Organic Chemistry 1
Lecture 5

Instructor: Prof. Duncan Wardrop

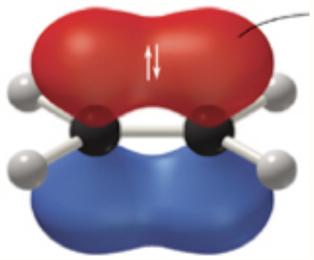
Time/Day: T & R, 12:30-1:45 p.m.

January 26, 2010

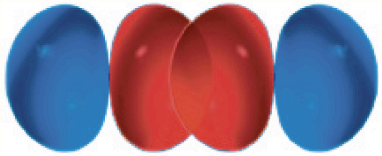
Self Test Question

Which of the following best depicts a π-bond?

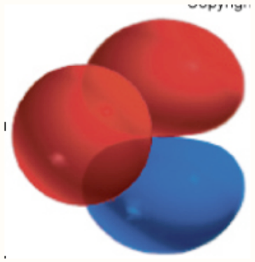
a.



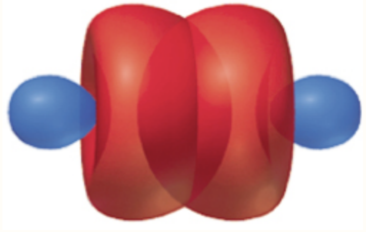
c.



e.



b.



d.

A. a

B. b

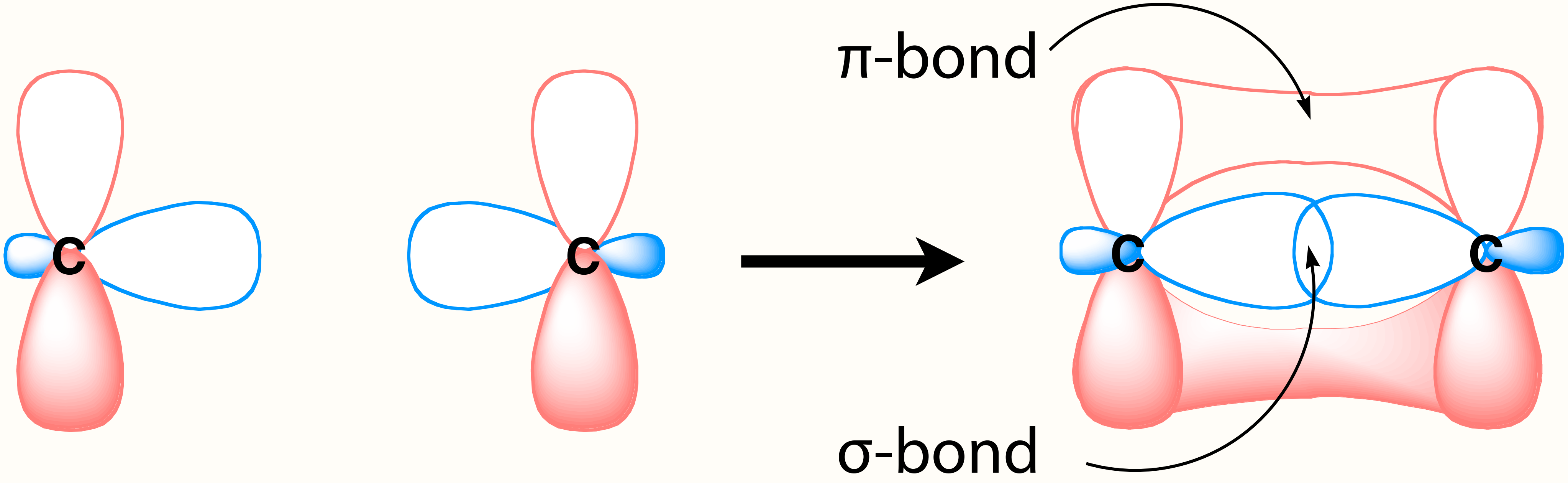
C. c

D. d

E. e

The answer is A: A bonding interaction exists when two orbitals overlap “in phase” with each other. The electron density in π bonds lie above and below the plane of carbon and hydrogen atoms. B depicts a C–C sigma bond between two sp-hybridized carbon atoms. C represents a sigma bond formed via the head-to-head overlap of two p-orbitals.

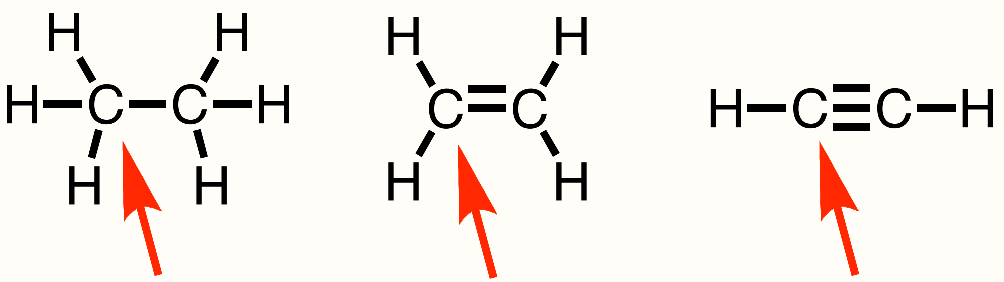
Summary of Bond Types



bond	**σ-bonds** (head-to-head)	**π-bonds** (side-to-side)
single	1	0
double	1	1
triple	1	2

Self Test Question

Rank the following hydrocarbons in order of *increasing* acidity.



ethane

four $2sp^3$

ethylene

one 2p

three $2sp^2$

ethyne

two 2p

two 2sp

A. ethane, ethylene, ethyne

B. ethane, ethyne, ethylene

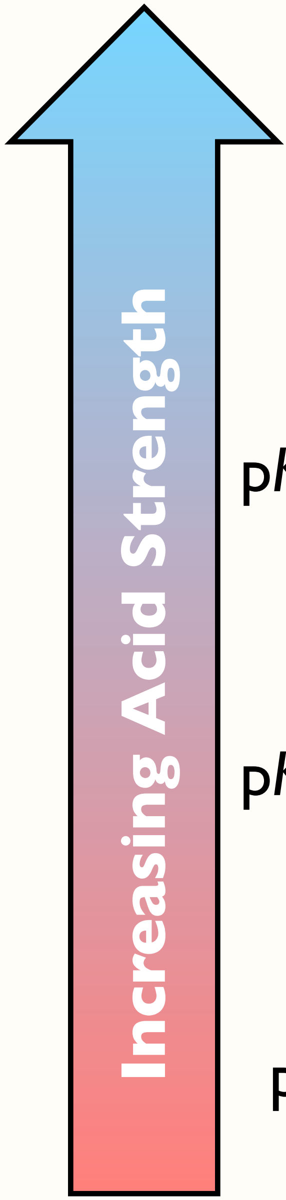
C. ethyne, ethylene, ethane

D. ethyne, ethane, ethylene

E. none of the above

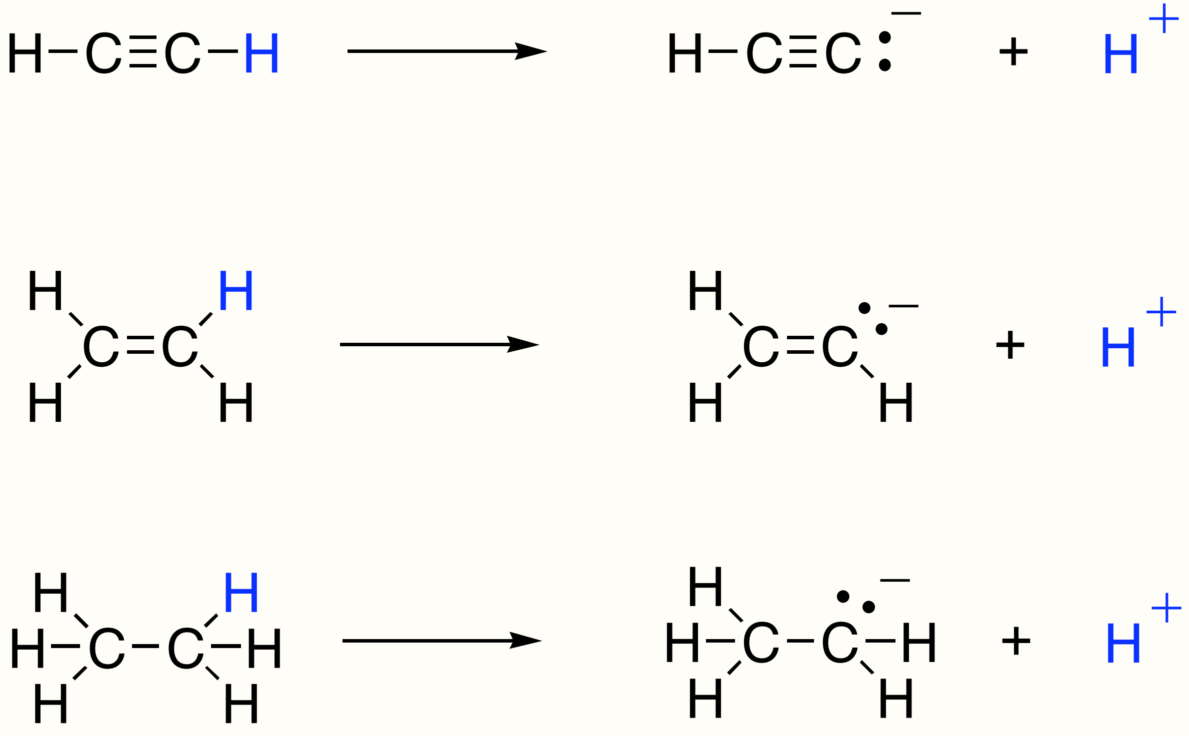
The answer is A.

Hybridization and Acidity



increased *s*-character =
increased electronegativity of carbon =
electrons closer to the nucleus =
stronger acid

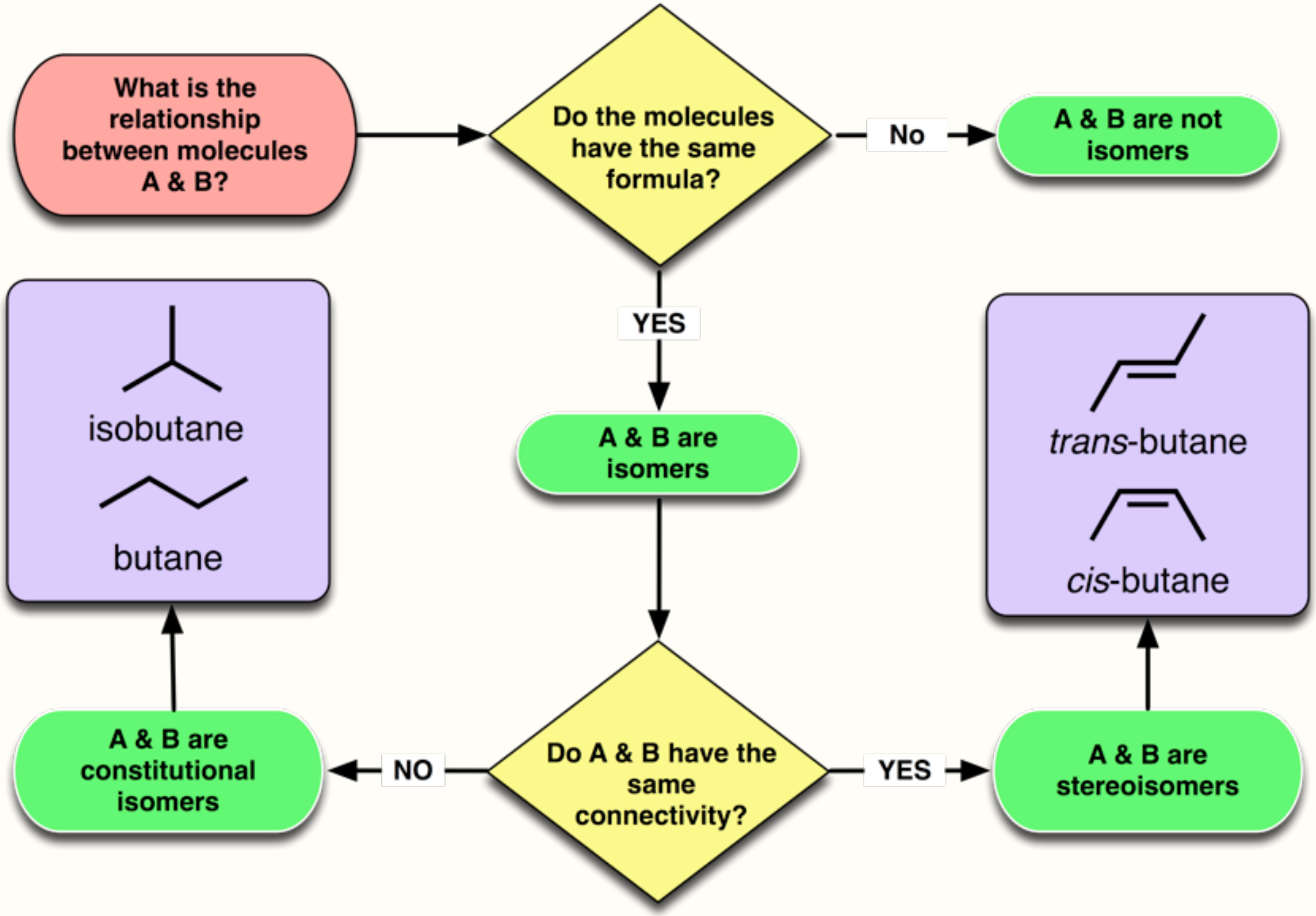
pK_a = 26	sp
pK_a = 45	sp^2
pK_a = 62	sp^3



Chapter 3: Conformational Isomers of Alkanes

Sections: 3.1-3.3

Isomer Classification



What is the relationship between molecules A & B?

Do the molecules have the same formula?

No

A & B are not isomers

YES

A & B are isomers

Do A & B have the same connectivity?

NO

A & B are constitutional isomers

isobutane

butane

YES

A & B are stereoisomers

trans-butane

cis-butane

Classification of Isomers

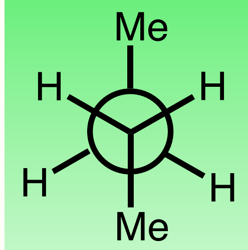
stereoisomers

Can the molecules be interconverted by rotation around single bonds?

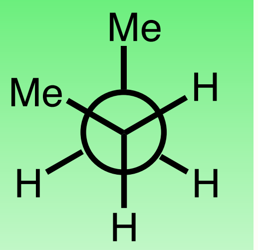
yes

no

conformational



anti butane



gauche butane

configurational

We will continue the isomer tree in Chapters 5 & 7 where we'll encounter subdivisions of configurational isomers

Model Activity

1. Make a model of butane.
2. Make a separate model of isobutane.
3. Using a *minimum number* of changes, convert your model of isobutane into butane.

Self Test Question

What action did you have to perform to convert isobutane to butane?

A. rotate around C2-C3 bond

B. remove methyl group from C-2

C. add one methyl group to C-1

D. add one methyl group to C-2

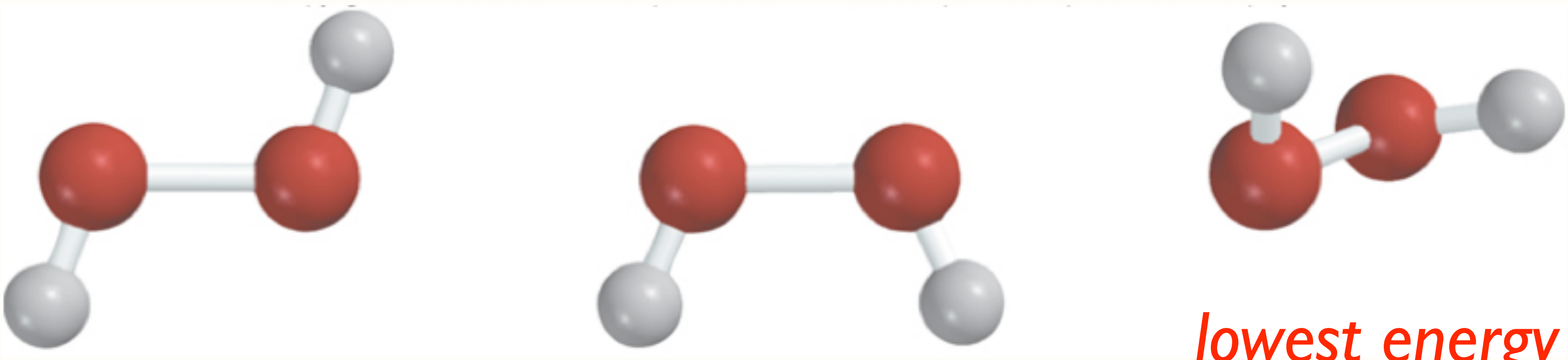
E. rotate around C1-C2

If you have to break bonds to interconvert isomers, they are constitutional (structural) isomers

Rotation Around Single Bonds

conformations: different spatial arrangements of atoms generated by rotation around single bonds

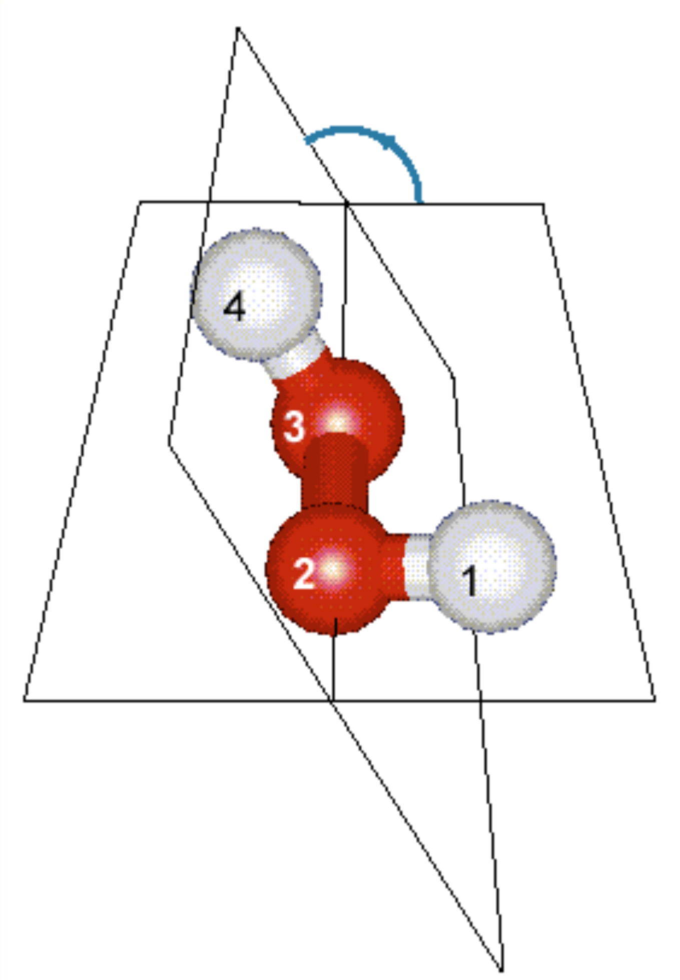
conformational analysis: comparison of the relative energies of different conformational isomers and how they influence properties and reactivity



lowest energy

Measuring Relative Positions of Atoms

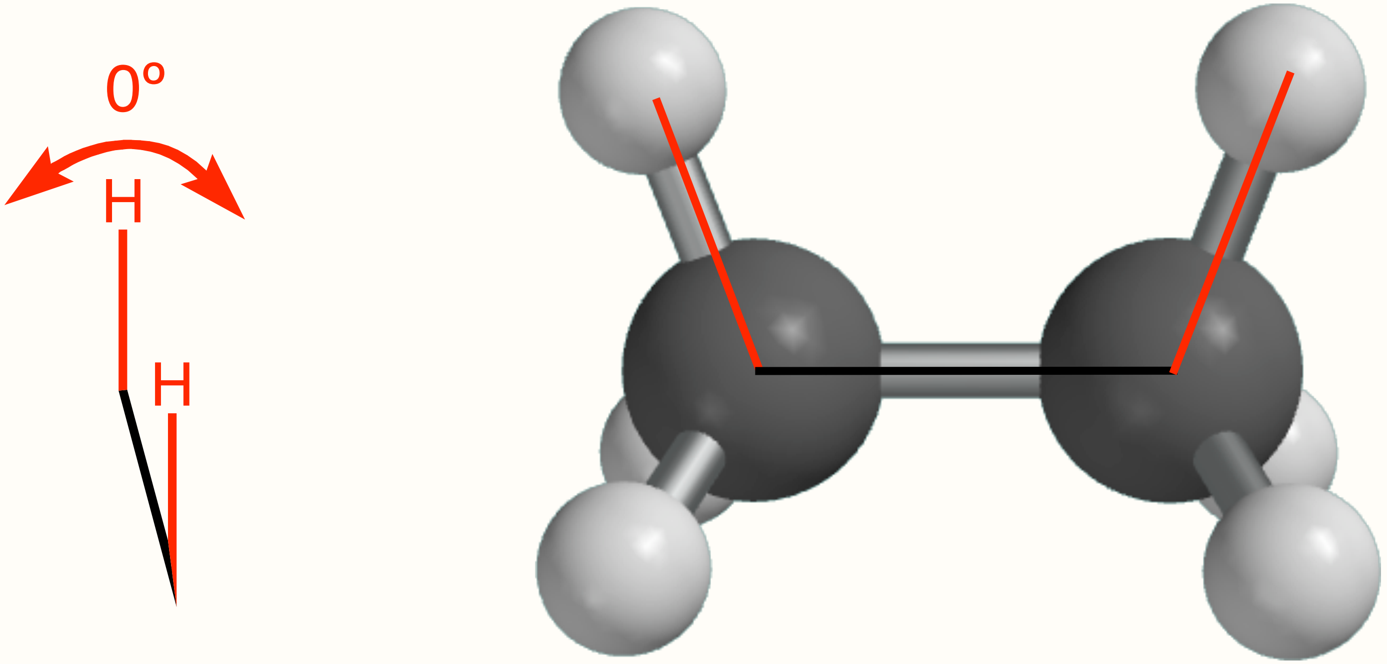
dihedral angle: angle between two intersecting planes; also called the **torsion angle**



plane can be defined by:

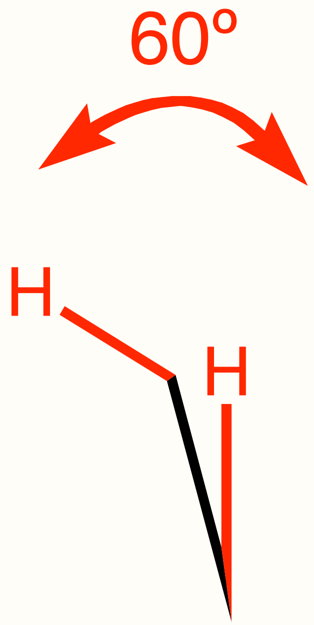
- 3 non-collinear points
- a line & a point not on that line
- two intersecting lines
- two parallel lines

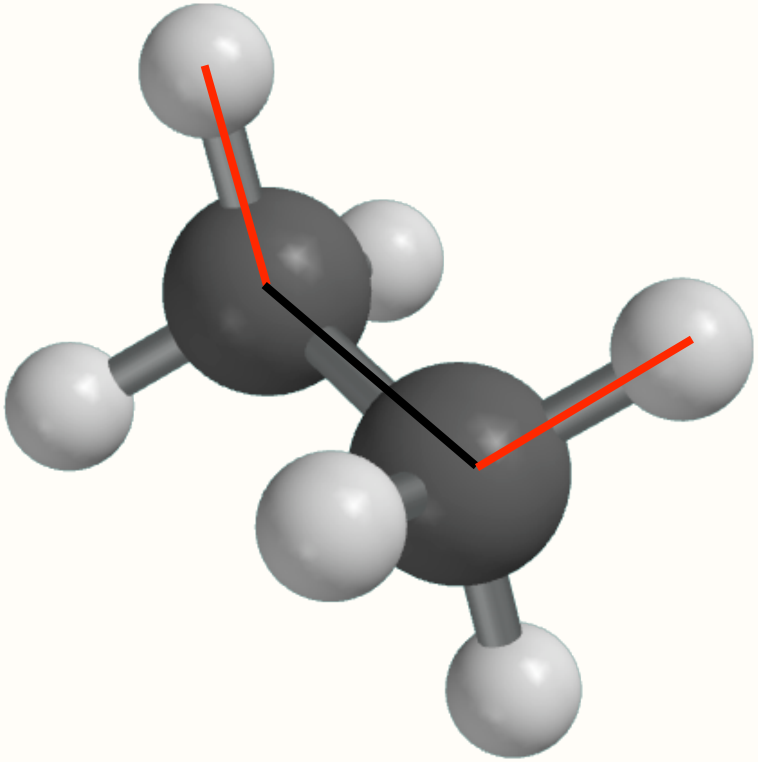
Eclipsed Conformation of Ethane



- C–H bonds on adjacent carbons are parallel (same plane)
- H–C–C–H angle (dihedral angle) = 0°
- highest energy conformation

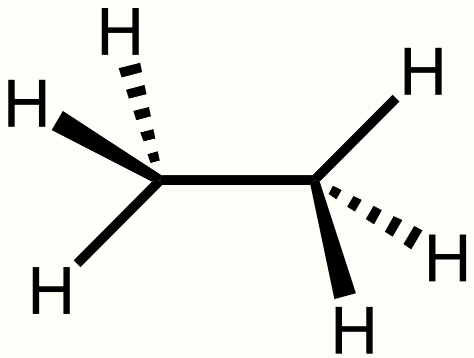
Staggered Conformation of Ethane

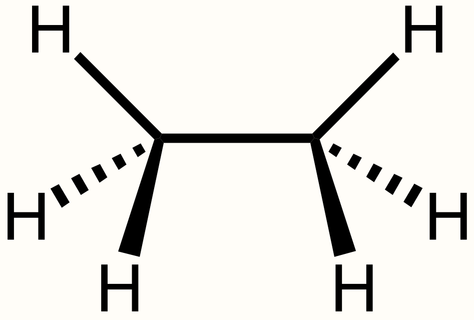


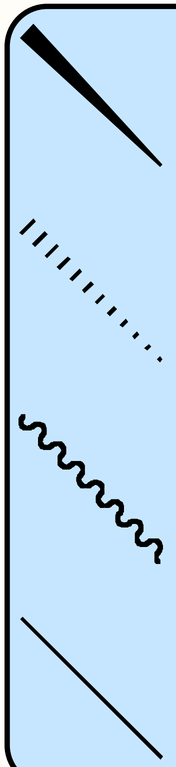


- C–H bond bisects (cuts in half) H–C–H angle on adjacent carbon
- H–C–C–H angle (dihedral angle) = 60º
- lowest energy conformation for ethane

Drawing Conformations: Wedge & Dash







= group is pointing toward you, in front of the plane of paper

= group is pointing away from you, behind the plane of paper

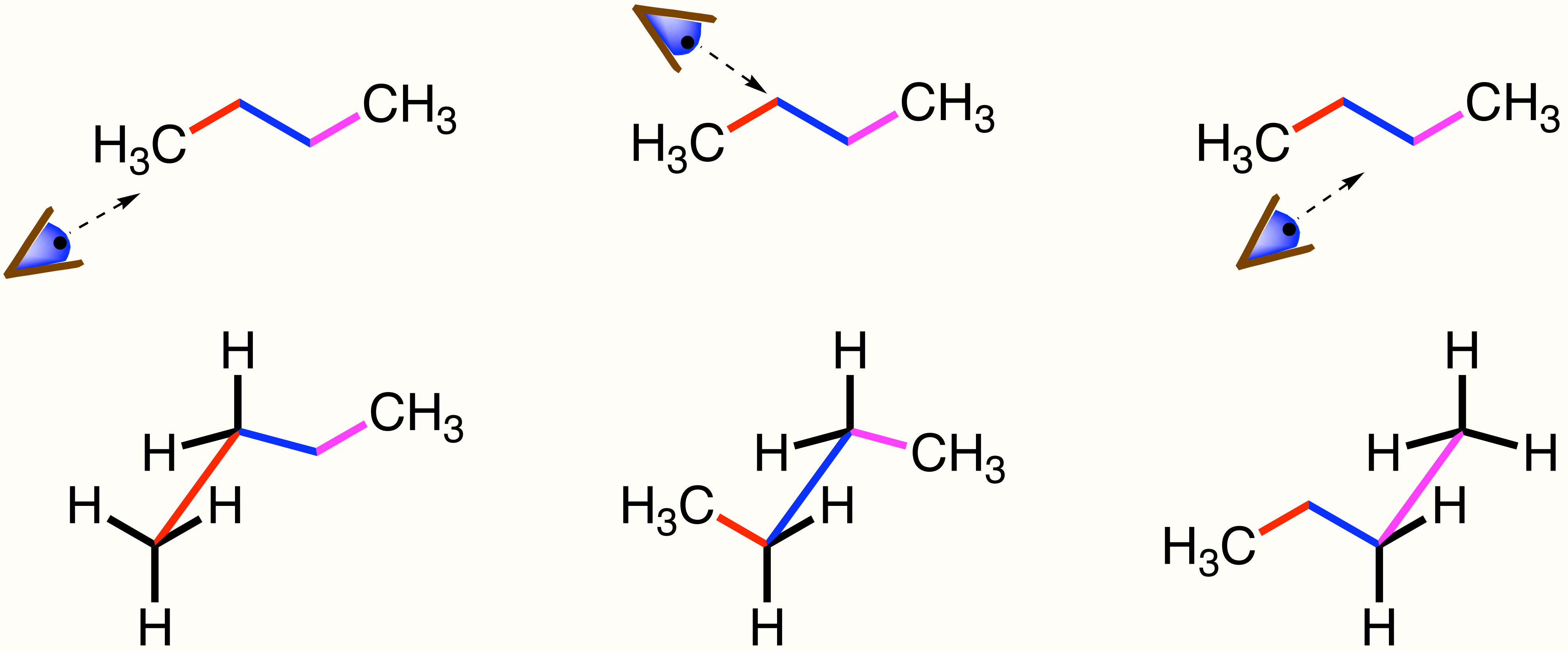
= group is *either* toward or away from you, usually denotes mixtures

= group lies in the plane of the drawing surface

rarely followed convention:

thickest part of wedge or dash is always closest to viewer

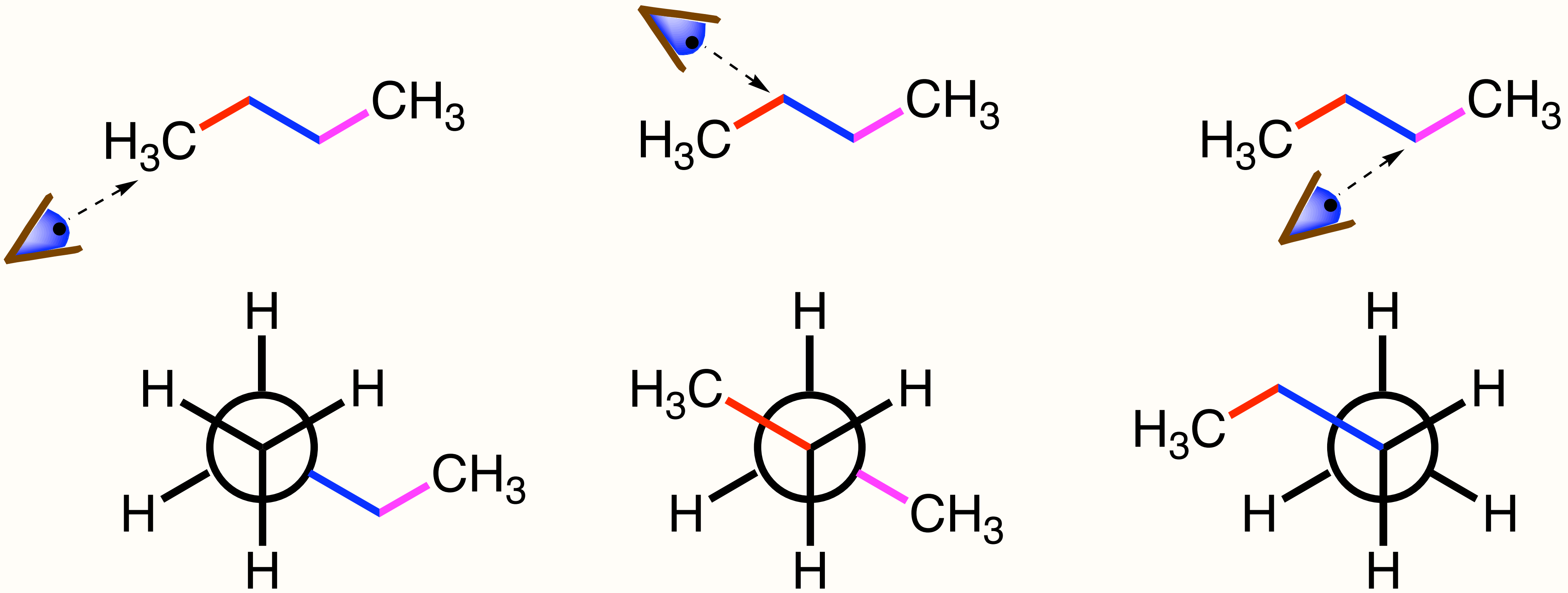
Drawing Conformations: Sawhorse



- one C–C bond viewed "head-on" from oblique angle (acute or obtuse, but not 0º, 90º or 180º); skewed
- all atoms on central C–C bond are shown

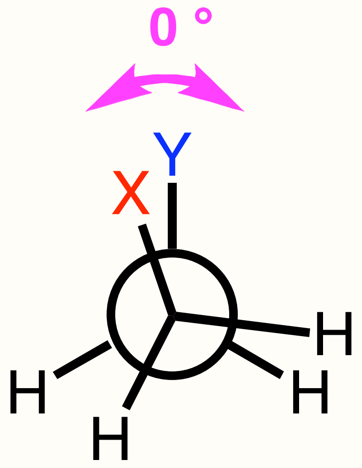
Why a Sawhorse?

Drawing Conformations: Newman Projection



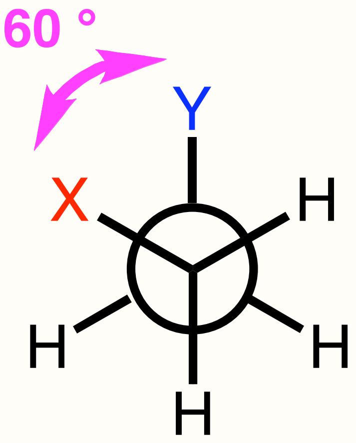
- <u>one</u> C–C bond viewed “head-on” at 0º angle
- all atoms on central C–C bond are shown
- circle represents back carbon atom

Spatial Relationships in Staggered Conformations: Anti & Gauche



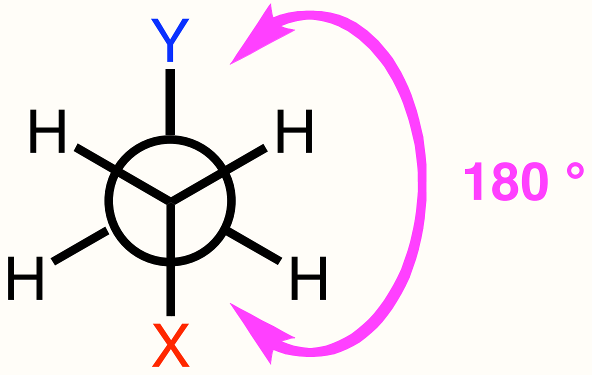
Torsion Angle = 0°

Eclipsed



Torsion Angle = 60°

Gauche

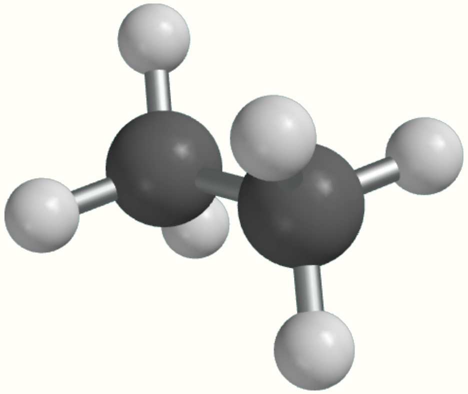
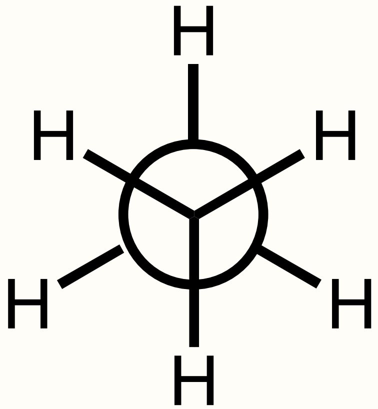
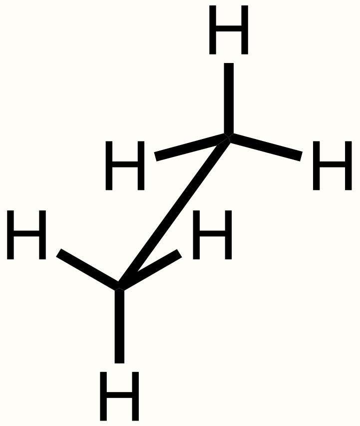
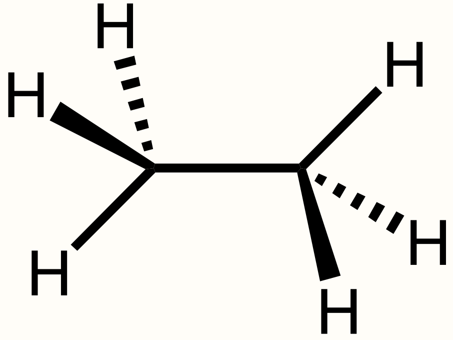
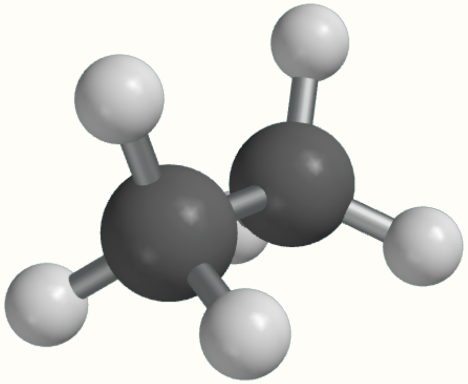
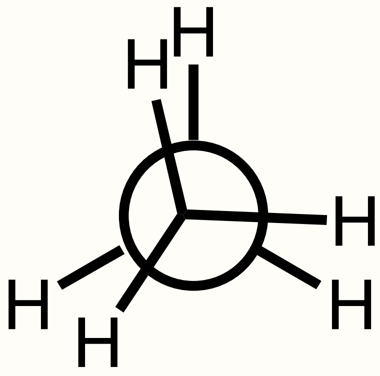
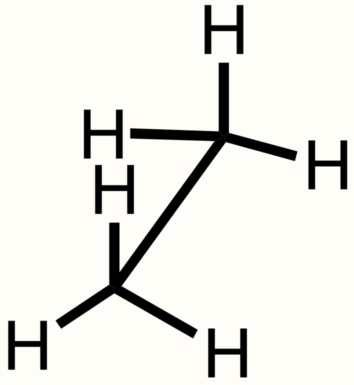
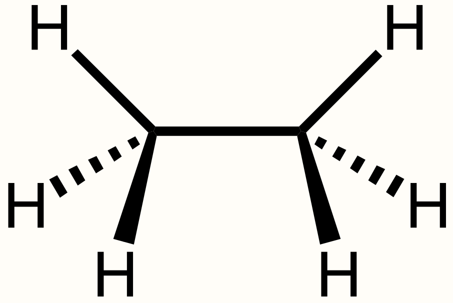


Torsion Angle = 180°

Anti-Periplannar

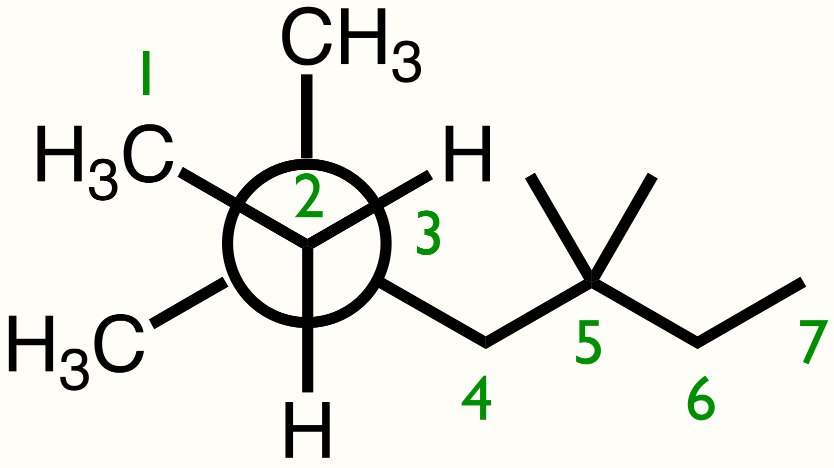
- *anti*: dihedral angle (torsion angle) = 180º
- *gauche*: dihedral angle (torsion angle) = 60º
- these relationships apply to *any* groups on <u>adjacent</u> carbon atoms

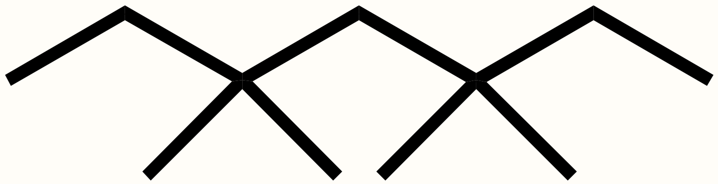
Comparison of Conformational Drawings of Eclipsed and Staggered Ethane

Ball & Stick	Newman	Sawhorse	Dash & Wedge
			
			

Self Test Question

What is the IUPAC name for molecule below?





A. 1,2,2,4,4-pentametnylhexane

B. 3,3,5,5-tetramethylheptane

C. 2-ethyl-2,4,4-trimethylhexane

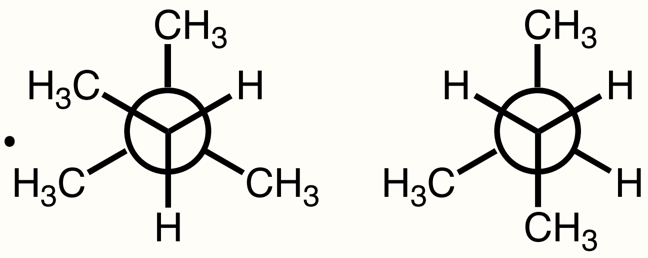
D. 1,2,4,4-tetramethylhexane

E. 3,3-dimethyl-5,5-dimethylheptane

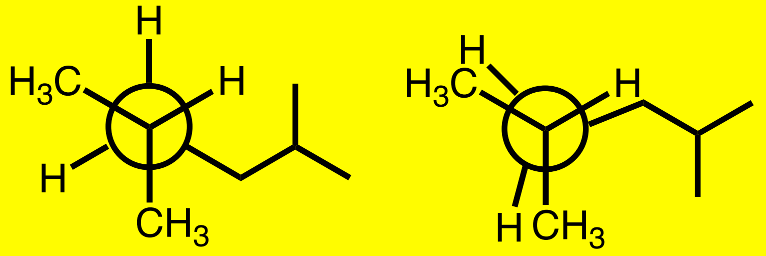
Self Test Question

Which set of molecules are conformational isomers?

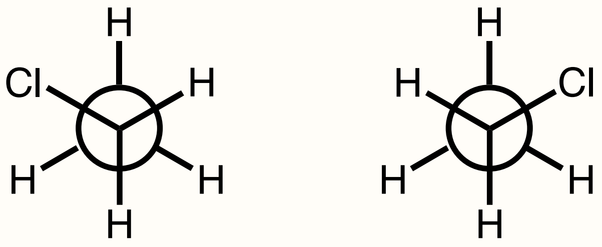
a.



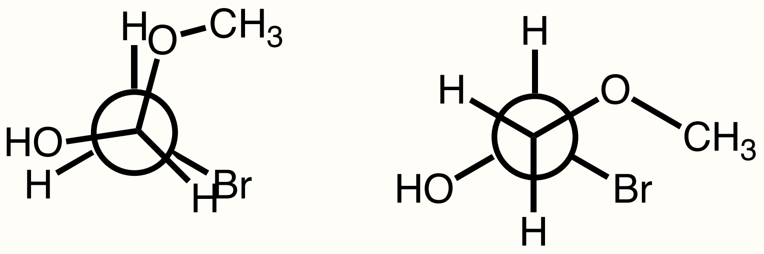
c.



b.



d.



A. a

B. b

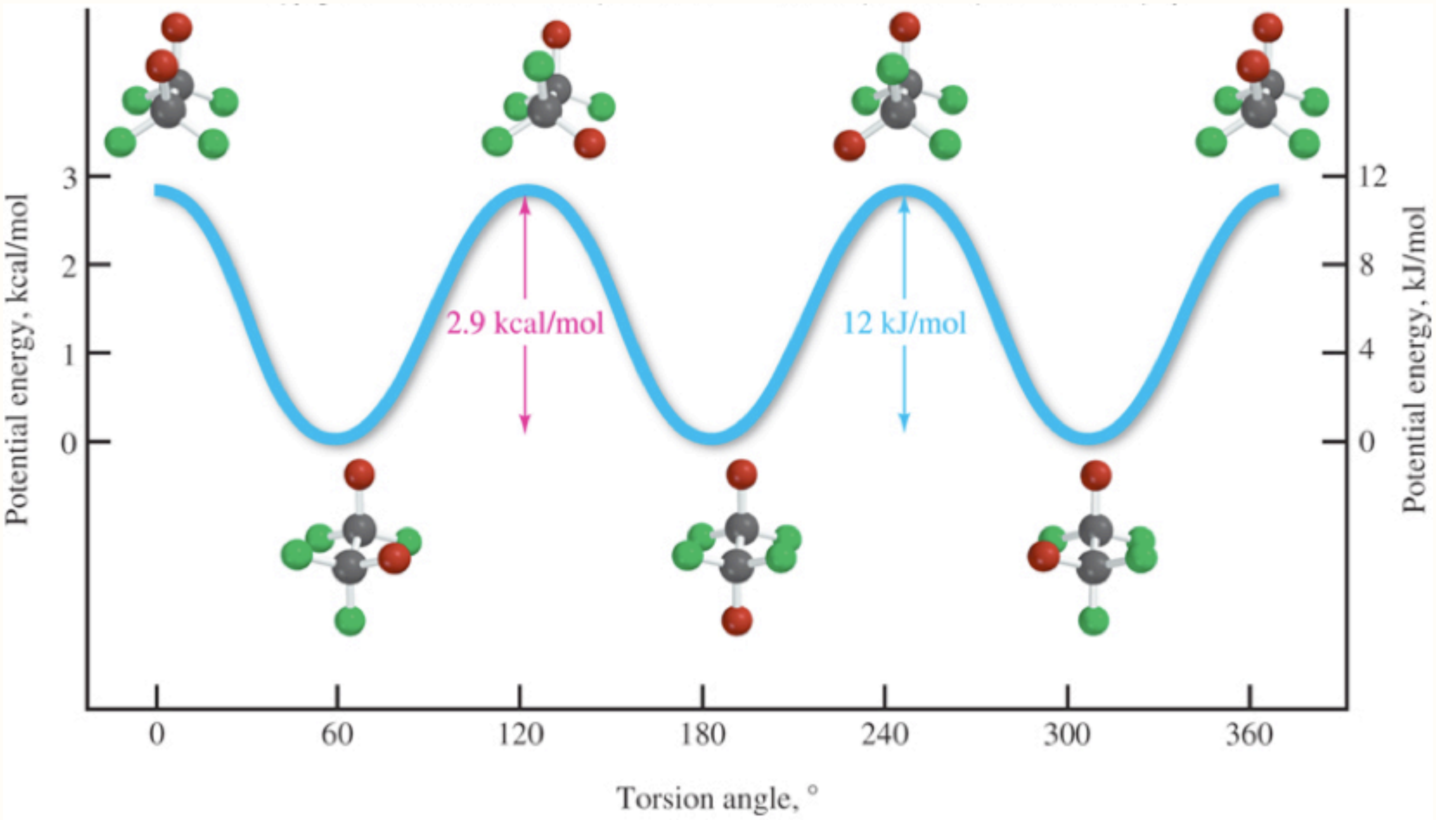
C. c

D. d

The answer is C. Pair A are different compounds and not isomers; Pair B are identical and therefore neither isomers or conformers of one another; Pair D share the same formula but differ in their constitution and therefore cannot be conformers of one another.

Conformational Analysis of Ethane

staggered conformation more stable than eclipsed



torsional strain: torsion angles (dihedral angles) are other than 60° (gauche)

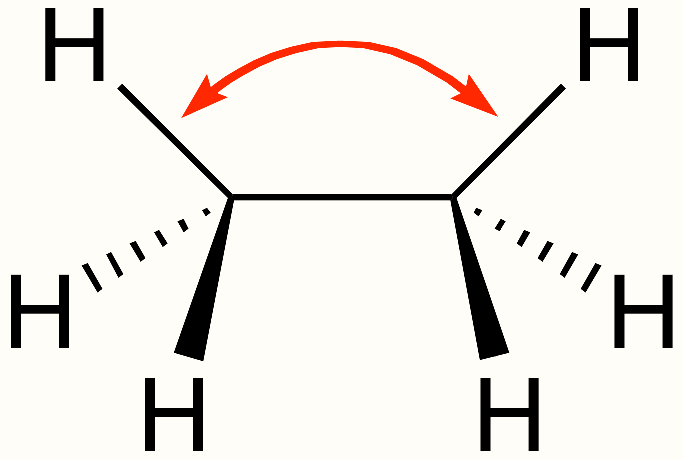
Two Conflicting Arguments Explain Preference for Staggered Conformation

1. **Steric Repulsion** Electrons in vicinal (adjacent) bonds destabilize (raise energy) in eclipsed conformations due to repulsion; they are closer.

2. **Hyperconjugation:** Electrons in vicinal (adjacent) bonds are delocalized by overlap between bonding and anti-bonding orbitals

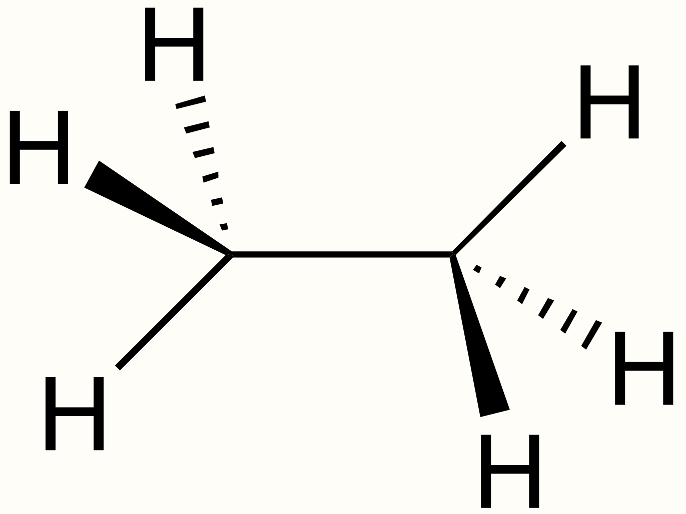
1. Steric Repulsion

maximum electron-electron repulsion



eclipsed

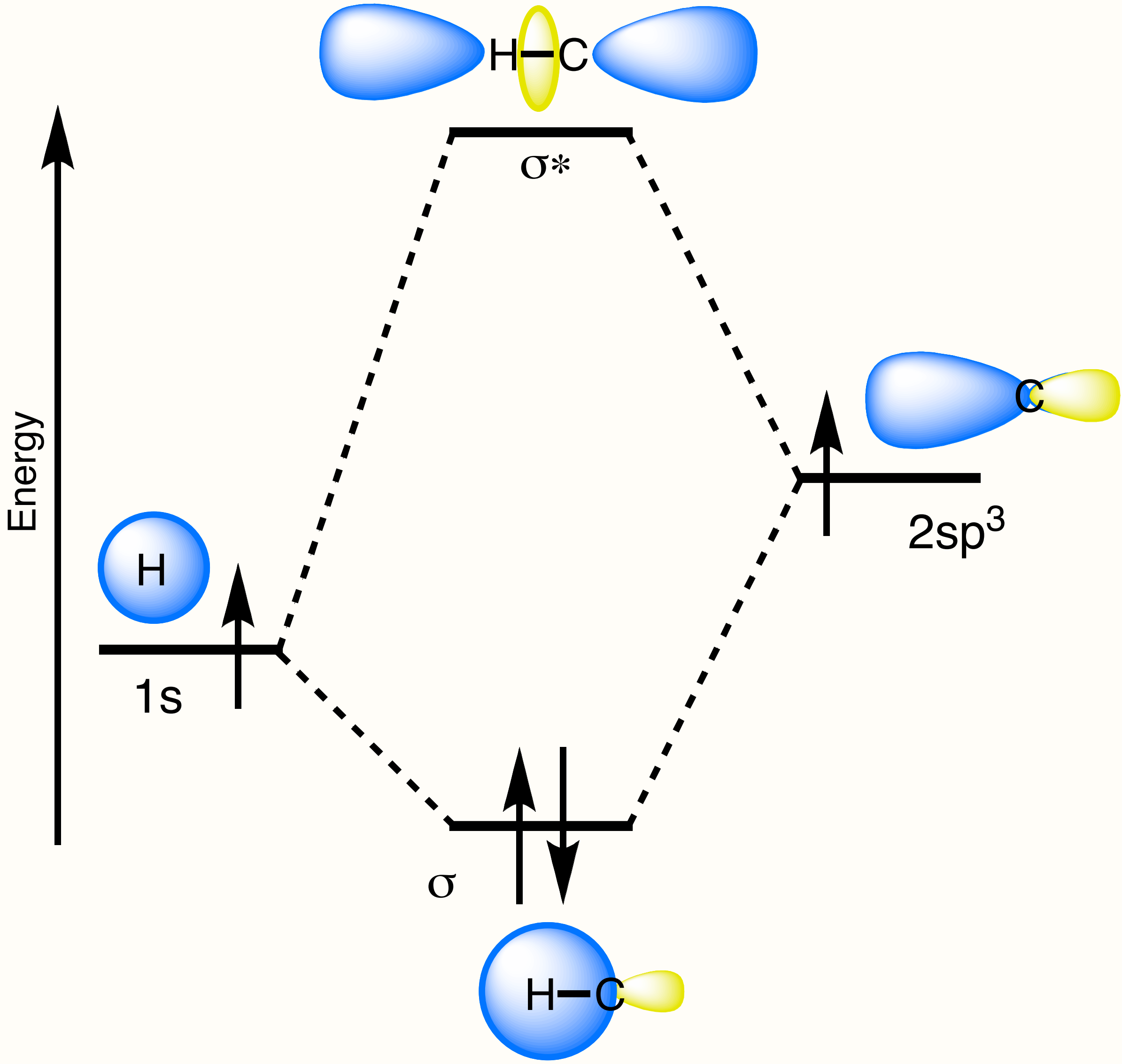
*Read on......



staggered

- widely accepted explanation until 2001*
- electron-electron repulsion is greatest in eclipsed conformation

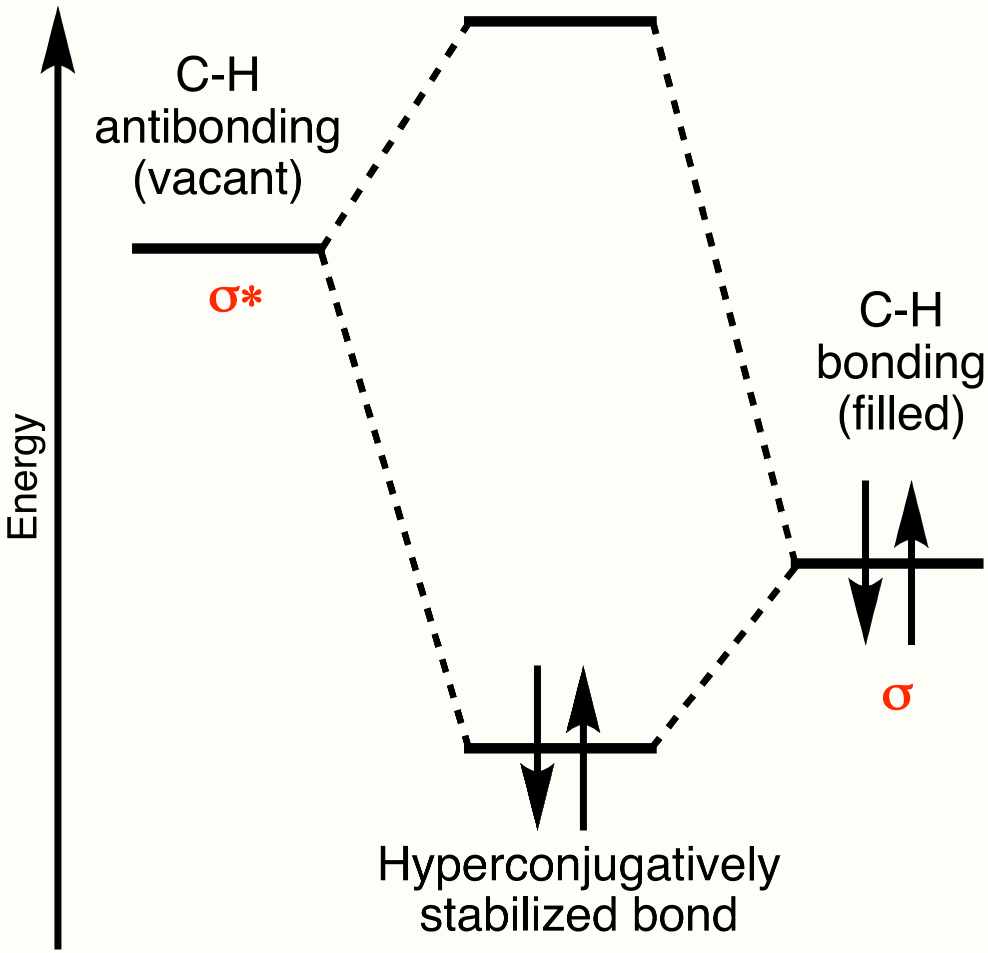
Brief Revision of Molecular Orbitals



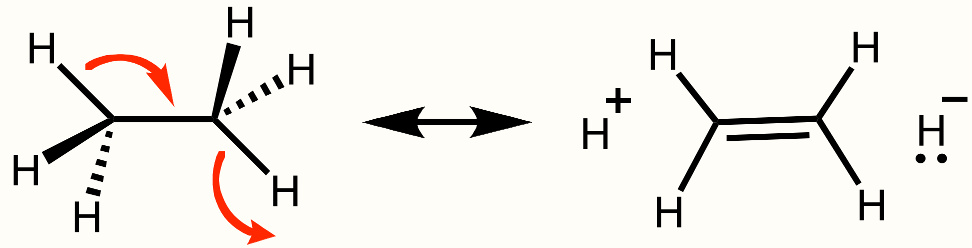
Molecular Orbitals Review:

- node = where orbitals change sign = no electrons found
- number of atomic orbitals = number of molecular orbitals
- bonding orbital (σ) is lower in energy than both atomic orbitals
- anti-bonding orbital (σ*) = less electron density between nuclei than if no bond at all; electrons from each atom repel each other
- even though an anti-bonding (s*) orbital may not be filled with electrons; it is still present in the molecule

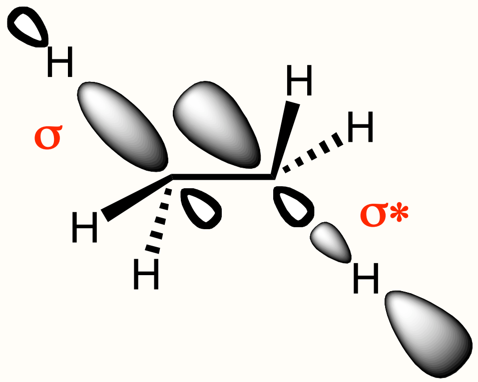
2. Vicinal Hyperconjugation



"Bond-No Bond Resonance"



A Stereoelectronic Effect

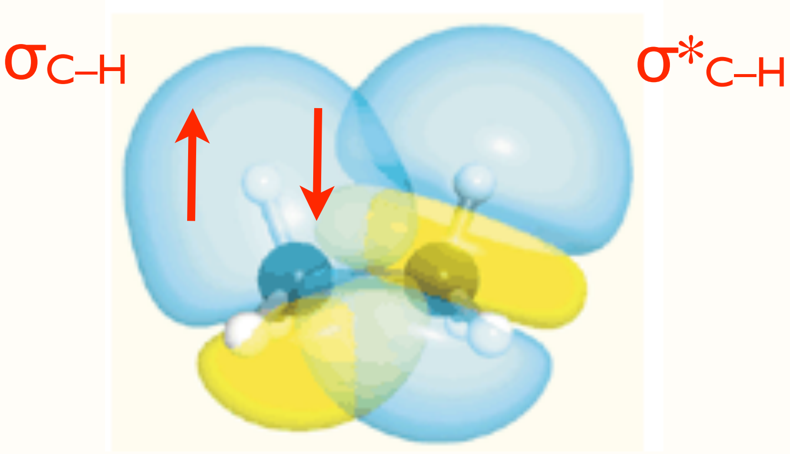


Stabilizing filled-empty orbital overlap only possible in staggered conformation

2. Hyperconjugation: Role in Conformations

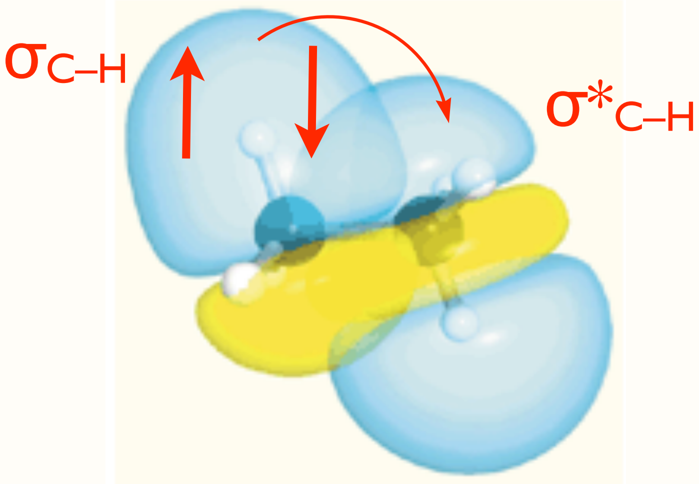
hyperconjugation: donation (transfer) of electrons from a filled orbital to an empty orbital; orbitals must overlap to allow transfer

Eclipsed



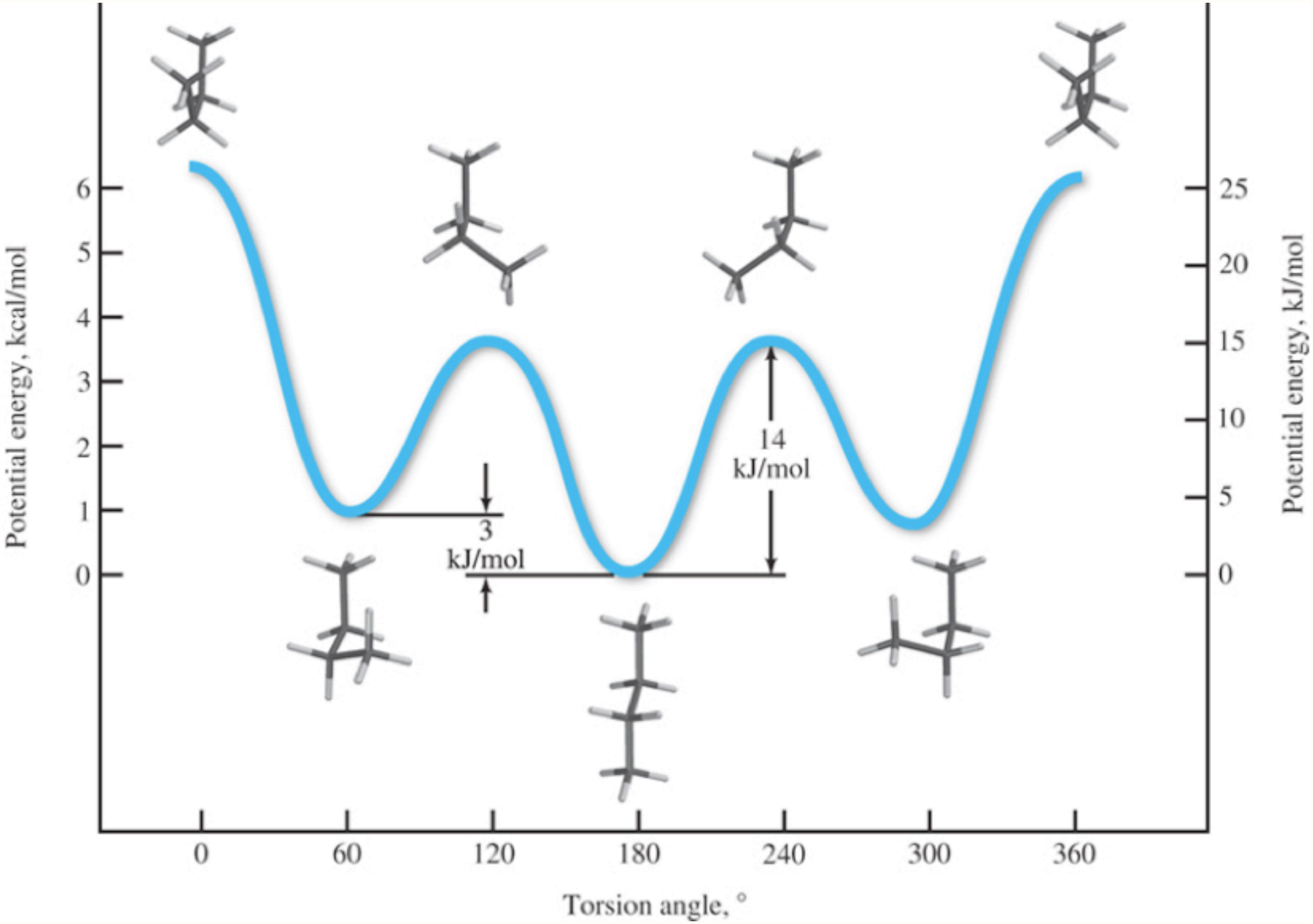
σ & σ* weak overlap =
no hyperconjugation =
no electron delocalization =
no additional stabilization

Staggered



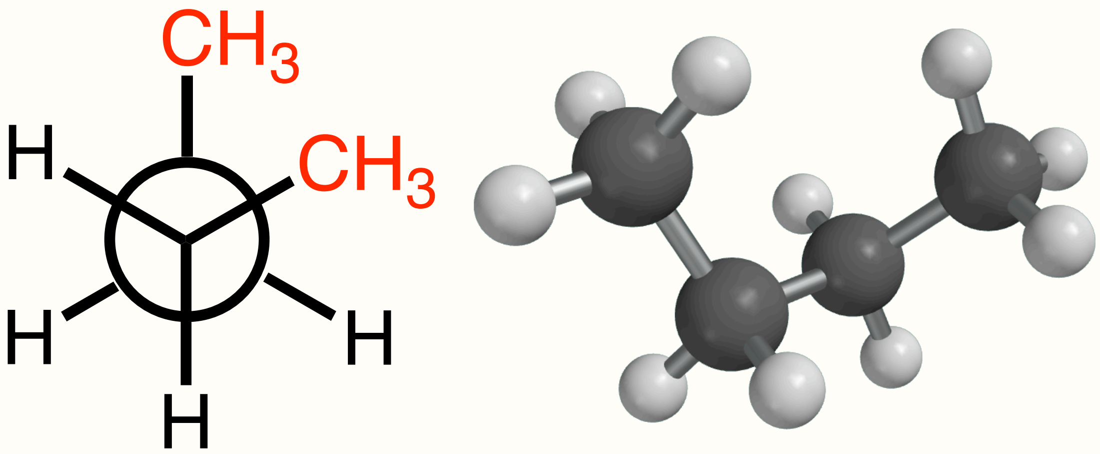
σ & σ* strong overlap =
hyperconjugation (σ→σ*) =
delocalized electrons =
lower energy (more stable)

Conformational Analysis of Butane

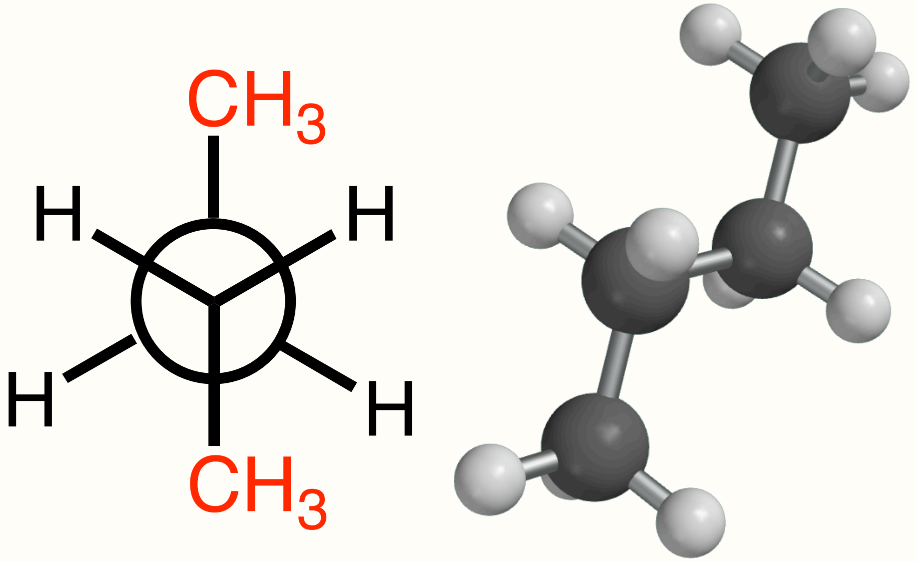


Van der Waals Strain (Steric Strain) in Staggered Conformations of Butane

Gauche

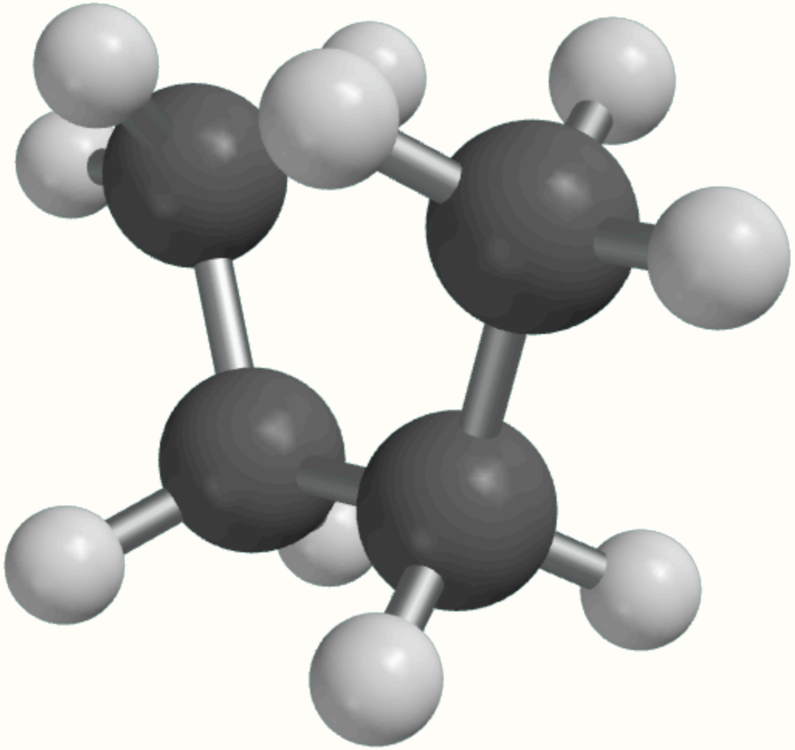


Anti



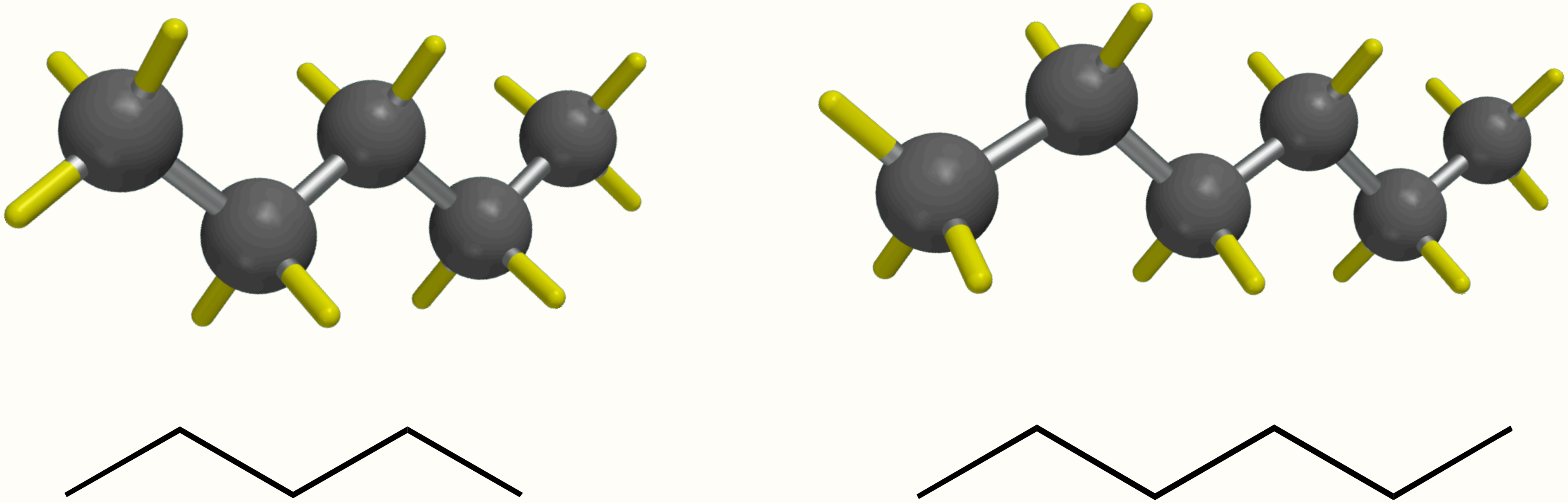
- The gauche conformation of butane is 3 kJ/mol less stable than the anti.
- The gauche conformation is destabilized by van der Waals strain (also called steric strain); repulsive van der Waals force between methyl groups
- **van der Waals strain** = destabilization that results from atoms being too close together; nuclear-nuclear & electron-electron repulsions dominate

Van der Waals Strain (Steric Strain)



- conformation of butane with two methyl group eclipsed is the least stable (highest in energy)
- destabilized by both torsional strain (eclipsed vicinal bonds) and van der Waals strain (atoms close together)

Conformation of Higher Alkanes



- *anti* arrangements of C-C-C-C units
- all vicinal (adjacent) bonds = gauche or anti
- minimize torsional strain; minimize steric strain
- described as "zig-zag" backbone

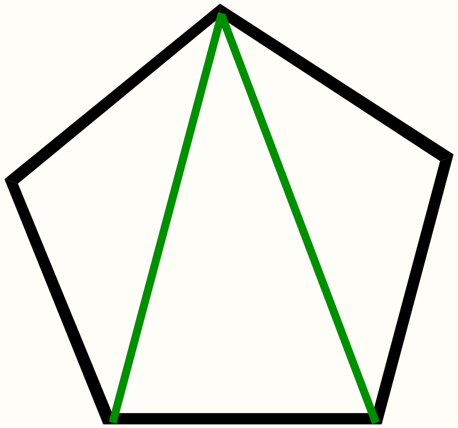
Conformational Isomers of 3-5 Carbon Cycloalkanes

Sections: 3.4-3.6

Self Test Question

Geometry: What are the angles in a regular pentagon?

$$\frac{3 \times 180°}{5} = 108°$$



A. 110°

B. 109.5°

C. 60°

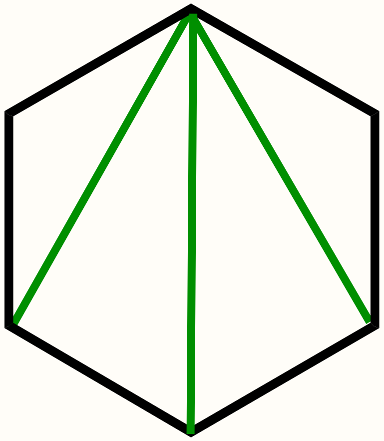
D. 120°

E. 108°

Self Test Question

Geometry: What are the angles in a regular hexagon?

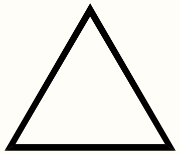
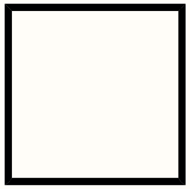
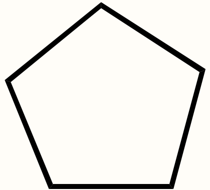
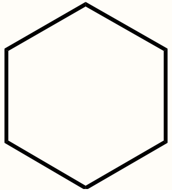
$$\frac{4 \times 180^\circ}{6} = 120^\circ$$



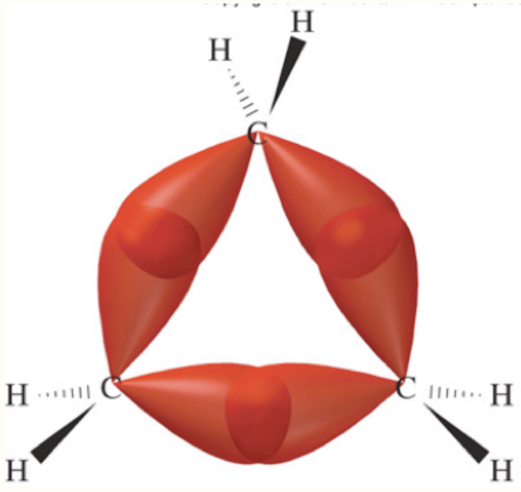
A. 90°
B. 120°
C. 144°
D. 150°
E. 30°

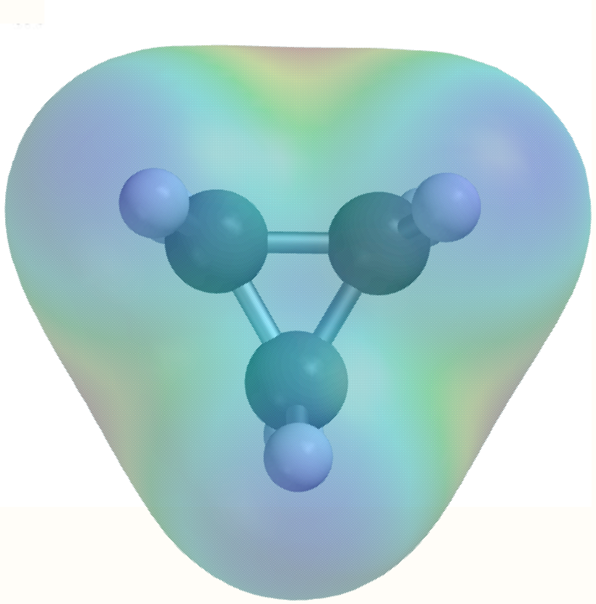
Heats of Combustion of Cycloalkanes

Angle strain (Baeyer strain): increase in energy associated with bond angles that deviate from tetrahedral (109.5°)

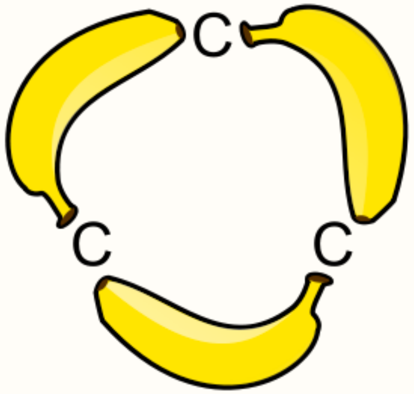
Cycloalkane	Shape	Geometric Angles	Difference from 109.5°	Heat of Combustion (-ΔH) per CH_2 Group
cyclopropane		60°	49.5°	167 kcal/mol
cyclobutane		90°	19.5°	163 kcal/mol
cyclopentane		108°	1.5°	157 kcal/mol
cyclohexane		120°	10.5°	156 kcal/mol

Cyclopropane & Banana Bonds!



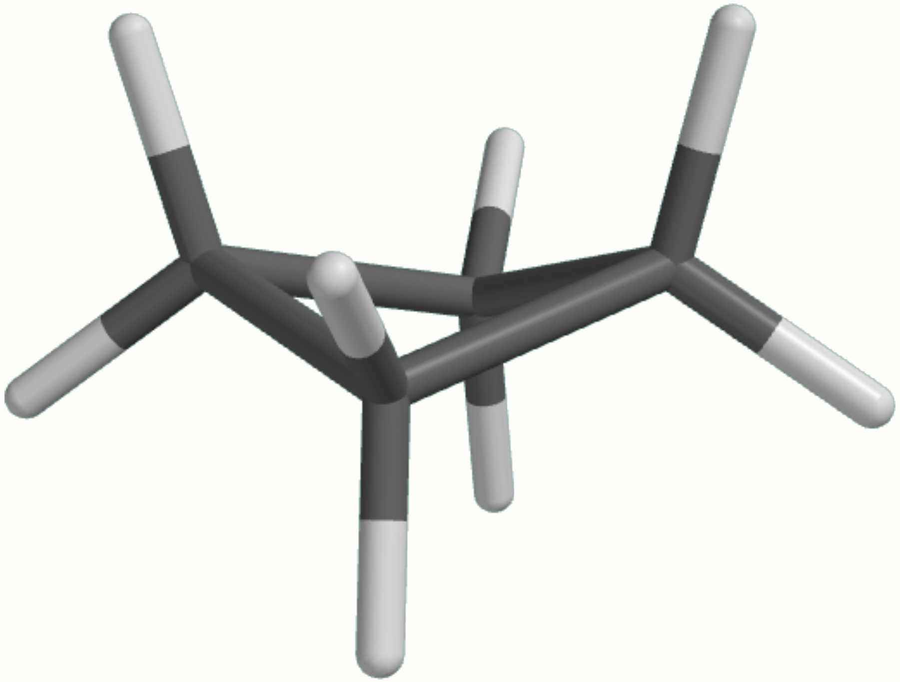


- only planar cycloalkane
- bent C-C bonds: sp^3 orbitals unable to overlap along internuclear axis; weaker C-C σ-bonds
- angle strain: 60° is a large deviation from 109.5°
- torsional strain: all bonds are eclipsed



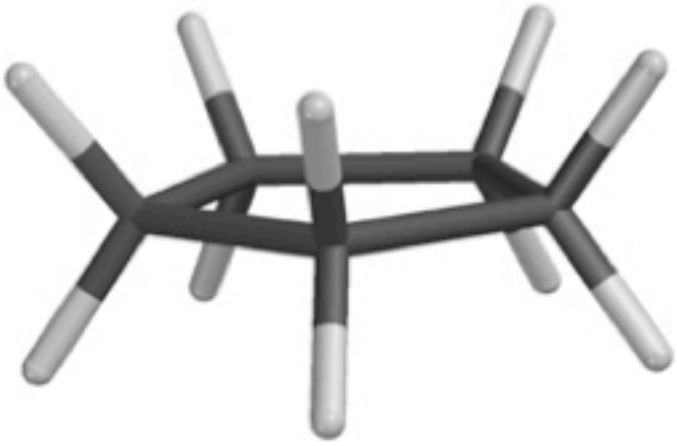
Conformations of Cyclobutane

Nonplanar "puckered" Conformation

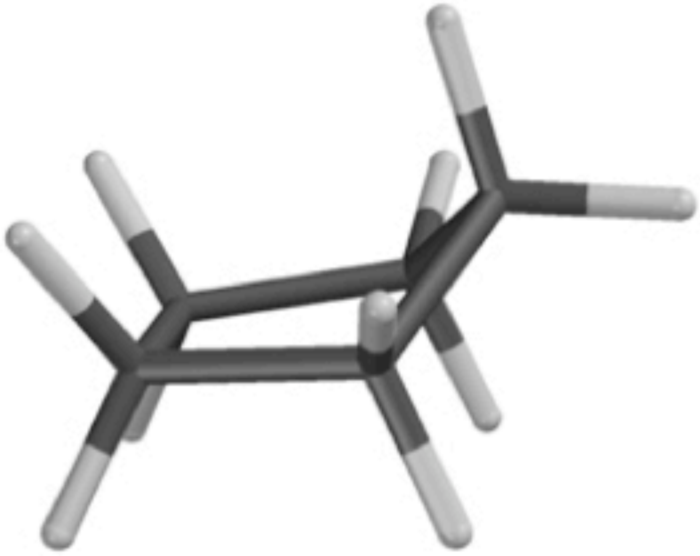


- torsional strain reduced in puckered conformation
- less angle strain than cyclopropane

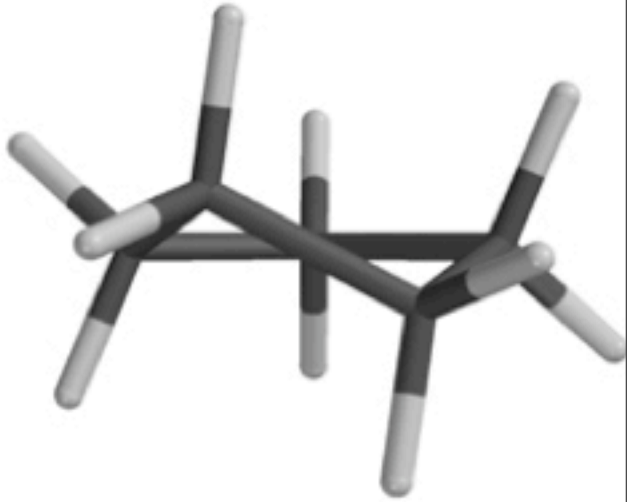
Conformations of Cyclopentane



Planar



Envelope



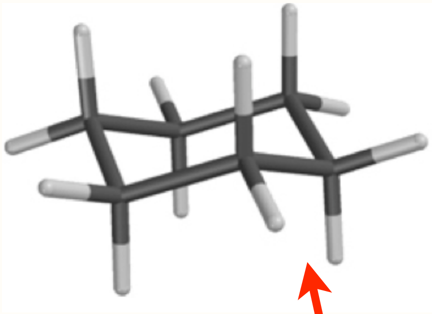
Half-Chair

- planar conformation least stable; all bonds eclipsed
- some torsional strain relieved in envelope and half-chair
- envelope & half-chair have similar energies; interconvert rapidly

Self Test Question

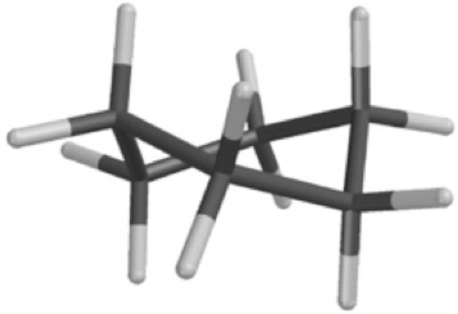
Which of the following conformations of cyclohexane would you expect to have the highest heat of combustion?

a.

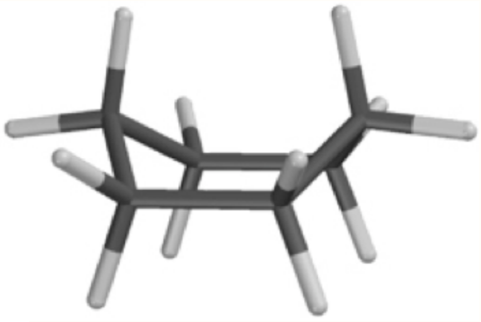


lowest NRG: all gauche & anti relationships

b.



c.



highest NRG: 4 eclipsed relationships

A. a

B. b

C. c

Quiz This Week

- Topic = Chapter 2
- Alkanes, Alkenes & Alkynes
- IUPAC Nomenclature
- Oxidation Numbers
- Heats of Combustion
- Bonding, Hybridization (ethene)

Next Lecture. . .

Chapter 3: Sections 3.7-3.12

You are responsible for sections 3.13-3.15