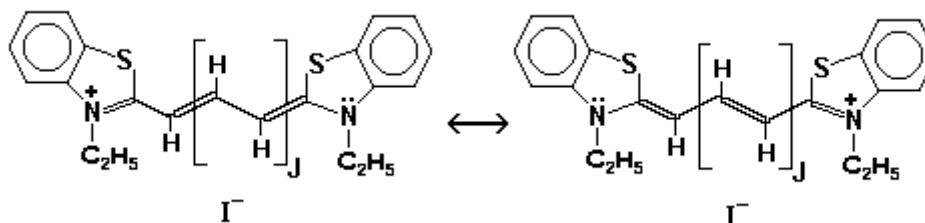


ABSORPTION SPECTRA OF CONJUGATED DYES

In this experiment the visible spectra of four symmetric cyanine dyes will be measured on an ultraviolet/visible spectrophotometer and interpreted in terms of the quantum mechanical particle in a box model. The dyes to be studied have the following general structure



where J can equal 0, 1, 2, or 3. Note that two resonance forms are drawn. This reflects the ability of three electrons from the nitrogen atoms and one electron from each carbon atom in the conjugated diene chain to move more or less freely along the chain. By assuming that these $2J+6$ electrons move in an infinitely deep square well potential, the quantum mechanical energies and wavefunctions for a particle in a box can be used to predict the positions and relative intensities of absorption bands in the visible spectrum of each dye.

THEORY

Figure 1a shows the nuclear skeleton of the smallest dye molecule to be studied in this experiment. The nuclei of the atoms constituting the conjugated diene chain are circled and lie in the same plane. Each carbon and nitrogen atom in the chain uses three of its valence

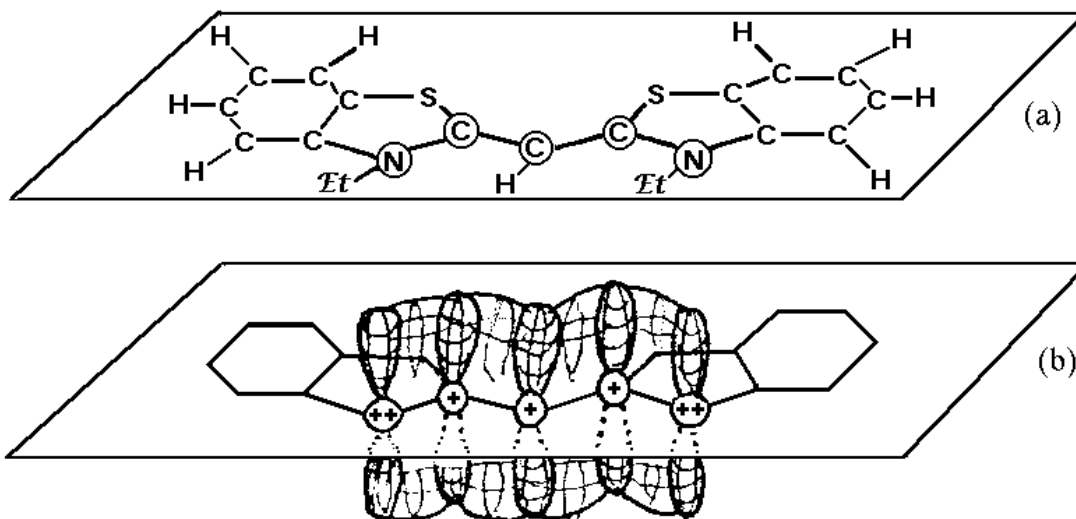


Figure 1

electrons to form three σ -bonds -- bonds possessing cylindrical symmetry about the internuclear axis. The remaining valence electrons form π -bonds which are characterized by electron density above and below the nuclear plane as shown in figure 1b.

The electrons in the π -bonds (π -electrons) are attracted by the positively charged carbon and nitrogen nuclei but repelled by the electrons forming the σ -bonds. The potential energy of a π -electron subject to these coulombic interactions as it zig-zags along the chain resembles the solid line shown in figure 2.

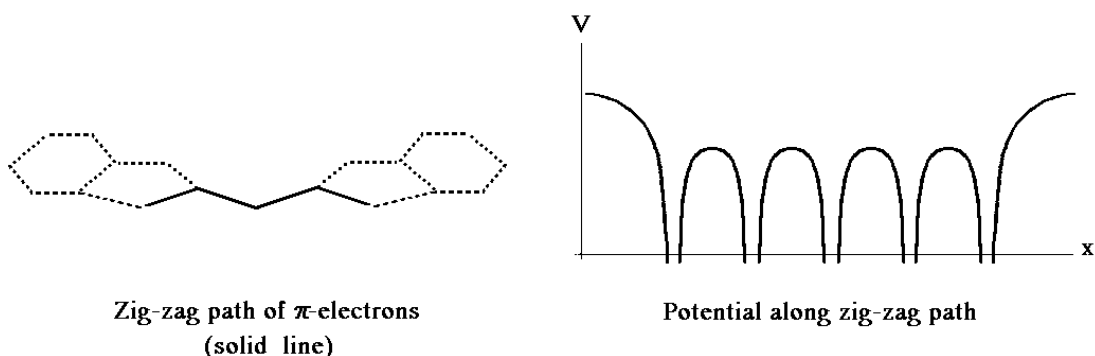


Figure 2.

Assume the π -electrons do not interact with one another and move on a straight path which extends the length of the molecule. If the potential is constant on this path but infinite off

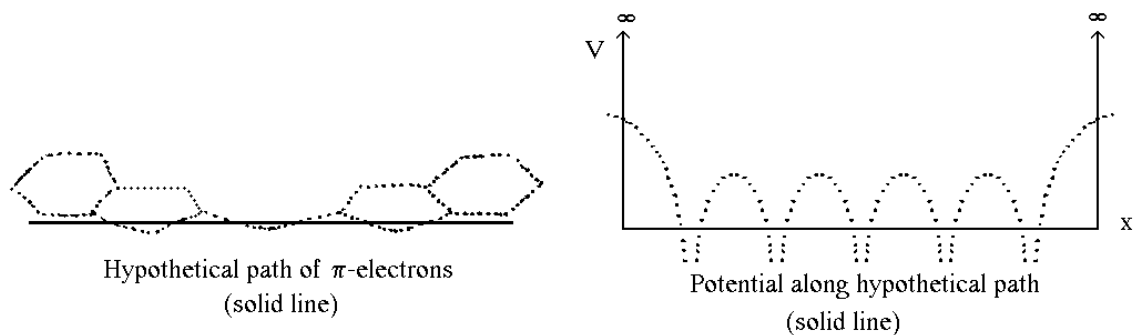


Figure 3.

the path (see figure 3), the π -electrons can be viewed as particles in a one dimensional box.

Interpretation of Absorption Wavelengths: The quantum mechanical behavior of one particle in a box is found by solving Schrodinger's equation with appropriate boundary conditions (see Hanna). The solutions reveal that the particle can occupy any one of an infinite number of discrete levels, the energy of the n th level given by

$$E_n = \frac{n^2 h^2}{8m_e L^2}$$

where L is the length of the box, m_e is the mass of the particle, h is Planck's constant, and n is a quantum number which can take the values 1,2,3,

The corresponding wavefunctions are

$$\Psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

For a one dimensional box with more than one particle, the same energy levels arise but they must be filled in accordance with the Pauli exclusion principle: no two electrons can have identical spin and quantum number. The lowest energy state of a $2N$ π -electron system therefore has two electrons of opposite spin in each of the N lowest particle in a box energy levels.

In this simple model, light is absorbed if it can induce an electron to jump to higher energy levels. This will occur whenever the wavelength of light satisfies Planck's relation

$$\lambda = hc/\Delta E$$

where c is the speed of light and ΔE is the transition energy - the difference in energy between the initial and final levels of the electron. Since wavelength is inversely proportional to transition energy, the longest absorption wavelength observed must correspond to the smallest possible transition energy. For a dye molecule in the ground state this will promote an electron from the highest filled to the lowest unfilled level.

To summarize, it is possible to predict the absorption wavelengths for a dye molecule from

- the number of π -electrons in the dye molecule
- the energy formula for the n th level of a particle-in-a-box
- the Pauli principle
- and Planck's relation.

Interpretation of Absorption Intensities: The intensities of electronic transitions have always proved extremely difficult to calculate accurately from molecular wavefunctions. The reason for this is that the calculated values are quite sensitive to the exact details of the wavefunctions, so that approximate wavefunctions tend to give poor agreement with experiment. However, different types of transitions observed in molecules have intensities which vary over a range of about eleven orders of magnitude, so that even approximate calculations of intensities can be very valuable in identifying observed spectral bands.

The intensity of an electronic transition, σ , is related to the integral of the electric dipole moment operator, μ , and the wavefunctions of the two states involved

$$\sigma \propto \left| \int \Psi_G \mu \Psi_E d\tau \right|^2$$

where Ψ_G and Ψ_E are wavefunctions for the ground and excited states of the molecule. If we represent the states of the molecule by an orbital approximation and assume that the center of the positive charges remains fixed during the transition, then the above integral reduces to one involving only the orbitals involved in the transition and the coordinates of the electron which changes orbitals.

For a one dimensional particle in a box model, we can write

$$\sigma = \frac{16 \pi^3 N_e^2 \omega}{3 (2303)hc} \left| \int_0^L \psi_i^* \psi_f dx \right|^2$$

$$= (5.023 \times 10^{19} \text{ liter} \cdot \text{mole}^{-1} \cdot \text{cm}^{-3}) \omega \left| \int_0^L \psi_i^* \psi_f dx \right|^2$$

where ω is the mean transition frequency in cm^{-1} , and ψ_i and ψ_f are the wavefunctions of the initial and final levels.

In this experiment, a spectrometer either simultaneously or sequentially measures I_0 , the amount of light transmitted by a reference cell containing solvents, and I , the amount of light transmitted by a cell containing a dye solution of known concentration, C , in moles per liter. As the spectrometer varies the wavelength of incident light, it records the absorbance, A , defined by the Beer-Lambert law as

$$A \equiv \log_{10} (I_0/I) = \epsilon C l$$

where l is the path length in cm (not to be confused with the particle in a box length, L) and ϵ is a quantity characteristic of the absorbing molecule called the molar extinction coefficient and has units of $\text{liters} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$.

The extinction coefficient evaluated at an absorption peak is frequently used for analytical purposes, since a knowledge of its value allows the determination of concentration by measurement of absorbance. But you will notice that the absorption peak associated with a given transition spans a range of wavelengths. The theoretical absorption intensity should therefore be compared to the integrated absorption coefficient

$$\sigma = \int_{\omega_{\min}}^{\omega_{\max}} \epsilon d\omega$$

where ω_{\max} and ω_{\min} are the maximum and minimum frequencies spanned by the absorption band. The integral should have units of $\text{liters} \cdot \text{mole}^{-1} \cdot \text{cm}^{-2}$.

When evaluating theoretical and experimental values of σ be very careful to express all quantities in the correct units. To avoid confusion with units, transition intensities are usually reported in terms of the dimensionless quantity f , the oscillator strength:

$$f = \frac{2302 m_e c^2}{\pi N_e^2} \sigma = (4.32 \cdot 10^{-9} \text{ moles} \cdot \text{cm}^2 \cdot \text{liter}^{-1}) \sigma$$

For transitions out of the ground state, values of the oscillator strength range from approximately 1.0 for strong transitions to 0.0 for forbidden transitions.

PROCEDURE

The four dyes used in this experiment are

J	Dye	Empirical Formula
0	3,3'-Diethylthiacyanine Iodide	C ₁₉ H ₁₉ IN ₂ S ₂
1	3,3'-Diethylthiacarbocyanine Iodide	C ₂₁ H ₂₁ IN ₂ S ₂
2	3,3'-Diethylthiadibocyanine Iodide	C ₂₃ H ₂₃ IN ₂ S ₂
3	3,3'-Diethylthiatricarbocyanine Iodide	C ₂₅ H ₂₅ IN ₂ S ₂

1) Obtain stock solutions of these dyes containing about 2.5 mg of dye in 50.0 ml of methanol. Dilute 1.0 ml of each stock solution to 25.0 ml with methanol using pipettes and volumetric flasks. Note the color of each dye.

2) Run the ultraviolet and visible spectrum of each dye on a visible-ultraviolet spectrophotometer using 1 cm path length quartz cells. (Be very careful with these cells -- they cost \$60 each). Start at a long wavelength limit where there is no absorption, and record the spectrum to a short wavelength limit of 200 nm. (Several different instruments in the lab can be used for this experiment. An instruction sheet will be supplied in the lab for whichever instrument you are assigned to use.)

ANALYSIS

1) Sketch the UV/visible spectra of the four cyanine dyes on a single plot, faithfully reproducing the positions and relative heights of all absorption peaks. On this plot show the extent of the visible spectrum and where the observed color of each dye lies.

2) From the Beer-Lambert Law and the molar concentration of each dye solution determine the extinction coefficient at the wavelength of maximum absorption (λ_{peak}). Brooker, et al (reference 3) report the following extinction coefficients for the dyes:

J	λ_{peak} (nm)	ϵ (liters·mole ⁻¹ ·cm ⁻¹)
0	423.0	8.45 x 10 ⁴
1	557.5	1.48 x 10 ⁵
2	650.0	2.29 x 10 ⁵
3	758.0	2.46 x 10 ⁵

Compare your extinction coefficients to these.

Note: Since cyanine dyes are light sensitive and can decompose, you may find that your extinction coefficients differ significantly from those of Brooker, et al. If your extinction coefficients are lower than Brooker's, recalculate the concentration of your dye solution using Brooker's extinction coefficient and use these values of concentration in subsequent calculations.

3) Determine the experimental integrated absorption coefficient and oscillator strength for the strongest band in each dye spectrum. Since $\omega = 1/\lambda$

$$\int_{\omega_{\min}}^{\omega_{\max}} \epsilon \, d\omega = \int_{\lambda_{\min}}^{\lambda_{\max}} \epsilon / \lambda^2 \, d\lambda = 1/C \int_{\lambda_{\min}}^{\lambda_{\max}} A / \lambda^2 \, d\lambda$$

where the Beer-Lambert Law has been used to obtain the right-most expression and λ_{\max} (λ_{\min}) is the maximum (minimum) wavelength of the absorption band. This integral can be evaluated by picking twenty or more wavelength-absorbance ordered pairs from the strong band of the spectrum, plotting A/λ^2 versus λ , and integrating the resulting curve either numerically using Simpson's rule or by the weight/density method.

4) Calculate the box length for each dye using the formula

$$L = m \cdot \cos 30^\circ \cdot 0.140 \text{ nm} + 2 \cdot 0.251 \text{ nm}$$

where m is the number of bonds in the conjugated chain. In this expression the .140 nm (1.40 Angstrom) aromatic C-C bond length has been projected onto a straight line and some additional length has been added for the two benzene groups.

5) Find the theoretical wavelengths and absorption intensities for the two lowest particle in a box transitions for each dye. From σ , compute oscillator strengths. Compare theoretical and experimental absorption wavelengths and oscillator strengths.

When evaluating theoretical σ 's, the following mathematical relations might be helpful.

$$\sin\theta \sin\phi = 1/2 [\cos(\theta - \phi) - \cos(\theta + \phi)]$$

$$\int y \cos y dy = \cos y + y \sin y$$

6) Calculate the wavelengths at which the next particle in a box transition should occur in each dye spectrum and see if there are any bands you can ascribe to these transitions. Finally, identify bands in your spectra that are due to the benzene groups in the dye molecule. These peaks should appear at approximately the same wavelength in all of the spectra.

NO ERROR PROPOGATION IS NECESSARY!

DISCUSSION

- Adequacy of the particle in a box model for interpreting the visible spectra of conjugated diene molecules.
- Why are absorption bands are observed rather than absorption lines?
- How might the model be improved to better mimic the molecule?

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