CHAPTER I

INTRODUCTION

INTRODUCTION

A) Literature survey on the spectra of azo dyes :

The absorption spectra of benzene azobenzene was investigated in a number of solvents by Brode(1) who found no shift of the band with change of solvent. The band of benzeneazophenol was not a simple one but consists of smaller bands (on the lower frequency side of the principle band) which were added to it to produce the observed absorption curve.

Takuvemura(2) studied the effect of varying pH on the UV-absoption spectra of solutions of azobenzene and some of its OH, NO_2 and Me derivatives. The bands shifted slightly towards longer wavelength with increasing pH value.

Ufimtsev(3) presented evidence supporting the chelate theory of the structure of these azo dyes which contained an OH group ortho to it. The insolubility of certain dyes e.g. 1-phenylazo-2-naphthol, in alkali may be due to their very limited solubility in water. The shift in the maximum of the absorption spectra was caused by the OH group.

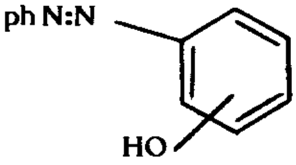
Nagakura(4) found that the solvent effect on absorption and dipole moment of p-aminoazobenzene and p-dimethylaminoazobenzene depends essentially on the refractive index of the solvent except for media leading to H-bond formation. The results were explained in terms of the electron migration effect. The energy of the H-bond was determined from the extinction of the absorption spectrum in mixed solvent e.g. ether and dioxane.

The influence of the substituents of the trans azobenzene isomers upon the energies of the individual electronic levels was investigated by Birnbaum(5). The changes in the energy levels were interpreted in terms of mesomeric and inductive effects of the substituent, while the behaviour of the cis form was complicated by the interaction of the benzene rings.

Costa(6) studied the UV spectra of asymmetric azo compounds and the corresponding isomeric azoxy compounds α and β , in particular the displacement of the K-band in the field from 320 to 415 nm which was found in all the studied compounds. The value of the ratio of the displacement of the frequency of the absorption $\Delta\nu$ of the K-band with respect to the unsubstituted compounds and the frequency ν of the various substituted compounds was examined in relation to the electronegativity and Hammet constant (σ) of the substituent. Within certain limits there was a linear relation between ($\Delta\nu/\nu$) and (σ). The values adopted for (σ) of the various groups and the electron accepting character of the phenylazo and phenylazoxy groups were discussed.

Mequire(7) concluded from the study of the spectra of benzene 4-dimethylaminoazobenzene and methyl orange, that the azo group had a relatively weak basicity and so when acids reacted with aminoazobenzene derivatives, the H^+ took a position on the dimethylamino group and not the azo group. This indicated that in the presence of strong acid a quinonoid structure was highly unlikely.

Mcdowell(8) found that alkali produced changes in the absorption spectra of azo dyes. These changes were completely reversed by acids. These changes were not produced by Na_2CO_3. Dyes of the type I show the absorption at 50-60 nm displacement of the maximum; together with a widening of the bands; if the OH is in the 2-position the displacement is 30-40 nm and the weaking was more pronounced. If the dye molecule contains 2 azo bridges with OH groups ortho to both, the displacement was in the opposite direction by 10-20 nm. A large electronegative group in the ortho position to the azo group decreased the sensitivity of the dye to alkali. The effects were duplicated when 4 model azo dyes were treated with NaOH. The NaCl solution did not produce similar effects on these models.



I

Skulski(9) found that the electron accepting groups in ortho position to the phenolic group of 4-hydroxyazobenzene and its derivatives produced a hypsochromic shift of the primary band. The spectra of 4-acetoxyazobenzene derivatives exhibit a band near 260 nm (suggested term K-band) which did not occur in 4-hydroxyazophenol. The electron acceptor substituents in the analogous derivatives of azobenzene obliterated completely the action of $OCOCH_3$ on the chromophoric system of azobenzene.

A means of working the activity of the groups, which were not included in the conjugated system was suggested. The described effect may be found in compounds of the type :

$1,3,4(4\text{-}AC_6H_4E{:}E)CBC_6H_3$

where E : E = N : N, CH : N, CH : CH

A = H, NO_2 , CHO

B = OH, $CONH_2$, NH_2, $NHCOCH_3$

C = NO_2, CHO, $COCH_3$, COOH.

Skulski(10) also studied the UV spectra of 2-acetamidoazobenzene (I), 2-benzamidoazobenzene (II) and 2-hydroxy-5-methylazobenzene (III) in a variety of polar and nonpolar solvents and compared them with the spectra of several related compounds having no intermolecular H-bonding. The effect of polar and nonpolar solvents on the B-band (in the region of 380 nm) indicated that I,II and III could form fairly strong chelate rings due to intermolecular H-bonding.

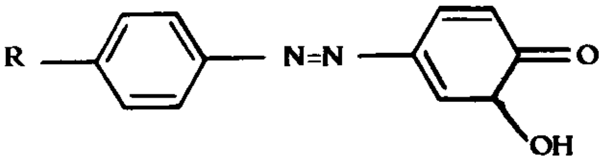
The electronic absorption spectrum of 2-(2-hydroxy-1-naphthylazo)-2'-hydroxy-5'-methylazoxybenzene in CCl_4 was studied by Elzbieta(11), which was found to exhibit 4-bands(λ_{max} in nm and log ε_{max} given) 314, 4.19, 440, 4.23, 510, 4.33 and 533, 4.30 respectively. Comparison with the spectrum of 1-benzeneazo-2-hydroxy-naphthalene and 2'-hydroxy-5'-methylazoxybenzene showed that the molecular part with the azo group has in fact the hydrazone structure, whereas that of the azoxy group has the azo structure. In both cases strong H-bonding was expected.

The characteristic spectra of some compounds of chloroazobenzene (I) e.g. of di-, tetra- and hexa-chloroazobenzene were found(12) to show K-band characteristics typical for the trans- isomers. The chloro substitution in the azobenzene caused bathochromic spectral shifts and for the disubstitution the magnitude of the shift increased in order of m-$<$ p-$<$o- (relative to the azo group) and had values of 2 nm, 2 nm and 6 nm respectively. In the tetra- and hexa- substitution, the effect was additive.

The uv spectra of azobenzene and stilbene derivatives were studied by Kozhevnikova(13). Bathochromic shifts were observed when two electron donor groups were present in the para-positions of the compounds. The symmetrical structure effect was the reason for the bathochromic shifts in compounds with identical electron donor groups. For nonsymmetrical structure a concept of counter effect of substituents was introduced to explain the bathochromic effect.

Skulski(14), showed that p-aminoazobenzene, p-hydroxyazobenzene and their Me and Ac -derivatives existed in the true azoid-forms in cyclohexane, MeOH and aqueous MeOH solutions. The electronic absorption spectra of the compounds showed no tautomeric rearrangements on passing from the nonpolar cyclohexane to the polar alcohol solvent.

Griffiths(15) investigated the electronic spectra in acid and alkaline medium of 5-(phenylazo)-tropolones (II,R=H,Me,OMe,F,Cl,I,NO_2,Ac,CN).

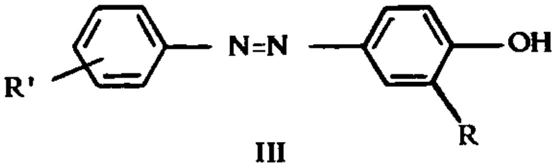


II

No hydrazone tautomerization was found either in the solid or in solution. The influence of the tropolone ring on the spectra was studied by comparison with that of the 4-(phenylazophenol). The frequency difference between the long wavelength bands of the neutral and ionized forms was correlated with the unmodified Hammett σ -values of the substituents.

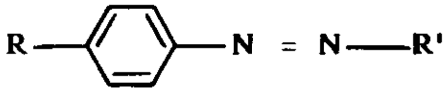
Vinogradova(16) showed that the basicity of azonaphthalenes in acid solutions decreased due to their protonation. The measured electronic absorption spectra of a series of azonaphthalenes in acid solutions differed markedly from that measured in neutral solutions. The electronic absorption spectra were applied for the determination of ionization constants of 1,1'-azonaphthalene, p-amino-1, 1'-azonaphthalene, 4-amino-4'-(1-naphthylazo)-1, 1'-azonaphthalene, azobenzene and 4-aminoazobenzene.

Issa et. al.(17) examined the ir spectra of some azobenzenes(III) where (R=H or COOH, R'= o-NO_2, p-SO_3H or p-Pr.) and the uv-visible of them in organic solvents and aqueous buffer solutions. The pk_a values of (III)



III

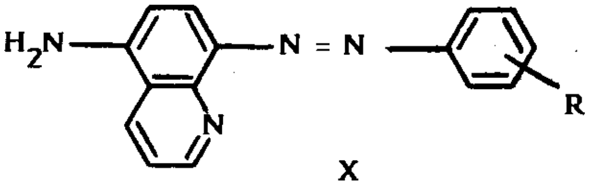
was determined via the pH dependence of the absorbance. The effects of the substituents on the spectra and pk_a data and the relations between



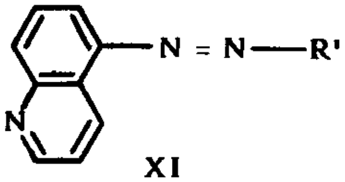
IX

9-phenanthrenyl, 6-hydroxy-5-chrysenyl, 5-hydroxy-6-chrysenyl, 2-hydroxy-1-acenaphthenyl) in the solid state. The main bands were assigned and considered briefly in the light of molecular structure. A change in the condensed ring system caused apparent shift in the position of the OH and N:N bands. The presence of a band in carbonyl region was discussed on the basis of an azo $\rightleftharpoons$ hydrazone equilibrium.

Etaiw et. al.(26) studied the UV-visible spectra of azo dyes containing quinoline nucleus, X (R = H, MeO, OH, Me, Cl, NO_2) and XI (R' = substituted ph or naphthyl, aminoquinolinyl) in organic solvents , H_2O and HCL.



X



XI

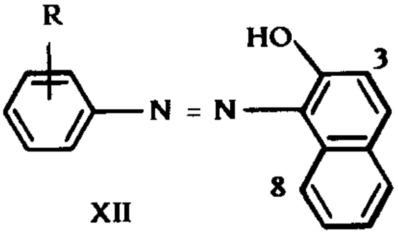
The observed bands were assigned to different $\pi - \pi^*$ and charge transfer transition. Spectra structure correlations were considered. The IR spectra of X and XI were discussed in relation to their molecular structure.

Etaiw et. al.(27) also examined the spectral behaviour and solvent effects of some aminoanthraquinone dyes. The acid dissociation constants of dyes containing OH, COOH or SO_3H groups were determined. The spectra in ethanol displayed 5 bands in the UV region and one in the visible region (450-560 nm). The last band was assigned to charge transfer transition which results from the interaction of the lone pair electron of the N atom with the ring bearing the carbonyl groups. The charge-transfer nature of the band was supported by calculating the value of E_{CT} and by the effect of solvent on band position.

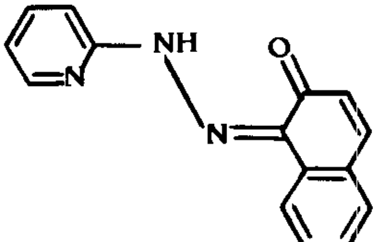
Solvent effects on the thermal cis-trans isomerization and position of the charge-transfer (CT) absorption of 4-(diethylamino)4'-nitroazobenzene studied by Schanze(28). The isomerization rates, the activation parameters and the absorption maximum were determined in a variety of protic and aprotic solvents. The data were analyzed and interpreted by using the Taft-Kamelt multiparameter linear free energy relationship (LFER) and the pyrene fluorescence parameter (py). The correlations suggested that the isomerization was accelerated in H-bonding solvent relative to aprotic solvents of similar polarity due to a H-bonding interaction between the solvent and the NO_2 group of the dye. Correlation of the absorption maximum with the taft-kamlet π^* parameter showed a similar dependence in protic and aprotic media. The absorption process was not affected by H-bonding as strongly as was the isomerization. The LFER of the isomerization rate vs the position of the CT absorption in different solvents suggested that the degree of charge transfer was similar in the transition state for the isomerization and in the Frank-Condon excited state.

Youssef et. al.(29) studied the different bands in the absorption spectra of 4-arylidene-1-(2,4-dinitrophenyl)-3-methyl-2-pyrazolin-5-ones where the bands were assigned and the solvatochromic behaviour was examined. The longer wavelength band shown by the OH derivatives was assigned to an intermolecular charge transfer transition. The H-bonding solvated complexes formed between DMF or EtOH and the p-OH derivatives were as well studied. The transition moment, free energy of formation and formation constant in the two solvents were determined.

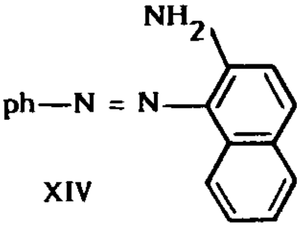
Haessner et. al.(30) studied the azo-hydrazone tautomerism in substituted 1-phenylazo-2-naphthols by ^{1}H nmr spectroscopy. The azo-hydrazo tautomerism in 38 title compounds XII (R = 2-NO_2, 4-F,3-OMe, 4-OH, 4-NH_2, etc.) was determined from the ^{1}H nmr chemical shifts of H(8) and H(3) using the pyridylazonaphthol XIII and the phenylazonaphthylamine XIV as model compounds. The equilibrium constant for the XII tautomerization have a linear free energy relationship with σ . The studied reaction entropy for the conversion of the azoic form into the hydrazone form was always negative and was substituent effect free. The quinoid hydrazone has a higher tendency to aggregate than does its tautomer.



XII



XIII



XIV

Gaber et. al.(31) studied the electronic absorption spectra of some phenylazohydrazone derivatives in ethanol and cyclohexane, as well as in some other organic solvents of different polarities and in buffer solutions of varying pH. The variation of absorbance with pH was utilized for the determination of pk_a. The IR spectra were recorded in the solid state as KBr pellets. The ^{1}H nmr spectra of some compounds in relation to their molecular structures were also discussed.

(B) Literature survey on the metal chelates of azo compounds :

Kandrace(32) investigated the chelation between 2-(5,5-dimethyl4,5,6,7, tetrahydrobenzenethiazolyl-2-azo)-5-hydroxybenzoic acid (I) and Cu(II) at pH 0.55-7. The studies showed that the reagent form 1:1 protonated and unprotonated complexes with absorbance maximum at 520 nm (molar absorptivity = 3.8141×10^4) and 607 nm (molar absorptivity = 4.844×10^4), respectively. The log stability constants were 6.27 and 10.46 for the protonated and unprotonated complexes respectively.

Drordzewski(33) measured the ir spectra for isotopic pair of Ni(II) and Zn (II) complexes of the type ML_2 where L denotes 1-(2-pyridylazo)-2-naphthol or 1-(2-pyridylazo) resorcinol. From the observed isotopic shifts the metal-ligand stretching bands were assigned in the region 150-350 cm^{-1}.

Agarwal(34) prepared the complexes of phenylazo-bis-acetaldoxime, p-chlorophenylazo-bis-acetaldoxime , p-tolylazo-bis-acetaldoxime and p-anisylazo-bis-acetaldoxime of Pd(II), Cu(II) and Ni(II) and characterized by element analysis, stability, free energy, thermogravimetric analysis, electronic spectra and magnetism. Conductometric and pH titrations confirmed the molar composition of 1:2 in all the complexes. The order of stability was Pd > Cu > Ni and for the same metal with different substituents on the ph ring the order was OMe > Me > H > Cl. Thermal decomposition started at 175°C with a maximum weight loss at ≈ 390, ≈ 350 and 300°C for Pd, Cu and Ni complexes, respectively.

and nickel chelates 6.30, 6.23, 6.29, 6.23, 6.77 and 6.36 respectively. The effects of various substitutions on the dye molecule upon the stability of their metal chelates have been discussed on the basic of steric hindrance affecting the chelating tendency of the amino acid of the dye molecule.

Issa et. al.(46) determined divalent cobalt using some Schaffer acid (2-hydroxynaphthalene-6-sulphonic acid) azo dyes as chromogenic reagents.

Gaber et. al.(47) studied the chelates of Co(II), Ni(II) and Cu(II) with some 3-arylazo-1,2,4-triazole dyes by conductometric titration, IR, electronic and ESR spectra. The formation of 1:1 and 1:2 (metal : ligand) complexes was established by elemental analysis and conductometric titration.

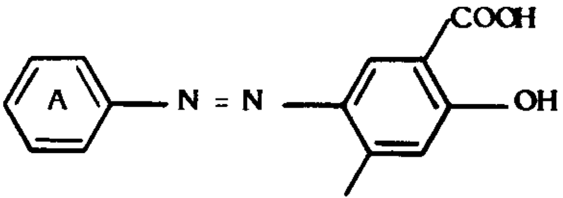
(C) Literature survey on dyeing processes of textiles, fibres and mixed blends with dyes and their chelates :

Shakra(48) studied the light fastness of some mono-azo dyes containing benzo[1,2,3]-thiodiazole, benzotriazole and benzo[b]-thiophene nuclei on nylone 6 fabric. It was showed that the resistance of fading increases as the λ_{max} of the N:N band decreases. Substituent effects on λ_{max} were briefly discussed.

Bishal(49) found a linear relationship between dipole moment, light fastness on nylon 66. The maximum absorption was observed for 6 mono-azo dispere dyes of azobenzene and (phenylazo) naphthalene type. The dipole moment were obtained from measurement of static dielectric constants and refractive index of dilute solutions in C_6H_6 and CCl_4 at 20-40°C.

Dessouki et. al.(50) investigated the effect of complexation of some azo salicylaldehyde derivatives with Co^{2+}, Ni^{2+} and Cu^{2+} ions in dyeing nylone 6 compared to that of the dye itself. The colour fastness to light, rubbing, perspiration and washing, to which the fibre was exposed during manufacture and subsequent use,was studied. The bonding of dye or its complexes to the fibre and the effect of the substituent groups on the colour fastness were discussed.

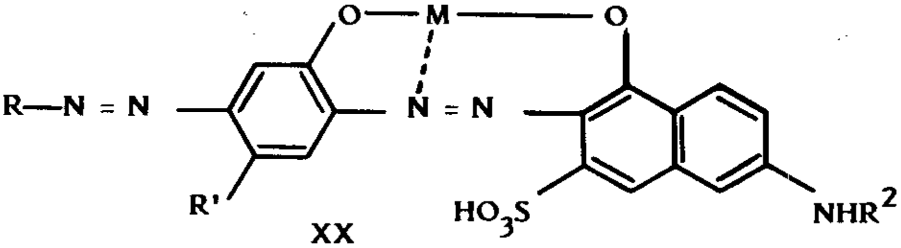
Data on a series of 65 azo disperse dyes XIX (R = C_1 - C_{15} alkyl; a mono - or disubstituted or unsubstituted)were reported(51). The dyes were suitable for application to polyamide fibres and produced yellow



XIX

to red-orange shades. Many correlations between the nature of substituents and the physical, spectroscopic properties of the dyes were established. Correlation between structure and color of dyed fabrics were also found.

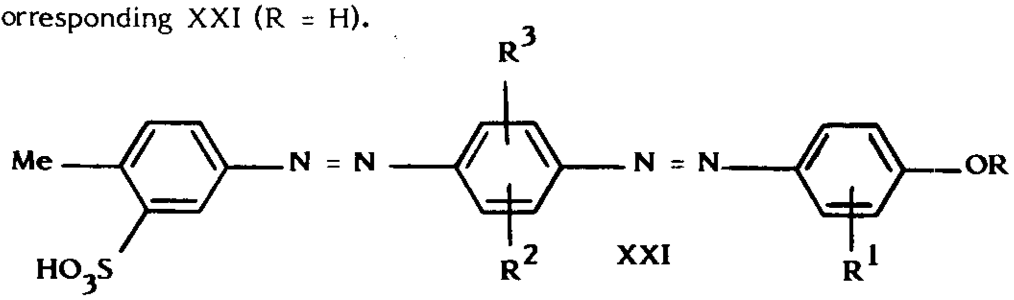
Sandoz(52) prepared the metal complex sulfo-group containing disazo dyes (XX) where R = ph containing a SO_3H or CO_2H group and optionally other substituents, or R = mono, di- or trisulfonaphthyl; R' = H, C_{1-4} alkyl, C_{1-14} alkoxy, C_{2-5} alkanoylamino, or H_2NCONH; R^2 = H, (un) substituted lower alkyl, ph, or (un) substituted phenyl-C_{1-3}-alkyl; and M = Cu^{2+} or Ni^{2+}.



XX

XX were water soluble, from storage-stable aqueous components and were useful for dyeing cotton, leather and especial paper. $2,4,8\text{-}H_2NC_{10}H_5(SO_3H)_2 \longrightarrow 5,2\text{-}Me(MeO)C_6H_3NH_2$ was diazotized, coupled with $2,5,7\text{-phNH(OH)-}C_{10}H_5SO_3H$ and copperized to give XX (M = Cu^{2+}, R = 4,8-disulfo-2-naphthyl, R' = Me, R^2 = ph), λ_{max} 595 which dyed paper in pure blue shades with good fastness to light and wet processing. Numerous other XX were prepared by the same method.

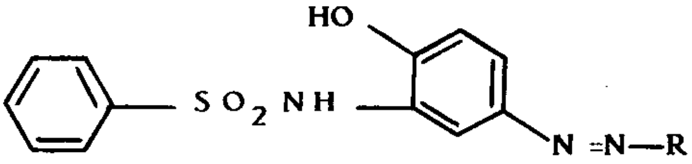
Nickel(53) prepared the Bis-azo dyes XXI (R = optionally substituted alkyl; R^1 = H, alkyl; R^2, R^3 = H, alkyl, alkoxy) by alkylation of the corresponding XXI (R = H).



XXI

These compounds in alkaline medium were fast yellow to orange dyes for polyamide fibres. A typical dye XXI (R = Me, R^1 = R^2 = H, R^3 = 2-OMe) produced golden yellow dyeing on nylon 6.

Some new dyes part XXII yellow to deep reddish violet azo disperse dyes (XXII; R = $C_{10}H_7$, substituted ph) were synthesized(54) by coupling N-(o-hydroxyphenyl)benzenesulfonamide with diazotized isomeric nitroanilines, chloroanilines, aminobenzoic acids, toluidine, and naphthylamines.



XXII

These dyes were applied to nylon 6 fabrics and the effects of dyes and carrier concentration, duration and temperature of dyeing and substituent position in R on the color strength of the dyeing were determined. Washing and light fastness of the dyeing were also examined.

Fadda(55) studied the synthesis of azo dispere dyes from meldrum's acid for dyeing acetate and other fibres. The diazotized aniline were coupled with Meldrum's acid to give 13 mono-azo dyes of structure XXIII (R = H, NO_2, OMe, Me, OEt , OC_6H_4Cl - p ; R_1 = H , Cl , NO_2 , OMe , CF_3 , OEt ; R_2 = H , Cl , NO_2 , OMe , CN ;