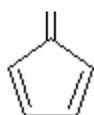


## Introduction to Aromaticity

### Historical Background

- ✓ Chemists of the early nineteenth century were puzzled by the structure of benzene – an unknown liquid with a pleasant “aroma” that was isolated from oil gas used to illuminate street lamps. Michael Faraday analyzed the substance, which was later termed benzene.
- ✓ Early chemists knew that benzene had a molecular formula of  $C_6H_6$  (from its molecular mass and C:H ratio of 1:1), which implies high reactivity. However, benzene was observed to be unusually stable at room temperature and did not undergo the reactions typical of alkenes.
- ✓ Based on these properties, along with the conclusions that carbon forms four bonds (Kekulé) and that carbon can form multiple bonds (Brown), some possible structures for Benzene were proposed, although these were shown to be incorrect later:<sup>1</sup>



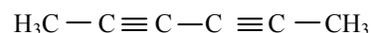
Fulvene



Prismane

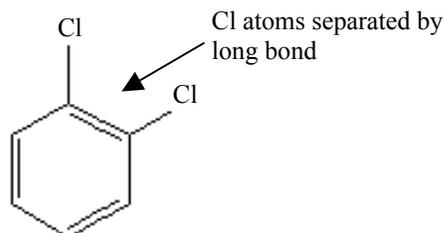
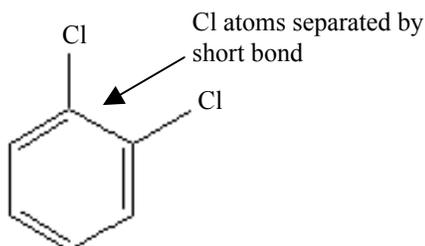
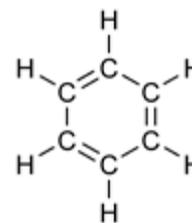


Dewar Benzene



2,4-Hexadiyne

- ✓ In fact, under certain conditions, both Dewar Benzene and Prismane rearrange to form Benzene (below) driven by the elimination of ring strain and preference for aromatic stabilization.
- ✓ According to Kekulé, the actual structure of benzene came to him in a dream in which he saw a snake biting its own tail. This suggested that benzene is a six-member ring with alternating single and double bonds.
- ✓ According to the structure proposed by Kekulé, there should be two isomers of 1,2-dichlorobenzene. In one structure, the chlorine atoms are separated by a single bond, and in the other, they are separated by a double bond. However, these isomers have never been isolated or detected.<sup>2</sup>



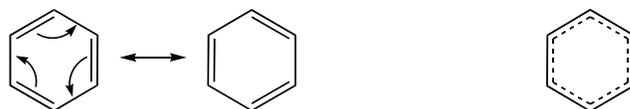
<sup>1</sup> Fulvene is from <http://www.steve.gb.com/images/molecules/arenes/fulvene.png>, visited 9/2/06; Prismane is from [http://www.angelo.edu/faculty/kboudrea/molecule\\_gallery/01\\_alkanes/prismane\\_01.gif](http://www.angelo.edu/faculty/kboudrea/molecule_gallery/01_alkanes/prismane_01.gif), visited 9/2/06; Dewar Benzene and 2,4-Hexadiyne were constructed on Microsoft Word

<sup>2</sup> 1,2-dichlorobenzene structures from <http://ntp.niehs.nih.gov/ntp/htdocs/structures/2d/TR255.gif>; site visited on 9/3/06

- ✓ Kekulé suggested that the reason the isomers are not observed is because there may be a very fast equilibrium between the two forms, meaning that they interchange so quickly that the individual structures are not even detected. But this still does not explain why benzene does not undergo typical alkene reactions.

### Why Benzene is Not a Normal Alkene

- ✓ A normal alkene undergoes an addition reaction when exposed to  $\text{Br}_2$ . The “three alkene” benzene shown above is expected to behave similarly. However, benzene does NOT react with  $\text{Br}_2$  unless a catalyst ( $\text{FeBr}_3$ ) is introduced. Since it is inert to  $\text{Br}_2$ , it cannot be a normal alkene.
- ✓ If the true structure of benzene was made up of alternating single and double bonds, as Kekulé originally suggested, then the bonds would also vary in length, since double bonds are shorter than single bonds. However, data obtained through x-ray crystallography confirms that all C-C bonds in benzene are of equal length.
- ✓ **Electron delocalization** through **resonance** provides a solution to the reactivity inconsistency, the bond length observation, and why isomers were not observed for 1,2-dichlorobenzene. The resonance contributors of benzene are pure fantasy. The resonance hybrid, which is a blend of the contributors, best represents reality. The electrons are spread throughout the ring, giving all the bonds partial double-bond character, which explains why the bonds are all the same length.<sup>3</sup>



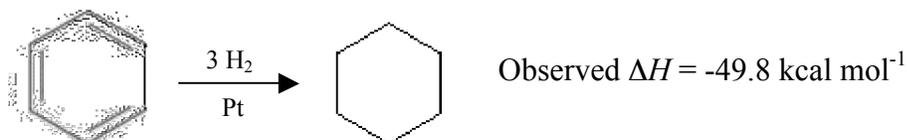
Benzene resonance contributors

Benzene resonance hybrid

- ✓ A final piece of information supporting the fact that benzene is not a normal alkene comes from **catalytic hydrogenation**, a method that utilizes a metal catalyst (such as Pt) to add hydrogen to a double or triple bond. This converts the pi bonds to C-H sigma bonds so that the energy change can be measured.
  - The heat of hydrogenation for cyclohexene is  $-28.6 \text{ kcal mol}^{-1}$
  - If benzene were simply three alkenes, we would expect its heat of hydrogenation to be three times the heat of hydrogenation of cyclohexene, since it has three double bonds.  $3(-28.6 \text{ kcal mol}^{-1}) = -85.6 \text{ kcal mol}^{-1}$ . This value would be a little lower due to conjugation.

<sup>3</sup> footnote deleted

- However, the experiment shows the heat of hydrogenation of benzene to be  $\Delta H = -49.8 \text{ kcal mol}^{-1}$ . This is “36  $\text{kcal mol}^{-1}$  less than three times the heat of hydrogenation of cyclohexene!”<sup>4</sup> This huge difference (which corresponds to extra stability) is not just explained by conjugation! The extra stability is the aromaticity (resonance energy).



### Overview

**Aromaticity**, also called **Resonance Energy**, is the extra stability observed in molecules such as benzene. To be considered aromatic, a compound must meet ALL FOUR of the following requirements:

1. The molecule must have a continuous ring or loop of  $p_z$  orbitals. This means that all atoms in the loop must be  $sp$  or  $sp^2$  hybridized.
2. Atoms forming the loop must be planar so that the  $p_z$  orbitals can overlap. A massive amount of torsional strain is required to override the amount of stability provided by aromaticity and thereby cause the molecule to lose planarity.
3. All of the pi bonds that are counted towards aromaticity must lie within a cyclic structure.
4. The molecule must obey **Hückel's Rule**: the aromatic loop must contain  $4n+2$  pi electrons, where  $n$  is any integer (whole number such as 0,1,2,...). In other words, “the pi cloud must contain an odd number of pairs of pi electrons”<sup>5</sup> totaling 2, 6, 10, 14, etc.

### Important Points to Remember

- ✓ **All aromatic molecules are conjugated, but not all conjugated molecules are aromatic.** This statement is true because “an aromatic molecule must have at least three adjacent, parallel  $p_z$  orbitals.”<sup>6</sup> This fits the definition of conjugation. However, in order for a conjugated molecule to be classified as aromatic, it must fit a number of other criteria. For instance, it must also be cyclic, planar, and contain the correct number of aromatic electrons.
- ✓ **All aromatic molecules have resonance, but not all molecules with resonance are aromatic.** All aromatic molecules have resonance because they must have at least three overlapping  $p_z$  orbitals occupied by a minimum of two pi electrons. However, not every molecule that has resonance is planar, cyclic, and obeys Hückel's Rule.

<sup>4</sup> Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 186

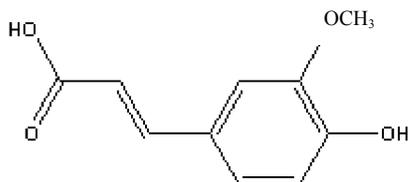
<sup>5</sup> Pg. 595 of Bruice, Organic Chemistry, 4<sup>th</sup> Edition, Ch. 15.2

<sup>6</sup> Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 191

- ✓ **Aromatic rings must be planar, yet they are more stable and less reactive than their non-aromatic counterparts.** This is true because the stability gained through aromaticity outweighs the strain caused by planarity.

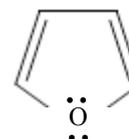
### Classifying Aromatic and Non-Aromatic Compounds

**EX:** Is the molecule shown below aromatic? Explain why or why not.<sup>7</sup>



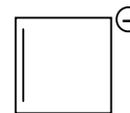
**ANSWER:** Yes, the molecule is aromatic. Remember that the entire molecule need not be cyclic for the molecule to be aromatic; only the atoms forming the loop of  $p_z$  orbitals must be cyclic, since these are the ones that will overlap. In this case, the benzene ring is planar, cyclic, contains a continuous ring of  $p_z$  orbitals, and has  $4n+2$  pi electrons ( $4n+2 = 6$ , so  $n = 1$ ). There is not enough torsional strain to override planarity.

**EX:** Is the molecule furan (shown on the right) aromatic? Why or why not?<sup>8</sup>



**ANSWER:** At first, it may appear that furan has only four  $sp^2$  hybridized electrons. However, the oxygen has two lone pairs, so the hybridization can be rearranged to give the correct number of pi electrons. If we take the oxygen to be  $sp^2$  hybridized instead of  $sp^3$ , then it can contribute a  $p_z$  orbital. Remember that for  $sp^2$  hybridization, there will be three filled  $sp^2$  orbitals (one with the sigma bond, one with the lone pair on the outside of the ring, and another with the remaining sigma bond) and one  $p$  orbital that contains the remaining lone pair. Thus, we will have a continuous loop of  $p_z$  orbitals, planarity, a cyclic ring, and  $4n+2$  pi electrons ( $4n+2 = 6$ ,  $n=1$ ). All of the requirements for aromaticity have been met, so furan is aromatic.

**EX:** Is the molecule shown on the right aromatic? Why or why not? (The negative formal charge is circled)<sup>9</sup>



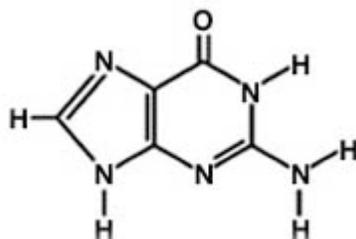
**ANSWER:** No, the molecule is not aromatic. The carbon on the bottom right corner has four bonds, so it must be  $sp^3$  hybridized. Thus, every atom in the ring does not have a  $p$  orbital. Also, it violates Hückel's Rule because it has two pairs of pi electrons (if we count the carbon on the top right corner as  $sp^2$  hybridized by putting its lone pair electrons into a  $p$  orbital).

<sup>7</sup> Image is a modified form of the one on <http://www.chembay.com/upimg/20029814570365.gif>, site visited 9/3/06; Also, the same structure was used in Chem 14C, Test #1, Summer 2006, by Professor Steven Hardinger

<sup>8</sup> Same question as CFQ #9 on Pg. 190 of Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version

<sup>9</sup> Structure adopted from Bruice, Organic Chemistry, 4<sup>th</sup> Edition, Ch. 15.2, Pg. 597

**EX:** The molecule guanine, shown below<sup>10</sup>, is a significant component of DNA. Is it aromatic? Explain why it makes sense for this compound to be aromatic.



**ANSWER:** All of the atoms making up the two rings are  $sp^2$  hybridized, so the molecule has a closed loop of  $p_z$  orbitals. There is not enough strain to force the molecule out of planarity, and there are two cyclic rings. The molecule has ten pi electrons (counting the lone pair electrons contributed by two of the nitrogen atoms). Thus, guanine is aromatic.

It makes sense for guanine to be aromatic. Aromaticity provides molecules with extra stability, so that they are not easily degraded. This “effectively preserves DNA function”<sup>11</sup> Also, since guanine is planar, the DNA bases can be stacked up on top of each other. This allows more genetic information to be stored in a smaller area.

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<sup>10</sup> Structure from [http://coris.noaa.gov/glossary/guanine\\_186.jpg](http://coris.noaa.gov/glossary/guanine_186.jpg), site visited 9/3/06

<sup>11</sup> Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 31