Chem 4A Scholars Note 2

Hückel Theory and Aromatic Stabilization Energy

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Hückel Theory The molecular orbital energy levels of conjugated ring system can be calculated using Hückel's Method.

1. First, we know from lecture that a conjugated ring system with 4n+2 electrons is **aromatic**, whereas a conjugated ring system with 4n electrons is **antiaromatic**. (We will see where this comes from soon!)

2. Before going into conjugated systems, let's consider a single π bond. Set the original energy level of the p orbital to be α, and the energy of the π bonding orbital to be $\alpha + \beta$. (**Note:** β **is a negative number!**)Thus for a regular π bond, the energy level diagram should be:

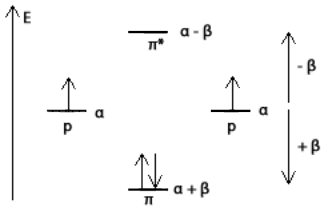

Figure 1: energy level diagram of a single π bond

Because there are 2 electrons in the π orbital, the stabilization energy is -2β. **Remember that** *stabilization energy***, like electron affinity, is a positive value.**

3. Now let's look at a simple ring system, benzene. There are six parallel p orbitals in benzene and one electron in each of the p orbitals. If no conjugation is allowed(i. e. electrons are localized in separate π bonds) The total stabilization energy contributed by the bonds are -6β. **However, this is not how benzene looks like!**

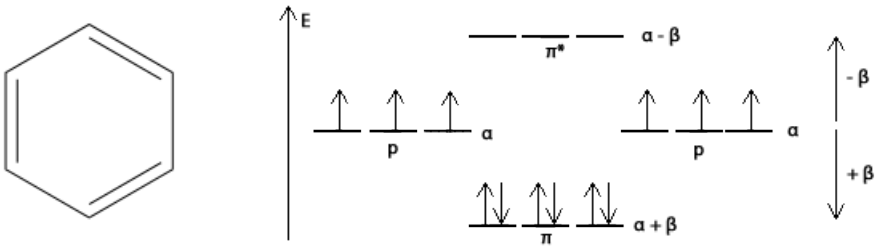

Figure 2: **Left:**One resonance structure of benzene **Right:**The MO diagram of π bonds in benzene if there is no conjugation.

4. In reality, π electrons are **delocalized** in the ring, this changes the energy structure of the molecular orbitals. The steps are rather straight forward.

5. First, we will draw a circle and fit the molecule into the circle, so that the vertices of the polygonal molecule all sit on the circle. **The polygon should have a single vertex at the lowest point in the circle.** On the energy scale, the center of the circle sits at α, and the radius of the circle is -2β, thus the bottom of the circle will have energy $\alpha + 2\beta$.

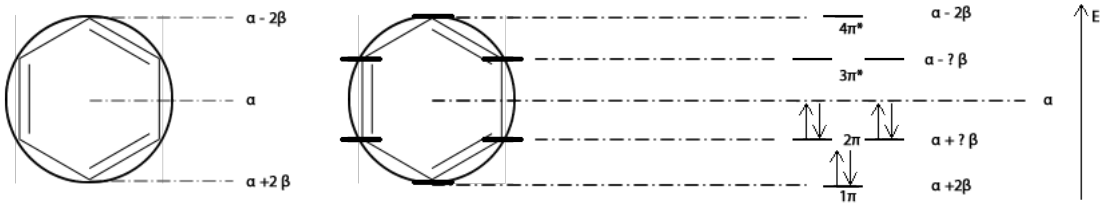

Figure 3: **Left:**Drawing the circle. **Right:** Drawing the energy level diagram.

6. Each vertex of the polygons correspond to one orbital, and the height of a vertex dictates the energy level of the molecular orbital. It's easy to determine the energy of the bottom and top energy levels. To calculate the energy of other levels, we can do some geometric calculations. The radius r of the circle is 2β, the angle of the vertex from the center line is θ, and the distance d of the vertex from the center line can be expressed as $d = 2\beta cos(\theta)$. In our case $\theta = 30°$, $cos(\theta) = 1/2$. Thus $d = \beta$. We now know all the energy levels of benzene.

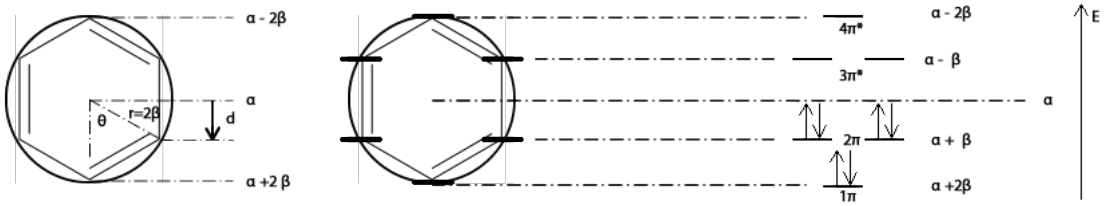

Figure 4: **Left:** Calculating the distance from one vertex to the center line. **Right:** The final MO diagram.

7. We can calculate the *total stabilization energy*. Here we have 2 electrons sitting in the lowest energy level 1π and 4 in 2π. The total stabilization energy due to both π bonding and conjugation is $-(2 \times 2\beta + 4 \times \beta) = -8\beta$. **Thus the total stabilization energy is -8β.**

8. We know that each double bond contribute 2β to the total stabilization energy. If there is extra stabilization energy it has to come from the ring conjugation.

$$\textit{aromatic stabilization energy} = \textit{total stabilization energy} - \textit{stabilization energy of separate double bonds} \quad (1)$$

The *aromatic stabilization energy* is then $-8\beta - 3 \times (-2\beta) = -2\beta$. **So aromatic stabilization energy for benzene is -2β.**

9. If we consider cyclobutadiene, we can easily see that the total stabilization energy is -4β, which is the same as in two separate double bonds, thus **there is no aromatic stabilization energy.** Thus cyclobutadiene is **antiaromatic**. It is always true that:

$$\text{For } \textbf{antiaromatic} \text{ system}, \quad \textit{aromatic stabilization energy} \leq 0 \quad (2)$$

$$\text{For } \textbf{aromatic} \text{ system}, \quad \textit{aromatic stabilization energy} > 0 \quad (3)$$

10. Generally, the energy levels of any conjugated polygonal ring system with N p orbitals can be approximated by the following equation:

$$E_n = \alpha + 2\beta cos(\frac{2(n-1)\pi}{N}) \quad n = 1, 2, 3..., \lceil N/2 \rceil \quad (4)$$

Note that some of the orbitals are degenerate(for the MOs in the middle of the diagram, each energy level has 2 orbitals) and n stand for the n*th* level of π orbitals.

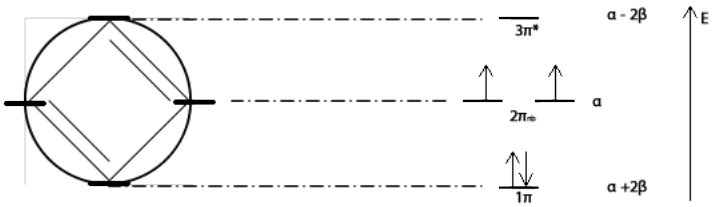

Figure 5: Cyclobutadiene has 4 electrons and 4 orbitals, it turns out that it's MO levels does not have extra stabilization energy. This is general true for any system with 4n electrons.

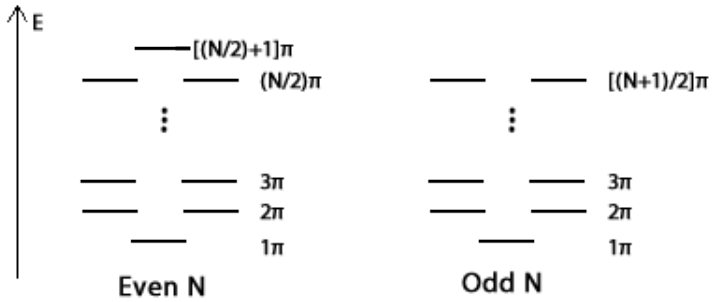

Figure 6: General Structure of any conjugated ring system with N parallel p orbitals.

11. Using equation 4, you can easily calculate the total stabilization energy of any conjugated ring systems. You can then calculate the aromatic stabilization energy. You should be able to distinguish between *total stabilization energy* from *aromatic stabilization energy*.

Linear conjugated systems In previous discussions, we have already used particle-in-a-box model to estimate the energy levels of a linear conjugated system. Hückel method gives a more accurate result. The energy level of a linear conjugated system can be calculated with the following equation:

$$E_n = \alpha + 2\beta cos(\frac{n\pi}{N+1}) \quad n = 1, 2, 3, ..., N \tag{5}$$

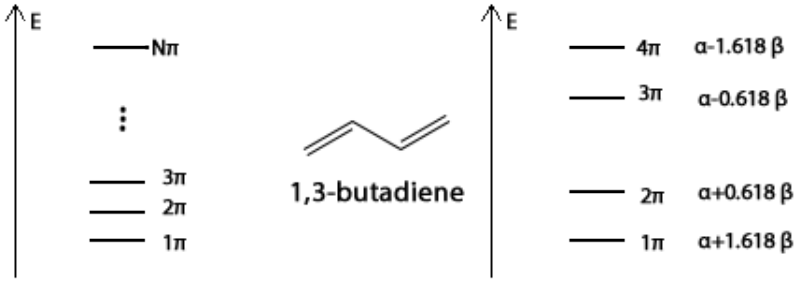

Figure 7: Linear conjugated system does not have degeneracy. 1,3-butadiene is a good example of such. The calculated energy levels are noted on the side of each orbital.

Exercises. Calculate the energy level of the following molecules. Using $\beta = -75kJ/mol$, determine the color of the molecules.

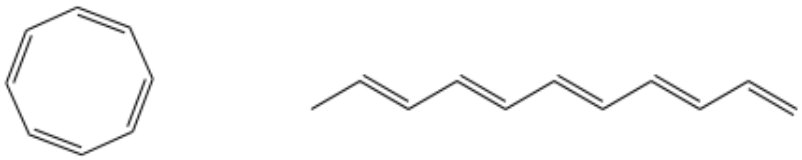

Figure 8: Exercise molecules

If you managed to get here, you should have learnt everything you need to know about aromaticity and conjugated π systems in Chem 4A. Specifically you will be able to solve question 3 in problem set 7 very quickly. Good luck! :)