

## 12BL Experiment 11: Diazo Dyes – An EAS Reaction

**Safety:** Proper lab goggles/glasses must be worn (even over prescription glasses). WEAR GLOVES – you are making very concentrated dyes and amines are very toxic. It is also highly encouraged to wear a lab apron to prevent any staining of your clothes. As always, ask where organic waste containers are located in the lab.

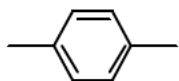
**Background:** Dyes are organic molecules that selectively absorb wavelengths of light within the visible range of the electromagnetic spectrum (~400-800 nm). The human eye responds to wavelengths within this range. The white light we receive from the sun contains all the wavelengths within the visible 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.

<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>

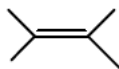
What determines the wavelength that is absorbed? The color in dyes is the consequence of the presence of a chromophore. Chromophores in dyes are generally large systems of conjugated double bonds (alternating double single bonds). It is this delocalized electron system that absorbs the energy from the 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 ( $\lambda$ ). 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 more stabilization, and the less energy it takes to excite the electrons.*

While the chromophore is the color-producing portion of the molecules, 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.

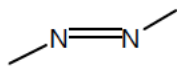
### Chromophores



Aryl group

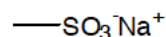
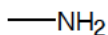
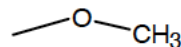
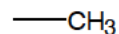


Double bonds



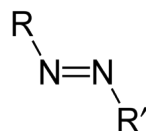
Azo group

### Auxochromes

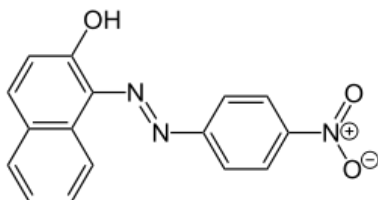


[http://depts.washington.edu/chemcrs/bulkdisk/chem242a\\_spr10/info\\_Azo%20Dye%20Lab.pdf](http://depts.washington.edu/chemcrs/bulkdisk/chem242a_spr10/info_Azo%20Dye%20Lab.pdf)

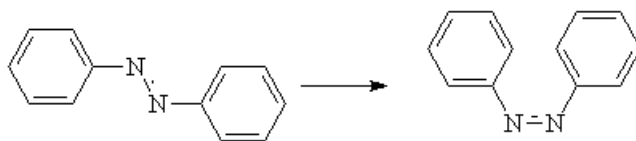
In this experiment, you will synthesize two different diazo dyes – Para-Red and a dye of your choice. The diazo dyes, otherwise known as azo dyes, account for 60-70% of all dyes. They all contain an azo group, -N=N-, which links two  $sp^2$  hybridized carbon atoms. Often, these carbons are part of aromatic systems, but this is not always the case. Most azo dyes contain only one azo group, but some contain two (*disazo*), three (*trisazo*) or more.



Azo dyes give bright, high intensity colours, much more so than the next most common dye class (anthraquinones). Azo dyes tend to supply more yellows, oranges and reds than any other colors. In fact, today you will synthesize para-red, the dye used in the American flag.

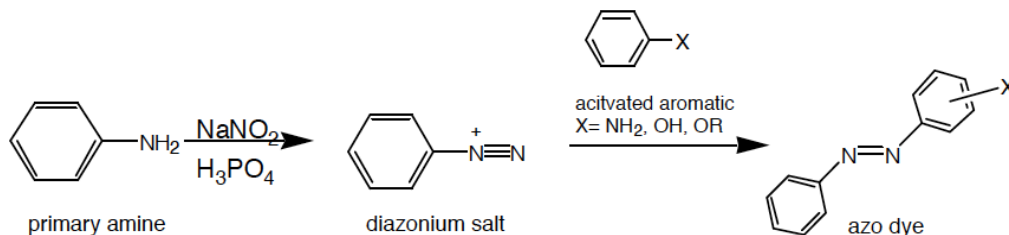


As with any double bond, the planar -N=N- bond shows geometrical isomerism. This change from *trans* to *cis* can be affected by exposure to UV radiation. This can lead to photochromism, a light-induced reversible colour change in some dyes.



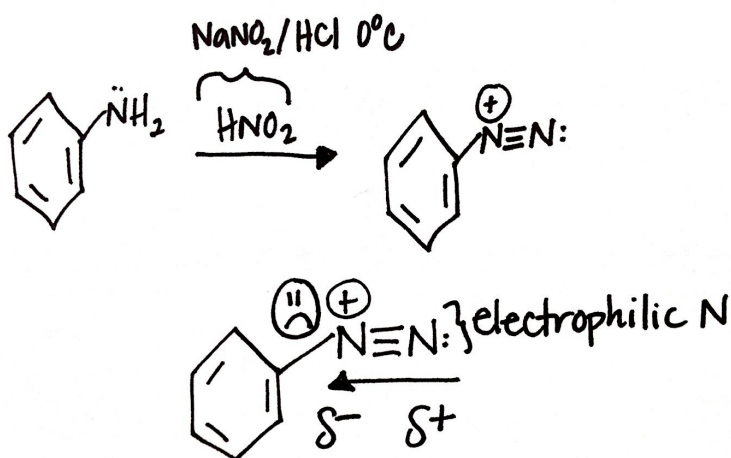
<http://www.chm.bris.ac.uk/webprojects2002/price/azo.htm>

Azo dye reactants include two organic compounds - a coupling component and a diazo component. Energy requirements for the reaction are low, since most of the chemistry occurs at or below room temperature. The environmental impact is reduced by the fact that all reactions are carried out in water.



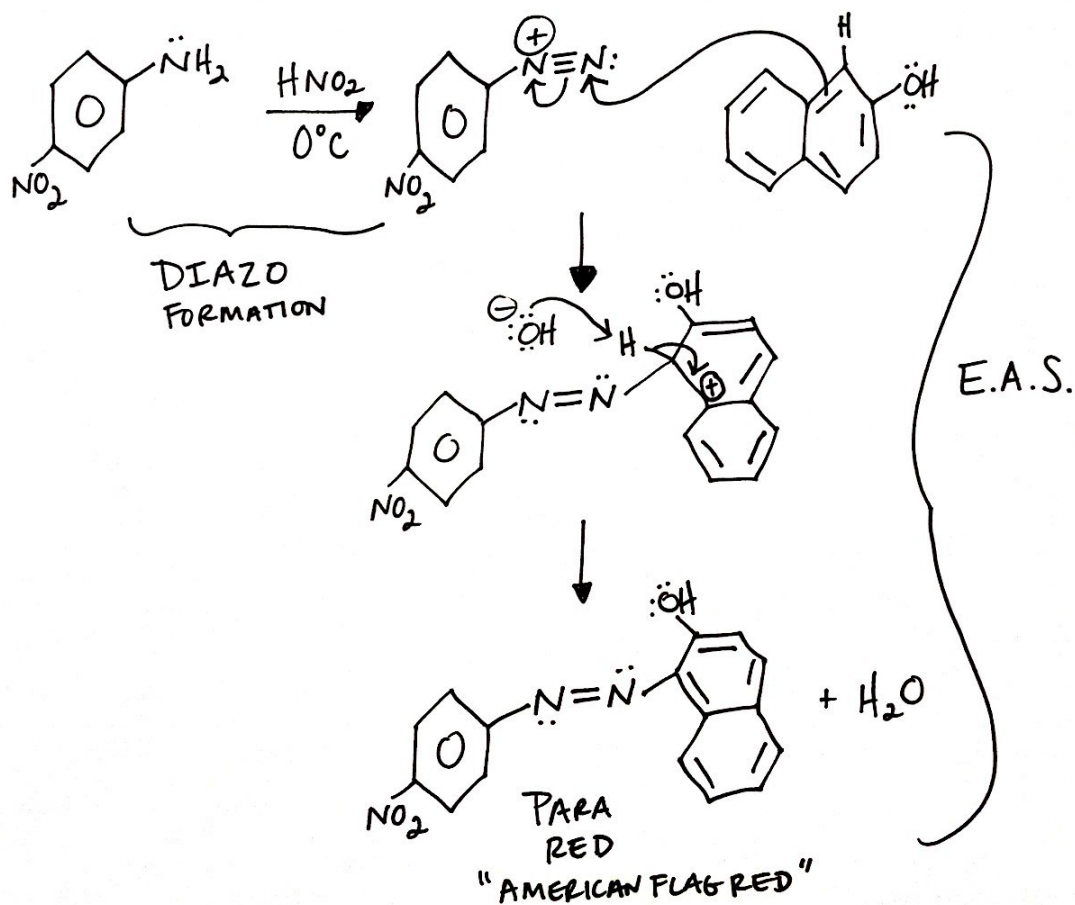
[http://depts.washington.edu/chemcrs/bulkdisk/chem242a\\_spr10/info\\_Azo%20Dye%20Lab.pdf](http://depts.washington.edu/chemcrs/bulkdisk/chem242a_spr10/info_Azo%20Dye%20Lab.pdf)

There are two main stages in the synthesis of your azo dye. First you must create your diazo component, the electrophile of your Electrophilic Aromatic Substitution reaction. A primary amine reacts with nitrous acid,  $\text{HNO}_2$ , under very cool temperatures to form a diazo salt. Recall, that an organic salt is simply considered an ionized/charged compound. Nitrous acid is commonly produced in solution from sodium nitrite and acid, like phosphoric or hydrochloric acid. Why is the diazo salt considered an electrophile?



Second, you perform your EAS reaction – the reaction between your electrophile (the diazo component) and your aromatic molecule (the coupling component). Because you are performing another EAS reaction, your coupling component must be aromatic. In addition, your coupling component must be extremely activated because your diazo salt is a very weak electrophile. Notice that while the diazo salt has a partially positive nitrogen from its dipole, the nitrogen atoms are still very electron rich which decreases its electrophilicity. Therefore, your coupling component must be a very strong nucleophile, activated by the presence of one or more of the strongest activators,  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OR}$ .

## Para Red Formation



**\*Not shown in mechanism above:** the initial inorganic deprotonation and final protonation of the hydroxyl group of the nucleophile while in a basic solvent, NaOH. Recall, inorganic reactions occur rapidly; organic reactions occur more slowly. See Postlab – make sure to show these mechanisms appropriately.

**Objective:** 1. To successfully synthesize two diazo dyes. 2. To understand the mechanisms of diazo synthesis, as well as review of EAS. 3. To learn about the properties of dyes including chromophores and auxochromes and understand how humans perceive color.

### Procedure:

#### Making of Diazo Electrophile:

- 1) Add 2.00 mmol of diazo component (an aromatic amine) with 1.6 mL of 3M HCL in 10 mL beaker.

- 2) If the diazo component does not dissolve completely heat it gently. You may add up to 2 mL of water to get it into solution (or most of it).
- 3) Cool the solution in an ice-water bath and stir with magnetic stirring bar for 5 minutes.
- 4) While the above stirring slowly add 2.0 mL of sodium nitrite drop wise over a 2-3 minutes period. (A color change may occur).
- 5) 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 (which is what you want). If the paper does not turn black then continue to add sodium nitrite solution drop wise until you get a positive test result.
- 6) Divide your solution into two equal parts and keep on ice. Label as Diazo Electrophile 1 and 2 or DE 1/ DE2.

#### **Coupling with a Phenol (Making Para Red):**

- 7) Dissolve 2.00 mmol of 2-naphthol (your phenol) in 4.0 mL of 1M NaOH.
- 8) Cool in ice water bath.
- 9) Slowly add Diazo Electrophile 1 made previously while manually stirring. Leave in Ice bath for 15 minutes.
- 10) If little or no colored solid appears adjust the pH with dilute NaOH or HCL to induce coupling. (A change in the pH on the color of the dye is sometimes very dramatic. This is generally due to a change in the charge on the dye molecules or a change in the level of conjugation.)
- 11) Collect by vacuum filtration, wash with water, and dry at room temp.
- 12) Weigh your product.

#### **Coupling with an Amine (pick your own):**

- 13) Dissolve 2.00 mmol of aromatic amine in 2.0 mL of 1 M HCL. (See Table 1, also think about why you don't need to dissolve the amine in NaOH as you did for the phenol).
- 14) Cool in ice water bath.

- 15) Slowly add Diazonium Electrophile 2 (made in part 1) to your solution while manually stirring.
- 16) Neutralize the solution with 3 M sodium carbonate (add very slowly) and test with pH paper.
- 17) Leave in ice bath for 15 minutes.
- 18) Collect azo dye by vacuum filtration; wash with water, and dry at room temperature.
- 19) Weigh your product.

**Fabric Dyeing:**

- 20) Using your dyes, dye two pieces of fabric to better view the color of your dyes. Dry and attach to postlab.
- 21) Now let's tie dye!

Procedure adapted by Shasta Ott

<http://faculty.clayton.edu/Portals/145/dye%20procedure.pdf>

<http://cnx.org/content/m15877/latest/>

<http://www.quimica.ufpr.br/armo/parared.pdf>

[http://depts.washington.edu/chemcrs/bulkdisk/chem242a\\_spr10/info\\_Azo%20Dye%20Lab.pdf](http://depts.washington.edu/chemcrs/bulkdisk/chem242a_spr10/info_Azo%20Dye%20Lab.pdf)

## 12BL Experiment 11 Prelab: Diazo Dyes – An EAS Reaction

1. Aromatic diazonium compounds (diazo salts) are formed from what reactants?
2. Nitrous acid is unstable at room temperature. What reactants are used to create nitrous acid in solution?
3. Draw the structure of an aromatic diazo salt. Show all bonds and charges.
4. Draw the structure of an Azo Dye (other than Para-Red) and circle the azo linkage. Be sure to label its name.
5. Diazo salts are considered weak electrophiles. Explain clearly why.
6. Because diazo salts are considered weak electrophiles, what type of aromatic molecule must be used in this electrophilic aromatic substitution reaction? Explain clearly AND give an example of this type of aromatic molecule.

## 12BL Experiment 11 Postlab: Diazo Dyes - An EAS Reaction

Mass of Dye 1 \_\_\_\_\_g

Mass of Dye 2 \_\_\_\_\_g

### \*Attach Fabrics

1. Show the reaction mechanism for the synthesis of the dye from Resorcinol & the Diazo compound created from the reagents shown in below. Mechanism must be neat & clear with all arrows, charges, bonds, etc clearly shown. \*Make sure you show the inorganic reactions that occur too! See background!  
(No mechanism necessary for amine to diazo conversion - see Ch 16 if you would like to see it).

(Anisidine +  $\text{NaNO}_2/\text{HCl}$ ) + Resorcinol



2. List ALL reagents needed to synthesize the following dyes:

a. American Flag Red

b. Aniline Yellow

3. What is a chromophore? What wavelengths of light (short or long) do large chromophores absorb and why? (make sure your explanation relates to energy)

4. What is an auxochrome? How does it affect a dye?

5. Redraw the structure of the "dye of your choice" you prepared in lab below. Label any auxochromes and circle the chromophore part of the molecule.