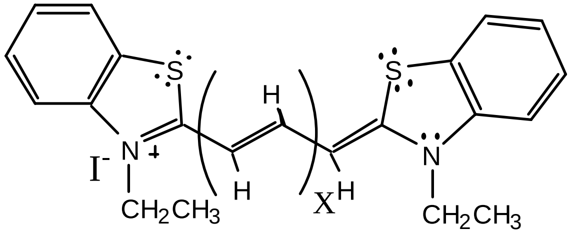
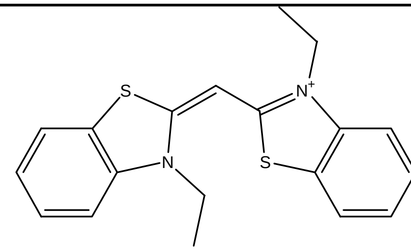
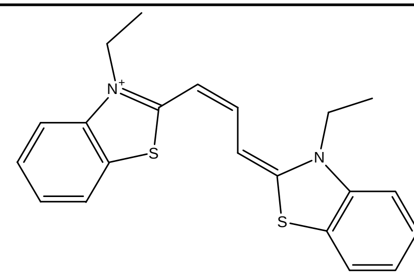
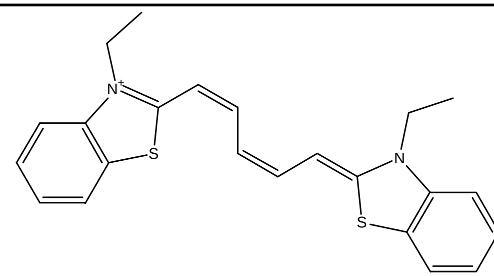
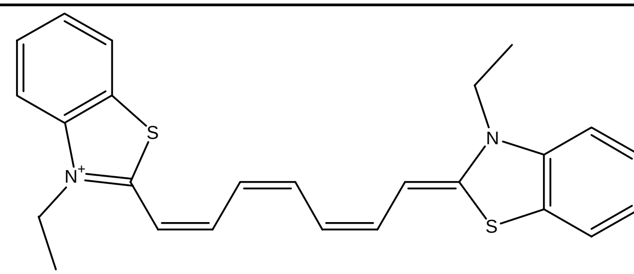
Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules

In this experiment, you are going to examine the spectroscopy of **cyanine dyes**.



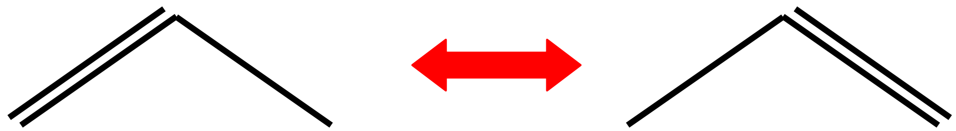
where x = 0,1,2,3

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules

X	Name	Structure
0	3,3í-diethylthiacyanine iodide	
1	3,3í-diethylthiacarbocyanine iodide	
2	3,3í-diethylthiadicarbocyanine iodide	
3	3,3í-diethylthiatricarbocyanine iodide	

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules

Each of the dyes contains alternating carbon double and single bonds:



These structures are in resonance with each other. So weíve really got:

C-C bond = 1 σ bond + 1/2 π bond

In the plane of the molecule

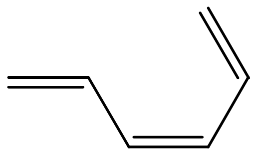
Perpendicular to the plane of the molecule

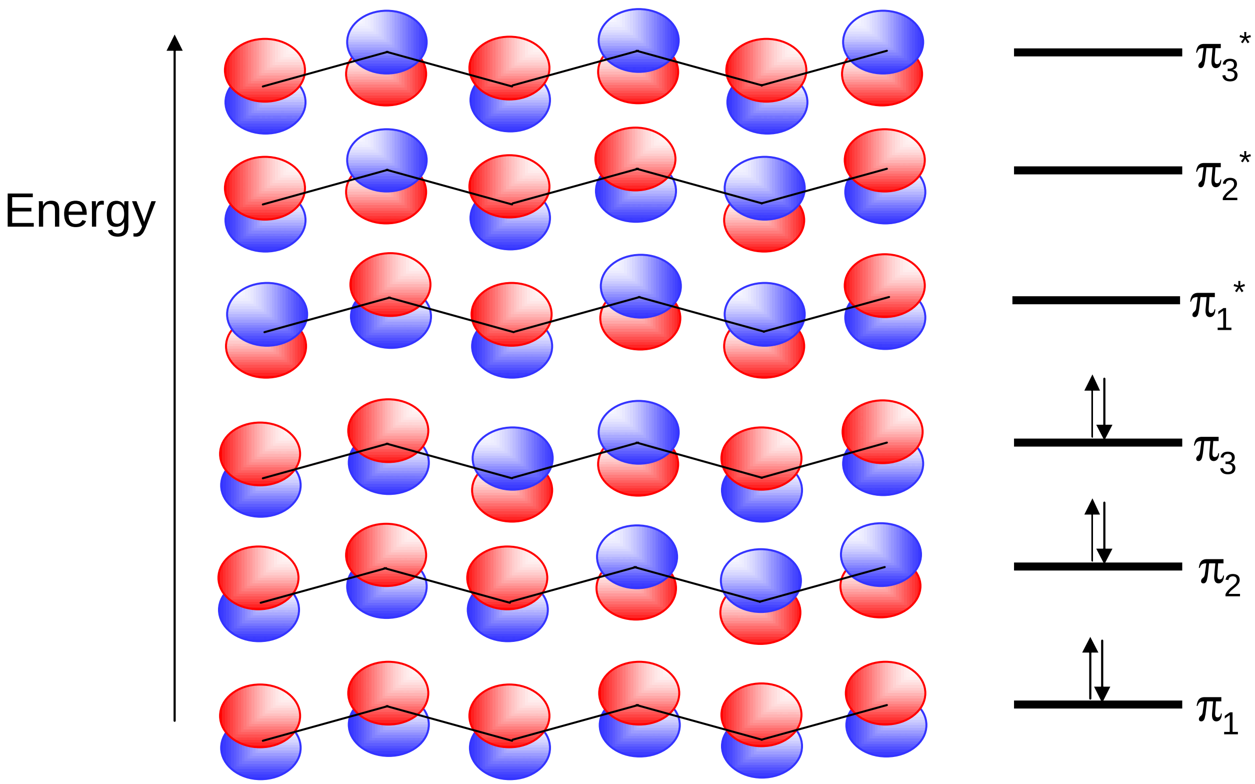
The π electrons from the carbon are **DELOCALIZED**.

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules

What does this have to do with the particle in a box?

The π electron system can be written as a series of the bonding and anti-bonding orbitals.

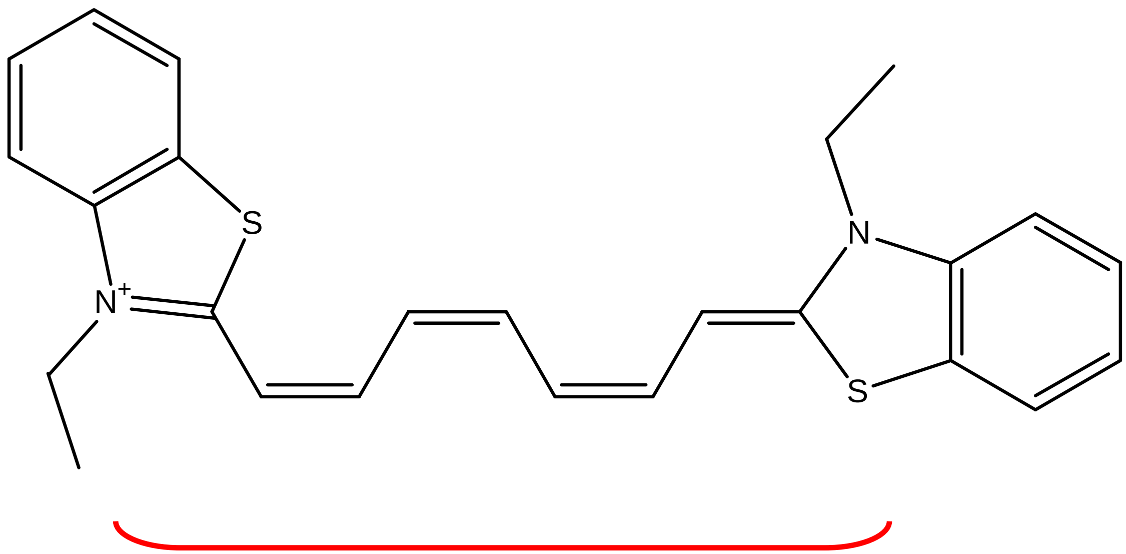
Eg. Hexatriene 



For each C, there is 1π electron.

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules
Particle in a Box

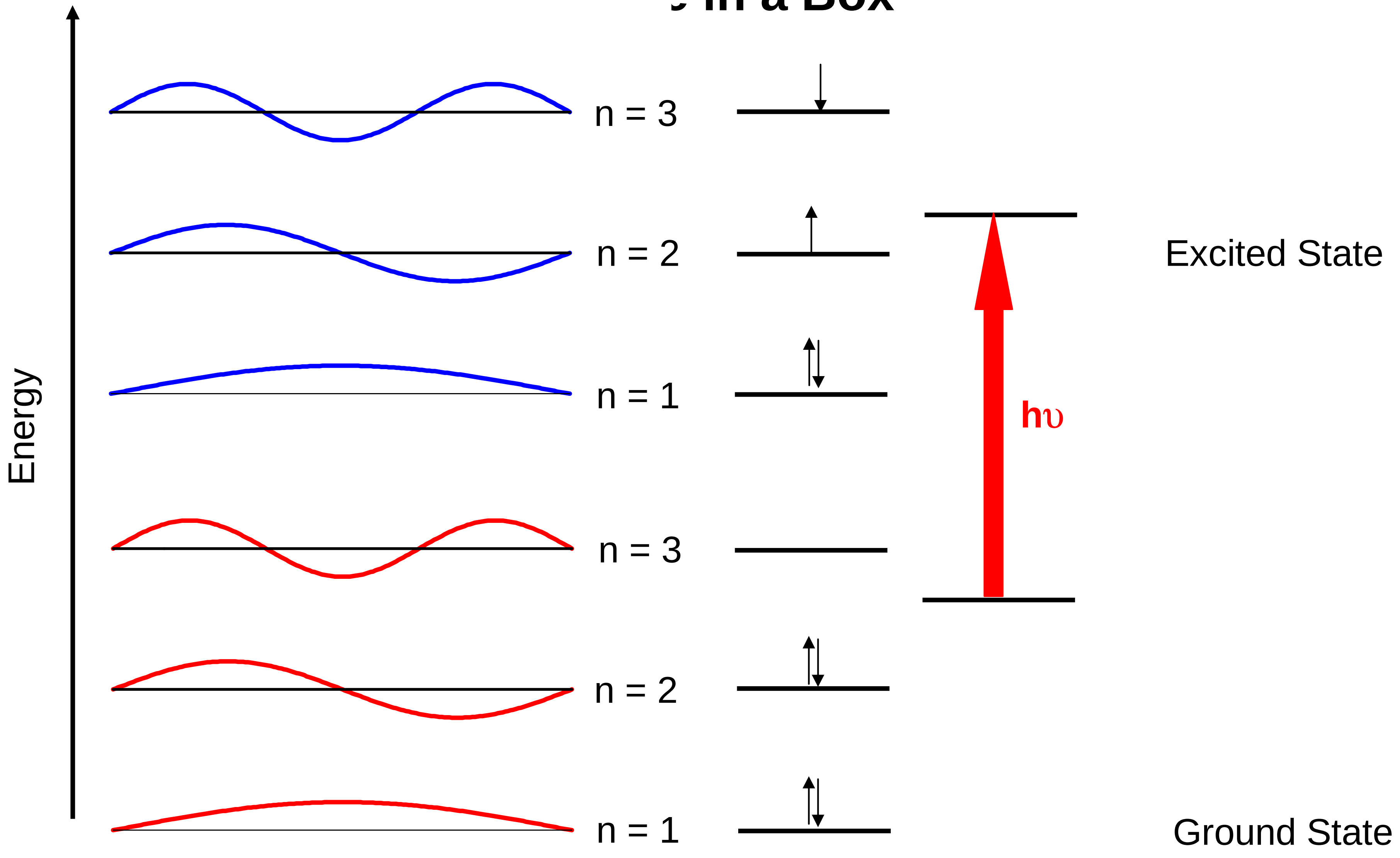
E.g. x = 3



Delocalized Electron System

We can consider the dye as a ìboxî with the electrons being the particles.

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules
Particle in a Box



Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules
Particle in a Box

The energy of the electron in the box is $$E_n = \left(\frac{h^2}{8m_eL^2}\right)n^2$$

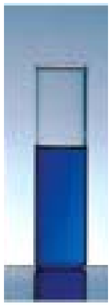
For a transition from 1 level to the next is $$\Delta E = \left(\frac{h^2}{8m_eL^2}\right)\left(n_{final}{}^2 - n_{initial}{}^2\right)$$

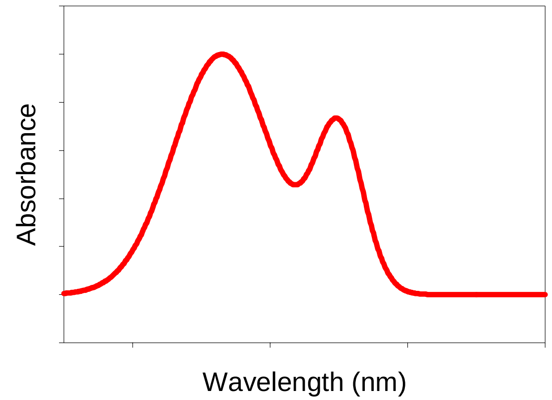
For the dye molecule (and the particle in a box)

$$\Delta E = \left(\frac{h^2}{8m_eL^2}\right)\left(N+1\right)$$

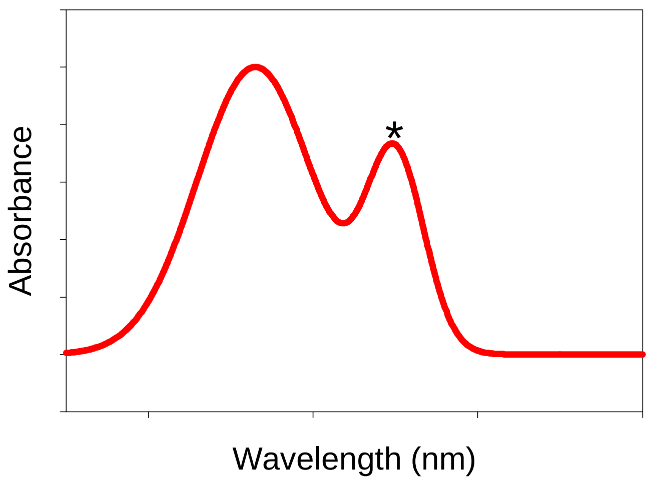
N = number of electrons in the ìboxî, i.e. the number of π electrons

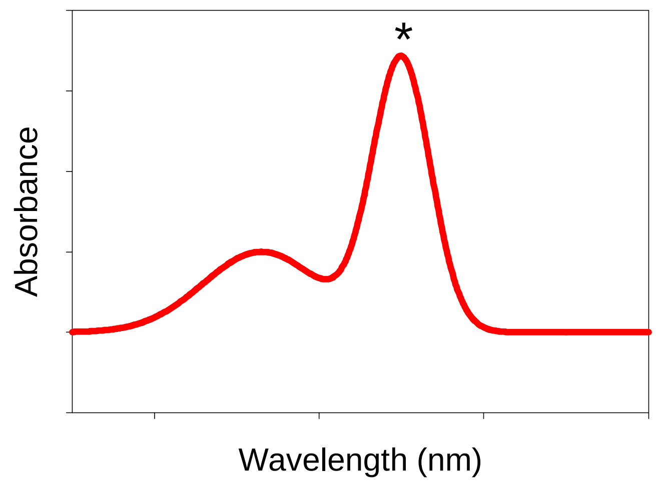
Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules Particle in a Box ñ Finding ΔE





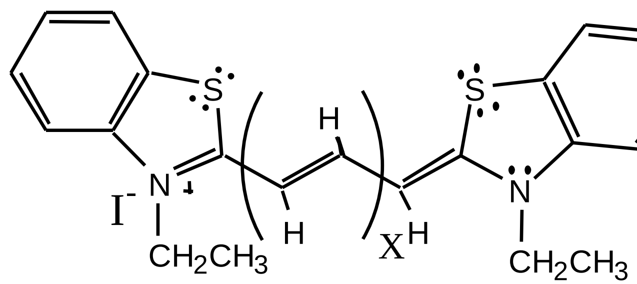
Note:





We want the lowest energy transition, i.e. the one with the longest wavelength. This does not mean the one with the highest absorbance ñ that depends on the orbital shapes.

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules Particle in a Box ñ Finding N

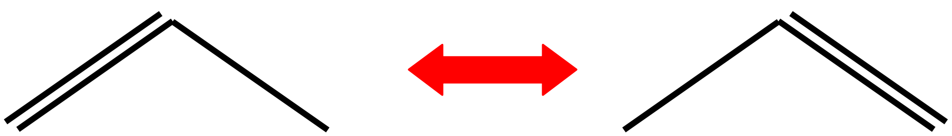


In the dye there are alternating C single and double bonds.

There are two nitrogens:

a) N^+ has 1 π electron with benzene ring

b) N has 2 π electrons from lone pair



C-C bond = 1 σ bond + 1/2 π bond

1e for every C atom

No. of carbon ñ carbon bonds = p

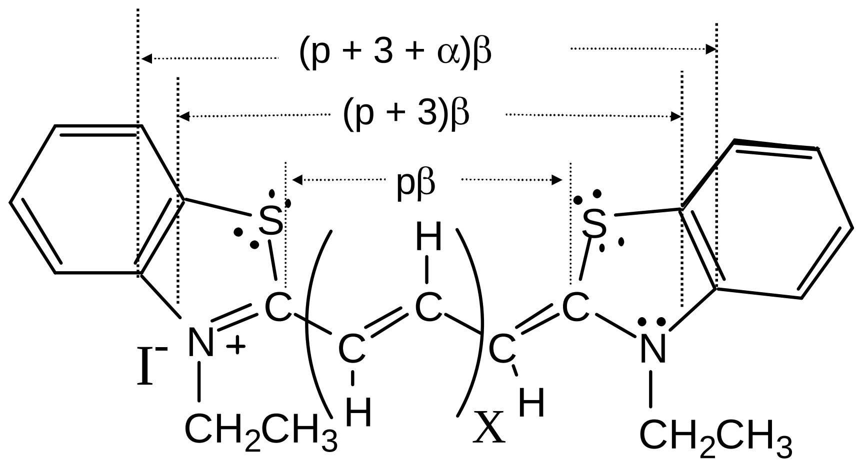
No. of carbon atoms = p + 1

No. of nitrogen π e = 3

No. of electrons = N = p + 4

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules Particle in a Box ñ Finding L

The length of the box, L, is the length of the delocalized electron system.



Length of box = L

= (number of C-C bonds x bond length) + (number of C-N bonds x bond length) + (number of C-N bonds x 0.5 bond lengths) + (α x bond length)

$\alpha = 1.6$

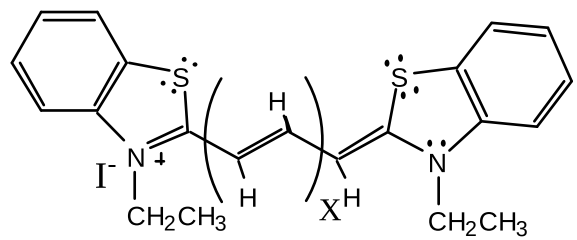
π electron density extends to half N-benzene ring bond length

$= p\beta + 2\ \beta + 2*0.5*\ \beta + \alpha\beta$

$= (p+4.6)\beta$

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules Particle in a Box

In this experiment you are going to find the number of ñCH=CH- units (x) there are in an unknown dye sample.



$$\Delta E = \left(\frac{h^2}{8 m_e L^2}\right)(N+1) = \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda = \left(\frac{8 c m_e L^2}{h(N+1)}\right)$$

$h = 6.62 \times 10^{-34}$ Js

$m_e = 9.11 \times 10^{-31}$ kg

$c = 2.998 \times 10^{8}$ ms^{-1}

N = p + 4

L = (p + 4.6) β
= (p + 4.6)(1.39×10^{-10}) m

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules
Particle in a Box
Relationship to x

$$\lambda = \left(\frac{8cm_eL^2}{h(N+1)}\right)$$

L = (p + 4.6) β
= (2x + 2+ 4.6) β
= (2x + 6.6) β

Number of C-C bonds = p = 2x + 2

Hence,

$$\lambda\ (nm) = 63.7\left[\frac{(2x+6.6)^2}{2x+7}\right]$$

Solve for x using the quadratic equation solution (Experiment 7 page 9).

Experiment 7: Spectroscopy and Quantum Chemistry of Dye Molecules
Other Tasks

1. Fill in the evaluation questionnaires about this class.
   ï You will fill out two evaluations ñ one about the whole class and one about your TA.
   ï It is **completely confidential**.
   ï We really appreciate your views!

2. Check out of your lab drawer.