LECTURE 5

The prototype aromatic compound is benzene but we can also have other atoms in the ring skeleton, such as nitrogen which leads to the compound pyridine, a so-called heteroaromatic:

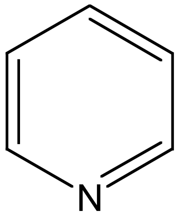


Fig. 1

We can also see aromatic character (aromaticity) in odd-sized rings provided they are charged species e.g.:

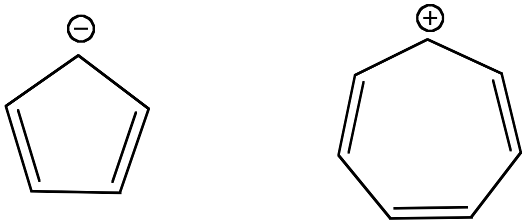
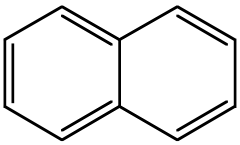
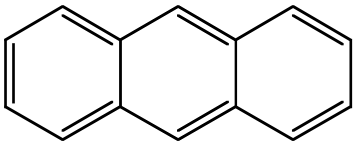


Fig. 2

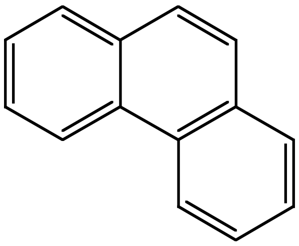
We may have polycyclic compounds both six-membered and other sizes:



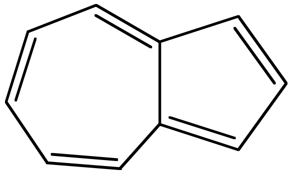
naphthalene



anthracene



phenanthrene



azulene

So how can we describe aromaticity so that it covers all these compounds and others?

1. Aromaticity: Resonance Theory

In 1865 Kekule proposed the structure of cyclohexatriene for benzene:

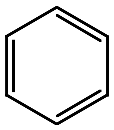


Fig. 3

However, it was clear that benzene could not be represented simply by this structure because

- The predicted enthalpy of hydrogenation for this structure (~350 kJ mole^{-1}) on the basis of those for cyclohexene (120 kJ mole^{-1}) and cyclohexadiene (232 kJ mole^{-1}) was too high by ~ 141 kJ mole^{-1} compared to the experimental value (209 kJ mole^{-1})
- Benzene, unlike alkenes, rarely undergoes addition reactions and is quite stable to oxidation and reduction
- Disubstituted benzenes, on the basis of this structure, should exist as two isomers (with either a double bond or a single bond between the two groups); however, they do not:

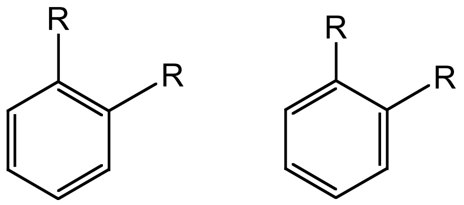
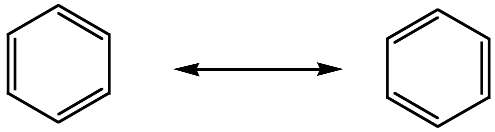


Fig. 4

- Subsequently, an X-ray crystallographic analysis of benzene showed a planar, regular hexagon in which all the C-C bond lengths are 139 pm, intermediate between that of the single bond in ethane (154 pm) and that of the double bond in ethene (134 pm)

In order to overcome these problems Kekule suggested that the two cyclohexatriene forms "oscillate" between each other. This far-sighted suggestion is very close to the Valence Bond (or Resonance) Theory of benzene where the "oscillation" is indicated by a double-headed arrow:
Fig. 5



It is important to realise that this theory states that benzene has neither structure (it is **not** an oscillation or equilibrium between the two forms) but rather is a resonance hybrid of these two so-called canonical forms i.e. it lies somewhere in between. Thus the π-electrons are not localised between two carbon atoms but are delocalised over the whole ring. This idea is often indicated by the following representation:

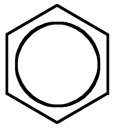


Fig. 6

although there is even a problem with this as we shall see shortly.

Resonance theory is very useful and subsequently we have seen its extensive use in looking at the reactions of benzene derivatives. However, it does have its shortcomings and the most spectacular of these is its failure to explain why cyclobutadiene, which may also be represented as a hybrid of two canonical forms, is **not** aromatic:

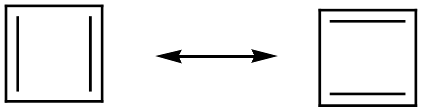


Fig. 7

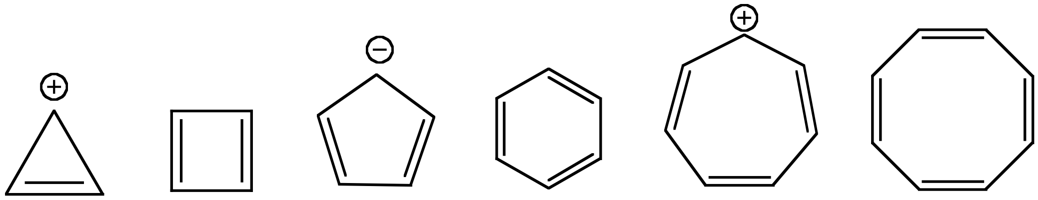
Indeed, cyclobutadiene is so reactive that it is said to be anti-aromatic.

2. Aromaticity: Huckel's Rules, Molecular Orbital Theory

In contrast to Resonance theory, Molecular Orbital theory can explain both of these different reactivities between benzene and cyclobutadiene and also provide an explanation for aromaticity in general. In the 1930s Huckel calculated the molecular orbital energies for a series of cyclic, conjugated (i.e. formally delocalised) poly-unsaturated systems and adumbrated Huckel's Rules which state that:

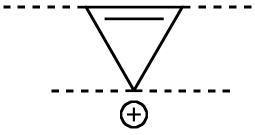
- Planar, cyclic systems of unsaturated atoms containing (4n + 2) π-electrons, where n is 0 or a positive integer, will be aromatic
- Planar, cyclic systems of unsaturated atoms containing 4n π-electrons, where n is a positive integer, will be anti-aromatic

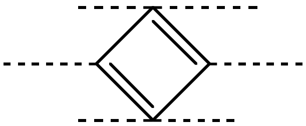
Let us now apply Huckel's rules to the molecular orbitals for a range of ring sizes.

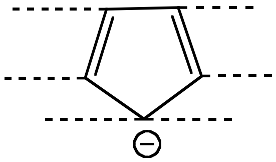


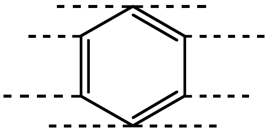
Notice that for odd-membered rings we must have one carbon with an atomic orbital on it and this orbital will either contain a pair of electrons (negative charge) or no electrons (positive charge). For aromaticity, the three and seven-membered rings are positively charged and the five-membered ring is negatively charged (the corresponding anti-aromatic compounds would have the opposite charge distribution e.g. cyclopentadienyl cation, not shown above). Thus according to Huckel's rules the compounds shown should be aromatic if they have two electrons (4n + 2, n = 0)(cyclopropenyl cation) or six electrons (4n + 2, n = 1)(cyclopentadienyl anion, benzene, cycloheptatrienyl cation) and anti-aromatic if they have four electrons (4n, n = 1)(cyclobutadiene) or eight electrons (4n, n = 2)(cyclooctatetraene).

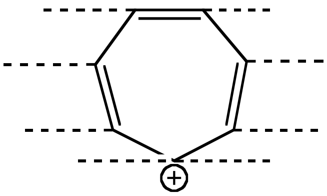
Although these rules are useful they do not tell us the reason why they work. The reasoning behind Huckel's rules follows from the arrangement of the energies of the molecular orbitals. This arrangement comes out of the mathematics, which I do not intend to cover, but there is an easy mnemonic for remembering the arrangement, called the Frost-Muslin diagrams. If you draw the rings with one apex pointing down and then draw horizontal lines through each carbon on the ring as below, the position of those horizontal lines represent the relative energies of the orbitals:

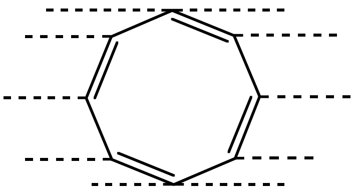












If we put the electrons in (see next page), we now see that all the 2 and 6 electron species can accommodate their electrons paired in low energy bonding orbitals whereas the 4 and 8 electron species have two electrons in separate, degenerate, non-bonding orbitals (they go into separate

orbitals because of Hund's rule) and thus the latter act as biradicals, which explains their extreme reactivity.
Notice that all the bi- and tricyclic aromatic compounds above (naphthalene, anthracene, phenanthrene, azulene) all contain 4n + 2 π-electrons and, therefore, are aromatic (the energies of their orbitals are more difficult to visualise).

Cyclooctatetraene avoids being a biradical by adopting a non-planar shape in which delocalisation does not occur because the orbitals are at right angles to one another (orthogonal) (note that Huckel's rules refer to planar species), a strategy which cyclobutadiene cannot follow:

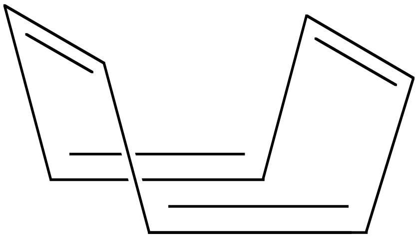


Fig. 8

We now see the problem of representing benzene as a hexagon with a ring in it (Fig. 6). Such a representation suggests that all six π-electrons are circulating the ring but these electrons are in three separate orbitals and only the least energetic of those orbitals encompasses the ring (see orbital pictures on next page).
Although a Kekule form is also not a good representation, it does allow us to see the mechanisms of aromatic compounds more clearly.