B.Sc. IV SEM

Organic Chemistry III, CHB 401 (B)

Unit IV:

Colour and Constitutions:

Synthesis of malachite green, fluorescein, synthesis and structure of Indigotin

A Key Notes

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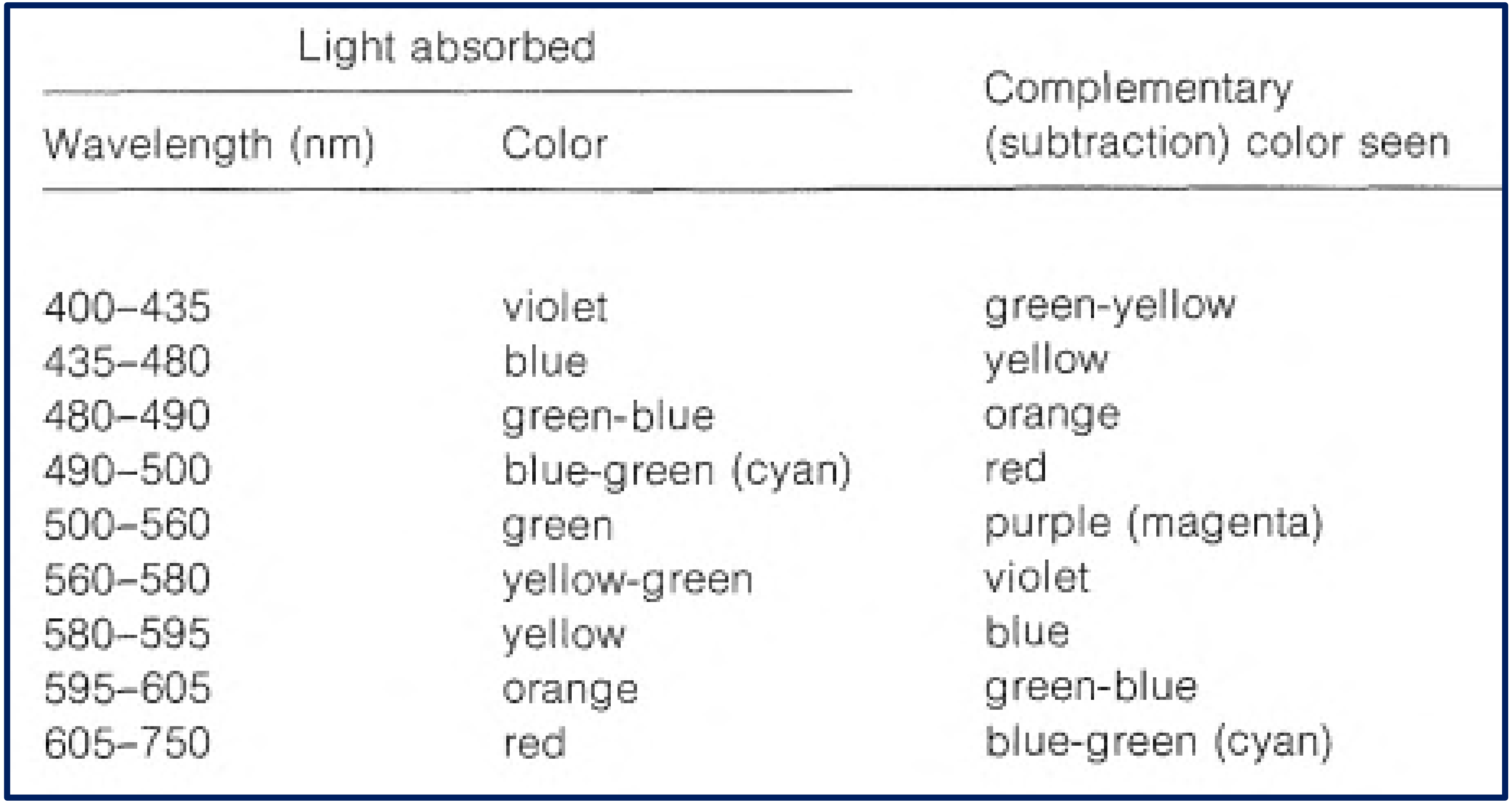
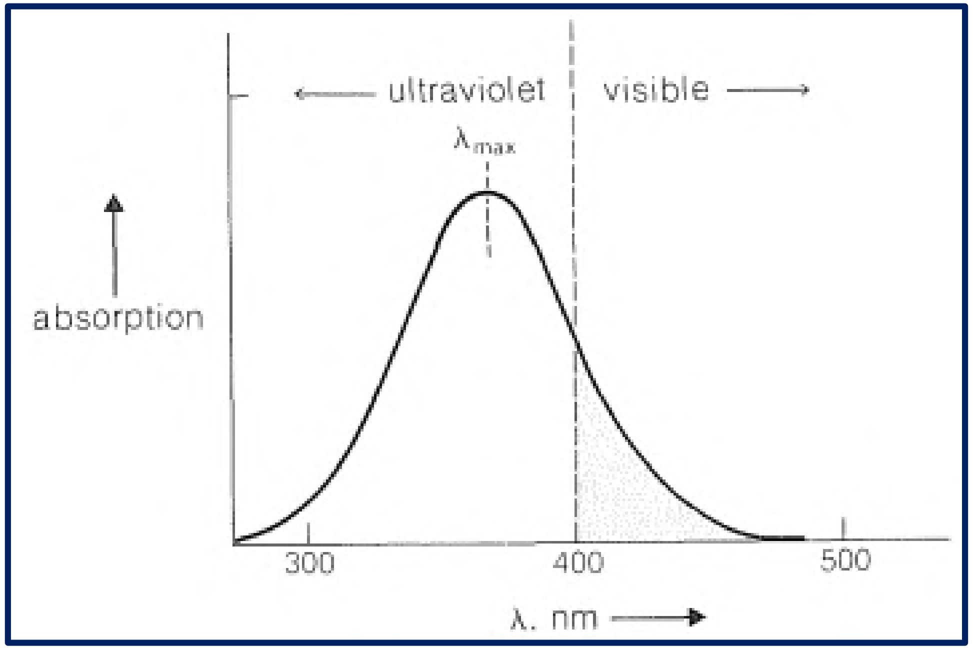
- Visible light is electromagnetic radiation having a rather narrow range of wavelengths (400-800nm).
- A black substance absorbs *all* wavelengths of visible light.
- Selective absorption of visible light by a substance imparts color, but the color is not that of the light absorbed but instead of the residual light that the substance transmits or reflects. ***For example***: a compound that absorbs in the region 435-480nm removes blue light from the visible spectrum, and the residual light is recognized by the eye as being yellow. The relationship of the observed color to wavelength of light absorbed is given below.
- It is customary to call the color observed the **complementary color** or the **subtraction color** to that absorbed.



Light absorbed		Complementary (subtraction) color seen
Wavelength (nm)	Color	
400–435	violet	green-yellow
435–480	blue	yellow
480–490	green-blue	orange
490–500	blue-green (cyan)	red
500–560	green	purple (magenta)
560–580	yellow-green	violet
580–595	yellow	blue
595–605	orange	green-blue
605–750	red	blue-green (cyan)

Note:-

- It is important to recognize that visible color will not necessarily depend on having the wavelength for maximum absorption (λ_{max}) in the visible region.
- Many substances with broad absorption bands will have λ_{max} below 400nm and yet appear strongly colored because their absorption bands extend into the visible spectrum.

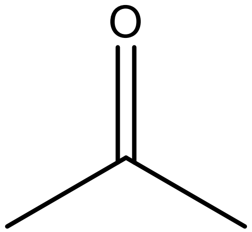


Absorption in the visible region by a colored substance that has λ_{max} in the ultraviolet

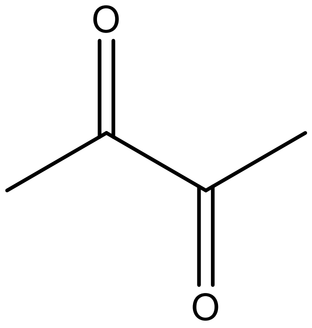
Color, Chromophore and Auxochromes

The carbonyl and ethylene (vinyl) groups have chromophoric properties only when they are present in the molecule in multiple conjugated order.

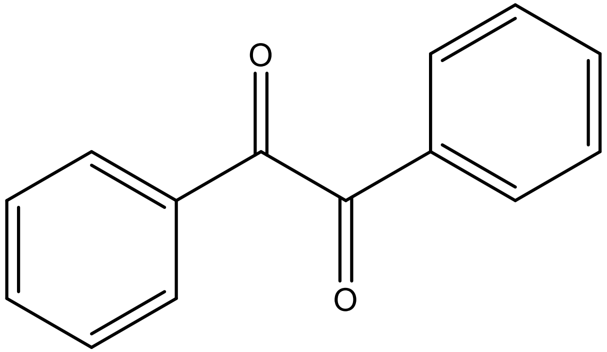
Thus, acetone is colorless, while diacetyl is yellow, as is benzil which is deeper yellow, and triketopentane is yellow-orange. Since it is the delocalization of π-electrons that is related to the production of color, it is evident from these examples that such delocalization accompanies multiple conjugated unsaturation.



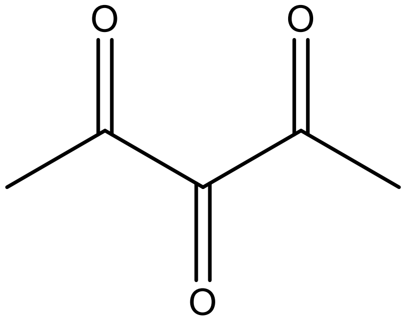
acetone



diacetyl



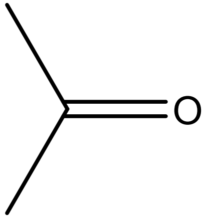
benzil



triketopentane

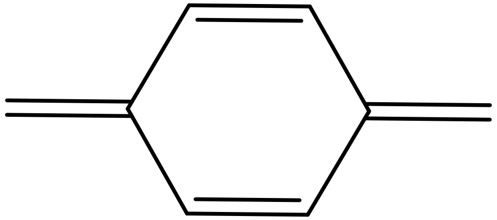
Chromophores:

O.N. Witt (1876) observed 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.

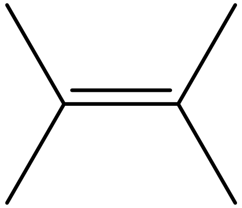


Keto

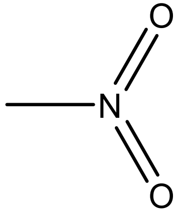
Nitroso



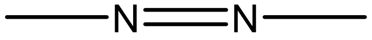
Quinonoid



Ethylenic



Nitro



Azo

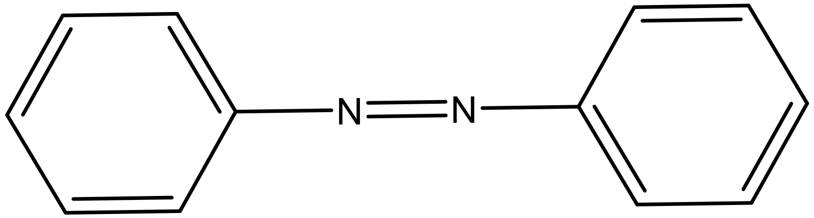
Auxochromes:

Auxochrome may be either acidic or basic like -OH or -NH_2.

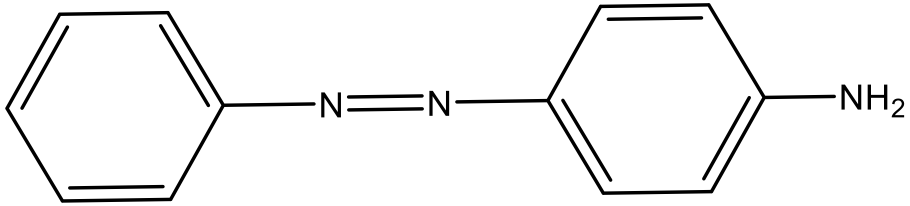
Other auxochromes include -COOH, -SO_3H, -NR_2

These groups form salts with either acids or alkalies.

They also form hydrogen bonds with certain groups (-OH of cellulose or NH_2 of wool, silk).



Azobenzene containing -N=N- chromophore
(Not serving as dye)

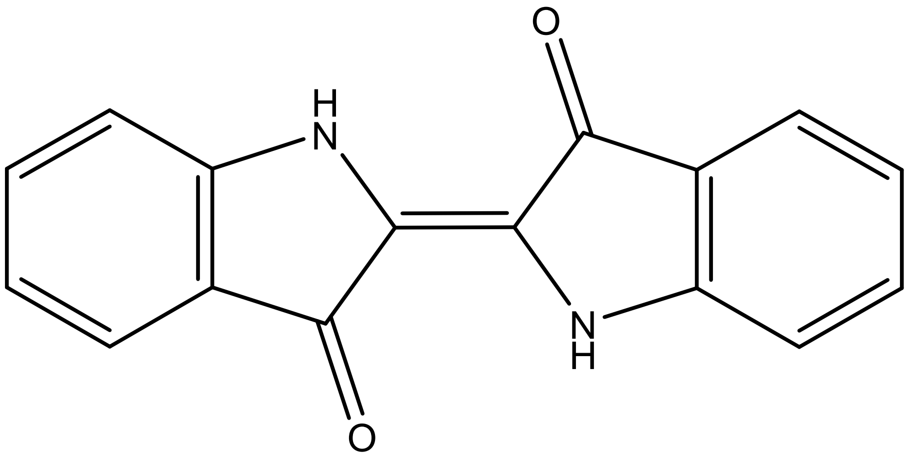


p-Aminoazobenzene containing -NH_2 auxochrome
(A disperse dye)

Classification based on chemical nature:

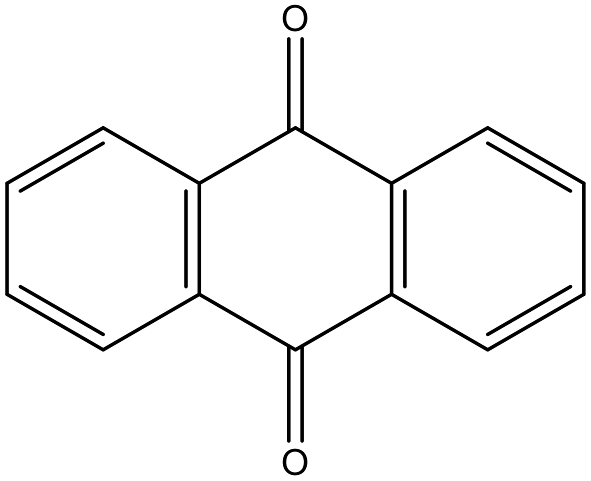
❑ Indigoid dyes:

- ✓ 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”.



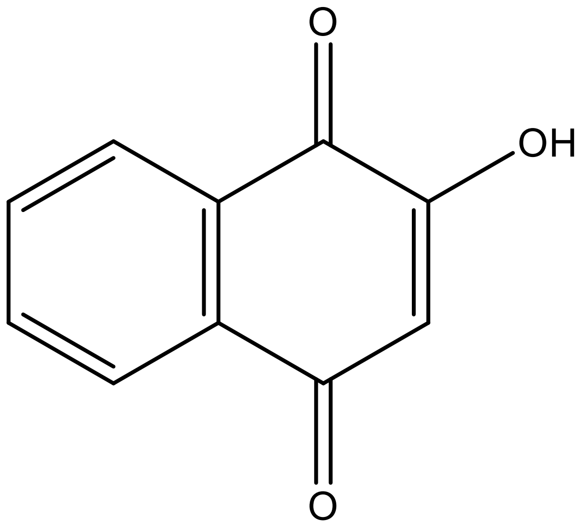
❑ Anthraquinone dyes:

- ✓ 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.



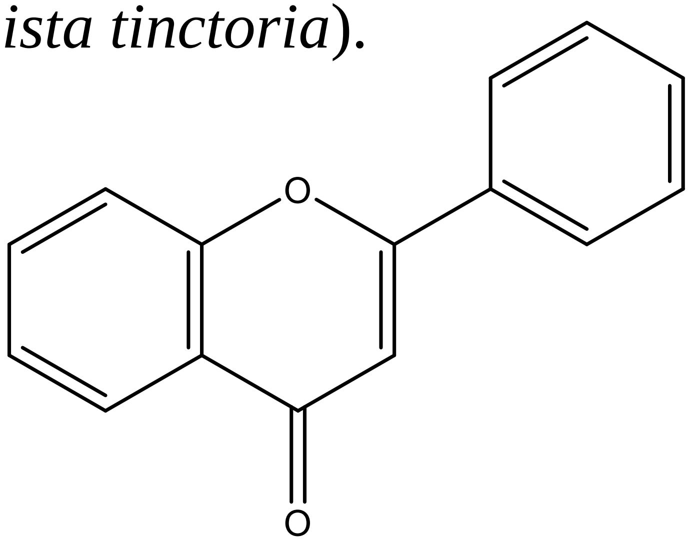
❑ Alpha-napthoquinones:

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



❑ Flavones:

- ✓ Flavone is colourless organic compound.
- ✓ Most of the natural yellow colours are hydroxyl 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.

Example: Benzene is colourless, whereas its isomer, fulvene is coloured.

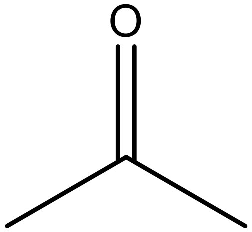
The following theories have been proposed to explain the observed general relationships existing between color and constitutions

➢ Witt's theory(Chromophore-Auxochrome theory):

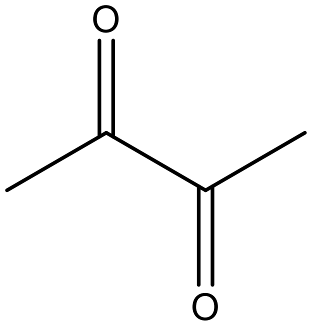
- In 1876 Witt put forward a theory according to which the color of a substance is mainly due to the presence of an unsaturated group known as chromophores (Greek *chroma-color, and phores-bearing*). The important chromophores are:

-C = C-; -C = N-; -C = O-; -N = N-; $-NO_2$; -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: -NO, $-NO_2$, -N=N, =N=N-N, $-N=N\rightarrow O$, p-quinonoid etc.
- When more than one chromophore is required to impart the color, example: >C=O, >C=C< etc. This can be exemplified by various examples. Acetone (having one >C=O as chromophore) is colourless, whereas diacetyl (with two >C=O) is yellow.



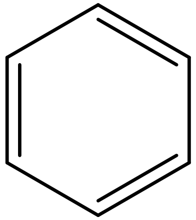
acetone



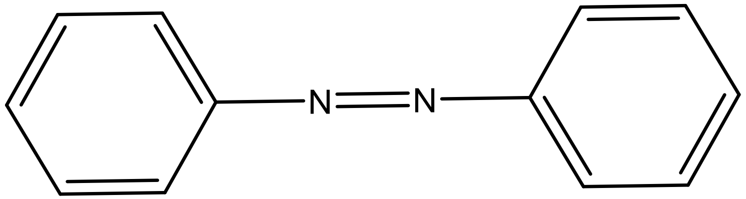
diacetyl

How does it work

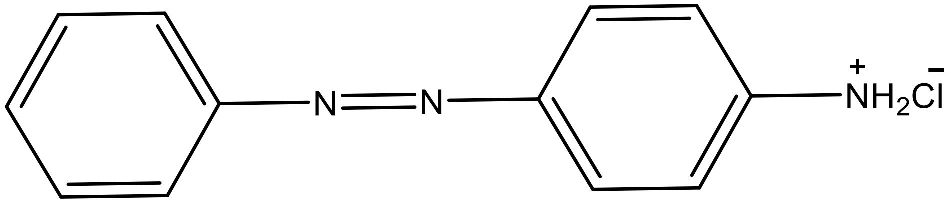
Since the auxochromes are capable of forming salts either with a basic or acidic groups, their presence also convert a coloured compound (devoid of salt forming groups) into a dye which must fix permanently to the fiber, i.e., it must be fast to water, light, soap and laundering, when fixed to the fiber. 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

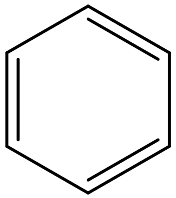


Diazobenzene

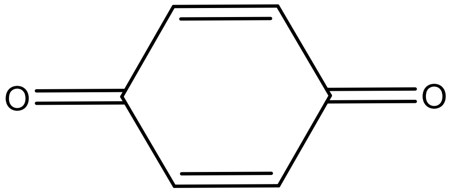


➢ Armstrong Theory (Quinonoid theory):

- Armstrong (1885) suggested that all colouring 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 coloured, otherwise it is colourless. Some of the important compounds, the colouring 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 colourless, where as benzoquinones are coloured.

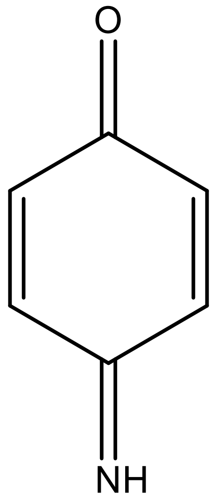


Benzene

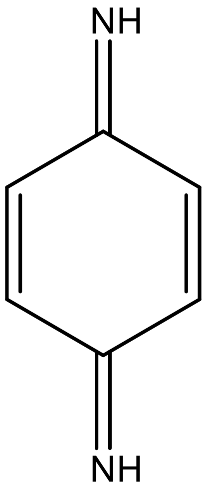


Benzoquinones

- But the quinonoid theory is not sufficient to account for the colouring characteristics of all the compounds. For example, iminoquinone and di-iminoquinone, both posses a quinoid structure even then they are colourless.



Iminoquinone



Di-iminoquinone

➢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

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.

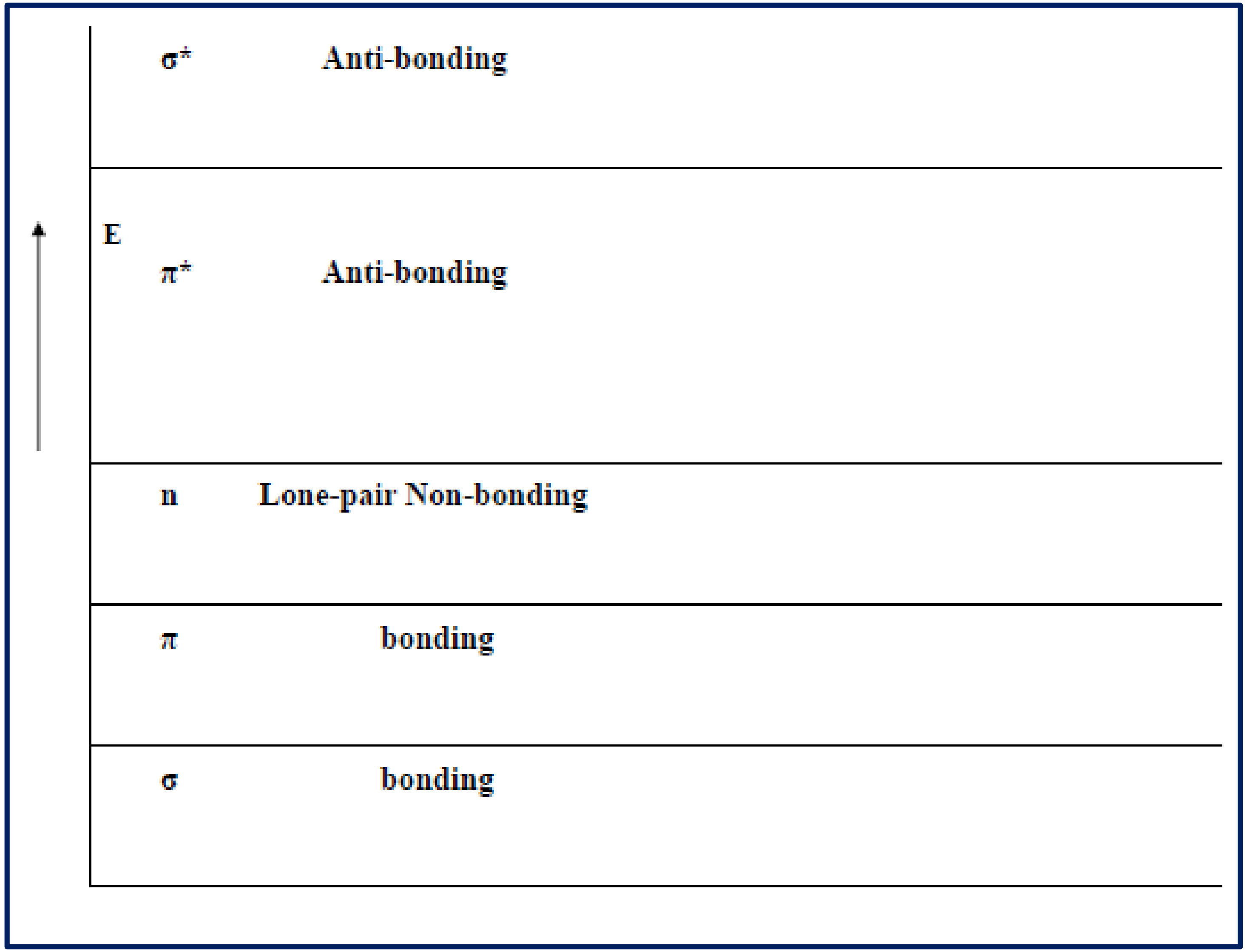
- Further, the dipole moment changes as a result of oscillation of electron pairs. The following order has been observed for the case of excitation of different groups.

  N=O > C=S > N=N > C=O > C=N > C=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

- 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.



σ* Anti-bonding

π* Anti-bonding

n Lone-pair Non-bonding

π bonding

σ bonding

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:

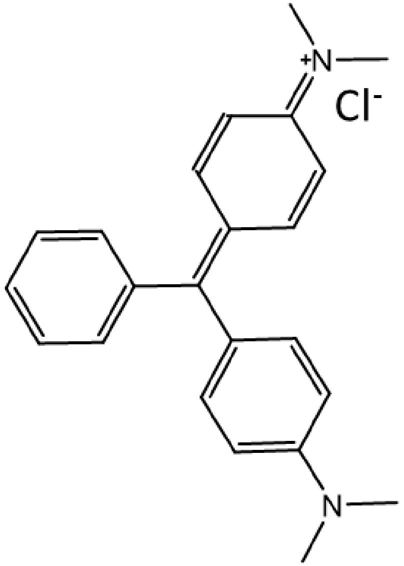
$n \rightarrow \sigma^*$

$n \rightarrow \pi^*$ 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 mμ.

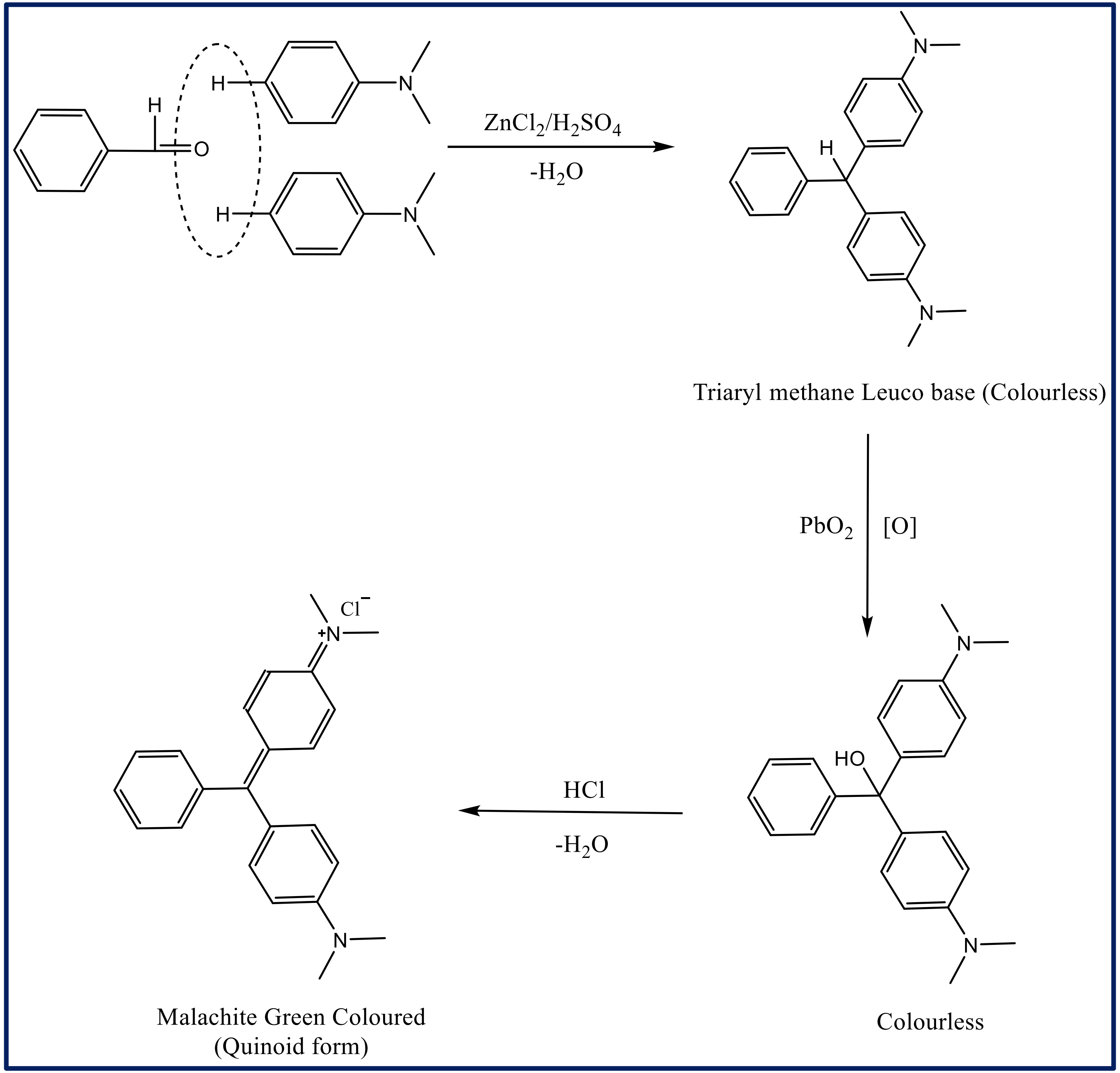
Malachite Green:

- It is a deep blue-green colour.
- It is used as a direct dye for wool and silk.
- It is obtained by treating benzaldehyde with *N*,*N*-dimethylaniline in presence of Con. H_2SO_4 to give *Leuco Base* (Greek; *Leuco* = Colourless). Oxidation of the *leuco base* with PbO_2 followed by treatment with HCl yields the dye.



Malachite Green

Synthesis:



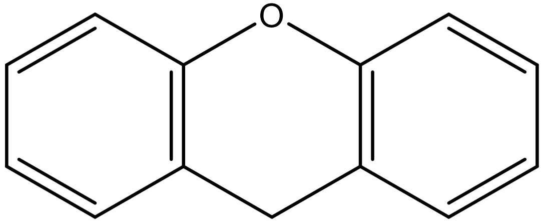
Triaryl methane Leuco base (Colourless)

Colourless

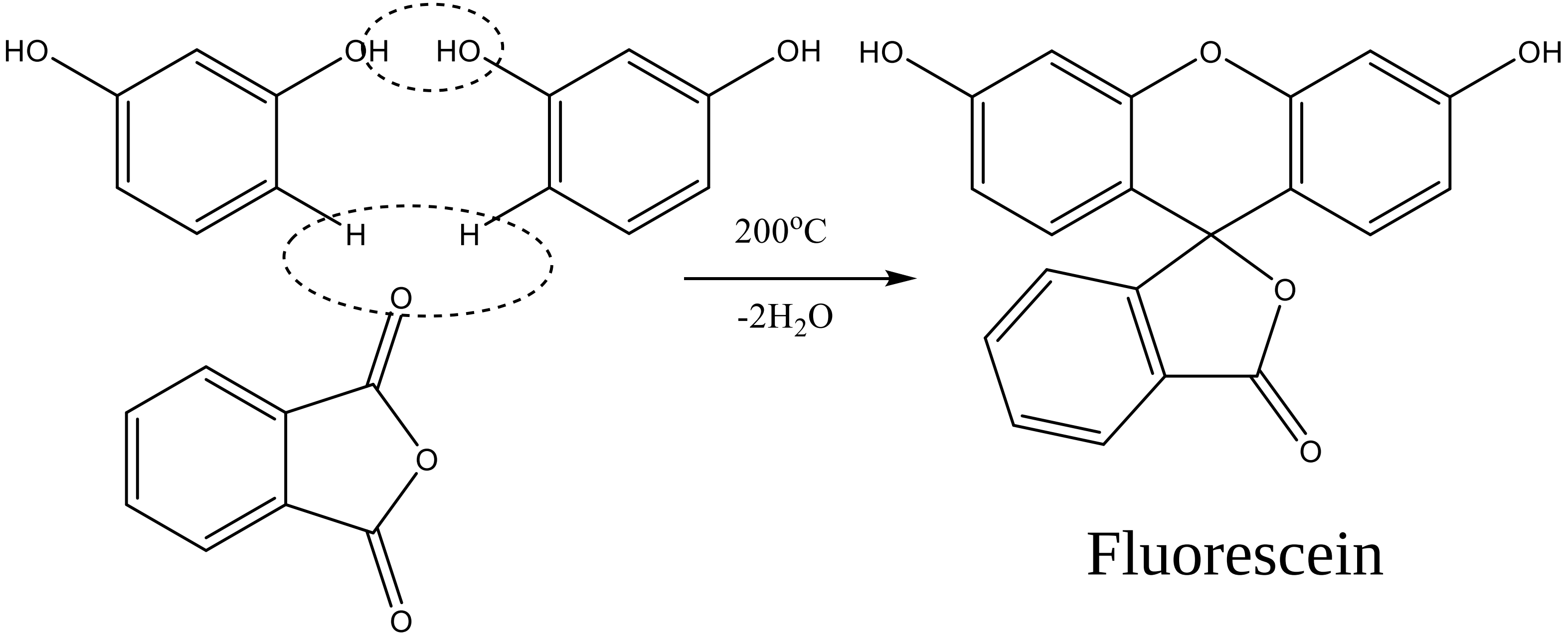
Malachite Green Coloured
(Quinoid form)

Fluorescein:

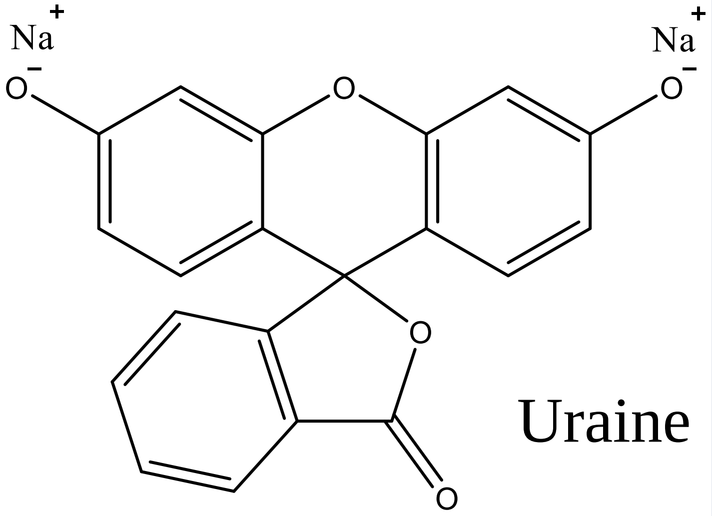
- It is a xanthene dye because it contains xanthene ring.



- It is a red powder insoluble in water but dissolves in dilute alkali and the solution gives beautiful Yellow-green fluorescence.
- The sodium salt of fluorescein is known as Uraine which is used for dyeing wool or silk yellow.
- It is obtained by heating resorcinol and phthalic anhydride with $ZnCl_2$ at 190^oC.



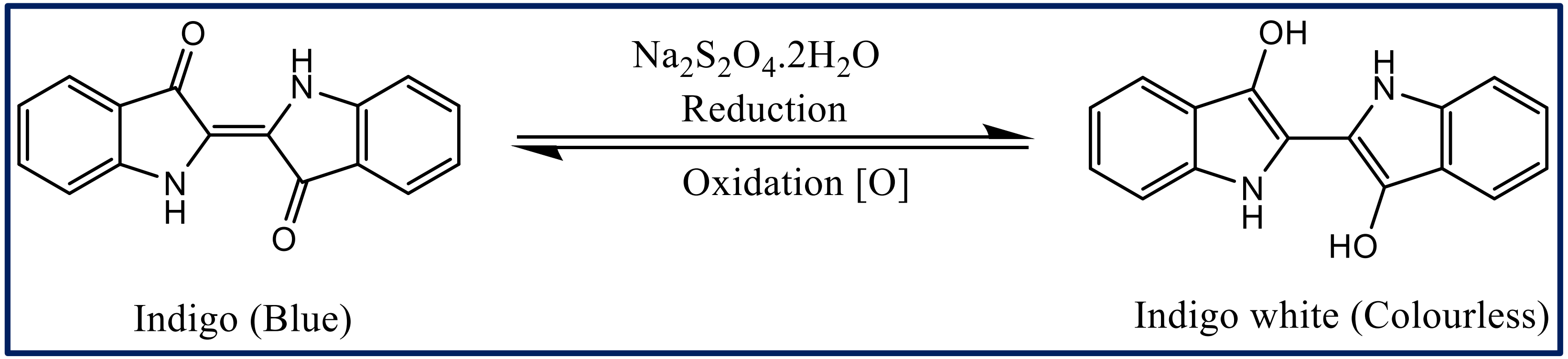
Fluorescein



Uraine

Indigotin:

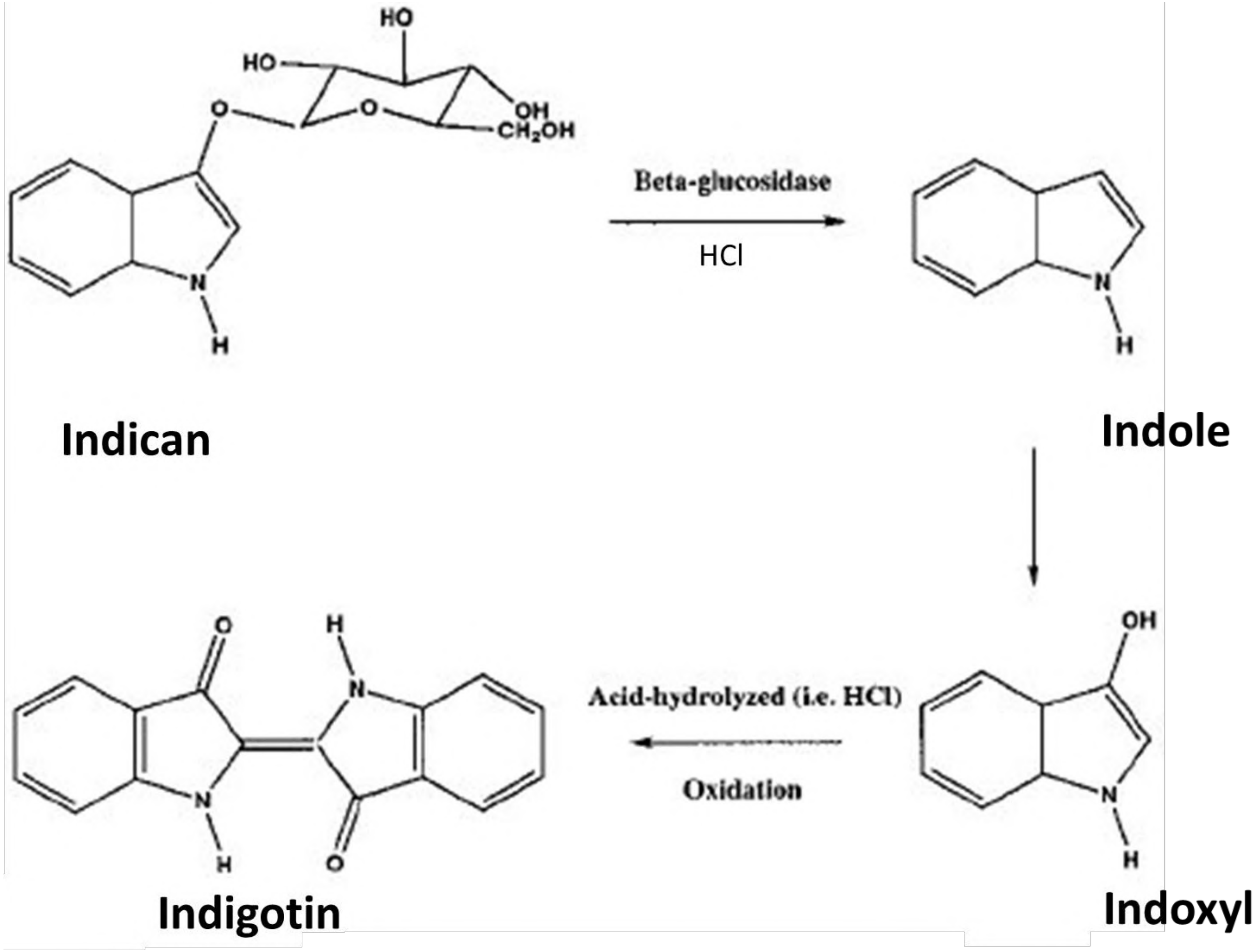
- It is a Vat dye. It is insoluble in water but on reduction with sodium hyposulphite, it forms a colourless compound which has great affinity with cotton and other cellulose. The cloth is soaked in this solution (reduced dye) and then hang in air. As a result, the colourless compound is oxidized back to the insoluble dye which is now bound to fabric.



Indigo (Blue)

Indigo white (Colourless)

- In nature, it is found in the plants of *Indigoferous* species and *Isatis tinctoria*. These plants do not contain indigotin but Indican, which is glucoside of Indoxyl. Indican on hydrolysis with HCl or enzyme is converted into Indoxyl and this on oxidation with air give Indigotin.


HO
HO
O
O
OH
CH_2OH
N
H
Indican
Beta-glucosidase
HCl
N
H
Indole
OH
N
H
Indoxyl
Acid-hydrolyzed (i.e. HCl)
Oxidation
O
H
N
N
H
O
Indigotin

Constitution of Indigotin:

☐ On the basis of vapour density, the molecular formula of Indigotin has been calculated as $C_{16}H_{10}O_2N_2$.

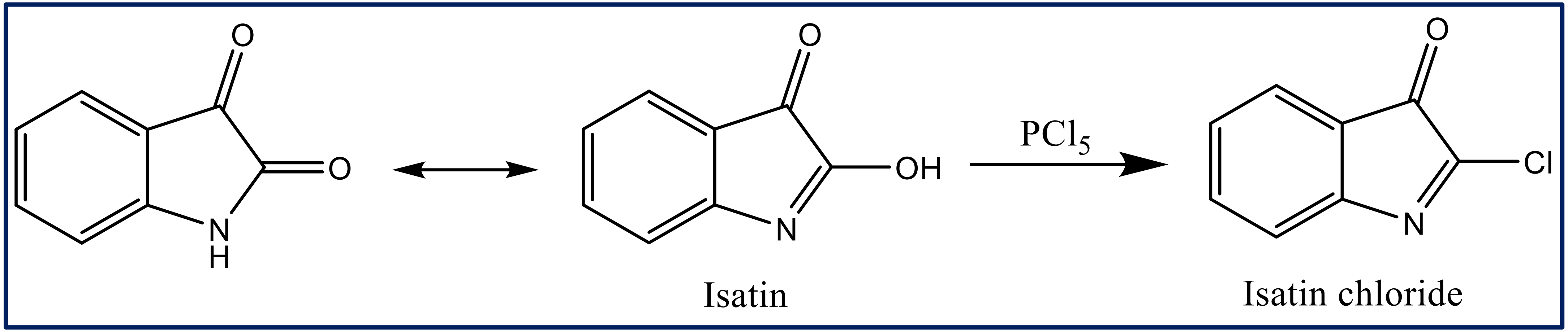
☐ On oxidation with HNO_3, it consumes two oxygen atoms and form two molecules of Isatin. From this, it is clear that the Indigotin is formed from two identical unit connected by a double bond.

$$C_{16}H_{10}O_2N_2 \xrightarrow[HNO_3]{[O]} \underset{\text{Isatin}}{2C_8H_5O_2N}$$

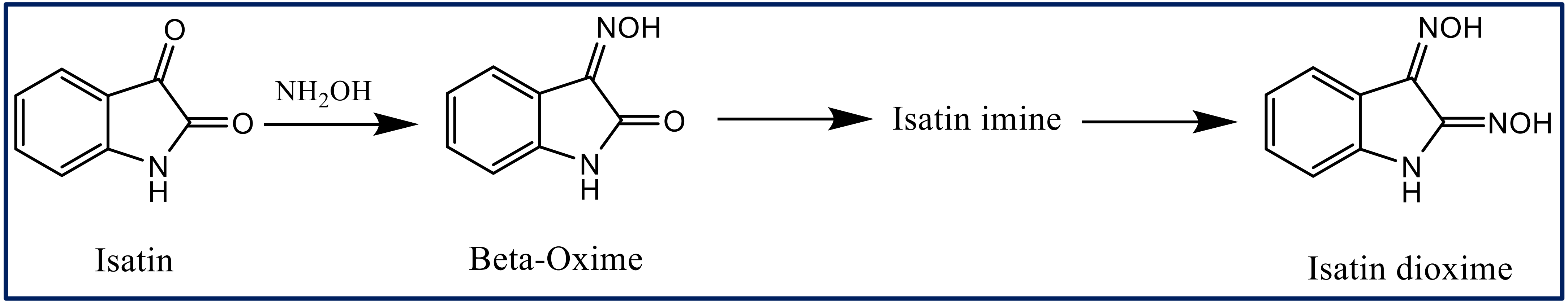
☐ **Structure of Isatin:**

✓ The molecular formula of Isatin is $C_8H_5O_2N$.

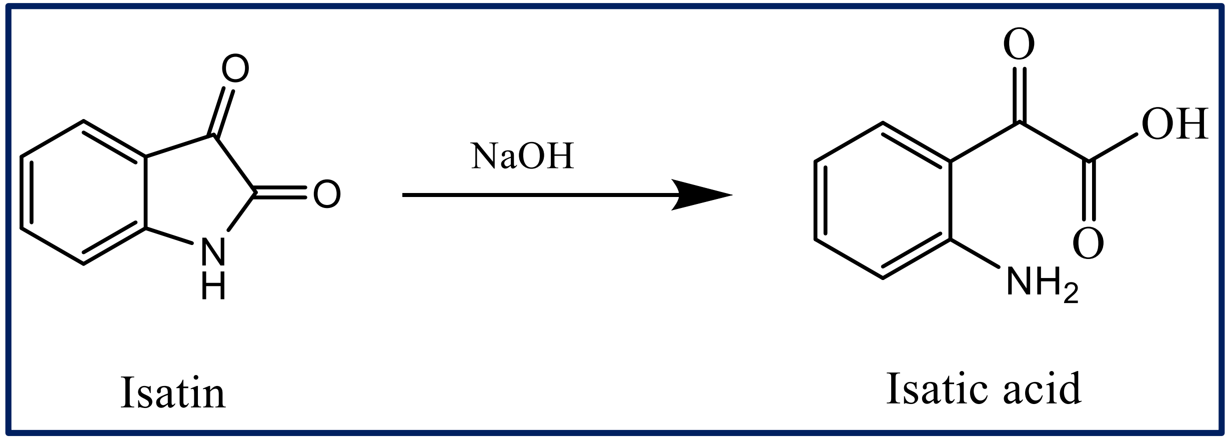
✓ On reaction with PCl_5, it forms Isatin chloride, indicates that it contains one OH group.



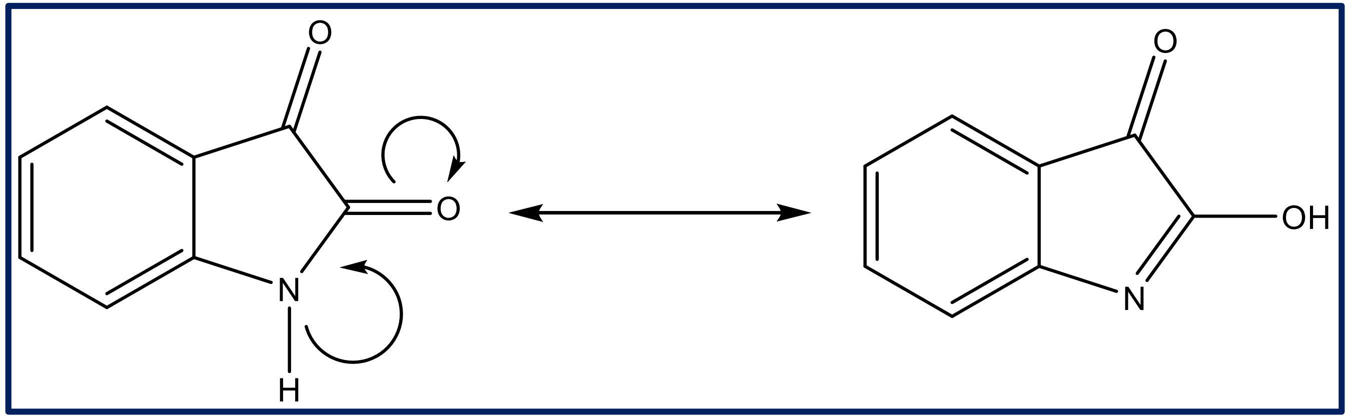
- ✓ On reaction with NH_2OH, it forms an imine, indicates the presence of carbonyl group.



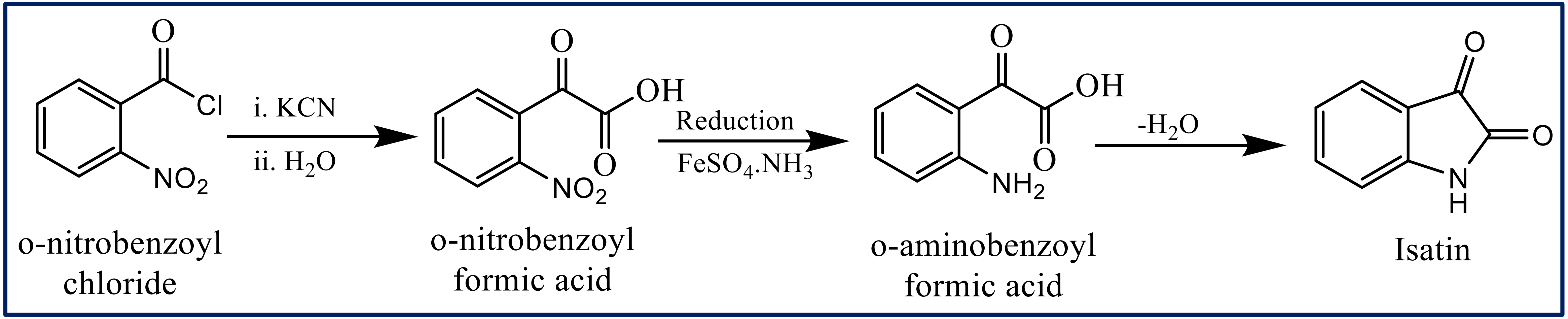
- ✓ On boiling with alkali, it gives Isatic acid.



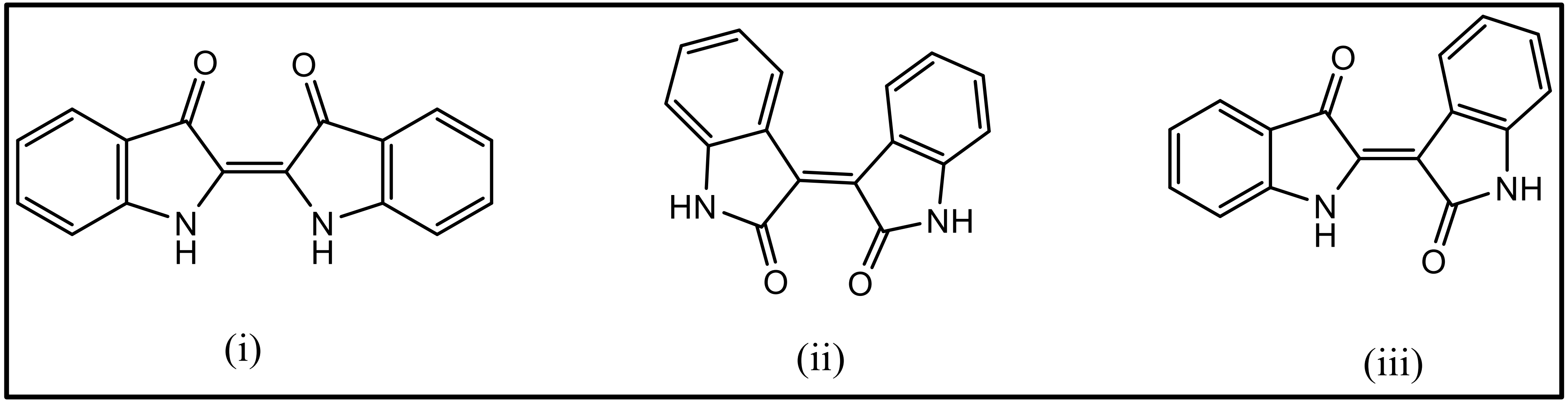
- ✓ On the basis of above facts, following structure could be assigned to Isatin, which is finally confirmed by synthesis.



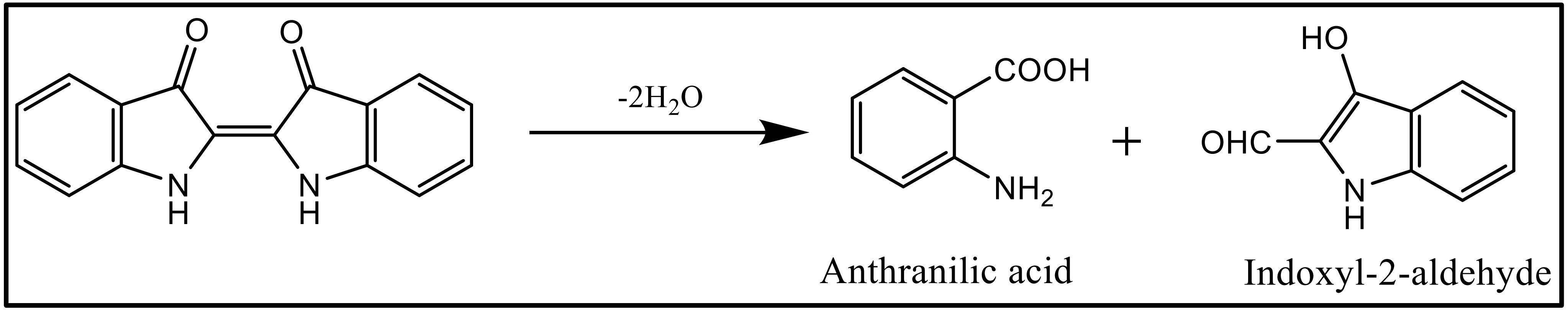
✓ Synthesis of Isatin:



❑ On the basis of above structure of Isatin, Indigotin may be assigned any of the following three structures (i), (ii), (iii). All of which upon oxidation could produce two molecules of Isatin.



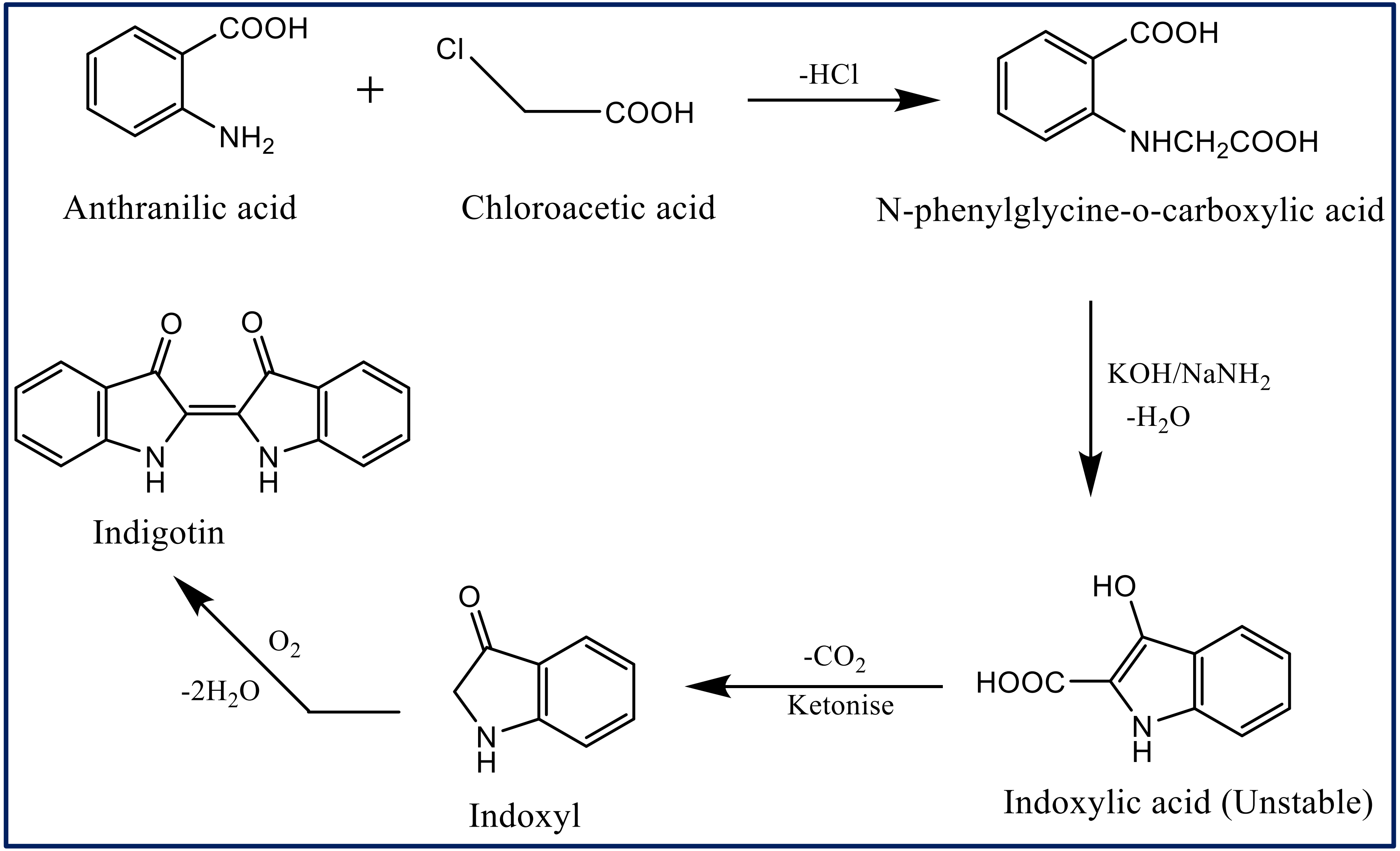
- ☐ Out of the above three possibilities, structure (i) has been confirmed for Indigotin by following facts;
- ✓ Upon hydrolysis with alkali, Indigotin produces anthranilic acid and Indoxyl-2-aldehyde.



- ✓ Conclusion evidence for the final structure of Indigotin was obtained from its unambiguous synthesis.

Synthesis of Indigotin:

(i)



Anthranilic acid

Chloroacetic acid

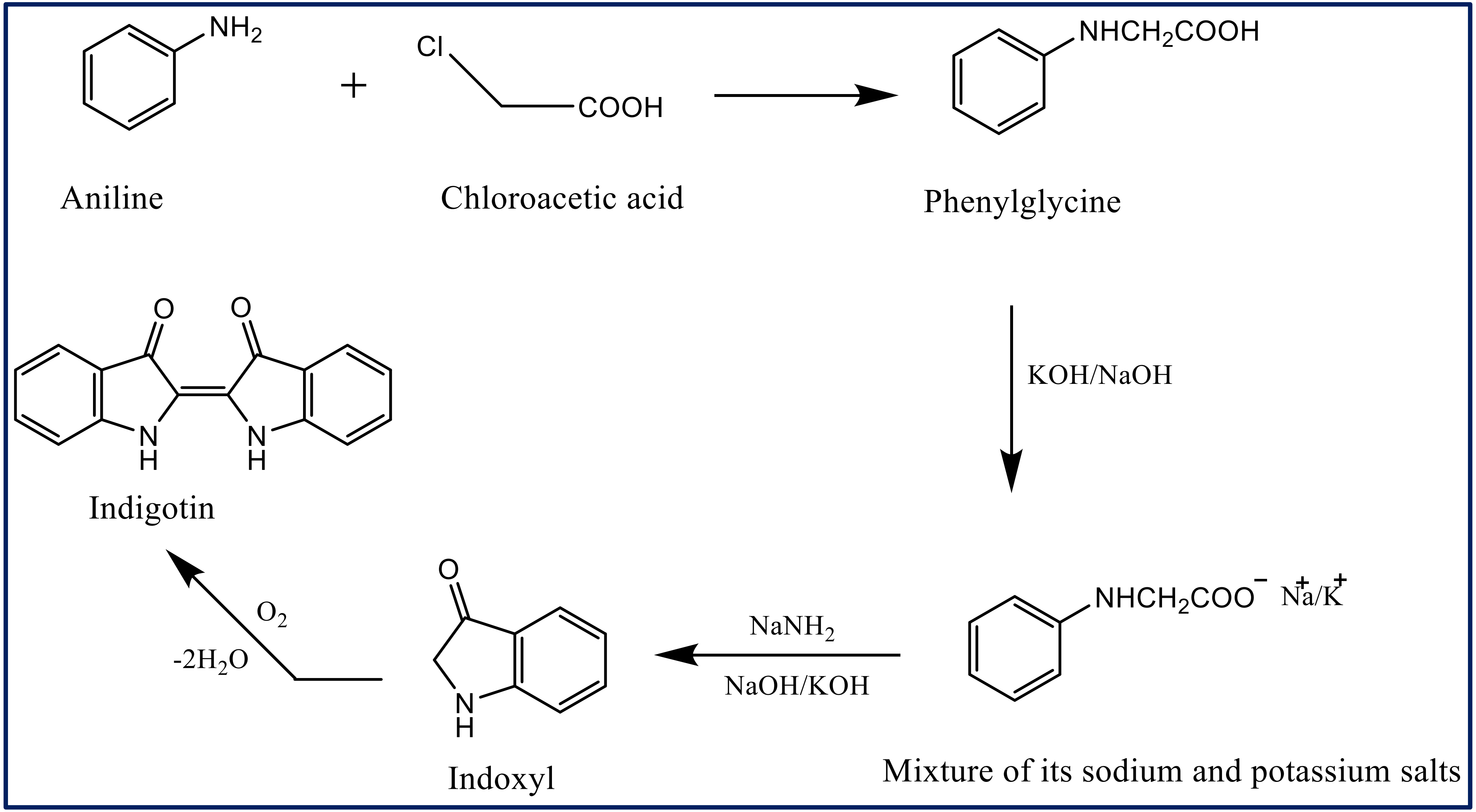
N-phenylglycine-o-carboxylic acid

Indoxylic acid (Unstable)

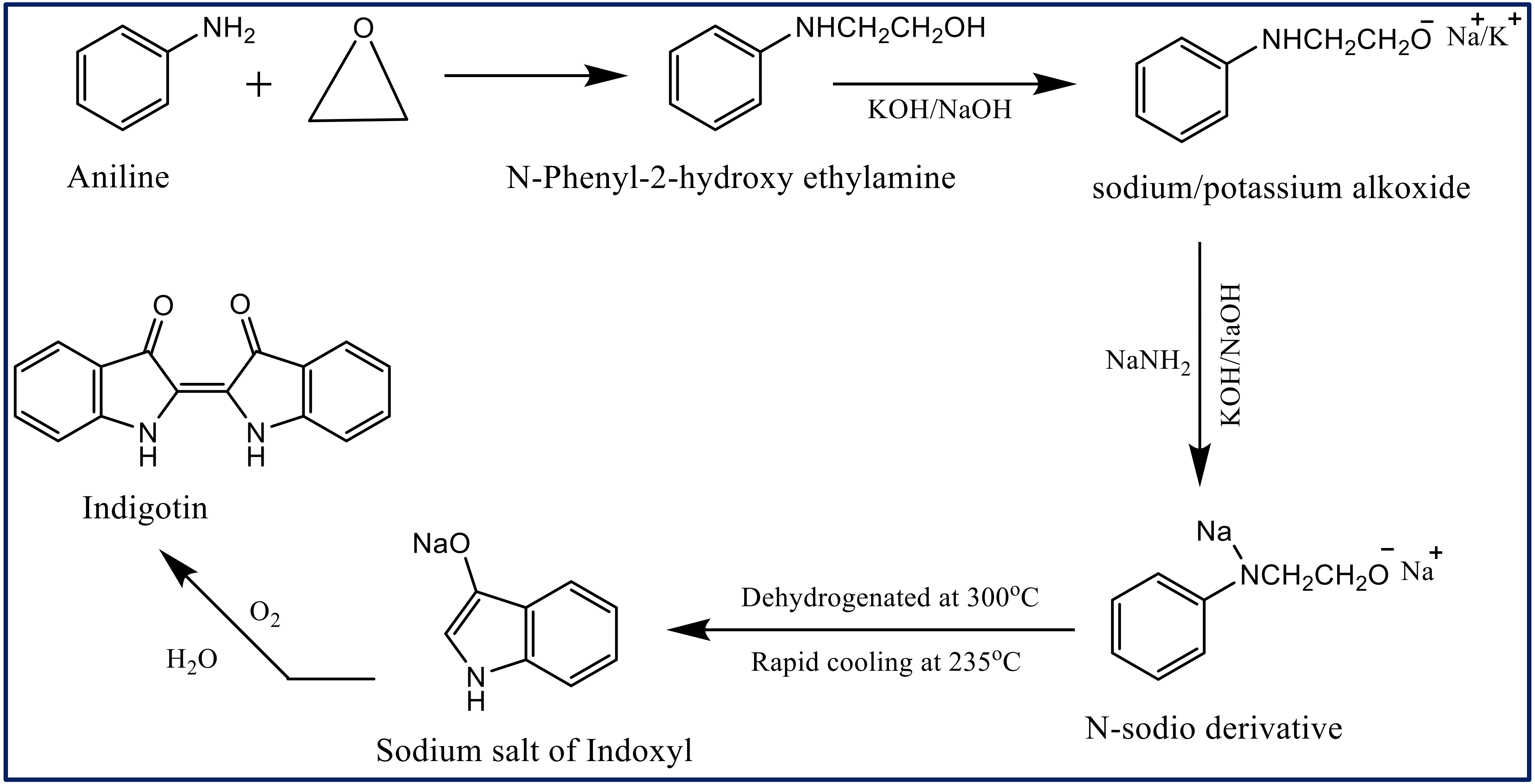
Indoxyl

Indigotin

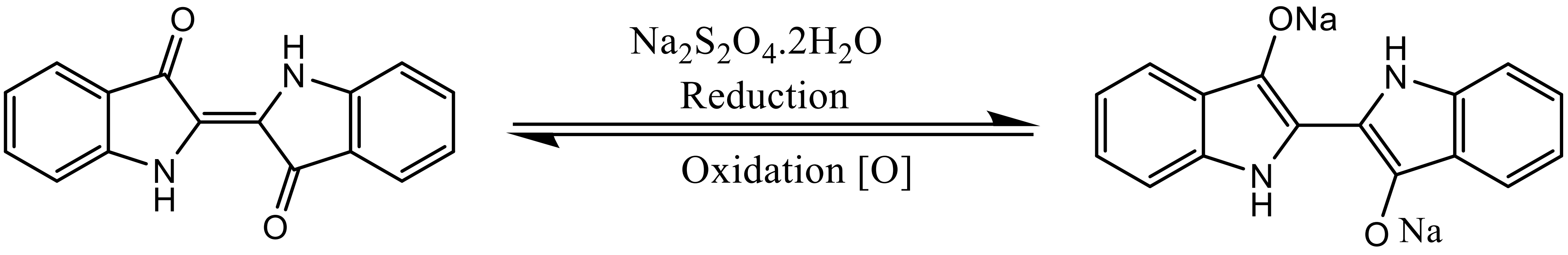
(ii)


NH2
Cl
COOH
Aniline
Chloroacetic acid
NHCH2COOH
Phenylglycine
KOH/NaOH
NHCH2COO⁻ Na⁺/K⁺
Mixture of its sodium and potassium salts
NaNH2
NaOH/KOH
O
N
H
Indoxyl
O2
-2H2O
O
O
N
H
N
H
Indigotin

(iii)


NH2
O
Aniline
NHCH2CH2OH
N-Phenyl-2-hydroxy ethylamine
KOH/NaOH
NHCH2CH2O− Na+/K+
sodium/potassium alkoxide
NaNH2
KOH/NaOH
Na
NCH2CH2O− Na+
N-sodio derivative
Dehydrogenated at 300°C
Rapid cooling at 235°C
NaO
N
H
Sodium salt of Indoxyl
O2
H2O
O
O
N
H
N
H
Indigotin

Indigotin is dark blue powder with metallic luster. It is insoluble in water. When it is agitated with sodium hyposulphite, a soluble Indigotin-white leuco compound is formed.



$Na_2S_2O_4.2H_2O$

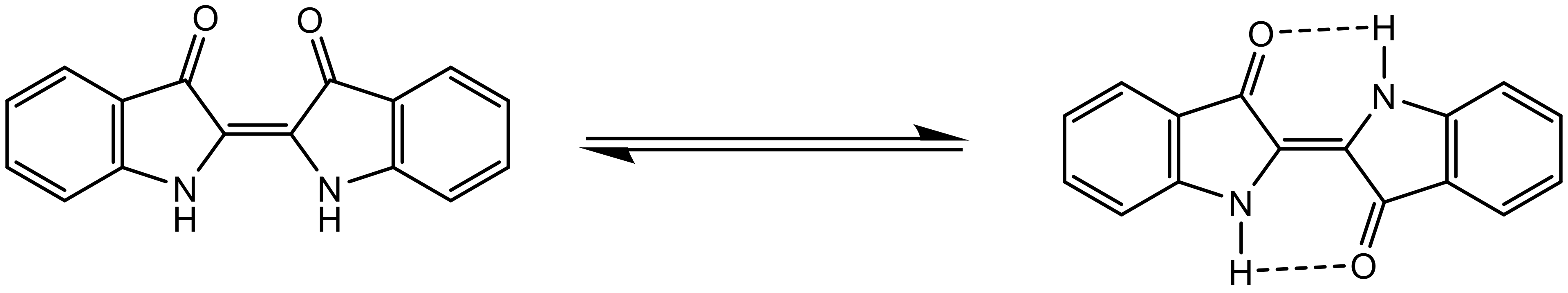
Reduction

Oxidation [O]

Indigotin (Blue)

Indigotin white (Colourless)

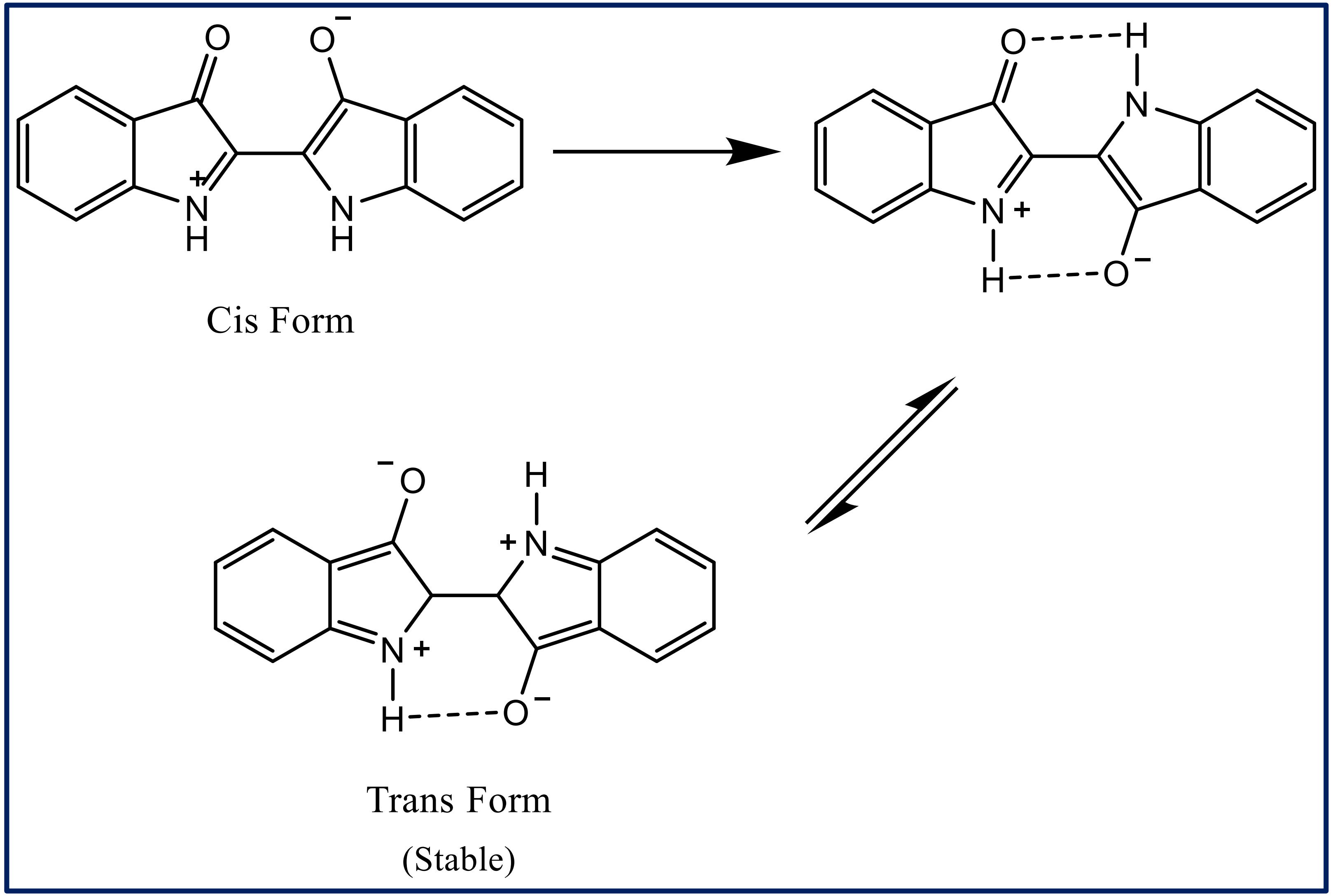
❑ Geometrical Isomers:



Cis-

Trans-
(Stable)

- Presence of centre of symmetry is possible only in Trans form.
- Trans form is stabilized by H-bonding which is absent in Cis-form.



Cis Form

Trans Form

(Stable)