Aromatic Heterocycles

While benzene is the archetypical aromatic compound, many unsaturated cyclic compounds have exceptional properties that we now consider characteristic of "aromatic" systems. The aromatic heterocycle pyridine is similar to benzene, and is often used as a weak base for scavenging protons. 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.

Pyrrole, furan, and thiophene 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 $sp^2$ 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 $\pi$-system is occupied by 6 electrons, 4 from the two double bonds and 2 from the heteroatom, thus satisfying the Hückel Rule.

Four additional examples of heterocyclic aromatic compounds are shown below.

The first example is azulene, a blue-colored 10 $\pi$-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 is weakly basic and behaves similarly to the electron pair in pyridine.

The Two Nitrogens of Imidazole

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 nitrogen is ‘pyridine-like’ (the lone pair is located in an $sp^2$ orbital, and is not part of the aromatic sextet). The diagram below shows how the lone pair electrons on the nitrogen atoms differ.

Basicity versus Aromaticity

When the nitrogen atom of an aromatic heterocycle contains a pi bond, then the lone pair occupies an $sp^2$ orbital and is available to react as a weak base. We can view these nitrogens as being “pyridine like”. When the nitrogen atom of an aromatic heterocycle has single bonds only, then the nitrogen is still $sp^2$ hybridized, but the lone pair occupies the unhybridized $p$ orbital to create aromaticity. This lone pair is part of the conjugated $pi$ electron system and is not available to react as a weak base.

Exercise

6. Draw the orbitals of thiophene to show that is aromatic.
7. The following ring is called a thiazolium ring. Describe how it is aromatic.

8. The nitrogenous bases for the nucleotides of DNA and RNA are shown below. Determine which nitrogen atoms are weak bases and which nitrogen atoms have lone pairs contributing to the aromaticity of the compound.

Answer

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

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