Analysis of the applicability of the particle-in-a-box model to conjugated systems of cyanine dyes

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Chemistry Department, Gustavus Adolphus College, 800 W. College, St. Peter, Minnesota 56082

Submitted: February 27, 2007

Abstract

The particle-in-a-box model was used to analyze the conjugated bonds and π electrons of several cyanine dyes. Analysis by UV-Vis spectrophotometry led to calculation of λ_{max} values for each dye, and values were compared to electronic spectra generated with the HyperChem program. The effective box length, *a*, was determined for six cyanine dyes and compared to the expected geometric box length, and the lengths of C-C bonds in each conjugated system was analyzed and compared to tabulated values. The applicability of the particle-in-a-box model to extract electronic and structural information is discussed and was deemed less than ideal for usage with cyanine dyes to predict spectral properties.

Introduction

Due to their extremely photosensitive nature, cyanine dyes have been studied for a variety of purposes. Cyanine dyes, such as those shown in Figure 1, are have been studied for their quenching properties of singlet oxygen,[1] and the large optical nonlinearity of the compounds has been utilized in organic and organometallic synthesis.[2] Such dyes are known to create aggregates in solution,[3] and such aggregates have significant effects during spectroscopic study of the dyes.
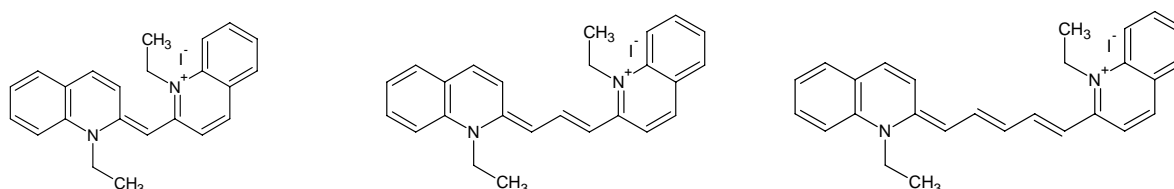

Figure 1: Cyanine dyes. From left to right: 1,1'-diethyl-2,2'-cyanine iodide, 1,1'-diethyl-2,2'-carbocyanine iodide, and 1,1'-diethyl-2,2'-dicarbocyanine iodide.

Also known for their cytotoxic effects, the usage of cyanine compounds as potential anticancer agents in the pharmaceutical sector has recently been explored at length. Photodynamic therapy (PDT) is one such endeavor that uses the cytotoxic and photosensitive

nature of cyanine compounds to effectively battle the growth of cancerous cells in an organism.[4]

The use of this therapy depends on the optical and spectroscopic properties of the cyanine

25   compounds: in order to determine such properties, several model systems can be applied.

      Cyanine dyes contain large conjugated systems, and these systems must be quantified to

determine, primarily, spectral properties of the compounds. A particle-in-a-box model, as was

used in this research, is a quantum chemical model that restricts conjugated electron movement

to the confines of the molecule itself, modeling the length of the conjugated chain as the sides of

30   a rigid box. Developed from the Schrödinger equation, this model allows for approximation and

basic representation of the conjugated system and permits scientists to predict spectral properties

of the cyanine dyes, as was endeavored in the research presented. In this work, solutions of three

cyanine dyes were prepared and studied via spectroscopy. The maximum wavelengths obtained

from the spectra and from the literature were used to calculate the effective box length, *a*, of the

35   particle-in-a-box model. The data was then compared to expected values, and errors were

discussed at length.

Experimental[5]

      Preparation of cyanine dyes. Cyanine dye dilutions were prepared from provided stock

solutions. The stock solutions of 1,1'-diethyl-2,2'-cyanine iodide (**1**), 1,1'-diethyl-2,2'-

40   carbocyanine iodide (**2**), and 1,1'-diethyl-2,2'-dicarbocyanine iodide (**3**) were stored in

volumetric flasks under cover of aluminum foil. Dilutions of **1** [0.003 mM], **2** [0.00385 mM],

and **3** [0.00352 mM] were prepared with methanol [neat] and stored in volumetric flasks with

limited exposure to natural laboratory light.

      Collection of spectral data. Using the OceanOptics UV-Visible spectrophotometer and

45   its companion software OOIChem [Ocean Optics, Inc.], absorbance spectra were collected from

450 nm to 800 nm. Each dilution was referenced against methanol in a plastic cuvette, and use

of OOIChem software led to the experimental determination of λ_{max} for each dye.

HyperChem analysis. Compounds **1**, **2**, and **3** were drawn and analyzed using the

HyperChem software program [Hypercube, Inc.]. The electronic spectrum for each molecule

50   was calculated with a semi-empirical CI method and PM3 theory and used to determine the

theoretical λ_{max} for each molecule. Molecular orbitals were calculated and analyzed using a

single-point energy calculation using the HyperChem program.

Determination of experimental parameters. The effective box length, *a*, was calculated

from the collected data via Equation 1

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$$a = \left(\frac{h\lambda(N+1)}{8mc} \right)^{\frac{1}{2}}$$

where N represents the number of π electrons in the system; all other variables represent their

commonly known constant values.

Results

A UV-Vis absorbance spectrum

60   (Fig. 2) was obtained and used to calculate

experimental λ_{max} values for each of the

studied cyanine dyes. Compound **1** was

found to have a λ_{max} of 530.55 nm, **2** had a

λ_{max} of 611.88 nm, and **3** had a computed

65   λ_{max} value of 713.02 nm. Using the

HyperChem-generated electronic

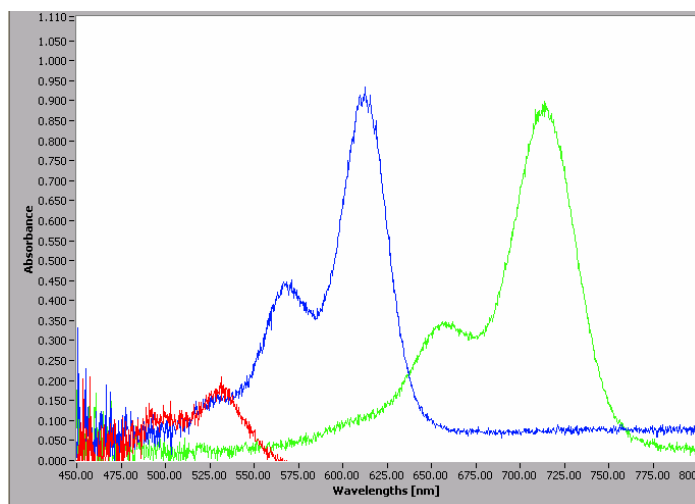spectrum, the calculated λ_{max} value of **1**

Figure 1. UV-Vis absorbance spectrum for Dyes 1-3, collected with the Oceans Optics UV-Vis spectrophotometer and the OOIChem software program. The λ_{max} value for Dye 1 (in red) is 530.55 nm, Dye 2 (in blue) is 611.88 nm, and Dye 3 (in green) is 713.02 nm.

was determined to be 467.63 nm (Fig. 2a). The theoretical λ_{max} values for **2** and **3** were 578.33

nm (Fig. 2b) and 694.78 nm (Fig. 2c), respectively.
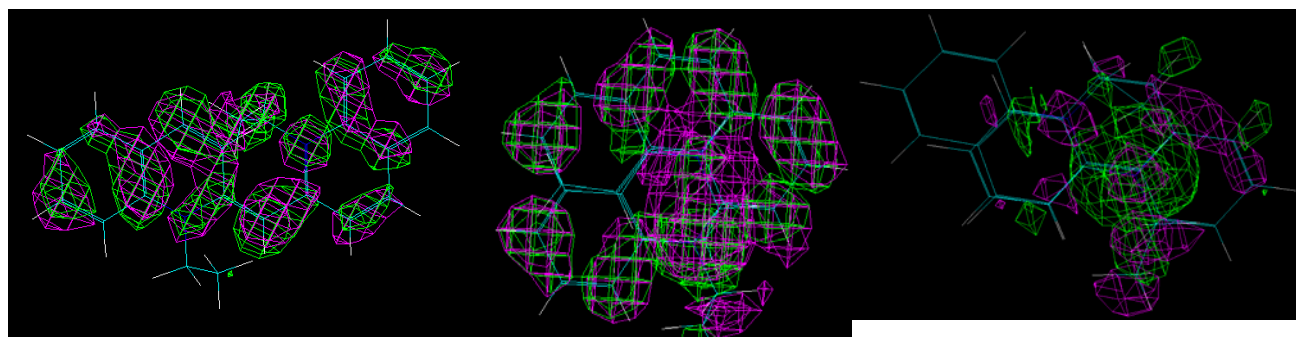

Figure 2. HyperChem molecular orbital representations. The green and purple orbitals represent the electron density of the molecule in its HOMO state. The wavelength calculated with the HyperChem software was 467.63 nm for compound 1 (2a). The λ_{max} values for compounds 2 and 3 were 578.33 nm and 694.78 nm, respectively, and are found in 2b and 2c.

70   The effective box length, *a*, was determined with Equation 1 (Table 1). Due to the

similar nature of compounds **1-3** and **4-6**, comparisons were made and conclusions drawn within

the two groups. Generally, the values for *a* and λ_{max} increased as more π electrons were

introduced to the respective systems. The calculated difference between geometric box length

and *a* decreased as π electrons were added to compounds **1-3**, but compounds **4-6** did not

75   demonstrate similar behavior: as values of N increased from 10 to 12 π electrons, the difference

decreased, but the addition of two π electrons in the system in **6** caused an over 50% increase in

the calculated difference.

Table 1. Compilation of collected data in calculation of effective bond length, *a*. The λ_{max} values for compounds 1-3 were determined via spectroscopy; λ_{max} values for compounds 4-6 were taken from the literature. The number of π electrons, N, and the number of bonds in the conjugated system, *q*, were determined from the compounds themselves. The experimental box length, *a*, was determined with Equation 1. The difference between experimental box length and geometric box length, *qb*, was determined, using a value of 0.139 nm for *b*, a uniform spacing of the conjugated bonds.

Code	Compound	N	λ_{max} (nm)	*a* (pm)	*q*	*(a-qb)* (pm)
1	1,1'-diethyl-2,2'-cyanine iodide	6	530.55	1067	4	511.1
2	1,1'-diethyl-2,2'-carbocyanine iodide	8	611.88	1299	6	465.4
3	1,1'-diethyl-2,2'-dicarbocyanine iodide	10	713.02	1551	8	438.8
4	1,1'-diethyl-4,4'-cyanine iodide	10	593	1414	8	302.3
5	1,1'-diethyl-4,4'-carbocyanine iodide	12	704	1675	10	285.2
6	1,1'-diethyl-4,4'-dicarbocyanine iodide	14	932	2070	12	402.4

In order to experimentally calculate the C-C bond length and the size of the endgroups, a

plot of a, experimental box length, and N, the number of C atoms in the conjugated system, was

80   constructed. For compounds **1-3**, the C-C bond length was calculated to be 121 pm, and the

effective size of the endgroups was determined to be 338 pm (Fig. 3). The chi-square value for

the regression line of the plot constructed for **1-3** was 6.67×10^{-23}. For compounds **4-6**, the C-C

bond length increased to 164 pm, but the effective size of the endgroups decreased to 248 pm

(Fig. 4). The chi-square value of the regression line of the plot of **4-6**, 2.99×10^{-21}, was larger
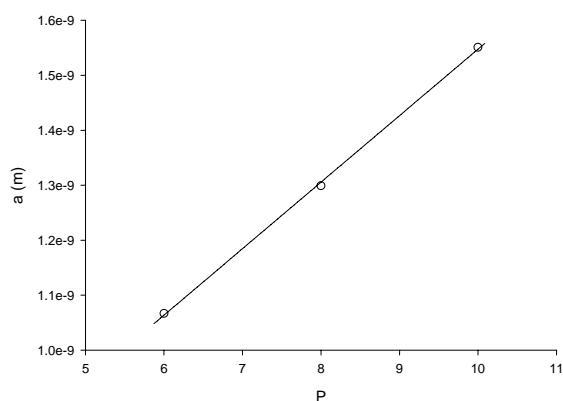
85   than that of the regression line for **1-3**.

Figure 3. Plot of box length, a, versus the number of C atoms in the conjugated chain, P, for Compounds 1-3**. The regression line was fit to the equation** $a = PL + E$**. The value of L, representing the C-C bond length, was determined to be 121 pm. The value of E, the effective size of the end group, was determined to be 338 pm. The chi-square for the regression fit was 6.67×10^{-23}.**
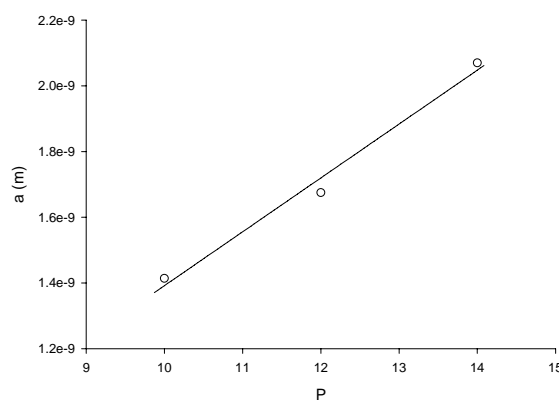
Figure 4. Plot of box length, a, versus the number of C atoms in the conjugated chain, P, for Compounds 4-6**. The regression line was fit to the equation** $a = PL + E$**. The value of L, representing the C-C bond length, was determined to be 164 pm. The value of E, the effective size of the end group, was determined to be -248 pm. The chi-square for the regression fit was 2.99×10^{-21}.**

Discussion

In order to evaluate the applicability of the particle-in-a-box model to study the spectra of

cyanine dyes, various experimental procedures were investigated and analyzed. The spectrum

90   obtained from the spectrophotometer revealed well-defined peaks for **2** and **3**, but a poorly

resolved peak for **1**. Experimental error is responsible for the lack of resolution – the dilution concentration of **1** was calculated incorrectly. The poor resolution is also due to the λ_{max} value of **1** (530.55 nm): the spectrophotometer had an abundance of noise at wavelengths up to 500 nm, so the noise overlapped much of the signal generated. The spectrum also revealed two distinct

95   peaks for compounds **1-3**, but only the value of the second, greater peak was recorded. The first hump was regarded as an indicator for the presence of the dye, but could not be contributed to methanol, as a background scan was taken. The hump seemed a bit too consistent to attribute to an impurity of the dyes.

The collected electronic spectra were quite useful in the comparison of experimental and

100   theoretically predicted λ_{max} values. The experimentally determined values were considerably larger than the predicted values, but the difference decreased as the λ_{max} values increased (i.e., there was a 53-nm difference for **1**, but only an 18-nm decrease for **3**.) The λ_{max} values of the compounds accounts for the great disparities: more background noise is present at lower wavelengths, so resolution is greater and determination of λ_{max} more precise at greater

105   wavelengths. From Figure 2, the theoretically predicted values lie closer to the valley than they do either peak. This may lead one to contemplate some sort of spectral splitting in which the spectrophotometer measures absorbance on either side of the predicted λ_{max}.

The experimental or provided λ_{max} values were used to determine the effective box length, *a*, determined to increase among **1-3** and **4-6** as π electrons were introduced into the

110   system. Such an increase is predicted, because an introduction of π electrons into a conjugated system indicates the introduction of C-C and C=C bonds, increasing the distance between the endgroups. The comparison of *a* with the geometric box length, *qb*, led to a positive difference for all studied compounds. The geometric box length is determined using an average value for

all the C-C or C=C bonds in the conjugated system. Compounds **1-3** demonstrated a decrease in

115   the difference as more π electrons were introduced, as expected. Again, as more π electrons are

introduced into the system, more C-C and C=C bonds must exist, and if more of these bonds

exist, they will be increasingly likely to demonstrate average bond length character. For **4-6**, a

similar trend was not determined. For **4** and **5**, an increase in C-C and C=C bonds did lead to a

decrease in the (a-qb) difference, but **6** did not, in fact demonstrating an increase in the

120   difference. The geometric structure of **6** is likely the determining factor to the increased

difference. The conjugated system has 12 π electrons, and such an abundance causes the

molecule to maintain more of the C-C character in its C-C bonds and more C=C character in its

C=C bonds; that is, there is less "averaging out" experienced by the bonds, making the geometric

box approximation less applicable to such a large conjugated system.

125   The experimentally determined C-C bond lengths were 121 pm and 164 pm for **1-3** and

4-6, respectively. The CRC Handbook lists a C-C bond in a conjugated system to be 145.5 pm

and a C-C bond in an alkane to be 151 pm[6]. Using this data, it is predicted that **1-3** exhibit more

conjugated character for C-C bonds, and **4-6** demonstrate more single-bond character in the

present C-C bonds. The effective size of the endgroups varied for the two groups of compounds

130   as well. The effective size of the endgroup of **1-3** was 338 pm, and for **4-6** it was 248 pm. The

comparison of the molecular structures of the endgroups reveals the difference. In compounds **1-3**, each endgroup is composed of eight carbon atoms in a bicyclic aromatic ring structure, and in

compounds **4-6**, each endgroup consists of just one aromatic ring. Spatially, as well as

electronically, the endgroups of **1-3** are larger than the endgroups for **4-6**, so it is expected and

135   demonstrated that the endgroups have different effective sizes. Additionally, differences are

found in the generated plots of effective box length, a, and the number of C atoms in the

conjugated system. The regression lines utilized to determine the effective size of the endgroups
and the length of the C-C bond had different values for **1-3** and **4-6**. The regression line,
generated with SigmaPlot, for **1-3** was 100 times more precise than the regression line generated

140   for **4-6**. Surprisingly, the line generated from experimentally derived quantities was more
accurate than the line generated from the values found in literature.[5]

From the experimental evidence and analysis, one would not likely find the particle-in-a-
box model to be an appropriate one to use to describe the spectra of cyanine dyes. The
difference between the calculated box length and the geometric box length was 511.1 nm for **1**, a

145   value that represents nearly four conjugated C-C bonds in a molecule. Also, the calculated bond
lengths for C-C bonds in each compound was far from the reported value, indicating that the
bond lengths determined from the particle-in-a-box approximation are not appropriate for
utilization in cyanine dye spectral analysis. The model used in this endeavor did support
conclusions drawn by other scientists using more appropriate and accurate approximations and

150   techniques, but the errors and differences determined in analysis would not make the selected
model system viable for further experimentation.

Conclusion

The particle-in-a-box model was deemed less than ideal for its projected applicability for
extraction of spectral information from cyanine dyes. Large differences existed between the

155   experimental, calculated effective box length and the geometric box length, indicating that the
experimental method utilized in this experimentation was inaccurate. Experimental and
calculation errors existed, but attempts were made to minimize these effects. For further
research, a model other than the quantum mechanical particle-in-a-box should be utilized for
more accurate and reliable results.

160   **References**

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