Alternative Compounds for the Particle in a Box Experiment

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A common experiment in many undergraduate physical chemistry laboratories is the study of how the absorption spectra of polymethine dyes can be used to determine the box length in the one-dimensional particle-in-a-box model (*1, 2*). A new series of compounds is proposed to replace the polymethine dyes in this experiment that are less expensive and less hazardous, and the length of the box is easier for students to visualize. The compounds are 1,4-diphenyl-1,3-butadiene; 1,6-diphenyl-1,3,5-hexatriene; and 1,8-diphenyl-1,3,5,7-octatetraene.

Experimental Box Length

To begin, each compound is dissolved in cyclohexane to make a 10^{-6} M solution. Then the absorption spectrum of each solution is acquired from 300 to 425 nm as shown in Figure 1. For each spectrum, the wavelength of the lowest energy peak is determined and converted to energy. This energy is used in the eigenvalue expression shown below for the one-dimensional particle in a box.

$$\Delta E = \frac{\left(n_f^2 - n_i^2\right) h^2}{8 m L^2}$$

To calculate the length, L, of the quantum mechanical (experimental) box, m is taken to be the mass of an electron, and n is the initial or final quantum level for the electronic transition. For each compound n is determined by counting the number of π electrons between the phenyl rings and then filling the energy levels with pairs of electrons. The lowest energy transition occurs from the highest occupied energy level to the lowest unoccupied energy level (*1, 2*). For example, 1,4-diphenyl-1,3-butadiene contains 4 π electrons between the phenyl rings. Thus, the two lowest quantum levels are filled and the lowest energy transition is from $n_i = 2$ to $n_f = 3$.

Theoretical Box Length

In this series of diphenyl compounds, the length of the box is taken to be the distance between the phenyl rings and the phenyl rings represent the walls of the box. In the polymethine dyes, the box length includes not only the distance between the rings, but extends into and beyond the rings (*1, 2*). As a result, students have great difficulty picturing where the walls of the box are and what length they are trying to measure. Students have a better understanding of the model when the diphenyl compounds are used.

To calculate the theoretical box length for the diphenyl compounds, use 0.139 nm as the average bond length of a carbon–carbon bond in the conjugated system between the rings. The theoretical box lengths are calculated by determining the number of bonds between the phenyl rings and multiplying by the length per bond. The theoretical box lengths are given in Table 1 along with the experimental box lengths determined from the absorption spectra. The theoretical and experimental box lengths for the polymethine dyes are included in Table 1 for comparison.

In conclusion, the experimental box lengths are in surprisingly good agreement with the theoretical box lengths. Further, the results are comparable to those obtained using the polymethine dyes, but the quantum mechanical box is much easier for students to recognize using the diphenyl compounds.

Literature Cited

1. Sime, R. J. *Physical Chemistry: Methods, Techniques, and Experiments*; Saunders College: Philadelphia, 1990; p 687.
2. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*; McGraw-Hill: New York, 1989; p 440.

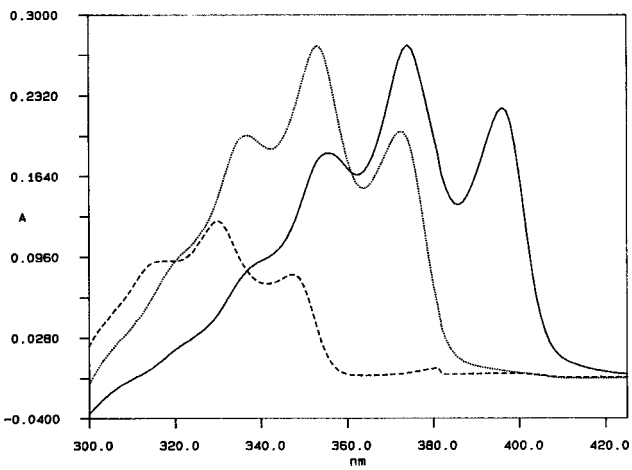

Figure 1. Absorption spectra of the diphenyl compounds in cyclohexane: --- 1,4-diphenyl-1,3-butadiene; ··· 1,6-diphenyl-1,3,5-hexatriene; — 1,8-diphenyl-1,3,5,7-octatetraene.

Table 1. Experimental and Theoretical Box Lengths

Compound	Experimental (nm)	Theoretical (nm)
Diphenyl Compounds		
1,4-diphenyl-1,3-butadiene	0.726	0.695
1,6-diphenyl-1,3,5-hexatriene	0.889	0.973
1,8-diphenyl-1,3,5,7-octatetraene	1.040	1.251
Polymethine Dyes		
1,1'-diethyl-2,2'-cyanine iodide	1.053	0.834
1,1'-diethyl-2,2'-carbocyanine chloride	1.285	1.112
1,1'-diethyl-2,2'-dicarbocyanine iodide	1.534	1.390