BENZENE - AROMATIC COMPOUNDS

Aliphatic Compounds: Open chain (acyclic) and those cyclic compounds with similar chemical properties. A typical reaction type of unsaturated aliphatic compounds: electrophilic addition.

Aromatic Compounds: Benzene, C₆H₆, and other unsaturated compounds that resemble it in chemical behavior. The aromatic properties of benzene are those that distinguish it from aliphatic hydrocarbons.

What are these properties?

Properties of Aromatic Compounds ---

�� Cyclic and each atom in the ring is a \( \pi \)-center (uses a \( p \) atomic orbital to form \( \pi \)-type bonds), \textit{i.e.}, \( sp^2 \) or \( sp \).

馬 Ring is flat or nearly so.
High degree of unsaturation but resistant to addition reactions --- generally undergo electrophilic substitution (an electrophilic reagent replaces a hydrogen [usually] attached to the ring).

Unusually stable.

π-Electrons delocalized above and below plane of ring.

*Benzene Molecular Orbitals*

σ-Orbitals —

Each carbon is sp² hybridized. The 18 carbon sp² atomic orbitals [(3/carbon)x(6 carbons)] and 6 hydrogen s atomic orbitals interact to form 12 σ and 12 σ* molecular orbitals. The 24 electrons from the atomic orbitals occupy the 12 σ orbitals giving 12 σ bonds.

= a σ-orbital; containing 2 electrons, a σ-bond
\(\pi\)-Orbitals —
\(\pi\)-Type orbitals form by the parallel overlap of p atomic orbitals.

P orbitals have two lobes. One lobe has a positive amplitude and the other a negative amplitude — metaphorically, a hill and a valley. If two adjacent p orbitals are in phase — hill next to hill and valley next to valley — they will overlap to form a molecular orbital in a constructive way: one hill will join with the other and one valley will join with the other. Electrons will be found wherever the amplitude \(\neq 0\). This situation — bonding — is shown in the figure to the right.
On the other hand, if two adjacent p orbitals are out of phase – hill next to valley and valley next to hill – they will overlap in a destructive way: the hills and valleys will be leveled and in some places the amplitude will be zero. [The places where the amplitude is 0 is called a node.] Electrons are not found at nodes. This situation – antibonding – is shown in the figure to the right.

Finally, it sometimes happens that the p orbital of a particular atom contributes nothing to a molecular orbital. The amplitude of the molecular orbital at that atom is zero. This is a nonbonding situation for that molecular orbital for that atom.
Before we consider benzene, let's look at a couple of simpler compounds (which happen to be aliphatic) that have π-bonds.

**Ethylene**

The π and π\* orbitals in ethylene are formed by a combining of the 2p atomic orbitals of the carbons. The π orbital is bonding between the two carbons – electrons in this orbital have less energy than they would have in an atomic 2p orbital. The π\* orbital is antibonding – electrons in this orbital have more energy than they would have in an atomic 2p orbital.
1. 3-Butadiene

At first glance we might think that this would be just like two ethylenes hooked together: a $\pi$ and $\pi^*$ orbital between carbons 1 and 2 and also between carbons 3 and 4. However, this overlooks the interaction that is possible between the p orbital on carbon-2 and the one on carbon-3. In fact, the four atomic p orbitals can interact with four different phase arrangements giving four $\pi$-type molecular orbitals. This is shown in the figure below. Each of the p atomic orbitals has the same energy and each contains one electron. Each can interact with a neighbor in a bonding way (the orbitals are in phase, $\Psi$, and can overlap), an antibonding way (the orbitals are out of phase, $\overline{\Psi}$, and cancel each other out between the atoms), or a nonbonding way (the neighboring p orbital makes no contribution to the molecular orbital that will form: $\overline{\Psi}$. The result of the interaction of the four p orbitals in 1,3-butadiene is the formation of four molecular orbitals, $\Psi_1$ through $\Psi_4$. This is shown schematically in the diagram below.
The orbital of lowest energy is $\Psi_1$; it is bonding between each of the carbons. The next higher in energy is $\Psi_2$; it is bonding between C-1 and C-2 and between C-3 and C-4, but antibonding between C-2 and C-3 because the orbital changes phase here. Both of these orbitals are bonding orbitals, overall: they are of lower energy than the isolated atomic p orbitals. [Since electrons in an atomic p orbital are nonbonding, the energy level of the p orbitals is called the nonbonding energy level.] $\Psi_3$ and $\Psi_4$ are antibonding orbitals, overall: they are of higher energy than the isolated atomic p orbitals.

The four electrons from the atomic p orbitals go into $\Psi_1$ and $\Psi_2$, the two bonding $\pi$ orbitals, because these are of lowest energy and each, like any orbital, can accommodate two electrons.
Finally, it might be noted that the conjugated 1,3-butadiene system is more stable than an isolated diene because the total energy of the four electrons in $\Psi_1$ and $\Psi_2$ turns out to be less than the energy of four electrons in two isolated $\pi$ bonds.

**Benzene**

Each carbon "starts" with a p atomic orbital containing one electron. These orbitals are perpendicular to the ring, but parallel to each other. These atomic "basis" orbitals are shown in the figure below. Each p orbital interacts ("overlaps") with two neighbors. This gives rise to six $\pi$-type orbitals, $\Psi_1$ through $\Psi_6$. $\Psi_1$ through $\Psi_3$ are bonding orbitals; $\Psi_4$ through $\Psi_6$ are antibonding. It turns out that $\Psi_1$ is the lowest energy orbital. $\Psi_2$ and $\Psi_3$ are *degenerate*, i.e. they have the same energy, and it is higher than the energy of $\Psi_1$. The electrons in the three occupied bonding orbitals give rise to one doughnut of electron density above the ring and one below, containing a total of 6 $\pi$ electrons. This aromatic electronic delocalization results in considerable stabilization – more than is observed in the case of conjugated aliphatic compounds.
Benzene Molecular Orbitals

\[ \Psi_6 = -\phi_1 + \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6 \]

\[ \Psi_4 = -\phi_1 + \phi_2 - \phi_3 - \phi_4 + \phi_5 - \phi_6 \]

\[ \Psi_5 = \phi_1 - \phi_3 + \phi_4 - \phi_6 \]

\[ \Psi_2 = \phi_1 + \phi_2 + \phi_3 - \phi_4 - \phi_5 - \phi_6 \]

\[ \Psi_3 = \phi_1 - \phi_3 - \phi_4 + \phi_6 \]

\[ \Psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \]

Six atomic 2p orbitals  Six benzene molecular orbitals
Because of the $\pi$-electrons, benzene, and other aromatic compounds, frequently act as Lewis bases or nucleophiles; thus, they are susceptible to *electrophilic attack*. Because of the stability associated with the delocalized electrons, this feature tends to be retained in the products; consequently, these reactions are usually *substitutions, not additions*.

\[
E^+ + \text{ benzene } \rightarrow E\text{ benzene} + H^+
\]

*How stable is benzene?*

*Compared to what?*

*Compared to isolated $\pi$-bonds, and conjugated, non-aromatic $\pi$-systems.*
Heats of Hydrogenation of Cyclic Unsaturated Molecules

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>$\Delta H^0_h$</th>
<th>$n \times \Delta H^0_h$ (C$<em>6$H$</em>{12}$)</th>
<th>&quot;Stability&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexene</td>
<td>cyclohexane</td>
<td>28.6 kcal</td>
<td>28.6 kcal</td>
<td>0 kcal</td>
</tr>
<tr>
<td>1,3-cyclohexadiene</td>
<td>cyclohexane</td>
<td>55.4</td>
<td>57.2</td>
<td>1.8</td>
</tr>
<tr>
<td>benzene</td>
<td>cyclohexane</td>
<td>49.8</td>
<td>85.8</td>
<td>36</td>
</tr>
</tbody>
</table>

Is aromatic stability shared by all monocyclic compounds with conjugated $\pi$ systems?

No.
Aromatic stability seems to be associated with

* completely filled $\pi$ bonding orbitals
* completely filled or empty $\pi$ non-bonding orbitals
* completely vacant $\pi$ antibonding orbitals.

Do I need to do Huckel MO calculations to tell what $\pi$ orbitals exist in one of these molecules and whether or not they are filled?
No.

Use the polygon mnemonic to find the orbitals, and fill them with the $\pi$ electrons in order of increasing energy.

**THE POLYGON MNEMONIC**

Draw the molecule as a regular polygon and rotate it around its center so one apex is pointing down. Each apex corresponds to a $\pi$ molecular orbital. The center of the polygon corresponds to the non-bonding energy level (same energy as an isolated p atomic orbital); orbitals of lower energy are bonding; orbitals of higher energy are anti-bonding.
**Examples**

```
 anti-bonding  
 non-bonding  
 bonding      

 Status        
 Anti-aromatic

 anti-bonding
 bonding      

 Aromatic

 anti-bonding  
 non-bonding  
 bonding      

 Not aromatic-non-planar, ordinary alkene

 anti-bonding
 bonding      

 Not aromatic-too much angle strain to be planar

 anti-bonding
 bonding      

 Not aromatic-too much steric strain to be planar

 Aromatic
```
Is this the simplest way to predict whether or not a monocyclic conjugated polyene is aromatic?

No.

Well...

If a monocyclic conjugated polyene consisting only of $\pi$ centers is planar,

- it will be aromatic if it contains $4n+2$ $\pi$ electrons, where $n$ is 0, 1, 2 ...
- it will be anti-aromatic if it contains $4n$ $\pi$ electrons.
Some examples ---

4n + 2 \( \pi \) Electrons: Aromatic Moieties

\( n = 0 \), 2 \( \pi \) electrons \hspace{1cm} \( n = 1 \), 6 \( \pi \) electrons

n = 0, 2 \( \pi \) electrons

n = 1, 6 \( \pi \) electrons

n = 2, 10 \( \pi \) electrons

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n = 2, 10 \( \pi \) electrons
4n \pi \text{ Electrons: Non- or Anti-Aromatic Moieties}

n = 1, \ 4 \pi \text{ electrons, antiaromatic}

n = 2, \ 8 \pi \text{ electrons, antiaromatic if planar}

n = 3, \ 12 \pi \text{ electrons, antiaromatic if planar}
Polycyclic (polynuclear) Aromatic Hydrocarbons

Examples ---

naphthalene  

anthracene  

phenanthrene  

benzo[a]pyrene, carcinogenic, found in cigarette smoke

These compounds are aromatic, but do not have as much stabilization per ring as benzene. Therefore, although they undergo electrophilic substitutions, they are more likely than benzene to undergo some addition reactions, especially if this results in benzene rings in the products.
Sources of Aromatic Compounds

Aromatic hydrocarbons may be obtained from ---

1) petroleum – not rich in aromatics, but has some.

2) reforming cycloalkanes from petroleum, eg

\[
\text{CH}_3 \quad \text{heat, catalyst} \quad \text{high pressure} \quad \text{CH}_3
\]
3) coal tar and coal gas.

Coal derives from plants which have suffered partial decay and been subjected to heat and pressure.

plants ---> peat ---> lignite ---> bituminous (soft) coal ---> ---> anthracite (hard)

Bituminous coal is a good source of aromatic compounds. Destructive distillation of it forms coal gas, coal tar, and coke. Coal tar is rich in aromatic hydrocarbons, bases (eg, pyridine), and phenolic (Ar-OH) compounds. [Ar- is shorthand for an aromatic ring, just as R- is shorthand for an alkyl group.]

Rich in aromatic compounds: benzene, toluene, xylenes, etc.