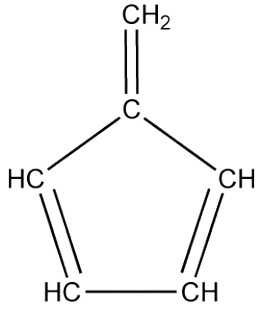
F. Experiment #6, Calculation of π-type Delocalized Molecular Orbitals Using Hückle Theory

Objectives:

1. Use Hückle theory to calculate the energy of conjugated organic molecules.
2. Predict the π electronic configuration of the molecules.
3. Predict the wavelength of the transition from the ground electronic configuration to the first excited state.

Procedure:

In spite of approximations made in the formulation of Hückle theory, it remains a powerful theoretical tool in predicting the energetic benefits of electron delocalization. In this lab, you will calculate the energy benefit of electron delocalization, among other electronic properties, in ethane and fulvene (5-methenyl-cyclopenta-1,3-diene), see below.



Start by working out the energy of the non-delocalized π-bond in ethane using the Hückle theory formalism described in McQuarrie (pgs. 390-398) as well as in class.

1. Setup the secular determinant including the interactions between all atoms.
2. Substitute α for H_{ii}, 1 for S_{ii}, 0 for S_{ij}, and β for H_{ij} where i and j correspond to neighboring atoms. Substitute 0 for H_{ij} when i and j correspond to atoms that don't neighbor each other.
3. Divide the entire matrix by β and let $x = (\alpha - E)/\beta$ to give:

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

4. Solve the determinant for x then substitute the previous definition and solve for E.
5. Let β = -75 kJ/mol.
6. Calculate the overall π-electron energy by summing the energies of all the electrons in your π-orbitals.
7. Calculate the energy difference (in J – not kJ/mol) between HOMO and LUMO by subtracting the energy of the HOMO level from the LUMO level.
8. The first spectroscopic transition would be where an electron is promoted from the HOMO to the LUMO when the molecule is irradiated with light having energy equivalent to the HOMO-LUMO gap. What wavelength, in nm, corresponds to this transition?

Repeat the procedure used for ethane for fulvene:

1. Show the determinant with H_{ij}, E, and S_{ij} written out explicitly.
2. Show the determinant after the appropriate substitutions of α and β.
3. Show the determinant after dividing by β and substituting the previous definition of x.
4. Solve the determinant for x.
5. Substitute the definition of x and solve for the energy levels.
6. Draw and energy-level diagram with the energy levels labeled with their energies.
7. Let β = -75 kJ/mol
8. Calculate the overall π-electron energy, the energy difference between the HOMO and LUMO in J and the energy benefit due to the electrons being delocalized in this molecule.
9. What wavelength of light, in nm, corresponds to the first spectroscopic transition?