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Fused heterocycle 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one based monoazo disperse dyes

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Abstract

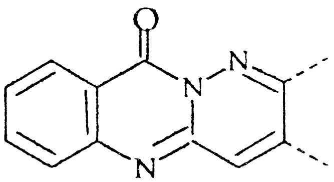
A series of new heterocyclic monoazo disperse dyes have been prepared by coupling 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one with various mono and di-N substituted derivatives of aniline. All the disperse dyes were characterized by their percentage yield, melting point, UV–visible spectroscopy, elemental analysis, infrared spectroscopy and dyeing performance on Nylon 66 and polyester fibres. The percentage dye bath exhaustion on different fibres have been found to be reasonably good and acceptable. The dyed fibres show fairly good to good fastness to light and very good to excellent fastness to washing, rubbing, perspiration and sublimation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: 11-Amino-13H-acenaphtho; Pyridazino[3,2-b]quinazoline-13-one; Synthesis; Nylon 66 fibres; Polyester fibres; Dyeing properties

1. Introduction

The development of new structure of disperse dyes have been a subject of interest and many novel structure of these dyes, useful in commercial application to polyester, polyamide or polyacrylic as well as their blends with other fibres have been discovered.

Novel colourants based on the 9-oxo-1,9a,10-triaza-9-hydro anthracene chromophoric system [1] derived from 3-amino-2-methyl-4-oxo-quinazoline and ortho quinones containing fused ring systems across the 2,3-positions, as examples of a new chromophoric system, are reported.



E. Dietz has also reported the condensation of 3-amino-2-methyl-4-oxo-quinazoline as well as its substituted derivatives with some dioxo compounds such as acenaphthenequinones, 5,6-dichloro acenaphthenequinones, phenanthrenequinones and isatin to produce various derivatives of polycyclic compounds. Which gave colour variation, like

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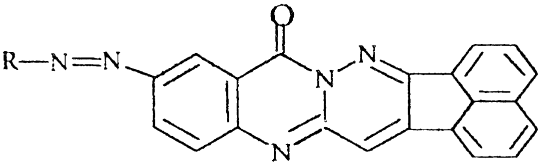
yellow, orange, brownish orange and greenish yellow [2].

In the present investigation we wish to report a new series of disperse dyes from 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one and various mono and di-N substituted derivatives of aniline. The general structure of the dyes (D_1–D_{16}) is as below



(F)

where R= various mono and di-N substituted derivatives of aniline as listed in Table 1.

2. Results and discussion

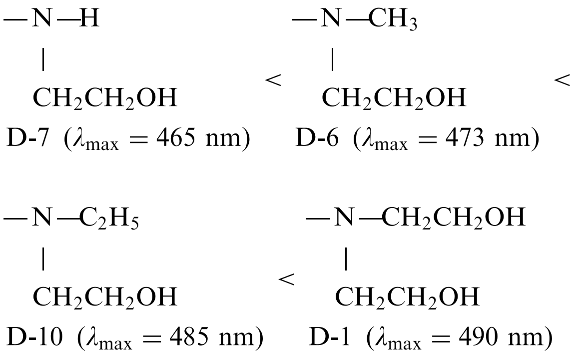
Fused heterocycle 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one **(D)** have been prepared by the condensation of 3-amino-2-methyl-6-nitro-4(3H)quinazolinone with acenaphthenequinone followed by reduction with Fe/HCl in methanol.

A series of monoazo disperse dyes (D_1–D_{16}) were prepared by the subsequent diazotization and coupling of **D**. Diazotization was carried out by the usual procedure using sodium nitrite and hydrochloric acid and the coupling was done in moderately acidic medium at 0–5 °C.

The characterization data, absorption maxima (λ_{max}) and logarithm of molar extinction co-efficient (log ε) of the 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one dyes are given in Table 1. The dyeing of Nylon 66 and polyester fibres with all the dyes were carried ut following a high temperature dyeing technique [3]. The absorption maxima of monoazo disperse dyes (D_1–D_{16}) were recorded in DMF (Fig. 2). The absorption maxima were in the range of 450–495 nm. The dyes were characterize by infrared spectra, all the dyes showed characteristic bands at 3200–3500 *br* cm^{-1} (N–H), and 1550–1575 cm^{-1} (–N=N–) stretching. The dyes D_9 and D_{11} showed a band at 700–850 cm^{-1} for C–Cl stretching. The dyes D_{11} and D_{12} showed a band at 1365–1385 cm^{-1} for (–$OCOCH_3$) stretching. The dyes D_{13}, D_{14}, D_{15} and D_{16} showed a band at 2240–2260 cm^{-1} for (–C≡N) stretching.

These dyes were applied on Nylon 66 and polyester fibres as disperse dyes, which gave variety of hues ranging from pink, golden yellow, light brown to dark brown.

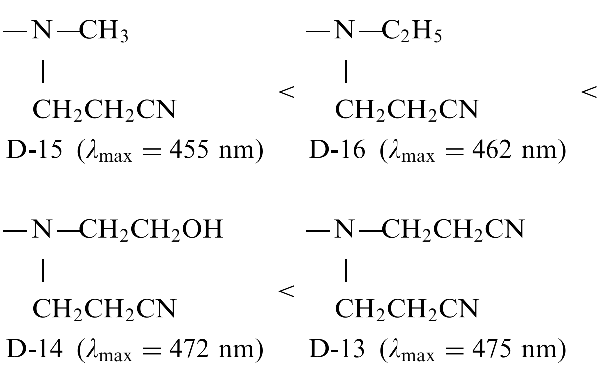
The data in the Table 1 reveals that the change in λ_{max} value depends on the nature of the substituents at the terminal amino group as well as on the phenyl ring. The bathochromic shift is observed with the nature of substituents at the terminal amino group in the following trend.



$$\begin{array}{c} -N-H \\ | \\ CH_2CH_2OH \\ \text{D-7 } (\lambda_{max} = 465 \text{ nm}) \end{array} < \begin{array}{c} -N-CH_3 \\ | \\ CH_2CH_2OH \\ \text{D-6 } (\lambda_{max} = 473 \text{ nm}) \end{array} <$$

$$\begin{array}{c} -N-C_2H_5 \\ | \\ CH_2CH_2OH \\ \text{D-10 } (\lambda_{max} = 485 \text{ nm}) \end{array} < \begin{array}{c} -N-CH_2CH_2OH \\ | \\ CH_2CH_2OH \\ \text{D-1 } (\lambda_{max} = 490 \text{ nm}) \end{array}$$

Similarly in case of cyano substituted derivatives of aniline, bathochromic shift is observed in the following trend.



$$\begin{array}{c} -N-CH_3 \\ | \\ CH_2CH_2CN \\ \text{D-15 } (\lambda_{max} = 455 \text{ nm}) \end{array} < \begin{array}{c} -N-C_2H_5 \\ | \\ CH_2CH_2CN \\ \text{D-16 } (\lambda_{max} = 462 \text{ nm}) \end{array} <$$

$$\begin{array}{c} -N-CH_2CH_2OH \\ | \\ CH_2CH_2CN \\ \text{D-14 } (\lambda_{max} = 472 \text{ nm}) \end{array} < \begin{array}{c} -N-CH_2CH_2CN \\ | \\ CH_2CH_2CN \\ \text{D-13 } (\lambda_{max} = 475 \text{ nm}) \end{array}$$

Table 1
Characterization data and percentage exhaustion of novel 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one mono azo disperse dyes

Dye	Coupling component (R)	Mol. formula	Mol. wt. g/mol	Yield (%)	m.p.[a] (°C)	λ_{max} (nm) (log ε)	% Found (Cal.)			% Exhaustion	
							C	H	N	N#[b]	P#[c]
D_1	*N,N*-bis(2-hydroxy ethyl)aniline	$C_{31}H_{24}N_6O_3$	528	70	223–225	490 (4.73)	70.44 70.46	4.52 4.55	15.90 15.91	60	55
D_2	*N,N*-bis(2-hydroxy ethyl)-*m*-amino acetanilide	$C_{33}H_{27}N_7O_4$	585	82	192–195	495 (4.50)	67.67 67.69	4.60 4.62	16.73 16.75	68	65
D_3	*N,N*-(diethyl)-*m*-amino acetanilide	$C_{33}H_{25}N_7O_2$	551	70	205–210	475 (4.30)	71.85 71.87	4.52 4.54	17.78 17.79	72	70
D_4	*N,N*-(diethyl)-*m*-amino propionate	$C_{34}H_{27}N_7O_2$	565	78	201–205	492 (4.35)	72.20 72.21	4.76 4.78	17.32 17.35	65	60
D_5	*N,N*-bis(2-hydroxy ethyl)-*m*-toluidine	$C_{32}H_{26}N_6O_3$	542	75	225–230	488 (4.60)	70.83 70.85	4.83 4.85	15.48 15.50	68	60
D_6	*N*-methyl-*N*-mono hydroxyethyl aniline	$C_{30}H_{22}N_6O_2$	498	72	220–222	473 (4.38)	72.26 72.29	4.40 4.42	16.85 16.87	65	62
D_7	*N*-mono-*N*-hydroxyethyl aniline	$C_{29}H_{20}N_6O_2$	484	82	215–220	465 (4.52)	71.88 71.90	4.10 4.13	17.35 17.36	62	58
D_8	*N*-mono-*N*-hydroxyethyl-*m*-toluidine	$C_{30}H_{22}N_6O_2$	498	71	230–235	470 (4.44)	72.27 72.29	4.40 4.42	16.85 16.87	62	60
D_9	*N,N*-bis(2-hydroxyethyl)-*m*-chloro aniline	$C_{31}H_{23}N_6O_3Cl$	562.5	79	225–227	483 (4.27)	66.10 66.13	4.07 4.09	14.91 14.93	62	55
D_{10}	*N*-ethyl-*N*-(2-hydroxyethyl)aniline	$C_{31}H_{24}N_6O_2$	512	73	200–205	485 (4.49)	72.65 72.66	4.66 4.69	16.39 16.41	70	65
D_{11}	*N,N*-bis(acetoxyethyl)-*m*-chloro aniline	$C_{35}H_{27}N_6O_5Cl$	646.5	85	228–230	471 (4.40)	64.95 64.97	4.16 4.18	18.06 18.08	65	63
D_{12}	*N,N*-bis(acetoxyethyl)aniline	$C_{35}H_{28}N_6O_5$	612	80	210–215	480 (4.38)	68.61 68.63	4.56 4.58	13.71 13.73	60	55
D_{13}	*N,N*-bis(2-cyanoethyl)aniline	$C_{33}H_{22}N_8O$	546	75	222–225	475 (4.42)	72.51 72.53	4.01 4.03	20.50 20.51	66	62
D_{14}	*N*-(2-cyanoethyl)-*N*-(2-hydroxyethyl)aniline	$C_{32}H_{23}N_7O_2$	537	72	210–212	472 (4.35)	71.49 7 1.51	4.26 4.28	18.23 18.25	70	68
D_{15}	*N*-methyl-*N*-cyanoethyl aniline	$C_{31}H_{21}N_7O$	507	78	222–225	455 (4.27)	73.35 73.37	4.12 4.14	19.31 19.33	60	58
D_{16}	*N*-ethyl-*N*-cyanoethyl aniline	$C_{32}H_{23}N_7O$	521	75	220–222	462 (4.46)	73.68 73.70	4.40 4.41	18.79 18.81	68	65

[a] All the melting points are uncorrected.
[b] N#—Nylon 66.
[c] P#—polyester.

Small bathochromic shift is also observed by introducing–$NHCOCH_3$ in the phenyl ring at the ortho position of the azo group (D-1–D-2), similarly comparison of D-3 and D-4 also shows bathochromic shift by displacing –$NHCOCH_3$ with –$NHCOC_2H_5$. Introduction of the methyl group in

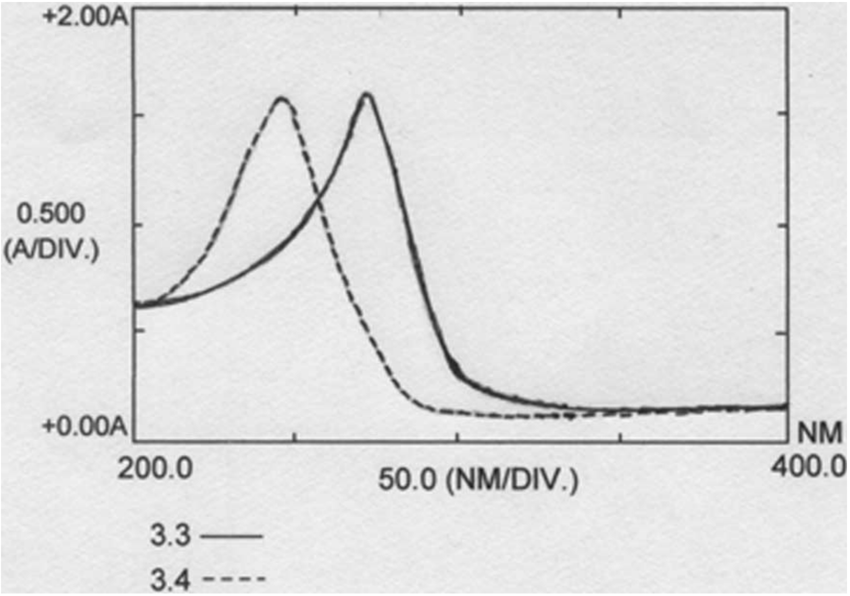


Fig. 1. UV–visible spectra of intermediate 3.3 and 3.4: 3.3 —— (λ_{max}: 270_{nm}); 3.4 - - - - (λ_{max}: 249_{nm}).

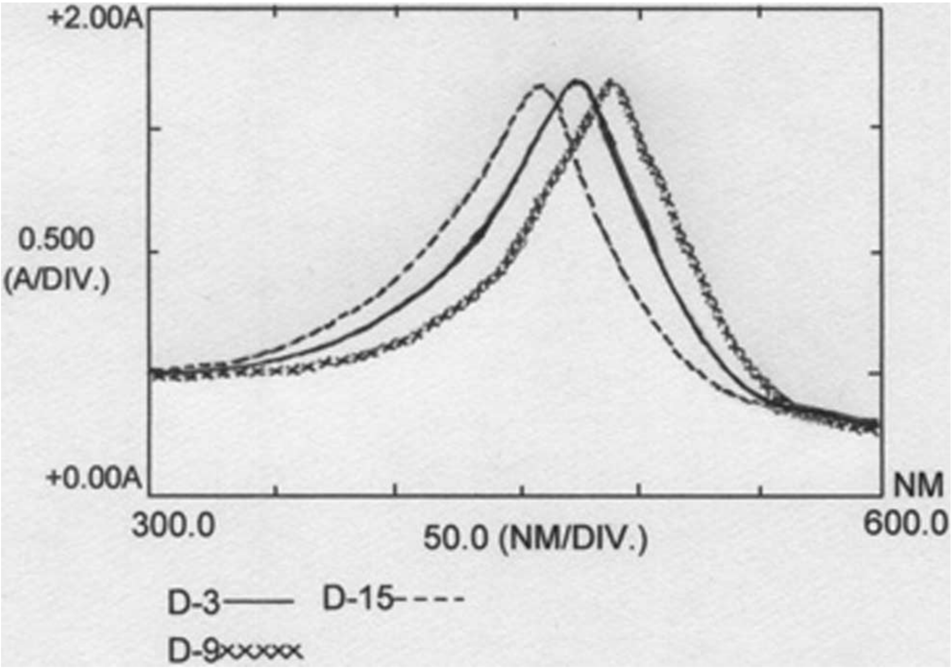


Fig. 2. UV–visible spectra of dyes D_3, D_9 and D_{15}. D_3 —— (λ_{max}: 475_{nm}), D_{15} - - - - (λ_{max}: 455_{nm}) D_9 (λ_{max}: 483_{nm}).

the phenyl ring at ortho to azo group is also shown as a bathochromic shift of 5 nm (D-7 and D-8). While hypsochromic shift is observed with the introduction of chlorine group in the phenyl ring (D-1 and D-9 plus D-11 and D-12).

The extent of exhaustion on the Nylon 66 and polyester fibres are also given in Table 1. The higher percentage exhaustion on the Nylon 66 fibre may be expected due to its relatively open structure.

The light fastness test was carried out using a Microseal light fastness tester in conjunction with a mercury lamp (MB/U 400-W) according to BS:1006-1978. Data of the fastness properties given in Table 2 show that the light fastness ranges from fairly good to good for all the disperse dyes for both the fibres except dyes D_1, $D_{3,}$ D_6 and D_7, which are fair to fairly good. The higher the rating, better is the fastness. The fastness to washing, rubbing, perspiration and sublimation are very good to excellent for all the disperse dyes. The fastness to washing is done by using cotton fabric for the evaluation of staining. This indicates good penetration and affinity of these disperse dyes for the fibres.

3. Experimental

All melting points are uncorrected and are expressed in °C. IR spectra were recorded on a Nicolet Impact −400 D FT–IR spectrophotometer using KBr pellets. The ^{1}H NMR spectra were recorded on Hitachi R-1500 instrument, using TMS as internal standard. Chemical shifts are given in δ (ppm). Absorption spectra of the dye solution in DMF were recorded on a Shimadzu UV 240 instrument.. Fastness test to light, sublimation and perspiration was assessed in accordance with BS: 1006-1978. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-1961, and the wash fastness test in accordance with IS: 765-1979.

3.1. Preparation of 3-amino-2-methyl-6-nitro-4(3H)-quinazolinone (A)

The title compound was prepared following a sequence of reactions according to the procedure described in the literature [4–7]. Yield 65%; m.p. 221–223 °C; IR(KBr). The compound showed characteristic bands at 3400–3500 cm^{-1} for–NH_2, at 1535–1550 s cm^{-1} for –NO_2 group, at 1690–1700 s cm^{-1} for the –C=O group and at 1310–1330 cm^{-1} for the –CH_3 group. Mol. formula $C_9H_8N_4O_3$, found: %C 49.05, %H 3.60, %N 25.44; calcd. %C 49.09, %H 3.64, %N 25.46. ^{1}H NMR ($CDCl_3$): 7.28 δ to 8.29 δ (6H, complex, aromatic proton); 4.94 δ (2H, singlet, aromatic-amine); 2.12 δ–2.70 δ (3H, singlet, aromatic-methyl).

3.2. Preparation of acenaphthenequinone (B)

The title compound was prepared according to the procedure described in literature [8]. Yield 70%; m.p. 260–261 °C; IR(KBr). The compound showed characteristic bands at 1690–1700 s cm^{-1} for –C=O group. Mol. formula $C_{12}H_6O_2$, found: %C 79.10, %H 3.29; calcd: %C 79.12, %H 3.30. ^{1}H NMR($CDCl_3$): 7.75 δ–8.76 δ (6H, complex, aromatic proton).

3.3. Preparation of 11-nitro-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one (C)

3-Amino-2-methyl-6-nitro-4(3H)-quinazolinone (2.5 g, 0.011 mol), acenaphthenequinone (2.002 g, 0.011 mol) and acetic anhydride (1.03 ml, 0.011 mol) were put into a round bottom flask. The reaction mixture was refluxed for 5–6 h. The contents were poured onto crushed ice. The product was isolated and crystallized by methanol. Yield 70%; m.p. 230–223 °C; absorption maxima (λ_{max}) recorded in DMF (Fig. 1); IR(KBr): the compound showed characteristic bands at 1535–1550 s cm^{-1} for the –NO_2 group and at 1690–1700 s cm^{-1} for (–C=O) group. Mol. formula $C_{21}H_{10}N_4O_3$, found: %C 68.84, %H 2.70, N 15.28; calcd: %C 68.85, %H 2.73, %N 15.30. ^{1}H NMR($CDCl_3$): 7.26 δ–8.58 δ (6H, complex, aromatic proton).

3.4. Preparation of 11-amino-13H-acenaphtho [1,2-e]pyridazino[3,2-b]quinazoline-13-one (D)

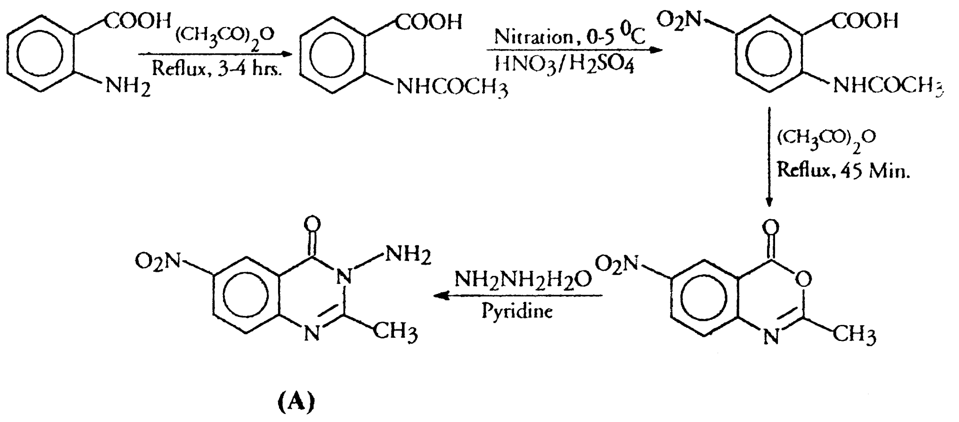
11-Nitro-13H-acenaphtho[1,2-e]pyridazino[3,2-b] quinazoline-13-one (3.29 g.,0.009 mol) dissolved in methanol (15 ml, 0.36 mol) and concentrated HCl

Table 2
Shade and fastness properties of novel 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one mono azo disperse dyes

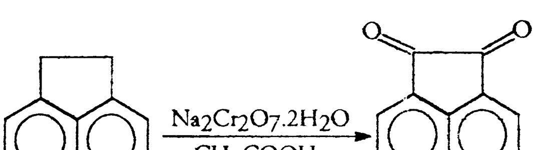
Dye	Colour of dyed fibres		Light fastness		Wash fastness		Rubbing fastness				Perspiration fastness				Sublimation fastness	
							$N^{\#}$		$P^{\#}$		$N^{\#}$		$P^{\#}$			
	$N^{\#a}$	$P^{\#b}$	$N^{\#}$	$P^{\#}$	$N^{\#}$	$P^{\#}$	Dry	Wet	Dry	Wet	Acid	Alkaline	Acid	Alkaline	$N^{\#}$	$P^{\#}$
D_1	Light brown	Light brown	3	3	4	4	4	4	4	4	4	4	4	4	4	4
D_2	Light brown	Light brown	3–4	3–4	5	5	4–5	4–5	4–5	4–5	5	5	5	5	4–5	4–5
D_3	Light brown	Light brown	3	3	4	4	4	4	4	4	4	4	4	4	4	4
D_4	Dark brown	Dark pink	4	4	4–5	4–5	4–5	4–5	4–5	4–5	5	5	5	5	4–5	4–5
D_5	Light pink	Light pink	3–4	3–4	4	4	4	4	4	4	4–5	4–5	4–5	4–5	5	5
D_6	Light yellow	Light yellow	3	3	4	4	4	4	4	4	4	4	4	4	4	4
D_7	Light pink	Light pink	3	3	4	4	4	4	4	4	4	4	4	4	4	4
D_8	Dark brown	Light brown	4	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
D_9	Brown	Brown	4–5	4–5	5	5	4–5	4–5	4–5	4–5	5	5	5	5	4–5	4–5
D_{10}	Brown	Brown	4	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
D_{11}	Light golden yellow	Light golden yellow	4–5	4–5	5	5	4–5	4–5	4–5	4–5	5	5	5	5	5	5
D_{12}	Brown	Light brown	4	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
D_{13}	Dark brown	Brown	4	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
D_{14}	Brown	Brown	4–5	4–5	5	5	4–5	4–5	4–5	4–5	5	5	5	5	5	5
D_{15}	Light brown	Light brown	4	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
D_{16}	Brown	Brown	4	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5

[a] $N^{\#}$—Nylon 66.

[b] $P^{\#}$— polyester.



Scheme 1.



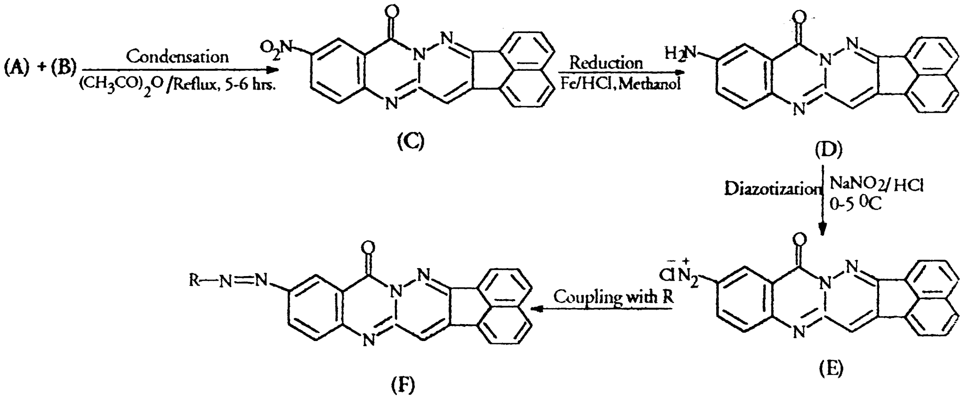
Scheme 2.

(6 ml) were added into a 250 ml round bottom flask and then heated in a water bath at reflux temperature. To this, iron powder (1.5 g) was added pinch by pinch within an hour with continuous stirring. The reaction mixture was further refluxed for 90 min and then hot filtered. The filtrate was neutralized with aqueous ammonia (50%) until the brown solid separated out.

This product was filtered and crystallized from DMF/EtOH to get fine dark brown powder. Yield 60%; m.p. 240–242 °C; absorption maxima (λ_{max}) recorded in DMF (Fig. 1); IR(KBr). The compound showed characteristic bands at 3400–3500 s cm^{-1} for C–NH stretching, at 1375–1400 s cm^{-1} for C–N stretching and at 1690–1700 s cm^{-1} for –C=O group. Mol formula: $C_{21}H_{12}N_4O$, found: %C 74.98, %H 3.55, %N 16.65; calcd: %C 75.00, %H 3.57, %N 16.66. ^{1}H NMR (DMSO-d_6): 7.25 δ–8.50 δ (6H, complex, aromatic proton) and 2.72 δ–3.16 δ (2H, singlet, aromatic-amine).

3.5. Diazotization of 11-amino-13H-acenaphtho [1,2-e]pyridazino[3,2-b]quinazoline-13-one (E)

Diazotization of title compound was carried out by usual method [9].



Scheme 3. R represents various mono and di-N substituted derivatives of aniline as lised in Table 1.

3.6. Coupling of diazo solution with N,N-bis(2-hydroxyethyl)aniline

Formation of dye D_1: *N,N*-bis(2-hydroxyethyl) aniline (0.6697 g, 0.0037 mol) was dissolved in hydrochloric acid (10% w/v), the solution was diluted with water (6 ml) and cooled at 0–5 °C. To this well stirred solution, a freshly prepared diazo solution was added at 0–5 °C dropwise in about 45 min maintaining the temperature below 5 °C. Stirring was continued for 24 h at 0–5 °C maintaining pH between 4 and 5 by adding the required amount of ice cold solution of sodium carbonate (10% w/v). The product was filtered, washed several times with water and dried at 40 °C. The reddish brown solid thus obtained was dissolved in DMF and precipitated by adding chloroform. Yield 70%, m.p. 223–225 °C.

4. Conclusion

Azo disperse dyes based on 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one have been synthesized. These dyes give mostly pink, yellow and brown shades on Nylon 66 and polyester fibres having 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.

Acknowledgements

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