Chemistry 121(01) Winter 2009

Introduction to Organic Chemistry and Biochemistry
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TR 9::00 - !0:00 am & 1:00-2:00 pm.

December 19, Test 1 (Chapters 12-14)
January 2 Test 1 (Chapters 15-16)
February 6 (Chapters 17-19)
February 27, (Chapters 20-22)
March 2, 2009, Make Up Exam:
Bring Scantron Sheet 882-E

Chapter 12. Saturated Hydrocarbons

Sections 12.4-12.14 & 12.6

Chapter 12. Saturated Hydrocarbons

Types of formula for organic compounds

Chemical formula: Indicate the kind and number of each type of atom in the molecule.

Condensed formula: Shows skeletal atoms in a molecule and places them in a sequential order that indicates bonding.

Structural formula: Shows each atom and bonds in a molecule.

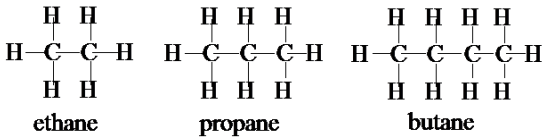
Line-angle formula: The hydrogen atoms are removed from carbon chains, leaving just a carbon line skeleton with functional groups attached to it.

Alicyclic Alkanes

Are saturated hydrocarbons:

•Noncyclic alkanes: General molecular formula, C_nH_{2n+2}

Structural formula:



ethane propane butane

Organic Nomenclature

Organic molecules can be very complex.

Naming system must be able to tell

- **Number of carbons in the longest chain**
- **The location of any branches**
- **Which functional groups are present and where they are located.**

The IUPAC Nomenclature System provides a uniform set of rules that we can follow.

Naming alkanes

1 Find the longest carbon chain.
Use as base name with an ane ending.

2 Locate any branches on chain.
Use base names with a yl ending.

3 For multiple branch of the same type, modify name with di, tri, ...

4 Show the location of each branch with numbers.

5 List multiple branches alphabetically
- the di, tri, ... don't count..

Alkanes

First four members of the alkanes

Name	# of C	Condensed formula
Methane	1	CH_4
Ethane	2	CH_3CH_3
Propane	3	$CH_3CH_2CH_3$
Butane	4	$CH_3CH_2CH_2CH_3$

Called a homologous series

- **"Members differ by number of CH_2 groups"**

Nomenclature: Unbranched or straight chain alkanes

General molecular formula: C_nH_{2n+2}

All bond angles about tetrahedral carbon are approximately 109.5°

Name	Molecular Formula	Name	Molecular Formula
methane	CH_4	nonane	C_9H_{20}
ethane	C_2H_6	decane	$C_{10}H_{22}$
propane	C_3H_8	dodecane	$C_{12}H_{26}$
butane	C_4H_{10}	tetradecane	$C_{14}H_{30}$
pentane	C_5H_{12}	hexadecane	$C_{16}H_{34}$
hexane	C_6H_{14}	octadecane	$C_{18}H_{38}$
heptane	C_7H_{16}	eicosane	$C_{20}H_{42}$
octane	C_8H_{18}		

Isomerism

Isomers - different compounds having the same molecular formula but different structural formulas

There are two type of Isomers:

Constitutional isomerism: Different connections among atoms in the

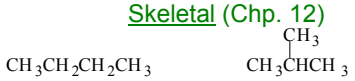
- Skeleton
- Position
- Functional group

Stereoisomerism: Same connectivity among atoms, but these atoms differ in spatial orientation

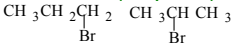
- geometric
- conformational
- optical

Constitutional Isomers

Skeletal (Chp. 12)



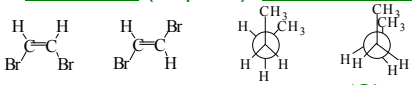
Positional (Chp. 12)



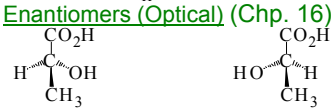
Functional (Chp. 14)

Stereoisomers

Geometric (Chp. 13) Conformational (Chp.12)



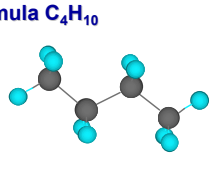
Enantiomers (Optical) (Chp. 16)

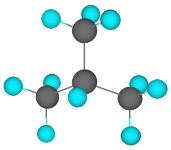


Constitutional isomers in butane

Constitutional isomers: compounds with the same molecular formula but a different connectivity of their atoms in the skeleton.

There are two constitutional isomers with molecular formula C_4H_{10}





$CH_3CH_2CH_2CH_3$

Butane
(bp -0.5°C)

CH_3CHCH_3 (CH_3 branch)

2-Methylpropane
(bp -11.6°C)

Constitutional isomers

Compounds with the same number and type of atoms but with different arrangements.

Molecular Formula C_5H_{12}

Condensed structural formulas.

$CH_3CH_2CH_2CH_2CH_3$	pentane
$CH_3CH(CH_3)CH_2CH_3$	2-methylbutane
$(CH_3)_4C$	2,2-dimethylpropane

All are constitutional isomers of C_5H_{12}.

Rules of IUPAC Nomenclature of Branched Alkanes

Parent name: the longest carbon chain

Substituent: a group bonded to the parent chain

Alkyl group: a substituent derived by removal of a hydrogen from an alkane; given the symbol R-

written in alphabetical order

CH_4 becomes CH_3- (methyl)

CH_3CH_3 becomes CH_3CH_2- (ethyl)

Prefixes: di-, tri-, tetra-, etc. are not included in alphabetization

Common alkyl groups

Name	Condensed Structural Formula	Name	Condensed Structural Formula
methyl	$-CH_3$	isobutyl	$-CH_2CH(CH_3)_2$
ethyl	$-CH_2CH_3$	*sec*-butyl	$-CH(CH_3)CH_2CH_3$
propyl	$-CH_2CH_2CH_3$	*tert*-butyl	$-C(CH_3)_3$
isopropyl	$-CH(CH_3)_2$		
butyl	$-CH_2CH_2CH_2CH_3$		

Names of Alkyl Groups

methyl	H_4 methane: CH_3- methyl
ethyl	CH_3CH_3 ethane: CH_3CH_2- ethyl
propyl	$CH_3CH_2CH_2$-
isopropyl	$(CH_3)_2CH$-
butyl	$CH_3CH_2CH_2CH_2$-
sec-butyl	$CH_3CH_2(CH_3)CH$-
isobutyl	$(CH_3)_2CHCH_2$-
tert-butyl	$(CH_3)_3C$-

IUPAC Nomenclature of branched alkanes

- suffix -ane specifies an alkane
- prefix tells the number of carbon atoms

Prefix	Carbons	Prefix	Carbons
meth-	1	undec-	11
eth-	2	dodec-	12
prop-	3	tridec-	13
but-	4	tetradec-	14
pent-	5	pentadec-	15
hex-	6	hexadec-	16
hept-	7	heptadec-	17
oct-	8	octadec-	18
non-	9	nonadec-	19
dec-	10	eicos-	20

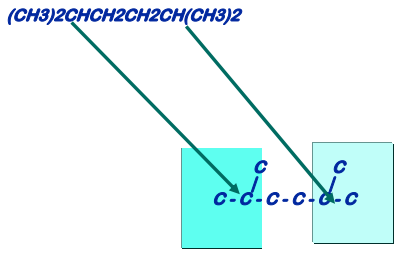
Example

Name the following.

$(CH_3)_2CHCH_2CH_2CH(CH_3)_2$

This is a condensed structural formula.

First convert it to a carbon skeleton, leaving out the hydrogen.



Now name it!

1. Longest chain is 6 - hexane
2. Two methyl groups - dimethyl
3. Use 2,5-dimethylhexane

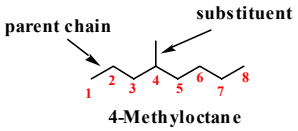
Giving IUPAC names

- $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_3$

Parent name: octane

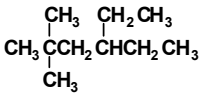
Substituent: Methyl at 4
4-mehtyl

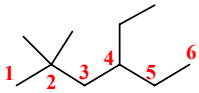
Name: 4-Methyloctane



4-Methyloctane

$CH_3C(CH_3)_2CH_2CH(CH_2CH_3)CH_2CH_3$

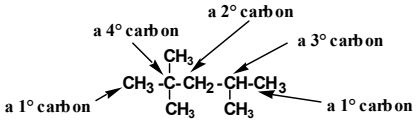




4-Ethyl-2,2-dimethylhexane

Types of carbon and hydrogen atoms

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



2,2,4-Trimethylpentane

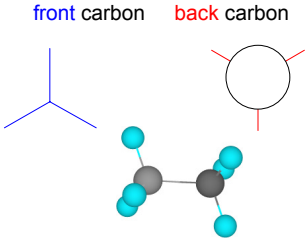
Primary (1°) hydrogen: a H bonded to primary (1°) carbon
Secondary (2°) hydrogen : a H bonded to secondary (2°) carbon
Tertiary (3°) hydrogen : a H bonded to tertiary (3°) carbon

Conformational Isomerism

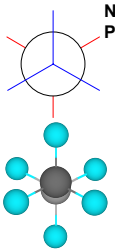
A type of stereoisomerism in which the isomers (known as conformers) differ by the degree of rotation around a carbon-carbon single bond

Newman projections: A way used to represent conformers using a projection that looks down a carbon-carbon bond

front carbon back carbon



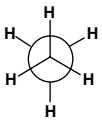
Newman Projection



Staggered and Eclipsed conformations of alkanes and cycloalkanes

Conformation Stereoisomerism: Any three-dimensional arrangement of atoms in a molecule that results from rotation about a single bond

Staggered conformation: A conformation about a carbon-carbon single bond where the atoms on one carbon are as far apart as possible from the atoms on an adjacent carbon



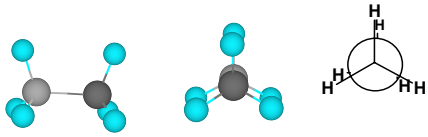
Newman Projection

Conformations of Alkanes

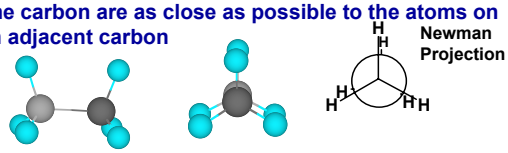
Conformers shown by Newman Projections

Ethane :staggered, ecliped

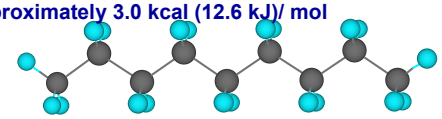
Butane: two staggered and two ecliped conformations



Eclipsed conformation: a conformation about a carbon-carbon single bond in which the atoms on one carbon are as close as possible to the atoms on an adjacent carbon



Lowest energy conformation of an alkane is a fully staggered conformation. The torsional strain between staggered and eclipsed ethane is approximately 3.0 kcal (12.6 kJ)/ mol



Sources of Alkanes

Natural gas

- 90-95% methane, 5-10% ethane

Petroleum

- gases (bp below 20°C)
- naphthas, including gasoline (bp 20 - 200°C)
- kerosene (bp 175 - 275°C)
- fuel oil (bp 250 - 400°C)
- lubricating oils (bp above 350°C)
- asphalt (residue after distillation)

Coal

Molecular Structure and Physical Properties

•Bp decreases with hydrocarbon chain branching due to decrease in surface area which results in fewer intermolecular attractions.

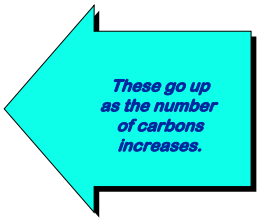
• Mp increases with hydrocarbon chain branching because the more compact molecules have a better fit in the crystal lattice making it more stable.

•Solubility - the quantity of solute that will dissolve in a solvent depends on polarity of solute and solvent. "Like dissolves like" refers to polar liquids tending to dissolve polar solutes and nonpolar liquids tend to dissolve nonpolar solutes. Alkanes are nonpolar.

Alkanes

Physical Properties

- Nonpolar molecules
- Not soluble in water
- Low density
- Low melting point
- Low boiling point



Physical Properties of Alkanes

Name	bp, °C	mp, °C	Density at 20 °C
Methane	-161.7	-182.6	0.000667
Ethane	- 88.6	-182.8	0.00125
Propane	- 42.2	-187.1	0.00183
Butane	-0.5	-135.0	0.00242
Pentane	36.1	-129.7	0.626
Hexane	68.7	- 94.0	0.659
Heptane	98.4	- 90.5	0.684
Octane	125.6	- 56.8	0.703
Nonane	150.7	-53.7	0.718
Decane	174.0	-29.7	0.730

Physical Properties of The Saturated Hydrocarbons

Name	Molecular Formula	Melting Point (oC)	Boiling Point (oC)	State at 25oC
methane	CH_4	-182.5	-164	gas
ethane	C_2H_6	-183.3	-88.6	gas
propane	C_3H_8	-189.7	-42.1	gas
butane	C_4H_{10}	-138.4	-0.5	gas
pentane	C_5H_{12}	-129.7	36.1	liquid
hexane	C_6H_{14}	-95	68.9	liquid
heptane	C_7H_{16}	-90.6	98.4	liquid
octane	C_8H_{18}	-56.8	124.7	liquid
nonane	C_9H_{20}	-51	150.8	liquid
decane	$C_{10}H_{22}$	-29.7	174.1	liquid
eicosane	$C_{20}H_{42}$	36.8	343	solid

Constitutional isomerism in alkane

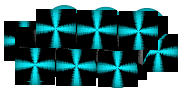
The number of constitutional isomerism increases with the carbon number in the alkane

Molecular Formula	Constitutional Isomers
CH_4	1
C_5H_{12}	3
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{25}H_{52}$	36,797,588
$C_{30}H_{62}$	4,111,846,763

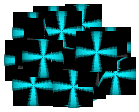
Physical Properties Constitutional isomers

Constitutional isomers are different compounds and have different physical properties

Name	Melting Point (°C)	Boiling Point (°C)	Density (g/mL)
hexane	-95	69	0.659
3-methylpentane	-6	64	0.664
2-methylpentane	-23	62	0.653
2,3-dimethylbutane	-129	58	0.662
2,2-dimethylbutane	-100	50	0.649



Hexane



2,2-Dimethylbutane

Reactions of alkanes

Halogenation

- A reaction where a halogen replaces one or more hydrogens.

$$CH_{4(g)} + Cl_{2(g)} \xrightarrow{\text{heat or light}} CH_3Cl_{(g)} + HCl_{(g)}$$

Used to prepare many solvents

- dichloromethane - paint stripper
- chloroform - once used as anesthesia
- 1,2-dichloroethane - dry cleaning fluid

Reactions of alkanes

Combustion

- $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

Many alkanes are used this way - as fuels

- **Methane** - natural gas
- **Propane** - used in gas grills
- **Butane** - lighters
- **Gasoline** - mixture of many hydrocarbons,

Reactions of Alkanes

Oxidation is the basis for the use of alkanes as energy sources for heat and power

heat of combustion: heat released when one mole of a substance is oxidized to carbon dioxide and water in a **combustion reaction**.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta H° = -212 \text{ kcal/mol}$$

Methane

$$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O \quad \Delta H° = -530 \text{ kcal/mol}$$

Propane

Synthesis Gas

A mixture of carbon monoxide and hydrogen in varying proportions, depending on how it is produced

$$\underset{\text{Coal}}{C} + H_2O \xrightarrow{\text{heat}} CO + H_2$$

$$\underset{\text{Methane}}{CH_4} + \frac{1}{2}O_2 \xrightarrow{\text{catalyst}} CO + 2H_2$$

Methanol and acetic acid are produced from synthesis gas

$$CO + 2H_2 \xrightarrow{\text{catalyst}} \underset{\text{Methanol}}{CH_3OH}$$

$$\underset{\text{Methanol}}{CH_3OH} + CO \xrightarrow{\text{catalyst}} \underset{\text{Acetic acid}}{CH_3\overset{\overset{O}{\|}}{C}OH}$$

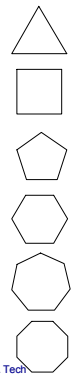
Cycloalknes

Cyclic alkanes: General molecular formula, C_nH_{2n}

Structure and nomenclature

- named similar to noncyclic alkanes
- to name, prefix the name of the corresponding open-chain alkane with cyclo-, and name each substituent on the ring
- if only one substituent, no need to give it a number
- if two substituents, number from the substituent of lower alphabetical order
- if three or more substituents, number to give them the lowest set of numbers, and then list substituents in alphabetical order
- in planar cyclopentane, all C-C-C bond angles are 108°, which differ only slightly from the tetrahedral angle of 109.5°consequently there is little angle strain

Naming simple of cycloalkanes:



cyclopropane

cyclobutane

cyclopentane

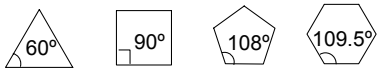
cyclohexane

cycloheptane

cyclooctane

Ring strain in cycloalkane

The stability of cycloalkanes depends on their ability to relieve ring strain when the bond angles are less than 109.5˚.



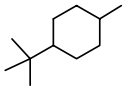
Least stable **Most stable**

Naming branched cycloalkanes

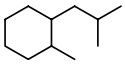
Commonly written as line-angle formulas

examples:

Isopropylcyclopentane



1-*tert*-Butyl-4-methyl-cyclohexane



1-Isobutyl-2-methyl-cyclohexane

1-Ethyl-1-methyl-cyclopropane

Cycloalkanes :saturated hydrocarbons with a carbon ring

Have C-C single bonds in a ring structure.

General formula C_nH_{2n}

cyclopropane

cyclobutane

Naming Cycloalkanes

Have the carbons connected in a ring. These compounds are known collectively as

To name a cycloalkane, use the prefix cyclo- with the parent. If there is only one substituent, a number is not needed.

Conformations of Cycloalkanes

Cyclohexane

Chair conformation-low energy

Boat conformation-higher energy

Geometrical (cis & trans) Isomers of Cycloalkanes

Carbon ring create a rigid structure

trans and cis is used to describe the arrangements of alkyl groups with respect to the plane of the ring

cis: on the same side

trans: on the opposite sides

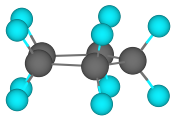
Cis and trans Geometrical isomers of Cycloalkanes

two groups are said to be located cis to each other if they lie on the same side of a plane.

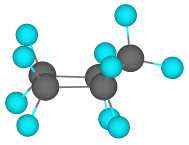
If they are on opposite sides, their relative position is described as trans.

Conformations of cyclopentane

- In planar cyclopentane, there are 10 fully eclipsed C-H bonds, which create torsional strain of approximately 10 kcal/mol
- Puckering to an "envelope" conformation relieves part of this strain
- In an envelope conformation, eclipsed interactions are reduced but angle strain is increased slightly (105°)

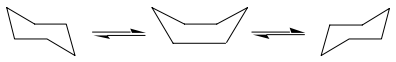


Planar conformation



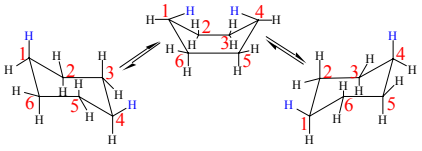
Envelope conformation

Cyclohexane Conformations:



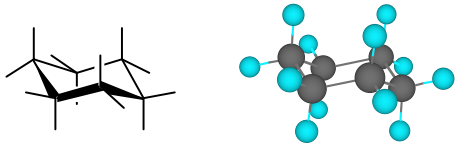
chair (most stable) — boat (unstable) — chair (most stable)

Why?



Chair conformations of cyclohexane

- The most stable conformation is a puckered chair conformation
- In a chair conformation, all bond angles are approx. 109.5°, and all bonds on adjacent carbons are staggered

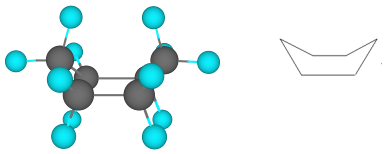


Chair conformation

Boat conformations of cyclohexane

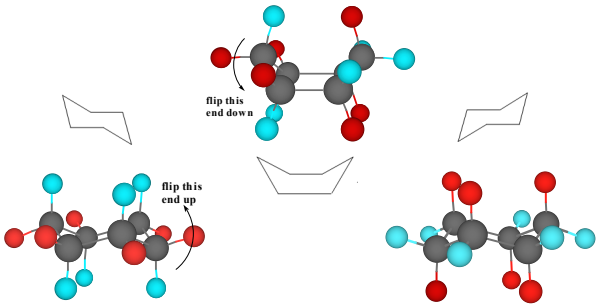
A puckered conformation in which carbons 1 and 4 are bent toward each other

- a boat conformation is less stable than a chair conformation by 6.5 kcal (27 kJ)/mol
- torsional strain is created by four sets of eclipsed hydrogen interactions
- steric strain (nonbonded interaction strain) is created by one set of flagpole interactions



Interconversions of conformations

Interconvert ion to alternative chair conformations (lower energy) via a boat conformation (higher energy



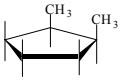
Cis and Trans Geometric Isomerism in Cycloalkanes

Geometric isomerism: A stereoisomer concerning the orientation differences of atoms or groups around a double bond or ring

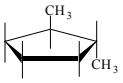
cis isomer - a geometric isomer where groups are on the same side of a ring or double bond

trans isomer - a geometric isomer where groups are on opposite sides of a ring or double bond

***cis*-1,2-dimethylcyclopentane**

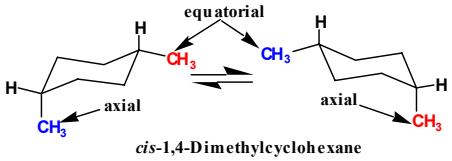


***trans*-1,2-dimethylcyclopentane**



***cis*-1,4-dimethylcyclohexane,**

Perspective drawing



cis-1,4-Dimethylcyclohexane
(these conformations are of equal stability)

Problem: draw the alternative chair conformations of this trisubstituted cyclohexane and state which is the more stable