CHEM40003

Aromatic Chemistry

LECTURE 1 - Aromaticity

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Format and scope of presentation

- **Aromaticity:**
  - Historical perspective (Kekulé)
  - Characteristics, NMR ring currents
  - Valence bond & molecular orbital representations (Hückel's rule)
  - Anti-aromaticity

**Key further reading:** Clayden, Greeves & Warren, *Organic Chemistry*, 2nd Ed., Chapter 7
- *conjugation* – pages 143 - 150
- *aromaticity* – pages 156 - 162
Aromaticity: historical perspective

- ‘Aromatic’ → ‘aroma’ → natural fragrances e.g. benzaldehyde (peaches)
- Unusual stability/unreactivity for an unsaturated hydrocarbon

- Late 1800’s: benzene combustion analysis → molecular formula $C_6H_6$

- No-decolourisation of bromine water (i.e. addition of $Br_2$ across double bonds)
Great events in Chemistry...

1865: Kekulé, moments before his brilliant insight into the structure of benzene.
Kekulé and his dream of snakes...

Loschmidt 1861

Kekulé 1861

Kekulé or Loschmidt?

• “It began with a daydream: the 150th anniversary of the Kekule benzene structure”, A. Rocke Angew. Chem. Int Ed. 2015, 54, 46-50 (DOI)
Aromaticity: stability and bond lengths

- **Quantification of unusual stability: heats of hydrogenation (calorimetry)**
  - see: Vollhardt *J. Am. Chem. Soc.* **2000**, *122*, 7819 ([DOI](https://doi.org/10.1021/ja000098q))

  ![Hydrogenation Reactions]

  \[
  \text{Pd/C-H}_2 \xrightarrow{\text{[T↑, P↑]}} \text{C}_6\text{H}_6 \quad \Delta H^\circ = -120 \text{ kJ mol}^{-1} \]

  \[
  \text{Pd/C-H}_2 \quad \Delta H^\circ = -232 \text{ kJ mol}^{-1} \quad \text{i.e. resonance 'worth' } \sim 8 \text{ kJ mol}^{-1} \quad \left[\begin{array}{c}
  \text{[V]} \\
  \text{[2x120)-232]} 
  \end{array}\right]
  \]

  \[
  \text{Pd/C-H}_2 \quad \Delta H^\circ = -208 \text{ kJ mol}^{-1} \quad \text{i.e. aromatic stabilisation 'worth' } \sim 152 \text{ kJ mol}^{-1} \quad \left[\begin{array}{c}
  \text{[X]} \\
  \text{[3x120)-208]} 
  \end{array}\right]
  \]

- **X-ray and neutron diffraction data show all bond lengths to be the same**
  - 1.39 Å *cf.* ave C-C 1.54 Å & ave C=C 1.34 Å
Aromaticity: NMR ring currents

- **Protons ‘INSIDE’ ring would experience SHIELDING** \((B_{\text{appl}} - B_{\text{ind}})\)
  - i.e. resonate @high field (small \(\delta/\text{ppm}\))
- **Protons ‘OUTSIDE’ ring experience DESHIELDING** \((B_{\text{appl}} + B_{\text{ind}})\)
  - i.e resonate @low field (large \(\delta/\text{ppm}\))

- Note that the field is induced as the result of electron movement within orbitals & resulting diamagnetic anisotropy, see [http://www.youtube.com/watch?v=AlUGILfmwSc](http://www.youtube.com/watch?v=AlUGILfmwSc) (11.30-13.30 min)
Aromaticity: NMR ring currents

• **Benzene gives a singlet at $\delta$ 7.27 ppm**
  - *i.e.* deshielding due to ring current (cf. $\delta$ 4.5-6.5 ppm for typical alkene protons)
  - *i.e.* singlet because all H’s are in identical environment ($C_6$ symmetry)

• **Higher aromatic systems have stronger ring currents resulting in dramatic shielding/deshielding:**

  ![18-annulene](image1.png)
  ![Vogel's hydrocarbon](image2.png)
  ![dimethylidihydropyrene](image3.png)

  - 18-annulene ($18\pi$ electrons)
  - $\delta$ **-1.8 ppm inside**
  - $\delta$ 8.9 ppm outside

  - Vogel's hydrocarbon ($10\pi$ electrons)
  - $\delta$ **-0.7 ppm inside**
  - $\delta$ $\sim$7.1 ppm outside

  - dimethylidihydropyrene ($14\pi$ electrons)
  - $\delta$ **-5.5 (Me) inside**
Benzene – Valence Bond and Molecular Orbital Representations of Aromaticity

**VALENCE BOND (VB) THEORY**
- resonance hybrids - imaginary structures which differ only in position of electrons (atoms/nuclei do not move)
- Not all resonance structures contribute equally - ‘real’ structure is weighted average of resonance structures

**MOLECULAR ORBITAL (MO) THEORY**
- Linear Combination of Atomic Orbitals (LCAO)
- σ-bonding framework formed from sp² hybridised carbons
- leaves a p-orbital on each C atom *orthogonal* to the ring
- 6× atomic p-orbitals (AOs) → [LCAO maths] → 6× Molecular Orbitals (MOs):
  - each MO capable of containing 2 electrons
  - 6 electrons available to occupy the 6 MOs → placed in 3 molecular orbitals of lowest energy: *bonding orbitals*
  - 3 *anti-bonding orbitals* remain vacant
Benzene - Molecular Orbital Description

- Linear Combination of Atomic Orbitals (LCAO) – $6 \times 2p$ atomic orbitals give $6 \times$ molecular orbitals:
  - The +/- signs (and associated blue/orange colour designations) do not represent charges, but refer to phase signs in the equations that describe these orbitals.
  - When the phases are the same, the orbitals overlap to generate a common region of like-phase; the orbitals having the greatest like-phase overlap are the lowest in energy (hence, $\pi_1$ is the lowest in energy).
Musulin-Frost diagrams:
MO diagrams without the maths

• **Graphical device for constructing MO energy diagrams:**
  
  - Draw appropriate regular polygon within a circle (with atoms touching circumference)
  - Ensure one atom is at lowest point → ring atom positions represent energy levels
  - Centre of circle is zero energy level (i.e. bonding orbitals below, anti-bonding above)
Hückel’s rule

- **Empirical rule for aromaticity:**
  - For compounds which are planar & have a contiguous, cyclic array of p-orbitals perpendicular to plane of ring:
    - Those with 4n+2 p electrons display special stabilisation: *i.e.* aromatic
    - Those with 4n p electrons display special instability: *i.e.* anti-aromatic:

<table>
<thead>
<tr>
<th>4n+2 $\pi$ electrons</th>
<th>4n $\pi$ electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>aromatic</strong></td>
<td><strong>antiaromatic (or non-aromatic if non-planar)</strong></td>
</tr>
<tr>
<td>( n = 0 )</td>
<td>( n = 1 )</td>
</tr>
<tr>
<td>cyclopropenyl cation</td>
<td>benzene</td>
</tr>
<tr>
<td>cyclobutenyldication</td>
<td>cyclopropenyl anion</td>
</tr>
<tr>
<td>cyclobutenyldianion</td>
<td>benzene</td>
</tr>
<tr>
<td>cyclopentadienyldianion</td>
<td>cyclobutadiene</td>
</tr>
<tr>
<td>cycloheptatrienyldianion (tropylium cation)</td>
<td>cyclopentadienyldianion</td>
</tr>
<tr>
<td>cyclooctatetraenyldication</td>
<td>cycloheptatrienyldianion</td>
</tr>
<tr>
<td>( n = 2 )</td>
<td></td>
</tr>
<tr>
<td>cyclooctatetraenyldianion</td>
<td>cyclooctatetraene</td>
</tr>
</tbody>
</table>

In practice, molecules that could be anti-aromatic tend to adopt structures which are non-aromatic – typically by twisting to preclude communication between adjacent p-orbitals (*e.g.* Cyclooctatetraene which adopts a ‘tub’ shaped conformation) or by adopting hybridisation states that do not present a contiguous cyclic array of p-orbitals (*e.g.* Cyclopropenyl anion, for which two low energy electronic configurations have been located computationally, neither of which is anti-aromatic).
Evidence for anti-aromaticity

- **Deprotonation of cycloprop(en)yl ketones**

\[
\begin{align*}
\text{Ph} & & \text{H} & & \text{Ph} & & \rightarrow & & \text{Ph} & & \text{H} & & \text{Ph} \\
\text{Ph} & & \text{H} & & \text{Ph} & & \rightarrow & & \text{Ph} & & \text{H} & & \text{Ph} \\
\text{Ph} & & \text{H} & & \text{Ph} & & \rightarrow & & \text{Ph} & & \text{H} & & \text{Ph}
\end{align*}
\]

\[
\text{NaOD} \quad \text{D}_2\text{O} \quad \rightarrow \quad \text{NaOD} \quad \text{D}_2\text{O}
\]

4 \(\pi\) electrons anti-aromatic

- **Silver assisted solvolysis of cyclopent(adien)yl iodides**

\[
\begin{align*}
\text{Cyclopentyl I} & & \rightarrow & & \text{Cyclopentyl} & & + & & \text{AgI} \\
\text{Cyclopentyl I} & & \rightarrow & & \text{Cyclopentyl} & & + & & \text{AgI}
\end{align*}
\]

'very fast'

\[
\begin{align*}
\text{Cyclopentyl I} & & \rightarrow & & \text{Cyclopentyl} & & + & & \text{AgI} \\
\text{Cyclopentyl I} & & \rightarrow & & \text{Cyclopentyl} & & + & & \text{AgI}
\end{align*}
\]

4 \(\pi\) electrons anti-aromatic