

SYNTHESIS OF AN AZO DYE

This is a 3 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)

Part A

In this lab you are going to synthesize an azo dye. You may not have thought about it before but; 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 (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. Filtering 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.

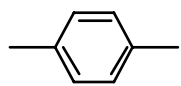
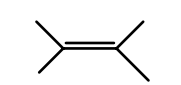
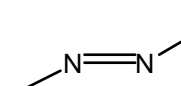
Complementary Colors

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

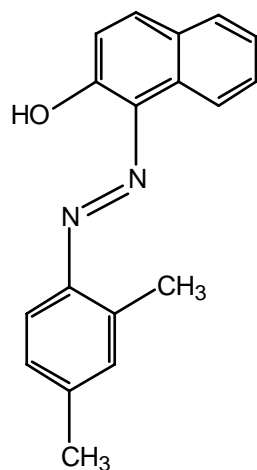
So now what determines what wavelength is absorbed? The color in dyes is the consequence of the presence of a chromophore. Chromophores in dyes are generally large systems of conjugated double bonds (alternating double single bonds). It is this delocalized electron system that absorbs the energy from 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 (λ). The longer the wavelength the lower the energy ($E = hc/\lambda$). If you look at the Table above you will see 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.

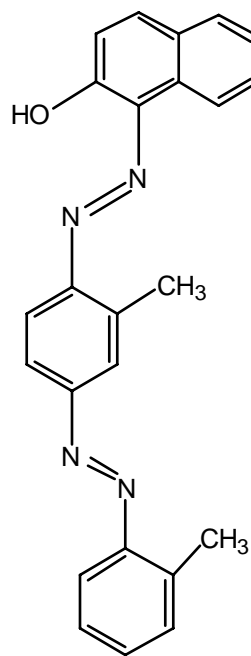
Examples of chemical groups that are chromophores and auxochromes are shown below.

<u>Chromophores</u>	<u>Auxochromes</u>
	—CH ₃
	—O—CH ₃
	—OH
	—NH ₂
	—SO ₃ ⁻ Na ⁺

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



Sudan II
 $\lambda_{\text{max}} = 493$



Sudan IV
 $\lambda_{\text{max}} = 520$

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 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

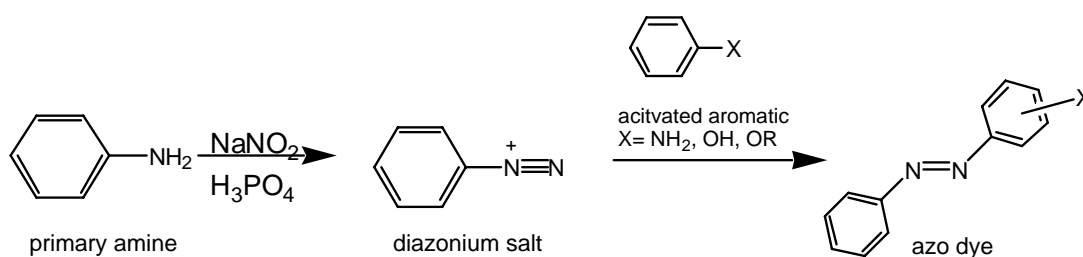
done in dyes can be considered as “trial and error”. You just try something and see what color you get.

AZO DYE SYNTHESIS

In this experiment you will use various organic amines to synthesize your azo dye. Once the dye is synthesized you will observe the effect of pH on the color, use your dye to color a variety of fabrics, and you will try to incorporate your dye into a binder to create a paint.

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 your lecture text (Bruice) sec 15.9, 15.10 and 15.11)



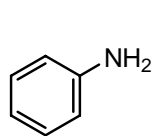
The aromatic ring can be substituted with different functional groups (auxochromes) and these substituents, due to their conjugation with the azo system, will affect the color of the dye (see sec 12.18 of Bruice for more details). In this experiment you will choose which dye to synthesize from the various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

Synthesis of your Dye:

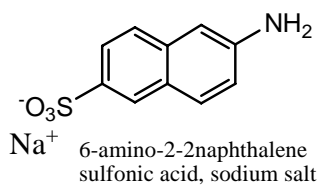
You will choose two compounds from the list on the next page. The first must be a primary amine (NH_2). This is the compound you will react with sodium nitrite in the first step of the reaction. The second compound you choose can be any of the ‘activated aromatic’ listed in the second group of compounds. 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.

Once you isolate the dye in this lab, later in the quarter you will try and incorporate your dye into a binder to create a paint mixture.

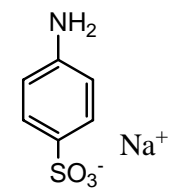
PRIMARY AMINES: Choose one of the below for the first step of the reaction



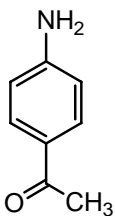
Aniline



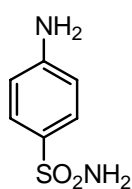
6-amino-2-naphthalene sulfonic acid, sodium salt



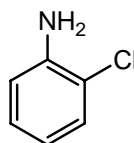
Sulfanilic acid sodium salt



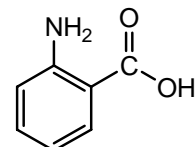
4-aminoacetophenone



Sulfanilamide

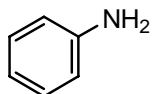


Chloroaniline

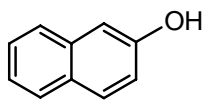


Anthranilic acid

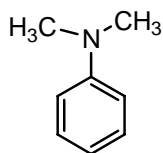
ACTIVATED AROMATICS: Choose one of the below for the second step of the reaction



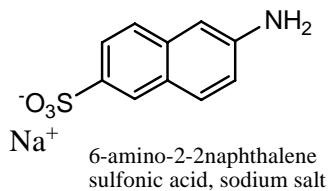
Aniline



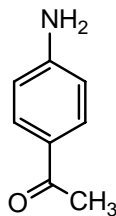
2-naphthol



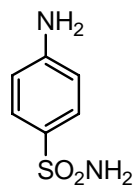
NN-dimethylaniline



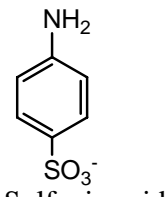
6-amino-2-naphthalene sulfonic acid, sodium salt



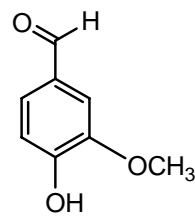
4-aminoacetophenone



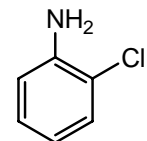
Sulfanilamide



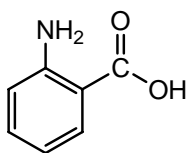
Sulfanilic acid



vanillin



Chloroaniline

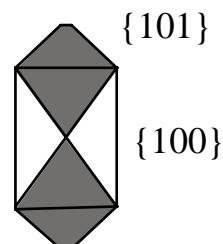


Anthranilic acid

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.

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). See below.



Part C: DYEING FABRIC

In the last part of the experiment (part C) 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

PROCEDURE

Part A. Synthesis of Azo Dye

Step 1--Formation of the diazonium salt: Add 2.0 mL of water and 20 drops of 10% sulfuric acid (H_2SO_4) to a 10 mL or 25 mL round bottom flask with spin bar. Cool the solution in an ice-water bath and stir. Add 1.0 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 0.03 g (30 mg). If the spin bar does not stir sufficiently, periodically stir with your spatula to break up clumps. Let the solution stir at 0° C for 10 minutes.

While the above solution is cooling, prepare a solution of 80 mg of sodium nitrite in 1 mL of water. Add the sodium nitrite solution dropwise to the reaction mixture (a color change may occur). Let this solution stir at 0° C for 10-15 minutes.

Step 2--Addition of the activated aromatic compound: Add 1.0 mmole of the aromatic amine or phenol to the diazonium salt solution. Stir at 0° C for 5 minutes (There may be a color change). If the solid does not mix well by the spin bar action stir with your spatula. At the end of 5 minutes let the solution stir at room temperature for 20 minutes. If necessary, periodically shake to help mixing. The solution will slowly turn color over time.

If the color formation is not sufficient it may be due to the activated aromatic being protonated at low pH (deactivated to reacting with the diazonium salt). Slowly add 1 M NaOH dropwise until the solution becomes neutral (or just basic). You may see a strong color change with the addition of base. If time permits you may want to let the reaction stir longer in order to insure completion of the reaction.

Step 3. Dye color dependence on pH When step 2 is complete you want to analyze the color of your dye depending on the pH of the solution

Measure the pH of your solution and note the color. Take about 0.5 mL of the solution and place it in a test tube and add either 1M NaOH or 1 M HCl to change the pH from either acidic to basic or visa versa. There may be a dramatic color change.

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

Change the reaction mixture to the pH that gives the 'best' color (use 1M NaOH or 1M HCl). Take about 1/3 of this solution to be used in part C 'Dyeing of fabric.'

Step 4. Isolation of the solid dye.

Cool your dye mixture on ice to crystallize the day. Once crystals have formed filter the solution. Wash the filtered solid with ice water (see next paragraph if you didn't get any solid). Scrape the isolated solid onto a watch glass and let them dry until next period. Time permitting, you may also try and recrystallize them using hot water as solvent.

If you didn't isolate a solid from the filtration, recover the colored filtrate by pouring it into a beaker. Let the beaker stand uncovered in your drawer until next period. Solid dye will crystallize over time. (Later in the quarter we will try to create paint from your solid dye by incorporating it into either Gum Arabic or Linseed oil. These are the two most common 'binders' used in paint chemistry).

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.

Crystallization is an Art. Crystal growth is effected by an array of subtle factors; concentration of the solution, amount of heat used to dissolve, rate of cooling, rate of evaporation and stillness 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)

Incorporation of Chicago sky blue or Amaranth red dye:

Label your crystallization dish with your name. Place the crystallization dish in the area marked for your section (Your instructor will show you where this is.) Eventually you will pour your crystallization solution into this beaker (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.

Part C Dying of Fabric.

Take the dye solution saved from step #3 in part A. 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).

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.