Part A: Aromaticity

(What structures are likely to exhibit the special stability known as aromaticity?)

Model 1: Amazing Benzene!
Figure 1: Heats of Hydrogenation

Critical Thinking Questions
1. Based on the data in Figure 1, estimate the heat of hydrogenation for benzene (heat released when benzene is reduced to cyclohexane).

2. The heat of hydrogenation for benzene is -49 kcal/mole. Add a solid line to Figure 1 indicating this value for benzene. Is benzene lower in P.E. than you expected?

Model 2: Aromaticity
- Benzene and other similar molecules exhibit an almost magical stability (lower than expected potential energy).
- Before it was understood, this “magical stability” was named aromaticity because many molecules in this class have a strong aroma (smell).
- Resonance alone cannot explain this amazing stability.

The Racetrack Explanation: The electrons of benzene “think” they are in a huge box (the larger = lower P.E.) because they can race endlessly around a track of conjugated p orbitals. This racetrack of p orbitals is called a cyclic conjugated pi system.

Aromatic Conjugated π System

Normal Conjugated π System
Figure 2: Not all cyclic conjugated pi systems are aromatic!

Aromatic  Aromatic  Aromatic  Aromatic

Critical Thinking Questions
3. Confirm that there is a p orbital (empty or half-filled) at each carbon in Figure 2.
   a) Label each cyclic conjugated pi system in Figure 2 with the total # of pi electrons in the "racetrack." (These are the electrons in p orbitals.)
   b) Certain "magic numbers" of pi electrons give rise to aromaticity. According to the data in Figure 2, circle the "magic numbers" in the list below.

   2  4  6  8  10  12  14  16  18  20

   c) Of 12-20, which do you expect to be "magic" numbers that allow aromaticity.

4. In 1938 German chemist Erich Hückel noticed this series and wrote what has come to be called "Hückel's Rule," which states: "a continuous, cyclic, conjugated pi system exhibits aromaticity (special stability) if it contains 4n + 2 pi electrons (where n can = 0, 1, 2, 3...etc.)."
   a) Do the numbers you circled in part b), above, agree with Hückel's Rule?
   b) Only one of the following molecules is aromatic. Label it aromatic.

   Aromatic

5. A molecule is considered aromatic if it contains an aromatic pi system as part of it.
   i) Cross out the three molecules below that are not aromatic.
   ii) Trace each aromatic pi system ("racetrack") in the remaining (aromatic) molecules. The first two are done for you. (Note that the second example has two aromatic rings. Even though these two aromatic rings are conjugated together, they are considered separate "racetracks.")

   Aromatic

   Aromatic
6. A molecule is considered aromatic if you can draw a resonance structure with a continuous cyclic \( \pi \) system containing \( 4n+2 \) \( \pi \) electrons.
   a) The resonance structure below has a 6-electron aromatic \( \pi \) system. Draw a resonance structure of this molecule containing a 10-electron aromatic system.
   ![Resonance structure](image)
   Note: there are a total of three resonance structures in this set. Draw the third one at home for extra practice.
   
   b) The resonance structure below does not contain an aromatic \( \pi \) system. Draw a resonance structure of this molecule that is aromatic (contains an aromatic \( \pi \) system).
   ![Resonance structure](image)
   Note: there are a total of 11 resonance structures in this set. Only four of them contain an aromatic \( \pi \) system. Draw them at home for practice.
   
   c) How many \( \pi \) electrons are involved in the aromatic resonance structure you drew in part b?
   
   d) Which of the two resonance structures you drew in each set is more important? Explain your reasoning.

7. Consider the following orbital representations of benzene.
   ![Benzene orbital representations](image)
   
   a) Which \( \pi \) system (planar or not planar) has better \( p \) orbital racetrack?
   
   b) Is your conclusion consistent with the fact that benzene is always planar?
   
   c) Explain why all conjugated \( \pi \) systems (not just aromatic ones) are lower in potential energy when they are planar.

   For Example: ![Planar and non-planar structures](image)
   For both: all atoms lie in the plane of the paper.

8. Review: for a molecule to be aromatic it must have a \( \pi \) system... that is cyclic that is conjugated and uninterrupted (no \( sp^3 \) hybridized carbons in the ring) that has \( 4n+2 \) \( \pi \) electrons (2 or 6 or 10 or 14 etc.) whose overall geometry is ______ (fill in the blank).