Novel Azo Disperse Dyes Countaining 2-Amino-6-Methyl Benzthiazole and Phenacyl Chloride

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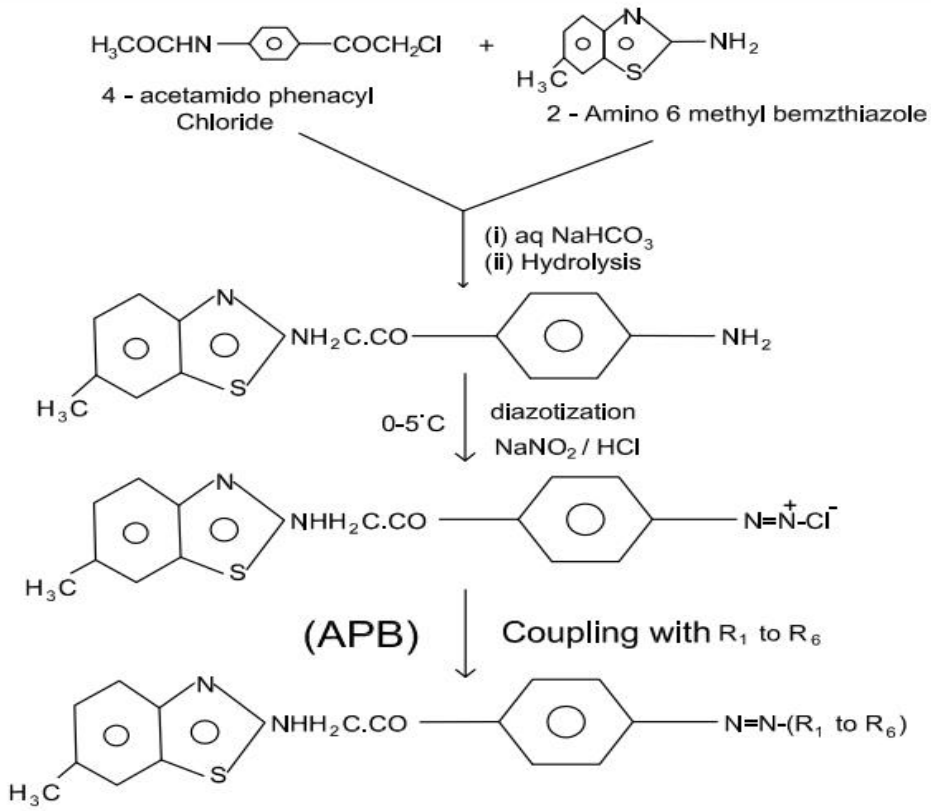
Abstract:
The aspect on novel azo disperse dyes countaining 2-amino -6-methyl benzthiazole and phenacyl chloride moieties has been undertaken.The novel aromatic amine countaining 2-amino-6-methyl benzthiazole and phenacyl chloride groups has been prepared.This was diazotiesed and coupled with different coupling components.All the resulting novel disperse dyes have been characterized by Elemental analysis IR,NMR,Visible spectroscopy.The produced disperse dyes were employed for dyeing of commercial Nylon and Polyester fibres and the fastness properties of dyes were evaluated.

Keywords: *Novel azo Disperse Dyes, IR, NMR, UV-Visible Spectroscopy, Wash Fastness and Light Fastness Properties.*

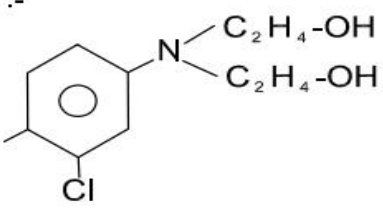
1. Introduction

In the field of dyes,numerous mono and bis azo dyes countributes major Industrial implementation.These dyes are mostly based on aeromatic amines,benzidine derivatives and naphthalene based couplers.[1].Recently most of the benzidine based dyes have been banned all over the world due to their carcinogenic and Toxic nature.[2].The Introduction of phenacyl group (PhCOCH2-) and 2-amino-6-methyl benzthiazole group into dye moiety may afford the dyes with better dyeing properties up to some extent.Till now,no such dye synthesis has been reported in literature.So it made interesting to explore the synthesis countaining phenacyl group.Hence,the present paper comprises synthesis,characterization and Fastness properties of phenacyl group countaining disperse azo dyes.The whole work is furnished into **scheme-1.**

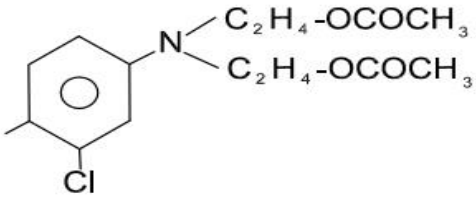


Where :- (R_1 - R_6)

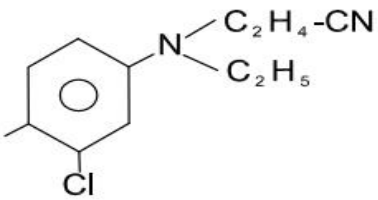
(I) R_1 :-



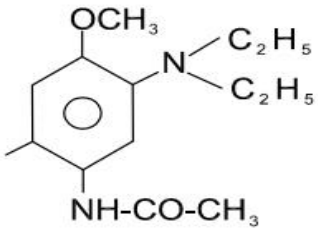
(II) R_2 :-



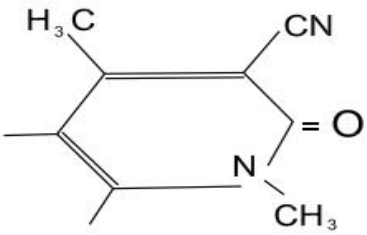
(III) R_3 :-



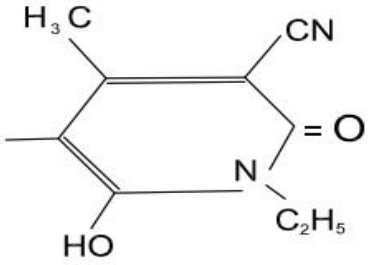
(IV) R_4 :-



(V) R_5 :-



(VI) R_6 :-



2. Experimental

2.1 Materials

4-(N-acetamido phenyl)-2-Chloroethanone (i. e 4-acetamido phenacly chloride) was prepared according to the method reparted in literature.[3] .2-amino-6-methyl benzthiazolyl was obtained from chitichous Ltd.Vadodara.

All the coupling component listed in Table-1 obtained from Jupiter Dyes, Vapi. Undyed nylon and polyesters fibres were obtained from kiran Threads Ltd, Vapi. All the other chemical were used of Laboratory grade.

2.2 Preparation of 1-(4-Aminophenacyl)-2-(2'-imino-6-methyl benzthazolyl)

Ethanone: To a mixture of 2-amino-6-methyl benzthiazol (0.05 mole) in 40 ml Anhydrous acetone few drops of pyridine and sodium bicarbonate as an acid acceptor in 250ml flask,4-acetamido phenacyl chloride (0.05 mole) was added gradually at 20^0C. The reaction mixture stirred and kept aside overnight keeping temperature below 20^0C. 1-(4-acetamido phenacyl)-2-(2-imino-6-methyl benzthazolyl) ethanone is filtered off-washing with cold acetone yield crystals of product. The melting point was 103-105^0C(Uncorrected). It was hydrolysed by alcoholic HCL.under reflux for 4-5 hours and the resultant cooled solution was neutralized by alkaline with Conc. NH_3 Solution to yield. The hydrolysed product designated according to IUPAC as 1-(4-aminophenacyl)-2-(2-imino-6-methyl-benzthazolyl) ethanone was obtained as Light Yellow coloured solid with melting point of the product is 123-125^0C (Uncorrected).

2.3 Diazotization 1-(4-amino phenacyl)-2-(2'-imino-6-methyl benzthazolyl amino) ethanone

1-(4-amino phenacyl)-2-(2'-imino-6-methyl-benzthazoly) ethanone (0.01 mole) dissolved in Hydrochloride acid (0.05 mole) with stirring and the solution was cooled to 0-5^0C in icebath. A Solution of sodium nitrite (0.01 mole) in 5 ml water cooled to 0^0 C was added and the stirred until the positive test of nitrous acid on starch Iodide paper. (i.e Blue colour on starch Iodide Paper). The Excess of nitrous acid was neutralized with **sulphamic acid. /Urea (1.0 grms)** and the mixture filtered to get the clear diazonium salt solution which was used for subsequent coupling reaction. Different couplers(R_1-R_8) were taken as their sodium salts.The solution of acid couplers in their respective medium was cooled and stirred.To this well stirred solution,the above mentioned diazo solution was added while maintaining pH at 6-7 by addition of sodium carbonate solution (10% w/v) maintaining the pH of the resulting solution.The solution was stirred continuously for three hours keeping temperature below 5^0 C.After completion of reaction,the solid material was filtered off and washed with water.[4,5] The disperse dye was purified from DMF- chloroform system.The melting points of all the dyes are Uncorrected.

3. Mesurements

C,H,N,S contents of all samples were estimated by C, H, N, S,P Elemental analyser,carlo Erba,Italy.The IR spectra of all the samples were scenned in KBr pellets on "Perkin Elmer" IR Spectrophotometer.The NMR spectral studies were carried out on "FT NMR DPX-300(Brucker)"Spectrophotometer.The dyeing assessment of all the dye samples was carried out on nylon and polyester by the method reported in literature.[6,7,8] Visible spectra of all the dyes are taken in distilled water using "JENWAY-6100R".

4. Results and Discussion

The novel amine 1-(4-amino phenyl)-2-(2'-imino-6-methylbenzthiazolyl) ethanone having the structure shown in **Scheme-1.** Confirmed by elemental and spectral analysis. The C, H, N contents and IR spectral features of all this amine are shown.in **Table-1.**are Consistant with the predicted structure.The azo disperse dyes obtained from this compound are shown in **Scheme-1.**The detailed analysis of all the dyes are presented in **Table-2.**The C, H, N contents of all the dyes samples are

consistent with the predicted structures **(Scheme-1).** The IR spectra of all the dyes comprises the important bands due to initial diazo component.The bands due to $–CH_2$ and CO of $COCH_2$ dimethyl amine $(CH_3)_2$ N groups are at their respective positions.Only the discernible difference in the spectra of dye samples is that the new band at 1650-1550 Cm^{-1} is assigned to the presence of azo group (–N=N-stretching).The bands at 1500,1200,1050 Cm^{-1} appeared in the double bond at 3600 Cm^{-1} to 3400 Cm^{-1} mainly arised due to –OH group.The observed bands in the spectra for each dye are shown in **Table-1**. The UV visible spectra of all the dye samples was recorded in distilled water.It is apparent that the Wave length of Maximum absorption is relatable to the azo grups in the compounds and it is observed in the region of 460-535 nm.Variation in λmax being attributed to structural vibration in the dye samples.All the dyes were dyed on polyester and Nylon fibers at 2% dye bath of shade and gave Coral pink to Mashroom to shades implied in **Table-3**.The dye bath exhaustion of dyes on both fibres was (about 20-30%). Thus, fixation of dye on Nylon and polyester is an excellent (70 to 80%). The light fastness and Washfastness of the dyes are shown in **Table-3**. The light fastness on fibres varied from good to very good. All the dyes have higher rating. The washing of the dyes is also very good compared with commercial dyes. The produced dyes have good exhaustion on dye pattern and better washing and light-fastness.

5. Conclusion

Unsymetrical Disperse azo dyes have been prepared using 1-(4-aminophenacyl)-2-(2-imino-6- methyl benzthiazolyl) ethanone. The dyes thus obtained gave dyeing having deeper shades and Excellent light fastness and wash fastness properties. Results of the work indicate that 1-(4-amino phenacyl)-2-(2'-imino-6-methyl benzthiazolyl) ethanone is a potential diazo component in the synthesis of Disperse dyes.

Table: 1 Analysis of 1-(4-amino phenacyl)-2-(2'-imino-6-methyl benzthiazolyl) ethenone

Elemental analysis:
C$_{16}$H$_{16}$N$_3$SO (298)

	%C	%H	%N	%S
Calc.	64.42	4.76	14.10	10.70
Found	64.36	4.68	14.06	10.60

IR (KBr) Cm^{-1}:
Ï of NH_2 : 3300, 3400

Ï co of $–COCH_2$: 1720,1735

Ï CH_2 of $–COCH_2$: 2890,2950

Ï aromatic : 3030,1400,1600

^{1}H-NMR ($CDCl_3$) :
Singlet X 7.2 ppm 4H (aromatic)=> Singlet X 7.4 ppm 4H(aromatic of Benzthiazolyl)
Singlet X 2.14 ppm 2H(-CH_2-)
Singlet X 2.6 ppm 1H (NH) => Singlet X 2-4 ppm (NH_2)

Table 2 Characterization of Novel Azo Disperse Dyes

Dye sample	MP⁰C (Uncorrected)	Mol.Wt (gm/mole)	% C		%H		%N		%S	
			Found	Cal.	Found	Cal	Found	Cal	Found	Cal
APB-R1	210	523.5	59.5	59.6	4.90	4.96	13.30	13.37	6.10	6.11
APB-R2	310	607.5	59.2	59.25	4.9	4.93	11.50	11.52	5.10	5.26
APB-R3	240	503	64.4	64.41	5.70	5.76	13.80	13.91	6.30	6.36
APB-R4	294	587	63.30	63.37	5.60	5.62	11.90	11.92	5.40	5.45
APB-R5	210	472	61.00	61.01	4.20	4.23	17.70	17.79	6.70	6.77
APB-R6	180	486	61.70	61.72	4.50	4.52	17.10	17.28	6.50	6.58
APB-R7	240	482	67.20	67.21	5.30	5.39	17.40	17.42	6.60	6.63
APB-R8	215	555	64.80	64.86	5.50	5.58	15.10	15.13	5.70	5.76

Table 3: Characterization and dyeing assessment of azo disperse dyes

DYE SHADE	λmax (nm)	Shade	Dyeing properties			
			Dyeing On Nylon		Dyeing On polyester	
			LF	WF	LF	WF
APB-R1	460.0	Coral pink	5	4	5	4
APB-R2	499.0	Candy	5	3	5	3
APB-R3	502.0	Sunrise	4-5	4	5	4-5
APB-R4	387.0	Deep Orange	4-5	4	4-5	4-5
APB-R5	420.0	Opaline Green	4	3	4-5	3-4
APB-R6	430.0	Pegion Blue	5	5	5	4
APB-R7	387.0	Royal Ivory	5	4	5	4-5
APB-R8	535.0	Mashroom	5-6	5	5	4-5

LF=Light FastnessWF=Wash Fastness

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