent is not conjugated with the azo residue, it can be concluded that only +I factors are operative.

Introduction of electron acceptor substituents into the diazo component results in a bathochromic shift due to more extensive electron delocalisation. Thus, dyes **IIa** and **IIb** containing the strong electron acceptor nitro substituent have λ_{max} at longer wavelengths than the corresponding dyes **Ia** and **IIa** with a methoxy substituent in the benzothiazole ring ($\Delta\lambda = 25$ and 32 nm respectively). The benz[2,1]isothiazole dyes **III**(**a** and **b**) have larger bathochromic shifts than the benzothiazole analogues **I**(**a** and **b**) and **II**(**a** and **b**). This could be related to the unusual structure of the dyes, which have quinonoid configuration in the ground state and an aromatic configuration in the charge transfer state.

Dyes **IV**(**a** and **b**) having a thiophene diazo component exhibit the highest bathochromic shifts, **IVa** being comparable to **IIIb**, which has a methoxy substituted coupling component. These bathochromic shifts afforded by five-membered ring sulphur heterocycles have been mentioned by several authors [4,5,12], indicating that these systems are useful in providing blue to greenish-blue dyes. The origin of the large shifts peculiar to these heterocyclic systems could not be explained only on terms of greater stabilisation of the excited state, but probably is correlated with the increased diene character of the heterocycle [13].

While the presence of the methoxy substituent in the coupling component results in bathochromic shifts for the dyes (**I–III**)**b** compared to the corresponding dyes (**I–III**)**a** which are of similar order for the three pairs of dyes ($\Delta\lambda_{Ia-Ib} = 15$ nm, $\Delta\lambda_{IIa-IIb} = 22$ nm, $\Delta\lambda_{IIIa-IIIb} = 20$ nm), dyes **IVa** and **IVb** show a significantly higher $\Delta\lambda = 52$ nm, implying that the effect of the methoxy substituent in the coupler is stronger in dye **IVa** than in the benzothiazole and-isothiazole dyes (**I–III**)**a**. This would indicate some colour insulting effect of the annelated benzene ring in dyes **I–III**. Similar results have been reported for a series of thiazole and benzothiazole dyes [14].

Even without any electron acceptor substitution, the heterocyclic ring is a powerful electron withdrawing residue. In particular, derivatives of thiazole, isothiazole and thiophene, i.e. heterocyclic systems containing sulphur as the π-excessive heteroatom, represent a very electronegative diazo component, and consequently have a marked bathochromic effect compared with the corresponding benzenoid compounds [3,4]. In Table 2 the absorption maxima of compounds **V**, **Ib**, **IIb** are given. Dye **V** derived from aniline and 2-methoxy-5-acetylamino-*N*,*N*-di-β-acetoxyethylaniline is deep yellow with $\lambda_{max} = 428$ nm; replacement of the phenyl moiety by the 6-nitrobenzothiazole residue results in a bathochromic shift of 148.5 nm. A large bathochromic shift 116.5 nm is observed, even when the benzothiazole residue is substituted with the electron donor methoxy group.

3.2. Dyeing and fastness properties

Adsorption of dyes **I–IV** on cellulose acetate varies from low to almost quantitative, the lowest dye uptake being observed for dye **IIb** (13.0–23.6% depending on the depth of dyeing) and the highest one (quantitative) for **Ib** (Table 3).

Table 2
Absorption maxima of aniline and benzothiazole based azo compounds

Compound	**V**	**Ib**	**IIb**
λ_{max}, nm	428	544.5	576.5
Colour	Deep yellow	Violet	Blue

Table 3
Dyeing and fastness properties of dyes (**I–IV**)**a** and (**I–III**)**b**[a,b]

Depth of dyeing (%) o.w.f.	mg dye/g fibre (% adsorbed dye) [2]			Wash fastness [11a]									Light fastness [11b]			Rate of dyeing [10]	Temperature range [10]
				Staining													
				Cotton			Acetate			Nylon							
Dye	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0	0.5	0.5
Ia	1.65 (66.1)	3.17 (63.4)	6.27 (62.7)	5	4–5	4	4–5	4	3	3–4	3	2–3	5–6	5–6	6	D	D
Ib	2.49 (99.6)	4.99 (99.8)	9.99 (99.9)	5	5	3–4	4–5	4–5	2–3	4–5	4	2–3	5–6	6	6–7	D	E
IIa	0.79 (31.7)	1.42 (28.4)	2.16 (21.6)	3–4	3–4	3–4	3	3	3	2–3	2–3	2–3	5	5	4	E	E
IIb	0.59 (23.6)	0.73 (14.6)	1.30 (13.0)	4–5	4–5	5	5	5	5	4–5	4–5	4–5	2	2	2	E	E
IIIa	1.34 (53.6)	1.74 (34.8)	2.60 (26.0)	5	5	4–5	5	4–5	3–4	2–3	2–3	2–3	6–7	6–7	6–7	E	E
IIIb	2.30 (92.0)	2.94 (58.8)	5.28 (52.8)	5	5	5	4–5	4–5	5	4	4	4	6–7	6–7	6–7	E	E
IVa	1.70 (68.0)	3.12 (62.0)	5.70 (57.0)	5	5	5	5	4	3–4	3	3	2–3	3–4	3–4	2–3	E	E

[a] For all dyes ratings of 5 for colour change except **IIb** [4–5 (Bl)].

[b] For all dyes ratings of 5 for acrylic, wool, polyester.

Wash fastness, expressed as colour change of the samples, was excellent while slight desorption of dye stained mainly nylon and cellulose acetate.

The light fastness of the dyeings was moderate, with the exception of the benzisothiazolylazo derivatives **III**(**a** and **b**),which showed a relatively high lightfastness, and dye **IIb** with a very low rating (Table 3). The latter could be correlated with the low dye uptake mentioned above.

The generalisation that the introduction of electron attracting substituents and, particularly, the increased electron mobility in the molecule decreases light fastness on non-protein substrates [8] is in accordance with the lightfastness ratings for the methoxy- and nitro-benzothiazolyazo dyes **I**(**a** and **b**) and **II**(**a** and **b**) and **IVa**, respectively. In contrast, the relatively high light fastness of the two benzisothiazole derivatives may be considered anomalous when correlated with the increased overall electron mobility in the molecule, as noted above.

The dyeing behaviour of dyes (**I–IV**)**a** and (**I–III**)**b** was also evaluated in respect of their rate of dyeing and the effect of temperature in dye uptake (Table 3). Both the rate-of-dyeing and temperature range tests were qualitative. According to these tests [10], dyes with the rating D are assessed “slow” and “very slow” with reference to their adsorption vs time behavior on cellulose acetate (rate-of-dyeing test) and “medium” and “poor” with reference to their temperature range properties. Poor temperature range properties indicate that the dye is slow-dyeing, since at equilibrium exhaustion for all dyes is much greater at lower than at higher temperatures.

4. Conclusions

N,*N*-di-β-hydroxy-ethylaniline and *N*,*N*-di-β-acetoxy-ethylaniline were used for coupling with some heterocyclic amines to produce ruby-red to greenish-blue azo dyes.The dyes obtained had moderate to high uptake on cellulose acetate, good wash fastness and low to moderate light fastness depending on the heterocyclic moiety and the depth of dyeing.

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