

Synthesis and application of novel heterocyclic dyes based on 11-amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one

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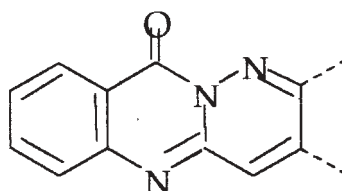
Abstract: A new fused heterocyclic compound, 11-amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one was synthesized and used to prepare a novel series of heterocyclic mono azo dyes by coupling with various naphthols. All the mono azo dyes were characterized by their melting point, elemental analysis, UV-visible spectrum, infrared spectrum and dyeing performance on nylon and polyester fibres. The percentage dye bath exhaustion on different fibres was found to be reasonably good and acceptable. The dyed fibres show fair to good fastness to light and very good to excellent fastness to washing, rubbing, perspiration and sublimation.

Keywords: 11-Amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one, synthesis, nylon fibres, polyester fibres, dyeing properties.

INTRODUCTION

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

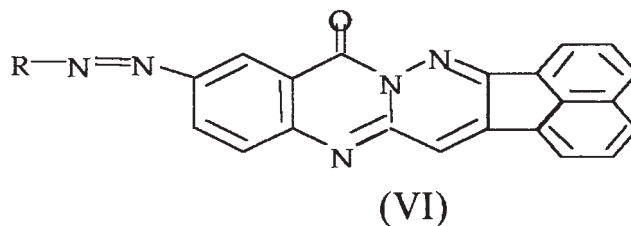
Novel colorants based on the 9-oxo-1,9a,10-triaza-9-hydroanthracene chromophoric system,¹ derived from 3-amino-2-methyl-4-oxo-quinazoline and ortho quinones containing fused ring systems across the 2,3-positions, as examples of a new chromophoric system have been reported.



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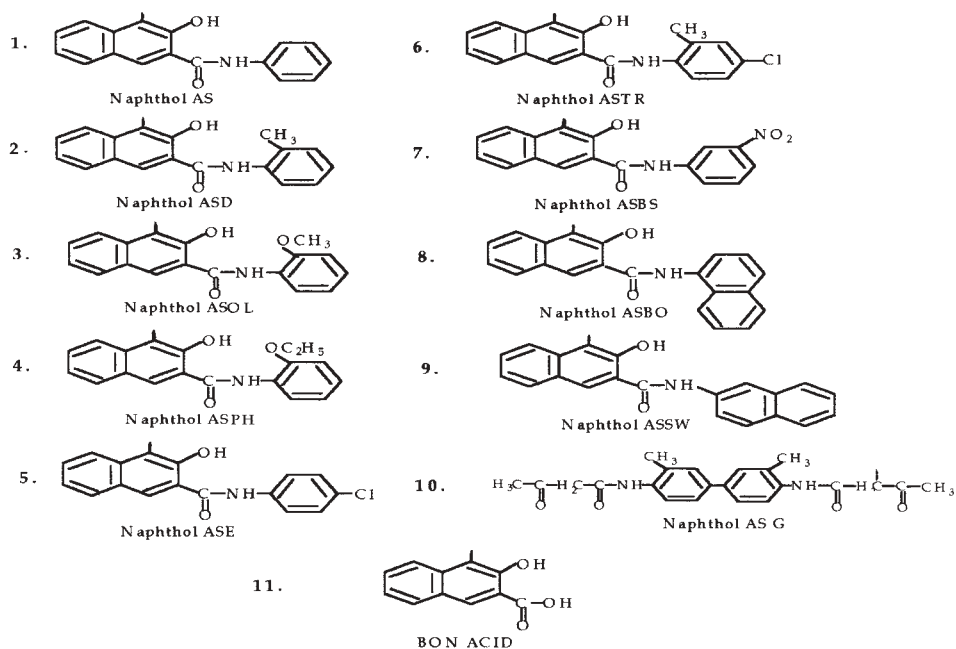
E. Dietz has reported the condensation of 3-amino-2-methyl-4-oxo-quinazoline, as well as its substituted derivatives, with some dioxo compounds such as acenaphthenequinones, 5,6-dichloro acenaphthenequinones, phenanthrenequinones and isatin to produce various derivatives of polycyclic compounds. These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

In the present investigation, a new series of mono azo dyes from 11-amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one and various naphthols is reported. The general structure of the dyes [D₁ to D₁₁] is as below

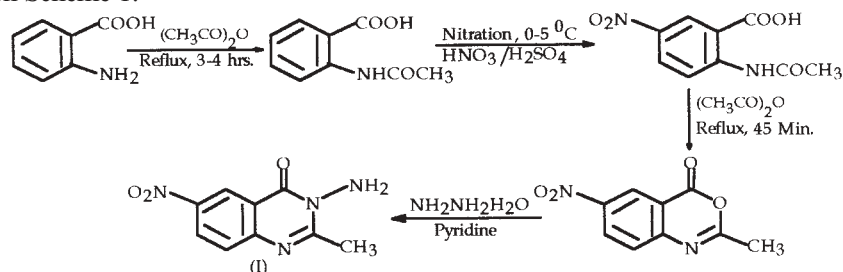


where R= various naphthols as shown in Chart 1

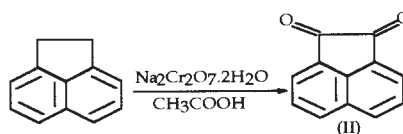
Chart 1



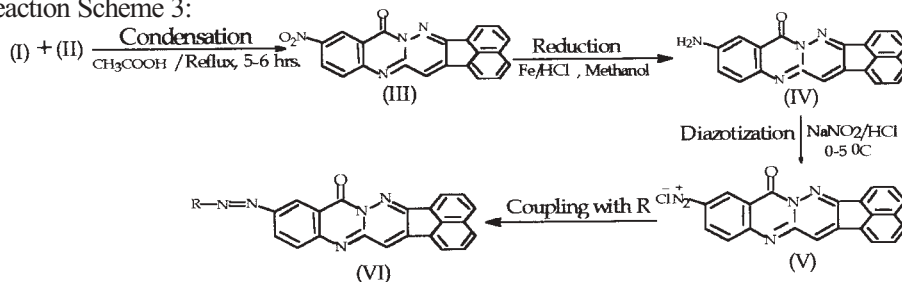
Reaction Scheme 1:



Reaction Scheme 2:



Reaction Scheme 3:



EXPERIMENTAL

All melting points are uncorrected and are expressed in °C. The IR spectra were recorded on a Nicolet Impact – 400 D FT-IR spectrophotometer using the KBr pellets technique. The ¹H-NMR spectra were recorded on a Hitachi R-1500 instrument, using TMS as the internal standard. Chemical shifts are given in δ (ppm). The absorption spectra of the dye solutions in DMF were recorded on a Shimadzu UV 240 instrument. The dyeing of nylon and polyester fibres with all the dyes were carried out using a glycerin bath “Laboratory High Temperature Dyeing Machine” containing twelve beakers.³ The fastness 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.

Preparation of 3-amino-2-methyl-6-nitro-4(3H)-quinazolinone (I)

The title compound was prepared following a sequence of reactions according to a procedure described in the literature.^{4,6} Yield 75%; m.p. 221–3 °C; IR(KBr): the compound showed characteristic medium intense bands at 3415 cm⁻¹ and 3496 cm⁻¹ corresponding to –NH stretching of –NH₂, strong bands at 1508 cm⁻¹ and 1360 cm⁻¹ for –N=O stretching of –NO₂ and at 1696 cm⁻¹ for the (N–C=O) group of quinazolinone. Mol. formula C₉H₈N₄O₃. Found: %C 49.05, %H 3.60, %N 25.44. Calcd: %C 49.09, %H 3.64, %N 25.46. ¹H-NMR(acetone-d₆): δ 7.28 to 8.29 (2H, *m*, aromatic proton); δ 4.94 (2H, *s*, aromatic amine); δ 2.12 to 2.70 (3H, *s*, aromatic methyl).

Preparation of acenaphthenequinone (II)

The title compound was prepared according to a procedure described in the literature.⁷ Yield 50%; m.p. 260–1 °C; IR(KBr): The compound showed characteristic bands at 1736 cm⁻¹ corresponding to the –C=O group. Mol. formula C₁₂H₆O₂. Found: %C 79.10, %H 3.29; Calcd: %C 79.12, %H 3.30. ¹H-NMR(CDCl₃): δ 7.75 to 8.76 (6H, *m*, aromatic proton).

TABLE I. Characterization data and percentage exhaustion of novel 11-amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one mono azo dyes

Dye	Coupling component R	Mol. formula	Mol. wt. g/mol	Yield %	M.p.* °C	λ_{\max}/nm (log ϵ)	%Found (% calcd.)			% Exhaustion	
							C	H	N	N*	P*
D ₁	Naphthol-AS	C ₃₈ H ₂₂ N ₆ O ₃	610	68	200–202	500 (4.10)	74.7 (74.8)	3.5 (3.6)	13.7 (13.8)	70	68
D ₂	Naphthol-ASD	C ₃₉ H ₂₄ N ₆ O ₃	624	70	180–185	515 (4.00)	74.8 (75.0)	3.6 (3.9)	13.4 (13.5)	65	60
D ₃	Naphthol-ASOL	C ₃₉ H ₂₄ N ₆ O ₄	640	65	205–208	520 (4.10)	73.0 (73.1)	3.6 (3.8)	13.0 (13.1)	72	70
D ₄	Naphthol-ASPH	C ₄₀ H ₂₆ N ₆ O ₄	654	60	190–195	528 (4.15)	73.2 (73.4)	3.8 (4.0)	12.7 (12.8)	62	58
D ₅	Naphthol-ASE	C ₃₈ H ₂₁ N ₆ O ₃ Cl	644.5	70	190–195	498 (4.16)	70.6 (70.8)	3.2 (3.3)	12.9 (13.0)	60	55
D ₆	Naphthol-ASTR	C ₃₉ H ₂₃ N ₆ O ₃ Cl	658.5	65	192–196	512 (4.15)	71.0 (71.1)	3.4 (3.5)	12.7 (12.8)	65	60
D ₇	Naphthol-ASBS	C ₃₈ H ₂₁ N ₇ O ₅	655	68	200–205	520 (4.12)	69.5 (69.6)	3.1 (3.2)	14.9 (15.0)	68	62
D ₈	Naphthol-ASBO	C ₄₂ H ₂₄ N ₆ O ₃	660	66	180–184	590 (4.12)	76.5 (76.4)	3.5 (3.6)	12.6 (12.7)	62	58
D ₉	Naphthol-ASSW	C ₄₂ H ₂₄ N ₆ O ₃	660	72	192–195	510 (4.20)	76.1 (76.4)	3.2 (3.6)	12.4 (12.7)	65	60
D ₁₀	Naphthol-ASG	C ₄₃ H ₃₃ N ₇ O ₅	1074	68	200–204	400 (4.54)	71.1 (71.5)	3.6 (3.9)	15.10 (15.6)	60	55
D ₁₁	BON-acid	C ₃₂ H ₁₇ N ₅ O ₄	535	65	185–190	515 (4.15)	71.6 (71.8)	3.1 (3.2)	13.0 (13.1)	68	62

All the melting points are uncorrected, N – nylon; P* – polyester.

TABLE II. Shade and fastness properties of novel 11-amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-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 ₁	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5
D ₂	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5
D ₃	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5
D ₄	4	4	5	5	5	5	5	5	4-5	4-5	5	5	5	5
D ₅	3-4	3-4	4-5	4-5	4	4	4	4	5	5	5	5	4-5	4-5
D ₆	4	4	5	5	4	4	4	4	4-5	4-5	5	5	5	5
D ₇	3-4	3-4	4-5	4-5	4	4	4	4	5	5	4-5	4-5	4-5	4-5
D ₈	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5
D ₉	3-4	3-4	4-5	4-5	4	4	4	4	5	5	5	5	4-5	4-5
D ₁₀	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5
D ₁₁	4-5	4-5	5	5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5	5

N* – nylon; P* – polyester.

Preparation of 11-nitro-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazolin-13-one (III)

3-Amino-2-methyl-6-nitro-4(3*H*)-quinazolinone (2.5 g, 0.011 mol), acenaphthene-quinone (2.002 g, 0.011 mol) and acetic acid (0.5 ml, 0.011 mol) were refluxed in a round bottom flask for 5-6 h after which the contents were poured onto crushed ice. The product was isolated and crystallized from methanol. Yield 70 %; m.p. 230–2 °C. IR(KBr): The compound showed characteristic bands at 1508 cm⁻¹ and 1360 cm⁻¹ corresponding to –N=O stretching of –NO₂ and at 1696 cm⁻¹ for the (N–C=O) group of quinazolinone. Mol. formula C₂₁H₁₀N₄O₃; found: %C 68.84, %H 2.70, %N 15.28; calcd: %C 68.85, %H 2.73, %N 15.30. ¹H-NMR(CDCl₃): δ 7.26 to 8.68 (10H, *m*, aromatic proton).

Preparation of 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazolin-13-one (IV)

11-Nitro-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one (3.29 g, 0.009 mol) dissolved in methanol (15 ml, 0.36 mol) and concentrated HCl (6 ml) were mixed in a 250 ml round bottom flask and then heated in a water bath at reflux temperature. Iron powder (1.5 g, 0.026 mol) was then 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 a brown solid separated out. This product was filtered and crystallized from DMF/EtOH to give a fine dark brown powder. Yield 60 %; m.p. 240–2 °C. IR (KBr): The compound showed characteristic broad bands at 3400–3500 cm⁻¹ for –NH stretching of –NH₂ and at 1696 cm⁻¹ corresponding to the (N–C=O) group of quinazolinone. Mol. formula: C₂₁H₁₂N₄O; found: %C 74.98, %H 3.55, %N 16.65; calcd: %C 75.00, %H 3.57, %N 16.66. ¹H-NMR (DMSO-*d*₆): δ 7.25 to 8.50 (10H, *m*, aromatic proton); δ 2.72 to 3.16 (2H, *s*, aromatic amine).

Diazotization of 11-amino-13H-acenaphtho[1,2-e]pyridazino[3,2-b]quinazolin-13-one (V)

Diazotization of the title compound was carried out by a usual method.⁸

Coupling of diazo solution with Naphthol-AS

Formation of dye D₁: Naphthol-AS (0.92 g, 0.0037 mol) was wetted with Tween-80 (1 % solution, few drops). To this mixture, hot water (25 ml) and sodium hydroxide solution (7 ml, 10 % w/v) were added slowly and the mixture was heated until a clear solution was obtained. The solution was cooled to 0–5 °C in an ice bath. Freshly prepared diazo solution was added to this solution drop by drop, over a period of an hour keeping the temperature below 5 °C. The reaction mixture was further stirred for two hrs. at 0–5 °C maintaining pH 8.0 by adding the required amount of sodium carbonate solution (10 % w/v). The product was filtered, washed several times with hot water whereby a dark red solid was obtained. The solid was dissolved in DMF and precipitated by adding chloroform. Yield 68 %; m.p. 200–202 °C.

Same general procedure was applied for the synthesis of the dyes D₂ to D₁₁.

IR(KBr): All the dyes showed a characteristic band at 1375 cm⁻¹ variable for –C=N stretching, at 3250–3500 cm⁻¹ for the free –OH group, at 1550 cm⁻¹ for the azo (–N=N–) group. The dyes D₅ and D₆ showed a band at 700–850 cm⁻¹ for C–Cl stretching. The dye D₃ showed a band at 2815 cm⁻¹ for (–OCH₃) stretching. The dye D₇ showed a band at 1535 cm⁻¹ for (N=O) stretching of an aromatic nitro group. Mol. formula: C₃₈H₂₂N₆O₃; found: %C 74.73, %H 3.60, %N 13.75; calcd: %C 74.75, %H 3.61, %N 13.77.

RESULTS AND DISCUSSION

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

A series of mono azo dyes (D₁ to D₁₁) were prepared by subsequent diazotization and coupling of IV with various naphthols. 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 °C.

The characterization data, absorption maxima (λ_{\max}) and logarithm of the molar extinction coefficient ($\log \epsilon$) of the 11-amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one dyes are given in Table I. The absorption maxima of D₁–D₁₁ were recorded in DMF. The absorption maxima were in the range of 400 nm to 528 nm. These dyes were applied on nylon and polyester fibres as mono azo dyes, resulting in a variety of hues on both fibres. 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. No particular trend was observed in the absorbance value for this dyes series. However, the dyes showed a bathochromic shift with the introduction of electron donating substituents in the phenyl ring of the various naphthols moiety in the sequence of H < CH₃ < OCH₃ < OC₂H₅. The data of percentage exhaustion on the nylon and polyester fibres are also given in Table I. The higher percentage exhaustion on the nylon fibre may be expected due to its relatively open structure.⁹

Data of the fastness properties given in Table II show that the light fastness ranges from fairly good to good for all the mono azo dyes for both the fibres except dyes D₄, D₇ and D₉, which are fair to fairly good. The fastness to washing, rubbing, perspiration and sublimation are good to excellent for all the mono azo dyes. This indicates good penetration and affinity of these mono azo dyes for the fibres.

CONCLUSION

Mono azo dyes based on 11-amino-13*H*-acenaphtho[1,2-*e*]pyridazino[3,2-*b*]quinazolin-13-one were synthesized. These dyes give mostly pink, red and yellow shades on nylon and polyester fibres having very good to excellent washing fastness, rubbing fastness, perspiration fastness and sublimation fastness on both substrates. The dyes have better exhaustion on nylon than polyester, probably due to the greater accessibility of the pore structure in nylon.

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ИЗВОД

СИНТЕЗА И ПРИМЕНА НОВИХ ХЕТЕРОЦИКЛИЧНИХ БОЈА ЗАСНОВАНИХ НА ДЕРИВАТИМА

11-АМИНО-13*H*-АЦЕНАФТО[1,2-*e*]ПИРИДАЗИНО[3,2-*b*]ХИНАЗОЛИН-13-ОНА

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Синтетизовано је ново хетероциклично једињење 11-амино-13*H*-аценафто[1,2-*e*]пиридазино[3,2-*b*]хиназолин-13-он, који је употребљен за добијање нове серије хетероцикличних моноазо боја купловањем са различитим нафтолима. Све моноазо боје карактерисане су тачкама топлења, елементалном анализом, UV-Vis спектрима, IR спектрима, као и способностима за бојење најлонског и полиетиленског влакна. Процентно исцрпљивање купатила за бојење за различита влакна показало се довољно добро и прихватљиво. Обојена влакна

имала су прихватљиву до добру отпорност на светлост, и врло добру до одличну отпорност на прање, трљање, зној и сублимацију.

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