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Chemistry of cyanine dyes in view of modern physics

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ABSTRACT

The Chemistry of Conjugated cyanine dyes were studied in view of Quantum Mechanical method. Particle in a box concept of modern physics is employed to describe the structural variation and electronic charge transfer (CT) inside the conjugated diene dyes.

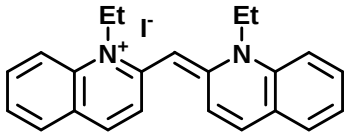
KEYWORDS

Cyanine dyes;
Charge transfer;
Modern physics;
Conjugated diene systems.

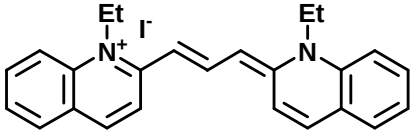
INTRODUCTION

Cyanine dyes consist of two heterocyclic nuclei containing nitrogen centers linked through an odd number of methine bonds, which are normally in the *trans* configuration, in such a way that resonance occurs through the conjugated diene system between the tertiary and quaternary nitrogen atoms[1], Figure 1. This class of organic compounds was reported in our previous work[2,8]. It was of great importance and have a wide application in various fields, such as nucleic acid detection[9-11], optical sensors[12], photovoltaic devices[13,14], near infrared laser dyes[15], histological staining[16], antimicrobial operations[17-23], dyes for polymers as well as sensitizers for various silver halide emulsions[24].

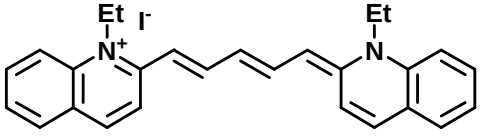
Great efforts, to employ concepts of modern physics, "particle in a box model", to describe the energy and other qualities of an electron of conjugated cyanine dyes were carried out[25]. There was a large disparity between the experimental data and the theoretical ones; hence the theoretical model remains incompatible with the experimental data. This intern encouraged us doing more research to decrease this disparity to a negligible value so that the theoretical model could adequately describe the electron CT inside the diene dye molecule.



1,1`-Diethyl-2,2`-cyanine iodide (Red dye)



1,1`-Diethyl-2,2`-carbocyanine iodide (Blue dye)



1,1`-Diethyl-2,2`-dicarbocyanine iodide (Green dye)

Figure 1: Mono-(Red dye), Tri- (blue dye) and penta- (Green Dye)-methine cyanine dyes

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The CT energy for an electron in a one dimensional box was given by:

$$\Delta E = \frac{h^2(n^2_{LUMO} - n^2_{HOMO})}{8mL^2} \quad (1)$$

whereas, $$\Delta E = \frac{hc}{v} \quad (2)$$

Therefore, $$\lambda = \frac{8mcL^2}{h(n^2_{LUMO} - n^2_{HOMO})} \quad (3)$$

Where m is the mass of an electron, c is the speed of the light L is the length of the one-dimensional box, h is Planck's constant, and the n values are the quantum number of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Thus, the importance of this research came from being able to compare and contrast the results of the experimentally determined data with the results of the empirically determined one. Also we can predict, to some extent, the energy and other qualities of an electron CT inside the diene dyes.

EXPERIMENTAL

In this experiment, three conjugated cyanine dyes were used, Scheme 1, and the experimental work according to literature[26] was carried out and the Experimental maximum wavelengths of the three dyes were recorded, TABLE 1.

TABLE 1 : Wavelengths (nm) obtained from the spectrophotometer

Dye	ΔE (joules)	Wavelength (nm)
Red	3.81×10^{-19}	522.00
Blue	3.29×10^{-19}	604.00
Green	2.81×10^{-19}	708.00

RESULTS AND DISCUSSION

Since each pathway introduces a quantized box inside which the electron can freely move according to Particle in a Box concept with approximately equal probability and different lengths, any available conjugated CT pathway inside the diene molecule should be considered. Thus, the three given cyanine dyes would have two conjugated CT pathways with different lengths, accordingly, the transition energy and its qualities should be averaged or binomially distributed to that of the two CT pathways, Figure 2.

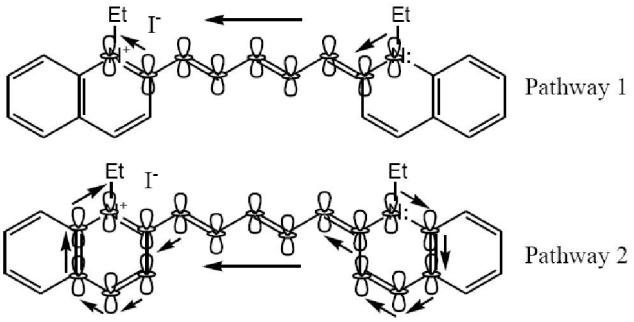

Figure 2 : The two possible CT pathways inside the dye (Green dye) molecule.

By determining the total number of π-electrons in each conjugated system for each CT pathway, it could be determined what the HOMO and LUMO levels are. This could be done by adding the number of π-electrons from each carbon atom (one electron per C atom in the methine chain) to the number of π-electrons donated by nitrogen atom, which are always three. Therefore, according to Pauli Exclusion Principle, the electrons are paired in the ground state, then successive electrons are added into the higher states until all π-electrons are accounted for, Figure 1. Hence, both the energy (E) for each CT pathway and the wavelength of maximum absorption (λ_{max}) could be calculated using Equation 1 and Equation 3, respectively, TABLE 2.

The length of the box is given by (L = kb) where K is the number of bonds involved in the conjugated diene CT pathway, and b is equal to 140×10^{-12} m, the length of a bond in benzene.

Looking at these data, it is possible to compare it with the data obtained from the spectrophotometer. As one can see, there is a large disparity between the experimental data and the theoretical data for each CT pathway separately, but this disparity could be minimized if the theoretical data for both CT pathways is averaged. This strongly recommended that all CT pathways inside the diene dye molecule should be considered to obtain approximately accurate results. Also, the data in, TABLE 2, may lead to assume that the electron charge transferred through the two CT pathways with equal probability, therefore, the averaged transition energy would represent the overall transition energy.

The above data, TABLE 2, leads us to believe that

TABLE 2 : Calculated energy and maximum wavelengths for each CT pathway and its average.

Dye	Pathway 1		Pathway 2		Average	
	ΔE (joules)	λ_{max} (nm)	ΔE (joules)	λ_{max} (nm)	ΔE (joules)	λ_{max} (nm)
Red	1.35×10^{-18}	147.57	0.32×10^{-18}	619.80	0.84×10^{-18}	383.69
Blue	7.70×10^{-19}	258.25	2.67×10^{-19}	744.37	5.19×10^{-19}	501.31
Green	5.29×10^{-19}	375.64	2.29×10^{-19}	869.89	3.79×10^{-19}	622.77

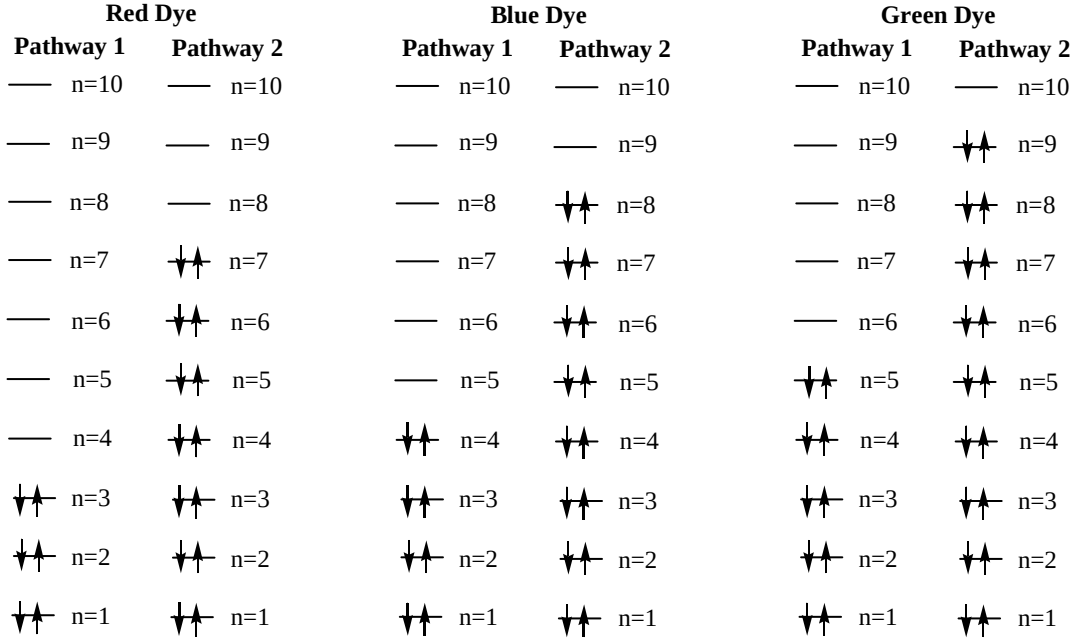

Figure 3: Graphical representation of HOMO and LUMO energy levels.

the electron CT occurs inside both pathways with equal probability; there is still small disparity between the averaged value and the experimental one which could be approximated to negligible value if the averaged value of the charge transition is distributed binomially between the two CT pathways, according to equations 4, 5, 6.

$$p\,\lambda_{max}(\text{path. 1}) + q\,\lambda_{max}(\text{path. 2}) = \lambda_{max}(\text{Exp.}) \quad (4)$$

Whereas, $p + q = 1$ (5)

$$\text{Thus } q = \frac{\lambda_{max.}(\text{Exp.}) - \lambda_{max.}(\text{Path.1})}{\lambda_{max.}(\text{Path.2}) - \lambda_{max.}(\text{Path.1})} \quad (6)$$

Where: p, the probability that the electron in CT pathway 1,q, the probability that the electron in CT pathway 2

Comparing the data embedded in TABLE 3 with that in TABLE 1 revealed that the disparity between the theoretical data and the experimental one were entirely neglected so that the theoretical model (particle in a box) adequately described the physical nature of the CT inside the conjugated diene cyanine dyes. Moreover, employing the concept of binomial distribution nature of the CT between the two available pathways adequately described the experimental data in view of this theoretical model and declared that the longer the CT pathway inside the conjugated diene system, the more probability the electron CT through (resonance stabilization).

TABLE 3 : Approximated wavelengths according to binomial distribution.

Dye	Pathway 1		Pathway 2		Total	
	P	$p\lambda_{max}$ (nm)	q	$q\lambda_{max}$ (nm)	ΔE (joules)	λ_{max} (nm)
Red	0.207	30.50	0.793	491.50	3.81×10^{-19}	522.00
Blue	0.289	74.70	0.711	529.30	3.29×10^{-19}	604.00
Green	0.327	122.57	0.673	585.43	2.81×10^{-19}	708.00

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CONCLUSION

As mentioned, concepts of modern physics adequately describe the experimental data of the CT inside the diene dye molecule. Moreover, either averaged or binomially distributed empirically calculated data minimized the disparity between experimental data and the theoretical one. Also we can employ theoretical models of modern physics either to describe or to predict the nature of CT inside the diene dye molecule and this intern opens a research window describing experimental chemical phenomena using theoretical physical one.

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