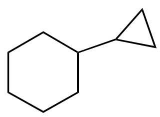
CHEM 261 September 23, 2021

General Molecular Formula of Alkanes

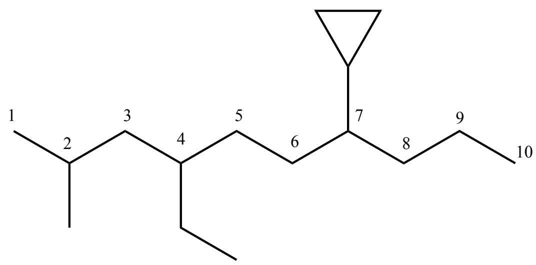
- No rings: general formula is C_NH_{2N+2}
- Each deviation of 2 hydrogens from the C_NH_{2N+2} formula is a **degree of unsaturation**
- 1 Degree of unsaturation : C_NH_{2N} Alkanes with one ring or double bond
- 2 Degrees of unsaturation: C_NH_{2N-2} Alkanes with two rings or double bonds, or one each

Examples of Naming Cycloalkanes:



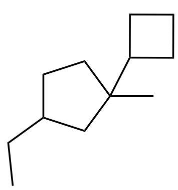
Degree of Unsaturation= 2

1-Cyclopropylcyclohexane



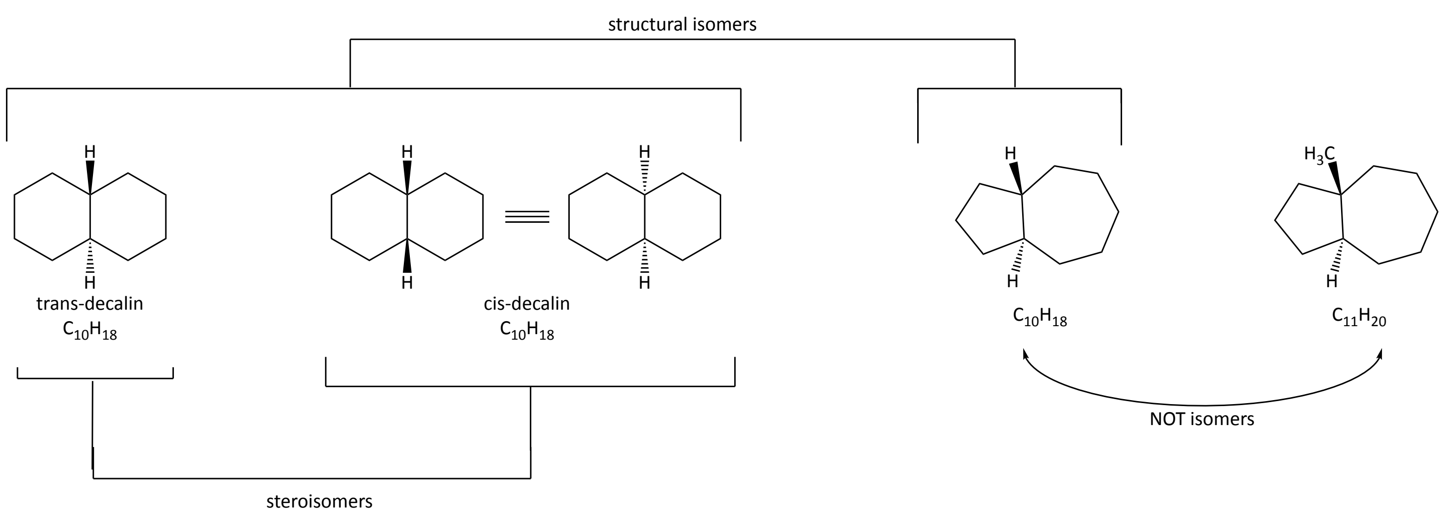
Degree of Unsaturation= 1

7-cyclopropyl-4-ethyl-2-methyldecane

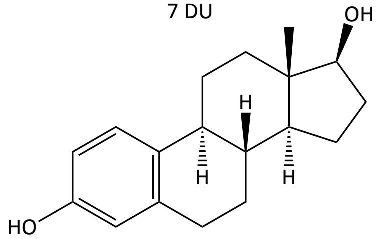


Degree of Unsaturation= 2

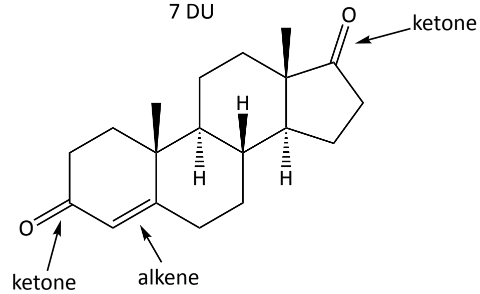
1-Cyclobutyl-3-ethyl-1-methylcyclopentane



estradiol
7 DU



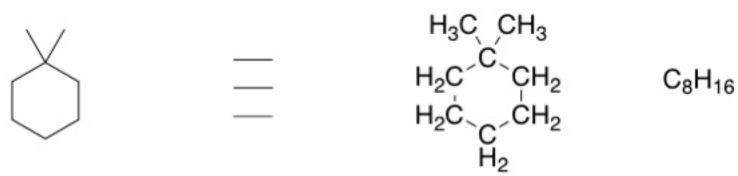
testosterone
7 DU



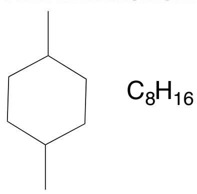
ISOMERS

Structural (Constitutional) Isomers

Share the same molecular formula but have the atomic bonds in different places



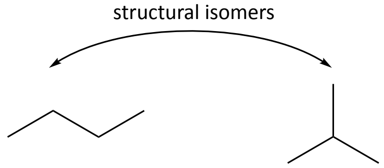
1,1-dimethylcyclohexane



1,4-dimethylcyclohexane

The above two compounds are structural (also known as constitutional) isomers

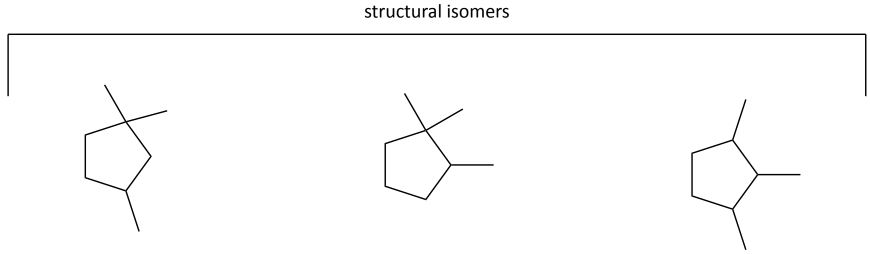
structural isomers



n-butane
C_4H_{10}

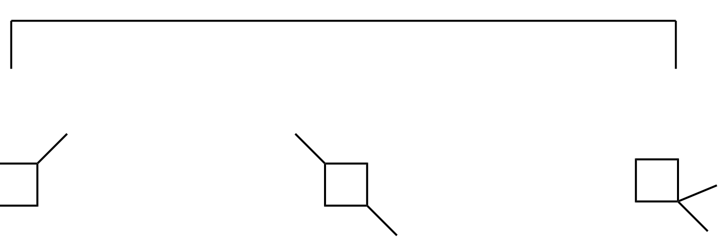
2-methylcyclopropane
C_4H_{10}

structural isomers



1,1,3-trimethylcyclopentane 1,1,2-trimethylcyclopentane 1,2,3-trimethylcyclopentane

Structural or constitutional isomers



1,2-dimethylcyclobutane 1,3-dimethylcyclobutane 1,1-dimethylcyclobutane

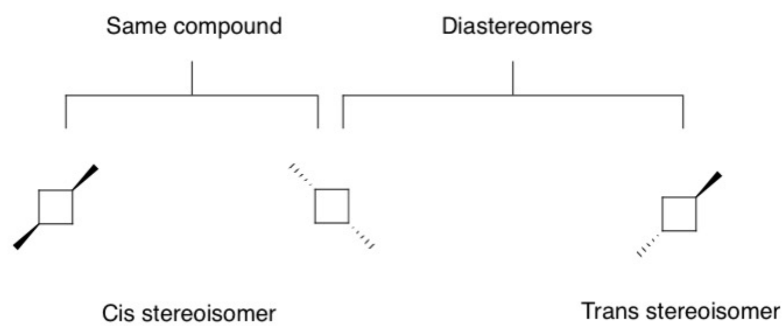
Stereoisomers

Compounds with the same molecular formula, same order of connection (base name) but connection of atoms that differ in 3D geometry

Two Types:

1. Diastereomers - stereoisomers that are not mirror images
2. Enantiomers - stereoisomers that are non-superposable mirror images of each other

Example: 1,3 dimethylcyclobutane

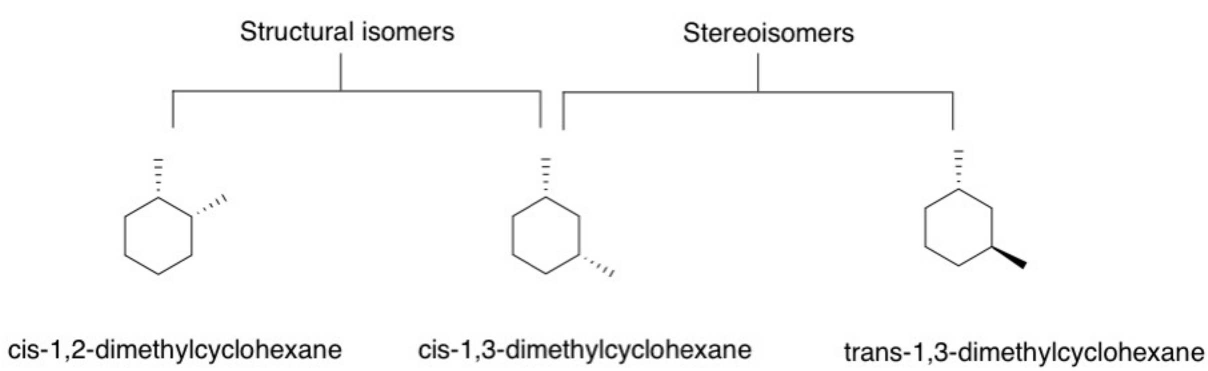


The first and second compounds are the same compound rotated in 3D space. The third compound has different geometry at one center, making it a stereoisomer, specifically a diastereomer.

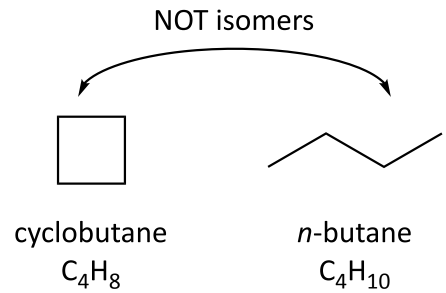
Cis - the substituents are on the same side of the ring

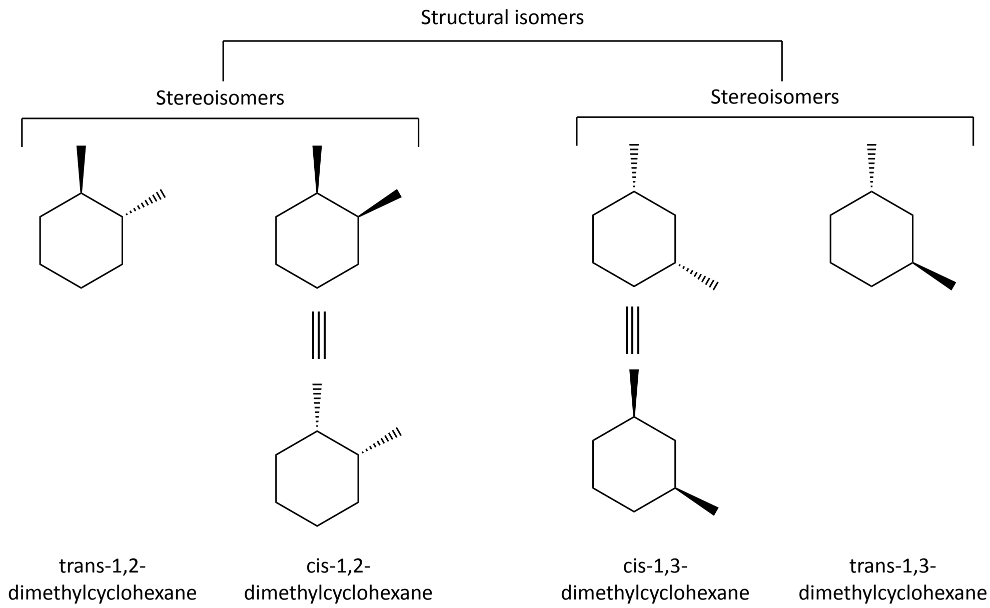
Trans - the substituents are on opposite sides of the ring

Example: 1,2-dimethylcyclohexane and 1,3-dimethylcyclohexane



The second two compounds are diastereomers of each other.



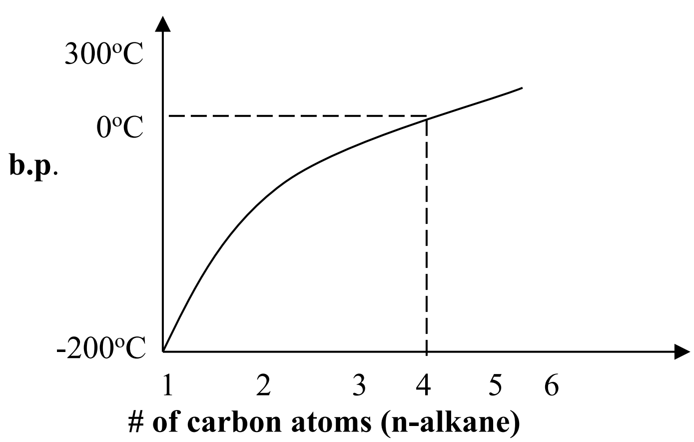


Physical Properties of Alkanes:

Boiling Point

Intermolecular forces are dominated by London forces

- Alkanes are non-polar because H and C have similar electronegativity leading them to interact with themselves through London Forces which causes a trend in boiling point:

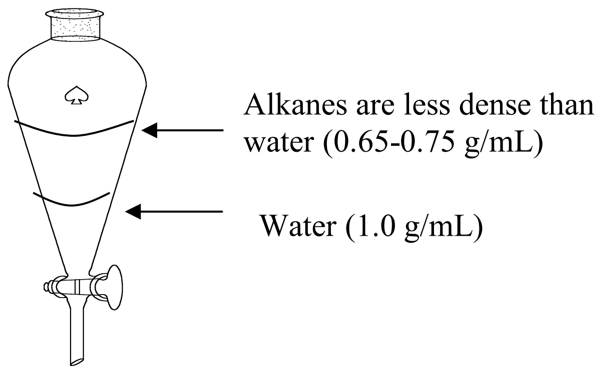


The boiling point increases as the size of the alkane increases because the longer carbon chains have greater surface area to experience London Forces. As the boiling point increases, the graph reaches a plateau where alkane starts to decompose (#C > 20)

Solubility

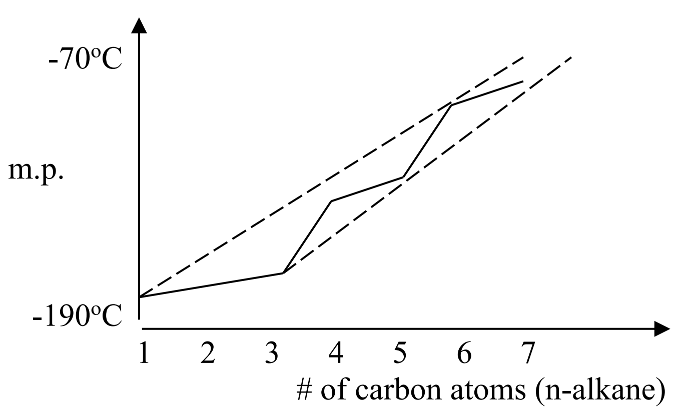
- Soluble in other organic solvents (like dissolves like)
- Not miscible with water → floats due to lower density
- Low density (ρ = rho = g/cm^3)
    - ρ water ~ 1 g/cm^3 or 1 g/mL
    - ρ alkanes ~ 0.7 g/cm^3

Separatory Funnel *(density separation)*

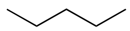
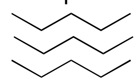
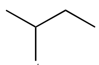
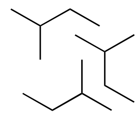
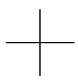


Melting point

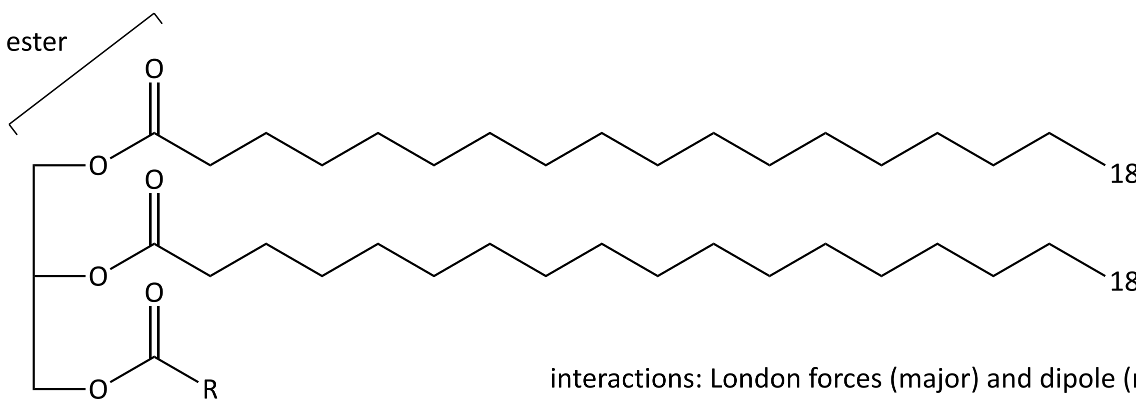
- Melting points are related to the crystal structure packing efficiency
- The predicted line (dotted line) is not what we observe, but a zig zag line (continuous) resulting from crystal structure packing.
- Alkanes are flammable and will combust into CO_2 and H_2O



e.g. Pentane

	mp (^oC)	bp (^oC)		
 n-Pentane	-129	36	well packed 	• n-pentane has high bp due to multiple contacts of straight chains (London Forces)
 Isopentane 2-methylbutane	-160	28	 less well packed	less well packed, less interacting surface area
 Neopentane 2,2-dimethylpropane	-13	9	"ball-like" shape, so B.P. comes down	mp of neopentane determined by good crystal packing of spherical shape. Ball-like shape means surface contact area small and boiling point lower

E.g.

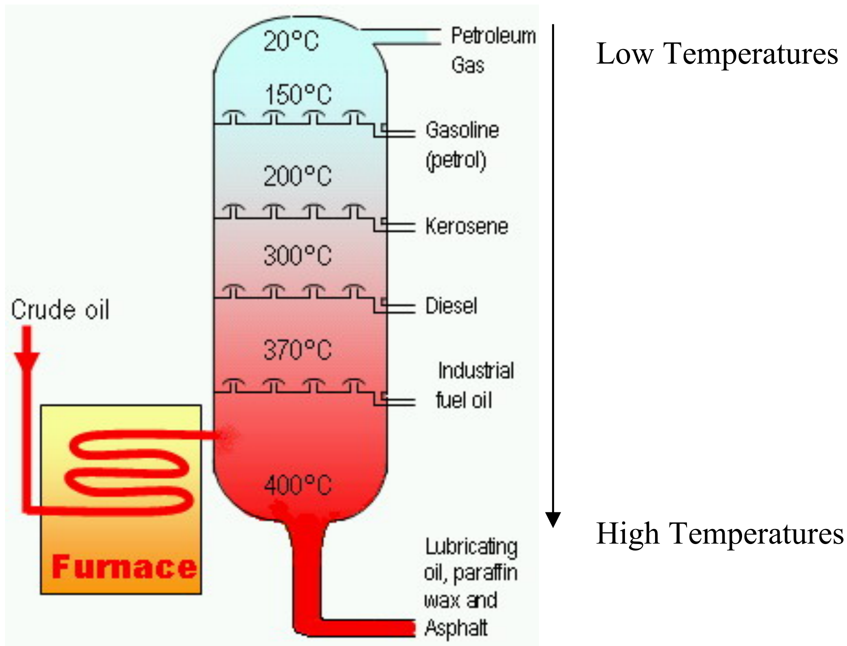


interactions: London forces (major) and dipole (min)

<u>Source of Hydrocarbons</u>

- Petroleum

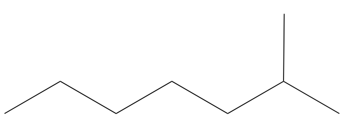
Distillation of Petroleum:



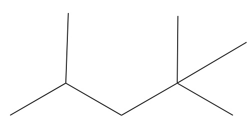
- Petroleum is a mixture of alkanes and other hydrocarbons (>>200 compounds)

Fuel (gasoline)

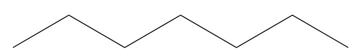
A fuel composed of 100% "isooctane" (incorrect name) will have an octane rating of 100. Heptane is bad for knocking (explosive burning). A fuel that knocks like a mixture of 90:10 "isooctane" to heptane has a 90 octane rating



isooctane



incorrectly also called "isooctane"



heptane

At the pump you typically see an octane rating between 88 and 94.

$Pb(CH_2CH_3)_4$ is known as tetraethyl lead
-Anti-knocking compound
-Toxic

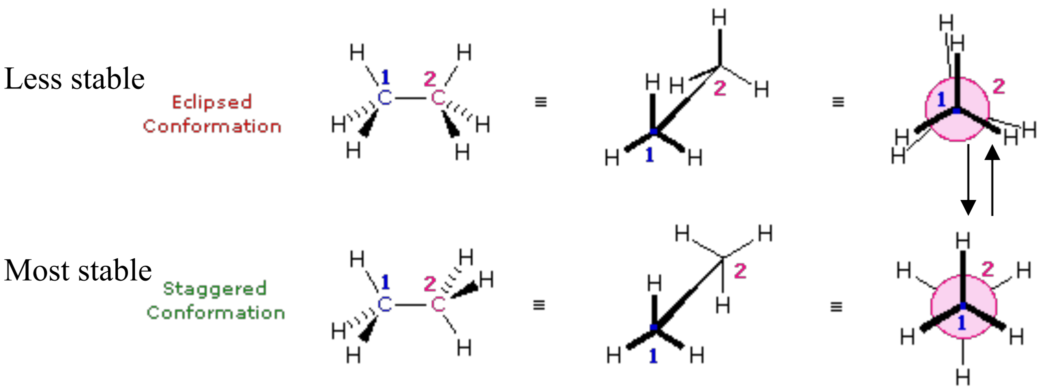
$Pb(CH_2CH_3)_4 + O_2$ + heat → PbO (bad for engine) + CO_2 and H_2O

To mitigate this problem: 1,2-dibromoethane ($Br\text{-}CH_2\text{-}CH_2\text{-}Br$) can be included. It reacts with PbO to form $PbBr_2$, which at high temperature is a gas that escapes into the atmosphere, harming the environment but leaving your vehicle unharmed

Conformation

Different 3D shapes of a <u>single (the same) molecule</u> obtained by rotation about single bonds

Example: Ethane



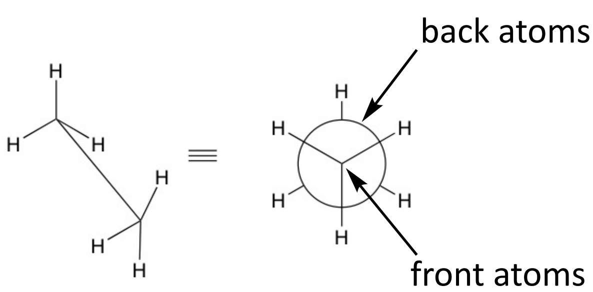
ΔG = 2.8 kcal/mol for rotation

At room room temperature (20 ºC): 15-20 kcal/mol of energy available. This allows for rotation around C-C to occur rapidly at room temperature. – Important to know

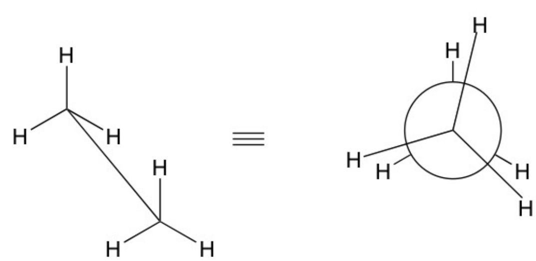
There is a **Steric effect** between neighboring bonds to hydrogens: **Repulsion of filled shells of e^-**

Newman Projections

This is a tool to examine the conformation (rotational 3D geometry) about one specific bond



Staggered conformation (hydrogens are anti)
Anti means opposite side -



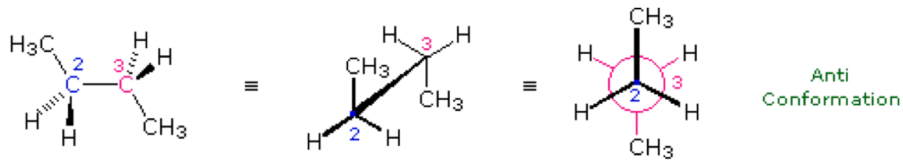
Eclipsed conformation (hydrogens are syn)
Syn means same side

Example: n-butane (C_4H_{10})

Rotation around all bonds still very rapid.

Most stable (most populated conformation) is called anti and has groups as far away as possible.

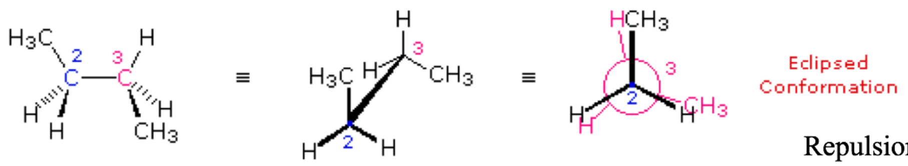
A



Most stable, staggered

Dihedral angle = 180°

B

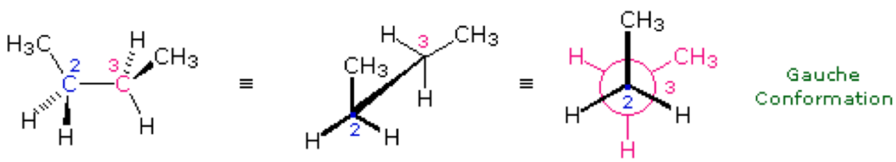


Dihedral angle = 120°

Repulsion = steric effect

Not as stable as anti

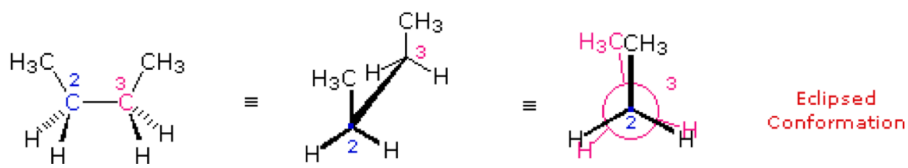
C



Dihedral angle = 60°

Least stable (syn) eclipsed

D



Dihedral angle = 0°