

Announcements

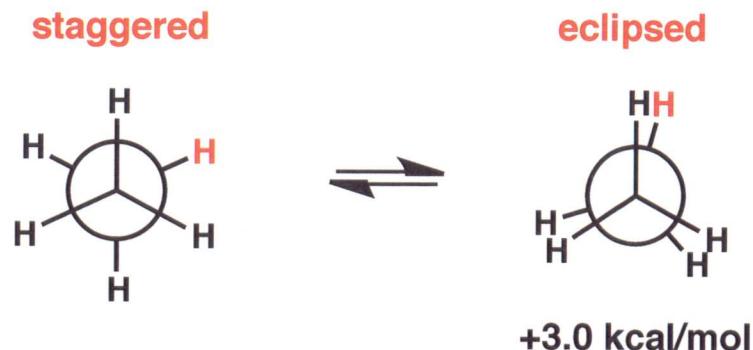
My office hours will be at **9** pm this Wednesday in 101 Schlinger

From last time:

Saturated hydrocarbons: alkanes consisting of carbon and hydrogen.

- generic formula: C_nH_{2n+2}
- prefix indicates number of carbons in longest chain

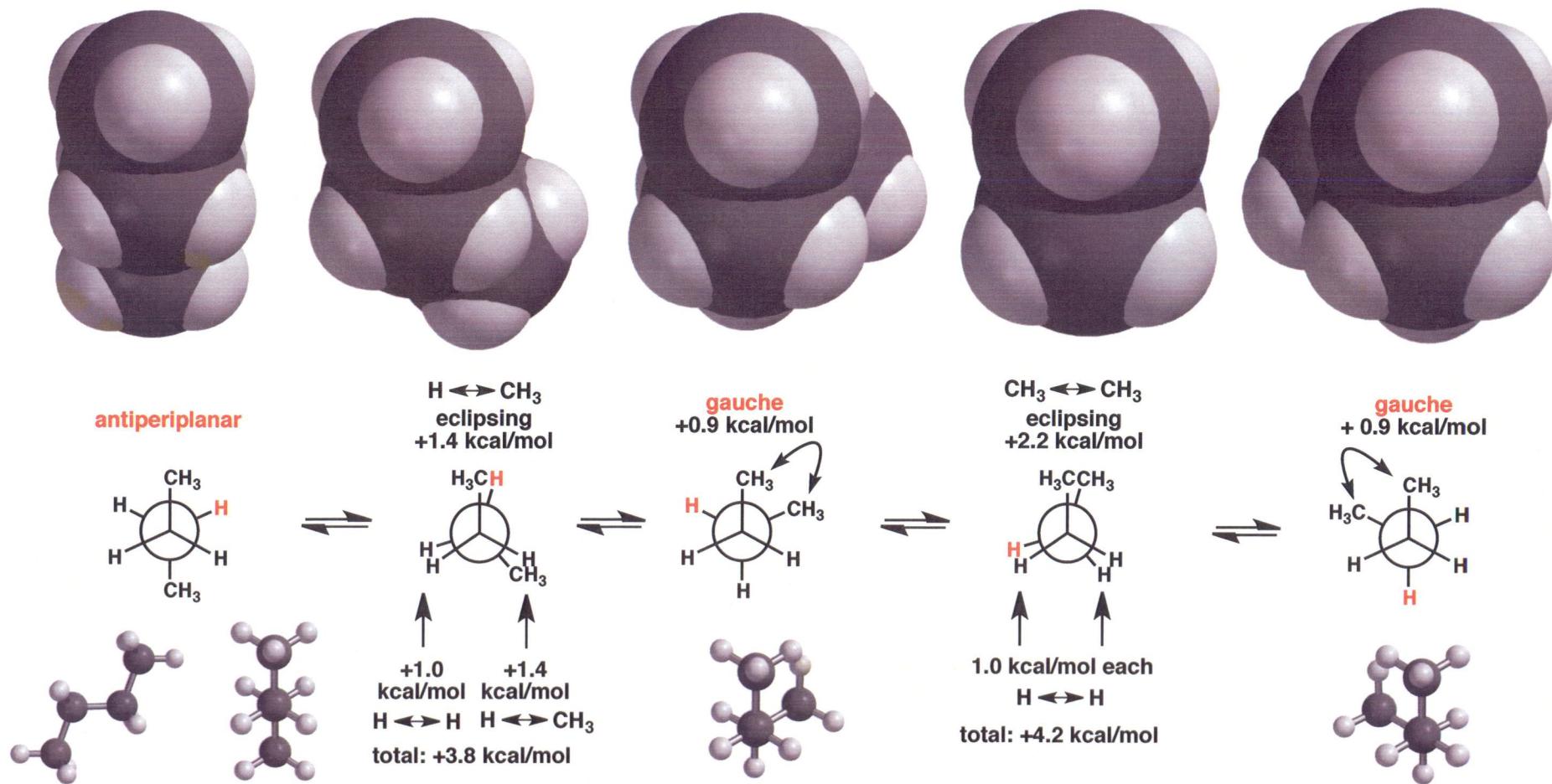
Ethane has two conformations:



Conformations of Alkanes

Conformational isomers: two isomers of a molecule which differ only in the spatial arrangement of the atoms; conformations can be interconverted by rotation about single bonds.

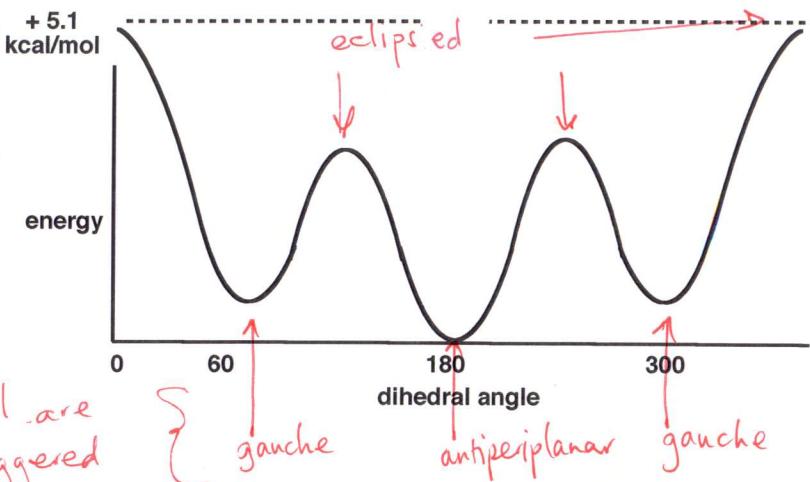
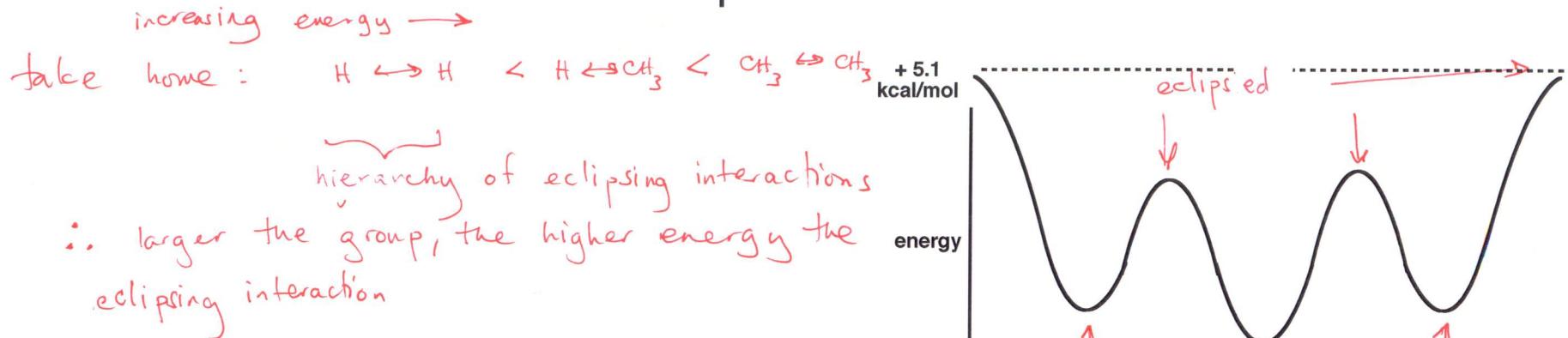
- Not all conformations are created equal



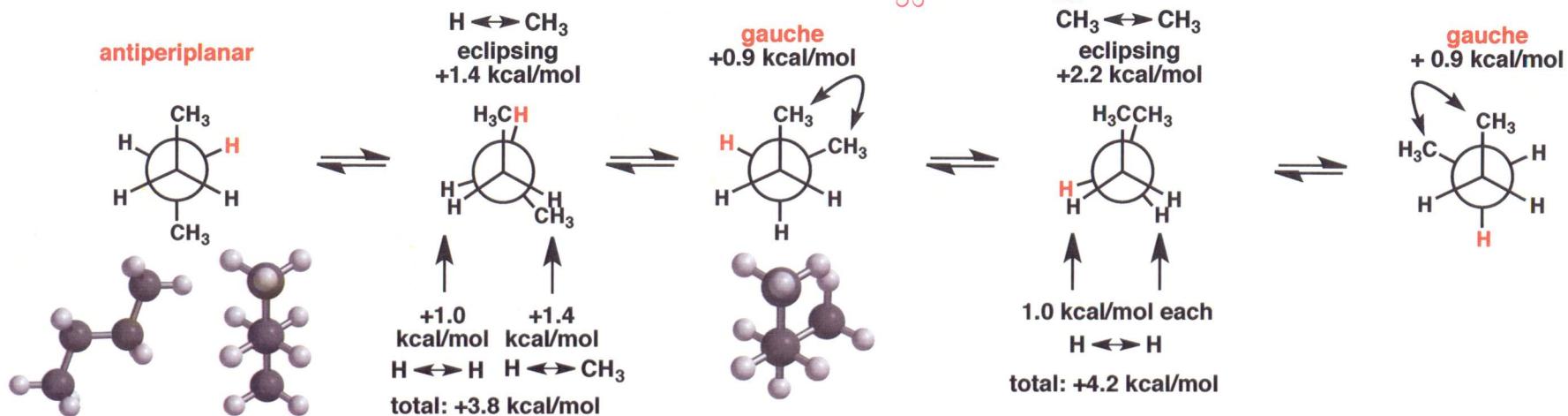
Conformations of Alkanes

Conformational isomers: two isomers of a molecule which differ only in the spatial arrangement of the atoms; conformations can be interconverted by rotation about single bonds.

- Not all conformations are created equal



In general, for hydrocarbons, staggered conformation << eclipsed conformation



Cycloalkanes

cycloalkanes: add “-cyclo” prefix

cyclopropane



cyclobutane



cyclopentane



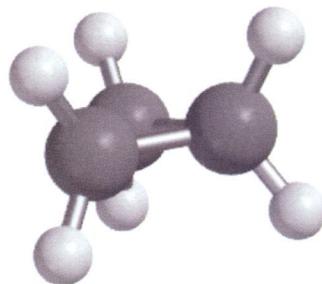
cyclohexane



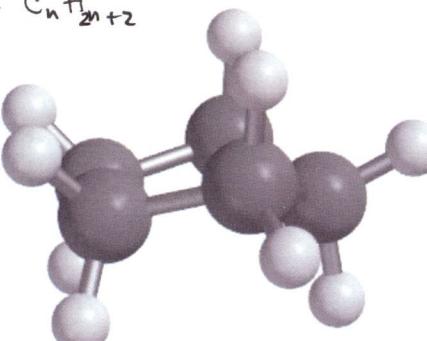
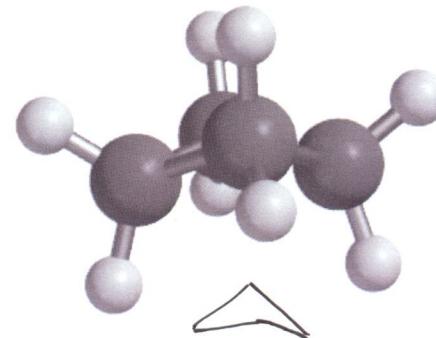
general formula = $C_n H_{2n}$ (1° unsaturation)

cycloalkane

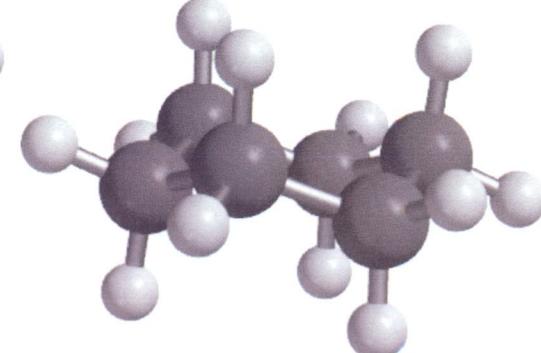
alkane = $C_n H_{2n+2}$



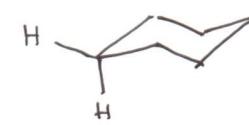
“butterfly”



“envelop”



“chair”



don't be misled: except for cyclopropane, cycloalkanes are not planar!

- cycloalkanes adopt conformations that:
 - provide bond angles closer to 109.5°
 - avoid eclipsing interactions

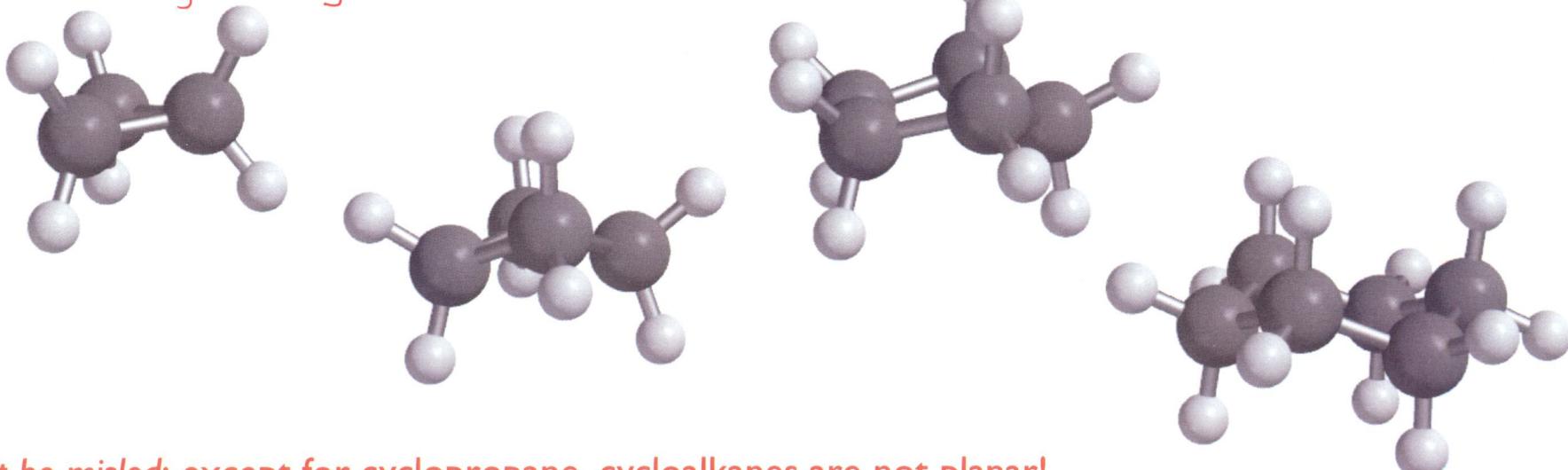
for more info, see RC, Ch 12

Small Rings Experience “Ring Strain”

- distortion from ideal bond angles results in “ring strain”

Cyclopropanes and cyclobutanes
are “less stable” than larger
ring sizes... sometimes this results
in interesting reactivity

	Heat of Combustion (kcal/mol)	Heat of Combustion per CH ₂ (kcal/mol)	total strain (kcal/mol)
cyclopropane	500	167	28
cyclobutane	656	164	26
cyclopentane	793	158	6
cyclohexane	945	157	0
cycloheptane	1108	158	6
open-chain alkane		157	



don't be misled: except for cyclopropane, cycloalkanes are not planar!

- cycloalkanes adopt conformations that:
 - provide bond angles closer to 109.5°
 - avoid eclipsing interactions

for more info, see RC, Ch 12

Carbons form bonds through sp^3 , sp^2 , and sp hybridized orbitals (remember Ch 1a)

ethylene (ethene, C_2H_4)

- planar
- sp^2 hybridized
- one σ bond, one π bond
- rotation around C–C bond is restricted
- generic name: alkene

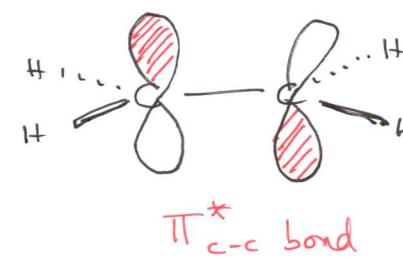
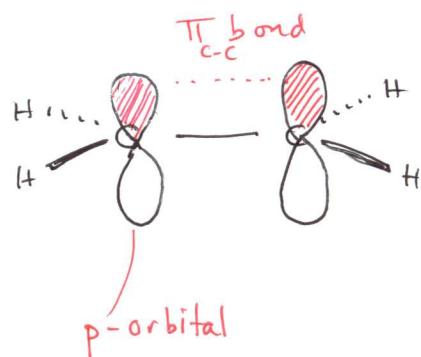
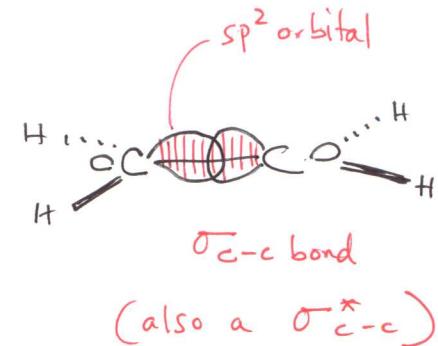
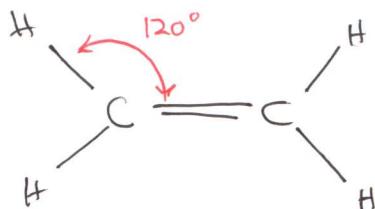
- in order for π -bond to form, the two p-orbitals must be parallel: maximizes the orbital overlap

- in order to rotate around C–C bond, you would lose orbital overlap, essentially break the pi-bond (~ 60 kcal/mol)

|
too high to happen at r.t.;

typically has to be ~ 26 – 27 kcal/mol or less for a process to occur in a reasonable time frame at room temp

the second bond fills the C valency



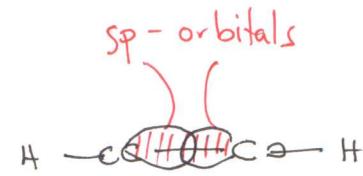
double bonds are $\sim 1.33 \text{ \AA}$



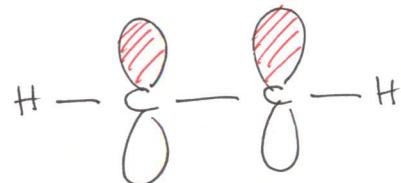
Carbons form bonds through sp^3 , sp^2 , and sp hybridized orbitals
 (remember Ch 1a)

acetylene (ethyne, C_2H_2)

- linear geometry
- sp hybridized
- one σ bond, two π bonds
- generic name: alkyne



(also σ_{c-c}^* orbital)
 antibonding



π_{cc} = in plane
 of board



π_{cc} = perpendicular
 to plane of board

each carbon has 2 p orbitals
 left for π -bonds

(and 2 π^*_{ccc} orbitals)



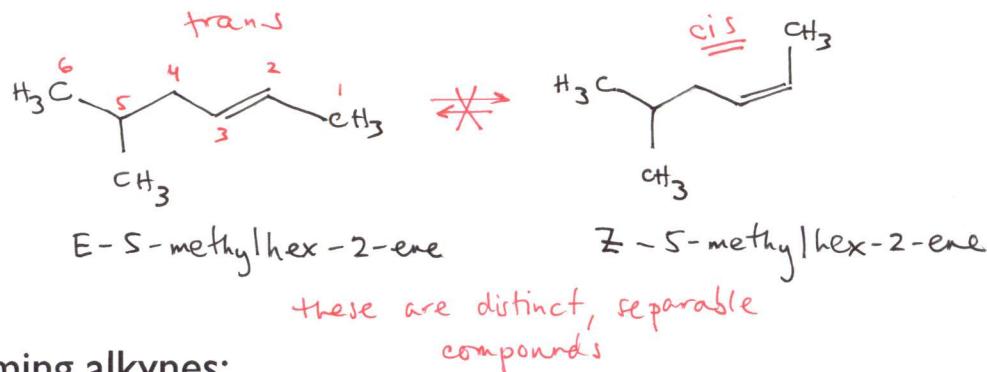
red and blue orbitals
 are orthogonal

Unsaturated Hydrocarbons: Alkenes and Alkynes

naming alkenes:

- prefix indicates number of carbons in longest chain, suffix is “-ene”
- number indicates location of double bond
- alkene geometry defined as *E* (trans) or *Z* (cis)

Alkene isomers: molecules with the same molecular formula and same connectivity of atoms, which differ only in alkene geometry



instead of “ene”

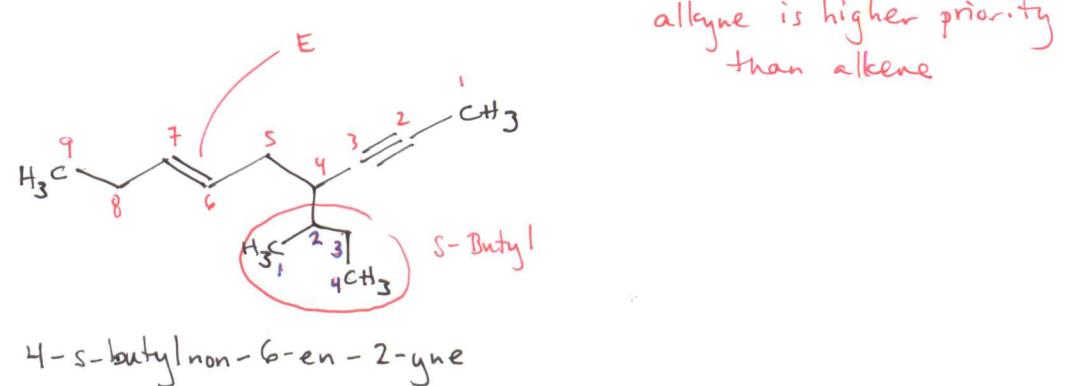
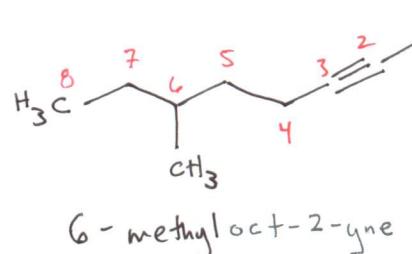
cis: on the same side
z = zusammen = together

trans: on the other side
E = entgegan = opposite

- trans alkenes are typically more thermodynamically stable than cis alkenes

naming alkynes:

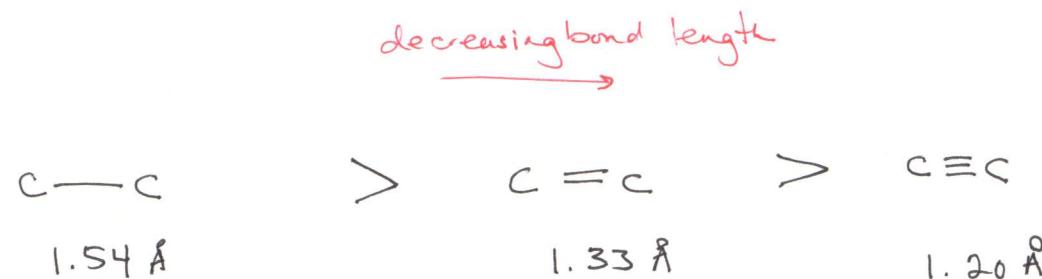
- prefix indicates number of carbons in longest chain, suffix is “-yne”
- number indicates location of triple bond



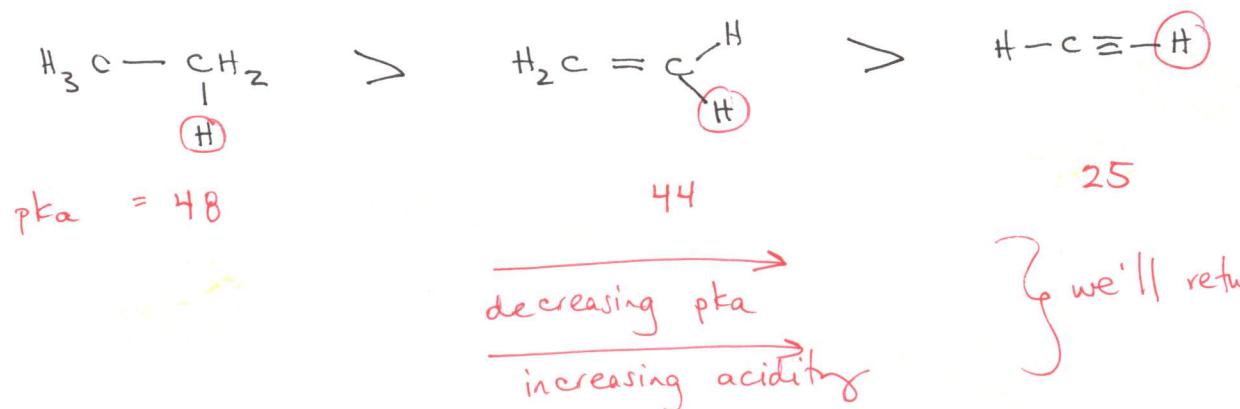
Alkanes, Alkenes, and Alkynes have Different Properties

Key trends:

- bond length:



- C–H acidity:

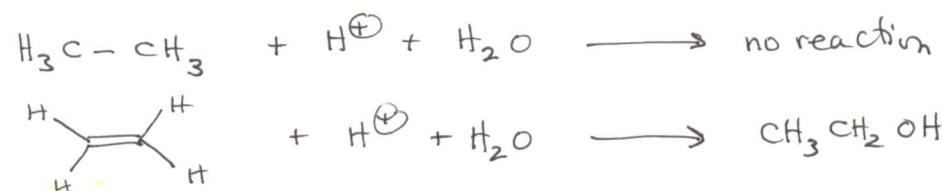


{ we'll return to this

- reactivity:

π bonds are higher in energy than σ bonds; they "react" first.

$$\text{H}-\text{C}=\text{CH}_2 + \text{H}^{\oplus} + \text{H}_2\text{O} \longrightarrow \text{no reaction}$$

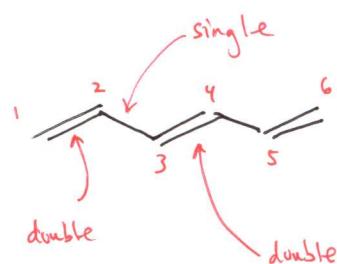


Delocalization and Conjugation in Polyalkenes

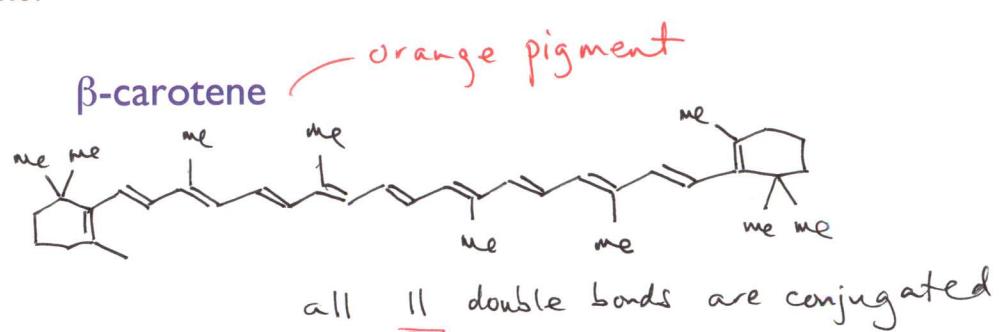
Conjugation: polyalkenes in which two double bonds are separated by just one single bond are “conjugated” polyalkenes.

- conjugated double bonds have different properties than isolated double bonds.
- electrons can “delocalize” in conjugated π -systems.

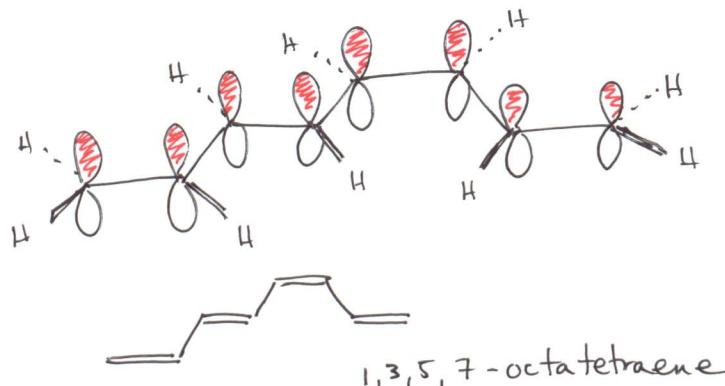
1,3,5-hexatriene



β -carotene



- the p-orbitals of the π -bonds must be coplanar for the alkenes to be conjugated:



all of the p-orbitals must be
in the plane of the board for good
overlap... influences the "conformation"
of the molecule

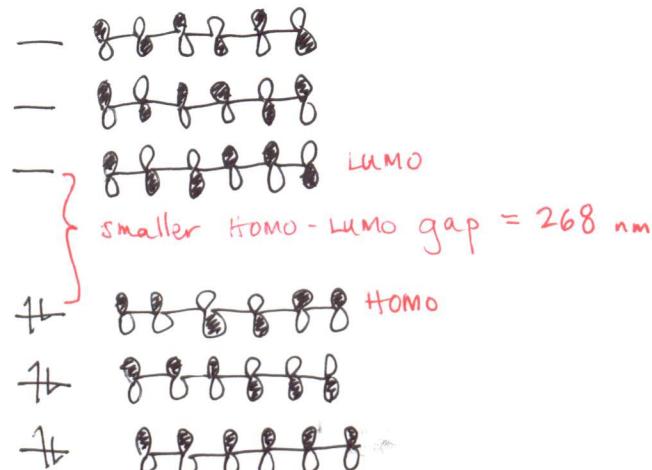
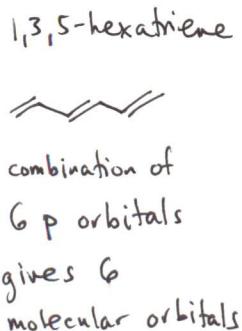
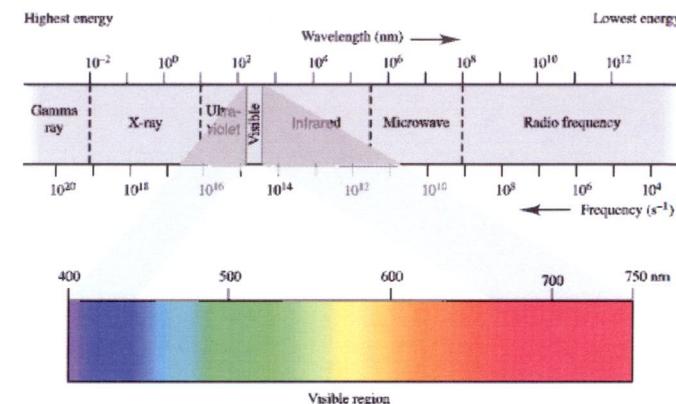
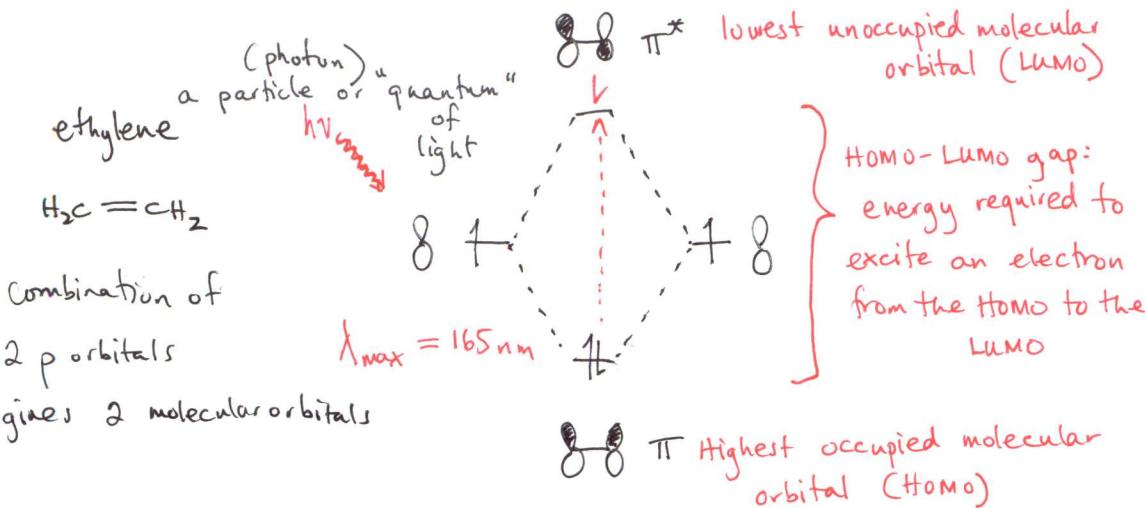


- delocalization in conjugated π -systems lowers the energy difference between the HOMO and LUMO.

Delocalization and Conjugation in Polyalkenes

Delocalization in conjugated π -systems lowers the energy difference between the HOMO and LUMO.

- highly delocalized π -systems can absorb lower energy (higher wavelength) light



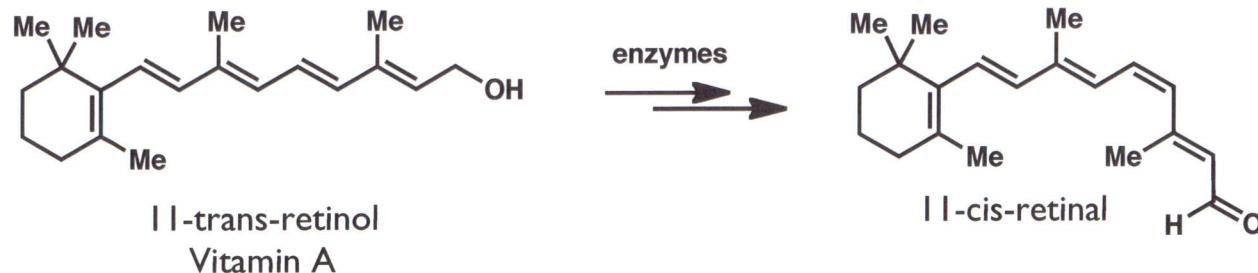
alkene	$\lambda_{\max} (\text{nm})$
$=$	165
$=\text{ }=\text{ }$	217
$=\text{ }=\text{ }=\text{ }$	268
$=\text{ }=\text{ }=\text{ }=\text{ }=\text{ }$	364

the HOMO-LUMO gap determines the λ_{\max} of absorption

reminder: $E = h\nu = hc/\lambda$

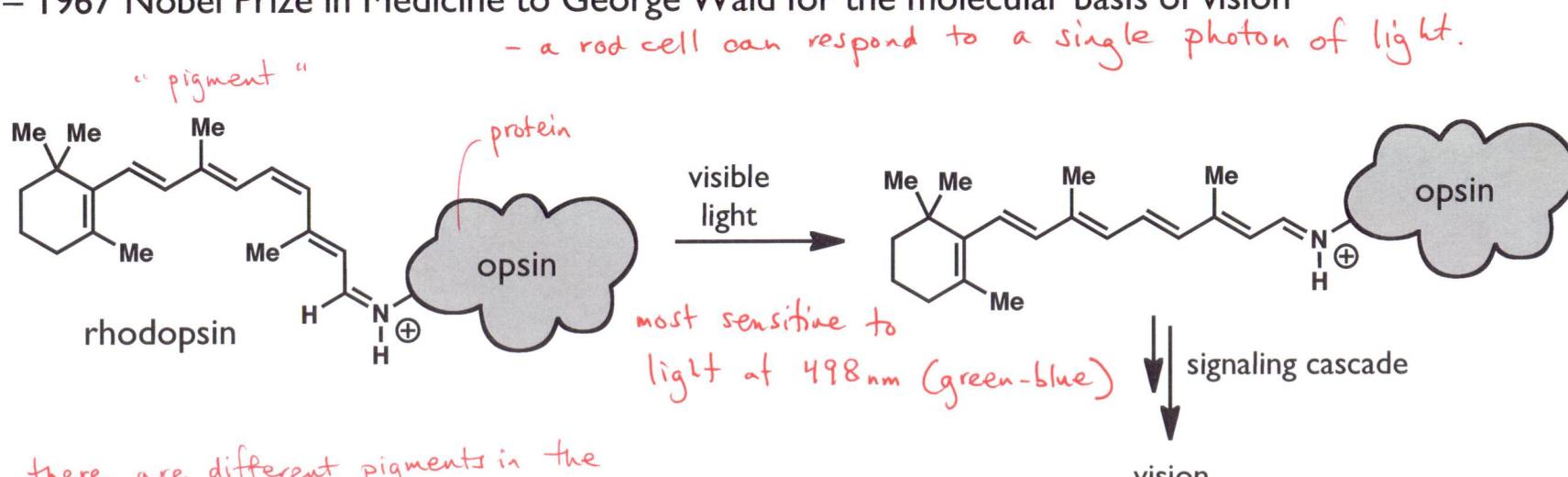
Molecules of the Day: Vitamin A and Retinal

retinol: Vitamin A, can be metabolized from β -carotene



How do we detect visible light?

- rod cells contain the pigment “rhodopsin” *↳ gives us night vision*
- isomerization from *cis* to *trans* results in a messenger cascade that is the basis for vision.
- 1967 Nobel Prize in Medicine to George Wald for the molecular basis of vision

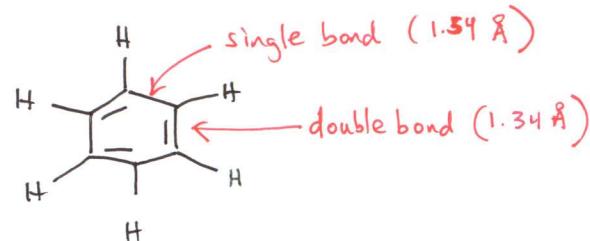
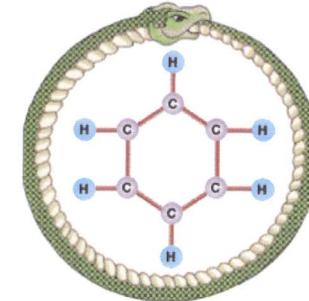


there are different pigments in the cones that allow us to see in color
(they absorb at different wavelengths)

Benzene is Special

Benzene (C_6H_6) was discovered in 1825

- all of the C-C bond lengths are identical (1.40 \AA)
- the heat of hydrogenation is substantially lower than that expected from a triene
- the structure was first proposed by Kekulé in 1865

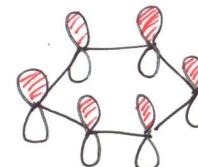


this structure implies that
not all bonds would be the
same length...

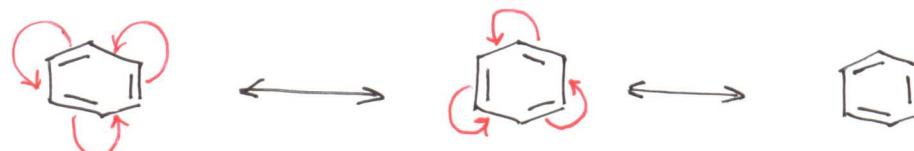
why is benzene exceptionally stable?

Delocalization! The π -system is completely delocalized!

All of the p-orbitals are coplanar, electrons can delocalize;
they are equally distributed among the p-orbitals of the 6 atoms



We can illustrate the delocalization using resonance structures:



benzene is an “aromatic” compound

Hückel's Rule

Hückel's Rule: planar, fully conjugated, cyclic systems with $(4n+2)\pi$ electrons have a closed shell of electrons all in bonding orbitals and are exceptionally stable. These systems are "aromatic."

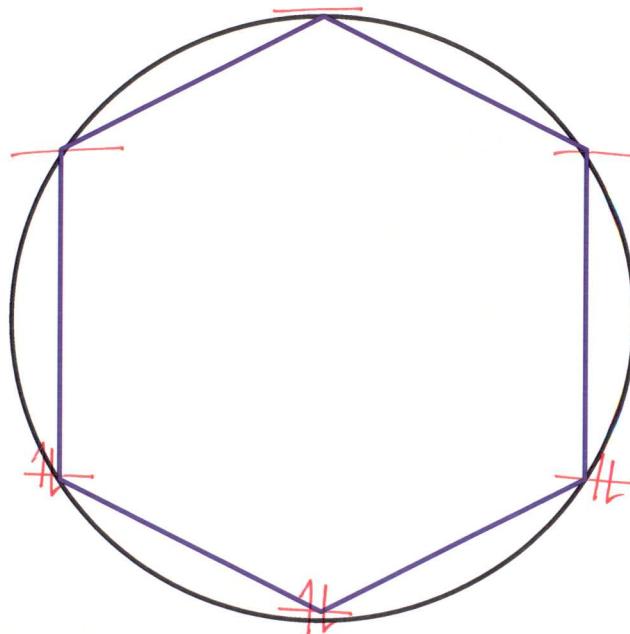


6 p orbitals combine to give

6 molecular orbitals

6 π -electrons, start filling at lowest energy MO

Frost Circle



- For a cyclic, conjugated, hydrocarbon with j sides, inscribe polygram of j sides into a circle with one vertex pointing down.
- Place an MO energy level at each vertex (there will be j MOs)
- The lowest energy level lies at the lowest vertex.
- Add π electrons to the MO energy levels following the Pauli principle and Hund's rules

Analogous systems with $4n\pi$ electrons are "anti-aromatic" (if planar) or "non-aromatic"

Hückel's Rule

Hückel's Rule: planar, fully conjugated, monocyclic systems with $(4n+2) \pi$ electrons have a closed shell of electrons all in bonding orbitals and are exceptionally stable. These systems are "aromatic."

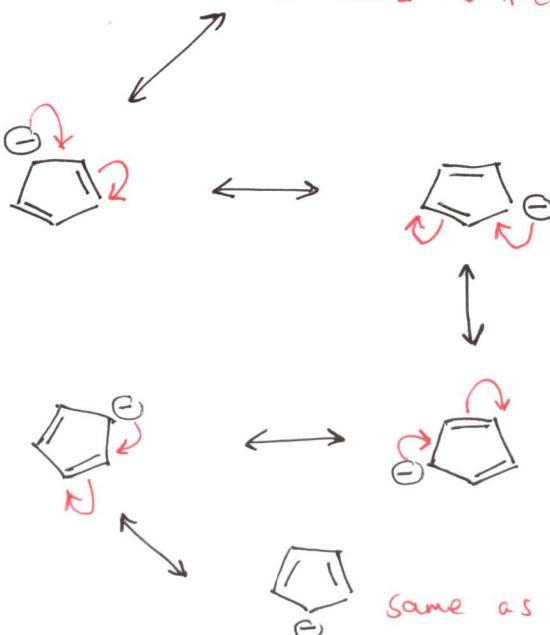
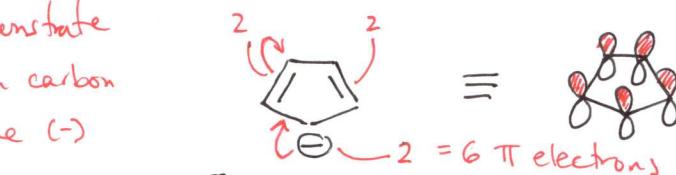
anthracene:



other examples of aromatic compounds:

cyclopentadienyl anion

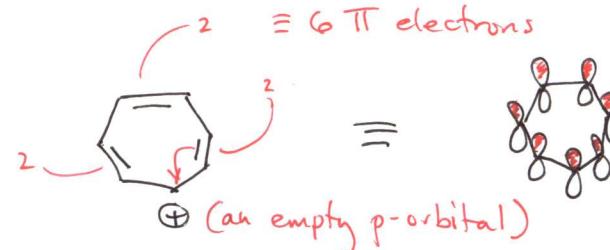
can demonstrate
that each carbon
shares the $(-)$
charge



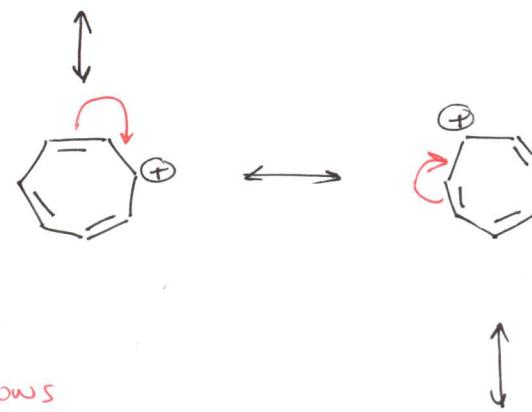
14 π -electrons

$$4(3) + 2 = \text{fits } 4n+2 \text{ rule}$$

cycloheptatrienyl cation



push electrons:
always draw arrows
from electron density



convince yourself
that the positive
charge is
distributed equally
over all 7
carbons



and so on...

analogous systems with $4n \pi$ electrons are "anti-aromatic"

cations are typically
very reactive, but aromatic

cations are more
stable

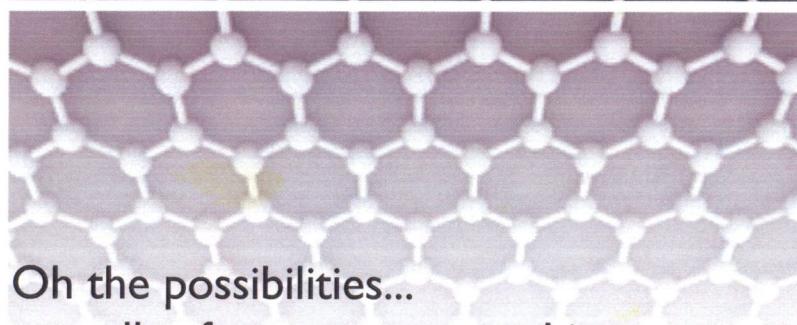
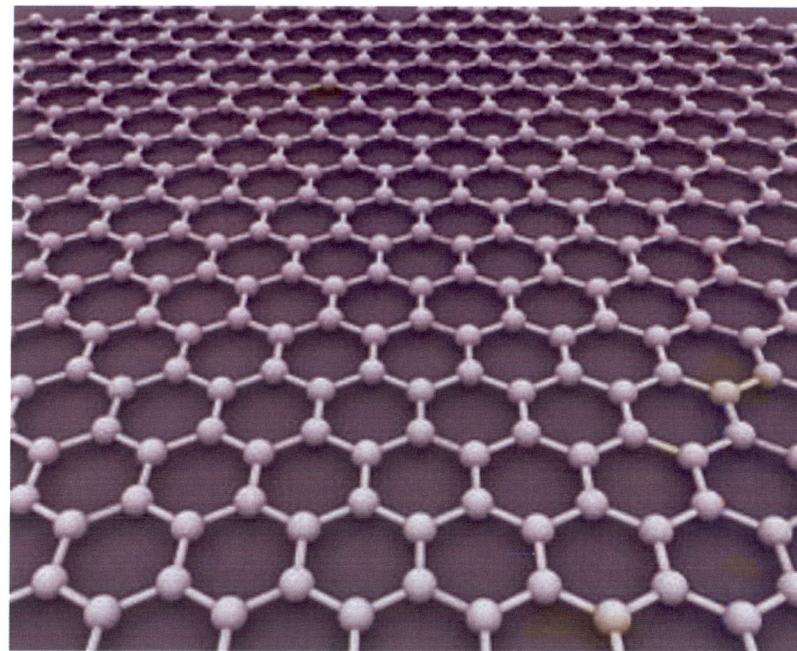
Molecule of the Day: Graphene

Graphene: single layer of sp^2 -hybridized carbons packed in a honeycomb lattice

- π -electrons are completely delocalized
- “organic” molecule that behaves like a metal (conducts electricity and heat)
- a lattice of fused benzene rings...the ultimate aromatic molecule!

2010 Nobel Prize awarded to Andre Geim and Konstantin Novoselov (U. Manchester) for their studies on the production, isolation, identification, and characterization of graphene.

“They simply stuck a flake of graphite debris onto plastic adhesive tape, folded the sticky side of the tape over the flake and then pulled the tape apart, cleaving the flake in two. As the experimenters repeated the process, the resulting fragments grew thinner. Once the investigators had many thin fragments, they meticulously examined the pieces—and were astonished to find that some were only one atom thick. Even more unexpectedly, the newly identified bits of graphene turned out to have high crystal quality and to be chemically stable even at room temperature.”



Oh the possibilities...

- smaller faster computer chips
- transparent touch screens
- solar panels
- plastic conductors

<http://www.scientificamerican.com/article.cfm?id=carbon-wonderland>
http://www.nobelprize.org/nobel_prizes/physics/laureates/2010/press.html

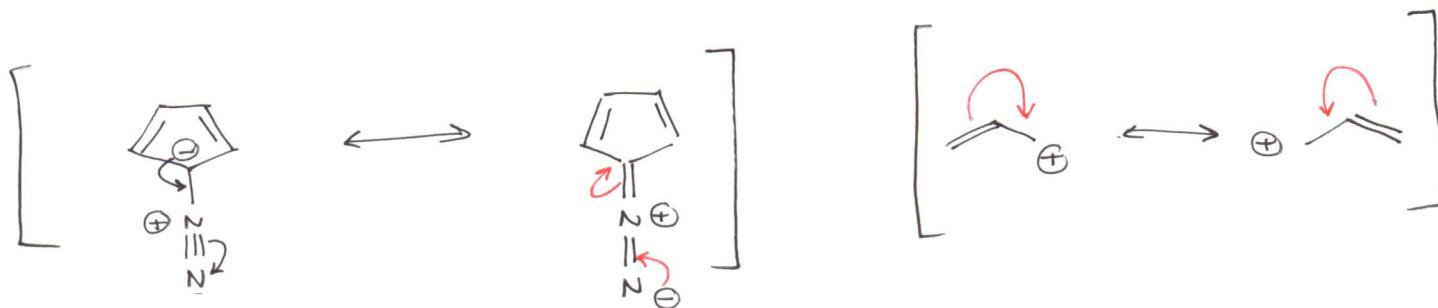
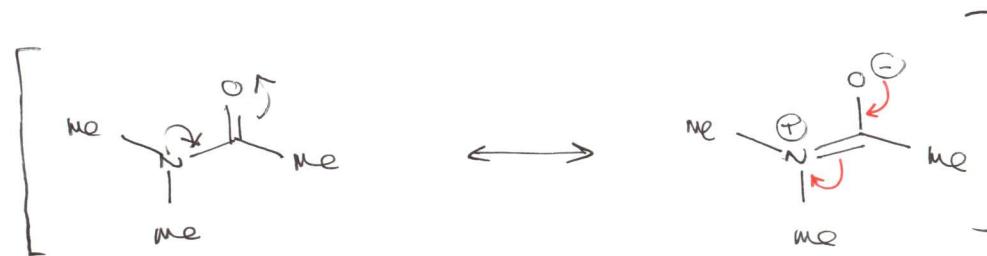
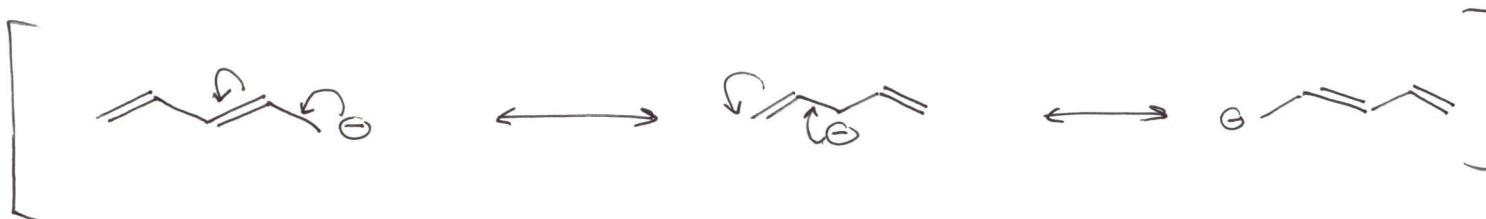
Drawing Resonance Structures

Resonance structures show the delocalization of electrons

- bonds, unshared electron pairs, carbocations, or single electrons can be moved using the curved arrow notation without moving any atoms
- arrows should originate at a source of electron density (i.e. a bond or a lone pair)

examples:

- resonance contributors that minimize charge are more dominant contributors



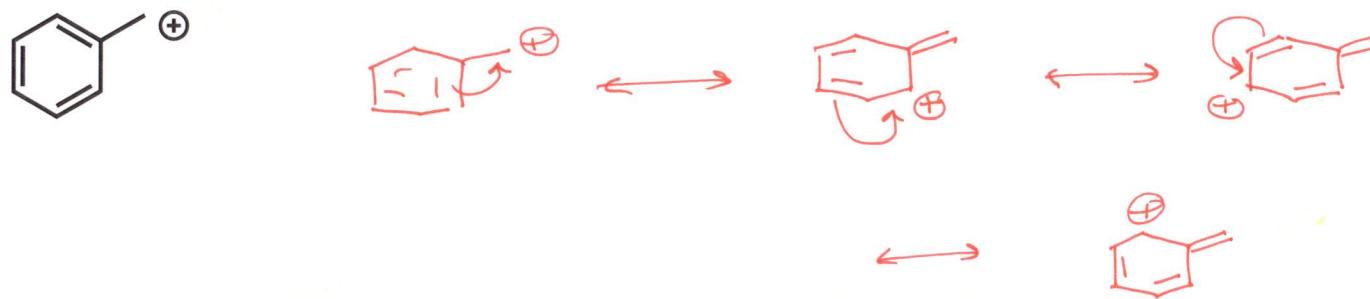
all resonance intermediates must still obey the octet rule... for a discussion of resonance, see RC Ch 6 sec. 5
no TEXAS carbons

Drawing Resonance Structures

Resonance structures show the delocalization of electrons

- curved arrows are used to demonstrate that π -electrons, unshared electron pairs (lone pairs), carbocations, or single electrons (radicals) can be delocalized over multiple atoms
- arrows should originate at a source of electron density (i.e. a bond or a lone pair)
- you must be able to push the electrons without moving any atoms

Which carbons share the positive charge?



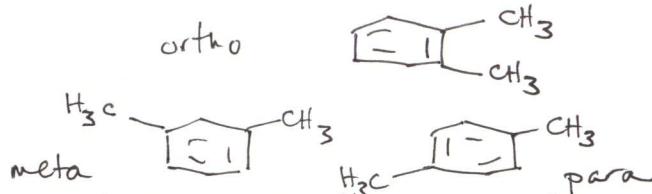
Naming Benzene Derivatives (aka Arenes)

Many aromatic compounds have common names

toluene



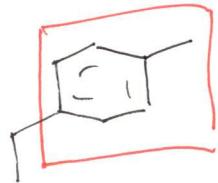
xylene



mesitylene

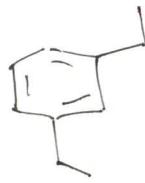


Disubstituted benzenes: use locator numbers or *ortho*, *meta*, or *para*



p-ethyltoluene

4-ethyltoluene



1,3-diethylbenzene

should be 1,3-diethylbenzene

Guidelines:

- Identify names of substituents
- Assign locator numbers to substituents alphabetically
- List substituents alphabetically, including locator numbers, with suffix “benzene”