Absorption Spectra of Cyanine Dyes

Reading/Preparation

The basic theory and the description of the experimental procedure are given in your lab text\(^1\) as experiment 34. Look carefully at the method and experimental sections in the text and only briefly at the other sections because we will analyze the spectra using an alternate approach described in an article by R. S. Moog\(^2\).

Prepare for this lab in advance by learning the start-up commands for the Shimadzu 2401 spectrophotometer and familiarizing yourself with control software. One of the purposes of this experiment is to become proficient in using this instrument.

Additions to and deviations from experimental procedure

You will study seven related cyanine dyes in methanol solution. The solutions are labeled IA, IIA, IIIA, and IVA corresponding to the compounds having 4, 6, 8, and 10 bonds along the delocalized electron chain between the nitrogen atoms in the 3, 3'-diethylthiacyanine iodide series of dye molecules. And solutions labeled IB, IIB, and IIIB corresponding to the compounds having 4, 6, and 8 bonds along the delocalized electron chain between the nitrogen atoms in the 1, 1'-diethyl-2-cyanine iodide series of dye molecules. (Note that the text and the Moog article both refer to the para-substituted structure rather than ortho-substituted structures that we are using.) Be VERY CAREFUL as you count the corresponding number of delocalized electrons for each dye.

Dilute each dye so that the peak absorbance is between 0.5 and 1.0. Carefully clean the sample cuvettes between use for different dyes. Record and print one good spectrum of each dye and include copies with your report sheet.

Dispose of your samples and any methanol used for cleaning in the container labeled "used cyanine dyes". CLEAN and REPLACE all equipment when finished.

References


SAFETY ISSUES

- Cyanine dyes are very toxic and are suspected carcinogens. Be careful to avoid skin exposure and especially ingestion.

- Methanol is toxic and especially hazardous to eyes. Avoid skin contact and exposure to vapors. Handle in a fume hood whenever possible.
Brief Report: Cyanine Dyes

Name: ________________________________

Partner(s): ________________________________

Date: ________________

1. List the range of available settings for each of these controls of the Shimadzu spectrometer:
   a) scan step (units?) ________________________________
   b) scan range (units?) ________________________________
   c) spectral resolution (units?) ________________________________
   e) scan rate (units? see manual) ________________________________

2. Draw the general structures for the "A" series of dyes we are using: ________________________________
   "B" series of dyes we are using: ________________________________

3. In Table I below, list your measured values for $\lambda_{\text{max}}$, $\lambda_{1/5}$, number of conjugated bonds, and measured peak absorbance (A) for each dye.

4. Use Beer’s Law to estimate the final concentration (c) of each dye assuming that the molar absorptivity coefficient for each is $5.0 \times 10^5$ L mol$^{-1}$ cm$^{-1}$. List the c values in Table I. Show how you calculated c for dye I.

5. Use Moog’s method to calculate the chain length (L) from $\lambda_{\text{max}}$ for each dye and list the values in Table I. Show how you calculated L for dye I:

6. Repeat the calculation of chain length using $\lambda_{1/5}$ for each dye and list these alternate values (L’) in Table I.
Table I: Data from Cyanine Dyes Experiment

<table>
<thead>
<tr>
<th>quantity</th>
<th>dye IA</th>
<th>dye IIA</th>
<th>dye IIIA</th>
<th>dye IVA</th>
<th>dye IB</th>
<th>dye IIB</th>
<th>dye IIIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{1/5}$ (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td># of bonds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c (mol/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L' (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7. Explain why Moog suggests that $\lambda_{1/5}$ may better indicate the actual HOMO – LUMO energy difference for the dyes.

8. Plot L vs # of bonds and show error bars for the "A" series. Do a weighted least-squares fit to find the slope, intercept, and their standard deviations. Include a copy of your plot with this report. How many degrees of freedom are in the fit to your data set?

Using the appropriate Student t value, estimate the 95% confidence interval for the slope and intercept. Show this calculation:

Plot, fit, and calculate C.I. for the "B" series. How many degrees of freedom for this set?

Next plot and fit using L' instead of L for both series. List all of the results in Table II below.

Table II: Results from Cyanine Dyes Experiment

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>slope (nm/bond)</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
</tr>
<tr>
<td>intercept (nm)</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
</tr>
</tbody>
</table>
9. Final results:
   average length of a conjugated bond for "A" dyes = ____________ ± ___________ pm
   "polarizability" of the end groups for "A" dyes = ____________ ± ___________ (include units)

   average length of a conjugated bond for "B" dyes = ____________ ± ___________ pm
   "polarizability" of the end groups for "B" dyes = ____________ ± ___________ (include units)

10. Use a general or organic chemistry text to find a reference value for the average length of a conjugated carbon-carbon bond. Cite that reference and write a few sentences comparing that bond length to your results, including their uncertainties, for the L plot in both "A" and "B" series.

Are the results from the L’ plot in better agreement with the literature? Why?

Would it help to take into account the actual 120° bond angles along the chains? Why?

Are the "polarizabilities" the same for the "A" and "B" series? Why?
Chem 3421 TA's Instructions: "Spectra of cyanine dyes" Lab

1) **Clean-up:** Clear away any old dye solutions that have been stored in the p-chem lab. Dispose of dye solutions as hazardous waste in the organic lab.

2) **Stock solutions:** (full procedure) Make concentrated solutions of the seven dyes:

<table>
<thead>
<tr>
<th>Label</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>3, 3'-diethylthiacyanine iodide</td>
</tr>
<tr>
<td>IIA</td>
<td>3, 3'-diethylthiacarbocyanine iodide</td>
</tr>
<tr>
<td>IIIA</td>
<td>3, 3'-diethylthiacarbocyanine iodide</td>
</tr>
<tr>
<td>IVA</td>
<td>3, 3'-diethylthiatricarbocyanine iodide</td>
</tr>
<tr>
<td>IB</td>
<td>1, 1'-diethyl-2, 2'-cyanine iodide</td>
</tr>
<tr>
<td>IIB</td>
<td>1, 1'-diethyl-2, 2'-carbocyanine iodide</td>
</tr>
<tr>
<td>&quot;IIB&quot;</td>
<td>1, 1'-diethyl-2, 2'-dicarbocyanine iodide</td>
</tr>
</tbody>
</table>

   a) The dyes are stored as solids below the center hood in MY 220. Be careful not to touch or breathe these materials as they are highly toxic. The strong air flow in a hood actually increases the hazard of working with these fine powders. Wear rubber gloves and wipe down all nearby surfaces with an acetone-soaked paper towel afterwards to remove the dust.

   b) Make solutions in the range of 10^{-3} M for each dye by dissolving ~30 mg of the powder into 50 mL of methanol. Label these solutions as indicated above and include "Chem 3421, Spring 2017" on the flask. Do the labeling in pencil directly on the flasks.

   c) Solutions must be ready before the first team does this experiment (see syllabus).

3) **Dilute solutions:** Provide small flasks, disposable pipets, and gloves for teams to make diluted dye solutions. Put approximately 500 mL of spectral grade methanol and a capped empty glass jug labeled "CHEM 3421 used cyanine dyes 2017" near the instrument.

4) **Disposal:** Discard all remaining dye solutions as organic waste at the end of Spring semester 2017.

5) **Spectrophotometer:**

   a) Clear the area around the Shimadzu spectrophotometer. Check that the manual is present.

   b) Store the chemicals in a plastic tray near the instrument.

   c) Locate two glass absorption cells for the spectrophotometer. Keep these in a drawer (i.e. hidden from random users or they will disappear).

   d) Ask each student group to sign the instrument log book when they have finished.

   e) Check that the instrument has been turned off each day to save lamp life time.

Please check the equipment and supplies each week to make sure that they have been cleaned properly after use and that they haven’t been removed from the area.