→ Synthetic dyes:→

→ Colour and constitution(electronic concept):→

- White light consists of seven primary colours viz. Violet, Indigo, Blue, Green, Yellow, Orange and Red (VIBGYOR).
- When white light falls on a substance, any of the following situations may arise –

(i) The light may be completely absorbed. In this case the substance appears to be black.

(ii) The light may be completely reflected. In this case the substance appears to be white.

(iii) The light may be partially absorbed and partially reflected. In this case the substance appears to be coloured.

The colour of the compound is that of the reflected light. The appearance of the colour may be due to anyone of the following –

(a) If the compound absorb a single band, the colour of the compound is the complementary colour of absorbed light.

(b) If the compound reflects only one band and absorb rest of light, the colour of the compound is that of the reflected light.

- It should be noted that if a substance is colourless it does not mean that it does not absorb any radiation. In such case, absorption takes place but it falls outside the visible range of radiation. i.e either it falls in the infrared or in the ultraviolet regions.

Table:- Relationship between the absorbed and reflected colour of white light.

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	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-blue
605-750	Red	Blue-green

- The range of electromagnetic radiations absorbed by a molecule depends upon its molecular structure.
- Following theories given for correlating colour with molecular structure:-

① Graebe and Liebermann theory
② Witt's theory
③ Modern or electronic theory of colour
(a) Valence bond theory (VBT)
(b) Molecular Orbital theory (MOT)

→ Dyes :→

- Dyes are those coloured compounds which upon treatment with textile fibres, paper, leather, hair, plastic, wax, cosmetic bases, impart colour to these objects.

Thus, all coloured compounds are not dyes. To act as a dye a coloured compound must have the following characterstics-

(i) It must have a suitable colour.

(ii) It should get fixed on the material to be dyed.

(iii) When fixed, it should be resistant to light, action of water, soap, detergent etc.

(iv) It should be resistant to organic solvent during dry cleaning.

→ Classification of dyes:→

I - On the basis of the source - Natural and synthetic dyes:-

- Natural dyes → Indigo (blue dye) and alizarin (red dye)
- Synthetic dyes → obtained from coal-tar and hence are called as coal-tar dyes.

II - On the basis of their constitution:-

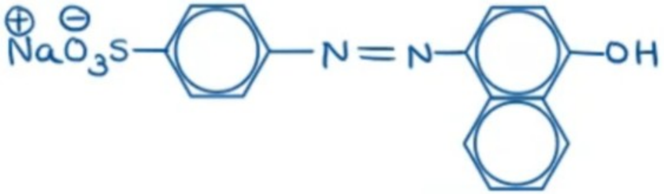
- The colour of the dyes depend upon their chemical composition and the functional group present.
- azo dyes, nitro dyes, nitroso dyes, triphenylmethane dyes, anthraquinone dyes, indigoid dyes, phthalein dyes, acridine dyes etc.

III - On the basis of their application to the material:→

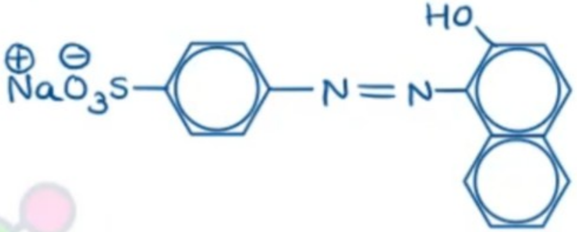
(a) Acid dyes:→

- Acid dyes are sodium salt of azo dyes containing sulphonic acid ($-SO_3H$) and carboxylic acid ($-COOH$) groups.

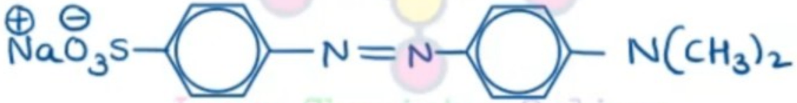
Example:-



orange-I



orange-II



Methyl orange

(b) Basic dyes:→

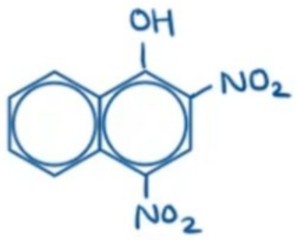
- Basic dyes are salts of bases having amino or alkyl amino group as auxochromes.

Aniline yellow

Butter yellow

(c) Direct or substantive dyes:→

- These are water soluble dyes which are directly applied to the fabric from an aqueous solution. These involve H-bonding between the dye and the fabric.

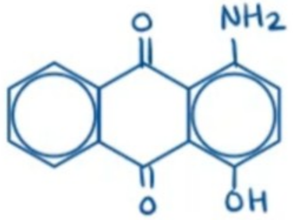


Maritius yellow

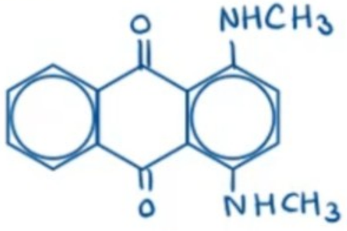
Congo red

(d) Dispersive dyes:→

- These are water insoluble dyes and are applied to the fabric from a dispersion.
- dispersion is made from finely divided dye and soap solution in presence of stabilising agents such as phenol, cresol or benzoic acid.



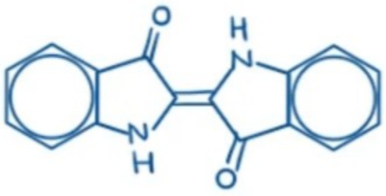
Celliton fast pink B



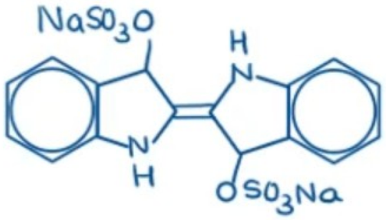
Celliton fast blue B

(e) Vat dyes:→

- These are water insoluble dyes which can not be applied directly to the fabric.
- These dyes are initially reduced to a soluble colourless form using a reducing agent.



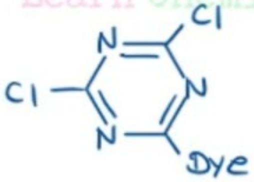
Indigo/Indigotin



Indigosol O

(f) Fibre reactive dyes:→

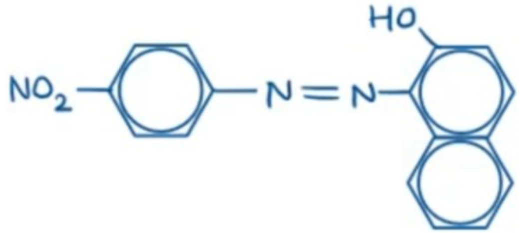
- These dyes contain a functional group which reacts directly with the hydroxy or amino group of the fibre due to which the colour of the dyed fabric is fast and has a long life.



derivative of
2,4-dichloro-1,3,5-triazine

(e) Ingrain dyes or insoluble dyes:→

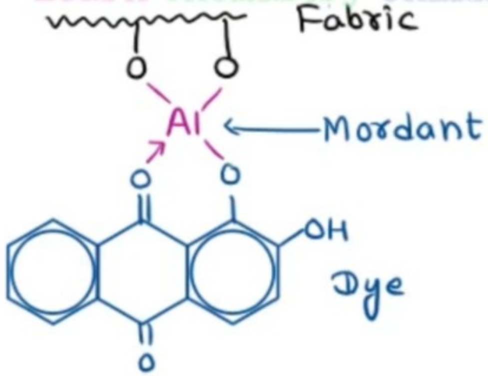
- These dyes are obtained by coupling reaction of phenols, naphthols, aryamine or aminophenol with diazonium salt



par red

(h) Mordant dyes:→

- They can not dye the fabric directly, but require some mordant.
- Mordant acts as a binding agent between the fibre and dye. Metal ions are used for acid dyes as mordant but for basic dyes tannic acid is used as the mordant.
- Same dye forms different colours depending upon the type of mordant used.
- Example:- Alizarin red gives rose-red shade with Al^{+3} ions, blue shade with Ba^{+2} ions red with Cr^{+6} and violet with Mg^{+2} ions.



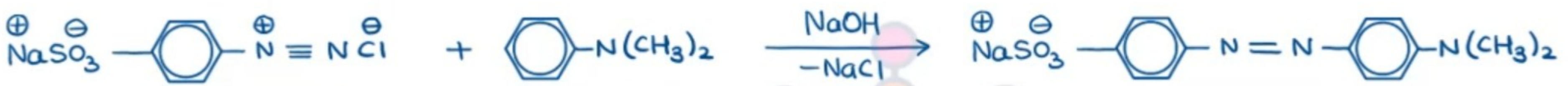
Alizarin - aluminium - fibre complex
(Rose red lake)

→ Methyl orange :→

- Methyl orange is a azo dye in which aromatic system is linked to azo group (—N=N—)
- Azo dyes are also known as ice colours because these are synthesised at low temp. (273 K).

- Synthesis :→

- It is a monoazo dye and is synthesised by coupling of N,N-dimethylaniline with sodium salt of diazotised sulphanilic acid.



Diazotised sulphanilic acid sodium salt

N,N-Dimethyl aniline

Methyl orange

- Properties :→

- Methyl orange is rarely used for dying purpose because its colour is not stable to washing and is also light.
- It is used as indicator in acid base titrations.
- Its colour changes to yellow above pH 4.4 and changes to red below pH 3.1 in solutions.
- In basic solution the chromophore is azo group while in acidic solution the chromophore is p-quinoid system.

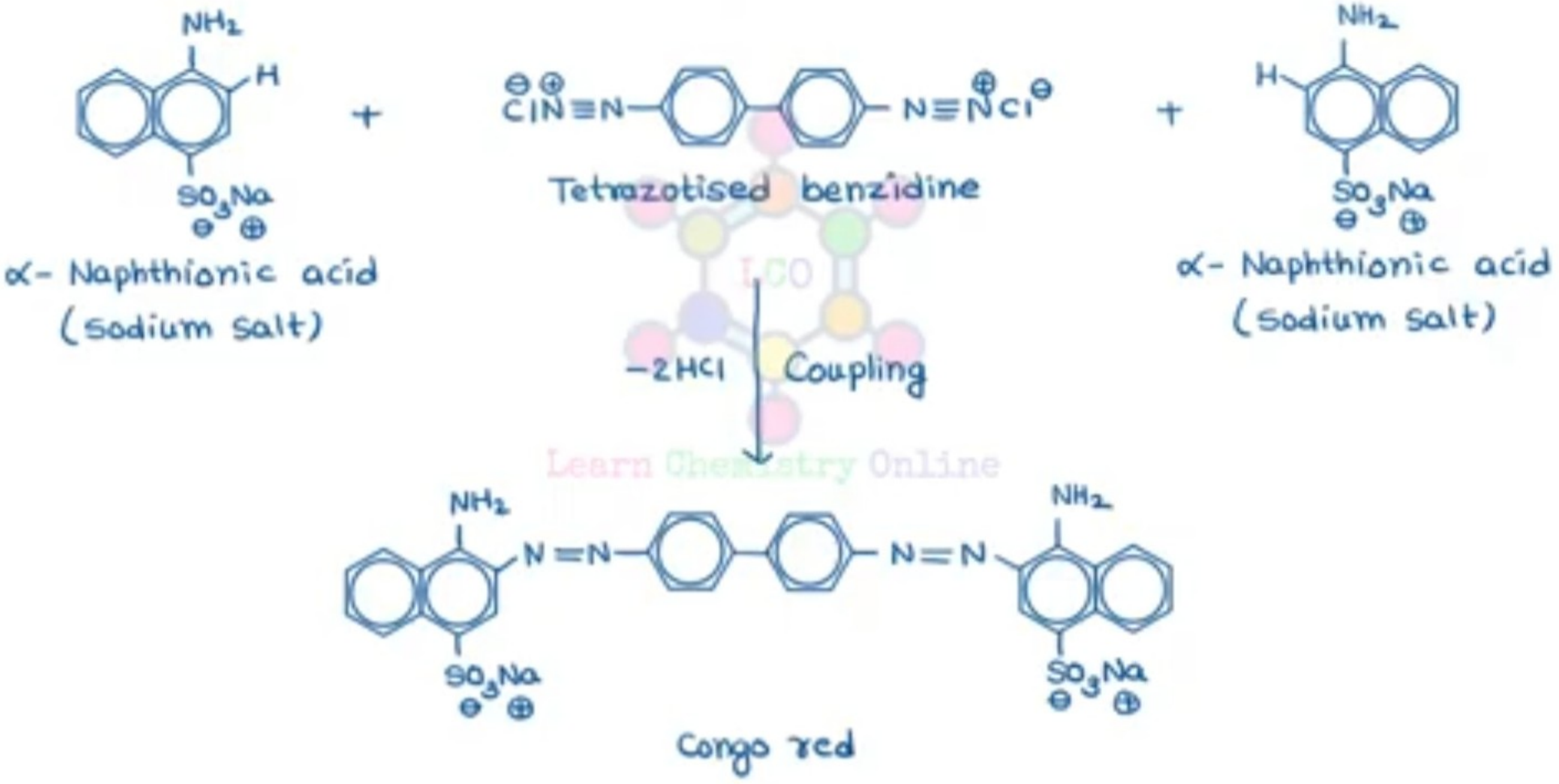
yellow (basic medium)

Red (Acidic medium)

→ Congo red :→

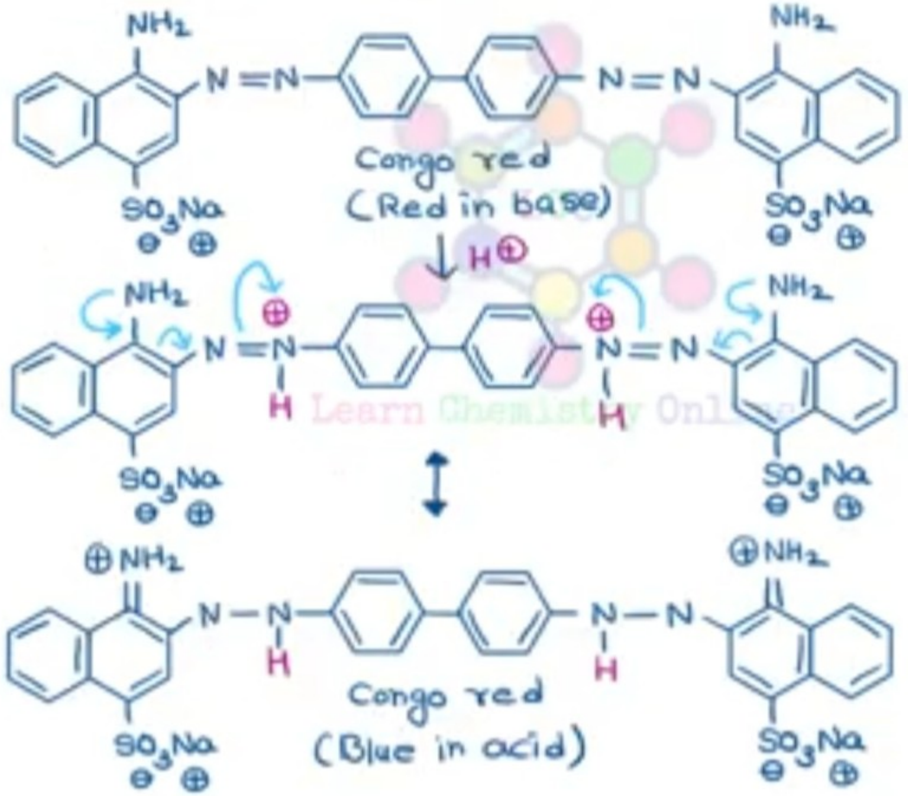
- Synthesis :→

- It is a bisazo dye and synthesised by coupling reaction of tetrazotised benzidine (4,4'-diamino diphenyl) with two molecules of α- naphthionic acid.



→ Properties:→

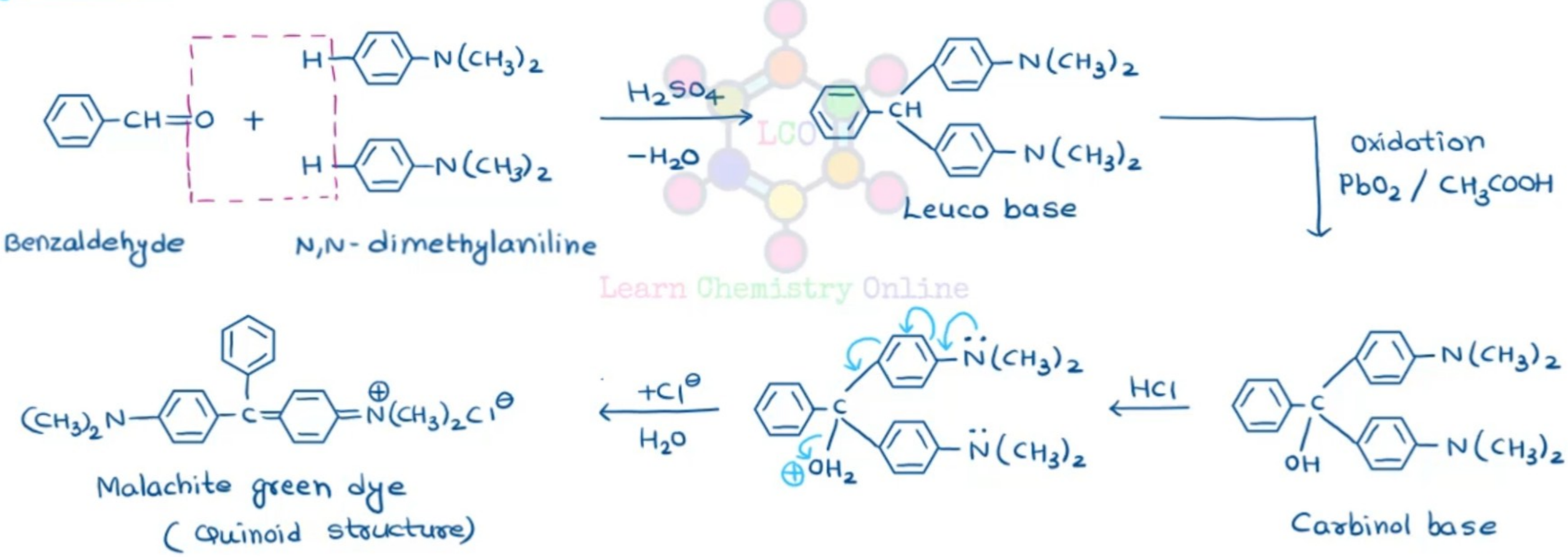
- Congo red is a direct dye which give red colour to cotton.
- It is not good dye because the colour changes when the acid is added.
- It is used as an indicator in acid-base titration.
- It is blue in acidic solution (below pH 3) and red in basic solution (above pH 3) due to resonance among the following canonical forms:



→ Malachite green :→

- Malachite green is a triphenylmethane dye.
- Derivatives of triphenylmethane containing $-NH_2$, $-NR_2$ and $-OH$ groups in the ring are called triphenylmethane dye which are generally colourless (leuco bases).
- This dye is called malachite green because its deep green colour resembles the colour of malachite (an ore of copper).

→ Synthesis :→



→ Properties:→

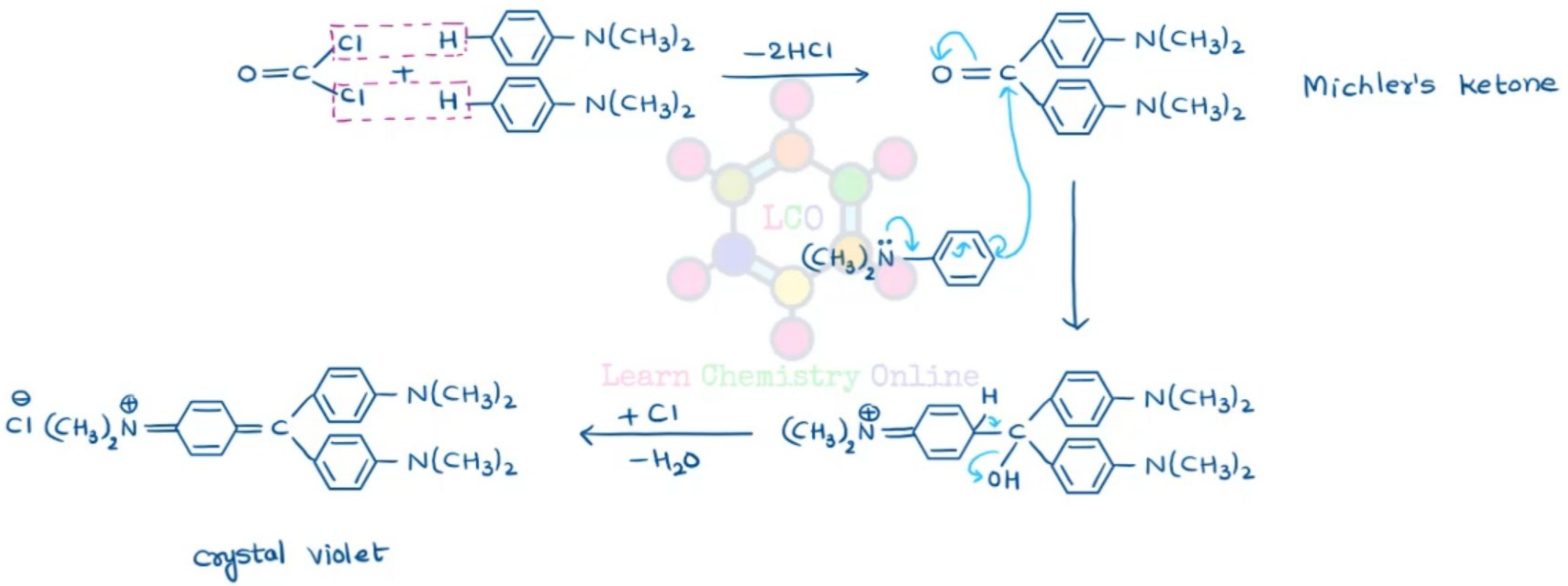
- Malachite green can be applied to wool and silk directly but for cotton it needs tannin as a mordant.
- In presence of acid or base the colour of malachite green fads slowly. In basic medium it fads due to the formation of colourless carbinol base while in acidic medium the colour fads due to addition of H^+ to the free dimethylamino group. Therefore, chances of resonance will decrease and colour would fade away.

→ Crystal violet :→

- Crystal violet is a type of triphenylmethane dye.

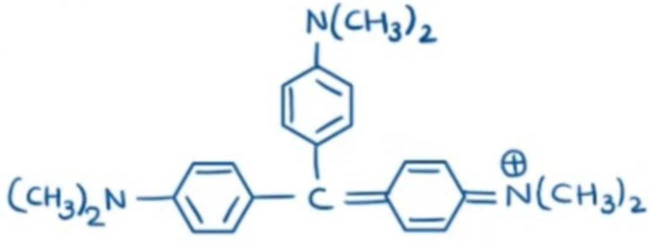
→ Synthesis :→

- This dye is obtained by heating N, N-dimethylaniline with $COCl_2$ (Phosgene).

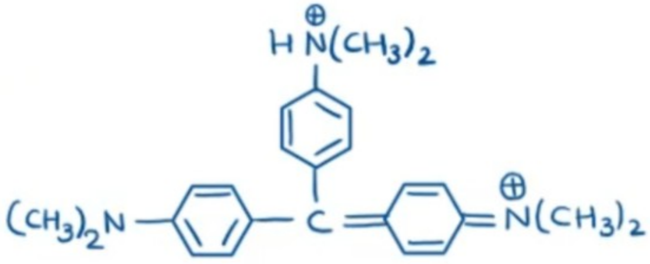


→ Properties:→

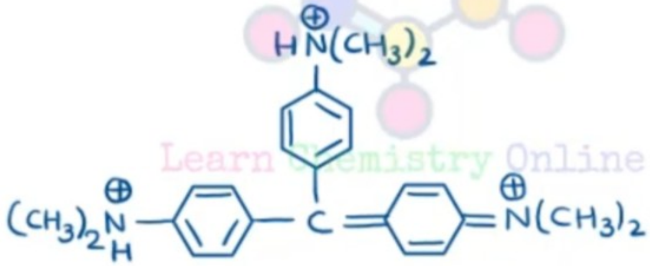
- The colour of the crystal violet dye depends upon pH of the solution.



Weakly acidic solution
Singly charged ion (purple)



strongly acidic solution
Doubly charged ion (Green)



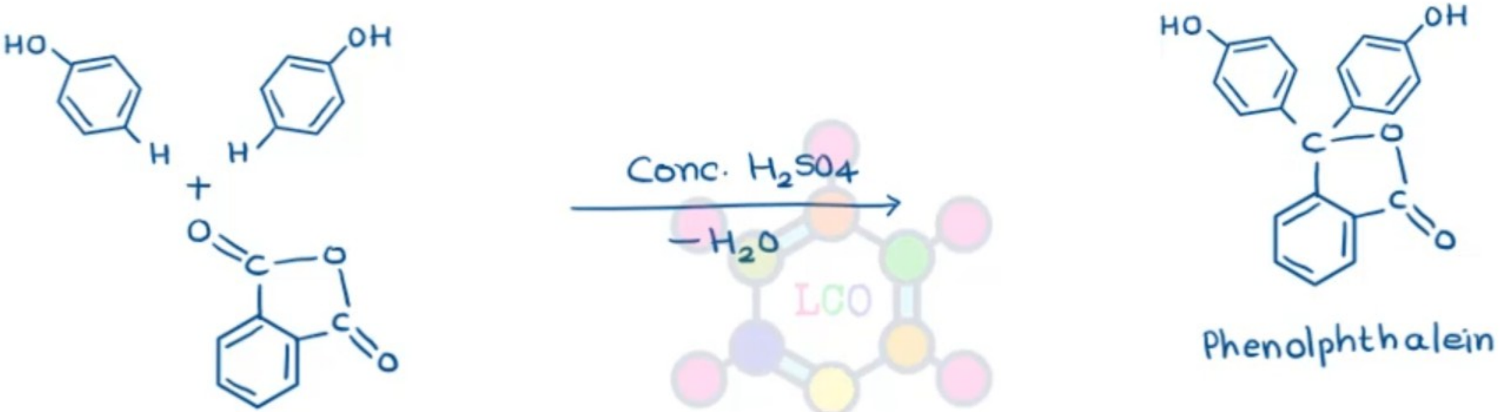
More strongly acidic solution
Triply charged ion (yellow)
Very little chance of resonance

→ Uses:- Manufacturing of inks, stamping pad and type writer's ribbons and as an indicator.

→ Phenolphthalein:→

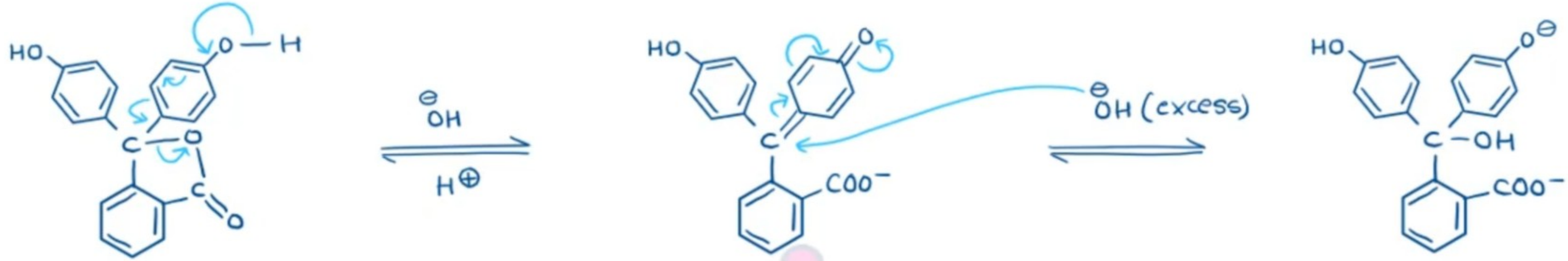
→ Synthesis:→

- Condensation of two molecules of phenol with one molecule of phthalic anhydride in presence of conc. H_2SO_4 gives phenolphthalein.



→ Properties:→

- It is not used as dye but is a very good indicator in acid base titration.
- It is insoluble in water and colourless in acid but becomes soluble and a deep red colour (pink when light) in basic medium because of resonance involving quinoid structure. However, in presence of excess of alkali, it again becomes colourless due to loss of the quinoid structure.



Phenolphthalein
(Colourless)

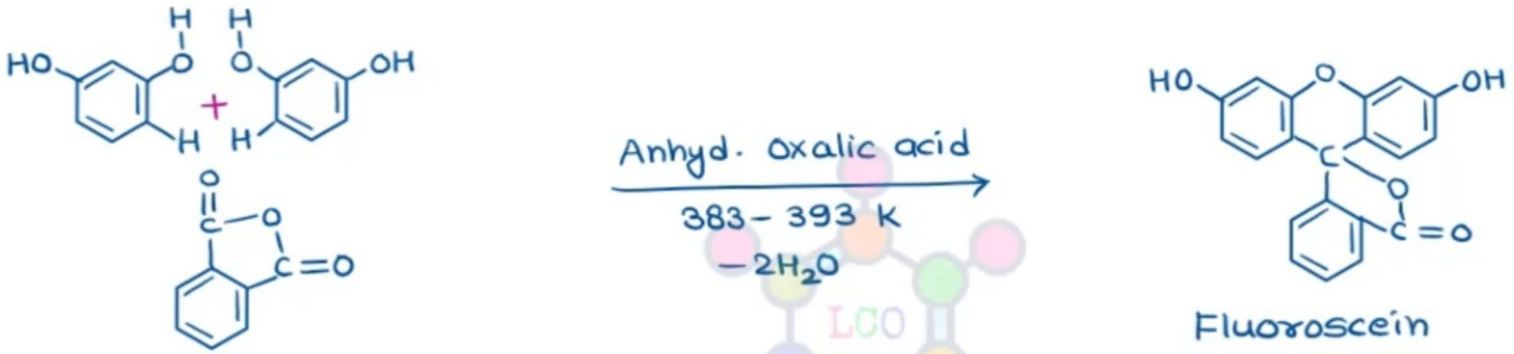
Red

Colourless

→ Fluorescein:→

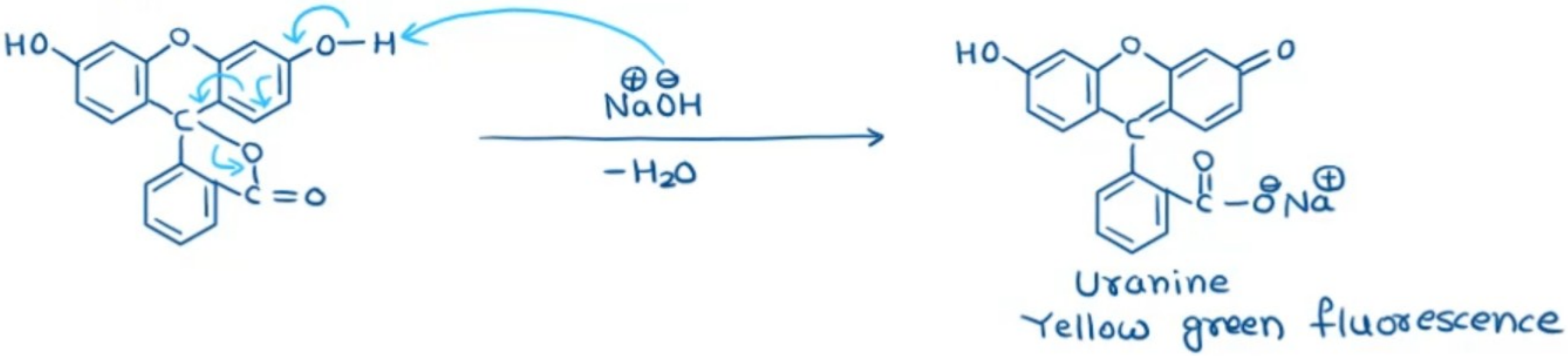
→ Synthesis:→

– Condensation of two molecules of resorcinol with one molecule of phthalic anhydride at 473 K or at 383-393 K in presence of oxalic acid gives fluoroscein.

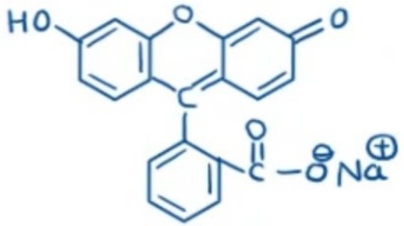


→ Properties:→

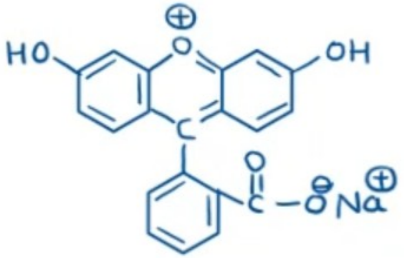
– It is a red powder insoluble in water but dissolves in alkalies to give a brown solution which produces a very strong yellowish green fluorescence due to formation of anion (uranine)



- The sodium salt of fluoroscein is called Uranine which is used to dye wool and silk
- The dark red colour of the dye is due to existence of two quinoid structures (para and ortho quinoids)



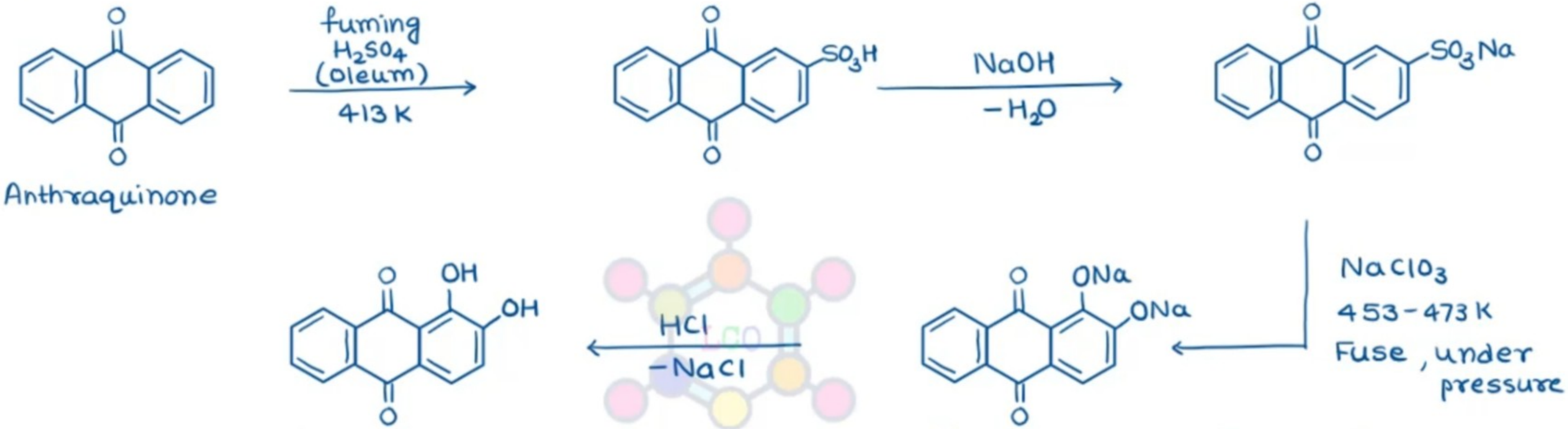
p-quinoid



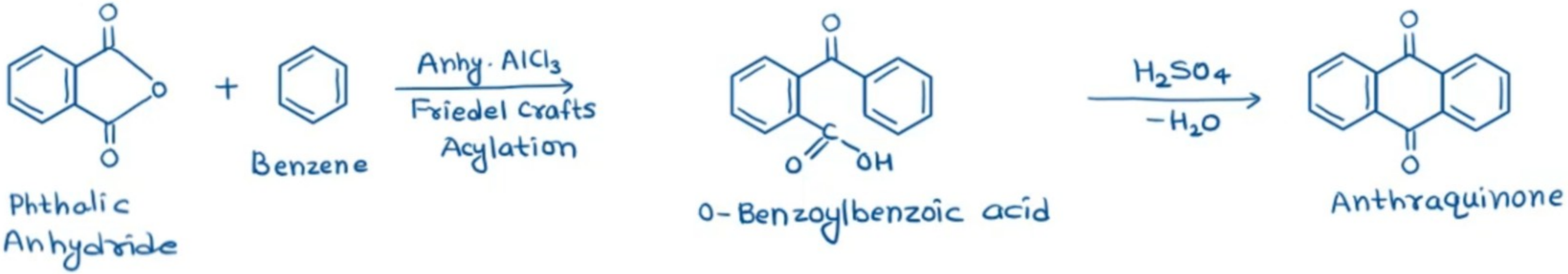
o-quinoid

→ Alizarin dye (1,2- dihydroxyanthraquinone) :→

→ Synthesis :→



– Anthraquinone used for this purpose can be obtained by Friedel-Crafts reaction.



→ Isolation of alizarin :→

- Alizarin occurs in madder root in the form of its glucoside called ruberthyric acid which on enzymatic or acid hydrolysis gives alizarin.

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

→ Physical properties :→

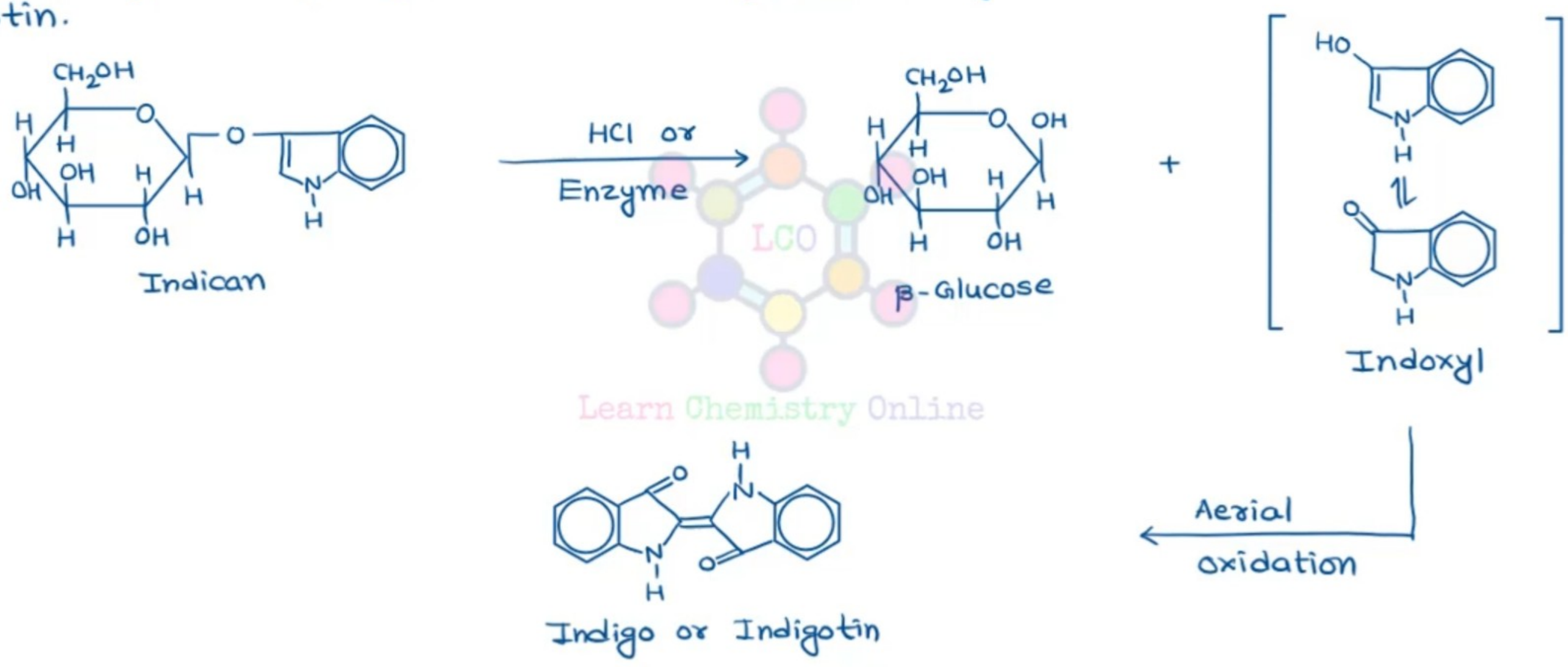
- Alizarin is a ruby red crystalline compound which sublimes on heating.
- m.p. → 563 K
- It is insoluble in water and alcohol but highly soluble in alkalies to give purple solution.

→ Uses :→

- Used as purgative.

→ Indigo :→

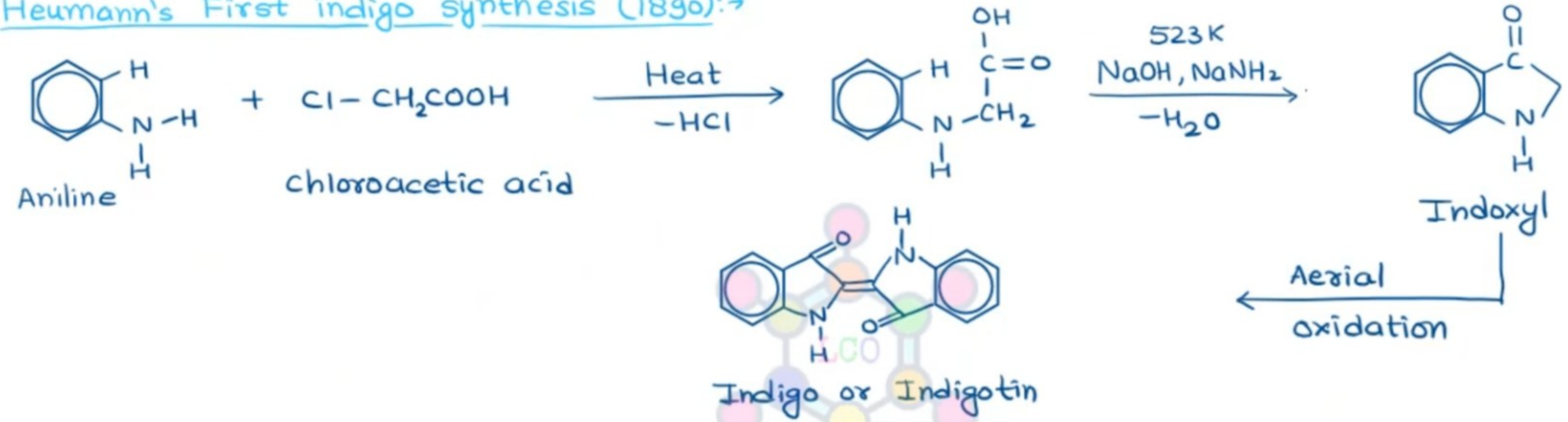
- Indigo is the oldest vat dye with india as its place of origin and is officially called indigotin.
- It is found naturally in indian plant, *indigofera tinctoria* and the European plant, *isatis tinctoria* as glucoside of indoxyl.
- Acid or enzymatic hydrolysis of indican yields indoxyl which on aerial oxidation gives indigotin.



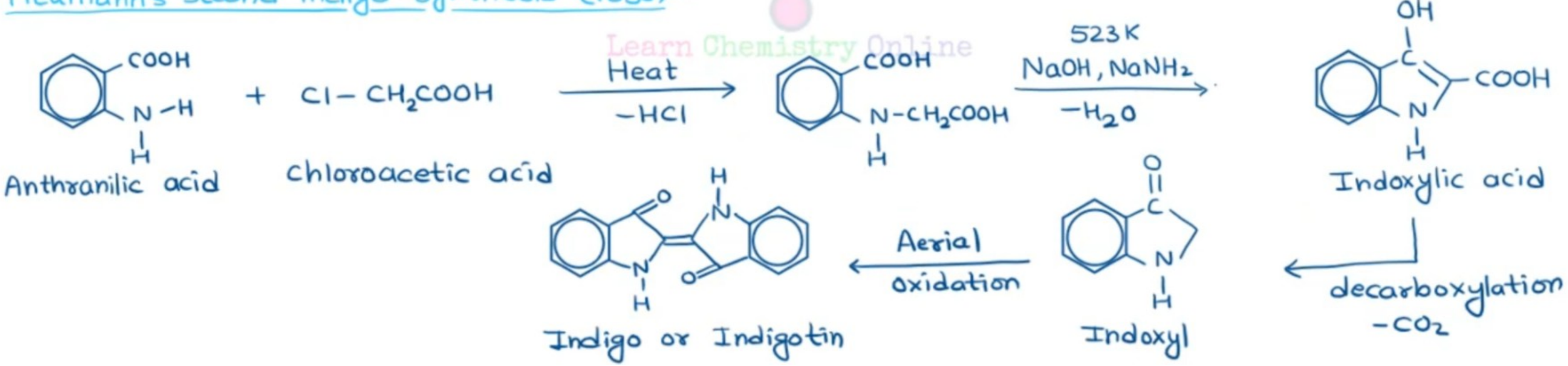
→ Synthesis of indigotin:→

– Indigotin can be synthesised by following three methods –

(i) Heumann's First indigo synthesis (1890):→



(ii) Heumann's second indigo synthesis (1896):→



→ Physical properties:→

- Indigotin is a dark blue compound.
- m.p. 663 K
- It is insoluble in water and many other organic solvents.

→ Chemical properties:→

- On reaction with alkaline sodium hyposulphite, insoluble indigotin is reduced to soluble colourless form (leuco form). The cloth to be dyed is soaked in this alkaline solution and then exposed to air when it imparts the original blue colour to the cloth due to aerial oxidation.

Indigo or Indigotin

Indigo white
(Leuco form, soluble in water)

→ Uses:→

- used as dye on large scale due to the following advantages.
  (i) colour is excellent (ii) Synthetic indigo is much cheaper than natural indigo.

→ Synthetic dyes:→

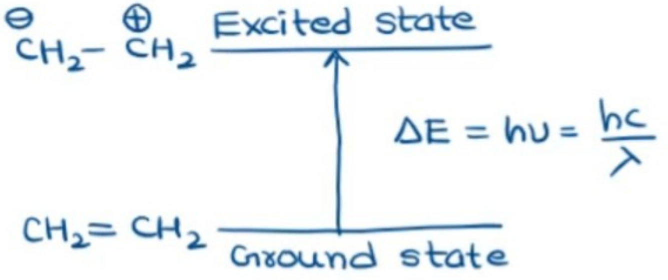
→ Modern or electronic theories of colour:→

→ Valence bond theory (VBT):→

- When a beam of light falls on a molecule, it absorb light of appropriate energy and gets excited.
- The wavelength of light absorbed depends upon the difference in the energy of ground state and the excited state (ΔE). The greater is this difference, the shorter is the wavelength of light absorbed.
- For example, ethylene is colourless but conjugated polyenes having more double bonds are coloured.
- According to VBT, the molecule of ethylene may be regarded as a resonance hybrid of the two structures (I) and (II) where structure (I) is for ground state while structure (II) is for excited state. The energy difference between these two states is quite large, due to which light (Photon) of very short wavelength (in UV range) is absorbed. This is the reason why ethylene appears colourless.

$$\underset{(I)}{CH_2=CH_2} \longleftrightarrow \underset{(II)}{\overset{\ominus}{C}H_2-\overset{\oplus}{C}H_2}$$

$$\boxed{\Delta E \propto \frac{1}{\lambda}}$$



- When the number of double bonds in conjugation increases the wavelength of absorption also increases.
- Example:-

$CH_2=CH_2$	$CH_2=CH-CH=CH_2$	$CH_2=CH-CH=CH-CH=CH_2$
Ethylene	1,3-butadiene	1,3,5-hexatriene
$\lambda_{max} = 175$ nm	$\lambda_{max} = 217$ nm	$\lambda_{max} = 258$ nm

- Based upon such observations, the following generalisations can be made-

(i) When charged structures are involved in resonance, there is lowering of energies of both the ground and the excited states.

(ii) Charged structures contribute more to the excited state than to the ground state.

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

- Hence it may be concluded that the colour of a compound will depend upon the following-

(a) Extent of conjugation:-

- The more extended is the conjugation greater is the contribution of the charged contributing forms and hence longer is the wavelength of absorption.

β-Carotene (pigment present in carrot)
(orange red) $\lambda_{max} = 478$ nm

(b) Presence of other groups:→

- The presence of both electron withdrawing or electron donating groups at the ends of the conjugated system will extend the conjugation further and hence will increase the contribution of the charged structures towards the resonance hybrid. Therefore the wavelength of light absorbed becomes longer and generally goes in the visible region i.e., the compound appears coloured.

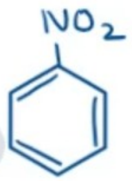
- Example:-

Colourless

$\lambda_{max} = 204$ nm

colourless

$\lambda_{max} = 230$ nm



pale yellow

$\lambda_{max} = 280$ nm

Dark yellow

$\lambda_{max} = 375$ nm

(c) Steric effect:→

- Resonance play a major role when the conjugated system is completely planar. if this coplanarity is destroyed by steric crowding, resonance will be restricted or inhibited (steric inhibition of resonance). consequently such compounds will absorb at a wavelength which is shorter than expected. Due to this intensity of colour is either decreased or the compound becomes completely colourless.

→ Synthetic dyes :→

→ Modern or electronic theories of colour :→

→ Molecular orbital theory (MOT) :→

- When an atom or molecule absorbs energy in the UV/visible region, it undergoes excitation involving transition between electronic energy levels.
- These transitions involve promotion of an electron from an occupied orbital (Ground State to an unoccupied orbital (excited state).
- Generally, the most probable transition takes place from Highest Occupied Molecular Orbitals (HOMO) to Lowest Unoccupied Molecular Orbitals (LUMO).

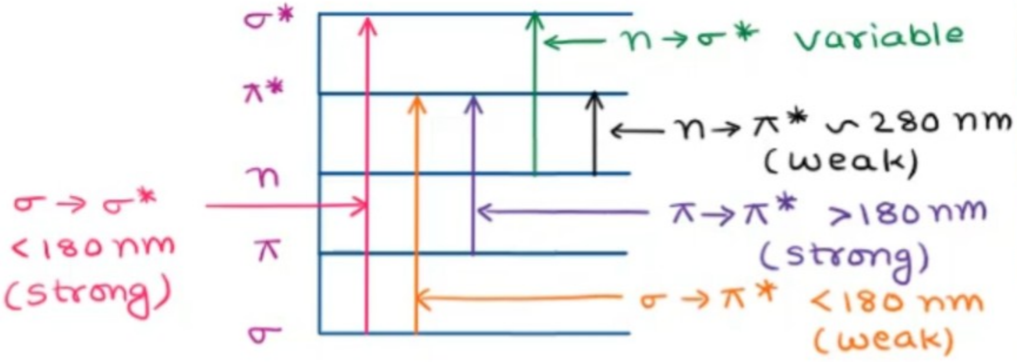
→ HOMO

- σ orbitals (σ bond)
- π orbitals (π bond)
- n orbitals (non-bonding orbitals)

→ LUMO

- σ* orbitals
- π* orbitals

→ Energy levels of various molecular orbitals



→ Various electronic transitions :-

1. From σ orbital to σ* orbital → $\sigma \rightarrow \sigma^*$
2. From σ orbital to π* orbital → $\sigma \rightarrow \pi^*$
3. From π orbital to π* orbital → $\pi \rightarrow \pi^*$
4. From n orbital to σ* orbital → $n \rightarrow \sigma^*$
5. From n orbital to π* orbital → $n \rightarrow \pi^*$

- The order of energies for various electronic transitions is as follows-

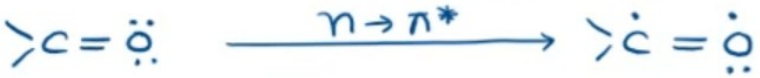
$$\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$$

$$\xrightarrow{\hspace{10cm}}$$

Decrease in energy (or increase in wavelength) of absorption.

- Out of all transitions, only $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions can occur in UV range.
- The $n \rightarrow \pi^*$ transition requires minimum energy and hence occurs at longer wavelength and such transition is always less intense because the electrons in the n-orbital are perpendicular to the plane of the π-bond (and hence to the plane of π^* orbital) due to which the probability of the jump of an electron from $n \rightarrow \pi^*$ orbital is very low or zero according to symmetry selection rule. However, vibrations of atoms bring about a partial overlap between the perpendicular planes due to which $n \rightarrow \pi^*$ transition does occur, but only to a small extent.

$n \rightarrow \pi^*$ transitions in carbonyl group can be shown as follows-



$$>C=\ddot{\underset{..}{O}} \xrightarrow{n \rightarrow \pi^*} >\dot{C}=\dot{\underset{..}{O}}$$

- Further $\pi \rightarrow \pi^*$ transitions are more intense than $n \rightarrow \pi^*$ transitions and hence are responsible for colour.

Simple alkenes, such as ethylene, absorbs at 175 nm. But 1,3-butadiene absorbs at 217 nm due to presence of two double bonds in conjugation. This may be explained as follows-

- A double bond consist 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 (Ψ_1 and Ψ_2) are bonding and are occupied by a pair of electrons each, while the other two (Ψ_3 and Ψ_4) are antibonding and are unoccupied.

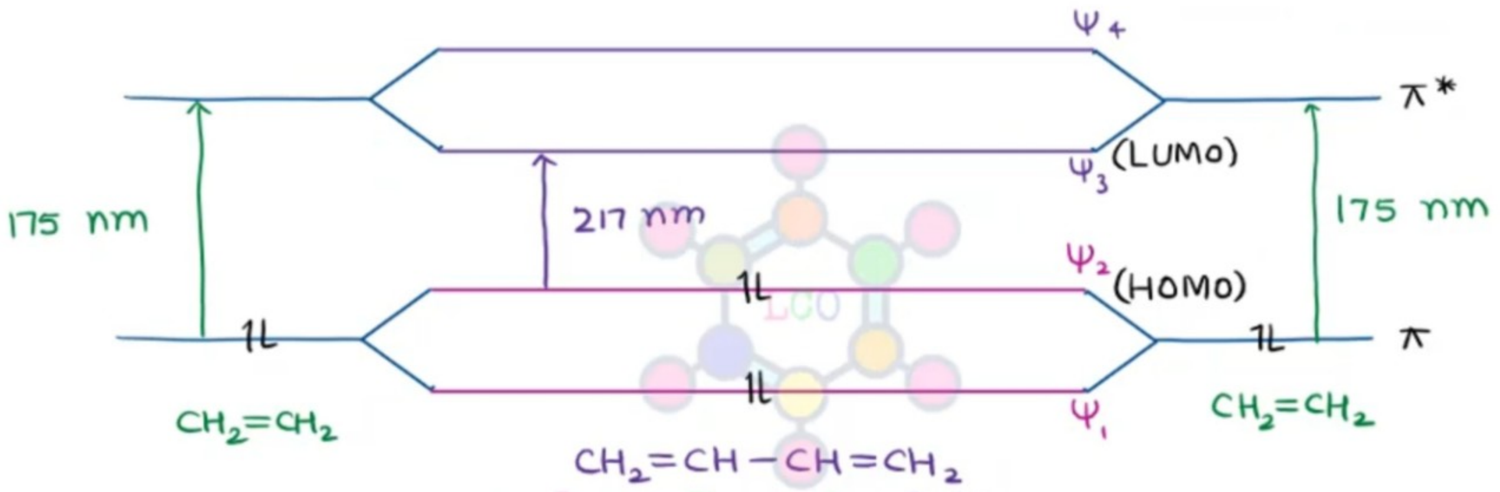


Fig:- Molecular orbitals of 1,3-butadiene

- It is clear from fig. that due to conjugation the energy of LUMO (Ψ_3) is decreases while that of the HOMO (Ψ_2) increases, thereby decreasing the gap between two orbitals and hence lesser amount of energy is required for the transition.
- So, with increasing conjugation in double bond, energy gap between HOMO and LUMO decreases and hence wavelength is increases.

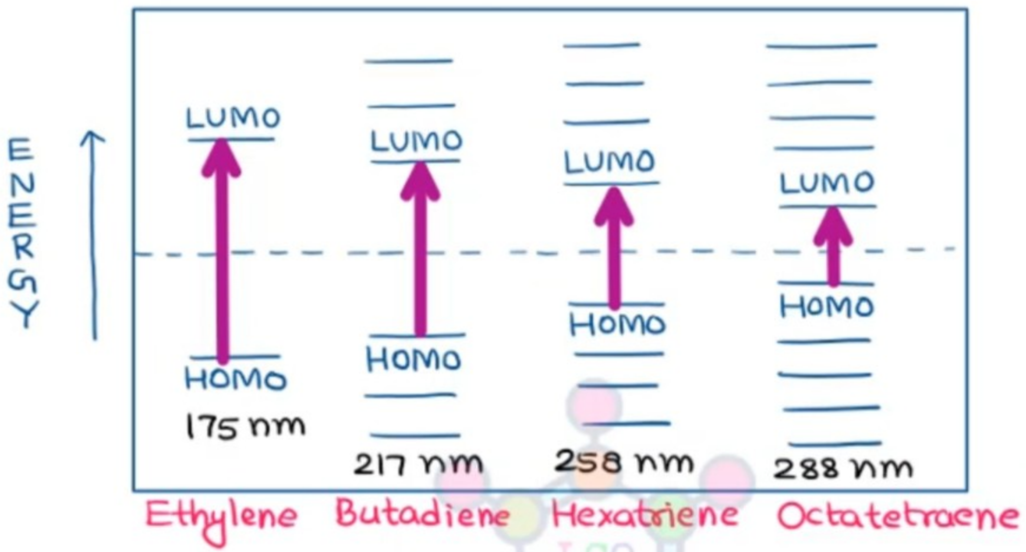


Fig:- As conjugation increases, the energy gap b/ω HOMO and LUMO decreases and absorption shifts to longer wavelength

- In case of higher polyenes, $CH_3(CH=CH)_nCH_3$, where $n>5$, the absorption band occurs in the visible region and the compound appears coloured.
- Further, in case of aromatic compounds, as the number of fused rings increases, the position of absorption approaches the visible region.

Naphthalene
$\lambda_{max} \rightarrow 275$ nm
(Colourless)

Anthracene
$\lambda_{max} \rightarrow 375$ nm
(Colourless)

Naphthacene
$\lambda_{max} \rightarrow 474$ nm
(Yellow)

Pentacene
$\lambda_{max} \rightarrow 580$ nm
(Blue)