Objectives

After completing this section, you should be able to

1. define aromaticity in terms of the Hückel $4n + 2$ rule.
2. use the Hückel $4n + 2$ rule to determine whether or not a given polyunsaturated cyclic hydrocarbon should exhibit aromatic properties.
3. describe the difference in properties between an aromatic hydrocarbon, such as benzene, and a non-aromatic polyunsaturated cyclic hydrocarbon, such as cyclobutadiene or cyclooctatetraene.
4. draw molecular orbital diagrams for aromatic species, such as benzene, the cyclopentadienyl anion and pyridine, and compare these diagrams with those obtained for non-aromatic species, such as cyclobutadiene and the cyclopentadienyl cation.

Study Notes

The following mnemonic device will help you establish the approximate energy levels for the molecular orbitals of various organic ring systems.

Whatever the size of the ring, place one point of the ring down to the bottom. The corners of the ring, where the carbons are located, will roughly approximate the location and pattern of the molecular orbital energy levels. Cut the ring exactly in half. The energy levels in the top half will be anti-bonding ($\Psi^*$) orbitals and those in the bottom will be bonding ($\Psi$) orbitals. If the carbons fall directly in the centre of the ring (e.g., four-membered rings) the energy levels there are non-bonding.

cyclopropenyl ring (three-membered ring)

cyclopentene structure and its molecular orbital levels

cyclobutadienyl ring (four-membered ring)

cyclobutadiene structure and its molecular orbital levels

cyclopentadienyl ring (five-membered ring)

cyclopentadiene structure and its molecular orbital levels

In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar molecule has $4n+2$ $\pi$ electrons, it is considered aromatic. This rule would come to be known as Hückel’s Rule.

Four Criteria for Aromaticity

When deciding if a compound is aromatic, go through the following checklist. If the compound does not meet all the following criteria, it is likely not aromatic.

1. The molecule is cyclic (a ring of atoms)
2. The molecule is planar (all atoms in the molecule lie in the same plane)
3. The molecule is fully conjugated (p orbitals at every atom in the ring)
4. The molecule has $4n+2$ $\pi$ electrons ($n=0$ or any positive integer)

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Why $4n+2$ $\pi$ Electrons?

According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. This is true of aromatic compounds, meaning they are quite stable. With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by $n$), leaving all bonding orbitals filled and no anti-bonding orbitals occupied. This gives a total of $4n+2$ $\pi$ electrons. You can see how this works with the molecular orbital diagram for the aromatic compound, benzene, below. Benzene has 6 $\pi$ electrons. Its first 2 $\pi$ electrons fill the lowest energy orbital, and it has 4 $\pi$ electrons remaining. These 4 fill in the orbitals of the succeeding energy level. Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electrons.

To apply the $4n+2$ rule, first count the number of $\pi$ electrons in the molecule. Then, set this number equal to $4n+2$ and solve for $n$. If $n$ is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six $\pi$ electrons:

\[
\begin{align*}
4n + 2 &= 6 \\
4n &= 4 \\
\quad n &= 1
\end{align*}
\]

For benzene, we find that $n=1$, which is a positive integer, so the rule is met.

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How Can You Tell Which Electrons are $\pi$ Electrons?

Perhaps the toughest part of Hückel's Rule is figuring out which electrons in the compound are actually $\pi$ electrons. Once this is figured out, the rule is quite straightforward. $\pi$ electrons lie in $p$ orbitals and $sp^2$ hybridized atoms have 1 $p$ orbital each. So if every molecule in the cyclic compound is $sp^2$ hybridized, this means the molecule is fully conjugated...
(has 1 p orbital at each atom), and the electrons in these p orbitals are the π electrons. A simple way to know if an atom is sp\(^2\) hybridized is to see if it has 3 attached atoms and no lone pairs of electrons. This video provides a very nice tutorial on how to determine an atom's hybridization. In a cyclic hydrocarbon compound with alternating single and double bonds, each carbon is attached to 1 hydrogen and 2 other carbons. Therefore, each carbon is sp\(^2\) hybridized and has a p orbital.

Let's look at our previous example, benzene:

Each double bond (π bond) always contributes 2 π electrons. Benzene has 3 double bonds, so it has 6 π electrons.

### Aromatic Ions

Hückel's Rule also applies to ions. As long as a compound has 4n+2 π electrons, it does not matter if the molecule is neutral or has a charge. For example, cyclopentadienyl anion is an aromatic ion. How do we know that it is fully conjugated? That is, how do we know that each atom in this molecule has 1 p orbital? Let's look at the following figure. Carbons 2-5 are sp\(^2\) hybridized because they have 3 attached atoms and have no lone electron pairs. What about carbon 1? Another simple rule to determine if an atom is sp\(^2\) hybridized is if an atom has 1 or more lone pairs and is attached to an sp\(^2\) hybridized atom, then that atom is sp\(^2\) hybridized also. This video explains the rule very clearly. Therefore, carbon 1 has a p orbital. Cyclopentadienyl anion has 6 π electrons and fulfills the 4n+2 rule.

### Heterocyclic Aromatic Compounds

So far, you have encountered many carbon homocyclic rings, but compounds with elements other than carbon in the ring can also be aromatic, as long as they fulfill the criteria for aromaticity. These molecules are called heterocyclic compounds because they contain 1 or more different atoms other than carbon in the ring. A common example is furan, which contains an oxygen atom. We know that all carbons in furan are sp\(^2\) hybridized. But is the oxygen atom sp\(^2\) hybridized? The oxygen has at least 1 lone electron pair and is attached to an sp\(^2\) hybridized atom, so it is sp\(^2\) hybridized as well. Notice
how oxygen has 2 lone pairs of electrons. How many of those electrons are \( \pi \) electrons? An \( sp^2 \) hybridized atom only has 1 p orbital, which can only hold 2 electrons, so we know that 1 electron pair is in the p orbital, while the other pair is in an \( sp^2 \) orbital. So, only 1 of oxygen's 2 lone electron pairs are \( \pi \) electrons. Furan has 6 \( \pi \) electrons and fulfills the \( 4n+2 \) rule.

\[
\text{O is } sp^2 \text{ hybridized}
\]

\[
\text{furan has 6 } \pi \text{ electrons}
\]

A Common Misconception

A very common misconception is that hybridization can be used to predict the geometry, or that hybridization somehow involves an energy cost associated with 'promoting' electrons into the hybrid orbitals. **This is entirely wrong.** Hybridization is always determined by geometry. You can only assign hybridization states to an atom if you already know its geometry, based on some experimental or theoretical evidence. The geometry of the oxygen in furan is trigonal planar and therefore the hybridization must be \( sp^2 \).

The **specific** rule is that if you have an \( \langle sp^2 \rangle \) conjugated system, the lone pair will be involved **if it makes the system more stable**. In this case, conferring Hückel \( \langle 4n+2 \rangle \) aromaticity. For furan with two lone pairs on the oxygen atom, if we count electrons from the carbon atoms, we have 4 (one per carbon). So adding two electrons from one of the lone pairs will give 6 = 4(1)+2, so Hückel rule is applicable and furan is aromatic.

Problems

Using the criteria for aromaticity, determine if the following molecules are aromatic:

\[
\text{Answers}
\]

1. Aromatic - only 1 of S's lone pairs counts as \( \pi \) electrons, so there are 6 \( \pi \) electrons, \( n=1 \)
2. Not aromatic - not fully conjugated, top C is \( sp^3 \) hybridized
3. Not aromatic - top C is \( sp^2 \) hybridized, but there are 4 \( \pi \) electrons, \( n=1/2 \)
4. Aromatic - N is using its 1 p orbital for the electrons in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1

5. Aromatic - there are 6 π electrons, n=1

6. Not aromatic - all atoms are sp² hybridized, but only 1 of S's lone pairs counts as π electrons, so there 8 π electrons, n=1.5

7. Not aromatic - there are 4 π electrons, n=1/2

8. Aromatic - only 1 of N's lone pairs counts as π electrons, so there are 6 π electrons, n=1

9. Not aromatic - not fully conjugated, top C is sp³ hybridized

10. Aromatic - O is using its 1 p orbital for the elections in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1

References


Exercises

Questions

Q15.3.1

To be aromatic, a molecule must be planar conjugated, and obey the 4n+2 rule. The following is the following molecule aromatic?

![Octagon](image)

Solutions

S15.3.1

No, it is not. It does not obey the 4n+2 rule. Also it is not planar.
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