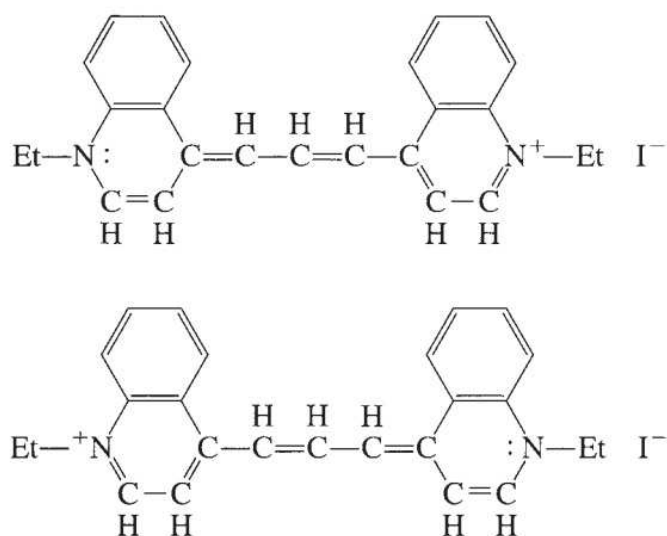


Absorption Spectrum of a Conjugated Dye

1 Introduction

Absorption bands in the visible region of the spectrum correspond to transitions from the ground state of a molecule to an excited electronic state that is 170 to 300 kJ/mol above the ground state. In many substances the lowest excited electronic state is more than 300 kJ/mol above the ground state and no visible spectrum is observed. Those compounds that are colored (i.e., absorb in the visible) generally have some weakly bound or delocalized electrons such as the odd electron in a free radical or the π electrons in a conjugated organic molecule. In this experiment we are concerned with the determination of the visible absorption spectrum of several symmetric polymethine dyes and with the interpretation of these spectra using the "free-electron,, or "particle-in-a-box,, model.

The visible bands for polymethine dyes arise from electronic transitions involving the π electrons along the polymethine chain. The wavelength of these bands depends on the spacing of the electronic energy levels. As an example, consider a dilute solution of 1,1'-diethyl-4,4'-carbocyanine iodide (cryptocyanine):



The cation can "resonate,, between the two limiting structures above, which really means that the wavefunction for the ion has equal contributions from both states. Thus all the bonds along this chain can be considered equivalent, with bond order 1.5 (similar to the C-C bonds in benzene). Each carbon atom in the chain and each nitrogen at the end is involved in bonding with three atoms by three localized bonds (the so-called σ bonds). The extra valence electrons on the carbon atoms in the chain and the three remaining electrons on the two nitrogens form a mobile cloud of π electrons along the chain (above and below the plane of the chain). We shall

assume that the potential energy is constant along the chain and that it rises sharply to infinity at the ends; i.e., the π electron system is replaced by free electrons moving in a one-dimensional box of length L . The quantum mechanical solution for the energy levels of this model is

$$E_n = \frac{h^2 n^2}{8mL^2} \quad n = 1, 2, 3 \dots \quad (1)$$

where m is the mass of an electron and h is the Planck constant.

Since the Pauli exclusion principle limits the number of electrons in any given energy level to two (these two have opposite spins: $+\frac{1}{2}, -\frac{1}{2}$), the ground state of a molecule with N π electrons will have the $N/2$ lowest levels filled (if N is even) and all higher levels empty. When the molecule (or ion in this case) absorbs light, this is associated with a one-electron jump from the highest filled level, so-called HOMO, ($n_1 = N/2$) to the lowest empty level, so-called LUMO, ($n_2 = N/2 + 1$). The energy change for this transition is

$$\Delta E = \frac{h^2}{8mL^2} (n_2^2 - n_1^2) = \frac{h^2}{8mL^2} (N + 1) \quad (2)$$

Since $\Delta E = h\nu = hc/\lambda$, where c is the speed of light and λ is the wavelength,

$$\lambda = \frac{8mc}{h} \frac{L^2}{N + 1}. \quad (3)$$

2 Method

It is necessary to define several terms commonly used in spectrophotometry. Absorption spectra are often characterized by the *transmittance* T at a given wavelength; this is defined by

$$T = \frac{I}{I_0} \quad (4)$$

where I is the intensity of light transmitted by the sample and I_0 is the intensity of light incident on the sample. When the sample is in solution and a cell must be used, I is taken to be the intensity of light transmitted by the cell when it contains solution, while I_0 is taken to be the intensity of light transmitted by the cell filled with pure solvent. Another way of describing spectra is in terms of the *absorbance* A , where

$$A = \log \frac{I_0}{I}. \quad (5)$$

A completely transparent sample would have $T=1$ or $A=0$, while a completely opaque sample would have $T=0$ or $A=\infty$.

The absorbance A is related to the path length d of the sample and the concentration c of

absorbing molecules by the Beer–Lambert law,

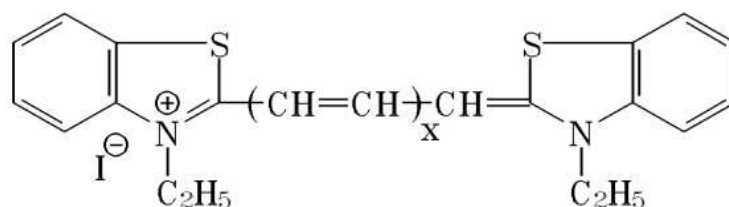
$$A = \varepsilon \cdot c \cdot d \quad (6)$$

where ε is called the *molar absorption coefficient* when the concentration is expressed in moles per unit volume. The quantity ε is an intrinsic property of the absorbing material that varies with wavelength in a characteristic manner; its value depends only slightly on the solvent used or on the temperature. The SI unit for ε is $\text{mol}^{-1} \text{m}^2$, but a more practical and commonly used unit is $\text{mol}^{-1} \text{L cm}^{-1}$, which corresponds to using the concentration c in mol/L and the path length d in cm.

For quantitative measurements it is important to calibrate the cells (or cuvettes) so that a correction can be made for any small difference in path length between the solution cell and the solvent cell. For analytical applications, one must check the validity of Beer's law, since slight deviations are often observed and a calibration curve of absorbance versus concentration is then required. Such corrections will not be necessary in the present work.

3 Experimental

Several polymethine dyes could be studied, preferably a series of dyes of a given type with varying chain length. In the experiment, the following diethyl thiacyanine iodides will be used where x is 1, 2, and 3.



The dyes are dissolved in absolute ethanol and their concentration is set to 4×10^{-6} M. All the materials are extremely expensive, thus extra caution is needed during the experimental work. For handling each compound, the appropriate pipet tip should be used.

1. Follow the spectrophotometer operating instructions carefully and switch on the equipment, wait 30 min for warm up. Set the appropriate parameters for the measurements. For automatic measurements the absorbance should be measured in the 390 – 870 nm range with 2 nm resolution.
2. While waiting for the warm up, two cuvettes should be rinsed with absolute ethanol 2-3 times using an automatic pipet.
3. The cuvettes should be filled with absolute ethanol up to 2/3.

- Obtain the spectrum of the cuvettes with ethanol.
- Fill one cuvette with the dye solution, place the cuvette into the holder and obtain the spectrum of the dye.
- Between each measurements, the cuvettes should be rinsed with absolute ethanol 2-3 times using an automatic pipet.
- Repeating the previous 2 steps measure all three known compound and the unknown.
- Rinse the cuvette with absolute ethanol 2-3 times using an automatic pipet.
- Convert the data from the spectrophotometer and download it as instructed.

4 Calculations

- Present all the spectra obtained by plotting A versus λ in one graph; label each plot clearly with the name of the compound and the concentration used.
- Determine λ_{max} , the wavelength at the peak for each dye studied.
- Calculate ϵ_{max} based on Lambert-Beer law.
- Calculate L based on Eq. (3).
- Summarize the results in the following table:

x	λ/nm	$\epsilon_{max}/(M^{-1}cm^{-1})$	N	L/nm

- Plot L vs x . From the slope estimate the bond length of C–C bond.
- Based on the experimentally determined λ_{max} , identify your unknown from below:

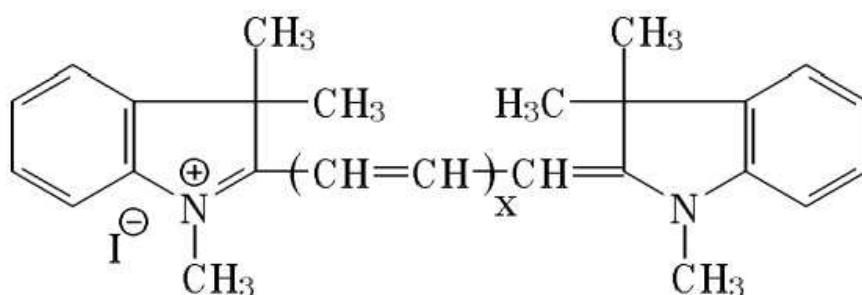


Figure 1: for $x=2$, the compound is 1,1',3,3,3',3'-hexamethyl-indo-dicarbocyanine-iodides
for $x=3$, the compound is 1,1',3,3,3',3'-hexamethyl-indo-tricarbocyanine-iodides

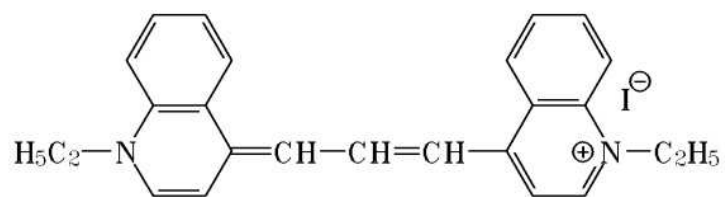


Figure 2: 1,1'-diethyl-4,4'-carbocyanin-iodides

8. Based on Eq. (2) predict the second absorption band of compound diethyl-tia-tricarboyanine ($x=3$). Is there any proof for it in the obtained spectrum? Discuss it briefly.
9. Explain the high energy broadening of the peak in the spectra.

5 Possible test questions

1. Define chromophore.
2. Draw the structure of the chromophore of the dyes going to be examined.
3. Write down the equation for the possible energy levels of the free electrons moving in a one-dimensional box of length L . Define the symbols.
4. Write down the equation for the energy difference between the highest occupied energy level and the lowest unoccupied energy level (HOMO \rightarrow LUMO), for a chromophore with N π -electrons. Define the symbols.
5. Write down the energy difference between the highest occupied energy level and the second lowest unoccupied energy level for a chromophore with N π -electrons. Define the symbols.
6. Write down the wavelength of the lowest energy absorption peak for a chromophore with N π -electrons. Define the symbols.
7. Define the Beer–Lambert law.
8. How can the length of the C–C bond be estimated from the measured data?
9. Why do we consider the electrons to be conjugated from nitrogen atom to nitrogen atom in case of the examined dyes?