Chem Factsheet

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Chemistry of Dyes

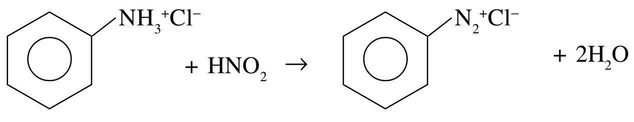
More than half of modern dyes are **azo compounds**. These contain the **C-N=N-C functional group**.

> *They are produced by an **azo-coupling reaction** in which carbon atoms in two **benzene rings** are linked by a nitrogen (C-N=N-C) bridge.*

> *The nitrogen atoms are provided by an **ionic diazonium compound** (containing C-N_2^+).*

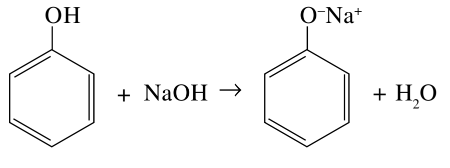
For example, the **benzenediazonium ion** has an N_2^+ group ($-N^+\equiv N$) attached to a benzene ring ($C_6H_5N_2^+$) and is present in **benzenediazonium chloride** ($C_6H_5N_2^+Cl^-$).

A diazonium compound is first made by reacting a **primary aromatic** (derived from benzene type compounds) **amine** with excess **hydrochloric acid and sodium nitrate(III)** ["sodium nitrite", $NaNO_2$] at 5-10°C. The acid and nitrate(III) mixture provides **nitric(III) ["nitrous"] acid (HNO_2)** in situ which then acts on the amine (present as the **ammonium salt** (C-NH_3^+) because of the excess acid.



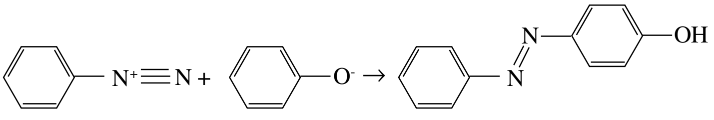
The temperature is critical. Any lower and the reaction is too slow; any higher and the diazonium compound decomposes to nitrogen and phenol (C_6H_5OH).

A solution of **sodium phenoxide** is also prepared by dissolving **phenol** in **sodium hydroxide** solution. This is often described as the "**coupling agent**".



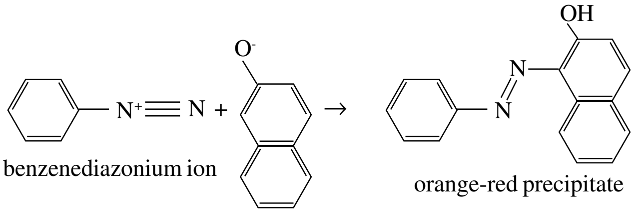
phenol sodium phenoxide

The final stage must be carried out at about 5°C, and so the reaction vessel is placed in a mixture of ice and water. The cold benzenediazonium chloride solution (prepared as above) is then added. The diazonium ion and the phenoxide ion react to form a yellow orange precipitate. This is the dye – **4-hydroxyazobenzene**.

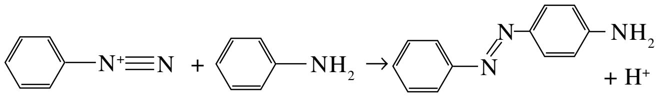


benzenediazonium ion phenoxide ion 4-hydroxyazobenzene

A similar example is the coupling reaction between napthalen-2-ol and benzenediazonium ion.The coupling ion is first prepared by dissolving **napthalen-2-ol in sodium hydroxide solution**, cooling and then mixed with the cold benzenediazonium chloride solution:



A third example is when a cold solution of benzenediazonium chloride is mixed with liquid phenylamine. A yellow dye is produced:



benzenediazonium ion phenylamine aniline yellow

Quick Question 1.
What structural features do these three azo dyes above have in common?

Quick Question 2.
Classify the reaction **mechanism** involved in forming each of these dyes.

Why Dyes are Coloured?

The electrons in the dye molecule are in specific energy levels. When they are excited by absorbing electromagnetic radiation they will move up to a higher energy level. When the energy absorbed by the electrons corresponds to the visible region of the electromagnetic spectrum then the compound will appear coloured. The colour of the light absorbed will depend on the difference in energy between the level the electron was in and the level to which it has been excited. This difference in energy corresponds to a specific wavelength or frequency of light and so will give rise to a specific colour. However the colour reflected and seen will not be the one absorbed but its complementary colour.

> $\Delta E = hf$,
> *where ΔE is the difference in energy between the ground and excited states of the electron, f is the frequency of the radiation absorbed, and h is Planck's constant.*

> *The colour of a dye is due to the fact that only certain colours which do not correspond to possible electron transitions are reflected or transmitted. These are called complementary colours.*

The excited electrons will lose their energy and decay back to their ground state by emitting electromagnetic radiation of a longer wavelength.

Why the Benzene Rings Bridged by Two Nitrogen Atoms Act as a Chromophore?

> *The term **chromophore** is used to describe groups which will absorb electromagnetic radiation in the visible region and hence cause compounds to be coloured.*

A highly **delocalised system of electrons extends over the benzene rings and the nitrogen atoms**. This delocalised system may also extend over the atoms or groups attached to the benzene rings. The atoms involved are said to be **conjugated** – linked by overlap of p-orbitals and d-orbitals). When white light (which is a mixture of all colours/frequencies) falls on one of these compounds the electron transitions which the delocalised electrons can undergo correspond to the visible region of the spectrum. Certain frequencies are absorbed and those which are not absorbed but reflected give the dye its characteristic colour.

The Effect of the Groups Attached to the Benzene Rings

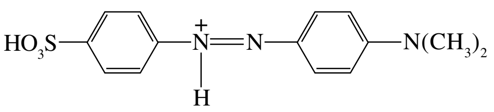
The delocalised system extends over the groups attached to the benzene and these will change the energy levels of the delocalised electrons slightly. This means that when an electron moves from one energy level to another the ΔE or energy change involved will be slightly different. Thus the frequency of radiation absorbed will be modified slightly. The frequencies of the reflected light (colour of the dye) will alter accordingly.

> *Modifying the groups present in a dye molecule can alter the frequencies absorbed and hence its colour. This may result from a change in pH.*

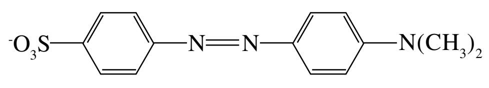
Azo Dyes as Indicators

The indicator methyl orange is an azo dye. It has two forms. The form which it adopts depends on the pH:

red methyl orange in acidic solutions (pH less than 3.1)



yellow methyl orange (pH greater than 4.4)



The change in colour which you see is due to a change in the delocalisation of the methyl orange molecule. Adding an acid causes the hydrogen ion to attach to give the red form, until at pH less that 3.1 it exists entirely in the red form. Between pH 4.4 and pH3.1 it exists as a mixture of the red and yellow forms.

> *The change in colour of dyes when groups are added is a result in a change of the delocalisation of the molecule. The delocalised energy levels are shifted slightly and this changes ΔE. The frequency absorbed changes slightly, giving a corresponding change in the colour of reflected / transmitted light.*

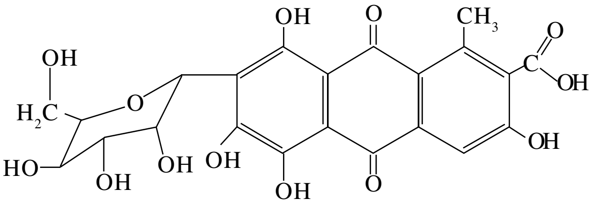
Traditional Natural Dyes

The dyes which were discovered in the past came from plants and animals and have a long history. They are still used in industry and in the home and for craft projects.

> *Pigments are insoluble molecules, whereas dyes are soluble.*

1. Cochineal

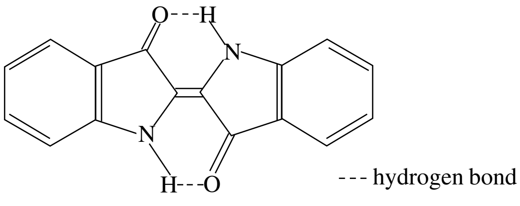
Cochineal is a natural traditional textile dye which produces scarlets, pinks and reds which have good lightfast and permanent properties. It was discovered in Peru and Mexico and has been used there for thousands of years. It is produced from an insect native to South America and Mexico which lives on the prickly pear cacti there. It was introduced into Britain in 1518 AD. However its industrial use here has declined due to the introduction of many competing artificial dyes from the mid-nineteenth century onwards.



carminic acid known as the dye cochineal

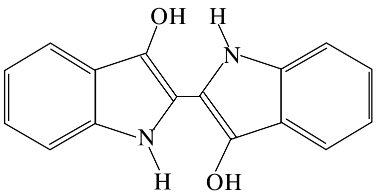
2. Indigo

Indigo is another natural textile dye which has been known and used for centuries. It originates from plant species containing the active ingredient Indican. In Great Britain a blue dye was extracted from the woad plant which contained indigo (which is used to colour jeans blue).



indigo

However, indigo dye is a pigment, which means it is not soluble in water. Woven fabrics will become stiff if treated with coloured pigments and flexing the material will cause the tiny pigment grains to fall out. Indigo must first be **reduced** to a form of white indigo.



indigo white is soluble in water

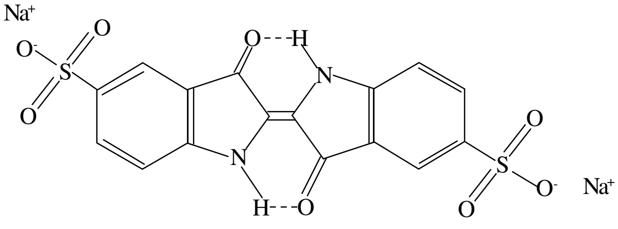
When the textiles are removed from the dye bath the white indigo is attached to the molecules of cloth and will rapidly be oxidised by oxygen in the air to form the dye indigo. One means by which dyes attach themselves to the material which is being dyed is hydrogen bonding. The structure of indigo is such that it forms hydrogen bonds with itself, whereas white indigo cannot do this. White indigo hydrogen bonds with water and this makes it soluble.

By the beginning of the nineteenth century chemists had begun to produce indigo synthetically. Synthetic dyes are often derived from coal tar. The chemical industry of the second half of the nineteenth century was able to obtain coal tar very cheaply because it was an unwanted by-product of the new coal-gas industry. Industrial chemists were able to make a range of traditional colours and also to discover many new coloured compounds.

> *Dyes may attach themselves to the fibres of material by hydrogen bonding, or by dipole-dipole bonds. They may also form stronger covalent or ionic bonds with the fabric.*

Practice Questions

1. The dye shown is formed by a modification of the benzene rings in indigo.



indigo carmine

   (a) Draw the structure of Indigo (1 mark).
   (b) Explain why indigo acts as a dye (6 marks).
   (c) A deep red dye called Thioindigo is a modification of Indigo in which the two NH groups are replaced by sulphur atoms. Draw Thioindigo (1 mark).
   (d) Suggest how Indigo Carmine (see above) might be prepared from Indigo (1 mark).
   (e) Thioindigo is deep red, Indigo Carmine is blue green whereas Indigo is blue.Explain why a colour difference occurs (4 marks).

2. Benzene rings are often found in the structure of compounds which act as dyes. However, benzene is a colourless compound with an electronic spectrum in the ultraviolet. Explain how the compounds are able to act as dyes. (5 marks)

3. How do dyes attach themselves to the molecules of the fabric to be dyed? (1 mark)

4. Dyes can be made from benzenediazonium chloride.Draw the chemical structure of this compound. (2 marks).

5. Give the name of the organic compound with which the benzenediazonium ion will couple to give aniline yellow dye. Give the reaction conditions.

6. Three dyes are yellow-orange, orange-red, and yellow. They each have a different chromophore containing benzene rings: A has 2 benzene rings, B has 3 benzene rings and C has 4 benzene rings. Match the dyes A, B and C to the correct colours (1 mark). Give a reason for your answer (3 marks).

Answer to Quick Question 1)

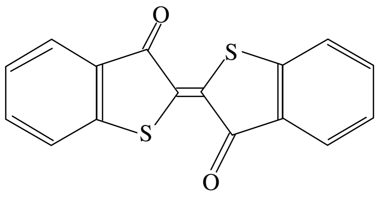
They all have an N=N and two benzene rings one bonded either side of the N=N.

Answer to Quick Question 2)

Electrophilic substitution – the diazonium ion is the electrophile.

Answers to Practice Questions

1. (a) see diagram in text. (1 mark)
   (b) Electrons are excited to a higher energy levels by the absorption of incident light photons. (1mark). The frequency of the light absorbed depends on the energy difference between the level the electron was in and the level to which it jumped (1 mark). Compounds containing conjugated benzene ring systems absorb in the visible region (1 mark). The energy levels are closer together for molecules with greater conjugation or more delocalisation / more than one benzene ring or a larger chromophore (1 mark). The frequency / energy of visible light is less than that of u.v. light (1 mark). The dyes reflect the complementary colour (1 mark).
   (c)



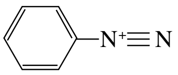
thioindigo

   (d) Indigo Carmine might be prepared from Indigo by treating with **sulphuric acid**. (1 mark)
   (e) Electrons are excited to higher energy levels by the absorption of light. (1 mark) The frequency of light absorbed depends on the difference in energy between the two levels, which depends on the degree of delocalisation (1 mark). The different substituents alter the delocalisation and so the energy levels by differing amounts and so the energy difference is not the same (1 mark). If the energy difference is altered then the frequency / energy of the light / photons absorbed will be different and so the colour will be different (1 mark).

2. As a result of light / photon absorption an electron jumps up from one energy level to another / is excited (1 mark). The frequency absorbed is dependent on the change in energy (1 mark). Dyes contain several benzene rings and this changes the energy levels of the system so that a lower energy / frequency change occurs (1 mark) than would occur if the benzene were alone as a single ring (1 mark). The energy absorbed is then in the visible region as visible light has a lower frequency / energy than u.v. light (1 mark).

3. Hydrogen bonding or dipole-dipole interactions or covalent or ionic bonding. (1 mark).

4.



benzenediazonium ion (1 mark) **and** the chloride ion Cl^- (1 mark)

5. Phenylamine (1 mark). 5-10°C (1 mark).

6. A is yellow, B is yellow-orange, C is orange-red (1 mark). The more conjugated and delocalised the electron system is the more the energy of the transition of an electron into an excited state is lowered (1 mark). The lower the photon energy absorbed the lower the frequency of light absorbed (1 mark). Lower frequency / longer wavelength corresponds to the more red end of the electromagnetic spectrum (1 mark).

Acknowledgements: *This Factsheet was researched and written by Christine Collier.*
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