Imam Muhammad ibn Saud Islamic University
College of Sciences
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Synthesis and application of amino-4-methyl-3-((4-nitrophenyl)diazenyl)naphthalen-2-ol

A graduation research project

submitted to the Department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

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Abstract

Azo dye was synthesized from aromatic amines containing and 1-amino-4-methyl-naphthalen-2-ol by diazotization and coupling reaction. This dye was characterized by FTIR and ^{1}H NMR analysis. The dyeing assessment of the synthesized dye was evaluated on wool. Spectral properties and colorimetric data (L*, a*, b*, C*, h*, K/S) have been investigated.

ملخص

تم تصنيع صبغة الآزو من الأمين العطري المحتوية على 1-أمينو-4-ميثيل-نفثالين-2-أول عن طريق تفاعل الاقتران. تم تحديد خصائص هذه الصبغة من خلال تحليل الأشعة تحت الحمراء والتحليل الطيفي .تم تقييم الصبغة المصنعة على الصوف و التحقيق من الخصائص الطيفية والبيانات اللونية.

Chapter 1

INTRODUCTION

General Introduction

The textile industry is one among the rapidly growing industries worldwide. Textile industry utilizes enormous amounts of synthetic dyes. The industrial base greatly expanded in the Kingdom including all activities, among them are paper industry and paper products whose number increased by 18%. Textile is one of the developing sectors in Kingdom. Indeed, during the last five years, the textile factories increased from 19 to 28 factories.

Synthetic azo dyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetics and other industries [1,2]. Among them the textile industry is a major consumer. These dyes have characteristically good tinctorial strength as well as stability. Azo dyes produce bright, high-intensity colors, have fair to good fastness properties, are economical to produce and account for more than half of all commercial dyes used. They have found wide application in dyeing of protein fibers such as wool, angora, cashmere, and silk, [3]. They attach to wool fibers via electrostatic linkages between the cationic, protonated amino end groups of wool (NH_3^+) and the anionic sulphonate groups of the dye (Dye-O^-) [4].

Azo compounds have also found their way into high-technology areas, such as colorants for liquid-crystalline materials and photoconductors for photoreceptors in copiers and laser printers [5].

Acid azo dyes containing aromatic heterocyclic moiety have been investigated due to their wide applications [6]. The use of heterocyclic diazo or coupling component has made the production of colorants having brilliant color and chromophoric strength [7].

In the same way, we have developed this work to synthesis a novel mono azo dyes and to investigates its application in textile dyeing. Moreover, spectral properties and colorimetric properties (L^*,a^*,b^*,C^*,H^*, K/S) have been also studied in detail.

In agreement with the aims defined for the present project, the manuscript began with a general introduction, and then a bibliographic revision is made, in chapter 1, concerning the most relevant topics related to the use of azo dye for wool dyeing.

The second part contains the general methods and the materials utilized in the scope of this project.

The third part presents a general discussion, the major results, conclusions and gives some perspectives for continuing the work in this research field.

Chapter 2

REVIEW OF LITRATURE

1. Introduction

Color and its various uses come over the horizon from pre-historical period by all cultural groups and on all major land masses. The ancestors of man must have noticed (perhaps with or without understanding) the abundance of multitude of colors worn by nature. Certainly, it would have been fascinating to them. Every civilization has its myth and association with color.

“Colorant” is used as a name for materials such as dyes and pigments. Ability of natural colorant to be used as natural dyes has been known since ancient times. A dye can generally be described as “a colored substance that has an affinity to the substrate to which it is being applied”.

The art of dyeing was as old as human civilization. From the historical records, it is learnt that natural colorants were available to people during Greco-Roman periods. Then, in 1856 William Henry Perkin, an English chemist, while attempting to synthesize quinine from aniline, a coal tar byproduct, accidentally produced and discovered "mauve" the first synthetic dye. The color quickly became the favorite of royal family and a new industry was born-Dyestuff Industry. The advent of synthetic dyes and their immediate acceptability throughout the world due to wide range of colors and good color fastness properties resulted in the limited use of natural dyeing.

2. DYES

2.1. Dye definition

Dyes are intensely colored substances used for the coloration of various substrates including paper, leather, fur, hair, foods, drugs, plastics, and textile materials. They are retained in these substrates by physical adsorption, salt or metal complex formation or by the formation of covalent chemical bonds [9]. Until the middle of nineteenth century all dyes were natural products, extracted in most cases from a variety of plants, but also from a few animal sources. Plant sources include roots, stems, leaves, flowers and fruits while animal sources include certain dried insects. At present practically all dyes are coloured organic chemicals synthesized from products of the petro-chemical and coal-tar industries [10].

Unlike most organic compounds, dyes possess colour because they absorb light in the visible spectrum (400–700 nm), they have at least one chromophore (colour-bearing group), they have a conjugated system, and they exhibit resonance of electrons, which is a stabilizing force in organic compounds. When any one of these features is lacking from the molecular structure the colour is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (colour helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colorant and they are most often used to influence dye solubility

2.2. Classification of dyes

Chemical structures determine the colors, properties, and uses of dyes, and provide the only rational basis of a classification of these compounds. The categories of colorants recognized in the COLOUR INDEX and in the first nine editions of Conn are set out in Table 1.1.

Table 1.1. Constitution (chemical) classes of dyes recognized in the *Colour Index*.

Nitroso dyes	Indophenol dyes
Nitro dyes	Azine dyes
Azo dyes	Oxazine dyes
Azoic dyes	Thiazine dyes
Stilbene dyes	Sulfur dyes
Carotenoid dyes	Lactone dyes
Diphenylmethane dyes	Aminoketone dyes
Triarylmethane dyes	Hydroxyketone dyes
Xanthene dyes	Anthraquinone dyes
Acridine dyes	Indigoid dyes
Quinoline dyes	Phthalocyanine dyes
Methine dyes	Natural organic coloring matters
Thiazole dyes	Oxidation bases
Indamine dyes	Inorganic coloring matters

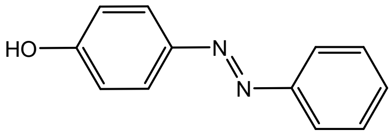
2.3. Specific interest to azo dyes

The azo group, -N=N-, is present in more commercially available dyes than any other chromophore. There are many applications in both industry and the laboratory for the dyes themselves and for the intermediate compounds that react with one another to form azo dyes or pigments.

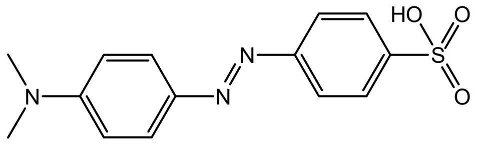
This linkage may be present more than one time and thus mono azo dyes have one azo linkage while two in diazo and three in triazo respectively. These azo groups are connected on both sides with aromatics like benzene and naphthalene moiety. Sometimes aromatic heterocyclic units are also present being connected with azo groups [11]. Different shades of the same dye having various intensities of color are due to these aromatic side groups. Azo dyes containing sulfonate groups as substituent are called as sulphonated azo dyes. Azo groups in conjugation with aromatic substituents or enolizable groups make a complex structure which lead to huge expression of variation of colors in dyes [12,13].

Some common examples of azo dyes are shown in Figure 1.1.

Yellow azo dye



Methyl Orange



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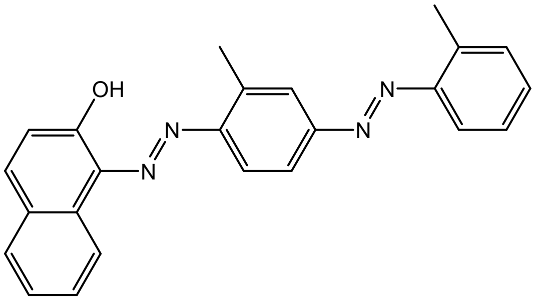
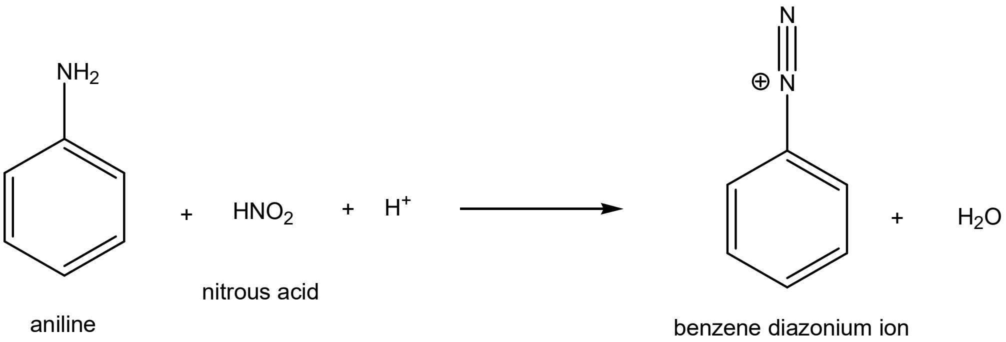
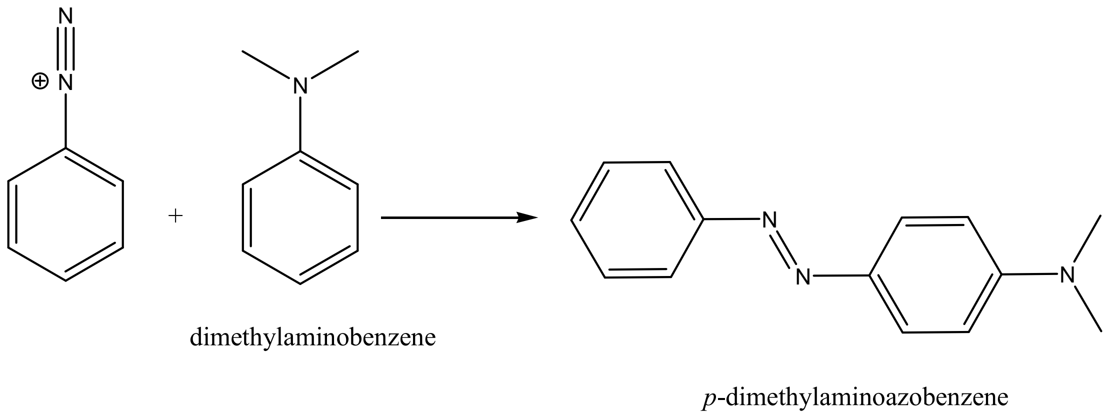


An azo group is formed when a diazonium ion, known as the diazo component, reacts with either a phenol or an amine, known as the coupling component. Diazonium ions are generated by the action of nitrous acid (from $NaNO_2$ and HCl) on aromatic primary amines at about 0° C (Scheme 1.1).



Scheme 1.1. Synthesis of benzene diazonium ion

Most diazonium salts are unstable, so they are used as soon as they have been made. In the azo coupling reaction, the end nitrogen atom of a diazonium ion displaces a hydrogen from the aromatic ring of aphenol or amine. The coupling occurs *para* or *ortho* to the hydroxyl or amine group. The *para* position is favored if it is not already occupied or hindered by other substituents. For example, benzene diazonium chloride couples with dimethylaminobenzeneto form *p*-dimethylaminoazobenzene (Scheme 1.2.).



Scheme 1.2. Synthesis of *p*-dimethylaminoazobenzene

The diazotate ion cannot couple. The synthesis ofthe dye must therefore be carried out at a pH that is a compromise between the alkalinity needed to generate the coupling component and the acidity that preserves the diazonium ion. The optimal pH is different for every pair of reactants; most phenols require more strongly alkaline conditions than most amines. Colored azo compounds can be synthesized by several methods other than coupling of diazonium salts [14], but such reactions are not often exploited commercially.

2.5. Classification of azo dyes

2.5.1.Cationic or basic azo dyes

These may have amine side chains, which are protonated in solutions at low pH, or quaternary nitrogen atoms, which are positively charged even under neutral or alkaline conditions. The charged group may be part of the chromogen (delocalized cationic dyes) or attached by a non-conjugated chain of carbon atoms (pendantcationic dyes).

2.5.2 Anionic or acid azo dyes

These have sulfonic or carboxylic acid groups attached to their aromatic rings. Sulfonic acids are strong (ionized at any pH), so the colored ions are always negatively charged. In acidic media, they are attracted to protonated amino groups of protein fibers (wool, silk). A carboxylic acid may not be entirely ionized at the pH of the dye bath.

2.5.3. Direct azo dyes

These anionic dyes have large molecules (two or more azo linkages) that can assume a coplanar conformation. Direct dyes bind to cellulose (cotton, linen) by nonionic, non covalent forces.

2.5.4. Reactive azo dyes

These have pendant side chains that can combine covalently with the substrate. Attachment to the hydroxyl groups of cellulose is amajor commercial application; the color has greater resistance to washing than can be obtained with any other type of dyeing.

2.5.5. Mordant azo dyes

In these, a hydroxyl group is adjacent to a ring carbon that is joined to either an azo nitrogen atom or a carboxyl group. Either arrangement can combine with a metal atom, such as chromium (III), to form a stable five- or six membered chelate ring. The dye-metal complex can be bound firmly by various types of substrates.

3.DYEING

3.1. Definition

Dyeing is a process of colouring textile fibres and other materials so that colouring matter becomes an integral part of the material rather than a surface coating. The mechanism of dyeing must differ with the nature of the material, that is, whether it is protein, cellulose or some synthetic substance [15]. The appropriate dye class for the fibre must be used along with specific dyeing conditions in order to gain an optimum result [16].

4.WOOL

4.1. Structure and chemical composition of wool fibre

Wool is a complex natural fibre composed mainly of proteins (97%) and lipids (1%), with a heterogeneous morphological structure [17]. Wool fibres have approximately the form of elliptical cylinders, with average diameters ranging from 15 μm to 50 μm and lengths determined by the rate of growth of the wool and the frequency of shearing. Wool and other keratin fibres consist of two major morphological parts: the cuticle layer (usually referred as scale layer of wool) which is composed of over lapping cells that surround the cortex (inner part of the fibre). The cortex comprises spindle-shaped cortex cells that are separated from each other by a cell-membrane complex (Figure 1.2), which consists of non-keratinous proteins and lipids [18].

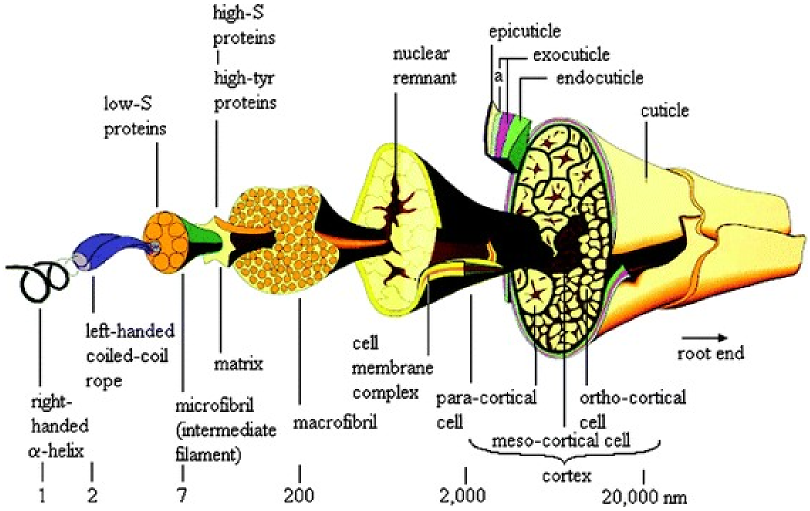


Figure 1.2 – Cross-section diagram of a merino wool fibre showing the structure at progressive magnifications.

The cuticle cells are laminar, rectangular structures which form a sheath of overlapping scales enveloping the cortex.

They comprise 10% of the total weight of the wool fibre. The cuticle cells are composed of three distinct layers. The outermost layer is the outer resistant surface membrane (epicuticle); the next layer from the surface of the cells is called the exocuticle, which is subdivided into two main layers (A and B-layers) that differ mainly in the cystine content. Finally the endocuticle is the cuticular layer nearest to the cortex [19].

The protein fiber wool consists of carbon, hydrogen, oxygen, nitrogen, and sulfur. The elemental analysis of wool is as follows:

Carbon	50.5 wt%
Hydrogen	6.8 wt%
Oxygen	22 wt%
Nitrogen	16.5 wt%
Sulfur	3.7 wt%
Ash	0.5 wt%

4.2. Chemical properties of wool fiber

4.2.1. Effect of acids

Concentrated acids damage it since they hydrolyze the salt linkages and hydrogen bonds. Dilute acids do not affect it.

4.2.2. Effect of alkali

It easily dissolves in alkaline solutions. Alkalis hydrolyze the disulphide bonds; hydrogen bonds and salt linkages of wool and cause the polymers to separate from each other, which is looked as dissolution of the fibre. Hydrolysis of the peptide bonds of wool polymers lead to polymer fragmentation and total destruction of the strand. Prolonged exposure to alkalis causes hydrolysis of the peptide bonds of wool polymers lead to polymer fragmentation and total destruction of the fibre.

4.2.3. Effect of bleach

Chlorine bleach is ordinary harmful to the wool. $KMnO_4$, Na_2O_2 are utilized for bleaching.

5.International Commission on Illumination: Color Systems

The CIE, or “Commission Internationale de l’Eclairage” (translated as the International Commission on Illumination), is the body responsible for international recommendations for photometry and colorimetry. In 1931 the CIE standardized color order systems by specifying the light source (or illuminants), the observer and the methodology used to derive values for describing color. The CIE Color Systems utilize three coordinates to locate a color in a color space. These color spaces include:

- CIE L*a*b*
- CIE L*C*h°

To obtain these values, we must understand how they are calculated. As stated earlier, our eyes need three things to see color: a light source, an object and an observer/processor. The same must be true for instruments to see color. Color measurement instruments receive color the same way our eyes do—by gathering and filtering the wavelengths of light reflected from an object. The instrument perceives the reflected light wavelengths as numeric values. These values are recorded as points across the visible spectrum and are called spectral data. Spectral data is represented as a spectral curve. This curve is the color’s fingerprint.

Once we obtain a color’s reflectance curve, we can apply mathematics to map the color onto a color space. To do this, we take the reflectance curve and multiply the data by a CIE standard illuminant. The illuminant is a graphical representation of the light source under which the samples are viewed. Each light source has a power distribution that affects how we see color. Examples of different illuminants are A — incandescent, D65 — daylight and F2 — fluorescent. We multiply the result of this calculation by the CIE standard observer. The CIE commissioned work in 1931 and 1964 to derive the concept of a standard observer, which is based on the average human response to wavelengths of light.

In short, the standard observer represents how an average person sees color across the visible spectrum. Once these values are calculated, we convert the data into the tristimulus values of XYZ. These values can now identify a color numerically.

5.1. CIELAB (L*a*b*)

When a color is expressed in CIELAB, L* defines lightness, a* denotes the red/green value and b* the yellow/blue value.

Figures 1.3 and 1.4 show the color-plotting diagrams for L*a*b*. The a* axis runs from left to right. A color measurement movement in the +a direction depicts a shift toward red. Along the b* axis, +b movement represents a shift toward yellow. The center L* axis shows L = 0 (black or total absorption) at the bottom.

At the center of this plane is neutral or gray.

To demonstrate how the L*a*b* values represent the specific colors of Flowers A and B, we've plotted their values on the CIELAB

Color Chart in Figure 1.3. The a* and b* values for Flowers A and B intersect at color spaces identified respectively as points A and B. These points specify each flower's hue (color) and chroma (vividness/dullness). When their L* values (degree of lightness) are added in Figure 1.5, the final color of each flower is obtained.

5.2. CIELCH (L*C*h°)

While CIELAB uses Cartesian coordinates to calculate a color in a color space, CIELCH uses polar coordinates. This color expression can be derived from CIELAB. The L* defines lightness, C* specifies chroma and h° denotes hue angle, an angular measurement.

5.3. Three-dimensional color system

Spectrophotometry’s applications are seemingly boundless. Colormatching measurements are made every day by those comparing a reproduced object to a reference point. Spectrophotometry-assisted color measurement can be useful in areas such as:

- Corporate logo standardization
- Color testing of inks
- Color control of paints
- Control of printed colors on packaging material and labels
- Color control of plastics and textiles throughout the development and manufacturing process
- Finished products like printed cans, clothing, shoes, automobile components, plastic components of all types

Each color has its own distinct appearance, based on three elements: hue, chroma and value (lightness). By describing a color using these three attributes, you can accurately identify a particular color and distinguish it from any other.

5.3.1. Hue

When asked to identify the color of an object, you’ll most likely speak first of its hue. Quite simply, hue is how we perceive an object’s color — red, orange, green, blue, etc. The color wheel in Figure 1.3 shows the continuum of color from one hue to the next. As the wheel illustrates, if you were to mix blue and green paints, you would get blue green. Add yellow to green for yellow-green, and so on.

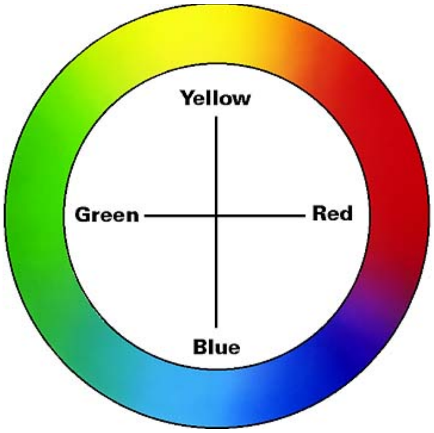


Figure 1.3. Hue

5.3.2. Chroma

Chroma describes the vividness or dullness of a color — in other words, how close the color is to either gray or the pure hue. For example, think of the appearance of a tomato and a radish. The red of the tomato is vivid, while the radish appears duller. Figure 1.4 shows how chroma changes as we move from center to the perimeter. Colors in the center are gray (dull) and become more saturated (vivid) as they move toward the perimeter. Chroma also is known as saturation.

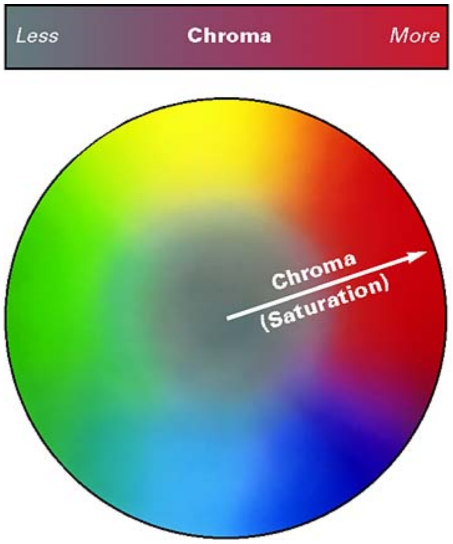


Figure 1.4. Chromaticity

5.3.3. Lightness

The luminous intensity of a color — i.e., its degree of lightness — is called its value. Colors can be classified as light or dark when comparing their value.

For example, when a tomato and a radish are placed side by side, the red of the tomato appears to be much lighter. In contrast, the radish has a darker red value. In Figure 1.5, the value, or lightness, characteristic is represented on the vertical axis.

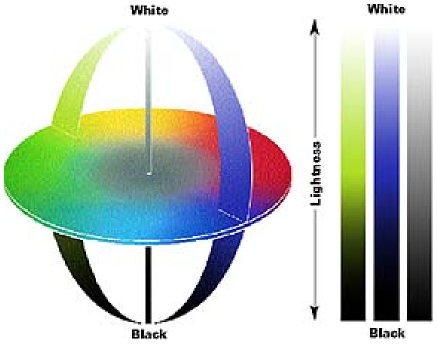


Figure 1.5. Three-dimensional color system depicting lightness

CHAPTER 3

Materials and Methods

1. Materials

1.1. Chemicals

1-Amino-4-methyl-naphthalen-2-ol, Sodium nitrite, *p*-nitro-aniline, hydrochloric acid, sulphamic acid and riboflavin were obtained from Sigma Aldrich (St Louis, MO, USA).

1.2. Proton NMR Spectrometer

NMR spectra were obtained on a Bruker AC 300 spectrometer operating at 300 MHz for ^{1}H. Chemical shifts are given in parts per million relatives to tetramethylsilane (TMS) and the coupling constants *J* are given in Hertz. The spectrum was recorded in DMSO as solvent at room temperature.

1.3. Infrared spectrometer

IR spectra were recorded on a Perkin-Elmer IR-197 spectrometer

1.4. Wool fabrics

The used wool was a scoured and bleached wool fabric of 205 g/m^2, 72 ends per inch and 64 picks per inch.

1.5. Equipment of Colour strength and colour depth measurements

The colour yield of samples was evaluated by light reflectance measurements using SF 300 spectrophotometer. Relative colour strengths (K/S values) were determined using the Kubelka-Munk equation [20]:

$$K/S = (1-R^2)/2R$$

Figure 2.3 : SF 300 spectrophotometer

2. Methods

2.1. Synthesis of azo dye

A solution of sodium nitrite ($NaNO_2$, 0.058 mol), in water (20 mL), was added slowly to a mixture of *p*-nitro-aniline (0.05 mol), in water (20 mL) and hydrochloric acid (30%, 0.125 mol), at 0-5 °C. After 30 min at 0-5 °C and pH less than 2, excess nitrous acid was destroyed by adding sulphamic acid. The resulting solution of benzene diazonium chloride was added slowly to a solution of 1-amino-4-methyl-naphthalen-2-ol (0.05 mol), at pH 6-6.5. The mixture was stirred for 30 min at room temperature and at pH 6.5. The solid product (1-amino-4-methyl-3-(4-nitro-phenylazo)-naphthalen-2-ol) was collected and purified by dissolving in distilled water (100 mL) and re-precipitating by slow addition of potassium chloride (30% w/v) to the stirred solution [21].

2.2. Wool pre-treatement

Before dyeing, wool fabric was further treated with a solution containing 5 g/L of sodium carbonate and 3 g/L of non-ionic detergent (Hostapal CV, Clariant), at 50 °C for 30 min. Then, it was thoroughly rinsed and air dried at room temperature.

2.3. Dyeing procedure

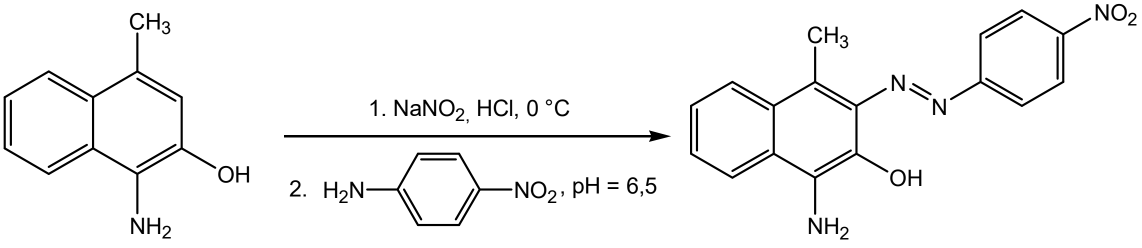
In a dye bath containing different amounts of dye (1 g/L) with liquor ratio 40:1, wool fabric was dyed using conventional heating (CH) at pH (3) for 30 minutes and at different temperatures (50 °C). The dyed sample was rinsed with cold water and finally dried at ambient temperature [22].

CHAPTER 4

Results and discussion

1. Synthesis and ^{1}H NMR study of azo dye 3

The synthesis of azo-dye **3** is produced in two steps. The first step is the formation of aromatic diazonium cation and the second step is the coupling reaction between this cation and 1-amino-4-methyl-naphthalen-2-ol **1** (Scheme 3.1).



1 **2** **3**

Scheme 3.1. Synthesis of azo dye 3

1.1. Structural study of azo dyes 3

A structure of a new compound **3** has been elucidated by FT-IR and ^{1}H-NMR measurements. Concerning the IR spectra of the azo dye **3**, structure was confirmed by functional group identification. Amino and alcohol group gave its peak at 3269 cm^{-1}, and appearance of the weak absorption band at 1548 cm^{-1} was due to the stretching band of azo group (Figure 3.1).

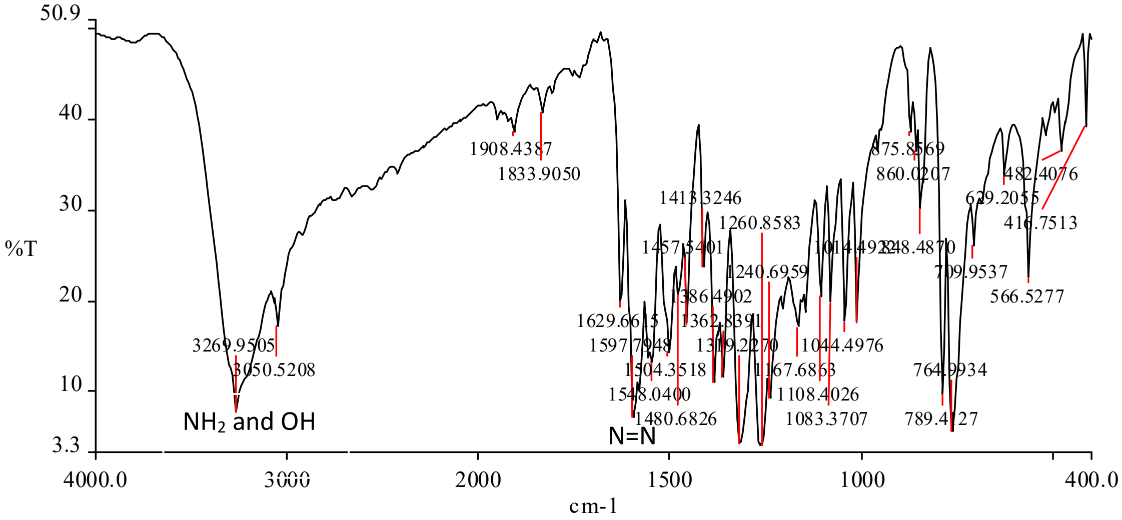


Figure 3.1 IR spectra of azo dye **3**

^1H NMR of azo dye **3** is recorded in DMSO. Dye show singlet at 2.37 ppm, which can be attributed to the methylene proton of phenyl ring. The aromatic protons are observed at 7.24-8.03 ppm, the four hydrogen atoms attached to the *para*-disubstituted ring gave an AA'BB' spin system. Compound **3** showed two broad absorptions as singlets at 10.05 ppm and 11.67 ppm, these confirmed the presence of NH_2 and OH groups (Figure 3.2).

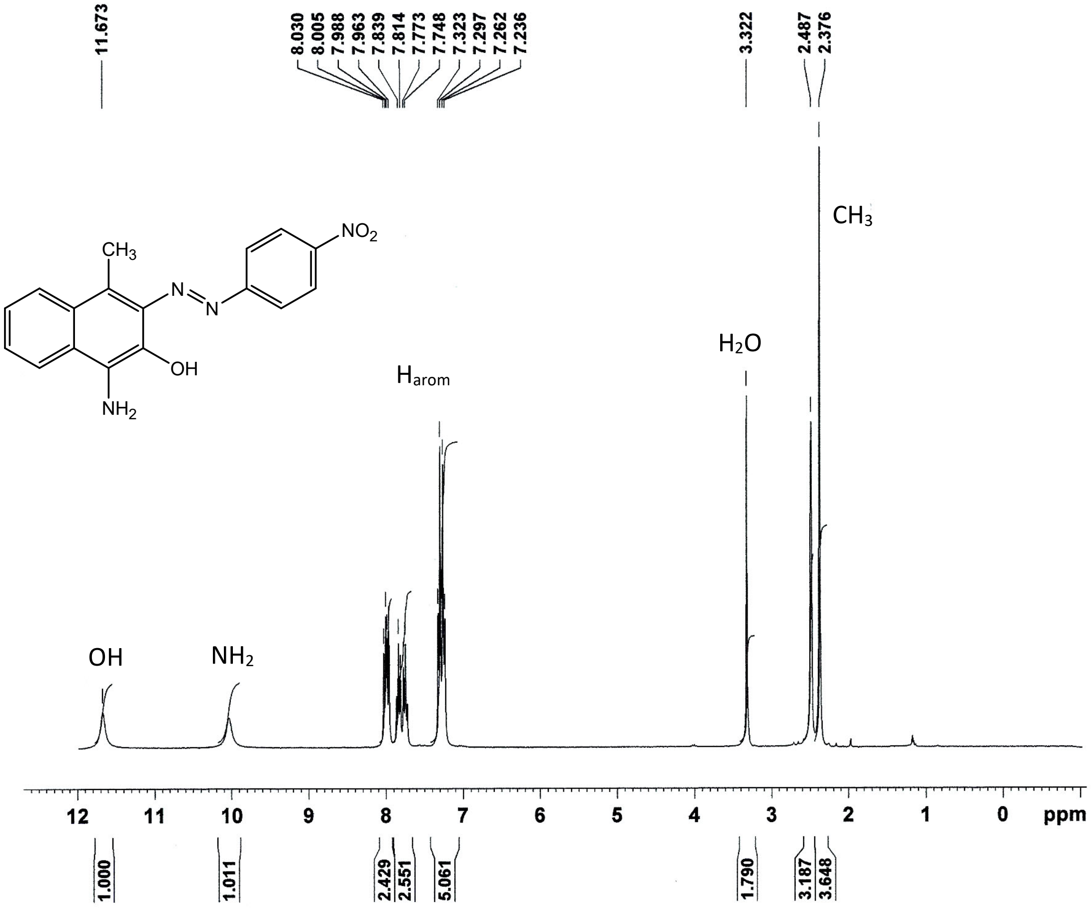


Figure 3.2. ^1H NMR spectra of azo dye **3**

2. Dyeing of wool fabrics with azo dye

Wool fabrics were dyed with azo dye at a liquor ratio of 40:1. The fabric was rinsed in tap water and air dried.

2.1. Colorimetric coordinates of wool fabric dyed with azo dye

Table 3.1 correspond to the color values (the colorimetric coordinates CILEAB) and the color strength (K/S) of the dyed wool samples which confirm the dyeability of the tested samples with the synthesized dye.

Table 3.1. Color values of azo dye on wool:

Dyeing conditions: pH 3, 30 min, 50 °C

$C_{molL}{}^{-1}$	L*	a*	b*	c*	h	K/S
1	51.53	29.70	20.55	36.12	34.68	9.40

CHAPTER 4

CONCLUSION

Conclusion

(*E*)-1-amino-4-methyl-3-((4-nitrophenyl)diazenyl)naphthalen-2-ol was synthesized and evaluated in dyeing wool fabric.

The structure of the synthesized compound was characterized using IR and ^{1}H-NMR spectroscopy.

Optimum conditions for the fixation of azo dye to the wool fabric were determined from the colour strength values on the dyed fabric.

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