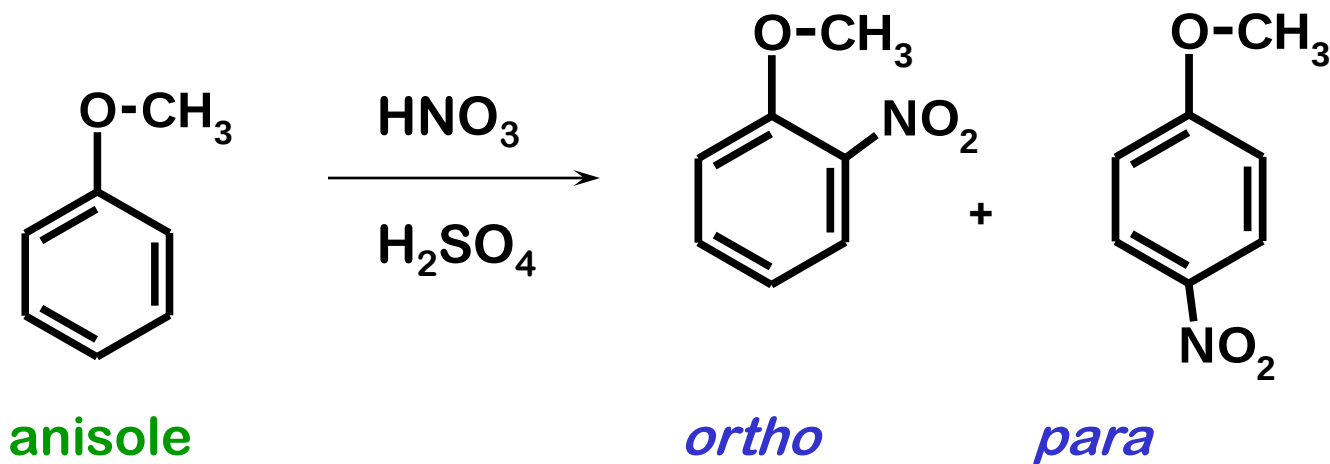


DIRECTIVITY AND RING ACTIVATION / DEACTIVATION

ACTIVATED RING

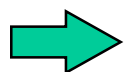
Nitration of Anisole



Reacts faster
than benzene

= “ACTIVATED”

The $-\text{OCH}_3$ group when it preexists on the ring gives only *ortho* and *para* products, and no *meta*.



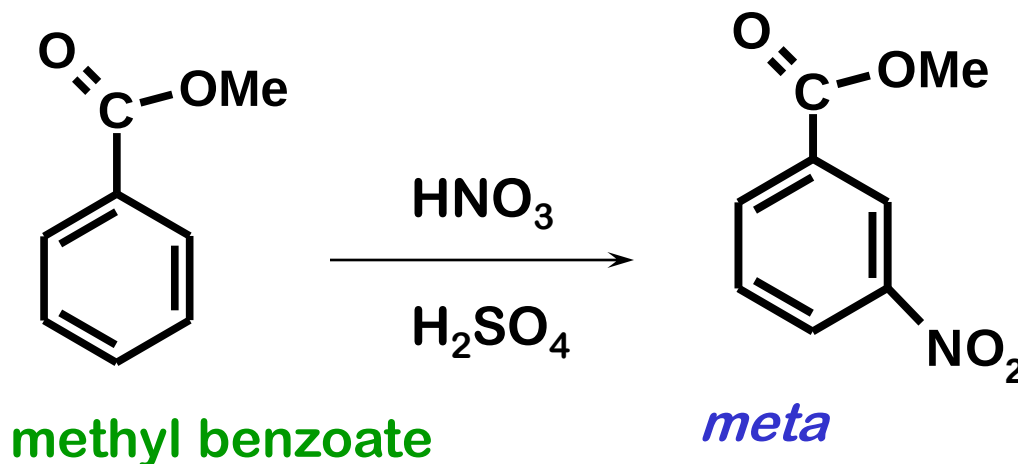
Substituents that cause this result are called

o,p directors

and they usually activate the ring.

DEACTIVATED RING

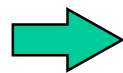
Nitration of Methyl Benzoate



Reacts slower
than benzene

= "DEACTIVATED"

The -COOMe group when it preexists on the ring gives only *meta*, and no *ortho* or *para* products.



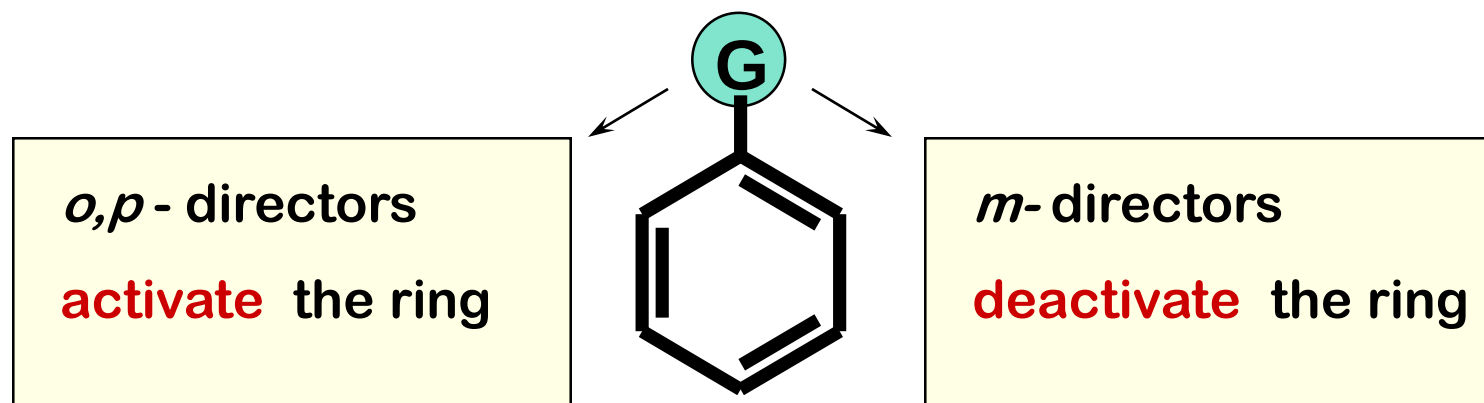
Substituents that cause this result are called

m directors

and they usually deactivate the ring.

SUBSTITUENT CATEGORIES

Most ring substituents fall into one of these two categories:

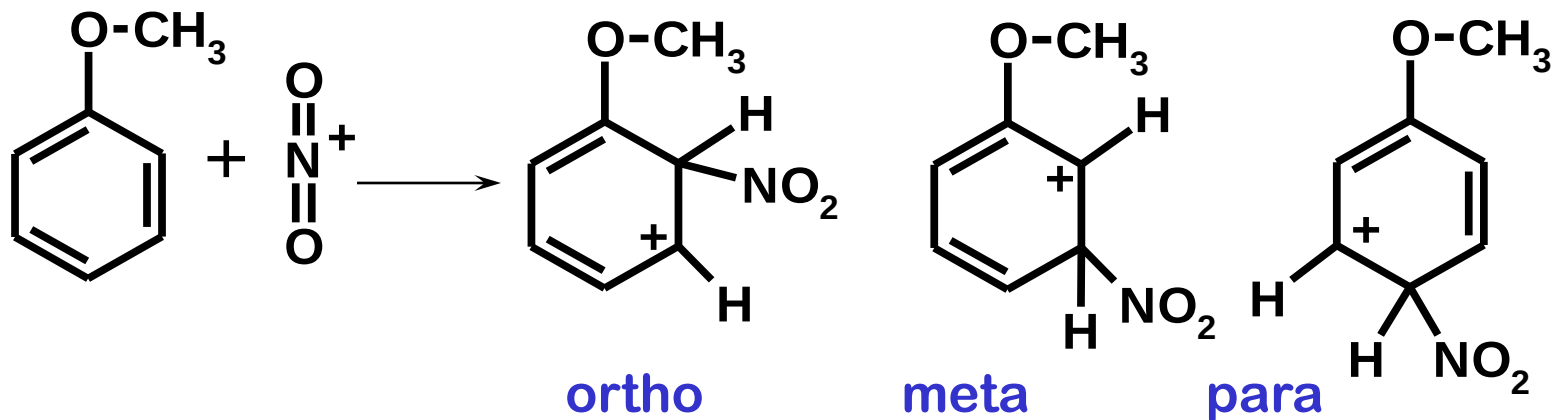


We will look at one of each kind in order to understand the difference.....

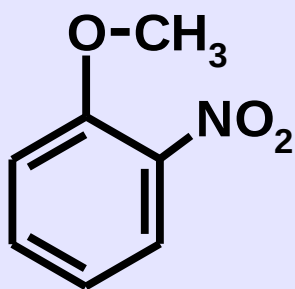
NITRATION OF ANISOLE

Nitration of Anisole

BENZENIUM ION INTERMEDIATES

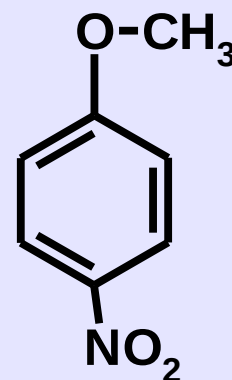


activated
ring

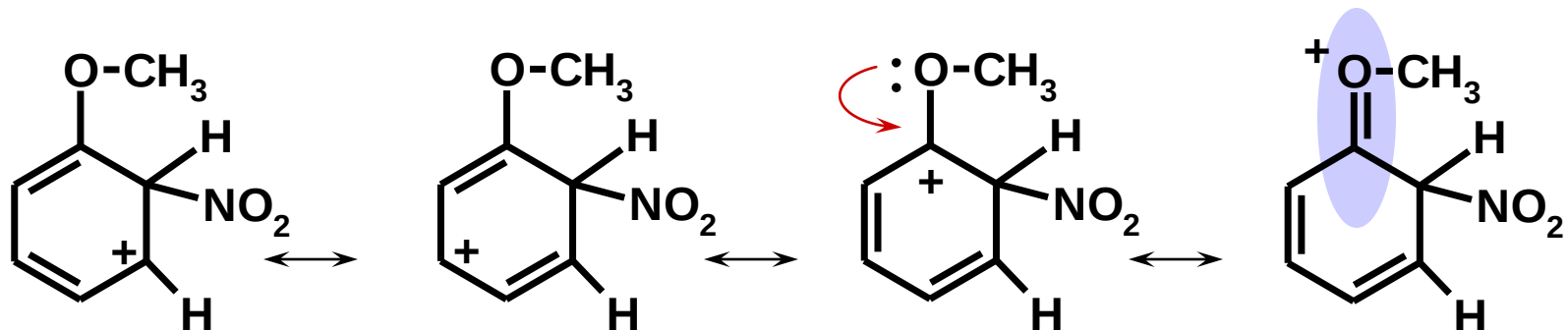


actual
products

ortho + para

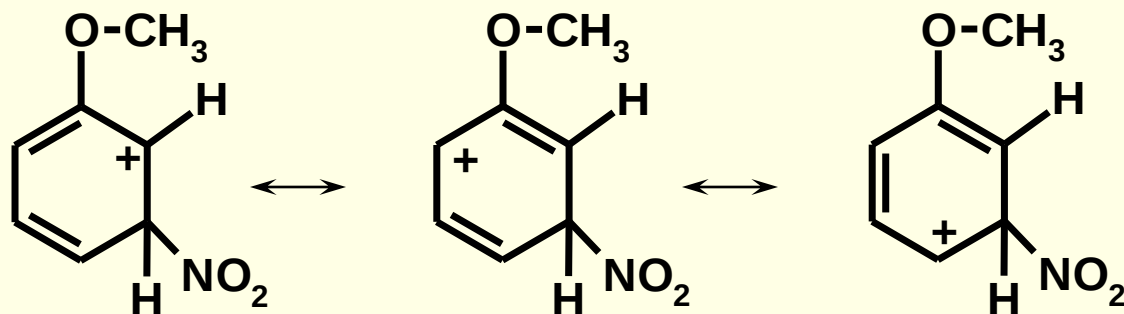


ortho

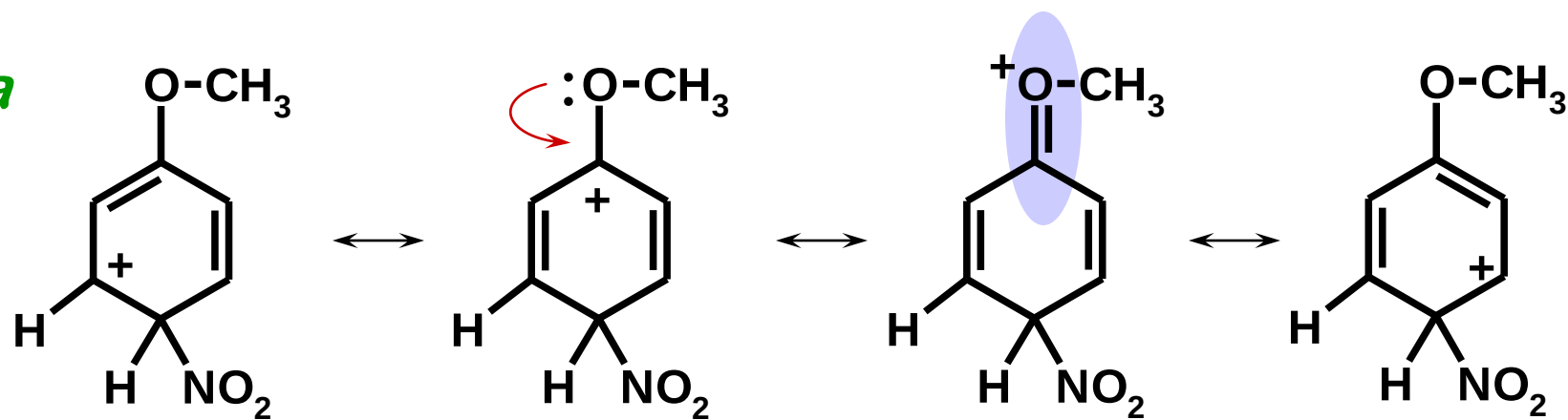


EXTRA!

meta



para

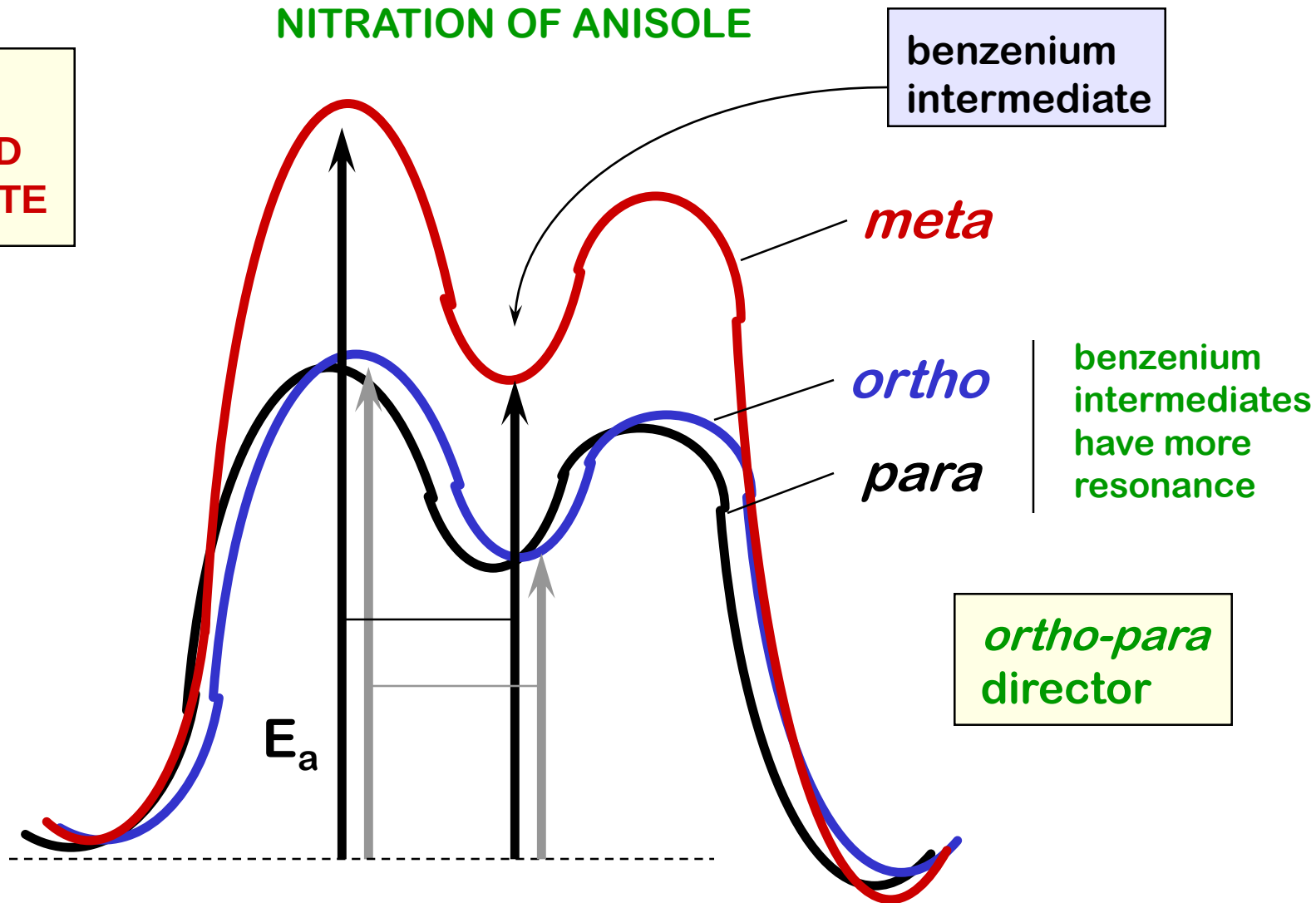


EXTRA!

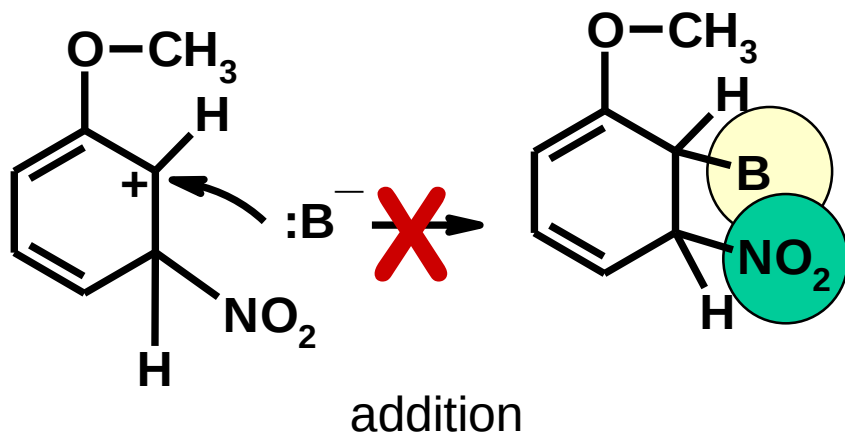
Energy Profiles

NITRATION OF ANISOLE

RECALL:
HAMMOND
POSTULATE

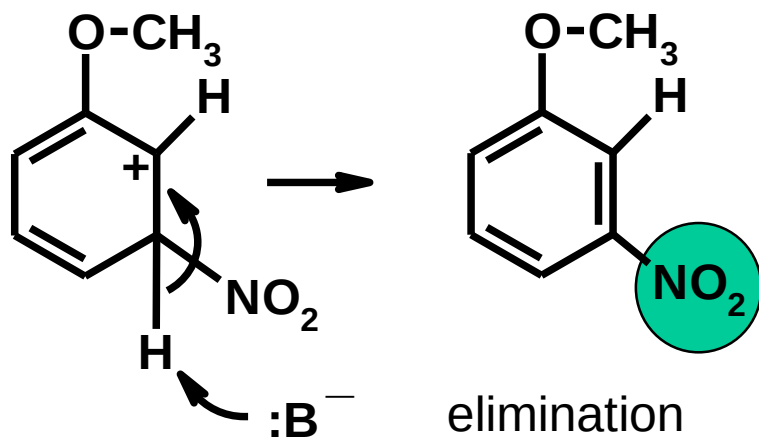


BENZENIUM IONS GIVE ELIMINATION INSTEAD OF ADDITION



ADDITION REACTION

doesn't happen
resonance would be lost



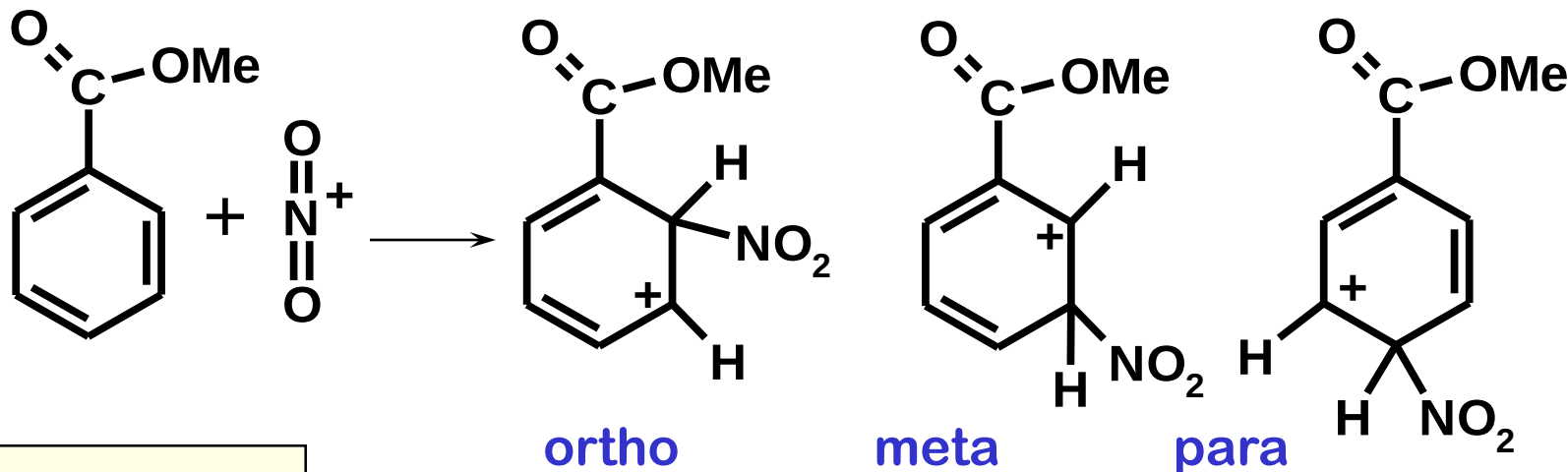
ELIMINATION REACTION

restores aromatic ring
resonance
(36 Kcal / mole)

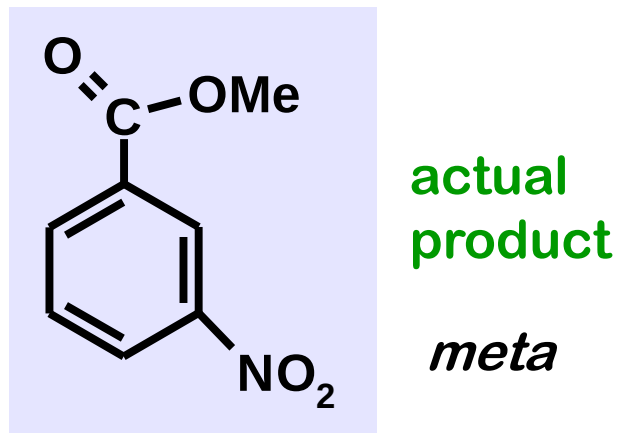
NITRATION OF METHYL BENZOATE

Nitration of Methyl Benzoate

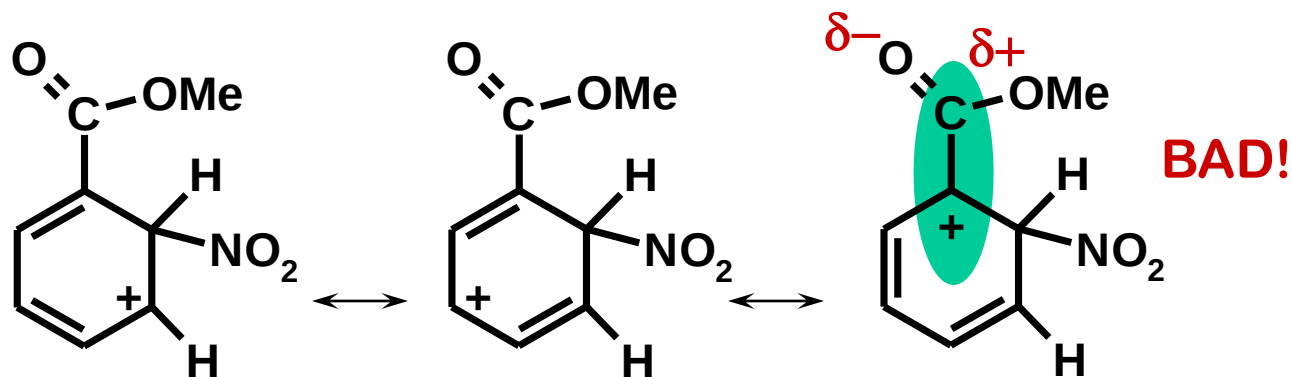
BENZENIUM ION INTERMEDIATES



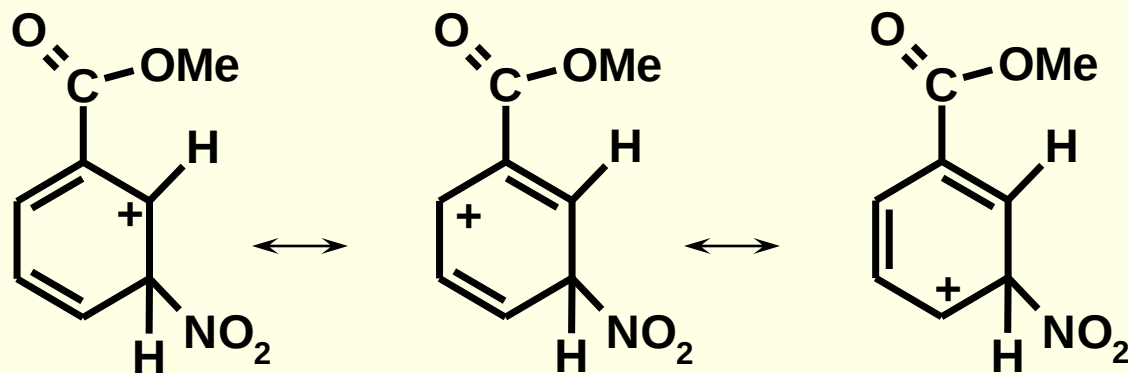
deactivated
ring



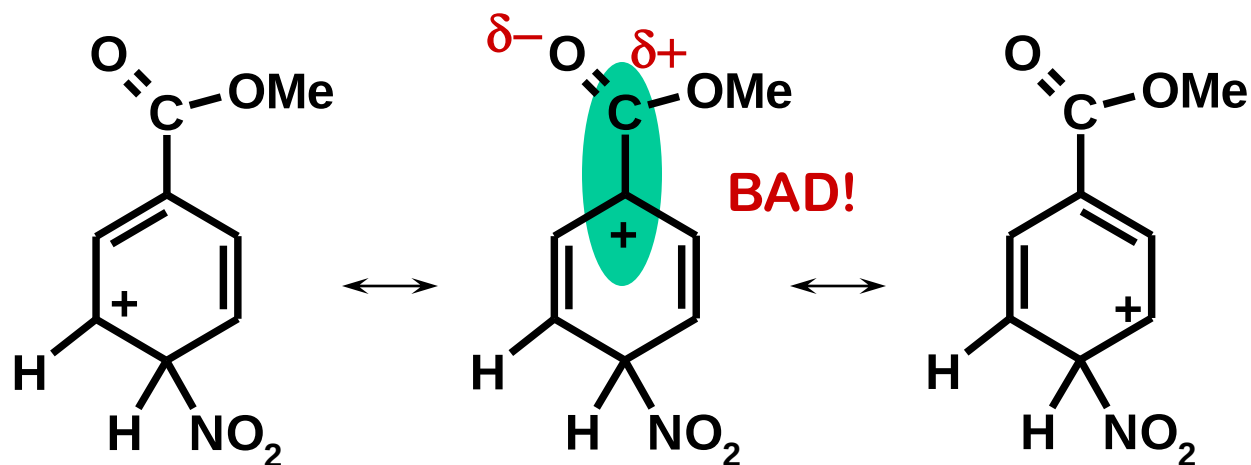
ortho



meta

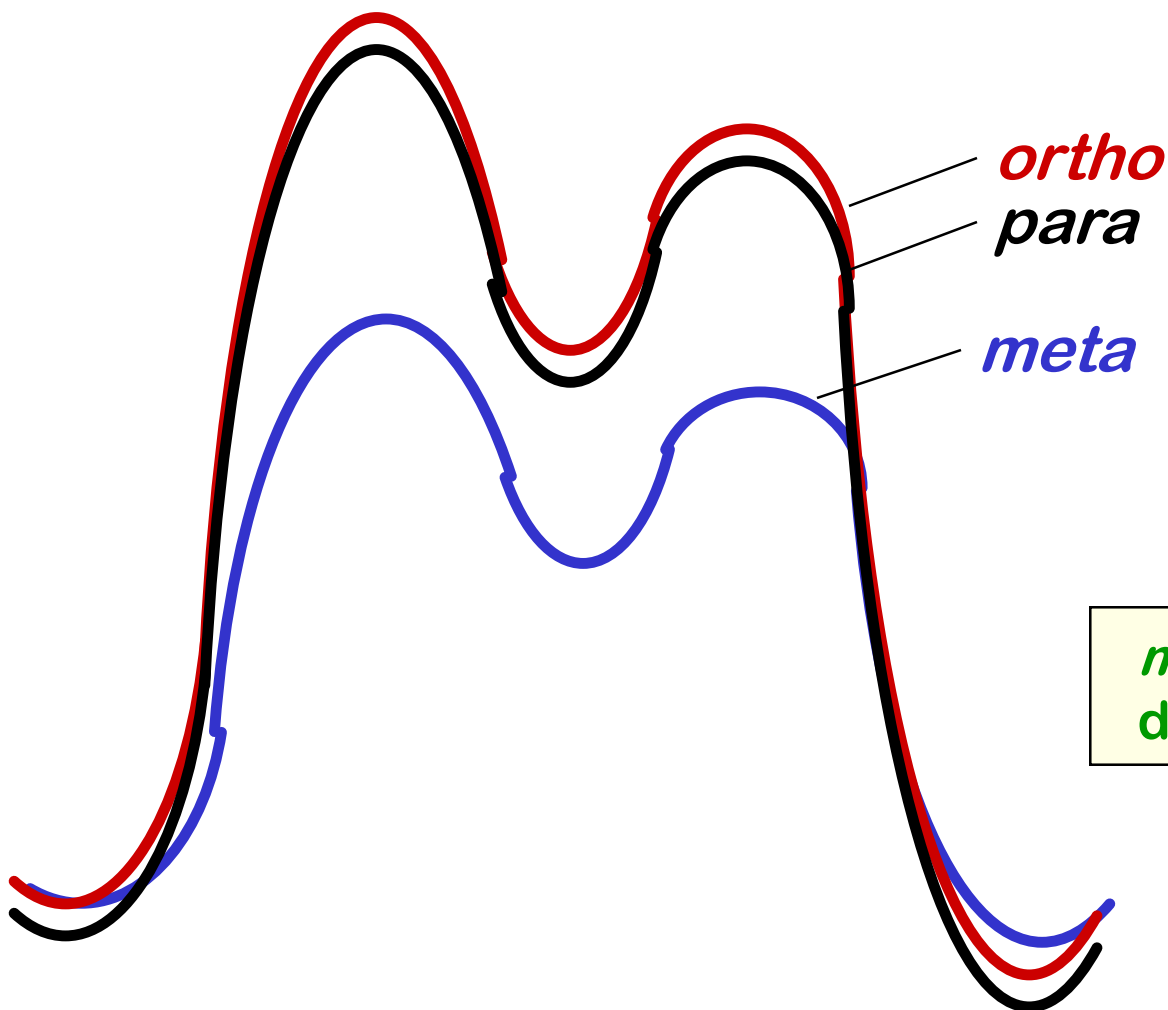


para



Energy Profiles

NITRATION OF METHYL BENZOATE



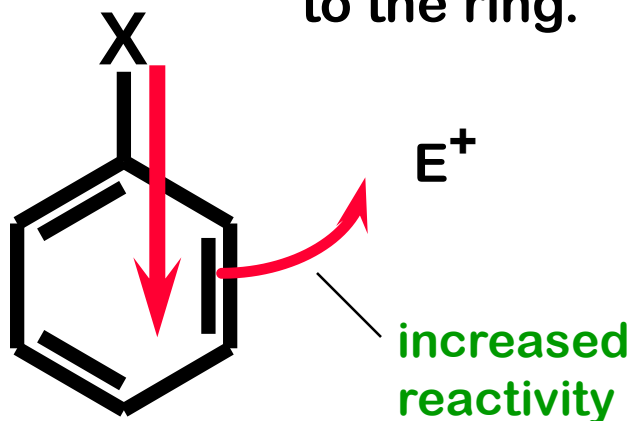
some
benzenium
resonance
structures
have a bad
situation

meta
director

DIRECTIVITY OF SINGLE GROUPS

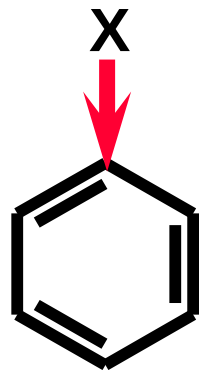
ortho, para - Directing Groups

Groups that donate electron density to the ring.

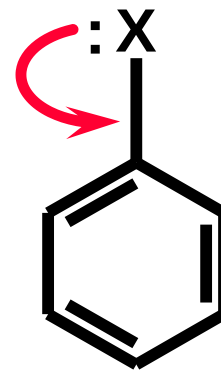


These groups also “activate” the ring, or make it more reactive.

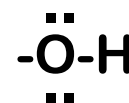
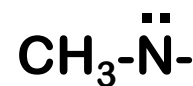
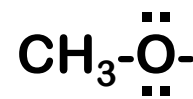
PROFILE:



+I Substituent



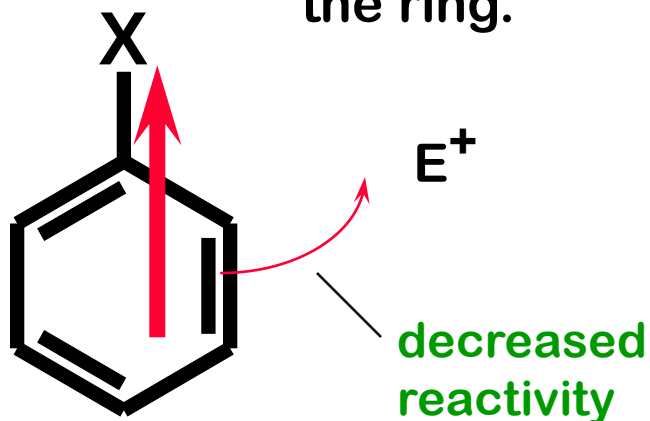
+R Substituent



The +R groups activate the ring more strongly than +I groups.

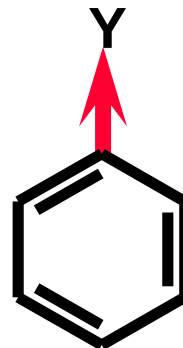
meta - Directing Groups

Groups that withdraw electron density from the ring.

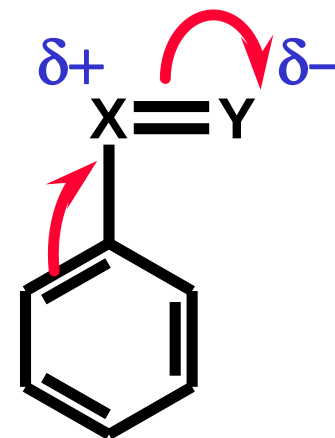
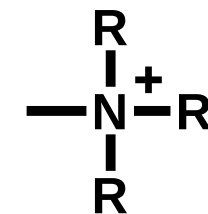


These groups also “deactivate” the ring, or make it less reactive.

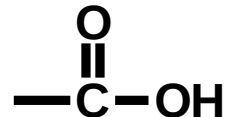
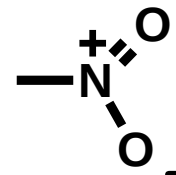
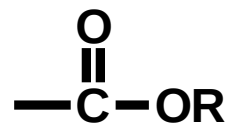
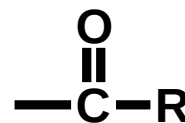
PROFILE:



-I Substituent

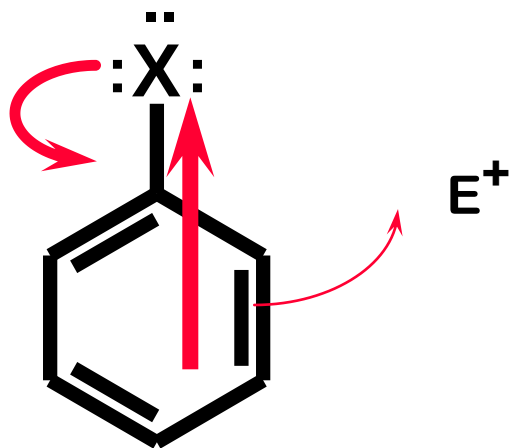


-R Substituent



THE EXCEPTION

Halides - *o,p* Directors / Deactivating



+R / -I / *o,p* / deactivating

-F
-Cl
-Br
-I

Halides represent a special case:

They are *o,p* directing groups
that are deactivating

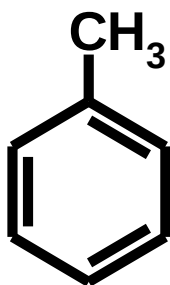
They are *o,p* directors (+R effect)

They are deactivating (-I effect)

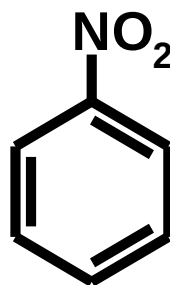
Most other other substituents fall
into one of these four categories:

- 1) +R / *o,p* / activating
- 2) +I / *o,p* / activating
- 3) -R / *m* / deactivating
- 4) -I / *m* / deactivating

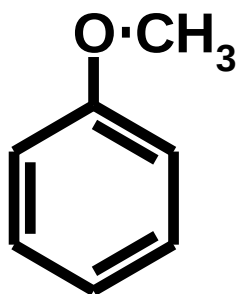
PREDICT !



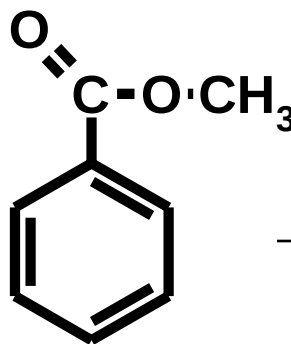
o,p



m



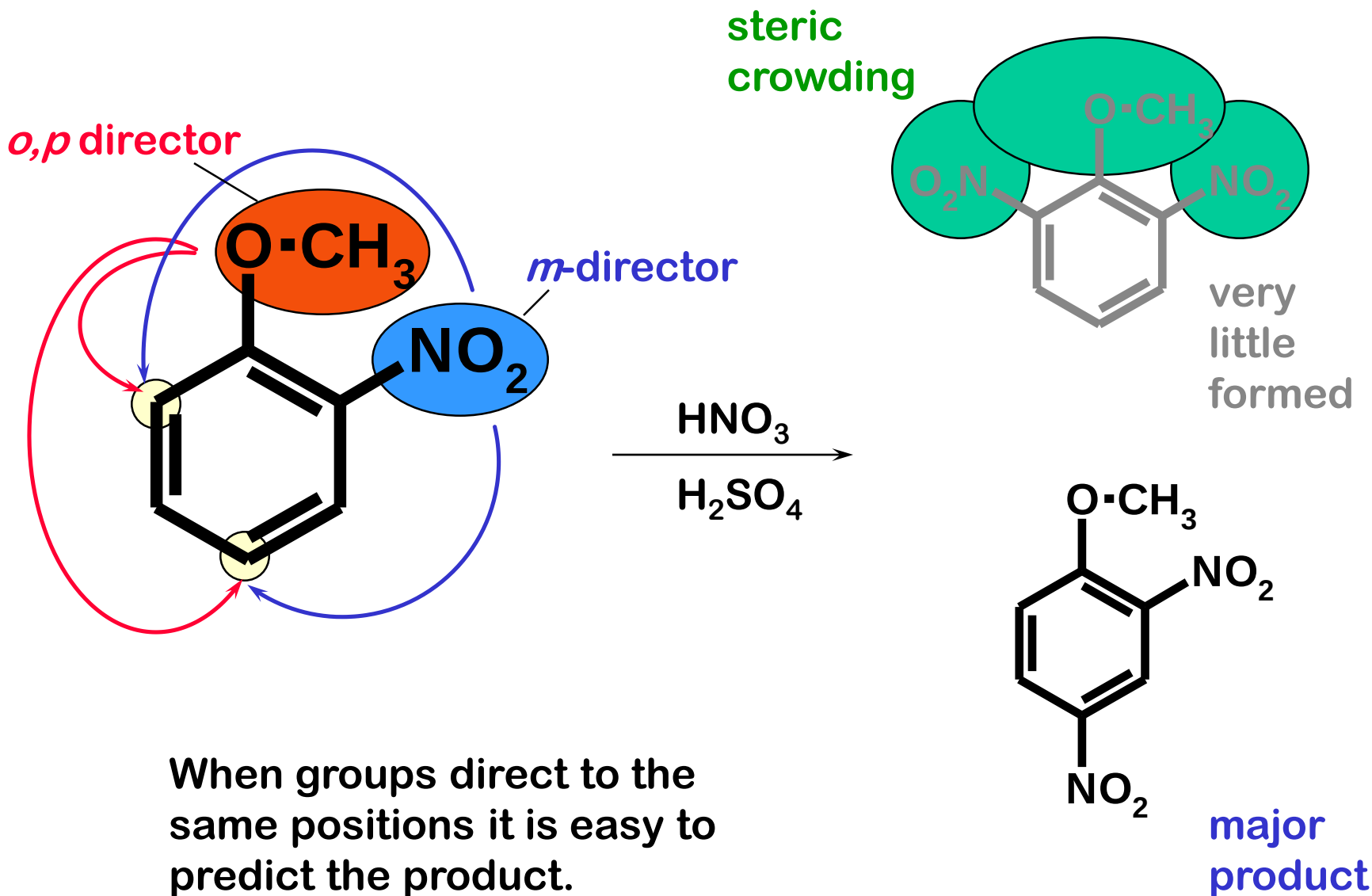
o,p



m

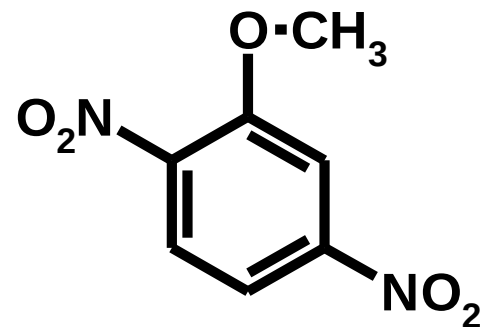
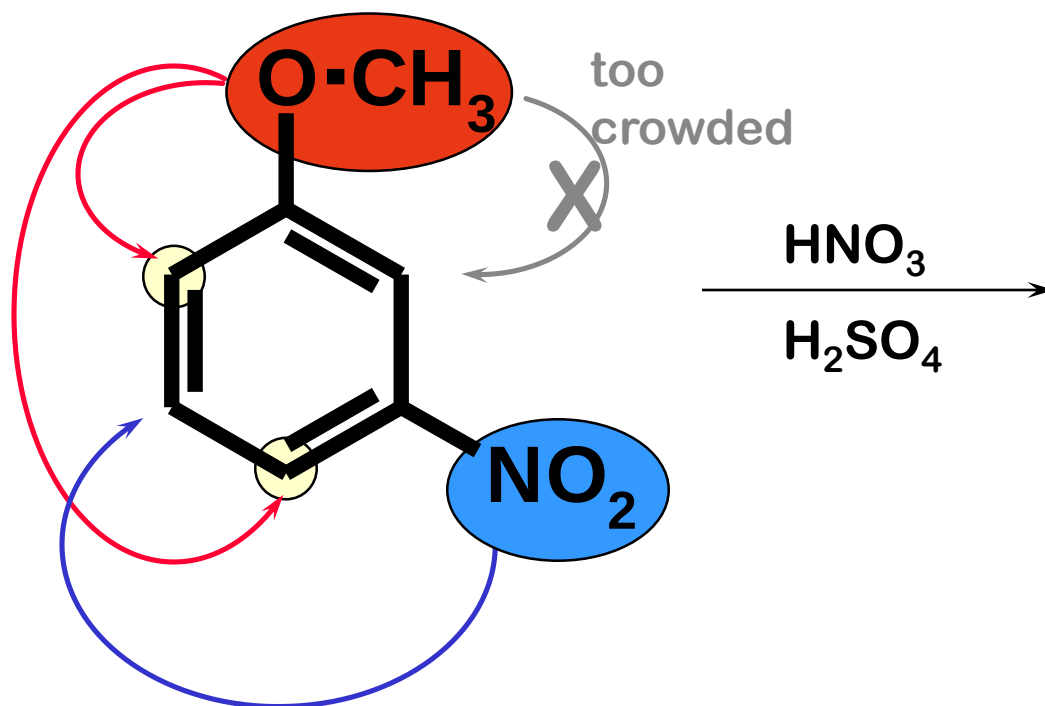
DIRECTIVITY OF MULTIPLE GROUPS

GROUPS ACTING IN CONCERT

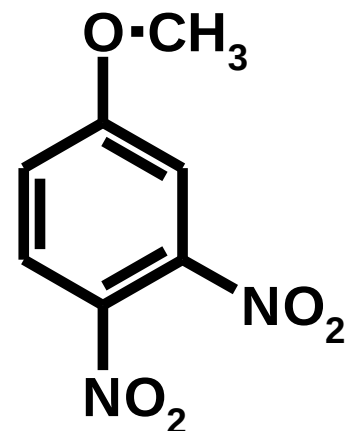


GROUPS COMPETING

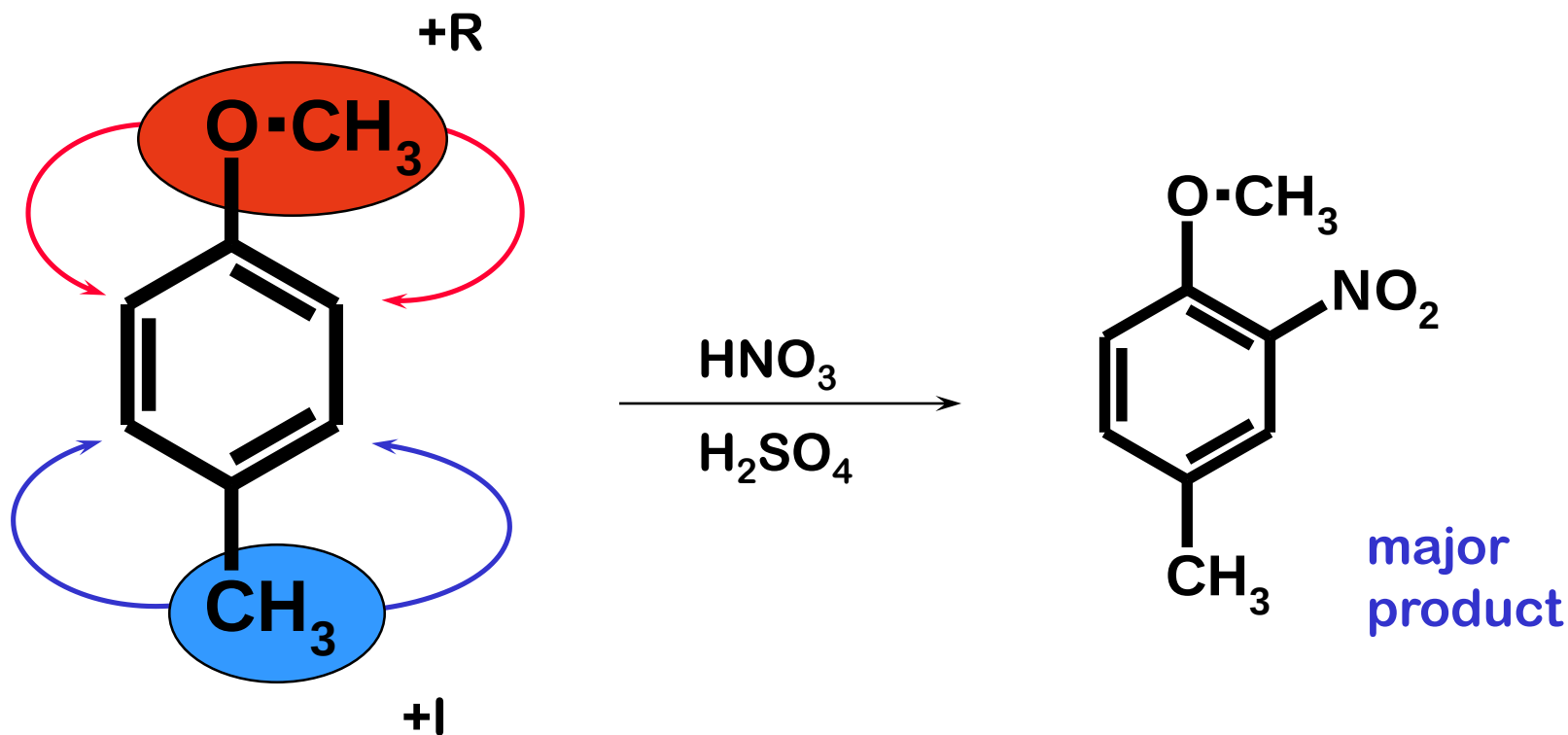
o,p-directing groups win
over *m*-directing groups



+



RESONANCE VERSUS INDUCTIVE EFFECT

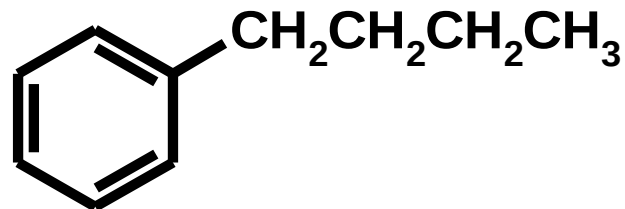
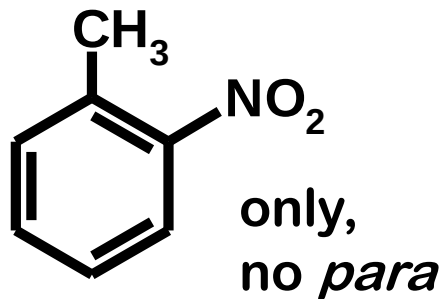
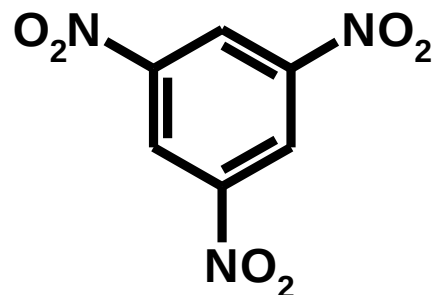
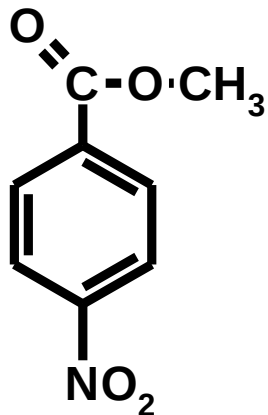


resonance effects are more
important than inductive effects

SOME GENERAL RULES

- 1) Activating (*o,p*) groups (+R, +I) win over deactivating (*m*) groups (-R,-I).
- 2) Resonance groups (+R) win over inductive (+I) groups.
- 3) 1,2,3-Trisubstituted products rarely form due to excessive steric crowding.
- 4) With bulky directing groups, there will usually be more *p*-substitution than *o*-substitution.
- 5) The incoming group replaces a hydrogen, it will not usually displace a substituent already in place.

HOW CAN YOU MAKE ...

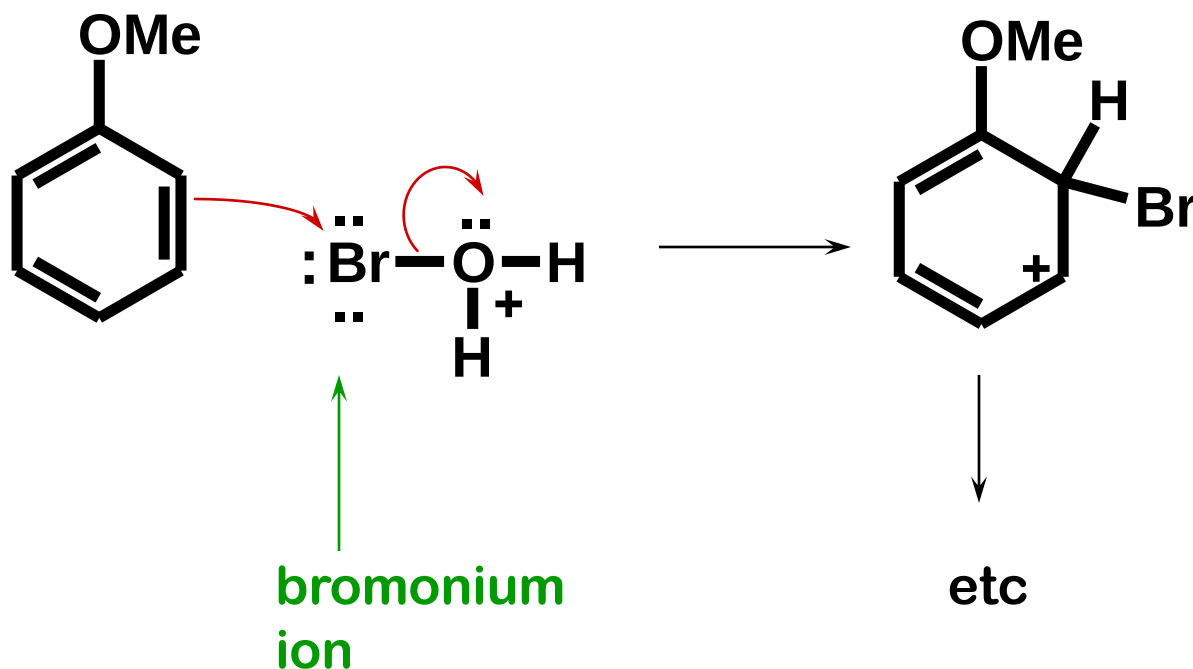
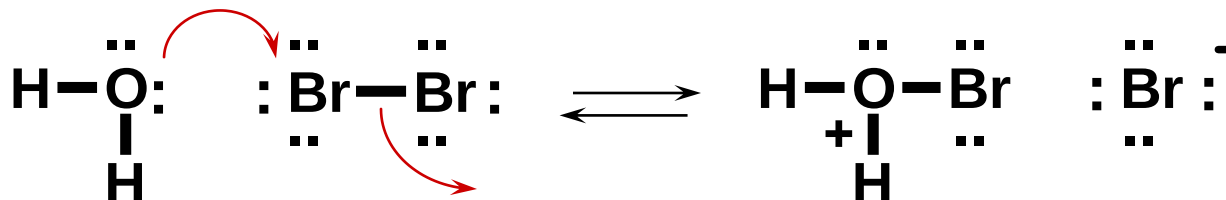


BROMINE - WATER REAGENT

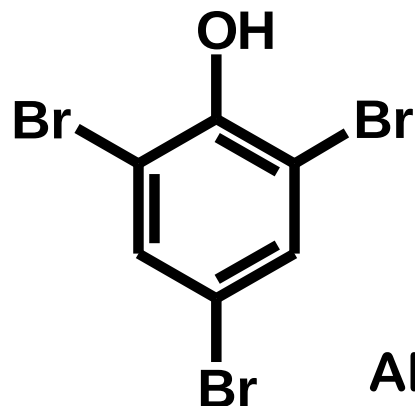
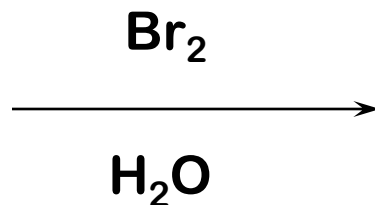
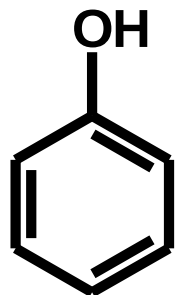
PHENOLS AND ANILINES

BROMINE IN WATER

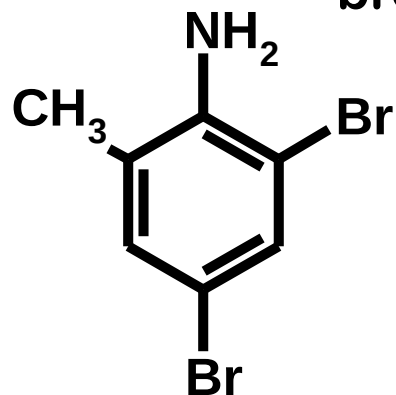
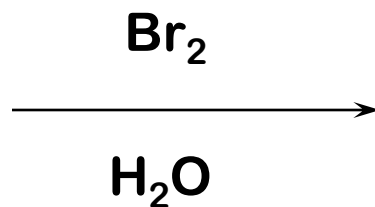
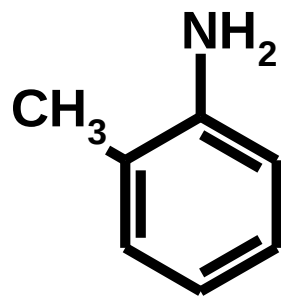
This reagent works only with highly-activated rings such as phenols, anisoles and anilines.



PHENOLS AND ANILINES REACT



All available positions are bromiated.



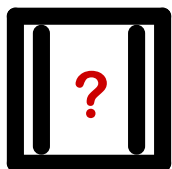
AROMATICITY

THE HUCKEL RULE

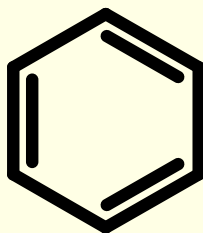
AROMATICITY

QUESTION:

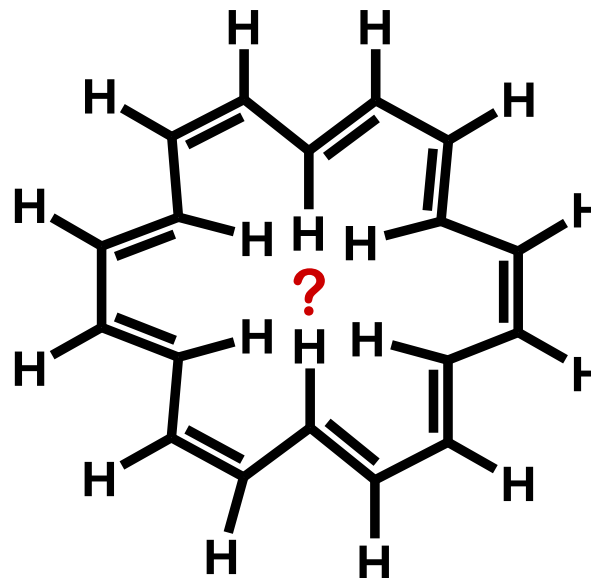
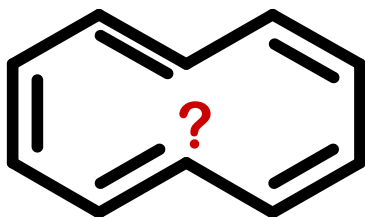
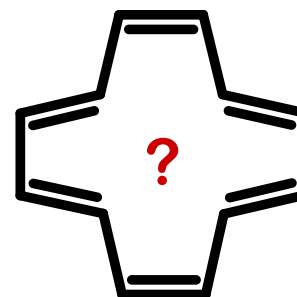
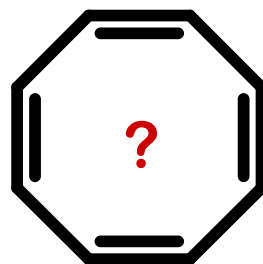
Are all fully-conjugated, cyclic systems aromatic?



36 kcal/mole RE



KNOWN
AROMATIC



Do these other rings have the same kind of stability as benzene?

AROMATICITY

HÜCKEL $4n+2$ RULE

Prediction: Compounds that have $4n+2$ pi electrons in a cyclic array will be aromatic.

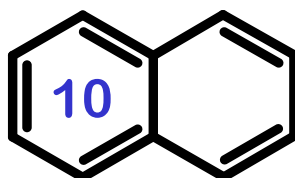
$4n+2$ series = 2, 6, 10, 14, 18, 22, 26, 30 etc.

The rule was derived by observation of

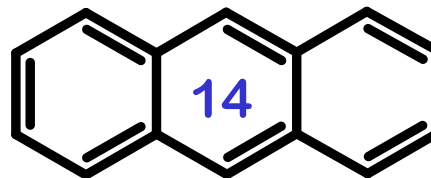
POLYCYCLIC AROMATIC COMPOUNDS



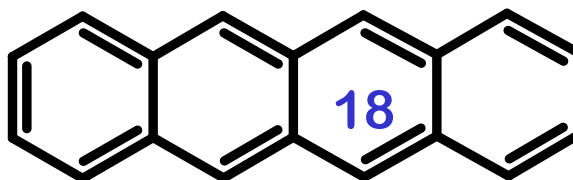
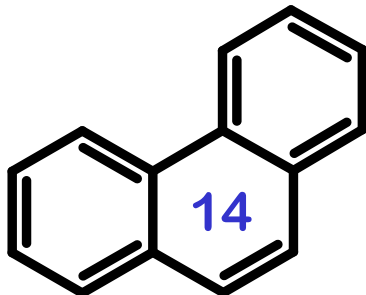
benzene



naphthalene



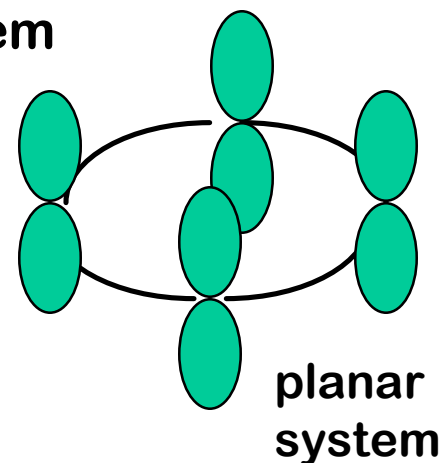
anthracene



Aromatic Compounds Have Special Properties

Aromatic compounds:

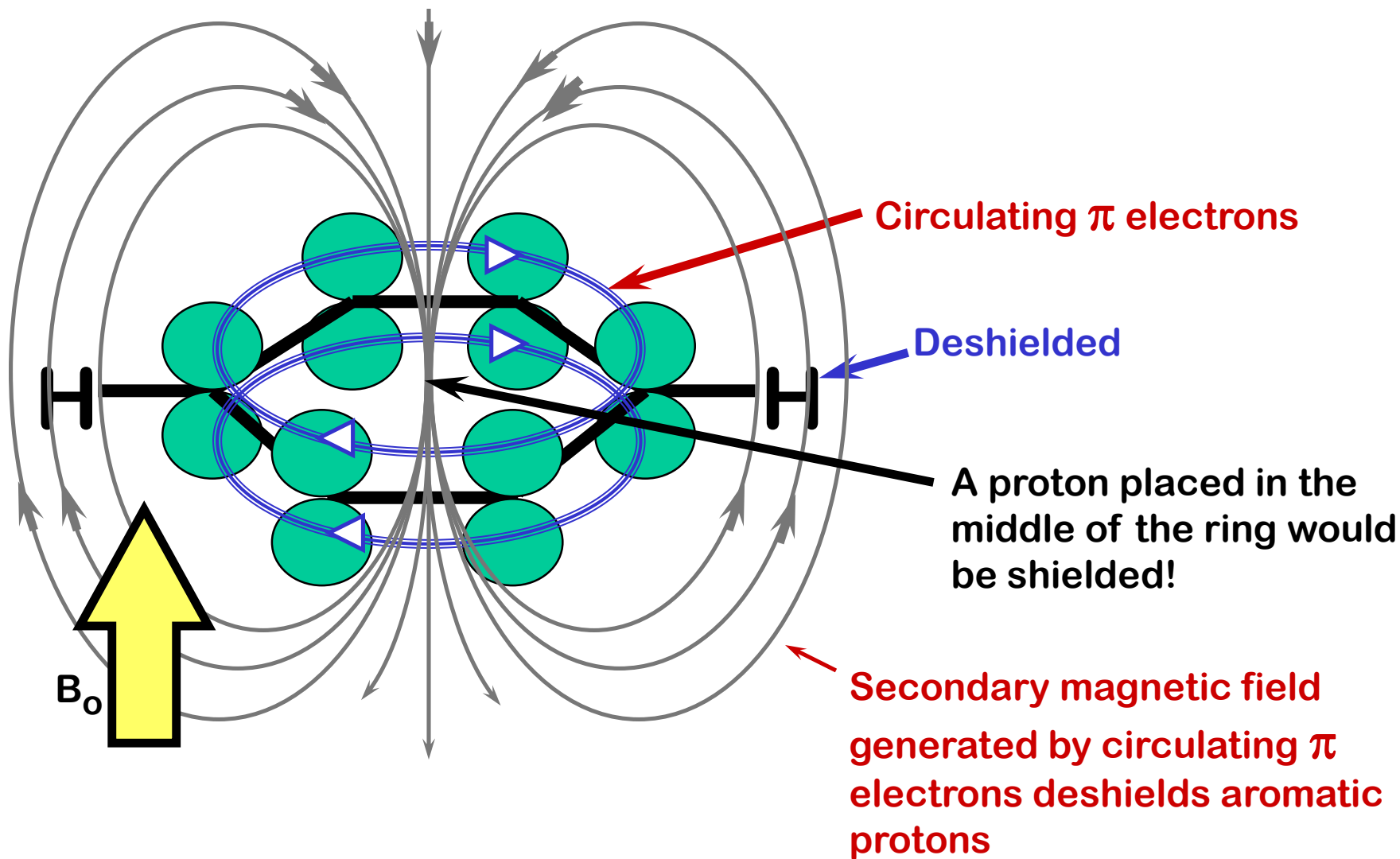
- 1) Must be cyclic and fully conjugated
- 2) Must have $4n+2$ π electrons in the system
- 3) Must have the entire system planar
- 4) Will have no unpaired electrons in the π system molecular orbitals



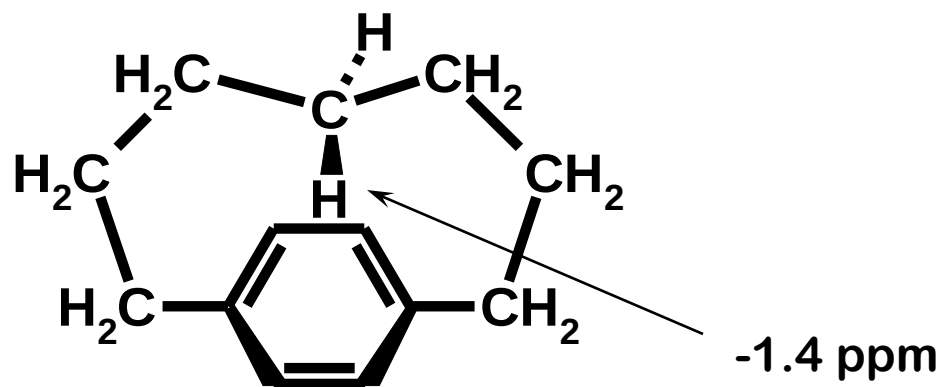
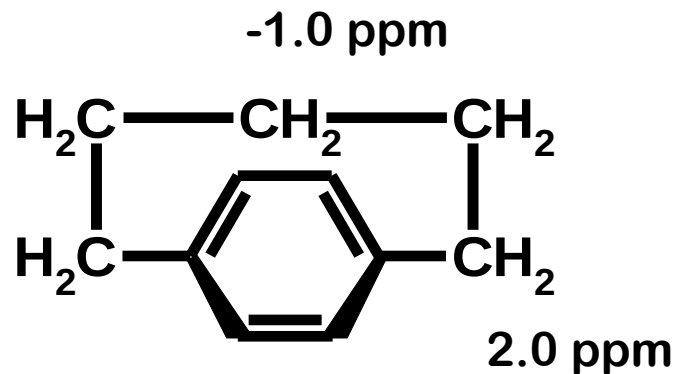
Characteristic Properties:

- 1) Special chemical stability
- 2) Give substitution reactions instead of addition
- 3) Show a ring current in the NMR
(Chapter 13, Section 13.8)

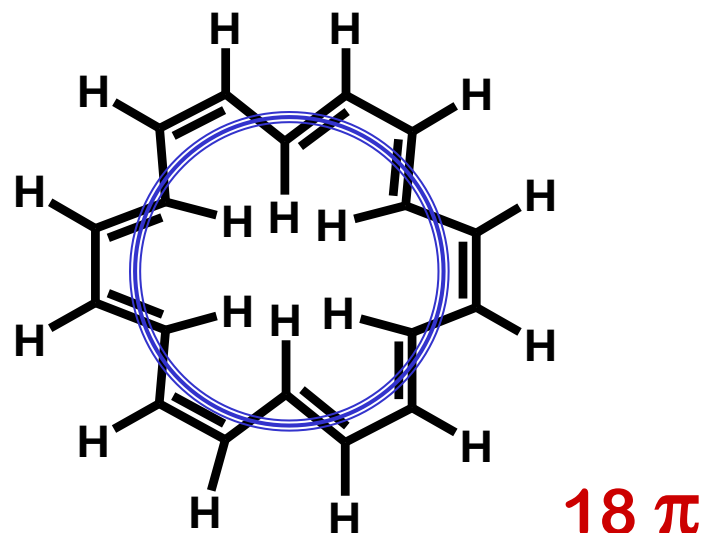
Ring Current in Benzene



RING CURRENTS CAN BE SEEN IN THE NMR



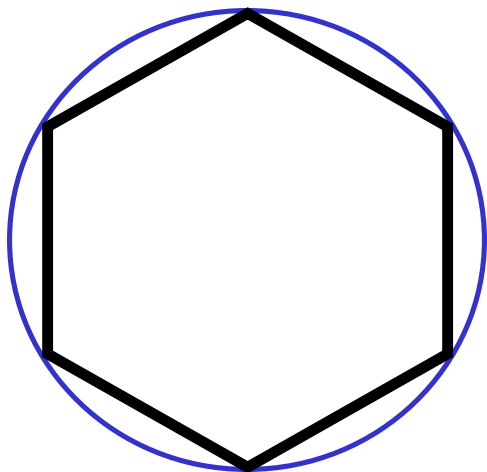
AROMATIC - SHOWS
A RING CURRENT



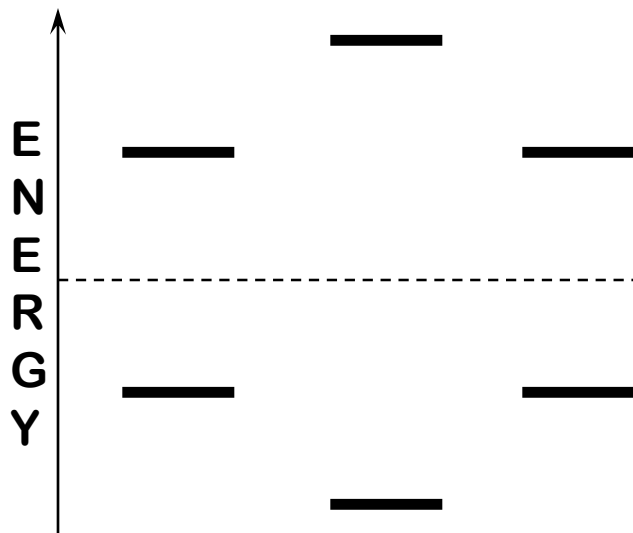
inner hydrogens -1.8 ppm
outer hydrogens 8.9 ppm

HÜCKEL MNEMONIC

CYCLIC π MOLECULAR ORBITAL ARRAYS



- 1) Draw a circle
- 2) Inscribe the ring in the circle point down
- 3) Each point where the polygon (ring) touches the circle represents an energy level.
- 4) Place the correct number of electrons in the orbitals, starting with the lowest energy orbital first.

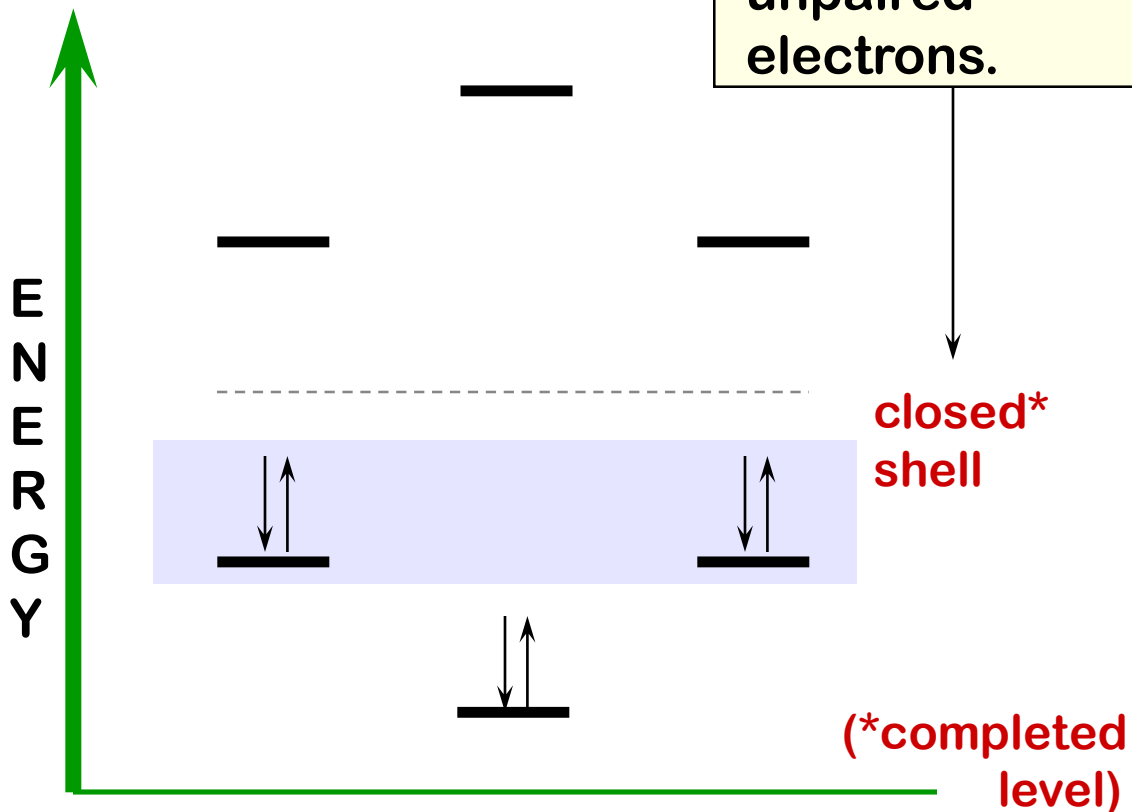
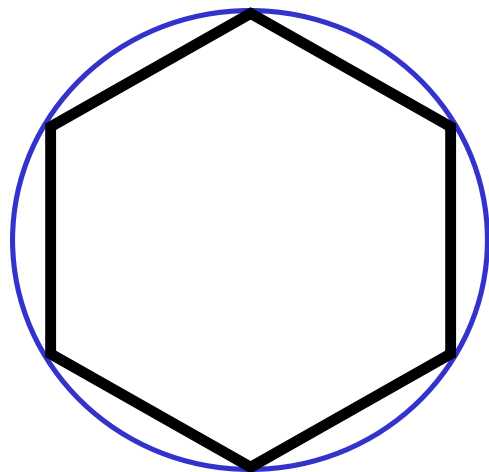


BENZENE



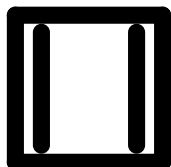
6π electrons

AROMATIC



Aromatic compounds will have all of the occupied π M.O. levels completely filled with no unpaired electrons.

CYCLOBUTADIENE

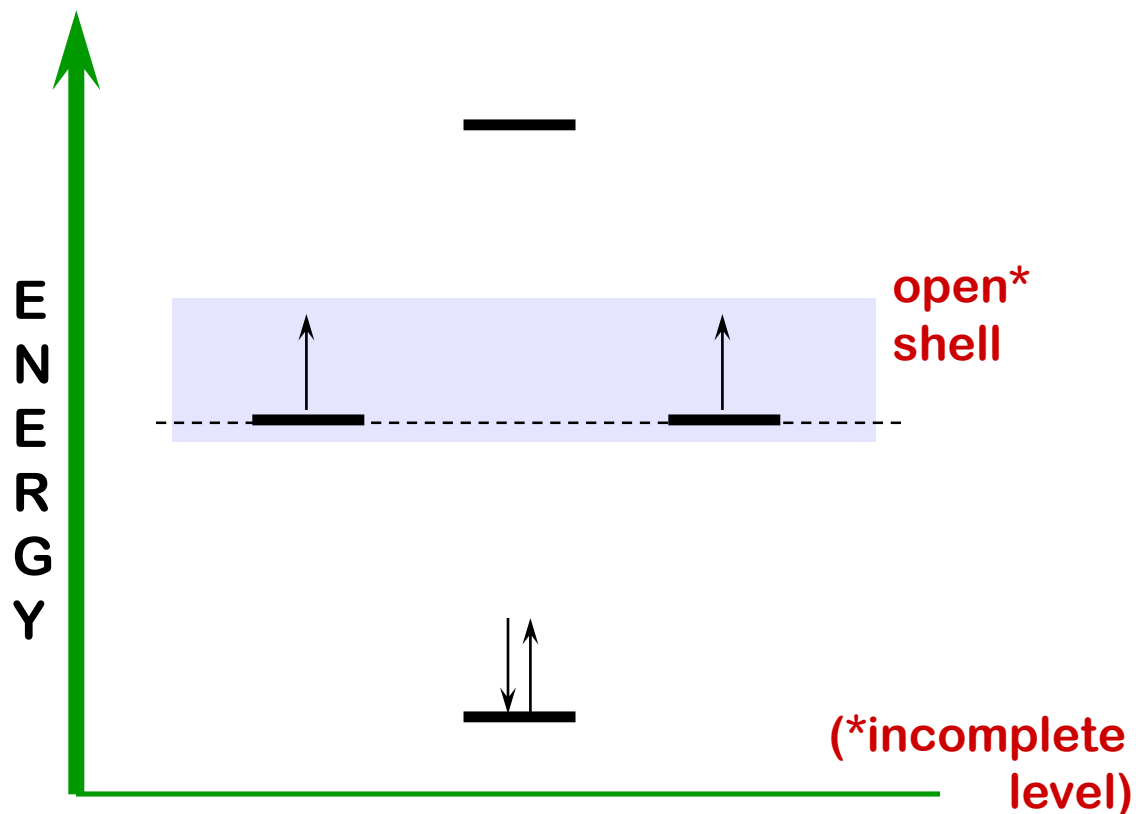
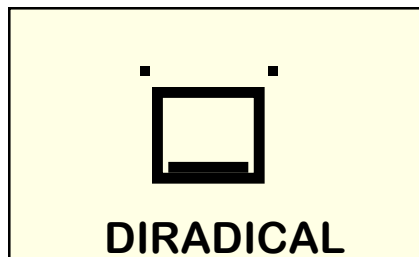
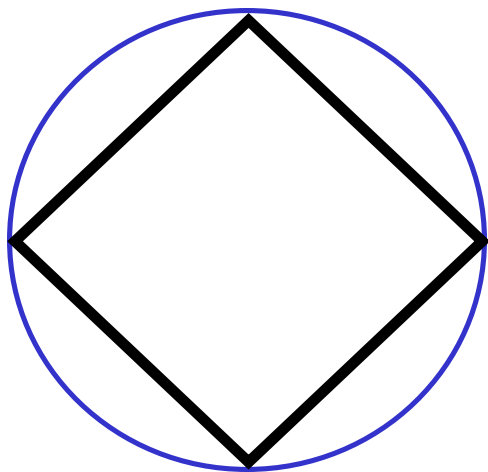


4π electrons

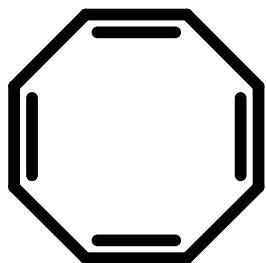
ANTI-AROMATIC

Does not have a completed shell and has unpaired electrons.

Does not have $4n+2 \pi$ electrons.



CYCLOOCTATETRAENE

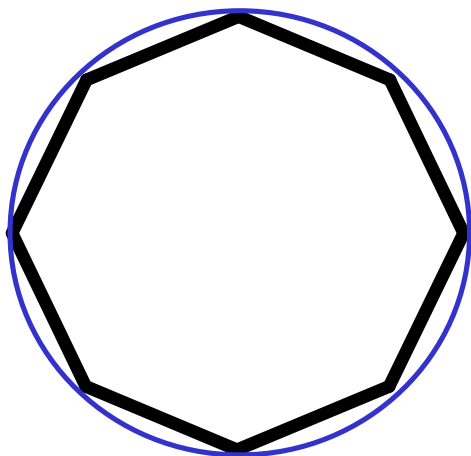


8π electrons

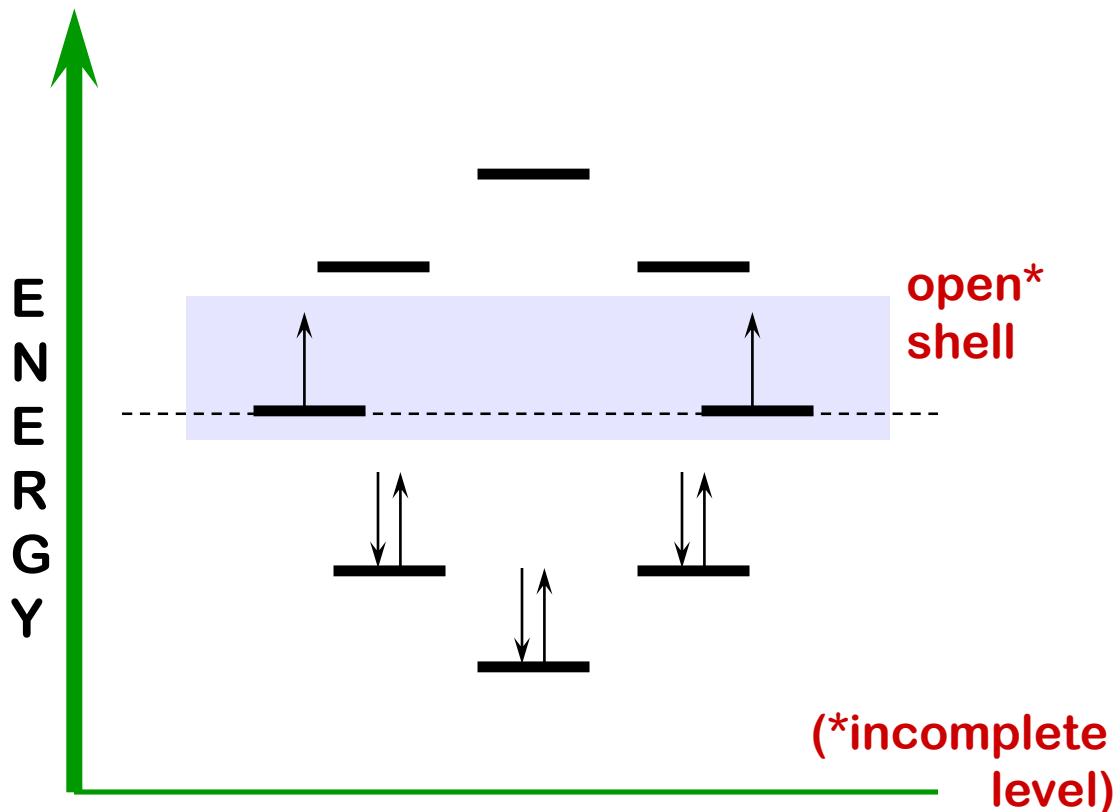
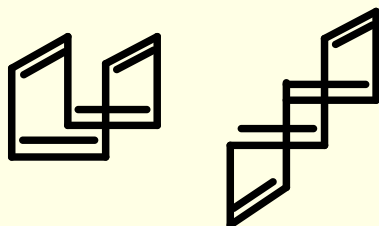
ANTI-AROMATIC

Does not have a completed shell and has unpaired electrons.

Does not have $4n+2 \pi$ electrons.

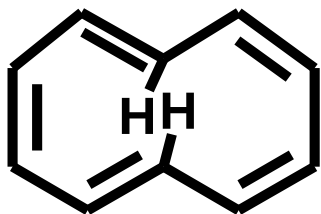


not planar



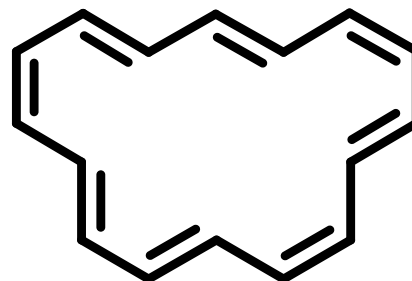
SOME CYCLIC POLYENES

ANNULENES



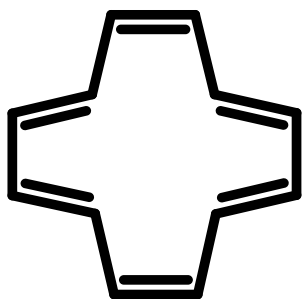
$10 \pi = 4(2) + 2$
BUT CANNOT BE PLANAR
(see the hydrogens)

[10]-annulene



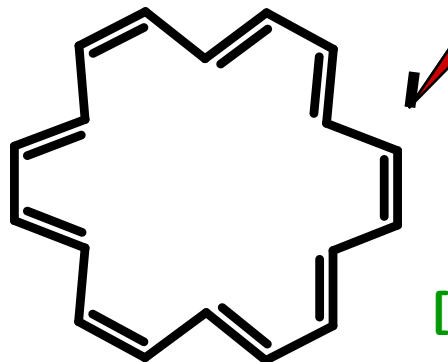
16π

[16]-annulene



12π

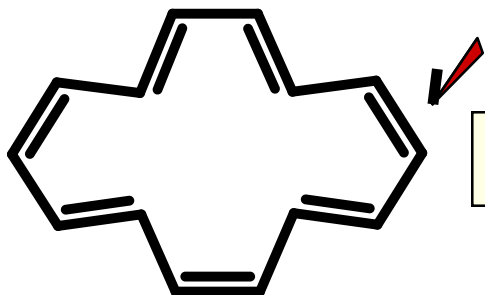
[12]-annulene



$18 \pi = 4(4) + 2$

AROMATIC

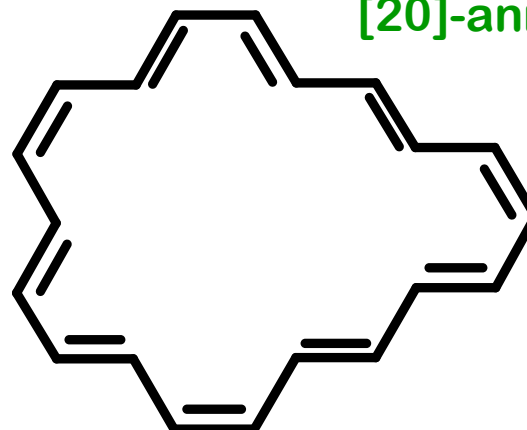
[18]-annulene



$14 \pi = 4(3) + 2$

AROMATIC

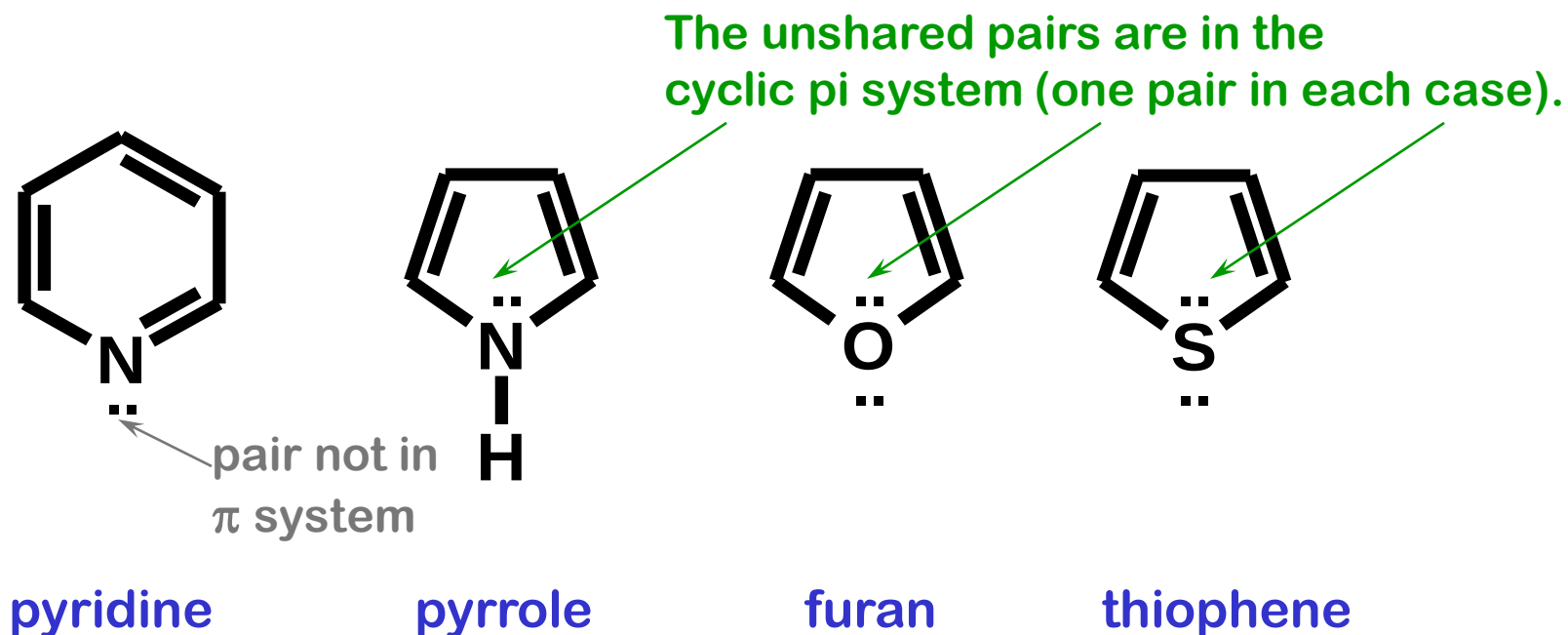
[14]-annulene



20π

[20]-annulene

HETEROCYCLIC COMPOUNDS

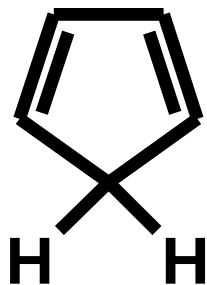


All have 6π electrons in a cyclic array.

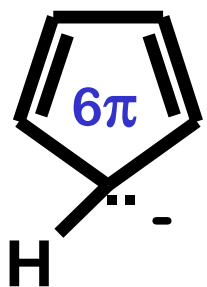
These compounds have reactions similar to benzene, rather than to alkenes. They will give substitution reactions under conditions similar to those for benzene.

CYCLOPENTADIENYL ANION AND CATION

The methylene hydrogens are acidic.



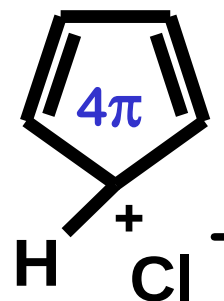
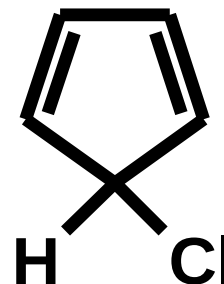
NaOEt
EtOH



AROMATIC

The anion forms readily.

This compound does not dissolve in water.

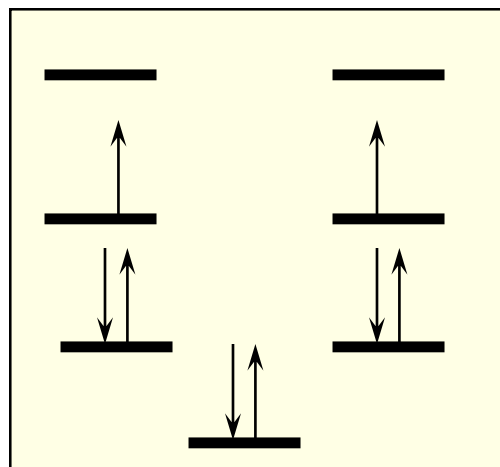


ANTI-AROMATIC

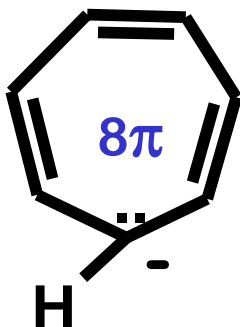
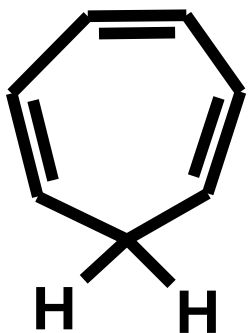
The cation does not form at all.

CYCLOHEPTATRIENYL ANION AND CATION

The methylene hydrogens are not acidic.

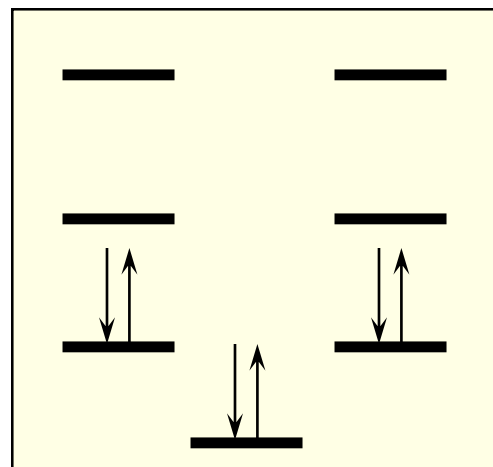


ANTI-AROMATIC

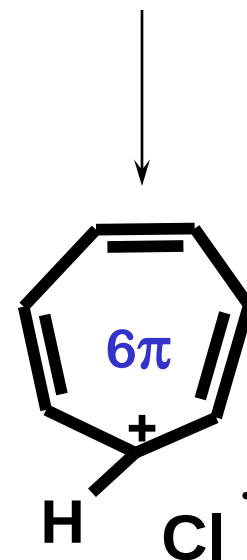
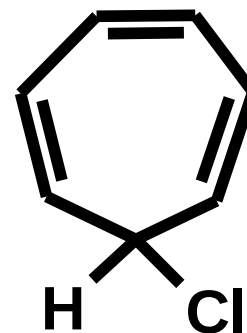


Doesn't form easily.

This compound ionizes easily in water.



AROMATIC



Dissolves in water.