

The Absorption Spectra of a Series of Conjugated Dyes

Determination of the Spectroscopic Resonance Integral

John J. Farrell

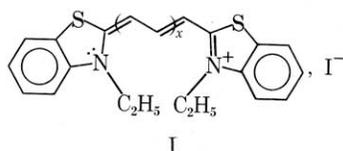
Franklin and Marshall College, Lancaster, PA 17604

Many cyanine dyes absorb radiation in the visible range of the electromagnetic spectrum (1, 2). These dyes may be considered as a classical example of the particle-in-a-box problem (3). They are often used in undergraduate laboratories because they provide a simple chemical application of elementary quantum mechanics (4, 5).

With the advent of the ubiquitous computer, simple Hückel Molecular Orbital calculations can be performed by undergraduates enrolled in courses where the topic is introduced. In this project HMO theory and particle-in-a-box theory are applied to the observed spectra of four thiacyanine dyes.

The Dyes

The dyes to be studied are shown below:



3,3'-diethylthiacyanine iodide	$x = 0$
3,3'-diethylthiacyanocarbyanine iodide	$x = 1$
3,3'-diethylthiadicyanocarbyanine iodide	$x = 2$
3,3'-diethylthiatriacyanocarbyanine iodide	$x = 3$

Each dye is referred to as Dye(x). Absorption maxima, Table 1, can be determined in $10^{-5} M$ methanolic solutions. The dyes can be purchased from K&K Labs, 121 Express Street, Plainview, NY 11803. Each dye costs about \$25/100 mg, but the long-term cost is not excessive because the solutions required are so dilute.

One-Dimensional Box Treatment

The quantum-mechanical solution for an electron in a one-dimensional box is

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (1)$$

where m is the mass of the electron and L is the length of the box. In this case, the box extends from nitrogen to nitrogen plus one-half of a bond length beyond each nitrogen. That is, $L = (p + 3)l$, where p = the number of carbon atoms in the chain and l is the average bond distance in the chain. The number of electrons in the chain, N , is $p + 3$. Each energy level can accommodate two electrons. Therefore, the highest occupied molecular orbital (HOMO) will be where $n = N/2$; and the lowest unoccupied molecular orbital (LUMO) will be where $n = (N/2) + 1$. To promote an electron from $E(\text{HOMO})$ to $E(\text{LUMO})$ requires a photon equal to this energy difference.

$$E(\text{LUMO}) - E(\text{HOMO}) = \frac{h^2(N + 1)}{8mL^2} \quad (2)$$

If we let $l = 1.39 \times 10^{-8}$ cm (the bond distance in benzene) the energy of transition is

$$\Delta E(\text{ev}) = 19.46 \frac{(p + 4)}{(p + 3)^2} \quad (3)$$

Table 1. Experimental and Particle-in-a-Box Transition Energies for Some Cyanine Dyes

Dye	x	Experimental		Theoretical	
		$\gamma(\text{nm})$	$\Delta E(\text{ev})$	$\Delta E(\text{ev}, \gamma = 0)$	$\Delta E(\text{ev}, \gamma = 0.68)$
Dye(0)	0	422	2.94	3.78	3.05
Dye(1)	1	555	2.23	2.74	2.32
Dye(2)	2	650	1.91	2.14	1.88
Dye(3)	3	760	1.63	1.76	1.57

Table 2. Coulomb and Exchange Integral Values Used in This Study

Atom	Bond	Example	Number of π electrons	h	k
C		benzene	1	0.0	1.0
N		pyrrole	2	1.5	0.8
S		thiophene	2	1.5	0.8

Agreement between predicted transition energies and experimental energies, Table 1, is not good (although the agreement is rather surprising in view of the approximations made). It can be improved, however, by introduction of a parameter, γ in eqn. (4), which is usually invoked by a need to correct the length of the box for the polarizable groups at the end of the chain (3, 4). The parameter is adjusted to give the best fit to a particular series of dyes. Inclusion of the appropriate parameter greatly improves the comparison between the theoretical and experimental values, Table 1.

$$E(\text{ev}) = 19.46 \frac{(p + 4)}{(p + 3 + \gamma)^2} \quad (4)$$

Hückel Molecular Orbital Treatment

The Hückel molecular orbital (HMO) method makes several assumptions which are listed below:

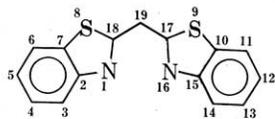
- 1) The wave function for the molecule can be factored into non-interacting portions representing the σ framework and the π system.
- 2) The π system is assumed to be composed of molecular orbitals constructed by a linear combination of atomic orbitals.
- 3) The resultant LCAO MO's are taken to be eigenfunctions of an effective one-electron Hamiltonian so that the variational principle may be applied.
- 4) The coulomb integrals, H_{ii} , are set equal to $\alpha + h\beta$, where α and β are the standard parameters for carbon and h has nonzero values for heteroatoms. The value of h increases as the valence orbital ionization energy increases. See Table 2.
- 5) The resonance, or bond, integrals, H_{ij} are set equal to zero if the orbitals are not on adjacent atoms. If the atoms are adjacent, $H_{ij} = k\beta$. See Table 2.
- 6) Overlap integrals, S_{ij} , are set equal to zero if the two atoms are not adjacent. All $S_{ii} = 1$.

Table 3. Elements 1,1–10,10 of the Secular Matrix for Dye(0)^a

1.5	0.8	0	0	0	0	0	0	0	0
0.8	0	1.0	0	0	0	1.0	0	0	0
0	1.0	0	1.0	0	0	0	0	0	0
0	0	1.0	0	1.0	0	0	0	0	0
0	0	0	1.0	0	1.0	0	0	0	0
0	0	0	0	1.0	0	1.0	0	0	0
0	1.0	0	0	0	1.0	0	0.8	0	0
0	0	0	0	0	0	0	0.8	1.5	0
0	0	0	0	0	0	0	0	0	1.5
0	0	0	0	0	0	0	0	0.8	0

^a See structure II for the numbering system and Table 2 for the coulomb and exchange integral values.

For these molecules the delocalization extends over the entire molecule. The ethyl group can be replaced by a hydrogen to simplify the HMO calculations; this should have little effect on the resultant energy levels. Examination of I, II, and Table 2 reveals that each molecule has $15 + 2x$ conjugated carbon atoms (atom numbers 2–7, 10–15, and 17–19), two sulfur atoms (atom numbers 8 and 9), two pyrrole-type nitrogen atoms (atom numbers 1 and 16), and a +1 charge on the molecule. The number of electrons is $22 + 2x$.



Arbitrary numbering system for Dye(0)

II

For Dye(0) the resultant secular matrix is 19×19 . Matrix elements 1,1–10,10 are shown in Table 3, after making the usual substitution, $\text{root} = (\alpha - E)/\beta$, and with the numbering system in II.

Solving for the characteristic roots of this matrix with pencil and paper in hand would be a formidable task indeed. However, the roots can be determined in less than a second on a mainframe computer (6); it takes only slightly longer on a PC. There are 19 roots to the secular matrix for Dye(0) and 19 energy states (all nondegenerate). The lowest 11 states are filled by the 22 electrons. Thus, the HOMO is $E(11)$ and the LUMO is $E(12)$. The HOMO's, the LUMO's, and the ΔE 's for all four dyes are given in Table 4.

A semiempirical value for the spectroscopic β can be found by plotting the HMO ΔE 's (abscissa) versus the observed ΔE 's (ordinate) and determining the parameters of the resultant straight line. For these data,

$$\Delta E(\text{ev, expt'l, } \pm 0.05) = -2.45(\pm 0.12) \times \Delta E(\text{HMO}) + 0.26(\pm 0.09) \quad (5)$$

Thus, $\beta = -2.45 \text{ ev}$ or 56 kcal/mole . This is, impressively, within the range of the accepted value of the spectroscopic exchange integral, $55\text{--}60 \text{ kcal/mole}$ (7). A comparison between the experimental transition energies and the theoretical HMO transition energies is given in Table 5.

Table 4. HOMO's and LUMO's for the Dye(x)'s

Dye	Number of π electrons	$E(\text{HOMO})$	$E(\text{LUMO})$	$\Delta E(\beta)$
Dye(0)	22	$\alpha + 0.4766\beta$	$\alpha - 0.6091\beta$	-1.086
Dye(1)	24	$\alpha + 0.3752\beta$	$\alpha - 0.4486\beta$	-0.824
Dye(2)	26	$\alpha + 0.3044\beta$	$\alpha - 0.3533\beta$	-0.658
Dye(3)	28	$\alpha + 0.2846\beta$	$\alpha - 0.2761\beta$	-0.561

Table 5. Experimental and HMO Transition Energies for Some Cyanine Dyes

Dye	x	Expt'l $\Delta E(\text{ev})$	Theoretical		
			$\Delta E(\beta)$	$\Delta E(\text{ev, } \beta = -2.45)$	$\Delta E(\text{ev, eqn. (5)})$
Dye(0)	0	2.94	-1.086	2.66	2.92
Dye(1)	1	2.23	-0.824	2.02	2.28
Dye(2)	2	1.91	-0.658	1.61	1.87
Dye(3)	3	1.63	-0.561	1.37	1.63

Additional Work

Students who master this simple HMO description of these dyes may wish to improve on the model. This can be tried in several ways. Four ways are suggested below (8, 9):

- 1) Treat the aromatic carbon and chain carbons differently; $h = 0.0$ and $k = 0.9$ for butadiene-type carbons.
- 2) Treat one nitrogen as a pyrrole type and the other nitrogen as a pyridinium type (one π electron; $h = 2.0$, and $k = 1.0$). Of course the two nitrogens would not be equivalent in this model.
- 3) Treat each sulfur atom as a pair of AO's with a total of two electrons.
- 4) Replace the pyrrole-hydrogen with a conjugative methyl.

Summary

The thiocyanine dyes studied in this experiment are reasonably stable and all four have absorption maxima in the visible range. Both particle-in-a-box theory and HMO theory can be applied to these molecules with satisfactory results. In addition to comparing the two theories, interested students can tinker with the models in an effort to improve the match between theory and experiment.

Literature Cited

- (1) Kuhn, H., *J. Chem. Phys.*, **17**, 1198 (1949).
- (2) Brooker, L. G. S., Keyes, G. H., and W. W. Williams, *J. Amer. Chem. Soc.*, **64**, 199 (1942).
- (3) Heilbronner, E., and H. Bock, "The HMO Model and its Applications," Vol. 1, John Wiley & Sons, London, 1976, pp 22–24.
- (4) Gerkin, R. E., *J. CHEM. EDUC.*, **42**, 490 (1965).
- (5) Shoemaker, D. P., Garland, C. W., and Steinfeld, J. I., "Experiments in Physical Chemistry," McGraw-Hill, Inc., New York, 1974, pp. 435–441.
- (6) Lowe, J. P., "Quantum Chemistry," Academic Press, New York, 1978, pp. 538–542.
- (7) Cotton, F. A., "Chemical Applications of Group Theory," John Wiley & Sons, Inc., New York, 1971, pp. 366–367.
- (8) Streitwieser, A., Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York, 1961.
- (9) Lowe, J. P., ref. (6), pp. 245–249.