INTERNATIONAL COLLEGE OF PHARMACEUTICAL INNOVATION
国际创新药学院

Fundamentals of Medicinal and Pharmaceutical Chemistry

FUNCHEM.15 Alkanes: Structural isomers and homologous series in organic chemistry

Professor Dan Wu

DATE: 8th November 2024

Learning outcomes

At the end of this lecture, the learner will be able to

- Recall and describe the general structure and bonding in alkanes.
- Recall and apply the rules of IUPAC method of nomenclature to name and identify acyclic alkanes.
- Recall and explain the physical properties of alkanes including branched and unbranched alkanes.
- Identify eclipsed and staggered conformers in sawhorse and Newman projection representations.
- Define torsional strain and explain how it affects the stability of conformers.
- Chirality

Recommended reading

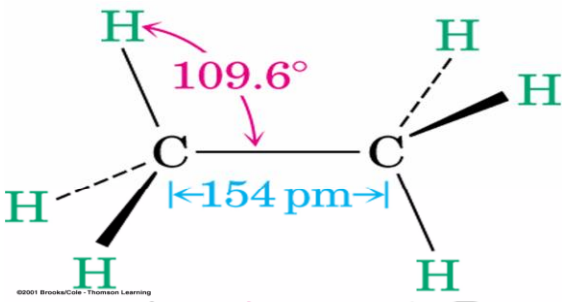
- Organic chemistry with biological application (John McMurry)
- Chapter 3: Organic Compounds: alkanes and their stereochemistry
- Chapter 4: Organic Compounds: Cycloalkanes and their stereochemistry
- Chapter 6: an overview of organic reactions

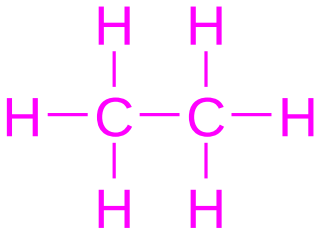
Alkanes

They are saturated hydrocarbons *i.e.* hydrocarbons with only single bonds.

(Hydrocarbons are organic compounds containing only C & H,
are the main components of petroleum and natural gas.)

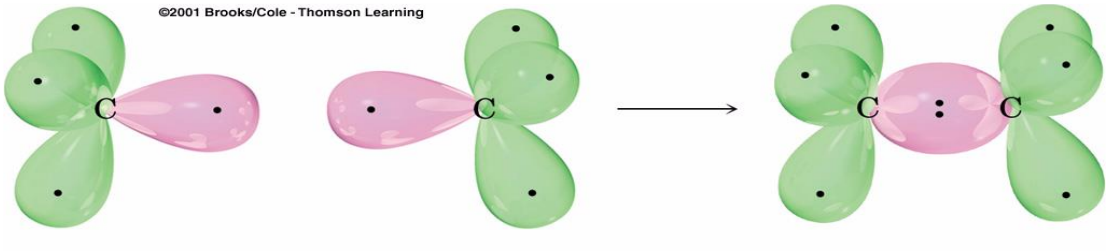
e.g. Structure of Ethane





Lewis structure

Geometric structure



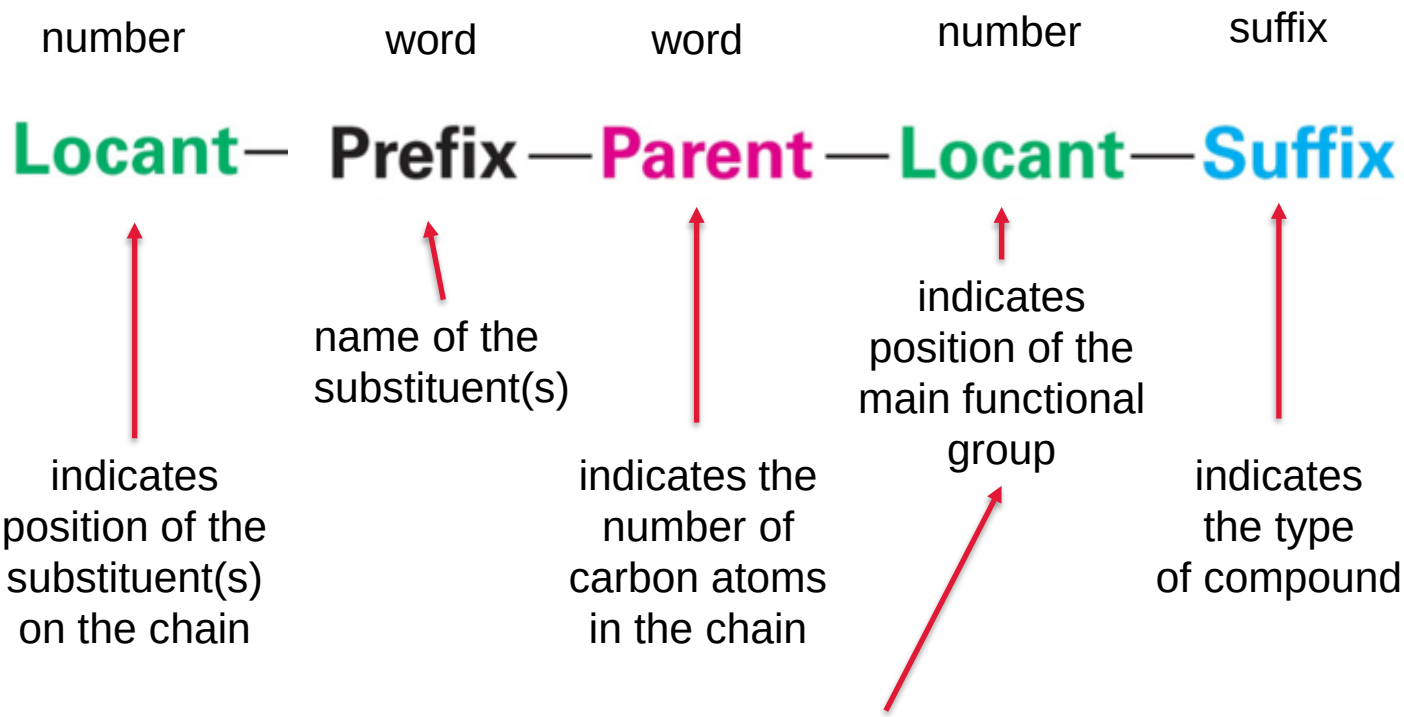
Three hybrid orbitals on each carbon atom overlap with three hydrogen orbitals.
The two carbons bond to each other by overlap of one hybrid orbitals on each.

Names & Formulas of the First Ten Unbranched Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

All acyclic alkanes fit the general molecular formula $\mathbf{C_nH_{2n+2}}$

IUPAC Naming Overview



Note – this locant is not needed for alkanes, you will see it being used in the naming of alkenes, alkynes and other compounds.

Alkane Nomenclature

IUPAC rules for naming alkanes (*International Union of Pure and Applied Chemistry*)

Systematic nomenclature enables accurate description.

1. The name ending for all alkanes is –ane. - **Suffix**

2. The parent chain is the longest continuous carbon atom chain in the structure. If two chains with equal length exist, choose the chain with the great number of branch points.

3. A word is attached to the name ending –ane indicating the number of carbon atoms in the **Parent** chain.

meth–	1C	hex–	6C
eth–	2C	hept–	7C
prop–	3C	oct–	8C
but–	4C	non–	9C
pent–	5C	dec–	10C
		undec-	11C

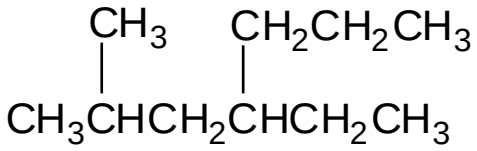
4. Number the carbon atoms of the parent chain starting from whichever end of the chain gives the location of the first branch the lower of two possible numbers.

5. Name each alkane–like branch (alkyl group) attached to the parent chain.

Alkane Nomenclature

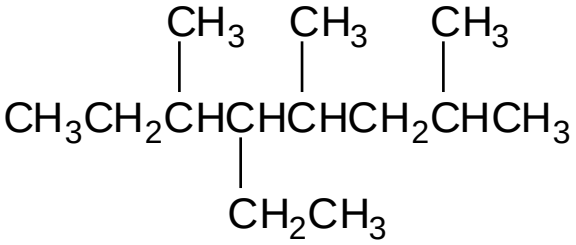
6. Attach the name of the alkyl group to the name of the parent as a **Prefix**. Place the location number of the group in front of the name separated by a hyphen.

7. When two or more groups are attached name each and locate each with a number. **Locant** The names of the alkyl groups are assembled in alphabetical order. Always use hyphens to separate numbers from words.



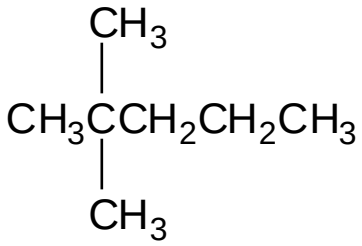
4-Ethyl-2-methylheptane

8. When two or more substituents are identical use prefixes such as *di-*, *tri-*, *tetra-*, *etc.* *Always separate a number from another number in a name by a comma.*



5-Ethyl-2,4,6-trimethyloctane

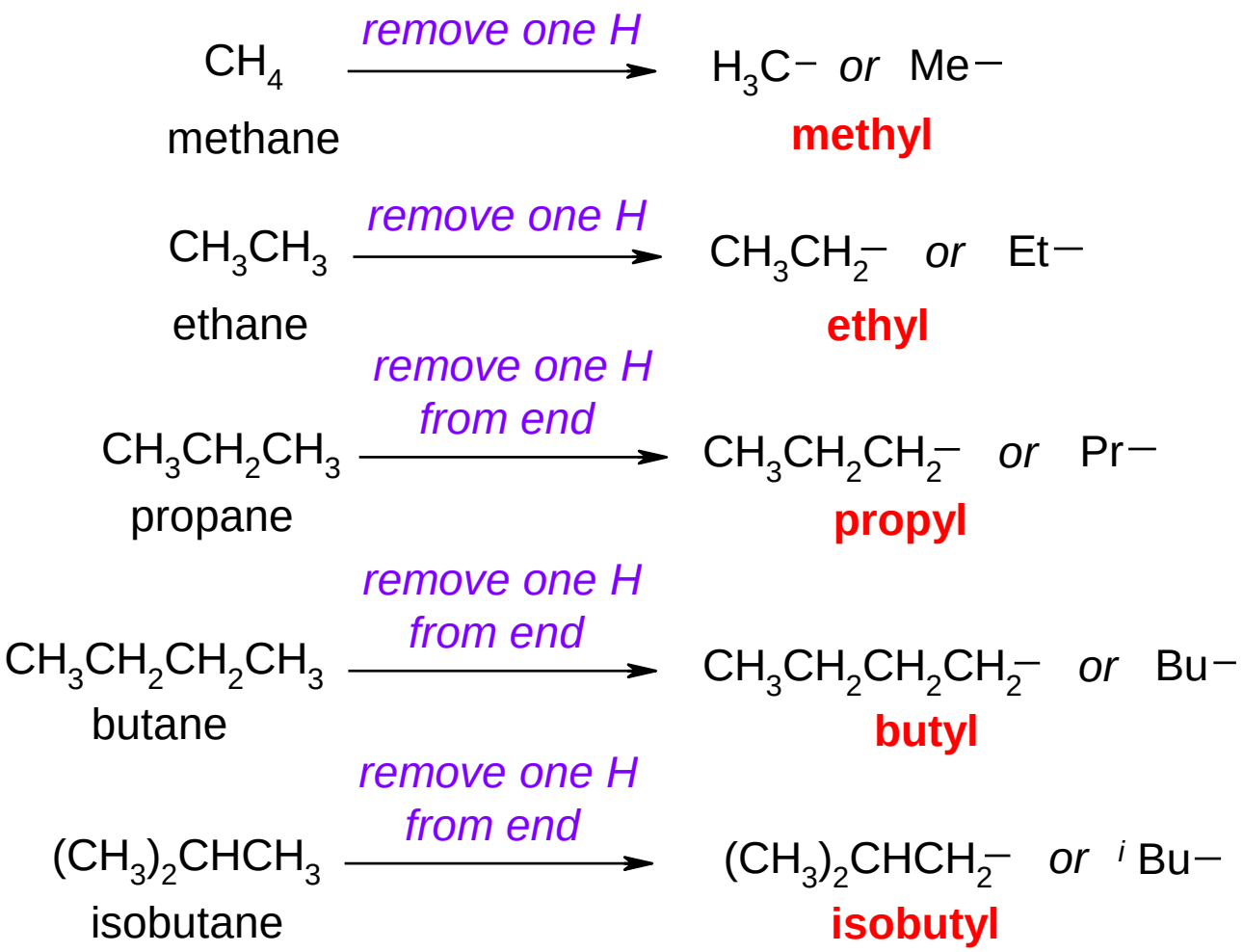
9. When identical groups are on the same carbon repeat the number locating this carbon in the name.



2,2-Dimethylpentane

Alkane Nomenclature

A primary alkyl group are named by taking the name of the alkane with the same number of carbon atoms and changing the *–ane* ending to *–yl*.



Alkane Nomenclature

Branched (secondary & tertiary) alkyl groups:

$CH_3CH_2CH_3$ — *remove one H from middle* → $H_3C\diagdown\ \diagup CH-$ *or* $^{i}Pr-$

propane

isopropyl

$CH_3CH_2CH_2CH_3$ — *remove one H from either of two interior carbons* → $CH_3CH_2\underset{|}{C}HCH_3$ *or* $^{s}Bu-$

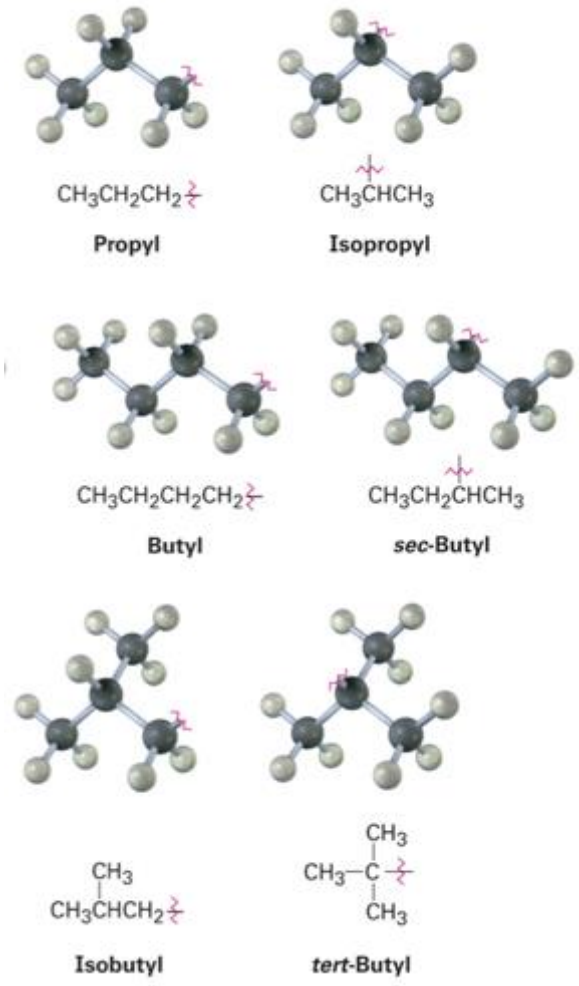
butane

***secondary* butyl or *sec*-butyl**

$(CH_3)_2CHCH_3$ — *remove one H from the tertiary carbon* → $(CH_3)_3C-$ *or* $^{t}Bu-$

isobutane

***tertiary* butyl or *tert*-butyl**



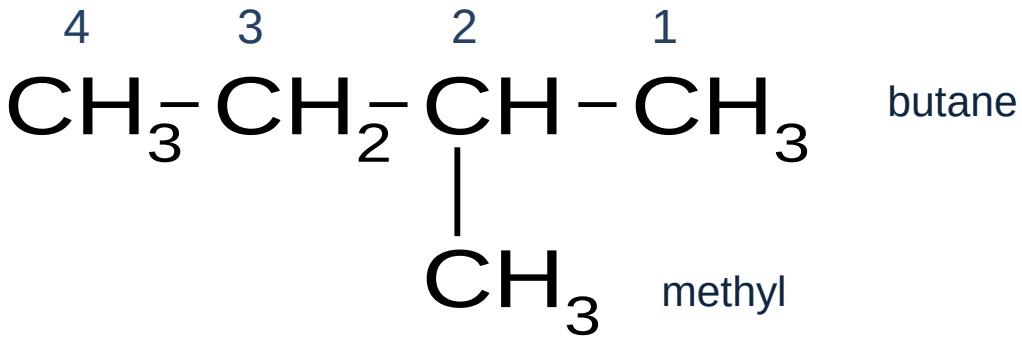
Note:

A primary carbon is one to which one other carbon atom is directly attached;

A secondary carbon is one to which two other carbon atoms are directly attached;

A tertiary carbon is one to which three other carbon atoms are directly attached.

Naming Examples



find longest chain

number from end nearest to a branch

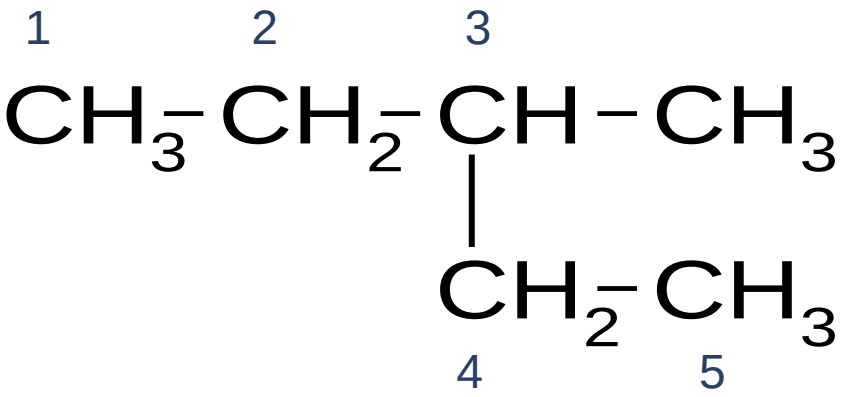
name substituent

2-Methylbutane

Locant **Prefix** **Parent** **Suffix**

NOTE: Numbers are separated from words by hyphens

Naming Examples



methyl

pentane

find longest chain

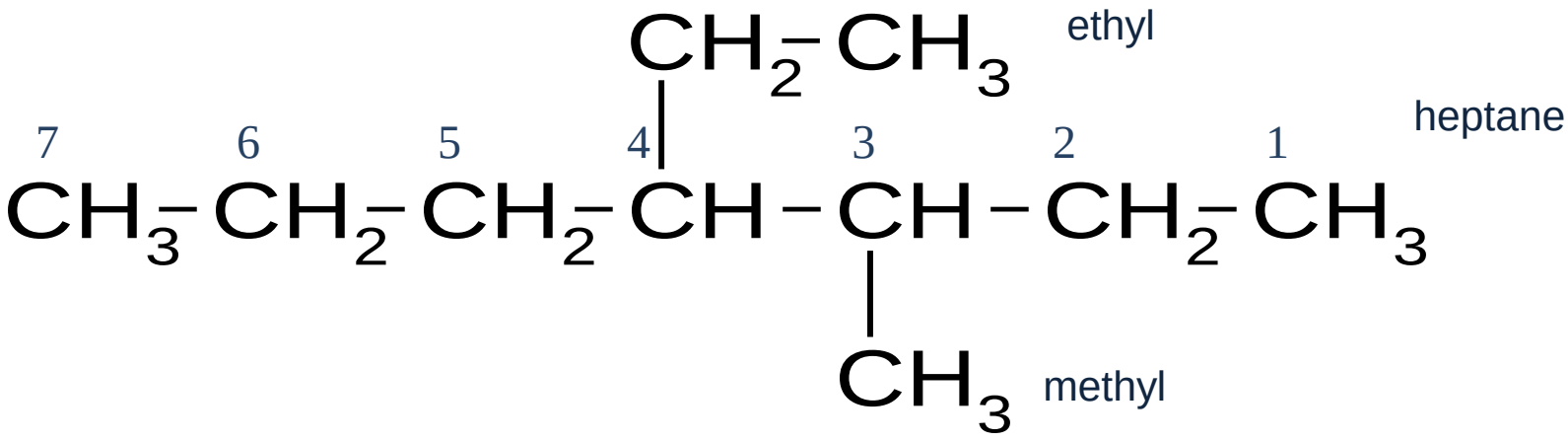
number from end nearest to a branch

name substituent

3-Methylpentane

Locant **Prefix** **Parent** **Suffix**

Naming Examples



find longest chain

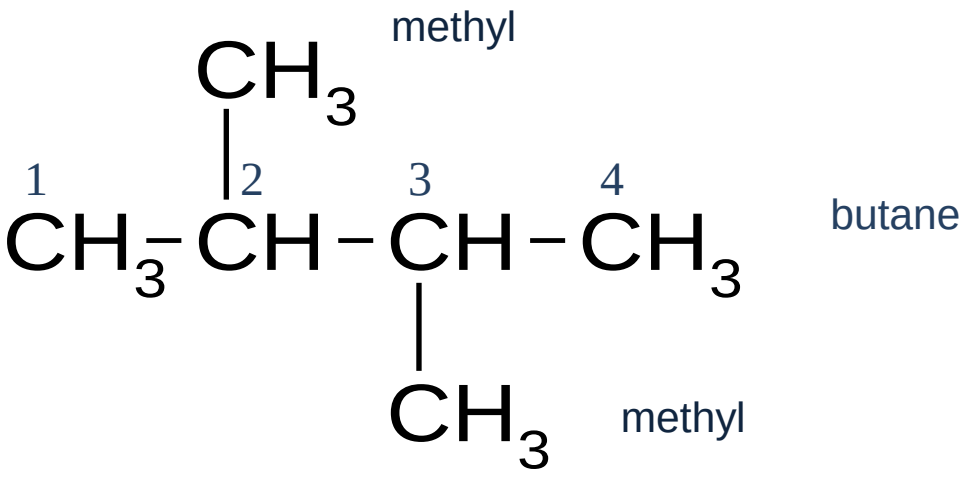
number from end nearest to a branch

name substituents in alphabetical order

4-Ethyl-3-methylheptane

Locant Prefix Locant Prefix Parent Suffix

Naming Examples



find longest chain

number from end nearest to a branch

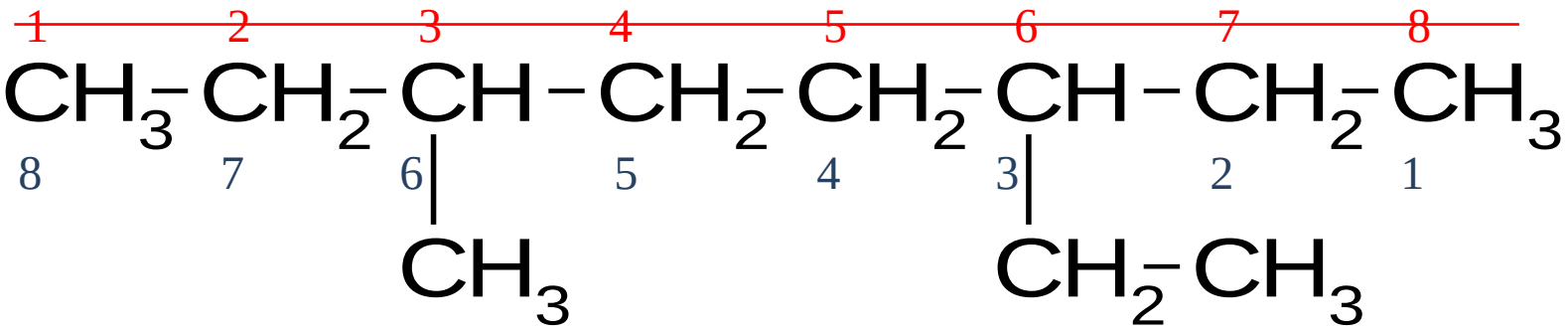
name substituents using “di-” for two identical substituents

2,3-Dimethylbutane

Locant **Prefix** **Parent** **Suffix**

NOTE: Numbers are separated from numbers by commas

Naming Examples



find longest chain

number from end nearest to a branch

if two substituents are same distance from end, “number alphabetically”

name substituents in alphabetical order

3-Ethyl-6-methyloctane

Locant **Prefix** **Locant** **Prefix** **Parent** **Suffix**

Physical Properties of Alkanes

Nonpolar molecules (C–C and C–H bonds are entirely non-polar)

Insoluble in water but soluble in non-polar solvents, *e.g.* CCl_4 ("*like dissolves like*")

Generally less dense than water

Boiling points *rise* as the chain length increases

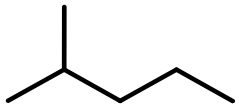
1-4 carbons are gases at room temp;

5-17 carbons are liquids at room temp;

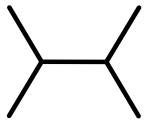
$\geq$ 18 carbons are waxy solids at room temp,

Boiling points *fall* as chains become branched

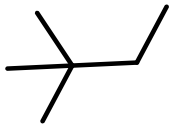
(*unbranched alkanes (n-alkanes) have higher boiling points than branched alkanes*)



C_6H_{14}
b.p. 60 C
m.p. -154 C

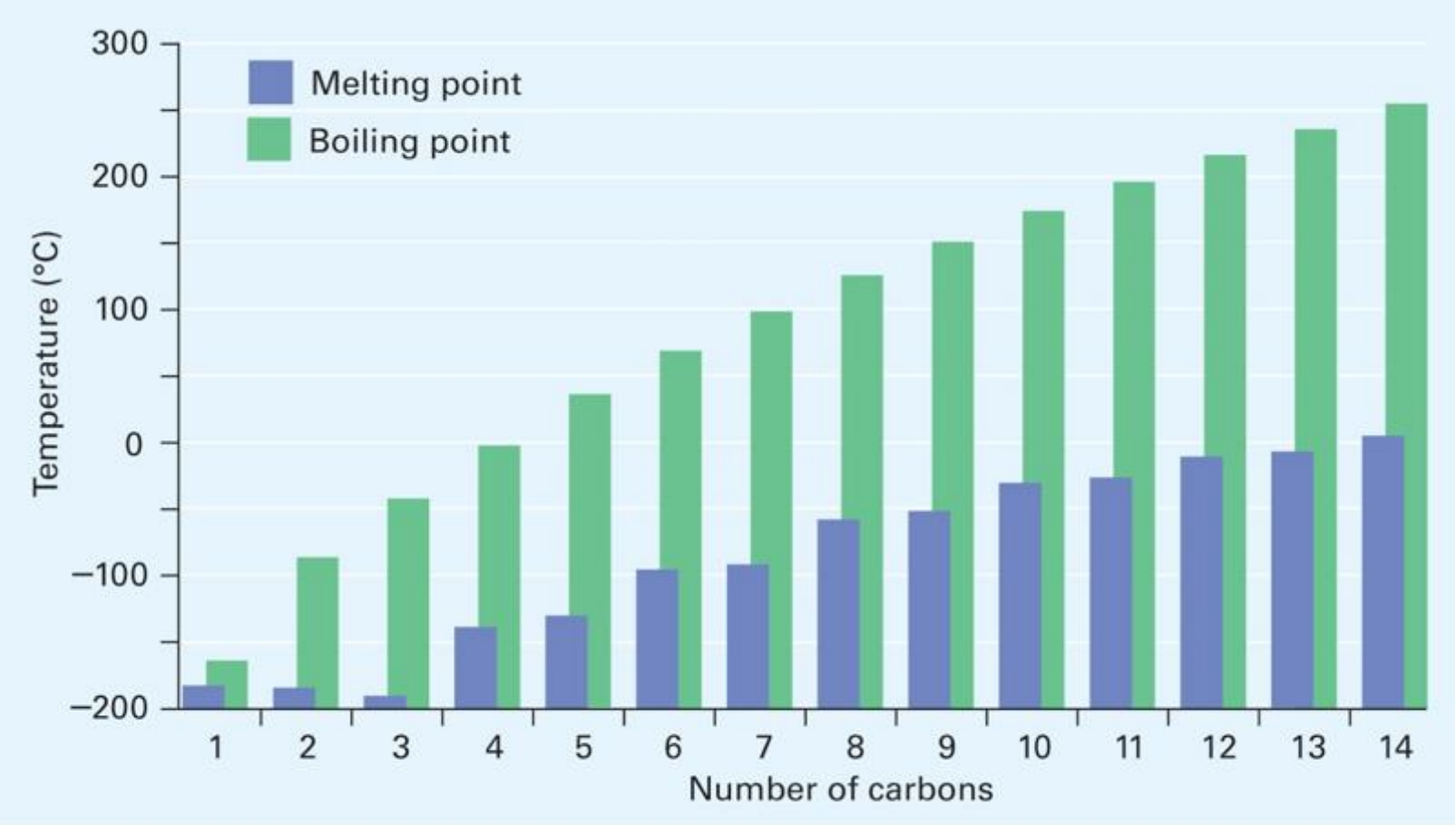


C_6H_{14}
b.p. 58 C
m.p. -135 C



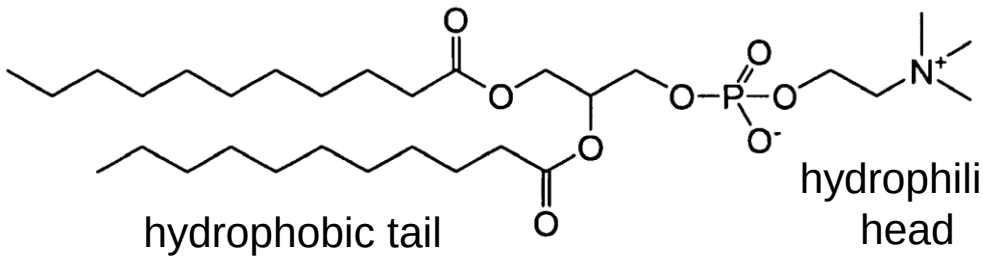
C_6H_{14}
b.p. 50 C
m.p. -98 C

Physical Properties of Alkanes



Increasing the number of carbons in the alkane molecule will increase the van der Waals forces experienced between molecules.

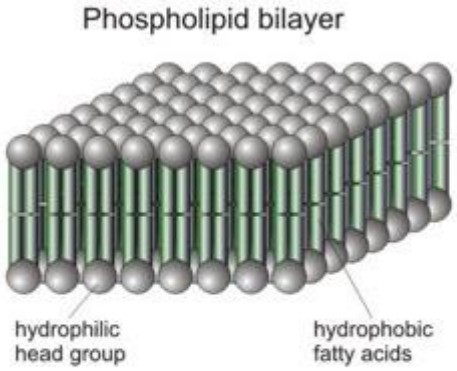
Alkanes in Biology: Phospholipids



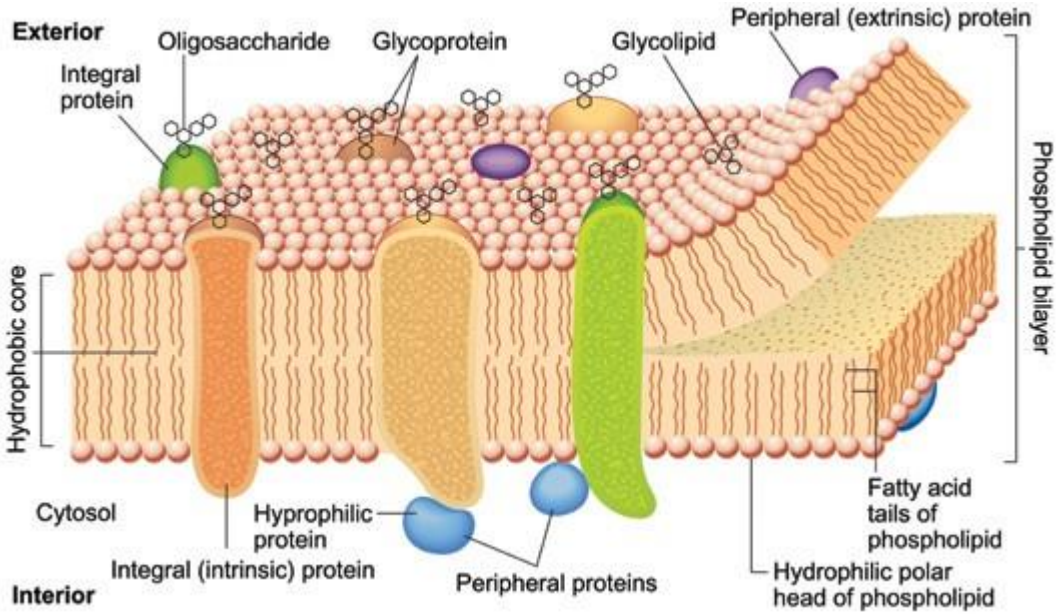
hydrophobic tail
(fatty acid)

hydrophilic
head

in water

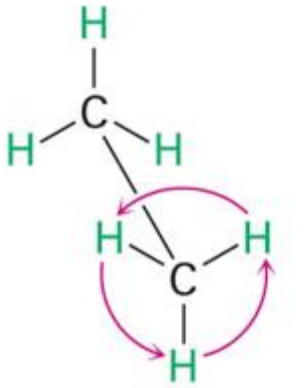


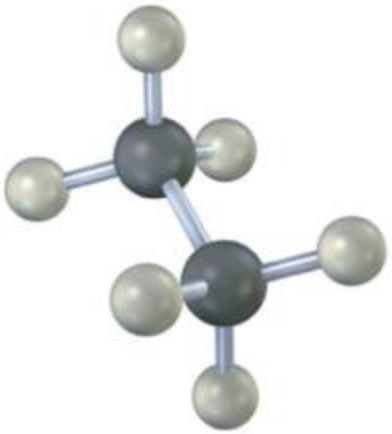
cell membrane



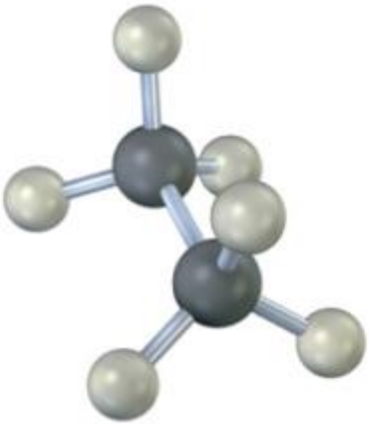
Conformations of Alkanes

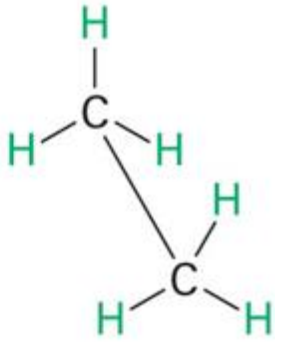
C-C single bonds can freely rotate resulting in a number of arrangements in space.





Rotate





Staggered

Eclipsed

The different arrangements of atoms that results from bond rotation are called conformations. Molecules that have different arrangements are called conformational isomers or conformers.

Conformers are represented in two ways. Sawhorse (shown above) or Newman projection (next slide).

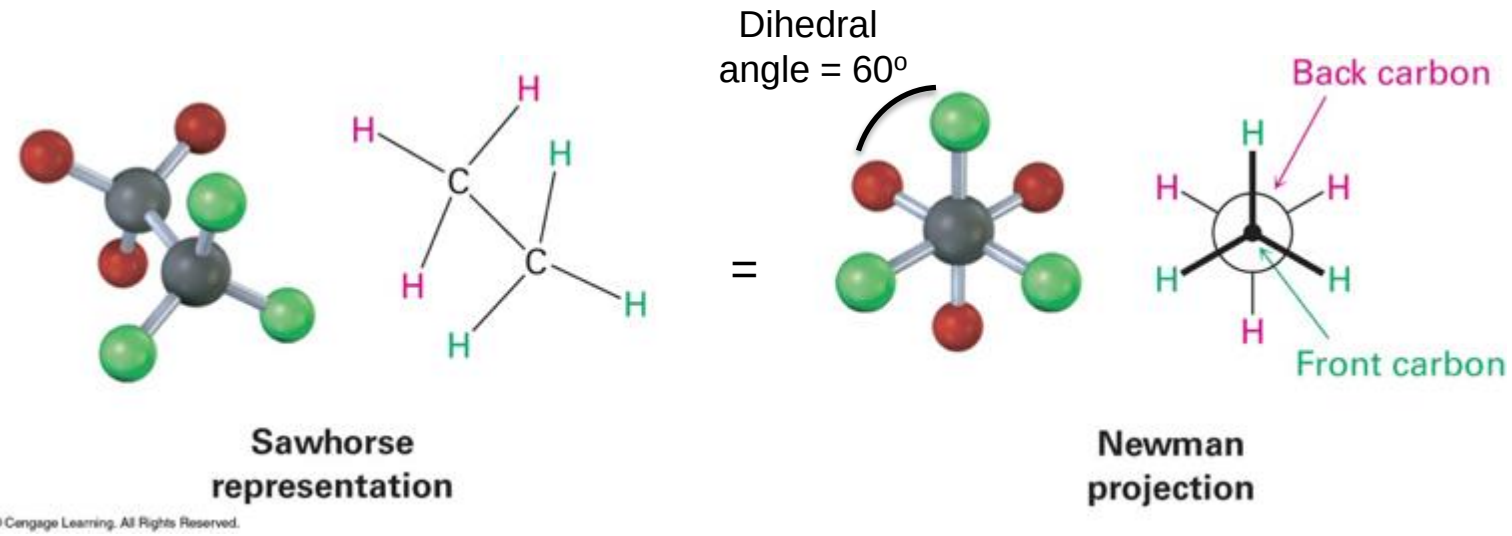
Newman Projection - Staggered Conformation

Newman projection can be used to specify the conformation of a particular bond

Newman projection represents the head-on look down the bond of interest

The circle in the Newman projection represents the atom at the back of the C-C bond and the lines radiating from the center are the bonds of that atom

The bonds of the rear atom emerge from the sides of the circle



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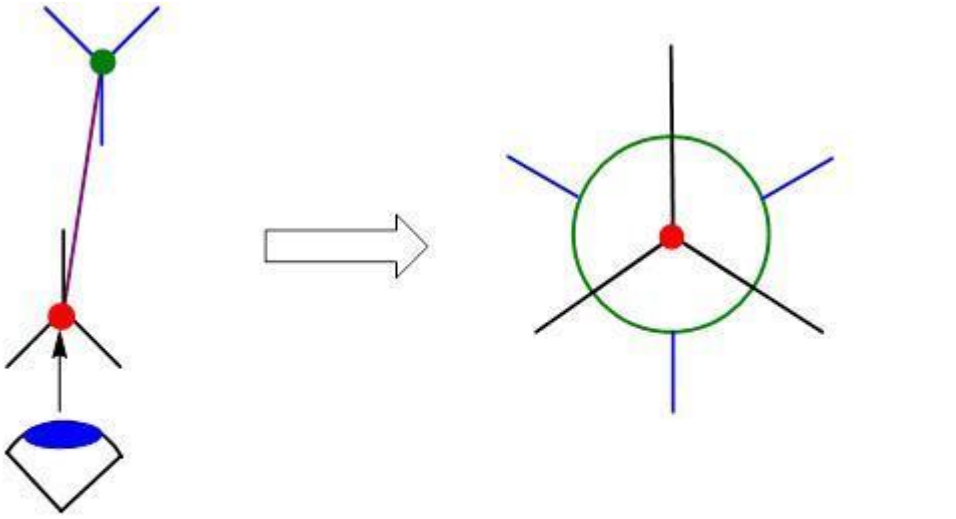
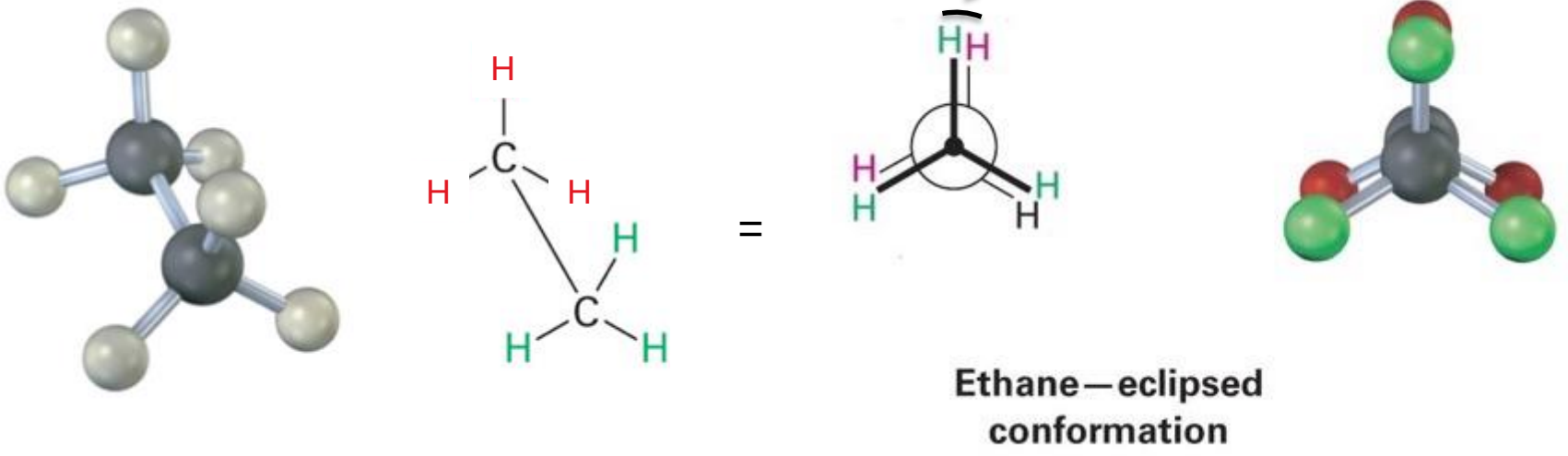


Sawhorse projection
(if we face it instead
of looking from the side

Corresponding **Newman Projection**
The **C-C bond** between the **Front** and
the **Back** carbon is hidden

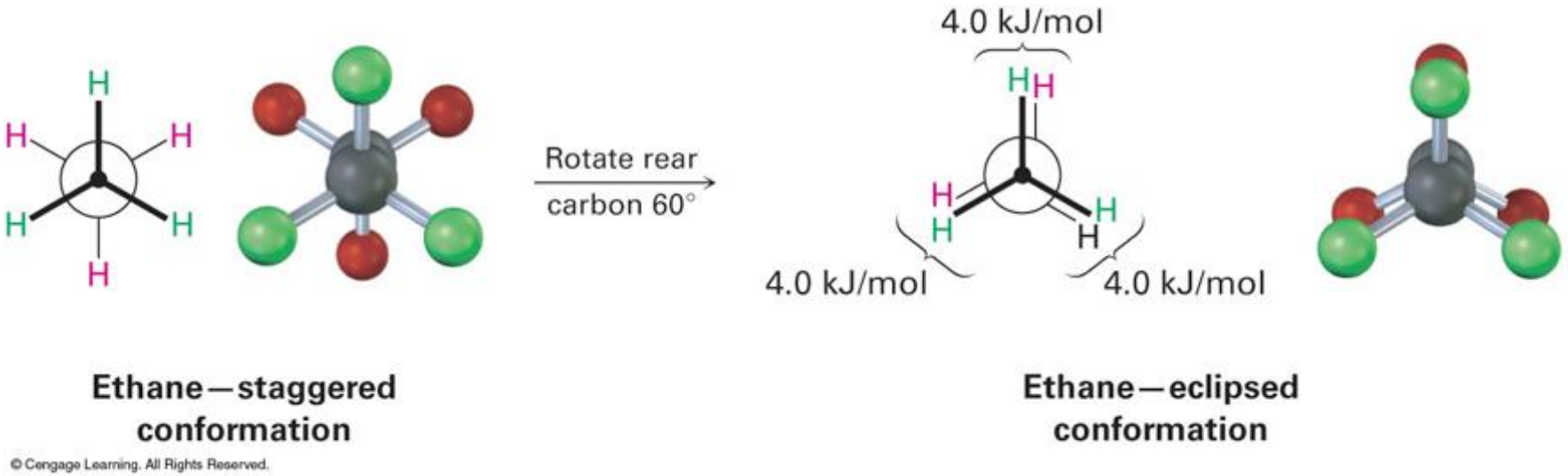
Newman Projection - Eclipsed Conformation

In the eclipsed conformation of a Newman projection the substituents of the rear carbon are placed at a slightly offset angle so that they can be displayed in the image. In theory they are exactly behind the substituents of the front carbon.



Ethane—eclipsed conformation

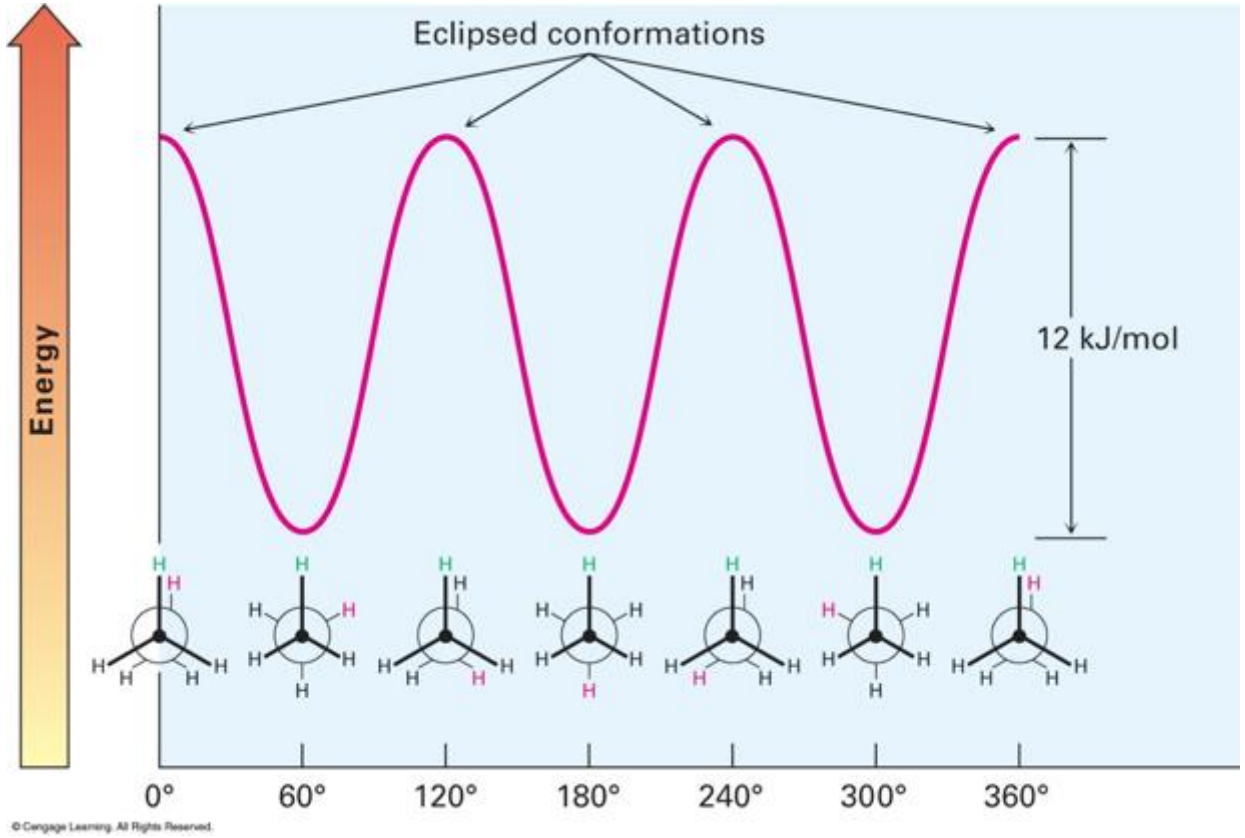
Two conformations of Ethane



99% of ethane molecules will be in staggered conformation and only about 1% will be close to eclipsed.
This is due to torsional strain (approx 12 kJ/mol) present in the eclipsed conformation not present in the staggered conformation.

Potential energy versus bond rotation in ethane

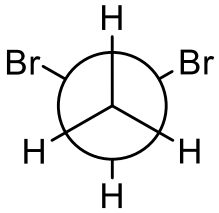
Energy differences during a complete C-C bond rotation



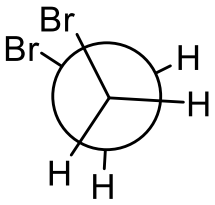
Try it yourself at
https://www.chemtube3d.com/stethanenewman/

Practice Example

Which of the following Newman projections shows the staggered confirmation of 1,2-dibromoethane?



1.



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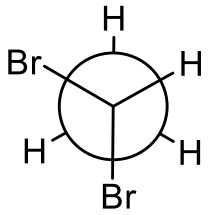

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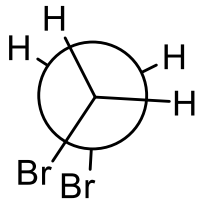

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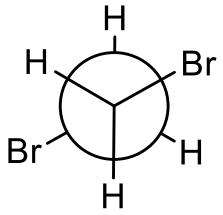
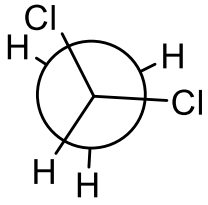


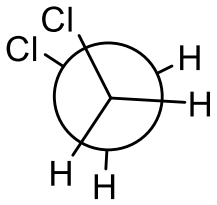
5.

Practice Example

How many of the following Newman projections shows an eclipsed confirmation of 1,2-dichlooethane?



1.



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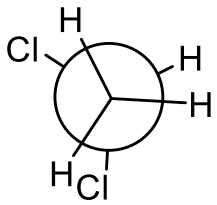
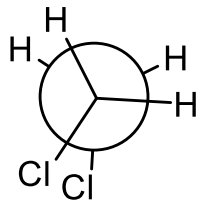


3.



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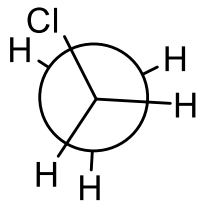

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