

Synthesis and Characterization of Hetarylazo Disperse Dyes Derived from Substituted *N*- β -Acetoxyethylanilines—Application on Cellulose Acetate

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ABSTRACT: The heterocyclic amines 2-amino-6-methoxy- and 2-amino-6-nitrobenzothiazole, 3-amino-5-nitro-[2,1]-benzisothiazole, and 2-amino-3,5-dinitrothiophene were diazotized and coupled to substituted *N*- β -acetoxyethylanilines to give dyes which colored cellulose acetate in red to deep blue hues. The color of the dyes is discussed with respect to the nature of the heterocyclic ring and to the substituents in the diazo and coupling component. Dyeing

and fastness properties of the dyes on cellulose acetate are also reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3479–3483, 2004

Key words: benzothiazolylazo, benzisothiazolylazo, thiophenylazo dyes; cellulose acetate; fastness properties; dyeing properties

INTRODUCTION

In continuation of our previous work^{1–3} on the synthesis and dyeing properties of a series of dyes obtained by coupling *N*-substituted naphthylamine and anilines with diazotized heterocyclic amines we report here the synthesis and characterization 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.

EXPERIMENTAL

Materials and apparatus

The following commercially available amines were used without further purification: 2-amino-6-methoxybenzothiazole, (1) 2-amino-6-nitrobenzothiazole, (2) 3-amino-5-nitro-[2,1]-benzisothiazole, (3) 2-amino-3,5-dinitrothiophene (Aldrich), (4) *N*-ethyl-*N*- β -acetoxyethylaniline (a) (Zhejiang) and 3-acetylamino-*N,N*-di- β -acetoxyethylaniline (b).

Melting points were determined with a Koffler hot stage apparatus and are given uncorrected. UV-visible spectra were recorded with a Shimadzu UV 2101 spectrometer using methanol as a solvent. ¹H-NMR data were obtained with a Bruker 300 AM spectrometer using CDCl₃/d₆-DMSO as a solvent and TMS as the internal standard. Mass spectra were obtained with a VG-TS250 spectrometer and elemental analyses using a Perkin–Elmer 2400-II Element Analyzer.

A Macbeth CE 3000 colereye spectrophotometer (PC Software Matchprobe 200, UV and specular component included, large area view 25.4 mm diameter) was used to measure the hue of the dyed fabrics.

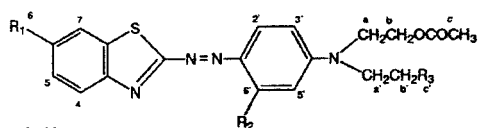
Synthesis and analytical data of azo dyes 1a,b–3a,b

Diazotization of amines 1–4 and coupling with a, b were reported previously.^{2,3} The dyes 1a,b–4a,b were obtained by conventional diazotization and coupling techniques.^{2,3}

Dye 1a

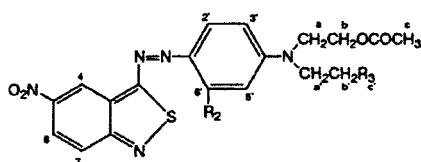
Dye 1a had the following properties: yield of crude product 91%; purified by recrystallization (ethanol); m.p. 101–104°C, λ_{\max} (nm, CH₃OH): 510.5; φ_{\max} (L · mol⁻¹ cm⁻¹, CH₃OH): 54,945; ¹H-NMR (δ , CDCl₃/day₆-DMSO): 1.24 t (3H, H-b'), 2.68 t (2H, H-b), 3.52 q (2H, H- α'), 3.71 s (3H, H-c) 3.76 t (2H, H-a), 3.89 s (3H,

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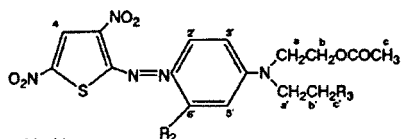
1 (a, b)
2 (a, b)

1a: R₁ = OCH₃, R₂ = H, R₃ = H
1b: R₁ = OCH₃, R₂ = NHCOCH₃, R₃ = OCOCH₃
2a: R₁ = NO₂, R₂ = H, R₃ = H
2b: R₁ = NO₂, R₂ = NHCOCH₃, R₃ = OCOCH₃



3 (a, b)

3a: R₂ = H, R₃ = H
3b: R₂ = NHCOCH₃, R₃ = OCOCH₃



4 (a, b)

4a: R₂ = H, R₃ = H
4b: R₂ = NHCOCH₃, R₃ = OCOCH₃

Scheme 1 Structure of dyes 1a,b–4a,b.

H-6), 6.74 days (2H, H-3', H-5'), 7.06 dd (1H, H-5), 7.28 days (1H, H-7), 7.96 dd (3H, H-2', H-6', H-4 overlapped); MS (*m/e*, %): 398 (16, M⁺), 325(9), 297(24), 206(20), 180(6), 165(11), 133(38), 91(36), 45(100); C(%), calcd, found): 60.28, 59.97; H:5.57, 5.27; N: 14.06, 13.90.

Dye 1b

Dye 1b had the following properties: yield of crude product 99%, purified by recrystallization (ethanol); m.p. 108–111°C; λ_{max} (nm, CH₃OH): 523.0; φ_{max} (L · mol⁻¹ cm⁻¹, CH₃OH): 54,348; ¹H-NMR (δ, CDCl₃/d₆-DMSO): 2.33 s (3H, NHCOCH₃), 2.73 t (4H, H-b, Hb'), 3.71 s (6H, H-c, Hc') 3.85 t (4H, H-a, H-a'), 3.90 s (3H, H-6), 6.52 dd (1H, H-3'), 7.07 dd (1H, H-5, 7.29 d (1H, H-7), 7.86 d (1H, H-2'), 7.92 d (1H, H-4), 8.10 d (1H, H-5'), 9.26 bs (1H, NHCOCH₃); MS (*m/e*, %): 513 (46, M⁺), 440(17), 427(7), 338(18), 180(82), 165(100), 91(69); C(%), calcd, found): 56.13, 55.73; H: 5.30, 5.03; N:13.64, 13.26.

Dye 2a

Dye 2a had the following properties: yield of crude product 82%, purified by recrystallization (ethanol); m.p. 150–152°C; λ_{max} (nm, CH₃OH): 541.5; φ_{max} (l.mol⁻¹.cm⁻¹, CH₃OH): 80,645; ¹H-NMR (δ, CDCl₃/d₆-DMSO): 1.27 t (3H, H-b'); 2.72 t (2H, H-b); 3.59 q (2H, H-α'), 3.74 s (3H, H-c) 3.81 t (2H, H-a), 6.78 d (2H, H-3', H-5'), 8.01 d (2H, H-2', H-6'), 8.11 d (1H, H-4), 8.33 dd (1H, H-5), 8.75 d (1H, H-7); MS (*m/e*, %): 413

(100, M⁺), 397(27), 366(25), 352(18), 339(49), 312(90), 207(52), 195(87); C(%), calcd, found): 55.20, 55.33, H: 4.63, 4.50; N: 16.94, 16.89.

Dye 2b

Dye 2b had the following properties: yield of crude product 87%, purified by recrystallization (ethanol); m.p. 137–140°C; λ_{max} (nm, CH₃OH): 545.0; φ_{max} (l.mol⁻¹.cm⁻¹, CH₃OH): 41,667; ¹H-NMR: 2.35 s (3H, NHCO[b]H₃), 2.75 t (4H, H-b, H-b'), 3.73s (6H, H-c, H-c') 3.90 t (4H, H-a, H-a') 6.61 d (1H, H-3'), 7.88 d (1H, H-4), 8.04 d (1H, H-2'), 8.06 s (1H, H-5'), 8.29 d (1H, H-5), 8.71 s (1H, H-7), 9.24 bs (1H, N[b]HCOCH₃); MS (*m/e*, %): 527 (7, [M-1]⁺), 455(7), 337(71), 195(87), 179(74), 133(79), 80(100); C(%), calcd, found): 52.27, 51.91; H: 4.58, 4.22; N: 15.90, 15.84.

Dye 3a

Dye 3a had the following properties: yield of crude product 82%, purified by column chromatography (silica gel, toluene-ethylacetate) and recrystallization (ethanol) of the appropriate fragment; m.p. 106–108°C; λ_{max} (nm, CH₃OH): 586.5, φ_{max} (l.mol⁻¹.cm⁻¹, CH₃OH): 46,948; ¹H-NMR: 1.29 t (3H, H-b'), 2.73 t (2H, H-b), 3.59 q (2H, H-a'), 3.74 s (3H, H-c), 3.82 t (2H, H-a), 6.80 d (2H, H-3', H-5'), 7.77 d (1H, H-7), 8.00 d (2H, H-2', H-6'), 8.22 dd (1H, H-6), 9.21 d (1H, H-4); MS (*m/e*, %): 413 (94, M⁺), 398(30), 340(88), 207(18), 133(100); C(%), calcd, found): 55.20, 55.29; H: 4.63, 4.69; N: 16.94, 16.66.

Dye 3b

Dye 3b had the following properties: yield of crude product 81%, purified by column chromatography (silica gel, toluene-ethylacetate) and recrystallization (ethanol) of the appropriate fragment; m.p. 195–197°C; λ_{max} (nm, CH₃OH): 594.5, φ_{max} (l.mol⁻¹.cm⁻¹, CH₃OH): 29,499; ¹H-NMR: 2.35s (3H, NHCO[b]H₃), 2.76 t (4H, H-b, H-b'), 3.73 s (6H, H-c, H-c') 3.90 t (4H, H-a, H-a') 6.58 d (1H, H-3'), 7.54 s (1H, H-5'), 7.76 d (1H, H-7), 8.19 d (1H, H-2'), 8.21 d (1H-H-6), 9.08 s (1H, H-4), 9.36 bs (1H, N[b]H COCH₃); MS (*m/e*, %): 528 (16, M⁺), 527 (61, [M-1]⁺), 455(50), 442(14), 337(16), 264(44), 207(16), 195(29), 55(100); C(%), calcd, found): 52.27, 52.28; H:4.58, 4.73, N: 15.90, 15.52.

Dyeing of cellulose secondary acetate

Aqueous dispersions of dyes 1a,b–3a,b² were used for dyeing cellulose secondary acetate and dye adsorbed on the fiber, fastness, and dyeing properties (wash-light and rate of dyeing-temperature range) of the dyeings were assessed by established procedures.^{2,4,5}

TABLE I
Electronic Spectra and Colorimetric Data of Compounds 1a,b–4a,b

Compound	λ_{\max} (CH ₃ OH, nm)	$\log \epsilon_{\max}$ (CH ₃ OH)	$h^{a,b}$
1a	510.5	4.74	20.70
1b	523.0	4.73	
2a	541.5	4.91	332.69
2b	545.0	4.62	326.69
3a	586.5	4.67	275.39
3b	594.5	4.47	256.10
4a	383.6	3.64	
4b	386.6		

Note. ^a Dyeing of cellulose acetate was not performed with 1b, 4a, and 4b.

^b Depth of dyeing 0.5% o.w.f.

RESULTS

Color

λ_{\max} and φ_{\max} of compounds 1a,b–4a,b in methanol are given in Table I. Methanol was used as a solvent for the measurements, because this solvent was found to be appropriate for the total extraction of the dye from the cellulose acetate.

Dyes (1–4)b derived from 3-acetylamino-*N,N*-di- β -acetoxyethyl-aniline have absorption maxima at longer wavelengths than the corresponding dyes (1–4)a derived from *N*-ethyl-*N*- β -acetoxyethyl-aniline, i.e., replacement of a *N*-ethyl with a *N*-acetoxyethyl group and primarily introduction of an electron donor acetylamino substituent in the coupling residue of dyes (1–4)a results in bathochromic shifts in the range of 4 (2b > 2a) to 13 nm (1b > 1a). These shifts can be mainly attributed to the presence of the

acetylamino group and the possibility of intramolecular hydrogen bonding formation with the azo residue rather than its electron donor character.^{6,7} The hypsochromic effect of the acetyl group in the coupling component seems to be not operative since its positive inductive effect practically could not affect the bathochromic shift of the compound due to the distance between the azo and acetyl groups.

However, when the nonacetylated 3-acetylamino-*N,N*-di- β -hydroxyethyl-aniline was used as a coupler,³ even higher absorption maxima were obtained,³ apparently due to the stronger +I effect of the hydroxy group.

On the other hand the introduction of electron withdrawing substituents in the diazo component increases the bathochromic shift due to more extensive electron delocalization. Dyes 2a and 2b with the strong electron acceptor nitro group show higher absorption maxima than the corresponding 1a and 1b dyes containing the electron donor methoxy group in the benzothiazole ring. The even larger bathochromic shifts of compounds 3(a,b) derived from aminobenzisothiazole could be attributed to the structure of the dyes, which have a quinonoid configuration in the ground state and an aromatic configuration in the charge transfer state.⁸

The above are in agreement with the hue h° values of dyes 1a,b–3a,b, which are generally correlated with the λ_{\max} of the corresponding dye and with the visual hue perception of the dyed cellulose acetate samples. The position of dyes 1a,b–3a,b in the CIELAB according to the hue angle h° is presented in Figure 1.

Finally, dyes 4(a,b) with the thiophene system as a diazo component exhibit the highest bathochromic

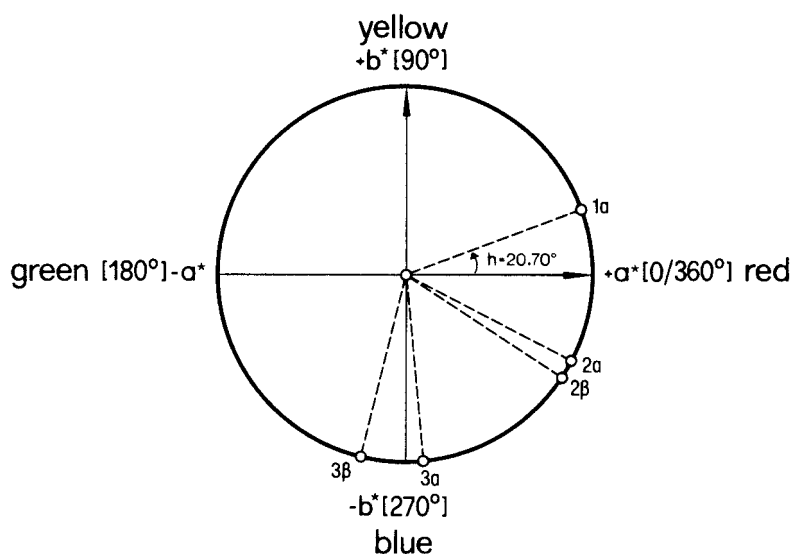


Figure 1 Hue angles of dyes 1a,b–3a,b at depth of dyeing 0.5% o.w.f. on cellulose acetate.

shifts, although the compounds as a whole are less extensively conjugated than the benzothiazole 1, 2 and isothiazole 3 dyes, thus providing blue to greenish-blue dyes of relatively low molecular weights. It is suggested that the increased diene character of the thiophene ring is responsible for this shift.⁹

Dyeing and fastness properties

Dye uptake on cellulose acetate, wash and light fastness of cellulose acetate dyeing, and rate of dyeing and temperature range for dyes 1a,b-3a,b are given in Table II.

As concluded from Table II, adsorption of the dyes on cellulose acetate varies from moderate to high depending on the depth of dyeing.

Wash fastness of the dyed samples, expressed as color change, was excellent. Slight desorption of dye mainly stained the synthetic fibers nylon, polyester, and cellulose acetate, as expected.

Contrary to some studies on the dye structure-light fastness relationship¹⁰ indicating that the introduction of electron withdrawing substituents and increase in electron mobility in the molecule decrease light fastness of nonprotein substrates, the results in Table II indicate that this is not occurring: Dyes 2(a,b) with the strong electron acceptor nitro group in the benzothiazolylazo moiety and the benzoisothiazolylazo dyes 3(a,b) exhibit significantly higher light fastness ratings than dye 1a with the electron donor methoxy group in the benzothiazolylazo component. Furthermore, the presence of the acetyl amino group and the replacement of the *N*-ethyl group with *N*-acetoxyethyl in the coupling component of dyes 2b and 3b and the subsequent increased electron mobility in the molecule compared to 2a and 3a does not result in a decrease of light fastness, but rather in a slight increase (light fastness of 2b and 3b in 1% o.w.f. depth a dyeing: 7, the corresponding value for 2a, 3a: 6-7). This is in agreement with data obtained using a similar series of dyes in the literature.^{8,11-13}

The dyeing behavior of dyes (1-3)a and (1-3)b was also evaluated with respect to their rate of dyeing cellulose acetate substrate and the effect of temperature on dye uptake (Table II). Both the rate of dyeing and the temperature range tests were only qualitative. According to these tests⁴ dyes with the ratings D and E (for the rate of dyeing test) are assessed as "slow" and "very slow," respectively, with reference to their adsorption versus time on cellulose acetate. Dyes with ratings D and E (for the temperature range test) are assessed as "medium" and "poor," respectively, with reference to their temperature range properties. Poor temperature range properties indicate that the dye is slow-dye-

TABLE II
Dyeing and Fastness Properties of Dyes 1a,b-3a,b

Depth of dyeing (% o.w.f)	Mg dye/g fiber (adsorbed dye) [Ref. 2]		Wash fastness [Ref. 5] ^{a,b} staining						Light fastness [Ref. 5]	Rate of dyeing [Ref. 4]	Temperature range [Ref. 4]	
	Cotton	Acetate	Nylon	Polyster	Cotton	Acetate	Nylon	Polyster				
Dye 1a	0.25 2.25 (90.3)	1.0 8.52 (85.2)	0.25 5	0.25 3-4	0.5 3	1.0 2-3	0.5 3-4	1.0 4-5	0.25 4	1.0 5	0.5 5-6	0-5 Δ
2a	1.78 (75.2)	2.66 (43.0)	5	4	2-3	2	2-3	3	6-7	6-7	E	Δ
2b	1.97 (78.6)	2.84 (51.4)	5	5	5	5	5	5	6-7	7	E	E
3a	1.30 (51.8)	1.96 (39.2)	5	4-5	4	4	4-5	4-5	6-7	7	E	E
3b	2.26 (90.4)	3.88 (75.9)	5	4-5	3-4	4	4-5	4-5	6-7	7	Δ	Δ

^a For all dyes ratings of 5 for color change.

^b For all dyes ratings of 5 for acrylic, wool.

ing, since, at equilibrium, exhaustion for all dyes is much greater at lower than at higher temperature. Thus, the corresponding results for the dyes in the study were to be expected.

CONCLUSION

3-Acetylamino-*N,N*-di- β -acetoxyethylaniline and *N*-ethyl-*N*- β -acetoxyethylaniline when used for coupling with some heterocyclic amines produce ruby-red to deep-blue azo dyes. These dyes had moderate to high uptake on cellulose acetate, excellent wash fastness, and moderate to high light fastness depending on the heterocyclic moiety and the depth of dyeing.

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