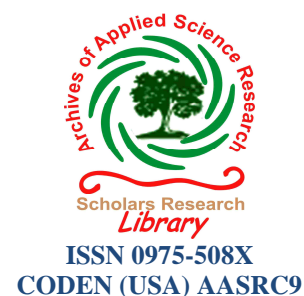




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## Studies on novel heteroaryl azo dyes

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### ABSTRACT

A series of new heteroaryl azo dyes were synthesized by coupling of diazonium salts of various phenyl amine with newly synthesized imidazole - thiazole combined compounds. Namely *N*-((1*H*-benzo[d]imidazol-2-yl)methyl)-4-phenyl-4,5-dihydrothiazol-2-amine. It was prepared by simple condensation reaction of 2-chloromethyl benzimidazol with 2-amino-4-phenylthiazole. It was characterized duly various aromatic amines were diazotized and the resultant diazonium salts were coupled with above compound. The so called result dyes *N*-((1*H*-benzo[d]imidazol-2-yl)methyl)-4-phenyl-5-(phenyldiazenyl)-4,5-dihydrothiazol-2-amine (Dye-A) obtained were characterized by elemental content, azo group determination and spectral studies. The dyeing performance of these dyes were assessed on polyester and nylon fabric. The dyes patterns were of various shades of red with good depth, brightness and leveling properties. The dyed fabric showed fairly good to very good light fastness and very good to excellent fastness to washing, perspiration and rubbing. The dye bath exhaustion and fixation on the polyester fabric was found to be very good.

**Key words:** 2-amino-4-phenylthiazole, benzimidazole, dyeing, polyester and nylon.

### INTRODUCTION

Azo dyes with thiazol components have been invented to produce shades ranging from red to greenish blue on synthetic fibre Colour Index described various dyes wherein thiazole nucleus occurs [1].

In this regard, azo dyes based on heterocyclic nucleus have been developed, and the resultant dyes have higher tinctorial strength and give brighter dyeings than those derived from simple diazo components. e.g amino-thiazoles, isothiazole, thiophene, and pyrazole compounds afford a pronounced bathochromic effect compared to benzenoid derivatives [3–9]. Hence the present author thought to study containing Imidazol-thiazol merged molecule. So the present paper comprises the study of novel heteroaryl azo dyes scanned in the scheme.

### MATERIALS AND METHODS

#### Material

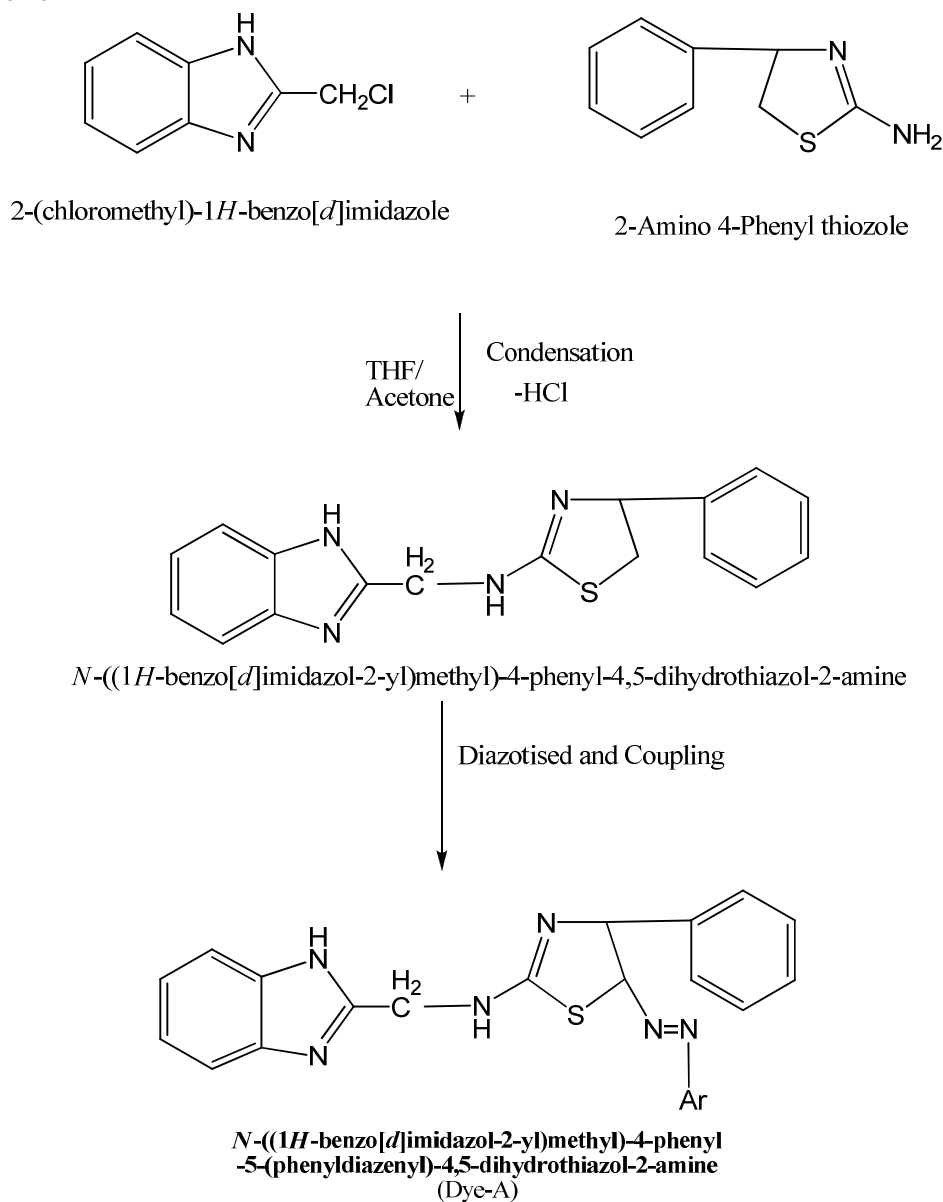
All the required reagents and solvents were of the commercial quality and purchased from local dealers.

#### General Information

2-amino 4-phenyl thiozole and 2-(chloromethyl)-1-*H* benzo[d]imidazole were prepared by methods reported [10,11]. All other chemical used of pure grade. Melting points were determined by a Kofler apparatus and UV-visible spectroscopy. Infrared spectra were recorded using Shimadzu (8400) FT-IR Spectrometer.

**Synthesis of imidazole - thiazole combined compound**

This was prepared by refluxing the mixture of 2-(chloromethyl)-1H-benzo[d]imidazole (0.9gm 0.006mole) with 2-amino 4-phenyl thiazole(1.056gm 0.006 mole) in the presence of  $K_2CO_3$  (mole) for 5 hour. The resultant product was washed by water-ethanol (50:50) mixture and finally by ethanol as air-dried. The product was dissolved in DMF and reprecipitated by solvent ether. The product is named as N-((1H-benzo[d]imidazol-2-yl)methyl)-4-phenyl-4,5-dihydrothiazol-2-amine.

**Reaction scheme**

**Where Ar =** a=Phenyl, b= 4-Chloro Phenyl, c=4-Bromo Phenyl, d=4-Methoxy Phenyl, e=4-Hydroxy Phenyl, f=2,4-Di Chloro Phenyl, g=2,4 Di Bromo Phenyl and h=4-Isopropyl Phenyl

**Coupling of diazotited arylamine with N-((1H-benzo[d]imidazol-2-yl)methyl)-4-phenyl-4,5-dihydrothiazol-2-amine combined compound**

The solution of different aryl amines (0.01 mole ) dissolved in HCl ( 6 ml, 50 % ) was cooled to 0 – 5°C in an ice – bath. A solution of sodium nitrite ( 0.01 mole, 0.69 gm ) in water (4ml) previously cooled to 0°C was added over a period of five minutes with stirring and maintaining the temperature at 0-5°C, stirring was continued for an hour, maintaining the same temperature with positive test for nitrous acid on starch iodide paper. Excess of nitrous acid was destroyed by adding required amount of sulphamic acid. The resulting solution was used for coupling reaction.

N-((1H-benzo[d]imidazol-2-yl)methyl)-4-phenyl-4,5-dihydrothiazol-2-amine (0.01mole) was dissolved in glacial acetic acid (30 ml). It was cooled below 5 °C in an ice-bath to this well stirred solution, above mentioned diazonium chloride solution was added drop wise over a period of 10-15 minutes, maintaining the pH 7.5 to 8.0 by simultaneous addition of aqueous sodium acetate.

(10 % w/v). The stirring was continued for 3 hours at 0–5 °C. To the reaction mixture was pour into ice the coloring material was precipitated. The dye was dried at 70 °C. It was crystallized from acetone.

The physical properties of the synthesized dyes are shown in table 1 and IR spectra are recorded in table 2.

### Dyeing of Polyester

The dye baths were prepared from the dye (2% O.W.F) with a dispersol-levelling agent (1gm/liter) and 5% toluene as carrier to a final liquor of 50:1, w/w. The pH value of the bath was adjusted to 4-5 with acetic acid (10%). The polyester fabrics, previously wetted, were placed into the liquor at 25°C-30°C. The temperature was raised to 100°C at the rate of 2°C/min, and dyeing continued for 60 min. After cooling, the dyed fabrics were reduction cleared in sodium hydroxide (2gm/liter), dispersing agent (1.5gm/liter) and sodium dithionite (2gm/liter) at 60°C for 30mins and then washed and dried. Percentage exhaustion was calculated to determine the dye absorption unto the fabric[12].

### Dyeing of Nylon

The procedure carried out for dyeing of the polyester fabric was repeated here but this time without a carrier.

### Fastness Tests

The various fastness tests such as washing, light, perspiration and rubbing was carried out. The wash fastness test was carried out using the ISO number 3 method, the light and perspiration fastness was assessed in accordance with BS:10061978 while the rubbing fastness test was carried out using crock meter (Atlas) in accordance with AATCC-1961. The %exhaustion and %fixation was carried out according to known method [13].

Table-1: Physical properties of synthesized dyes

Dye No.	Molecular weight (gm)	Melting point °C	% yield	Colour
A	412	209	73	Red
B	446.5	171	71	Light red
C	491	169	76	Deep red
D	442	180	65	Light red
E	428	177	68	Red
F	481	201	75	Red
G	570	173	77	Red
H	480	175	64	Light red

### Infrared spectra of the Dyes

Table-2: IR Spectra features of synthesized Dyes cm<sup>-1</sup>

Dyes NO.	Ar-CH Bend	C-H Stretch	NH stretch	Aromatic Stretch	N=N	C-N Stretch	N=C=S	O-H
A	771.23	2911.10	3314.5	1532.20	1413.60	1203.50	1980.0	-
B	775.45	2850.51	3250.23	1530.10	1423.00	1205.14	1922.1	-
C	750.13	2915.21	3435.21	1550.11	1432.61	1206.11	2125.93	-
D	751.23	2916.23	3455.21	1511.23	1453.10	1231.10	2212.90	-
E	823.0	2878.14	3475.14	1575.0	1413.10	1212.11	2214.80	3436.1
F	825.23	2914.0	3478.10	1544.40	1465.10	1250.30	2210.10	-
G	841.21	2844.14	3452.21	1611.10	1450.10	1225.21	2229.10	-
H	832.11	2875.13	3315.25	1551.21	1423.11	1231.2	2231.15	-

### Visible Absorption spectra of Dyes

The visible absorption spectra of all the synthesized compounds were recorded in different solvent system and their data are shown in Table 3. The solvatochromic properties of these dyes were systematically investigated in different solvents with different polarities[14-17].

Table-3: Visible Absorption spectral band of Synthesized Dyes

Dyes No	$\epsilon_{\text{max}}$ acetone $\text{mole}^{-1} \text{cm}^{-1} \times 10^4$	Acetone $\lambda_{\text{max}}(\text{nm})$ a	DMF $\lambda_{\text{max}}(\text{nm})$ b	Ethanol $\lambda_{\text{max}}(\text{nm})$ c	Ethanol+HCl $\lambda_{\text{max}}(\text{nm})$ d	Change in $\lambda_{\text{max}}(\text{nm})$ d-c
A	2.342	515	511	500	510	+10
B	2.254	523	516	515	520	+5
C	2.248	510	511	490	495	+5
D	1.664	411	409	415	415	+0
E	1.334	415	408	410	420	+10
F	2.411	616	596	538	550	+17
G	2.786	601	611	611	590	-21
H	2.421	564	571	526	531	+5

### Dyeing and Fastness properties

The dyes were applied to polyester, nylon and polyester/cotton blend using the methods described above. The dyes gave very good levelness and fiber penetration on polyester nylon and polyester/cotton blend. The exhaustion was good up to 95% and fixation values up to 93%. The dyes gave very-good to moderate wash, perspiration and rubbing fastness while the light fastness result was between good to fair. The results show that nylon gave higher exhaustion values than polyester for most of the dyes this can be attributed to the amorphous nature of the nylon fabric and hence easy penetration of the dye molecules than the polyester fabric which is highly crystalline. It can also be seen from table 5 that the %fixation was higher for those in which alkaline fixation were carried out indicating that alkaline fixation is necessary when dyeing polyester cotton blend with disperse-reactive dyes to fix the reactive dyes on the cotton component of the blend.

## RESULTS AND DISCUSSION

The present study revealed that prepared thiazole-imidazole junction derivative showed wide range of shade. This thiazole-imidazole junction derivative was obtained using conventional methods and the synthesis is extremely convenient and relatively inexpensive. These dyes provide bright shades of red and an outstanding property of these dyes is their high affinity and intensity of colour with only a small molecule of the dyes. The nature of the substituents in the diazo component has little or no effect in the visible absorption spectra and shade of the dyeing. Furthermore these dyes show good exhaustion, fixation, and uniform dyeing properties in addition to the good fastness properties. Some of the dye have good rating for fastness properties on both nylon and polyester fabrics. These dyes can hence be used commercially.

Exhaustion and fixation data, Washing and Light Fastness Result, Perspiration Fastness Result, and Rubbing Fastness Results are shown in the Table number 4,5,6 and 7 respectively.

TABLE 4 % Exhaustion and fixation of Synthesized DYES

Dye no.	%Exhaustion Polyester	%Exhaustion Nylon	%Exhaustion Polyester-cotton blend	%fixation	%Exhaustion Polyester-cotton blend Without alkali fixation	% fixation
			With alkali Fixation			
A	91	92	92	90	86	60
B	89	95	93	86	81	50
C	87	56	91	76	71	58
D	92	45	82	74	75	60
E	65	56	46	74	48	12
F	64	65	62	78	64	41
G	55	74	51	67	61	16
H	52	45	63	65	67	15

Table 5 Washing and Light Fastness Result

Dye no.	Polyester		Nylon		polyester-cotton	
	Wash	light	Wash	light	Wash	Light
A	4-5	3	2	4	5	3
B	3-4	2	3	4	4-5	6
C	3	3	5	3	5	4
D	4-5	4	4	4	4	5
E	3-4	5	5	3	3-5	4
F	4	5	4	3	4	3
G	4	4	2	3	3-4	5
H	3-4	5	3	2	4	3

Table 6 Perspiration Fastness Result

Dye no.	Polyester		Nylon		polyester-cotton	
	acid	Alkaline	Acid	Alkaline	Acid	Alkaline
A	4	4-5	4-5	4	4-5	5
B	3	3-4	3-5	3-4	3	5
C	3	3-4	2-3	2-3	3-4	4-5
D	2	3	2-3	2-3	3	4
F	3	3	3-4	3-4	2-3	4-5
G	3-4	3	2-3	2-3	3	5
H	2-3	3-4	4-5	2-3	4	2-3

Table 7 Rubbing Fastness Results

Dye no	Polyester		Nylon		Polyester-cotton Dry	
	dry	wet	dry	wet	Dry	wet
A	5	5	4-5	4-5	5	4-5
B	3-4	4	3-4	3-4	4-5	3-4
C	4	4	3-4	4-5	3-4	3
D	3-4	3	3	2-3	3-4	4
E	4	3	4	2-3	4	4-5
F	4	3-4	2-3	3-4	4	4
G	5	2-3	3-4	3-4	5	4-5
H	2-3	3-4	3-4	2-3	3-4	4

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