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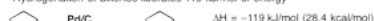
Introduction to Aromaticity

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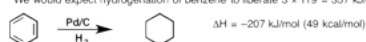
Note - this sheet is not meant to be comprehensive. Your course may provide additional material, or may not cover some of the reactions shown here. Your course instructor is the final authority.

1. An introduction to resonance energy and aromaticity

Hydrogenation of alkenes liberates 119 kJ/mol of energy



We would expect hydrogenation of benzene to liberate $3 \times 119 = 357 \text{ kJ/mol}$.



Instead, 207 kJ/mol is liberated (150 kJ/mol less than we expect!)

So it is 150 kJ/mol (36 kcal/mol) **more stable**.

The extra stability of benzene is called the "resonance energy".

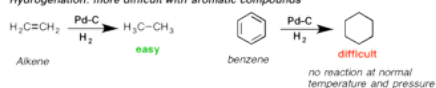
Benzene has a particularly large resonance energy, which leads us to classify it as "aromatic".

Resonance energy of some compounds:

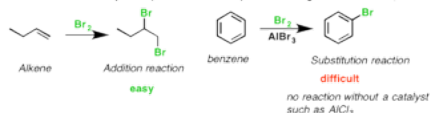


2. Two major ways in which reactions of aromatic compounds differ from alkenes

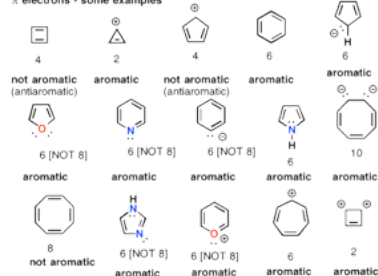
Hydrogenation: more difficult with aromatic compounds



Reaction with electrophiles (such as bromine): aromatics give substitution, not addition

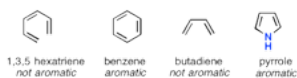


π electrons - some examples



3. How to tell if a molecule is aromatic?

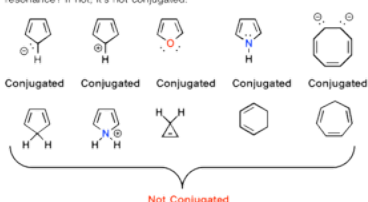
Rule 1. It must be a ring. No acyclic molecule is aromatic. Ever!



Rule 2. The molecule must be conjugated

Meaning: there must be a continuous line of p orbitals around the ring. p orbitals can come from 1) π -bonds 2) lone pairs 3) carbocations

A good test: Can you push electrons all the way around the ring through resonance? If not, it's not conjugated.

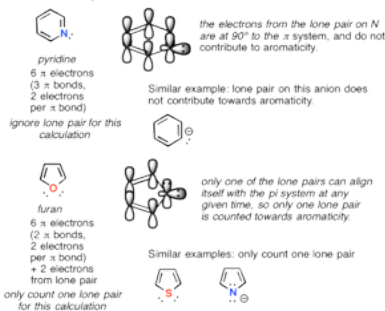


Rule 3. There must be $4n + 2 \pi$ electrons i.e. 2, 6, 10, 14... π electrons

π electrons can come from double bonds or lone pairs. Note: A carbocation indicates the absence of π electrons.

One tricky part: for a given atom, you can only count electrons from a lone pair if the atom is not part of a π bond. And in that case you can only count a maximum of one lone pair.

This is due to the fact that each atom can only share one p orbital with the π system of the molecule.



For more examples, see section on left

Rule 4. It must be flat

Most molecules that obey the first 3 rules are also flat. One exception is [10]-annulene, which is bent due to repulsion of the hydrogens.



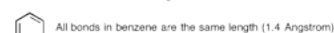
4. Antiaromaticity

Molecules that obey rules 1,2 and 4 but have $(4n) \pi$ electrons instead of $(4n + 2) \pi$ electrons have special instability. This special instability is called "antiaromaticity".



5. Some physical evidence for aromaticity:

- Shows a different reactivity profile than for alkenes (see section on reactivity at left)
- All π bonds are of the same length & do not alternate



Compare this to cyclobutadiene, which has short double bonds and long single bonds - like a rectangle.

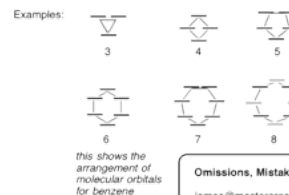
3. Ring currents in NMR

Resonances for aromatic protons in NMR typically show up in the region 6.8-8.0 ppm, whereas those for "normal" alkenes show up in the region from 5.0-6.5 ppm.

6. "Frost circles" - a trick for obtaining the molecular orbital structures of aromatic rings.

General idea: Inscribe a polygon of n sides in a circle. Make sure one of the apices is pointing down. Then, each apex will represent a level in the molecular orbital energy diagram.

Frost, J. Chem. Phys. 1953, 21, 572



Omissions, Mistakes, Suggestions?

james@masterorganicchemistry.com
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