Week 5

Aromaticity

5.1 Aromaticity 1

- Office hours: Tuesday and Friday at 4:00 PM.

- PSet 3 is due 2/17.

- Aromatic compounds are called such because they're often fragrant. They're heavily associated with biological systems.

- History of aromatic comounds.

  - 1825: Michael Faraday isolated a compound from his oil lamp having a C : H ratio of 1 : 1.
  - 1834: Benzoic acid plus heat makes $(CH)_n + CO_2$.
    - ■ Even hex-1,3,5-triene still has more hydrogens than carbons.
  - Benzene.
    - ■ There are about 60 possible structures for C_6H_6.
    - ■ **Dewer benzene** is two fused 4-member rings with alkenes on opposing sides.
    - ■ But benzene is highly unreactive in alkene reactions. . .
  - 1865: Kekulé proposed a "cyclohexatriene" structure.
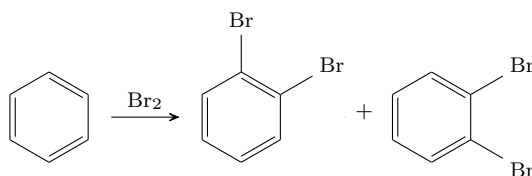

Figure 5.1: Bromination of cyclohexatriene.

  - ■ Evidence: You would expect bromination of cyclohexatriene to produce two products, but it only produces one (the two molecules must be rapidly interconverting, i.e., via resonance).
  - Chemists began looking for more similar compounds.
  - 1911: Cyclooctatriene was made.
    - ■ It can be hydrogenated, so not consistent with the low reactivity of benzene.
  - Cyclobutadiene was impossible to isolate due to a self-Diels-Alder reaction at any temperature greater than $-260\,°C$.

- Enthalpies of hydrogenation.

- Hydrogenation of cyclohexene has $\Delta H = -28.6$ kcal/mol.
    - Hydrogenation of cyclohex-1,4-diene has $\Delta H = -57.2$ kcal/mol.
    - Hydrogenation of cyclohex-1,3-diene has $\Delta H = -55.4$ kcal/mol.
        - ■ The 1.8 kcal/mol difference between the previous two comes from conjugation as predicted by resonance.
    - Hydrogenation of benzene has $\Delta H = -49.3$ kcal/mol.
        - ■ That is a huge stabilization effect.
- The bond lengths in benzene are all equally 1.39 Å.

- MO theory: We need a method to draw the MOs for flat, cyclic conjugated compounds. We will use the **Frost method**.

- For hexa-1,3,5-triene, six p-orbitals combine to make six MOs.
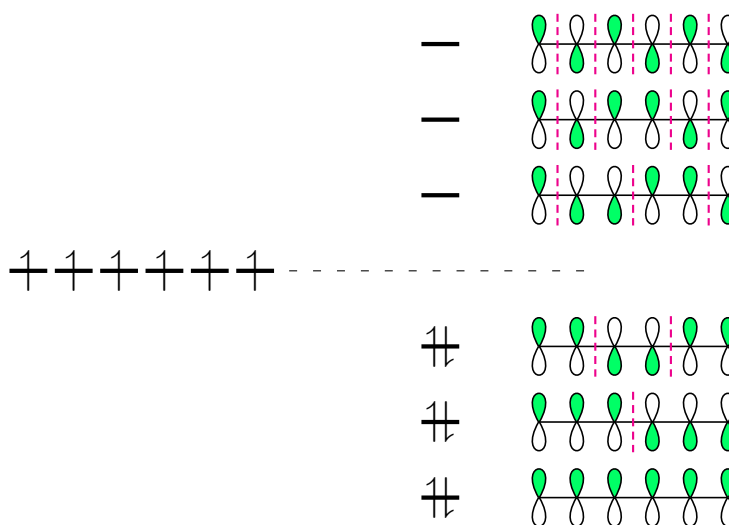

Figure 5.2: Hexa-1,3,5-triene MO diagram.

- Three are bonding; three are antibonding. We can guess at what the SALCs look like with a nodal analysis.

- For benzene, six p-orbitals combine to make six different MOs.

    - See Figures III.1 and III.2 in Labalme [1].
    - For conjugated cyclic systems with an even number of atoms, there will always be a single high and single low MO energy level.

- **Frost method**: The following procedure for drawing MOs for flat cyclic conjugated compounds.

    1. Draw a polygon of the molecule without double bonds and with a vertex at the bottom.
    2. Draw a line halfway through the structure.
    3. Put an MO at each vertex.

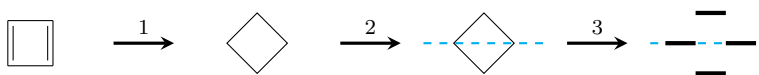- For example, if we want to find the MOs of butadiene, we do the following.

Figure 5.3: Frost method: Butadiene.

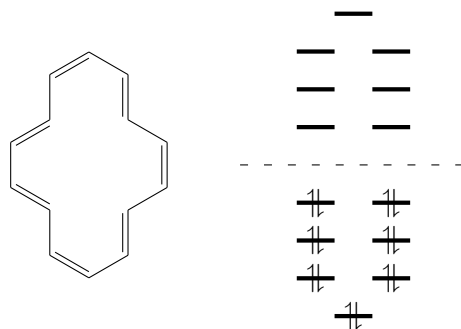- We can even apply this to cyclotetradecaheptaene.

Figure 5.4: Frost method: Cyclotetradecaheptaene.

- **($4n + 2$) rule**: If a system has $4n + 2$ π-electrons for $n \in \mathbb{N}_0$, then it is aromatic.

  - Alternatively, if all bonding orbitals are filled and there are no electrons in non-bonding or anti-bonding orbitals, then the compound is aromatic.

- **Anti-aromatic** (molecule): A flat cyclic conjugated molecule with an uninterrupted flow of p-orbitals that does not satisfy the ($4n + 2$) rule.

  - Alternatively, the molecule must have electrons in non-bonding or antibonding orbitals and six or fewer atoms in the cycle.

- **Non-aromatic** (molecule): A molecule with electrons in non-bonding or antibonding orbitals and seven or more atoms in the cycle.

- Unpaired electrons in nonbonding orbitals can be very destabilizing.

  - But since cyclooctatetraene is not flat (it's tub-shaped), it avoids the MO overlap that leads to anti-aromaticity.