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Synthesis and Applications of Isoindoline-Monomethine Disperse Dyes

N. SEKAR* and R.N. RAJULE
Institute of Chemical Technology, University of Mumbai, Mumbai-400 019, India
E-mail: nnsekar@udct.org and rajulern@yahoo.com

Monomethine styryl dyes have been synthesized by reacting 1-amino-3-imino isoindoline first with active methylene compound in presence of base followed by reaction with electron-rich aromatic compounds in acetic anhydride and catalytic amount of sulphuric acid. The dyes are evaluated on polyester fabric.

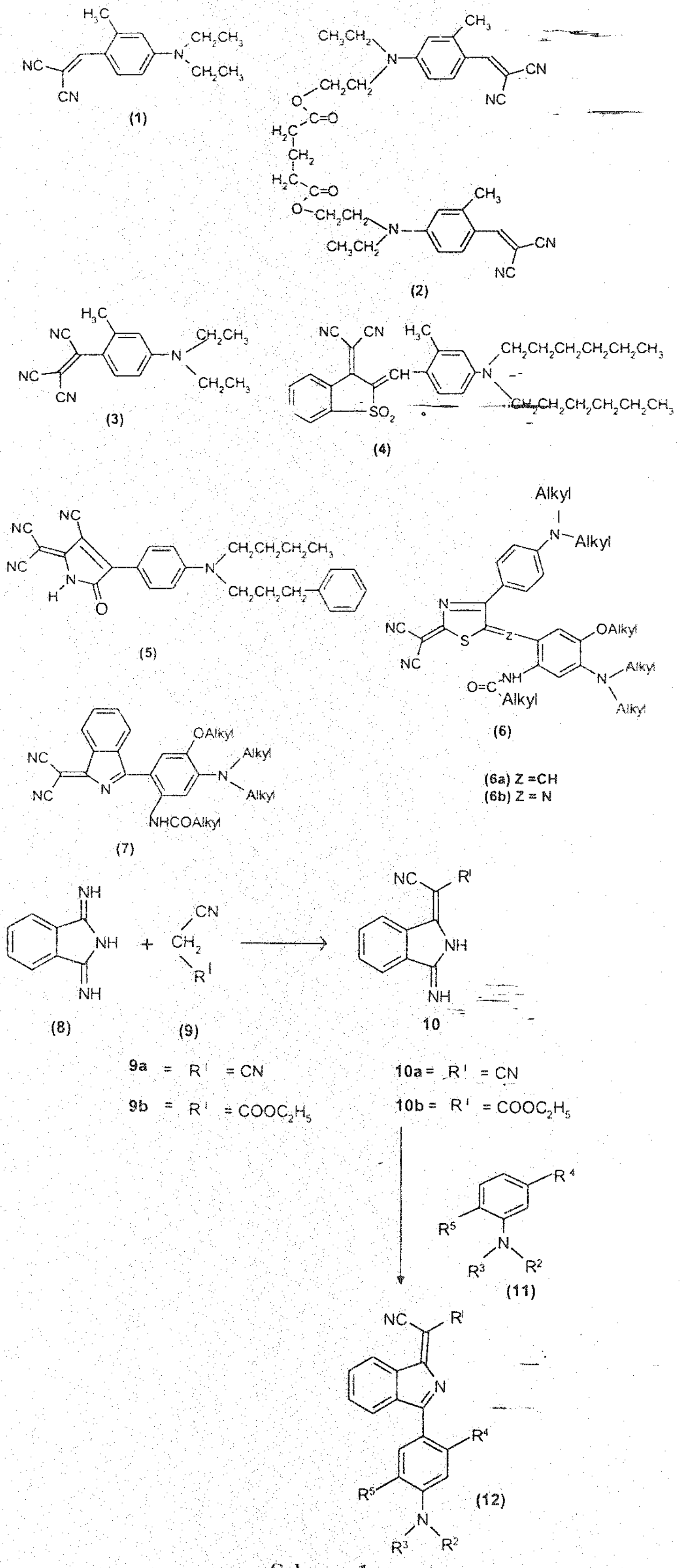
Key Words: **Methine dyes, Blue disperse dyes.**

INTRODUCTION

Methine or styryl dyes represented by the formula (1) are technically important as yellow disperse dyes[1]. The sublimation fastness of this kind of dyes can be improved by introducing suitable substituents into the alkyl residue of the amino group or by doubling the molecular size as exemplified in CI Disperse Yellow 99, (2)[1–3]. A strong bathochromic shift of hue has been observed through the introduction of cyano group in the alpha position as in the dye (3)[4,5]. Such red tricyanoethylene dyes are also widely described in the patent literature[6–9]. The discovery of blue styryl disperse dyes such as CI Disperse Blue 354 (4) by Sandoz in the late 1970s[10] is considered to be a landmark in the replacement of the aristocratic anthraquinone disperse dyes[11]. This discovery opened up a new avenue for having modified styryl dyes incorporating 1,1-dicyanobutadiene moiety into a heterocyclic system to obtain blue disperse dyes which are technically equivalent to anthraquinone based blue disperse dyes[12–17]. Several innovative variations of these structures have been studied in obtaining tinctorially strong blue disperse dyes; they are pyrrole dyes represented by CI Disperse Blue 365 (5)[18–23]. Further variation to these structures are (6)[24–26] and (7)[27–30].

It is known that 1-amino-3-iminoisoindoline (8) can be reacted with one molar equivalent of an active methylene compound like ethyl cyanoacetate (9b) and malononitrile (9a) to give monomethine compound of the type (10)[29–31] which on further condensation with electron-rich aromatics (11) in acetic anhydride and catalytic amount of sulphuric acid give isoindoline monomethine dyes (12)[27, 28]. This paper describes the synthesis and application of such monomethine disperse dyes of the general structure (7).

The reaction sequence is outlined in **Scheme-1.**



Scheme-1

TABLE-1
STRUCTURE OF THE ISOINDOLINE MONOMETHINE DYES SYNTHESIZED

Dye No.	R^1	R^2	R^3	R^4	R^5
12a	CN	CH_3	CH_3	H	H
12b	CN	C_2H_5	C_2H_5	H	H
12c	CN	C_2H_5	$CH_2C_6H_5$	H	H
12d	CN	C_2H_5	C_2H_4CN	CH_3	H
12e	CN	C_2H_5	C_2H_5	$NHCOCH_3$	H
12f	CN	C_2H_5	C_2H_5	$NHCOCH_3$	OCH_3
12g	CN	C_2H_5	C_2H_4CN	$NHCOCH_3$	OCH_3
12h	$COOC_2H_5$	C_2H_5	C_2H_5	$NHCOCH_3$	H
12i	$COOC_2H_5$	C_2H_5	C_2H_5	$NHCOCH_3$	OCH_3
12j	$COOC_2H_5$	C_2H_5	C_2H_4CN	$NHCOCH_3$	OCH_3

EXPERIMENTAL

Commercially available 1-amino-3-imino isoindoline, N,N-dialkylated aniline derivatives, malononitrile and ethylcyanoacetate were used.

Elemental analysis was carried out in microanalytical laboratories of University of Mumbai, Institute of Chemical Technology. IR spectra were recorded in FTIR/5300 spectrophotometer. Ultraviolet spectra were recorded on Perkin-Elmer Lambda 3B UV-Vis spectrophotometer. Data Colour Spectra Flash SF 300 spectrophotometer (Data Color International, NJ, USA) linked to a personal computer with Lyn SLIFORM NG software (She Lyn Inc., Greensboro, NC, USA) was used to measure reflectance spectra of dyed samples and calculated CIELAB colorimetric data. AATCC grey scale ratings were used for dyed samples. Colorimetric data were obtained using specular included, illuminant D65 and CIE 1964 10^O supplemental standard observer. Each fabric was measured three times and average data was taken. ^{1}H-NMR spectra were recorded on a Brucker DRX instrument at 300MHz.

Synthesis of methine compound (10a): In a 100 mL three-necked round bottom flask fitted with a mechanical stirrer and air condenser, 20 mL of methanol, 1-amino-3-iminoisoindoline (7.25 g, 0.05 mol) and malononitrile (4.2 mL, 0.005 mole) were taken. The mixture was refluxed for 3 h; it was then cooled, washed with water and dried. Yield 7.5 g (76% of theory); m.p. 220°C (recrystallised from DMF). IR spectra recorded in KBr pellet showed absorption band at 3360 cm^{-1} ν(NH) and 2200 cm^{-1} ν(CN). Analysis %, Found (Calcd.): C 68.2 (68.1), H 3.2 (3 .1), N 28.1 (28.2).

Synthesis of methine compound (10b): In a 100 mL three-necked round bottom flask fitted with a mechanical stirrer and air condenser, 30 mL of methanol, 1-amino-3-imino isoindoline (7.25 g, 0.05 mol) and ethyl cyanoacetate (5.32 mL, 0.005 mol) were taken. The mixture was refluxed for 3 h; it was then cooled, washed with water and dried. Yield 7.0 g; m.p. 205°C (recrystallised from DMF), IR spectra recorded in KBr pellet showed the following absorption bands:

1. Absorption band at 3284 cm^{-1} for –NH function,
2. Absorption band at 2214 cm^{-1} for –CN function,
3. Absorption band at 1686 cm^{-1} for carbonyl group.

C 68.2 (68.1), H 3.2 (3.1), N 28.1 (28.3).

Synthesis of disperse dye (12c): In a 100 mL two-necked round bottom flask equipped with mechanical stirrer, an air condenser protected by calcium chloride guard tube was placed **9a** (1.94 g, 0.01 mol), N-ethyl N-benzyl aniline (3.88 g , 0.01 mol) and acetic anhydride (10 mL). A drop of sulphuric was added and the reaction mass was heated to 90°C on an oil bath and maintained for 3 h. The reaction was monitored by thin layer chromatography (which showed two spots: one blue spot presumably for the product and second, yellow spot corresponding to the starting compound **9a.**

The reaction mass was run into cold methanol (10 mL). The solid that separated was filtered and extracted in benzene (20 mL). The benzene layer was washed with 100 mL of 5% aqueous sodium hydroxide. The benzene layer was separated and dried over anhydrous magnesium sulphate (5 g). Benzene was then removed by distillation under line vacuum to get pure dye **12c.** The dye was crystallized from ethanol. Yield: 37%; m.p. 184°C. Analysis %, Found (Calcd.): C 80.2 (80.4), H 4.8 (5.1), N 14.3 (14.4).

Synthesis of disperse dye (12a): Synthesis was carried out analogously as carried for **12c**, by taking **9a** (1.94 g, 0.01 mol), N,N′-dimethylaniline (2.98 g, 0.01 mol) and acetic anhydride (10 mL). Yield: 38%; m.p. 210°C. ^{1}H NMR (DMSO-d_6): δ (ppm) 2.9δ (s, 6H, —CH_3), 6.6–6.8 δ (2d, 2H), 7.0–7.2 δ (2d, 2H), 7.4–7.8 (2m, 4H, proton). Analysis %, Found (Calcd.): C 76.3 (76.5), H 4.9 (4.7), N 19.0 (18.0).

Synthesis of disperse dye (12b): Synthesis was carried out analogously as for **12c**, by taking **9a** (1.94 g, 0.01 mol), N,N′-diethylaniline (3.26 g, 0.01 mol) and acetic anhydride (10 mL). Yield: 32%; m.p. 232°C. Analysis %, Found (Calcd.): C 77.2 (77.3), H 5.3 (5.5), N 17.4 (17.2).

Synthesis of disperse dye (12d): Synthesis was carried out analogously as for **12c**, by taking **9a** (1.94 g, 0.01 mol), N-ethyl, N-cyanoethylaniline (3.51 g, 0.01 mol) and acetic anhydride (10 mL). Yield: 30%; m.p. 238°C. Analysis %, Found (Calcd.): C 75 (75.2), H 5.1 (4.8), N 19.6 (19.9).

Synthesis of disperse dye (12e): Synthesis was carried out analogously as for **12c**, by taking **9a** (1.94 g, 0.01 mol), 3-acetamido N,N′-diethyl aniline (2.06 g, 0.01 mol) and acetic anhydride (30 mL). Yield: 65%; m.p. 215°C. Analysis %, Found (Calcd.): C 72 (72), H 5.4 (5.4), N 19.1 (18.2).

Synthesis of disperse dye (12f): Synthesis was carried out analogously as for **12c**, by taking **9a** (1.94 g, 0.01 mol), 3-acetamido, 6-methoxy-N,N′-diethyl aniline (2.36 g, 0.01 mol) and acetic anhydride (30 mL). Yield: 75%; m.p. 210°C. Analysis %, Found (Calcd.): C 69.4 (69.7), H 5.5 (5.5), N 16.5 (16.9).

Synthesis of disperse dye (12g): Synthesis was carried out analogously as for **12c,** by taking **9a** (1.94 g, 0.01 mol), 3-acetamido, 6-methoxy-N-ethyl, N-cyanoethyl aniline (2.61 g, 0.01 mol) and acetic anhydride (30 mL). Yield: 67%; m.p. 248°C. Analysis %, Found (Calcd.): C 68.3 (68.4), H 5.2 (5.0), N 19.2 (19.1).

Synthesis of disperse dye (12h): In a 100 mL two-necked round bottom flask equipped with a mechanical stirrer and an air condenser protected by calcium guard tube was placed **9b** (2.41 g, 0.01 mol), N,N′-3-acetamido, N,N′-diethyl aniline (2.06 g, 0.01 mol) and acetic anhydride (30 mL). A drop of sulphuric acid was added and the reaction mass was stirred and gradually heated to 90°C on an oil bath and maintained at this temperature for 5 h. The reaction was monitored by TLC. The reaction mass was added to ice-cold water .The dye with impurities precipitated, which was filtered, washed with water and dried. The impurities presenting the product were separated by washing the product with methanol. The solid that separated was filtered and extracted in benzene (20 mL). The benzene layer was repeatedly washed with 100 mL of aqueous NaOH solution (5%). The benzene layer was separated and distilled out under line vacuum to get pure dye **12h.** Yield: 51%; m.p. 235°C. Analysis %, Found (Calcd.): C 69.8 (69.7), H 6.1 (6.04), N 13.1 (13.02).

Synthesis of disperse dye (12i): Synthesis was carried out analogously as for **12h,** by taking **9b** (2.41 g, 0.01 mol), 3-acetamido-6-methoxy-N,N-diethyl aniline (2.36 g, 0.01 mol) and acetic anhydride (30 mL). Yield: 70.6%; m.p. 228°C. Analysis %, Found (Calcd.): C 67.6 (67.8), H 6.1 (6.04), N 12.2 (12.17).

Synthesis of disperse dye (12j): Synthesis was carried out analogously as for **12h,** by taking **9b** (2.41 g, 0.01 mol), 3-acetamido-6-methoxy-N-ethyl, N-cyanoethyl aniline (2.61 g, 0.01 mol) and acetic anhydride (30 mL). Yield: 64.9%; m.p. 185°C. Analysis %, Found (Calcd.): C 66.50 (66.80), H 5.70 (5.56), N 14.60 (14.43).

Dyeing procedure: The synthesized disperse dyes were applied on polyester using standard dyeing methods[33–36].

Colour and fastness measurements: Light fastness and wash fastness tests were carried out using standard methods and assessed according to international blue scale (1–8) and grey scale (1–5) respectively[37, 38].

Assessment of light fastness: A xenon arc lamp weathering tester model 60X-H machine was used to assess light fastness of dyed samples by comparison with relative blue scale standards of AATCC (16E-1964R). The xenon arc lamp employed in this apparatus was of water-cooled variety.

The specimens used were exposed in a well-ventilated exposure chamber. The air temperature in the chamber was maintained at 30°C. The variation of the light intensity over area covered by specimen and standard should not exceed 20%. The samples and the standard were exposed simultaneously under the same condition for the same time (100 h).

Pick up values: The pick up values of the dyes were determined by comparing the dyeing with standard depths:

5 = 1 × standard depth (commercial)
4 = 1/3 × standard depth (commercial)
3 = 1/4 × standard depth (commercial)
2 = 1/6 × standard depth (commercial)
1 = 1/12 × standard depth (commercial)

RESULTS AND DISCUSSION

The reaction of 1-amino-3-iminoisoindoline **(8)** with 1 mol of malononitrile **(9a)** gave the expected intermediate 3-dicyanomethylene-1-iminoisoindoline **(10a)** and the analogous reaction with ethylcyanoacetate **(9b)** gave the intermediate 3-(1-cyano 1-carbethoxy methylene)-1-iminoisoindoline **(10b).**

The structures of **(10a)** and **(10b)** were confirmed by elemental analysis and IR spectra.

The reaction of the intermediate **(10a)** and **(10b)** with N,N-disubstitued anilines having a free *para*-position gave the dyes **12a–j.**

These dyes are presented in Table-1. The structures of all these dyes were confirmed by elemental analysis and IR spectra.

The visible spectra of the dyes were recorded methanol and the data are presented in Table-2.

TABLE-2
VISIBLE ABSORPTION SPECTRA AND COLOR OF THE DYES

Dye No.	Color of dye solution	λ_{max}	ε_{max}	Colour on polyester
12a	Reddish blue	562	4.54	Reddish blue
12b	Reddish blue	549	4.41	Reddish blue
12c	Reddish blue	575	4.43	Reddish blue
12d	Reddish blue	514	4.48	Reddish blue
12e	Reddish blue	541	4.26	Reddish blue
12f	Light green	640	4.70	Light green
12g	Pink	538	4.82	Pink
12h	Blue	526	4.15	Yellow (decomp)
12i	Blue	528	4.22	Yellow (decomp)
12j	Blue	493	4.39	Yellow (decomp)

It is seen that the colour of the dyes ranged from red to green. The molar absorptivity of the dyes were uniformly good.

The dyes **12a–j** were applied on polyester.

All the dyes exhausted well on the polyester. The dyes **12h, 12i** and **12j** were not stable under the condition of dyeing as reported[1]. The light fastness and the sublimation fastness of dyes are presented in Table-3. It is seen that the light fastness and sublimation fastness ratings are reasonably good.

TABLE-3
FASTNESS PROPERTIES OF THE DYES

Dye No.	Pick up	Xeno light fastness	Sublimation fastness
12a	1	1	4
12b	4	1	4
12c	1	1	4
12d	4	1	4
12e	5	6	5
12f	4	8	5
12g	5	6	5
12h	3	3	6
12i	3	3	8
12j	3	3	6

Conclusion

1-Amino-3-iminoisoindoline **(8)** can be used as an intermediate in the synthesis of blue monomethine disperse dyes **(12a–h)** by first reacting **(8)** with malononitrile **(10a)** and **(10b)** followed by the reaction with electron-rich aromatic compound **(11)** to give disperse dyes having red to blue shade. The dyes based on ethyl cyanoacetate **(9b)** were not stable under the condition of dyeing. They were susceptible to hydrolytic cleavage under the condition of dyeing.

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