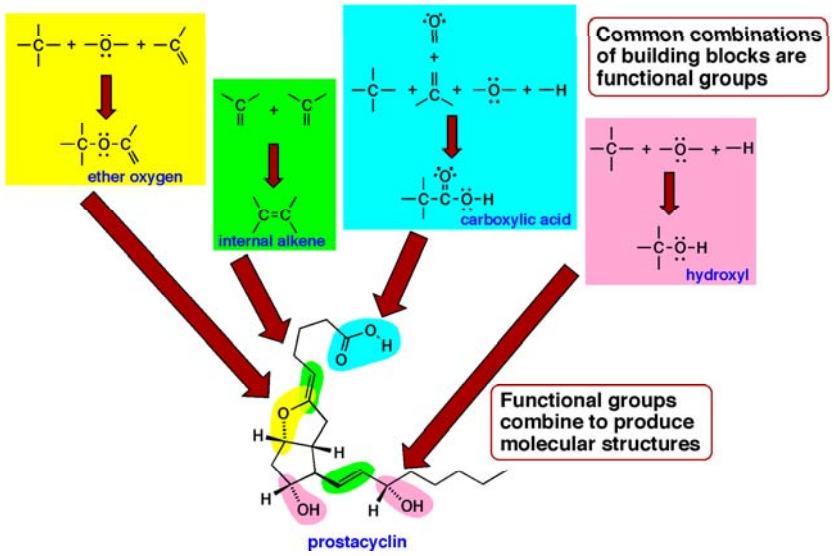
Functional Groups in Organic Chemistry



Functional Groups in Organic Chemistry

alkane

alkene

alkyne

arene

halide

X = F, Cl, Br, I

Heteroatoms (any atom other than C or H)

memorize

alcohol

ether

amine

primary (1°)

secondary (2°)

tertiary (3°)

nitrile

Functional Groups in Organic Chemistry
The Carbonyl Compounds

carbonyl

aldehyde

ketone

carboxylic acid

phenol

ester

amide

acid chloride

acid anhydride

aniline

nitro

sulfide (thioether)

thiol

imine

epoxide

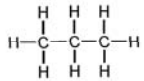
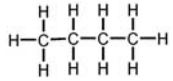
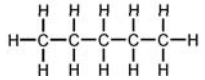
The Normal Alkanes

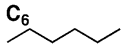
Read: Chapter 2 of Vollhardt or Chapter 3 of McMurry

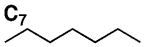
Hydrocarbons are compounds composed of only hydrogen and carbon
Alkanes are hydrocarbons containing only single bonds
The **n-alkanes** are homologs of the *straight-chain* series of H-$(CH_2)_n$-H

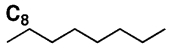
carbon number	name	Kekulé structure	condensed formula	ball & stick model
C_1	methane		CH_4	
C_2	ethane		CH_3CH_3	

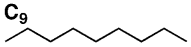
The Normal Alkanes

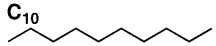
carbon number	name	Kekulé structure	condensed formula	skeletal structure
C_3	propane		$CH_3CH_2CH_3$	
C_4	butane		$CH_3CH_2CH_2CH_3$	
C_5	pentane		$CH_3(CH_2)_3CH_3$	

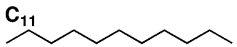

hexane

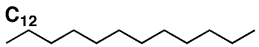

heptane


octane


nonane


decane


undecane


dodecane

The skeletal structure shows the carbon-carbon bonds as lines and does not show the carbon-hydrogen bonds

For names of longer normal alkanes: pp. 71 (Vollhardt) or pp. 82 (McMurry)

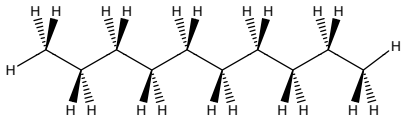
Shortcut Conventions

Stable conformation:

Heavy wedged line: coming out of the plane of the page toward the viewer;

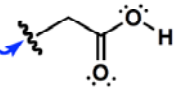
Dashed line: receding back behind the page, pointing away from the viewer;

Regular lines: in plane with the page

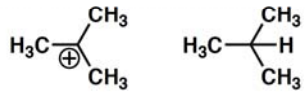

decane

- the carbon chain is represented as zigzag line
- leave out C and H when not necessary
- show electron lone pairs and formal charges
- when only a small portion of the structure is of interest, use a partial structure convention:

partial structure convention



Note the difference between these structures:



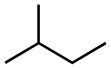
Compounds with the Same Formula

Compounds that have the same molecular formula but differ in physical and/or chemical properties are known as isomers.

Isomers that differ in connectivity are known as constitutional isomers.

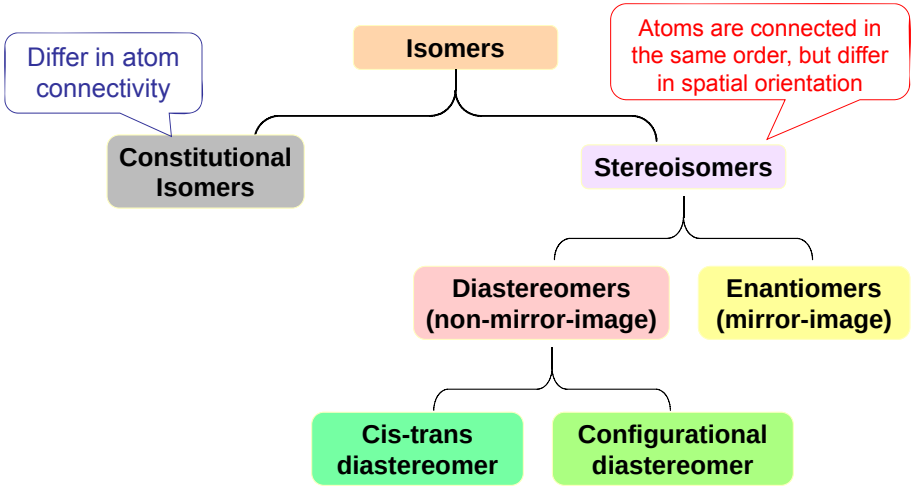
The constitutional isomers of pentane


$CH_3CH_2CH_2CH_2CH_3$
pentane
(or *n*-pentane)

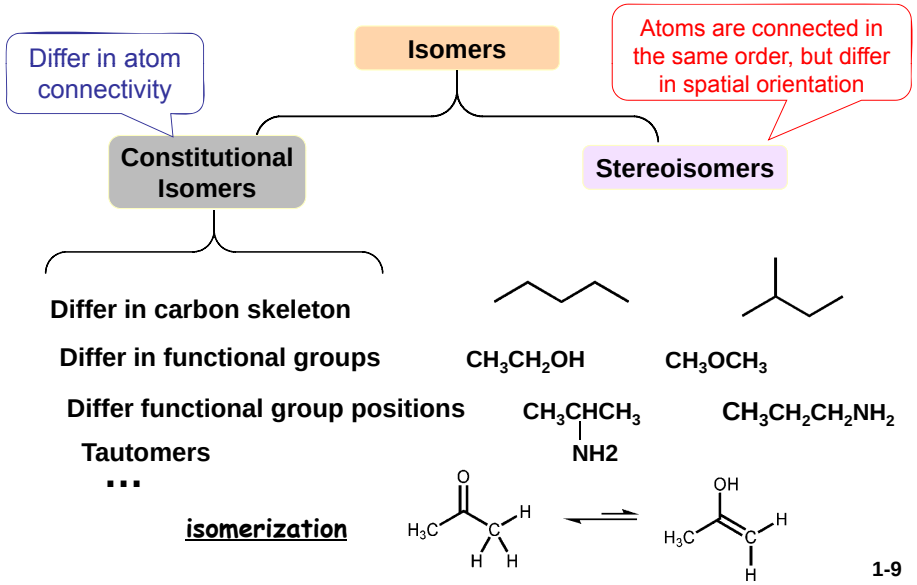

$CH_3CHCH_2CH_3$
CH_3
isopentane


CH_3
CH_3CCH_3
CH_3
neopentane

Classification of Isomers

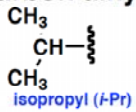


Classification of Isomers



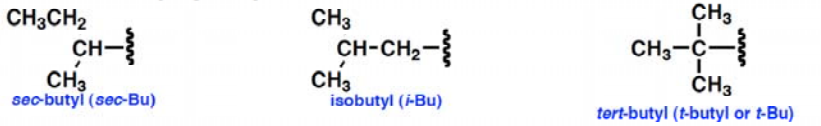
Alkyl Structure Units

3-carbon alkyl groups

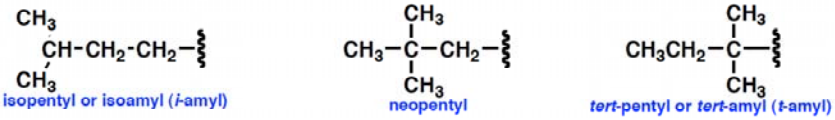


An alkane from which a single hydrogen has been removed is an __alkyl__ group.

4-carbon alkyl groups



5-carbon alkyl groups



(common names)

A generic alkyl group is represented by: __-R__

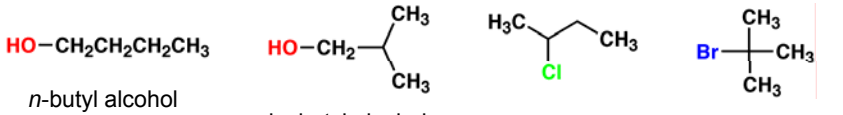
Classifying sp^3 Carbon Atom Type by C-C Connectivity

Primary carbon	(1°)	bonded to one other C
Secondary carbon	(2°)	bonded to two other C
Tertiary carbon	(3°)	bonded to three other C
Quaternary carbon	(4°)	bonded to four other C

Classifying Halides and Alcohols by C-C Connectivity

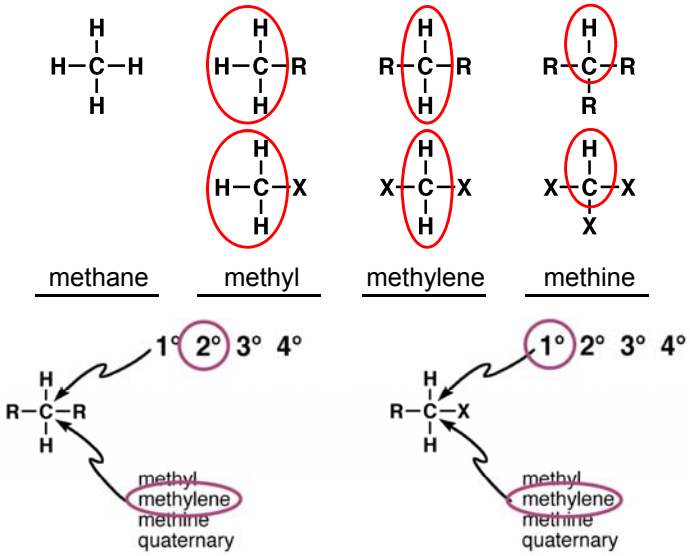
X = -F, -Cl, -Br, -I	1° halide	2° halide	3° halide
X = -OH	1° alcohol	2° alcohol	3° alcohol

Used for naming compounds that contain butyl structural units:



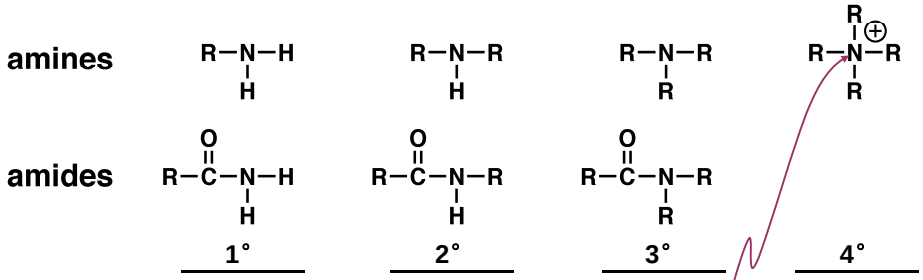
(common names)

Classifying sp^3 carbon-atom-type by C-H connectivity



Classifying sp^3 nitrogen-atom-type by C-N connectivity

For amines and amides, the notation 1° , 2° , 3° , and 4° refers to the number of N-C bonds

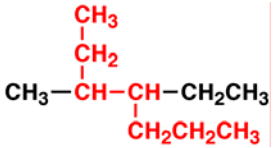


The ium suffix denotes "+" charge: quaternary ammonium ion

The ide suffix denotes "-" charge

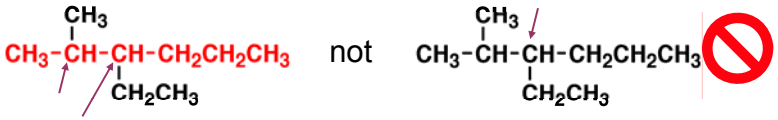
Systematic Process for Naming Alkanes - Step 1
(IUPAC Nomenclature)

Choose the longest continuous carbon chain (the Parent part)



Named as a substituted heptane

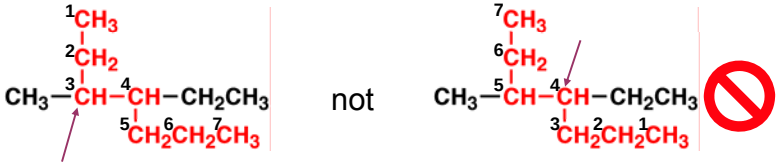
If two different chains of equal length are present, choose the one with the greater number of branch points.



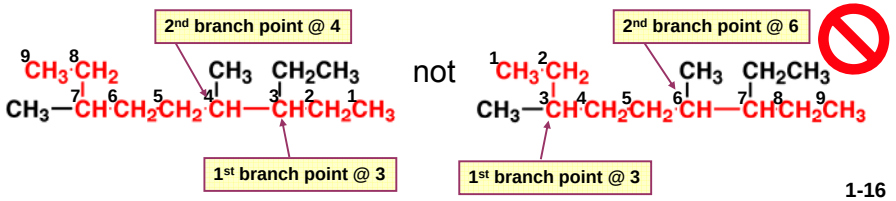
Naming Alkanes - Step 2
Numbering the atoms in the main chain

Number the atoms in the main chain

- Begin at the end nearer the first branch point



- If first branch point is equidistant from both ends, begin numbering at the end nearer the second branch point

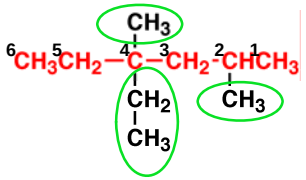


Naming Alkanes - Step 3
Identify and number substituents

The three parts of a chemical name

Prefix—Parent—Suffix

Substituents and their locations | **The main carbon chain** | **Functional group family**



Parent chain named as hexane

Substituents: 2-methyl, 4-methyl, 4-ethyl

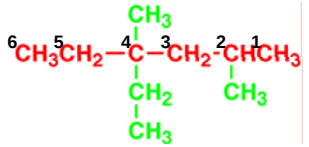
Arrange in alphabetical order

Substituents: 4-ethyl, 2-methyl, 4-methyl

Naming Alkanes - Step 4
Write the name as a single word

Prefix—Parent—Suffix

- Substituents named in prefix (alphabetical order)
- Hyphens separate different prefixes
- Commas separate numbers
- Identical substituents use di-, tri-, tetra-

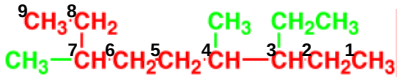


Parent chain named as hexane

Substituents: 4-ethyl, 2-methyl, 4-methyl

Name the compound: 4-ethyl-2,4-dimethylhexane

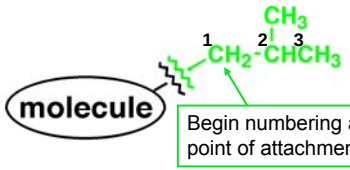
Naming Alkanes - Examples



Parent chain named as nonane

Substituents: 3-ethyl, 4-methyl, 7-methyl

Name the compound: 3-ethyl-4,7-dimethylnonane



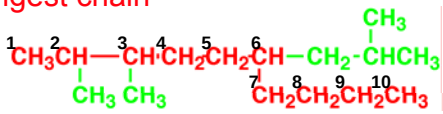
The parent chain of the substituent is named as: **propane**

Name the substituent **2-methylpropane** **2-methylpropyl**

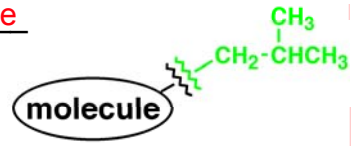
As a substituent, we drop the -ane and add -yl

Naming Alkanes that have Branched Substituents

Find the longest chain



The parent chain is named as: decane



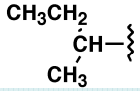
One substituent is branched. It will be named as a complex substituent:
- By applying the systematic rules
- By using common names

Complex Substituents Named with Common Names

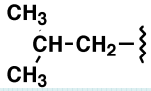
3-carbon alkyl groups

1-methylethyl (*i*-Pr)

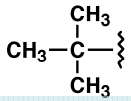
4-carbon alkyl groups



1-methylpropyl (*sec*-Bu)

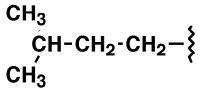


2-methylpropyl (*i*-Bu)

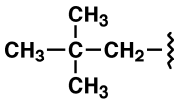


1,1-dimethylethyl (*t*-Bu)

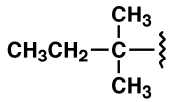
5-carbon alkyl groups



3-methylbutyl (isopentyl or *i*-amyl)

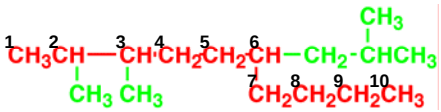


2,2-dimethylpropyl (neopentyl)



1,1-dimethylpropyl (*t*-amyl)

Naming an Alkane that has a Branched Substituent



The parent chain is named as: decane

	systematic	common
Complex substituent:	2-methylpropyl	isobutyl (*i*-Bu)

Chemical name: 2,3-dimethyl-6-(2-methylpropyl)decane 6-isobutyl-2,3-dimethyldecane

Enclose complex substituent in ( )

"Iso" and "neo" are consider part of the substituents and counted in alphabetic ordering, while *i*-, *n*-, *sec*-, *tert*-, *s*-, *t*-, di, tri, tetra, and etc. are not counted.

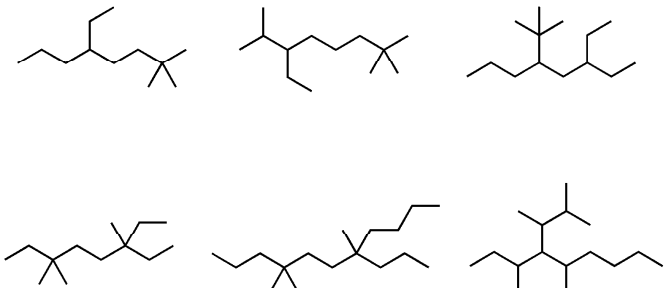
The Eight Laws of Learning

The four laws of learning are explanation, demonstration, imitation, and repetition. The goal is to create a correct habit that can be produced instinctively under great pressure.

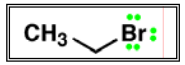
To make sure this goal was achieved, I created eight laws of learning: namely explanation, demonstration, imitation, repetition, repetition, repetition, repetition, and repetition.

-John Wooden, Basketball Coach

Name the following compounds:

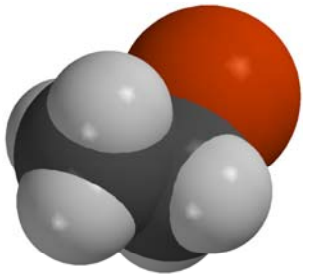


Types of Computer Models



Wireframe

Ball & Stick

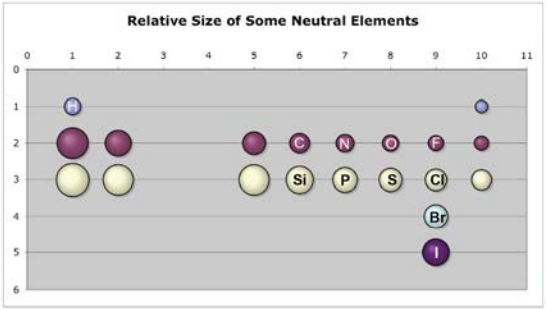


Spacefilling

Each atom is a sphere of fixed radius. The model consists of interpenetrating spheres.

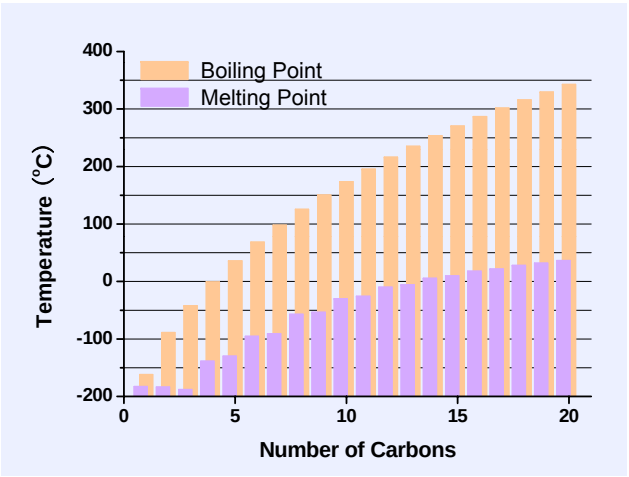
van der Waals Radii

Atomic numbe r	Element	Van der Waals radii (Å)
1	H	1.20
6	C	1.70
7	N	1.55
8	O	1.52
9	F	1.47
14	Si	2.10
15	P	1.80
16	S	1.80
17	Cl	1.75
35	Br	1.85
53	I	1.98



The relative sizes of the neutral atoms are shown as a function of their position within the periodic table. Within a given row, the atoms get smaller as the atomic number increases. Within a given column, the atoms get larger as the atomic number increases.

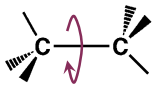
Physical Properties of Normal Alkanes



Dispersion forces increase with molecular size, thus generally higher bp and mp for larger alkanes; increased branching lowers bp and mp.

Conformations of Alkanes

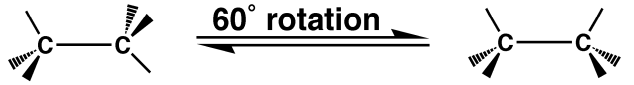
Rotation about single bonds generates a set of different spatial arrangements of the atoms known as a conformational isomer (conformers)



Representations:

staggered — eclipsed

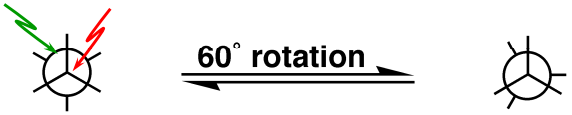
perspective formula



sawhorse projection

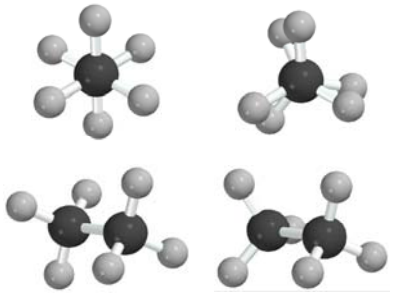
back carbon front carbon

Newman projection



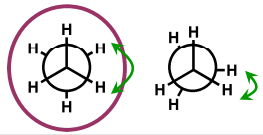
Conformation and Energy

The energy of the molecule depends on the angle of rotation.



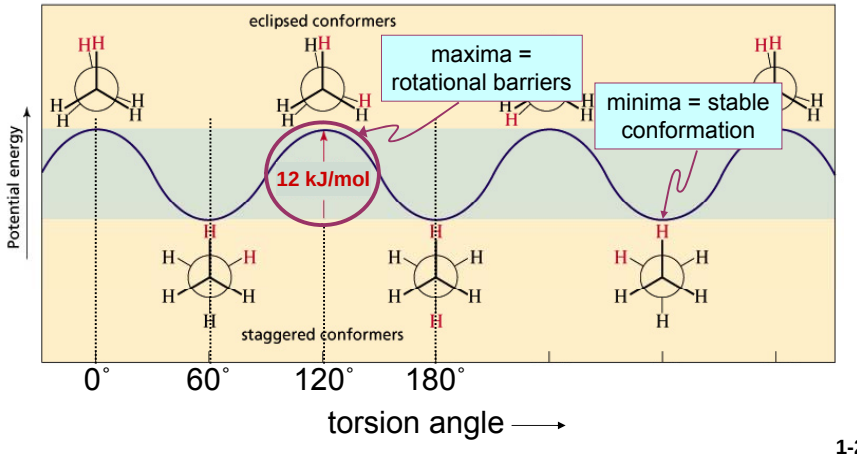
The angle of rotation is called the dihedral or torsion angle

Which conformer is more stable?

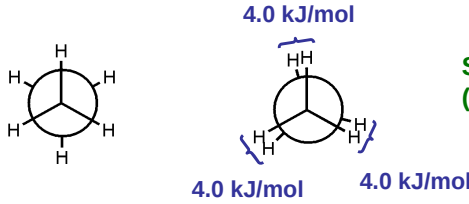


Conformational Energy

The energy changes continuously as a function of the torsion angle. We represent this on a plot called the potential energy surface (PES).



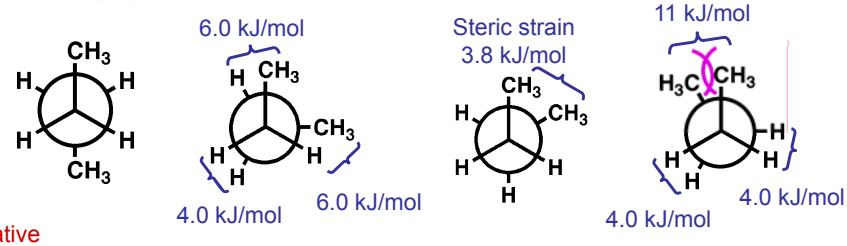
Rotational Barrier



Steric repulsion? (MO interaction)

Relative energy 0 12 kJ/mol

What about propane?



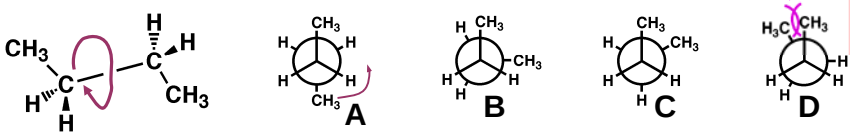
Relative energy (kJ/mol)	0	16	3.8	19

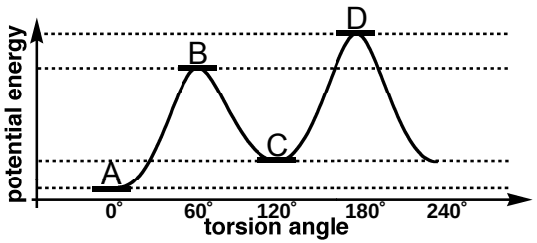
Butane Conformations

There are two different rotational barriers and two different different stable conformations for butane.

- Barrier heights equal? Y (N)
- Energy of stable conformations equal? Y (N)

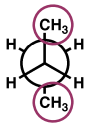
denotes steric interaction



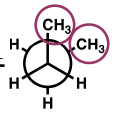


The Staggered Conformers of Butane

anti-periplanar or anti



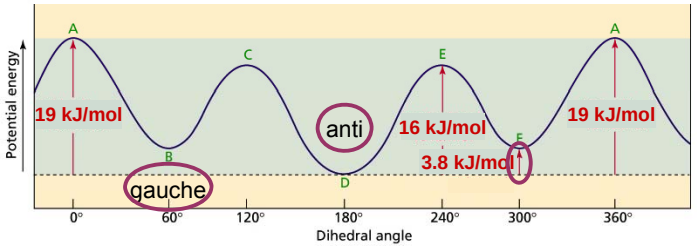
interconvert rapidly



gauche

If you took a snapshot of a large number of butane molecules, the anti population would not equal the gauche population because their energies differ

- Which conformer will be more populated? (anti) / gauche
- What is the ratio of anti to gauche conformers?



Which energy parameter is relevant to this question?

3.8 kJ·mol^{-1}

Estimating Anti / Gauche Populations

gauche $\rightleftharpoons^{K}$ **anti** $\qquad K = \dfrac{[\text{anti}]}{[\text{gauche}]}$

$$\text{mol\% anti} = \frac{[\text{anti}]}{[\text{gauche}] + [\text{anti}]} = \frac{K}{1 + K}$$

Convention: use capital *K* for equilibrium constant (and small k for rate constants)

We know $\Delta G = -RT \ln K$

For butane $\Delta G = -3.8$ kJ·mol^{-1} @ 25 °C: $K = 0.22 = [\text{gauche}] / [\text{anti}]$

% *gauche* = 100% × 2 × [gauche] / (2 × [gauche] + [anti])

% *gauche* = 30% % *anti* = 70%

Experimentally observed: 72% *anti* at 25 °C

Rates vs. Amounts

$$\mathbf{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{B} \qquad K = \frac{k_f}{k_b}$$

What energy determines k_b, the rate of backward conversion?

This energy difference (between the minimum and the maximum, $\Delta G^{\neq}$) determines the: rate of forward conversion, k_f (how fast)

This energy difference (between the two minima, ΔG) determines the: relative amounts of A and B, *K* (how much)