Chemistry 239 Spring 2007

SYNTHESIS OF AN AZO DYE FOR INCORPORATION INTO CRYSTALS

This is a three-part lab in which you will synthesize an azo dye (part A), grow crystals with dye incorporation (part B) and stain various fabrics with your dye (part C).

INTRODUCTION

What is it about a dye that makes it colored? Dyes are organic molecules that selectively absorb **wavelengths** of light within the visible range of the **electromagnetic spectrum** (λ = 400 - 800 nm). The human eye responds to wavelengths within this range. The white light we receive from the sun contains all the wavelengths within the visible range. When an object absorbs a particular wavelength, we see the wavelengths that are left over, and the object appears colored. Removing orange light out of "white" light, for example, results in blue-green (cyan) hue. The hue resulting from the removal of a color from white light is the latter's **complementary** color.

Complementary Colors

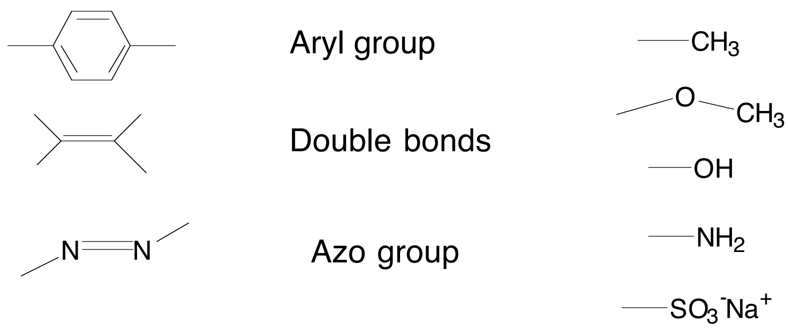
Color absorbed	***Wavelength absorbed (nm)***	***Color observed***
Red	***647-700***	***Green***
Orange	***585-647***	***Cyan (green-blue)***
Yellow	***570-585***	***Blue***
Green	***491-570***	***Red***
Blue	***424-491***	***Yellow***
Violet	***400-424***	***Yellow-green***

So now what determines the wavelength absorbed? The color in dyes is the consequence of the presence of a **chromophore**. Chromophores in dyes are generally large systems of conjugated bonds (alternating double and single bonds). It is this delocalized electron system that absorbs the energy from the light. For example, if the electrons in the dye require only a small amount of energy to be rearranged into new energy state, then the substance absorbs a low energy wavelength. Recall that the longer the wavelength the lower the energy ($E = hc/\lambda$). The table above shows that the longest wavelength is associated with the absorption of red light. If the incident light is white and red light is absorbed, then the light reflected is perceived as green (the complementary color of red). If a lot of energy is required for the electrons promoted to a higher energy state, then it absorbs only a short wavelength light, since short wavelengths correspond to high energy. If it absorbs blue light, then the light it reflects is perceived as yellow. In general, the more conjugation (more double bonds) you have in a dye the less energy it takes to excite the electrons.

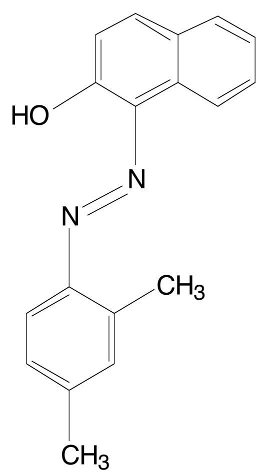
But there is more to it than that. While the chromophore is the color-producing portion of the dye molecules there are other factors. Dyes also contain **auxochromes**, which are a group of atoms attached to a chromophore that modify the ability of that chromophore to absorb light. In general, auxochromes influence the intensity of the dye; but they can also provide a site by which the dye can chemically bond to the fabric.

Examples of chemical groups that are chromophores and auxochromes are shown below.

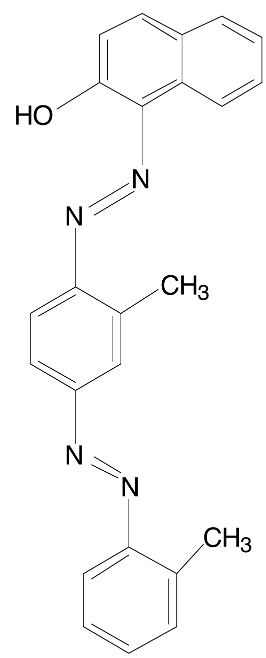
Chromophores Auxochromes



In this lab you are going to synthesize a dye that contains both aryl and azo functionalities (see above). To look at the impact of conjugation on the wavelength absorbed, let's look at two commercially available azo dyes.



Sudan II
$\lambda_{max} = 493$



Sudan IV
$\lambda_{max} = 520$

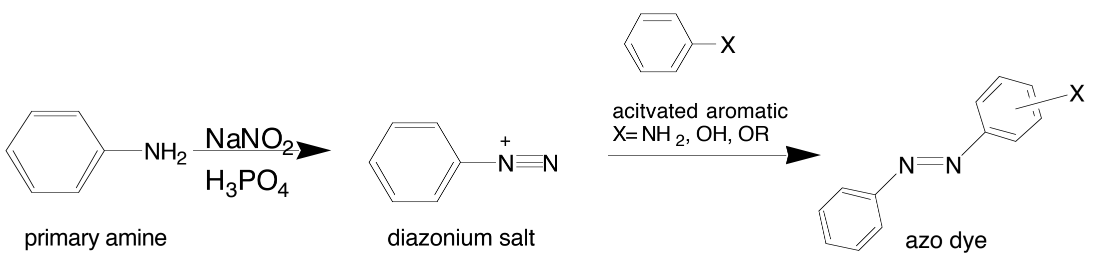
Notice that Sudan IV has a more extensive system of conjugation and thus absorbs a longer, lower energy wavelength.

Life would be simple if we could just look at conjugation but the color we see is also dependent on the auxochrome, what molecule the dye is bound to in the fabric, the pH— the list goes on. As part of this lab you will look at the effect of a change in the pH on the color of the dye, and sometimes it is very dramatic. This is generally due to a change in the charge on the dye molecules or a change in the level of conjugation. Adding or subtracting auxochromes can also effect the electron delocalization and thus change the color. Therefore, much of the work done in dyes can be considered as "trial and error". You just try something and see what color you get.

PART A: AZO DYE SYNTHESIS

Azo dyes, which were developed in the mid 1800s, are one of the most common dye materials. They contain the basic structure of Ar-N=N-Ar. Their color is due to the high level of conjugation that extends through N-N double bond to the aryl unit.

Azo dyes are synthesized via the following reaction. A primary amine (R-NH_2) is converted to a diazonium salt, and this is reacted with another aryl unit (see Bruice, sections 15.9, 15.10 and 15.11)



The aromatic ring can be substituted with different functional groups (auxochromes) and these substituents, due to their conjugation with the azo system, will affect the color of the dye (see section 12.18 of Bruice for more details). In this experiment you will choose which dye to synthesize from the various amines and activated aryl compounds shown on the next page. Different combinations will lead to different colors.

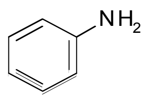
Synthesis of your Dye:

You will choose two compounds from the list on the next page. The first must be a primary amine (NH_2). This is the compound you will react with sodium nitrite in the first step of the reaction. The second compound you choose can be any of the 'activated aromatic' listed in the second group of compounds. This compound will be used in the second step of the reaction when you add this to the diazonium salt that you generate in the first step.

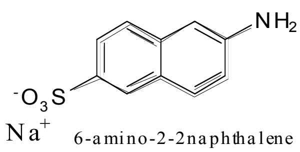
PART B: DYEING CRYSTALS

Researchers have shown that molecules in solution – even molecules that are very different from the crystal molecules and ions – can arrange themselves on a growing crystal surface so that they make specific non-covalent bonds. If these interactions are strong enough, and crystal growth is fast enough, the crystal can actually grow around and entomb the impurity. However, this only works for molecules with particular structures that match structural features of the growing crystals.

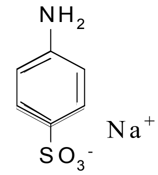
PRIMARY AMINES: Choose one of the below for the first step of the reaction



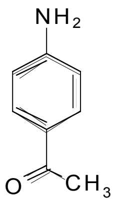
Aniline



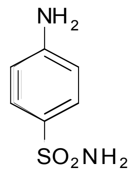
6-amino-2-2naphthalene sulfonic acid, sodium salt



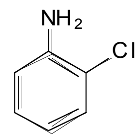
Sulfanic acid sodium salt



4-aminoacetophenone

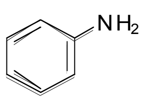


Sulfanilamide

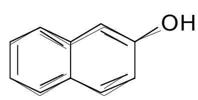


Chloroaniline

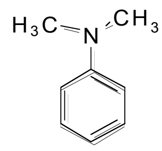
ACTIVATED AROMATICS: Choose one of the below for the second step of the reaction



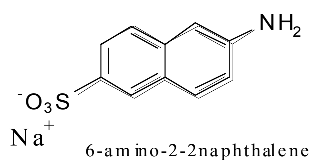
Aniline



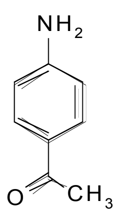
2-napthol



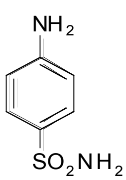
NN-dimethylaniline



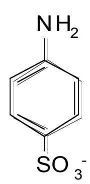
6-amino-2-2naphthalene sulfonic acid, sodium salt



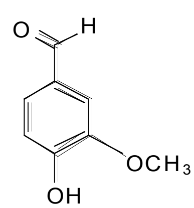
4-aminoacetophenone



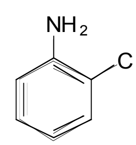
Sulfanilamide



Sulfanic acid

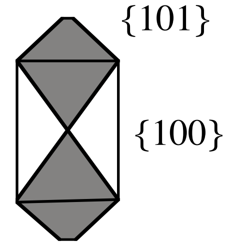


vanillin



Chloroaniline

In part B of this lab, we will attempt to grow dyed crystals of KH_2PO_4 (potassium dihydrogen phosphate) with an azo dye. These dyes will tend to selectively stain the pyramid faces (called {101} in crystallographic language), as shown in the figure below.



PART C: DYEING FABRIC

In the last part of the experiment you will use your synthesized dye to color a special swatch of fabric. The swatch is woven such that it contains bands of some of the more common fibers used in making clothing. The fibers included are both natural fibers and synthetic. Here you will explore how the interaction of the dye with the fiber affects the color.

The fibers contained in the swatch are shown below.

Fabric type (starting a end with black thread)
Acetate
SEF
Arnel (bright)
Bleached cotton
Creslan 61
Dacron 54
Dacron 64
Nylon 6.6
Orlon 75
Spun silk
Polypropylene
Viscose
Wool

• Pre-lab:

Read: This handout

Prepare for class on Monday, April 9: "Purpose" and "Materials and methods"

Decide which amine and which activated aromatic compound you want to use. **Write the chemical reactions** of your synthesis after the "Purpose" section, including all reagents. Note that this is a two-step synthesis.

Pre-lab calculation: For both your amine and your activated aromatic compound, calculate the mass of 0.1 mmol (millimole) for each (show the steps of the calculation, please). This should be written near the chemical equation above.

You may tape the procedure on the next several pages into your notebook (right-hand page only).

• During lab:

Since this is a lab about color, in the "Data" section, you should writing your observations of what occurs at which step of which part.

• Post-lab:

Examine the results of Parts B and C on Wednesday to complete your “Data” section.

· **Lab Result Report: (Due Monday, April 16 at the beginning of lab)**

Photocopy the non-procedure parts of this lab.

No conclusion or abstract is required.

PROCEDURE

Part A. Synthesis of Azo Dye

Step 1. Formation of the diazonium salt: Add 2 mL of water and 10 drops of phosphoric acid to a 5 mL conical vial with spin vane. Cool the solution in an ice-water bath and stir. Add 0.1 mmole of the amine to be converted into a diazonium salt. **Note**: if your amine is a liquid, you can assume that one drop weighs about 0.015 g (15 mg). If the spin vane does not stir sufficiently, periodically stir with your spatula to break up clumps. Let the solution stir at 0^o C for 10 minutes.

While the above solution is cooling, prepare a solution of 20 mg of sodium nitrite in 1 mL of water. Add 10 drops of the sodium nitrite solution to the conical vial (a color change may occur). Let this solution stir at 0^o C for 10 minutes.

Step 2. Addition of the activated aromatic compound: Add 0.1 mmole of the aromatic amine or phenol to the diazonium salt solution. Stir at 0^o C for 5 minutes (There may be a color change). If the solid does not mix well by the spin vane action stir with your spatula or periodically cap the vial and shake for 10 seconds. At the end of 5 minutes let the solution stir at room temperature for 30 minutes. If necessary, periodically shake to help mixing. The solution will slowly turn color over time. If time permits you may want to let the reaction stir longer in order to insure getting a more concentrated color.

Step 3. Dye color dependence on pH While you are waiting for the completion of step 2, prepare 2 test tubes as described below:

In test tube #1 add 2 mL of 1 M NaOH
In test tube #2 add 2 mL of distilled water (this will be acidic once you add your solution)

After stirring at room temperature add 1 mL of the reaction mixture to test tubes #1 and #2. Note the colors.

Place one drop from each test tube on a piece of filter paper and note the color.

Part B. Incorporation of Dye into crystals of potassium dihydrogen phosphate (KDP)

In this section you will make a crystallization solution containing the dye Chicago Sky Blue or Amaranth Red (your choice). The Chicago sky blue and Amaranth red dyes are known to incorporate into KDP but for your dye it is unknown whether it will incorporate. At your option you may also try to incorporate your dye.

Crystallization is an art. Crystal growth is affected by an array of subtle factors: the concentration of the solution, the amount of heat used to dissolve, the rate of cooling, the rate of evaporation and the turbulence of the crystal solution all can make a critical difference in the shape and beauty of the crystals you grow.

For this lab it is important that you get your KDP to dissolve by heating at low temperature. It is also important that once you have dissolved your KDP and have added the solution to the beaker that you do not move it — it is important that the solution remains still (and, to be on the safe side, still your mind as well).

Step 1. Incorporation of Chicago sky blue or Amaranth red dye

Label the crystallization dish with your name. Place that in the area marked for your section (your instructor will show you where this is). Eventually you will pour your crystallization solution into this dish; once this has been done **it cannot be moved**.

Preset the heat knob of your stirring hot plate to a low heat setting and let it warm up.

Weigh 17 grams of potassium dihydrogen phosphate (KDP), and transfer into a 250 mL beaker. Add 50 mL of distilled water and a magnetic stirrer.

Cover the beaker with a watch glass and place the beaker on a hot plate. Stir the solution with the heat set at a medium setting for 2 minutes, then turn down to 'low' and continue stirring until all solid has dissolved (if the KDP does not dissolve after 10 minutes you may turn up the heat a little bit).

Once the KDP has dissolved add 2 mL of Chicago Sky blue dye solution or 3 mL of Amaranth Red. Choose the color that pleases you the most. Stir this solution for 1 minute (be ready to do the next step immediately after the minute stir).

While the solution is still warm, carefully pour it (but not the stir bar) into your crystallization dish that you have placed in the designated area. Immediately after pouring, cover the crystallization dish with a watch glass. Once poured, be careful not to move the solution. You will recover the crystals during the next lab meeting.

At the next lab meeting, carefully gravity filter to recover your crystals and let air-dry.

Describe the color, shape and size of your crystals. You may either describe the largest crystal you recover, or the "typical" crystal in your batch.

Step 2. Incorporation of your dye (optional)

In a large beaker labeled with your name, dissolve KDP in the same manner as described above. Once dissolved, add 1 mL of your dye. Once the dye has mixed for one minute, cover the solution with a watch glass and quickly and carefully place this solution in the space designated for your lab section.

Part C. Dyeing of Fabric

Caution: Use gloves for this part

Choose a solution from test tube #1 or #2 (from Part A) that is of a preferable color. Dilute this dye solution with 10-15 mL of distilled water. Obtain a piece of multibanded fabric and submerge the fabric into the dye solution and gently heat on a hot plate for 10-15 minutes (cover with a watch glass to avoid evaporation). If you want to increase the concentration of your dye, you may add the remains of the original reaction vial.

Once you are done heating, rinse with water and leave the cloth in your drawer. In some cases the dye color and intensity will change once the fabric has dried out. **Warning**: Be careful not to touch your dye solution or the cloth without gloves. Your azo dye may be toxic and/or a skin irritant.

Note which fabric(s) were the best at retaining the dye with its original color, and which fabric(s) were worst. You may speculate as to the reasons for these observations.