1. Use a Frost circle to determine the relative energies for the molecular orbitals for the following structures. Show the proper electron occupancy of the molecular orbitals.

![Molecular Orbitals](image)

See Next Page for Answers

2. Which of the molecules in question 1 will be aromatic?

See Next Page for Answers

3. Explain whether each of the following structures is aromatic, antiaromatic, or neither.

![Structures](image)

The cyclopropene carbanion has 4 π electrons and will be anti-aromatic since the ring must be planar. The definition for a ring being anti-aromatic is to contain 4\(\pi\) electrons and be planar. The cyclopentadiene carbanion has 6 π electrons (4\(n\) + 2) and will be aromatic. The cycloheptatriene dianion contains 8 π electrons (4\(n\)) and will be antiaromatic if the ring is flat. If the ring is not flat, then the compound will be non-aromatic.

4. Cyclooctatetraene readily reacts with potassium metal to form a dianion. Discuss the electronic structure and geometry of this dianion and explain why it is formed so readily.

![Reaction](image)

The cyclooctatetraene dianion will contain 10 electrons in its π system (4\(n\) + 2). Therefore, the ring will become flat and gain the aromatic stabilization energy. This dianion is easily formed because the molecule is aromatic.
Answer to Question 1

\[
\begin{align*}
\text{Aromatic} & \quad \Rightarrow \quad \text{Anti-aromatic} \\
\text{Anti-aromatic if ring is flat} & \quad \Rightarrow \quad \text{Aromatic} \\
\text{Anti-aromatic} & \quad \Rightarrow \quad \text{Aromatic} \\
\text{Aromatic} & \quad \Rightarrow \quad \text{Anti-aromatic} \\
\text{Anti-aromatic if ring is flat} & \quad \Rightarrow \quad \text{Aromatic} \\
\text{Aromatic} & \quad \Rightarrow \quad \text{Anti-aromatic} \\
\text{Aromatic} & \quad \Rightarrow \quad \text{Anti-aromatic if ring is flat} \\
\text{Non-aromatic} & \quad \Rightarrow \quad \text{Anti-aromatic if ring is flat}
\end{align*}
\]
5. Draw the six molecular orbitals for the 1,3,5-hexatriene $\pi$-system and identify the HOMO and LUMO.

\[ \begin{align*}
\Psi_6 & \\
\Psi_5 & \\
\Psi_4 & \quad \text{LUMO} \\
\Psi_3 & \quad \text{HOMO} \\
\Psi_2 & \\
\Psi_1 &
\end{align*} \]

6. Looking at the molecular orbitals for butadiene and ethylene shown below, identify the HOMO and LUMO for each compound’s molecular orbitals.

\[ \begin{align*}
\Psi_4 & \\
\Psi_3 & \quad \text{LUMO} \\
\Psi_2 & \quad \text{HOMO} \\
\Psi_1 & \quad \text{HOMO} \\
\text{Butadiene MO’s} & \\
\text{Ethylene MO’s} &
\end{align*} \]

7. Briefly explain why a Diels Alder reaction can easily occur between the two molecules above.

The bonds being formed in a Diels-Alder reaction are between the terminal carbons in the above two $\pi$ systems. The interaction must be from the HOMO of one molecule (butadiene) and the LUMO of the other (ethylene). In the above case, the reaction will be symmetry allowed. Look at the shading of the p-orbitals on the terminal carbons in $\Psi_2$ of butadiene (HOMO) and $\Psi_2$ of ethylene (LUMO). These orbitals will allow for constructive overlap and the formation of two new $\sigma$ bonds via a Diels-Alder reaction.

Consider the following reaction:

\[ \begin{array}{c} \text{Butadiene} \\
\text{Ethylene} \end{array} \rightarrow \text{Cyclohexadiene} \]

8. Briefly explain why this reaction does not easily occur. (Look back at the MO’s for butadiene in question 6)

Looking at the MO’s for butadiene, the HOMO and LUMO do not have the proper symmetry to allow new $\sigma$ bonds to form by overlap of the p orbitals on the terminal carbons.
9. If an electron is photochemically promoted in some butadiene molecules into $\Psi_3$, the reaction shown above proceeds easily. Briefly explain why.

The molecules which have had an electron photochemically promoted to $\Psi_3$ have $\Psi_5$ as their HOMO. These molecules will be able to react with the unexcited molecules which have $\Psi_3$ as the LUMO because the orbital symmetries match.

10. 2,4-Cyclopentadienone is unstable and cannot be isolated, whereas 2,4,6-cycloheptatrienone is quite stable and can be readily isolated. Use arguments based on resonance and aromaticity to explain these experimental observations. (HINT: Recall a resonance structure that is commonly written for the carbonyl group.)

The carbonyl group is polarized with the electrons closer to the more electronegative oxygen atom. The carbocation-like character this places on the carbon atom has differing effects in the above two molecules. 2,4,6-Cycloheptatrienone will be stable because the ring easily moves to the carbocation extreme because it will form an aromatic ring. 2,4-Cyclopentadienone, on the other hand, will be anti-aromatic if the carbocation is formed at the carbonyl carbon.

11. The following fluorinated compound is a stronger acid than nitric acid. Briefly explain this.

When the above compound loses the acidic hydrogen, a cyclopentadienyl carbanion is formed. This ring system is stable because it is aromatic. The trifluoromethyl groups help further stabilize the carbanion by pulling electron density towards the fluorines through inductive effects.

12. The amino acid histidine contains an imidazole ring. In many enzymes this ring acts as a base for catalysis. Explain which nitrogen of the imidazole ring is more basic and show the structure of the conjugate acid of imidazole.

The $sp^2$ hybridized nitrogen is more basic. The imidazole ring can become aromatic if it can get two more electrons from one of the nitrogens. Only the $sp^3$ hybridized nitrogen is in a position to donate its lone pair of electrons into the $\pi$ system of the imidazole ring. The lone pair of electrons on the $sp^2$ hybridized nitrogen are perpendicular to the $\pi$ system of the ring. Therefore, the $sp^3$ hybridized nitrogen will use its lone pair of electrons to make the imidazole ring aromatic. This means that those electrons are not available to be donated to an electrophile.
13. When 7-fluoro-1,3,5-cycloheptatriene is dissolved in SbF$_5$/SO$_2$, a species is produced that shows a singlet at a chemical shift of 9.2 ppm in its H$^1$-NMR spectrum. Show the structure of this species and briefly explain why its chemical shift is so far downfield.

![Chemical structure](image)

The product of the above reaction will be the aromatic cycloheptatrienyl cation. Since the ring is aromatic, the $\pi$ electrons are evenly distributed around the ring and all of the hydrogens will be magnetically equivalent (this accounts for the singlet in the NMR). The chemical shift is quite downfield because of the positive charge on the molecule. Chemical shift is related to electron density with an increased downfield shift as the electron density decreases.