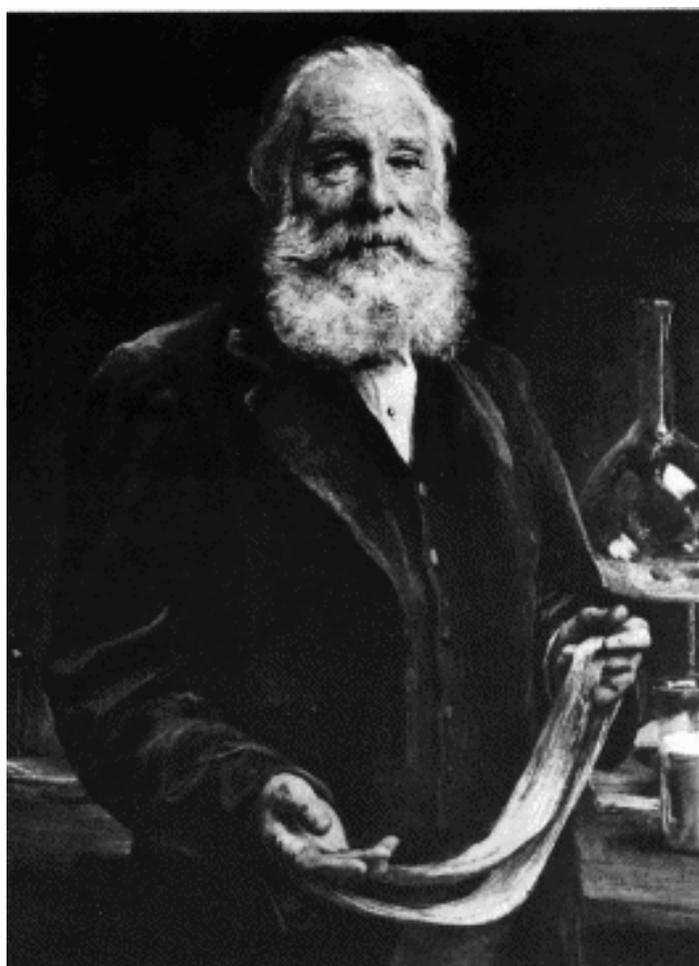


E36

Chemistry of Blue Jeans: Indigo Synthesis and Dyeing



William Henry Perkin (1838-1907)

The Task

The goal of this experiment is to synthesise the vat dye, indigo and compare the properties of cloth that has been dyed with indigo and a mordant dye alizarin.

Skills

At the end of this laboratory session you should be able to:

- vacuum filtrate.
- accurately weigh out samples.

Other outcomes

At the end of the laboratory session you should be able to:

- synthesise indigo.
- dye cloth using a vat.
- dye cloth using a mordant dye.
- observe the colours of the mordant dyes formed with different divalent metal ions.
- test and compare the dyed material for solubility and fading.

History

Indigo

The blue dye indigo has been used in India for about the last 4000 years. It was derived from the plant *Indigofera tinctoria*. Phoenician traders and migrating peoples gradually introduced this dye to the Mediterranean area and then spread to Europe. In Northern Europe from the Bronze Age (2500 – 850 BC) people used a blue dye, woad from the plant *Isatis tinctoria*. It has since been discovered that this plant contains the chemical indigo, but due to other compounds in the plant it is not a ‘pure’ blue like the *Indigofera*.¹

Indigo is a vat dye. The plant was fermented and then treated with urine. The fibre was dipped into the colourless dye bath and then hung out in the sun to contain a blue insoluble dye on the fibre.¹

In 1865, the German chemist Johann Friedrich Wilhelm Adolf von Baeyer began working with indigo. In 1880, his work resulted in the first synthesis of indigo and three years later the announcement of its chemical structure. BASF developed a viable manufacturing process that was in use by 1897, and by 1913 natural indigo had almost been replaced by synthetic indigo. In 2002, 17000 tons of synthetic indigo was produced worldwide.²

Denim

Denim originated in the ancient textile centre of Nimes, France and was called “serge de Nimes”. Columbus is reported to have used denim for his sails on the Santa Maria. At approximately the same time in India, the sailors of Dhunga, were using denim material for their pants, which became known as dungarees. Later on, the word “jeans” came into existence from Genoa, Italy, where working men wore denim trousers.³

In 1849, Levi Strauss, an unsuccessful miner in the Californian gold rush in the U.S.A, became rich by making denim pants for the more successful miners. The first western “Levis” jeans were born. Over the next hundred years they remained working pants.³

About 1947, denim started to move into sportswear and rainwear. Since 1960, the jeans business has undergone a transformation from tough, cheap clothing to a fashion conscious market. In 1970 the American youth adopted denim as their favourite material.³

Alizarin

Alizarin was used for dyeing cloth in Asia in ancient times. It has been found in the excavations at Pompeii and in Egyptian textiles from as early as 1567 BC and in Corinth from 146 BC. In 972 AD, alizarin was first used on paper in ink for a marriage certificate of Empress Theophou, then later as a pigment in paint. In the Advocates Library in Edinburgh, alizarin paint has been found in an illustration book dated 1465-1489.⁴

Alizarin is found in the madder root from the Mediterranean and Asian plant *Rubia tinctorium*.¹ The plant was usually harvested three years after planting for maximum yields of the dye. After uprooting, it was left to dry, placed in larger piles for 2-3 days and then dried in warm air drying houses. The dried roots were crushed and separated from the bark and ground into a fine powder. Some madder must be fermented for 1-2 years before it can be used. Other madder that has significantly better quality can be used straight away, but it is better if stored first.⁴

Sir William Henry Perkin (1838 – 1907), at 18 years of age, synthesised the first synthetic dyestuff, from chemicals derived from coal tar, called mauveine or aniline purple, whilst trying to synthesis a different compound, quinine.⁵ In 1869, Perkin synthesised alizarin. The German company BASF beat him to the patenting process by one day! It was decided that Perkin would sell to Britain (400 tonnes a year) and BASF to the rest of the world.⁶

The Birth of the Pharmaceutical Industry

A medical student, Paul Ehrlich (awarded the Nobel Prize in 1908), had been impressed with the ability of certain dyes to stain tissues selectively. Ehrlich believed that staining was a result of a chemical reaction between the dye and the tissue, so he sought dyes that had an affinity for micro-organisms, hoping that the dye could be modified to become specifically lethal to the micro-organisms.⁷

Ehrlich discovered in 1907 the curative properties of the dye, Trypan Red I, when used against experimental trypanosomiasis and salvarsan in 1909, as a remedy for syphilis. Through these discoveries he invented the term “chemotherapy”. His research was looking for “magic bullets” – chemicals that would be toxic to infectious micro-organisms but harmless to humans.⁷

In 1935, the daughter of Gerhard Domagk, a doctor employed by a German dye manufacturer (I. G. Farbenindustrie), contracted a streptococcal infection from a pin prick. As his daughter neared death, her father decided to give her an oral dose of a dye called Pronstil, which had been developed by the company. Tests had shown that it inhibited the growth of streptococci in mice. Within a short time the little girl recovered. Domagk’s gamble not only saved his daughter’s life, but it initiated a new and wonderful productive phase in modern chemotherapy.⁷

Chemistry

Indigo

Today you will be synthesising indigo using the Baeyer-Drewson reaction,⁸ which is an Aldol Condensation reaction,^{8,9} shown in Figure 1. This is the method developed by J. F. W. Adolph von Baeyer in 1880 to produce the first synthetic indigo. This reaction works well for small scale reactions and is not used today in industry for producing large quantities of indigo.

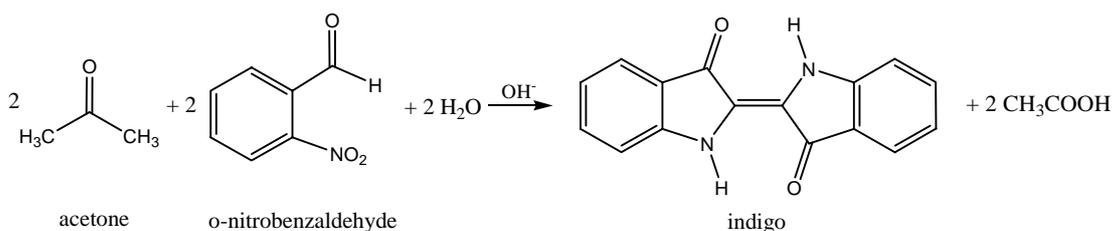


Figure 1: The Baeyer-Drewson reaction of 2-nitrobenzaldehyde with acetone in basic conditions to produce indigo.

Indigo is not soluble in water, so to dye cloth the indigo needs to be made into a water soluble form. Therefore, indigo is called a vat dye. In this experiment, the insoluble indigo dye is synthesised and then reduced with sodium hydrosulfite (sodium dithionite), as shown in Figure 2, to the water soluble leucoindigo (sometimes called indigo white). When the clear yellow leucoindigo solution comes into contact with air it oxidises back to the insoluble blue indigo compound.¹⁰

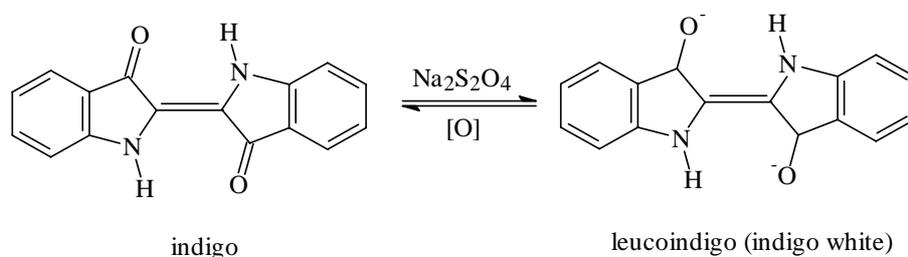


Figure 2: The reaction showing the conversion of the insoluble blue indigo dye to the clear yellow, water soluble leucoindigo or indigo white.

Why is leucoindigo water soluble?

Alizarin

Alizarin (Figure 3) is a mordant dye. A mordant dye requires that the fibres of the fabric be treated with a metal salt solution (such as an aluminium, chromium or copper salt) before the dye. The metal ions form strong complexes between the fibre and the later applied dye.¹ When different metal ions are used, the colour of the dyed cloth changes. Today you will be dyeing cotton material. Figure 4 shows the structure of cotton¹¹, cellulose, a polymer made from D-glucopyranose¹² sugar molecules. The metal ions bond to the hydroxyl groups on the cellulose. When alizarin is added, it binds to the metal as shown in Figure 5, dyeing the cotton fabric.

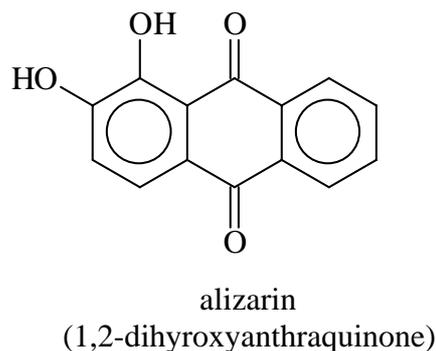
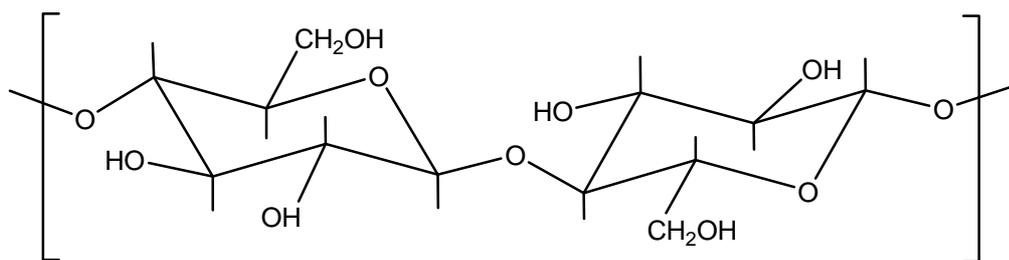
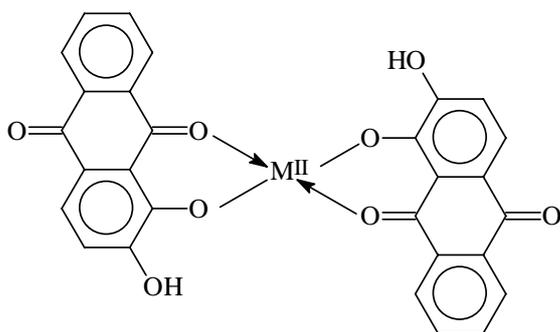


Figure 3: The chemical structure of alizarin.



Cellulose (cotton)

Figure 4: The structure of cellulose, cotton.¹¹



1,2-dihydroxyanthraquinone form neutral 2:1 complexes with divalent metals such as copper and zinc.

Figure 5: The complex the alizarin forms with the divalent metal ion.¹³

Experimental

Part A: Synthesis of the Vat Dye Indigo

Chemical Hazards

2-nitrobenzaldehyde – hazardous: flammable, toxic and an irritant

Acetone – hazardous: flammable, toxic and an irritant

Ethanol – hazardous: flammable, toxic and an irritant

Sodium hydroxide – hazardous: corrosive, hygroscopic and an irritant

Sodium hydrosulfite - hazardous: flammable, toxic, hygroscopic and an irritant

Sodium hydrosulfite can spontaneously ignite in moist air. Make sure that you follow the instructions given exactly. Do not leave the powder exposed to air.

Indigo is not considered to be hazardous but it will stain skin and clothes. Follow the instructions carefully and minimize contact with it.

Do not touch the dye or dyed material with your fingers.

Synthesis of Indigo

- 1) On a watchglass, weigh 1.0 g of 2-nitrobenzaldehyde and transfer it to a 100 mL beaker.
- 2) Pour 20 mL acetone into the beaker with the 2-nitrobenzaldehyde.
- 3) Dilute the solution with 35 mL of deionised water (use 100 mL measuring cylinder).
- 4) Using a 10 mL measuring cylinder, measure 5 mL of 2 M sodium hydroxide.
- 5) Using a glass rod, stir the solution in the beaker vigorously and carefully pour in the sodium hydroxide.
- 6) The solution turns a deep yellow, then darker and within 20 s. a dark precipitate of indigo will appear.
- 7) Continue to stir the mixture for 5 min.
- 8) Collect the purple-blue precipitate by suction filtration.
- 9) Wash the product with deionised water until the washings are colourless (*ca.* 100 mL of water needed), then with 20 mL of ethanol.
- 10) Take out about 0.1 g of the indigo and place it in a 100 mL beaker for vat dyeing the cotton (about ½ the size of a pea).
- 11) The waste solution may be disposed of by washing it down the sinks in the fume cupboards with plenty of water.

Vat Dyeing of Cotton

- 1) To the beaker with the indigo sample add a few drops of ethanol and make a paste by rubbing the mixture with a glass rod.
- 2) Using a 10 mL measuring cylinder, measure 1 mL of deionised water and add it to the paste. Make a suspension by stirring with a glass rod.
- 3) Using a 10 mL measuring cylinder, add 3 mL of 2 M sodium hydroxide solution to the suspension.
- 4) Put 20 mL of deionized water into a 100 mL beaker, add a small amount (the end of a spatula full) of sodium hydrosulfite (sodium dithionite) and stir.
BE CAREFUL NOT TO SPILL THE SODIUM HYDROSULFITE AND RETURN THE CAP TO THE BOTTLE AFTER USE.
- 5) Add the solution made in Step 4 to the beaker that contains the indigo dye.
- 6) Cover the beaker with a watchglass.
- 7) Heat the mixture up to 50 °C on a steam bath (check the temperature occasionally with a thermometer always returning the cover afterwards). As soon as a clear yellow solution is obtained, add 40 mL of deionised water.
- 8) Immerse three small pieces of cotton in the 'vat' and leave for 1 h. at 50 °C, occasionally moving the fabric to ensure even dyeing and checking the temperature.
- 9) Remove the cotton with metal tongs and squeeze dry; hang it in the air for about 30 min. to develop the colour.¹⁰
- 10) Hang the cloths to dry.
- 11) After they are dry, rinse with cold water until the washings are clear to remove any residue of indigo which is not incorporated into the fibres of the cloth, and hang to dry.

Part B: Alizarin

Chemical Hazards

$\text{Al}_2(\text{SO}_4)_3$ – hazardous: an irritant which causes serious damage to eyes.

CuSO_4 – hazardous: toxic and an irritant which causes serious damage to eyes.

FeSO_4 – hazardous: toxic and an irritant which causes serious damage to eyes.

CaSO_4 – an irritant which causes serious damage to eyes.

Alizarin is not considered to be hazardous but it will stain skin and clothes. Follow the instructions carefully and minimize contact with it.

Do not touch the dye or dyed material with your fingers.

Dyeing with the mordant dye Alizarin

In this experiment, different colours of the mordant (metal ions) will be discovered and then a piece of material will be dyed using the different colours observed.

You and a partner need to make up a series of stock solutions of the metal ions which will be used as the mordant. You will need five clean dry 100 mL beakers.

Beaker 1 – Cu^{2+} mordant - dissolve a spatula of CuSO_4 in ~ 80 mL of deionised water.

Beaker 2 – Fe^{2+} mordant - dissolve a spatula of FeSO_4 in ~ 80 mL of deionised water.

Beaker 3 – Al^{3+} mordant- dissolve a spatula of $\text{Al}_2(\text{SO}_4)_3$ in ~ 80 mL of deionised water and add ~1 mL of 2 M NaOH.

Beaker 4 – Ca^{2+} mordant- dissolve a spatula of CaSO_4 in ~80 mL of deionised water.

Beaker 5 – Tap water mordant - in another clean dry 100 mL beaker, dissolve a spatula of alizarin in ~ 80 mL of deionised water.

Dyeing the Cotton

1. Pour 10 mL of the alizarin solution into a 250 mL beaker.
2. Take a small piece of cloth and dip it into the copper mordant (Beaker 1) using the metal tongs.
3. Place the cloth into the alizarin solution making sure that it is completely covered.
4. Using the tongs squeeze as much solution as possible out of the material and hang to dry.
5. Label a 400 mL beaker 'waste'; tip the remaining solution from Step 4 into the waste beaker. Rinse the 250 mL beaker using a small amount of deionised water.
6. Repeat steps 1-5 with the remaining mordants (Beakers 2-4).
7. Repeat steps 1-5 using tap water as the mordant.
8. Repeat steps 3 and 4 with cloth dyed in alizarin with no mordant.
9. When the cloth has dried, wash the cloth with cold water until the water is clear. Dry the cloth again and fill out Table 1.

Using the mordants to make patterns on the cotton material.

1. Use a large piece of material.
2. Using the tongs dip different parts of the material into the mordants **or** place your material on a large white tile and 'paint' the mordant on using the plastic disposable pipettes.
3. Hang the material up to dry, and dry it with a hair dryer.
4. Pour 20 mL of the alizarin into a petri dish.
5. Using the metal tongs pull the material through the alizarin solution and hang to dry.
6. When the cloth has dried, wash the cloth with cold water until the water is clear. Dry the cloth again.

Part C: Testing the Dyed Cotton Material

Chemical Hazards

Cyclohexane – hazardous: flammable, toxic and an irritant.

Ether – hazardous: flammable and an irritant.

3% Hydrogen peroxide– hazardous: toxic and an irritant.

Hydrogen peroxide is incompatible with cyclohexane, ether and nitrobenzaldehyde.

Mixing these materials can cause a serious risk of fire and explosion.

Cyclohexane and ether are to be handled in the fume cupboards and not on the bench.

Hydrogen peroxide is to be handled on the bench and not in the fume cupboards.

Before and when handling any of these materials, make that your working area is free from the incompatible substance.

Indigo and alizarin are not considered to be hazardous but will stain skin and clothes.

Follow the instructions carefully and minimize contact with them.

Do not touch the dye or dyed material with your fingers

Solubility of the dye

Can you dissolve the dye from the material?

- 1) Cut each of the following into 4 pieces;
 - Cloth dyed with alizarin only;
 - One piece of cloth dyed with single metal mordant;
 - One piece of cloth dyed with indigo.
- 2) In the fumehood make up a cyclohexane (non-polar solvent) bath and an ether (very non-polar solvent) bath as shown in Figure 6.

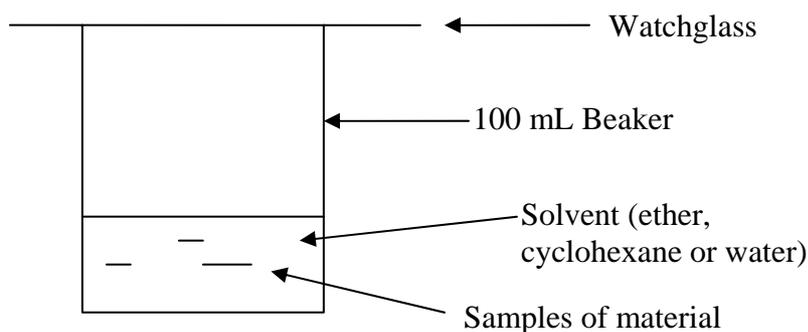


Figure 6: Diagram of a solvent bath.

- 3) Place one of each dyed sample into each bath and leave for 10-15 min.
- 4) On your bench, make a water solvent bath and place one of each dyed sample into the water bath and leave for 10-15 min.
- 5) Observe the colour of the solution and allow the cloths to dry.
- 6) Compare the colour of the cloth that has been soaking in the solvent baths with the original piece of cloth remaining. Record in Table 2 whether the dye is soluble (most of the dye was removed from the cloth), slightly soluble (a little bit of the dye was removed from the cloth) or insoluble (no dye was removed from the cloth).
- 7) Dispose of the cyclohexane and ether solvents in the 'Organic Solvent Waste' bottle in the fume cupboard.

Fading

Make that your working area is free from the solvent baths used above before beginning this part of the experiment..

To test the property of the dye for fading, we are going to speed up the process of fading by using dilute hydrogen peroxide.

- 1) Cut off a piece of each of the following
 - Cloth dyed with alizarin only;
 - One piece of cloth dyed with a single metal mordant;
 - One piece of cloth dyed with indigo.
- 2) On your bench make a solvent bath with 3 % hydrogen peroxide.
- 3) Place the samples of dyed cloth in the solvent bath and leave for 10-15 min.
- 4) Observe the colour of the solution and allow the cloths to dry.
- 5) Compare the colour of the cloth that has been soaking in the solvent baths with the original piece of cloth remaining and record in Table 3 whether there has been any fading by the hydrogen peroxide (was there no fading, a little bit of fading or a lot of fading?).

Results

Table 1: The colours you obtained from using the following mordants.

Mordant	Colour of Cotton Material
Copper	
Iron	
Aluminium	
Calcium	
Tap water	
No mordant	

Question 1

Look at the colours of the dyed cotton. What ions are present in the tap water used?

Table 2: The solubility of Dyes. (Is the dye soluble, slightly soluble or insoluble?)

	Water	Ether	Cyclohexane
Indigo			
Alizarin with mordant			
Alizarin without mordant			

Table 3: Fading of the dyes.

	Did the dye fade?	How much did the dye fade?
Indigo		
Alizarin with mordant		
Alizarin without mordant		

Group Discussion

A dye is something that has the following properties:

- Highly coloured, so that it can be used in small concentrations;
- Capable of being attached strongly to the fabric, so that it won't wash out;
- Resistant to fading and discolouring;
- Non-toxic.

1) Did the indigo dye fulfil these qualities?

2) Did the alizarin dye fulfil these qualities?

3) Was there a difference in the above qualities between the alizarin dye when there was mordant used and no mordant?

4) List some of the differences between the indigo dye and the alizarin dye.

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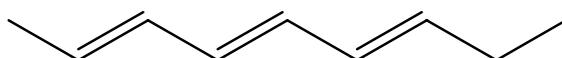
Appendix A

What is Colour?

When a compound is coloured it absorbs visible light (gains energy) as its electrons are excited. The colour of the compound is the complementary colour of the light which is absorbed. Have another look at the colour wheel and discussion in the pre-work for E1.

Conjugated double bonds – where double bonds are separated by only one single bond.

There are three conjugated double bonds here.



Visible light has wavelengths between 800 nm and 400 nm. The greater the number of conjugated bonds a compound contains, the longer will be the wavelength at which the compound absorbs light.* Looking at Figure A1a, indigo has conjugated double bonds throughout the whole molecule; the reduced compound, leucoindigo (Figure A1b), no longer has conjugated double bonds throughout molecule. Therefore the indigo is a blue colour and leucoindigo is yellow.

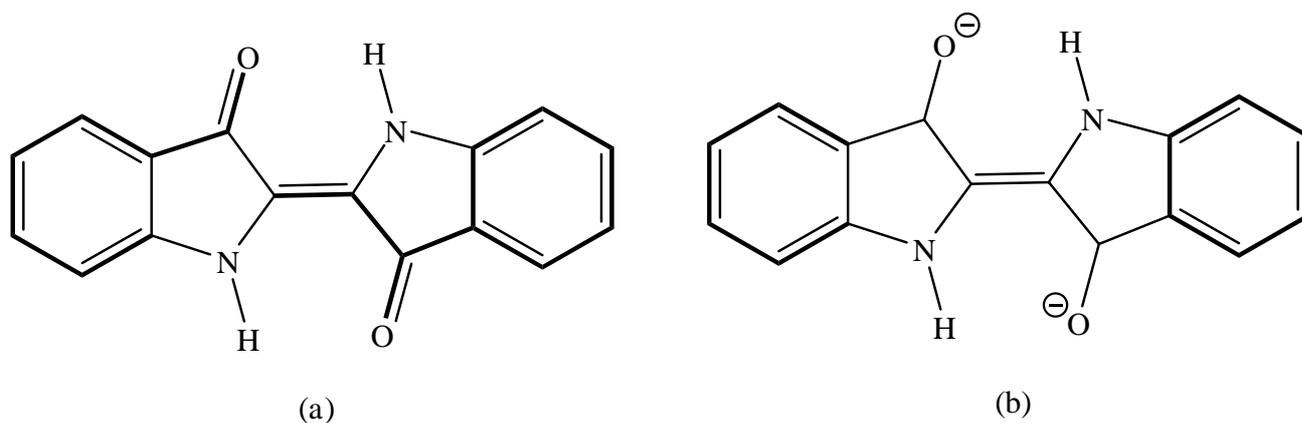


Figure 1A: **a)** the structure of indigo showing the conjugated bonds in bold; **b)** the structure of the leucoindigo showing the conjugated bonds in bold.

Visible and ultraviolet spectra, or electronic spectra, show the absorbance of energy at a given wavelength. The energy measured is from the electrons in the compound being excited and the releasing of that energy and going back to where it came from. The maximum height of the biggest peak is called the maxima.

From the electronic spectra of these compounds (Figures 2A(i) (ii)) it can be seen that the indigo compound has its absorbance maxima at 675 nm, which is higher than the leucoindigo which has its absorbance maxima at 396 nm. This is expected because the indigo has a greater number of conjugated double bonds than the leucoindigo.

The electronic spectrum of indigo shows where it absorbs light. As it absorbs wavelengths around 675 nm (in the red region), we see it as blue (see E1). The electron spectra of leucoindigo shows that it absorbs light in the violet and blue regions and we see it as yellow.

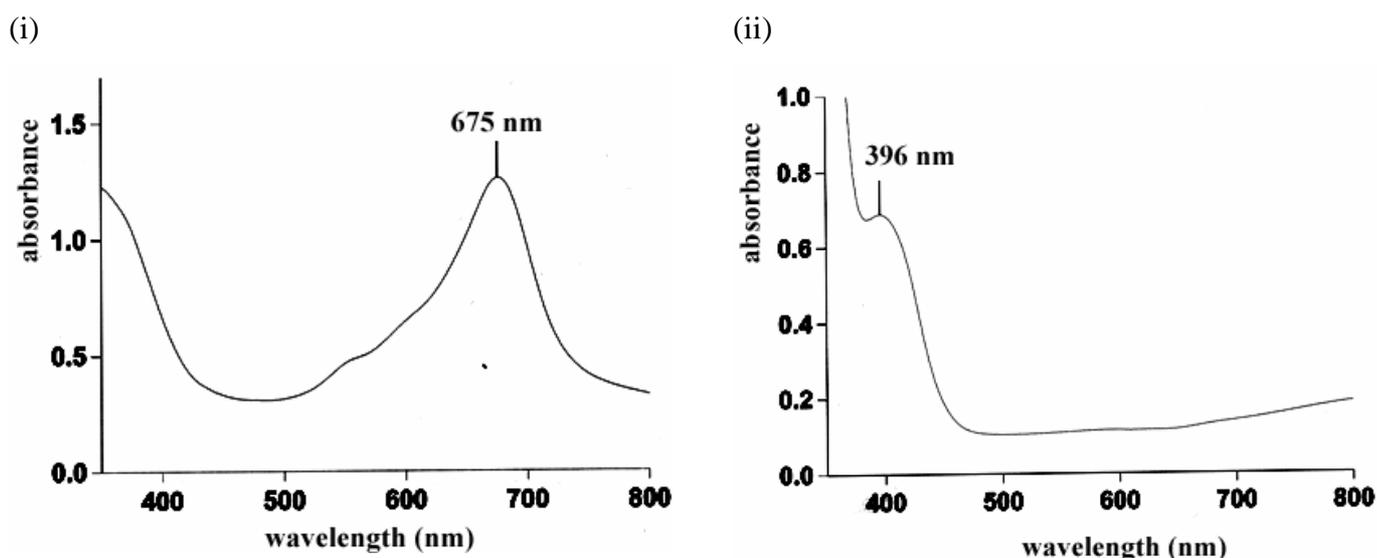


Figure 2A: Electronic spectra of (i) indigo showing the maxima absorbance at 675 nm and (ii) leucoindigo showing the maxima absorbance at 396 nm.

* T. W. Graham Solomons, "*Organic Chemistry*", 4th Ed., p 571 (1988) John Wiley & Sons.