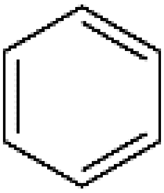
UNDERSTANDING BENZENE STRUCTURE

LESSON 4 **A STRUCTURE THAT FITS WITH THE EVIDENCE**

Over the last three weeks, you have discovered that;



- the **molecular formula of benzene is C_6H_6**
- There are many possible structures that could have the formula **C_6H_6**
- ***Kekulé*** suggested a structure that we refer to as ***Kekulé benzene.***
- There are reasons to doubt this proposed theoretical structure. These include,
  - Failure to react with **bromine water**
  - **Bond lengths between carbons are all equal** AND **between the length of a C-C and C=C**
  - The **enthalpy of hydrogenation for 'real' benzene** is significantly less exothermic than we would expect if the structure was the ***Kekulé benzene*** structure. This difference is around **150** $kJmol^{-1}$

We now need to consider a modified version of the ***Kekulé benzene*** structure that is consistent with the evidence above.

Electronic Configurations and Structure

Complete the electronic configurations for the following species.

H	**$1s^1$**	**Na^+**	**$1s^2 2s^2 2p^6$**
C	**$1s^2 2s^2 2p^2$**	**O**	**$1s^2 2s^2 2p^4$**
Cl^-	**$1s^2 2s^2 2p^6 3s^2 3p^6$**	**Sc**	**$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$**
Cr	**$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$**	**Ge**	**$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$**
Br	**$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$**	**Kr**	[Ar]**$3d^{10} 4s^2 4p^6$**

How many types of **subshell**, does Na^+ contain? **2 (s &p sub-shells)**

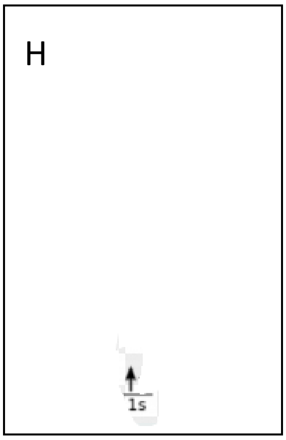
How many filled **orbitals** does O contain? **3 (2 filled s orbitals and a filled p orbital)**

How many completed shells does Kr contain? **3 (1st, 2nd and 3rd shells are filled. 4th shell is only partially filled)**

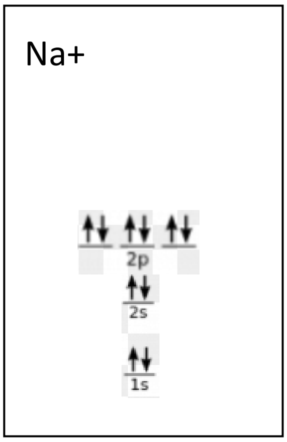
We can represent these configurations in an **energy level diagram** that illustrates the **'Aufbau' order**. (This 'building up' order is based upon the '*aufbau'* principle which, in turn obeys *Hund's Rule* and the *Pauli Exclusion principle*. These are some of fundamental rules that govern the behaviour of electrons in atoms.)

Draw **labelled energy level diagrams** for H, Na^+, C, Sc. Use boxes ↑↓ or lines ↑↓

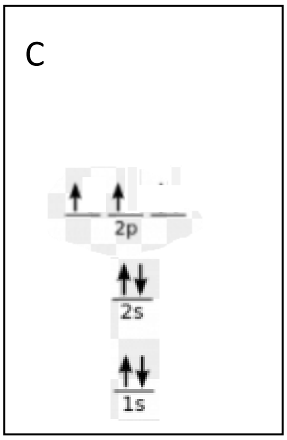
H



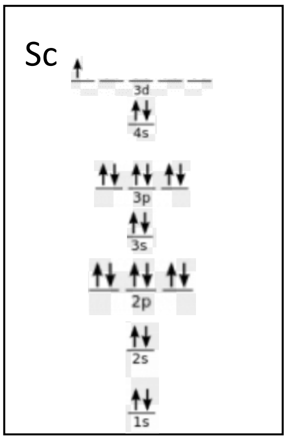
Na+



C

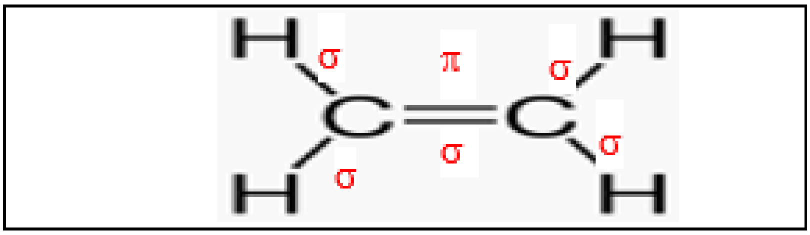


Sc



Now let’s concentrate on carbon and hydrogen.

Draw a ***displayed formula*** of ethene and label the all the bonds with either σ or π



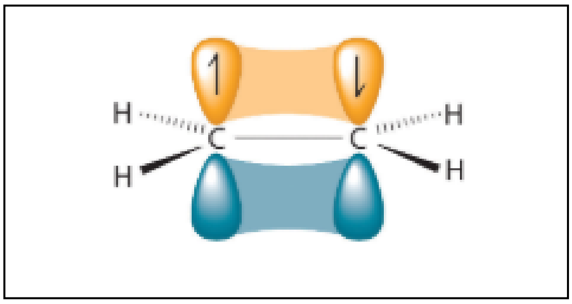
What type of overlap of atomic orbitals leads to a ***sigma*** bond? **‘end-on overlap’**

Electrons in which type of orbital are involved in forming a ***pi*** bond? **p**

In a ***pi*** bond, what type of overlap of electrons takes place? **‘sideways-on overlap’**

The double bond in an alkene makes them especially attractive to what type of species? **electrophile**
The **weakness of the pi bond** leads to the **high reactivity** of alkenes.

Complete the 3D diagram of ethen to show the orbitals that overlap to form the pi bond

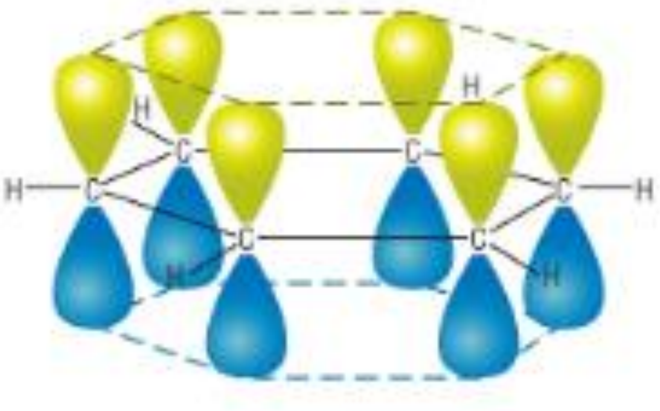


What are the bond angles between all the **σ** bonds in ethene? **120°**

What is the bond geometry around each of the carbons in ethene? **trigonal planar**

If benzene was simply cyclohexa-1,3,5-triene, then you could apply the same bonding ideas as illustrated above.

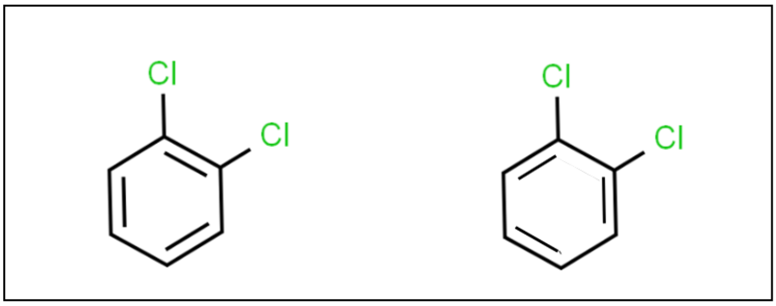
Add the relevant orbitals to the diagram below.



Now, if you decide to overlap **pairs of p-orbitals** to form **3 double bonds** over the ring of 6 carbons, which pairs would you choose? You may agree that which ever 3 you choose , the compounds are identical.

If the choice is random, then the **1,2-dichlorobenzene** would exist as **2 isomers** with the 3 double bond in a different position relative to the 2 chlorine atoms.

Draw the 2 isomers of **1,2-dichlorobenzene**

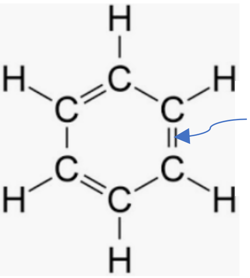


If this is the case, then these isomers would react differently, producing 2 different products when they each react with electrophiles. When **1,2-dichlorobenzene** reacts, only one product of that reaction has ever been observed. (BTW, this is a 4th piece of evidence to doubt the Kekulé structure! This is not required at A level.)

Well, it turns out that the **overlap of 6 π electrons takes place over the whole ring of 6 carbons**.

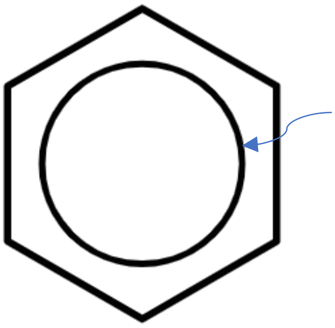
All **6 electrons** form one **ring of 6 π electrons**. The pairs of electrons don't produce 3 **localised** double bonds, Instead, the 6 π electrons become completely **delocalised** over all six carbon atoms

So, we can't draw the structure a Kekulé suggested, *i.e.*



Localised double bonds that are in a fixed position

A more representative way to draw benzene is as follows:



The ring represents **6 delocalised π electrons**

This 'smearing out' of the electrons by **delocalisation** makes arenes much more resistant to electrophiles. Therefore, they **don't react with bromine water** (evidence we saw earlier).

The equal electron density between each carbon and its neighbour means that the distance between the carbon nuclei are all the same. So, the **bond lengths are all equal** (evidence we saw earlier).

Make no mistake, benzene does many chemical reactions! The relative stability of benzene does not prevent reactions, they simply need a bit more ‘pushing’. Next year we will cover several reactions of benzene.

The general type of reaction is electrophilic substitution **NOT** addition. Those **6 delocalised π electrons** are extremely reluctant to being broken up.

Remember, benzene is only one example of a large family of related compounds called **arenes**.

Arenes are a broad family of organic compounds that exhibit this same resistance to electrophilic addition.

A compound falls into the family of arenes, if obeys all of **Hückels rules** (<u>not required at A level</u>!)

If you want to understand **Hückels rules**, then continue.

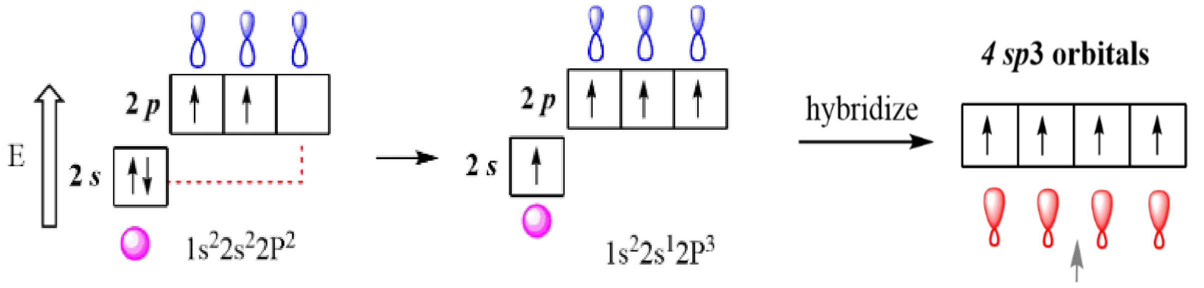
Stretch and Challenge

Before we can understand **Hückels rules**, we need to understand a little about **orbital hybridisation theory** (Proposed by *Linus Pauling*).

Earlier in this work, you drew an energy level diagram for CARBON.

Well, this is only accurate for individual CARBON atoms in their lowest energy state (ground state). Even in elemental carbon, any allotrope you consider, the carbon atoms are bonded with each other. Under these conditions (basically, always!) the electrons in the 2*s* and three 2*p* orbitals merge to produce 4 new **hybrid orbitals** of **equivalent energy**. They are called ***sp*^{3} orbitals**.

They have a shape that reflects the contributions from both *s* and *p* orbitals. This is illustrated below. Note that before the hybridisation takes place, one of the 2s electrons is first promoted to the 'excited state'.

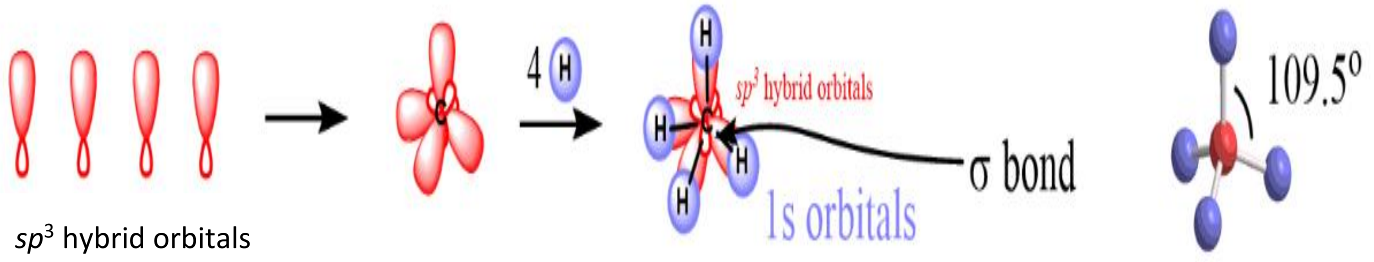


ground state for carbon

excited state for carbon

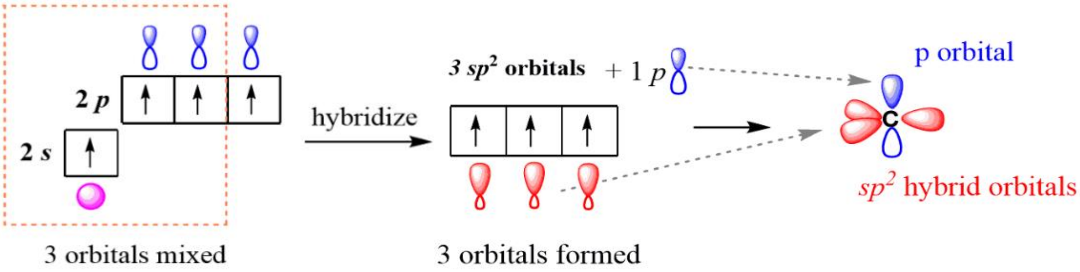
4 equivalent orbitals formed

These 4 individual sp^3 hybrid orbitals are **all equivalent** and form strong sigma bonds with other carbon atoms in diamond. They also bond tetrahedrally (the (unrelated) VSEPR rules can now be applied). Therefore, methane is a tetrahedral molecule.

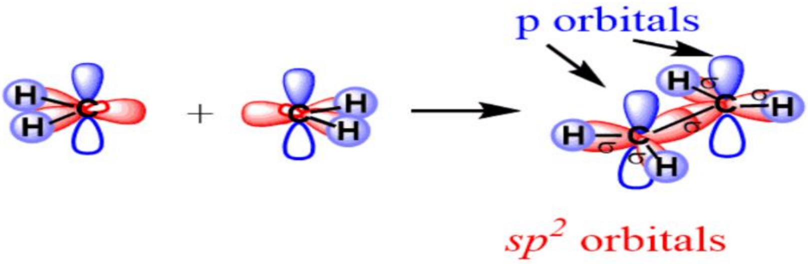


sp^3 hybrid orbitals

Now let’s consider the hybridisation in the case of **ethene**. In this case, not all the 2*p* orbitals hybridise. One *p* orbital (that happens to contain 1 electron) is unhybridized.

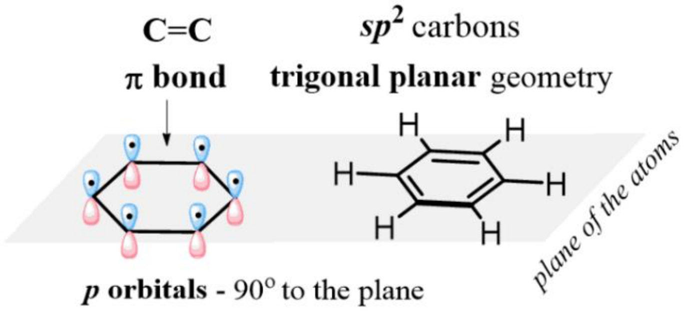


Each carbon atom forms a sigma bond with its neighbouring carbon and 2 hydrogens:

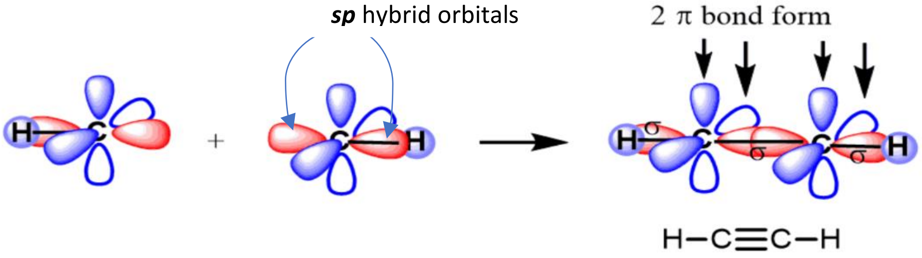


The sideways overlap of the unhybridized *p* electrons forms the π bond.

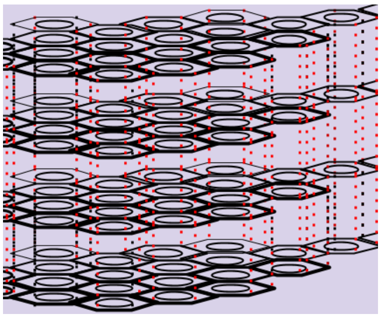
In **benzene**, all the carbon atoms are *sp*^{2} hybridised.



This theory can be extended to the compound **ethyne**, C_2H_2. In this compound, p_x and p_y orbitals (each containing 1 electron) are unhybridized.



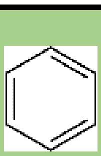
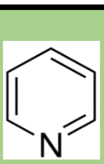
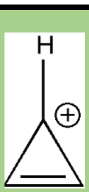
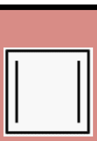
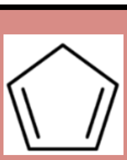
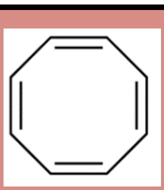
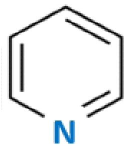
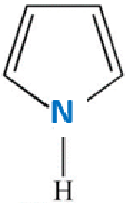
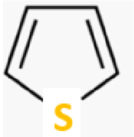
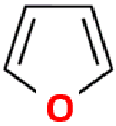
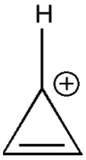
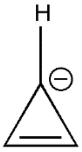
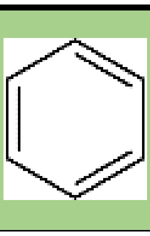
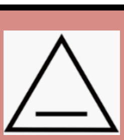
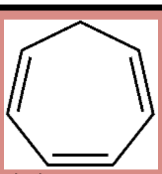
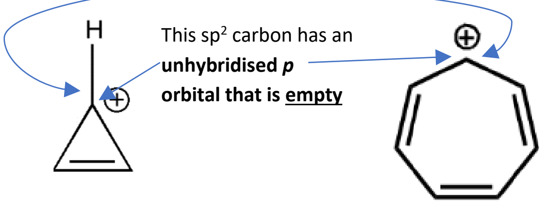
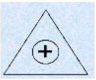
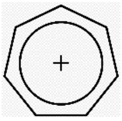
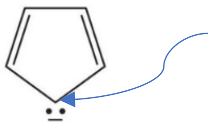
The bonding in graphite contain layers of carbon atoms that are *sp*^{2} hybridised. Each layer has weak intermolecular attractions with the layers above and below.

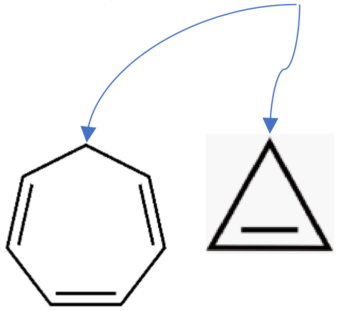


Hϋckels rules

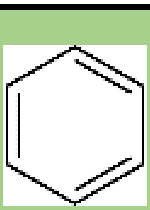
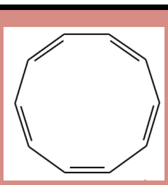
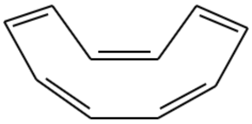
The challenge is to try and work out what are these rules that make a molecule an arene.

In the table below, there are molecules that are either arenes (aromatic) or antiaromatic (non-aromatic).

<table>
<tr><th>Aromatic</th><th>antiaromatic (not an arene)</th></tr>
<tr><td>1.
 
Number of π electrons=6 & 2</td><td>
Number of π electrons=4 & 8</td></tr>
<tr><td colspan="2">There is a pattern in the number of π electrons that the ring must contain.
Find the nth term expression that gives the number of delocalised π electrons in an arene. = 4<i>n</i> +2</td></tr>
<tr><td colspan="2">So you now know that the first rule is that an arene must have 4<i>n</i> +2 π electrons
Work out whether these molecules fulfil that criterion. You will need to think about the hybridisation and the number of unhybridized <i>p</i> electrons on the highlighted atoms.
Pyridine 
Pyrrole 
Thiophene 
Furan 
cyclopropenyl cation 
cyclopropenyl anion  </td></tr>
<tr><td colspan="2">According to the first of Hϋckels rules, cyclopropane and cycloheptatriene should be an arene but they fail based on a second rule. See below</td></tr>
<tr><td>2.
</td><td>
cyclopropene cycloheptatriene</td></tr>
<tr><td>The molecules below allow for conjugation because the 2 or 6 π electrons can delocalise over the whole ring. The carbon highlighted is sp^2 hybridised.

This sp^2 carbon has an unhybridised <i>p</i> orbital that is <u>empty</u>
In fact, it is better to draw these as arenes.

Also,

This sp^2 carbon has an unhybridised <i>p</i> orbital that contains 2 electrons that contribute to the ring</td><td>The double bonds must follow the sequence;
<i>double bond, single bond, double bond, single bond etc</i>
This is known as conjugation.

The delocalisation can’t ‘spread’ through a sp^3 hybrid carbon.
</td></tr>
</table>

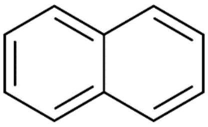
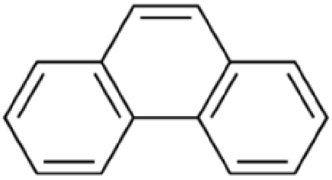
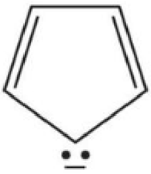
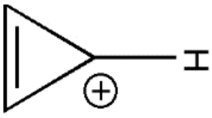
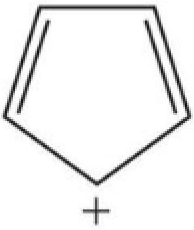
According to the first two rules, cyclodecapentene should be an arene.
It has 10 π electrons (first rule met).
It appears to be conjugated (second rule met).
BUT it isn’t an arene. The diagrams below might illustrate a third simple rule.

3.  Number of π electrons=6	  A more realistic diagram! Number of π electrons=10

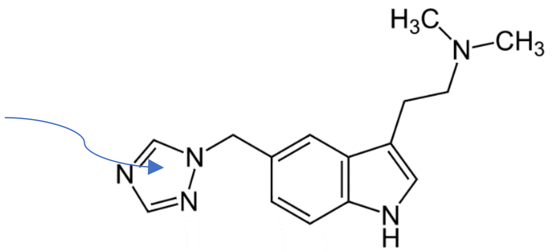
This third rule simply states that **for there to be delocalisation**, **the molecules must also be planar.** The bond strain on each cyclodecapentene simply makes it impossible for cyclodecapentene to form a flat ring. Therefore, it isn’t an arene.

Hϋckel’s rules

1. The system must contain 4n+2 **π electrons**
2. The π electron system must be a **conjugated ring** (every atom in the ring has p orbitals perpendicular to the ring)
3. The π electron system must be **planar**

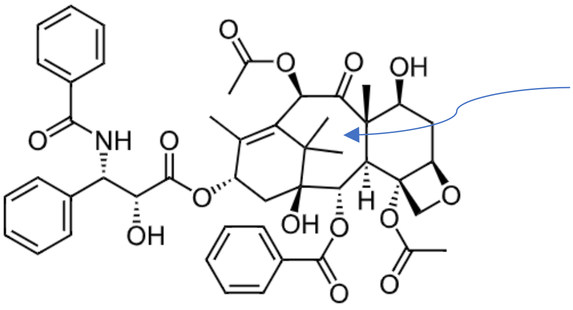
Aromatic	antiaromatic (not an arene)
$10\ \pi$ e$^-$ **Conjugated** **Planar**  $14\ \pi$ e$^-$ **Conjugated** **Planar**  $6\ \pi$ e$^-$ **Conjugated** **Planar**  $2\ \pi$ e$^-$ **Conjugated (due to empty and unhybridised p orbital)** **Planar** 	Fails due to there being **4π e$^-$** 

Some more interesting arenes



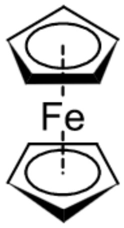
The nitrogen containing ring (triazole) is also an aromatic ring.

2-(5-((1H-1,2,4-Triazol-1-yl)methyl)-1H-indol-3-yl)-N,N-dimethylethanamine ‘***Maxalt’*** Migraine drug.



An **8 membered ring** which is extremely difficult to synthesise in the lab!

(1S,2S,3R,4S,7R,9S,10S,12R,15S)-4,12-bis(acetyloxy)-1,9-dihydroxy-15-({(2R,3S)-2-hydroxy-3-phenyl-3-[(phenylcarbonyl)amino]propanoyl}oxy)-10,14,17,17-tetramethyl-11-oxo-6-oxatetracyclo[11.3.1.$0^{3,10}$.$0^{4,7}$]heptadec-13-en-2-yl benzoate
Better known as ***Taxol*** (brand name, ***Placlitaxel***) A powerful cancer treatment. Plenty of rings but not all aromatic!



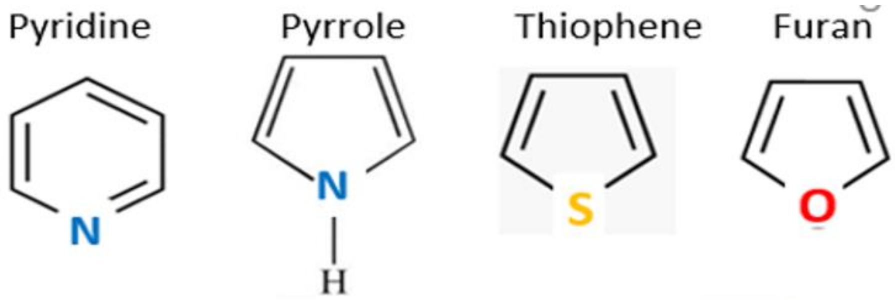
Ferrocene.

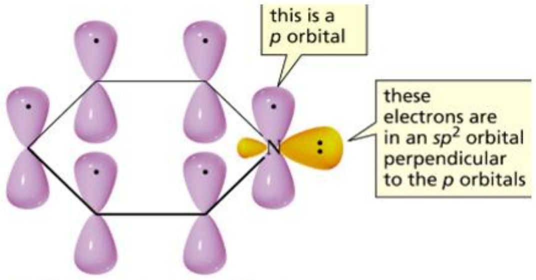
This unusual compound exists as orange crystals which are stable in air. Note the sandwich like nature of the compound. The Fe is in oxidation state +2 .

The rings above and below are cyclopentadienide anions with an Fe^{2+} ion as the filling. It has the formula:

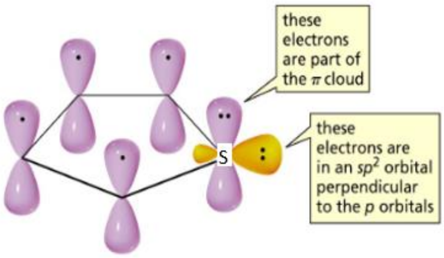
$Fe(C_5H_5)_2$

Are these ARENES?

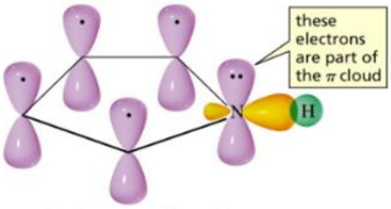




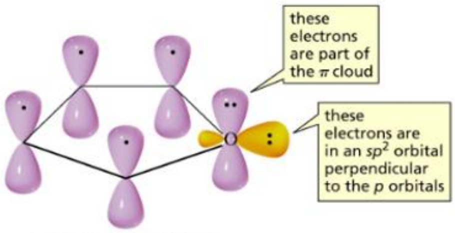
orbital structure of pyridine



orbital structure of thiophene



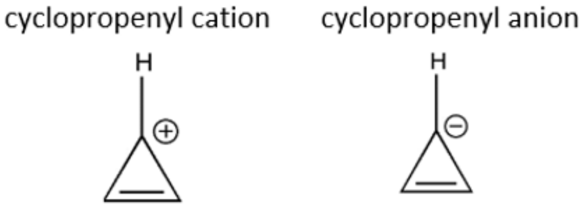
orbital structure of pyrrole



orbital structure of furan

All of these molecules are arenes (aromatic) because the all have:

1. 6 π electrons (4n + 2)
2. All the π electrons are delocalised in a conjugated system
3. All molecules are planar



Cyclopropenyl cation is an arene because it has:

1. 2 π electrons (4n + 2)
2. Both the π electrons are delocalised in a conjugated system
3. It is planar

Cyclopropenyl anion is not an arene because it fails the first rule. It has 4 π electrons so is antiaromatic.

REMEMBER! This is not required at A Level!