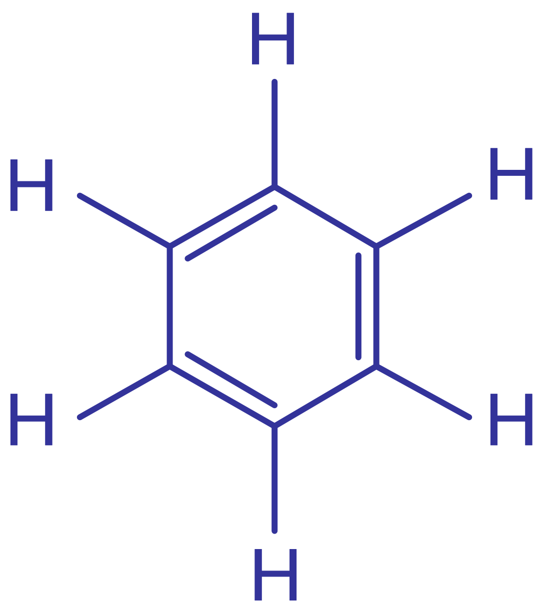
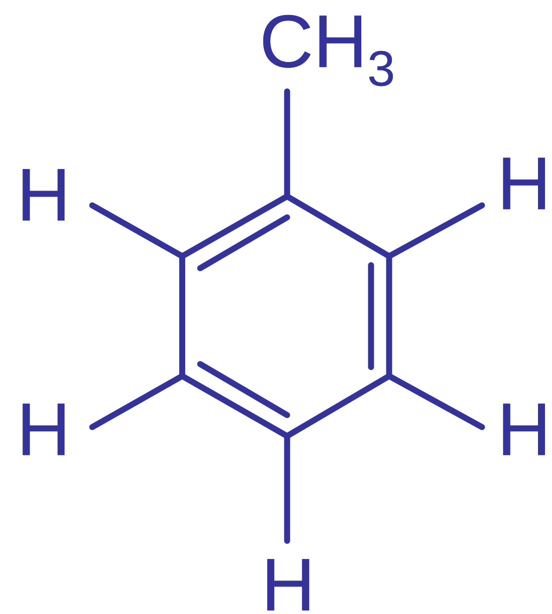
Chapter 11
Arenes and Aromaticity

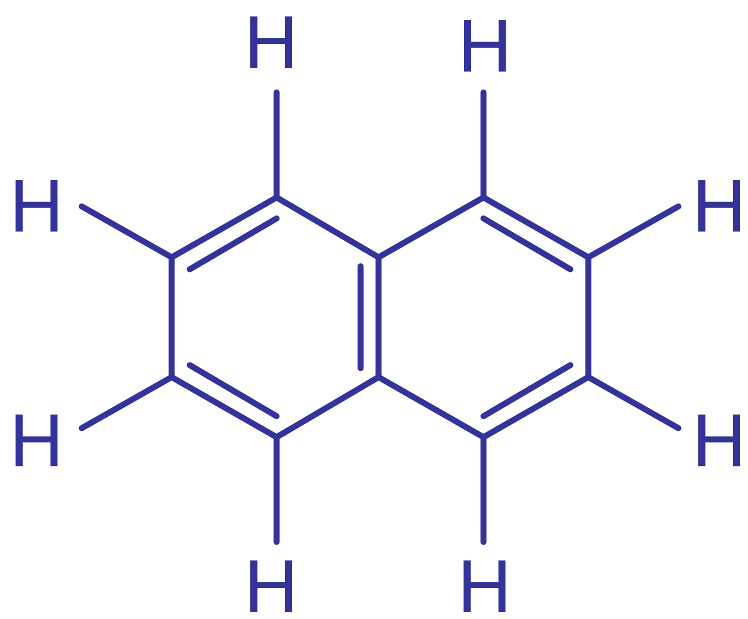
Examples of Aromatic Hydrocarbons



Benzene



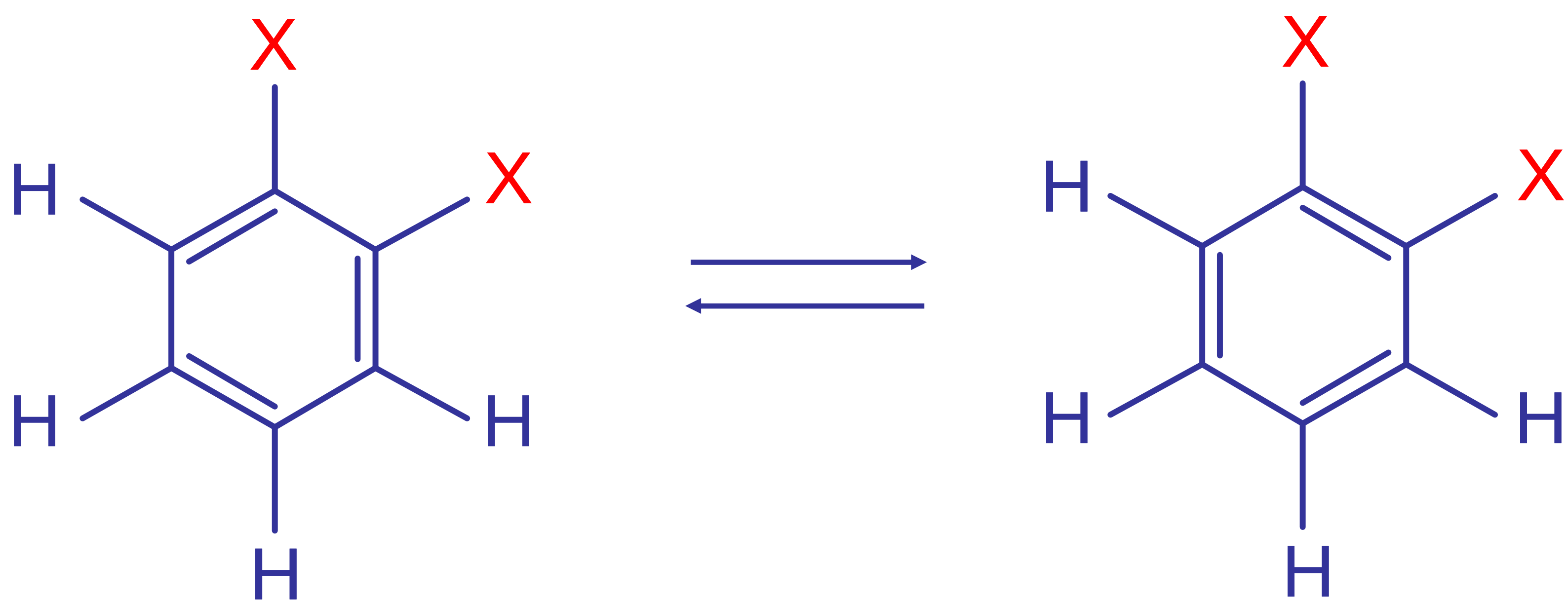
Toluene



Naphthalene

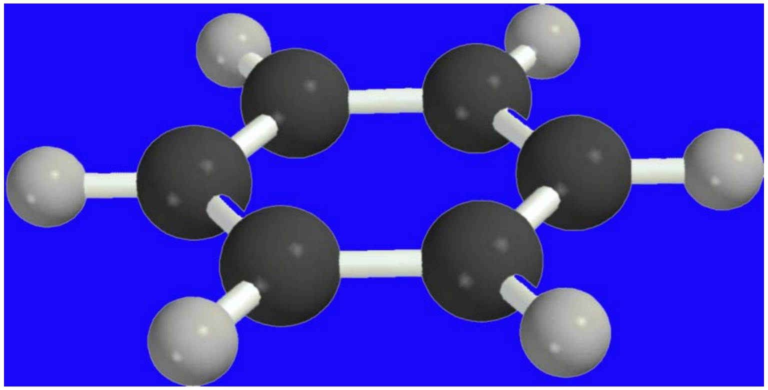
11.2. The Structure of Benzene

- Kekulé (1866) proposed a cyclic structure for C_6H_6 with alternating single and double bonds.
- Later, Kekulé revised his proposal by suggesting a rapid equilibrium between two equivalent structures.
- However, this proposal suggested isomers of the kind shown were possible. Yet, none were ever found.



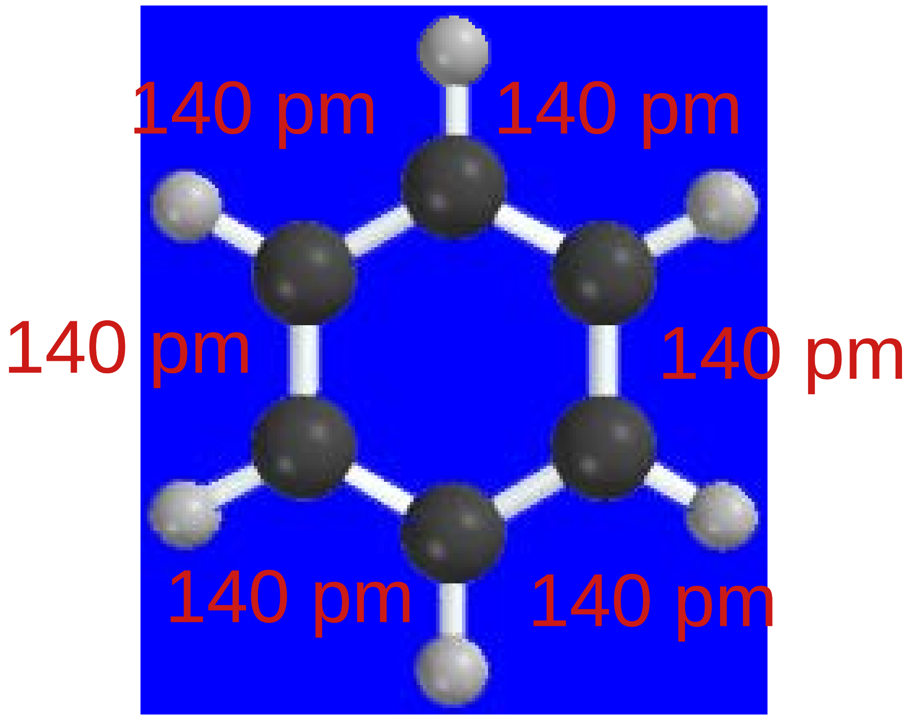
Structure of Benzene

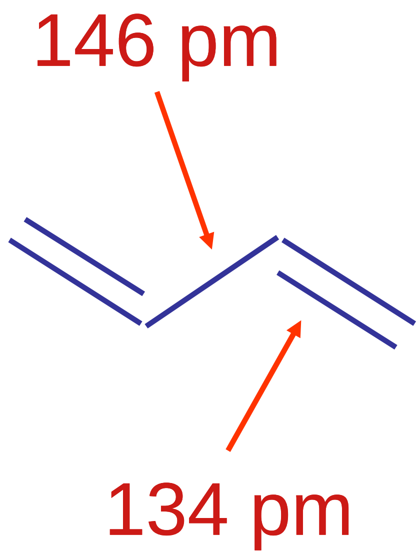
➢ Structural studies of benzene **DO NOT** support the Kekulé formulation. Instead of alternating single and double bonds, all of the C—C bonds are the same



Benzene has the shape of a regular hexagon

All C—C bond distances = 140 pm



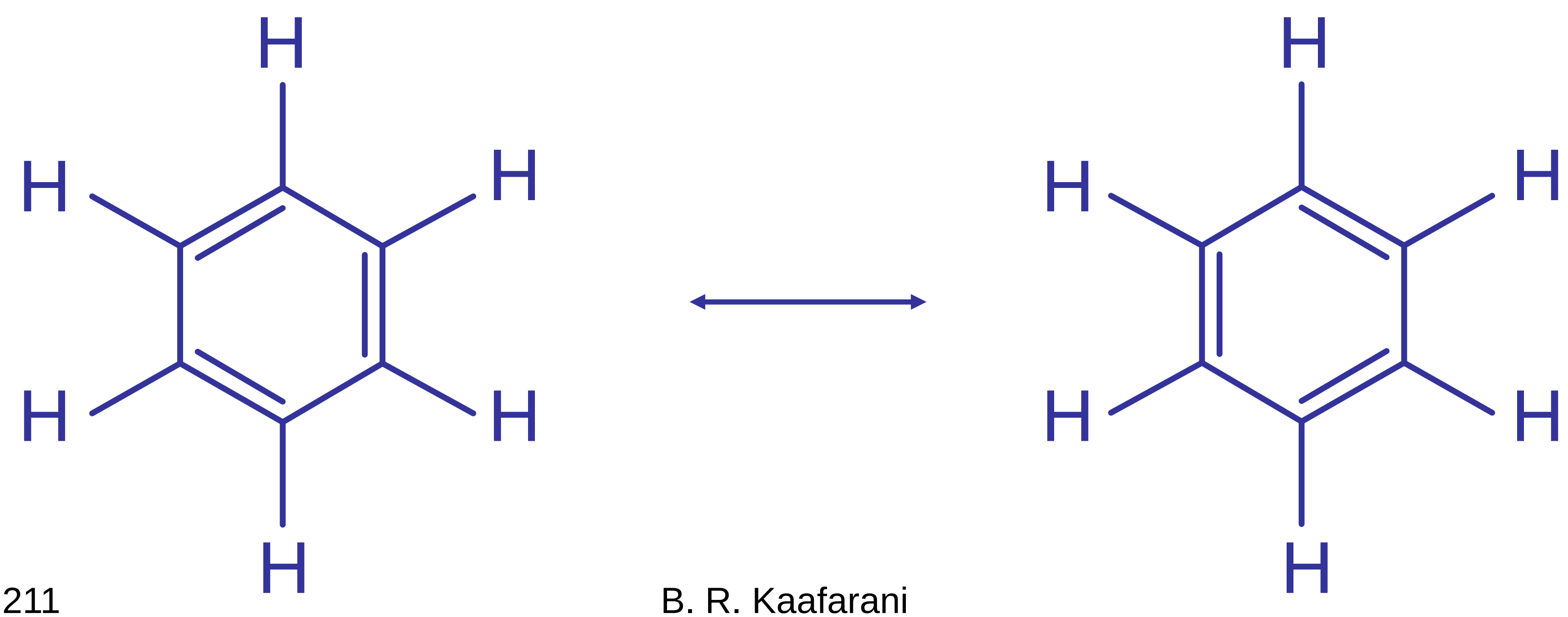


- 140 pm is the average between the C—C single bond distance and the double bond distance in 1,3-butadiene.

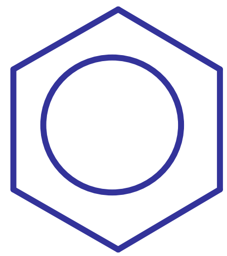
Resonance Picture of Bonding in Benzene

➢ Instead of Kekulé's suggestion of a rapid equilibrium between two structures.

➢ Express the structure of benzene as a *resonance hybrid* of the two Lewis structures. Electrons are not localized in alternating single and double bonds, but are delocalized over all six ring carbons.



Resonance Formulation of Benzene



- Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two Kekulé structures).

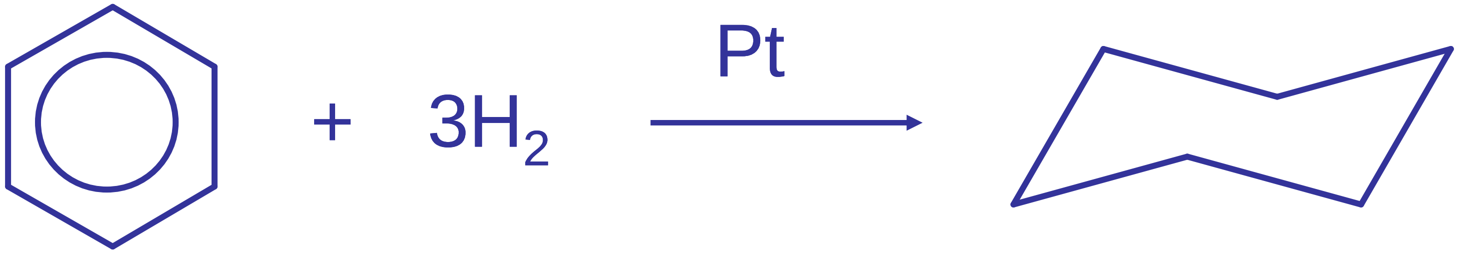
11.3. The Stability of Benzene

- Benzene is the best and most familiar example of a substance that possesses "special stability" or "aromaticity".

- Aromaticity is a level of stability that is substantially greater for a molecule than would be expected on the basis of any of the Lewis structures written for it.

Thermochemical Measures of Stability

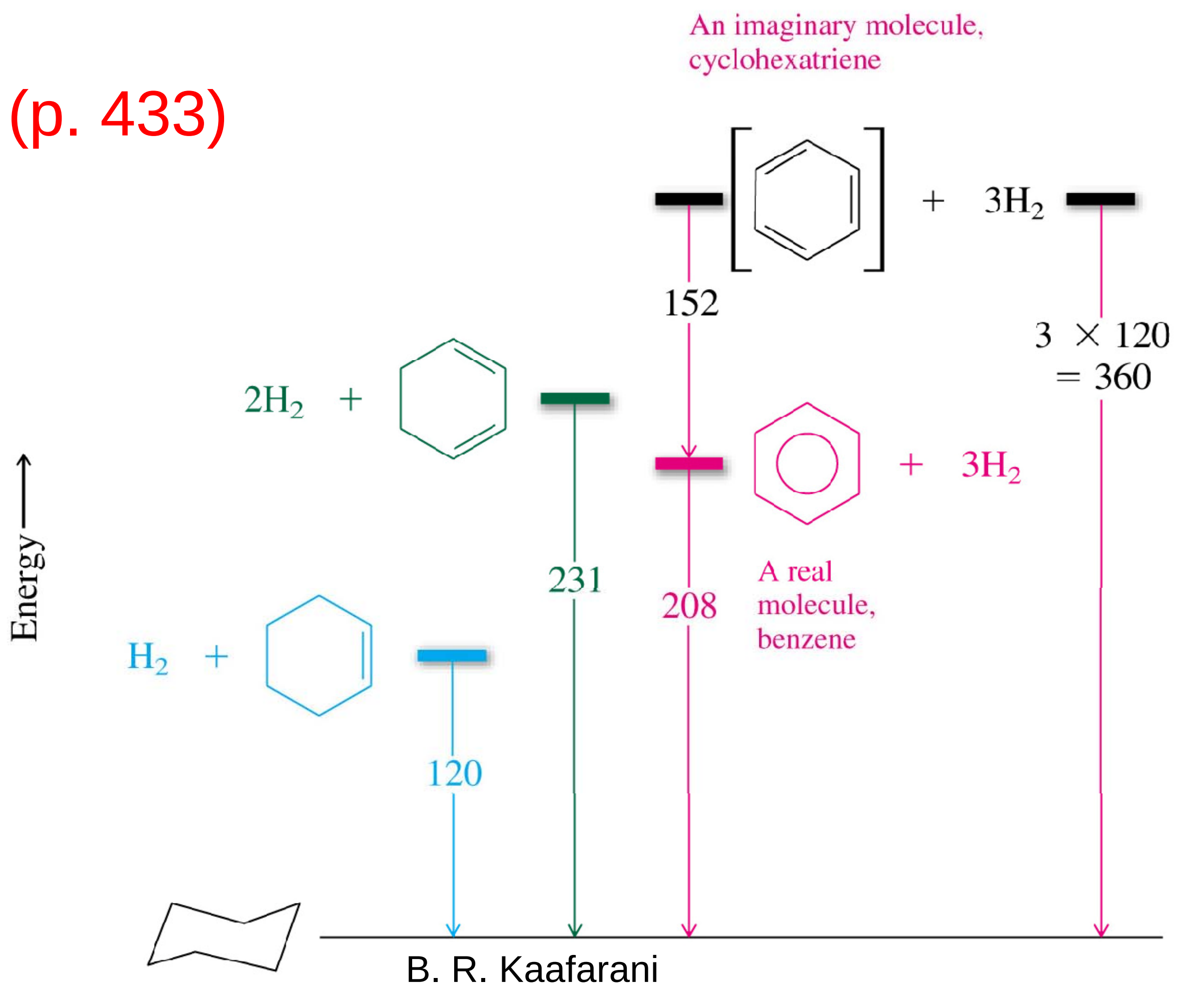
- *Heat of hydrogenation:* compare experimental value with "expected" value for hypothetical “cyclohexatriene”.



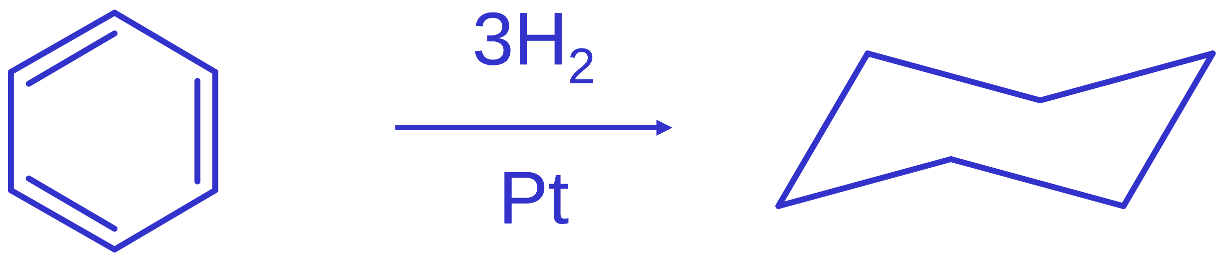
$$\Delta H° = – 208 \text{ kJ}$$

- Observed heat of hydrogenation is 152 kJ/mol less than "expected“.
- Benzene is 152 kJ/mol more stable than expected.
- 152 kJ/mol is the resonance energy of benzene.

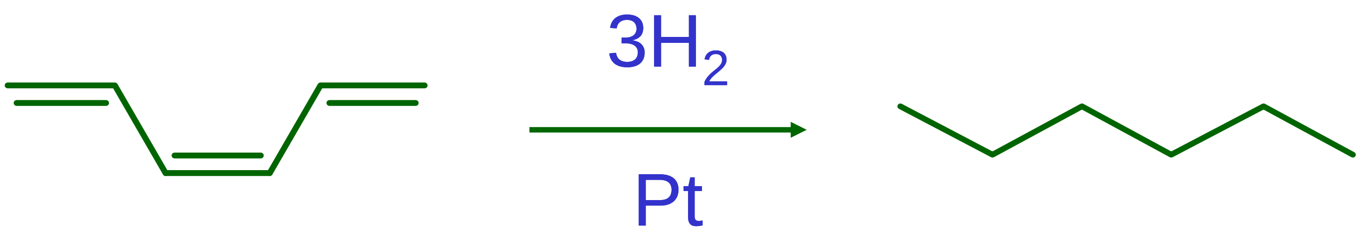
Figure 11.2 (p. 433)



Cyclic conjugation versus noncyclic conjugation



Heat of hydrogenation = 208 kJ/mol



Heat of hydrogenation = 337 kJ/mol

Resonance Energy of Benzene

- Compared to localized 1,3,5-cyclohexatriene

  152 kJ/mol

- Compared to 1,3,5-hexatriene

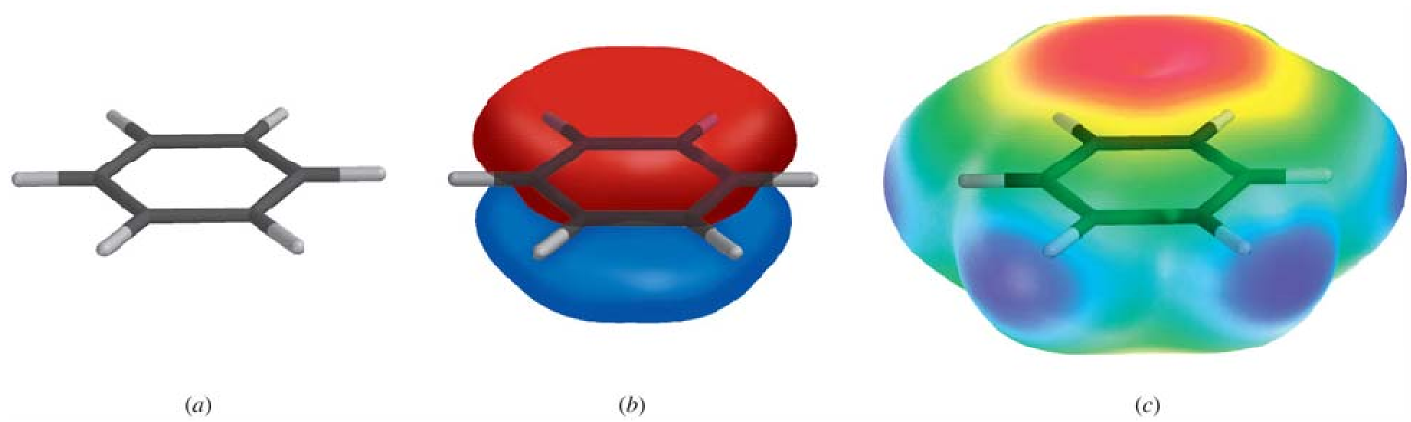
  129 kJ/mol

- Exact value of resonance energy of benzene depends on what it is compared to, but regardless of model, benzene is more stable than expected by a substantial amount.

11.4. An Orbital Hybridization View of Bonding in Benzene

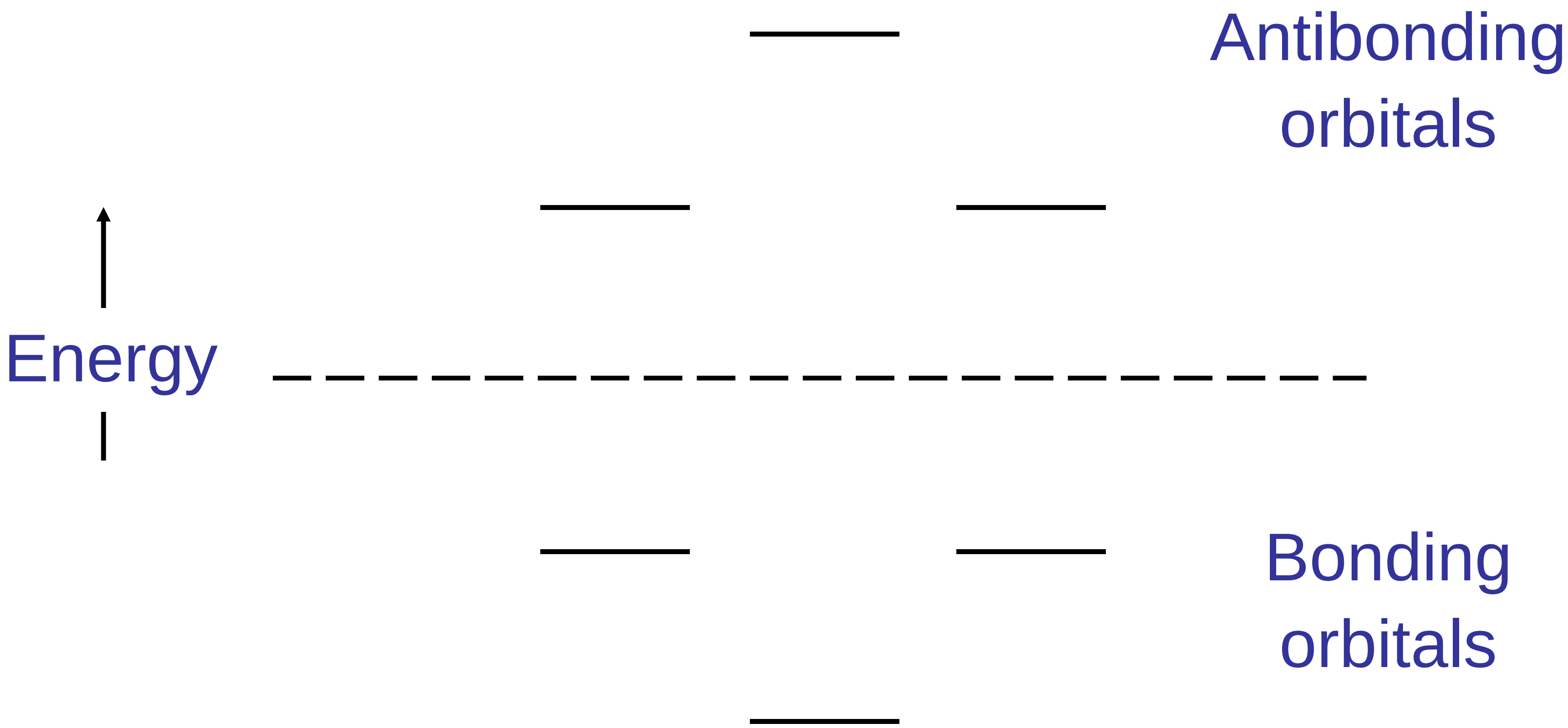
Planar ring of 6 *sp*^{2} hybridized carbons

Figure 11.3



- Each carbon contributes a *p* orbital.
- Six *p* orbitals overlap to give cyclic π system; six π electrons delocalized throughout π system.
- High electron density above and below plane of ring.

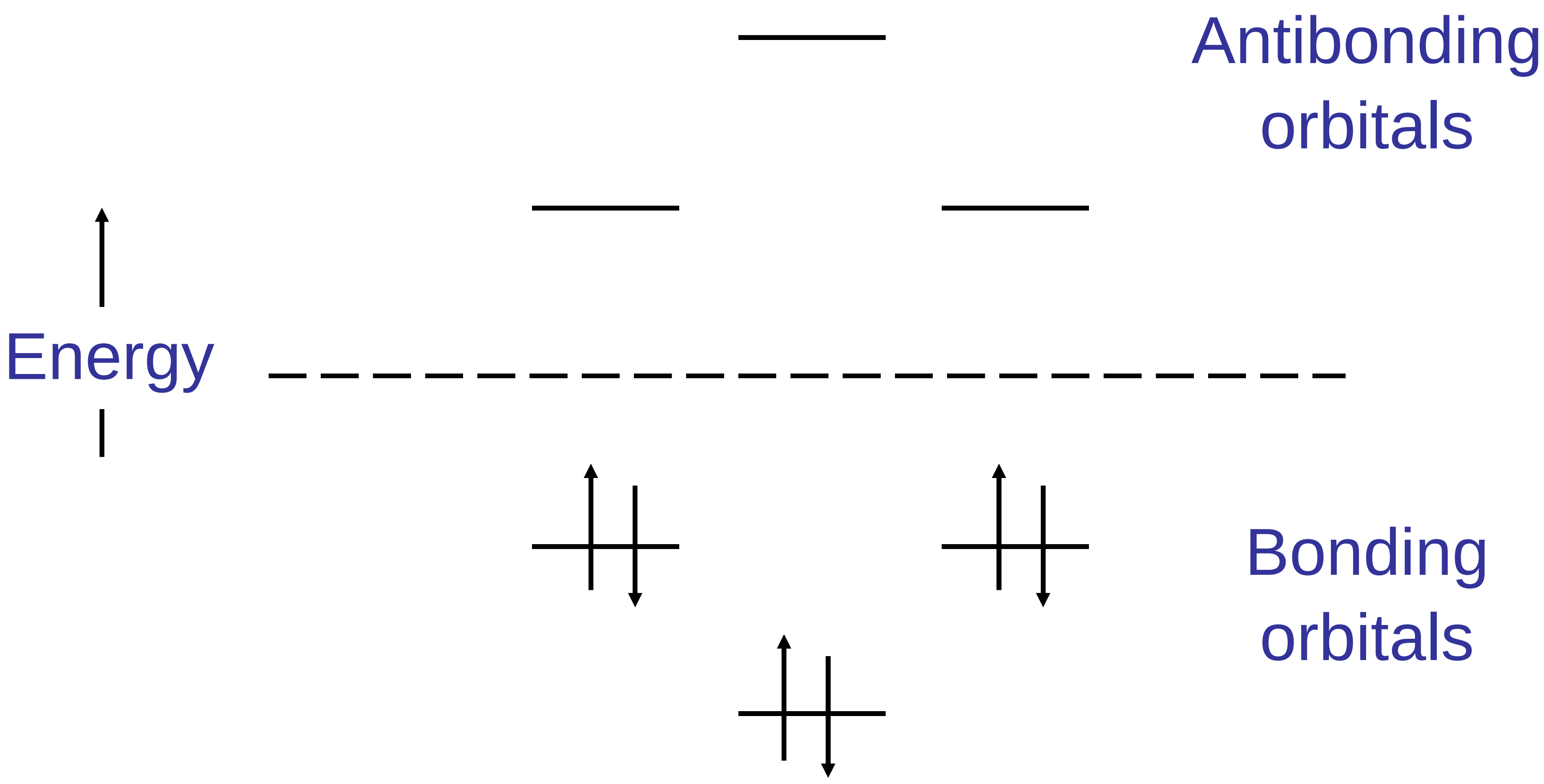
11.5. The π Molecular Orbitals of Benzene



6 *p* AOs combine to give 6 π MOs

3 MOs are bonding; 3 are antibonding

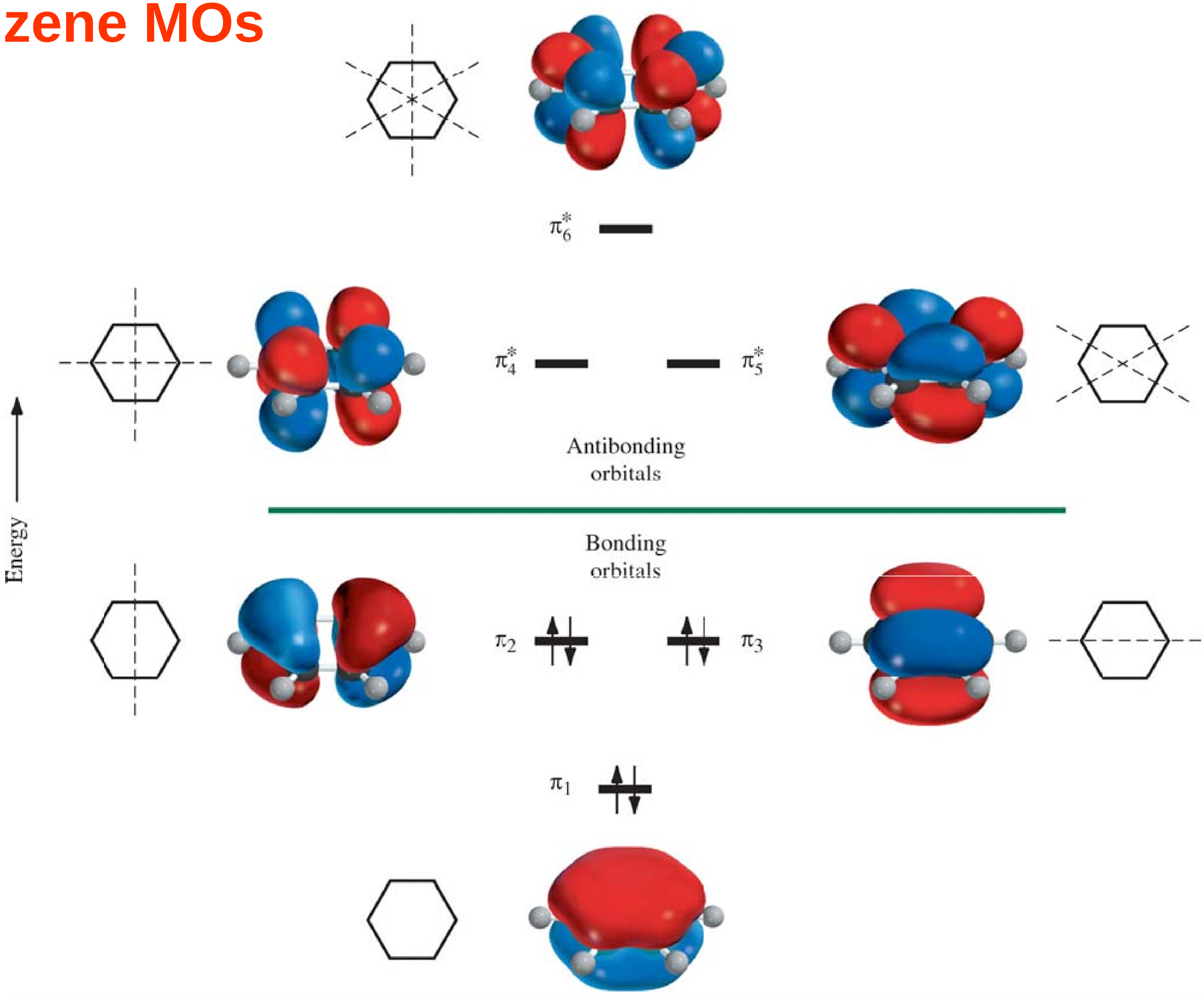
Benzene MOs



All bonding MOs are filled

No electrons in antibonding orbitals

Benzene MOs

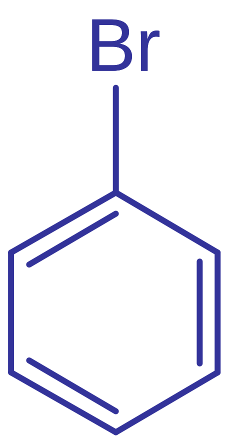


π_6^*
π_4^*
π_5^*
Antibonding orbitals
Energy
Bonding orbitals
π_2
π_3
π_1

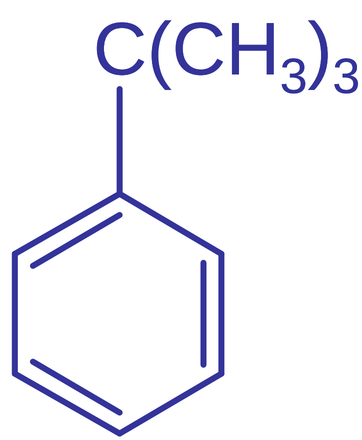
11.6
Substituted Derivatives of Benzene and Their Nomenclature

General Points

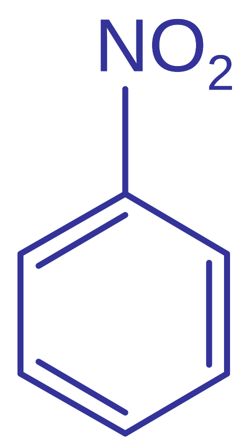
1) Benzene is considered as the parent and comes last in the name.



Bromobenzene



tert-Butylbenzene



Nitrobenzene

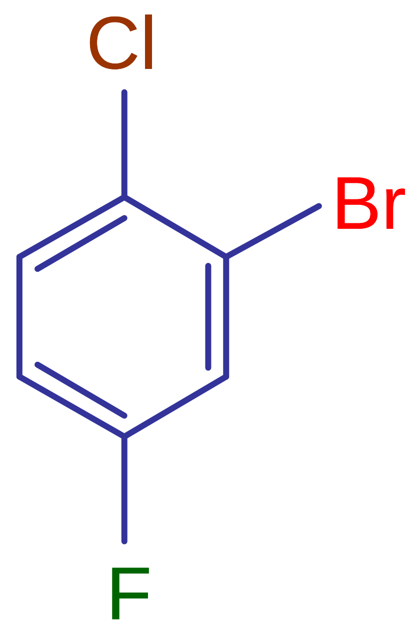
General Points

1) Benzene is considered as the parent and comes last in the name.

2) List substituents in alphabetical order.

3) Number ring in direction that gives lowest locant at first point of difference.

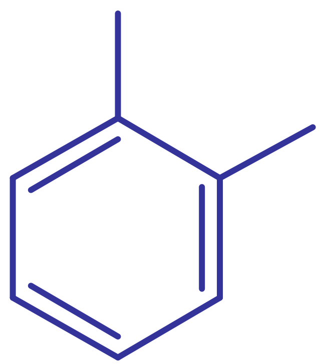
Example



2-Bromo-1-chloro-4-fluorobenzene

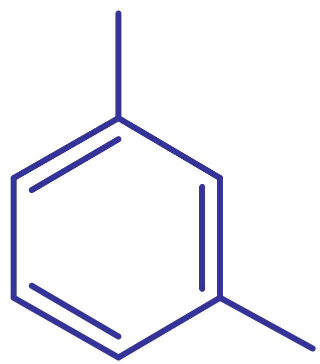
Ortho, Meta, and Para

Alternative locants for disubstituted derivatives of benzene



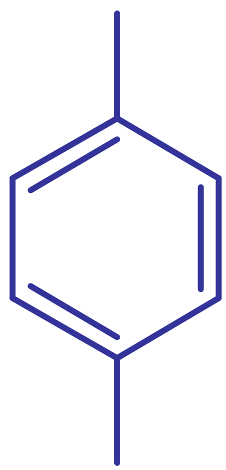
1,2 = *ortho*
(abbreviated *o*-)

o-Xylene



1,3 = *meta*
(abbreviated *m*-)

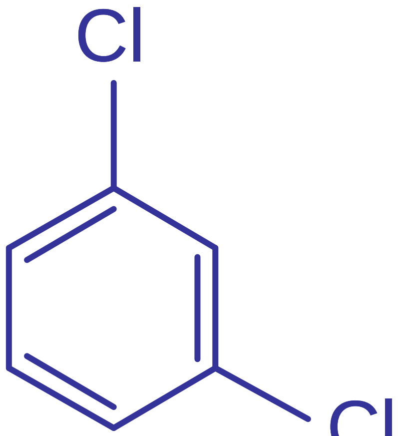
m-Xylene



1,4 = *para*
(abbreviated *p*-)

p-Xylene

Examples



o-Ethylnitrobenzene

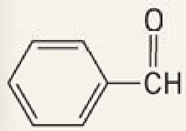
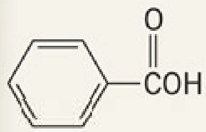
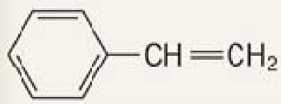
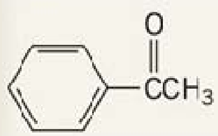
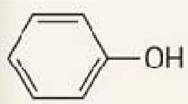
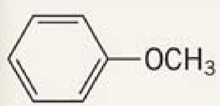
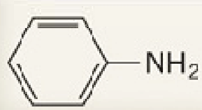
(1-Ethyl-2-nitrobenzene)

m-Dichlorobenzene

(1,3-Dichlorobenzene)

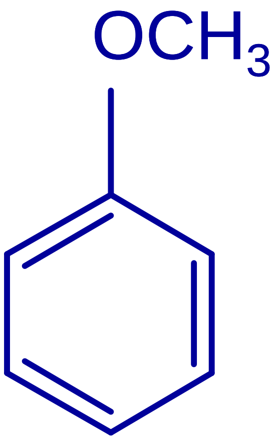
Benzene Derivatives

TABLE 11.1 Names of Some Frequently Encountered Derivatives of Benzene

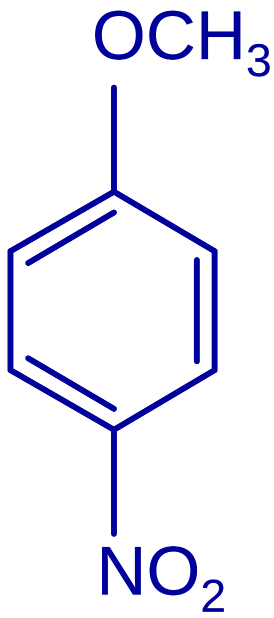
Structure	Systematic name	Common name*
	Benzenecarbaldehyde	Benzaldehyde
	Benzenecarboxylic acid	Benzoic acid
	Vinylbenzene	Styrene
	Methyl phenyl ketone	Acetophenone
	Benzenol	Phenol
	Methoxybenzene	Anisole
	Benzenamine	Aniline

*These common names are acceptable in IUPAC nomenclature and are the names that will be used in this text.

Benzene Derivative names can be used as parent



Anisole



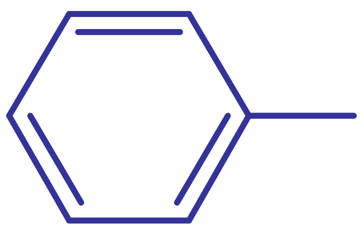
p-Nitroanisole

or

4-Nitroanisole

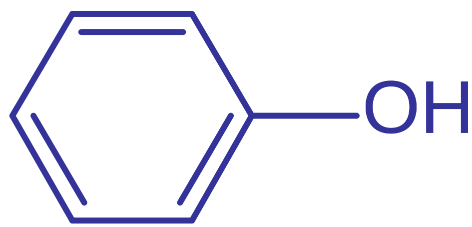
Easily confused names

phenyl



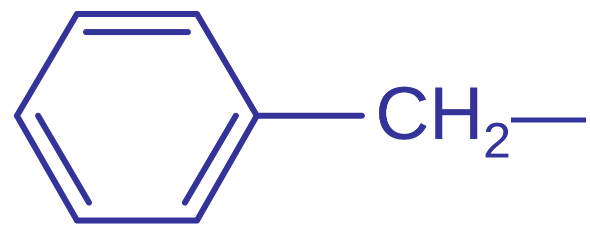
a group

phenol



a compound

benzyl

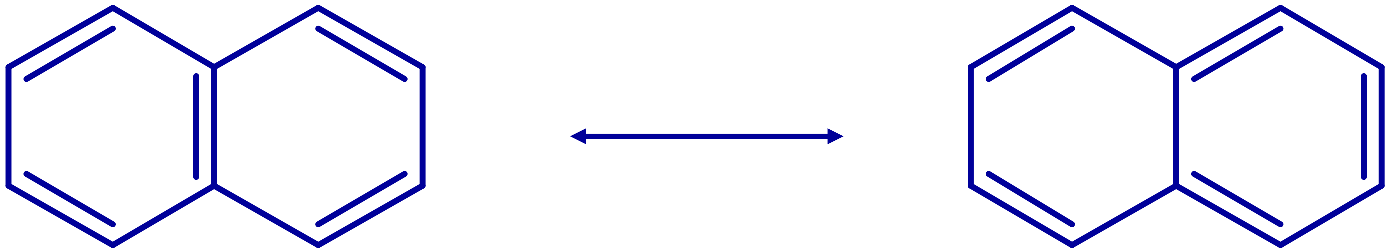


a group

11.7. Polycyclic Aromatic Hydrocarbons

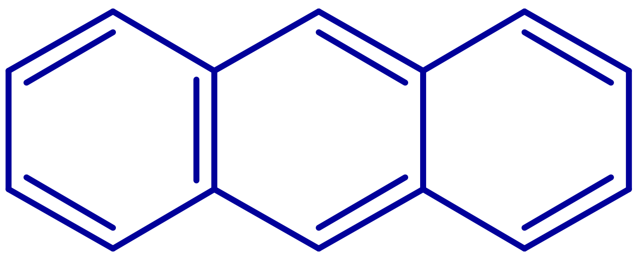
Naphthalene

Resonance energy = 255 kJ/mol

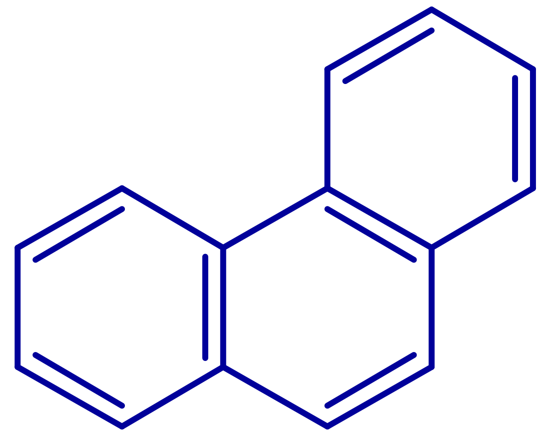


Most stable Lewis structure; both rings correspond to Kekulé benzene.

Anthracene and Phenanthrene



Anthracene



Phenanthrene

Resonance energy:

347 kJ/mol

381 kJ/mol

11.8. Physical Properties of Arenes

- Resemble other hydrocarbons:
  - Nonpolar.
  - Insoluble in water.
  - Less dense than water.

11.9. Reactions of Arenes: A Preview

1. Some reactions involve the ring.
2. In other reactions the ring is a substituent.

A. Reactions involving the ring

a) Reduction

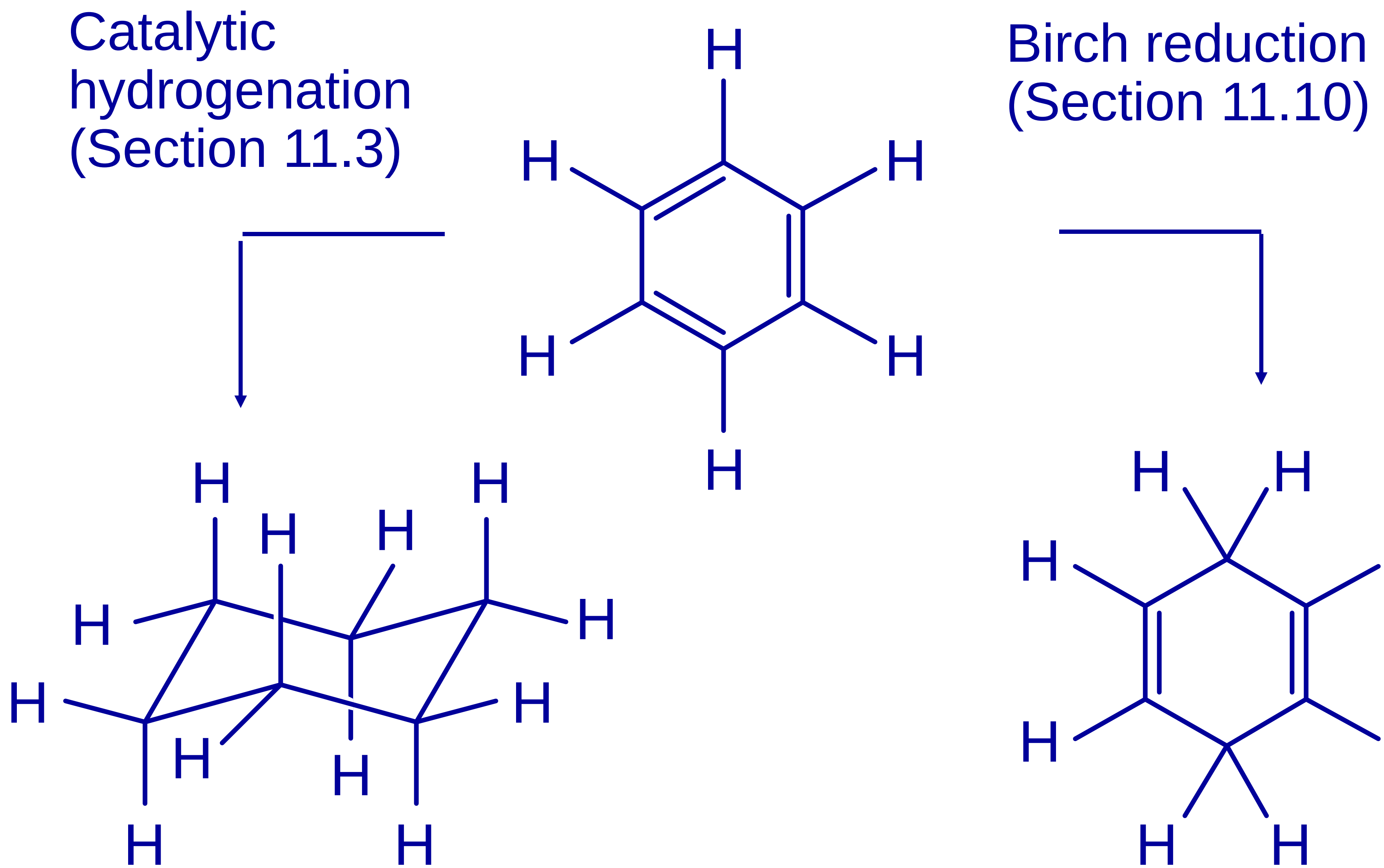
Catalytic hydrogenation (Section 11.3).
Birch reduction (Section 11.10).

b) Electrophilic aromatic substitution (Chapter 12).

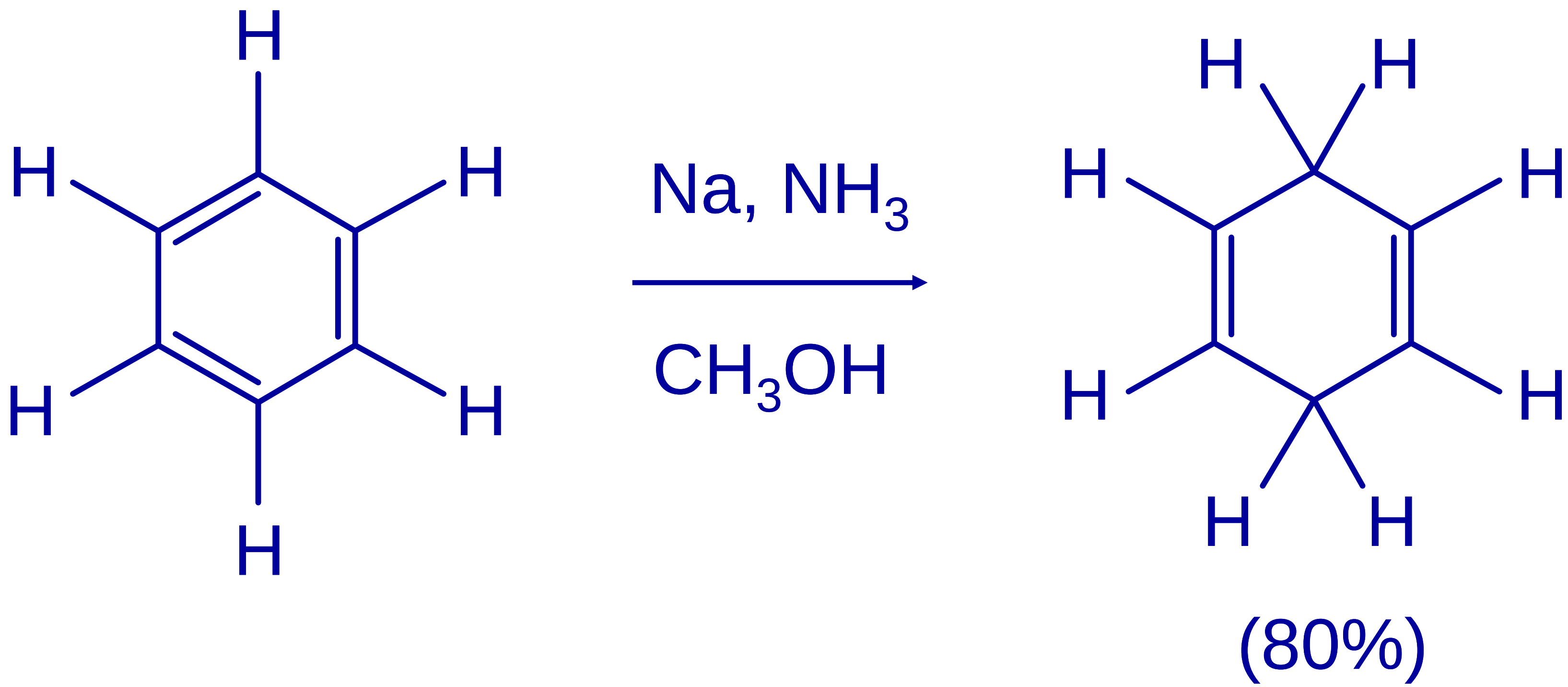
c) Nucleophilic aromatic substitution (Chapter 12).

B. The ring as a substituent (Sections 11.11-11.16).

Reduction of Benzene Rings



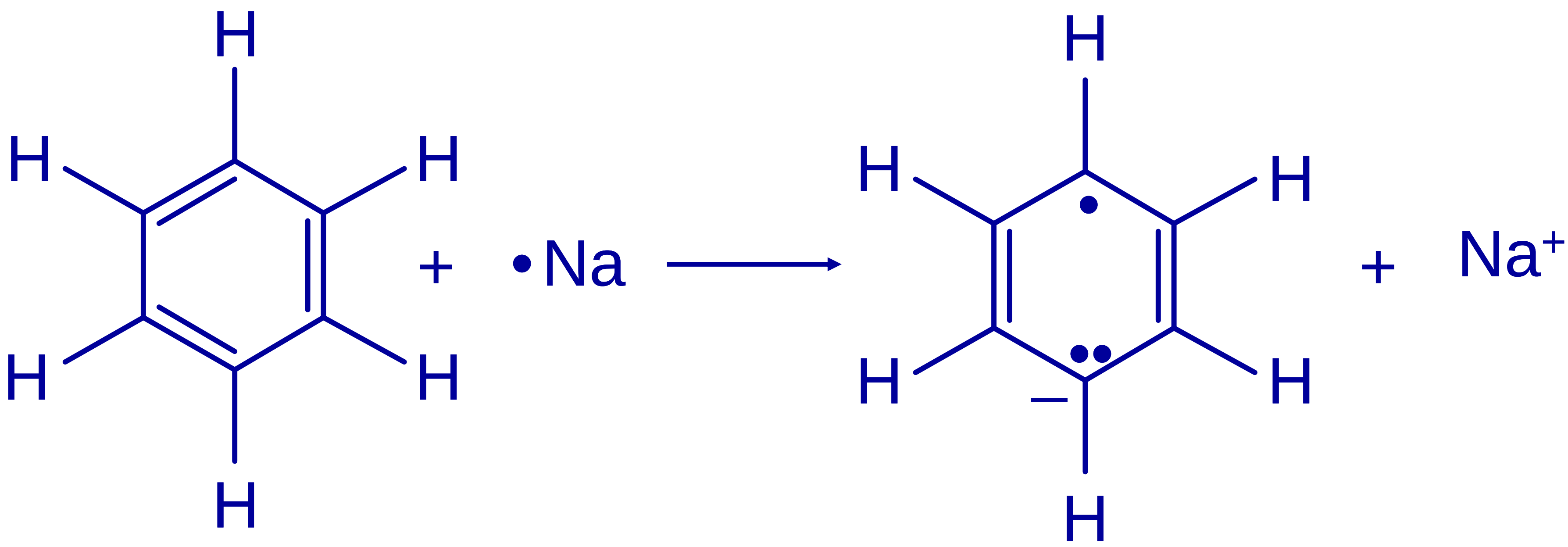
11.10. Birch Reduction of Benzene



- Product is non-conjugated diene.
- Reaction stops here. There is no further reduction.
- Reaction is not hydrogenation. H_2 is **NOT** involved in any way.

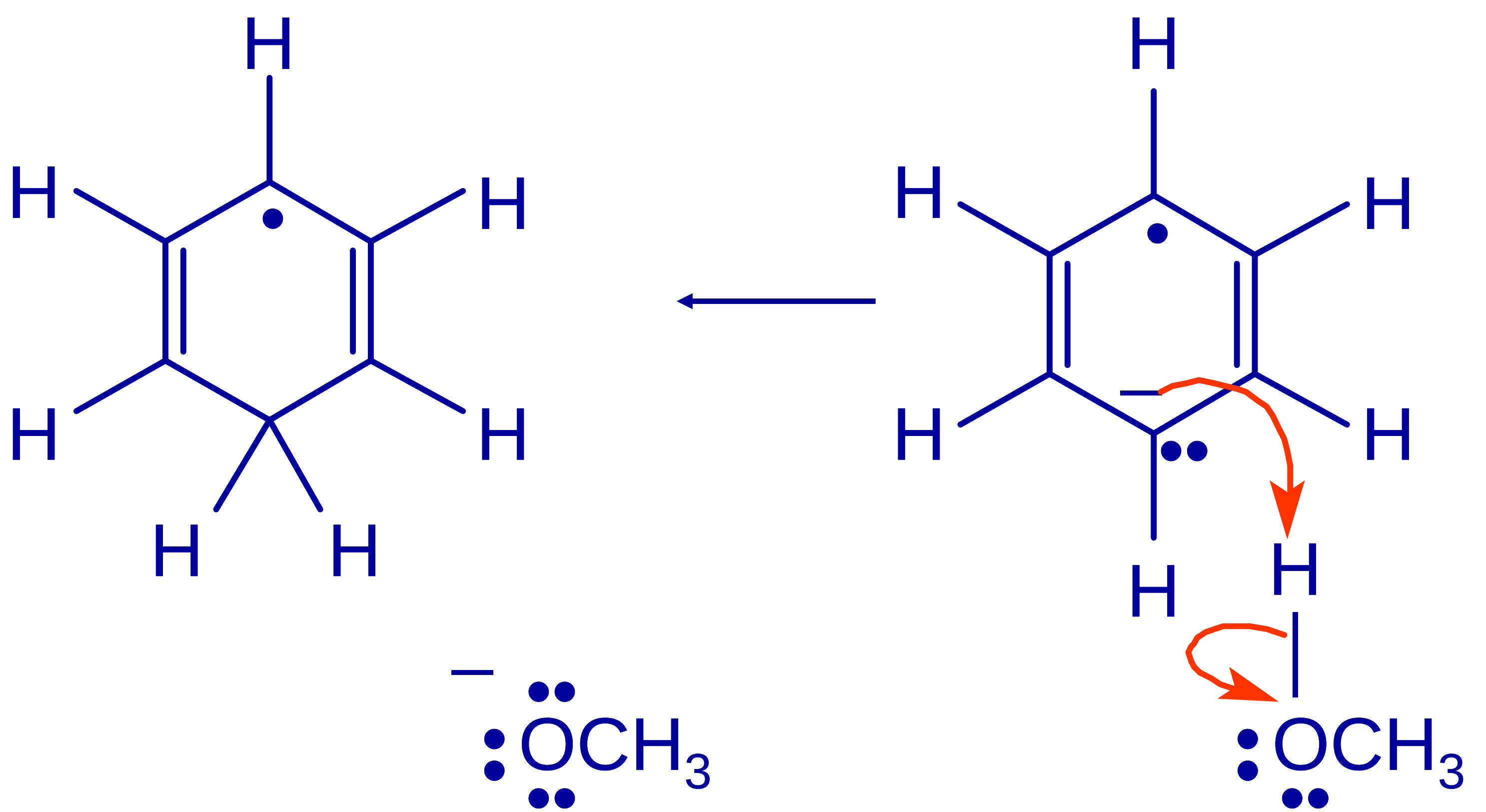
Mechanism of the Birch Reduction (Mechanism 11.1)

Step 1: Electron transfer from sodium



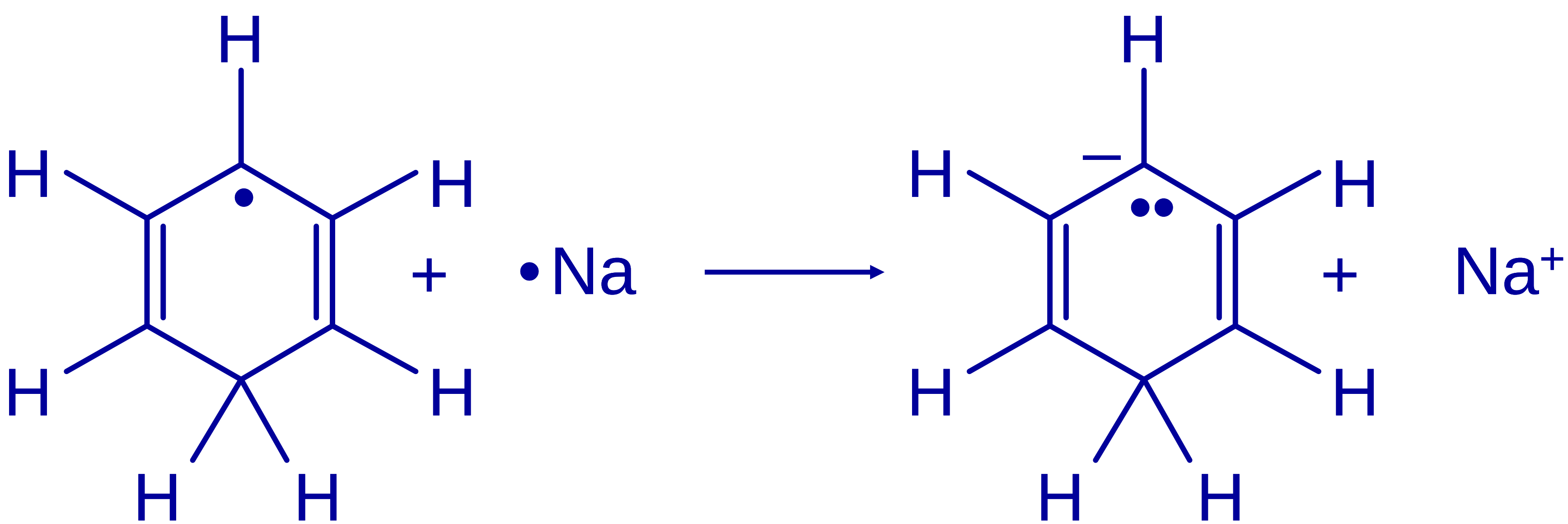
Mechanism of the Birch Reduction (Mechanism 11.1)

Step 2: Proton transfer from methanol



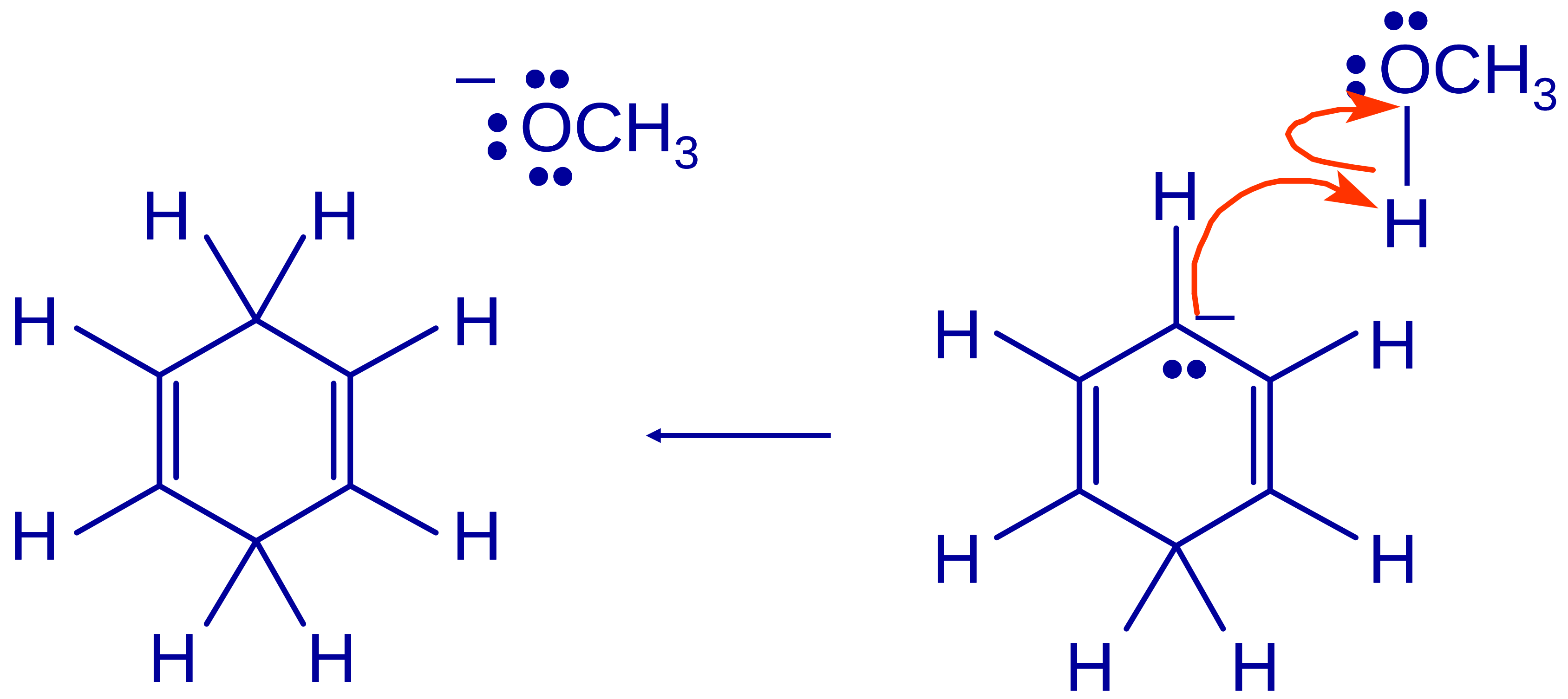
Mechanism of the Birch Reduction (Mechanism 11.1)

Step 3: Electron transfer from sodium

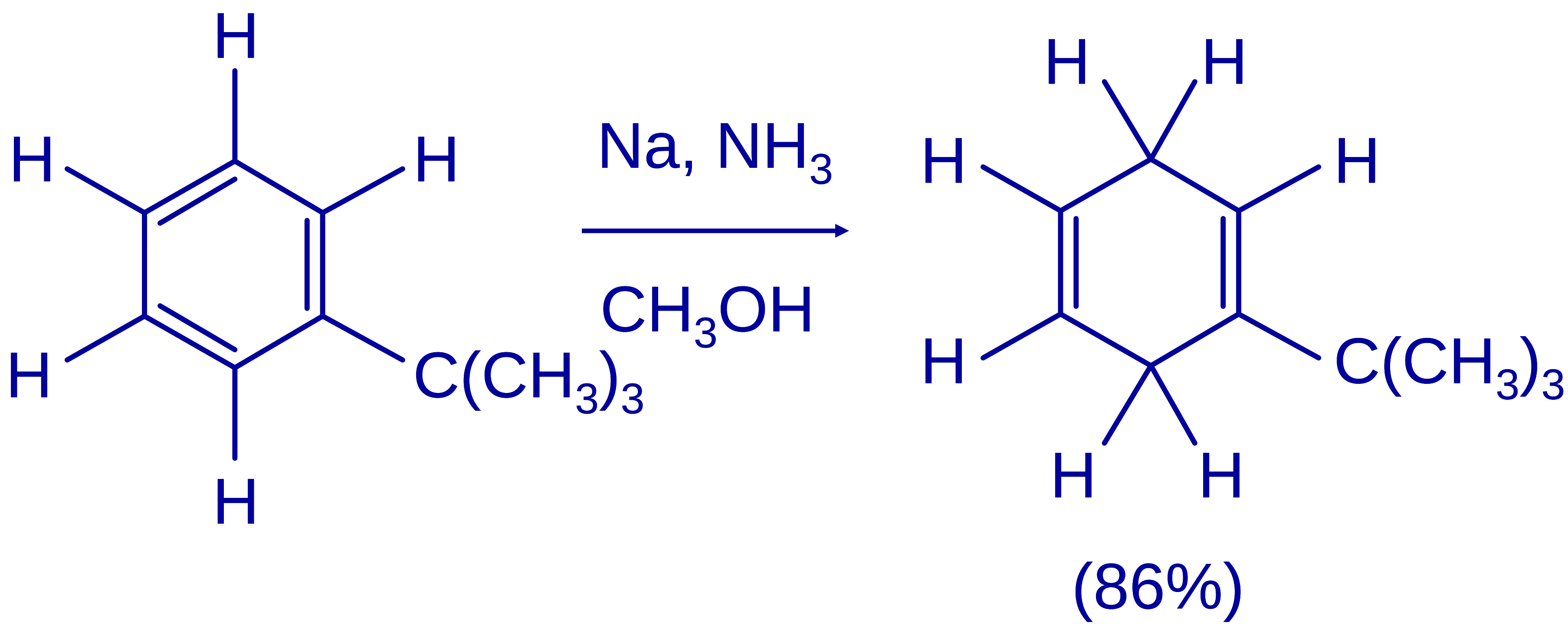


Mechanism of the Birch Reduction (Mechanism 11.1)

Step 4: Proton transfer from methanol



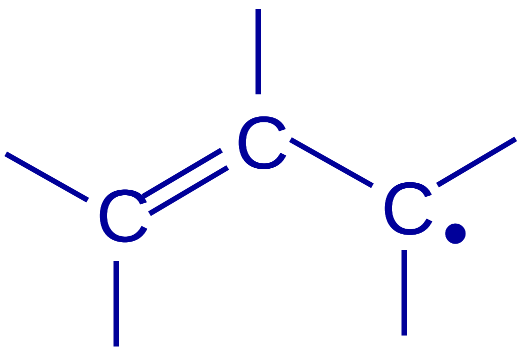
Birch Reduction of an Alkylbenzene



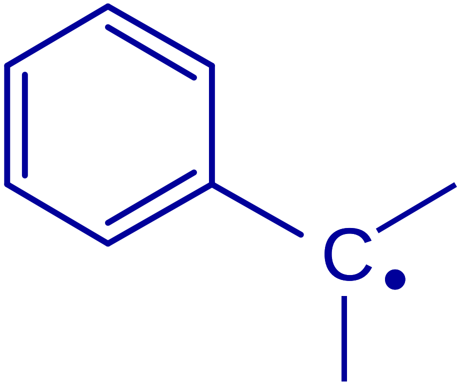
- If an alkyl group is present on the ring, it ends up as a substituent on the double bond.

11.11. Free-Radical Halogenation of Alkylbenzenes

The Benzene Ring as a Substituent



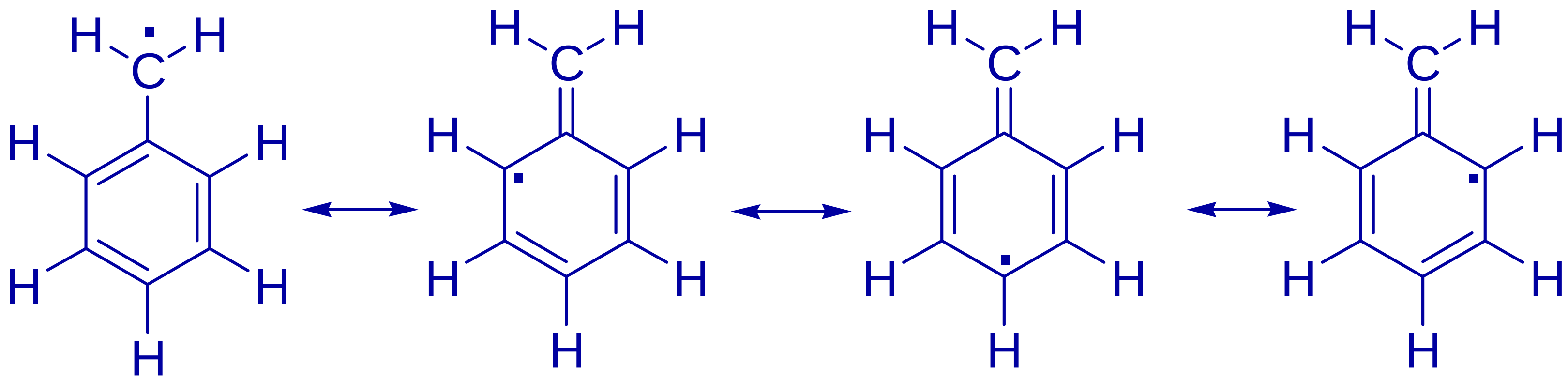
Allylic radical



Benzylic radical

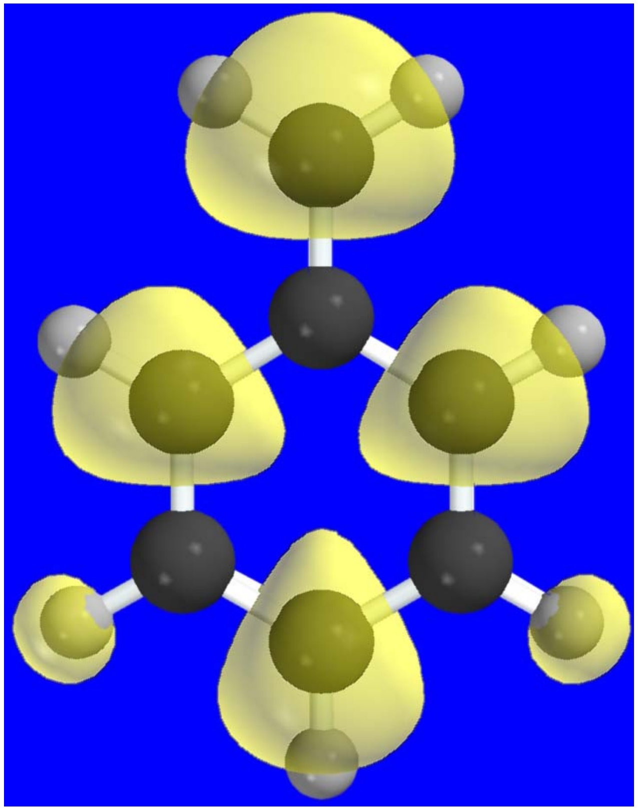
Benzylic carbon is analogous to allylic carbon.

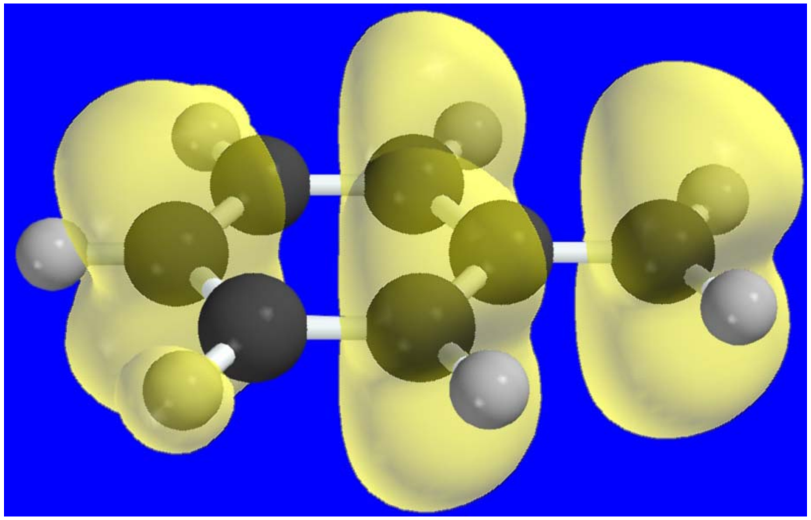
Resonance in Benzyl Radical



- Unpaired electron is delocalized between benzylic carbon and the ring carbons that are *ortho* and *para* to it.

Spin Density in Benzyl Radical (Figure 11.9, p 444)

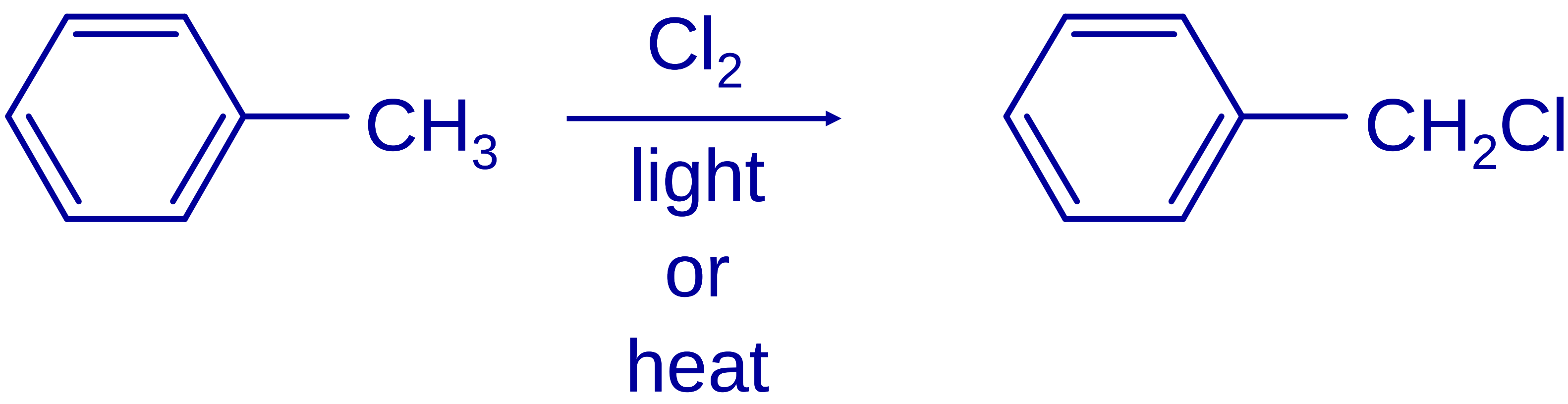




- Unpaired electron is delocalized between benzylic carbon and the ring carbons that are *ortho* and *para* to it.

Free-Radical Chlorination of Toluene

- Industrial process.
- Highly regioselective for benzylic position.

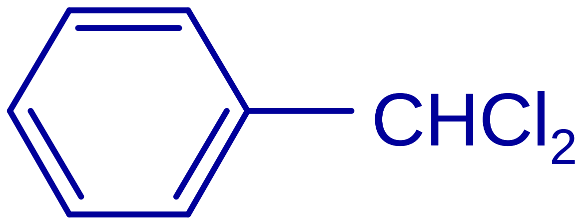


Toluene

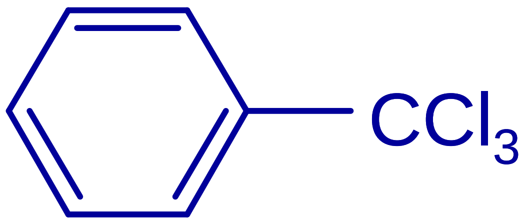
Benzyl chloride

Free-Radical Chlorination of Toluene

- Similarly, dichlorination and trichlorination are selective for the benzylic carbon. Further chlorination gives:



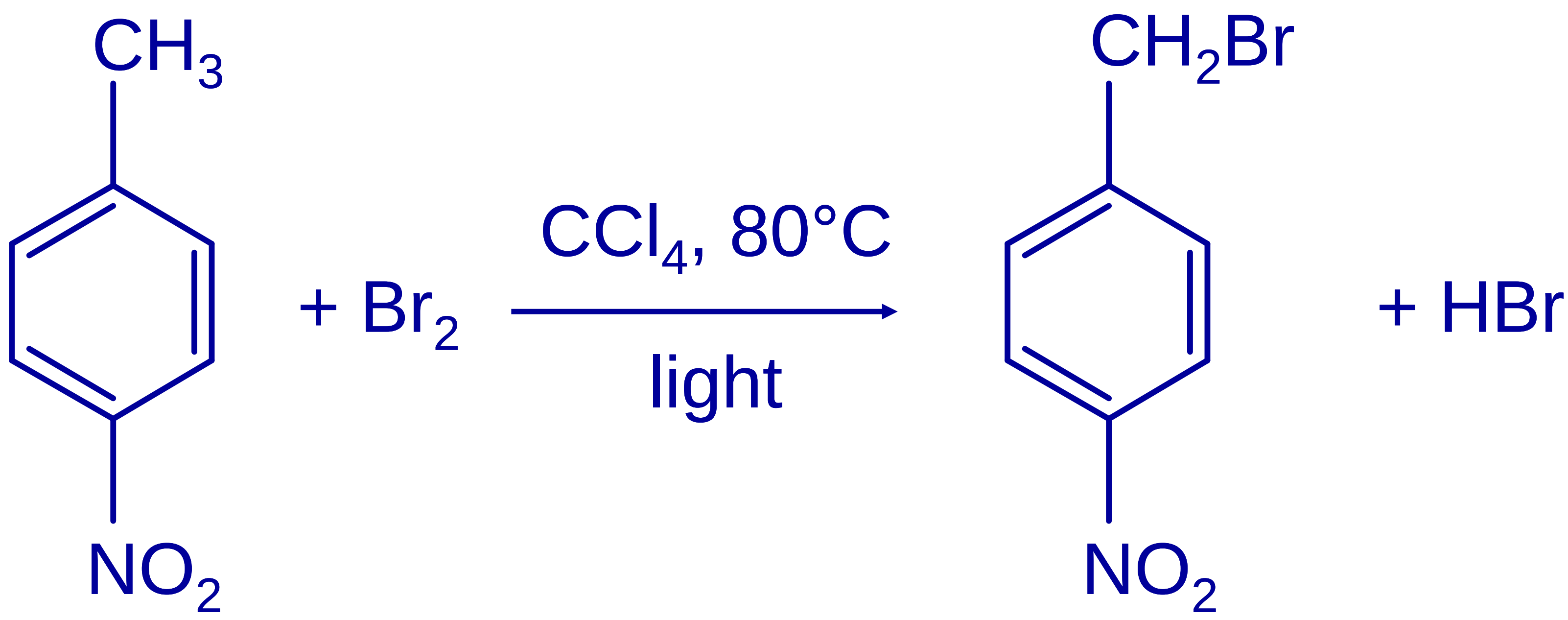
(Dichloromethyl)benzene



(Trichloromethyl)benzene

Benzylic Bromination

- Is used in the laboratory to introduce a halogen at the benzylic position.

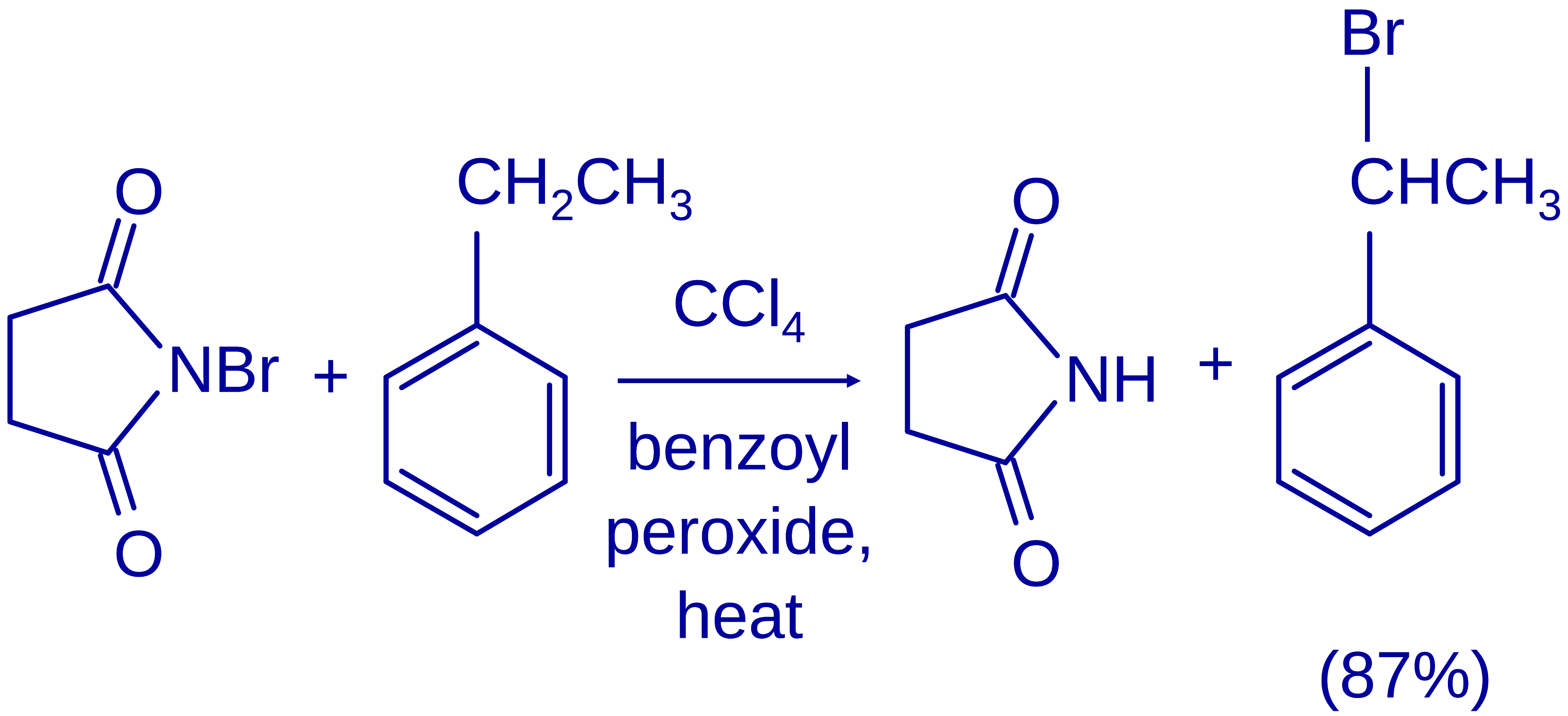


p-Nitrotoluene

p-Nitrobenzyl bromide (71%)

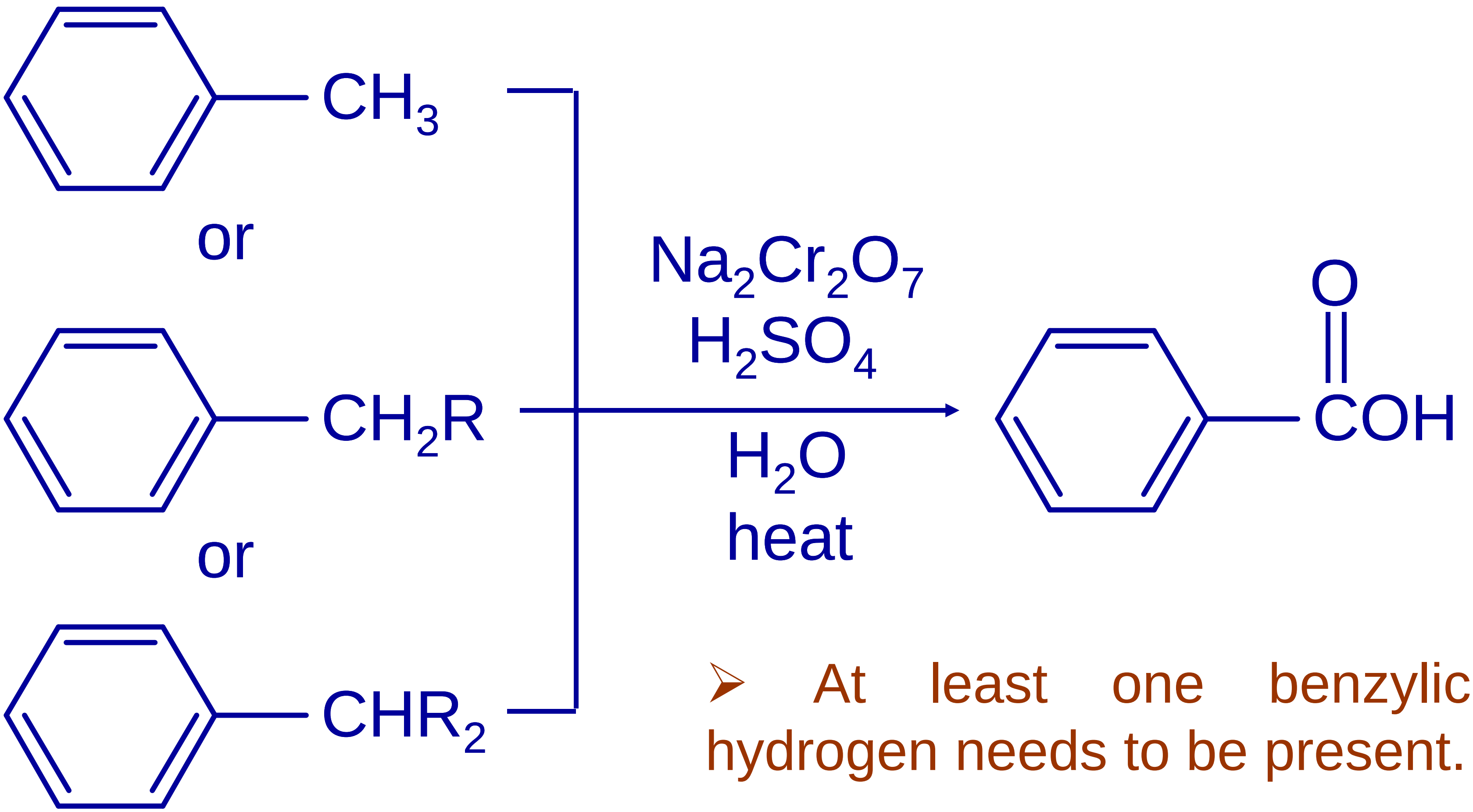
N-Bromosuccinimide (NBS)

- NBS is a convenient reagent for benzylic bromination.



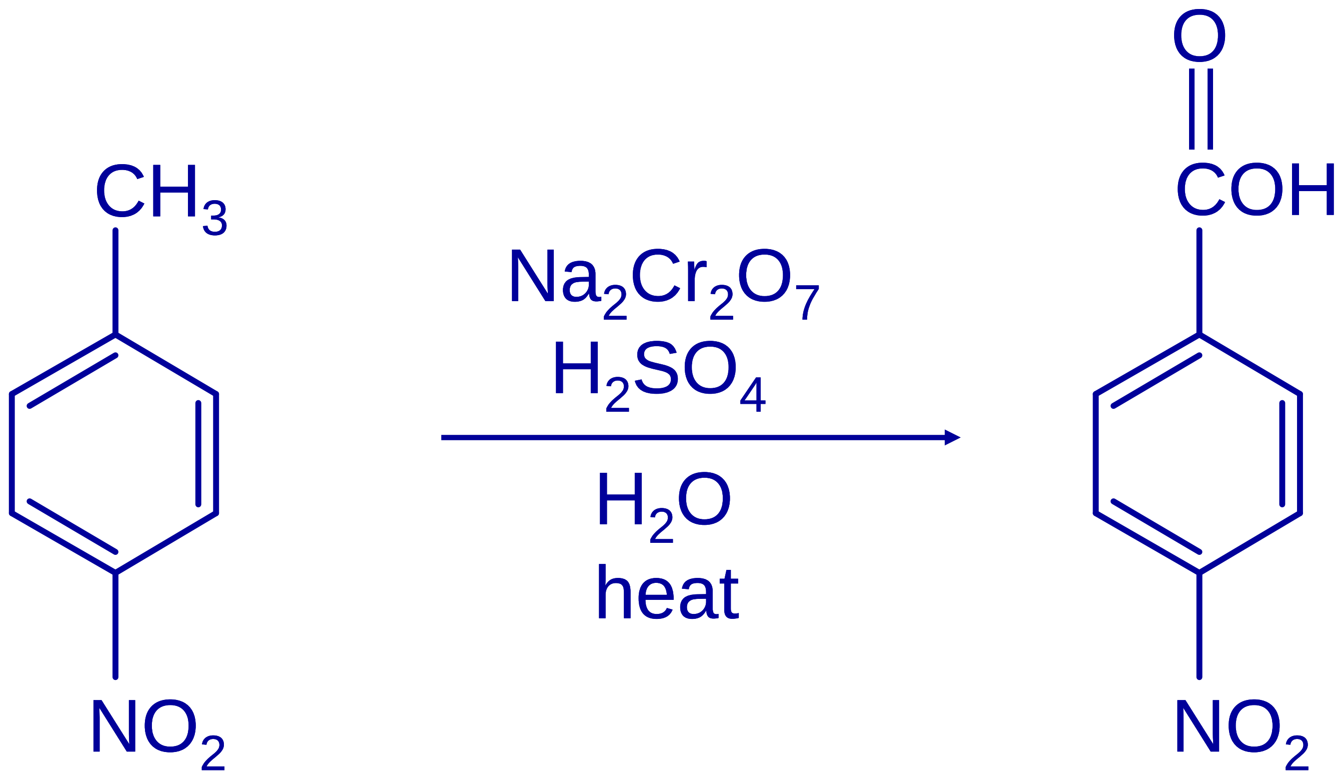
11.12. Oxidation of Alkylbenzenes

Site of Oxidation is Benzylic Carbon



- At least one benzylic hydrogen needs to be present.

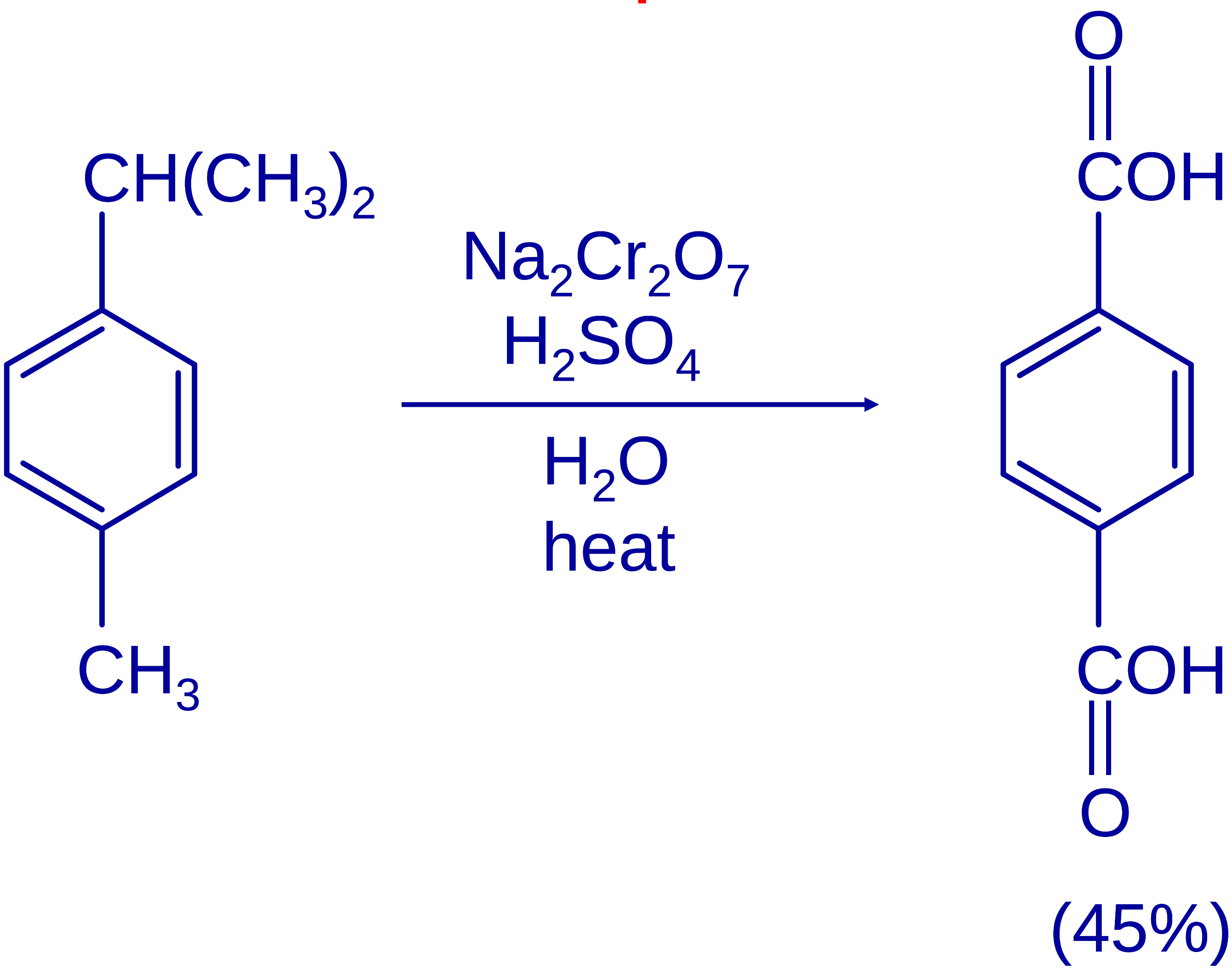
Example



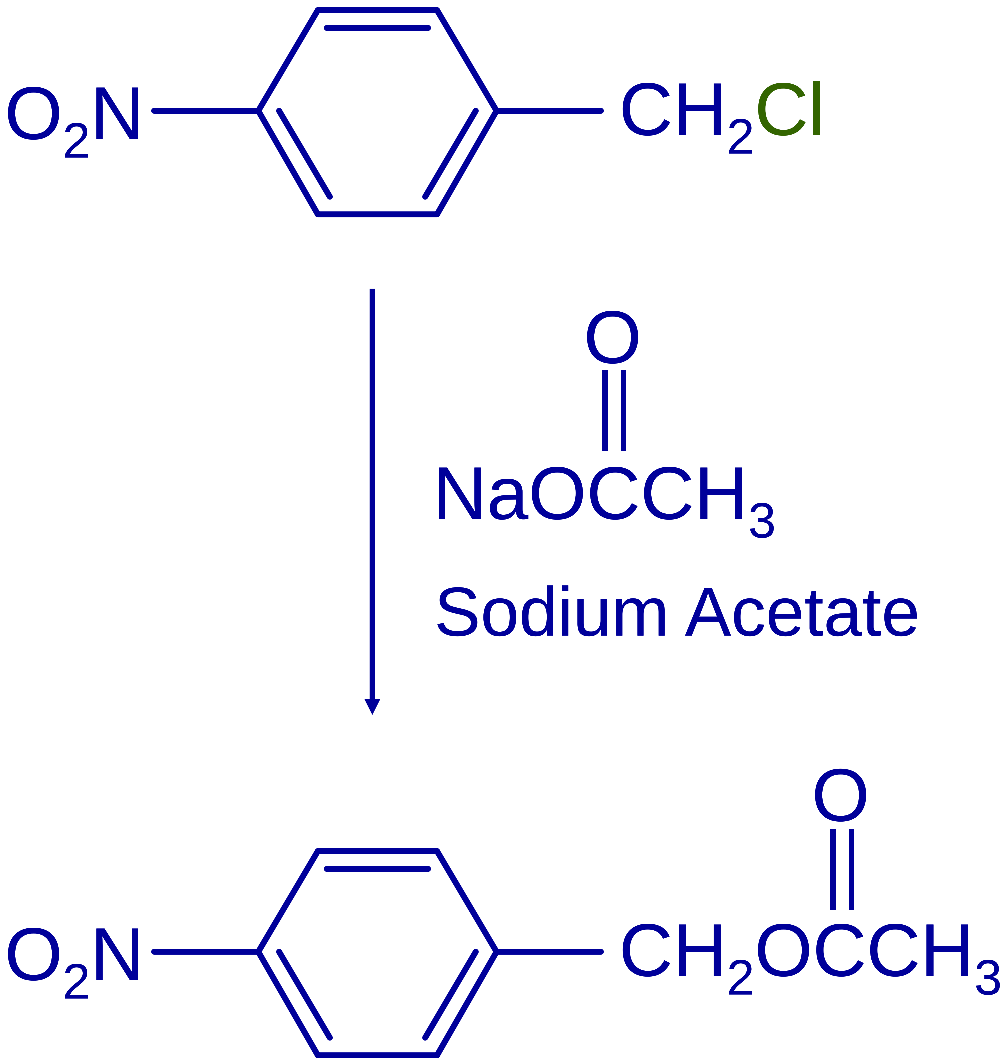
p-Nitrotoluene

p-Nitrobenzoic acid (82-86%)

Example



Nucleophilic Substitution in Benzylic Halides

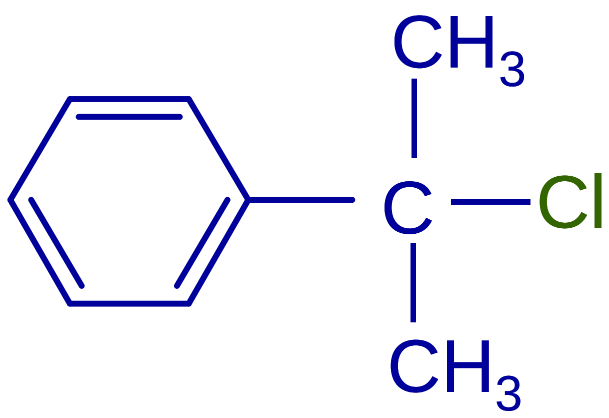


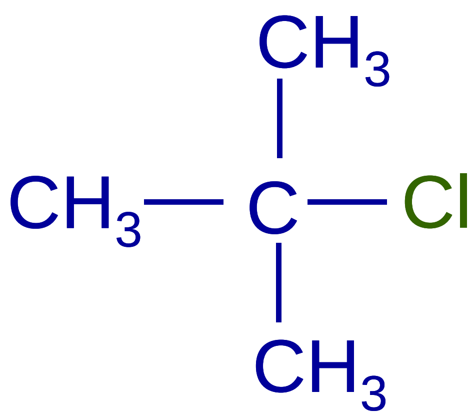
(78-82%)

Mechanism is S_N2

What about S_N1?

Relative solvolysis rates in aqueous acetone



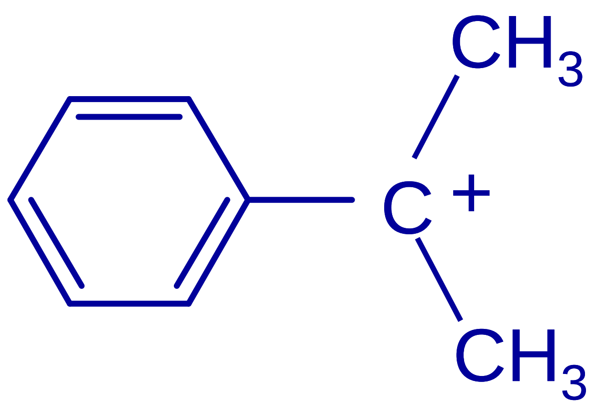


600 1

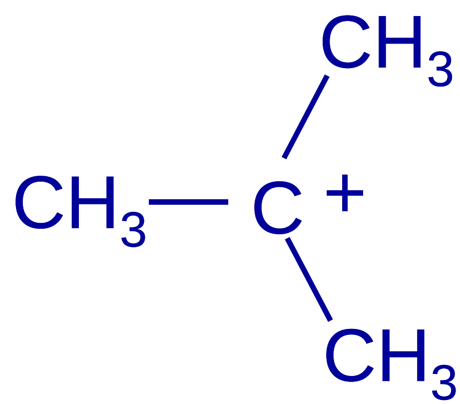
- Tertiary benzylic carbocation is formed more rapidly than tertiary carbocation; therefore, more stable.

What about S_N1?

Relative rates of formation:

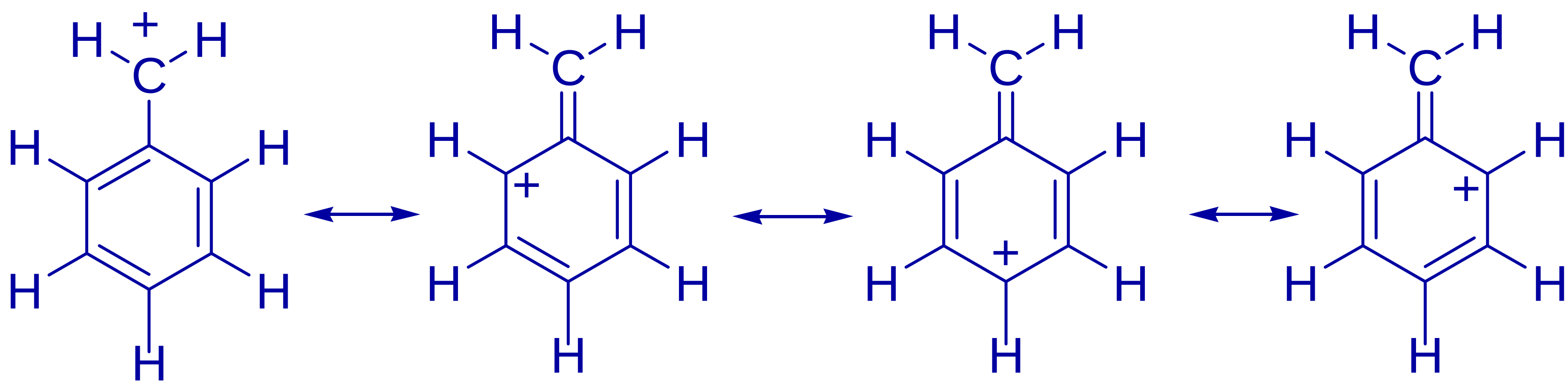


more stable



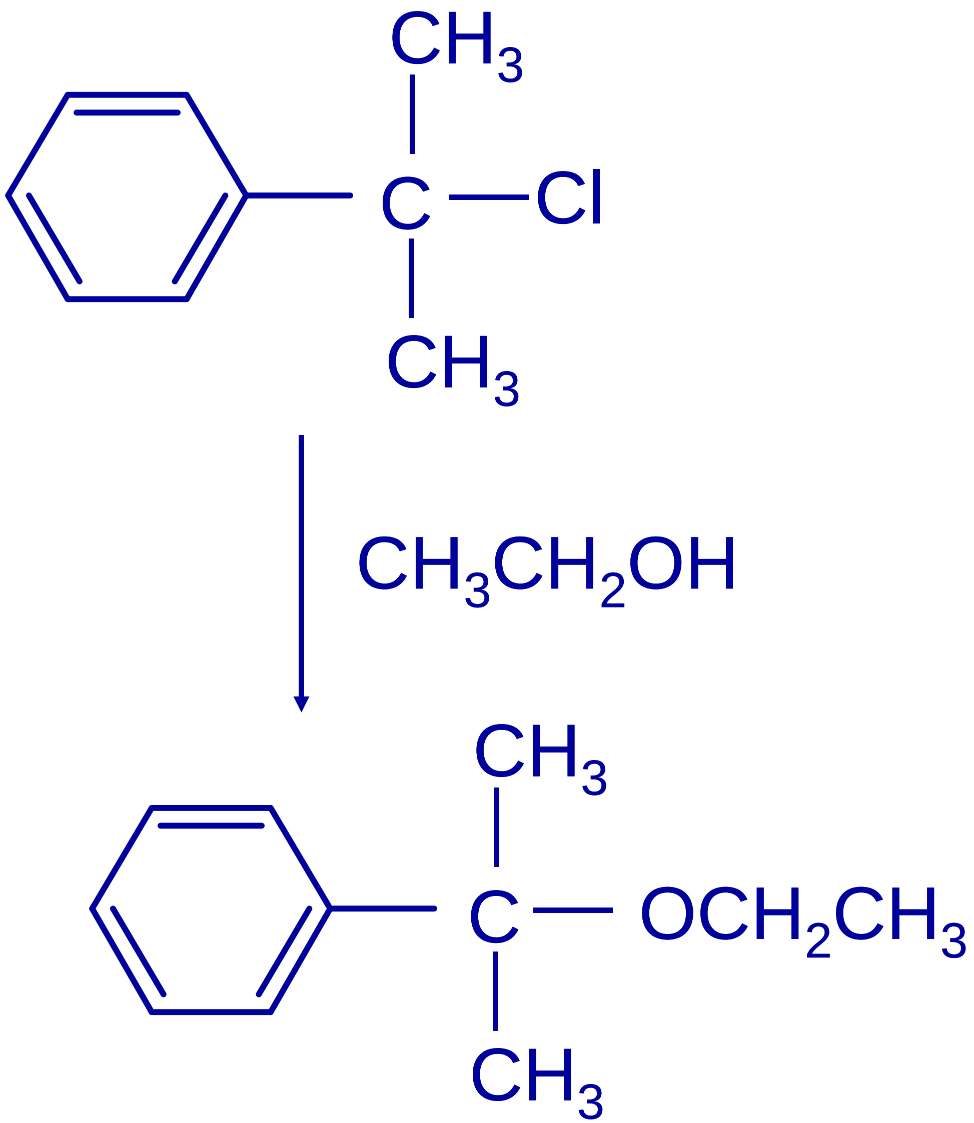
less stable

Resonance in Benzyl Cation



➢ Positive charge is delocalized between benzylic carbon and the ring carbons that are *ortho* and *para* to it.

Solvolysis



(87%)

11.15
Preparation of Alkenylbenzenes

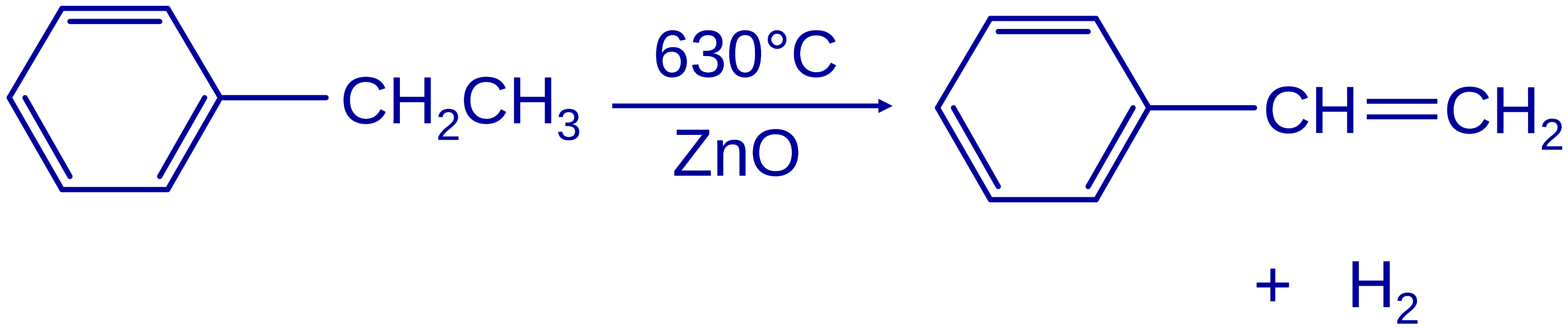
Dehydrogenation

Dehydration

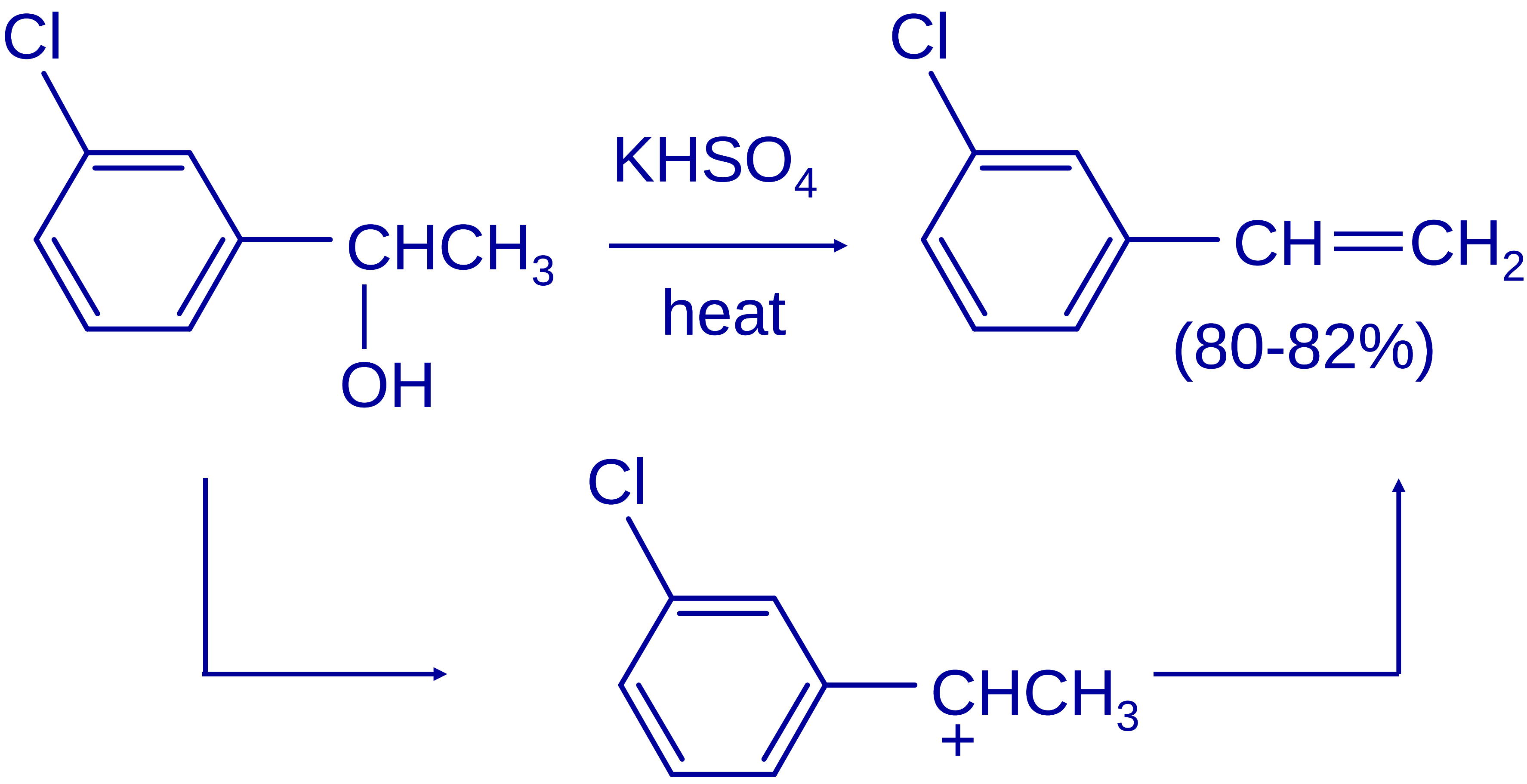
Dehydrohalogenation

Dehydrogenation

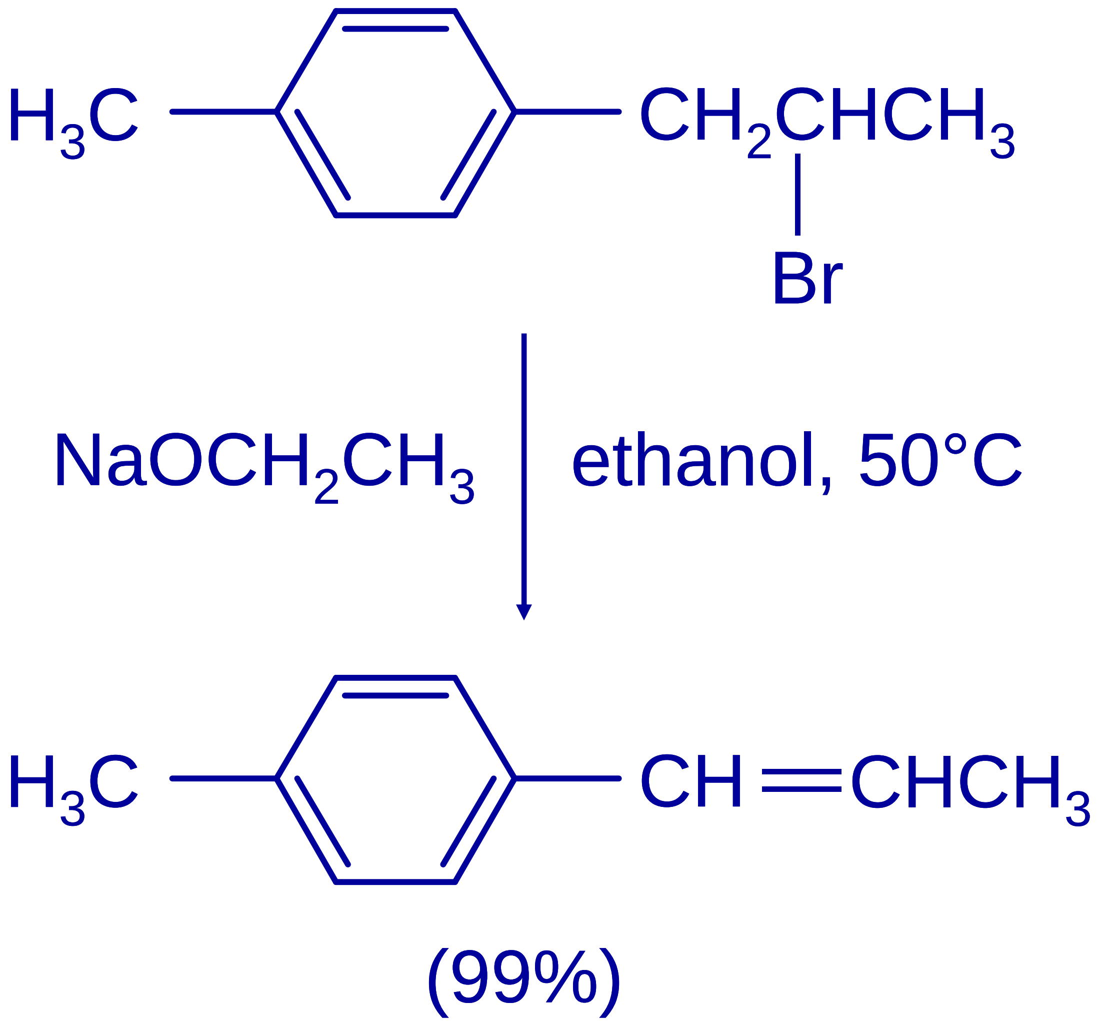
- Industrial preparation of styrene.



Acid-Catalyzed Dehydration of Benzylic Alcohols



Dehydrohalogenation



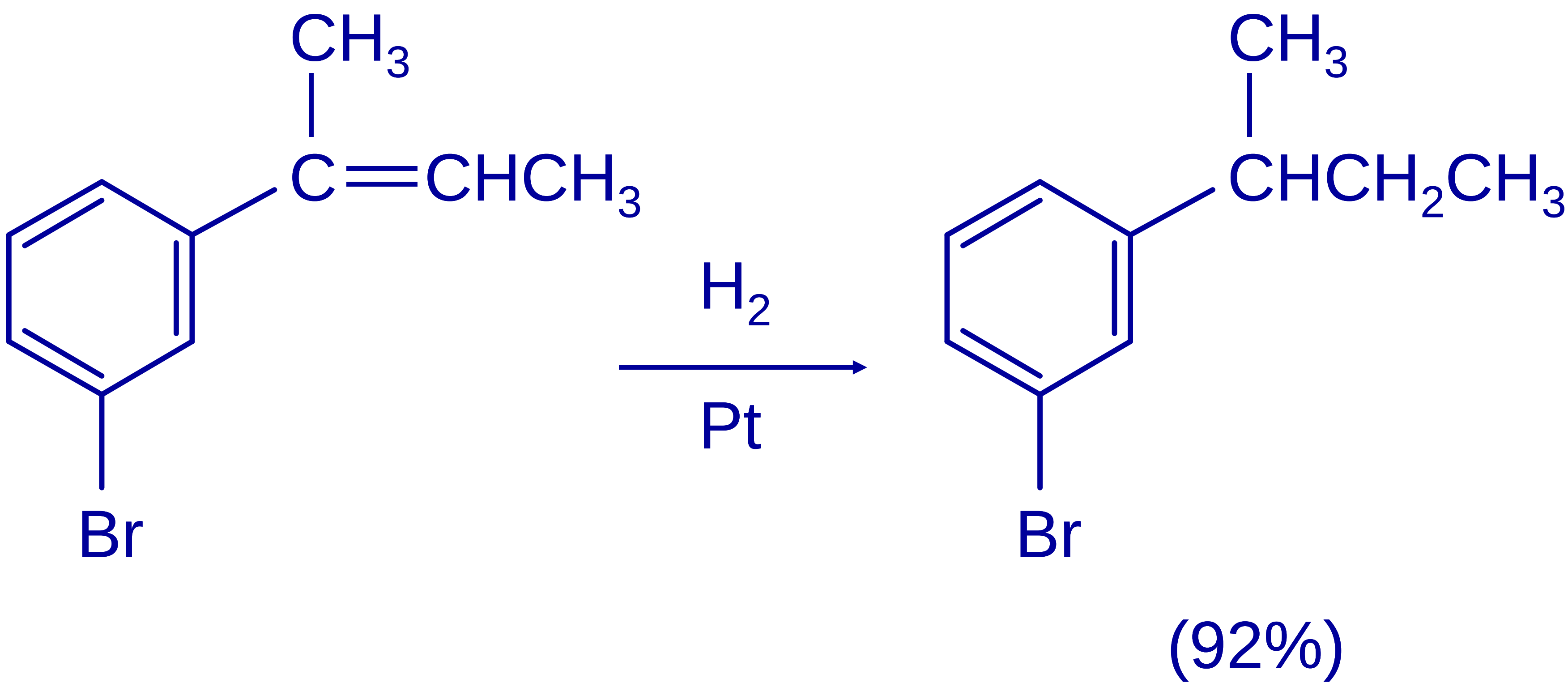
11.16
Addition Reactions of Alkenylbenzenes

Hydrogenation

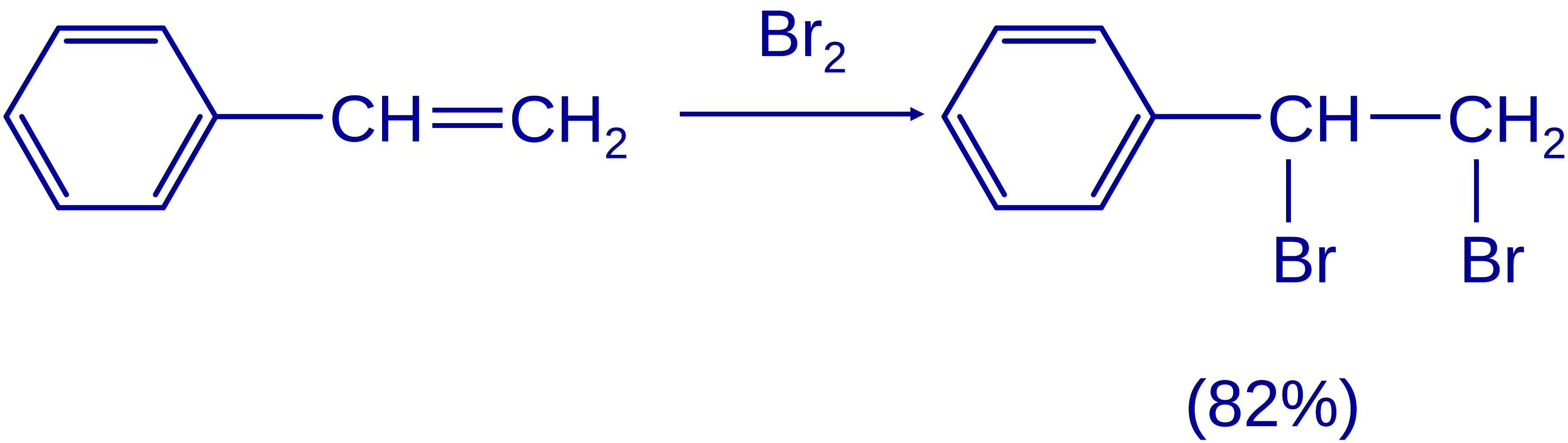
Halogenation

Addition of hydrogen halides

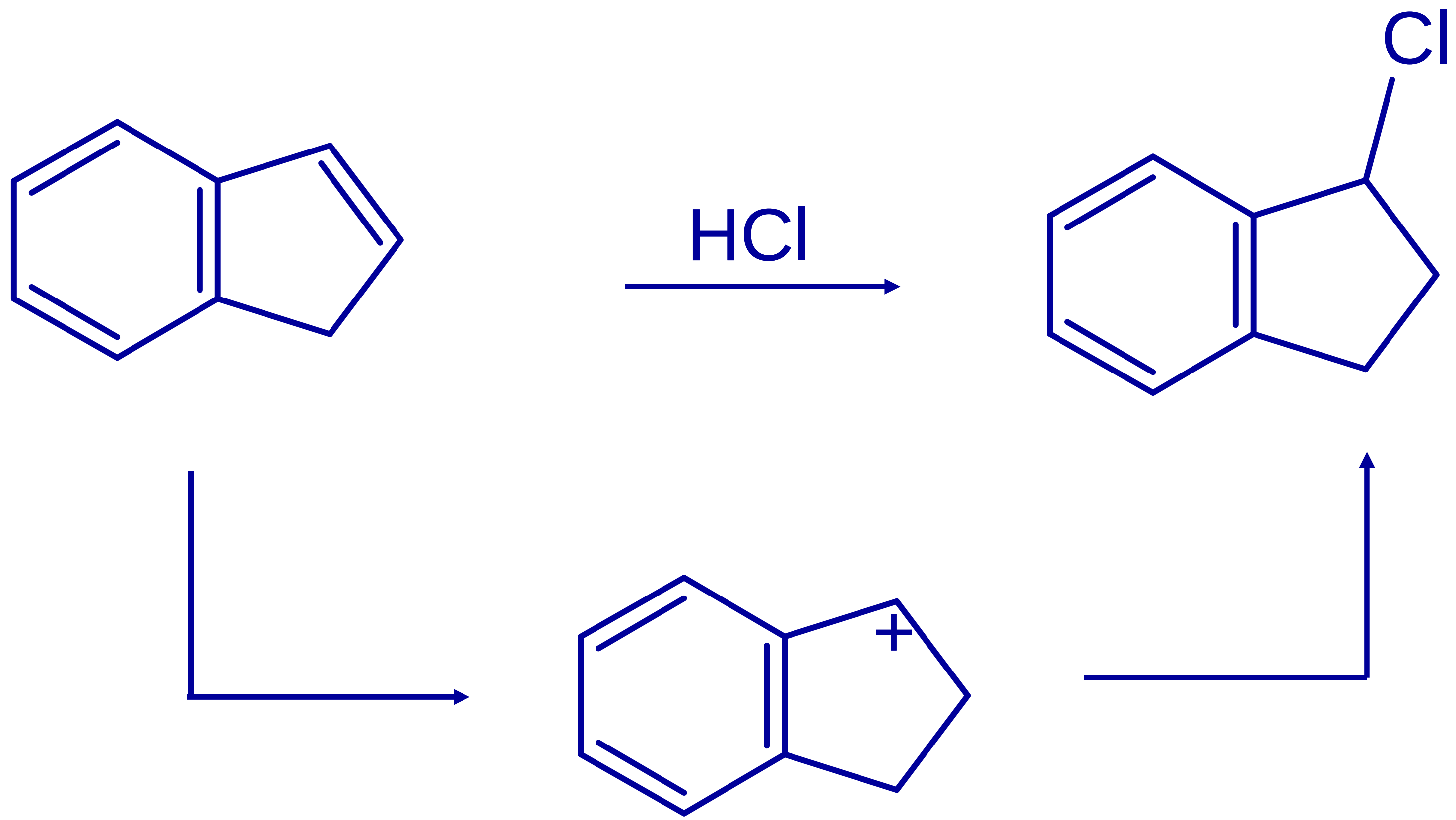
Hydrogenation



Halogenation

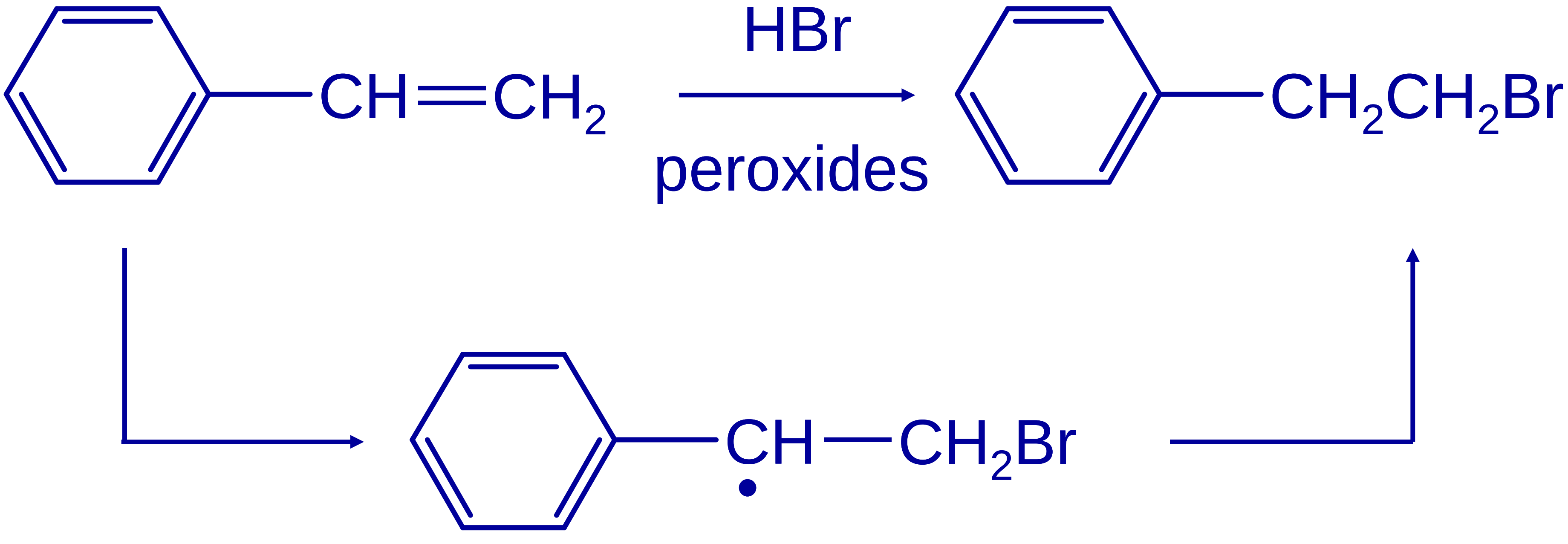


Addition of Hydrogen Halides



via benzylic carbocation

Free-Radical Addition of HBr



via benzylic radical

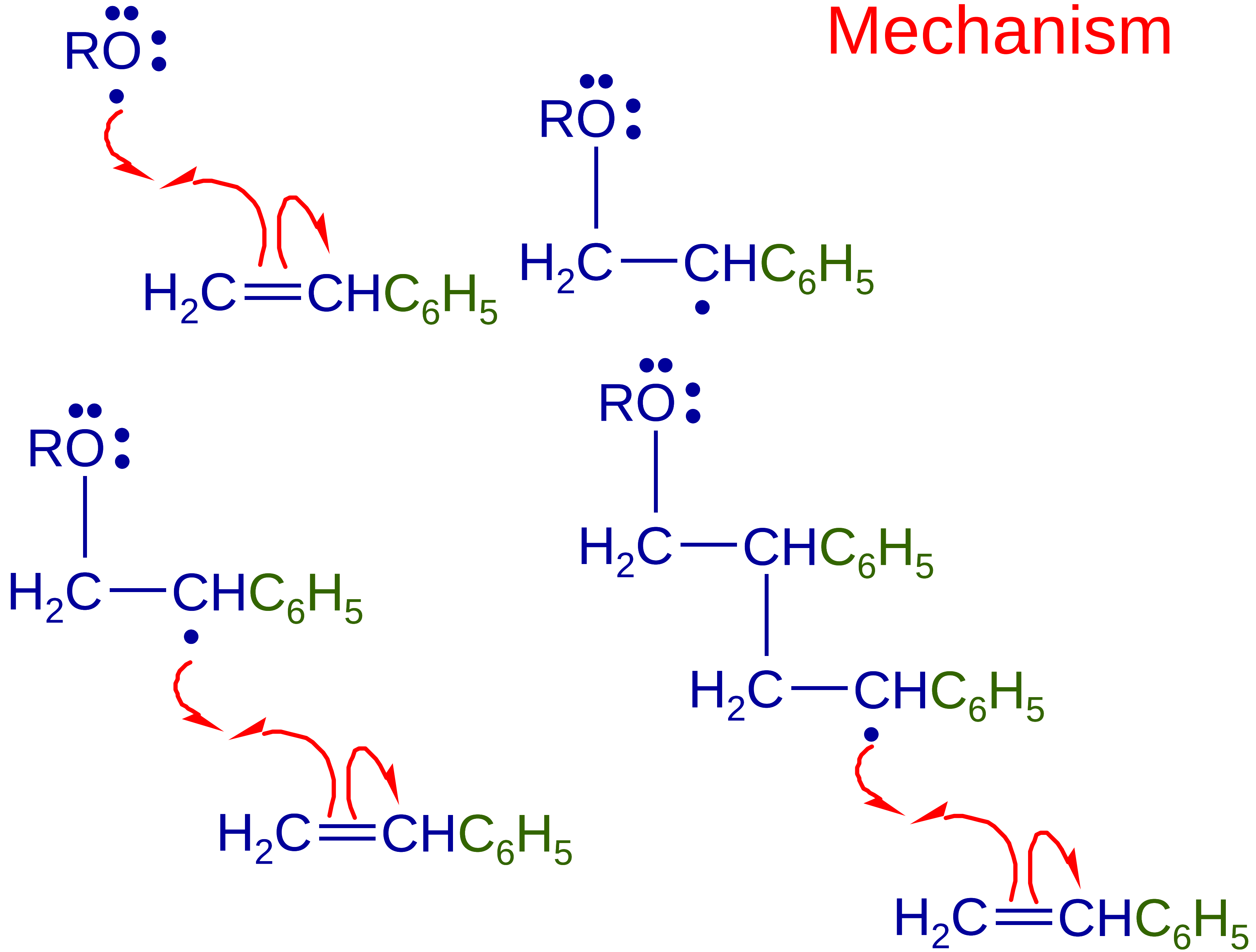
11.17. Polymerization of Styrene

$$H_2C{=}CHC_6H_5 \longrightarrow$$

$$—CH_2—\underset{C_6H_5}{\underset{|}{CH}}—CH_2—\underset{C_6H_5}{\underset{|}{CH}}—CH_2—\underset{C_6H_5}{\underset{|}{CH}}—$$

polystyrene

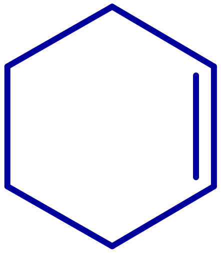
Mechanism


RO
H2C=CHC6H5
RO
H2C—CHC6H5
RO
H2C—CHC6H5
H2C=CHC6H5
RO
H2C—CHC6H5
H2C—CHC6H5
H2C=CHC6H5

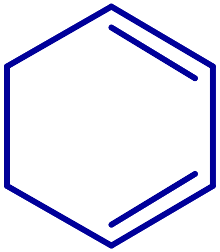
11.18. Cyclobutadiene and Cyclooctatetraene

Heats of Hydrogenation

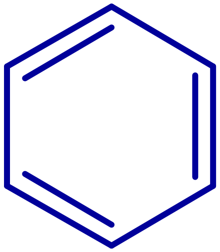
to give cyclohexane (kJ/mol)



120



231

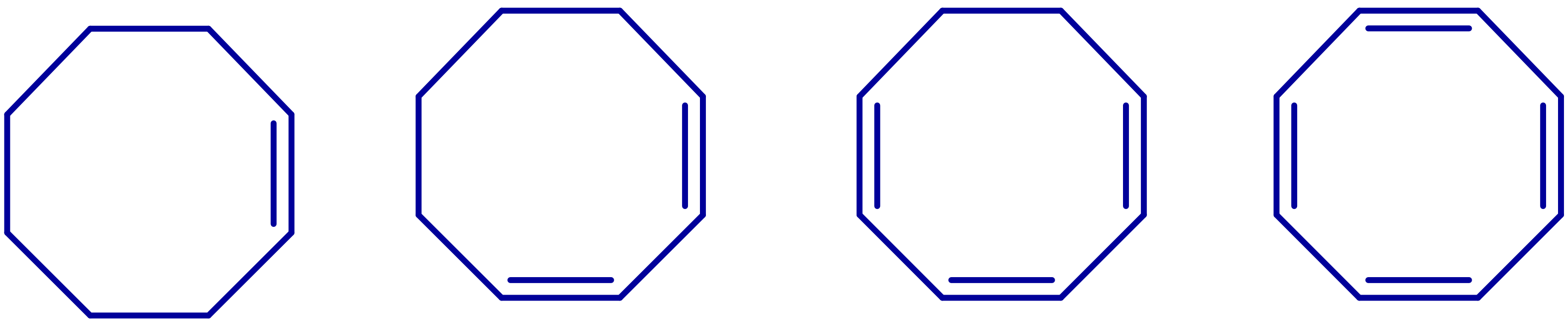


208

- Heat of hydrogenation of benzene is 152 kJ/mol less than 3 times heat of hydrogenation of cyclohexene.

Heats of Hydrogenation

to give cyclooctane (kJ/mol)



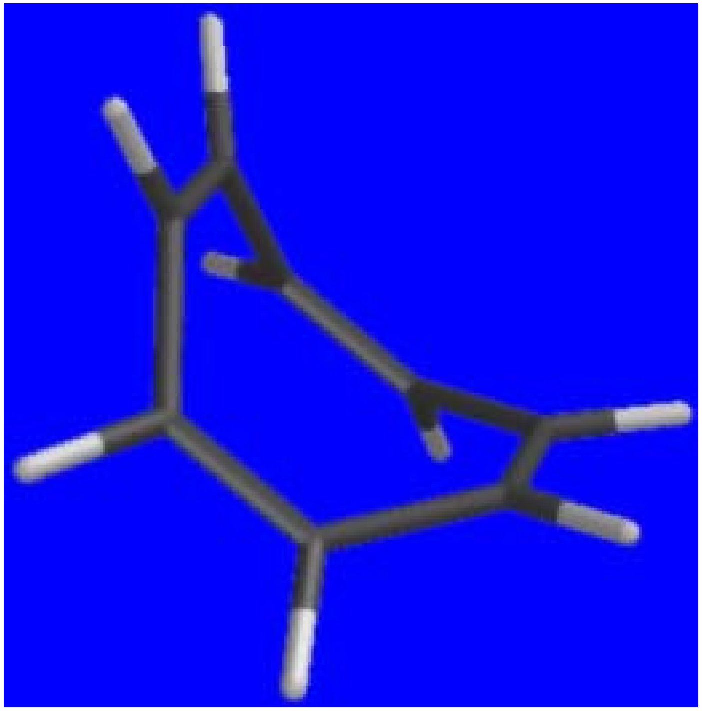
97 | 205 | 303 | 410

- Heat of hydrogenation of cyclooctatetraene is more than 4 times heat of hydrogenation of cyclooctene.

Structure of Cyclooctatetraene

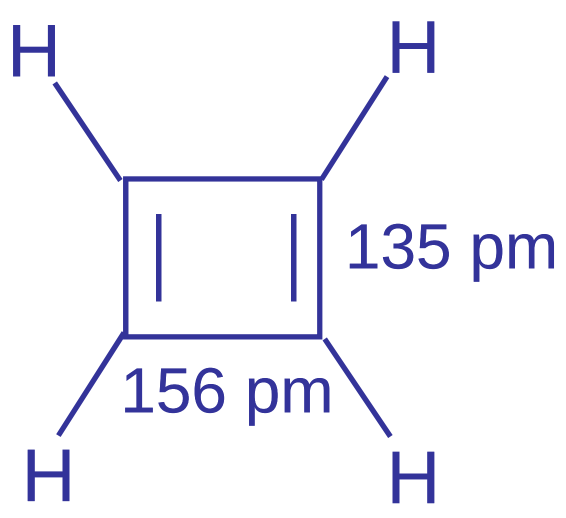
Cyclooctatetraene is not planar.

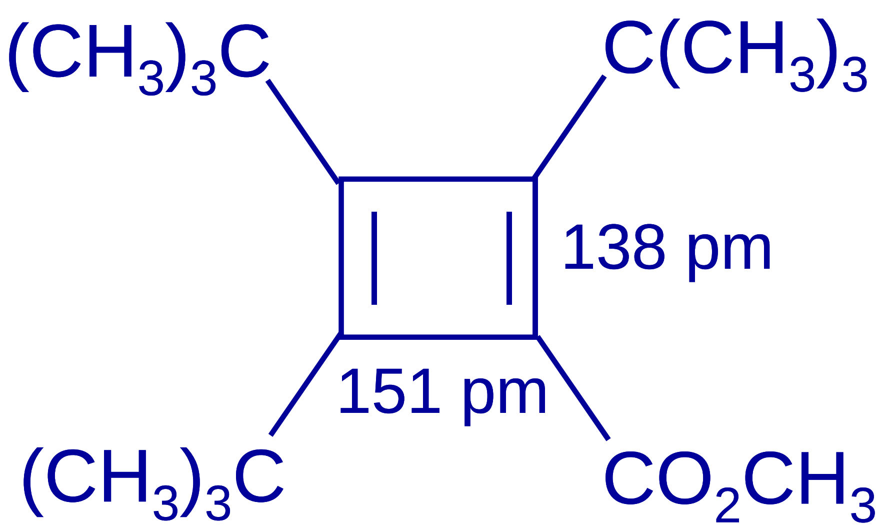
Has alternating long (146 pm)
and short (133 pm) bonds.



Structure of Cyclobutadiene

➢ MO calculations give alternating short and long bonds for cyclobutadiene.





Stability of Cyclobutadiene

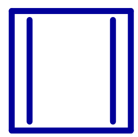
- Cyclobutadiene is observed to be highly reactive, and too unstable to be isolated and stored in the customary way.

- Not only is cyclobutadiene not aromatic, it is *antiaromatic*.

- An antiaromatic substance is one that is *destabilized* by cyclic conjugation.

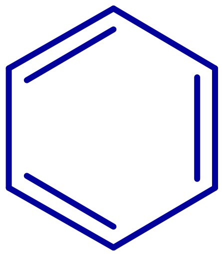
Requirements for Aromaticity

- Cyclic conjugation is necessary, *but not sufficient.*

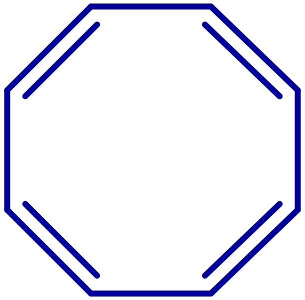


not aromatic

Antiaromatic when square



aromatic



not aromatic

Antiaromatic when planar

Conclusion

There must be some factor in addition to cyclic conjugation that determines whether a molecule is aromatic or not.

11.19. Hückel's Rule: Annulenes

The additional factor that influences aromaticity is the number of π- electrons.

Hückel's Rule

➢ Among planar, monocyclic, completely conjugated polyenes, only those with $4n+2$ π electrons possess special stability (are aromatic):

n	4*n*+2	
0	2	
1	6	Benzene!
2	10	
3	14	
4	18	

Hückel's Rule

- Hückel restricted his analysis to planar, completely conjugated, monocyclic polyenes.

- He found that the π molecular orbitals of these compounds had a distinctive pattern.

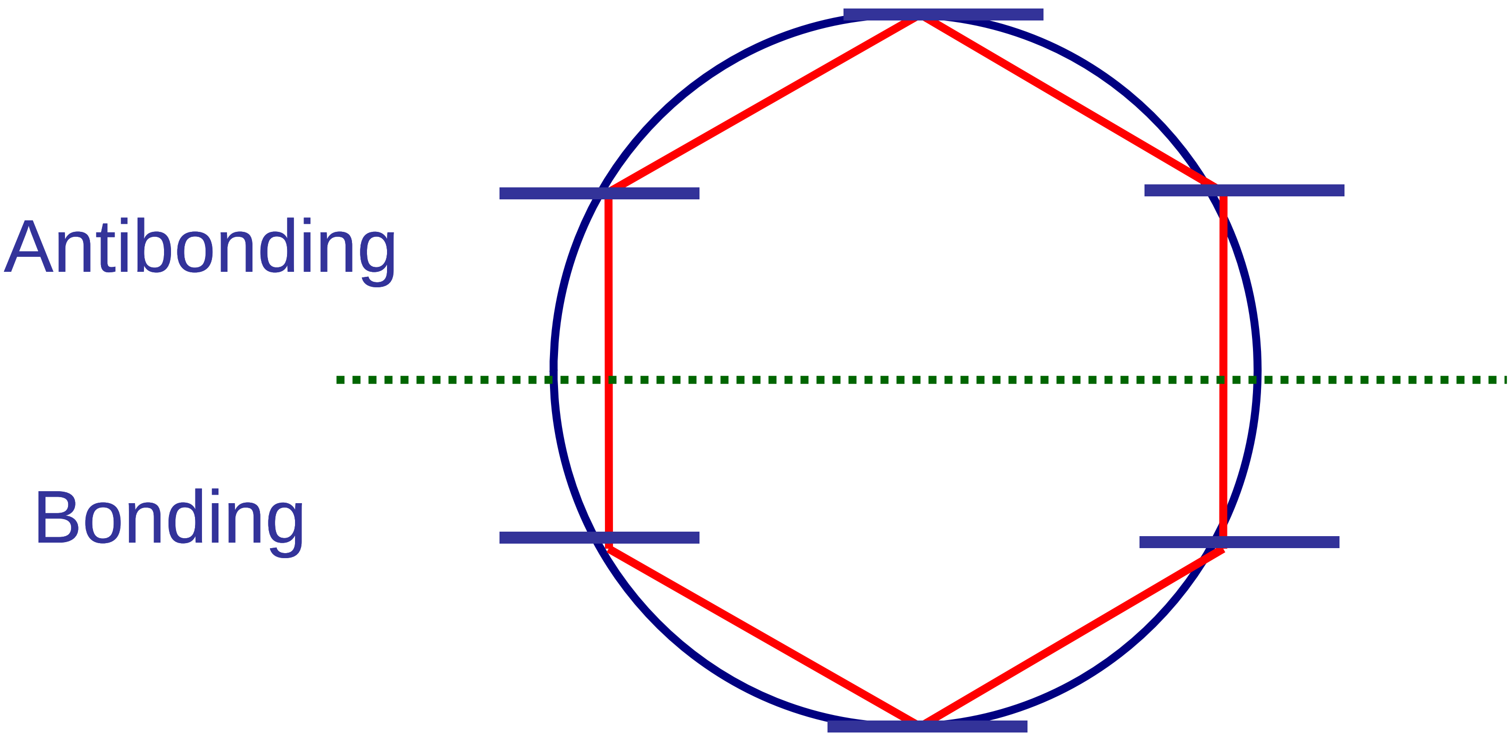
- One π orbital was lowest in energy, another was highest in energy, and the others were arranged in pairs between the highest and the lowest.

Hückel's Rule

- *Frost's circle* is a mnemonic that allows us to draw a diagram showing the relative energies of the π orbitals of a cyclic conjugated system.

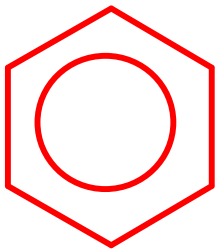
1) Draw a circle.
2) Inscribe a regular polygon inside the circle so that one of its corners is at the bottom.
3) Every point where a corner of the polygon touches the circle corresponds to a π electron energy level.
4) The middle of the circle separates bonding and antibonding orbitals.

Frost's Circle

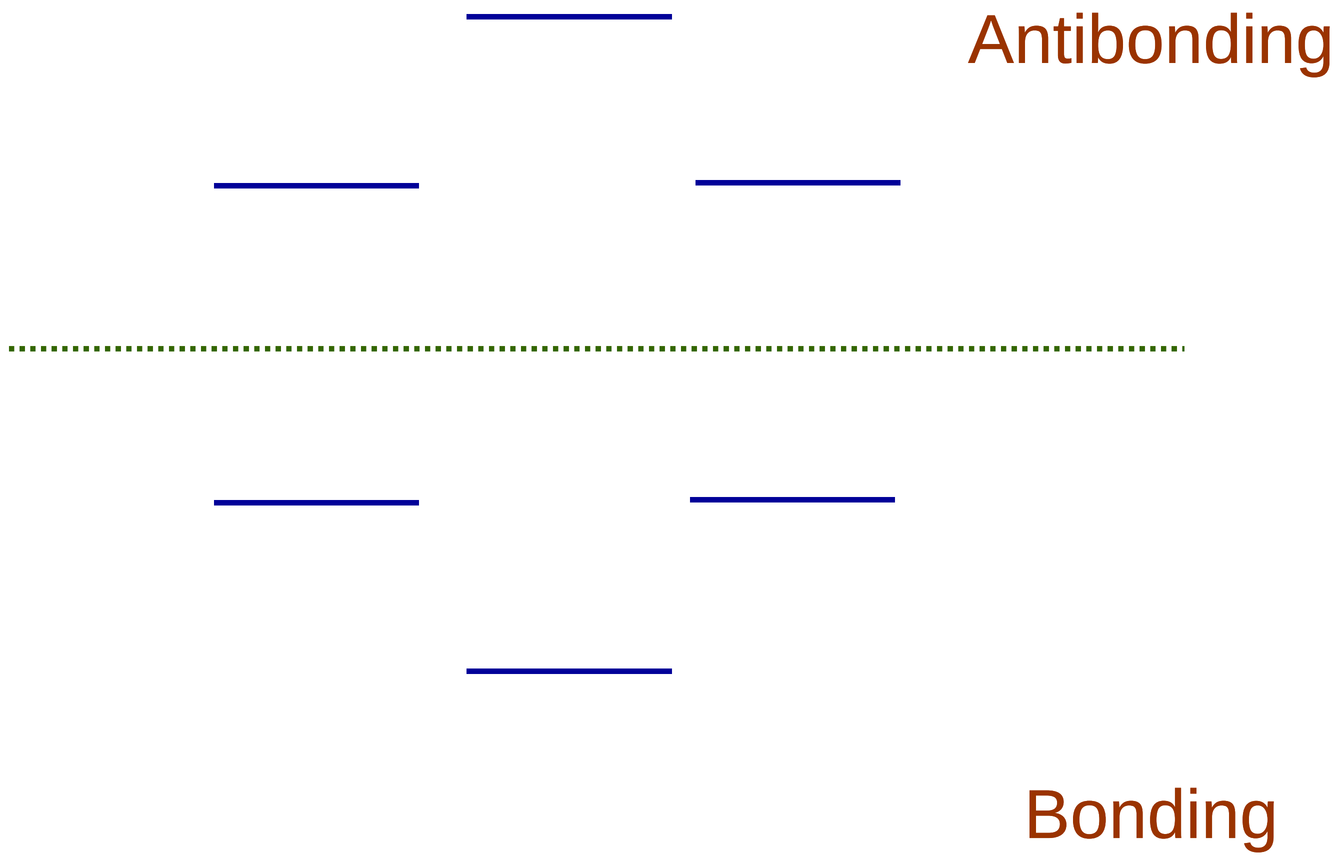


π MOs of Benzene

π-MO's of Benzene



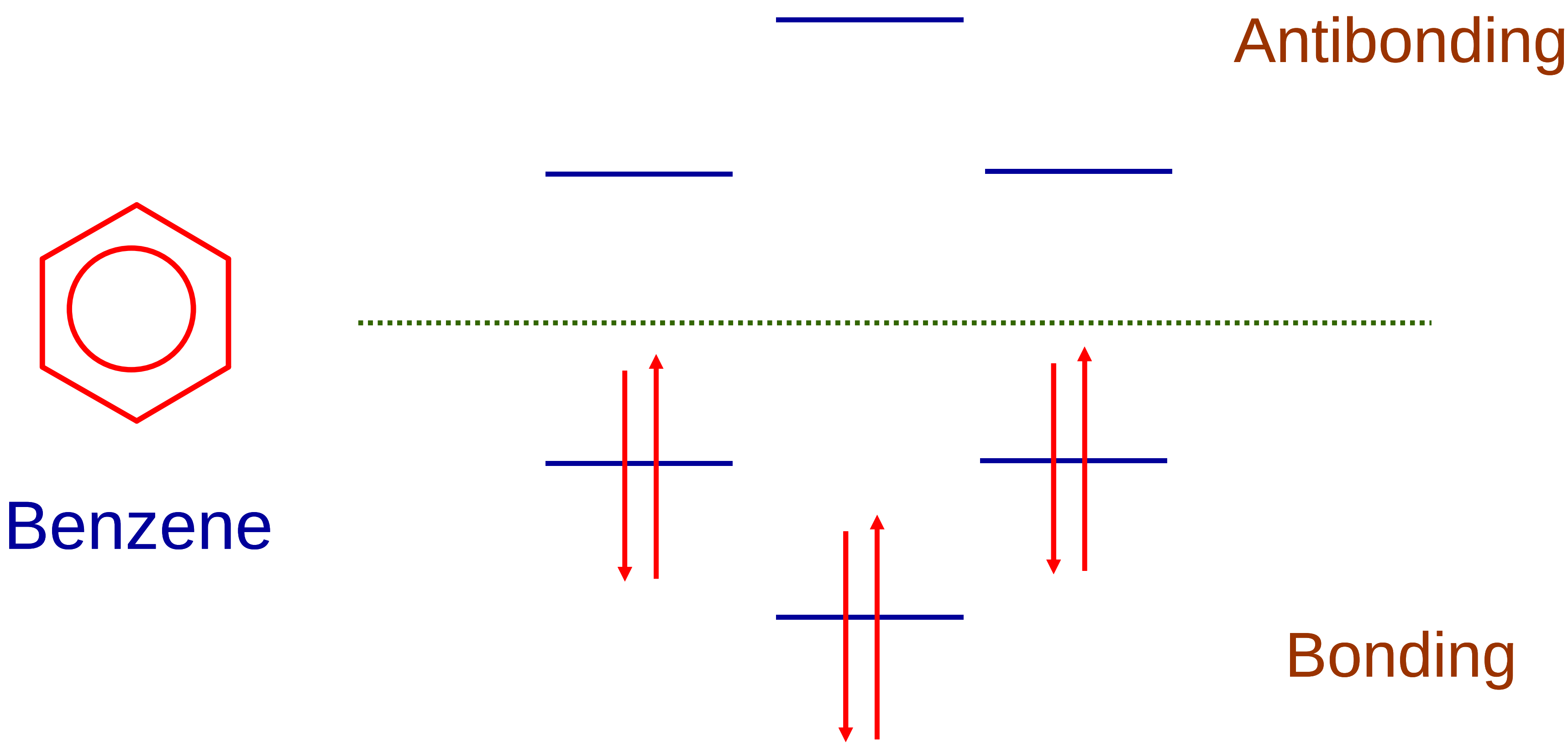
Benzene



6 *p* orbitals give 6 π orbitals.

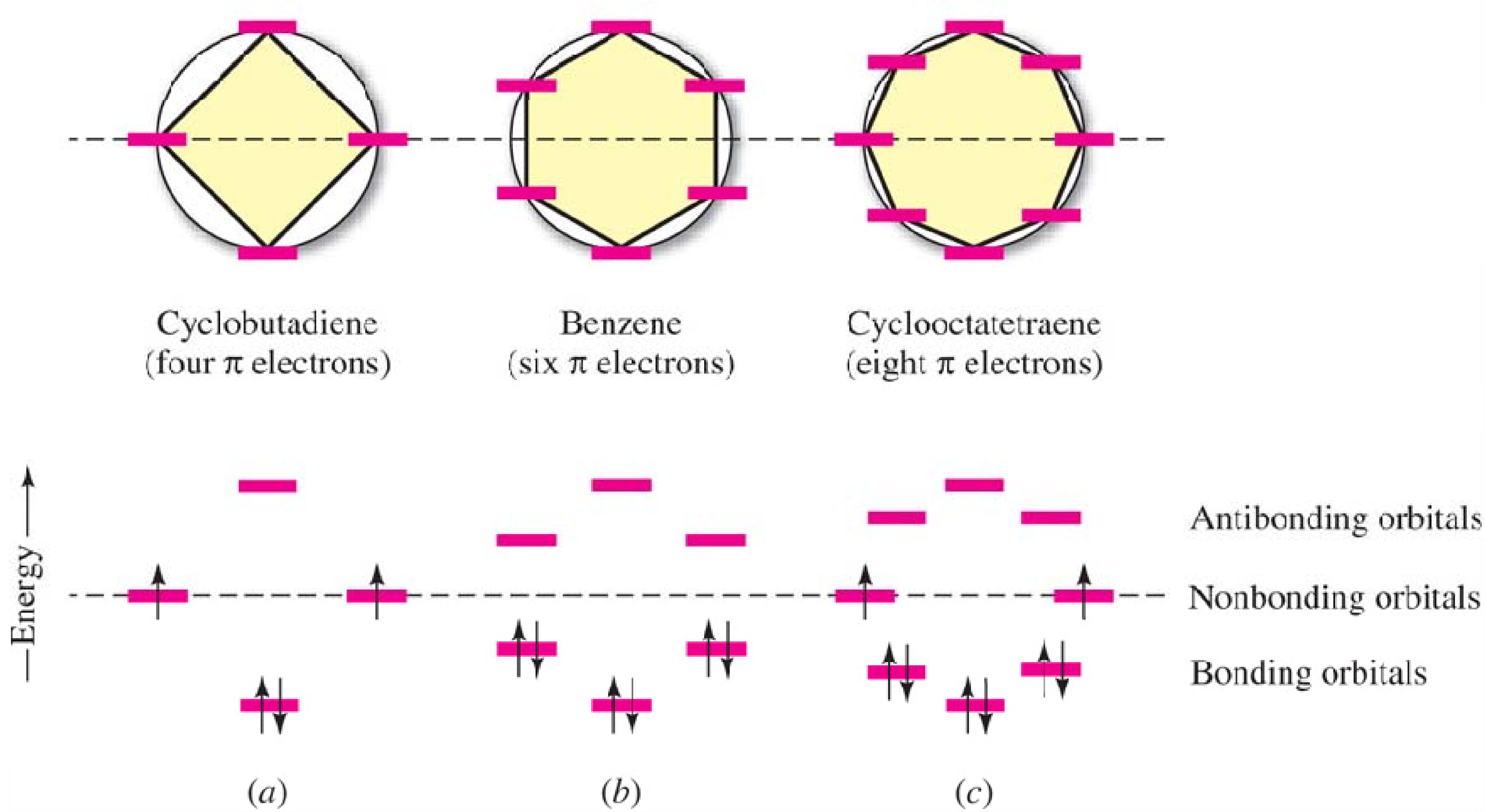
3 orbitals are bonding; 3 are antibonding.

π-MO's of Benzene

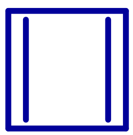
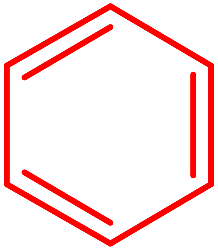
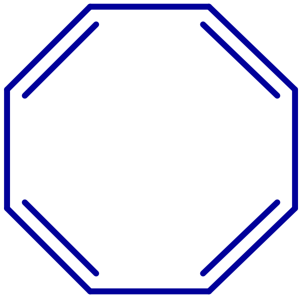


6 π electrons fill all of the bonding orbitals.

all π antibonding orbitals are empty.

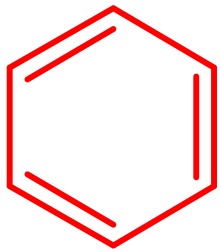

Cyclobutadiene
(four π electrons)
Benzene
(six π electrons)
Cyclooctatetraene
(eight π electrons)
Energy
Antibonding orbitals
Nonbonding orbitals
Bonding orbitals
(a)
(b)
(c)

π-Electron Requirement for Aromaticity

4 π electrons	6 π electrons	8 π electrons
		
not aromatic	aromatic	not aromatic

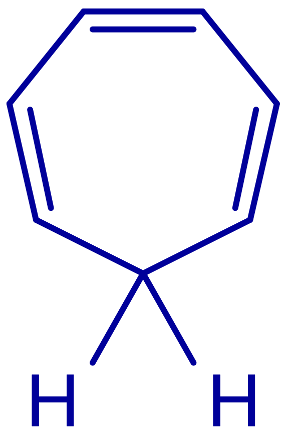
Completely Conjugated Polyenes

6 π electrons;
completely conjugated



aromatic

6 π electrons;
not completely conjugated

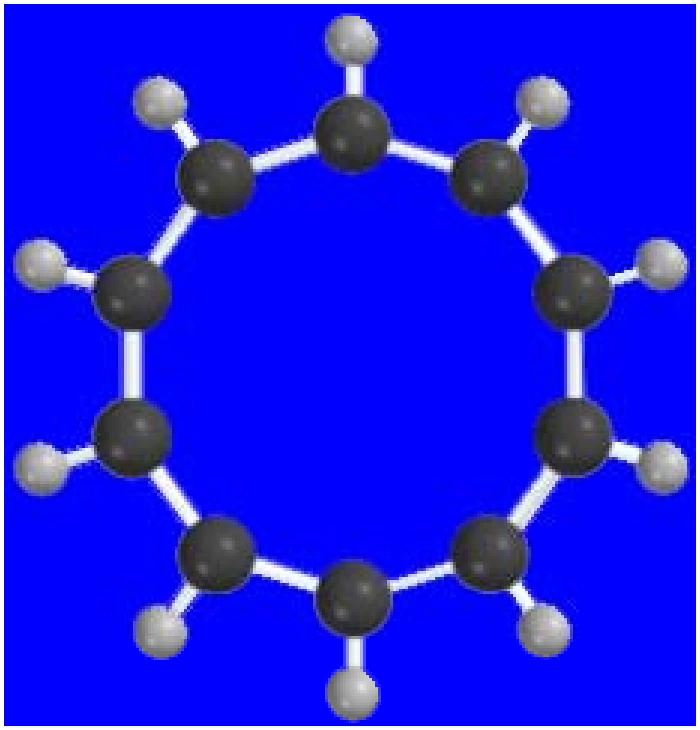


not aromatic

11.20. Annulenes

- Annulenes are planar, monocyclic, completely conjugated polyenes. That is, they are the kind of hydrocarbons treated by Hückel's rule.

[10] Annulenes

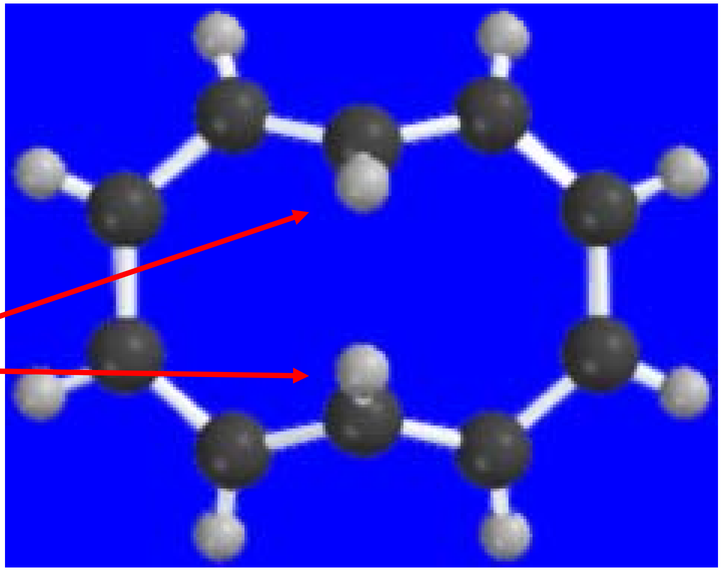


- Predicted to be aromatic by Hückel's rule, but too much angle strain when planar and all double bonds are *cis.*

- 10-sided regular polygon has angles of 144°.

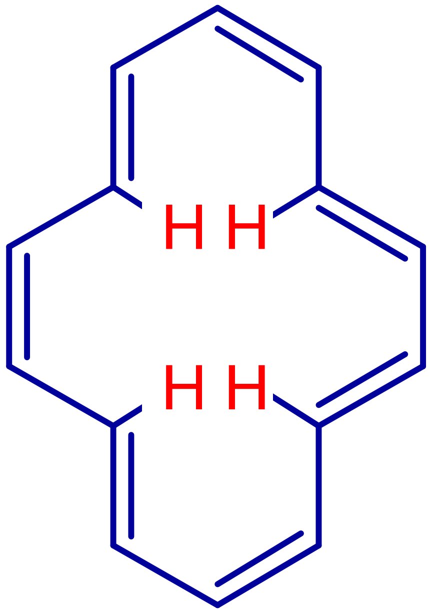
[10] Annulenes

van der Waals
strain between
these two hydrogens



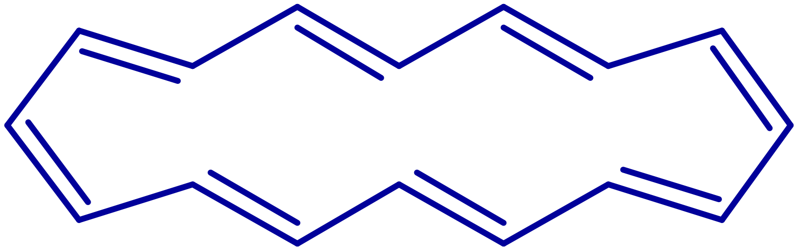
➢ Incorporating two *trans* double bonds into the ring relieves angle strain but introduces van der Waals strain into the structure and causes the ring to be distorted from planarity.

[14] Annulenes



- 14 π electrons satisfies Hückel's rule.
- van der Waals strain between hydrogens inside the ring.

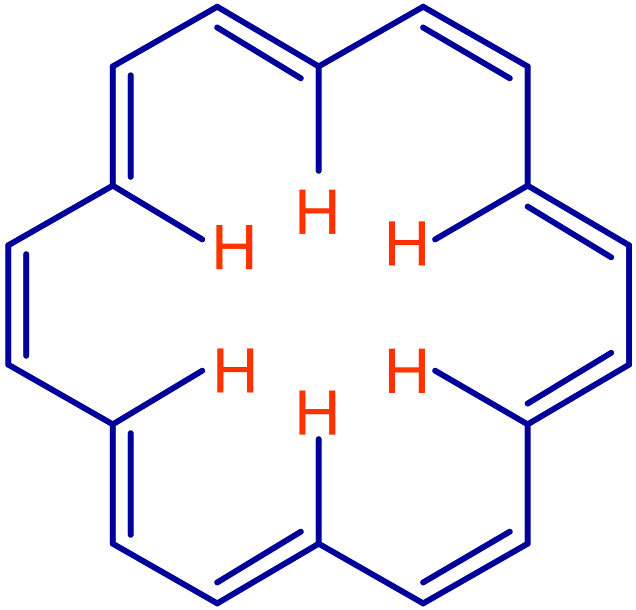
[16] Annulenes



- 16 π electrons does not satisfy Hückel's rule.
- Alternating short (134 pm) and long (146 pm) bonds

not aromatic.

[18] Annulenes

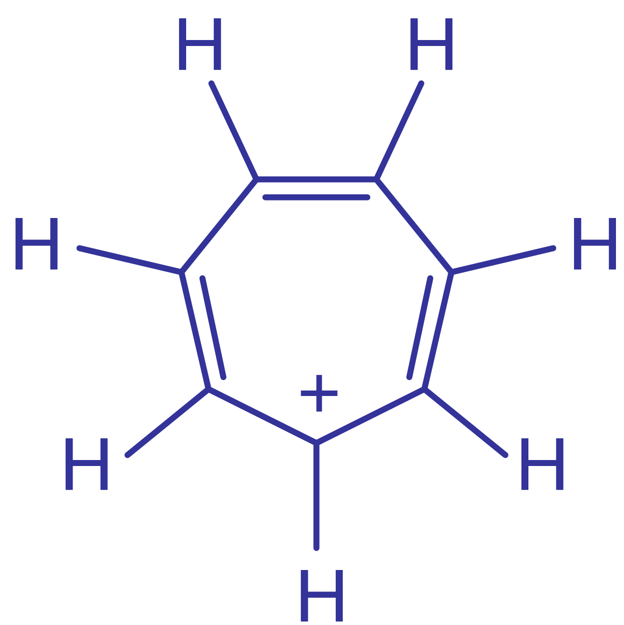


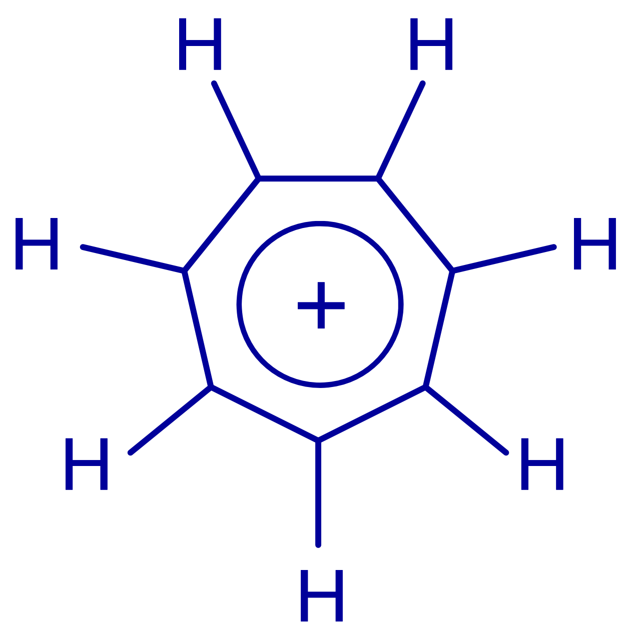
- 18 π electrons satisfies Hückel's rule.
- Resonance energy = 418 kJ/mol.
- Bond distances range between 137-143 pm.

11.21. Aromatic Ions

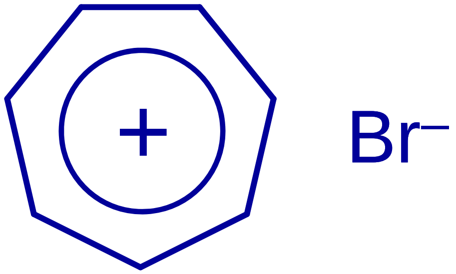
Cycloheptatrienyl Cation

- 6 π electrons delocalized over 7 carbons.
- Positive charge dispersed over 7 carbons.
- Very stable carbocation also called tropylium cation.

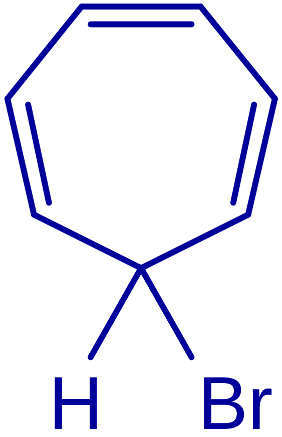




Cycloheptatrienyl Cation



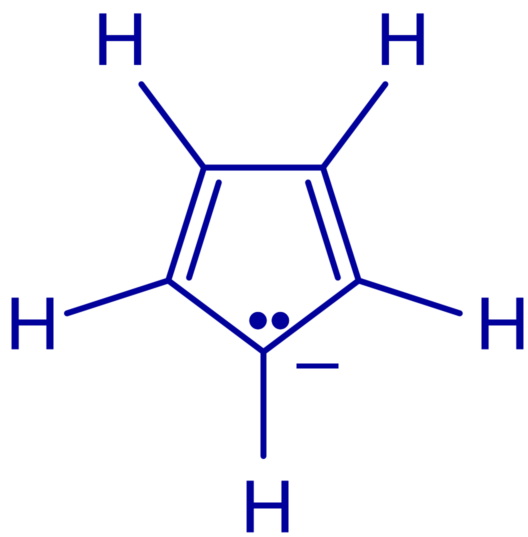
Ionic



Covalent

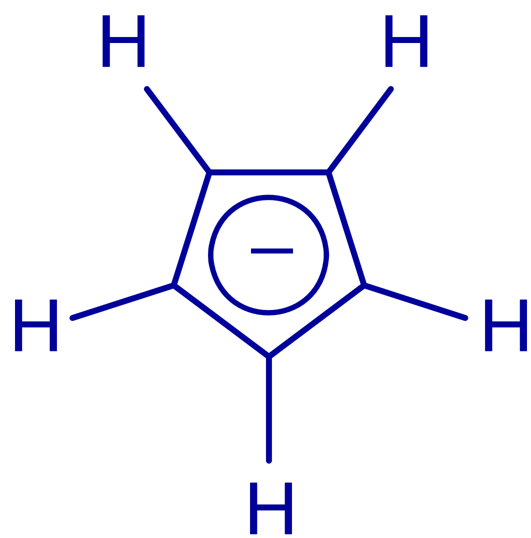
- Tropylium cation is so stable that tropylium bromide is ionic rather than covalent.
- mp 203 °C; soluble in water; insoluble in diethyl ether.

Cyclopentadienide Anion

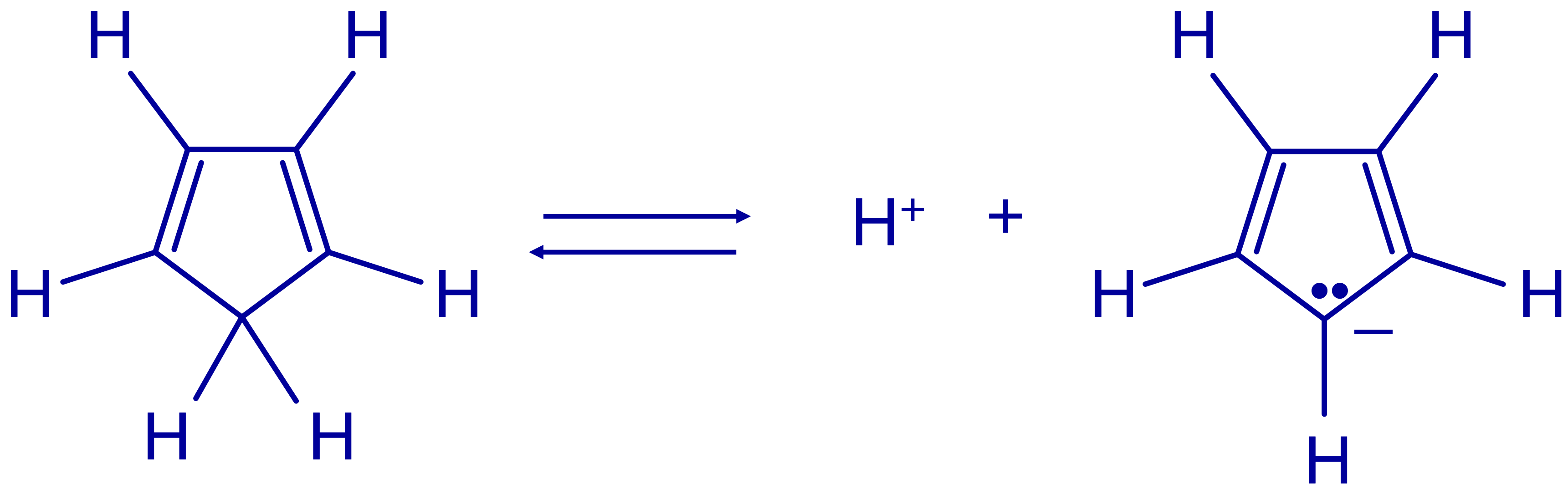


6 π electrons delocalized over 5 carbons.

Negative charge dispersed over 5 carbons stabilized anion.



Acidity of Cyclopentadiene

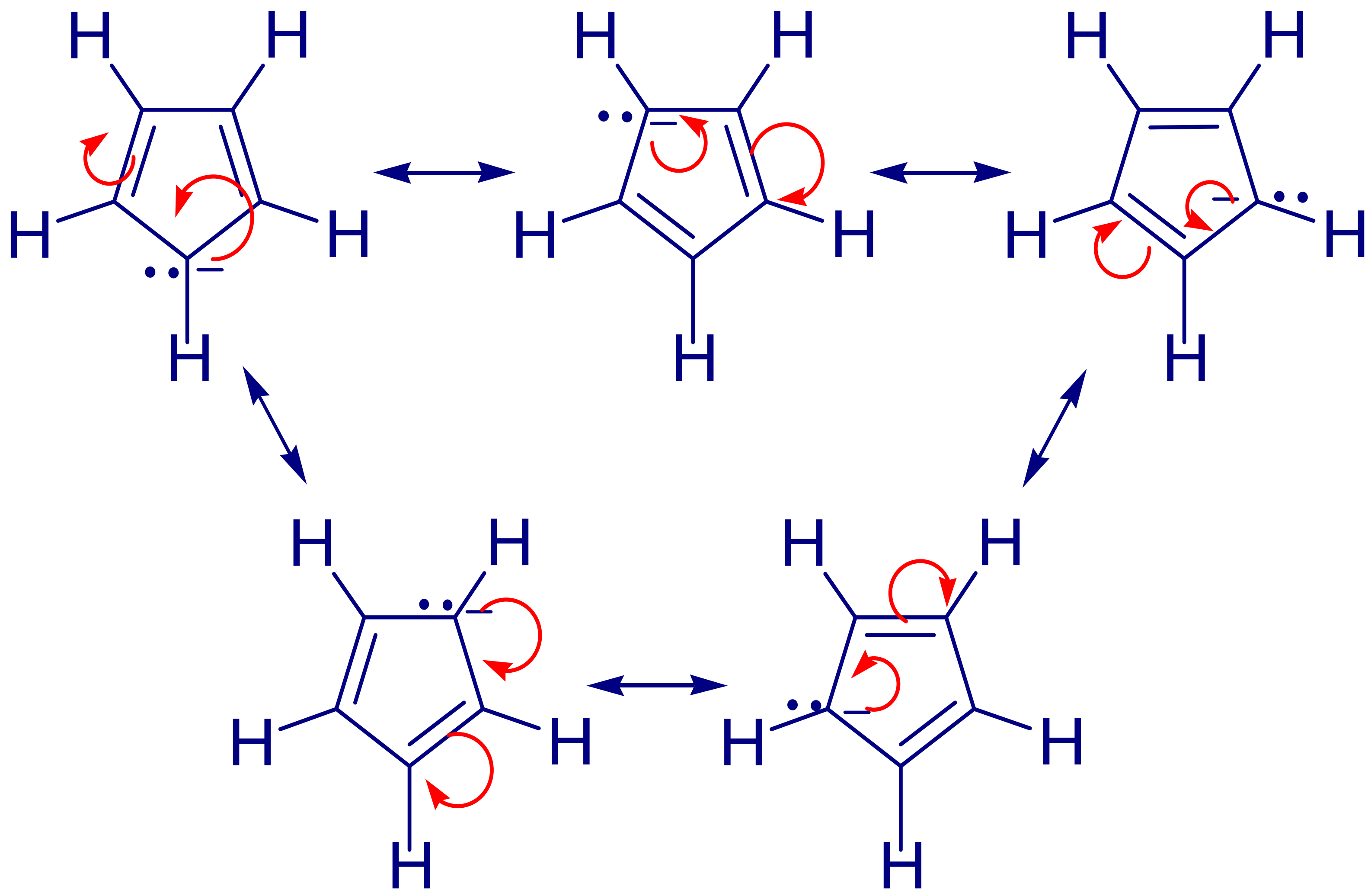


pK_a = 16

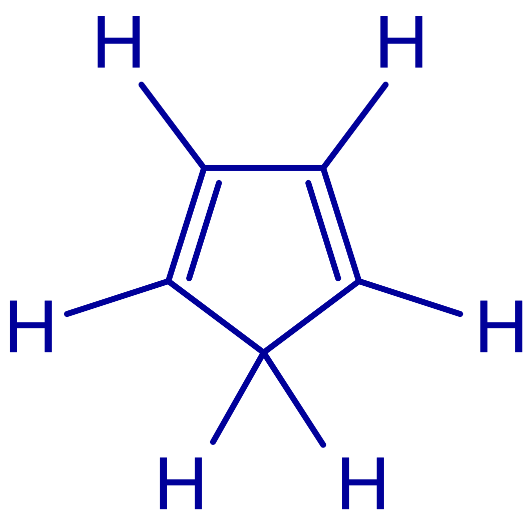
$K_a = 10^{-16}$

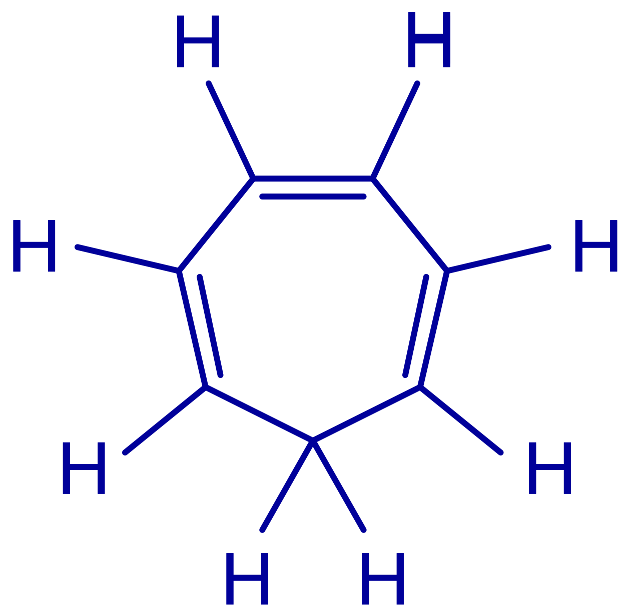
- Cyclopentadiene is unusually acidic for a hydrocarbon.
- Increased acidity is due to stability of cyclopentadienide anion.

Electron Delocalization in Cyclopentadienide Anion



Compare Acidity of Cyclopentadiene & Cycloheptatriene





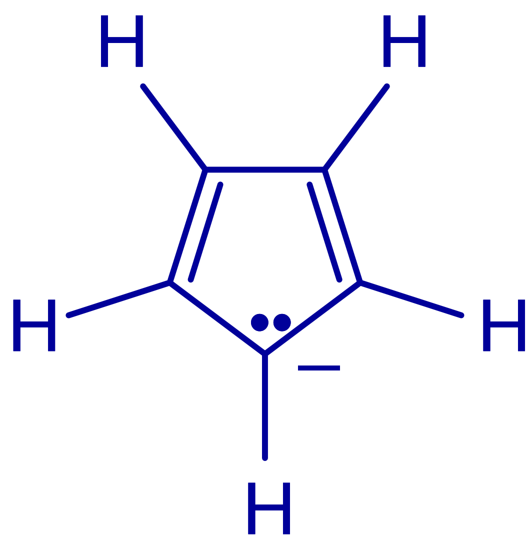
pK_a = 16

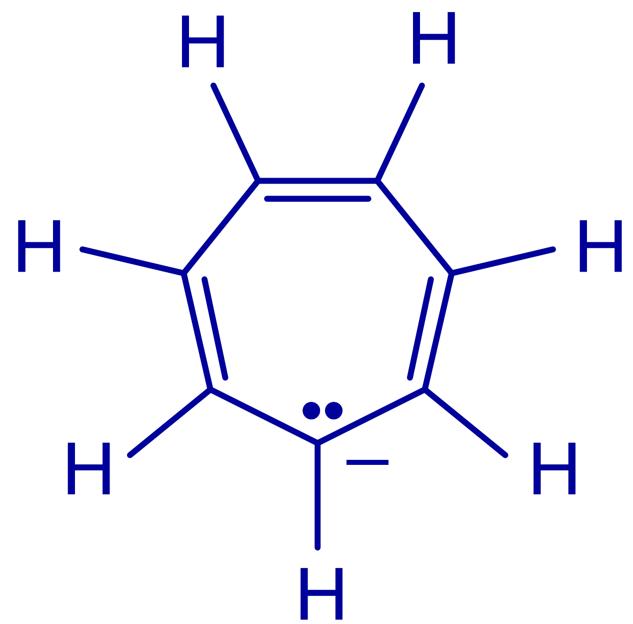
$K_a = 10^{-16}$

pK_a = 36

$K_a = 10^{-36}$

Compare Acidity of Cyclopentadiene & Cycloheptatriene

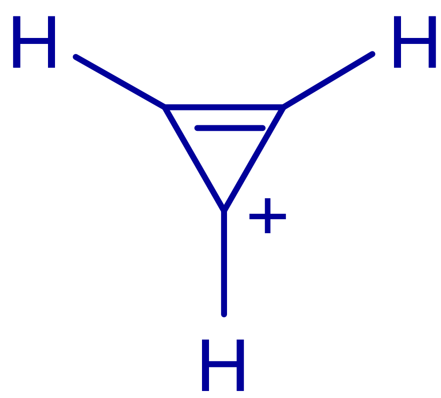




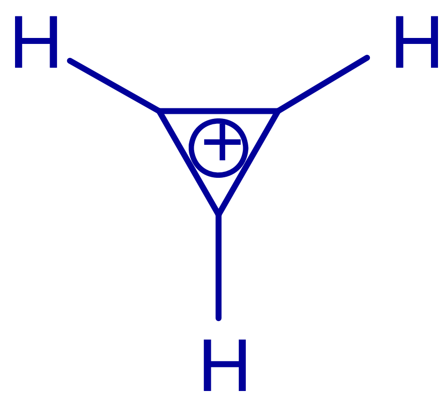
Aromatic anion
6 π electrons

Anion not aromatic
8 π electrons

Cyclopropenyl Cation



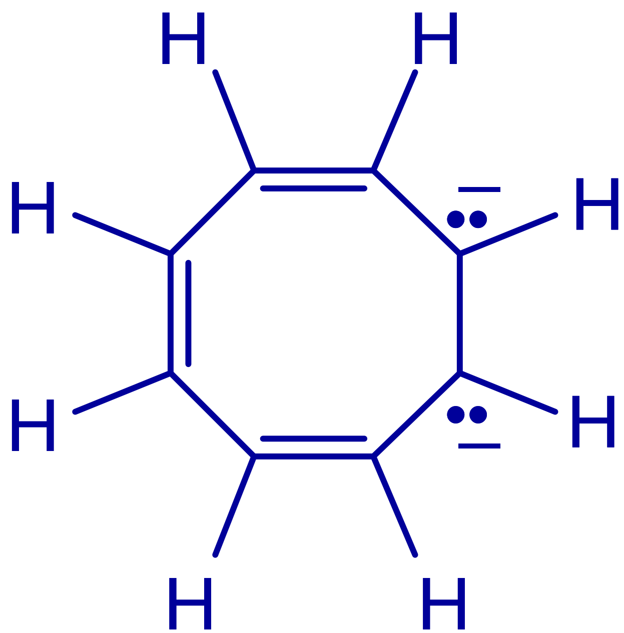
also written as



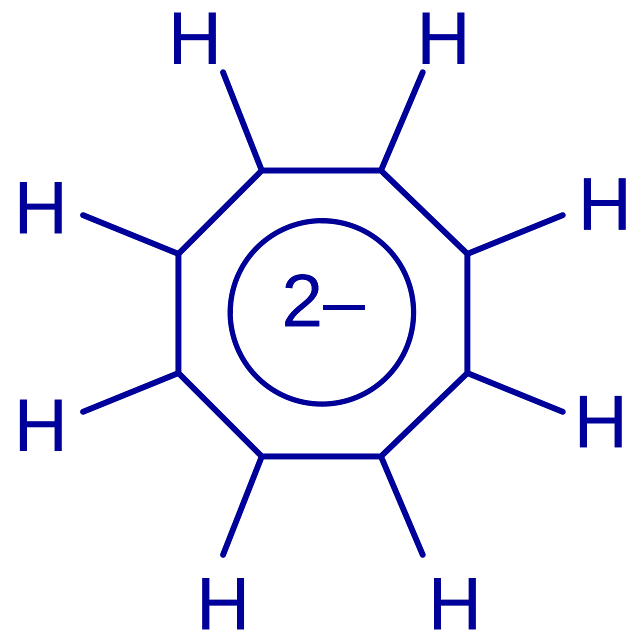
$n = 0$

$4n + 2 = 2\ \pi$ electrons

Cyclooctatetraene Dianion



also
written as

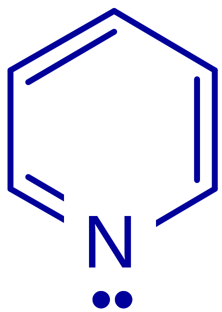


$n = 2$

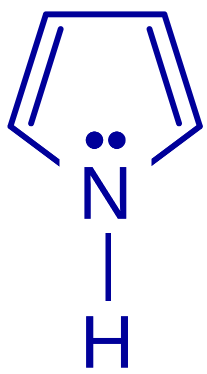
$4n + 2 = 10\ \pi$ electrons

11.22. Heterocyclic Aromatic Compounds

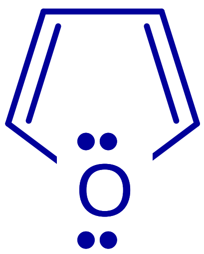
Examples



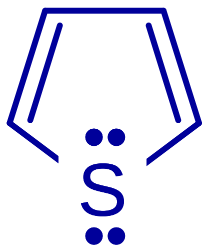
Pyridine



Pyrrole



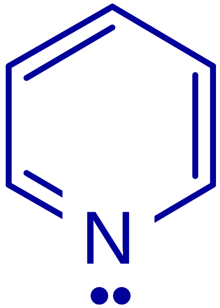
Furan



Thiophene

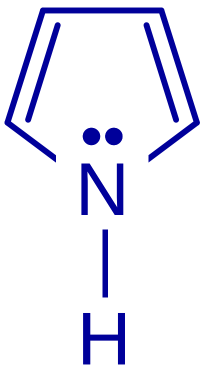
11.23. Heterocyclic Aromatic Compounds and Hückel's Rule

Pryridine



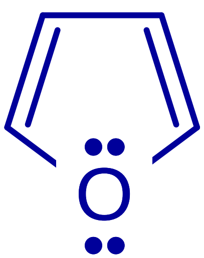
- 6 π electrons in ring.
- Lone pair on nitrogen is in an *sp*^{2} hybridized orbital; not part of π– system of ring.

Pyrrole



- Lone pair on nitrogen must be part of ring π– system if ring is to have 6 π-electrons.
- Lone pair must be in a *p* orbital in order to overlap with ring π-system.

Furan



- Two lone pairs on oxygen one pair is in a *p* orbital and is part of ring π-system; other is in an sp^2 hybridized orbital and is not part of ring π-system.