Dyes

Definition

Dye is a natural or coloured subs-tances which is used in solution to stain materials specially fabrics, paper, leather, etc. All the coloured substances are not dyes. A coloured substance is termed as a dye if it fulfils the following conditions:

i) It must have a suitable colour.
ii) It can be fixed on the fabric either directly or with the help of mordant
iii) When fixed, it must be stable in light and washing. i.e; it must be resistant to the action of water, washing soda and soap.
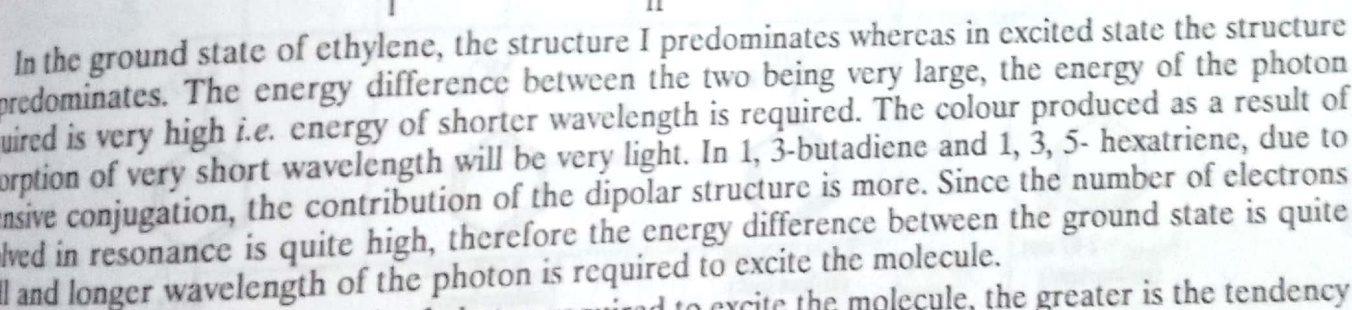
(RCO) grou...

2. Electronic theories – Modern theories of colour. Two electronic theories – Valence Bond (VB) Theory and Molecular Orbital (MO) Theory have been proposed for explaining the origin of colour. The valence band theory explains colour of dyes on the basis of electron pairs while molecular orbital theory explains the colour of dyes in terms of single electrons.

(a) Valence Bond Theory

According to this theory electron pair of a molecule in its ground state are in a state of constant oscillation and when such a molecule is placed in light, it absorbs photon of appropriate energy and gets excited. The wavelength of light (photon) absorbed depends upon the energy difference of the ground and excited states of the molecule. The smaller is this difference, the greater is the wavelength of light absorbed. According to this theory
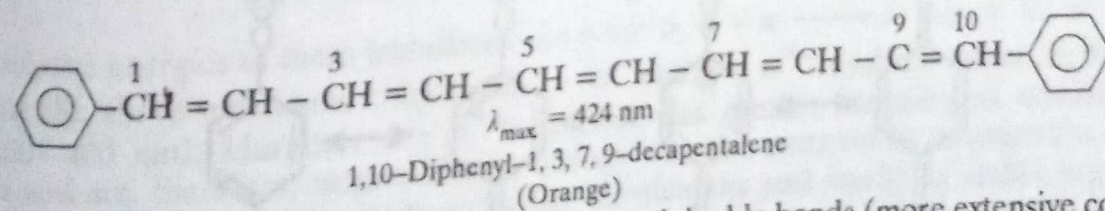
(i) Resonance is involved between various structures of the molecule which dipolar structures also contribute.

(ii) Due to contribution of dipolar structure, the energy difference between the ground and exerted states is also decreased or the energy of both, the ground state and excited state, is decreased.

(iii) The greater the number of electrons participating in the resonance, the smaller is the energy difference between the ground and excited state of the molecule and greater the wavelength of light absorbed.

(iv) The contribution of the dipolar structure is greater in excited state in comparison to the ground state.

Ethylene is colourless while butypolyene is coloured. Infact, the intensity of colour increases with the increase in number of double bonds in the molecule. This can be explained on the basis of valence bond theory. Ethylene can be considered as a resonance hybrid of following structures I and II.

$$CH_2 = CH_2 \longleftrightarrow \overset{+}{CH_2} - \overset{\ominus}{CH_2}$$
$$\text{I} \qquad\qquad \text{II}$$

In the ground state of ethylene, the structure I predominates whereas in excited state the structure II predominates. The energy difference between the two being very large, the energy of the photon required is very high i.e. energy of shorter wavelength is required. The colour produced as a result of absorption of very short wavelength will be very light. In 1, 3-butadiene and 1, 3, 5- hexatriene, due to extensive conjugation, the contribution of the dipolar structure is more. Since the number of electrons involved in resonance is quite high, therefore the energy difference between the ground state is quite small and longer wavelength of the photon is required to excite the molecule.

The longer is the wavelength of photon required to excite the molecule, the greater is the tendency produce the colour. Hence the colour producing tendency is an the following order.

$$CH_2 = CH_2 \qquad CH_2 = CH-CH = CH_2 \qquad CH_2 = CH-CH = CH-CH = CH_2$$
$$\lambda_{max} = 175 \text{ nm} \qquad \lambda_{max} = 217nm \qquad\qquad \lambda_{max} = 258 \text{ nm}$$
Ethylene (colourless)   1, 3-Butadiene   1,3, 5–Hexatriene
                         (Colourless)   (Colourless)

$$\bigcirc\text{-}\overset{1}{C}H = CH - \overset{3}{C}H = CH - \overset{5}{C}H = CH - \overset{7}{C}H = CH - \overset{9}{C} = \overset{10}{C}H\text{-}\bigcirc$$
$$\lambda_{max} = 424 \text{ nm}$$

1,10–Diphenyl–1, 3, 7, 9–decapentalene
(Orange)

...has 11 conjugated double bonds (more extensive conjugation) the ...colour

It may be noted here that the colour of the compound is actually the complementary colour of the light absorbed.

When some group, which exerts electron donating inductive or resonance effect (i.e. groups with $+I$ ($+$ R-effect) or electron with drawing inductive or resonance effect (i.e. group with $-I/-$ R effect) is present at the end of the conjugated system, then the conjugation becomes more extensive due to the involvement of the lone pairs of electrons present on the heteroatoms with the π electrons of the conjugated system. This results in the increase of the contribution of the charged structures (i.e. dipolar) towards the resonance hybrid.
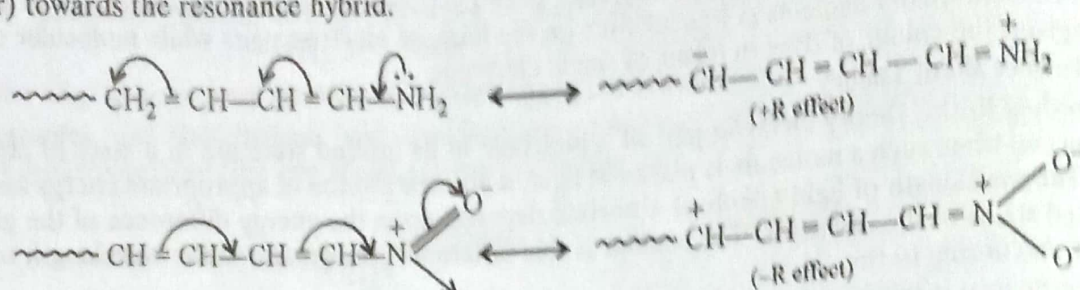
As a consequence, the required wavelength of the photons to produce the colour, becomes still longer. *This can be explained as below.*

Benzene is resonance hybrid of two ketone structures together with some contribution by the dipolar (charged) structures also. Though benzene itself is a chromophore, yet it is colourless.
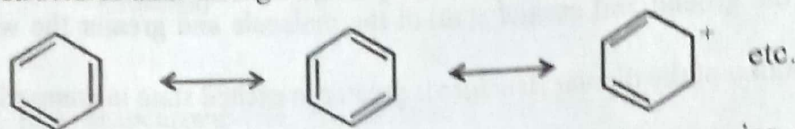

When some chromophore like $-NO_2$ group is attached with the benzene ring, then the compound absorbs at a higher wavelength. Similarly, when auxochromes like $-NH_2$ and $-OH$, group are attached with the benzene ring, then increase in resonance takes place and wavelength of the photon required to excite the molecule increases.
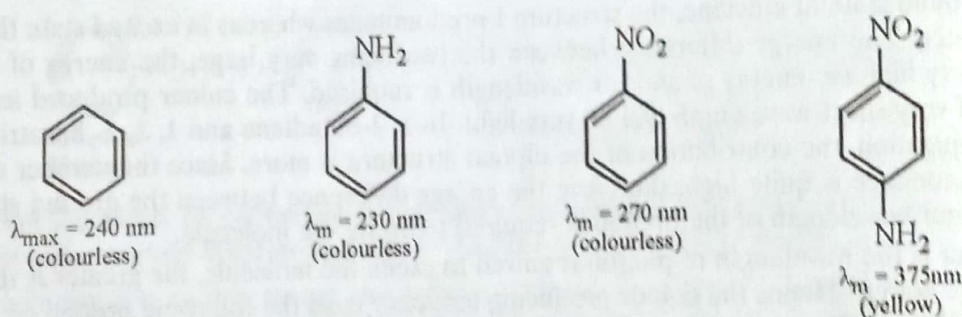
The colour of quinones may be explained by resonance among the charged structures.
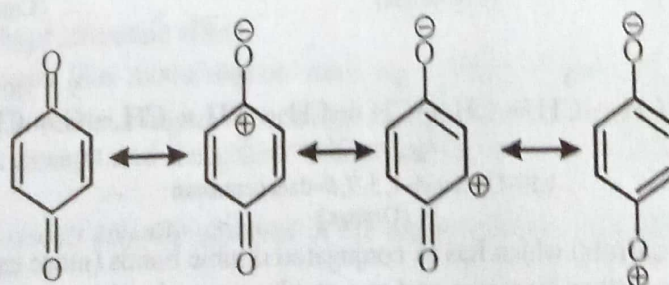
There are similar resonating structures for o-benzoquinone.
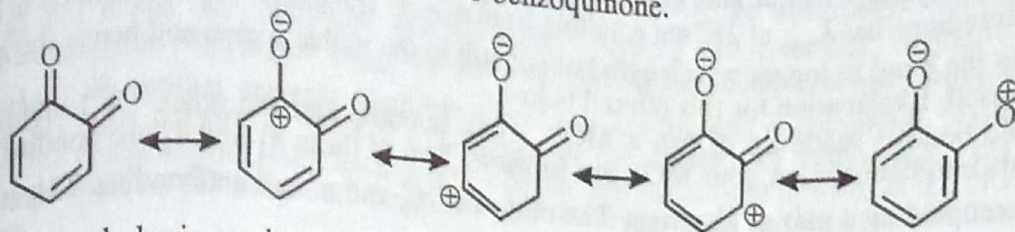
All compounds having quinonoid structures (ortho or para) are coloured Further greater the number of resonating structures for a compound, deeper will be its colour. For example, ortho form can be represented by greater number of resonating structures than the para form, the former will be deeper in colour. For example o-quinone is red and p-quinone is yellow.

Resonance in a conjugated system is maximum or effective when the system is planar or nearly planar. If due to some steric effects, the resonance is hindered, the colour of the compound which was due to resonance will diminish or disappear.

(b) Molecular Orbital Theory.

According to molecular theory, one electron gets transferred from bonding or non-bonding orbital to an antibonding orbital when a molecule absorbs a photon of light on being placed in the path of a beam of light. Different types of electron transitions take place depending on various types of electrons present in a molecule.

A transition in which a bonding σ electron is excited to an antibonding σ-orbital is called $\sigma - \sigma^*$ transition.

A transition in which a bonding π electron is excited to an antibonding π-orbital is called $\pi - \pi^*$ transition.

A transition in which one electron of a lone pair (i.e. non bonding pair of electrons) to an antibonding π^* orbital is called the $n - \pi^*$ transition. This is shown in Fig. 1.
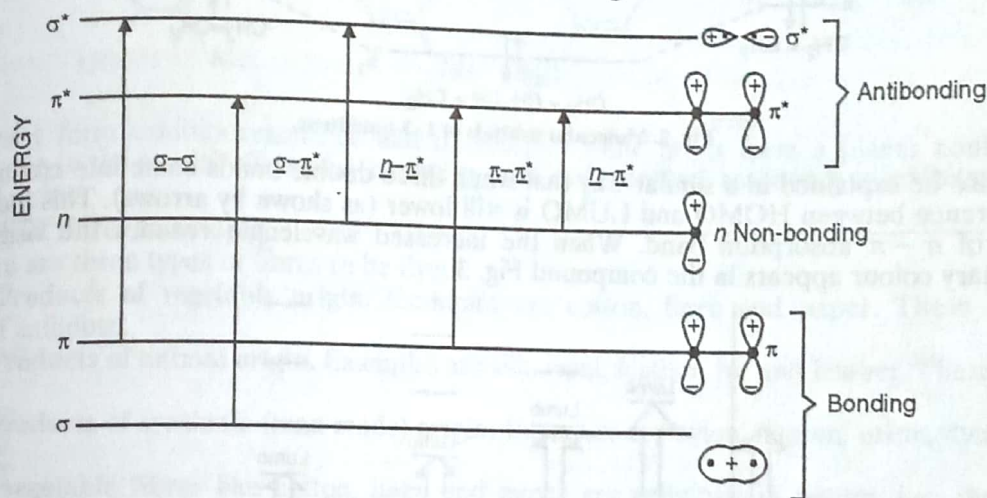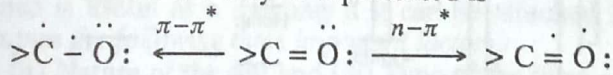

Fig. 1. Electronic transitions in molecules.

This type of transition takes place in molecules containing double bonds involving heteroatoms, e.g. $>C = O$, $>C = S$, $>C = N-$ etc. and may be represented is

$$>\overset{..}{C} \overset{..}{-} \overset{..}{O}: \overset{\pi - \pi^*}{\longleftarrow} >C = \overset{..}{O}: \overset{n - \pi^*}{\longrightarrow} >\overset{.}{C} = \overset{.}{O}:$$

The relative energies of there transitions are $\sigma - \sigma^* > \sigma - \pi^* \longrightarrow \pi - \sigma^* > n - \pi^*$

Among the above mentioned transitions $\pi - \pi^*$ and $n - \pi^*$ transition occur in the ordinary UV region (200–400 nm). Moreover $\pi - \pi^*$ transitions has greater intensity as compared to $n - \pi^*$ transitions and are, therefore, responsible for colour with the increase in conjugation, the absorption resulting from $\pi - \pi^*$ transitions shifts to longer wavelengths and finally to visible region and is thus responsible for colour. This is explained as below :

In case of ethylene, there are two types of transitions viz, $\sigma - \sigma^*$ and $\pi - \pi^*$. As the longest wave

length band absorbs at 175 nm and hence this band occurs in the far ultraviolet region, ethylene is colourless. Butadiene has λ_{max} at 217 nm resulting from $\pi - \pi^*$ transition. The conjugation in butadiene has shifted to the band to longer wavelength but not still in the visible region and hence the intensity is greatly increased. Explanation for this offered below.

A double bond is made up of two π MO's — one bonding and the other. On bringing the two double bonds into conjugation, four MO's are forward. Two of these π_1 and π_2 are bonding and each of them is occupied by a pair of electrons. The other two π_3^* and π^* are antibonding. This is shown in Fig. 2.

From Fig. 2 it is evident that the energy of **HOMO** (*highest occupied molecular orbital*) H_2 increases and that of **LUMO** (*the lowest unoccupied molecular orbital*) π_3^* decreases. As a consequence, the energy levels involved in $\pi - \pi^*$ transition come closer and therefore smaller energy is required. Thus the energy difference between π_2 and π_3^* orbitals in 1, 3-butadiene is considerably smaller than that between the corresponding energy difference in ethylene. It is because of this 1, 3-butadiene absorbs at a longer wavelength (217 nm) than ethylene (175 nm). Moreover because the energy levels come closer, their interaction in the excited state is increased and thus the intensity of absorption in 1, 3-butadiene is higher.
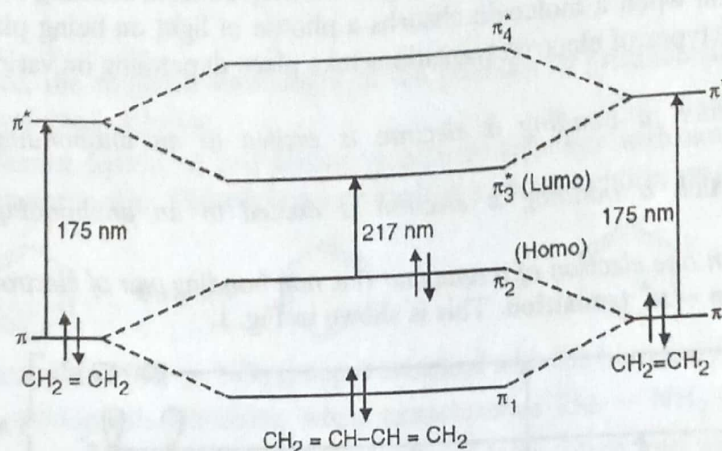

Fig. 2. Molecular orbitals of 1, 3-butadiene.

It can also be explained in a similar way that when three double bonds come into conjugation the energy difference between HOMO and LUMO is still lower (as shown by arrows). This increases the wavelength of $n - \pi$ absorption band. When the increased wavelength reaches the visible region, complementary colour appears in the compound Fig. 3.
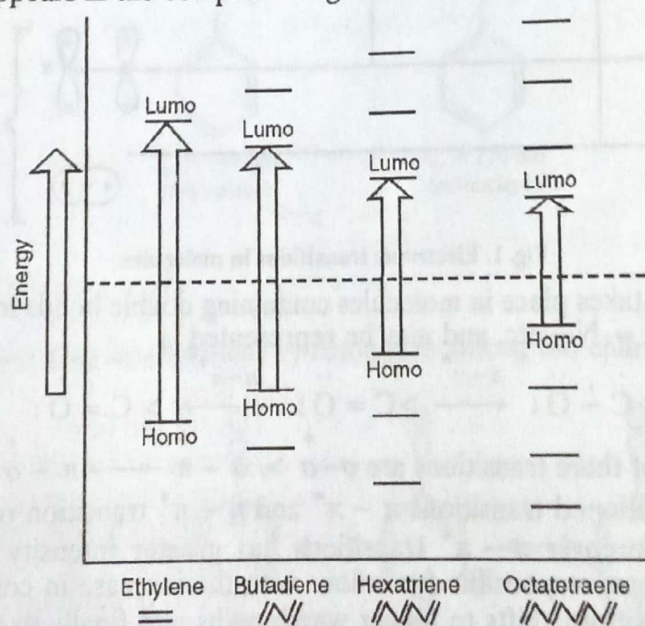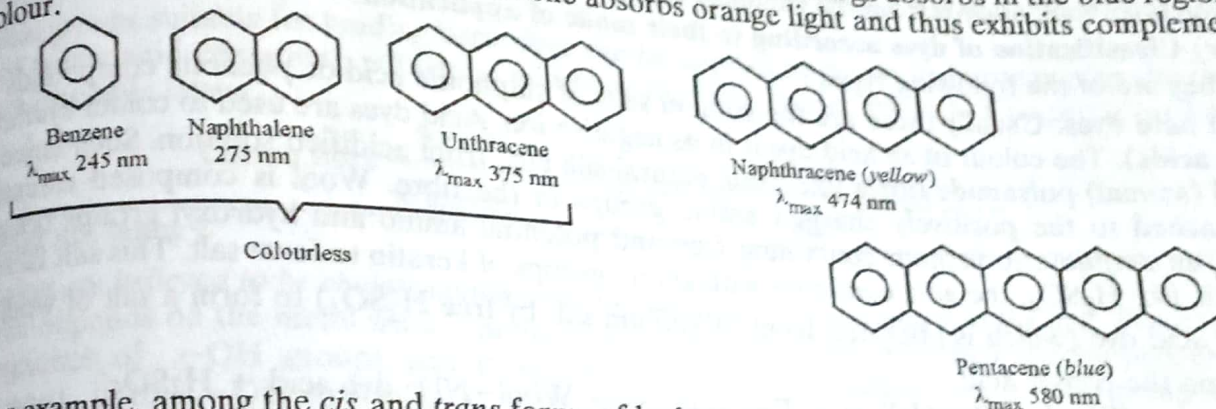

Fig. 3. The energy difference between HUMO and LUMO decreases with the increase in conjugation this shifting the absorption bands to longer wavelengths.

For example, in polyenes, $CH_3(CH = CH)_n CH_3$, when $n = 6$, the absorption band occurs in the blue region and hence the compound exhibits complementary yellow colour. Similarly, β-carotene absorbs in the greenish blue region (λ_{max} 478 and 422) and exhibits complementary orange colour.

Let us take up another example. Benzene absorbs at 254 nm and is colourless. Naphthalene and anthracene are also colourless. With the increases in the number of fused rings, the absorption approaches the visible region. Naphthacene with four linearly fused rings absorbs in the blue region and exhibits complementary yellow colour. Pentacene absorbs orange light and thus exhibits complementary blue colour.

Benzene
λ_{max} 245 nm

Naphthalene
275 nm

Unthracene
λ_{max} 375 nm

Naphthracene (yellow)
λ_{max} 474 nm

Colourless

Pentacene (blue)
λ_{max} 580 nm

For example, among the *cis* and *trans* forms of hydroxyazo compound, azophenol, the *trans* form is coloured where the *cis* form is colourless.

cis
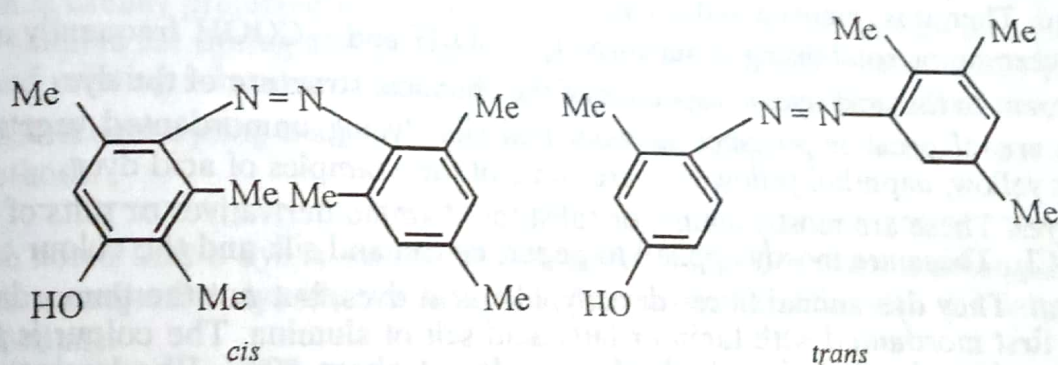
trans

The *trans* form exhibits resonance and is coloured while in *cis* form a planar configuration is prevented due to the spatial effect of *o*–methyl groups and therefore resonance is inhibited. Hence *cis* form is colourless.