THE EFFECTS OF INCORPORATING HIGHLY ELECTRON WITHDRAWING GROUPS ON COLOUR AND DYEING PROPERTIES OF MONO AZO DISPERSE DYES

BY

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December, 1992

DECLARATION

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



YAKUBU, M. Kabir

Date: 5 - 1 - 1994

CERTIFICATION

This thesis entitled "The effects of incorporating highly electron withdrawing groups on colour and dyeing properties of mono azo disperse dyes" by Yakubu M. Kabir meets the regulations governing the award of the degree of master of science of Ahmadu Bello University and is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

This work is dedicated to Him who is knowledge itself. Who entails us to ponder and wonder about His creation.

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My foremost unreserved gratitude goes to my supervisor, Dr. K.A. Bello whose ingenuity alone saw me to the completion of this work. Infact no words will be enough to thank him for all the pains he took to groom me for this task, gather materials, constructively criticise and patiently took in all my shortcomings with fortitude. I hope that Almighty Allah will reward him here and there.

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Mohammad Kabir Yakubu.

ABEIBACX

Highly electros withdrawing groups, bromine and oyano, were substituted into 2' , and 6' - positions in the acceptor ring of azo dyes, with c o n d e n e s a b l e aldehyde group in the 4-position. The formyl group of the resulting dyes were condensed with active methylene compounds to give series of dyes. Characterisation and spectrophotometry analysis of the derived dyes were carried out. The dyes were applied to polyester and their dyeing properties were investigated.

It was found that the incorporation of these highly electron withdrawing groups led only to slight bathochromic shifts of visible absorption bands. Seasons such as steric interference were given to explain the effect. However, it was found that the dyes derived from 2',6'-dicyano para-aminoaeompounds were more bathochromic than their 2',6'-dibromo para-aminoazo conterparts.

Most of the dyes exhibit, negative halochromism due to the. effect of electron withdrawing groups incorporated in the

acceptor ring. Most of the. dyes also show bathochromic shifts as the solvent polarity was increased.

The dyes are generally fast to washing but very poor to light.

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CHAPTER 1

1.0 INTRODUCTION

1.1 GENERAL INTRODUCTION

Dyes are described as chemical substances which are coloured and can impart their colour onto a substrate either from a solution or aqueous dispersion. The substrate may be either textile fibre, leather, food items, hair or cosmetics etc.

Dyes and pigments owe their colour to their ability to absorb light of wavelength ranges within the visibe region of the electromagnetic spectrum (λ; 400 - 800nm). This is due to the electronic transition between different molecular orbitals within the molecule and the wavelengths absorbed are determined by the energy difference between the orbitals[1].

The colour seen when a chemical substance absorbs a particular wavelength within the visible spectrum is however the complementary colour of the reflected light.

Table 1.1, gives pairs of complementary colours with their wavelengths in the visible spectrum.

Table 1.1 Pairs oc Complementary Colours[2]

Colour absorbed	Wavelengths absorbed	Colour seen
Violet	400 - 435nm	Yellow-green
Blue	455 - 480nm	Yellow
Greenish-blue	480 - 490nm	Orange
Bluish-green	490 - 500nm	Red
Green	500 - 560nm	Purple
Yellow-green	560 - 580nm	Violet
Yellow	580 - 595nm	Blue
Orange	595 - 605nm	Greenish-blue
Red	605 - 750nm	Bluish-green

1.2 COLOUR AND CHEMICAL CONSTITUTION

The theory of modern synthetic dye is attributed to the pioneer work of Perkin when he discovered mauveine in 1856[3]. New chromophoric dye classes were developed in the 1860's. The field of triarylmethane dyes was discovered in 1859 by the synthesis of Magenta by Verguin. In 1862, the first Acridine dye, Phosphine was discovered by Nicholson. In 1858 dye synthesis and organic chemistry in general was revolutionized by the discovery of diazotisation reactions by Griess[4]. The first azo dye, Aniline Yellow was thus synthesized in 1861, Bismarck brown by Martin in 1863 etc. In 1868, Graebe and Liebermann synthesized the natural dye Alizarin thus marking the beginning of anthraquinone chemistry.

At all these times, structural chemistry was very much in its infancy. Electron was unknown, bonding in molecules was based on empirical valency ideas. Kekule had provided the cyclohexatriene formulation for benzene in 1865[5]. This was later modified to a dynamic structure involving a continuous oscillation between the two triene forms.

The first observation on the relation between chemical constitution and colour was made by Graebe and Liebermann[6]. They postulated that colour arise from the presence of unsaturation in a molecule. This idea was based on the experimental observation that all known dyes could be reduced and the colour disappears on reduction.

In 1879, Professor Nietzki[7] extended this idea and formulated a rule that the colour of a dye was deepened (shifted bathochromically) by the addition of groups to the molecule thus increasing the molecular weight. This rule was however left open to criticism due to ready availability of practical exceptions; however, the rudiments of the ideas of extended conjugation can be recognised in it.

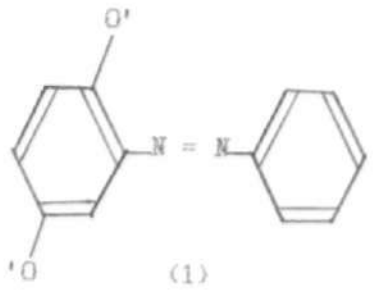
Hewitt and Mitchell[8] stated the rule correctly in terms of the dependence of colour on the conjugation length in a molecule. Schutze[9] in 1892 examined Nietzkis rule in depth pointing out many exceptions and in so doing coined the terms bathochrome and hypsochrome. These are now used to describe red (bathochromic) and blue (hypsochromic) shifts in absorption spectroscopy.

The first real attempt to establish a general theory relating depth of colour to molecular constitution was made by Witt in 1876[10]. He provided what has proved to be one of the most durable theories surviving to the present day and having its indelible mark on the everyday terminology of electronic absorption spectroscopy. Witt considered that a dye molecule could be dissected into discrete units, the total combination of which gave rise to colour. He noted that all dyes known at that time contained a benzene or naphthalene moity and that attached to this moity were simple unsaturated groups such as $-NO_2$, -NO, -N=N-, -C=O. He termed these groups chromophores. Combination of an aromatic nucleus and chromophores generally give rise to feeble colour or none at all. Such a union was called a chromogen. Intense colour could be developed from a chromogen by attaching weakly basic groups i.e $-NH_2$, $-NR_2$, -OH etc called auxochromes. In modern times a chromophore is more clearly defined as a -M (mesomerically electron withdrawing) and auxochrome as a +M (mesomerically electron donating) substituents.

This approach was adopted by Kauffmann[11] in the 1990's, systematically extended and developed. He established that the relative effectiveness of the common auxochromes for producing colour is

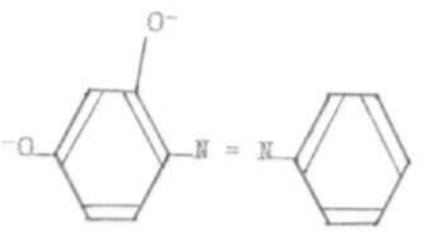
$$C_2H_5- < OCH_3 < NHAc < -NH_2 < NMe_2 < NHPh.$$

Recognizing that chromophores were opposite in Acid-Base characteristics to auxochromes, Kauffmann redesignated them anti-auxochrome. Kauffmann also examined the influence of multi auxochromic substitution on colour and the importance of the relative position of auxochrome and anti-auxochromes in a dye molecule. Kauffmann showed that the deepest colour was obtained when two auxochromes were ortho, meta relative to a single anti-auxochrome. The organic chemist however thinks that ortho and para arrangement is potentially the most bathochromic. This is well exemplified by the two azo dyes anions (1) and (2).



(1)

blue



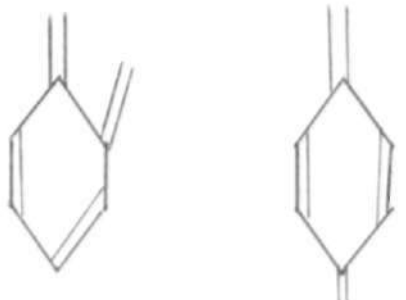
(2)

orange

Although a greater number of low energy resonance structures can be drawn for (2) than for (1), it is the latter compound that absorbs at longer wavelength. This highlighted one of the weakness of the resonance interpretation of colour, in which seemingly resonance forbidden structures are often ignored, yet this can make a very important contribution to the excited state of the molecule and hence its colour. Adequate consideration of such structures predict (1) to have lower transition energy.

Witts theory was developed further by Pfeffer, Delthy and Wizinger[12]. To explain the intense colour of di- and triarylmethane cationic and anionic dyes which contain no obvious chromophores, the concept of lonogenes was introduced (e.g $-\overset{+}{C}-$, $-\bar{C}-$, $-\bar{N}-$) which were powerful antiauxochromic groups. Witts theory though applicable to quinone and azo dyes, could not be applied to the cationic dyes known at that time.

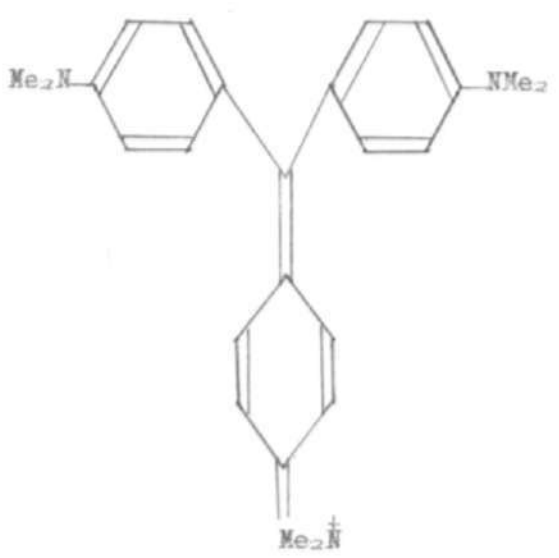
In 1888, the quinonoid theory was proposed by Armstrong[13]. This approach enjoyed wide acceptance in its day because of its immediate relevance to the cationic dyes which were most numerous at that time. This theory no longer survive and has no relevance in modern interpretation of colour. The theory was based on the idea that the exocyclic double bonds peculiar to ortho and para quinonoid structures (3) and (4) were in some way strained and this was associated with colour. Thus any molecule that had such quinonoid units in its structure would exhibit colour.



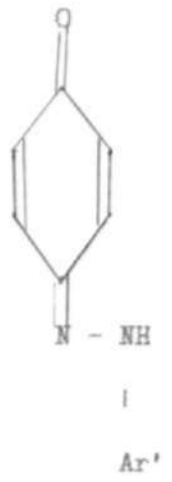
(3) (4)

Cationic dyes e.g (5) also owe their intense colour to the quinonoic structures. The azo dyes are adopted to this theory by

assuming that they actually existed as hydrazone tautomers e.g (6).

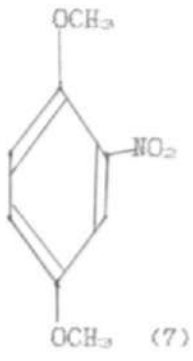


(5)



(6)

Many exceptions to the quinonoid theory were advanced. Some quinonoid compounds were synthesized with no colours e.g 1,4-benzoquinone diamine and also many intensely coloured compounds with no possibility of quinonoid sbstituents were synthesized e.g yellow, 1,4-dimethoxy-2-nitro-benzene (7).



(7)

In 1913, Watson[14] suggested that if a dye could show a quinonoid structures in its possible tautomeric forms, then it would be deeply coloured however small its molecular size, e.g indamine (8) which is blue, contrasted with 4,4'-diaminoazo benzene (9) which is yellow and yet the latter has the greater degree of conjugation. It was then possible to rationalize various pronounced differences between dyes of similar molecular size, as Watson demonstated for hydroxy-anthraquinones, triary-methane, indophenol dyes and many others.



(8)



(9)

In 1904, Baly and Desch[15] promoted by the discovery of the phenomenan of keto-enol tautomerism, presumed that near uv light absorption was associated with the very rapid bond alternation occuring between tautomeric forms of a molecule (dynamic isomerism) for example ket-enol tautomerism).

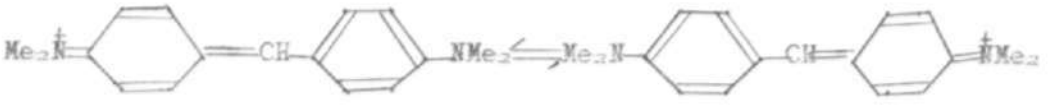


(10a) (10b)

However many coloured compounds are incapable of exhibiting tautomerism.

Analogous oscillation theories were proposed by Von Baeyer[16] for triarylmethane dyes and by Willstatter[17] for quinhydrones and oscillation between benzonoid and quinonid rings structures was assumed to occur.

Watson[14] extended these ideas to include other dye systems and suggested that the oscillating process in a dye molecule corresponded to the reversal of double bond and single bonds along the whole conjugated chain i.e.



(11a) (11b)

The longer the chain the slower the period of the oscillation and then one could account qualitatively for the effect of conjugation length on absorption. The idea that light absorption involved the electrons in a molecule was introduced later but was accepted reluctantly by organic chemists. Drude[18] showed theoretically that whereas atomic vibration corresponded to frequencies in the I.R. range, U.V. frequencies required the oscillation of particles of much smaller mass i.e electron and visible region involved interractions of the radiation with electrons.

1.3 Qualitative Methods of Colour Prediction

1.3.1 Predictive Method Of Colour Assessment

Coloured organic molecules can be of the following chromogenic types.

(i) n-π* chromogen

(ii) donor-acceptor chromogen

(iii) polyene chromogen

(iv) cyanine type chromogen

Most organic dyes however belong to the donor-acceptor class. Such chromogens are characterized by having one or more substituents with lone pair of electrons (donor groups) and one or more electron attracting substituents (acceptor groups) attached to the same conjugated π electron system (conjugating bridge). Absorption of visible light results in the migration of π-electrons density from the donor groups to the acceptor groups. The transition energy of such process will depend critically on the relative strengths of the donor and acceptor residues and also the nature of the bridging group. Most empirical quantitative work is based on the numerical definition of the donor strength (ionization potential) and acceptor strength (electron affinity, Hammett σ constants), and the correlation of these quantities with absorption maxima.

The order of electron donor strengths for some common donors based on ionization potential is

$$OAc < OH < NHAc \approx OMe < SH < NH_2 < SMe < O^- < NH^-$$

The colour of donor-acceptor chromogens generally deepen as the donor strength is increased. An example of a linear correlation between absorption wavelength and ionization potential of donor is given by the 2-donor substituted anthraquinone[19]. Corresponding compounds substituted in the 1-position are complicated by steric interraction and hydrogen bonding effects.

Prediction of spectra properties based on electron acceptor strength using the Hammetts substituents σ constant are met with complexities because the σ-constant derived on the basis of ground state properties of aromatic compounds containing the relevant acceptor group, may have little relevance in the excited state of the chromogen.

1.3.2 Resonance Theory

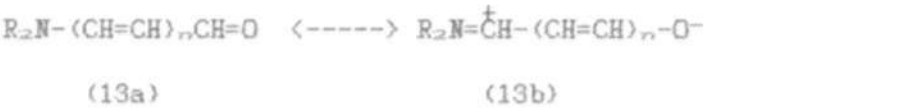
This theory states that if an unsaturated organic molecule can be represented reasonably as a hybrid of two extreme canonical forms, then, the closer the two forms are in energy, the smaller will be the gap between the ground and first excited state, i.e the more bathochromic will be the light absorption band. 12a and 12b are two canonical forms of a cyanine dye; they are equal in energy, thus resonance theory suggests that these should absorb at particularly long wavelengths. Such chromogens

are generally the most bathochromic of all organic π-π^* chromogens for a given molecular size.



(12a) (12b)

The merocyanines (13) have none-equivalent extreme forms (13a) and (13b), they are predicted to absorb at shorter wavelengths than the cyanines of equivalent chain length. The merocyanines and related chromogens have a ground state structure corresponding more closely to the neutral form and thus show some degree of double bond - single bond alternation along their conjugated systems.



(13a) (13b)

The hydrocarbon polyenes on the other hand represent an extreme situation where one canonical form (14a) is much lower in energy than the charge separated form (14b), these are thus relatively hypsochromic chromogen.



(14a) (14b)

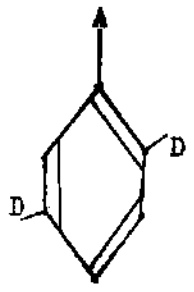
All general qualitative treatments of colour and constitution recognise the fundamental significance of the transition of a

chromogen from the ideal so called polymethine state as in (12) to the polyene state as in (14) although some place greater stress on this than others.

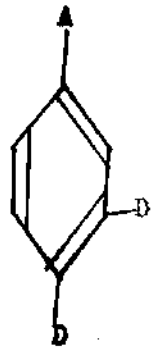
When several low energy resonance forms for a molecule are possible, it is generally assumed that the greater the number of these, the more bathochromic will the molecule be.

However, the main weakness of resonance theory lies in the assumption that only a few, low energy canonical forms contribute to the hybrid molecular structure. It has been found out that various high energy forms may make an important contribution to the excited state of a molecule, neglect of this can lead to the prediction of high energy absorption bands where infact low energy transition exist.

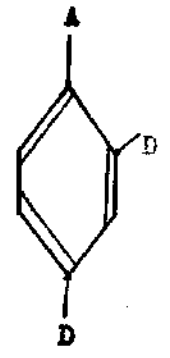
Some of the exceptions to the above rule predicted by resonance theory is given in (15). A and D are acceptor and donor groups respectively. It is observed that the relative order of λ_{max} values for these systems will be (15a) > (15b) > (15c). The reverse order is predicted by the resonance theory.



(15a)

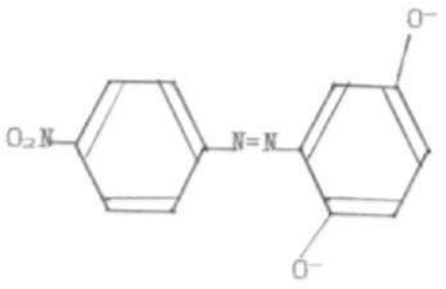


(15b)



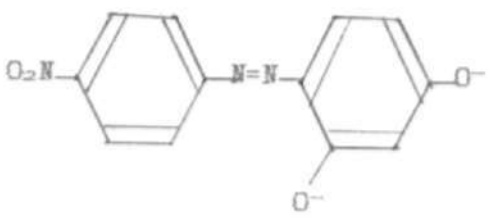
(15c)

The ionized dihydroxyazo benzene derivatives (16) and (17) provide other examples of such systems.



(16)

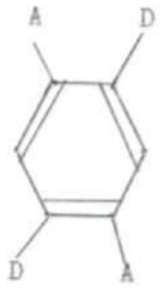
λ_{max} 655nm



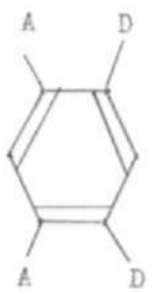
(17)

λ_{max} 574nm

Other exception can be been in the case of benzene derivatives bearing one donor and one acceptor group, as in (18a) and (18b), the meta isomer in most cases absorbs at longer wavelength than the para isomer, the resonance theory predicts the reverse.

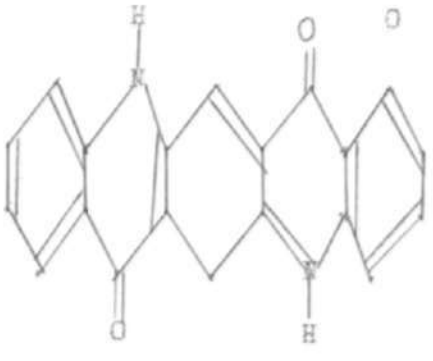


(18a)



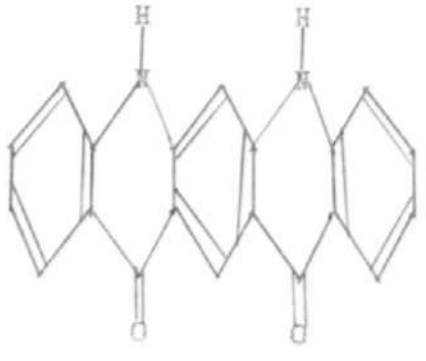
(18b)

Also quinacridone (19) is red-violet, whereas its isomer (20) is yellow in colour.



(19)

red-violet



(20)

Yellow

Resonance theory is of considerable value in helping one to understand the colour and constitution behaviour of cyanine type chromogens, because of its conceptual simplicity. However, this approach cannot be extended with any confidence to other more complex types of chromogen.

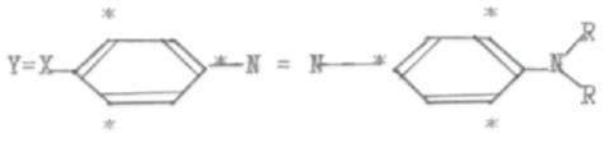
1.3.3 Perturbational Molecular Orbital Theory (PMO)

The (PMO) method considers the electronic structure of a complex molecule to arise by the modification or perturbation of a simpler model compound[51].

Such a perturbation might result from the attachment of substituents to the model structure or the replacement of a carbon atom in the molecular frame work by a heteroatom. By focussing attention on the highest unoccupied molecular orbital (H.U.M.O) and lowest unoccupied molecular orbital (L.U.M.O), Dewar[20] was able to draw up a set of rules for predicting the

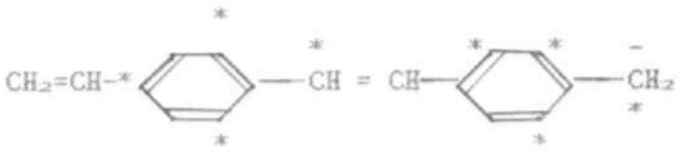
effect of structural changes on the colour of alternant molecules.

An alternant molecule is defined as one that contains a system of overlapping atomic p-orbitals such that the contributing atoms are linked to form open chains or even-numbered rings. If the contributing atoms are indexed by 'starring' every alternate atom, it is found that in such systems no two adjacent atoms will carry the same index. Starring is initiated at any of the terminal positions of the π-electron system and it is found that all odd alternants have at least one more starred atom than there are unstarred atoms. The following scheme can be used to explain the starring in the Dewar's analysis.



(21)

Y=X- represents typical electron acceptor group such as $-NO_2$, -CN-, -CHO etc.



(22)

However slight modification as summarised below have been made to the general approach.

(i) Alteration of the electronegativity of an atom in an even numbered alternant system has only a small effect on the wavelength of the first absorption band.

For odd numbered alternants the following rules apply.

(ii) Replacing a carbon atom at a starred position by a more electronegative heteroatom will cause a hypsochromic shift of the first absorption band whereas similar replacement at an unstarred position will cause a bathochromic shift.

(iii) Attaching electron donating substituents (+M, +I) to a starred position will cause a bathochromic shift of the first absorption band, attaching them to unstarred position will cause hypsochromic shift. The reverse is true of electron withdrawing substituents (-M, -I).

(iv) Attachment of a neutral conjugating specie (±M) i.e, phenyl, vinyl etc to any position in the chromogen will result in a bathochromic shift.

So many examples can be given to confirm the rules but still some limitations to the rules have been found out. One of the problems concerns what is meant by an 'electron donating' or 'electron withdrawing' groups, for some substituents both characteristics are observed depending on their particular relationship to the reaction centre in a given molecule. The methoxy group (-OCH_3), for example shows typical donor properties when it is in the para position of a phenyl ring and in this case

the +M effect of the group is dominant. In contrast, the same substituent in the meta position of a phenyl ring is weak electron acceptor and in such case the -I effect is dominant. Many substituents have similar opposed inductive and mesomeric effects (e.g -OH, NH_2, -F, -Cl).

Dewar's rules are based on the orbital pairing properties peculiar to alternant hydrocarbons and as long as heteroatomic dye structures bear a close similarity to such compounds, the rules should work well.

.However, there is evidence that in more complex systems containing several heteroatoms and exhibiting some polyene character the anology between such systems and iso-π-electronic odd alternant hydrocarbon breaks down, and the rules are inapplicable, e.g the aminoazobenzenes illustrated by (21). Rule 3 would suggests that attachment of electron donor groups e.g OMe, NHAc, Me) to the 2-position (formally unstarred) should produce a hypsochromic shift, whereas it is well known that such structural modifications give useful bathochromic shifts. Conversely, hypsochromic displacement were produced when electron acceptor groups were attached to the same position.

Failure of Dewar's rules also occurs in other systems e.g the anthraquinones and in certain cases the rules cannot be applied at all, if a chromogen is non alternant system (e.g the indigoids). In such cases the 'starring' procedure breaks down.

1.3.4 The Triad Theory of Dahne

Dahne[21] developed some ideas concerning the basic theories of colour and constitution in organic chemistry. This theory developed in 1965 is an overall restatement of the well known molecular orbital and electronic properties of alternant hydrocarbon and the extension of these principles to include heteroatomic dye structures and complex donor-acceptor chromogens containing several donor and acceptor groups.

Dahne postulated that there are three ideal states for unsaturated compounds.

(i) The aromatic state structure. This is believed to have a stabilised electronic structure with equal π-bond orders and equal π-electron densities at all atoms.

(ii) The polyene state. In this system there is no special resonance stabilisation of the conjugated system and thus there is a high degree of single-double bond alternation.

(iii) Polymethine state. Structures falling under this correspond to the odd-altenant hydrocarbon anions and cations and also include the even alternant polyene radical anions and cations, such systems possess a high resonance energy, equal π-bond orders and a strongly alternating π-electron density.

Electronic excitation gives a maximum change in π-electron density at all atoms.

Dahne's general formula is represented by structure (25)

$$\text{-----}(N\pm1)\pi\text{----}$$

$$X\text{-}(Y)_{n-2}\text{-}X^{-}$$

(25)

Based on this, the following rules are made for predicting colour and constitution.

(i) If a polymethine system is pertubed by replacing carbon atom by a heteroatom or attaching a substituent, if the characteristic charge density alternation of the polymethine is preserved, then the first absorption band will be unaffected or displaced slightly to shorter wavelength. The resultant structures are designated.

(ii) If modification such as described alters the characteristic polymethine charge alternation, then the resultant chromogen will absorb at significantly longer wavelengths than the parent system.

(iii) If an alternating or non-alternating polymethine can adopt a more favourable aromatic structure, the chromogen will absorb generally at shorter wavelength than the corresponding unbranched polymethine chromogen.

(iv) The gradual transition from an ideal polymethine structure to an aromatic or polyene structure results in an increasing hypsochromic shift[22].

Some important criticism of the Dahne's approach to colour and constitution theories is that it attempts to interprete the

behaviour of all donor-acceptor chromogens within the polymethine concept, as a result in a few cases lead to the wrong prediction.

1.4 QUANTITATIVE MOLECULAR ORBITAL METHODS

The most successful procedures for computing the transition energies and intensities of complex organic molecules are based on the linear combination of atomic orbitals (LCAO) theory. This assumes that the molecular orbitals of a particular structure can be represented as a linear combination of the individual atomic orbitals present in the system. By calculating the energy of each molecular orbital it is then possible to calculate the transition energies for the promotion of an electron from a low energy orbital to the various high energy unoccupied orbitals. From the L.C.A.O. form of the two orbitals involved in a transition, it is possible to estimate the absorption intensities.

It is assumed that the σ and π orbitals of an unsaturated molecule can be treated independently and attention is directed to the higher energy set of π-orbital only. Electron repulsion effects are ignored hopefully to be compensated for by suitable choice of empirical parameters. We have various methods under this category some of the more important ones are:

1.4.1 The Free Electron Model (F.E.M.O)

The (FEMO) method is the simplest molecular orbital calculation procedure and works surprisingly well with polymethine systems because of their high degree of bond uniformity along the molecular axis. The approach restricts attention to the conjugated π-electron systems which are regarded as mainly responsible for the colour of dyes.

It is assumed that the electrons are free to move within the conjugated system, based on this, Kuhn[23] showed that the wavelength of the maximum absorption over the first absorption band λ_1 is calculated by means of the Schroedinger expression[24].

$$\lambda_1 = \frac{8mcl^2}{h(n+1)} \quad \ldots\ldots\ldots\ldots (1)$$

and the transition energy is given by

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

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

However, one important source of error identified with this approach is due to its assumption that all bond lengths along the molecular axis are identical which assumes a constant potential

energy along the chain, this situation does not hold for polyenes which are known to exhibit strong bond alternations.

Though many refinements of the method have been suggested, these are more of academic than practical value because of ready availability of other far superior methods.

1.4.2 The Huckel Method (HMO)

The Huchel method is based on the assumption 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 orbital, with each atomic orbital having the wave function ϕ, ω can be written as a linear sum.

$$\omega = C_1\phi_1 + C_2\phi_2 + + + \ldots\ldots C_n\phi_n \quad \ldots\ldots (3)$$

C is the mixing coefficient and the energy of the eigen value, E, of the molecular orbital is defined by the equation.

$$H_\omega = E_\omega \quad \ldots\ldots (4)$$

where H =- Hamilton operator.

$$E = \frac{\int_{-\infty}^{+\infty} E_n C_n \phi_n + \Sigma_n C_n \phi_n dx}{(\Sigma_n C_n \phi_n)^2 dt} \quad \ldots\ldots (5)$$

w = wave function.

Thus the energy of a molecular orbital is expressed in terms of the atomic orbital wave function.

The HMO model provides the π-orbital energies of a molecule, these energies can be expressed in the general form[23].

$$E_n = \alpha + X_n\beta \quad \ldots\ldots\ldots (6)$$

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.

Although the HMO method is more generally applicable than the latter procedure, it suffers from the same major disadvantage, namely that it neglects electronic interaction effects.

The method can however be refined in various ways, and in particular it can be made self-consistent by carrying out several consecutive calculations on the same molecule, adjusting the parameters at each state to allow for the charge densities and bond orders predicted by the previous calculation. Eventually convergence is achieved, i.e, predicted charge densities and bond orders show no change between two consecutive calculations. Such a procedure has been used recently to calculate the spectra of a wide range of heteroatomic conjugated molecules, including retinals and porphyrins[25].

1.4.3 The Pariser-Parr-Pople (PPP) Method

Both the HMO and the FEMO methods suffer 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. The PPP method takes into account electronic interaction, and because it is self-consistent it is well suited to handle heteroatomic structures.

Since it is also based on the LCAO approach, it assumed that each molecular orbital can be expressed as a linear sum of the individual atomic orbitals. A set of equations are obtained which are similar in general form to the HMO equation, differing only in the energy terms α_i (coulomb, integral), β_i (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 orbital j without reversal of spin (singlet-singlet transition) is given by[26]

$$\Delta E_{i \longrightarrow j} = (E_j - E_i) - \gamma_{ij} + 2\delta_{ij} \quad \ldots\ldots (7)$$

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

Additional advantages of the method over the previous two (FEMO and HMO) are that

(i) The ability to distinguish molecular geometry like the cis-trans isomers.

(ii) The ability to distingish between singlet and triplet states.

The main disadvantage of this method is that it relies on the assumption that the σ^- and π^- electrons behave independently of each other, and thus the σ-elecrons are ignored.

1.4.4 All-Valence-Electron Methods

All valence-electron MO calculations are based more or less on the same formular as the PPP procedure but with the major difference that all orbitals involved in bonding, i.e both σ^- and π-electrons are specifically considered. Obviously the choice of parameters is a greater problem than in π-electron methods, and in addition, the demands made on computer time are much greater.

Important calculations of spectra is the CNDO/S method designed by Jaffe and Del Bene[27], this was applied for the polyenes and polyacetylenes[28], acetylinic, cyanines[29] porphyrins[30] and the aminoazobenzene[30].

1.4.5 Molecules in Molecules Method

Molecules in molecules (MIM) calculations have both quantitative and qualitative applications in colour and constitu-

tion studies. When MIM and PPP are combined, the procedure is known as 'configuration analysis'[31].

The MIM procedure was developed by Languet-Higgins and Murrel[32] and is consequently also known as the LHM method.

In this method a complex unsaturated molecule is dissected into smaller sub-units, the molecular orbital properties of which are known, and the state wave function for the complete molecule are calculated on the basis of these smaller units. For example a donor-acceptor chromogen is considered to consist of three units: the donor, a single atom with lone pair of electrons; the acceptor, consisting of two atoms linked together by a double bond; and the conjugating bridge, a more complex system of conjugated doube bonds. If the units are brought together and still retain their separate identities, then various electronic excitation processes are possible. These may be classed as local excitation, where an electron is promoted from a bonding orbital to an antibonding orbital within the same unit, and gives rise to locally excited (LE) configurations. Alternately they can be classed as charge transfer transition, where an electron from the bonding orbital of one unit is promoted to the antibonding orbital of a different unit and gives rise to charge transfer (CT) configurations.

To obtain a closer approximation to the true situation, the ground state or no bond (NB) configuration, the LE and CT configurations are considered to interact and the configuration

interaction procedure gives rise to state wave function and energies, the former expressed as a linear sum of the NB, CT, and LE configurations, which is later retained and simplified in the work of Baba, Suzuki and Tekemura[31] where they based their calculations on the PPP-Cl method on the concept of delocalised molecular orbitals.

$$\omega = C_{N\omega NB} + cc_{T,1} + C_{\varepsilon T,2}\omega_{\varepsilon T,2} +++ \ldots\ldots$$
$$+ Cl_{\varepsilon,1}\ \omega_{1\varepsilon,1} + C^{1E,S}\ \omega_{LE3} ++++ \ldots\ (8)$$

where ω is the wave function

1.5 DISPERSE DYES

In early 1920s, secondary cellulose acetate then called 'synthetic silk' was synthesized. Unfortunately it was soon discovered that all available dyes both natural and synthetic known then could not dye this fibre, apart from some few acid, mordant and basic dyes none of which gave dyeings of satisfactory fastness properties.

Disperse dyes owe their name due to the fact that they are only sparingly soluble in water and are applied from finely dispersed particles in aqueous media.

Disperse dyes are the most important class of dyes in the colouration of cellulose acetate and polyesters.

1.5.1 Physical Properties of Disperse Dyes

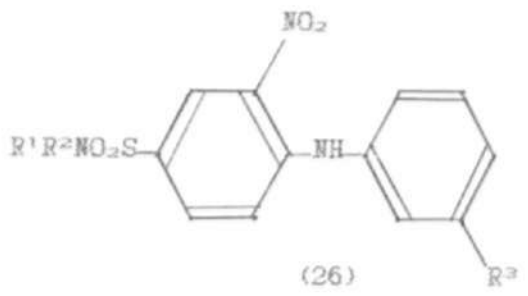
Disperse dyes are nonionic, crystalline when pure, are of comparatively low molecular weight and when heated above melting point sublime without decomposing. They are very sparingly soluble in water at dyebath temperatures. Chemical groupings in the dye responsible for solubility are normally those which can form hydrogen bonds with water, notably -N=N-, -OH, $-NH_2$, -O-Alkyl, -NHAlk.

1.5.2 Chemical classification of Disperse Dyes

Chemically disperse dyes belong to three more important and two less important chemical groupings:

1.5.2.1 Nitrodiphenylamine Dyes

The basic structure of this type of dye is



(26)

R^1 and R^2 = H, Alk or Ar; R^3 = H or substituent.

They are generally prepared by chlorosulphonating 2-nitrochlorobenzene and condensing the products with ammonia and

alkylamino or aniline to give the corresponding sulphonamide followed by further condensation with an arylamine at a higher temperature to form the nitrodiphenylamine. Probably the best known commercial dye of this type is C.I. Disperse Yellow 42 (26, R^1 = ph; R^3 = R^2 = H).

This is a relatively small class of dyes which are still used on account of their low cost, ease of manufacture, very good fastness to light in pale colours and their usefulness in producing greens with blue anthraquinone dye whilst maintaining good fastness to light.

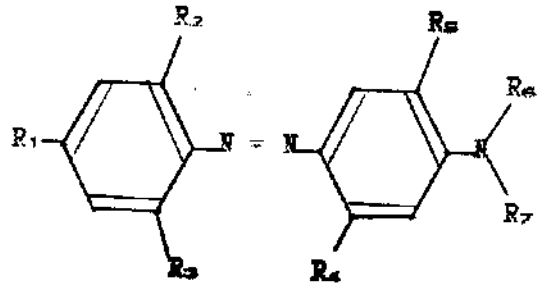
One of their main problems is that their sublimation fastness is not very good.

Recently research work has aimed at improving the sublimation fastness either by the incorporation of polar groups or by increasing the molecular size[33-36].

1.5.2.2 Azo Dyes

Basically azo dyes can be defined as the dyes made by the diazotisation of primary aromatic amines and then coupled to a suitable coupling component.

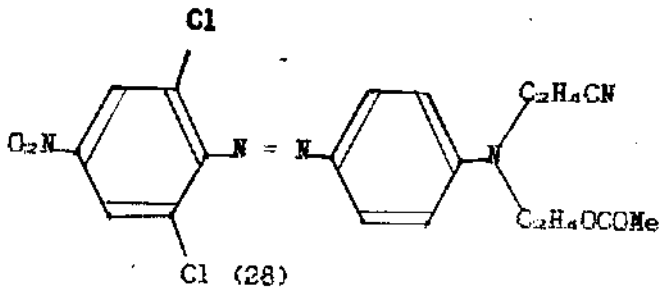
The general formula for azo disperse dye is:



(27)

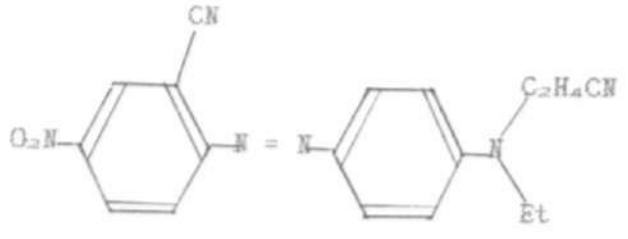
R_1 = an electron attracting group especially a nitro group; R_2 and R_3 = H or electron attracting groups, R_4 and R_5 = H or electron repelling groups, R_6 and R_7 = H or especially alkyl groups which may be further substituted.

In general this type of structure is used to cover the orange to blue area of the spectrum using 4-nitroaniline and 2-chloro-4-nitroaniline for oranges and scarlets, 2,6-dihalogeno-4-nitroanilines for browns, 2-cyano-4-nitroaniline for reds and reddish violets, 6-bromo-2-cyano-4-nitroaniline for violets and reddish blues and 6-halogeno-2,4-dinitroaniline for blues. Several structures of this type of comercial dye have recently been disclosed[37].



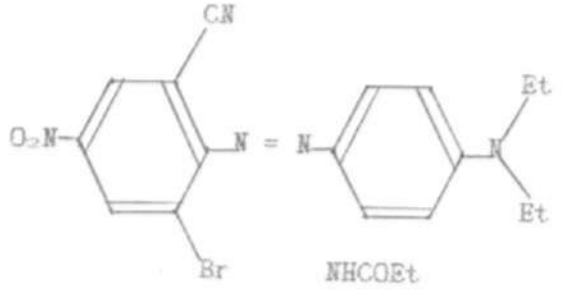
(28)

C.I. Disperse orange 30.



(29)

C.I. Disperse Red 73



(30)

C.I. Disperse Blue 183

Azo disperse dyes continue to be the major area of research activity because of the following reasons.

(i) The colour of dyeings produced by azo dyes now range from greenish yellow to bluish green.

(ii) It is possibe to prepare these dyeings with moderate to very good fastness properties.

(iii) The dyes are relatively cheap and generally do not require numerous intermediate stages.

1.5.2.3 Anthraquinone Dyes

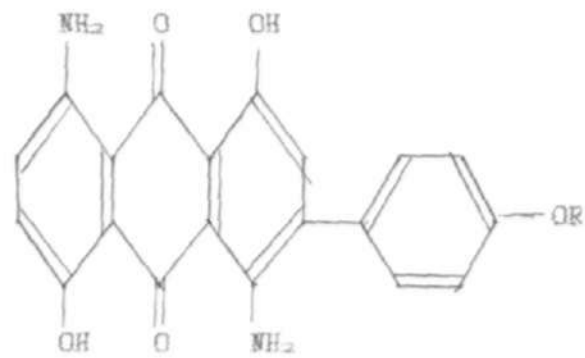
These give wide coverage of the spectrum. However, they are no longer popular with the dyestuff chemists and manufacturers due to the following reasons:

(i) Their tinctorial strength is weak.

(ii) Several intermediate stages are often required in their production.

(iii) Most of the intermediates are derived from anthraquinone-α-sulphonic acids which require a mercury catalyst.

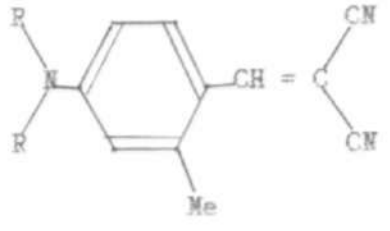
An example of anthraquinonoid dye is C.I. Disperse Blue 73.



(31)

1.5.2.4 Styryl Dyes

These are useful for the production of bright greenish yellow colours with good fastness to light on polyester fibres. They have the general formula:



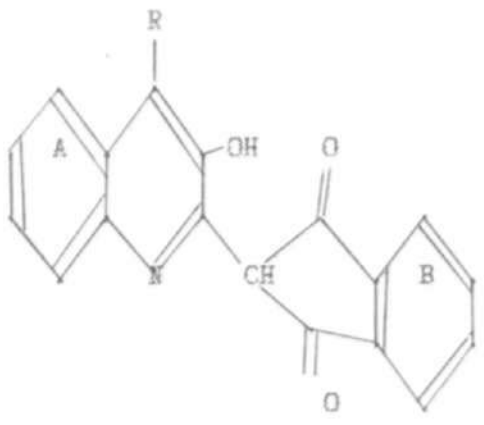
(32)

Some of the early members of this class of dyes were lacking in sublimation fastness and rather unstable when applied at high temperature especially under alkaline conditions.

1.5.2.5 Quinophthalone Dyes

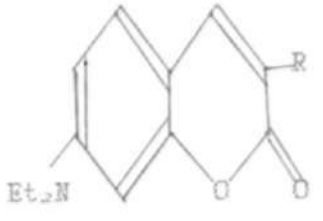
They produce greenish yellow colour effect on polyester. They are however limited in their colours. They possess good fastness to light with the advantage of a high degree of stability under most application conditions.

A typical structure is:



(33)

Though there are other chemical groups that can produce disperse dyes, they are not important as these groups. Some of the other important chemical groups that produce disperse dyes include coumarine dyes.



R is a heterocyclic radical

(34)

1.5.2.6 <u>Development in Azo Disperse Dyes Synthesis</u>

Colour and constitution studies have in the recent years centred on what might be termed 'donor-acceptor' monoazo dyes generalised by formula (35).

$$D_n - X - N = N - Y - A_n$$

(35)

D represents one or more donor groups, such as $-NH_2$, MeO, CH_3, $-NHCOCH_3$ etc, and X represents an aromatic ring system which may be carbocyclic or heterocyclic and together they constitute the donor half of the chromogen. The residue Y and the attached electron acceptor groups A form the acceptor half of the chromogen.

The visible absorption band of (35) can be equated with the movement of electron density from the donor groups D to the acceptor groups A, but in addition there is significant movement in the azo group itself, and thus it has been suggested[52] that the residue -N=N-Y-A_n be classed as a complex acceptor.

In the general sense, any factor that lowers the ionization potential of the unit D-X-, will cause a bathrochromic shift of the visible band. This can be achieved where X is benzene ring by

(i) Increasing the electron donor strengths of group D

(ii) Increasing the number of groups D

(iii) Varying the position of attachment of groups D relative to the point of attachment of the azo group.

(iv) The benzene ring can be replaced by a heterocyclic residue.

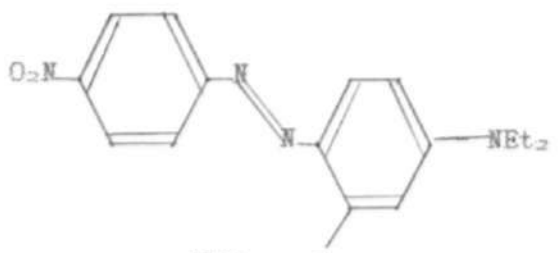
As far as (i) is concerned for maximum intensity in an amino azo benzene, the donor group should be para to the azo group. Though, meta and ortho donor groups give more bathochromic effects[38], they have very low absorption intensity (ϵ_{max} < 6,000), the intensity cannot be greatly enhanced by increasing the electron withdrawing strength of the acceptor ring.

The electron donor strength of the amino group in the para position can be modified in various ways[39].

Modifiction of the side chain substituents in the amino-donor group causes hpsochromic shifts as most heteroatomic substituents

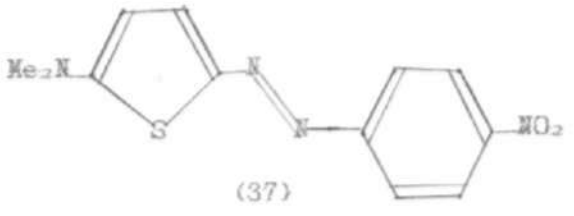
exert an electron withdrawing inductive effect which is transmitted through the σ-bonds of the alkyl chain to the nitrogen atom.

Substituent effects in the donor ring of dyes of type (36) has been examined in detail by Gregory and Thorp[41]. It was noted that donor groups R produced bathochromic shifts. The largest shifts were obtained when R = NEt_2 (λ_{max} in ethanol) and R = $-O^-$; 567nm, when compared with the parent dye, R = H, which has the value 486nm.



(36) R

As already mentioned, bathochromic shifts can also be produced by replacing the donor aromatic ring by a heterocyclic residues, the net effect being a general lowering of ionization potential of the donor moiety for example the thiopen analogue of the amino benzene (37) absorbs at 554nm in ethanol whereas its benzene counterpart absorbs at 478nm in the same solvent[42].



(37)

The colour properties of the donor-acceptor azobenzene are equally dependent on structural variation within the acceptor ring. This has been studied elaborately[43].

1.6 Objective of the Present Work

The objectives of the present study are many and notably among them are to synthesize new azo dyes. The effect of incorporating highly electron withdrawing groups on colour and chemical constitutions of the resulting dyes will also be examined. The effect of solvent polarity and few drops of HCl on the visible absorption spectra of the dyes will also be investigated. Finally all the dyes will be characterized and a comparative study of the influence of these substituents on the dyeing and fastness properties will be examined.

CHAPTER TWO

2.0 EXPERIMENTAL

2.1.0 General Information

2.1.1 Chemicals

Bromine

Glacial acetic acid

Para dimethyl amino benzaldehyde

Ethanol

Malononitrile

Idan-1,3-dione

Anhydrous sodium acetate

Hydrochloric acid

Sodium acetate trihydrate

3-Acetamido-6-methoxy aniline

3-Acetamido-N,N-diethyl aniline

2,5-Dimethoxyl aniline

Dimethylformamide

Toluene

Cuprous cyanide

Piperidine

Phenol

Detergent

Sodium carbonate

Liquid paraffin

2.1.2 Instruments

Mechanical stirrer

50ml three necked flask

Colorimeter 253

Xenon arc light fastness measuring instrument

Linitest washing machine

Dyeing master

Electronic weighing balance

Oven

2.1.3 Materials

Polyester fabric

Cotton fabric

Filter papers

Ice blocks

2.1.4 Melting Point determination

Gallamkemp melting point apparatus was used to determine the melting points of the synthesised samples.

2.1.5 Infrared spectroscopic measurements

A mule was prepared by grinding a mixture of the dyes in liquid paraffin. The paste was placed in between sodium chloride discs. Spectra of the samples were got using a Beckmann single beam infra-red spectrophotometer obtained at the Bayero University, Kano.

2.1.6 Visible absorption spectroscopic measurements

Colorimeter 253 was used. Five solvents were used to determine the wavelength of maxima absorption (λ_{max}) of the dyes. The solvents are dimethyl formamide, carbon tetrachloride, toluene, acetone and ethanol.

In either case, the determination of the λ_{max} involved taking so many readings while maintaining the concentration constant and varying the wavelengths by 2nm interval and taking the absorbance values. This was continued until a point was reached where the absorbance value continued to decrease with increasing wavelength. A graph plotted of wavelength versus absorbance revealed that the λ_{max} is that point where the absorbance started to decline with increasing wavelength (λ).

2.1.7 Determination of Halochromism effect

After obtaining the λ_{max} for the various dyes in ethanol, few drops of HCl was added and a change in colour was noticed. Colorimeter 253 was then used to determine the new λ_{max} following

the procedure described in section 2.1.6. The change of λ_{max} due to protonation of any centre of the dye is described as halochromism.

2.1.8 Determination of molar extinction coefficient

A known quantity of dye was dissolved in a known volume of DMF. The absorbance of the dye solution was determined at the appropriate λ_{max} for the dyes in DMF. Beer's and Lamberts law was used to determine the molar extinction coefficient.

2.1.9 Dyeing of polyester

The polyester sample was cut into 0.4gms samples. Each sample was dyed in a dyebath made up as follows:

10ml of 50g/l phenol as carrier

20ml of 17g/l anionic detergent

and 70ml of water.

The liquor:goods ratio being 250:1, the depth of shade being 1.4%. Dyeing was carried out for one hour at a temperature of 100°C. A thorough rinsing was then followed. The dyed samples were dried overnight. All dyeings were carried out using dyeing master.

2.1.10 Determination of dye exhaustion

All the dyed samples were weighed (ygm), small specimens were cut out from these samples and also weighed (xgm).

A known weight of each dye (dgm) was dissolved in 5cm³ of pyridine, λ_{max} and the absorbance values were noted. 5cm³ of pyridine was used to strip the dye from the specimens. The absorbance of the dyes stripped from the specimen was determined using the colorimeter set at the appropriate wavelength determined. By using Beers and Lamberts law, the quantity of the dye absorbed by the specimen was determined using the formular:

$$c = A_2 d / A_1$$

where c = the quantity in grammes of the dye absorbed by the specimen

A_1 = the absorbance of dgm of te dye in 5cm³ pyridine

A_2 = the absorbance of cgms dye stripped from the specimen in 5cm³ pyridine

The total dye in the sample = c/x . y

$$\text{Exhaustion (\%)} = \frac{c/x \,.\, y}{0.0056} \times 100$$

0.0056gm being the quantity of dye in the dye liquor from section 2.1.9.

2.1.11 Wash fastness test

This was done according to I.S.O. 3^{S2} standard washing procedure. The specimens were prepared by cutting the dyed samples into 10cm x 4cm dimensions. These samples were made into composites by stitching a test specimen made up of the dyed sample place in between a cotton piece and a polyester piece of dimension 5cm x 4cm. The composite was agitated in a solution made up in the following way:

5g/l soap solution

2g/l soda ash

Liquor ratio 50:1

The washing was carried out in the linitest machine at 60 ± 2°C for 30 minutes. The composites were then separated and dried.

2.1.11.1 Assessment of change in colour

Grey scale for evaluating change in colour was used to determine the change in colour after the washing test. The procedure involved comparing the degree of contrast between the originally dyed sample and the specimen tested, compared to the degree of contrast between the pairs of colours in the standard grey scale for assessing change in colour. The fastness rating of the specimen under test is the number of this grey scale contrast.

2.1.11.2 Assessment of staining

The degree of staining of the adjacent white polyester in the composite was assessed using the grey scale for assessing staining.

A white polyester material and the stained specimen were assessed according to the manner used for assessing change in colour as in section 2.1.11.1.

2.1.12 Light fastness testing

Light fastness testing of the dyed samples were assessed by the use of xenon arc light fastness instrument obtained at the Chemistry Department, Bayero University, Kano.

The procedure involved aligning both the eight dyed samples wool standards together with the dyed sample specimens on a card which was later attached to stainless steel metal strip and then inserted into a compactment which was maintained at a constant relative humidity by the use of distilled water during exposure. The compactment was then placed into position along the radial exposure chamber. Exposure was carried out for 24 hours until the last sample specimen to fade have faded to the extent of standard three of the standard grey scale for evaluating change in colour. The test was then terminated.

The rating of a dyed sample is that standard wool dyed sample which faded to the same extent as the specimen exposed at the same time.

2.2 PREPARATION OF THE INTERMEDIATES

2.2.1 Preparation of 3,5-dibromo para-amino benzaldehyde

Bromine, 68.39g (0.428 moles) was dissolved in 40cm^3 of glacial acetic acid. The solution was added dropwise to 30g of 4-dimethyl amino benzaldehyde (0.2moles) in 96cm^3 glacial acetic acid over a period of 15 minutes. Stirring was continued for 45 minutes while cooling in an icebath. Orange crystals were obtained, and these were washed thoroughly with benzene and then dried overnight over sodium hydroxide. The product obtained after drying was then oven heated for 3 hours at 135°C. This yielded 50.3gm of 3,5-dibromo-para-amino benzaldehyde. The compound was recrystallised from ethanol, melting point 148-150° (Lit[44] m.pt. 149.5-150.6°C). The yield was 89.68%.

2.2.2 Preparation of 3-oxo-$\Delta^{1,3}$-indandione

Indandione 3.13g (0.021moles) and malononitrile 2.83g (0.042moles) were dissolved in 35.7cm^3 absolute alcohol, 2.29g of anhydrous sodium acetate was added at room temperature, with rigorous stirring. An immediate red colouration occured, the suspended solid slowly dissolved. After 40 minutes, the mixture was diluted with 92cm^3 of water and then acidified with HCl to a pH of 1-2. The suspension was stirred for 10 minutes and the solid material filtered off and washed thoroughly with water to give a colourless solid.

The crude product was recrystalized twice from acetic acid to give 3-oxo-^{1,3}-indandione, melting point 225°C (Lit[45] m.pt. 223-229°C). The yield was 3.84g which was 98.4%.

2.2.3 Preparation of 2,2-indene-1,3-diylidene bispropanedinitrile

Indan-1,3-dione, 4.38g (0.03 moles) and malononitrile 5.94g (0.12mole) were dissolved i 50cm^3 of absolute alcohol at room temperature and 5.168g sodium acetate trihydrate was added. The mixture was heated under reflux for 5 hours. After cooling the blue solution was filtered to remove the mono condensate products. The filterate was acidified with HCl to pH 1-2, the grey precipitate was filtered off and washed thoroughly with water. It was then dried to give the product as a grey poweder. Yield 68.6% (4.49g) and the melting point was 257°C.

2.3 Synthesis of dyes

2.3.1 General Procedure for diazotisation of 3,5-dibromo amino benzeldehyde

3,5-Dibromo amino benzaldehyde 5.58g (0.02moles) was dissolved in a mixture of 24cm^3 acetic acid and 6cm^3 water. The solution was cooled with stirring to 12°C. To this solution was added dropwise 1.5g (0.02moles) sodium nitrite dissolved in 10cm^3 of water. 10cm^3 of HCl was then added immediately and the mixture maintained at 15-20°C for 15 minutes.

Excess nitrous acid was destroyed with a small amount of urea. The solution was diluted with 200cm^3 ice water, giving a clear solution of the diazonium salt.

2.3.2 General procedure for coupling

0.02 moles each of the 3-acetamido-N,N-diethylaniline, 3-acetamido-6-methoxy aniline and 2,5-dimethoxy aniline was dissolved in a mixture of 200cm^3 ice water and 5cm^3 HCl. The pH of this solution was 4. The diazonium salt solution formed in section 2.3.1 was then added dropwise with stirring at 0-5°C. The pH was maintained at 4 by the addition of sufficient quantity of sodium acetate. Stirring was continued for 2 hours. The dyes obtained using each of the coupling components were washed thoroughly with water and then recrystallized from suitable solvents. The yield and melting points of the three dyes are summarised in Table 3.1.

2.3.3 General procedure for condensation with active methylene compounds

Equal moles of the benzaldehyde dyes (I-III) and the active methylene compounds which are indan-1,3-dione, 3-oxo-$\Delta^{1,3}$-indandione, 2,2-indene-1,3-diylidene bispropanedinitrile and malononitrile respectively were condensed in ethanol under reflux for 2 hours with 2 drops of piperidine. The products obtained were washed thoroughly with water and then recrystallised from suitable solvents. Yields, melting points for the dyes are summarised in Table 3.2.

2.3.4 General method for the preparation of 3,5-dicyano para benzaldehyde azo dyes (IV-VI)

Equimolar amounts of each of three formyl azo dyes (I), (II) and (III) (obtained in section 2.3.2) and cuprous cyanide were reacted in dimethylformamide under reflux for 30 minutes. The suspension formed was poured into 100cm^3 cold water. The precipitated solid was washed thoroughly with water and then dried in the oven overnight. Pure samples were obtained by recrystallisation from suitable solvents to give dyes (IV), (V) and (VI) respectively. The yield and melting points are summarised in Table 3.5.

2.3.5 General procedure for condensation of 2',6'-dicyano para-benzaldehydes with active methylene compounds

Equimolar quantities of each dyes (IV), (V) and (VI) and each of the active methylene compounds, indan-1,3-dione, 3-oxo-$\Delta^{1,3}$-indandione, 2,2-indene-1,3-diyldene bispropanedinitrile and malononitrile were condensed in ethanol under reflux with catalytic amount of piperidine for 30 minutes to give dyes in series (IV)-(VI) respectively. The dyes were purified by recrystallisation from suitable solvents. Yield and melting points for the dyes are summarised in Tables 3.6 - 3.8 respectively.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

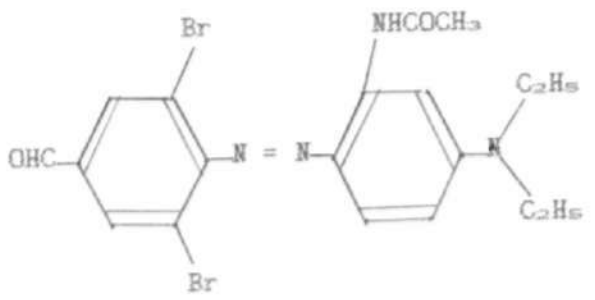
3.1 Synthesis of Intermediates and Dyes

The principal intermediate 3,5-dibromo para-aminobenzaldehye was synthesised from N,N-diethylaminobenzaldehyde by direct bromination and elimination of the ethyl radical by baking as illustrated in the equation below.



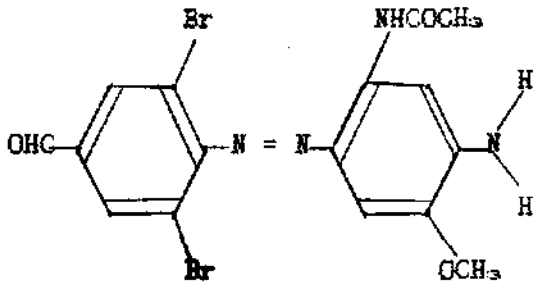
The yield obtained was good and the melting point corresponded with what was reported in the literature[45].

The three dyes (I) - (III) were then prepared by the diazotization of 3,5-dibromo para-aminobenzaldehyde and coupled to 3,acetamido-N,N-diethylaniline, 2-methoxy-5-acetamidoaniline and 2,5-dimethoxyaniline respectively.



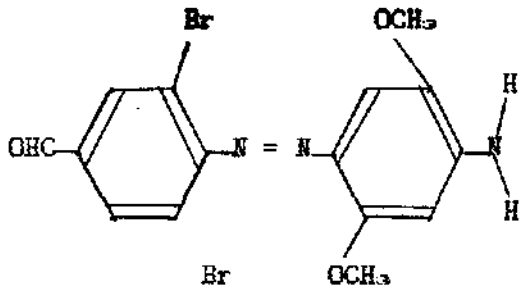
(I)

4'-formyl-2',6'-dibromo-4-N,N-diethyl amino-2-acetamidoazobenzene



(II)

4'-formyl-2',6'-dibromo-4-amino-2-acetamido-5-methoxylazobenzene



(III)

4'-formyl-2',6'-dibromo-4-amino-2,5-dimethoxyazobenzene

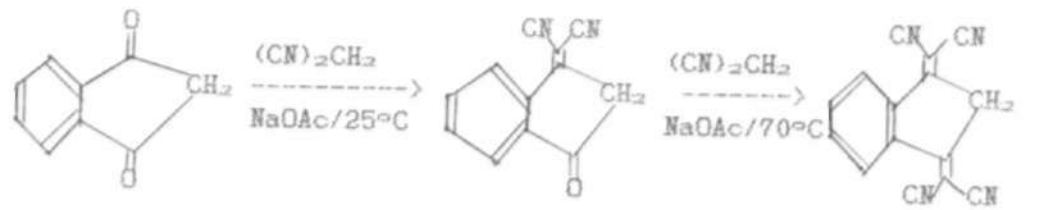
Table 3.1: Yield and melting points for the formyl dyes

Dye No:	Yield (%)	Molecular weight	Melting point °C:	Recrystallisation solvent:	Colour of crystal
(I)	40.4	495.9	100-105	Ethanol	orange
(II)	63.5	469.9	130.132	Ethanol	red
(III)	32	442.9	125-130	Ethanol	red

The yield obtained as summarised in Table 3.1 were not high and this could be due to the deactivation of the benzene ring by the electron withdrawing strength of -CHO and -Br groups.

Dyes (I) -(III) were condensed with active methylene compounds in order to push the λ_{max} to the longer wavelength of the visible absorption region.

The active methylene compounds used are indanedione, 3-oxo-$\Delta^{1,3}$-indanedione, 2,2-indene-1,3-diyledene bispropandinitrile and malononitrile. Indanedaione and malononitrile were supplied from the chemical company (BASF), while 3-oxo-$\Delta^{1,3}$-indanedione and 2,2-indene-1,3-diyledene bispropandinitrile were prepared by following scheme 3.1.



indanedione | 3-oxo-$\Delta^{1,3}$-indanedione | 2,2-indene-1,3-diyledene bis-propandinitrile

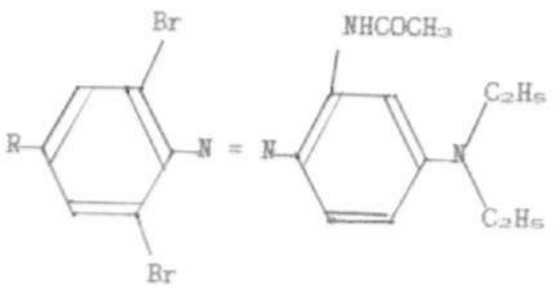
Scheme 3.1

Reaction of indanedione with malononitrile in absolute alcohol in the presence of sodium acetate at room temperature gave 3-oxo-$\Delta^{1,3}$-indanedione on dilution of the reaction mixture with water

followed by acidification with hydrochloric acid. It was purified by recrystallisation from acetic acid and was isolated as colourless solid. 2,2'-indene-1,3-diyledene bispropandinitrile was similarly prepared by refluxing a mixture of indanedione and malononitrile in ethanol in the presence of sodium acetate trihydrate for 5 hours. The mixture was cooled, left overnight, diluted with water and acidified, giving the compound as a white precipitate. Pure sample was obtained by recrystallisation from acetic acid.

These active methylene compounds were then condensed with the aldehyde dyes (I)-(III) by refluxing in ethanol to give dyes in series (Ia)-(Id), (IIa)-(IId) and (IIIa-IId) as summarised in Table 3.2 - 3.4 respectively.

Table 3.2: Yield and characterisation data for dyes derived from condensation products of dye (I)



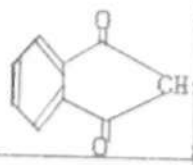
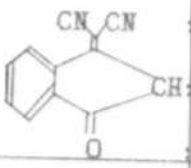
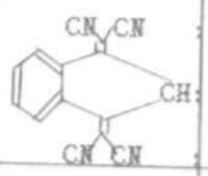
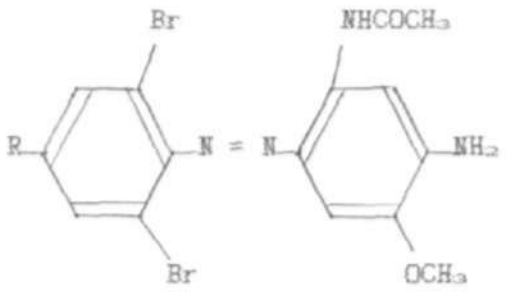
Dye No	Substituent (R)	Mol. Wt	Yield (%)	M.Pt. °C	Rec. Solvent	Colour
I(a)		623.9	38.8	150-160	Toluene	Grey crystal
I(b)		659.9	25.0	114	Ethanol	dark crystal
I(c)		695.9	29.13	119-120	Toluene	leaflet
I(d)	$(CN)_2C=CH$	543.9	10.98	215-323	Toluene	powder crystal

Table 3.3: Yield and characterisation data for dyes derived from condensation products of dye (II)



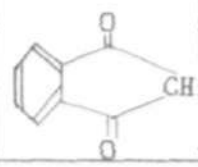
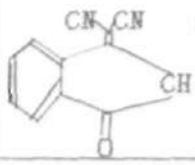
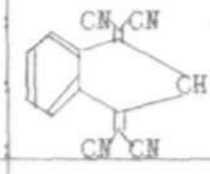
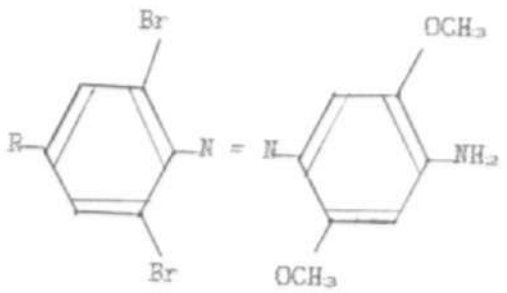
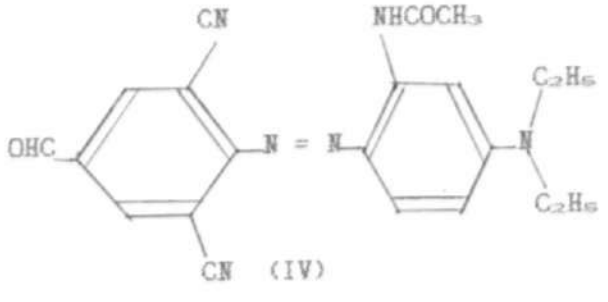
Dye No	Substituent (R)	Mol. Wt	Yield (%)	M.Pt (°C)	Rec. Solvent	Colour
II(a)		597.9	15.68	200-215	Ethanol	dark crystal
II(b)		633.9	25.55	240	Toluene	dark crystal
II(c)		669.9	259	259	Toluene	leaflet needle
II(d)	$(CN)_2C=CH-$	517.9	77.15	200	Toluene	dark crystal

Table 3.4: Yield and characterisation data for dyes derived from condensation products of dye (III)



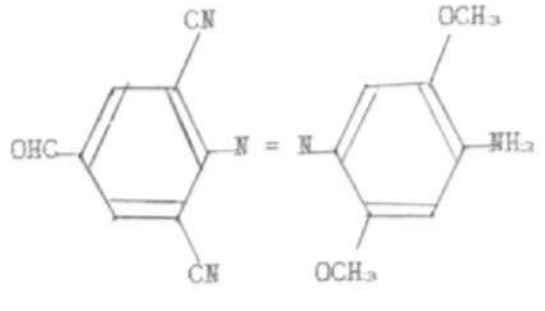
Dye No	Sbstituent (R)	Mol. Wt	Yield (%)	M.Pt. (°C)	Rec. solvent	Colour
III(a)	O CH O	570.9	49.24	190	Ethanol	leaflet needles
III(b)	CN CN CH O	606.9	49.04	215	Toluene	Dark crystal
III(c)	CN CN CH CN CN	642.7	38.78	250-256	Toluene	Dark crystal
III(d)	$(CN)_2C=CH$	490.9	40.3	193-194	Ethanol	dark powder

The corresponding dicyano derivatives of dyes (I) - (III) were prepared by the nucleophilic substitution reaction of the bromine by cyano group to give dyes (IV), (V) and (VI) respectively. Yield and characterisation data for these dyes are summarised in Table 3.5.



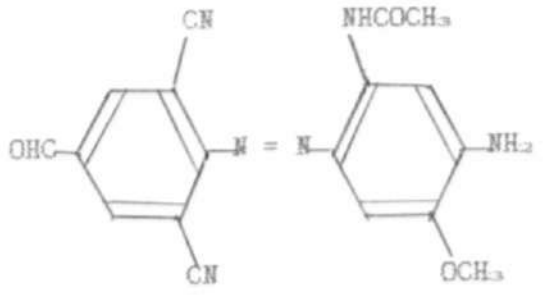
(IV)

4'-formyl-2',6'-dicyano-4-N,N-diethyl-2-acetamidoazobenzene



(V)

4'-formyl-2',6'-dicyano-4-amino-2,5-dimethoxyazobenzene



(VI)

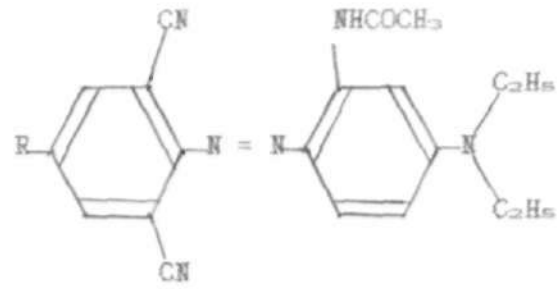
4'-formyl-2',6'-dicyano-4-amino-2-acetamido-5-methoxyazobenzene

Table 3.5: Yield and characterisation data for 2',6'-dicyano-benzaldehyde dyes (IV) - (VI)

Dye No	Yield (%)	Mol. Wt	M. Pt. (°C)	Rec. solvent	Apprearance
(IV)	93.12	362	250-262	Toluene	Dark crystals
(V)	95	309	217-225	Toluene	Leaflet needle
(VI)	96	336	315	Ethanol	dark needle

Condensation of dyes (IV), (V) and (VI) with the active methylene compounds summarised in Scheme 3.1 gave series of dyes in (IVa) - (IVd), (Va)-(Vd) and (VIa) - (VId) respectively as summarised in Tables 3.6 - 3.8.

Table 3.6: Yield and characterisation data for dyes derived from condensation product of dye (IV)



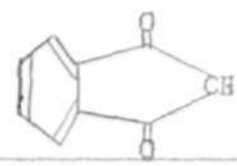
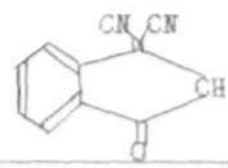
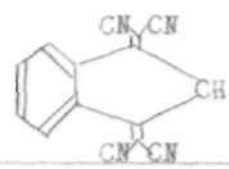
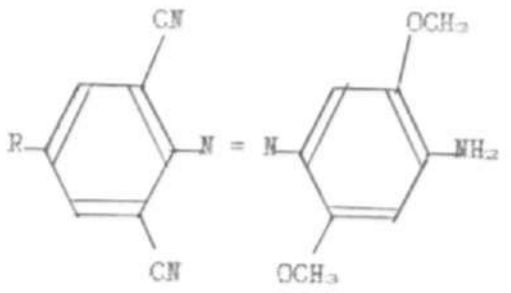
Dye No	Substituent (R)	Mo. Wt.	Yield (%)	M.Pt. (°C)	rec. solvent	Colour
IV(a)		490	13.3	313-316	Ethanol	Dark crystal
IV(b)		526	28.70	307-310	Toluene	Powder
IV(c)		562	18.6	316-320	Toluene	Leaflet needles
IV(d)	$(CN)_2C=CH-$	410	22	290-300	Ethanol	Dark crystal

Table 3.7: Yield and characterisation data for dyes derived from condensation products of dye (V)



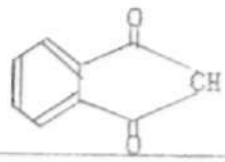
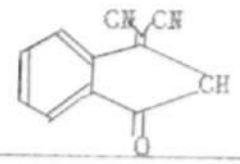
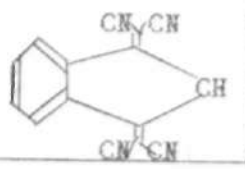
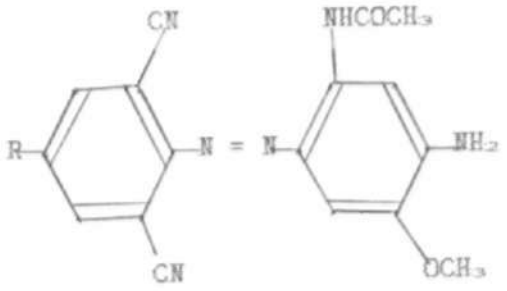
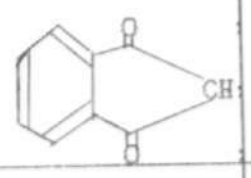
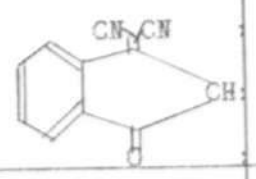
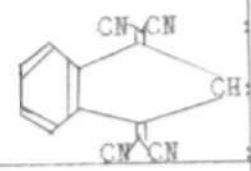
Dye No	Substituents (R)	Mo. Wt.	Yield (%)	M.Pt. (°C)	Rec. solvent	Colour
V(a)		437	25	300	Ethanol	Dark crystal
V(b)		473	74.7	280-290	Toluene	Dark crystal
V(c)		509	70.5	283-287	Toluene	leaflet needles
V(d)	(C)N_2C=CH-	357	70.78	280	Ethanol	Dark needles

Table 3.8: Yield and characterisation data for dyes derived from condensation product of dye (VI)



Dye No	Substituents (R)	Mol. Wt	Yield (%)	M.Pt. (°C)	Rec. Solvent	Colour
VI(a)		464	66	298-305	Ethanol	Dark crystal
VI(b)		500	79	310	Toluene	Dark crystal
VI(c)		536	73.13	317	Toluene	Leaflet needles
VI(d)	$(CN)_2C=CH-$	384	59	290-301	Ethanol	Dark needles

3.2 Visible Absorption spectra of the dyes

Visible absorption spectra of the dyes were measured by the use of colorimeter 253 spectrophotometer. Five different solvents, ethanol, acetone, dimethylformamide, toluene and carbon tetrachloride were used. The extinction coefficient was calculated from dimethylformamide. The results obtained are summarised in Table 3.9 for dibromo derivatives and Table 3.10 for dicyano derivatives respectively.

Dye (I) which was obtained by coupling 3-acetamido N,N-diethylaniine with 3,5-dibromo-para-amino-benzaldehyde absorbed at 555nm in toluene and is violet in colour. When the formyl group of this dye was condensed with indanedione as the electron withdrawing group, the dye absorbed at 557nm in the same solvent, indicating a bathochromic shift of 2nm. Replacement of one of the carbonyl group in dye I(a) by dicyanovinyl group gave dye I(b) which absorbed at 559nm in the same solvent as dye I(a) and this shows a bathochromic shift of 2nm relative to dye I(a). However, when the second carbonyl group of dye I(b) is replaced by second dicyanovinyl, the resulting dye I(c) absorbed at 585nm in the same solvent, giving a bathochromic shift of 26nm in toluene. Condensation of dye (I) with malononitrile gave dye I(d) and this is relatively hypsochromic when compared with I(c), but the dye is still more bathochromic than the parent dye (I) and even when (I) is condensed with indanedione.

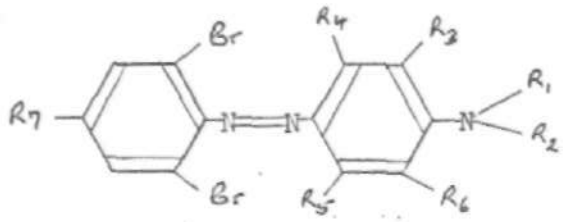
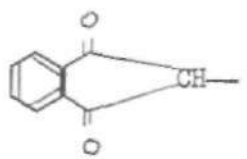


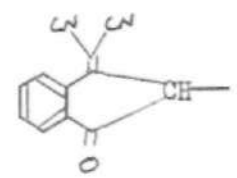
Table 3.9 Visible absorption spectra of dye derive from 3,5-dibromoparaami benzaldehyde

Substituents								Wavelength of maximum absorption (max)					Molar absorption coefficient in DMF (fmax X 10^4
Dye No.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	CCl_4	Toluene	Ethanol	Acetone	DMF	
I	$-C_2H_5$	$-C_2H_5$	H	$-NHCOCH_3$	H	H	-CHo	560	555	525	555	585	1.289
Ia	"	"	"	"	"	"	X1	565	557	527	590	590	3.957
Ib	"	"	"	"	"	"	X2	525	559	543	557	592	9.554
1c	"	"	"	"	"	"	X3	527	585	585	596	595	6.186
Id	"	"	"	"	"	"	$(CN)_2C=CH-$	526	560	535	692	585	3.131
II	"	"	"	"	"	$-OCH_3$	-CHO	480	517	515	555	515	1.857
IIa	"	"	"	"	"	"	XI	517	525	522	557	525	3.847
IIb	"	"	"	"	"	"	X2	520	560	525	590	555	9.667
IIc	"	"	"	"	"	"	X3	527	570	583	600	590	3.129
IId	"	"	"	"	"	"	$(CN)_2C=CH-$	-	556	526	537	545	3.11
III	"	"	$-OCH_3$	H	$-OCH_3$	"	-CHO	495	512	526	554	566	4.834
IIIa	"	"	"	"	"	"	X1	500	560	555	592	583	5.11
IIIb	"	"	"	"	"	"	X2	513	563	552	600	587	6.937
IIIc	"	"	"	"	"	"	X3	515	575	565	603	608	3.606
IIId	"	"	"	"	"	"	$(CN)_2C=CH-$	-	562	555	590	570	2.161

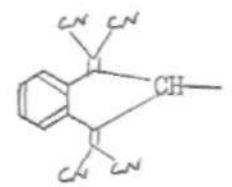
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X3 =



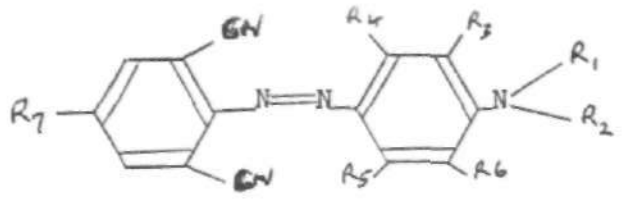
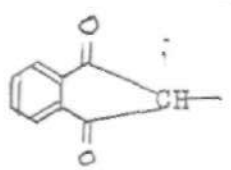
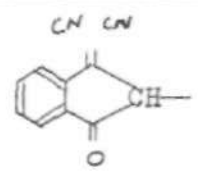
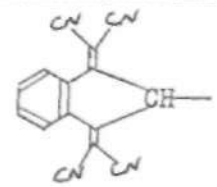


Table 3:10 Visible absorption spectra of dyes derived from 3,5-dicyano paraamino benzaldehyde

Substituents								Wavelengths of maximum absorption (max)					Molar absorption Coefficient in DMF(£max X 10^4)
Dye No.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	CCl_4	Toluene	Ethanol	Acetone	DMF	
IV	$-C_2H_5$	$-C_2H_5$	H	$-NHCOCH_5$	H	H	-CHO	602	603	600	603	610	5.147
IVa	"	"	"	"	"	"	X1	587	585	582	595	605	5.8696
IVb	"	"	"	"	"	"	X2	592	587	581	605	600	7.416
IVc	"	"	"	"	"	"	X3	605	604	600	607	587	6.663
IVd	"	"	"	"	"	"	$(CN)_2C=CH-$	-	590	510	598	600	8.59
V	"	"	$-CCH_3$	H	OCH_3	H	-CHO	555	565	591	590	585	7.96
Va	"	"	"	"	"	"	X1	560	557	588	595	590	8.30
Vb	"	"	"	"	"	"	X2	565	565	590	591	595	8.787
Vc	"	"	"	"	"	"	X3	593	590	585	605	603	5.00
Vd	"	"	"	"	"	"	$(CN)_2C=CH-$	560	550	591	600	602	2.85
V1	"	"	H	$-NHCOCH_3$	H	$-OCH_3$	-CHO	515	560	557	593	600	4.569
VIa	"	"	"	"	"	"	X1	535	572	560	578	533	1.431
VIb	"	"	"	"	"	"	X2	-	581	570	582	601	4.555
VIc	"	"	"	"	"	"	X3	540	600	593	590	608	2.086
VId	"	"	"	"	"	"	$(CN)_2C=CH-$	-	562	565	561	595	5.196

X1 = 

X2 = 

X3 = 

The results summarised in Table 3.9 has clearly showed that the visible absorption spectra of the dye based on 3,5-dibromo para-amino benzaldehyde is very insensitive to the effect of incorporating electron withdrawing groups in the acceptor half of the chromogen. This lack of sensitivity may be due to steric effect of the bromo atoms in position 2,6 which prevented the dye from assuming a complete planarity with the rest of the chromogen.

As already mentioned in the literature[39], that the azo dye can be classified as donor-acceptor chromogen, in which the π-electron density of the donor group can be enhanced either by increasing the number of electron donating groups or by increasing the strength of this electron donating substituents. When this occurs, a bathochromic shift in colour is usually the result. In order to investigate this effect, an additional electron donating methoxy group was incorporated in dye (I) to give dye (II) and this dye absorbs at 517nm which is very hypsochromic when compared with dye (I) in the same solvent. This hypsochromic effect may be due to the fact that the N,N-diethyl group in dye (I) has also been replaced by the amino group and this means that the N,N-diethylaniline can release more electron into the acceptor group of the chromophore than the simple aniline.

When dye (II) was condensed with all the active methylene cmpounds as was done with dye (I), the same small bathochromic

shift was observed in the same solvent and this further confirms that dyes based on this diazo component are very insensitive to the action of incorporating strong electron withdrawing groups and similarly little change in colour was obtained when an additional electron donating group was incorporated in the donor group of this dye.

Dye in series (III) were similarly prepared by replacing the acetamido group with two methoxy groups in position 3 and 5 relative to the azo groups. As can be seen from the data summarised in Table 3.9, similar results are obtained. This means that it will be very difficult to push the λ_{max} of the dyes based on this diazo component into longer wavelength of the visible absorption region.

It is however evident from the data summarised in Table 3.9 that the bathochromic effect of the active methylene compounds incorporated into the acceptor half of the chromogen follows a similar pattern irrespective of the electron donating groups in the donor half of the chromogen. This order is generally observed that dye in series (c) is more bathochromic than (b) and this is more than (d) and more than those in series (a) and lastly followed by the dye with formyl -CHO groups.

Series c > series b > series d > series a > with - CHO group.

Dyes in series (c) represent all dyes derived from 2,2-indene-1,3-diyledene bispropandinitrile, and those in series (b) represents all dyes derived from 3-oxo-$\Delta^{1,3}$-indanedione while those in series (a) represent dyes derived from indandione and lastly those in series (d) represent dyes derived from the condensation with malononitrile.

The reasons for the small bathochromic shift observed when the active methylene compounds are incorporated are not far fetched. Quantitatively, bathochromic shift is determined by two opposing factors at the acceptor ring; these are electron withdrawal strengths of the acceptor group and the steric influence of the atoms attached to the acceptor ring. Dyes in series (c), though might suffer from steric hinderance due to the positioning of two cyano groups at one carbon atom is not much affected adversely because cyano groups are rod like in shape. Whatever this steric interference might incur on the λ_{max} is much counter balanced by the strength of electron withdrawal, cyano group being strongly (-M). A strong -M effect group attached to the acceptor ring in a situation as this is believed to lead to increased conjugation thus lowering the ionization potential across the molecule and therefore bringing about a bathochromic shift.

Members of dyes in series (d) gave more bathochrmic shift than the members of dyes in series (a) simply because the former have two cyano groups i.e. increased conjugation than the latter.

A similar trend was observed between series of dyes in (a) and dyes containing the terminal -CHO.

The results summarised in Table 3.10 shows the effect of replacing the bromine groups with cyano groups and comparison of the data in Table 3.9 and Table 3.10 clearly showed that dyes in Table 3.10 are more bathochromic than those in Table 3.9 even when the corresponding pairs of dyes were compared. For example dye (I) absorbs at 555nm in toluene and when the two bromo groups are replaced by cyano groups giving dye (IV), the λmax changed to 603nm in the same solvent, indicating a bathochromic shift of 48nm which is a very significant change in colour and infact the colour of the dye changed completely from violet to blue. Similar trends were observed when different electron donating groups and electron withdrawing groups were incorporated into the dyes.

It is however, very surprising to note that incorporation of electron withdrawing groups into dye (IV) gave hypsochromic effect. For example dye (IV) absorbed at 603nm in toluene and when the formyl group is condensed with indandione the resulting dye (IVa) absorbed at 585nm which is relatively hypsochromic. Similar effect were observed with other electron withdrawing groups incorporated with this dye. This effect is very difficult to explain as the data in Table 3.9 showed that when the electron withdrawing groups were incorporated with dyes derived from the bromo derivatives a small bathochromic effect were observed which is in good agreement with the results of the other workers[45].

The general red shifts observed when the cyano groups were substituted for bromo groups can be explained in terms of the size of the bromo group, which is large in nature, producing marked steric hindrance interfering with the lone pair of electron on the ß-nitrogen of the azo nitrogens. It was reported[45] that amino azo dyes exist in the trans configuration, as such, a large substituent can exercise strong steric hinderance between it and the lone pair orbital of the ß-nitrogen atom as shown in the configuration in Figure 3.1.

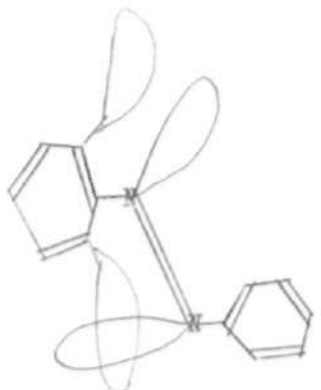


Fig 3.1

This will effectively reduce p-orbital overlap thus reducing delocalization of the lone pair of electron on that atom, reducing the resonance energy, increasing ionization potential and thus introducing some hypsochromic shift as compared with groups that could not exhibit such behaviour. Cyano group being rod-like in nature reduces such effect to a minimum and as compared to the dibromo substituents, they were favourably more bathochromic.

3.3 Solvatochromism

This describes the influence of solvent polarity on the absorption maxima of the dyes. Extensive work has been done on this over the year[47]. It was reported that the influence of polarity of the solvent is on the π-π^* transition which is believed to exhibit bathochromic shift with increasing solvent polarity and on the n-π^* transition which is shifted hypsochromically with increasing solvent polarity.

Yet another report[45] stated that certain donor-acceptor chromogen with low resonance energy might record hypsochromic shift with increasing polarity while a high resonance energy form might record bathochromic shift.

The solvents in the study as shown in Table 3.9 and 3.10 are arranged in order of increasing polarity. An observation of the dyes derived from 3-acetamino-5-methoxyaniline in CCl_4, ethanol and DMF, chosen because they are wider apart in polarity, for dyes (II) and (VI) showed that there was a general bathochromic shift with increasing polarity of the solvents.

In Table 3.9 and 3.10 for dyes (IIa) the λ_{max} CCl_4 517nm < λ_{max} 522nm ethanol < λ_{max} 525nm in DMF.

(VIa); λ_{max} CCl_4 535nm < λ_{max} ethanol 560nm < λ_{max} DMF 583nm.

Similarly the dyes based on 3-acetamido-N,N-diethylaniline typified by dyes (I) and (IV) showed this trend.

(Ia); λ_{max} CCl_4 565nm > λ_{max} ethanol 527nm < λ_{max} DMF 590nm.

(IVa); λ_{max} CCl_4 587nm > λ_{max} ethanol 582 < λ_{max} DMF 605nm.

It could be observed that as the polarity of the solvent is

enhanced the bathochromic shift is progressively increased, however, these are not as pronounced as in the case of the dyes based on 2-methoxy-5-acetamido aniline.

Similarly the dyes based on 2,5-dimethoxy aniline showed this trend:

(IIIb), λ_{max} CCl_4 513nm < λ_{max} ethanol 552nm < λ_{max} DMF 587nm.

(Vb), λ_{max} CCl_4 565nm < λ_{max} ethanol 590nm < λ_{max} DMF 595nm.

A general increase in bathochromic shift with reapect to increasing polarity was also recorded in this group.

The reason for these results which become readily obvious is that 3-acetamido-5-methoxy aniline is more exposed to participate in H-bonding interaction making it easily solvated, reducing energy between the cannonical forms with increasing solvent polarity. The same explanation applied with the case of the dye derived from 2,5-dimethoxy aniline which showed the trend to a lesser extent.

Solvatochromism is due to various solute-solvent interaction in both the ground and excited states. The red shift on changing to a more polar solvent also suggested that the dye molecule has a more polar excited state than the ground state and a polar solvent can stabilise this more than the ground state, and this will lower the energy of the transition. Light absorption causes the π-electrons to migrate from amino donor group to the various electron acceptor residues and hence the excited state has a larger dipole moment (that is, is more polar) than the ground state.

3.4 Halochromism

It has been observed for a long time that most dyes derived from 4-aminoazo benzene undergo a pronounced colour change on addition of few drop of acid[50]. In view of this it became necessary to study the effect of hydrochloric acid addition on the λ_{max} of the dyes synthesised.

The halochromism of the azo dyes synthesized were studied in ethanol as solvent and the shifts of the absorption maxima on acidification with hydrochloric acid are summaried in Table 3.11 and 3.12. In all cases, the protonated solutions were neutralised carefully with weak alkali (sodium bicarbonate) to verify that the original spectra were completely resorted, showing that decomposition of the dyes had not occured during protonation.

As can be seen from the data summarised in Table 3.11 and 3.12, most of the dyes showed negative halochromism which may be due to the strength of the electron withrawing groups incorporated in the acceptor half of the chromogen.

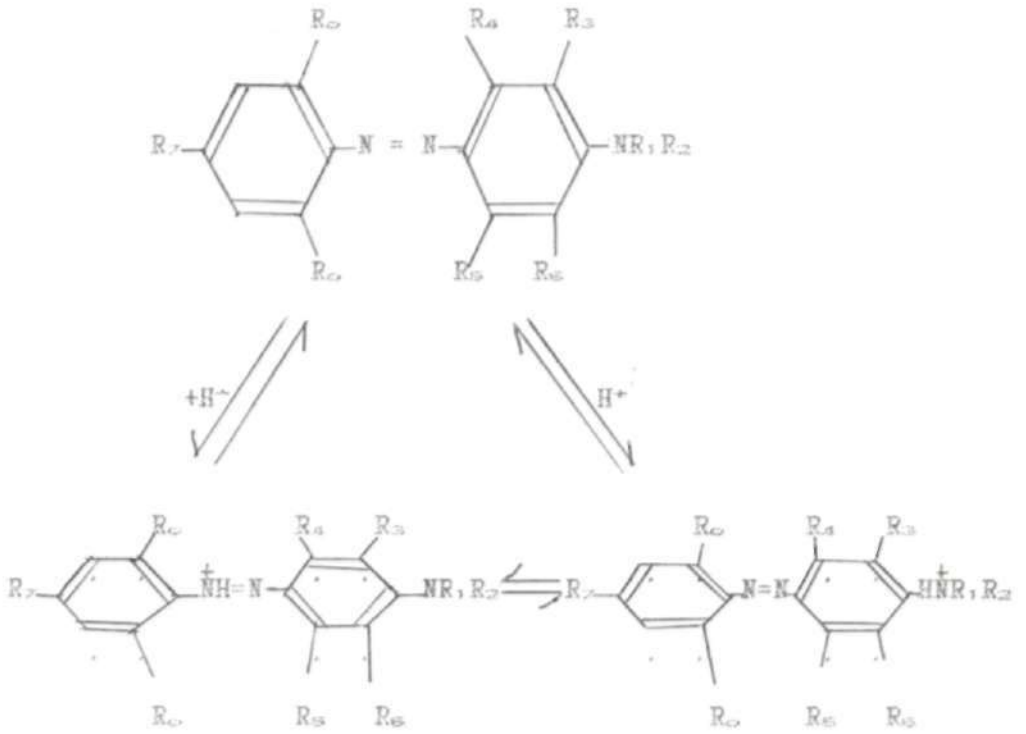
Addition of acid to 4-aminoazobenzene dyes have been explained to lead to two equilibrium tautomeric forms. One tautomeric isomer resulted from the protonation of the ß-nitrogen in the azo linkage to form an azonium ion leading to bathochromic shift. The second isomer leads to the formation of an ammonium cation at the terminal amino group, this prevents lone pair donation at this terminal and as such leads to hypsochromic shift.

Table 3.11: Absorption maxima of dyes derived from 3,5-dibromo Para-aminobenzaldehyde in neutral and acidic ethanol

Dye No :	λ_{max}/nm		: $\Delta\lambda_{max}$
	Neutral	+ HCl	: $\lambda_{acidic} - \lambda_{neutral}$
(I) :	525	515	: - 10
(Ia) :	527	480	: - 47
(Ib) :	513	595	: + 82
(Ic) :	585	485	: -100
(Id) :	535	490	: - 45
(II) :	515	468	: - 50
(IIa) :	522	418	: -104
(IIb) :	525	463	: - 62
(IIc) :	583	460	: -123
(IId) :	526	455	: - 71
(III) :	560	545	: - 15
(IIIa) :	550	535	: - 15
(IIIb) :	552	525	: - 27
(IIIc) :	565	495	: - 70
(IIId) :	555	515	: - 40

Table 3.12: Absorption maxima of dyes derived from 3,5-dicyano para-amino benzaldebyde in neutral and acidic ethanol

Dye No :	λ_{max}/nm		$\Delta\lambda_{max}$
	Neutral	+ HCl	$\lambda_{acidic} - \lambda_{neutral}$
(IV)	600	510	- 90
(IVa)	582	500	- 82
(IVb)	581	505	- 72
(IVc)	600	510	- 90
(IVd)	510	487	- 23
(V)	591	580	- 11
(Va)	583	555	- 33
(Vb)	590	515	- 75
(Vc)	585	590	+ 5
(Vd)	591	505	- 86
(VI)	557	498	- 59
(VIa)	560	510	- 50
(VIb)	570	500	- 70
(VIc)	593	499	- 94
(VId)	545	505	- 40



Scheme 3.2

Substituents are believed to cause inverse variation of the two forms since they stabilize one form or the other.

$$\text{The tautomeric equilibrium constant } k_T = \frac{[\text{azonium}]}{[\text{ammonium}]}$$

k_T depends on the solvent, acid concentration and the substituents[50].

From this explanation, it is understandable why there was a general hypsochromic shift. The 2,6-disubstittution must have

effectively blocked the orbital of the α-nitrogen so that accessibility to it by a proton became hindered therefore reducing k_T.

This line of thought is even reinforced when it was realised that the 2,6-dibromo substituted azo dyes recorded higher $\Delta\lambda_{max}$ hypsochromically being larger in volume than their dicyano substituted counterparts.

For members of different donor groups, it was observed that the dyes derived from 2,5-dimethoxy suffer less hypsochromic shift because the methoxy group at R_5 position can be viewed as partially blocking the lone pair of electrons on the terminal nitrogen thus reducing the [ammonium] and increasing k_T. It was reported[45] that methyl group has been used to bock -N-alkyl group against protonation.

It is also true that 2-methoxy-5-acetamido derivative dyes could also exercise such influence due to the strategic positioning of a methoxy group at R_5 position, but it is also true that the bulky $-NHCOCH_3$ group can interfere with the p-orbital at the β-nitrogen therefore from the former effect there is increased [azonium] and the latter effect there is increased [ammonium], the two effect reaching equilibrium with the result that the dyes derived from 2-methoxy-5-acetamido aniline suffered more hypsochromic shift than those derived from 2,5-dimethoxy aniline.

The dyes derived from 3-acetamido-N,N-diethylaniline suffered more hypsochromic shift. Two corresponding reasons account for

this. The bulky ethyl group at the terminal nitrogen sterically blocks the approach of a proton, but the high +I strength of these groups concentrating the lone pair at the nitrogen atom encourage proton affinity, it appears that the last effect over rides the steric factor, also the large acetamido group can interfere with the p-orbital at the β-azo nitrogen, so that the overall effect is marked hypsochromic shift as was recorded for the dyes derived from 3-acetamido N,N-diethyl aniline.

3.5 Interpretation of IR Spectra

The fundamental reactions of concern in this analysis involved the condensation of the aldehyde functional group -CHO in the parent dye (I), (II), (III), (IV), (V) and (VI) to form their respective condensation derivatives and the nucleophilic substitution reactions of bromine in the dyes (I), (II) and (III) by cyano groups to form dyes (IV), (V) and (VI) respectively.

The basis of infrared spectroscopy in this respect was to ensure that the aldehyde groups were actually condensed as observed by the disappearance of their absorption peaks when the spectra of respective derivatives were compared with those of the parent dyes.

Aromatic aldehyes are believed to absorb in the following regions of the infrared spectrum[48-49].

Strong band at 1650-1750cm^{-1}

Medium bands 2700 - 2750cm^{-1}

1225 - 1300cm^{-1}

1160 - 1200cm^{-1}

830 - 970cm^{-1}

All the dyes in group (IV), (V) and (VI) contained cyano groups while those in group (I), (II) and (III) contained aldehyde groups. So dyes (IV), (V) and (VI) were easily distinguished from (I), (II) and (III) by the presence of -CN group. This functional groups absorbs a stretching vibration at 2120-2260cm^{-1}. It can also absorbs between 2200-2300cm^{1} [48-49].

Another approach of distinguishing dyes in groups (IV), (V) and (VI) from those in groups (I), (II) and (III) is the absent of bromine absorption peaks in the former. But this is used to a leser extent because bromine absorption is not constant with respect to structure.

Observation of the ir spectrum of dye (I) showed a strong band at 1715cm^{-1}, (Ia), (Ib), (Ic) and (Id) did not show similar peaks. This confirmed that condensation had taken place. Dyes (Ib)-(Id) showed a medium-strong absorption peak at 2400cm^{-1}. This is a characteristic absorption band of a -CN group. Dye (I) and (Ia) did not show this peak, indicating that the -CN group is absent.

There is a strong band at 1700cm^{-1} for dye (II) due to the presence of -CHO stretching. This is absent in dye (IIa-(IId). The presence of a medium absorption peak at 2400cm^{-1} for dye (IIb)-(IId) but not in (IIa) indicated the presence of -CN.

The ir spectra of (IIIb)-(IIId) indicated a strong absorption band between 2400-2420cm^{-1} due to the presence of the same -CN

group. However dyes (III) and (IIIa) did not show the presence of CN group.

All the dyes in groups (IV)-(VI) showed strong absorption band at 2120cm^{-1} indicatig the presence of the -CN- group and this clearly showed that the bromine has been replaced by the cyano groups.

3.6 Dye Exhaustion and Substantivity for Polyester

All the dyes synthesised were applied on polyester and the percentage dye absorbed estimated to assess the substantivity of the dyes for the fibre. The results obtained are shown in Table 3.13 and 3.14 for the dibromo derivaties and cyano derivatives respectively.

As can be seen from the results summarised in Table 3.13 and 3.14, dyes based on dicyano derivatives have higher substantivity on polyester than the dibromo derivatives. This can be attributed to their lower molecular weight favouring high diffusion coefficient. It is generally the case with disperse dyes of low molecular weight that the rate of diffusion is normally high because the polyester fibre is more compact in structure and therefore dye possessing large molecular weight usualy find it difficult to penetrate the interior of the fibre molecule.

Table 3.13: Dye exhaustion on polyester for dyes based on 2,6-dibromo para substituted azo dyes

Dye No	Per cent Exhaustion	Shade	Sample
(I)	65	pink	
(Ia)	53	light-pink	
(Ib)	20	bright pink	
(Ic)	38	dull pink	
(Id)	60	light violet	
(II)	63.5	Orange	
(IIa)	60	light pink	
(IIb)	45	pink	
(IIc)	55	deep pink	
(IId)	63	Stained	
(III)	60.1	pink	
(IIIa)	40	light pink	
(IIIb)	37	light pink	
(IIIc)	53	Stained	
(IIId)	59	Stained	

Tale 3.14: Exhaustion of dyes on polyester for dyes based on 2,6-dicyanopara substituted azo dyes

Dye No	Exhaustion (%)	Shade	Sample
(IV)	70	Purple	
(IVa)	63	blue	
		blue	
(IVb)	56	bright blue	
(IVc)	50	blue-violet	
(IVd)	62.3	blue	
(V)	63	violet-blue	
(Va)	50	reddish-violet	
(Vb)	55	violet	
(Vc)	70	deep blue	
(Vd)	68	violet	
(VI)	77	violet-blue	
(VIa)	60.3	blue	
(VIb)	73	bright blue	
(VIc)	75	blue	
(VId)	77	violet blue	

The surprisng result is the percentage dye exhausted of the dyes based on 2,2-indene-1,3-diyledene bispropandinitrile which proved to have higher substantivity than their 3-oxo-$\Delta^{1,3}$-indane-dione malononitrile counterpart and in some cases even better than the dyes based on indane-1,3-dione.

It can be explained that both indane-1,3-dione and 3-oxo-^{1,3}-indandione malononitrile are having at least an oxygen atom in their structure. This is believed to participate in hydrogen bond formation inside the fibre structure, while dyes based on 2,2-indene-1,3-diylidene bispropanedinitrile does not carry any oxygen atom in its structure. This hydrogen bonding capability of the former dyes can hinder their diffusion into the fibre as reported by Glenzel et al[50]. Another possible explanation is that oxygen atom is more spherical and might contribute to more molar volume factor than the cyano group which are rod like and denser and therefore less molar volume factor[50]. These reasons could also be fowarded to explain why dyes based on 2,6-dicyano dyes are having more substantivity than their 2,6-dibromo derivatives

3.7 Wash fastness properties

All the dyeings obtained on polyester fabrics were assessed for wash fastness test by following the I.S.O 3 standard procedure. The results of this investigation using grey scale for assessing both change in shade and staining of the adjacent

fabric are shown in tables 3.15 and 3.16 respectively for dibromo and cyano derivatives.

Table 3.15: Wash fastness of dyes derived from bromo derivatives

Dye No	Change in colour	Staining of white polyester
(I)	3	4
(Ia)	3	3-4
(Ib)	3-4	4
(Ic)	4-5	4
(Id)	4-5	4-5
(II)	3	4
(IIa)	4-5	3-4
(IIb)	4-5	3
(IIc)	4-5	4
(IId)	2-3	4
(III)	4	4
(IIIa)	4	4
(IIIb)	2-3	4
(IIIc)	4	4
(IIId)	3	3

Table 3.16: Wash fastness of dyes derived from dicyano derivatives

Dye No	Change in colour	Staining of white polyester
(IV)	2-3	4
(IVa)	3	3
(IVb)	3-4	3-4
(IVc)	2-3	4-5
(IVd)	3-4	4
(V)	3-4	3
(Va)	3	4
(Vb)	3	3-4
(Vc)	1-2	3-4
(Vd)	3	3-4
(VI)	4	3
(VIa)	4-5	3-4
(VIb)	4	4
(VIc)	4	4
(VId)	4-5	4-5

The results of the washness fastness summarised in tables 3.15 and 3.16 generally showed that the washing fastness of dyes derived from dibromo derivatives were better than those based on dicyano derivatives. However, both series of dyes have moderate to good fastnsss rating.

The excellent fastnes of the dibromo derevatives relative to the cyano derivatives is due to the large molecular size of the former which afforded them low diffusion and made them have higher resistance to washing than the relatively low molecular weight dicyano derivatives.

With respect to the substituent effects on washing fastness, it could be observed that lower grades were obtained for the dyes based on 2,5-dimethoxy aniline dyes (III) and (V). (IIIb) gave the lowest for 2,6-dibromo derivatives while (Vc) gave the lowest for the dicyano derivatives.

It is however, generally observed that with increase in the molecular weight of the dyes higher fastness properties were recorded.

3.8 Light fastness test

Light fastness testing was carried out by the help of xenon arc lamp whose spectra composition almost equal that of the natural day light. Exposure was carried out for 24 hours when the specimens have faded to the extent of grade 3 on the standard grey scale for evaluating washing fastnes. The results obtained are summaried in tables 3.17 and 3.18 for the dibromo and diyano dyes derivatives respectively.

Table 3.17: Light fastness rating for dibromo derivatives on polyester

Dye No	:	Light fastness rating
II	:	3 - 4
(IIa)	:	2 - 3
(IIb)	:	2
(IIc)	:	2
(IId)	:	2-3
(III)	:	4
(IIIa)	:	3
(IIIb)	:	2
(IIIc)	:	1
(IIId)	:	4-5

Table 3.18: Light fastness rating for dicyano derivatives on polyester

Dye No	:	Light fastness rating
(V)	:	3
(Va)	:	2-3
(Vb)	:	2
(Vc)	:	3-4
(Vd)	:	3
(VI)	:	3
(VIa)	:	2
(VIb)	:	2
(VIc)	:	2-3
(VId)	:	2

As can be seen from the results in tables 3.17 and 3.18 for for series of dyes, the light fastness of these dyes are very poor.

Comparison of the two series shows that 2,6-dibromo derivatives have slightly fair light fastness than the 2,6-dicyano derivatives. This is no doubt due to the influence of the bromine atoms.

CHAPTER Four

CONCLUSION

It was observed generally that to obtain bathochromic shift, incorporation of highly electron withdrawing group at acceptor group of the azo dye could achieve this objective. But the presence of two bromo or 2 cyano groups in positions 2 and 6 relative to the azo group made the dyes under study to be relatively insensitive to this effect due to steric interference affecting the delocalization of the lone pair of electron at the β-nitrogen and this also reduced the extinction coefficients of the dyes.

It was also found out that there is a general negative halochromism which reflected the high electron withdrawing nature of the substituents incorporated.

Incorporation of relatively low molecular weight cyano groups had negative effect on the washing fastness and to some extent also on the light fastness. Though the relative low molecular weight of cyano derivatives had more substantivity. There was also a general bathochromic shift with increase in polarity of the solvents.

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