WEEK 2: CONJUGATION & AROMATICITY

(Chapter 13)

Announcements: Labs start this week!

This week:

Aromatic Systems
Planar, cyclic, fully conjugated molecules having $4n+2 \pi$ electrons, where $n$ is integer (0, 1, 2, 3, ...)

Ex.: Benzene

$\text{H}_2\text{C} = \text{C} = \text{H}_2$ = $\text{C}_6\text{H}_6$

1) Planar
2) Cyclic
3) Fully conjugated
4) $6\pi$ electrons $\rightarrow 4n+2 = 6$

Recall (last week):

Conjugated Systems
- Arrangement of $\pi$-bonds in a 1,3-fashion.

Reactions:

\[ \text{H}_2\text{Br} \rightarrow \text{Br} \quad \text{H}_2 \text{Br} \quad \text{1,2-addn} \]

\[ \text{H}_2\text{PtCl}_2 \rightarrow \text{H}_2 \quad \text{R} \quad \text{R} \quad \text{Δ} \quad \text{Diels-Alder} \]

\[ \text{H}_2 \text{Br} \rightarrow \text{Br} \quad \text{H}_2 \text{Br} \quad \text{1,4-addn} \]

\[ \text{R} \quad \text{R} \quad \text{R} \quad \text{Δ} \quad \text{Diels-Alder} \]

\[ \text{Section 12.16} \]

Benzene = stable & not very reactive:

1) $\text{H}_2\text{Br} \rightarrow \text{No Rxn}$

2) $\text{H}_2\text{PtCl}_2 \rightarrow \text{Very Slow}$

3) $\text{R} \quad \text{R} \quad \text{R} \quad \text{Δ} \quad \text{Diels-Alder} \rightarrow \text{No Rxn.}$

We are going to discuss why benzene is so stable (not just a conj. polyene) this week...

Structure of Benzene?

$\text{C}_6\text{H}_6$, first isolated from whale blubber

Proposals:
1) Sir James Dewar "Dewar" Benzene

2) Albert Ladenburg "Ladenburg" Benzene

3) Friedrich Hekulé cyclohexatriene

Almost right.

Current Structural Understanding of Benzene

1) Regular hexagon

2) All C-C bond lengths $= 1.39\text{Å}$

3) Each C $= sp^2$ hybridized.

Resonance Depiction:

\[
\begin{align*}
\text{\textbf{1}} & \rightarrow \text{\textbf{2}} \\
\text{\textbf{3}} & \rightarrow \text{\textbf{4}} \\
\text{\textbf{5}} & \rightarrow \text{\textbf{6}} \\
\end{align*}
\]

Dbi bond character between all C's!
<table>
<thead>
<tr>
<th><strong>Quick</strong> Orbital Depiction:</th>
<th><strong>Quantifying Delocalization Energy:</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>2p orbitals (all parallel)</td>
<td>Heats of Hydrogenation:</td>
</tr>
</tbody>
</table>
| Orbital overlap among all  | [\(\text{Cyclohexene} + \text{H}_2 \xrightarrow{\text{Pd}} \text{Cyclohexane}\)]
| neighbor C atoms           | \(\Delta H = -28.6 \text{ kcal/mol}\) |
| \(\text{DELocalization}\)  |                                  |
| Form circle of e- density  | Hypothesize/Guess:              |
| above \& below ring.       | \(\Delta H = 3 \times (-28.6 \text{ kcal/mol})\) |
| Can draw as                | Actual:                          |
| ![Diagram](image)          | \(\Delta H = -49.3 \text{ kcal/mol}\) |
| Circle denotes 2p overlap  | \(\Delta H_{\text{guess vs. actual}} = 32.9 \text{ kcal/mol}\) |

<table>
<thead>
<tr>
<th><strong>Energy Diagram:</strong></th>
<th><strong>Aromaticity:</strong> Aromatic compounds are stable bc of this delocalization energy.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Energy Diagram" /></td>
<td>IS benzene the only aromatic cmpd? NO.</td>
</tr>
<tr>
<td>32.9 kcal/mol (Guess)</td>
<td>Criteria for Aromaticity:</td>
</tr>
<tr>
<td>49.3 kcal/mol (Actual)</td>
<td>1) Molecule must be cyclic.</td>
</tr>
<tr>
<td>85 kcal/mol (Guess)</td>
<td>2) Fully conjugated (2p orbital on every atom in ring)</td>
</tr>
<tr>
<td></td>
<td>3) Molecule is planar</td>
</tr>
<tr>
<td></td>
<td>Benzene is planar. 2p orbitals can overlap. Delocalization 0</td>
</tr>
</tbody>
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<table>
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<tr>
<th><strong>Ex:</strong> Cyclooctatetraene</th>
<th>**Must have ((4n+2)) \pi \text{ electrons, } \Rightarrow \text{Hückel's Rule}</th>
</tr>
</thead>
<tbody>
<tr>
<td>not aromatic.</td>
<td>(n=\text{integer}) ((0,1,2,\ldots))</td>
</tr>
<tr>
<td>not planar</td>
<td>(4n+2 = 6) (4n = 4) (n=1\ \text{OK!})</td>
</tr>
<tr>
<td></td>
<td>(4\pi \cdot e^- \Rightarrow 4n+2 = 4)</td>
</tr>
<tr>
<td></td>
<td>(4n = 2) (n=1/2)</td>
</tr>
<tr>
<td>lost overlap; broke connectivity.</td>
<td>(n=1/2)</td>
</tr>
</tbody>
</table>
Why does Hückel's Rule Work?

Molecular Orbital Diagrams:

Recall: Ethylene $\text{H} = \text{C} = \text{H}$

\[
\begin{align*}
\pi & - \text{bond: } 2p_c + 2p_c \\
& = \phi_A \phi_A \text{ antibonding (1 node)} \\
\pi^* & = \phi_B \phi_B \text{ bonding (1 node)} \\
2 \text{ p orbitals} & \Rightarrow 2 \text{ MOs} (\pi, \pi^*)
\end{align*}
\]

Benzene $\text{C}_6\text{H}_6$

$\text{L} \text{ MO's (Cyclic \Rightarrow Some degenerate (equal energy) orbitals.}$

$\text{MO's:}$

\[
\begin{align*}
\phi_1 & \quad 2 \text{ nodes} \\
\phi_2 & \quad 3 \text{ nodes} \\
\phi_3 & \quad 2 \text{ nodes} \\
\phi_4 & \quad 1 \text{ node} \\
\phi_5 & \quad 1 \text{ node} \\
\phi_6 & \quad \text{nonbonding level (energy of single 2p orbital)}
\end{align*}
\]

Frost Circle: easily generates molecular $\pi$ orbitals for planar, cyclic, fully conjugated molecules.

1. Draw Circle $\text{C}_6$ vertex down.
2. Draw ring corresponding to molecule inside circle $\text{C}_6$ vertex down.
3. Where ring meets Frost's Circle $\Rightarrow 2 \text{ MOs}$.
4. Cut Frost's circle in half $\Rightarrow$ n.b. level

Radius $= 2\beta$ energy units

E $= -\frac{1}{2} \beta$ n.b. level

Now unit for energy:

\[
\beta = -18 \text{ kcal/mol}
\]

Note: All bonding orbitals filled & no e-s in antibonding orbitals.

Hückel's Rule w/ MO's in Mind:

When $4n + 2 = n \text{ integer}$, all e-s will be in bonding MO's (stable) $\Rightarrow$ AROMATIC.

When $4n + 2 = n \text{ not integer}$, there will be unpaired e-s @ the nonbonding level (unstable).

\[\Rightarrow\text{ ANTIAROMATIC}\]

Frost Circle / MO's for Butadiene: $\text{C}_4\text{H}_6$

1. Draw circle
2. Ring w/ vertex down
3. Intersections $= \phi_4$
4. Find n.b. level
5. Put in e-s (H $\pi$ e-s) $\phi_2 = -\phi_3$ antibonding

\[
\begin{align*}
\text{Not stable!} \\
\text{Unpaired e-s @ nonbonding level} \Rightarrow \text{Radical Character.}
\end{align*}
\]

$4n + 2 = 4 \Rightarrow n = \frac{1}{2}$

\[\Rightarrow \text{ NOT AROMATIC}\]
19. Examples: Aromatic or Not?

**Neutral Compounds**

**Substituted benzenes**

- Toluene
  - Cyclic ✓
  - Fully conj ✓
  - Planar ✓
  - Hückel's Rule: \(4n+2=6\) \(n=1\) ✓

**AROMATIC**

**Heteroaromatics**

- Pyridine
  - Cyclic ✓
  - Fully conj ✓
  - Planar ✓
  - \(4n+2=6\); \(n=1\) ✓

**AROMATIC**

Why not \(4n+2=8\)? Geometry of orbitals.

- Two \(\sigma\) bonds are in \(sp^2\).
- \(sp^2\) is parallel to conjugated \(p\)-orbitals.

- Furan
  - Cyclic ✓
  - Fully conj ✓
  - Planar ✓
  - \(4n+2=6\); \(n=1\) why?

**AROMATIC**

- Sp^2 orbital is perpendicular to conj. p-orbitals.

20. Polynuclear Aromatics

- Cyclic ✓
- Fully conj ✓
- Planar ✓
- Hückel's Rule: \(4n+2=10\) \(n=2\) ✓

**AROMATIC**

- Naphthalene
  - Cyclic ✓
  - Fully conj ✓
  - Planar ✓
  - \(4n+2=10\); \(n=2\) ✓

**AROMATIC**

- Polynuclear containing a heteroatom

- Quindine
  - Cyclic ✓
  - Fully conj ✓
  - Planar ✓
  - \(4n+2=10\); \(n=2\) ✓

**AROMATIC**

Ex: benzene = [6]-annulene

Ex:

[4]-annulene

Cyclic ✓
2) Fully conj ✓
3) Planar ✓ (Build model)
4) \( 4n + 2 = 14; n = 3 ✓ \)

26. [10]-annulene (all cis bonds)

1) Cyclic ✓
2) Fully conj ✓
3) Planar? NO

Make Model.

Not AROMATIC.

27. Aromatic Ions

Cyclopentadienyl Anions

\[ \text{cyclopentadiene \quad \text{not aromatic}} \]

\[ \text{anion} \quad \text{stable for anion (not as stable as benzene)} \]

pKa 10

(relatively acidic because aromatic system obtained upon deprotonation)

28. Cyclopropenyl Cation

1) Cyclic ✓
2) Fully conj ✓
3) Planar ✓
4) \( 4n + 2 = 2; n = 0 \)

AROMATIC

5) empty \( \text{p} \)

29. Tropylium Ion

Aromatic
1) Cyclic ✓
2) Fully conj ✓
3) Planar ✓
4) \( 4n + 2 = 6; n = 1 ✓ \)

empty \( \text{p} \)
Substituted Benzenes

Benzene = \[ > = \bigcirc = \text{Ph}H \]
\[ \text{Ph}= \text{phenyl} \]

Monosubstituted benzenes:

- Phenyl group = \[ C_6H_5 = \sigma \]
- Benzylic group = \[ C_6H_5CH_2 = \text{Bn} \]

Disubstituted:

- \[ CH_3 \]
- \[ CH_3 \]
- \[ CH_3 \]

\[ \text{E}-\text{xylene} \]
\[ \text{1,2-Dimethylbenzene} \]

\[ \text{M}-\text{xylene} \]
\[ \text{p}-\text{xylene} \]

\[ \text{Br-M}-\text{bromophenol or 3-bromophenol} \]

Common Monosubstituted Benzenes

- Toluene
- Aniline
- Phenol

Reactions of benzene derivatives

1. Birch reduction:

\[ \text{Benzene} \rightarrow \text{Diene} \]

Mechanism:

- Electron transfer to antibonding orbital
- Radical anion
- \[ \text{E}-\text{oct} \]
- \[ \text{H}-\text{oct} \]

Substituent Effects:

A) Electron-withdrawing groups (EWG):

- Diene w/ EWG substituent in between 2 double bonds

B) Electron-donating groups (EDG):

- Diene w/ EDG substituent on single bond.

Why? EWG:

\[ \text{H-OEt} \rightarrow \text{H-OEt} \]
\[ \text{H-OEt} \rightarrow \text{H-OEt} \]
\[ \text{H-OEt} \rightarrow \text{H-OEt} \]
\[ \text{H-OEt} \rightarrow \text{H-OEt} \]
\[ \text{H-OEt} \rightarrow \text{H-OEt} \]
The Bonylic Position

**Rxns at benzylic position = facile.**

**A** \(\text{SN}1\) Rxns:

- Benzylic position/carbon
- Aromacity retained
- Pt. e-
- Highly resonance stabilized!

**B** \(\text{SN}2\) Rxns:

- S\(\text{N}^+\) in T.S. is delocalized.
- Lower energy barrier for this rxn.

**C** Radical Rxns:

- 1\(\rightarrow\)CH\(_3\)  NBS  CC\(_4\)  hv  1\(\rightarrow\)CH\(_3\)  via \(\left[\begin{array}{c}H \\ \text{CH}_3\end{array}\right]\)
- "resonance-stabilized" intermediate.

**D** Oxidation

- Benzylic position highly prone to oxid.
- Mechanism is vague (not fully known)
  - \(\text{CH}_3\)  KMnO\(_4\)  \(\rightarrow\) CH\(_3\)  KMnO\(_4\)  \(\rightarrow\) CH\(_3\)  KMnO\(_4\)  \(\rightarrow\) CH\(_3\)
- No Rxn.
- Fully substituted benzylic carbons don't react!
  - Must be \(\geq 1\) H @ benzylic position for rxn to proceed.