# Nuggets of Knowledge for Chapter 17.5 – Aromatic Compounds I Chem 2320

## I. Aromaticity

### The problem of benzene

- Benzene was first isolated in 1825 by Michael Faraday. He measured the boiling point at 800 and found its empirical formula to be CH, an unusually low carbon to hydrogen ratio.
- In 1834, the molecular weight was found to be 78, which meant that the molecular formula was C<sub>6</sub>H<sub>6</sub>. Many structures were proposed, but they did not match the properties or reactivity of the compound.
- In 1866, a cyclic structure with alternating single and double bonds was proposed by Freidrich Kekule.
  - However, this structure predicted the existance of two isomers of 1,2-dichlorbenzene, and only one was known to exist. It was thought that perhaps these two isomers were in rapid equilibrium with each other, but this turned out to be false.
- Several pieces of evidence led to a resonance model of benzene: all C-C-C bond angles are 120°, all of the C-C bonds are the same length (1.397 angstroms), the ring is planar, and all carbons are sp<sup>2</sup> hybridized. All of this observations are explained by having two resonance structures in which the double bonds are shared between all carbons, making the bond order 1.5 for all bonds.
  - Because of this, benzene rings are often drawn with a circle in the middle, rather than 3 alternating double bonds. This is more accurate, but makes it harder to keep track of the electrons.
- Benzene shows very different reactivity than alkenes.
  - Alkenes react with KMnO<sub>4</sub> to give vicinal diols, and with bromine to give vicinal dibromides, both of which are used as chemical tests. Benzene shows no reaction with these reagents.
  - $\circ$  If FeBr<sub>3</sub> and bromine are reacted with benzene, a product is formed, but it is a substitution rather than an addition product.
  - These observations lead to the conclusion that benzene is unusually stable, more so than would be predicted from just the resonance structures.
- Heats of hydrogenation can be used to determine the stability of hydrocarbons which give the same product. To calculate the stability of benzene, we compare the following:

- The heat of hydrogenation of cyclohexene is -120 kJ/mol, while the heat of hydrogenation of 1,4-cyclohexadiene is -240 kJ/mol. This is exactly double, showing that for every double bond in a compound, we would expect -120 kJ/mol to be generated.
- The heat of hydrogenation of 1,3-cyclohexadiene is -232 kJ/mol. This is 8 kJ/mol less than we would expect, so we conclude that the conjugated diene is more stable than the isolated one by 8 kJ/mol.
- The heat of hydrogenation of benzene is -208 kJ/mol. This is an amazing 151 kJ/mol below what we would predict for three double bonds. This is much more stable than can be accounted for simply by having two resonance structures.
- Other cyclic compounds with alternating double bonds do not all show this special stabilization.
  - $\circ$  Cyclobutadiene (C<sub>4</sub>H<sub>4</sub>) is so unstable it cannot be isolated except when synthesized in frozen argon.
  - $\circ$  Cyclooctadiene (C<sub>8</sub>H<sub>8</sub>) behaves just like a regular diene, undergoing alkene reactions.
  - $\circ$  [14]annulene (C<sub>14</sub>H<sub>14</sub>) shows some stabilization similar to benzene.
- The key to explaining the properties of benzene (and other aromatic compounds) is in the molecular orbitals.
  - Benzene has 6 p orbitals which combine to form 6 pi orbitals. The energy of these orbitals has the shape of a hexagon one lowest, two next at the same energy, then two more, then one highest.
    - The lowest pi orbital has no nodes, the second two have one node, the next two have two nodes, and the last one has three nodes. (The orbitals with the same number of nodes and the same energy are called "degenerate" orbitals.)
    - The three lowest orbitals are occupied by 3 pairs of electrons, making a stable compound.
  - Cyclobutadiene has 4 p orbitals which combine to form 4 pi orbitals. The energy of these orbitals has the shape of a diamond one lowest, two next at the same energy, then one highest.
    - The lowest pi orbital has no nodes, the second two have one node, and the highest one has two nodes.

• The lowest orbital is occupied by a pair of electrons, but the next two are occupied by only one electron each, making the compound a diradical and very unstable.

#### Rules for aromaticity

- Aromatic compounds can be identified using the following rules.
  - The compound must be cyclic. The pattern of pi orbitals that is characteristic of aromatic compounds only works if the pi orbitals are in a circle; in noncyclic compounds, the pattern of the pi orbitals is simply one on top of the other.
- Each atom in the ring must have an unhybridized p orbital to contribute to the pi system. That means that all atoms must be sp<sup>2</sup> (or sp).
  - $\circ$  If there are any atoms that are sp<sup>3</sup>, then the compound cannot be aromatic.
  - If the compound contains a triple bond, only one set of p orbitals can participate in the pi system, because the other one will be perpendicular rather than in line with it.
  - $\circ$  Carbocations are sp<sup>2</sup> hybridized, so they can be involved in aromatic compounds.
  - $\circ$  Atoms with lone pairs and no double bonds are usually sp<sup>3</sup> hybridized; however, if all other atoms in a ring have a p orbital, the atom with the lone pairs will actually be sp<sup>2</sup>.
- The number of electrons in the pi orbitals must fit the formula 4n +2, where n is any integer. In other words, the number of pi electrons must be 2, 6, 10, 14, etc. This is called Huckel's rule.
- If the compound meets all of the other criteria for aromaticity (cyclic, p orbital on every atom) but has a number of pi electrons that fits the formula 4n (such as 4, 8, 12, etc), then the compound will be antiaromatic. This means that it will be particularly unstable, like cyclobutadiene.
  - A five-membered ring with two double bonds and a pair of electrons will be aromatic, since it has 6 pi electrons.
  - A five-membered ring with two double bonds and a carbocation will be antiaromatic, since it has 4 pi electrons.
- The compound must be planar in order to be aromatic or antiaromatic.
  - In general, if a compound would be aromatic if it were planar, it will be planar unless there is too much ring strain.

- [10]annulene with all cis C=C's would be aromatic if it were flat, but there is too much ring strain, so it is nonaromatic.
- [14]annulene with 4 trans C=C's is flat, and has the right number of pi electrons, so it is aromatic.
- In general, if a compound would be aromatic if it were planar, it will bend and twist to avoid this.
  - Cyclooctatetraene would be antiaromatic if it were flat, so it takes a boat conformation and is nonaromatic.
  - Pentalene is antiaromatic because it is too rigid to avoid being planar.
- If a compound has non-carbon atoms in the ring, it is important to determine what kind of orbital the lone pairs are in only electrons in p orbitals can participate in the pi system.
  - If the atom is involved in a double bond, its lone pair electrons are in one of the sp<sup>2</sup> orbitals rather than a p orbital (because the p orbital is involved in making the double bond), so they cannot be counted as part of the pi electrons.
  - If the atom has two lone pairs, only one of them can be in a p orbital at a time; the other one will be in an sp<sup>2</sup> orbital.
- Not all aromatic compounds are as stable as benzene. The amount of resonance energy varies for each aromatic compound. To say a compound is aromatic simply means that it is unusually stable compared to similar compounds which are not aromatic.

### Effects of Aromaticity on Reactions

- If a compound forms an aromatic anion, then it will be unusually acidic.
  - For example, cyclopentadiene has a pKa of 16, while cyclopentane has a pKa of around 50 that's10<sup>35</sup> times more acidic!
- If a compound forms an aromatic carbocation, then it will be able to dissociate unusually well, and be more stable than regular carbocations. On the other hand, if it would form an antiaromatic carbocation, it will not dissociate.
- If a cyclic compounds containing N is aromatic, then its basicity will be decreased if the conjugate acid is not aromatic. The conjugate acid will have unusually high acidity.

# **II. Introduction to Compounds Containing Benzene Rings**

#### Nomenclature

- When a benzene ring is the principle chain and there are no principle groups, the name ends in benzene.
- If there is a principle group (such as an alcohol) that is on a chain separate from the ring, the chain takes priority.
  - When the benzene ring is named as a substituent, it is called a phenyl group.
  - The term "benzyl" is only used in common names such as benzyl chloride.
- There are several compounds with a benzene ring and one substituent; many of these have common names which should be memorized.
  - You will need to know toluene, phenol, anisole, aniline, styrene, acetophenone, benzaldehyde, and benzoic acid.
  - When using these names as the principle chain, the group that gives the name is assumed to be in the first position, but a number isn't included in the name: 2-hydroxyacetophenone.
- A nitro group (-NO<sub>2</sub>) is most commonly found on benzene rings. It has a positively charged nitrogen bonded to two oxygens, each with 1.5 bonds and 1/2 a negative charge. It is usually represented using resonance structures (or, more simply, the formula).
- When there are only two substituents on a benzene ring, an older system of naming is sometimes used (note: this cannot be used with cyclohexane rings).
  - ortho: substituents which have a 1,2 relationship
  - meta: substituents which have a 1,3 relationship
  - para: substituents which have a 1,4 relationship
- In compounds with an OH and a functional group containing a C=O, the C=O group has priority.

### **Physical Properties**

• Solubility: Aromatic compounds with no polar groups or only one polar group are insoluble or slightly soluble in water; compounds with two polar groups or a negatively charged group are soluble in water.

- Density: Aromatic hydrocarbons are less dense than water; aryl halides are more dense than water; many other aromatic compounds are about the same density as water.
- State of matter: Aromatic compounds with one substituent are usually liquids at room temperature; exceptions are phenol and benzoic acid. Aromatic compounds with two substituents or more than one benzene ring are usually solids at room temperature.
- Melting and boiling points: Boiling points are affected by molecular weight and intermolecular forces; melting points are affected by molecular weight, intermolecular forces, and symmetry.

### Spectroscopy

- IR: IR spectra of compounds containing benzene rings contain 3 characteristic bands. IR is not always a good way of determining if a compound is aromatic because these bands are not always obvious.
  - C-H on C=C at 3100-3000cm-1
  - C=C aromatic at 1600 and 1500 cm-1 (these are not always easy to see)
  - overtones at 2000-1600 cm-1 (these are only obvious when the ring is monosubstituted)
- NMR: Proton NMR spectra of aromatic compounds have a very characteristic range of 6.5-8.5 ppm for H's on the ring (it is usually enough to remember that they show up around 7 ppm). H's on carbons next to benzene rings show up around 2-3 ppm.
  - Para-substituted rings with two different substituents are easy to spot because they always have two clear doublets in the aromatic region.
  - 13C NMR spectra of aromatic compound show benzene rings carbons between 120 and 150 ppm.

### **III. Reactions of Benzylic Carbons**

- Benzylic carbons are those which are right next to a benzene ring. They have a few reactions that are different from other carbons.
- Benzylic carbons can form carbocations even when they are primary because the positive charge can delocalize inside the ring, with 3 additional resonance structures. However, only the benzylic carbon reacts, since otherwise aromaticity would be destroyed.

- Benzylic radicals are more stable than other radicals because of resonance with the benzene ring. When an aromatic compound with an alkyl substituent reacts with NBS and light, the bromine is substituted onto the benzylic carbon only.
- If an aromatic compound with an alkyl substituent reacts with KmnO<sub>4</sub> followed by treatment with aqueous acid, the benzylic carbon is oxidized all the way to a carboxylic acid. All other carbons (not including the ring) are oxidized to CO<sub>2</sub>.

## IV. Substitution Reactions of Aryl Halides

- Aryl halides do not react under typical  $S_N 2$  or  $S_N 1$  conditions.
- Two exceptions to this include:
  - Putting a strong electron-withdrawing group on the ring allows a stabilized carbanion to form (nucleophilic aromatic substitution).
  - Using a base that is strong enough to cause elimination to occur (elimination-addition).

#### Nucleophilic Aromatic Substitution

- When strong electron-withdrawing groups are present, a strong nucleophile can attack not by pushing off the halide, but by pushing a pair of electrons out of a double bond and onto a carbon. The halide then leaves, and the electrons go back into the ring.
  - The carbanion intermediate is stabilized by resonance with the electron-withdrawing groups; this intermediate is called a Meisenheimer complex.
  - Electron-withdrawing groups only work in the ortho and para positions, because in the meta position the negative charge is not shared with that carbon.
  - Nitro groups are the most common electron-withdrawing groups used in this reaction, but other groups such as CF<sub>3</sub> groups, cyano groups, and carbonyl groups can also work (though not as well).
  - The nucleophile may be hydroxide (forming a phenol), alkoxides (forming aryl ethers), thiolates (forming aryl sulfides), and ammonia or amines (forming anilines).
- The rate of reaction with the halides is reversed from what is observed with  $S_N1$  and  $S_N2$  reactions: F >> Cl > Br > I.
  - $^{\circ}$  This is because the breaking of the C-X bond is NOT the rate limiting step, as it is in  $S_N 1$  and  $S_N 2$  reactions. The rate limiting step is the attack of the nucleophile, since aromaticity is temporarily lost; the more electronegative the atom, the more it can stabilize the negatively charged intermediate, which makes F the fastest.

• The main limitation of this reaction is that electron-withdrawing groups must be present in ortho and/or para positions, so only these kinds of compounds may be made.

#### **Elimination-addition**

- If an aryl halide reacts with sodium amide (NaNH<sub>2</sub>), a very strong base, it undergoes elimination and forms a benzyne intermediate.
  - This is a highly strained compound containing 2 double bonds and a triple bond in a 6-membered ring.
  - The benzyne then reacts with another ion of sodium amide and a molecule of ammonia to give an aniline.
- This reaction differs from the previous one in that it doesn't require electron-withdrawing groups, and has a very different intermediate.
- Because the two carbons in the triple bond of the benzyne are equivalent, the NH<sub>2</sub> can end up on either one. This can cause constitutional isomers to form when there are other substituents on the benzene ring.
- An industrial variation on this reaction is to use NaOH at 350° C at this temperature, it becomes a strong enough base to do the same reaction as sodium amide, forming a phenol.
- The main limitation of this reaction is that it is only good for forming anilines (at least at laboratory temperatures); also, it often creates constitutional isomers.