**1** / VOL. 2, NO. 4
THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
10.1007/s00897970135a

Computers in Chemistry

# Evaluating Experiment with Computation in Physical Chemistry: The Particle-In-A-Box Model with Cyanine Dyes

**JEFFREY R. BOCARSLY*** AND **CARL W. DAVID***
Department of Chemistry
University of Connecticut
Storrs, CT 06269
bocarsly@nucleus.chem.uconn.edu

The results from a classic experiment in the undergraduate physical chemistry laboratory, the particle-in-a-box model for spectroscopic transitions of conjugated dyes, is compared to computational results obtained using a molecular mechanics structural approach and the extended Hückel molecular orbital picture. The goal of this exercise is to help students to think critically about their experimental data and to use comparisons of mathematical and computational models to try to understand departures of an experiment from expectations.

*Students can learn the power of independent approaches to a given problem as a tool for the advancement of scientific knowledge.*

---

## Introduction

A classic experiment in the undergraduate physical chemistry laboratory is the elucidation of conjugated dye spectroscopy using the particle-in-a-box model for electrons, where the "box" in which the electron is confined is defined by the extent of conjugation [1]. These conjugated systems may be

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

examined on a more sophisticated level using molecular mechanics calculations and the extended Hückel molecular orbital picture. In order to induce students to think critically about the quality of their data and the use of mathematical analyses of data, we have employed a computational chemistry approach to explaining experimental deviations from expectations.

## Theory

The particle-in-a-box experimental exercise begins with measuring the energies of maximum visible absorbance ($\lambda_{\text{max}}$) for a series of commercially available dyes. The experimental absorbance energies are analyzed using a one-dimensional particle-in-a-box model for the $\pi$ systems of the dyes, leading to a calculation of the theoretical absorbance wavelength for these systems.

The determination of the theoretical absorbance wavelength is as follows. The one dimensional particle-in-a-box kinetic energy Hamiltonian is:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{1}$$

where $x$ is the position of the particle in the one-dimensional box and m is the mass of the particle. The function that satisfies the operator relation $H\Psi = E\Psi$ turns out to be:

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

when the energy $E$ is:

$$E = \frac{n^2h^2}{8mL^2} \tag{3}$$

where the quantum number n is 1, 2, 3, ... and $L$ is the box length. The electronic absorptions for this system are due to spectral transitions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). A system of $N$ $\pi$ electrons will have $N$ energy levels, and half of these levels will be filled, since each orbital can accommodate two electrons. Therefore, the quantum numbers $n_{\text{HOMO}} = N/2$ and $n_{\text{LUMO}} = (N/2)+1$. The energies of these levels depend on

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

*n* (eq 3), and the transition energy will depend on the difference in energy between the LUMO and the HOMO:

$$\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$$

$$= \frac{h^2}{8mL^2}\left[\frac{N}{2}+1\right]^2 - \frac{h^2}{8mL^2}\left(\frac{N}{2}\right)^2 = \frac{h^2}{8mL^2}\left[\frac{N^2}{4}+N+1-\frac{N^2}{4}\right] = \frac{h^2}{8mL^2}(N+1) \tag{4}$$

Since the transition energy and the absorption wavelength are related by $\Delta E = \frac{hc}{\lambda}$, the wavelength of absorbance is related to the box length *L* and *N*:

$$\lambda = \frac{hc}{\Delta E} = \frac{8mc}{h}\frac{(L)^2}{N+1} \tag{5}$$

where $\lambda$ is the predicted absorbance maximum (in meters).

Equation 5 reflects one of the key assumptions of the particle-in-a-box model, namely that the shape of the potential well (i.e., the box) is that of a square well potential. Conjugated dye molecules, however, may depart from this assumption, due, for example, to the polarizability of the end groups of the conjugated chain (which has the effect of changing the effective length of the conjugated box by causing the potential walls to slope more gently than in a square well potential). In order to account for departures from the ideal square potential box, we can define a modified box length $L' = L + \alpha$:

$$\lambda = \frac{8mc}{h}\frac{(L+\alpha)^2}{N+1} = \frac{8mc}{h}\frac{(L')^2}{N+1} \tag{6a}$$

where the empirical constant $\alpha$ accounts for departures from the ideal square box potential. Generally, $\alpha$ is found in the range $-1 < \alpha < 1$; the experimental value of $\alpha$ for the cyanine dyes used in this experiment is ~1 Å. Equation 6a can be rearranged by solving for the spectroscopic box length:

$$L' = L + \alpha = \sqrt{\frac{\lambda h(N+1)}{8mc}} \tag{6b}$$

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

showing that when the box length is calculated from spectroscopic data, the value obtained for the spectroscopic box length is intrinsically corrected by $\alpha$.

## Experimental

We have performed the spectroscopic experiment using 1,1'-diethyl-2,2'-cyanine dyes (I, 1,1-diethyl-2,2'-cyanine iodide; II, 1,1'-diethyl-2,2'-carbocyanine iodide; III, 1,1'-diethyl-2,2'-dicarbocyanine iodide), although other conjugated dyes should also be appropriate.

### *Molecular mechanics calculations*

While a full discussion of molecular mechanics is beyond the scope of this article, a few general comments about the method are appropriate. In the interests of computational frugality, molecular mechanics does not use physical first principles (i.e., quantum mechanics) to calculate molecular structure. Rather, it uses computationally less-expensive relations from classical mechanics, such as Hooke's law and Lennard–Jones potentials to model the ground-state electronic interactions between atoms in molecules.

The computational strategy is as follows: assign an algebraic relation from classical mechanics to each bond-stretch, angle-bend, dihedral angle rotation, Van der Waals interaction and electrostatic interaction in a molecule. The sum of these terms forms an $n$-dimensional potential energy surface, where $n$ is the number of independent geometric variables for the molecule. Each point on the surface represents a unique combination of bond lengths, angles, and interatomic distances that describes a possible geometry for the molecule. The lowest point on this surface (the global minimum) represents that combination of bond lengths and angles corresponding to the ground-electronic-state structure of the molecule. A number of extensive descriptions of the method are available [2, 3]. We have used the MacroModel suite produced at Columbia University by W. Clark Still and co-workers [4], using the MM2* force field for molecular mechanics minimizations. No counterions were included in the computations and no solvent models were included. Starting with a minimized structure, a Monte Carlo search for the global minimum energy structure (1000 steps) was conducted for each dye structure. Only the lowest energy structures found were considered. The conjugated box for these structures is defined as the total

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

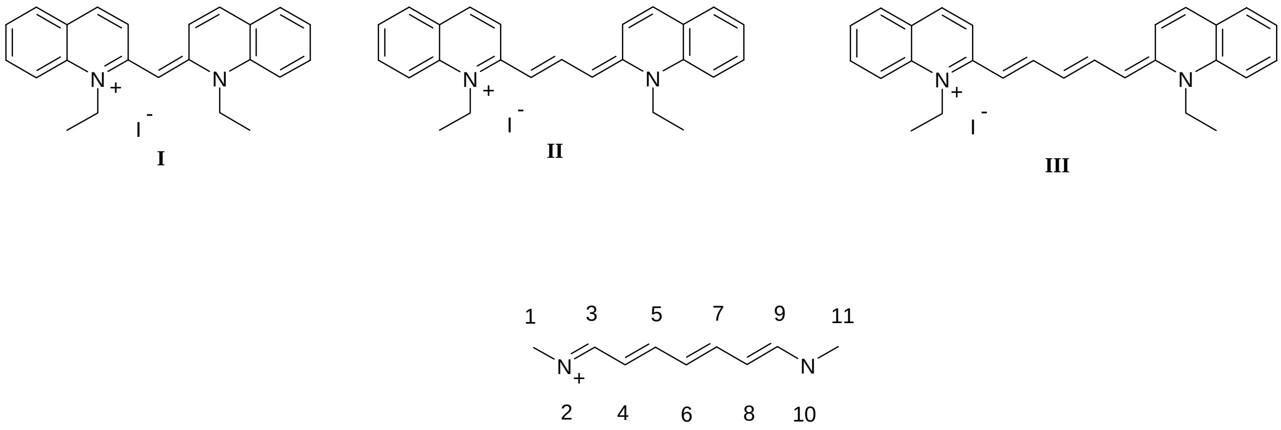

**FIGURE 1**. DYES I, II, AND III WITH THE NUMBERING SCHEME FOR THE CONJUGATED BOX.

bond length of the chain between nitrogen atoms of the dyes plus one bond distance on each side, as in previous work on this model [5].

### *Hückel calculations*

HyperChem 4.5 (HyperCube, Inc.) was used for extended Hückel calculations [6]. Computations were performed on a Silicon Graphics Indy workstation equipped with 64 MB RAM. These computations can also be run over a network using an X-Windows emulator from a Macintosh or a DOS system, or from Linux-equipped DOS machines.

## Results and Discussion

### *Particle-in-a-box model*

The dyes used in this experiment are shown in Figure 1. Spectroscopic data are presented in Table 1 for the experimental $\lambda_{\max}$ values for dyes I–III, with the $L'$ values calculated using equation 6. As shown in Table 1, the conjugated-box lengths increase with increasing wavelength, consistent with equation 5 ($\lambda$ proportional to $L^2$). The box lengths calculated with MM2* molecular mechanics diverge from the spectroscopic $L$ values, and are consistently shorter. Even when the molecular mechanics box lengths are corrected by $\alpha$ for the polarizability of the dye end groups, there is still a deviation between the geometric and the spectroscopic model.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

**TABLE 1.** Comparison of Spectroscopic and MacroModel (MM2*) structural calculations of cyanine dye box lengths.

| dye | $N^a$ | experimental $\lambda_{max}$ (nm) | spectroscopic box length $L'$ (Å) (eq 6b) | molecular mechanics calculated box length, $L^b$(Å) | corrected molecular mechanics calculated length, $L + \alpha$, ($\alpha \sim 1$Å) |
|---|---|---|---|---|---|
| I | 6 | 524 | 10.5 | 8.4 | 9.4 |
| II | 8 | 614 | 12.9 | 11.2 | 12.2 |
| III | 10 | 707 | 15.4 | 14.0 | 15.0 |

[a] $N$ = C + 3, where C is the number of carbon atoms between the nitrogen atoms in the conjugated chain.

[b] Based on low-energy structure from a Monte Carlo search of 1000 structures. "Box length" is defined as the sum of the bond lengths of the conjugated chain between nitrogen atoms of the dyes plus one bond distance on each side.

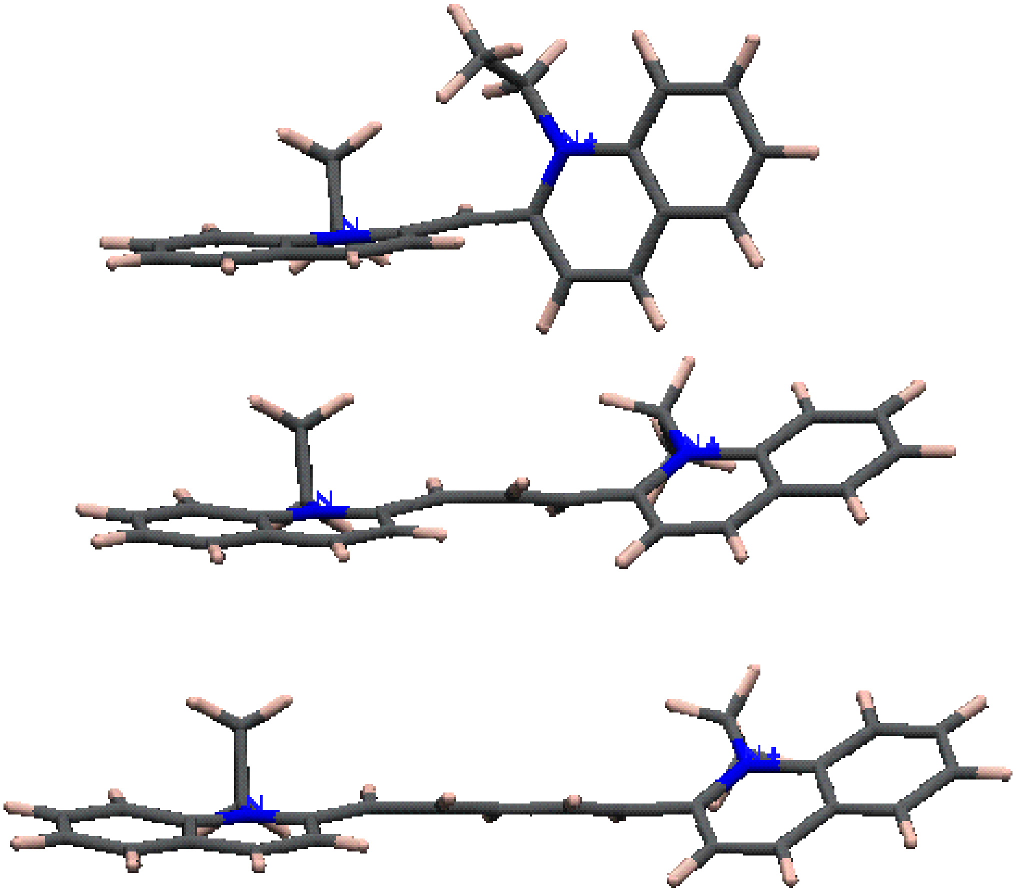

**FIGURE 2**. MOLECULAR-MECHANICS-MINIMIZED STRUCTURES OF DYES I, II, AND III.

THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

**TABLE 2.** Dihedral angles of Conjugated-Box Carbons (Absolute Value) in Dyes I–III From Molecular Mechanics-Minimized Structures.

| dihedral number | Conjugated “box” carbons forming dihedral angles | I | II | III |
|---|---|---|---|---|
| | | Dihedral andgles | | |
| 1 | 1-2-3-4 | 178.76 | 177.66 | 177.67 |
| 2 | 2-3-4-5 | 99.544 | 135.91 | 135.32 |
| 3 | 3-4-5-6 | 179.28 | 177.52 | 179.85 |
| 4 | 4-5-6-7 | 172.45 | 161.00 | 179.78 |
| 5 | 5-6-7-8 | | 177.37 | 177.64 |
| 6 | 6-7-8-9 | | 172.20 | 162.32 |
| 7 | 7-8-9-10 | | | 177.52 |
| 8 | 8-9-10-11 | | | 172.15 |
| | average absolute values of angles | 157.5 | 166.9 | 170.3 |
| | RMS deviation from plane of C | 0.254 Å | 0.244 Å | 0.217 Å |

It is noteworthy that agreement between the molecular mechanics structural model and the spectroscopic model increases with increasing conjugated length. Examination of the calculated dye structures provides insight into the reasons that the spectroscopic model departs from the computed geometry. The molecular-mechanics-minimized structures show that the dyes differ in their overall molecular conformation (Figure 2).

The short conjugated chain of I is forced to be nonplanar to a significant extent, relative to the longer chains of II and III, due to steric interactions of the aromatic end groups. This nonplanarity can be crudely measured by examining the dihedral angles along the conjugated box of each dye, or by considering the deviation from the mean plane of the atoms in the conjugated box (Table 2). The average dihedral angle of dye I is ~158°, indicating a large deviation from planarity, while the average angles for II and III are substantially closer to 180°. The rms deviations from the plane follow a similar trend. This suggests that systems of greater conjugated length more closely approach planarity. This effect can be seen in a plot (Figure 3) of dihedral angle vs. dihedral angle number, using the atom numbering scheme in Figure 1 and the data in Table 2.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

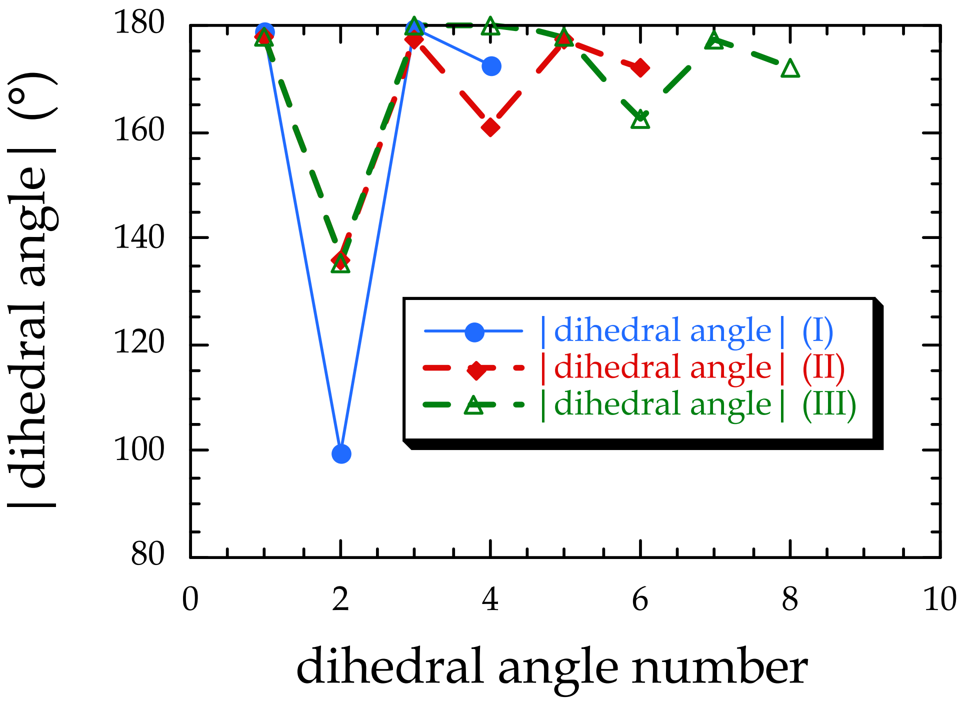

**FIGURE 3**. PLOT OF THE ABSOLUTE VALUE OF THE DIHEDRAL ANGLE VS. THE DIHEDRAL ANGLE NUMBER FOR DYES I, II, AND III.

---

From Figure 3, it is clear that each dye contains a highly strained dihedral angle at the beginning of each chain (dihedral no. 2). In each case, this angle involves the terminal positively charged nitrogen of the dye (the molecular mechanics calculation used does not assume charge delocalization). Each conjugated chain also has a second site of lesser nonplanarity, located close to the opposite end of the conjugated box, one bond farther in. In dye I, the shortest dye, these two sites of nonplanarity coincide, as indicated by the large single deviation in this conjugated chain. This implies that the nonplanarity is caused by steric interactions between the end groups of the dyes and the atoms near the ends of the conjugated chains. Since all dyes have roughly the same degrees of nonplanarity at their termini, the increased planarity of longer conjugated dyes is due to the increase in the intervening chain length, which is not sterically affected by the end groups. Since it is the planar geometry of these systems that allows *p*-orbital overlap to form conjugated π systems, nonplanarity suggests a disruption of the π system of the dye.

This nonplanarity should result in an effective shortening of the conjugated length of the box. However, the polarizability of the dye end groups creates an effective

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

**TABLE 3.** Extended Hückel HOMO an LUMO energies and predicted $\lambda_{max}$ for dyes I–III.

| dye | HOMO energy ($cm^{-1}$) | LUMO energy ($cm^{-1}$) | Hückel $\lambda_{max}$ | Hückel box lengths (Å)[a] |
|---|---|---|---|---|
| I | 89866 | 79447 | 960 | 14.3 |
| II | 90329 | 80117 | 980 | 16.4 |
| III | 89987 | 80519 | 1056 | 18.8 |

[a] equation 5.

lengthening of the conjugated box. Both of these factors are reflected in the empirical parameter $\alpha$. Since $\alpha > 0$, end-group polarizability more than compensates for the effects of nonplanarity in dyes I–III. When the MM2* $L$ is corrected by $\alpha$, the agreement between the molecular mechanics structural model and the particle-in-a-box spectroscopic model increases substantially (Table 1). We note that each of the structures depicted in Figures 2 and 3 has subtle differences in the degrees of nonplanarity of the conjugated chain. This means, of course, that the correction factor $\alpha$ should be specific to the structure of each molecule. A single value for $\alpha$ is used for each class of dye on the assumption that the variation in $\alpha$ for a class of dyes of analogous structure is small compared to the differences in $\alpha$ for dyes of divergent structure (e.g., dyes with different end groups).

### *Hückel calculation*

In order to explore further the relationship between molecular geometry and electronic structure, an extended Hückel calculation [6] was performed on the minimized structures. The difference in energies of the HOMO and LUMO for each of the dyes can be used to predict the spectroscopic $\lambda_{max}$ values. Table 3 shows the calculated Hückel energies for the HOMO and the LUMO of each dye, with the energy difference and the resulting conjugated box length. As can be seen from Table 3, the trend of increasing spectroscopic box length with increasing conjugation found in the experimental data (Table 1) is reproduced in the Hückel calculation. However, the calculation overestimates the transition energies of the dyes, leading to overestimates of box length. The real value of the Hückel calculation for the problem posed here is in the geometric characteristics of the Hückel LUMOs for the three dyes, shown in

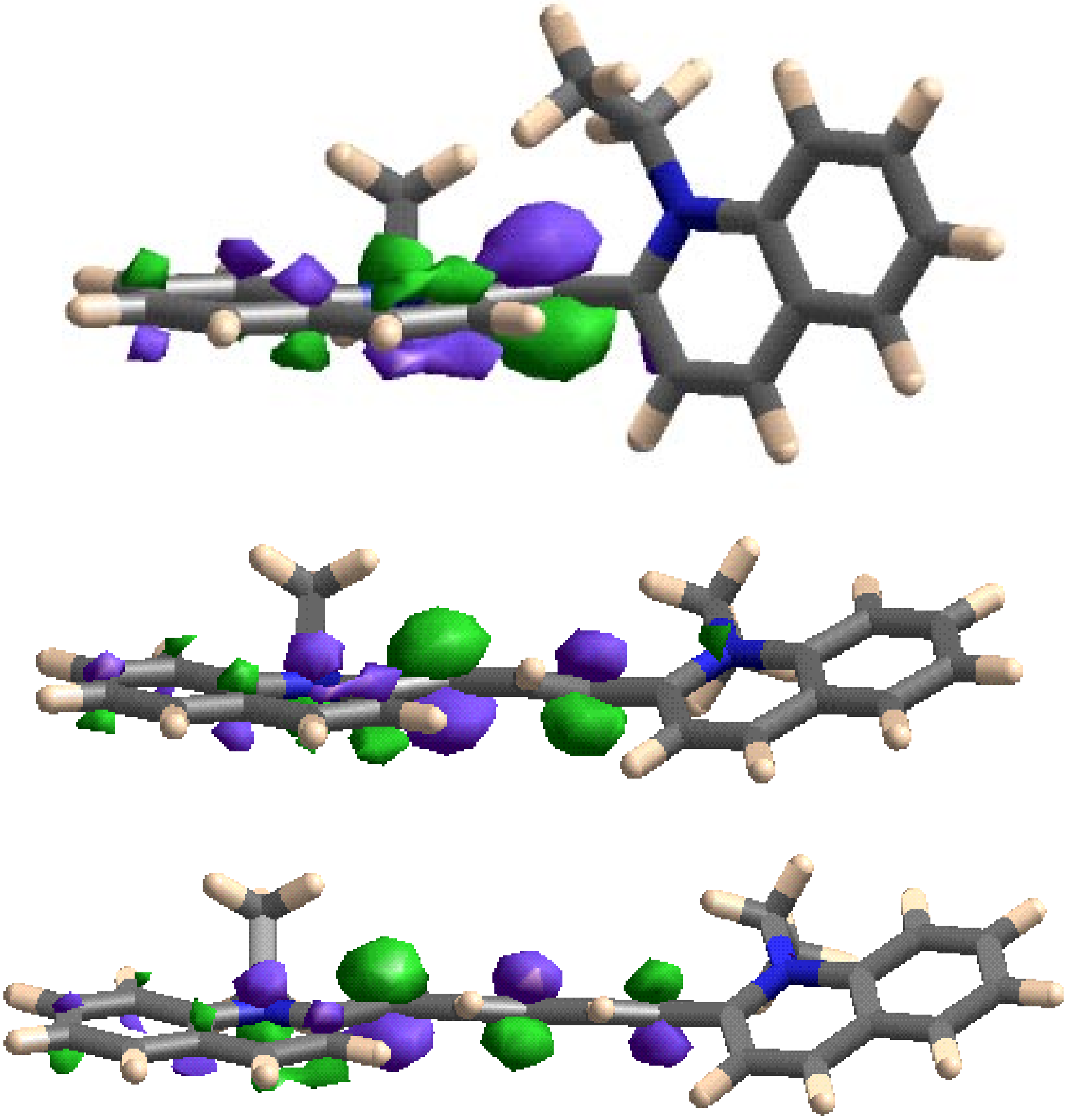

**FIGURE 4**. REPRESENTATION OF THE EXTENDED HÜCKEL LUMOS FOR DYES I–III.

---

Figure 4. In these depictions, it is clear that the nonplanar nuclear geometry of the conjugated unit disrupts the spatial extension of the conjugated π orbital, and little orbital extends onto the most highly "kinked" end group. The graphical depictions of the Hückel MOs clearly show that the geometries of the calculated orbitals exhibit longer conjugated-box lengths in the longer dyes than in the shorter.

Both the corrected molecular mechanics box lengths ($L + \alpha$) and the Hückel molecular orbital method are linear with respect to the spectroscopic box lengths, $L'$, which itself

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

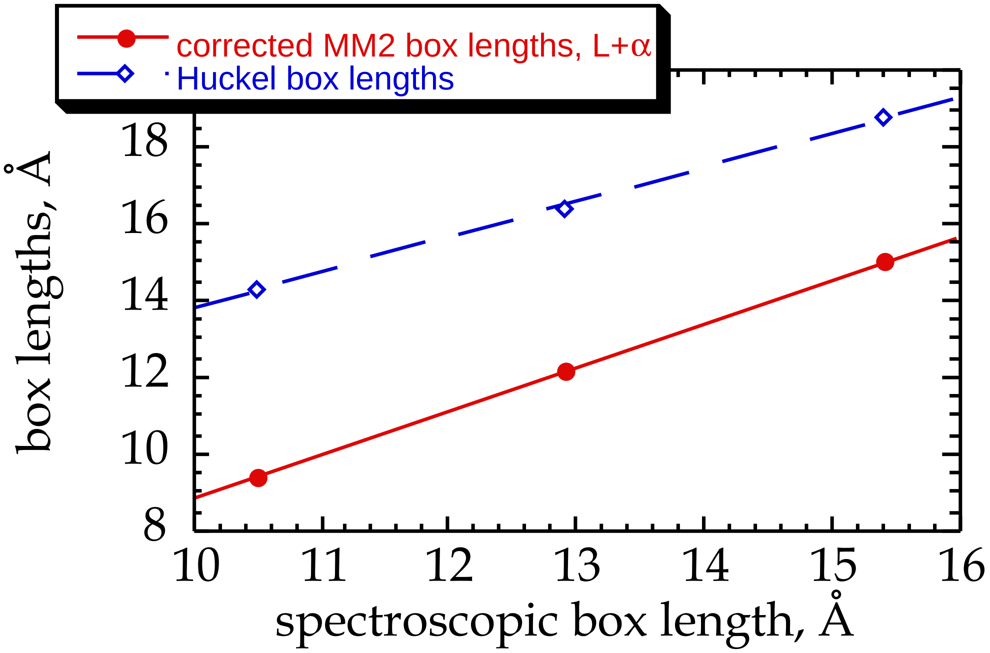

**FIGURE 5**. PLOT OF MOLECULAR MECHANICS (*L* + *α*) AND HÜCKEL BOX LENGTHS VS. THE SPECTROSCOPIC BOX LENGTH, *L′*.

is a linear function of the experimental variable $(\lambda)^{0.5}$. The slopes of these relationships are both ~1 (Figure 5), suggesting that each method produces the correct trend for agreement with the one-dimensional particle-in-a-box model, which is significant, given that molecular mechanics is a purely structural method that contains no explicit quantum mechanical information, while the Hückel approach is the simplest of the quantum approaches.

## Educational Comments

The overall goal of this exercise is to sensitize undergraduate chemists to the need for critical examination of data and theoretical models from the perspectives of either other data or models. Students can learn the power of independent approaches to a given problem as a tool for the advancement of scientific knowledge. Since most laboratory courses try to present a survey of different problems, it is somewhat rare that students have the opportunity to focus on a question with more than one approach. The exercise presented here allows them to do this while simultaneously presenting students with modern computational techniques.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04135-2

## ACKNOWLEDGEMENT

We thank the National Science Foundation for support (NSF-ILI grant DUE-9451383).

## REFERENCES

1. Shoemaker, D. P; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 6th ed.; McGraw-Hill: New York, 1996; Chapter 14.

2. DeKock, R. L.; Madura, J. D.; Rioux, F.; Casanova, J. *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; **1993**, *4*, 149.

3. Williamson, K. L. *Macroscale and Microscale Organic Experiments*, 2nd ed.; D. C. Heath: Lexington, MA, 1994; Chapter 16.

4. Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C., *J. Comp. Chem.* **1990**, *11*, 440.

5. Kuhn, H. *J. Chem. Phys*. **1949**, *17*, 1198.

6. Levine, I. N. *Quantum Chemistry*, 3rd ed.; Allyn and Bacon: Boston, 1983; Chapter 15.