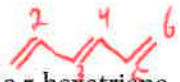
Quiz 9.3 – Molecular Orbital Theory: Polyatomic Molecules

Name: Key

Resonance in 1,3,5 hexatriene



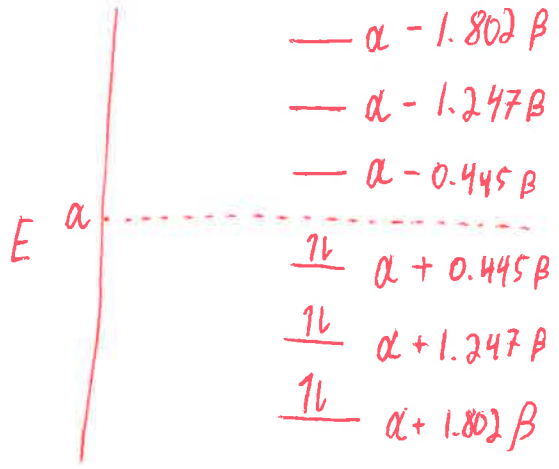
○ Show the Hückel theory determinant for 1,3,5 hexatriene. You may either show the matrix populated with α and β terms, or the simplified matrix with only 1s and 0s

let $x = \frac{\alpha - E}{\beta}$

$$H = \alpha \mathbb{1} + \beta \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \quad \text{-or-} \quad \begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix} = \emptyset$$

○ Solve for the energy levels (You may use WolframAlpha or similar software to either find the determinant or diagonalize the matrix) and draw the energy level diagram

$$H = \alpha \mathbb{1} + \beta \begin{vmatrix} -1.247 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.445 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1.802 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1.802 & 0 & 0 \\ 0 & 0 & 0 & 0 & -0.445 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1.247 \end{vmatrix}$$

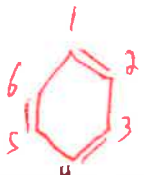


○ Give the total bonding energy of the π system, as well as the resonance stabilization energy

$E_{bonding} = 2 \cdot 0.445\beta + 2 \cdot 1.247\beta + 2 \cdot 1.802\beta = 6.988\beta$

$E_{resonance} = E_{bonding} - 6\beta = 0.988\beta$

↑ 2 · # of double bonds



Resonance in benzene

- Show the Hückel theory determinant for benzene. You may either show the matrix populated with α and β terms, or the simplified matrix with only 1s and 0s

Let $x = \frac{\alpha - E}{\beta}$

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

-or-

$$H = \alpha \mathbb{I} + \beta \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

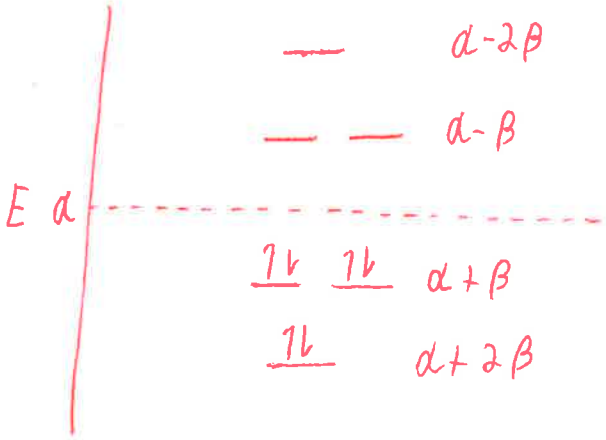
- Solve for the energy levels (You may use WolframAlpha or similar software to either find the determinant or diagonalize the matrix) and draw the energy level diagram

$$x^6 - 6x^4 + 9x^2 - 4 = \emptyset$$

$$(x^2 - 4)(x^2 - 1)^2 = 0$$

$$x = 2, 1, 1, -1, -1, -2$$

$$E = \alpha + x\beta$$



- Give the total bonding energy of the π system, as well as the resonance stabilization energy

$$E_{bonding} = 4 \cdot \beta + 2 \cdot 2\beta = 8\beta$$

$$E_{resonance} = E_{bonding} - 6\beta = 2\beta$$

- Compare these values to those found for 1,3,5 hexatriene and comment on why they are different

More than double the resonance stabilization energy

Benzene has 2 equally stable resonance structures, so the electrons fully delocalize around the ring. 1,3,5 hexatriene only partially delocalizes