THE EFFECT OF SUBSTITOENTS ON PROPERTIES OF MONOAZO DYES DERIVED FROM H-ACID

BY

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Being a Thesis submitted to post graduate school
in partial fulfilment of the
requirements for the
award of Master of Science (M.Sc) Degree in
Textile Science and Technology,
Ahmadu Bello University,
ZARIA,

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MAY 1994

D E C L A R A T I O N

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 derived from the published work of others have been duly acknowledged in the text by means of reference.

OWETE O. Valerie

Date:

C E R T I F I C A T I O N

This thesis entitled "The Effect of Substituent on properties of Monoazo Dyes Derived From H- Acid" by Owete, Valerie Obiajulu meets the regulations 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

To Him who created me and everything else for His pleasure and to the progress of the textile industry and related fields in Nigeria.

A C K N O W L E D G E M E N T

I thank God who has made all things possible inspite of the many obstacles.

I am indeed grateful to my supervisor Dr. K. A. Bello, whose patience and forbearance go without saying. Without it I would not have had much to show for all my effort.

Many thanks go to all my lecturers, the academic staff in the department who have given their best to improve my knowledge and skills in the course, including Professor E. G. Kolawole, Dr O.K. Sunmonu, Dr P. O. Nkeonye, Mr E.B. Iliya and all the non- academic staff whose moral support have been highly invaluable.

Dr Ajayi (and family) of Abubakar Tafawa Balewa University, Bauchi who took care to ease my ordeal whilst there, and Professor Olagbemiro, of the same university for the help offered me in his department; Andrew Omachi, Chemistry Department ABU and Mr Michael Adeyemi of United Nigerian Textiles Plc, Kaduna for making their facilities available to me in their laboratories; also Associate Professor B. B. Dambatta, Mallam Ibrahim Marmara, his late predecessor Danladi Ayok and Mohammed S. D. Gumel for enabling me to carry out various tests in the chemistry department of Bayero University Kano.

My special thanks go to the family of Professor & Mrs E. O. Gyang who took care of me in ways too numerous to mention; Semira Adejumo and her family, the Adohs whose kindness towards me has been unique, Mr Patrick Azunna who also helped me while in Kano; Mr and Mrs C.B. Theophilus F.R.S.C., Bauchi, I also wish to thank Mr C. A. Offor for his contribution towards the completion of this thesis.

To all my friends within and outside ABU e.g. Bitrus Dlagai B.Sc. Tech. 89/90, Austin Jacob whose company made it worthwhile, my family in the church for the support throughout the course.

Finally, I wish to thank my parents Chief & Mrs O. W. E. Owete, my brothers and sister for their patience, consistent encouragement, assistance and material support which have helped in bringing this programme to an end, I am truly grateful.

May God bless them all.

OWETE, Valerie O

A B S T R A C T

A variety of azo dyes were synthesized based on H- acid (1-amino,8- naphthol, 3,6- disulphonic acid) coupled to diazotised aniline and its substituted derivatives.

Electron releasing substituents - acetyl, benzoyl and paratoluene sulphonyl groups - were introduced into the amine group of the coupling component and aniline derivatives containing various electron withdrawing groups were used as the diazo components.

The structural features of the dyes synthesized were ascertained by the analysis of their individual I.R. (infrared) spectra, measured in paraffin.

The effect of different substituent groups on the colour of the dyes synthesized were studied by measuring the relative change of wavelength of maximum absorption in distilled water, and the solvatochromic effects in dimethyl formamide.

The fastness properties of the dyes on Nylon 6.6 (woven) were also investigated.

Results obtained showed the N- paratoluene sulphonyl groups as having the highest electron releasing strength resulting in marked bathochromic shifts. Marked trends were not observed for the various diazo ring substituents due to the interplay of steric hindrance and non-planarity of dyes formed.

N- benzoylated H- acid dyes showed high wash, perspiration and light fastness properties due to intra molecular aggregation.

N- acetylated H- acid favoured high perspiration and light fastness properties due to weak electron releasing strength which increases the dye's inherent stability.

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CHAPTER ONE

I N T R O D U C T I O N

The white light given out by the sun is made up of all wave lengths of electro magnetic waves. The part we see as light makes up only a small fraction known as "the visible spectrum". In this fraction, different wavelengths appear as different colours of light.

A given colour is 'perceived' as a result of the selective absorption of the radiation of the visible spectrum by the substrate being observed. The visible region of the spectrum is illustrated as shown below:

THE VISIBLE SPECTRUM 400 - 750 nm

Radiation: ultraviolet (uv)	Blue	Green	Yellow	Red	Infrared (IR)
	<--[visible region]-->				
Wavelength (nm)	400 nm			750 nm	

The light reflected by the substrate or transmitted through it to the observer produces the sensation of colour when incident on the retina of the eye (the retina is the light sensitive surface within the eye). The retina then transfers electric impulses to

the brain via the optic nerves which join up the retina to the brain. The impulses received are then converted into the coloured images seen, within the brain.

The retina contains specialized cells (rods and cones) for the purpose of responding to the light stimuli received in different conditions (i.e, photopic and scotopic vision).

The colour seen is complementary to that absorbed by the object. This can be seen from Table 1 below:

Table 1: THE RELATION BETWEEN COLOUR ABSORBED AND COLOUR SEEN

Wavelength nm	Colour of Light absorbed	Colour of Light Seen
400 - 435	Violet	Yellow - Green
435 - 480	Blue	Yellow
480 - 490	Green - Blue	Orange
490 - 500	Blue - Green	Red
500 - 560	Green	Purple
560 - 580	Yellow - Green	Violet
580 - 595	Yellow	Blue
595 - 605	Orange	Green - Blue
605 - 750	Red	Blue - Green

The strong absorption of selected narrow bands of light wavelength give rise to bright colours while dull colours are produced where there is absorption across a broad region of the visible spectrum. At high concentration, such dull colours tend towards black[1]

1.1 THE MEASUREMENT OF COLOUR [2]

The measurement of colour absorbed and the intensity of absorption can be done using an Absorption Spectrophometer or Colorimeter. Here an artificial light source (e.g a mercury discharge lamp or deuterium lamp) is used to illuminate identical cells containing the dye solution at a known concentration (c) in one and the pure solvent in the other referred to as the reference cell. The choice of wavelength of light incident on the cells at a given time is determined by the position of a prism or diffusion grating through which the artificial light obtained from the lamp source is directed and thereafter focussed on the cells.

Measurement can be made over the entire visible spectrum by the slow rotation of the prism throughout, while the absorbance (A)/Optical density (O.D)/Intensity of absorption (I) is being read.

An automatic recorder receives electric impulses from a photo-electric ell, within which the intensities of beams emerging from the pure solvent (Io) and dye solution (I) have been compared. The results obtained (i.e Absorbance) are recorded as intensity of absorption against wavelength on a graph sheet. For a given dye a particular curve is expected/obtained on a standard uv-visible

spectrophotometer. Any variations that occur may simply be in intensity of absorption (which changes with dye concentration) or otherwise due to the presence of impurities.

The absorbance (A) for a given dye in solution can be calculated using the Beer Lambert- law [2]

$$A = \text{Log } \frac{Io}{I} = \epsilon cl$$

where

I = intensity of emergent light

Io = intensity of incident light

ϵ = molar extinction coefficient

c = concentration of solute in moles per litre

l = thickness of the solution in centimetres

The above equation is also useful in calculating the molar extinction coefficient (ϵ) of a dye which is a direct measure of its tinctorial power.

1.2 NATURAL DYES AND PIGMENTS

Dyes are coloured compounds which when applied on a given substrate produce a lasting coloration of appreciable intensity. Dyes are applied on a fabric or material from an aqueous system either directly; or indirectly by chemical conversion to a soluble form which is reversible or precipitated chemically after application to the parent dye.

Pigments unlike dyes are applied onto a substrate in an insoluble form and anchored or bound onto it with some resinous

material.

The earliest form of artificial coloration was carried out by Stone Age Men who made paintings on cave walls with plant extracts[3].

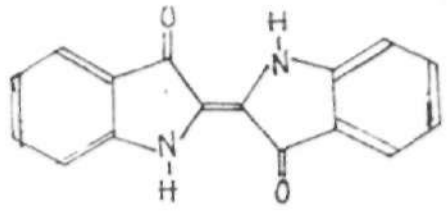
They also dyed furs and textiles; as described in ancient hieroglyphics[4]

Dyes need to have affinity for the substrate and reasonable fastness to washing and, light and by experience in the use of natural plant and animal dyes, a few gained international acceptance. The natural dye market flourished and was a highly profitable venture until the middle of the nineteenth century when the synthetic dye industry emerged.

1.2.1 INDIGO AND WOAD (C.I NATURAL BLUE 1 15780)

This has the oldest record of use compared to other natural dyes. Sanskrit writings show that over four thousand years ago the cloth wrappings of Egyptian mummies were dyed with indigo. Woad has an equally long history and there is record of laws being passed in England, France and Germany prohibiting the use of Indigo on the grounds that Indigo was the 'devil's dye' and was quoted to be 'harmful, deceitful and corrosive'. This was because Woad and Indigo had similar colours but Indigo was made more available and therefore threatened the European Woad market. Indigo (Figure 1) is obtained from Longocarpus cyanescens in Nigeria.

(Fig 1)



Mode of extraction of Indigo:

(1) Plant fermentation in warm water for 12 hours after beating the leaves and stem to a pulp.

(2) Aerial oxidation of the liquor from fermentation after removal of the fermented plant pulp at the end of fermentation.

The dye precipitated is filtered off and pressed into three inch cubes and dried.

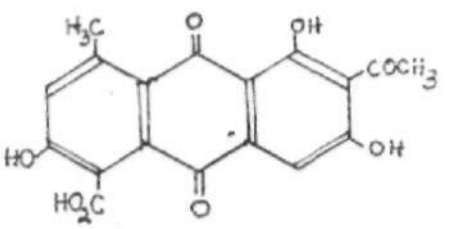
1.2.2 KERMES[5] (C.I NATURAL RED 3, 75460)

Until the 16th century, this was a popular red colouring and reference is made to its being used in dyeing of the tabernacle curtains of the temple according to Moses (6,7) instructions.

It was used for dyeing of wool when mordanted with alumina and tatar to give a rich crimson and scarlet colour respectively.

Its mode of extraction is highly labourious involving breeding thousands of the female insect Coccus elicas. They are collected just before they hatch their eggs and killed by exposure to the vapour of vinegar and dried.

The structure is represented in Figure (2)



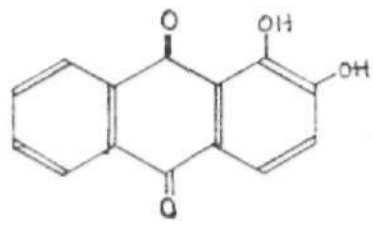
(Fig 2) Kermisic Acid active colorant of Kermes.

Logwood can be used for dyeing silk, wool, leather, cotton, rayon, wood, fur, hog, bristles, cattle, and horse hair and of nylon[9] and as a bleachable printing ink for paper thus allowing for reprocessing of paper pulp[10]. It is also used as a natural colorant for food drugs and cosmetics where synthetic colorants are not allowed.

Method of Extraction: Wood chips are extracted with boiling water and the extract concentrated to 5% moisture retention to give Logwood dye crystals of haematoxylin.

1.2.4 MADDER[5] (C.I NATURAL RED 8, 75330)

An age old natural dye used by the predynastic era of the Egyptians in their tombs. It is obtained from plants of the order Rubiceae and is generally found in their roots. the structure is as shown in Figure 5.



(Fig 5) Madder(also known as alizarin)

It gives turkey red dyeings on cotton and with salts of various metals. It gives a variety of fast colours e.g.

with chromium - bluish red

with calcium - dull bluish red

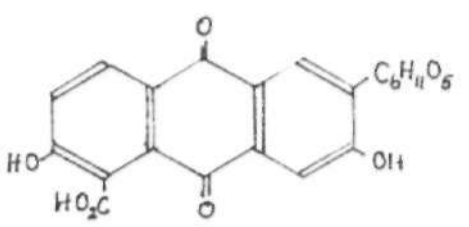
with tin - orange yellow

1.2.5 COCHINEAL[11] (C.I NATURAL RED 75470)

The native country of cochineal was Mexico but it's use as a dyestuff was not known until the Spaniards conquered Mexico in 1518. When the Spaniards realized that the cochineal was more superior to than the already popular Kermes, they tried to maintain the monopoly of it's production.(The dye was obtained from the dried bodies of the insect **coccus cacti** which feeds on cactus in Mexico). However, because it was not possible to limit the cultivation of the insect to Mexico alone for an indefinite period of time, it wasn't possible to maintain it's monopoly[11]

Method of extraction[5] involves exposing the insect to heat and 70,000 insects were needed to produce one pound of the dye. the dye was used for dyeing wool and silk. With salts of aluminium and tin, crimson and vivid scarlet dyeings respectively were obtained. The colours were fast to light but sensitive to alkaline conditions.

Carminic acid shown in (Figure 6) below is used as colorant of cochineal dye. It is also used as a food, drug and cosmetic colorant today.



(Fig 6) Carminic Acid

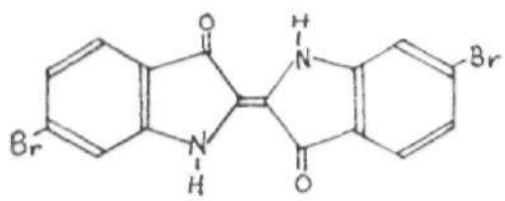
1.2.6 TYRIAN PURPLE[5] (C.I NATURAL VAT DYE 75800)

In Tyre the dye industry was believed to have begun as early as 3,000 - 2,000 B.C.It was obtained from the glands of Shellfish(**Murex brandis**) found in the Mediterranean Sea.

Extraction:

It was gotten from a pus like secretion present in the snail. This secretion had to be exposed to sun to produce the real dye . Extraction of 1.4 grammes of the dye required 12,000 Molluscs.

454 g of the dye cost about one hundred and fifty dollars[12]. Due to it's purple coloration of wool and cost of production, a rich man was aptly described as being born to (wear the expensive) purple. Tyrian purple is shown in (Figure 7) below.

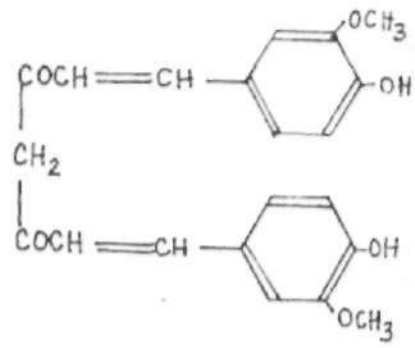


(fig.7)

A few other dyes of commercial importance today include:-

1.2.7 CURCUMIN(5) (C.I NATURAL YELLOW 3, 75300)

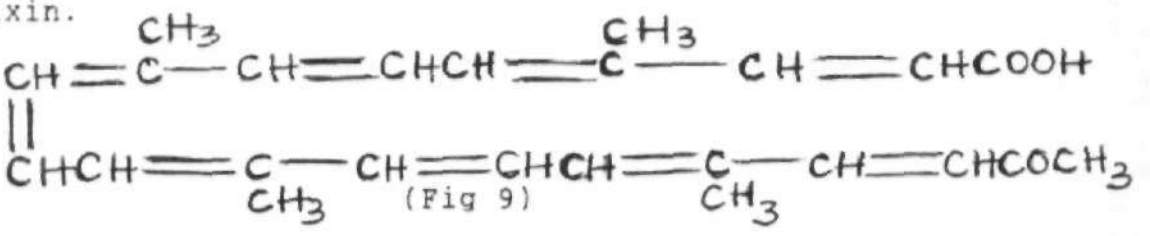
It is obtained from the roots and shoots of curcumin tinctoria (see fig.8) below) and used in food colouring.



(Fig.8)

1.2.8 ANNATTO[5] (BIXIN) (C.I NATURAL ORANGE 4, 75120)

It is obtained from the seed and pulp of the shrub **Bixa** orellana. It is an important food and cosmetic colouring which is converted in animal organisms to Vitamin A and is therefore categorized as a provitamin. Shown in Figure (9) is the structure of Bixin.



(Fig 9)

From the above review it can be seen that Natural dyes represent a very wide range of organic chemical structures found in flowers, fruit, seeds, leaves, bark, wood and roots of various plants, in certain insects and in a few selected animal tissues.

There also exist a category of `**Mineral Dyes**'[12] made from various minerals found in the earth's crust. These were more fast than the plant and animal dyes e.g ultramarine blue. Various kinds of rocks were pounded into a powder and used as dyes. Certain black muds and also water containing minerals such as sulfur were used.

Today the use of natural colouring material is restricted largely to highly sensitive material e.g food, drugs, and cosmetics.

In general use, such as dyeing of textiles, they have been replaced by synthetic dyes which can be produced more cheaply than other dyes and with a greater variety of colours. They also give more permanent and level colorations.

1.3.1 HISTORICAL DEVELOPMENT OF SYNTHETIC DYES

The first major breakthrough in dye synthesis which has become a historical landmark is the accidental discovery of mauveine by W.H Perkin [1,2] while trying to synthesize quinine from a mixture of anilines. This was in the year 1858. It gained great significance because of his ability to develop a successful industrial manufacturing process for its large scale production. Mauveine was used for the purple coloration of silk.

Earlier records of dyes synthesized though without any industrialized process for production include:

-Picric Acid by Woulfe in 1777[4]. It was used in dyeing silk yellow. Earlier attempts had been made to manufacture synthetic dyes by modifying the natural ones already present. For example W. H. Perkin and his collaborators worked on Logwood in this direction without much success[13]. After the discovery of mauveine, other dyes were synthesized without any experimental guidelines or laid down theories to account for the reactions observed viz:

In 1859, E. Verguin synthesized Fuschine in Lyon[4], Magenta, Rosaniline Blue, Methyl Violet. Hoffman Violet, Aniline Black and Aldehyde Green were produced between 1857 - 1867[14]. However, in 1858, August Von Kekule brought forward his discovery of the 'quadrivalency of carbon' as well as the constitution of the benzene ring[4]. With this discovery the research into the development of the synthetic dyes became more directional and gave rise to the elucidation of already proven dyes as well as the

development of analogues of some natural dyestuff.

The synthesis of alizarin was achieved in 1868[14,15] by C. Graebe and C. Liebermann.

Alizarin was subjected to zinc distillation which yielded anthracene Figure (10) below:

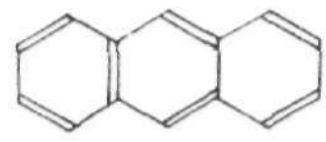
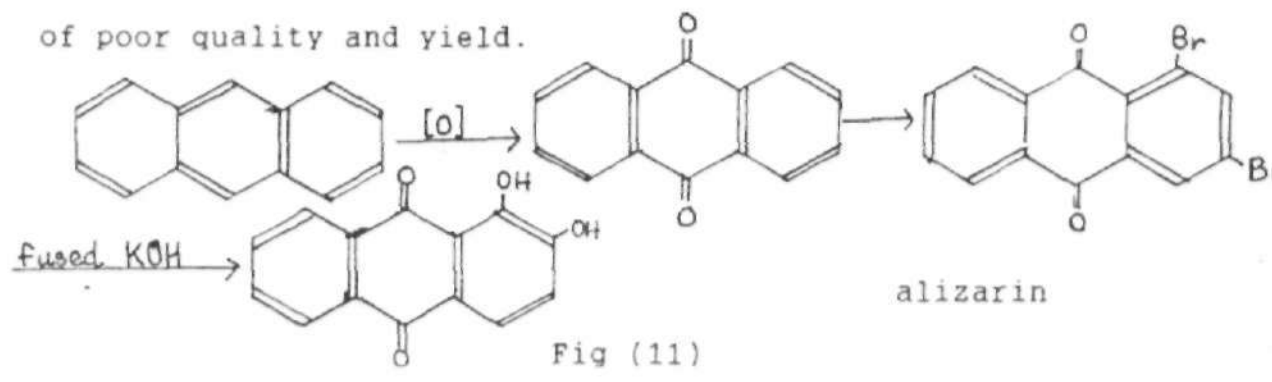


Fig (10)

Anthraquinone was therefore dibrominated, anthraquinone being the oxidation product of anthracene. The dibrominated product was fused with potassium hydroxide to give alizarin. The product was of poor quality and yield.



alizarin

Fig (11)

By 1869, Perkin in collaboration with Caro, Graebe and Liebermann [14] improved and patented alizarin having developed improved methods of synthesis. They were also able to produce one tonne of the dye at the time. Perkin was able to reach an annual production capacity of four hundred and thirty five tonnes per year by 1873[14].

The synthesis of Indigo was started in 1870 with the elucidation of its structure by Professor Adolf Von Baeyer[4]. Large scale production began in 1897 following the investment of

about one million pounds for intensive research by German dye manufacturers Badische Anilin and Soda Fabrick. (BASF) The company had earlier bought the patent from Professor Von Baeyer and had K. Heumann (1890) develop a technically sound process for its manufacture.

In an attempt to compete with the synthetic version, the natural Indigo producers tried to modify the natural dye for improved qualities but to no avail[16].

P. Griess 1862 [14.1] discovered the azo functional group as being very important in the synthesis of dyes thus forming the largest chemical class of dyes. The first azo dye is credited to a man called Martius[4].

With time, there has evolved synthetic dyestuff for natural fibres which are virtually insoluble in water and exist within the dyed material as large sized molecules which are not easily removed by washing e.g Phthalocyanine dyes discovered in 1936 and Nolan Dyes in 1915, which are metal complex dyes[4] Vidal produced Sulfur dyes for weighted cotton (1873). Vat dyes and Azoic dyes were created in 1906 and 1912 respectively[17].

By the year 1951/52 and 1956, Reactive dyes for Wool and Cellulose respectively had been developed; their advantage over natural dyes being that they formed covalent linkages with the natural fibres thus becoming one entity with the fibre and requiring a high amount of chemical or physical energy to separate the dye from the material fibre.

The majority of the synthetic dyes which have been

specifically synthesized for the purpose of dyeing synthetic fibres include: disperse and eationic dyes Disperse dyes were developeed for hydrophobic man made fibre e.g acetate fibers, polyester and nylon (produced in 1923) while cationic dyes were created for acrylic fibers in the year 1957 [17].

To date there are over 60,000 synthetic dyes and over 35,000 different trade names thus proving the versatility of the synthetic dye industry.[17]

1.3.2 ADVANTAGES OF SYNTHETIC DYES OVER NATURAL DYES AND ITS INFLUENCE ON THE SYNTHETIC DYE INDUSTRY.

Natural dyes had many disadvantages compared with the synthetic dyes and their inadequacies became more obvious as time passed in the development of the synthetic dye industry.

The dyeing of natural fibres with the natural dyes involved intricate fixation processes. Hardly any of the colours known to the early natural dyers were capable of dyeing the four main fibres being used - wool, flax, silk, and cotton from a simple dyebath i.e they could not be dyed by dissolving the dyestuff in water and then introducing the material into the dye liquor.

Many modern dyes can be used in a simple way. Most ancient dyes involved one or other of two different techniques.

1. Treating the dyed fabric/dye liquor with solutions of metallic salt (mordants) before the dye can be properly fixed on the fabric e.g Alizarin.
2. Reducing the dye to its soluble leuco form dissolving it in an alkaline liquor. The material is steeped in to the alkaline

dyebath and the final colour (blue and purple for Indigo and Tyrian Purple respectively developed on the fabric by oxidation in the air.

Varieties of fast colours were produced using different metals for mordanting though somewhat dull.

With the advent of new synthetic fibres as from 1938 (Nylon - E. I. du Pont Nemours & Co[18]) having very different physical and chemical properties from the natural fibres, it becomes even more difficult to develop methods of fixing the natural dyes on to synthetic fibres.

Methods of natural dyeing were developed further (by trial and error) but the pace at which new fibres have been continually manufactured has made it virtually impossible for the natural dyers to make any impact in synthetic fibre dyeing. Exceptions to the rule include Logwood which is popular due to the unique black it gives with copper or chrome mordants. It is presently used for production of weighted silk fabrics and for nylon. It serves as a biological staining ink in the laboratory.

As seen earlier, the mode of extraction of some of the natural dyes (Kermes, Cochineal, Tyrian purple) are also highly tedious and time consuming. Dyeings of cochineal mordanted with aluminium were fast to light but sensitive to alkaline conditions[5] such as are present in domestic washing. The shades obtained tend to be a bit dull due to the use of mordants and the presence of some amount of impurity. In spite of disadvantages some natural dyes were expensive e.g Tyrian purple costing as much as one hundred and

fifty dollars per pound or four hundred and fifty four grammes.

Synthetic analogues of the natural dyestuff and other synthetic dyes made subsequently were not subject to 'seasonal' fluctuations in production or affected by unfavourable climates because the raw materials were available all the year round. They are obtained from coal, tar, natural gas and petroleum products. The production level can be adjusted to meet up with the daily increase in population demand as well as in the number of outlets for its use over the years.

Synthetic dyes are outstanding for purity and for dyeing silks for which most of the expensive and moderately effective natural dyestuffs were used.

The use of mordants is reduced as the synthetic dyes have higher affinities than most of the natural dyes. In addition the synthetic dye were much cheaper to produce.

A variety of application classes of synthetic dyes exist for any one type of fibre and with a larger range of colours that can be obtained from them. Mixtures of synthetic dyes are easily made in order to obtain unique shades. The limited number of fast natural dyes and varying fixation methods were bound to make such mixing techniques difficult. They lacked the versatility of synthetic dyes hence the overwhelming success of the synthetic dye market over that of the natural dyes.

1.3.3 THE ESTABLISHMENT OF THE SYNTHETIC DYE INDUSTRY

With the acquisition of the systematic knowledge of synthetic

organic chemistry along with the effective reaction mechanisms practised by the various industrialists, highly efficient methods of synthesis and brilliant industrialization techniques were developed. This brought about a high level of production and this was not restricted to dyes of a particular chemical class. In fact, a variety of dyes having various functional groups were produced[14].

Perkin who pioneered the synthetic dye industry at the age of 18[14] retired at an early age of 36 and had manufactured the following dyes by that time: Mauveine, Dalula, Magenta, Alizarin, Ethyl Mauveine and Perkin Green.

Though Perkin's work particularly in the synthesis of mauveine and alizarin and in the field of industrial chemistry were quite important, the British industry did not develop much at the early stages. This was due to the fact that for various reasons they preferred to export the raw coal tar product and import the dyes made with it from Germany. Not until after the first World war did other countries deem it important to go into dye synthesis as an industry. Even then the Germans had the advantage of a good sales organization world-wide and they also supplied technical service to the dyers. Thus converting old craft traditions into a near scientific industry.[19]

One of the main reasons for the expansion of the German synthetic dye industry over that of the British is due to the fact that the dye chemistry lecturers in the Royal College of Chemistry at the time of Perkin's study were mainly Germans. These included

Hoffmann (Perkin's lecturer) Caro, Martius, Bottiger and Griess; and when Hoffmann returned home before the war most of them went back except Griess. As a result the research and development that went with the establishment of the synthetic dye industry was more intensive and directional on the side of the Germans than that of the Britons.

Most of the dyes were made in Europe until the beginning of World War I. When the U.S could no longer obtain dyes from abroad the American Chemical Industries started to manufacture dyes. Now most of the dyes used in the U.S are produced within.

Development of synthetic dyes within the developing countries is still on a very limited scale, for example in Nigeria, there is no known dye industry for the manufacture of synthetic dyes.

1.4.0 COLOUR AND CONSTITUTION OF ORGANIC DYES

In 1858, it was discovered by Graebe and Liebermann that the reduction of coloured compounds results in the loss of coloration. This implied that the colouring matter had to be unsaturated to be able to emit colour[20].

O. N. Witt in 1876[21] further developed the unsaturation theory stating that dyes[1] were made up of

(i) chromophores (GK-color bearers) - give potentiality for colour.

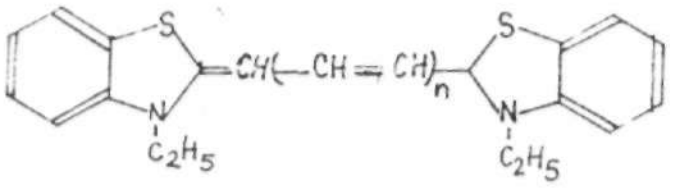
(ii) salt forming radicals auxochrome (GK-increase colour) - in order to dye efficiently and intensify colour.

Nietzki's rule (1897)[1] proposed that the introduction of substituent weighting groups e.g methyl, phenyl, ethoxy, bromo,

nitro deepened the colour of a given dye as its molecular weight is increased. However, there arose many exceptions to this rule.

Armstrong (1888)[19] suggested that all dyes must be able to obtain a quinonoid structure with the benzene ring and substituents. Although several exceptions existed the idea was generally helpful.

In 1907, Hewitt having compared some series of azo dyes came to conclusion that the longer the chain of conjugated bonds in the dye, the deeper the colour of the compound.

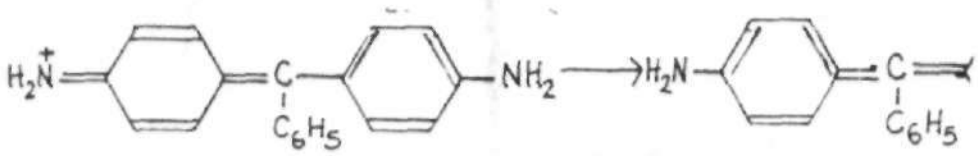


(Fig 12)

and for Figure (12) above.

where n =	1	2	3
λmax values	550	640	760

Bury in (1935)[1] attributed the colour observed to the movement of electrons which give rise to two distinct but identical structures, as shown below in Figure (13)



Doebner Violet

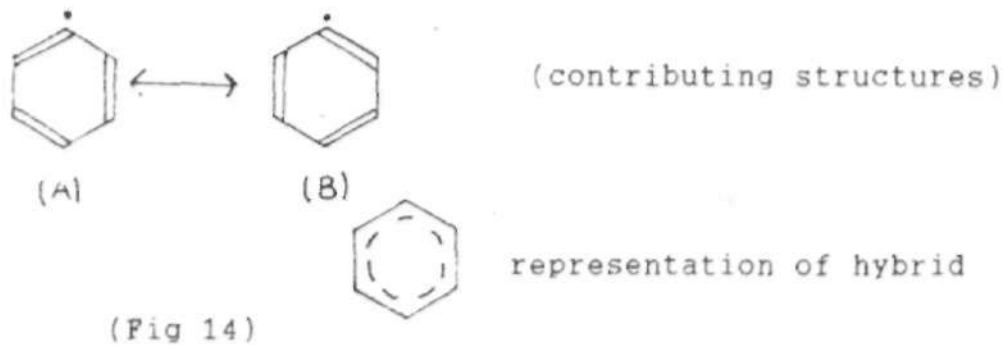
(Fig 13)

(He described dyes as resonance hybrids of classical structures of similar stability but different charge distribution)

With this theory scientists began to consider colour and constitution from the standpoint of the resonance theory.

1.4.1 RESONANCE THEORY[1][2]

Resonance (mesomerism) in resonating organic compounds results in the formation of hybrids from two or more contributing structures. The number of contributing structures depends on the number of possible arrangements of electrons. This can be easily seen with benzene Figure (14) below:



(contributing structures)

representation of hybrid

(Fig 14)

The contributing structures always have the same arrangement

of atomic nuclei but different arrangement of bonding electrons. Each of these structures have different energy levels.

In the ground state, the more stable low energy structures make the highest contribution and on excitation (after absorption of light energy) the less stable high energy structures do most of the contribution to the structure of the excited hybrid molecule. Hence in either state, the molecule is a single species which can be called `a perfect blend' of the contributing structures.

The fundamental structures for many dyes can be represented as

$$A{=}C{-}(C{=}C){-}_{n}B \longleftrightarrow A{-}C({=}C{-}C)_{n}{=}B$$

(a) (b)

(Fig 15)

showing extreme resonance structures. The unsaturated chain can represent Witt's chromophore. While A & B may be either nitrogen or oxygen atoms in that case, they would have to be auxochromes (Auxochromes are electron donors having a lone pair of electrons) e.g Doebner's violet, phenol blue.

If two auxochromes are linked together (as above) it facilitates the transfer of electrons from one end to another along the conducting chain(chromophore).

The greater the number of interactions the smaller the energy differences between the ground and excited state. Also the energy levels of the intermediate structures will be higher compared to the levels of the extreme structures.

Interaction between the contributing structures is progressive

and cumulative going from one extreme classical structure to another . Resonance stabilisation decreases in the same order and the greater the energy difference between resonance structures the less the interaction will be.

After interaction between the energy levels of the two extreme classical structures through the intermediate structures they tend to split into the ground and excited states.

As mentioned earlier, excitation by light photons of the visible region causes excitation of the resonance hybrid to higher energy levels.This is a result of a larger proportion of the contributing structures being able to exist in the less stable high energy state.

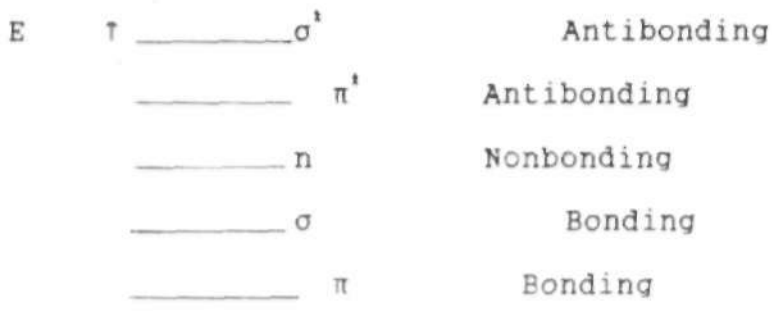
1.4.2 SPECTRAL LINE AND ABSORPTION BAND

Absorption of Radiation as shown by Graebe and Liebermann[22], Witt[21] and Armstrong[22] unsaturation is necessarily present in every dye molecule. The unsaturated chain normally has equal numbers of (alternating) single and double bonds which serve to conduct an electron form one part of the molecule to the other.

On absorption of the visible radiation by the ground state of the resonance hybrid of the dye molecule, the mobile electrons present as the lone pair on the auxochrome group or the π electrons of the double bonds become excited and jump into the contributing structures which have higher energy values[1] and thus give rise to an excited resonance hybrid of the dye molecule. Radiation from the ultraviolet region of the electromagnetic spectrum causes the

excitation of π electrons as well as σ bond electrons i.e. covalent bonds.

DIAGRAM SHOWING THE VARIOUS ENERGY LEVELS IN A DYE MOLECULE[2]



(Fig 16)

In the ground state of energy dye molecules there are three categories of electrons.

(i) covalent (σ) bond electrons

(ii) unsaturated (π) bond electrons

(iii) lone pair of electrons

As shown in the diagram above, categories (i) and (ii) are found in the bonding orbitals.

Covalent bonds are formed by the headlong overlap of valence orbitals of the combining atoms.

Category (iii) is thus termed because the pair of electrons (n) are not involved in the formation of any bonds but are present in the non-valence orbitals of atoms such as oxygen,

nitrogen ,..etc. The electronic energy for excitation of the third category of electrons (n) absorbs the least amount of energy. Absorption due to this transition is seen nearer the longer wavelength end of the visible spectrum (620-750nm). This accounts for the fact that the auxochromes (substituents with oxygen or nitrogen attached directly to the aromatic framework of the molecule) produce a `red shift' in the absorption band which is also referred to as a bathochromic shift[21]. Shift of absorption bands to regions of shorter wavelength is referred to as a blue shift or hypsochromic shift.

1.5.0 CLASSIFICATION OF SYNTHETIC DYES

There are 2 broad classifications of dyes according to

(i) application method

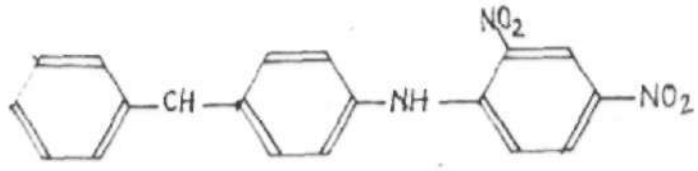
(ii) chemical constitution

However, dyes belonging to one application method group are neither restricted to substrate type or chemical constitution. It is also highly unlikely that dyes of a given chemical constitution class will only dye a specific fibre via a particular application method.

1.5.1 CLASSIFICATION ACCORDING TO CHEMICAL CONSTITUTION[2][4][24]

1. **Nitro Dyes** :- Phenols or amine containing nitro groups in the ortho and para positions.

e.g.

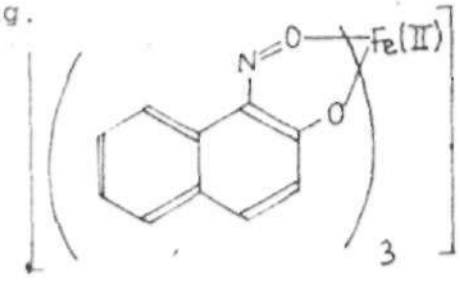


Amido Yellow E

(Fig 17)

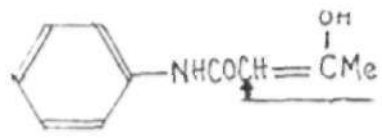
2. **Nitroso Dyes** :- Phenols or naphthols with nitroso group in ortho and or para position used as metal complexes in mordant dyeing.

e.g.



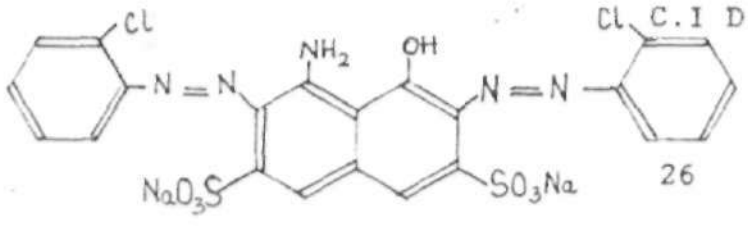
Pigment Green B (Fig 18)

3. **Azo Dyes** :- Characterized by one or more azo (-N=N-) group formed by diazotising aromatic amines and coupling the resulting diazonium salt with either a phenol, naphthol or aromatic amine having a free ortho and or para position or certain other compounds having reactive groups . e.g. acetanilide (see Figure (19) below) or acetaryl amides.



point of attack by diazo component

(Fig 19)

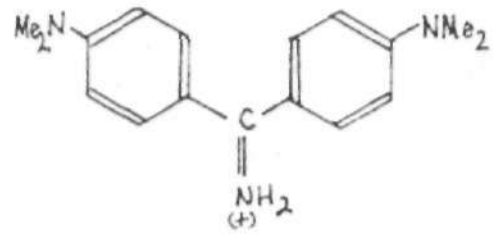


C.I Disperse Acid Blue 87 (Fig 20)

A Disazo dye

Azoic dyes are formed insitu to give insoluble dye molecules.

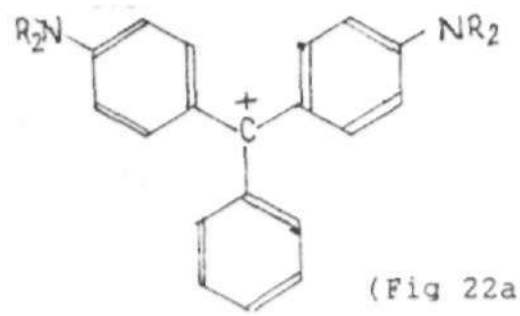
4. **Diphenyl methanes** :- These are dimethyl aminophenyl methane derivatives e.g. Auramine Figure (21)



(Fig 21)

5. **Triphenyl methanes** :- derivatives of triphenyl methane or triphenyl carbinol having one or more primary, secondary or tertiary amino group para to the methane carbon atom.

i. **Malachite Green series**



(Fig 22a)

ii. **Rosaniline series**

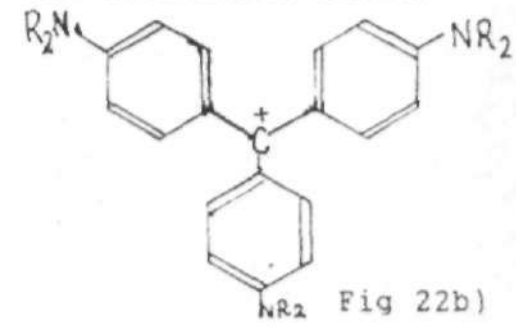
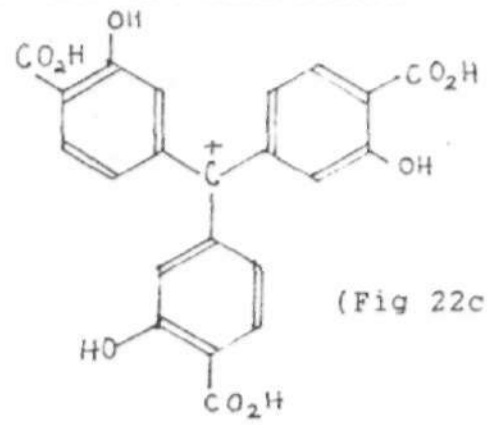


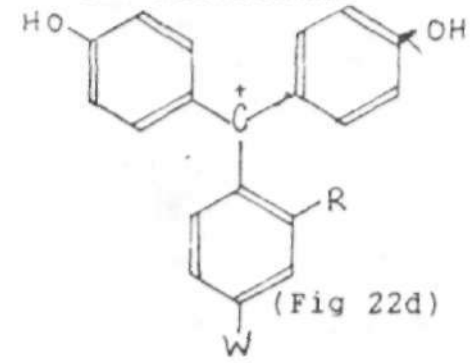
Fig 22b)

iii. **Rosolic acid series**



(Fig 22c)

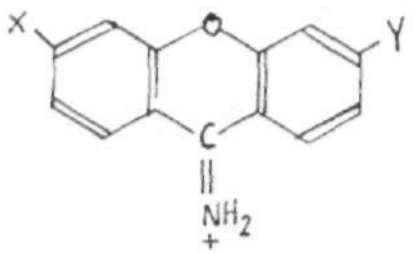
iv. **Phthaleins**



(Fig 22d)

6. **Xanthenes** :- Resemble the di and triarylmethane classes. The only difference being the presence of an oxygen atom linking two of the aromatic rings.

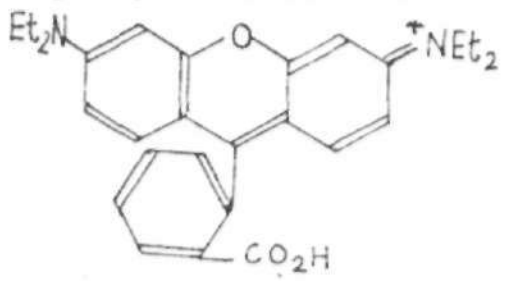
7. **Diphenyl methane derivatives**



e.g. Pyroline G

(Fig 23a)

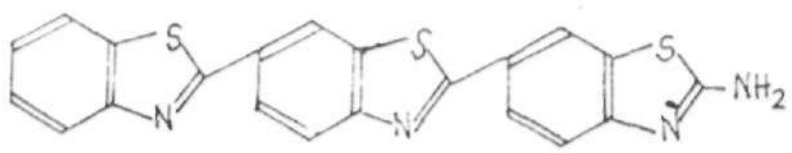
ii. **Triphenyl methane derivatives**



Rhodamine B

(Fig 23b)

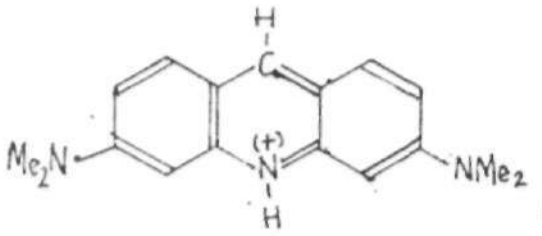
7. **Thiazoles** :- Aminothiazole or azothiazole sulphonic acid, or thiazolinium salt. e.g.



Primuline

(Fig 24)

8. **Acridines** :- salts of 9-hydroxy, 9, 10-dihydroacridine with amino groups in 3, 6 positions

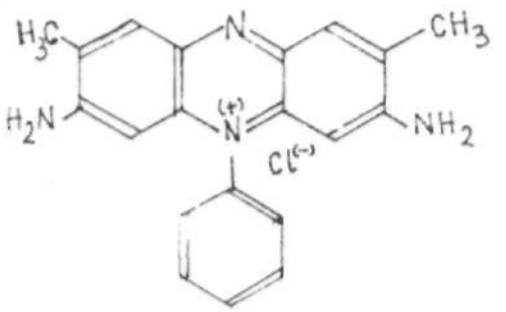


Acridine Orange NO

(Fig 25)

9. **Azines** :- contain dihydrophenazine derivatives.

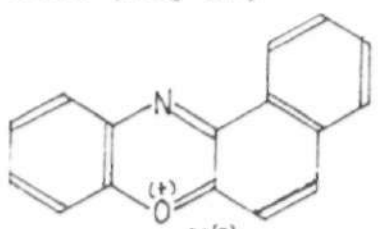
e.g.



Safranine T

(Fig 26)

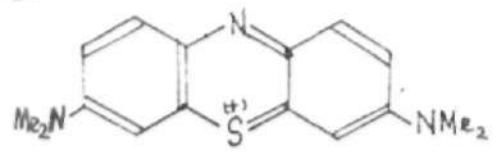
10. Oxazines :- contain phenoxazine derivatives e.g. Meldola's Blue (Fig 27)



(Fig 27)

11. Thiazines :- contain phonoxazine derivatives

e.g.



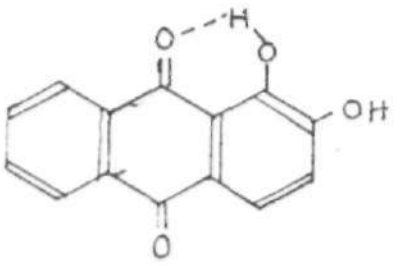
Methylene Blue

(Fig 28)

12. **Sulfur Dyes** :- obtained by heating organic compounds with sulfur or alkali polysulphides. The resultant compounds have high molecular mass but with undefined structure .

e.g. Vidal Black

13. **Anthraquinone Dyes** :- made up of Anthraquinone or Anthrone derivatives e.g.

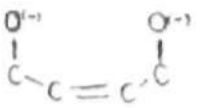


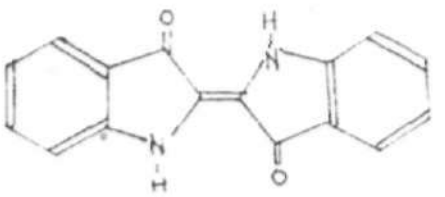
Alizarin

(Fig 29)

Further classified according to application group viz Anthraquinone disperse, mordant, acid and vat dyes.

14. **Indigoid and Thioindigoid Dyes** :- 2 units of indole or Thionaphthene are linked to form a dye molecule. Chromophoric group represented by :-





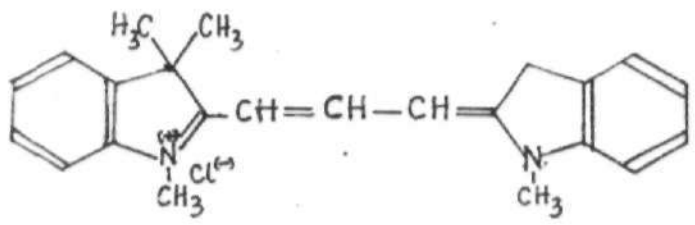
(Fig 30)

15. **Phthalocyanines** :- comprises of ring system of indole units and nitrogen atoms. It combines with various metals to form coloured compounds. Brilliant colours and excellent heat fastness.

16. **Methine, Cyanine, and Polymethine Dyes** :- contain one or

more methine linkage(s) in their chromophoric system.

e.g.



Astraphloxine FF

(C. I. Basic Red 12)[2]

(Fig 31)

They mainly serve as photographic sensitizers in colour photography. Only limited use on textiles. e.g. Bixin serves as food and drug colorant.

1.5.2 CLASSIFICATION OF DYES ACCORDING TO APPLICATION

1.5.2.1 Acid Dyes are water soluble dyes which are applied basically from acid solutions onto fibres possessing basic nitrogen groups e.g. wool, silk and nylon. Water solubility is imparted by the presence of sulphonic groups, or in rare cases carboxylic groups.

Acid dyes are found in nitrophenols, azo compounds, triphenyl methane anthraquinoids or indigoid compounds.[24]

There are 3 categories of acid dyes which is in accordance to their molecular mass and ease of levelling. Those of higher molecular mass which do not level easily (Groups 2 & 3) are known

as acid milling and neutral milling dyes.[25] They are used for dyeing loose wool fibres which undergo milling (felting/fulling) after dyeing. Dyeings in these categories are done from weakly acid to neutral dyebaths. Group 1 dyes level more easily due to their small size and they are known as levelling or equalising acid dyes.

1.5.2.2 **Chrome Dyes** also known as mordant dyes are acid dyes which have been applied in conjunction with metallic mordants. Chrome today is the most popular metallic mordant hence the generalised term `chrome dyes'.

The resultant metal complex dye has a larger molecular size and gives dyeings of higher wash fastness than acid dyes without chrome treatment. On wool, they have improved lightfastness and good fastness to drycleaning.[26]The wool may be treated with the solution of chrome salt before or after dyeing.

1.5.2.3 **Premetallised Dyes** are as the name implies acid dyes which have been complexated before dyeing. They are mainly used on wool.

Acid dyeing premetallised dyes are 1:1 metal azo complexes. Neutral dyeing, premetallised dyes are 1:2 metal azo dye complexes. The metal being either chromium or cobalt.

1.5.2.4 **Basic Dyes** are also referred to as cationic dyes and are salts of organic coloured bases. They are characterized by the presence of a basic ammonium group.[24] It may also be present as

a part of a heterocyclic ring as a tetracovalent atom, hence triphenyl methane dyes, xanathenes, acridenes, oxazines and thiazines are considered or are used as basic dyes.

Basic dyes are used on acrylic fibres producing brilliant shades with good light fastness properties. Previous usage on mordanted cotton gave poor light fastness. They are also used on modified nylon and polyester fabrics. They occasionally serve as topping colours.[27]

They can be applied to a substrate from a neutral or weakly acid dyebath.

1.5.2.5 Direct Dyes also known as `substantive' dyes are commonly used for cotton and other cellulosic fibres. They are applied from an aqueous medium with the aid of an electrolyte to achieve dye fixation.

The main chemical class to which direct dyes belong are the di, tris, tetrakis azo compounds. Other classes are stilbene, copper, phthalocyanine, dioxazine, quinoline or thiazole compounds.[27]

In the process of washing the dye molecules tend to become desorbed easily although generally they have high light fastness values.

Improved wetfastness is obtained by

(i) coupling the dye molecule insitu either with

(a) a diazotised aromatic amine where the dye molecule has free site for coupling ortho or para to a substituent

amino or hydroxy group; or

(b) a naphtholic developer[26] having diazotised the molecule insitu.

(ii) the formation of metal complexes of copper chrome by treating the dyed fabric with solution of their metal salts.

(iii) the formation of cross linkages between the direct dye molecules using formaldehyde.

(iv) the application of resins (used for anticrease finishes) on the fabric thus trapping the dye molecules.

Direct dyes are also used on leather and paper.

1.5.2.6 **Disperse Dyes** were known as cellulose acetate dyes because the disperse dye series was first developed for the fibre. Now their use has been extended to most other synthetic fibres e.g. nylon, polyester, acrylic. Dyeing is by solid solution, wherein the fibre absorbs the dye from an aqueous dispersion of it at high temperatures. Dispersions of the dyes (which are largely insoluble in water) are achieved by using small quantities of wetting agents e.g. naphthalene sulphonic acid formaldehyde condensate.[28] Substituents are present in the dye molecule which help to make the dye molecule readily dispersible in water e.g. -N=N-, -OH-NH2, O-alkyl, -NH alkyl. They form weak hydrogen bonds with water.[28,29] General chemical classification groups to which the dye molecules belong are amino azo and amino anthraquinone derivatives.

For highly crystalline fibres e.g. polyester having low

penetration at the boil, temperatures for dyeing are increased(120 - 130^{0}c) to aid dye molecule penetration.

1.5.2.7 Azoic Dyes are insoluble azo dyes which are prepared insitu (i.e. within the fibre) giving rise to fast prints and dyeings on cotton mainly.

Appropriate components commonly known as Fast salts or Fast bases (diazotised amines salts stabilized and undiazotised amines respectively) are coupled with a naphtholic compound that has been previously padded or printed into the fabric from an alkaline solution. The diazo component is applied by the same padding or printing method used for the naphthol.

The early coupling components were B - naphthol and their derivatives[27] but after the year 1912 a range of Naphthols were produced which had a higher affinity for cotton and produced shades of wider variety and improved light, washing and rubbing fastness, viz the Naphthol AS series which are derivatives of the anilide of 2-hydroxy, 3-naphthoic acid [Greisheim Elektron firm][28]

Soaping of the final dyed material is usually required to remove surface absorbed dyes.

1.5.2.8 Vat Dyes are so called because the early dyeing processes for the application group involved reducing the soluble parent dye in large `vats' to form the soluble leuco form. The fibres or fabrics to be dyed, having been saturated with the alkaline leuco solution, were exposed to air for the subsequent

oxidation and reformation of the insoluble parent dye within the fibre. These vats have however, in modern industries been replaced by the continuous feed methods where the fabric having passed through the alkaline leuco bath for a while is then passed on to an oxidation bath while more of the fabric is fed into the leuco dye bath. Sodium hydrosulphite (hydros)is the chemical used to effect the reduction.

Other types were developed for viscose, nylon, wool, silk and acrylics.

Their small size makes them give bright colours and are also easy to apply with the high levelling power on all fibres.

1.5.2.9 **Reactive Dyes** are characterised by the presence of a reactive group that combines chemically with a suitable group in the fibre e.g hydroxyl in cotton, amine in protein and polyamide. Examples of such are the mono and dichloroazinyl group.

There are 3 chemical classes of reactive dyes viz: azo, anthraquinoid and phthalocyanine. The cost of reactive dyes are decreasing gradually as they are being developed rapidly with research. They have extremely good wash fastness but are susceptible to chlorine.

1.5.2.10 **Solvent Dyes** are insoluble in water but soluble in a range of organic solvents such as alcohols, esters, ethers, aliphatic and aromatic hydrocarbons. The choice of solvent depends on the type of application involved. Applications

include for varnishes, printing inks, colouring candles, soaps, petrol and dope dyeing of synthetic polymers.

1.6.0 Fibre structure in relation to dyeing Present day textile fibres can be classified broadly into the following categories:

(i) natural vegetable

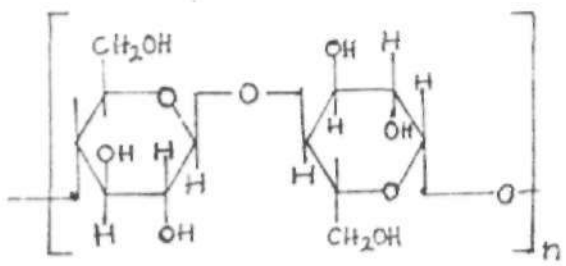
(ii) animal hair

(iii) mineral matter

(iv) regenerated chemically from natural animal and vegetable fibres.

(v) synthesized wholly from chemicals.[26]

However, they all have polymers as their fundamental units. Polymers are large sized molecules (macromolecules) which are made up of repeating units of a particular monomer joined together by characteristic linkages e.g for cellulose having B glucoside linkages as shown in cellulose Figure (32) below [30,31]



Cellobiose

(Fig 32)

Functional groups within the polymers retain their chemical properties and determine the type of dyestuff for which the fibre would have an afffinity for. Generally fibres having many polar

functional groups will have a greater affinity for the ionic dyestuff while these having very few polar groups or none at all will have greater affinity for non-ionic dyestuff.

The absorption and penetration of water between the polymer molecules is necessary for the creation of voids for the dye molecules to diffuse into from an aqueos dyebath



(Fig 33)

swelling of fibres on wetting due to lateral seperation of chains by infiltration of water molecules[18]

Fibres with many polar functional groups are hydrophillic in nature. This is because water is also a polar compound. Those fibre having little or no polar functional groups are described as being hydrophobic i.e water repelling since it would have a low affinity for polar water molecules. This means that hardly any voids would be created for the easy diffusion of dye molecules into the fibre. As a result dyeing of these fibres with disperse dyes is called solid solution.

The chemical structure of the polymer chains also determines what chemical assistants may be added to the dyebath from which it is being dyed e.g wool and silk have low resistance to alkali[27] and therefore can not be dyed with alkali. Reactive dyes as such would lead to hydrolysis of its peptide linkage . See Figure (34) below.



(Fig 34)

The micromolecular structure which has to do with the arrangement of the polymeric molecules within the fibres also has a great role to play in the dyeing properties of any given fibre type. As shown in the cross section of a typical fibre Figure [35], a fibre possesses regions with different degrees of order and disorder in arrangment of the polymer molecules.

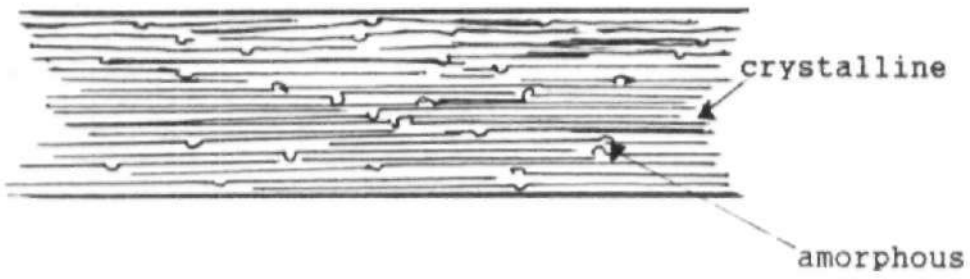
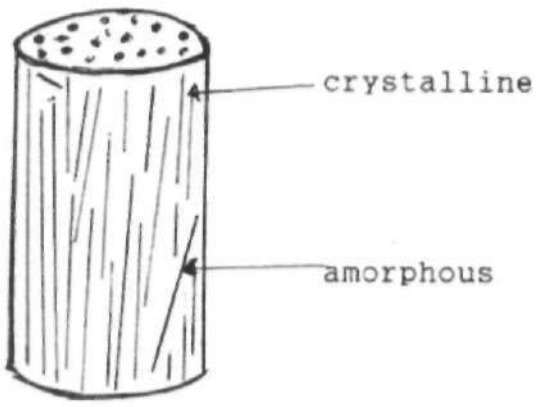


Fig 35)a - a typical fibre showing crystalline (ordered) and amorphous (disordered) regions of the fibre.



(Fig 35)b - a cross section of cotton fibre

When synthetic fibres are freshly spun the molecules within the fibre are in a highly disordered state and the fibres

themselves are of low tenacity. Their quality in terms of tenacity is therefore improved by drawing the fibre. This drawing causes the molecules to slip and slide over one another and become oriented (aligned to the fibre axis). Increased crystallinity is therefore attained. This can be compared to the spinning of cotton yarns from cotton slivers (slivers are weak rope like arrangements of combed out short fibres) and the stretching out of the sliver with a twist to hold in the fibres form a much stronger 'yarn'.

A skin effect is however observed with man made fibres which is due to the resistance which the outer flow of molecules encounters with the walls of the orifice of the spinnerets. This results in a much higher degree of orientation on the outside of the yarn than those within. During dyeing at the early stage, wetting of the fibre and penetration of the dyestuff is made difficult. This results in a ring effect during dyeing that is best observed through the cross section of the fibre. Subsequent levelling is achieved by internal migration of the dye molecules.

Cystallinity tends to impart hydrophobicity to fibres even having polar functional groups. This is due to the screening off of polar functional groups with possible intermolecular hydrogen bonds. Also, the close arrangement of polymer molecules leaves little or no space for dye molecules to penetrate into it from the dyebath.

Effective exhaustion of a dyebath by crystalline man made fibres is made possible by having a knowledge of their Glass Transition Temperatures (Tg). This temperature of dyeing marks the onset of dyeing for the fibre being dyed because at temperatures below the Tg value, the polymeric molecules are frozen into their closed arrangement relative to each other. As the dyeing temperature approaches and exceeds Tg for the fibre, the polymer molecules rotate about their bonds till free volumes (voids) are created for the dye molecules to diffuse into.

The mechanical properties of the fibres play an important role in determining the type of dyeing machine to be used e.g loose wool can not be dyed on a jig machine wherein dyeing is done under high tension as this can disintegrate the tow.

1.6.1 Physical and Chemical Properties of Nylon in relation to Dyeing

Nylon is the generic name for a group of polyamide fibres whose long polymer chains have the recurring amide [CONH] linkage predominant in the molecule.

The most common species of Nylon are Nylon 6.6 [discovered by Wallace Carothers of E.I. Du Pont de Nemours and co in 1920 [18] and Nylon 6. [formed by I.G. Faberin Industries in 1937 [18]. Nylon 66 is synthesized from hexamethylene diamine and adipic acid to give hexamethylene adipamide.

$$H[NH(CH_2)_6NHCO\ (CH_2)_4CO]_nOH$$

$n = 67-80$

Nylon 6 is synthesised from E-caprolactam to give polycaprolactam.

$$H\text{-}[NH(CH_2)_5CO]_{n130\text{-}160}OH$$

Acid dye fixation is possible on nylon due to the presence of amino end groups. Depending on the proportion of amino end groups (AEG) per kilogramme or polymer chain, a variety of Nylon types are available viz: light dyeing nylon - where some of the amino end groups have been converted to imines to reduce acid dye absorption; deep and ultra deep dyeing nylon - where carboxylic acid end groups have been converted to amino end groups by the means of diamines to increase acid dye absorption. Basic dyable Nylon prepared by converting amino end groups to acidic groups e.g. sulphonic acid thus increasing its affinity for cationic dyestuffs[51].

Disperse dyes are insensitive to the polarity of the Nylon and are taken up by solid solution into the fibre.

Nylon has a high resistance to alkali even at high temperatures. Dilute acids have no significant effect on it but it is hydrolysed by concentrated hydrochloric acid at the boil[12].

Nylon is a semicrystyalline fibre with amorphous region for the dye molecules to migrate into. However effective sites of dye attachment are screened off from the dye molecules in crystalline regions[51]. Drawing, for improved tenacity and flexibility tends to increase the crystallinity of the nylon

fibres[53]. The minimal swelling of the fibres in water (2%)[54] and its smooth circular surface which causes water to slide off the fibre surface further compounds the dyeing of nylon with water soluble dyes e.g. acid dyes. Therefore total and continuous immersion is necessary for dyeing and this is done at temperatures above its glass transition temperature. (Tg), solvents (which possibly lower the Tg) are sometimes used to enable the polymer chains rotate and create voids for dye uptake at lower temperatures i.e. by plasticization[55]. Due to its thermoplastic properties Nylon dyeing is done on a jig where it can be held out smooth or having been preset by steaming in a roll, in a rope form on the winch[18].

Depending on the ease of penetration and levelling of the chosen dye in the nylon fibre substrate, the nylon fabric may be heat set to obtain permanent pleats before or after dyeing.

Effective control of polymerisation, extrusion and processing of the Nylon fibres is necessary to avoid barriness due to irregular distribution of amino end groups. Likewise the drawing, heat setting and texturising processes need to be controlled to prevent barriness due to the screening off of amino end groups by irregular portions of crystalline and amorphous regions.

Barriness is a major problem with acid dyes.

Barriness [18,28] can be overcome by the use of disperse dyes in dyeing Nylon fibres especially since its mode of attachment to the fibre is not site specific. A specilized range of acid dyes (Nylomnine A dyes-ICI) have been developed to improve

coverage of barry Nylon.

Level dyeings are enhanced by pH and temperature control in conjunction with dyebath additives; solvents, e.g benzyl alcohol, anionic and cationic retardants which help to lower the strike (rate of dye uptake by the fibre) e.g Matexil LA - NS & LC - CWL, and assistants to promote dye fixation when padding of the dye onto the fabric e.g Levagal KST. Enclosed jiggers and pressuresed beam dyeing allow for uniformity in exposure of the fabric to heat during "high temperature" dyeings.

1.7.0 Factors Affecting Fastness Properties of Dyed Samples

The colour fastness of dyed or printed textiles is the measure of change in the depth of colour, hue, and brightness observed when it undergoes exposure to agencies such as are encountered during further processing of the dyed sample as well as in use.

Such changes in depth of colour, hue or brightness may be as a result of one or more of the following reasons:

(i) The Chemical breakdown of the colorant while still held within the fibre to give uncoloured or differently coloured compounds.

(ii) Detachment of the colorant molecules from within the fibre i.e without any chemical degradation of the colorant.

(iii) Changes in the physical and chemical structure of the

fibre during processing or in use which in turn may affect (i) & (ii).

(iv) Staining of undyed areas of the sample or adjacent materials occurs under conditions similar to those that facilitate dyeing e.g temperature, PH, and substantivity of the dye for the fibre is an obvious facture.

A generalised consideration of the factors that affect or bring about the conditions (i - iv) leading to changes in depth of colour, hue, and brightness is made below.

1.7.1 Structure of the Colorant

Decomposition and loss or change in colour of the dye molecules may occur as a result of interaction of the dye molecules with

(1) Chemical substances within the dye-fibre system, in the immediate surrounding; or

(2) Photochemically activated species also within the dye fibre system or in the immediate surrounding.

The inherent stability of the dye molecule on a given substrate to the various types of chemical interactions possible is what determines the degree and type of colour change that it undergoes. This is in turn directly related to the chemical structure of the dye.

An example is the higher light fastness of anthraquinoid

An example is the higher light fastness of anthraquinoid acid dyes on wool compared to triaryl methane acid. dyes on the same substrate. This implies that the anthraquinoid acid dyes are more stable to photochemical interaction and are thus decomposed at a lower rate than triaryl methane acid dyes[32].

Dye oxidation by oxidising bleaching agents is less obvious with anthraquinoid vat dyes on cellulose compared to most other dye types. Chemical composition of the chromphores undergo changes which result in the final colour observed.

A colorant may act as a catalyst to others present within the same fibre system, whereas the dyes which are so catalysed in their decomposition would remain stable if present alone. This is a common occurence with some mixtures of vat dyes resulting in the later prominence of one colour over the other e.g. greens fading to give yellowish tinges. The decomposition of the blue dye made the yellow dye to gain prominence.

1.7.2 The State of the Colorant in the Fibre

This mainly has to do with the strength of dye-fibre / dye-resin and dye-dye molecule bonds formed within the fabric. These bond strengths are important in that they determine the ease of desorption of the dye molecules from within. The dye-fibre system when exposed to wet agencies may release the dye molecule to go into the liquid media likewise rubbing which makes use of the mechanical means of desorption.

Covalent bonds formed between reactive dyes and their

Covalent bonds formed between reactive dyes and their substrate fibres have the strongest dye fibre strength and unless under severe conditions or in the presence of water containing chlorine, these bonds are not easily broken. This results in the high wet fastness and wash fastness of most reactive dyeings. Here the dye and the fibre are said to have become one entity.

Direct dyes employ hydrogen bonds (and Van Der Waals bonds where the molecule is planar) to hold these molecules onto the fibre substrate. These dye-fibre bonds are more easily broken as there is competition between the fibrous substrate and the liquid medium for the formation of hydrogen bonds with the dye molecules. Also in the case of cellulose where the cellulose material acquires a negative charge in water, which further enhances the repulsion of the direct dyestuff molecules are fully or partially detached. As such salt is recommended for use when washing the dyed fabric (i.e preferably plain material) to neutralise the repulsing or negative charge and allow for weak readsorption of the direct dyes.

Dye-dye molecule bonds e.g intra-molecular hydrogen bonds are induced/formed under certain conditions so that effectively larger dye molecules are formed which are desorbed much less easily, moreso when they are insoluble in water. Large aggregates of virtually insoluble dye molecules are formed insitu in vat and azoic dyeings as on cellulose.

Ingrain dyes e.g Phthalogen based dyes are typically large molecules which are insoluble.

The dye molecule aggregates tend to serve as molecular screens from chemical attack thus providing improved chemical stability of the dye while in the material. Also where the dye molecules are insoluble, water carrying corrosive or decomposing chemicals are not easily taken up by the dye molecules from the liquid medium.

1.7.3 The Amount of Colorant in the Fibre

The presence of dye molecules of a given type in large quantities within a fibrous substrate makes for the observation of apparently high fastness values compared to pale shades of the same dye molecule that is where the concentration of the dye molecules is low. This is the case with all agents of colour fading e.g a deeply dyed material using a given dye would require much more exposure to light to achieve a significant change in the shade depth than a pale shade of the same dye where the dye is easily prone to photochemical degradation.

Exceptions arise where the dye molecule is present in the fibre in large insoluble particles even in pale shades as with pale dyeings and prints of pigments resin bonded to the fibre.

Where the fastness of a given dye on substrate is determined by the rate of desoprtion of dye molecules e.g in wash fastness, rubbing fastness, dry heat fastness (i.e the

dye sublimes at high temperatures) the higher the concentration of the dyestuff the lower the fastness ratings observed particularly with respect to staining.

1.7.4 The Nature of the Fibre

The nature of the fibre on which the dye is present contributes a great deal towards the colourfastness of the dyed fibres. This is due to the chemical and physical interaction between the dye molecule and fibre.

Chemically certain functional groups within the fibre could in the presence of agencies such as light, react with the dye molecule in its excited state. Thus as the dye fades, the fibre also loses some of its features e.g the phototendering of cotton by some vat dyes[33].

Increased light fastness is observed[34] when acid dyes are used in the colouring of anodized aluminium This was supposedly due to the trapping of excitons formed by the polar substrate which would result in the stabilization of the dye[25]

Similarly a non polar substrate which would prevent the transfer of secondary charge carriers from dye molecule to dye molecule and reduce the possibilities of the fading mechanism operating.

The physical properties of the fibre substrate are important in that they determine:

(1) The ease of desorption of the dye molecules and

(2) The rate of diffusion during dyeing.

These are directly related to the density of the fibre and therefore compactness of the polymer molecules within the fibre. With increase in fibre density and or/size of the dye molecule, the washing, rubbing, dry heat fastness increases e.g the wash fastness of disperse dyes on polyster fibres are much higher than on secondary cellulose acetate.

The compactness of the fibre determines its permeability to various components of the environment that can have a detrimental effect on the colorant[33] e.g alkali and acid in wash baths etc.

The moisture regain of the fibre along with the relative humidity and the temperature of the environment determine the value of the "effective humidity" at the fibre surface. The effecitve humidity affects the rate of fading of a coloured textile on exposure to light.

1.7.5 Presence of Foreign Substances

These may be obtained as

(i) residues during processing e.g dyeing assistants such as carriers, after treatment agents or

(ii) chemicals used in the application of various type finishes e.g delustering (T_iO_2) anticrease finish, water proof finish, etc.

Titanium dioxide is particularly well known for photochemical catalysis of dyes in fibres treated with them.

Traces of certain carriers on dyed and printed polyester

materials can reduce the light fastness values significantly.

The decomposition of fluorescent brighteners within the fibre could impart a yellowish coloration to it. This would mask or alter any initial coloration present within the fibre substrate[25]

1.8 Aim of this Study

The aim of this present study is to synthesize new azo dyes based on H-acid by varying substituents on the coupling components and on the diazo component of the parent dyes.

Infra-red spectra of dyes shall be analysed to ascertain the chemical constitution of the dyes synthesized.

Spectroscopic investigations shall be carried out in the uv-visible region of the electromagnetic spectrum to see the effect of change in chemical constitution on colour seen or emitted. Measurements were done in both distilled water and dimethyl formamide.

The effect of changes made in chemical constitution of the dyes on their fastness properties will also be studied.

CHAPTER TWO

2.0 E X P E R I M E N T A L

2.1.0 General Information

2.1.1 Chemicals:

The reagents used for the purpose of the experiments carried out include;1-amino - 8-hydroxy - 3,6-disulphonic acid (H-acid), Benzoyl Chloride, Acetic anhydride, Acetic acid, Para Toluene sulphonyl chloride, Sodium Nitrite, Sodium carbonate anhydrous, Hydrochloric acid, Sulphuric acid, Aniline, p-nitroaniline, 2,4-dinitroaniline, 2,4-dinitro- 5-chloroaniline, 2-Cyano-4-nitroaniline, 2-cyano - 4-chloroaniline . ., Sulphanilic acid, Aminobenzoic acid, Sodium Chloride, Disodium hydrogen orthophosphate, Histidine monohydrhochloride monohydrate, Sodium dihydrogen orthophosphate, Sodium hydroxide, Acetone, Liquid paraffin, Dimethyl formamide, Urea Petroleum ether bp 40-60^{0}C

2.1.2. Instruments

Apparatus used in during the experiement include an AATCO persprometer, a Dye Master, and Atlas Laundrometer, a Bausch and Lomb Spectronic 20 (spectrophotomela), an IR Machine (Perkin-Elmer), a Xenon Arc Lightfastness Measuring Instrument.

2.1.3 Materials

The materials used in assessing the colour properties of the dyes syntheisised were cotton (woven) fabric and Nylon 6.6 (woven) fabric.

2.2.0 SYNTHESIS OF DYES AND INTERMEDIATES

2.2.1 General Method of Acetylation of H-acid

1g (0.0033 Moles) of H-acid was dissolved at 50^0C in $7.0cm^3$ of water containing (0.0019 moles) 0.1992g Soda Ash in a three necked round bottom flask fitted with a mechanical stirrer and reflux condenser.

The stirrer was started and 0.5840g (0.0057 moles) acetic anhydride added into the flask over a period of 8 minutes. Stirring was continued for at least one hour to ensure complete acetylation of the H-acid.

1.6589 (o.0165 moles) Soda Ash was then added to the reaction mixture to hydrolyse off any acetyl group that may have substituted the hydrogen atom in the hydroxyl group of the H-acid.

The treatment was necessary to prevent loss of starting material and contamination of the final dye by decomposition products of the diazocompounds.

The alkaline solution obtained at the end was what was used for the coupling with the different diazocompounds.

2.2.2 Benzoylation of H-acid[36]

1.0g (0.0033 moles) of H-acid was measured into a strong boiling tube and 20 ml of 10% NaOH solution (0.05 moles) used to dissolve it. 2 ml of benzoyl chloride (0.0148 moles) was added dropwise while shaking vigorously in the securely corked boiling tube till the mixture was used directly for coupling.

2.2.3 Tosylation of H-acid[36]

1.0g (0.0033 moles) of H-acid was treated with 20 mls of 10% NaOH (0.05 moles) and 1.5 ml (3g, 0.0065 moles) of toluene-p-sulphonyl chloride was added in small portions in a boiling tube, securely covered with constant shaking.

To remove excess acid chloride the mixture was warmed slightly till its characteristic odour was gone. The alkaline solution was used directly for coupling with diazonium ions.

2.3.0 Diazotisation of the Amines:

2.3.1 Diazotisation of aniline, p-nitroaniline (substituents a and b)

0.054 moles of aniline was dissolved in 1.5 cm^3 concentrated hydrochloric acid. This was diluted with about 2.5 cm^3 of water and cooled to temperatures between $(0-5)^2C$ in ice. A cold solution of 0.5g (0.007 moles) sodium nitrite in 5 cm^3 of water was added drop wise and stirring continued for 4 minutes. The solution of diazoaniline was used directly for coupling. The entire procedure was repeated for the same amount of p-nitroaniline.

2.3.2 *Diazotisation of Sulphanilic acid and Aminobenzoic acid* (substituents c and d)

These amines are not soluble in acid but readily soluble in alkali hence the inverse or indirect method of diazotisation was used.

0.054 moles of sulphanilic acid was dissolved in 13 ml of water containing 0.3614g of sodium carbonate (0.0034 moles) to dissolve the amine.

2.89 ml of concentrated hydrochloric acid was added to the solution, then ice to lower the temperature to 8 - 10^0C with continuous stirring.

A solution of 0.4096g (0.0059 moles) sodium nitrite in 2.40 ml of water was added over a period of 8 minutes.

Stirring was continued after a further 10 minutes to give a suspension of diazosulphanilic acid.

The above procedure was repeated for aminobenzoic acid.

2.3.3 Diazotisation of 2 - chloro- 4- nitro and 4- chloro- 2- nitro aniline (substituents e and f)

0.054 moles of each was dissolved in 1.5 ml of hot concentrated sulphuric acid. This was cooled directly with ice to temperatures between 0 - 5^0C. A cold solution of 0.5g (0.007 moles) sodium nitrite in 5 cm^3 of water was added drop wise with continuous stirring for 4 minutes. The solution was used directly for coupling.

This method of diazotisation is known as the suspension method because the amine, on cooling in the sulphruic acid

solution, forms a fine suspension in the acid.

2.3.4 *Diazotisation of 2- cyano- 4- nitro aniline, 2- cyano- 4- chloro aniline, 2,4- dinitro aniline and 2,4- dinitro- 5- chloro aniline (substituents g, i h, and j)*

Nitrosyl sulphuric acid ($NO^+ H SO_4^-$) was used in place of the aqueos solution of sodium nitrite where nitrous acid ($NO^+ OH^-$) is formed. The method of preparation is as follows:

Powdered sodium nitrite (0.02 moles) 1.38g was added portion wise to concentrated sulphuric acid (20 ml) with good stirring at 0^0C so that no fumes were given off. The mixture was stirred for 10 minutes and then put on a water bath and heated gradually until the temperature reached 65^0C. Stirring was continued until all the nitrite had dissolved. The solution was kept at 0^0C in a freezer until ready for use.

The nitrosyl sulphuric acid solution was used in 5 cm^3 portions with 0.054 moles of each of the substituents g, h, i and j while in solutions made with hot concentrated sulphuric acid. Addition of the cold nitrosyl sulphuric acid was done drop wise to the cooled suspensions of the amines in the acid, at temperatures between 0 - 5^0C with continuous stirring over 5 - 10 minutes.

The solutions of diazoamines in sulphuric acid were used directly for coupling.

2.3.5 General method of coupling H- acid and it's derivatives with the various amines.

Cold alkaline solutions of the coupling components

containing 0.0029 moles of the various couplers (H- acid and derivatives) were coupled directly with the cold diazoamines earlier produced (0.054 moles) in sections 2.10.1 - 4.

The reaction was carried out within a temperature range of (0 - 5)^{0}C. both the diazo and coupling components were maintained within the temperature range by placing them in an ice bath.

The diazonium ion solutions were added drop wise to each of the alkaline solutions of the coupling components to avoid the generation of nitrogen fumes from decomposing nitrous acid or nitrosyl sulphuric acid. The addition was done with continuous stirring over a period of about 8 minutes. Stirring was continued for another 30 minutes in order to facilitate the coupling reaction.

In the case of any foaming, urea solution was used to destroy the excess nitrous acid or nitrosyl sulphuric acid.

The dyes formed were salted out and filtered. then dried in an oven at temperatures not exceeding 60^{0}C.

2.3.6 General Method of Dyes Purification.

The dried dyes in their salted form were dissolved in Dimethyl formamide (D.M.F.) and the D.M.F. was evapourated on a water bath to bring the dye solution to it's maximum possible concentration such that the dyestuff could be readily precipitated by the addition of another solvent to it's solution in D.M.F viz acetone.

On precipitation, the dyestuff was refiltered using the sintered glass crucible (pore size 3) and rinsed with

petroleum ether (bp 40 - 60^{0}C). The precipitate was then dried in an electric oven at 60^{0}C.

2.4 Infrared Spectral Measurement

A small amount of each dye sample was worked into a paste using liquid paraffin. This in turn was rubbed on one side of a sodium chloride disc. The disc was placed in the pathway of an artificial light source of a Perkin elmer infra-red spectro photometer. An electric recording device plotted the absorption values for each dye sample over the entire infra-red spectral region/band. Most of the tests were carried out in the Chemistry Department, Bayero University, Kano while some were carried out in the Chemistry Department, Abubakar Tafawa Balewa University, Bauchi at a later date.

2.5 Visible Absorption Spectroscopic Measurement

A Bausch and Lomb Spectromic 20 was used to determine the maximum wavelength value for each dye. Readings were taken over 5 nm intervals.

Solutions of each sample were made using distilled water and Dimethyl formamide and the maximum wavelength values measured in each case. Values obtained are recorded in Tables 3.5 - 3.8.

2.6 Determination of Molar Extinction Coefficients

Molar extinction coefficients for all the dyes were calculated using distilled water as the solvent.

The Absorbance (A) (Optical Density O.D) values at the maximum wavelength earlier determined were recorded for dye solutions of known concentrations (c).

Where the thickness of the cell in which the dye solution is placed is given as (l) and the concentration (c) of the solution measured in moles, the molar extinction coefficient (ϵ) was calculated using

The Beer-Lambert Law viz:

$$A\ (O.D) = \epsilon .\ c .\ l.$$

$$\therefore\ \epsilon = \frac{A\ (O.D)}{c.l}$$

2.7 Dyeing of Nylon

All dyeing were done using Nylon 6.6 woven fabric, commercial grade, by the exhaustion method.

The fabric was cut into several pieces measuring 5 cm by 4 cm and the average weight noted (0.5g).

Each of the dyes was made into a 0.1% stock solution by dissolving 10 mg of every dye in 10 ml of distilled water.

Dyeings were done in the Dyeing master (Waterman dyeing machine) consisting of several tubes for simultaneous dyeings of many samples at once.

Where a liquor ratio of 50.1 was to be maintained and a 1% shade obtained, the following measurements were made to

complete each dyebath.

(i) Amount of dye stock solution required:

Using the equation

$$\frac{WP}{c}$$

where W, weight of the fabric is 0.5g

P, Percent shade required is 1%

c, concentration of stock solution is 0.1%

$$\therefore \quad \frac{0.5\% \times 1\%}{0.1\%} = 5 \text{ ml}$$

(ii) Amount of 1% Acetic acid solution required:

Using the equation

$$\frac{W \times P}{c}$$

where W, weight of the fabric is 0.5g

P, percent shade required is 1%

c, concentration of stock solution is 1%

$$\therefore \quad \frac{0.5 \times 1\ \%}{1\%} = 0.5\text{ml}$$

For the liquor ratio of 50:1 i.e Volume of a dyebath to weight of fabric. the total amount of liquor required would be 25 cm^3 of liquor to 0.5g of Nylon 6.6. Therefore {25 - (0.5

+ 5.0)}cm^3 of water is required to top the dyebath viz: 19.5cm^3.

For every dyebath, a sample piece of Nylon 6.6 was wetted thoroughly in water and squeezed out before fixing them onto four pronged hooks. These hooks were then fixed onto hangers in the machine which oscillate vertically when it is switched on.

With the machine on and oscillation in progress, the temperature of the water bath in which all the tubes are immersed was raised to 100^{0}C, from a starting temperature of 60^0, over a period of 15 minutes.

Dyeing was continued at the boil for 45 minutes. The dyed samples were then unhooked, rinsed and dried at 60^0 in an electric oven. This process was repeated until all the dyeings were done.

2.8 Wash Fastness Testing

The stability of the Dye-Fibre bonds to Alkaline washing was investigated for each dyed sample by passing them through ISO 3 Wash Fastness Test, a standard procedure documented by the International Organisation for Standardization (I.S.O)[7].

Composites of the dyed samples were made with nylon and cotton fabrics of the same size sandwiching the dyed samples.

Soap solution was prepared using 5g/l of soap and Soda Ash (Na_2CO_3) added at a concentration of 2g/l.

The composite samples were immersed in soap solution, using a liquor ration of 1:5, in the wash cannisters of an 'Atlas Laundrometer AATC Standard Instrument'. The cannisters were sealed and fixed into a rotary frame within the laundrometer.

The laundrometer was filled to the designated water level and heated to 60^{0}C. After washing the composites were dried and dismantled for evaluation using the Grey scales.

Evaluation was done in three respects:

(i) change in colour of the dyed sample

(ii) staining on Nylon 6.6

(iii) staining on cotton

Results obtained are summarised in Tables 3.9 - 3.12.

2.9 Acid and Alkali Perspiration Fastness Testing[85]

Composite specimens of the dyed samples were prepared as for the wash fastness testing. These were then treated in freshly prepared alkaline and acid `perspiration testing' solutions.

These were prepared as follows:

(a) Alkaline Perspiration Solution

5g sodium chloride

0.5g Histidine monohydrochloride monohydrate

2.2g sodium dihydrogen orthophosphate

The solution was brought to PH 8.0 with 0.1N solution of sodium hydroxide.

(b) Acid perspiration solution

5g sodium chloride

2.2g disodium hydrogen orthophosphate

0.5g histidine monohydrochloride monohydrate

The solution was brought to PH 5.5 with 0.1N sodium hydroxide.

Both solutions were made up to one litre.

For each test a composite was immersed in the two perspiration solutions separately with liquor ratio being 20:1.

Having removed the composites from the perpiration solutions, they were arranged separately in between glass plates one on top of another and a weight of 4.5 kg placed on top. The entire assembly was then placed in an oven at 37 ± 2°C for 4 hours.

At the end of the 4 hours, the assembly was removed from the oven, the composites dismantled and air dried at temperatures not exceeding 60°C.

The change in colour of the specimens and staining of the undyed nylon and cotton samples were assessed using Grey scales.

Values obtained were recorded in Tables 3.13 - 3.16.

2.10 Light Fastness Testing

An artificial light source (Xenon Arc) was used to

determine the light fastness values of each dye on the dyed Nylon 6.6 samples.

Strips of the dyed samples were arranged on a card alongside strips of Blue Wool Standards for light fastness testing numbered 1 - 8. Three cards were thus made for the forty dyed samples. Each card was placed within a glass frame after having screwed them into a rigid steel frame. One side of the samples was covered with an opaque cardboard to shield it from exposure to the source of light. Each glass casing had a small water reservoir screwed 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 samples to the light source was continued until on each card the most resistant sample faded to an extent equal to the contrast rating of 4 on the Grey scale.

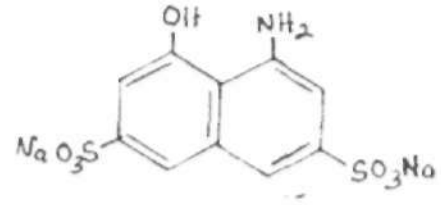
Light fastness values for each sample were obtained by comparing the degree of fading of each sample with that observed with the Blue Wool Standard. Ratings are given according to the wool standard with which the dyed sample's fading is comparable. The light fastness values obtained are shown in Tables 3.17 - 3.20 of Chapter 3.

CHAPTER THREE

3.0 R E S U L T S A N D D I S C U S S I O N S

3.1 Synthesis of Intermediates and Dyes

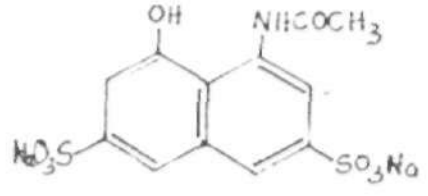
The main intermediate used was 1- amino, 8- naphthol, 3,6-disulphonic acid (I)(H- acid)



(I)

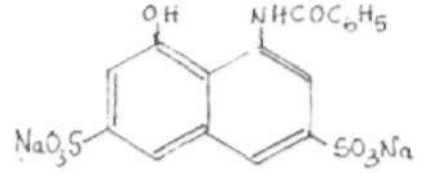
H- acid.

and three derivatives (II, III, IV) below were made from it wherein substituents were introduced onto it's primary amine group.



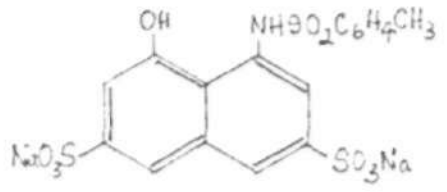
(II)

N- acetylated H- acid.



(III)

N- Benzoylated H- acid.



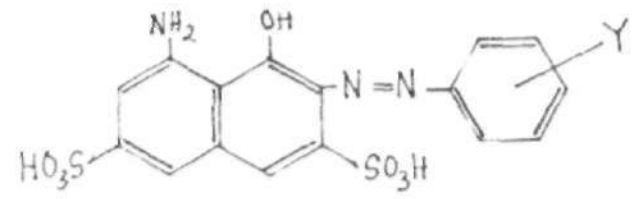
(IV)

N- paratoluene sulphonyl H- acid.

The dyes formed by coupling the various amines to the couplers I-IV belonged to the series 1(a-j), 2(a-j), 3(a-j) and 4(a-j) as

described in Tables 3.1 - 3.4. The tables also show the dye structures and characteristion data.

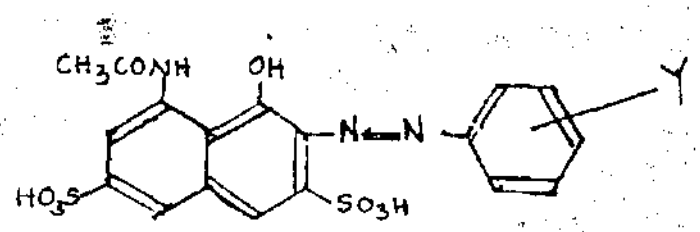
Table 3 1: Dyes Derived from 1- amino- 8- naphthol- 3,6 disulphonic acid (I)



(I)

Dye No.	Y Substituents	Mol. Wt.	Colour of crystals
1a	H	423.0	Dark crystals
1b	4- NO_2	468.0	Dark crystals.
1c	4- SO_3H	503.0	Dark crystals
1d	4-COOH	467.0	Dark, with yellow tinged crystals.
1e	2-Cl, 4- NO_2	502.5	Dark red powder.
1f	2- NO_2, 4- Cl	502.5	Dark and powdery.
1g	2- CN, 4- Cl	482.5	Dark and powdery.
1h	2, 4- NO_2	513.0	Dark and powdery.
1i	2- CN, 4- NO_2	493.0	Dark blue tiny crystals.
1j	2,4- NO_2,5-Cl	547.5	Dark crystals

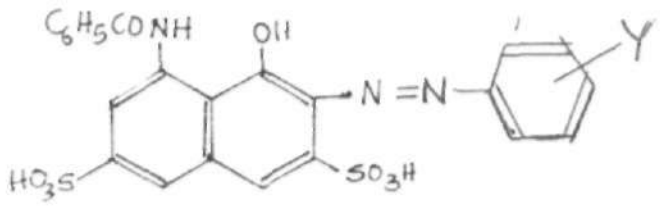
Table 3.2: Dyes Derived from N- acetyl- 1- amino- 8- naphthol- 3,6- disulphonic acid II



(II)

Dye No.	Y Substituents	Mol. Wt.	Colour of crystals
2a	H	465.0	Dark, crystalline
2b	4- NO_2	510.0	Dark tiny crystals.
2c	4- SO_3H	545.0	Brownish powder.
2d	4-COOH	509.0	Dark brown tiny crystals.
2e	2-Cl, 4- NO_2	544.5	Dark and crystalline.
2f	2- NO_2, 4- Cl	544.5	Dark and crystalline.
2g	2- CN, 4- Cl	524.5	Dark brown and leaflet.
2h	2, 4- NO_2	555.0	Brown and powdery.
2i	2- CN, 4- NO_2	535.0	Dark and crystalline.
2j	2,4- NO_2,5-Cl	589.5	Black and powdery.

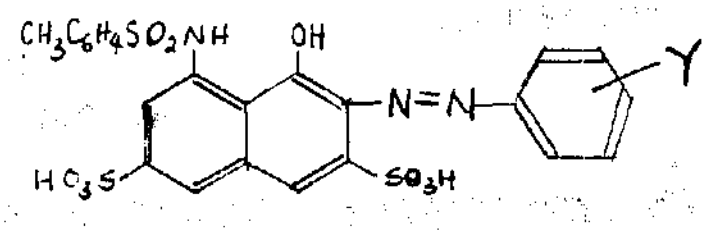
Table 3.3 Dyes Derived from N- Benzoyl- 1- amino- 8- naphthol- 3,6- disulphonic acid (III)



(III)

Dye No.	Y Substituents	Mol. Wt.	Colour of crystals
3a	H	527.0	Brownish red leaflets.
3b	4- NO_2	572.0	Dark red tiny crystals.
3c	4- SO_3H	606.0	Brownish leaflets.
3d	4-CO_2H	571.0	Brown and crystalline.
3e	2-Cl, 4- NO_2	606.5	Wine red and powdery.
3f	2- NO_2, 4- Cl	606.5	Wine red and powdery.
3g	2- CN, 4- Cl	586.5	Wine red and powdery.
3h	2, 4- NO_2	617.0	Reddish brown powder.
3i	2- CN, 4- NO_2	597.0	Dark red leaflets.
3j	2,4- NO_2,5-Cl	651.5	Reddish violet powder.

Table 3.4 : Dyes Derived from N- paratoluene sulphonyl- amino-8- naphthol- 3,6- disulphonic acid (IV)



(IV)

Dye No.	Y Substituents	Mol. Wt.	Colour of crystals
4a	H	577.0	Dark amorphous powder.
4b	4- NO_2	622.0	Dark brown crystals.
4c	4- SO_3H	656.0	Dark violet powder.
4d	4-COOH	621.0	Dark and crystalline.
4e	2-Cl,4-NO_2	656.5	Dark, Maroon, crystalline
4f	2-NO_2,4-Cl	656.5	Dark brown, amorphous.
4g	2-CN,4-Cl,	636.5	Maroon, amorphous.
4h	2,4-NO_2	667.0	Dark powder.
4i	2-CN,4-NO_2	647.0	Blackish fine powder.
4j	2,4-NO_2,5-Cl	701.5	Dark red crystals.

3.2 INTERPRETATION OF I.R DATA [44,45,46]

The main reactions carried out on the H-acid coupling component were acetylation, benzoylation and tosylation.

The variety of amines according to their substitutents were used, viz:

a - aniline

b - 4-nitroaniline

c - sulphonic acid

d - 4-aminobenzoic acid

e - 2-chloro- 4-nitroaniline

f - 2-nitro- 4-chloroaniline

g - 2-cyano- 4-chloroaniline

h - 2,4-dinitroaniline

i - 2-cyano- 4-nitroaniline

j - 2,4-dinitro- 5-chloroaniline

The infrared spectral analysis is therefore expected to show absorption peaks respective to substitutions on the amino group of the coupling components and the various substituents on the aniline ring.

The acetylation of H-acid is expected to give absorption peaks for the carbonyl group of the acetyl group. This is characterised by strong absorptions at about 1,720 - 1670 cm^{-1} [41] for free dilute solutions and 1680 - 1630 cm^{-1} for the associated solid state.

All acetylated and benzoylated H-acid dyes absorbed mainly at 1700 - 1720 cm^{-1} Dye (3a) and (2f) absorbed at 1680 - 1650 cm^{-1} showing an associated solid state for the carbonyl group.

N-Tosylation of the H-acid dyes is expected to introduce peaks for the sulphonyl group and the methyl group as follows:

1,260 - 1,150 cm^{-1} very strong (SO_2 assymetric stretch)

1,080 - 1,010 cm^{-1} very strong (SO_2 symmetric stretch)

700 - 650 cm^{-1} strong (S-O-stretch)

and 1,000 cm^{-1}, 1,450 cm^{-1} for C-H and H-H bending vibrations respectively.

Inspections of the spectra for the n-paratoluene sulphonyl H-acid dyes showed that Dyes (4a - 4h) absorbed between 1030 and 1060 (4f), (h), (i) and (j) absorbed bewtween 1160 and 1240 cm^{-1} for assymetric stretch.

Absorptions at 1000 cm^{-1} for the N-paratoluene sulphonyl H-acid dyes were all relatively weak while absorptions at 1,450cm^{-1} were masked by a strong peak for paraffin (the solvent used in making the mull) in the same region.

Aryl cyano groups absorb between 2,100 - 2300 cm^{-1}[44,45,46]. However, the intensity of absorptions for the cyano group expected to be strong were generally lowered by the prescence of electron withdrawing groups adjacent.

Absorption was observed between 2,100 - 2,400 cm^{-1} for the (g) and (i) dyes.

For all the dyes containing nitro groups peaks were observed between 1,300 - 1,590 cm^{-1}. The position for the absorptions due to symmetric stretching in the nitro group is affected by the planarity of the nitro group and phenyl ring as well as the extent

to which conjugation of electrons within the group is favoured. Aryl nitrogroups generally absorb between 1570 - 1300 with strong peaks.

For the sulphonic acid group the following absorptions were expected:

1260 - 1150 cm^{-1} SO_2 symmetrical stretch (very strong)

1080 - 1010 cm^{-1} SO_2 symmetrical stretch (very strong)

700 - 650 cm^{-1} S-O stretch, strong

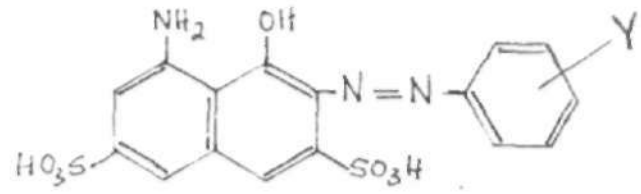
Absorptions for the (c) dyes were observed for the 1st and 2nd categories viz 1260 - 1150 cm^{-1} and 1080 - 1010cm^{-1}.

The (d) dyes were characterised by absorptions between the range of 1,300 cm^{-1} - 1200 cm^{-1} for C-O stretch vibrations in dimers.

3.3 Visible Absorption Spectra of the dye.

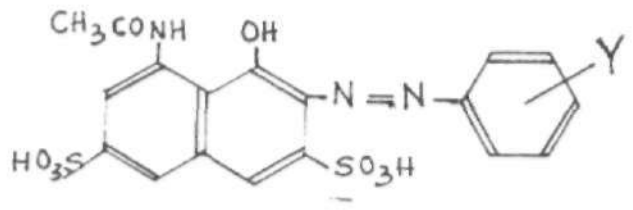
The measurement of visible absorption spectra of the dyes was done using a Bausch and Lomb spectronic 20 colorimeter. Two solvents were used;distilled water and dimethyl fomramide. The extinction coefficient was calculated from distilled water.Values obtained were recorded in Tables 3.5 - 3.8 for the dyes derived from H-acid and it's derivatives.

Table 3.5 : Visible Absorption Spectra of Dyes derived from 1-amino-8- naphthol- 3,6- disulphonic acid (I)



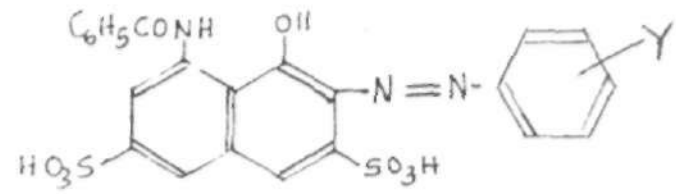
Dye No.	Y Substituents	Max. wavelength of absorption		Molar Extinction Coefficient
		Dist.H_2O	D M F	
1a	H	530	530	1.25×10^5
1b	4- NO_2	510	530	5.55×10^5
1c	4- SO_3H	525	540	7.64×10^5
1d	4-COOH	525	530	1.28×10^5
1e	2-Cl,4-NO_2	525	500	8.93×10^5
1f	2-NO_2,4-Cl	510	510	4.18×10^5
1g	2-CN,4-Cl,	500	535	1.25×10^5
1h	2,4-NO_2	525	560	3.08×10^5
1i	2-CN,4-NO_2	520	615	1.00×10^4
1j	2,4-NO_2,5-Cl	500	495	2.46×10^5

Table 3.6 : Visible Absorption Spectra of Dyes derived from N-acetyl- 1- amino- 8- naphthol- 3,6- disulphonic acid(II)



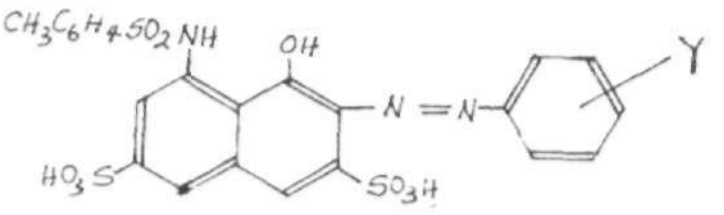
Dye No.	Y Substituents	Max. wavelength of absorption(nm)		Molar Extinction Coefficient
		Dist.H_2O	D M F	
2a	H	510	533	1.89×10^5
2b	4- NO_2	500	530	9.44×10^5
2c	4- SO_3H	515	540	3.75×10^5
2d	4-COOH	520	530	7.38×10^5
2e	2-Cl,4-NO_2	530	540	6.40×10^5
2f	2-NO_2,4-Cl	495	500	2.72×10^5
2g	2-CN,4-Cl,	530	520	1.49×10^5
2h	2,4-NO_2	485	500	6.81×10^5
2i	2-CN,4-NO_2	530	540	1.39×10^5
2j	2,4-NO_2,5-Cl	520	420	1.86×10^5

Table 3.7 : Visible Absorption Spectra of Dyes synthesised from N- Benzoyl- 1- amino- 8- naphthol- 3,6- disulphonic acid (III)



Dye No.	Y Substituents	Max Wavelength of absorption(nm)		Molar Extinction Coefficient
		Dist.H_2O	D M F	
3a	H	530	530	2.24×10^5
3b	4- NO_2	515	530	8.87×10^5
3c	4- SO_3H	515	525	7.12×10^5
3d	4-CO_2H	510	525	2.85×10^5
3e	2-Cl,4-NO_2	530	540	1.14×10^5
3f	2-NO_2,4-Cl	535	540	2.03×10^5
3g	2-CN,4-Cl,	520	535	7.99×10^5
3h	2,4-NO_2	490	500	4.63×10^5
3i	2-CN,4-NO_2	525	495	2.27×10^5
3j	2,4-NO_2,5-Cl	570	500	2.75×10^5

Table 3.8 : Visible Absorption Spectra of Dyes synthesised from N- paratoluene sulphonyl- 1- amino- 8- naphthol- 3,6- disulphonic acid (IV)



Dye No.	Y Substituents	Max. Wavelength of absorption(nm)		Molar Extinction Coefficient
		Dist.H_2O	D M F	
4a	H	510	545	1.20×10^5
4b	4- NO_2	505	515	8.09×10^5
4c	4- SO_3H	530	540	2.71×10^5
4d	4-COOH	530	540	6.21×10^5
4e	2-Cl,4-NO_2	520	530	9.19×10^4
4f	2-NO_2,4-Cl	525	540	1.03×10^4
4g	2-CN,4-Cl,	505	520	4.77×10^5
4h	2,4-NO_2	580	545	1.75×10^5
4i	2-CN,4-NO_2	530	596	3.75×10^5
4j	2,4-NO_2,5-Cl	500	495	4.00×10^5

Dye(1a)(H-acid->aniline)absorbs at 530nm in distilled water.The introduction of a nitrogroup para to the azo functional group in Dye(1b) caused an hyposochromic shift of 20nm. Dyes(1c & 1d), where H-acid was coupled to sulphanilic acid and aminobenzoic acid respectively, gave blue shifts of 5nm each. For Dye(1e) (H-acid -> 2-chloro-4-nitroaniline)->λmax was recorded as 525 nm. Dye (1f) (H-acid--->2 nitro- 4-chloroaniline) absorbed at 510nm in distilled water giving a blue shift of 20 nm same as for dye (1b). With Dye (1h) H-acid -2,4-dinitroniline) an hypochromic shift of 5 nm as in dyes (1c, d and e) was observed. Dye (1g) H-acid-->2-cyano, 4-chloroaniline) gave a blue shift of 30nm relative to dye (1a), but relative to dye (1f) gave a blue shift of 10 nm. A blue shift of 10 nm was observed for dye (1i) (H-acid --->2-cyano- 4-nitroaniline). Dye 1j was formed by coupling H-acid to 2,4-dinitro-5-chloroaniline. It shows a blue shift 30 nm relative to (1a) same as for (1g).

From the results obtained all the substituents gave hypsochromic shifts relative to Dye (1a). However, relative to one another, the y substituents in Dye (1g) and (1j) gave the highest blue shifts, in other words they had the lowest electron withdrawing affect on the acceptor ring of the dyes.

When dye (1e) is compared to dye (1b) it is seen that a bathochromic shift (15 nm) occurs when a chlorogroup is introduced into the 2-position of the nitroaniline ring. A lower bathochromic shift occurs when a cyano group is introduced instead of the chlorogroup in dye (1i) viz 10 nm. This would imply that the cyano

group is a weaker electron withdrawing substituent than the chloro group in the two dyes. Introducing a second nitro group into the same 2-position in dye 1b (to give dye 1h) causes a bathochromic shift of the same magnitude as when a chloro group was fixed there. Thus implying that for this series of dyes, the nitrogroup and the chlorogroup exert the same effect in withdrawing electrons from the H-acid coupler. However, literature[37] shows that the electron withdrawing inductive effect of the functional groups utilised with respect to hydrogen are in the following descending order of power NO_2, CN, Cl. This may not be unconnected to the strain on the two nitro groups forcing them out of plane of the aniline ring.[38]

When another chloro is introduced into the 5-position of dye 1h (dye 1j) a much greater blue shift is observed relative to dye (1a). This may be due to increased new planarity of the dye as a result of repulsion between the nitro group and the chloro group or a possible electron releasing effect I$^+$ (using it's lone pair of electrons) by the chloro group.

When the nitro group in dye (1i) is substituted with a chloro group to give dye (1g) a blue shift is observed in the latter. This may once again imply a relative electron releasing effect by the chloro group compared to the nitro group in the presence of the electron withdrawing cyano group. Comparison of dyes (1f) and (1g) shows that the nitro group is a stronger electron withdrawing group than the cyano group when meta to a chloro group. The sulphonic and carboxylic groups exhibit electron withdrawing strengths of the same magnitude as the 2-chloro-4-nitro and 2,4-dinitro substituents

on the acceptor ring in dyes (1e & h) respectively.

In dye (1f) when the nitro and the chloro groups switch places as placed in (1e) a hypsochromic shift of 15 nm is observed for the former. This may confirm the possibility of the chloro group releasing electrons more than withdrawing at the 4-position of the acceptor ring or may be due to steric hindrance between the substitutents ortho to the azo group or increased non planarity of the dye molecule thus shortening the distance/path along which resonance occurs upon excitation of the dye molecule.

Molar extinction coefficients were largely in the range of 10^5 mol^{-1} cm^{-1} with Dye (1e) having the highest value of 8.93×10^6 mol^{-1} cm^{-1}. Dye (1i) had the lowest value of 1.00×10^{-4} mol^{-1} cm^{-1} Bathochromic shifts were observed for most of the y substituents on the diazo or acceptor ring when coupled to N-acetylated H-acid.

In comparison to dye (2b) λ max- (1500 nm) in dye (2e) λ max (530 nm) chlorine is seen exerting a strong electron withdrawing effect complementary to the nitro group at the 4-position. The cyano group in dye (2i) λ max 530nm, seems to have the same electron withdrawing strength with the chloro group in dye (2e). However, dye (2h) where a nitro group has been fixed in the number 2 position of dye 2b, shows a relative hypsochromic shift of 15 nm. This must be due to the non-planar posture taken up by the dye molecule due to the two bulky substituents. Introduction of a chloro group into the number 5 position of dye (2h) to give (2j)

seems to rectify the planarity of the dye molecule as a bathochromic shift of 10nm is observed for dye (2j) relative to dye (2a). There is no difference in λ max values recorded for dyes (2i) and (2g), λ max 530 nm; whereas there is a difference in the para substituent on the acceptor ring, nitro and chloro respectively. It was expected that higher values would be obtained for (2i) where the nitro group which is a stronger electron withdrawing group is. As with dyes (1e) and (1f) a hypsochromic shift is observed with (2f) λ max 495 nm relative to dye (2e) λ max 530 nm. However, unlike with dyes (1f) and (1g) a bathchromic shift was observed for dye (2g) λ max nm relative to dye (2f).

Unlike in series 1 dyes, dye (2d) has a higher bathochromic shift than dye (2c), and Dye (2d) has the same λ max value as dye (2j), thus implying that the carboxylic acid group is quite a powerful electron withdrawing group in the presence of the acetyl group.

Molar extinction coefficient values for the N-acetylated H-acid dyes were lower than that for for their H-acid analogues, many more had values in the range of 10^5 mol^{-1} cm^{-1} Dye (2a) was observed as having the highest tinctorial power with molar extinction coefficient of 1.89 x 10^5 mol^{-1} cm^{-1} and Dye (2j) had the lowest value of 1.86 x 10^5 mol^{-1} cm^{-1}.

For the series 3 dyes most of the shift observed where hypsochromic for the various y substituents. Again as with dyes 1b and 2b, the nitrogroup on dye 2b exerted a relatively weak (if at all) electron withdrawing effect, but the introduction of a

chlorogroup into the number 2-position of the dye 3b, once again caused a bathochromic shift for the dye 3e formed. As with dyes (1e) and (1i) a blue shift of 5nm was observed for dye 3i relative to dye 3e. The substituent effect observed for the 2,4-dinitroaniline ring is that of non planarity between the substituent and on the dye molecule causing it to absorb at shorter wavelengths (λ max (3h):- 490 nm, (3a) 530 nm) relative to dye 3a.

As with dyes (1f) and (1g) the nitrogroup in dye (3f) proves to be a stronger electron withdrawing group than the cyano group in dye (3g) a bathochromic shift of 15 nm was observed going from dye (3g) to (3f). However in the series 1 and 2 dyes, series f is less bathochromic than the series g dyes. This is obviously due to the effect of the benzoyl group on the H-acid amine group.

Dyes 3c and 3d do not follow any of the trends observed for the series c and d dyes in the 1 and 2 series as this time the N-benzoylated H-acid---> Sulphanilic acid (3c) is more bathochromic relative to (3a), than N-benzoylated H-acid ----> 4 aminobenzoic acid (3d).

The N-benzoylated H-acid dyes had molar extinction coefficients ranging between 8.87 x 10^5 mol^{-1} cm^{-1} for dye 3b and 2.85 x 10^5 mol^{-1} cm^{-1} for dye 3d. This range of values is higher than those obtained for H-acid analogues.

Looking at the shifts for dyes in series (4) coupled with nitroaniline one might conclude since the hypsochromic pattern of absorption relative to their aniline dyes is consistent, that the

N-paratoluene sulphonyl H-acid derivative is the most electron releasing coupling component of all the coupling components. The series (e) where N-paratoluene sulphonyl H-acid is coupled to 2-chloro - 4-nitroaniline, gives like the other couplers, a bathochromic shift relative to dye 4b. This confirms the significant electron withdrawing effect of the chloro atom in the number 2 position of the ring relative to the nitrogroup in the 4-position.

Changing the position of the nitro and chloro groups in (4e) to give (4f) results in a bathochromic shift of 5nm similar to that observed for dyes 3e and 3f. If it was considered that the initial positioning of the nitro group at the 4-position caused non planarity of the dyes (hence the hyprochromic shifts) it could be suggested that the bulky substituents on the amino groups of the series 3 and 4 upon interacting with the 2-nitro group of the (3f) and (4f) dyes forced the molecules back into the plane of resonance and thus favoured the bathochromic shifts.

Going from dye (4e) to (4i), N-paratoluene sulphonylated H-acid coupled to 2-chloro-4-nitroaniline and 2-cyano- 4-nitroaniline respectively, we find an increase in λ max implying in this series that the cyano groups in this series is a much stronger electron withdrawing group than the chloro atom. A greater bathochromic shift of 70 nm is observed with the substituent 2, 4-dinitroaniline in dye (4h) unlike with the series 1,2, and 3 series where hypsochromic shifts were observed relative to their aniline dyes. This could be attributed also to the possible interaction of the

bulky substituents with the 2-nitrogroup of the aniline ring as suggested earlier. This time around, when a chloro group is introduced into the 5-position of dye (4h) rather than rectify planarity of the dye molecule, it distorts it giving rise to a hypsochromic shift for (4j) relative to 4a.

As with the dyes (1i) and (1g), (3i) and (3g) the incorporation of a chlorogroup at the 4 position of the aniline ring rather than the nitrogroup (as in 4i) causes a hypsochromic shift. The same bathochromic shift is observed going from dye (4e) to (4f) as with (3e) to (3f). The bathochromic shift observed going from dye (4f) to (4g) implies that the nitrogroup is a stronger electron withdrawing group than the cyano group at the 2 position of the aniline ring relative to chlorine at the 4-position.

Dyes (4c) N-paratoluene sulphonyl H-acid ---> sulphanilic acid and (4d) N-paratoluene sulphonyl H-acid---> carboxylic acid exhibit bathochromic shifts comparables in strength to the 2-cyano- 4-nitro substitutes. They have the same max values as dyes (1c) and (1d) had the same values.

Dye (4e) like (1e), had the highest molar extinction coefficient of 9.79 x 10^{4} mol^{-1} cm^{-1} and is the highest value obtained overall. Dye (4f) had the lowest molar extinction coefficient of 1.03 x 10^{4} mol^{-1} cm^{-1}.

In considering the general shifts of each y substituent from the H-acid (i.e dyes in series 1) derivatives to each of the H-acid derivates coupling components viz 2, 3, 4 analogues, it was seen

that there was

(i) a general hypsochromic shift for dyes coupled to N-acetylated H-acid except for dyes

(2e)- N acetylated H-acid---> 2-chloro- 4 nitroaniline

(2g)- N-acetylated H-acid---> 2 cyano- 4 chloroaniline

(2i)- N acetylated H-acid---> 2 cyano- 4-nitroaniline

(2j)- N-acetylated H-acid---> 2,4-dinitro- 5-chloroaniline

(ii) a general bathochromic shift for dyes coupled N- benzoylated H-acid, except dyes

(3a)- N-benzoylated H-acid--->aniline

(3c)- N-benzoylated H-acid--->sulphanilic acid

(3d)- N-benzoylated H-acid---->4-aminobenzoic acid

(3h)- N-benzoylated H-acid---->2,4-dinitroaniline

(iii) a general bathochromic shift for dyes coupled to N-paratoluene sulphonyl H-acid except dyes

(4a)- N-paratoluene sulphonyl H-acid--->aniline

(4b)- N-paratoluene sulphonyl H-acid---> 4-nitroaniline

(4e)- N-paratoluene sulphonyl H-acid---> 2-chloro – 4-nitroaniline.

(4j)- N-paratoluene sulphonyl H-acid----> 2,4-dinitro- 5-chloroaniline.

(No visible change in λ max relative to their 1 analogue viz for dye 1a - 3a and dye 1j - 4j.)

It can be concluded therefore that the N-acetylated amino group is a weaker electron releasing group than the amino group. This is confirmed by literature[39]. Also it can be infered that the N-benzoylated amino group and the N-paratoluene sulphonylated amino group are more electron releasing than the unsubstituted amino group due to the general bathochromic shifts observed between the 3 and 4 dye series and their H-acid analogues. Of the 3 and 4 dye analogues, the 4-series (dyes derived from N-paratoluene sulphonyl H-acid) shows more bathochromic shifts with the various y substituents on the aniline ring hence the N-paratoluene sulphonylated amino group is a stronger electron releasing group than the N-benzoylated amino group.

A general analysis of (y) substituents (b)-(j) shows the following general trends:

With 4-nitroaniline (b) all the H-acid derivatives gave hypsochromic shifts shifts relative to dyes formed with aniline (a), the lowest being with N-paratoluene sulphonyl H-acid.

The sulphonic acid group as in substituent (c) and carboxylic acid group in substituent (d) show no specific trend but vary with the coupler.

They give maximum hypsochromic shifts of the same value with H-acid and maximum bathochromic shifts of the same value with N-paratoluene sulphonyl H acid. The (c) and (d) substituents generally exhibit the same electron withdrawing strengths and except with N-benzoylated H-acid, they show either the same strength as the Nitro group in 4-nitro aniline or higher in

withdrawing electrons from the acceptor ring. Sekido & Injima show sulphonate and nitro groups having the same strength in affectiing light fastness values.(40)

Dyes in (e) (coupled to 2-Cl-4-NO_2aniline) show general bathochromic shifts relative to the (a) dyes. They also showed consistently bathochromic shifts relative to the 4-nitroaniline dyes,thus highlighting the highly complementary electron withdrawing effect of the chloro group at the number 2 position of the aniline ring relative to the nitrogroup at the number 4 position of the same.

Dyes in (f) series (H-acid derivatives coupled to 2-nitro- 4-chloroaniline) show hypochromic shifts for the two less electron releasing coupling components -1 and 2, and bathochromic shifts for the others i.e 3 and 4. They show the same trends relative to the (e) dyes (H-acid derivatives coupled to 2-Cl-4-NO_2aniline). It may be that the chloro group at number 4 position has a positive inductive effect i.e is electron releasing and that the nitro group for dyes are out of the plane of maximum resonance but the bulky rings of the coupling components in (3) (N-Benzoylated H-acid) and (4) N-Paratoluene sulphonyl H-acid) force the aniline ring into the plane.

Dyes in (g) series (H-acid derivatives coupled to 2-cyano-4-chloro aniline)show general hyposochromic shifts relative to their (a)dyes.The only exception is with N-acetylated H-acid. In comparison with the series(f)dyes,the (f)dyes show a greater hypsochromic shift implying that the nitro group is a stronger

electron withdrawing group than the cyano group.The only execption again is found with (2f)&(2g).Where (2f)is more hypsochromic relative to (2g).

Series (h) dyes (H-acid derivatives coupled to 2,4-dinitroaniline) are generally hypsochromic in the decreasing order of coupling components (3)--->(2)--->(1). Dye (4h) only is bathochromic and the highest bathochromic shift for all the dyes is recorded with dye(4h).This may be attributed to unfavoured non planarity of the dyes with the coupling components (3), (2) and (1). It is likely to be due to steric hindrance repulsion between the bulky substituents ortho to the azo functional group that resonance is further restrained in dye (3h). With dye (4h) it may be that the high electron releasing strength of N-Paratoluene sulphonyl H-acid and the possible rearrangement of the dye molecule structure to give a favoured planar structure that enhanced the high bathochromic shift observed.The dye (3h) also recorded the highest hypsochromic shift of all the dyes relative to their (a) dyes.

Series (i) dyes (H-acid derivatives coupled to 2-cyano-4-nitroaniline) showed hypsochromic shifts for H-acid and N-Benzoylated H-acid and bathochromic shifts for N-acetylated H-acid and N-Paratoluene sulphonyl H-acid. In relation to the (g) dyes (H-acid derivatives coupled to 2-cyano- 4-chloroaniline) except for dye (2g) there was a bathochromic shift for all series (i) dyes over (g) dyes. This shows that the nitro group at the 4 position is a stronger electron withdrawing group than the chloro group in

the same position of the aniline ring.

Comparing series (i) dyes with series (e) dyes, only dye (4i) gave a bathochromic shift over its (e) analogue largely implying that the chloro group at the 2 position relative to a nitro group in 4 position of the ring is a stronger electron withdrawing group than the cyano group when at the 2 position of the same aniline ring. The cyano group is only favoured when the coupling component has a strongly electron releasing substituent such as N-paratoluene sulphonyl amino group is. Series (j) dyes (H-acid derivatives coupled to 2, 4-dinitro-5-chloroaniline) show marked hypsochromic shifts for H-acid (1) and N-paratoluene sulphonyl H-acid (4) and bathochromic shifts for N-acetylated H-acid (2) and N-benzoylated H-acid (3) (the bathochromic shift as much more marked for the latter) relative to their (a) dyes.

Except for dyes (1h), the introduction of a chloro group at the 5 position of the (h) dyes caused a shift opposite to that observed prior to its introduction. This affirms the role of steric hindrance between bulky substituents ortho to the azo group in the (h) dyes. The chloro group added automatically adjusts the structure to become favourable as in (3j) and (2j) or unfavourable as in 4j. With (1h), hypsochromic shifts are observed when the chloro group is introduced at the 5-position to give (1j).

Dye (3j) gave the second most bathochromic shift for all dyes and dyes (4j) and (1j) the second most hypsochromic shifts for all the dyes relate to their respective (a) dyes for their coupling

components.

3.4 SOLVATOCHROMISM

The wavelength of maximum absorption of a given dye varies according to the polarity of the solvent in which the measurement is made. It may induce either a blue shift (negative solvatochromy) or a red shift (positive solvatochromy) depending on how it affects the stability of the ground state or the excited state of the molecule.

$\pi \rightarrow \pi^*$ transitions[41] in the excited state of the molecule result in a higher electron density than in the ground state of the molecule. At the same time it is higher than in the excited state of the molecule caused by $n-\pi^*$ and $n-\sigma^*$ transitions. As a result of this, polar solvents stabilise $\pi-\pi^*$ excited state, thus lowering the energy required for its excitation. This is done by hydrogen bonding with hydrogen atoms of the solvent molecules[42]. With the $n-\pi^*$ or $n-\sigma^*$ transitions the ground state is more likely to be stabilised by the hydroxyl groups of polar solvents. Thus a greater amount of electromagnetic energy would be needed to achieve the transitions[43] i.e $n-\pi^*$, $n-\sigma^*$.

Most of the shifts in maximum absorption wavelengths observed were bathochromic for the generality of the dyes where measurements were done in DMF. This implies that most of the favoured transition for the dye molecules were $n-\pi^*$ or $n-\sigma^*$ transitions[41]. This is to be expected as the electron releasing group on the coupling components were amino based derivatives, the nitrogen atom having a lone pair of electrons which could be used in extending

the resonance of mobile electrons within the dye molecules. The most outstanding red shifts observed when the dyes were dissolved in dimethyl formamide, were obtained with 4i (+95nm) and (1i) (+67.5nm) viz N-paratoluene sulphonyl H-acid---> 2-cyano- 4-nitroaniline and H-acid ---->2-cyano- 4-nitroaniline respectively. This brings into question the electron releasing ability of N-benzoylated H-acid. From section 3:3, it is supposed to have a higher electron releasing ability than H-acid yet the dye (3i) gives a blue shift of -30 nm unless however there is repulsion between the benzene ring and cyano group. It is also seen that the 2-cyano- 4-nitro substituents on the aniline ring are highly electron withdrawing. The highest blue shifts were observed with dye (2j) N-acetylated H-acid---> 2,4-dinitro- 5-chloroaniline), -100nm. Negative solvatochromy as mentioned earlier is an indication of $\pi - \pi^*$ transitions being favoured probably due to the restraint of the lone pair of electrons by the coupling substituent and the functional group ortho to the azo group on the acceptor ring (viz the nitro group) Dyes (3i), (1e), (2g), (1j) and (4j) also give blue shifts in dimethyl formamide in decreasing order of shifts observed. All series (j) dyes showed negative solvatochromy in dimethyl formamide. In other words the 2,4-dinitro- 5-chloro substituents on the aniline ring favour $\pi - \pi^*$ transitions which require more transition energy than $n-\pi^*$ transitions. This means that they are highly electron withdrawing substituents over all the other substituents. However dyes (1e) (H-acid--->2-chloro- 4-nitroaniline) and (4h) (N-paratoluene sulphonylated H-acid---> 2,4-

dinitroaniline) showed higher Blue shifts in dimethyl formamide than dyes (1j) and 4j) respectively. In other words, the much lower blue shifts of (1j) and (4j) compared to dyes (2j) and (3j) may be due to the lack of planarity of the dye molecules (proposed in 3.2) which would hinder the resonance of mobile electrons in the π-π^* transitions.

The nitroaniline dyes of N-acetylated H-acid and N-benzoylated H-acid gave the highest red shift for the (2) and (3) dyes in D.M.F (for the 3 dyes). The aminobenzoic acid, 2-cyano- 4-chloroaniline substituents gave equal red shifts). The nitro substituent is seen playing a prominent role in favouring n-π^* or n-σ transition in the (2) and (3) dyes as the case may be.

Some of the dyes exhibited Halochroism in their weakly acidic dyebaths when compared to their aqueos solutions e.g Dye (3h) N-benzoylated H-acid coupled to 2,4-dinitroaniline changed colour from brown to pink. Dye 3i, N-benzoylated H-acid coupled with 2-cyano- 4-nitro aniline changed colour in water from purple to blue upon addition of 1% acetic acid in the process of preparing their dyebaths.

3.5 Wash Fastness Results

The results of wash fastness tests are shown in Tables 3.1 - 3.12.

Table 3.9 : Wash fastness ratings of dyes derived from 1- amino-8- naphthol- 3,6 disulphonic acid

Dye No	Change in colour	Staining on Nylon	Staining on cotton
1a	5	5	5
1b	4 - 5[D]	5	5
1c	2 - 3	5	5
1d	5	5	5
1e	2 - 3	5	5
1f	2 - 3	5	5
1g	2 - 3[Bl.]	5	5
1h	3[Bl.]	5	5
1i	2[Bl.]	5	5
1j	2[Bl.]	5	5

KEY:

Bl - bluer

D - darker

Br - brighter

Table 3.10 : Wash fastness ratings of dyes derived from N-acetyl-1- amino- 8- naphthol- 3,6 disulphonic acid

Dye No	Change in colour	Staining on Nylon	Staining on cotton
2a	4 - 5	5	5
2b	2 - 3	5	5
2c	2	5	5
2d	4	5	5
2e	3^{Bl}	5	5
2f	4 - 5	5	5
2g	4 - 5	4 - 5	5
2h	$3 - 4^{Bl}D$	5	5
2i	$4 - 5^{Bl}D$	5	5
2j	3^{Bl}	4 - 5	5

Table 3.11 : Wash fastness ratings of Dyes derived from N- benzoyl- 1- amino- 8- naphthol- 3,6 disulphonic acid

Dye No	Change in colour	Staining on Nylon	Staining on cotton
3a	3 - 4	5	5
3b	4 - 5[3]	5	5
3c	2 - 3	5	5
3d	2	5	5
3e	2	5	5
3f	4[1]	5	5
3g	4	5	5
3h	3 - 4[3]	5	5
3i	4 - 5[3]	5	5
3j	3 - 4[3]	5	5

Table 3.12 : Wash fastness ratings of dyes derived from N-paratoluene sulphonyl- 1- amino- 8- naphthol-3,6 disulphonic acid

Dye No	Change in colour	Staining on Nylon	Staining on cotton
4a	3	5	5
4b	2 - 3[Br]	5	5
4c	4 - 5	5	5
4d	4	5	5
4e	4 - 5[Br]	5	5
4f	4[Br]	5	5
4g	3	5	5
4h	3 - 4	5	5
4i	3[Br]	5	5
4j	3	5	5

(1) High wash fastness values of dyes are observed generally in relation with:

(i) increased coplanarity of the substitutents with the rings of the aromatic framework of the dye. These induce higher substantivity and thus higher wash fastness.

(ii) intramolecular aggregation of dye molecules possessing increasingly non-polar substituents[17].

(iii) Polarisable auxochromes which induce fixation on to fibre by hydrogen bonds[17].

In otherwords, the wash fastness is a measure of how easy or difficult it is separate the dye molecules from the fibre and break intramolecular bonds of the dye molecules while in the fibre.

On the average dyes synthesized from N-Benzoylated H-acid showed the highest wash fastness where seven out of the ten synthesized have ratings of 3-4 to 4-5 (See table 3.11) this is most likely due to the additional benzene ring on the coupling component which may increase the planarity and thus surface area of contact of the dye molecules with themselves and the fibres. This would enhance Van der Waals short range bonding as well as hydrogen bonds between any polarisable substituents on either fibre or dye molecule[7].

For the N-paratoluene sulphonyl H-acid dyes, nine out of the ten synthesized distributed broadly over ratings of 4-5 and 3 (See 3.12).

The lowered fastness values are most likely due to the additional sulphonyl and methyl on the benzene ring of the amino

group on the coupling component, introducing some non planarity in the structure of the dye molecule compared to the N-Benzoyl- derivatives. Intramolecular repulsion may come into play since the series (j) crystals were all 'fine' sized particles.

The N-benzoyl dyes, when made into dyebaths always turned out as suspensions of the dye molecules. This goes to show that indeed intramolecular aggregation of the N-benzoyl dyes was favoured within the Nylon 6.6 susbstrate. Hence the relatively high wash fastness values. The dyes (3c) N-benzoylated H-acid---> sulphanilic acid (3d) i.e N-benzoylated H-acid---> 4-aminobenzoic acid and (3e) i.e N-Benzoylated H-acid---> 2-chloro- 4-nitro aniline had wash fastness values of 2-3 for (3c) and 2 for (3d) and (3e) respectively. With dyes (3c) and (3d) the presence of solubilizing groups may have resulted in polar disparity between the dye molecules and non-alignment with the fibre molecules due to the increased number of fixation groups on the dye molecule[47].

Nine out of ten of the N-acetylated H-acid dyes are distributed between ratings of 4-5 and 2-3 with most concentrated at the higher wash fastness ratings. The carbonyl groups could have formed hydrogen bonds with the fibre.

For dyes derived from H-acid, seven out of ten dyes have their ratings between 3 and 2. This must be due to their smaller size which does not favour intramolecular aggregation as an added advantage to its site specific fixation on the nylon fibres. In addition, a smaller surface area would mean inter surface contact between dye molecules and fibres would be reduced thus making it

more easily desorbed during the alkaline washing.

Dyes (1a) and (1d) H-acid coupled to aniline and 4-amino benzoic acid respectively, gave the highest wash fastness values of 5 out of all the dyes synthesized of all the dyes obtained from aniline.

Dye (4a) has the lowest wash fastness, likely due to the lack of an auxochrome on the acceptor ring of the molecule to give added substantivity to the large molecular framework it has. Dye (3d) has the lowest wash fastness of 2 compared to other (d) 4-aminobenzoic acid dyes with ratings of 4 and above. The dye molecule (3d) has in addition to the polarisable carboxyl group at the amino group of the coupling component, an extra solubilizing group that can act in site specific fixation with the protonated amino group of the amine group of the fibre. Thus it is likely that the dye molecule may not be aligned to the fibre.

The (y) substituents follow no specific trend in influencing the wash fastness ratings of the dyes. They are influenced mainly by the size of the molecules and planarity which in turn is affected by the number of substituents on the dye molecule and their polarisability.

With 2-chloro- 4-nitroaniline-(e), (1), (2) and (3) coupling components have poor wash fastness ratings of 3 and below while (4) N-paratoluene sulphonyl H-acid has a marked fastness of 4-5. However, 2-nitro- 4-chloroaniline (f) gives fastness ratings of 4 and above for (2) (3) and (4) coupling components and 2-3 for (1) H-acid.

Dyes (1c) (2c) and (3c) have poor wash fastness rating of 2-3 whereas (4c) has a high wash fastness rating of 4-5, showing that presence of the additional sulphonic acid group favours the alignment of the bulky (4c) molecule on the fibre unlike with other coupling components.

Amongst the (j) dyes a generally poor wash fastness is observed but with (3j) of greater planarity and inter surface contact the highest ratings of 3-4 was observed.

Apart from dye (1h), probably due to its small size all the (h) 2, 4-dinitroaniline dyes had a wash fastness rating of 3-4. This is the most consistent trend observed for the (y) substituent effect on the wash fastness of the dyes synthesized. A uniformity in mode of fixation is thus implied probably via the 2,4-dinitro chloro ring and the 2 sulphonic acid groups on the coupling component.

It was a general observation that the amines with strong electron withdrawing groups such as 4-nitroaniline (b) 2-cyano- 4-chloroaniline (g) 2,4 - dinitroaniline (h), 2-cyano- 4-nitroaniline (i), 2,4-dinitro- 5-chloroaniline (j) gave dyeings which turned brighter, bluer or darker upon washing. This trend was less obvious for the N-paratoluene sulphonyl derivatives. This might not be unrelated to the possible ionization of the coupler [II] which enhances deepening of colour due to increased resonance within the dye molecule. This occurs under the influence of electron withdrawing groups in the alkaline washing condition.

3.6 Perspiration Fastness Test Results

Table 3.13 : Acid & Alkali Perspiration Fastness test results for dyes derived from 1- amino- 8- naphthol- 3,6 disulphonic acid (I)

Dye No	Alkali Perspiration rating			Acid Perspiration rating		
	Δ in col.	Staining on Nylon	Staining on Cotton	Δ in col.	Staining on Nylon	Staining on Cotton
1a	4	3	4	4 - 5	4	2 - 3
1b	4 - 5	4	3 - 4	3 - 4[D]	5	2 - 3
1c	2 - 3	4	3 - 4	3	3 - 4	4
1d	4[Bl]	4	2 - 3	4 - 5[Bl]	4 - 5	2 - 3
1e	1 - 2	4 - 5	4	1 - 2	4 - 5	5
1f	2 - 3[Bl]	3	2 - 3	2 - 3	4 - 5	5
1g	2 - 3[Bl]	3	2 - 3	4 - 5[Bl]	3	2 - 3
1h	2 - 3	5	5	2	5	5
1i	2 - 3	5	5	4 - 5	3	2 - 3
1j	4 - 5	5	5	5	5	5

KEY:

Bl - bluer

Br - brighter

D - darker

3.6 Perspiration Fastness Test Results

Table 3.13 : Acid & Alkali Perspiration Fastness test results for dyes derived from 1- amino- 8- naphthol- 3,6 disulphonic acid (I)

Dye No	Alkali Perspiration rating			Acid Perspiration rating			Dye No
	Δ in col.	Staining on Nylon	Staining on Cotton	Δ in col.	Staining on Nylon	Staining on Cotton	
1a	4	3	4	4 - 5	4	2 - 3	
1b	4 - 5	4	3 - 4	3 - 4[D]	5	2 - 3	
1c	2 - 3	4	3 - 4	3	3 - 4	4	
1d	4[Br]	4	2 - 3	4 - 5[Br]	4 - 5	2 - 3	
1e	1 - 2	4 - 5	4	1 - 2	4 - 5	5	
1f	2 - 3[Bl]	3	2 - 3	2 - 3	4 - 5	5	
1g	2 - 3[Bl]	3	2 - 3	4 - 5[Bl]	3	2 - 3	
1h	2 - 3	5	5	2	5	5	
1i	2 - 3	5	5	4 - 5	3	2 - 3	
1j	4 - 5	5	5	5	5	5	

KEY:

Bl - bluer

Br - brighter

D - darker

Table 3.14 : Acid & Alkali Perspiration Fastness test results for dyes derived from N- acetyl-1- amino- 8- naphthol- 3,6- disulphonic acid (II)

Dye No	Alkali Perspiration rating			Acid Perspiration rating			Dye No
	Δ in col.	Staining on Nylon	Staining on Cotton	Δ in col.	Staining on Nylon	Staining on Cotton	
2a	2 - 3	2 - 3	2	3	4 - 5	2 - 3	
2b	5	5	5	2	5	5	
2c	3 - 4	4 - 5	2 - 3	3 - 4	4	4	
2d	3 - 4	3	2	4 - 5	3	2	
2e	3 - 4	5	4 - 5	5	5	5	
2f	2 - 3	5	5	2	5	5	
2g	5	5	2	3 - 4	5	2	
2h	3 - 4[3l]	5	4	4[3r]	5	5	
2i	4	4 - 5	3	3	3 - 4	3	
2j	3[3l]	5	5	5	3 - 4	3 - 4	

Table 3.15 : Acid & Alkali Perspiration Fastness test results for dyes derived from N- benzoyl-1- amino- 8- naphthol- 3,6- disulphonic acid (III)

Dye Number	Alkali Perspiration rating			Acid Perspiration rating		
	Δ in col.	Staining on Nylon	Staining on Cotton	Δ in col.	Staining on Nylon	Staining on Cotton
3a	4 - 5[Br]	2 - 3	2 - 3	4	4 - 5	2 - 3
3b	4 - 5	4 - 5	4 - 5	4	5	5
3c	3 - 4	4 - 5	2 - 3	3 - 4	4	4
3d	2	5	3	3 - 4	3	2
3e	4 - 5	4 - 5	4 - 5	4	4 - 5	3
3f	4 - 5	4 - 5	2 - 3	3 - 4	4	4
3g	4 - 5	4 - 5	4 - 5	3	4 - 5	2
3h	4 - 5[Bl]	3	2 - 3[Bl]	4 - 5[Bl]	4 - 5	2
3i	4 - 5[Bl]	1 - 2	2 - 3	3 - 4	3	1 - 2
3j	3 - 4[Bl]	5	5	4[Bl]	5	5

Table 3.16 : Acid & Alkali Perspiration Fastness test results for dyes derived from N- paratoluene sulphonyl- 1- amino- 8- naphthol- 3,6- disulphonic acid (IV)

Dye No	Alkali Perspiration rating			Acid Perspiration rating		
	Δ in col.	Staining on Nylon	Staining on Cotton	Δ in col.	Staining on Nylon	Staining on Cotton
4a	3 - 4	3	2	4 - 5	3	2
4b	4 - 5	5	5	4 - 5	5	5
4c	4 - 5	5	4 - 5	3	4 - 5	4 - 5
4d	4 - 5	5	3	4 - 5	5	4
4e	3	4 - 5	4 - 5	4	4 - 5	4 - 5
4f	4 - 5[Bl]	5	5	3	5	5
4g	4[Br]	5	4	4 - 5	5	4
4h	3	4 - 5	4	1	3	2 - 3
4i	2 - 3	4 - 5	3	2[Bl]	4	2 - 3
4j	3	5	5	4 - 5[Bl]	5	5

Tables 3.13 - 3.16 show the results obtained for acid and alkaline perspiration tests carried out at the United Nigerian Textile Public Limited Company, Kaduna.

The standard acid and alkali perspirations are semblances of actual perspiration containing Histidine as the main reagent Histidine is an amino acid containing an amino group which has a lone pair of electrons. This lone pair of electrons may or may not affect the fastness of the dyes adversely under normal conditions of perspiration. It is recorded that the light fastness of acid dyes on wool is lowered due to the presence of Histidine acting as hydrogen donors for photo reduction of the azo dyes[48].

Under both acid and alkaline conditions the dyes synthesized from N-acetylated H-acid; coupled to 4-nitroaniline (b) and 2-cyano- 4-chloroaniline (g) for the latter and coupled to 2-chloro- 4-nitroaniline and 2,4-dinitro- 5-chloro aniline for the former gave the highest perspiration fastness ratings of 5.

A definite trend can not readily be developed or deciphered from the results obtained with regards to y substituent effects, but the following general statements can be made, viz:

The N-benzoylated H-acid dyes tend to cluster between a narrow range of wash fastness values; 4-5 for alkaline perspiration and 3-4 to 4 for acidic perspiration. It seems

that the intra molecular aggregation provided a kind of screening effect towards the perspiration solution such that the y substituents hardly made distinct differences in ratings of the dyes.

The N-acetylated H-acid dyes were more spread out in both acidic and alkaline conditions with higher values under alkaline conditions. The N-acetylated H-acid dyes stand out, as shown earlier, as having the highest perspiration fastness values. This may not be unrelated to the electron withdrawing effect of the N-acetylated amino group on the coupling component of the dyes.

With dyes synthesized from H-acid it was consistently observed that Dyes (1j) (H-acid---> 2,4-dinitro- 5-chloroaniline) and (1e) H-acid --->2-chloro- 4-nitro aniline) had the highest and lowest ratings respectively for the series. Clustering of dye ratings was observed at 2-3 under alkaline conditions. In acid conditions 4 of the dyes had fastness ratings of 4-5.

The N-paratoluene sulphonyl H-acid dyes were less affected by the acidic solution (as with the N-acetylated H-acid dyes) in that five of the dyes had fastness ratings of 4-5 under acidic conditions. Yet under acidic conditions ratings as low as 1 was obtained for (4h), and this was the lowest fastness value for all the dyes synthesized. Where the degradation mechanism is by reduction of the azo group by the hydrogen from histidine, high electron releasing groups such

as N-paratoluene sulphonyl H-acid (4) would tend to increase the electronegativity of the azo nitrogen atom immediately adjacent to it thus making it more susceptible to reduction. The N-acetylated H-acid (2) dyes though not having much screening effect would then be expected to be of relatively higher perspiration fastness ratings due to its lower electron releasing effects.

Stainings on cotton were worse under acidic testing conditions but better for Nylon. Dye (3i) (N-benzoylated H-acid ---> 2-cyano- 4-nitroaniline had the lowest staining values, under both acidic and alkaline conditions.

The absence of a flowing medium i.e of perspiration solution during testing must partly contribute to the similarities of ratings because there would not be much active outward migration of dyes from within the fabric.

3.7 Light Fastness Test Results

Table 3.17 : Light fastness results for dyes derived from 1-amino- 8- naphthol- 3,6- disulphonic acid.

Dye No	Light fastness Rating
1a	2
1b	3
1c	2
1d	2
1e	2
1f	2
1g	3
1h	2
1i	2
1j	1

Table 3.18 : Light fastness results for dyes derived from N-acetyl-1- amino- 8- naphthol- 3,6- disulphonic acid.

Dye No	Light fastness Rating
2a	4
2b	3
2c	1 - 2
2d	3 - 4
2e	1 - 2
2f	1
2g	2
2h	1
2i	2
2j	3

Table 3.19 : Light fastness results for dyes derived from N-benzoyl- 1- amino- 8- naphthol- 3,6- disulphonic acid.

Dye No	Light fastness Rating
3a	4 - 5
3b	3
3c	3
3d	2
3e	2
3f	2
3g	2
3h	2
3i	1
3j	2

Table 3.20 : Light fastness results for dyes derived from N-paratoluene suphonyl- 1- amino- 8- naphthol- 3,6- disulphonic acid

Dye No	Light fastness Rating
4a	3 - 4
4b	1 - 2
4c	1[D]
4d	3
4e	2
4f	3
4g	1
4h	1[D]
4i	1
4j	1

Tables 3.17 - 3.20 show the results obtained from carrying out light fastness testing using the Xenon Arc Tester. The sample cards were each exposed until the most resistant dyed sample changed up to a contrast rated 4 on the grey scales.

The most resistant specimen was obtained as dye (3a) with a light fastness of 4-5. Dye (2a) follows closely with a rating of 4. Dyes (4a) and (2d) have ratings of 3-4. All the other dyes have fastness ratings of 3, 2 and 1.

Apparently none of the electron withdrawing (y) substituents groups favour the light fastness of the dyes because apart from dye (1a) whose light fastness rating is lower than dyes (1b) and (1g) all the other (a) dyes have the highest ratings in their series. Trotman[11] showed that the introduction of auxochrome substituents to a dye molecule or chromogen may improve its washfastness but lower its light fastness. This is due to dye intramolecular repulsion caused by polar disparity or direct ionic repulsion. Larger planar molecules, such as the N-Benzoylated H-acid derivatives, are favoured by intramolecular aggregation which provides a high screening effect from degradation by light. Evans and Stapleton[11] discovered that for a given dye structure, on the coupling component, electron withdrawing groups increase light fastness because they help to lower the release of the n, lone pair of electrons on the Nitrogen atom. On the other hand, electron releasing groups lower light fastness ratings due to

the fact that they release electrons to the azo group which is basically the site of photochemical interaction and later destruction. In the light of this, it becomes obvious why Dye (4a) has a lower light fastness than dyes (2a) and (3a). Some screening effect may come into play making dye (4a) have a higher ligh fastness rating than dye (1a) even though N-paratoluene sulphonyl H-acid has a greater electron releasing effect than H-acid. Generally the larger the size of a dye molecule the more prone it is to photochemical attack hence for a good number of N-paratoluene sulphonyl Acid dyes, a very poor rating of 1 for light fastness was observed.

Prior investigation by Sekido and Injima[1] and Zafi J. Lawi[2] showed that acetylation of the amino group (introduction of a relatively electron withdrawing group into the coupling component) increased the light fastness of the H-acid analogues.

CHAPTER FOUR

4.0 CONCLUSION

The coupling component N-paratoluene sulphonylated H-acid proved consistently to be the most electron releasing group of all the donor groups. N-acetylated H-acid was observed to be powerfully electron withdrawing compared to H-acid. The N-benzoylated H-acid dyes seemed to fall between the two extremes.

Of the y substituents, the nitro group though a strong electron withdrawing group did not effect, on its own, consistent bathochromic shifts. it seemed to, especially in the para position of the acceptor ring, be electron releasing in strength. The chloro group introduced into the ortho position of a 4-nitroaniline acceptor ring seems to be highly complementary to the electron withdrawing influence of the nitro group causing marked bathochromic shifts going from one structure to the other. It was generally observed the chloro group at the para position of the acceptor ring may have more of an electron releasing rather than electron withdrawing effect. The 2,4-dinitro- 5-chloroaniline substituents were powerfully electron withdrawing but shifts observed were either bathochromic or hypsorchromic depending on the geometry of the dye molecule which in turn was influenced by the presence of steric hindrance from adjacent substituents. The

same was observed for the dyes synthesized from 2,4-dinitroaniline.

Solvatochromic investigation showed that majority of electron transitions within the dye molecules were due to $n-\pi^*$ or $n-\sigma^*$ transitions. $\pi-\pi^*$ transitions occured where powerful electron withdrawing groups e.g 2,4-dinitro- 5-chloroaniline could force double bond electrons into forming bonds with adjacent carbon atoms.

The larger the size of dye molecules the higher the wash fastness rating. The H-acid dyes showed the lowest range of ratings generally. The N-benzoylated H-acid dyes in Nylon 6.6 fibre showed a high degree of susbstantivity due to intramolecular aggregation within the fibre which in turn is related to its larger surface area and planarity. Increasing in the number of substituents as with 2,4-dinitro- 5-chloroaniline generally gave poor wash fastness values. It was observed that alkaline washings favoured strongly electron withdrawing susbtituents as with the (h), (i) and (j) dyes causing bluer and darker colours on the fabric i.e improved bathochromic shifts within the dye molecules.

Perspiration fastness testings showed that electron withdrawing (as with the N-acetylated H-acid dyes) by the coupling component favoured dye perspiration fastness on Nylon 6.6. It was only then that substituent effect became distinct, as in the acid perspiration testing for N-acetylated H-acid dyes. The screening effect by intramolecular

same was observed for the dyes synthesized from 2,4-dinitroaniline.

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aggregation of the N-benzoylated H-acid dyes favoured its perspiration fastness ratings. It can be seen that the degradation action of Histidine must be electrophillic in nature and directed towards the azo group.

Light fastness of the N-Benzoylated H-acid dyes is again favoured by intramolecular screening and the larger sized N-paratoluene sulphonyl H-acid dyes were more prone to attack. Also the relative electron with drawing effect of the N-acetyl group on the coupler favours higher light fastness results.

REFERENCES

1. "Color and Constitution of Organic Dyes" Kirk Othmer Encyclopaedia of Chemical Technology Vol. 5. 2nd Edition. Interscience Publishers. New York. 1965. PP 763 ff
2. Abrahart, E. N., "Dyes and their Intermediates",2nd edition Edward Arnold Publishers Limited ,London (1977). PP (1,3,8 & 72).
3. "Encyclopaedia Africana", AMERICANA CORPORATION, International Edition, Volume 9 (1965)
4. P. Rys and H. Zollinger,"Fundamentals of the Chemistry and Application of Dyes", WILEY INTERSCIENCE London(1972) PP 1 ff.
5. "Dyes, Natural"; Kirk Othmer Encyclopaedia of Chemical Technology Vol. 7, 2nd Edition. INTERSCIENCE Publishers,New York. 1965. pp 614 ff.
6. Brown B.,"Textile Colorist", 65, 189 (1943).
7. "Dyes Evaluation and Application", Kirk Othmer Encyclopaedia of Chemical Technology Vol. 7, 2nd Edition. Interscience Publishers New York 1965. P 505 ff.
8. "Cheuvreul M. E." Ann Chim et Phys", 81, 128 (1812); 82, 53, (1812).
9. (a) Drew R. L., "Am Dyestuff Reporter", 26, 623 (1937).
   (b) Tisdale H. B., "Rayon Textile Monthly", 29(7), 79, (1948)
10. Knagg N. S., "Am Dyestuff Reporter", 45, 595 (1956)

11. Edelstein S. M., "Am Dyestuff Reporter", 47, 1 (1958).

12. Cody K. M., "Am Dyestuff Reporter", 26, 539 (1937).

13. Perkin E. G. and Everest E., "The Natural Organic Colouring Matter", Longman Green and Co., New York (1918).

14. "Dyes and Dye Intermediates", Kirk Othmer Encyclopaedia of Chemical Technology Vol. 7, 2nd Edition, Interscience Publishers New York 1965. P.462 ff.

15. Graebe C. and Liebermann C., "Ber Pent Chem", 1,(1868) 49

16. Zaenber W., J.,Soc "Dyers and Colorists", 15, (1899) 194

17. Giles C. H., "A Laboratory course in Dyeing", 3rd Edition, S. D. C.Bradford. (1971) PP(182).

18 Moncrieff R. W., "Man Made Fibres", 6th Edition, Newnes - Butterworth 1975 PP (336, 348,354 & 376).

19. Porting, "The Dictionary of Dyes and Dyeing". Mills and Boons Limited London. 1980. PP (57, 162 & 163).

20. Graebe C., Liebermann C., "Ber. Pent. Chem" 1, (1868)106.

21. Witt. O.N. "Ber. Bent. Chem. (1876) 522

22. Armstrong H. E., "Proc. Chem. Soc." 4 (1888), 27

23. Sircar A. G. , J. "Chem Soc" 109. 1976 157 - 19.

24. "Dyes and Dye Intermediates", Small Business Publication of Consultants and Engineers (Chemical Engineering Series No. 50', Delhi PP 236 ff.

25. Stevens C. B. and Nunn D. M.(Ed)., " The Dyeing of Synthetic Polymer and Acetate Fibres, Bradford Dyers Co. Publishing Trust, Bradford (1979) .

26. Stout, E.E., "Introduction to Textiles". 3rd Edition, John Wiley and Sons, Inc. New York. 1970 P.36.

27. Trotman E. R., "Dyeing and Chemical Technology of Textile Fibres", 5th Edition, Griffith, London 1975.

28. Nkeonye P. O., "Fundamental Principles of Textile Dyeing, Printing and Finishing", ABU Press Limited, Zaria (1990). PP (115 & 164)

29. Bird C. L., Palette, 15, (1964) 25, Sandoz Publication, Basle.

30. Freudenberg K. and Blonquist, C."Ber Pent. Chem" 68B (1935) 2070.

31. Wolfram H. L.,and Dacon J. C. J., "American Chem. Soc." 74 (1952) 533.

32. Evans and Stapleton, "The Chemistry of Synthetic Dyes", Vol 6, Ed Venkataraman (N. Y. Acad Press 1978) PP 221, 247 & 258.

33. McKellar J. F., Radiat Res. Rev. 3, (1971)141

34. Patterson D. and Piling B., "The Photoconductivity of Dyes", Bios Report 1661, p. 19.

35. Nigerian Industrial Standard 5175. U. D. 566.5 "Standard Method For Determination of Colourfastness to Perspiration". Nigerian Standards Organisation, Federal Ministry Of Industries, Lagos.

36. Vogel A. I., "A Textbook of Practical Organic Chemistry", Longman, 3rd Edition, Longman Group, London, 1978.

37. Norman R. O. C. and Waddington D. J., " Modern Organic Chemistry", 4th Edition, English Language Book Society.Unwin Hyman Limited, London, 1983. PP 65.

38. Trotter, J., "Acta. Cryst." 14 (1961) 244.

39. Kaufmann,"Die Auxochrome, samlung citem und chem - Techn. Voltrage", Vol 12 (Stuttgart: Ence 1907).

40. Sekido M. and Injima T., Sen'i Gakkaishi, 155, 214 (1959) A53, 9673 (1969).

41. Cundall., R.B and Gilbert, A., "Photochemistry", Nelson, London (1970) PP 60

42. Wells, C.H.J., "Introduction to Molecular Photochemistry", Chapman and Hall Limited, London (1972) PP 21.

43. Daruwalla E. H., Rao S. S. and Tilak B. D., J. Soc. Dyers and Colourists., 76, (1960) 413.

44. Nakanishi, K., and Solomon, P.H. "Infrared Absorption Spectroscopy" (2nd Edition) Holden-day Incorporated. San Francisco.

45. Rao, C.N.R., "Chemical Application of Infrared spectroscopy" Academic Press Incorporated. New York. 1963. PP (175 - 178, 246. 258 and 296)

46. Walker, S., and Straw, H.,"Spectroscopy" volume 2. Chapman and Hall. London. 1967 PP 126.

47. Derbyshire A. N., and Peters, R.H., "J. Soc. Dyers and Colourists" 71 (1955) 530.

48. Bello K. A. Kari I. A. and Martins C. M. O. A., "Bathochromic and Hypsochromic Shifts", (Paper - 15th National Conference of the Chemical Society of Nigeria, Narict, Zaria (1990).

49. Giles G. H.and McEachram A. E., "J. Soc. Dyers and

Colourists", 72, (1956) 373

50. Lawi Z. J., " Synthesis and Application of Azo Dyes", B.Sc. Desertation. (Textile Science and Technology) Ahmadu Bello University, Zaria (1990).

51. Berg, "Melliland Textilber" 52 (1971) 448.

52 Peters, R.H., and Ingamells, W., "J. Soc. Dyers and Colourists" 76 (1960) 617.

53. Munden and Palmer, "J. Text. Inst". 41 (1950) 609.

54. Khorana, H.G., "Chem. Rev". 53 (1953) 145.

55. Cassie, A.B., J. Soc. Dyers and Colourists" 76 (1960) 617.