Computational Comparative Studies of Azo disperse Dyes

Anita Gour
Department of Chemical Science, Christian Eminent College Indore (M.P.), India.
dranitagour@gmail.com

Abstract

In present paper we have experimented various methods of synthesis of above mentioned Azo dyes and presented comparative between the same. Colour in dyes is invariably explained as a consequence of the presence of a Chromophore. Since, by definition, dyes are aromatic compounds their structure includes aryl rings, which have delocalised electron systems. These are responsible for the absorption of electromagnetic radiation of varying wavelengths, depending on the energy of the electron clouds. In this paper we have shown the comparatively study about Four Azo disperse DyesC_1 to C_4 to give the corresponding various azo disperse dyes (R_1 to R_4) by attachment of coupling components. These dyes were applied to polyester fabric and their fastness properties were evaluated(1,2)

Keywords:*coupling component of diazonium salt,* primary aromatic amino compound, *polyester fabric, synthesis, fastness etc.*

INTRODUCTION

Dyes are coloured, ionising,aromatic organic compoundsColour in dyes isinvariably explained as a consequence of thepresence of a Chromophore. Since, by definition,dyes are aromatic compounds their structureincludes aryl rings, which have delocalised electron systems. These are responsible for the absorption of electromagnetic radiation of varying wavelengths, depending on the energy of the electron clouds. For this reason, Chromophores do not make dyes coloured in the sense that they confer on them the ability to absorb diation.Rather, Chromophores function by altering theenergy in the delocalised electron cloud of the dye,and this alteration results in the compoundabsorbing radiation from within the visible rangeinstead of outside it (3,4,) Our eyes detect thatabsorption and respond to the lack of a completeColour in dyes isinvariably explained as a consequence of thepresence of a Chromophore. Since, by definition,dyes are aromatic compounds their structureincludes aryl rings, which have delocalisedelectron systems. These are responsible for theabsorption of electromagnetic radiation of varyingwavelengths, depending on the energy of theelectron clouds. For this reason, Chromophores donot make dyes coloured in the sense that theyconfer on them the ability to absorb radiation.Rather, Chromophores function by altering theenergy in the delocalised electron cloud of the dye,and this alteration results in the compoundabsorbing radiation from within the visible rangeinstead of outside it2., 3,4,5 Our eyes detect thatabsorption and respond to the lack of a completerange of wavelengths by seeing colour. Dye shouldbe fast to light, water, soap, acid and alkali. So itmust be permanently attached to the fibre by stablechemical bond. This stable chemical bond formeddue to presence of auxochrome group in dye may
be either acidic or basic in nature.(5)

MATERIALS AND METHODS

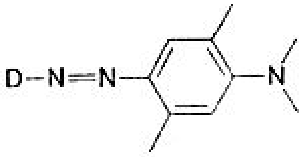
These are synthesized by two-stage process viz. Diazotisation & Coupling.

Diazotisation: The process in which primary aromatic amino compound convert into the diazonium salt is known as Diazotisation, this reaction is carried out in presence of HNO2 at low temperature 0-5 ^{0}C.

$$NaNO_2 + HCl \xrightarrow{0\ \text{to}\ 5\ ^\circ C} HNO_2 + NaCl$$

$$ArNH_2 + HNO_2 + HCl \longrightarrow \underset{\text{Aryl Diazonium Chloride}}{ArN_2Cl} + 2H_2O$$

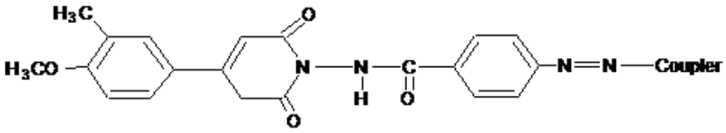
Coupling: When diazonium ring gets attached to another aromatic ring, then it is called coupling. It can be represented by general formula given below, where D is Aromatic or Heterocyclic group of the diazo component.(6)



D = Aromatic or heterocyclic group
of the diazo component.

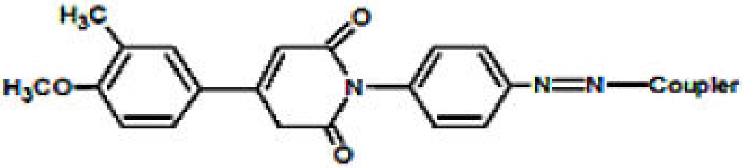
Preparation of C$_1$1-{4-[4-N,N-di(2-hydroxyethyl)amino-2-methyl]phenylazo} benzamido- 4 -(4-methoxy-3-methylphenyl)-2,6(1H,5H)-pyridinedione:

A solution of 4(0.365 gm, 0.001mole) in propionic acid (1ml) and glacial acetic acid (5ml) was added drop wise with stirring over a period of 45 minutesto a cold (50C) mixture of nitrosyl sulphuric acid [prepared by dissolving solid sodium nitrite(0.069gm, 0.001mole) in conc. sulphuric acid (8ml) at 700C]. The reaction mixture was stirred for an additional period of 2 hours at 5-100C. The reaction mixture was then added to propionic acid-acetic acid mixture (2ml-10ml) under stirring. The excess of nitrous acid was destroyed using urea (about 0.2gm). The mixture was filtered to get a clear diazonium salt solution.16,173-Methyl-N,N-di(2-hydroxyethyl)aniline (0.195gm, 0.001 mole) was dissolved in propionic acid-acetic acid mixture (4ml-20ml). The solution was externally cooled to 50C. The previously cooled diazonium salt solution was slowly added to the above solution maintained at 5-100C over a time period of 1 hour. The pH of the reaction mixture was maintained acidic (4-5) throughout the coupling period by addition of solid sodium acetate. After the addition of diazonium salt solution was over the reaction mixture was stirred further, for a period of 3 hours. The mixture was neutralized with sodium acetate solution. The separated monoazo dye was filtered, washed thoroughly with cold water and dried. All the other dyes of C$_1$ (R $_1$ to R$_6$) were synthesized by using the same method.(7)



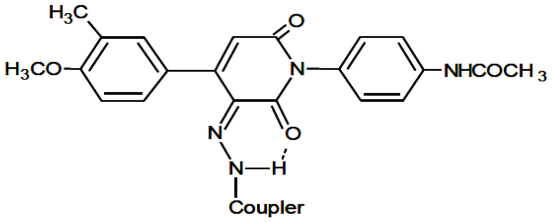
Preparation of $C_2$1-(4-Aminophenyl)-4-(4-methoxy-3-methylphenyl)-2,6-(1H,5H)-pyridinedione:

A solution of C_1 (0.322 gm, 0.001mole) in propionic acid (1ml) and glacial acetic acid (5ml) was added drop wise with stirring at period of 45 minutes to a cold (50C) mixture of nitrosyl sulphuric acid [prepared by dissolving solid sodium nitrite (0.069gm, 0.001mole) in conc. sulphuric acid (8ml) at 70oC]. The mixture was stirred for an additional period of 2 hours at 5-10oC. The mixture was then added to propionic acid 2ml and acetic acid mixture 10ml under stirring. The extra nitrous acid was destroyed using 0.2gm urea. The mixture was filtered to get a clear diazonium salt solution. 3-Acetamido-4-N,N-diethylaniline (0.206gm, 0.001mole) was dissolved in propionic acid 4ml and acetic acid 20ml mixture. The resultant was externally cooled to 50 C.[6] The previously cooled diazonium salt solution was slowly added to the above mixture maintained at 5-10oC over 1 hour. Throughout the coupling period by addition of solid sodium acetate, the pH was maintained acidic (4-5). After addition of diazoniumsalt , the reaction mixture was stirred further for a period of 3 hours,. The mixture was neutralized with sodium acetate solution. The separated monoazo dye was filtered, washed thoroughly with cold water and dried. All the other dyes of C_2 (R_1 to R_6) were synthesized by using the same method.(8)

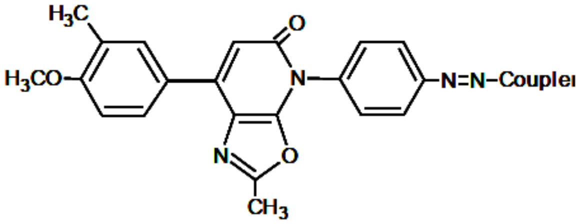


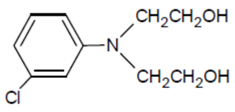
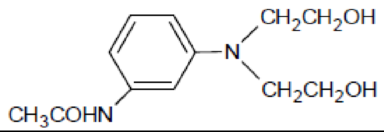
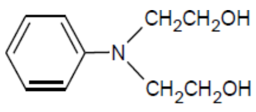
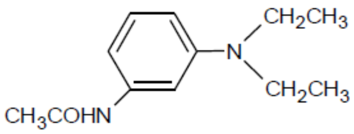
Preparation of C_3 5- [(2-Acetamido-4-N,N-diethylamino)phenyl] hydrazono-1-(4-acetamidophenyl) - 4 -(4-methoxy-3-methylphenyl) -2, 6-(1H)-pyridinedione:

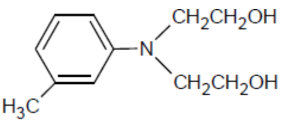
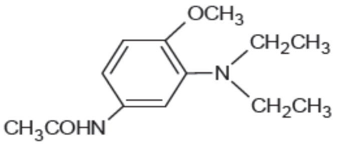
Compound C_3(0.379 gm, 0.001 mole) was dissolved in propionic acid (1 ml) and acetic acid (4 ml) mixture.The solution was cooled to about 10^0C. It was added drop wise to a cold solution (5^0C) of nitrosyl sulphuric acid [prepared by dissolving solid sodium nitrite (0.075 gm, 0.001 mole) in conc. sulphuric acid (8 ml) at 70^0C]. The added to propionic acid – acetic acid mixture (2ml-10 ml) under stirring. The excess of nitrous acid was destroyed using urea (about 0.2 gm). The mixture was filtered to get a clear reaction mixture was stirred further, for an additional period of 2 hours at $5\text{-}10^0$C. The reaction mixture was then diazonium salt solution.3-Acetamido-4-N,N-diehtylaniline coupler (0.206gm, 0.001 mole) was dissolved in propionic acid – acetic acid mixture (4ml-20 ml) .The solution was externally cooled to 50C. The previously cooled diazonium salt was slowly added to the reaction mixture maintained at 5-100C over a time period of 1 hour. The pH of reaction mixture was aintained acidic (4-5) throughout the coupling period by addition of solid sodium acetate. After the addition of diazonium salt solution was over the reaction mixture was stirred further, for a period of 3 hours.All the other dyes of C_3 (R_1 to R_6) were synthesized by using the same method.(9)



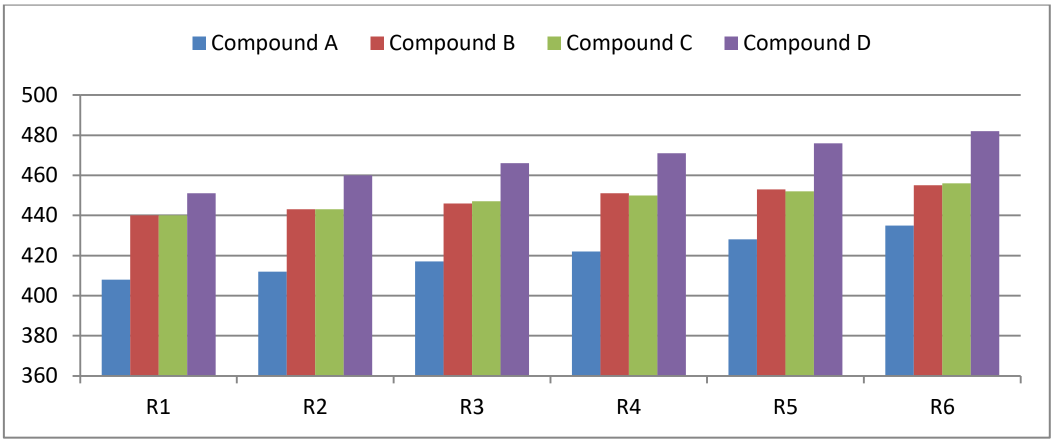
Preparation of C_4 7-{4-[2- Chloro- 4-N,N-di (2-hydroxyethyl)amino]phenylazo} phenyl- 6-oxo-2-methyl-4-(4-methoxy- 3-methylphenyl)- oxazolo [5,4-b] pyridine:
A solution of compound **W** (0.361 gms, 0.001 moles) in glacial acetic acid (5 ml) and propionic acid (1 ml) was added drop wise with stirring over a period of 45 minutes to a cold (50C) mixture of nitrosyl sulphuric acid [prepared by dissolving solid sodium nitrite (0.075 gms, 0.001 moles) in conc. sulphuric acid (8 ml) at 70^0C]. The reaction mixture was stirred for an additional period of 2 Hrs. maintained at 5 –100C. The reaction mixture was then added to propionic acid – acetic acid mixture (2-10 ml) under stirring. The excess of nitrous acid was removed using urea (about 0.2 gms). The mixture was filtered to get a clear diazonium salt solution. 3-Chloro-4-N,N-di (2-hydroxyethyl) aniline (0.215 gms, 0.001 moles) was dissolved in propionic acid –acetic acid mixture (4-20ml) . The solution was externally cooled at 50C. The previously cooled diazonium salt solution was slowly added to the mixture maintained at 5-100C over a time period of 1 Hr. The pH of the reaction was maintained acidic (4 –5) throughout the coupling period by addition of solid sodium acetate. After the addition ofdiazonium salt solution was over, the reaction mixture was stirred further , for a period of 3 Hrs. The mixture was neutralized with acetate solution.All the other dyes of C_4 (R_1 to R_6) were synthesized by using the same method.(10)



R	Coupler	R	Coupler
R1		R4	
R2		R5	

R3		R6	

R	Colour of different Dye andAbsorption Maxima							
Coupler	**Compound A**		**Compound B**		**Compound C**		**Compound D**	
	Colour	**λ_{Max} (nm)**	**Colour**	**λ_{Max} (nm)**	**Colour**	**λ_{Max} (nm)**	**Colour**	**λ_{Max} (nm)**
R_1	Pale Yellow	408	Pale Golden Yellow	440	Golden Yellow	440	Yellow	451
R_2	Pale Yellow	412	Pale Golden Yellow	443	Golden Yellow	443	Yellowish orange	460
R_3	Pale Yellow	417	Pale Golden Yellow	446	Golden Yellow	447	Yellowish orange	466
R_4	Pale Yellow	422	Golden Yeiiow	451	Yellowish Orange	450	Yellowish orange	471
R_5	Yellowish Orange	428	Reddish Orange	453	Yellowish Orange	452	Reddish Orange	476
R_6	Yellowish Orange	435	Reddish Orange	455	Yellowish Orange	456	Reddish Orange	482



Graphical representation of different dyes

RESULT AND DISCUSSION :

Numerous possibilities to modify the azo dyes synthesis is being utilized to produce desired range of hue of industrial use. In current scenario of Make in India, above synthesis research could be developed to produce economic dyes in our country and we could save significant foreign investment through import.The pyridone skeleton as diazo component and different N,N-dialkylsubstitutedaniline derivatives as couplers of monoazo dyes $R_1$to R_6 showed an absorption range 408 nm to 456 nm respectively. It was observed that the value of the absorption maxima increased with increasing number of electron donating substituent on dyes. In these chromophore systems coupler serves as donor end, while the pyridone skeleton is the acceptor end. Preparation of some novel disperse azo dyes $C_1$to C_4 have been prepared using based on 1-(4-Aminobenzamido)-4-(4-methoxy-3-mehylphenyl)-5-(4-nitrophenylhydrazono)-2,6-(1H)-pyridinedione. dyesR_1 to R_6gave yellow to orange shades on polyester. The dyes derived from diazo component having electron donating substituent's show bathochromacity compared to dyes derived from diazo components having electron withdrawing substituent's.

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