CHAPTER 5

Natural and Synthetic Dyes

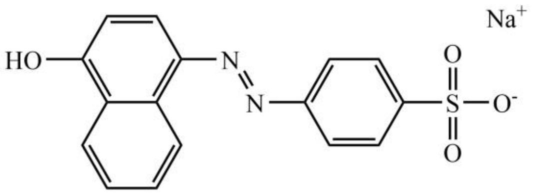
❖ Various Classes of Synthetic Dyes Including Heterocyclic Dyes

A dye may simply be defined as a colored compound that binds chemically or physically to the substrate to which it is applied; and depending upon the type of source, they are classified as synthetic or natural. In this section, we will further classify the synthetic dyes (azo and non-azo types) based upon their method of application.

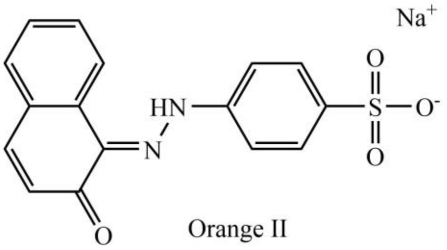
- ***Acid Dyes***

An acid dye may simply be defined as the sodium salt of azo dyes which contains carboxylic or sulphonic acid.

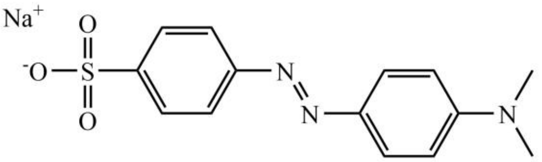
These types of dyes are applied to fiber from their acid solution and are typically employed to color wool, nylon, polyurethane, and silk. Acid dyes have a greater affinity for nylon which is obviously due to the presence of more free amino groups in polycaprolactam. These types of dyes cannot be applied to cotton due to little to no affection. Some of the typical examples of acid dyes are orange-I, orange-II, congo red, and methyl orange.



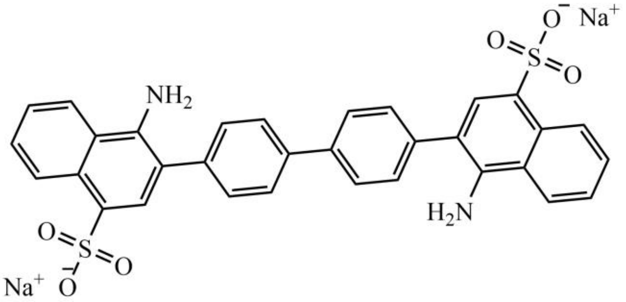
Orange I



Orange II



Methyl Orange



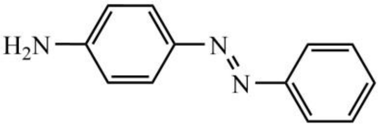
Congo Red

It is also worthy to note that besides dying the fabric, some special acid dyes are also used as food colorants, to stain organelles in the medical field.

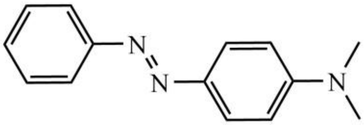
- ***Basic Dyes***

A basic dye may simply be defined as the salt of colored bases which contains amino groups as auxochromes.

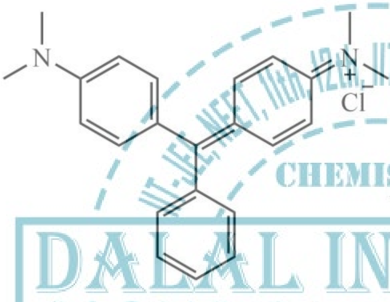
The amino groups of basic dyes generate water-soluble cations; which in turn, can bind with the anionic sites on the fabric used. These dyes can be used to color modifies nylons and polyesters. Some of the typical examples of basic dyes are aniline yellow, butter yellow, chrysoidine G, and malachite green.



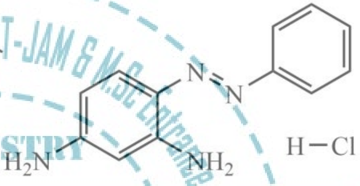
Aniline Yellow



Butter Yellow



Malachite Green



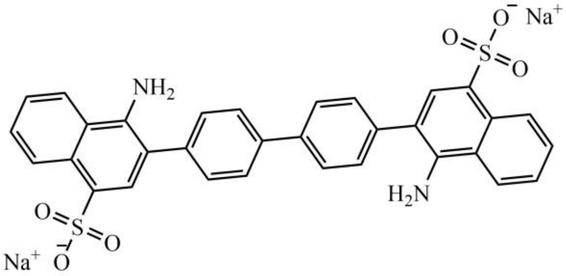
Chrysoidine G

It is also worthy to note that besides dying the fabric, some special basic dyes are also used as paper colorants in the paper industry.

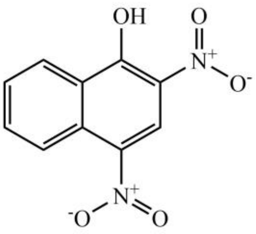
- ***Direct Dyes***

A direct dye may simply be defined as the dye which can be applied to the fabric directly from its aqueous solution.

These dyes are water-soluble and appropriate for the fabrics that can bind to the dye molecule via hydrogen bonding. Direct dyes are primarily used to color nylon, silk, rayon, cotton, and wool. Some of the typical examples of direct dyes are martius yellow and congo red.



Congo Red

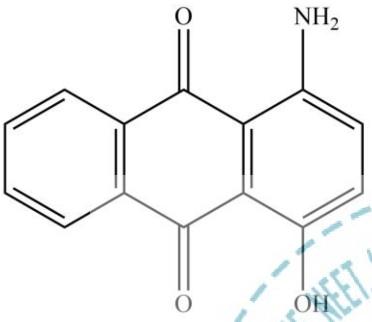


Martius Yellow

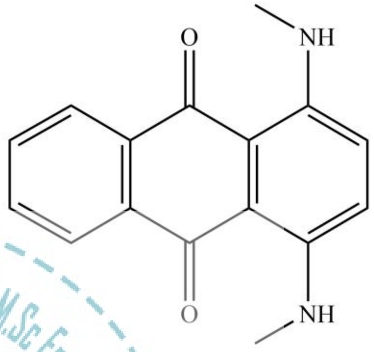
➢ *Disperse Dyes*

A disperse dye may simply be defined as the dye which can be applied to the fabric in the form of dispersion dye material in a soap solution stabilized by benzoic acid, cresol, or phenol.

These dyes are water-insoluble (correspond to the anthraquinone class) and are appropriate for the synthetic polyamide fibers. Some of the typical examples of disperse dyes are celliton fast pink B and celliton fast blue B.



Celliton Fast Pink B

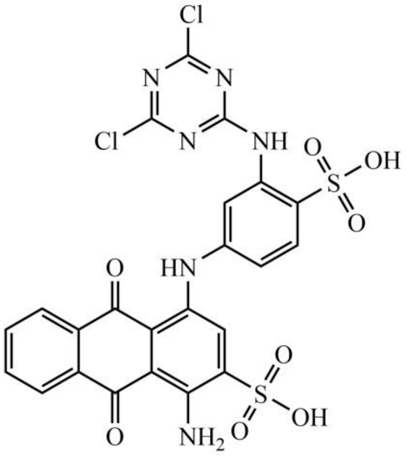


Celliton Fast Blue B

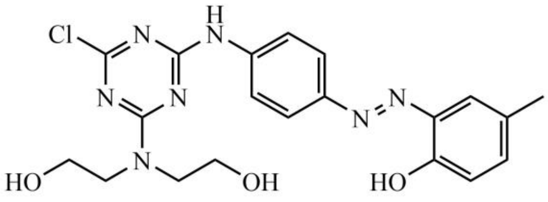
➢ *Reactive Dyes*

A reactive dye may simply be defined as the dye that has reactive groups capable of binding with the amino or hydroxyl groups of the fiber.

These dyes bind very strongly with the fiber which can be attributed to the chemical nature of the bonding interaction. These dyes are primarily used to color wool, silk, and cotton. Some of the typical examples of disperse dyes are reactive blue 4 and 2-[[4-[[4-[bis(2-hydroxyethyl)amino]-6-chloro-1,3,5-triazin-2-yl]amino]phenyl]azo]-p-cresol.



Reactive Blue 4

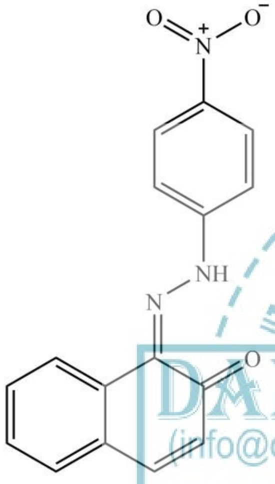


2-[[4-[[4-[bis(2-hydroxyethyl)amino]-6-chloro-1,3,5-triazin-2-yl]amino]phenyl]azo]-p-cresol

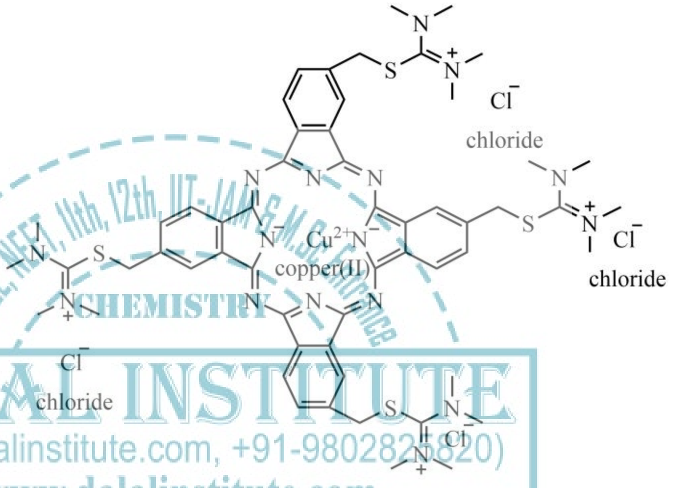
➢ *Ingrain Dyes*

An ingrain dye may simply be defined as the dye that is produced within the fiber from chemical precursors and binds itself by an irreversible chemical change in such a way that fastness is improved upon the dyeing.

These dyes are created by the coupling of the diazonium salt with naphthols, phenols, aminophenols, or arylamines on the fiber's surface. Ingrain dyes are not considered as fast because the dye molecules bind to the fiber via adsorption. These dyes are primarily used to color nylon, silk, polyester, leather, polypropylene, polyacrylonitriles, polyurethanes, and cellulose. Examples of ingrain dyes are para red and Ingrain blue 1.



Para Red

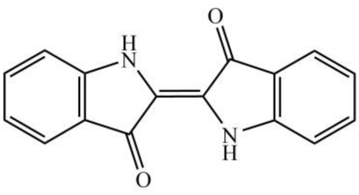


Ingrain Blue 1

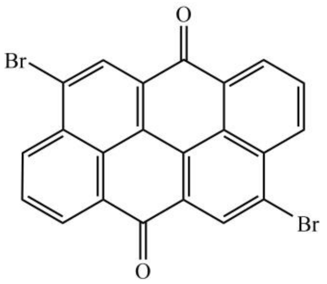
➢ *Vat Dyes*

A vat dye may simply be defined as the dye that is applied in its reduced form to the fabric in a bucket or vat with a reducing agent like sodium hydrosulfite's alkaline solution.

These dyes are water-insoluble and cannot be applied directly to the fiber. However, their reduced form (generally colorless) becomes soluble in water and does have an affinity for cellulose fiber. Owing to this special feature, vat dyes are primarily used to color cotton cloths. Some of the typical examples of vat dyes are indigo (also a naturally occurring dye) and vat orange 3.



Indigo

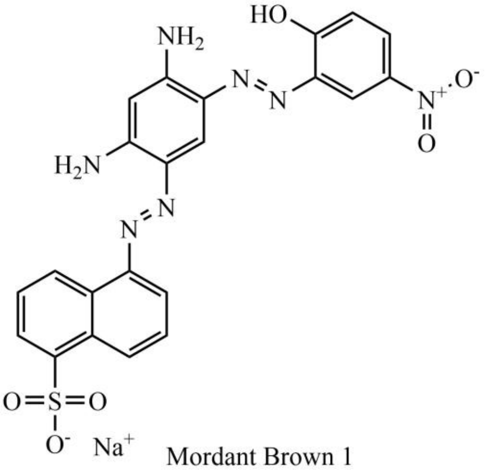


Vat Orange 3

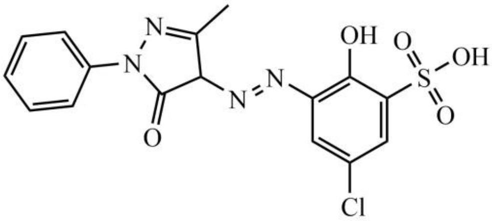
➢ *Mordant Dyes*

A mordant dye may simply be defined as the dye that is applied to the fabric via some mordant acting as a binding agent between the fiber and dye.

Tannic acid and metal ions are used as mordant basic and acid dyes, respectively. The fabric is first soaked in the mordant provider and then the dye is applied. These dyes are primarily used to color wool. Two of the typical examples of mordant dyes are mordant brown 1 and mordant red 19.



Mordant Brown 1



Mordant Red 19

It is also worthy to note that mordants not only increase the fastness of the dye but can also change the color of both the dye-plus-mordant solution and influence the shade of the overall product.

❖ Interaction Between Dyes and Fibers

In the process of dying, the dye molecules bind with the fiber by some sort of attractive force which can be physical or chemical in nature. The fastness of the dye depends upon the nature and extent of these dye-fiber forces. In this chapter, we will discuss the types of interactions between dye and fiber.

➢ *Physical Theory*

According to the physical theory of dye-fiber interaction, dye molecules are retained by the fiber via van der Waal forces or hydrogen bonding.

Some of the most important characteristic features of the physical theory of dye-fiber interaction are given below.

1. The fastness of dye in this type of interaction increases with increasing molecular size.
2. Dye’s fastness decreases as the solubility increases.

One of the most common examples of dyes showing this type of interaction is the coloring of the cellulosic by solubilized vat, direct, sulfur, and vat dyes.

➢ *Chemical Theory*

According to the chemical theory of dye-fiber interaction, dye molecules are retained by the fiber via the chemical bond.

Some of the most important characteristic features of the chemical theory of dye-fiber interaction are given below.

1. The dye as well as fiber, are required to have reactive groups.

2. Dye's fastness decreases as the number of reactive sites increases.

3. In most cases, the bonding's nature is ionic but can also be covalent in some.

4. An electrolyte is added after the 'half dying process' to exhaust the bath.

5. Sometimes the dying-rate is so high that leveling agents are needed for a more uniform effect.

Some of the most common examples include dying of wool or nylon or silk with acid dye, dying of acrylic or silk or cationic polyester with a basic dye, and coloring of anionic polyester with sulfur, vat, reactive or direct dyes. Furthermore, the coloring of cotton by reactive dye material also results in the formation of chemical bonds (covalent interaction).

➢ *Physio-Chemical Theory*

According to the physio-chemical theory of dye-fiber interaction, dye molecules are retained by the fiber via physical bonds.

Some of the most important characteristic features of the physio-chemical theory of dye-fiber interaction are given below.

1. The fastness of dye in this type of interaction is enhanced by increasing molecular size by the reaction of fiber-retained dye with some other chemical species.

2. One component must be the dye; however, the other component can be the dye or non-dye chemical.

Some of the most common examples of dyes showing this type of interaction are mordant dyeing of wool, mordanting of cotton in basic dyeing, back tanning of dyed protein fiber.

➢ *Fiber-Complex Theory*

According to the fiber-complex theory of dye-fiber interaction, dye molecules are retained by the fiber via the formation of a complex.

Some of the most important characteristic features of the fiber-complex theory of dye-fiber interaction are given below.

1. The dye on its own is not able to enter the fiber's matrix due to lack of affinity or large molecular structure.

2. The reaction of two different compounds under feasible conditions.

One of the most common examples of dyes showing this type of interaction is cotton's coloring with insoluble azoic.

- ***Solid Solution Theory***

According to the solid-solution theory of dye-fiber interaction, dye molecules are trapped inside by the fiber material under suitable conditions.

Some of the most important characteristic features of the solid-solution theory of dye-fiber interaction are given below.

1. The dyestuff as well fiber, both are in the solid phase.
2. Dye gets trapped in the hydrophobic fiber, forming a solid solution.
3. The dyeing is carried out at a higher temperature to facilitates the passage of dye molecules into the fiber.

One of the most common examples of dyes showing this type of interaction is dying man-made material with disperse dye.

- ***Pigment or Mechanical Theory***

According to the pigment or mechanical theory of dye-fiber interaction, dye molecules are attached to the fiber via a binding agent.

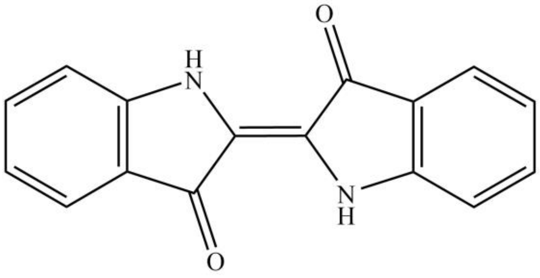
Some of the most important characteristic features of the pigment theory of dye-fiber interaction are given below.

1. The dye has no reactive sites, no affinity for the fiber, and is insoluble in most of the solvents.
2. The fiber becomes more stiff and the dye’s fastness depends upon the film’s longevity.

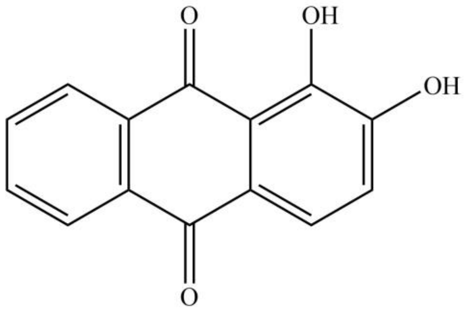
Some of the most common examples of dyes showing this type of interaction are the dying of fabric, pigment colors.

❖ Structure Elucidation of Indigo and Alizarin

Two of the most popular examples of natural dyes are indigo and alizarin which have a cultural history all across the globe. In this section, we will discuss the general method of structure elucidation of alizarin and indigo as well.



Indigo



Alizarin

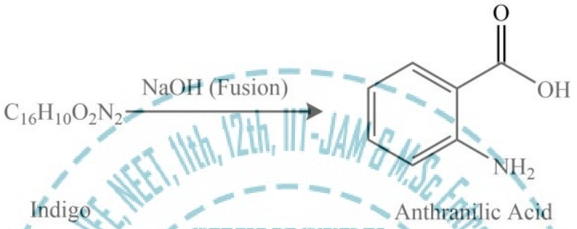
➢ ***Structure of Indigo***

Indigo is a naturally occurring blue dye whose molecular structure can be elucidated by the general method as given below.

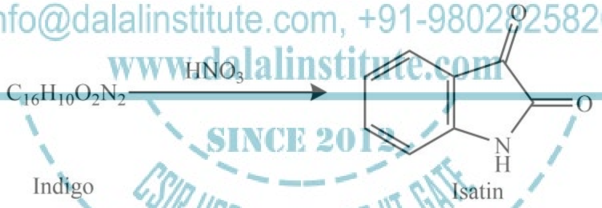
1. The combined study of elemental analysis and mass spectrum suggested that $C_{16}H_{10}O_2N_2$ is the molecular formula of indigo.

2. The double bond equivalent (D.B.E) for indigo was found to be 13 suggesting that there must be more than one benzene ring.

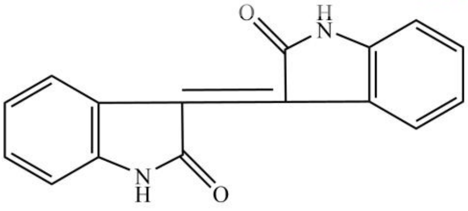
3. Indigo's fusion at low-temperature results in anthranilic acid suggesting that there must be at least one ortho-substituted benzene ring where one position is bind by nitrogen and the other by carbon.



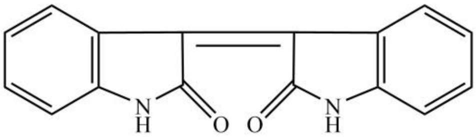
4. Indigo's oxidation with nitric acid results in two moles of isatin indicating two identical units in indigo that are connected with each other such that one molecule of isatin is generated from each unit.



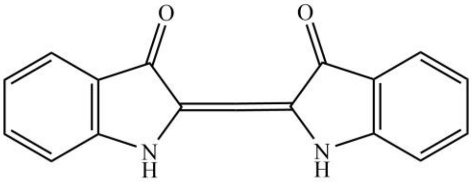
5. Three possible structures can be concluded from the isatin structure.



Structure 1

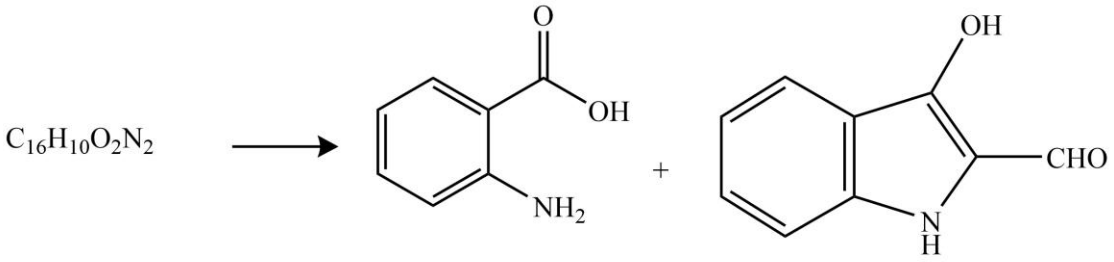


Structure 2



Structure 3

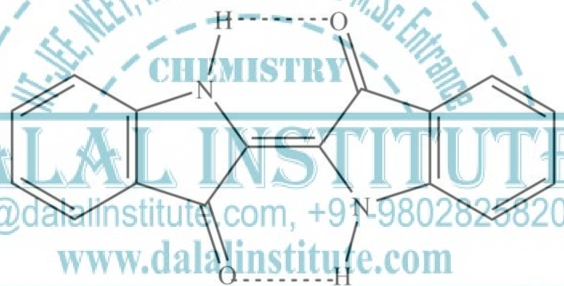
6. The treatment of indigotin with dilute alkali results in the formation of indoxyl-2-aldehyde and anthranilic acid.



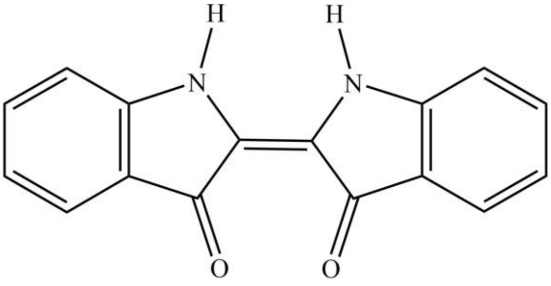
Indigo Anthranilic Acid Indoxyl-2-aldehyde

7. Finally, we may conclude that two identical units must be joined via the second position of the indoxyl fragment, and an oxygen-containing functional group must be present at position 3. All this suggests following two structures for indigotin.

Stablized by hydrogen bonding



trans-Indigo



Not stablized by hydrogen bonding

cis-Indigo

Now since trance configuration is stabilized by H-bonding, it must be the primary choice. Similar results were obtained by qualitative analysis of mass spectra and NMR data.

➢ *Structure of Alizarin*

Indigo is a naturally occurring blue dye whose molecular structure can be elucidated by the general method as given below.

1. The combined study of elemental analysis and mass spectrum suggested that $C_{14}H_8O_4$ is the molecular formula of alizarin.

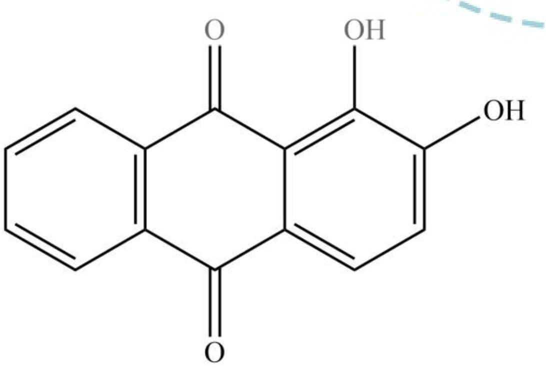
2. The double bond equivalent (D.B.E) for alizarin was found to be 11 suggesting that there must be at least one benzene ring.

3. The reduction of alizarin with zinc at 675K results in anthracene indicating that alizarin must a derivative of the anthracene molecule.

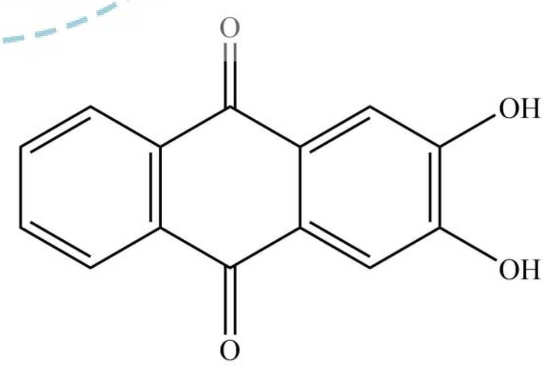
4. The reaction of alizarin with acetic anhydride results in diacetate showing two hydroxyl groups are expected in the alizarin molecule.

5. Since the condensation of phthalic anhydride with catechol at 455K results in alizarin, it can be concluded that this dihydroxy derivative of anthraquinone must be having OH groups in the same cycle.

6. Therefore, following structures can be proposed for alizarin molecule.

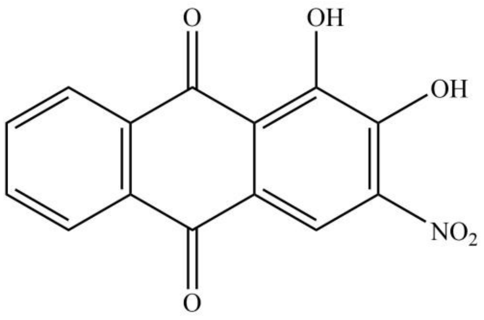


Structure I

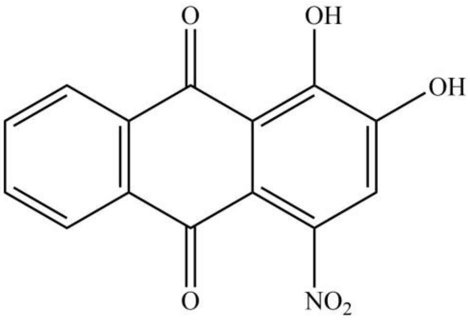


Structure II

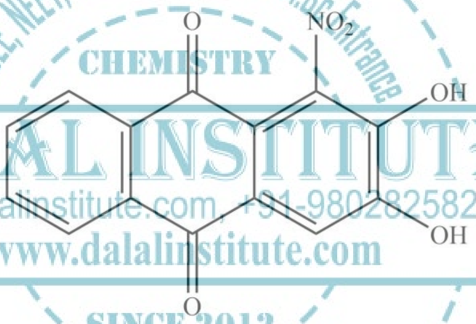
7. The nitration of alizarin results in two isomers of mono-nitro derivative, which in turn produce phthalic acid upon oxidation; indicating the presence of the nitro group in the same cycle as the hydroxy group. Now since structure I can give two mono-nitro derivatives but the second structure can produce only one mono-nitro derivative, the correct answer should be structure I.



Structure IA



Structure IB



Structure IIA

Now since trance configuration is stabilized by H-bonding, it must be the primary choice. Similar results were obtained by qualitative analysis of mass spectra and NMR data

❖ Problems

Q 1. What is a dye? How would you classify them based on their source?

Q 2. Discuss the classification of various forms of dyes on basis of their method of application.

Q 3. What is the difference between mordant and vat dyes?

Q 4. Give the points of similarity and differences between the physical and chemical theory of dye-fiber interaction.

Q 5. State solid-solution theory of dye-fiber interaction. Also give is salient features.

Q 6. Discuss the general method of structure determination of indigo.

Q 7. What is the chemical formula of alizarin? Also, discuss its structure elucidation.

❖ Bibliography

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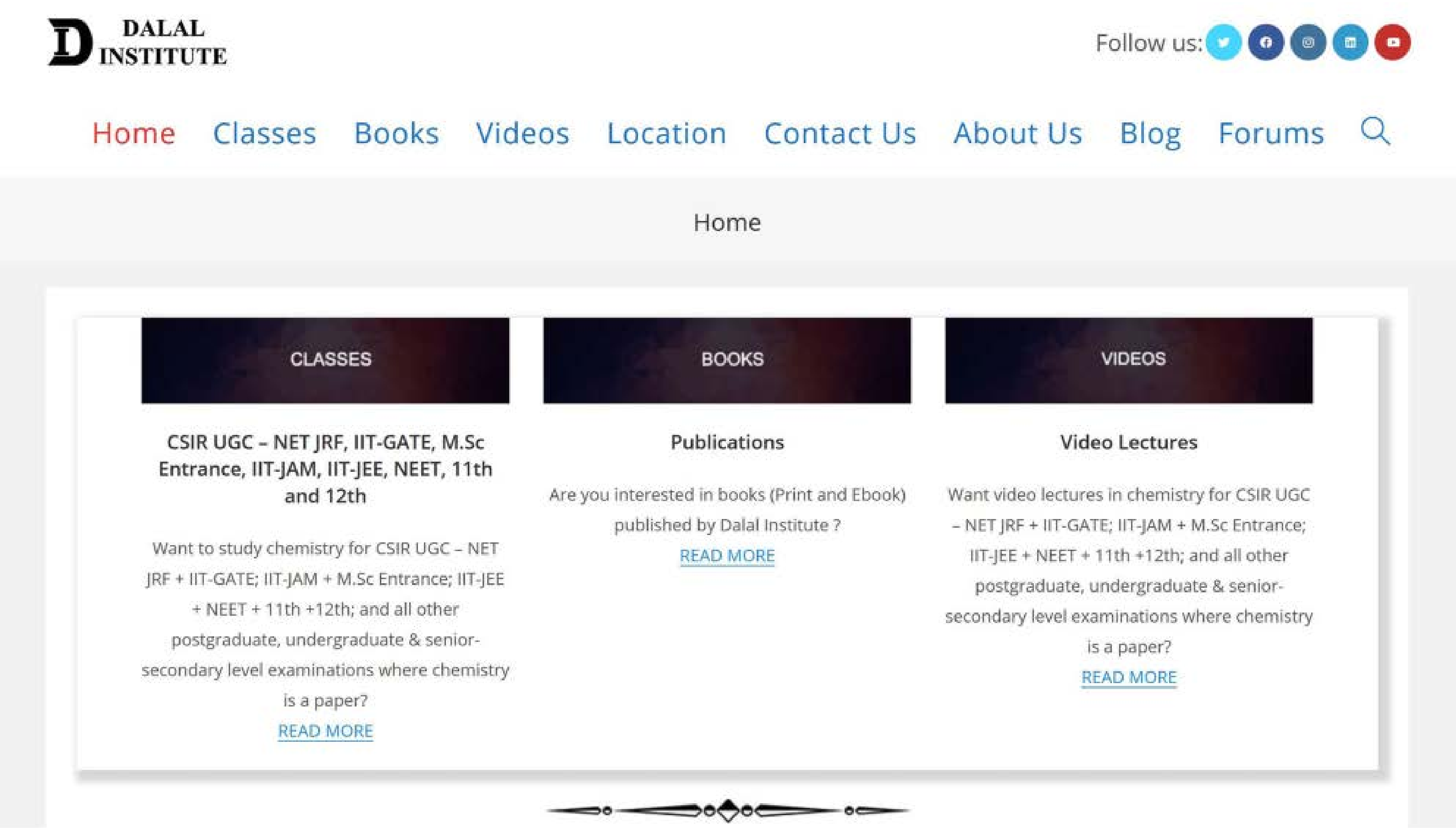

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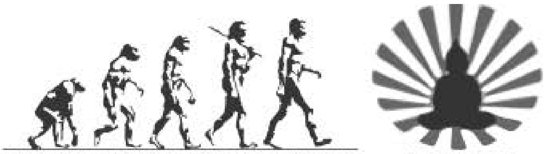

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