

CHEM 202

Module 2

Aromaticity and Functional group manipulations in Aromatic Chemistry

Dr Andrea Vernall

andrea.vernall@otago.ac.nz

Module Outline

L1	Aromaticity and Valence Bond Pictures of Unsaturated Hydrocarbons
L2	A Molecular Orbital Approach to π Bonding
L3	Electrophilic aromatic substitution – introduction, mechanism, reactions
L4	S _E Ar - Synthesis of Alkylbenzenes and Substituent Effects
L5	Effect of Substituents on Orientation in S _E Ar
L6	Functional Group Interconversions, including diazonium chemistry
L7	Functional interconversions and more “Synthesis problems”
L8	Nucleophilic Aromatic substitution, benzyne
L9	The effect of a benzene ring on a substituents, acidity, free radical and carbocation stability, the benzylic carbon.

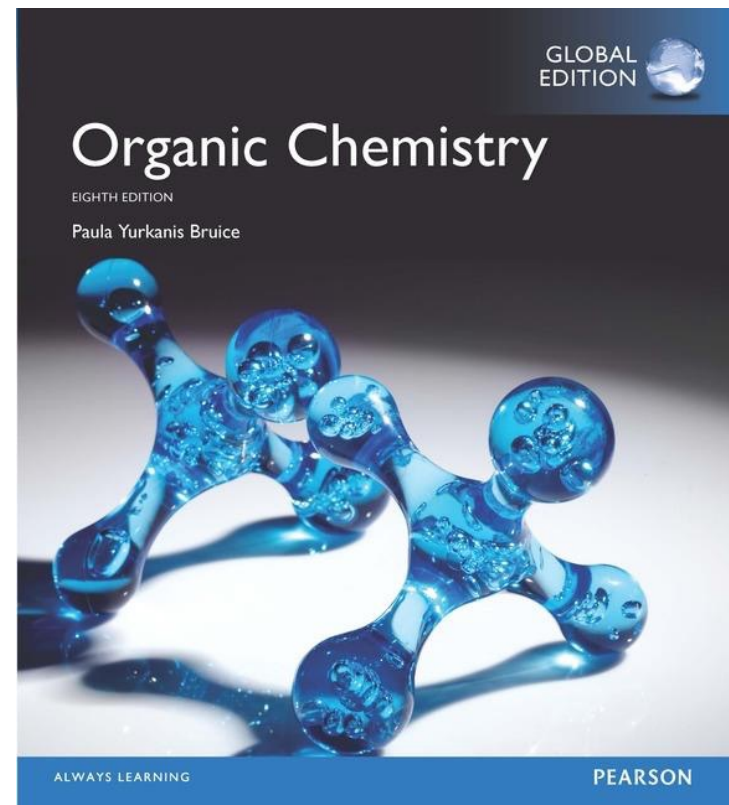
Learning Objectives – 9 lecture module + tutorials

Refer to Blackboard

- Course information,
 - **'Aims and objectives for lecture courses'**
 - Module 2
-
- 4 Pages of “Aims and objectives” for this module
 - Document is in approximately the same order as the lecture material
 - The relevant sections from the above document are written word-for-word as Learning Objectives at the start of the relevant lecture.

Reference textbook

- “Organic Chemistry” by Paula Yurkanis Bruice, 8th Edn.
- The E-book is available for \$60 through the following link;
<http://www.pearsoned.co.nz/9781292160344>
- Page/section numbers in this lecture module refer to the **8th Edition**



Lectures 1 and 2, predominantly refer to Chapter 8, sub sections concerning aromatic compounds, resonance

Lecture I

Aromaticity and Valence Bond Diagrams of Unsaturated Hydrocarbons

Dr Andrea Vernall

andrea.vernall@otago.ac.nz

Learning Objectives – Lecture 1

Section 1 – Valence bond and molecular orbital pictures of unsaturated hydrocarbons

Discuss experimental evidence which refutes the 1,3,5-cyclohexatriene structure for benzene proposed by Kekule, to include data on bond lengths and the thermodynamic stability of benzene compared to that predicted for 1,3,5-cyclohexatriene

Draw resonance (canonical) structures for molecules containing π and non-bonded electrons

Depict benzene and its derivatives using the Kekule and delocalised structures

Use Hückel's rule to determine if a given structure is aromatic

Lecture Outline: L1

1. History and properties of benzene

- What is benzene? What is aromaticity?
- Discovery
- Stability

2. Resonance, delocalization

- Drawing resonance structures

3. Requirements for aromaticity

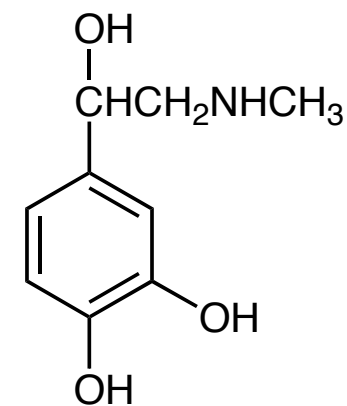
- Physical requirements
- Hückel's rule

1. History and properties of benzene

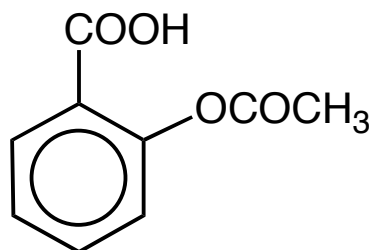
What's an aromatic compound?

Anything that contains an aromatic ring.....

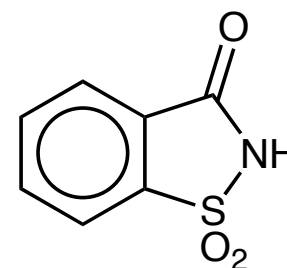
This could be something that contains a *benzene-like* substructure -



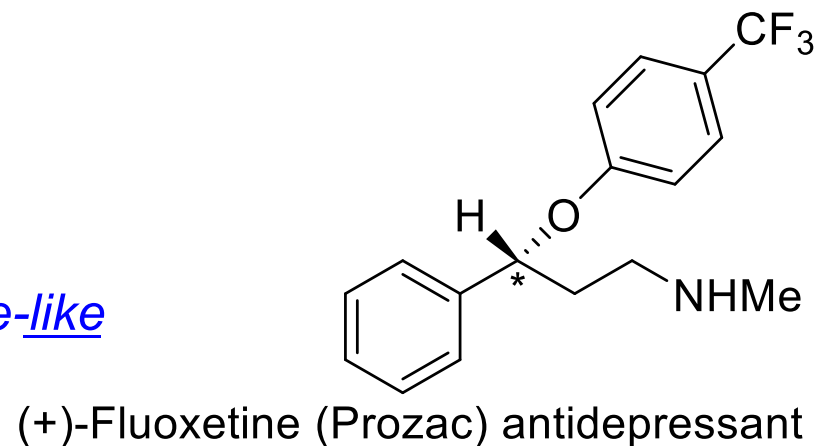
adrenalin



aspirin



saccharin



What does the name 'benzene' represent ?

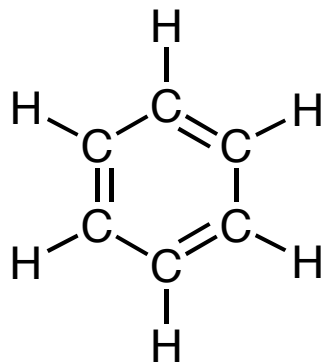
How was benzene discovered ?

What's with the double bonds or 'circle' ?

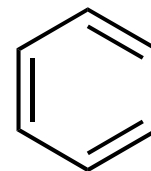
1. History and properties of benzene

What is benzene ?

- A regular hexagon of carbon atoms with **6 hydrogens**
- Planar structure, all C's are sp^2 hybridised



Which is abbreviated as:



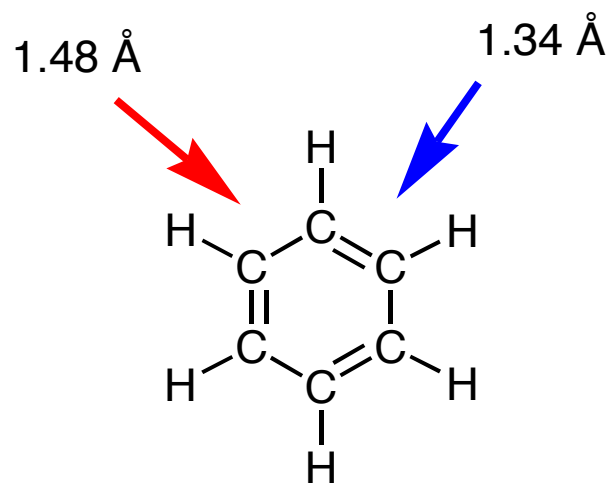
The 'double' bonds are alternating (separated by one 'single' bond).

BUT it is a **CONJUGATED** system

1. History and properties of benzene

How was benzene discovered, what's the evidence for the conjugation?

- Early chemists knew benzene has a Mr of C_6H_6 and it was unusually **stable**
- One explanation for C_6H_6 could be a 1,3,5-cyclohexatriene

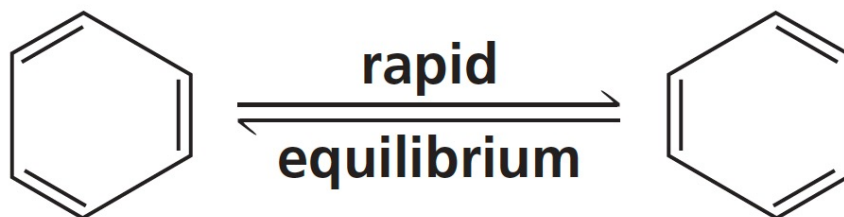


It was thought that cyclohexatriene should have 3 short bonds and 3 longer bonds (alternating).

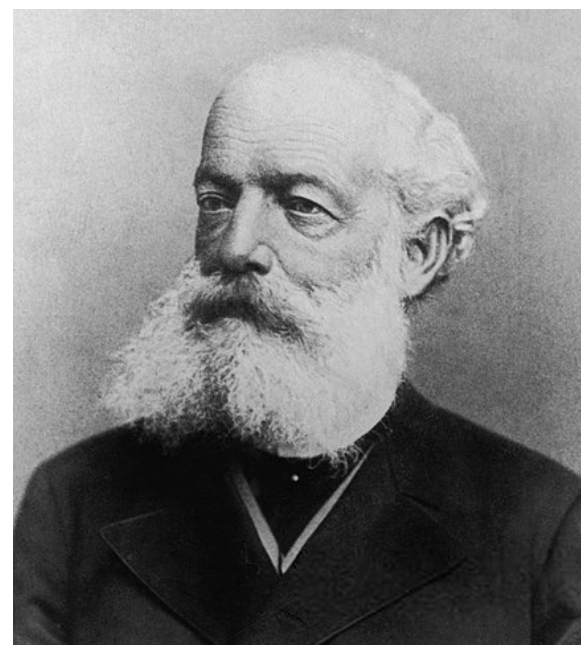
1. History and properties of benzene

How was benzene discovered, what's the evidence for the conjugation?

- To explain reactivity patterns, in 1865 the German chemist **Kekulé** proposed benzene was a mixture of 2 compounds in equilibrium



Kekulé structures of benzene

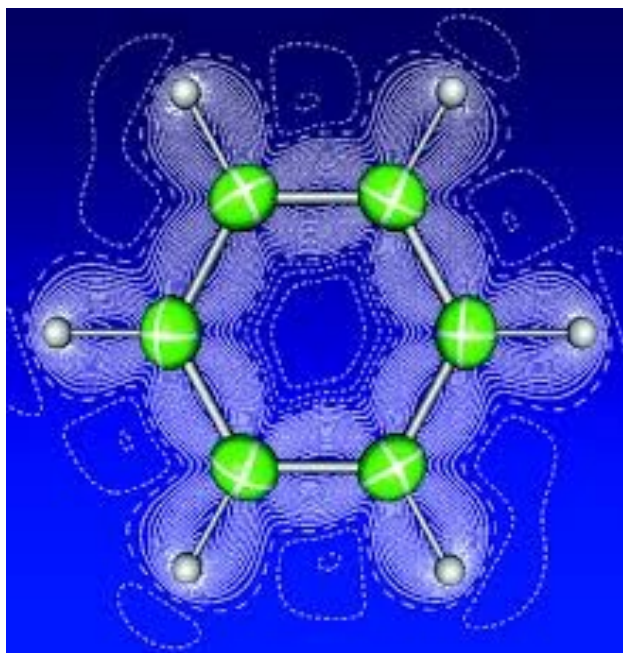


- But benzene didn't react like an 'alkene'*

1. History and properties of benzene

How was benzene discovered, what's the evidence for the conjugation?

- In the 1930s the then new techniques of X-ray and electron diffraction produced a surprising result -

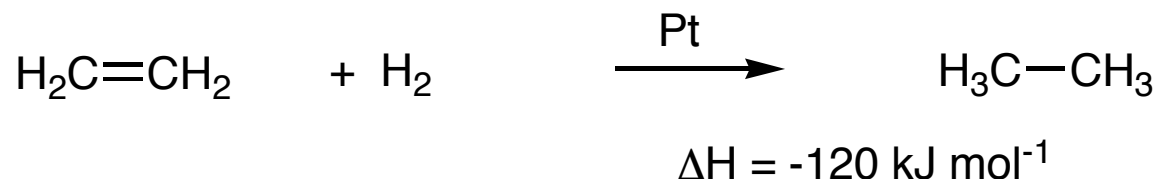


- Benzene is **PLANAR**
- All carbon-carbon bonds have the **same bond length**, 1.39 Å

1. History and properties of benzene

Stability

- Benzene is quite a stable compound
- We can use the heat of hydrogenation to demonstrate this
 - The heat of hydrogenation is the heat evolved when one mole of an unsaturated compound is hydrogenated $\approx 120 \text{ kJ per double bond}$.

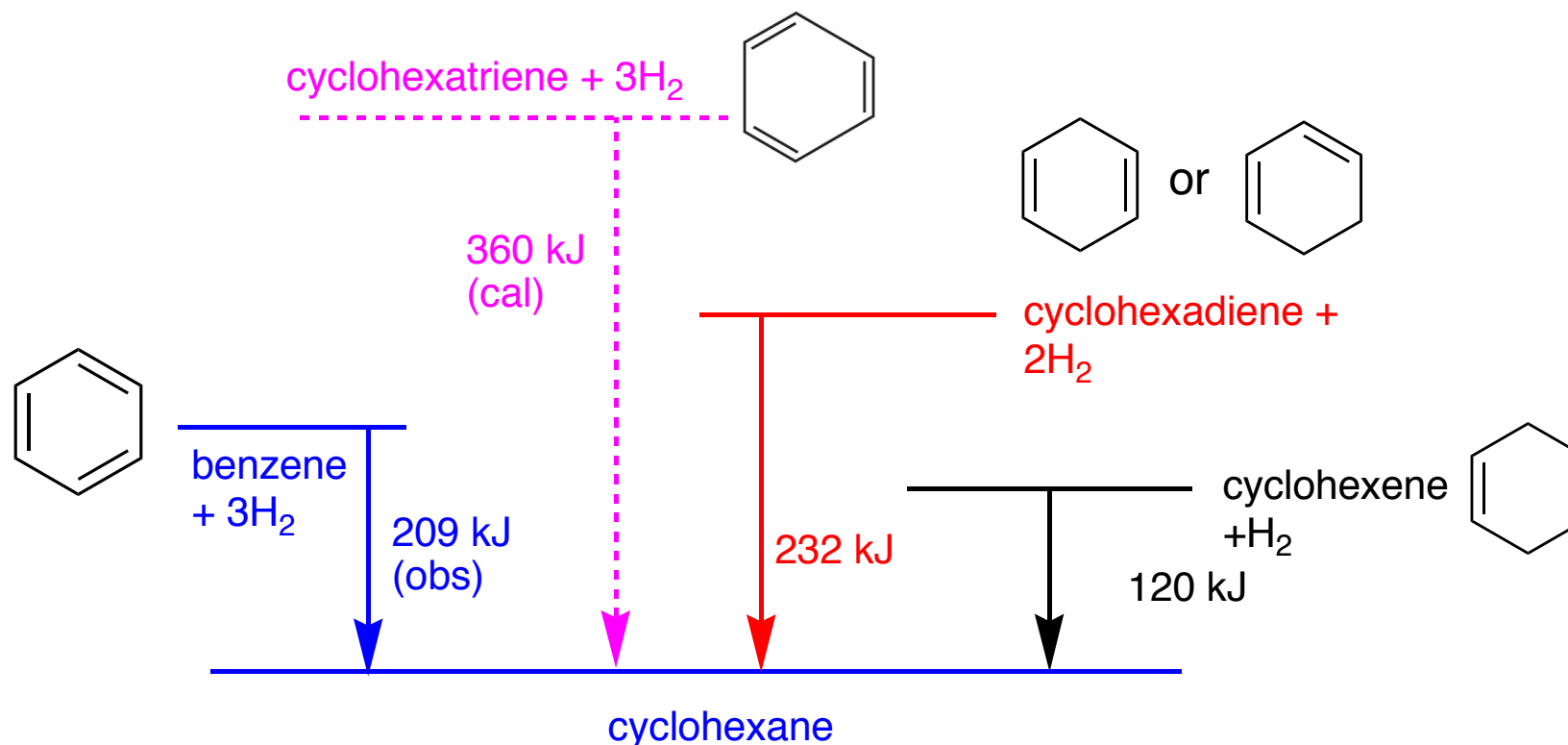


- Thus **if** 1,3,5-cyclohexatriene **theoretically exists** it should evolve approximately 360 kJ mol^{-1} of energy upon complete hydrogenation

1. History and properties of benzene

Stability

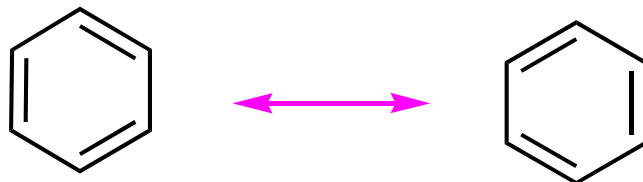
- Heat of hydrogenation, ≈ 120 kJ per double bond.



Benzene is more stable than the **hypothetical** cyclohexatriene structure.
We will see in Lecture 2 is it because benzene's electrons sit in lower energy MOs

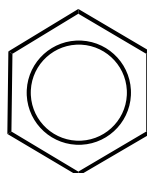
2. Resonance, delocalisation

- The structure of benzene is that of a hybrid of :



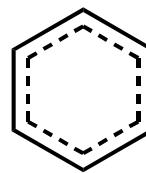
resonance contributors

- Where each contributor is an approximate *hypothetical structure* with delocalised electrons (NOT 'alkenes')
- The actual structure is a **resonance hybrid** with **DELOCALISED** electrons.



resonance hybrid

or



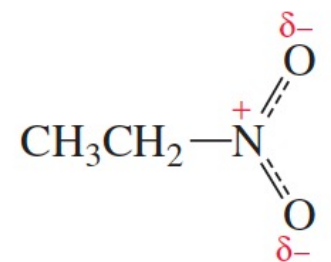
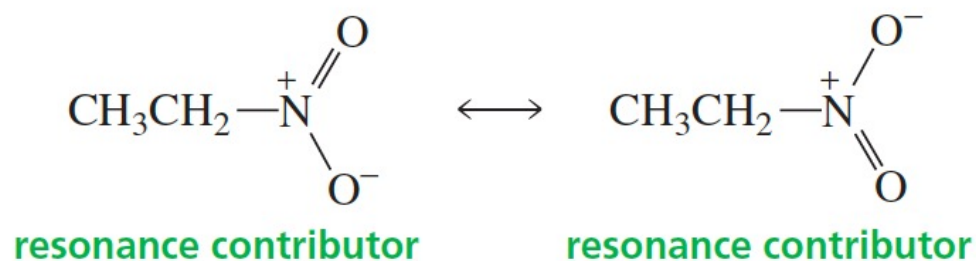
bond order = 1.5

2. Resonance, delocalisation

Definition

Resonance structures are two or more structures **representing** a molecule:

- that differ only in their arrangement of electrons
- have the same arrangement of atomic nuclei



resonance hybrid

2. Resonance, delocalisation

Rules for drawing resonance structures

First draw the Lewis structure (this is the first resonance contributor)

Then follow the rules below to move electrons -

- Only electrons move, not atoms.
- Only π and non-bonded electrons (e.g. lone electron pairs) move.
- The total number of electrons in the molecule does not change.

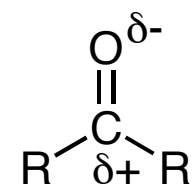
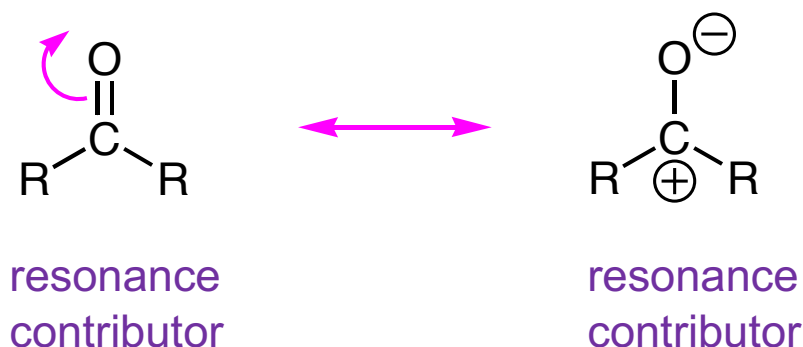
Move the electrons in one of the following ways -

- Move the π electrons between two different atoms towards the electronegative atom (*example 1*)
- Move π electrons towards a positive charge (*example 2*)
- Move the π electrons towards a π bond (*example 3*)
- Move non-bonding electrons towards a positive charge.
- Move non-bonding electrons towards a π bond (*example 4*)

2. Resonance, delocalisation

Move the π electrons between two different atoms towards the electronegative atom (*example 1*)

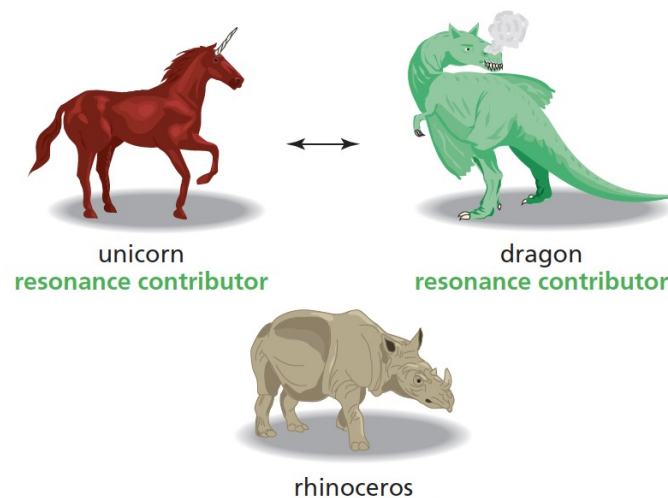
e.g. a ketone



Is best represented by this as the 'real' structure

This resonance is **NOT** an equilibrium

- Page 359 in Bruice
- The unicorn and dragon are 'imaginary' and don't really truly exist, but are just a way of representing what the real species (the rhino) looks like
- Only the 'rhino' is real



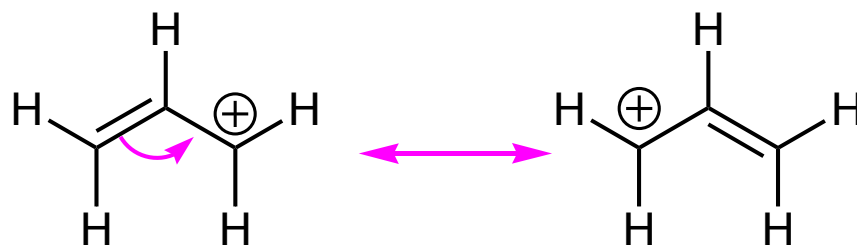
Hybrid or 'real' structure

BREAK

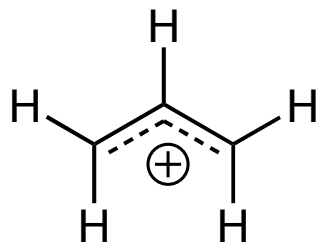
2. Resonance, delocalisation

Move π electrons towards a positive charge (*example 2*)

e.g. allyl cation



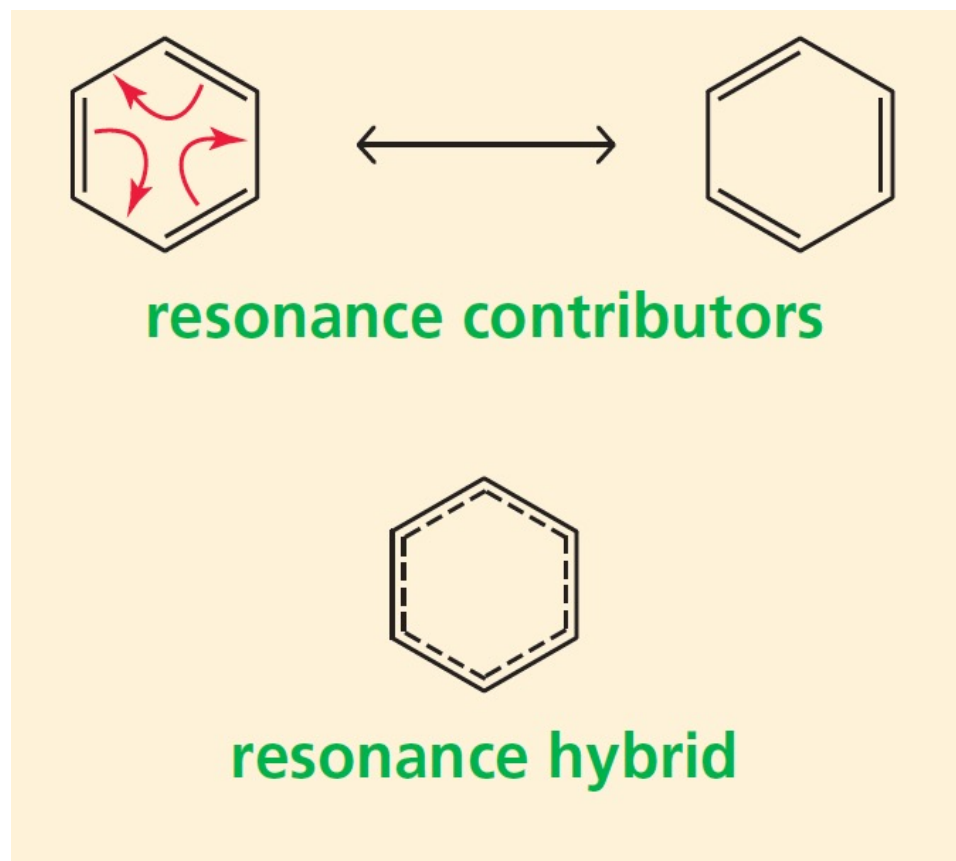
Resonance contributors



'real' structure

2. Resonance, delocalisation

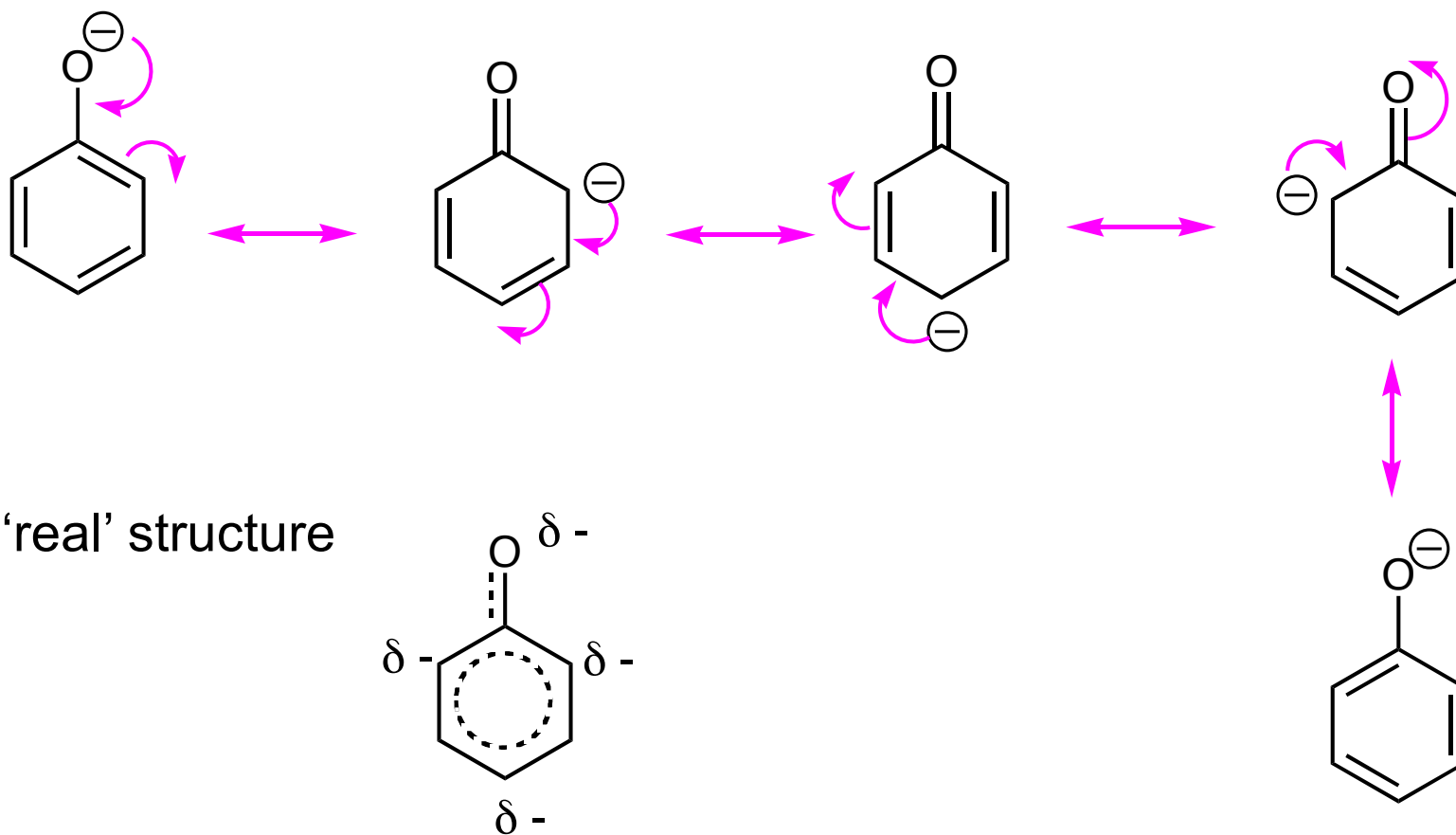
Move the π electrons towards a π bond (*example 3*)



2. Resonance, delocalisation

Move non-bonding electrons towards a π bond (*example 4*)

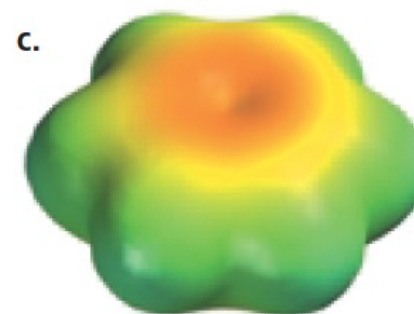
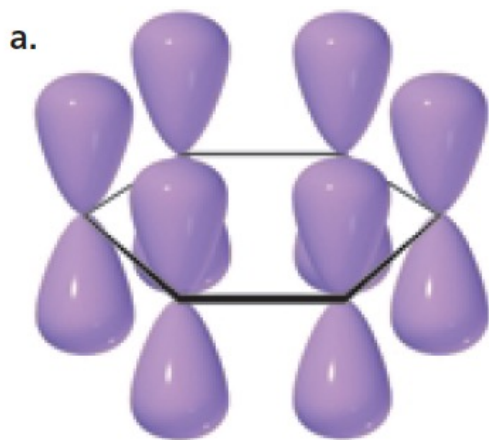
e.g. the phenoxide ion



3. Requirements for aromaticity

To be classified as aromatic, a compound must meet both the following -

1. It must have an uninterrupted cyclic cloud of π electrons above & below the molecule
 - For the π cloud to be cyclic, the molecule must be **cyclic**
 - For the π cloud to be uninterrupted, **every atom** in the ring must have a **p orbital**
 - For each p orbital to sufficiently overlap, the molecule must be **planar**
2. The π cloud must contain an **odd number of pairs** of π electrons

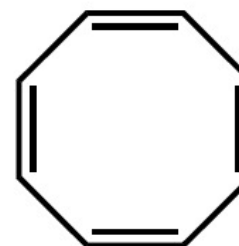
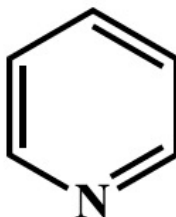
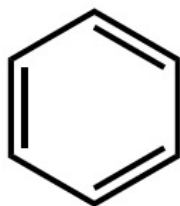


3. Requirements for aromaticity

Hückel's Rule

- “The π cloud must contain an **odd number of pairs** of π electrons” was recognized by German physicist Hückel, who described the ‘ $4n+2$ rule’.

The uninterrupted π electron cloud must have **$(4n + 2)$ π electrons**, where **n is any whole number**


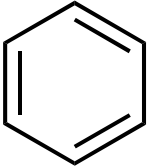
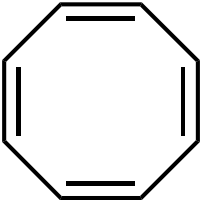
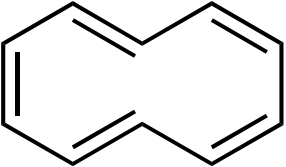
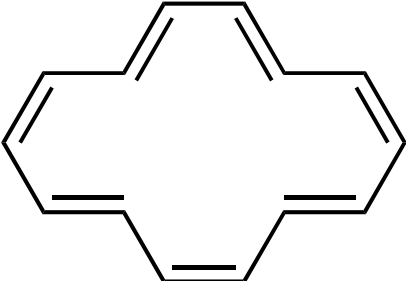


Historically an ‘aromatic’ compound was defined by a smell



3. Requirements for aromaticity

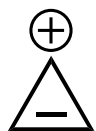
Applying the criteria for aromaticity

	planar	π -electrons	C/C bonds	aromatic
	no			
	yes			
	no			
	no			
	yes			

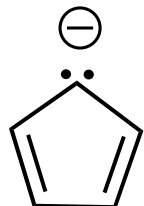
3. Requirements for aromaticity

Applying the criteria for aromaticity

Charged systems can also be aromatic.



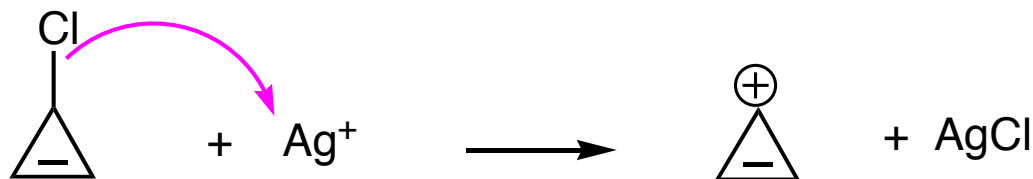
cyclopropenyl cation



cyclopentadienyl anion

both are easily formed because they are relatively stable.

e.g.



3. Requirements for aromaticity

Applying the criteria for aromaticity

Conversely, NOT aromatic -

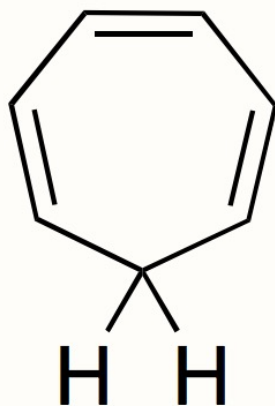


Are very difficult to form. eg:

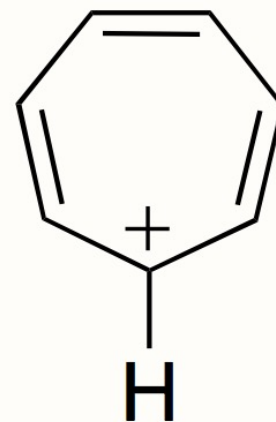


3. Requirements for aromaticity

Applying the criteria for aromaticity



6 π -electrons
not fully conjugated =
not aromatic

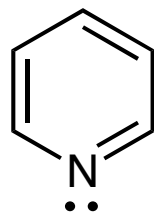


6 π -electrons
fully conjugated =
aromatic

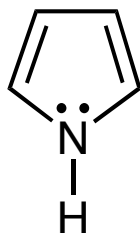
3. Requirements for aromaticity

Applying the criteria for aromaticity

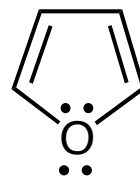
Many HETEROCYCLES are also aromatic



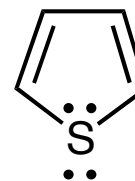
pyridine



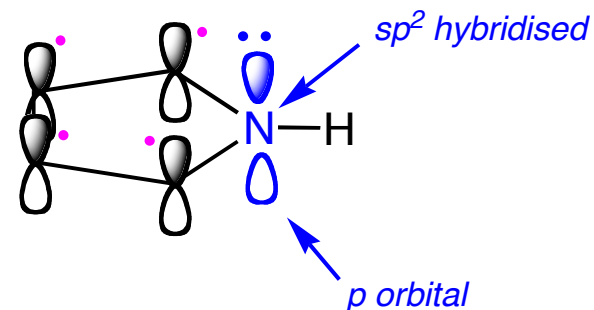
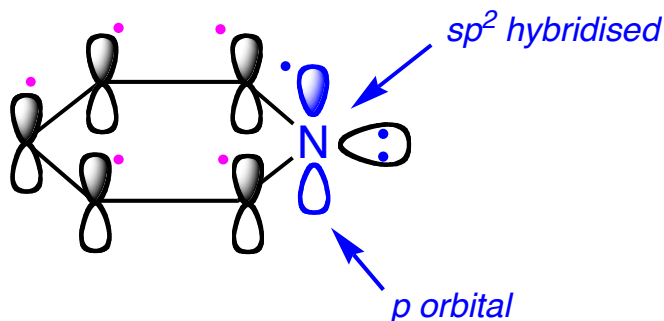
pyrrole



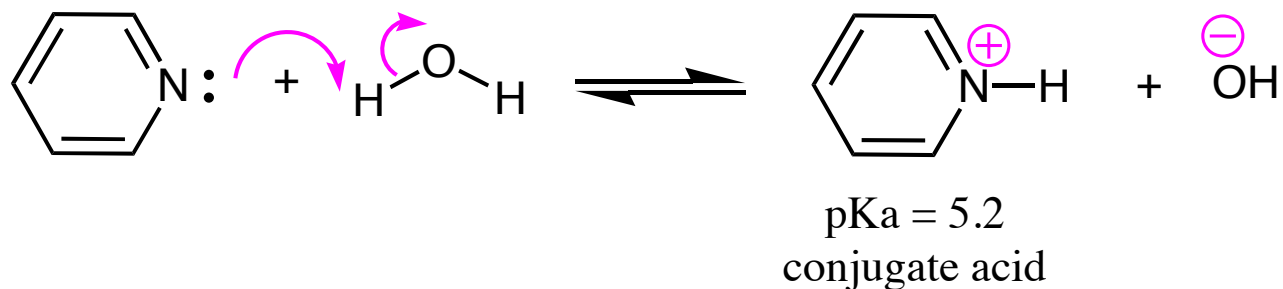
furan



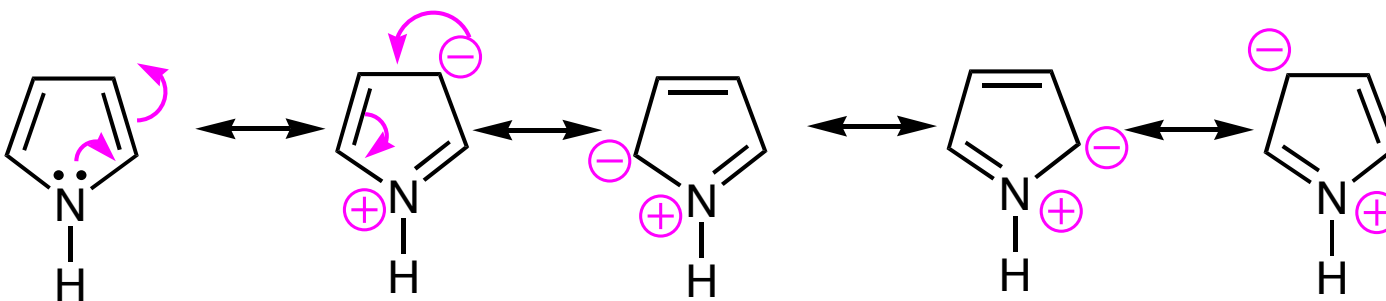
thiophene



Thus pyridine is basic, nitrogen lone pairs are not part of the aromatic ring:



Pyrrole is not basic, because nitrogen's lone pair of electrons are **part of the aromatic ring**:



Can you draw the resonance hybrid, the 'rhino' for pyrrole?