

Relation between Color and constitution

Electro magnetic radiation

Light is electromagnetic radiation (that is, it has both electrical and magnetic components) vibrating in transverse wave packets, or quanta.

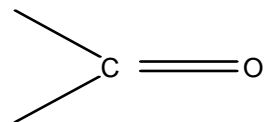
The vibration may occur in all planes or in one only (plane polarized light), each plane having right and left circular vector components. We may measure the amplitude of the wave quantum (intensity of the light), its frequency, ν , and/or wavelength, λ (color or tone), and its velocity in a given medium, v .

Color, Chromophore and Auxochromes

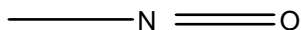
The carbonyl and ethylene (vinyl) groups have chromophoric properties only when they are present in the molecule in multiple conjugated order. Thus, acetone is colorless, while diacetyl is yellow, as is benzil which is deeper yellow, and triketopentane is yellow-orange. Since it is the delocalization of pi-electrons that is related to the production of color, it is evident from these examples that such delocalization accompanies multiple conjugated unsaturation.

Chromophores

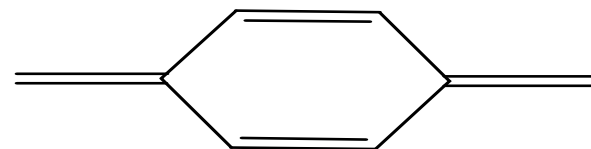
- O.N. Witt observed in 1876 that coloured compounds contain certain unsaturated groups which he called chromophores and compound containing a chromophore is called a chromogen. When certain groups called auxochrome are present in the chromogen a dye is obtained.



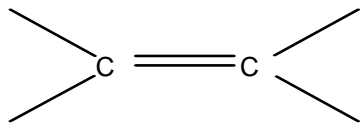
K e t o



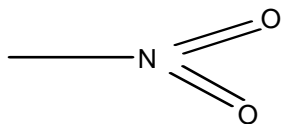
N i t r o s o



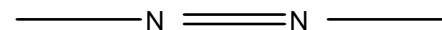
Q u i n o n o i d



\ E t h y l e n i c



N i t r o

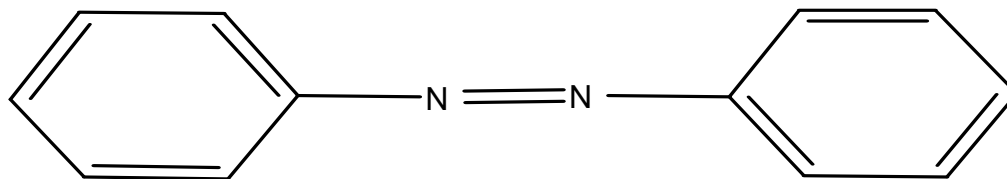


A z o

C h r o m o p h o r e s

Auxochromes

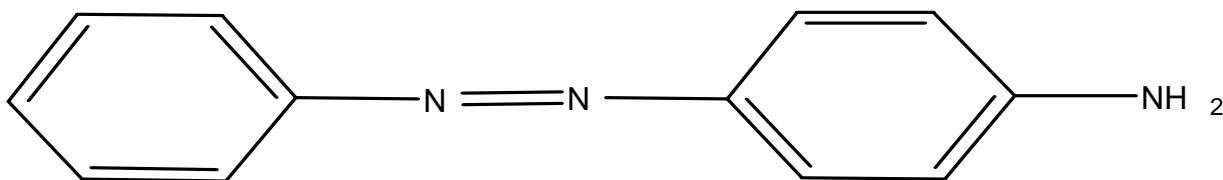
Auxochrome may be either acidic or basic like -OH or -NH₂. Other auxochromes include -COOH, -SO₃H, -NR₂ these groups form salts with either acids or alkalies. they also form hydrogen bonds with certain groups (-OH of cellulose or NH₂ of wool, silk).



(Azobenzene)

containing -N=N- chromophore

Not serving as dye



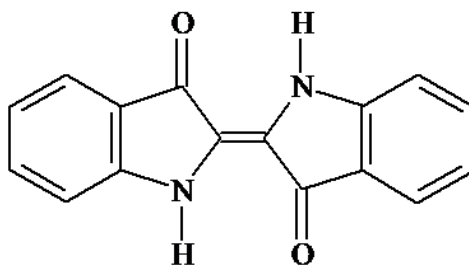
(p-Aminoazobenzene)

-NH₂ auxochrome

A disperse dye

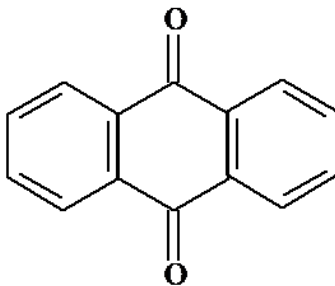
CLASSIFICATION BASED ON CHEMICAL NATURE

- **Indigoid dyes:** This is the most important group of natural dyes. The dyestuff is extracted from *Indigofera tinctoria*, a bush pea family. The dye was used pre-historically in India, where it probably originated. The word is derived from “Indican”.



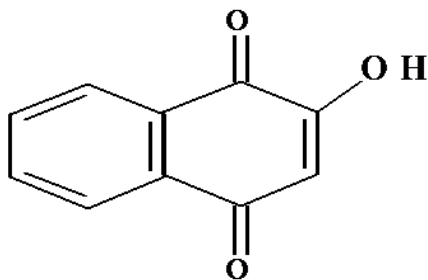
Anthraquinone dyes

Anthraquinone dyes: Some of the most important red dyes are based on the anthraquinone structure. They are obtained both from plants and insects. These dyes are characterized by good fastness to light. They form complexes with metal salts and the resultant metal-complex dyes have good wash fastness.



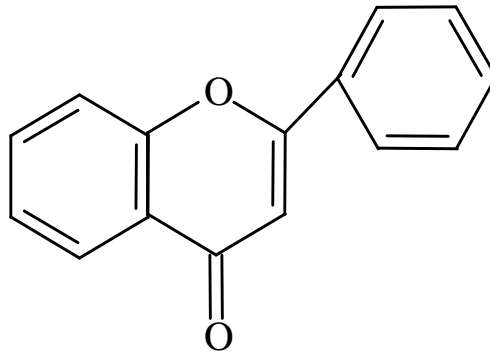
Alpha-naphthoquinones

Alpha-naphthoquinones: The most prominent member of this class of dyes is lawsone. It is obtained from *Lawsonia inermis*



Flavones:

Flavones: Flavone is colorless organic compound. Most of the natural yellow colors are hydroxy and methoxy derivatives of flavones and isoflavones. It is obtained from as dust on flowers and seeds of various *Primula* species, in buds of various varieties of poplar, in yellow dahlias, in weld (*Reseda luteola*) and dyer's broom (*Genista tinctoria*).

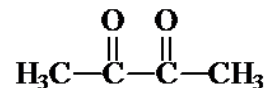
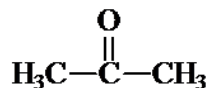


RELATION BETWEEN COLOR AND CONSTITUTION

Like the physical and chemical properties of organic compounds, there is a definite relationship between the color and constitution e.g., Benzene is colorless, whereas its isomer, fulvene is colored. The following theories have been proposed to explain the observed general relationships existing between color and constitutions

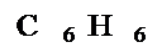
- **Witt's theory (Chromophore-Auxochrome theory):** In 1876 Witt put forward a theory according to which the color of a substance is mainly due to the presence of an unsaturated group known as chromophores (Greek *chroma* - color, and *phores* - bearing). The important chromophores are:
 - - C = C -
 - - C = N -
 - - C = O -
 - - N = N -
 - - NO₂
 - - Quinoid rings

- The compounds possessing chromophores are known as chromogens. The chromopheric groups are of the following two types.
- When a single chromophore is sufficient to impart color to the compound. Examples are: -NO, -NO₂, -N=N, =N=N-N, -N=N→O, p-quinonoid etc.
- When more than one chromophore is required to impart the color, e.g. >C=O, >C=C< etc. This can be exemplified by various examples. Acetone (having one >C=O as chromophore) is colorless, whereas biacetyl (with two >C=O) is yellow.

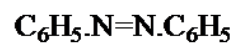


How does it work

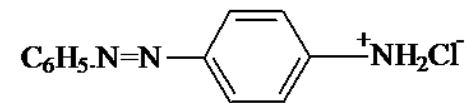
Since the auxochromes are capable of forming salts either with a basic or acidic groups their presence also convert a colored compound (devoid of salt forming groups) into a dye which must fix permanently to the fiber, i.e., it must be fast to water, light, soap and laundering, when fixed to the fiber. The permanent fixing of dye to the fiber is generally due to the formation of chemical bond between the fiber and the auxochrome. This can best be exemplified by the following examples.



Benzene

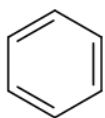


Diazobenzene

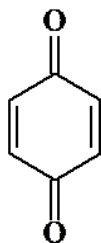


Armstrong Theory (Quinonoid theory):

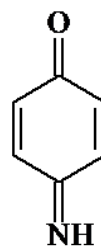
- **Armstrong Theory (Quinonoid theory):** Armstrong in 1885 suggested that all coloring matters may be represented by quinonoid structures (p- or o-), and thus believed that if a particular compound can be formulated in a quinonoid form it is colored, otherwise it is colorless. Some of the important compounds, the coloring properties of which can be explained on the basis of this theory are given below.
- On the basis of this theory we can see that benzene is colorless, where as benzoquinones are colored.
- But the quinonoid theory is not sufficient to account for the coloring characteristics of all the compounds. For example, iminoquinone and di-iminoquinone, both posses a quinoid structure even then they are colorless.



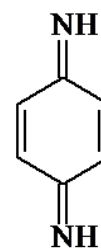
Benzene



Benzoquinones



Imnoquinone



Di-iminoquinone

Modern Theory

- **Modern Theory:** The above two theories were discussing the relationship between color and constitution are found to be only empirical. The next two important theories, which explain plausibly the relation between color and constitution, require somewhat theoretical background about the effect of light on the molecule.
 - Valence bond theory
 - Molecular orbital theory

Valence bond theory

Valence bond theory: The various postulates of this theory are as follows:

- Chromophores are groups of atoms, the π -electrons of which may get transferred from ground state to excited state by the absorption of radiation, thus producing the color.
- Auxochromes are groups, which tend to increase resonance by interacting the unshared pair of electrons on nitrogen or oxygen atoms of the auxochromes with the π electrons of the aromatic ring. This increase in resonance increases the intensity of absorption of light and also shifts the absorption band to longer wavelength. Hence there occurs the deepening of the color. From this it is evident that increase in resonance must deepen the color and actually it has been found to be so.

Further More

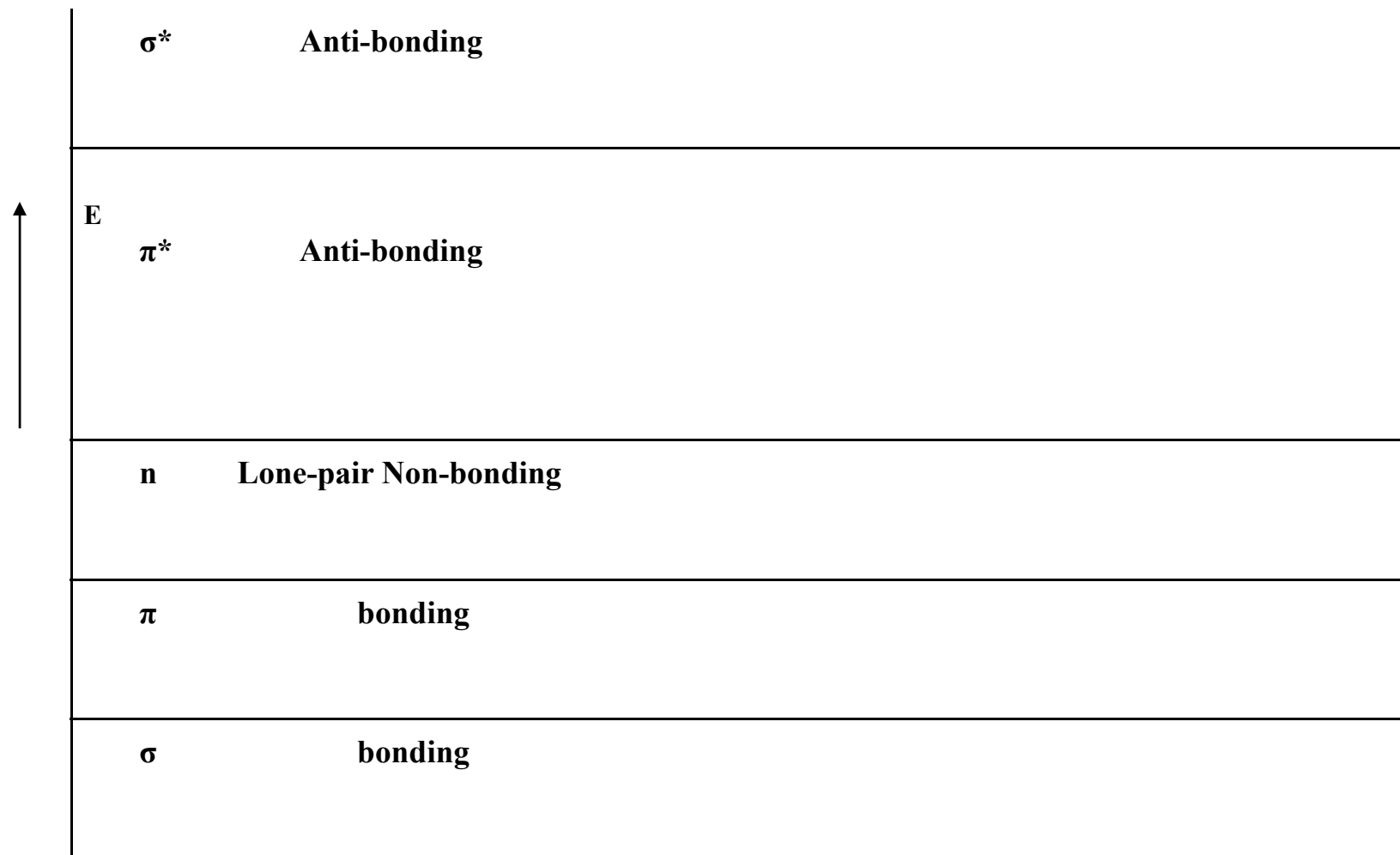
The dipole moment changes as a result of oscillation of electron pairs. The following order has been observed for the case of excitation of different groups.

- $\text{N}=\text{O} > \text{C}=\text{S} > \text{N}=\text{N} > \text{C}=\text{O} > \text{C}=\text{N} > \text{C}=\text{C}$
- Resonance theory explains the relation of the color and the symmetry of the molecule or transition dipole of the molecule because as the number of charged canonical structures increases, the color of the compound deepens. The more the possibility and longer the path for a change to oscillate in a compound, the longer wavelength of light will be absorbed and therefore deeper would be the color of the compound.

Molecular orbital theory

Molecular orbital theory: According to this theory the excitation of a molecule means the transference of one electron from an orbital of lower energy to that of higher energy. These electrons may be σ , π or n (non-bonding) electrons. The higher energy states are commonly known as anti-bonding orbitals. The anti-bonding orbitals associated with σ and π bonds are called σ^* and π^* orbitals respectively. However, there are no anti-bonding orbitals associated with n (non-bonding) electrons because they do not form bonds. Chart of the simplest form, the essential types of energy are given in the next slide:

Chart showing molecular orbitals



Electronic transitions

- The electronic transitions can occur by the absorption of ultraviolet and visible radiation. Although transitions are possible, only the following types are allowed:
 - $n \rightarrow \sigma^*$
 - $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$
- A $\sigma \rightarrow \sigma^*$ transition takes place when a bonding σ –electron is excited to an antibonding σ –orbital, i.e. σ^* . This type of transition requires a very large amount of energy as σ –electrons are very tightly bond. Hence the compounds like saturated hydrocarbons which do not have any π or σ electrons may undergo only $\sigma \rightarrow \sigma^*$ transitions. However, these transitions do not take place by absorbing in the ordinary ultra-violet region, e.g., ethane absorbs at 135 m μ .