Lecture 5: Introduction to Aromaticity
Discussion Section Problems Solutions

1. **Similarities:**
   - Conjugation and aromaticity both provide special stabilization relative to nonconjugated or nonaromatic isomers.
   - Both involve extended pi electron systems, featuring parallel and overlapping $p$ orbitals.
   - Both require that the atoms bearing the $p$ orbitals of the pi electron cloud to be planar, in order to maximize the overlap of these adjacent $p$ orbitals.

**Differences:**
- The $p$ orbitals that overlap to form the $\pi$ molecular orbitals of an aromatic molecule must be in a continuous loop whereas conjugated molecules may be cyclic or acyclic.
- An aromatic molecule incorporates $4n + 2$ pi electrons whereas a conjugated molecule does not have this restriction.

*Other similarities and differences exist.*

2. (a) Phenanthrene has a closed loop of $p$ orbitals (the circled atoms shown below), and no significant strain issues that prevent planarity. It has fourteen pi electrons ($n = 3$). Therefore phenanthrene is aromatic.

(b) Two $sp^3$ carbons interrupt the $p$ orbital loop, so Dewar benzene is not aromatic.

(c) Pyrrole is aromatic. The nitrogen atom uses $sp^2$ hybrid orbitals in order to place the lone pair in a $p_z$ orbital and give six pi electrons (two each from the two C=C and two more from the nitrogen lone pair).
(d) Oxazole is aromatic.

(e) If the nitrogen is $sp^2$, tryptophan has a closed loop of $p$ orbitals and ten pi electrons: Eight in the four C=C and two in the $sp^2$ nitrogen lone pair, so $n = 2$. (The atoms with $p$ orbitals that are part of the aromatic electron cloud are shown below). There are no significant strain issues that prevent planarity. Therefore tryptophan is aromatic.

(f) In a planar conformation, there is a severe nonbonded (van der Waals) interaction (torsional strain) between two hydrogens. (Verify this with a model!) The energy increase due to this strain more than offsets the stability due to aromaticity. Therefore the molecule adopts the lowest energy conformation: nonplanar but without severe hydrogen-hydrogen repulsion. (The problematic hydrogens adopt “axial” positions.)

3. Only two solutions are presented for each part, but many other solutions are possible.

(a) ![Furan](image1) ![Thiophene](image2)  
Furan  
Thiophene

(b) ![Cyclopropenyl cation](image3) ![Thiazole](image4)  
Cyclopropenyl cation  
Thiazole

4. Each face of the benzene molecule bears a cyclic cloud of pi electrons formed by overlap of the six $p_z$ orbitals, as shown below. The electron clouds comprise the two
halves of the bagel, and the carbon ring is the cream cheese (or whatever else you like on your bagel).

Examine a model to explore more thoroughly the nature of benzene’s pi electron cloud.

5. Each of the five heterocycles is not forced out of planarity by strain. Each nitrogen atom within the ring must be \(sp^2\) to allow for the closed loop of \(p\) orbitals. Contributions to each base’s pi electron cloud are shown below.

**Adenosine:** \(3 \times C=N + C=C + N\) lone pair = 10 pi electrons.

\[
\text{Adenosine: } 3 \times C=N + C=C + N\text{ lone pair} = 10\text{ pi electrons.}
\]

\[
\text{Cytosine: } C=N + C=C + N\text{ lone pair} = 6\text{ pi electrons.}
\]

\[
\text{Guanine: } 2 \times C=N + C=C + 2\text{ N lone pair} = 10\text{ pi electrons.}
\]

\[
\text{Thymine: } C=C + 2\text{ N lone pairs} = 6\text{ pi electrons.}
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\[
\text{Uracil: } \text{Uracil is similar to thymine, minus the methyl group. The absence of this methyl group does not alter the aromaticity.}
\]

6. (a) Kekulé benzene is the structure with three alternating \(C=C\) inside a six-membered ring.
Kekulé benzene resonance contributors

5-Fluorouracil resonance contributors

(b) The 5-fluorouracil “benzenoid” resonance contributor is aromatic. It has a continuous loop of $p$ orbitals (the two nitrogens are $sp^2$), no significant torsional strain issues that prevent planarity, and six pi electrons ($n = 1$).

(c) The single most important resonance contributor for 5-fluorouracil conforms to the greatest number of resonance contributor preference rules. Aromaticity must be considered as well. (An aromatic resonance contributor that violates one preference rule might be more significant than other nonaromatic resonance contributor that obeys all the preference rules.) The “diamide” contributor obeys all preference rules, and is also aromatic, so it is the best resonance contributor.