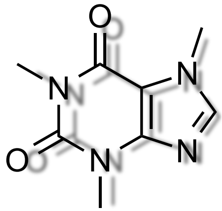


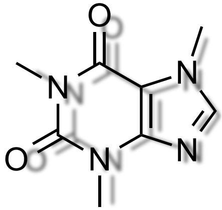
Chem 2500

Chapter 9

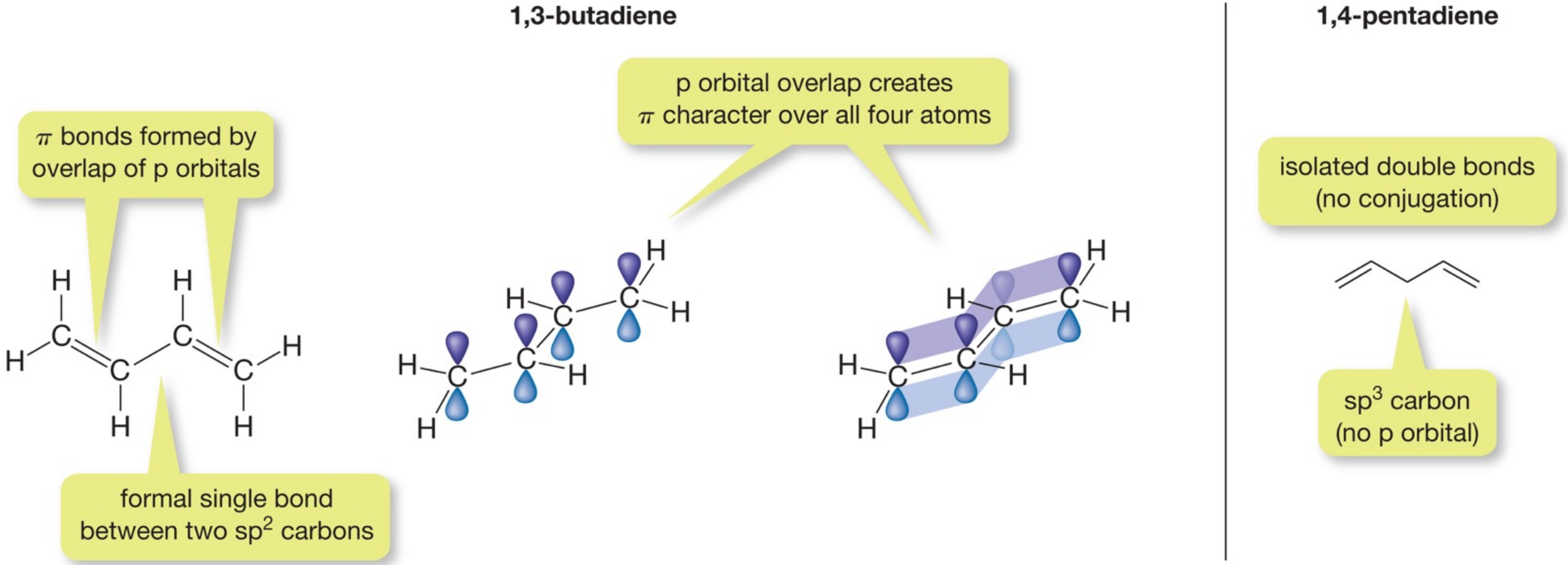
Conjugation and Aromaticity

(9.1-9.5)

Conjugated Systems – Molecular Orbitals



- Molecules with alternating double and single bonds are said to be conjugated.
- The p orbitals in the conjugated system are aligned with each other making the electrons delocalized.



1,3-butadiene

π bonds formed by overlap of p orbitals

formal single bond between two sp^2 carbons

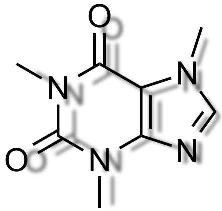
p orbital overlap creates π character over all four atoms

1,4-pentadiene

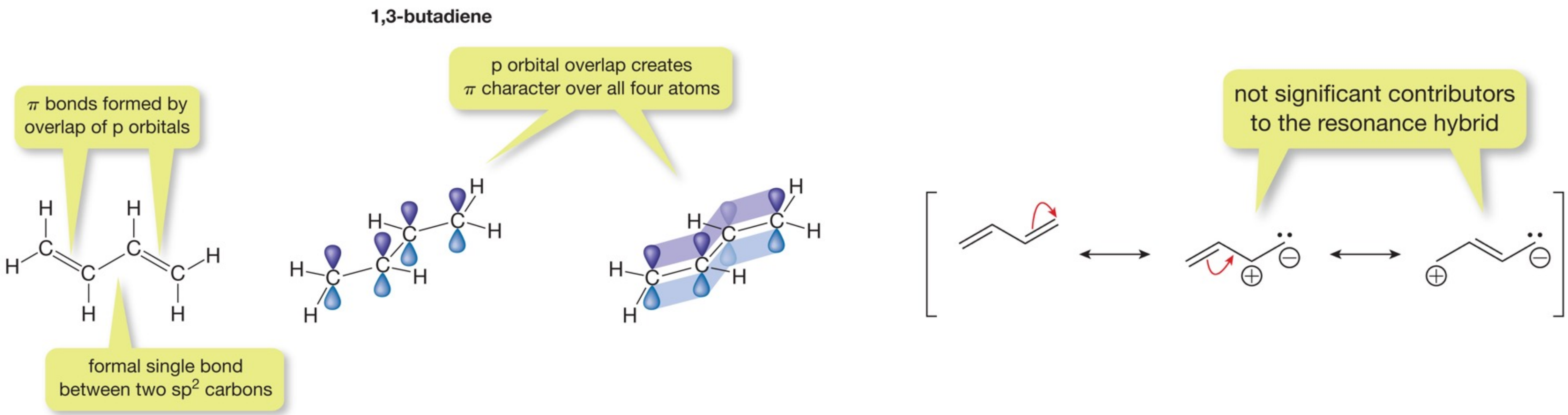
isolated double bonds (no conjugation)

sp^3 carbon (no p orbital)

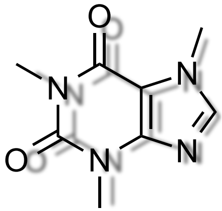
Conjugated Systems – Molecular Orbitals



- The representation of alternating double and single bonds, however, is not accurate.
- Lewis and/or resonance structures can sometimes describe the bonding in conjugated systems, however, they are more accurately described using π molecular orbitals.

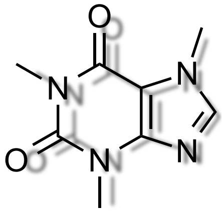


π Molecular Orbital Diagrams



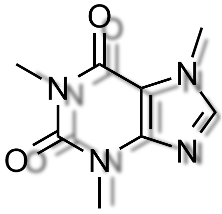
- According to molecular orbital (MO) theory, all π-symmetric orbitals in a π-system combine to give a set of π-MOs in which:
  - The number of π-MOs is equal to the number of *p* orbitals which combined to make them.
  - In a linear π-system, # energy levels = # π-MOs.
  - In a cyclic π-system, use the polygon-in-a-circle trick to predict energy levels; the polygon should always point down. *Note that, while benzene has a cyclic π-system, 1,3-cyclohexadiene does not!*
  - The number of delocalized π-electrons is equal to 2 electrons per double bond + 2 electrons per **lone pair that is part of the π-system**. *We are primarily interested in the HOMO and LUMO of any given π-system, so make sure you count your electrons carefully to correctly identify the HOMO and LUMO!*

π Molecular Orbital Diagrams

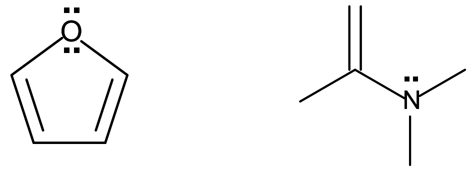


- The shape of each MO can be predicted using symmetry and nodes:
  - The lowest energy π-MO has all p orbitals aligned in phase, giving no nodes perpendicular to the plane of the π–system.
  - The next π–MO will have one node perpendicular to the plane of the π–system, the next π–MO will have two such nodes, etc.
  - The highest energy π–MO will have every *p* orbital out-of-phase with the *p* orbitals on neighbouring atoms.
  - As long as the π–system is symmetric (via mirror plane), every MO will be either **symmetric** or **antisymmetric** (with respect to phase).

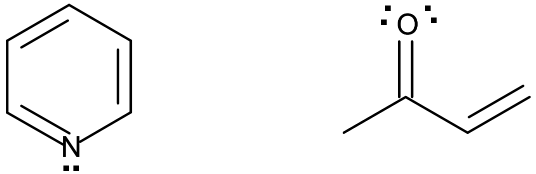
π Molecular Orbital Diagrams



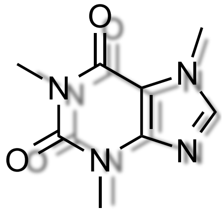
- A π-MO diagram is a simplified MO diagram that is missing the σ-MOs for clarity. You will need to be careful to include the correct number of electrons. Include two electrons for every pi bond on your Lewis structure and two electrons for every lone pair involved in the pi system.
  - A lone pair is involved in the pi system if the atom with the lone pair is bonded to at least one **other** atom which has a pi bond in the pi system. Only one lone pair per atom can be part of the same pi system.



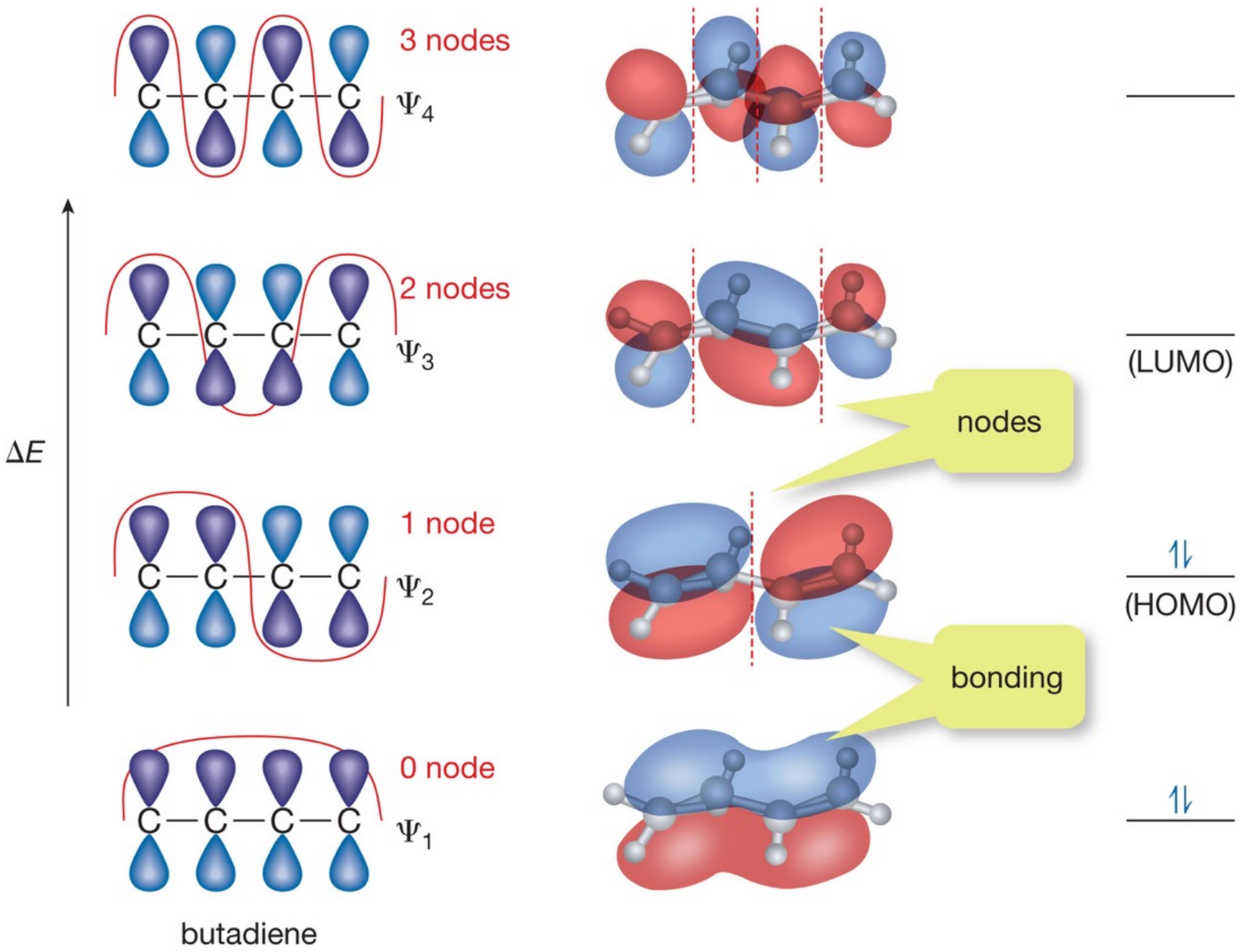
  - A lone pair is **not** involved in the pi system if the atom has a pi bond in the pi system.



Conjugated Systems – Molecular Orbitals

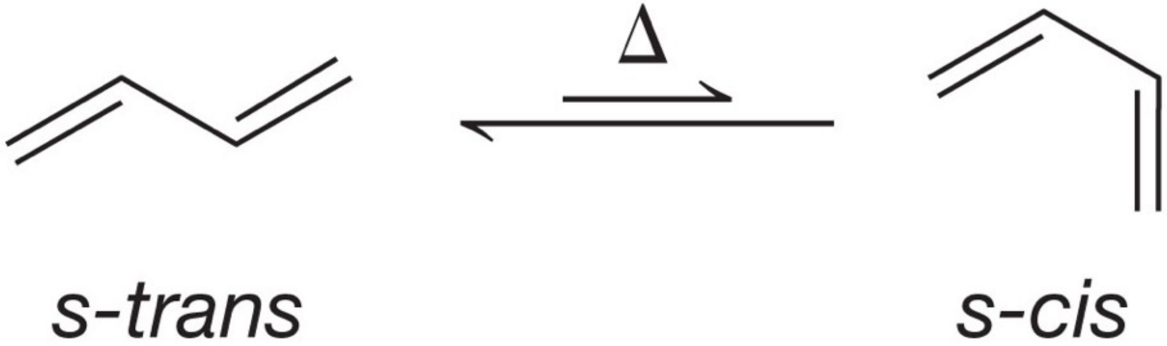


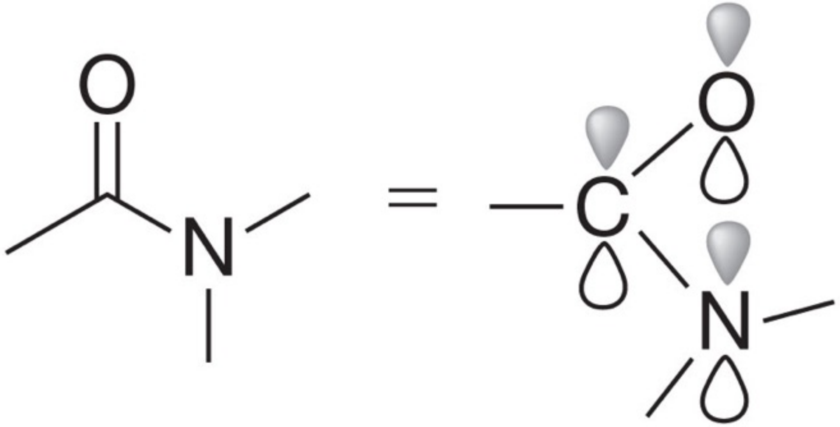
- 4 atomic p orbitals overlap to produce 4 MOs.
- The relative energies of the MOs are dependent on the orbital phases and symmetry.
- The ***highest occupied molecular orbital*** (HOMO) and ***lowest unoccupied molecular orbital*** (LUMO) give us a better understanding of the structure and reactivity of these conjugated systems.



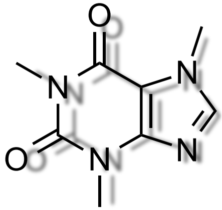
Conjugated Systems – Bond Rotation

- The extent of π character between atoms in conjugated systems can affect properties such as bond rotation and bond length.
- Singles bonds typically rotate freely at room temperature while double bonds do not.
- The 'single' bond in 1,3-butadiene has a higher than normal barrier to rotation because of the significant double bond character between these atoms.

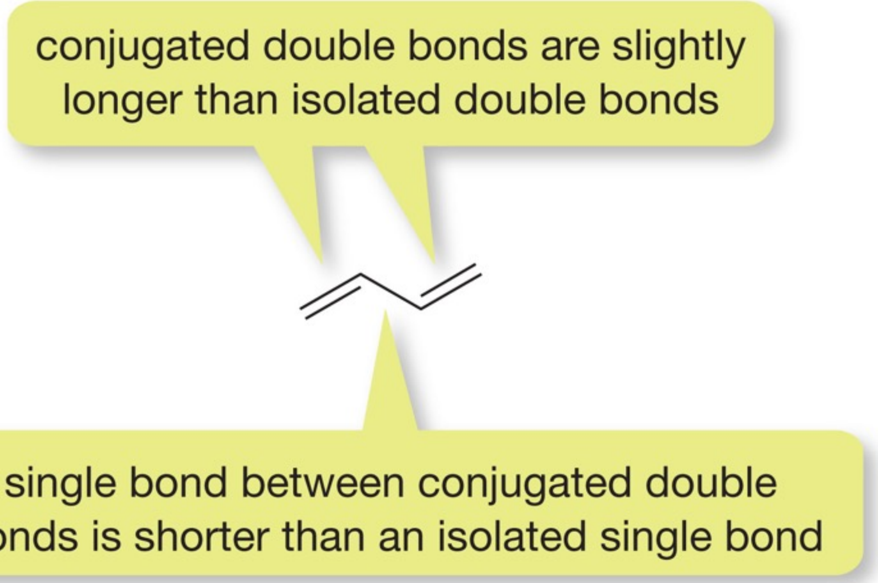




Conjugated Systems – Bond Lengths



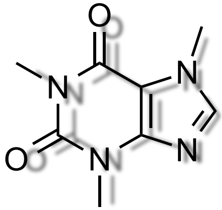
- For 1,3-butadiene, the MO diagram suggests that the central bond (C2-C3) has some double bond character and that the double bonds (C1-C2 and C3-C4) have some single bond character.
- Experimentally this is found to be true as the double bonds are longer than expected and the single bond is shorter than expected.



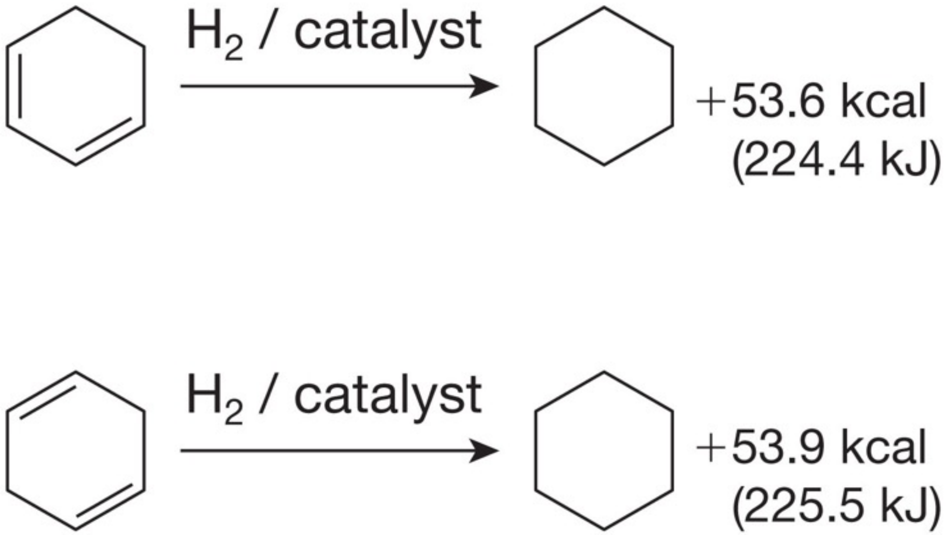
conjugated double bonds are slightly longer than isolated double bonds

single bond between conjugated double bonds is shorter than an isolated single bond

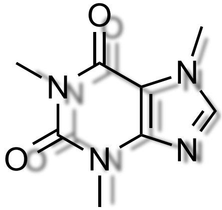
Conjugated Systems – Heat of Hydrogenation



- One method of determining the relative stability of molecules is to measure their heats of hydrogenation; that is, the amount of energy released when an alkene is saturated to and alkane by a catalytic hydrogenation reaction.



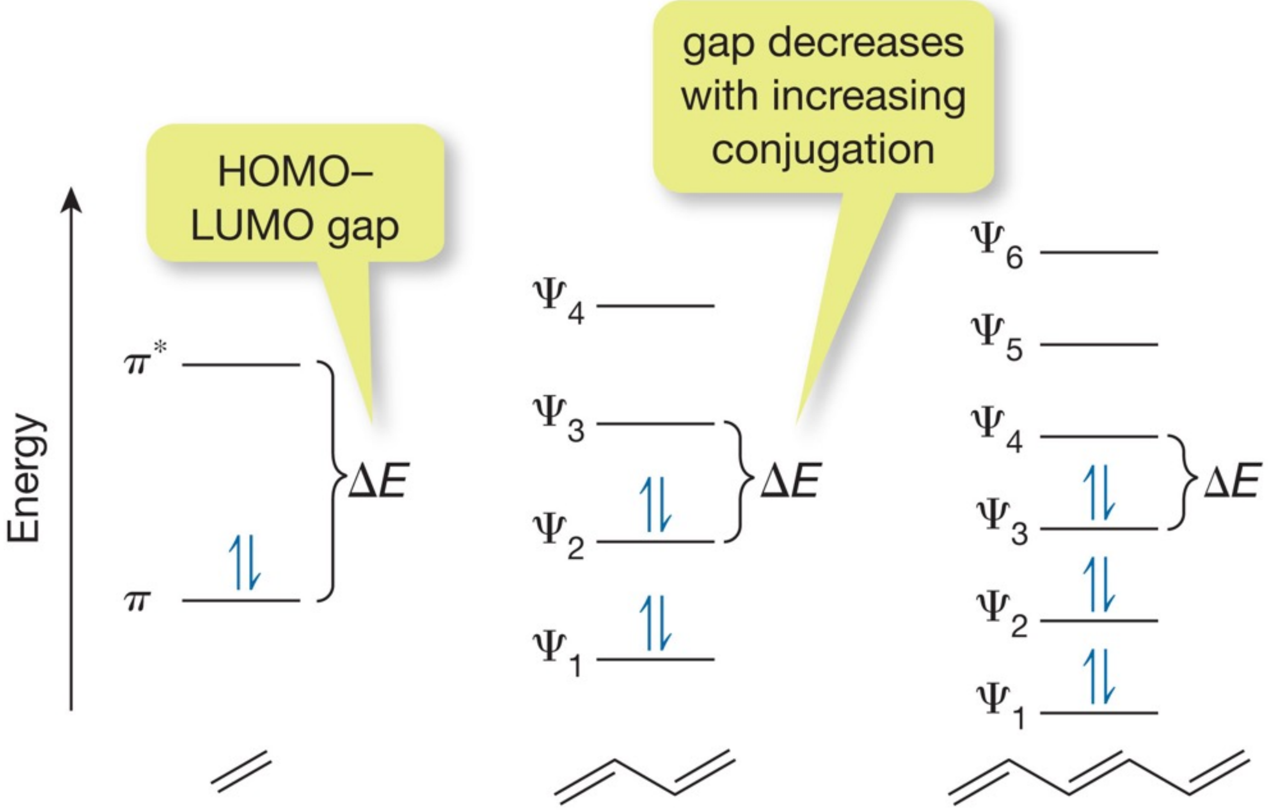
more stable



UV-visible Absorption

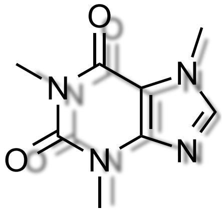
- When molecules are exposed to light, they absorb light of the energy that matches the energy gap between the HOMO and the LUMO.
- For alkenes, the HOMO-LUMO gap corresponds to the π and π* MOs.
- Note that as the conjugation increases, the HOMO-LUMO gap decreases.

$$E = \frac{hc}{\lambda}$$



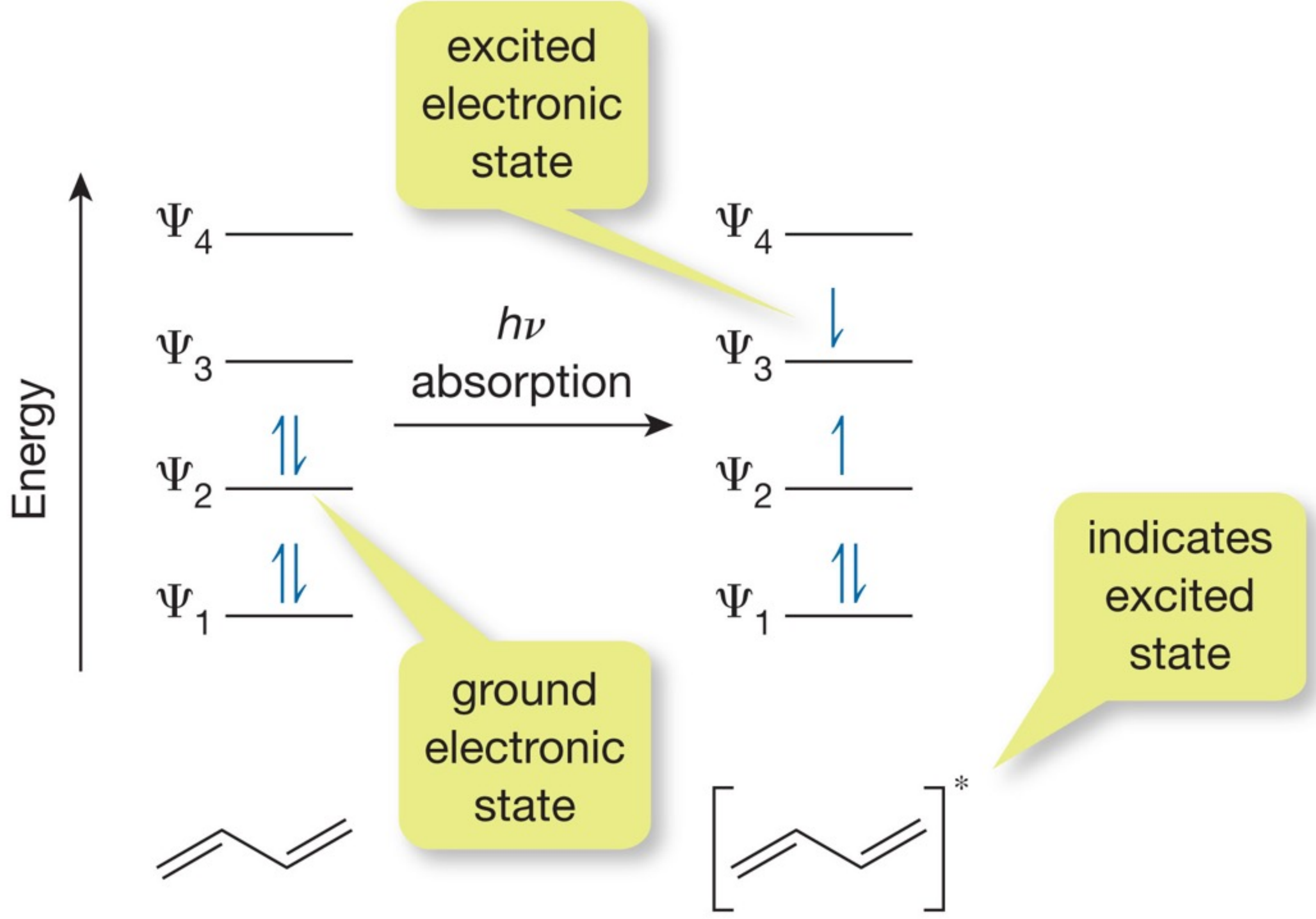
HOMO–LUMO gap

gap decreases with increasing conjugation



UV-visible Absorption

- When light is absorbed, electrons in the ***ground state*** are promoted to an ***excited state***.



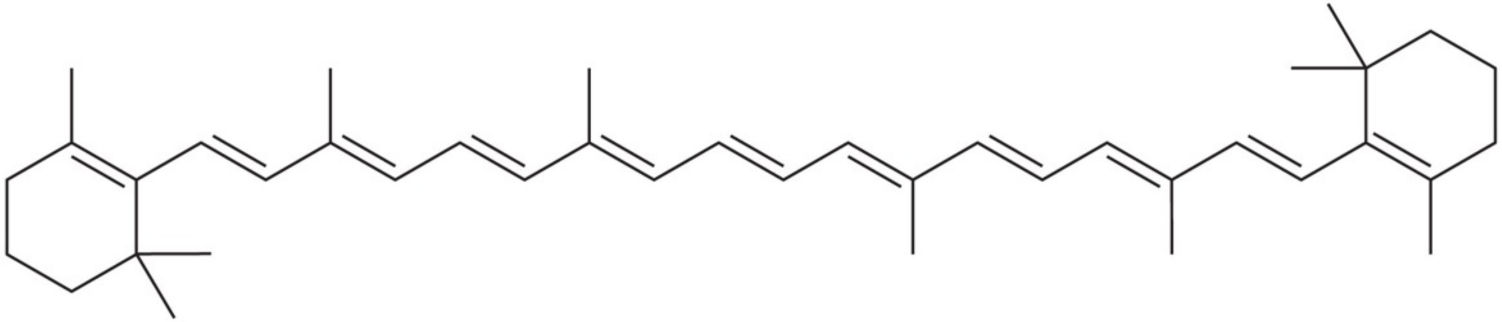
excited electronic state

ground electronic state

indicates excited state

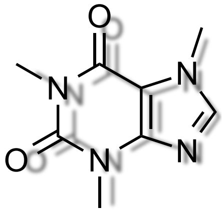
UV-visible Absorption

- With sufficient conjugation, the HOMO-LUMO gap becomes small enough that the absorbed light moves from the ultraviolet region into the visible region.
- When this happens, molecules appear coloured.
- For example, β-carotene, found in carrots, absorbs light with a λ_{max} of 465 nm and is orange in colour.



β-carotene
$\lambda_{\text{max}} = 465$ nm

UV-visible Absorption



- The colour that we ‘see’ is from the wavelengths that are ***not*** absorbed and are reflected into the eyes of the observer.
- β-carotene absorbs in the blue-violet region, but the reflected light from the remaining visible region is orange.

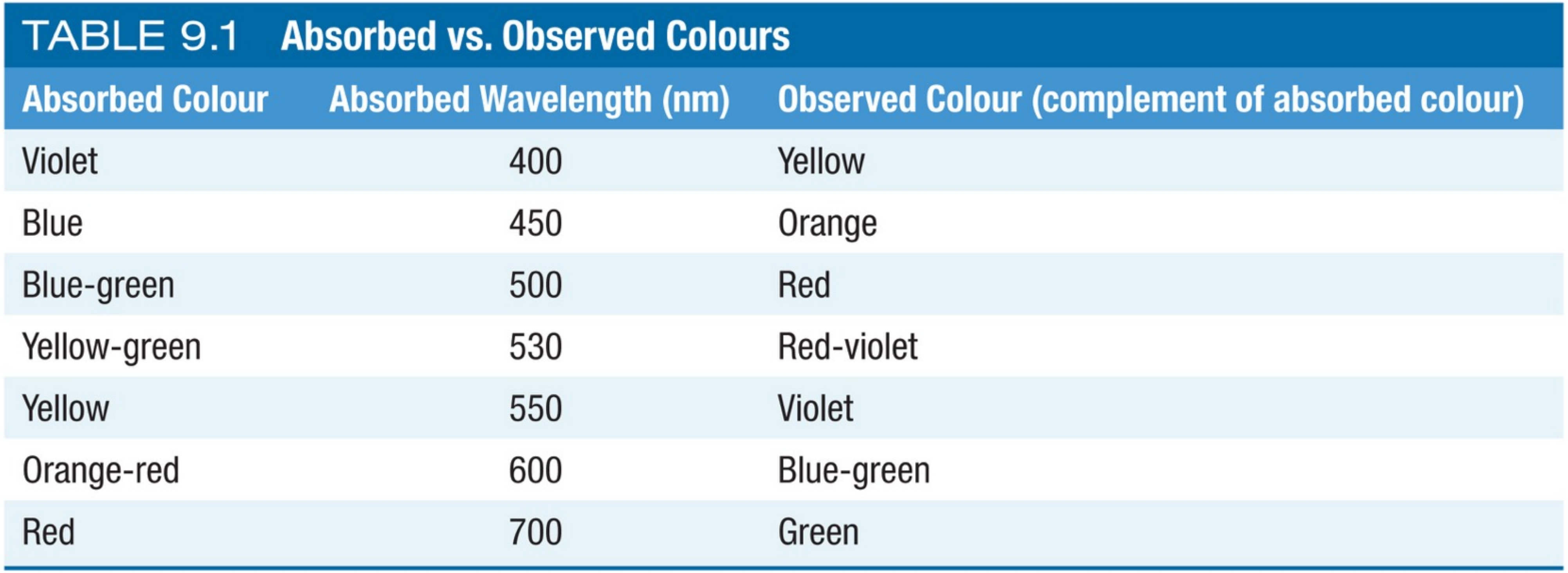
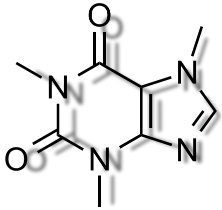


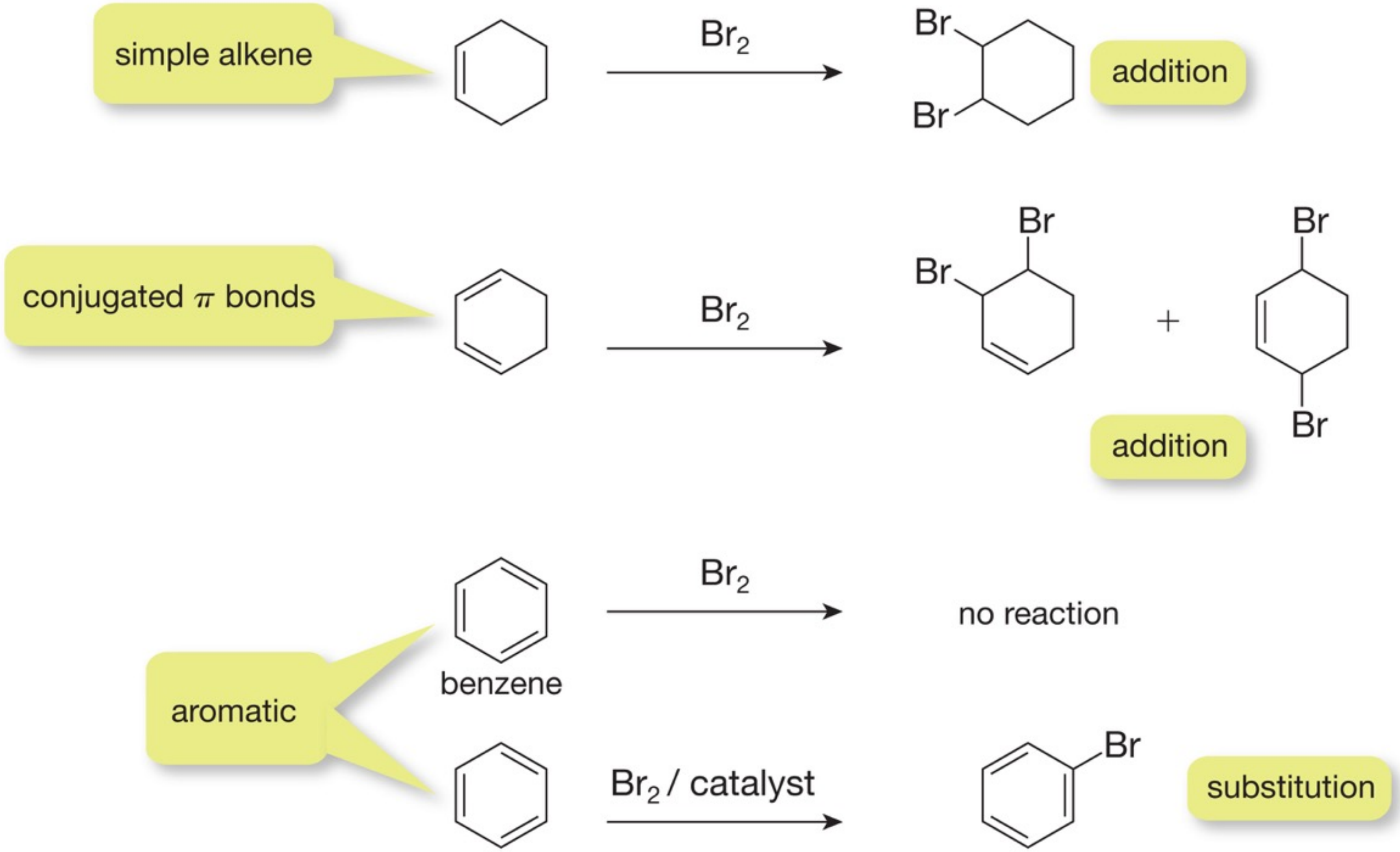
TABLE 9.1 Absorbed vs. Observed Colours

Absorbed Colour	Absorbed Wavelength (nm)	Observed Colour (complement of absorbed colour)
Violet	400	Yellow
Blue	450	Orange
Blue-green	500	Red
Yellow-green	530	Red-violet
Yellow	550	Violet
Orange-red	600	Blue-green
Red	700	Green

Aromaticity

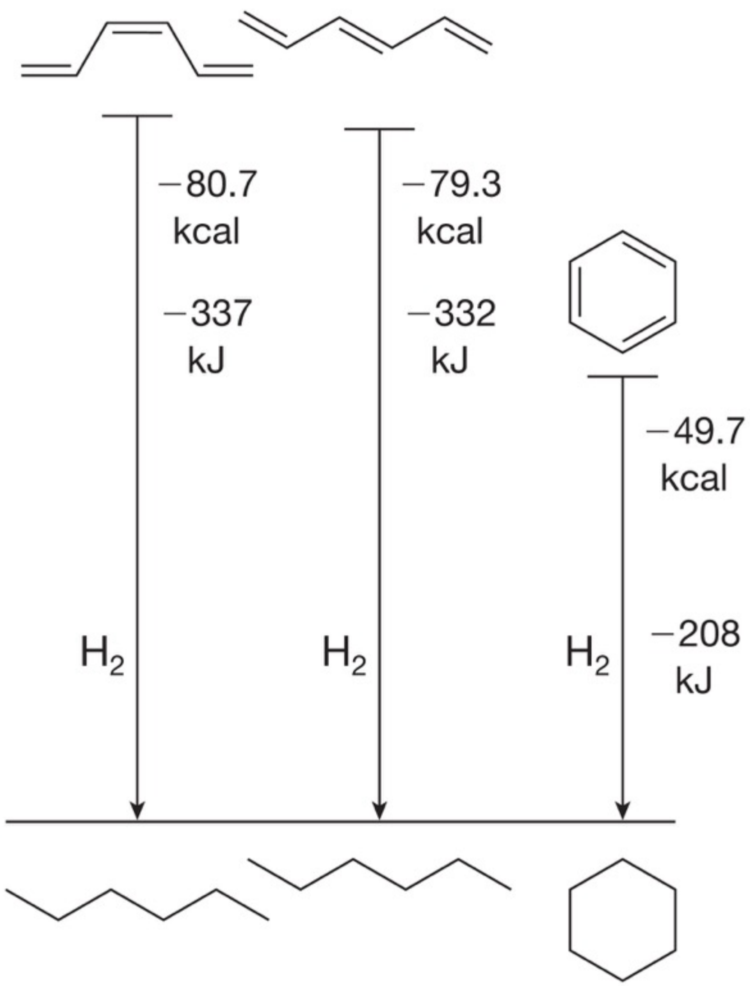


- ***Aromaticity*** is a special property we sometimes see in molecules with ***cyclic, conjugated π systems***.
- Aromatic molecules have a higher than expected stability and this aromaticity alters their chemical reactivity.



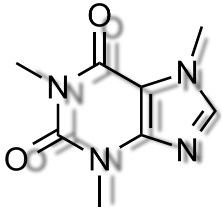
Aromatic Stability

- A comparison of heats of hydrogenation, shows that aromatic molecules have a much higher than expected stability.



hydrogenation of benzene releases much less heat because it is more stable to begin with

Criteria for Aromaticity



- For a molecule to be aromatic, it must meet the following requirements:
  - Be cyclic.
  - Have an atomic p orbital on all participating ring atoms, (each ring atom is sp or sp^2 hybridized).
  - Be planar.
  - Have $4n + 2$ π electrons in the cyclic π system (where n is an positive integer).
- This last point was articulated by Erich Hückel in 1931 and is known as Hückel's rule.

Criteria for Aromaticity

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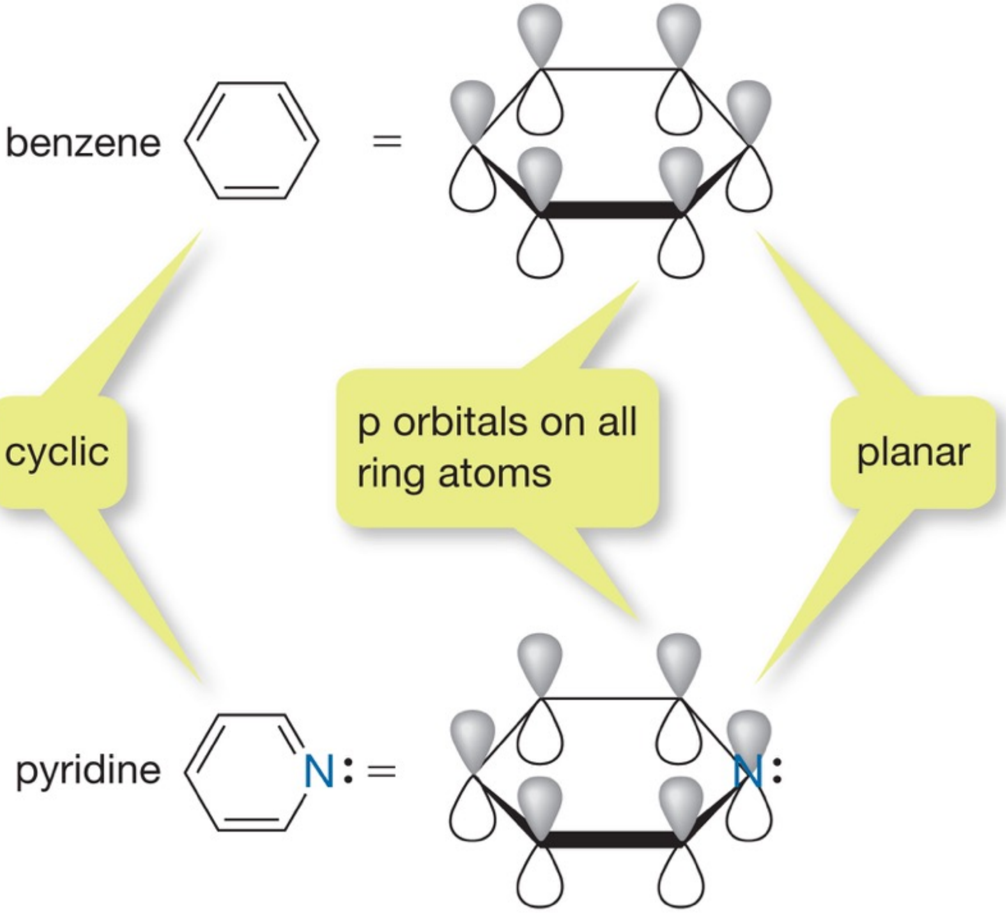
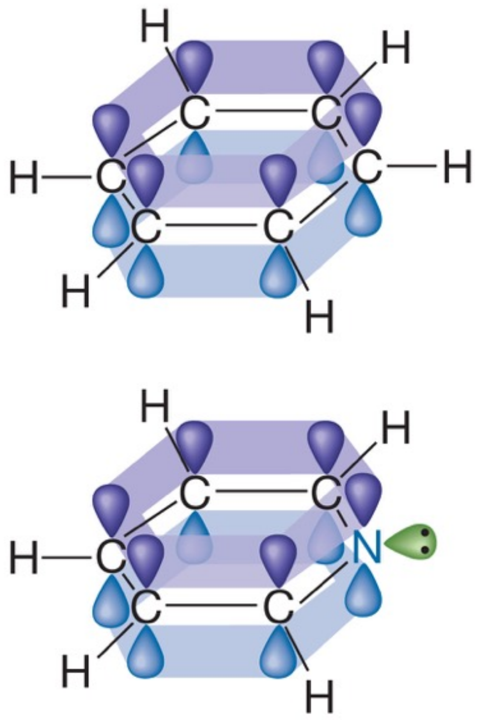


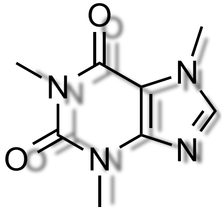


Anti-Aromaticity

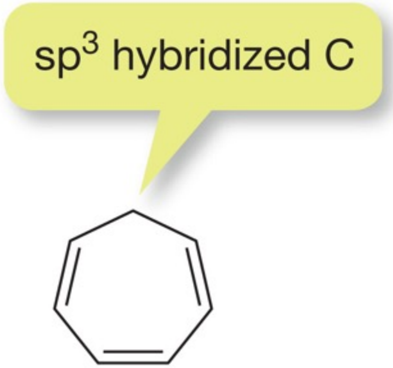
- Why $4n + 2$ π electrons? For some molecules, the delocalization of π electrons is destabilizing. These molecules are known as anti-aromatic molecules.
- Anti-aromatic molecules follow the exact same criteria as those of aromatic molecules except they have $4n$ π electrons, not $4n + 2$.
- Where aromatic molecules are more stable than expected, anti-aromatic molecules are ***less stable*** than expected.
- Most often, anti-aromaticity prevents molecules from adopting expected geometries or from even forming.

4 π electrons
(anti-aromatic)

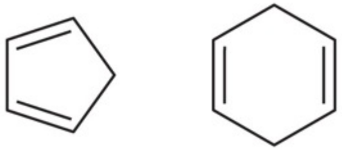
Non-Aromatic Compounds

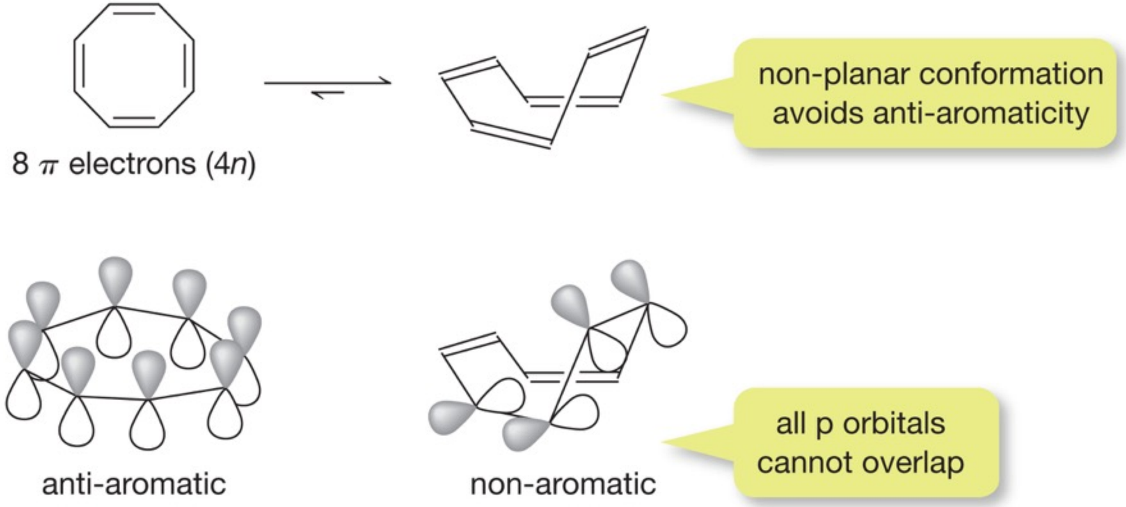


- Any other conjugated molecule that is neither aromatic nor anti-aromatic is non-aromatic.
- Typically these molecules are acyclic, or non-planar, or have at least one sp^3 atom as part of the ring.


sp^3 hybridized C

non-aromatic!

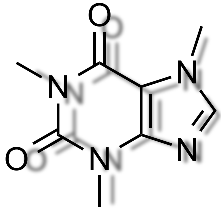

other non-aromatics



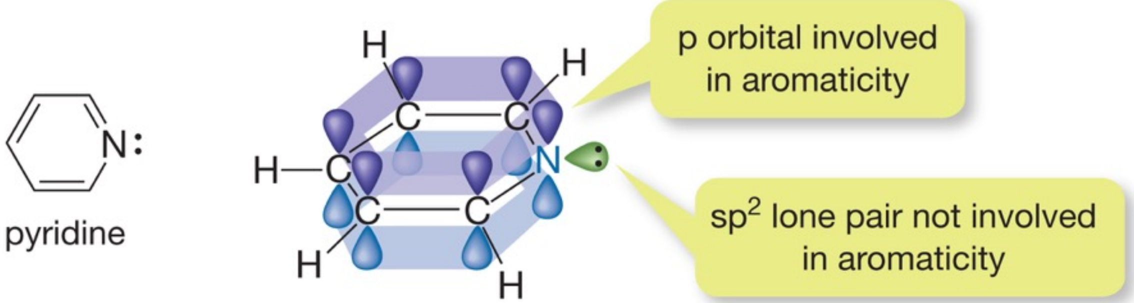
non-planar conformation avoids anti-aromaticity

all p orbitals cannot overlap

Contribution of Electrons Pairs to Aromaticity

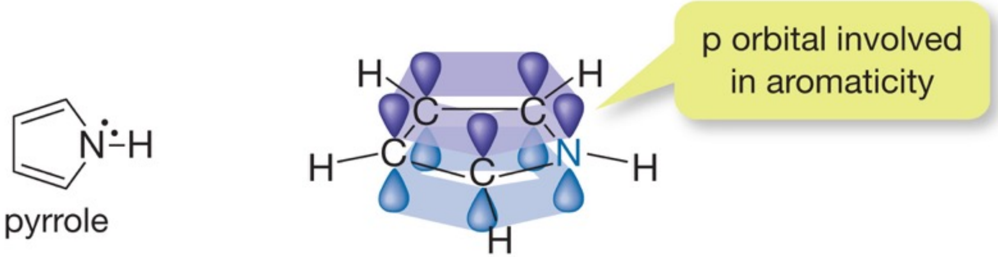


- The only difference between aromatic and anti-aromatic molecules is the number of π electrons in the cyclic π system.
- Therefore, understanding which electrons are part of the π system is of paramount importance (see slide #6!).
- Pyridine, pyrrole, and furan all have 6 π electrons!

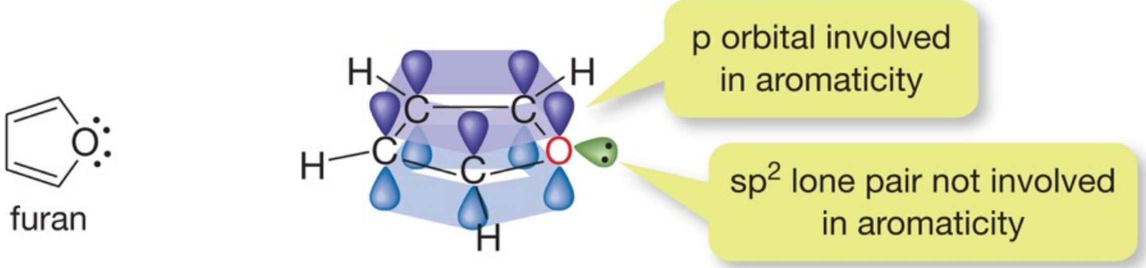

pyridine

p orbital involved in aromaticity

sp^2 lone pair not involved in aromaticity


pyrrole

p orbital involved in aromaticity

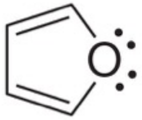

furan

p orbital involved in aromaticity

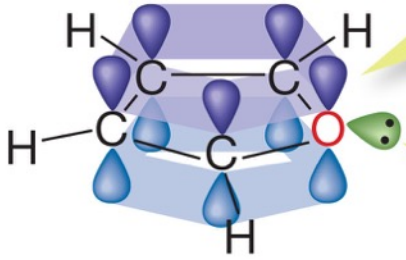
sp^2 lone pair not involved in aromaticity

Contribution of Electrons Pairs to Aromaticity

- Atoms in molecules adopt ***whatever geometry*** results in the greatest stability.
- The oxygen atom in furan is trigonal planar, not tetrahedral as predicted by VSEPR theory.
- In the corresponding seven membered ring, the oxygen atom is tetrahedral, not trigonal planar.

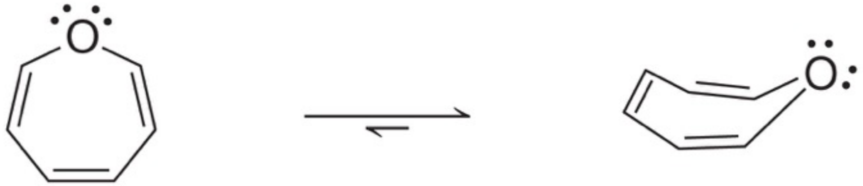


furan



p orbital involved in aromaticity

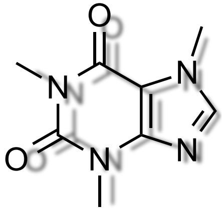
sp^2 lone pair not involved in aromaticity



sp^3 oxygen

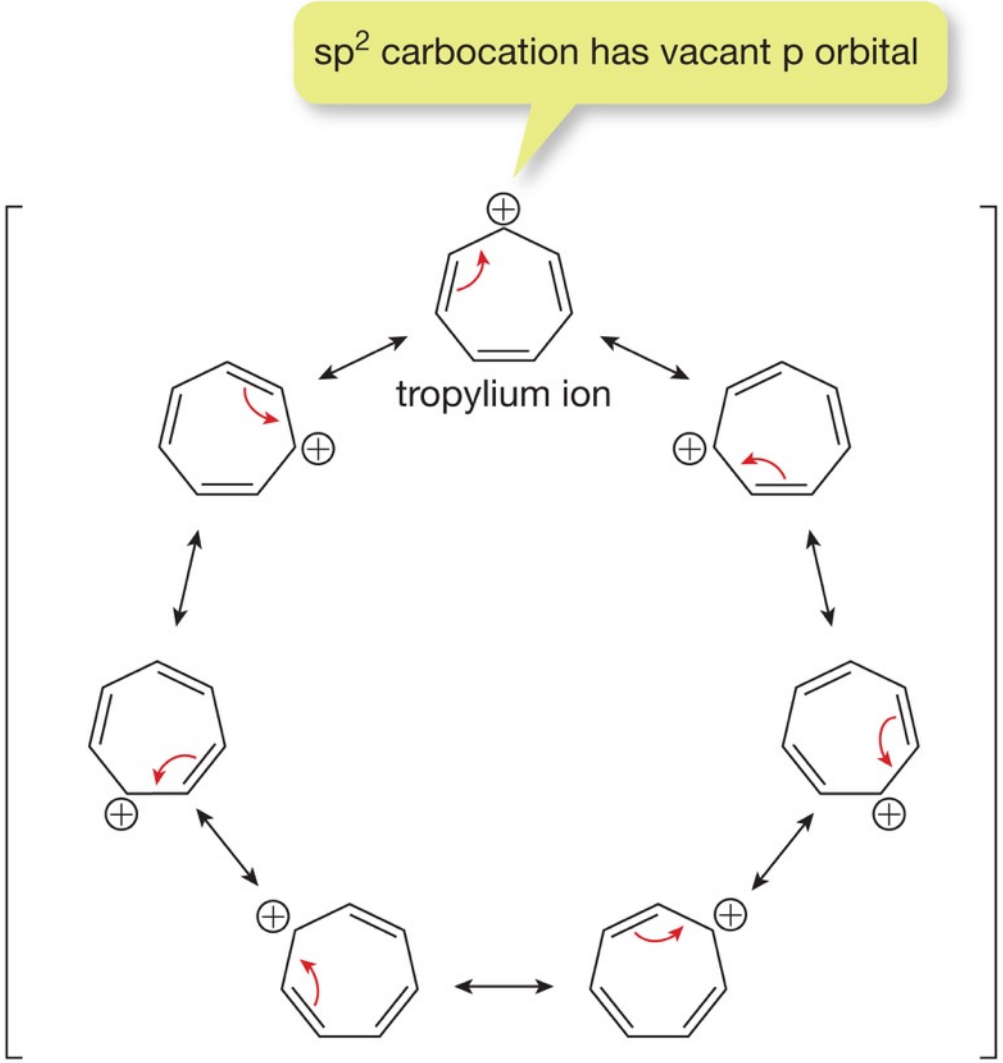
anti-aromatic if planar

non-aromatic



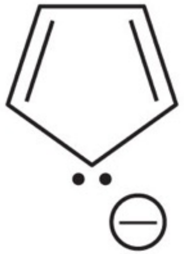
Aromatic Ions

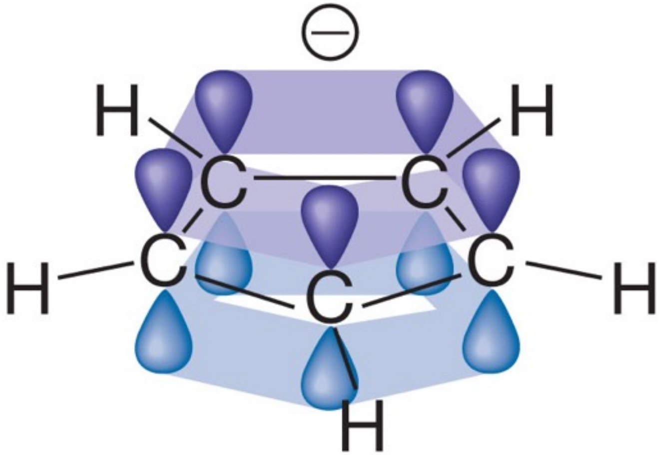
- Anions and cations can also be aromatic.
- Carbocations are sp or sp^2 hybridized and their empty p orbital can participate in aromaticity if it is part of a ring of p orbitals delocalizing $4n + 2$ π electrons.
- Consider the tropylium ion (notice how the + charge is delocalize on every atom of the ring.



Aromatic Ions

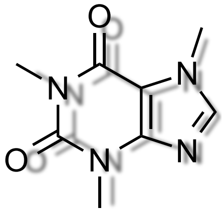
- Anions can also be aromatic if the electron pair occupies a p orbital.
- In cyclopentadienyl anion, the lone pair is found in an sp^2 hybridized p orbital that is delocalized with 4 other sp^2 hybridized carbon atoms.
- Because of aromatic stability of the cyclopentadienyl anion, neutral cyclopentadiene is 10^{30}-10^{45} times more acidic than cyclopentane!



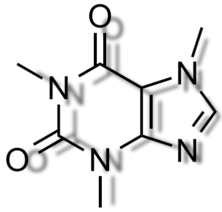


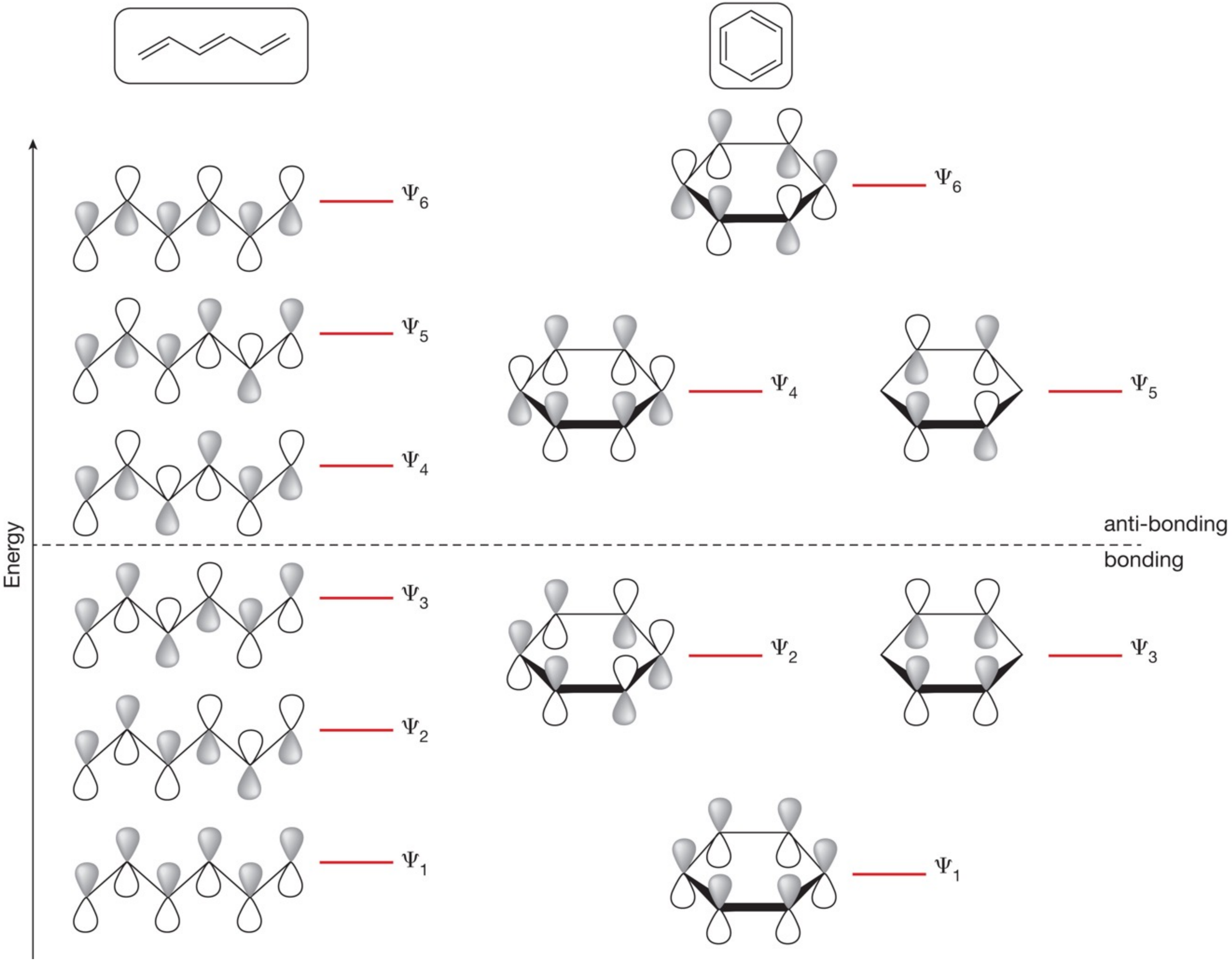
charge delocalized over the whole aromatic ring

Molecular Orbital Analysis of Aromatic Rings

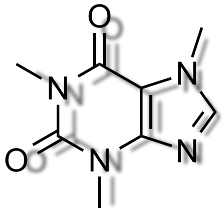


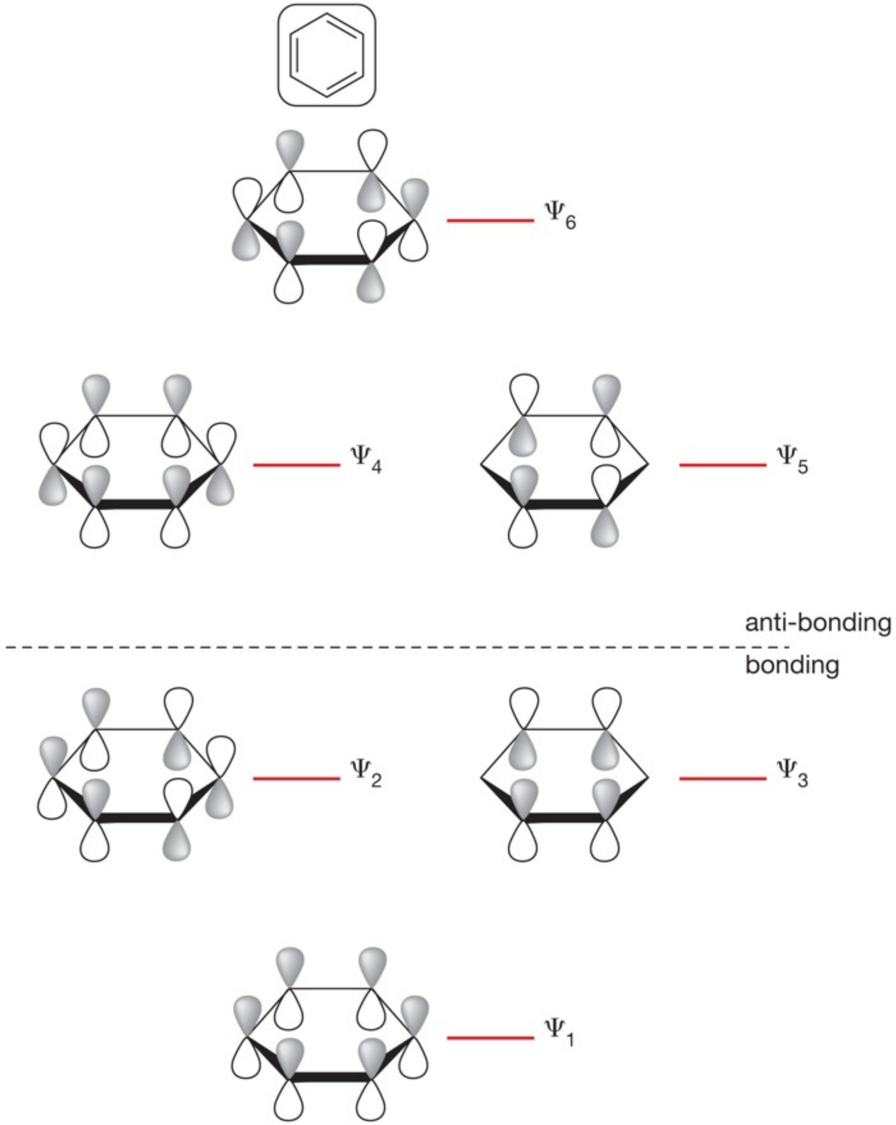
- The basis for Hückel's rule lies in the energies of the π molecular orbitals.
- As we saw for the π molecular orbital diagrams for linear systems, the number of p orbitals equals the number of MOs of differing energies.
- For cyclic π systems, the number of energy levels differs as some of the MOs have the same energy; these are referred to as ***degenerate*** energy levels.

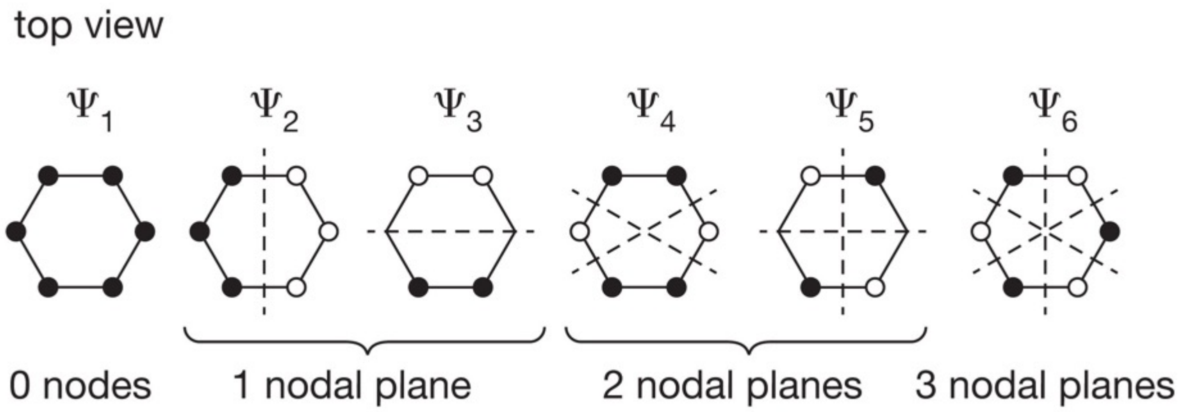



Energy
Ψ_6
Ψ_5
Ψ_4
Ψ_3
Ψ_2
Ψ_1
Ψ_6
Ψ_4
Ψ_5
anti-bonding
bonding
Ψ_2
Ψ_3
Ψ_1

Molecular Orbital Analysis of Aromatic Rings







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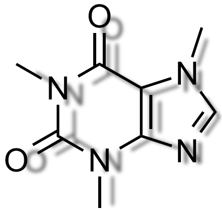
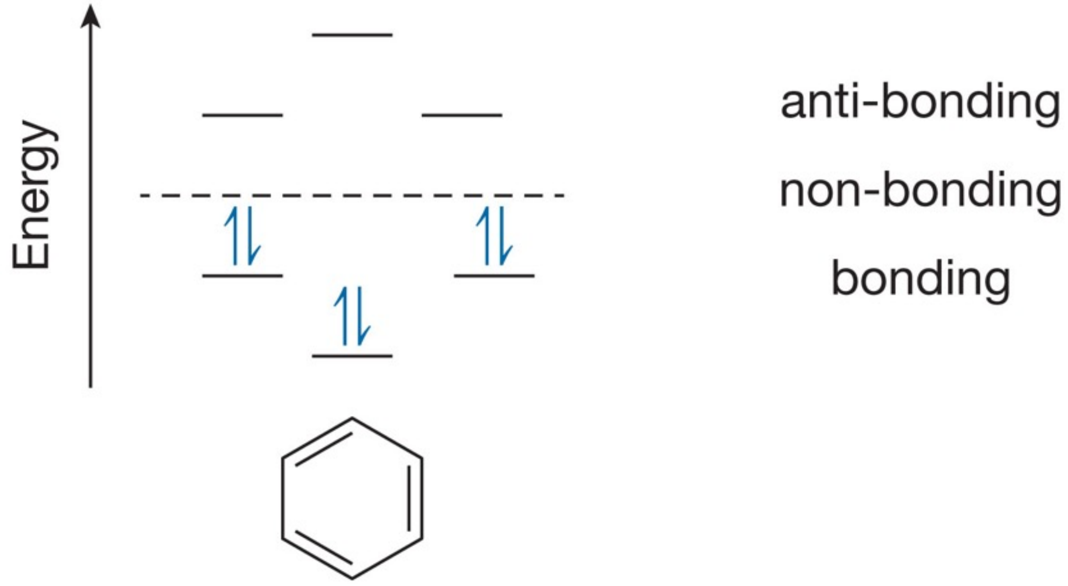


- The ground state configuration of benzene places its six π electrons in the lowest energy MOs, which are all bonding, producing a very stable structure that is aromatic.



all electrons in bonding orbitals
stable structure

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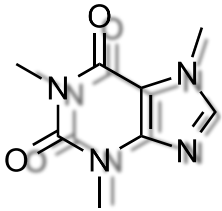
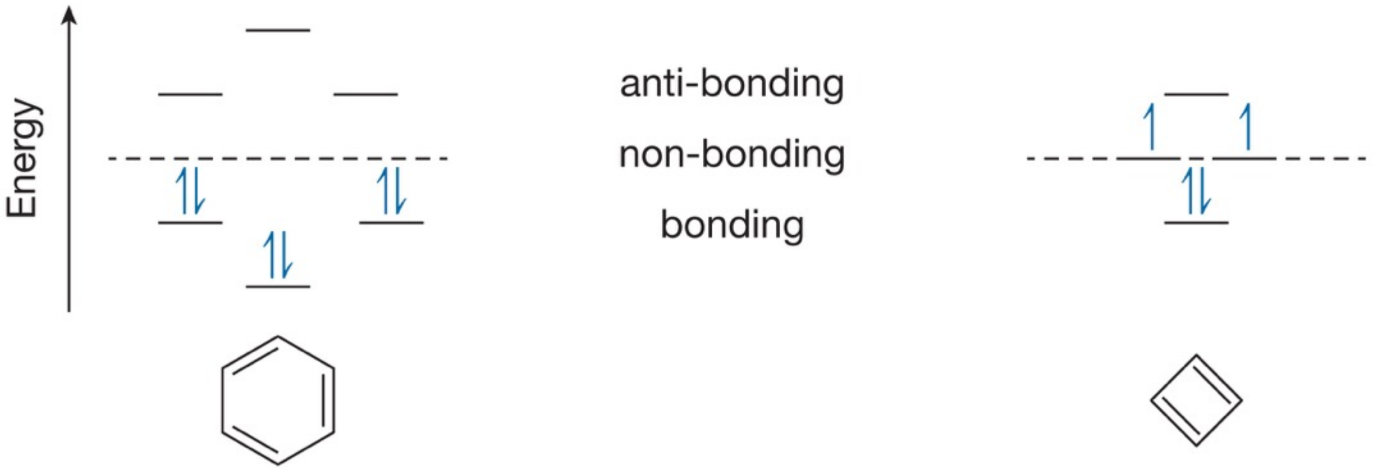


- By comparison, the ground state configuration of cyclobutadiene requires 2 electrons in 2 non-bonding MOs. This produces an unstable structure that would be anti-aromatic.
- In order to avoid anti-aromaticity, cyclobutadiene forms a rectangle instead of a square.



all electrons in bonding orbitals
stable structure

unpaired electrons
in non-bonding orbitals
unstable structure

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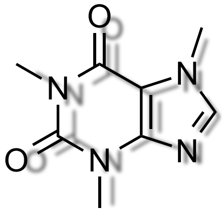
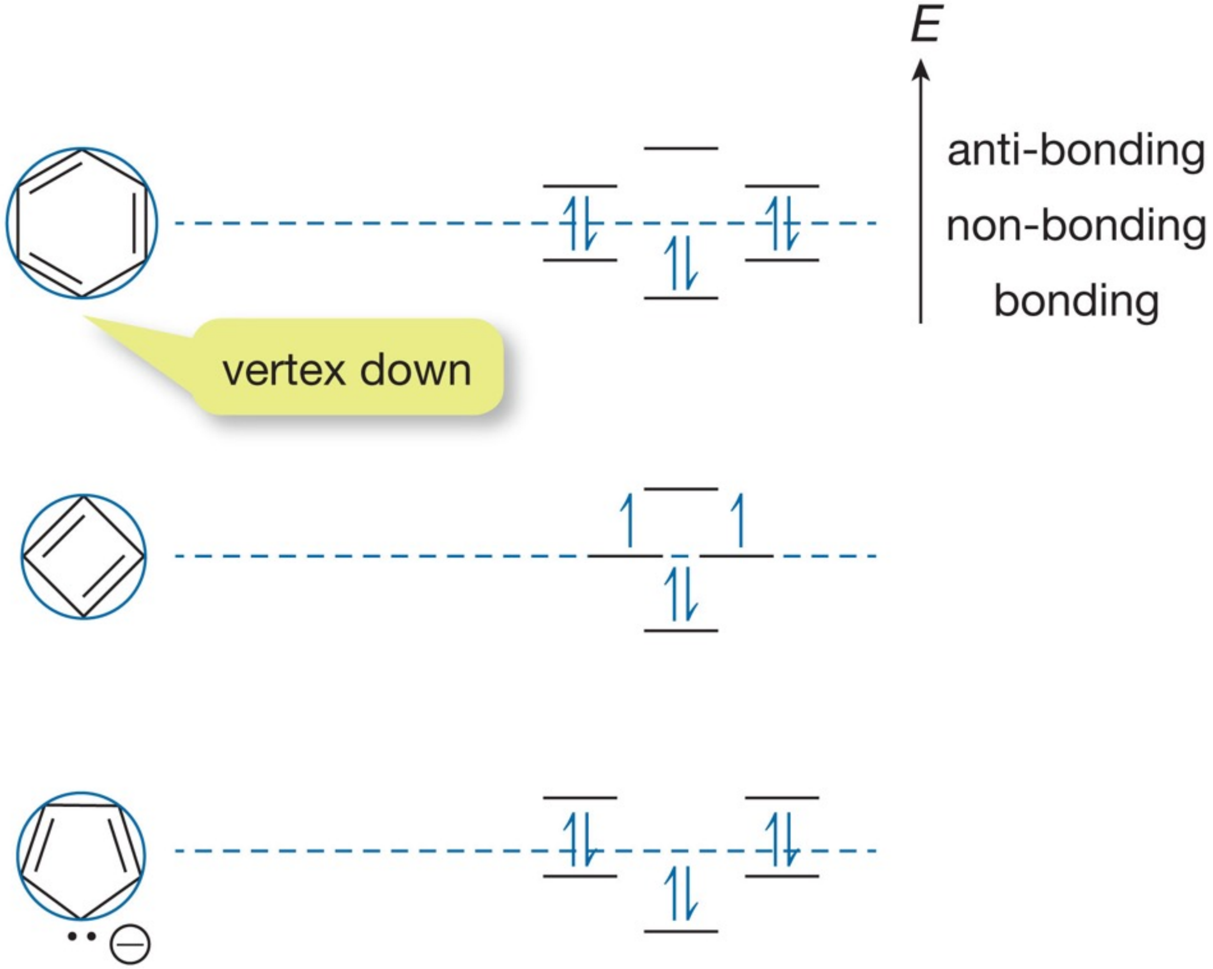


- The relative energies of the MOs for simple conjugated ring structures can be constructed using ***Frost Circles***.
- Frost Circles are made by drawing the appropriate polygon with *<u>one vertex pointing down</u>* within a circle connecting all the vertices.
- Each vertex corresponds to the relative energies of the π MOs.
- The centre of the ring corresponds to the non-bonding energy level.



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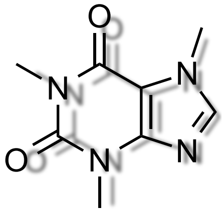
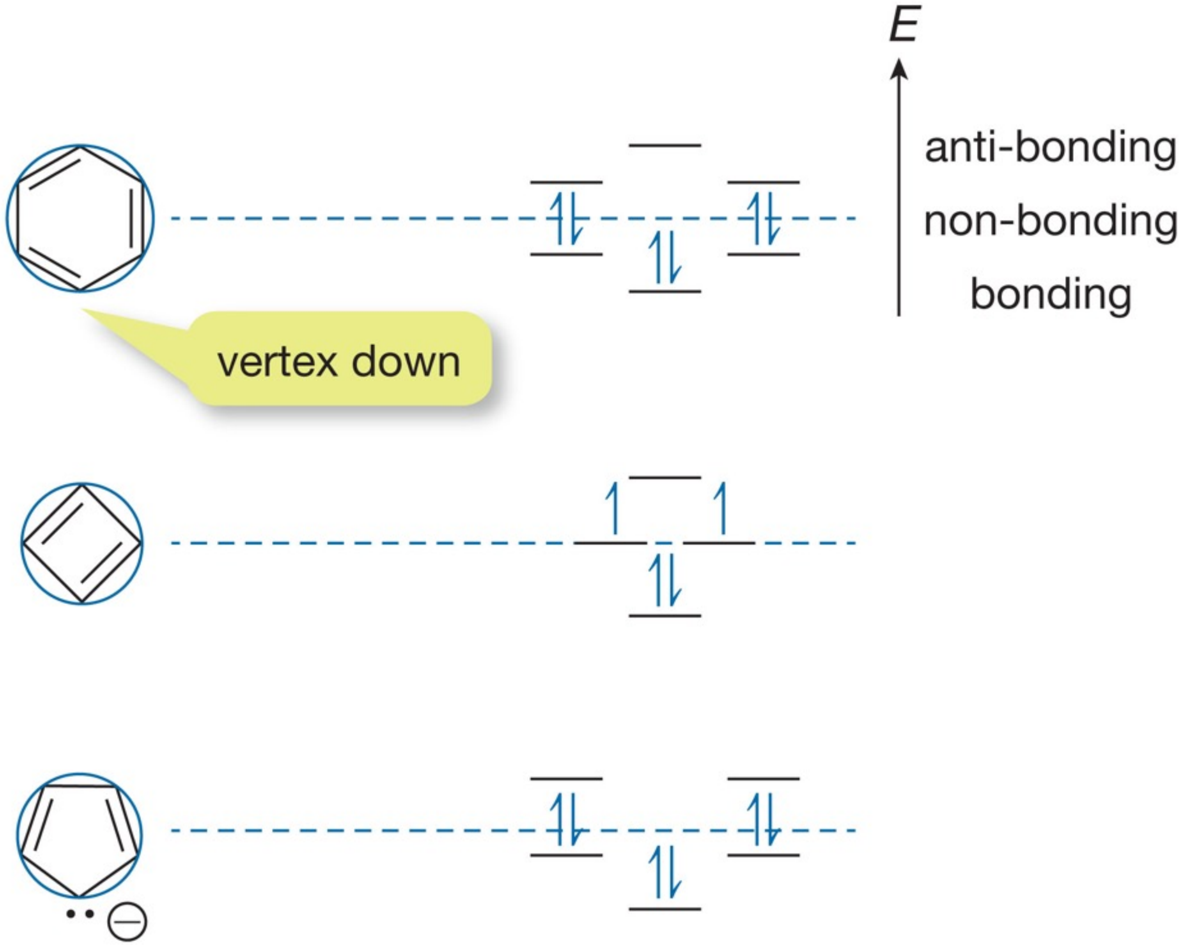


- Frost circles can predict whether a molecule is aromatic or anti-aromatic.
- Benzene and the cyclopentadienyl anion are aromatic – all 6 of their π electrons are paired and found in the bonding MOs.
- Cyclobutadiene is anti-aromatic – 2 unpaired π electrons are found in the non-bonding MOs.



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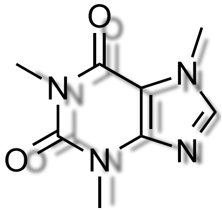
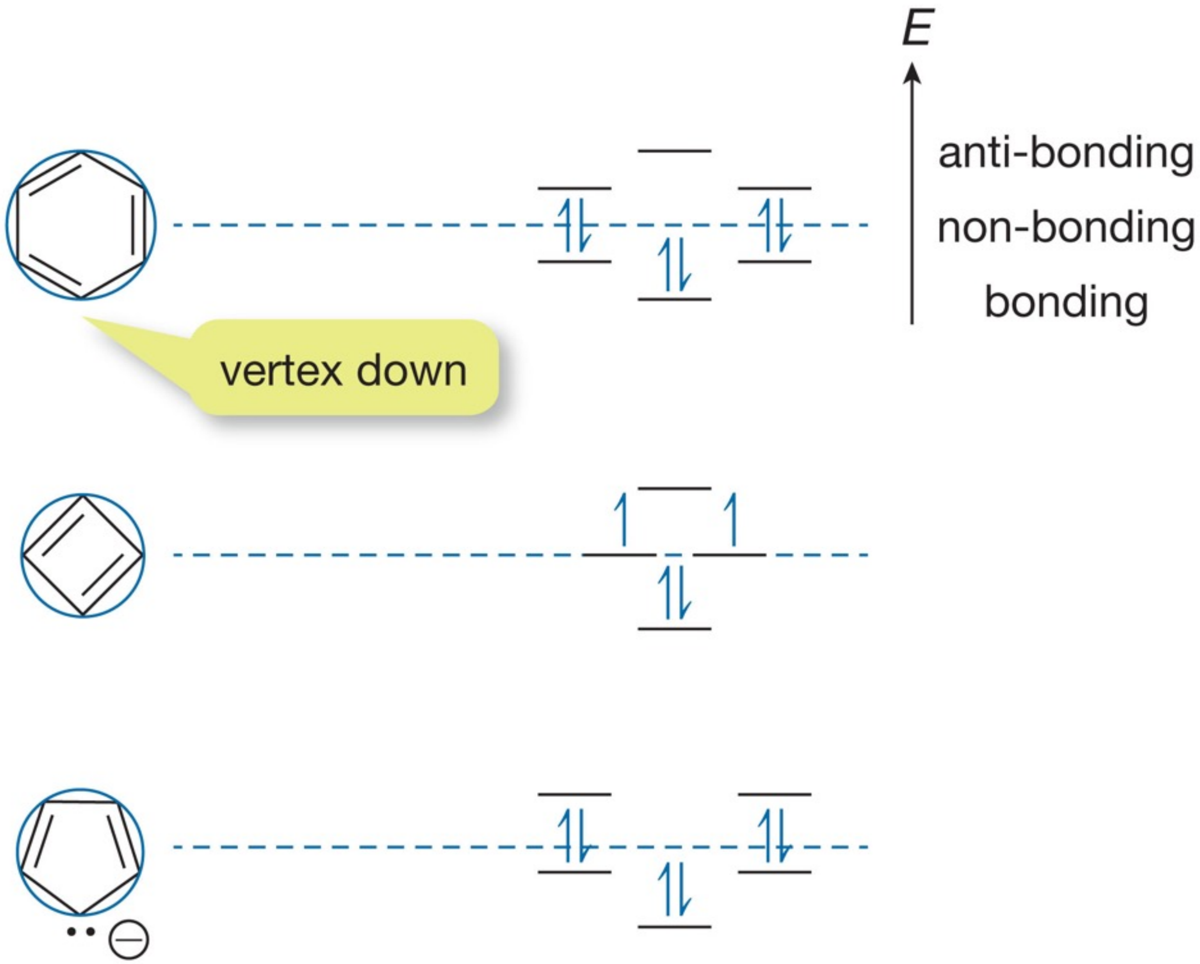


- Instead of existing as a high energy, anti-aromatic compound, most structures predicted to be anti-aromatic avoid anti-aromaticity by adopting a conformation that does not permit the overlap of p orbitals over the entire ring system.
- This is why cyclobutadiene adopts a rectangular structure rather than a square structure.



Molecular Orbital Analysis of Aromatic Rings

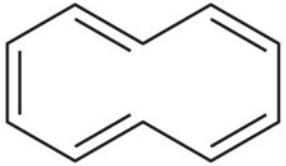
- Using the Frost Circle provided, draw the π MOs for the cyclopentadienyl anion.

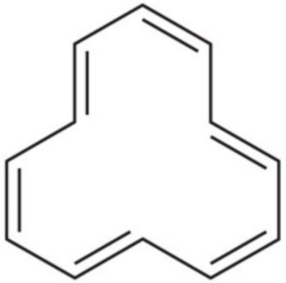
Aromatic Hydrocarbon Rings – Annulenes

- ***Annulene*** is a general term for any cyclic, fully conjugated system.
- Annulenes have an even number of carbon atoms in the ring and are named [*n*]-annulene, where *n* specifies the ring size.


[6]-annulene
(4*n*+2 electrons)


[8]-annulene
(4*n* electrons)

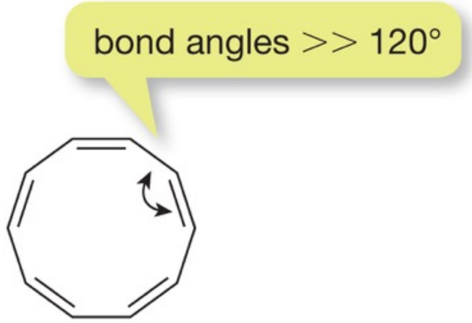

[10]-annulene
(4*n*+2 electrons)


[12]-annulene
(4*n* electrons)

- Some annulenes are aromatic if they follow Hückel's rule and are planar.
- Those that are anti-aromatic according to Hückel's rule will adopt non-planar conformations to avoid anti-aromaticity.

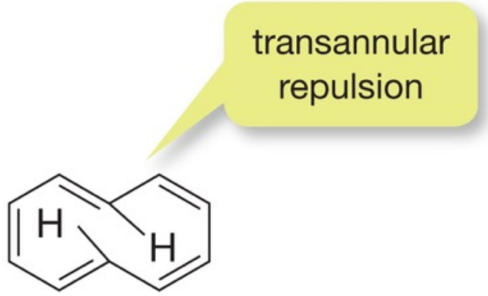
Aromatic Hydrocarbon Rings – Annulenes

- Some rings cannot be planar due to steric interactions or bond angles and cannot be aromatic even if they satisfy the other criteria.



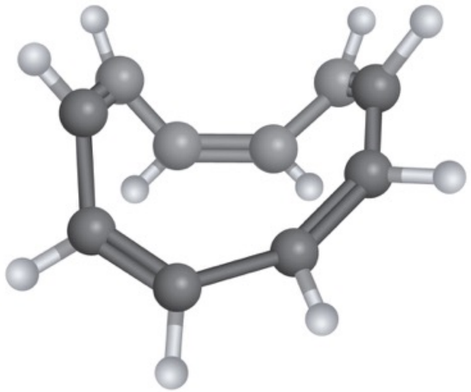
bond angles >> 120°

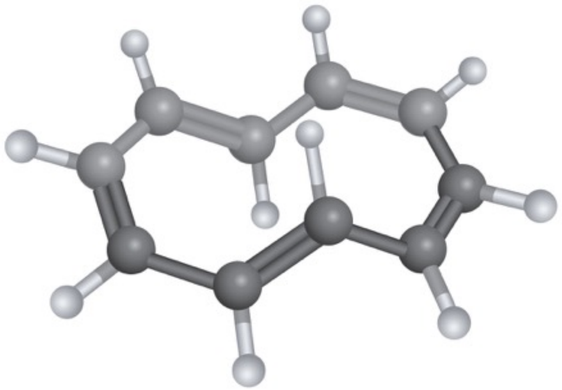
all-*cis* isomer



transannular repulsion

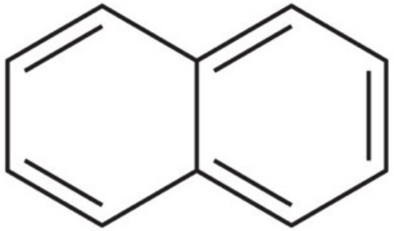
cis-trans-cis-trans-cis isomer



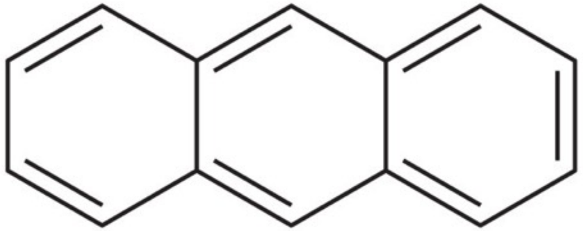


Polycyclic Aromatic Rings

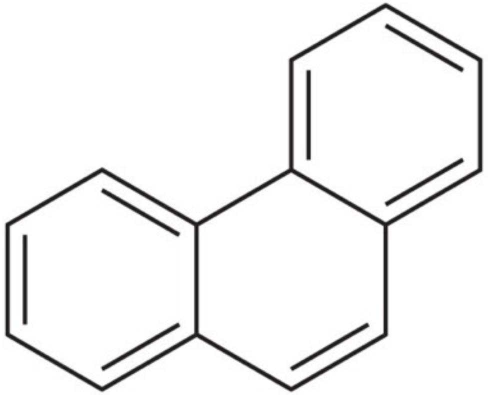
- Aromatic rings can be fused, producing polycyclic aromatic compounds such as naphthalene, anthracene, and phenanthrene.
- These molecules satisfy Hückel’s rule and are planar.



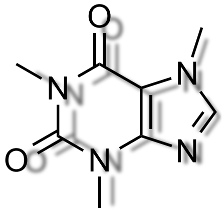
naphthalene



anthracene

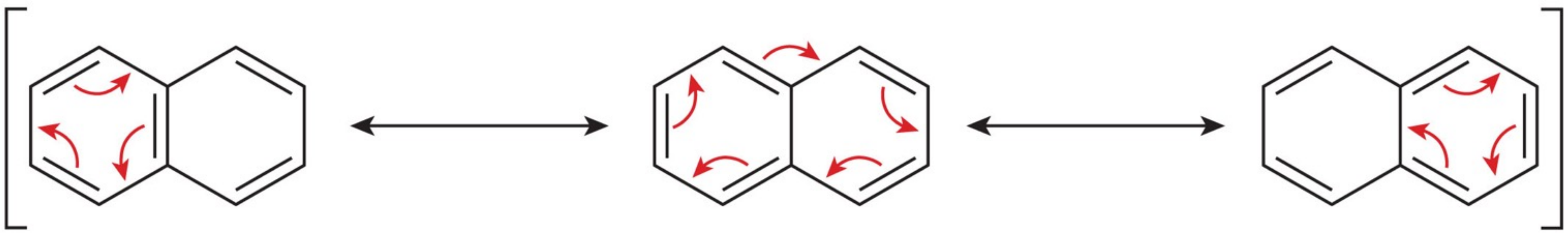


phenanthrene



Polycyclic Aromatic Rings

- Resonance structures can be drawn to illustrate their aromaticity, however, because the actual structure is a weighted average of all the resonance contributors, these molecules have less aromatic stabilization than benzene.



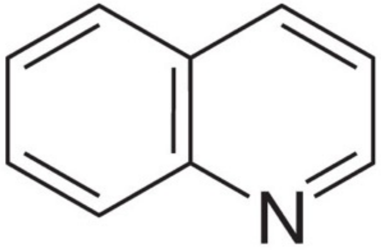
both rings aromatic

left ring aromatic

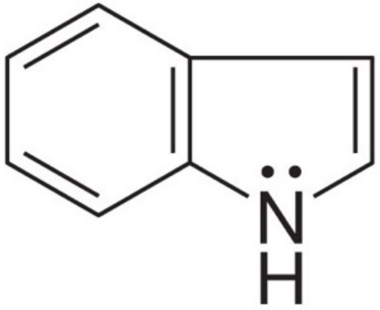
right ring aromatic

Polycyclic Aromatic Rings

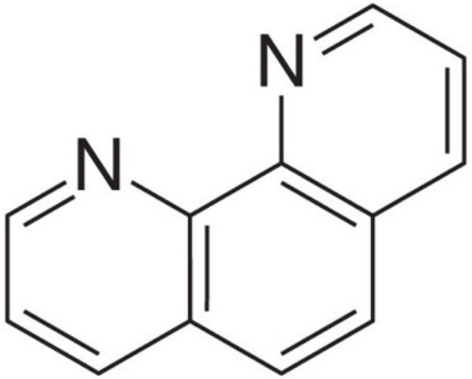
- Polycyclic aromatic heterocycles are also common.



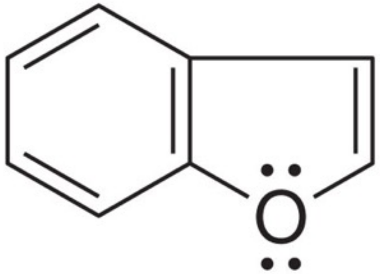
quinoline



indole



phenanthroline

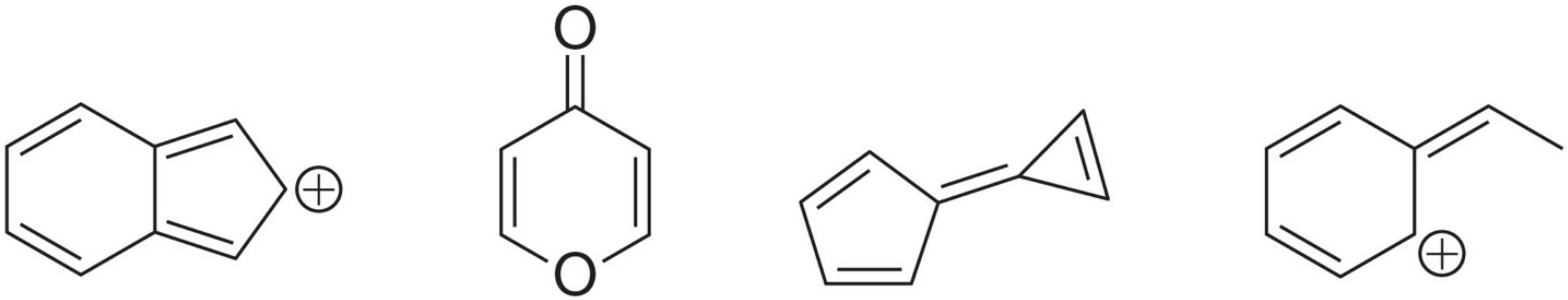


benzofuran

Practice

9.16

The following compounds are aromatic, but do not appear so in the resonance structures shown. For each molecule, show the resonance structure that explains the observed aromatic properties.



Practice

9.21

Imidazole acts as a base, forming a conjugate acid with a pK_a of 7.05. Which nitrogen atom is protonated in the following acid-base reaction?