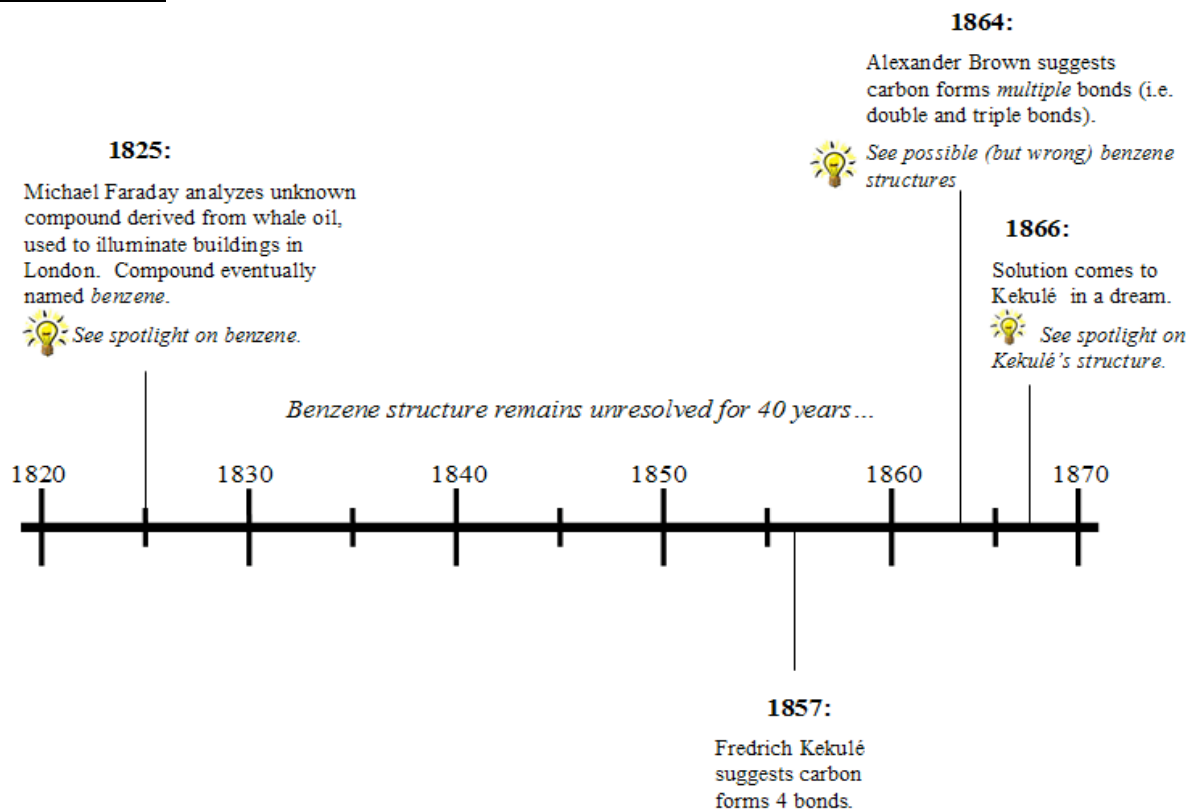


# Introduction to Aromaticity

## Historical Timeline:<sup>1</sup>



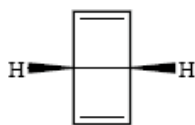
### Spotlight on Benzene:<sup>2</sup>

- Early 19<sup>th</sup> century chemists derive benzene formula (C<sub>6</sub>H<sub>6</sub>) and molecular mass (78).
- Carbon to hydrogen ratio of 1:1 suggests high reactivity and instability.
- However, benzene is fairly inert and fails to undergo reactions that characterize normal alkenes.
  - Benzene remains inert at room temperature.
  - Benzene is more resistant to catalytic hydrogenation than other alkenes.



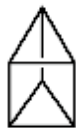
### Possible (but wrong) benzene structures:<sup>3</sup>

*Dewar benzene*



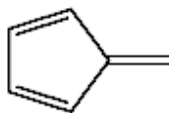
- Rearranges to benzene at room temperature.
- Lots of ring strain.

*Prismane*



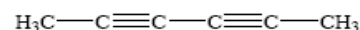
- Rearranges to Faraday's benzene.
- Lots of ring strain.

*Fulvene*



- Undergoes catalytic hydrogenation easily.

*2,4-Hexadiyne*



- Undergoes catalytic hydrogenation easily
- Lots of ring strain.

<sup>1</sup> Timeline is computer-generated, compiled with information from pp. 92-93 of *Principles of Organic Chemistry*, Ch. 15.2, and from *Chemistry 14C Thinkbook* by Dr. Steven Hardinger, Version 4, p. 26

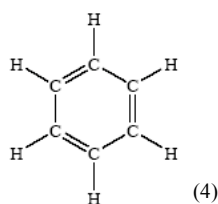
<sup>2</sup> *Chemistry 14C Thinkbook*, p. 26

<sup>3</sup> Images of Dewar benzene, prismane, fulvene, and 2,4-Hexadiyne taken from *Chemistry 14C Thinkbook*, p. 26.



### **Kekulé's solution:**

- "snake bites its own tail"



### **Problems with Kekulé's solution:**

- If Kekulé's structure were to have two chloride substituents replacing two hydrogen atoms, there should be a pair of 1,2-dichlorobenzene isomers: one isomer with single bonds separating the Cl atoms, and another with double bonds separating the Cl atoms.
- These isomers were never isolated or detected.
- Rapid equilibrium proposed, where isomers interconvert so quickly that they cannot be isolated or detected.
- Regardless, Kekulé's structure has C=C's and normal alkene reactions are still expected.
  - But the unusual stability of benzene still unexplained.

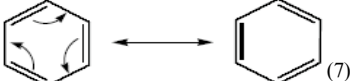
### **Comparison of Benzene and Three Alkenes**

- Table of laboratory experiments and observations:<sup>4</sup>

|  | Normal alkene reaction  | Expected observation of benzene in analogous alkene reaction  | Actual observation of benzene   | Conclusions                                 |
|--|-------------------------|---|---|---|
| <b>Addition reaction with Br<sub>2</sub></b>         | <p>(see footnote 4)</p> | <p>(4)</p>  | <p>(4)</p> <p><i>Substitution</i> reaction, not addition reaction. Benzene is inert to Br<sub>2</sub>, unless catalyst (FeBr<sub>3</sub>) present</p> | Benzene not a normal alkene                 |
| <b>Bond length</b>                                   | N/A                     | In cyclohexene, C-C and C=C alternate, along with bond lengths  | X-ray crystal structure does not reveal bonds of alternating length   | C=C bonds in benzene are not simple alkenes |
| <b>Heat of hydrogenation (<math>\Delta H</math>)</b> | <p>(4)</p>              | <p>(4)</p> <p><math>\Delta H</math> for benzene = 3 times that of cyclohexene:<br/> <math>3(-28.6 \text{ kcal mol}^{-1}) = -85.6 \text{ kcal mol}^{-1}</math> (5)</p> | $\Delta H$ for benzene = -49.8 kcal mol <sup>-1</sup> . This is 36 kcal mol <sup>-1</sup> less than 3 times $\Delta H$ for cyclohexene <sup>6</sup>   | Benzene is more stable than expected        |

<sup>4</sup> All images (including Kekulé structure at top of page) from *Chemistry 14C Thinkbook*, p. 27.

- Potential solution to reactivity discrepancies between benzene and alkenes: resonance

- Possible benzene “isomers,” or resonance contributors: 

- These “isomers” *do not* exist! The resonance hybrid is the best representation<sup>8</sup>. The hybrid shows *electron delocalization*: the spreading of electron density from a fixed place (i.e. a lone pair or covalent bond), such that they are free to distribute over several other atoms. In benzene, electrons spread throughout the ring.

- Overall conclusions: differences between benzene and normal three alkenes are not just attributable to resonance or conjugation.
- Extra stability is *aromaticity*.

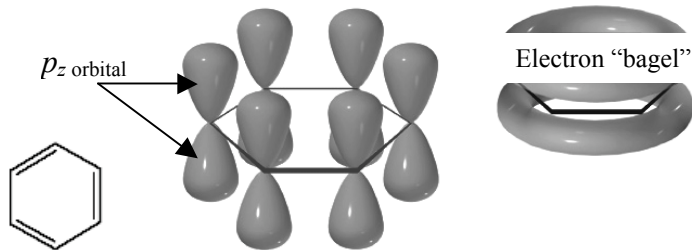


### **Requirements for Aromaticity:**

- Pi bonds participating in the aromatic system must form a closed loop.
- Each participating atom must have a  $p$  orbital to contribute to the loop of parallel  $p_z$  orbitals.
- All atoms must be  $sp^2$  or  $sp$  hybridized; almost always  $sp^2$ .
- All  $p_z$  orbitals must overlap and be planar; disruption of planarity negates stability and is energetically unfavorable.
- Arrangement must obey *Hückel's rule*:  $4n + 2$  pi electrons ( $n$  is an integer: 0, 1, 2...)



### **Epitome of Aromaticity: Benzene<sup>10</sup>**



- Three pi bonds lying within a ring.
- Each atom is  $sp^2$ , forming overlapping loop of  $p_z$  orbitals (electron “bagel”).
- Planarity.
- 6 pi electrons ( $4n + 2 = 6$ ,  $n = 1$ ).
- “All C-C bond lengths are equal, and halfway between C-C and C=C. All C-H bonds are equal. All C-C-C bond angles are equal, and all H-C-C bond angles are equal at  $120^\circ$ ”<sup>10</sup>

### **Things to Remember:**

<sup>5</sup> *Chemistry 14C Thinkbook*, p. 27

<sup>6</sup> *Chemistry 14C Thinkbook*, p. 27

<sup>7</sup> Image from *Chemistry 14C Thinkbook*, p. 27

<sup>8</sup> Image from *Chemistry 14C Thinkbook*, p. 27

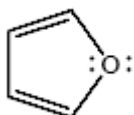
<sup>9</sup> Information compiled from *Chemistry 14C Thinkbook*, p. 30, and from *Organic Chemistry*, p. 595

<sup>10</sup> Two-dimensional benzene image from *Chemistry 14C Thinkbook*, p. 27. Three-dimensional images from *Organic Chemistry*, p. 595. Information regarding benzene from *Chemistry 14C Thinkbook*, p. 187

- Every aromatic molecule is conjugated because an aromatic molecule must have at least three adjacent, parallel, or overlapping  $p$  orbitals, which is sufficient to meet the requirements of conjugation.
- Every conjugated molecule is not necessarily aromatic because a conjugated molecule with resonance can be acyclic, which would violate the rule for aromaticity that requires a closed loop.

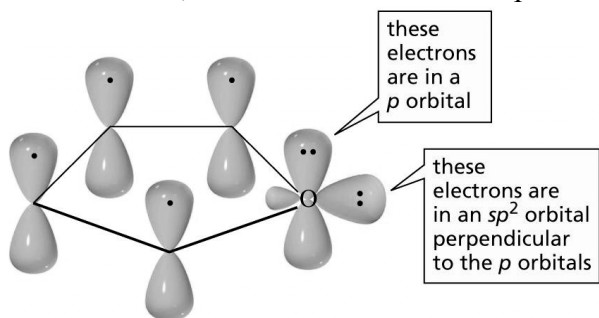
### Example Problems:

1) Is furan<sup>11</sup> (see structure below) aromatic? Why or why not?



Answer:

Furan is aromatic. The oxygen within the cyclic structure can assume an  $sp^2$  hybridization as opposed to an  $sp^3$  (which normally characterizes atoms bonded to four electron groups). With  $sp^2$ , one of the two lone pairs occupies a  $p_z$  orbital, allowing oxygen to contribute to the continuous loop of  $p_z$  orbitals and maintains the ring's flat shape. The other lone pair occupies an  $sp^2$  orbital, perpendicular to the pi electron cloud. This pair is not involved in the pi electron cloud (i.e. the  $p_z$  orbital overlap seen in the electron "bagel"). Furan also obeys Hückel's rule ( $4n + 2 = 6$  pi electrons,  $n = 1$ ). Because furan has a continuous, closed loop of  $p_z$  orbitals, planarity, and obeys Hückel's rule, it is aromatic. See 3D representation:



orbital structure of furan

(12)

2) I. (see structure below) aromatic? Why or why not?

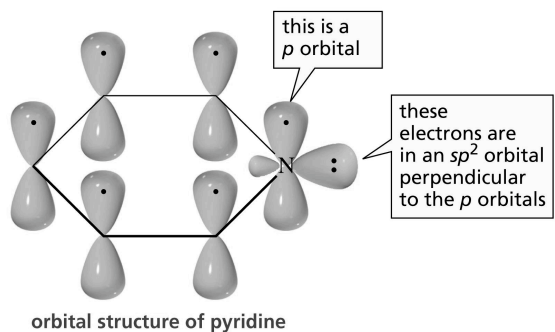
Answer: Pyridine is aromatic. As in furan, nitrogen's lone pair occupies an  $sp^2$  orbital as opposed to a  $p_z$  orbital, so it does not contribute to the pi electron cloud. However, it contributes a  $p$

<sup>11</sup> Image from *Chemistry 14C Thinkbook*, p. 30. Question adopted from example problem in *Chemistry 14C Thinkbook*, p. 30.

<sup>12</sup> Image from *Organic Chemistry*, p. 595

<sup>13</sup> Image from *Chemistry 14C Thinkbook*, p. 29. Question adopted from practice problem in *Chemistry 14C Thinkbook*, p. 188

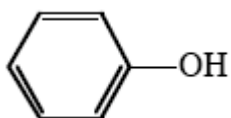
orbital just like the remaining carbons in the ring. The molecule is planar, has a closed loop of  $p_z$  orbitals and meets Hückel's rule ( $4n + 2 = 6$  pi electrons,  $n=1$ ). See 3D representation:



(14)

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3) Is phenol<sup>15</sup> (see structure below) aromatic? Why or why not?



*Answer:* Phenol is aromatic. At first glance, the OH group of phenol appears to disrupt possible aromaticity. While it is true that OH is acyclic and its lone pairs do not participate in aromaticity, the molecule is still considered aromatic overall because it contains a "normal" benzene ring, which meets all of the requirements of aromaticity.

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<sup>14</sup> Image from *Organic Chemistry*, p. 599

<sup>15</sup> Image from *Chemistry 14C Thinkbook*, p. 29. Question adopted from practice problem in *Chemistry 14C Thinkbook*, p. 189