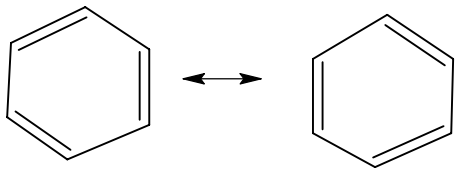
AROMATICITY – THE FIRST CHECK

Consider only π-electrons of conjugated cyclic systems like benzene

Hückel rule: cyclic systems with (4n+2) π-electrons, n=0,1,2…., are stable (aromatic)

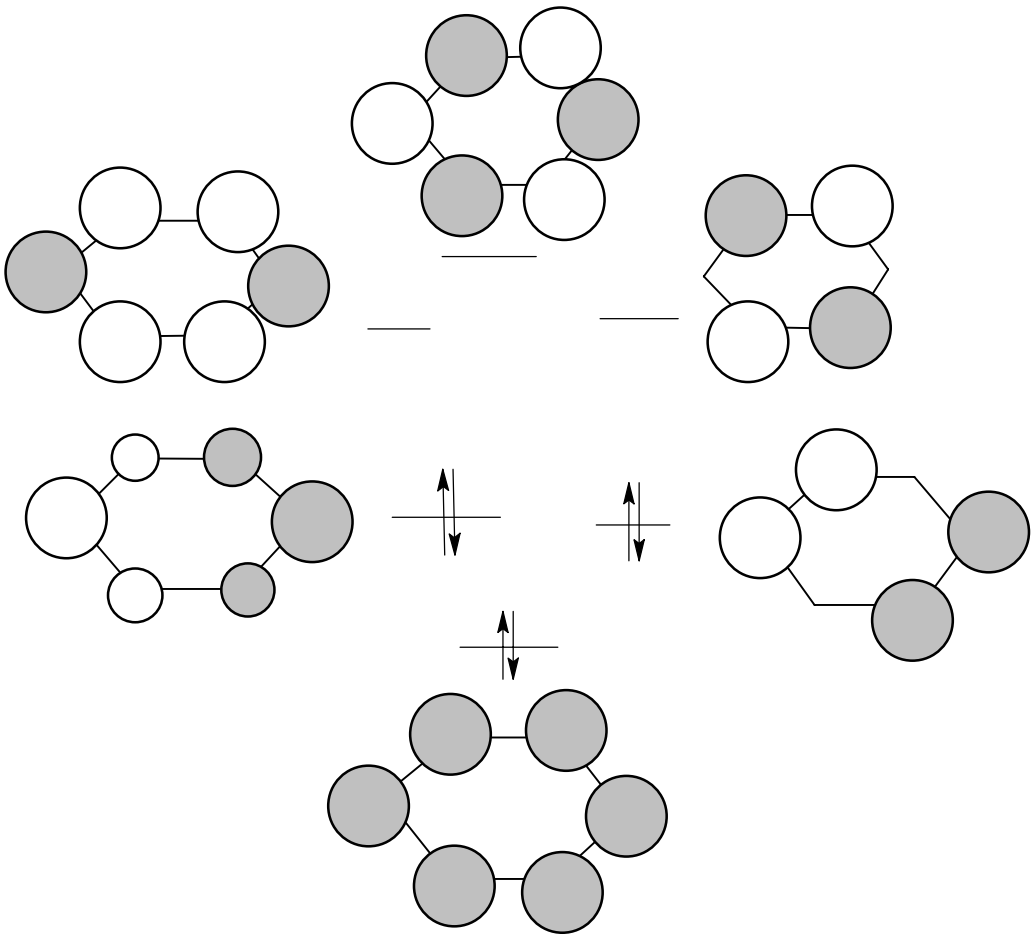
cyclic systems with (4n) π-electrons, n=0,1,2…., are unstable (antiaromatic)



D_{6h}

Consider π- MO of benzene (6 π electrons)

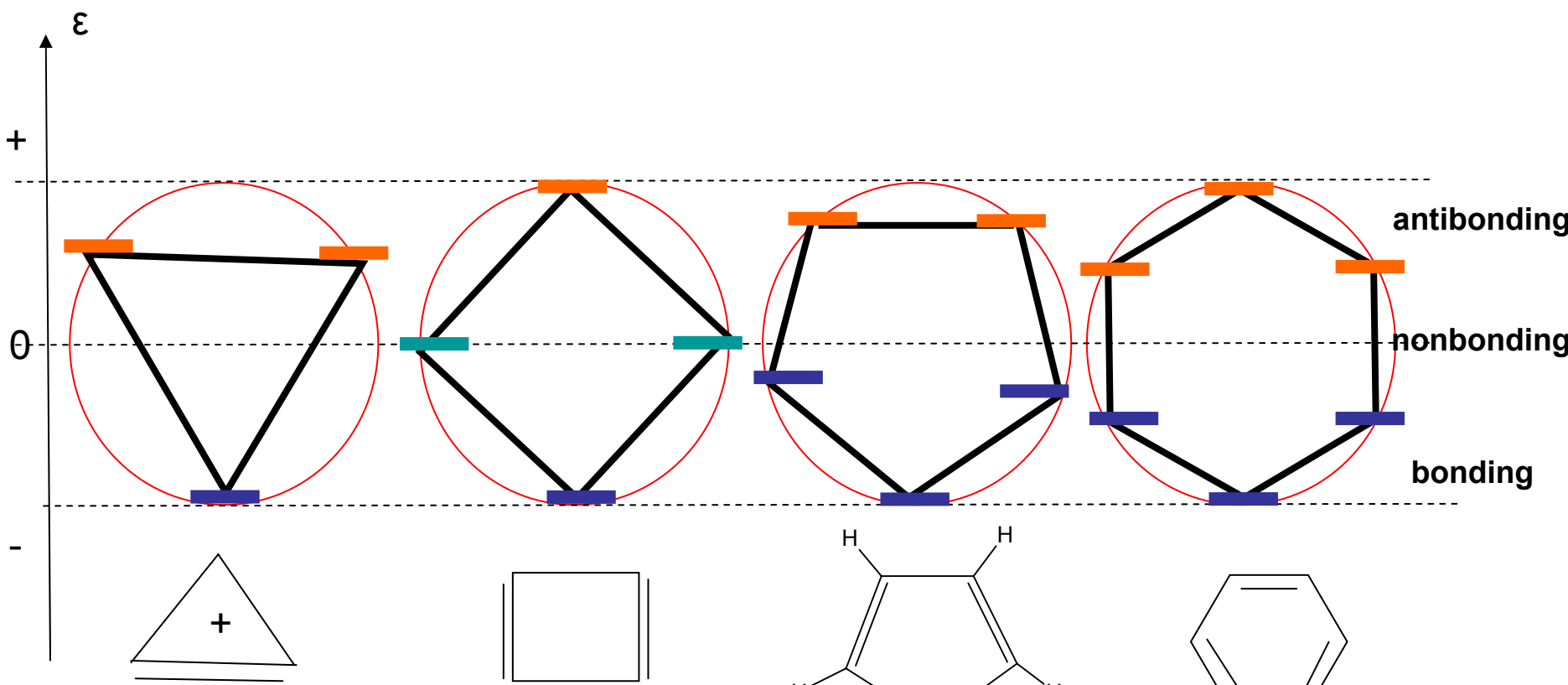
D_{6h} symmetry implies double degeneracy of MO
(there is no preference for x or y direction assuming that z is perpendicular to the molecular plane)



π-electrons occupy only bonding orbitals

SHMO (Simple Hückel MO calculator) //www.chem.ucalgary.ca/SHMO

The circle method



Cyclopropenyl cabocation
2π electrons
(4n+2), n=0
aromatic

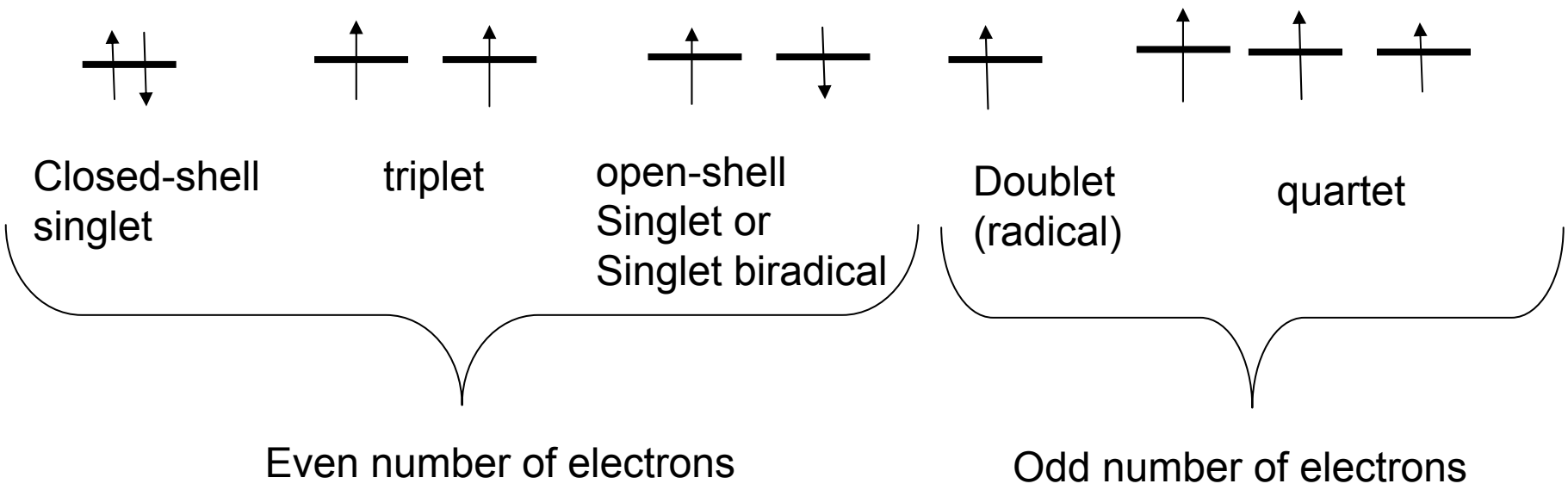
Cyclobutadiene
4π electrons –
antiaromatic (not stable). Dication and dianion-aromatic

Cyclopentadienyl anion
6π electrons –
aromatic

Benzene
6π electrons –
aromatic

Systems with 2 and 6 electrons in the π-system have closed-shell electronic state (closed-shell singlet)

Systems with 4 and 8 electrons in the π-system have unpaired electrons, each on different MO, with open-shell electronic state (usually triplet)



NEXT OBSERVATION

2 and 6 π-electron cyclic systems have E_{π} energy lower than reference (localized or open) systems with the same number of π-electrons

This is also true for

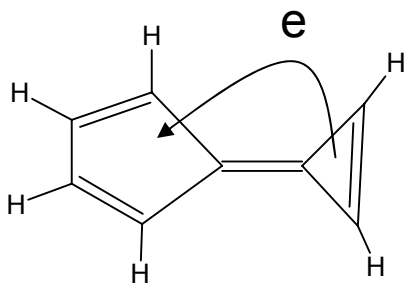
2 6 10 14 18…. (4n+2)

4 8 12 16 20… (4n) – cyclic systems are not stable

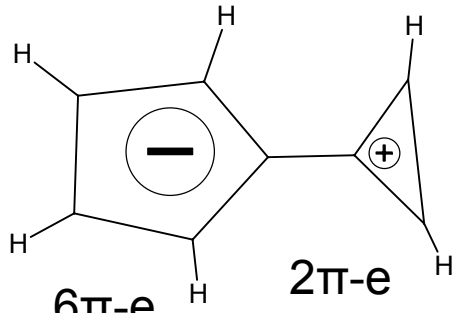
Hückel rule: (4n+2) π-electron systems are especially stable compared to acyclic analogues. They are AROMATIC systems.

(4n) π-electron cyclic systems are unstable compared to acyclic analogues. They are ANTIAROMATIC systems.

For larger annulenes, n>20, (annulenes are the cyclic compounds composed from alternating single and double bonds), the difference between cyclic and acyclic forms disappears.

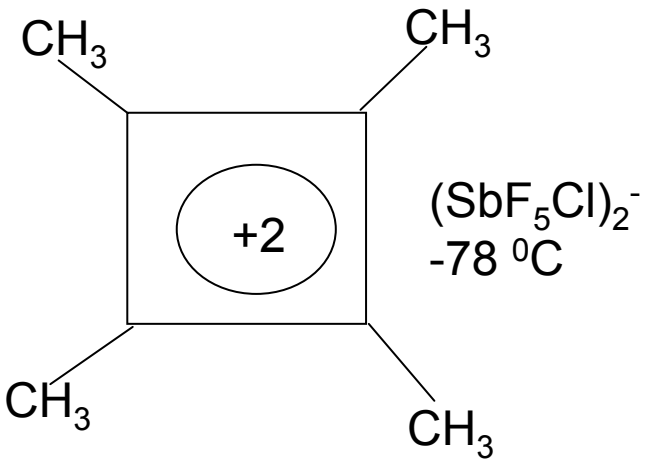


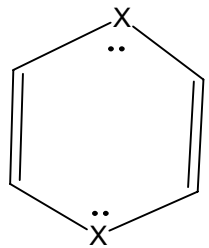
Should have a high barrier to rotation about a double bond and a small dipole moment



Zwitter-ion

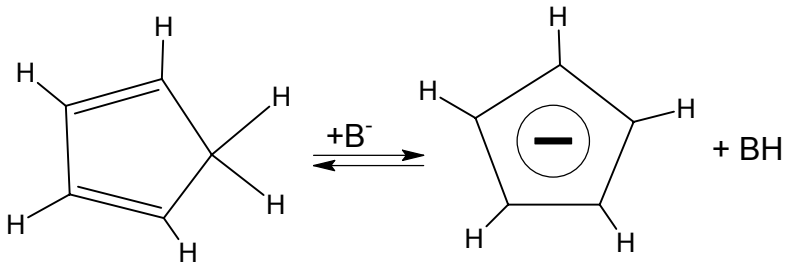
In fact, the barrier is ca. 20 kcal/mol; μ= 6.3 D





X= N, O

Nonplanar, reactive, oxidized readily



High acidity of cyclopentadiene:
Anion is stable