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Short communication

Monoazo disperse dyes derived from 11H-7-amino-2-chloro-isoindolo[2,1-a] benzimidazole-11-one

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Abstract

A series of new heterocyclic disperse dyes were prepared by diazotising 11H-7-amino-2-chloro-isoindolo[2,1-a]benzimidazole-11-one and coupling with various mono- and di-N-substituted aniline derivatives. The resultant dyes were characterised using standard spectroscopic methods and their dyeing performance on nylon 66 and polyester fabrics was assessed. Results of the latter studies indicated that dye bath exhaustion was moderate to good and the dyed fabrics had good to very good fastness properties. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: 11H-7-Amino-2-chloro-isoindolo[2; 1-a]benzimidazole-11-one; Synthesis; Disperse dyes; Nylon 66 and polyester fibres; Dyeing properties

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1. Introduction

Isoindolo[2,1-a]benzimidazoles, the condensation products of phthalic anhydrides and *ortho*-phenylenediamines [1–3], are known to be suitable as dyes [4], dye precursors [5], sedatives and tranquilizers [6], and electrostatographic toners [7]. These compounds are also used in polymeric materials for gas and fluid separation membranes [8,9] and to provide thermal stability [10]. However, no report involving the use of an amino derivative of this heterocycle in the preparation of azo disperse dyes is evident in the open literature. In the present paper, we report the synthesis and dyeing properties of some monoazo disperse dyes derived from 11H-7-amino-2-chloro-isoindolo[2,1-a] benzimidazole-11-one. The general structure for the target dyes (**D$_1$–D$_{15}$**) is given in Fig. 1.

2. Experimental

2.1. General

All melting points are uncorrected and are expressed in °C. IR spectra were recorded in KBr on a Nicolet Impact 400 D FT-IR spectrophotometer and ^{1}H NMR spectra were recorded on a Hitachi R-1500 instrument, using TMS as the internal standard, and chemical shifts are given in δ (ppm). Absorption spectra were recorded in DMF on a Shimadzu UV 240 instrument. Fastness to light, sublimation and perspiration was assessed in accordance with BS 1006-1978 [11]. For light

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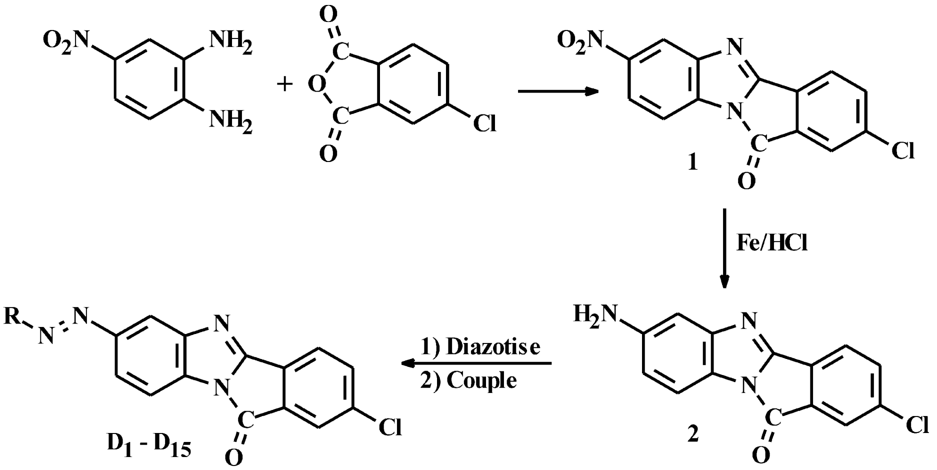

Fig. 1. Route used for the synthesis of dyes and intermediates reported in this study.

fastness testing, a Microseal instrument equipped with an MB/U 400-W mercury lamp was employed, and light exposures were conducted for 150 h. Rubbing fastness was carried out with an Atlas crockmeter in accordance with AATCC TM 8-1961 [12] and wash fastness was conducted in accordance with ISO: 765-1979 [13].

2.2. Synthesis

2.2.1. 11H-7-Nitro-2-chloro-isoindolo[2,1-a] benzimidazole-11-one (1)

4-Nitro-*ortho*-phenylenediamine (4.21 g, 0.027 mol) and 4-chlorophthalic anhydride (5 g, 0.027 mol) were powdered and transferred to a round bottom flask. The mixture was stirred for 45 min at 140–150 °C, acetic anhydride (2.45 ml, 0.027 mol) was added, and heating was continued for 6 hrs. The hot reaction mixture was poured over crushed ice, stirred, and the product was isolated by filtration. Recrystallisation from dioxane gave 5.89 g (72%), m.p. 212–214 °C. Calculated for $C_{14}H_6N_3O_3Cl$: C, 56.09%; H, 2.00%; N, 14.03%. Found: C, 56.05%; H, 1.98%; N, 13.98%. UV-visible: $\lambda_{max} = 270$ nm.

2.2.2. 11H-7-Amino-2-chloro, isoindolo[2,1-a] benzimidazole-11-one (2)

A solution of compound **1** (3.0 g, 0.01 mol) in methanol (6 ml) and HCl (12 M, 8 ml) was stirred under reflux, as iron powder (1.6 g) was added in small portions over 1 h. Stirring under reflux was continued for 90 min and the resultant mixture was filtered hot. The filtrate was neutralized with aqueous ammonia (50%) to give a brown solid that was collected and recrystallised from DMF/ethanol. The light brown powder (2.18 g, 81%) had m.p. 230 °C. Calculated for $C_{14}H_8N_3OCl$: C, 62.34%; H, 2.97%; N, 15.58%. Found: C, 62.30%; H, 2.91%; N, 15.54%. IR (KBr): 3300–3500 (C–NH), 1690–1710 (C=O), 1600–1640 (C=N), 750–850 (C–Cl). NMR: δ3.04 (2H, s, Ar–NH), δ 7.1–8.0 (6H, m, Ar–H). UV-visible: $\lambda_{max} = 259$ nm.

2.2.3. Diazotisation of amine 2

Diazotisation was carried using nitrosyl sulphuric acid according to the following procedure. H_2SO_4 (16 g, 18 M) was placed in a small beaker and stirred at 0–5 °C, as dry powered $NaNO_2$ (0.69 g, 0.01 mol) was slowly added. After the addition was complete, stirring was continued for 30 min, and the reaction temperature was raised gradually to room temperature. The reaction mixture was then stirred at 70 °C until a clear solution formed. The resultant solution was cooled to 5–10 °C and compound **2** (2.69 g, 0.01 mol) was added very slowly with stirring. The reaction mixture was stirred for 1 h at <5 °C, crushed ice (10 g) was added, and excess HNO_2 was destroyed by adding urea. The resultant solution was used in the subsequent coupling reactions.

2.2.4. Dye synthesis

The synthesis of dyes $\mathbf{D_1}$–$\mathbf{D_{15}}$ is illustrated in the preparation of dye $\mathbf{D_1}$: *N,N*-bis(2-hydroxyethyl-aniline (0.67 g, 0.004 mol) was dissolved in HCl (1.5 ml, 10% w/v), and the solution was diluted with water (6 ml) and cooled to 0–5 °C. To this well-stirred solution, the freshly prepared diazonium salt solution was added dropwise over 45 min, maintaining the temperature below 5 °C. Stirring was continued for 1 h at 0–5 °C, maintaining pH 4–5 using cold Na_2CO_3 (10% w/v). The product was collected, washed several times with water, and dried at 40 °C. The reddish brown solid was dissolved in DMF (12 ml) and precipitated by adding $CHCl_3$ to give (1.07 g, 63%), m.p. 191 °C.

2.2.5. Dyeing procedure

A paste composed of dye (40 mg), dispersing agent (Dodamol, 80 mg), and 3–4 drops of wetting agent (Tween-80, 1%) was prepared by grinding the mixture very well with a small mortar and pestle. To this paste, water (100 ml) was added with rapid stirring to obtain an aqueous dispersion of dye. The pH of the dispersion was adjusted to 4.5–5.0 by adding HOAc (1%). The dyeing of nylon 66 and polyester fabric was conducted at elevated temperatures [14] using a "Laboratory High Temperature Dyeing Machine" equipped with 12 beakers. In dyeing nylon 66 (2 g), the bath temperature was raised to 115 °C at a rate of 2 °C per min, held there for 60 min, and then allowed to cool to 35 °C. The dyed fabric was washed several times with water and dried. The dyeing of polyester was carried out at 125 °C for 90 min. The dyed fabric was further treated with a solution of detergent (0.2 g) and Na_2CO_3 (0.1 g) in water (200 ml) at 60 °C for 30 min, washed thoroughly with water and dried. A 20-min reduction clear treatment was given to all dyed fabric, using a solution of $Na_2S_2O_4$ (4 g) and Na_2CO_3 (4 g) in water (200 ml) at 60 °C. The fabrics were then washed thoroughly with water and dried.

3. Results and discussion

The 11H-7-amino-2-chloro-isoindolo[2,1-a]benzimidazole-11-one (2) was obtained via the condensation of 4-chloro-phthalic anhydride and 4-nitro-*ortho*-phenylenediamine in the presence of acetic anhydride followed by reduction of the nitro intermediate (**1**) with Fe/HCl. (Fig. 1). For dye synthesis, amine **2** was diazotised and coupled with the mono and di-*N*-substituted aniline derivatives listed in Table 1. The λ_{max} values for the resultant dyes $\mathbf{D_1}$–$\mathbf{D_{15}}$ are also given in Table 1, and a comparison of the absorption spectra for intermediates **1–2** and dyes $\mathbf{D_1}$ and $\mathbf{D_3}$ is shown in Fig. 2. The absorption maxima for the dyes were in the range of 490–520 nm, with a broad shoulder near 500–505 nm. These results indicate that the absorption band from the heterocyclic system is preserved in the dyes produced.

IR spectra for the dyes showed absorption bands at 1550–1575 (–N = N– group [15]), 1690–1700 (–C = O group), 1600–1640 (–C = N group), and 750–850 (–C–Cl group). Dyes $\mathbf{D_2}$ and $\mathbf{D_3}$ gave absorption bands at 1520–1580 (N–H group) and at 1660–1685 (–C = O group), $\mathbf{D_7}$, $\mathbf{D_{11}}$ and $\mathbf{D_{12}}$ gave a band at 2240–2260 (–C≡N), and $\mathbf{D_{10}}$ and $\mathbf{D_{15}}$ gave a band at 1385–1365 (–C–H of O–acetyl group).

The dyes where applied to nylon 66 and polyester fabric at a 2% shade. The hues of the dyed fabrics are shown in Table 2. As expected, the use of the mono *N*-substituted couplers tended to give absorption maxima at lower wavelengths than the *N,N*-disubstituted couplers.

Data on dye fastness properties are also given in Table 2. Except for dyes $\mathbf{D_1}$, $\mathbf{D_4}$, $\mathbf{D_{10}}$, and $\mathbf{D_{13}}$, light fastness was good to very good on nylon 66, and except for $\mathbf{D_2}$, $\mathbf{D_5}$and $\mathbf{D_{12}}$ it was good to very good

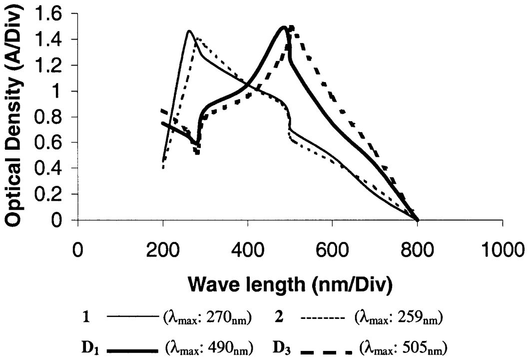

Fig. 2. UV-visible spectra of intermediates **1–2** and dyes $\mathbf{D_1}$ and $\mathbf{D_3}$.

Table 1
Characterization of monoazo disperse dyes D_1–D_{15}

Dye	Coupling component (R)	Mol. formula	Mol. wt. (g/mol)	Yield (%)	M.p.^{a} (°C)	λ_{max}^{b} (log €)	Found (Cal.) (%)			% Exhaustion	
							C	H	N	N	P
D_1	*N*,*N*-Bis(2-hydroxy ethyl)aniline	$C_{24}H_{21}N_5O_3Cl$	462.5	63	191	490 4.12	62.35 62.40	4.50 4.54	15.13 15.16	64	70
D_2	*m*-Acetamido *N,N*-bis(2-hydroxyethyl) aniline	$C_{26}H_{24}N_6O_4Cl$	519.5	65	195	500 4.21	60.14 60.17	4.55 4.61	16.18 16.20	69	60
D_3	*m*-Acetamido *N,N*-bis (diethyl) aniline	$C_{25}H_{24}N_5O_2Cl$	487.5	65	210–212	505 4.03	64.11 64.13	4.88 4.92	17.23 17.26	75	70
D_4	*N*,*N*-Bis(2-hydroxyethyl)-*m*-toluidine	$C_{25}H_{23}N5O_3Cl$	476.5	65	205	495 4.25	63.05 63.09	4.76 4.86	14.69 14.72	65	60
D_5	*N*,*N*-Bis(2-cyanoethyl)aniline	$C_{26}H_{19}N_7O_2Cl$	480.5	62	189	515 4.43	65.01 65.06	3.91 3.95	20.40 20.43	68	60
D_6	*N*,*N*-Bis(2-hydroxyethyl)-*m*-chloroaniline	$C_{24}H_{20}N_5O_3Cl_2$	496	59	182	520 4.05	58.02 58.06	4.01 4.03	14.08 14.11	65	62
D_7	*N*,*N*-Bis(2-cyanoethyl)-*m*-toluidine	$C_{27}H_{21}N_7OCl$	494.5	63	179	510 4.21	65.62 65.65	4.19 4.24	19.81 19.85	72	68
D_8	*N*-(2-Hydroxyethyl)aniline	$C_{22}H_{17}N_5O_2Cl$	418.5	58	190	485 4.11	63.21 63.23	4.01 4.06	16.72 16.76	64	60
D_9	*N*-Ethyl-*N*-(2-hydroxyethyl)aniline	$C_{24}H_{21}N_5O_2Cl$	446.5	70	197	495 4.28	53.85 53.87	4.66 4.70	15.68 15.71	62	55
D_{10}	*N*,*N*-Bis(acetoxyethyl)aniline	$C_{28}H_{25}N_5O_5Cl$	546.5	71	188	498 4.10	61.55 61.59	4.51 4.57	12.80 12.83	70	65
D_{11}	*N*-(2-Cyanoethyl) aniline	$C_{23}H_{16}N_6OCl$	427.5	69	200	496 4.25	64.65 64.71	3.68 3.74	19.63 18.74	74	68
D_{12}	*N*-Methyl-*N*-cyanoethylaniline	$C_{24}H_{18}N_6OCl$	441.5	65	210	498 4.27	65.35 65.38	4.05 4.07	19.04 19.06	60	58
D_{13}	*N*-(2-Hydroxyethyl)-*m*-toluidine	$C_{23}H_{19}N_5O_2Cl$	432.5	62	215	500 4.09	62.88 62.93	4.36 4.39	16.65 16.68	68	62
D_{14}	*N*-Methyl-*N*-(2-hydroxyethyl)aniline	$C_{23}H_{19}N_5O_2Cl$	432.5	64	219	505 4.19	63.94 63.96	4.34 4.39	16.18 16.22	73	68
D_{15}	*N*,*N*-Bis(acetoxyethyl)-*m*-chloroaniline	$C_{28}H_{24}N_5O_5Cl_2$	580	70	203	505 4.55	55.91 55.95	4.10 4.13	12.05 12.08	60	58

[a] Melting points are uncorrected.

[b] Solvent = DMF.

Table 2

Shades and fastness properties of monoazo disperse dyes D_1–D_{15}

Dye No.	Colour of dyed fabric		Light fastness		Wash fastness		Rubbing fastness				Perspiration fastness				Sublimation fastness	
							N		P		N		P			
	N	P	N	P	N	P	Dry	Wet	Dry	Wet	Acid	Alkaline	Acid	Alkaline	N	P
D_1	Reddish brown	Reddish brown	4–5	4–5	5	5	4–5	5	5	5	5	5	5	4–5	5	5
D_2	Purple red	Purple red	5	5	4–5	5	5	5	5	5	4–5	5	5	5	5	5
D_3	Reddish purple	Reddish purple	5	5	5	4–5	5	4–5	5	5	5	5	4–5	5	5	5
D_4	Reddish brown	Reddish brown	4–5	5	5	5	4–5	5	4	5	5	5	5	4–5	4–5	5
D_5	Wooden brown	Wooden brown	5–6	4–5	5	5	5	4	5	4–5	5	5	5	5	5	5
D_6	Purple	Purple	5–6	5	5	4–5	5	5	5	5	5	4–5	5	4	5	5
D_7	Brownish orange	Brownish orange	5	5–6	5	5	5	5	4–5	5	5	5	4–5	5	5	5
D_8	Reddish brown	Brown	5	5	5	5	4–5	4–5	5	5	5	5	5	5	4–5	5
D_9	Orange brown	Orange brown	5–6	5	5	5	5	5	5	4–5	5	5	5	4–5	5	5
D_{10}	Dark brown	Reddish brown	4–5	5	4–5	5	5	5	5	5	5	5	4–5	5	5	4–5
D_{11}	Light brown	Light brown	5	5	5	5	5	5	5	5	4–5	4–5	5	5	5	5
D_{12}	Orange	Orange brown	5	4–5	5	5	4–5	5	5	4–5	5	5	5	5	5	5
D_{13}	Reddish orange	Reddish orange	4–5	5	5	5	5	5	5	5	5	4–5	5	5	4–5	4–5
D_{14}	Dark purple brown	Purple brown	5–6	5	4–5	5	5	5	5	5	5	5	5	4–5	5	5
D_{15}	Reddish brown	Purple Brown	5–6	5	5	5	5	5	4–5	5	5	5	4–5	5	5	5

N—Nylon 66; P—Polyester; rating scale = 1 (lowest) to 8 (highest) for light fastness and 1 to 5 for washing, perspiration, rubbing and sublimation fastness.

on polyester. Washing and rubbing fastness properties were good to excellent on both fabric types and perspiration and sublimation fastness properties were excellent.

4. Conclusions

Azo disperse dyes based on 11H-7-amino-2-chloro-isoindolo[2,1-a]benzimidazole-11-one have been synthesized. These dyes give mostly orange, red, and brown shades on nylon 66 and polyester fibres that have very good to excellent washing fastness properties on both substrates. The dyes have better exhaustion on nylon than polyester, probably due to the greater accessibility of the pore structure in nylon.

References

[1] Arient J, Marhun J. Collection Czechoslov Chem Commun 1961;26:98–106.
[2] Jaff EE. Eur Pat 4 56 609, 1991 (as cited in Chem Abstr 1992;116:131253).
[3] Arient J, Slosar J, Havlickova J. Collection Czechoslov Chem Commun 1965;30(16):1913–22.
[4] Arient J, Havlickova L. Collection Czechoslov Chem Commun 1963;28:1885–94.
[5] Kashizaki Y. Jpn Kokai Tokkyo Jap Pat 03,39,751, 1991 (as cited in Chem Abstr 1992;116:31312).
[6] William HJ. US Pat 3,329,684, 1967 (as cited in Chem Abstr 1967;67:108656).
[7] Orient Chemical Industries Ltd. Jpn. Kokai Tokyo Koho., Jap Pat 59,185,349, 1984 (as cited in Chem Abstr 1985;102:176456).
[8] Zhou W, Gaoxue S. J Appl Polym Sci 1994;51(5):855–61.
[9] Koros WJ, Walker DRB. US Pat 5,262,056, 1993 (as cited in Chem Abstr 1994;121:85159).
[10] Bilow N, William L. Wire-Wire Production 1973;48(1):52–8 (as cited in Chem Abstr 1973;78:112332).
[11] Standard Test method. BS 1006, 1978 (UK); ISO 105, 1994 (India).
[12] AATCC Test Method 8, 1961.
[13] Indian Standard. ISO: 765, 1979.
[14] Mardiya HA, Patel VS. Indian J Chem Tech 2001; 8(2):140–8.
[15] Desai JA, Patel MH, Patel KK, Patel RG, Patel VS. Indian J Text Res 1985;10:71–4.