A N I N V E S T I G A T I O N O F
P H O T O T R O P I S M I N S O L U T I O N

by

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Summary:

Phototropism is the phenomenon which applies to compounds that can undergo reversible photochemical reactions. The phototropic effect is known to occur in the solid state and in solution, but it is only in recent years that attention has been paid to the phototropism of dissolved molecules.

Saturated aqueous solutions of ammonium thiocyanate containing traces of ferrous ions exhibit a reversible colour change on exposure to ultraviolet light. The change has been shown to be due to the photo-induced atmospheric oxidation of the ferrous ions and the formation of an intensely coloured ferrithiocyanate complex. In the absence of light, the ferric ion is reduced by the thiocyanate ions.

Solutions of the leucocyanides and leucobases of some Triarylmethane dyestuffs are phototropic. Irradiation results in a reversible change from the colourless, covalent form to the intensely coloured ionic form of the dyestuff. Reversible photo-ionisation reactions of this sort have been shown to be generally applicable to the leucocyanides and leucobases of the Basic dyes.

The quantitative study of phototropism in solution presents some

difficulties, in that the phototropic equilibrium state is usually dependent upon the relative rates of three distinct chemical processes. Two methods have been developed whereby equilibrium mixtures, containing large and reproducible amounts of the unstable photoproduct, can be examined. One of these techniques has been used to examine the effects of chemical structure and concentration of the solute, and polarity of the solvent, on the reversible cis-trans photo-isomerisation of aromatic azo compounds in solution. Phototropic behaviour has been characterised by the change in the molecular absorption spectrum, ΔA, at the wavelength of maximum absorption of the photoproduct, the half-life time and the quantum yield for the forward photochemical process, and the half-life time and rate constant for the reverse (thermal) process. The light sensitivity of the metal complexes of five hydroxy-azo compounds has been studied.

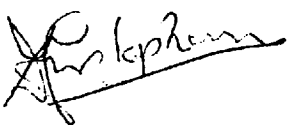
Acknowledgements

The work recorded in this thesis was carried out in the Chemistry Department of the Imperial College of Science and Technology between October, 1964, and August, 1967. It is entirely original, except where due reference is made, and no part has previously been submitted for any other degree.

I wish to express my gratitude to my supervisor, Professor T.S. West, for his invaluable assistance during this research project.

Thanks are also due to the Imperial Chemical Industries, Ltd., (Agricultural Division) for the provision of a research grant, and to the Science Research Council, which supplied much of the instrumental equipment used.

Finally, I would like to thank Mr. D.M. Alger, of the Instrument Workshop, for constructing the Irradiation unit used in this work.



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CONTENTS

CHAPTER 1.

Introduction

1.1 Nomenclature

Marckwald [1] used the term 'phototropy' to describe the phenomenon by which a solid changes its colour when exposed to light but reverts to its original state in the dark. His choice of nomenclature was unfortunate in that the term has also been used by botanists and biochemists to describe the photo-induced tropistic behaviour in plant life. However, the term has now largely been replaced by 'Phototropism' and 'Photochromism'.

The term phototropism, by virtue of its derivation Viz: Greek φωτο , pertaining to light, and τρόπος , turning or changing [62], implies a general change induced by radiation, and will be used exclusively throughout this thesis in this sense. Photochromism is concerned specifically with photo-induced changes in the visible range of the spectrum, and as such, many phototropic compounds are photochromic, but we are dealing with reversible systems, and reversibility of colour does not necessarily mean

chemical reversibility.

1.2 Definition

Phototropism may be defined as the phenomenon by which a system undergoes a reversible change in its spectral absorption characteristics on exposure to ultra violet or visible light. In the absence of activating radiation then, the system will exist in a stable 'dark' state, exhibiting a characteristic absorption spectrum. On exposure to a suitable source of radiation, an equilibrium state between the stable form and the photo-induced form will be established, resulting in a change in colour, and characterised by an 'equilibrium' spectrum. When the light source is removed, the system will revert to the stable state by a thermal (dark) process. It should be noted here that it is frequently possible to accelerate this reversal by irradiation with light of a different wavelength to that initially used. i.e. the photo-chemical reaction can operate in both directions. For complete reversal, however, total absence of absorbed light is necessary.

A comparison of the phenomenon with the closely related ones of fluorescence and phosphorescence is worthwhile at this stage.

Absorption of electromagnetic radiation of the ultraviolet and visible spectrum by a molecule results in the transfer of electrons from vibrational levels in the ground state, to vibrational levels in various electronic excited states. This absorbed energy may be dissipated in several ways.

(1) Internal conversion of the electronic energy to molecular vibrational and rotational energy, resulting in a radiationless (thermal) return to the ground state.

(2) Radiationless transfer to the lowest vibrational level of the first excited singlet state, and subsequent return to the ground state by photon emission. This is termed Fluorescence, and takes place within 10^{-7} seconds of initial excitation.

(3) Intersystem crossing to metastable triplet states, and subsequent return to the ground state by photon emission. This is termed phosphorescence, and takes place at least 10^{-4} seconds after the initial excitation. The triplet state in solution is, however, more likely to be deactivated by collisional encounters with solvent molecules, etc.

(4) Transfer of the excited electronic energy to vibrational and

torsional twisting modes rendering them sufficiently energetic to cause atomic rearrangement, or dissociation of the molecule. This may take place via the excited singlet or triplet states.

(5) Electron migration or stabilisation away from the point of initial excitation. (Intra-molecular charge transfer.) This may lead to ionisation or intermolecular electron transfer and the production of different chemical species.

(4) and (5) are processes involved in photochemical change. It is when the photochemical change so produced is reversible that the term phototropism is applicable.

1.3 Historical

The first application of phototropic materials dates back to the time of Alexander the Great, who issued his troops with a strip of chemically treated cloth which was worn on the left forearm. Insolation of this material produced visible colour changes dependent on exposure-time and thus provided Alexander's Macedonian troops with the world's first wristwatch. Among historians this device is known affectionately as "Alexander's Rag Timeband."[2]

The earliest reports of the phenomenon in the scientific literature came from ter Meer [3] who observed photoinduced colour changes with the potassium salt of dinitromethane, and Phipson [4], who painted his gatepost with 'lithopone' paint pigment and referred to the resulting phototropic effect as the "actinic phenomenon." It was Marckwald [1] however, who first considered the phenomenon in terms of a truly reversible photo-reaction, after examining the light-labile compounds benzo(C)(1,8) naphthyridine and tetrachloro - 1(2) - naphthalenone.

Since this early work several hundreds of phototropic systems have been cited in the literature. The phenomenon has been the subject of a number of reviews, namely those of Stobbe [5], Chalkley [6], Van Overbeek [7], Bhatnagar et al [8], and more recently, Brown and Shaw [9] in 1961, Dessauer and Paris [10] in 1963, and Exelby and Ginter [11] in 1965.

1.4 Phototropic compounds - mechanisms

Both inorganic and organic compounds exhibit phototropism. The known inorganic systems are solids, mixtures of solids, or solids supported in rigid matrices, e.g. organic solvents at low

temperature or silicate glasses. Since this thesis is concerned with the phototropism of molecules dissolved in mobile solvents at normal temperatures, inorganic phototropism will not be discussed further.

Organic compounds exhibit the phenomenon in both the solid state and in solution, and a considerable amount of data has been accumulated on the subject. Some of this work will now be presented and discussed, in relation to the processes involved. Examples of solid phototropism will be included where appropriate, but the emphasis will be placed on phototropic behaviour in solution.

The subject may be divided into four main categories, according to the general nature of the photo-induced processes.

A ISOMERISATION

(1) Cis-trans isomerisation

In 1938 Hartley [12] observed that solutions of ordinary (trans) azobenzene in various solvents were phototropic.

He succeeded in isolating the photoproduct and deduced that it was the cis isomer. A number of derivatives of azobenzene were also found to be phototropic in solution, presumably due to isomerisation, but the photoproducts were too unstable to effect a separation.

The cis-trans photo-isomerisation of aromatic azo compounds has subsequently been examined by several workers [13-21]. The stable form in all cases is the trans isomer, which undergoes partial conversion to the cis form on irradiation.

FIG. 1
Phototropism of Azo Compounds

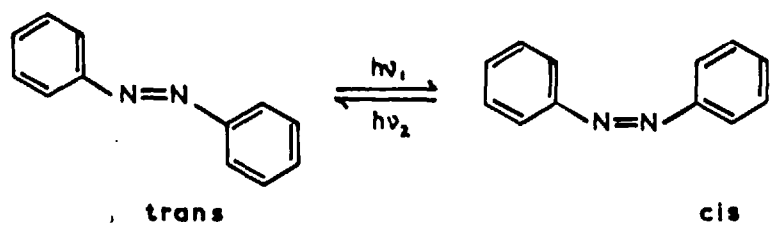
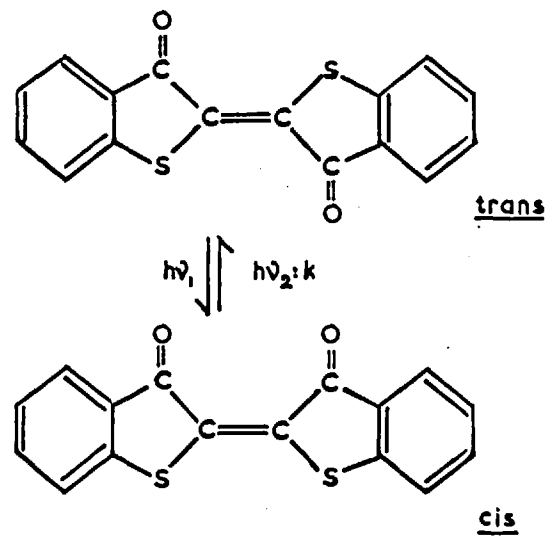


Fig. 1 shows the general reaction scheme. The isomerisation is accompanied by a hypsochromic and hypochromic shift in the absorption spectrum of the dissolved molecules. It should be noted that the reaction may also be reversed photochemically. This appears to be true of all cis-trans phototropic reactions.

Thioindigo dyestuffs in solution also exhibit photoisomerisation, about the carbon-carbon double bond (Fig. 2)

FIG. 2



Phototropism of Thioindigo.

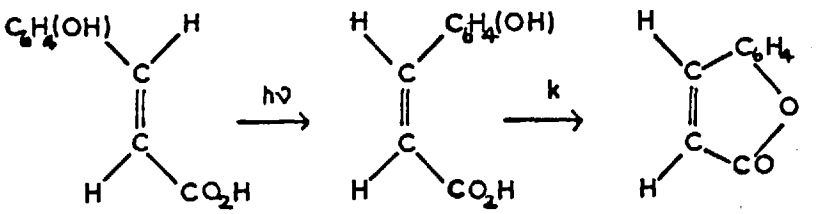
The light sensitivity of these compounds was first reported by Stearns [22] and subsequently examined by Brode and Wyman [23, 24]. Again, the trans isomer is the more stable form. The cis forms of thioindigo derivatives appear, in general, to be more stable than those of the corresponding azobenzenes. A chromatographic

separation of the isomers of thioindigo and 5,5' dichloro-4,4',7,7'-tetramethyl thioindigo has been effected, and the absorption spectra of the almost pure cis and trans products plotted.[24] As would be expected, the trans isomers have higher R_f values than the cis, due to the more polar character of the latter. The absorption spectral changes accompanying the isomerisation are more complicated than those of the aromatic azo compounds, but in all cases the main long-wave absorption peak for the cis isomer is at a shorter wavelength than that of the trans form.

A large number of substituted ethylenes, both aromatic and aliphatic, exhibit cis-trans photo-isomerisations in solution. The majority of the compounds examined to date have been simple substituted ethylenes, and consequently no visible colour change occurs during the isomerisation, since the reactants and products absorb ultra violet light only. Vaidya[25] examined the light sensitivity of aqueous solutions of the geometric isomers, maleic (cis) and fumaric (trans) acids, and similar unsaturated mono- and dicarboxylic acids. With the exception of cis-o-coumaric acid (which undergoes intramolecular esterification to form the lactone (coumarine), Fig. 3), the cis and trans forms are stable in the

absence of activating irradiation. The cis isomers absorb at

FIG. 3



shorter wavelengths, and with lower extinction coefficients, than the corresponding trans isomers.

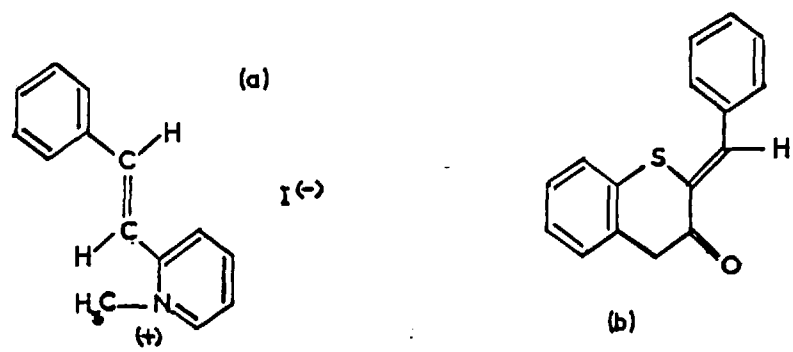
Stilbene ($C_6H_5.CH{:}CH.C_6H_5$) in iso-octane is phototropic [26], the photoproduct being the relatively stable cis-isomer, but the behaviour of the derivatives of stilbene towards light is more complicated. Henry [27] found that trans 4,4'-diamidinostilbene in solution underwent dimerisation as well as photo-isomerisation. The latter process was dark-reversible, but the former could be reversed by ultra violet irradiation. Derivatives of 4,4'-diamino-2,2'-stilbene disulphonic acid are phototropic in the solid state [28],

the colour change being from colourless or yellow in the dark, to pink in the light. The process requires the presence of atmospheric oxygen and consequently cannot be due entirely to a simple isomerisation.

Benzalacetone ($C_6H_5.CH:CH.CO.CH_3$) and benzalacetophenone, ($C_6H_5.CH:CH.CO.C_6H_5$) undergo <u>cis-trans</u> photo-isomerisation in the solid state [29].

The coloured compounds 2-styrylpyridine methiodide [30], (Fig.4 (a)) and 2-benzylidene 3-oxo-2,3- dihydrothianaphthalene [31] (Fig.4 (b)) are also phototropic. Resolution and subsequent examination of the

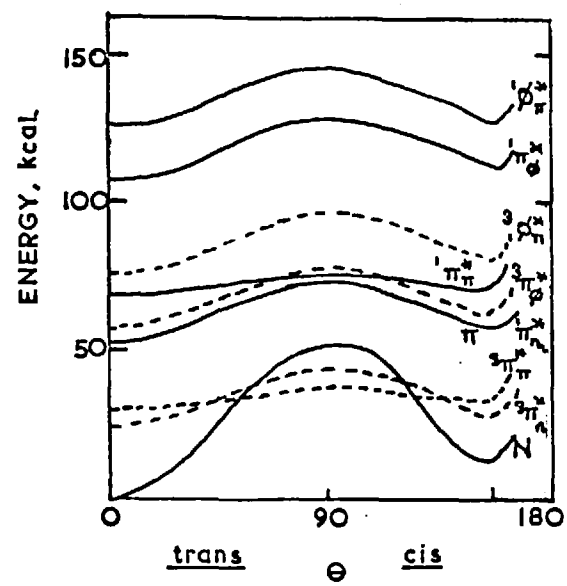
FIG. 4



isomers of the former compound showed that the trans form was the stable one. The thianaphthalene derivative was allotted the stable configuration shown in Fig.4 (b), since it is sterically more favourable.

The exact mechanism by which cis-trans photoisomeration occurs is still not fully understood, and several suggestions have been put forward as to how the excited trans molecules are converted to the cis form. Birnbaum and Style [17] estimated the energy of the azobenzene molecule in the ground and in several excited states as a function of the angle of twist about the central double bond. (Fig. 5). They concluded that the energy barrier separating the cis and trans forms in their excited states was sufficiently small to allow rotation between the two forms, and that isomerisation occurred via an excited state common to both isomers, in which, presumably, the nitrogen-nitrogen double bond possessed considerable single-bond character. If such a common state did exist, however, the cis isomers, since they are less the stable (i.e. have a higher ground-state energy) would absorb light at longer wavelengths than the trans. The opposite effect is observed in practice. The hypsochromic shift in the absorbance spectra accompanying trans-cis

FIG. 5



Potential energy of azobenzene vs. Angle of twist about N=N

—— singlet states

---- triplet "

isomerisation is due to steric interaction of the aromatic groups in the cis isomer, resulting in distortion of the molecule, and consequent loss of conjugation.

Theoretical investigations [32, 33] (based on studies of the carbon-carbon double bond in ethylenes) indicate that the $^3\pi^*$ state is

of minimum energy for the 90° twist configuration, and not as shown in Fig. 5 for azobenzene. In this case, isomerisation might occur by intersystem crossing from excited singlet states to the $^3\pi^*$ triplet and thence by a thermal process.

The idea of a separate thermal process, involving the excited state molecules, is supported by Fischer [21] and Zimmerman et al [19] in connection with the isomerism of azobenzene and the azonaphthalenes. The latter workers base their argument on the fact that the quantum yields for the forward and reverse photochemical processes do not add up to unity, thus ruling out a common excited state. This is scarcely conclusive evidence, but the proposals are consistent with the observed absorbance spectra. Whether the isomerisation occurs from the short lived singlet states, or whether conversion to a metastable triplet is necessary, has not yet been ascertained.

A mechanism for the photochemical isomerisation of stilbene has been proposed from a study of the fluorescence properties of the two isomers [26] and on the basis of earlier work on the isomerisation of α-β unsaturated acids [34].

Trans stilbene is fluorescent, but the cis-trans photo-reaction

competes with the fluorescence. i.e. some of the molecules do not lose their excess electronic energy by emission but convert it into rotational energy and thus isomerise. Cis-stilbene, on the other hand, does not fluoresce, and this is explained in terms of the 'loose bolt' theory of Lewis and Calvin [35]. Because of steric distortion of the cis molecule, the oscillating electronic field in the excited molecule has components in the axes of vibration and rotation of the benzene rings. The excited state electronic energy is thus rapidly converted into molecular vibrational and rotational energy and subsequently dissipated in the form of heat. The electronic excited states are, therefore, too short-lived to exhibit fluorescence, and the loss of the vibrational and rotational energy will result in the formation of either cis or trans molecules. This latter explanation appears to be quite sound and may well be applicable to isomerisation about the nitrogen-nitrogen double bond. It is noteworthy however, that none of the above workers has attempted to draw a distinction between isomerisation via rotation or via an N-N-C bond angle of 180°.

Finally, the following general conclusions may be drawn from the

above data, concerning cis-trans photo-isomerisation.

(i) Both the cis-trans and the trans-cis conversions can be effected photochemically.

(ii) The trans form is the more stable.

(iii) The stability of the cis-form varies greatly according to the degree of steric hindrance to its formation.

(iv) The cis form absorbs at shorter wavelengths because of molecular distortion and loss of conjugation.

(v) The trans-form generally exhibits a higher extinction coefficient, since it has the greater transition dipole moment.

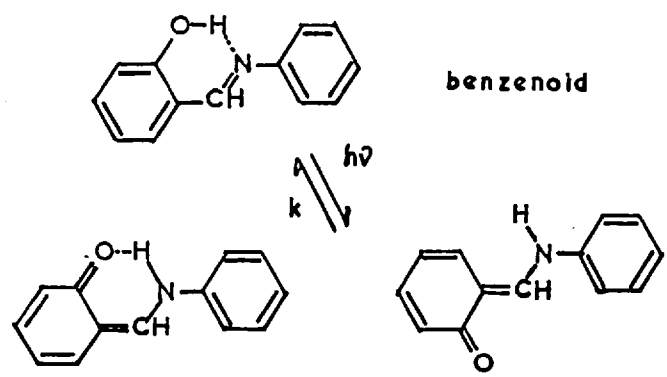
(2) Tautomerism

Isomers which exist in dynamic equilibrium with one another, and which differ in the location of one of the atoms or groups within the molecule, are termed tautomers, and the phenomenon is known as tautomerism. In this section we are concerned with a specific form of tautomerism involving the intramolecular transfer of hydrogen atoms.

Schiff's Bases (Anils) are the products of condensation between aldehydes and primary amines. (General formula = R.CH:N.R'). Of some 300 of these compounds investigated, 25 are reported to be phototropic. Irradiation results in colour changes from pale yellow to orange or red, though the time required for this change, and for the subsequent thermal reversal varies greatly from compound to compound.

Originally, the phototropic effect was observed in the solid state only, and for this reason, was believed to be the result of a material interaction of the molecules in the crystalline lattice, and not an intramolecular rearrangement.[36-40] However, Cohen and Schmidt[41] showed that solid solutions of Schiff's Bases (e.g. in paraffin oil at -80°C) were phototropic and thus concluded that the phenomenon was a property of the isolated molecules and that an intramolecular process was involved. These workers observed phototropism only with compounds derived from salicylaldehyde. Arguing that the presence of a hydroxyl group in the ortho-position was a necessary feature, and that the pronounced bathochromic shifts on irradiation indicated a quininoid photoproduct, they postulated the tautomeric mechanism shown in Fig. 6. for the photochemical reaction.

FIG. 6



Note that the photoproduct itself may exist in one of two isomeric forms.

Unfortunately, while this mechanism offers a reasonable explanation for the behaviour of salicylaldehyde derivatives, and, possibly, for the phototropic effect observed with some derivatives of p-hydroxybenzaldehyde [42,43], it cannot account for the phototropism of Schiff's Bases derived from o-nitrobenzaldehyde.[44]

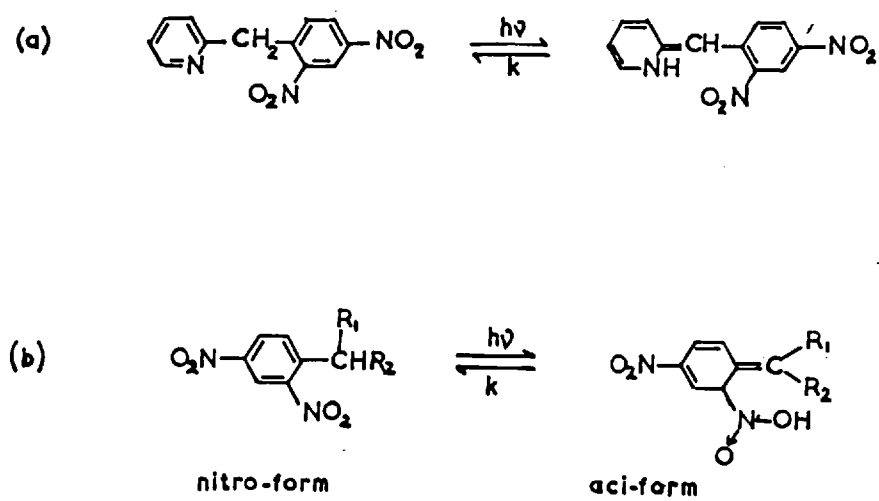
The phototropic activity of 2(2',4'-dinitrobenzyl) pyridine (colourless to deep violet on irradiation) has been observed both

in the solid state [45, 46] and in solution at low temperatures.[47] The tautomeric equilibrium illustrated in Fig. 7 (a) was proposed to account for the change, in which a hydrogen atom is transferred from the methylene group to the heterocyclic nitrogen atom. [45] Hosher et al [48] however, observed similar photochromic behaviour with 4-(2;4'-dinitrobenzyl) pyridine and suggested that hydrogen transfer to the o-nitro group was more feasible. A recent study [49] of solutions of twenty-one aromatic nitrocompounds of this type has shown that while a nitro group in the ortho position is a necessary requirement for phototropic activity, the presence of a pyridyl group is not. This further supports a mechanism involving hydrogen transfer to the ortho nitro group, and the reaction scheme shown in Fig. 7 (b) is now generally accepted, where R_1 can be H, CH_3, C_6H_5, etc., and R_2 is an electron withdrawing group, increasing the acidity of the central C-H bond.

The phototropism of these compounds in monomolecular films has also been examined. [50, 51]

The light sensitivity of twenty four metal complexes of diphenyl-thiocarbazone, "Dithizone" has recently been examined. [52] The mercury complex was found to be phototropic in the solid state and

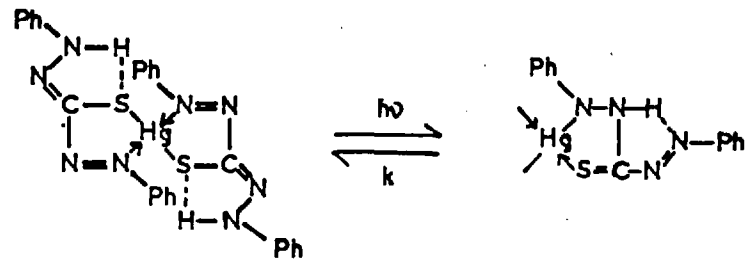
FIG.7



in solution, and eight other metal complexes exhibited phototropism in solution. The colour change on irradiation varies considerably (e.g. orange-blue: green-yellow) and the rate of thermal reverse reaction is greatly dependent on the metal ion complexed. (The half-life time for the activated Mercury complex in solution at 25°C is 30 seconds: for the cadmium and lead complexes at -80°C, less than 1 second.)

On the basis of kinetic and infra-red studies [53] Meriwether et al have suggested the structures shown in Fig. 8 for the complex and

FIG. 8



the activated form. The photo-induced change involves both a proton shift and the cis-trans isomerisation of an azo-methine group. It is suggested that this process occurs independently in each ligand attached to the central metal ion, and that it also accounts for the phototropic behaviour of the other dithizone complexes.

B DISSOCIATION

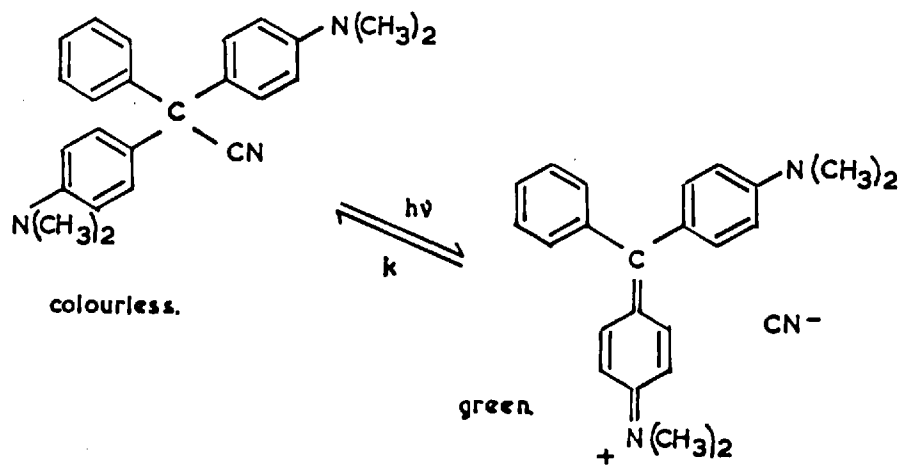
This section deals with phototropic systems in which irradiation results in the dissociation of the stable form into ionic or free radical species.

The most important group of compounds in this class are the leuco derivatives of triarylmethane dyestuffs. The compounds are

phototropic in solution at ordinary temperatures. The stable form is almost always colourless, but the activated form exhibits an intense visible absorption spectrum.

The leucocyanides and leuco bases of dyestuffs such as p-Rosaniline, Crystal violet, Malachite green, Brilliant green and Victoria blue have been extensively studied in a variety of solvents. [54-61, 63-66] There is much controversy over the phototropic mechanism involved. Litschitz et al [54-56] proposed the mechanism in Fig. 9 for the phototropism of Malachite green leucocyanide. There can be little doubt that the photoproduct is ionic in nature, since the colour observed is indistinguishable from that of the parent dyestuff, Malachite green, which is itself ionic. However, it has been suggested [60, 61] that the reaction is not strictly phototropic, in that the colourless leuco carbinol was produced by a hydrolytic thermal reversal. This is supported by chemical evidence. Germann and Gibson [63] suggest that neither the cyanide nor carbinol result on reversal of the activated form, but they fail to suggest a suitable alternative. De Gauock and Le Fèvre, [39] on the basis of conductivity studies, showed that the reaction only became reversible after the first irradiation and subsequent thermal process.

FIG.9. Phototropism of Malachite green leucocyanide.



Later work by Holmes,[64] and Sporer [65] indicates that no one mechanism can account for the phototropic behaviour of the leucocyanides. It is suggested that the cyanide, carbinol, or the ethyl ether could result, on the removal of irradiation, from solvent interactions. Irradiation itself could lead to the production of ionic or free radical species, and to side reactions resulting in the destruction of the dye molecule.

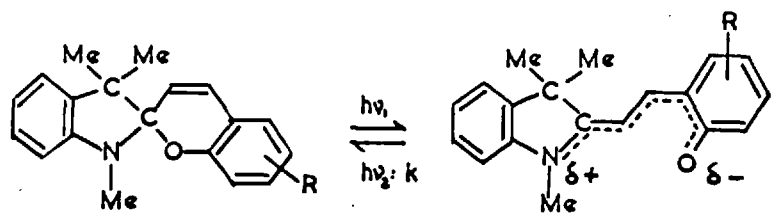
The quantum yields for the photochemical reaction are close to

unity [59,61,65,66] and the leuco-compounds have been examined for their use in actinometry.[58,60] No evidence has yet been given for any photochemical reversal of the colour reaction, similar to that occurring in photo-isomerisation reactions.

Certain spiropyrans undergo reversible photo-dissociation in solution.[66,67] Much of the investigation of these compounds has been carried out at low temperatures, due to the marked temperature dependence of the reverse process.

Fig. 10 illustrates the phototropic behaviour of substituted

FIG. 10



colourless coloured

1,3,3 trimethylindolinobenzopyrylspiran (R = substituent.)

Irradiation with ultraviolet light results in the dissociation of the C-O bond to yield the highly coloured (e_{max} - 10^4) merocyanine form. The rate of the thermal reversal varies greatly with the

nature of the ring substituents. [69] The process can be reversed photochemically though with less efficiency than in the forward process because of the necessary molecular alignment to effect ring closure. The activated molecule is believed to exist in various stereo-isomeric forms depending on the conditions under which irradiation is carried out. [71]

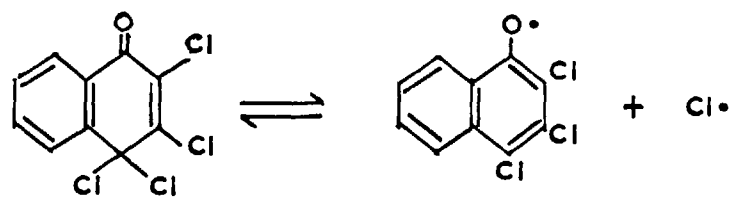
The phototropism of these compounds in rigid media has been examined for possible data storage applications. [76] To this end a number of patents have been issued to the National Cash Register Company.

The photo-dissociation of a number of substituted quinols, both in the solid state and in solution, has been reported. [78] The existence of free radical species in the activated solutions was established, and a mechanism of the type shown in Fig. 11 for tetrachloro-1 (4H) naphthalenone, was suggested.

Prolonged irradiation leads to irreversible side reactions, possibly involving dimerisation.

Other compounds which have been shown to undergo reversible photo-dissociation into free radical species are Octaarylbypyrroles, [79]

FIG. II



colourless coloured

and the products of reaction between fluorescent dyestuffs and complex mercaptans, such as glutathione, cysteine and thioglycollic acid. [80]

C OXIDATION / REDUCTION

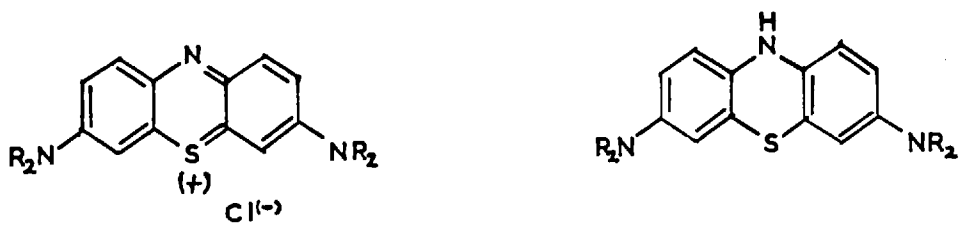
Phototropic systems of this type differ from the two previously described in that intermolecular reactions between two or more species are involved in the photochemical process.

The fundamental step is the excitation and subsequent migration of the electronic field associated with one of the species present

(charge transfer within the molecule.) This will facilitate inter-molecular charge transfer i.e. oxidation/reduction, and the formation of new chemical species. Provided that the oxidised and reduced forms are stable (i.e. do not undergo irreversible side reactions), reversibility of the above process is possible in the absence of light.

Solutions of the Thiazine dyes, Thionine and Methylene blue, (Fig.12) undergo reversible photoreduction in the presence of ferrous

FIG.12



basic dye (coloured) leuco dye (colourless)

R=H: thionine. R=CH_3: methylene blue

ions.[81-83, 85] The reduction is a two electron process, but is believed to pass through an unstable Semiquinone intermediate.[83, 84] Contrary to the majority of phototropic processes, irradiation causes irradication of colour, to yield the leuco dyes. The forward

and reverse processes are rapid (of the order of a few seconds.) Oxygen must be absent since it reoxidises the leuco dyes, resulting in an accumulation of ferric ions in the system, rendering it non-phototropic. The phototropic effect is enhanced by the presence of phosphate and fluoride ions, which form complexes with the photoproduced ferric ions, thus reducing the rate of reversal.

Other Thiazine dyes, namely Methylene green, Toluidine blue and Thiocarmine, and the Xanthene dyes, Brilliant cresyl blue, Eosin and Uranine have also been reported as phototropic in the presence of ferrous ions. [83, 85] Alternative reductants, e.g. ascorbic acid and hydroquinone have also been used. [86]

A saturated solution of ammonium thiocyanate containing ferrous ions becomes red on exposure to light and decolourises in the dark. This has been reported by Sharma [87] to be due to the formation of a 'loose, additive complex' between the ferrous ion, oxygen, and the thiocyanate ions. The Fe(II)-thiocyanate system will be considered in a later chapter.

The reversible photobleaching of chlorophyll is believed due to a charge transfer reaction. In this case the solvent molecules may

act as the electron acceptors.[88]

D MISCELLANEOUS

Reversible photo-isomerisation, dissociation, and oxidation/reduction account for the phototropic behaviour of the compounds to which mechanisms have been assigned to date. There are, however, many more phototropic systems which have yet to be characterised mechanistically, and elucidation of the (more complex) processes involved requires further experimental work. The more important of these compounds are listed below, together with the appropriate references:

(1) Hydrazones [5, 89-93, 95]

(2) Semicarbazones [95-102]

(3) Ozazones [103-107]

(4) Disulphoxides [108, 109]

(5) Succinic Anhydrides [110-113]

1.5 Solid and Solution Phototropism: Distinguishing Features

The three main processes responsible for phototropic change, viz. Isomerisation, Dissociation, and Oxidation/reduction, are applicable to materials both in the solid state and in solution. However, phototropic solids rarely retain their light labile properties on dissolution. The probable reason for this is that enhancement of the thermal reverse reaction occurs to such an extent on solvation that the photoproduct is formed in quantities too small for detection. Whilst it has been suggested [36-40] that the orientation of the molecules within the crystalline lattice might be a prerequisite for the phototropism of certain solids, in which case solvation would prevent the forward photochemical process, no conclusive evidence of this has been reported.

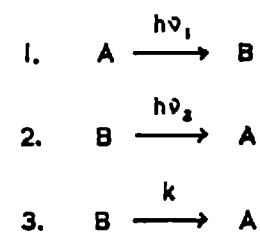
The dissolved molecules will have greater freedom of movement (rotationally and vibrationally) and interchange of energy with solvent molecules is possible. These facts may result in increased or decreased efficiency of the photochemical reaction, but are unlikely completely to prevent it.

1.6 Factors influencing Phototropic Equilibrium in Solution

Fig. 13 illustrates the three reactions, the rates of which will determine the nature of the phototropic equilibrium between the stable photo-reactant A and the unstable photoproduct B. The first two of these are photochemical processes and will depend on

FIG. 13

Reactions determining phototropic equilibrium between A (stable form) and B (unstable photoproduct.)



the following factors:

(a) Wavelength of irradiation

The Grotthus-Draper law states that only absorbed quanta, yielding excited state molecules, can produce a chemical change. The

wavelength most effective in promoting the forward photochemical process will thus be that at which A absorbs most strongly, assuming that the excited state molecules so produced are sufficiently energetic. In cases where reaction 2 is operative the absorbance of the photoproduct has also to be considered. This should be at a minimum, particularly if the reverse reaction is very efficient, in order to increase the conversion of A to B.

(b) Intensity of irradiation

The rate of photochemical change will be dependent on the rate of photon absorption, which in time will depend on the rate at which photons are being supplied to the system.

(c) Quantum Yield, Φ

The quantum yield for a photochemical process is defined as the number of photoproduct molecules produced per photon of absorbed radiation. If the reaction occurs with 100% efficiency, the quantum yield will equal unity, but this is rarely the case. For a given photo-chemical system then, the quantum yield will be a fractional quantity, the dimensions of which will depend on competing excited state behaviour, such as that outlined on pages 8 and 9.

The Φ values for the reactions 1 and 2 will differ, which complicates the selection of an optimum wavelength for the A$\longrightarrow$ B conversion if there is spectral overlap between A and B.

The reverse reaction, 3, is generally a straightforward thermal process, and, for a given compound, will be dependent upon:

(a) Concentration of solute (assuming 1st order kinetics or greater)

(b) Temperature of the solution

(c) Nature of the solvent

1.7 Fatigue

This is the process by which some systems lose their phototropic character on repeated exposure to light. Fatigue may occur as the result of irreversible photochemical reactions involving either reactant or photoproduct, or by irreversible thermal processes involving the photoproduct, producing new chemical species. These reactions may only occur to a very small extent during each exposure and fatigue may not be detected until several hundred phototropic changes have been effected. For this reason very little information is available on the phenomenon, though it is of considerable

importance in the commercial applications of phototropism.

1.8 Summary and Objectives

It will now be appreciated that a considerable amount of information concerning phototropic behaviour has accumulated during the 60 years or so since it was first recognised. However, much of this data is of limited value in that detailed studies of individual phototropic systems have rarely been made. This is particularly true of phototropism in solution, which has only received interest during more recent years. Much of the quantitative information published is of doubtful accuracy, since the analytical study of phototropic systems, which are influenced by so many factors, requires carefully controlled instrumental techniques. The purpose of the research work outlined in this thesis was

(1) to develope reliable equipment for the quantitative examination of phototropic solutions.

(2) to carry out an investigation of the phototropism of solutions containing selected organic molecules.

(3) to examine the possible application of the phenomenon to analytical chemistry.

CHAPTER 2.

Apparatus

2.1 Preface

Both the qualitative and the quantitative evaluation of phototropic systems present some difficulties in that,

(i) The system must be in an equilibrium state

(ii) The factors determining the equilibrium (Section 1.6) must be carefully controlled.

Failure to observe (i) will result in irreproducibility and, when the analytical process is a lengthy one, (e.g. spectral scanning) in gross errors. This is particularly relevant when the photoproduct is very unstable and may result in the failure to record any phototropic change. Likewise, failure to observe (ii) will lead to irreproducible results.

The variety of physical differences between reactants and photoproducts allows the use of a number of analytical techniques; e.g. measurement of paramagnetism, [79] conductivity, [39] and optical rotation. [114] Molecular absorption spectrophotometry, however, offers

the most complete method of analysis, though the difficulties of using light beams in both the activating and monitoring processes are considerable.[115-117]

Two methods have been developed whereby the absorption spectra of solutions containing large and reproducible quantities of the photoproduct species can be measured under equilibrium conditions.

2.2 Flow-through Irradiation/Absorption

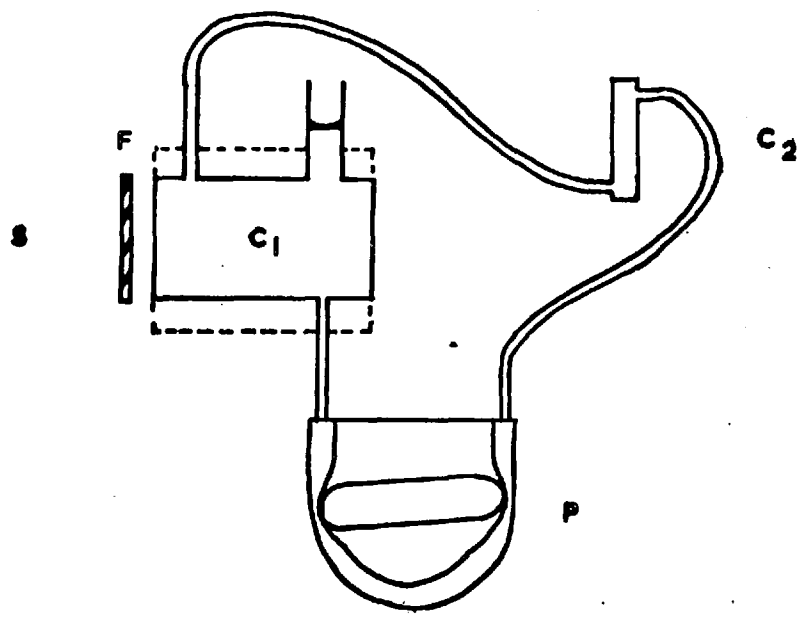
The technique is illustrated in Fig. 14.

Approximately 90 ml. of a sample solution is circulated in the closed circuit illustrated, by means of the peristaltic pump, P. Filtered light from the source S enters the irradiation cell, C_1 and the absorption spectrum of the resultant solution is followed at the quartz cuvette C_2, contained in the cell compartment of a recording spectrophotometer.

The cell C_1 is a closed quartz cylinder, length (internal) 7.6 cm., and internal diameter 3.5 cm., and contains about 85% of the total sample volume. A film of aluminium has been evaporated on to the outer sides and remote end, to ensure maximum absorption of

FIG. 14

ARRANGEMENT FOR FLOW-THROUGH IRRADIATION/ABSORPTION.



irradiant light. The cell is housed in a cooling jacket which maintains a solution temperature of 25 ± 1°C. The large side-arm illustrated is used to fill and drain the circuit, to minimise pressure fluctuations during pumping, and to allow the sample solutions to degas. (The removal of trapped air bubbles, which affect the performance of the spectrophotometer, proved a serious problem in earlier modifications of this technique.) The side-arm is graduated to ensure constant sample volume.

The peristaltic pump operates by means of two rollers on each end of a rotating arm, which successively squeeze a flexible tube along its length, so forcing the liquid in the tube to move forward. The tubing must be both elastic and inert. Silicone rubber tubing (Esco Rubber Ltd., 0.5 cm.I.D.), though suitable for the circulation of aqueous solutions, was found to contaminate organic solvents. In this case, fluorosilicone rubber (Esco, Ltd: 0.3 cm.I.D.) is necessary. The latter can not be used universally however, since aqueous solvents cause binding between the tubing walls.

The rate of pumping was determined from the following considerations:

(a) Too slow a rate gives inadequate sample mixing, and erratic

results.

(b) Too rapid a rate gives excessive pressure fluctuation with the risk of tube fracture.

Connections are made with Nylon 66 tubing (Portland Plastics Ltd. 0.2 cm.I.D.) which gave no spectral contamination for $\lambda \geqslant 280$ mμ with the solvents used.

Finally the entire system is blacked out to eliminate extraneous effects from laboratory lighting.

Table 1 summarises the data associated with the flow-through technique.

When fluorosilicone tubing is used in the pump (ref. Table 1) the sample is circulated every 22 seconds. Of this time, 15% (3.3 seconds) is spent outside the irradiation cell.

When the source S is switched on the solution entering the irradiation cell contains solute molecules in the dark (stable) state only. As the solution passes through, these molecules will absorb photons and the solution leaving the cell will contain a proportion of the photoproduct. At this point the irradiation is effectively shut off while the sample completes the circuit. If the reverse

TABLE 1.

	Organic Solvents (fluorosilicone rubber)	Aqueous Solvents (Silicone rubber)
Total circuit volume	86 ml.	87 ml.
Volume of C_1	73.1 ml.	73.1 ml.
% Sample in C_1	85%	84%
Path length, C_2	0.5 cm.	0.5 cm.
Pump tube diameter	0.3 cm.	0.5 cm.
Circulation time (assuming 100% efficiency)	22.1 secs.	16.1 secs.

reaction is not completed during this interval the solution re-entering the cell will contain a proportion of photoproduct molecules. Recirculation will thus result in an increase in photoproduct concentration which will continue until the amount of (concentration dependent) reversal taking place during the total circulation time is equal to the photochemical change taking place during the 85% of this time that the sample is being irradiated. Thus an equilibrium will be established at which the rate of the forward photochemical process is but slightly greater than that of the thermal reversal.

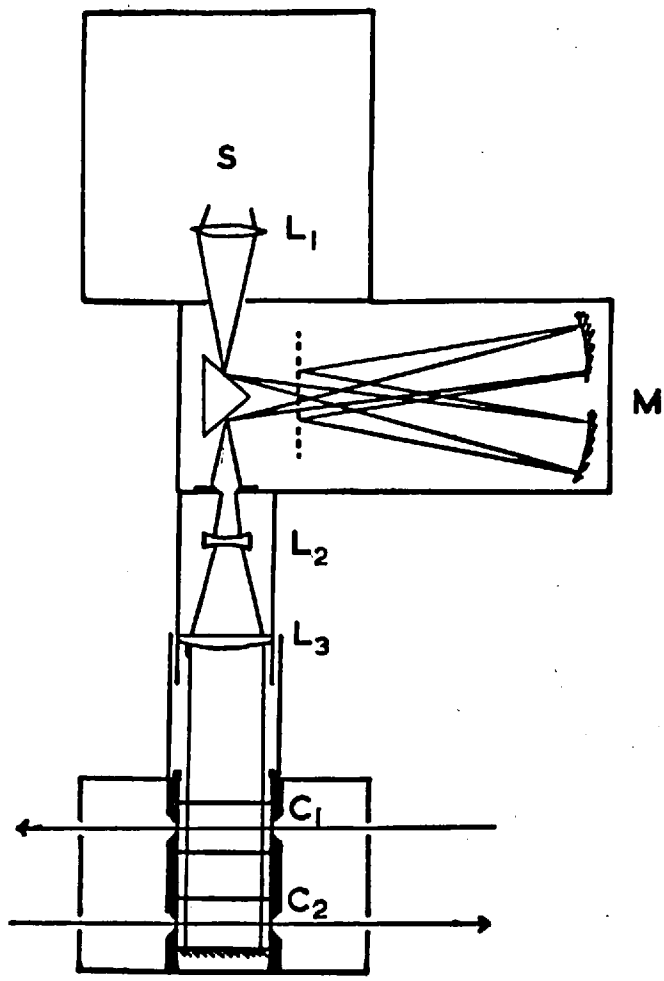
The photochemical change is followed immediately after irradiation. With the possible exception of very rapid phototropic systems, the equilibrium mixture analysed here will not differ measurably from that elsewhere in the system, and in any case, a difference will not affect the reproduceability of the results. The measuring beam is of negligible intensity compared to the activating one.

2.3 Direct Irradiation/Absorption

Here, (Fig. 15) light from the source S is focussed by the quartz condenser L_2 into a 'straight through' diffraction grating monochromator, M. The emergent monochromatic beam passes through the quartz optics L_2 and L_3 and a wide, collimated beam is incident at the two cuvettes, housed within the spectrophotometer, containing the sample and reference solutions (6 ml.). Adjustable slits set in the cell house door can be used to control the width of the beam, but the collimating optics were chosen so as to make the adjustment slight. The collimator may be telescoped to facilitate access to the cell compartment.

The extreme sensitivity of the spectrophotometer detecting system to light necessitated the following precautionary measures to eliminate

FIG. 15



ARRANGEMENT FOR DIRECT IRRADIATION/ABSORPTION.

interference from the activating beam.

(a) The (2 cm. x 1 cm.) cuvettes are optically polished on all four sides, and the reference cell C_2 is aluminised on the remote side, to prevent light scatter in the cell compartment. (N.B. The mirrored cell can equally well be placed in the 'sample' position. It was originally used in the 'reference' position so that light scatter at both cells would be approximately equal and the two effects would cancel out. This later proved to be unnecessary.)

(b) The cell holder is of a special design, incorporating knife-edge slits through which the monitoring beams pass. The cells are held in place by small phosphor-bronze clips at the top edge of each, and are effectively 'walled off' from the rest of the cell compartment.

(c) The height and lateral position of the source S and the position of the plano-convex optic L_3 are adjustable to ensure that the activating beam is collimated and perpendicular to the monitoring beams. In this respect the mirrored cuvette proves useful, because an image of the monochromator exit slit is produced, at the slit, when the optical alignment is correct.

(d) Diffraction of the monitoring beams at the knife-edge slits (ref. (b)) causes a sluggish response of the pen recorder to absorbance changes. Reduction of the wavelength scanning speed prevents this from resulting in spectral errors.

N.B. The monitoring beam in the recording spectrophotometer used is deflected alternately from sample to reference cuvette by a 'chopping' device, which consists of a polished, segmented disc rotating at 50 cps., alternately transmitting and reflecting the light beam. An attempt was made to eliminate interference between the irradiant and absorbing beams by chopping the irradiant beam with an identical device. Thus, intermittent irradiation of the sample could take place while the monitoring beam was passing through the reference cuvette. The cuvette could be sealed off from the irradiating beam and no stray light would reach the photomultiplier. Whilst this device is theoretically sound, in practice it was found that the two chopping discs could not be synchronised to operate exactly out of phase with one another.

By the direct technique then, phototropic changes can be monitored simultaneously with irradiation. The wide activating beam ensures complete sample irradiation, so reducing the likelihood of errors

due to insufficient mixing within the cuvette.

2.4 Instrumentation

The source used in the above techniques is a 500 watt D.C. Xenon arc lamp, which provides a stable high intensity ultraviolet and visible continuum.

The filters (Fig. 16) and monochromator provide the necessary wavelength selection (Section 1.6). The ultraviolet and visible spectrophotometer has the following accessories:-

(a) Absorbance vs. Time Scanning:

The absorbance of the sample at a predetermined wavelength can be plotted as a function of time, thus facilitating kinetic studies of the forward and reverse processes.

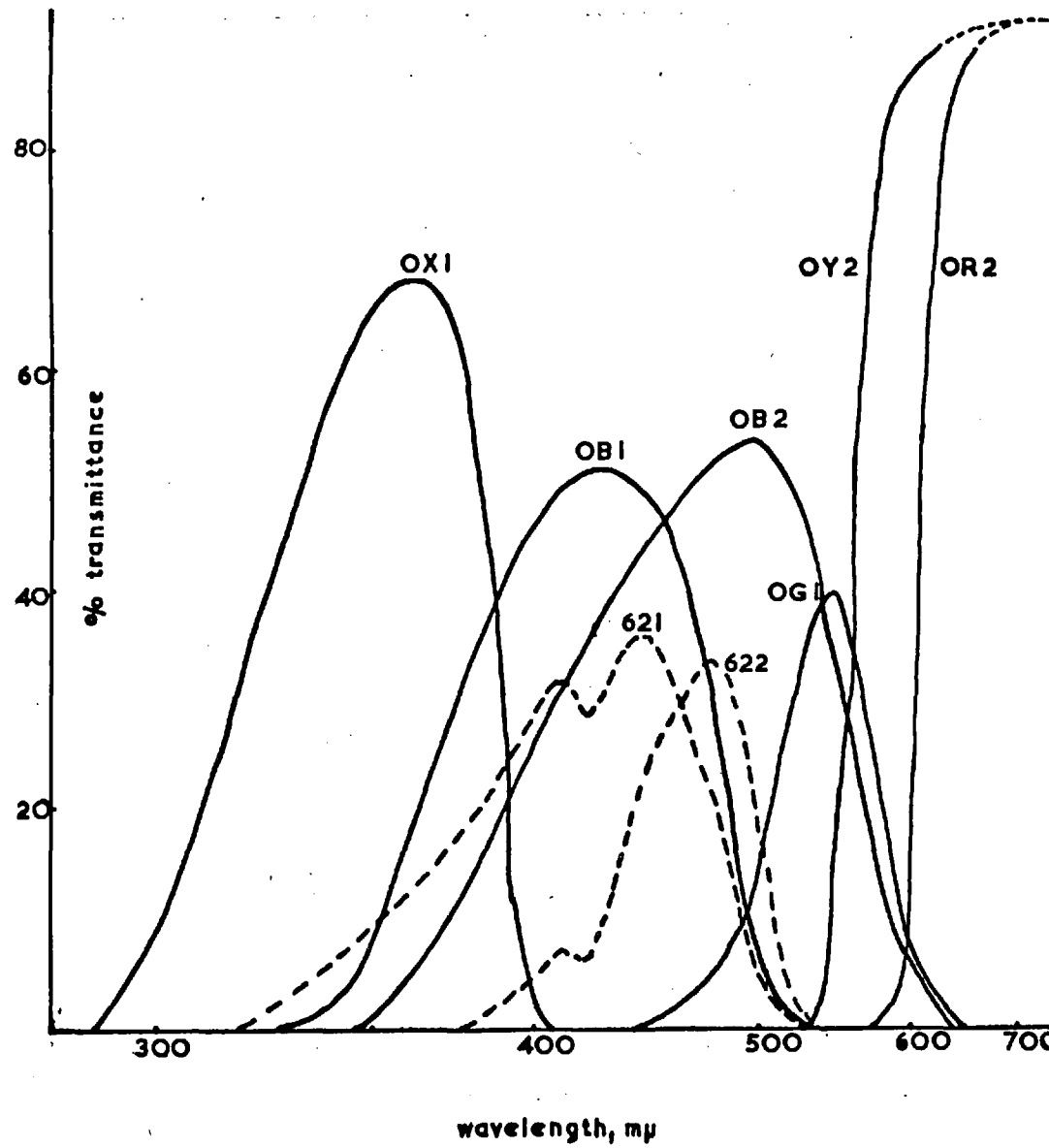
(b) Automatic rescanning:

The absorbance spectrum of the sample can be automatically re-plotted at preselected time intervals.

Specifications of Manufactured Equipment

Spectrophotometer: Ultrascan (Hilger and Watts Ltd.), H999, with

FIG.16. Transmission Characteristics of Optical Filters.



accessories H981, H1027, H1028.

Lamp: Compact source, high pressure Xenon discharge (Mazda: AEI Ltd.), 500 w. D.C. Type XE/d. Ref. 98-1002. with 25 amp starter unit (AEI: 66/90101) and Power supply (Westinghouse Brake and Signal Co. Ltd., R19810).

Monochromator: Quartz grating (Hilger and Watts Ltd.), D292.

Filters: Chance Bros. Ltd., and Ilford Ltd.

Cuvettes: 5 mm. quartz flow-through (Hellma (England) Ltd.) 137-QI. 20 mm. fluorimeter (Thermal syndicate Ltd., Spectrosil).

Pump: Gallenkamp & Co. Ltd., WN-200, with accessories MX-720 and EU-068.

Optics: Optical works, Ltd.

2.5 Determination of Lamp Intensity

Actinometry provides the most accurate technique for the determination of the intensity of the activating irradiation, since the actinometer solutions can be irradiated in exactly the same way as the phototropic

solutions are. Thermopile data is less accurate, particularly when optical filters are used, but can be used over a greater range of wavelengths.

A Flow-through Irradiation/Absorption

(i) Actinometry

The intensity of the filtered light incident just within the irradiation cell C_1 (Fig. 14) has been determined by ferrioxalate actinometry.[118] The intensity is evaluation from measurement of the rate of photolytic decomposition of acid potassium ferrioxalate solutions to yield ferrous ions. The absorbance characteristics of the solution limits determination to light of wavelengths less than ~500 mμ.

Procedure:

Preparation of potassium ferrioxalate: Ferric chloride hexahydrate, A.R.(81.1g) was dissolved in distilled water (200 ml.) and the solution was slowly added to a rapidly stirred solution of potassium oxalate monohydrate, A.R. (165.5g) in distilled water (600 ml.) The product was removed by filtration, washed with cold water, and

recrystallised from warm distilled water. The pure potassium ferrioxalate was dried in a current of warm air and stored in a dark container. The entire preparation was performed in a dark room illuminated by a Wratten, Series OA, safelight.
Yield (purified), $K_3Fe(C_2O_4)_3 . 3H_2O$ = 100g = 68% theoretical.

The oxalate present was determined titrimetrically using standard potassium permanganate solution.

Mean oxalate found = 53.85% (Theoretical = 53.75%)

Irradiation: The flow through circuit was filled with a solution of potassium ferrioxalate (0.15M) in sulphuric acid (0.05M). (Volume = 87.0 ml.), and the peristaltic pump was operated at 75 r.p.m. Irradiation, with the appropriate filter in place, was carried out for between 15 and 30 minutes, the exposure time being accurately recorded. 1 ml. and 2 ml. aliquots of the exposed solution were removed and the concentration of ferrous ion present was determined spectrophotometrically using o-phenanthroline. (N.B. Laboratory illumination for above = Wratten OA safelight).

Analysis: A calibration curve for the Fe(II): o-phenanthroline colour system was prepared using ferrous ammonium sulphate, standardised by

titration with standard potassium permanganate solution.

10 aliquots between 0 and 5 ml. of standard ferrous solution (10^{-4}M) were taken. Each was treated with 0.1% aqueous o-phenanthroline solution (2 ml.), buffered to pH = 3.5 with a sodium acetate/sulphuric acid buffer, and diluted to 25.0 ml. The solutions were stored in the dark for 30 minutes. The absorbance of the coloured species was measured at 510 mμ, vs. a reagent blank, in 1 cm. glass cuvettes. (Unicam SP 600 spectrophotometer).

The system was found to obey Beers' law throughout the concentration range used, with a molar extinction coefficient of $\epsilon_m^{510} = 1.13 \times 10^4$. (Cf. approximate value of 1.11×10^4 obtained by Hatchard and Parker.[118])

The ferrous ion concentration in the exposed ferrioxalate solutions was determined by the same procedure as above, the absorbance being read against a blank prepared from an identical aliquot of the unexposed ferrioxalate solution. The analysis was performed under Wratten OA safelight illumination.

Results: Ref. Table 2.

Calculation: The following equations are applicable:-

$$n_{Fe^{2+}} = \frac{6.023 \times 10^{20}\, V_1 V_3 \log_{10}(I_0/I)}{V_2 l\, \epsilon_m} \qquad 2.1$$

$$I_0 = n_{Fe^{2+}} / \Phi_{Fe^{2+}} . t\left(1 - \frac{I'}{I_0}\right) \qquad 2.2$$

where: $n_{Fe^{2+}}$ = Number of ferrous ions formed photolytically.

V_1 = Volume of ferrioxalate solution irradiated. (ml.)

V_2 = Volume of the aliquot taken for analysis. (ml.)

V_3 = final volume to which V_2 is diluted for analysis (ml.

$\log_{10}(\frac{I_0}{I})$ = absorbance of the o-phenanthroline complex at 510 mμ.

l = path length of cuvettes used in analysis (cm.)

ϵ_m = molar extinction coefficient for the Fe(11)-: o-phenanthroline complex

I_0 = Intensity of activating light (quanta/second)

$\Phi_{Fe^{2+}}$ = Quantum yield for the production of Fe^{++} ions.

t = Exposure time, (seconds)

$(1-\frac{I'}{I_0})$ = fraction of irradient light absorbed by the ferrioxate solution.

Equation (2) above simplifies to $I_0 = n_{Fe^{2+}} / \Phi_{Fe^{2+}} . t$, under the

experimental conditions. i.e. the ferrioxalate solution in the irradiation cell (effective path length, ~16cm.) is of sufficient concentration to absorb all of the light transmitted by the filters used.

The quantum yield for the photolysis with each filter was determined by an averaging procedure based on the quantum yields recorded at discreet wavelengths within the limits of transmission of the filter, and the shape of the transmission ourve (Fig. 16). Any inaccuracy here will be no greater than that asssociated with the original values of $\Phi_{Fe^{2+}}$ [118, 119].

Applying the above equations, the number of ferrous ions formed during the photolysis can be found, and hence the intensity of the activating light. Table 2 shows the results obtained for the four filters which show no appreciable transmission at wavelengths greater than 500 mμ.

(2) Thermopile

The e.m.f. produced by a thermopile bears a linear relationship to the energy of illumination falling on the active surface. The thermopile can be calibrated using a standard lamp, and the measurement of unknown radiation intensities is then readily achieved using a suitable potentiometer circuit.

TABLE 2

Filter	Irradiation Time, t (seconds)	Aliquot for Analysis, V_2 (ml.)	Absorbance at 510 mμ	$\Phi_{Fe^{2+}}$	Mean Intensity, I_0, (Quanta/second)
OXI	900	1	0.305	1.23	3.09×10^{16}
		2	0.605		
	1,200	1	0.427		
		2	0.853		
OBI	900	1	0.220	1.13	4.99×10^{16}
		2	0.437		
	900	2	0.444		
621	1,800	1	0.335	1.12	3.82×10^{16}
		2	0.665		
622	1,800	1	0.186	0.93	2.58×10^{16}
		2	0.363		

In order to use the technique for the determination of the intensity of the filtered light entering the irradiation cell C_1 (Fig. 14) it was necessary to replace the latter with a plano-convex quartz lens. The light could then be focussed on to the active surface of the thermopile. The technique is subject to considerable error in this case because:

(i) The combined amount of light reflected interfacially at the lens, and

protective window over the thermopile will differ from that reflected at the irradiation cell window.

(ii) Any infra-red irradiation transmitted by the filters and lens will produce an extraneous response from the thermopile.

(iii) The conversion of thermal intensity (watts) to quantal intensity involved a wavelength term, and may result in an error of approx. 5% with the filters used.

The results obtained by this method are shown in Table 3. Note that they are considerably higher, where comparable, than those obtained by actinometry, but are useful in that they show the relative variation in intensity with the filters used. With the exception of OG1, these results are in keeping with the recorded transmission characteristics of the filters. (Fig. 16).

N.B. Full experimental details of the use of the thermopile will be given in the next section.

P.T.O.

TABLE 3

Filter	Intensity, Quanta/second	Filter	Intensity, Quanta/second
OXI	5.29×10^{16}	OY2	1.44×10^{18}
OB1	1.25×10^{17}	OR2	1.49×10^{18}
OB2	2.53×10^{17}	621	6.55×10^{16}
OG1	3.89×10^{17}	622	5.33×10^{16}

B Direct Irradiation Absorption Technique

(1) Actinometry

Procedure

Irradiation: A solution of potassium ferrioxalate (0.15M) in sulphuric acid (0.05M) was used (cf. Page 54). A 6 ml. aliquot was transferred to the sample cuvette, C_1 (Fig.15) and irradiated at the appropriate wavelength for one hour, using the maximum monochromator slit width (2.3 mm.) The total sample was transferred to a 50 ml. graduated flask and the Fe(11): o-phenanthroline colour was developed and measured as described previously. The process was repeated using an irradiation time of 30 minutes. The experiment was performed under safelight conditions.

Calculation: Refer equations 2.1 and 2.2.

The irradiation wavelengths were chosen to correspond to those at which quantum yields for the ferrioxalate photolysis have been reported. [119] Total absorbance of the activating light can be assumed, in this wavelength region, with the concentration of ferrioxalate solution used.

Results: Refer to Table 4.

TABLE 4

Wavelength mμ	Irradiation time, t (seconds)	Absorbance at 510 mμ	$\Phi_{Fe^{2+}}$	Mean Intensity I_0 (Quanta/second)
302	3600	0.181	1.24	$1.07(5) \times 10^{14}$
	1800	0.089	"	
334	3600	0.261	1.23	1.59×10^{14}
	1800	0.132	"	
366	3600	0.370	1.21	2.26×10^{14}
	1800	0.185	"	
405	3600	0.413	1.14	2.68×10^{14}
	1800	0.204	"	
436	3600	0.448	1.01	3.30×10^{14}
	1800	0.226	"	

The intensity values are plotted as a function of wavelength (Fig. 17).

(2) Thermopile

The thermopile used was of the area (surface) type (Kipp, Delft, Holland: Serial No. 323) and was previously calibrated. (e.m.f. = 380 mV/watt/sq.cm.)

Procedure

Irradiation: The cell holder (Fig. 15) was replaced by the thermopile, and the lens L_3 was adjusted to ensure that all the irradiant light fell on the active surface. The thermopile was protected from draughts and extraneous light. Emf values were obtained, using a Tinsley Vernier potentiometer and rotating mirror galvanometer, by the null method. (The potentiometer was calibrated with a Weston cell). With the appropriate wavelength selected, The emfs of the thermopile in the exposed (V_1), and unexposed (V_2) state were alternately recorded until the difference ($V_1 - V_2$) assumed a steady value. The process was repeated at 10 mμ and 20 mμ intervals in the wavelength range 280 mμ to 700 mμ.

Calculation: The energy of the incident light beam is given by

$$= \frac{V_1 - V_2}{380} \quad x \quad 4.155 \text{ watts},$$

where V_1 and V_2 are measured in millivolts. The numerical values in the equation relate to the calibration and dimensions of the thermopile.

The intensity, in quanta per second, is given by

$$I_0 = \frac{E \times 10^7}{h\nu} \qquad (2.5)$$

where h is planck's constant (6.625×10^{-27} erg.sec.) and ν is the radiation frequency. (sec^{-1}.) Converting frequency to wavelength, and combining the constants in (2.4) and (2.5) we have

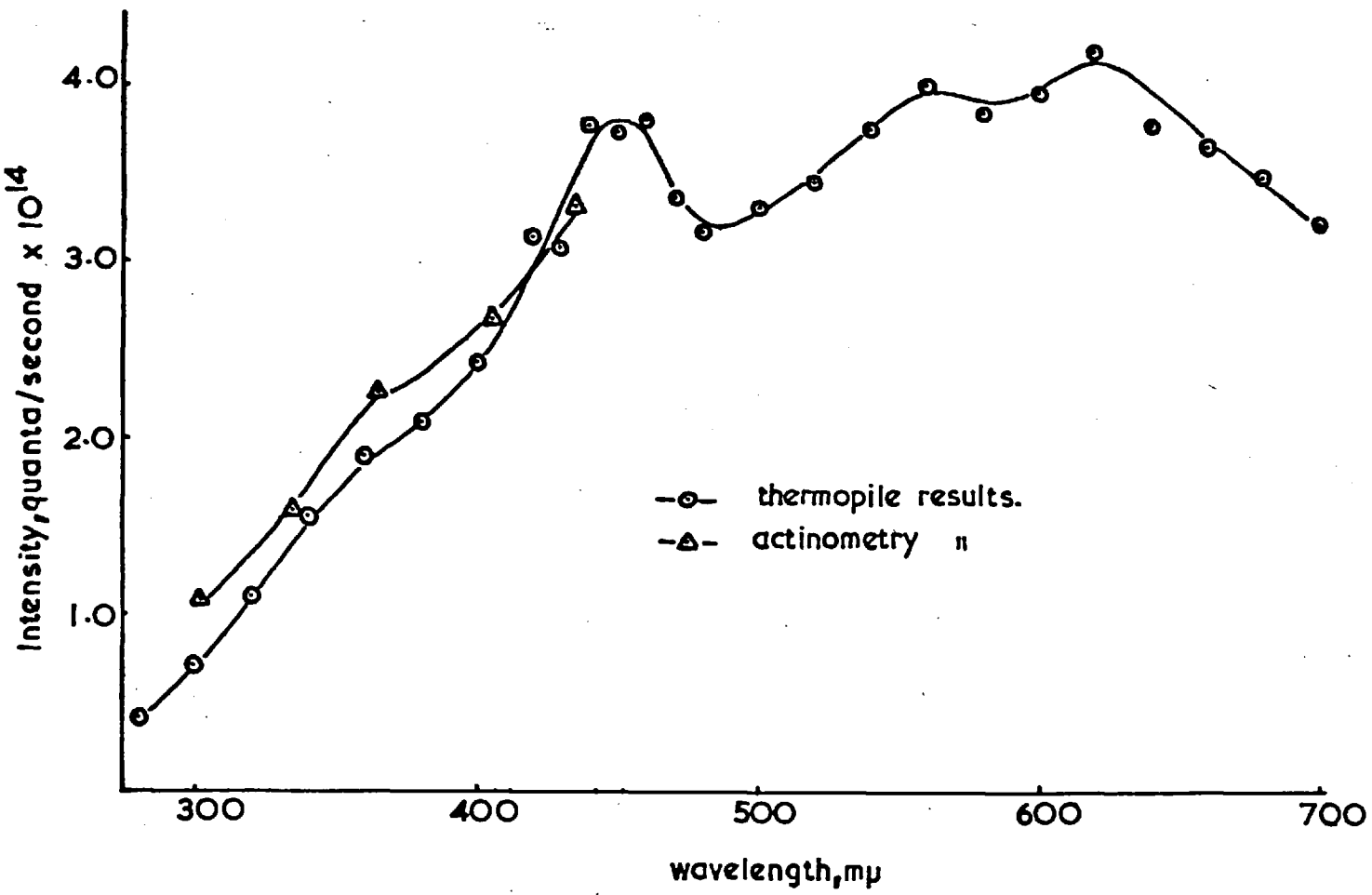
$$I_0 = (V_1 - V_2) \times \lambda(m\mu) \times 5.505 \times 10^{13} \text{ quanta/second} \qquad (2.6)$$

from which I_0 can be determined.

Results: These are displayed graphically (Fig. 17). They compare favourably with those obtained by actinometry because:

(i) Reflections at the plane quartz window over the thermopile will

FIG. 17. Intensity of light incident at sample cuvette vs. wavelength.



approximate to those at the near face of the sample cuvette.

(ii) The diffraction grating monochromator eliminates heating effects.

(iii) The light used is monochromatic.

2.6 Comparison of Methods

Consider the reactions outlined in Fig.13, the rates of which govern the degree of phototropic change.

From Tables 2 and 4, it can be seen that the intensity of the activating light used in the flow-through technique is 100–200 times greater than in the direct technique. The difference in the rates of formation of photoproduct molecules will, therefore, be of the same order, provided all the activating light is absorbed in each case. However, in order to produce the same spectral change as in the direct technique, the filtered light must convert 4 times as many molecules per unit volume, in $\sim$ 15 times the volume of solution. (i.e. to take into account the differences in the path lengths of the monitoring cuvettes, and the sample volume.) The rate of spectral change for the forward photochemical process will

thus be greater for the flow-through technique, by a factor of 2-3.

The non-monochromaticity of the optical filters may, however, result in a considerable rate of photochemical reversal if the reactant and photoproduct have closely spaced absorption spectra, thus reducing the degree of change at the equilibrium state.

The thermal reverse process will be more rapid in the flow technique because of the necessity to use higher concentrations, but, if the reaction is of 1st order, the spectral changes resulting will be the same for both techniques.

Few generalisations can therefore be made as to which technique is the more effective for the examination of a phototropic system. The direct method offers the more quantitative approach, but necessitates irradiation for more prolonged periods. For systems characterised by very rapid thermal reactions, the flow-through technique is the better choice, since the activating intensity becomes critical. Solutions of compounds which show photochemical change in both directions, but little thermal reaction, are better studied using direct irradiation, since the wavelength, and not the intensity, will be the controlling factor.

CHAPTER 3

Reversible photo-oxidation/reduction.
The Fe(II) - ammonium thiocyanate system

3.1 Preface

Liesgang[145] reported the reversible formation of a pink colouration when concentrated aqueous solutions of ammonium thiocyanate were exposed to sunlight. The colour change was later attributed[122] to the transient formation of colloidal sulphur as a result of the irreversible photochemical reaction:

$$NH_4CNS \longrightarrow NH_4CN + S$$

The photooxidative formation of a red polymeric form of thiocyanogen has also been suggested,[123] and Werner and Bailey[126] considered the possibility of tautomerism of thiocyanic acid.

Later workers[124, 125], however, noted that the presence of traces of ferrous ion was necessary in order to obtain the colour change. Montignie[124] suggested that the reaction could be summarised by the following equation:

$$2FeSO_4 + 6HCNS + O \rightleftharpoons H_2O + 2H_2SO_4 + 2Fe(CNS)_3$$

i.e. that the colour produced was that of the well-known ferric thiocyanate complex. Sharma [87] compared the photoproduct with ferric thiocyanate solutions and concluded that the formation of ferric thiocyanate was doubtful. He postulated the formation of a 'loose, additive' complex between ferrous ion, thiocyanate ion and oxygen, but offered no suggestion as to its structure.

The following characteristics of the reversible colour change were noted by the workers cited above:

(1) The forward photochemical process could be effected within a few minutes on exposure, to sunlight, of a saturated aqueous solution of ammonium thiocyanate containing ferrous ions.

(2) Reversal, in the absence of light, was less rapid. Complete disappearance of the colour took at least fifteen minutes.

It was decided to investigate the Fe(II)-ammonium thiocyanate system in this study because the doubtful conclusions drawn by previous workers indicated that a more thorough examination should be made. In addition, the phototropic process appeared to be sufficiently slow to permit its investigation with less refined

equipment than that which was currently undergoing development at the beginning of the investigation. It would also prove useful in that some of the practical problems associated with the handling of phototropic systems would be more fully appreciated. A variety of experimental techniques was applied during the investigation, in order to determine that which gave the most reliable results.

3.2 Results

Preliminary investigations showed that ferrous ions were involved in the phototropic process. It was established that, although saturated aqueous solutions of ammonium thiocyanate (analytical reagent grade) were phototropic, the small colour change observed was due to iron impurities in the crystalline solid. Ammonium thiocyanate (A.R.) contains a maximum of 0.0001% by weight of iron, and the solubility of the compound in water at 20°C is 162g. per 100 ml.[127]. A saturated aqueous solution thus contains 1.62 p.p.m. of iron. This would account for the previously reported phototropism of 'pure' ammonium thiocyanate solutions.[121-123, 126]

Attempts to remove the traces of iron by heating the thiocyanate solutions with activated charcoal, and by coprecipitation with

aluminium hydroxide from the slightly alkaline solution, proved inadequate. The activated charcoal could not itself be rendered iron free and further contaminated the solutions. It was noted, however, that a coloured iron-thiocyanate species could be extracted from both the irradiated and non-irradiated thiocyanate solutions, using iso butyl methyl ketone. A purification procedure was developed, based on this extraction.

The rate of development of colour on irradiation of saturated thiocyanate solutions containing ferrous ions was examined using three light sources viz: a tungsten filament lamp, a mercury vapour lamp and a xenon arc lamp. The first of these produced no photo-tropic effect, indicating that the activating wavelengths must lie in the ultraviolet region. The intensity of the final colour developed was independent of lamp intensity, but the rate of development was greater for the xenon arc (full colour development in 15 minutes) than for the mercury lamp (full colour development in 35 minutes). The reaction appears to obey first order kinetics with respect to the ferrous ion concentration. (Fig. 19).

The photoproduct solution exhibited a broad absorption band in the visible region, λ_{max}= 480 mμ, due to the red colouration. (Fig.18)

Light of wavelengths below 375 mμ was totally absorbed by the ammonium thiocyanate. The spectrum was found to be practically identical with that of a non-irradiated saturated thiocyanate solution containing ferric ions.

The rate of fading of the coloured species produced by irradiation was examined. (Fig. 20). The disappearance of the colour was less rapid than that indicated by earlier reports. Complete disappearance required the absence of light for at least 12 hours. The reaction initially follows first order kinetics, but thereafter varies in a more complete manner. A similar fading of the non-irradiated ferric solutions was observed.

The intensity of the coloured photoproduct was found to be proportional to the initial concentration of ferrous ions. Calibration data show that Beer's law is obeyed in the concentration range 1.25 - 6.25 x 10^{-6}M, with a calculated molecular extinction coefficient of 20,250. Again, similar results were obtained for the non-irradiated ferric solutions (ϵ_m= 20,850) (Fig.22).

Dilution of the ammonium thiocyanate solutions was found to inhibit the phototropic effect for a given ferrous ion concentration. (Fig.21)

The final concentration of the coloured species formed shows a linear dependence upon thiocyanate ion throughout most of the concentration range used.

Prolonged irradiation, either of the pure saturated thiocyanate solution, or that containing ferrous ions, led to the irreversible decomposition of the thiocyanate and the formation of a yellow substance in solution.

Absence of oxygen completely inhibited the phototropism. On addition of persulphate, the non-irradiated ferrous thiocyanate solutions became yellow. Conversely, treatment of the irradiated solutions with sulphur dioxide caused immediate destruction of the red complex, but again a pale yellow colour slowly developed. The red colour corresponding to the irradiated ferrous and the non-irradiated ferric systems was destroyed on heating. Continued heating resulted in the decomposition of thiocyanate to yield a yellow product.

The extraction of the red species into a number of organic solvents was examined.

3.3 Experimental Procedure

(1) Chemicals + Apparatus

Saturated Ammonium Thiocyanate solution(S.A.T.) 1000g. of iron-free ammonium thiocyanate crystals (prepared from ammonium thiocyanate (A.R.) as described in section (2)) were shaken with distilled water, (500 ml.) The supernatant liquid was decanted as required.

Ferrous ammonium sulphate solution, 10^{-1}M 16.21g. of $(NH_4)_2 SO_4 FeSO_4, 6H_2O$ (A.R.) were dissolved in 10^{-1}M sulphuric acid solution (500 ml.) The solution was standardised titrimetrically using standard potassium permanganate solution. Dilutions of the stock solution were prepared as required.

Ammonium ferric sulphate solution, 10^{-1}M. 48.22g. of $(NH_4)_2 SO_4 Fe_2(SO_4)_3, 24H_2O$(A.R.) were dissolved in 2M. sulphuric acid solution (500 ml.) Dilutions of the stock solution were prepared as required.

Iso-butyl methyl ketone G.P.R. grade.

Irradiation

150 w.D.C. Xenon arc lamp, focussed by an off-axis ellipsoidal

reflector.

Mercury spectral discharge lamp (Welmeck corporation, Hg/3) 50 c.p.s. focussed by a 9" parabolic mirror.

Each was used in conjunction with an optical heat filter.

Absorbance

Beckmann DB recording spectrophotometer

Hilger Uvispeck spectrophotometer

1 cm. and 4 cm. quartz cuvettes.

Both irradiation, and absorbance measurements, were carried out in the same cuvettes.

Agfa microsyringe pipette (Boroughs Wellcome & Co.)

(2) Preparation of iron-free ammonium thiocyanate

Ammonium thiocyanate (A.R.) was dissolved in water (250 ml.) to give a saturated solution. The solution was shaken with iso-butyl methyl ketone (50 ml.) and the coloured organic phase was separated. The extraction was repeated. A sample of the aqueous phase showed no visible change on exposure to light from the Xenon arc for 15 minutes. The solution became yellow on irradiation for 45 minutes. The

procedure was repeated with a further 3 aliquots of the ammonium thiocyanate solution. The aqueous phases were combined and the product was allowed to crystallise out, in the absence of light, at room temperature. The product was air dried on a filter pad and stored in a dark container.

(3) Absorption spectrum of the irradiated Fe(11): S.A.T. system

10.0 ml. of S.A.T. solution were transferred to a 4 cm. (optical path length) x 4 cm. x 1 cm. quartz cuvette. 0.0025 ml. of ferrous ammonium sulphate solution (10^{-1}M) was added using the microsyringe pipette. The sample was irradiated for 40 minutes (mercury vapour lamp). The absorption spectrum of the sample was recorded immediately after irradiation, in 1 cm. cuvettes, against a non-irradiated reagent blank. (Fig. 18).

(4) Absorption spectrum of the Fe(111): S.A.T. system

The procedure in Section (3) was repeated using 0.0025 ml. of ammonium ferric sulphate solution (10^{-1}M). The colour developed immediately, and was unaffected by irradiation. (Fig. 18).

(5) Rate of colour development, Fe(11): S.A.T. system

0.005 ml. Fe(11) solution (10^{-2}M)

10.0 ml. S.A.T. solution

The solution, contained in a 4 cm. quartz cuvette, was irradiated with light from the Xenon Arc lamp. The cuvette was removed at recorded time intervals and the absorbance measured, in situ, at 480 mμ against a reagent blank. (It was assumed that no change in the system occurred during this period (approx. 30 seconds).) The procedure was repeated using 0.0025 ml. of Fe(11) solution (10^{-2}M). The rate of development of colour was studied in a similar manner, using the mercury vapour lamp. The results are shown on Fig. 19.

(6) Rate of reversal

0.005 ml. Fe(11) solution (10^{-2}M)

10.0 ml. S.A.T. solution

The solution, contained in a 4 cm. cuvette, was irradiated with light from the Xenon arc lamp for 15 minutes. The cuvette was placed in the cell compartment of the spectrophotometer. The absorbance at 480 mμ, was measured at recorded time intervals for

three hours. (A non-irradiated blank was used.) The procedure was repeated using 0.0025 ml. of Fe(11) solution (10^{-2}M). Results are shown on Fig. 20.

(7) Effect of ammonium thiocyanate concentration on colour development

Solutions: 0.005 ml. Fe(11) solution (10^{-2}M)

x ml. S.A.T. solution

(10.0 - x) ml. distilled water

x = 2.0, 3.0, 4.5, 5.5, 6.5, 7.5, 8.5, 9.5 or 10.0 ml. consecutively.

Each aliquot was prepared in a 4 cm. cuvette, and irradiated for 35 minutes (mercury vapour lamp). The absorbance was measured immediately after irradiation, at 480 mμ, against the appropriate blank solution. No further change in absorbance occurred on irradiation for a further 5 minutes. The results are shown graphically on Fig. 21.

(8) Effect of ferrous ion concentration on colour development

Solutions: x ml. Fe(11) solution (2.5×10^{-3}M)

10.0 ml. S.A.T. solution

x = 0.005, 0.01, 0.015, 0.02, 0.025 or 0.03 ml. consecutively.

Each aliquot was prepared in a 4 cm. cuvette and irradiated for 35 minutes (mercury vapour lamp). The absorbance was measured at 480 mμ against the appropriate blank solution. The calibration curve for the Fe(11): S.A.T. system is shown on Fig. 22.

(9) Calibration data for the Fe(111): S.A.T. system

Solutions: x ml. Fe(111) solution (2.5×10^{-3}M)

10.0 ml. S.A.T. solution

x = 0.005, 0.01, 0.015, 0.02, 0.025, or 0.03 ml. consecutively

The absorbance of the solutions was measured at 480 mμ in 4 cm. cuvettes against a reagent only blank solution. The calibration curve is shown on Fig. 22.

(10) Effect of atmospheric oxygen

0.005 ml. Fe(11) solution (10^{-2}M)

10.0 ml. S.A.T. solution

A stream of oxygen-free nitrogen was passed through the solution for 5 minutes. Gassing was continued during irradiation. (Mercury lamp.) No colour change was observed after 35 minutes exposure.

(11) Effect of sulphur dioxide

0.005 ml. Fe(11) solution (10^{-2}M)

10.0 ml. S.A.T. solution

Irradiation - 35 minutes - mercury lamp.

A stream of sulphur dioxide gas was passed through the solution. Decolorisation occurred immediately. The solution became yellow on gassing for a further 10 minutes.

(12) Effect of persulphate

0.005 ml. Fe(11) solution (10^{-2}M)

10.0 ml. S.A.T. solution

ca 30 mg. sodium persulphate

A red colour developed immediately i.e. before irradiation. Absorbance at 480 mμ, in 4 cm. cells against a reagent blank = 0.425. On standing for 15 minutes, the solution became yellow.

(13) Solvent Extraction

0.005 ml. Fe(11) solution (10^{-2}M)

10 ml. S.A.T. solution

Irradiated (35 minutes - mercury lamp) and non-irradiated samples were treated with the solvent (5 ml.) Results are tabulated below:

Solvent	Extraction of Coloured Species	
	Non-Irradiated	Irradiated
Carbon tetrachloride	None	None
Benzene	None	None
Chloroform	None	None
Ether	None	Incomplete
Amyl acetate	None	Complete
Iso-butylmethylketone	Complete	Complete

3.4 Comments on Experimental technique

The injection of very small quantities of ferrous and ferric ion solutions was necessary in order to maintain a high thiocyanate concentration, and to limit the consumption of the ammonium thiocyanate. From the experimental data obtained, it would appear that the microsyringe was capable of delivering reproducible quantities of solution at the 0.0025 ml. level.

The intensity of the sources was not measured because reproducible conditions of irradiation could not be guaranteed. Of the two

sources, results indicate that the Xenon arc emits more activating irradiation than the mercury lamp. Since the thiocyanate solutions appeared to be stable to diffuse daylight and laboratory lighting, no safelight conditions were necessary. In general, irradiation and subsequent absorption measurements were carried out in the same cuvettes to minimise transference errors. The heating effects of the lamps was much reduced by the use of the infra red filter. A rise in temperature of a few degrees did occur during irradiation, but was neglected.

Quantitative evaluation of phototropic data was impossible with such limited apparatus, but a general interpretation of the reasons for the reversible colour change was possible.

3.5 Discussion of Results

The Fe(11): S.A.T. system is not strictly phototropic, since oxygen is consumed during the cycle, and the system is, therefore, not chemically reversible.

Adherence of the coloured photoproduct to Beer's law indicates the formation of a discreet complex species. There can be no doubt that the iron present is in the ferric state (cf. absorption spectra

FIG. 18. Absorbance spectra of: 1. Fe(II)-S.A.T., irradiated.
2. Fe(III)-S.A.T., non-irradiated.

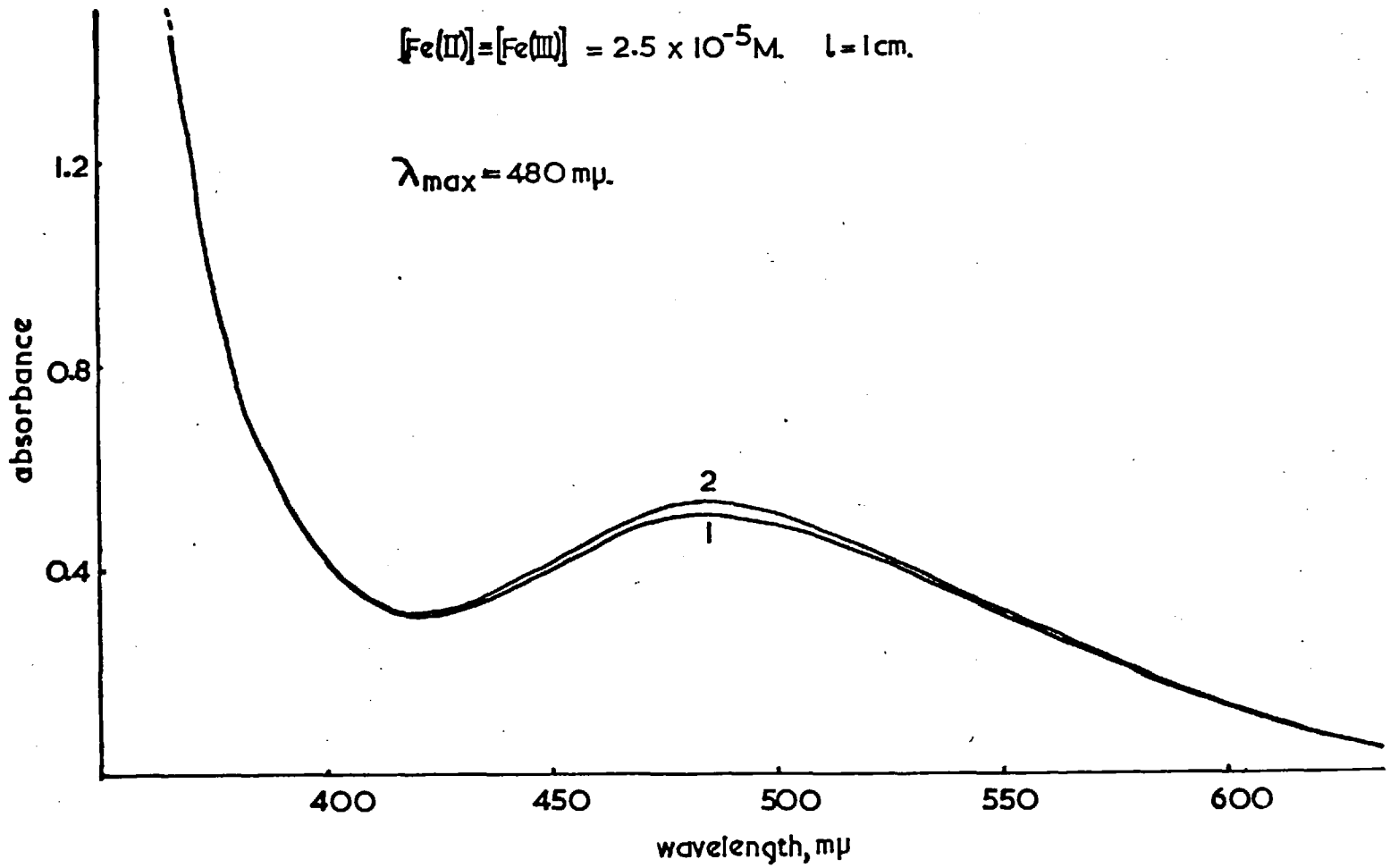
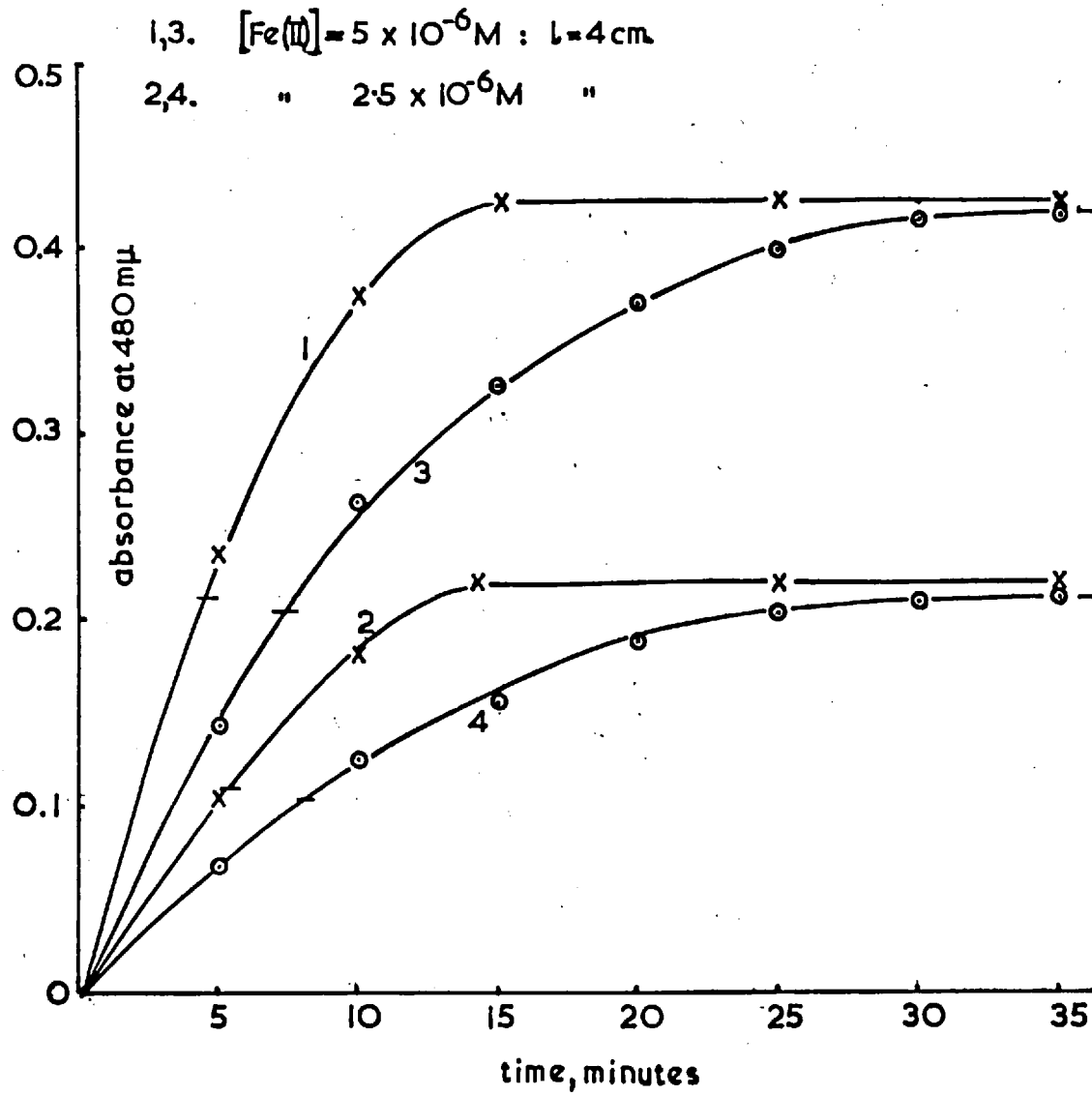


FIG 19 Rate of colour development of Fe(II)-S.A.T. system.



1,2. Irradiation with xenon arc.
3,4. " " " mercury vapour lamp.

FIG. 20. Rate of reversal.

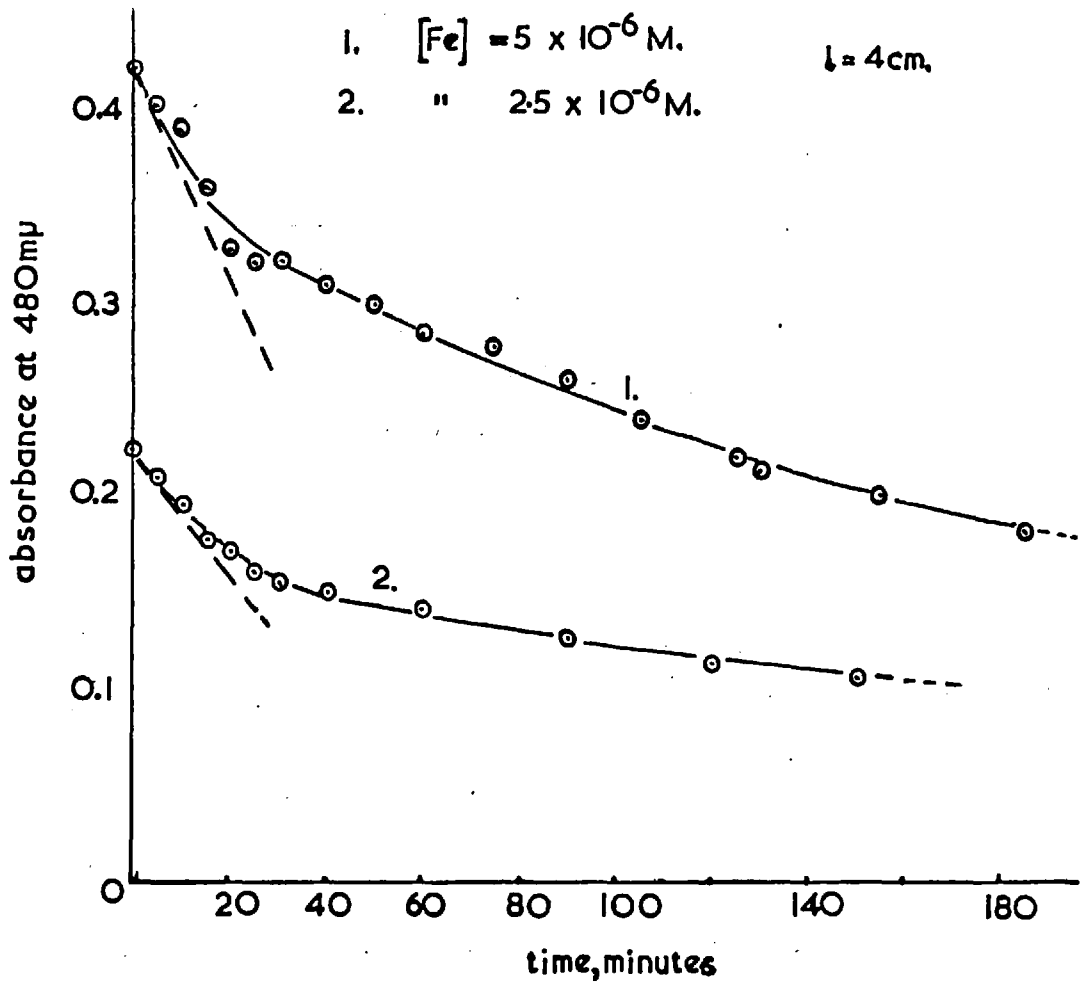


FIG. 21. Effect of thiocyanate concentration on development of colour.

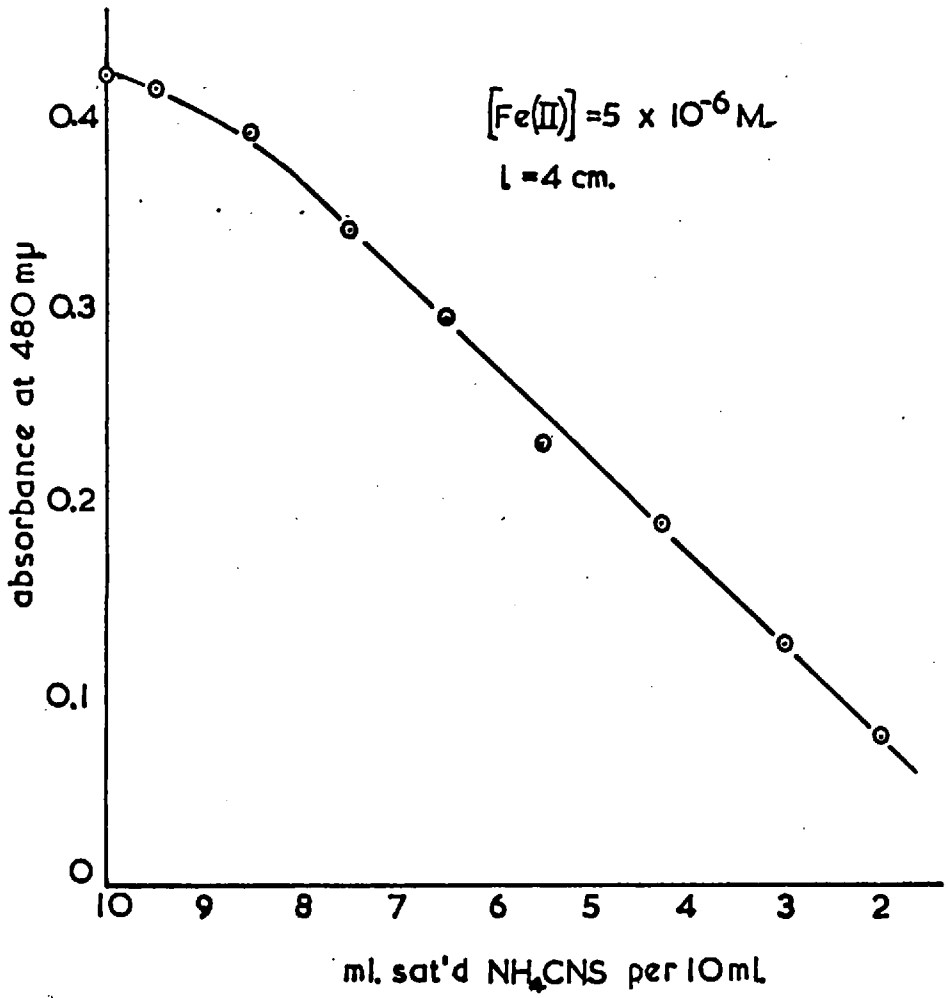
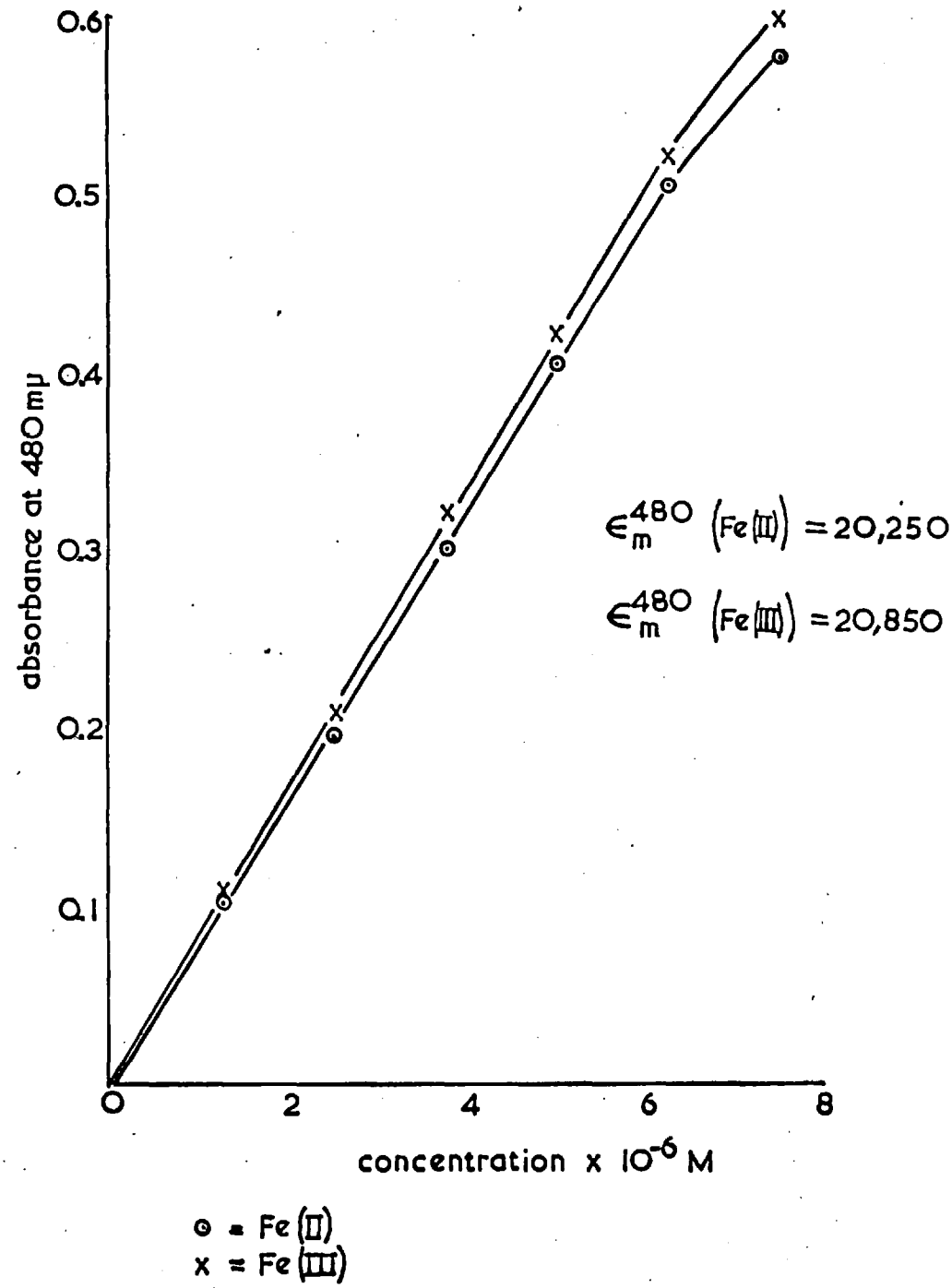


FIG. 22. Calibration data: Fe(II)-S.A.T., irradiated
Fe(III)-S.A.T., non-irradiated



and ϵ_m values), but the structure of the complex is debatable. Various formulae have been assigned to the coloured species formed between ferric and thiocyanate ions [128-130], ranging from the di-positive cation $Fe(CNS)^{++}$ to the triply charged anion $Fe(CNS)_6^{\equiv}$. Bent and French [130] found evidence for the existence of the di-positive cation in aqueous solutions but it appears generally accepted that the triply charged anion is the dominant species when thiocyanate is present in excess. Whether this anion is associated with another ferric ion, i.e. $Fe[Fe(SCN)_6]$, or with other cations present, is not clear.

In the saturated (ca 160%) ammonium thiocyanate solutions, a complex of the type $(NH_4)_3[Fe(CNS)_6]$ is likely because of the vast excess of NH_4^+ ions and CNS^- ions present. The molar extinction coefficient for the photoproduct is considerably higher than that reported for the Fe(111) - thiocyanate complex formed in acid 0.8% ammonium thiocyanate solution ($\epsilon_m = 6.3 \times 10^3$), i.e. under the conditions used for the spectrophotometric determination of Fe(111). [131] This would indicate complete association of the $Fe(CNS)_6^{3-}$ anion, and association of this anion with the ammonium ions to give a high thiocyanate: ferric ion ratio for the complex

in the saturated solutions.

The forward process involves the direct photo-oxidation, in the presence of atmospheric oxygen, of ferrous ions. Whilst a mechanism involving an oxidised thiocyanate intermediate (see below) is conceivable, this would not be in keeping with the observed kinetics of the reaction.

The thiocyanate ion bears many resemblances with the halogen anions.[132] It can thus act as a reducing agent, according to the following equation:

$$2\ CNS^- \longrightarrow (CNS)_2 + 2e^- \quad (\underline{cf}.\ 2I^- \longrightarrow I_2)$$

The thiocyanogen so produced is extremely unstable. In water it is hydrolysed to give hydrocyanic and thiocyanic acids.[134] The latter further decomposes to give a yellow substance, iso-pexthiocyanic acid.[127]

$$3HCNS \longrightarrow H_2C_2N_2S_3 + HCN$$

It is clear that the reverse reaction is a reductive process and a reaction of the type below is likely:

$$2Fe^{+++} + 2CNS^{-} \longrightarrow 2Fe^{++} + (CNS)_2 \downarrow \text{decomposition}$$

The kinetics of the reaction indicate that the reversal takes place in a complex manner.

The effect of dilution of the ammonium thiocyanate solutions on the observed colour changes cannot be explained in terms of either a decreased forward photochemical process, or an increased thermal reversal, which suggests that a photochemical reversal is taking place. The fading of the ferrithiocyanate colour, in dilute thiocyanate solutions on exposure to light, is well known. [87,130]

The direct oxidation of the thiocyanate by atmospheric oxygen explains the observed effects on prolonged exposure of the iron-free solutions. Note that the decomposition of the ferrithiocyanate complex will be continually occurring in the irradiated equilibrium state, and will contribute to the formation of the per-acid on prolonged irradiation of the Fe(11):S.A.T. solutions. Oxidation of the thiocyanate by persulphate is much more rapid, as is the reduction of the ferric ion in the complex by sulphur dioxide. Sulphur dioxide is known to form a yellow addition compound with

ammonium thiocyanate.[134]

The extraction of the coloured species from the non-irradiated Fe(11) S.A.T. solutions can be explained by assuming reduction of the solvent. It is noteworthy that of the solvents used, only the ketone is readily reduced.

The results may be summarised as follows:

(1) A concentrated aqueous solution of ammonium thiocyanate is photochromic (but not phototropic) in the presence of ferrous ions.

(2) The forward process occurs by the irreversible atmospheric oxidation of ferrous ions under irradiation by ultra violet light.

(3) The coloured photoproduct is a ferrithiocyanate complex, probably consisting of the $Fe(CNS)_6^{\equiv}$ anion with associated ammonium ions.

(4) The thermal process involves the irreversible reduction of Fe(111) ions by the thiocyanate ions.

(5) The thiocyanate ions are also directly and irreversibly oxidised by the atmospheric oxygen.

The explanation offered for the photochromic change is very empirical. With a complex oxidation/reduction system of this sort, many (unrecognised) side reactions can be expected. No account has been taken, for instance, of the behavious of byproducts formed on oxidation of the thiocyanate ions.

The high sensitivity of the system to both ferrous and ferric ions, and the selectivity of extraction offered by the solvents, amyl acetate and iso-butyl methyl ketone, might render the technique useful in the quantitative determination of the two cations in admixture, but this can be effected by various other methods.[120] Any procedure developed would be limited by the difficulties inherent in handling saturated solutions of an extremely soluble compound.

CHAPTER 4

Reversible photoionisation. The Basic Dyes

4.1 Preface

Solutions of the leucocyanides of the dyes p-Rosaniline, Crystal Violet, Malachite green, Brilliant green and Victoria blue are phototropic, the coloured, ionised dye molecule being reversibly formed on irradiation of the generally colourless, non-ionised leuco-compound with ultraviolet light. (ref. Fig. 9) The phototropic behaviour of solutions of the leucobases of some of these dyes has also been reported. [54,60] The dyes listed above belong to an important group of dyestuffs known as the Triarylmethane series, and numbered between 42000 and 44990 in the 'Colour Index'.[94] In addition, all are Basic dyes as are the majority of the Triarylmethane dyes.

A Basic dye is defined as "A cationic dye characterised by its substantivity for tannin-mordanted cotton"! [94] Essentially, the dye molecule is itself positively charged and is associated with a simple anion, such as chloride or bisulphate. The Basic dyes are distinguished by the brilliancy of their hues, some of them having

fluorescent properties, and also occur in a number of other dye series. Viz: the Xanthene (45000-45999), Acridine (46000-46999), Thiazole (49000-49399), Azine (5000-50999), Oxazine (51000-51999) and Thiazine (52000-52999) series.

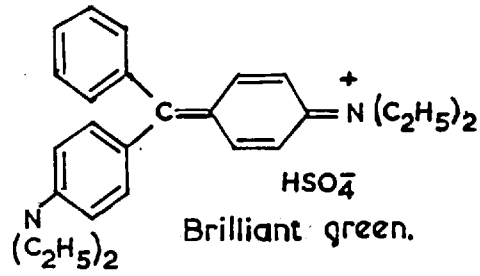
The purpose of the investigation outlined herein was to discover whether phototropic behaviour is exhibited by the leucocyanides and leucobases of the Basic dyes in general; i.e. is not a restrictive property of the triarylmethane series. The known phototropic leucocyanides and leucobases exhibit the phenomenon in a variety of solvents.[54] It was decided to compare the phototropic behaviour of these compounds with those of typical Basic dyes from the other dye series in acid neutral and alkaline aqueous solution, and in the chloroform extracts from these solutions. Such a procedure would provide information as to the normal, chemical equilibrium between the non-ionised and ionised forms, and indicate the effect of solvent polarity on the phototropism. The work has been carried out on a purely qualitative basis. Phototropic behaviour was determined by visual comparison, as were the rates for the forward and reverse processes.

4.2 Results

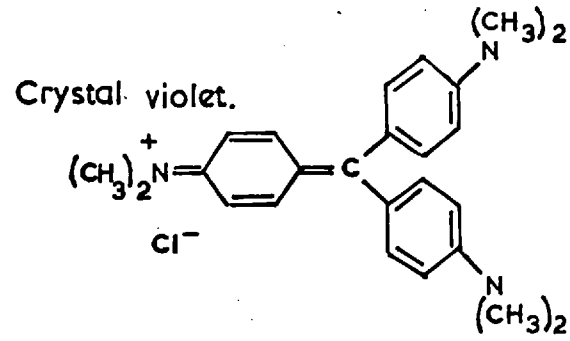
The triarylmethane compounds chosen for examination are shown on Fig. 23. Note that two of the dyes, namely, Erioglaucine A and Erio green B are amphoteric compounds, i.e. the positive charge on the dye molecule is associated with an anion covalently bound to the molecule. As such these are not Basic dyes, and were chosen for comparative purposes. The other Basic dyes selected are shown on Figs. 24 and 25. Of these, the neutral molecule Erythrosine (Fig. 24 (a)) is an exception, and was chosen for comparison with the related Xanthene dye, Rhodamine B.

The results of the investigation have been tabulated below, but some explanation of these tables is necessary. The left hand side of each table deals with the aqueous solutions of the compounds studied under the various conditions, and the right hand side with the separated chloroform extracts from the non-irradiated aqueous solutions. Note that the leucocyanides were prepared in situ in the neutral aqueous solutions. Phototropic behaviour is indicated by the reversibility sign ($\rightleftharpoons$). A broken arrow ($\dashrightarrow$) indicates the transient formation of the photoproduct (i.e. rapid reversal), and the broken arrow ($\dashleftarrow$) indicates the formation

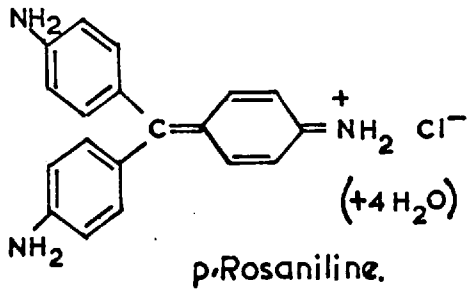
FIG. 23. Triarylmethane Dyes. (42000 - 44999)



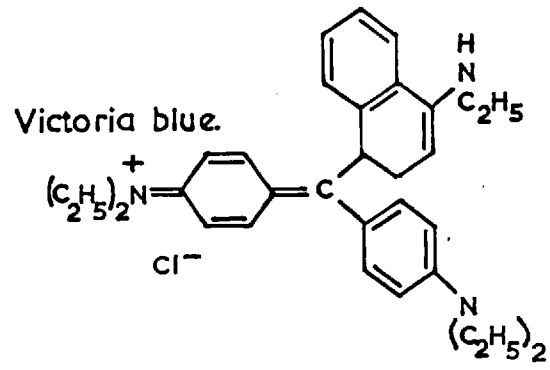
Brilliant green.



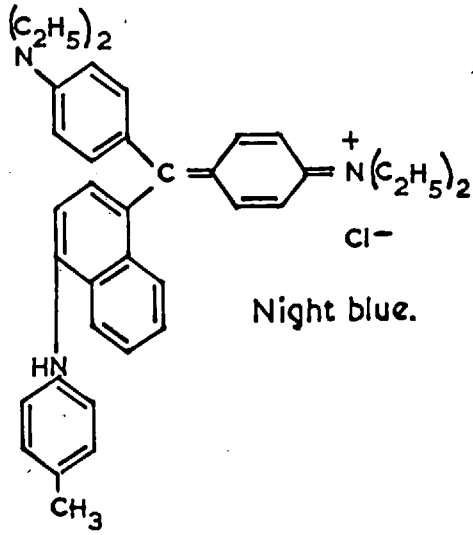
Crystal violet.



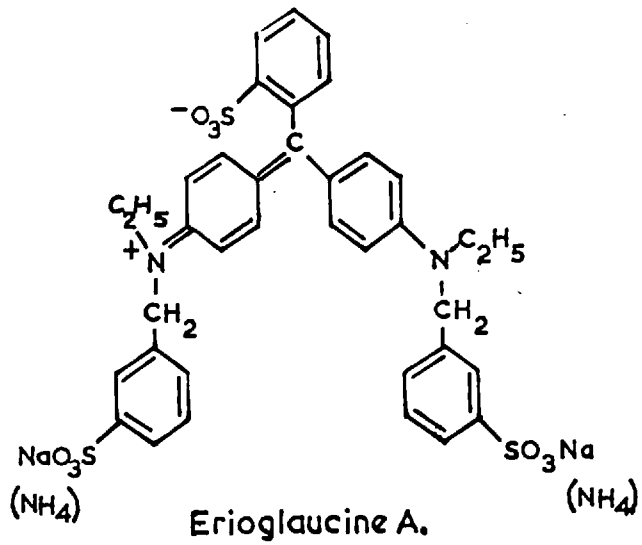
p.Rosaniline.



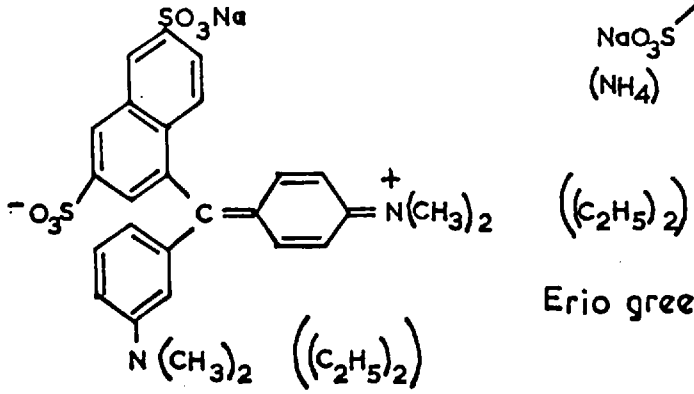
Victoria blue.



Night blue.



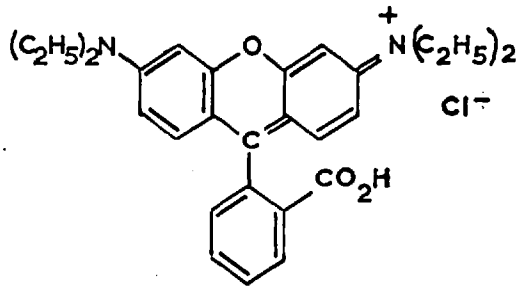
Erioglaucine A.



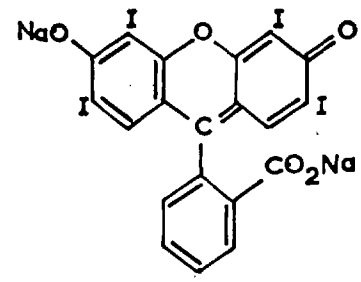
Erio green B.

FIG. 24. Basic Dyes.

(a) Xanthene (45000-45999)

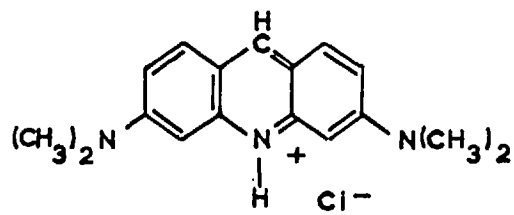


Rhodamine B (45170)



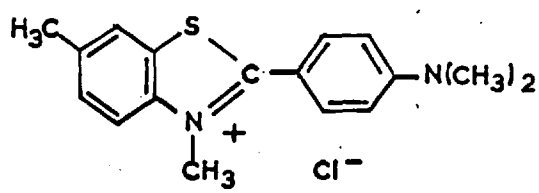
Erythrosine (45430)

(b) Acridine (46000-46999)



Acridine orange R (46005)

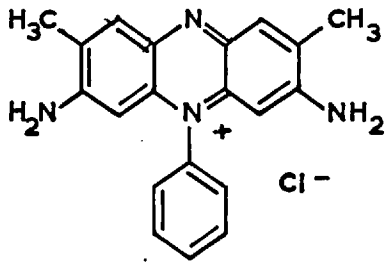
(c) Thiazole (49000-49399)



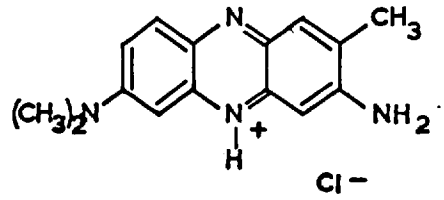
Acronol yellow TC (49005)

FIG. 25. Basic Dyes (cont.)

(d) Azine (50000-50999)

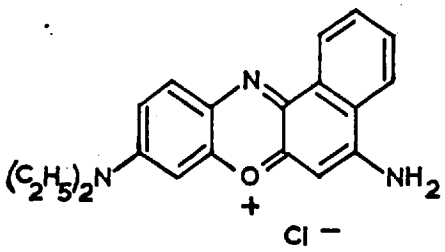


Saffranine T (50240)

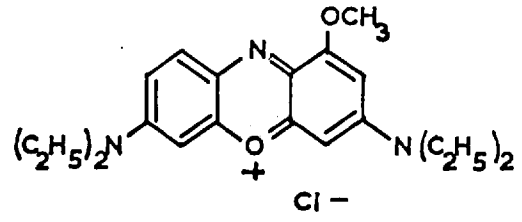


Neutral red (50040)

(e) Oxazine (51000-51999)

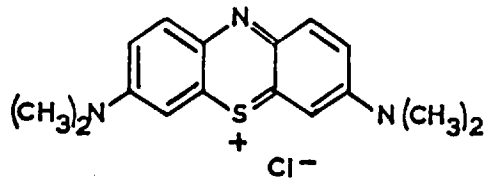


Nile blue A (51180)



Acronol sky blue 3G (51004)

(f) Thiazine (52000-52999)



Methylene blue BP (52015)

of a relatively stable photoproduct (i.e. slow reversal). The degree of extraction into the chloroform phase was determined by visual comparison, or, in the case of the colourless aqueous solutions, by separation of the aqueous phase, regeneration of the coloured species by acidification, and visual comparison with a suitable blank. In some cases, comparison of the fluorescence of the colourless aqueous and organic phases was possible.

Table 5. p-Rosaniline

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	red	-	0	-	-
pH = 7	red	-	0	-	-
pH = 10	colourless	-	100	colourless	⇌ red
pH = 7 + CN^-	colourless	⇌ red	100	colourless	⇌ red

P.T.O.

Table 6. Crystal Violet

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	violet	-	> 90	violet	-
pH = 7	violet	-	> 90	violet	-
pH = 10	colourless	-	100	colourless	⇢ violet
pH = 7 + CN^-	colourless	⇢ violet	100	colourless	⇢ violet

Table 7. Malachite Green

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	green	-	~ 30	green	-
pH = 7	green	-	~ 30	green	-
pH = 10	colourless	-	100	colourless	⇢ green
pH = 7 + CN^-	colourless	⇢ green	100	colourless	⇢ green

Table 8. Brilliant Green

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	green	-	30	green	-
pH = 7	green	-	30	green	-
pH = 10	colourless	-	100	colourless	⇌ green
pH = 7 + CN^-	colourless	⇌ green	100	colourless	⇌ green

Table 9. Victoria Blue

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	blue	-	100	blue	-
pH = 7	blue	-	100	pink	⇌ blue
pH = 10	pink	-	100	pink	⇌ blue
pH = 7 + CN^-	pink	⇌ blue	100	pink	⇌ blue

Table 10. Night Blue

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	blue	-	100	blue	-
pH = 7	blue	-	100	pink	⇌ blue
pH = 10	pink	-	100	pink	⇌ blue
pH = 7 + CN^-	pink	⇌ blue	100	pink	⇌ blue

Table 11. Erioglaucine A

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	turquoise	-	0	-	-
pH = 7	turquoise	-	0	-	-
pH = 10	turquoise	-	0	-	-
pH = 7 + CN^-	turquoise	-	0	-	-

Table 12. Erio Green B

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	green	-	0	-	-
pH = 7	green	-	0	-	-
pH = 10	green	-	0	-	-
pH = 7 + CN^-	green	-	0	-	-

Table 13. Rhodamine B

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	pink	-	100	pink	-
pH = 7	pink	-	~50	pale pink	⇌ pink
pH = 10	pink	-	~50	pale pink	⇌ pink
pH = 7 + CN^-	pink	-	~50	pale pink	⇌ pink

Table 14. Erythrosine

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	pink	-	100	colourless	-
pH = 7	pink	-	0	-	-
pH = 10	pink	-	0	-	-
pH - 7 + CN^-	pink	-	0	-	-

Table 15. Acridine Orange R

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	orange	-	~50	orange	-
pH = 7	orange	-	~80	yellow	⇄ orange
pH = 10	orange	-	100	yellow	⇄ orange
pH = 7 + CN^-	yellow	-	100	yellow	⇄ orange

Table 16. Acronol Yellow TC.

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	yellow	-	~ 70	yellow	
pH = 7	yellow	-	100	colourless	⇌ yellow
pH = 10	yellow	-	100	colourless	⇌ yellow
pH = 7 + CN^-	pale yellow	-	100	colourless	⇌ yellow

Table 17. Saffranine T

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	pink	-	0	-	-
pH = 7	pink	-	0	-	-
pH = 10	pink	-	~ 50	pink	-
pH = 7 + CN^-	pink	-	~ 50	pink	-

Table 18. Neutral Red

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	red	-	~50	orange	-
pH = 7	orange-red	-	100	yellow	⇌ orange
pH = 10	yellow	-	100	yellow	⇌ orange
pH = 7 + CN^-	yellow	-	100	yellow	⇌ orange

Table 19. Nile Blue A.

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	blue	-	100	blue	-
pH = 7	blue	-	100	pink	⇌ blue
pH = 10	blue	-	100	pink	⇌ blue
pH = 7 + CN^-	pink	-	100	pink	⇌ blue

Table 20. Acronol Sky Blue 3G

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	blue	-	100	blue	-
pH = 7	blue	-	100	blue	-
pH = 10	blue	-	100	pink	⇌ blue
pH = 7 + CN^-	blue	-	100	pink	⇌ blue

Table 21. Methylene Blue BP

Aqueous Phase			Chloroform Phase		
Conditions	Colour	Effect of Irradiation	% Extraction	Colour	Effect of Irradiation
pH = 3	blue	-	~50	blue	-
pH = 7	blue	-	<10	blue	-
pH = 10	blue	-	100	pink	⇌ blue
pH = 7 + CN^-	pale blue	-	100	pink	⇌ blue

The following observations are not included in the above tables:

(1) The phototropic solutions, in all cases, showed full colour development after irradiation for 30 seconds.

(2) Reversal of the phototropic aqueous solutions was complete within 30 seconds of removing the sample from the light source.

(3) Addition of excess CN^- ion, i.e. over that just sufficient to cause complete formation of the leucocyanide, inhibited phototropism in the aqueous phase.

(4) The photoproducts in the separated chloroform phases were stable for at least two hours. Reversal was incomplete after standing for 12 hours.

(5) The phototropic chloroform extracts exhibited the phenomenon in presence of the aqueous phase. Reversal of the colour system under these conditions was more rapid (< 3 hours) and could be effected immediately by shaking the chloroform with the aqueous phase, after irradiation.

4.3 Experimental

(1) Chemicals and Apparatus

The dyestuffs below are listed with the characteristic Colour Index number and name[94] in parentheses in order to avoid ambiguity over the use of trivial and commercial names. Each was dissolved in water (500 ml.) to give a solution of suitable optical density for visual comparisons.

(0.02 - 0.05g $\longrightarrow$ 10^{-5} - 10^{-4} M solutions)

p-Rosaniline	(42500: C.I. Basic Red 9) J.J.Griffith & Sons Ltd.
Crystal Violet	(42555: C.I. Basic Violet 3) G.Grühler & Co., Leipzig.
Malachite Green	(42000: C.I. Basic Green 4) Hopkin & Williams Ltd.
Brilliant Green	(42040: C.I. Basic Green 1) Geigy Co.Ltd.
Victoria Blue	(42595: C.I. Basic Blue 7) Source unknown
Night Blue	(44085: C.I. Basic Blue 15) Source unknown
Erioglaucine A	(42090: C.I. Acid Blue 9) Geigy Co.Ltd.
Erio Green B	(44025: C.I. Acid Green 16) Geigy Co.Ltd.
Rhodamine B	(45170: C.I. Basic Violet 10) Hopkin & Williams Ltd.

Erythrosine (45430: C.I. Acid Red 51)

Acridine Orange R (46005: C.I. Basic Orange 4) I.C.I. Ltd.

Acronol Yellow TC (49005: C.I. Basic Yellow 1) I.C.I. Ltd.

Saffranine T (50240: C.I. Basic Red 2) Source unknown

Neutral red (50040: C.I. Basic Red 5) Hopkin and Williams Ltd.

Nile blue A (51180: C.I. Basic Blue 12) Allied Chemical & Dye Corpn., New York

Acronol Sky blue 3G (51004: C.I. Basic Blue 4) I.C.I. Ltd.

Methylene blue BP (52015: C.I. Basic Blue 9) I.C.I. Ltd.

Potassium cyanide solution, 10^{-2}M. 0.65g. of KCN (analytical reagent grade) were dissolved in distilled water (1 litre).

Buffer solutions: Prepared by admixture of 20% v/v aqueous acetic acid, and 20% v/v aqueous ammonia solutions.

Chloroform: General purpose reagent.

Irradiation: 150w. D.C. Xenon arc lamp, unfiltered, focussed by an off-axis ellipsoidal mirror.

Absorption spectra (Nile blue A leucocyanide): Unicam SP 800 spectrophotometer: 2 cm. quartz cells.

(2) Procedure

(a) Examination of aqueous solutions The aqueous solution of the dyestuff (5 ml.) was treated with the appropriate buffer solution (4 drops) and allowed to stand until no further change in colour took place. The solution was irradiated for 5 minutes, and a comparison made with an identical non-irradiated solution.

(b) Examination of aqueous leucocyanide solutions The aqueous solution of the dyestuff (5 ml.) was treated with buffer, pH = 7, (4 drops). Potassium cyanide solution (10^{-2}M) was added dropwise until no further change in colour took place (3-10 drops). In some cases gentle warming was necessary to effect the change. The solution was irradiated for 5 minutes, and a comparison made with a non-irradiated sample. If a colour change occurred, the irradiated and non-irradiated solutions were allowed to stand in the absence of light to determine reversibility. Where phototropism occurred, the procedure was repeated using twice the quantity of potassium cyanide solution.

(c) Examination of Chloroform extracts The non-irradiated aqueous solutions outlined in sections 2 (a) and 2 (b) were treated with

chloroform (5 ml.) and shaken for 1 minute to effect the extraction. The phototropic behaviour of the organic extracts was examined in the presence of the aqueous phase, and after separation, as outlined in section 2 (b).

4.4 Discussion of Results

Of the 17 dyes examined, 13 exhibit phototropic behaviour under suitable conditions, and only one of the basic dyes, the Azine dye Saffranine T is not phototropic under the conditions used. The phototropic process is clearly attributable to a reversible photo-ionisation reaction. The fact that in the presence of excess OH^- or CN^- ions, the dyes yield a product which is completely extracted into chloroform, and which absorbs light at shorter wavelengths than the original dyestuff, is consistent with the formation of a covalent species, and the change from a quininoid to a benzenoid structure. (cf. Fig. 9) (N.B. The thiazole dye, Acronol yellow TC (Fig. 24 (c)) does not contain a quininoid system in the ionic state. The hypsochromic shift in this case is due to the existence of a single bond between the nitrogen and the central carbon atom in the covalent state, and resultant loss of conjugation.) The solution of photo-product, when formed, is identical in appearance with the original

(ionic) dyestuff solution. The absence of the phototropic effect in the presence of excess cyanide ions and high pH (excess hydroxyl ions) indicates that these ions are formed during the phototropic process. Hence the stability of the photoproduct in chloroform. The enhanced stability of the photoproduct in the chloroform phase after separation of the aqueous phase results from the prevention of interchange of ionic and covalent species between the two solvents.

In acid medium, all the dyes exist in the coloured (ionised) forms and extract to varying degrees into chloroform, depending on their relative ionic character. Thus, in the triarylmethane series, p-Rosaniline, by virtue of its free amino groups, shows no extraction, whereas the 4,4',4" tris dimethylamino derivative, Crystal violet, is almost completely extracted. The larger molecules, Victoria blue and Night blue, are completely extracted. The greater charge delocalisation in the case of Crystal violet (the positive charge in the coloured form may reside on any one of the 3 tertiary nitrogen atoms) explains the increased extraction of this compound with respect to the 4,4' bis dimethylamino compound, Malachite green. (Fig. 9) The complete extraction of the coloured form of Rhodamine B is the result of suppression of the ionisation of the carboxylic acid grouping in acid

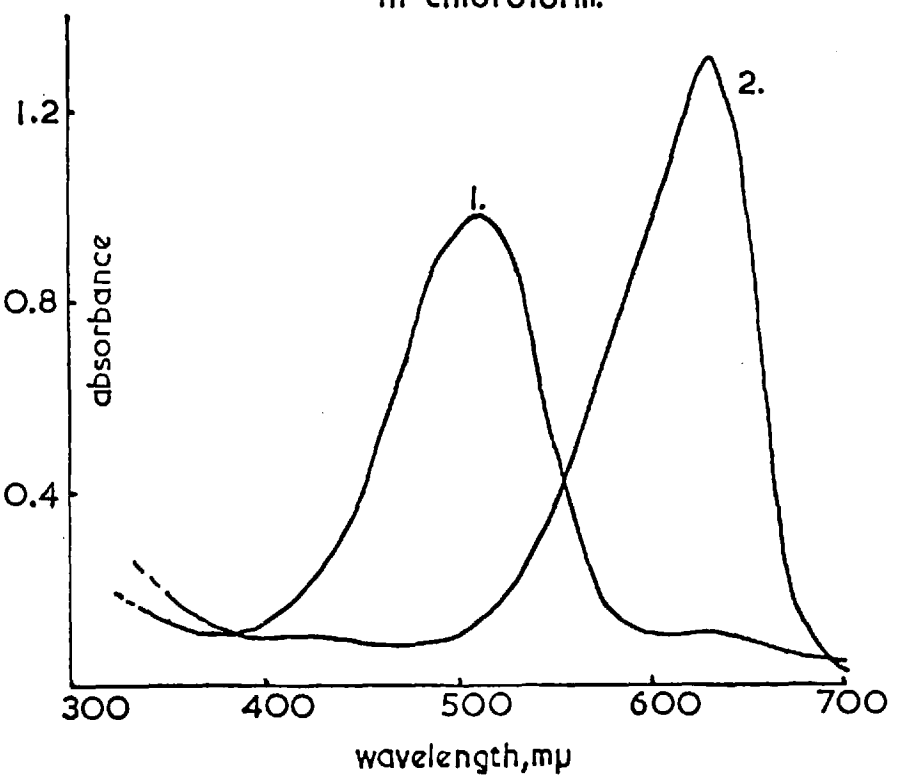
medium. Erythrosine is extracted as a colourless species, presumably the enol form, (common with Fluorone dyes in the Xanthene series), involving a bond between the central carbon atom and a carboxyl oxygen. (cf. Fig. 27). The dyes exist in the normal coloured form in neutral aqueous solution, but there is evidence of an equilibrium between ionic and covalent species in some cases. Victoria blue, Night blue, Nile blue A, Acronol yellow TC, Acridine orange R, Neutral red and Rhodamine B show colour changes on extraction, indicating a shift in equilibrium in favour of the covalent species in the chloroform phase.

The covalent leucobases are extracted from alkaline solutions of all the basic dyes, with the exception of Saffranine T (and possibly Rhodamine B, vide infra). The partial extraction of a coloured form of Saffranine T may be due to the 'salting out' of an ionic base. The leucobases formed directly in aqueous solution e.g. p-Rosaniline, Victoria blue, are not phototropic, the effect being inhibited by the excess OH^- ions. The chloroform extracts in all cases show phototropic behaviour. The dyes which readily react with CN^- ion give phototropic leucocyanides in neutral aqueous medium. In the remaining cases, the excess of cyanide ion required to form the covalent

derivatives inhibits the phototropic behaviour of the product. All the chloroform extracts from the neutral solutions containing cyanide ions are phototropic.

The colour change accompanying phototropism is striking. Fig. 26

FIG. 26. Absorption spectra of Nile blue A leucocyanide in chloroform.



1. Normal. 2. After irradiation.

shows the absorption spectra of Nile blue A leucocyanide (10^{-4}M) in chloroform in the normal (dark) state, and after 30 seconds' exposure

to the Xenon arc. The leucocyanide is fluorescent in the normal state, λ max (excitation) = 500 mμ: λ max (emission) = 560 mμ. The photoproduct solution exhibits an unusual light scattering effect, initially believed due to fluorescence of the dissolved molecules. However, the position of the emission band is dependent upon the wavelength of excitation, according to the following relation:

$$\lambda_{max}\ (\text{emission}) = \lambda_{max}\ (\text{excitation}) + 70\text{m}\mu$$

$$\text{in the range}\quad 400\ \text{m}\mu \leqslant \lambda_{max}\ (\text{excitation}) \leqslant 500\text{m}\mu$$

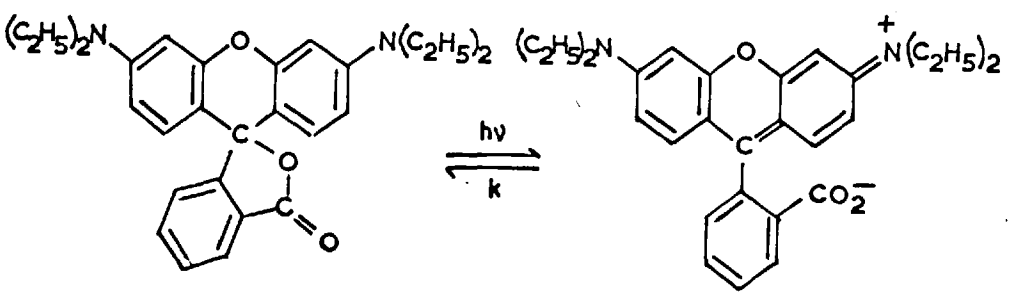
In this respect the phenomenon shows similarity with Raman scattering.

The structure put forward for the leucocyanide of Malachite green indicates the formation of a covalent bond between the cyanide ion and the central tertiary carbon atom. (Fig. 9) However, this is not possible for basic dyes other than the Triarylmethane, Xanthene and Thiazole dyes, because no such carbon atom is present. A C—CN or C—OH bond could be formed with central, secondary carbon atom in Acridine orange R, but it seems likely that bonding occurs between the cyanide or hydroxyl ion and the bridge nitrogen which is common to the remaining dyes. A similar structure, in which a bond is formed between the bridge nitrogen atom and a hydrogen atom, has been

postulated for the reduced (leuco) form of Methylene blue. (Fig.12)

The behaviour of Rhodamine B (Table 21) is of interest. There is no evidence for the formation of a leucocyanide, since the compound behaves similarly in neutral solution in the absence of CN^- ions. Indeed the phototropic effect may be the result of the change shown below. (Fig. 27)

FIG. 27.



I. colourless. II. pink.

The colourless lactone, I, could be formed directly or as a result of condensation between a hydroxyl group attached to the central carbon atom (a leucobase) and the o-carboxylic acid group.

It has been suggested [60,61] that the leucobases and not the original leucocyanides are the products of the reversal of the photoproduced

ionic Triarylmethane cyanides. However, the phototropic Triarylmethane leucocyanides exhibit the phenomenon in aqueous solution under conditions such that the leucobases are not stable forms. Similarly, the absence of hydroxyl ions in the separated chloroform solutions of the leucocyanides precludes the possibility of phototropic reversal to give the leucobase.

The amphoteric Triarylmethanes failed to form leucocompounds under the conditions used: similarly the Acid Xanthene dye, Erythrosine. The formation of light labile leucocompounds is therefore concluded to be a property of the basic dyes only.

CHAPTER 5

Reversible photo-isomerisation. The cis-trans photo-isomerisation of aromatic azo compounds

5.1 Preface

As stated in Chapter 1, the stable form of azobenzene is that in which the aromatic rings are in the trans configuration about the N=N. Irradiation of solutions of azobenzene results in the formation of the cis isomer. The process is both thermally and photochemically reversible, and is also applicable to a number of azobenzene derivatives.

Substituted aromatic azo compounds constitute the great majority of commercially available dyestuffs (Numbers 11000-36999).[94] They are also widely used in analytical chemistry as indicators in chelatometry, and as reagents for quantitative analysis by molecular absorption spectrophotemetry. In such applications, the stability of the compounds to light is of great importance, and it is for this reason that azo compounds were chosen for an extensive examination of their phototropic behaviour.

The two methods which have been developed for the quantitative

examination of phototropic systems (ref: Chapter 2) were compared in order to determine that which was more suitable for use in this investigation. Solutions of two azo compounds which had been reported to be phototropic, namely, 4-dimethylaminoazobenzene in benzene [14] and Chrysophenine (4,4'-bis (4-ethoxyphenylazo)-stilbene -2,2'-disulphonic acid (disodium salt)) in water [20] were examined using both techniques. The absorption spectral changes, and the rates of the phototropic processes are illustrated on Figs. 54, 56, 57, 63 and 64. The Flow-through technique was found to be preferable, since although the final equilibrium attained between the cis and trans forms is less in favour of the cis isomer, (particularly in the case of Chrysophenine, which has a very stable cis isomer), the time required to reach equilibrium is much shorter. In addition, the kinetic curves obtained using the Direct technique were very erratic, especially when the rate of change was high, i.e. at the onset of the phototropic or reverse processes. For this reason, such kinetic curves for 4-dimethylaminoazobenzene in benzene have not been recorded, and that recorded for chrysophenine is of doubtful accuracy. The erratic behaviour is due to the inadequate mixing of the two isomers in solution, and while this does not affect the final equilibrium attained, no useful data could be gathered

concerning the rate of phototropic change.

The Flow-through technique has been used to examine the light lability of 25 substituted hydroxy- and amino-azobenzenes and azonaphthalenes, in order to determine the relations between position and nature of the substituent and the phototropic behaviour of the compound in solution. The effect of solvent polarity on the degree of phototropism attained has been investigated using solutions of the compounds in a non-polar solvent, benzene, and in various ethanol/benzene mixtures. Each of the phototropic solutions has been characterised by recording the 'dark' or stable absorption spectrum, and the 'equilibrium' absorption spectrum resulting from the exposure of the sample, until no further change took place, to activating light of the most suitable wavelength. Kinetic curves, on which the rate of change in absorbance at the wavelength of maximum absorption of the trans isomer is recorded, have been used to evaluate the Quantum yield for the forward photochemical process, the rate constant for the thermal reversal, and the half-life times of both processes.

Preliminary investigations of the effect of the wavelength of irradiation showed that the filtered light most suitable for the

generation of the cis isomer was that which most closely corresponded in spectral characteristics with the main absorption band of the trans isomer in solution. This behaviour is expected from consideration of the Grotthus-Draper law (Ref.p.36) provided that absorption by the cis isomer, and the resultant photochemical reversal, are at a minimum in this wavelength range. The choice of the optimum filter was not always obvious, however, since the intensity has to be taken into account, and in some cases, phototropic data are recorded for more than one filter.

The azo compounds used in this investigation were either prepared in the laboratory, or obtained as commercial dyes. The usual method of preparation, as used in the manufacture of the dyes, is by diazotization of an aromatic amine and a subsequent coupling reaction. Such a process is notorious for its indeterminate nature and the resultant azo compound invariably contains quantities of similar derivatives resulting from self-coupling reactions and coupling at alternative positions in the acceptor molecule. The purification of the reaction products by the conventional method of recrystallisation is thus a difficult operation. A method of chromatographic purification using a 30" x 1" alumina column has been developed and

was found to give good results with many of the azo compounds used.

5.2 Results

Table 22 shows the R_f values of the azo compounds which were found suitable for chromatographic purification. Where more than one R_f value is recorded, that underlined corresponds to the major constituent. The R_f values were recorded on thin layer alumina plates, after chloroform elution. In the subsequent large scale purification, a 50% chloroform/acetone solvent was used, where necessary, to increase both the solubility and the R_f values of the more polar compounds. Purity was determined either by melting point determination or by elemental analysis. (The Figures in parenthesis in the right-hand column of Table 22 correspond to the melting points obtained from the literature, [136] or to the calculated analytical results.)

The dark and equilibrium absorption spectra of the solutions of the pure azo compounds in the various solvents are shown on Figs.28-55, 58-63 and 65-66. Where a phototropic change is observed, the change in the two spectra is recorded as the difference in absorbance, ΔA at the wavelength ($m\mu$) corresponding to the absorption peak of the dark spectrum. The non-phototropic solutions are recorded as

exhibiting identical dark and equilibrium spectra. A solution was only taken to be non-phototropic if no change in the absorption occurred on exposure of the sample to filtered light at all wavelengths absorbed by the sample, and also to unfiltered light from the Xenon arc. Where the difference between the absorption of the solutions in benzene and ethanolic benzene is appreciable, the dark and equilibrium spectra in both solvents have been recorded.

The kinetic data obtained for the phototropic solutions is summarised in Table 23. The half-life times, at 25 ± 1°C, for the changes resulting from irradiation with the appropriate filter ($t_{\frac{1}{2}}$ forward), and the half life times for the thermal reaction, ($t_{\frac{1}{2}}$ reverse), were taken directly from the absorbance vs time curves, which correspond to concentration vs time curves provided Beer's law is obeyed.

The quantum yield (Φ) values were calculated from the slopes, at the onset of the forward reaction, of the absorbance vs time curves. The following assumptions were necessary for this purpose.

(1) The absorption spectra of both the cis and trans forms in solution adhere to Beer's law.

(2) The absorbance of the pure cis form in solution is approx. 5%

of that of a similar concentration of the pure trans form in solution, at the wavelength of maximum absorption of the trans form.

(3) The activating light is completely absorbed by the sample at the onset of the photochemical reaction.

Over the concentration range used, deviation from Beer's law is expected to be slight. The second assumption is reasonable if the predicted hypsochromic and hypochromic shifts of the absorption spectra, with isomerisation, take place (Ref. p. 12), in which case there will only be 'background' absorption by the cis isomer at the wavelength of the trans absorption peak. This is known to be true for azobenzene itself, for which the pure cis form has been isolated and examined [19] and appears likely from a study of the dark and equilibrium spectra recorded herein. The final assumption is valid provided there is complete, or near complete, overlap between the transmission spectrum of the filter used and the absorption spectrum of the trans isomer in solution. This is the case for those filters which result in the most pronounced phototropic change. With this condition satisfied, the light lost will be negligible, since a solution of sufficient concentration to give an absorbance reading of, say, 0.1 units in the monitoring cuvette will absorb in excess

of 99.9% of the light at that wavelength entering the irradiation cell.

The quantum yields were evaluated as follows:

If $\triangle(A/t)$ $sec.^{-1}$ is the rate of change in absorbance at the onset of the forward photochemical process, then

$$\frac{1.05\,\triangle(A/t)}{\epsilon\, 1} \qquad mole.litre^{-1}\ sec.^{-1}$$

is the rate of change in concentration of the <u>trans</u> form, where ϵ is the molar extinction coefficient of the <u>trans</u> form at maximum absorption, 1 is the path length of the monitoring cuvette (= 0.5 cm) and the factor 1.05 is the correction term for the absorbance of the <u>cis</u> form. (<u>N.B.</u> At the start of the forward reaction, the photochemical and thermal reverse reactions are absent.) Thus,

$$2.10\,\frac{\triangle(A/t)}{\epsilon} \times 6.023 \times 10^{23}\ mol.litre^{-1}\ sec.^{-1}$$

is the rate of change of molecular concentration. The total number of <u>trans</u> molecules destroyed, or the total number of <u>cis</u> molecules formed, per second, will be

P.T.O.

$$12.65 \frac{\Delta(A/t)\ V}{\epsilon} \times 10^{20} \text{ mol. sec.}^{-1},$$

where V is the volume (ml.) of the flow-through curcuit. The quantum yield, of the number of molecules formed per photon, is thus given by the relation

$$\Phi = \frac{12.65\,\Delta(A/t)\ V \times 10^{20}}{\epsilon I_o},$$

where I_o is the intensity of the light, in quanta per second, transmitted by the filter, as determined actinometrically (Ref. Chapter 2).

The thermal constants from the reverse reaction were calculated from the relation

$$k = \frac{\log_e 2}{t_{\frac{1}{2}}} = \frac{0.6932}{t_{\frac{1}{2}}}$$

which assumes adherence to Beer's law ($t_{\frac{1}{2}}$ value) and that the reverse reaction is 1st order. The latter is to be expected for a simple isomerisation reaction, and is confirmed in the next chapter.

TABLE 22

Azo Compound	R_f Values	Purity of Product
azobenzene	0.67 : 1.0	mp = 68°C (68°C)
4-hydroxyazobenzene	0.13	152°C (152°C)
4-methoxyazobenzene	0.60 : 0.90	53-54°C (56°C)
1-phenylazo-2-naphthol	0.65	132-3°C (134°C)
2-methoxy-1-phenylazo naphthalene	0.65	60-61°C (62°C)
4-phenylazo-1-naphthol	0.10 0.73	C=77.14% (77.41%) H= 4.74% (4.84%)
1-methoxy-4-phenylazo naphthalene	0.74	C= 78.2% (77.95%) H= 5.27% (5.33%)
1-(4'-hydroxyphenylazo) naphthalene	0.15	C=77.16% (77.41%) H= 4.79% (4.84%)
1-(4'-methoxyphenylazo)-naphthalene	0.67 : 1.0	C=77.96% (77.95%) H= 5.24% (5.33%)
2,4-dihydroxyazobenzene	0.10 : 0.46	C=66.90% (67.2%) H= 4.56% (4.67%)
2,2'-dihydroxyazo benzene	0.40 : 0.63	C= 67.0% (67.2%) H= 4.57% (4.67%)

(Continued...

TABLE 22 (Continued)

Azo Compound	R_f Values	Purity of Product
2-hydroxy-1,1'-azo naphthalene	0.73	229-230°C (230°C)
1,5-dihydroxy-4-phenylazo naphthalene	0.13 : 0.24:1.0	C=72.01% (72.73%) H= 4.45% (4.54%)
4-aminoazobenzene	0.37	mp=125-6°C (126°C)
4-dimethylaminoazobenzene	0.73	mp=115-6°C (116-7°C)
2,4-diaminoazobenzene	0.22	mp=116-117°C (118°C)
4-(4'-aminophenylazo)-1-naphthylamine	0.13	73.05% (73.29%) 5.26% (5.34%)
2-methoxy-4-nitro-4'-dimethylaminoazo benzene	0.58	C=60.02% (60.0%) H=5.13% (5.33%)

TABLE 23

Azo compound	Solvent	Filter	$t_{\frac{1}{2}}$, minutes		Φ	k, minutes^{-1}
			forward	reverse		
Azobenzene	C_6H_6	OX1	14.4	-	0.15	-
"	10% EtOH/C_6H_6	OX1	15.9	-	0.13	-
4-Hydroxyazobenzene	C_6H_6	OX1	3.75	5.55	0.26	1.26×10^{-1}
"	1% EtOH/C_6H_6	OX1	2.45	2.60	0.24	2.67×10^{-1}
4-Methoxyazobenzene	C_6H_6	OX1	8.25	-	0.24	-
2-Methoxy-1-phenylazonaphthalene	C_6H_6	OB2	4.85	-	0.12	-
	C_6H_6	OG1	5.20	-	-	-
"	50% EtOH/C_6H_6	OB2	4.90	-	0.12	-
1-Methoxy-4-phenylazonaphthalene	C_6H_6	OB1	2.80	-	0.14	-
	10% EtOH/C_6H_6	OB1	2.70	-	0.14	-
"	50% EtOH/C_6H_6	OB1	2.75	-	0.14	-
1-(4'-Hydroxyphenylazo)-naphthalene	C_6H_6	OB1	2.00	10.5	0.28	6.60×10^{-2}
	1% EtOH/C_6H_6	OB1	1.60	2.05	0.25	3.38×10^{-1}
"	5% EtOH/C_6H_6	OB1	0.3	0.5	-	1.39
1-(4'-Methoxyphenylazo)-naphthalene	C_6H_6	OB1	3.15	97.2	0.29	7.13×10^{-3}
	C_6H_6	OX1	7.25	102	0.28	6.79×10^{-3}

TABLE 23 (cont.)

Azo compound	Solvent	Filter	$t_{\frac{1}{2}}$, minutes		Φ	k, minutes^{-1}
			forward	reverse		
1-(4'-Methoxyphenylazo)-naphthalene	5% EtOH/C_6H_6	OX1	7.45	-	0.28	-
	50% EtOH/C_6H_6	OX1	7.15	-	0.28	-
4,4'-Dihydroxyazobenzene	C_6H_6	OX1	1.50	-	0.28	-
2-Methoxy-5-phenylazobenzoic acid	50% H_2O/EtOH	OX1	3.30	20.7	0.35	3.35×10^{-2}
4-Acetamido-2-phenylazo phenol	C_6H_6	-	0.5	0.85	-	8.15×10^{-1}
4-Aminoazobenzene	C_6H_6	621	1.80	4.90	0.32	1.41×10^{-1}
"	1% EtOH/C_6H_6	621	0.65	0.90	0.40	7.70×10^{-1}
"	5% EtOH/C_6H_6	621	0.3	0.5	-	1.39
4-Dimethylaminoazobenzene	C_6H_6	622	2.10	-	0.36	-
"	C_6H_6	OB1	2.10	6.85	0.31	1.01×10^{-1}
"	10% EtOH/C_6H_6	OB1	1.45	2.45	0.31	2.83×10^{-1}
2-Methoxy-4-nitro-4'-dimethylaminoazobenzene	C_6H_6	OB2	0.70	1.50	0.35	4.62×10^{-1}
	0.5% EtOH/C_6H_6	OB2	0.60	1.25	0.35	5.55×10^{-1}
"	2% EtOH/C_6H_6	OB2	0.50	0.90	0.35	7.70×10^{-1}
"	5% EtOH/C_6H_6	OB2	0.40	0.40	0.35	1.73

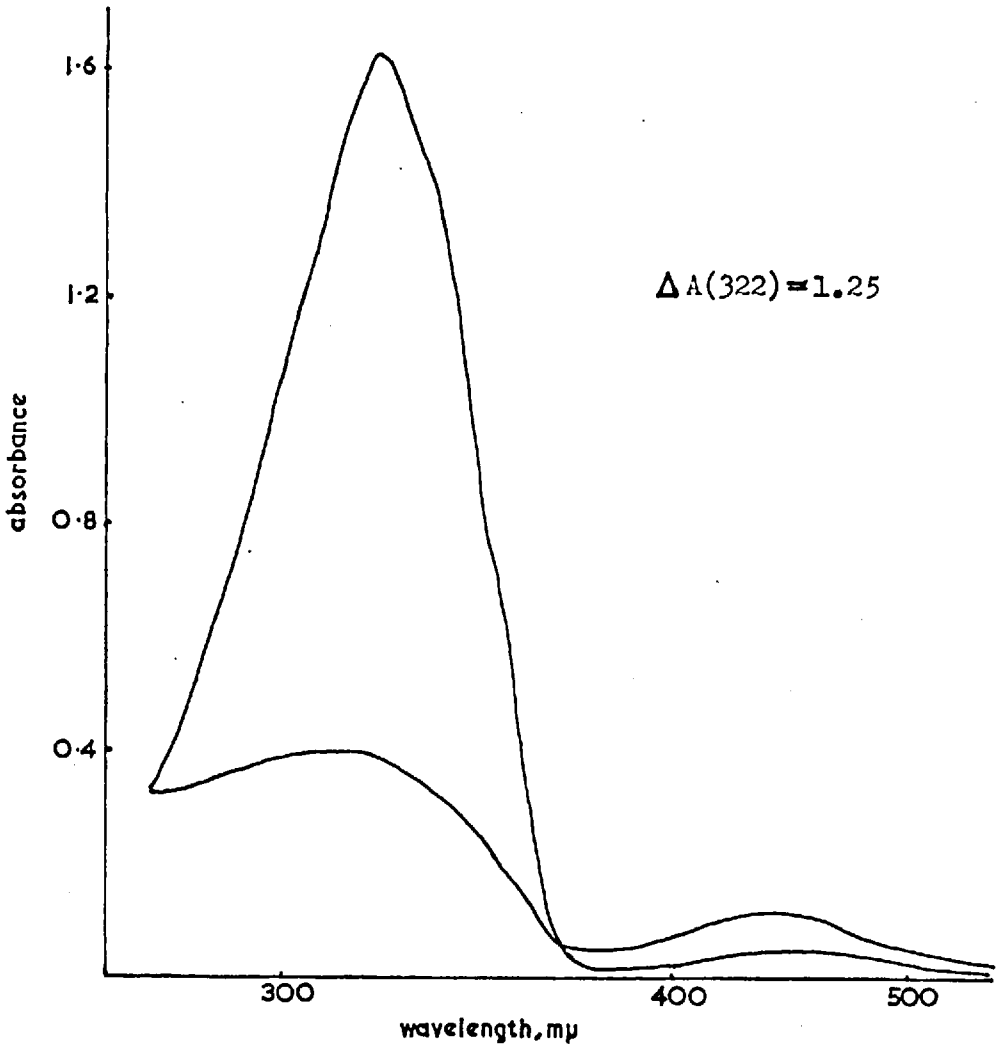
TABLE 23 (cont.)

Azo compound	Solvent	Filter	$t_{\frac{1}{2}}$, minutes		Φ	k, minutes^{-1}
			forward	reverse		
2-(4'-Dimethylaminophenylazo) pyridine	C_6H_6	OB1	1.25	2.00	0.33	3.77×10^{-1}
	1% EtOH/C_6H_6	OB1	0.70	1.10	0.32	6.30×10^{-1}
Chrysophenine	H_2O	OB1	2.50	-	0.12	-
"	H_2O	622	3.50	-	0.11	-

FIG. 28

AZOBENZENE.

(1.5×10^{-4}M in benzene)



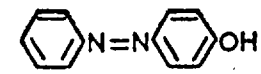
1. Dark spectrum.

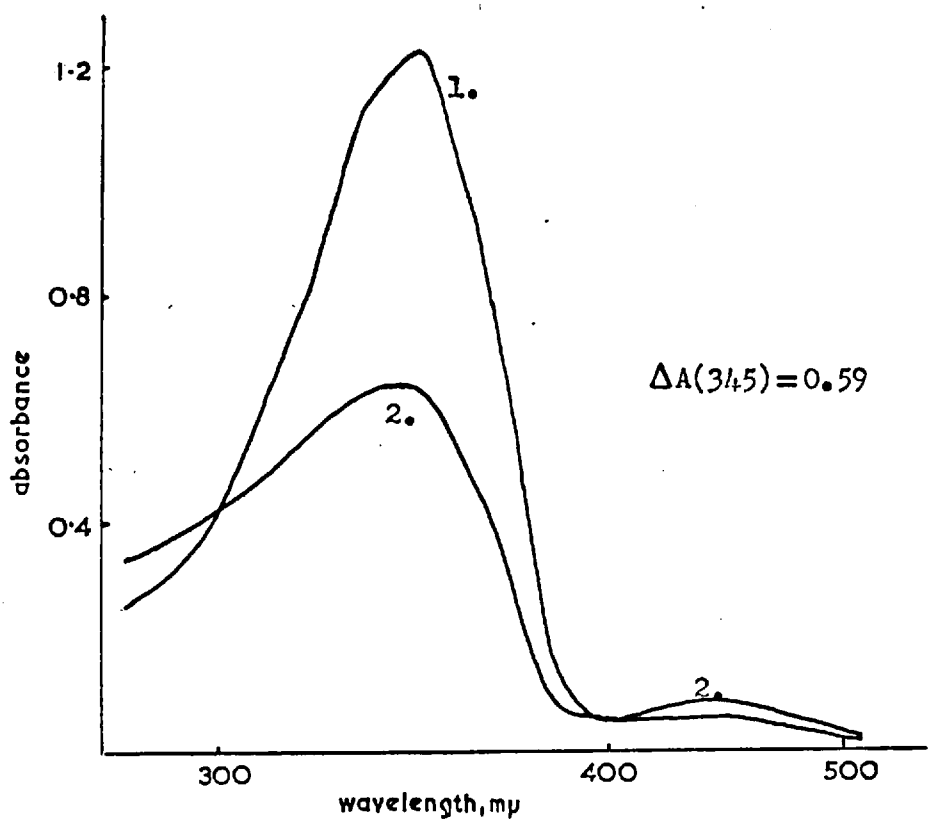
2. Equilibrium spectrum, irradiation OX1.

FIG. 29

4-HYDROXYAZOBENZENE.

(10^{-4}M in benzene)





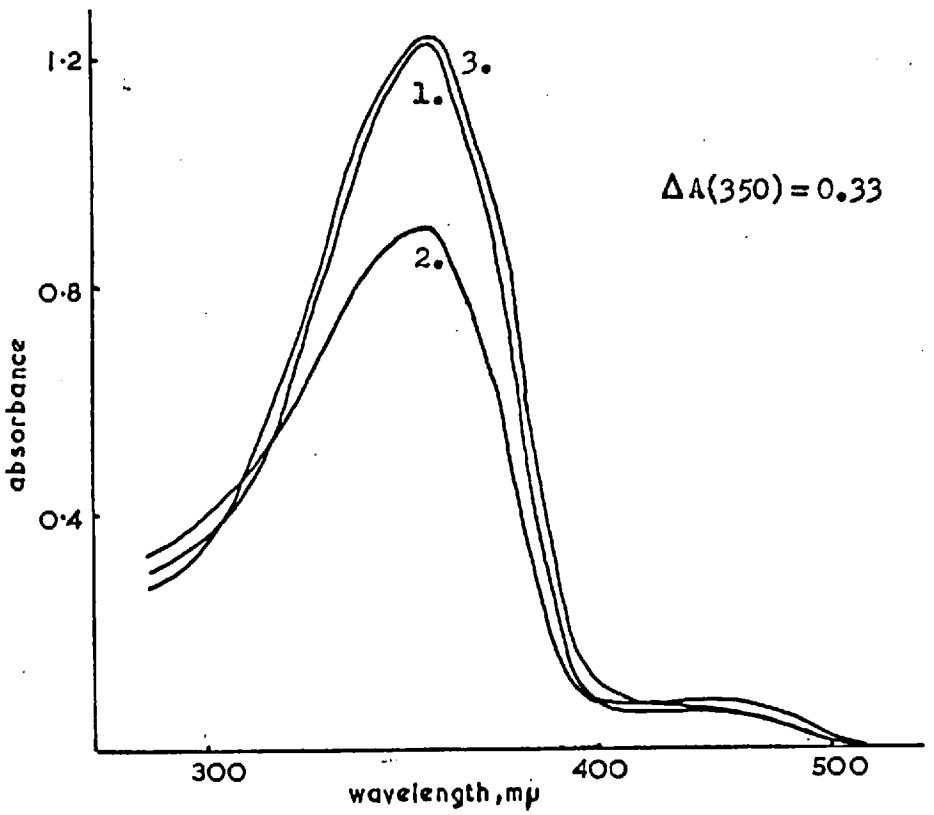
1. Dark spectrum.

2. Equilibrium spectrum, irradiation 0X1.

FIG.30

4-HYDROXYAZOBENZENE.

(10^{-4}M)



1. Dark spectrum in 1% v/v ethanolic benzene.

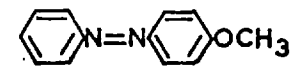
2. Equilibrium spectrum in 1% v/v ethanolic benzene, irradiation 0X1.

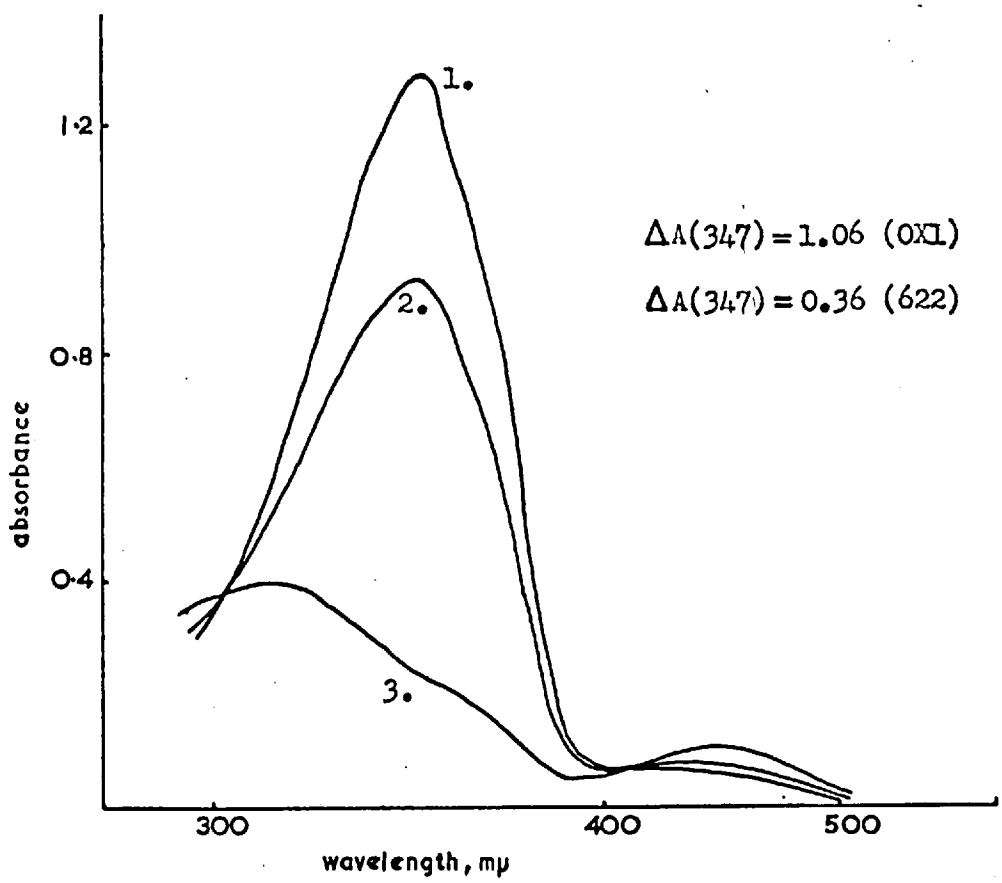
3. Dark and equilibrium spectra in 10% v/v ethanolic benzene.

FIG. 31

4-METHOXYAZOBENZENE.

(10^{-4}M in benzene)





1. Dark spectrum.

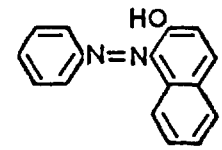
2. Equilibrium spectrum, irradiation 622.

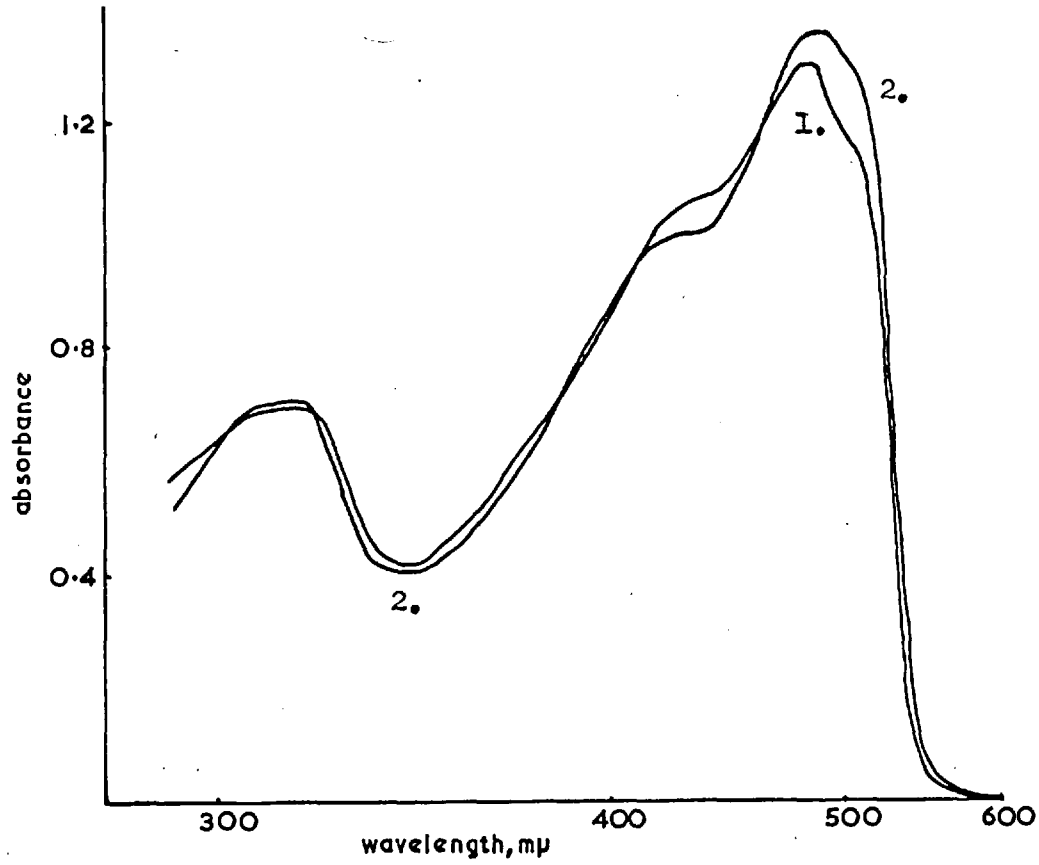
3. Equilibrium spectrum, irradiation OX1.

FIG.32

1-PHENYLAZO-2-NAPHTHOL.

(2×10^{-4}M)





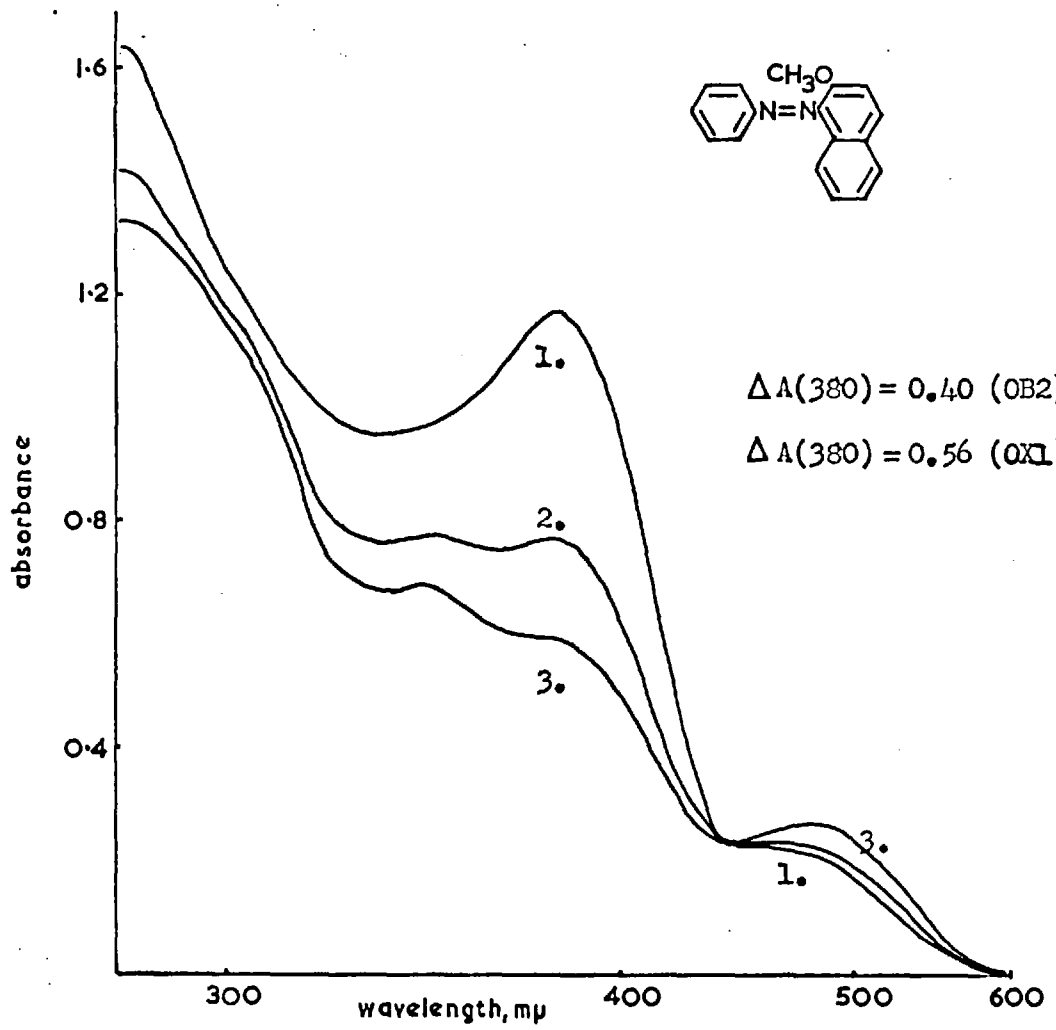
1. Dark and equilibrium spectra in benzene.

2. Dark and equilibrium spectra in 50% ethanolic benzene.

FIG.33

2-METHOXY-1-PHENYLAZONAPHTHALENE.

(3×10^{-4}M in benzene)



1. Dark spectrum.

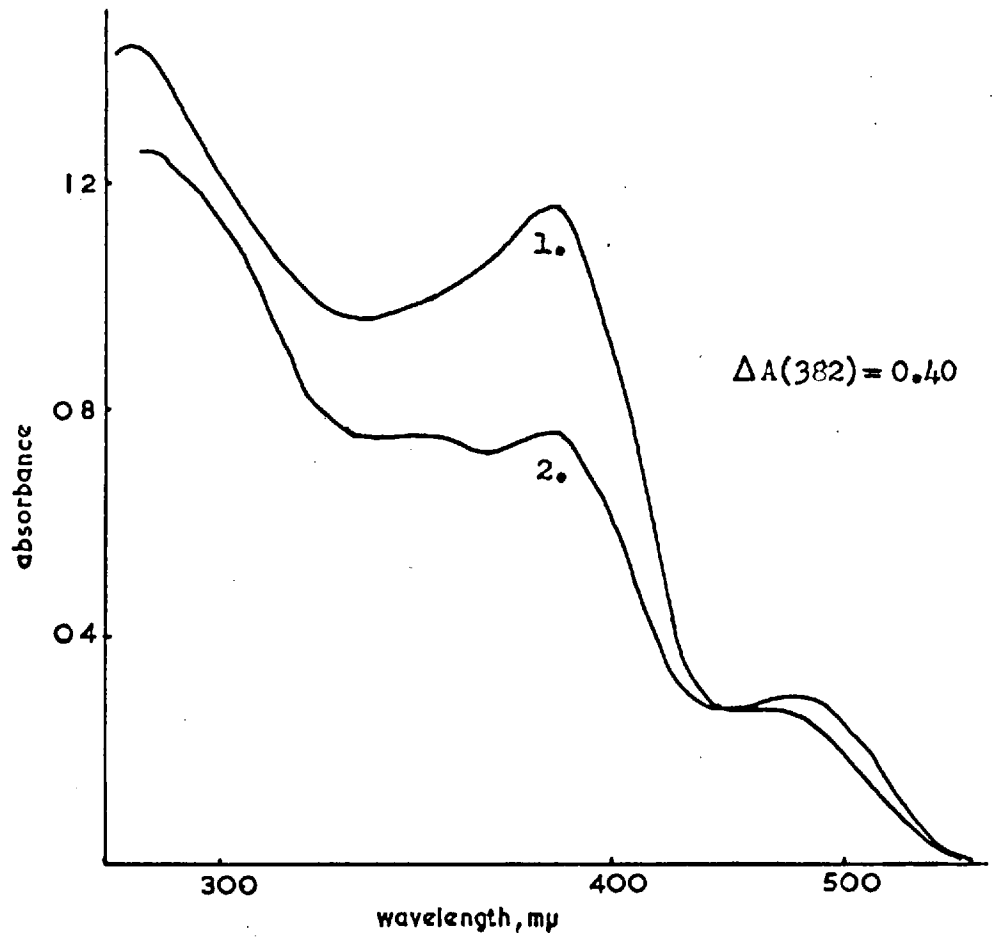
2. Equilibrium spectrum, irradiation OB2.

3. Equilibrium spectrum, irradiation OX1.

FIG. 34

2-METHOXY-1-PHENYLAZONAPHALENE.

(3×10^{-4}M in 50% v/v ethanolic benzene)



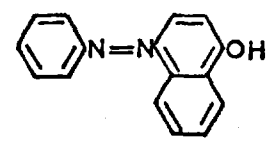
1. Dark spectrum.

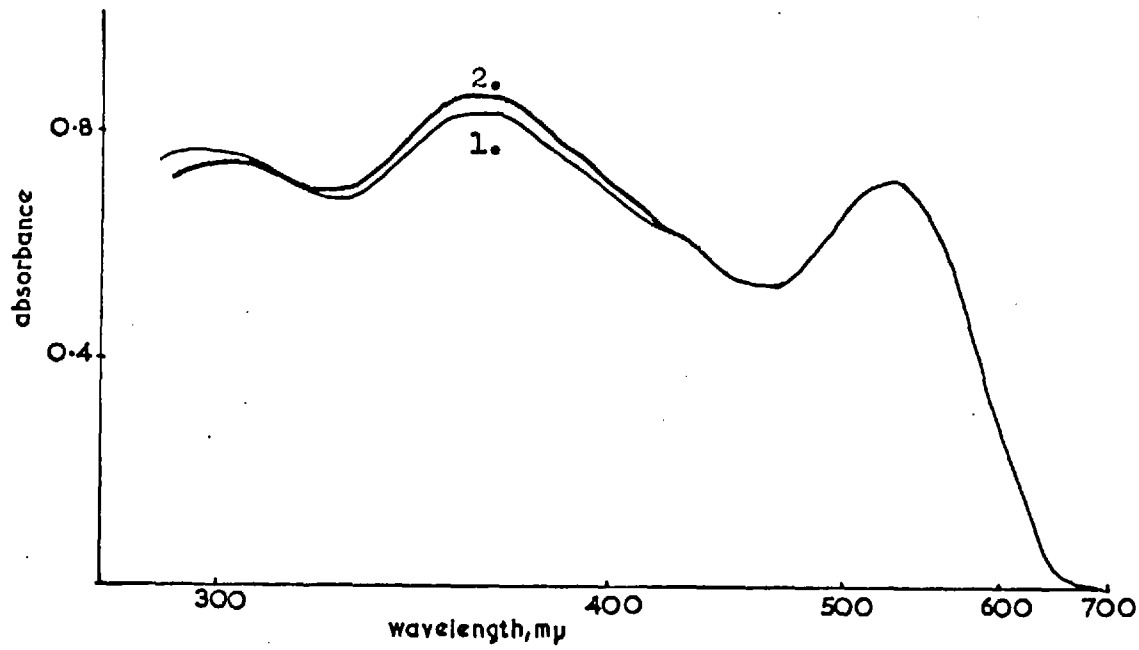
2. Equilibrium spectrum, irradiation 0B2.

FIG.35

4-PHENYLAZO-1-NAPHTHOL.

(3×10^{-4}M)





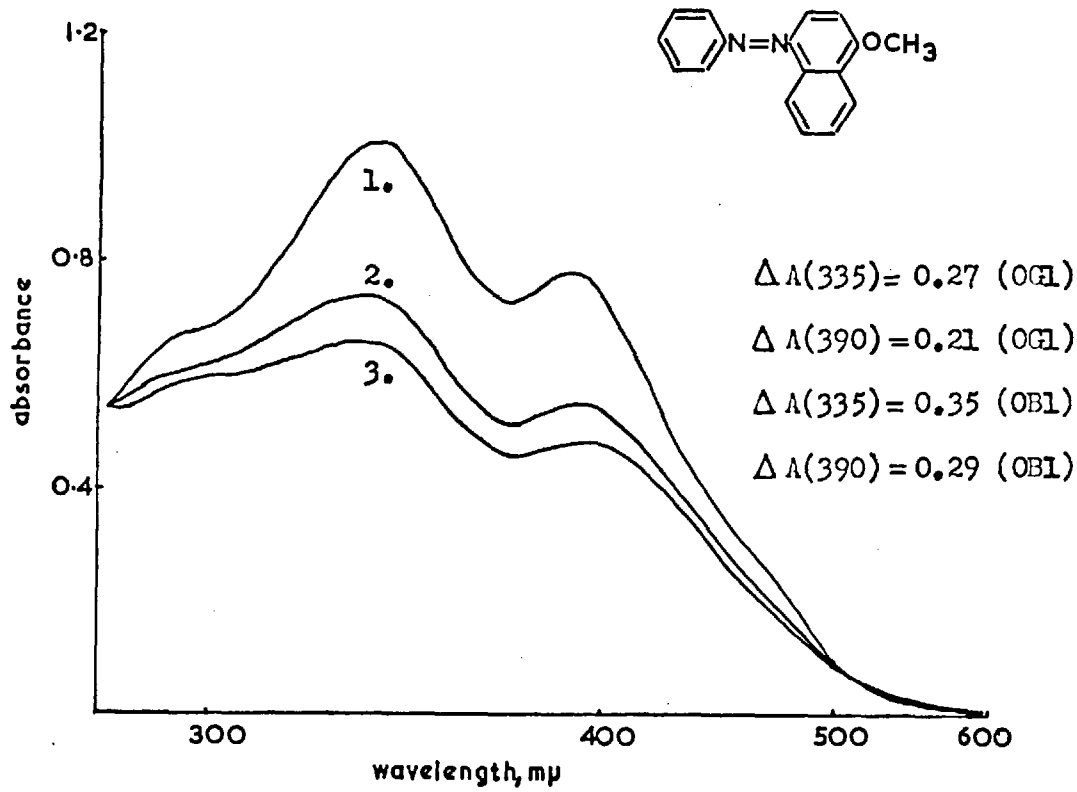
1. Dark and equilibrium spectra in benzene.

2. Dark and equilibrium spectra in 50% v/v ethanolic benzene.

FIG. 36

1-METHOXY-4-PHENYLAZONAPHTHALENE.

(10^{-4}M in benzene)



1. Dark spectrum.

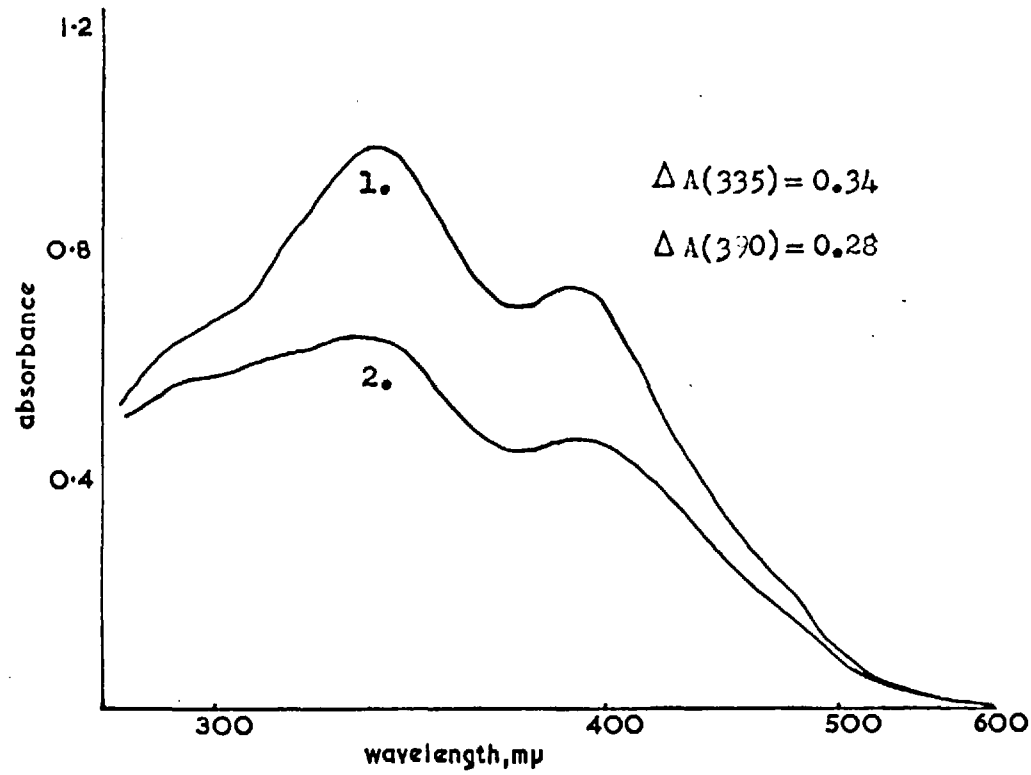
2. Equilibrium spectrum, irradiation OG1.

3. Equilibrium spectrum, irradiation OH1.

FIG.37

1-METHOXY-4-PHENYLAZONAPHTHALENE.

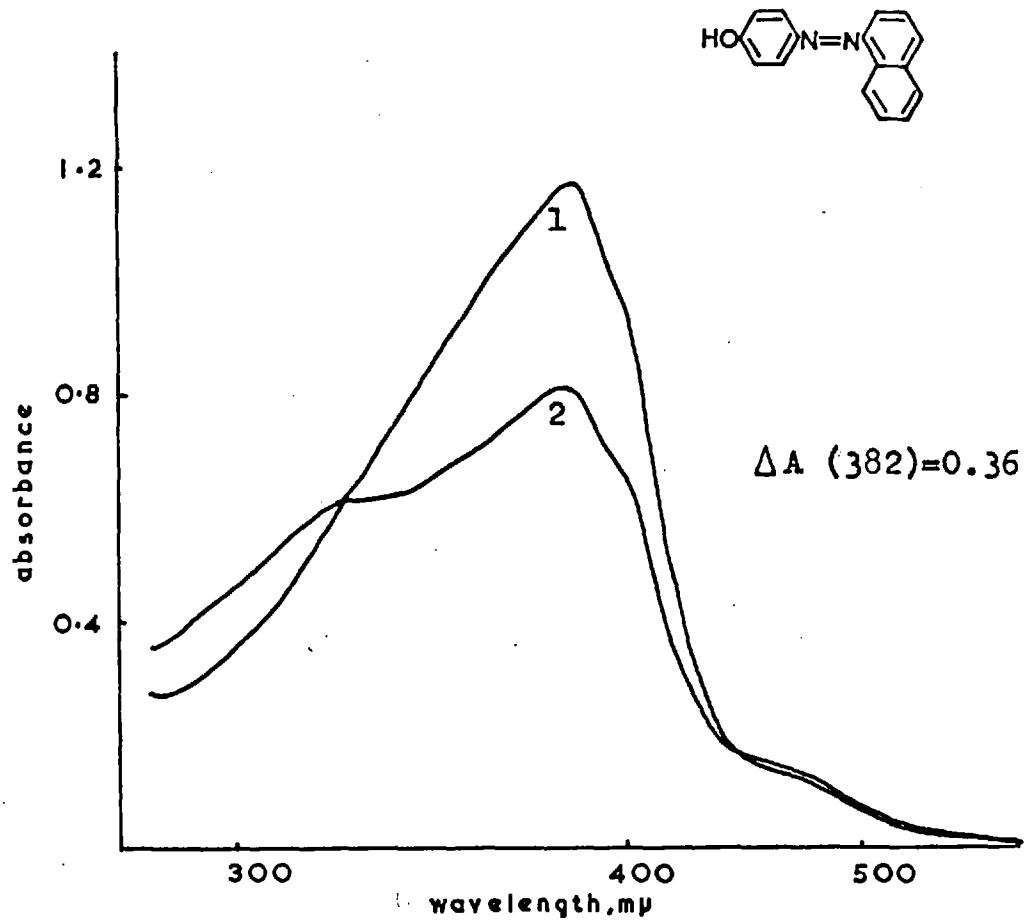
(10^{-4}M in 10% v/v ethanolic benzene)



1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.

FIG. 38

1-(4'-HYDROXYPHENYLAZO)-NAPHTHALENE.
(1.5 x 10^{-4}M in benzene)

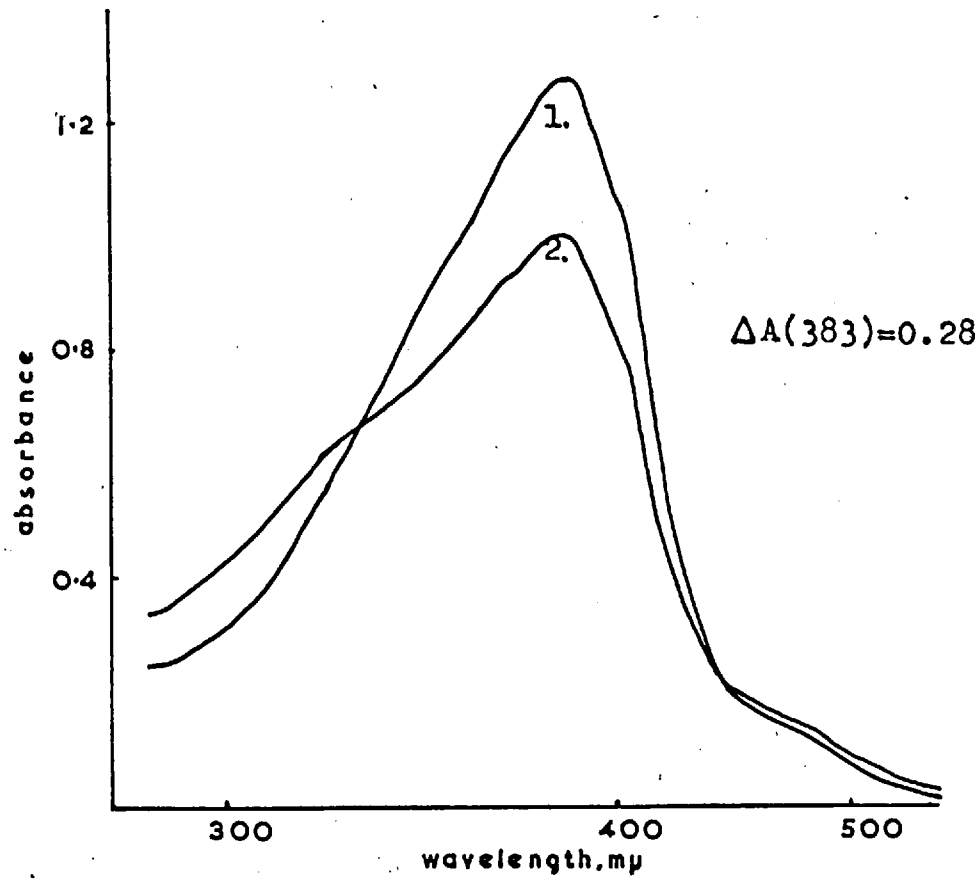


1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.

FIG. 39

1-(4'-HYDROXYPHENYLAZO)-NAPHTHALENE.

(1.5 x 10^{-4}M in 1% v/v ethanolic benzene)

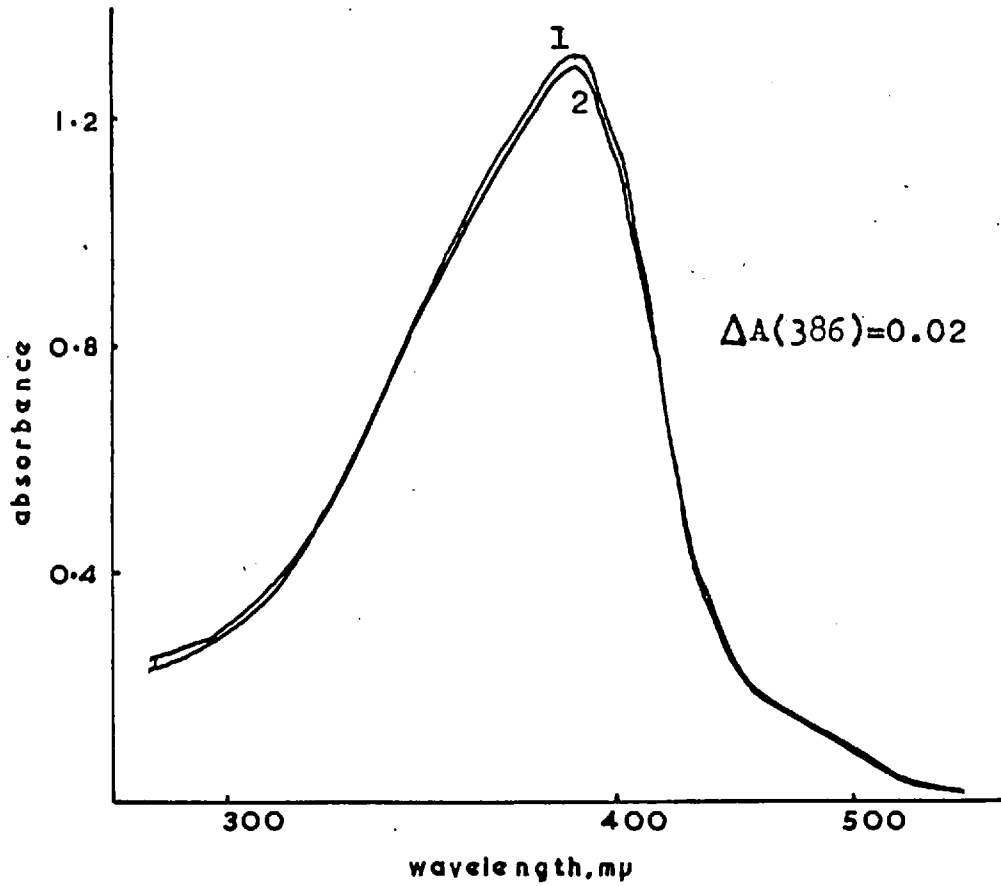


1. Dark spectrum.
2. Equilibrium spectrum, irradiation 0B1.

FIG.40

1'-(4'-HYDROXYPHENYLAZO)-NAPHTHALENE.

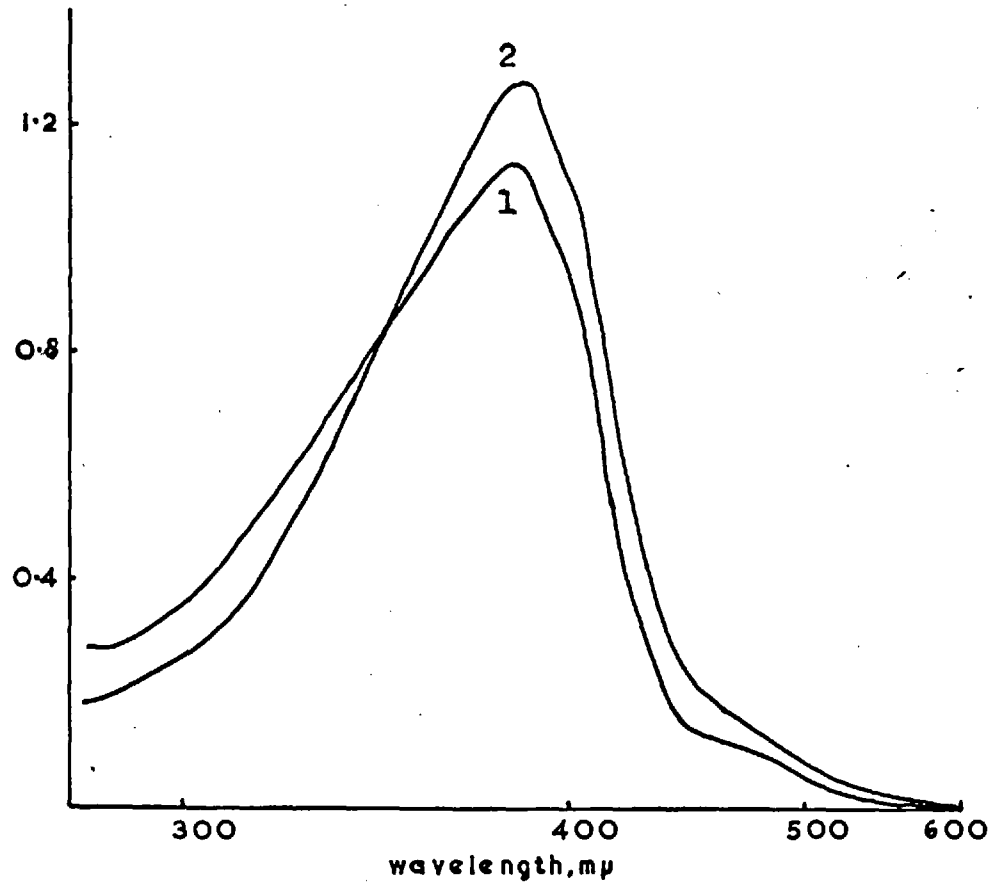
(1.5 x 10^{-4}M in 5% v/v ethanolic benzene)



1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.

FIG.41

1-(4'-HYDROXYPHENYLAZO)-NAPHTHALENE.
(1.5×10^{-4}M)

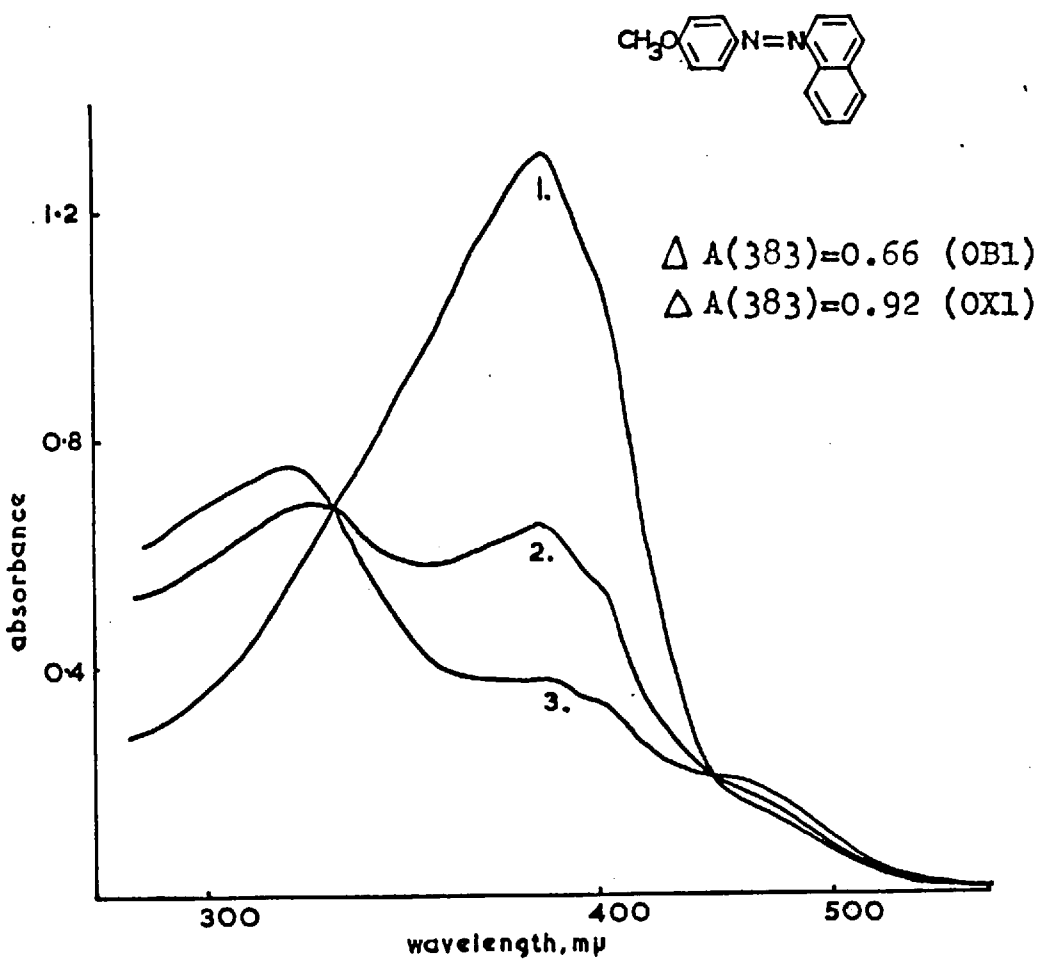


1. Dark spectrum in benzene.
2. Dark and equilibrium spectra in 50% ethanolic benzene.

FIG.42

1-(4'-METHOXYPHENYLAZO)-NAPHTHALENE.

(1.5 x 10^{-4}M in benzene)

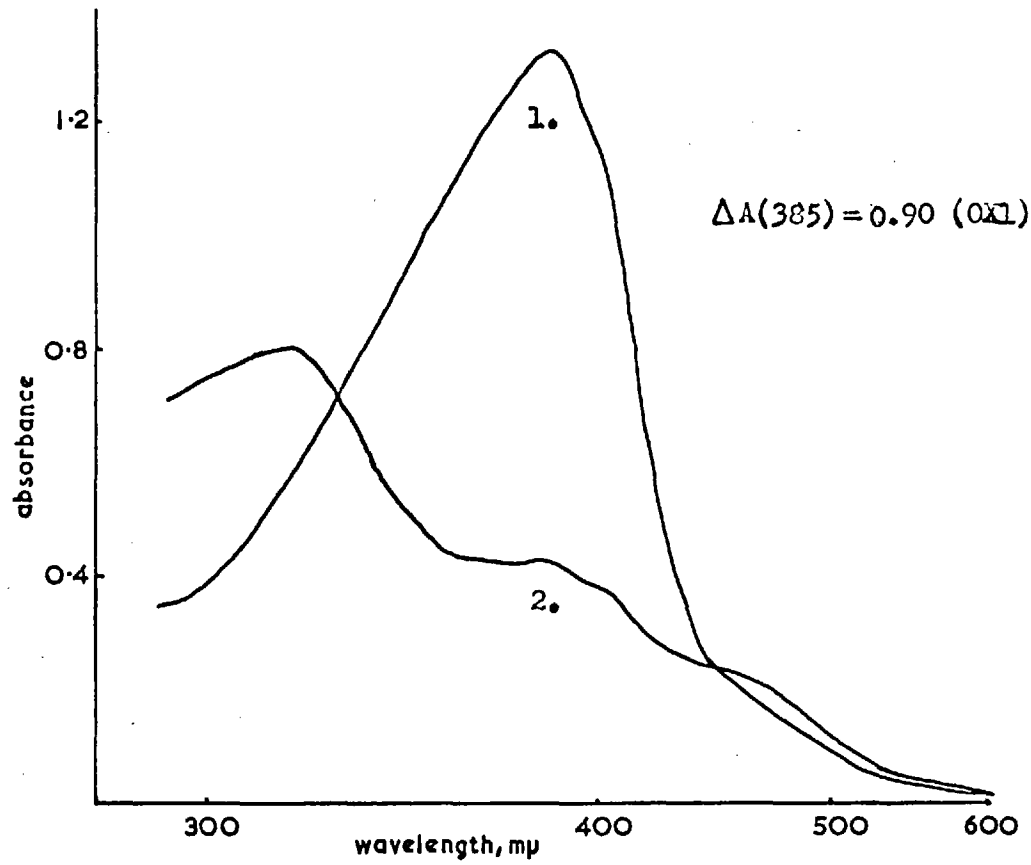


1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.
3. Equilibrium spectrum, irradiation OX1.

FIG.43

1-(4'-METHOXYPHENYLAZO)-NAPHTHALENE.

(1.5×10^{-4} M in 50% ethanolic benzene)



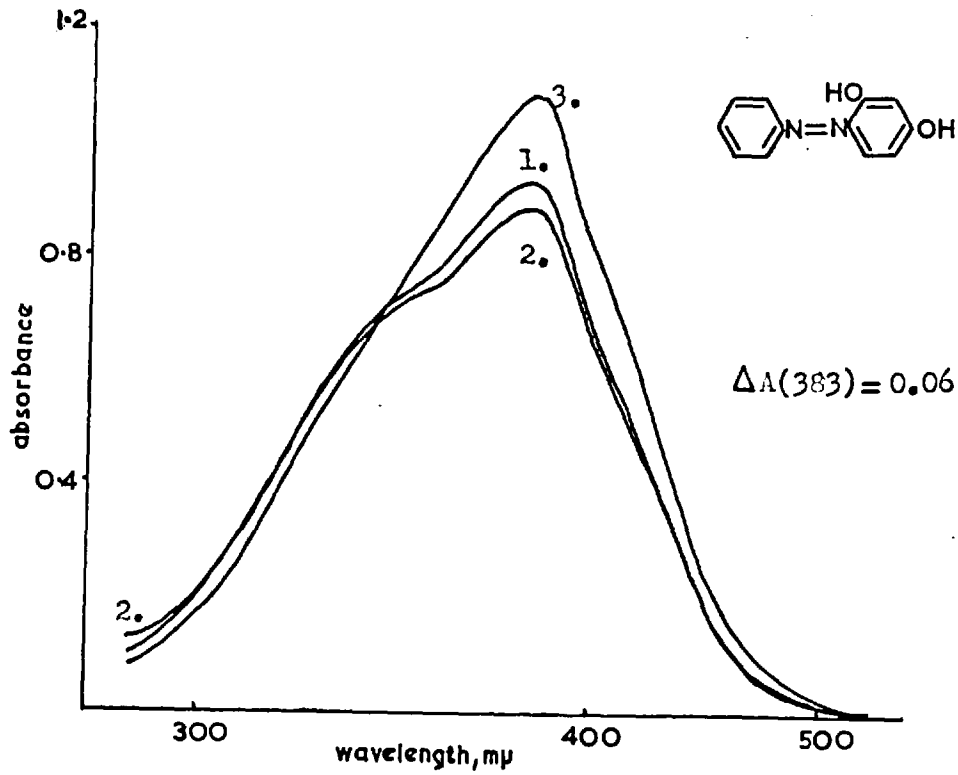
1. Dark spectrum.

2. Equilibrium spectrum, irradiation 0X1.

FIG. 44

2,4-DIHYDROXYAZOBENZENE.

(1.5×10^{-4}M)



1. Dark spectrum in benzene.

2. Equilibrium spectrum in benzene, irradiation OB1.

3. Dark and equilibrium spectra in 50% v/v ethanolic benzene.

FIG.45

2,2'-DIHYDROXYAZOBENZENE.

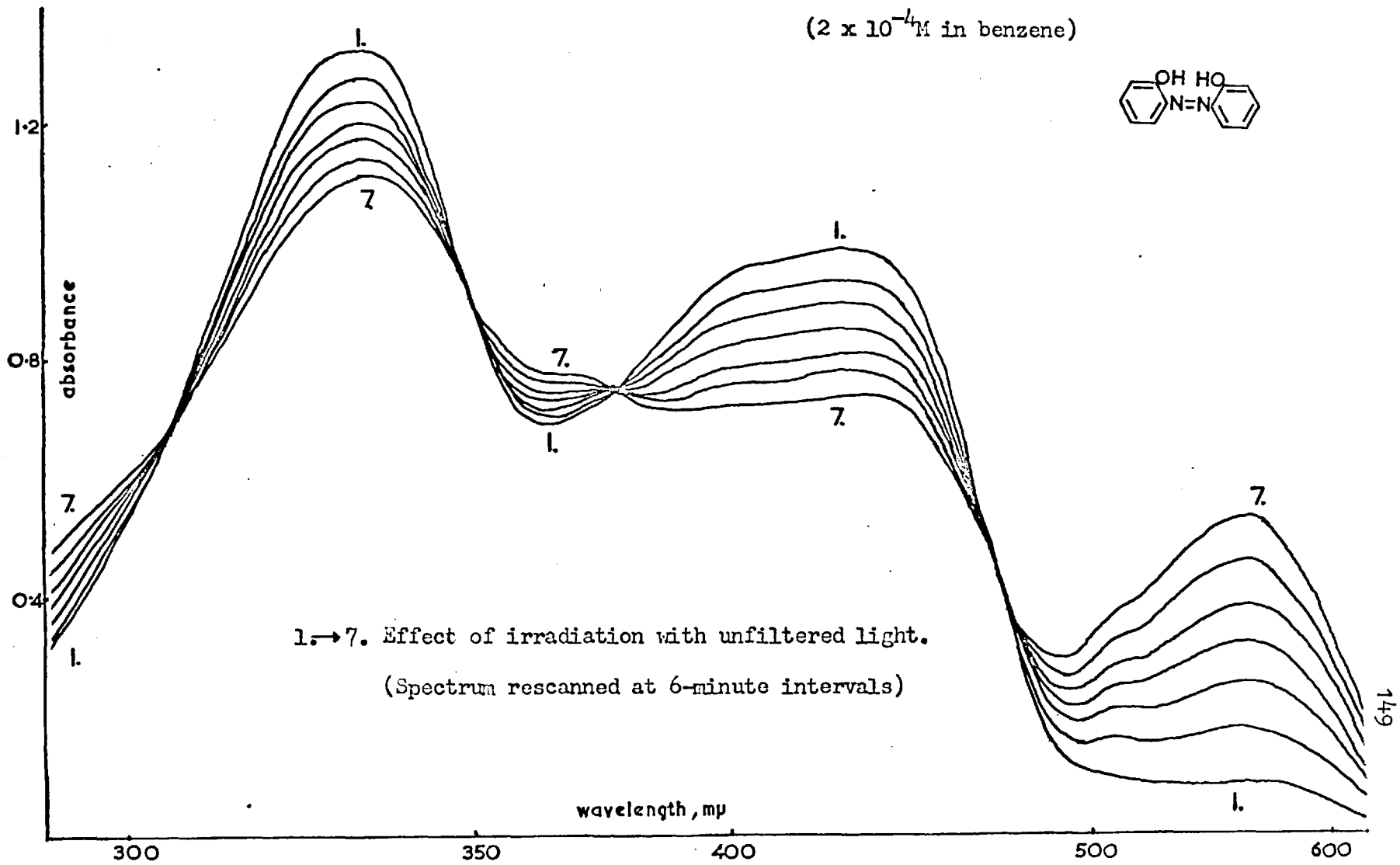
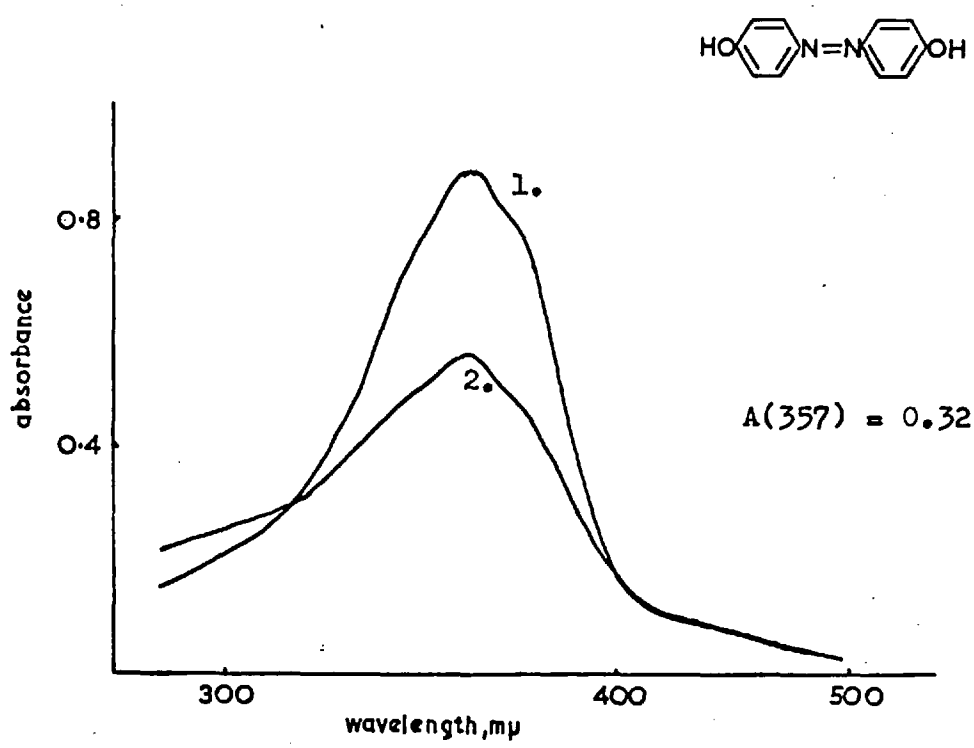


FIG.46

4,4'-DIHYDROXYAZOBENZENE.

(7.5×10^{-5}M)



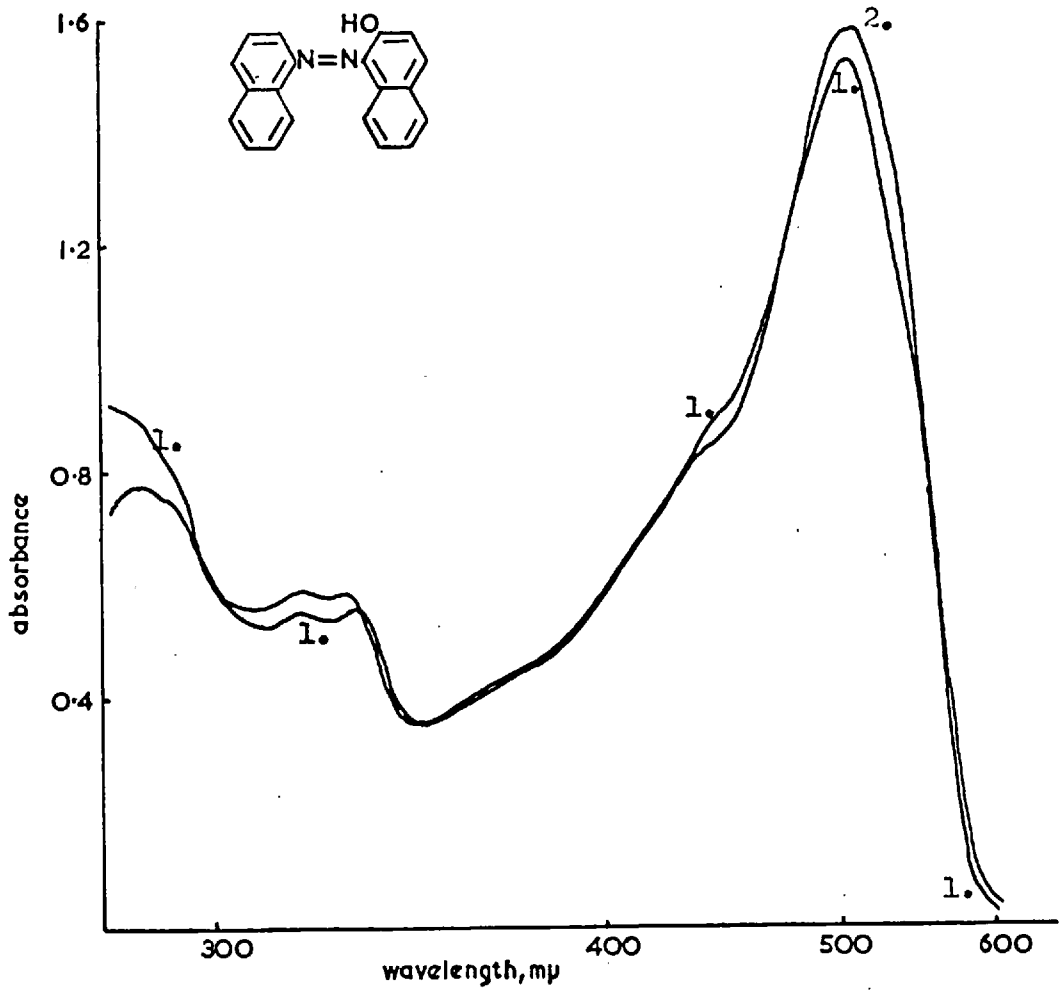
1. Dark spectrum in benzene, and dark and equilibrium spectra in 1% v/v ethanolic benzene.

2. Equilibrium spectrum in benzene, irradiation 0X1.

FIG.47

2-HYDROXY-1,1'-AZONAPHTHALENE.

(1.5×10^{-4}M)



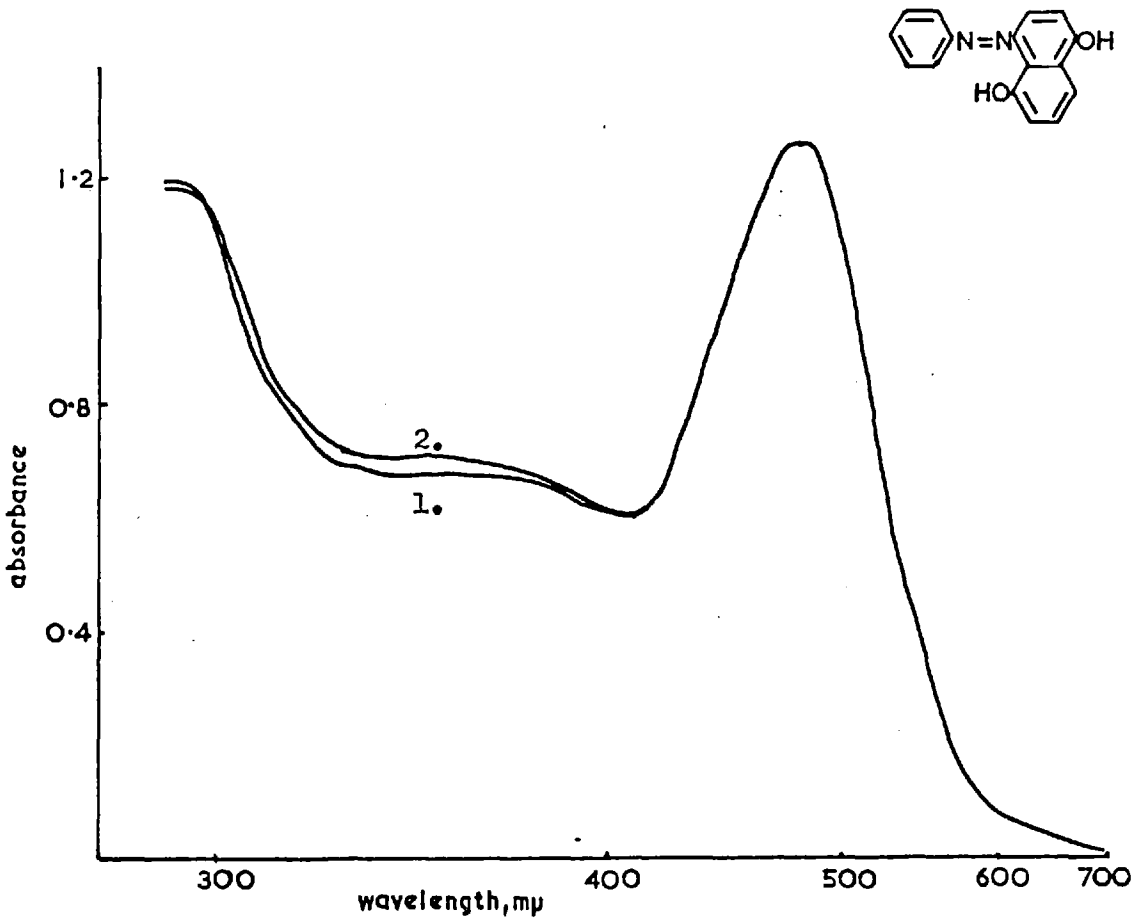
1. Dark and equilibrium spectra in benzene.

2. Dark and equilibrium spectra in 50% v/v ethanolic benzene.

FIG.48

1,5-DIHYDROXY-4-PHENYLAZONAPHTHALENE.

$(2.5 \times 10^{-4}M)$



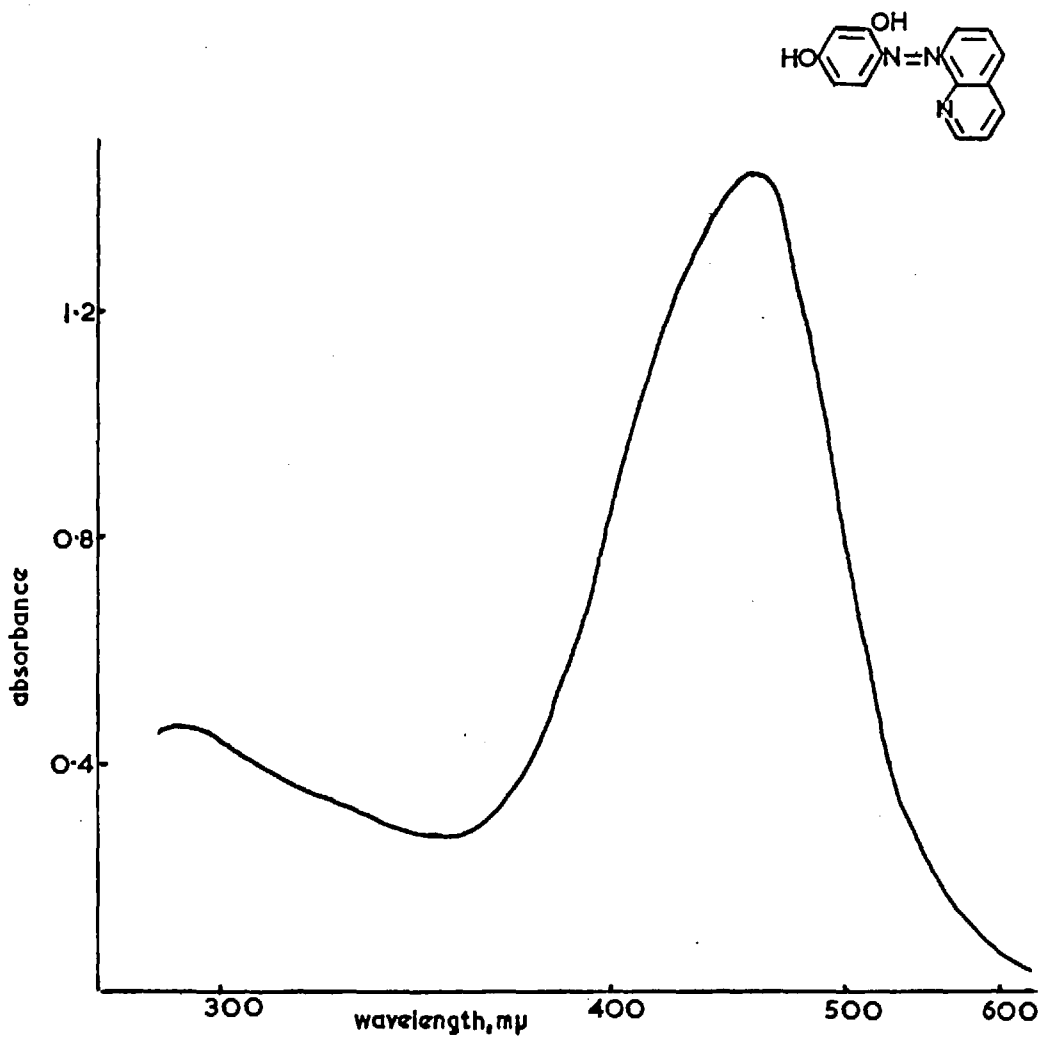
1. Dark and equilibrium spectra in benzene.

2. Dark and equilibrium spectra in 50% ethanolic benzene.

FIG. 49

8-(2',4'-DIHYDROXYPHENYLAZO)-QUINOLINE.

(1.5×10^{-4} M in benzene)

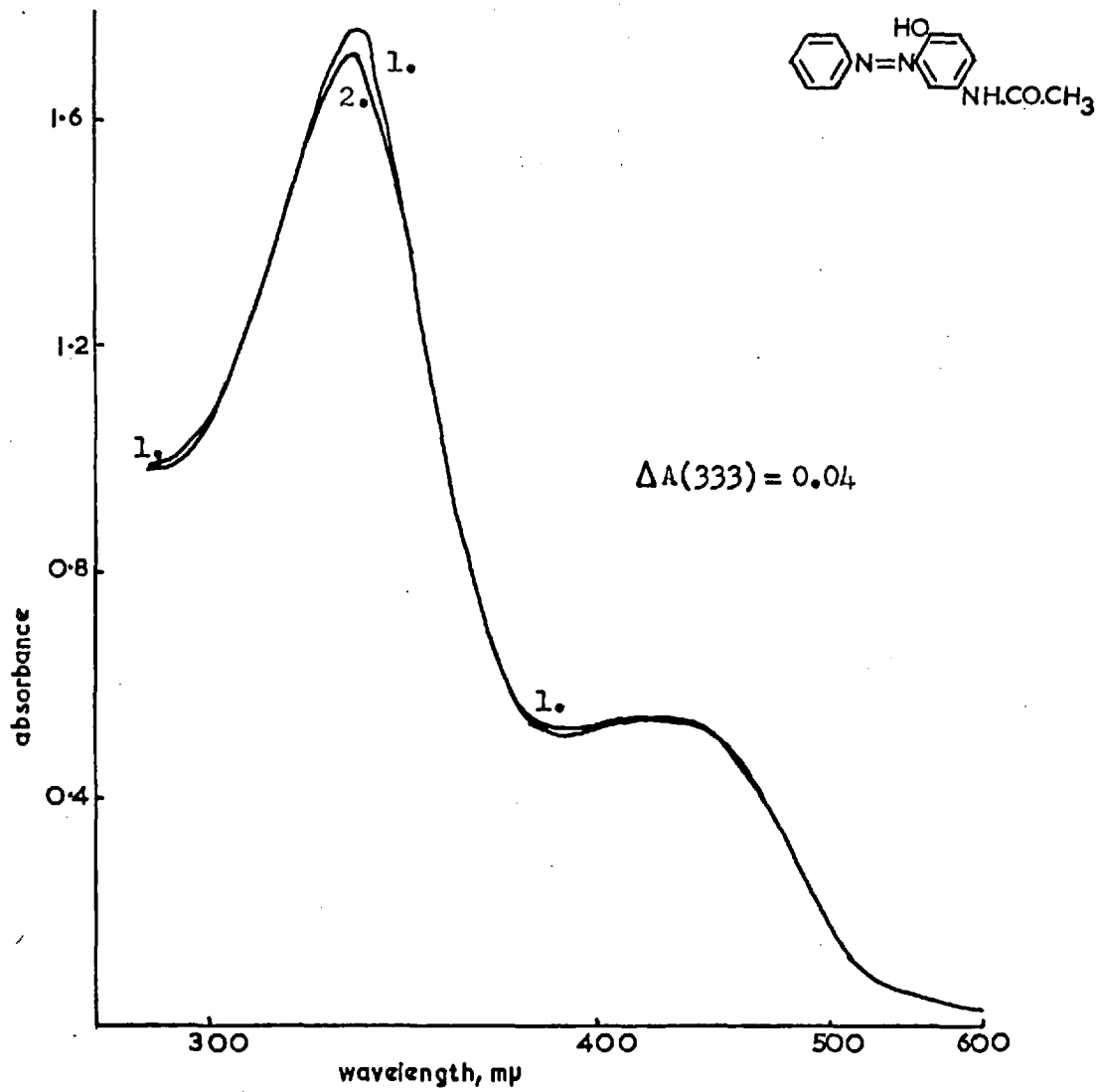


Dark spectrum.

FIG.50

4-ACETAMIDO-2-PHENYLAZOPHENOL.

(2 x 10^{-4}M in benzene)



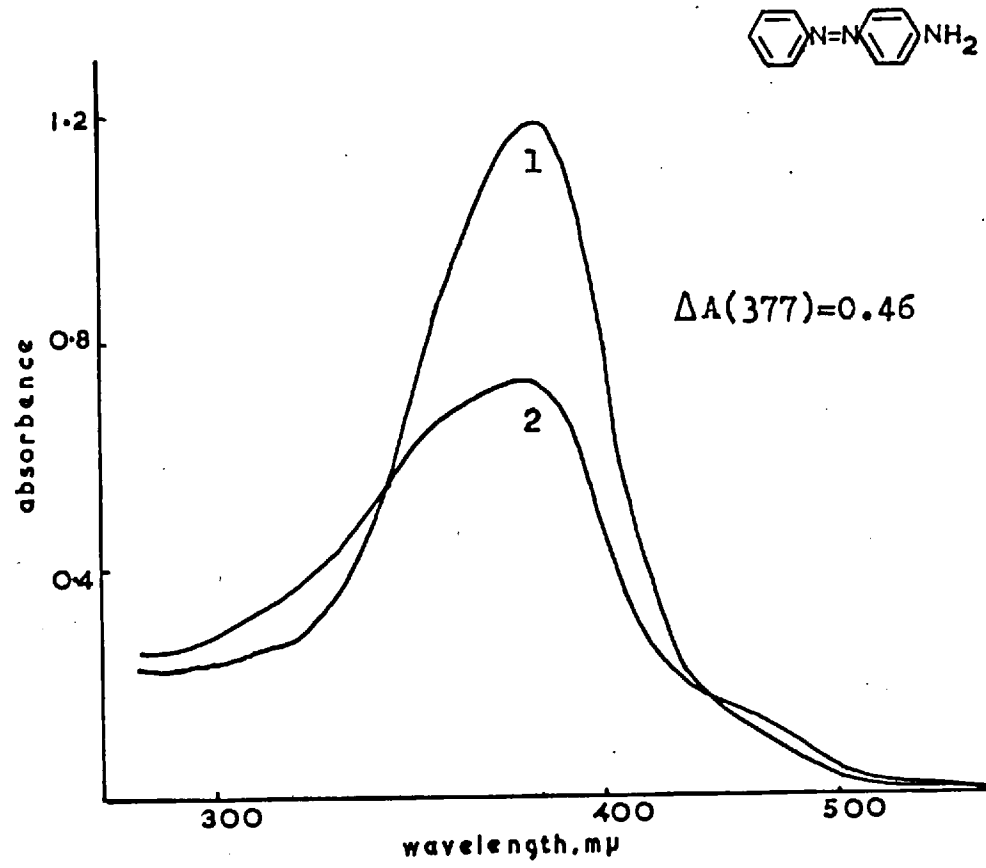
1. Dark spectrum.

2. Equilibrium spectrum, irradiation with unfiltered light.

FIG. 51

4-AMINOAZOBENZENE.

(10^{-4}M in benzene.)

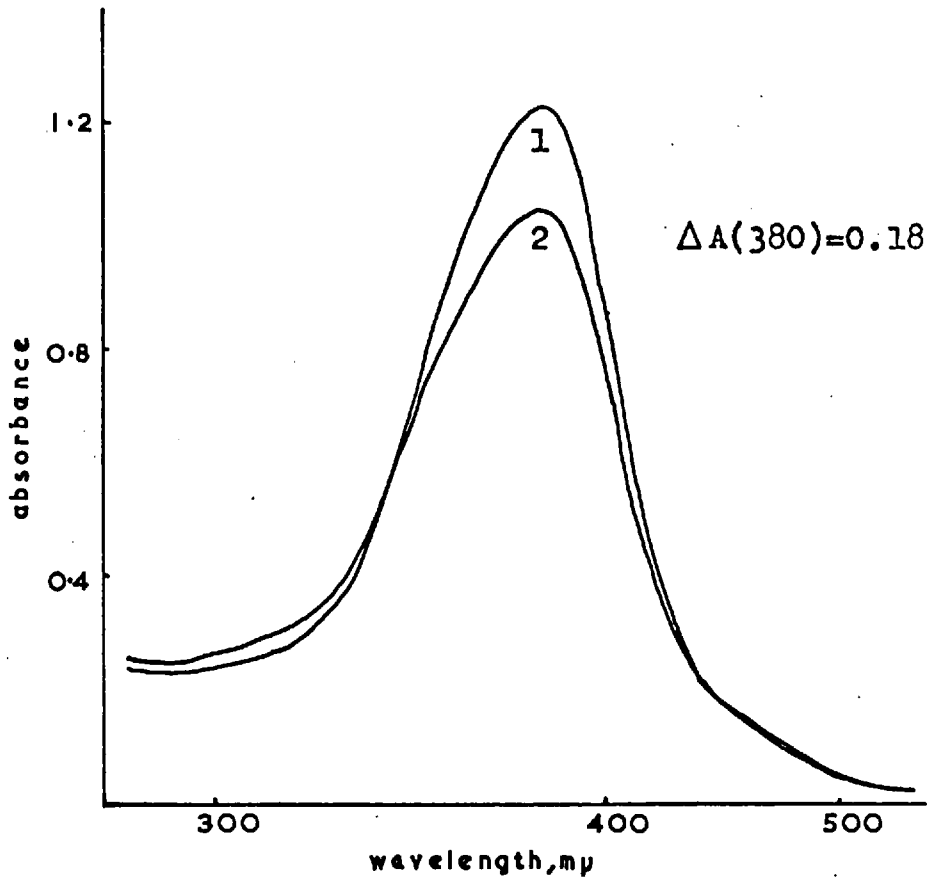


1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.

FIG. 52

4-AMINOAZOBENZENE.

(10^{-4}M in 1%v/v ethanolic benzene)

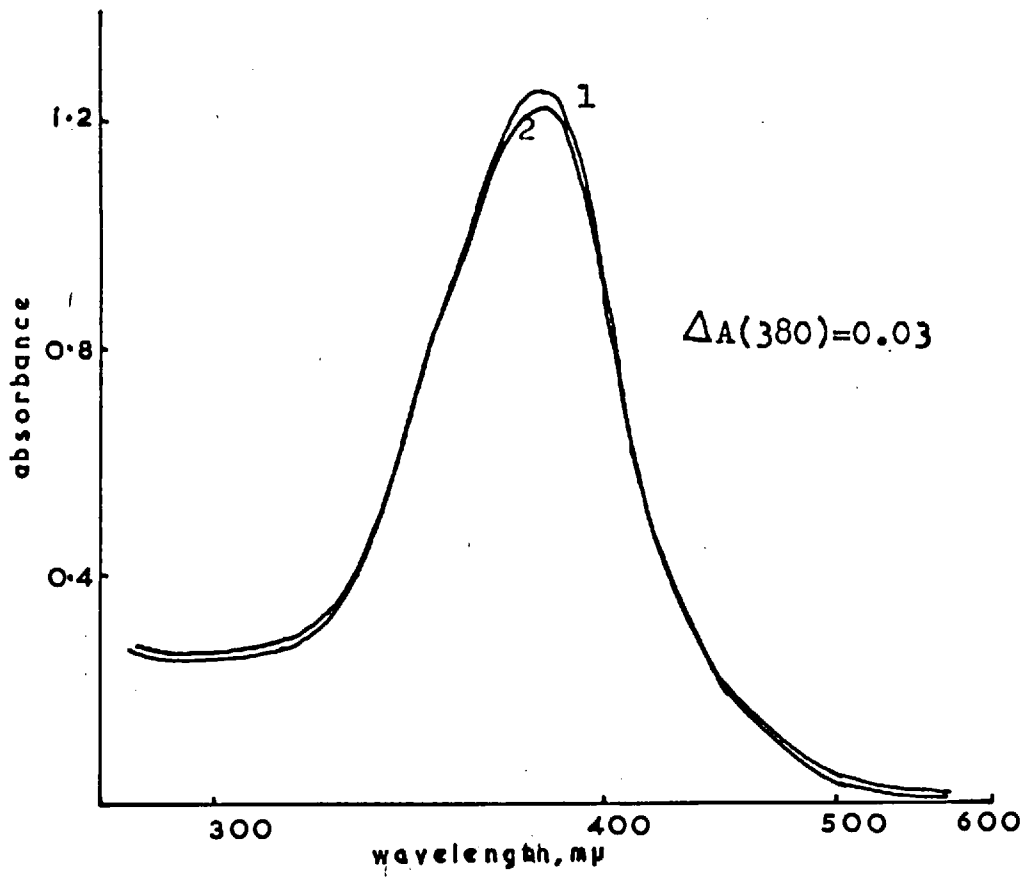


1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.

FIG.53

4-AMINOAZOBENZENE

(10^{-4}M in 5% v/v ethanolic benzene)

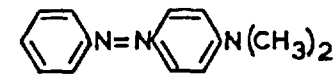


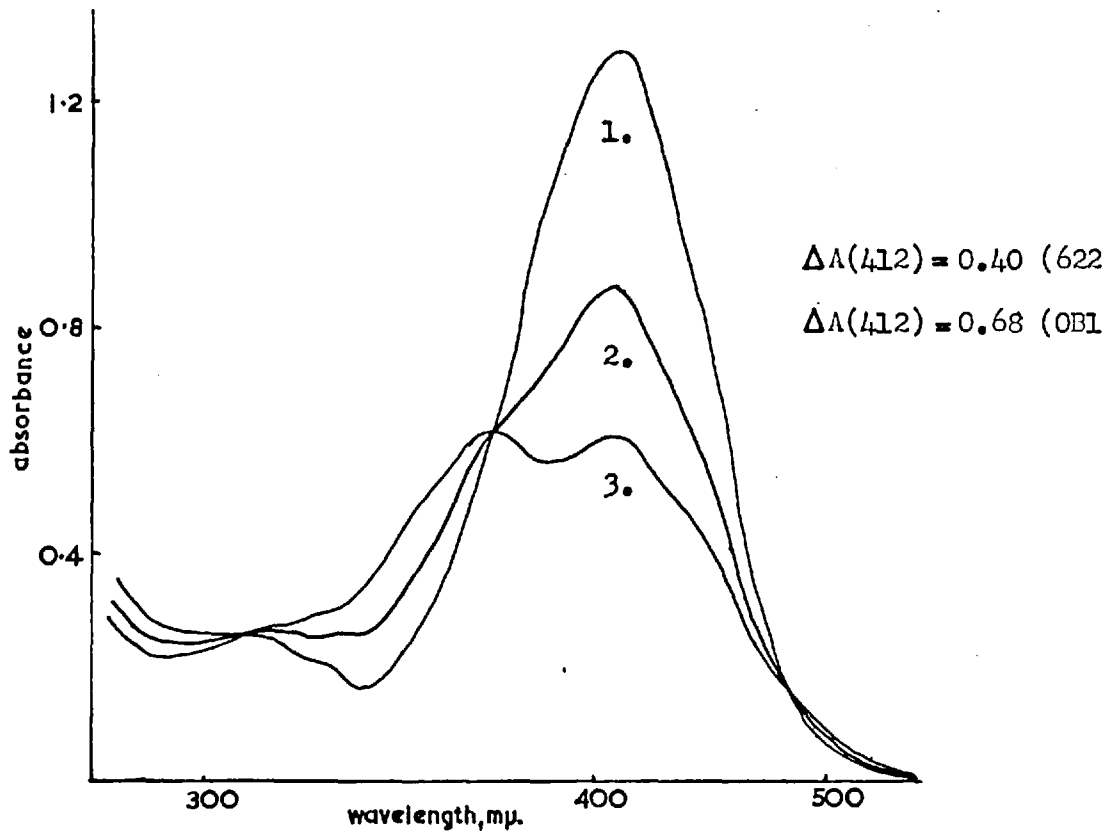
1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.

FIG.54

4-DIETHYLAMINOAZOBENZENE.

(10^{-4}M in benzene)





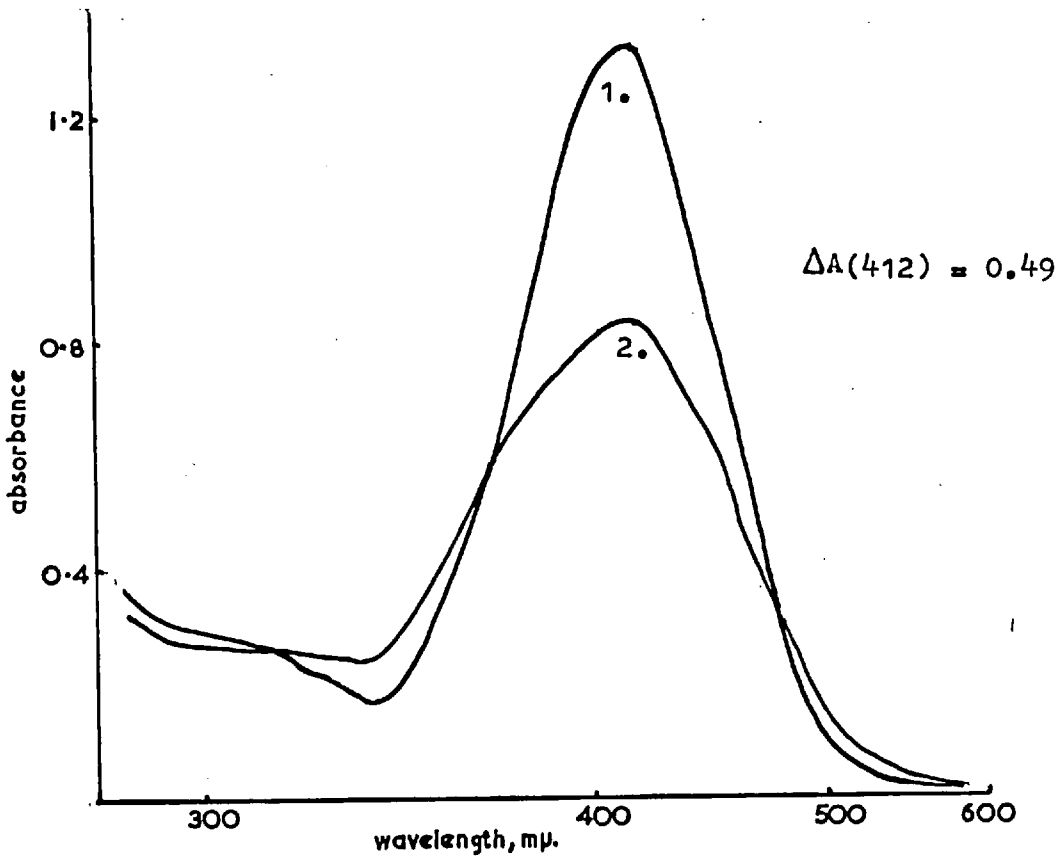
1. Dark spectrum.

2. Equilibrium spectrum, irradiation 622.

3. Equilibrium spectrum, irradiation OB1.

4-DIMETHYLAMINOAZOBENZENE.

(10^{-4}M in 10% v/v ethanolic benzene)

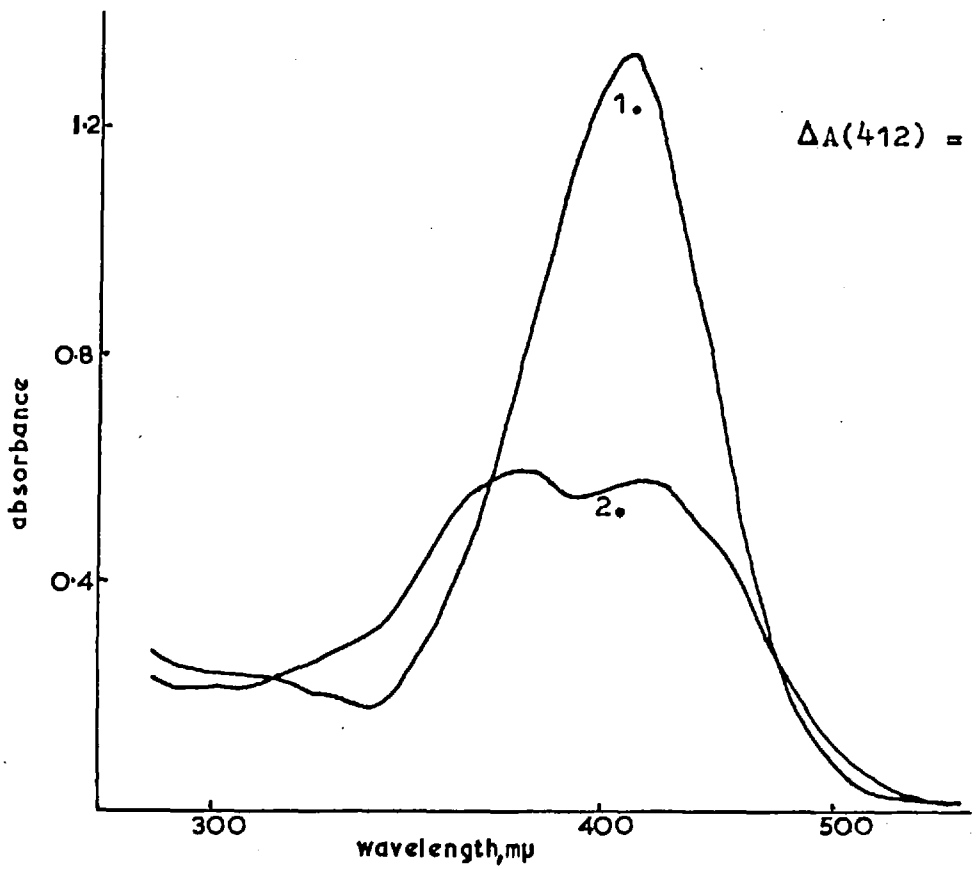


1. Dark spectrum.
2. Equilibrium spectrum, irradiation OB1.

FIG. 56

4-DIMETHYLAMINOAZOBENZENE.

(2.5×10^{-5}M in benzene)



1. Dark spectrum.
2. Equilibrium spectrum, irradiation at 410mu.

FIG.57

4-DIMETHYLAMINOAZOBENZENE in benzene.

Rates of trans-cis photo-isomerisation and reversal.

(10^{-4}M solution)

1. Irradiation 622.
2. Irradiation OB1.
3. Dark (thermal) reaction.

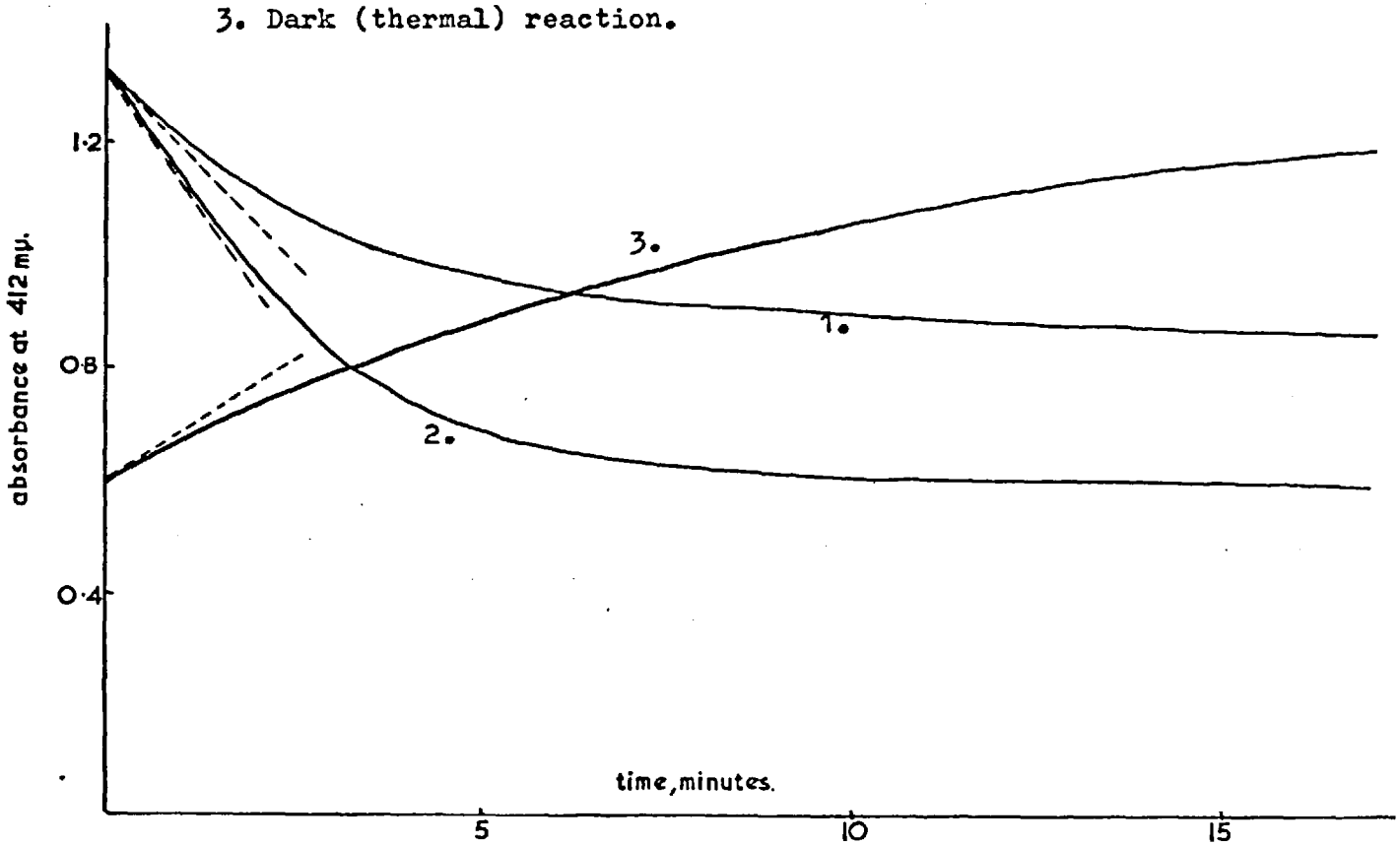
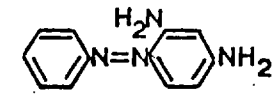
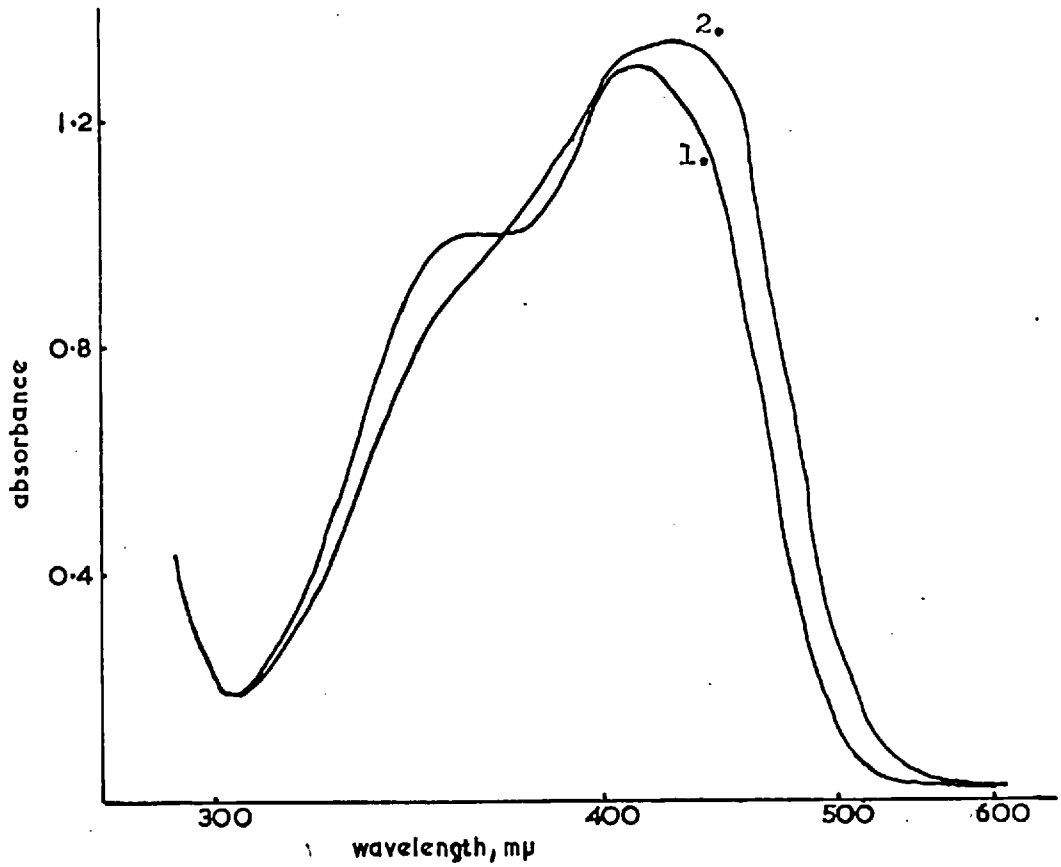


FIG.58

2,4-DIAMINOAZOBENZENE.

(1.5×10^{-4}M)





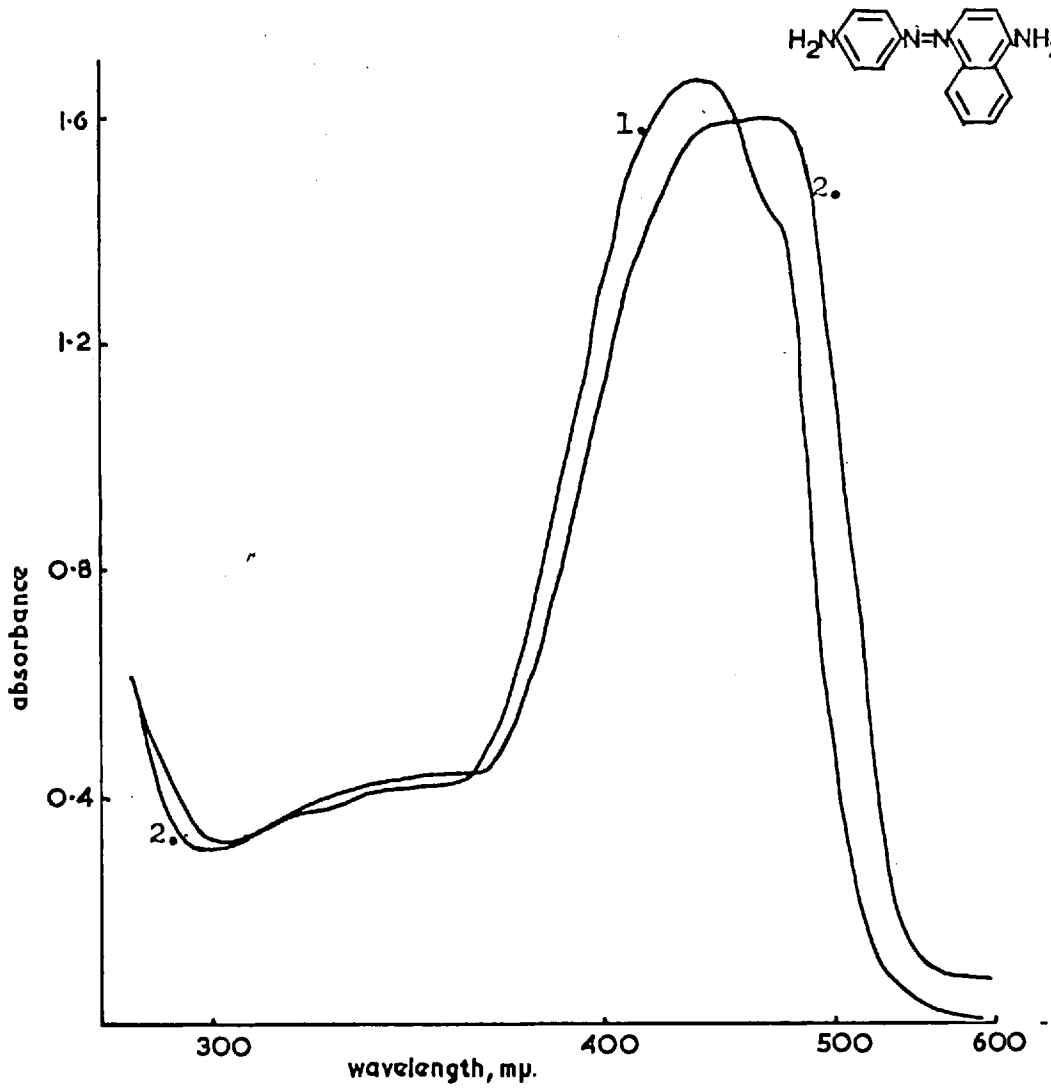
1. Dark and equilibrium spectra in benzene.

2. Dark and equilibrium spectra in 50% v/v ethanolic benzene.

FIG.59

4-(4'-AMINOPHENYLAZO)-1-NAPHTHYLAMINE.

(1.5×10^{-4}M)



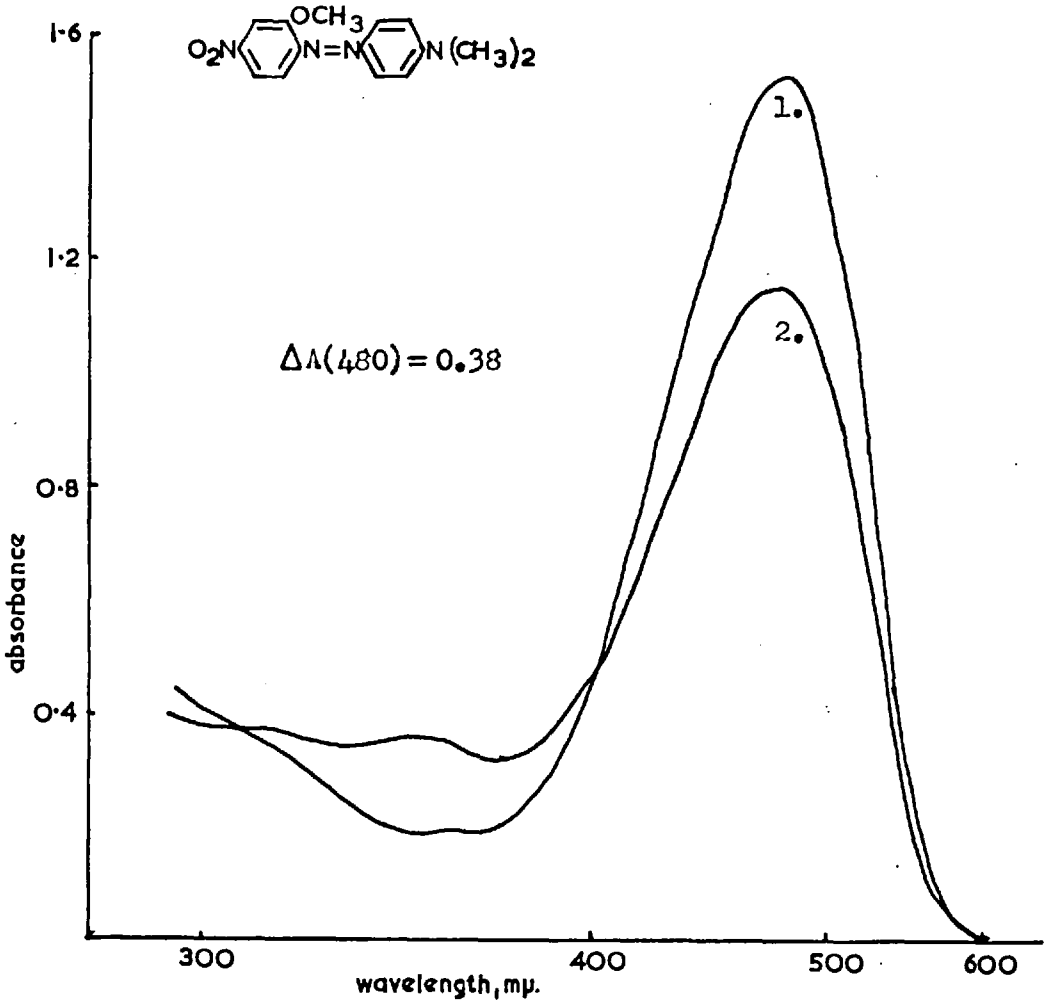
1. Dark and equilibrium spectra in benzene.

2. Dark and equilibrium spectra in 50% v/v ethanolc benzene.

FIG.60

2-METHOXY-4-NITRO-4'-DIMETHYLAMINOAZOBENZENE.

(10^{-4}M in benzene)



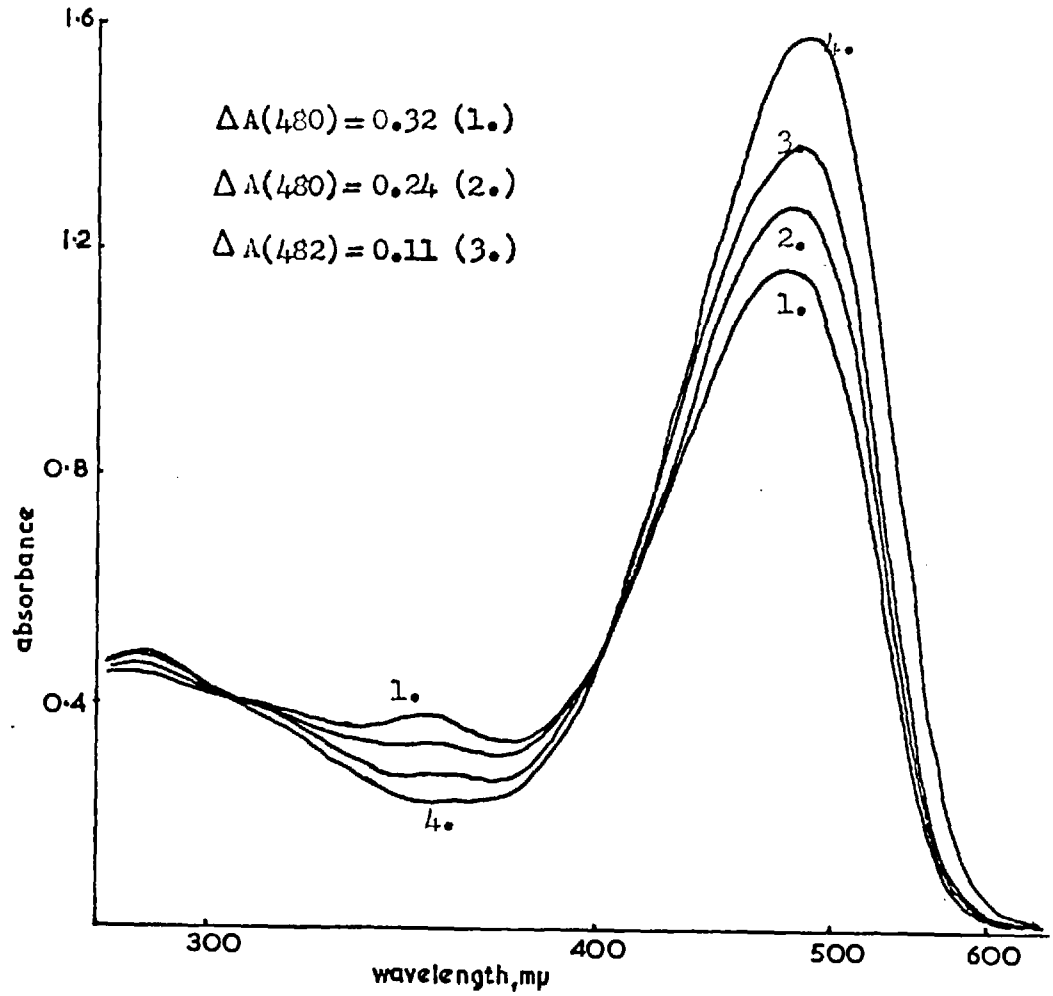
1. Dark spectrum.

2. Equilibrium spectrum, irradiation OB2.

FIG.61

2-METHOXY-4-NITRO-4'-DIMETHYLAMINOAZOBENZENE.

(10^{-4}M)



1. Equilibrium spectrum in 0.5% v/v ethanolic benzene, irradiation OB2

2. Equilibrium spectrum in 2% v/v ethanolic benzene, irradiation OB2.

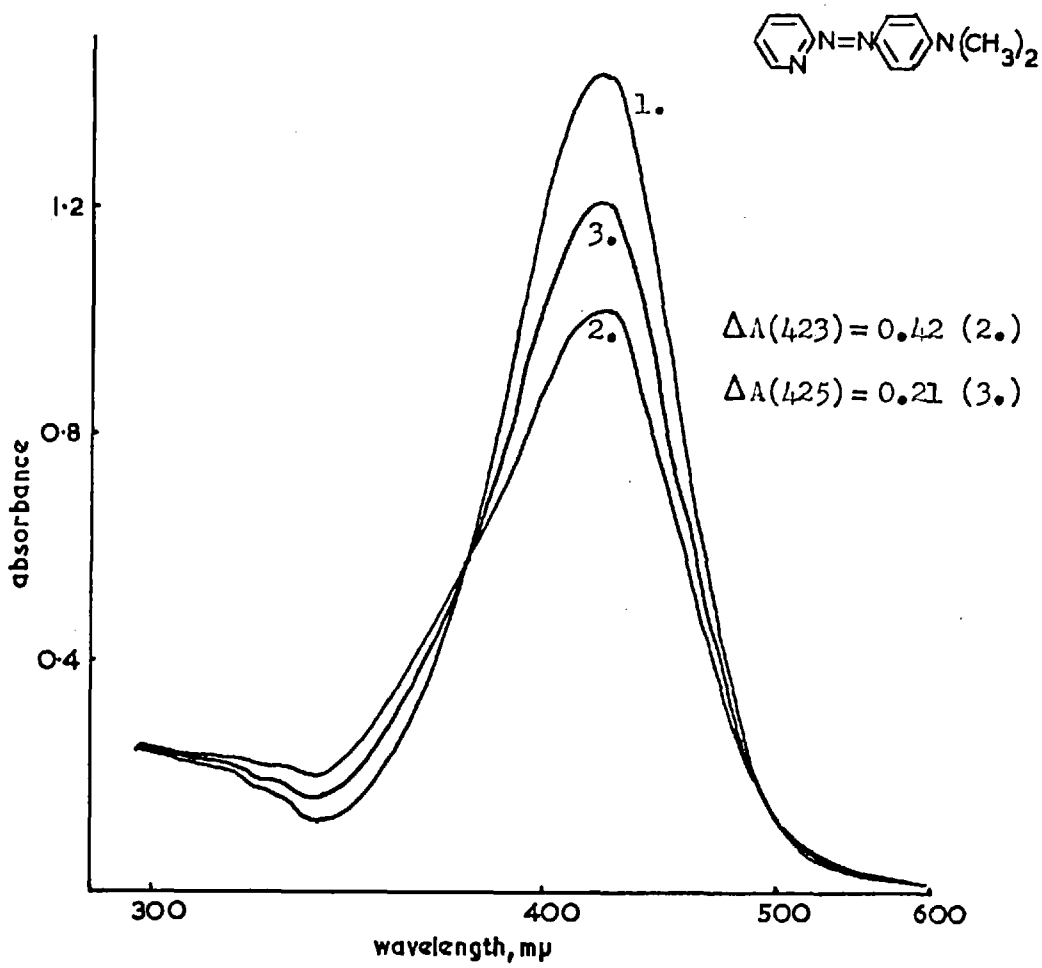
3. Equilibrium spectrum in 5% v/v ethanolic benzene, irradiation OB2.

4. Dark and equilibrium spectra in 50% v/v ethanolic benzene.

FIG. 62

2-(4'-DIMETHYLAMINOPHENYLAZO)-PYRIDINE.

(10^{-4}M)



1. Dark spectrum in benzene.
2. Equilibrium spectrum in benzene, irradiation OB1.
3. Equilibrium spectrum in 1% v/v ethanolic benzene, irradiation OB1.

FIG.63

CHRYSOPHENINE in water.

1. Dark spectrum (30ppm-flow-through:7.5ppm-direct)
2. Equilibrium spectrum, irradiation OB1 (30ppm-flow-through)
3. Equilibrium spectrum, irradiation at 405mμ (7.5ppm-direct)

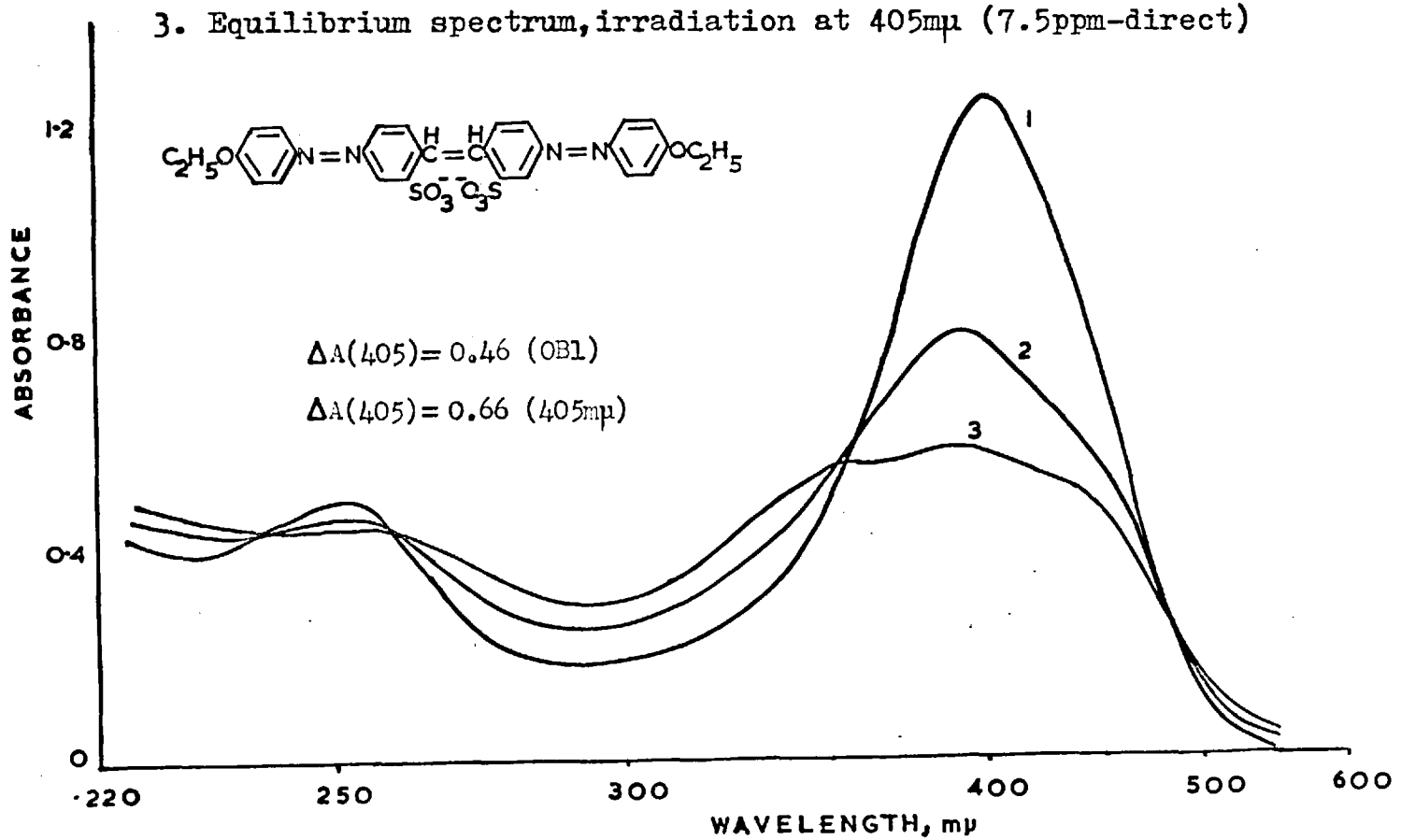


FIG.64

CHRYSOPHENINE in water.

Rates of trans-cis photo-isomerisation and reversal.

1. Irradiation OB1 (30ppm - flow-through): scale II
2. Irradiation OG1 (30ppm - flow-through): scale II
3. Dark (thermal) reaction (30ppm - flow-through): scale II
4. Irradiation at 405 mμ (7.5ppm - direct): scale I

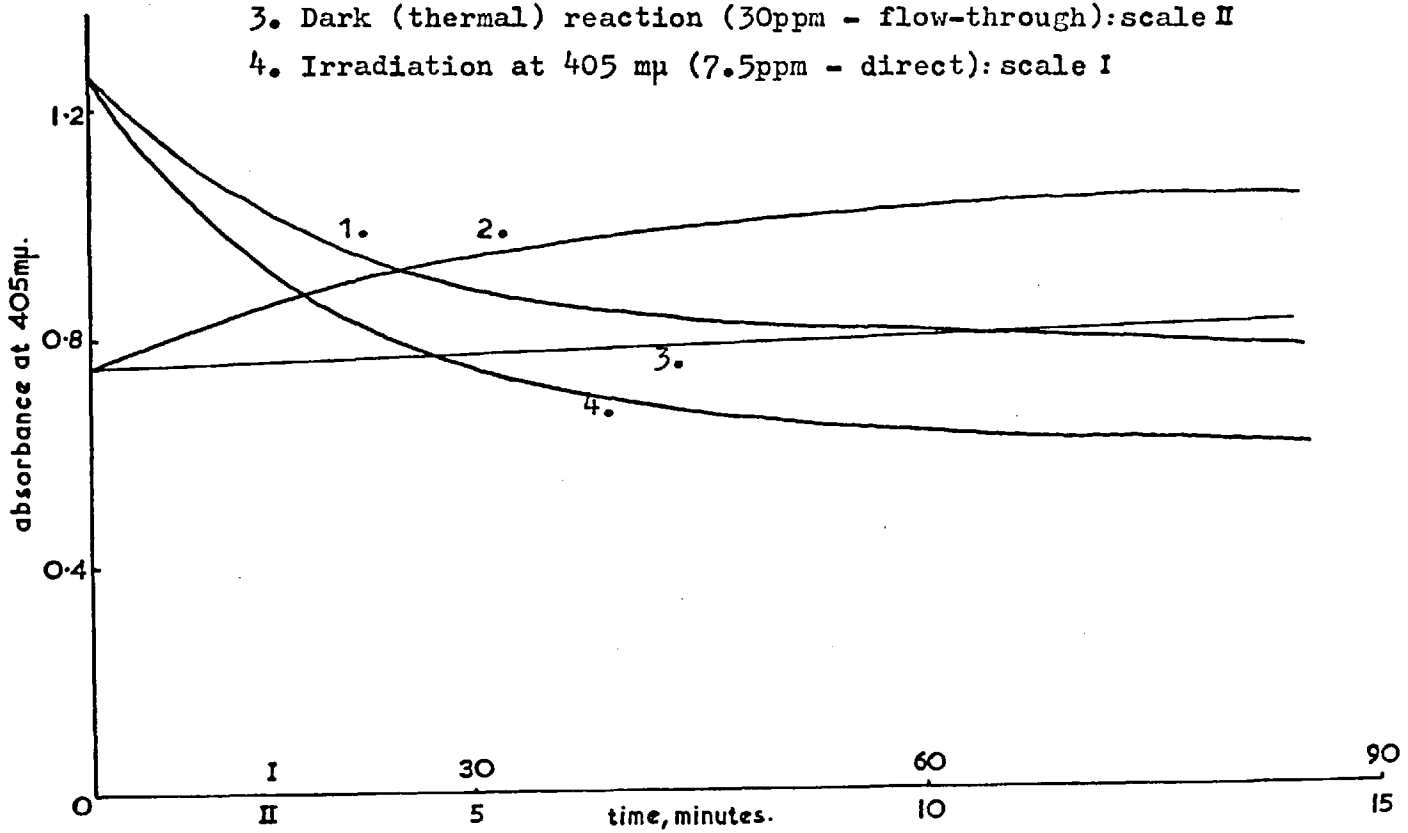
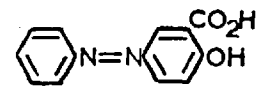
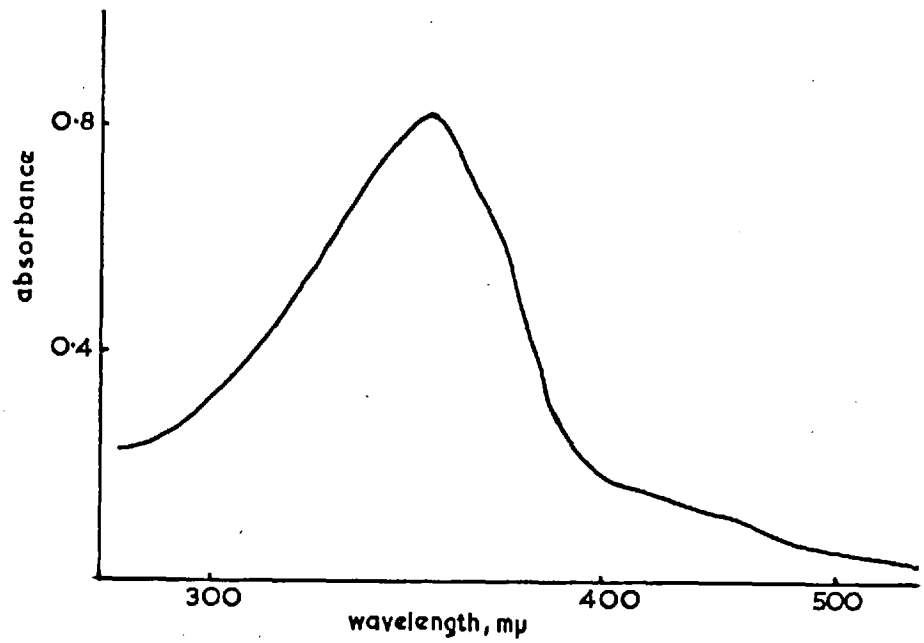


FIG. 65

2-HYDROXY-5-PHENYLAZOBENZOIC ACID.

(10^{-4}M in 50% v/v aqueous ethanol)



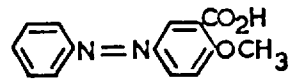


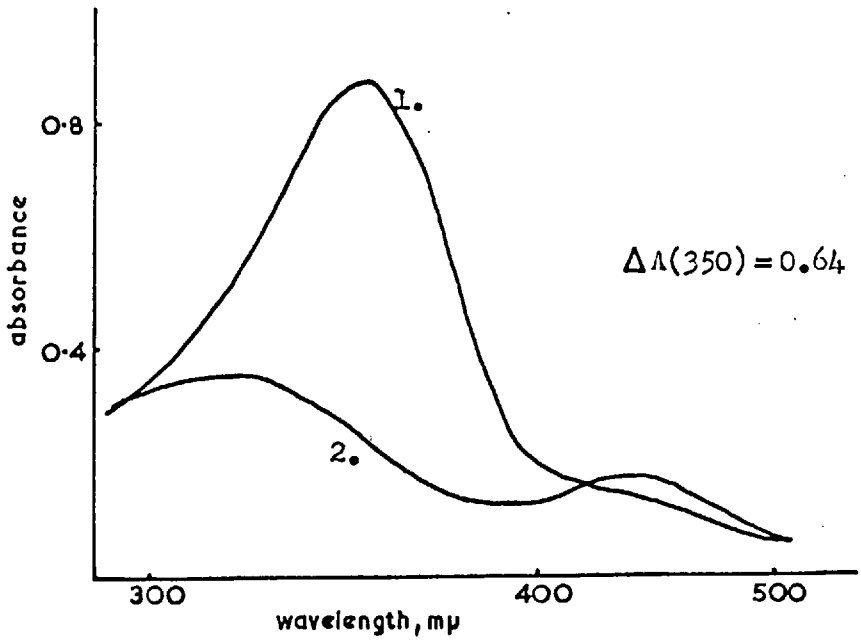
Dark and equilibrium spectra.

FIG. 66

2-METHOXY-5-PHENYLAZOBENZOIC ACID.

(10^{-4}M in 50% v/v aqueous ethanol)





1. Dark spectrum.

2. Equilibrium spectrum, irradiation 0X1.

5.3 Experimental

(1) Chemicals and Apparatus

Azo compounds: Ref: Section (2). The dyes were dissolved in benzene, aqueous ethanol, or distilled water to give 10^{-3}M solutions. The solutions were stored in the absence of light for at least one week before examination.

Benzene	Analytical reagent grade
Ethanol	Analytical reagent grade
Chloroform	Analytical reagent grade
Aluminium oxide, M.F.C.	Hopkin and Williams Ltd.

Irradiation and absorption measurement Ref: Chapter 2

(2) Azo Compounds

The source of each compound, or the details of its preparation are given below. Unless otherwise stated, the dyes were purified chromatographically (Ref: Section 3)

Azobenzene Hopkin and Williams Ltd.

4-hydroxyazobenzene The compound was prepared as follows [135]:

Aniline (9.3g:9.1ml) was dissolved in 2:1 v/v aqueous hydrochloric acid solution (60 ml) and the solution was cooled to 0°C. Sodium nitrite solution (approx. 8M) was added slowly, with stirring, until diazotisation was complete. (Immediate reaction with starch/iodide indicates the presence of excess nitrite.) The cooled ($t \leqslant 5^{\circ}C$) diazonium solution was slowly added to a cooled ($t \leqslant 5^{\circ}C$) solution of phenol, (9.4g) in 10% w/v aqueous sodium hydroxide solution (300 ml). The mixture was allowed to stand for 30 minutes, was acidified with hydrochloric acid, and the insoluble product separated by filtration. The crude product was suspended in water (500 ml) and subjected to steam-distillation to isolate the 2-hydroxy derivative. The ethereal extract of the distillate contained 2-hydroxyazobenzene, but in quantities too small for further purification and examination. The non-volatile 4-derivative was filtered off and recrystallised from absolute ethanol. Yield = 13.8g = 70% theory.

4-methoxyazobenzene 4-hydroxyazobenzene (5g) was dissolved in acetone (100 ml) containing a few ml. of distilled water. Alternate portions (1-2ml) of dimethyl sulphate and 20% w/v aqueous sodium hydroxide solution were added to the stirred solution during 3 hours, such that the solution remained slightly alkaline at all times

(pH = 7-9) . A sample of the mixture showed no colour change on dilution (aqueous acetone) and acidification. Stirring was continued for a further 1 hour. The excess dimethyl sulphate was destroyed by heating with excess sodium hydroxide solution. The acetone was distilled off and the oily product extracted into chloroform (250 ml). The solvent was removed by evaporation and the resultant oil was crystallised from 60-80°C petroleum ether by cooling the solution rapidly in acetone/dry ice. Yield = 4g.

1-phenylazo-2-naphthol Waxoline Yellow 15 (12055: C.I. Solvent Yellow 14) Imperial Chemical Industries Ltd. (I.C.I.)

2-methoxy-1-phenylazonaphthalene Waxoline Yellow 15 (5g) was methylated as outlined for the preparation of 4-methoxyazobenzene. The product was crystallised from a rapidly cooled solution in 60-80°C petroleum ether. Yield = 4g.

4-phenylazo-1-naphthol Brun Organol PPN (12000: C.I. Solvent brown 4) Française des Matières Colorantes S.A. (Fran.)

1-methoxy-4-phenylazonaphthalene 4-phenylazo-1-naphthol (5g) was methylated as outlined for the preparation of 4-methoxyazobenzene. The product was crystallised from cold 60-80°C petroleum ether.

Yield - 4g.

1-(4'-hydroxyphenylazo)-naphthalene Jaune organol ANP (11810: C.I. Solvent yellow 8). Fran.

1-(4'-methoxyphenylazo)-naphthalene The compound was prepared by methylation of the parent alcohol (5g.), as outlined for the preparation of 4-hydroxazobenzene, and crystallised from cold 60-80°C petroleum ether. Yield = 4g.

2, 4-dihydroxazobenzene Aniline (4.5 ml) was dissolved in 2:1 v/v aqueous hydrochloric acid (30 ml) and diazotisation was carried out as described previously. The cold diazonium solution was added slowly to a cooled solution of resorcinol (5.5g) in 10% w/v aqueous sodium hydroxide (60 ml). The mixture was stood in ice for one hour and acidified to precipitate the product, which was removed by filtration, washed with water, sucked dry, and recrystallised from absolute ethanol. Yield = 5g = 48% theory.

2,2'-dihydroxyazobenzene The compound was prepared as follows [136]: A paste of 2-nitrophenol (10g) and sodium hydroxide (50g) in distilled water (10ml) was cautiously heated to 200°C. The resultant mixture was shaken with 4N hydrochloric acid solution (300 ml). The product

was extracted into (peroxides free) ether (2 x 250 ml) and the ethereal solution evaporated to dryness. The residue was recrystallised from aqueous ethanol. Yield = 1g = 15% theory.

4,4' dihydroxyazobenzene The compound was prepared from 4-nitrophenol (5g) as described above. The reaction was less vigorous. The product was recrystallised, to constant melting point, from aqueous ethanol. Yield (pure) = 1.5g = 22.5% theory. m.p. = 214°C. (215°C [136]).

2-hydroxy-1,1'-azonaphthalene Waxoline red BNS (12170: C.I. Solvent Red 4) I.C.I.

1,5-dihydroxy-4-phenylazonaphthalene Aniline (9.1 ml) was diazotised, and the product coupled with 1,5-dihydroxyazonaphthalene (16g) as outlined for the preparation of 2,4-dihydroxyazobenzene. Yield = 18g = 68% theory.

8-(2',4'-dihydroxyphenylazo) quinoline The pure compound was prepared in this laboratory from 8-aminoquinoline and resorcinol. [137]

2-hydroxy-5-phenylazobenzoic acid The compound was prepared from the sodium salt, Solochrome yellow 3GS (13990: C.I. Mordant yellow 18)

I.C.I., by precipitation from acid solution. The product was recrystallised, to constant melting point, from absolute ethanol m.p. = 216-217°C. (218°C [136]).

2-methoxy-5-phenylazobenzoic acid Solochrome yellow 3GS (5g) was dissolved in water (150 ml), and methylated as outlined for the preparation of 4-methoxyazobenzene. The product solution was boiled with excess sodium hydroxide solution to destroy the excess dimethyl sulphate and to saponify any methyl ester present. The cooled solution was acidified, the product removed by filtration and recrystallised, to constant melting point, from aqueous ethanol. Yield (pure) = 3g. m.p. = 107-108°C (106°C [136]).

4-acetamido-2-phenylazophenol The compound was prepared, as follows, during the second stage in a 4-stage preparation of 2-hydroxyazobenzene from 4-aminophenol [138] which failed at the third stage.

4-aminophenol ⟶ 4-acetamidophenol A solution of 4-aminophenol (25g) in glacial acetic acid (23.8ml., 25g) was refluxed for 12 hours. The product was removed by filtration and recrystallised, twice, from hot distilled water. Yield = 22g = 59% theory. m.p. = 163-164°C (166-167°C [138]).

4-acetamidophenol ⟶ 4-acetamido-2-phenylazophenol Aniline (12.7 ml, 12.4g) was dissolved in a solution of hydrochloric acid (38 ml) in distilled water (270 ml) and diazotised in the usual manner. The cold diazonium solution was added slowly, with stirring, to a cold solution of 4-acetamidophenol (20.1g) and sodium acetate (50g) in ethanol (500 ml). The mixture was allowed to stand in ice for 30 minutes. On dilution with distilled water, a brown oil separated which converted to a yellow-green crystalline form on heating. The product was filtered off and a sample recrystallised to constant m.p. from aqueous ethanol. m.p. = 220-221°C (226°C [138]).

4-aminoazobenzene Hopkin and Williams Ltd.

4-dimethylaminoazobenzene Hopkin and Williams Ltd.

2,4'-diaminoazobenzene The free base was isolated from the monohydrochloride, Chrysoidine YS (11270: C.I. Basic orange 2) I.C.I., by precipitation from alkaline solution. The product was recrystallised from ethanol.

4-(4'-aminoazo) 1-naphthylamine Dispersol diazo black B. (11365: C.I. Disperse black 1) I.C.I.

2-methoxy-4-nitro-4'-dimethylaminoazobenzene Rouge acétaquinone 2JZ (11040: C.I. Disperse red 41) Fran.

2-(4'-dimethylaminoazo)pyridine Eastman Chemical Co.

4,4'-bis-(4-ethoxyphenylazo)-stilbene-2,2'-disulphonic acid. (disodium salt). Trivial name, Chrysophenine. This compound was available in the laboratory, in the pure state.

(3) Purification of azo compounds

(a) Thin layer chromatograms The azo compound (a few milligrams) was dissolved in chloroform, and the chromatogram prepared on alumina plates using chloroform as eluent. The R_f values were recorded. (Table 22). The position of colourless, or near colourless bands was established by standing the plates in iodine vapour for a few hours.

(b) Column chromatography The azo compound (0.3-0.5g) was shaken with chloroform or 50% v/v acetone/chloroform (3 ml). The filtrate was placed at the top of a 30" x 1" packed alumina column, and eluted with the pure solvent at a rate of 30 drops per minute. The eluent containing the major constituent was filtered and evaporated

to yield the pure azo compound.

(4) Absorbance Spectra and Phototropic Properties

(a) Flow-through Irradiation/Absorption: A known volume of the solution of azo compound (10^{-3}M) was transferred to the irradiation cell C_1 (Fig. 14). For studies in ethanolic benzene the requisite volume of ethanol was similarly transferred. The circuit was filled to the graduation with benzene (total volume = 86 ml), 50% aqueous ethanol, or distilled water (total volume = 87 ml.) A loose fitting cap was placed over the side-arm to prevent solvent losses by evaporation. The Xenon arc was struck, with a shutter in place to prevent light from reaching the sample, and the peristaltic pump was operated at the optimum rate (ref: page 45). The sample was circulated for 30 minutes, to effect adequate mixing, to degas the solution, and to allow an equilibrium temperature to be reached. The absorption spectrum was recorded. The spectrum was recorded again after an interval of 30 minutes, to check the solution stability. The spectrophotometer was converted for absorbance vs. time recording, the sample was exposed to irradiation, with the appropriate filter in place, and the kinetic curve for the forward reaction was plotted until an equilibrium state was reached.

Absorbance was measured at the wavelength corresponding to the maximum absorbance value of the solution in the normal 'dark' state. The absorption spectrum of the solution in the equilibrium state was recorded. The irradiation was shut off, and the absorbance vs time curve corresponding to the thermal reverse reaction was recorded, at the same wavelength as that used for the forward reaction. Care was taken throughout the procedure to avoid exposing the sample to laboratory lighting.

(b) Direct irradiation/absorption: The solution (6.0 ml) was transferred to the cuvette C_1 (Fig. 15). The absorption spectrum was recorded, and again after 30 minutes. The sample was exposed to irradiation of a wavelength at which absorbance was at a maximum, and the absorbance vs time curve was recorded, monitoring the sample at the same wavelength as that of irradiation. The equilibrium absorption spectrum was recorded. With the irradiation shut off, the absorbance vs time curve for the reverse process was recorded using the same monitoring wavelength as above. Care was taken to avoid exposure of the sample to stray light either before or during the investigation.

5.4 Discussion of Results

The absorption spectra of solutions of the *para*-substituted *trans* azobenzenes (Figs. 28, 29, 31, 51, 54) follow the expected pattern. The main absorption bands are the result of $\pi-\pi^*$ electron transitions, and the weak absorption at somewhat longer wavelengths is due to the forbidden $n-\pi^*$ transition from non-bonding orbitals on the nitrogen atoms. The introduction of auxochromes in the *p*-position has the expected bathochromic shift, increasing in the order

$$-H < -OH \simeq -OCH_3 < -NH_2 < -N(CH_3)_2,$$

which agrees with results previously reported for these compounds.[14] The double, or broad single, peaks exhibited by the *ortho*-substituted azobenzenes in solution (Figs. 32, 33, 44, 50, 58) is probably due to the alternate paths of resonance possible between the substituent and the azo group.[139]

Solutions of the naphthyl azo derivatives absorb light at longer wavelengths than the corresponding phenylazo compounds because of increased conjugation. Substitution in the 2- or 4- positions in the naphthalene ring leads to more complex absorption spectra (Figs. 32-37, 47-48, 59) again believed due to the alternate resonance

paths possible. Chrysophenine in solution (Fig. 63) absorbs light at shorter wavelengths than would be expected for such a long conjugated molecule, probably because of steric distortion at the central C = C bond.

Irradiation of the phototropic solutions results in the hypochromic and hypsochromic shifts in the absorption spectra consistent with the formation of sterically distorted cis isomers (Ref: pp.17-18). The slight increase in absorption at longer wavelengths is presumed due to the greater probability of $n-\pi^*$ transitions in the cis isomer.

The quantum yields for the forward photochemical process lie, with few exceptions, between the values 0.24 and 0.35 (Table 23). The variation in these values with the structure of the azo compounds and the polarity of the solvent is insignificant with respect to the observed variation in the degree of phototropism attained. The results obtained for azobenzene compare favourably with that given by Zimmerman et al [19] viz: 0.12 at 365 mμ, but are nevertheless considered to be low, because the light transmitted by the OXI filter (Fig. 16) does not correspond closely with the absorption spectrum of trans azobenzene. (Fig. 28). The figure given by

Birnbaum and Style [17] of 0.20 at 365 mμ is considered to be more accurate. The low results obtained for 2-methoxy-1-phenylazonaphthalene and 1-methoxy-4-phenylazonaphthalene are believed due to light absorption by the cis isomer at the wavelength of maximum absorption by the trans form. (Ref. pp. 123-4 and Figs. 33, 36). The low result for chrysophenine is to be expected for a complex molecule containing more than one azo group.

The half-life times for the photochemical trans-cis conversions are of limited value, since they are dependent upon the rate of the thermal reaction, and on the relative rates of the forward and reverse photochemical processes. The latter will depend, for a given intensity of irradiation, on the distribution of the absorbed (polychromatic) light between the cis and trans forms in solution, which will vary continuously, and in an indeterminate manner, during isomerisation. It is for this reason that it has not been possible to evaluate quantum yields for the reverse photochemical process. For the purposes of this discussion it is assumed that, while the Φ values for the photochemical reversal may be somewhat larger [17,19,21] than those for the forward process, they show a similar insignificant variation with chemical structure and solvent polarity.

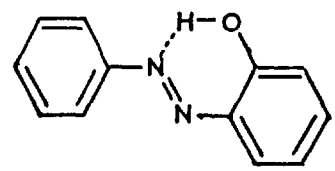
The photochemical reversal could be used to accelerate the cis-trans conversion in solutions where the thermal reversal was negligibly slow, thus confirming their phototropic (as opposed to irreversible photochemical) properties. Azobenzene, for instance, could be converted from the ΔA (322) = 1.25 (OXI) state (Fig. 28) to a ΔA (322) = 0.10 state in approx. 12 minutes on exposure of the solution to light transmitted by the OB2 filter (Fig. 16). (N.B. Cis azobenzene in solution absorbs more light than the trans isomer at wavelengths greater than 360 mμ).

The factor which predominantly influences the degree of phototropism attained for the azo compounds studied is the rate of the thermal reversal. This is clearly seen from a comparison of the results given in Table 23, and the corresponding dark and equilibrium spectra recorded. The effects of the structure of the solute, and the polarity of the solvent on phototropic behaviour will therefore be discussed in terms of the variation in the rate of the thermal cis-trans reaction.

With the exception of 4-acetamido-2-phenylazophenol in benzene (Fig. 50) which shows a small, reversible, spectral shift on exposure to unfiltered light, compounds containing hydroxyl or amino groups in

the ortho position relative to the azo bond are not phototropic under the conditions used. (Figs. 32, 47, 49, 58). This behaviour has been suggested [14], in the case of o-hydroxyazo compounds, to be due to hydrogen bonding between the hydroxyl hydrogen and the β-nitrogen atom (Fig. 67), thus stabilising the trans isomer. The

FIG. 67



observed bathochromic shifts in the spectra of the solutions of o-hydroxy- and o-aminoazo compounds with respect to the o-methoxyazo compounds and related p-substituted derivatives tends to support this suggestion.

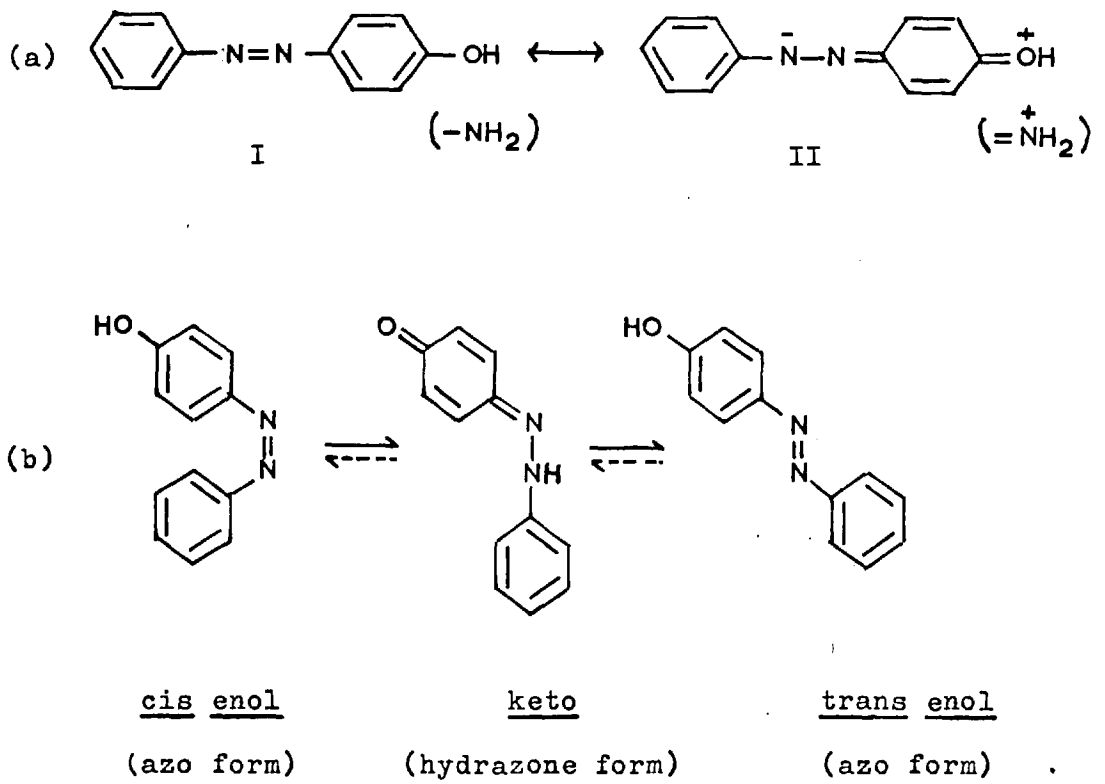
Azobenzene, and the o- and p- methoxy derivatives of azobenzene and benzeneazonaphthalene, (Figs. 28, 31, 33-34, 36-37, 42, 43) are characterised by the stability of their cis isomers. (Thermal cis-trans conversion was generally too slow for the measurement of half-life times and rate constants (Table 23).) The degree of photo-tropism attained is very much in favour of the cis isomer, and is

independent of solvent polarity.

The benzene solutions of azo compounds containing hydroxyl or amino groups in the para position either exhibit no phototropic effect (Figs. 35, 48, 59) or are limited in their phototropic behaviour (Figs. 29, 38, 51) by rapid thermal reverse reactions. The rates of these thermal reactions increase markedly with solvent polarity (Figs. 30, 39-41, 52-53) and none of the above compounds exhibited phototropism in solvents more polar than 10% v/v ethanolic benzene.

The instability of the cis isomers of 4-hydroxy- and 4-aminoazobenzene in solution has been suggested by Hartley [12] to be due to mesomerism between the two extreme forms shown in Fig. 68 (a). Whilst the equilibrium between the two forms will lie far to the left, the azo bond will have appreciable single bond character, thus facilitating the cis-trans isomerisation. A mesomeric effect of this sort could explain the phototropic behaviour of p-hydroxy and p-aminoazocompounds in more polar solvents, in that the ionised mesomeric form, II (Fig. 68 (a)) would be more favourable. However, mesomerism alone cannot account for the apparent stability of the cis, p-methoxyazo compounds, which would be expected to behave similarly, or for the enhanced phototropic behaviour of 4-dimethylaminoazobenzene in benzene (Fig.

FIG. 68



54) with respect to the 4-amino derivative (Fig. 51).

The existence of intermediate tautomeric forms (effectively stabilised forms of the extreme mesomeric form, II (Fig. 68 (a)) might account for the ease of the cis-trans conversion in p-hydroxyazo compounds. The thermal reverse reaction could then proceed as indicated in Fig.

68 (b). The *cis*-end ⟶ keto ⟶ *trans*-enol reaction would be more rapid in more polar solvents because of the greater ease of initial protonation of the β-azo nitrogen atom. The stability of the methylated derivatives in the *cis* form would follow from their inability to form such tautomers. The suggestion is supported by the fact that 4-phenylazo-1-naphthol is known to be tautomeric [140]. (The unusual absorption spectrum of the compound insolution (Fig. 35), and the absence of phototropism, indicates the presence of a more stable keto form.)

The behaviour of the 4-aminoazo compounds (Figs. 51-53, 59) could be accounted for in terms of *amine*-*imine* tautomerism. Similarly, the non-phototropic behaviour of the *o*-hydroxy and *o*-aminoazo compounds could be due to the formation of tautomeric forms *via* an intermediate hydrogen bond.* *i.e.* as opposed to stabilisation of the *trans* form by hydrogen bonding (see above). The phototropism exhibited by the *o*-methoxy azo compounds (Figs. 33, 34) follows from either of these arguments.

The effects of solvent polarity on the phototropism of solutions of 4-dimethylaminoazobenzene (Figs. 54, 55), 2-methoxy-4-nitro-4'-

* *cf.* The phototropism of Schiff's Bases (pp 22-23)

dimethylaminoazobenzene (Figs. 60, 61), and 2-(4'-dimethylaminoazo) pyridine (Fig. 62) cannot be explained on the basis of tautomer formation. A mesomeric effect, in which the extreme (ionised) form has greater stability, cf. Fig. 68 (a), because of the presence of a tertiary nitrogen atom in the p-position, could account for the behaviour of these compounds.

It appears then, that the stability of the cis isomers of the azo compounds studied is governed by a combination of the phenomena of mesomerism and tautomerism. The variation in the spectral properties of some of the non-phototropic solutions with solvent polarity (Figs. 32, 58, 59) points towards the existence of a tautomeric equilibrium in the 'dark' state. Conversely, the simple absorption spectra exhibited by 4-hydroxyazobenzene, 1-(4'hydroxyphenylazo) naphthalene, and 4-aminoazobenzene in benzene and ethanolic benzene (Figs. 29-30, 38-41, 51-53) indicate that the keto (or imine) form can only exist as an unstable intermediate between the cis and trans enol (or amine) forms.

The effect of solvent polarity was extended to an examination of 5-phenylazo-2-hydroxybenzoic acid, and the methyl ether thereof, in 50% aqueous ethanol (Figs. 65, 66). While the parent alcohol is non-

phototropic, the methyl ether shows extensive phototropic behaviour. The complex ethylated molecule, Chrysophenine (Fig. 63,) also forms a stable cis isomer in polar solvents.

The behaviour of the dihydroxyazobenzenes in solution is anomalous and has not been discussed above. 4,4'-Dihydroxyazobenzene is phototropic in benzene, the phototropism being very sensitive to the presence of ethanol in the solvent (Fig. 46). However, the rate of the reverse reaction could not be recorded, and the dark and equilibrium spectra are of doubtful accuracy, because of extensive solute adsorption by the nylon tubing used in the flow-through technique. Such adsorption is also believed to account for the apparent irreversible photochemical change shown by 2,4-hydroxyazobenzene in benzene. (Fig. 44). 2,2'-Dihydroxyazobenzene in benzene (Fig. 45) undergoes an irreversible photochemical reaction. The rate of change is linear, and the isobestic points suggest a simple rearrangement of the molecule, but elucidation of the exact nature of the reaction requires further investigation.

CHAPTER 6.

Cis-trans photo-isomerisation of aromatic azo compounds. Effect of concentration. Examination of phototropic mixtures

6.1 Preface

The previous chapter was concerned with the effects of chemical composition of the solute and the polarity of the solvent on the phototropic behaviour of solutions of aromatic azo compounds. This chapter deals with the effects of solute concentration on the light lability of two typical phototropic solutions, namely, 1(4'-hydroxyphenylazo) naphthalene in benzene, and 1(4'-methoxyphenylazo) naphthalene in benzene. (Ref: Figs. 38, 42).

An examination of the phototropism of mixtures of solutions which have closely related absorption spectra, but differ in their phototropic properties, has been carried out to determine whether the phototropic effect can be used as a means of resolution of such mixtures. Mixed solutions of 1-(4'-hydroxyphenylazo) naphthalene, 1-(4'-methoxyphenylazo) naphthalene and 2, 4-dihydroxyazobenzene in

benzene and ethanolic benzene have been investigated. As was established in chapter 5, the first of these compounds exhibits phototropism in benzene, but not in 10% v/v ethanolic benzene, and the second is equally phototropic in both these solvents. 2, 4-Dihydroxyazobenzene shows only a small irreversible change in either solvent.

6.2 Results

Figs. 69 and 70 show the effects of concentration on the dark and equilibrium absorption spectra of 1-(4'-hydroxyphenylazo) naphthalene and 1-(4'-methoxyphenylazo) naphthalene in benzene. Figs. 70-74 show the corresponding variations in the rates of the forward photochemical reaction and the thermal reversal.

The graphs on Figs. 75 and 76 depict data compiled from the results shown on the previous six figures. Graph I, in each case, shows the variation in the maximum absorbance of the 'dark' solution, A_{trans} (380), (curve (a)), and the variation in the difference between the dark and equilibrium spectra, ΔA (380), (curve (b)), with total concentration. Graph II, in each case, is a plot of the rate of decrease in the concentration of the cis isomer, $-\frac{d[cis]}{dt}$, due to

thermal reversal, vs the concentration of cis isomer, [cis], at the phototropic equilibrium. The $-\frac{d[cis]}{dt}$ values were obtained from the slopes of the absorbance vs. time curves at the onset of the reverse reaction, and the [cis] values at equilibrium were evaluated from the $\Delta A(380)$ values, after correction for the cis absorbance at 380 mμ. (Ref: p.123).

The phototropic data for the various mixtures is shown on Table 25. The Φ and k values were determined as described in Section 5.2.

N.B. The 'apparent' Φ values recorded in Table 25 represent the number of cis molecules of the active species formed per photon of light absorbed by the mixture.

TABLE 25

Composition of Mixture*	Solvent	$\Delta A(380)$	$t_{\frac{1}{2}}$, minutes forward	reverse	$\Phi_{app.}$	k, mins.$^{-1}$
A (0.5) C (0.5)	C_6H_6	0.19	4.15	9.5	0.12	7.30×10^{-2}
"	10% EtOH/ C_6H_6	0.01	-	-	-	-
A (0.5) C (1.0)	C_6H_6	0.15	5.1	7.9	0.09	8.77×10^{-2}

(Continued...

TABLE 25 - Continued

Composition of Mixture*	Solvent	ΔA(380)	$t_{\frac{1}{2}}$, minutes forward	reverse	$\Phi_{app.}$	k, mins.$^{-1}$
A (0.5) C (1.0)	10% EtOH/ C_6H_6	0.04	-	-	-	-
A (1.0) C (0.5)	C_6H_6	0.25	3.6	8.0	0.16	8.66×10^{-2}
"	10% EtOH/ C_6H_6	0.01	-	-	-	-
B (0.5) C (0.5)	C_6H_6	0.35	5.5	-	0.11	-
B (0.5) C (1.0)	C_6H_6	0.31	8.5	-	0.08	-
B (1.0) C (0.5)	C_6H_6	0.64	8.0	-	0.17	-
A (0.5) B (0.5)	C_6H_6	0.63	4.65	-	-	-
A (0.5) B (0.5)	10% EtOH C_6H_6	0.31	4.9	-	0.15	-
A (0.5) B (0.5) C (0.5)	C_6H_6	0.40	7.0	-	-	-

(Continued...

TABLE 25 - Continued

Composition of Mixture*	Solvent	$\Delta A(380)$	$t_{\frac{1}{2}}$, minutes forward	reverse	$\Phi_{app.}$	k, mins.$^{-1}$
A (0.5) B (0.5) C (0.5)	10% EtOH/ C_6H_6	0.12	5.0	8.2	0.16	8.45×10^{-2}

* A = 1(4'-hydroxyphenylazo) naphthalene

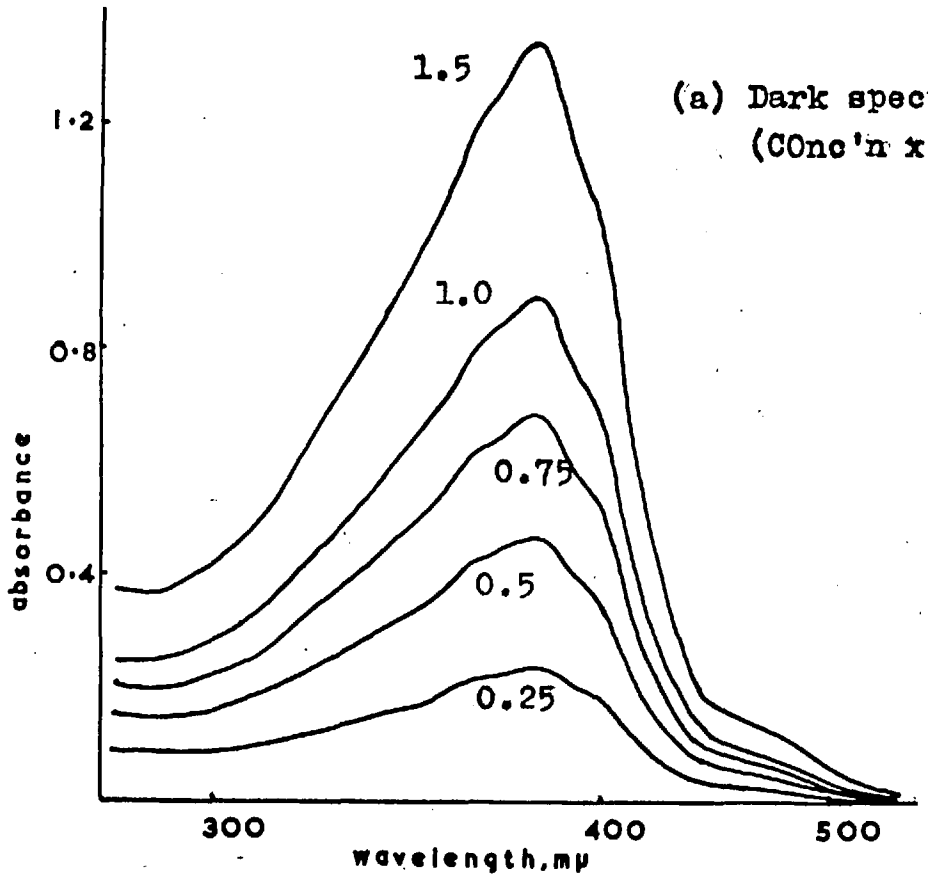
B = 1(4'-methoxyphenylazo) naphthalene

C = 2,4 - dihydroxyazobenzene

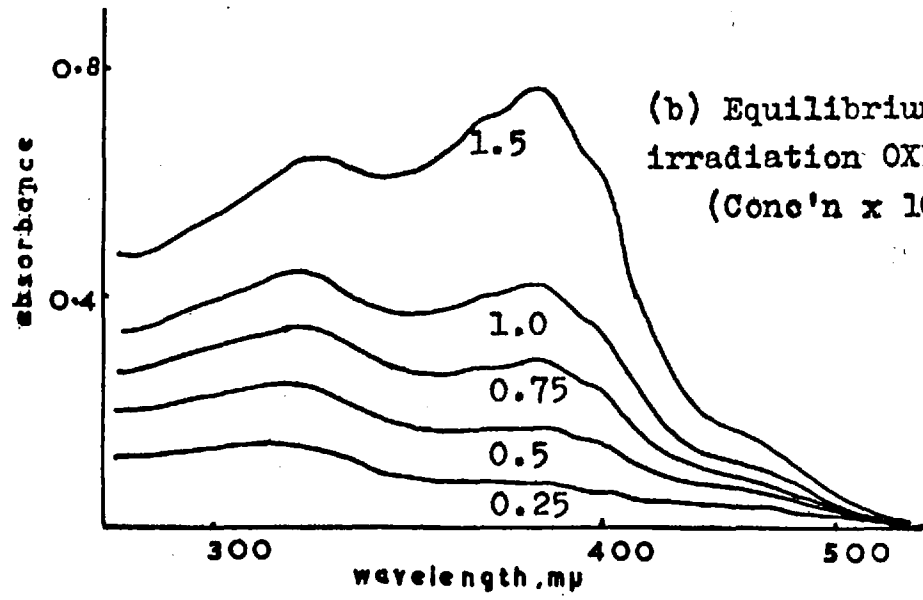
The concentration of each species (x 10^{-4}M) is recorded in parenthesis.

FIG. 69

Photo-isomerisation of 1-(4'-HYDROXYPHENYLAZO) NAPHTHALENE in benzene.



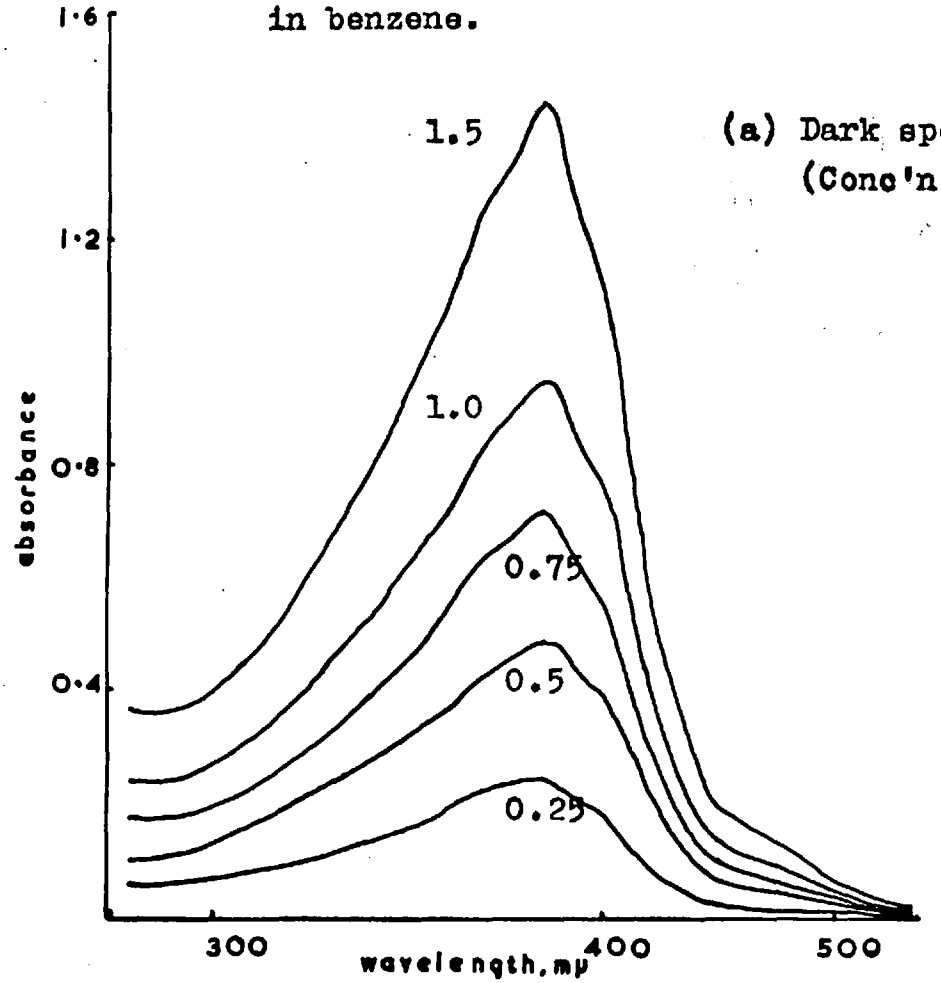
(a) Dark spectra.
(Conc'n x 10^{-4}M)



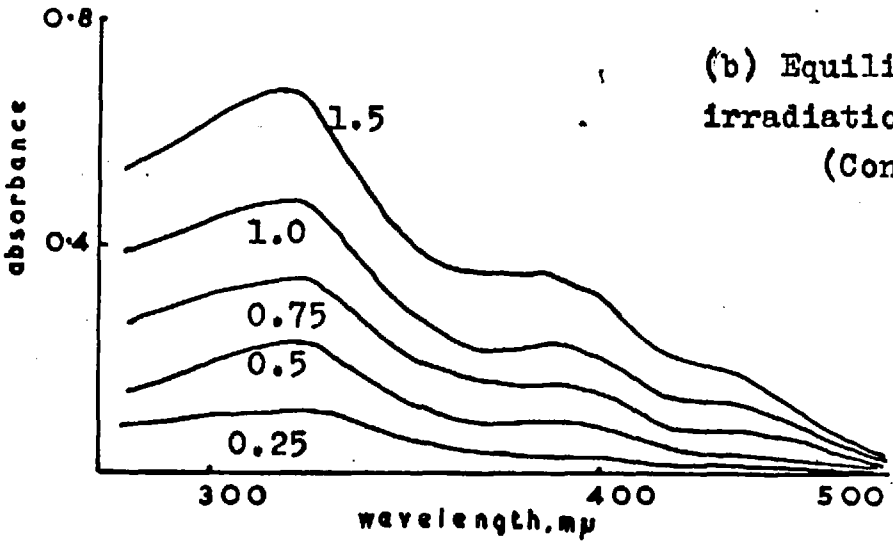
(b) Equilibrium spectra, irradiation 0X1.
(Conc'n x 10^{-4}M)

FIG. 70

Photo-isomerisation of 1-(4'-METHOXYPHENYLAZO) NAPHTHALENE in benzene.



(a) Dark spectra.
(Conc'n x 10^{-4}M)



(b) Equilibrium spectra, irradiation 0X1.
(Conc'n x 10^{-4}M)

FIG.7I

1-(4'-HYDROXYPHENYLAZO) NAPHTHALENE in benzene.

Rate of <u>trans-cis</u> photo-isomerisation vs. concentration.

(conc'n x 10^{-4}M:irradiation OX1:t=25±1°C.)

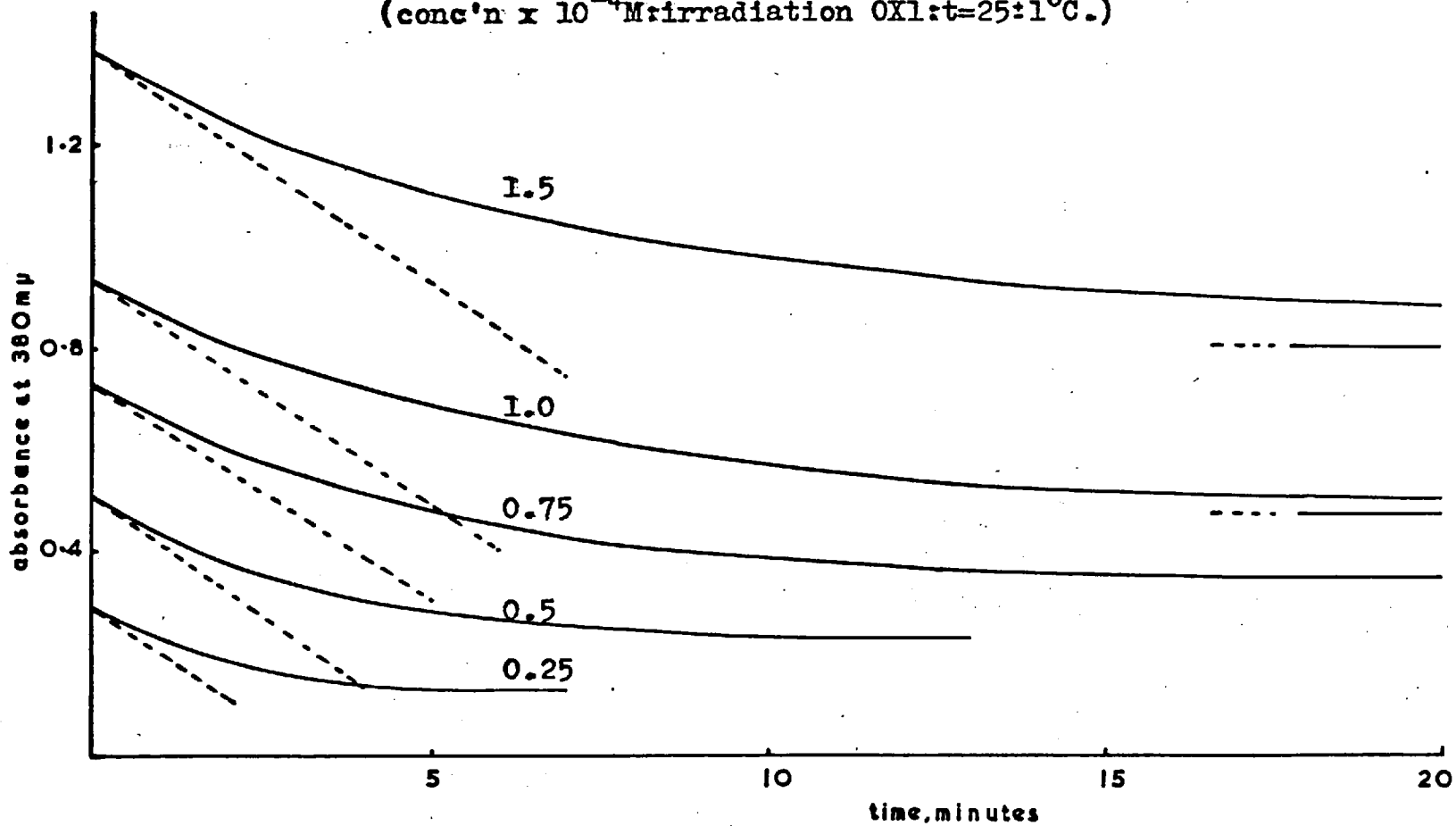


FIG. 72

1-(4'-METHOXYPHENYLAZO) NAPHTHALENE in Benzene.

Rate of <u>trans</u>-<u>cis</u> photo-isomerisation vs. concentration.

(Conc'n x 10^{-4}M: Irrad'n OX1: t=25±1°C)

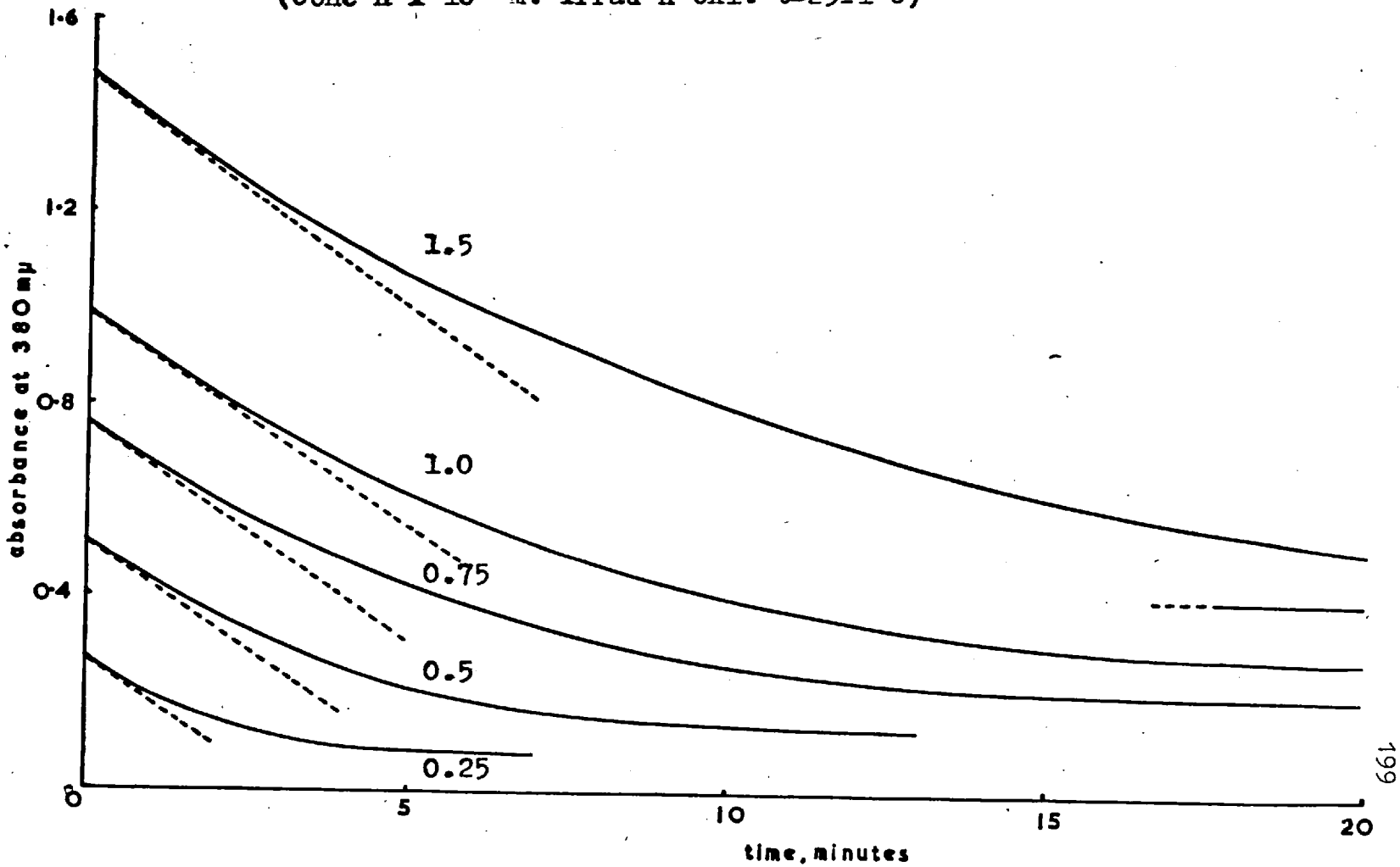


FIG. 73

1-(4'-HYDROXYPHENYLAZO) NAPHTHALENE in Benzene.
Rate of dark (thermal) reaction vs. concentration.

(Conc'n x 10^{-4}M: T=25±1°C.)

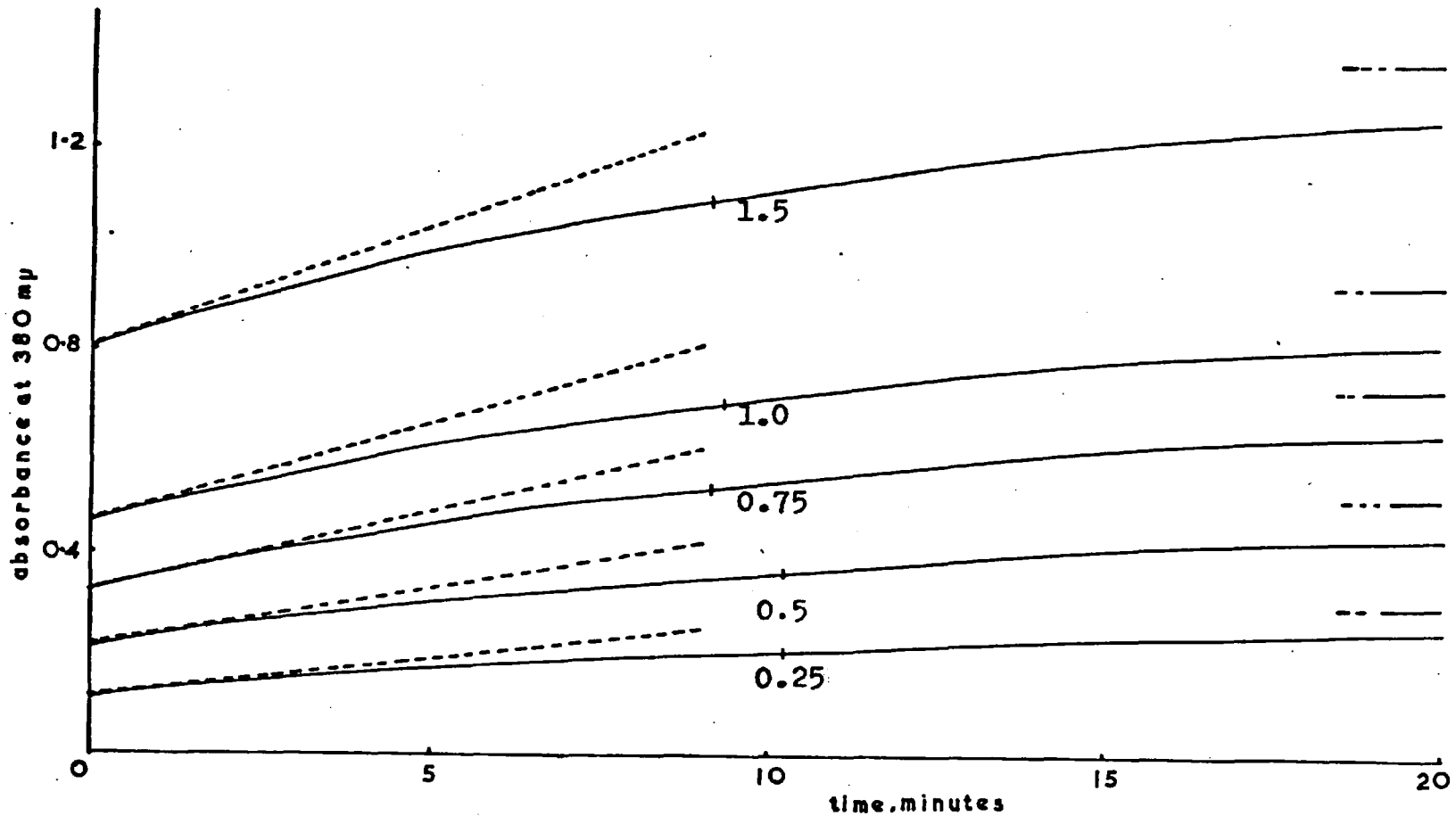


FIG.74

1-(4'-METHOXYPHENYLAZO) NAPHTHALENE IN BENZENE.
Rate of Dark (thermal) Reaction vs. Concentration
(Conc'n x 10^{-4}M;t=25±1°C.)

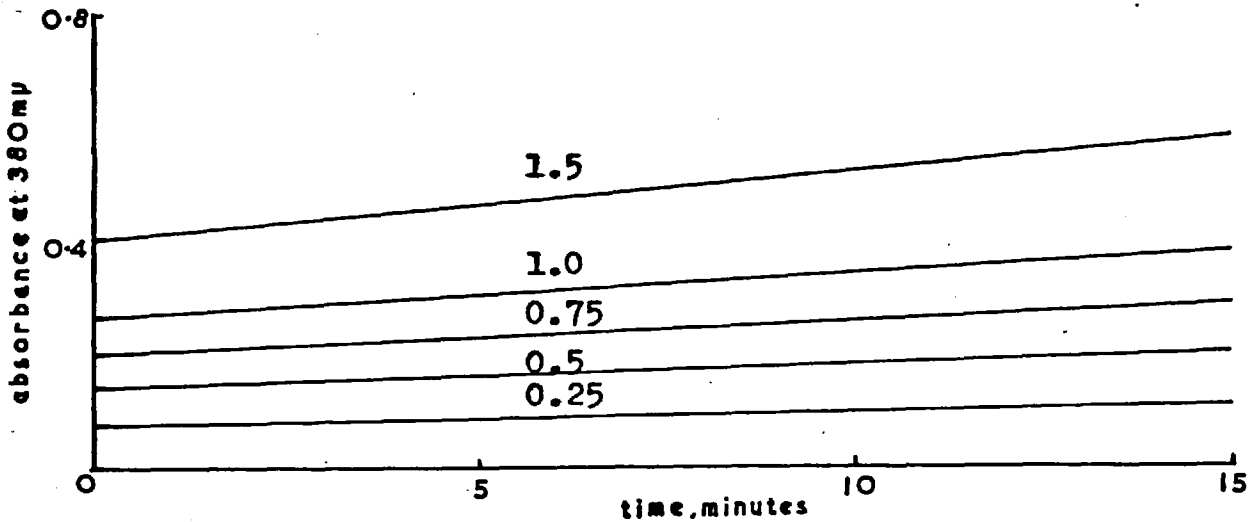
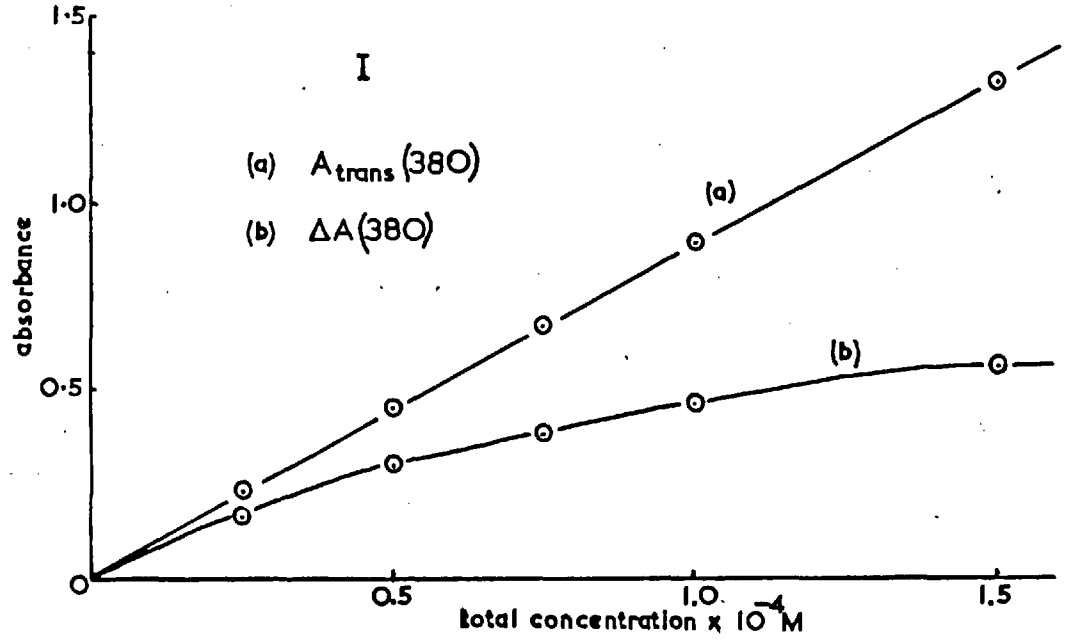


FIG. 75

1-(4'-HYDROXYPHENYLAZO) NAPHTHALENE in benzene.



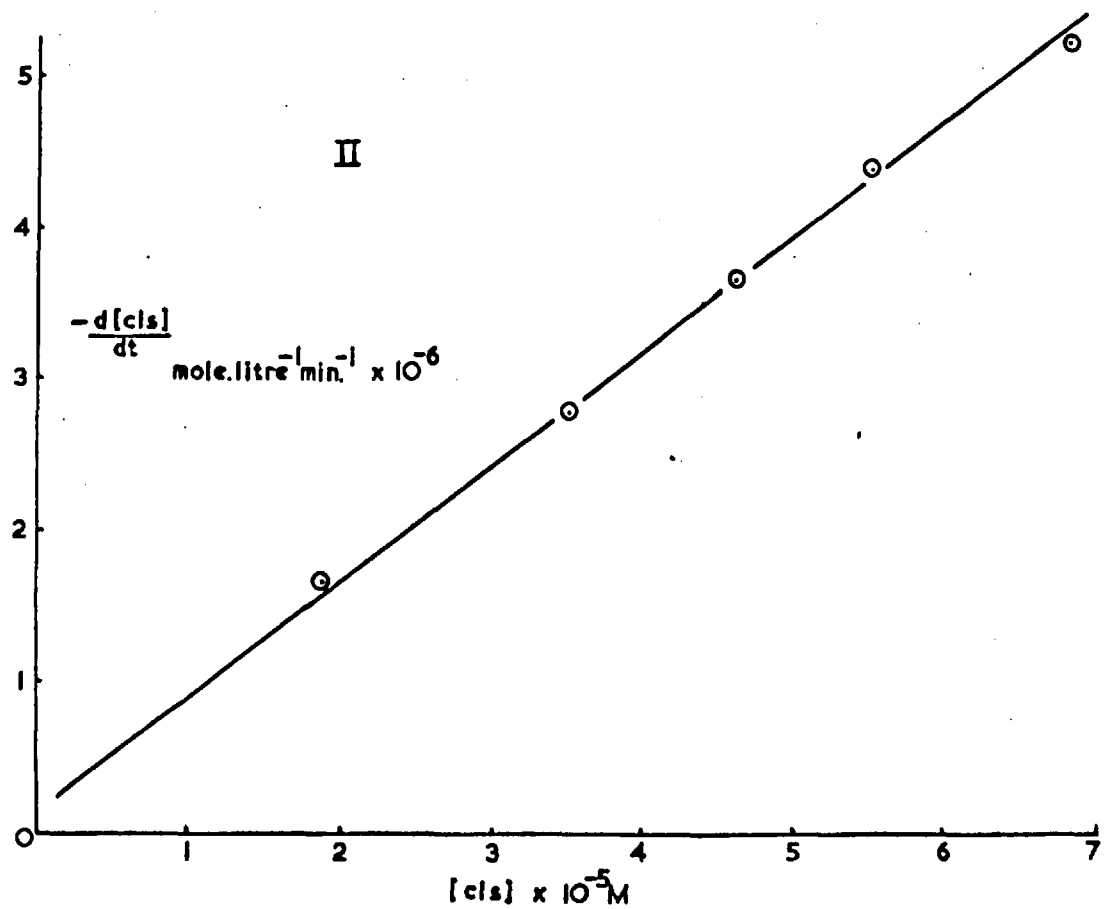
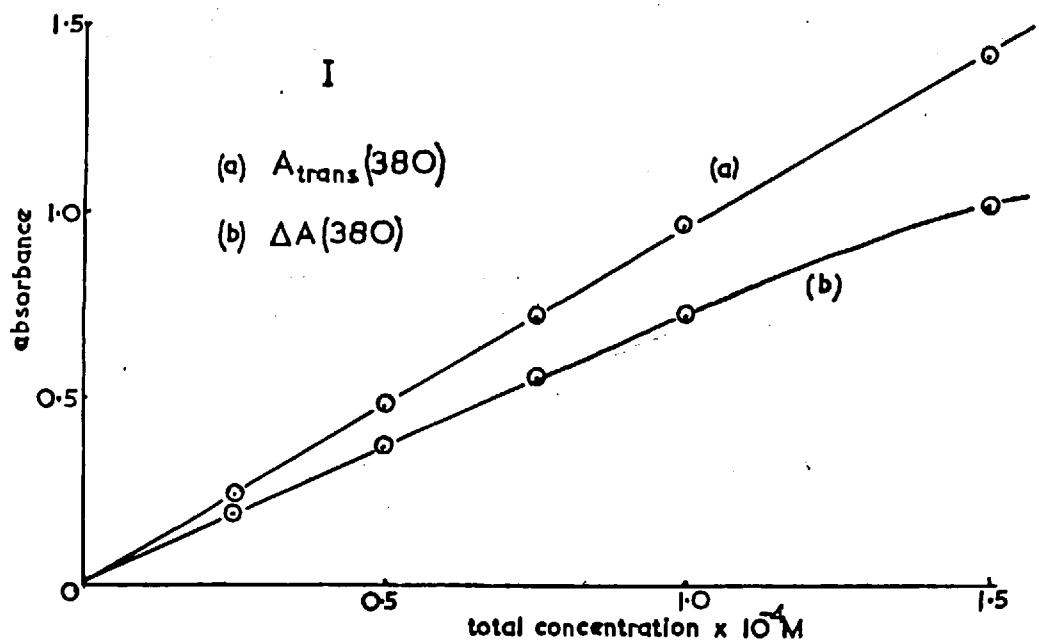
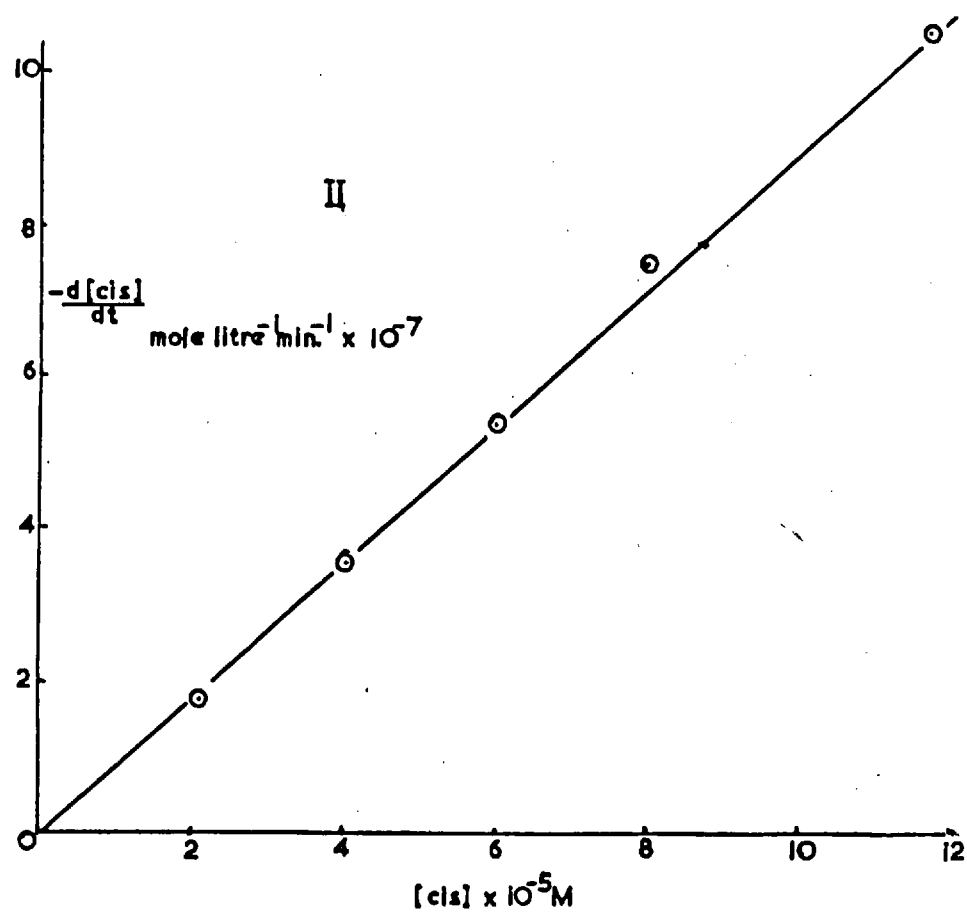


FIG. 76

1-(4'-METHOXYPHENYLAZO) NAPHTHALENE in benzene.





6.3 Experimental

(1) Chemicals and Apparatus

1-(4'-hydroxyphenylazo)-naphthalene: 10^{-3}M solution in benzene

1-(4'-methoxyphenylazo)-naphthalene: 10^{-3}M solution in benzene

2,4 - dihydroxyazobenzene: 10^{-3}M solution in benzene

Irradiation/Absorption measurement: Flow-through technique.

OXI filter.

(2) Effect of Concentration

2.15, 4.3, 6.45, 8.6, and 12.9 ml. aliquots of the stock solution of 1(4'-dihydroxyphenylazo) naphthalene were taken and diluted to 86 ml. with benzene in the flow circuit. The dark and equilibrium spectra, and the absorbance *vs.* time curves were recorded as outlined in Section 5.3. The process was repeated for 1(4'-methoxyphenylazo) naphthalene in benzene.

(3) Examination of Mixtures

The mixtures were prepared *in situ* in the flow circuit by dilution of aliquots of the stock solutions. Phototropic behaviour was examined as outlined in Section 5.3.

6.4 Discussion of Results

(1) Effect of Concentration

The absorption spectra of the solutions of the trans isomers of 1-(4'-hydroxyphenylazo) naphthalene and 1-(4'-methoxyphenylazo) naphthalene adhere to Beer's law over the concentration range examined. (Figs. 75 and 76, I (a)). The calculated maximum molar extinction coefficients are 1.75×10^4 and 1.85×10^4, respectively.

The initial rate of the photochemical trans-cis conversion is independent of concentration (Figs. 71, 72) which confirms the assumption (Ref: p.124) that all the available activating light is absorbed by the sample, even at low solute concentrations, and indicates that the quantum yield is independent of concentration. The mean quantum yields calculated from the absorbance vs. time curves are $\Phi = 0.28$ for 1-(4'-hydroxyphenylazo) naphthalene, and $\Phi = 0.27$ for the methoxy derivative. (cf. Table 23).

The linearity of the plots on Figs. 75 and 76, II, shows that the thermal reactions follow first order kinetics (p. 126). The rate constants calculated from the slopes of these curves are $k = 7.73 \times 10^{-2}$ min^{-1}, and $k = 9.20 \times 10^{-3}$ min^{-1}, for the phenol and ether,

respectively. Both values are higher, but will be more accurate, than those evaluated from the $t_{\frac{1}{2}}$ (reverse) values (Ref: Table 23).

At low solute concentrations, the ΔA (380) values for 1-(4' methoxyphenylazo) naphthalene in benzene increase linearly with total concentration (Fig. 76, I (b)). i.e. the percentage of cis isomer at equilibrium is constant. This is because, in the effective absence of a thermal reaction, the phototropic equilibrium is governed by the rates of the forward and reverse photochemical processes, which are independent of the concentration of the equilibrium mixture. The slight departure from linearity at higher concentrations is due to the effect of the slow thermal reaction on the phototropic equilibrium.

The ΔA (380) values for 1-(4'-hydroxyphenylazo) naphthalene in benzene tend towards a constant value with increasing concentration. (Fig. 75, I'' (b)), i.e. the concentration of cis isomer at equilibrium becomes constant. Because of the instability of the cis isomer, the phototropic equilibrium is governed by the rate of the (concentration dependent) thermal cis-trans reaction.

(2) Phototropic behaviour of mixtures

The differences in phototropic behaviour permitted the examination of the phototropism of one component in each mixture with respect to the other component(s). For instance, in a mixture of 1-(4'-hydroxyphenylazo)-naphthalene (A) and 1-(4'-methoxyphenylazo)-naphthalene (B) in 10% ethanolic benzene, only the latter compound is phototropic. The small, irreversible changes in the spectra of mixtures containing 2, 4-dihydroxyazobenzene (C) were determined by examination of mixtures of A and C in 10% ethanolic benzene, and could thus be deducted from the ΔA values recorded for mixtures of A and C, and B and C in benzene.

A comparison of the ΔA (380) values given in Table 25 with those on Figs. 75 and 76, I (b), shows that the degree of phototropism attained by the active component in the mixtures is less than that for the pure component at the same concentration. This is because the absorption of activating light is divided between the active and passive species in solution. In addition, the proportion of light absorbed by the labile trans isomers decreases rapidly with isomerisation. Light absorption by the cis molecules, since it occurs

predominantly at shorter wavelengths, is less affected by the presence of the passive species. The net rate of the trans-cis photochemical isomerisation at equilibrium is thus reduced. The effect of this on the equilibrium attained is particularly noticeable when the thermal reverse process is rapid.

It is clear, then, that even when the cis isomer is very stable, the ΔA values cannot be used for a quantitative determination of the active species present.

The apparent quantum yields are directly related to the distribution of light between the active and passive forms in solution. An approximate determination of the amount of the phototropic constituent present in each solution is thus possible.

CHAPTER 7

Cis-trans photo-isomerisation of aromatic azo-compounds. Effect of complex formation

7.1 Preface

It has been established (Chapter 5) that azo compounds containing hydroxyl groups in the ortho or para position with respect to the azo bond do not exhibit phototropism in polar solvents. Methylation of the hydroxyl groups, however, yields compounds which show a considerable phototropic effect in solution, regardless of the polarity of the solvent. It was suggested that this is because the hydroxyazo compounds, unlike the methyl ethers, can exist in tautomeric forms, with the result that the photoproducts are too unstable to exist in measureable quantities.

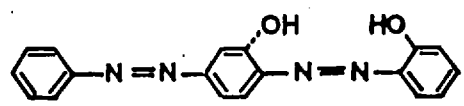
The main purpose of the research work outlined in this chapter was to determine whether or not complex formation between suitable hydroxy azo compounds and metal ions can produce the same effect as methylation. This would mean that a non-phototropic reagent could yield

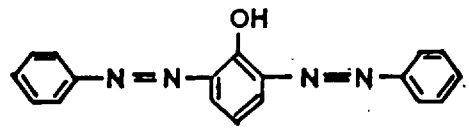
phototropic complexes, under suitable solvent conditions. Fig. 77 shows the empirical structures of some of the compounds suitable for examination. Note that in each case the hydroxyl group or groups can take part in complex formation, leaving at least one azo bond 'free' to isomerise.

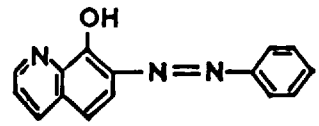
The work presented herein is that part carried out by the author in a joint programme [141] of investigation of the phototropic properties of azo compounds containing selected cation complexing centres. The compounds which have been examined are 5-phenylazo-8-hydroxyquinoline, 'phenazoxine', the 4'-sulphonic acid derivative 'sulphenazoxine', and the monohydroxy bis azo dyestuffs, Coomassie red PGS, and Beibrich scarlet (vide infra).

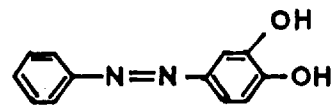
A brief investigation was also made of solutions of 2-(4'-dimethyl-aminophenylazo) pyridine. The phototropic behaviour of this compound in benzene has already been established (Fig. 62). The compound is known to form metal complexes [142] involving bond formation between the metal cation, the heterocyclic nitrogen atom and the azo nitrogens. Such bonding rules out any possibility of isomerisation about the N=N bond.

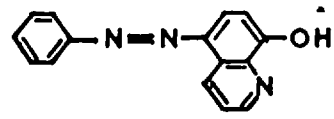
FIG. 77

1. 

2. 

3. 

4. 

5. 

7.2 Results

1) Phenazoxine

This compound was chosen for initial work because it is soluble in non-polar solvents. The extractability of 21 cations into a solution of phenazoxine in chloroform was examined. Of these cations, only mercury (1) and mercury (11) yielded coloured complexes on extraction from aqueous solution, containing an excess of the cation, in the pH range 3-9. The light lability of the complexes in chloroform was compared with that of the pure reagent, using the Direct irradiation/absorption technique. The mercury (1) and mercury (11) complexes gave identical absorption spectra, and behaved in analagous manner on irradiation. Both reagent and complexes underwent irreversible photochemical reactions. (Fig. 79)

2) Sulphenazoxine

The behaviour of this compound, and the complexes thereof, was examined in 50% v/v aqueous ethanol. Out of 21 cations, 15 formed soluble complex species with the reagent in the pH range 3-9. Sulphenazoxine solution was found to be stable to irradiation throughout this pH range.

The complexes formed between the reagent and the following cations were too unstable, in the absence of irradiation, to permit an examination of their phototropic properties:

Ag (1) (pH = 3;5), Be (11) (pH = 7), Cu (11) (pH = 7), Fe (11) (pH = 3 - 9), Fe (111) (pH = 9), Hg (11) (pH = 3), Mg (11) (pH = 9), Mn (11) (pH = 9), Ni (11) (pH = 3 - 9).

Al (111) (pH = 5 - 9), Cd (11) (pH = 3;5), Fe (111) (pH = 3 - 7), Ga (111) (pH = 3 - 9), In (111) (pH = 3 - 9), and Zn (11) (pH = 3), yielded stable species. The Pd (11) (pH = 3;5) complex was also stable, but required at least 3 hours for complete formation. The spectra of the aluminium, cadmium, gallium and indium complexes showed intense, single absorption peaks (λ_{max} = 425 - 475 mμ), indicative of strong complex formation.

Of the 'dark-stable' solutions, only those containing aluminium at pH = 7 and pH = 9, and gallium at pH = 7, showed any change on exposure to light. The spectra of the aluminium complexes underwent small irreversible hypochromic shifts on irradiation (ΔA (425) = 0.04 (OB1). Similar changes were recorded after irradiation with light transmitted by the OB2 filter. The gallium complex was found

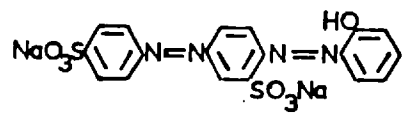
to be phototropic. The dark and equilibrium spectra are shown on Fig. 80. The phototropic effect was enhanced when 15% (cf. 50%) aqueous ethanol was used as the solvent (Fig. 81). The kinetics of the phototropic change in the less polar solvent gave the following (approximate) values for the quantum yield, and the rate constant for the thermal reversal.

$$\Phi = 0.2 : k = 7.5 \times 10^{-1} \text{ min.}^{-1}$$

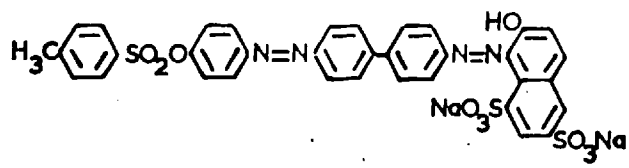
3) Beibrich scarlet: Coomassie red PGS

The structures of these compounds are shown on Fig. 78. Both were

FIG.78



Beibrich scarlet



Coomassie red PGS

examined in 50% aqueous ethanol. Of 21 cations, Copper (11), Nickel (11) and Palladium (11), formed complex species with Beibrich scarlet, in the pH range 3-9, and only Palladium (11) yielded a complex with Coomassie red PGS. Neither the reagents, nor the complexes, were affected by irradiation using the flow-through technique.

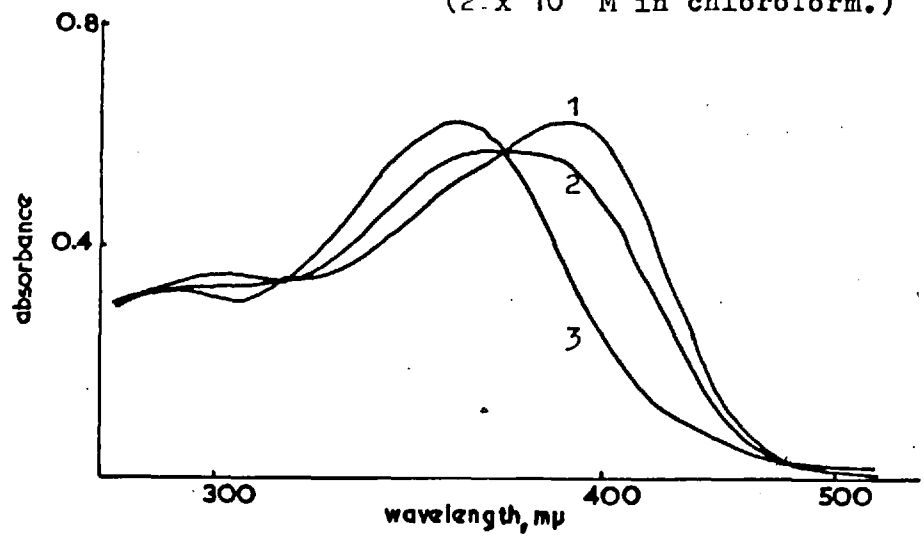
4) 2(4'-dimethylaminophenylazo) pyridine

The reagent forms complexes with copper (11), mercury (11) and nickel (11), and weak complexes with cobalt (11), manganese (11) and zinc (11) in aqueous solution in the pH range 5-7. [142] The copper (11) complex at pH = 7, and the mercury (11) complex at pH = 6, were examined for phototropic behaviour in 50% aqueous ethanol. As expected, neither was phototropic.

Fig. 82 shows the variation in absorption spectra and phototropic activity of the reagent with respect to the pH of the aqueous ethanolic solvent. A slight phototropic effect is exhibited in the pH range 8-12. The solutions at lower pH values are stable to irradiation.

Hg (II) - PHENAZOXINE.

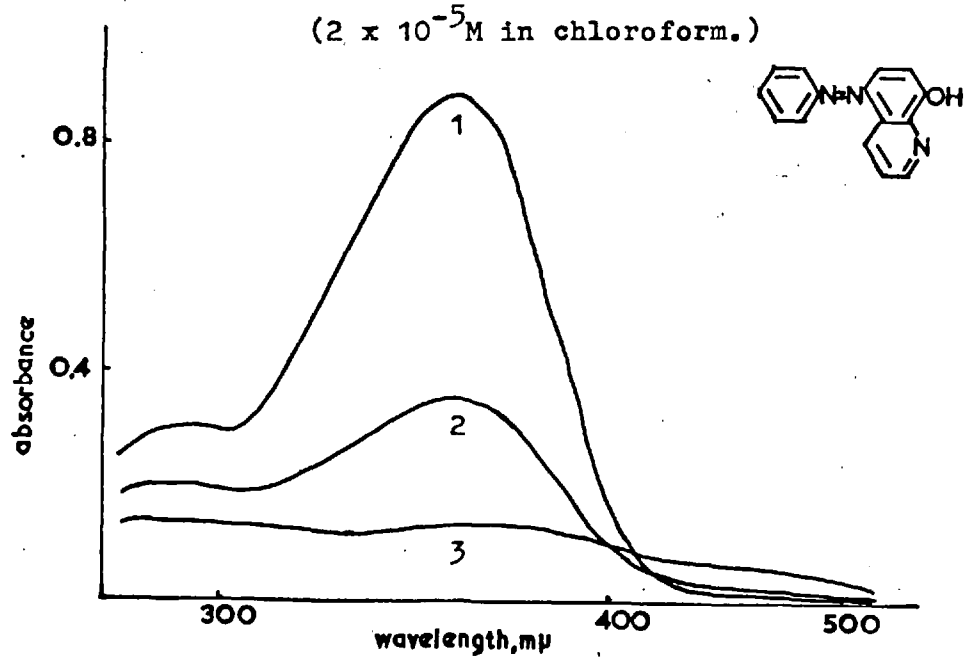
(2×10^{-5}M in chloroform.)



1-2-3: Effect of prolonged irradiation, 350mμ

PHENAZOXINE.

(2×10^{-5}M in chloroform.)



1-2-3: Effect of prolonged irradiation, 350mμ

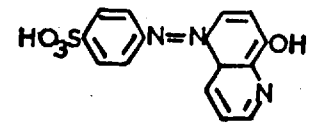
FIG. 80

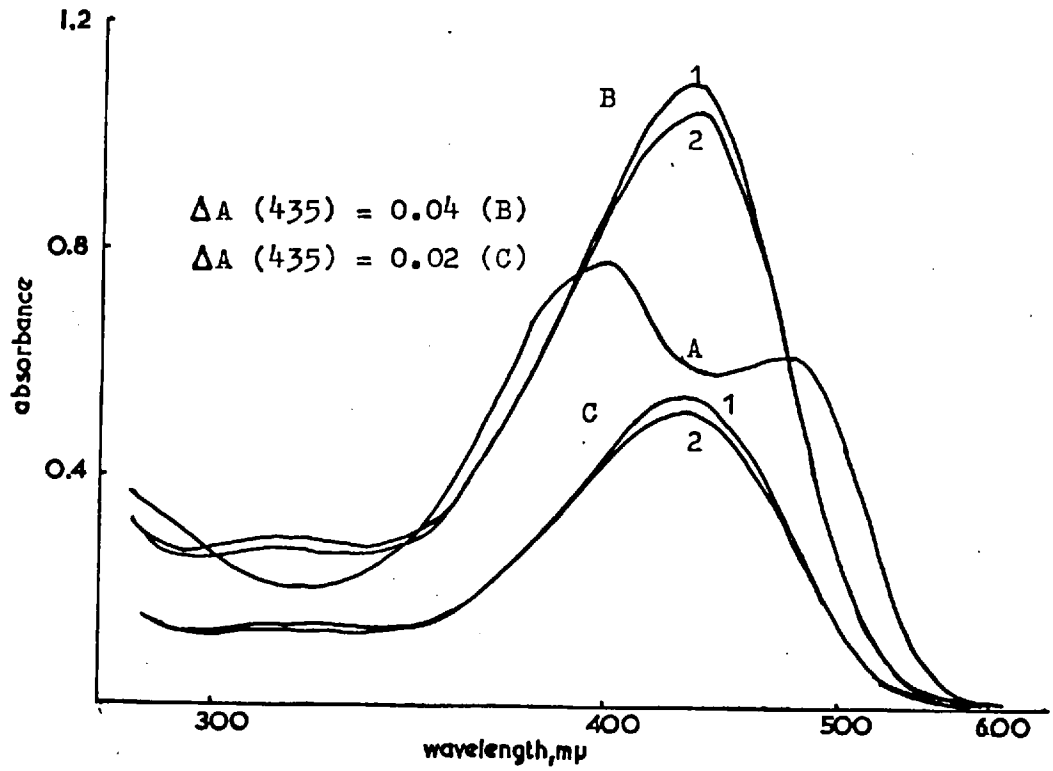
SULPHENAZOXINE in 50% v/v aqueous ethanol.

A Reagent only (10^{-4}M), pH = 7. Non-phototropic.

B 1:1 Ga (III) - sulphenazoxine (10^{-4}M), pH = 7.

C 1:1 Ga (III) - sulphenazoxine (5×10^{-5}M), pH = 7.





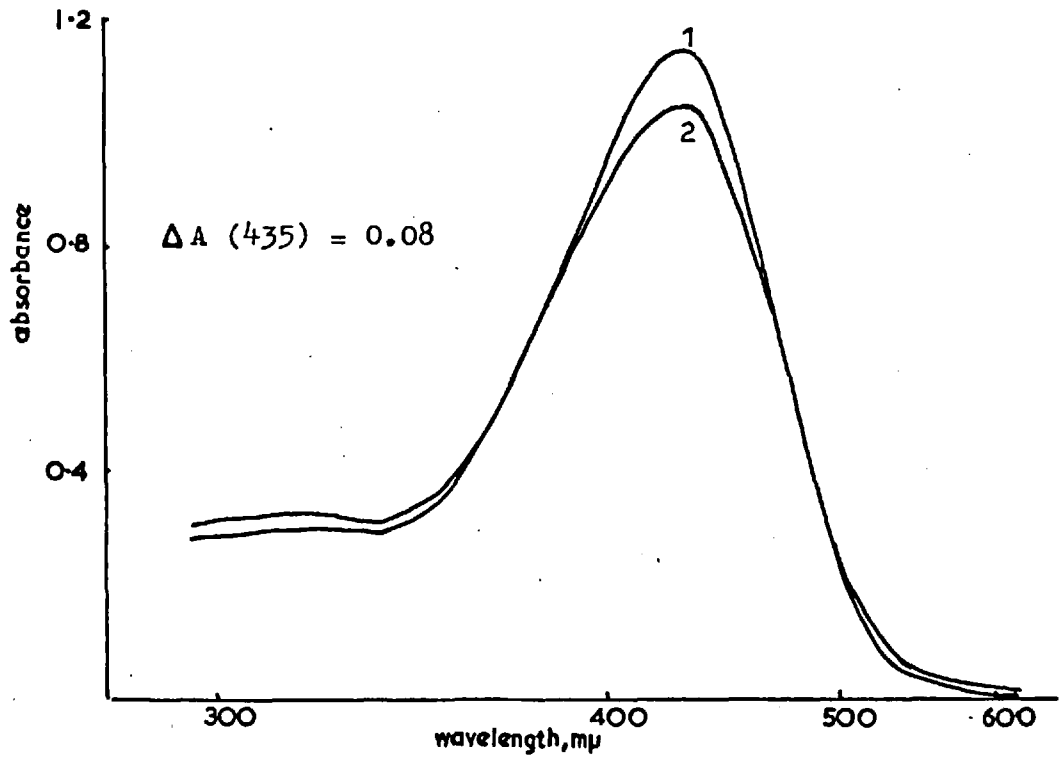
1 Dark spectra.

2 Equilibrium spectra, irradiation OB1.

FIG. 81

1:1 Ga (III) - SULPHENAZOXINE.

(10^{-4}M in 15% aqueous ethanol)



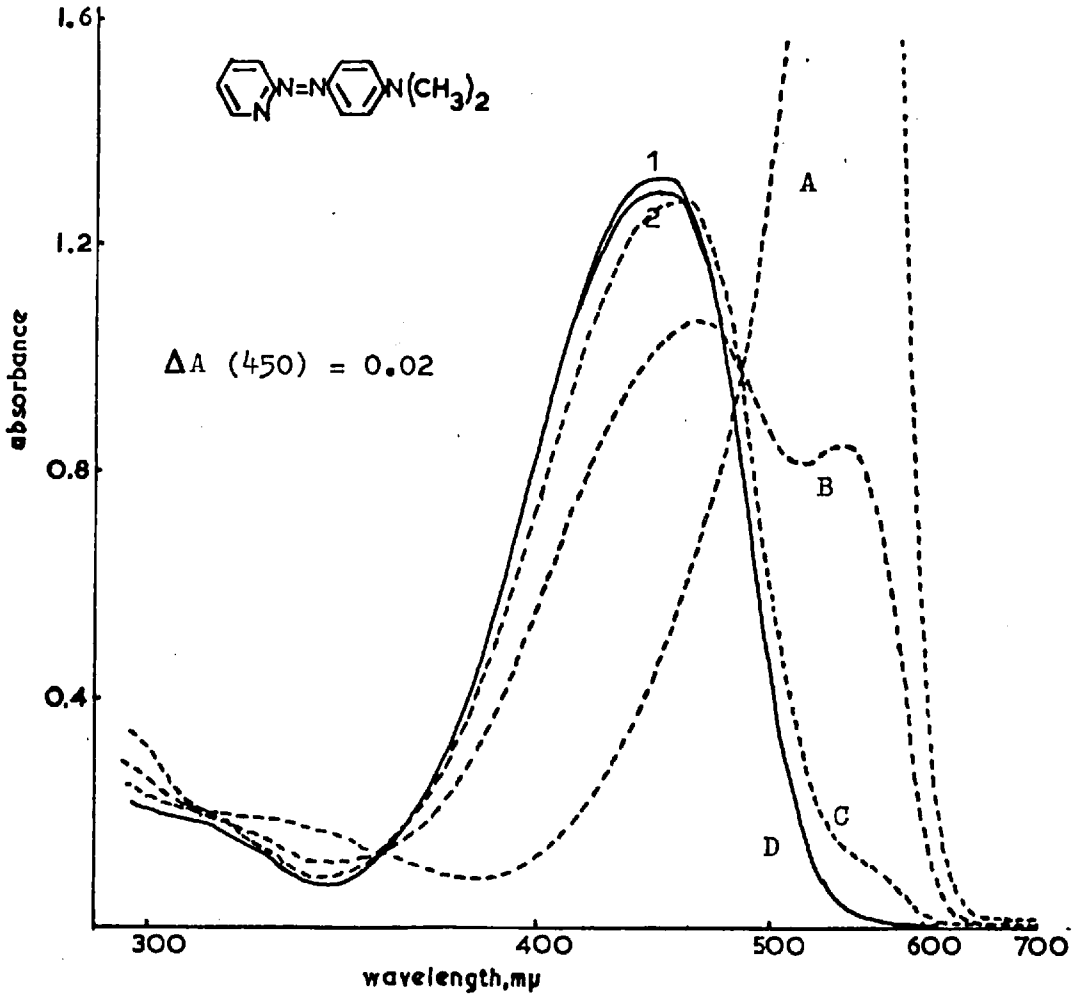
1 Dark spectrum.

2 Equilibrium spectrum,irradiation OB1.

FIG.82

2 (4'-DIMETHYLAMINOPHENYLAZO) PYRIDINE.

(10^{-4}M in 50% v/v aqueous ethanol)



A pH < 1: B pH = 3: C pH = 5: - non-phototropic.

D pH = 7 - 12:

1 Dark spectrum (pH = 8 - 12); dark and equilibrium spectrum (pH = 7).

2 Equilibrium spectrum (pH = 8 - 12), irradiation OB1.

7.3 Experimental

1) Chemicals and Apparatus

Phenazoxine: The compound was prepared as follows: [121, 143] Aniline (4.5 ml) was dissolved in 2:1 aqueous hydrochloric acid (30 ml) and the mixture cooled to 0°C. Diazotisation was carried out using an aqueous solution of sodium nitrite (3.7g) (Ref: Section 5.3). The resultant solution was added, slowly, with stirring to a cold solution of 8-hydroxyquinoline (6.7g) in 1:1 aqueous hydrochloric acid (35 ml). The mixture was neutralised with solid sodium carbonate, and the product removed by filtration. The crude phenazoxine was washed with water and recrystallised three times from hot absolute ethanol. Yield (purified) = 4.5g. = 38% theory. Found: C = 70.12%, H = 4.20%. $C_{15}H_{11}ON_3$ requires: C = 72.30%, H = 4.43%.

A 10^{-3}M solution in chloroform was prepared.

Sulphenazoxine: Sulphanilic acid (6g) was dissolved in a solution of sodium carbonate (2g) in water (35 ml). The solution was acidified with concentrated hydrochloric acid (10 ml), cooled, and diazotised using 20% aqueous sodium nitrite solution (13 ml). The product was coupled with 8-hydroxyquinoline (5g) as described above. The crude

sulphenazoxine was recrystallised 3 times from aqueous ethanol. Yield (purified) = 5g. = 40% theory. Found: C = 46.54%, H = 3.43%. N = 11.18%. $C_{15}H_{11}O_4N_3S.2H_2O$ requires: C = 49.32%, H = 3.56%, N = 11.50%.

A 10^{-3}M solution in 50% aqueous ethanol was prepared.

Beibrich Scarlet (26905: C.1. Acid red 66)
Hopkin and Williams Ltd. A 10^{-3}M solution in 50% aqueous ethanol was prepared.

Coomassie Red PGS (22245: C.1. Acid red 85)
Imperial Chemical Industries,Ltd. 10^{-3}M solution in 50% aqueous ethanol.

2 (4'-dimethylaminophenylazo) pyridine Eastman Chemical Co. 10^{-3}M solution in aqueous ethanol.

Metal ions: 10^{-2}M aqueous solutions of the following cations were prepared: Ag (1), Al (111), Ba (11), Be (11), Ca (11), Cd (11), Co (11), Cu (11), Fe (11), Fe (111), Ga (111), Hg (1), Hg (11), In (111), Mg (11), Mn (11), Ni (11), Pb (11), Pd (11), Sr (11), Zn (11).

Buffer solutions: pH = 3.0: pH = 5.0: pH = 7.0: pH = 9.0; pH = 12
(Solvent = 50% aqueous ethanol)

Chloroform: Analytical reagent grade

Ethanol: Analytical reagent grade

Irradiation and Absorption measurement: Flow-through technique. Direct technique.

2) Complexing capabilities of reagents

a) Phenazoxine: The 10^{-3}M solution in chloroform (5 ml) was shaken with the aqueous solution of the cation (5 ml), containing a few drops of the appropriate buffer solution. The colour of the organic extract was compared with a suitable blank.

b) Sulphenazoxine, Beibrich scarlet, Coomassie Red PGS: The 10^{-3}M solution in aqueous ethanol (10ml) was buffered to the required pH value, and treated with the cation solution (1 ml). Complex formation was determined by visual comparison with an appropriate 'blank' solution.

3) Effect of Irradiation

a) Hg (II) - phenazoxine: An aliquot (2.0 ml) of the mercury complex extracted from neutral aqueous solution (section 2) (a)) was diluted to 100 ml. with chloroform. 6 ml. of this solution was transferred to the cuvette C_1 (Fig. 15). The absorption spectrum was recorded, vs. a solvent blank, and again after an interval of 30 minutes. The sample was exposed to irradiation at 350 mμ, and the absorption spectrum was scanned at 15 minute intervals until no further change took place. The procedure was repeated using a reagent blank, prepared in an identical manner, but in the absence of Hg (II) ions.

b) Sulphenazoxine: Beibrich scarlet: Coomassie red PGS: 2 (4' - Dimethylaminophenylazo) pyridine: The reagent solution (8.7 ml) was treated with the appropriate buffer solution (8 ml), and diluted to the mark in the flow-through circuit with 50% aqueous ethanol. The absorption spectra (vs. the pure solvent), and the light-sensitivity of the solutions were examined as described in Chapter 5. The process was repeated after the addition of an aliquot (0.87 ml) of the metal ion solution. For the examination of the Ga (III)-sulphenazoxine complex in 15% aqueous ethanol, the

sample was diluted to the mark with 96% v/v aqueous ethanol.

7.4 Comments on experimental technique

The chloroform solutions of phenazoxine were examined using the direct technique because the solvent was found to have adverse effects on the tubing used in the flow-through circuit. For the examination of the remaining reagents aqueous ethanol was preferred as a solvent to distilled water. The latter became somewhat opaque on prolonged circulation due to separation of dissolved air.

7.5 Discussion of Results

The photochemical behaviour of phenazoxine in chloroform is not understood, though the near-complete annihilation of colour indicates that N=N bond fission is taking place. The spectral change in the mercury complex on irradiation cannot be due to cis-trans photo-isomerisation, because a reverse photochemical reaction is clearly absent. The explanation of the photochemical reaction and the reason for the apparent stabilisation of the colour in the presence of mercurous or mercuric ions requires further experimental work.

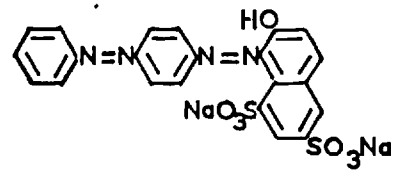
The phototropic behaviour of the gallium sulphenazoxine complex

indicates that cis-trans photoisomerisation is taking place. Thus, the postulated effect of complexation of the free hydroxyl group is confirmed. The apparent specificity of the phototropic reaction for the gallium complex is, again, not understood. However, the phototropic behaviour will be influenced by factors such as the stability constants and the general stereochemistry of the complexes. A weak complex allows rapid interchange between the free reagent molecules and those bound up in the complex, thus precluding stabilisation of the cis isomer by complex formation. Where more than one reagent molecule is involved in the complex (the gallium : sulphenazoxine ratio is probably 1:3 [121]) isomerisation may either be sterically favoured or restricted. It is clear that the pH of the solution also has a significant effect. The slight irreversible change in the spectrum of the aluminium complex is not due to isomerisation, since if the cis isomer were stable, a much larger phototropic change would have been recorded.

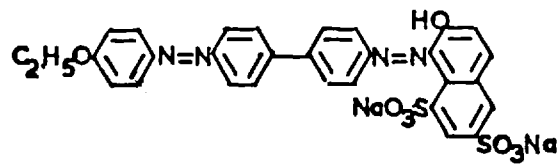
2 (4'-dimethylaminophenylazo) pyridine undergoes limited cis-trans photo-isomerisation in solution at high pH. The absence of the effect in acid solution is readily explained in terms of protonation of the molecule and delocalisation of the positive charge.

The dyestuffs Beibrich scarlet and Coomassie red PGS were chosen for examination because it was believed that the free o-hydroxyl groups, since they can enter into conjugation with the more remote azo groups in each molecule, would prevent photoisomerisation of these groups in the same way as do hydroxyl groups in the p position in mono azo compounds. The light-stability of the dyes in solution suggests that this is the case. Whilst the behaviour of the complexes of these compounds is disappointing, the Beryllium complexes of two similar dyes, Brilliant crocein and Diazol scarlet B, (Fig. 83), do

FIG.83



Brilliant crocein (27290)



Diazol scarlet B (22240)

exhibit a slight phototropic effect in alkaline solution. [141] The iron (111) complex of Brilliant crocein is also phototropic under similar conditions. [141]

CHAPTER 8

Conclusion. Suggestions for future work

The brief review of the subject, and the work outlined in this thesis indicates that the number of compounds which do, or can be expected to, exhibit phototropism in solution is considerable. In addition, it has been demonstrated, with the aromatic azo compounds, that phototropic solutions can be qualitatively and quantitatively characterised by the controlled production of 'equilibrium' absorption spectra. Investigation of the various other groups of phototropic compounds in this way would provide detailed knowledge of the phototropism of individual molecules, and would allow correlations to be made between chemical structure, within each group, and phototropic behaviour.

In view of the preliminary results obtained, continued investigation of the complex-forming azo dyes is worthwhile. A programme to examine the cation complexes of several mono- and di-hydroxy- *bis*, *tris* and *tetrakis* azo derivatives has been initiated. Derivatives of 7-phenylazo-8-hydroxyquinoline are known to form two types of cation complex [144], in which the azo group is either bound up with the metal atom, or is free to undergo possible photo-isomerisation. Studies of the

complexes of these compounds and of the similar 1, 8-dihydroxy-2-aryl-azonaphthalenes could prove fruitful. Compounds containing alternative ligand groups, e.g. the di (N,N) acetic acid derivatives of aminoazo compounds, are also worthy of examination.

The photochemical behaviour of the leucocyanides of Basic dyes provides a basis for the controlled release of cyanide ions. Since an intensely coloured dye molecule is released for each cyanide ion formed, the sensitivity of the system to metal ions which form $M(CN)_4^{n-}$ and $M(CN)_6^{n-}$ complexes will be very high, and the additional factors which will control the formation of these complex species offers a means whereby the selectivity of the cyanide ion may be increased. Systems of this sort could thus be profitably examined.

Finally, the work initiated by Meriwether et al [52,53] on the metal dithizonates is worth following up, in view of the importance of these complexes in the analytical chemistry of metal ions.

Of the two methods developed for the analysis of phototropic solutions, Flow-through irradiation/absorption has been used almost exclusively. It has been shown capable of examining reproducible amounts of photoproducts so unstable that either phototropism had not been

previously detected, or the phototropic change measured was subject to considerable inaccuracies. For fundamental research, the technique requires little improvement. A more intense light source, or sources which give line or band spectra, might be used, in conjunction with suitable optical filters, to accelerate the forward photochemical processes. A much shorter irradiation cell, but of similar volume, would also achieve this object.

Direct irradiation/absorption is potentially a more accurate analytical technique. Whilst the recording of the kinetics of phototropic reactions by this method is at present unsatisfactory, a suitable stirring device will overcome this problem. However, the technique is both tardy and difficult to operate, and is therefore more suited as an extension of the Flow-through technique for the occasional examination of individual systems of particular interest. It is unlikely that activating light of intensities greater than 10^{14} quanta/second can be used in this method, without it having adverse effects on the response of the spectrophotometer.

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