Absorption Spectroscopy of Linear Polyenes

Larry Hartman, (CHEM 3723, 2016-10-13)
College of Math and Sciences, Augusta University

Abstract

Energies derived from optical absorption wavelengths of 3,3'-diethylthiadicarbocyanine iodide and 3,3'-diethylthiatricarbocyanine iodide were compared to Spartan software molecular models to determine validity of "particle-in-the-box" manual calculations with built in error factors. Peak absorption wavelengths for the two molecules were obtained via spectrometry. Several simplified Spartan models were prepared to obtain ΔE values between HOMO and LUMO orbitals. The compared energy values were 25% to 50% higher than manual calculations. "Particle-in-the-box" calculations appeared to give only rough approximations. Results are questionable due to molecule size limitations in the student version of Spartan software; therefore, consideration should be given to re-execution of the experiment with a more robust version.

Supervising Instructor: Eric Zuckerman
College of Math and Sciences, Augusta University

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Introduction

Using the "particle-in-the-box" model, the predicted wavelength formula as a function of the number of carbon atoms is:

$$\lambda_{absorp} = 63.7 * \frac{(C + 3 + \alpha)^2}{C + 4} \tag{1}$$

where:

$\lambda_{peak} =$ Absorption peak wavelength
$C =$ Number of carbon atoms
$\alpha =$ Arbitrary error factor, should resolve to value between 0 and 1

The derivation of the wavelength formula from quantum principles is provided in *Appendix B: Derivation of the Wavelength Formula*. The predicted wavelengths for 3,3'-diethylthiadicarbocyanine (P7) and 3,3'-diethylthiatricarbocyanine (P9) when $\alpha = 0$ are 579 nm and 706 nm respectively. Values of α are expected to fall between 0 and 1. The wavelength formula was rearranged to determine α from experimental data:

$$\alpha = \sqrt{\frac{\lambda_{peak} * (C + 4)}{63.7}} - C - 3 \tag{2}$$

The arbitrary error factor will differ for each polyene and for each change in spectroscopic parameter, i.e. a change in the concentration solvent. Once a wavelength is obtained from the spectrometer, its associated energy is easily calculated:

$$\Delta E = \frac{hc}{\lambda_{peak}} \tag{3}$$

where:

$\lambda_{peak} =$ Absorption peak wavelength
$h =$ Plank's constant (6.62608E-34)
$c =$ Speed of light (3.0E+8)

The spectrometer used must be capable of plotting wavelengths in the 600 to 900 nm range. Specific setup parameters depend upon manufacturer and model. Spartan models to determine energy values were executed from the following parameters:

- Algorithm: B3LYP/6-31G*
- cation
- no unpaired electrons

The "cation" setting was chosen because the target molecules are both ionic and only the cation portion was modeled.

Experimental Procedure

Four solutions for spectrometry were prepared using 25 mL volumetric flasks. The first two used approximately 0.13 mg (2.5 μ mol) of 3,3'-diethylthiadicarbocyanine (P7) in each with one flask using water as the solvent, and another using ethanol. The second two used approximately 0.16 mg (2.5 μ mol) of 3,3'-diethylthiatricarbocyanine (P9) in each with one flask using water as the solvent, and another using ethanol. Weight measurement was particularly difficult due to the small amount required and the tendency of the two chemicals to absorb water from the atmosphere. A small amount from each solution was used to fill four separate cuvettes. Subsequent spectroscopies were performed. The remainder of each solution was labeled and stored for future use.

Owing to the molecule size limit in the student version of Spartan software, trimmed down approximations were made of the P7 and P9 molecules. The following graphic depicts where the limiting approximations were made on the molecules:

FIGURE HERE.

Each student chose different R1 and R2 groups, executed the models for both P7 and P9 molecules with the attached R groups, then rebuilt/re-executed the molecules switching the positions of the R1 and R2 groups. It was expected that 4 energy values for each student would be returned via Spartan. However, one of the students used R groups that still exceeded the limitations of the software and executed four models with differing groups. The results for the various student models are found in *Appendix C: Student Spartan Results*

Observations and Results

Of the four solutions, the ethanol solvent dissolved both solutes more efficiently and yielded solutions with richer colors. The ethanol variants (as a result of the better dissolution) also yielded a better quantitative transfer of chemical to the volumetric flask. Use of ethanol as a solvent also yielded slightly higher peak wavelengths (*Table 1, P7 and P9 Peak Wavelengths*). The wavelengths returned from spectroscopy were much higher than predicted wavelengths. Since absorption peak wavelengths are directly proportional to the carbon chain length (eqs 16 and 22 in *Appendix B*), P9 exhibits a deeper blue hue.

Table 1: P7 and P9 Peak Wavelengths

Molecule	Solvent	Wavelength (nm)
P7	water	647
P7	ethanol	657
P9	water	751
P9	ethanol	762

Energies were calculated using eq. 3 (*Table 2, P7 and P9 Energies Derived from Peak Wavelength*). Energy values are discrete in nature, constrained by the length of the carbon chain, the number of π bonds, and Pauli exclusion principle (eqs 15 through 22 in *Appendix B*). The energy values obtained from spectroscopy differed from values returned by various Spartan models executed by students (*Appendix C*) from approximately 25% to 50% higher than values calculated from experimental data. Student F reported the lowest variant using the same model configuration as the other students. In another model with a different configuration, student F was able to return values with a lower difference from the experimental values. However, returning energy values from a model that are close to energy values calculated from experimental is not wholly sufficient to validate the accuracy of either set of calculations without knowing the basis for

the models and the assumptions made. The most that can be concluded from student F's approach is that more research should be completed to understand the factors involved.

Table 2: P7 and P9 Energies Derived from Peak Wavelength

Molecule	Solvent	Energy (eV)	Error value (α)
P7	water	1.918	0.570
P7	ethanol	1.888	0.651
P9	water	1.652	0.380
P9	ethanol	1.628	0.470

Error values (α) fell within the expected range between 0 and 1. The values of α are different for each chain length and solvent; however, table 2 data can be used to predict higher values for P5 and lower values for P11, assuming a linear model (on the surface it seems that an inversely proportional relationship exists between P7 and P9 results):

$$\begin{aligned}
\Delta\alpha &= m * \frac{1}{\Delta C} \\
m_{etoh} &= (0.470 - 0.651) * (9 - 7) \\
m_{etoh} &= -0.362 \\
b &= 0.470 - (-0.362 * 9) \\
b &= 3.728 \\
\alpha_{p3-etoh} &\approx -0.362 * (9 - 3) + 3.728 = 1.556
\end{aligned}$$

Similar calculations can be performed for other variants. Note that α prediction for P3 (Etoh) exceeds the expected upper limit of 1.

Conclusion

The Spartan molecular model that returned the best conformity is student F's model, with R groups Cl and OH. The energy values for student F's model range from 27% to 56% higher than the energies calculated from experimental results. All energy values returned by Spartan were higher than energy values calculated from experimental values. The error factor ranged from 0.380 to 0.651, apparently lowering as the carbon chain grows.

Appendix A: General Chemical Properties and Safety Data
(presented in alphabetical order)

3'3'-diethylthiadicarbocyanine (P7)

Source:
https://pubchem.ncbi.nlm.nih.gov/compound/5702697

* CAS: 71-23-8
* $C_{23}H_{23}IN_2S_2$
* 518.47659 g per mole
* Blue powder
* Toxic by mouth

3'3'-diethylthiatricarbocyanine (P9)

Source:
https://pubchem.ncbi.nlm.nih.gov/compound/9937256

* CAS: 3071-70-3
* $C_{25}H_{25}IN_2S_2$
* 544.51387 g per mole
* No safety data given

ethanol

Source:
https://pubchem.ncbi.nlm.nih.gov/compound/702

* CAS: 64-17-5
* C_2H_6
* 46.06844 g per mole
* Boiling Point: $78.29°$ C
* Density: $0.7893 g/cm^3$ $20°$ C
* Miscible in water
* Colorless liquid with fragrant odor
* Highly flammable liquid and vapor
* Irritation to skin, eyes, and nose
* May cause headaches and drowsiness
* May induce coughing

Appendix B: Derivation of the Wavelength Formula

Source: Laboratory Instructions

Momentum (p) and position (x) energy Hamiltonian function for particle moving on one-dimensional surface:

$$H(p,x) = \frac{1}{2}mv^2 + V(x) \tag{4}$$

$$= \frac{p^2}{2m} + V(x) \tag{5}$$

Momentum Hamiltonian function:

$$p \to \frac{h}{2\pi i}\frac{\partial}{\partial x} \tag{6}$$

Replace momentum variable in equation 5 with momentum Hamiltonian:

$$H(x) = -\left(\frac{h}{2\pi}\right)^2 \frac{1}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{7}$$

Multiply by wave function Ψ to find time independent eigenvalue, E. This is the energy of the particle:

$$H(x)\Psi = -\left(\frac{h}{2\pi}\right)^2 \frac{1}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi = E\Psi \tag{8}$$

Solution for the quantum mechanical particle with $V(x) = 0$:

$$\Psi = \sin\left[\frac{2\pi}{\lambda}(x - x_0)\right] \tag{9}$$

$$E = \frac{(h/\lambda)^2}{2m} \tag{10}$$

Approximations for potential $V(x)$ to use as boundary conditions:

$$V(x) = 0, \qquad 0 < x < L \tag{11}$$

$$V(x) = \infty \tag{12}$$

Set boundary conditions in the solution to find corresponding wave function for electron. The quantum electron can only take on discrete energy levels:

$$\Psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \tag{13}$$

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{14}$$

Set length L as related to polyene chain length, C (an integer), and quantum number n. The variable N is the number of π electrons in the chain. The variable α is an error factor because the boundaries can not be exactly ascertained. The variable l is the C$-$C bond length:

$$N = C + 3 \tag{15}$$

$$L = (C + 3 + \alpha)l \tag{16}$$

N is related to n, via optical transition from highest ocupied molecular orbit to lowest occupied molecular orbit and Pauli exclusion principle. This implies an energy transition $\Delta E.$:

$$n_{homo} = \frac{N}{2} \tag{17}$$

$$n_{lumo} = \frac{N}{2} + 1 \tag{18}$$

$$n_{homo}^2 = \frac{N^2}{4} \tag{19}$$

$$n_{lumo}^2 = \frac{N^2}{4} + N + 1 \tag{20}$$

$$n_{lumo}^2 - n_{homo}^2 = N + 1 \tag{21}$$

$$\Delta E = \frac{h^2}{8mL^2}(N+1) \tag{22}$$

Energy is also related to the product of its momentum h/λ and the speed of light, c. Solve for wavelength, λ:

$$E = \frac{hc}{\lambda} \tag{23}$$

$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2}(N+1) \tag{24}$$

$$\lambda = \frac{8mc}{h}\frac{L^2}{N+1} \tag{25}$$

where:

$$m_e = 9.110 * 10^{-31} kg \tag{26}$$

$$c = 2.998 * 10^8 m/s \tag{27}$$

$$h = 6.626 * 10^{-34} J * s \tag{28}$$

The resulting equation, taking into account defined constants, and substitution of N and L from eqs 15 and 16:

$$\lambda_{nm} = 63.7\frac{(C+3+\alpha)^2}{C+4} \tag{29}$$

Appendix C: Student Spartan Results
Source: Student Notes

Student	R1	R2	P7 eV	P7 eV (R-switched)	P9 eV	P9 eV (R-switched)
A	CH_3	Cl	2.84	2.81	2.42	7.22
B	CH_3	SH	3.3	2.9	2.7	2.5
C	NH_2	F	3.1	2.8	2.4	2.5
D	OH	CH_3	2.8	3.1	2.6	2.8
E	F	H	2.9	3.2	2.4	2.6
F	Cl	OH	2.8	2.7	2.4	2.4
F	Cl	OH	2.3	2.7	2.1	2.2
G	CH_3	NH_2	3.0	2.9	–	–
G	CH_3	H	–	–	2.5	–
G	NH_2	H	–	–	2.3	–

Student F ran models with two settings. The first was with "equilibrium geometry" as the other students. The second with "energy." Student G had difficulties with building models within the size constraints of the student edition of Spartan.

Author Information

Larry Hartman: lahartman@augusta.edu