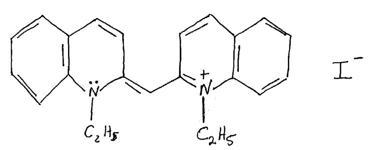
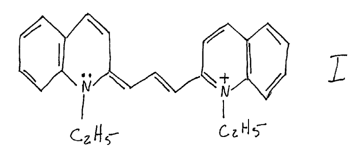
# Chemistry 351: Laboratory
# Conjugated systems

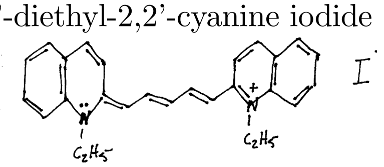
In this lab we investigate the visible absorbance spectrum of six related conjugated systems. **Family 1**: 1,1'-diethyl-2,2'-cyanine iodide, 1,1'-diethyl-2,2'-carbocyanine iodide, 1,1'-diethyl-2,2'-dicarbocyanine iodide and **family 2**: 1,1'-diethyl-4,4'-cyanine iodide, 1,1'-diethyl-4,4'-carbocyanine iodide, and 1,1'-diethyl-4,4'-dicarbocyanine iodide (see below).



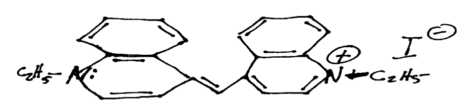
1,1'-diethyl-2,2'-cyanine iodide



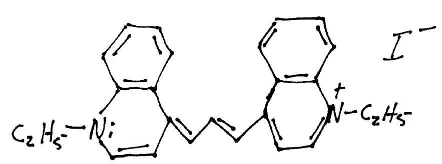
1,1'-diethyl-2,2'-carbocyanine iodide



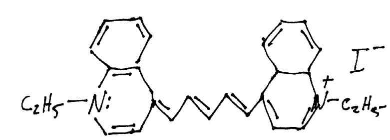
1,1'-diethyl-2,2'-dicarbocyanine iodide



1,1'-diethyl-4,4'-cyanine iodide



1,1'-diethyl-4,4'-carbocyanine iodide



1,1'-diethyl-4,4'-dicarbocyanine iodide

Conjugated systems are molecules which have alternating double bonds. The $\pi$ electrons are 'delocalized' across the entire conjugated network. One says that these electrons occupy delocalized molecular orbitals. The visible spectrum that we will be investigating is due to the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In other words we are using visible light to probe the HOMO–LUMO gap.

## PART I: EXPERIMENT

1. We shall use methanol as a solvent for the six molecules we are investigating. It will also serve as the blank for this experiment. Methanol is a nonconjugated system and as a result it will not absorb light in the region we are concerned with.

2. It is your job to prepare a blank and samples solutions for each of the above six dyes. All six of these molecules absorb visible light very strongly, so very dilute solutions are needed. Place only a few grains of dye in about 10ml of methanol.

3. Start the Ocean Optics software and acquire a blank spectrum. Consult the instruction sheet for acquiring absorbance spectra (this should by on the computer cart).

4. Run your first sample. Adjust the concentration until the peak absorbance is about 1 unit. Any where in the range from 0.2 to 1.2 absorbance units will be fine. If you are outside of this range dilute or make you solution more concentrated as appropriate.

5. Save and print your final spectrum.

6. Repeat with the other samples. If you don't change any of the data acquisition parameters you do not have to re-blank the instrument for each run.

## PART II: PARTICLE IN A BOX MODEL

1. Count the number of $\pi$-electrons in each of the dye molecules (the number will not be the same for all the molecules.)

2. Determine the HOMO and LUMO energy levels.

3. Using the one dimensional particle in a box model and the acquired spectra, work out effective lengths for each of the molecules. Plot the effective length of the molecule versus the number of bonds in the "bridging" carbon chain for each family of dyes. How do the effective lengths compare to the actual lengths of the respective molecules? Usual convention is to take the effective length for the box to be the

length of the molecule plus one bond length on either end of the molecule (to account for the polarizability of the molecule). Hoe do your effective lengths compare with this convention?

4. Separately for each of the two families of dyes find the difference in effective lengths for all pairs of dyes (for example length of 1,1'-diethyl-2,2'-carbocyanine iodide minus length of 1,1'-diethyl-2,2'-cyanine iodide). Dividing this difference in effective length by the difference in the number of carbon–carbon bonds between the two dyes gives the length of the carbon–carbon bond in conjugated systems. Could you also fish out the carbon-carbon bond length from your plot?

5. Compare your result with the literature value for carbon–carbon bonds in conjugated systems. Consult the CRC handbook which is available in the lab. (Note: in the CRC handbook the bonds we are interested in are referred to as aromatic.)

6. Include in your written report, the average and standard deviation for the carbon–carbon bond. Also report a percent error versus the accepted value. Among other things your report should discuss why we focussed on the "bridging" carbons for the dyes rather than the entire molecule.