

Absorption Spectra of Conjugated Molecules

Introduction

The purpose of this experiment is to measure the absorption spectra of two series of cyanine dyes and diphenyl polyenes, and to try to correlate the experimental observations using a simple quantum mechanical model. The model for these molecules will be the "particle-in-a-box" which we will consider in class. Structures for the compounds labeled A-F are on page I-3.

Procedure

This experiment is taken directly from Shoemaker *et al.* Prior to laboratory you should familiarize yourself with the experiment, and with the structure and nomenclature of the molecules being used. The most significant parameters in the model are the length of the molecule and the nature of the potential at the ends. You should therefore decide which of the molecules form appropriate homologous series.

Stock solutions containing the cyanine dye molecules in methanol will be provided. These solutions must first be diluted before measurements are taken. Record the spectra for a series of dilutions, remembering to keep track of the accuracy and precision of the concentration of each solution. Obtain spectra over at least an order of magnitude difference in concentration. Spectra should be recorded using either the Cary/OLIS 14 spectrophotometer, or the HP8452 diode-array spectrophotometer. Be sure to consider the absorption spectrum of the sample cuvettes.

Report

Your report should include a table comparing experimental values with theoretically calculated values determined from the model. The following quantities should be considered.

1. The wavelength of maximum absorption and the energy of the transition. These values should be calculated first by a model which assumes no adjustable parameter, α , for end effects, and then using the end effect parameter as suggested in ref. 1. Note that among the cyanine dyes which you have available you can study series of varying length but constant α , and constant length but varying α . (Note, you may find that some values of α do turn out to be greater than one.)
2. You should know the concentrations with sufficient accuracy that you can determine the extinction coefficient at λ_{\max} as a function of chain length.
3. Note any changes in color and absorption band shape as you dilute your solutions. As pointed out in ref. 1, this is evidence of polymerization at higher concentrations. Also note the change in color upon going from the solid to the solution phase. Can you give an explanation for this?
4. (Optional) Consider the true potential energy function for an electron in a typical cyanine dye. What simple model potentials might be used to approximate the actual potential. Investigate how these spectra might be interpreted using, for example, a particle-in-a-box model in which the potential energy function ends of the boxes have steps, rather than sharp transitions to infinite potential. You might also investigate other simplifications of the particle-in-a box model, such as its one-dimensionality and neglect of electron-electron repulsion, and how they could be overcome.

Diphenyl polyenes:

I - Stilbene (1,2-diphenyl ethylene)	$\phi\text{-CH=CH-}\phi$
II - 1,4-diphenylbutadiene	$\phi\text{-(CH=CH)}_2\text{-}\phi$
III - 1,8-diphenyloctatetraene	$\phi\text{-(CH=CH)}_4\text{-}\phi$
IV - 1,12-diphenyldodecahexaene	$\phi\text{-(CH=CH)}_5\text{-}\phi$
V - 1,16-diphenylhexadecaoctaene	$\phi\text{-(CH=CH)}_8\text{-}\phi$

Due to the scarcity of these compounds, simply observe the color of the solids and try to relate the colors to chain length. Photographs of several of these compounds are available in the laboratory. Obtain absorption maxima from the literature.

Cyanine dyes available for detailed study:

- A = 1,1'-diethyl-2,2'-cyanine iodide
- B = 1,1'-diethyl-2,2'-carbocyanine bromide
- C = 1,1'-diethyl-2,2'-dicarbocyanine iodide
- D = 1,1'-diethyl-2,4'-cyanine iodide
- E = 1,1'-diethyl-4,4'-cyanine iodide
- F = 1,1'-diethyl-4,4'-carbocyanine iodide

Solutions are provided for compounds A-F, you will need to dilute them and record their absorption spectra. Solids are also available for observation.

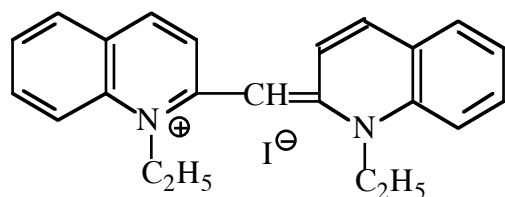
References

1. D. P. Shoemaker, C. G. Garland, J. I. Steinfeld and J. W. Nibler, *Experiments in Physical Chemistry*, 4th Ed., p. 412, McGraw-Hill, 1981. (Other editions contain the same experiment. 5th edition page 440.)
2. H. Kuhn, *J. Chem. Phys.* **17**, 1198 (1949).
3. K. W. Hausser, R. Kuhn, A. Smakula and K. H. Krenchen, *Z. Phys. Chem.* **B29**, 363 (1935). This article might be on reserve in the Chemistry Library.
4. K. W. Hausser, R. Kuhn and G. Seitz, *Z. Phys. Chem.* **B29**, 391 (1935).

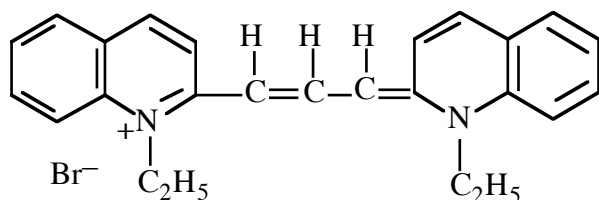
Safety Notes

Compound A is listed as highly toxic; methanol, C, D, E, and F are toxic, and all 6 A-F are irritants. Gloves are available in the lab – it would be wise to wear them. Waste methanol with trace amounts of dye and/or waste neat methanol should be placed in the appropriately labeled waste bottle. Prolonged exposure to methanol vapors is not good for your health. Prepare the solutions in the fume hood if possible and keep the cuvette covered outside the hood.

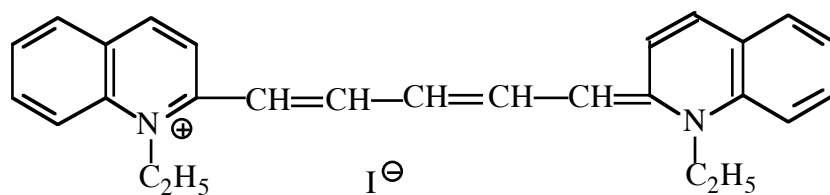
Feb-91 JT, Jan-92 epl, March-97 BK, Jan 2000 JT, Jan 2001 JT



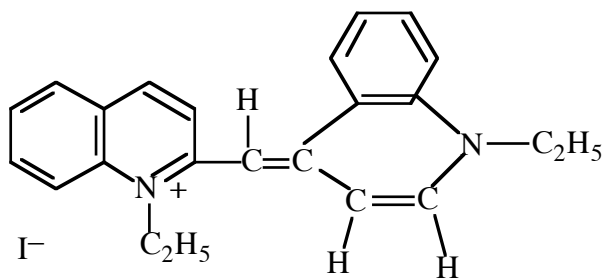
A = 1,1'-diethyl-2,2'-cyanine iodide
MW 454.36 g/mole
(stock solution: 0.0114 g in 25 ml)



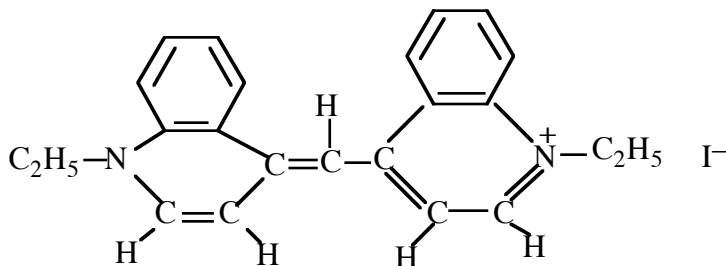
B = 1,1'-diethyl-2,2'-carbocyanine bromide
MW 433.4 g/mole
(stock solution: 0.0108 g in 25 ml)



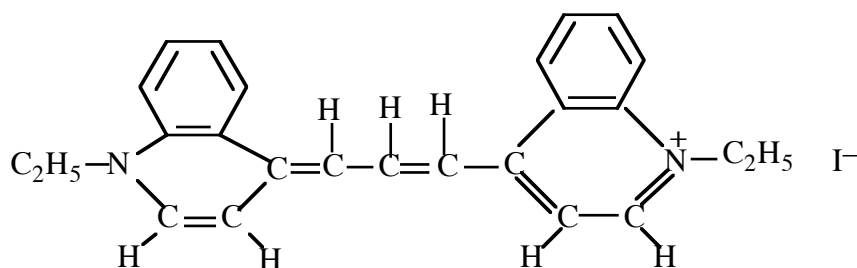
C = 1,1'-diethyl-2,2'-dicarbocyanine iodide
MW 506.43 g/mole
(stock solution: 0.0127 g in 25 ml)



D = 1,1'-diethyl-2,4'-cyanine iodide
MW 454.36 g/mole
(stock solution: 0.0114 g in 25 ml)



E = 1,1'-diethyl-4,4'-cyanine iodide
MW 454.36 g/mole
(stock solution: 0.0114 g in 25 ml)



F = 1,1'-diethyl-4,4'-carbocyanine iodide
MW 480.4 g/mole
(stock solution: 0.0120 g in 25 ml)

HP 8452A Instructions

If it isn't already on, turn on the HP 8452A diode array spectrophotometer by the rocker switch on the back left side of the instrument. Check that the IBM PC 300GL computer is on. It should remain on.

Use control-alt-delete to log onto the Novell Network.

- Log on with 02ABC.student, then your password, and click OK
- Click CLOSE to get rid of the Windows NT promotional material
- Click NO to avoid the Internet explorer tour

Using the Windows NT START button, go to
programs -- UV-Visible ChemStations -- Instrument 1 Online

In the UV-vis ChemStation window, log on as operator name "chem302" with no password

After the program loads, pull down the "Instrument" menu item "Lamp(s)"

- Click the radio button "ON" for the deuterium lamp
- Click the OK button
- Wait patiently until the HP 8452A no longer reads "busy"
- The cartoon lamp will light up on the lower right of the screen

In the "Task" window, select "Spectrum/Peaks"

- Click the "setup" button
- Adjust parameters as desired:
 - 3 peaks is a reasonable start
 - do have the program prompt you for a sample ID
 - Data Type = Absorbance
 - Display Spectrum 350 to 750 nm
- Click "OK"

In the "Sampling" window, chose "Manual"

- Under setup -- pathlength = 1cm "OK"
- Load a blank/reference sample in the spectrophotometer
- Click "blank" to record a background spectrum
- (You can watch the cartoon animation of the spectrophotometer in action)
- This should produce a spectrum with absorbance less than 0.001 throughout

Load your sample in the spectrophotometer

- Click on the "Sample" box to record the spectrum
- Type in the sample name, solvent, comment, and click "OK"

If you want to find more or fewer peaks, then click the set-up box in the task window and change the number of "Find an annotate up to ___ peaks", click "OK", and wait for about 5 seconds.

To print, click the printer icon. A hardcopy will appear on the laser printer in the back room of room 210 TCL (the chemistry student computer room). Novell will send a confirming message.

To save a spectrum, first click on the spectrum to highlight it. There are several ways to save a spectrum. One method that seems to work is: under the File menu, select "Export Selected Spectrum As -- WAV format", Save into C:\hpchem\1\data\CHEM 302. Type filename.WAV in the filename box.