SYNTHESIS AND PROPERTIES OF MONOAZO DYES DERIVED FROM ARYAMINES

BY

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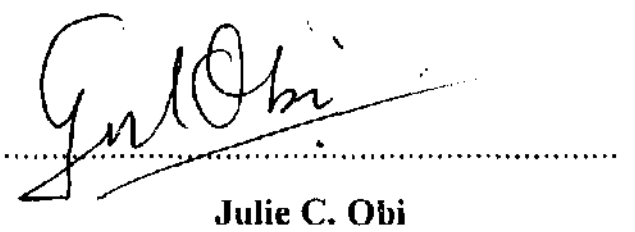
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ZARIA

NOVEMBER, 1997

DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other university or institution. The information acquired from the published work of others has been duly appreciated in the text by means of reference.



Julie C. Obi

Date: 21/11/97

CERTIFICATION

This thesis entitled "Synthesis and properties of monoazo dyes derived from arlyamines" by Julie C. Obi meets the regulation governing the award of the degree of Master of Science of Ahmadu Bello University and is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

This work is dedicated to God Almighty who granted me an opportunity to be alive up till this time. And also to my parent Mr. and Mrs. S.I. Obi.

ACKNOWLEDGEMENT

All thanks and praises be to our Lord Jesus Christ for bringing me up to this stage in life.

The successful completion of this research work would not have been possible without the collaborative efforts of many individuals among whom I wish to acknowledge are as follows:-

I am particularly grateful to my supervisor, Dr. K.A. Bello of the Department of Textile Science and Technology whose immeasurable co-operation, guidance, suggestions and criticisms were invaluable to the successful completion of this work.

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ABSTRACT

The synthesis of azo dyes derived from different diazo components and coupling components was undertaken and their spectroscopic properties in different solvents (ethanol, toluene and acetone) were measured. The results show that substituents have a marked effect on the colour of the azo dyes. Some of the subtituents shift the max of the dyes bathochromically while others cause a significantly hypsochromic shift in the max observed. The max of the dyes in ethanol is higher compare to other solvents (i.e acetone and toluene) due to high dielectric constant and hence more polar character of the former.

Analysis of the synthesised dyes by i,r, comfirmed the different groups present in the molecule. The effect of halochromism on the colour of the dyes syntheised were examined and protonation of azo dyes occurs readily.

Finally, all the dyes synthesised were applied to polyester and nylon fabric and their fastness characteristics assessed. It was found generally, that the dyes are very resistant to wash fastness and are also found suitable for transfer printing.

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CHAPTER ONE

1.1 INTRODUCTION

Dyes are coloured substances, which when applied to a substrate impart colour to this substrate by a process which at least temporarily destroys any crystal structure of the coloured substances. The dyes are retained in the substrate by adsorption, solution and mechanical retention or by ionic or covalnt chemical bonds. Dyes that are characterised by satisfactory permanence in spite of exposure to light, air and normal handling are referred to as fast dyes while others are fugitive.

All coloured substances, dyes and pigments have the power of absorbing radiation selectively from the visible region of the electromagnetic spectrum (λmax 400nm - 750nm). Such absorption being the characteristic of the molecular species concerned. There is an electronic transition between different molecular orbitals within the molecule and the wavelenghts absorbed are determined by the energy difference between the orbitals.

If a mixture of electromagnetic radiations of all wavelenghts of visible region (white light) falls on a substance, three results may be obtained. In the first case, they may be completely absored, in which case practically none is reflected and the substance appears black. Secondly, very little of the light may be absorbed, almost all be reflected and the substance appears white. Lastly, light of a particular wavelenght may be absorbed and the rest reflelted, in this case the substance appears coloured.

Therefore, when an electronic transition is in the visible range (400 - 750nm) the compound will appear coloured. The colour perceived for different wavelenghts of light are summarised in Table 1.1 (Griffiths, 1976). However, light of a given wavelenght is perceived as colours but if that wavelenght is absorbed, we perceive the complementary colour.

Some compounds appear to have a yellow colour even though their λmax are in the ultraviolet region. In such cases a "tail" of an absorption band stretches into the visible region (Andrew and Clayton, 1973). Since the light absored is violet or blue, we see the compound as the complementary colour of yellow.

Intensively coloured materials have absorptions in the visible region. For organic compounds, such electronic absorptions are generally $\pi \rightarrow \pi^*$ or n--> π^* transitions and involved extended electronic systems. That is, colour in organic compounds is generally a property of π structure. If the absorption band is narrow or sharp, the colour will appear bright or brilliant and clean. A broad absorption band or more than one band in the visible region gives colours that we perceive as dull or muddy.

Table 1.1 Pairs of Complementary Colours

Colour Absorbed	Wavelength Absorbed	Colour Seen
Violet	400 - 435nm	Yellow-green
Blue	435 - 480nm	Yellow
Greenish-blue	480 - 490nm	Orange
Bluish-green	490 - 500nm	Red
Green	500 - 560nm	Purple
Yellow-green	560 - 580nm	Violet
Yellow	580 - 595nm	Blue
Orange	595 - 605nm	Green-blue
Red	605 750nm	Blue-green
Red + Violet	750 - 435nm	Green

1.2 Spectroscopic and Quantum Chemistry of Organic Colourants

The visual colour of organic compounds results from absorption of light in the 400-750nm region. Although the spectral response of the human eye is involved in colour perception, the measurement of the spectral absorption feature in the ultraviolet and visisble region is important for discussing colour structural relationships.

Quamtum chemistry has established that light absorption of organic colourants in the uv-visible region arises from electronic excitation. The electronic excitation energy and transition probability determine the position and intensity of the absorption band, while the molecular vibration in the excited state account for the shape of the obsorption band.

The first attempts in interpreting light absorption of organic colourants made use of the knowledge that long wavelenght absorptions are observed for conjugated systems (Bury, 1935). This suggests that only electrons involved in conjugated bonds need to be considered. As the theoretical counterparts of the empirical mesomerism conception, the valence bond (VB) theory of conjugated systems (resonance theory) seemed to be at first, the most attractive approach in deriving colour-structureal relationships (Pauling, 1975).

Forster described dye molecules in both the ground and lowest energy excited states as mixture of two interacting reasonance structures (Lewis, 1939). Along these lines, the simplest streptocyanine dyes were studied by Herzfield and Sklar (1942). The wave functions of the two resonance structures, in which positive charge is positioned either at the one or at the other terminal nitrogen, are used to define the state wave functions of the dye molecules. The symmetrical conbination of the starting functions represents the ground state Ψ_0, the antisymmetrical combination, the excited state Ψ_1. The energy difference of both states represents the transition energy DE. According to Pauling (1975), the two resonance structures do not overlap appreciably. The calculated resonance spliting is therefore, too low and further structures must be included. The large number of resonance structures make valence bond calculations very time consuming and hardly feasible. In spite of the fact that several relationships between colour and chemical structure have been successfully interpreted (such as substitution and solvent effects), the valence bond theory lost its paramount importance in elucidating colour-structure relationships.

Later, the theory of molecular orbitals (MO theory) attracts more and more attention in accounting for absorption features of organic colourants. According to this theory, the electronic states are described by means of molecular one-electron functions Yi (molecular orbitals, MO_s). This method seems to be less suited as no information is obtained about the wave functions of the ground and lowest excited state Yo and Yi, respectively.

Much attention in colur chemistry was first paid to the free electron model (MO-FE theory) which was developed by Kuhn, Bayliss and Platt (1948). Here, they assumed that the potential energy of the π-electrons moving along a chain structure or along a cyclic structure, is independent of their positions. In the simplest cases, one examines the energies of an electron in a one dimensional box. The MO's are then given in closed form shown, for example, for strepto-polymethine dyes. In the ground state of the molecule two electrons of anti-parallel spin occupy the lowest energy orbitals.

According to this model, light absorption results from exciting an electron from one of the occupied to one of the unoccupied orbitals. Excitation from the highest occcupied molecular orbital (HOMO) to the lowest unoccupied molecylar (LUMO), that is, excitation between frontier molecular orbital's (FMO's) gives rise to the lowest energy $\pi \rightarrow \pi^*$ transition. This model has been succcessfully applied by Kuhn to rationalize the colour of various natural and artificial dyes (Forsterling & Kuhn, 1975), but its application is limited in scope.

In the molecular orbital-linear combination of atomic orbital (MO-LCAO) approximation each molecular orbital Yi is represented by a linear combination of atomic orbitals Qr, where the expansion coefficient (Cir) are algebraic numbers. Therefore, if an electron occupies the MO Yi, Cir^2 means the probability to find the electron in the region of the atom r, π-type MO's are generated by combining P^{π} orbitals. Hence, LCAO-MO's show much resemblance to FE-MO's. The colour determining lowest transition energy can be similarly calculated from the frontier orbital energies.

Also, the most serious drawback of the HMO method represents the explicit neglect of electron-electron interaction. This led to development of semi-empirical treatments which take into account electron-electron interaction explicitly e.g. Pople's SCF-method (Parr, 1964). In this frame work transition energies are no longer simply equal to energy differences between occupied and unoccupied orbitals, but contain additional electron-electron interaction terms. This method has been further improved by adding the configuration interaction (CI) procedure, as described by Parise and Parr (1975). The semi empirical SCF-CI treatment is known as PPP method, named after Pariser Parr and Pople.

PPP calculations of various colourants showed that the singly excited configuration which results from electron excitation from the HOMO to the LUMO, contribute dominantly to the resulting excited state. In contrast to HMO theory, PPP calculations also permit a discussion about the shorter wavelenght absorption. Also, PPP calculations proved to be highly useful in

elucidating the chromophoric systems in all classes of organic colourants. Therefore, compounds absorbing at long wavelenghts such as substituted azo, amino, anthraquinone dyes, indigo, quinacridone and polymethine dyes are mostly calculated at shorter wavelenghts than experimentally found.

Finally, all the calculations mentioned above refere to the isolated molecule while the observed colour or spectral data are more or less influenced by the surrounding medium givig rise, in many cases, to considerable bathochromic or hypsochromic shifts (positive or genative solvatochromism).

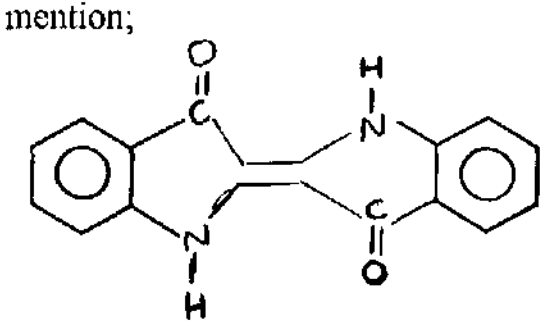
1.3 TYPES OF DYES

The knowledge and use of colour began with dawn of civilization. In the beginnig, men utilized the colours he found in the earth and in the products of the earth. It is probable that the earliest dyes were discovered by accident, by products of stains from berries, fruits or nuts as food. But as generation succeeded earh other, man started looking for a way of getting colours, brighter colours and more varied colours. This then led to discovery of science and technology. Therefore, in the broadest sense, dyestuffs are divided into natural and synthetic dyes.

NATURAL DYES

This group comprises all dyes obtained from animal or vegetable matter with little or no chemical processing. Example include, berries, roots, bark, flowers and marine growth, such as indigo, woad, madder and logwood from plants and tyrian purple from shells. These dyes can also be used to dye furs, textilss fibres etc. Among the natural dyes extracted and use, the following deserve mention;

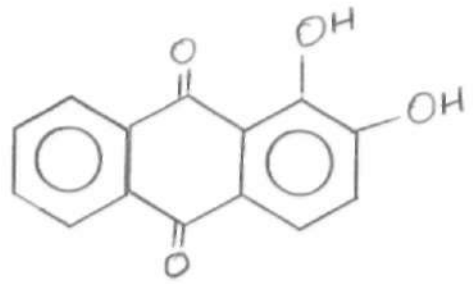
(i) **Indigo**



(i)

Indigo was obtained from dyers wood indigenous in Europe and from Indigo fera tinctoria, a native plant of Asia. Unlike most other natural dyes, it has not been replaced by some superior synthetic product, instead the colouring matter in the original dye has been replaced synthetically in the same form. The analysis and synthesis of indigo was one of the greatest chemical achievements of the late nineteenth century and a major triumph of the German dye making industry. Indigo has always been a more satisfactory dye for cotton than wool.

(ii) **Alizarine**

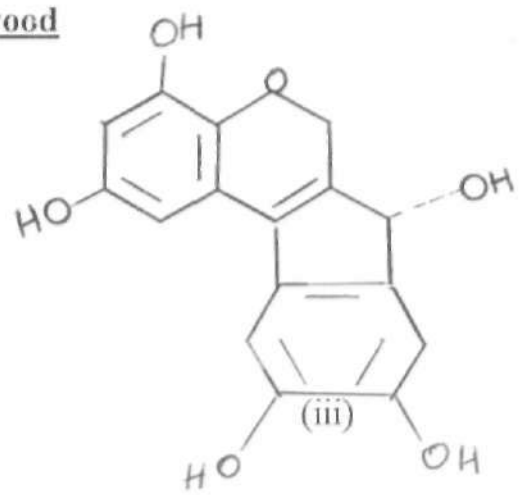


(ii)

Madder was second only in importance to indigo and was for many centuries the best red. The colouring matter in natural madder is Alizerine (ii) and the synthetic production of this was one of the early triumphs of the dyestuff chemists of the nineteenth century. Once Alizerine had been produced synthetically the use of natural madder ceased because the quantity of actual colouring matter in the natural madder was only about two percent (2%).

Madder was a mordant dye and its two greatest uses were first, in the production of the turkey red shade and secondly in the printing trade. Alizerine obtained from madder extracted from Africa was used to dye wool, silk, fur etc.

(iii) **Logwood**



(iii)

Logwood (CI natural black 75290) was the first satisfactory homogenous black dye and came into general use after the discovery of America. Previously blacks were normally dyed woad and after treated with another dye such as madder or weld, so as to turn the blue of the woad to as near black as possible.

When logwood was introduced the dyers woad made repeated and in many cases successful efforts to prohibit its use. This prohibition was justified because the dyers at first tended to use logwood to give a blue. When dyers gave up using logwood and turned to producing satisfactory black which in conjuction with a copper or chrome mordant, it became recognised for what it really was, the first true black. It remained the only one until the coming of the synthetic dyes. Logwood is used for dyeing of silk, nylon, viscose acetate fibres etc.

Other examples of natural dyes include Saffron, henna cochineal from insect Cochina etc. Most natural dyes have no direct affinity for textile fibres and therefore applied by means of mordants which function as fixing agent. The name mordant is derived from the French word "Modrs" and is based on the early belief that these mordants corroded the fibres. opening the pores for the dye molecules to enter. But it was later discovered that the mordants combine with the dye molecules to form insoluble compound or colour lakes inside the fibre. Usually, the mordants not only fix the dye but are essential for colour formation and a single dye may give a range of hues with different mordants.

Historically, the chief mordant was alum but during the twentieth century, chrome has so much dominated the scene that now mordant dyes are usually called chrome dyes. Others are aluminium, copper etc. These are metal salts.

1.3.1 LIMITATIONS OF NATURAL DYES

The extraction and application of natural dye was the main concern of the industry that flourished in the nineteenth century. A lot of problems were encountered in the production and application but their degree of fastness was something less than good.

Natural dyes require the use of mordant for colour fixation. The concentration of these mordants can result in non-uniformity of dyeings. Also some mordants are very expensive. The extraction procedure of natural dyes are very cumbersome and expensive for large scale production. Dyes can take from two to ten months to make and are most difficult to make correctly in shade and strenght because they have to satisfy the human eye.

Natural dyes from plants spoil, ferment or mold at room temperature within two to three days unless precautions are taken to preserve them. Though, this effect can be minimized by keeping the dyebath in cool place or even in the refrigerator. Fermented dyes produce toxic substance.

Also, most of the natural dyes cannot be applied on synthetic fibres such as polyester, nylon, acrylics, polyolefins, polyethelene etc. Therefore,

due to their large size molecules and its high solubility, they have poor wash fastness.

The shades range of the natural dyes are limited. The common hues are blues obtained from woad, blacks (in conjuction with madder and green (from old vats)), but gradually replaced by indigo. Natural dyes are hydrophilic in nature i.e water soluble dyes, consequently, do not suit hydrophobic materials.

Finally, to produce bright and clear colour, the dyebath has to contain soft water which is obtained normally by the application of washing soda to boiling water, that is, later filtered before vegetable dyeing ensued. This leads to time wastage and also expensive.

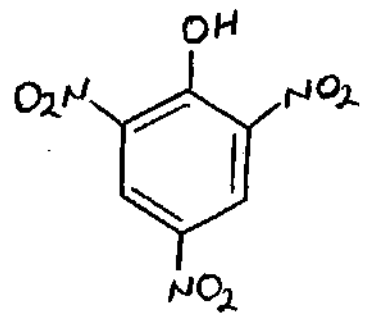
1.4 HISTORICAL DEVELOPMENT OF SYNTHETIC DYES

Despite the fact that Hoffmann was the brain behind the synthetic dyestuff industry, it is usual to start the story of the industry with the discoveries of W.H. Perkin and there are good reasons for this.

In 1858, when Perkin was a students under Hoffmann at the Royal College of Chemistry, he acquired from his master the enthusiasm for experiment which was the mark of all who worked there. Perkin continued his experiments at home and the first synthetic dyes made came from one of these (Abrahart, 1968). The actual remark of Hoffmann that led to Perkin's

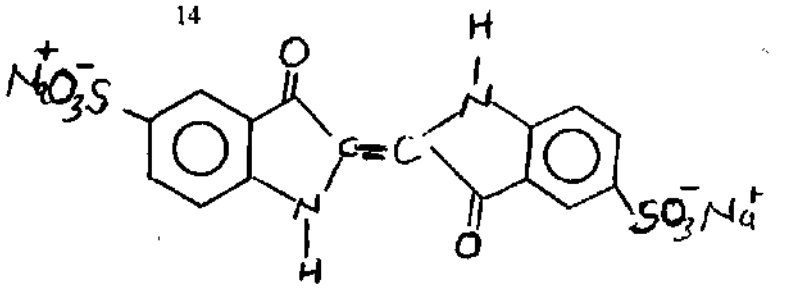
discovery of Mauve (purple) was a suggestion that it would be a good idea to synthesise quinine. From Perkin's experiment, quinine was not obtained and chemists now known that it was not possible to obtain it in that way. Instead, Perkin obtained a dark precipitate and having repeated the experiment again, he obtained similar precipitate. On working with this precipitate, he found that he was able to obtain a deep mauve or purple colour from it.

Although, purple dye was regarded as the start of the synthetic dye era this was actually neither the first synthetic dye to be manufactured in the laboratoey nor even the first to be produced. The first synthetic dye belongs to picric acid and the simplest dye known. It is a yellow colouring matter formed by the action of concentrated nitric acid on many organic substances including skin and was manufactured in 1845 by nitrating phenol obtained from coal-tar.



(iv) Picric acid

Picric acid is a member of acid dye class which does not occur in nature. The first acid dye, howver, was the sodium salt of indigo-5,5'-disulphonic acid manufactured by Barth in 1740 (Noller, 1951). It was sold under the name Saxe blue. The structure is shown below;

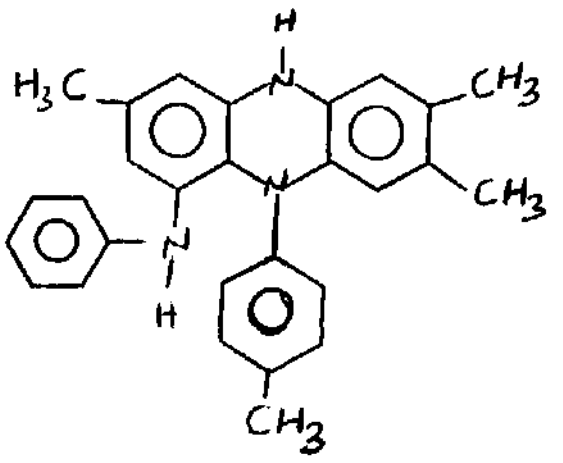


(v) 5,5'-disuphonic acid

The second synthetic dye was synthesised by Pront in 1818 (Trotmann, 1976) by treating uric acid with nitric acid followed by ammonia. Such a source was "gnano" the dry excreta of sea-birds imported from Peru for use as a fertilizer and murexide began to be manufactured in 1853 in Mulhouse and in 1855 in Manchester (Allan, 1971).

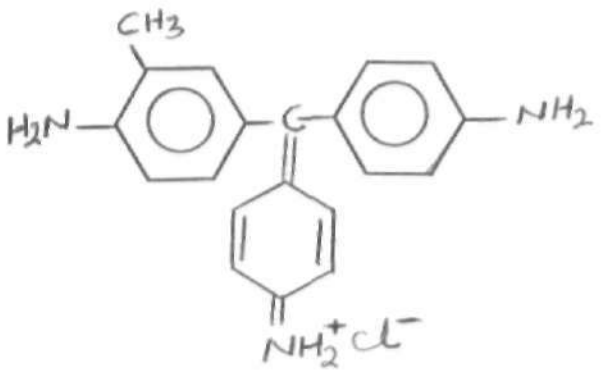
Therefore, the observation that a coloured compound could be obtained from Aniline was not new as Runge has discovered them over twenty years previously. Though, Perkin was

pressumably unaware of this, but he was the first to recognised that a coloured compound might be a dye. The structure of the main constitution of aniline purple was believed as written below;



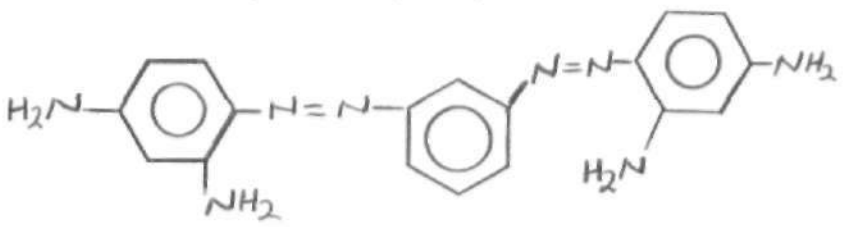
(vi) Mauve

The fact that a commercially successful dye could be produced from aniline prompted many others particularly in France to try the effect of reagent on aniline. Verguin (1952) heated impure aniline with stanic red (basic dye) which was later named as maganata.



(vii) Maganata dye

Also in 1958 (Witt, 1976), a reaction was discovered which eventually yielded more dyes, than all the others put together. This was diazo reaction discovered by Peter Greiss (1976). The first commercially successful azo dyes ws Bismark Brown discovered by Martin (1975).



(viii) Bismark Brown

Therefore, within fifteen years of Perkin discovery, it was possible to dye every natural fibre in a very much wider range of shade with synthetic dye called "Coal tar colour" or aniline colour (dyes) than with natural dyes.

1.5 COLOUR AND CHEMICAL CONSTITUTION OF ORGANIC DYES

The origin of the colour of organic substances could only be successfully explained when the molecular constitution of the first dyes had been established and the first synthesis carried out. As more and more dyes were discovered and their properties studied, working rules emerged, whereby colour and dyeing properties could be related with structure. To mention but few concepts which have significantly contributed to the theory of colour and structure, the following are paramount.

The first relations between colour and molecular constitution can be traced back to Graebe and Liebermann (1868), who related the colour of the organic substances to a system of unsaturated bonding. About a decade later after the elucidation of the constitution of several dye molecules. Witt (1975) founded the classical theory of colour. He attributed the visual colour to the presence of particular groups - the chrommophores. Examples of chromophores include; $-NO_2$, -N=N-, >C=O, and also >C=C<. Structures containing chromophores were termed as "chromogens". When the chromophore is colourless itself, the so called auxochromic groups may be introduced to give it colour. Auxochrome has the ability to retain charge more readily than carbon atom. Examples of auxochrome include:- $-NH_2$, $-NR_2$, -OH in addition to hydrophilic groups $C-SO_3$, $-SO_3^-$ Na+ or hydrophobic substituents which regulate their water affinity.

Witt's theory of colour was extended and refined in the course of this century by Kauffman, Dilthey and Wizinger (Dilthey, 1928; Dilthey and

Wizinger, 1975). During this time the meaning of the terms chromophore and auxochrome underwent considerable change (Mohler, 1975). The term "anti auxochromes" was newly introduced for groups which induce a brightening of the colour (Fabian and Hartman, 1975). Antiauxochromes are example; -N=O or C=O, that is groups which formerly belonged to the Chromophores. Wizinger attributed the colour of organic colourants to the presence of intra molecular ionic states, which were modelled by coupling of auxochromes and antiauxochromes with conjugated systems.

These approaches obviously consist in a partitioning of the whole conjugated systems of the dye molecule into several molecular building blocks. Although, the explanations given in Witts-Dilthey-Winzinger's colour theory later proved to be less satisfactory or even completely wrong, the idea of molecular partitioning retained much of its appeals. Thus Griffiths most recently has regarded important synthetic dye as being composed of donor and acceptor fragments ("donor-acceptor chromogens") (Griffiths, 1964).

On the other hand, already soon after the foundation of Witt's theory of colour, also concepts were developed which clearly contrast with those just mentioned. In these concepts the colour was attributed to larger conjugated bond system as a whole. Thus Nietzky (1889) and Armstrong (1975) related the colour to quinoid structures. According to them, triphenyl methine dyes owe their colour to quinoid structures. Also Izmailskii (1913) stated that dyes molecues exist in a "mesotropic equilibrium state" which gives rise to the colour ("chrome-state"). The comceptions resembles in the later introduced

and widely used mesomerism approach and its equivalent presentation in terms of quantum mechanical resonance (Allen, 1971). The colour determining conjugated system has now been generally designed the chromophore.

Colour determining conjugated systems, however, are not exclusively cyclic structures. Already early studies pointed out that some coloures compounds contain chain molecules. Later Konig recognised the basic polymethine chromophore (Konig, 1975). He defined polymethine as chain molecules containing an odd number of methine or hetero analogues groups ("mesochrome") and terminal groups ("perichromes"). These structure give rise to the "chromo-state". According to Konig the chrome-state is characterized by a high degree of bond equalisation and charge alternation along the conjugated chain. The terminal perichomes are mono-valent groups. They determine whether the dye molecules is neutral or ionic.

Finally, all the above mentioned concepts of the classical theory of colour are phenomenological in essence, based on the chemists' experience and intuition ("chemical theories"). Although, each concept possesses its own features, there is one principle inherent in all conceptions, the deeply coloured conjugated system is, in principle, responsible for the colour. But the colour can also often be rationalised alternatively by assembling the conjugated system from chromophoric subunits. The latter approach has an appreciable heuristic value: a great variety of chromophores can be conceived by combination of only a few basic chain and cyclic subchromophores.

1.6 RAW MATERIALS FOR SYNTHETIC DYES

The primary source of organic raw materials for the dye industry has traditionally been product recovered from the fractional distillation of coal-tar. Hence, the name "coal-tar dyes" is frequently used in place of the more correct "synthetic dyes". Coal tar is a product of the gasification (or carbonization) of coal, the primary purpose of which is the production of coke for steel manufacture and coal gas for industrial and domestic heating. The coal-tar is refined by distillation and from over 300 products which have been isolated and characterised the most important for the dye industry are benzene, toluene, xylene, naphthalene, anthracene, acenaphthene, pyrene, pyridine, carbazole, phenol and cresols.

In addition to the organic materials mentioned above, a great variety of inorganic chemicals are used in the dye industry. These include sulphuric acid and oleum for sulphonation, nitric acid for nitration, chlorine and bromine for halogenation, caustic soda and caustic potash for fusion and neutralization and sodium nitrite for diazotisation, as well as hydrochloric acid, sodium carbonate, sodium sulphate, sodium hydrosulphite, sodium sulphide, aluminium chloride, sodium dichromate, mangese dioxide, iron powder and many others.

The great number of intermediates are also used to manufactures dyes. The intermediates employed are J- acid, H-acid, Tobias acid. The use of these

intermediates make manufacture by continous process uneconomical. Therefore, anthraquinone, produced from anthracene by catalytic air oxidation is one of the very few intermediates used solely by the dye industry that is made by continuous peocess.

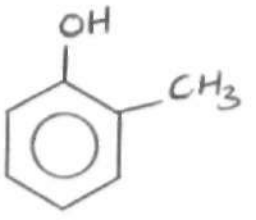
Some of the primaries obtained for dyestuff industries at high temperature carbonization of coal tar and also the intermediates are summarized below;



Benzene
(ix)



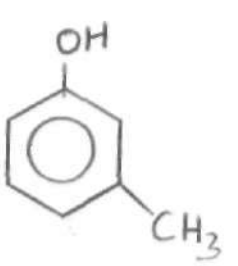
Toluene
(x)



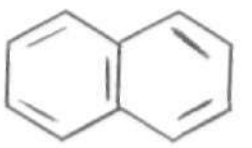
O-Cresol
(xi)



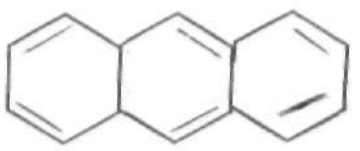
Xylene
(xii)



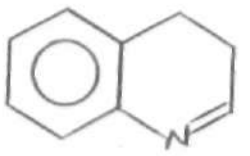
M-Cresol
(xiii)



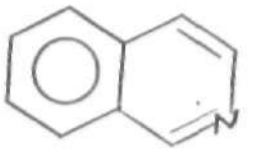
Naphthalene
(xiv)



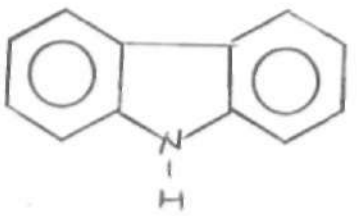
Anthracene
(xv)



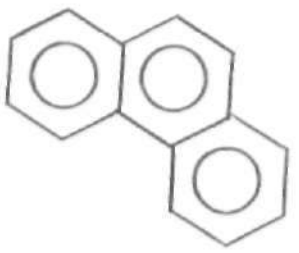
Quinoline
(xvi)



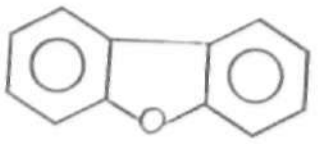
ISO-quinoline
(xvii)



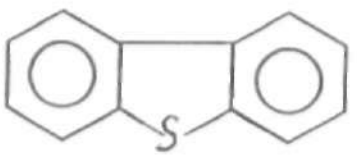
Carbozole
(xviii)



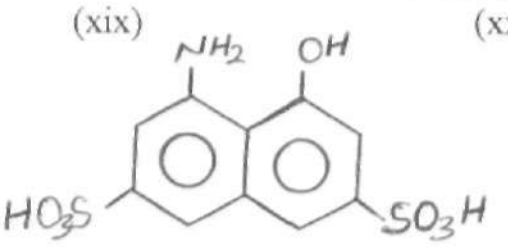
Phenanthrene
(xix)



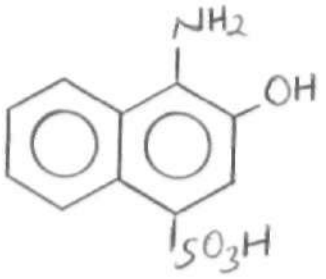
Dibenzofuran
(xx)



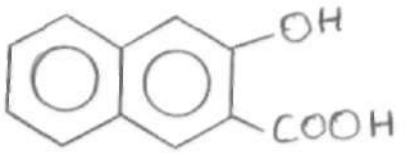
Dibenzothiophene
(xxi)



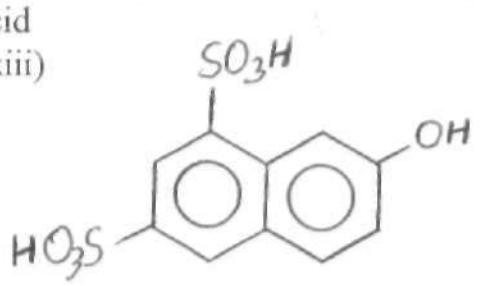
(8-amino-1-Naphthl-3,6-disulphonic acid)
H-acid
(xxii)



(-amino-2-Naphthol-4-sulphonic)
acid
(xxiii)



(2-Naphol-3-Carboxylic)
acid
130n-acid
(xxiv)



(2-Naphthol-6,8-disulphonic)
acid
(G-aind)
(xxv)

1.7 CLASSIFICATION OF DYES

Dyes have been classified according to a variety of schemes. Classes based on usage and application are especially useful to the dyers but result in groups containing a great diversity of chemical structures. To the chemist, the classification by related chemical constitution is, therefore, much more desirable. Today, the chemical and usage classification of dyes used in colour index are the most widely accepted throughout both the manufacturing and dyeing industries.

1.7.1 CLASSIFICATION OF DYES ACCORDING TO METHOD OF APPLICATION

The organic dyes can be classified according to the method of application to the fibres as follows;

(a) **Acid dyes**

Acid dyes contain both a chromophoric group and a water-solubilizing group. Usually the solubilizing group is the sulphonic acid radical, $-SO_3H$. Acid dyes are not generally acids (dye-SO_3Na) of strong sulphonic acid groups. In most cases where solubility is not due to a sulphonic group, the dye contains either a carboxyl group or a hydroyl group. Acid dyes have little or no affinity for pure cotton, even in the presence of 0.5% sodium chloride or sodium sulphate. But they can be used to dye protein and polyamide fibre.

(b) **Basic or cationic dyes**

Historically, the first synthetic dye, mauve, prepared by Perkin in 1856, was a basic dye. Prior to the discovery of acrylic and polyester textile fibres the major application area for basic dyes was on mordanted cotton, linen, rayon when bright tinctorically strong shades were required. The light and wash fastness properties of basic dyes applied by the mordant method are poor. Basic dyes are applied to wool and silk when brightness and tinctorial strenght are more important than fastness to light and washing.

(c) **Direct dyes**

Direct dyes are water-soluble dyes that exhaust onto cellulosic fibres, such as cotton, linen and rayon, from a salt bath without mordanting of the fibre. Due to these properties, direct dyes are called substantive.

Chemically, nearly all direct dyes are azo product containing one or more sulphonic radicals, which impart water solubility. A few also contain carboxyl groups ortho to hydroxyl, a configuration which permits aftertreatment for improvement of fastness. Direct dyes are easier to salt out from aqueous solution than the acid dyes.

(d) **Disperse dyes**

Disperse dyes are water-insoluble, coloured organic substances, which can be dispersed in water in a very fine particle size. Disperse dye was initially developed for dyeing acetate, but also find applicable to colouring of

nylon and many of the newer synthetic hydrophobic fibres. The newer fibres have a more compact structure than the secondary acetate. Current developments in disperse dyes have been towards improvement in the dyeing or fastness properties, by introduction of modifying substituent groups rather than by building of larger molecules.

Finally, the fastness properties of disperse dyes vary depending upon the fibre to which they are applied. Wet fastness properties are generally better when applied to the new hydrophobic fibres e.g polyester or triacetate that they are on nylon or secondary acetate.

(e) **Oxidation dyes**

This is a small group of dyes, only one type of which is of importance in textile colouration and even this is restricted largely to printing. They are so called because on chemical oxidation they are converted to insoluble colourants inside the fibre. The classical oxidation dye is Aniline Black.

(f) **Chrome dyes**

In the colour index, these dyes are classified as mordant dyes, but since the only mordants used to any extent commercially in textile dyeing are chromium compounds the term "chrome dyes is generally used. The essential feature of these dyes is that the basis of their apllication is the formation inside the fibre of a very stable co-ordination complex of the chrome dye and

chromium from the mordant. After the application of the dyes to the substrate, they are essentially irreversible whereby dyeings of very high wet fastness are obtained.

(g) **Vat dyes**

These are water insoluble pigment characterised by the presence in their struture of the least two keto or quinone groups (- C=O) which enable them to be converted into alkaline soluble leuco compounds which when absobed by the fibre are subsequently oxidised to the insoluble pigment. They are applied to the fibre in reduced form, they are then oxidised to the original insoluble pigments. Vat colours are widely used on cotton, viscose ravon, linen and other vegetable fibres.

(h) **Reactive dyes**

This is a new type of dyestuff first marketed in 1956 which react chemically with the cellulose in fibres, wool, silk and nylon under alkaline condition. They are applied with final hot wash (Beach, 1970). The major problems in the use of reactive dyes is the reaction of the dye with water instead of the substrate and this leads to hydrolysis and this can be minimized when dyeing by exhaustion technique, by adding the alkali required for the fixation at a later stage of dyeing process or by using small liquor ratio.

(i) **Ingrain dyes**

This is the name given to a small group of dyes, almost all of them based on phthalocyanine precursors, which under the prescribed conditions of application form insoluble phthalocyanine inside the fibre.

1.7.2 CLASSIFICATION OF DYES ACCORDING TO CHEMICAL CLASS

Organic dyes can be classified according to chemical class as follows;

(i) **Azo dyes**

The azo dyes and pigments form the largest groups of all the synthetic colourants and play a prominent part in almost every type of application. Azo dyes are characterised by the presence of one or more azo groups (-N=N-) which form bridges between organic residue. Simple azo compound have the general formula R_1-N=N-R_2 in which the residue R_1 and R_2 are saturated, unsaturated or aromatic groups.

Azo dyes are made almost exclusively by the diazotiation of a diazo or diazonium salt, a reaction of fundamental importantce to the industry discovered by Greiss (1976). The diazonium salt is coupled with phenols, naphthols, arylamines, pyrazolenes, or other suitable compound to give hydroxy-azo or amino azo compound or their tautomeric equivalent. In the resulting dyes the azo group is the chromophore and the hydroxyl or amino group is an auxochrome.

The importance of the azo colourant is shown by the fact that they embrace over 60% of the total number of dye structure known to be manufactured. The application involves acid dyes for wool and polyamide, basic dyes for acrylic fibres, direct dyes for cotton and viscose rayon, disperse dyes for polyester and reactive dyes for cellulose. Further areas of their application are dyeing of paper and leather and their use as pigments. The azo dyes comprise practically every shade from yellow to black.

Azo dyes are further sub-divided into mono azo, disazo, trisazo, or polyazo depending on wether there are one, two, three or more azo chromophoric groups respectively in the dye molecule. They all cover the whole of visible region of the spectrum. Thus yellow, red, blue, green etc can be synthesized by introducing a suitable substituents in the acceptor and donor ring of the chromogen.

(ii) **Sulphur dyes**

Sulphur dyes are water insoluble substances which are brought into soluble form for dyeing by treatment with a hot solution containing alkali and sodium sulphide. Sulphur dyes are relatively few in number but important in quantity. They are the dullest of the dyes but economical. Sulphur dyes have moderate to good fastness to light, poor fastness to bleach and are reasonable fast to washing and perspiration. They are applied to cotton, viscose rayon,

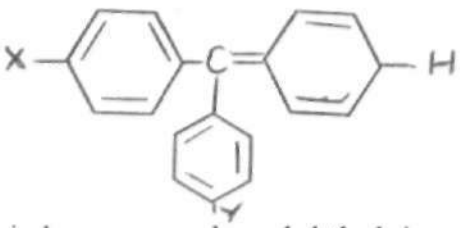
linen and mixtures. They produce a range of dull sades limited to yellow, blue, grey, black, brown etc.

(iii) **Diphenylmethine and Triphenyl methine dyes**

These dyes belong to the earliest synthetic dyes which were discovered in the nineteenth or early twentieth century. The yellow, red, violet, blue or green dyes are characterised by extreme brilliance and high colour depth, but to low fastness to light, they partly lost their importance in dyeing of wool, silk or cotton. Some of them are still manufactured for colouring paper and leather, printing inks, indicators in analytical chemistry and various other application (Hall, 1975). They have also found application in textile technology in dyeing polyacrylonitrile and its copolymers.

Diphenyl and triphenylmethine dyes are characterised by their chromonohoric system consisting of a central carbon atom linked to two and three aromatic rings respectively. The colour and dyeing properties depend on the nature and number of auxochromic group such as -OH, NR_2, NHR, NH_2, NHAr or a combination of these in the 3-para position (Cassebaum, 1962).

Typical examples of this class of dyes are melachite green where X = Y = NR^1R The structure is written below:

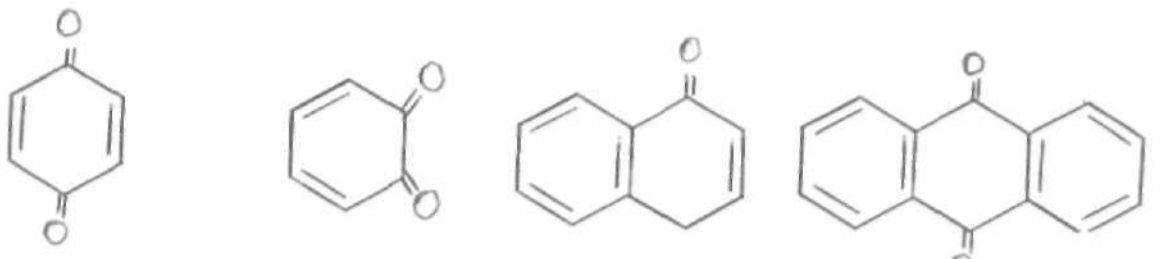


(xxvii)

When X = Y = CH_3 the structure is known as phenolphthalein.

(iv) **Quinold dyes**

Quinoid dyes posses at least two carbonyl groups which are involved into a cyclic structure. They participate mostly in a six-membered ring (for example ortho- and para-benzoquinones) but they can also be situated in different rings. A few examples of the first types of compounds and given above:



(xxviii) (xxix) (xxx) (xxxi)

The molecular structure of these quinones is evidently characterized by the fact that the molecules consist of more or less localized carbonyl groups and of ethennoid, polyenoid or benzenoid subunits.

Quinoid dyes are applied as vat dyes and are therefore related to indigoid colourants. This means, they can be reduced to leuco compounds,

which are reoxidated then to the dye on substrates such as cellulosic fibres. Quinoid compound also belong to the acid. mordant, disperse and reactive application classes. They cover all shades between yellow and black. Also a large number of natural dyes contains quinoid structures (Thomson, 1954).

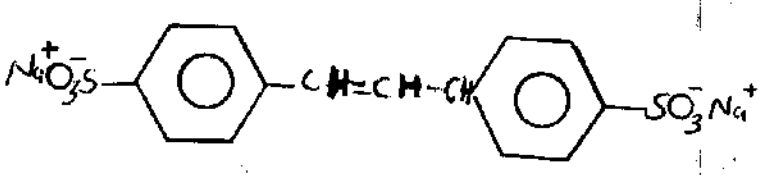
(v) **Stilbene dyes**

The stilbene dyes contain the residue of 2,2'- stilbenedisulphonic acid (i). They form a subdivision of the azo dyes but, owing to these common structural features and to the fact that many of them are not prepared by the classical azo coupling reaction, they are treated as a separate class.

The stilbene dyes are mainly direct dyes used for the dyeing of natural or man made cellulosic fibre e.g, cotton, viscose rayon etc. Their affinity to cellulose is due to stilbene system. Some of stilbene dyes are used in the dyeing of paper and leather.

The hue range of stibene dyes, originally covering only yellow and orange shades, has been extended to red, brown, khaki, green and grey. Lightfastness, in general, is rather high. Stilbene dyes are inexpensive and have come to be classed among the most important direct dyes, especially for orange and brown shades.

Another important application of the stilbene system is to be found in some optional brighteness derived from diaminostilbenedi sulphonic acid or from stilbene triazoles.

(xxxii) 

(vi) **Azine, Oxazine and Thiazine dyes**

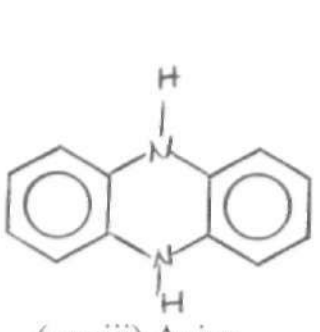
The colourless parent compounds are represented by formula (xxxiii), (xxxiv) and (xxxv) respectively. Characteristically, when dyes of these classes have been decolourized by reduction, exposure to air suffices to restore their colour.

The dyes contain not only the chromogens, but also auxochromes, of which amino and substituted amino groups are the most important. These groups are always located in positions 3 and 7, the cationic mesomeric colour system formed being the aza analog of that present in diphenylmethane dyes.

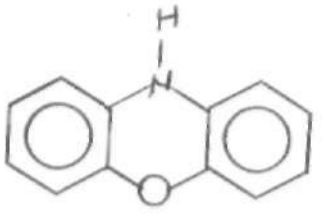
The dyeing classes to which the azines, oxazine and thiazines belong. together with the hue of their dyeing are summarised in Table 1.2

Table 1.2 Subdivision of Azine dyes according to dyeing class and hue

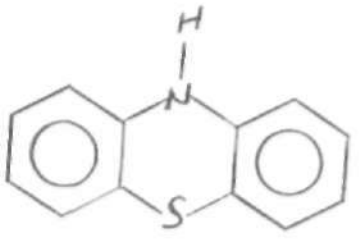
Chemical class	:	Dyeing class:	Hues
Azine	:	Basic	: Red, violet, blue, black
Oxazine	:	Direct	: Violet, blue
Thiazine	:	Mordant	: Blue



(xxxiii) Azine



(xxiv) Oxazine

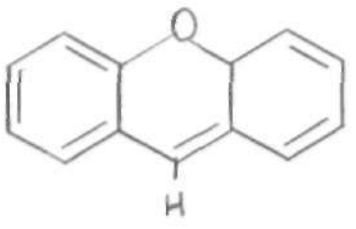


(xxv) Thiazine

(vii) **Xanthene dyes**

The dyes of the xanthene class dated from 1871, when Baeyer (1883) synthesized fluorescein (acid yellow 73, CI 45350) from phthalic anhydride and resorcinol. Xanthene dyes are characterized by the presence of xanthene (xxxvi) or dibenzo-pyran nucleus. They are also characterized by pure, brilliant hues and by fluorescene. They range in shade from yellow to violet.

Xanthene dyes are cationic (basic) dyes. The class comprises acid and spirit soluble dyes and mordant colours and lakes. The fluoresceines, which contain carboxyl and phenolic hydroxyl groups, are acid dyes.



(xxxvi) Xanthene

(viii) **Cyanine dyes**

The cyanines, which comprise a large group of dyes, are among the very synthetic dyes known (Hamer, 1964). The first member of the series was described by its discoverer, C. Greville Williams at a meeting of the Royal Society of Edinburge on April 7, 1856.

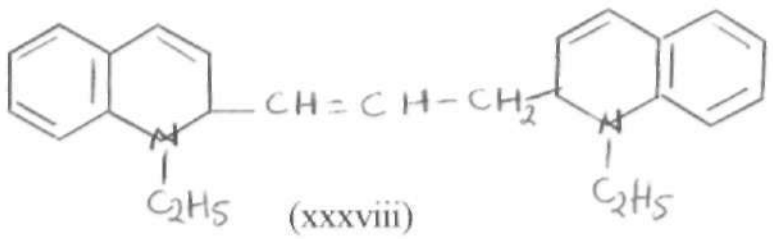
Cyanine dyes has a beautiful blue shade and hence used in photography, while some are used as an infrared absoring tracer for blood dilution studies in medical diagnosis.

According to Brooker (1954), the cyanines are polymethine dyes, which conform to the amidinium ion system represented by the resonance scheme (xxxvii) wherein both nitrogens are members of heterocyclic ring systems.

$$>N\text{-}C(=C\text{-}C) = \overset{+}{N}< \;\longleftrightarrow\; \overset{+}{>}N=C(\text{-}C=C)_n\,N<$$

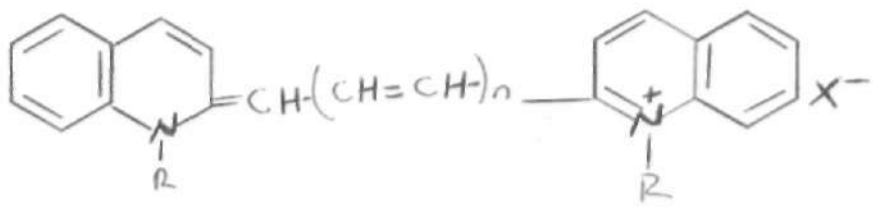
(xxxvii)

The conjugated chain joining the nitrogn atoms passes through a part of each heterocyclic ring. A typical cyanine is (xxxviii) in which the nitrogen atom and included in Quinoline rings.



(xxxviii)

Cyanines may be classified according to the number of -CH= or methine groups in the chain between the ring system, as illustrated below in which R is an alkyl or aryl group, n = 0, 1, 2, 3, etc and X is the anion.



(xxxix)

This shows that increasing the lenght of the amidinum conjugated in the dyes must be effected by introducing two -CH= groups, in a "vinylene" unit, -CH=CH, giving rise to the concept of a "vinylogous" series.

Otehr chemical class of dyes include

- Nitroso dyes
- Nitro dyes
- Indamine and indophenol dyes
- Phthalocyanine

1.8 AIMS AND OBJECTIVES OF THE PRESENT RESEARCH

This research is important in view of the fact that there is a strong drive towards technological development which is locally biased. Hence, the Nigerian government encourages groups and individuals to utilize local raw materials in producing goods like chemicals, drugs, machine tools, dyes etc. This has become necessary due to global economic crises whereby importation of goods intc Nigeria is telling negatively on Nigeria's foreign

exchange reserve. To achieve this objective, the Nigerian government placed embargo on importation of a number of goods among which are dyes and their various mordants.

This therefore, led to the scarcity of dyes. The aim therefore, is to study the methods which can be used to synthesis some useful dyes for the local consumption by our textile industries. The major raw materials are obtained from petroleum which can be obtained from our petrol chemical plant in Nigeria. The primaries are first of all converted to intermediaries and finally is the conversion of the intermediates to the useful dyes.

In this reseach, all the dyes to be synthesised are azo dyes and the effects of substitutuents on the colour and fastness properties of the dyes will be examined. Another objectives of this research is to examine the effect of acid solvent polarity on the absorption wavelenght of the dyes synthesised.

CHAPTER TWO

2.0 EXPERIMENTAL

2.1.0 GENERAL INFORMATION

2.1.1 CHEMICALS

Acetone

Potassium hydroxide pellets

Tetraoxo sulphate (VI) acid (concentrated)

N,N-dimethylaniline

Ethanol (95%)

Aniline

Acetic acid

Propionic acid

Hydrochloric acid (concentrated)

Toluene

Sodium ethanoate (anhydrous)

Dimethyl formamide

Sodium trioxo carbonate (VI)

Sodium Nitrite

Sodium chloride

Sulphanilic acid

4-Amino benzoic acid

4-Nitro aniline

1-Naphthol

2-Naphthol

2-Chloro-4-nitro aniline

2-Cyano-4-chloro aniline

4-Chloro-2-nitro aniline

2,5-dimethyl aniline

2-Cyano-4-nitro aniline

0-Phenyl-phenol

Pyridine

Potassium iodide starch paper

2.2.1 MATERIALS

Polyester fabric (100%)

Nylon fabric (100%)

Cotton fabric (100%)

Viscose rayon

2.2.0 PREPARATION OF THE DYES

The general method of the synthesis of the dyes involves diazotisation and coupling as described below.

2.2.1 GENERAL PROCEDURE FOR PREPARATION OF DYES (1), (3), (4), (6), (7) AND (8) PROCEDURE FOR DIAZOTISATION

In a 250cm^3 beaker, 5.0g (0.036mole) of the amine was dissovled in a warm mixture of concentrated hydrochloric acid (13cm^3) and water (13cm^3). The solution was immersed in an ice bath and cooled to 0-5^{0}C with vigorous strirring. Sodium nitrite (3.7g, 0.054 mole) was dissolved in water (8cm^3) and the solution was added slowly and with strirring to an end-point tested with

potassium iodide starch paper which turned blue-black. The temperature is maintained below 5^0C to avoid decomposition of the diazonium salt throughout the preparation.

Procedure for coupling

In a 250cm^3 beaker, the coupling compound (5.2g 0.035 mole) wasd dissolved in a solution of sodium hydroxide pellets (7g) and water (25cm^3). The solution was cooled in an ice bath at 5^0C. The diazonium salt was added slowly and with strirring into the solution. The solution was filtered with a Buchner funnel and then washed with water until all the acid are being washed away. It is then dried in the oven at a temparature of 50^0C.

2.2.2 GENERA PROCEDURE FOR PREPARATION OF DYES (2) & (5)

Procedure for diazotisation

In a 250cm^3, amine (10.50g, 0.05 mole) was dissolved in hot water (100cm^3) containing anhydrous sodium carbonate (2.65g, 0.025 mole). The solution was filtered and concentrated hydrochloric acid (10.5cm^3) was added to the solution, followed by ice (60g). The mixture was stirried at (8^0C - 10^0C) and a solution of sodium nitrite 53.7g) and water (10.0cm^3) was added dropwise over 15 minutes. The mixture was then strirred for further 15 minutes to give a suspension of diazonium salt. The presence of cecess

nitrous acid was confirmed using starch iodide paper which gave a faint blue colouration.

Procedure for coupling

In a 250cm^3 beaker, the coupling compound (7.2g, 0.05 mole) was dissovled in 10% cold solution of sodium hydroxide (40cm^3). The solution was cooled to 5^{0}C in an ice bath and then poured slowly and with stirring into the diazonium solution. The solution was strirred very well for 10 minutes and the mixture was then heated until all the solid dissolved. Sodium chloride (20g) was added in order to decrease the solubility further. The solution was warmed until the sodium chloride dissolved completely. The solution was then allowed to stand for one hour in the air and the cooled in an ice-bath until crystallisation is completed. The product is collected in a buchner funnel with gentle suction. It is then washed with little saturated salt solution and dried at 60^{0}C.

2.2.3 PURIFICATION OF THE DYES (Vogel. 1978)

The dyes were recystallised by boiling in ethanol (30-35cm^3). The solution was filtered hot and then allowed to cool in an ice bath. The crystals formed were filtered, weashed and driend in the oven at 50^{0}C.

2.3.0 CHARACTERIZATION OF THE DYES

2.3.1 MELTING POINT DETERMINATION

The melting point of the dyes were determining using Gallenkamp melting apparatus.

2.3.2 ULTRAVIOLET-VISIBLE ABSORPTION SPECTROSCOPY

The ultraviolet-visible spectra of the dyes in different solvents were recorded on ultraviolet-visible spectrophotometer unicam SP 800 in the Department of Chemistry, Ahmadu Bello University, Zaria.

2.3.3 INFRA-RED SPECTROSCOPY

The infrared spectra of the dyes were recorded in Nujol solution on Perkin-Elmer 1310 infrared spectrophotimeter in the Department of Chemistry, Tafawa Balewa University, Bauchi.

2.4.0 DETERMINATION OF MOLAR EXTINCTION COEFFICIENT

The molar extinction coefficient (E) of the dyes were calculated using the formula

$$A = EC1$$

$$E = A/C1$$

Where,

A = absorbance

C = Concentration (moles per litre)

I = Lenght of the cell in (cm)

The solvent used for this determination was ethanol and the methods of calculation are shown above. The absorbance was measured using colorimeter in the Department of Chemistry, Ahmadu Bello University, Zaria.

2.5.0 DYEING OF THE FABRIC (Diserens, 1951)

Dyeing was carried out on nylon 6.6 and polyester fabric using all the dyes synthesised in the laboratory at a liquor of 1:50 with the Dye Master in the Department of Textile Science and Technology, Ahmadu Bello University, Zaria. A 2% stock solution of each of the dyes was prepared and 5cm^3 was taken for each dye solution and put in the dye bath containing small amount of dispersing agent (2cm^3) and water was added to make up the dye bath to 50cm^3. After the dye bath is set, the fabrics (2g each) were wetted out and excess water squeezed out with the aid of filter papers and then introduced into the dyebath, this was done at a temparature of 50^{0}C. The temperature was then raised to the boil over 15 minutes and dyeing continued at this temperature for one hour. In the case of polyester dyeing, 50g/l (10ml) o-phenyl phenol carrier was added to the dye bath before dyeing. After dyeing, the fabric was removed and rinsed thoroughly with water and dried.

2.6.0 TRANSFER PRINTING (Reuther, 1977)

A strip of whatmann chromatography paper (4 x 4cm) was immersed for two minutes in 0.01M solution of the dyes. The excess solution on the surface of the paper was squeezed out between two glass rods and the strip

was allowed to dry at room temperature before being wrapped in a piece of polyester and then enclosed in an alluminium foil. The composite specimen was then iron with very hot iron for 60 seconds. The transfer printed polyester fabrics were rinsed with water and dried in an open air.

2.6.1 EXTRACTION OF DYES FROM PRINTED POLYESTER FABRIC

The absorbance of the transfered dyes on the polyester was measured by cutting a small piece of printed polyester material (1 x 1cm). This small piece was dipped into 25cm^3 (10% pyridine) and the solution was boiled for 15 minutes, so that the printed dyes on the polyester will be stripped off. The absorbance was measured using colormeter in the Department of Chemistry, Ahmadu Bello University, Zaria.

2.7.0 DETERMINATION OF LIGHT FASTNESS

An artificial light source (Xenon Arc) was used to determine the light fastness values of each dye on the dyed nylon and polyester materials. Strips of the dyed materials were arranged on a card along side strips of blue wool standards for light fastness testing numbered 1-8.

Seven cards were thus made for fifty dyed materials. Each card was placed within a glass frame after having screwed them into a rigid steel frame. One side of the materials was covered with an opaque carboard to shield it from exposure to the source of light. Each glass casing had a small water reservoir screened into its base in order to attain the optimum/standard

effective humidity at the surface of the fabrics as this affects the rate of fading if it is either too low or too high.

Exposure of the dyed materials to the light source was continued until on each card the most resistant materials faded to an extent equal to the contrast rating of 5 on the Grey Scale. Light fastness values for each material was obtained by comparing the degree of fading of each material with that observed with the Blue wool standard. Ratings are given according to the wool standard with which the dyed materials fading is comparable.

2.8.0 DETERMINATION OF WASH FASTNESS (SDC, 1962)

All the dyed materials were assessed for washing fastness by following the ISO No. 3 test procedure. The test was carried out using the "Lintest wash wheel" machine with a shaft rotating at a speed of 40 ± 2 revolution per minute in Bayero University, Kano.

The soap solution contained 5g (Lux soap) per litre and 2g sodium carbonate per litre of distilled water. The dyed fabric was cut (2cm x 5cm) and placed between the two adjacent white fabric of similar dimensions and stapled all the four edges to form a composite specimen. The composite specimen was treated at $60^0C \pm 2^0C$ for 30 minutes. After washing the fabric was removed and the material was seperated from the white fabric, dried and then analysed for change in colour and staining of the adjacent white material using the grey scales.

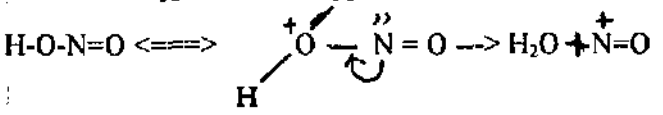
CHAPTER THREE

3.0 RESULTS AND DISCUSSION

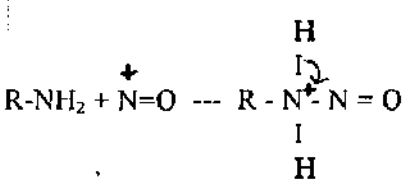
3.1 SYNTHESIS OF THE MONOAZO DYES

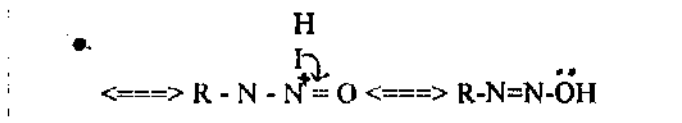
In order to know the effect of substituents on the colour and dyeing properties of the monoazo dyes, the compound containing different auxochromes such as hydroxyl (-OH), carboxylic (-COOH), nitro ($-NO_2$), chloro (-Cl), cyano (-CN), dimethoxy $(-OCH_3)_2$ and derivatives of amino groups were diazotised and coupled to diffeent coupling components like 2-naphthol, 1-naphthol, toludine and N,N-dimethyl aniline as shown in scheme 1 below.

SCHEME 1

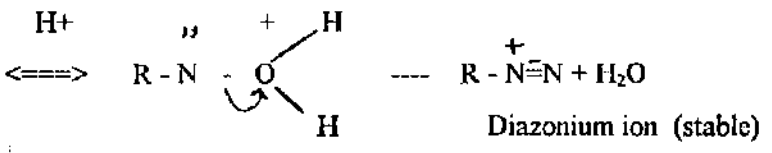


Nitrozonium ion



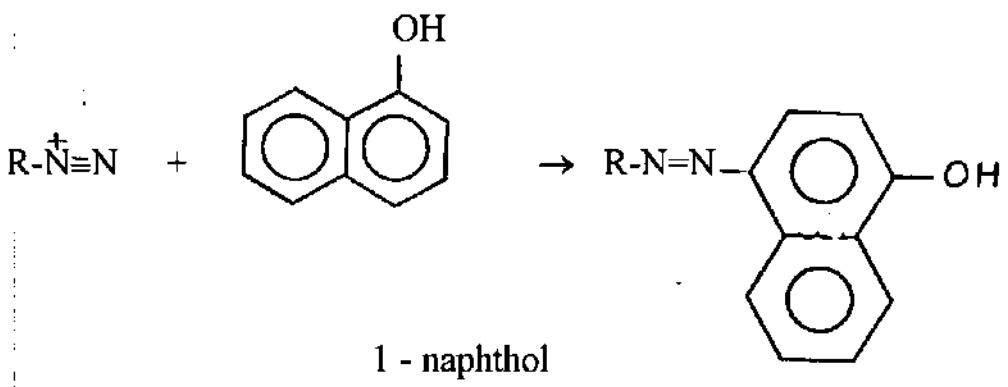


Diazohydroxide



Diazonium ion (stable)

Diazonium ion couple with aromatic compound such as 1-naphthol at the 4th position as shown below:



1 - naphthol

The diazonium ion solution prepared were used as soon as they were produced. This is due to the fact that solution of diazonium ions are of limited stability and are also sensitive to high temparatures which can cause their decomposition. Coupling was carried out by careful addition of diazonium ion solution at 0-5°C to avoid decomposition. Coupling occurs at the 4th position for all the coupling components used. Good yields of the dyes were obtained as summarised in Table 3.2

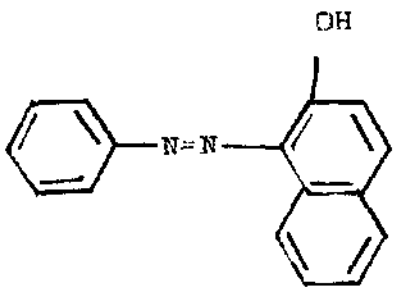
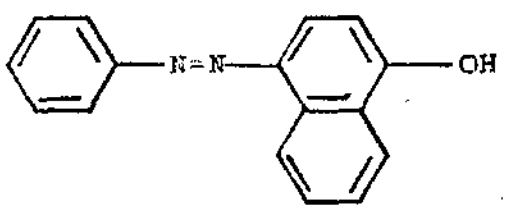
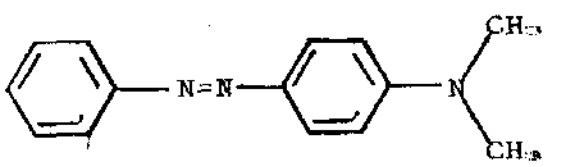
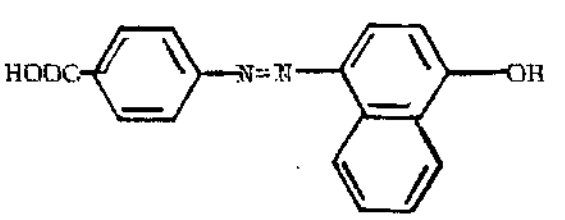
3.2.0 PURIFICATION OF THE DYES

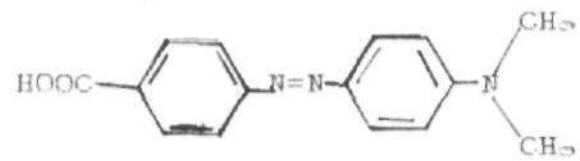
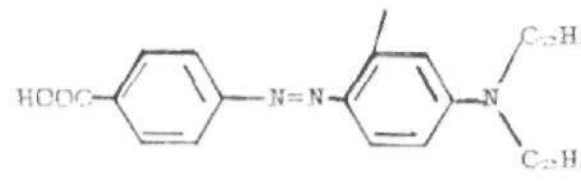
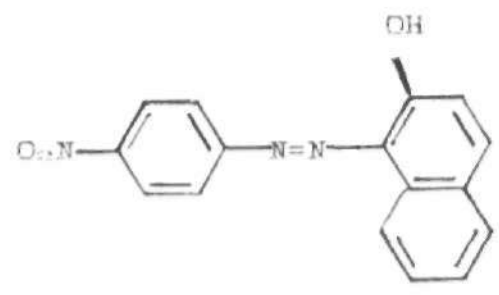
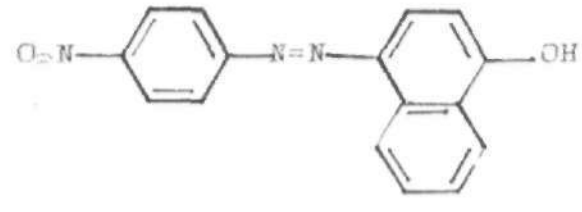
Purification were carried out in order to remove the impurities contained in the dyes. More, also, some dyes e.g, (2) and (5) were in the form of sodium salts. However, it was necessary to remove impurities such as buffer salts and other electrolytes which could lower the colour strenght of

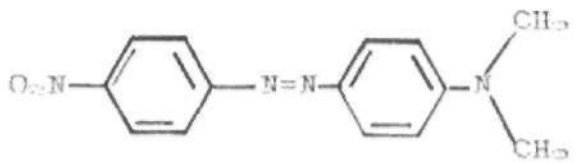
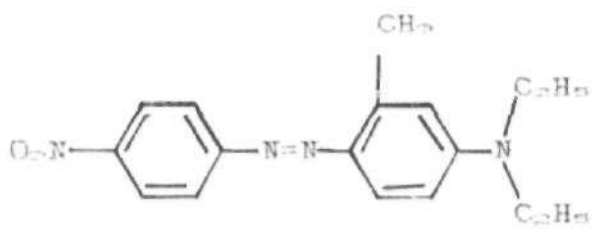
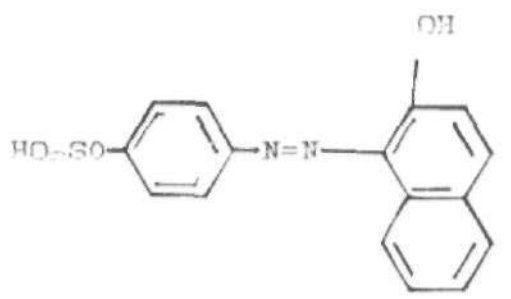
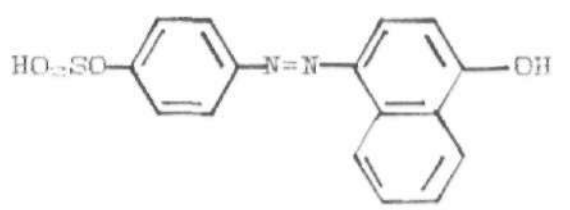
the dyes. The impurities were removed in each case by subjecting the dye to further purification process. This was carried out by recystallisation from ethanol. The basic structures and the molecular weight of the dyes are summerised in Table 3.1. The melting points, physical appearance on purification, colour of the dyes and percentage yields of the dyes are tabulated in Table 3.2.

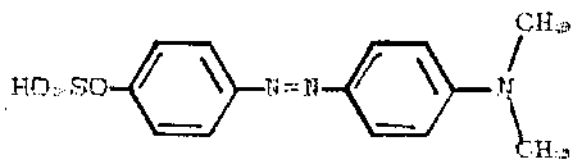
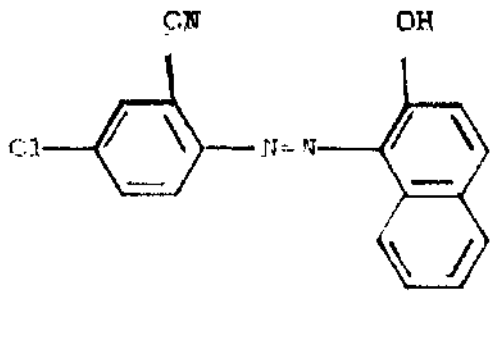
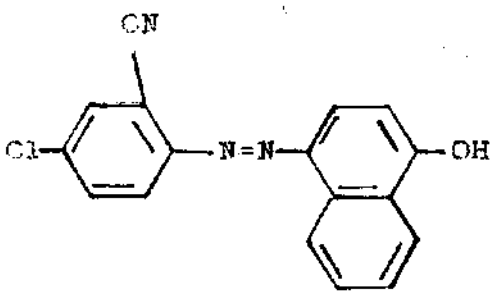
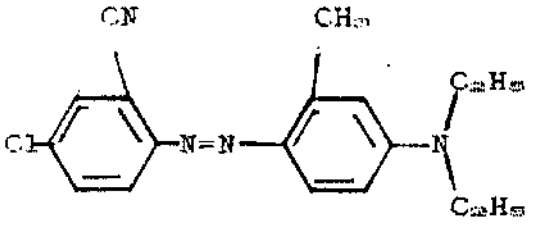
Fron the data summerised in Table 3.2 good yields of the dyes were obtained with the exception of dyes (6c) and (8a) which gave 38.76% and 38.92% respectivcly.

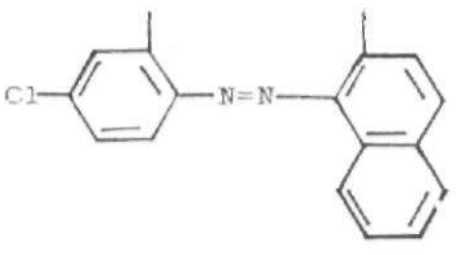
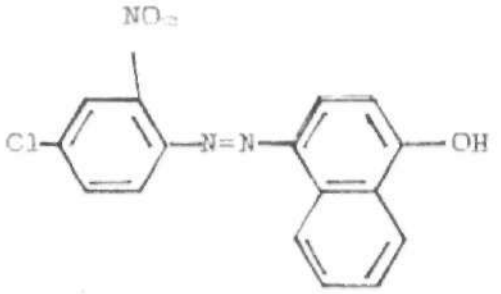
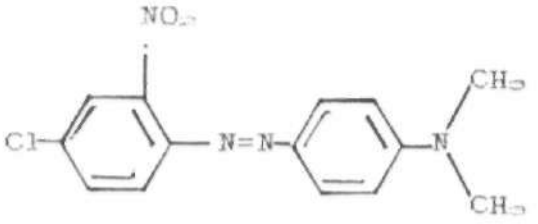
Table 3.1 Structures and molecular weight of the dyes

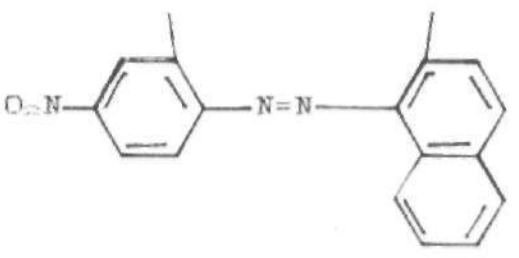
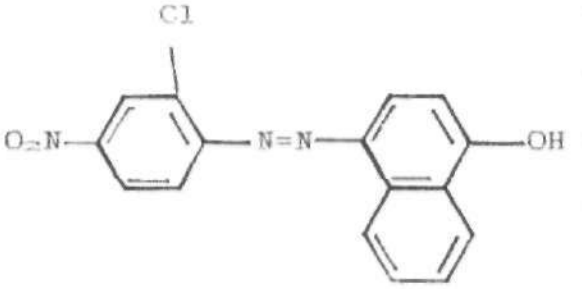
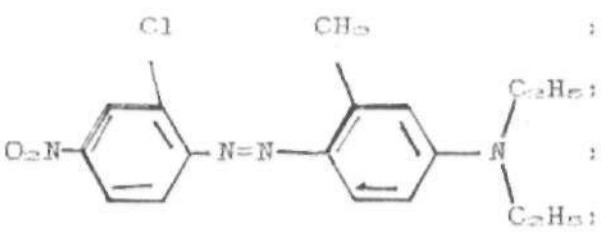
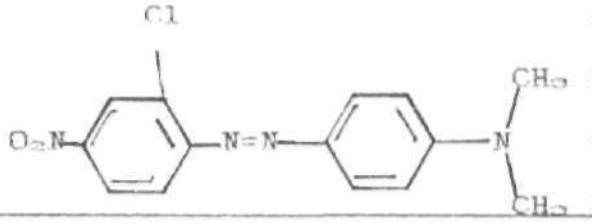
Dye No:	Structure	Molecular weight (g)
1a		265.0
		265.0
1c		237.0
2a		309.0

Dye No:	Structures	Molecular weight (g)
2b		281.0
2c		328.0
3a		309.0
3b		309.0

Dye No.	Structures	Molecular weight (g)
3c		282.0
3d		278.0
4a		367.0
4b		367.0

Dye No:	Structures	Molecular Weight (g)
4c		319.0
5a		324.5
5b		324.5
5c		338.5

Dye No:	Structures	Molecular weight (g)
6a		343.5
6b		343.5
6c		316.5

Dye No:	Structures	Molecular weight (g)
7a		343.5
7b		343.5
7c		358.5
7d		316.5

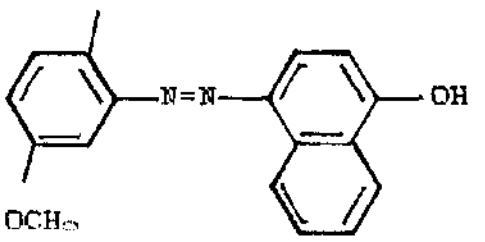
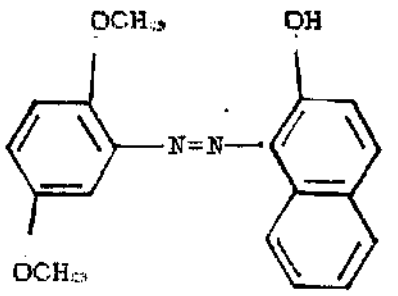
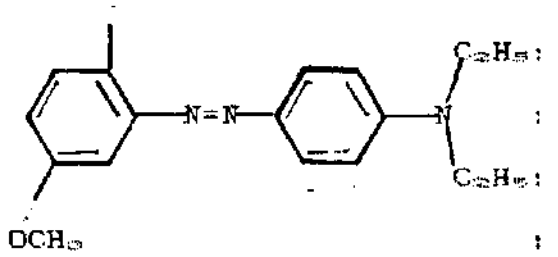
Dye No:	Structures	Molecular Weight (g)
8a		333.0
8b		333.0
8c		336.0

TABLE 3.2 PHYSICAL CHARACTERISTICS OF THE DYES

Dye No.	Appearance	Colour	Weight (g)	Yield (%)	Melting °c
1a	Powder	Orange	4.6	92.41	285
1b	"	Brown	4.5	90.52	280
1c	"	Yellow	4.7	94.23	230
2a	Crystal	Black	8.0	76.19	250
2b	Powder	Orange	7.2	68.57	275
2c	"	Orange	7.4	70.84	330
3a	"	Red	4.4	88.32	265
3b	Powder	Brown	4.2	84.20	213
3c	"	Red	3.6	72.62	200
3d	"	Purple	4.0	79.44	284
4a	"	Orange	3.4	68.82	340
4b	"	Brown	3.8	76.54	342
4c	"	Yellow	4.1	81.10	315
5a	"	Orange	5.8	49.10	305
5b	"	Brown	6.1	58.13	290
5c	Crystal	Purple	5.8	55.62	288
6a	Powder	Orange	2.7	54.82	280
6b	"	Red	2.9	58.76	240
6c	"	Red	1.9	38.76	284
7a	"	Black	2.8	56.34	302
7b	"	Black	2.6	51.12	293
7c	"	Black	3.0	60.02	270
7d	"	Black	2.7	54.15	241
8a	"	Black	1.9	38.92	310
8b	"	Red	3.0	60.14	320
8c	"	Red	3.2	63.40	310

3.3 VISIBLE ABSORPTION SPECTRA OF THE DYES

TABLE 3.3 VISIBLE ABSORPTION SPECTRA OF THE DYES

DYE NO. λMAX IN DIFFERENT SOLVENTS (nM)

	TOLUENE	ACETONE	ETHANOL
1a	430	440	449
1b	406	408	418
1c	400	408	410
2a	458	470	474
2b	478	488	491
2c	450	488	474
3a	451	454	460
3b	448	452	458
3c	445	450	457
3d	456	460	480
4a	440	465	472
4b	472	479	489
4c	398	416	445
5a	436	442	460
5b	447	449	457
5c	451	462	466
6a	460	466	471
6b	430	438	450
6c	415	421	432
7a	447	459	468
7b	438	453	458
7c	410	420	433
7d	400	405	430
8a	456	460	472
8b	471	478	480
8c	451	454	463

The visible absorption spectra of the dyes were determined using different solvents such as ethanol, acetone and toluene. The λmax was measured using spectrophotometer. The results of the λmax obtained are summerised in Table 3.3. From the data in Table 3.3, dye (1a) obtained by coupling aniline with 2-naphthol absorbs at 430nm in toluene and at 440nm and 449nm in acetone and ethanol respectively. The reason for the difference in λmax values in different solvents is due to the fact that solvents have marked effect on the colour of the dyes. The measure of solvent's ability to insulate opposite charges from each other is known as dielectric constant (Chapmann, 1972). The greater the dielectric constant, the greater is the solvent polarity. The dielectric constant of the solvents used are summerised below.

Solvent	:	Dielectric Constant
Toluene	:	2.379
Acetone	:	20.740
Ethanol	:	24.300

Therefore, the result of the present work confirm the order of polarity i.e

Ethanol > Acetone > Toluene

Also according to Venkataraman (1952), π---π* transition exhibits bathochromic effect (red shift) when the polarity of the solvent is increased, while the n--->π* transition exhibits hypsochromic effect (blue shift) with

decrease in solvent polarity. This shows that π---> π^* transition is responsible for the increase in the λmax of the series of dye synthesised.

Changing the relative positions of the substituent, for example hydroxyl group in dye (1a) to be para to the azo group as in dye (1b) leads to hypsochromic shift. For instance, dye (1a) absorbed at 430nm in toluene and dye (1b) absorbs at 406nm in the same solvent. This is because hydrogen bonding can occur between the azo group in dye (1a) and the hydroxyl group in the ortho position. This can lead to bathochromic effect in comparing dye (1a) and dye (1b).

Also, by changing the coupling component as in dye (1c) with N,N-dimethylaniline decreases the λmax of the dye when compared with dyes (1a) and (1b) with naphthol ring. From the data, dye (1c) absorbs at 400nm in toluene and dye (1a) and (1b) absorb at 430nm and 460nm respectively in the same solvent. The reason for the decrease in λmax in dye (1c) compared to dye (1a) and (1b) is as a result of extensive conjugation in dyes (1a) and (1b). Naphthol ring is more highly conjugated than the benzene ring. Conjugation brings about a shift of λmax to longer wavelenght. When a molecule absorbs at its longest wavelenght, an electron is excited from its highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). For compounds with multiple bonds, for example, benzene and naphthol the highest occupied molecular orbital is a bonding π orbital and the lowest unoccupied molecular orbital is the antibonding π^* orbital. The wavelenght of the absorption maximum is determined by the difference in

energy between these two levels i.e π---> π^*. Therefore, for compounds with extensive conjugation, the energy difference between π--> π^* is shorter. This narrow gap is due to conjugation. Hence, the greater the number of conjugated multiple bonds a compound contains, the longer will be the wavelenght at which the compound absorbs light (chapmann, 1772). Therefore, all the series of dyes synthesised show a higher show a higher λmax with naphthol ring than with benzene ring.

Also incorporation of election withdrawing group in the acceptor ring of the azo dye increase the λmax of the dye. For example, dye in series (2) absorbs at a longer wavelenght than dye in series (1). This is as a result of carboxylic (-COOH) group which is a strong electron withgrawing group. The stronger the electron withdrawing group, the more bathochromic in colour the dye becomes. Similar trend was also observed when the cargoxylic group in dye series (2) was subtituted with sulphonic group as in dye in series (4). For example, dye (2a) absorbs at 458nm in toluene, while dye (4a) absorbs at 440nm in the same solvent. The result shows a bathochromic shift for dye (2a) and hysochromic for dye (4a). This can also be explained in terms of electro-negativity of (-SO_3H) and (-COOH) groups. The carboxylic group is a strongly electron withdrawing groups as indicated by the result and hence a shift to the longer wavelenght of the dye.

Considering dye (7c) and (7d) which contain the same substituents on the diazo component of the dyes but coupled with different coupling components. For instance, dye (7c) which was coupled with N,N-diethylaniline absorbs at 410nm in tolnene, while dye (7d) which was coupled with N,N-dimethyl-aniline absorbs at 400nm in the same solvent. The result shows

a bathochromic shift for dye (7c). The reason for the difference in >λmax is due to the electron donating power of the two groups, diethyl and dimethyl groups. Since the electron donating power of the N,N-diethyl is more than that of the N,N-dimethyl, dye (7c) shows a bathochromic effect. Therefore, the higher the electron donating power of the substituents, the higher the wavelenght (>λmax) observed. Hence, all the dyes synthesised confirm to this theory.

Similarly, dye in series (7) show a hypsochromic shift when compared to dye in series (3) with only the nitro group at the diazo component. Dye in series (3) absorbs at higher wavelenght than dye in series (7), this is because chlorine atom is a weakly deactivating group and hence increase the energy of the transition. The higher the energy of the transition, the shorter the wavelenght.

Finally, dye in series (8) has higher >λmax value when compared to some other dyes, for example, dyes in series (7) and dyes in (6). This is because the (-OCH_3) group has moderate activating power therefore, any factor which activate the ring, increases the rate of reaction and thereby decreasing the energy of the transition. Hence, a shift to a longer wavelenght, that is bathochromic shift.

3.4 EFFECT OF HYDROCHLORIC ACID ON λMAX

Halochromism is the effect of addition of acid on the >λmax of a compound. The results of adding a few drops of concentrated hydrochloric acid to azo dye solution is given in Table 3.4. In this investigation most of the dyes show a red shift on addition of a few drop of concentrated hydrochloric acid. The change in colour or λmax value of the azo dye on addition of acid has been attributed to protonation at the -nitrogen atom of the azo group and this gave a red shift for the dye synthesised.

Table 3.4 Halochromism in Monoazo dyes

Dye No: Ethanol: Ethanol (2cm3): λmax

	(nm)	+ 1 drop of HCL (nm)	(nm)
1a	449	455	+ 6
1b	418	425	+ 7
1c	410	420	+ 10
2a	474	490	+ 16
2b	491	493	+ 3
2c	474	475	+ 1
3a	460	466	+ 6
3b	457	475	+ 18
3d	480	488	+ 8
4a	472	480	+ 8
4b	489	494	+ 5
4c	445	447	+ 2
5a	460	468	+ 8
5b	457	472	+ 15
5c	466	483	+ 17
6a	471	483	+ 12
6b	450	458	+ 8
6c	432	449	+ 17
7a	468	472	+ 4
7b	458	460	+ 2
7c	433	481	+ 47
7d	430	478	+ 48
8a	472	485	+ 13
8b	480	484	+ 4
8c	463	470	+ 7

3.5 MOLAR EXTINCTION COEFFICIENT (E)

The molar extinction coefficient of the dyes were calculated using relationship described in Section 2.4.0.

The solvent used for this determination was ethanol and the results of this investigation are summaerised in Table 3.5.

From the data in Table 3.5, molar extinction coefficient (E) values ranges from 1.2×10^4 to 4.8×10^4, which is quite adequate for any commercial dye. For a dye to be suitable for textile application, the molar extinction coefficient must be around 20,000 and above. Hence, all the dyes synthesised are suitable for textile application with the exception of dyes (1b) and (7d) whose molar extinction coefficient are 1.3×10^4 and 1.2×10^4 respectively.

Table 3.5 Molar Extinction Coefficient of the Dyes

Dye No.	λmax in Ethanol (nm)	Absorbance "A"	Molar Extinction Coefficient $Imol^{-1}cm^{-1}$
1a	449	0.75	3.8×10^4
1b	418	.025	1.3×10^4
1c	410	0.40	2.0×10^4
2a	474	0.74	3.7×10^4
2b	451	0.56	2.8×10^4
2c	474	0.70	3.5×10^4
3a	460	0.78	3.9×10^4
3b	458	0.77	3.9×10^4
3c	457	0.79	4.0×10^4
3d	480	0.95	4.8×10^4
4a	440	0.81	4.1×10^4
4b	460	0.70	3.5×10^4
4c	412	0.45	2.3×10^4
5a	453	0.92	4.6×10^4
5b	457	0.90	4.5×10^4
5c	466	0.96	4.8×10^4
6a	471	0.74	3.7×10^4
6b	450	0.85	4.3×10^4
6c	432	0.57	2.9×10^4
7a	468	0.80	4.0×10^4
7b	458	0.63	3.2×10^4
7c	433	0.24	2.5×10^4
7d	430	0.24	1.2×10^4
8a	472	0.60	3.0×10^4
8b	480	0.90	4.5×10^4
8c	463	0.63	3.2×10^4

3.6 APPLICATION OF THE DYES TO THE FABRIC

All the dyes synthesised were applied to nylon 6.6 and polyester fabrics using standard dyeing conditions. Different shades were obtained on these fabrics. Dyed sample material obtained from the application of each dye on nylon and polyester are shown in Appendix II a & b, the shades of colours obtained for nylon fabrics are deeper in hue than that of the polyester fabrics. This is because the rate of difussion in polyester fabric is slower due to its compact structure, i.e they are highly crystalline. While, nylon has a more open structure i.e amphous, hence dye molecules diffuse faster in nylon.

It was also observed that dyes (4) and (2) cannot be used to dye polyester fabric. This is due to the fact that they are acid dyes. Acid dyes are anionic, with high molecular weight size and therefore find it difficult to penetrate a highly crytalline structure of the polyester fabric. Therefore, nylon fabrics can be dyed more easily with acid dyes because of their amophons structures. The shades of dyeing obtained on the fabrics are summerised in Appendix III.

3.7 WASHING FASTNESS RATING

Washing fastness is the resistance of the colour of a coloured textile to the destructive action of washing with water and alkali (Nkeonye, 1987). The test was conducted by adopting the general procedure by the International Standard Organisation. Procedure number three (ISO) was followed. The results obtained are shown in Table 3.6.

The evaluation of washing fastness was conducted using the grey scale. The results show that on polyester fabric, all the dyes with the exception of dye (7d), (6c) (5c) and (3a), show a very good fastness to washing. Similarly, on nylon, all the dyes are good to washing except dye (7d), (1c), (5b), (5c) and (6c) which are poor to washing.

From the result of the evalusation on Table 3.6, dyes synthesised give dyeing of higher wash fastness on polyester than they do on nylon, and this is in line with the usual experience that dyestuff which have been difficult to get into a fibre are usually hard to get out, i.e they are fast. As mentioned before, polyester fabrics have compact structure and the dye molecules find it difficult to penetrate, hence decreasing the rate of diffusion of the dye.

Also, from the data in Table 3.6, dye (2) and (4) cannot be used to dye polyester fabric but can dye nylon fabric. This is because they are acid dyes. Acid dyes are anionic.

Table 3.6 Wash Fastness Rating on Nylon and Polyester

Dye No	Change in Colure		Adjacent Staining	
	Polyester	Nylon	Polyester	Nylon
1a	4	3	4	2
1b	4	3	3	2-3
1c	3-4	2	4	2
2a	none	4	none	4
2b	none	3-4	none	4
2c	none	4	none	3-4
3a	3	2-3	4	2-3
3b	4	3	4	3
3c	4	3	3	2-3
3d	4	3	3	3
4a	none	4	none	3-4
4b	none	3-4	none	3
4c	none	3	none	4
5a	4	4	4	3
5b	4	2	4	3
5c	3	2	4	3
6a	4	3	3	2-3
6b	4	2	3	2
6c	3	3	4	3
7a	4	4	4	3
7b	4	4	4	3
7c	5	4	4	3
7d	3	2	3	2-3
8a	4	3	4	4
8b	4	3	4	2-3
8c	5	3	4	3

numbers of negatively charged carboxyl acid and positively charged amine end-groups, ionisation of the carboxyl acid groups is depressed, leaving a net positive charge on the fibre (Nunn, 1987). The mechanism of adsorption of acid dyes by nylon follows thus;

$$H^{+}X^{-}$$

$$H^{+}\text{N-Nylon-COO-} \quad \text{----> X-H}_3\text{ N-Nylon-COOH}$$

$$D^{-}Na^{+}\downarrow$$

$$D^{-}H_3{}^{+}\text{N-Nylon-COOH} + Na^{+}X^{-}$$

Acid dyes have high affinity on nylon and therefore, wash fastness rating are very good because acid dyes have large molecular weight and nylon being amphous, the dye molecule will penetrate easily.

The results of adjacent staining for both polyester and nylon fabrics showed that polyester fabric are only slightly stained or stainless. While the nylon fabrics are deeply stained except for dye (2) and (4) series which are acid dyes. For example dye (1a) which showed a good fastness rating for both polyester and nylon 4 and 4 respectively, while the rating for adjacent staining 4 and 3 respectively for polyester and nylon. The results showed that polyester is unstained while nylon is a bit stained. This can again be explained, based on the structures of the fabrics. Since polyester is crystalline and nylon amophous instructure, hence easy in, easy out.

In general, if the dyed material is to have satisfactory fastness, the dye must remain on the fibre and not migrate back into water on subsequent laundering. For this to be possible, an interaction must occur between the dye

and the fibre. The nature and extent of this interaction affect the strength of attachment between dye and fibre and hence the level of wash fastness attained. Therefore, several type of interaction are possible in dye-fibre systems. Since the dyes synthesised are disperse and acid dyes. These forces can be responsible for dye-fibre interaction.

Disperse dyes being non-ionic and therefore do not dissolve to an appreciable extent in water (hydrophobic) hence like dissolves like. Therefore, the dye-fibre attraction is retention by solid solution. For acid dyes-nylon interaction, dye attachment onto nylon is by ionic or salt links, the fixation being enhanced by the non-polar Van der waals' forces (Derbyshire & Perters; 1987) as well as by hydrogen bonding. Also, if both the dye and fibre are long and flat (linear), the Van der waals' force is effective and the strenght of attraction depends on the area of possible contact.

In summary, therefore, the observation that polyester fibre has good wash fastness can be attributed to strong Van der waal's force of attraction as well as retention by solid solution. While for nylon with moderate fastness ity is a weak van der waal's force of attraction. Also, nylon, showing good fastness with acid dyes, is due to strong ionic or salt link bwteen the dye and fibre.

3.8 LIGHT FASTNESS RATING

Light fastness is the resistance of a colour to the destructive effects of daylight or of an artificial light souce whose spectra composition is similar to that of daylight. The test was conducted using an artificial light source (xenon Arc) and the evaluation was conducted using standard blue wool fabrics. The results obtained are summerarised in Table 3.7.

The light fastness properties of the nylon and polyster dyed fabrics are generally moderate on both substances, but slightly better on nylon than polyester. This may be attributed to the carrier used for the polyester dyeing. Carriers increase the rate of dye uptake by the fibre, and hence enable dyeing to be completed in an economic time at the boil. Carriers can be well cause reduction in the light fastness properties of the disperse dyes when they are not completely removed. The carrier used in this case is O-phenyl-phenol.

Table 3.7 Light Fastness Rating of Polyester & Nylon

Dye No.	Polyester	Nylon
1a	2	3
1b	4	3
1c	3	4
2a	none	3
2b	none	4
2c	none	4
3a	2	2
3b	3	4
3c	4	4
3d	4	5
4a	none	3
4b	none	4 - 5
4c	none	3
5a	4	4
5b	4	3
5c	5	5
6a	3	3
6b	2 - 3	3
6c	4	4
7a	3	4
7b	3	3
7c	4	4
7d	2 - 3	3
8a	2	3
8b	2 - 3	3
8c	4	3 - 4

3.9 WASH FASTNESS OF TRANSFER PRINTED FABRICS

The dyes synthesised were also applied onto the polyester and nylon by transfer printing technique and the printed samples subjected to ISO 3 test for wash fastness properties. The results obtained are summerised in Table 3.8.

The fastness properties on both printed fabrics are moderate but slightly better on polyester than nylon. This is because polyester has a compact structure and once the dyes enter the crystalline region of the fibre, it is not easy to desorb. The colours obtained on transfer printing are shown in Appendex 1c.

3.10 LIGHT FASTNESS ON TRABSFER PRINTED FABRICS

This test was also conducted using an artificial light source (xenon Arc) and the evauation was conducted using standard blue wool fabrics. The result obtained are shown in Table 3.9.

From the data summerised in Table 3.9, printed polyester and nylon fabrics showed poor fastness while the dyed polyerter and nylon have moderate fastness to light. The reason beig that, the amount of colourant on the fibre effect the light fastness printed polyester and nylon are not deeply coloured when compared to dyed polyester and nylon. A deeply coloured fabric exhibits higher fastness to light because more dye molecules must be destroyed before a change in colour become apparent.

Table 3.8 Wash Fastness Rating of Printed Fabrics

Dye No.	Polyester	Nylon
1a	4	3
1b	3 - 4	3
1c	4	3
2a	none	4
2b	none	3
2c	none	3
3a	3	2
3b	3	3
3c	4	3
3d	4	3
4a	none	4
4b	none	3
4c	none	3
5a	4	4
5b	4	4
5c	3	2 - 3
6a	4	3
6b	3	3
6c	3	4
7a	4	3
7b	4	4
7c	4	3
7d	3 - 4	3
8a	4	4
8b	4	3
8c	3	4

Table 3.9 Light Fastness Rating of Printed Fabrics

Dye No.	Polyester	Nylon
1a	2	2
1b	4	3
1c	2 - 3	3
2a	none	1
2b	none	2
2c	none	2
3a	3	2
3b	4	4
3c	4	3
3d	4	4
4a	none	3
4b	none	3
4c	none	4
5a	4	4
5b	3	3
5c	3	4
6a	4	4
6b	2	3
6c	2	3
7a	3	2
7b	3	3
7c	4	4
7d	2 - 3	3
8a	2	2
8b	2	4
8c	3	2

3.11 MOLES OF DYE EXTRACTED FRO M THE PRINTED FABRICS

The printed dye on the polyester fabric was extracted using pyridine and the absorbance of the extracted dyes were measured using colourimeter in the Department of Chemistry, Ahmadu Bello University, Zaria. The moles of dye extracted were calculated using the equation given in section 2.4.0 and the result obtained are summerised in Table 3.10.

Table 3.10 Moles of Dye Extracted (c) from the Fabric

Dye No.	Absorhance	Moles of Dyes Extracted/Litre (c)
1a	0.48	0.0013
1b	1.00	0.0077
1c	1.80	0.0009
2a	none	none
2b	none	none
2c	none	none
3a	1.90	0.0049
3b	0.10	0.0003
3c	0.41	0.0001
3d	0.09	0.0002
4a	none	none
4b	none	none
4c	none	none
5a	0.07	0.0002
5b	0.27	0.0006
5c	0.14	0.0003
6a	0.13	0.0004
6b	0.30	0.0007
6c	0.44	0.0015
7a	0.06	0.0002
7b	0.13	0.0004
7c	0.16	0.0006
7d	0.11	0.0009
8a	0.07	0.0002
8b	0.02	0.0004
8c	0.40	0.0013

From the data above, little amount of dyes were absorbed by the polyester fabric during the transfe printing. This is due to polyester compact structure and the dye molecules being large find it difficult to penetrate this compact structure of the polyester.

Dye (1b) has the highest number of moles (0.0077 mole/litre) of the extracted, followed by dye (3a) 0.0049 mole/litre. Dyes in series (2) and dyes in series (4) showed no absorption because they are acid dyes. Acid dyes are suitable for dyeing nylon due to their loose structures.

3.12 IR SPECTRA DATA OF THE DYES

The infra red spectra of the dyes showed absorption below 1400cm-^{1} representing the vibration frequency of the whole dye molecule. The absorption above 1400cm-^{1} represents the stretching or bending vibrations of groups incorporated in the dye molecule.

Thus dye (1a) showed an absorption at 2940cm-^{1} due to OH stretching vibration while a sharp peak at 1490cm-^{1} confirms the presence of aromatic ring. These peaks are found in the dyes in the series except dye (1c) which showed absorption at 3400cm-^{1} due to $N(CH_3)_2$ stretching vibration. The peak is not very sharp due to absence of hydrogen atom. The incorporation of carboxylic group in dye (2) showed absorption at 1660cm-^{1} corresponding to >C=O stretching vibration. This absorption peak is absence in dye (1c). There is also absorption at 2940cm-^{1} confirming presence of OH group in the dye.

Dye in series (3) showed longer wavelenght and sharp absorption peaks than dye (1). This is due to incorporation of two electron withdrawing groups. The absorption peak at 820cm-^{1} represent the -C1 stretchig vibration while the absorption at 1520cm-^{1} is due to -NO_2 stretching vibration. The chlorine and nitro groups are electron withdrawing groups, thereby causing the absorption peaks to be sharp. There is also absorption at 2920cm-^{1} representing OH stretching vibration.

Comparing dye (2) and (3), dye in series (2) showed stronger and sharper absorption peaks than dye in series (3). This is also attributed as a result of electron withdrawing ability of the two groups (the carboxylic and nitro groups).

So also, dye (4) showed strong absorption peak at 2940cm-^{1} due to OH stretching vibration while a sharp peak at 1460cm-^{1} is as a result of -SO_2O vibration. The same peaks are found in the other dye series. Dye (5), in addition to showing absorption corresponding to -CI strectching vibration at 720cm-^{1}.Also, the presence of absortion peak at 2760cm-^{1} confirms OH stretching, vibration, these are found in all the dyes in series (5).

Finally, in dye (6), there is absorption at 1550cm-^{1} due to -NO_2 stretching vibration and also a slight absorption peak at 790cm-^{1} representing -CI stretching vibration. The same peaks are also found in dye (7) but with slight difference in the wavelength. This is as a result of different positions of the substituents, e.g in dye (6) and (7), the nitro group is ortho and para position respectively. The spectra of the dyes are shown in Appendix IV.

CHAPTER FOUR

4.0 CONCLUSION

From the result of the investigation, it can be seen that substituents have a marked effect on the colour of the dyes in general and the relative position of these substituents also effects the colour of the dyes. Similarly, the effects of solvent polarity as indicated in the results shows that polar solvent have bathochomic (red shift) effect on the colour observed. All the dyes synthesised show positive halochromism which is the effect of addition of few drops of hydrochloric acid, this is typical of azo dyes.

Also, the colours obtained on dyeing of both polyester and nylon fabrics with the disperse dyes show a deep shade with nylon and pale with polyester, as a result of the compact nature of the polyester fabrics. Hence. polyester fabrics are dyed at a longer time which is uneconomical. The colour fastness of dyed polyester and nylon is good and is within the range acceptable for quality dyeing in the textile industries.

Though, the colour fastness of polyester fabric was slightly better than the nulon because the colour fastness depends on the following factors: First, the types of fibre; thus diperse dyes generally show higher wash fastness property on polyester than nylon. Secondly, the amount of colourant on the fibre also affects the colour fastness. Deep dyeings or prints often differ markedly from that of a pale dyeing or prints of the same dye on the same

material. Deep dyeing fabrics exhibit higher fastness to light because more dye molecules must be destroyed before a change in colour is observed but lower fastness to washing than a pale dyeing. Therefore, nylon have higher fastness to light and lower fastness to washing than the polyester. Also, the presence of foregn substances like dyeing assistance, example, carriers, used for polyester dyeing can reduce light fastness by as much as two points on the 1-8 scale. Due to poor yield of disperse dyes on polyester by dyeing at the boil and also the initial lack of pressure equipment prompted an early search for carriers.

Carriers for polyester are usually hydrophobic organic molecules, for example, o-phenyl phenol, with sufficient affinity to permit their absorption from aqueous dyebath. Carriers, when used in dyebath for polyester fabrics, increase the rate of dye uptake by the fibre thereby enabling dyeing to be completed in an economic tine at the boil (Ingamells and Peters; 1955).

In addition, the number of moles of dye extracted from the printed polyester is quite significant. The efficiency of the dye transfer from paper to the fabric is assisted by the fact that the disperse dye has affinity for the synthetic fibre but virtually no affinity for the cellulosic paper support; the disperse dye vapour is readily adsorbed by the fibre under transfer conditions. Therefore, for the dieperse dyes to be useful in the transfer printing technique, it should have the following properties. It must sublime in the region of 180-23^{0}C, it must have no affinity for the cellulose based paper support. The dye must be readily absorbed in the vapour state by the synthetic fibre and also,

give adequate depth of colour and fastness on the fibre to be printed in order to meet end-use requirements.

The infra-red spectra of all the dyes synthesised, showed the various substituents attached to the dye molecule. The absorption peaks are very sharp and strong.

Recent research works (Noah, 1997) have indicated that disperse dyes can be applied to cotton fabrics by transfer printing technique. This however, was not studied and it is recommended that future studied can be carried out to assess the suitability of these dyes for transfer printing on cotton fabrics.

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APPENDIX 1a

DYED FABRICS WITH THE MONAZO DYES

NYLON 6,6.

DYE NO Colour Samples.

I series	a	b	c	d
2 "	a	b	c	d
3 "	a	b	c	d
4 "	a	b	c	d
5 "	a	b	c	d
6 "	a	b	c	d
7 "	a	b	c	d
8 "	a	b	c	d

APPENDIX 1b

DYED FABRICS WITH THE MONAZO DYES

POLYESTER

DYE NO	Colour Samples			
I series	a 	b 	c	d
2 "	a None	b None	c None	d
3 "	a 	b 	c 	d 
4 "	a None	b None	c None	d
5 "	a 	b 	c 	d
6 "	a 	b 	c 	d
7 "	a 	b 	c 	d 
8 "	a 	b 	c 	d

APPENDIX 1c

COLOURS OF THE PRINTED MONAZO DYES

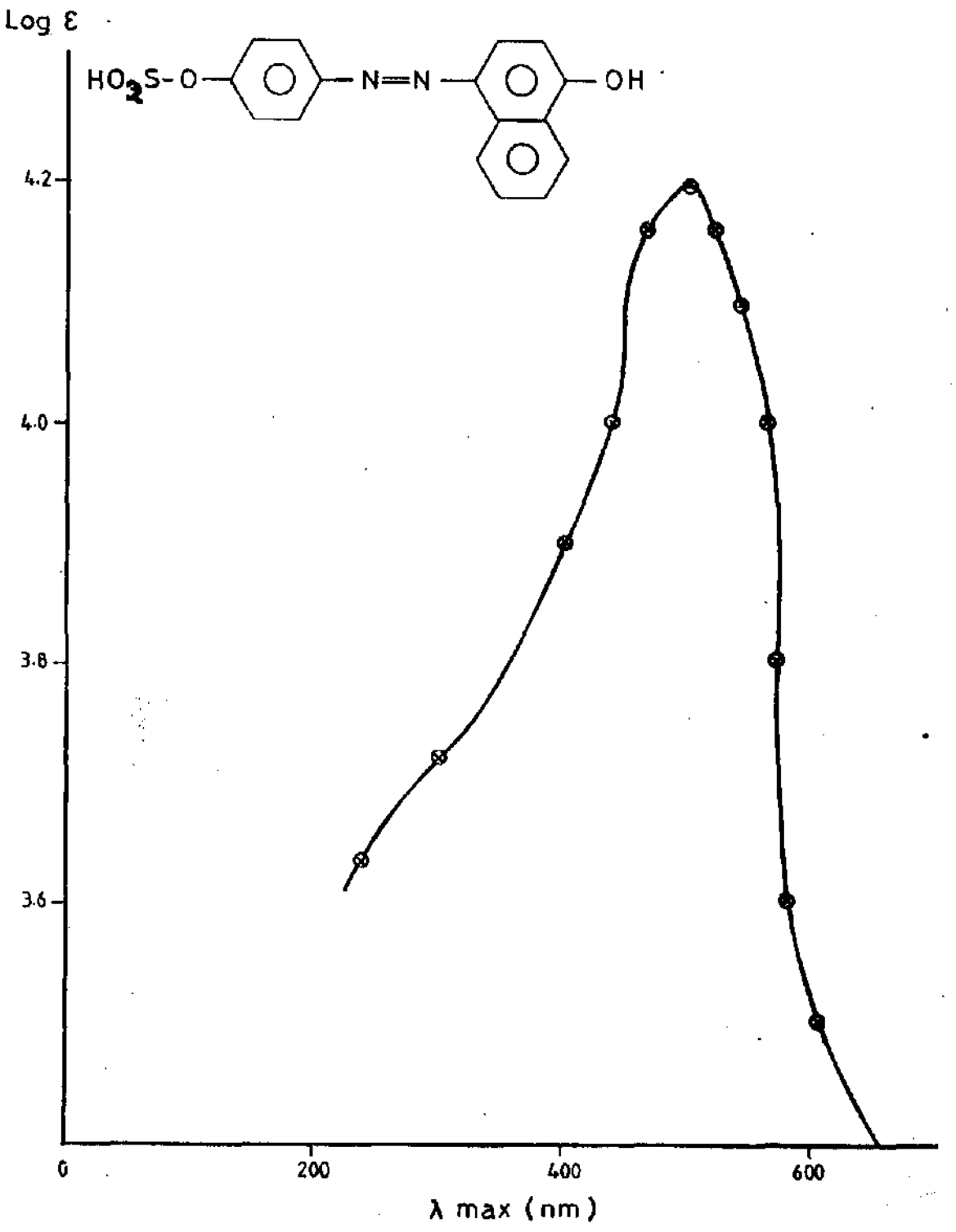
POLYESTER

DYE NO	Colour Samples.			
I series	a 	b 	c	d
2 "	a None	b None	c None	d
3 "				
4 "	a None	b None	c None	d
5 "	a	b		d
6 "	 a	 b	c	d
7 "	a	b	 c	 d
8 "	a	 b	 c	d

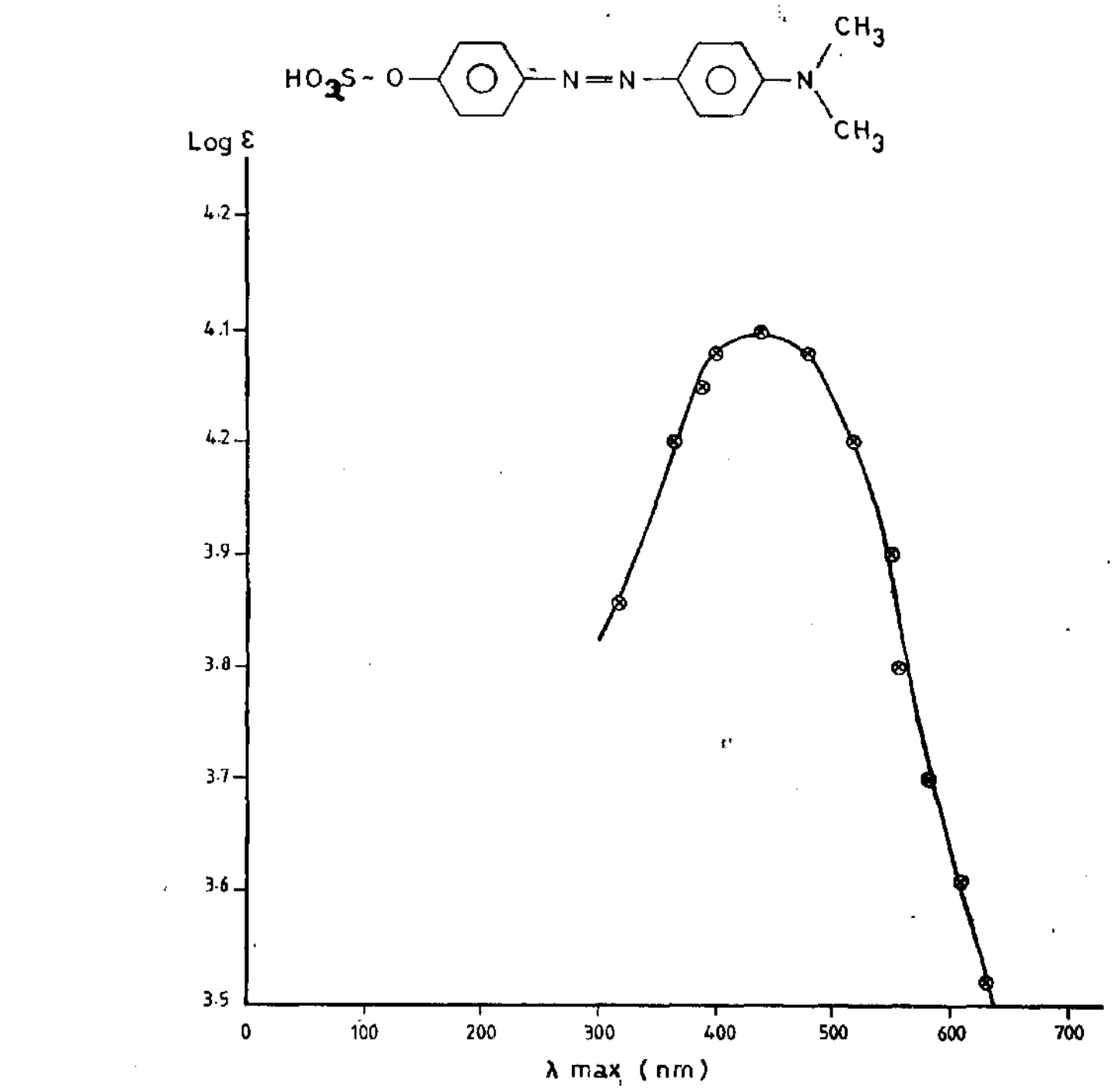
APPENDIX II

SHADES OF DYEINGS OBTAINED ON THE FABRICS

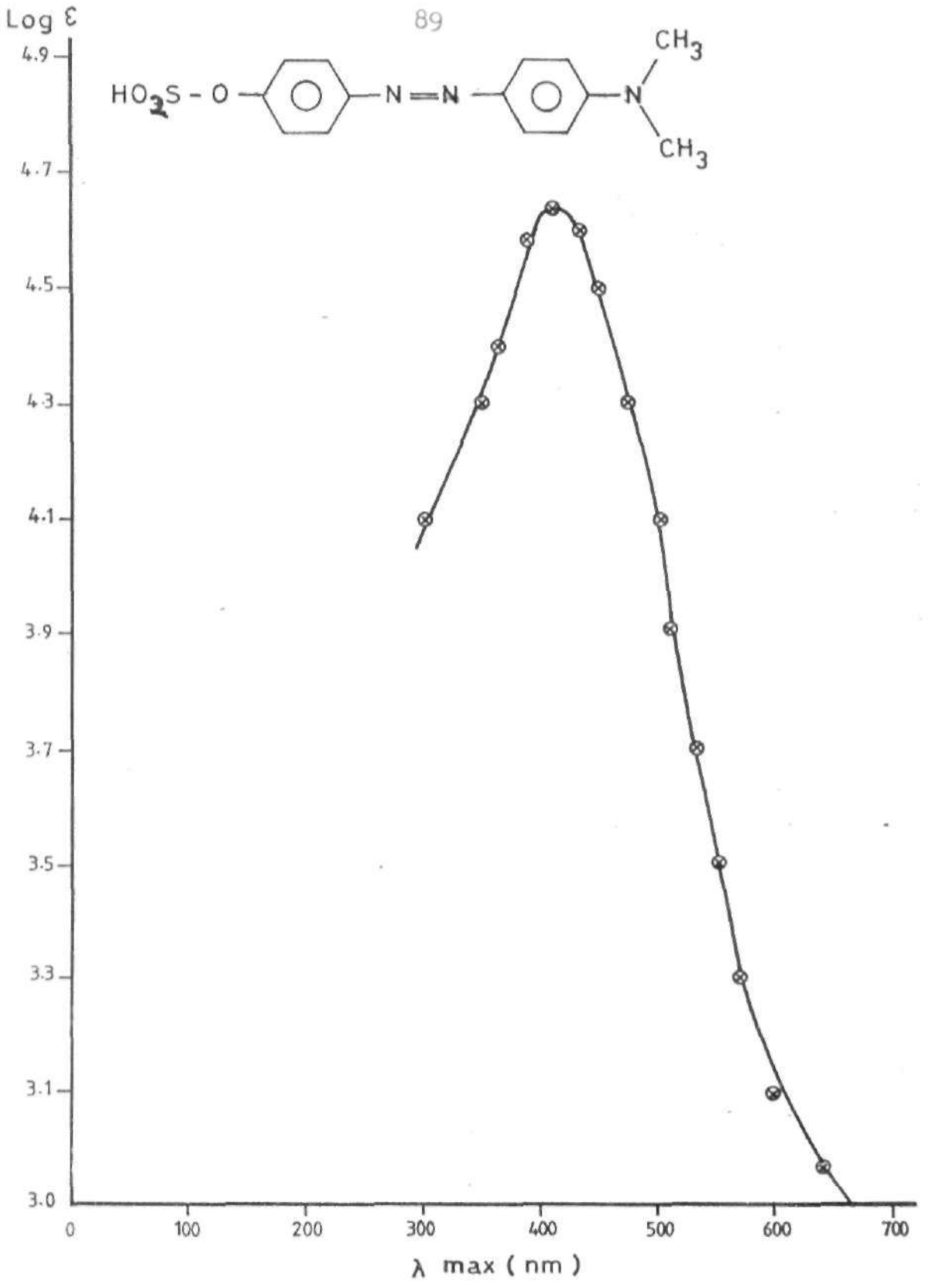
Dyes No.	Colour on Polyester	Colour on Nylon
1a	Deep Orange	Deep Orange
1b	Orange	Orange
1c	Yellow	Yellow
2a	None	Yellow
2b	None	Yellow
2c	None	Orange
3a	Orange	Orange-Yellow
3b	Orange	Orange-red
3c	Orange	Orange-red
3d	Orange-red	Orange-red
4a	None	Orange
4b	None	Light Orange
4c	None	Yellow
5a	Orange	Orange
5b	Orange	Orange
5c	Red Orange	Orange
6a	Brown	Orange
6b	Orange-red	Orange
6c	Orange	Orange
7a	Orange	Orange
7b	Orange	Orange
7c	Orange	Purple
7d	Orange-red	Orange-red
8a	Brown	Brown
8b	Orange	Orange
8c	Purple	Purple



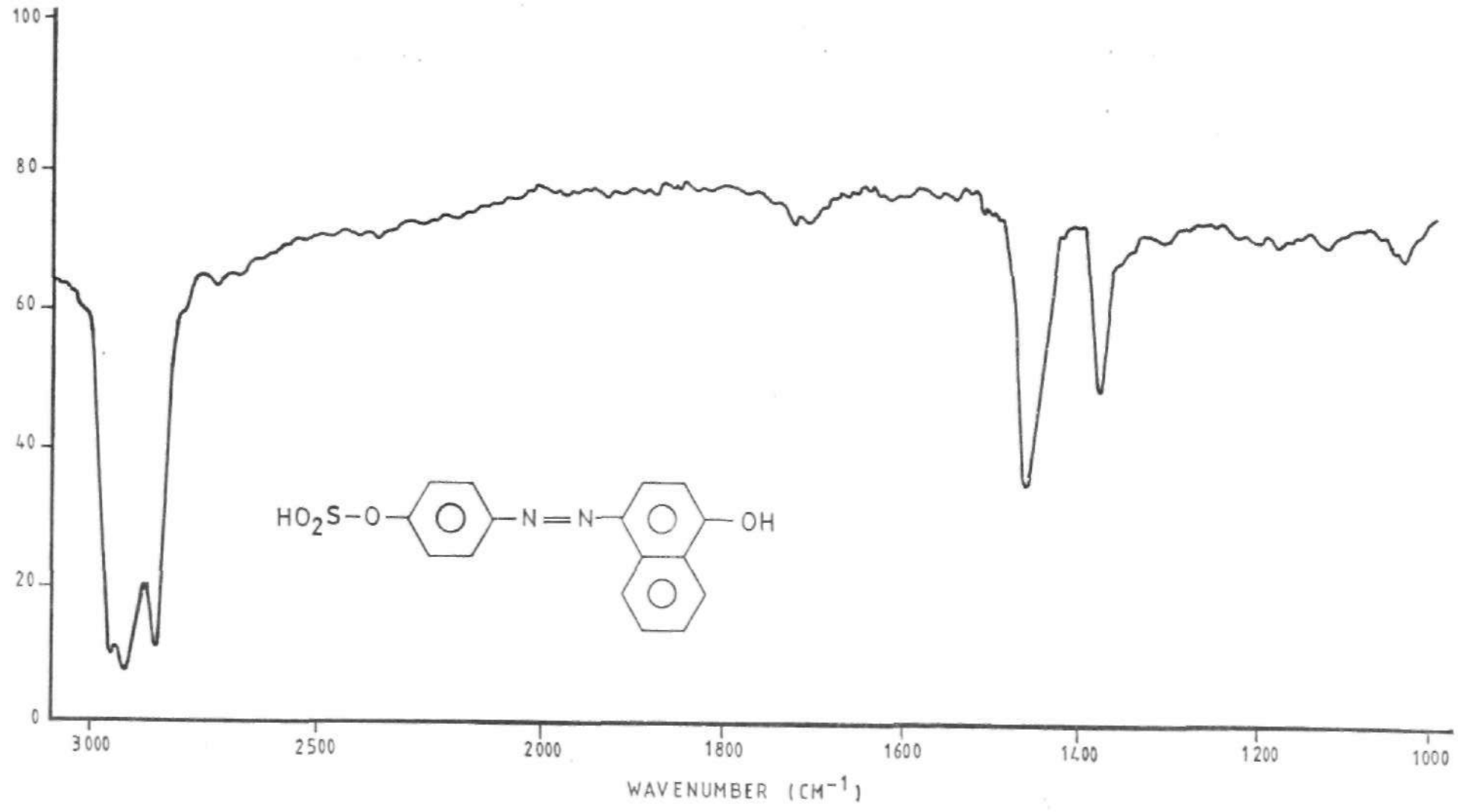
UV SPECTRUM OF DYE (4b) IN ETHANOL .

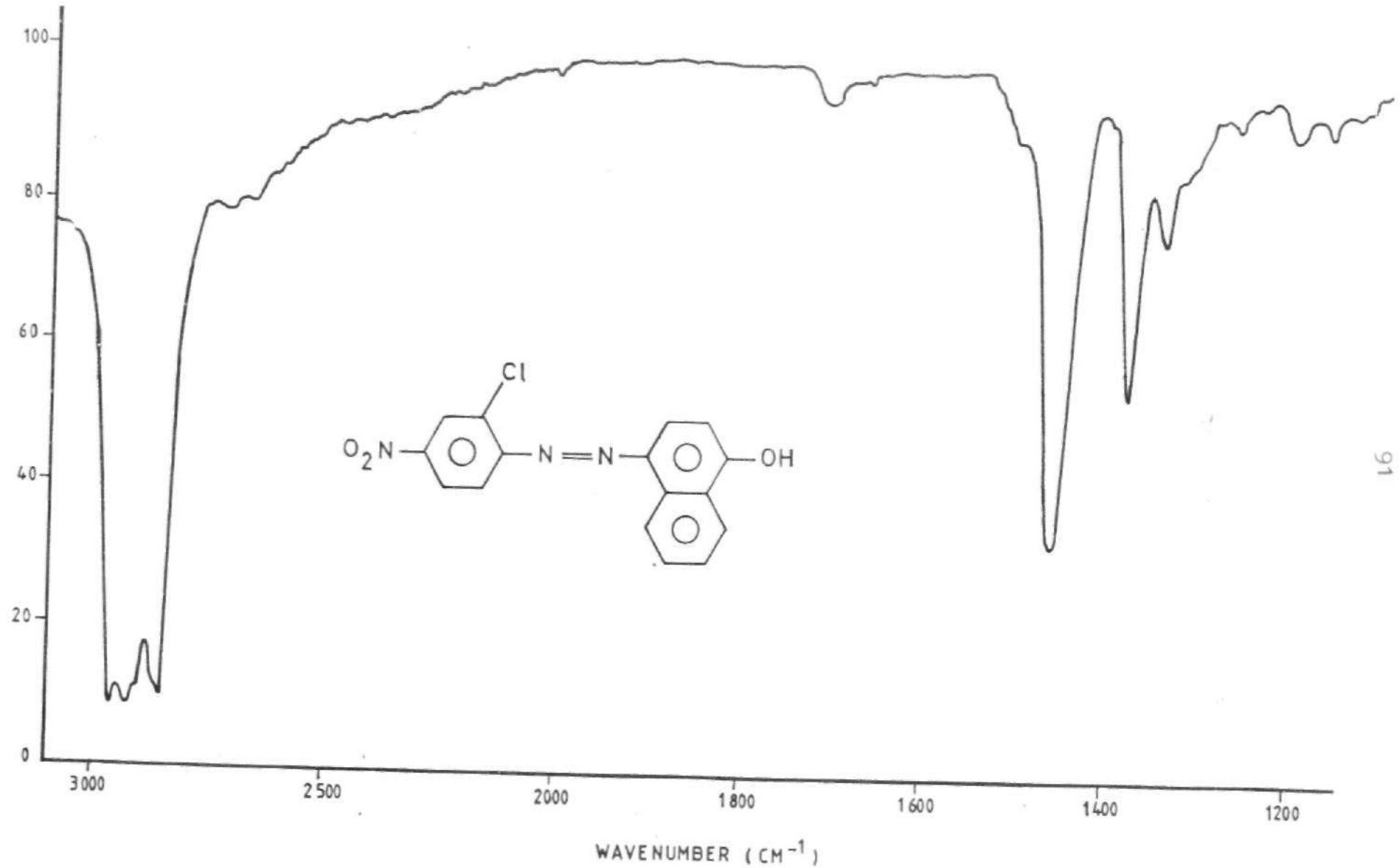


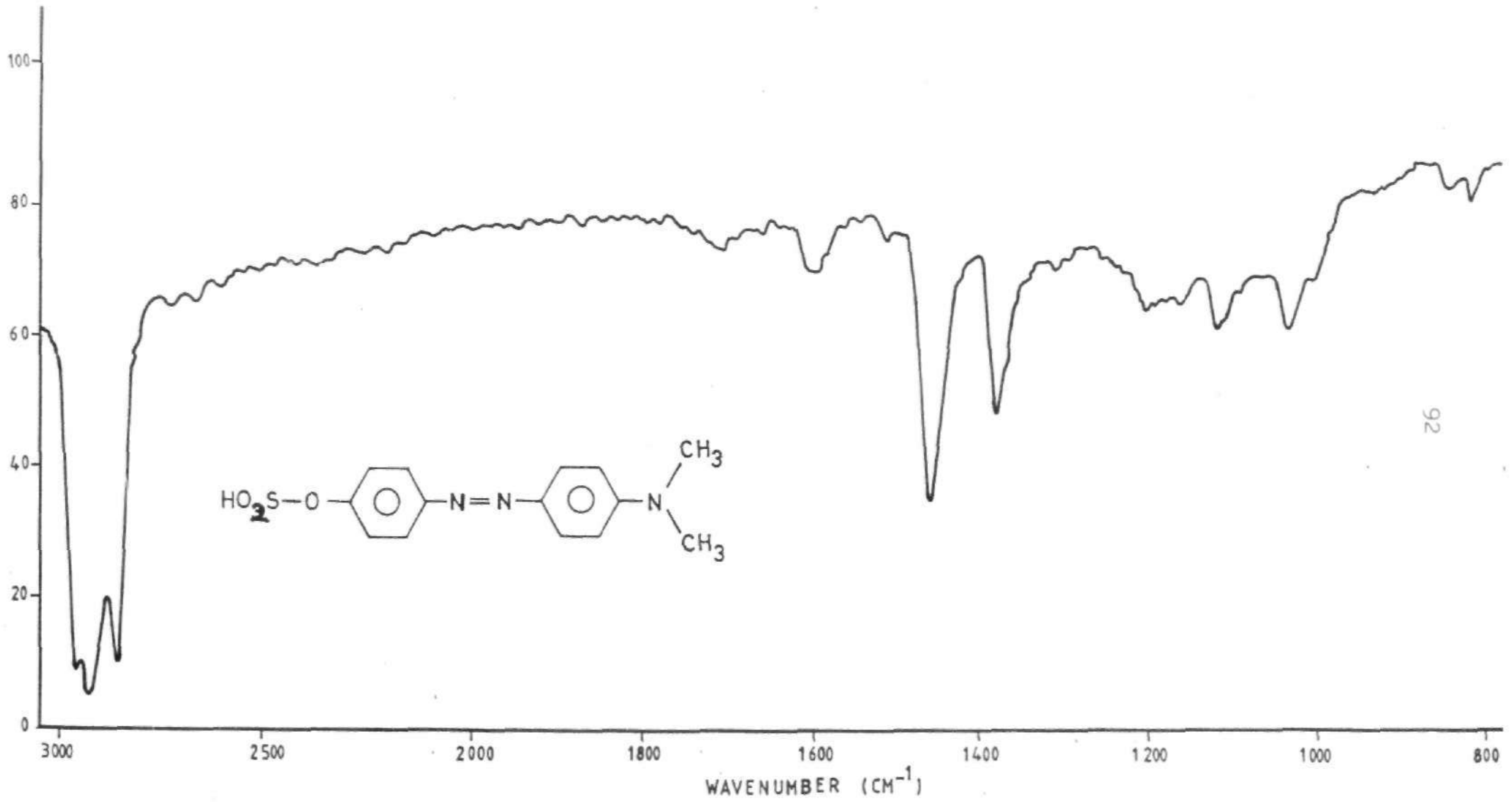
UV SPECTRUM OF DYE (4c) IN ETHANOL .

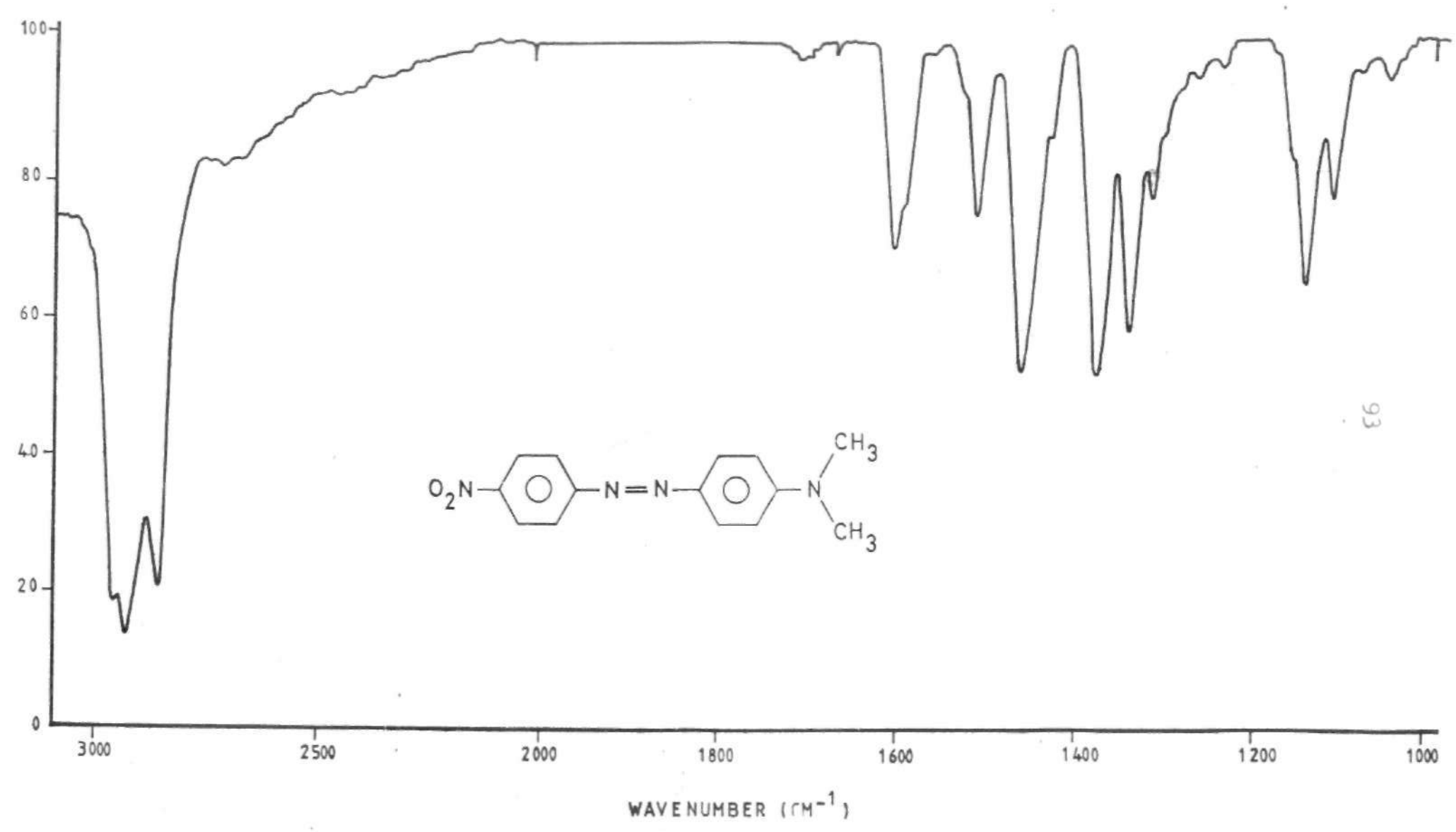


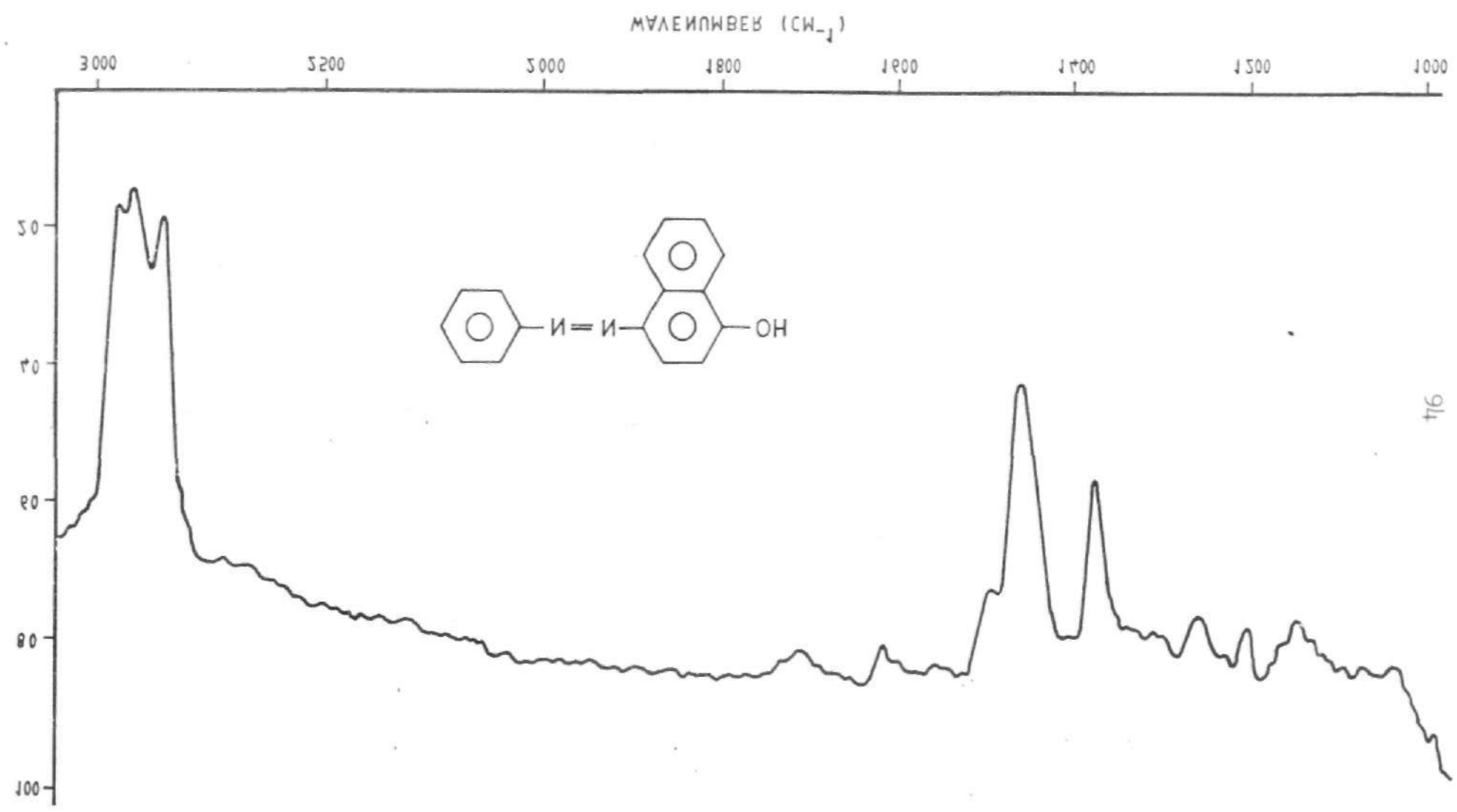
UV SPECTRUM OF DYE (4c) IN ACETONE .


100
80
60
40
20
0
3000
2500
2000
1800
1600
1400
1200
1000
WAVENUMBER (CM⁻¹)
HO2S–O
N=N
OH


100
80
60
40
20
0
3000
2500
2000
1800
1600
1400
1200
WAVENUMBER (CM⁻¹)
Cl
O₂N
N=N
OH


100
80
60
40
20
0
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM^{-1})
HO$_3$S—O
N=N
N
CH$_3$
CH$_3$
CH$_3$


100
80
60
40
20
0
3000
2500
2000
1800
1600
1400
1200
1000
WAVENUMBER (CM^{-1})
O_2N
N=N
N
CH_3
CH_3


WAVENUMBER (CM⁻¹)
4000
3200
3000
1800
1600
1400
1300
1000
50
40
30
20
100
HO
N=N