Objectives

After completing this section, you should be able to

1. draw the structure of the common aromatic heterocycles pyridine and pyrrole.
2. use the Hückel $4n + 2$ rule to explain the aromaticity of each of pyridine and pyrrole.
3. draw a diagram to show the orbitals involved in forming the conjugated six-pi-electron systems present in aromatic heterocycles such as pyridine, pyrrole, etc.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- carbocycles
- heterocycles

Aromatic Heterocycles

Many unsaturated cyclic compounds have exceptional properties that we now consider characteristic of "aromatic" systems. The following cases are illustrative:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structural Formula</th>
<th>Reaction with Br₂</th>
<th>Thermodynamic Stabilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Reaction</td>
<td>Result</td>
<td></td>
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<tr>
<td>---------------------------</td>
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<tr>
<td>1,3-Cyclopentadiene</td>
<td>Addition</td>
<td>Slight</td>
<td></td>
</tr>
<tr>
<td>1,3,5-Cycloheptatriene</td>
<td>Addition</td>
<td>Slight</td>
<td></td>
</tr>
<tr>
<td>1,3,5,7-Cyclooctatetraene</td>
<td>Addition</td>
<td>Slight</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>Substitution</td>
<td>Large</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>Substitution</td>
<td>Large</td>
<td></td>
</tr>
<tr>
<td>Furan</td>
<td>Substitution</td>
<td>Moderate</td>
<td></td>
</tr>
<tr>
<td>Pyrrole</td>
<td>Substitution</td>
<td>Moderate</td>
<td></td>
</tr>
</tbody>
</table>

Benzene is the archetypical aromatic compound. It is planar, bond angles=120°, all carbon atoms in the ring are sp² hybridized, and the pi-orbitals are occupied by 6 electrons. The aromatic heterocycle pyridine is similar to benzene, and is often used as a weak base for scavenging protons. Furan and pyrrole have heterocyclic five-membered rings, in which the heteroatom has at least one pair of non-bonding valence shell electrons. By hybridizing this heteroatom to a sp² state, a p-orbital occupied by a pair of electrons and oriented parallel to the carbon p-orbitals is created. The resulting planar ring meets the first requirement for aromaticity, and the π-system is occupied by 6 electrons, 4 from the two double bonds and 2 from the heteroatom, thus satisfying the Hückel Rule.

Four illustrative examples of aromatic compounds are shown above. The sp² hybridized ring atoms are connected by brown bonds, the π-electron pairs and bonds that constitute the aromatic ring are colored blue. Electron pairs that are not part of the aromatic π-electron system are black. The first example is azulene, a blue-colored 10 π-electron aromatic
hydrocarbon isomeric with naphthalene. The second and third compounds are heterocycles having aromatic properties. Pyridine has a benzene-like six-membered ring incorporating one nitrogen atom. The non-bonding electron pair on the nitrogen is not part of the aromatic \( \pi \)-electron sextet, and may bond to a proton or other electrophile without disrupting the aromatic system. In the case of thiophene, a sulfur analog of furan, one of the sulfur electron pairs (colored blue) participates in the aromatic ring \( \pi \)-electron conjugation. The last compound is imidazole, a heterocycle having two nitrogen atoms. Note that only one of the nitrogen non-bonding electron pairs is used for the aromatic \( \pi \)-electron sextet. The other electron pair (colored black) behaves similarly to the electron pair in pyridine.

Heterocycles - cyclic structures in which the ring atoms may include oxygen or nitrogen - can also be aromatic. Pyridine, for example, is an aromatic heterocycle. In the bonding picture for pyridine, the nitrogen is \( sp^2 \)-hybridized, with two of the three \( sp^2 \) orbitals forming sigma overlaps with the \( sp^2 \) orbitals of neighboring carbon atoms, and the third nitrogen \( sp^2 \) orbital containing the lone pair. The unhybridized \( p \) orbital contains a single electron, which is part of the 6 \( \pi \)-electron system delocalized around the ring.

Why do we not assume that the nitrogen in pyrrole is \( sp^3 \)-hybridized, like a normal secondary amine? The answer is simple: if it were, then pyrrole could not be aromatic, and thus it would not have the stability associated with aromaticity. In general, if a molecule or group can be aromatic, it will be, just as water will always flow downhill if there is a downhill pathway available.

Imidazole is another important example of an aromatic heterocycle found in biomolecules - the side chain of the amino acid histidine contains an imidazole ring.

In imidazole, one nitrogen is 'pyrrole-like' (the lone pair contributes to the aromatic sextet) and one is 'pyridine-like' (the
lone pair is located in an $sp^2$ orbital, and is \textit{not} part of the aromatic sextet).

### Exercises

#### Questions

**Q15.5.1**

Draw the orbitals of thiophene to show that is aromatic.

![Thiophene orbital diagram](image)

**Q15.5.2**

The following ring is called a thiazolium ring. Describe how it is aromatic.

![Thiazolium ring](image)

#### Solutions

**S15.5.1**

This drawing shows it has 6 electrons in the pi-orbital.

![Thiophene solution](image)

**S15.5.2**

Similar to the last question, the drawing shows that there is only 6 electrons in the pi-system.
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