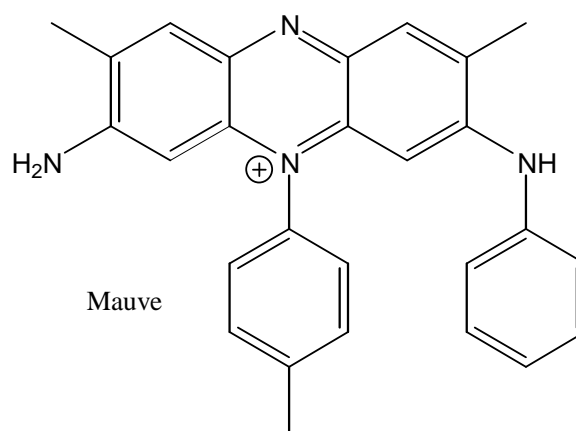


Many plants yield dyestuffs that will dye wool or silk, but there are few of these that will dye cotton as well. Most will not dye synthetic fibers like polyester or rayon. In addition, the natural dyes, with a few exceptions, do not cover a wide range of colors, nor do they yield “brilliant” colors. Even though some people prefer the softness of the “homespun” colors from natural dyes, the synthetic dyes, which give rise to deep, brilliant colors, are much preferred today. Also, synthetic dyes that will dye the popular synthetic fibers can now be manufactured. Thus, today we have available an almost infinite variety of colors, as well as dyes to dye any type of fabric.

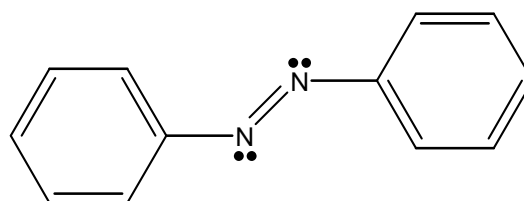
Before 1856, all dyes in use were obtained from natural sources. However, an accidental discovery by W.H. Perkin, an English chemist, started the development of a huge synthetic dye industry, mostly in England and Germany. Perkin, then only age 18, was trying to synthesize quinine. Structural organic chemistry was not very well developed at that time, and the chief guide to the structure of a compound was its molecular formula. Based on formulas, Perkin thought that it might be possible to synthesize quinine by the oxidation of aniline and toluidine (methylaniline).

He obtained no quinine, but he did recover a blackish precipitate with properties that could be extracted with ethanol to give a beautiful purple solution. This purple solution subsequently proved to be a good dye for fabrics. After receiving favorable comments from dyers, Perkin resigned his post at the Royal College and went on to found the British coal tar dye industry. He became a very successful industrialist and retired at age 36 to devote full time to research. The dye he synthesized became known as mauve. The structure of mauve was not proved until much later. From the structure it is clear that the aniline which Perkin used was not pure and that it contained all three toluidine isomers as well.

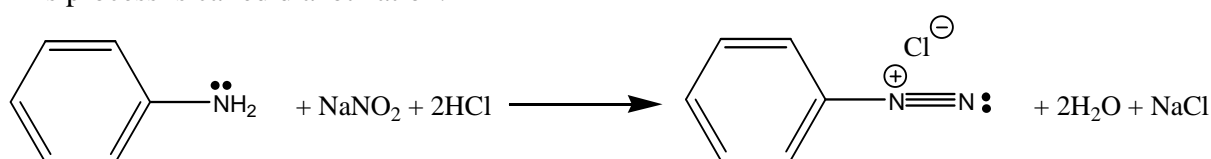


Mauve was the first synthetic dye, but soon the triphenylmethyl dyes, paraosaniline, malachite green, and crystal violet were discovered in France. The triphenylmethyl dyes were soon joined by synthetic alizarin, synthetic indigo, and the azo dyes. The azo dyes, also manufactured from aromatic amines, revolutionized the dye industry.

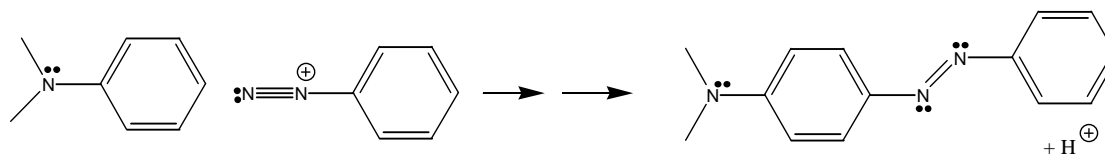
The azo dyes are one of the most common types of dyes still in use today. They are used in dyes for clothing as food dyes and as pigments in paints. In addition, they are used in printing inks, and in certain color printing processes. Azo dyes have the following basic structure:



The group containing the nitrogen-nitrogen double bond is called an azo group. To produce an azo dye, an aromatic amine is treated with nitrous acid to give a diazonium ion intermediate. This process is called diazotization.



The diazonium ion is an electron deficient (electrophilic) intermediate. An aromatic compound, suitably rich in electrons (nucleophilic) will add to it. The most common used nucleophilic species are aromatic amines and phenols. The addition of the amine or the phenol to the diazonium ion is called diazonium coupling reaction.



Azo dyes are both the largest and most important group of synthetic dyes. In making the azo linkage, many combinations are possible. These combinations give rise to dyes with a broad range of colors, encompassing yellows, oranges, reds, browns, and blues.

The azo dyes, the triphenylmethyl dyes, and mauve are all synthesized from the anilines and aromatic substances. All of these substances can be found in coal tar, a crude material that is obtained by distilling coal. Perkin's discovery led to the formation of a multimillion dollar industry based on coal tar, a material that was once widely regarded as a foul smelling nuisance. Today, these same materials can be recovered from crude oil or from petroleum as by-products in the refining of gasoline. Although we no longer utilize coal tar, many of the dyes are still in extensive use.

Azo compound are easily reduced at the nitrogen-nitrogen double bond by reducing agents such as sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$).

Azo Dye history at DU:

Year	amine(s)	Aromatic coupling reagent(s)
2004	4-aminobenzene sulfonic acid	dimethyl aniline
2005	2, 3, and 4-aminobenzene sulfonic acids	1 & 2-naphthol, salicylic acid
2006	2, 3, and 4-aminobenzene sulfonic acids	1 & 2-naphthol, salicylic acid
2008	2, 3, and 4-aminobenzene sulfonic acids	1 & 2-naphthol, 1-bromo-2-naphthol
2009	2, 3, and 4-aminobenzene sulfonic acids	1 & 2-naphthol, 1,5-dihydroxynaphthalene
2011	2, 3, and 4-aminobenzene sulfonic acids	1 & 2-naphthol, 1-nitroso-2-naphthol

Swatches from Spring Semesters 2006, 2008, and 2009 are on the course webpage.

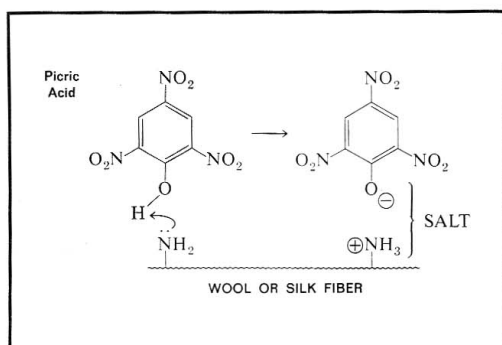


FIGURE 1. Direct dye.

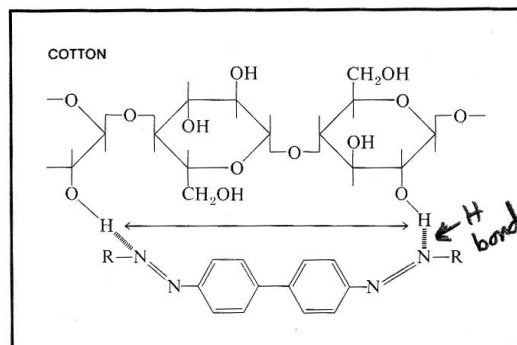


FIGURE 2. Disazo dye.

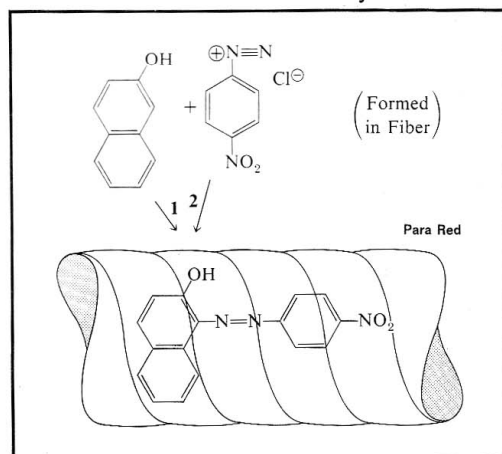


FIGURE 3. Ingrain dye.

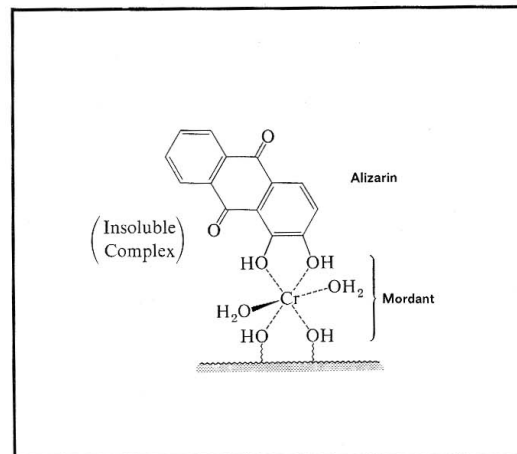


FIGURE 4. Mordant dye.

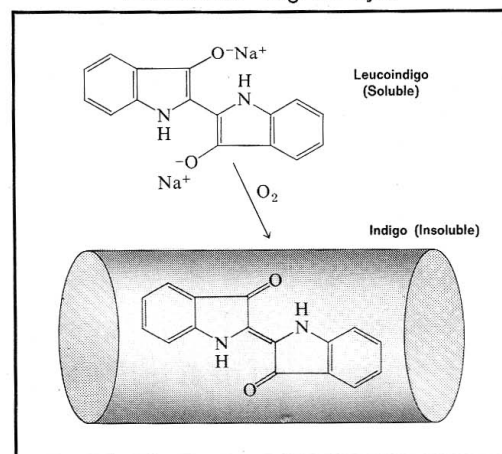


FIGURE 5. Vat dye.

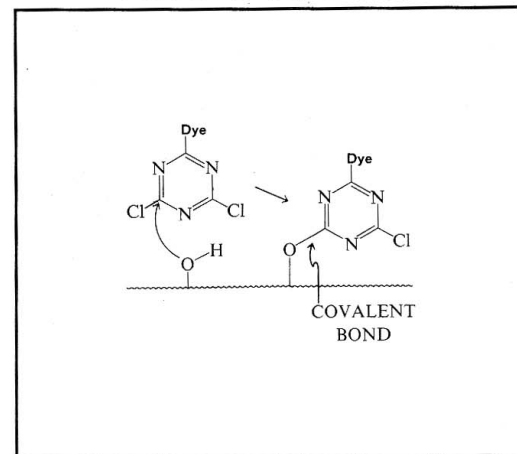


FIGURE 6. Fiber reactive dye.

From "Introduction to Organic Chemistry Laboratory Techniques: a contemporary approach."
1976 By D.L. Pavia, G.M. Lampman & G.S. Kriz Jr. WB Saunders Company

As shown on the previous page, in order for a dye to be effective it must “stick” to the fabric that is being dyed. There are several ways that dyes interact with fibers including:

1. Physical “trapping” of dye molecules in fiber matrices.
2. Binding by chemical weak forces such as
 - a. Hydrogen bonding,
 - b. Van der Waals forces,
 - c. Ionic forces and
 - d. Hydrophobic interactions.
3. Dye molecules can also be covalently bound to fibers.

The chemical composition of fibers and the chemical nature of the dye determine their interaction.

We will be dyeing fabric swatches containing strips of spun diacetate, bleached cotton, nylon 6.6, Dacron 54, orlon 75 and worsted wool are available.

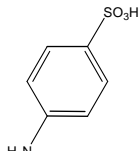
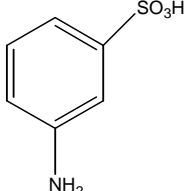
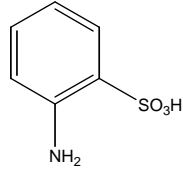
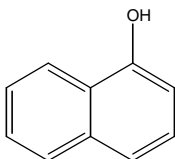
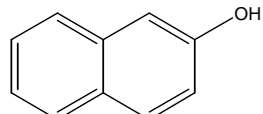
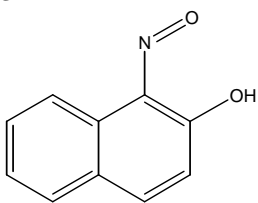
Diacetate (shiny)	Cotton	Nylon	Dacron	Orlon	Wool (Fuzzy Off-white)
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This gives us not only the ability to test the dye with different fabrics but also creates a sort of color “fingerprint” for each dye compound.

Arguably, the most notable development in synthetic organic chemistry in the last decade is probably the so called combinatorial chemistry. The goal of combinatorial chemistry is to prepare a large number of structurally diversified but related compounds efficiently. A new journal has emerged that is devoted entirely to combinatorial chemistry. The pharmaceutical industry has embraced this new development and invested millions of dollars into the area. The products from a combinatorial synthesis are usually called a library, which must be screened for a desired activity. This desired activity could range from anti-tumor or anti-HIV properties to effective catalytic properties.

In this experiment, the principle of combinatorial chemistry is shown through preparing azo dyes using the combinatorial approach. The coupling reactions involve an aromatic diazo compound and a nucleophilic, water-soluble aromatic compound as the coupling partners. Each aromatic ring can be diversified by substitution pattern. Each student is assigned a unique coupling reaction. The entire class will perform the same basic reaction, but will attain a variety of products. Assay and the identification of individual compound are a straightforward process for this parallel experiment. A fabric dyeing experiment follows the coupling experiment. The color of the dyed multi-fiber strip serves as the final assay for this experiment. At the end of this experiment, the colors of the dyed multi-fiber strips from the entire class should be compared. Any conclusions from the correlation of the product structures to the colored strips should be discussed in the lab report.

The product designations are arranged on a grid with aminobenzenesulfonic acid going across and the nucleophilic benzene derivatives (aromatic coupling reagents) going down. Each square of the grid is a unique combination of two reactants.

	A  Sulfanilic acid	B  Metanilic acid	C  2-aminobenzene sulfonic acid
1  1-naphthol	A1	B1	C1
2  2-naphthol	A2	B2	C2
3  1-nitroso-2-naphthol	A3	B3	C3

“Warm red, intensified by a suitable yellow, is orange. This blend brings red almost to the point of spreading towards the spectator. But the element of red is always sufficiently strong to keep the color from flippancy. Orange is like a man, convinced of his own powers. Its note is always that of the angelus, or of an old violin.” V. Kandinsky, Concerning the spiritual in art.

Procedure:**I. Diazonium Salt Preparation**

In a small Erlenmeyer place 1 g of an aminobenzenesulfonic acid and 10 mL of 2.6 % aqueous sodium carbonate (solution already made). Make a solution of 0.4 g of sodium nitrite in 1 mL of water. Combine the two solutions into the small Erlenmeyer. Into a 100 mL beaker place 1 mL of concentrated HCl and 6 g of ice. The solution from the small Erlenmeyer is added dropwise with a disposable pipet to the beaker. The resulting mixture is placed in ice-water bath to induce formation of diazonium salts. The mixture is used in the next step.

II. Coupling reaction

In a small beaker place 5.2×10^{-3} mole of one aromatic coupling reagent (1- or 2-naphthol, 1-nitroso-2-naphthol) and add 4 mL of a 2.5 M aqueous solution of sodium hydroxide. Place the beaker in an ice-water bath. The suspension of the diazonium salts prepared in the first step is added portionwise to the beaker. The reaction mixture is stirred with a glass rod after each addition. The color of the solution should change during this period of reaction. Let the reaction proceed for about 10 min with occasional stirring. Then heat the suspension on a hot plate till the solid dissolves. Add 2 g of NaCl and continue heating to dissolve it. Cool the beaker to room temperature first. Then cool it in an ice-water bath. Use a Hirsch or Buchner funnel to vacuum filter the solid. Wash the solid with 4 mL of saturated NaCl solution and let it dry in the air. Weigh the azo dye product when it is fully dry.

III. Dying a fiber strip

Disposable gloves should be worn in this experiment. Dissolve approximately 0.1 g of the azo dye prepared in the previous step in about 40 mL of water in a 100 or 150-mL beaker. Put a multi-fiber strip in the solution of the azo dye and keep it immersed. Boil the solution for about 5 minutes. Remove the multi-fiber strip from the hot solution with a tweezers and rinse the multi-fiber strip in a large beaker of tap water. Pat dry the dyed multi-fiber strip with a paper towel, record the fabric colors, and compare the colors with your colleagues.

IV. Analysis

Take a UV-vis spectrum between 300 and 600 nm of your dye in water. You may use the previously prepared dye bath.

Enter the dye designation (A1, A2, etc..) and lambda max on a spreadsheet before you leave the lab.

Hand in your synthetic dye in a properly labeled vial:

Your name, compound designation (A1, A2, etc...) and the date.
(Hand in your dyed swatch with your lab report.)

V. Clean up: Dispose of filtrate and dye bath in a container in the waste hood.

Checklist for completing the "Prelab" section:

(refer to Laboratory Syllabus for complete directions)

*Title and date**Purpose.**Physical constants.* Create a table of physical constants and safety data for the chemical compounds referred to in the procedure: <http://domin.dom.edu/faculty/jbfriesen/chem254lab.htm>

Name	Formula	M.W. g/mole	m.p. °C	b.p. °C	density g/mL
sulfanilic acid 4-aminobenzene sulfonic acid	C ₆ H ₇ NO ₃ S	173.19	288 (dec) CF		
metanilic acid 3-aminobenzene sulfonic acid	C ₆ H ₇ NO ₃ S	173.19	(dec) CF		
orthanilic acid 2-aminobenzene sulfonic acid	C ₆ H ₇ NO ₃ S	173.19	325 (CF)		
aqueous sodium carbonate	Na ₂ CO ₃	105.99	~0	~100	~1.0
sodium nitrite	NaNO ₂	69.00	271		
aqueous hydrochloric acid	HCl	36.46	~0	~100	~1.0
2-naphthol	C ₁₀ H ₈ O	144.17	122 (CF)	286 (CF)	
1-naphthol	C ₁₀ H ₈ O	144.17	96 (CF)	279 (CF)	
1-nitroso-2-naphthol	C ₁₀ H ₇ NO ₂	173.17	106-108 (dec) (AC)		
2.5M aqueous sodium hydroxide	NaOH	40.00	~0	~100	~1.0
sodium chloride	NaCl	58.44			
saturated aqueous NaCl	NaCl	58.44	~0	~100	~1.0
sodium hydrosulfite	Na ₂ O ₄ S ₂	174.11			

Name	Solubility	Safety Information
sulfanilic acid	Soluble in aqueous base	Warning: Corrosive!
metanilic acid	Insoluble in aqueous acid and neutral water	Caution: Moderately toxic by various routes.
orthanilic acid	soluble in alcohol insoluble in nonpolar solvents	Caution: Moderate fire and explosion hazard.
aqueous sodium carbonate	Soluble in water, Insoluble in alcohol Insoluble in nonpolar solvents	Caution: Irritation of eyes, nose and throat.
sodium nitrite	Soluble in water soluble in alcohol insoluble in nonpolar solvents	Caution: Irritation of eyes, nose and throat. Caution: Flammable
aqueous hydrochloric acid	Soluble in water soluble in alcohol insoluble in nonpolar solvents	Caution: Caustic

glacial acetic acid	miscible with water, Miscible with alcohol immiscible with nonpolar solvents	Warning: Caustic, can cause burns Warning: Vapor irritating to eyes, nose and throat. Caution: Flammable
1 or 2-naphthol 1-nitroso-2-naphthol	Some soluble in water, soluble in alcohol and nonpolar solvents	Moderately toxic. Irritating to eyes, skin and respiratory system.
10% aqueous sodium hydroxide	soluble in water some soluble in alcohol insoluble in nonpolar solvents	warning: Caustic
sodium chloride	soluble in water some soluble in alcohol insoluble in nonpolar	Not harmful
sodium hydrosulfite	soluble in water, some soluble in alcohol insoluble in nonpolar	Caution: Irritation of eyes, nose and throat. Caution: Flammable

References: MI = Merck Index, 11th ed.
CF = www.chemfinder.com
Hazardous Chemical Desk Reference, Lewis and Sax, 1987
AC = Aldrich catalog online

___ (1 point) *Flowchart*. Refer to "Procedure." The following products will be synthesized according hood and the table on page 5 of the handout. 1R&8R → A1; 2R&7R → A2; 3R&6R → A3; 4R&9 → B1; 4L&5L → B2; 3L&6L → B3; 2L&7L → C1; 1L&8L → C2; 5R&10 → C3

(3 points) *Structures and equations*.

Please use you assigned aminobenzenesulfonic acid and aromatic coupling reagent to complete these questions.

___ Draw the structure of your diazo intermediate as a chloride salt.

___ How many possible positional isomers could be produced with your reactants?

___ Draw the structure of your azo dye (all atoms neutral).

___ Write the balanced equation for the synthesis with structural formulas:

aminobenzenesulfonic acid + sodium nitrite + HCl + aromatic coupling reagent → azo dye + water + sodium chloride

(3 points) *Calculations*.

___ Calculate the number of moles in 1.0 g of your aminobenzenesulfonic acid.

___ Calculate the number of moles in 0.40 g of sodium nitrite.

___ Calculate the mass of 5.2×10^{-3} mole of your aromatic coupling reagent.

___ Calculate the molecular weight of your dye (all atoms neutral).

___ Calculate the theoretical yield of your dye.

___ *Safety Question*: (1 point) Give at least 2 reasons why is it necessary to do toxicology and carcinogenic studies of new clothes dyes before they can be used on commercial fabrics?

Experimental Observations and Data:

Hand in a copy of your experimental observations and data before you leave lab.

(4 points)

Experimental Observations: Refer to Laboratory Syllabus for guidelines.

Raw Data: Refer to Laboratory Syllabus for guidelines.

<p>Cold hearted orb that rules the night, Removes the colours from our sight. Red is grey and yellow white, But we decide which is right. And which is an illusion? The Moody Blues, Days of Future Passed</p>

Lab Report:

Write a Journal of Organic Chemistry style "Results and Discussion" for this experiment.

(8 points)

Address, at minimum, the following points in your discussion...

1. Report the percent yield of your dye. (include a chemical equation with molecular structures)
2. Discuss the UV-vis and fabric strip class data. (include at least one table or graph)
 - a) The general trend observed by changing the amine for the same aromatic coupling reagent (A1, B1, C1, for example).
 - b) The general trend observed by changing the aromatic coupling reagent for the same amine (A1, A2, A3, for example).
3. Discuss the reasons why the same dye gives a different color with different fabrics. (include at least one table or graph)
4. Discuss the reasons why the same fabric gives a different color with different dyes. (include at least one table or graph)

<p><i>Now Israel loved Joseph more than any of his other sons, because he had been born to him in his old age; and he made him a coat of many colors.</i> Genesis 37:3</p>
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Experimental procedures are based on the lab manual: Daniel R. Palleros, *Experimental Organic Chemistry*, John Wiley & Sons, Inc., New York, 2000, pp. 627-628.

A Combinatorial Experiment Suitable for Undergraduate Laboratories

Benjamin W. Gung and Richard T. Taylor

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