Experiment 6 – Colorful Chemistry: Synthesis & Application of Organic Dyes

Learning Objectives

- Synthesize ~~azo and~~ indigo dyes
- Dye fabric swatches containing multiple types of fibers to observe the different colors or qualities that can be obtained with one dye
- Perform and observe different dyeing methods: direct, mordant, and vat dyeing
- Observe the correlation between dye structure and its absorbance & emission properties (color)

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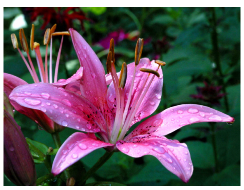
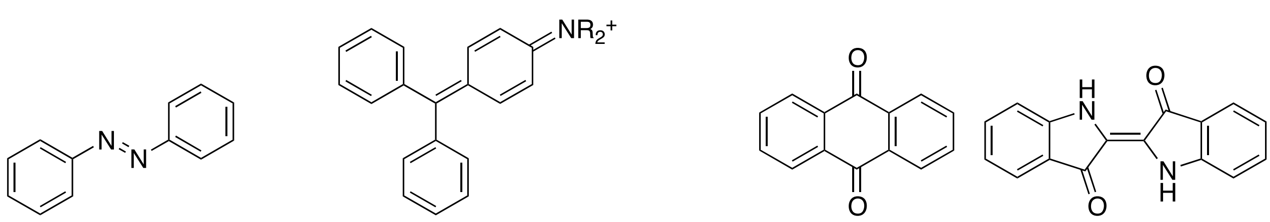
* Please find "How to Prepare for Lab & Assignments" after the procedure in this doc.



Background: Organic Dyes

DYES AND PIGMENTS are colorful compounds used to change the appearance of objects. Nature produces them to make flowers attractive to insects and to people, to tell predators to back off, and to catch the sunlight for energy. Humans have learned to use such naturally colored substances from a very early time, as cave paintings and ceramic artifacts testify. It was not until the past century or so that we have discovered how to make our own dye molecules. The creation of new colors and their applications in the textile and printing industries was at least partially responsible for bringing synthetic organic chemistry to the foreground of scientific research!

THE DIFFERENCE BETWEEN DYES AND PIGMENTS is that dyes are water-soluble and pigments are not. Dyes can be classified according to their structures and also based on their mode of application to fibers. According to structural differences, the most common dyes can be classified as *azo, cationic, anthraquinone,* and *indigo* (**Figure 1**). Depending on their mode of application, dyes can be grouped into the following types: *direct, mordant, ingrain, vat, disperse, reactive,* and *solvent*.



Azo Benzene (Parent of azo dyes) — **Alkylmmonium triphenylmethane** (Parent of some cationic dyes) — **Anthraquinone** — **Indigo**

Figure 1. Structural families of dyes

THE NATURE OF COLOR. Objects appear a certain color to our eyes and brains because the materials absorb certain wavelengths of the visible spectrum (400 – 750 nm) and reflect the complementary colors. Thus, a compound that absorbs blue light will appear orange and one that absorbs red will appear green. But what is it about the structures of these compounds that make them absorb certain wavelengths? A short explanation is the *extent and nature of the conjugation* present in the compound. A conjugated compound has a network of linked p-orbitals (forming pi-bonds), appearing structurally as alternating double and single bonds. This is apparent in all of the examples of dyes in **Figure 1** above. In general, the more extended a conjugated system (the larger the number of pi electrons involved), the longer the wavelength absorbed (towards red), and the shorter the wavelength emitted (towards violet). There are many other factors involved, as you will observe, including contribution of *ortho/para*-activators and *meta*-deactivators.

The azo dye synthesis is no longer performed in the teaching labs due to safety hazards.
Optional reading for fun…

Azo Dyes encompass the largest family of dyes. They contain an azo group, -N=N-, linking two aromatic rings. Because of their extended conjugated pi-orbital systems, these aromatic compounds absorb in the visible region of the electromagnetic spectrum and are deeply colored, often vibrant orange. This implies that azo dyes *absorb* relatively short wavelengths of light. TO BE USEFUL AS DYES, AZO COMPOUNDS MUST BE SOLUBLE IN WATER. This can be achieved by having polar and ionic groups attached to the aromatic rings. Sodium salts of sulfonic ($-SO_3Na$) and carboxylic ($-CO_2Na$) acids work well for this purpose. Easter purple and American flag red (AFR) are examples of ionic azo dyes (**Figure 2**). Recalls that nitro (NO_2) group contain a positively charged nitrogen and negatively charged oxygen. Simple changes in substituents and substitution patterns can make significant enough changes to be noticed by the naked eye, as evidenced by the comparison of **Solochrome Orange M** to **AFR**.

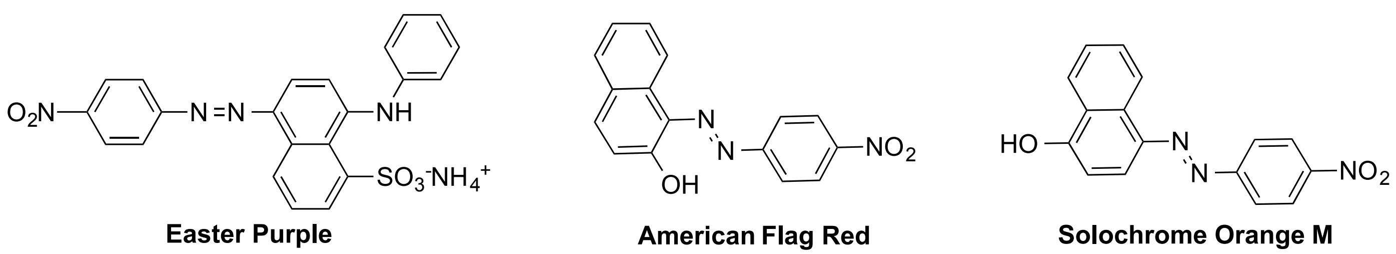


Figure 2. Examples of water-soluble azo dyes

THE SYNTHESIS OF AZO DYES is accomplished in two steps (**Figure 3**). In the first step, an aromatic amine (aniline) is transformed into a diazonium salt by the reaction of nitrous acid (HNO_2) obtained *in situ* by mixing sodium nitrite and a mineral acid. Diazotization reactions are usually performed at low temperatures to avoid the decomposition of the diazonium salts. These compounds are unstable at higher temperatures due to their tendency to expel nitrogen gas. Some **diazonium salts are explosive when dry and must be kept in solution**. In the second step, the diazonium salt is coupled to an aromatic compound, usually an aniline or phenol derivative, to yield an aromatic azo compound.

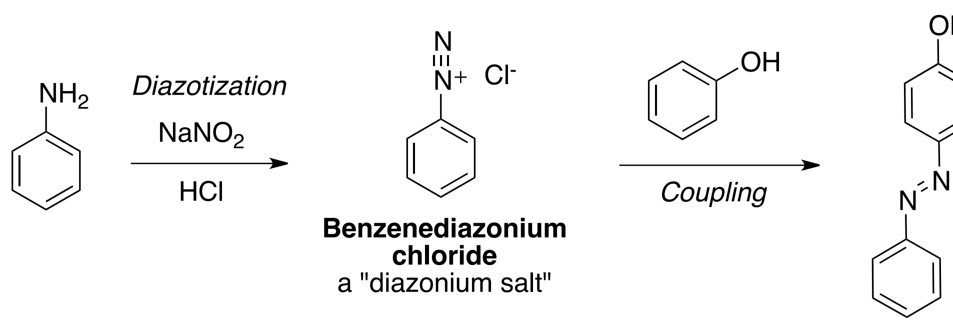


Figure 3. Synthesis of azo dyes.

The azo dye synthesis is no longer performed in the teaching labs due to safety hazards.

Cationic Dyes

THERE ARE SEVERAL CHEMICAL CLASSES OF *CATIONIC DYES*, the most important being the derivatives of triphenylmethane, such Malachite Green (**Figure 5**). In triphenylmethane dyes, three aromatic rings are directly attached to a central sp^2-hybridized carbon atom. At least two of the rings have a dialkylamino group ($-NR_2$) *para* to the central carbon. These molecules are highly conjugated and have the positive charge delocalized among all three aromatic groups. Notice that just one extra lone pair from the methyl amine group donating into the system drastically changes the color from green to violet!

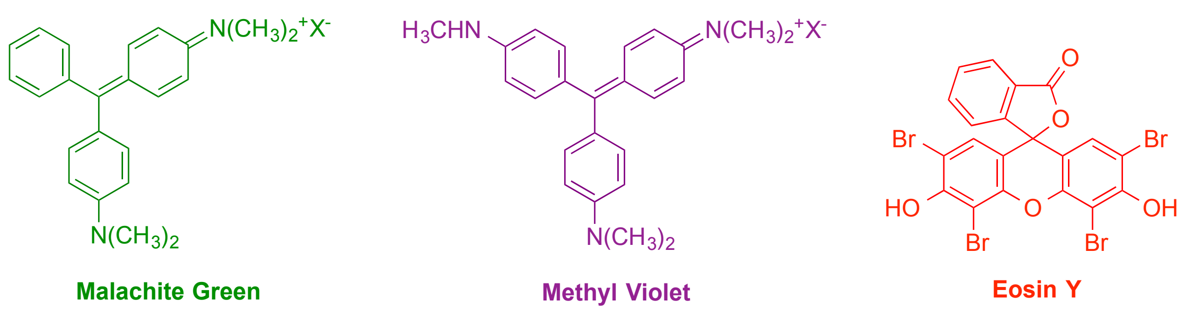


Figure 5. (a) Cationic green and violet dyes and (b) an uncharged dye

Mordant Dyeing

THESE DYES OF NATURAL ORIGIN were used for centuries to dye cotton and leather with beautiful red hues. The most important dye of this class is **alizarin**, which is the main component of the dyestuff obtained from the roots of the madder plant *Rubia tinctorum*. These dyes are applied to fabrics in the presence of metal ions such as aluminum, iron, tin, and chromium. This method is called *mordant dyeing*, where the fabric is pre-treated (soaked) in a specific salt solution before dyeing to create coordination complexes. The metal cation is the center of the complex while the dye and fiber molecules are bound as *ligands* through strong **ion-dipole interactions** (**Figure 6**).

When **alizarin** is used to dye cotton, a red hue is obtained if the metal is aluminum or tin, a deep violet shade with Fe^{2+}, and brown-black if Fe^{3+} is used instead. The connection between metal and dye is strongest when the dye can be ionized (protonated or deprotonated). One of alizarin's phenol protons is removed in a basic dye bath. This creates a negatively charged conjugate base (**Figure 6b**), which is very happy sharing its extra electron with the metal in a stronger **ionic bond**! The difference in size and charge of the metal can drastically affect the conjugated electrons in the dye, causing different colors of dyed fabric. In this lab, you'll investigate the effects of pre-treating fabric with $CuSO_4$, $AlKSO_4$, and $FeSO_4$ on the observed colors of an alizarin dye swatch.

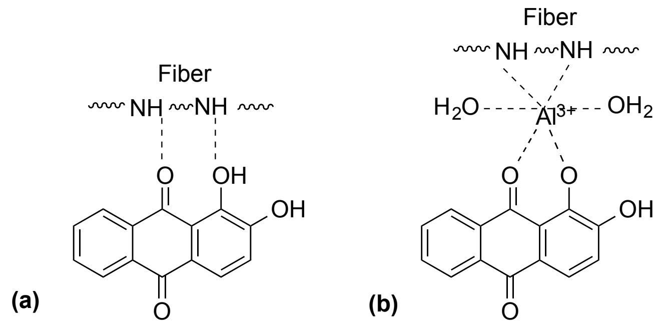


Figure 6. (a) Direct and (b) mordant dyeing with alizarin under basic conditions.

Indigo Dye

THE USE OF INDIGO, the dye of blue jeans, goes back at least 4000 years. The pigment was obtained from several indigenous plants from India and was introduced into the Middle East by Phoenician merchants. From there its use spread around the Mediterranean region and the rest of Europe. Indigo and its derivatives give blue-purple colors.

INDIGO IS SYNTHESIZED BY THE CONDENSATION of *o*-nitrobenzaldehyde and acetone under basic conditions (**Figure 7a**). The reaction is complete in a matter of minutes. *Vat dyes* such as indigo are insoluble in water but dissolve upon reduction with sodium dithionite ($Na_2S_2O_4$) under basic conditions. The reduced dye, called the *leuco* form, is soluble in water and is applied onto the fiber by immersion. Upon drying and exposure to atmospheric oxygen, the dye is re-oxidized and acquires its original color (**Figure 7b**). Notice that the carbonyl carbon of blue indigo is reduced (how many C-O bonds are in the reactant vs. product?). Dithionite is oxidized to sulfite in the process. While in the leuco-indigo solution, the fabric is yellow, but it quickly turns blue after it is removed.

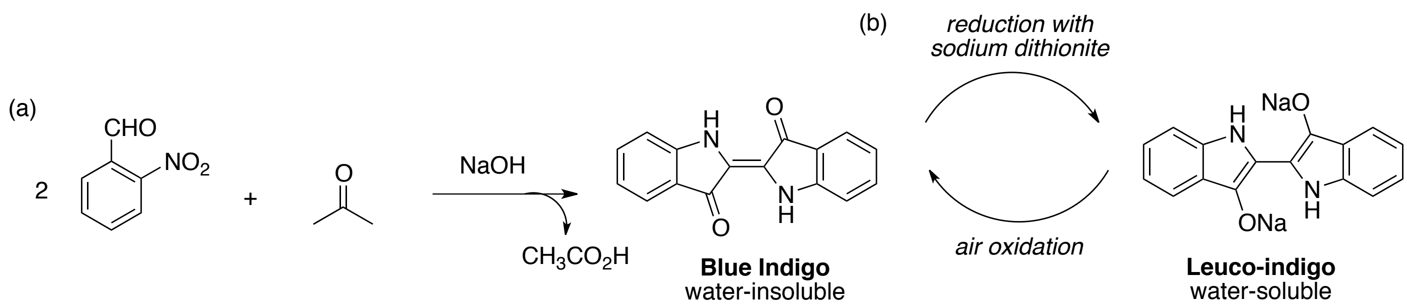


Figure 7. (a) Synthesis of Indigo and (b) reduction to leuco-indigo

Dying to Learn about Dyeing?

TO UNDERSTAND THE PROCESS OF DYEING we must consider the chemical nature of fibers and fabrics. Different fibers subjected to the same dyeing process produce different color shades because each type of fiber reacts with the dye molecules in a unique way. Fibers with an abundance of polar groups like the alcohol (OH) groups in cotton and wool, are easier to dye. Polyesters, acetates, and acrylics contain less polar functional groups like esters and nitriles. These synthetic fibers are generally less absorbent than natural ones and require special methods for color application. Polyesters dyes require high pressure and temperature to adequately adhere to the fabric.

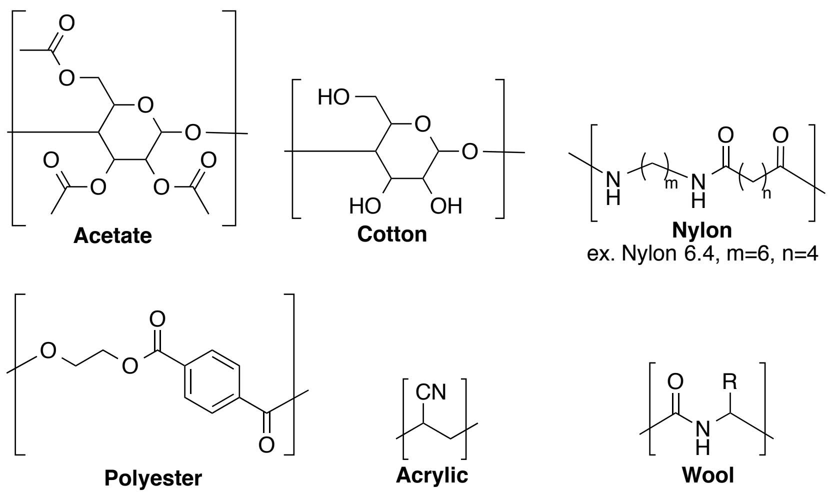


Figure 8. Structures of the repeating units of fibers

EXPERIMENT OVERVIEW

In this experiment, students synthesize dyes and use them to dye fabric swatches containing multiple types of fabric (**Figure 8**). The overall objective is to observe the different colors or qualities of fabrics that can be obtained with one dye, as well as comparison of different dyes and dyeing methods.

Thread a paperclip through the acetate (smoother) end of the fabric swatch *before* dyeing. The order is: acetate (smooth), cotton, nylon, polyester, acrylic, and wool (tan). Label each fabric strip with your name, the dye, mordant, or other conditions if applicable on a securely fastened tag. Attach this tag to the paperclip immediately after dyeing and rinsing.

Down time during reactions or dyeing? If you are prepared for the next steps of the experiment and looking for a way to kill time, take this opportunity to write a draft of the experimental methods section. It is to your benefit to do this in lab while you can ask your TA questions!

**** EXPERIMENTAL PROCEDURE ****

Parts A & B omitted due to safety concerns with the diazocoupling reaction.

Part C. Synthesis and Vat Dyeing with Indigo

Indigo requires a special dyeing process because it is not soluble in water. Once synthesized, **blue indigo** is made solution by a reduction reaction with a solution sodium dithionite ($Na_2S_2O_4$).

C.1. Synthesis of Blue Indigo

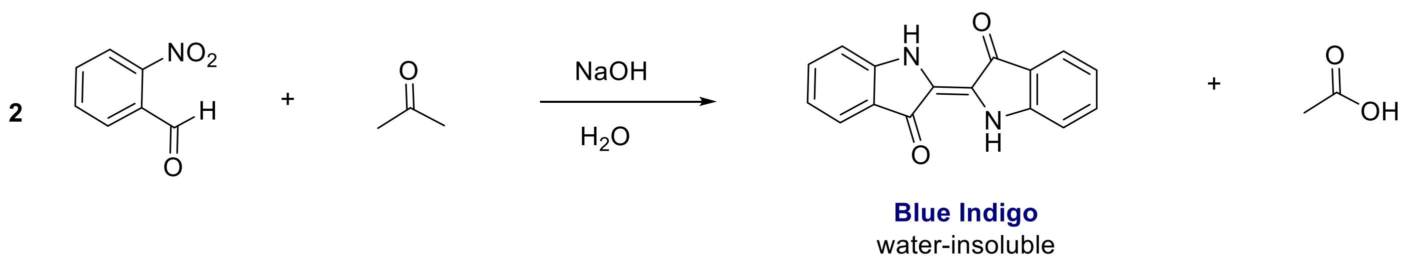


Figure 9. Synthesis of blue-indigo

Perform this reaction in the fume hood. In a 50-mL beaker add a stir bar, 100 mg of *o*-nitrobenzaldehyde, 1 mL of acetone, and 1 mL of water. Stir the suspension on a stir-plate and add 1 mL of a 2.5 M NaOH solution drop-wise. Dark blue indigo should start to form immediately as a black-blue sludge. Bring the beaker back to your bench-top and let the reaction mixture stand undisturbed at room temperature for 10 minutes. Transfer to an ice-water bath for an additional 10 minutes. Collect the solid by vacuum filtration onto pre-weighed filter paper, performed at your bench-top. Use a magnet to keep the stir bar from falling into the funnel.

Wash the solid on the filter with 2 mL COLD water, allowing all the liquid to pass through before following with 2 mL of ethanol.** Let the solid air dry with the vacuum on for 15 minutes, weigh the product, and calculate the % yield. If the yield is greater than 100%, place the filter paper with solid back on the funnel and dry for an additional 10 minutes. Rinse the stir bar over the liquid waste, then leave it in a shared dithionite bath for at least 10 minutes, which should remove any residual blue indigo and make for easier cleaning.

C.2. Dyeing with Indigo

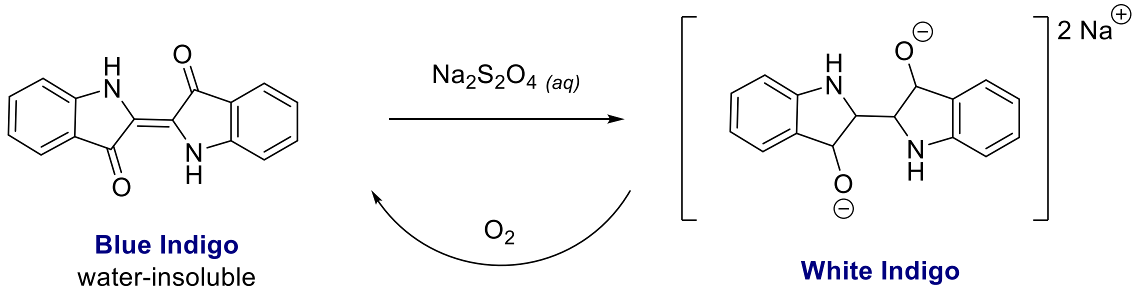
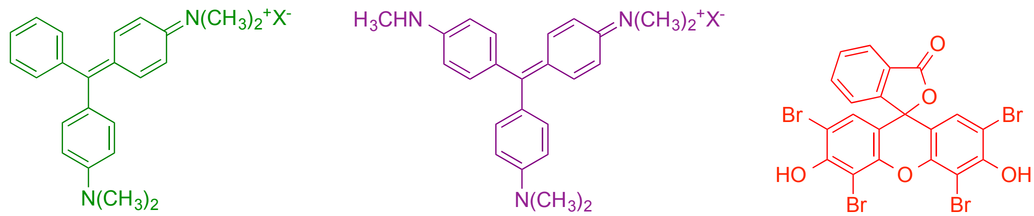


Figure 10. Vat dyeing: reduction of the carbonyl carbons in blue indigo and oxidation of white indigo

To a 100-mL beaker equipped with a magnetic stir bar, add 25 mL of water and dunk the filter paper containing indigo directly into the beaker with the aid of tweezers. If possible, take out the filter paper after most of the indigo has dissolved, otherwise the paper can remain in the beaker. Add 5 mL of 2.5 M NaOH and cover with a watch glass.** Boil on a hotplate with stirring with magnetic stir bar. Once the solution is boiling, add 7 mL of a freshly made solution of sodium dithionite. Boil and observe any color change. If the blue color persists add more sodium dithionite (1 mL at a time), allowing the solution to return to a boil between additions (up to 3 mL), until most of the solid has dissolved and solution turns yellow.** The solution may not be clear yellow. Once 10 mL is added and the solution is boiling, proceed to the next step.

Turn off the heat, add a strip of fabric (don't forget to paperclip the acetate side!) and let it sit in the hot bath for 3 minutes. Use tweezers to remove from heat. Rinse well into a labeled waste beaker, dry with paper towels, then let it air dry. Wait a few minutes to record observations, as it takes time for the indigo to dry and completely undergo oxidation in the air.

Part D. Direct Dyeing with Malachite Green and Eosin Y



Malachite Green **Methyl Violet** **Eosin Y**

Figure 5. (a) Cationic green and violet dyes and (b) an uncharged dye

Perform this step in the fume hood. Obtain 20 mL of the Malachite Green or Eosin Y solution in a beaker and cover with a watch glass. Add a strip of fabric and bring the system to a *gentle* boil on a hot plate, keeping it covered.** After about 3 minutes of gentle boiling, use tweezers to remove from the heat and rinse the swatch into the waste beaker. Pat dry between paper towels and clean the tip of the squirt bottle.**

Part E. Mordant Dyeing with Alizarin

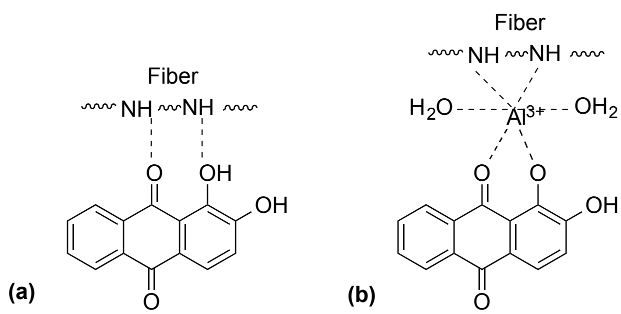


Figure 6. (a) Direct and (b) mordant dyeing with alizarin.

In a 100-mL beaker place 20 mg of alizarin and 20 mL of 0.5 % $NaHCO_3$ $_{(aq)}$. Warm on a hot plate to dissolve the dye, then bring to a gentle boil. Pre-treated mordant fabric swatches will be available in the lab. Add your assigned strip of fabric (untreated, $CuSO_4$, $AlKSO_4$, or $FeSO_4$) and gently boil for 5 minutes. Remove the strip from the bath with tweezers, soak in tap water for a minute, then rinse with tap water into the waste until the rinse water runs clear. Dry on paper towels. Dispose of the solutions in the liquid waste. Record your observations and those for the other three fabric swatches.

Table 1. Clean-up & Safety - *Copy the pertinent notes into the specific pages of your notebook.*

Clean-up	Safety
Keep isolated solids on the filter paper and dispose in solid waste after you're sure you're done with them!	4-nitroaniline, 2-naphthol, and malachite green are highly toxic – minimize exposure
Liquid waste: mother liquors, dye baths, and other liquids	Sodium nitrite is a toxic oxidizer
	Ethanol and acetone are flammable
Solid waste: filter papers, pipets, and contaminated paper towels	Hydrochloric acid and sodium hydroxide are corrosive
Part B: Rinse pipets or anything used with diazonium salts with water or liquid from ice baths and dispose in solid waste; wash glassware immediately!	Parts A & B: Diazonium salts are explosive in solid state! Wash this glassware immediately.
	Irritants: naphthols, salicylic acid, *o*-nitrobenzaldehyde, $Na_2S_2O_4$, and ANS

Experiment adapted from Palleros, D. R. "Dyes and Pigments," *Experimental Organic Chemistry*, **2000**. Wiley: New York. p. 611 - 634.

Pre-lab Questions / Quiz Prep

1. What structural characteristics give dyes their color? List two examples that fit this trend.

2. List the main **functional group** and associated **intermolecular force (IMF)** in the fibers of cotton, wool, nylon, polyester, acetate, and acrylic.
   - Examples of IMF's include hydrogen-bonding (H-bonding) and dipole-dipole interactions. "Polar" and "non-polar" are technically not IMF's!

3. Consider the structure of the dye **indigo** and indicate its predominant IMF (**Figure 2**). Do you expect this dye to adhere better to cotton or to polyester? Base your response on the information in #2 above.

4. Briefly explain the difference between **ingrain and mordant dyeing**. What is the role of the mordant and of the sodium bicarbonate solution? Why do mordant-dyed fabrics keep their colors so well?

5. Explain the general process of **vat dyeing**. Which atom on indigo is being reduced in the vat dyeing process (**Figure 7b**)?

6. Calculate the **mmoles** of *o*-nitrobenzaldehyde and acetone used. Determine the **limiting reagent** and report the **theoretical yield** of blue indigo in mmol and mg. Show your work.

How to Prepare for Lab + Assignments

Follow Canvas Exp 6 Module…

Before Lab

- Read this PDF – background, procedure, safety, pre-lab and in-lab questions
- Attend and/or watch **lab lecture** – we go over everything you need for your assignments!
- Practice the lab online *via* **Slugs@home platform** - sites.google.com/ucsc.edu/slugshome/home
- Complete the **pre-lab questions** at the end of this doc - incorporated into Canvas quiz ☺
  - **Quiz** due the Monday before your enrolled section – check Canvas for due date
- Download the **Exp 6 worksheet** and prepare your **lab notebook**…

Lab Notebook Preparation – *worksheet = template / outline to copy by hand into lab notebook*

- **Purpose:** one-sentence summary of the main lab goals plus the reaction scheme
- **Reagent Table** – add chemical properties; Wikipedia is a reliable source for chemical properties!
- **Procedure with Diagrams** – complete before starting lab; sample on Canvas
  - Use the procedure on the previous pages to create your hand-drawn experimental instructions
    - Simple sketches & labels for all **equipment, chemical names** with **amounts**, & **transfers**
  - Format: Break it up with flow charts, bullet-points, comic strip, and/or whatever works for you!
    - Avoid copying the procedure word-for-word.
    - Make it easy for anyone to follow your procedure without referring to this document.
  - **Slugs@home Exp 6 website** - Equipment & Safety pages; pictures & videos of the whole lab
  - The **class notes** include useful diagrams as well

During Lab

- Check the **safety rules** to dress for lab and arrive a few minutes early to **Thimann Labs**
- **Pre-lab talk:** tips for success and open Q&A
- Show your **lab notebook pages** to your TA
- Perform the experiment with a partner, fill out data & observations in a **lab notebook**

After Lab – each partner submits separate, individual assignments

- Upload **Notebook Pages** to Canvas by midnight on lab day – graded on completeness/participation
- Complete & upload the **Lab Report** on GradeScope (GS) – due date on Canvas
  - In-lab questions only – see last page of this document

LAB REPORT

Canvas > **Experiment 6 Report** for submission details

Upload to GradeScope (GS) after both parts of the lab – see due date on Canvas

- **Select Pages** to correlate your responses to the GS outline ☺
- OPTION to work with a partner – one person uploads the PDF then **"Select Group Members"** – gives both students the same grade

In-lab Questions

1. Re-submit your **dye-fabric observations** from the worksheet. You do not need to type this table for the report but do make sure your observations are *neat and easy to read, please* ☺

3. Report the **yield** (in mg and %) for the **synthesis of indigo** *in one complete sentence*. Show your work.

4. *For any one dye under normal conditions (without mordant)*, briefly comment on the abilities of different fabrics to absorb the dye (color intensity). Include comments on the **structural features of both the fiber and the dye**.

5. Discuss the results of **mordant dyeing**. What were the differences using the dye with and without a mordant (metal salt)? What were the differences using the same dye with different mordants?

6. Comment on how the extent in **conjugation** (number of pi-electrons, electron withdrawing/donating groups) affects the observed **color** of the dyed fabric. Choose 2-3 examples that best exemplified this trend.