SYNTHESIS OF SOME NEW 2,6-DIAMINO-4-(P-ARYLAZO)ANILINOPYRIMIDINE AND SOME RELATED 5-ARYLAZOPYRIMIDINE DERIVATIVES FOR DYEING SYNTHETIC FIBRES

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ABSTRACT

Synthesis of some 2,6-diamino-4-(p-arylazo)anilinopyrimidine (IIIa-c) and 2,6-diamino-5-(arylazo)-4-(p-arylazo)anilinopyrimidine (IVa-h) are described. Compounds IIIa-c were synthesized by condensation of 2,6-diamino-4-chloropyrimidine (I) with the appropriate aminoazobenzene (IIa-c), while compounds IVa-h by coupling IIIa with diazotized arylamines. The effects of the nature and orientation of the substituents on the colour and dyeing properties of these dyes on polyester and acrylic fibres were evaluated.

1- INTRODUCTION

Heterocyclic diazo components, especially the derivatives of pyrimidine have played a significant role in the technology of disperse dyes. Interest has developed in recent years with respect to their uses as potential antineoplastic and antimicrobial agents[1,2]. We have been particularly interested in studying if the reaction of this ring might be extended to include a more general synthesis of new heterocyclic compounds, as well as its uses as an intermediate for new azo disperse dyes. In previous papers[3-9] , and in continuation of the work in this area, the synthesis of some 2,6-diamino-4-(p-arylazo) anilinopyrimidine (IIIa-c) and some related 5-arylazopyrimidine derivatives (IVa-h) was investigated. No details regarding the synthesis and the dyeing behaviour of such disperse dyes for dyeing synthetic fibre have been published.

2- Results and Discussion

In the present investigation some new 5-arylazopyrimidines (IVa-h) were prepared. The effect of the nature of substituents on the colour of the azo dyes is discussed. Their dyeing behaviour and performance on polyester and acrylic fibres were assessed. No details of the synthesis and disperse dyeing behaviour of such compounds have been published hitherto. The pyrimidine azo dyes (IVa-h) used in this paper have been identified by IR, ^{1}H-NMR and mass spectroscopy and characterized by the melting point and UV-Visible spectrophotometeric data as shown in Table 1.

The IR spectrum of compound (III_{a-c}) showed bands at 1555 cm^{-1} (-N=N-), at 3310 cm^{-1} (NH absorption) and 3400-3450 cm^{-1} (NH_2 stretching). The infrared measurements of the prepared arylazo derivatives (IV_{a-h}) show the presence of a band at 1610 cm^{-1}, indicating the presence of C=N group of the pyrimidine ring. The -N=N- stretching were recorded at 1580 and 1585 cm^{-1}, the NH absorption at 3300 cm^{-1}, and the NH_2 group at 3450 cm^{-1}. The ^1H-NMR and mass spectra of these compounds are in complete agreement with the proposed structures (cf. Experimental part).

Since the compounds obtained (IV_{a-h}) varied in colour from brown to yellowish, a convenient method of measuring the colours of these compounds was to study the absorption spectra of their solutions.

The UV spectra of compounds IVa-h in chloroform showed four bands in the region 250-440 nm. The relatively small difference in λ_{max} may be caused by the polarity change of the absorbing system caused by the interactions due to the general solvent effect[10]. It has been reported that the UV spectra of the azo compounds show two absorption bands at 400-410 and 290-300 nm corresponding to n-π^* and π-π^* transitions respectively[11].

It is clear that the band at the longer wavelength seems to be modified by polar substituents in the arylazo moiety, whereas the shorter wavelength band is unaffected. Table 1 shows that both electron-donating and withdrawing groups cause the absorption at higher wavelengths.

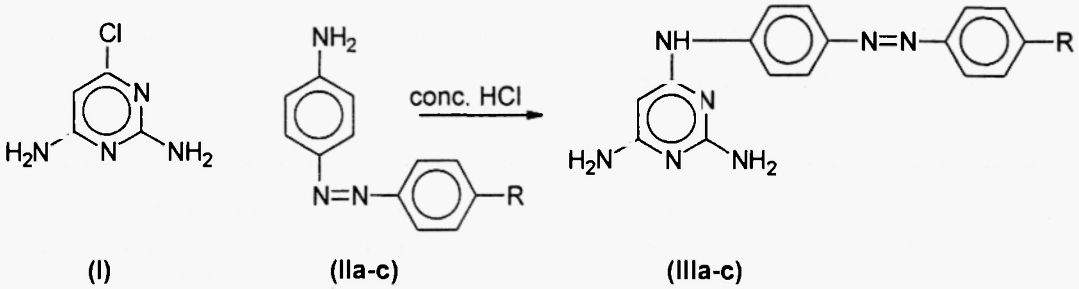
Table 1 also shows that the presence of electron-donating or-withdrawing groups has not brought about any marked increase or decrease in λ_{max} in the visible region.

Generally, variation in colour of the dyes (IV_{a-h}) depends on substitution in the azobenzene and pyrimidine components. Within the series of azo dyes investigated, the relationship between the shift observed in the absorption maxima, and polar characteristics of substituent, may be summarized as follows:

1- The introduction of a nitro group does not alter the absorption maximum. However, it gives a better exhaustion and colour yield of the dye (see Table 2).
2- The introduction of an electron-donating group in the p-position gives a bathochromic shift.

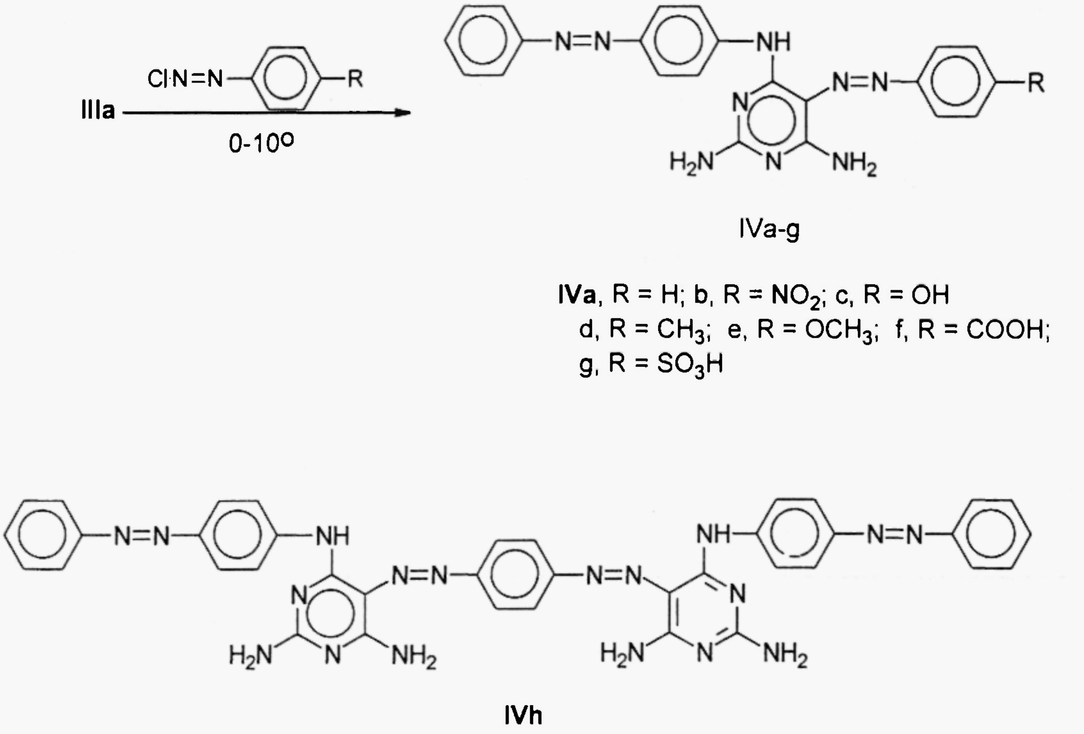
The application of substituted 5-arylazopyrimidine derivatives (IV_{a-h}) to polyester and acrylic fibres gave satisfactory results.

As the disperse dyes do not give full depth or colour on polyacrylic and polyester fibres and their behaviour depend upon the individual dye and the type of fibre[12], the compounds IVc, IVf and IVg exhibited low affinity towards polyester and polyacrylic fibres. Generally, the presence of electron-donating groups in the p-position of the aryl nuclei of the azo benzene moiety (IV_{d-e}) increases the vibrational energy of the molecule which in turn increases the strength (K/S) values of the dyed polyester and modifies the colour toward reddish and yellowish directions on the red-green and yellow-blue axes respectively.



Dye No.	R
IIIa	H
b	NO_2
c	CH_3

Scheme 1



IVa, R = H; b, R = NO_2; c, R = OH
d, R = CH_3; e, R = OCH_3; f, R = COOH;
g, R = SO_3H

Scheme 2

Table 1. Characterization data of 2,6-diamino-4-(p-arylazo)anilino-pyrimidine derivatives (IIIa-c) and 5-arylazopyrimidine derivatives (IVa-h)

Compd. No.	**R**	**M.p., (°C)**	**Colour of Crystals**	**Yield %**	**Mol. formula**	**Analysis (%)**		**λ_{max} (nm)**
						Calc.	**(Found)**	
						C	**H**	
IIIa	H	220	Yellowish brown	76	$C_{16}H_{15}N_2$	62.9 (62.7)	4.9 (4.7)	265.380
b	NO_2	170	Yellow	70	$C_{16}H_{15}N_8O_2$	54.8 (54.7)	4.0 (3.8)	260. 370
c	CH_3	130	Yellow	73	$C_{17}H_{17}N_2$	63.9 (63.8)	5.3 (5.1)	260. 380
IVa	H	90	Yellowish brown	65	$C_{22}H_{19}N_9$	64.5 (64.3)	4.6 (4.5)	250.285. 400.420
b	NO_2	305	Red	70	$C_{22}H_{18}N_{10}O_2$	58.1 (57.5)	3.9 (3.7)	250. 290. 395. 435
c	OH	230	Brown	30	$C_{22}H_{19}N_9O$	62.1 (62.0)	4.4 (4.3)	252. 295. 395. 433
d	CH_3	290	Red	72	$C_{23}H_{21}N_9$	65.2 (65.1)	4.9 (4.8)	245. 295. 400. 420
e	OCH_3	238	Yellowish brown	76	$C_{23}H_{21}N_9O$	62.8 (62.6)	4.7 (4.6)	256, 290. 400, 433
f	COOH	>300	Orange	60	$C_{23}H_{19}N_9O_2$	60.9 (60.5)	4.2 (4.1)	250. 290. 410, 435
g	SO_3H	130	Yellowish brown	63	$C_{22}H_{19}N_9SO_3$	53.9 (53.7)	3.9 (3.8)	255. 295. 395, 430
h	-	180	Brown	35	$C_{38}H_{30}N_{18}$	61.7 (61.6)	4.0 (3.8)	250, 295, 405, 435

Table 2. Colour differences between dyeings IVa-h and Dyeing IVa as standard on different fibres

Dye	%R	K/S	Tristimulus values									Colour difference			
No.			L	a*	b*	X	Y	Z	L*	C*	H*	ΔL	ΔC	ΔH	ΔE
							Polyester fibres								
IVa	6.16	7.03	65.1	39.4	51.0	44.7	34.2	9.4	65.1	64.4	52.3	-	-	-	-
b	3.22	14.4	55.6	41.0	52.4	32.4	23.5	4.8	55.4	66.5	52.0	-9.55	2.14	-0.37	9.8
c	5.65	7.8	64.1	39.9	52.4	43.3	32.9	8.4	64.1	65.9	52.7	-1.04	1.48	0.4	1.87
d	2.36	20.08	50.9	44.2	53.7	27.9	19.2	3.1	50.9	69.6	50.6	-14.2	5.15	-2.0	15.2
e	2.60	18.3	50.8	38.3	50.1	26.3	10.1	3.7	50.8	63.1	52.6	-14.4	-1.3	0.3	14.4
f	6.01	7.21	63.5	39.7	49.4	42.5	32.2	9.1	63.5	63.3	51.2	-1.59	-1.0	-1.2	2.27
g	6.03	7.23	64.8	38.8	50.1	44.0	33.8	9.5	64.8	63.5	52.3	-0.37	-0.9	0.005	1.02
h	2.58	18.35	47.7	40.0	45.3	23.6	16.6	3.6	47.7	60.4	48.6	-17.4	-3.96	-4.0	18.3
							Acrylic fibres								
IVa	18.34	1.5	79.1	18.0	44.4	59.3	55.1	22.9	79.0	47.8	68.3	-	-	-	-
b	9.28	4.12	71.5	24.6	53.5	49.3	43.0	13.0	71.5	58.9	65.0	-7.54	11.0	-2.8	13.6
c	19.9	1.3	79.2	17.3	42.0	59.2	55.2	24.6	79.0	45.2	67.0	0.07	-2.6	-0.6	2.7
d	3.21	14.3	61.0	32.4	62.4	36.3	28.9	4.6	60.7	70.0	62.0	-18.4	22.5	-5.8	29.6
c	6.57	6.3	71.0	29.3	60.0	49.8	42.0	9.6	70.8	66.9	64.0	-8.28	19.0	-4.2	21.2
f	12.29	2.8	72.8	23.7	46.7	51.0	44.8	16.2	72.8	52.3	63.0	-0.28	4.5	-4.5	9.85
g	12.94	2.6	72.1	24.9	43.1	50.0	43.7	17.3	72.0	49.8	60.0	-7.3	1.9	-7.1	11.2
h	8.69	4.5	64.0	27.9	22.4	39.0	32.7	11.7	63.9	35.8	38.8	15.3	-12.0	-1.0	28.0

Table 3. Colour fastness of dyeings IVa-h on polyester and acrylic fibres

Dye	Washing		Rubbing		Sublimation		Acid persipiration			Light
No.	Change	Staining	Dry	Wet	Change	Staining	Sample	Cotton	other	
					Polyester Fibres					
IVa	4-5	3-4	4	3-4	3-4	3	4-5	4-5	4-5	3-4
b	4-5	4	3	3-4	3-4	3-4	4-5	4-5	4-5	4-5
c	2-3	2-3	2-3	3-4	3	3	3	3-4	3-4	2-3
d	4-5	4	2	3-4	4	4	5	5	5	4-5
e	4-5	4-5	3-4	4	4	4	4	4-5	4-5	3-4
f	2-3	2-3	2	2	3	3	3	3	3	1-2
g	2-3	2-3	2-3	3	3	2-3	2-3	3	3	1-2
h	4-5	3	4	4	4	4-5	4-5	4-5	4-5	3-4
					Acrylic Fibres					
IVa	4-5	4-5	4	4	4	4	4-5	4	4	4-5
b	4-5	4-5	4	4	4	4	4-5	4-5	4-5	5
c	2-3	2-3	2-3	2-3	3	3	3	3	3-4	3-4
d	5	4-5	3-4	3-4	4	4	4-5	4-5	4-5	5-6
e	4-5	5	3-4	3	4	4	4	4-5	4-5	6
f	2	2	3	3-4	2-3	3	3	3	3	3-4
g	2	2	2	3	2-3	3	3	3	3-4	3-4
h	5	4-5	3	3	4-5	4	4-5	4-5	4-5	6

On the other hand, on dyeing acrylic fibres these dyes ($IV_{d,e}$) decreases the K/S values (Table 2). Also the colour is shifted towards the greenish and bluish directions on the red-green and yellow-blue axes respectively, as shown from the tristimulus values (X,Y,Z). According to the results of the colour measurements (Table 2), the lightness (L*) value for dyeing of the unsubstituted control dyes (IV_a) on both fibres were in the 65-80 region, but in most instances the presence of a 4-nitro substituent in the azobenzene moiety (IV_b) resulted in a marked decrease in lightness (negative DL-value). Also, from the colour differences (Table 2), it was noticed that H always has a negative value on polyacrylic indicating that the colour tends towards red, whereas on polyester fibres H can be positive or negative.

The fastness properties of (IV_{a-h}) on different fibres (Table 3) show that the dyed polyester and polyacrylic fibres have good fastness to washing according to the International Geometric Grey Scale. Also, there is not much difference in the fastness due to the variation in the structure of the dye molecule.The good fastness properties of the dyes($IV_{a,b,d,e,h}$) could be attributed to the absence of solubilizing groups and the big size of dyes molecules. The fastness to acid perspiration is generally good. This may be due to the good stability of these compounds in acid medium. The majority of the compounds show moderate sublimation fastness (3-4) according to the International Geometric Grey Scale.

Light fastness on polyacrylic is better than that on polyester. The rubbing fastness test was carried out using an Atlas crockmeter as per the AATCC8-1961 standard method of testing. The fastness to rubbing (wet and dry) is satisfactory (3-4), which may be attributed to the intra-fibre diffusion of dye molecules.

3- Materials and Methods

3.1 Synthesis of the trisubstituted-primidines (IIIa-c).

To a solution of 2,6-diamino-4-chloropyrimidine (I) (0.005 mol) in hot water (6 ml), the corresponding p-aminoazobenzene derivatives (II_{a-c}, 0.0075 mol), ethanol (3 ml) and concentrated HCl (3 drops) were added. The solution was refluxed for 4 h. and then diluted with water (25 ml), treated with norite and filtered. The filterate was cooled to room temperature and ammonical (pH 7-7.5) with 2N NH_4OH when a precipitate appeared, and kept in a refrigerator for 12 h. The coloured precipitate was then filtered, washed with suitable solvent to remove impurities, dried and recrystalized from ethanol. The characterization data are listed in Table 1. The infrared spectra of compounds IIIa-c showed stretching frequencies at 3400-3450 cm^{-1} (NH_2), 3310 cm^{-1} (NH) and 1555 cm^{-1} (-N=N-). The ^1H NMR spectrum (δ ppm) of compound IIIc showed peaks at: 2.6 (s, 3H, CH_3), 4.2 (bs, 2H, NH_2), 6.6 (bs, 2H, NH_2), 6.8-7.9 (m, 9H, Ar-H), 8.4 (bs, 1H, NH).

3.2 General method for the synthesis of 5-arylazopyrimidine derivatives (IVa-h):

To a suspension of 2,4,6-trisubstituted pyrimidine IIIa (0.004 mol) in water (150 ml), glacial acetic acid (15-20 ml) was added dropwise with stirring until a clear solution was obtained. The solution was cooled in ice-water and a cold solution of an equimolar amount of the diazotized arylamine (prepared by adding a cold solution of 0.004 mol $NaNO_2$ in 10 ml water with stirring to an ice-cold solution of 0.04 mol amine in 20 ml 1N HCl; the diazotized solution containing excess of HCl) was added slowly with stirring (5 min). Then 1N NaOH solution was added to it dropwise to bring pH of the solution to 6-8 when precipitate appeared. Stirring was continued further for 4 h. In case of compound IVf, IVg and IVh , the solution became coloured instead of giving precipitate. In such cases, after stirring for 4 h, pH was adjusted to 3-4 by adding 1N HCl when a heavy precipitate appeared. The mixture was kept in a refrigerator for 12 h and the crude product filtered, washed several times with water, dried and purified by crystallisation. In case of (IVh), to a cold solution of IIIa (0.008 mol) in water (200 ml), glacial acetic acid (30 ml) was added a cold solution of a tetrazotized p-phenylene diamine (0.004 mol). The results are listed in Table 1.

IR spectra of compounds IVa-h generally showed bands at 3450 (stretching of the NH_2 group), 3300 (NH group), 1610 (cyclic C=N), 1585 and 1580 cm^{-1} (two N=N- azo groups).

The ^{1}H-NMR spectrum (δ ppm) of compound IVd showed peaks at: δ2.6 (s, 3H, CH_3), 4.6 (bs, 2H, NH_2), 6.6 (bs, 2H, NH_2), 6.8-7.7 (m, 13H; Ar-H), 10.2 (bs, 1H, NH), and for compound IVe showed peaks at 3.9 (s, 3H, OCH_3), 4.4 (bs, 2H, NH_2), 6.6 (bs, 2H, NH_2), 6.8-7.8 (m, 13H, Ar-H), 10.2 (bs, 1H, NH).

The MS of compound IVa produced the following m/z values: M^+ 410 (60), 341 (50), 279 (18), 256 (10), 197 (15), 149 (10), 105 (44), 77 (100), 410 (60).

MS compound IVc (m/z): M^+ 455 (10), 380 (60), 318 (11), 259 (10), 213 (47), 167 (100), 138 (37), 77 (70).

MS compound IVd (m/z): M^+ 425 (10), 423 (10), 368 (35), 313 (6), 256 (15), 236 (24), 149 (35), 129 (39).

MS compound IVh (m/z): M^+ 738 (5), 434 (10), 424 (10), 409 (10), 368 (30), 305 (10), 259 (60), 198 (50), 168 (100), 122 (60), 93 (70).

3.3 Dyeing of polyester and acrylic fibres

Dyeing of these fibres was carried out in accordance with the procedure reported in Ref. 8.

3.4 Colour fastness tests

Fastness to washing, prespiration, light and sublimation was tested according to the method reported in Ref. 9.

3.5 Colour measurements

All the synthesized dyes were used for dyeing polyester, and acrylic fibres at 1% shade. The percent reflectance (%R) of the dyed material was measured at different wavelengths in the visible region (400-700 nm) using the ACS-600 colour control system. The K/S values at λ_{max} was calculated using the Kubelka-Munk equation.

The K/S value at λ_{max} was used to compare the colour depth of a dye on different fibres. The colour difference between different dyed materials was calculated using CIELAB units.

All melting points are uncorrected. FTIR spectra (KBr) were recorded on a Nicolet Magna-IR model 550 spectrophotometer. ^{1}H-NMR spectra in $CDCl_3$ were determined on a Brucker Wpsy. 200 MHz spectrometer with TMS as internal standard. UV spectra on Perkin-Elmer spectrophotometer (Model 402) using chloroform as solvent and mass spectra were recorded at 70 eV with a Varian MAT 311. Elemental analysis (C, H) were formed to yield anticipated with the calculated values.

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