Unit IV: Dyes

Adapted from A Text Book of Organic Chemistry by Tewari and Vishnoi
Wikipedia and http://www.jku.at/cto/content/e34502/e116152/e128964/OT2colors12_ger.pdf

Color Sensation

The electromagnetic spectrum ranges from ultra low frequency, low energy and high wave length (1000 KM) radio waves to very high frequency, high energy and low wavelength (1 picometer) gamma rays. Electromagnetic radiation interacts with matter in different ways across the spectrum. These types of interaction are so different that historically different names have been applied to different parts of the spectrum, as though these were different types of radiation. Thus, although these "different kinds" of electromagnetic radiation form a quantitatively continuous spectrum of frequencies and wavelengths, the spectrum remains divided for practical reasons related to these qualitative interaction differences.

Electromagnetic radiation with a wavelength between approximately 400 nm and 700 nm is directly detected by the human eye and perceived as **visible light** (Figure 1). Other wavelengths, especially nearby infrared (longer than 700 nm) and ultraviolet (shorter than 400 nm) are also sometimes referred to as light, especially when not used in the context of visibility to humans.

The basic structure of matter involves atoms bound together in many different ways. When electromagnetic radiation is incident on matter, it causes the atoms and the charged particles that constitute these atoms to oscillate and gain energy. The ultimate fate of this energy depends on the matter as well as the nature of the radiation.

In the case of visible radiation, the incident radiation could be reradiated as (i) scattered, (ii) reflected, or (iii) transmitted radiation. Some of the radiation maybe absorbed leading to excitation of electrons. When the atoms relax, the energy is transmitted at characteristic frequencies.

The transmitted light can strike the retina of the eye causing the sensation of colour. White light is a composite mixture of all colors of the visible spectrum. When white light strikes an object, it can be either

(i)   Totally absorbed – which make the object appear black

(ii)   No absorption leading to total reflection – which will make the object appear white

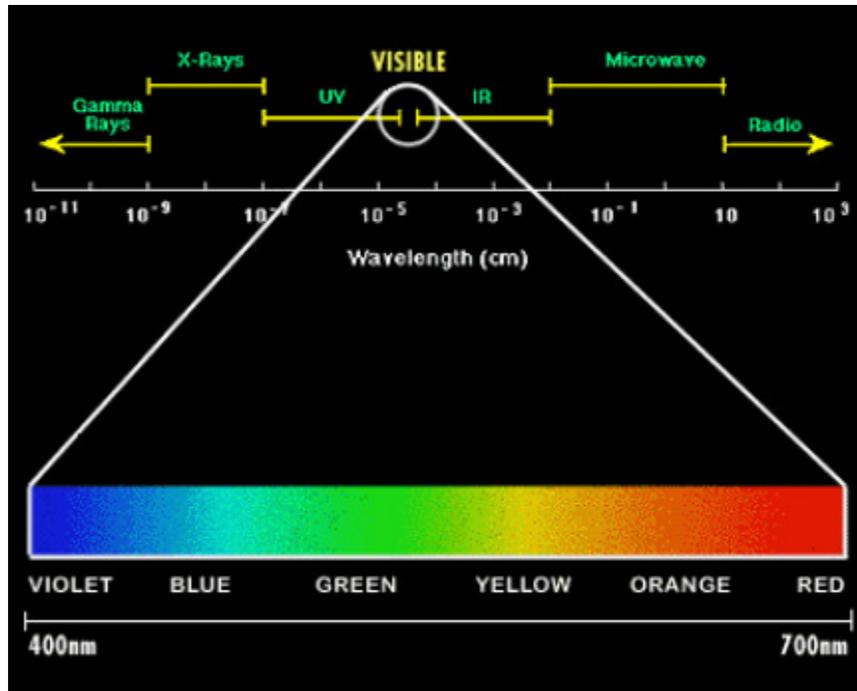(iii)   Partly absorbed and rest reflected – which lead to the sensation of color to the eye.

Figure 1

The object may appear, say red in color (605 to 750 nm) due to absorption of all light except red by the object, thereby reflecting only red light to the eye.

The object may also appear red in color due to a second reason: it might be because the object absorbs color that is complementary to red, ie. Blue-green (Table 1).

Wavelength [nm]	Absorbed color	Complementary color
650-780	red	blue-green
595-650	orange	greenish blue
560-595	yellow-green	purple
500-560	green	red-purple
490-500	bluish green	red
480-490	greenish blue	orange
435-480	blue	yellow
380-435	violet	yellow-green

Table 1

Color and Chemical Constitution

Different objects produce different colors depending on the color transmitted to the eye. For e.g. Tyrian purple, a modified form of Indigo dye is blue in color, whereas picric acid dye is yellow.
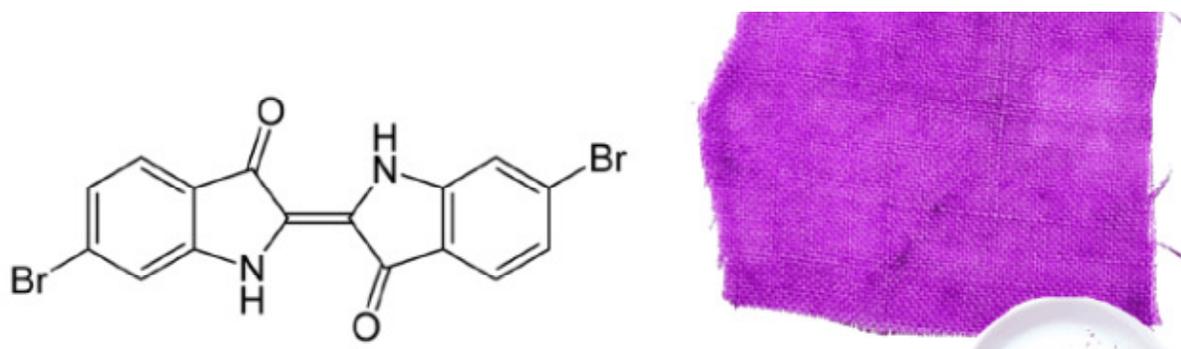

Figure 3a: 6,6'-Dibromoindigo: Chemical structure and Tyrian Purple dye color.

Figure 3b: Picric Acid Chemical Structure and dyed yellow bird feathers.

In the nineteenth century, when chemistry was in its infancy, dye chemists proposed that the color produced by dyes may be due to the interaction of light with the specific moieties present in the chemical structures of these molecules. Two theories were proposed based on this, (i) Quninonoid theory and (ii) Chromophore-Auxochrome theory.

Quinonoid Theory

Armstrong in 1885 observed that quinines were colored compounds and hence theorized that all dyes could be represented by quinonoid structures (figure 4). However his theory was disproved soon and the theory was not
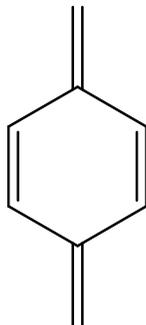
Quinonoid Structure

Figure 4

Chromophore-Auxochorme Theory:

As far back as 1868, Grabe and Liebermann suggested that **unsaturation** as a criterion for color formation in organic compounds. This was further emphasized by Witt in 1876 with his "Chromophore-Auxochrome" theory. The theory proposed that:

(i) The color of organic compounds is mainly due to the presence of groups of unsaturation, *ie.* Groups containing multiple bonds. He named these groups as **chromophores** (Derived from greek*,* where *Chromo*= Color and *Pherein*= to bear). In contrast, colorless compounds were found to have no unsaturation centers. The compounds containing these chromophores were called **chromogens**. So, Trypan-blue and picric acid described above are chromogens. Some of the important chromophores are:

CHROMOPHORIC STRUCTURE

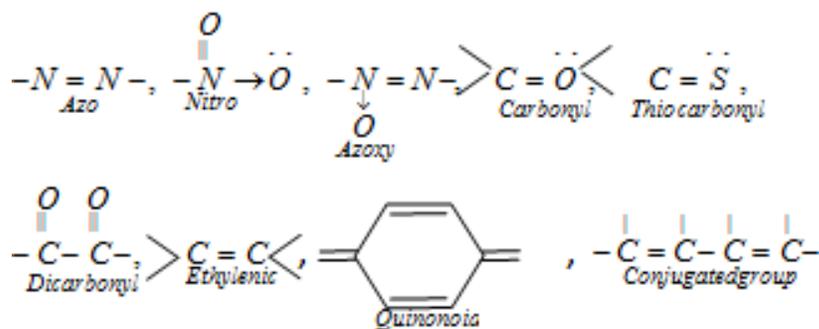| Group	Structure	nm
Carbonyl	$>C=O$	280
Azo	$-N=N-$	262
Nitro	$-N=O$	270
Thioketone	$-C=S$	330
Nitrite	$-NO_2$	230
Conjugated Diene	$-C=C-C=C-$	233
Conjugated Triene	$-C=C-C=C-C=C-$	268
Conjugated Tetraene	$-C=C-C=C-C=C-C=C-$	315
Benzene	⬡	261

Figure 5: Some important chromophores

The presence of a chromophore is not necessarily sufficient for color. To make a substance colored, the chromophore has to be conjugated with an extensive system of alternate single and double bonds, for eg. as shown in the figure 4 above. Thus the chromophore part of the colored substance (dye) absorbs some wavelengths from white light and reflects back the complementary color. This nonuniform absorption of while light and transmission of complementary colored light contributes to the formation of colored dye substances.

(ii) The intensity of the color increases with increase in the number of chromophores in a chromogen. This effect is particularly marked if the chromophore is **conjugated**. For *eg.* Ethylene, $CH_2=CH_2$ has one double bond, but is colorless. However, polyene CH_3-$(CH_2=CH_2)_6$-CH_3 with multiple conjugated double bonds is yellow in color.

(iii) Certain groups, while not producing color themselves, when present along with a chromophore in an organic substance, enhance the density of the color. Such color support groups are called **auxochromes** (Greek word, *Auxanien* = to increase; *Chrome* = color), *i.e.* they make the color deep and fast and fix the dye to the fabric. The auxochromes are basic or acidic functional group sets. The important type of auxochromes are:
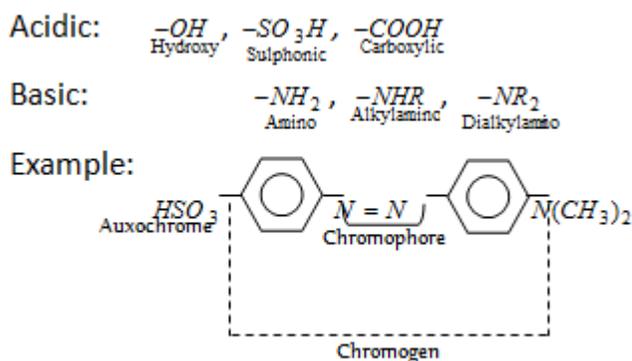

Figure 6 Some important auxochromes

For eg. Napthalene is colorless. But the presence of a chormophore in the form of two nitro groups provides a pale yellow color to 2,4-dinitronaphthalene. The color is enhanced by the

addition of a hydroxyl group as auxochrome in this compound. The new compound, 2,4-dinitro-1-naphthol is called Martius yellow and is used as a yellow dye. In contrast, the presence of only the hydroxyl group in 1-naphthol does not produce any color. This proves that the hydroxyl group acts as merely the auxochrome, *ie.* aids the chromophore and is not a chromophore by itself.
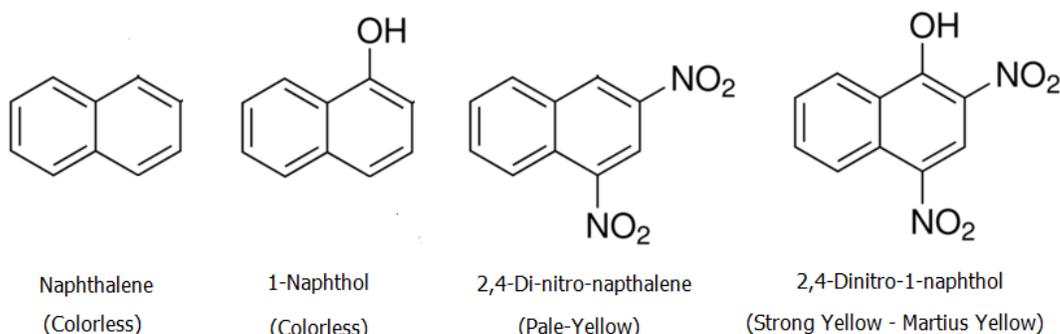

Naphthalene	1-Naphthol	2,4-Di-nitro-napthalene	2,4-Dinitro-1-naphthol
(Colorless)	(Colorless)	(Pale-Yellow)	(Strong Yellow - Martius Yellow)

Figure 7.Significance of auxochromes in chromogens.

For *eg.*, Benzene (C_6H_6) has an absorption maximum at 255 nm with an extinction coefficient of 203. The substitution of an auxochrome, NH_2 to the benzene ring to form aniline (C_6H_5-NH_2) shifts the absorption maximum at 280 nm with an extinction coefficient of 1430. This shows that the presence of the auxochrome shifts the absorption maximum as well as enhances the UV absorption.

Bathochromic shift is a change of spectral band position in the spectrum of a molecule to a longer wavelength (lower frequency and energy). Hypsochromic shift is a change of spectral band position in the spectrum of a molecule to a shorter wavelength (higher frequency and energy). Auxochromes that cause deepening of the color are called bathochromic groups and the spectral shift is called bathchromic shift, while groups causing the opposite effect are called hypsochromicgroups and hypsochromic shifts respectively.

Although this theory seemed to provide a satisfactory explanation for the observations, it could not explain them from the point of view of atoms and molecules.
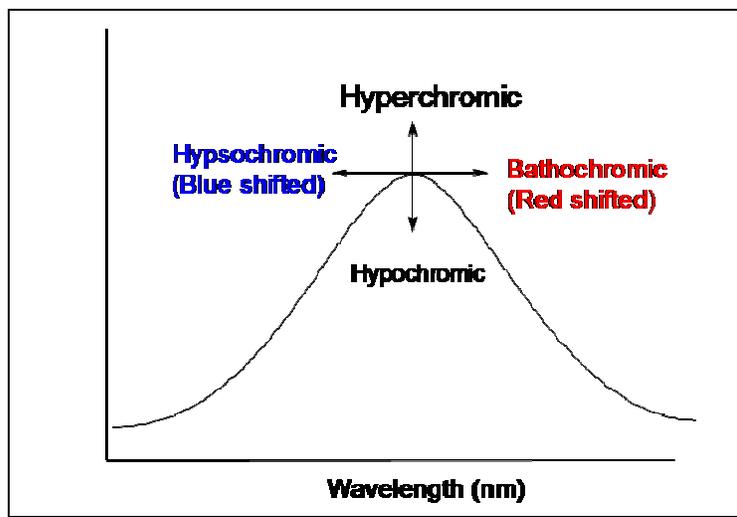

Figure 8: Direction of Bathochromic and Hypsochromic Shifts in Spectrum

Revised Chromophore-Auxochrome Theory

The chromophore-auxochrome theory has been reinterpreted and revised later with development in the electronic theory of atoms and molecules (as described below).

Thus a **chromophore** is an isolated functional group which shows absorption in ultra-violet and visible regions (200 to 800 nm). An **auxochrome** is any group that increases the absorption of the chromophore.

Just as the valence electrons of atoms occupy atomic orbitals (AO), the shared electron pairs of covalently bonded atoms may be thought of as occupying molecular orbitals (MO). In general, this mixing (hybridization) of **n** atomic orbitals always generates **n** hydbridized molecular orbitals. Figure 9 belows show the 2 bonding orbitals, (sigma – σ and pi – π), one non-bonding (n) orbital and 2 anti-bonding, (σ* and π*) orbitals respectively. When electromagnetic waves in the 200 – 800 nm range strike the electrons present in the bonding orbitals, they can get sufficiently excited to promote a molecular electron to a higher energy orbital.

When organic molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown below in figure 9. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum.
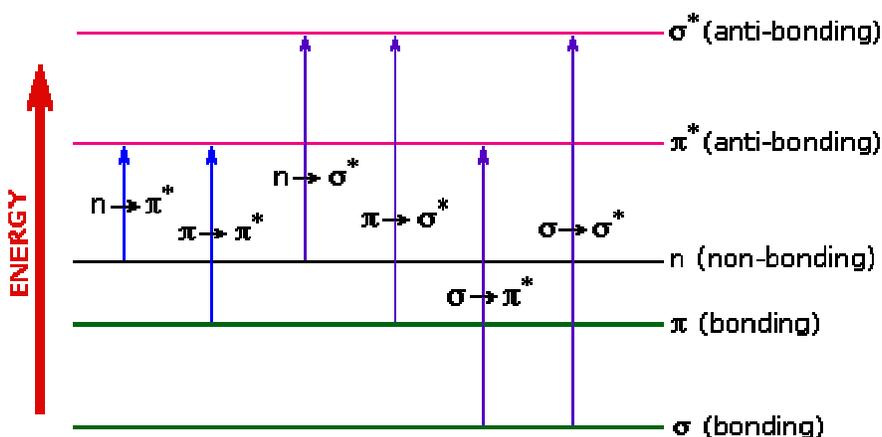

Figure 9: Electronic Transitions

When light is incident on a dye chromophore group having pi electrons, it can absorbs energy and undergo the $\pi \rightarrow \pi^*$ transitions. When these electrons relax, they transmit energy in the visible range providing us the sensation of color. This is further enhanced when the pi bonds are present in resonance with adjacent pi bonds, for eg. in conjugated state with alternate double and single bonds. Hence the $\pi \rightarrow \pi^*$ transitions, especially in conjugated double bonds are good chromophores.

When light in incident on a dye group having non-bonding electrons, it can undergo the $n \rightarrow \pi^*$ transitions. Also these groups can enhance the resonance in the chromophores. This aids the shifting of absorption of chromophores to higher wavelengths (shorter frequencies and energy). These groups which contain the non-bonding groups in dyes molecules and present in close proximity to the chromphore are called auxochromes.

Dyes

Dyes maybe natural of synthetic organic molecules having the property of imparting their color to other substances such as textile fibers. A good dye should be:

(i)   A suitable color
(ii)   Capable of fixing itself on the fiber
(iii) Resist the action of alkali, acid or solvents, ie. be "fast". In contrast, dyes which are susceptible to this are called "fugitive"

Natural dyes such as indigo from *Indigo tinctoria* and Alizarin from *madder genus* root have been known since civilization.
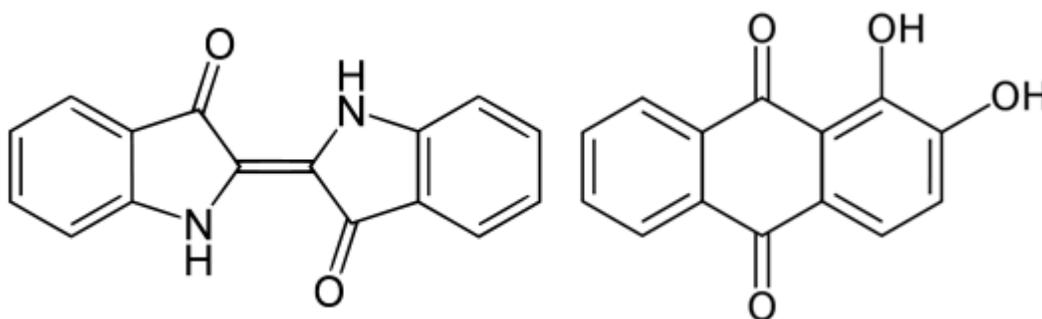

Figure 10: Chemical structures of Indigo (Blue color on the left) and Alizarin (Red color on right)

However it was not until 1771 that the first synthetic dye, picric acid (yellow color) was discovered. This was followed by many synthetic dyes.

Nomenclature of Dyes

Due to the complex and diverse nature of the chemical structure and action of dyes, a systematic nomenclature has not been attempted. The nomenclature follows from the common names given in literature for these classes of compounds.

Classification of Dyes

Dyes maybe classified according to two types: (i) Application (ii) Chromophore based (Chemical Classification). We will follow the chromophore based classification to understand the properties and synthesis methods of these dyes.

Dyes maybe classified mainly according to chromophores :

1. Nitro and Nitroso dyes
2. Diphenylmethane dyes
3. Triphenylmethane dyes
4. Phthalene dyes
5. Xanthene dyes
6. Azo dyes – Monoazo, Bisazo
7. Anthraquinone dyes - Mordant
8. Carbazole dyes
9. Heterocyclic Dyes
10. Pthalocyanine dyes

We will study some of them as discussed below.

1. **Nitro and Nitroso Dyes**: They contain nitro (NO_2) or nitroso ($N=O$) groups in their structure and are generally polynitro derivatives of phenol. They have the nitro group as the chromophore and hydroxyl or amino group as auxochrome. Picric acid (figure 3b) is an example. Another example is martius yellow, whose synthesis is depicted below.
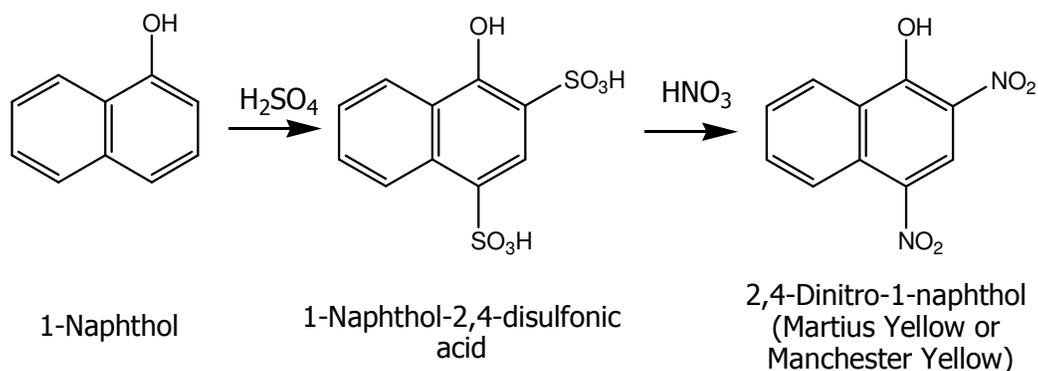

1-Naphthol   1-Naphthol-2,4-disulfonic acid   2,4-Dinitro-1-naphthol (Martius Yellow or Manchester Yellow)

Figure 11: Synthesis of Nitro Dye Martius Yellow

1-Naphthol in sulfonated to produce 1-naphthol-2,4-disulfonic acid, which in turn is subjected to nitric acid treatment to produce 2,4-dinitro-1-naphthol. This is used to dye silk and wool, but it is fugitive and does not stand treatment with acid, alkali and solvents. It is also used as a staining agent in microbiology.

Figure 12: Dyeing with Martius Yellow
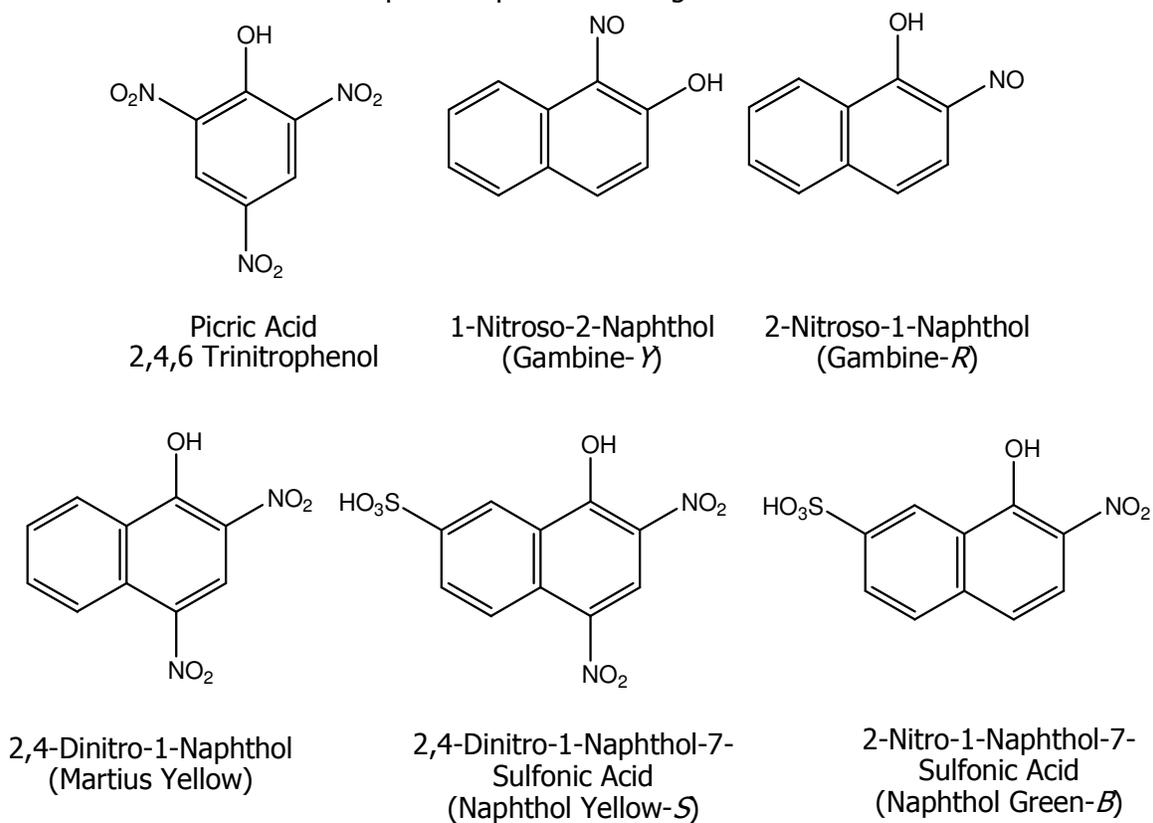
Other examples are provided in Figure 13.

Picric Acid
2,4,6 Trinitrophenol

1-Nitroso-2-Naphthol
(Gambine-*Y*)

2-Nitroso-1-Naphthol
(Gambine-*R*)

2,4-Dinitro-1-Naphthol
(Martius Yellow)

2,4-Dinitro-1-Naphthol-7-Sulfonic Acid
(Naphthol Yellow-*S*)

2-Nitro-1-Naphthol-7-Sulfonic Acid
(Naphthol Green-*B*)

Figure 13: Examples of Nitro and Nitroso Dyes

2. **Diphenylmethane Dyes**: These dyes contains two phenyl groups attached to a methane group (C_6H_5-CH_2-C_6H_5). For eg. Auramine O was discovered in 1883 and is prepared by heating p-p'-tetramethyl-diaminodiphenylmethane with sulphur, ammonium chloride and sodium chloride in a current of ammonia at 200^oC. The product on treatment with hydrochloric acid forms yellow colored Auramine O, a basic dye (Figure 14). It is used for dyeing silk, wool, jute, paper and leather. However, the color is fugitive!

Figure 14: Auramine O Yellow Dye
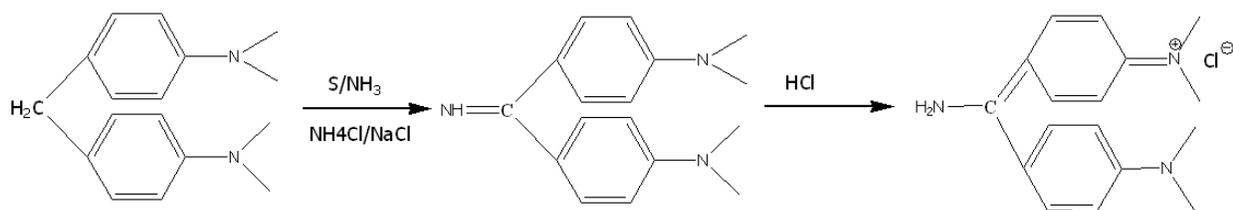
Figure 15: Synthesis of yellow colored Auramine O, a diphenylmethane dye

3. **Triphenylmethane Dyes:** These dyes have 3 phenyl groups attached to a methane. In these dyes, amino and/or hydroxy groups acts as auxochrome. However, it is only the salt form of these dyes that act as dyes.

a) **Malachite Green** is a dye prepared by Fisher in 1877 by condensing dimethylaniline with benzaldehyde with a dehydrating agent such as sulfuric acid at 100ºC. The resultant product is oxidized and treated with hydrochloric acid to produce the green colored dye. It is used to dye wook and slik. It is also used as a staining agent in microbiology. It is a bacteriostat and used as an antiseptic (Figure 16 and 17).

Figure 16: Malachite Green Dye
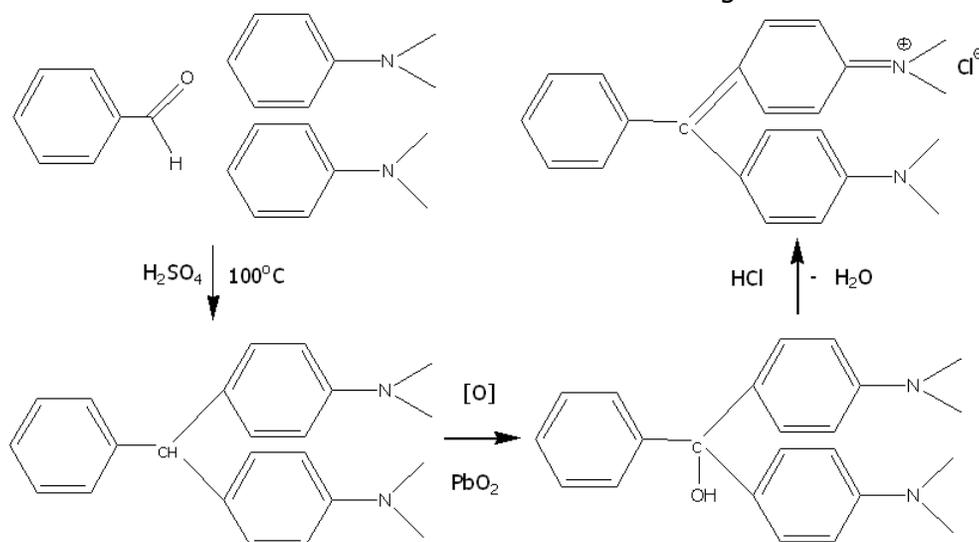
Figure 17: Synthesis of Malachite Green

b) **Rosaniline** (also known as **Magenta** and **Fuchsine**): It was discovered by Veruin in 1859 and it is the o-methyl derivative of para-rosaniline. It is prepared by oxidizing an equimolar mixture of aniline (C_6H_5-NH_2), ortho-methylaniline and para-methylaniline (H_3C-C_6H_4-NH_2) in nitrobenzene in the presence of iron filings (Figure 18).

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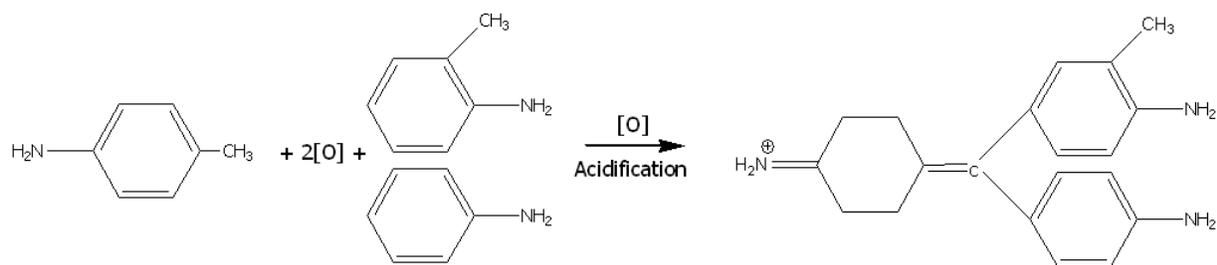
Figure 18: Synthesis of Rosaniline

It is used to dye wool and silk directly and cotton after treatment with tannin as a mordant (helps the dye attach to the fabric). It produces a violet-red color (Figure 19).

Figure 19: Fuchsine Colored Fabric

c) **Crystal Violet**: It was first prepared in by Kern in 1883 by heating Michelor's ketone with dimethylaniline in the presence of $COCl_2$ (Figure 21).
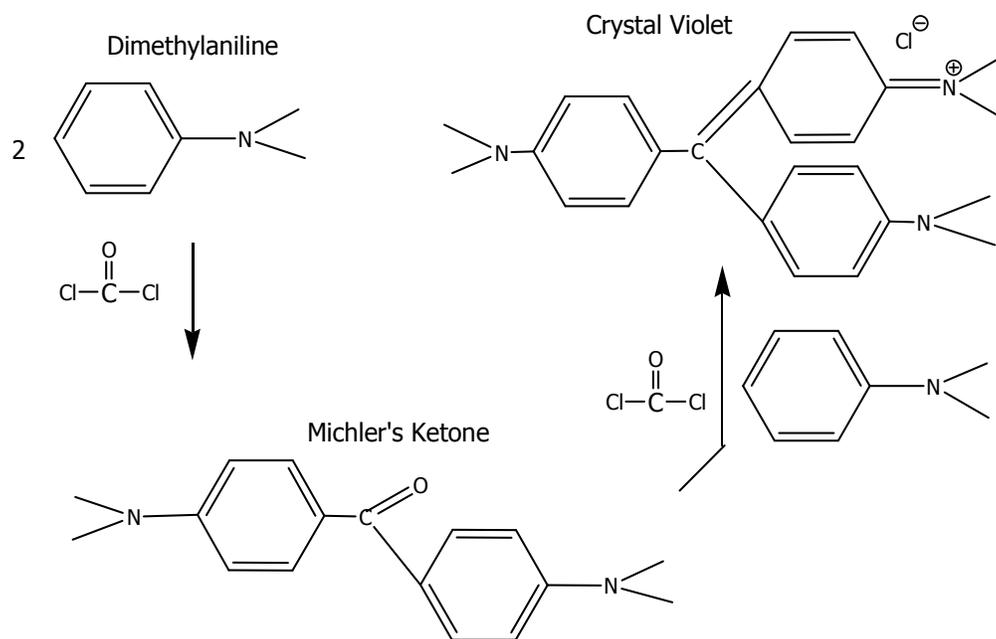

Figure 20: Crystal Violet Dye

Figure 21: Synthesis of Crystal Violet

Crystal Violet is used to dye wool and silk directly, but cotton with the help of a mordant (fixing agent). It is also used as a microbiological staining agent, antiseptic and antifungal agent.

4. **Phthalene Dyes**: They are obtained by condensing phenols with phthalic anhydride in the presence of a dehydrating agent. Phenolphthalein is the most popular phthalene dye that is also used as an indicator in acid-base titrations

a) **Phenolphthalein**: It is prepared by reacting phthalic anhydride with 2 equivalents of phenol at 200°C in the presence of concentrated sulfuric acid which acts as the dehydrating agent (Figure 23).
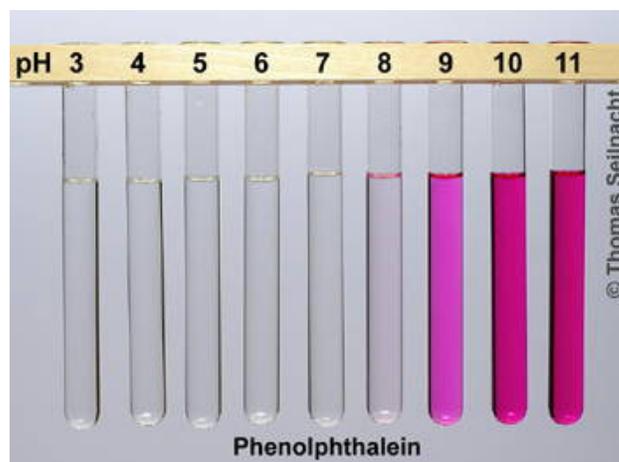
Figure 22: Phenolphthalein at different pH
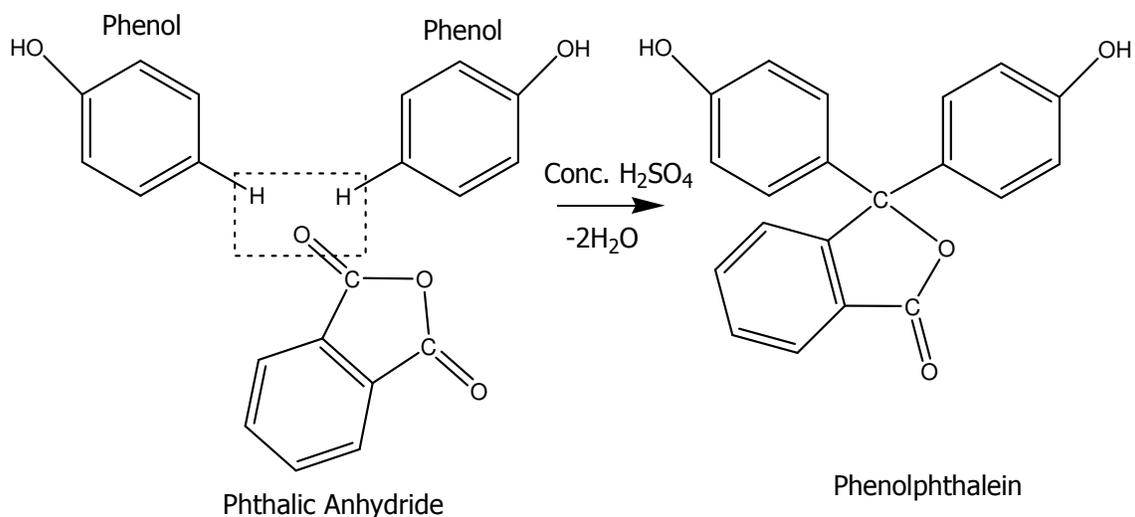
Figure 23: Synthesis of Phenolphthalein

It is white crystalline solid, which is remains colorless in acid or neutral soltuions, but turns pink in alkaline solutions. This is used as an indicator in acid-base titrations.

b) **Fluorescein**: It is prepared by heating phthalic anhydride with resorcinol (dihydroxy benzene) in 1:2 molar ratio in the presence of concentrated sulfuric acid at 200°C (Figure 24).
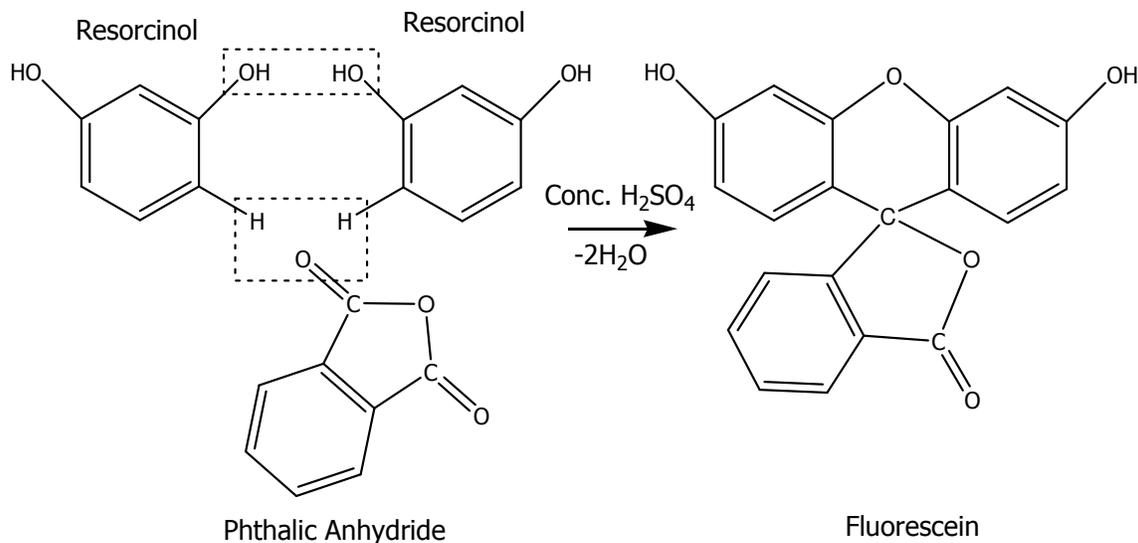

Figure 24: Synthesis of Fluorescein

Fluorescein gives an yellow-green fluorescence in dilute alkaline solutions and is used as a dye for wool and silk. It is also used as a tracer for detecting water leakages in pipelines, as a staining agent in microscopy, as a purgative and antiseptic. (Figure 25)

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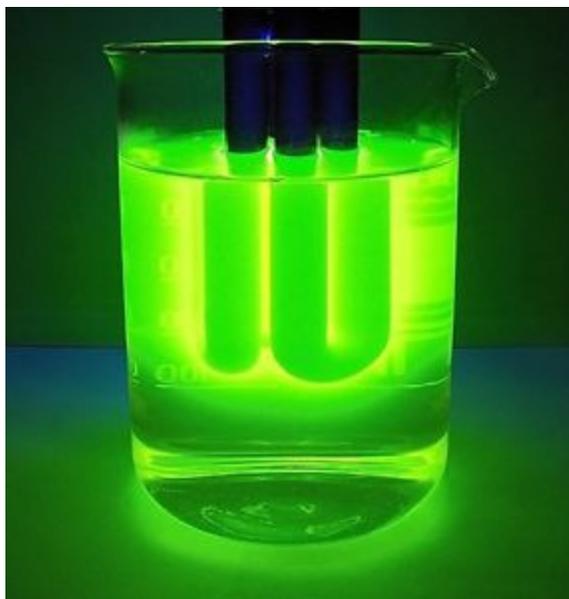
Figure 25: Fluorescein Dye Solution

5. **Xanthene Dyes**: These dyes are related to phthalein dyes and the parent substance for these dyes are xanthenes (di-benzo-1,4- pyran). An important xanthenes dye is eosin described below.

Fluorescein described above is a type of xanthenes dye, but is described under phthalene dyes as the parent substance is phthalic anhydride.

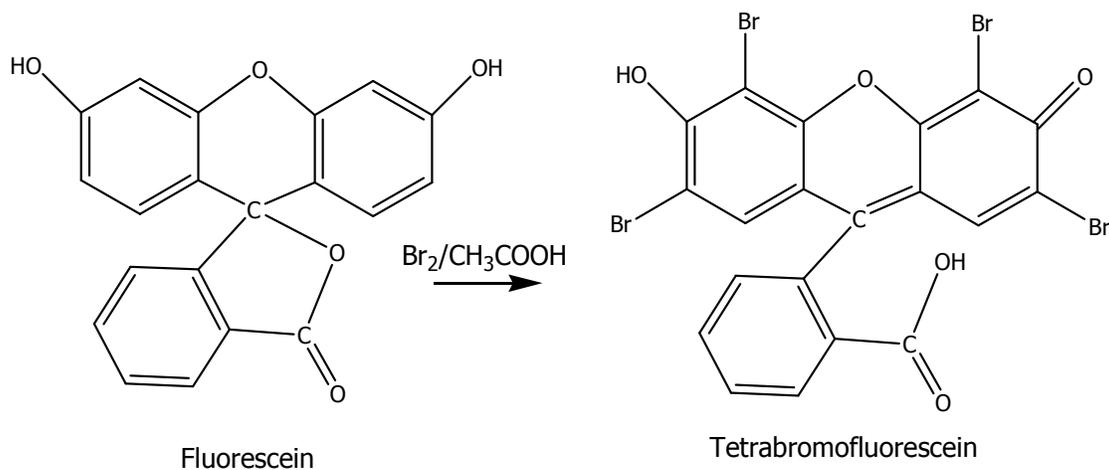a. **Eosin**: It is obtained by heating fluorescein with bromine in the presence of glacial acetic acid.

Fluorescein

Tetrabromofluorescein

Figure 26: Synthesis of Eosin (Tetrabromofluorescein)

b. A subgroup of xanthenes dyes are **Rhodamine** Dyes. These are prepared by condensing phthalic anhydride with m-hydroxyamines in the presence of dehydrating agent. **Rhodamine B** also known as Basic Violet 10 is a typical example of this. It is prepared (Figure 27) by condensing together m-diethylamino phenol (2 moles) with phthalic anhydride (one mole) in the presence of zinc chloride.
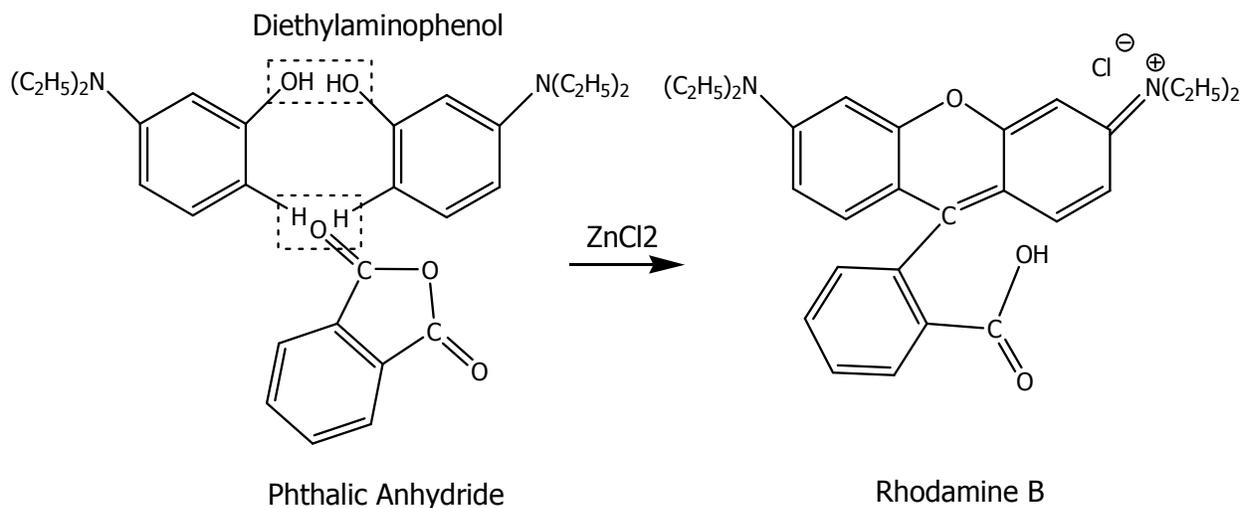

Figure 27: Synthesis of Rhodamine B

c. A subgroup of Xanthene dyes is **Pyronine** dyes. These are prepared by condensing formaldehyde (1 mole) with m-dialkylaminophenols (2 moles) in the presence of concentrated sulfuric acid as dehydrating agents. The produce is oxidized with ferric chloride to pyronine dyes. The important member of this class is **Pyronine G**.
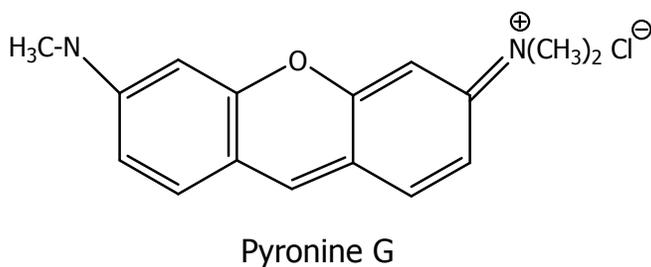

Pyronine G

Figure 28: Structure of Pyronine G

6. **_Azo Dyes:_** This constitutes the single largest group of dyes and have the complete ranges of colors. The term azo suggests that it has the "–N=N–" group. They also contain sulfonic acid, hydroxyl and/or amino groups. These additional groups impart water solubility, variations in color etc.

They are prepared by coupling a diazotized amine (known as the primary component) with a phenol or amine (known as the secondary component). This coupling usually occurs at the para

position to hydroxyl or amino groups present in benzene derivatives. If the para position is filled up, then it can occur in the ortho position.

Azo dyes can be divided into monazo-, bisazo-, triazo- etc dyes depending on the number of azo groups present. They can be further subdivided into acid, basic, direct, ingrain or developed dyes depending on the mode of application. So azo dyes could be monoazo acid, monoazo basic, bisazo acid, bisazo basic dyes *etc*. Some azo dyes are given below as examples.

Monoazo dyes: In monoazo dye, 2 acid dyes are used as an example.
   a. **Acid Dye - Orange II or Acid Orange**: It is prepared by coupling diazotized sulphanilic acid with β-Naphthol.
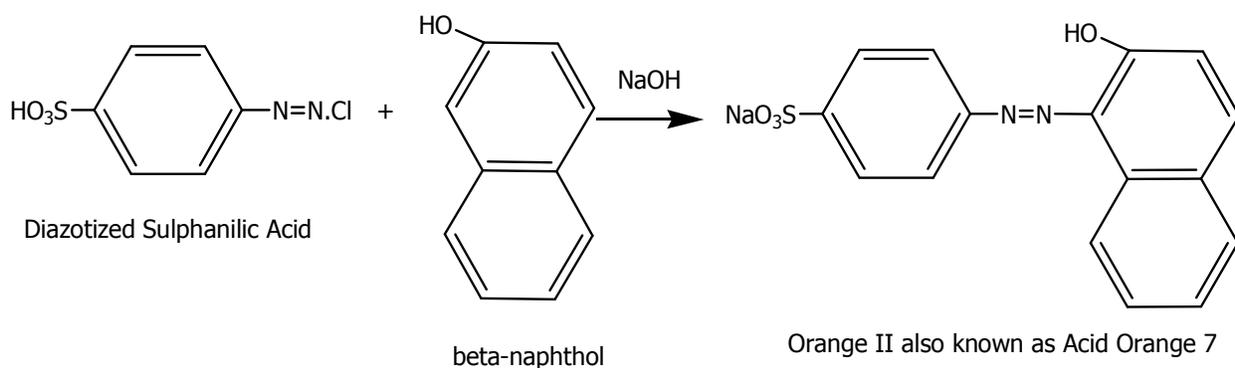

Figure 29: Synthesis of Acid Orange Dye

It is used to dye wool, silk, nylon, leather *etc*.

   b. **Acid Dye - Methyl Orange (Helianthin)** – It is an important acidic azo dye prepared by coupling diazotized sulphanilic acid with demethyl aniline.
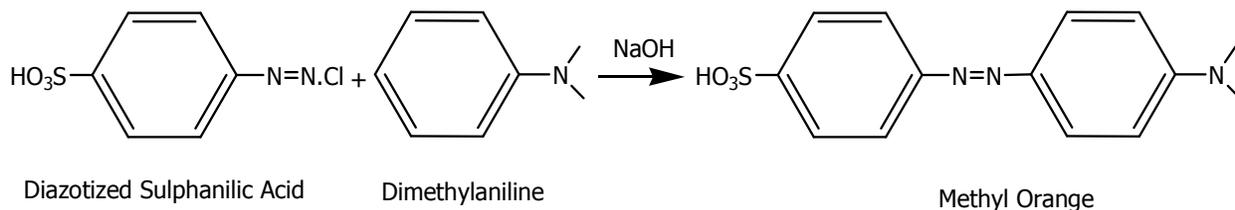

Figure 30: Synthesis of Methyl Orange

It imparts orange color to wool and silk, but the color is fugitive. It is used as an acid-base indicator in titrations as it gives orange color in alkaline pH conditions and red color in acidic pH conditions.

Bisazo Dyes : In bisazo dyes, a basic dye and a direct dye are used as an example.

a. Basic Dye - Bismark Brown: It was first prepared by Martius in 1863 by the action of nitrous acid on excess m-phenylenediamine. It is a mixture of mono and bisazo compounds I and II. It is a brown dye used in boot polish and wood polish. It dyes wool and mordanted cotton.
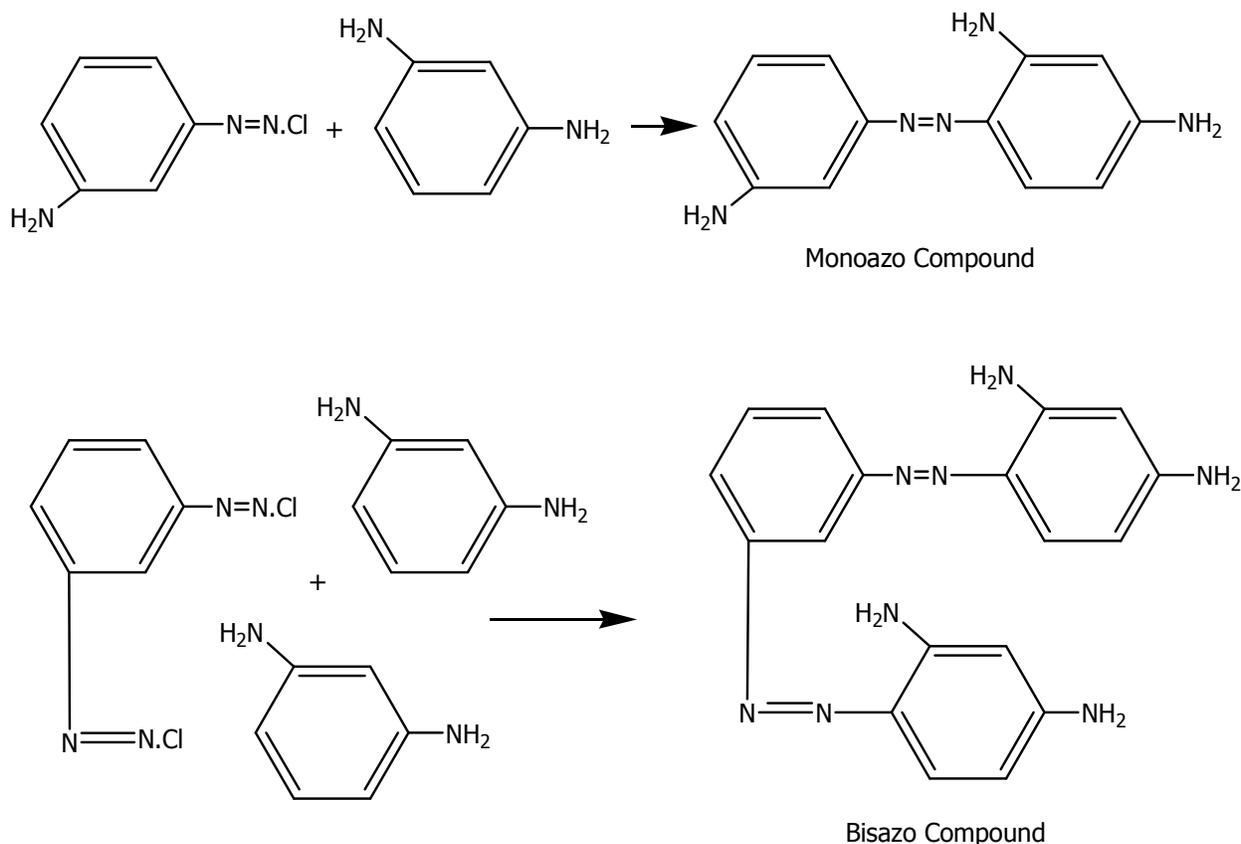

Figure 31: Synthesis of Bismark Brown

b. Direct Dye - Congo Red: It is prepared by coupling tetraazotised benzidine with naphthionic acid (1-naphthylamine-4-sulfonic acid). It was the first synthetic dye that could dye cotton directly.

It is red in alkaline solution and it sodium salt is used for dyeing cotton from water solution. It is very sensitive to acids and in the presence of mineral acids the color changes from red to blue. Hence it is used as a acid-base indicator.
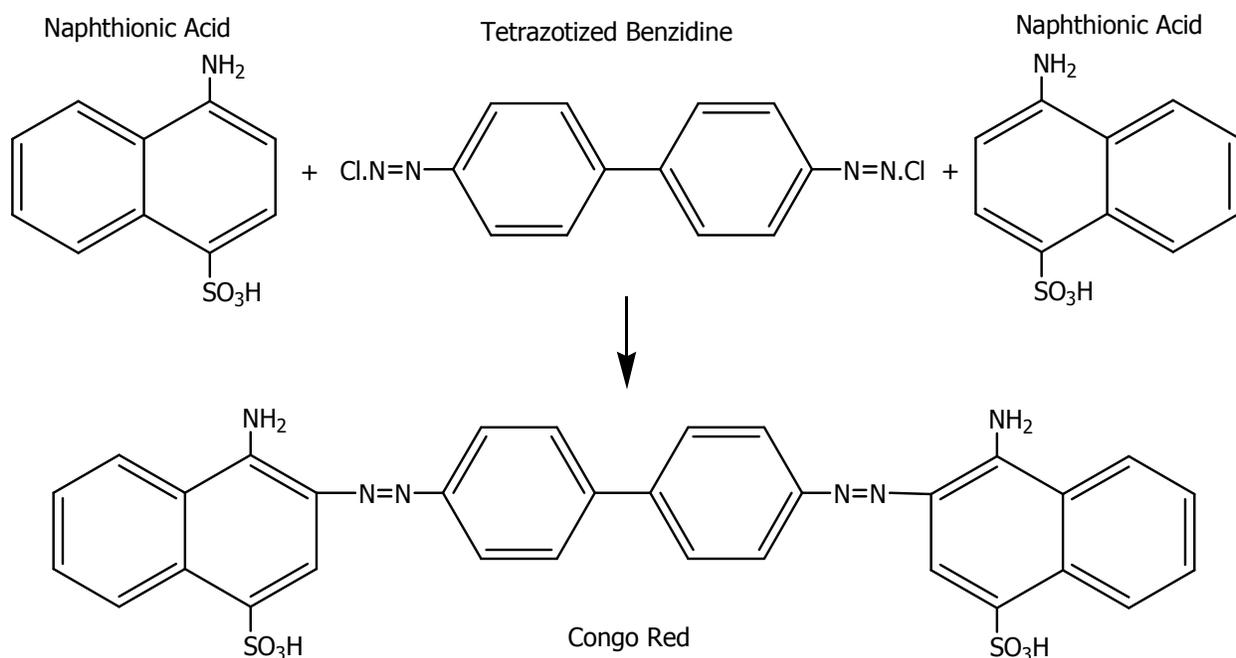
Figure 32: Synthesis of Congo Red

7. **Anthraquinone Dyes:** These are derivatives of anthraquinone. Alizarin obtained from madder root is the most important member of this class. Anthraquinone dyes can be categorized into various groups depending on the application such as mordant dye and vat dye. Each application is provided with an example below.

a. **Mordant Anthroquinone Dyes – Alizarin** (1,2-Dihydroxy Anthraquinone)

It is the most important anthraquinone dye. It occurs in madder root (*Rubia tinctoria*) as a glucoside, ruberythric acid, from which it is obtained by acidic hydrolysis. Industrially it is obtained by sulphonating anthraquinone with oleum at $140^{o}C$. The sodium salt of the resulting β-sulphonic acid, anthraquine -2-sulphonic acid (also known as silver salt) on fusion with sodium hydroxide, in the presence of sodium or potassium chlorate at $200^{o}C$, under pressure given alizarin.

Mordant dyes have no natural affinity for the fabric and are applied to it with the help of certain additional substances known as mordants. A mordant (Latin mordere = *to bite*) is any substance which can be fixed to fabric and reacts with the dye to produce colors on fabric.

Three types of mordants are commonly used,
- Acidic mordants such as tannic acids which are used with basic dyes.
- Basic mordants such as albumin or metallic hydroxides which are used with acidic dyes.
- Metallic mordants like salts of aluminum, chromium, iron, tin, etc., which are used with acidic dyes
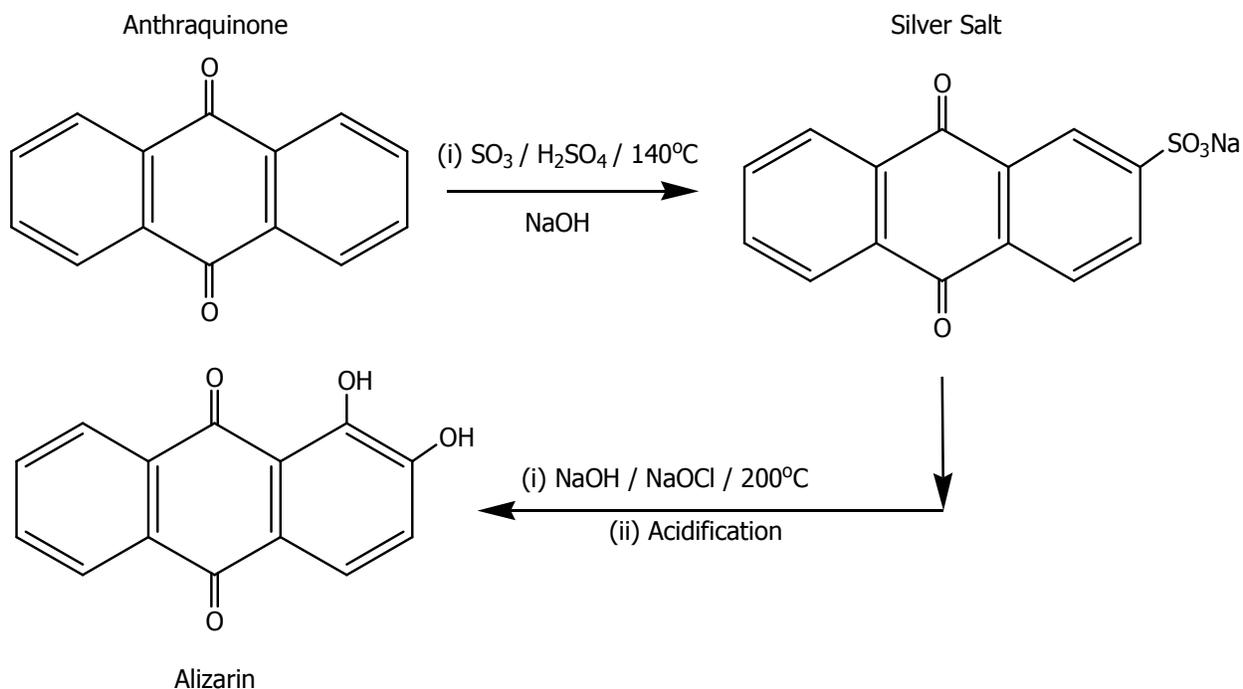
Figure 33: Synthesis of Alizarin (1,2-Dihydroxy Anthraquinone)

The mordant forms an insoluble coordination compound between the fabric and the dye and binds the two. The procedure of mordant dyeing consists in impregnating the fabric with mordant in presence of wetting agent followed by soaking of the fabric into the solution of dye.

Alizarin is a classic mordant dye. It provides different colours depending on the metal ion used. For example, with Al^{3+}, alizarin gives a rose red color; with Ba^{2+}, a blue color; with Fe^{3+}, a violet color and with Cr^{3-}, a brownish red color. Alizarin was used widely for dyeing wool, cotton etc. A structure showing binding of Alizarin to fabric with Al^{3+} as mordant is provided below.
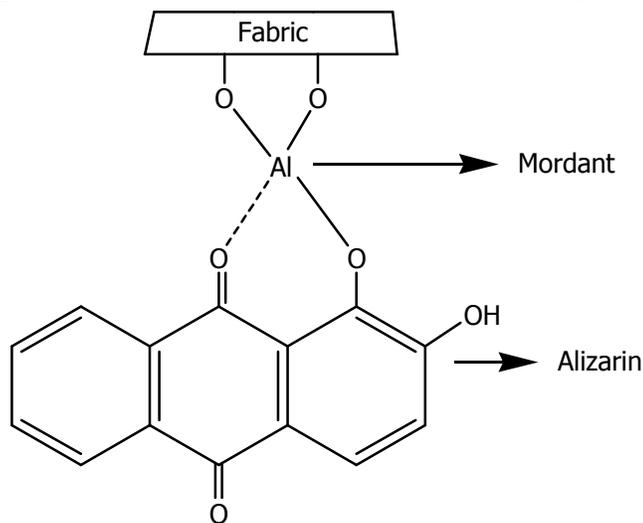
Coordination Compound of Alizarin with Al3+ as Mordant

Figure 34: Alizarin with Al^{3+} as mordant for attachment to fabric

b. Vat Dyes - Indanthrone blue dye

These dyes constitute a major class of dyes of the present day textile industry. They are available in brilliant colors of exceptional fastness. Indanthrone blue (Vat O) is an important dye belonging to this class.

Indanthrone blue can be prepared by fusion of 2-aminoanthraquinone with potassium hydroxide in the presence of oxidizing agent like potassium nitrate or potassium chlorate at 250°C. This dye is used in coloring cotton, wool, silk and pulp in paper industry.
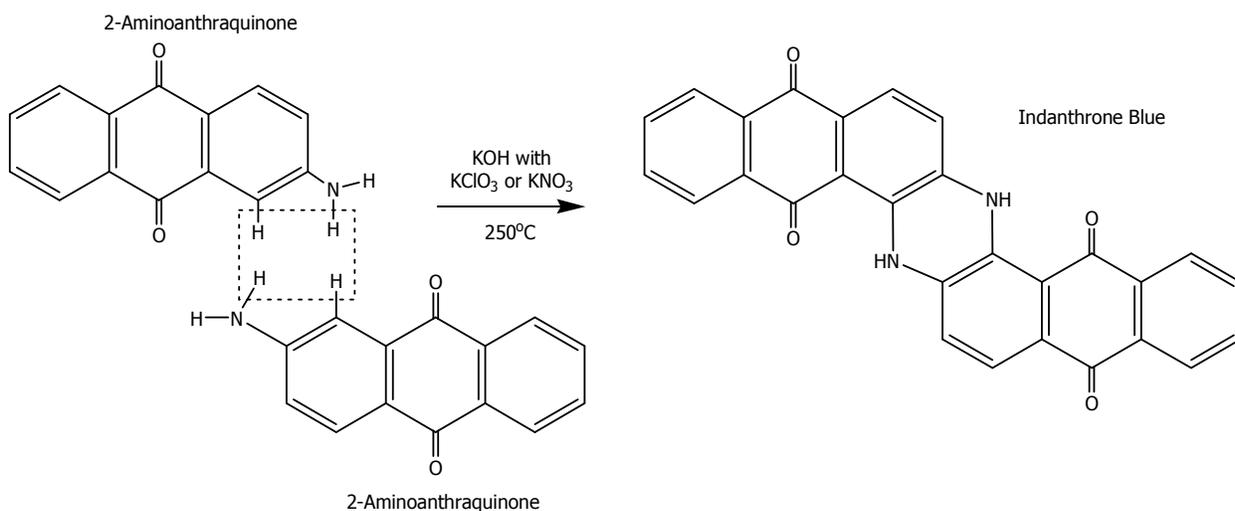

Figure 35: Synthesis of Indanthrone Blue

Carbazole Dyes:

Carbazole is the name given to an aromatic heterocyclic tricyclic organic compound. It consists of two six-membered benzene rings fused on either side of a five-membered nitrogen-containing ring. (Figure 36)
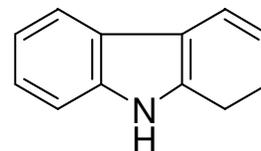

Figure 36: Carbazole Structure

A typical example of carbazole dye is Indanthrene Brown R. This dye is produced from a dianthramide intermediate by treatment with sulphuric acid. This leads to ring closure to form a the carbzole ring structure. (Figure 37)
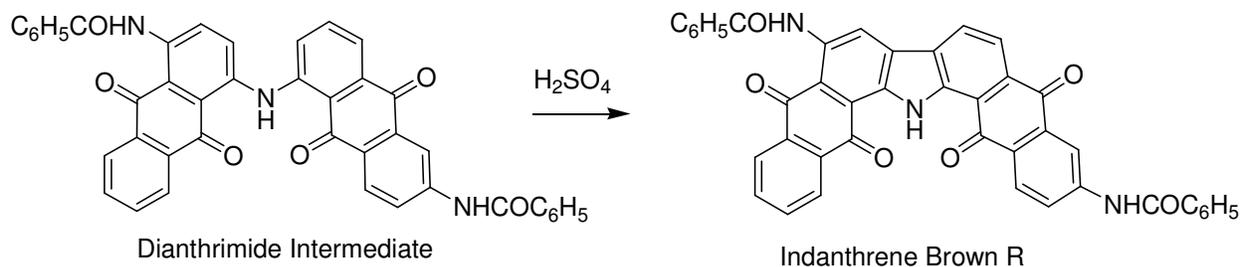
Figure 37: Synthesis of Indanthrene Brown R

Heterocyclic Dyes:

They contain atleast one heterocyclic ring in their structure. Heterocyclic compounds contain an atleast one atom other than carbon in their ring structure. Heterocyclic atoms found in such structures are usually nitrogen, sulfur and oxygen. Sub-groups of heterocyclic dyes are acridine, cyanine and azine type of dyes. Acridine dyes are provided as an example below.

Acriflavine synthesis

The acetylation of 2,8-diaminoacridine followed by hydrolysis forms 2,8-diamino-10-methylacridium also known as acriflavine.
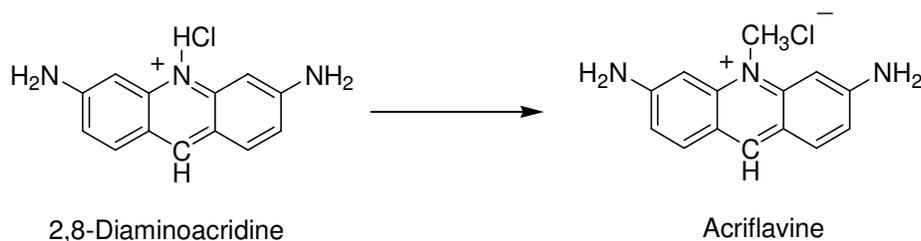

Figure 38: Acriflavine Synthesis

Phthalocyanine Dyes and Pigments
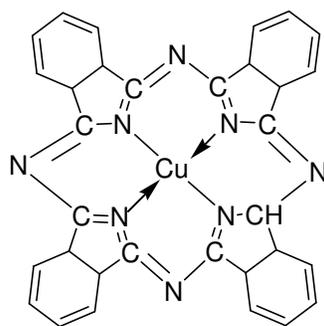
These are analogs of chlorophyll containing nitrogen atoms instead of methylidyne groups (Figure 39).

Figure 39: Monastral Fast Blue