SYNTHESIS AND APPLICATION OF NOVEL HETEROCYCLIC DYES BASED ON 11-AMINO-3-BROMO-13H-ACENAPHTHO[1,2-e]PYRIDAZINO[3,2-b]-QUINAZOLI NE-13-ONE

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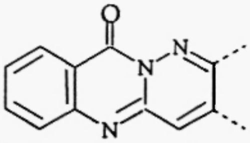
Abstract:

Synthesized a new fused heterocyclic compound, 11-Amino-3-Bromo-13H-acenaphtho[1,2-e]pyridazino[3,2-b]-quinazoline-13-one and is used to synthesize a novel series of heterocyclic mono azo dyes by coupling with various naphthols. All the 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 has been found to be reasonably good and acceptable. The dyed fibres showed fair to fairly good fastness to light and very good to excellent fastness to washing, rubbing, perspiration and sublimation.

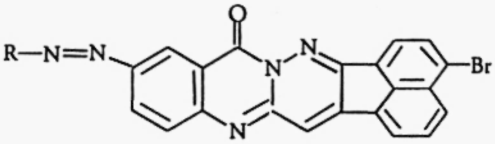
1. Introduction:

The development of new structure of azo 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(**I**) 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.



As no report seems to be available in the literature on the use of 11-Amino-3-Bromo-13H-acenaphtho[1,2-e]-pyridazino[3,2-b]quinazoline-13-one azo dyes, an attempt has been made to synthesize a series of azo dyes by diazotizing this heterocyclic amino compound and coupling with various naphthols. The general structure of the dyes [D_a to D_k] is as below



(VII)

Where R= various naphthols as listed in chart-1.

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2. Experimental:

All melting points are uncorrected. 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 dye solution in DMF were recorded on a Shimadzu UV 240 instrument. Fastness test to light, sublimation and perspiration was assessed in accordance with AATCC/15/1985. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC/88/1988 and the wash fastness test in accordance with IS: 765-1979.

2.1 Preparation of 3-Amino-2-methyl-6-nitro-4(3H)-quinazolinone (I):

The title compound was prepared following a sequence of reactions according to the procedure described in literature (2-5). Yield 65 %; m.p. 221-3 °C, IR(KBr): The compound showed characteristic medium intense bands at 3415 cm^{-1} and 3496 cm^{-1} for -NH stretching of -NH_2, strong bands at 1347 cm^{-1} and 1528 cm^{-1} for -N=O stretching of -NO_2 and at 1696s cm^{-1} for (N-C=O) group. Mol. Formula $C_9H_8N_4O_3$, Found: %C 49.05, %H 3.60, %N 25.44; Calculated: %C 49.09, %H 3.64, %N 25.46; ^{1}H NMR(acetone-d_6): 7.28δ to 8.29δ (4H, multiplet, aromatic proton); 4.94δ (2H, singlet, aromatic- amine); 2.12δ to 2.70δ (3H, singlet, aromatic- methyl).

2.2 Preparation of 5-Bromo-acenaphthene (II):

The title compound was prepared according to the procedure described in literature (6).

Yield 79%; m.p. 51-52 °C; IR(KBr): The compound showed characteristic bands at 775 cm^{-1} for C-Br stretching. Mol.Formula $C_{12}H_9Br$, Found: %C 61.38, %H 3.54; Calculated: %C 61.83, %H 3.86; ^{1}H NMR($CDCl_3$): 7.82δ to 8.75δ (5H, multiplet, aromatic proton); 2.30δ to 2.70δ (4H, triplet, aromatic -CH_2- proton).

2.3 Preparation of 5-Bromo-acenaphthenequinone (III):

The title compound was prepared according to the procedure described in literature (7).

Yield 50%; m.p. 244-46 °C; IR(KBr): The compound showed characteristic bands at 1736s cm^{-1} for -C=O group and at 775 cm^{-1} for C-Br stretching. Mol. Formula $C_{12}H_5O_2Br$, Found: %C 54.78, %H 1.57; Calculated: %C 55.19, %H 1.92; ^{1}H NMR($CDCl_3$): 7.82δ to 8.75δ (5H, multiplet, aromatic proton).

2.4 Preparation of 3-Bromo-11-nitro-13H-acenaphtho[1,2-e]pyridazino[3,2-b]- quinazoline-13-one (IV):

3-Amino-2-methyl-6-nitro-4(3H)-quinazolinone (2.5gms, 0.011mole) was fused with 5-Bromo-acenaphthenequinone (2.965gms, 0.011mole) for 30 minutes at 220 °C followed by addition of acetic acid (0.5ml, 0.011mole) (8) and reaction was refluxed for 5-6 hrs. The contents were poured onto crushed ice. The product was isolated and crystallized from methanol. Yield 65 %; m.p. 225-30 °C; IR(KBr): The compound showed characteristic strong bands at 1347 cm^{-1} and 1528 cm^{-1} for -N=O stretching of -NO_2, at 1696s cm^{-1} for (N-C=O) group and at 775 cm^{-1} for C-Br stretching. Mol.Formula $C_{21}H_9N_4O_3Br$, Found: %C 56.22, %H 1.69, %N 12.18; Calculated: %C 56.64, %H 2.02, %N 12.59; ^{1}H NMR($CDCl_3$): 7.03δ to 7.83δ (9H, multiplet, aromatic proton).

2.5 Preparation of 11-amino-3-Bromo-13H-acenaphtho[1,2-e]pyridazino[3,2-b]-quinazoline-13-one (V):

3-Bromo-11-nitro-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one(5.0gms,0.0112mole) dissolved in methanol (25ml, 0.056mole) and concentrated HCl (9ml) were added into a 250ml round bottom flask and then heated in water bath at reflux temperature. To it iron powder (1.25gms, 0.022mole) was added pinch by pinch within an hour with continuous stirring. The reaction mixture was further refluxed for 90 min. and then filtered hot. 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. 235-40 °C; IR(KBr): The compound showed characteristic bands at 3422_{br} cm^{-1} for -NH stretching of NH_2 group, at 1696s cm^{-1} for (N-C=O) group and 775 cm^{-1} for C-Br stretching. Mol. Formula: $C_{21}H_{11}N_4OBr$, Found: %C 60.31, %H 2.29, %N 13.08; Calculated: %C 60.74, %H 2.65, %N 13.50; ^{1}H NMR (DMSO-d_6): 7.25δ to 8.50δ (9H, multiplet, aromatic proton) & 2.72δ to 3.16δ (2H, singlet, aromatic- amine).

2.6 Diazotization and coupling of 11-amino-3-Bromo-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one (VI):

Diazotization of title compound was carried out by usual method (9).

3. Dye application:

The dyeing of nylon 66 and polyester fibres with all the dyes were carried out following the high temperature dyeing technique using the glycerin bath "Laboratory High Temperature Dyeing Machine" containing twelve beakers (10).

4. Results and Discussion:

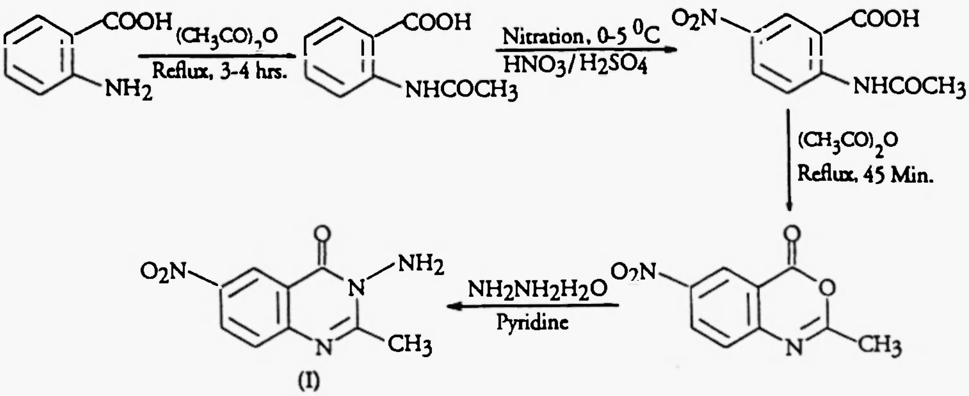
Fused heterocycle 11-Amino-3-Bromo-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one (V) have been prepared by the condensation of 3-Amino-2-methyl-6-nitro-4(3H)quinazolinone with 5-Bromo- acenaphthenequinone followed by reduction with Fe/HCl in methanol.

A series of azo dyes (D_a to D_k) were prepared by the subsequent diazotization and coupling of **V**. Diazotization was carried out by the usual procedure using sodium nitrite and hydrochloric acid and the coupling was done in moderately alkaline medium at 0-5 ^{0}C.

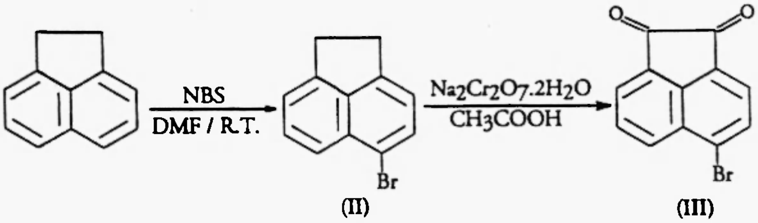
The characterization data, absorption maxima (λ_{max}) and logarithm of molar extinction co-efficient (log∈) of the 11-Amino-3-Bromo-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one dyes are given in Table-1. The absorption maxima of mono azo dyes (D_a-D_k) were recorded in DMF. The absorption maxima were in the range of 392nm to 530nm. No particular trend have been observed in the absorbance value for this series dyes, however, the dyes showed bathochromic shift with the introduction of the electron donating substituents in the phenyl ring of the various naphthols moiety in the sequence of $H< CH_3< OCH_3< OC_2H_5$. The dyes were characterized by infrared spectra, all the dyes showed characteristic bands at 3469br cm^{-1} for (-OH) stretching, at 1696_s cm^{-1} for (-N-C=O) stretching, at 775_s cm^{-1} for (-C-Br) stretching and at 1559_s cm^{-1} for (-N=N-) stretching. The dyes D_e and D_f showed a medium strong band at 836_s cm^{-1} for (-C-Cl) stretching. The dyes D_b, D_f and D_j showed a strong band at 1330_s cm^{-1} for (-C-CH_3) stretching. The dye D_g showed both strong band at 1540_s cm^{-1} and 1360_s cm^{-1} for (-C-NO_2) stretching.

These dyes were applied on nylon 66 and polyester fibres as azo dyes, which gave variety of hues ranging from pink, red and brown. The variation of the shades of the dyed fibres results from the alternation in the coupling components, but difference arises from both, the nature and position of the substituent. The data of percentage exhaustion on the

Reaction Scheme 1:



Reaction Scheme 2:



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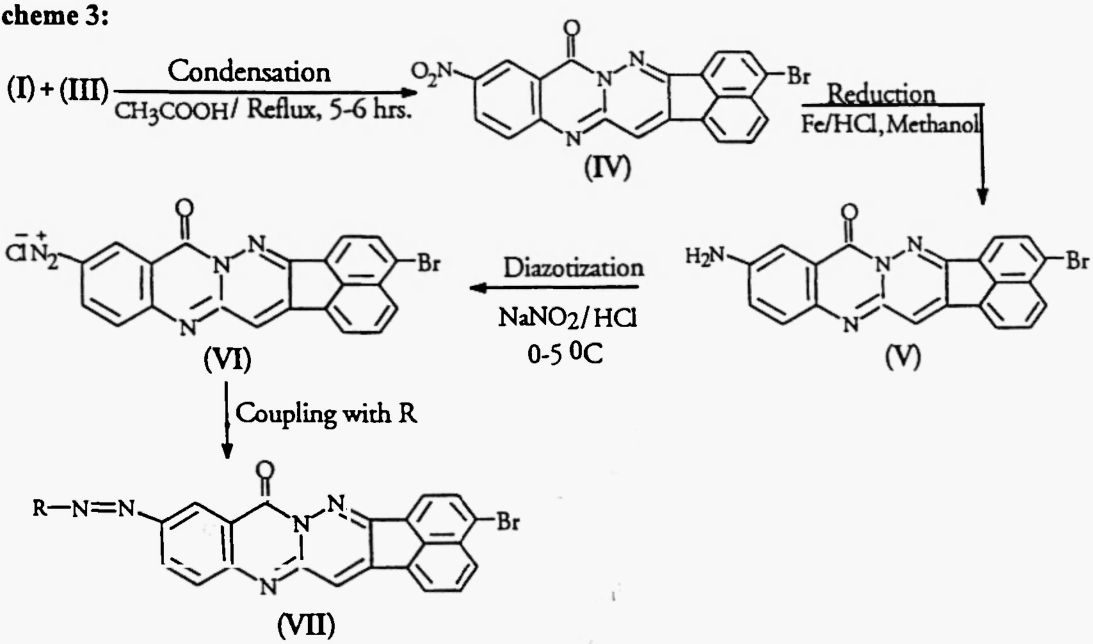
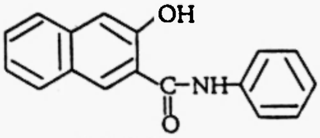


Where R= various naphthols as listed in chart-1

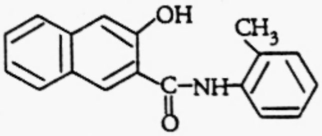
Chart:1

a.



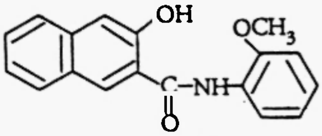
Naphthol AS

b.



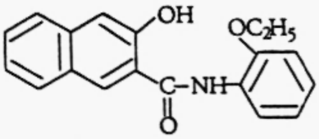
Naphthol ASD

c.



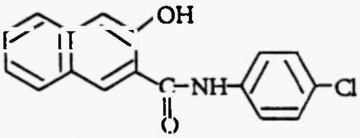
Naphthol ASOL

d.



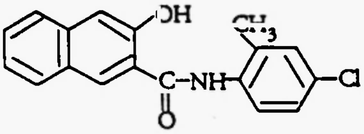
Naphthol ASPH

e.



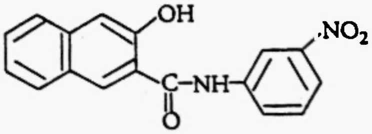
Naphthol ASE

f.



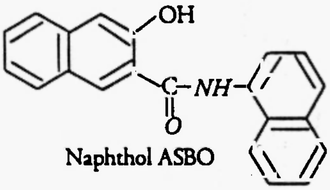
Naphthol ASTR

g.



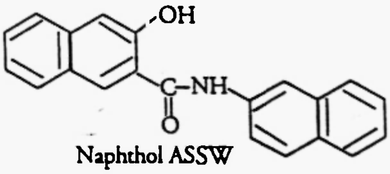
Naphthol ASBS

h.



Naphthol ASBO

i.



Naphthol ASSW

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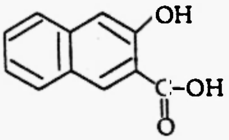
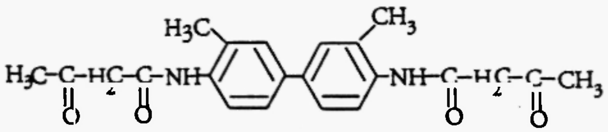


BON ACID

j.



Naphthol ASG

TABLE- 1

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

Dye	Coupling Component (R)	Mol. Formula	Mol. Wt. gm/mol	Yield (%)	m.p.* ^0C	λ^*_{max} nm (log ∈)	% Found, %(Cal.)			% Exhaustion	
							C	H	N	N*	P*
D_a	Naphthol-AS	$C_{38}H_{21}N_6O_3Br$	688	80	222-225	510 (4.20)	65.92 (66.28)	2.65 (3.05)	11.71 (12.21)	65	62
D_b	Naphthol-ASD	$C_{39}H_{23}N_6O_3Br$	702	82	220-222	520 (4.39)	66.32 (66.67)	2.96 (3.28)	11.55 (11.97)	63	60
D_c	Naphthol-ASOL	$C_{39}H_{23}N_6O_4Br$	718	75	200-205	522 (4.12)	64.77 (65.18)	2.80 (3.20)	11.34 (11.70)	69	65
D_d	Naphthol-ASPH	$C_{40}H_{25}N_6O_4Br$	732	72	203-205	530 (4.70)	65.15 (65.57)	3.01 (3.42)	10.98 (11.48)	70	66
D_e	Naphthol-ASE	$C_{38}H_{20}N_6O_3ClBr$	722.5	70	200-202	520 (4.15)	62.70 (63.11)	2.37 (2.77)	11.17 (11.63)	62	60
D_f	Naphthol-ASTR	$C_{39}H_{22}N_6O_3ClBr$	736.5	74	210-212	525 (4.27)	63.16 (63.54)	2.64 (2.99)	16.96 (11.41)	68	65
D_g	Naphthol-ASBS	$C_{38}H_{20}N_7O_5Br$	733	72	205-210	522 (4.22)	61.83 (62.21)	2.25 (2.73)	12.87 (13.37)	65	62
D_h	Naphthol-ASBO	$C_{42}H_{23}N_6O_3Br$	738	79	195-198	495 (4.35)	67.94 (68.29)	2.71 (3.12)	10.91 (11.38)	72	69
D_i	Naphthol-ASSW	$C_{42}H_{23}N_6O_3Br$	738	75	208-210	515 (4.30)	67.90 (68.29)	2.70 (3.12)	10.89 (11.38)	68	65
D_j	Naphthol-ASG	$C_{43}H_{31}N_7O_5Br$	804	85	215-218	409 (4.25)	63.80 (64.18)	3.48 (3.86)	11.74 (12.19)	65	62
D_k	BON-acid	$C_{32}H_{16}N_5O_4Br$	613	76	200-202	525 (4.36)	62.22 (62.64)	2.31 (2.61)	10.93 (11.42)	70	65

* All the melting points are uncorrected, N* – Nylon 66; P* – Polyester;

TABLE- 2

Fastness properties of Novel 11-Amino-3-Bromo-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one mono azo dyes

Dye	Light Fastness		Washing Fastness		Rubbing Fastness				Perspiration Fastness				Sublimation Fastness	
					N'		P*		N'		P*			
	N'	P*	N'	P*	Dry	Wet	Dry	Wet	Acidic	Alkaline	Acidic	Alkaline	N'	P*
D_a	3	3	5	5	5	5	5	5	5	5	5	5	5	5
D_b	4	4	5	5	5	5	5	5	5	5	5	5	5	5
D_c	3	3	5	5	5	4	5	5	4	4	5	5	5	4
D_d	3	3	5	5	5	5	5	5	5	5	5	5	5	4
D_e	4	4	5	5	5	5	4	4	5	5	4	4	5	5
D_f	3	3	5	4	5	4	5	5	4	4	5	5	4	5
D_g	3	3	4	5	4	5	5	5	5	5	5	5	5	5
D_h	3	3	4	5	4	5	4	4	5	5	5	5	5	4
D_i	3	3	4	4	4	5	4	4	5	5	5	5	5	4
D_j	4	4	5	5	4	4	5	5	4	4	4	4	5	5
D_k	4	4	5	5	5	5	5	5	5	5	5	5	5	5

N' – Nylon 66; P* – Polyester;

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 the straight light mercury lamp (MB/U 400-W) under the standard condition set out in AATCC/15/1985. Data of the fastness properties given in the Table-2 show that the light fastness ranges from fair to fairly good for all the dyes for both the fibres. The fastness to washing, rubbing, perspiration and sublimation are very good to excellent for all the dyes. This indicates good penetration and affinity of these dyes for the fibres.

5. Conclusion:

Azo dyes based on 11-Amino-3-Bromo-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazoline-13-one mostly gave pink, red and brown shades on nylon 66 and polyester fibres having fair to fairly good light fastness and very good to excellent washing fastness, rubbing fastness, perspiration fastness and sublimation fastness on both substrates. The dyes have better exhaustion on nylon 66 than polyester, probably due to the greater accessibility of the open structure in nylon 66.

6. Acknowledgement :

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