THE EFFECT OF SUBSTITUENTS

O N T H E S P E C T R O S C O P I C A N D

DYEING PROPERTIES OF

M O N O A Z O A N D M E T H I N E D Y E S

BY

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DECLARATION

I declared 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 has been duly acknowledged in the text by means of reference.

ISUWA, A. Kari

Date: _____

CERTIFICATION

This thesis entitled "The effects of substituents on the spectroscopic and dyeing properties of monoazo and methine dyes" by ISUWA Adamu 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 literaty presentation.

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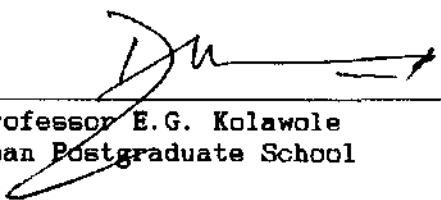Chairman Supervisory Committee

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DEDICATION

This work is dedicated to my mother

Juma, late father (Adamu)

my brothers Joseph, Solomon, Peter, Tiko and

my sisters Christiana, Mura, Gloria and Mary.

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All thanks and praises be to GOD ALMIGHTY and to his son our Lord and Saviour JESUS CHRIST for bringing me up to this stage in life.

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ABSTRACT

The synthesis of azo dyes derived from 2-aminothiazole derivatives was undertaken and their spectroscopic properties in different solvents examined. From the results of the investigation, the incorporation of electron withdrawing group in the acceptor ring of the chromogen gives a bathochromic shift of the visible absorption band, while the incorporation of electron donating group in the same position of the chromogen results in hysochromic effect. The dyes were applied to polyester and nylon fabrics and their fastness characteristics assessed. It **was** found generally that the dyes are very resistant to alkaline washing and are also suitable for transfer printing.

Series of methine dyes were also synthesised by condensing highly electronegative active methylene compounds with formyl group of aromatic compounds and the dyes obtained were applied on polyester and nylon fabrics. The colours obtained are very brilliant, ranging from yellow to green with good resistance to alkaline hydrolysis.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 General Introduction

Dyes are coloured substances that can be applied in solution or dispersion to a substrate to give coloured appearance. The substrate to which a dye is applied is usually a textile fibre but may be leather, paper, fur, hair, pulp, food, cosmetics etc. In most cases the material to be dyed possesses a natural affinity for appropriate dyes and readily absorbs them from solution or acqueous dispersion under suitable conditions of concentration and temperature. The presence of other substances called additives to regulate the rate of dyeing and the pH of the solution may sometimes be necessary.

Most coloured materials owe their colour to the presence of substances that absorb light of wavelength ranges within the visible region of the electromagnetic spectrum ($\lambda 400 - 800nm$) and this property is not destroyed by pulverisation[1]. The absorption of light by a coloured substance is due to electronic transition between different molecular orbitals within the molecule and the wavelengths absorbed are determined by the energy difference between the orbital[2].

Every dye or pigment therefore exhibits a pattern of absorption arising from its chemical structure and this may be represented by an abosrption spectrum consisting of a graph in

which the degree of absorption (i.e absorbance) or transmittance is plotted as ordinate and frequency or wavelength is plotted as abscissa.

Dyes and pigments absorb light in a characteristic manner and the unabsorbed light, called the complementary colour, is usually reflected or transmitted. Thus a dye or a pigment absorbing light within the green range (500-560nm) is seen in day light as purple, which is the complementary colour of that absorbed.

Table 1 shows the relationship of complementary colour observed to wavelength of light absorbed named after Mohler[3].

Table 1: PAIRS OF COMPLEMENTARY COLOURS

Colour absorbed	Wavelengths absorbed	Colour seen
Violet	400-435nm	Yellow-green
Blue	435-480nm	Yellow
Greenish-blue	480-490nm	Orange
Bluish-green	490-500nm	Red
Geen	500-560nm	Purple
Yellow-green	560-580nm	Violet
Yellow	580-595nm	Blue
Orange	595-605nm	Green-blue
Red	605-750nm	Blue-green
Red + Violet (Purple)	400-435nm	Green

As no single wavelength of light corresponds to the colour purple, a mixture of red and violets has to be removed from white light to give a visual effect of green. Thus all green dyes have two absorption bands, in the region of 650nm and 420nm.

The absorption spectrum of a dye may be complex and the purity of the colour observed depends on the shape of the curve, thus bright colours are the result of narrow absorption bands with sharp peaks while dull colour is associated with broader bands lacking such peaks. Non spectral bands such as brown are associated with absorption spreading fairly evenly over wide wavelength range, black is a result of absorption throughout the visible region and white is due to no absorption of light, almost all reflected.

It should be noted however, that many substances absorb radiation of wavelengths above or below the visible region. These substances do not give rise to colour appearance because of the limited sensitivity of the eye rather than to any difference in phenomena.

Young-Helmoholzt theory[4] in order to explain the above observation assumes that the human eye possesses three types of receptors which respond to light of the colours red, green and blue or violet and the conversion of light energy into electrical energy takes place in the retina of the eye where sensitive tissues namely, rods and cones are embeded and the inability of

these tissues to respond to electromagnetic waves of such wavelength is responsible for the colourless appearance.

1.2   Natural dyes

The dyes used earliest by the prehistoric man were obtained from plants and animals via extraction while others were obtained as minerals from ground. In essence therefore, all dyes that are obtained naturally without any chemical transformation are referred to as natural dyes. These dyes are also used to dye furs, textiles, etc.

Among the natural dyes extracted and used, the following deserve mention.

Indigo (i) was obtained from dyers wood indigenous in Europe and from Indigofera tinctoria a native plant of Asia. It was used to dye cotton fabrics.

(i)
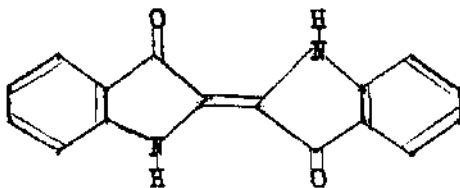
Alizarin (ii) was obtained from madder campheachi wood extract from Africa and was used to dye wool, silk, fur etc.

(ii)
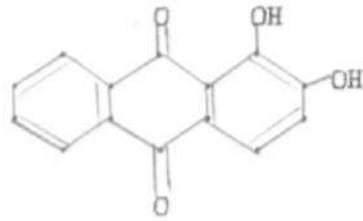
Also "Logwwod" (CI Natural black 75290) the only natural dye
that is still in production in large scale today is obtained from
haematoxylon which is cultivated but also grow wild in central
America.   Logwood is used for the dyeing of silk, nylon, viscose
acetate fibres and give cheap blacks of good fastness properties.
When freshly cut, the wood contains haematoxylon (iii) the leuco
compound of the colouring matter haematin (iv).   Oxidation to
haematin occurs during ageing or by deliberate oxidation of the
extract[s].
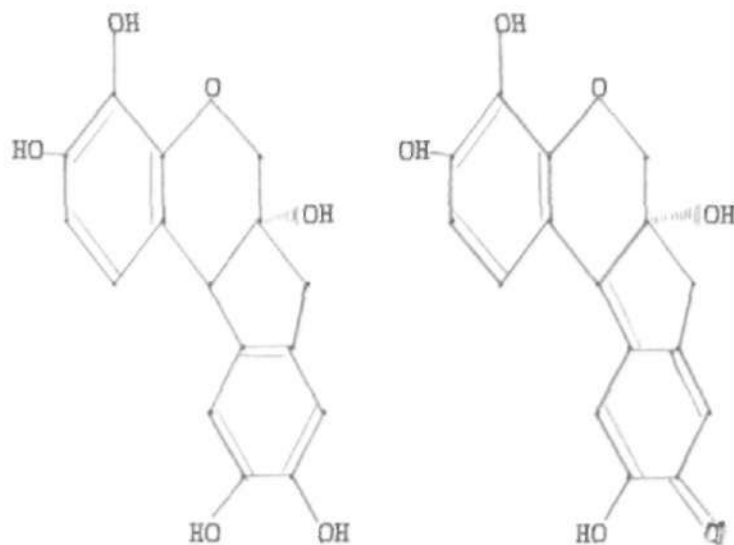
(iii)   (iv)

Other examples of natural dyes include Saffron, henna cochineal from insect cochina etc.

Most natural dyes have no direct affinity for textile fibres and are applied by means of mordants which function as fixing agents[6]. The name mordant is derived from the French word modrs and is based on an early belief that these agents corroded the fibres, opening the pores so that dye particles might enter. Later it was recognised that mordants combine with dye molecule to form insoluble compounds or "colour lakes" inside the fibre. Usually the mordants not only fix the dye but is essential for colour formation and a single dye may give a range of hues with different mordants. Mordants are normally metal salts of Cr, Al, Cu etc.

Dyeing with natural dyes is usually undertaken in three steps, namely, scouring, mordanting and dyeing[7]. The scouring process involves the preparation of the dye bath using generous amount of warm water containing a water softner and soap solution to which the fabric is immersed for sometimes, rinsed and dried. The mordanting process involves the application of the mordant. This is either done before dyeing, during dyeing or after dyeing. Chromium salt is one of the mordant in common use and the mordanting process is named in respect of the chromium metal e.g when chromium is added during dyeing the mordanting process is called the metachrome process, while the after chrome process refers to the application of the mordant before dyeing. The third

process is the application of the mordant after dyeing and this is often referred to as pre mordant method. The dyeing process involves the absorption of the colour by the substrates. This requires different pH, pressures and temperature condition depending on the dye and fibre in use.

1.2.1 Limitations of natural dyes

The extraction and application of natural dye became a substantial industry that flourished until the later part of the 19th century when it was gradually superseeded by the new synthetic dyes industry. This came about as a result of the inherent disadvantages accrued in the production and application of natural dyes.

One of the disadvantages being that natural dyes have no affinity for textile fibres and always require a mordant for their fixation to the fabric. These mordants produce colour ranges peculiar to the particular kind of metal from which the salt is made and unusual results were sometimes obtained by mixing mordants with different level of contaminants. At times the concentration of these mordants result in non uniform dyeings while other mordants are very expensive.

Also the extraction procedure are normally too cumbersome and expensive for large-scale production. Natural dyes also differ according to climatic conditions and geographical region, their

dyed products lack uniformity of hues with fastness properties which are inadequate for most quality dyeings.

Natural dyes from plants spoil, ferment or mold at room temperature within two or three days unless precautions are taken to preserve them. This effect could only be minimised if the dye bath is stored in a cool place or refrigerated[e]. Some of the dyes when fermented produce toxic substances, examples of which is the poke weed berry which ferments to give repugnant odour and fumes. Thus mordanting and dyeing have to be performed in ventilated environment.

Lastly, to produce bright and clear colour, the dyebath has to contain soft water which is obtained normally by the application of washing soda to boiling water, that is later filtered before vegetable dyeing ensued. This is of a great disadvantage in view of the time wastage and the cost involved. Thus natural dyes have limited uses and are nowadays used mainly in the dyeing of the leather.

1.3 Historical development of synthetic dyes

Synthetic dyes are coloured substances obtained by chemical transformation. They were an early result of trial synthesis of quinine through the oxidation of a mixture of aniline bases by Willaiam H. Perkin in England[e]. In the course of his oxidation reaction he accidentally obtained a black precipitate which after extraction with alcohol resulted into a purple dye

called mauve or mauveine instead of the expected quinine. The brilliant violet hue of mauve on silk immediately stimulated attention of many chemists and in 1859, Vergum in Lyon discivered fuschine, whilst the discovery of diazo compound by Peter Griess[10] in England laid the foundation for the development of the currently largest class of synthetic dyes namely the azo compounds.

It should be noted however, that mauveine was not the first synthetic dye to be proved in the laboratory, nor even the first to be manufactured but Perkin mauve is regarded as the starting point of the synthetic dye era because it was the first to be recognised and used as a dye. Also with primitive means then at his disposal Perkin was able to prepare a relatively pure and technically interesting product which later resulted to large scale production in his industry set up the following year after the discovery.

After the discovery of the quadrivalency of carbaon by Kekule (1858) and the constitution of benzene (1865) a way was opened up for processes leading to the production of purely synthetic dyes, as well as for the artificial production of natural dyes.

The first success to be mentioned is the discovery and synthesis immediately afterwards of alizarin (1,2-dihydroxyanthr-anquinine by Graebe and Liberman (1868) by the fusion of sulphonated anthraquinone with caustic alkali[11]. The elucidation of the constitution and the synthesis of indigo by Adolf Von

Baeyer[12] and K. Heuman[13] and also of indigoid dyes by G. Engi and P. Friedlander[13] who synthesized Ciba blue 4B and thio indigo respectively.

Vidal[13] opened up the field of sulphur dyes whilst the year 1901 was characterized by the discovery of indanthrone, the first anthraquinone vat dye discovered by R. Bohn[14]. Other classes of dyes discovered in the 20th centuray include Neolan dyes (1915), phathalocynines (1936) and the 1:2-metal complex dyes (irgalan dyes)[15].

R. Clavel and H. Dreffuss[13] solved the problem of dyeing hydrophobic fibres by means of disperse dyes. The post war era is characteristised by the development of pigments which achieved importance for colouring plastics, example of which include quinacridone[16], cromophthalic dyes[17].

In 1951-52 reactives dyes for wool were developed. Typical examples include Remalan, Cibanlan produced by Ciba and procion dyes produced by ICI. These possess very brilliant shade on the substrate and the fastness characteristics are very excellent. The synthesis and the application of reactive dyes has further opened up a way for dyestuff research to graduate from purely empirical synthesis of coloured molecules to the study of the mechanism of interaction of substrates and dyes with already known chromogens such as azo, anthraquinone and cyclic aza compounds.

Nowadays, thousands of dyes of different constitution are commercially available the manufacture of which spread over a large number of countries like Germany, Switzerland, Italy, Japan etc. This clearly shows that a thorough knowledge of organic synthesis leading to preparation of new dyes, optimization of manufacturing process is yielding success.

1.3.1 Raw materials for synthetic dyes

Since some of the earliest synthetic dyes were obtained from aniline which was known to be constituent of coal tar and were referred to as aniline dyes whether or not they were actually derived from aniline or coal tar. The term synthetic dyes is now preferred since primaries are increasingly obtained from petroleum sources rather than from coal tar[18].

The manufacture of synthetic dyes proceeds from simple pure chemical substances used as raw materials and are called primaries. The most important of which include benzene, toluene, the xylenes, phenols, the cresols, napthalenes, anthracenes, carbazole etc. Although aromatic compounds are present in petroleum the content is usually so low that they cannot be isolated economically, thus, the petroleum industry and other related industries have developed several processes whereby aromatic compounds are obtained from non-aromatic fractions. The first of these were cracking processes which were designed to bring about the cleavage of high-boiling component into more

volatite fractions, but, which with the aid of suitable catalyst
also enable naphthalene to be dehydrogenated with formation of
aromatic products. The application of these processes was
limited by the presence of suitable precusors in the natural oil,
and they were chiefly of value for the production of fuel of
increased octane rating. Later, various reforming processes were
developed, making use of wider range of aliphatic compound to
yield lower boiling aromatic derivatives.

Thus benzene is obtained by dehydrogenation of cycloparaffins
like cyclohexane or by dehydrogenation with rearrangement of
methyl cyclopentane using a suitable catalyst such as alumina.
The reaction is represented below[9]:-

Cyclohexane   Benzene

Using n-hexane,

$CH_3(CH_2)_4CH_3$ ----------> (Zeolite) ----------> (Silica)
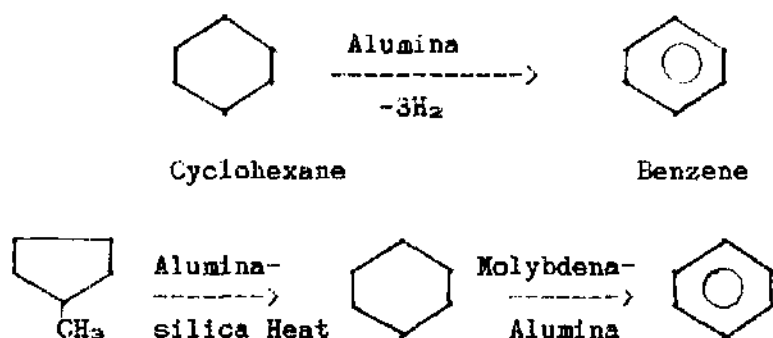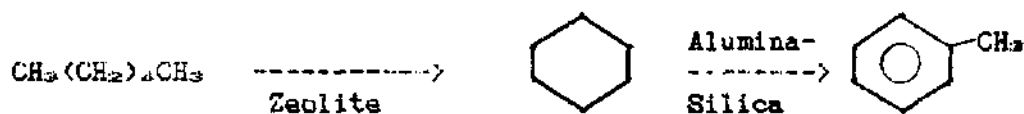
Toluene (methylbenbene) is produced by several analogous
processes for example by dehydrogenation of methylcyclohexane in

the presence of a catalyst which could be molybdena-alumina, platinium, cobalt molybdate or chrome-alumina. For instance, the catarole process developed by petrochemicals Ltd converts paraffinic hydrocarbons at 630-680°C by means of a copper or copper-iron catalyst to a liquid aromatic product and a gas consisting mainly of ethylene and propylene[9]. Also the thermal hydrodealkylation process developed by the Gulf research and development company is stated to convert toluene into benzene with at least 95% efficiency without a catalyst[20].

1.4.1 Colour and Chemical Constitution

After Perkin synthesis of mauvine in 1857, little was known of the chemistry of dyes and infact the constitution of mauveine was not establshed until many years later. As more and more dyes were discovered and their properties studied, working rules emerged, whereby colour and dyeing properties could be related with structure.

Graebe and Libermmann[19] in 1868 observed that all organic dyes then known were decolourised on reduction and they suggested that colour is associated with unsaturation. Witt[21] in his own studies associated the colour of organic dyes to the presence of certain unsaturated groups of atoms which he called chromophores[21]. Examples of such groups include the nitro (-NO_2), nitroso -(-N=O), azo -(-N=N-)-, ethylene -(-CH=CH-)- and carbonyl groups -(-C=O). This however, is in good agreement with

Graebe and Libermann suggestion. Witt[21] ascribed the name chromogen to compounds containing such groups and showed that although they are coloured, they do not behave as dyes for fibres unless they are also substituted by basic or weakly acidic groups such as $-NH_2$, $-N(CH_3)_2$, or OH. The presence of these groups greatly increase the colour yielding power of a chromophore and for this reason they are called auxochromes. The presence of the auxochromes make the compound to have affinity for the substrate and also intensify the colour.

Nietzki[22] pointed out that the colour of dyes is deepened by the incorporation of substituents, the deepening effect being roughly proportional to the increase in molecular mass[22]. Certain groups however, when incorporated produce hypsochromic effect (i.e. shift of λmax to shorter wavelength) and serve as exception to this rule.

The next major development was the quinoid theory advanced by H. E. Amstrong[23]. Amstrong[22] pointed out that most dyes can be represented in a quinonoid form since quinones were known to be component of several colours. This is referred to as quinonoid theory, however, Amstrong did not explain the reason why they gave rise to colour.
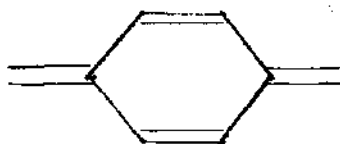
(v)

Baeyer[24] in 1907 put further the view that colour might be due to "rhythmic" vibration in ether caused as a result of oscillation of the quinonoid condition between two benzene ring.[24] In the same year Hewitt and Mitchell observed that in azo dyes the depths of colour increases with the length of a chain of alternating single and double bonds (conjugated chain) and ascibed this effect to the dimunition in frequency of the chief oscillation[25]. This was confirmed in quantitative experiments by Vatson and Meek[13].

More recently Brooker et al found that in a series of methine dyes of general structures (vi), in which n has values of 0, 1, 2 and 3, the wavelengths of absorption maximal in methanol solution are 423nm, 557.5nm, 650nm and 758nm respectively[26].
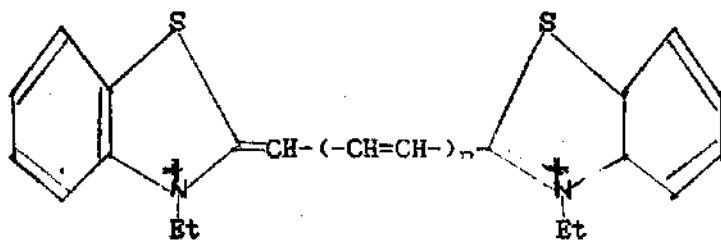
(vi)
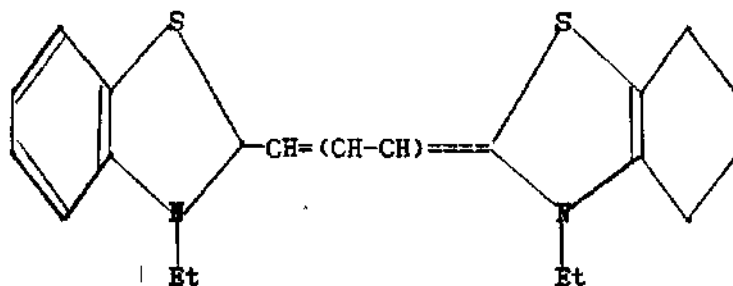
Watson[14] also pointed out that the depth of colour is affected by other factors beside the length of the conjugated chain because if the dye molecule is weighted without altering the lengths of the conjugated chain, vibrations become slower and the shade is rendered bluer. Thus on brominating fluorescein, erosine with much deeper hue is obtained. This system was likened to a stretched string whose vibrations are slowered by the increase in either its length or weight with the tension kept constant. The presence of an additional auxochrome as in polyhydroxyanthraquinone or the modifications of an auxochrome as when an amino group is alkylated or arylated has also a marked deepening influence on hue[5].

Although most dyes contain an axochrome the presence of such groups is not a precondition for dyeing ability because many vat dyes with one or more keto groups as chromophores have no auxochromes. However, on reduction to leuco form the vat dye possesses the hydroxyl group which function as the auxchrome during dyeing.

It is now usual to regard the molecule of a dye as consisting of a chromophoric system in which the classical chromophore forms part of a conjugated system of a single and double bonds often terminating in a polar atom or group which can exist in two adjacent states of covalency.

1.4.2 Resonance theory in relation to colour

Bury (1935)[39] pointed out that majority of dyes existed in resonance hybrids i.e a compound having two extreme structures, but in between the extreme structures are some intermediate ones. e.g benzene exists in two extreme structures with respect to bond

|(a)   (vii)   (b)
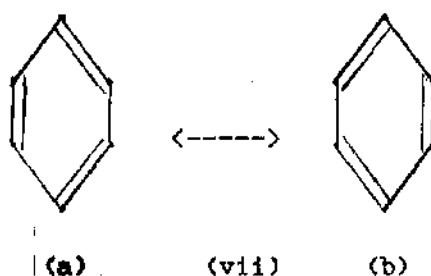
distribution within the molecule. There is no difference in the chemical properties between the two forms. In fact benzene does not exist in either of the forms but as a resonance hybrid of the two, a condition described as a mesomeric state. The energy of the mesomeric state is less than that of either of the two structures shown above (vii). In its simplest form, resonance theory states that if an unsaturated organic compound can exist in two extreme canonical forms, then the closer the two forms are in energy, the smaller will be the gap between the ground and first excited state, i.e the more bathochromic will be the absorption band, e.g.

$$R_2\overset{..}{N}-(CH=CH)_nCH=\overset{+}{N}R_2 \quad \longleftrightarrow \quad R\overset{+}{N}=CH-(CH=CH)_n-\overset{..}{N}R_2$$

(a)   (viii)   (b)
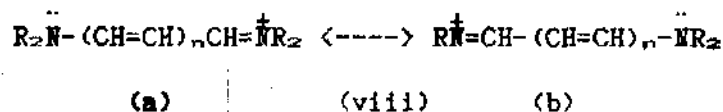
The two structures (viiia and b), are equal in energy, and thus resonance theory suggests that these should absorb at longer wavelengths.

Another good example of the effect of resonance on colour is shown by the indicator methyl organge, and also demonstrating the mode of action of the azo group chromophore. In alkali medium methyl orange exist in the form (ix):

$$-O_3S-\bigcirc-N=N-\bigcirc-NMe_2$$
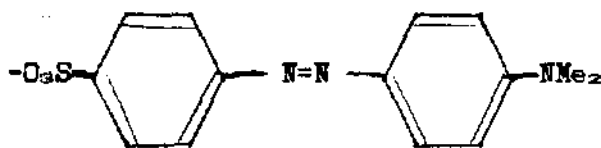
(ix)

The resonance is restricted to valency changes within the benzene rings. As acid is added, as in acid-base titration, there is excess hydrogen ions in the system resulting in the protonation of the azo group chromophore. There is charge transfer so that the methyl orange can exist in two canonical structures (x):

$$HO_3S-\bigcirc-NH-N=\bigcirc=\overset{+}{N}Me_2$$

$$\updownarrow$$

$$HO_3S-\bigcirc-\overset{+}{N}H=N-\bigcirc-NMe_2$$
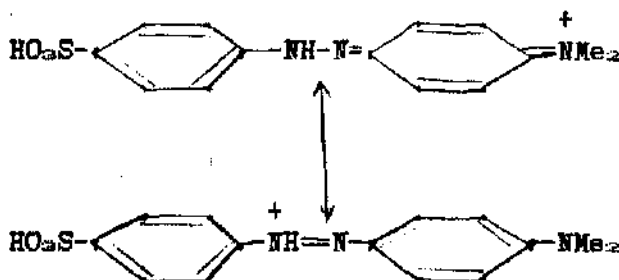
(x)

These structures are intensely coloured and responsible for the characteristic colour change in acid-base titration when methyl orange indicator is used. The association of colour with resonance is due to the fact that the energy required to bring the mesomeric structure from ground state to excited state is comparatively low, hence absorption in the visible and then colour.

In general, according to resonance theory, the more the structures that could be drawn for a molecule i.e the higher the resonance energy, the lower the transition frequency and hence the more bathochromic a dye becomes.

A mathematical analysis of resonance between members of a series of ionic structures in polymethines and other dyes have also been carried out by means of the valence bond method[27,29], and the results of this work are in good agreement with the observed absorption characteristics of dyes concerned[29]. The resonance theory is however, impracticable for quantitative prediction of colour-structure relationship being very useful only in the qualitative treatment.

The quantitative treatment of colour-structure relationship has been approached with greater success by the molecular orbital methods.

1.4.3 Molecular Orbital Method in relation to colour

The molecular orbital method assumes that a molecular orbital is formed by the overlapping of outer singly occupied orbitals of two or more atoms, resulting to several types of

molecular orbitals. This is called the linear combination of atomic orbitals (LCAO) method[30]. Each molecular orbital has a characteristic shape, size and energy and are denoted by symbols such as σ(sigma), $\sigma*$ (sigma star) or antibonding orbital π-bonding and $\pi*$ (pi antibonding). Atomic orbitals that are incapable of combination such as those containing inner shell or lone pair electrons are described as non-bonding (n) orbital. The order of orbitals energy is as shown below. In the lowest or

$$\sigma*$$
$$\pi*$$
$$n \qquad \text{Increasing energy}$$
$$\pi$$
$$\sigma$$
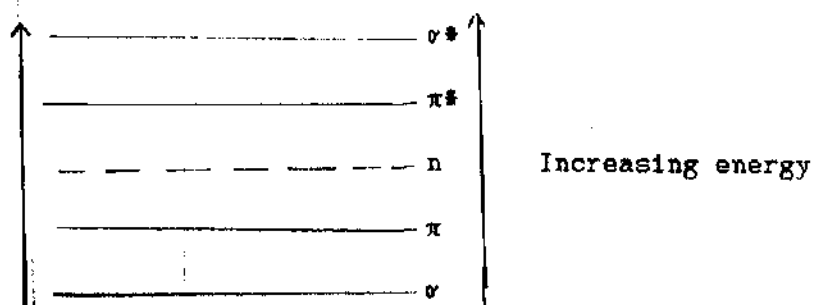
ground electronic state of most organic molecules all the bonding and non-bonding orbitals are fully occupied while the antibonding orbitals are empty[31]. Absorption of a quantum of energy of a wavelength within the visible region causes a σ or π bonding electron associated with a covalent bond or a non-bonding (n) electron to be promoted to an empty antibonding level, thus bringing about the excited state.

In simple molecules, the electronic energy level are in the order $\sigma < \pi < n < \pi* < \sigma*$. Transition of the type n $\longrightarrow \pi*$ normally give rise to spectral bands at longer wavelengths than

those due to transition $\pi \rightarrow \pi*$ or $\sigma \rightarrow \sigma*$ (in the u.v. region).

In dye molecules the $\pi \rightarrow \pi*$ is more probable since there are as many π-levels as there are conjugated atoms. The energy gain ΔE is in the first approximation equal to the energy difference between the two molecular orbitals concerned in the transition and is related to the wavelength (λ) of the light absorbed by the equation

$$\Delta E = E\omega_A - E\omega_D = \frac{hc}{\lambda} \qquad \ldots\ldots\ldots (1)$$

where ω_A and ω_D are the acceptor and donor orbitals wavefunction respectively, h = planks' constant and c = velocity of light.

In the molecular orbital (MO) method, the Huckel method called "linear combination of atomic orbital method" (LCAO) leads to a more successful prediction of colour in organic compounds[33].

1.4.4 Linear Combination of Atomic Orbital (LCAO)

Huckel Molecular Orbital (HMO) Method

In this approach, the assumption is made that a molecular orbital wave function (ω) can be expressed as a linear combination of the component atomic orbital wave function (ϕ). Thus for a system of n overlapping p orbitals, with each atomic orbital having the wave function ϕn, ω can be written as a linear sum

$$\omega = c_1\phi_1 + c_2\phi_2 + \ldots\ldots c_n\phi_n \qquad ------ (2)$$

where c is the mixing coefficient and the energy or eigein value, E, of the molecular orbital is defined by the equation

$$H\omega = E\omega \qquad -----------\quad (3)$$

where H = Hamitonian operator. This is equal to

$$E = \int_{-\infty}^{+\infty} \frac{\Sigma_n c_n \emptyset_n + \Sigma_n c_n \emptyset_n d\tau}{\int_{-\infty}^{+\infty} [\Sigma_n c_n \emptyset_n]^2 d\tau} \qquad ---------\quad (4)$$

ω = wave function

Thus the energy of a molecular orbital is expressed in terms of the atomic orbital wavefunction. In short the HMO method provides the π-orbital energies of a molecule, and these energies can be expressed in the general form[36].

$$E_n = \alpha + x_n\beta \qquad ....\quad (5)$$

The transition energy for the promotion of one electron from one orbital to the other is then given by the energy difference between the two relevant π orbital energies. In its original form the HMO has been applied specifically to hydrocarbon system in which there is some justification for assuming that all atoms have the same coulomn integral α and all pair of adjacent atoms have the same resonance integral (β value). The HMO has also

been applied successfully to symmetrical cyanines type molecules because of the high tendency to bond length equalisation along the conjugated chain of this system. For other system LCAO treatment is less successful and generally not applicable.

1.4.5 The Pariser-Parr-Pople (PPP) Self-consistent Field Molecular orbital method

The Huckel molecular orbital suffers serious disadvantages especially in the calculation of electronic transition energies and thus can only be used in the prediction of spectra for some few cases. One of these more reliable methods is that due to Periser-Parr-Pople[34] and although this procedure retains the $\sigma-\pi$ separation principle of the HMO method, it has the great advantage of including interelectronic interaction in the calculations.

The PPP method is based on the same LCAO approach i.e, it is assumed that each molecular orbital can be expressed as a linear sum of the individual atomic orbital. Thus a set of secular equations are obtained which are similar in general form to the HMO equations, differing only in the energy terms α, (coulomb integral) β (resonance integral) which include repulsion energies due to the presence of electronic interaction.

Thus it can be shown that the transition energy for the promotion of a single electron from orbital i to orbitals j without reversal of spin (singlet-singlet transition) is given by[35]:

$$\Delta E_{i \longrightarrow j} = (E_j - E_i) - \tau_{ij} + 2\delta_{ij} \quad \dots \dots \dots \quad (6)$$

E_j and E_i are the eigen values for orbitals j and i respectively. The energy quantity τ_{ij} is the total repulsion energy between the molecular orbitals i and j assuming there is one electron each.

The PPP method is particularly suitable for the treatment of large conjugated molecules and can be used routinely and inexpensively. Additional advantages of the method when compared with the HMO or FEMO procedures are:

(1) The ability to handle heteroatomic systems reliably.

(2) The ability to distinguish molecular geometry like the cis-trans isomers unlike the HMO or FEMO

(3) The ability to distinguish between singlet and triplet states.

The disadvantage of the PPP method is a host of assumption and approximations made in the calculation to arrive at reasonable prediction of colour in organic compounds.

1.4.6 The Free Electron Method

The free electron method provides a somewhat simpler approach by restricting attention to the conjugated π-electron systems which are regarded as mainly responsible for the colour of dyes. Assuming that electron are free to move within the conjugated system, Kuhn[36] showed that the wavelength of the

maximum of the first absorption band ($\lambda 1$) can be calculated by means of the Schroedinger expression[40]:-

$$\lambda 1 = \frac{8mcl^2}{h(n + 1)} \quad \ldots\ldots\ldots\ldots (7)$$

and the transition energy is given by

$$\Delta E_{n\longrightarrow n+1} = \frac{h^2}{8ml^2} (2n + 1)$$

where m = mass of an electron, c = velocity of light, h = plank's constant, n = number of π-electrons, l = length of the conjugated chain.

Calculations with this method of appoach have shown good agreement with observed values of lamda (λ) maximum for several cyanine and triphenylmethane dyes and it may become of practical value in the study of dyes in other classes like the cyclic conjugated system by assuming that the electron is confined in a circle of constant potential.

One important source of error in this method stems from the assumption that all bond lengths along the molecular axis are identical, which inturn assumes a constant potential energy along the chain. This situation certainly does not hold for polyenes which are known to exhibit strong bond alteration.

The development of synthetic dyes were hampered by the lack of suitable theory to explain light absorption process untill the development of quantum mechanic - "The wave-particulate theory of electron" by Schroedinger[37]. The earlier theories were qualitative in treatment of light absorption process and stem from the valence bond or resonance theory introduced by Bury[38].

1.5.0 Chemical classification of dyes

The classification of dyes on the basis of the type of chromophoric group present in the dye molecule is referred to as chemical classification. The most important group of dyes based on this method of classification are discussed below.

1.5.1 Azo dyes

The azo dyes account for more than 60% of the total dyes known to be manufactured. They are characterized by the presence of one or more azo (-N=N-) chromophoric group(s) in the dye molecule which form bridges between organic residue, one of which is usually an aromatic nucleus. They are further subdivided into monoazo, disazo, trisazo or polyazo depending on whether there is one, two, three, or more azo chromophoric group respectively in the dye molecule. They cover the whole of the visible region of the spectrum. Thus yellow, red, blue, green etc can be synthesized by introducing a suitable substituents in the acceptor and donor ring of the chromogen.

They are manufactured by diazotising primary aromatic amine and coupling to suitable coupling component such as phenols, naphthols, arylamines and active methylene compounds. Another method of synthesis is the oxidative coupling reaction developed by Hunig, this method however, is not widely used.[39]

1.5.2 Anthraquinone dyes

The characteristic chromophoric group present in the anthraquinone series consist of one or more carbonyl group $-\overset{O}{\underset{}{C}}-$ in association with a conjugated system, one of which is an aromatic nucleus or condensed aromatic rings (xi).
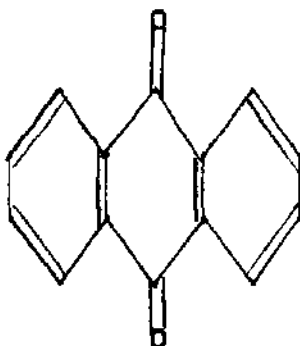
(xi)

Anthraquinone is a faintly yellow compound and does not possess dyeing properties until it is being introduced with electron donors such as -OH, NH_2, NR_2, NHAr etc. The introduction of these substituents involve unit processes such as hydroxylation, nitration, reduction, etc.

These electron donors also provide the compound the ability to absorb in any desired region of the visible spectrum. Thus as

with the azo dyes, it is possible to have yellow, red, blue, and green anthraquinone dyes. They are often synthesized by cyclisations and reduction reactions between components containing several reactive positions, consequently, some of the commercial products of anthraquinone dyes are mixtures[49].

1.5.3 Triaryl Methane Dyes

These dyes are characterized by their chromophoric system consisting of a central carbon atom linked to three aromatic rings and usually contain two or three substituted amino groups. The hue and dyeing properties depends on the nature and number of auxochromic groups such as -OH, NR_2, NHR, NH_2 NHAr or alkyl group or a combination of these in the 3-para position.[41]

Typical examples of this class of dyes are malachite green where X = Y = NR'R, V = H in structure (xii).
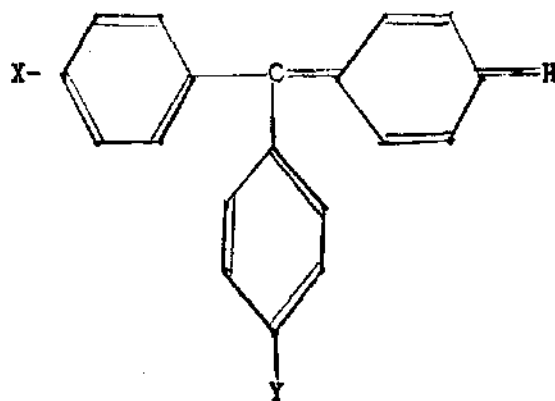
(xii)

When X = Y = OH, the structure (xii) is known as phenolphthalein and a popular colour known as magenta results when X = Y = W = NH₂ in the above structure (xii).

All the dyes of this series are derived from the triphenyl-methane or tripenylcarbinol which are both colourless. They can also be synthesized by condensation of benzene with carbontetra-chloride to form the aluminium complex of triphenylmethylchloride which is then reduced to the hydrocarbon by ether[42(a)]. The application of triaryl methane dyes is in dyeing of silk, wool, paper, office stationary, cosmetic and in printing ink.

1.5.4 Nitroso dyes

The charateristic feature of nitroso dyes is the presence of the nitroso chromophoric group (-N=O) in conjugation with aromatic residue.

$$R \longrightarrow N = O$$

(xiii)

The shade produced on fabric by these dyes depend on the substituents attached to R, which is usually an aromatic nucleus. They are prepared by nitrosation reaction of the aromatic compounds. A few green dyes of the nitroso class are of importance, for instance, a mordant dye discovered by Fuchs[42(b)]

is obtained by nitrosating β-naphthol in the one position and converting the product into its bisulphite derivative. The dye gives brownish olive shade on a chromium mordant or yellowish green with iron. The fastness properties of the nitroso dyes are excellent on most fabrics.

1.5.5 Nitro dyes

These are phenols or amines containing the nitro (-NO$_2$) group in the o and/or p-positions in conjugation with aromatic residue. The water soluble members of the series are acid colours while the insoluble members are useful pigments. The nitro chromophoric group is often found in dyes having a different chromophoric group. In a few dyes however, the nitro group is the only chromophore, a hydroxyl or amino group is then invariably present as auxochrome and resonanate between two or more tautomeric forms giving rise to colour. The first commercial nitro dye was picric acid[43] (CI 110305) (3,5-dinitrophenol (xiv) formerly used as an acid dye giving greenish yellow on silk.

OH

NO$_2$ NO$_2$
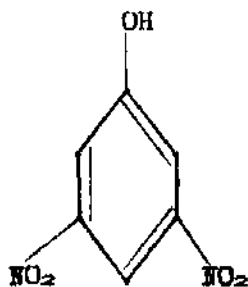
(xiv)

1.5.6 Methine, polymethine and cyanine dyes

The methine, polymethine and cyanine dyes fall into one group since their chromophoric system is characterized by an acyclic link of methine group (-CH=) with a structure (xv).

$$-(=C-C-)n-$$
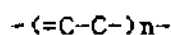
(xv)

where n = 0 or a positive integer or (xvi)

$$-(C=C-)n-$$ where n = a positive integer

(xvi)

The cyanine dyes are known for their photographic sensitizing action and form an important class of dyes with links or chains of the first type containing an odd number of carbon atoms attached to two basic heterocyclic residues. The first cyanine dye was discovered by W. Grevile by heating crude quinoline containing lepidine with isoamyl iodide and caustic soda[44]. The cyanines are not as suitable as the isocyanines in photographic action because of their tendency to produce fogging on photographic plate[45].

The methine and polymethine are used for dyeing cellulose acetate e.g Celliton fast Yellow 7G (I.G)[46], CI Disperse Yellow 31, (CI 48000) is used to dye acetate and nylon with good fastness to light, gas fumes and hot pressing properties. In general, the application of polymethine dyes for the dyeing of

textiles is limited by the fact that they generally have very poor light fastness, but by choice of a suitable heterocyclic nucleus, the light fastness properties can be enhanced greatly. For example, the aza analogue have outstanding fastness properties.

1.5.7 Sulphur dyes

These are obtained by heating certain organic compound with sulphur. This class of dyes are characterized by the presence of a sulphur linkage serving as the chromophore within the dye molecule. However, little is known about the chemical structure of these dyes, despite their long history. The first commercial sulphur dye made in France by Croissant and Bretonniere (1973) was produced by heating variety of organic materials of animals or vegetable origin with aqueous sodium sulphide or polysulphide. The shade obtained could often be varied by adjusting the temperature and duration of heating [47,48] Sulphur dyes can be applied to cotton and other fibres by the vating processing using sodium sulphide bath.

1.5.8 Indamine and Indophenol

This consists of derivatives of benzoquinone mono or diimine or corresponding napthalene compound. Dyes of this class are mainly used for color photography and also as intermediates for sulphur dyes.

(xvii)   (xviii)
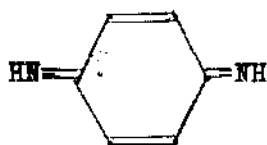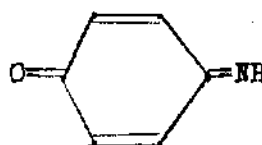
indamine   indophenol

Typical example of this class of dyes is CI solvent Blue 22 (CI 49705) (xix) which is obtained by oxidising a mixture of N,N-diethyl-p-phenylenediamine and α-naphthol in alkaline solution. It is used for colouring spirits, lacuers, fats and waxes.
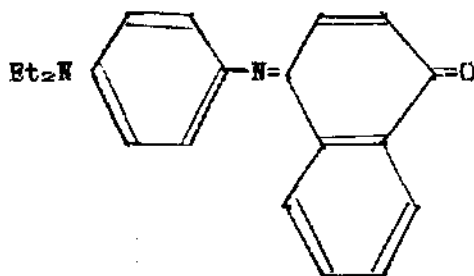
(xix)

1.5.9 Stilbene dyes

The stilbene dyes are characterised by the presence in their structure of the stilbene (xx) residue. The first stilbene dye was discovered by J. Walter (1983) and is still manufactured by many firms under various brand names such as curcumines (FBY) CI Direct Yellow 11, (CI 4000), it gives yellow shade of low fastness to light and is widely used for dyeing and printing of papers.
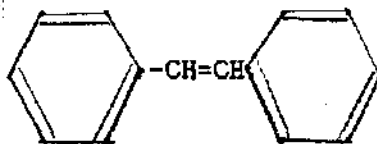
$$\text{(xx)}$$

Other chemical class of dyes include:-

- The phthalocyanines

- Quinoline dyes

- Xanthene dyes

- Thiazole dyes.

1.6.0 Colouristic classification of dyes

The classification which is based on the method by which the dye is applied to the fabric and also to the type of fabric to which apllication is made is known as colouristic classification. This is of interest to the dyers than the chemical classification. Based on this method of classification, the following are of paramount importance.

1.6.1 Azoic dyes

The term azoic describes a system of producing an insoluble azo dye in situ i.e inside the fibre. One intermediate, the coupling component having affinity for cellulosic fibre being padded onto the material, the material is always impregnated with a coupling component and dried and then

brought in contact with a solution of the second intermediate known as the diazo component where upon the insoluble dye is formed. The major application of this dye is in dyeing and printing of cellulosic fibres, especially cotton, giving bright, intense hues and shade of high standard of fastness to light and wet treatments.

1.6.2 Vat dyes

Vat dyes are insoluble dyes which are converted to the leuco form by vatting using sodium hydrosulphite. The application of these dyes involve three different stages viz: (i) reduction to leuco form, (ii) adsorption of the leuco dye by the fibre and (iii) oxidation of the dye to insoluble colour pigment inside the fibre. The water soluble leuco esters are valuable for producing pale shades, or for colouring materials that are difficult to penetrate. The original dye is regenerated by simultaneous hydrolysis and oxidation. The dyes possess outstanding fastness properties due to the fact that after oxidation the dyes remain permanently in the insoluble form inside the fibre.

1.6.3 Acid dyes

Acid dyes are water soluble, the solubility depends on one or more sulphonic or carboxylic groups present in the dye

molecule. These dyes are used in dyeing textiles such as wool, silk, polyamide, acrylic, and leather.

They are normally applied from a dyebath containing tetraoxosulphate (VI) acid, formic acid or acetic acid (ethanolic acid). Neutral and even slightly alkaline dyebaths may sometimes be used. These dyes give very bright hues on substrate with wide range of fastness properties ranging from poor to very good fastness.

1.6.4 Direct dyes

The direct dyes are also called substantive azo dye because they have substantivity for cellulosic materials. They are water soluble due to the presence of two or more sulphonic group in their structure. They are used in dyeing cellulosic fibres from aqueous dyebath using approximately neutral condition. Inorganic salts are often used to enhance exhaustion onto the fibre. The substantivity of the dyes onto the fibre depends on the combination of van der waals forces, hydrogen bonding and possibly physical entrapment by aggregation. The fastness properties of direct dyes are not outstanding and thus for quality dyeing, vat, azoic, and reactive dyes are preferred.

1.6.5 Reactive dyes

These are dyes that form covalent linkages with the fibre molecule and because of the covalent attachment, the fastness

properties of these are excellent on all the substrates to which they are applied. They are also water soluble and are used in the dyeing and printing of cellulosic fibre, wool, silk and nylon. The presence of hydroxyl or amino group/carboxylic group play a role in the attachment of the reactive dyes to the fibres. The major problem in the use of reactive dyes is the reaction of the dye with water instead of the substrate and this leads to hydrolysis, however, this can be minimised when dyeing by exhaustion technique, by adding the alkali required for the fixation at a later stage of dyeing process or by using small liquor ratio.

1.6.6 Disperse dyes

This is a class of water insoluble dyes originally introduced for dyeing cellulose acetate and usually applied from fine aqueous dispersion.[49] Recently work have also established that such dyes slightly dissolve in water and the degree of solubility influence the dyeing and leveling properties. Disperse dyes belong to three main classes, viz, nitroarylamine, azo and anthraquinone, almost all contain amino or substituted amino groups, but do not contain solubilising groups such as sulphonic acid or carboxylic acid groups. They are usually ground in a mill to fine particle size $(1-10\mu)$ in an aqueous medium containing a dispersing agent, the later being acting as a restraining and retarding agent. The principal uses of disperse dyes are in the

dyeing of cellulose acetate, nylon, polyester and polyacrilonitrile fibres. The fastness properties vary on different fibres, for example the washing fastness is higher on polyester than on nylon and the rate of dyeing is in reverse condition.

1.6.7 Ingrain dyes

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

1.6.8 Oxidation dyes

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

1.6.9 Basic dyes

They are so called because they give coloured cations in aqueous solution; hence these dyes are often referred to as the cationic dyes. They are used to dye negatively charged fibres such as modified acrylonitrile fibres.

1.6.10 Chrome dyes

In the Colour Index these dyes are classified as "mordant dyes", but since the only mordants used to any extent commercially in textile dyeing are chromium compounds the term "chrome dyes" is generally used. The essential feature of these dyes is that the basis of their application is the formation inside the fibre of a very stable co-ordination complex of the chrome dye and chromium from the mordant. After the application of the dye to the substrate, they are essentially irreversible whereby dyeings of very high wet fastness are obtained.

1.7 Aims and objectives of the present work

Dyes are used in large quantities by the textile industry in Nigeria and no single manufacturing plant is in the country at present, therefore a large amount of hard currencies are spent for the importation of these vital materials for our industries. The main aims of the present work is to study the methods which can be used to synthesis some useful dyes for the local consumption by our textile industry.

The principal raw materials for the synthesis are derived from petroleum which can be obtained in large quantities from our petrol-chemical plant in Nigeria. The conversion of the primaries to intermediates can be done locally and the final stage which is the conversion of the intermediates to useful dyes can similarly be done successfully.

In the present work, efforts have being made to synthesise some azo and methine dyes and the effect of incorporating different substituents in different positions of the dye chromogen. Another objective of the present study is to examine the effect of these substituents on the colour and fastness properties of the dyes synthesised. Some azo dyes are used as indicator e.g methyl orange because of their sensitivity to acid-alkali, it is also the objective of the present study to examine the effect of acid on the absorption wavelengths of both methine and azo dyes synthesised. The effect of solvent polarity on the absorption wavelengths of the dyes was also investigated.

This research is of necessity in view of the need for a successful dye industry take off in a developing country like Nigeria. This then calls for exploring the possibility of synthesising and applying dyes with improved fastness to different agencies.

It is my hope that apart from testing these dyes for textile dyeing, the application could be extended to photographic printing technology, especially the methine dyes.

CHAPTER TWO

EXPERIMENTAL

2.1.0 General Information

2.1.1 Chemicals

Bromine

Iodine crystals

Ethylacetoacetate

Acetophenone

Priopiophenone

Acetone

Thiourea

Ammonia solution

Potassium hydroxide pellets

Ethanol (95%)

Tetraoxosulphate (VI) acid (concentrated)

Aniline

N,N-dimethyl aniline

N,N-diethyl aniline

Acetic acid glacial

Propionic acid

Chloroform

Hydrochloric acid

Phthalic anhydride

Triethylamine $N(CH_2CH_3)_3$

Toluene

Malononitrile $CH_2(CN)_2$

Sodium acetate (anhydrous) CH_3CO_2Na

Sodium acetate trihydrate $CH_3CO_2Na.3H_2O$

4-N,N,-Dimethylaminobenzaldehyde

4-Hydroxybenzaldehyde

2-Methoxybenzaldehyde

4-Nitro-2-aminobenzaldehyde

4-Nitrobenzaldehyde

Dimethyl formamide

Dichloromethane

4-Acetamido benzaldehyde

Sodium trioxo carbonate (Na_2CO_3)

2.1.2 **Materials**

Polyester fabric

Nylon 6 fabric

100% cotton

2.2.0 Characterisation of Intermediates and Dyes

2.2.1 Melting point determination

The melting point of various intermediates and dyes were determined using Gallenkamp melting point apparatus - open-tubular in the department of chemistry, A.B.U., Zaria.

2.2.2 Ultraviolet-Visible absorption spectroscopy

The UV-Visible spectra of the dyes in different solvents were recorded on uv-visible spectrophotometer Unicamp SP 800 in the department of chemistry, A.B.U., Zaria.

2.2.3 Infra-red spectroscopy

The infra-red spectra of thiazole intermediates and dyes were recorded in Nujol solution on Perkin-Elmer 710B Infra-red spectrophotometer in the department of chemistry, A.B.U., Zaria.

Indane-1,3-dione intermediates and dyes were recorded in nujol solution on Perkin-Elmer 710B Infra-red spectrophotomer in the department of chemistry Tafawa Balewa University, Bauchi

2.3 Dyeing of the fabrics

Dyeing was carried out on nylon 6, 100% cotton, and polyester fabrics using all the dyes synthesised in the laboratory at a liquor ratio of 1:50 with the 'dye master' in the Department of Textile Science and technology, A.B.U. Zaria. A 1%

stock solution of each of the dyes were prepared and 10cm³ was taken for each dye solution and put in the dyebath containing small amount of dispersing agent, enough water was then added to the dyebath to make up to 50cm³. After the dyebath is set, the fabrics (1gm each) were wetted out and excess water squeezed out with the aid of filter papers and then introduced into the dyebath this was done at a temperature of 50°C The temperature was then raised to the boiled over 15 minutes and dyeing continue at this temperature for 1 hour. After dyeing, the the fabric was removed and rinsed thoroughly with water and dried.

2.4 Transfer printing

A strip of whatman chromatography paper (4 x 4cm) was immersed for 2 minutes in 0.01M solution of the dye in dichloromethane (15cm³). The excess solution on the surface of the paper was squeezed off between two glass rods and the strip was allowed to dry at room temperature before being wrapped in a piece of polyester, nylon and cotton fabric and then enclosed in a metal foil (Aluminium foil).

The composite was placed between hot press plate suitable for transfer printing at 180°C for 40 and 60 seconds respectively. The transfer printed fabrics were rinsed with water, and dried.

2.5 Washing fastness test

All the dyeings were assesed for washing fastness by following the ISO No 3 test procedure[1]. The test was carried out using the linitest washing machine in the department of Textile Science and Technology, A.B.U., Zaria.

2.6 Preparation of 2-Amino-4-methylthiazole (1a)[2]

0.5 mole of halogen (I or Br) was added to a suspension of 1.0mole of thiourea (26g) in 100cm^3 of acetone. After the addition was complete, the reaction mixture was refluxed for 2 hours, the reflux condenser was removed and the open vessel was heated overnight on a steam bath. The heated mixture was then stirred slowly and 20g of solid sodium hydroxide pellets were added with cooling. The upper oily layer was separated in a separatory funnel and the aqeous layer was extracted three times with ether using a total volume of 300cm^3.

The dark red oil was combined with the ether extract and the solution was dried over 30g of solid sodium hydroxide and filtered under suction. The ether was removed by distillation from a steam bath and after a small fore-run, 2-amino-4-methylth-iazole (1a) was collected, filtered and recrystallised from ethanol. This gave a yield of 56% and the melting point was found to be 48°C (Lit.[3] m.pt 45°C)

2.7 Preparation of 2-Amino-4-phenylthiazole (1b)

0.2mole (28cm³) acetophenone and 0.4mole of thiourea (30.4g) were reacted with 0.2mole of halogen (I = 25.4g, Br = 20cm³)[54]. The reaction mixture was heated overnight on a steam bath, then diluted with water and heated again until most of the solid had gone into solution. The solution was then filtered, cooled and made alkaline with concentrated ammonia solution. The precipitated compound (1b) was filtered and recrystallised from absolute ethanol. Yield, 60%, m.pt. 170°C (Lit.[55] m.pt. 173-174°C).

2.8 Preparation of 2-Amino-4-phenyl-5-methylthiazole (1c)

The same procedure was followed as for the preparation of compound (1a) except that propiophenone was used instead of acetophenone. Yield, 48%; melting point 119-120°C (Lit.[56] 118-120°C).

2.9 Preparation of 2-Amino-4-methyl-5-carbethoxythiazole (1d)

The same proceddure as for compound (1b) and (1c) except ethylacetoacetate was used as the active methylene compound in this case. Yield, 53%; melting point 150-151°C. (Lit.[57] 147°C).

Vmax nujol >C=O 1710cm⁻¹

Table 1: <u>Yield and characterisation data for the thiazole</u>
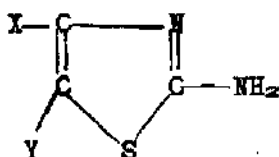
(1)

No	Substituents	Name	Yield (%)	M.Pt (°C)	ir
(1a)	X = CH₃; Y = H	2-amino-4-methyl-thiazole	56	48	
(1b)	X = C₆H₅; Y = H	2-amino-4-phenyl-thiazole	60	174	
(1c)	X=C₆H₅; Y = CH₃	2-amino-4-phenyl-5-methylthiazole	48	119-120	
(1d)	X =CH₃; Y=COC₂H₅	2-amino-4-methyl-5-carbethoxylthia-zole	53	150-151	>C=O 1710cm⁻¹

2.10 General Procedure for diazotisation of Amino Thiazole

Sodium nitrite (0.2mole, 1.38g) was added portionwise to concentrated tetraoxosulphate VI acid (20cm³) with stirring at 0°C so that no brown fumes were given off. The mixture was stirred for 10 minutes and then placed on a water bath and heated gradually until the temperature reached 65°C. Stirring was continued until all the nitrite had dissolved. Acetic acid and

propionic acid mixture 1:4 (20cm³) was added and the solution was cooled to 0°C. To this mixture was then added portionwise 0.2mole (1.38g) of the amino thiazle and the solution stirred for about 10 minutes to form the diazonium salt.

2.11 General Procedure for coupling

0.02mole of the coupling component [aniline (2cm³), N,N-dimethylaniline (2.5ml)] respectively was suspended in 200g of crushed ice in a beaker. to this suspension was added 5cm³ of concentrated tetraoxosulphate VI acid followed by the addition of the diazonium ion solution with stirring. The precipitated dye (2), was filtered with sintered glass funnel porosity 4. The dyes were purified by column chromatography and recrystallised from suitable solvents. Yield, melting point and characterisation data for the dyes are summarised in Table 2.
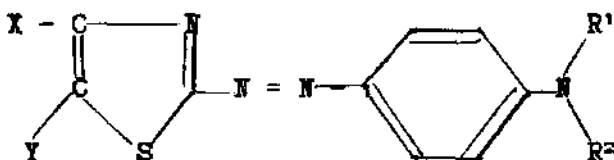
(2)

Table 2: Yield and characterisation data for the azo dyes

Dye No.	:Yield: m.pt : ir : U.V
	: (%) : °C : :
2(a) X = Me, Y = CO$_2$C$_2$H$_5$, R^{1}R^2 = H	: 35 :178-179:1710 :180 n->π*
	: : :>C=O :300 π->π*
2(b) X = Ph, Y = H, R^{1}R^2 = H	: 40 : 196 : :
2(c) X = Me, Y = H, R^{1}R^2 = Me	: 30 :136-137: :
2(d) X = Me, Y = CO$_2$C$_2$H$_5$, R^{1}R^2 = Me: 55 :168-169:>C=O :190 n->π*
	: : :1715 :
2(e) X = Ph, Y = H, R^{1}R^2 = Me	: 50 : 151.5 : :
2(f) X = Me, Y = H, R^{1}R^2 = Et	: 45 : 119 : :
2(g) X = Me, Y = CO$_2$Et, R^{1}R^2 = Et	: 48 :124-126:>C=O :
	: : :1685 :
2(h) X = Ph, Y = Me, R^{1}R^2 = Et	: 52 :189-190: :
2(i) X = Ph, Y = H, R^{1}R^2 = Et	: 43 : 160.5 : :

2.12.0 Preparation of Active methylene compounds

2.12.1 Preparation of 1,3-Indanedione

Triethylamine (278cm^3) and acetic anhydride (95cm^3) were stirred together on a water bath. Phthalic anhydride (145g) was added with stirring followed by dropwise addition of acetoacetic ester (126.5cm^3) at a temperature between 30-35°C for 15minutes.

The mixture was heated to 75°C for 1½hrs and cooled to 40°C. The resulting deep orange brown solution was poured into the mixture of the ice and water (500cm³) containing hydrochloric acid (190cm³), effervescence occured and on cooling overnight, the product was precipitated out and was filtered off as a yellow solid. The precipitate was washed with water (3 x 250cm³) then with toluene (500cm³) in small portions untill the brown oil was removed. The precipitate was finally washed with petroleum ether (b.p. 60-100°C), the crude product was recrystallised once from toluene to give indane-1,3-dione as a yellow needle. The yield obtained was (105.2g, 72%), m.pt. 132-134°C. (Lit⁹⁹ 129-132°C).

Vmax nujol >C=O 1710 cm⁻¹

2.12.2 Preparation of 3-oxo-Δ¹,³-Indandedione-malononitrile

Anhydrous sodium acetate (16g) was added to a stirred mixture of 1,3-indanedione (21.9g), malononitrile (19.8g) and absolute alcohol (250cm³) at 22°C. An immediate red colouration occured and the suspended solid slowly dissolved. After 40 minutes, the mixture was diluted with water (500cm³) and acidified to pH 1-2 by the addition of HCl. The suspension was stirred for 10minutes and the solid material filtered off and washed thoroughly with water. The crude material was recrystallised twice from acetic acid to give 3-oxo-Δ¹,³-indanedione malononitrile as a colurless solid (26.4g, 90%). M.pt 232°C Lit⁵⁹ (223-229°C).

Vmax nujol >C=O 1700cm⁻¹

-C≡N 2210cm⁻¹.

2.12.3 Preparation of 2,2-Indane-1,3-diylidenebispropanedinitrile

A mixture of 1,3-indanedione (8.76g) and malononitrile (11.88g) in absolute alcohol (100cm³) was stirred at room temperature for 15minutes and sodium acetate trihydrate was added. The mixture was heated under reflux for 5 hours. After cooling, the blue solution was filtered to remove the monocondensation products. The filerate was acidified with HCl to pH 1-2. The white precipitate was filtered off washed with water untill the washing was blue. It was then dried to give the resulting 2,2-indane-1,3-diylidenebispropandinitrile as an off white solid (13g, 80%). An analytically pure sample was obtained by recrystallisation from acetic acid followed by vacuum sublimation. M.pt. 257°C.

Vmax nujol >C≡N 2220cm⁻¹

2.13 Condensation of benzaldehydes with active methylene compounds

2.13.1 Condensation of benzaldehydes with Indane-1,3-dione

0.03mole (4.38g) of 1,3-indadione was reacted with 0.03mole of 4-N,N-dimethylaminobenzaldehyde (4.41g), 2-methoxybenzaldehyde (4.1g), 4-acetamidobenzaldehyde (4.92g) and

4-hydroxylbenzaldehyde (3.66g) respectively in 50cm³ acetic anhydride with stirring at 60°C for 1hr. The resulting dye on cooling was filtered, washed with acetic anhydride and recrystallised from the same solvent to give series of dyes (3). The characterisation data for the dyes are summarised in Table 3.
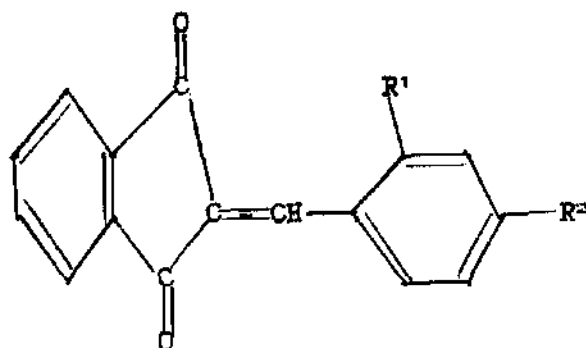
(3)

Table 3: Yield and characterisation data for methine dyes derived from indane-1,3-dione.

Dye No	Substituents	M.pt (°C)	Yield (%)	uv	ir
3(a)	R¹ = H, R² = N(Me)₂	218-220	80	132n->π*	1690cm⁻¹
					>C=O
3(b)	R¹ = H, R² = OH	223	75	190	1685cm⁻¹
				n-->π*	>C=O
3(c)	R¹ =H, R² = NHCOCH₃	189-192	68	194	1730cm⁻¹
				n-->π*	>C=O
3(d)	R¹ = OCH₃, R² = H	210-213	85	190	1700cm⁻¹
					>C=O

2.13.2   Condensation of Aldehydes with 3-oxo-Δ'.³-indandione

3-oxo-Δ'.³-indanedione (0.06mole, 11.76g) was reacted with 0.06mole of appropriate benzaldehyde [4-N,N-dimethylamino-benzaldehyde (8.82g), 2-methoxylbenzaldehyde (8.2g), 4-hydroxyl-benzaldehyde (7.32g), 4-acetamidobenzaldehyde (9.84g), and 2-nitro-4-aminobenzaldehyde (10.08g)] in ethanol at room temperature for ½hour with stirring and then heated to 60°C for another ½hour. The crystalline product was filtered off, washed with ethanol and recrystallised from ethanol to give dyes in series (4). Yield, m.pt. and characterisation data for the dyes are summarised in Table 4.
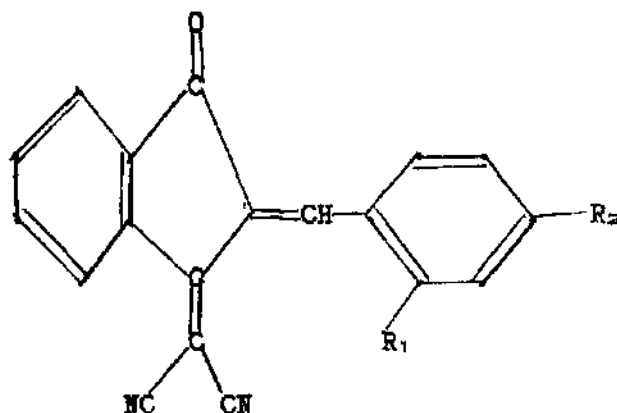
(4)

Table 4: Yield and characterisation data for dyes derived from
3-oxo-$\Delta^{1,\alpha}$-indanedione

Dye No	Substituents	M.pt °C	Yield %	ir	uv
4(a)	X = Me, Y = $CO_2C_2H_5$, R_1R_2 = H	178-179	35	1710	190
				$>C=O$	$n-\pi^*$
				str	300
					$\pi-\pi^*$
4(b)	X = Ph, Y = H, R_2 = H	196	40		
4(c)	X = Me, Y = H, R_1R_2 = Me	136-137	30		
4(d)	X = Me, Y = $CO_2C_2H_5$, R_1R_2 = Me	168-169	55	1715	190
				$>C=O$	$n-\pi^*$
				str	
4(e)	X = Ph, Y = H, R_1R_2 = Me	151.5	50		
4(f)	X = Me, Y = H, R_1R_2 = Et	119	45		
4(g)	X = Me, Y = CO_2Et, R_1R_2 = Et	124-126	48	$>C=O$	
				1685	
				str	
4(h)	X = Ph, Y = Me, R_1R_2 = Et	189-190	52		
4(i)	X = Ph, Y = H, R_1R_2 = Et	160.5	43		

2.13.3 Condensation of benzaldehyde with bispropandinitrile

The same procedure as in 2.13.1 is followed except that
2,2-indene-1,3-diylidenebispropandinitrile is used in place of
1,3-indandione. Yield, melting point and characterisation data
obtained for dyes (5) in this series are summarised in Table 5.
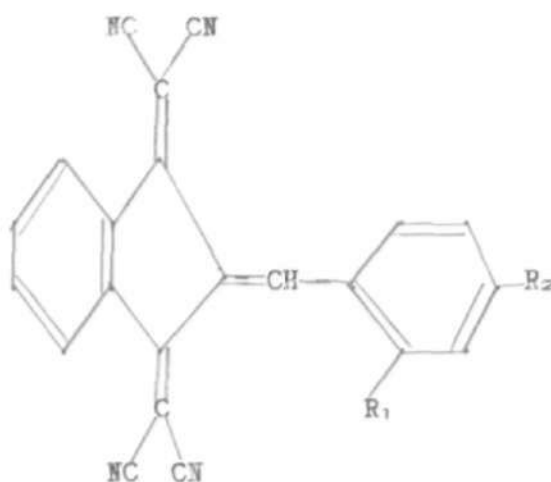
(5)

Table 5: Yield and characterisation data for dyes derived from
bispropaninitrile

Dye No	Substituents	Melting point	Yield	ir
5(a)	R_1 = H, R_2 = NMe$_2$	190°C	85%	C=C 1635cm⁻¹
				-C≡N 2220cm⁻¹
5(b)	R_1 = H, R_2 = OH	209–211°C	70%	-C=C- 1630cm⁻¹
				-C≡N- 2226cm⁻¹
5(c)	R_1 = OCH$_3$, R_2 = H	238°C	55%	-C=C- 1645cm⁻¹
				-C≡N- 2220cm⁻¹
5(d)	R_1 = NO$_2$, R_2 = NH$_2$	179	66%	-C=C- 1650cm⁻¹
				-C≡N- 2222cm⁻¹

CHAPTER THREE

3.0   RESULTS AND DISCUSSION

3.1 Synthesis of intermediates and Monoazo dyes

The intermediates used for the preparation of azo dyes are the derivatives of 2-aminothiazole. They are 2-amino-4-methylthiazole 1(a), 2-amino-4-phenylthiazole 1(b), 2-amino-4-phenyl-5-methylthiazole 1(c) and 2-amino-4-methyl-5-carbethoxythiazole 1(d). These were prepared by adopting Dodson method[o], in which ketones were reacted with thiourea and a halogen to give substituted 2-aminothiazole, as shown in scheme 1.

$$X - C = O$$

$$Y - CH_2 \qquad + \quad 2NH=C-SH \qquad + \quad I_2 \ (Br_2, \ Cl_2)$$
$$\qquad\qquad\qquad\qquad\qquad NH_2$$

$$X-C=N$$
$$Y-C \qquad C-NH_2HI \ (Br, \ Cl) \qquad + \ H_2O \ + \ NH=C-SH$$
$$\qquad S \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad NH_2HI(Br, \ Cl)$$
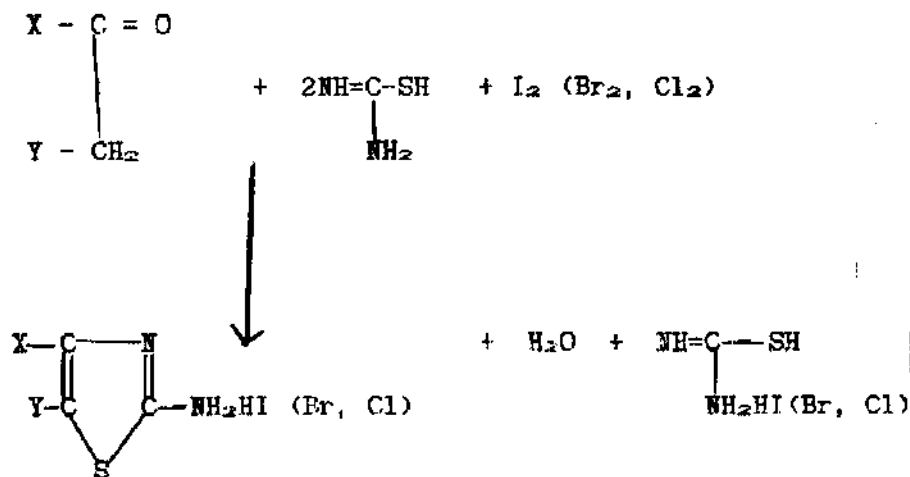
1(a)   X = CH_3,   Y = H

1(b)   X = C_6H_5,   Y = H

1(c)   X = C_6H_5,   Y = CH_3

1(d)   X = CH_3,   Y = $-CO_2CH_2CH_3$

Scheme 1.

In scheme 1, acetone, propiophenone, acetophenone and
ethylacetoacetate were reacted respectively overnight on a steam
bath with thiourea in equimolar ratio in the presence of half
mole of halogen. Iodine and bromine were used respectively for
the halogen in the present study. In each case, the 2-
aminothiazole obtained from the reaction mixture agreed in ir and
physical properties with those reported in the literature[61].

The 2-aminothiazole derivatives obtained were recrystallised
in absolute ethanol and diazotised satisfactorily at 0-5°C by
adding the solid aminothiazole to nitrosylsulphuric acid prepared
by adding concentrated tetraoxosulphate (VI) acid. The resulting
diazonium solutions were generally used within a few hours since
decomposition takes place on long standing even when cold.

The diazonium salts were coupled to aniline, N,N-
dimethylaniline and N,N-diethylaniline respectively to obtain a
series of dyes (2). Coupling was usually accompanied by some
evidence of decomposition, however, by careful addition of the
diazonium salts solution at 0-5°C to the solution of the coupler
in acetic-propionic acid mixture in ratio 1:4, good yields of the
dyes were obtained. Series of dyes (2) obtained using the
different 2-amino thiazole derivatives are summarised in Table
3.1

Table 3.1: Series of monoazo dyes derived from 2-aminothiazole

(2)
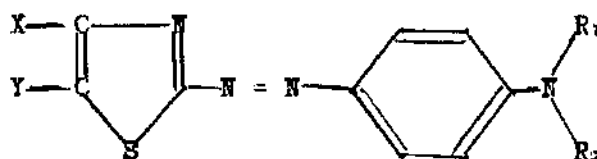
Dye No	Substituents		
2(a)	X = CH$_3$,	Y = -CO$_2$CH$_2$CH$_3$,	R$_1$ = R$_2$ = H
2(b)	X = C$_6$H$_5$,	Y = H	R$_1$ = R$_2$ = H
2(c)	X = CH$_3$,	Y = H	R$_1$ = R$_2$ = CH$_3$
2(d)	X = CH$_3$,	Y = -CO$_2$C$_2$H$_5$	R$_1$ = R$_2$ = CH$_3$
2(e)	X = C$_6$H$_5$,	Y = H	R$_1$ = R$_2$ = CH$_3$
2(f)	X = CH$_3$,	Y = H	R$_1$ = R$_2$ = C$_2$H$_5$
2(g)	X = CH$_3$,	Y = -CO$_2$C$_2$H$_5$	R$_1$ = R$_2$ = C$_2$H$_5$
2(h)	X = C$_6$H$_5$,	Y = CH$_3$	R$_1$ = R$_2$ = C$_2$H$_5$
2(i)	X = C$_6$H$_5$,	Y = H	R$_1$ = R$_2$ = C$_2$H$_5$

3.2 Visible absorption spectra for the azo dyes

The visible absorption spectra of the dyes were measured in ethanol and chloroform and their molar extinction coefficients were calculated from ethanol solution. The results obtained are summarised in Table 3.2

Table 3.2 Visible absorption spectra for the azo dyes

Dye No	Ethanol $\lambda max(nm)$	Chloroform $\lambda max(nm)$	Ethanol-chloroform $\Delta\lambda max$ (nm)	ϵmax in ethanol
2(a)	494	470	+ 24	5931
2(b)	504	494	+ 10	5762
2(c)	412	506	+ 6	5251
2(d)	526	510	+ 16	4512
2(e)	520	512	+ 8	5100
2(f)	523	514	+ 9	5700
2(g)	532	520	+ 12	5339
2(h)	500	492	+ 8	4520
2(i)	524	498	+ 20	5371

Dye 2(a) obtained by coupling aniline with 2-amino-4-methyl-5-carbethoxy-thiazole absorbs at 494nm in ethanol, when the methyl group in 3(a) was replaced by a phenyl ring and the electron withdrawing carbethoxyl group in position-5 was removed, the resulting dye 2(b) absorbs at 504nm in the same solvent indicating an increase in wavelength or a bathochromic shift of 10nm. In this case, the attachment of electron donating methyl group in the acceptor ring of the dye 2(a) causes a hypsochromic effect on the absorption maximum of dye 2(a) relative to dye 2(b). The increase in the wavelength of absorption observed for

dye 2(a) in comparison with 2(b) can be attributed to the increase in the conjugation of the dye molecule by the incoporation of the phenyl ring.

This result is comparable to that obtained on the effect of conjugation on the absorption maxima of cyanine dyes by L.G.S Brooker[62,63]. Qualitatively, as conjugation increases the ground electronic state of the molecule is lowered even further due to stabilisation resulting from a rapid increase in the number of charged structures. This makes the difference in energy of the excited electronic state from the ground electronic state, ΔE becomes progressively smaller and hence the bathochromic effect.

In dye 2(d), the electron donating ability of the coupler in 2(a) has been enhanced by replacing the simple aniline with N,N-dimethylaniline and the new dye 2(d) aborbs at 526nm, indicating a bathochromic shift of 32nm relative to dye 2(a). Comparison of dye 2(d) and dye 2(c) also reveals the effect of the electron withdrawing carbethoxy group in position-5 of dye 2(d), and in this case dye 2(c) without the electron withdrawing groups in the acceptor rings shows maximum absorption at 512nm and when the electron withdrawing group is incorporated, a bathochromic shift of 14nm was observed (dye 2(d) λmax 526nm and 2(c) λmax 512 respectively in the same solvent). This result is very similar to the report on the effect of electon withdrawing nitro group on the absorption maxima of monoazo dyes derived from 5-nitrothiazoles and substituted anilines by J.B. Dickey et al[65].

Furthemore, replacement of electron donating methyl group in dye 2(c) with phenyl group as in dye 2(e) also gives a bathochromic shift of 8nm relative to dye 2(c). This is constistent with the results obtained when alinine was used as a coupler.

In the series of dyes 2(f)-2(i), the electron donating methyl group was replaced by ethyl group in the donor half of the chromogen and from the results summarised in table 2.2, the electron donating strength of N,N-diethylaniline is more than the N,N-dimethyl aniline as indicated by the red shift displayed when the corresponding pairs of dyes 2(c)-2(e) are compared with those in series 2(f)-2(i). In each case, the dyes with N,N-diethylaniline are more bathochromic in colour.

The results summarised in Table 3.2, clearly show that the incorporation of electron donating group in the acceptor ring of the azo chromogen leads to blue shift of the visible absorption band, while the incorporation of powerful electron withdrawing group in this position leads to red shift. In the same manner, when the electron donating ability of the coupler is enhanced, the more deepened in colour the resulting dyes become. The shift in λmax to longer wavelength is due to increase in polarisation of the dye molecule resulting to enhanced electron density displacement from the donor half of the chromogen to the acceptor half of the chromogen. Consequently, the energy between the highest occupied molecular orbital and the lowest unoccupied

molecular orbital LUMO is decreased, i.e the $\pi \rightarrow \pi^*$ transition frequency decreases and the electron transition takes place at lower frequency photon resulting to the bathochromic shift of the visible absorption band.

3.3 Effect of solvent polarity on λmax of monoazo dyes

The effects of the solvent polarity on the absorption maxima of the dyes were also investigated and the results obtained are also summarised in Table 3.2. The results show a general red shift when the solvent polarity is changed from less polar solvent-chloroform to the more polar solvent-ethanol as summarised in Table 3.2. More dramatically the λmax values are displaced to longer wavelengths by around 6-26nm in ethanol when compared with less polar solvent - chloroform. For example, dye 2(i) absorbs at 524nm in ethanol and at 500nm in chloroform. Similarly, dye 2(c) absorbs at 512nm in ethanol whereas, it shows maximum absorption at 506nm in chloroform, indicating a red shift of 6nm. Similar trends were observed for all the dyes in this series.

The effect of solvent polarity on the visible absorption band of the dyes have been thoroughly studied and well documented in the literature[19]. The report indicated in the literature has shown that $\pi \rightarrow \pi^*$ transition exhibit bathochromic effect when the polarity of the solvent is increased while, the $n \rightarrow \pi^*$ transition show hypsochromic effect with increase in solvent polarity. This

clearly indicates that in the present study, the visible band is due to $\pi \rightarrow \pi*$ transition since a general positive solvatochromic effect was observed on increasing the polarity of the solvent.

Solvatochromism is due to various solute-solvent interaction in both the ground and excited states. The red sift on changing to a more polar solvent suggests that the dye molecule has a more polar excited state than the ground state and this will lower the energy of the $\pi \rightarrow \pi^*$ transition. Thus light absorption causes the π-elecron to be displaced from the amino donor group to the various elecron acceptor residues and hence the excited state has a larger dipole moment i.e. more polar than the ground state.

3.4 Effect of Hydrochloric acid on Visible absorption band (Halochromism)

Halochromism is the effect of acid on the visible absorption band which could be decrease or increase of the wavelength of absorption maxima. The decrease of λ_{max} in acidic medium is referred to as negative halochromism while the increase of λ_{max} in the same acidic medium is known as positive halochromism.

The halochromism properties of the 2-aminothiazole dyes synthesised were examined and the shifts of the absorption bands in acidified ethanol are listed in table 3.3.

Table 3.3   Halochromism in monoazo dyes

Dye No	Ethanol λmax (nm)	Ethanol + HCl λmax (nm)	$\Delta\lambda$max
2(a)	494	500	+ 6
2(b)	504	550	+ 46
2(c)	512	596	+ 84
2(d)	526	560	+ 34
2(e)	520	570	+ 50
2(f)	523	538	+ 12
2(g)	532	570	+ 44
2(h)	500	594	+ 94
2(i)	524	570	+ 46

$\Delta\lambda$max = λmax in acidic ethanol - λmax in ethanol

In all cases, the protonated solutions were neutralised carefully with base (sodium trioxocarbonate IV) to ensure that the original spectra were completely restored thus confirming that decomposition of the dyes had not occured during protonation.

The halochromism of p-aminoazobenzene has been the subject of prolonged controversy among chemist[64], but it is now believed that protonation of p-aminoazo benzene dyes occurs almost exclusively at the β-azo nitrogen atom to form the azonium[65] tautomer and the protonated form is in all respect different from

the neutral azo compound. This is due to factors such as resonance stabilisation of the resulting azonium cation[66].

In the case of the thiazole dyes, protonation may take place at the heterocyclic nitrogen atom to generate a diazohemicyanine cation and the increase in electronic symmetry results in an ehanced bathrochromic effect (positive halochromism).

Diazohenicyanine cation

As can be seen in Table 3.3, all the dyes studied, show pronounced positive halochromism i.e. shift of the absorption band to longer wavelength on addition of acid. The most striking example is dye 2(h) which is violet (λmax 500nm) in neutral solution but turns blue (λmax 594nm) in acidic ethanol solution indicating a bathochromic shift of +94nm. Other members of the series like 2(f) gives λmax in neutral ethanol of 523nm but gives

λmax of 535nm in acidic ethanol; 2(g) gives λmax of 532nm in neutral ethanol and 576nm in acidic ethanol indicating a positive halochromism of +44nm. In all the cases of dyes under study, protonation leads to enhanced electron density displacement from the donor to the acceptor ring leading to decrease in energy of the π^* orbital and hence $\pi \rightarrow \pi^*$ transition frequency.

The halochromic effect for dye 2(h) is very remarkable where a bathochromic shift of +94nm was obtained when the dye solution in ethanol was acidified. This large shift can be attribited to the incorporation of the electron donating methyl group in the 5-position of the acceptor ring of the chromogen.

3.5 Application of the azo dyes to the fabrics

All the dyes synthesised were applied on polyester and nylon fabrics using standard dyeing conditions[87]. The different shades obtained on these fabrics are summarised in Table 3.4.

As can be seen in table 3.4, the colour produced ranges between red and violet on both fabrics. A typical example is dye 2(a) which produced red-orange shade on polyester and nylon. When the two hydrogen of the amino group of dye 2(a) were substituted with two electron donating methyl group to produce dye 2(d), the shade produced is violet on polyester and nylon indicating the deepening effect of the colour resulting from an increase in electron donating strength of the donor ring.

Table 3.4   Shades of dyeings obtained on the fabrics

Dye No	Colour on polyester	Colour on nylon
2(a)	Red-orange	Red-orange
2(b)	Red-orange	Red-orange
2(c)	Pink-red	Pink-red
2(d)	Pink-violet	Pink-violet
2(e)	Pink	Pink
2(f)	Pink	Pink
2(g)	Pink	Pink
2(h)	Red-orange	Pink
2(i)	Pink	Pink

A similar observation was noticed on the shade of dye 2(i) compared with dye 2(h) where Y substituent has been substituted with methyl group.   2(h), produce red-orange shade on polyester and nylon fabrics while 2(i) produce pink shade on both fabrics. In this case a negative deepening effect (hypsochromic effect) was observed.   This is explained on the basis of the substituents which in turn affect the $\pi \rightarrow \pi^*$ transition wavelengths as explained in section 3.2.

With all the other dyes under study, the change in shade is not appreciable on both fabrics, for example, dye 2(f) gives pink

shade on nylon and polyester but on substitution of Y which is H in 2(f) by electron withdrawing carbethoxy group at such position to give dye 2(g), the same shade i.e. pink was produced on the fabrics. This is however, consistent with the fact that their visible absorption maxima is not wide enough as to produce any conspicous colour change on the fabrics.

The colours obtained on the application of the azo dyes to polyester and nylon are shown in Appendix 1.

3.6 Washing fastness rating

Washing fastness is the resistance of dyeings to alkaline hydrolysis. This test is considered very useful since dyed fabrics are subjected to various washing conditions during use. The test was conducted by adopting the general procedure by the International Standard Organisation. Procedure number three (ISO No 3 procedure was followed)[68]. The results obtained are shown in Table 3.5.

As can be seen in Table 3.5, dye 3(a) has fastness rating of 4 on nylon and polyester indicating good fastness to washing, while staining of the dyeings on the adjacent material is rated 3 on nylon and 4 on polyester indicating that the adjacent material was fairly stained with dyeings of nylon and almost stainless on polyester.

Table 3.5 Washing Fastness rating of Monoazo dyes

Dye No	Change in Shade		Staining on adjacent fibre	
	Nylon	Polyester	Nylon	Polyester
2(a)	4	4	3	4
2(b)	3	4	4	3
2(c)	2-3	3	4	3
2(d)	3-4	4	2-3	4
2(e)	3-4	4	3	4
2(f)	4	4	3	4
2(g)	3	3-4	2-3	3
2(h)	3-4	4	3	4
2(i)	4	3	3	4

On the other hand dye 2(c) shows moderate fastness on both polyester and nylon and was rated 3 and 2-3 respectively on these fibres. The degree of staining in this case being fair and is rated 4 on nylon and 3 on polyester fibre.

In General, the process of attachment of dye molecule can be by mechanical entrapment or by chemical linkage between the dye and the fibres molecules. Fastness characteristics of individual dyes depend on so many factors which include the relative orientation of the dye molecule with the fibre molecule and the various forces involved in the dye-fibre interaction, i.e

whether ionic, covalent, van der waals, dipole interaction etc. Also the fastness characteristics of the dyes depend on the structure of the dye and the fibre molecule to which the dye is being applied.

In the present study, all the dyes synthesised are disperse dyes since they all lack solubilising groups the force involves in the dye-fibre interaction is mainly due to physical entrapment, involving van der waals forces of attraction. These forces are as a result of second-order wave mechanical interaction of the π-orbital of the dye and the fibre molecule and are very effective when the dye molecule is linear and having groups such as alkyl or aryl which approach the fibre molecule closely.

Thus the observation that some of the dye have good wash fastness is attributed to the strong van der waals interaction and some dipole-dipole interaction between the dye and fibre molecules. While dyeings having moderate fastness indicates weak interaction of these forces.

3.7 Wash Fastness of Transfer Printed Fabrics

The monoazo dyes synthesised were also applied onto the polyester and nylon by transfer printing technique and the printed fabrics were subjected to ISO 3 washing test to assess the fastness characteristics of the printed samples. The results obtained are summarised in Table 3.5b.

Table 3.5b   Fastness rating of Azo   Dyes Transfer printed

Dye No	Change in shade		Staining of white sample	
	Polyester	Nylon	Polyester	Nylon
2(a)	4	3	4	3
(b)	4	3-4	4	3-4
(c)	3-4	3	3	2-3
(d)	4	3	3	2-3
(e)	4	3	4	3
(f)	3	3	4	3
(g)	4	4	4	3
(h)	3-4	3	3-4	3-4
(i)	3-4	3	4	3

The fastness properties of the transfer printed samples are generally good on both substrates and slightly better on polyester than on nylon and this may be attributed to the crystalline nature of the polyester material. This means that once the dyes are able to enter the crystalline region of the fibre, it is not easy to desorb. The colour obtained on transfer printing are similar to those obtained during dyeing and this are shown in appendix 2.

3.8 IR Spectra of the monoazo dyes

The infra red spectrum of dye 2(a) shows an absorption due to $>C=O$ stretch vibration at 1700cm^{-1}. The absence of such peak in dye 2(b) is a strong evidence of the absence of the electron withdrawing carbethoxy $-CO_2Et$ group in such dye. The absorption at 3300cm^{-1} for 2(a) and 2970cm^{-1} for 2(b) is due to the N-H stretching vibration.

The replacement of methyl group of 2(a) which absorbs at 1400-1456cm^{-1} and 1378cm^{-1} (finger print region) with phenyl group resulted to 2(b) which gives a broad absorption at 3000-3100cm^{-1}. The same trend was observed on comparing 2(c) and 2(d), 2(f) and 2(g) with absorption at 1710cm^{-1} for 2(d) and 1705cm^{-1} for 2(g) while no such band was observed for 2(c) and 2(f).
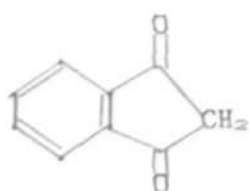
Dye 2(e) and 2(f) give very similar spectrum except at the absorption at 1500cm^{-1} which is slightly different for the ethyl group of 2(f) by the broadening of $-CH_2$ at 1490cm^{-1} and $-CH_3$ at 1500cm^{-1} for dye 2(f).

In general, each dye gives its characteristic absorption spectrum in the finger print region (1400cm^{-1}-660cm^{-1}) but an absorption band between the region 1300cm^{-1} - 1500cm^{-1} for all the dyes indicates the vibration frequency due to the $-N=N-$ streching vibration. Also a general absorption between 1180cm^{-1} - 1360cm^{-1} is due to $-C-N-R'R$ stretching vibrational frequency.

The absence of some bands in the spectra is being attributed to the presence of overtones (hamonics) frequency[**].

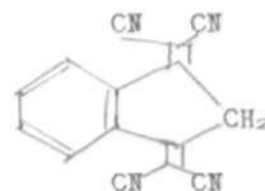### 3.8 Sythesis of Methine Intermediates and Dyes

The dyes synthesised in thise section were derived by condensing active methylene compounds with various benzaldehyde under base catalysed reaction. The active methylene compounds used are 1,3-indanedione (3), 3-oxo-$\Delta'\cdot{}^3$-indanedionemalononitrile (4) and 2,2-indene-1,3-diylidenebispropandinitrile (5).
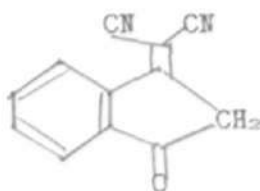
(3)   (4)   (5)

1,3-Indanedione was synthesised by reacting equimolar amount of phthalic anhydride with ethylacetoacetate in the presence of triethylamine as base for 1½hours. The deep orange solution that was obtained was acifidied with hydrochloric acid. The resulting compound was recrystallised from toluene to get 1,3-indanedione as yellow needles.


Phthalic anhydride   (3)

3-oxo-$\Delta^{1,3}$-Indanedionemalononitrile (4) and 2,2-indene-1,3-diyledenebispropandinitrile (5) were prepared by reacting (3) with malononitrile in the presence of anhydrous sodium acetate and sodium acetate trihydrate respectively as shown in the reaction scheme below.


(4)

(5)
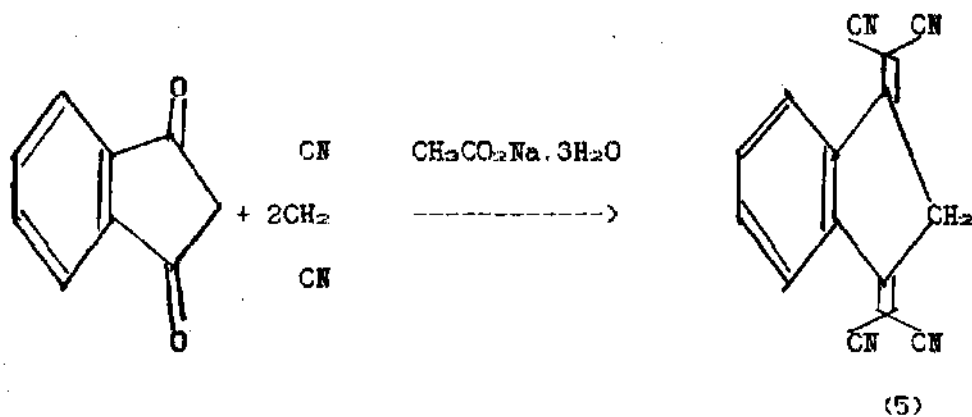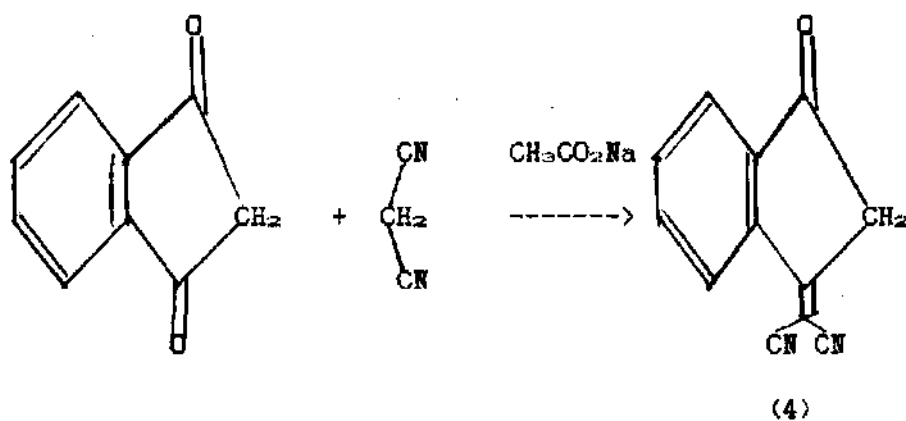
In each case the intermediates obtained agreed in their ir spectra and physical properties with that reported in the literature[55].

The active methylene compounds (3), (4) and (5) were recrystallised respectively in toluene and then condensed in turns with various benzaldehyde derivatives, namely 4-N,N-dimeth-
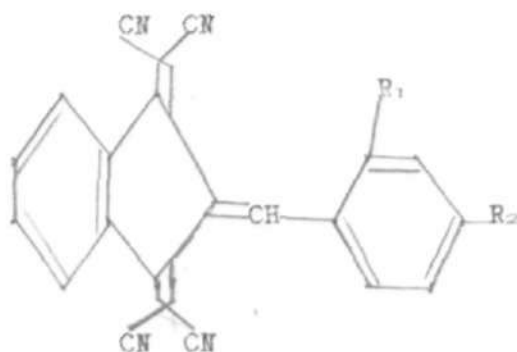
yaminobenzaldehyde, 4-hydroxybenzaldehyde, o-methoxybenzaldehyde, 4-nitro-2-aminobenzaldehyde, 3-acetamidobenzaldehyde and p-nitrobenzaldehyde to produce series of methine dyes (6), (7) and (8) respectively.
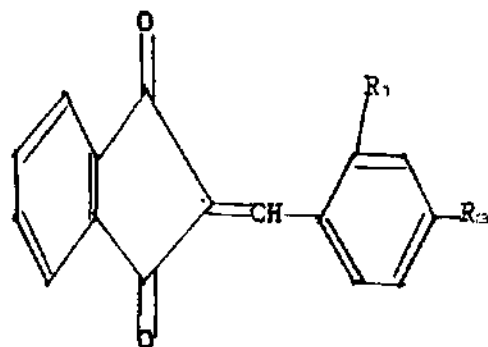
6(a) R_1 = H, R_2 = N(Me)$_2$

(b) R_1 = H, R_2 = OH

(c) R_1 = H, R_2 = NHCOCH$_3$

(d) R_1 = OCH$_3$, R_2 = H
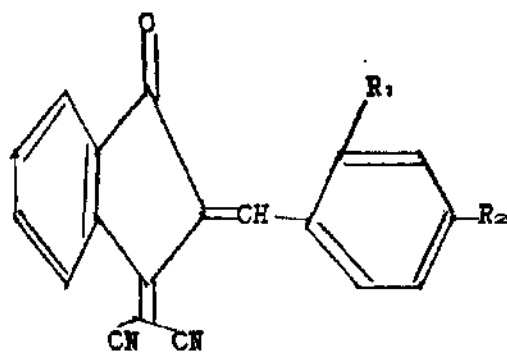
7(a) R_1 = H, R_2 = N(CH$_3$)$_2$

(b) R_1 = H, R_2 = OH

(c) R_1 = OCH$_3$, R_2 = H

(d) R_1 = NO$_2$, R_2 = NH$_2$

(e) R_1 = H, R_2 = NO$_2$

(f) R_1 = H, R_2 = NHCOCH$_3$

8(a)   R₁ = H, R₂ = N(CH₃)₂

   (b)   R₁ = H, R₂ = OH

   (c)   R₁ = OCH₃, R₂ = H

   (d)   R₁ = NO₂, R₂ = NH₂

3.9 Visible Absorption Spectroscopic properties of Methine Dyes

The visible absorption spectra of the dyes were measured on the Unicamp SP 800 spectrophotometer in different solvents and their molar extinction coefficients were calculated from absolute alcohol. The results of the condensation of indane-1,3-dione with various benzaldehydes are summarised in table 3.9a.

Table 3.9a   Visible absorption spectra of dyes derived from 1,3-indanedione

Dye No	DMF/λmax (nm)	Ethanol /λmax	Chloroform /λmax (nm)	DCM λmax	ϵ max (ETOH) x 10^5
6(a)	490	486	470	468	6.21
(b)	455	445	420	412	5.24
(c)	500	485	468	465	6.05
(d)	495	470	460	440	8.50

As can be seen in the table 3.9a, dye 6(a) which was obtained by condensation of 1,3-indanedione with 4-N,N-dimethylamino benzaldehyde absorbs at 490nm in dimethylformamide and it is yellow in colour. When the electron donating dimethylamino group was replaced by hydroxyl group, the resulting dye 6(b) absorbs at 455nm in the same solvent indicating an hypsochromic shift of 35nm relative to dye 6(a). Dye 6(c), obtained by the same condensation reaction of 1,3-indanedione with 4-acetamidobenzaldehyde absorbs at 500nm and this is relatively more bathochromic when compared with dyes 6(a) and (b). In this case the electron donating ability of acetamido group is stronger than that of the dimethylamino group and hydroxy group. Dye 6(d) with the methoxy group in the o-position gives an absorption maximum at 495nm in DMF and this shows an hypsochromic shift of 5nm relative to dye 6(c).

When one of the carbonyl groups in dye (6) was replaced by dicyanovinyl group another series of dyes (7) were obtained and the spectroscopic data of these dyes are similarly measured in different solvents and the results are summarised in table 3.9b.

Table 3.9b: Visible Absorption spectra of dyes derived from

3-oxo-Δ¹·ᵗ-Indanedione malononitrile

Dye No	DMF λmax(nm)	Ethanol λmax(nm)	Chloroform λmax (nm)	DCM λmax(nm)	εmax ethanol ethanol x 10⁵
7(a)	610	605	600	580	6.15
(b)	550	545	440	435	4.9
(c)	565	562	444	430	5.7
(d)	572	570	456	452	5.8
(e)	570	535	455	450	9.6
(f)	605	600	500	490	5.6

Comparison of the data summarised in table 3.9a and (b)
generally show that dyes in table 3.9b are more bathochromic when
compared with their corresponding analogues. For example, dye
7(a) absorbs at 610nm in dimethylformamide, whereas, the
corresponding dye 6(a) absorb at 490nm in the same solvent. This
shows that replacement of one of the carbonyl group in dye (6)
results in large bathochromic shift of 120nm. It is interesting
to note that the incorporation of electron withdrawing nitro
group as in dye 7(e) gives a dye which is hypsochromic when
compared with dye 7(f) which has an electron donating acetamido
group. This shows that the incorporation of electron withdrawing
group in the donor half of the methine chromogen will lead to
dyes which are less bathochromic than when electron donating
groups are substituted in this position.

Similar trend was observed when different solvents were used. For example 7(a) shows λmax of 605nm in ethanol, whereas, the corresponding dye 6(a) in table 3.9a absorbs at 486nm, showing a bathochromic shift of 119nm. When chloroform was used the shift was +130nm relative to dye 6(a) (i.e. 7(a) λmax in chloroform is 600nm and 6(a) λmax 470nm in the same solvent).

When the intensity of the dyes in table 3.9a and 3.9b are compared, it can be seen that when one of the carbonyl group was replaced as in dye (7), the extinction coefficient is reduced. For example, the extinction coefficient of dye 7(a) is 6.15×10^5 and that of 6(a) is 6.21×10^5 this may be due to steric interaction of the cyano group in series (7).

The results summarised in table 3.9b suggest that further bathochromic shift can be obtained if the second carbonyl group can be replaced by dicyanovinyl groups. To investigate this, the dyes in series (8) were prepared by condensation of the benzaldehyde with 2,2-Indene-1,3-diylidenebispropandinitrile (5). The visible absorption spectra of dyes (8) are summarised in table 3.9c.

Table 3.9c   Visible absorption spectra of dyes derived from

2,2-Indene-1,3-diylidenebispropandinitrile

| Dye No. | λmax in different solvent | | | | εmax EtOH |
	:DMF (nm):Ethanol (nm):Chloroform (nm):DCM :				x 10⁵
8(a)	: 625	: 615	: 605	: 600:	5.92
(b)	: 578	: 573	: 466	: 460:	3.83
(c)	: 580	: 474	: 470	: 465:	4.60
(d)	: 576	: 570	: 460	: 455:	4.89

Key: DMF = Dimethylformamide;   DCM = Dichloromethane

The dyes in this series are more bathochromic than the corresponding analogue in Table 3.9(a) and (b).   For example, dye 8(a) absorbs at 625nm in DMF, and the corresponding dye in Table 3.9b (dye 7a) absorbs at 610nm indicating a bathochromic shift of 15nm.   Similar effects are observed when the corresponding dyes are compared.   This shows that the replacement of the second carbonyl group in dye 7 results in an increase in the wavelength of maximum absorption.   This can be accounted for in terms of the resonance theory which states that the more the canonical structures which can be drawn for a compound the more bathochromic the colour of the resulting compound.   This is because the interaction between these structures will give rise to a set of energy states, namely, the ground and the excited states which will be better approximations to the actual molecular state.   The energy difference between the ground state and the first excited state is equal to that associated with the

longest wavelength of absorption band. Thus, applying this theory, it can be said that dye in series (7) are generally more bathochromic than dye in series (6) because of increase in resonance energy arising from greater number of the classical structures of (7) than (6). For example four classical structures can be drawn for (7) while only three can be drawn for (6) as shown below:
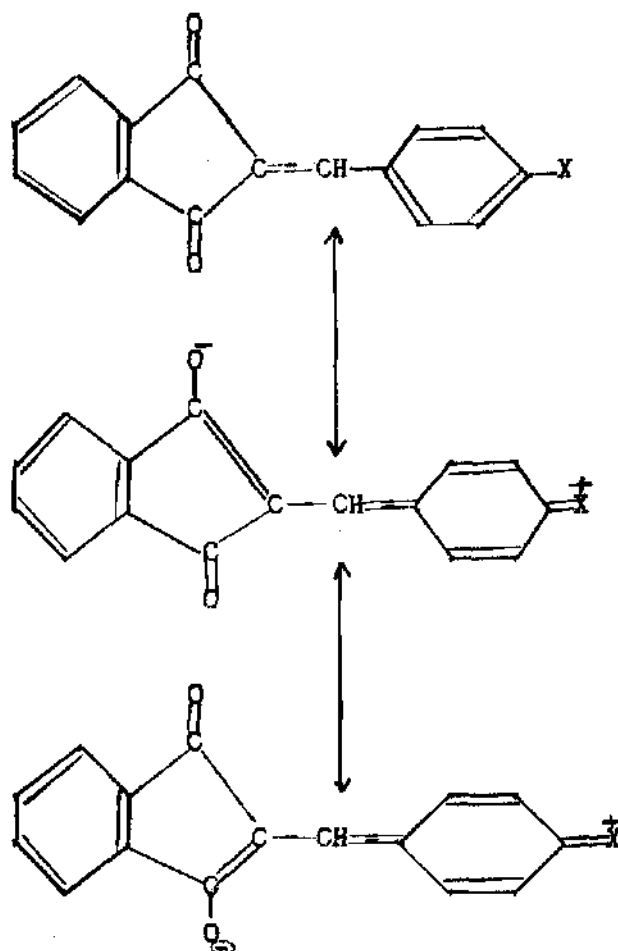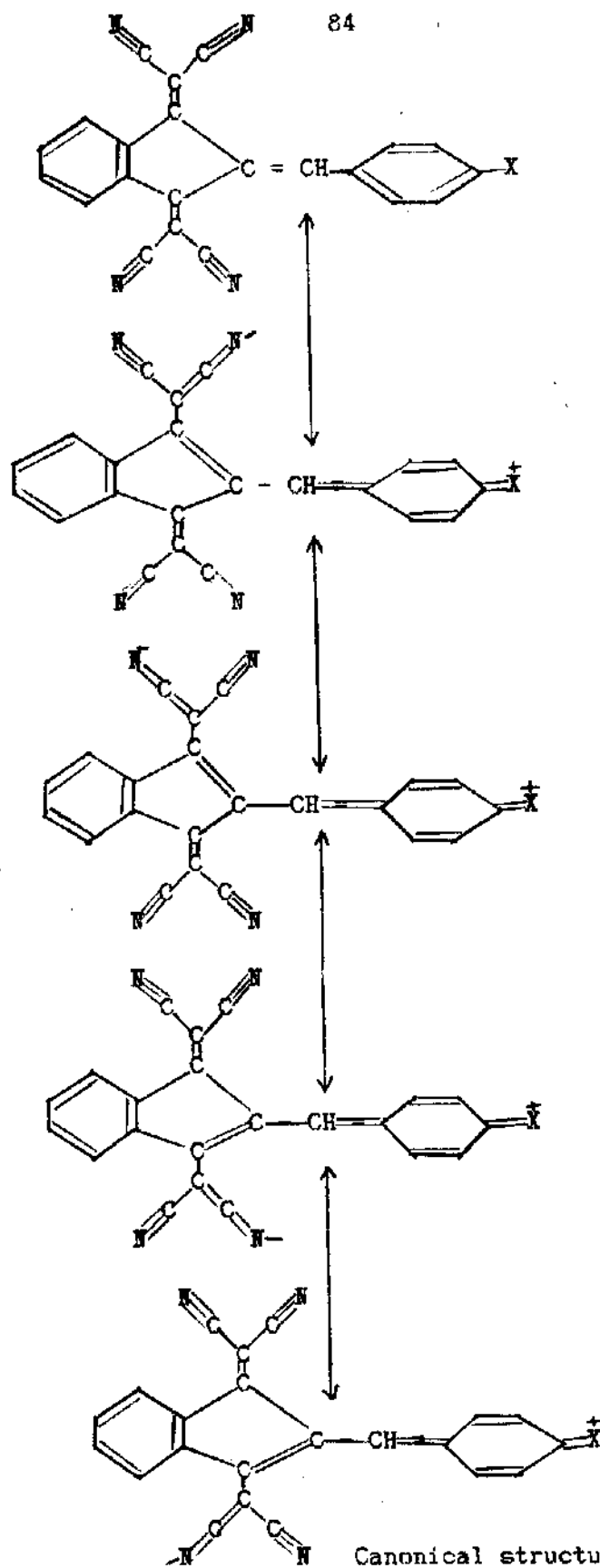

Canonical structures of dye (6)
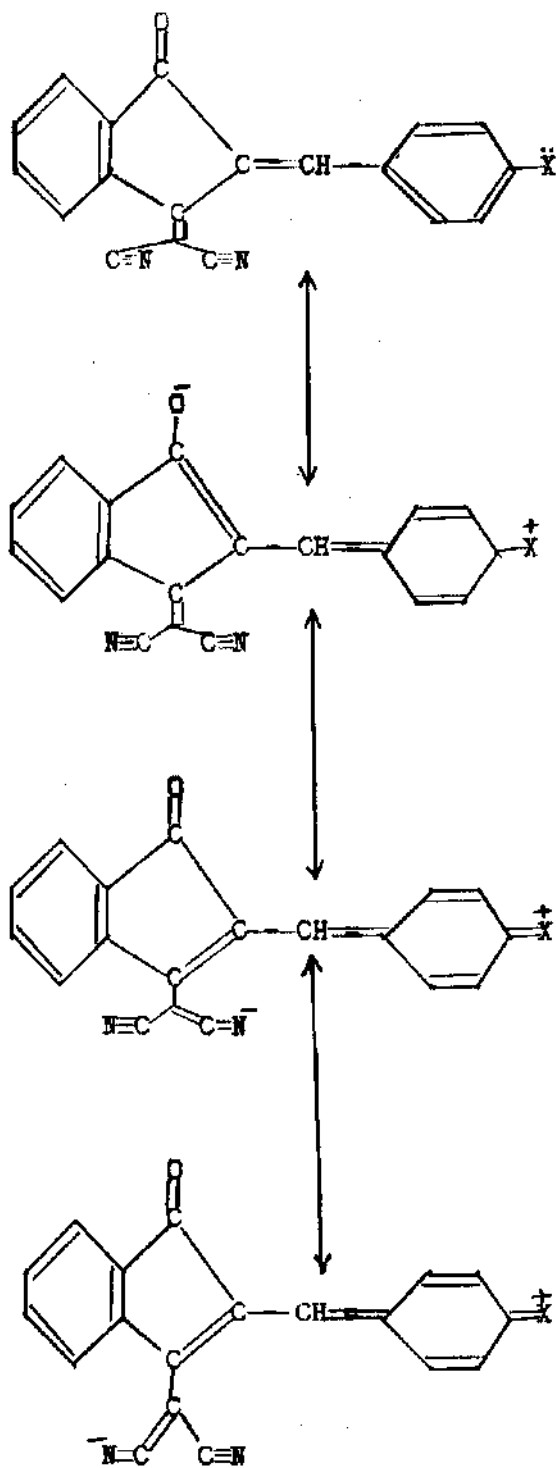
Canonical structures of dye (7)

In general the more structures there are contributing to the resonance, the greater will be the resonance energy, i.e. the lesser the transition frequency and hence the more bathochromic the dye becomes. The red shift observed on comparing dyes (7) with (6) can also be explained as resulting from increase in congugation when the carbonyl group is replaced by a more electro negative cyano group. Qualitatively as conjugation increases, the ground state is lowered i.e resonance energy increases but the first excited state is lowered even further due to stabilisation by a rapid increase in the number of charged structures. The transition frequency progressively diminish and the λmax is shifted to longer wavelength. Furthermore, the replacement of the second carbonyl group as in dyes (8) by the second dicyanovinyl group increases the conjugation further and more resonance structures can be written for dyes (8) and in consequence λmax is further increased bathochromically.

As can be seen from the canonical structures below, five resonance structures can be drawn for dye (8) while only four can be written for dye (7) and only three for dye (6). The order of increasing bathochromic shift of the dyes can be arranged thus: Dye (8) > dye (7) > (6) when the corresponding dyes are compared.
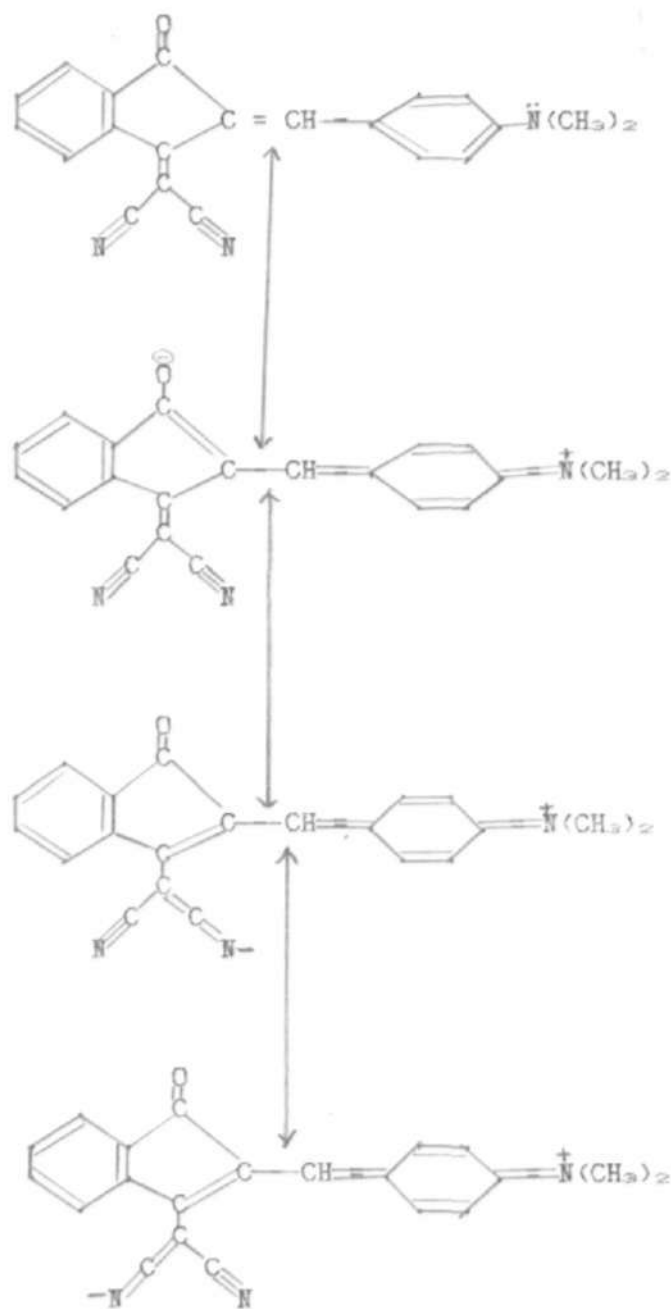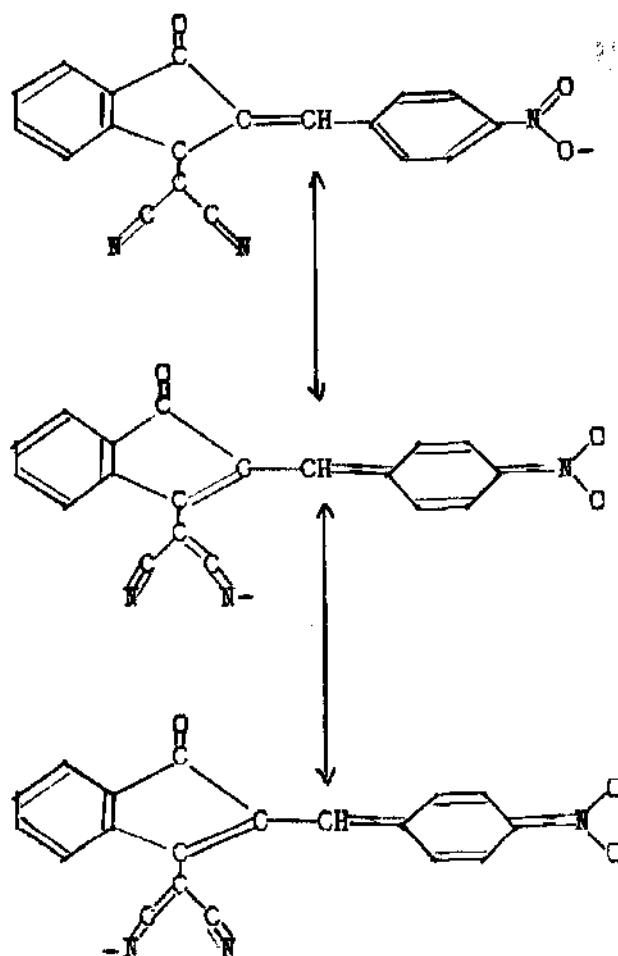
Canonical structure of dye (8)

When individual dye in the series (6), (7) and (8) are compared with each other, it is noted that a hypsochromic effect is observed when electron withdrawing groups are attached at the donor half of the chromogen. This can also be explained in terms of resonance theory. It is evident that these substituents decrease the symmetry of the molecule instead of increasing the conjugation. Consequently, the degree of degeneracy of the canonical structures is decreased, giving rise to increase in $\pi \rightarrow \pi^*$ transition frequency. For example, dye 7(a) with dimethylamino group absorbs at 610nm while dye 7(c) with electron withdrawing group in the donor half of the chromogen absorbs at 565nm in the same solvent.

As can be seen from the canonical structures below, only three canonical structures can be drawn for dye 7(c) and all structures are charged, the degree of charge separation in this case being great. This implies that there is greater assymetry of the dye molecule and a decrease in resonance energy. An hypsochromic effect is therefore expected and the transition frequency is increased. This explains why dye 7(c) absorbs at 565nm indicating a blue shift of 45nm relative to dye 7(a) (λmax 610nm in the same solvent).

In general, the stronger the electron withdrawing power of a substituent at the donor half of the chromgen the lesser is the degree of symmetry of the dye molecule and the smaller the wavelength of absorption maximum of the dye becomes.

Canonical structures of dye 7(a)

Canonical structures of dye 7(c)

3.10 Solvatochromism in methine dyes

The effect of solvent polarity on absorption maxima was also investigated in dimethylformamide, ethanol, chloroform and dichloromethane. The results are summarised in tables 3.9a, 3.9b and 3.9c for the three series of dyes.

As can be seen in the tables, for all the dye in the series, there is a general red shift when the solvent is changed from a less polar solvent to a more polar solvent, i.e from

dichloromethane-chloroform-ethanol to the more polar dimethylformamide. The magnitude of the shift being of the order of 16-145nm. A typical example is dye 7(a) which absorbs at 580nm in dichloromethane but absorbs at 600nm in the more polar chloroform indicating a bathochromic shift of 20nm. When the λmax of the same dye was measured in still more polar solvent than chloroform, a further increase in λmax was observed (e.g the same dye absorbs at 605nm in ethanol and 610nm in dimethylformamide.

Similar results were obtained for all the methine dyes studied. Solvatochromism is due to solute-solvent interaction and in this class of coloured organic molecules it means that the ground state is less polar than the excited state. A polar solvent thus tend to stabilise the excited state more than the ground state i.e lowering the π^* transition without changing the non bonding molecular orbital (NBMO) and in consequence giving rise to a bathochromic effect.

Using 8(b) as an example, it is evident that an increase in solvent polarity will only have a small effect on the stability of neutral 8(b)i, whereas the stability of the charged separation forms 8(b)ii, 8(b)iii, 8(b)iv and 8(b)v will be greatly enhanced.

8(b)i

8(b)ii

8(b)iii

8(b)iv

8(b)v
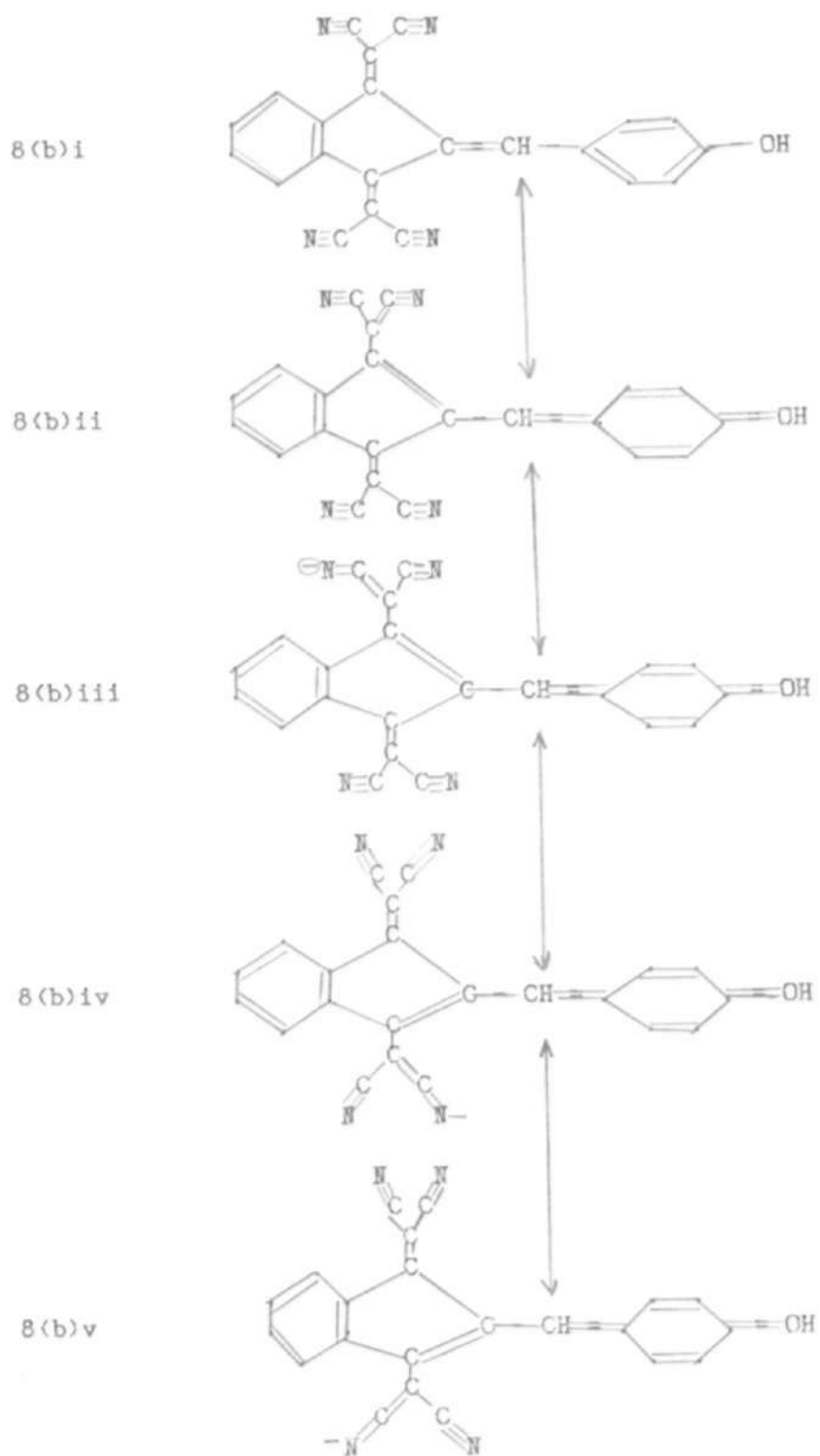
Thus a change in the solevent polarity will bring 8(b)ii, 8(b)iii, 8(b)iv and 8(b)v closer together in energy and after allowing for resonance interaction, the gab between the ground and the excited state in the more polar solvent like dimethylformamide will be reduced relative to that in a less polar solvent like dichloromethane. A bathochromic shift will then result[71]. However, in few cases like merocyanines hypsochromic shift of the λmax has been observed as the polarity of the solvent increases, this being peculliar to a type of donor-acceptor chromogen that has a lower energy resonance form of greater polarity than the higher energy resonance form[72].

3.11 Allopolar Isomerism

Allopolar isomerism is a phenomenon arising from a combination of steric and electronic effects and is shown by a chromogen having a banched π-electron system. Allopolar isomerism occurs when a dye molecule shows two well defined visible bands, one near 600nm and the other near 500nm and the relative intensities of the two bands show a marked dependence on solvent polarity[73]. This is being attributable to the presence of two different molecular species in solution.

Among the series of dyes studied, the following indicated the existence of this isomerism; 6(d), 7(a), 7(d) and 8(a) as shown in table 3.11.

Table 3.11 Allopolar properties of the methine dyes

Dye No	λmax DMF		λmax EtOH		λmax CLF		λmax DCM	
	λ1(nm)	λ2(nm)	λ1(nm)	λ2(nm)	λ1(nm)	λ2(nm)	λ1(nm)	λ2(nm)
6(d)	495	425: 470	420	460	410	440	402	
		$\epsilon=8.5\times10^{5}$:6.9×10^{5}						
7(a)	610	450: 605	445	600	–	580	–	
		$\epsilon=6.2\times10^{5}$:7.2×10^{5}						
7(d)	572	442: 570	438	456	–	452	–	
		$\epsilon=5.8\times10^{5}$:6.3×10^{5}						
8(a)	625	456: 615	452	600	–	605	–	
		$\epsilon=5.9\times10^{5}$:5.9×10^{5}						

As can be seen in Table 3.11, dye 7(d) give two absorption bands, one at 570nm and the other at 438nm with molar extinction coefficient of 5.8 x 10^5 and 12.1 x 10^5 respectively in ethanol. Both bands show marked dependence on solvent polarity, for example when the polarity of the solvent is changed from dimethylformamide to chloroform the λmax changed from 572nm to 456nm, while the second peak changed from 442nm to zero. Also the molar extinction coefficient of the second band is almost twice that of the first band showing a remarkably absorption intensity of the second band relative to the first band. This observation can be explained in terms of the steric crowding of the substituents which prevents the coplanarity of the dye

molecule.   Thus for dye 7(d), it is possible that both the nitro and the dicyanovinyl groups prevent the system from achieving coplanarity and two isomeric entities are then possible as shown below.

7(d)i

meropolar form (uncharged

form)

Halopolar form
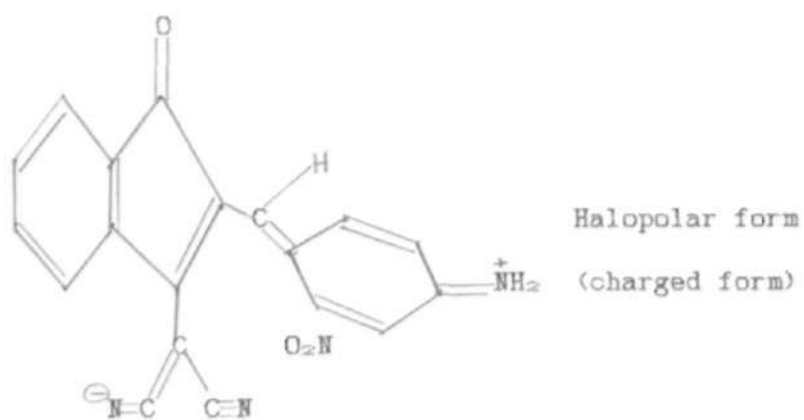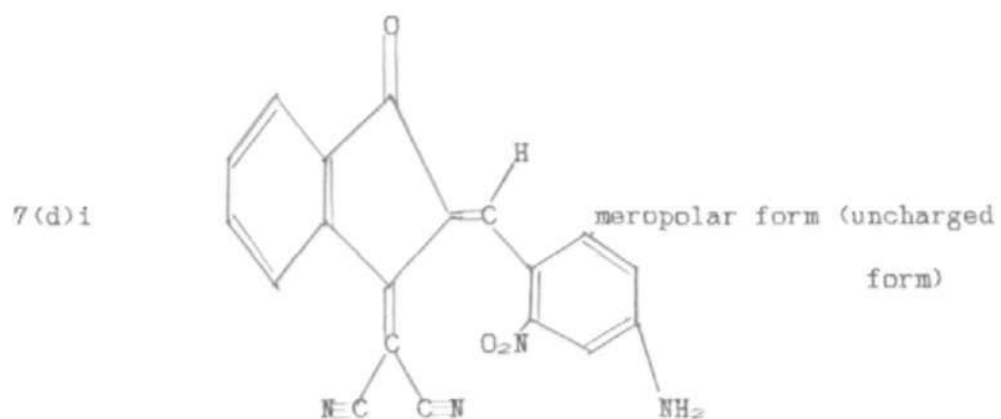
(charged form)

The first can be represented by 7(d)i in which the amino group is twisted out of the plane of the carbonyl ring. This is the meropolar (uncharged) form and give rise to the band at 438nm in ethanol. The second specie can be represented by 7(d)ii which is the ionised dicyanvinyl ring and non coplanar to the donor half of the cyanine chromogen. This is called the halopolar form and gives absorption at 572nm.

For the same reason, the meropolar form of 7(c) is responsible for the absortion band at 470nm in dimethylformamide while the halopolar form is responsible for the λmax at 580nm. In dye 6(d) the meropolar form with the amino group twisted out of the plane give absorption at 425nm while the halopolar form being non coplanar with the donor half of the ring gives absorption at 445nm in dimethylformamide. The extinction coefficient of the meropolar form is lower (6.9×10^5) than the holopolar form $(\epsilon = 8.50 \times 10^5)$ in ethanol solution.

Similarly, the absorption at 445nm for dye 7(a) $(\epsilon = 7.2 \times 10^5)$ in ethanol is due to the meropolar form while the holopolar form absorbs at 605nm $(\epsilon = 6.15 \times 10^5)$

For the same reason the meropolar form of dye 8(a) is responsible for the absorption at 615nm $(\epsilon = 5.89 \times 10^5)$ while the holopolar form is responsible for that at 452nm $(\epsilon = 5.72 \times 10^5)$ in ethanol.

It should be noted that the two isomeric forms are no resonance forms but are distinct chemical entities. Also the

appearance of one absorption band i.e the one with the longest
λmax at around 500nm for dyes exhibiting this isomerism in less
polar solvent indicates the predominance of one form, in this
case the meropolar form, over the other, the holopolar form.
This is because the uncharged form predominates in solvent that
are non or least polar as charge separation is unlikely. A clear
example is dye 8(c) where only one absorption band was observed
in chloroform 470nm and dichloromethane 465nm. This shows that
in less polar solvent the charged forms (allopolar) are less
stable and are overwhelmed by the meropolar form which absorbs at
the 470nm and 465nm in chloroform and dichloromethane
respectively.

3.12 Halochromism in methine dyes

For all the methine dyes studied, no change in λmax of the
visible absorption band was observed when a few drops of
hydrochloric acid was added i.e, no halochromic effect. This is
due to the absence of protonation at any electronegative atom or
group such as the azo group which is protophilic.

3.13 I.R Spectra of the Methine dyes

The i.r spectra of the dyes show absorption below $1400cm^{-1}$
representing the vibration frequency of the whole dye molecule.
This is characteristic of each dye sample and is referred to as
the finger print region. The absorptions above $1400cm^{-1}$ repres-

ents the stretching or bending vibrations of groups incorporated in the dye molecule. Thus dye 6(a) gives an absorption at $1632cm^{-1}$ due to C=C- stretching vibration, while a sharp peak at $1710cm^{-1}$ is due to the carbonyl >C=O stretching vibration frequency. These peaks are found in the rest of the members of the dyes in series (6) with absorption differing a little in wavenumber. For example the absorption at $1685cm^{-1}$ for 6(b) corresponds to >C=O stretch vibration frequency, while 6(c) gives the same absorption at $1720cm^{-1}$. The absorption corresponding to the C=C stretching vibration remains almost constant for all the dyes in this series (6) i.e at $1632cm^{-1}$.

When one of the carbonyl group in dye (6) was replaced by dicyanovinyl group to give series of dyes (7), a very sharp peak at the region $2220-2266cm^{-1}$ corresponding to the stretching vibration frequency of -C-N- is observed for the dyes. The peak also differing slightly from one member to the other as a result of the structural differences.

Dye 7(a) in addition to showing absorption corresponding to >C=O stretching vibration at $1700cm^{-1}$, C=C stretching vibration at $1630cm^{-1}$ also gives a sharp peak at $2220cm^{-1}$ corresponding to the -C≡N stretching vibration frequency. Showing clearly the presence of the cyano group. Additional absorption band were observed in the finger print region.

The replacement of the second carbonyl group from dyes (7) giving rise to series of dyes (8) show the complete absence of

the absorption peak around 1700 - 1735cm⁻¹ and indicating the absence of the carbonyl group. However, the absorption corresponding 2220cm⁻¹ due to the presence of cyano groups becomes sharper and more intense. A typical example is dye 6(a), which gives no absorption around 1700cm⁻¹-1735cm⁻¹ but give an intense and sharp peak at 2220cm⁻¹ corresponding to the C≡N stretching vibration frequency.

3.14 Dyeing and colour range of Methine dyes

All the methine dyes synthesised were applied to polyester, nylon and cotton fabrics using standard dyeing procedure. The colour produced are summarised in Table 3.14

Table 3.14 Colour range of methine dyes

Dye No.	Colour on Polyester	Colour on Nylon	Colour on cotton
6(a)	orange	orange	orange
(b)	Yellow	yellow	yellow
(c)	red	red	red
(d)	orange	orange	orange
7(a)	Blue-green	blue-green	blue-green
(b)	violet	violet	violet
(c)	violet	violet	violet
(d)	Blue	blue	blue
(e)	Blue	blue	blue
(f)	Green-blue	green-blue	green-blue
4(a)	Blue-green	Blue-green	Blue-green
(b)	blue	Blue	Blue
(c)	Blue	Blue	Blue
(d)	Blue	Blue	Blue

From the data on Table 3.14, dye 6(a) produced orange shade on polyester, nylon and cotton fabrics while the corresponding analogue (8a) produce blue-green shade on all the fabrics. This is attributated to the deepening effect of the incorporation of dicyanovinyl group in 8(a). When the shades of the dyeings obtained with all the dyes in the three series are compared, it was found that dyeings obtained with series (6) are yellow to orange in shade, while those in series (7) are violet to blue and those in series (8) are blue and blue-green in colour.

3.15 Washing fastness properties of Methine dyes

The resistance of the dyeings to alkaline hydrolysis was investigated using I.S.O. No 3 washing procedure, the results obtained are summarised in Table 3.15.

The dyeings are very resistant to alkaline washing treatment indicating good washing fastness for all the dyes. For instance, wash fastness of dye 6(a) is rated 4 on polyester and 4 on nylon, while on cotton the rating is 3. This shows a very slight loss in depth on both polyester and nylon and moderate fastness on cotton fibre. The higher resistance on nylon and polyester may be due to high crystalline structure of both fibres.

Fastness properties depend on how strongly the dyes molecules are held by the fibre molecule and so many factors are responsible for this which ranges from weak Van der waal's forces to strong dipolar interactions. These forces in turn depend on

Table 3.15 Washing Fastness Rating

Dye No	Change in Shade			Staining of adjacent fibres		
	Polyester	Nylon	Cotton	Polyester	Nylon	Cotton
6(a)	4	4	3	4-5	4	3
(b)	3-4	4	4	4	3	3-4
(c)	4	3-4	3	3-4	4	3
(d)	3	3	4	4	3	3-4
7(a)	4-5	4	2-3	4	3	2-3
(b)	4	3	3	4-5	3	3-4
(c)	4	3-4	3	4	3	3
(d)	4-5	2-3	3	4-5	3-4	3-4
(e)	3-4	3-4	3	3-4	3-4	3
(f)	4-5	4	3	3	3-4	4
8(a)	3-4	4-5	4	4	3-4	3
(b)	4	3-4	3-4	3-4	4	2-3
(c)	4-5	3	3-4	4-5	4-5	3
(d)	4	3	2-3	4	3	2-3

the geometry or the relative stoichimetry of the dye molecule and
fibre molecule. The geometrical factors depend on the nature,
the number and position of substituents in the chromogen.
Therefore, the good fastness properties exhibited by the dye
indicates strong dye-fibre interaction with so many forces coming
into play, with the dye molecules possibly assuming a better
geometry for interaction.

3.16 Transfer printing properties of the Methine Dyes

The transfer printing property of the methine dyes under study was investigated using the procedure described in section 2.4 and the colour of the printed materials on nylon, polester and cotton are tabulated in table 3.16 and shown in Appendix 4.

Table 3.16 Colour of Printed Samples

Dye No	Colour on polyester	Colour on Nylon	Colour on cotton
6(a)	orange	orange	orange
(b)	light-yellow	yellow	yellow
(c)	red	red	red
(d)	orange	orange	orange
7(a)	Blue-green	blue-green	blue-green
(b)	violet	violet	violet
(c)	violet	violet	violet
(d)	blue	blue	blue
(e)	blue	blue	blue
(f)	green-blue	green-blue	green-blue
8(a)	blue-green	blue-green	blue-green
(b)	blue	blue	blue
(c)	blue	blue	blue
(d)	blue	blue	blue

3.17 Washing fastness properties of Printed materials

The washing fastness of the tansfer printed materials are also studied using the I.S.O. No. 3 washing procedure. The results are tabulated in Table 3.17.

Table 3.17 Washing Fastness properties of printed fabrics

Dye No	Change in shade			Staining of white sample		
	Polyester	Nylon	Cotton	Polyester	Nylon	Cotton
6(a)	4	3	4	4	3-4	3-4
(b)	3-4	3	4	4	3	3
(c)	4	3-4	3-4	3	3	3
(d)	4	3-4	3	3-4	3	3-4
7(a)	4	3	4	4	3	3-4
(b)	4	3-4	4	3-4	3-4	2-3
(c)	3-4	3	3-4	4	2-3	4
(d)	4	3-4	3	3-4	3-4	3
(e)	4	4	3	4	3-4	4
(f)	4	3	3-4	4	4	3-4
8(a)	4	3-4	3	3-4	4	2-3
(b)	4	3	2-3	3	3	3
(c)	3-4	2-3	3	2-3	2-3	3
(d)	3	3	3	3-4	3	3

From the data summarised above, the printed samples are also very fast to washing with little staining of the adjacent white materials.

Chapter Five

Conclusion

In the series of the azo dyes prepared, it can be concluded that the incorporation of the electronwithdrawing groups in the acceptor half of the chromogen results in bathochromic shift of the visible absorption band, while the incorporation of electron donating group in this position gives a hypsochromic effect.

Similarly, when the strength of an electron donating group incorporated in the donor ring of the chromogen is increased, the colour of the dyes become more bathochromic. The effect of solvent polarity on the visible absorption band generally show a red shift on changing from less polar solvent to more polar solvent. Also, all the azo dyes show pronounced halochromic effect on addition of few drops of acid, this is typical of azo dyes.

The colours obtained on dyeing of both polyester and nylon fabrics with azo dyes synthesised show a very billiant shade with good washing fastness rating which is quite in the range acceptable for quality dyeings.

The colour obtained from methine dyes ranges from yellow to green. Replacement of the carbonyl groups of the parent dyes investigated results in highly bathochromic shift and this shows that the cyano groups are strongly electronegative to induce such highly bathochromic displacement.

The methine dyes synthesised are also very suitable for transfer printing and the resistance of the printed materials to washing are excellent.

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APPENDIX 1

DYED FABRICS WITH THE MONOAZO DYES

DYE NO	Polyester	Nylon
2(a)		
2(b)		
2(c)		
2(d)		
2(e)		
2(f)		
2(g)		
2(h)		
2(i)		

APPENDIX 3

COLOUR OF METHINE DYED SAMPLES

DYE NO	NYLON	POLYESTER	COTTON
6(a)			
(b)			
(c)			
(d)			
7(a)			
(b)			
(c)			
(d)			
(e)			
(f)			
8(a)			
(b)			
(c)			
(d)			

APPENDIX 4

COLOUR OF METHINE PRINTED SAMPLES

DYE NO	NYLON	POLYESTER	COOTON
6(a)			
6(b)			
6(c)			
6(d)			
7(a)			
7(b)			
7(c)			
7(d)			
7(e)			
7(f)			
8(a)			
8(b)			
8(c)			
8(d)			