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Synthesis of 4-Chlorophenylazo 1-Naphtholazo-4-Bromobenzene

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ABSTRACT

The synthesis of 4-chlorophenylazo-1-naphtholazo-4 bromobenzene, was achieved by using diazotization and coupling methods. The characterisation of the synthesized dye was determined. The UV Spectra shows that the dye absorbed at the visible region of 400-600nM with distinct peaks at 400–500nM conforming it as a good dye. The dye was applied on 100% cotton, polyester, doctor flannels worsted wool, fine worsted wool, acrylic fibre 58 west laid acrlan, Nylon, polystyrene. The dye exhausted well on fabrics. The fastness property shown that the dye has very good – excellent (4-5), wash fastness property for polystyrene, very good - excellent (4-5), light and heat fastness for all the fabrics. From the starting point for our investigation, continuous and serial investigations on the study of different dyes were made on 4-chlorophenylazo-1-naphtholazo-4 bromobenzene in the present study with the similar standard methods. Similar findings as pervious study were observed (A. Regina, 2015).

INTRODUCTION

As we know that the dye can generally be described as a coloured substance that has an affinity for the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve its fastness on the fibre (www.apparel search, 2004). The colour of a compound is related to its chemical constitution (Gurdeep, 1990 and Mariam *et al*. 2014). The relationship between colour and chemical constitution of a substance has been explained by different theories, including Witt's Theory which states that there existed a relationship between colour and chemical constitutions of a substance of a compound and that, a dye is made up of two parts: chromophores and auxochromes. According to him, colour usually appears in an organic compound if it contains certain unsaturated groups. These groups are referred to as chromophores {*e.g.* azo (N=N), carbonyl (> C=0) *etc*}. He also referred to compounds containing a chromophoric groups as chromogens and further pointed out that the presence of certain groups in a chromogen leads to a deepening of the colour though these groups are not chromophores themselves and do not impart colour to the compounds when present without the chromophores.He referred to these groups as auxochromes {*e.g.* Amino (NH_2), hydroxyl (OH), chloro (Cl) *etc*.} Other theories relating colour and chemical constitution include; Amstrong's theory, Baeyer's theory, Nietzki's theory, Watson's theory *etc*. Any group or factor that produces the deepening of colour in accordance with the sequence yellow → orange → red → purple → violet → blue → green is known as a bathochrome and the effect *i.e.*, the deepening of colour is known as bathochromic effect (Galanty andBujtas,1992).Any group or a factor that will lighten the colour of the dye in accordance with the sequence Green → blue → violet → purple → red → orange →yellow is known as hypsochrome and the effect produced is known as hypsochromic effect (Simeon, 2000). Colour influences our mood and emotions and generally enhances the way in which we enjoy our surroundings (Ohme *et al.*, 1988). Our experience of colour emanates from a rich diversity of sources, both natural and synthetic (Mark *et al*., 1980). Natural colours are all around us; in the earth, the sky, the sea, animals and birds and in the vegetation, for example in the trees, leaves, grasses and flowers(Hunger, 2003). Colour is an important aspect in our enjoyment of the food we eat. Infact we frequently judge the quality of meat products, fruits and vegetables by the richness of their colour (Hofenk *et al.*, 2014) solution to the fibres at some point in the dyeing process (Cho *et al.*, 1996 and Moldovan *et al*. 2011).

Azo Dyes:

Azo dyes are a large class of very effective synthetic dyes used for colouring a variety of consumer goods such as foods, cosmetics, car paint, clothes, leather and textiles. Azo dyes are synthetic organic dyes that contain azo group. The Azo compounds bear the functional group R – N = N – R′, in which R and R′ can be either aryl or alkyl group. IUPAC defines azo compounds as “Derivatives of diazene (diimide), HN = NH, wherein both hydrogens are substituted by hydrocarbyl groups, *e.g*. PhN = Nph azo benzene or diphenyldiazene. The more stable derivatives contain two aryl groups. The N = N group is called an azo group. The name azo comes from *azote*, the French name for nitrogen that is derived from the Greek *a* (not) + *Zoe* (to live). More than half the commercial dyes belong to this class. Depending on other chemical features, these dyes fall into several categories defined by the fibres for which they have affinity or by the methods by which they are applied (Fernandez, 2004).

Classification of Dyes:

Dyes are classified in various ways according to (a) their chemical constitution (b) the methods of application to the fibre. Neither system of application is satisfactory by itself; the same chromophoric system may be present in dyes differing widely in use and application, the presence or absence of solubilising groups, proton-accepting groups, long-chain alkyl groups *etc*, are among factors determining dyeing characteristics and suitability for a particular technical purpose. However, the first two types of classification of dyes are considered the most important (Schmeyers *et al.*, 1998).

Classification according to Chemical Constitution:

One of the ways of classifying dyes is based on their chemical constitution, particularly considering the chromophoric system present in the dye molecule. The chemical constitution of dyes are so varied that it is not possible to classify all the dyes into proper group. However the main classes of dyes according to their chemical constitution are given below:-

C.I. Basic Orange Solvent Orange 15
(Acridine orange) 4600Where Me=Methyl group $(CH_3)_2$

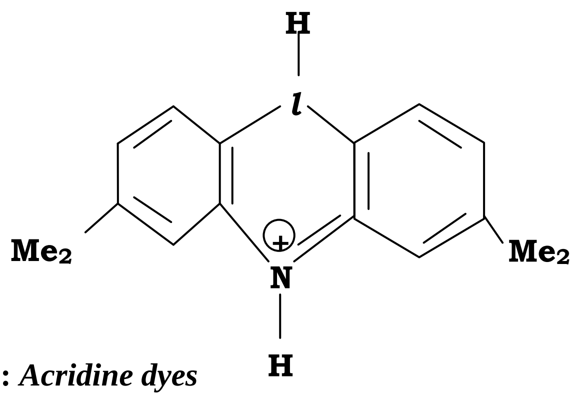


Fig. 1: ***Acridine dyes***

MATERIALS AND METHODS

Synthesis of 4-chlorophenylazo-1-Naphtholazo-4-Bromobenzene:

A concentrated hydrochloric acid (22.0cm^3) was mixed with 100cm^3 of distilled water. The solution mixture was used to dissolve 12.8g of 4-chloroaniline and the resultant solution was cooled to 0^{o}C. A cold 2M sodium nitrate solution (50cm^3) was slowly added with stirring for 10minutes, maintaining the temperature at 0^{o}C. Thereafter, 1-naphthol prepared by dissolving 14.4g of the compound in 150.0cm^3 of 2M solution of sodium hydroxide was coupled with the diazonium salt solution (prepared above) by mixing the solutions slowly with stirring for 30minutes. A red dye was obtained, filtered, washed with distilled water, dried and recrystallized using acetone as solvent. The TLC and percentage yield were determined. A second diazotiization was carried out by dissolving 4.3g of 4-bromoaniline in a mixture of 100cm^3 water and 22.0cm^3 of concentrated hydrochloric acid and the solution mixture cooled to 0^{o}C. A 50cm^3 cold 2M sodium nitrate solution was slowly added with stirring for 10 minutes, maintaining a temperature of 0^{o}C. Meanwhile, 7.1g of the pure red dye prepared previously was thoroughly dissolved in a sodium hydroxide solution prepared by dissolving 1.5g of sodium hydroxide in 38.0cm^3 of water. This was coupled to the bromoaniline diazonium salt solution over 30 minutes with continuous stirring. A maroon dye was obtained, filtered with Whatman filtered paper No 1 (11.0cm size), washed with distilled water, dried and recrystallized in acetone. The TLC and percentage yield were obtained.

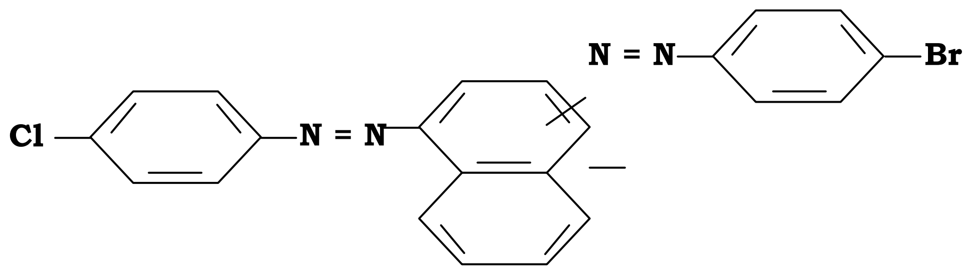


Fig. 2: 4-Chlorophenylazo-1-naphtholazo 4-bromobenzene Colour: (Maroon red)

Melting Point:

Melting point tubes were made by sealing one end of a capillary tube (about 5cm long) in a Bunsen flame. A little bit of the dry dye sample was put in the melting point tube. The tube was inserted into a melting point apparatus (Stuart MP 3). The apparatus was switched on and the temperature at which the sample begins to melt was recorded.

Tin Layer Chromatography (TLC):

A 0.1g of each dye sample was melted in a test tube. With the help of capillary tube, the sample solution was picked and dotted twice along a base line drawn on the chromatographic paper. It was inserted into a chromatographic tank containing 10cm^3 of methanol as the organic solvent. The movement of the mobile phase was monitored. When it stopped moving, a pencil mark was drawn along the chromatographic paper where the mobile phase stopped. The distance travelled by the compound and that travelled by the solvent front were recorded and the $\boldsymbol{R_f}$ calculated as follows:

$$\boldsymbol{R_f} = \frac{\text{Distance travelled by the compound}}{\text{Distance travelled by the solvent front}}$$

UV-Visible Analysis:

0.001g of the dye sample was dissolved with 10cm^3 of methanol and ensured thorough dissolution. Sample was collected in a cuvet and inserted into the UV and scanned from 900nm to 200nm. The distinct peaks were observed between 400 – 500nm and printed (Schultz & Julius, 1908).

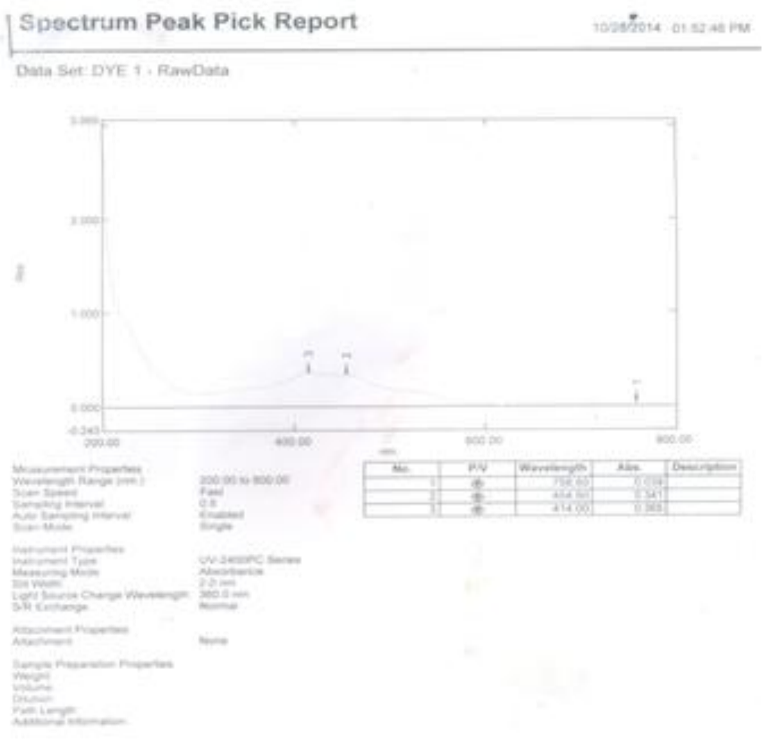
Fastness Test:

A 3g of OMO detergent was dissolved in cold water. 1000cm^{3}distilled water was added to make a standard solution. 1 g of disazo dye was weighed and dissolved. 0.5cm^3 of Ethanol and 100cm^{3}of ethanol was further added and stirred properly to make 1% solution maintaining pH of 4.5 – 5.2. The dyed fabrics were introduced into the dye bath at 42^{o}C and the temperature maintained at 32^{o}C for 24 hours. The fabric removed and rinsed with cold water using a wash bottle and dried on a cardboard sheet.

RESULTS AND DISCUSSION

The percentage yield of the synthesized dye was 95.10%, R*f* value of 0.56 and melting point value of 190^{0}C. These showed that the dye synthesized was pure.

Table 1
UV-Visible Spectrophotometer



The result of the UV-Visible spectrophotometer analysis of the dye showed that the dye sample absorbed at the visible region of 400 – 600nm with a distinctive peaks at 400 – 500nm, confirming to be a good dye (Schultz and Julius 1908).

Fastness Properties of Synthesized dye:

The dye was applied at 20% depth on the fine worsted wool, 100% cotton, Acrylic fibre, polyester (Dacron 54), Doctor Flannel worsted wool, polystyrene and nylon fabrics. The heat, light and wash fastnesses were given in Tables 2, 3 and 4 respectively.

1. Very Poor
2. Poor
3. Good
4. Very Good
5. Excellent

Wash Fastness:

The wash fastness of dye showed (2-3), 100% Cotton (3), Acrylic fibre (3), Polyester (Dacon 54) (3), Doctors flannel worsted wool (2-3), Polystyrene (4-5), Nylon (2). This showed that the dye has good fastness property for polystyrene which has very good – excellent (4-5), showed the dye had good affinity for polystyrene.

Table 2
Wash Fastness

The Dye	Fabrics						
	Fine Worsted Wool	100% Cotton	Acrylic fibre	Polyester (Dacon 54)	Doctors flannel worsted wool	Polystyrene	Nylon
	2-3	3	3	3	2-3	4-5	2

Light Fastness:

The light fastness of dye shows (5), 100% Cotton (5), Acrylic fibre (4-5), Polyester (Dacon 54) (4), Doctors flannel worsted wool (5), Polystyrene (4-5), Nylon (4), showing the dye had good affinity for all the fabrics.

Table 3
Light Fastness

The Dye	Fabrics						
	Fine Worsted Wool	100% Cotton	Acrylic fibre	Polyester (Dacon 54)	Doctors flannel worsted wool	Polystyrene	Nylon
	5	5	4-5	4	5	4-5	4

Fastness to Heat:

The heat fastness of dye showed, 100% Cotton (5), Acrylic fibre (4-5), Polyester (Dacon 54) (4), Doctors flannel worsted wool (5), Polystyrene (4-5), Nylon (4), showing the dye had good affinity for all the fabrics.

Table 4
Fastness to Heat

The Dye	Fabrics						
	Fine Worsted Wool	100% Cotton	Acrylic fibre	Polyester (Dacon 54)	Doctors flannel worsted wool	Polystyrene	Nylon
	4-5	4-5	5	4-5	4-5	5	5

CONCLUSION AND RECOMMENDATIONS

From the present findings it was observed that the dye made was a disazo dye, pure and possess the necessary characteristics like colour intensity. Further study needs to be carried out for confirmatory and hazardous effects of this dye to the environment. The investigation of fastness properties should be extended to other destructive agents like rubbing and sublimation should be further studied in order to ascertain the level of dis-changeability of this dye in the environment. The carcinogenic and/or environmental friendliness of the synthesized dyes should be analyzed to assess their possible health hazards so far

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