SYNTHETIC DYES

10.1. INTRODUCTION

In our day-to-day life, we come across many substances which have specific colours. In this unit, we shall discuss what is colour ? How is it related to the constitution of the molecules ? What type of coloured substances called **dyes** (natural or synthetic) are currently being used to colour various articles of our daily use ?

10.2. COLOUR AND CONSTITUTION

3.2.1. Colour

When white light (400–750 nm) falls on a substance, three processes may occur :

(*i*) *If the light is totally reflected, the substance appears* **white.**

(*ii*) *If the light is totally absorbed the substance appears* **black.**

(*iii*) *If a certain portion of the light is absorbed and the rest reflected, the substance has the colour of the* **reflected light.**

If only a single band is absorbed, the substance has the *complementary colour* of the absorbed band.

Wavelength (nm)	Colour absorbed	Colour reflected (Complementary colour)
400–435	Violet	Yellow-green
435–480	Blue	Yellow
480–490	Green-blue	Orange
490–500	Blue-green	Orange
500–560	Green	Purple
560–580	Yellow-green	Violet
580–595	Yellow	Blue
595–605	Orange	Green-blue
605–750	Red	Blue-green

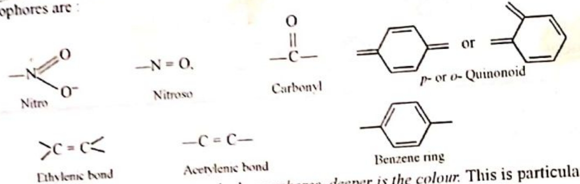
If a substance absorbs all visible light, except one band which it reflects, the substance will have the colour of the reflected band. For example, it is evident from the above table that if a substance absorbs *blue colour*, it will appear *yellow* which is the complementary colour of blue. *In fact, no substance absorbs a single band and hence no dye has a pure shade.* For example, malachite green predominantly reflects green light but also to small extent, it also reflects red, blue and violet light.

It may, however, be noted that substances which appear to be colourless also have absorption spectra. In such cases, *absorption takes place in the infra-red* or *ultra-violet regions but not in the visible region of the electromagnetic spectrum.*

10.2.2. RELATION BETWEEN COLOUR AND CONSTITUTION

Many theories have been put forward from time to time to correlate colour with the molecular structure. e of these are described below

1. Witt's theory. In 1876, it was observed by **Otto Witt** *a German Chemist*, that the intrinsic colour ny compound is due to the presence of certain groups containing multiple bonds. *These groups which art colour to a particular compound are called* **chromophores.** (Greek : *Chroma* = Colour, *phoros* = ring) and the *compound containing the chromophoric group is called the* **chromogen.** Some important omophores are :



Further, greater the number of such chromophores, deeper is the colour. This is particularly marked when the chromophores are in conjugation with one another. For example,

(*i*) As the number of conjugated double bonds increases, the colour of diphenyls, $C_6H_5(CH = CH)_nC_6H_5$ deepens :

$C_6H_5CH = CHC_6H_5$ Colourless

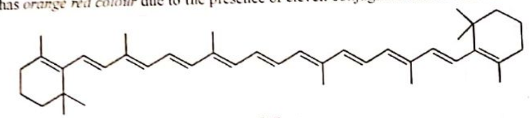
$C_6H_5(CH = CH)_2C_6H_5$ Colourless

$C_6H_5(CH = CH)_3C_6H_5$ Pale yellow

$C_6H_5(CH = CH)_4C_6H_5$ Yellow

$C_6H_5(CH = CH)_5C_6H_5$ Orange

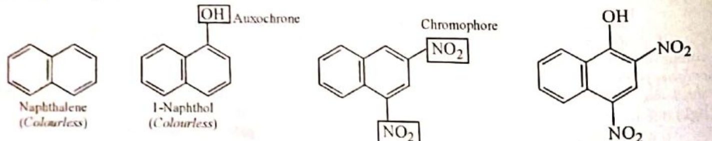
(*ii*) Ethylene, 1, 3-butadiene and 1, 3, 5-hexatriene are colourless, but β-carotene (the pigment present in carrots) has *orange red colour* due to the presence of eleven conjugated double bonds.



β-Carotene

Auxochromes. *Witt* also observed that there are certain *groups which themselves are not chromophores but deepen the colour when introduced into a coloured molecule. Such groups are called auxochromes.* For example, OH, NH_2, NHR, NR_2, X (Cl, Br or I), CO_2H. Even alkyl groups exert weak auxochrome effect.

Let us now examine the effect of auxochromes on the intensity of colour. Both naphthalene and naphthol are colourless. 1, 3–dinitronaphthalene is pale yellow but 2, 4-dinitro-1-naphthol (the dye *Martius yellow*) is orange red.



Naphthalene (*Colourless*)

1-Naphthol (*Colourless*)

1, 3-Dinitronaphthalene (*Pale yellow*)

2,4-Dinitro-1-naphthol (*Martius yellow, orange red dye*)

Thus, the presence of auxochrome, *i.e.* OH group has deepended the colour of 1, 3-dinitronaphthalene chromophore from pale yellow to orange red in *Martius yellow*.

Two other terms which are also commonly used in connection with dyes are **bathochromic and hypsochromic groups.** *Whereas bathochromic groups bring about the deepening, hypsochromic groups bring about the lighening of colour.* In dye industry, deepening of colour means colour changes from yellow → orange → red → purple → blue → green → black. This is exactly the order of the complementary colour of the colour absorbed (Table 3.1). Thus, when we say, that the colour of one compound is deeper than the other, it simply means, that the wavelength of maximum absorption of the former is longer than that of the latter. Since visible colour is the complementary colour of the absorbed band, *bathochromic groups cause red shift while hypsochromic groups cause blue shift* etc.

2. Modern theories or Electronic theory of colour. Two electronic theories have been proposed to explain the origin of colour. These are *Valence Bond (V.B.) Theory and Molecular Orbital (M.O.) Theory.* The most important difference between V.B. and M.O. theories is that in the *V.B. theory, electrons are dealt with in pairs but in M.O. theory they can be dealt with singly.*

(*i*) **Valence bond theory.** According to V.B. theory, the electron pairs of a molecule in the ground state are in a state of oscillation and when placed in the path of a beam of light, they absorb a photon of appropriate energy and get excited. The wavelength of photon of light absorbed depends upon the energy difference between the ground and the excited state. *The smaller is this difference, longer is the wavelength of light absorbed.*

To illustrate V.B. theory of colour, let us first consider a molecule of ethylene which may be regarded as resonance hybrid of the following two structures (I and II)

$$\underset{\text{I}}{CH_2 = CH_2} \longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2—CH_2^-}$$

To a first approximation, ground state is represented predominantly by structure (I) while excited state is represented by structure (II). The energy difference between these two states is very large and hence a photon of short wavelength is absorbed.

In general, it has been shown that

(*i*) *Resonance among charged structures lowers the energy of both the ground as well as the excited states.*

(*ii*) *Charged structures, however, stabilize the excited state more than they do the ground state.*

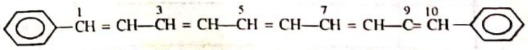
(*iii*) *Larger the number of electrons involved in resonance, smaller is the energy difference between the ground and the excited states.*

From the above discussion, it follows that more extended the conjugation in a molecule, *greater is the contribution of charged structures, smaller is the energy difference between the ground and the excited states, and hence longer is the wavelength of absorption. When this wavelength of absorption is long enough to lie in the visible region, we observe colour.* For example,

$CH_2 = CH_2$ Ethylene (*Colourless*) λ_{max} 175 nm

$CH_2 = CH—CH = CH_2$ 1, 3-Butadiene (*Colourless*) λ_{max} 217 nm

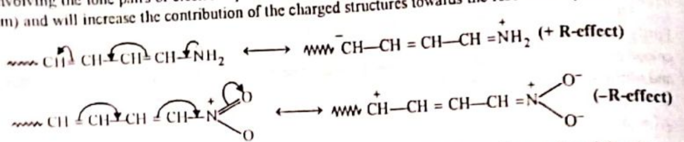
$CH_2 = CH—CH = CH—CH = CH_2$ 1, 3, 5-Hexatriene (*Colourless*) λ_{max} 258 nm



1, 10-Diphenyl-1, 3, 5, 7, 9-decapentaene (*orange*) λ_{max} 424 nm

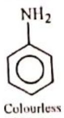
It may, however, be remembered that the colour of the compound is actually the complementary colour of the light absorbed.

Further, the presence of both electron-donating groups (*i.e.* groups with +I/+R-effect) or electron-withdrawing groups (*i.e.* groups with –I/–R effect) at the ends of conjugated system will *extend* the conjugation (by involving the lone pairs of electrons present on the heteroatom with the π-electrons of the conjugated system) and will increase the contribution of the charged structures towards the resonance hybrid.

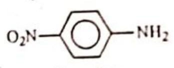


Consequently, the wavelength of light absorbed becomes longer and when this wavelength lies in the visible region, the compound appears coloured. For example,


Colourless
204 nm


Colourless
230 nm


Colourless
270 nm


Pure yellow
375 nm

Steric effects and colour. We know that resonance is maximum when the system is completely or almost completely planar. If due to steric hindrance, resonance is inhibited, the depth of colour will diminish or the compound may even become colourless.

(*ii*) **Molecular Orbital theory.** According to M.O. theory, whenever a molecule absorbs a photon of light, one electron is transferred from *bonding (or non-bonding) orbital to an anti-bonding orbital*. Depending upon the types of electrons present in a molecule, different types of electronic transitions are possible. A transition in which a bonding σ-electron is excited to an antibonding σ-orbital is called **σ-σ* transition**. In the same way, π-π* represents the transition of a bonding π-electron to an anti-bonding π*-orbital. A *n*-π* transition represents the transition of *one* electron of a *lone pair i.e.* non-bonding pair of electrons, to an antibonding π*-orbital (as shown in Fig. 10.1). This type of transition occurs in molecules containing double bonds involving hetero-atoms, *e.g.* $>C=O$, $>C=S$, $>C=N-$ etc. and may be represented as follow

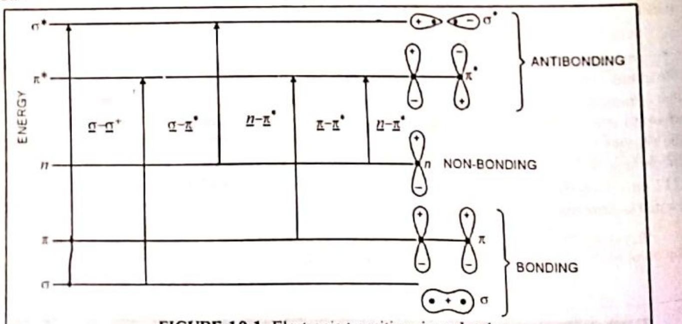


FIGURE 10.1. Electronic transitions in molecules.

$$>\dot{C}-\ddot{O}: \xleftarrow{\pi-\pi^*} >C=\ddot{O}: \xrightarrow{n-\pi^*} >C\dot{=}\dot{O}$$

The relative energies of these transitions are :

$$\sigma\text{-}\sigma^* > \sigma\text{-}\pi^* > n\text{-}\sigma^* > \pi\text{-}\pi^* > n\text{-}\pi^*.$$

Of all these transitions, only π–π* and *n*–π* transitions lie in the ordinary UV region (200–400 nm). Further more π–π* transitions are much more intense than n-π* transitions and hence are responsible for colour. Further, as conjugation increases, absorption due to π–π* transitions gets shifted to longer wavelengths and ultimately to the visible region and hence is responsible for colour as explained below

In ethylene, there are two types of transitions, *i.e.*, σ–σ* and π–π*. The longest wavelength band, *i.e.* π–π* absorbs at 175 nm (ε = 5000)*. Since this band also lies in the far ultraviolet region, therefore, *ethylene is colourless*. Butadiene has λ_{max} at 217 nm (ε = 21000) due to π–π* transition. Thus, conjugation has shifted the band to longer wavelength (but still not into the visible region) and the intensity has greatly increased. This may be explained as follows :

A double bond consists of two π-MOs—one bonding and the other antibonding. But when two double bonds are brought into conjugation, four MOs are formed—two of these *i.e.* π_1 and π_2 are bonding and are occupied by a pair of electrons each while the other two are antibonding *i.e.* π_3^* and π_4^* as shown in Fig. 10.2.

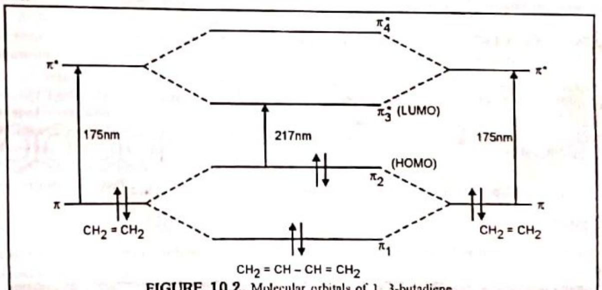


FIGURE 10.2. Molecular orbitals of 1, 3-butadiene.

Thus, it is clear that the energy of highest occupied molecular orbital (HOMO), *i.e.* π_2 increases while that of the lowest unoccupied molecular orbital (LUMO), *i.e.*, π_3^* decreases. As a result, the energy levels involved in π–π* transition now come closer and hence lesser amount of energy is needed. In other words, the energy gap between π_2 and π_3^* orbitals in 1, 3-butadiene is much lower than in the corresponding energy gap in π and π* orbitals in ethylene and hence 1, 3-butadiene absorbs at a longer wavelength (217 nm) than ethylene (175 nm). Further, since the energy levels come closer, their interaction in the excited state increases and hence ϵ_{max} also goes up.

In a similar way, we can show that when three double bonds are brought into conjugation the energy gap between the HOMO and LUMO becomes still smaller (as shown by arrows in Fig. 10.3) and wavelength

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*ε means molar absorptivity. Higher the ε-value, more intense is the absorption.

of $\pi-\pi^*$ absorption band increases, and when it reaches the visible region, colour (complementary) will appear in the compound. For example, in the polyenes, $CH_3(CH = CH)_nCH_3$, when $n = 6$, the absorption band occurs in the blue region and so the compound is yellow (complementary colour). Similarly, β-carotene (an orange pigment of carrots) absorbs in the greenish blue region. (λ_{max} 478 nm, ϵ = 139,000) and 422 nm, C = 122, 000) and hence has orange colour.

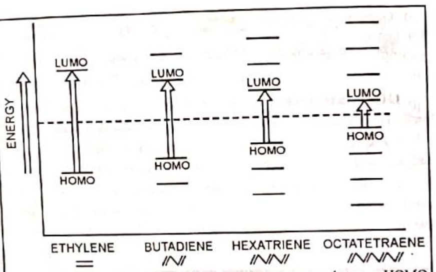
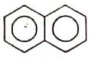


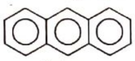
FIGURE 10.3. As conjugation increases, the energy gap between HOMO and LUMO decreases and absorption shifts to longer wavelengths.

Now let us cozsider benzene. It absorbs at 254 nm and is, therefore, colourless. Similarly, naphthalene and anthracene are colourless. As the number of fused rings increases, the position of absorption approaches the visible region. Thus, naphthacene with four linearly fused rings absorbs in the blue region and hence is yellow while pentacene which absorbs *orange light is blue* (complementary colour).

Benzene
$_{max}$ 254nm

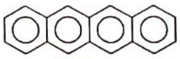


Napthalene
275nm

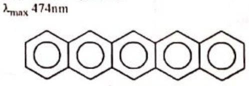


Unthracene
λ_{max} 375nm

Colourless



Napthracene (*yellow*)
λ_{max} 474nm



Pentacene (*blue*)
λ_{max} 580nm

10.3. DYES

A dye is a coloured substance, which can be applied in solution or dispersion to a substance such as textile fibres (cotton, wool, silk, polyester, nylon) paper, leather, hair, fur, plastic material, wax, a cosmetic base, giving it a coloured appearance.

Conditions which a dye must satisfy. A substance can be used as a dye for the textiles only if it satisfies the following conditions :

(*i*) It must have a suitable colour.

(*ii*) It must be able to fix itself or capable of being fixed to the fabric from the solution.

(*iii*) When fixed, it must be fast to light, resistant to the action of water, soap, detergents etc. during washing or to the organic solvents during dry cleaning etc.

10.3.1. NOMENCLATURE

The chemical names of dyes are very complicated and hence *trade names are more popular.* These trade names often include one or more alphabetical letters and a number. *Whereas the number indicates the shade, alphabetical letter s refer to the colour.* For example, G for yellow (German : *gelb* = yellow), R for red (German, *rot* = red). Sometimes alphabets may also refer to some specific properties. For example, WE for fast to washing (German = *was checht*). Sometimes the letter also stands for intensity of colour. For example, 6 B stands for deep purple (close to blue) but sometimes these letters may have entirely different meanings. For example, Alizarin *blue D*, here D stands for direct which means it is direct dye for cotton.

10.4. CLASSIFICATION OF DYES

Dyes may be classified into a number ways as discussed below :

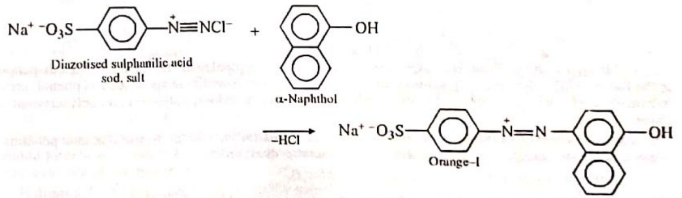
I. Natural and Synthetic Dyes. Since early times, man has been trying to extract dyes from the plants for using them to beautify his clothes. Such dyes are known as natural dyes. Two examples of natural dyes known since early times are *indigo* (a blue dye) and *alizarin* (a red dye). India has been the main producer and exporter of indigo. However, natural dyes have only limited shades. Hence, now a days, most of the dyes used are the synthetic dyes which can have a variety of shades. Most of these dyes are aromatic compounds obtained from coal-tar. Hence these are also called *coal-tar dyes.*

II. Classification of Dyes based on their Constitution (Chemical classification). In this system, dyes are classified on the basis of chemical constitution or the functional group to which the dyes owe their colour. Some important classes are : *azo dyes, nitro dyes, nitroso dyes, triphenymethane dyes, anthraquinone dyes, indigoid dyes, phthalein dyes, acridine dye etc.*

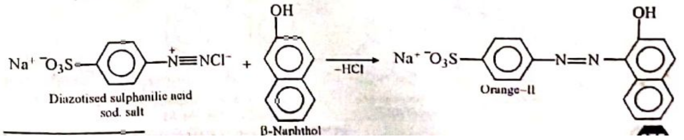
III. Classification of Dyes based on their Application. The application of a dye on a particular fibre depends on the nature of both the fibre and the dye. There are four different ways in which a dye molecule may be attached to the fibre : through (*i*) *covalent bonds* ; (*ii*) *hydrogen bonds* ; (*iii*) ionic bonds ; (*iv*) *van der Waals forces.* Based upon the methods of application, dyes have been classified into the following categories :

(*i*) **Acid dyes.** *The sodium salts of azo dyes containing sulphonic acid* (—SO_3H) *and carboxylic acid* (—CO_2H) *groups are called* **acid dyes.** These dyes are applied to the fabric from their acid solutions and are used to dye wool, silk, nylon and polyurethane fibres. The affinity of acid dyes for nylon is higher than that for other types since polycaprolactam fibres contain a higher proportion of free amino groups. These do not have affinity for cotton and hence cannot be used to dye cotton. Typical examples of acid dyes are orange-I, orange-II, methyl orange and congo red.

Orange-I is a versatile dye prepared by coupling diazotised sulphanilic acid with α-naphthol.

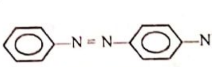


The dye orange-II is similarly obtained by coupling diazotised sulphanilic acid with β– naphthol.

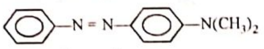


structure and chemistry of methyl orange and congo red will be discussed later in this unit.

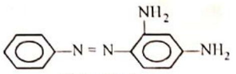
Basic dyes. These dyes are the salts of the coloured bases containing amino groups (—NH_2 or —
he *auxochromes*. These include azo and triphenylmethane dyes. In the acid solution, these amino
rm water soluble cations which then react with anionic sites present on the fabrics and thus get
o them. Modified or reinforced nylons and polyesters can be dyed with these dyes. Some common
. of this class are aniline yellow, butter yellow, chrysodine G and malachite green (discussed later
nit).



Aniline yellow



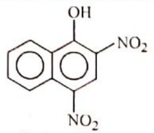
Butter yellow



Chrysodine G

rysodine G is an orange dye and is obtained by coupling benzenediazonium chloride (1 mole) with
ylenediamine. It is generally used to dye silk, wool, cotton, leather and paper.

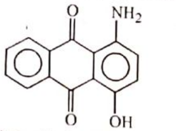
i) **Direct or substantive dyes.** These are water soluble dyes. As the name suggests, these are those
hich can be directly applied to the fabric from an aqueous solution. These are most suitable for
which can form hydrogen bonds with the dyes. Thus, these are usually used for dyeing cotton, wool,
on and nylon. Congo red and martius yellow are the two well known examples of this class of dyes.



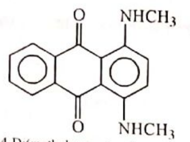
Martius yellow

Disperse dyes. These are water insoluble dyes and are applied to the fabric in form of a dispersion
ely divided dye in a soap solution in the presence of some stabilizing agent such as phenol, cresol
ic acid. These dyes are used to dye synthetic fibres such as nylons, polyesters and polyacrylonitrile

ese dyes belong to the class of anthraquinone dyes and are suitable for dyeing synthetic polyamide
nportant examples of disperse dyes (anthraquinone dyes) are :
elliton fast pink B and (*ii*) *Celliton fast blue B*.

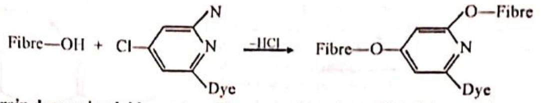


1-Amino-4-hydroxyanthraquinone
(*Celliton fast pink B*)

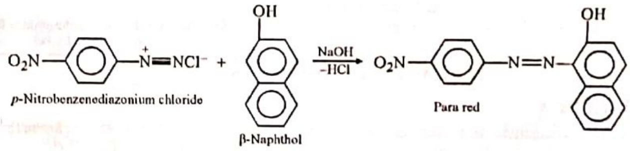


1,4-Di(methylamino) anthraquinone
(*Celliton fast blue B*)

(*v*) **Fibre reactive dyes.** These are those dyes which contain a reactive group which combines directly with the hydroxyl or the amino group of the fibre. Because of the formation of permanent chemical bonds between the fibre and the dye, the colour of the dyed fabric is fast and has a long life. Cotton, wool or silk can be dyed with this type of dyes. Dyes which are derivatives of 2, 4-dichloro-1, 3, 5-triazine are important examples of fibre reactive dyes.



(*vi*) **Ingrain dyes or insoluble azodyes.** These constitute about 60% of the total dyes used. These are obtained by coupling of phenols, naphthols, arylamines, aminophenols adsorbed on the surface of a fabric with a diazonium salt. As there is only surface adsorption of the dye on the fabric, the colour is not fast. These dyes can be used to dye cellulose, silk, polyester, nylon, polypropylene, polyurethanes, polyacrylonitriles and leather. An example of this type of dye is para red.



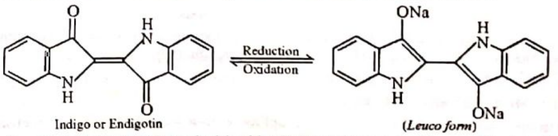
p-Nitrobenzenediazonium chloride

β-Naphthol

Para red

Azodyes also find use in foodstuffs, cosmetics, drugs, biological stains such as indicators in chemical analysis. However, because of their toxic nature, these dyes are no longer permitted to dye foodstuffs.

(*vii*) **Vat dyes.** Vat dyes are insoluble in water and hence cannot be used directly for dyeing. Therefore, they are first reduced to a soluble colourless form (*leuco form*) in large vats with a reducing agent such as an alkaline solution of sodium hydrosulphite. Under these alkaline conditions, the leucoform develops affinity for cellulose fibres. Therefore, these dyes are mainly used to dye cotton fibres.



Indigo or Endigotin

(*Leuco form*)

The cotton fabric to be dyed in soaked in this alkaline solution and then oxidised to the insoluble coloured form by exposure to air or by some oxidising agents such as chromic acid or perboric acid. A well known example of vat dyes is *indigo*.

Indigosol O, on the other hand, is readily soluble in water. It has affinity for cellulose and can be rapidly and quantitatively oxidised on the fibre with formation of indigo. It is especially suitable for wool.

Indigosol O

(*viii*) **Mordant dyes.** These dyes do not dye the fabric directly but require a mordant. The mordant, in fact, acts as the binding agent between the fibre and the dye. (Fig. 10.4).

For acid dyes, metal ions are used as mordants but for basic dyes, tannic acid is used as the mordant. These dyes are primarily used to dye wool. The fabric to be dyed is first soaked in the solution of a suitable metal salt (mordant) and the soaked fabric is then dipped in the solution of the dye when insoluble coloured complexes called *lakes* are formed on the fabric. In this way, the metal ions first get attached to the fabric and then the dye molecules are linked to the metal ion through covalent and or coordinate bonds. The same dye can give lakes of different colours depending upon the metal ion used. For example, alizarin gives *rose-red* (*turkey red*) colour with aluminium ions *blue colour* with barium ions, *brownish red* with chromium ions, *violet* with magnesium and *red* with strontium ions.

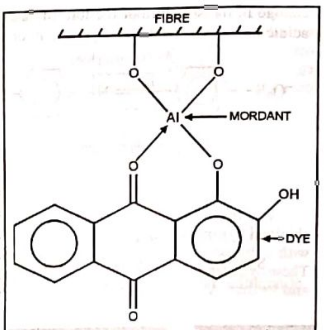


FIGURE 10.4 Alizarin-aluminium fibre complex (*rose red lake*)

CHEMISTRY OF SOME IMPORTANT DYES

10.5. AZO DYES

Azo dyes constitute the largest class of synthetic dyes. Their chromophore is Ar, *i.e.*, aromatic system joined to the azo (—N = N—) group and the common auxochromes are : NH_2, NR_2, OH etc.

The usual method of preparation of azo dyes involves direct coupling between a diazonium salt and a phenol or an amine. The structures of azo dyes is elucidated by reduction with $SnCl_2/HCl$ or sodium hyposulphite (dithionite) when azo group is ruptured with the formation of primary amines which are then identified.

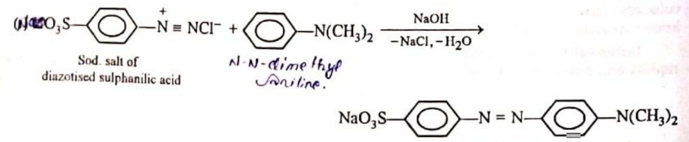
$$\underset{\text{Azo dye}}{Ar—N=N—Ar'} \xrightarrow{e^-,\,H^+} \underset{1°\ \text{Amines}}{Ar—NH_2 + H_2N—Ar'}$$

Azo dyes are classified according to the number of azo groups in the molecule, *i.e.* monoazo, disazo, trisazo etc. They are also classified as basic (cationic) dyes, acid (anionic) dyes etc.

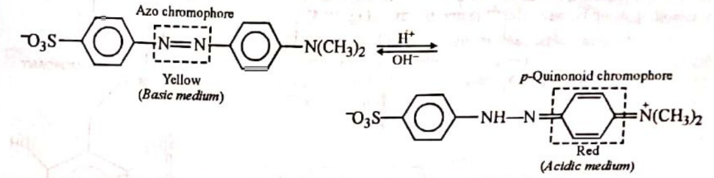
Two important azo dyes are described below :

10.5.1. Methyl Orange, Helianthin

Synthesis. Methyl orange is obtained by coupling N, N-dimethylaniline with diazotised sulphanilic acid.



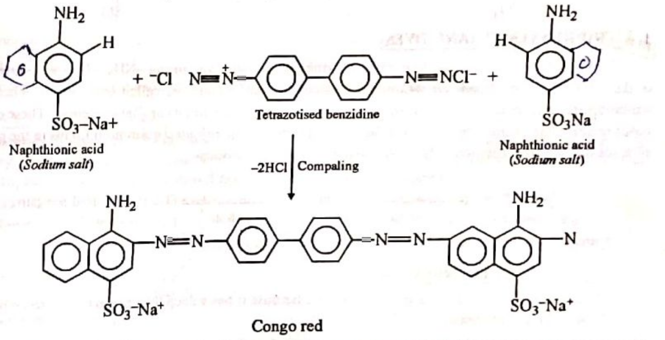
Properties. It is an *acid dye* for wool and silk but its colour fades on exposure to light and washing. Therefore, it not used as a dye but is better used as an *indicater in acid-base titrations*. It is *yellow in basic solutions* (above pH 4·4) while *red in acidic solutions* (below pH 3·1). The change in colour is attributed to change in the structure of the ion. In basic medium, the ion contains the azo chromophore while in the acidic medium, it contains *p-quinonoid chromophore.*



10.5.2. Congo Red.

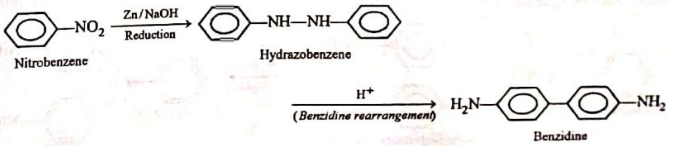
Congo red is an example of disazo dye, *i.e.*, it contains two azo groups.

Synthesis. It is obtained by coupling tetrazotised benzidine (4, 4′-diaminodiphenyl) with two molecules of naphthionic acid (4-aminonaphthalene-1-sulphonic acid).

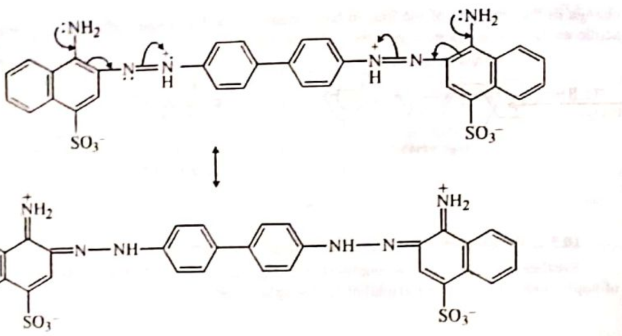


Congo red

Benzidine needed for the purpose may be prepared by rearrangement (called **benzidine rearrangement**) of hydrazobenzene in presence of acid. Hydrazobenzene, in turn, is prepared from nitrobenzene by reduction with Zn/NaOH



Properties. It is a *direct dye* and its sodium salt dyes cotton a full red. However, it is not a good dye because the colour changes when the acid is added. Therefore, it is used as an indicator. It is *blue in acidic solutions* (*below pH 3*) *and* **red in solutions** (*above pH 3*). This change in colour from red to blue in acid solutions is due to resonance among charged canonical structures.



6. TRIPHENYLMETHANE DYES

Triphenylmethane dyes are derivatives of triphenylmethane containing $-NH_2$, $-NR_2$ and $-OH$ groups he rings. The compounds so obtained are usually colourless and are called *leuco bases*. These upon dation are converted into the corresponding colourless tertiary alcohols or *carbinol bases*. These carbinol es readily change from the *colourless* **benzenoid forms** to the *coloured* **quinonoid forms** in the presence cids due to salt formation. These changes are summarised below :

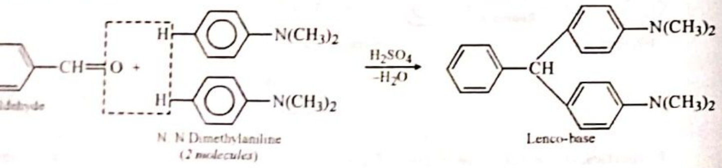
$$\underset{(Colourless)}{\text{Leuco-base}} \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} \underset{(Colourless)}{\text{Carbinol base}} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} \underset{(Coloured)}{\text{Dye (Quinonoid structure)}}$$

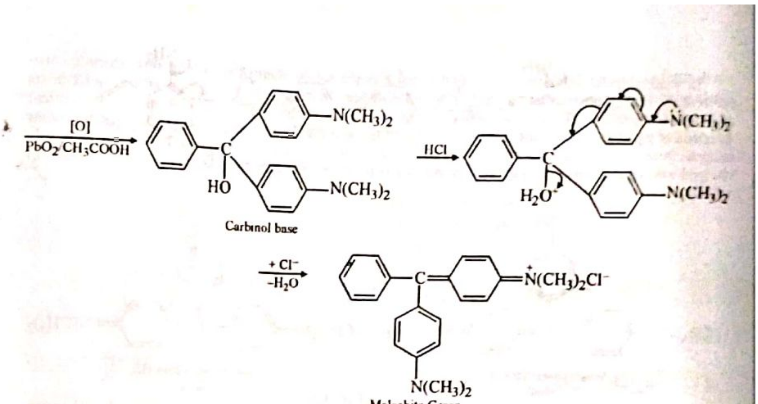
Some important triphenylmethane dyes are discussed below :

10.6.1. MALACHITE GREEN

The name malachite green is given to this dye because it has a deep blue green colour resembling that alachite–an ore of copper.

Synthesis. It is prepared by condensing N, N-dimethylaniline (2 molecules) with benzaldehyde olecule) at 373 K in presence of conc. H_2SO_4. The leuco-base so produced is oxidized with lead dioxide $_2$) in a solution of CH_3COOH and HCl. The carbonol base so produced reacts with excess of HCl to Malachite green.



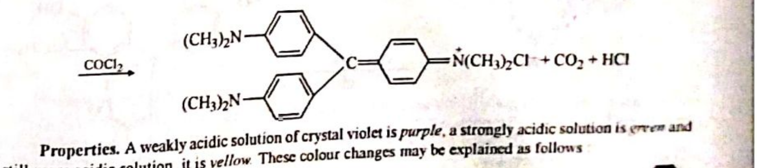


Malachite Green

Properties. Malachite green dyes wool and silk directly and cotton mordanted with tanin.

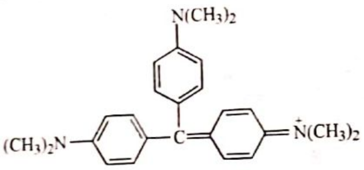
10.6.2. CHRYSTAL VIOLET

Synthesis. It is prepared by heating either N, N-dimethylaniline with carbonyl chloride (phosgene) or by heating *Michler's ketone* with dimethylaniline in presence of $POCl_3$. In the first case, Michler's ketone initially formed condenses further with dimethylaniline to form crystal violet.

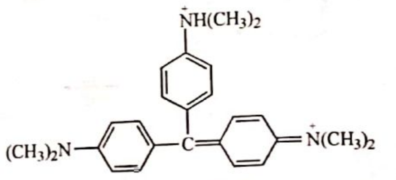


Properties. A weakly acidic solution of crystal violet is *purple*, a strongly acidic solution is *green* and still more acidic solution, it is *yellow*. These colour changes may be explained as follows :

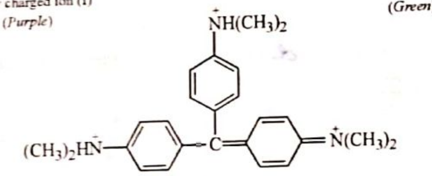
In weakly acidic solution, crystal violet exists as the singly charged ion (I). In this structure, *two-rds* of the charge can oscillate in the horizontal direction. In strongly acidic solution, crystal violet exists doubly charged ion (II). Here the whole unit of charge can oscillate in horizontal direction (the vertical rection of oscillation is inhibited due to fixation of the lone pair by proton addition) and hence the colour eepens from *purple to green*. In very strongly acidic solution, another proton is added to form the triply harged ion (III). In this ion, only little resonance is possible and hence the colour lightens from *green to ellow*.



Singly charged ion (I)
(Purple)



Doubly charged ion (II)
(Green)



Triply charged ion (III)
(Yellow)

Uses. Crystal violet is used in the manufacture of inks, stamping pads and type-writing ribbons. It is also used as an indicator for determining hydrogen ion concentration in solutions.

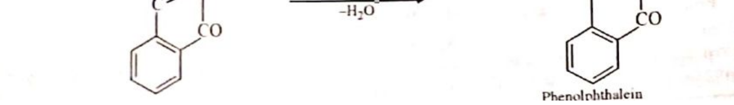
10.7. PHTHALEIN DYES

These are obtained by condensing phenols with phthalic anhydride in the presence of certain dehydrating agents such as conc. H_2SO_4, $ZnCl_2$ or anhydrous oxalic acid.

10.7.1. PHENOLPHTHALEIN

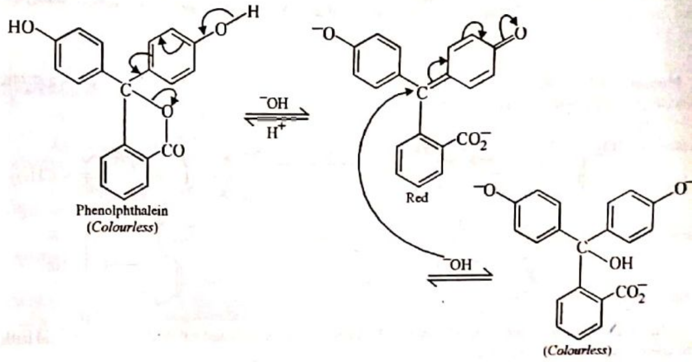
Phenolphthalein is a phthalein dye. It may also be regarded as a triphenylmethane derivative.

Synthesis. It is prepared by heating phthalic anhydride (1 molecule) with phenol (2 molecules) in the presence of conc. H_2SO_4.



Phenolphthalein

Properties. Phenolphthalein is not a dye. It is insoluble in water but dissolves in alkalies to form red solution. This is due to the formation of disodium salt which undergoes resonance and has quinon structure. When excess of strong alkali is added, the solution of phenolphthalein becomes colourless due to loss of quinonoid structure and resonance as shown below :

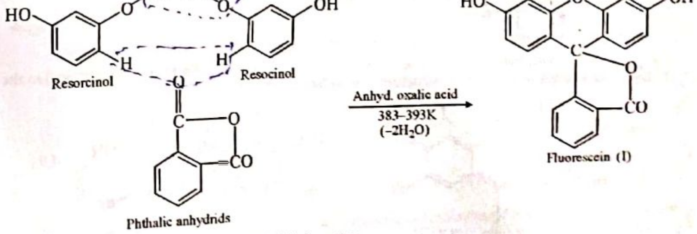


Uses. Because of the colour changes shown above, phenolphthalein is used as an indicator in acid base titrations. It is also a powerful laxative.

10.7.2. FLUORESCEIN

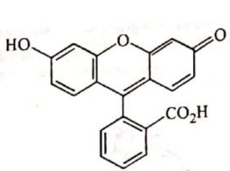
It is a xanthen derivative. In preparation and properties it more closely resembles phthalein dyes.

Synthesis. It is prepared by heating phthalic anhydride (1 molecule) with resorcinol (two molecule at 473 K or at 383–393 K with anhydrous oxalic acid.

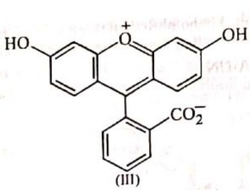


Properties. It is a red powder insoluble in water.

Since it is coloured, therefore non-quinonoid uncharged structure (I) is not satisfactory. To account for the red colour, two quinonoid structures are possible in which the conjugation is totally different, one having the *p*-quinonoid structure (II) and the other the *o*-quinonoid structure (III).

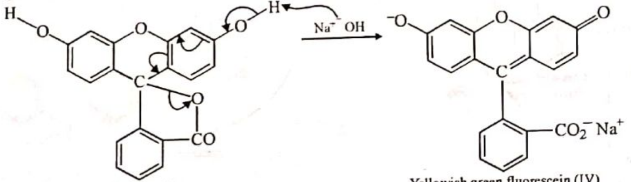


(II)



(III)

Fluorescein dissolves in alkalies to give a reddish brown solution which, on dilution, gives a strong yellowish green fluorescence due to formation of anion (IV)

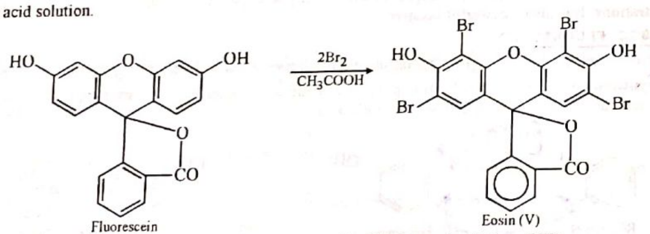


Fluorescein

Yellowish green fluorescein (IV)

The sodium salt of fluorescein is known as **Uranine** and dyes wool and silk yellow from an acid bath. The colours are, however, fugitive.

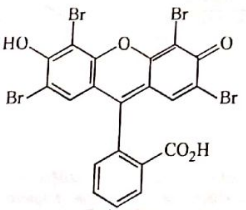
EOSIN is tetrabromofluorescein and is obtained by the action of bromine on fluorescein in glacial acetic acid solution.



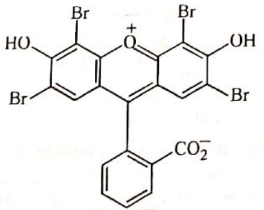
Fluorescein

Eosin (V)

Since Eosin is a red powder, so its structure cannot be (V). It may be (VI) or (VII)



Eosin (VI)



Eosin (VII)

Eosin dyes wool and silk pure red with a yellow fluorescence in case of silk. Eosin in form of lead lake called *Vermilionette* is used for poster printing. Most of the red inks are dilute solutions of Eosin.

10.8. ALIZARIN

Alizarin is one of the most important *anthraquinoid dye*. It occurs in madder root (Fr. *Alizari*, madder) in form of its glucoside called, *ruberthyric acid*.

$$\underset{\text{Ruberthyric acid}}{C_{26}H_{28}O_{14}} + 2H_2O \xrightarrow[(\textit{Hydrolysis})]{H^+ \text{ or Enyzyme}} \underset{\text{Alizarin}}{C_{14}H_6O_2(OH)_2} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Alizarin ~~Alizarin~~ is 1, 2-dihydroxy anthraquinone

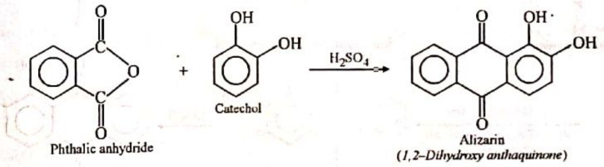
Structure. The structure of Alizarin has been deduced as follows :

1. Elemental analysis and molecular weight determination have shown that the molecular formula of alizarin is $C_{14}H_8O_4$.

2. On reduction with zinc dust at 673K, alizarin gives anthracene. This implies that alizarin is a derivative of anthracene.

3. With acetic anhydride, alizarin forms a diacetate thereby suggesting that alizarin contains *two hydroxyl groups.*

4. Alizarin can be prepared by condensing phthalic anhydride with catechol in presence of conc. H_2SO_4 at 453 K. This shows that alizarin in a dihydroxy derivative of anthraquinone in which both the —OH groups are present in the same ring.

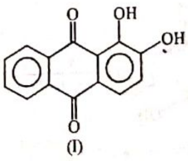


Phthalic anhydride

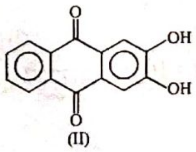
Catechol

Alizarin
(*1,2–Dihydroxy anthaquinone*)

On the basis of the above condensation reaction, the following two structures (I and II) are possibe for alizarin



(I)



(II)

5. Alizarin on nitration gives two isomeric mononitro derivatives, both of which on oxidation give phthalic acid. This suggests that in both these nitroderivatives, NO_2 group is present in the same ring which contains the hydroxy groups. Since structure (I) has two different positions available for nitration, therefore, it can give two different nitro derivatives (III and IV). Structure (II), on the other hand, can give only *one* nitro derivative (V) since the two vacant positions are equivalent.

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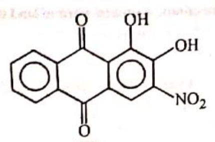
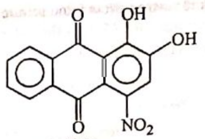
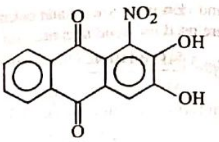
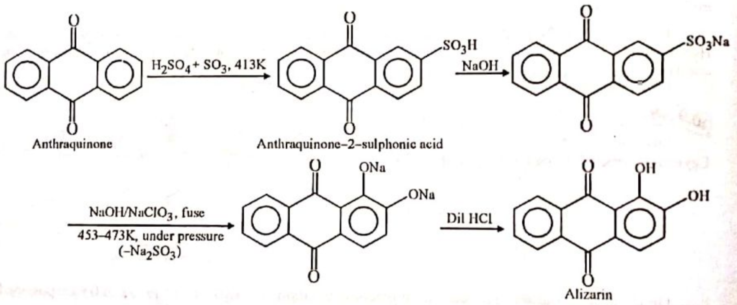

(III)


(IV)


(V)

Since structure (I) can explain the formation of two different nitro derivatives, therefore, the actual structure of alizarin is (I), *i.e.*, it is 1, 2-dihydroxyanthraquinone and not structure (II), ***i.e.* 2, 3-**dihydroxyanthraquinoe.

Manufacture. It is manufactured by sulphonating anthraquinone with fuming sulphuric acid (oleum) at 413 K and fusing the sodium salt of product, *i.e.* anthraquinone-2-sulphonic acid with NaOH, containing a calculated quantity of sodium or potassium chlorate at 453-473 K under pressure. Acidification of the product with dil. HCl gives alizarin. The function of sodium or potassium chlorate is to provide oxygen for the oxidation of C_1–H into C_1–OH.

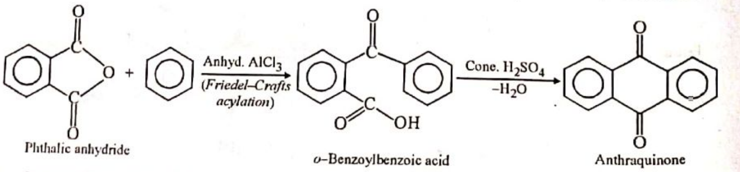


Anthraquinone

Anthraquinone–2–sulphonic acid

Alizarin

Anthraquinone needed for the purpose can be prepared from benzene and phthatic anhydride as follows :



Phthalic anhydride

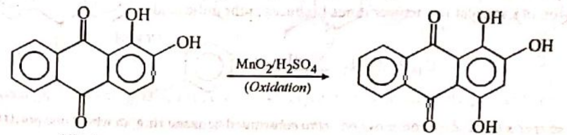
o–Benzoylbenzoic acid

Anthraquinone

Properties. 1. Alizarin forms *ruby red crystals* m.p. 563 K. It is Insoluble in water and alcohol but issolves is alkalies to from *puple solution.* It sublimes on heating..

2. It is a mordant dye, and the colour of the lake depends on the metal used. Aluminium gives a red ke (*Turkey red*), ferric salts give *violet-black* while chromium salts form *brown-violet* lake. Aluminium and iron lakes are usually employed for cotton dyeing and printing while aluminium and chromium lakes are used for wood dyeing.

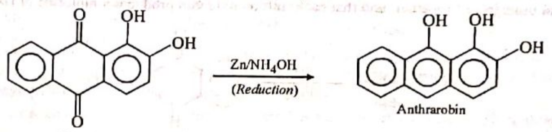
3. Oxidation. On oxidaton with MnO_2 and H_2SO_4, it gives purpurin



Alizarin

Purpurin

4. Reduction. On reduction with zinc dust and NH_4OH, it forms anthrarobin.



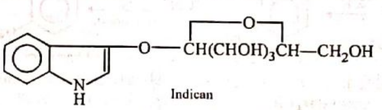
Anthrarobin

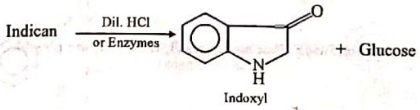
Alizarin

Uses. Alizarin is used as a mordant dye and also as a purgative

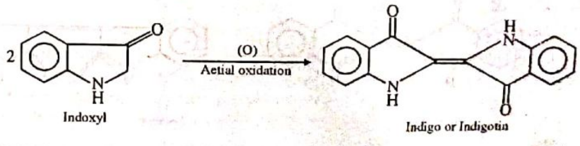
10.9. INDIGO

India is the birth place of *indigo*, its official name being *indigotin.* It is the oldest vat dye known. Egyptian mummy clothes, 5000 years old, were dyed with it. It occurs as *indican* which is the glucoside of indoxyl in Indian plant, *indigofera tinctoria* and the European plant, *isatis tinctoria.* The indican on hydrolysis with either HCl or enzymes gives indoxyl which upon areial oxidation gives indigotin.


Indican



Indoxyl



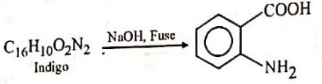
Indoxyl

Indigo or Indigotin

Structure. The strucure of indigo has been deduced as follows :

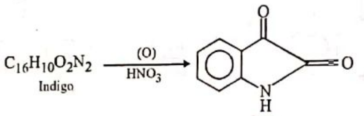
1. Elemental analysis and molecular weight determination have shown that the molecular formula of indigo is $C_{16}H_{10}O_2N_2$.

2. Fusion of indigo at low temperatures produces anthranilic acid.



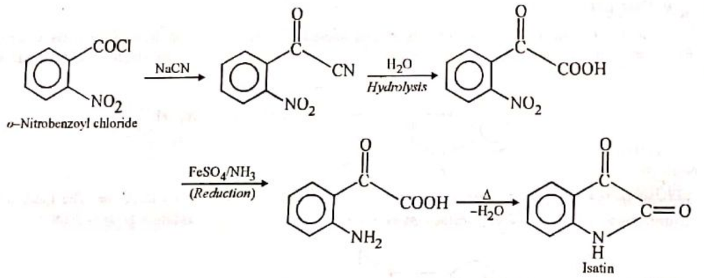
This suggests that indigo contains one *ortho* substituted benzene ring, in which one position is attached to a carbon atom while the other is linked to nitrogen atom.

3. Oxidation of indigo with HNO_3 yields two molecules of isatin. This suggests that indigo contains two identical units joined together, and that each unit on oxidaton produces a molecule of isatin.



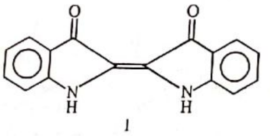
Isatin

The structure of isatin has been confirmed by its synthesis as sketched below :

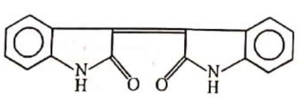


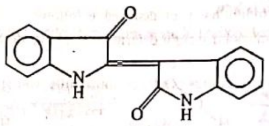
Isatin

4. On the basis of the structure of isatin, the following three structures (I, II and III) are possible for indigotin.



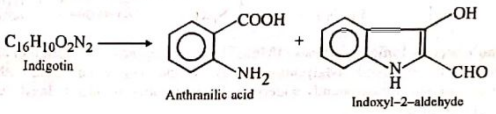
I





III

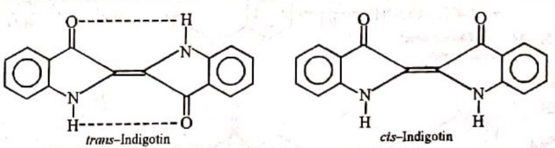
5. Indigotin on treatment with dilute alkali yields anthranilic acid and indoxyl-2-aldehyde.



Indoxyl–2–aldehyde

Formation of indoxyl-2-aldehyde suggests that the two identical units in indigotin are connected through position-2 of indoxyl moiety while position-3 carries an oxygen containing functional group. These arguments suggest that most probable structure of indigotin is I.

Further X-ray analysis has revealed that indigotin has the more stable *trans*-configuration.

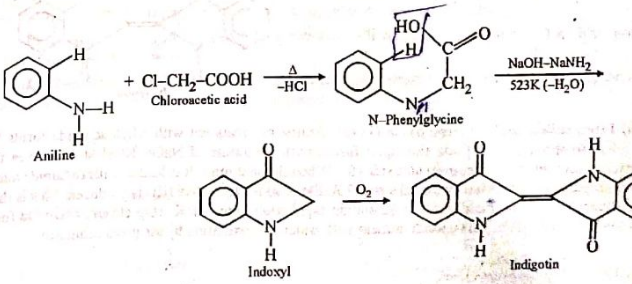


trans–Indigotin (stabilized by H–bonding)

cis–Indigotin

This structure has been confirmed by the following three syntheses :

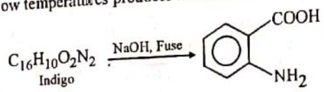
1. Heumann's First indigo synthesis (1890). Condensation of anline with chloroacetic acid produces. N-phenylglycine. This upon fusion with NaOH and $NaNH_2$ at 523 K gives indoxyl which upon subsequent oxidation by air gives indigotin.



Structure. The strucure of indigo has been deduced as follows :

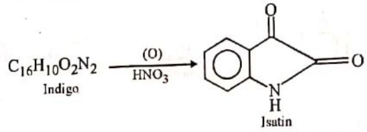
1. Elemental analysis and molecular weight determination have shown that the molecular formula of indigo is $C_{16}H_{10}O_2N_2$.

2. Fusion of indigo at low temperatures produces anthranilic acid.

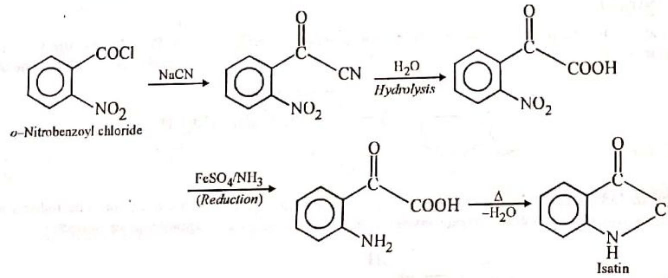


This suggests that indigo contains one *ortho* substituted benzene ring, in which one position is attached to a carbon atom while the other is linked to nitrogen atom.

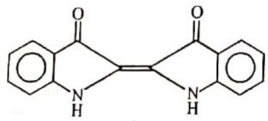
3. Oxidation of indigo with HNO_3 yields two molecules of isatin. This suggests that indigo contains two identical units joined together, and that each unit on oxidaton produces a molecule of isatin.



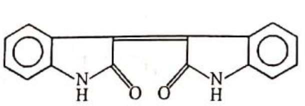
The structure of isatin has been confirmed by its synthesis as sketched below :

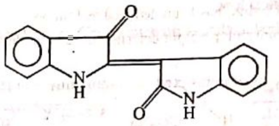


4. On the basis of the structure of isatin, the following three structures (I, II and III) are possible for indigotin.



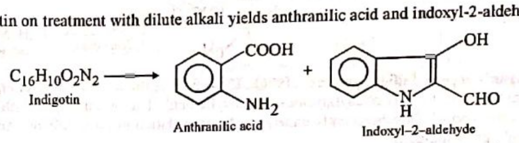
I





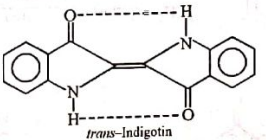
III

5. Indigotin on treatment with dilute alkali yields anthranilic acid and indoxyl-2-aldehyde.

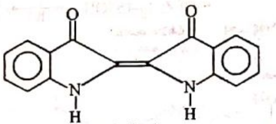


Formation of indoxyl-2-aldehyde suggests that the two identical units in indigotin are connected through position-2 of indoxyl moiety while position-3 carries an oxygen containing functional group. These arguments suggest that most probable structure of indigotin is I.

Further X-ray analysis has revealed that indigotin has the more stable *trans*-configuration.



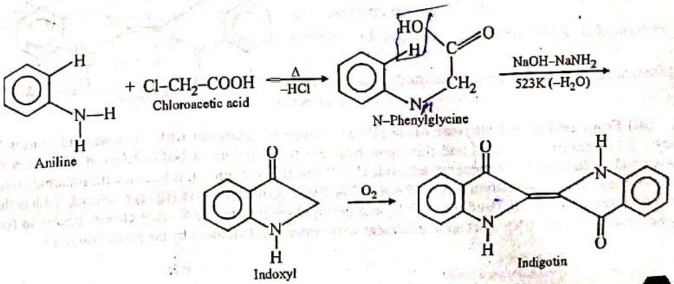
trans–Indigotin
(stabilized by H–bonding)



cis–Indigotin

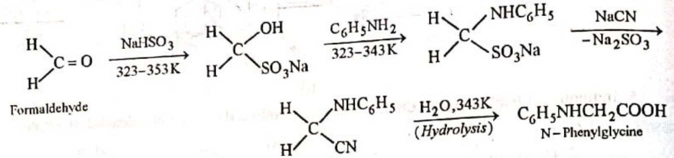
This structure has been confirmed by the following three syntheses :

1. **Heumann's First indigo synthesis (1890).** Condensation of anline with chloroacetic acid produces N-phenylglycine. This upon fusion with NaOH and $NaNH_2$ at 523 K gives indoxyl which upon subsequent oxidation by air gives indigotin.

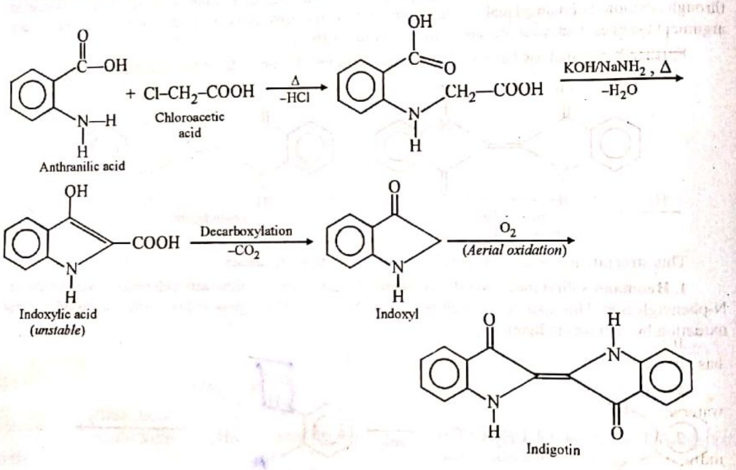


The overall yield of indigotin is low.

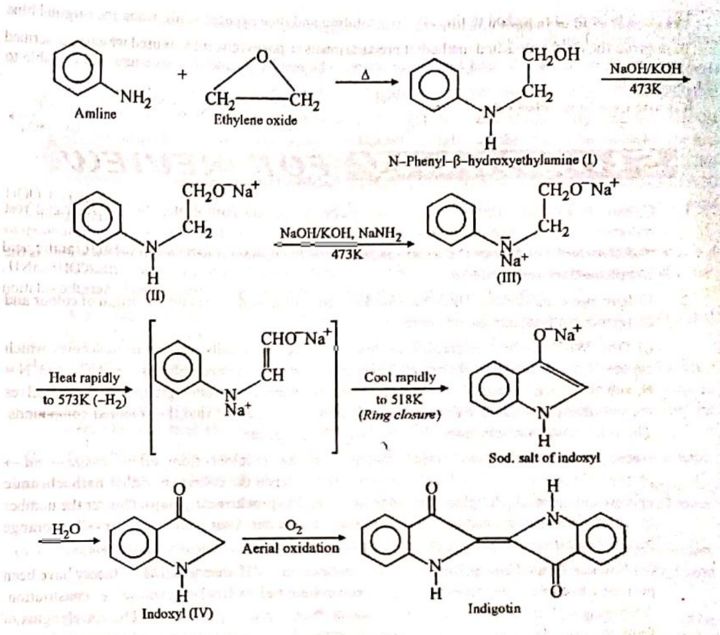
To improve the yield a modified method of preparation of N-phenylglycine was used which is described below :



2. Heumann's Second Indigo synthesis (1896). This involves the condensation of anthranilic acid with chloroacetic acid to form N-phenylglycine-*o*-carboxylic acid. This when fused with KOH/NaNH$_2$ produces indoxylic acid which subsequently undergoes dicarboxylation to form Indoxyl. Aerial oxidation of indoxyl finally gives indigotin.



(iii) From aniline and ethylene oxide (1943). Anline on treatment with ethylene oxide forms N-phenyl β-hydroxyethylamine (I) and this upon fusion with a mixture of NaOH/KOH at 473 gives the corresponding sodium (and potassium) alkoxide (II). When this sodium salt is heated with sodamide and a mixture of sodium and potassium hydroxides at 473 K, the N-sodio derivative (III) is produced. This is then dehydrogenated on heating rapidly to 573 K, and on rapid cooling to 578 K, ring closure occurs to form sodium salt of indoxyl (IV). This upon treatment with water and oxidation by air gives indigotin.



It may be noted that synthetic indigo is much cheaper than natural indigo. In fact, synthetic indig has virtually wiped out the indigo plantation so popular at one time in India.

Properties. 1. Indigotin is a dark blue powder, with coppered lustre, m.p. 663 K. It is insoluble i water and most-organic solvents.

2. When a paste of indigotin is agitated with alkaline sodium hyposulphite in large vats, the insolubl indigotin is reduced to the soluble leuco compound, called *indigotin white*.