# Determination of Carbon–Carbon Bond Length from the Absorption Spectra of Cyanine Dyes

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The study of the absorption spectra of a series of cyanine dyes is often used in the undergraduate laboratory as an example of the application of elementary quantum mechanics to a chemical system (*1–4*). The lowest electronic transition of these dyes involves the conjugated $\pi$ system and generally lies in the visible region. Although some fairly sophisticated calculations (*5*) have been made for these types of dyes, the agreement with experimental results is poor. The simple particle-in-a-box (or free electron) model, originally proposed by Kuhn (*6*) has been found to provide more satisfactory agreement, even though some of the assumptions made are somewhat unrealistic.

Consider, for example, the polymethine dyes shown in Figure 1. The conjugated $\pi$ systems of these dyes are commonly modelled as providing a "particle-in-a-box" potential energy surface, in which the $\pi$ electrons are allowed to move freely (the free electron model). That is, it is assumed that the potential energy is constant along the polymethine chain and that it rises sharply to infinity at the two ends (the nitrogen atoms). The energy levels for this system are given by the eigenvalues of the Schrodinger equation for a particle constrained to a one-dimensional box of length $L$:

$$E_n = h^2n^2/[8mL^2];\ n = 1,2,3,\ldots \tag{1}$$

where $m$ is the mass of the electron and $h$ is Planck's constant. *The Pauli principle is then applied to this set of* energy levels, resulting in the determination that the lowest energy transition will occur from the level with $n = N/2$ to that with $n = (N/2) + 1$, where $N$ is the total number of $\pi$ *electrons in the chain. This model predicts that the lowest* energy transition in these systems is described by

$$\Delta E = hc/\lambda = h^2(N + 1)/[8mL^2] \tag{2}$$

Note that eq 2 relates the "length" of the box to the absorption energy and wavelength for each dye.

The analysis described by many previous workers is to determine a chain length, $L$, for each dye using eq 2 and the energy corresponding to the experimentally obtained absorption maximum ($\lambda_{\max}$). This "experimental" chain length is then compared to a "theoretical" length, generally provided by a relation of the form

$$L = (b' + \alpha) \times r \tag{3}$$

where $b'$ represents the "number of bonds" in the chain, $r$ is the average bond length, and $\alpha$ is an empirical parameter which increases the effective number of bonds in the chain to account for the polarizability of the groups at the two ends. The value of $r$ is set equal to the bond length of benzene (0.139 nm), and the value of $b'$ is generally (although not universally) increased by 2 over the actual number of bonds to account for the extension of the $\pi$ system for one bond length beyond each of the terminal nitrogen nuclei.[1] This leaves only the value of $\alpha$ to be determined. This parameter is expected to be constant for a given series of dyes. Table 1 shows the values of $\alpha$ which provide fits to the experimental data.[2] It is clear that $\alpha$ does not remain constant for a given series of dyes, as has been noted previously (*1*).

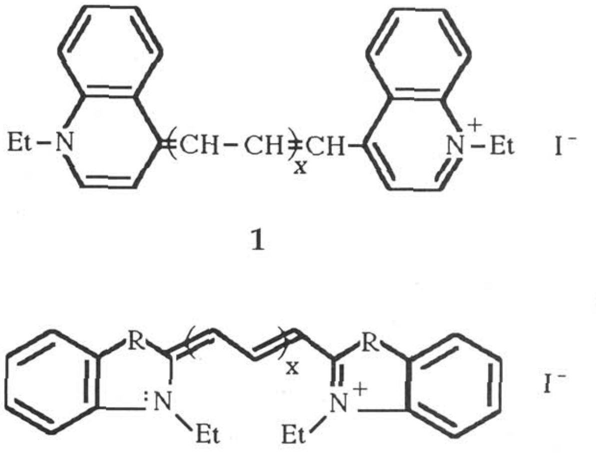

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Figure 1. Dye 1: 1,1′-diethyl-4,4′-cyanine iodides ($x = 0, 1, 2, 3$); Dye 2a ($R = S$): 3,3′-diethylthiacyanine iodides ($x = 0, 1, 2, 3$); Dye 2b ($R = O$): 3,3′-diethyloxacyanine iodides ($x = 1, 2, 3$).

**Table 1. Particle-in-a-Box Parameters for Three Series of Polymethine Dyes**

| | | $b$ | $N$ | $\lambda_{\max}$ (nm) | $L_{\max}$ (nm)[a] | $\alpha$[b] |
|---|---|---|---|---|---|---|
| Dye I | $x = 0$ | 8 | 10 | 592[c] | 1.40 | 0.111 |
| | $x = 1$ | 10 | 12 | 708[c] | 1.67 | 0.020 |
| | $x = 2$ | 12 | 14 | 813[c] | 1.92 | −0.164 |
| | $x = 3$ | 14 | 16 | 929[c] | 2.19 | −0.255 |
| Dye IIa | $x = 0$ | 4 | 6 | 422 | 0.946 | 0.810 |
| | $x = 1$ | 6 | 8 | 556 | 1.23 | 0.863 |
| | $x = 2$ | 8 | 10 | 651 | 1.47 | 0.602 |
| | $x = 3$ | 10 | 12 | 757 | 1.73 | 0.429 |
| Dye IIb | $x = 1$ | 6 | 8 | 483 | 1.15 | 0.261 |
| | $x = 2$ | 8 | 10 | 578 | 1.39 | −0.0096 |
| | $x = 3$ | 10 | 12 | 681 | 1.64 | −0.211 |

[a] Effective length calculated using $\lambda_{\max}$ and eq 2.
[b] Calculated using eqs 2 and 3.
[c] Data from ref *1*.

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[1] Previous authors (*7*) have commented that "[t]he point . . . must be decided arbitrarily. Apparently the most satisfactory convention is to place this wall [at the end of the "box"] . . . one bond distance beyond the end atoms of the conjugated system."

[2] Some authors omit the parameter $\alpha$ completely. In this case, the agreement between "experimental" and "theoretical" lengths is generally very poor—see, for example, refs *1* and *2*.

## An Alternative Approach

This standard approach and the results obtained raise a number of questions. Why is the "number of bonds" often increased by 2 (as opposed to 1 or 0 or some other value) over the number actually present? Why is there an additional and separate adjustment to the "number of bonds" in the chain with the parameter $\alpha$? Why is $\alpha$ not constant for a given series of dyes? What is the physical interpretation of a negative value of $\alpha$? Many (if not all) of these questions are difficult to answer, suggesting that a more easily interpretable model is desirable.

An alternative approach to the applications of the particle-in-a-box model to these systems is to slightly modify eq 3 to the following:

$$L = (b \times l) + \gamma \qquad (4)$$

where $b$ is the *actual* number of bonds between the nitrogens, $l$ is the average bond length along the chain for a given series of dyes, and $\gamma$ is an empirical parameter expected to be constant for a series of dyes and that accounts for *all of the additional lengthening of the chain* beyond the two end atoms.[3] Rather than setting the average bond length in the chain to be equal to the bond length in benzene, *the value of $l$ is to be determined* from the data. Note that within a given series of dyes only the number of bonds along the chain, $b$, varies. The values of $l$ and $\gamma$ are assumed to be constant and unknown. Thus, from the absorption spectra, the effective chain length, $L$, for each dye in a series can be determined using eq 2. If $L$ is then plotted against the total number of bonds, $b$, in the chain, the result is expected to be a straight line with slope $l$, the average bond length, and an intercept, $\gamma$. This analysis thus provides an example of a typical application of spectroscopy to chemical problems, in which a model is applied to observed spectra to elucidate some aspect of molecular structure—in this case the bond length. This is similar in spirit to the analysis of, for example, the HCl infrared spectrum using the rigid rotator model to determine the equilibrium bond distance in that molecule.

The plot of effective length, $L$, versus number of bonds, $b$, for the thiacyanines (Dyes 2a) using this analysis is shown in Figure 2. The values for $l$ and $\gamma$ obtained from the best fit line to the data are given in Table 2. The results from fits to similar plots for the other two series of dyes are also presented in Table 2 for comparison. In all cases, excellent fits are obtained.

The values of $l$ obtained are somewhat shorter than the expected value of about 0.139 nm (the bond length in benzene). Still, all three sets of data give excellent fits to straight lines and the resulting bond length is within about 10% of the benzene value in all cases. Note that, although there is some variation in these spectroscopically obtained bond lengths, they are relatively constant, as would be expected. (It is possible that the observed deviations may be attributed to, at least in part, the choice of wavelength for determining the transition energy. See below.) The obtained values of $\gamma$ are physically reasonable. The approximation of infinite potential at the ends of the box should become less valid as the polarizability of the end groups is increased, leading to an expected increase in the effective box length. The relative values of $\gamma$ for oxygen- and sulfur-containing end groups are consistent with the differences in polarizability of those two species.

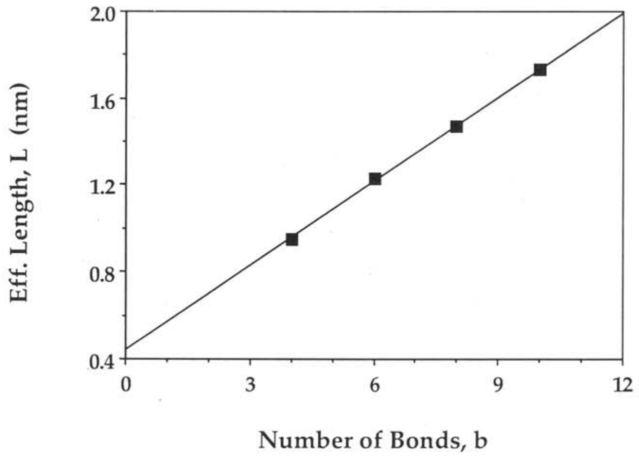

Figure 2. Plot of effective length, $L$, versus number of bonds, $b$, for dye series IIa (3,3′-diethylthiacyanine iodides).

**Table 2. Calculated Carbon–Carbon Bond Length and "Chain Lengthening" for Three Series of Dyes**

| | $l$ (nm)$^a$ | $\gamma$ (nm)$^a$ | $l$ (nm)$^b$ | $\gamma$ (nm)$^b$ |
|---|---|---|---|---|
| Dye I | 0.131 | 0.354 | | |
| Dye IIa | 0.130 | 0.437 | 0.132 | 0.448 |
| Dye IIb | 0.123 | 0.413 | 0.130 | 0.380 |

$^a$ Results of fits of data for each series to eq 4 using $\lambda_{max}$.
$^b$ Results of fits of data for each series to eq 4 using $\lambda_{1/5}$.

**Table 3. Values of $\lambda_{1/5}$ and Calculated Chain Length for Two Series of Dyes**

| | | $\lambda_{1/5}$ (nm) | $L_{1/5}$ (nm)$^a$ |
|---|---|---|---|
| Dye IIa | $x = 0$ | 440 | 0.966 |
| | $x = 1$ | 575 | 1.25 |
| | $x = 2$ | 673 | 1.50 |
| | $x = 3$ | 789 | 1.76 |
| Dye IIb | $x = 1$ | 496 | 1.16 |
| | $x = 2$ | 601 | 1.42 |
| | $x = 3$ | 714 | 1.68 |

$^a$ Calculated using $\lambda_{1/5}$ and eq 2.

## Another Possible Refinement

Although it is the simplest to measure, the absorption maximum is not necessarily the most appropriate indicator of the energy of transition. This wavelength is indicative of the Franck–Condon maximum, rather than the electronic origin, of the transition. If there is a significant change in the equilibrium nuclear distances in going from the ground state to the excited electronic state, the most intense transition will be to an excited vibrational level. Since significant geometry changes have been observed upon excitation of linear polyenes and their derivatives (*8*), such an effect is not unreasonable for these dyes. The expected vibrational structure in the absorption band could be masked by the large inhomogeneous broadening present for ionic species such as these in polar (and hydrogen-bonding) solvents. Thus, although the true position of the origin is unclear from the absorption spectra, it is quite possibly located on the rising edge of the absorption. As an approximate (and admittedly arbitrary) estimation of the origin, the wavelength corresponding to the absorption which is $\frac{1}{5}$ that of the maximum ($\lambda_{1/5}$) may be used. (See Table 3.) The calculated values for $l$ and $\gamma$ are then altered slightly. These are presented in Table 2 for Dyes 2a and 2b. Excellent fits are obtained in both cases.

Note that the average bond lengths obtained are both increased over the results presented above (Table 2) and

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[3] This approach assumes that the C–N bonds are treated as equivalent to C–C bonds. If this assumption is not made, then $b$ becomes the number of C–C bonds in the chain, and $\gamma$ includes in addition the length of two C–N bonds.

that the difference between them is significantly decreased. Thus, the agreement between these values is better than that obtained using $\lambda_{max}$ and *is consistent with the expectation* that the carbon–carbon bond length should not be significantly affected by alterations in the end groups. The values of $\gamma$ are changed slightly, but their relative magnitudes remain consistent with the corresponding differences in chemical structure of the two dye series. All of these results are essentially unaffected if the "origin" is located at $\lambda_{1/4}$ or $\lambda_{1/10}$. The use of this approach (as opposed to using the absorption maximum) to determine the transition energy may provide a more accurate method of applying the particle-in-a-box model to these systems. However, for many beginning physical chemistry students the use of a wavelength other than $\lambda_{max}$ may be an excessive complication considering the necessity to discuss more detailed aspects of molecular spectroscopy and the fact that the true electronic origin of these systems is not readily determined.

## Summary

A new method of analyzing the traditional conjugated dyes absorption experiment provides a method for calculating the average bond length along a polymethine chain. This new approach is conceptually simpler than previous methods and provides values for the bond length that are within 10% of the benzene bond length for several different series of dyes. In addition, if an approximate electronic origin of the examined transitions is used in place of the absorption maximum, the calculated bond lengths are found to be in better agreement among various dyes.

## Acknowledgment

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