University of Illinois
at Chicago UIC

Lecture 24
Organic Chemistry 1

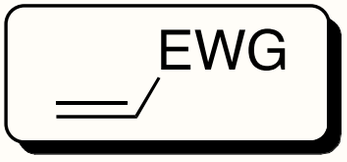
Professor Duncan Wardrop

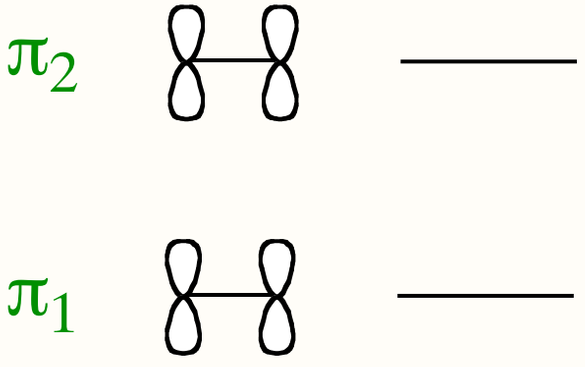
April 6, 2010

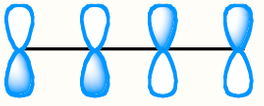
Self Test Question

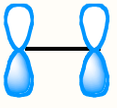
Which shorthand orbital diagram best represents the LUMO of a dienophile in a Diels-Alder reaction?

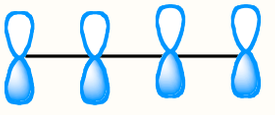
1. Step one: determine the number of p AOs in the π-system.
2. Step two: draw the same number of unshaded molecular orbitals as p AOs.
3. Assign nodes to MOs. Lowest = 0. Each higher MO has one more node.
4. Shade MOs to reflect node assignment in step 3.
5. Determine # of electrons in π-system. Place those electrons into MO according to Hund, Pauli & Aufbau principles.

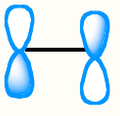


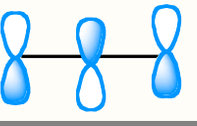


A. 

B. 

C. 

D. 

E. 

Self Test Question

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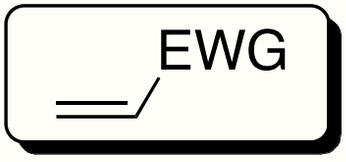

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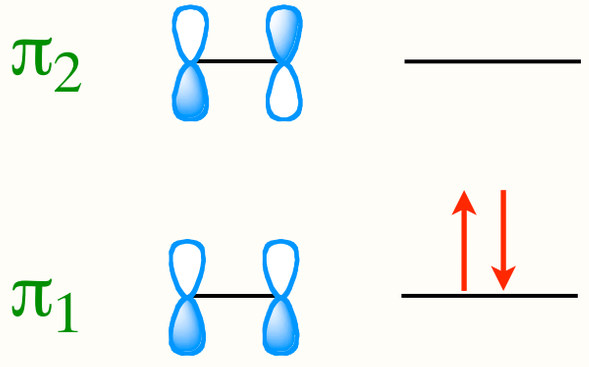
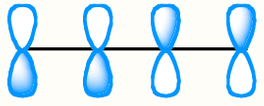
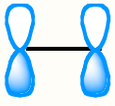
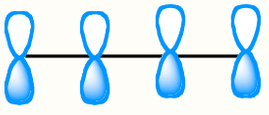
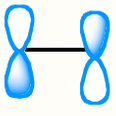
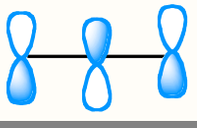


A. 

B. 

C. 

D. 

E. 

Chapter 11
Arenes & Aromaticity

Sections 11.1-11.7
You are responsible for sections 11.8-11.10.

Classes of Hydrocarbons

Hydrocarbons

- only C & H atoms
- framework for fxnl groups
- generally, non-reactive

Aliphatic

- *aleiphar* Greek for "fat"
- sources were fats and oils

Aromatic

- aka: arenes
- many isolated from plants;
- benzene
- cyclic conjugated alkenes

Alkanes

- **only** single bonds
- nomenclature: -ane suffix

Alkenes

- contain a double bond
- nomenclature: -ene suffix

Alkynes

- contain a triple bond
- nomenclature: -yne suffix

Examples of Aromatic Hydrocarbons

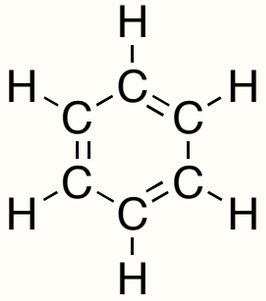
Aromatic

- aka: arenes
- many isolated from plants; impurities were fragrant
- cyclic conjugated alkenes

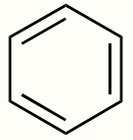
- many are derivatives of benzene
- resonance: delocalized electrons
- adjacent double bonds
- planar (120° bond angles)
- polyaromatic hydrocarbons (PAHs) contain two or more aromatic rings; highly carcinogenic and environmental toxin

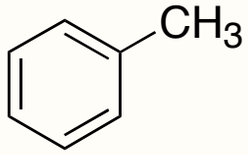
Arene: aromatic hydrocarbon

Aromatic: (not smell) typically based on structure of benzene; we'll define aromaticity later

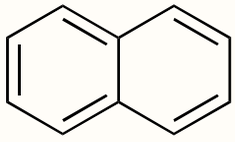


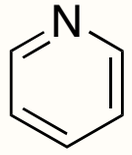
benzene


benzene



toluene


napthalene

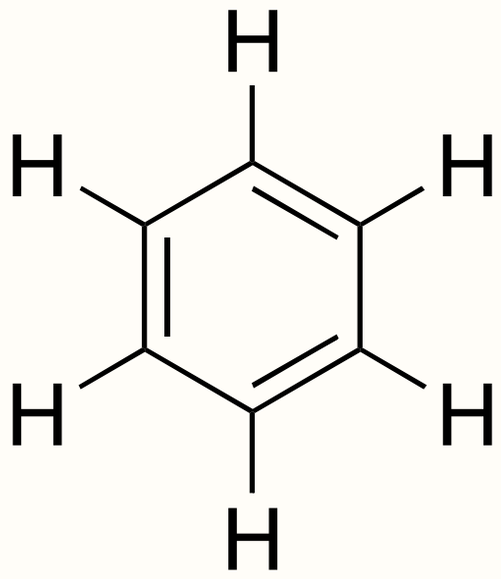


pyridine

furan

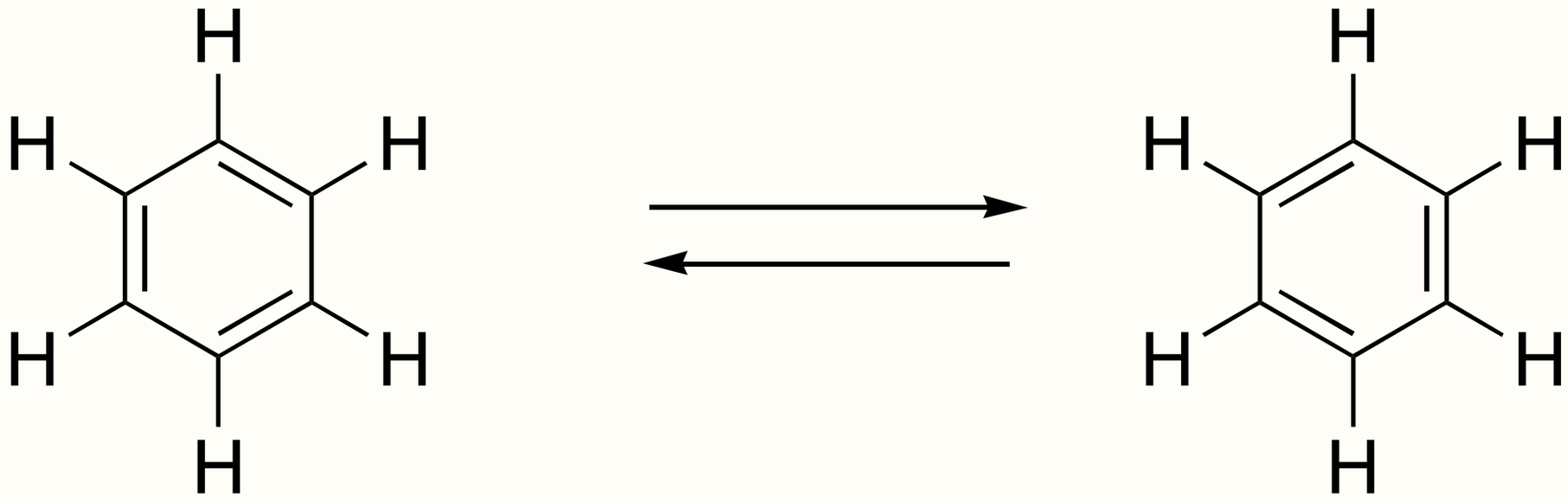
Kekule Formulation of Benzene

Kekule proposed a cyclic structure for C_6H_6 with alternating single and double bonds.



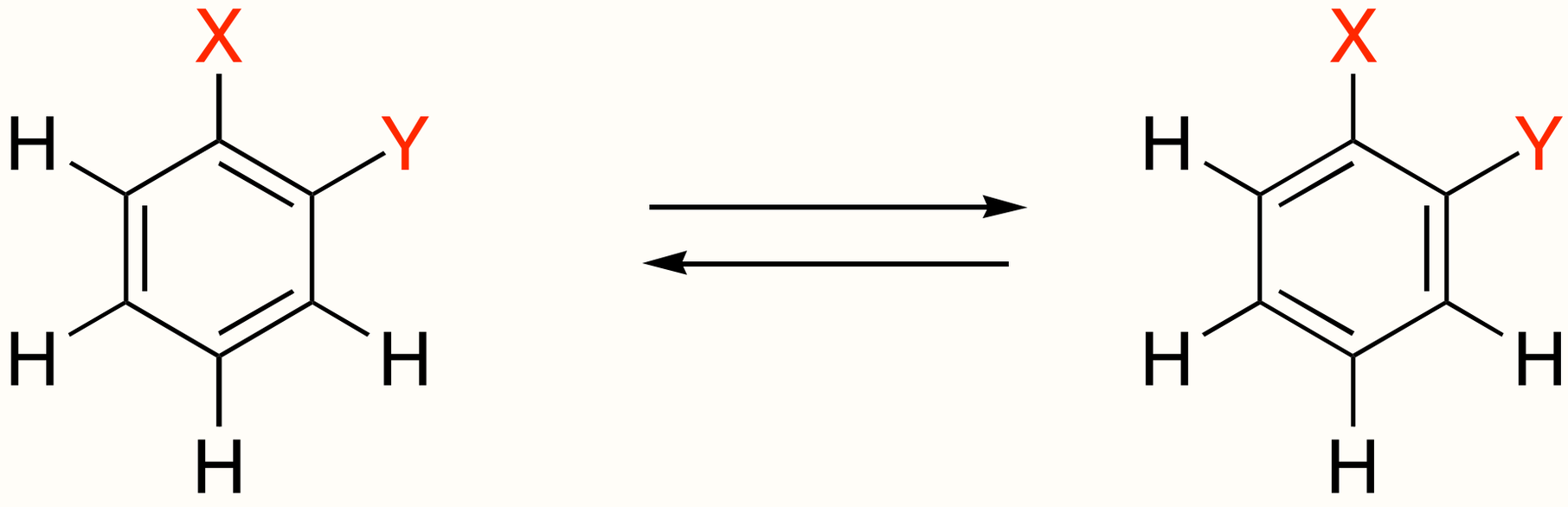
Kekule Formulation of Benzene

Later Kekule revised his proposal by suggesting a rapid equilibrium between two equivalent structures.



Kekule Formulation of Benzene

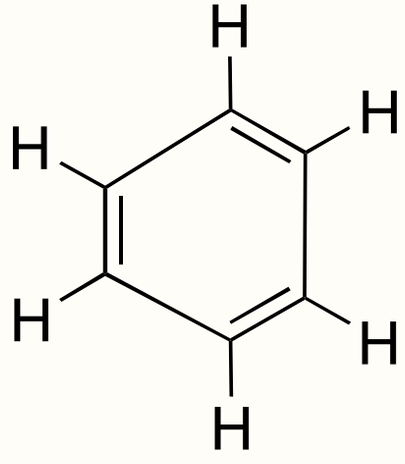
However, this suggested that isomers of the kind shown were possible. Yet, none were ever isolated.



Curious Case of Benzene

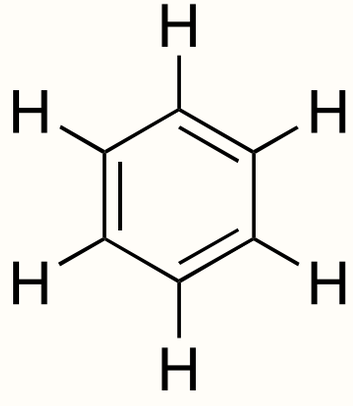
Furthermore, structural studies did support the Kekule model. Instead of alternating single and double bonds, all of the C-C bonds are the same length.

Predicted



C–C bond length: 150 pm
C=C bond length: 134 pm

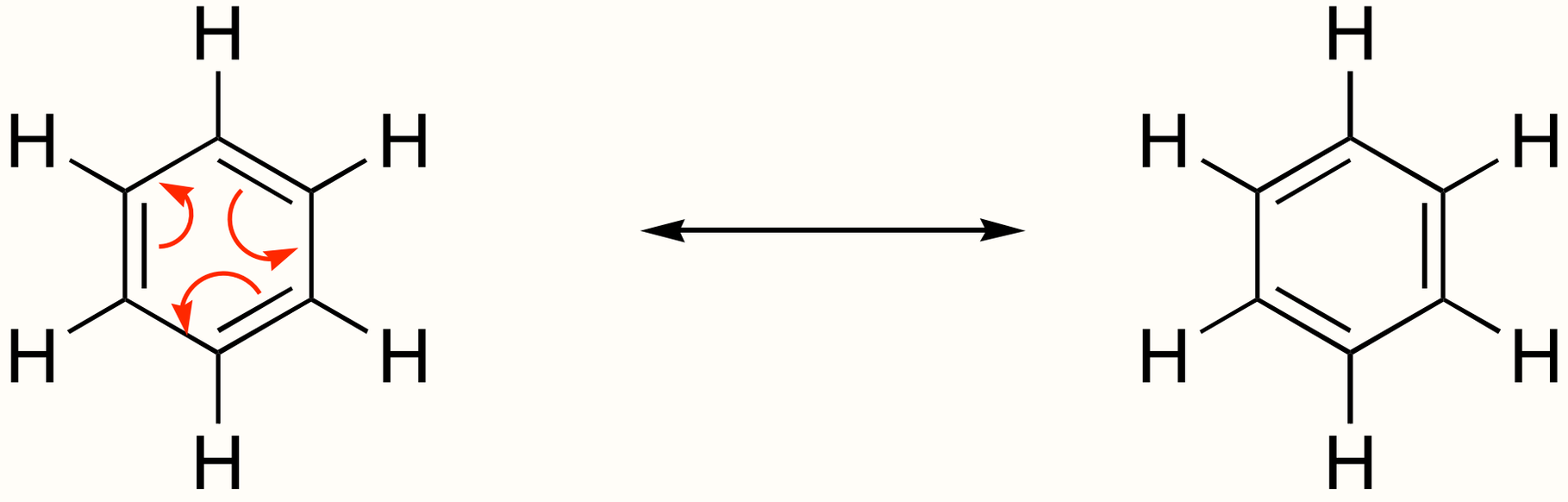
Actual



All bonds = 140 pm

Resonance Formulation of Benzene

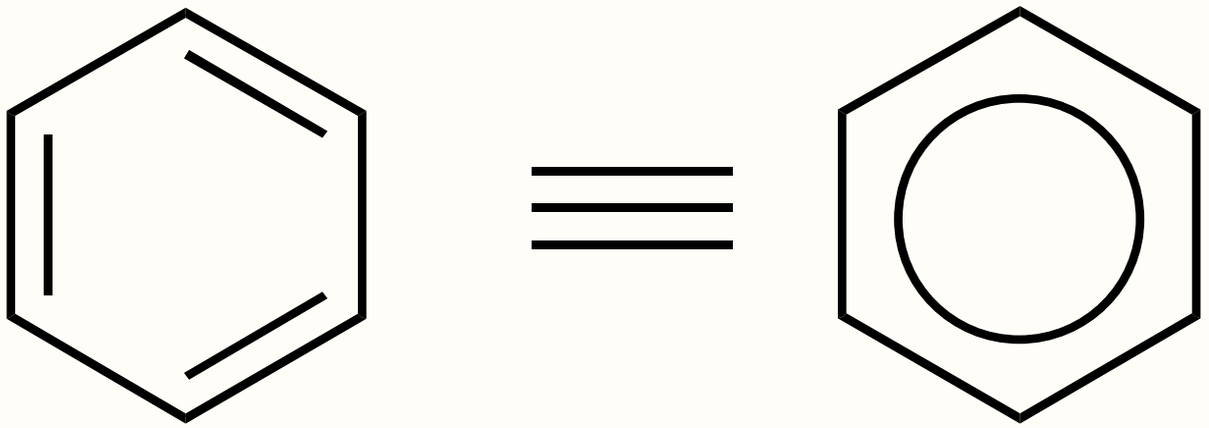
The structure of benzene is best represented, not as an equilibrium between two isomers, but as a resonance hybrid of two Lewis structures.



Electrons are not localized in alternating single and double bonds, but are delocalized over all six ring carbon atoms.

Resonance Formulation of Benzene

A common representation for benzene resonance is a circle inscribed in a hexane ring (Robinson symbol); the circle represents the 6 delocalized π-electrons.



Kekule ≡ Robinson

While common, this representation will not be used in this class. The Kekule structure is preferred since it allows us to more easily keep track of electrons and electron-flow in mechanism.

Electrons are not localized in alternating single and double bonds, but are delocalized over all six ring carbon atoms.

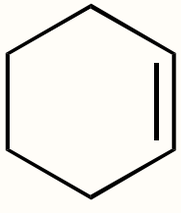
Self Test Question

Based upon what you've already learned about hydrogenation, rank the molecules below in order of increasing heat of hydrogenation ($\Delta H_{hydrog} = -\Delta H$).

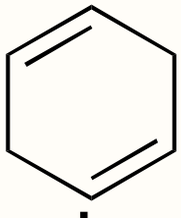
If you've already read this chapter, do not consider aromaticity when answering this question.

Current Assumptions:

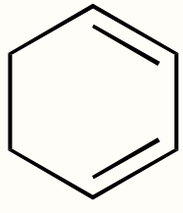
1. ↑ double bonds = ↑ ΔH_{hydrog}
2. conjugation = ↓ ΔH_{hydrog}



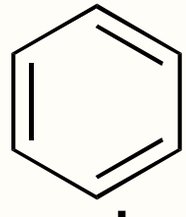
a



b



c



d

A. a,b,c,d

B. a,c,b,d

C. d,c,b,a

D. d,b,c,a

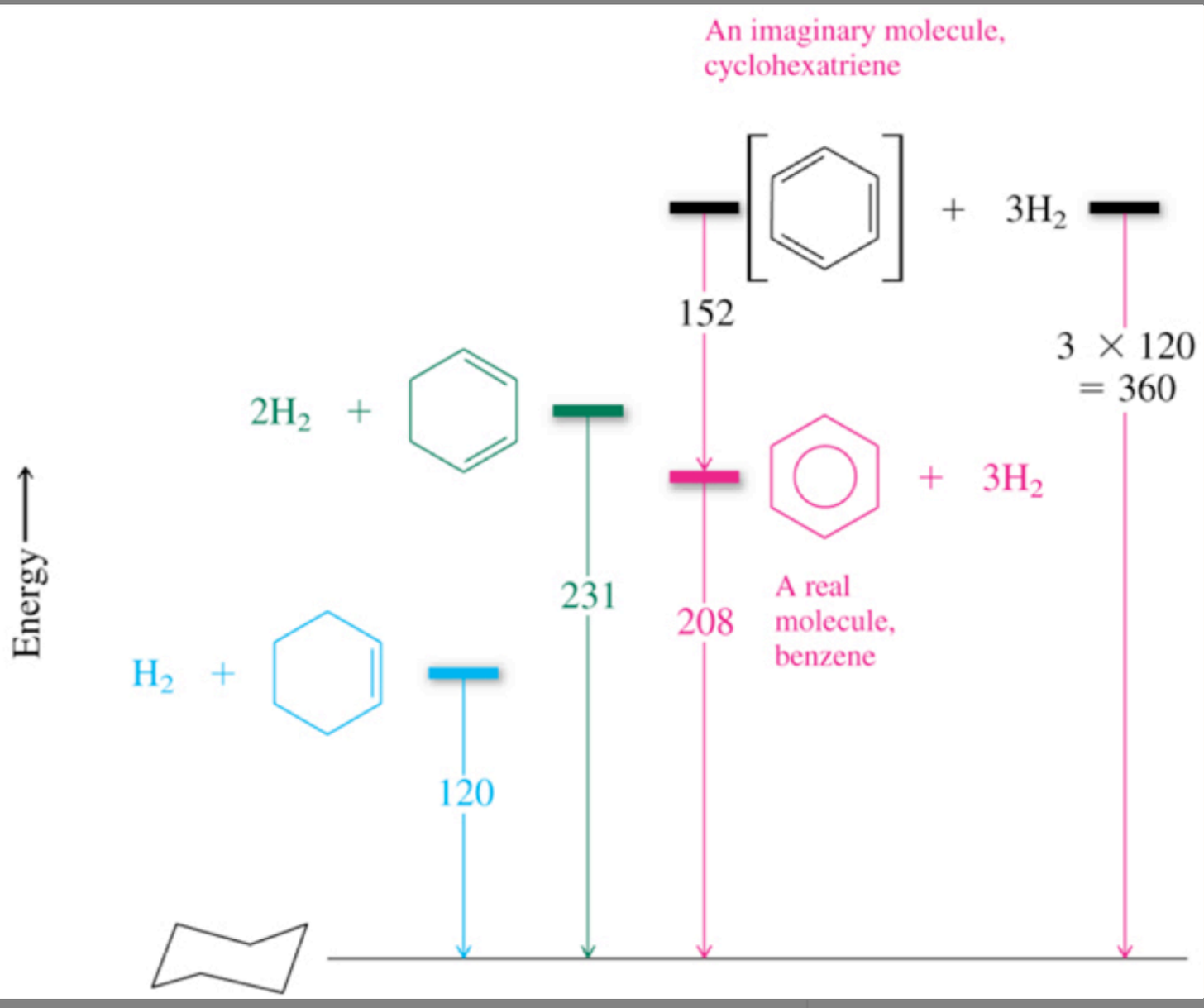
E. d,c,a,b

Resonance Energy of Benzene

Observed ΔH_{hydrog} is 152 kJ/mol less than "expected" for cyclohexatriene

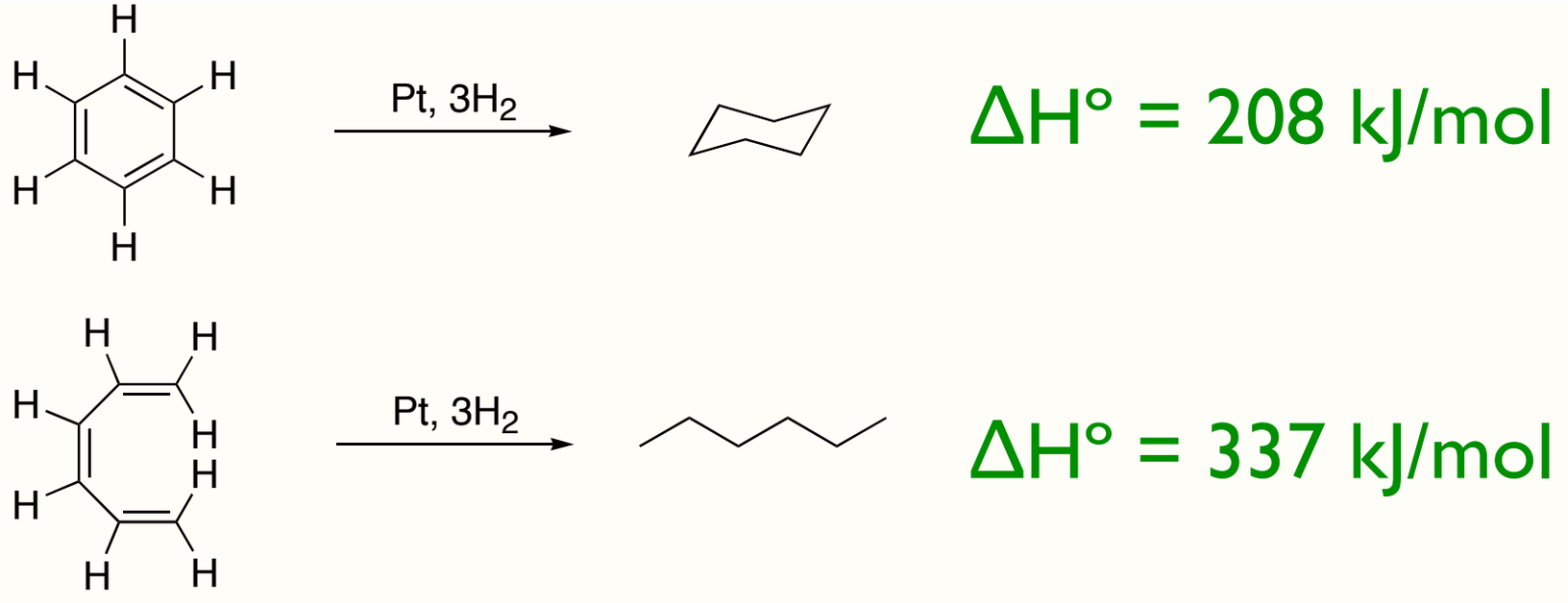
Benzene is 152 kJ/mol more stable than "expected" for cyclohexatriene

The extra 152 kJ/mol stability of benzene is called resonance energy



Resonance Energy of Benzene

When compared to (*Z*)-1,3,5-hexatriene, conjugation alone cannot account for the extra stability of benzene.



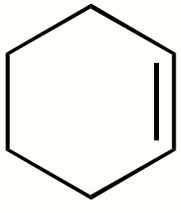
- *initial observation: benzene posses a "cyclic conjugation" that imparts a significant amount of extra stability*
- *benzene and similar compounds with this extra stability as a result of cyclic conjugation are called* ***aromatic****; we'll refine this definition later*

Self Test Question

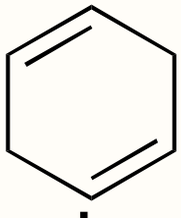
Now, considering the extra stability imparted by aromaticity (crudely: cyclic conjugation), rank the molecules below in order of increasing heat of hydrogenation ($\Delta H_{hydrog} = -\Delta H$).

Revised Assumptions:

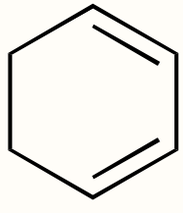
1. ↑ double bonds = ↑ ΔH_{hydrog}
2. conjugation = ↓ ΔH_{hydrog}
3. aromatic = more stable = ↓ ΔH_{hydrog}



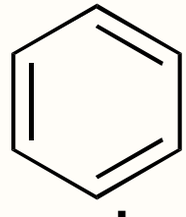
a



b



c



d

A. a,b,c,d

B. a,c,b,d

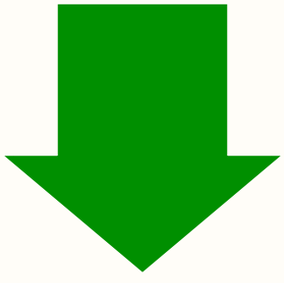
C. a,d,c,b

D. a,c,d,b

E. a,b,d,c

Resonance Energy of Benzene

The extra stability of benzene compared to 1,3,5-hexatriene implies that the electrons in the molecular orbitals (MOs) of benzene are lower in energy than the MOs of 1,3,5-hexatriene.



We must consider the energies of the MOs for both molecules to explain this mysterious extra stability inherent in benzene.

Molecular Orbitals of Benzene

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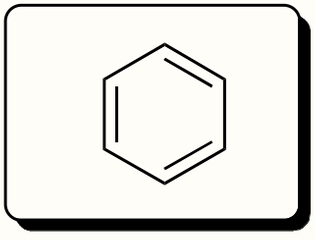

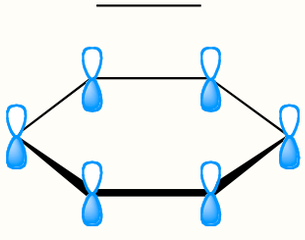

0 nodes

Fronteir Molecular Orbitals of Benzene

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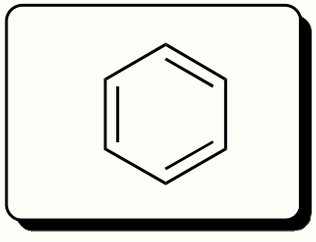
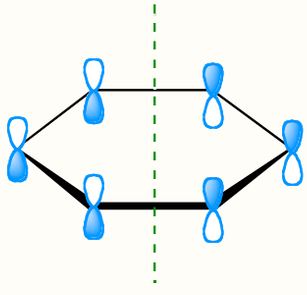
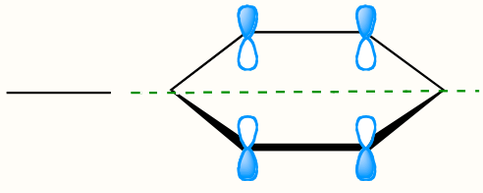
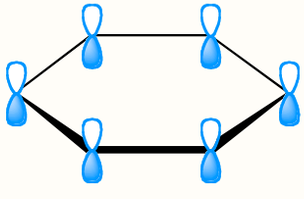


2 nodes





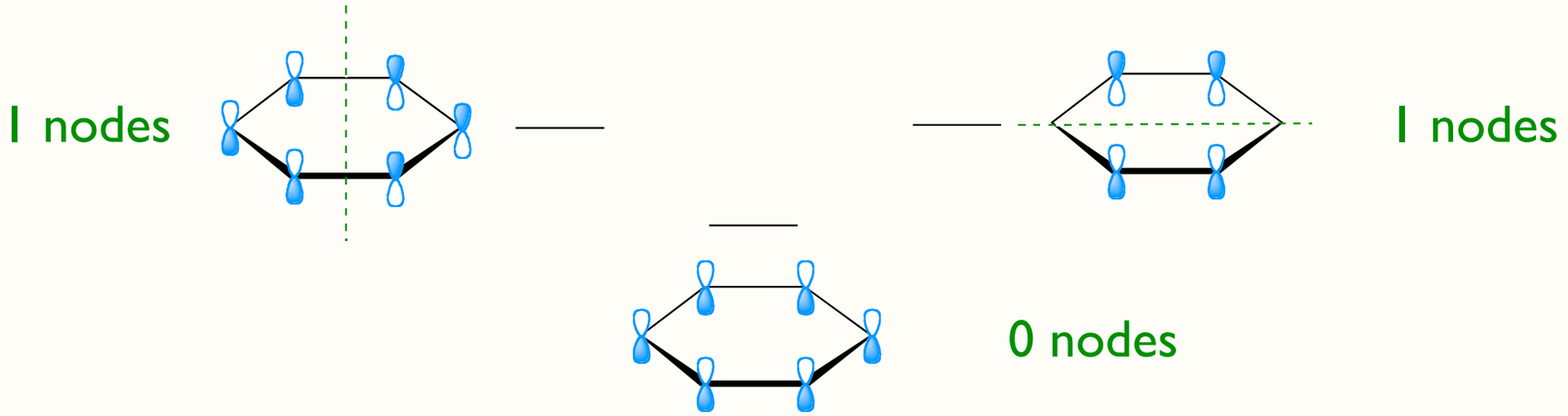
1 nodes



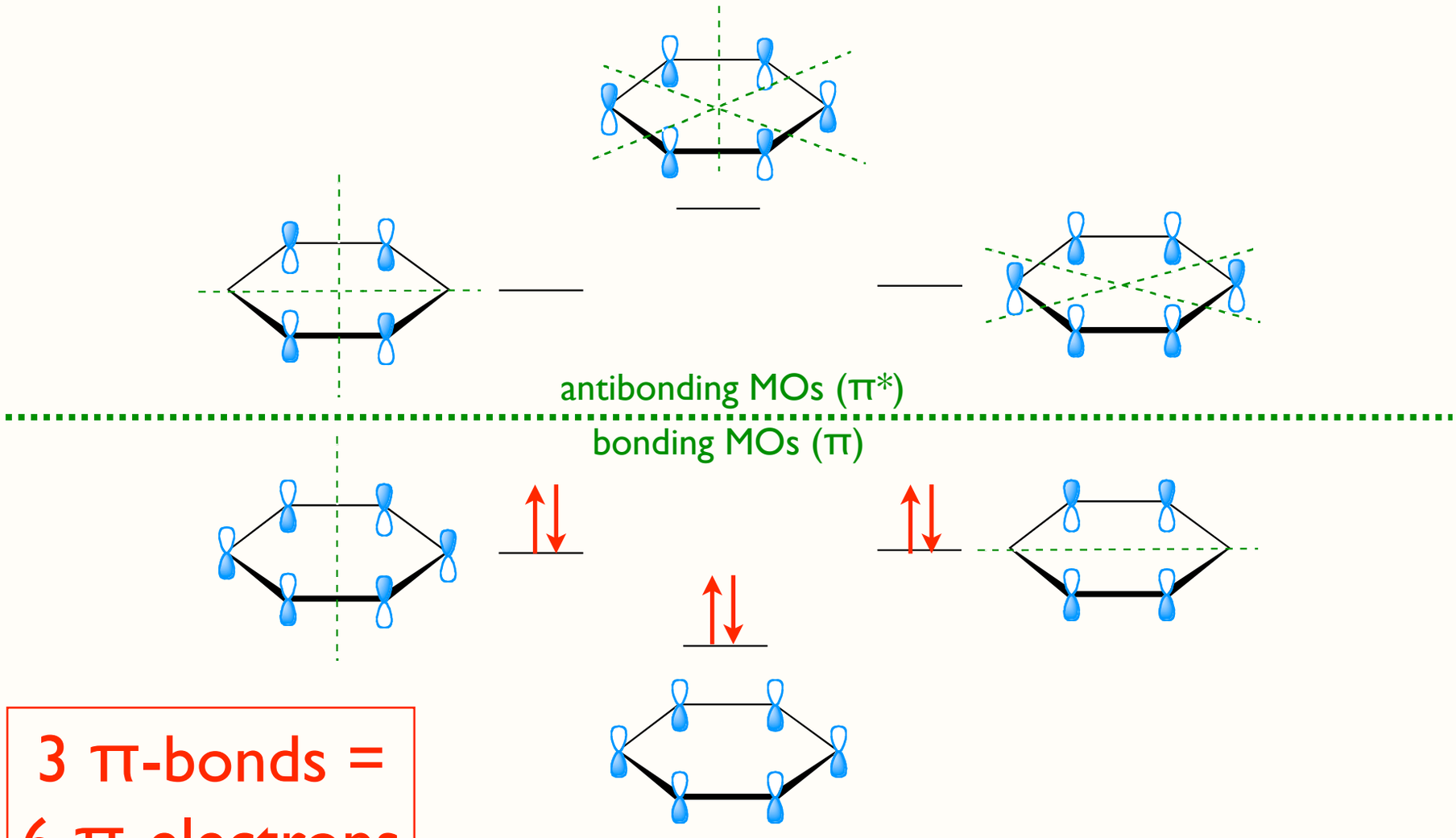
0 nodes

Fronteir Molecular Orbitals of Benzene

degnerate orbitals = orbitals with the same number of nodes = orbitals with the same energy

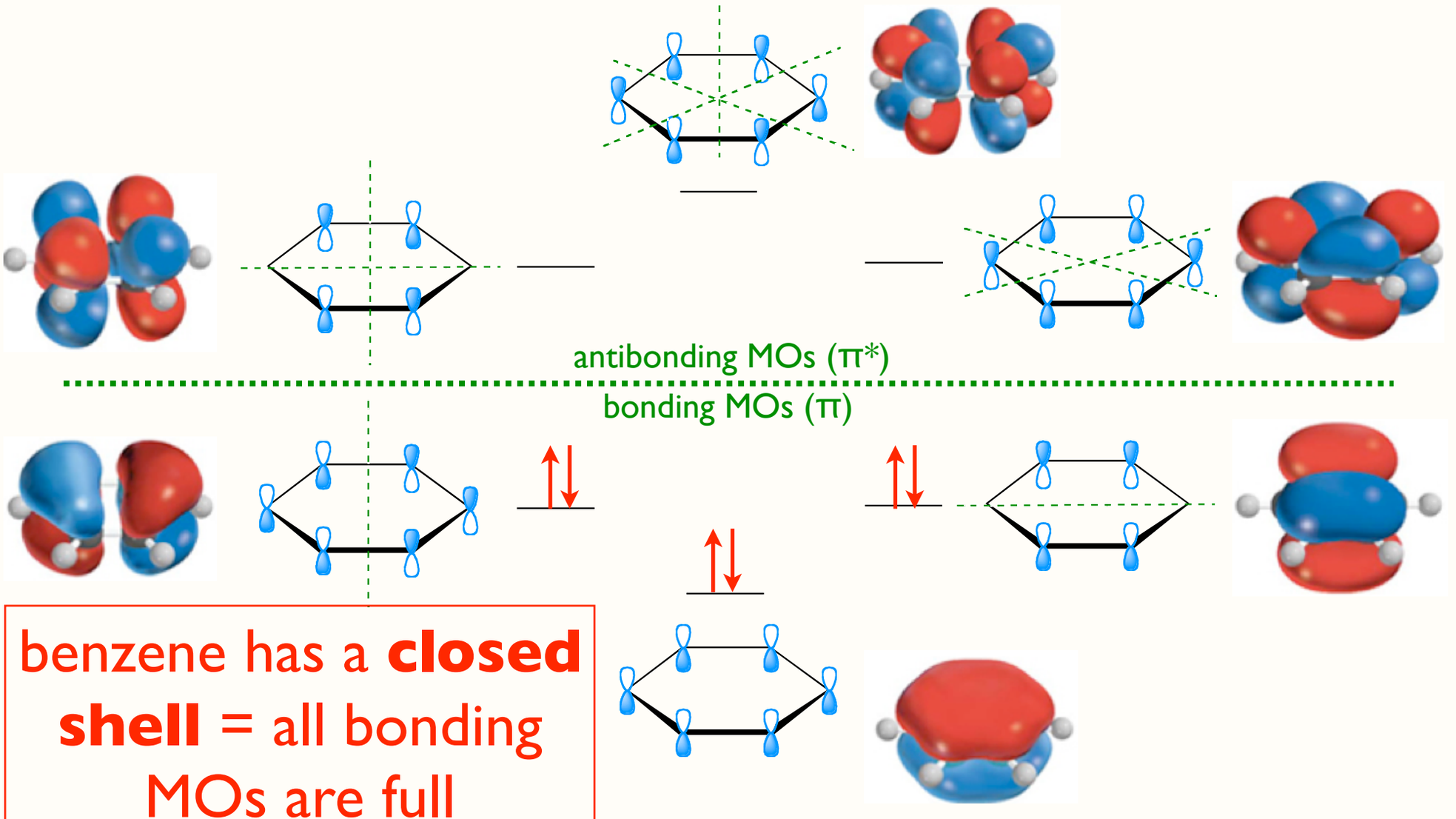


Fronteir Molecular Orbitals of Benzene



3 π-bonds =
6 π-electrons

Fronteir Molecular Orbitals of Benzene



benzene has a **closed shell** = all bonding MOs are full

Bonding vs. Antibonding MOs
Qualitative Observation

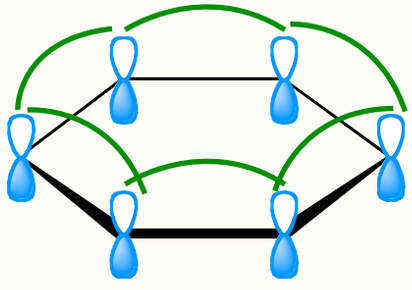
net bonding = bonding interactions – antibonding interactions

bonding interaction: constructive interference between adjacent orbitals

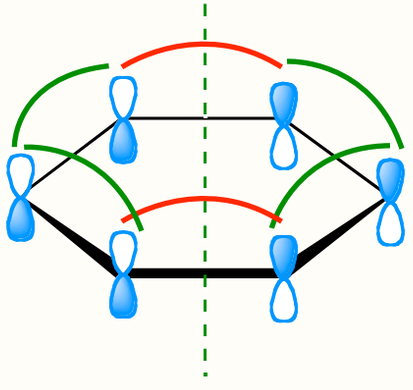
antibonding interactions: destructive interference between adjacent orbitals

more bonding interactions = more stable = lower in energy

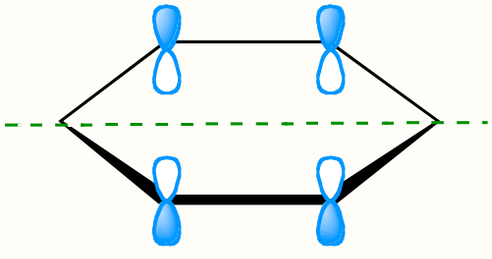
6 bonding
- 0 antibonding
6 net bonding



4 bonding
- 2 antibonding
2 net bonding



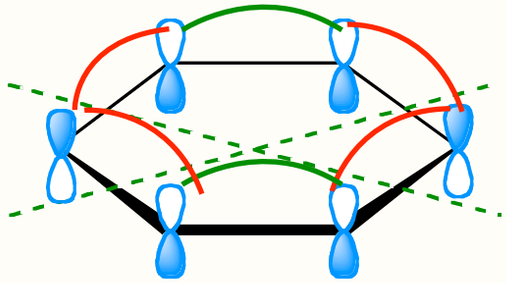
2 bonding
- 0 antibonding
2 net bonding



Self Test Question

What is the *net bonding* in the MO below?

2 bonding
- 4 antibonding
2 antibonding



A. 4 bonding

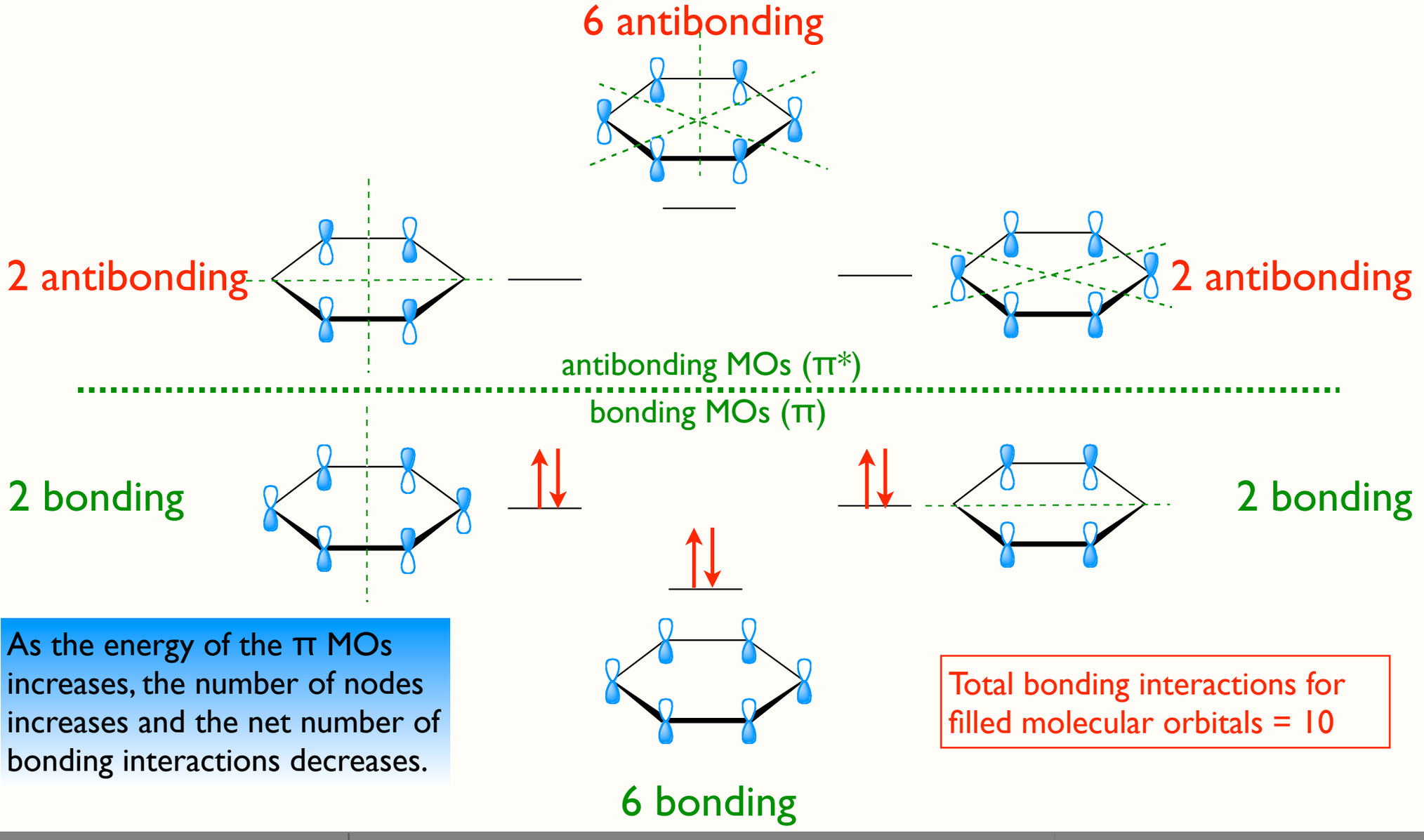
B. 2 bonding

C. 2 antibonding

D. 4 antibonding

E. 6 antibonding

Bonding vs. Antibonding MOs Qualitative Observation



As the energy of the π MOs increases, the number of nodes increases and the net number of bonding interactions decreases.

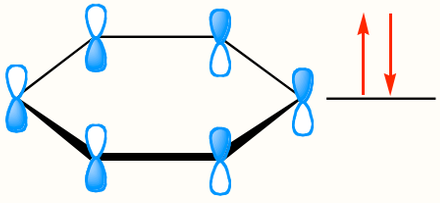
Total bonding interactions for filled molecular orbitals = 10

Aromaticity Revealed

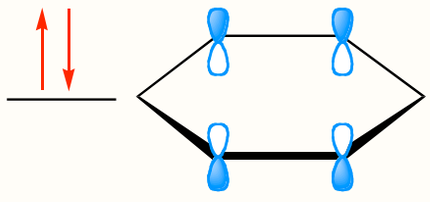
Q: Why is benzene more stable than 1,3,5-hexatriene?

A: Benzene contains filled MOs with more *net bonding*.

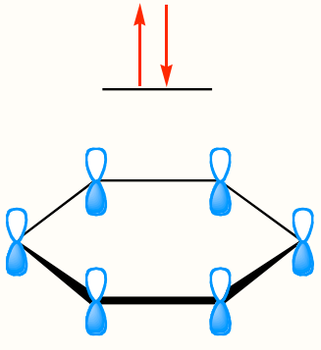
net bonding interactions for filled MOs = **10**



2 bonding



2 bonding

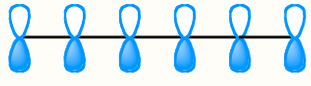


6 bonding

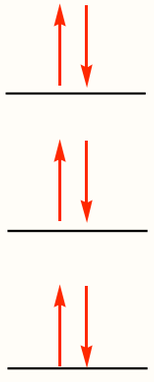
net bonding interactions for filled MOs = **9**

1 bonding

3 bonding



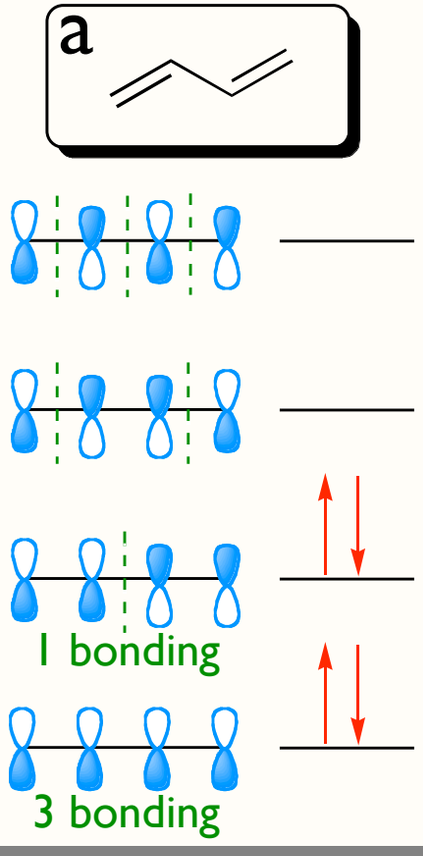
5 bonding

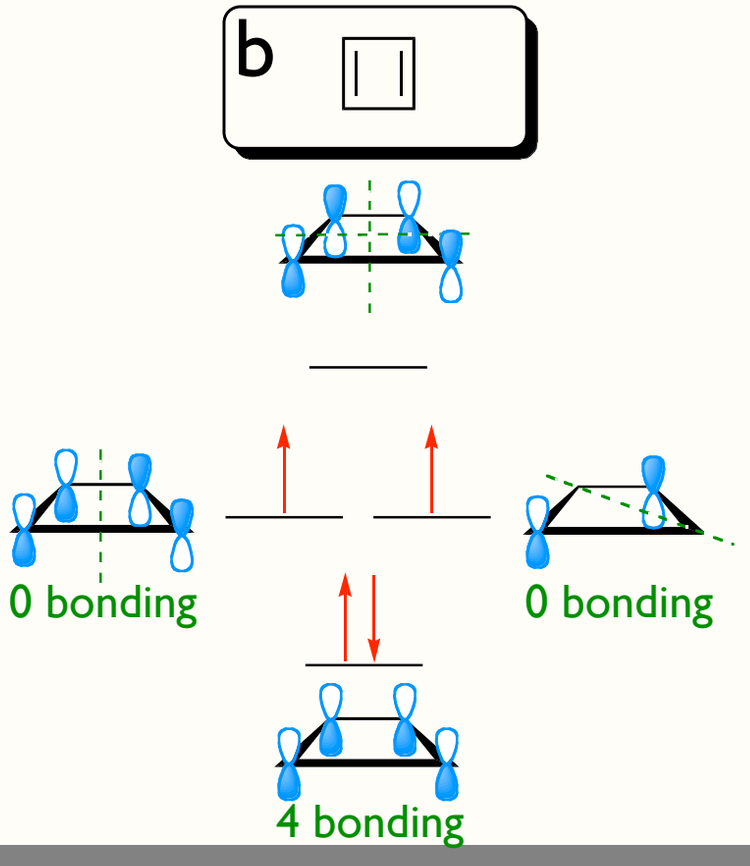


Only the first three MOs for each are shown.

Self Test Question

Unlike benzene, cyclobutadiene is not stabilized by resonance. Using the MO diagrams below, determine the **total** number of bonding interactions in **all** filled orbitals for each molecule. List them in the order a,b.

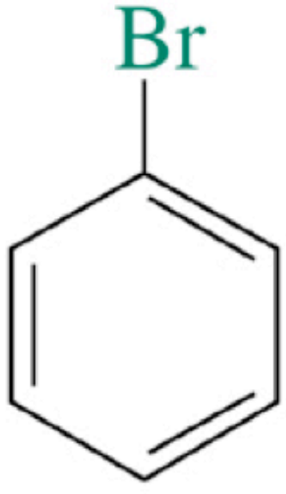




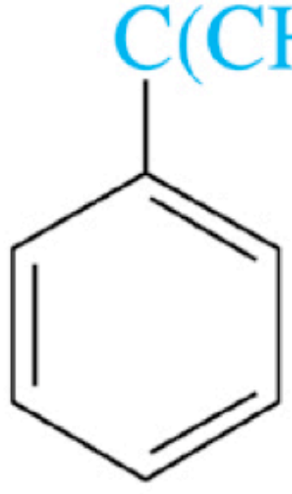
A. 4,4
B. 4,3
C. 2,3
D. 1,1
E. 0,0

Nomenclature: Monosubstituted Benzene

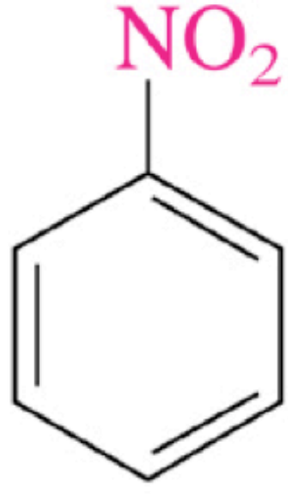
Benzene is considered the parent and comes last in the name .



Bromobenzene



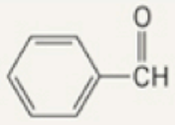
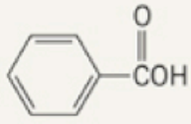
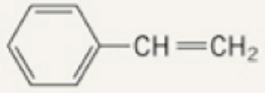
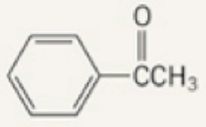
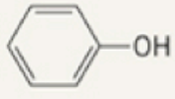
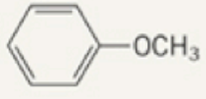
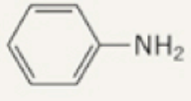
tert-Butylbenzene



Nitrobenzene

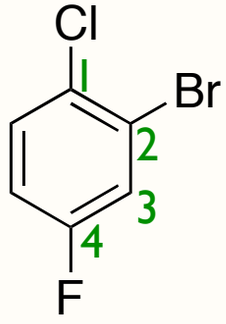
Frequently Encountered Monosubstituted Benzene Derivatives

TABLE 11.1 Names of Some Frequently Encountered Derivatives of Benzene

Structure	Systematic name	Common name*
	Benzenecarbaldehyde	Benzaldehyde
	Benzenecarboxylic acid	Benzoic acid
	Vinylbenzene	Styrene
	Methyl phenyl ketone	Acetophenone
	Benzenol	Phenol
	Methoxybenzene	Anisole
	Benzenamine	Aniline

Nomenclature: Polysubstituted Benzene

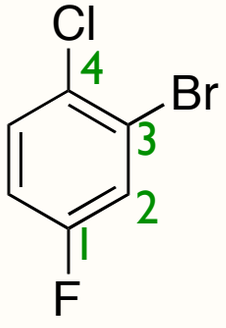
1. Benzene is considered as the parent and comes last in the name.
2. List substituents in alphabetical order in the name.
3. Number ring in the direction that gives lowest locant at first point of difference. *Do not base numbering on CIP rules!!!*



2-bromo-1-chloro-4-fluorobenzene ✓

locants: 1,2,4

First point of difference

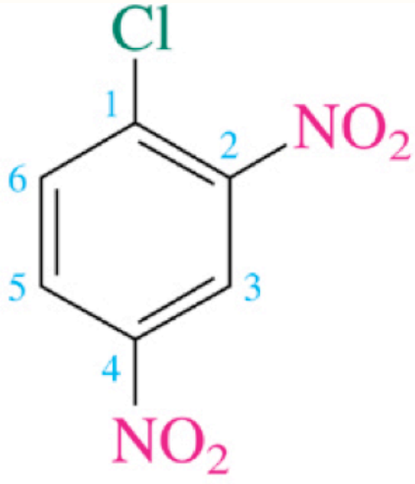


locants: 1,3,4

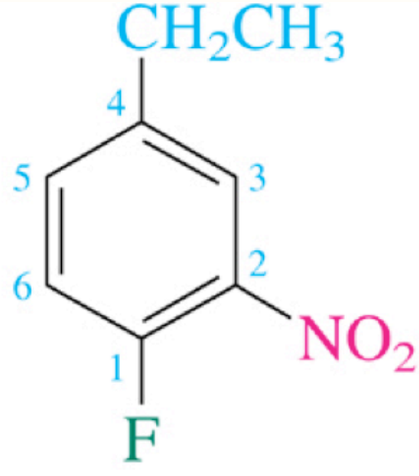
3-bromo-4-chloro-1-fluorobenzene X

Nomenclature: Polysubstituted Benzene

1. Benzene is considered as the parent and comes last in the name.
2. List substituents in alphabetical order in the name.
3. Number ring in the direction that gives lowest locant at first point of difference. *Do not base numbering on CIP rules!!!*



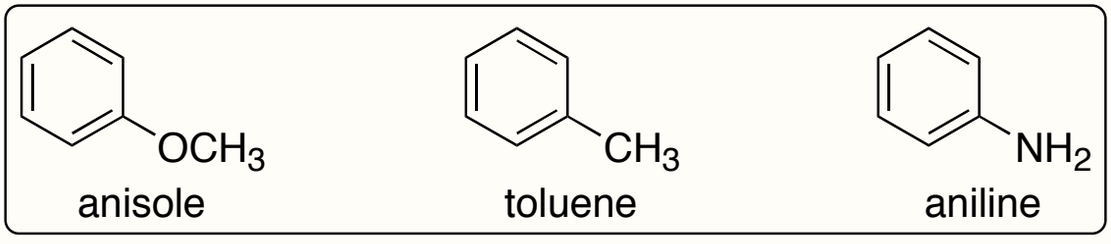
1-Chloro-2,4-dinitrobenzene

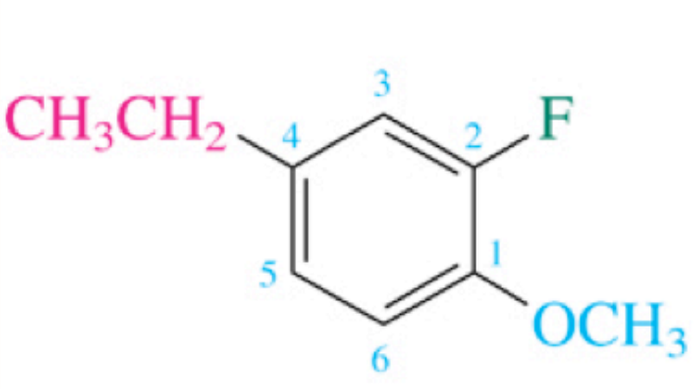


4-Ethyl-1-fluoro-2-nitrobenzene

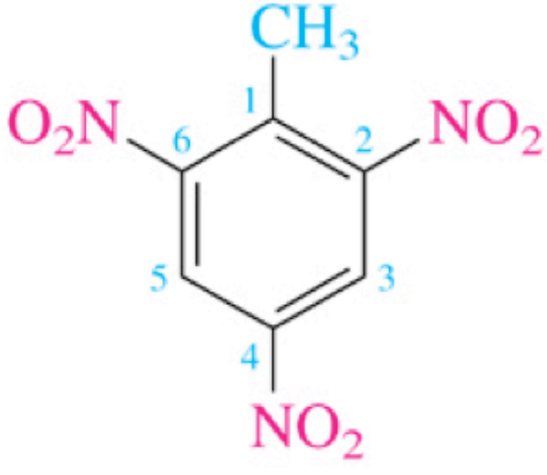
Nomenclature: Polysubstituted Benzene

4. Common names of benzene derivatives *may* be used as the parent name.
5. In this case, the substituent that defines the derivative is at C-1.

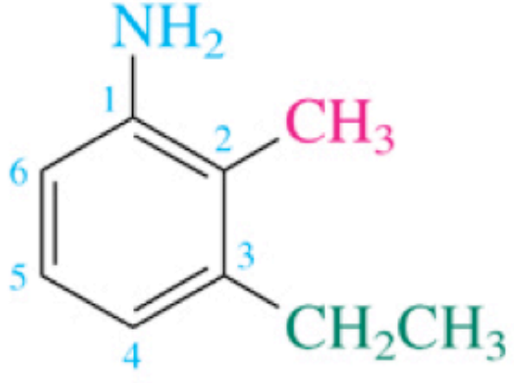




4-Ethyl-2-fluoroanisole



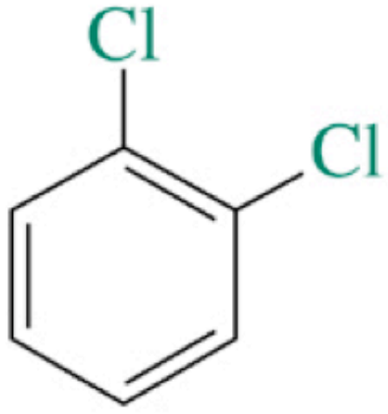
2,4,6-Trinitrotoluene



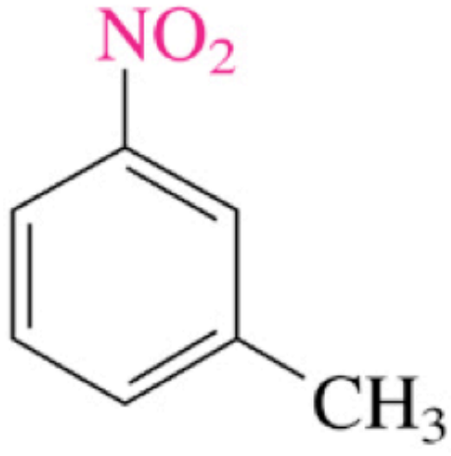
3-Ethyl-2-methylaniline

Nomenclature: Disubstituted Benzene

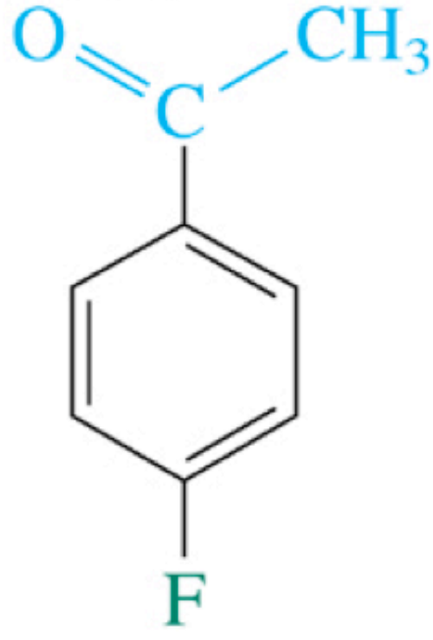
6. *ortho (o), meta (m) and para (p)* may be used to indicated 1,2-; 1,3; and 1,4 substituted benzene, respectively.



o-Dichlorobenzene
(1,2-dichlorobenzene)



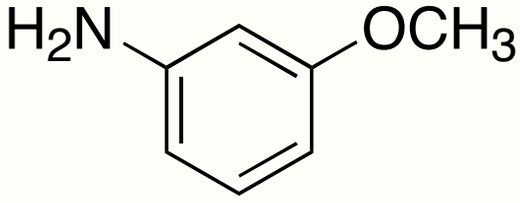
m-Nitrotoluene
(3-nitrotoluene)



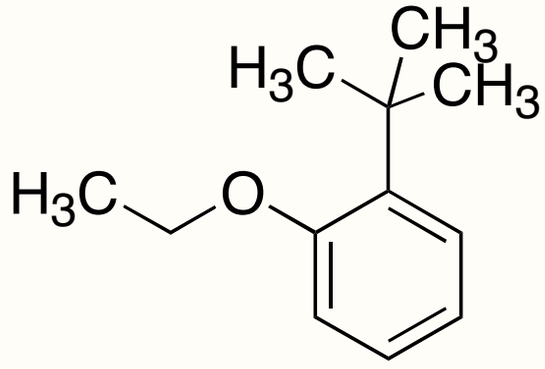
p-Fluoroacetophenone
(4-fluoroacetophenone)

Nomenclature: Benzene

7. If the substitution is symmetrical (and *ortho*, *meta* & *para* are not used) the substituents are numbered in alphabetical order.



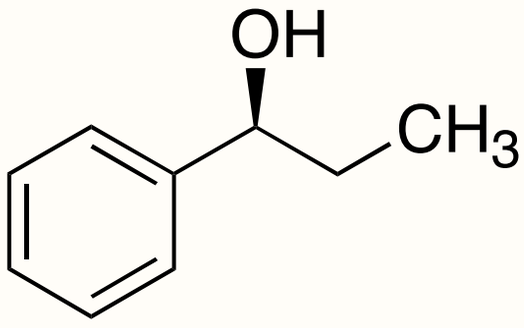
1-amino-3-methoxybenzene
(*m*-aminomethoxybenzene)



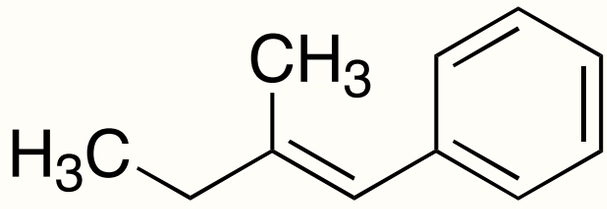
1-*tert*-butyl-2-ethoxybenzene
(*o*-*tert*-butylethoxybenzene)

Nomenclature: Benzene as a Substituent

6. When benzene is not the highest priority group, it is named *phenyl* (substituent name).



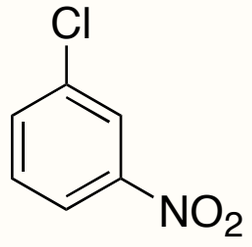
(*S*)-1-phenyl-1-propanol



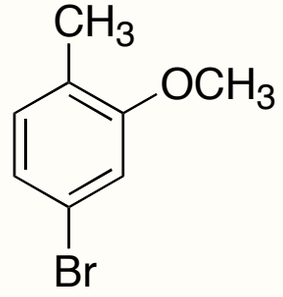
(*E*)-2-methyl-1-phenyl-1-butene

Self Test Question

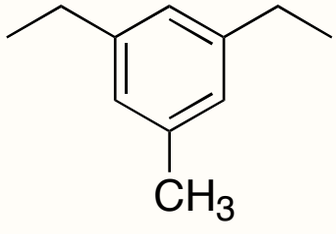
Which IUPAC name is *correct*?

A 

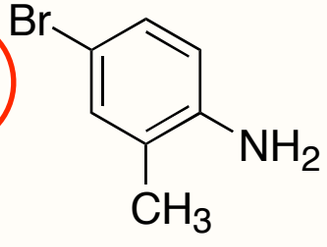
p-chloronitrobenzene

C 

5-bromo-2-methyl-1-methoxybenzene

B 

3,5-diethyl-1-methylbenzene

D 

4-bromo-2-methylaniline

Next Lecture...

Chapter 11: Sections 11.11-11.25

Quiz Next Week. . .

Synthesis Problem

Chapter 11