

***Year 1 CHEM40006***  
***Reactivity at Carbon Centres***

***LECTURE 12 - Reactivity at  $sp^2$  Centres:  
Introduction to Aromatic Compounds & Aromaticity***

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# Format and scope of presentation

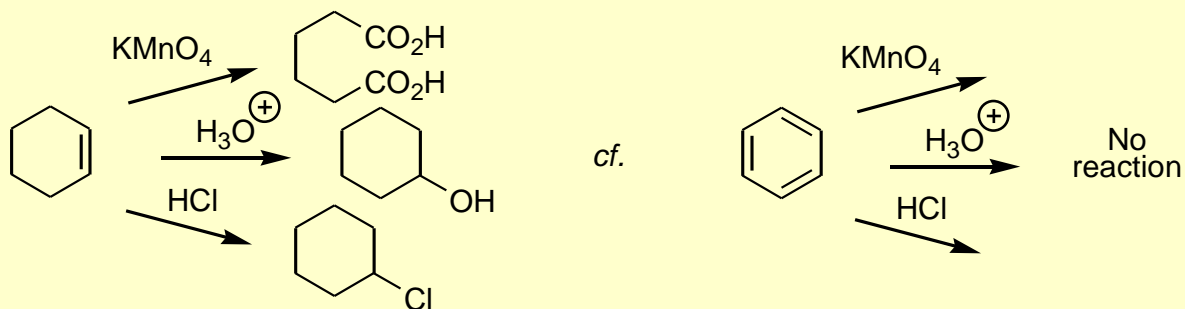
- **Aromaticity:**
  - Historical perspective (Kekulé)
  - Characteristics, NMR ring currents
  - Valence bond & molecular orbital representations (Hückel's rule)
  - Anti-aromaticity

**Key further reading:** Clayden, Greeves & Warren, *Organic Chemistry*, 2<sup>nd</sup> Ed., Chapter 7

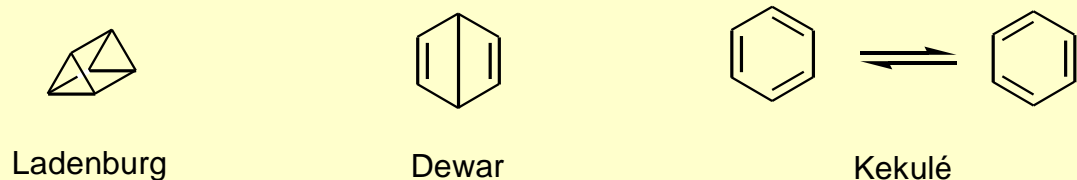
- *conjugation* – pages 143 - 150
- *aromaticity* – pages 156 - 162

# Aromaticity: historical perspective

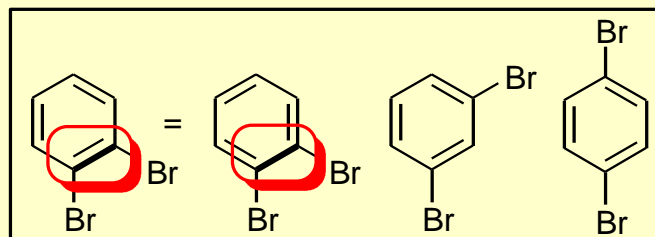
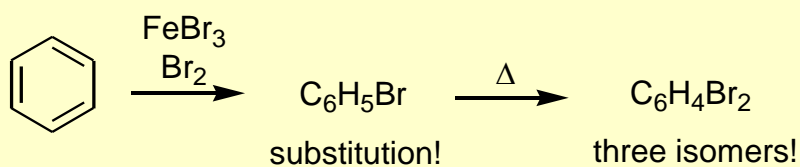
- **'Aromatic' → 'aroma' → natural fragrances e.g. benzaldehyde (peaches)**
- **Unusual stability/unreactivity for an unsaturated hydrocarbon**



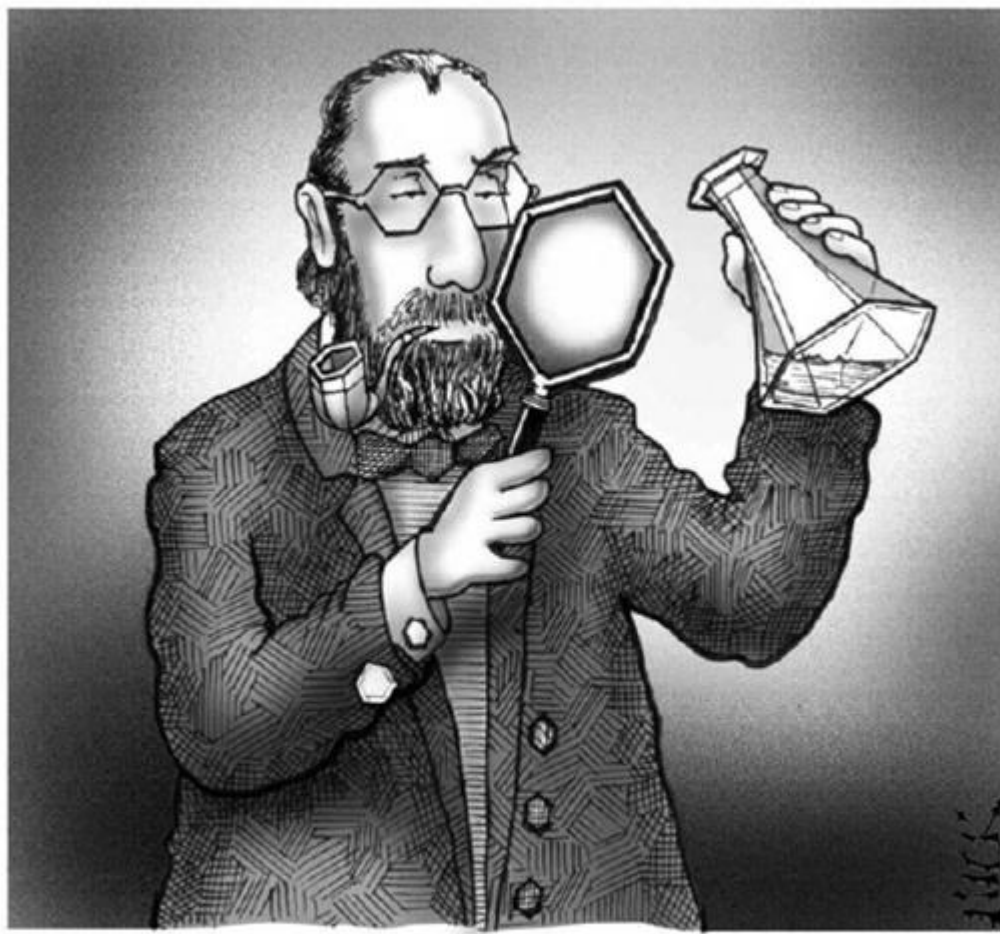
- **Late 1800's: benzene combustion analysis → molecular formula  $\text{C}_6\text{H}_6$**



- **No-decolourisation of bromine water (i.e. addition of  $\text{Br}_2$  across double bonds)**

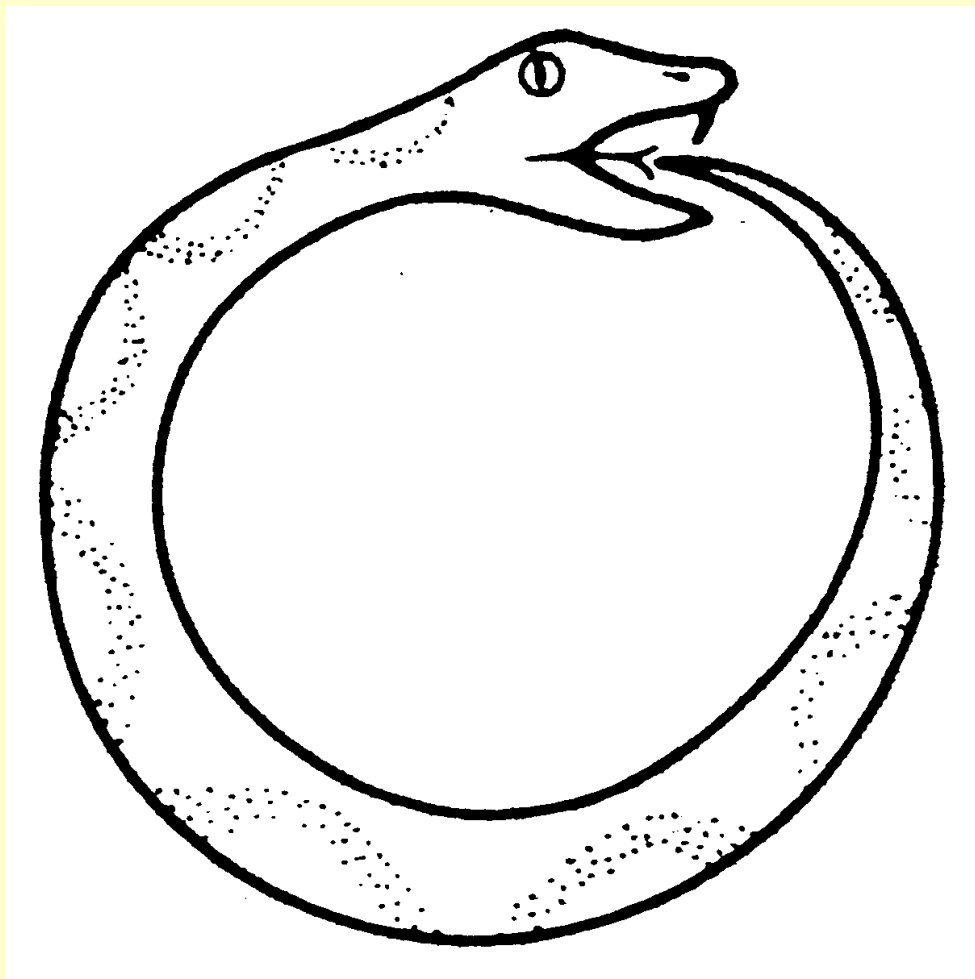


*Great events in Chemistry...*

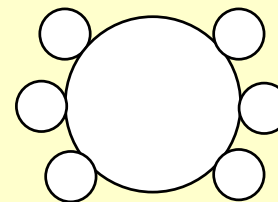


1865: Kekulé, moments before his brilliant insight into the structure of benzene.

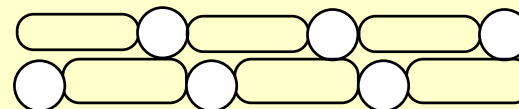
## Kekulé and his dream of snakes...



Ouroboros



Loschmidt 1861



Kekulé 1861

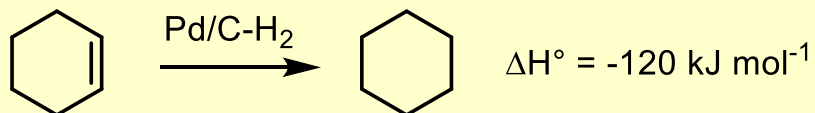
### Kekulé or Loschmidt?

- 'It began with a daydream: the 150<sup>th</sup> anniversary of the Kekule benzene structure', A. Rocke *Angew. Chem. Int Ed.* **2015**, 54, 46-50 ([DOI](#))
- "I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by the repeated visions of the kind, could now distinguish larger structures of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis."

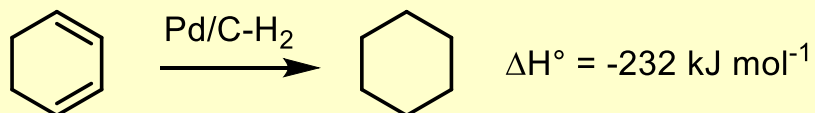
# Aromaticity: stability and bond lengths

- Quantification of unusual stability: heats of hydrogenation (calorimetry)**

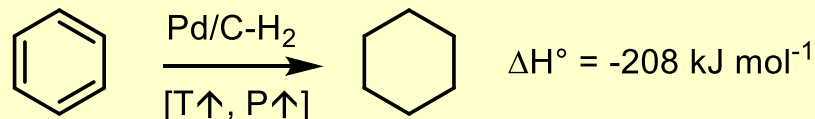
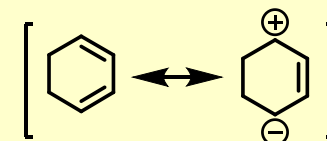
- see: Vollhardt *J. Am. Chem. Soc.* **2000**, 122, 7819 ([DOI](#))



N.B. 1 kcal = 4.18 kJ



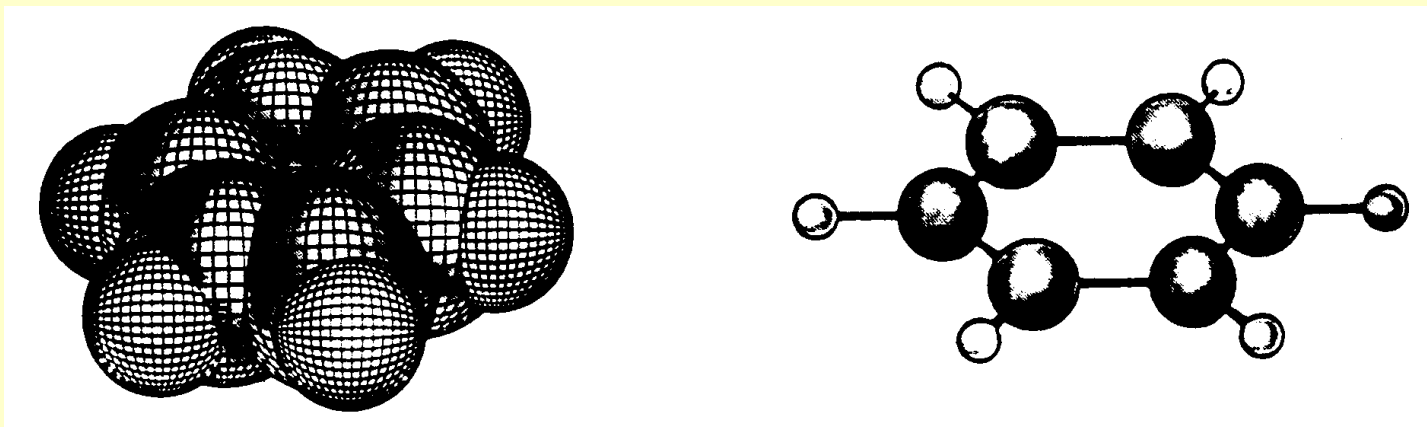
i.e. resonance 'worth'  $\sim 8 \text{ kJ mol}^{-1}$   
 $[(2 \times 120) - 232]$



i.e. aromatic stabilisation 'worth'  $\sim 152 \text{ kJ mol}^{-1}$   
 $[(3 \times 120) - 208]$

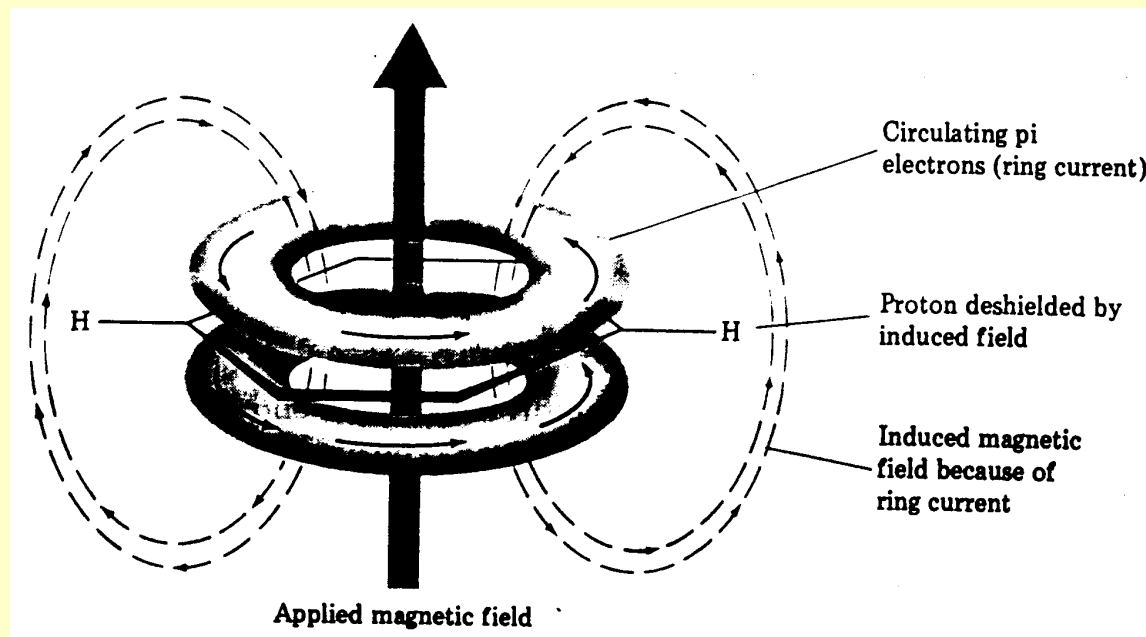
- X-ray and neutron diffraction data show all bond lengths to be the same**

- 1.39Å cf. ave C-C 1.54Å & ave C=C 1.34Å



# Aromaticity: NMR ring currents

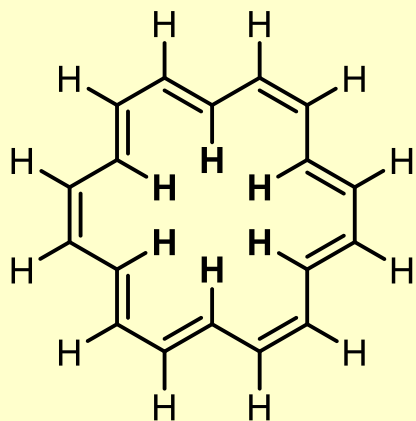
- **Protons 'INSIDE' ring would experience SHIELDING ( $B_{\text{appl}} - B_{\text{ind}}$ )**
  - *i.e.* resonate @high field (small  $\delta/\text{ppm}$ )
- **Protons 'OUTSIDE' ring experience DESHIELDING ( $B_{\text{appl}} + B_{\text{ind}}$ )**
  - *i.e.* resonate @low field (large  $\delta/\text{ppm}$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



- Note that the field is induced as the result of electron movement within orbitals & resulting diamagnetic anisotropy, see <http://www.youtube.com/watch?v=AIUGILfmwSc> (11.30-13.30 min)

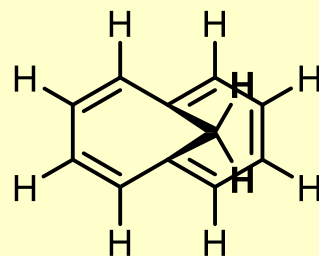
# Aromaticity: NMR ring currents

- **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:**



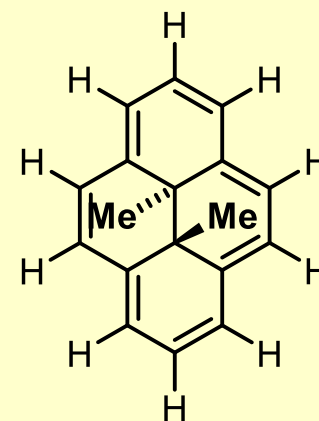
18-annulene  
( $18\pi$  electrons)

$\delta$  -1.8 ppm inside  
 $\delta$  8.9 ppm outside



Vogel's hydrocarbon  
( $10\pi$  electrons)

$\delta$  -0.7 ppm inside  
 $\delta$  ~7.1 ppm outside



dimethyldihydropyrene  
( $14\pi$  electrons)

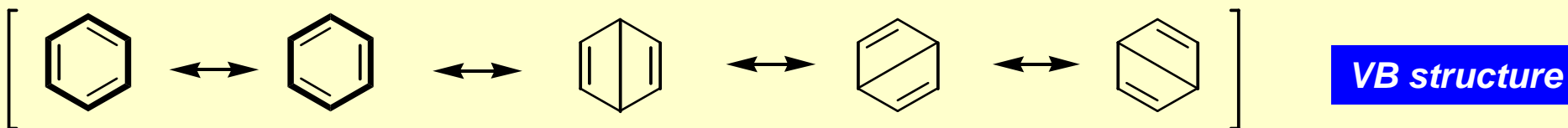
$\delta$  -5.5 (Me) inside



# 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
- Reviews: Hiberty *et al. Chem. Rev.* **2011**, 111, 7557 ([DOI](#)) & *Angew. Chem. Int. Ed.* **2018**, 57, 5994 ([DOI](#))

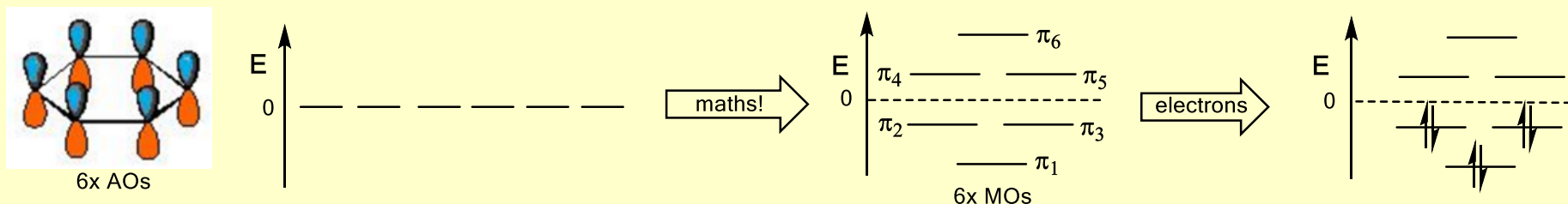


## MOLECULAR ORBITAL (MO) THEORY

- Linear Combination of Atomic Orbitals (LCAO)
- $\sigma$ -bonding framework formed from  $sp^2$  hybridised carbons
- leaves a p-orbital on each C atom *orthogonal* to the ring
- 6x atomic p-orbitals (AOs)  $\rightarrow$  [LCAO maths]  $\rightarrow$  6x Molecular Orbitals (MOs):



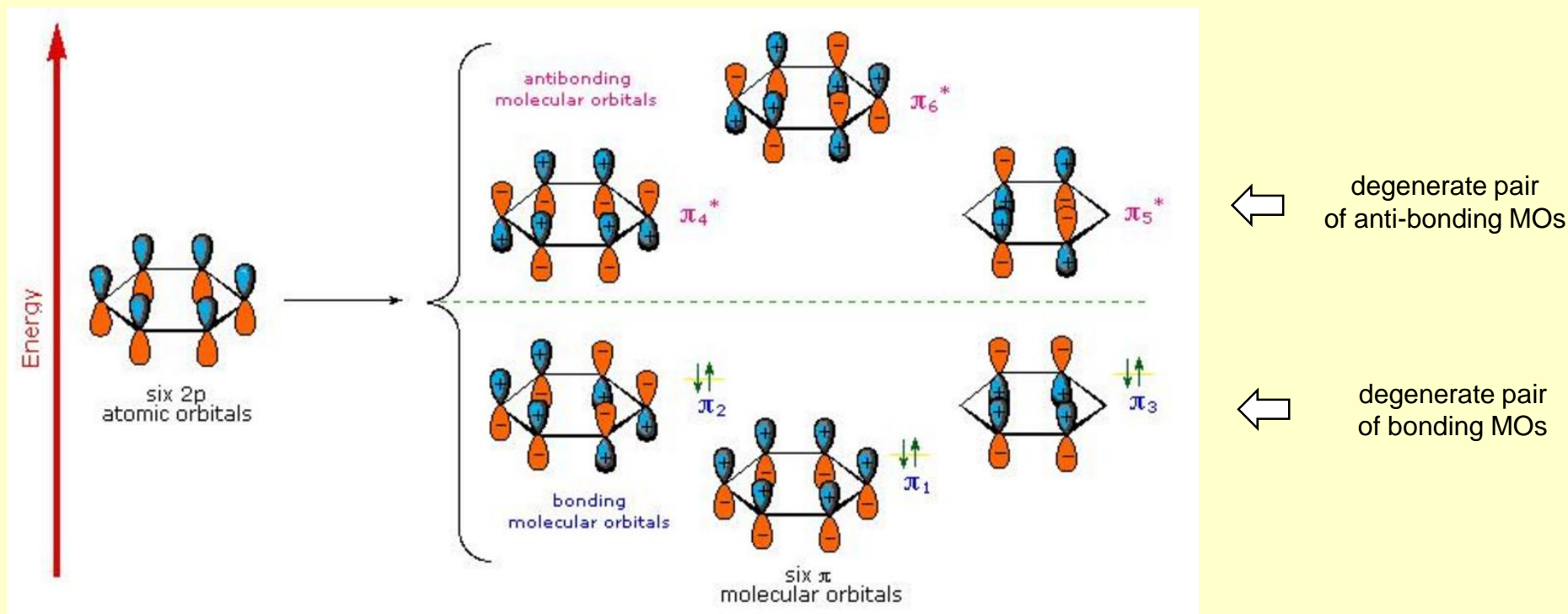
**MO structure**



- each MO capable of containing 2 electrons
- 6 electrons available to occupy the 6 MOs  $\rightarrow$  placed in 3 molecular orbitals of lowest energy: **bonding orbitals**
- 3 **anti-bonding orbitals** remain vacant

# Benzene - Molecular Orbital Description

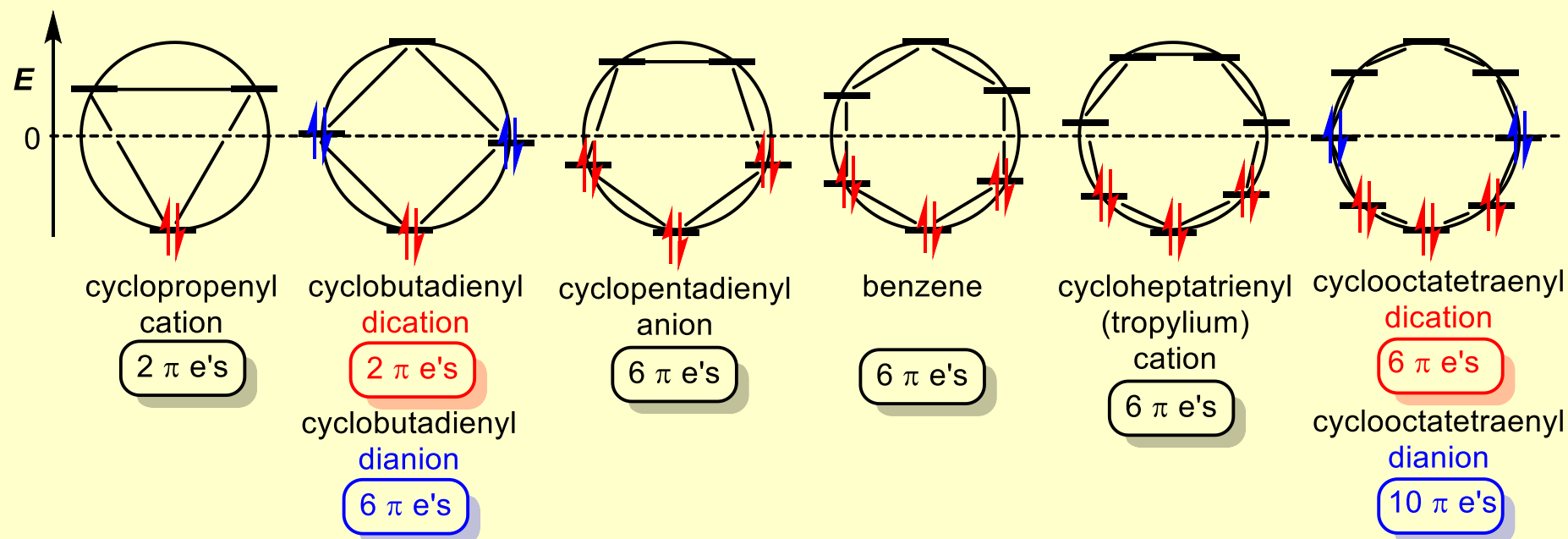
- Linear Combination of Atomic Orbitals (LCAO) – 6x 2p atomic orbitals give 6x molecular orbitals:



- 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:**
  - Frost & Musulin *J. Chem. Phys.* **1953**, 21, 572 ([DOI](#)) & Zimmerman *J. Am. Chem. Soc.* **1966**, 88, 1564 ([DOI](#))
  - 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:**

- Hückel *Z. Phys.* **1931**, 70, 204; **Review:** Berson *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 2750 ([DOI](#))

- **For compounds which are planar & have a contiguous, cyclic array of p-orbitals perpendicular to plane of ring:**

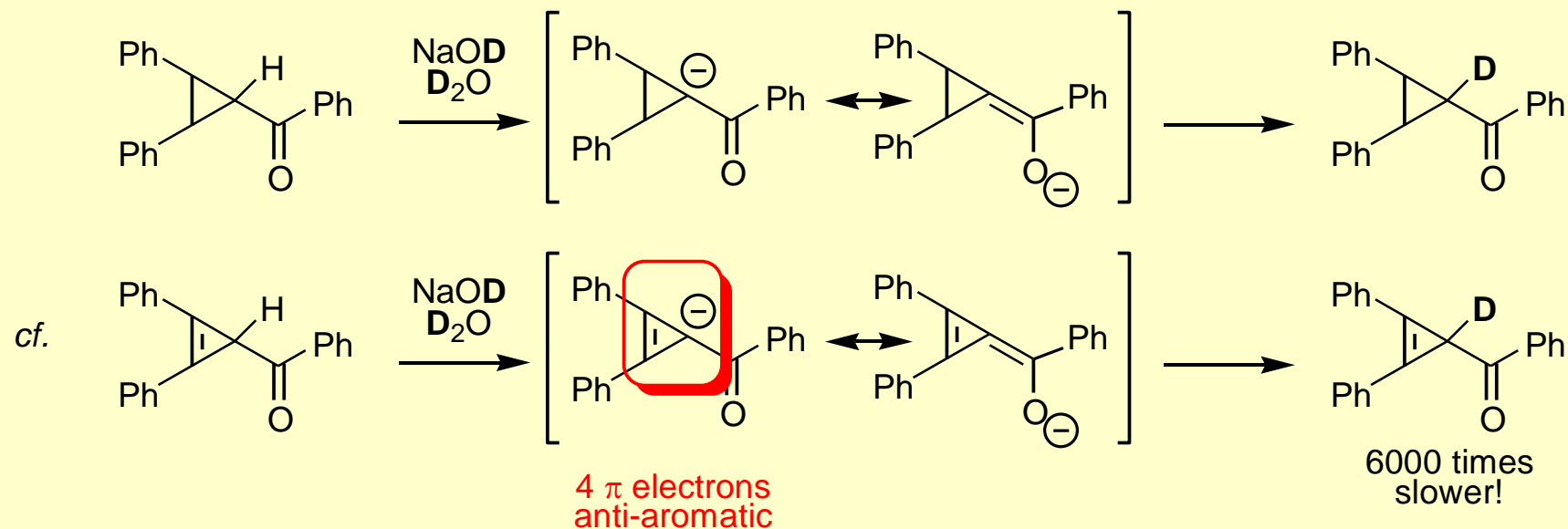
- Those with  $4n+2$  p electrons display special stabilisation: *i.e.* **aromatic**
- Those with  $4n$  p electrons display special instability: *i.e.* **anti-aromatic:**

$4n+2$ $\pi$ electrons aromatic	$4n$ $\pi$ electrons antiaromatic (or non-aromatic if non-planar)
<b>n = 0</b>  cyclopropenyl cation  cyclobutenyl dication	
<b>n = 1</b>  cyclobutenyl dianion  benzene  cyclopentadienyl anion  cycloheptatrienyl cation (tropylium cation)  cyclooctatetraenyl dication	 cyclopropenyl anion  cyclobutadiene  cyclopentadienyl cation
<b>n = 2</b>  cyclooctatetraenyl dianion	 cycloheptatrienyl anion  cyclooctatetraene

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**



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

