EXPERIMENT 6

ABSORPTION SPECTRA OF CONJUGATED DYES

INTRODUCTION

This experiment is a study of the visible spectra of several dye molecules. Absorption of electromagnetic radiation (EMR) in the visible (ca. 400-750 nm), ultraviolet (ca. 180-400 nm), and vacuum UV (ca. 10-180 nm) regions is associated with the promotion of a valence electron from its lowest energy (ground state) level to a higher energy level. For most organic molecules the energy spacing between levels is greater than about 400 kJ/mol. However, in certain cases, the energy spacing's are smaller and the compound absorbs visible wavelengths. Such a compound (or a solution of the compound) is colored and the observed color is the complement of the color that is absorbed. For example, a red solution must absorb blue-green (also called cyan) light (400-600 nm region) and transmit red wavelengths (600-700 nm).

The four molecules studied in this lab are shown in Figure 7.1 and their names and relevant data are given in Table 7.1. These compounds are all intensely colored, many with a bluish tinge, and have been historically called cyanine dyes[1]. Structurally, their distinguishing feature is the chain of alternating double bonds connecting the two rings. The delocalization of the π-electrons shifts the electronic absorption into the visible region, and, as this experiment will demonstrate, the length of the conjugated system affects the specific characteristics of the transition. It is advised that the student read Chapter 13 of the 9th edition of Physical Chemistry by Atkins & de Paula [2].
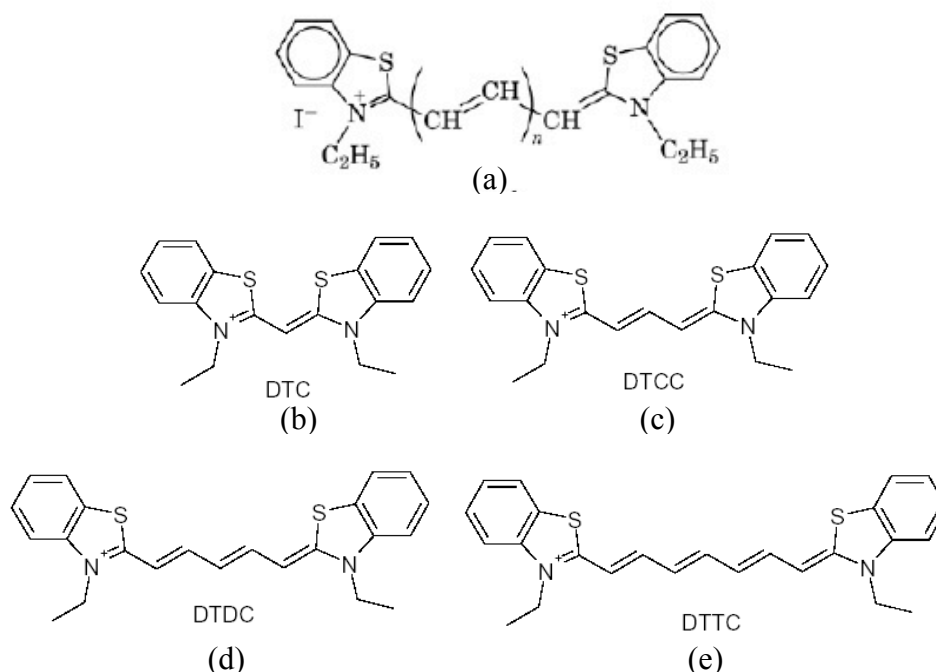
Figure 7.1. Structures of the thiacyanine dyes studied. (a) general structure of the thiacyanine dyes; (b) 3,3'-diethylthiacyanine iodide (DTC); (c) 3,3'-diethylthiacarbocyanine iodide (DTCC); (d) 3,3'-diethylthiadicarbocyanine iodide (DTDC); (e) 3,3'-diethylthiatricarbocyanine iodide (DTTC).

Table 7.1. The names, abbreviations used, number of ethylene units between rings, λ_{max}, and molar absorptivity of the dyes studied. Data taken from Sturmer[1].

Name (Abbrev.)	n	λ_{max} (nm)	ε (L/mol cm)
3,3'-diethylthiacyanine iodide (DTC)	0	423	8.5×10^4
3,3'-diethylthiacarbocyanine iodide (DTCC)	1	557	1.5×10^5
3,3'-diethylthiadicarbocyanine iodide (DTDC)	2	650	2.3×10^5
3,3'-diethylthiatricarbocyanine iodide (DTTC)	3	758	2.5×10^5

The Particle-in-a-box Model

This system can be treated theoretically using the "free electron" model, as proposed by Kuhn[3]. In this model, the spectral characteristics in the visible region are determined solely by the π-electrons, which are "freely" in motion along the chain, with the electrons in the sigma framework localized between the connected atoms and excited only by EMR in the

vacuum UV range. Thus, the π-electrons of a conjugated dye molecule can be modeled using a one-dimensional "particle-in-a-box" (PIB).

When applying the PIB model to conjugated systems, the following assumptions are made:

- All the carbon-carbon bonds in a conjugated system have equivalent bond lengths
- Each carbon atom forms 3 sigma bonds.
- Each carbon atom contributes one valence electron to form a mobile π electron cloud.
- This π electron cloud moves along the carbon chain, above and below the plane of the chain.
- Potential energy of the π electrons is constant along the chain.
- Potential energy of the π electrons rises sharply to infinity at the ends of the chain.

The quantum mechanical solution for the energy levels of an electron placed in a one-dimensional box of length L is given by equation (7.1), where h is Planck's constant and m is the mass of an electron. The following figure (Figure 7.2) displays the first five energy levels in a conjugated system containing six π-electrons.

$$E_n = \frac{n^2 h^2}{8mL^2}; n = 1,2,3,... \tag{7.1}$$

The Pauli exclusion principle limits the number of electrons in each level to 2 (one with spin function α, or spin-up, and the other with spin function β, or spin-down). Therefore, if there are N π-electrons, the ground state of the molecule will have N/2 number of levels completely filled (if N is an even number). In Figure 7.2, N = 6 because we have drawn the diagram for a conjugated carbon chain with 6 π electrons. When this conjugated system absorbs light, the valence electrons will be excited from the highest occupied molecular orbital (HOMO; $n_1 = N/2$) to the lowest unoccupied molecular orbital (LUMO; $n_2 = N/2 + 1$). An orbital is a wave function for a single electron. The energy change for this electronic transition is given in equation 7.2.
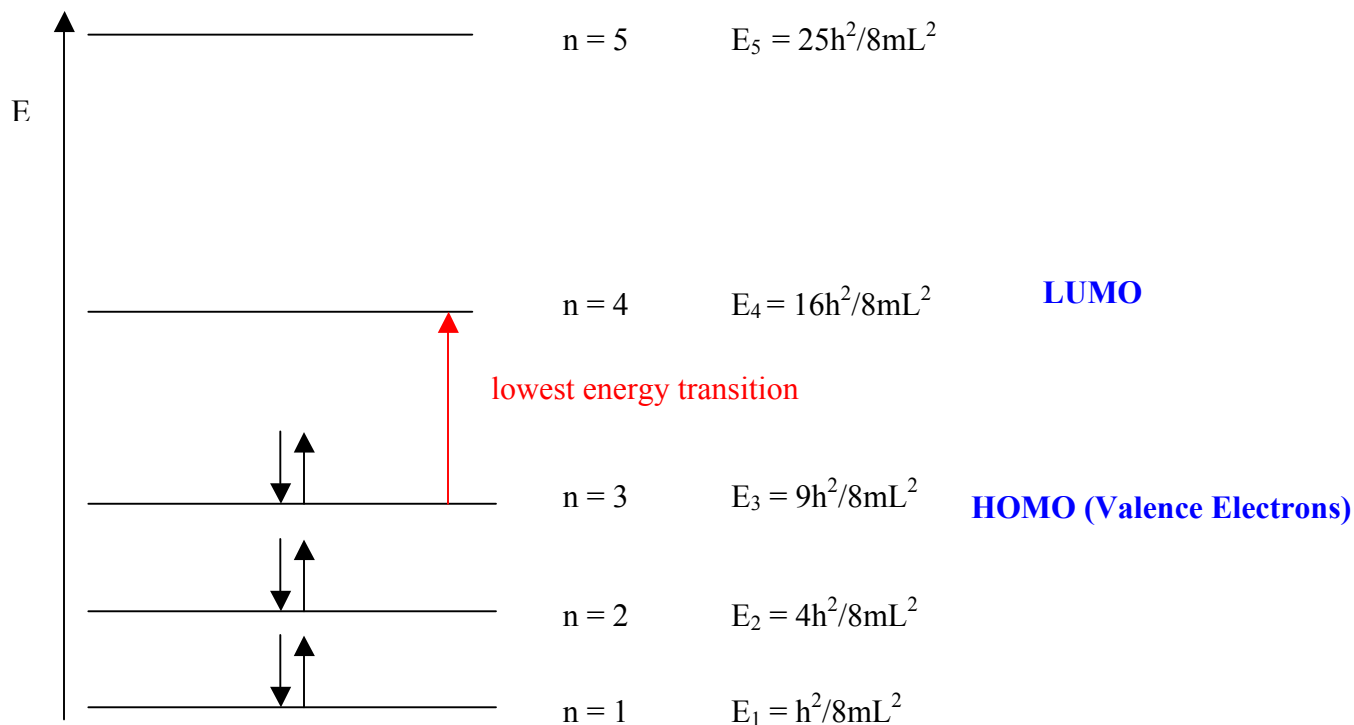
Figure 7.2: Energy diagram for a conjugated carbon chain with six π-electrons (N = 6)

$$\Delta E = E_{n_2} - E_{n_1} = \frac{[\frac{N}{2}+1]^2 \ h^2}{8 \ m \ L^2} - \frac{[\frac{N}{2}]^2 \ h^2}{8 \ m \ L^2} = \frac{[N+1] \ h^2}{8 \ m \ L^2} \tag{7.2}$$

This transition will occur when it is illuminated with light that has a frequency of ν (Equation 7.3) and wavelength of λ (equation 7.4). Kuhn assumed that L was the length of

$$\nu = \frac{\Delta E}{h} = \frac{[N+1] \ h}{8 \ m \ L^2} \tag{7.3}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{8 \ m \ L^2 \ c}{h \ [N+1]} \tag{7.4}$$

the conjugated system plus one C-C bond distance on each side (in order to take into account that the box boundary is not perfectly vertical), which can be estimated from average bond

lengths, *l*. For conjugated carbon-carbon bonds the value for benzene, *l*=1.39 Å, is used and for carbon-heteroatom bonds, values of *l*=1.43 Å for C-N and *l*=1.68 Å for C-S, are used.

The energy of interaction, ε, between a system of charged particles and an electric field is given by the scalar product of the electric field, **E**, and the dipole moment for the system, **μ**, (equation 7.5), both of which are vectors. Note here that the symbol ε is also used for the extinction coefficient, which expresses the strength of a spectroscopic absorption.

$$\varepsilon = -\bar{\mu} \cdot \bar{E} \tag{7.5}$$

The dipole moment is defined as the summation of the product of the charge q_j times the position vector $\mathbf{r}_j$ for all charged particles j (equation 7.6). To calculate an expectation value

$$\bar{\mu} = \sum_{j} q_j \bar{r}_j \tag{7.6}$$

for this interaction energy, the integral in equation 7.7 is evaluated.

$$\langle \varepsilon \rangle = \int \Psi_n^* (-\hat{\mu} \cdot \hat{E}) \Psi_n d\tau \tag{7.7}$$

Typically, the wavelength of light used in electronic spectroscopy is considerably longer than the length of the molecule and the magnitude of the electric field is essentially a constant. Thus, the expectation value of the interaction energy is linearly proportional to the expectation value of the dipole moment (equation 7.8).

$$\langle \mu \rangle = \int \Psi_n^* \hat{\mu} \Psi_n d\tau \tag{7.8}$$

To obtain the strength of the interaction that causes transitions between states, the transition dipole moment is used rather than the dipole moment. The transition dipole moment integral is very similar to the dipole moment integral (equation 7.8) except the two wave functions are different, one for each of the states involved in the transition. Two different states are involved in the integral (equation 7.9) because the transition dipole

$$\langle\mu\rangle_{\mathrm{T}} \;=\; \int \Psi_f^* \,\hat{\mu}\, \Psi_i \,d\tau \tag{7.9}$$

moment integral has to do with the magnitude of the interaction with the electric field that

causes a transition between the two states. Just like the probability density is given by the

square modulus of the wave function, the probability for a transition, as measured by the

extinction coefficient, ε, is proportional to the absolute square of the transition dipole

moment, $|\mu_T|^2 = \mu_T^* \mu_T$. Within the PIB model, the wave function is given by equation 7.10

and the dipole moment operator by equation 7.11, which, when substituted into equation 7.9

gives the transition dipole moment presented in equation 7.12.

$$\psi_n \;=\; \left(\frac{2}{L}\right)^{1/2} \sin\!\left(\frac{n\pi x}{L}\right) \tag{7.10}$$

$$\hat{\mu} = -e\hat{x} \tag{7.11}$$

$$\langle\mu\rangle_{\mathrm{T}} \;=\; \frac{-2e}{L} \int_0^L \sin\!\left(\frac{n_f\pi x}{L}\right) x \sin\!\left(\frac{n_i\pi x}{L}\right) dx \tag{7.12}$$

OBJECTIVE

To obtain spectra for several dyes with different lengths of conjugation; to observe how the

spectral properties change with length of conjugation; to compare the experimental results

with predictions from the particle-in-a-box theoretical model and ZINDO-type calculations.

PROCEDURE

CAUTION! The toxicity of the dyes used in this lab should be considered unknown and as

such all should be treated as toxic. Conjugated dyes are known sensitizers; take care when

handling the dyes and wash your hands after handling them. The dyes are light sensitive, and

so if it is necessary to store the dye solutions, protect them from light.

1. The instructor will supply you with the appropriate dye stock solutions. Record the

   concentrations. Using a 1 mL pipette, transfer an aliquot of each stock solution into

separate, and labeled, 100 mL volumetric flask and fill to the mark with Reagent Grade methanol.

2. Rinse a cuvette, which has a path length of 1 cm, thoroughly with Reagent Grade Methanol. Carefully wipe the cuvette windows and place a cell filled with methanol in the cell compartment. Close the compartment and collect a reference spectrum (See your instructor for directions on instrument operation; absorbance will be measured as a function of wavelength from 350 nm to 850 nm). This spectrum will be stored in the instrument's computer and will be subtracted from future spectra.

3. Remove the cell, rinse with methanol and fill the cuvette 3/4 full with dye #1. Put the cuvette back in the instrument and collect the spectrum. Locate the long wavelength maximum absorbance in the spectrum for each dye and annotate the peak with λ_{max} and the corresponding absorbance.

4. Rinse the cuvette with methanol and repeat this process for each of the remaining dyes. You should collect a spectrum for each of the dyes in the series (a total of four dyes).

5. Save a copy of each spectrum on your "disk" and print out copies of the full, annotated, spectrum for your report.

WRITE-UP

(1) Include a table of results listing concentration, λ_{max}, intensity, and extinction coefficient.
(16 marks)

(2) Calculate the absorbance for DTC at λ_{max} using the Beer-Lambert law ($A=\varepsilon cl$), the information in Table 1.1, and a dye concentration of 1.00×10^{-5} M. (5 marks)

(3) Determine the "length" of DTC using the values at the top of page 5. How does this compare with the smallest wavelength used in the experimental section? (6 marks)

(4) Calculate the absorption energy when a particle with a mass of 1.0×10^{-23} g, confined to a box 1.0×10^{-9} m long, is excited from the n=5 to the n=6 energy level. (5 marks)

(5) Calculate $|\mu_T|^2$ for the transition given in (4). (12 marks)

(6) Determine the number of π-electrons in DTC given that atoms donate the following number of π-electrons to the conjugated π-system: carbon, one; a neutral nitrogen, two; a positively charged nitrogen, one; a sulfur atom, two. (4 marks)

(7) For each dye, compare your experimentally obtained results for λ_{max} and the extinction coefficient with: (16 marks)
      (a) Those from the literature
      (b) Those obtained using the particle-in-a-box model – how might you improve the given model?
      (c) Those obtained from ZINDO calculations performed in Lab 2

REFERENCES

1. D.M. Sturmer, *in Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2000.
2. P.W. Atkins and J. de Paula, *Physical Chemistry*, 9th Ed., Oxford University Press, 2010.
3. H. Kuhn, *J. Chem. Phys.*, **1949**, 17, 1198.