LAB #1: ABSORPTION SPECTRA OF CONJUGATED DYES

Abstract
Ultraviolet-visible spectroscopy is used to explore the electronic structure of several conjugated polyene dyes, and a Particle-in-a-Box model is used to extract structural information.

Related Reading
McQuarrie and Simon, *Physical Chemistry: A Molecular Approach*, Section 3-5: "The Energy of a Particle in a Box is Quantized", pp. 81-83.

Background
Molecules and atoms absorb light only when the energy of an impinging light quantum or photon matches the energy **difference** between the state in which the molecule initially finds itself and some excited state of the molecule. In order for light absorption to take place

$$E_{photon}= h\nu = \Delta E_{molecule}= E_{upper\ state} - E_{lower\ state} \tag{1}$$

Thus to interpret the color of an object we must know the array of possible energy levels for its molecules. In general these include states of quantized rotational, vibrational, and electronic energy. With rare exceptions, visible absorptive coloration arises when visible photons are absorbed and excite molecules from their ground (the lowest-energy electronic) state to a higher-energy **electronic** state. Thus **transitions between electronic states are responsible for the majority of the colors** we see in the natural world. Note that the transition must result in absorption of a photon of visible light in order for our eyes to detect it.

Conjugated polyenes, such as β-carotene, are very ubiquitous pigments in nature and generally absorb light in the visible portion of the electromagnetic spectrum. These polyenes have a structure with alternating π-electron character (i.e, double bonds) in which the electrons are delocalized over the entire conjugated system. By changing the size of the conjugated system, the effective "box" length over which the electrons can move is changed. This crude model of electrons moving along a chain of carbon atoms can be successfully modeled with the Particle in a Box quantum mechanical model.

For example, consider hexatriene, a compound with three π-bonds (6 π-electrons) in the conjugated chain. Two of these electrons are placed in each energy level (Pauli Exclusion Principle), starting from the lowest energy level (Aufbau Principle).
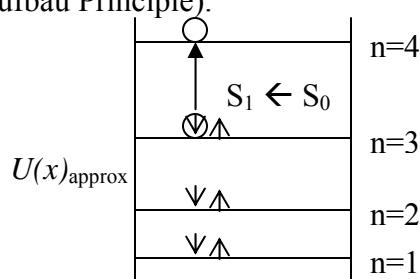
For hexatriene, it can be seen that the $S_1 \leftarrow S_0$ transition corresponds to a $n=4 \leftarrow n=3$ transition in the Particle in a Box model. The energy for the Particle in a Box model is given below. (See book for details on obtaining this energy.)

$$E_n = \frac{h^2 n^2}{8ma^2} \qquad (2)$$

where $n = 1, 2, 3\ldots$, $h = 6.62608 \times 10^{-34}$ J·s (Planck's constant), $m = 9.10939 \times 10^{-31}$ kg (mass of an electron), and a = length of the box (in meters if using SI units).

For the $S_1 \leftarrow S_0$ transition, the energy difference is:

$$\Delta E = E_{S_1} - E_{S0} \qquad (3)$$

$$\Delta E = \frac{h^2}{8ma^2}\left(n_{S_1}^2 - n_{S_0}^2\right) \qquad (4)$$

where $n_{S_0} = N/2$ (for hexatriene, $n_{S_0} = 6/2 = 3$) and $n_{S_1} = N/2 + 1$ (for hexatriene, $n_{S_1} = 6/3+1 = 4$) and N is the number of π-electrons. ΔE can then be expressed in terms of N:

$$\Delta E = \frac{h^2}{8ma^2}(N+1) = h\nu = \frac{hc}{\lambda} \qquad (5)$$

Solving for the box length, a, gives:

$$a = \left(\frac{h\lambda(N+1)}{8mc}\right)^{\frac{1}{2}} \qquad (6)$$

The box length, a, may also be related to the polyene structure with the empirical formula:

$$a = (P \cdot l) + E \qquad (7)$$

where P is the number of C atoms in the conjugated chain, l is the C-C bond length in the chain, and E is the effective size of the endgroups.

Note on wavelengths: If only changes in electronic energy accompany absorption of light, a very sharp maximum in absorption should be observed at the characteristic wavelength. Although sharp lines are observed for isolated atoms, broad absorption bands are observed for substances in liquid phases (due to the accompanying vibrational and rotational transitions). In the experiment, we shall assume that the wavelength λ_{max}, the wavelength at which the dyes absorb most strongly, is the wavelength to use in Eq (6).

You will carry out experiments on three cyanine dyes for which particle-in-a-box theory works very well. Additional calculations will be done on three other cyanine dyes. The structural formulas of Dye #1 (1,1'-diethyl-2,2'-cyanine iodide), #2 (1,1'-diethyl-2,2'-carbocyanine iodide), #3 (1,1'-diethyl-2,2'-dicarbocyanine iodide), #4 (1,1'-diethyl-4,4'-cyanine iodide), #5 (1,1'-diethyl-4,4'-carbocyanine iodide) and #6 (1,1'-diethyl-4,4'-dicarbocyanine iodide) are shown below, along with some tabulated information on the dyes.

The two nitrogen atoms in each dye represent a substantial disruption of the conjugated system, so that these atoms can be thought of as the walls of the box. The box length can be taken as the distance between the two nitrogen atoms, measured along the intervening carbon-carbon bonds. In order to determine the energy levels occupied by the electrons, we must count the number of π-electrons in the conjugated system. In Dye #2, for example, there are three double bonds in the conjugated chain. Each of these bonds, as well as the lone pair of electrons on the left-side nitrogen atom, has two π-electrons; thus, for Dye #2 there are 8 π-electrons. The general formula: $N = P + 3$ also works for determining the number of π-electrons in the conjugated chain of each dye. So, for Dye #2, the $S_1 \leftarrow S_0$ transition corresponds to a $n = 5 \leftarrow n = 4$ transition in the Particle in a Box model.
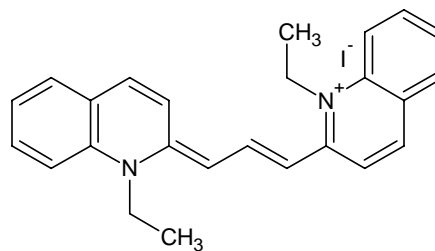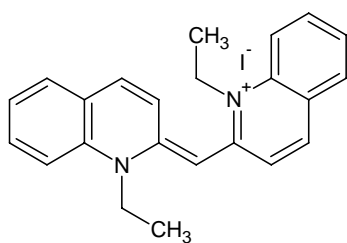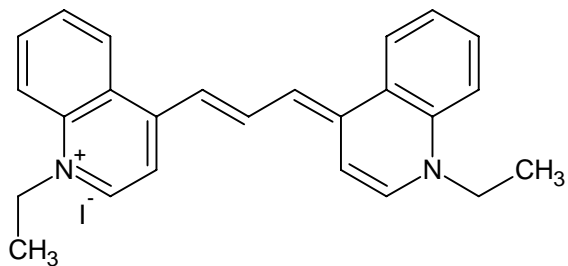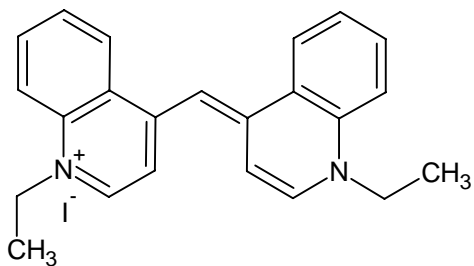
Dye #1: 1,1'-diethyl-2,2'-cyanine iodide   **Dye #2**: 1,1'-diethyl-2,2'-carbocyanine iodide
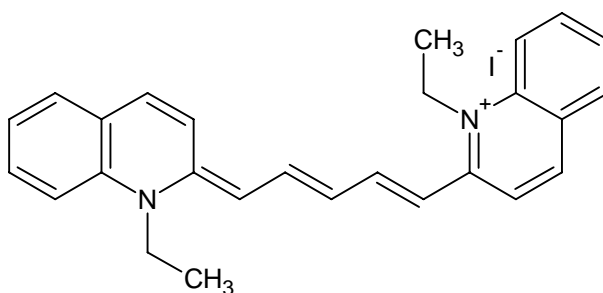
Dye #3: 1,1'-diethyl-2,2'-dicarbocyanine iodide

Dye	M.W. (g·mol^{-1})	ε (10^5 M^{-1} cm^{-1})[a]
1	454.4	0.75
2	480.4	1.95
3	506.4	2.13

[a] Molar absorption coefficient in methanol.

Dye #4: 1,1'-diethyl-4,4'-cyanine iodide   **Dye #5**: 1,1'-diethyl-4,4'-carbocyanine iodide
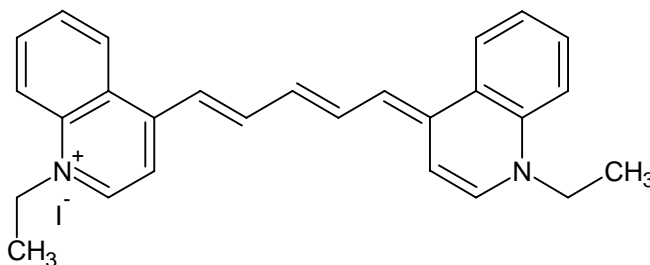
Dye #6: 1,1'-diethyl-4,4'-dicarbocyanine iodide

Dye	λ_{max} / nm
4	593
5	704
6	932

Procedure

Safety and Other Concerns: The dyes you will be using in this experiment are toxic. You should be careful in working with them, and avoid getting the solutions on your skin. In addition, these dyes will slowly degrade in the presence of light, so you should keep the solutions in the dark when they are not in use.

In the Lab:
1. Stock solutions of Dyes #1-3 are already prepared (with methanol as the solvent).
2. Prepare dilute solutions of Dyes #1-3 (in methanol) such that the final concentrations will give an absorbance between 0.5 and 1 for a 1-cm pathlength. (Recall that Beer's Law says $A = \varepsilon cb$.) When making your solutions, try to minimize the amount of solute and solvent used (you need ~2-3 mL of each).
3. Record spectra against a solvent reference, scanning from 400-800 nm, using the Ocean Optics UV-Visible spectrometer to record the spectrum of each dye.
4. Save and print your spectra for your notebook.
5. Determine λ_{max} for each dye. Make a table of λ_{max} in your notebook.

6. Draw these molecules in HyperChem and, using a semiempirical CI method, calculate the electronic spectrum. Place this spectrum in your notebook. Explore the molecular orbitals of this series of compounds.
7. Dispose used methanol/dye solutions in the appropriately marked container. Clean the glass cuvettes thoroughly with methanol or, if you used plastic cuvettes, throw them away.

Analysis:

The following steps, questions, and suggestions are things for you to consider when writing your lab report and preparing your notebook. Don't simply follow these steps and answer the questions in the report. Instead, use these questions for guidance of what important points should not be missed in presenting your results and discussion. (Refer to the 'How to Write a Lab Report' handout when writing the report.) Your notebook should include a summary of the experiment, including the spectra and any analysis.

Things to do/include in report:
*   Plot UV-Vis absorbance spectra for Dyes #1-3. (These can be combined into one figure). Note λ_{max} for each dye.
*   Comment on the electronic spectrum obtained with HyperChem.
*   Calculate the effective box length, a, for each of the dyes *(Dyes #1-6)*. Include an example calculation in the report.
*   Prepare a table with columns for compound code, compound name, total number of π-electrons in the conjugated chain, λ_{max}, and experimental box length, a.
*   Compare the experimental length with the geometric box length, qb, based on a uniform spacing of $b = 0.139$ nm for each of the q bonds in the conjugated system. Evaluate and tabulate the difference $(a - qb)$ for each dye. This difference is usually positive and can be ascribed to an increase of the effective free-electron box length due to potential energy rising not as abruptly (to infinity) right at each terminal nitrogen atom.
*   For each group of dyes, grouped #1-3 and #4-6, plot the box length, a, versus the number of C atoms in the conjugated chain, P to determine experimental determinations of the C-C bond length, l, and the size of the endgroups, E. Compare the experimental C-C bond values to literature values (e.g., from the CRC handbook). Also comment on the quality of the regression fit (preferably from SigmaPlot; Excel is okay). Compare the E's for the two series and try to explain any differences based on differences in the molecular structures.
*   Comment on the appropriateness of the free electron/particle-in-a-box model for describing the spectra of the cyanine dyes. Your answer to this question should go beyond simply stating whether the model is "good" or "bad."

References
Dr. Smith's site: http://www.gustavus.edu/academics/chem/pchem/quantum_lab.html
NMSU Chem435 site: http://www.chemistry.nmsu.edu/studntres/chem435/Lab5/
Hope College: http://mulliken.chem.hope.edu/~krieg/Chem346_2002/Polyene_lab.html
Also see references listed on these sites and your textbook.