Experiment #1

SYNTHESIS OF AN AZO DYE FOR INCORPORATION INTO CRYSTALS

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.

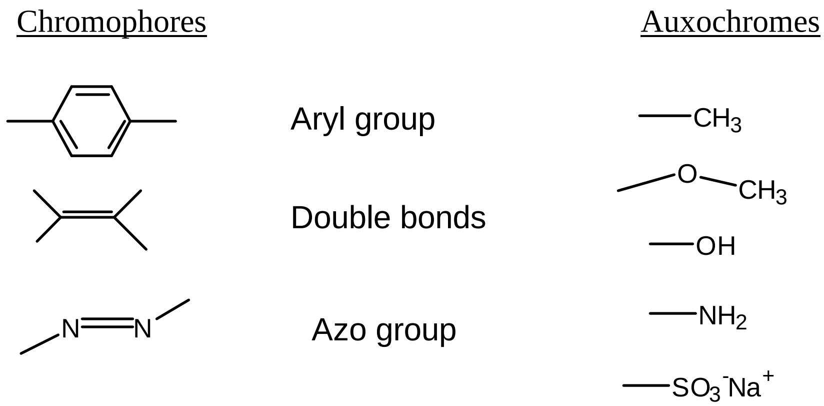
Complementary Colors

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

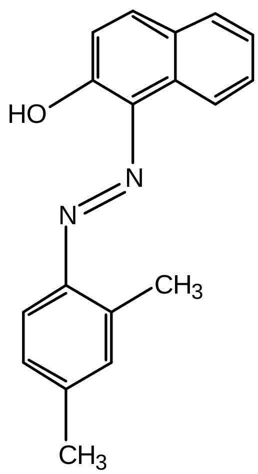
So now what determines what wavelength is absorbed? The color in dyes is the consequence of the presence of a chromophore. Chromophores in dyes are generally large systems of conjugated double bonds (alternating double single bonds). It is this delocalized electron system that absorbs the energy from 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.

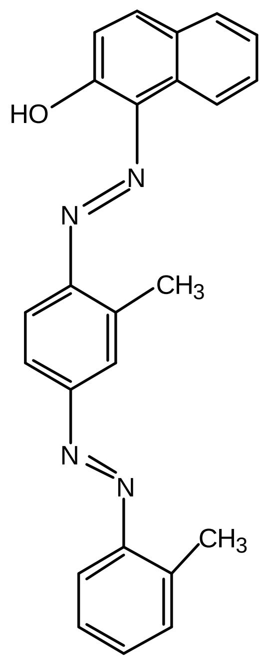
Examples of chemical groups that are chromophores and auxochromes are shown below.



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
λ_{max} = 493



Sudan IV
λ_{max} = 520

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

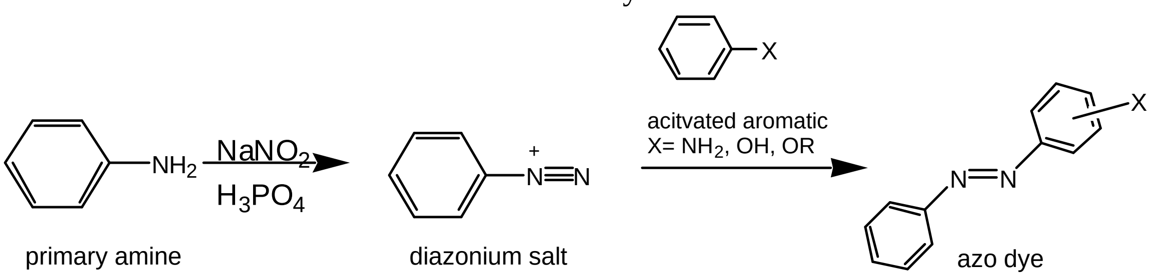
Life would be simple if we could just look at conjugation but the color we see is also dependent on the auxochrome, what the dye is bound to in the fabric, the pH - the list goes on. As part of this lab you will look at the effect of a change in the pH on the color of the dye, and sometimes it is very 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. In essence, this is what you are going to do in lab.

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 crystal of potassium dihydrogen phosphate (KDP).

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.

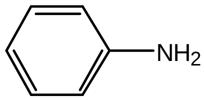
Azo dyes are synthesized via the following reaction. A primary amine (R-NH_2) is converted to a diazonium salt and this is reacted with another aryl unit.



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. 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.

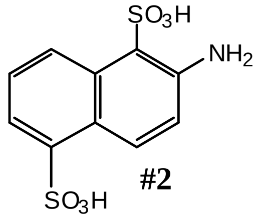
Synthesis of your Dye:

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. 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.



aniline

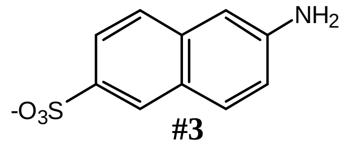
#1



#2

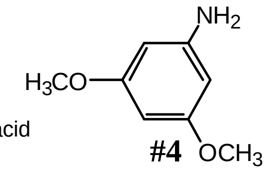
2-amino-1,5-naphthalenedisulfonic acid

mw 303



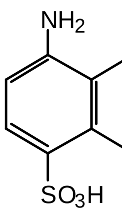
#3

6-amino-2-naphthalenesulfonic acid
mw 241



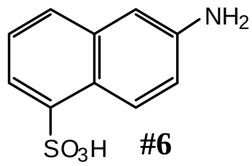
#4

3,5-dimethoxy aniline
mw 153



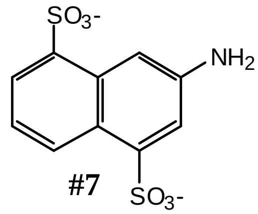
#5

8-amino-1,5-naphthalenedisulfonic acid
(mono sodium salt)
mw 325



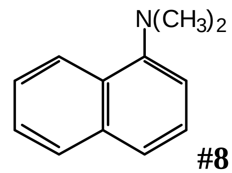
#6

6-amino-1-naphthalene-
sulfonic acid mw 223



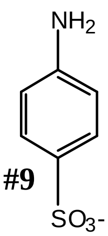
#7

3-Amino-1,5-naphthalene-
disulfonic acid, disodium salt



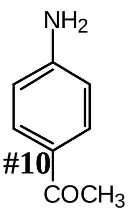
#8

N,N-Dimethyl-
1-naphthylamine
mw 171



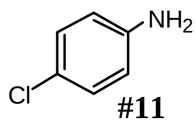
#9

sulfanilic acid,
sodium salt
mw 231



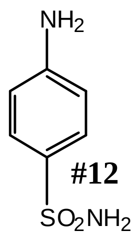
#10

4-Aminoacetophenone
mw 135



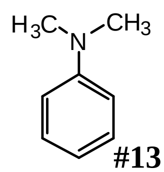
#11

p-chloroaniline
mw 127



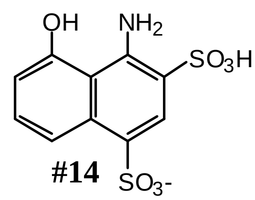
#12

sulfanilamide
mw 172



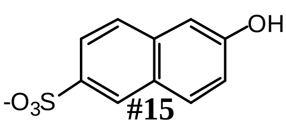
#13

N,N-dimethylaniline
mw 121



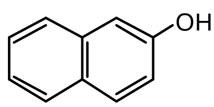
#14

8-amino-1-naphthol-
5,7-disulfonic acid
monosodium salt mw 341



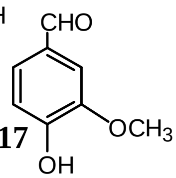
#15

2-napththol-6-sulfonic acid sodium salt
mw 246



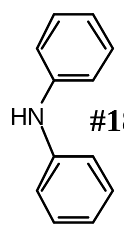
#16

2-napthol
mw 144



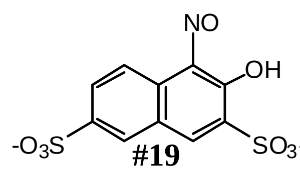
#17

Vanillin mw 152



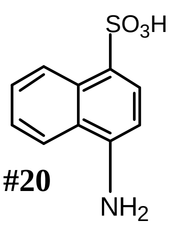
#18

diphenylamine
mw 169



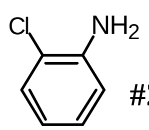
#19

1-nitroso-2-naphthol-
3,6-disulfonic acid disodium salt
mw 377



#20

4-aminonaphthalene sulfonic aicd
MW 223



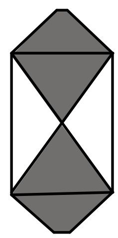
#21

o-chloroaniline
mw 127

Warning*: Amines are, in general, toxic compounds; avoid skin contact.*

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 azo dye that you have synthesized. These dyes will tend to selectively stain the pyramid faces (called {101} in crystallographic language).



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 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 approx. 7 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.

After 10 minutes, test the reaction solution for excess sodium nitrite using starch-Iodide paper*. If the paper *immediately* shows a dark blue/black spot then this means that all of the amine has been converted to the diazonium salt. If the paper does not turn black then add another 3-4 drops of sodium nitrite solution and let stir for another 5 minutes. After 5 minutes of stirring proceed onto step 2, (or if the starch Iodide paper turns black) where you will add the aromatic compound you chose for the second component of your dye.

*Dip a micro capillary it into the reaction vial and then touch the capillary onto a piece of Starch Iodide paper and let the solution bleed onto it.

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 6 M NaOH (check the pH to make sure it’s basic)
- 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 2 different crystallization solutions. One will contain the dye you synthesized and the second will contain 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.

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 crystallizing dish 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 your dye:

Label your crystallizing dish with your name and lab section. Place the crystallization dish in the area marked for your section (Your TA 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 level ‘2’ 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 ‘2’ for 2 minutes, then turn down to ‘low’ and continue stirring until <u>all</u> 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 1 mL of the solution prepared in test tube 1 or 2. 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 the crystallizing dish that you have placed in the designated area. Immediately after pouring, cover the dish with a watch glass. Once poured, be careful not to move the solution. You will recover the crystals during the next lab meeting.

Incorporation of Chicago sky blue or Amaranth red Dye
In a 250 mL beaker labeled with your name and lab section, dissolve KDP in the same manner as described above. Once dissolved add 3 mL of Chicago Sky blue dye solution or 4 mL of Amaranth Red instead 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: Dying of Fabric

Choose a solution from test tube #1 or #2 above 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 glove. Your azo dye may be toxic and/or a skin irritant.