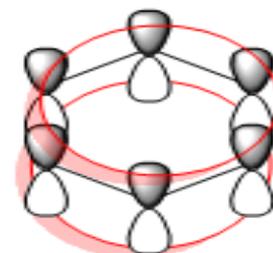


Aromaticity and Benzene Introduction

Aromatic substances are incredibly unreactive in comparison to cycloalkenes. For example, in the halogenation of alkenes the compound readily undergoes an addition reaction across the double bond. You would expect this to happen in benzene (Refcode BENZEN) with its appearance of having double bonds, but this is not the case. If benzene was reacted with bromine in the same way as alkenes no reaction would occur. This can be explained by the existence of a system of delocalised π -electrons, as pictured below.

Like normal π -bond across alkenes, there is an overlap between $2p^2$ orbitals above and below the carbon ring. However, in benzene the π -bonds are continuous across the whole ring, forming a network of delocalised electrons. These electrons are evenly distributed across the whole molecule, resulting in a much stronger bond in comparison to a standard π -bond. This is because the delocalised electrons are stable and an addition reaction would break this stability so is unfavorable. This means that reactivity to addition of halogens is much lower and will not take place, compared to the reactivity of a standard C=C bond which react readily with halogens.



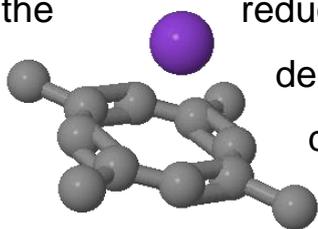
Whether a molecule is aromatic is not can be worked out by Huckel's rule (This is not covered at A-Level). The rule states that for a molecule to be aromatic:

1. It must have $4n+2$ delocalised electrons e.g. 6, 10, 14..... electrons
2. It must be cyclic
3. It must be planar
4. Every atom in the ring must contribute to delocalisation via a p-orbital

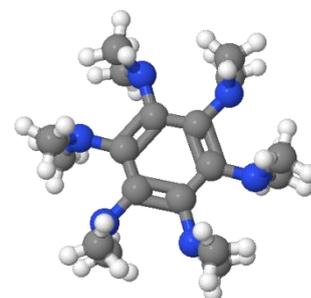
Benzene has 6 delocalised electrons, is cyclic, is planar and all atoms in the ring contribute to delocalisation via a p orbital so is aromatic. The effect of this rule on aromatics is shown on the next page.

Observation and Measurements

An experiment which can be conducted to change the shape of cyclic molecules is the reduction/oxidation of the rings, which changes the number of delocalised p-electrons. A good example of this would be the differences between 1,3,5,7-tetramethylcyclooctatetraene (Refcode: TMCOTT) and its dianion counterpart (Refcode: TMOCKE), which is produced when the substance is treated with an alkaline metal. By comparing these structures, you may notice the exact same differences found between benzene and the neutral tetra-methyl cyclooctatetraene where the neutral compound maintains the non-planar tub-shape, but the anion takes on the planar molecule shape much like the benzene ring.



Conversely, you can compare benzene in the same manner but with a different effect; Although benzene itself can't be oxidised easily due to its stability, some alternate compounds can due to the attachment of reactive groups. For instance, hexakis(dimethylamino)benzene (Refcode: GENFAG) when oxidised with iodine forms a di-anion (Refcode: GENFEK) and again, the contrast is quite striking as the molecule has now become non-planar and has undergone quite a transformation.



Explanation

In a cyclic substance, as you gain certain numbers of electrons, the substance enters a state where it is planar. There must be some force providing stability to these structures to make it preferable, otherwise the molecule would take a different form, this is force is aromaticity and the delocalisation of electrons. This effect is explained by Huckel's rule.