

COMPUTERISED

STUDIES IN HETEROCYCLIC
CHEMISTRY - SYNTHESIS OF
HETEROCYCLIC QUINONOID
DISPERSE DYES.

A THESIS
SUBMITTED TO THE
UNIVERSITY OF BOMBAY
FOR THE DEGREE OF
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Dedicated to My Grandmother,
Parents
Dr. B. B. Gaitonde
And
Shri Anil Kumar

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No part of this work has been submitted for a degree or diploma or other academic award. The literature concerning the problem investigated has been surveyed and all the necessary references are given. The experimental work has been carried out entirely by me. In accordance with the usual practice, due acknowledgement has been made wherever the work presented is based on the results of other workers.

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GENERAL REMARKS

Visible spectra were taken in dimethylformamide on a Perkin-Elmer 350 spectrophotometer. Infrared spectra were recorded as nujol mulls on a Perkin-Elmer Infra-cord 137 spectrophotometer. The absorption values are recorded in cm^{-1} . Nuclear magnetic resonance spectra were recorded on Varian T-60 spectrometer using tetramethyl silane as external standard and the chemical shifts are cited on δ scale. Coupling constants (J) are in Hz. The following abbreviations are used: s - singlet; d - doublet; t - triplet; q - quartet; m = multiplet. Mass spectra were obtained with a CEC 21-110B double focussing mass spectrometer operating at 70 ev using a direct inlet system. Spectral charts, wherever necessary, have been reduced to standard size and attached at the end of the discussion. The actual values are given in the discussion.

Temperatures are in $^{\circ}\text{C}$. Melting points are uncorrected and are given immediately after the solvent of crystallisation. Melting points have been taken in capillaries.

Figures shown in brackets (underlined) are structure numbers and the figures in superscript are literature references.

Abbreviations

AsCl ₃	-	Arsenic trichloride.
CCl ₄	-	Carbon tetrachloride.
DMF	-	Dimethyl formamide.
DMS	-	Dimethyl sulphate.
DMSO	-	Dimethyl sulphoxide.
DCNQ	-	2,3-Dichloro-1,4-naphthoquinone.
IR	-	Infrared.
M ⁺	-	Molecular ion.
m.p.	-	Melting point.
m.m.p.	-	Mixed melting point.
NMR	-	Nuclear magnetic resonance.
UV	-	Ultraviolet.

Patents

Be. P.	-	Belgium patent.
B. P.	-	British patent.
F. P.	-	French patent.
G. P.	-	German patent.
Neth. Appl.	-	Netherlands Application.
U.S.P.	-	United States patent.

Concerning nomenclature :

The following names

- (1) naphthindolizinedione, and
- (2) phthaloylpyrrocoline

refer to the same class of compounds.

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CHAPTER - I A

**STRUCTURAL FEATURES OF DISPERSE DYES
AND THEIR DYEING PROPERTIES**

1

The present investigation is related to the synthesis of naphthoquinone dyes and study of their properties as disperse dyes. This chapter gives a brief review of important earlier developments in disperse dyes as regards their structural features and dyeing properties. 'Disperse Dyes', are so called since they are applied as aqueous dispersions. They are substantially water-insoluble and were originally introduced for dyeing cellulose acetate in the form of fine aqueous suspensions¹. It is well known now that they are not entirely water insoluble and dissolve in water to the extent of 0.1 to 7.1 mg/liter at 25° and 0.5 to 240 mg/liter at 80°². In fact, this small solubility is essential for the dyeing process. According to the solution theory of dyeing, the suspended dye slowly dissolves in water to a small extent giving an aqueous saturated solution of the dye along with insoluble dye. In the dyeing process the dissolved dye is extracted by the polymeric fiber. As dye molecules are absorbed by the fiber from the aqueous solution, more dye passes into solution from the suspension in order to maintain the concentration of the dye in solution. An equilibrium is ultimately established whereby the concentration of the dye in the solution is equivalent to that of the dye in the synthetic fiber substrate.

The main use of disperse dyes is for dyeing cellulose acetate and polyester fibers. They are also used

for dyeing nylon. The dyes also cover Barre effects (non-uniformities introduced into the fiber during processing). However, their somewhat limited fastness properties restrict their use for dyeing pale shades on hosiery and carpets. Attempts have also been made to synthesise dyes with improved wet fastness. Such dyes are useful for dyeing light and medium shades on acrylic fibers. These dyeings show very good lightfastness, but their use is restricted because of their limited build-up properties. Other fibers, e.g. polypropylene are often mentioned in claims in patents on disperse dyes, but they are generally only of academic interest. The recently introduced elastomeric fibers can also be dyed with disperse dyes.

The early history of the development of dyes for cellulose acetate fibers is now wellknown. It will be recalled that when this fiber was marketed after the first world war, very few of the existing commercial acid, wool and direct cotton dyes (which were water soluble by virtue of the presence of sulfonic acid groups) had any affinity for cellulose acetate. The hydroxyl groups in cellulose play a key role in the affinity of these dyes on cotton. Cellulose acetate in which most of the hydroxyl groups in cellulose are acetylated has a compact crystalline structure and the fiber is therefore hydrophobic and differs from cellulose in its dyeing properties.

In the early days, attempts were made to dye cellulose acetate by a preliminary swelling treatment with cellosolve or by saponification of the acetyl groups with hot alkaline solutions and then dyeing with direct cotton dyes, acid dyes, solubilized vats and azoics³. In view of the difficulty in obtaining a homogeneous product after saponification and the danger of weakening the fiber, this process is now almost outdated.

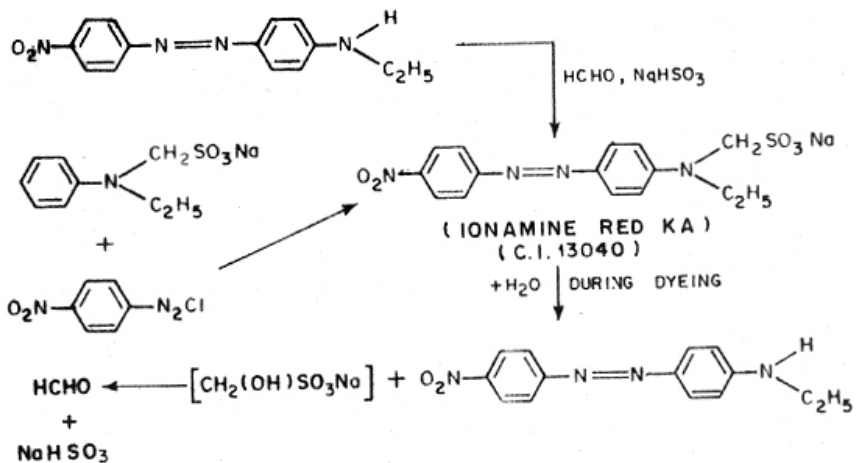
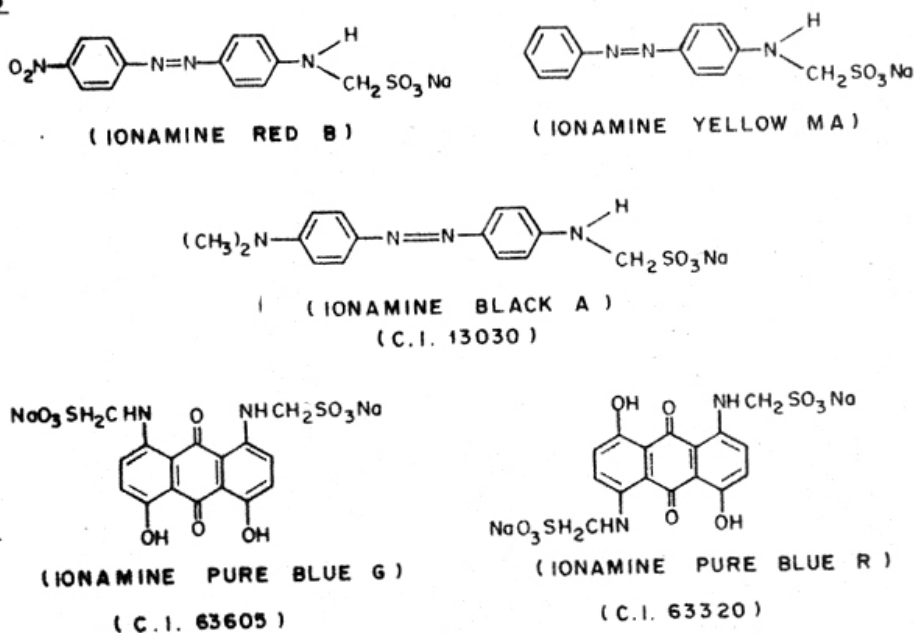
The precursors of currently used disperse dyes are the 'Ionamines', 'Tonamine dyes' were the first special range of dyes for cellulose acetate introduced by British Dyestuffs Corporation and British Celanese⁴. These dyes were solubilized aminoazo and anthraquinone compounds which had no affinity for cotton and other cellulosic fibers. Solubilization was effected by means of an N-sulphomethyl group. These dyes were prepared by (a) reacting an insoluble azo dye containing a primary or secondary amino group with formaldehyde bisulphite or (b) more conveniently, by coupling a diazonium salt with an N-methylaniline- ω -sulphonate. The product was soluble in water and was applied to cellulose acetate from a warm weakly acid or alkaline bath. During the dyeing process the dyes were hydrolysed yielding the water insoluble dye containing the aminoazo group. The insoluble dye as it is being formed is taken up by the fiber substrate (Chart I). Ionamine dyes are now obsolete. However, earlier they were

useful as they could be applied in a manner similar to direct cotton dyes and gave shades which had good fastness to washing, light and rubbing. They, however, suffered from the defect of hydrolysing at different rates which made their use in mixtures somewhat unsatisfactory due to difficulty in matching. The colour of the final dyeings were also different from those of the original dye solutions, owing to the hypsochromic effect associated with the absence of dialkyl group on the amino function which carries a solubilizing group⁵.

From the study of dyeing properties of Ionamine and other dyes then used for dyeing cellulose acetate, theories relating chemical constitution with affinity for cellulose acetate were postulated. It was realized that suitable dyes should be basic in character and have a relatively simple chemical structure. It was also concluded that such dyes should be insoluble or have comparatively low solubility in water. Thus solubilization of dyes has to be accomplished without changing or destroying that part of the chemical structure which is responsible for imparting affinity for the fiber (Chart I).

The problem was solved by Holland Ellis⁶ of British Celanese Ltd. who observed that water insoluble aminoazo and hydroxyazo dyes when ground with sulphoricinoleic acid or its alkali salts became so finely dispersed on dilution with

CHART - I.
IONAMINE DYES

A**B**

water that they were capable of dyeing cellulose acetate from a weakly alkaline bath at 70-80°. These dispersions would pass through filter paper leaving no residue. Such dispersed dyes, were marketed under the name SRA (name derived from Sulpho-Ricinoleic Acid) Colours. These dispersed dyes ranged from golden yellow to blue.

Whereas the SRA Colours were the first to enable the dyer to dye and print cellulose acetate with comparative ease, they were not without drawbacks. Thus discharge printing was difficult since the decomposition products of SRA Colours were retained tenaciously by the fiber and could not be readily removed by washing or hot soaping.

Later in 1924, Baddiley and Shepherdson⁷ improved the 'Dispersion Process' using much stronger dispersing agents like the condensation products of naphthalene sulfonic acids with formaldehyde. The azo dyes so dispersed came to be known as 'Dispersols' and the aminoanthraquinone derivatives as 'Duranols'. Particularly important were the dyes built up on the pattern of Disperse Red 17 which was first described by Green and Saunders⁴. The presence of N-hydroxyalkyl groups did not render aminoazo dyes water soluble, but they greatly facilitated the

dispersion of such dyes. The dyes in the form of such dispersions showed good affinity for cellulose acetate fibers. So successful was the 'Dispersion Technique' that many other dyestuff companies also marketed similar dyes using different dispersing agents. Examples are SRA (BrC), Dispersols and Duranols (I.C.I.), Cibacets (Ciba), Cellintons (BASF), Celanthrenes (DUP), etc.

'Solacet' dyes were introduced by I.C.I. some 10 years later. These dyes were water soluble azo dyes containing sulfated N-hydroxyalkylarylamines as coupling components. These dyes had superior washing fastness and better penetration. Their rate of dyeing could be controlled by the addition of electrolytes thus making levelling and matching easier.

Current developments are mainly aimed at improvement in fastness properties of disperse dyes towards washing, light, gas fumes and hot pressing. Advances in this field have gone hand in hand with production of a variety of various synthetic fibers. Largest growth in production and development of disperse dyes is due to widespread use of polyester fibers.

The advent of hydrophobic fibers, such as polyester created new problems for the dyer and the dye chemist. It also opened up possibilities of using insoluble

coloured compounds which hitherto were only employed as intermediates and pigments. The polyester fiber behaves different in dyeing from cellulose acetate and nylon (polyamides fibers). Being more hydrophobic than cellulose acetate, polyester fabrics are comparatively difficult to dye⁸. On screening available dyes it was found that soluble dyes such as Solacets, solubilized vats, acid and direct dyes had insufficient affinity for polyester fibers. Duranol and Dispersol dyes did not dye polyester as readily as cellulose acetate, rayon and nylon. In order to determine whether this was due to the fiber being incapable of absorbing sufficient dye or whether the dye had difficulty in entering and diffusing into the fiber, the diffusion coefficients and saturation values of a number of disperse dyes were measured for polyester fibers. It was found that (a) polyester fibers ultimately absorb more dye than nylon and only slightly less than cellulose acetate rayon, (b) the relative diffusion coefficients within polyester fiber, acetate rayon and nylon at 85° are approximately 1:500:700. This meant that the dominant factor in the colouration of polyester was the very slow rate of diffusion into the fiber and therefore, conditions for the application of dyes on polyester should be so adjusted that diffusion of the dye into the fiber was facilitated to the maximum extent possible.

The conventional methods used for the application of disperse dyes to polyester may be conveniently classified into three groups.

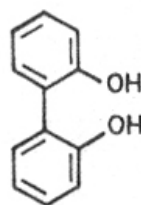
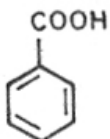
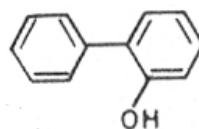
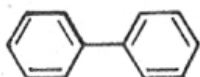
[A] CARRIER DYEING

A considerable advance in the dyeing of polyester fibers was made when the carrier method of dyeing was introduced. It was discovered that quite a number of organic compounds such as phenols, amines or aromatic hydrocarbons, when either dissolved or suspended in the dye bath accelerated the adsorption of disperse dyes on the polyester fiber. The carrier dissolves in the fiber in much the same way as disperse dyes. Once in the fiber, they act as swelling agents for the hydrophobic polyester fiber and convert the amorphous fiber regions into a gel. In other words, the role of carriers in hydrophobic fibers is the same as that of water in hydrophilic fibers viz. making the fiber substrate more accessible to the dye molecules for dyeing to occur. Thus the carriers penetrate into the fine structure of polyester fiber substrate and push adjacent long chain molecules apart. This loosens up the molecules. The water insoluble carriers also appear to form a surface film on the fiber in which the disperse dye is highly soluble. The transfer of dye, in such circumstances, does not take place between the aqueous phase and the fiber but between dyestuff dissolved in the carrier and fiber⁸. For a

carrier to be commercially useful, it should pose no health hazard in dyeing, it should be inexpensive and should not impair light fastness. Balmforth et al⁹ showed that there is an optimal concentration of the carrier above which the dye uptake by the fiber decreases. This optimum carrier concentration corresponds approximately to the amount necessary to saturate both the fiber and dye bath systems. Excess of carrier will introduce a third phase, namely undissolved carrier, which will compete with the dye in uptake by the fiber. Increase in absorption of disperse dyes at equilibrium is brought about by bisphenyl, orthophenyl phenol and phenylsalicylate in that order. Benzoic acid, on the other hand, decreases adsorption by the fiber at equilibrium and only increases the dyeing rate, probably by promoting the solubility of the dye¹⁰. It is suggested that water soluble carriers such as benzoic acid really act as extremely efficient dispersing agents. Substances suitable as carriers are shown in Chart (II).

[B] HIGH TEMPERATURE DYEING

There are many advantages associated with dyeing polyester at temperatures ranging between 120° and 130°. Heavy shades can be dyed with disperse dyes without a carrier, saving expense and also time since rinsing out carriers is a lengthy operation. A wider range of dyes is

CHART - IITYPICAL CARRIERS USED IN DISPERSE DYEING

also available because some of them possessing good light fastness exhaust badly in conventional machines but can be dyed successfully at temperature above 100° . When dyeing at atmospheric pressure, only dyes of low molecular weight, which tend to sublime during plating can be used, but more satisfactory colours with higher molecular weights can be applied at temperatures between 120° and 130° . There is no perceptible loss of elasticity or tensile strength when polyester is dyed under neutral or slightly acidic conditions at 130° , but degradation becomes apparent in the presence of even traces of alkali. Any alkali used during scouring, therefore, must be removed entirely before high temperature dyeing. Scouring should be carried out at $90-95^{\circ}$ in a liquor containing 1-2 kg. of detergent and 1/4 kg. of sodium carbonate per 100 gal. during a period of 1/4 hr. After scouring, a rinse by water should be followed by a second rinse with water containing a little acetic acid to ensure that no alkali is left. With the more level dyeing disperse dyes, no advantage is gained by using temperature above 120° so long as the initial adsorption is reasonably uniform. On the other hand, if dyes which are known to give unlevel dyeing have to be used, dyeing at 130° is preferred.

[C] THERMOFIXATION PROCESS

Another newer application process which has stimulated research in disperse dyes is transfer printing. The thermosol process of DuPont, or similar thermofix methods are used extensively for continuous dyeing of fabrics made of polyester alone or when mixed with other fibers. The process is based upon padding with a disperse dye or a finely divided vat dye in its pigment form. This is followed by drying causing a film containing the dye to adhere to the surface of the fibers. The next stage consists of heating the fiber to 180-220° for period of 30-60 seconds. The process requires the dye to sublime, so it is interesting to recollect that many dyes that are either obsolete or were never introduced commercially because of poor sublimation fastness may become very useful for transfer printing.

CONSTITUTIONAL FEATURES OF DISPERSE DYES
AND CORRELATION WITH DYEING PROPERTIES

An optimum structure for disperse dye should provide, apart from the greatest possible colour fastness (sublimation, light and wash fastness), an ideal balance between water solubility and hydrophobic properties during the dyeing process. However, since the structural requirements for both these properties conflict, it is necessary to strike a compromise that will suit a

commercial dyeing operation. The constitutional features required of a disperse dye are : (a) small molecular size and simplicity of structure, (b) coplanarity of the dye, (c) a balance of hydrophilic-hydrophobic nature of the dye vis-a-vis hydrophilic-hydrophobic character of the fiber, (d) adsorption forces.

(a) Small size and simplicity
of the dye molecule

The polyester and other polymer fibers have a large number of microscopic pores. During dyeing the dye penetrates through these pores into the fiber substrate with which they are then bound by hydrogen bonds or Van der Waal's forces (in the case of disperse dyes). Polyester fibers (terylene) are highly crystalline and markedly hydrophobic. These fibers are, therefore, not easily penetrated by dyes of complex structure having large molecular dimensions. The fibers have also no polar groups such as hydroxy, amino and cannot combine, therefore, with dye anions, cations or reactive chlorine and similar groups present in reactive dyes.

The exhaustion of disperse dyes at equilibrium is quite good, but the diffusion into the fiber is extremely slow. The time required to reach equilibrium, therefore, is much longer than would be permissible in commercial dyeing practice. By selecting disperse dyes with the rapid

rate of diffusion it is possible to dye pale to medium shades at the boil at a reasonable rate. Carrier dyeing facilitates dyeing of a variety of shades on polyester fibers.

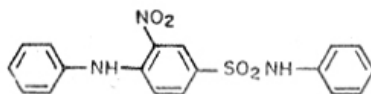
Typical disperse dyes are shown in (Chart III). It will be observed that they all possess simple chemical structures and are of small size (mol. wt. generally < 500).

(b) Interrelation of coplanarity and substantivity of disperse dyes

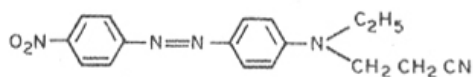
Tilak, Daruwala and Rao¹¹ studied the interrelation of coplanarity of some typical specially tailor-made naphthoquinonoid disperse dyes with substantivity. Although the necessity of coplanar configuration of quinonoid dyes in vat dyeing is generally taken for granted, systematic work was done to experimentally establish the essentiality or otherwise of coplanarity as a contributory factor regarding substantivity of quinonoid dyes for cellulosic and synthetic fibers¹³.

The above authors have discussed the unsatisfactory character of the evidence cited in the literature regarding the above relationship. To study the significance of coplanarity of the dye molecule in dyeing of cellulosic and hydrophobic fibers two series of naphthoquinonoid vat and disperse dyes were synthesised and quantitative determination

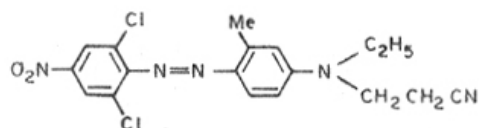
CHART — III
TYPICAL DISPERSE DYES



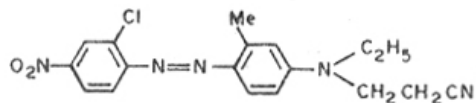
YELLOW



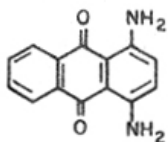
ORANGE



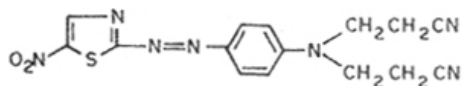
ORANGE, (BROWN)



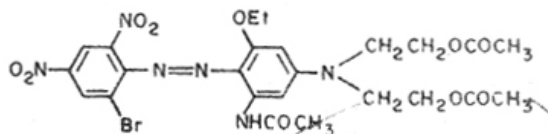
RED, (RUBINE)



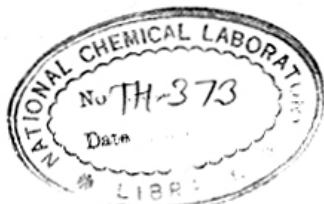
VIOLET



BLUE



GREENISH BLUE



of substantivity and affinity values was made. The first set of dyes comprised a set of coplanar quinonoid dyes derived from 2,3-dichloro-1,4-naphthoquinone and a corresponding non-coplanar analog for each of the coplanar dyes derived from endo-9,10-o-phenylene-2,3-dichloro-9,10-dihydro-1,4-anthraquinone. The non-coplanar dyes were identical with the coplanar dyes as regards the number and location of hydrogen bonding groups and had nearly the same Van der Waal's forces of attraction^{11,12}. (Chart IV).

The results of substantivity studies on this series of dyes made on cellulose¹¹, cellulose acetate¹¹ and other hydrophobic fibers such as nylon, terylene and orlon¹⁴ showed that whereas the coplanar dyes were substantive, the non-coplanar analogs had very little affinity for these fibers. The low substantivity of these dyes for cellulose acetate and other hydrophobic fibers was not a solubility effect since these dyes had the same (in some cases more) solubility in amyl acetate as their coplanar analogs.

In the second series of dyes investigated, Tilak et al^{15,16} synthesised dyes of increasing non-coplanarity by positioning substituents such as chlorine in a manner which results in steric crowding, thereby making the molecule non-coplanar to a varying degree, as in series A of Chart V. Non-coplanarity was also brought about by having two hetero atoms in the molecule, as in the case of naphtho-

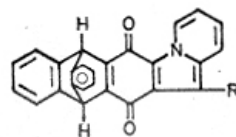
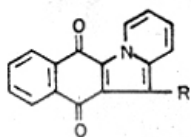
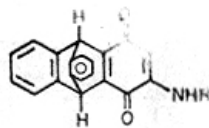
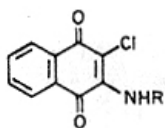
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thiazinequinone series (B). Removal of either of the hetero atoms results in planar derivatives such as 2,3-benzo[g]thiafluorine-1,4-dione or 2,3-phthaloylindole. The latter is the wellknown vat dye Helindone Yellow R. 2,3-Phthaloylpyrrocoline was also studied for its affinity values. The effect of Van der Waal's forces brought about by extended conjugation to offset the influence of non-coplanarity was studied by the determination of affinity values of dyes of the series (C) which have an additional benzene ring (Chart V).

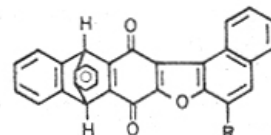
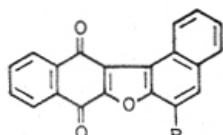
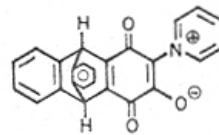
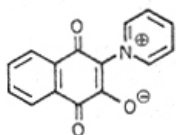
From the determination of affinity and saturation values on cellulose acetate, nylon and terylene, it was found that coplanarity of the molecule influenced affinity and saturation values, the affinity value decreasing progressively with progressive increase in non-coplanarity. Affinity values of a series of dyes of related chemical constitution also varied with different fiber substrates. With extended conjugation in the dye molecule, affinity and saturation values for all fibers increased. The work leads to the conclusion that in the quinonoid dyes examined, coplanarity was essential for substantivity to cellulosic and hydrophobic fibers.

The chemical constitutional features like conjugated unsaturation, presence of hetero atom and presence or absence of certain groups has a large impact on substantivity. It was suggested that substantivity is associated with a polynuclear system of conjugated double bonds, the residual valency of

CHART - IV.

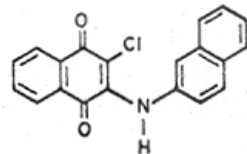
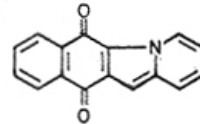
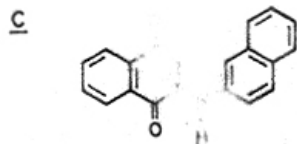
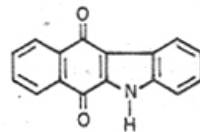
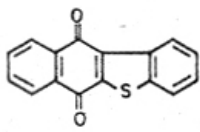
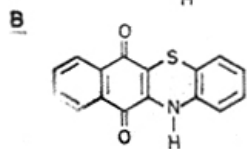
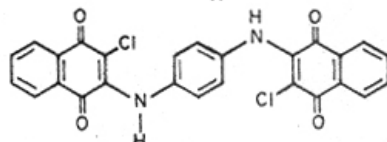
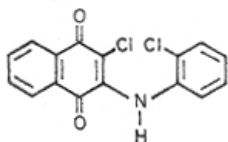
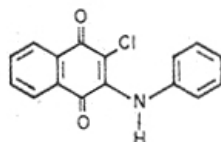
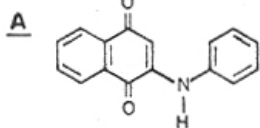


R = COOEt, CONHR', CONHAr



R = H, CONHAr

CHART - V.



which, in conjugation with the auxochromes present, is responsible for substantivity. The groups which interfere in conjugation weaken and may even destroy substantivity. Increase in substantivity with an increase in length of a conjugated chain of double bonds is to be anticipated in view of the electron cloud associated with conjugated chain of double bonds and the electronic dispersion forces. Among condensed polynuclear systems substantivity increases from benzene to naphthalene, anthracene and the more complex polynuclear aromatic systems.

According to Ruggli et al¹⁷ sulfur atoms in any form lead to increased substantivity, but a restriction to ring systems containing sulfur would be more justified. Substantivity is increased not only by sulfur containing rings but also by pyrazolone and other heterocyclic ring systems.

Presence of certain groups like azo group, amide groups etc. increase substantivity but sulfonic acid group while increasing water solubility and leaving power, decreases substantivity.

(c) Hydrophobic-hydrophilic balance

The dyeing of polyester fiber by disperse dyes depends on the partition of the dyes between the polyester and the medium in which the dye is dispersed. Disperse dyes for polyester fiber are non-ionic organic compounds which dissolve in the polyester fiber substrate but are only very slightly soluble in water. They are employed as dispersions in water and when the fiber is immersed in such dispersions a very small amount of dye which is dissolved in the water is extracted from aqueous medium by fiber substrate which thus becomes coloured. The consequent depletion of the aqueous solution causes further dye molecules to pass from the dispersed aqueous phase into aqueous solution phase and then into fiber substrate, thus giving the dyed fiber.

Dyeing thus depends on the ability of the dyestuff to diffuse into the fiber and is strongly dependent upon the internal conditions of the latter. The capacity of fibers to absorb dye is the property of the amorphous regions, and the more highly oriented or the more crystalline the fiber, the less readily absorption takes place. The mechanism discussed above, requires the penetration of dye directly between polymer chains in absence of water i.e. non-ionic dyes pass from the water phase into the polymeric fiber and travel apparently beyond the water filled region into the easily penetrable polymer substrate. This can most

readily be appreciated from the figure for normal water content of polyester fibers in air dry conditions, which is ca. $0.05-0.1 \text{ mol kg}^{-1}$, whereas simple anthraquinone disperse dyes can be absorbed (at 100°) to the extent of ca. 0.18 mol kg^{-1} ¹⁸ which, having regards to the differences in area of a water and a dye molecule, represents substantially greater penetration of the polymer structure by the dye than by water vapour.

Since polyester is a hydrophobic fiber and slight water solubility is essential for disperse dyeing, the balance between hydrophobicity and hydrophilicity has to be maintained. The dye-dye aggregates can markedly influence the concentration gradients. The large size of the dye molecules can also retard diffusion when the pores are small. Due to the hydrophobic nature of polyester, water within the fiber would slow down the diffusion. Additions of alcohols, urea, etc. destroys the dye-dye aggregates and/or the ice like structure of the water in the pores¹⁹. The hydrophilicity of the dye can also be adjusted so that maximum dye can reach the fiber pores. This can be achieved by positioning some polar groups in a dye molecule thereby making it more hydrophilic. Relatively simple aminoazo compounds, the amino-anthraquinone derivatives containing ethanolamine ($-\text{NHCH}_2\text{CH}_2\text{OH}$) or similar groups are excellent disperse dyes, since these groups render them more readily dispersible in water and also

facilitate their absorption by hydrophobic fiber. The work of Marian¹⁸ has shown that the presence of certain groups such as -OH, -CONH, -SO₂N- or O-alkyl in the dye molecule confers affinity and fastness properties on diverse dye-fiber combinations. Chart VI shows a few dyes where the structures are modified for increasing hydrophilicity.

(d) Adsorption forces

Since in dyeing of dispersed dyes the dye molecule does not react chemically with the fiber, the adsorption forces gain importance. Naturally, the type and the nature of the adsorption forces which cause the fixation of dyes by fibers has been the subject of much study²⁰. These forces can be classified as (i) forces attributed to hydrogen bonding, (ii) physical or Van der Waal's forces, and (iii) forces coming from ion exchange. Of these (iii) are most readily identifiable and they play a role mainly in dyeing of nylon and protein fibers. The role of the above forces in disperse dyeing is briefly discussed below.

(i) Forces attributed to hydrogen bonding

The very small size of hydrogen and its high polarising power causes it, under certain conditions, to form bonds with two atoms simultaneously. The required condition is that the H atom must be covalently bound to an

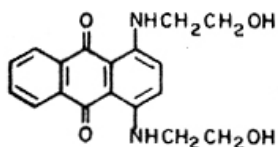
atom of high electron affinity, whereby it is positively polarised. This occurs when hydrogen is bound to N, O and F and also in some cases when it is bound to Cl, S and C^{21,22,23}.

Chart VII shows three typical disperse dye structures. Since neither in the dye nor in the fibers there are ionic groups, dye attraction clearly must originate in one or more of the various types of polar and dispersion forces. An apparently linear relation between saturation adsorption of disperse dyes on (non-ionic) secondary cellulose acetate and on (ionic) nylon suggests that the mechanism of disperse dyeing on these fibers is the same, but nylon absorbs less dye because of its lower content of amorphous material. Simple model non-ionic proton donors, e.g. phenol are readily adsorbed by cellulose acetate and this is due to hydrogen bonding as was first suggested by Marsden and Urquhart²⁴. Vikerstaff¹³ later extended this concept to dyeing with disperse dyes, all of which contain simple polar groups. Most disperse dyes contain proton donor groups, e.g. OH or NH₂, as well as proton acceptors e.g. >C=O, -N=N-, -N(CH₃)₂ and O-alkyl.

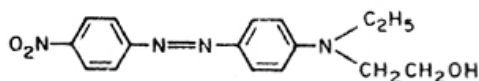
The hydrogen bond is relatively weak [(ca. 8.4-41.9 kJ) (2-10 Kcal.) mol⁻¹] and therefore can be readily formed and readily broken - one of its important features. It can be regarded as being formed by partial

CHART - VI

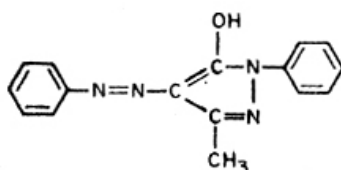
DYES WITH INCREASED HYDROPHILICITY



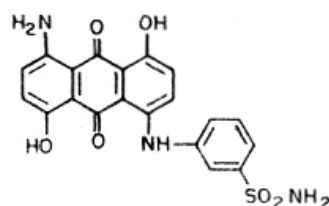
CI DISPERSE BLUE 7
(C.I. 62500)



CI DISPERSE RED 1
(C.I. 11110)



CI DISPERSE YELLOW 16
(C.I. 12700)



CI DISPERSE BLUE 40
(C.I. 63302)

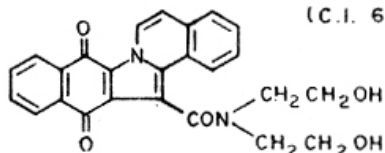
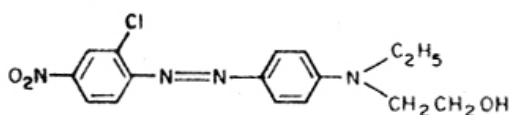
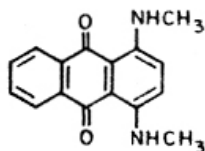


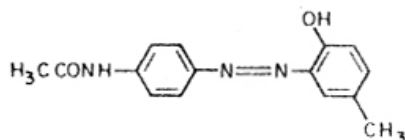
CHART - VII



CI DISPERSE RED 13
(C.I. 11115)

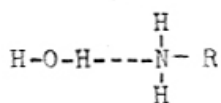


CI DISPERSE BLUE 14
(C.I. 61500)



CI DISPERSE YELLOW 3
(C.I. 11855)

proton donation and acceptance or, alternatively, by partial electron acceptance and donation by the receptive groups. Thus, in the solvation of an amino group by water, in a disperse dye, a proton of water is partially held by the nitrogen of the amino group and the unshared electrons of nitrogen are partly held by this proton



Examination of the structure of most dyes and fibers show that they have many groups which would be expected to form intermolecular hydrogen bonds and consequently these bonds are often considered to take part in the dyeing operation. A complicating factor, however, is the presence of water in the dyebath, which by itself bonding strongly with these groups, may inhibit their attachment to other molecules.

(ii) Physical or Van der Waal's Forces

These forces are so named because they were first recognised by Van der Waal in 1873 in his study of the cause of non-confirmity of gases to the ideal gas laws. They are usually divided into two main groups known respectively as polarisation (or electrostatic) and dispersion forces.

Polarisation Forces - The symmetrical distribution of electrons around atoms is disturbed when the atoms are chemically combined. In many cases this results in a permanent unsymmetrical distribution of electrons in the resulting molecule which therefore has an electric or dipole moment. Such compounds excluding hydrocarbons are polar. Molecules with dipole moments attract each other in two ways, viz. by permanent dipoles and by induced dipoles. The disperse dyes are weakly polar by virtue of presence of groups such as amino, hydroxy etc. Similarly the hydrophobic fibers are also polar. As a result polarizing forces play a role in disperse dyeing.

Dispersion or London Forces - These forces are named from the author F. London who first stated that non-polar molecules can also attract one another due to the electron clouds associated with them. In non-polar molecules, electrons which are constantly in motion may be so disturbed that there is a separation of positive and negative charge and therefore a dipole moment. When two such molecules come very close they are attracted to one another due to these electron dispersion forces. The energy of the system is thus lowered and a weak bond is established. With the increase in molecular size as in polycyclic aromatic systems the dispersion forces increase and they become relatively more effective than polarisation forces. Since both the fiber and dye molecules are large, electron dispersion forces play

a significant role in dye fiber affinity. If the dye and the fiber are unable to align themselves close enough (e.g. through steric hindrance), the dye will not be able to get attached to the fiber substrate since Van der Waal's forces will not be operative. The dye therefore has to align itself as closely as possible to the fiber substrate.

IMPACT OF STRUCTURAL MODIFICATION ON DYEING PROPERTIES

The relation between chemical constitution and dyeing properties is a complex one, because of the fact that the properties not only depend on chemical constitution but on several other factors. Although it is possible to have an approximate idea of the grade of fastness of a particular group of dyes of similar structures, it is not possible to generalize for all types of dyes as regards their fastness properties when applied to a fiber substrate. The various constitutional features described earlier put several limitations on structural modifications which one can make to achieve the desired dyeing properties. Quite often a structural change introduced to achieve improvement in one dyeing fastness property leads to adverse effect on another and hence balances and compromises have to be made. The important fastness properties required of disperse dyes are fastness to light, sublimation, burnt gas fumes and washing.

Light fastness

Light fastness is influenced not only by the chemical constitution of the dye but by several other factors, such as the type and physical structures of the fiber, the physical state of the absorbed dye, the method of dyeing used, the nature of the bonds holding dyestuff on the fiber and the after treatments likely to be given to the dyed fabric. In general, with a few exceptions, fastness ratings compared with dyeings on cellulose acetate are lower on nylon and about the same on terylene²⁵. In order to discuss the influence of constitution on the fading mechanism, it is necessary to be in possession of exact data on the energy relations of excited state. Since this data is lacking, one must revert to empirical rules.

Dyed fabric when exposed to light undergoes changes in two ways involving phototropism and fading⁵. Phototropism is a reversible change in shade shown by some disperse dyes on short exposure to light, the original shade is, however, restored on keeping the dyed fabric in dark^{26,27}. This is much more common in yellow and orange dyes of aminoazo series. This phenomenon is attributed to trans-cis rearrangement. This defect can be reduced by the introduction of electron withdrawing groups, such as nitro, cyano and acetyl in the p-position to the aminoazobenzene moiety, or by attaching an electron withdrawing group to the

amino nitrogen in such dyes. Thus reduced basicity of the amino group seems to have a favourable effect on light fastness(see Table I).

The most important action of light is fading involving an irreversible change. In the case of disperse dyeings, especially on polyester fiber, it has been found by Shrouder and Boyd²⁸ that the best dyes are those which are stable aromatic structures with a minimum of reactive groups. Amino and alkylamino groups are powerful auxochromes. These groups, however, are very vulnerable to attack by light and thus such dyes were fugitive to light. Substituents which lower basicity of amino groups in the dye molecule lead to increased light fastness²⁹. N-dialkyl groups in earlier disperse dye are therefore replaced by $-N(C_2H_4CF_2)_2$, $N-(C_2H_4CN)_2$ groups in commercial disperse dyes now in use. As with azo dyes, structural modification of aminoanthraquinone disperse dyes which reduce basicity of the amino group leads to reduced fading caused by gas fumes, ozone or light³⁰. Thus dyes of improved resistance to fading are obtained by the introduction of strong electronegative groups such as SO_2NH_2 , $SO_2N(CH_2CH_2OH)_2$, $-COCH_3$, $CONH_2$, CF_3 etc. Table (IIA, B) and Table III show the effect of structural modifications on light and sublimation fastness in a series of typical disperse dyes.

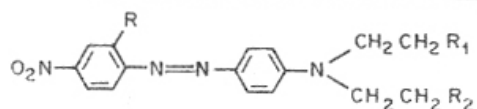
TABLE - I.

STRUCTURE	PHOTOTROPISM
	PHOTOTROPIC
	NON - PHOTOTROPIC
	NON - PHOTOTROPIC

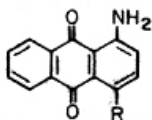
TABLE - II.

EFFECT OF SUBSTITUENTS ON LIGHT AND SUBLIMATION
FASTNESS OF DYES ON POLYESTER FIBER

A



NO.	R	R ₁	R ₂	LIGHT FASTNESS	SUBLIMATION FASTNESS
1	NO ₂	H	CN	2	3-4
2	OCH ₃	H	CN	3-4	2-3
3	CH ₃	H	CN	4-5	2
4	H	H	CN	5	2
5	Cl	H	CN	6	2-3
6	CN	H	CN	6-7	3-4
7	Cl	H	OH	3	2-3
8	Cl	H	H	3-4	1-2
9	Cl	OH	CN	4	4-5
10	Cl	H	CN	5-6	2-3
11	Cl	OCOCH ₃	CN	7-8	3-4
12	Cl	CN	CN	7-8	4

B

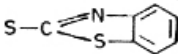
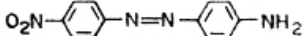
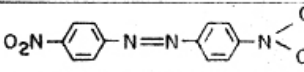
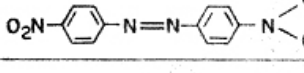
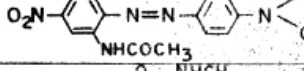
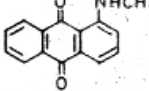
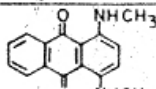
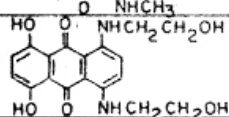
NO.	R	LIGHT FASTNESS	SUBLIMATION FASTNESS
1	OCH ₃	1-2	1
2	NHCH ₃	3	1-2
3	NHC ₆ H ₅	4-5	2-3
4	OH	5-6	1
5	S-Ph	5-6	2-3
6	NHCOPh	6	3
7		7	4

TABLE - III.
EFFECT OF POLAR GROUPS SUBSTITUTION ON SUBLIMATION
AND LIGHT FASTNESS

NO.	STRUCTURE	SUBLIMATION FASTNESS 210° (30 sec)	LIGHT FASTNESS
1		3	6
2		4	5
3		5	4
4		5	—
5		3	5
6		4-5	5
7		5	4

A study of structures of various disperse dyes reveals that the compounds having intramolecular hydrogen bonding usually have high light fastness. The hydrogen bonded structure becomes coplanar and also more stable. Hydrogen bonded imino groups make them less vulnerable to attack. This is seen in the case of nitrodiphenylamine disperse dyes which are known for their excellent light fastness. Good fastness is considered to be due to their ability to exist in the bonded form (see Chart VIII). Intriguing fact, however, in such dyes is that when a second nitro group is substituted in the p -position light fastness decreases although intramolecular hydrogen bonding is present.

It has been shown by Marian³¹ that disperse dyes are monomolecularly distributed in hydrophobic fibers; but there are differences in the mode of physical adsorption. The dyes of hydroxyazobenzene series are attacked on exposure to light undergoing rearrangement from the trans to cis form. In *o*-hydroxyazobenzene dyes, where this is precluded, the attack takes the form of oxidation on the β -carbon atom. *O*-acetylaminoazobenzene dyes which possess no intramolecular hydrogen bridges are rearranged in the cis form. Both effects can be greatly reduced by introducing bulky groups into the dye molecules and/or by heavy stretching of the fiber to increase their anisotropy.

The light fastness also depends on the rate of diffusion of gases into the fiber substrate³². This can be improved by increasing the crystallinity of the dyed fiber. The lower rate of diffusion of gases in the more crystalline fiber is the reason why many dyes have higher light fastness on polyester than on nylon or cellulose acetate fiber. This is known as diffusion restriction effect and probably operates to some extent in all fading of colourants in fibers or films.

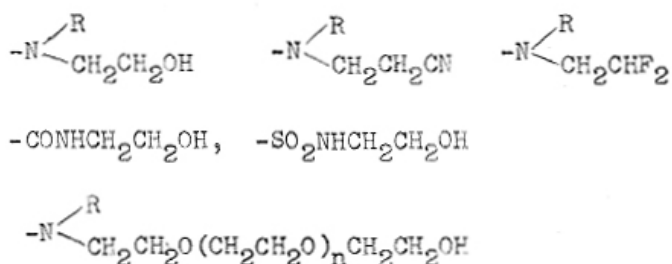
Sublimation fastness

Another important aspect of a disperse dye is its fastness to sublimation. Disperse dyes are comparatively simple in structure which permit their permeability into compact synthetic fibers. They are also devoid of ionic solubilizing groups. Because of these structural characteristics they often have significant vapour pressure. When a dyed fabric is exposed to high temperature, as during setting of plates or in hot pressing, the dye sublimates from the fiber, which may be then absorbed by the adjoining fibers leading to staining.

Disperse dyes possess melting points ranging from 120-300° and can be recovered unchanged after melting. There is no relationship between melting point and fastness to sublimation³³. Sublimation tendency of dyes decreases as

polar character of the dye increases and as the number of groups capable of hydrogen bonding increases^{20,34}.

Following are typical groups which improve sublimation fastness^{28,30} and also substantivity of disperse dye for synthetic fiber



The effect of substituents on sublimation is shown in Table IV in addition to Table II (A and B) and Table III.

Washing fastness

Fastness of dyes to washing is important for wash n' wear fabrics. Wash fastness is dependent on molecular complexity of dyes, their substantivity and nature of the substrate. Fastness of dyes to washing on cellulose acetate is relatively lower as compared with polyester. Cellulose acetate being less compact is dyed at 50-80°. Washing which is also carried out around this temperature causes desorption of the applied dye. In the case of polyester, dyeing is carried out at 100-120° whereas washing is usually carried at a much lower temperature, consequently desorption of the dye from the dyed fiber is much less.

CHART-VIII.

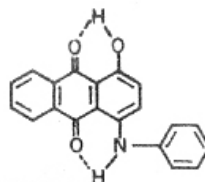
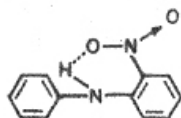
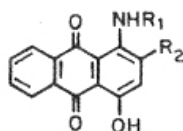


TABLE-IV.
EFFECT OF SUBSTITUTION ON SUBLIMATION FASTNESS
OF DISPERSE DYES ON POLYESTER FIBER



NO.	R ₁	R ₂	SUBLIMATION FASTNESS 210° FOR 30 sec.
1	H	H	1-2
2	Ph	H	1-2
3	C ₂ H ₄ COOC ₂ H ₅	H	2-3
4		H	2-3
5		H	2-3
6		H	3-4
7	NHCOCH ₃	H	4-5
8	H	OCH ₃	1-2
9	H		2-3
10	H	S-CH ₂ CH ₂ CN	3-4
11	H	Br	1-2
12	H		4-5

Table (V) shows clearly how molecular complexity increases washing fastness³⁵. However, affinity of the dyes for the substrate is adversely affected. In other words, improvement in washing fastness is obtained at the cost of dye and build up.

Fastness to gaseous fumes

Discolouration by gas fumes is much different from that caused by light and it occurs more commonly in industrial than in rural areas. Earlier work on this subject showed that oxides of nitrogen present in the atmosphere were responsible for gas fading^{36,37}. It has now been shown that nitrogen dioxide is the causative agent³⁵. Gas fading is a major problem with dyed cellulose acetate fabrics since nitric oxide is soluble in cellulose diacetate. The same sensitive dyes when applied on wool, nylon do not fade and their fading on cotton is much slower. Polyester fibers also absorb nitric oxide but at a much slower rate than acetate and hence dyes, which fade on cellulose acetate are much more resistant on polyester fiber substrate.

It has been observed that the dyes which have low gas fastness on cellulose acetate also have low light fastness on polyester³⁴. This suggests that basic character of the amino group in the molecule is responsible for low gas and light fastness³⁴. Thus gas fading can be improved by reducing

TABLE - V.
EFFECT OF MOLECULAR SIZE OF DYES ON THEIR
WASH FASTNESS

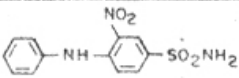
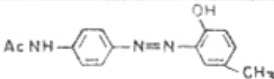
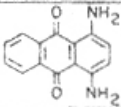
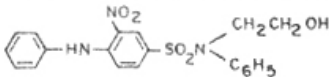
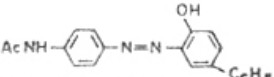
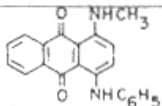
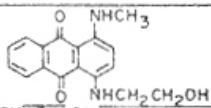
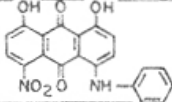
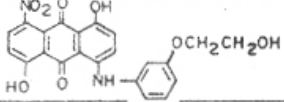
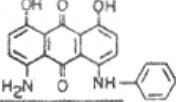
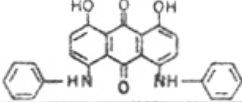
NO.	STRUCTURE	WASH FASTNESS	REMARKS
1		1-2	LESS FAST
2		2	LESS FAST
3		1-2	LESS FAST
4		3	MORE FAST
5		3-4	MORE FAST
6		3-4	MORE FAST

TABLE - VI.

NO.	STRUCTURE	AFFINITY	GAS FASTNESS
1		VERY GOOD	0-1
2		FAIR	4
3		VERY GOOD	4-5
4		GOOD	2
5		VERY POOR	4

the basic character of the amino group by introducing electron withdrawing groups or by eliminating the amino group altogether from the dye structure. Thus the dye 1,5-dihydroxy-4-arylamino-8-nitroanthraquinone has adequate substantivity and excellent light and gas fading properties. The phenyl ring acting as an electron sink is sufficient to reduce electron density at amino nitrogen to make it resistant to gas fading. Gas fading can also be reduced by adding some inhibitor in the dyebath alongwith the dye. Such inhibitors (mclamine, triethanolamine, sodium formate, etc.) preferentially react with nitrogen dioxide leaving the dye unaffected. Table VI shows affinity and gas fading fastness of some disperse dyes.

Fading of dyes is also due to ozone present in the atmosphere. Percentage of ozone in atmosphere is comparatively more in the countryside. Because of its strong electrophillic nature (more than nitrogen dioxide) it can react even with weakly basic amines or nucleophillic groups.

REFERENCES

1. Definition given by Society of Dyers and Colourists, J. Soc. Dye. Col., 74, 41 (1958).
2. Bird C. L., ibid, 70, 68 (1954).
3. Venkatraman, K., 'Chemistry of Synthetic Dyes', Academic Press, New York, 1, 637 (1952).
4. Green A. G., Saunders K. H., J. Soc. Dye. Col., 39, 10 (1923)
5. Knight A. H., ibid, 66, 169 (1950).
6. Ellis G. H., Br. C., B. P., 219,349 (1923); C. A., 19, 579 (1925).
7. Baddiley, Shepherdson, B. P., 211, 720 (1924); C. A., 18, 1914 (1924).
8. Michie A. G. H., J. Soc. Dye. Col., 70, 13 (1924).
9. Balmforth D., Bowers C. A., Bullington J. W., Guion T. H., Roberts T. S., ibid, 82, 405 (1966).
10. Vickerstaff T., Hexagon Digest., 20.
11. Tilak B. D., Rao S.S., Daruwalla E. H., J. Soc. Dye. Col., 76, 418 (1960).
12. Tilak B. D., Rao, S.S., Chem. Ind. (London), 1320 (1957).
13. Vickerstaff T., 'The Physical Chemistry of Dyeing', Oliver and Boyd: Edinburgh, (1950); 2nd edn. (1964).
14. Daruwalla E. H., Rao S. S., Bhatt N. J., Textil - Rundschau 20, 133 (1965).
15. Venkateswaran M.R., Ph.D. (Tech.) Thesis, University of Bombay (1967).
16. Tilak B. D., Venkateswaran M. R., Chimia., 22 (Suppl.) 95 (1968).
17. Ruggli, J. Soc. Dye. Col., Jubilee Vol., 77 (1934).
18. Schuler, Remington, Disc. Faraday Soc., 16,201 (1954).

19. Rys P., Zollinger H., 'Fundamentals of the Chemistry and Application of Dyes', Wiley-Interscience, 182 (1970).
20. Giles C. H., 'The Theory of Colouration of Textiles', Ed. by Bird and Boston, 41 (1975).
21. Pimentel, McClellan, 'The Hydrogen Bond', W. H. Freeman and Co. ; San Francisco, (1960).
22. Murrell., Chem. in Britain, 5, 107 (1969).
23. Vinogradov, Linnell, 'Hydrogen Bonding', Van Nostrand Reinhold Co., London, (1971).
24. Marsden, Urquhart, J. Textile Inst., 33, T 105 (1942).
25. Giles C. H., J. Soc. Dye. Col., 73 127 (1957).
26. Michel L. V., Stauffer H., Helv. Chim. Acta., 24, 151 E (1941).
27. Zollinger H., 'Azo and Diazo Chemistry', Interscience, New York, 60 (1961).
28. Shrouder H. E., Boyd S. N., Textile Research J., 27, 275 (1957).
29. Dickey, Ind. Eng. Chem., 45, 1730 (1953).
30. Salvin V. S., Walker R. A., Textile Research J., 30, 381-88 (1960).
31. Merian E., ibid, 36, 612-18 (1966).
32. Giles C. H., Shah C. D., Johari D. P., Sinclair R.S., J. Soc. Dye. Col., 88 (2), 59 (1972).
33. Rhode Island Intersectional Paper, Amer. Dyestuff Reprtr., 54, 26 (1965).
34. Salvin V. S., ibid, 55, 490 (1966).
35. Sunthakar S.V., 'Chemistry of Natural and Synthetic Colouring Matters, T. S. Gore, 528 (1962).
36. Rowe F. M., Chamberlain K. A. J., J. Soc. Dye. Col., 53, 268-78 (1937).
37. Green Span F. P., Spoerri P. E., Amer. Dyestuff Reprtr., 445-50 (1941).

CHAPTER - I B

**SYNTHESIS OF NAPHTHINDOLIZINEDIONES
(PHTHALOYL PYRROCOLINES)
FROM SUBSTITUTED NITROTOLUENES**

SYNTHESIS OF NAPHTHINDOLIZINEDIONES OR
PHTHALOYLPIRROCOLINES

Background and Recent Developments

The α, β -unsaturated carbonyl system in quinones readily undergoes Michael condensation with compounds containing active methylene groups. However, the strongly basic conditions associated with these reactions also produce tarry products and early workers got only poor yields of reaction products¹. Many authors have continued to explore reactions of quinones with active methylene compounds. Thus reactions of 1,4-naphthoquinone with compounds containing reactive methylene groups and other reactive compounds have been widely studied.

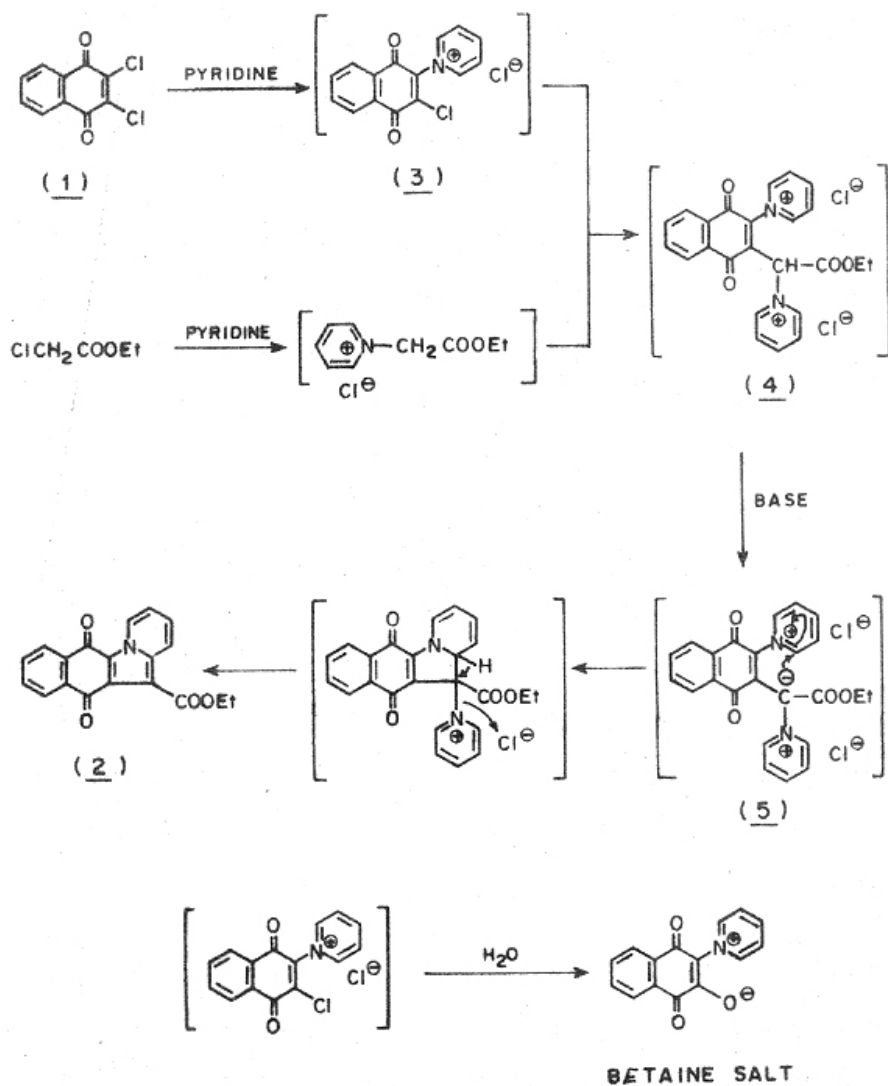
The reaction of 2,3-dichloro-1,4-naphthoquinone (DCNQ) (1) with ethyl chloroacetate and pyridine provided an interesting heterocyclic quinone, 1-carboethoxy phthaloyl-pyrrocoline^{2,3} [12-carbethoxynaphth(2',3'-b)indolizine-6,11-dione] (2). This reaction was explored by many authors with the view to synthesise a series of dyes and pigments. A wide variety of active methylene compounds such as acetoacetic ester⁴, cyanoacetic ester⁴, acetylacetone⁴, dibenzoylmethane⁵, diethylmalonate⁵, etc. have been reacted with 2,3-dichloro-1,4-naphthoquinone in presence of tertiary heterocyclic bases. Besides pyridine several substituted pyridines such as 4-picoline⁶, collidines⁷, phenylpyridine⁸,

etc. have also been employed. Isoquinoline⁶ also reacts with (1) to give phthaloylpyrrocolines. The possible mechanism for these reactions postulates formation of the key intermediate (3) as a first step⁹ (see Chart I).

Phthaloylpyrrocoline is usually prepared by heating a mixture of DCNQ, active methylene compounds and the heterocyclic base in an inert solvent. Dioxan or xylene usually give high yields. The yields of these heterocyclic quinones⁴ vary from trace to very good for pyridine, but when isoquinoline is used, the yields are generally better. Pyridine reacts with DCNQ and ethyl chloroacetate to give the salt (4). In presence of a base, (4) readily gives a carbanion intermediate (5) which cyclises eliminating pyridine hydrochloride to give 1-carbethoxy-2,3-phthaloylpyrrocoline (2) (Chart I).

The interest in the phthaloylpyrrocoline chemistry has been stimulated because of the discovery that several derivatives of this class are useful as vat dyes for cotton and as pigments¹⁰. Thus several patents⁸ describe the preparation of carboxamide derivatives (6) (Chart II) prepared by the condensation of 2,3-phthaloylpyrrocoline-1-carboxylic acid chloride with arylamines. These dyes are claimed to be red pigments of good fastness. A Russian patent¹¹ has described phthaloylpyrrocolines of

CHART - I.

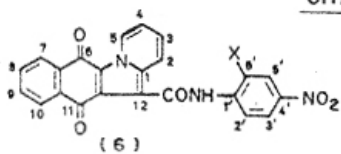


the type (7) (Chart II) prepared by the condensation of 5-nitro-2,3-dichloro-1,4-naphthoquinone with pyridine and active methylene compounds e.g. $\text{CNCH}_2\text{COOEt}$, Ac_2CH_2 , BzCH_2COCN , BzCH_2Ac . These dyes are described as disperse dyes. Xerox Corporation¹² has taken a patent on synthesis of pyrrocolines of the type (8) (Chart II) claiming that these are intensely brilliant oranges suitable for paints and inks.

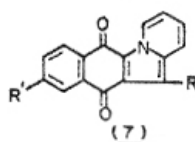
The compounds of the general formula (9) (Chart II) are useful as intermediates for synthesis of heterocyclic dyes and pigments¹³. 1-Aminonaphthindolizine diones of type (10) (Chart II) have been prepared by condensing DCNQ or substituted DCNQ with 3-amino pyridine and reactive methylene compounds in boiling ethanol. Such quinones¹⁴ are red coloured compounds which are used for the preparation of heterocyclic dyes. Substituted phthaloyl-pyrrocolines (11) (Chart II) have also been reported by Ciba¹⁵. It is claimed that very high yields can be obtained by carrying out the reaction in dioxan.

Geigy^{16,17} has recently taken out a series of patents relating to pyrrocoline pigments. The substituted phthaloylpyrrocolines (12) (Chart II) have been synthesised by two general schemes A and B shown in Chart III. 2,3-Phthaloylpyrrocoline-1-carboxylic acid is first prepared, converted to the acid chloride and then reacted with the

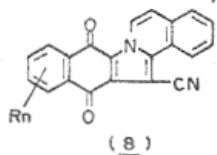
CHART - II.



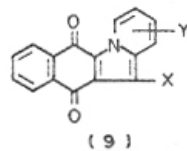
X = Cl, LOWER ALKYL, ALKOXY or NIRO



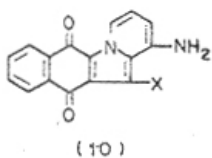
R = CN, COOEt R' = NO₂, NH₂, NHAc



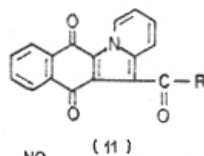
Rn = SAME or DIFFERENT NO₂, ACETAMIDO, CN, ALKOXY, NH₂, or HALOGEN n=1-3



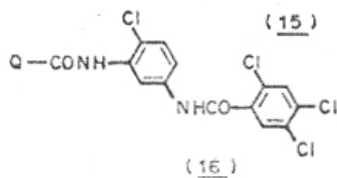
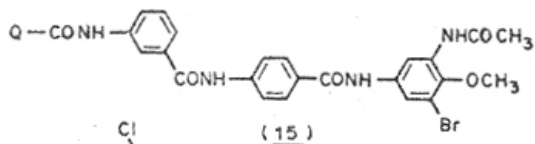
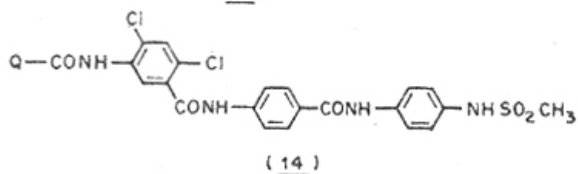
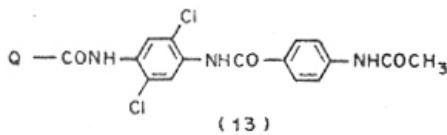
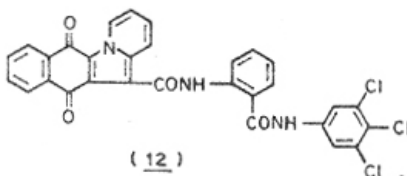
X = SUBSTITUTED PYRIDINES
X = NO₂, NH₂ etc.



X = COOEt, COOMe, CN, CONHPh



R = , -NH- , - ,



aminobenzoic acid. The pyrrocoline derivatives containing carboxylic acid group can be used as such as pigments or can be further reacted with arylamines after conversion to the carboxylic acid chloride as before. Such compounds are said to be useful for the dyeing of inks, rubbers, synthetic polymers, paper and textiles.

Naphth(2',3'-b)indolizine-6,11-dione-12-carboxamides (13-15) (Chart II) prepared by the above general method have been reported to be pigments of good fastness for paper and polyvinyl chloride^{18,19,20}. Light fast pigments of general formula (16) (Chart II) can be used for printing papers and for PVC²⁰.

Substituted pyrrocoline pigments prepared by the method described in route C have been represented²¹. Also, (17) can be prepared as shown in route D (Chart IV).

Quinoline derivatives such as benzo[g]naphth[2",3"—b]indolizine-8,13-dione-14-carboxamides have been similarly prepared by the condensation of the relevant carboxylic acid chloride with arylamines. These pigments are claimed to give enamels of very good light fastness and possess very good heat stability in polyethylene and natural rubber^{22,23}. A few examples are (18-21) (Chart V). The compound (18) has been used for dyeing²³ PVC film (Geon-121) stoving lacquer, polyethylene rubber and printing ink. The

CHART - III.

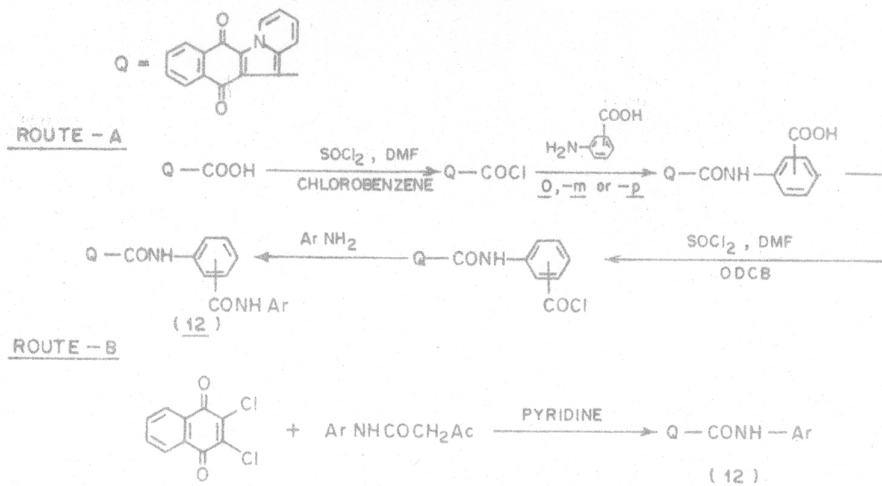


CHART - IV.

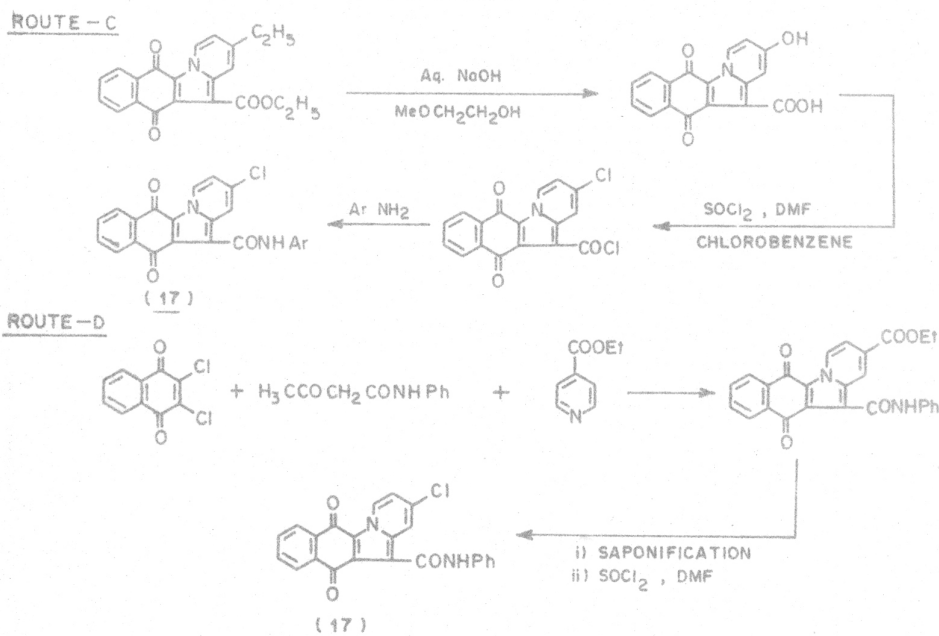
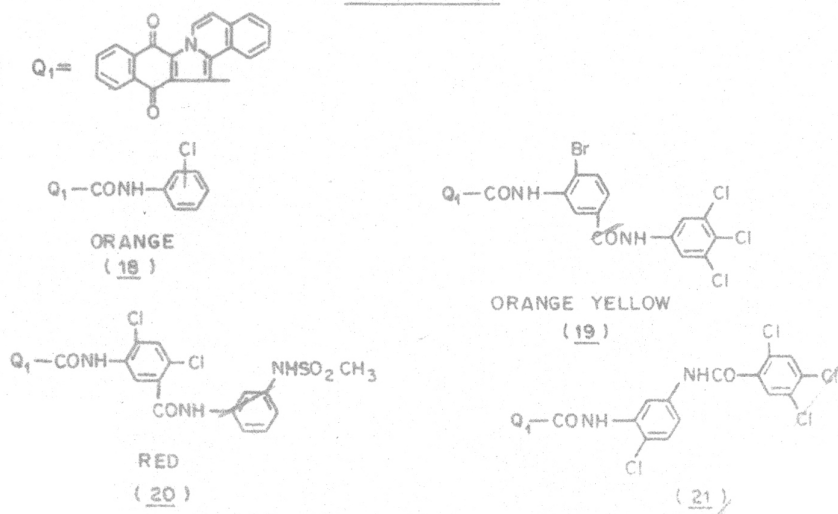


CHART - V.

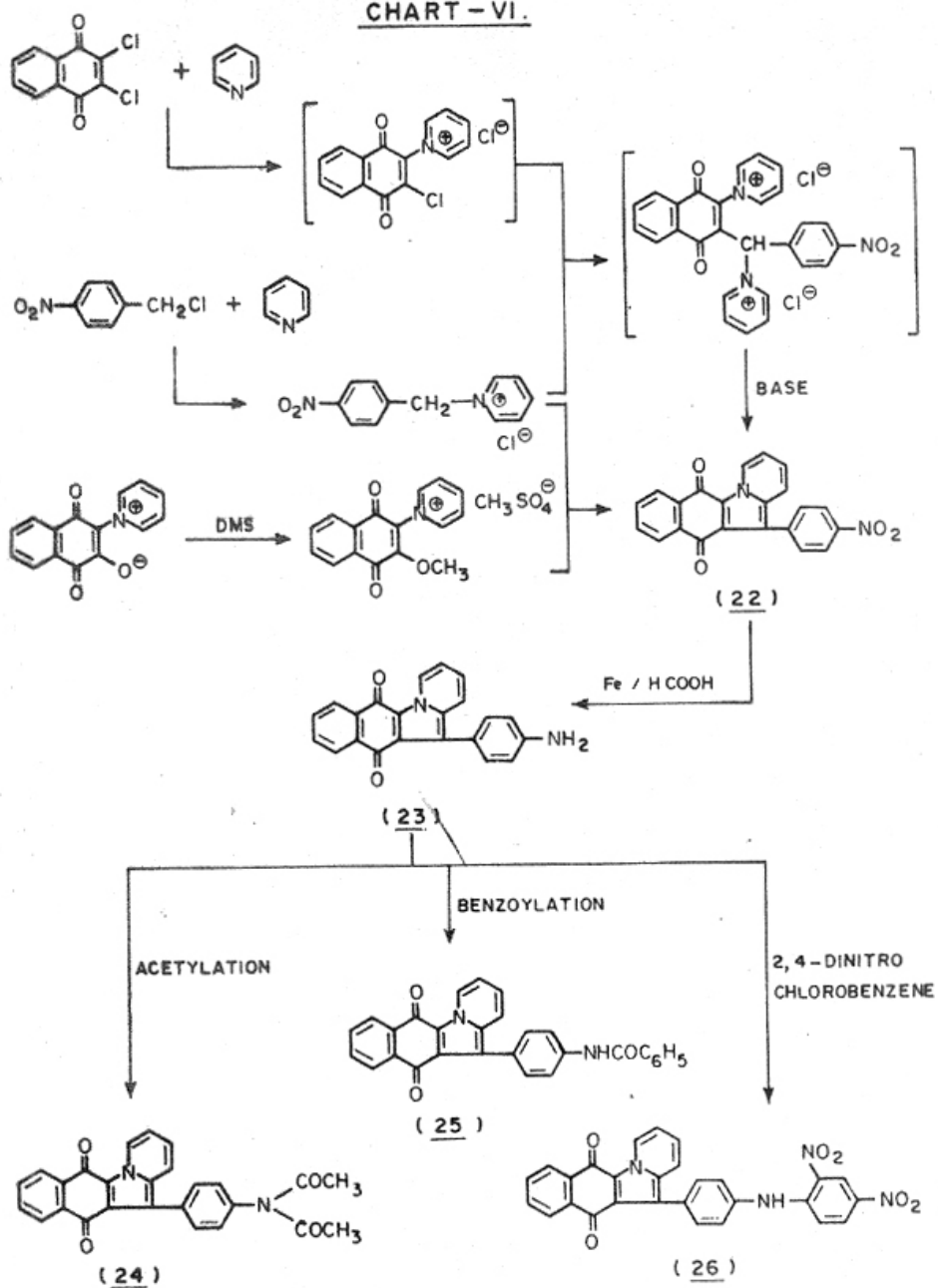


pigments such as(19-21) are useful for dyeing and pigmenting high molecular weight hydrophobic materials and possess good resistance to light, cross-lacquering, migration, heat and solvents^{24,25}.

Naphthindolizinediones such as 12-(p-nitrophenyl)-naphth[2',3'-b]indolizine-6,11-dione were synthesised in this laboratory by Tilak et al. The synthesis involved interaction of p-nitrobenzyl chloride with DCNQ in presence of pyridine²⁶. The required naphthindolizinedione was obtained in 54% yield. 12-(p-Nitrophenyl)naphthindolizinedione(22) can also be prepared by the reaction of pyridinium methosulphate and ethyl p-nitrophenylacetate. The p-nitro group in (22) was reduced with iron and formic acid to give 12-(p-aminophenyl)naphthindolizinedione (23) . Although attempts to diazotize amino group in (23) failed, various derivatives like diacetyl (24) benzoyl (25) were prepared. Interaction of 2,4-dinitrochlorobenzene with (23) yielded a bluish red dinitrophenylamino derivative (26) [see Chart VI].

The thermolysis of 2-chloro-3-azido-1,4-naphthoquinone (27) in excess of γ -picoline resulted in a mixture of (28), (29) and (30)²⁷. It is evident that two different reactive species, a nitrene generated from (27) and an active methylene group generated from γ -picoline are involved in the reaction. Product (30) was isolated in 65% yield when DCNQ

CHART - VI.



was refluxed with excess of γ -picoline. The activity of the methyl group in γ -picoline was exploited and a number of compounds were synthesised in this laboratory²⁷. In order to prove the structure of (30) the compound was unambiguously prepared by treating 1-(4-pyridylmethyl)pyridinium bromide or 1-(4-quinolylmethyl)pyridinium bromide with appropriate quaternary salts as shown in Table 1. The resulting dyes were then quaternized by treatment with methyl iodide²⁷. Charts VII, VIII and Table I give few representative examples of these compounds.

CHART -VII.

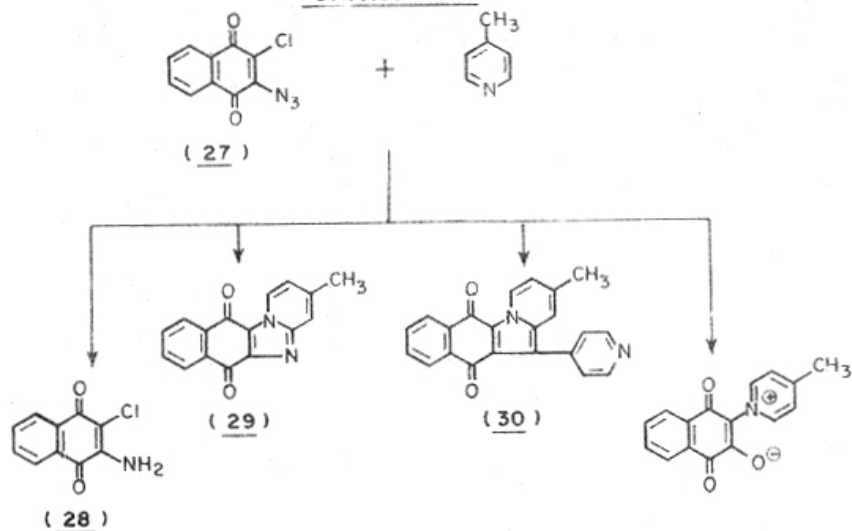


CHART -VIII.

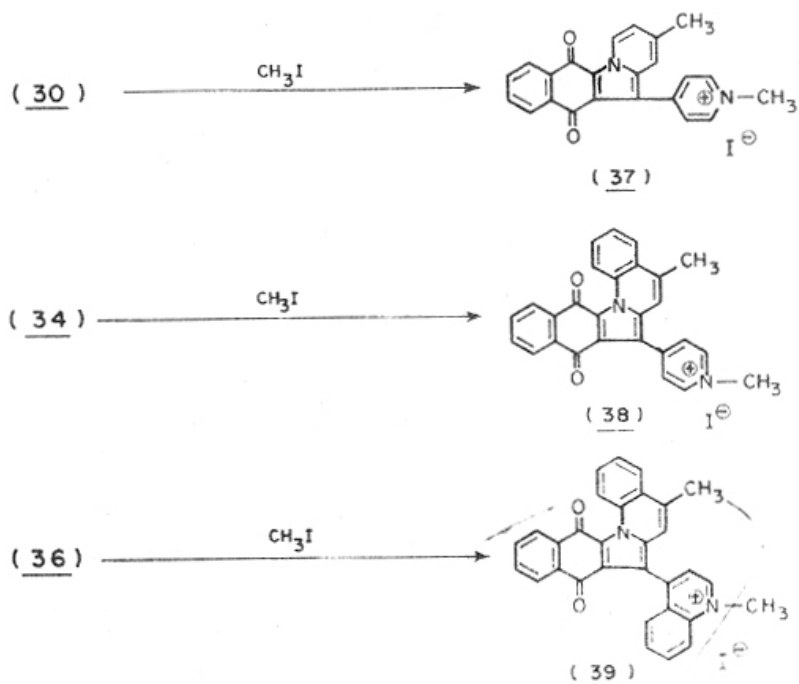
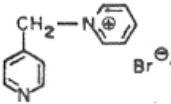
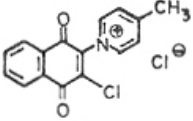
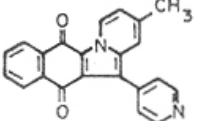
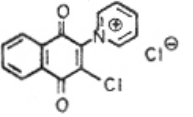
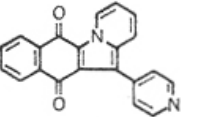
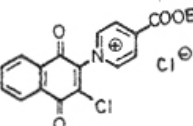
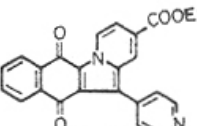
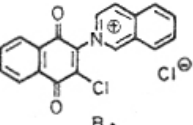
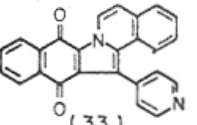
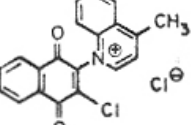
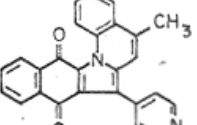
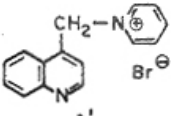
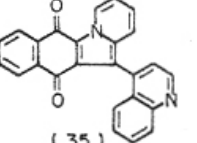
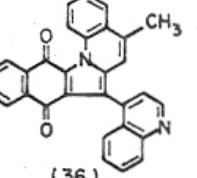


TABLE -1.

NO.	REACTIVE METHYLENE COMPOUND	QUATERNARY SALT	PRODUCT	COLOUR AND MELTING POINT
1	 <p>A</p>	 <p>B₁</p>	 <p>(30)</p>	REDDISH ORANGE 340°
2	A	 <p>B₂</p>	 <p>(31)</p>	ORANGE 298°
3	A	 <p>B₃</p>	 <p>(32)</p>	RED 248°
4	A	 <p>B₄</p>	 <p>(33)</p>	ORANGE 358°
5	A	 <p>B₅</p>	 <p>(34)</p>	RED 285°
6	 <p>A'</p>	B ₂	 <p>(35)</p>	REDDISH ORANGE 290°
7	A'	B ₅	 <p>(36)</p>	ORANGE 335°

Present Work

Despite the fact that 2,3-phthaloylpyrrocolines are brilliant dyes, they do not appear to have been as yet included in the commercial range of dyes. This is presumably due to the fact that (1) the yields of these dyes are low of the order of 10-60%, (2) the dyes show poor substantivity when applied as vat dyes to natural fibers¹³ and (3) the light fastness of these dyes is low¹³.

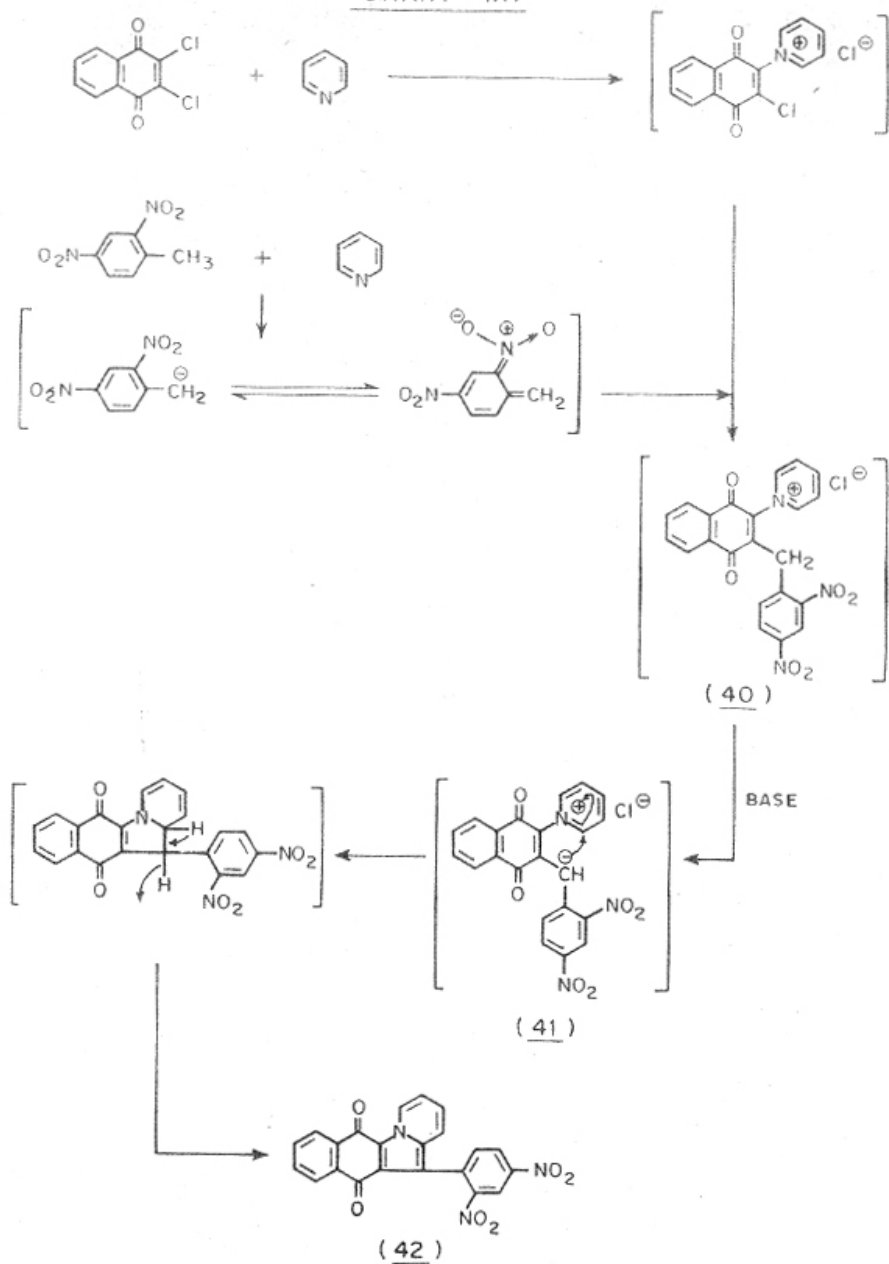
Yields in the synthesis of pyrrocoline dyes depend on the reactivity of an active methylene compound since pyridinium salt of DCNQ is readily hydrolysed by moisture to form the betaine salt^{2,3}. Generally, the reaction rate of betaine formation is higher than that of pyrrocoline. Hence dry reaction conditions are essential for success of the reaction. However, it is observed that betaine formation cannot be entirely avoided even under dry conditions.

Poor light fastness is probably due to the fact that there are no groups present in the dye molecules which could form hydrogen bonds as in the case of hydroxy or N-methylaminoanthraquinone dyes. 1,5-Dihydroxy-8-nitro-4-anilinoanthraquinone disperse dyes are known to have good light fastness, which is probably due to the ability of these dyes to exist as a hydrogen bonded structures. Further, such dyes form hydrogen bonds with fibers which facilitate fixation of the dye to the fiber.

The present work was undertaken to synthesise new phthaloylpyrrocolines by the interaction of 2,3-dichloro-1,4-naphthoquinone, tertiary heterocyclic bases like pyridine, isoquinoline etc. and compounds containing a methyl group activated by o-, p-substituted electron withdrawing groups. Thus when electron withdrawing groups are present in 2,4- or 2,4,6-position in toluene, the methyl group is capable of losing a proton in presence of a tertiary heterocyclic base to give a reactive carbanion (Chart IX). This carbanion reacts with DCNQ in presence of a base to yield 2,3-phthaloylpyrrocoline. By insertion of groups like CN and NO₂, it was expected to synthesise 2,3-phthaloylpyrrocoline pigments which can be used as disperse dyes of superior light fastness. The low yields of the final products precludes the work of any commercial interest.

Mechanism^{9,27} of formation of a typical phthaloylpyrrocoline is shown in Chart IX which illustrates the reaction of 2,4-dinitrotoluene, pyridine and DCNQ. Dichloronaphthoquinone reacts with pyridine to give first 3-chloro-1,4-naphthoquinone-2-pyridinium chloride (3). 2,4-Dinitrotoluene loses a proton in presence of pyridine to form a carbanion which then attacks the pyridinium salt (3) to form the complex (40). One more mole of pyridine abstracts a proton forming (41) to generate a second carbanion which cyclises to give 12-(2',4'-dinitrophenyl)naphth(2'',3''-b)indolizine-6,11-dione (42).

CHART - IX.



The above reaction was exploited to synthesise a number of phthaloylpyrrocolines (naphth-2',3'-indolizine-6,11-dione). The synthesis of phthaloylpyrrocolines by the interaction of di or trisubstituted toluene with DCNQ and heterocyclic bases has been studied in some detail. It was found that anhydrous conditions and proper solvent choice were important factors.

The general method of preparation of above disperse dyes consists in heating the mixture of 1 mole of DCNQ with 3 moles of the heterocyclic base in a suitable solvent for 20 minutes. This was followed by dropwise addition of compound containing the reactive methyl group (dissolved in solvent) during another ten minutes. The mixture was then refluxed for two hours and poured in water. The residue was filtered and washed thoroughly with boiling water and dried under vacuum. The aqueous filtrate contains the yellow coloured pyridinium (or the respective heterocyclic base) betaine. The reaction product was adsorbed either on silica gel or alumina and chromatographed. Work-up yielded the respective 1-aryl-2,3-phthaloylpyrrocolines. These compounds gave characteristic coloured solutions in concentrated sulfuric acid.

The choice of solvent remarkably influences the yield of dyes. When the reaction of DCNQ and 2,4-dinitrotoluene was carried out in 98% ethanol containing molar quantities of pyridine no appreciable amount of pyrrocoline was isolated but instead 80% yield of betaine salt was obtained. When the reaction was carried out in dry benzene, above 7-8% of pyrrocoline was isolated; whereas pyridine itself as a solvent yielded 14-15% of the phthaloyl pyrrocoline.

Polar media such as dimethylformamide gave poor yields of the 1-aryl-2,3-phthaloylpyrrocolines. When the synthesis was repeated at higher temperature in solvents such as dimethyl sulphoxide, trichlorobenzene or nitrobenzene the yields of the pyrrocolines were still lower. Chlorobenzene gave about 16-17% yield of the dyes. In toluene the yield was around 10-12%.

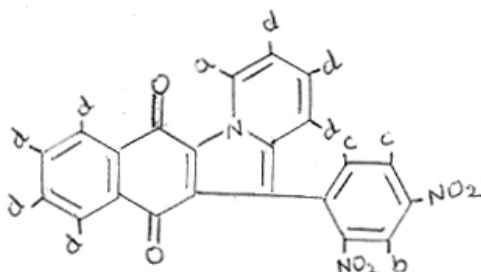
Among all solvents dry dioxan and xylene gave best results. Dry dioxan gave the best yield which also, however, did not exceed 27-30%. The reaction mixture, when dioxan was used as solvent, was also easy to work up. Various modifications in the reaction procedure were tried without much success as regards yield improvement.

In addition to pyridine, stronger bases like triethylamine and sodamide were used with the view to facilitate proton abstraction from dinitrotoluene. However, this led to formation of side products with reduction in yield of the desired pyrrocolines.

The structure of the compound (42) was established on the basis of spectral and elemental analysis. The IR spectrum of (42) (Fig. 1) shows two bands between 1650 and 1630 cm^{-1} which can be assigned to two carbonyl groups. In addition to this, the spectrum shows two bands at 1360 cm^{-1} and 1530 cm^{-1} which indicate the presence of nitro group. Since nujol also shows peaks in the region of nitro groups, IR was also recorded in hexachlorobutadiene. This confirmed the presence of nitro group.

Compounds of the type (42) being less soluble in usual organic solvents, NMR spectrum (Fig. 2) was recorded in arsenic trichloride. Almost all the compounds of the present work were found to have good solubility in arsenic trichloride. NMR shows a complex pattern of aromatic protons appearing in a narrow range. The eleven protons present appeared as a multiplet of seven protons and four doublets having

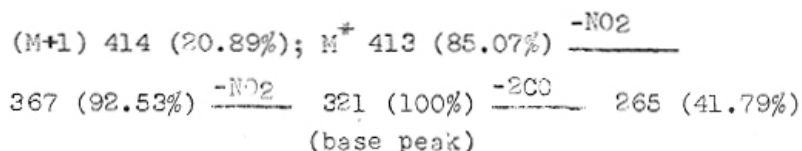
one proton each (Fig. 2).



A characteristic doublet was consistently found in every spectrum of above naphthindolizinedione derivatives. This one proton doublet, centered at 9.8δ ($J = 1.7$ Hz), can therefore be assigned to proton a. Further, the spectrum shows a doublet at 9.0δ which can be assigned to a proton situated in between the two nitro groups of dinitrophenyl moiety (b). The reason for its downfield appearance is the deshielding effect of two nitro groups. The doublet is due to m-coupling i.e. coupling with proton c which is situated in meta position with respect to b. Two doublets at $8.6-8.9\delta$ can be assigned to two c protons of dinitrophenyl moiety. Finally the complex multiplet between $7-8.4\delta$ corresponding to seven protons can be assigned to d protons (see Fig. 3).

The mass spectrum (Fig. 4) of (42) shows ($M + 1$) peak at 414 (20.89 %) and is followed by molecular ion peak at 413 (85.07%). Fragmentation pattern clearly shows the loss of two nitro groups which confirms their existence in the

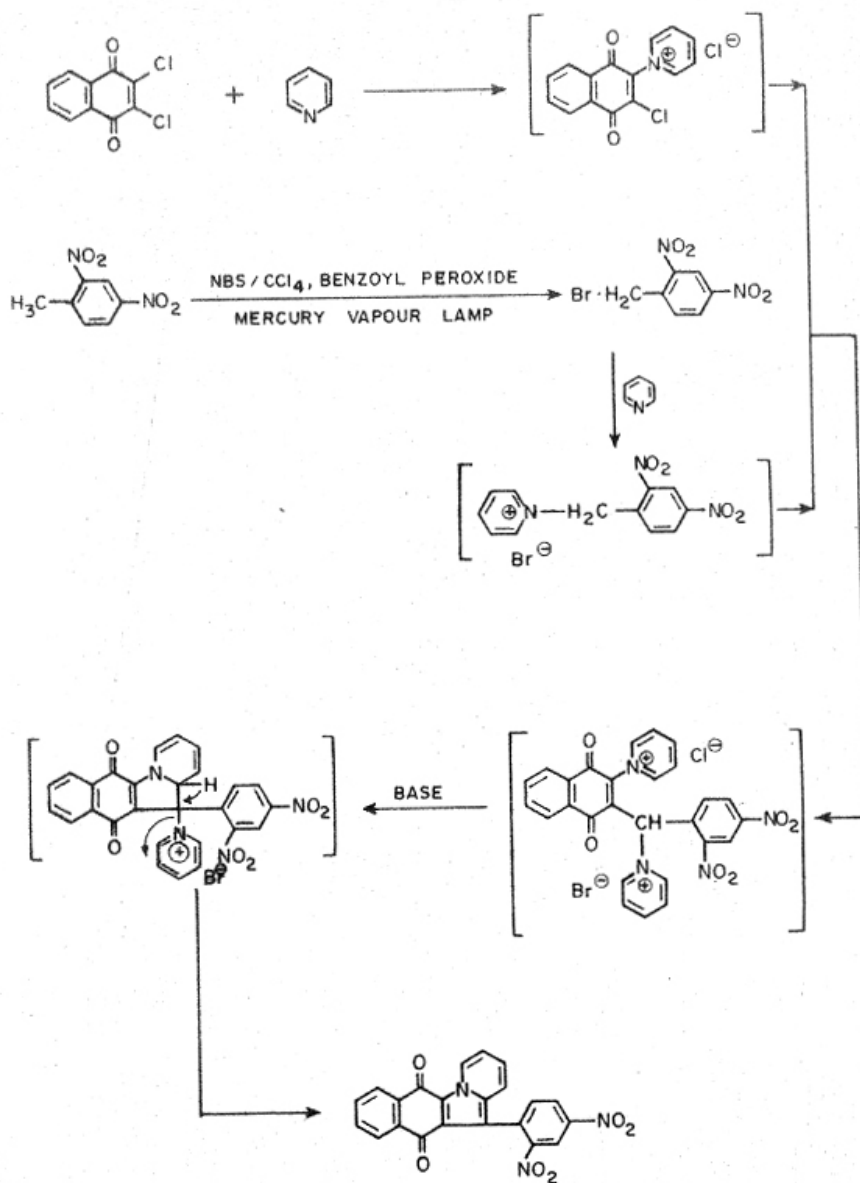
molecule. The successive loss of two carbon monoxide molecules in the fragmentation pattern is suggestive of two carbonyl groups as part of the ring structure:



Structure of (42) was further confirmed by microanalysis. Figs. 1, 2 and 4 show IR, NMR and mass spectrum of compound (42).

Compound (42) was also synthesised unambiguously as shown in Chart X. 2,4-Dinitrotoluene was brominated with N-bromosuccinimide in presence of benzoyl peroxide. Reaction was rapid and smooth when photolysed. 2,4-Dinitrobenzyl bromide thus obtained was reacted with pyridine to yield 2,4-dinitrobenzylpyridinium bromide (A). The latter interacts with the pyridinium salt (3) derived from DCNQ. The pyridinium salt (A) was not isolated but its presence was inferred since the test for the presence of an active methylene group (in 2,4-dinitrobenzylpyridinium bromide) was established by means of picryl chloride test of Krohnke²⁸. The pyridinium salt (A) in 2N NaOH solution reacted with picryl chloride to give a dark red colour indicating the presence of reactive methylene group in 2,4-dinitrobenzylpyridinium bromide. Many authors²⁹ have reported the synthesis of reactive quaternary salts and the use of picryl chloride test for showing the presence of an active methylene group in such salts.

CHART -X.



(42)

The reaction of pyridinium salt (A) with (3) resulted in the formation of 12-(2',4'-dinitrophenyl)naphth [2",3"-b]indolizine-6,11-dione (42). The yield of the latter at best was only 30%. Compound (42) thus prepared was identical in all respects with the product prepared from DCNQ and 2,4-dinitrotoluene described above.

A reexamination of the earlier work in this laboratory on the interaction of DCNQ, acetylacetone and pyridine showed that along with compound (43), which was reported earlier, acetaldehyde is also formed. The latter was trapped as its 2,4-dinitrophenylhydrazone. Further confirmation of the mechanism of the reaction between DCNQ and reactive methylene derivatives was afforded by the interaction of DCNQ, acetacetanilide and pyridine (in boiling ethanol). The reaction afforded (43), (44) (as the major products), ethyl acetate and acetaldehyde (trapped as 2,4-DNP derivative) (Chart XI).

Ethylbenzene, when nitrated gave 2,4-dinitroethylbenzene along with its 2,6-isomer. 2,4-Dinitro derivative was checked by VFC technique to ensure the absence of 2,4-dinitrotoluene. 2,4-Dinitroethylbenzene was then reacted with DCNQ instead of 2,4-dinitrotoluene. Work up gave an orange red solid which proved to be identical with (42). The formation of (42) by interaction of DCNQ, pyridine

and 2,4-dinitroethylbenzene indicates a loss of methane molecule in the reaction (Chart XII). However, we failed to trap methane from the reaction. Yield of compound (42) in this reaction was only 3-4%.

Lastly (42) was also prepared by the route suggested by J. A. Van Allen³⁰. Reaction between DCNQ and pyridine in butanol gives the pyridinium salt which when heated with dimethyl sulphate yields pyridinium methosulphate of DCNQ. Van Allen reacted this methosulphate with a number of compounds containing a reactive methylene group to give phthaloylpyrrocolines in good yields. Following this procedure the methosulphate was reacted with 2,4-dinitrotoluene in presence of pyridine (with dry dioxan as solvent). However, the yield of (42) under these conditions was only 4-5% (Chart XIII).

The above synthesis of (42) was further exploited to prepare several 1-aryl-2,3-phthaloylpyrrocolines. 2,4,6-Trinitrotoluene may be expected to readily give the carbanion by proton abstraction by a base. However, steric crowding of the methyl group by two *o*-nitro groups was to reduce its accessibility for interaction with DCNQ. Interaction of DCNQ, 2,4,6-trinitrotoluene and pyridine in dry dioxan gave a 30% yield of 12-(2',4',6'-trinitrophenyl)-naphth(2'',3''-b)indolizine-6,11-dione (45). The reaction

when carried out in benzene gave 10-12% yield of (45). Yield was much lesser when 90% ethanol was used. Reaction in pyridine gave about 16-17% yield of (45). Carrying out the reaction in higher boiling solvents was not tried due to the danger inherent in use of TNT and an oxidising agent such as DCNQ. Structure of (45) was confirmed by its IR, NMR, mass spectra and microanalysis.

2-Cyano-4-nitro toluene (prepared by Sandmeyer reaction from fast scarlet G base, 2-amino-4-nitro toluene) was interacted with DCNQ and pyridine as above (Chart XIV). Final work-up gave 12-(2'-cyano-4'-nitro)naphth(2",3"-b) indolizine-6,11-dione(46) where structure was confirmed by IR, NMR, mass spectra and microanalysis. Fig.5 indicates the IR spectrum of (46).

Replacement of pyridine in above reactions by substituted pyridines did not lead to higher yields of the relevant dyes. This may be attributed to lower basicity of these bases and lower reactivity towards DCNQ. These results are tabulated later in this chapter. The influence of these factors will be clear from the good yield (~60%) of the desired pyrrocoline dye (47) obtained from DCNQ, pyridine and ethylchloroacetate as compared to only 4-5% yield of (48), when DCNQ was reacted with 3-cyanopyridine and ethyl chloroacetate.

CHART - XI.

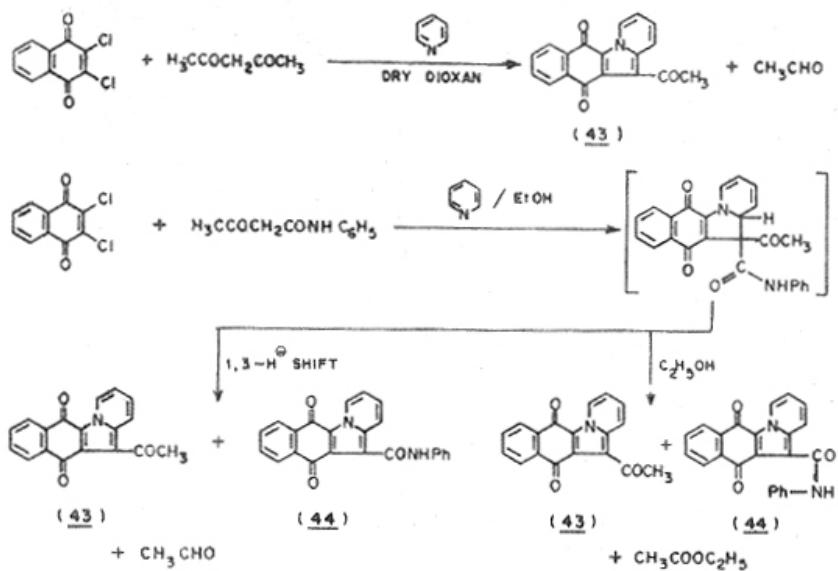


CHART - XII.

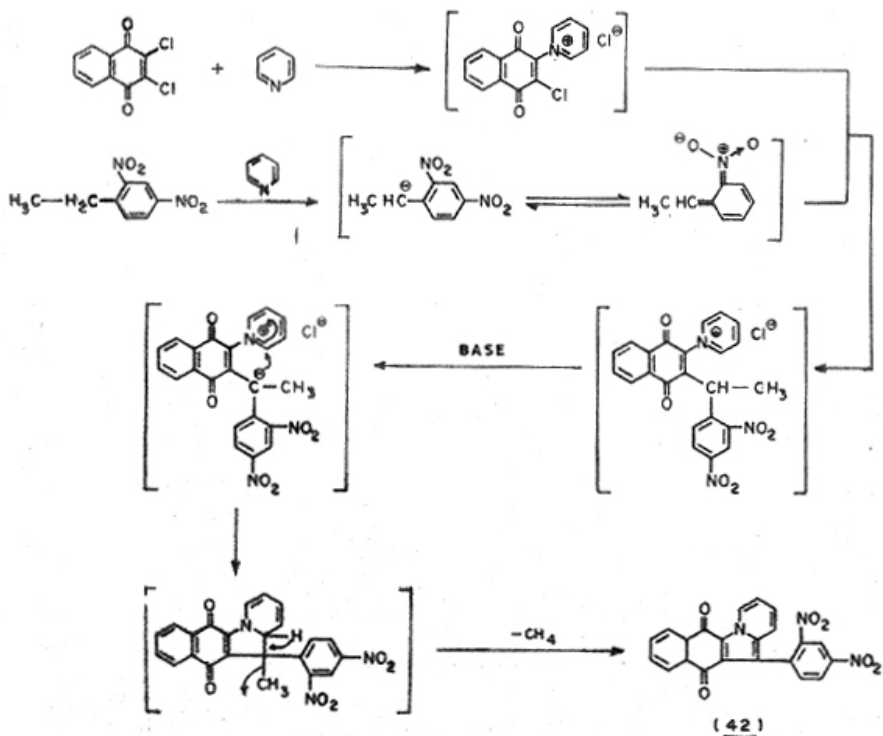


CHART - XIII.

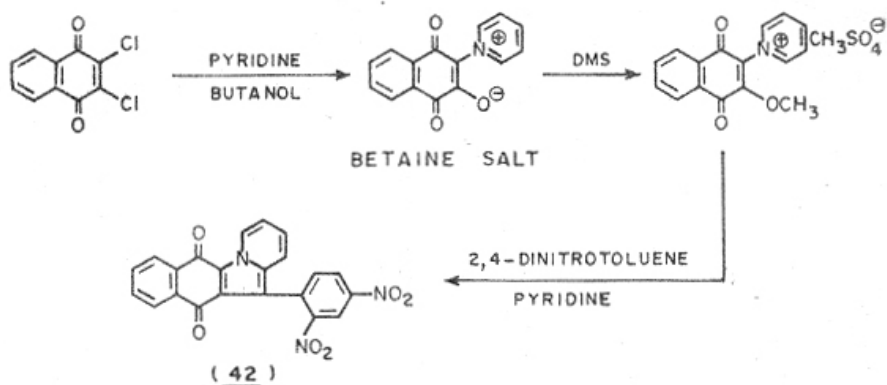
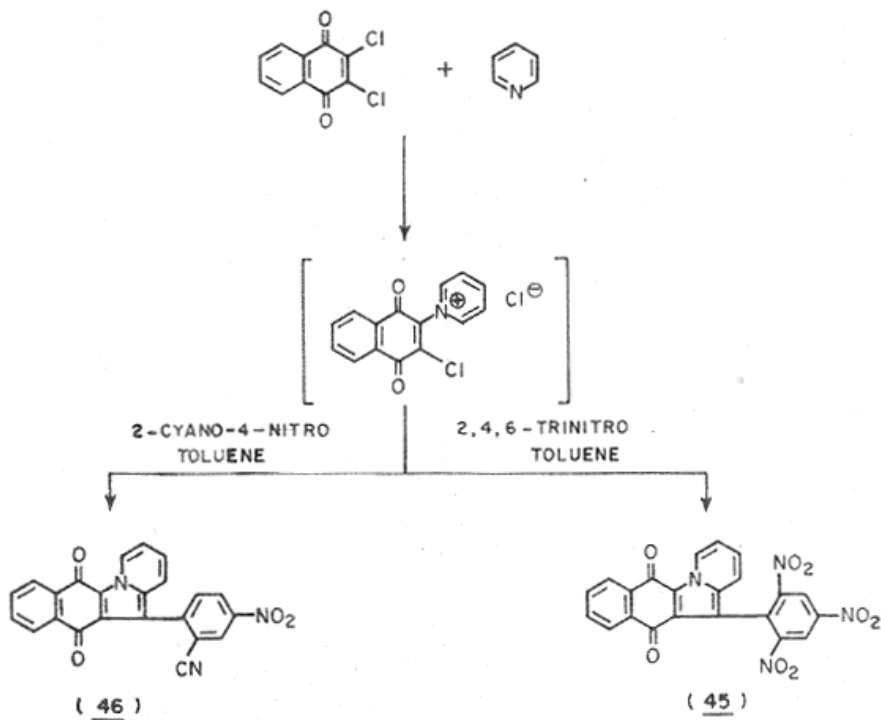


CHART - XIV.



This result is explicable on the basis of lower basicity of 3-cyanopyridine as compared to pyridine. In another case when pyridinium salt of DCNQ was treated with excess of γ -picoline, the major product obtained was (50) and not (49). This too was explained on the ground of higher basicity of γ -picoline than pyridine (Chart XV).

Pyridine in above reactions was then replaced by isoquinoline. Earlier reports show that yield of above heterocyclic quinones are better when pyridine is replaced by isoquinoline. However, with nitrotoluenes this was not the case. A possible reason may be the steric hindrance between *o*-nitro substituted phenyl group and isoquinoline moiety in the isoquinolinium salt. The yields of dyes using isoquinoline and nitrotoluenes were in the range of 5-25%.

When DCNQ was reacted with 2,4-dinitrotoluene in presence of isoquinoline the orange compound 14-(2',4'-dinitrophenyl)benzo[g]naphth[2'',3''-b]indolizine-8,13-dione (51) was obtained in 20% yield. The reaction when carried out in several solvents gave varying yields of (51) which are given (as % yield) in brackets against each solvent, viz. dioxan (20%), benzene (7-8%), isoquinoline (10%), DMSO, DMF, nitrobenzene, trichlorobenzene [very low yields of (51)].

Compound (51) was also prepared by two unambiguous syntheses. In the first route DCNQ was interacted with

2,4-dinitrobenzyl bromide as in the synthesis described earlier. The reaction was carried out in dry dioxan when (51) was obtained in 15-17% yield. In the second synthesis 2,4-dinitrotoluene was replaced by 2,4-dinitroethylbenzene. Later synthesis also supports the mechanism of methane evolution as suggested in case of previous reaction with pyridine. Chart XVI describes above alternative synthesis. Figs. 6 and 7 show the NMR and mass spectrum of (51).

Reaction of trinitrotoluene with DCNQ and isoquinoline gave a poor yield of 14-(2',4',6'-trinitrophenyl)benzo[g]naphth[2'',3''-b]indolizine-8,13-dione (52). Highest yield of (52) (yield— 10%) was obtained when dry xylene was used as solvent. When ethanol, benzene and dioxan were used as solvents the yield of (52) was even lesser (3-7%). Structure of (52) was confirmed by its IR, NMR and elementary analysis.

Interaction of DCNQ, 2-cyano-4-nitrotoluene and isoquinoline in dioxan gave 14-(2'-cyano-4'-nitrophenyl)benzo[g]naphth[2'',3''-b]indolizine-8,13-dione (53) (yield 9%). As in the previous case, use of ethanol, benzene and xylene gave still lower yields (2-6%) of (53). Structure of (53) was confirmed by its IR, NMR spectra and micro-analytical data.

CHART - XV.

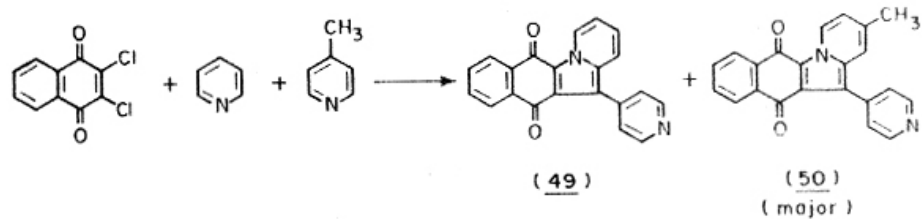
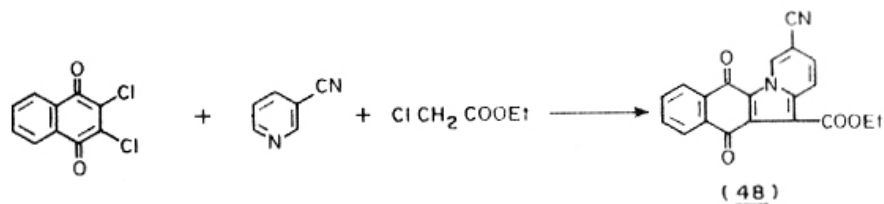
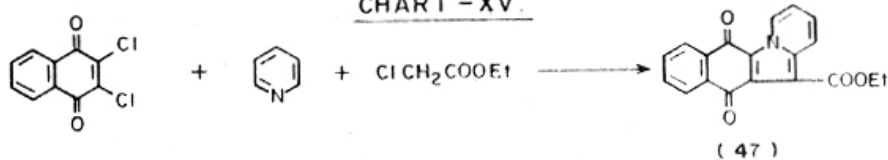
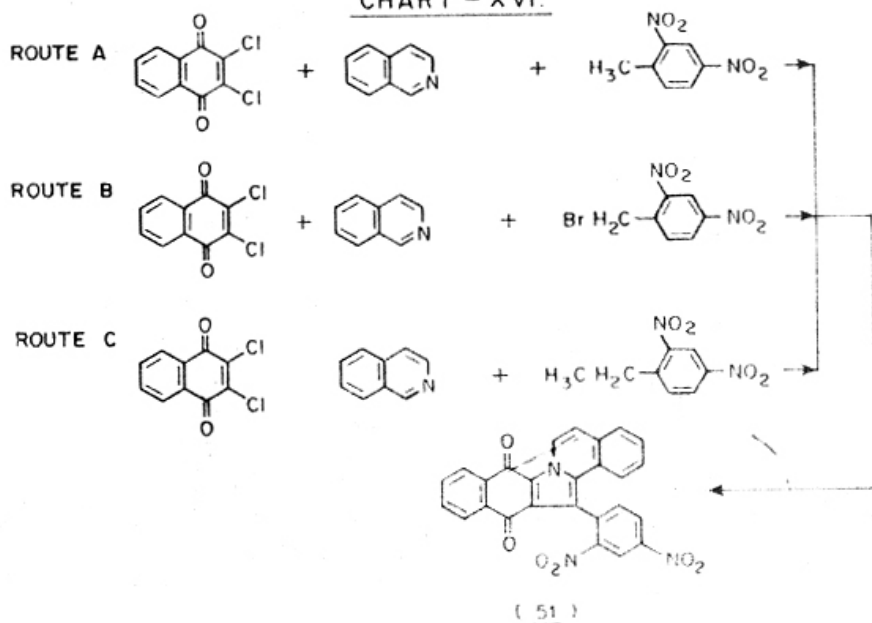


CHART - XVI.



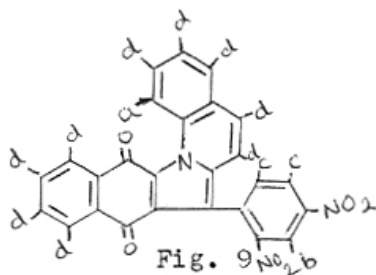
As in previous cases (53) was also prepared by interaction of isoquinolinium methosulphate of DCNQ, 2-cyano-4-nitrotoluene and isoquinoline in dry dioxan as solvent. The reaction gave (53) only in very low yield (~2%). Chart XVII indicates the reactions of 2,4,6-trinitrotoluene and 2-cyano-4-nitrotoluene when isoquinoline is used as base. Fig. 8 shows the NMR spectrum of compound (53).

A few naphthindolizinediones were also prepared by using other heterocyclic bases such as quinoline, ethyl isonicotinate, 4-aminopyridine and 4-acetamidopyridine. However, the yield of the relevant naphthindolizinedione was very low (5-10%).

Interaction of quinoline with DCNQ and compounds containing active methylene group do not normally yield relevant pyrrocolines. This is largely due to overlap of hydrogen at (a) and adjacent CO group of the naphthoquinone [see Fig. 9]. However, recently, a few pyrrocolines with 2- and 4-methylquinoline have been prepared in our laboratory. When we used quinoline as heterocyclic base we did get positive results though the yields were low.

Interaction of DCNQ, quinoline and 2,4-dinitrotoluene in dry xylene gave 14-(2',4'-dinitrophenyl)benzo[i]naphth[2'',3''-b]indolizine-8,13-dione (54) (yield - 6%). Use of other solvents, such as ethanol, benzene

and chlorobenzene instead of xylene gave even poorer yields (2-4%) of (54). Structure of (54) was confirmed by its IR, NMR, mass and microanalytical data.



Compound (54) was also synthesised, as in the case of previous compounds, by starting from 2,4-dinitroethylbenzene and 2,4-dinitrobenzyl bromide (Chart XVIII). NMR and mass spectrum of (54) are shown in Figs. 10 and 11.

Interaction of DCNQ, 2-cyano-4-nitrotoluene and ethylisonicotinate in dry xylene gave 3-carbethoxy-12-(2'-cyano-4'-nitrophenyl)naphth[2'',3''-b]indolizine-6,11-dione (55). Its structure was followed by usual analytical methods. Fig. 12 shows the IR spectrum of compound (55).

Reaction of DCNQ, 2,4-dinitrotoluene and 4-acetamidopyridine in dry dioxan yielded 3-acetamido-12-(2',4'-dinitrophenyl)naphth[2'',3''-b]indolizine-6,11-dione (56). Compound (56) was also prepared in very poor yield by interaction of 2,4-dinitrobenzyl bromide, DCNQ and 4-acetamidopyridine.

CHART - XVII

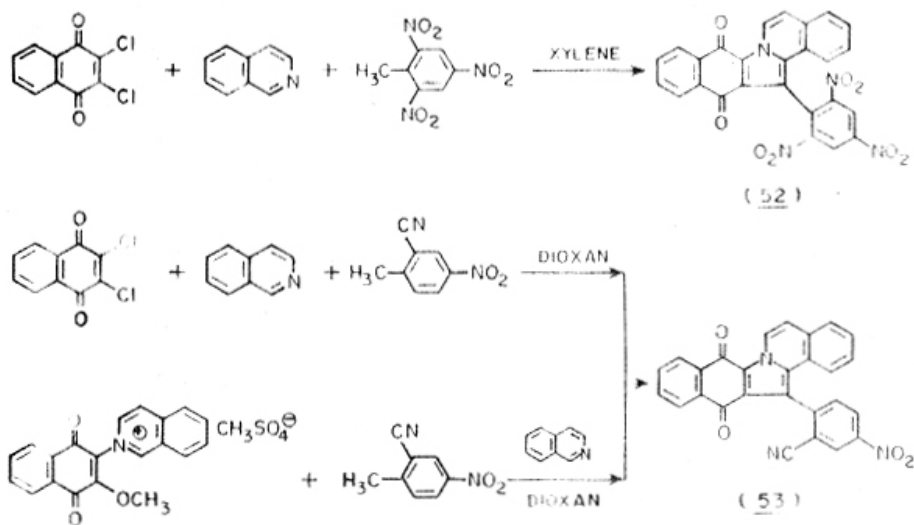
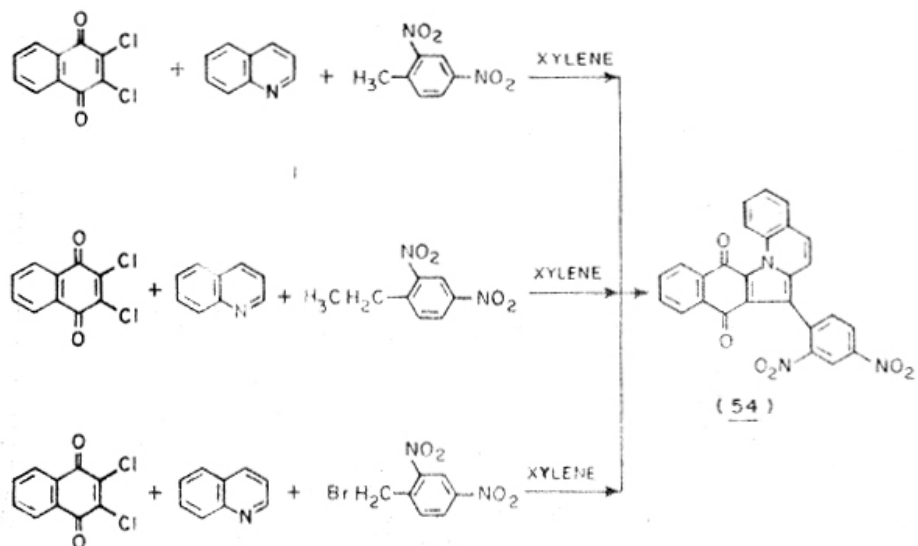


CHART - XVIII



Reaction of DCNQ, 4-acetamidopyridine and 2-cyano-4-nitrotoluene in dry dioxan gave 3-acetamido-12-(2'-cyano-4'-nitrophenyl)naphth(2",3"-b)indolizine-6,11-dione (57) in low yield ($\approx 5\%$). When the reaction was carried out in DMF as solvent a dark violet product was formed alongwith the above red coloured compound (57). Both these products were isolated and their structure was determined by a study of their spectra and elementary analysis.

Coloured compound (57) gave a single band in the region of 3300 cm^{-1} in IR indicating the presence of -NH group. The violet coloured compound on the other hand gave two bands at 3525 cm^{-1} , 3510 cm^{-1} in IR indicating the presence of a free amino group. The elementary analysis of the violet coloured compound and its IR spectrum shows that it is 3-amino-12-(2'-cyano-4'-nitrophenyl)naphth[2",3"-b]indolizine-6,11-dione (58). Thus during reaction in DMF the acetamido group gets partly hydrolysed yielding compound (58).

Figures 13 and 14 show the IR spectra of compounds (57) and (58).

The above violet coloured compound (58) was also obtained through interaction of DCNQ, 2-cyano-4-nitrotoluene and 4-aminopyridine in dry dioxan. The reaction, as may be

expected, yields a mixture of a large number of products from which (58) was isolated in very small yield (2-3%).

The reactions of ethyl-isonicotinate, 4-acetamidopyridine and 4-aminopyridine with DCNQ and compounds containing active methyl group are shown in Chart XIX.

Interaction of DCNQ and compounds containing a reactive methyl group with a variety of heterocyclic bases was studied. Most of them were, however, unsuccessful. These unsuccessful attempts of the synthesis of the relevant phthaloylpyrrocolines are summarized in Chart XX and XXI.

CHART - XIX

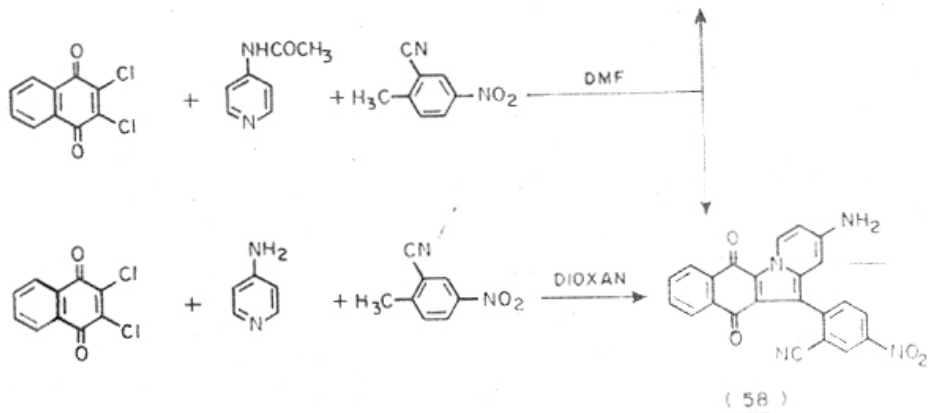
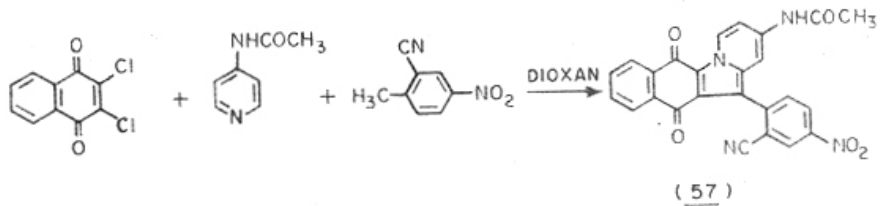
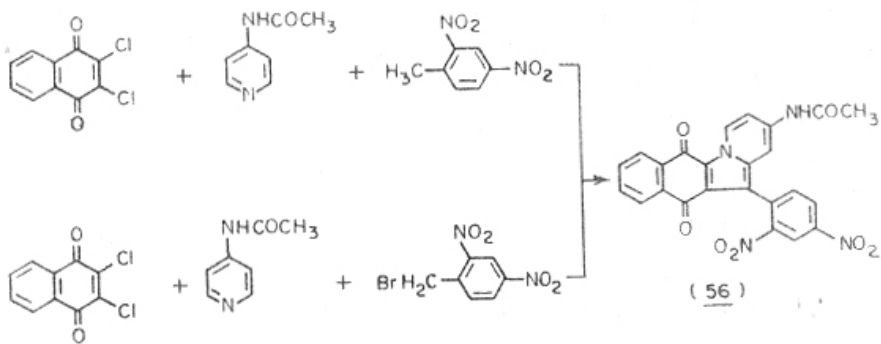
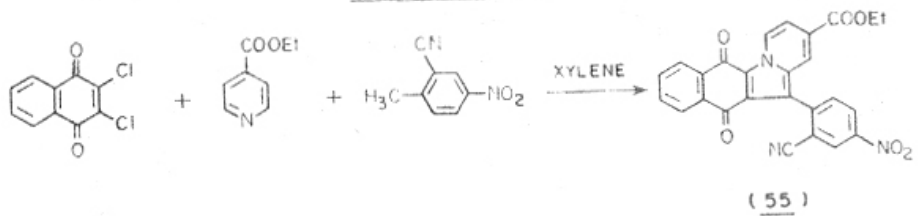


CHART - XX.

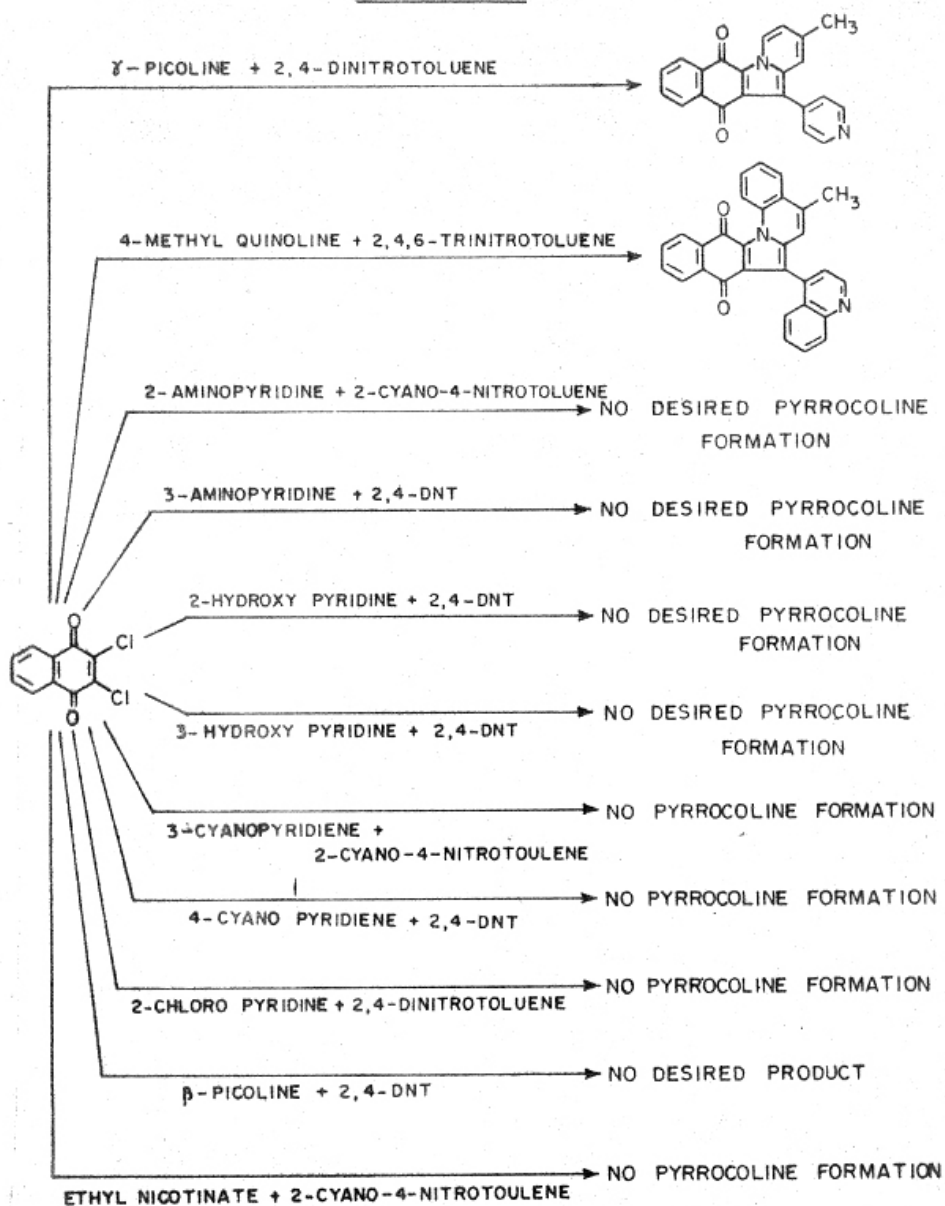
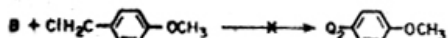
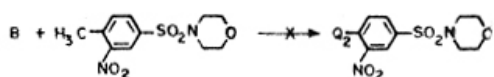
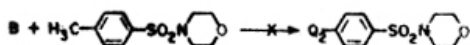
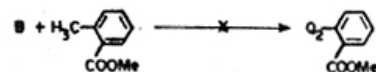
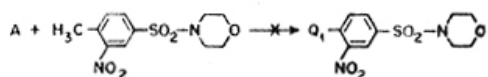
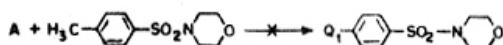
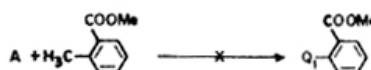
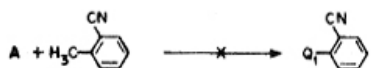
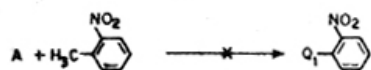
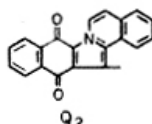
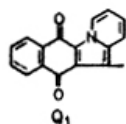
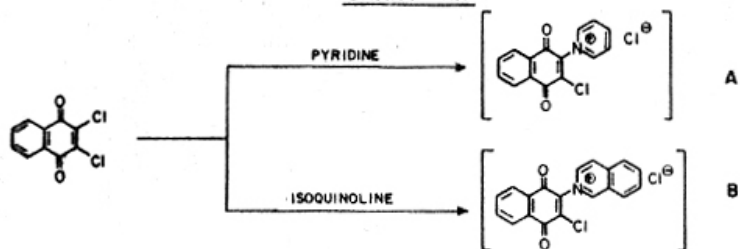


CHART-XXI



EXPERIMENTAL

The four general routes (A to D) used presently for the synthesis of naphthindolizinedione or phthaloylpyrrocoline are described below :-

ROUTE [A]Naphthindolizinediones from 8,8-dichloro-1,4-naphthoquinone (DCNQ) and di- or tri-substituted nitrotoluenes

DCNQ [2.27 g., 0.01 mol] and the heterocyclic base (0.03 mol) were heated in appropriate solvents (dry xylene or dry dioxan) at 80° for 20 minutes. During the course of reaction the mixture turned dark green. To this mixture di- or tri-substituted nitrotoluenes (0.01 mol) dissolved in appropriate solvent was added within 15-20 minutes. During the addition, reaction mixture turned bluish green. The reaction mixture was further heated to reflux temperature. Initial bluish green solution turned red and finally became reddish brown at reflux.

The reaction mixture was then cooled to room temperature and poured over crushed ice. When xylene was used as solvent the reaction mixture was distilled under reduced pressure to remove the solvent and the mixture was poured into crushed ice. When other high boiling solvents

such as chlorobenzene, isoquinoline, quinoline, trichlorobenzene, nitrobenzene etc. were used, the same procedure for work up was followed. When excess of heterocyclic base was used, the reaction mixture was added to 5% aqueous copper sulphate instead of crushed ice.

The reddish brown reaction product was filtered, washed thoroughly with hot water (to remove betaine salt), then with 5% copper sulphate solution to remove traces of heterocyclic base. Final washings were given with cold water and the mixture was dried under vacuum. The reaction product was dissolved in DMF and chromatographed on a silica gel or neutral alumina column. Compounds containing cyano group were preferably chromatographed over alumina.

In all the above reactions first fraction eluted with 50% petroleum ether and benzene yielded unreacted DCNQ (0.5-0.7 %). The second red to reddish orange fraction eluted with various solvent systems, ranging from 5% ethyl acetate-benzene to 50% ethyl acetate-benzene, yielded the desired naphthindolizinediones which were rechromatographed and finally purified by crystallisation from suitable solvents.

The compounds were characterised by IR, NMR, mass spectra and elementary analysis. Mass spectrum of a few compounds could not be recorded as they did not sublime. Some NMR spectra could not be recorded due to low solubility

of the compounds in usual solvents. The NMR spectra were recorded in arsenic trichloride whereas IR spectra were recorded either in nujol or hexachlorobutadiene.

ROUTE [B]

Synthesis from DCNQ and substituted nitrobenzyl bromide

This method was particularly useful for synthesis of 12-dinitrophenyl naphthindolizinediones. The method consists in the interaction of 2,4-dinitrobenzyl bromide, DCNQ and a heterocyclic base.

A mixture of 2,4-dinitrotoluene [1.82 g.; 0.01 mol], N-bromosuccinimide (0.02 mol) and benzoyl peroxide (catalytic amount) was refluxed in carbon tetrachloride in the presence of a mercury vapour lamp for 3 hours. Completion of reaction was traced by TLC. Reaction mixture was filtered hot and the filtrate was thoroughly washed with water. The solvent layer was dried over anhydrous sodium sulphate. To the carbon tetrachloride extract, the relevant heterocyclic base (0.01 mol) was added with stirring. The mixture was then heated under reflux for 2 hours. Excess solvent and the base were removed by distillation and the dark brown coloured residue (A) was used directly in the next step as it decomposed on keeping for more than a few hours. An aqueous

solution of (A) on treatment with picryl chloride in 2N NaOH solution gave a transient red colour which quickly faded thus indicating the presence of a reactive methylene group in (A).

A mixture of DCNQ [2.27 g.; 0.01 mol] and the heterocyclic base (0.04 mol) was heated to 80° for 20 minutes in a suitable solvent. Product (A) obtained above and the heterocyclic base (0.01 mol) were then added to the reaction mixture over a period of 15 minutes. The mixture was further refluxed for two hours. The reaction mixture on work up gave products which were identical with those obtained by Route A.

ROUTE [C]

From the methosulphate of the respective
betaines derived from DCNQ and pyridine/
isoquinoline

DCNQ [11.3 g.; 0.05 mol] and the heterocyclic base (0.05 mol) were refluxed in n-butanol for about 15 minutes. A vigorous reaction ensued and the reaction mixture solidified. The reaction gave 11 gms. of 1,4-dioxo-3-(pyridinium or isoquinolinium)2-naphthoxide.

A suspension of 5 gms. of the respective naphthoxide in dimethyl sulphate (25 ml) was heated on a steam bath until all naphthoxide had gone into solution. The solution

was cooled and poured into ether. The oil which separated out on scratching gave the methosulphate of the respective betaines derived from DCNQ and pyridine/isoquinoline.

The methosulphate (0.01 mol) was heated with equimolar proportions of the heterocyclic base and the substituted nitrotoluene derivatives for 2 hours. Dry dioxan or dry xylene was used as solvent. The reaction mixture was cooled and worked up as in Route A. The pyrrocolines obtained were identical with those obtained in Route A and B.

ROUTE [D]

From 2,4-dinitroethylbenzene

DCNQ [2.27 g.; 0.01 mol] and the heterocyclic base (0.03 mol) were heated in dry dioxan/xylene for 20 minutes. To this green coloured reaction mixture 2,4-dinitroethylbenzene (1.9 g.; 0.01 mol) in 10 ml of dry dioxan/xylene was added in 20 minutes. The mixture was then heated under reflux for 2 hours. The reaction mixture on work up as in Route A gave naphthindolizinediones which were identical with those obtained by Route A, B and C.

2,4-Dinitroethylbenzene was prepared by nitration of ethylbenzene as follows:- To a mixture of ethylbenzene (53 g.) and concentrated sulphuric acid (117.5 ml) was added fuming nitric acid (85 ml). Temperature was maintained at 60° for three hours and the reaction mixture was poured

over ice. Product obtained by ether extraction, steam distillation and then vacuum distillation gave the following three fractions :

- (a) 2,6-Dinitroethylbenzene (9 g) (b_1 113-17°).
- (b) Mixture of 2,6-dinitroethylbenzene and 2,4-dinitroethylbenzene (9.2 g).
- (c) 2,4-Dinitroethylbenzene (65.7 g) (b_1 124-7°)
 η_{25}^D - 1.5655.

Purity of 2,4-dinitroethylbenzene was confirmed by IR and NMR spectra. Absence of 2,4-dinitrotoluene in 2,4-dinitroethylbenzene was confirmed by V.F.C. analysis.

12-(2',4'-Dinitrophenyl)naphth[2'',3''-b]indolizine-6,11-dione (42).

The above compound is the reaction product of the interaction of 2,4-dinitrotoluene DCNQ and pyridine. This compound was prepared via Routes A-B.

Route A was followed for the interaction of DCNQ [2.27 g.; 0.01 mol], 2,4-dinitrotoluene (1.82 g.; 0.01 mol) and pyridine (3.0ml.; 0.04 mol) with dry dioxan (15 ml) as solvent. The reaction product crystallised from DMF (m.p. 300°) gave (42) as orange red needles (1.3g.;30%). (Found: C,64.3; H, 2.9; N, 10.3; $C_{22}H_{11}N_3O_6$ requires : C, 63.9; H, 2.7; N, 10.7%).

IR (Nujol): γ_{max} - 1650, 1630, 1570, 1530, 1490, 1400, 1360, 1320, 1270, 1230, 1160, 1140, 1075, 1055 and 1030 cm^{-1} .

NMR (AsCl_3): 9.8 δ [1H, d, J = 7Hz H-a]; 9.0 δ [1H, d, J = 2Hz H-b]; 8.85 δ [1H, d, J = 3 Hz H-c]; 8.6 δ (1H, d, J = 2Hz H-c); 7.25-8.3 δ [7H, m H-d].

Mass spectrum : m/e - 414 [(M+1), 21%], 413 (M^+ , 85), 368 (24), 367 (92.5), 327 (21), 322 (28.5), 321 (100), 320 (18), 265 (42), 263 (24), 262 (36), 195 (21), 189 (21), 188 (18), 104 (30), 78 (22.5), 76 (28.5).

Compound (42) was also prepared through Routes B, C and D. In Route B, interaction of DCNQ [2.27 g.; 0.01 mol] 2,4-dinitrobenzyl bromide [2.61 g.; 0.01 mol] and pyridine [3 ml, 0.04 mol] gave compound (42) [1.3 g., 30%]. In Route C, N-(1,4-dioxo-2-methoxynaphthyl-3)pyridinium methosulphate [3.77 g.; 0.01 mol] was reacted with 2,4-dinitrotoluene [1.82 g.; 0.01 mol] and small excess of pyridine. Work up gave compound (42) [0.150 g., 4%]. Route D consisted in reacting DCNQ [2.27 g.; 0.01 mol], 2,4-dinitroethylbenzene [1.91 g.; 0.01 mol] and pyridine [3 ml; 0.04 mol] as in the general method described earlier. The reaction mixture on work up gave (42) [0.160 g., 4%].

All the naphthindolizinediones (42) obtained via Routes B, C and D were confirmed to be identical with the one obtained via Route A by superimposable IR. These reactions by Routes A-D were also repeated using various solvents.

12-(2',4',6'-Trinitrophenyl)naphth
[2'',3''-b]indolizine-6,11-dione (45).

A mixture of DCNQ [2.27 g.; 0.01 mol], 2,4,6-trinitrotoluene [2.27 g.; 0.01 mol] and pyridine [3 ml; 0.04 mol] in dry dioxan (15 ml) as solvent were reacted as described in Route A. The product after work up was crystallised from DMF (m.p. 231°). Compound (45) crystallised in red needles (1.37 g, 30%). (Found: C, 58.2; H, 2.4; N, 12.00; C₂₂H₁₀N₄O₈ requires : C, 57.6; H, 2.2; N, 12.2%). IR (Nujol) ν_{\max} 1650, 1630, 1590, 1550, 1500, 1470, 1400, 1340, 1330, 1270, 1230, 1165, 1150, 1095, 1085, 1060, 1030 and 1020 cm⁻¹. NMR (AsCl₃) : 10.05 δ [1H, d, J = 7Hz H-a]; 9.4 δ [2H, s H-b]; 7.6-8.6 δ [7H, m H-c]. Mass spectrum: m/e -459 [(M+1), 24.5 %], 458 (M⁺, 100), 412 (11), 366, 320 (43), 292, 264 (20), 263 (16.5), 252 (15), 160 (14), 104 (28), 78 (15).

12-(2'-Cyano-4'-nitrophenyl)naphth
[2'',3''-b]indolizine-6,11-dione (46).

DCNQ [2.27 g.; 0.01 mol], 2-cyano-4-nitrotoluene [1.62 g.; 0.01 mol] and pyridine [3 ml; 0.04 mol] were inter-acted as in Route A with dry dioxan (15 ml) as solvent. The reaction product (46) which showed bright fluorescence in benzene crystallised in red needles (m.p. 307°) from chloroform (0.98 g., 25%).

(Found: C, 69.9; H, 2.7; N, 10.6; $C_{23}H_{11}N_3O_4$ requires :
C, 70.2; H, 2.8; N, 10.7%).

IR (Nujol): γ_{max}^{ν} - 2200, 1660, 1620, 1590, 1550, 1500,
1470, 1400, 1340, 1330, 1270, 1230, 1165, 1150, 1095,
1085, 1060, 1020 and 1015 cm^{-1} .

NMR ($AsCl_3$) : 9.7 δ [1H, d, J = 7Hz H-a]; 9 δ [1H, s H-b];
8.3 δ [1H, d, J = 3Hz H-c]; 8.1 δ [1H, d, J = 2Hz H-c]; 7.1-8 δ
(7H, m H-d).

Mass spectrum: m/e -394 [(M+1), 28%], 393 (M⁺, 100), 363,
317, 289 (19), 264 (15), 263 (15), 261 (17), 239 (11.5),
215 (19), 214 (32), 213 (23), 212 (23), 134 (10), 133 (13),
111 (13), 104 (15), 94 (19), 88 (28.5), 78 (53), 76 (58.5),
75 (45).

14-(2',4'-Dinitrophenyl)benzo[g]naphth
[2'',3''-b]indolizine-8,13-dione (51).

Compound (51) was prepared via Routes A, B and D.
In Route A DCNQ [2.27 g.; 0.01 mol], 2,4-dinitrotoluene
[1.82 g.; 0.01 mol] and isoquinoline [5 ml; 0.04 mol] were
interacted with dry dioxan [15 ml] as solvent. The product
after work up was crystallised from DMF (m.p. 324). Compound
(51) crystallised in yellowish orange needles (0.950 g.,
20%). (Found: C, 67.7; H, 3.0; N, 8.9; $C_{26}H_{13}N_3O_6$ requires:
C, 67.4; H, 2.8; N, 9.1%).

IR (Nujol) : ν_{\max} - 1650, 1620, 1590, 1525, 1500, 1460, 1380, 1340, 1300, 1280, 1270, 1240, 1220, 1160, 1100, 1080, 1050 and 1030 cm^{-1} .

NMR (AsCl_3): 9.8 δ [1H, d, J = 7Hz H-a]; 9.4 δ [1H, d, J = 2Hz H-b]; 9 δ [1H, d, J = 3Hz H-c]; 8.85 δ [1H, d, J = 2Hz H-c]; 7.6-8.55 δ [9H, m H-d].

Mass spectrum : m/e - 464[(M+1), 9%], 463 (M^+ , 39), 418 (18), 417 (60.5), 387 (44.5), 371 (100), 360 (21), 359 (27), 358 (32), 344 (15), 343 (10), 342 (11), 341 (13), 315 (29), 314 (48), 313 (64), 312 (55.5), 238 (27), 185 (28), 184 (18.5), 157 (37.5), 156 (60), 155 (28), 154 (21), 151 (34), 150 (23.5), 143 (29), 142 (26.5), 137 (16), 105 (20), 104 (38), 77 (35), 76 (36).

In Route B, DCNQ [2.27 g.; 0.01 mol], and 2,4-dinitrobenzyl bromide [2.61 g.; 0.01 mol] and isoquinoline [5 ml; 0.04 mol] were interacted in dry dioxan [15 ml] as solvent. Work up gave (51) (0.750 g., 15%) which is identical with product obtained via Route A. In Route D the reactants were DCNQ [2.27 g.; 0.01 mol], 2,4-dinitroethylbenzene [1.91 g.; 0.01 mol] and isoquinoline [5 ml; 0.04 mol]. Dry dioxan [15 ml] was used as solvent. Work up gave (51) (0.150 g.; 4%). The above reactions (Routes A, B and D) were also repeated in various solvents.

14-(2',4',6'-Trinitrophenyl)benzo[g]
naphth[2'',3''-b]indolizine-8,13-dione (52).

DCNQ [2.27 g.; 0.01 mol], 2,4,6-trinitrotoluene [2.27 g.; 0.01 mol] and isoquinoline [5 ml; 0.04 mol] were interacted in dry xylene [15 ml]. On work up the product was crystallised from DMF (compound did not melt below 360°). Compound (52) crystallised in yellowish orange needles (0.375 g., 10%). (Found: C, 61.3; H, 2.2; N, 10.9; $C_{26}H_{12}N_4O_8$ requires : C, 61.4; H, 2.4; N, 11.0 %).

IR (Nujol): γ_{\max} - 1650, 1630, 1600, 1575, 1560, 1530, 1510, 1500, 1460, 1415, 1400, 1380, 1370, 1320, 1300, 1280, 1250, 1240, 1170, 1100, 1060 and 1040 cm^{-1} .

NMR (AsCl_3) : 9.75 δ [1H, d, J = 7Hz H-a]; 8.4 δ [2H, s H-b]; 7.4-8.3 δ [9H, m H-d].

14-(2'-Cyano-4'-nitrophenyl)benzo
[g]naphth[2'',3''-b]indolizine-8,13-dione (53).

Interaction of DCNQ [2.27 g.; 0.01 mol], 2-cyano-4-nitrotoluene [1.62 g.; 0.01 mol] and isoquinoline [5 ml; 0.04 mol] in boiling dry dioxan [15 ml] via Route A on usual work up gave (53). Compound (53) crystallised from DMF (compound did not melt below 360°) in orange needles (0.380 g., 9 %).

(Found: C, 73.0; H, 2.8; N, 9.3; $C_{27}H_{13}N_3O_4$ requires :
C, 73.1; H, 2.9; N, 9.5%).

IR (Nujol) : γ_{\max} - 2200, 1650, 1630, 1600, 1500, 1460,
1380, 1300, 1270, 1240, 1230, 1170, 1160 and 1030 cm^{-1} .

NMR (AsCl_3) : 9.5 δ [1H, d, J = 7 Hz H-a]; 9 δ [1H, s, H-b];
8.2 δ [1H, d, J = 2Hz H-c]; 8.1 δ [1H, d, J = 3Hz H-c];
7-8 δ [9H, m H-d].

Compound (53) was also prepared through Route C as follows :- N-(1,4-dioxo-2-methoxynaphthyl-3)isoquinolinium methosulphate [4.27 g.; 0.01 mol], 2-cyano-4-nitrotoluene [1.62 g.; 0.01 mol] and isoquinoline [5 ml; 0.04 mol] were reacted in boiling dry dioxan (15 ml). Work up gave (53) (m.p. > 360°), (0.059 g., 2%). Compound obtained by Route C was identical with that obtained by Route A.

14-(2',4'-dinitrophenyl)benzo[1]
naphth[2",3"-b]indolizine-8,13-dione (54).

DCNQ [2.27 g.; 0.01 mol], 2,4-dinitrotoluene [1.82 g.; 0.01 mol] and quinoline [5 ml; 0.04 mol] were interacted as in Route A. Dry xylene [15 ml] was used as solvent. The usual work up gave (54) crystallised from DMF (m.p. 336°) in yellowish orange needles (0.275 g., 6%).
(Found: C, 67.3; H, 2.7; N, 8.9; $C_{26}H_{13}N_3O_6$ requires :
C, 67.4; H, 2.8; N, 9.1%).

IR (Nujol) : γ_{\max} - 1650, 1620, 1580, 1510, 1460, 1410, 1375, 1350, 1290, 1280, 1240, 1200, 1170, 1160, 1140 and 1030 cm^{-1} .

NMR (AsCl_3) : 9.6 δ [1H, d, J = 7Hz H-a]; 9.2 δ [1H, s H-b]; 8.6-8.7 δ [2H, 2m H-c]; 7.4-8.3 δ [9H, m. H-d].

Mass spectrum: m/e - 464 [(M+1), 10%], 463 (M^+ , 36), 418 (16.5), 417 (58.5), 387 (45), 373 (35.5), 372 (58), 371 (100), 359 (28), 344 (16), 343 (20), 315 (28.5), 314 (47.5), 313 (65), 312 (50.5), 238 (24), 213 (10), 138 (18), 137 (11.5), 102 (11), 101 (26), 77 (30), 74 (25).

DCNQ [2.27 g.; 0.01 mol], 2,4-dinitrobenzyl bromide [2.61 g.; 0.01 mol] and quinoline [5 ml; 0.04 mol] were interacted as in Route B, dry xylene [15 ml] being used as solvent. In another reaction DCNQ [2.27 g.; 0.01 mol], 2,4-dinitroethylbenzene [1.96 g.; 0.01 mol] and quinoline [5 ml; 0.04 mol] were interacted as in Route D with dry xylene [15 ml] as solvent. Both these reactions were monitored on TLC with benzene - 20% ethyl acetate, chloroform, acetone along with authentic sample of (54) obtained through Route A. Yield of (54) via Route B was 5%.

3-Carbethoxy-12-(2'-cyano-4'-nitro-phenyl)naphth(2'',3''-b)indolizine-6,11-dione (55).

DCNQ [2.27 g.; 0.01 mol], 2-cyano-4-nitrotoluene [1.62 g.; 0.01 mol] and ethyl isonicotinate [3 ml; 0.04 mol] were interacted as in route A with dry xylene [15 ml] as solvent. The usual work up gave (55). Compound (55) crystallised from chlorobenzene (m.p. 344°) in orange needles (0.280 g., 6%). (Found: C, 67.0; H, 3.1; N, 8.9; C₂₆H₁₅N₃O₆ requires : C, 67.1; H, 3.2; N, 9.0 %).

IR (Nujol): γ_{\max}^{ν} - 2200, 1660, 1630, 1560, 1450, 1400, 1360, 1270, 1240, 1160, 1060, 1030 and 1010 cm⁻¹.

3-Acetamido-12-(2',4'-dinitrophenyl)naphth(2'',3''-b)indolizine-6,11-dione (56).

DCNQ [2.27 g.; 0.01 mol], 2,4-dinitrotoluene [1.82 g.; 0.01 mol] and 4-acetamidopyridine [5.44 g.; 0.01 mol] were interacted in dry dioxan [15 ml] as in Route A. The usual work up gave (56). Compound (56) crystallised from chlorobenzene (compound did not melt below 360°) in dark red needles (0.225 g., 5%). (Found : C, 61.2; H, 2.8; N, 11.8; C₂₄H₁₄N₄O₇ requires : C, 61.3; H, 3.0; N, 11.9%).

IR (Nujol) : γ_{\max}^{ν} - 3300, 1670, 1660, 1630, 1600, 1590, 1560, 1520, 1400, 1340, 1270, 1220, 1165, 1065, 1045 and 1020 cm⁻¹.

3-Acetamido-12-(2'-cyano-4'-nitrophenyl)
naphth[2",3"-b]indolizine-6,11-dione (57).

DCNQ [2.27 g.; 0.01 mol], 2-cyano-4-nitrotoluene [1.82 g.; 0.01 mol] and 4-acetamidopyridine [5.44 g., 0.01 mol] were interacted in dry dioxan [15 ml] as in Route A. The usual work up gave (57). Compound (57) crystallised from chlorobenzene (compound did not melt below 360°) in dark red needles (0.250 g., 6%). (Found: C, 66.5; H, 3.0; N, 12.3; C₂₅H₁₄N₄O₅ requires : C, 66.7; H, 3.1; N, 12.4%). IR (Nujol) : γ_{\max}^- - 3300, 2200, 1680, 1655, 1630, 1590, 1560, 1480, 1380, 1260, 1220, 1160, 1090, 1070, 1050 and 1000 cm⁻¹.

When the above reaction was carried out in DMF (15 ml) a violet coloured product (58) was also obtained along with (57). Compound (58) crystallised from chlorobenzene (compound did not melt below 360°) in violet flakes (0.120 g., 3%). (Found: C, 67.5; H, 2.8; N, 13.6; C₂₃H₁₂N₄O₄ requires : C, 67.6; H, 2.9; N, 13.7%). IR (Nujol) : γ_{\max}^- - 3415, 3410, 2200, 1640, 1610, 1580, 1560, 1490, 1460, 1390, 1345, 1300, 1260, 1230, 1210, 1190, 1160, 1070, 1040 and 1015 cm⁻¹.

3-Amino-12-(2'-cyano-4'-nitrophenyl)naphth
(2'',3''-b)indolizine-6,11-dione (58).

DCNQ [2.27 g.; 0.01 mol], 2-cyano-4-nitrotoluene [1.62 g.; 0.01 mol] and 4-aminopyridine [3.76 g.; 0.01 mol] were interacted in dry boiling dioxan [15 ml] as in Route A. The usual work up gave (58). Compound (58) crystallised from chlorobenzene (compound did not melt below 360°) in violet flakes (0.150 g., 4%). (Found: C, 67.5; H, 2.8; N, 13.6; $C_{23}H_{12}N_4O_4$ requires : C, 67.6; H, 2.9; N, 13.7%).

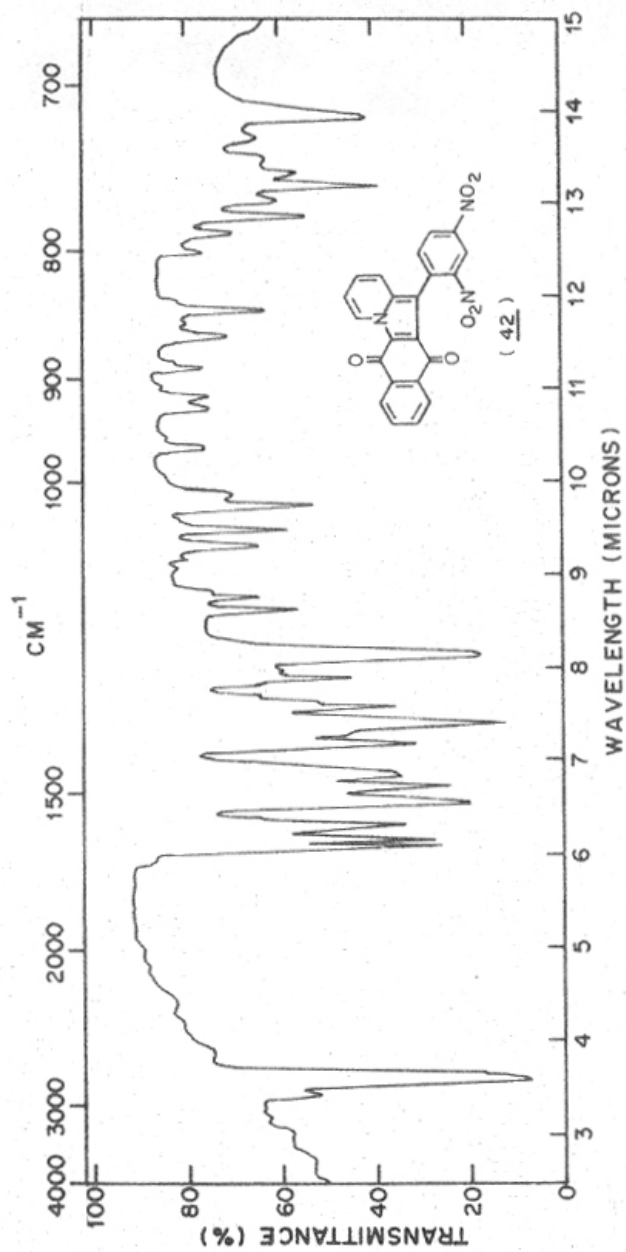


FIG.-1.

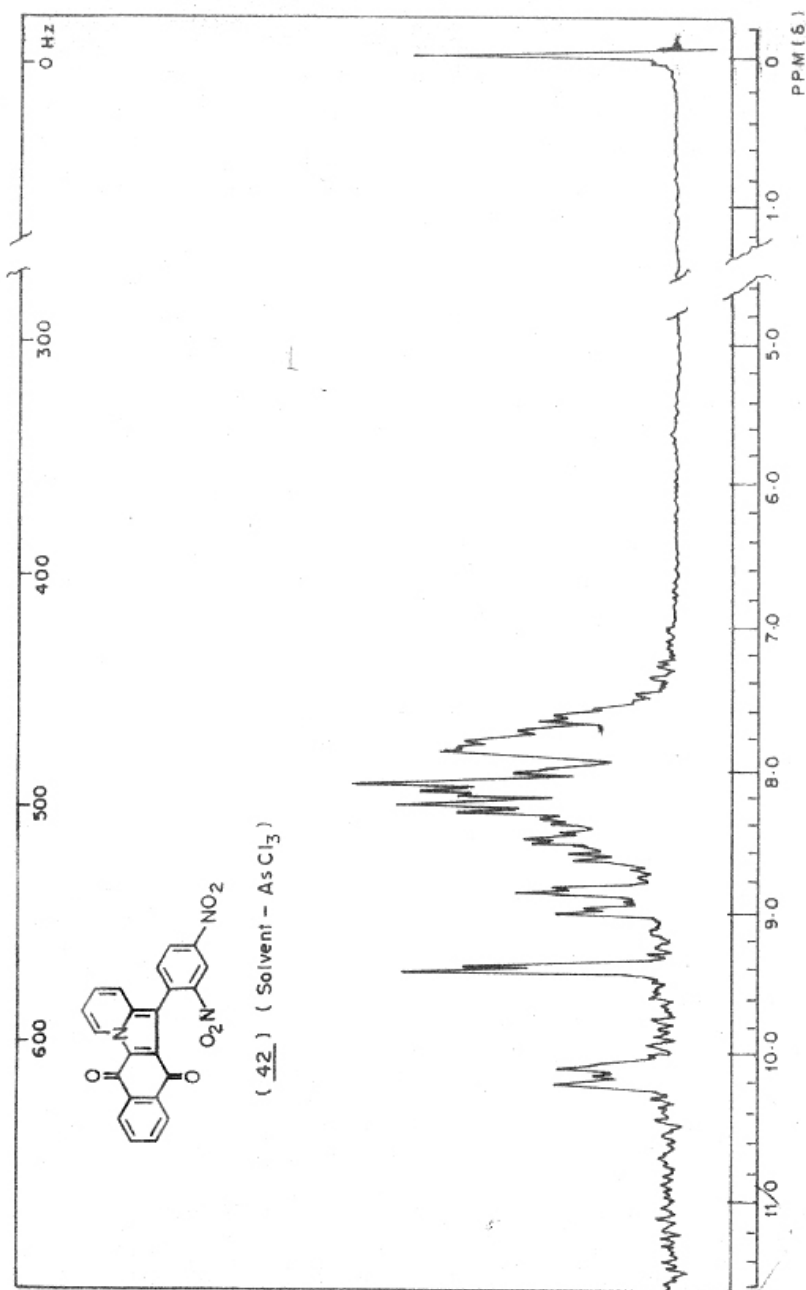


FIG. - 3.

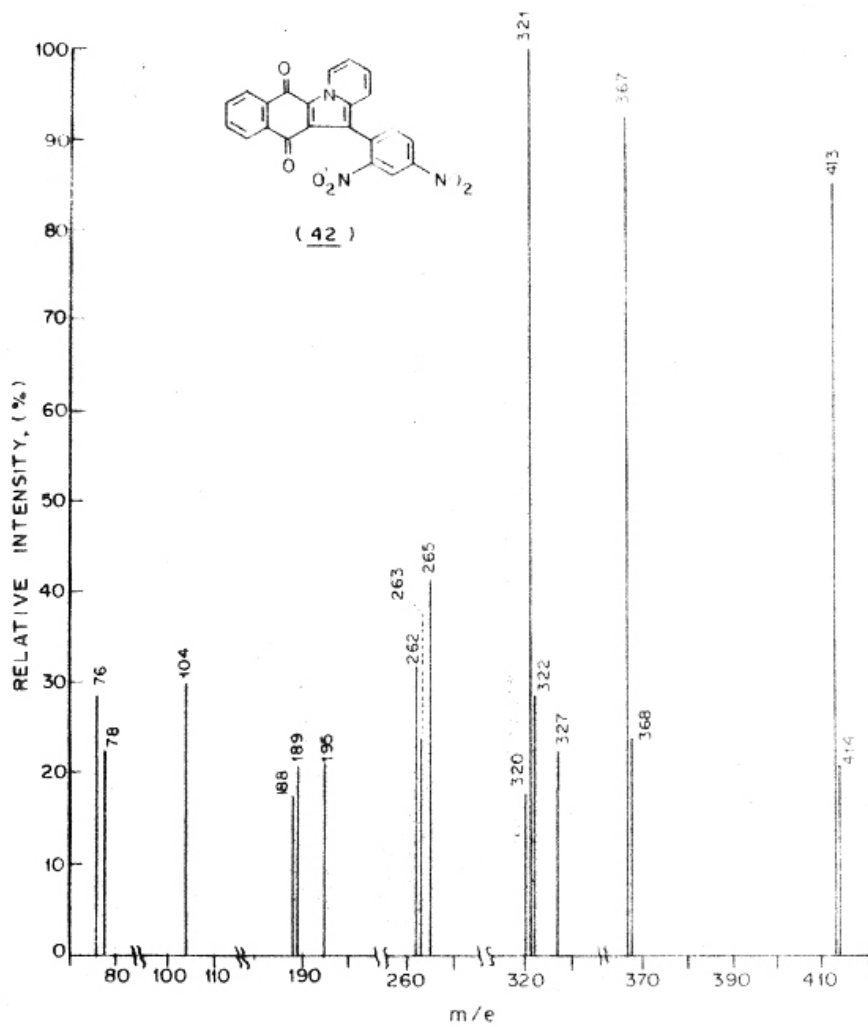


FIG. -4.

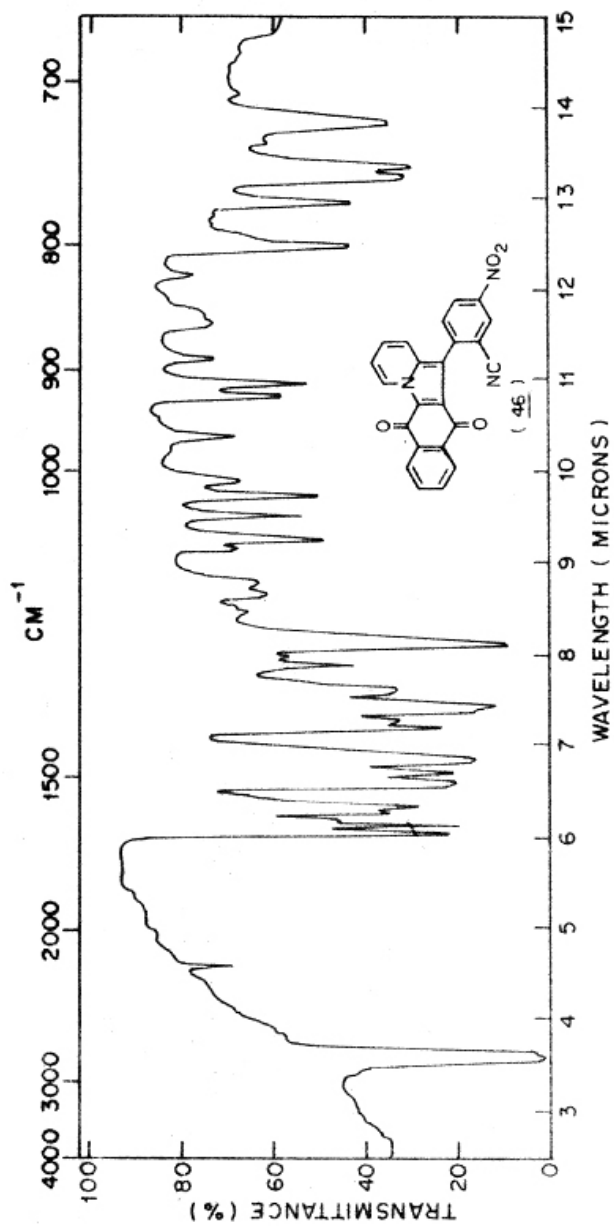


FIG - 5.

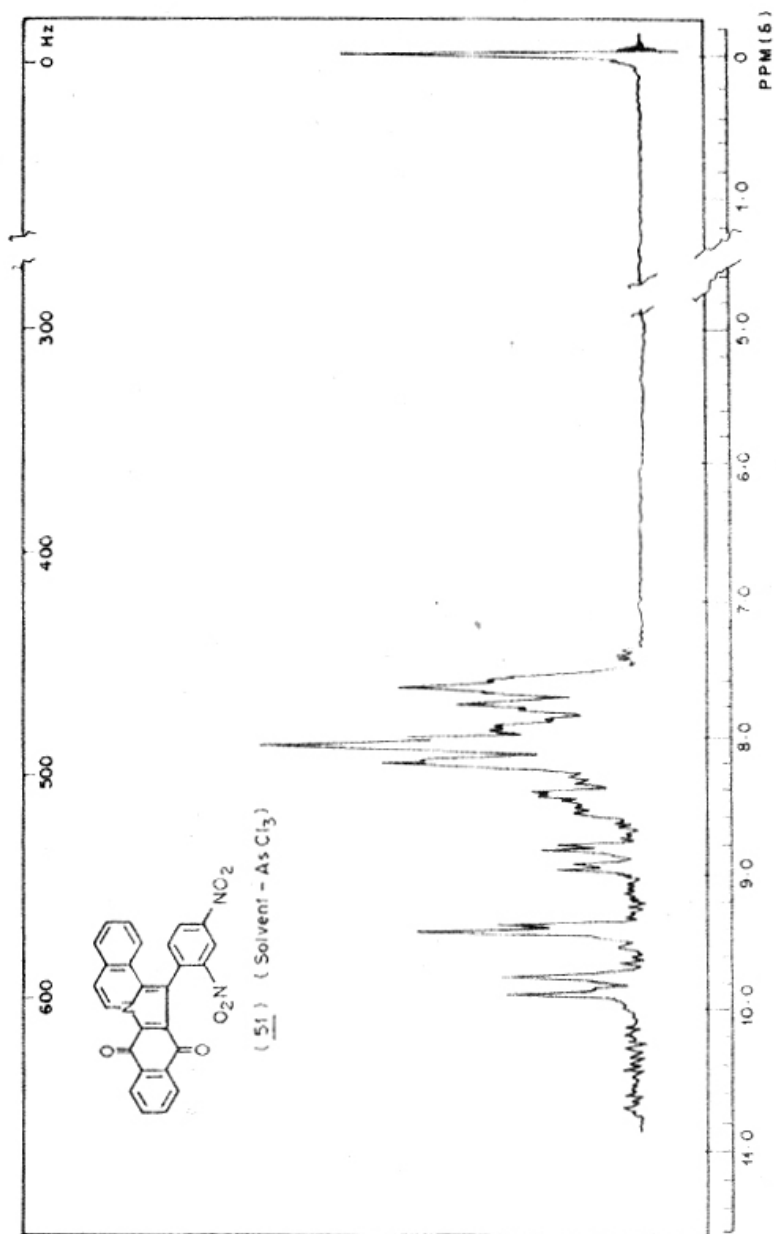


FIG - 6

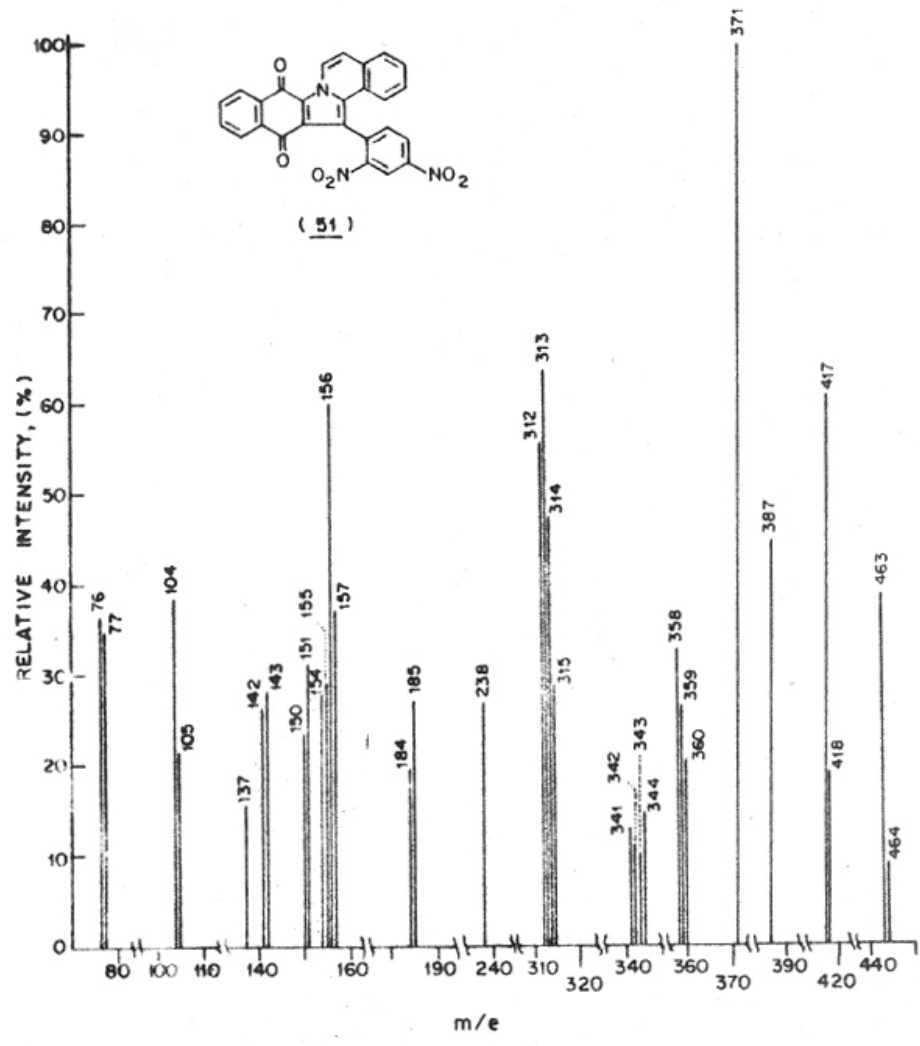


FIG. - 7.

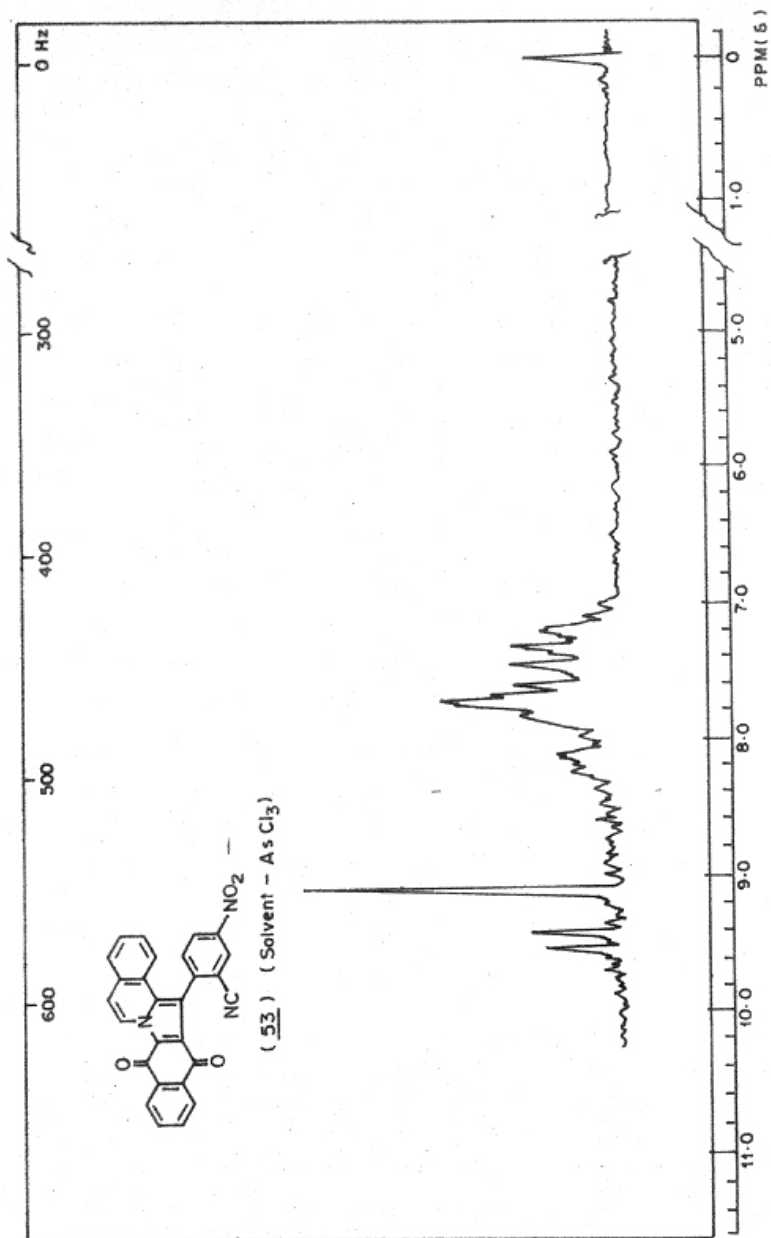


FIG. - 8.

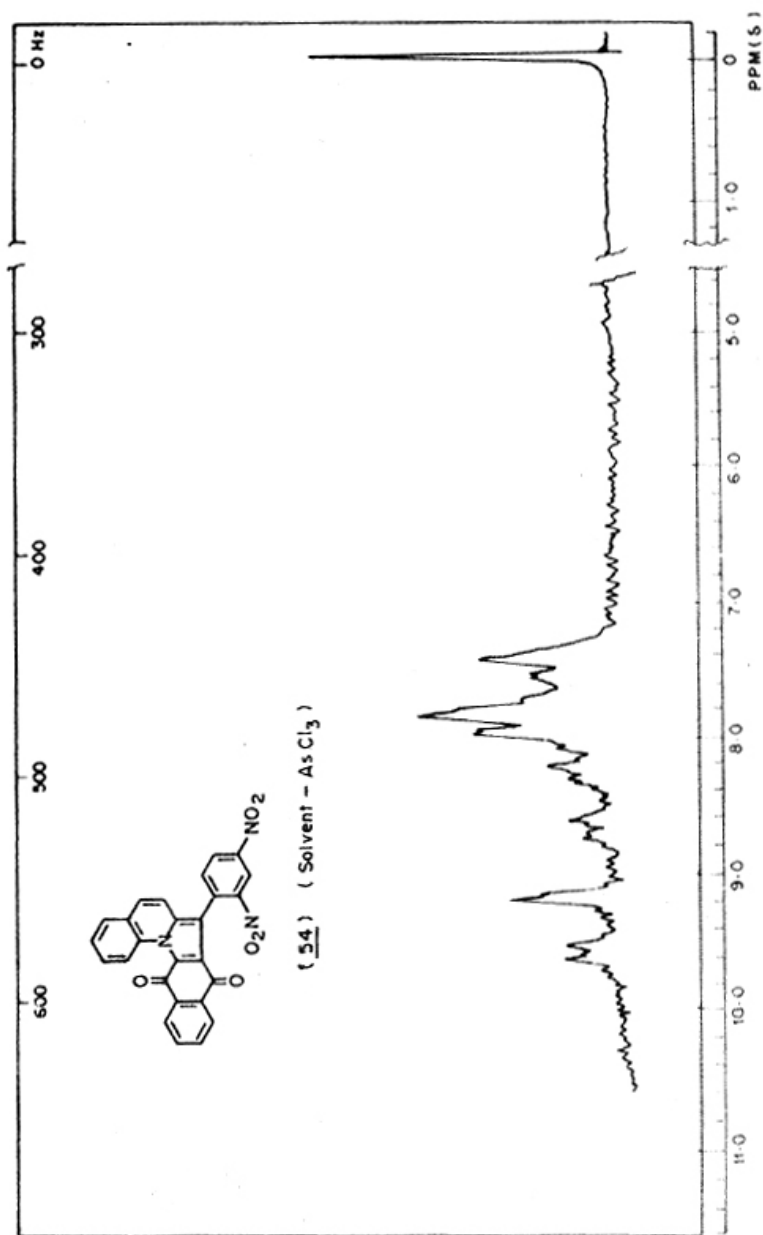


FIG - 10

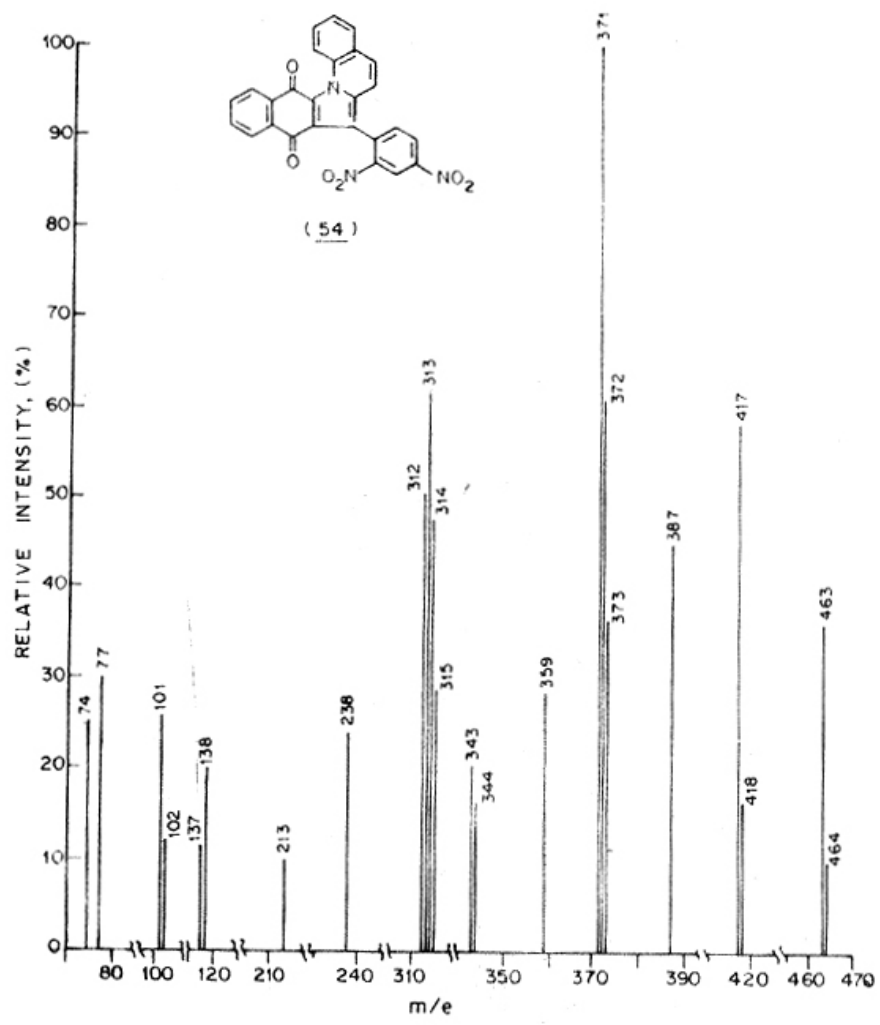


FIG. 11.

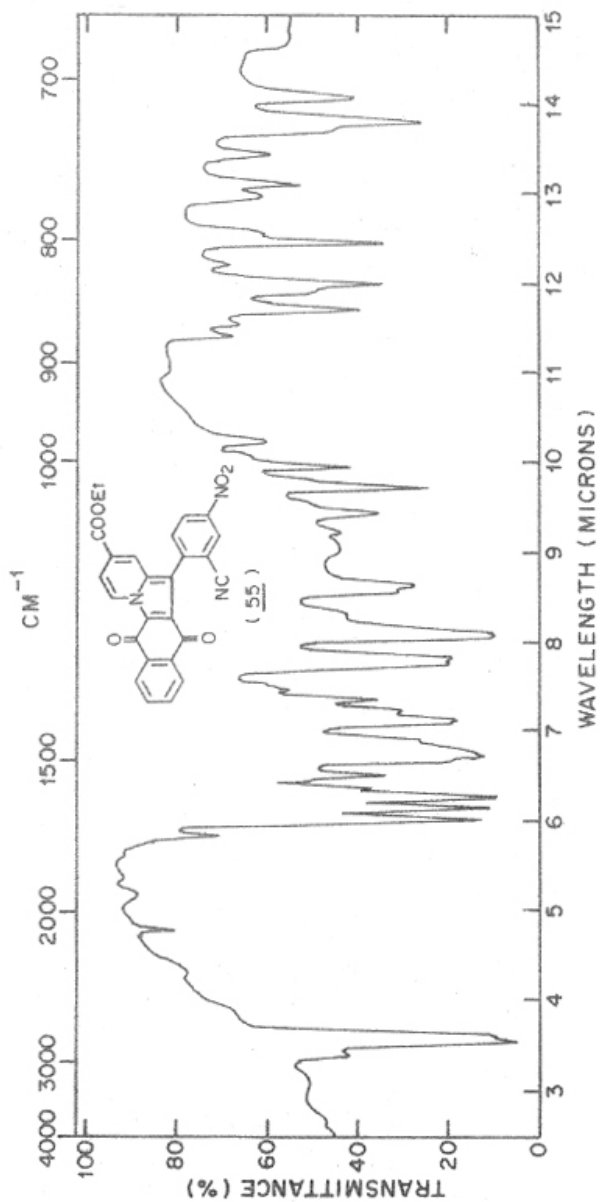


FIG. -12

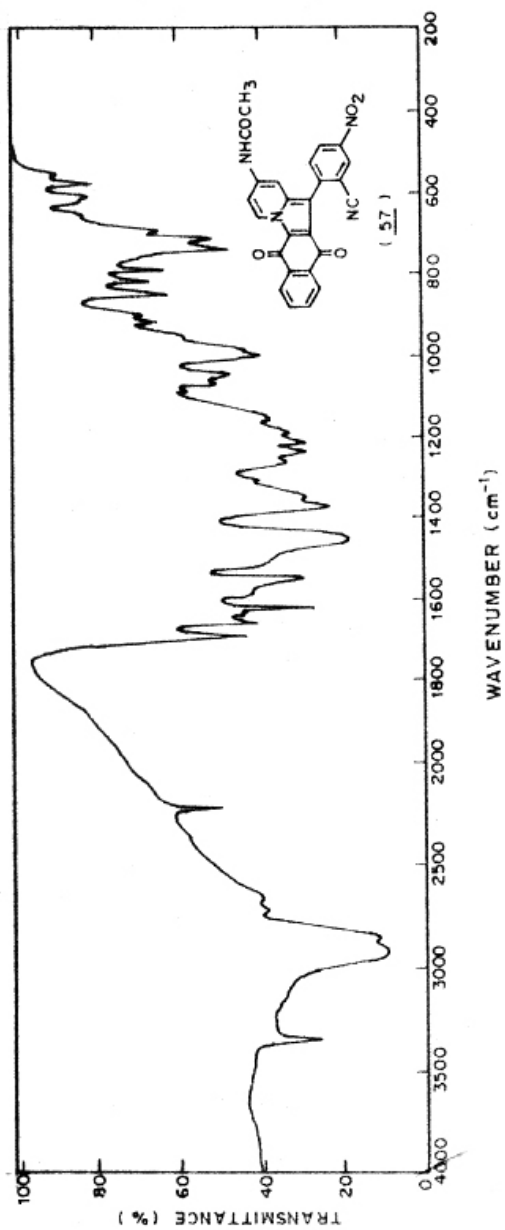


FIG. - 13.

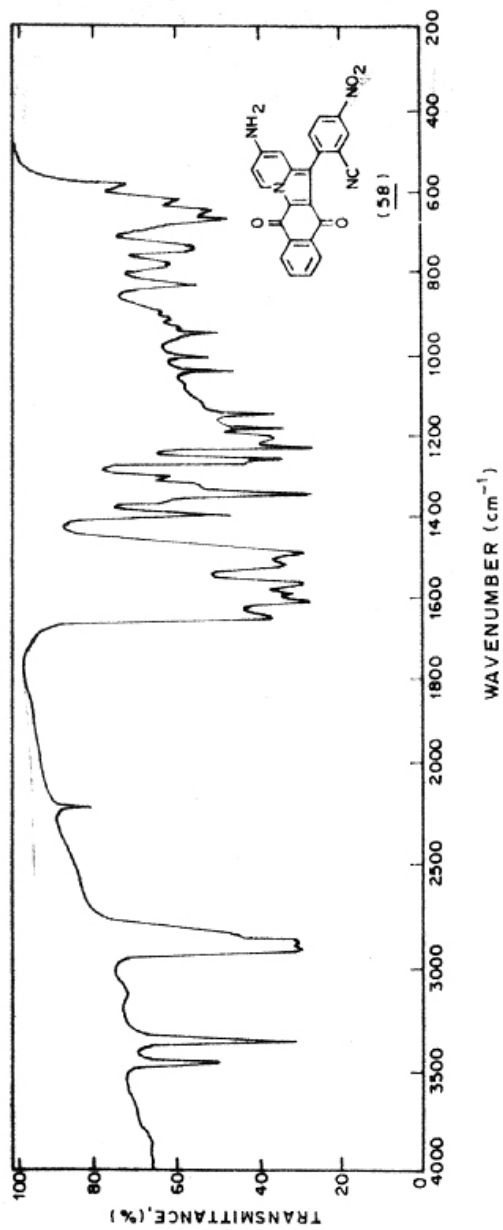


FIG - 14

REFERENCES

1. Finley T. K., 'The Chemistry of Quinonoid Compounds', ed. by S. Patai., Interscience, New York, (1974).
2. Tilak B. D., Suryanarayan B., Curr. Sci., 22, 171 (1953).
3. Pratt E. F., Lukenbaugh R. W., Erickson R. L., J. Org. Chem., 19, 176 (1954).
4. Pratt E. F., Lukenbaugh R. W., Price R. G., J. Am. Chem. Soc., 79, 1212 (1957).
5. Tilak B. D., Acharya R. W., Suryanarayan B., J. Sci. Ind. Res. (India), 14(B), 394 (1955).
6. Tilak B.D., Mathur M.S., ibid, 17(B), 33 (1958).
7. Long R. S., Boyle R. J. U.S.P., 2,863,714 (1958); C. A., 53, 6633 (1959).
8. Amer Cyan. U.S. P., 2,877,230 (1959); J. Soc. Dye. Col., 75, 562 (1959).
9. Tilak B. D., 'The Chemistry of Synthetic Dyes', Vol. V, Ed. by K. Venkataraman., Academic Press, New York, (1972).
10. Saroti M.F., Chem. Rev. , 63, 279 (1963).
11. Zitkov V. A., Raetskaya, Trocheshnikova, USSR . P., 138682 (1960); C.A. 56, 8888 d (1962).
12. Xerox Corpn., U.S.P., 3,531,309 (1967). J. Soc. Dye. Col., 87, 397 (1971).
13. Geigy, Fr. P., 1,385,278 (1965); C.A., 62, 11950e(1965).
14. Geigy, Belg. P., 660,291(1965); C.A., 62, 18054a (1965).
15. Ciba, Belg. P., 646,397 (1963); C.A., 63, 11521a (1965).
16. Geigy, Neth. Appl., 6,505,682 (1964); C.A., 64,12850b (1966).
17. Geigy, Neth. Appl., 6,410,993 (1963); C.A., 63,8527g (1965)
18. Geigy, B.P., 1,078,366 (1967); C.A., 67, 101013v (1967).

19. Geigy, Fr. P., 1,466,795 (1967); C.A., 67, 101014w (1967).
20. Geigy, Neth. Appl., 6,414,313 (1965); C.A., 64, 2202d (1966).
21. Geigy, G.F., 1,810,411 (1969); C.A., 71, 103179k (1969).
22. Geigy, Neth. Appl. 6,504,888 (1965); C.A., 64, 14322 (1966).
23. Geigy, B.F., 1,076,482 (1964); C.A., 67, 109624r (1967).
24. Geigy, Neth. Appl., 6,514,409 (1966); C.A., 65, 10706b (1966).
25. Geigy, Neth. Appl., 6,514,411 (1966); C.A., 65, 10706f (1966).
26. Kulwant Singh., Ph. D (Tech.) Thesis, University of Bombay (1973).
27. Tilak B. D., Ayyangar N.R., Lugade A. G., Ind. J. Chem., 19 (B), 24 (1980).
28. Krohnke F., Schmeiss, Ber., 70, 728 (1937).
29. a) Reid W., Bender H., Chem. Ber., 89, 1893 (1956).
b) Karroll King L., Abramov S.V., J. Org. Chem., 23, 1609 (1958).
30. Van Allen J. A., Reynolds G. A., Adel R. E., ibid, 28, 3502 (1963).

CHAPTER - II

SYNTHESIS OF NAPHTHINDOLIZINEDIONES FROM NITROMETHANE AND ACETONITRILE

SYNTHESIS OF NAPHTHINDOLIZINEDIONES
FROM NITROMETHANE AND 2,3-DICHLORO-
1,4-NAPHTHOQUINONE (DCNQ) (1)

In the preceding study of condensation of DCNQ, nitrotoluenes and heterocyclic compounds the reactivity of the activated methyl group was discussed. This study was further extended to aliphatic nitro and cyano compounds viz. nitromethane and acetonitrile which on interaction of DCNQ (1) and pyridine yielded 12-nitro- and 12-cyano-naphthindolizinediones.

12-Nitronaphthindolizinediones have been reported by Allan et al¹ and in patents². Allan and Reynolds found that N-(1,4-dioxo-2-methoxynaphthyl-3)pyridinium methosulphate (A) reacts with amines to give products in which the methoxy group in (A) is replaced by the amino group. This reaction of (A) with nucleophilic agents was further extended to include active methylene compounds. The reaction was carried by interaction of an equimolar quantity of (A) and the reactive methylene compound and two or more equivalents of sodium acetate in boiling methanol. Reactive methylene derivatives also included nitromethane when 12-nitronaphthindolizinedione (2) was obtained. In all these cases, highly coloured blue solutions were immediately formed which rapidly changed to reddish brown after a short time. Mechanism of the reaction with nitromethane and N-(1,4-dioxo-

2-methoxynaphthyl-3)pyridinium methosulphate (A) may be explained as shown in Chart I.

The above authors have not mentioned the yield obtained for the reaction products. Repetition of the reaction in our hands gave about 20% yield of the desired naphthindolizinedione. 12-Cyanonaphthindolizinedione was also obtained by Allan et al¹ by interaction of ethyl cyanoacetate with (A).

12-Nitronaphthindolizinedione (2) has also been prepared by nitration of the parent naphthindolizinedione (3)². The latter was obtained by the interaction of DCNQ (1) and α -picoline or by decarboxylation of naphthindolizinedione-12-carboxylic acid (4) by heating with copper bronze^{3,4,5}. The latter method gave better yield of (3). Nitration of the parent naphthindolizinedione was carried by interaction with nitrosylsulphuric acid below 15° whereby nitronaphthindolizinedione (2) was obtained in 65% yield (see Chart II).

Synthesis of 12-nitronaphthindolizinedione by the interaction of DCNQ (1) heterocyclic base (e.g. isoquinoline) and nitromethane was first attempted by Pratt⁶. However, he isolated parent naphthindolizinedione instead of 12-nitro derivative. Chart III shows the probable mechanism for the formation of (3) in the reaction.

CHART - I.

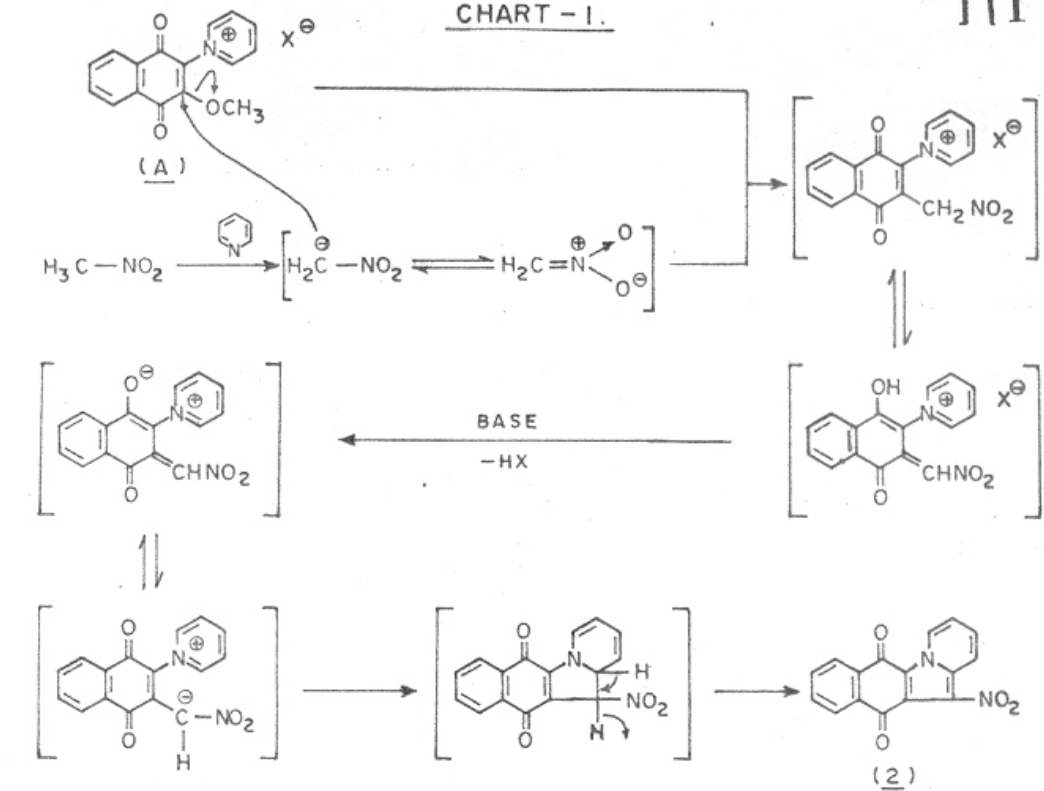
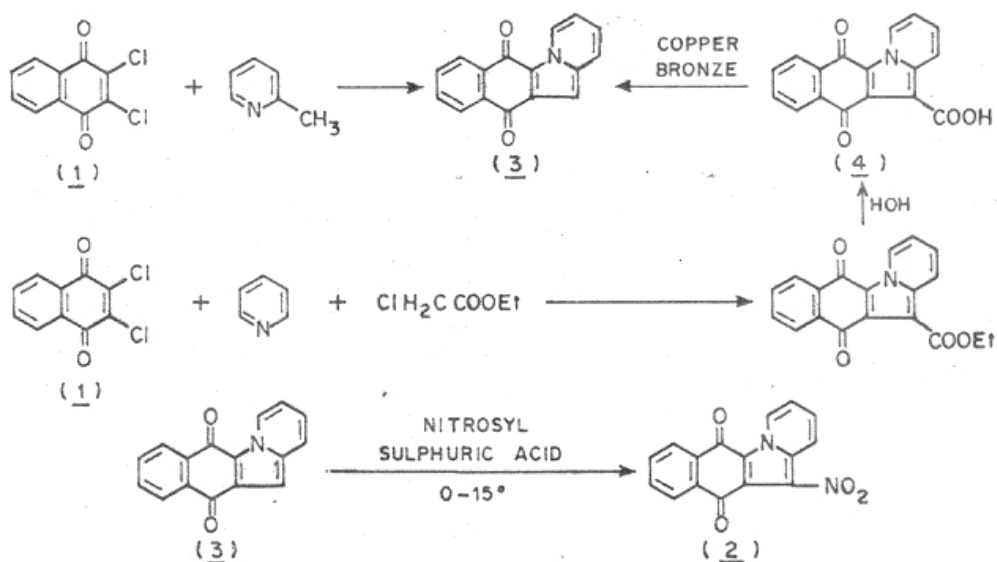


CHART - II.



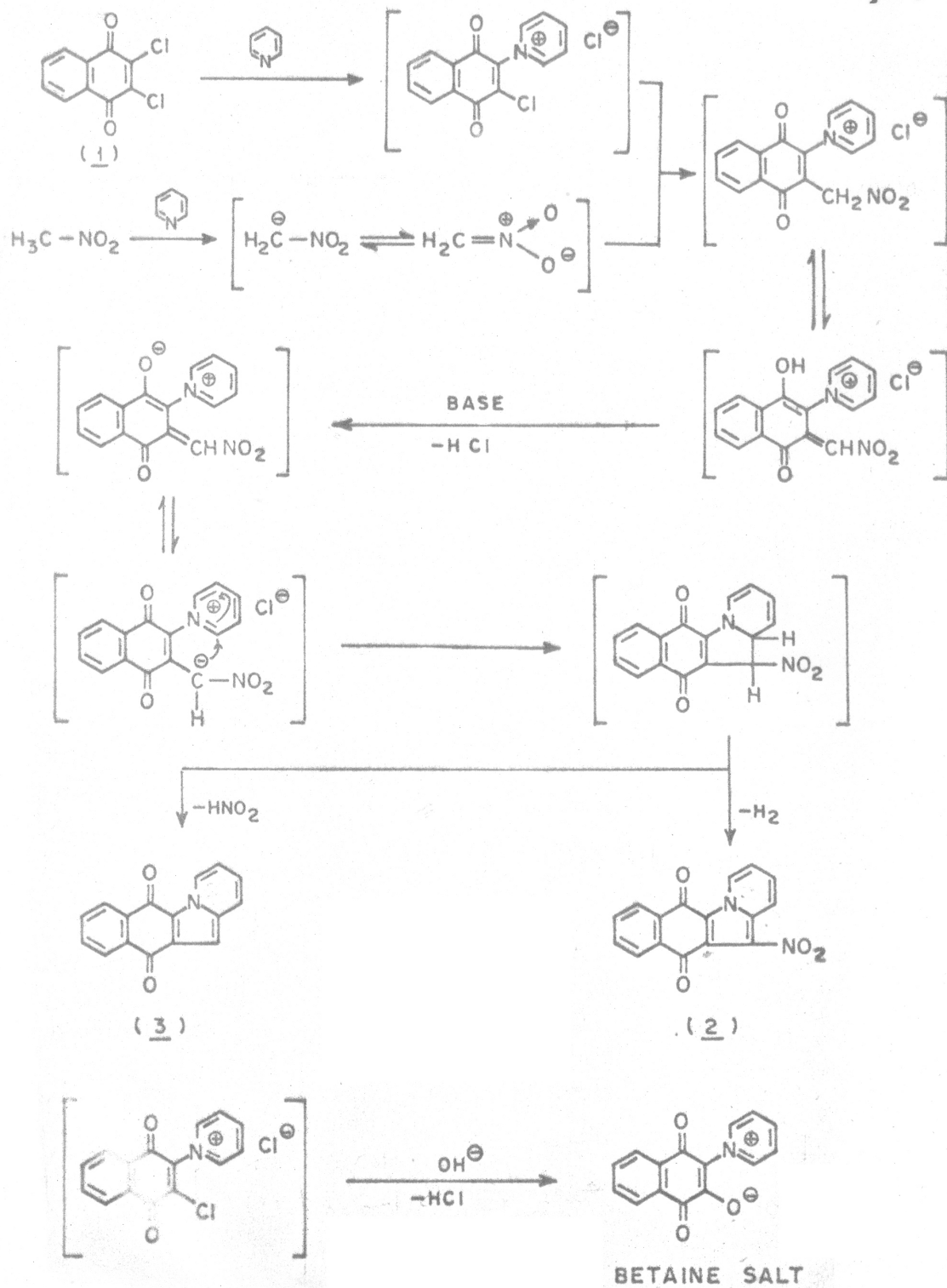
PRESENT WORK

As stated earlier a direct synthesis of 12-nitro-naphthindolizinedione or 1-nitrophthaloylpyrrocoline by the interaction of DCNQ (1), the heterocyclic base and nitromethane was attempted. The reaction was found to be sensitive to reaction conditions. A detailed study of these reactions is described below :-

The general method of synthesis of 12-nitro-naphthindolizinedione consisted in heating DCNQ (1) and nitromethane at 80° for 15 minutes. To the clear solution was added nearly three equivalents of the heterocyclic base over a period of 15 minutes. The mixture was further refluxed for two hours and cooled. Further cooling at 0° for 15 minutes gave a solid which was filtered off. The residue was thoroughly washed with hot water, air dried, adsorbed on silica gel and chromatographed first with the help of 50% petroleum ether - benzene to recover unreacted DCNQ (1). Further elution with benzene gave the desired 12-nitronaphthindolizinedione.

The interaction of DCNQ (1), pyridine and nitromethane is shown in Chart III.

Since nitromethane showed good reactivity in the above reaction, the pyridine moiety was replaced by various heterocyclic bases like isoquinoline, quinoline, ethyl



isonicotinate and 4-cyanopyridine. As per the earlier observation⁶, isoquinoline gave better yields of naphthindolizinedione than pyridine. Ethyl isonicotinate and 4-cyanopyridine also gave better yields though it failed in an earlier study. Although interaction of DCNQ (1), reactive methylene compound and quinoline do not yield the relevant benzonaphthindolizinedione, quinoline showed fair reactivity in the present study.

For the **success** of the reaction, dry reaction conditions, choice of solvent and reaction period had to be optimised. It was observed that higher boiling solvents favour the loss of nitrous acid in the final step of mechanism to yield the parent naphthindolizinedione instead of 12-nitronaphthindolizinedione. Reaction in dry benzene gave about 5% yield of nitronaphthindolizinedione, whereas use of absolute ethanol did not lead to the desired product. Reaction in dry dioxan as solvent or in nitromethane itself proved to be optimal for the synthesis of 12-nitronaphthindolizinedione. Both the solvents gave about same yield of desired nitro derivative. Reaction when carried out in dry xylene gave 20% yield of parent naphthindolizinedione and 11% yield of the 12-nitro derivative. When the synthesis was repeated at higher temperature in solvents such as dimethylformamide, chlorobenzene, o-dichlorobenzene, trichlorobenzene and nitrobenzene, either the reaction gave exclusively the

parent naphthindolizinedione (3) or decomposition products. This may be the reason for the failure of Pratt to isolate nitronaphthindolizinedione, since the reaction was carried by him in boiling 1,2,3-trichloropropane (b.p. 148°).

Reaction period is also one of the important factors in the reaction. It was clearly seen from the decrease in yields by continued heating. Thus when reaction mixture of DCNQ, pyridine and nitromethane was refluxed for two hours, about 30-32% yield of 12-nitronaphthindolizinedione (2) was obtained. Further continuation of the reaction, monitored by TLC, indicated the formation of side products. Work up after 6 hours reflux gave only 15-17% yield of (2). Isolation of the desired reaction product became more difficult due to the formation of side products having close Rf. values.

The above synthetic route appears to be more convenient than the previous syntheses since the yield of the final product was better and the reaction involved a single step. Although patents report a yield of 65-70% of 12-nitronaphth [2',3'-b]indolizine-6,11-dione (2) in nitration of parent naphthindolizinedione, the latter cannot be obtained in more than 40% yield starting from DCNQ.

Acetonitrile was another active methylene compound used for the synthesis of naphthindolizinedione. Earlier reports mention the inactivity of acetonitrile as an active

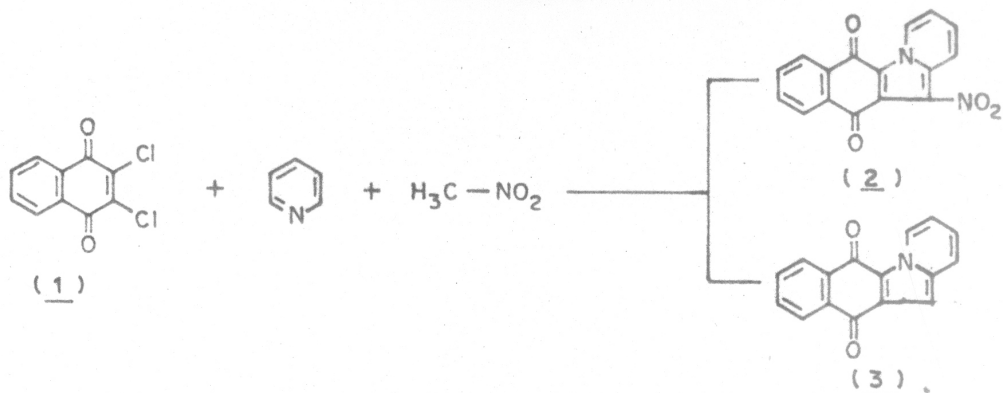
methylene compound. When the reaction was carried out in the presence of a strong proton abstractor like sodamide or sodium hydride, acetonitrile formed a carbanion which then reacted with DCNQ and pyridine and gave finally 12-cyanonaphthindolizinedione (9) albeit in low yield. The 12-cyanoderivative was also prepared unambiguously by interaction of DCNQ, pyridine and ethyl cyanoacetate.

Structural determination of the above compounds was on IR, NMR, mass spectra and elementary analysis. Confirmation of the structures was also made by comparison of the compounds with samples prepared by alternative route followed by Allan et al.¹ Details of the preparation of above compounds are described below:-

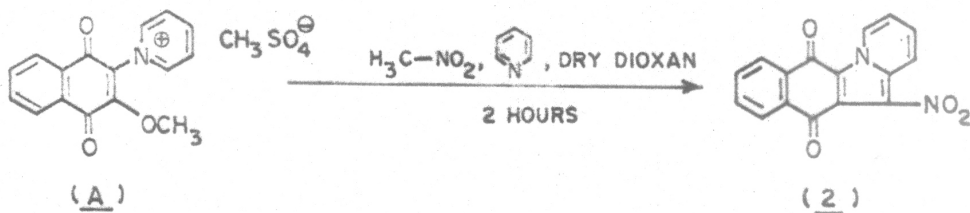
Interaction of DCNQ (1), nitromethane and pyridine yielded 12-nitronaphth[2',3'-b]indolizine-6,11-dione (2). The reaction was repeated under various conditions and solvent systems. These are tabulated in Chart IV.

Pyridine in the above reaction was then replaced by isoquinoline. Interaction of DCNQ, nitromethane and isoquinoline in dry dioxan as solvent for 2 hours gave 14-nitrobenzo[g]naphth[2',3'-b]indolizine-8,13-dione (5) in 35% yield. [Chart V, Route A]. Solvents such as benzene ethanol and higher boiling solvents like xylene, chlorobenzene, dimethylformamide, ODCB gave less (or no) yield of (5).

CHART - IV.



SOLVENT	REACTION PERIOD	% YIELD OF 12-NITRO NAPHTHINDOLIZINEDIONE (2)	% YIELD OF PARENT NAPHTHINDOLIZINEDIONE (3)
BENZENE	2 HOURS	4-5 %	—
ETHANOL	2 HOURS	—	—
DIOXAN	2 HOURS	30-32 %	—
NITROMETHANE	2 HOURS	30-32 %	—
XYLENE	2 HOURS	11 %	20 %
HIGHER BOILING SOLVENTS	2 HOURS	—	—
DIOXAN OR NITROMETHANE	6 HOURS	15-17 %	—

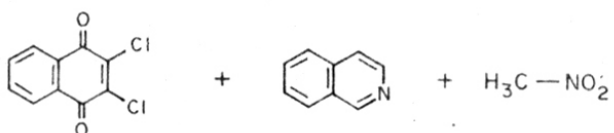


Compound (5) was also prepared in 20% yield according to Route B (Chart V). Figs. 1 and 2 indicate the NMR and mass spectra of compound (5).

Interaction of DCNQ (1), quinoline and nitromethane gave 16% yield of 14-nitrobenzo[*i*]naphth[2',3'-*b*]indolizine-8,13-dione (6). Use of dry dioxan as a reaction medium gave optimum yield of (6). Importance of reaction period and solvent variation was similar to the reaction of pyridine and isoquinoline with DCNQ and nitromethane described earlier. Figs. 3 and 4 indicate IR and NMR spectrum of compound (6). Chart VI represents the above reaction of DCNQ, quinoline and nitromethane. The yield of the 12-arylnaphth-indolizinedione obtained by interaction of DCNQ (1), ethyl isonicotinate and 2-cyano-4-nitrotoluene was low, as already reported in previous chapter. However, when ethyl isonicotinate was reacted with DCNQ (1) and nitromethane the yield of 3-carbethoxy-12-nitronaphth[2',3'-*b*]indolizine-6,11-dione (7) was fairly good. This may be attributed to high reactivity of nitromethane as compared to nitrotoluenes. Dry nitromethane was found to be the best solvent for the reaction. The yield of (7) was 16%. Fig. 5 indicates the NMR spectrum of compound (7). The reaction of DCNQ (1), ethyl isonicotinate and nitromethane is shown in Chart VI.

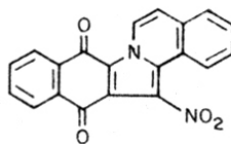
CHART - V.

ROUTE A



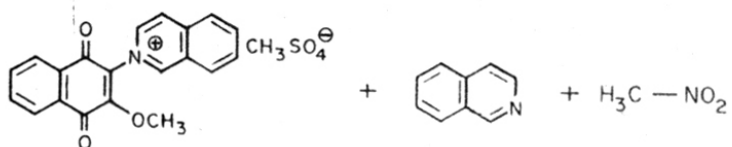
(1)

DRY DIOXAN



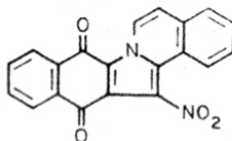
(5)

ROUTE B



(A')

DRY DIOXAN



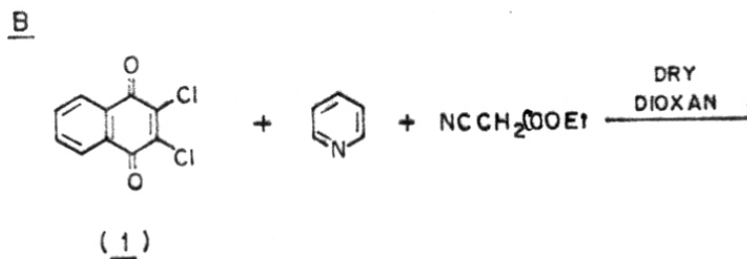
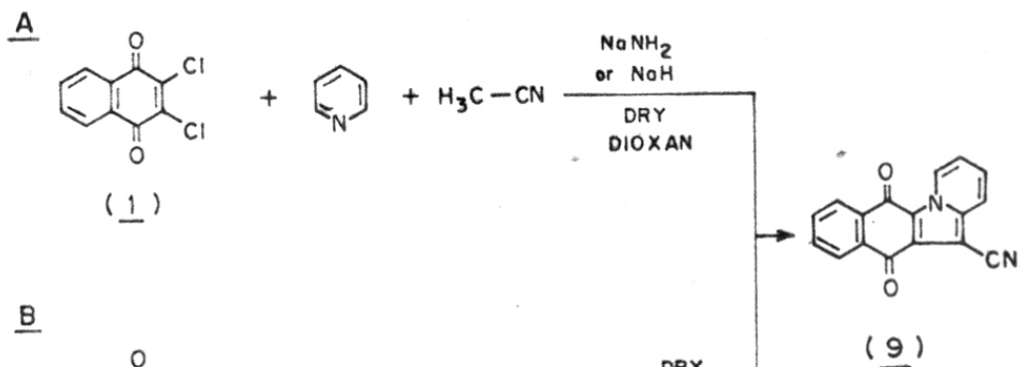
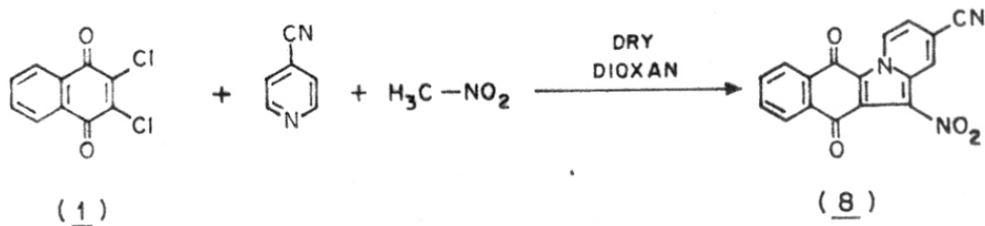
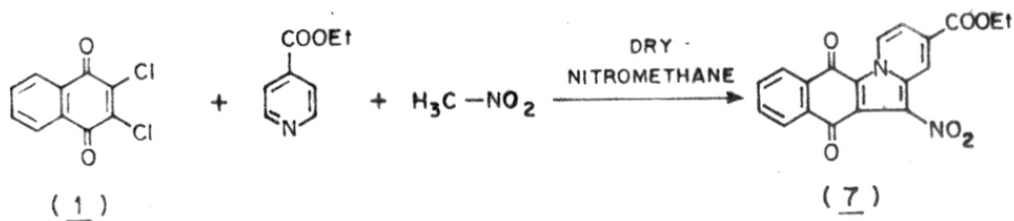
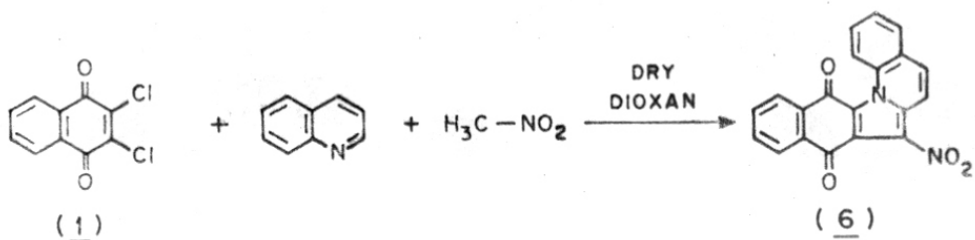
(5)

Interaction of 4-cyanopyridine, DCNQ (1) and nitromethane in dry dioxan gave 12% yield of 3-cyano-12-nitronaphth[2',3'-b]indolizine-6,11-dione (8) (Chart VI).

12-Cyanonaphth[2',3'-b]indolizine-6,11-dione (9) was earlier prepared by the interaction of DCNQ (1), ethyl cyanoacetate and pyridine. Acetonitrile was not used earlier as a reactive methylene compound in view of its low reactivity. Under usual conditions of interaction of DCNQ, pyridine and acetonitrile, only the betaine salt was obtained. However, when a strong external base like sodamide or sodium hydride (1-1.2 moles) was used, compound (9) was obtained in 4% yield. Authentic sample of (9) was prepared for comparison by reported method⁷. It was identical with the compound prepared above (Chart VI).

Reduction of nitro/nitroarylnaphth-indolizinediones

Few representative nitro/nitroarylnaphthindolizinediones described above and in Chapter I were reduced to corresponding amino derivatives. Earlier, 12-(p-nitrophenyl)naphth[2'',3''-b]indolizinedione was reduced to the corresponding amino derivative in our laboratory by treatment with iron and formic acid⁸. As mentioned in the Chapter I, a number of electron withdrawing groups like nitro or cyano were introduced in the naphthindolizinedione moiety with the view to improve the fastness properties of these disperse dyes (for



polyester fibers). For modifying tinctorial and dyeing properties further, it was of interest to partially reduce the nitro/nitroarylnaphthindolizinediones to the corresponding amino derivatives and to use the latter as dyes or to further modify them by acylation, benzylation etc.

12-Aminonaphth[2',3'-b]indolizine-6,11-dione (10) was prepared according to the patented procedure². Compound (10) has been reported to be a useful intermediate for preparation of pigments and heterocyclic dyes. As per the procedure given, 12-nitronaphthindolizinedione (2) was boiled with alkaline sodium sulphide. The reaction gave almost pure (10) which was further purified by crystallisation from chlorobenzene.

Though dinitroarylnaphthindolizinediones were partially reduced by interaction with aqueous sodium sulphide, it was difficult to locate the specific nitro group which had undergone reduction. Reduction of dinitrotoluenes has been reported by several workers^{9,10,11}. It was found that when 2,4-dinitrotoluene was reduced with alkaline sulphides or hydrazine hydrate 2-nitro-4-aminotoluene was obtained; whereas reduction with sodium amalgam gave 2-amino-4-nitrotoluene. To confirm this work, which was reported many years ago, 2,4-dinitrotoluene was reduced with alkaline sodium sulphide and hydrazine hydrate. Both the reductions

gave 2-nitro-4-aminotoluene which was identical with an authentic sample.

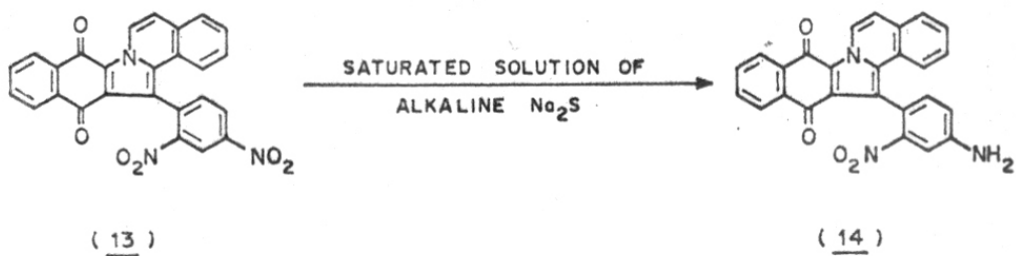
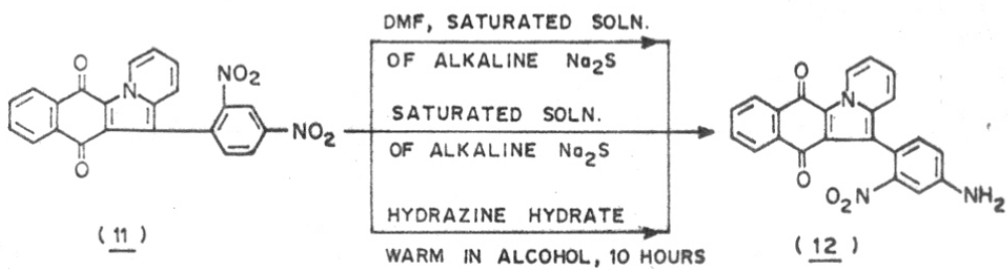
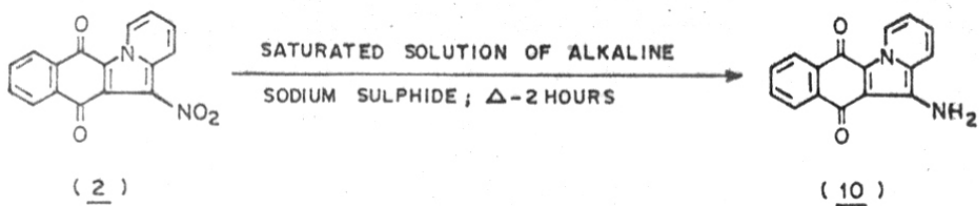
Reduction of 12-(2',4'-dinitrophenyl)naphth [2'',3''-b]indolizine dione (11) with either aqueous alkaline sodium sulphide or hydrazine hydrate gave an identical 12-nitroaminophenyl naphthindolizinedione which has been assigned the structure 12-(2'-nitro-4'-aminophenyl)naphth [2'',3''-b]indolizine-6,11-dione (12) (Chart VII). The presence of amino, nitro and carbonyl functions in (12) were confirmed by IR. Figs. 6 and 7 indicate IR and mass spectrum of compound (12).

14-[2',4'-Dinitrophenyl]benzo [g]naphth [2'',3''-b] indolizine-8,13-dione (13) on similar reduction gave 14-(2'-nitro-4'-aminophenyl)benzo [g]naphth [2'',3''-b] indolizine-8,13-dione (14) (Chart VII).

Acetylation and benzylation of amino/aminoarylnaphthindolizinediones

12-Aminonaphthindolizinedione (10) when acetylated by treatment with acetic anhydride gave 12-acetamidonaphth [2',3'-b]indolizine-6,11-dione (18). 12-(p-Aminophenyl) naphth [2'',3''-b]indolizine-6,11-dione (15) when acetylated earlier in our laboratory gave 80% yield of diacetyl derivative (16) and only 10% of monoacetyl derivative (17)⁸. The diacetylation of aromatic primary amines has also been

CHART - VII.



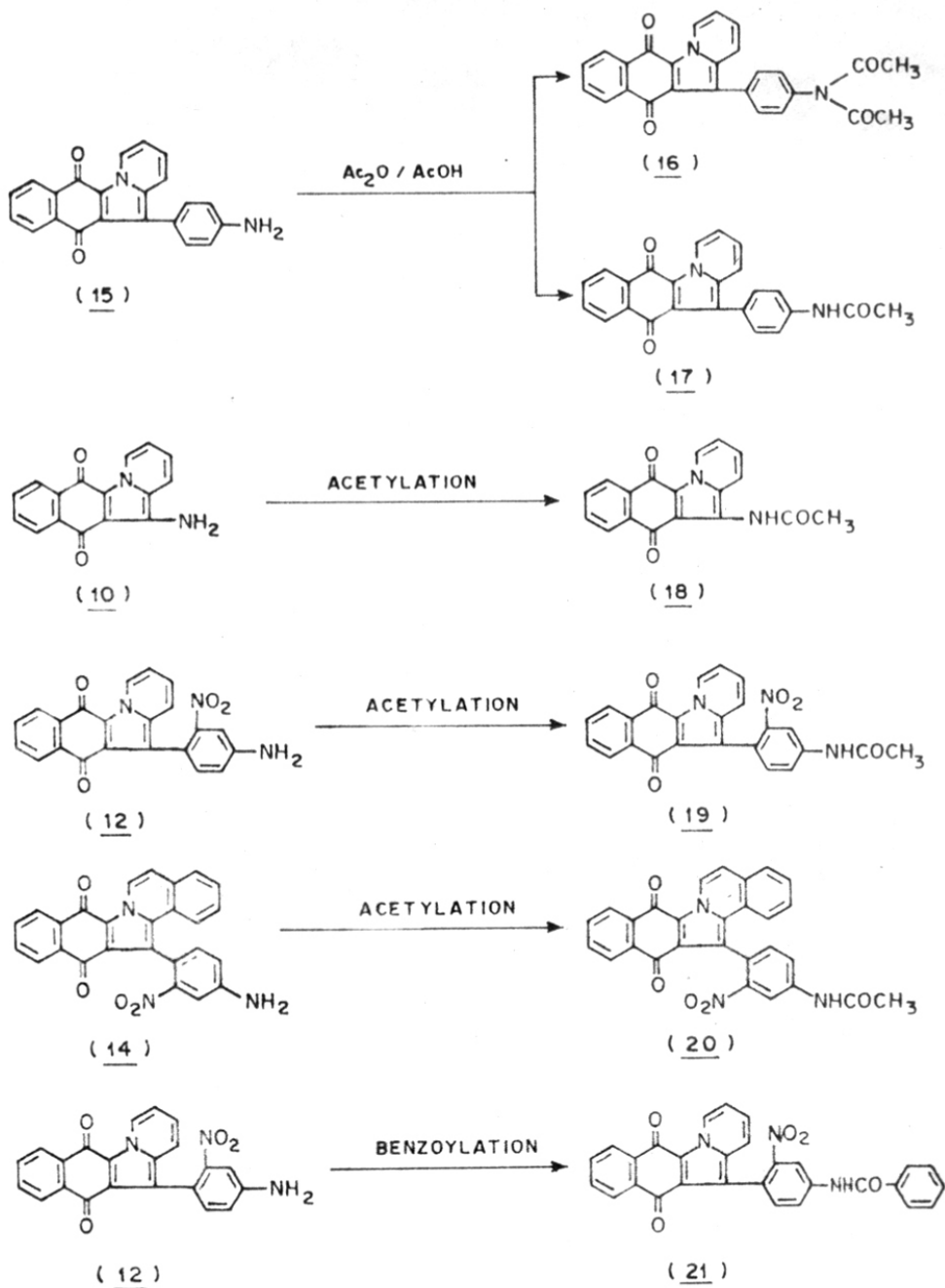
reported earlier. For example, diacetyl derivatives of aniline; o, m and p-toluidine; o, p-anisidine; α and β naphthylamines are known and their infrared spectra have been studied¹². Nevertheless, when acetylation of 12-(2'-nitro-4'-aminophenyl)naphth[2'',3''-b]indolizine-6,11-dione (12) was carried out by treatment with acetic anhydride, it exclusively gave the monoacetyl derivative (19) in 90% yield. 14-(2'-Nitro-4'-aminophenyl)benzo[g]naphth[2'',3''-b]indolizine-8,13-dione was also acetylated to the corresponding monoacetyl derivative (20) by treatment with acetic anhydride (Chart VIII). Fig. 8 shows the IR spectrum of compound (19).

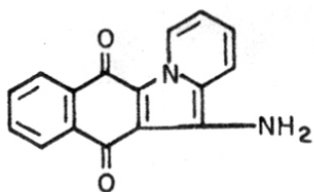
Benzoylation of 12-(2'-nitro-4'-aminophenyl)naphth[2'',3''-b]indolizine-6,11-dione (12) by treatment with benzoyl chloride gave the benzoyl derivative (21) in 90% yield (Chart VIII).

Reaction of aminonaphthindolizine-diones with acrylonitrile

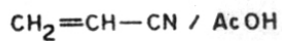
Interaction of 12-aminonaphth [2',3'-b]indolizine-6,11-dione (10) and 12-(2'-nitro-4'-aminophenyl)naphth [2'',3''-b]indolizine-6,11-dione (12) with acrylonitrile gave N,N-biscyanoethyl derivatives, 12-(biscyanoethylamino)naphth [2',3'-b]indolizine-6,11-dione (22) and 12-[2'-nitro-4'-(biscyanoethylaminophenyl)]naphth[2'',3''-b]indolizine-6,11-dione (23) respectively (Chart IX).

CHART - VIII.

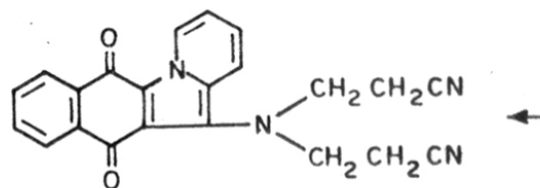




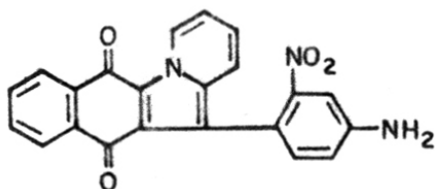
(10)



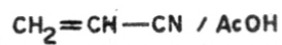
COPPER ACETATE



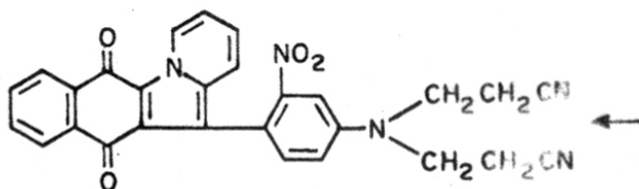
(22)



(12)



COPPER ACETATE



(23)

EXPERIMENTAL12-Nitronaphth [2',3'-b]indolizine-6,11-dione (2).

The compound was prepared by two methods A and B.

Method (A) :-From 2,3-dichloro-1,4-naphthoquinone(DCNQ) (1).

A mixture of DCNQ [2.27 g.; 0.01 mol] and nitromethane [5 ml] in dry dioxan [20 ml] was heated at 80° till a clear yellow solution is formed. Pyridine [3 ml; 0.04 mol] in dry dioxan [5 ml] was then added over 20 minutes under stirring. During the addition the reaction mixture turned bluish green. The mixture was then heated under reflux for 2 hours. Initial bluish green mixture turned red and finally became reddish brown at reflux.

The reaction mixture was then cooled to room temperature and poured over crushed ice. When xylene was used as solvent, it was distilled off under reduced pressure and the residue was then added to crushed ice. Work up of the reaction mixture when other high boiling solvents like dimethylformamide, chlorobenzene, were used was also carried out similarly. The reddish orange coloured reaction product was filtered off and washed thoroughly with hot water to remove the betaine salt formed during the reaction. The reaction product was further washed with 5%

copper sulphate solution to remove last traces of pyridine. Final washings were given with cold water and the reaction product was dried under vacuum. The reaction product was then adsorbed on silica gel or alumina (alumina was preferably used for purification of cyano compounds) and then chromatographed.

The first fraction eluted by 50% pet. ether and 50% benzene yielded 1% unreacted DCNQ (1). The second yellowish orange fraction obtained by eluting with 10% ethyl acetate and benzene yielded 12-nitronaphthindolizinedione (2). The product was again chromatographed through a short column and finally crystallised from DMF. [Effect of various reaction conditions and solvent choice on yield is tabulated in the discussion part of this chapter (see Chart IV)]. Compound (2) crystallised from DMF (m.p. 266°) in yellowish orange needles (0.810 g.; 30%) (Found: C, 65.6; H, 2.5; N, 9.5; calculated for $C_{16}H_8N_2O_4$: C, 65.8; H, 2.7; N, 9.6%).

IR (Nujol) : γ max - 1650, 1620, 1580, 1500, 1455, 1400, 1390, 1340, 1290, 1275, 1240, 1165, 1135, 1040 and 1020 cm^{-1} .
NMR ($AsCl_3$) : 9.7 δ (1H, d, J = 7Hz); 7-8.5 δ (7H, m).

Mass spectrum: m/e - 293 [(M+1), 25%], 292 (M^+ 22), 272 (5), 247 (30), 246 (100), 218 (30), 217 (40), 191 (22.5), 190 (33), 164 (17.5), 163 (23), 137 (4), 138 (5), 124 (4), 110 (16), 92 (26), 78 (12).

Method B :-From N-(1,4-dioxo-2-methoxynaphthyl-3)
pyridinium methosulphate (A)

Compound (A)* [3.77 g.; 0.01 mol], pyridine [3 ml; 0.04 mol] and nitromethane [5 ml] were interacted with dry dioxan [15 ml] as solvent. The reaction mixture was worked up on similar lines as Method A to get 12-nitronaphth[2',3'-b]indolizine-6,11-dione (2) (0.500 g., 17%). Both the products from Methods A and B were identical.

14-Nitrobenzo[g]naphth[2',3'-b]
indolizine-8,13-dione (5).

DCNQ [2.27 g.; 0.01 mol], isoquinoline [5 ml; 0.04 mol] and nitromethane [5 ml] were heated in boiling dry dioxan [15 ml] for two hours, as described in Method A. The reaction mixture was cooled to 0° and the reaction product was filtered off. Further work up was on similar lines as Method A to get (5). Compound (5) crystallised from chlorobenzene (m.p. 336°) in orange needles (1.19 g., 35%). (Found : C, 70.2; H, 3.4; N, 8.0; calculated for C₂₀H₁₀N₂O₄ : C, 70.3; H, 3.4; N, 8.2%). IR (Nujol): γ_{\max} - 1650, 1620, 1580, 1500, 1455, 1400, 1390, 1340, 1290, 1275, 1240, 1165, 1150, 1135, 1040 and 1020 cm⁻¹. NMR (AsCl₃) : 9.6 δ (1H, d, J = 7Hz); 7.3-8.6 δ (9H, m).

* Preparation of Compound (A) is given in experimental part of Chapter I.

Mass spectrum : m/e - 343 [(M+1), 21.5%], 342 (M⁺, 25), 312 (17), 296 (100), 268 (47), 257 (43.5), 240 (23.5), 239 (15.5), 229 (12), 228 (9), 215 (29.5), 214 (40), 202 (10), 201 (11.5), 200 (10), 164 (15), 147 (15), 120 (45.5), 113 (9.5), 78 (13), 77 (7).

Compound (5) was also prepared through Method B as follows :- N-(1,4-dioxo-2-methoxynaphthyl-3)isoquinolinium methosulphate (A') [4.27 g.; 0.01 mol], isoquinoline [5 ml; 0.04 mol] and nitromethane [5 ml] in dry dioxan [15 ml] were refluxed for 2 hours. Work up gave (5) (0.680 g., 20%). Compounds obtained by both the above methods were identical, as shown by mixed melting point and superimposable IR spectra.

14-Nitrobenzo[1]naphth[2',3'-b]
indolizine-8,13-dione [6].

DCNQ [2.27 g.; 0.01 mol], quinoline [5 ml; 0.04 mol] and nitromethane [5 ml] and dry dioxan [15 ml] were refluxed together for 2 hours. Work up as in general method A gave (6). Compound (6) crystallised from DMF (m.p. 304°) in orange needles (0.525 g., 16%). (Found : C, 70.1; H, 3.5; N, 8.3; C₂₀H₁₀N₂O₄ requires : C, 70.3; H, 3.4; N, 8.2%).. IR (Nujol) : γ_{\max} - 1650, 1620, 1580, 1510, 1460, 1410, 1390, 1350, 1295, 1280, 1240, 1200, 1175, 1160, 1140, 1090, 1050 and 1030 cm⁻¹.

NMR (AsCl_3) : 9.6 δ (1H, d, J = 7 Hz); 7.6-8.5 δ (9H, m).

Mass spectrum : m/e - 343 [(M+1), 8%], 342 (M^+ , 12), 312 (8), 296 (100), 241 (38), 240 (64), 239 (23), 238 (19), 213 (10), 164 (10), 139 (12), 138 (16.5), 137 (11.5), 135 (10), 134 (30), 122 (10), 120 (48), 119 (26), 113 (16), 107 (24), 101 (25), 100 (11), 94 (40), 78 (30).

3-Carbethoxy-12-nitronaphth[2',3'-b]
indolizine-6,11-dione (7).

Compound (7) was prepared by Method A by interaction of DCNQ [2.27 g.; 0.01 mol], ethyl isonicotinate [5 ml, 0.04 mol] and nitromethane [20 ml]. Work up gave (7) which crystallised from chlorobenzene (m. p. 321°) in yellowish orange needles (0.420 g., 16%). (Found : C, 62.5; H, 3.2; N, 7.6; $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_6$ requires : C, 62.6; H, 3.3; N, 7.6%).

IR (Nujol): γ_{max} - 1700, 1650, 1620, 1580, 1460, 1370, 1320, 1290, 1250, 1220, 1160, 1130, 1060 and 1010 cm^{-1} .

NMR (AsCl_3) : 9.75 δ (1H, d, J = 7 Hz); 9.3 δ (1H, s); 7.5-8.7 δ (5H, m); 5.0 δ (2H, q); 1.8 δ (3H, t).

Mass spectrum : m/e - 365 [(M+1), 12%], 364 (M^+ , 17), 334 (8), 320 (13.5), 319 (21), 318 (100), 303 (15), 289 (14), 273 (16), 246 (8), 245 (15), 217 (16.5), 189 (28.5), 188 (8), 164 (15), 124 (14), 110 (18), 92 (30), 78 (15).

3-Cyano-12-nitronaphth[2',3'-b]
indolizine-6,11-dione (8).

Interaction of DCNQ [2.27 g.; 0.01 mol], 4-cyano-pyridine [4.16 g.; 0.04 mol] and nitromethane [5 ml] in boiling dioxan [15 ml] for 2 hours gave on work up (8). Compound (8) crystallised from chlorobenzene (compound did not melt below 360°) in yellow needles (0.400 g., 13%). (Found : C, 66.4, H, 2.3; N, 13.4; $C_{17}H_7N_3O_4$ requires : C, 66.4; H, 2.2; N, 13.2%).

IR (Nujol): ν_{\max} - 2200, 1670, 1610, 1590, 1550, 1495, 1460, 1375, 1350, 1320, 1280, 1240, 1210, 1180, 1130, 1090 and 1000 cm^{-1} .

12-Cyanonaphth[2',3'-b]indolizine-6,11-dione (9).

A mixture of DCNQ [2.27 g.; 0.01 mole], pyridine [3 ml; 0.04 mol], acetonitrile [5 ml] and sodium hydride [0.300 g.; 0.012 mol] in dry dioxan were heated under reflux for 2 hours. Work up gave (9). Compound (9) crystallised from chlorobenzene (m.p. 319°) in yellowish orange needles (0.400 g., 4%). (Found: C, 74.9; H, 3.0; N, 10.4; calculated for $C_{17}H_8N_2O_2$: C, 75.0; H, 2.9; N, 10.3%).

IR (Nujol) ν_{\max} - 2180, 1650, 1630, 1520, 1500, 1460, 1320, 1260, 1230, 1170, 1140, 1070 and 1020 cm^{-1} .

Mass spectrum : m/e - 273 [(M+1), 21.5], 272 (M⁺, 100),
258 (16.5), 246 (59.5), 218 (83), 190 (81), 167 (32),
163 (39), 130 (30), 129 (27), 124 (44), 92 (37), 78 (39).

12-Aminonaphth[2',3'-b]indolizine-6,11-dione (10).

12-Nitronaphthindolizinedione (2) [1.07 g.; 0.04 mol] was suspended in a saturated solution of sodium sulphide and the mixture was refluxed for 3 hours. The solution was cooled and the blue coloured reaction mixture was filtered off. The residue was washed thoroughly till free of alkali. The resulting compound (10) was crystallised from chlorobenzene (m. p. 203^o) in violet plates (0.950 g., 90%). (Found: C, 73.4; H, 3.8; N, 10.8; calculated for C₁₆H₁₀N₂O₂: C, 73.3; H, 3.8; N, 10.7%).

12-(2'-Nitro-4'-aminophenyl)naphth
[2'',3''-b]indolizine-6,11-dione (12).

12-(2',4'-Dinitrophenyl)naphth[2'',3''-b]indolizine-6,11-dione (11) [2.065 g.; 0.05 mol] was dissolved in dimethylformamide and warmed. To this hot solution was added a saturated solution of alkaline sodium sulphide. The mixture was heated at reflux for 2 hours. After cooling the mixture was poured over ice, filtered, washed thoroughly with water and vacuum dried. Compound (11) can also be reduced as described in previous compound (10). The 12-amino-nitrophenylnaphthindolizinedione (12) crystallised from DMF (m. p. 296^o)

in violet plates (1.650 g., 87%). (Found : C, 68.8; H, 3.3; N, 10.8; $C_{22}H_{13}N_3O_4$ requires : C, 68.8; H, 3.4; N, 11.0%).

IR (Nujol) : ν_{\max} - 3440, 3360, 1650, 1620, 1580, 1530, 1510, 1480, 1390, 1340, 1310, 1300, 1280, 1260, 1220, 1150, 1130, 1080, 1040 and 1010 cm^{-1} .

IR (HCB) : ν_{\max} - 3440, 3360, 1650, 1610, 1560, 1480, 1390, 1340, 1300, 1280, 1265, 1225, 1165, 1130, 1085, 1065 and 1020 cm^{-1} .

Mass spectrum : m/e - 384 [(M+1) 9%], 383 (M^+ , 37), 337 (100), 321 (62), 320 (17), 293 (23), 265 (40), 252 (20), 238 (18), 227 (23), 211 (16), 189 (20), 176 (15), 168 (17), 155 (20), 140 (18), 126 (18), 111 (18), 97 (31), 94 (29), 78 (30).

Compound (12) was also prepared by an alternate route as follows :- A mixture of dinitrophenyl-naphthindolizine-dione (11) [2.065 g., 0.05 mol] and hydrazine hydrate [5 ml; 80% solution] and ethanol [20 ml] was heated at 60-70° for 10 hours under stirring. The violet coloured product was further purified by crystallisation from dimethylformamide. Yield of the amine was only 50% (0.950 g.) and there were several side products. The products obtained from both the methods were identical as shown by mixed m.p. and super-imposable IR.

12-(2'-Nitro-4'-aminophenyl)benzo[g]naphth
(2'',3''-b]indolizine-8,13-dione (14).

14-(2',4'-Dinitrophenyl)benzo[g]naphth[2'',3''-b]indolizine-8,13-dione (13) [2.3 g.; 0.05 mol] was reduced by two routes described in previous compound (12). The amine (14) crystallised from nitrobenzene (compound did not melt below 360°) in reddish violet plates (1.75 g., 80%). (Found : C, 71.9; H, 3.4; N, 9.6; C₂₆H₁₅N₃O₄ requires : C, 72.1; H, 3.5; N, 9.7%).

IR (Nujol) : ν_{\max} - 3430, 3300, 1650, 1620, 1580, 1550, 1510, 1460, 1420, 1410, 1390, 1310, 1290, 1265, 1245, 1230, 1220, 1200, 1180, 1160, 1140, 1090, 1070 and 1030 cm⁻¹.

12-Acetamidonaphth[2',3'-b]
indolizine-6,11-dione (18).

A mixture of 12-aminonaphthindolizinedione (10) [0.525 g.; 0.002 mol] and acetic anhydride [3 ml] was refluxed gently for 30 minutes. The reaction mixture was cooled, poured into ice — cold water (20 ml), boiled to decompose excess acetic anhydride and the acetyl derivative obtained was filtered and washed. The acetyl derivative (18) crystallised from chlorobenzene (m.p.265°) in orange red needles (0.490 g., 80%). (Found : C, 70.9; H, 3.8; N, 9.1; C₁₈H₁₂N₂O₃ requires : C, 71.1; H, 3.9; N, 9.2%)-

IR (Nujol) : γ_{\max} - 3370, 1700, 1660, 1630, 1610, 1540, 1520, 1480, 1470, 1350, 1320, 1300, 1270, 1240, 1210, 1160, 1130, 1100, 1080, 1050 and 1020 cm^{-1} .

Mass spectrum : m/e - 305 [(M+1), 12%], 304 (M^+ , 100), 290 (8), 289 (18), 261 (21), 246 (48), 218 (23.5), 191 (11), 190 (21), 163 (16), 138 (95), 110 (10.5), 92 (27.5), 78 (10.5).

12-(2'-Nitro-4'-acetamidophenyl)naphth
[2'',3''-b]indolizine-6,11-dione (19).

Compound (12) [0.575 g.; 0.015 mol] was acetylated as above. The acetyl derivative (19) crystallised from chlorobenzene (m.p. 280°) in red needles (0.510 g.; 80%). (Found : C, 67.8; H, 3.6; N, 10.0; $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_5$ requires : C, 67.8; H, 3.5; N, 9.9%).

IR (Nujol) : γ_{\max} - 3400, 1700, 1660, 1630, 1590, 1565, 1550, 1520, 1485, 1470, 1390, 1370, 1345, 1310, 1270, 1250, 1230, 1150, 1130, 1100, 1090, 1070, 1050 and 1020 cm^{-1} .

Mass spectrum : m/e - 426 [(M+1), 7%], 425 (M^+ , 55), 380 (33), 379 (100), 364 (29), 336 (21), 321 (42), 293 (14), 265 (30), 252 (14), 238 (12), 227 (21), 211 (15), 168 (16), 140 (17), 126 (14), 114 (18), 91 (24), 78 (32).

14-(2'-Nitro-4'-acetamidophenyl)benzo [g]
naphth[2'',3''-b]indolizine-8,13-dione (20).

Compound (14) [0.435 g.; 0.001 mol] was acetylated with acetic anhydride. The acetyl derivative (20) crystallised from chlorobenzene (compound did not melt below 360°) in red needles (0.360 g., 74%). (Found : C, 70.6; H, 3.5; N, 8.7; C₂₈H₁₇N₃O₅ requires : C, 70.7; H, 3.6; N, 8.8%). IR (Nujol) : γ_{\max} - 3300, 1670, 1630, 1600, 1580, 1550, 1510, 1460, 1420, 1390, 1370, 1310, 1300, 1270, 1240, 1220, 1170, 1150, 1120, 1075, 1030 and 1010 cm⁻¹.

12-(2'-Nitro-4'-benzamidophenyl)naphth
[2'',3''-b]indolizine-6,11-dione (21).

A mixture of compound (12) [0.575 g.; 0.0015 mol] and benzoyl chloride [5 ml] was heated at 100° for 30 minutes. The reaction mixture was cooled and excess 5% NaOH solution added under vigorous stirring. The solution was boiled to destroy benzoyl chloride and to dissolve excess benzoic acid. The benzoyl derivative (21) was filtered, washed and dried. Compound (21) crystallised from chlorobenzene (compound did not melt below 360°) in red needles (0.570 g., 80%). (Found : C, 71.4; H, 3.4; N, 8.6; C₂₉H₁₇N₃O₅ requires : C, 71.5; H, 3.5; N, 8.6%). IR (Nujol) : γ_{\max} - 3290, 1650, 1630, 1600, 1580, 1575, 1550, 1540, 1510, 1490, 1420, 1390, 1370, 1350, 1330, 1310, 1300, 1270, 1240, 1220, 1170, 1150, 1120, 1070 and 1020 cm⁻¹.

12-(Biscyanoethylamino)naphth
[2',3'-b]indolizine-6,11-dione (22).

Compound (10) [0.525 g.; 0.002 mol] was reacted with excess acrylonitrile [5 ml] and copper acetate dissolved in acetic acid. The reaction mixture was refluxed for 30 minutes, cooled and poured over crushed ice. The residue was filtered and washed thoroughly with cold water. The biscyanoethyl derivative (22) was purified by crystallisation from chlorobenzene. Compound (22) crystallised from chlorobenzene (Compound did not melt below 360°) in red plates (0.580 g., 80%). (Found : C, 71.6; H, 4.3; N, 15.1; C₂₂H₁₆N₄O₄ requires : C, 71.7; H, 4.3; N, 15.2%).

IR (Nujol) ν_{\max} - 2200, 1665, 1635, 1630, 1600, 1580, 1530, 1490, 1470, 1450, 1410, 1350, 1340, 1310, 1280, 1240, 1225, 1200, 1160, 1140, 1090, 1050 and 1020 cm⁻¹.

12-[2'-nitro-4'-(biscyanoethylamino)phenyl]
naphth[2'',3''-b]indolizine-6,11-dione (23).

Compound (12) [0.575 g.; 0.0015 mol], acrylonitrile [5 ml], catalytic amount of copper acetate and glacial acetic acid [10 ml] were refluxed for 30 minutes. On work up as above gave (23) which crystallised from chlorobenzene (compound did not melt below 360°) in red needles (0.590 g., 80%).

(Found: C, 68.6; H, 3.8; N, 14.3; C₂₈H₁₉N₅O₄ requires : C, 68.7; H, 3.9; N, 14.3%).

IR (Nujol) : ν_{\max} - 2200, 1660, 1630, 1585, 1570, 1480, 1390, 1370; 1350; 1320; 1310, 1290, 1230, 1160, 1140, 1100, 1090, 1070, 1050 and 1020 cm⁻¹.

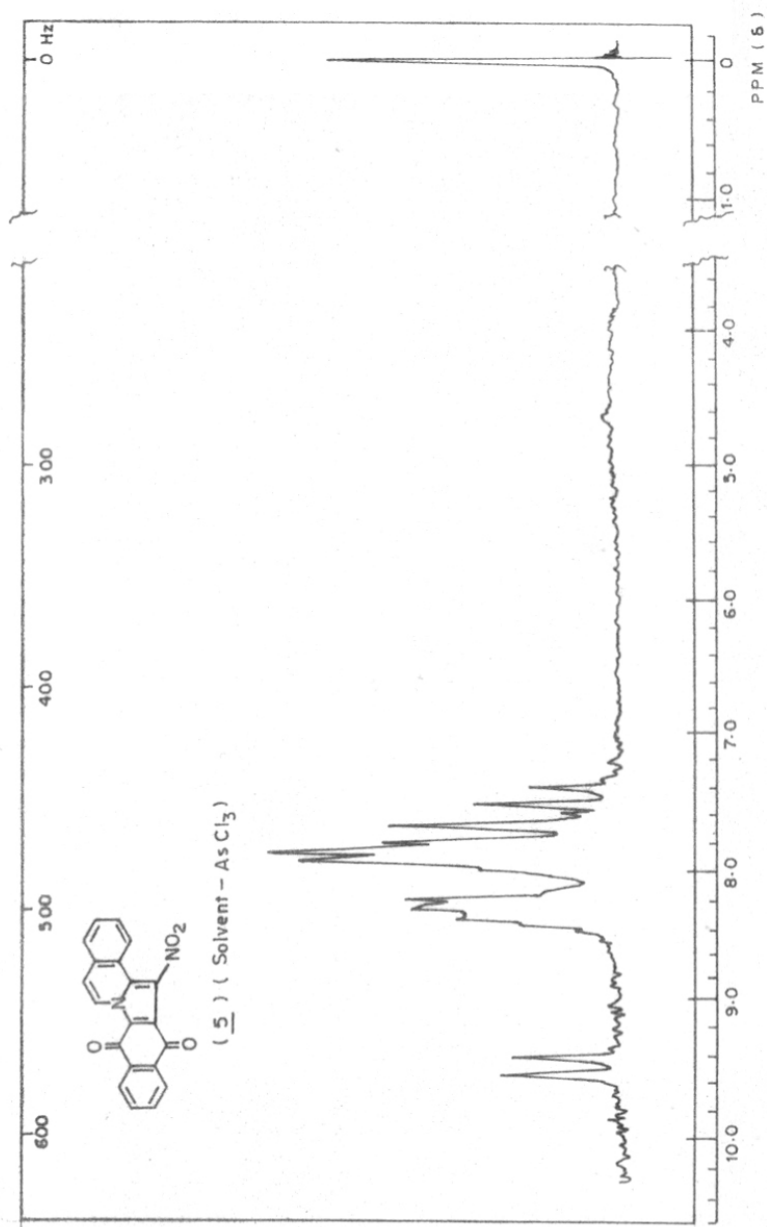


FIG. - 1.

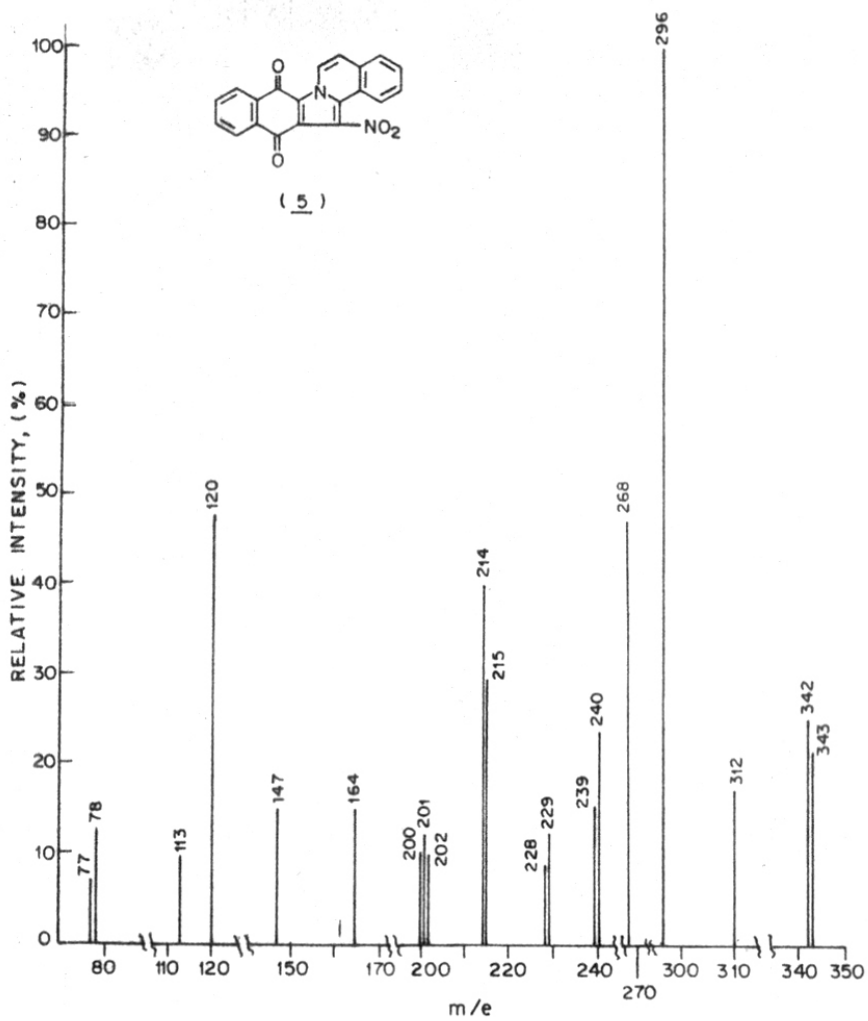


FIG. - 2.

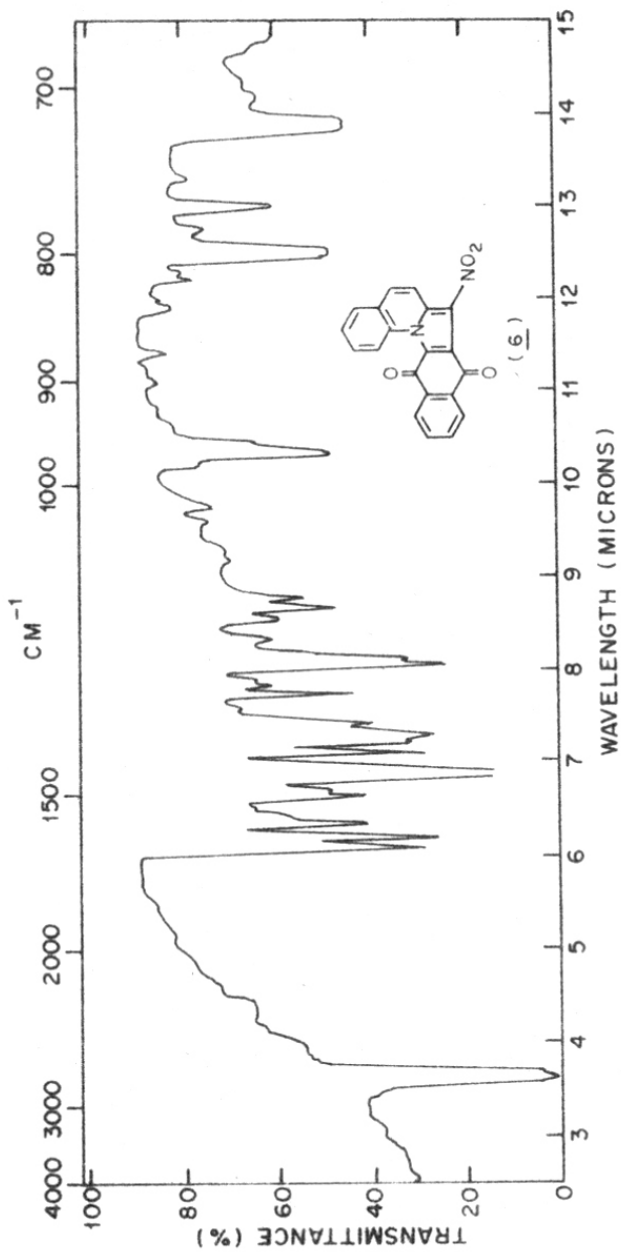


FIG. 3

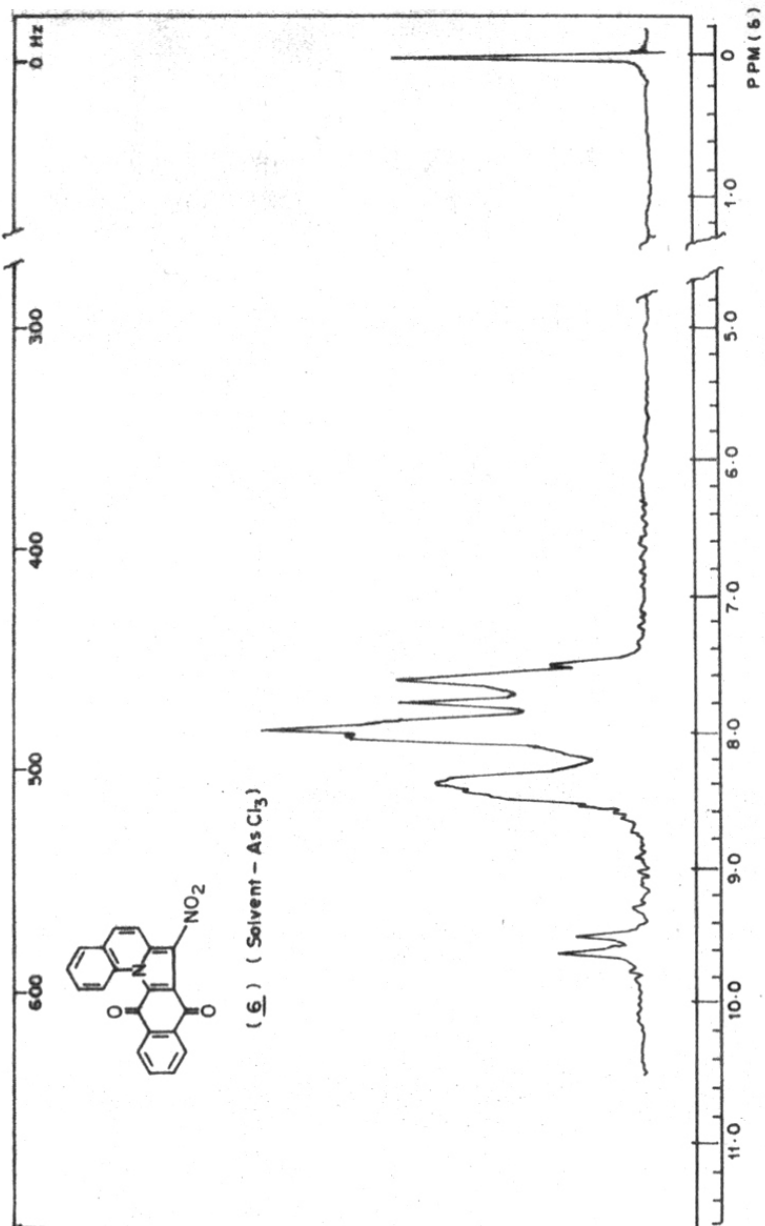


FIG. - 4.

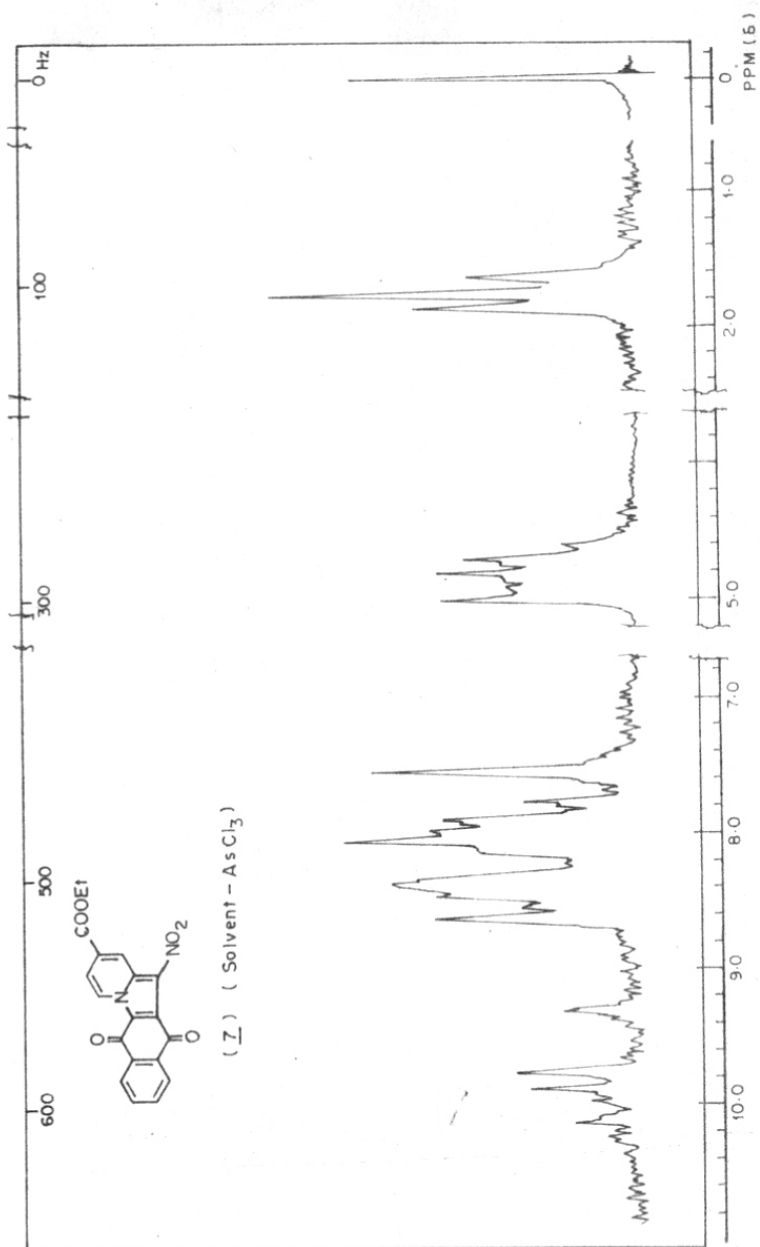


FIG. -5

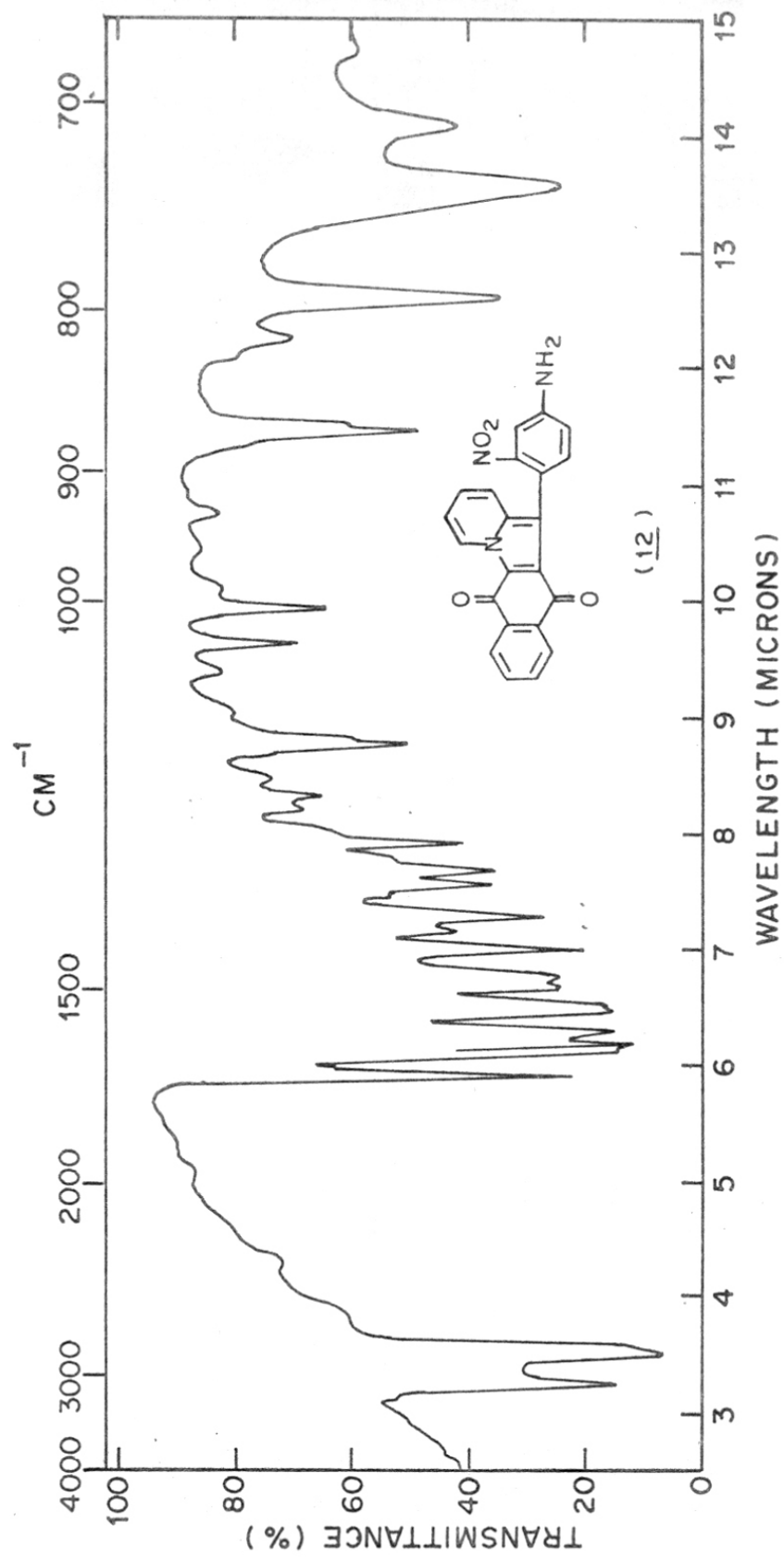


FIG. 6.

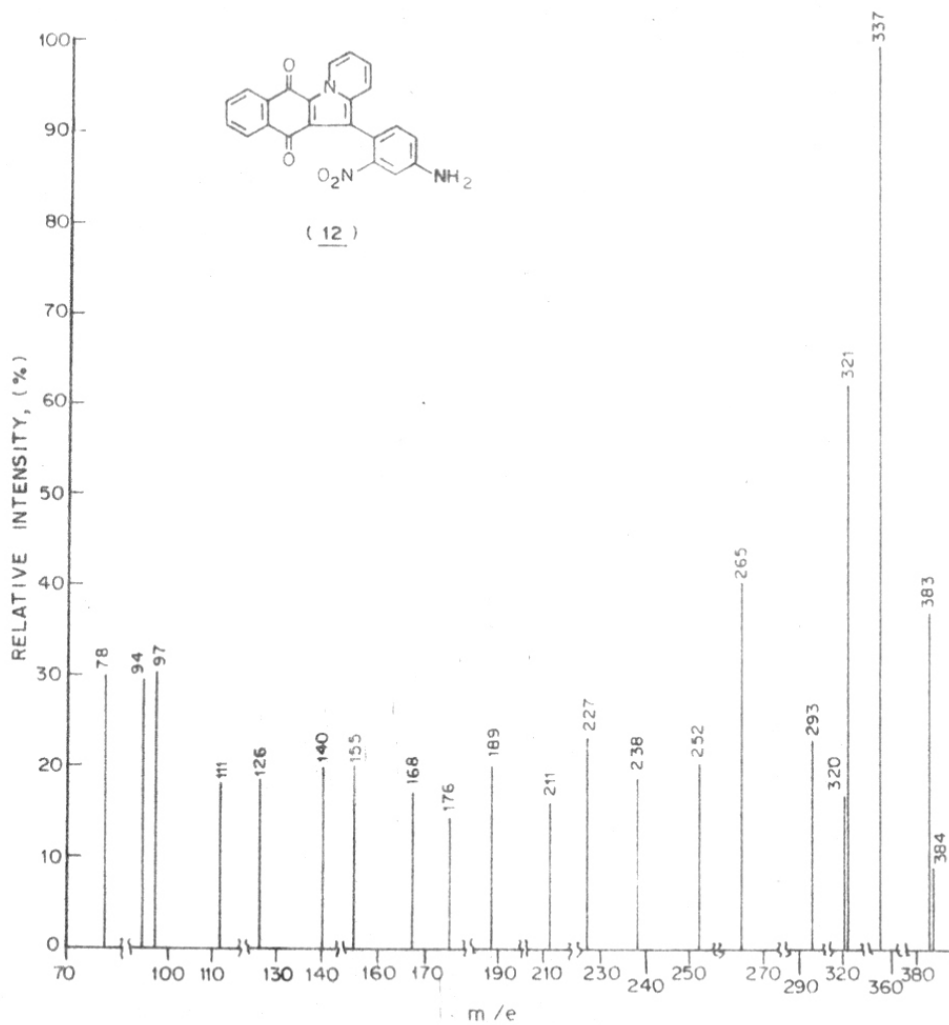


FIG. - 7.

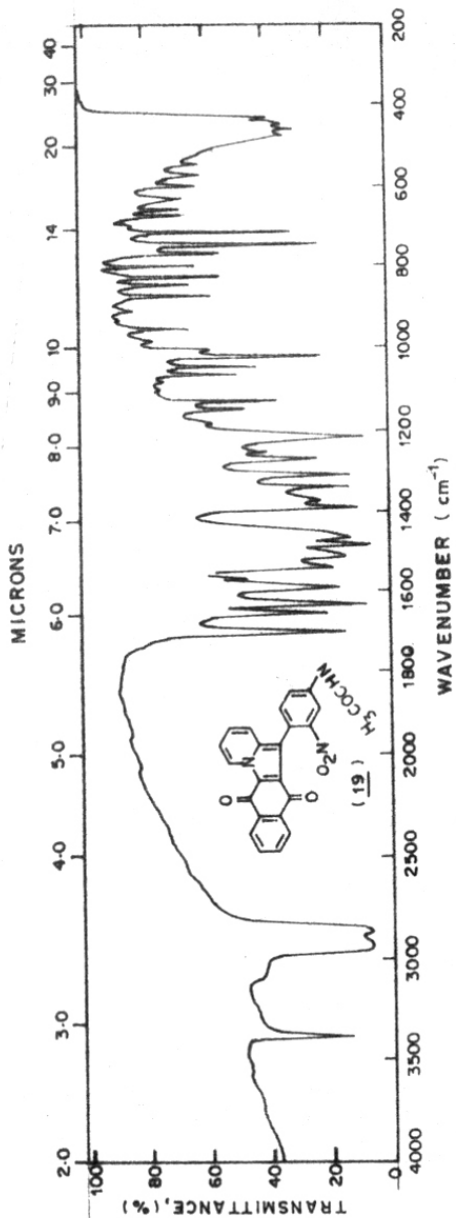


FIG. - 8.

CHAPTER – III

SPECTRAL STUDIES AND DYEING PROPERTIES
OF NAPHTHINDOLIZINEDIONES

REFERENCES

1. Van Allan J. A., Reynolds G. A., Adel R. E.,
J. Org. Chem., 28, 3502 (1963).
2. Geigy, Fr. P., 1,385,278 (1965); C.A., 62, 11950e
(1965).
3. Tilak B. D., Acharya R. V., Venkiteswaran M. R.,
J. Sci. Ind. Res., 14(B), 250-2 (1955).
4. Tilak B. D., Suryanarayan B., Acharya R. V.,
ibid, 14(B), 394 (1955).
5. Tilak B. D., Mathur M. S., ibid, 17(B), 33 (1958).
6. Pratt E. F., Rice R. G., Lukenbaugh R. W.,
J. Am. Chem. Soc., 79, 1212-17 (1957).
7. Saroti M. F., Chem. Rev., 63, 279 (1963).
8. Kulwant Singh, Ph. D. (Tech.) Thesis, University
of Bombay (1973).
9. Wingrove A. S., Caret R., in 'Organic Chemistry',
Harper and Row Publishers, New York, 1122 (1981).
10. Limpriet H., Ber., 18, 1400 (1885).
11. Miller Earnst., J. Prakt. Chem., 111, 273-6 (1925).
12. Abramovitch R. A., J. Chem. Soc., 1413-17 (1957).

INTRODUCTION

A series of naphthindolizinediones (2,3-phthaloyl-pyrrocolines) from 2,3-dichloro-1,4-naphthoquinone (DCNQ) and benzodindolizinediones from chloranil have been prepared in our laboratory.¹ These products were prepared with the view to synthesise a new series of vat dyes. In view of their structural analogy with anthraquinonoid cellulose acetate dyes and also because many of the above dyes were weakly substantive to cellulose as vat dyes, it was considered of interest to study their possible application to cellulose acetate. Among the quinonoid dyes prepared earlier, 12-carbethoxynaphth[2,3-b]indolizine-6,11-dione (also termed as 1-carbethoxy-2,3-phthaloylpyrrocoline) (A) (Chart I), had good substantivity and dyed an attractive golden yellow shade on cellulose acetate. The fastness of the dye was, however, only moderate : light fastness of the order of 2 and sublimation fastness 5. Dye (A) was also evaluated as a disperse dye for cellulose acetate and the relationship between coplanarity and substantivity of quinonoid dyes on secondary cellulose acetate was also established². The coplanar dye (A) and its analogues appear to be of technical interest for dyeing of cellulose acetate since they have good substantivity as well as good build up properties owing to their high saturation values².

Encouraged by these results it was decided to synthesise certain specifically tailored naphthindolizinedione dyes and to examine their dyeing properties to study the interrelation between structure and dyeing properties. The above study showed that coplanarity was essential for affinity of quinonoid dyes such as naphthindolizinediones for synthetic fibers as well as for cotton (as vat dyes)².

In view of the affinity of naphthindolizinedione disperse dyes for cellulose acetate, it was decided to study these compounds as dyes for polyester fabrics. Thus a series of 12-substituted naphthindolizinediones was prepared starting from DCNQ^{3,4}.

PRESENT WORK

As stated earlier a large number of naphthindolizinediones have been synthesised in this laboratory. Naphthindolizinediones are also the subject of a large number of recent patents. Majority of these dyes are reported by Ciba-Geigy. However, the interrelation between chemical structure, spectra and dyeing properties of these dyes with reference to polyester fabrics has not been reported. One of the important objectives of the present work is to synthesise a series of closely related naphthindolizinedione disperse dyes for polyester fabrics and to systematically study the above co-relation. With this end in view a number of dyes which have been reported earlier (mostly in patents) as well as several new dyes were prepared by conventional methods reported earlier as well by synthetic procedures described earlier in the thesis (Chapters IB and II).

The naphthindolizinedione dyes prepared may be classified in three groups:

Group a : Group a comprises of carboxamide derivatives prepared by the condensation of naphthindolizinedione-12-carboxylic acid chloride with a variety of aromatic, aliphatic and heterocyclic amines as given in the general procedure described below. Carboxamide derivatives

prepared for this study are tabulated in Table I. Of the compounds listed in Table I, compounds (2² in all) marked by an asterisk are hitherto unreported. Their physical characteristics are tabulated in Table I.

General method for the synthesis of 12-carboxy-amidonaphth[2',3'-b]indolizine-6,11-diones

(a) Synthesis of 12-carbethoxy naphth[2',3'-b]indolizine-6,11-dione

2,3-Dichloro-1,4-naphthoquinone [22.7 g.; 0.1 mol] and pyridine [30 ml, 0.4 mol] were heated in dry dioxan at 80° for 20 minutes. To this mixture was added ethylchloroacetate [12 ml, 0.1 mol] over a period of 20 minutes. The mixture was refluxed for 2 hours. After cooling the reaction mixture in an ice bath, the solid so obtained was filtered off and thoroughly washed with hot water. The product was dried and crystallised from chloroform to get 12-carbethoxy naphth[2',3'-b]indolizine-6,11-dione in shining orange needles [m.p. 157°. Lit. m.p. 157-8°], [19 g., 60%].

(b) Synthesis of naphthindolizinedione-12-carboxylic acid.

A solution of carboxylic ester (obtained from the above reaction) [19 g.] in 200 ml. of hot absolute alcohol was poured into a cold solution of clean sodium [16. g.] in 200 ml. of absolute alcohol. Upon refluxing the reaction

T A B L E - I

12-CARBOXYAMIDONAPHTHINDOLIZINEDIONES

Compound No.	Solvent of crystallisation	Colour and shape	Melting point in °C
(1)	Chlorobenzene	Red needles	264
(2)	Benzene	Bluish red needles	218
(3)	Xylene	Violet needles	264
* (4)	DMF	Red needles	355
* (5)	DMF	Red needles	310
* (6)	Chlorobenzene	Dark red needles	360
* (7)	DMF	Red needles	307
* (8)	ODCB	Bluish red plates	312
* (9)	Chlorobenzene	Reddish orange plates	319
* (10)	DMF	Reddish orange needles	323
* (11)	Chlorobenzene	Red needles	329
* (12)	Chlorobenzene	Red needles	230
* (13)	DMF	Reddish violet needles	236
(14)	Benzene	Bluish violet needles	248
(15)	Toluene	Bright red needles	275
(16)	Benzene	Scarlet needles	273
* (17)	DMF	Reddish orange needles	341
(18)	Chlorobenzene	Violet needles	331-2
* (19)	Chlorobenzene	Red needles	286

(20)	ODCB	Bluish violet needles	340-1
*(21)	Chlorobenzene	Red needles	344
(22)	Benzene	Light reddish orange needles	230
(23)	DMF	Reddish orange needles	252
(24)	Benzene	Reddish orange elongated plates	279
(25)	Acetone	Red needles	245
*(26)	Ethanol	Yellowish orange needles	249
(27)	Benzene	Red needles	219
(28)	Ethanol	Reddish orange elongated plates	255
(29)	Benzene	Reddish orange plates	219
*(30)	Chlorobenzene	Reddish orange needles	282
*(31)	Chlorobenzene	Red needles	298
*(32)	ODCB	Red needles	317
*(33)	Nitrobenzene	Red plates	342
*(34)	Chloroform	Yellowish orange needles	287
*(35)	DMF	Bluish red needles	348
*(36)	Chlorobenzene	Red needles	291
*(37)	Nitrobenzene	Red plates	287

* These compounds are unreported.

mixture for 10 minutes a red gelatinous mass precipitated. This was filtered off and washed with 100 ml. of absolute alcohol. The resultant red powder was extracted with glacial acetic acid in a soxhlet apparatus for 14 hours. The red solution was allowed to stand for several days whereupon maroon needles of 12-carboxylic acid were obtained [m.p. - 313° . Lit. m. p. 314.5°], [13 g; 75%].

(c) Synthesis of carboxamide derivatives.

The carboxylic acid [1 g] was converted into its acid chloride by treatment with excess of thionyl chloride. The dark red reaction mixture turned orange within 10 minutes. Excess thionyl chloride was distilled off and to the residue appropriate amine and dry dioxan [15 ml] were added. The mixture was further refluxed for 2 hours. After cooling the reaction mixture in an ice bath the solid obtained was filtered. The carboxamides thus obtained were almost pure and were further purified by crystallisation from appropriate solvents.

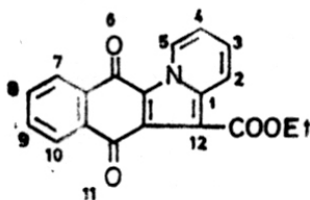
Group b : Group b comprises of dyes derived by the interaction of DCNQ, a heterocyclic base and substituted nitrotoluenes, nitromethane and acetonitrile (Chapters IB and II).

Group c : It is a group of dyes where a heterocyclic base containing a methyl group acts as an active methylene compound.

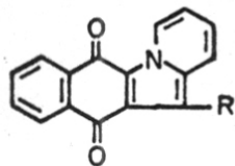
Structures (B), (C) and (D) in Chart I represent the above three groups.

12-(4'-Nitrophenyl)naphthindolizinedione and its derivatives (amino, acetamido, benzamido, etc.) prepared earlier in this laboratory had poor fastness as disperse dyes for polyester fabrics (light fastness 1, sublimation fastness 3-4)⁵. Low fastness to light of these dyes indeed prompted the present work (Chapters IB and II) in which dyes were prepared with substituents such as NO₂, CN,

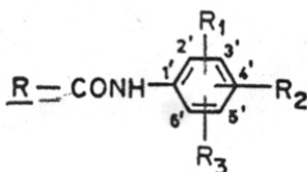
N(CH₂CH₂CN)₂ groups to improve dyeing and fastness properties especially to light. Similarly other workers in this laboratory have also studied the influence of introduction of 12-pyridyl or 12-quinolinyl groups in naphthindolizinediones [e.g. structure (D)]⁶. Several dyes of this type were synthesised and evaluated as dyes for polyester fabric. Their fastness properties were found to be moderate to good on polyester fabric^{6,7}. In order to study the effect of quaternisation on such naphthindolizinediones, they were methylated using methyl iodide as methylating agent.



(A)



(B)



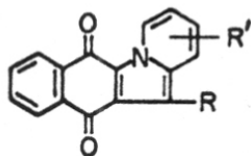
(1), $R_1 = R_2 = R_3 = H$ (TABLE - II)

$R_1, R_2, R_3 = Cl, Br, CN, NO_2, NH_2, CH_3, OCH_3$ etc.

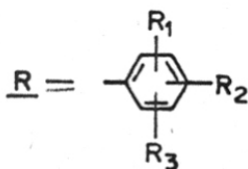
$R = CONHR'$ WHERE $R' =$, , ,

$R = COR''$ WHERE $R'' =$, ,

$-NH-N(CH_3)_2$, , ,



(C)

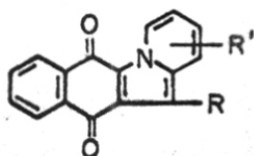


(1), $R_1 = R_2 = R_3 = H$ (TABLE - III)

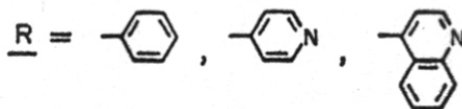
$R_1, R_2, R_3 = NO_2, CN, NH_2, NHCOCH_3, N(CH_2CH_2CN)_2$

$R = H, CN, NO_2, NH_2, NHCOCH_3, N(CH_2CH_2CN)_2$

$R' = 2,3$ BENZO ; $4,5$ BENZO ; 3 - CARBETHOXY ; 3 - CYANO
 3 - $NHCOCH_3$, 3 - AMINO



(D)



$R' = H, CH_3$

VISIBLE SPECTRA OF NAPHTHINDOLIZINEDIONES

Visible spectra of a large number of substituted naphthindolizinediones were recorded in dimethylformamide to make a comparative study of their spectral properties.

Comparative spectral study of naphthindolizinedione-12-carboxyamides

Group a : Effect of substituents on spectral data of naphthindolizinedione-12-carboxyamides was studied by comparison of visible spectra of these compounds with that of 12-substituted anilide (1) [$R=CONHC_6H_5$; Table II]. Compound (1) absorbed in the visible region at 508 nm (DMF) with ϵ -6000. Substitution in the 4'-position of phenyl ring (see structure B, Chart I) by acetamido group [(20); Table II] showed a pronounced bathochromic shift. Substitution by a carboxylic acid and amino group in the 4'-position of the phenyl ring [(18), (35), Table II] showed a considerable bathochromic shift. Methoxy group substitution in 2',3' and 4'-position [(12), (13) and (14); Table II] also showed a considerable bathochromic shift. The carboxyamide 8 (Table II) prepared from 2-methoxy-5-nitroaniline led to a considerable bathochromic shift but the one prepared from *p*-amino-*p*'-methoxydiphenylamine [(21); Table II] showed a hypsochromic shift. Although, substitution of nitro group in the 4'-position of phenyl ring [(6); Table II] led to a bathochromic shift, insertion of second nitro group in 2'-position [(10); Table II]

showed a hypsochromic shift. Halogen substitution in nitro-phenyl or in dinitrophenyl moiety of compounds (6) and (10) respectively also led to a hypsochromic shift as is evident from compounds (7), (9) and (11) [Table II]. It was also observed from the present data that halogen substitution in the phenyl ring showed a hypsochromic effect [(7), (9), (11) and (15) - (17); Table II].

The phenyl ring of 12-substituted anilide (1) was replaced by heterocyclic rings by the interaction of naphth-indolizinedione-12-carboxylic acid chloride with 2-aminopyridine, 3-aminopyridine, 2-aminothiazole and 2-amino-6-methoxy benzothiazole to get (30), (31), (32) and (33) respectively [Table II]. Although compound (30) showed a hypsochromic shift, replacement of the anilido group by heterocyclic amido group did not significantly affect the absorption maxima although the intensity of absorption was lower in these cases. When the phenyl ring^{of}/(1) was replaced by aliphatic substituents like morpholino, diethanolamino and dimethyl hydrazino groups to get compounds (24) - (26), a hypsochromic shift was observed. Hypsochromic shift was more pronounced in the morpholino derivative (24).

Comparative spectral study of 12-
substituted naphthindolizinediones
(Group b)

Comparative study of spectral data of naphthindolizinediones derived from substituted nitrotoluenes was also undertaken. These compounds were compared with 12-phenylnaphthindolizinedione [(1); Table III]. 12-Phenylnaphthindolizinedione (1) [Table III] absorbed in the visible region at λ_{max} 500 nm (DMF) with ϵ 8500. In almost all the compounds, substitution of electron withdrawing groups like cyano or nitro in 2', 4' or 2',4',6'-position of phenyl ring led to a hypsochromic shift [compounds (2) - (9); Table III]. The shift was more pronounced when pyridine moiety was replaced with isoquinoline, quinoline and ethylisonicotinate. The hypsochromic shift after the insertion of two nitro groups in phenyl ring was also observed in case of carboxamide series. Substitution of acetamido and amino group in pyridine moiety in compounds (2) and (4) led to a pronounced bathochromic shift [(10) - (12); Table III]. Partial reduction of the dinitrophenyl moiety also showed a considerable bathochromic shift [(13) and (14); Table III]. However, acetylation of amino group, i.e. acetamido group in phenyl ring led to a hypsochromic shift [(15); Table III]. Biscyanoethyl derivative of (15) showed a bathochromic shift [(16); Table III].

Spectral data of 12-cyano and 12-nitronaphthindolizinediones and their derivatives [(18) - (26); Table III] was compared with that of unsubstituted naphthindolizinedione [(17); Table III]. Compound (17) [Table III] absorbs at 484 nm (DMF) with ϵ - 6300. Except for the compound derived from pyridine, nitromethane and DCNQ [(18); Table III] all the 12-nitro and 12-cyano derivatives showed hypsochromic shift. A pronounced bathochromic shift was observed when compound (18) was reduced to the amino derivative [(24); Table III]. This series of compounds showed an absorption between 460-600 nm.

Comparative spectral study of 12-
substituted naphthindolizinediones
(Group c)

Spectral data of the compounds, where 12-position of naphthindolizinedione was substituted with heterocyclic rings [(2) - (5); Table IV] was compared with that of 12-phenylnaphthindolizinedione [(1); Table IV]. Compound (1) [Table IV] absorbs at 500 nm (DMF) with ϵ - 8500. Except for the compound derived from DCNQ, pyridine and α -picoline [(5); Table IV], all the compounds of this series showed hypsochromic shift. However, quaternisation of compound (2) gave a water soluble quaternary salt which showed bathochromic shift [(6); Table IV].

Figures 1, 2, 3, 4, 5 show the spectra of representative naphthindolizinediones where (λ) in DMF is plotted against $\log \epsilon$. Spectral data is also presented in Tables II, III and IV.

Dyeing behaviour

The dyeing properties of the above dyes were investigated on polyester (polyethyleneterephthalate) fiber [Tables II, III and IV]. Dyeings were carried out as follows :-

Dispersions (1%) of the dyes were prepared by ball milling a mixture of 0.1 g. of the dye, 0.1 g. of Tammol (NNO) and 10 ml of water for 48 hours. The 10% solution thus obtained were used as stock solution for dyeing polyester fabric. Polyester fabric was dyed in 1% shade by high temperature dyeing method. The dye bath was set with 1% dye dispersion, 5% Unisperse P (a heat resistant levelling agent of HICO), 10% ammonium sulphate and 1% formic acid; keeping the material-liquor ratio at 1:50. The polyester fabric was entered at 60° and the temperature raised to 130° in 30 minutes. The pressure was raised to 40 lbs. and dyeing continued for one more hour. After cooling to 90°, temperature was further brought down by water circulation in dyeing machine. The dyeings were taken out and given a 'reduction clear' in a bath containing 2 g./l sodium hydrosulphite, 4 ml/l sodium

hydroxide 30° Be and 1 g/l Unipersol AC (EASF) (a cationic oxyethylation product of a fatty amine acts as a dispersing agent during dyeing and after cleaning synthetic fibers) at 70° for 30 minutes. Finally, it was rinsed and dried at 60°.

The naphthindolizinedione dyes synthesised above gave a wide range of shades from yellow to bluish-violet. Few representative dyes are shown in Shade Card No. I-IX.

Few representative examples of dyeing behaviour of naphthindolizinediones are given below:-

The effect of the substituents attached to amido group in carboxyamido series (Group a) on dyeing behaviour could be clearly established by studying the Shade Cards I-VI.

When unsubstituted phenyl ring was attached to CONH group [(1); Shade Card I] the dyeing was bright red with good build up property. However, when phenyl ring was replaced with heterocyclic units like pyridine and thiazole [(30), (31), (32); Shade Card I] the less substantive dyes were obtained giving more pale shades. The incorporation of benzothiazole unit gave slightly better shade [(33); Shade Card I]. The effect of more bulky naphthyl group [(37); Shade Card II] also led to pale shades with less affinity towards polyester fabric.

The substituted phenyl ring also exhibited some characteristic dyeing behaviour on polyester fabric. If methyl or methoxy groups were present in 2'-position of phenyl ring [(2), (12); Shade Card II] the bright attractive shades were obtained. The presence of these groups in 4'-position of phenyl ring [(3), (14); Shade Card II], however, resulted in less substantive dyes, giving pale shades on the fabric. If more bulky group like NO₂ was introduced in addition to methyl group less substantive dye was obtained [(4),; Shade Card III]. The effect of 2'-bromo-6'-cyano and 2'-bromo-6'-nitro in addition to para nitro group [(9), (11); Shade Card III] also led to poor substantive dyes since the coplanarity of these dyes get affected by the insertion of bulky substituents like cyano and nitro group. The presence of only one nitro group in addition to methyl or methoxy group led to slightly better substantivity [(5), (8); Shade Card IV]. The presence of nitro group alone did not increase the substantivity [(6); Shade Card III], however, nitro group in conjugation with only one methyl, chloro or methoxy group led to improved substantivity [(5), (7), (8); Shade Card IV]. The presence of chloro group alone gave dye with good build up property [(15); Shade Card IV], but with 2',4'-dichloro substitution in phenyl ring there was no exhaustion of dye bath [(17); Shade Card IV]. The auxochromic amino group in 4'-position of phenyl ring did not enhance the build up

properties [(18); Shade Card V]. The acetylation or arylation of amino group [(20), (21); Shade Card V] did not alter the dyeing behaviour and dyeings with poor build up were obtained.

The effect of morpholino group was more striking [(24); Shade Card V]. It led to bright attractive orange shade. This could be attributed to the swelling of polyester fiber due to morpholino unit and hence improved dye affinity. Dimethylamino group attached directly to CONH linkage also led to bright attractive deep orange shade on polyester fabric [(26); Shade Card V]. Incorporation of hydrophilic groups like $(\text{CH}_2\text{CH}_2\text{OH})_2$ and COOH [(25), (35); Shade Card VI] led to poor substantivity due to their strong affinity towards aqueous phase. Incorporation of an additional azo chromophore para to CONH linkage did not lead to considerable improvement in build up properties of the dye [(36); Shade Card VI].

Regarding the other two sets of naphthindolizine-diones (Groups b and c), the dyeings were generally uniform. However, the dyes obtained from nitromethane and acetonitrile (Group b) showed poor light fastness. Group b dyes prepared from pyridine, 4-acetamidopyridine and 4-aminopyridine gave deeper shades as compared to those obtained from isoquinoline, quinoline and ethyl isonicotinate. This was due to high exhaustion in case of former dyes [Shade Cards VII-IX].

ϵ -max represents the tinctorial strength of dyes. For naphthindolizinediones-12-carboxyamides (Group a) ϵ -max value for the dyes prepared from 2-bromo-4-nitroaniline, 2,4-dinitro-6-bromoaniline and *p*-aminobenzene [(9), (11), (36); Table II] was higher as compared to other dyes. However, these dyes showed low affinity for polyester fabric. In general, the tinctorial power of dyes from Group b, i.e. those prepared from substituted nitrotoluenes, nitromethane and acetonitrile (refer Table III) was better than 12-carboxyamido dyes. In Group b, the tinctorial strength of dyes prepared by using quinoline as heterocyclic base was very good. ϵ -max value of biscyanoethylamino derivative of 12-(2'-nitro-4'-aminophenyl)naphthindolizinedione was highest among the dyes studied [(16); Table III]. A general tendency towards a decrease in tinctorial depth of dye was noticed when acetamido group was inserted in naphthindolizinediones [(20); Table II; (10), (11), (15) and (25); Table III].

FASTNESS PROPERTIES

The sublimation and light fastness of above dyes on polyester (polyethyleneterphalate) fabric were determined and are presented in Tables II, III and IV.

Sublimation fastness

A 1.5" x 1.5" of undyed polyester fabric (stain cloth) was stitched on dyed polyester. The fastness was determined by treating the specimen samples at 180° for 3 minutes. Any staining on the undyed pieces, change in shade and depth, were assessed with the following ratings:

1 - poor; 2 - moderate; 3 - fair; 4 - good;
5 - excellent.

The sublimation fastness of these dyes varied from poor to excellent depending on the nature of the substituents.

In carboxamide series (Group a) the simple 12-anilido dye [(1); Table II] and that with CH₃ substituent in 2'-position of phenyl ring [(2); Table II] exhibited excellent fastness. Methoxy substitution in 4'-position of phenyl ring and methoxy and nitro group substitution in 2' and 5'-positions of phenyl ring respectively exhibited excellent sublimation fastness [(14) and (8); Table II]. Substitution of bromo, nitro and cyano group in 2', 4' and 6'-position of phenyl ring [(9); Table II], substitution of one or two chloro groups in 2' or 2', 4'-position of phenyl ring [(15), (16); Table II] and a free amino group substitution in 4'-position of phenyl ring [(18); Table II] showed excellent sublimation fastness. Though

substitution of nitro group in 4'-position of phenyl ring showed good sublimation fastness of Grade 4, insertion of second nitro group in 2'-position reduced it to 3-4 range, [(6) and (10); Table II]. When phenyl ring of carboxyanilide was replaced with aliphatic substituents like morpholino and diethanolamino group the dyes exhibited excellent sublimation fastness [(24), (25); Table II]. Anilino group when replaced with heterocyclic moieties like 3-aminopyridine and 2-aminothiazole, the dyes showed excellent fastness to sublimation [(31), (32); Table II].

Naphthindolizinedione dyes from Group b, where the phenyl ring was di- or tri-substituted with electron withdrawing groups, exhibited sublimation fastness in the range of good to excellent [(2) - (12); Table III]. Aminonitro derivatives obtained by the partial reduction of dinitrophenyl moiety and acetylation of amino group reduced the fastness to sublimation [(13) - (15); Table III]. However, biscyanoethyl derivative of compound (13) improved the sublimation fastness [(16); Table III]. 12-Nitro and 12-cyanonaphthindolizinediones exhibited moderate to good sublimation fastness [(18) - (23); Table III]. Reduction of nitro group and subsequent acetylation of NH_2 group did not make much difference in sublimation fastness but biscyanoethylamino derivative improved the fastness [(24) - (26); Table III].

In Group c all the compounds of this series exhibited sublimation fastness of good to excellent grade [(2) - (5); Table IV].

LIGHT FASTNESS

This was determined by exposing the dyed polyester on Atlas Fadometer equipment for 25 hours according to the prescribed procedure⁸. The changes in shade were assessed as given below:

1-poor; 3 - moderate; 5 - good; 6 - very good;
7 - excellent; 8 - maximum.

The light fastness of these dyes varied from poor to excellent. The relationship between the light fastness and the change of substituents on the phenyl ring attached to CONH linkage (Group a) is not clear. Light fastness in most of the cases was independent of different substituents on phenyl ring. In some cases dyes with 2'-chloro substituent on phenyl ring showed excellent light fastness [(15), Table II] than the dyes with 4'-chloro and 2',4'-dichloro substituents [(16), (17); Table II]. Carboxamide with methoxy group in 4'-position of phenyl ring showed excellent light fastness [(14); Table II] whereas those with methoxy group in 2'- and 3'-position showed moderate light fastness [(12), (13); Table II]. Similarly, carboxamide with methyl group substitution in 4'-position of phenyl ring had light fastness of 5-6 [(3),

Table II] whereas substitution of methyl group in 2'-position, reduced it to 4-5 [(2); Table II]. In some cases the effect of substituent attached to amide linkage is clear and certain empirical relationship can be established. Thus, when the substituent attached to amide is a heterocyclic ring, the light fastness of the dye was better than the corresponding dyes when the substituent was unsubstituted aryl ring, e.g. dye with 3-aminopyridine [(31); Table II] showed good light fastness of grade 5, whereas phenyl and naphthalene substituted dyes had light fastness of the order of 3-4 [(1), (37); Table II]. When phenyl ring of carboxyanilide was replaced with aliphatic moieties, the dyes showed reduced light fastness in the range of 2-4 [(22) - (28); Table II].

The dyes prepared from substituted nitrotoluenes (Group b) consistently showed moderate light fastness. Since the dyes prepared from p-nitrobenzyl chloride show poor light fastness [(27), (28) and (29); Table III] improvement can be claimed due to incorporation of more than one electron withdrawing substituents like nitro and cyano groups. 12-Nitro and 12-cyanonaphthindolizinediones, however, showed poor to moderate light fastness [see Table III]. Introduction of heterocyclic rings in 12-position of naphthindolizinedione (Group c, Table IV) also showed moderate light fastness in the range of 3-4.

A distinctive feature of the work presented here is the fact that naphthindolizinediones presently described had better all round fastness properties than dyes reported earlier by Tilak et al. They also dyed a wide range of shades on polyester fabric than the earlier naphthindolizinediones. However, the yields of nearly all dyes synthesised presently were uniformly very low so as to make this work more of academic interest rather than of commercial value.

SPECTRA (IN DMF) AND DYEING PROPERTIES OF
12-CARBOXYAMIDO NAPHTHINDOLIZINEDIONES


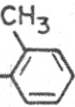
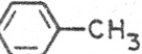
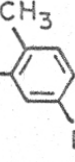
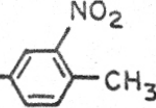
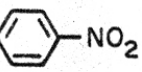
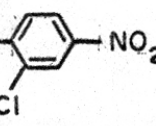
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2	CONH- 	4-5	M-G	5	E	518	6250
3	CONH- 	5-6	G-V.G.	4	G	—	—
4	CONH- 	4-5	M-G	4	G	504	5300
5	CONH- 	4-5	M-G	3-4	F-G	504	5900
6	CONH- 	3-4	M	4	G	514	4600
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TABLE - II. (Continued)

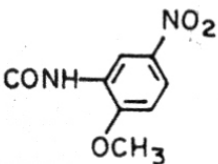
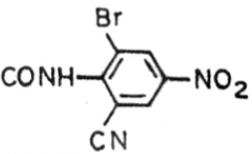
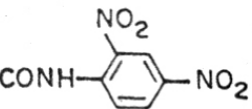
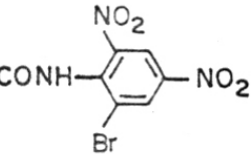
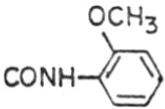
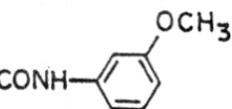
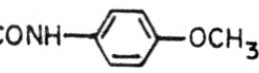
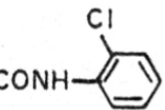
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9		3-4	M	5	E	502	7400
10		3-4	M	3-4	F-G	495	3900
11		3-4	M	3-4	F-G	504	7400
12		3-4	M	4	G	510	6000
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TABLE - II. (Continued)

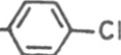
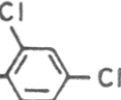
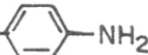

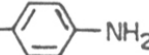
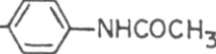

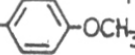


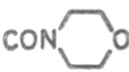
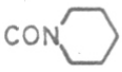



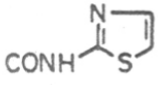
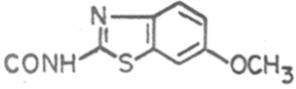
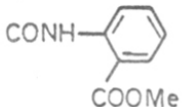
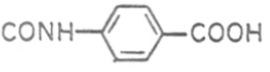
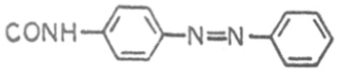
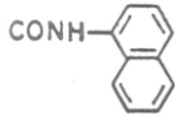
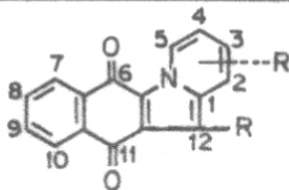
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17	CONH-  -Cl	4	M-G	5	E	496	5400
18	CONH-  -NH ₂	4-5	M-G	5	E	522	2200
19	CONH-  -  -NH ₂	6	V.G.	-	-	-	-
20	CONH-  -NHCOCH ₃	4	M-G	4-5	G-E	532	1900
21	CONH-  -NH-  -OCH ₃	5-6	G.-V.G.	4	G	500	4250
22	CON-  CH ₂ CH ₂ OH	3	M	-	-	-	-
23	CONH-  -OCH ₂ CH ₂ OH	3	M	-	-	-	-

TABLE - II. (Continued)

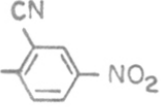
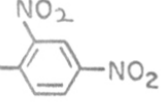
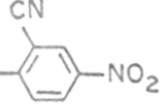
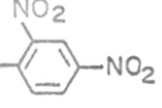
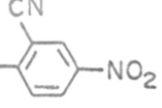
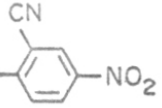
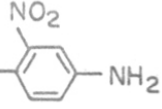
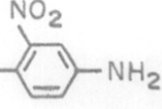
NO.	R	LIGHT FASTNESS		SUBLIMATION FASTNESS		λ MAX	ε
		NO	GRADE	NO	GRADE		
24	CON 	4	M-G	5	E	484	4400
25	CON(CH ₂ CH ₂ OH) ₂	3-4	M-G	5	E	504	4200
26	CONHN(Me) ₂	3-4	M-G	3-4	F-G	495	4400
27	CONHCH ₂ CH ₂ OH	3	M	-	-	-	-
28	CON 	3	M	-	-	-	-
29	CONH- 	2	P	-	-	-	-
30	CONH- 	5	G	4-5	G-E	498	3850
31	CONH- 	5	G	5	E	506	4800

NO	R	LIGHT FASTNESS		SUBLIMATION FASTNESS		λ MAX	ϵ
		NO	GRADE	NO	GRADE		
32		3-4	M-G	5	E	508	4950
33		3	M	3-4	F-G	507	6300
34		3-4	M-G	5	E	488	5900
35		1-2	P	3-4	F-G	522	4250
36		4-5	M-G	4-5	G-E	507	8050
37		3	M	3-4	F-G	517	5250

SPECTRA (IN DMF) AND DYEING PROPERTIES OF
12-SUBSTITUTED NAPHTHINDOLIZINEDIONES DERIVED FROM
SUBSTITUTED NITROTOLUENES, NITROMETHANE
AND ACETONITRILE



NO	R ₁	R ₂	LIGHT FASTNESS		SUBLIMATION FASTNESS		λ MAX	ε
			NO	GRADE	NO	GRADE		
1		H	-	-	-	-	500	8500
2		H	3	M	5	E	414 497	4600 7650
3		H	3-4	M	4-5	G-E	495	7450
4		H	3	M	5	E	500	7450
5		2,3-BENZO	3-4	M	5	E	468	7900
6		2,3-BENZO	4	M	5	E	462	6100

NO	R ₁	R ₂	LIGHT FASTNESS		SUBLIMATION FASTNESS		X MAX	ε
			NO	GRADE	NO	GRADE		
7		2,3-BENZO	3-4	M	5	E	454	5000
8		4,5-BENZO	3-4	M	5	E	472	8500
9		3-CARBETHOXY	2-3	P-M	4-5	G-E	488	6900
10		3-ACETAMIDO	3-4	M	5	E	537	5200
11		3-ACETAMIDO	3-4	M	5	E	528	4500
12		3-AMINO	2-3	P-M	4	G	440 557	3900 8500
13		H	3-4	M	4	G	538	6100
14		2,3-BENZO	3-4	M	4	G	530	4500

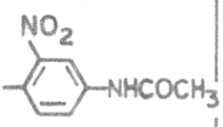
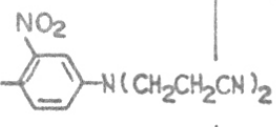
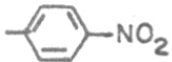
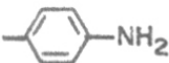

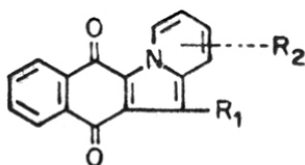
NO	R ₁	R ₂	LIGHT FASTNESS		SUBLIMATION FASTNESS		λ MAX	ε
			NO	GRADE	NO	GRADE		
15		H	3-4	M	4-5	G-E	424 498	3450 5700
16		H	4	M	5	E	516	10,000
17	H	H	—	—	—	—	484	6300
18	NO ₂	H	2	P	4	G	362 489	6400 6800
19	NO ₂	2,3-BENZO	2-3	P-M	3-4	F-G	467	7300
20	NO ₂	4,5-BENZO	2-3	P-M	3-4	F-G	464	9650
21	NO ₂	3-CARBETHOXY	2	P	4	G	476	7500
22	NO ₂	3-CN	2-3	P-M	4-5	G-E	474	6600

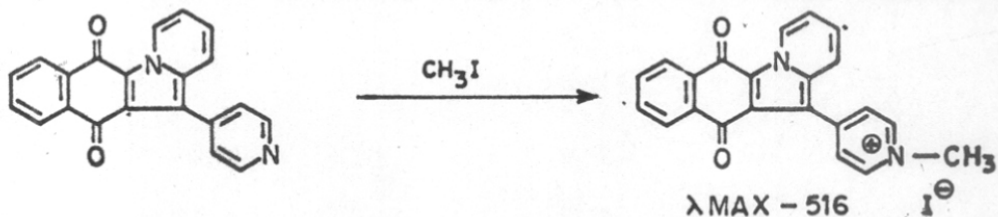
TABLE - III. (Continued)

NO	R ₁	R ₂	LIGHT FASTNESS		SUBLIMATION FASTNESS		λ MAX	ε
			NO	GRADE	NO	GRADE		
23	CN	H	2	P	4	G	352 476	8000 6800
24	NH ₂	H	2-3	P-M	3	F	382 454 601	12896 4150 6050
25	NHCOCH ₃	H	2-3	P-M	3-4	F-G	488	4950
26	N(CH ₂ CH ₂ CN) ₂	H	3	M	4-5	G-E	493	7600
27		H	1	P	3-4	F-G	-	-
28		H	1	P	2-3	M-F	-	-
29		H	1	P	3-4	F-G	-	-

SPECTRA (IN DMF) AND DYEING PROPERTIES OF
12-SUBSTITUTED NAPHTHINDOLIZINEDIONES DERIVED FROM
HETEROCYCLIC BASES HAVING A METHYL GROUP



NO	R ₁	R ₂	LIGHT FASTNESS		SUBLIMATION FASTNESS		λ MAX	ε
			NO	GRADE	NO	GRADE		
1		H	-	-	-	-	500	8500
2		3-CH ₃	5	G	5	E	490	-
3		3-CH ₃	2	P	5	E	490	-
4		H	1-2	P	3	F	482	-
5		3-CH ₃	1-2	P	5	E	506	-



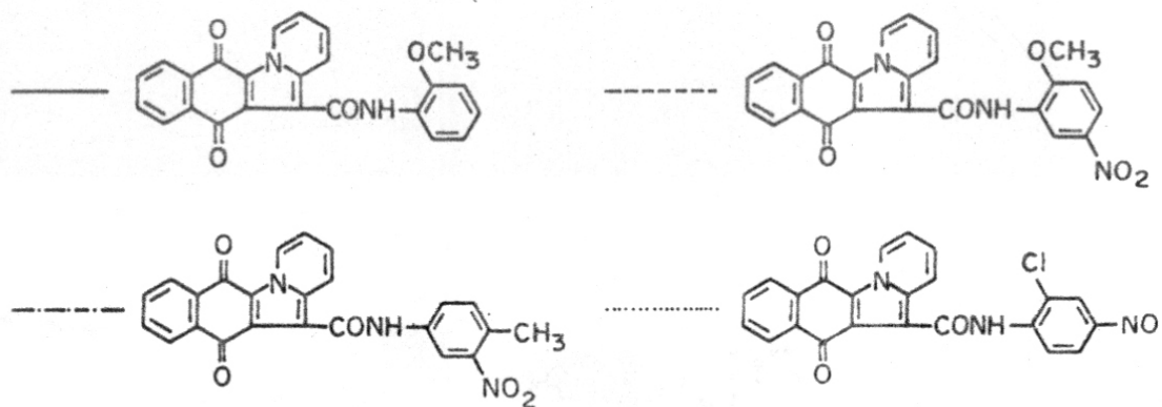
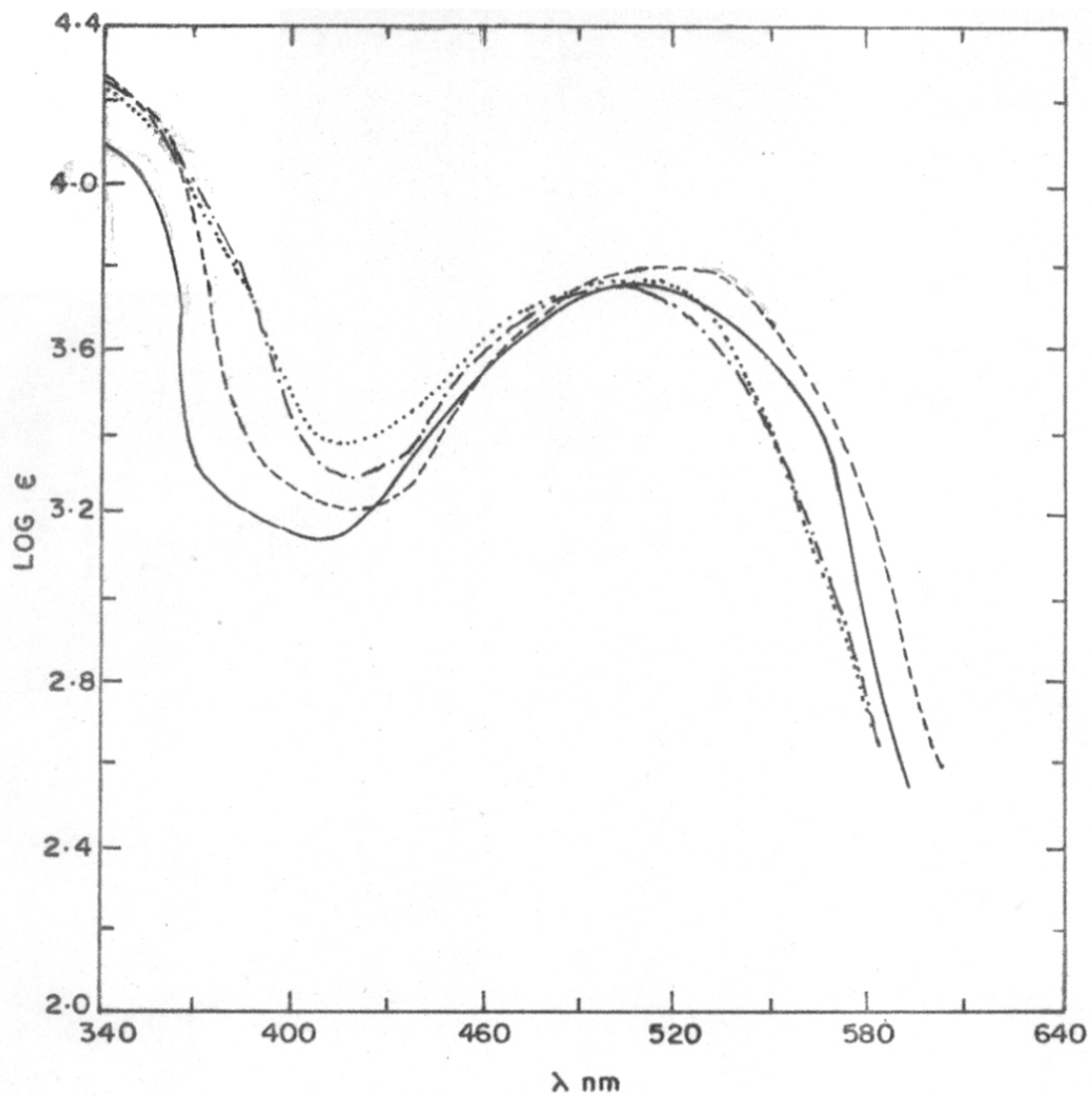


FIG. - 1.

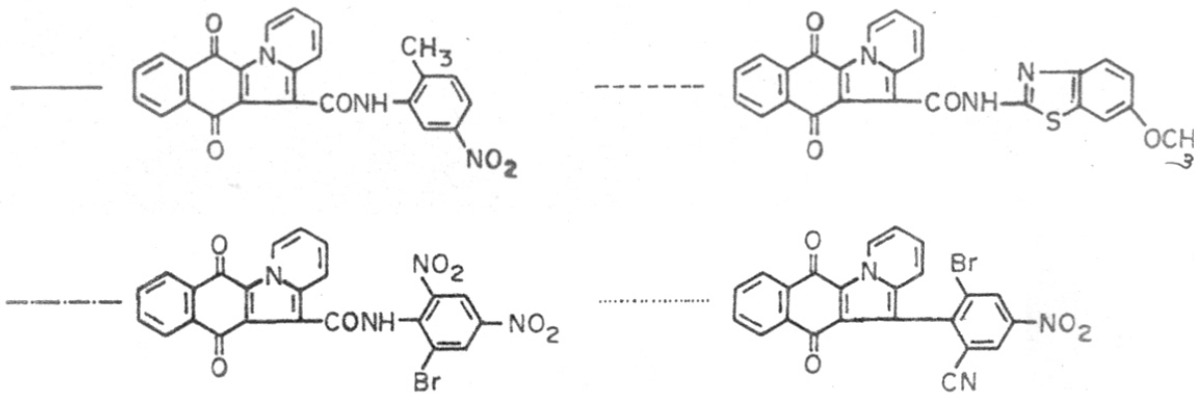
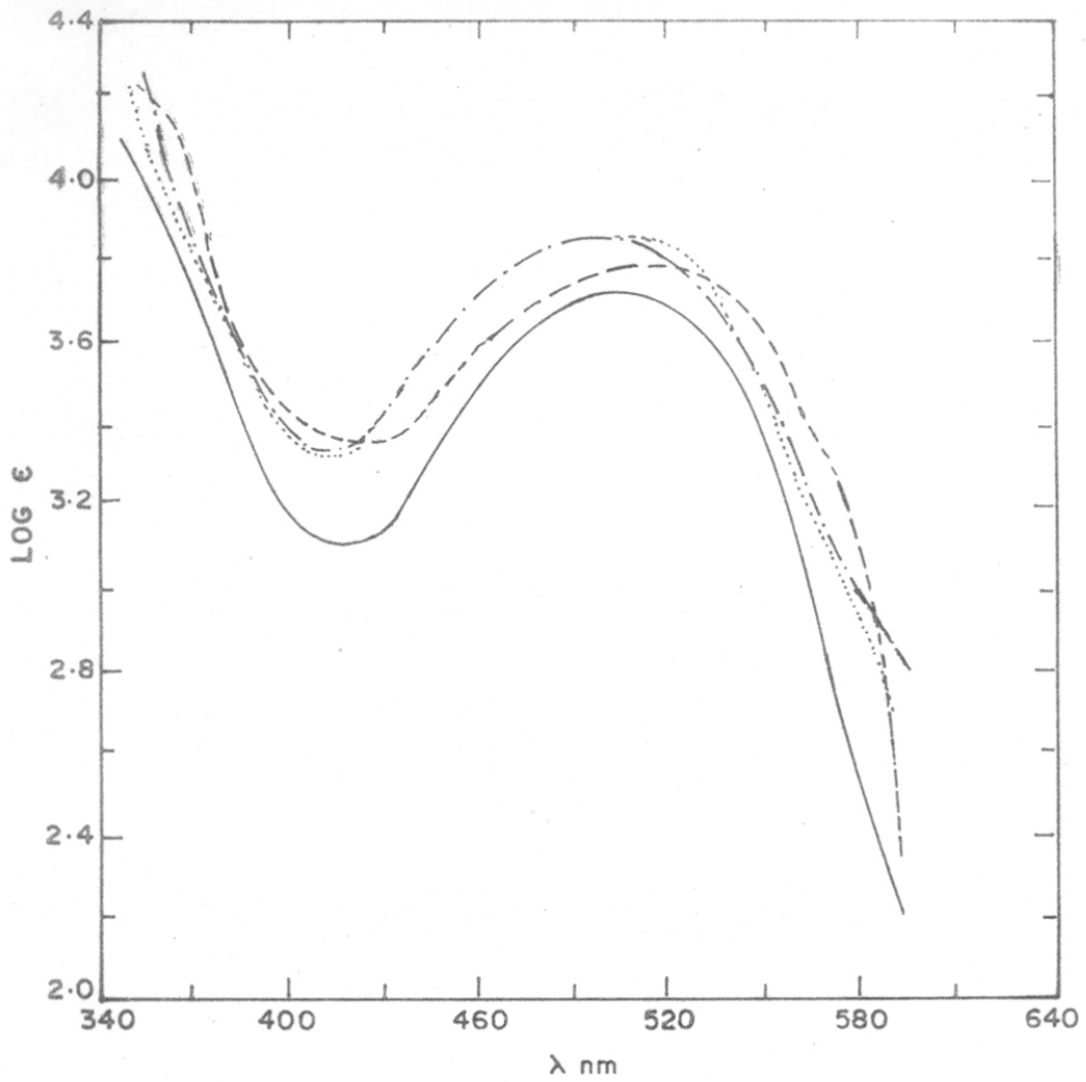


FIG. - 2.

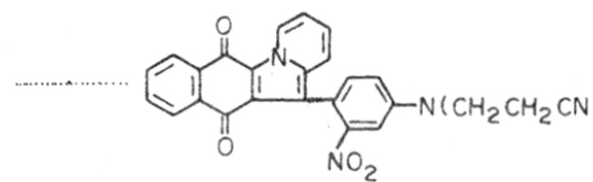
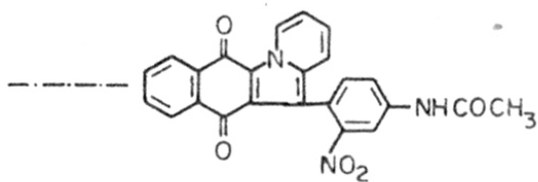
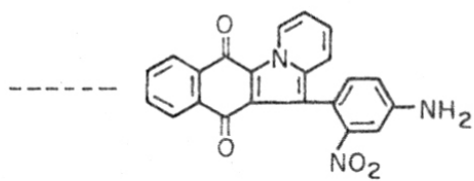
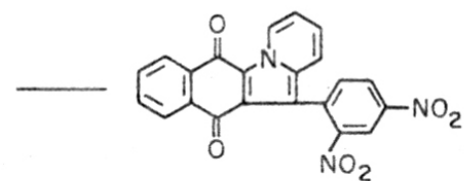
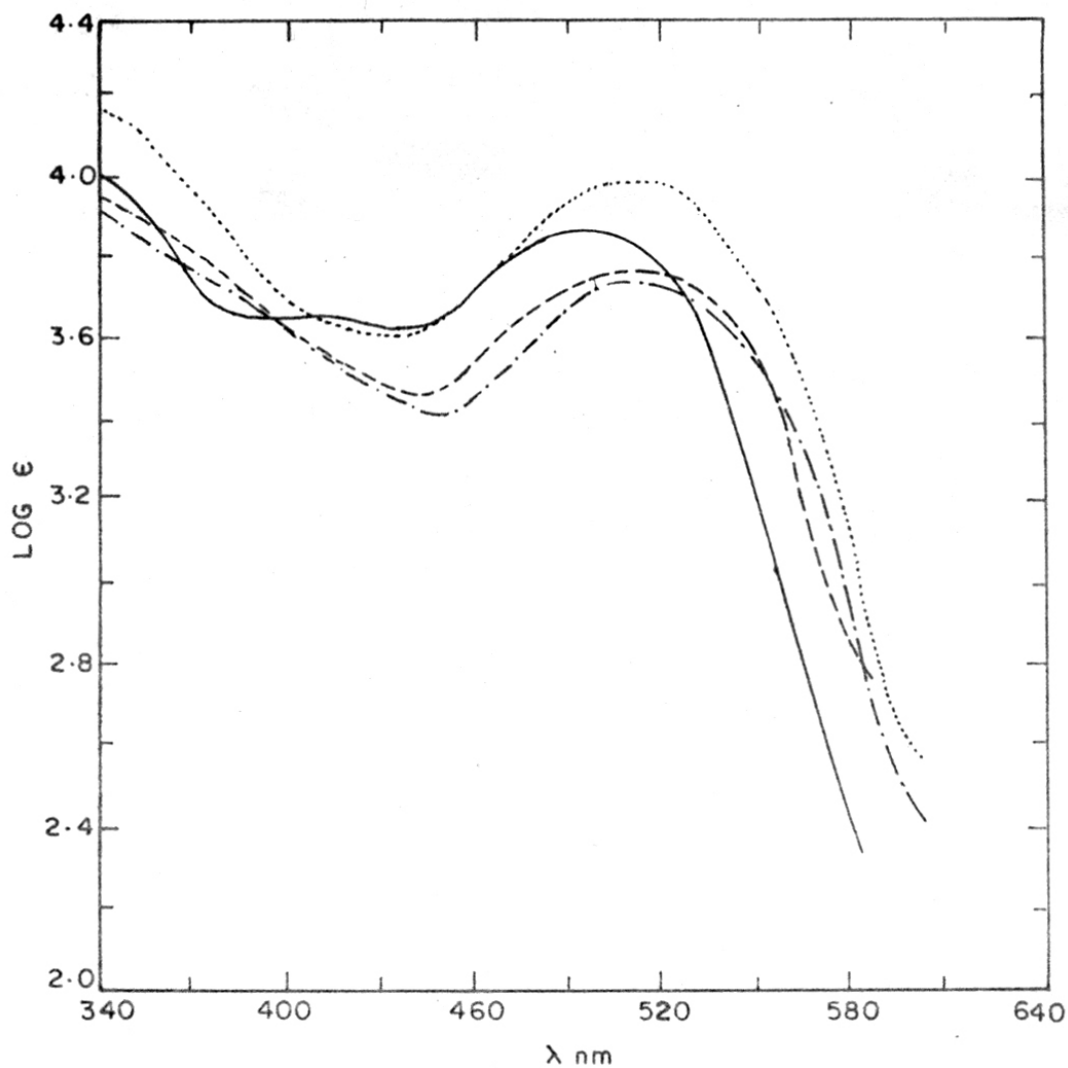


FIG. - 3 .

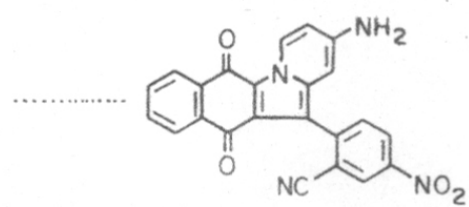
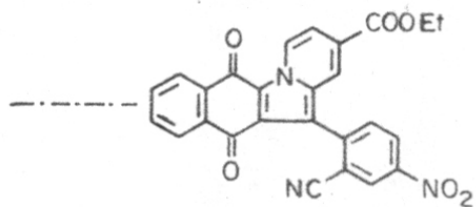
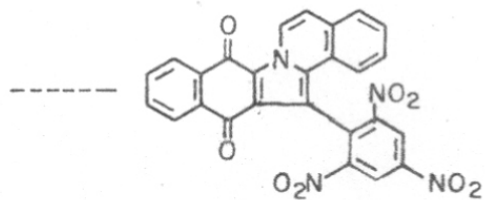
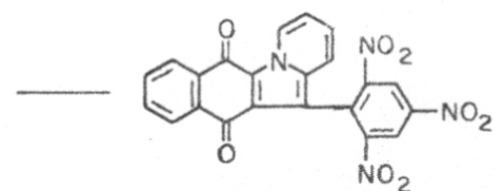
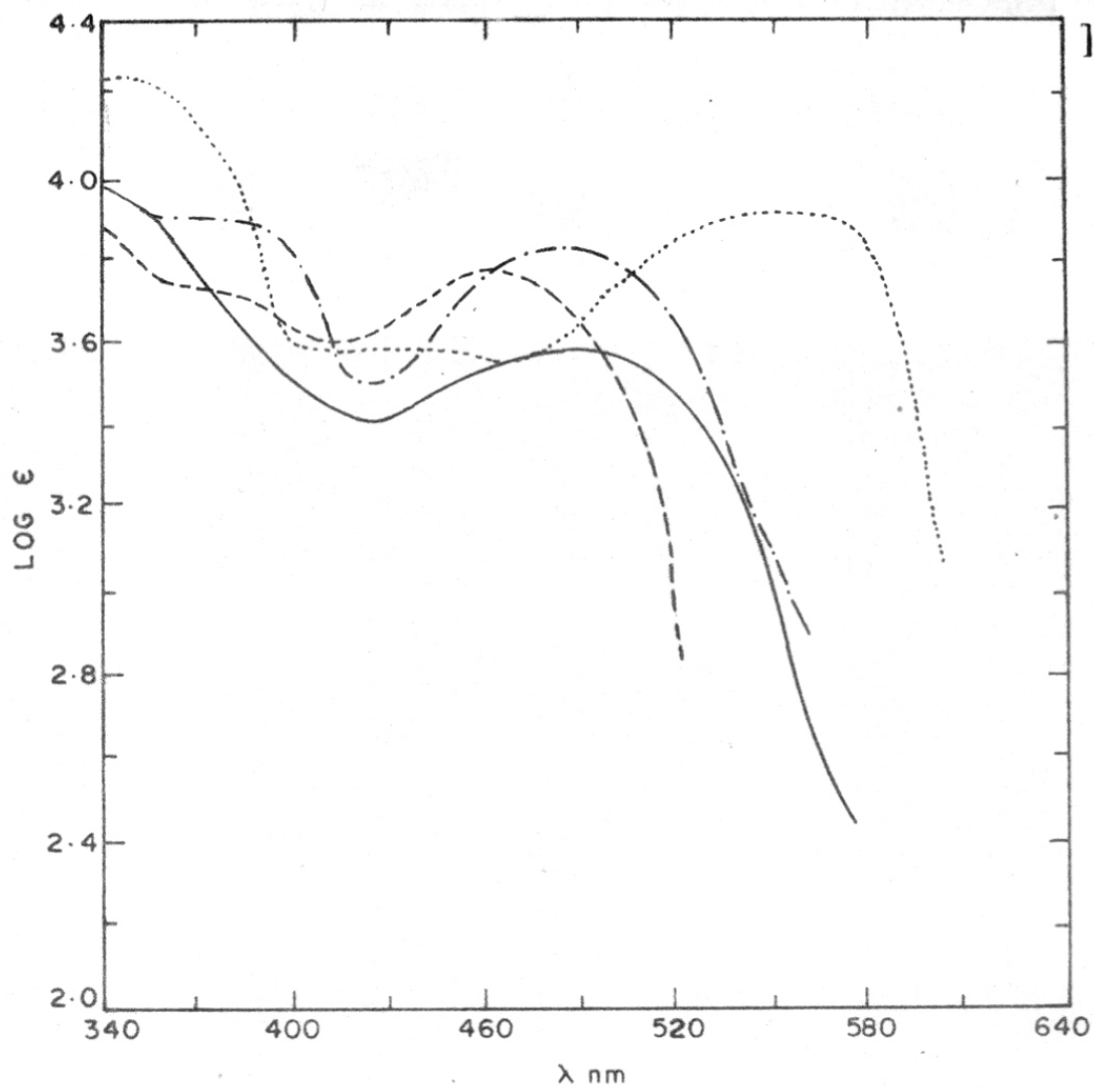


FIG. -4 .

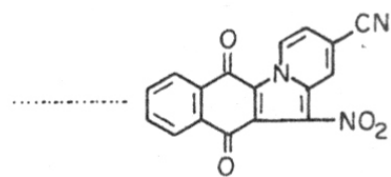
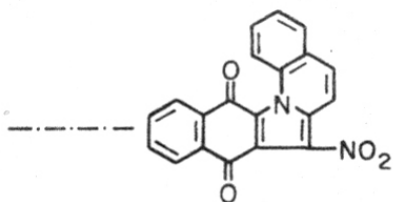
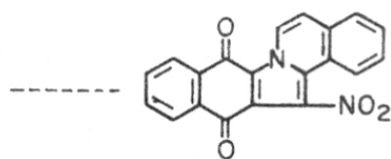
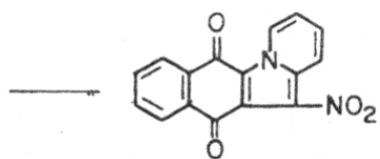
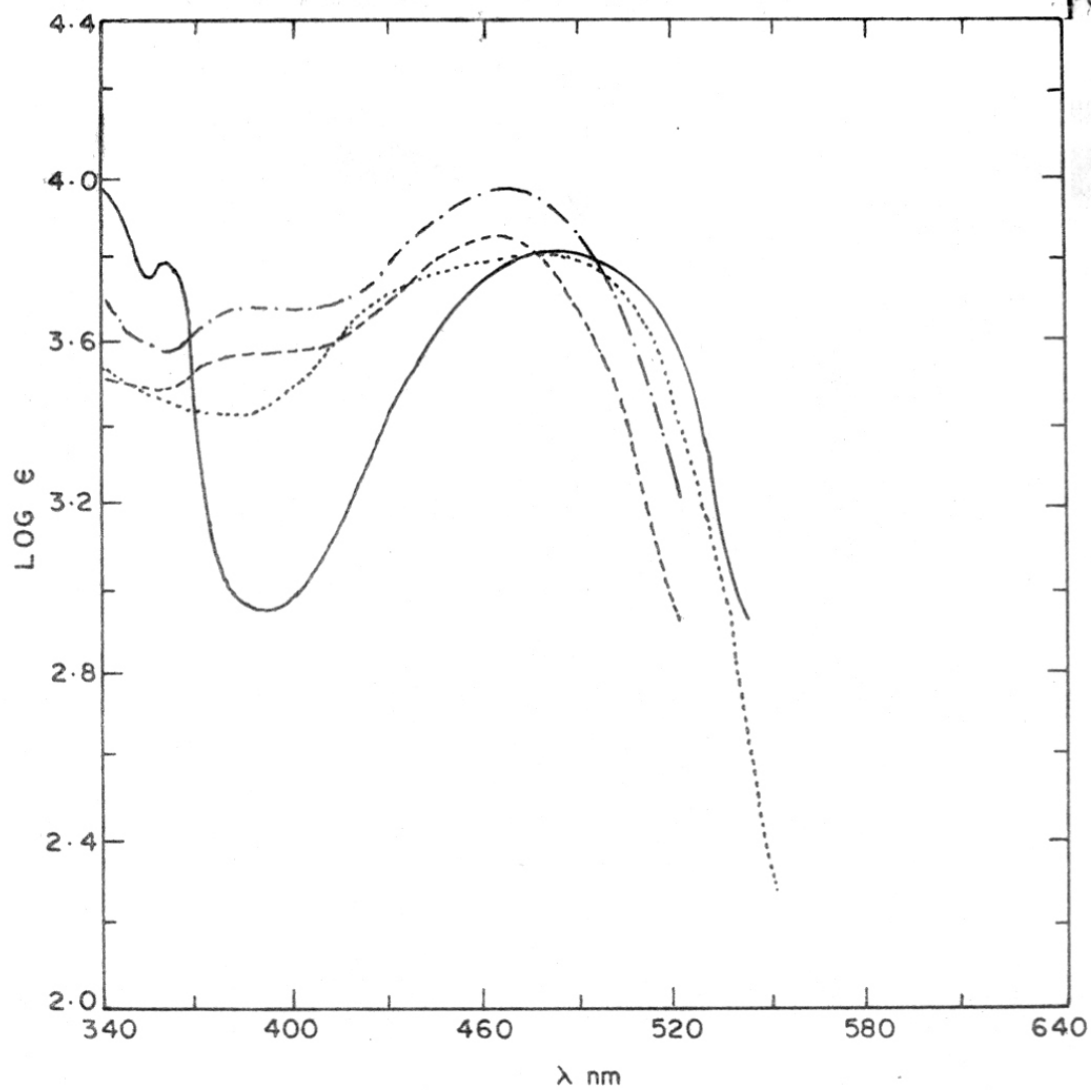
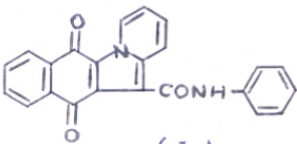

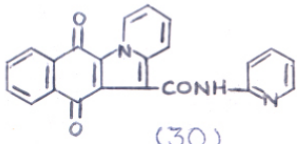

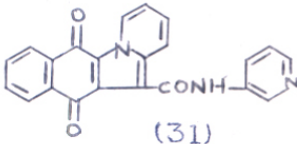

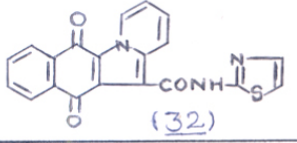

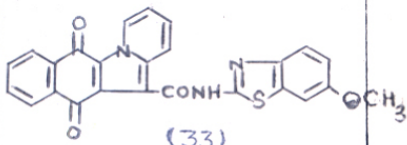



FIG. - 5 .

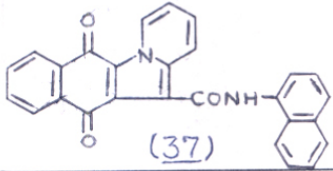

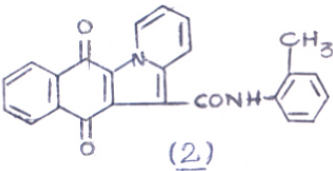

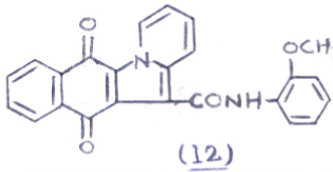

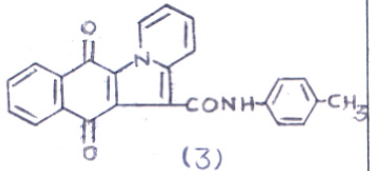

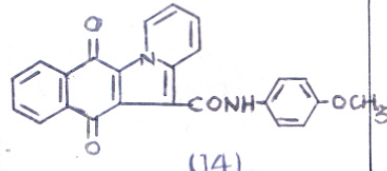

SHADE CARD No. I
LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
 (1)		4	5
 (30)		5	4-5
 (31)		5	5
 (32)		3-4	5
 (33)		3	3-4

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate
 5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum .
 Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;
 4 : Good ; 5 : Excellent .

SHADE CARD No. II

LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
 (37)		3	3-4
 (2)		4-5	5
 (12)		3-4	4
 (3)		5-6	4
 (14)		5-6	5

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate

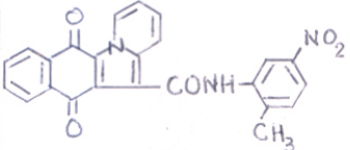

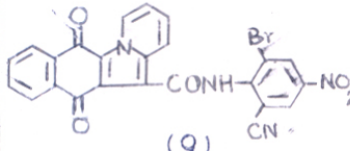

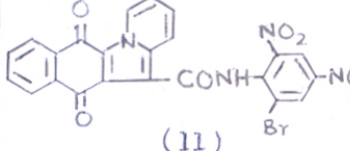

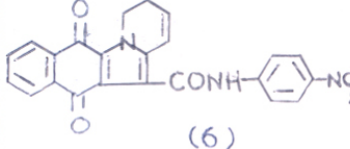

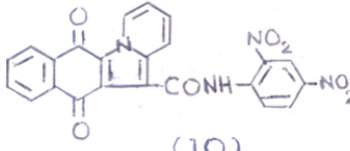

5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum

Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;

4 : Good ; 5 : Excellent

SHADE CARD No. III

LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

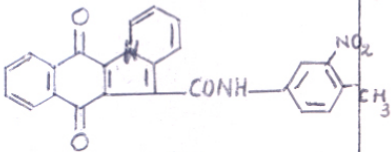

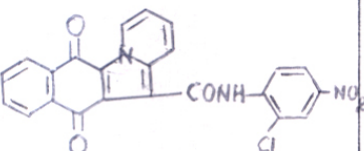

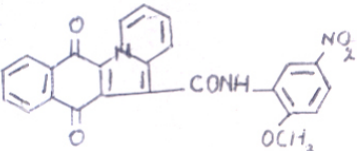

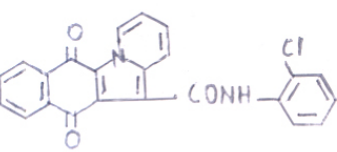

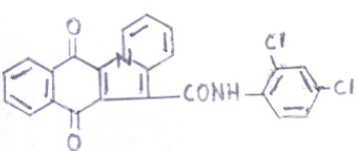

STRUCTURE	SHADE (1%)	XENO	THERMO
 <p style="text-align: center;">(4)</p>		4-5	4
 <p style="text-align: center;">(9)</p>		3-4	5
 <p style="text-align: center;">(11)</p>		3-4	3-4
 <p style="text-align: center;">(6)</p>		3-4	4
 <p style="text-align: center;">(10)</p>		3-4	3-4

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate
 5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum

Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;
 4 : Good ; 5 : Excellent

SHADE CARD No. IV

LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
 <p style="text-align: center;">(5)</p>		4-5	3-4
 <p style="text-align: center;">(7)</p>		3-4	3-4
 <p style="text-align: center;">(8)</p>		5-6	5
 <p style="text-align: center;">(15)</p>		7-8	4-5
 <p style="text-align: center;">(17)</p>		4	5

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate

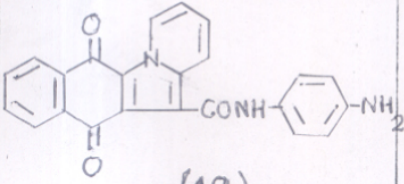

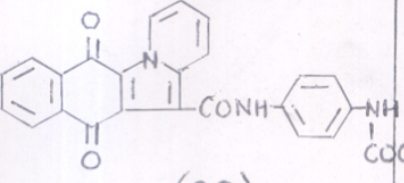

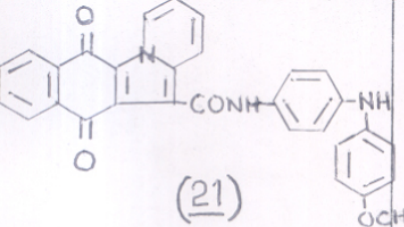

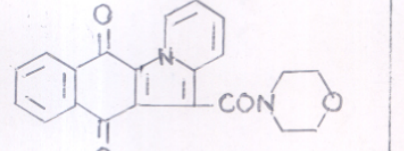

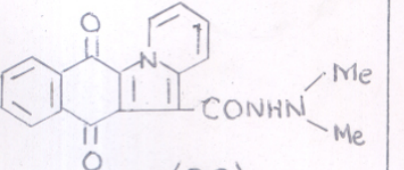

5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum.

Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;

4 : Good ; 5 : Excellent

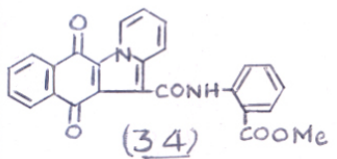

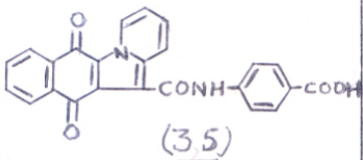

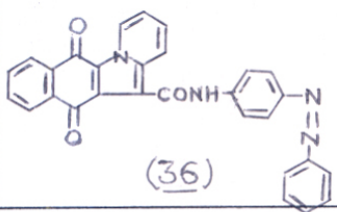

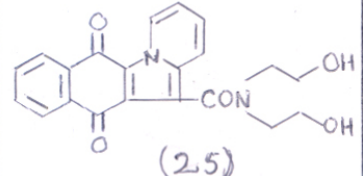


SHADE CARD No. V

LIGHT AND SUBLIMATION FASTNESS OF
 NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
 <p style="text-align: center;">(18)</p>		4-5	5
 <p style="text-align: center;">(20)</p>		4	4-5
 <p style="text-align: center;">(21)</p>		5-6	4
 <p style="text-align: center;">(24)</p>		4	5
 <p style="text-align: center;">(26)</p>		3-4	3-4

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate
 5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum
 Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;
 4 : Good ; 5 : Excellent

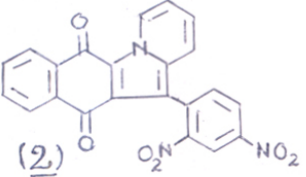

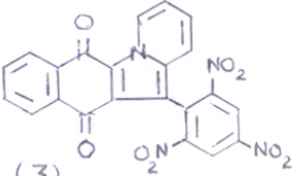

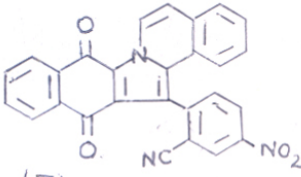

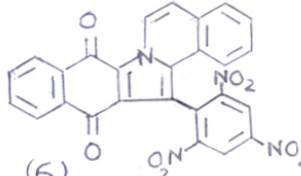

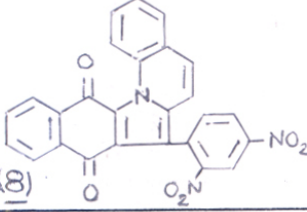

LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
 <p>(34)</p>		3-4	5
 <p>(35)</p>		1-2	3-4
 <p>(36)</p>		4-5	4-5
 <p>(25)</p>		3-4	5
			

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate
 5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum .

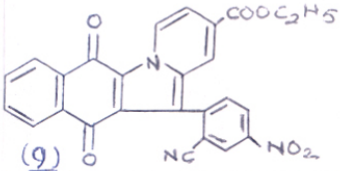

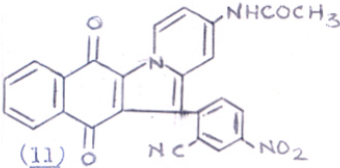

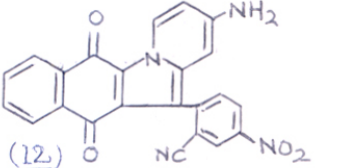

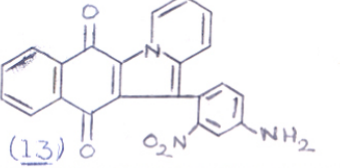

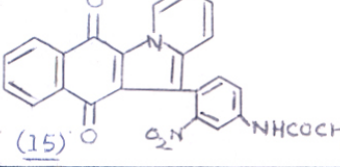

Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;
 4 : Good ; 5 : Excellent .

LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
 <p>(2)</p>		3	5
 <p>(3)</p>		3-4	4-5
 <p>(7)</p>		3-4	5
 <p>(6)</p>		4	5
 <p>(8)</p>		3-4	5

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate
 5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum
 • Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;
 4 : Good ; 5 : Excellent .

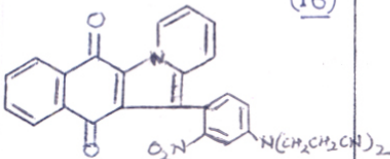

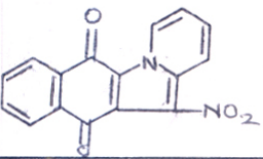

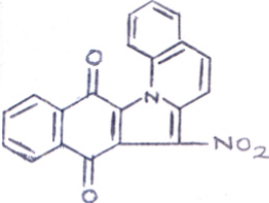

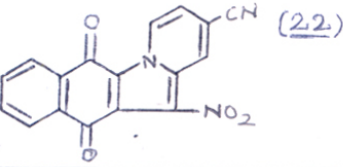

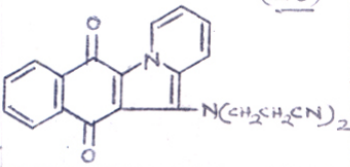

LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
 <p>(9)</p>		2-3	4-5
 <p>(11)</p>		3-4	5
 <p>(12)</p>		2-3	4
 <p>(13)</p>		3-4	4
 <p>(15)</p>		3-4	4-5

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate
 5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum.
 Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;
 4 : Good ; 5 : Excellent

SHADE CARD No. IX

LIGHT AND SUBLIMATION FASTNESS OF
NAPHTHINDOLIZINEDIONE DISPERSE DYES
 (1% SHADE ON POLYESTER)

STRUCTURE	SHADE (1%)	XENO	THERMO
<p style="text-align: right;">(16)</p> 		4	5
<p style="text-align: right;">(18)</p> 		2	4
<p style="text-align: right;">(20)</p> 		2-3	3-4
<p style="text-align: right;">(22)</p> 		2-3	4-5
<p style="text-align: right;">(26)</p> 		3	4-5

Grading scale : Light fastness (Xeno) : 1 : Poor ; 3 : Moderate
 5 : Good ; 6 : Very good ; 7 : Excellent ; 8 : Maximum .
 Sublimation fastness (Thermo) : 1 : Poor ; 2 : Moderate ; 3 : Fair ;
 4 : Good ; 5 : Excellent .

REFERENCES

1. Tilak B.D., Venkiteswaran M.R., J. Sci. Ind. Res., 15 (B), 561 (1956).
2. Tilak B. D., Daruwalla E. H., Rao S.S., J. Soc. Dye. Col., 76, 418 (1960).
3. Tilak B.D., 'The Chemistry of Synthetic Dyes', Vol.V Ed. by K. Venkatraman, Academic Press, New York (1972).
4. Tilak B.D., 'Chemistry of Natural and Synthetic Colouring Matters', T. S. Gore, p. 537 (1962).
5. Kulwant Singh, Ph. D.(Tech) Thesis, University of Bombay (1973).
6. Kolhe, P. Y., Ph. D. Tech. Thesis, University of Bombay (1980).
7. Tilak B.D., Ayyangar, N.R., Lujade A.G., Kolhe P.Y., Ind. J. Chem., 24 (1980).
8. Procedure Followed by Indian Dyestuff Industries Ltd., Kalyan, Colour Index, Vol. 4 (2nd Edn.).

SUMMARY

The thesis is presented in the following Chapters.

CHAPTER - IA

Structural features of disperse
dyes and their dyeing properties.

Important developments in disperse dyes have been reviewed. Dyeing properties of these dyes on polyester, in relation to their structural features is discussed. A detailed presentation of constitutional features includes (a) limitation of molecular weight, (b) coplanarity of the dye, (c) a balance of hydrophilic-hydrophobic nature vis-a-vis hydrophilic-hydrophobic character of the fiber substrate and (d) adsorption forces. Lastly, the influence of structural modifications of dyes on fastness to light, sublimation, gas fading and washing is discussed.

CHAPTER - IB

Synthesis of phthaloylpyrrocolines or naphth-
indolizinediones from substituted nitrotoluenes.

The syntheses of dyes containing naphthindolizinedione moiety are discussed.

Despite the fact that naphthindolizinediones are brilliant dyes they do not appear to have been included in commercial range of dyes and pigments. Poor lightfastness is a major drawback. The present work was undertaken with

a view to synthesise new naphthindolizinedione dyes of improved lightfastness by insertion of electron withdrawing groups (i.e. NO_2 and CN groups). The dyes were synthesised by interaction of 2,3-dichloro-1,4-naphthoquinone (DCNQ), heterocyclic compounds such as pyridine and its derivatives and compounds containing a reactive methyl group. The methyl group was activated by the presence of electron withdrawing groups located in o and p positions in the aromatic ring.

The mechanism of formation of the above dyes is discussed. This includes dyes derived from DCNQ and substituted nitrotoluenes (e.g. 2,4-dinitrotoluene; 2,4,6-trinitrotoluene and 2-cyano-4-nitrotoluene). Heterocyclic bases which were reacted were pyridine, isoquinoline, quinoline, ethyl isonicotinate, 4-acetamidopyridine and 4-aminopyridine.

Three alternate routes for the synthesis of above naphthindolizinedione dyes were employed and the reaction mechanisms involved are discussed.

CHAPTER - II

Synthesis of naphthindolizinediones from nitromethane.

A one step synthesis of 12-nitronaphthindolizinedione is presented in which nitromethane is used as an active methylene compound. Temperature control, solvent

choice and reaction period critically affect the course of the reaction and yield of the desired nitronaphth-indolizinedione. The above reaction along with related earlier work and the mechanisms involved are discussed. Reaction with acetonitrile under various conditions is also presented.

Some of the above nitro compounds were reduced to the respective amines. Dinitrophenylnaphthindolizinedione on reduction with sodium sulphide gave aminonitrophenylnaphthindolizinedione. The amino compounds were further reacted with (a) acrylonitrile, (b) acetic anhydride and (c) benzoyl chloride. The dyes thus formed when dyed on polyester gave a variety of shades ranging from yellow to bluish violet. The dyeings showed good fastness to light, sublimation and washing.

CHAPTER - III

Spectral studies and dyeing behaviour of naphthindolizinediones.

A large number of phthaloylpyrrocoline (naphth-indolizinedione) disperse dyes have been synthesised in this laboratory by the reaction of 2,3-dichloro-1,4-naphthoquinone with compounds containing a reactive methyl group in the presence of heterocyclic bases. However, the

absorption spectra in relation to tinctorial properties of these dyes on polyester have not been studied earlier. The present chapter describes this study. These dyes have been evaluated with reference to their light and sublimation fastness. The chapter also outlines the effect of substituents on the colour and depth of shades obtained on polyester.

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

It is with deep sense of gratitude that I wish to thank Professor B. D. Tilak, for assigning me this research problem and offering inspiring advice and guidance throughout the course of this investigation.

I profusely thank Dr. N. R. Ayyangar for lending me a helping hand during this work. Grateful thanks are also due to Dr. A. G. Lugade for valuable suggestions and discussions.

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Words fail me in expressing my gratitude towards Mr. N. R. Warerkar for his invaluable help during my stay in Poona.

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M. N. Rajadhyaksha