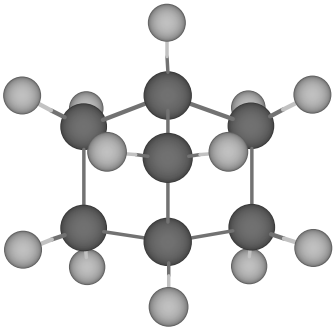
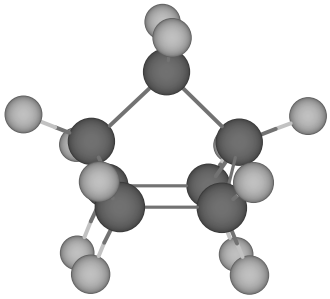
Alkanes and Cycloalkanes



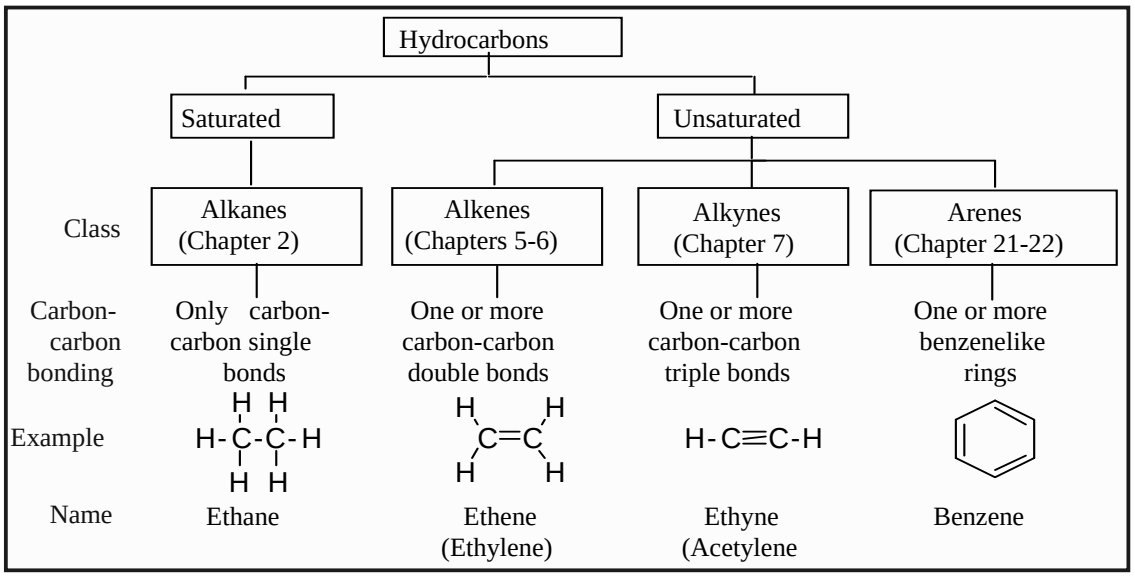


Chapter 2

Structure

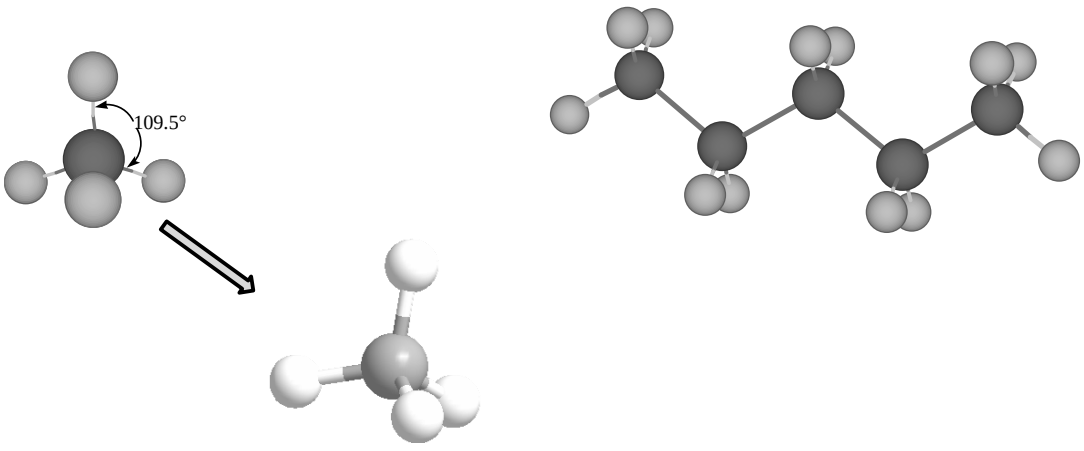
- **Hydrocarbon:** A compound composed only of carbon and hydrogen.
- **Saturated hydrocarbon:** A hydrocarbon containing only single bonds.
- **Alkane:** A saturated hydrocarbon whose carbons are arranged in an open chain.
- **Aliphatic hydrocarbon:** Another name for an alkane.

Hydrocarbons



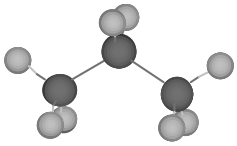
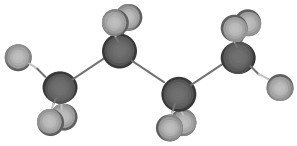
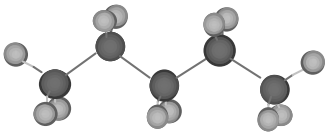
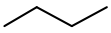
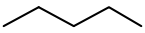
Structure

- Shape
  - tetrahedral about carbon
  - all bond angles are approximately 109.5°

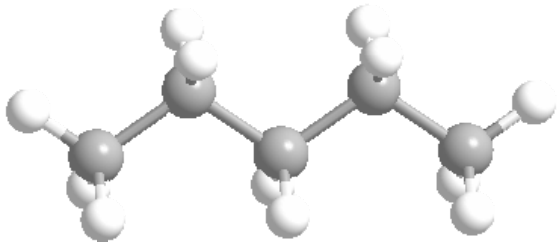


Drawing Alkanes

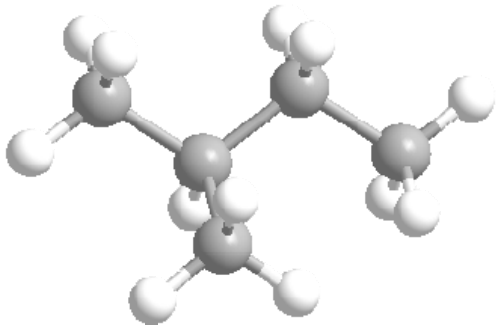
- Line-angle formulas:
  - an abbreviated way to draw structural formulas.
  - each vertex and line ending represents a carbon.

Ball-and-stick model			
Line-angle formula			
Structural formula	$CH_3CH_2CH_3$	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$
	Propane	**Butane**	**Pentane**

$$CH_3CH_2CH_2CH_2CH_3$$

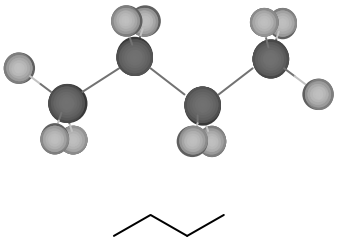


$(CH_3)_2CHCH_2CH_3$

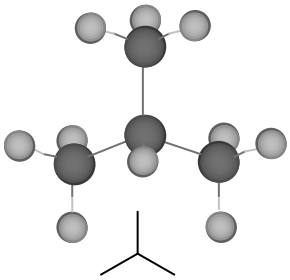


Constitutional Isomers

- Constitutional isomers: Compounds with the same molecular formula but a different connectivity of their atoms.
  - example: C_4H_{10}



$CH_3CH_2CH_2CH_3$
Butane
(bp -0.5°C)



CH_3CHCH_3 (CH_3 above the central CH)
2-Methylpropane
(bp -11.6°C)

Nomenclature IUPAC

- Suffix -ane specifies an alkane, e.g. ethane.
- Prefix tells the number of carbon atoms.

Commit to Memory

Prefix	Number of carbons	Prefix	Number of 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

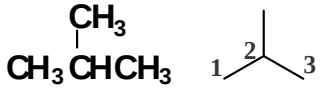
Nomenclature IUPAC

- 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-**.

Alkane	Name	Alkyl group	Name
CH_4	Methane	CH_3-	Methyl group
CH_3CH_3	Ethane	CH_3CH_2-	Ethyl group

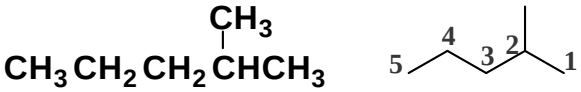
Nomenclature IUPAC

1. The name of a saturated hydrocarbon with an unbranched chain consists of a prefix and suffix.
2. The parent chain is the longest chain of carbon atoms.
3. Each substituent is given a name and a number. Use a hyphen to connect the number to the name.

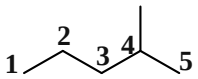


2-Methylpropane

4. If there is one substituent, number the chain from the end that gives it the lower number.



2-Methylpentane



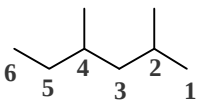
(not 4-methylpentane)

Nomenclature IUPAC

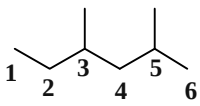
5. If there are two or more identical substituents, number the chain from the end that gives the lower number to the substituent encountered first.

Indicate the number of times the substituent appears by a prefix di-, tri-, tetra-, etc.

Use commas to separate position numbers.



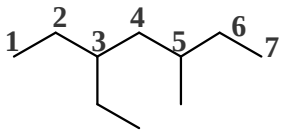
2,4-Dimethylhexane



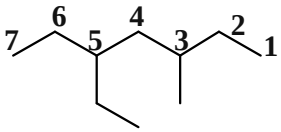
(not 3,5-dimethylhexane)

Nomenclature IUPAC

6. If there are two or more different substituents,
– list them in alphabetical order.
– number from the end of the chain that gives the substituent encountered first the lower number.



3-Ethyl-5-methylheptane

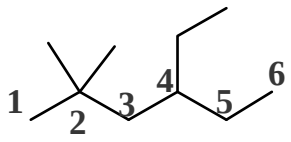


(not 3-methyl-5-ethylheptane)

Nomenclature IUPAC

7. The prefixes di-, tri-, tetra-, etc. are **not** included in alphabetization.

Alphabetize the names of substituents first and then insert these prefixes.



4-Ethyl-2,2-dimethylhexane

(not 2,2-dimethyl-4-ethylhexane)

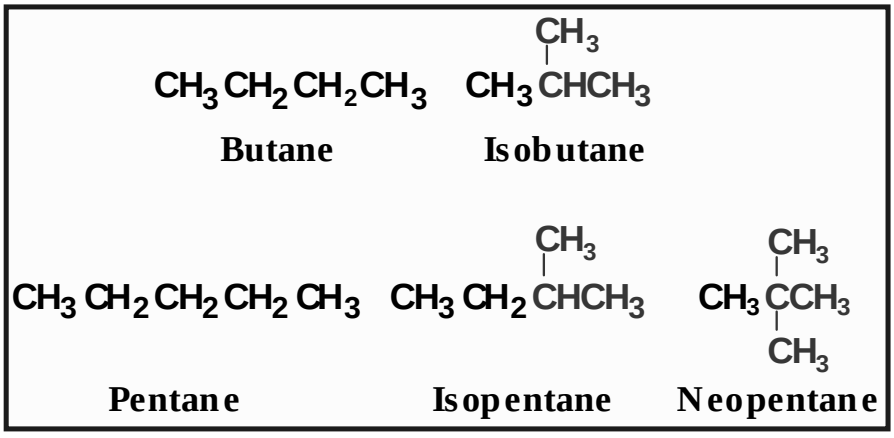
Nomenclature - IUPAC

- Alkyl groups

Name	Condensed Structural Formula	Name	Condensed Structural Formul
methyl	$-CH_3$	butyl	$-CH_2CH_2CH_2CH_3$
ethyl	$-CH_2CH_3$	2-methylpropyl (isobutyl)	$-CH_2CH(CH_3)_2$
propyl	$-CH_2CH_2CH_3$	1-methylpropyl (*sec*-butyl)	$-CH(CH_3)CH_2CH_3$
1-methylethyl (isopropyl)	$-CH(CH_3)_2$	1,1-dimethylethyl- (*tert*-butyl)	$-C(CH_3)_3$

Nomenclature - Common

- The number of carbons in the alkane determines the name.
  - All alkanes with four carbons are butanes, those with five carbons are pentanes, etc.
  - iso- indicates the chain terminates in $-CH(CH_3)_2$; neo- that it terminates in $-C(CH_3)_3$.



Classification of C & H

Primary (1°) C: A carbon bonded to one other carbon.

1° H: a hydrogen bonded to a 1° carbon

Secondary (2°) C: A carbon bonded to two other carbons.

2° H: a hydrogen bonded to a 2° carbon

Tertiary (3°) C: A carbon bonded to three other carbons.

3° H: a hydrogen bonded to a 3° carbon

Quaternary (4°) C: A carbon bonded to four other carbons.

IUPAC - General

- prefix-infix-suffix
  - Prefix:Tells the number of carbon atoms in the parent chain.
  - Infix : Tells the nature of the carbon-carbon bonds in the parent chain.
  - Suffix : Tells the class of the compound.

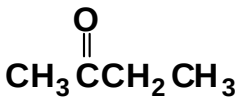
Infix	Nature of Carbon-Carbon Bonds in the Parent Chain
-an-	all single bonds
-en-	one or more double bonds
-yn-	one or more triple bonds

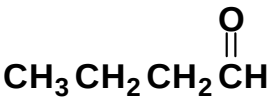
Suffix	Class
-e	hydrocarbon
-ol	alcohol
-al	aldehyde
-amine	amine
-one	ketone
-oic acid	carboxylic acid

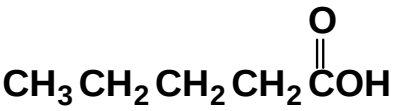
IUPAC - General

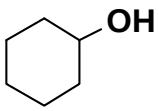
prop-en-e = propene $CH_3CH{=}CH_2$

eth-an-ol = ethanol CH_3CH_2OH

but-an-one = butanone 

but-an-al = butanal 

pent-an-oic acid = pentanoic acid 

cyclohex-an-ol = cyclohexanol 

eth-yn-e = ethyne $HC{\equiv}CH$

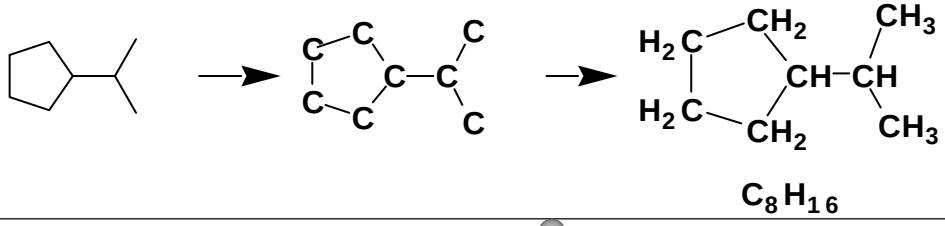
eth-an-amine = ethanamine $CH_3CH_2NH_2$

Cycloalkanes

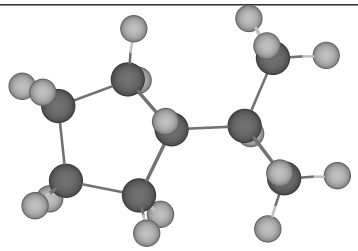
- General formula C_nH_{2n}
  - Five- and six-membered rings are the most common.
- Structure and nomenclature
  - Add the prefix cyclo- to the name of the open-chain alkane containing the same number of carbons.
  - If only one substituent, no need to give it a number.
  - If two substituents, number 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.

Cycloalkanes

- Line-angle drawings
  - Each line represents a C-C bond.
  - Each vertices and line ending represents a C.

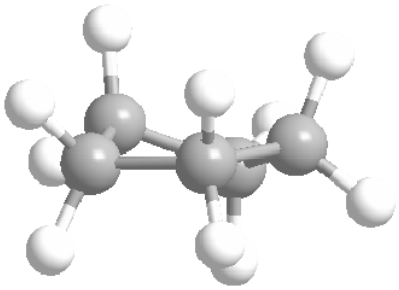


C_8H_{16}

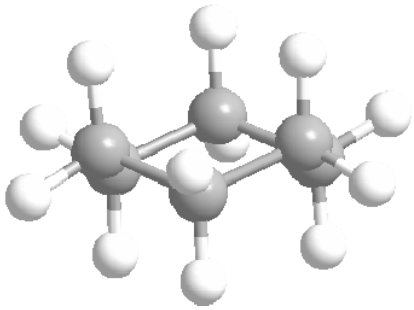


Cycloalkanes

- Line-angle drawings
  - Each line represents a C-C bond.
  - Each vertices and line ending represents a C.
  - Most common are 5 & 6 member rings



cyclopentane



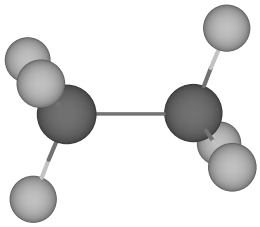
cyclohexane

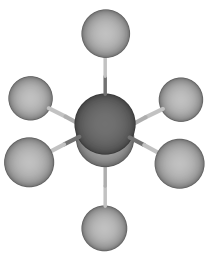
Conformations

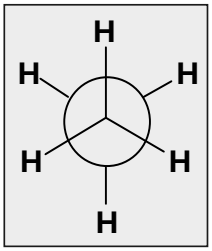
Conformation: Any three-dimensional arrangement of atoms in a molecule that results from rotation about a single bond.

Conformations

- Staggered conformation: A conformation about a carbon-carbon single bond in which the atoms or groups on one carbon are as far apart as possible from the atoms or groups on an adjacent carbon.
- Newman projection: A way to view a molecule by looking along a carbon-carbon single bond.

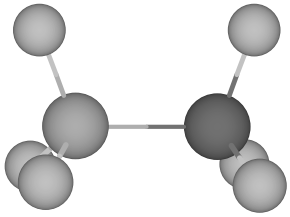


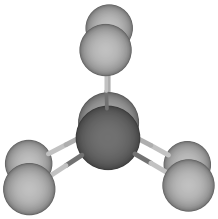


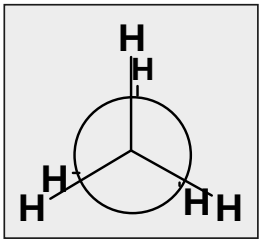


Conformations

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

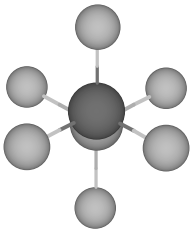


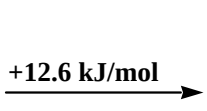


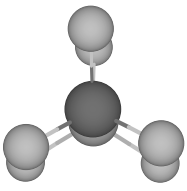


Conformations

- Torsional strain
  - strain that arises when nonbonded atoms separated by three bonds are forced from a staggered conformation to an eclipsed conformation.
  - also called eclipsed interaction strain.
  - the torsional strain between eclipsed and staggered ethane is approximately 12.6 kJ (3.0 kcal)/mol.

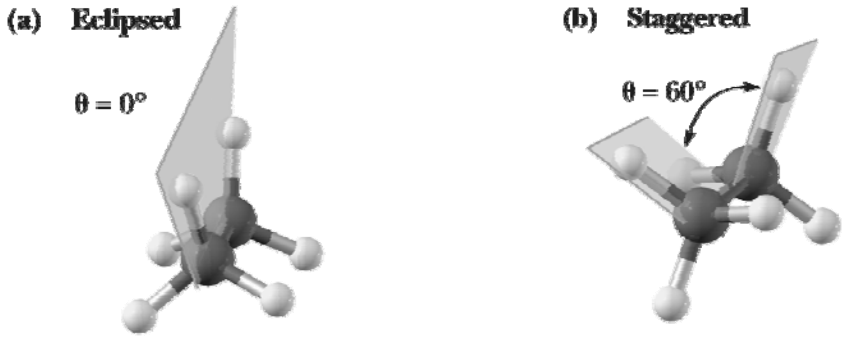






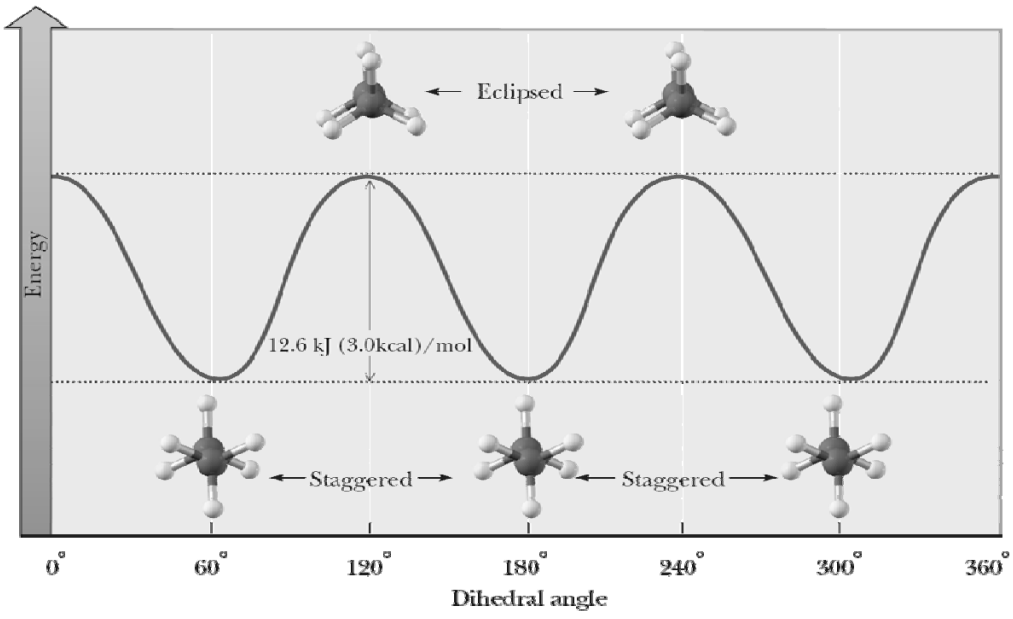
Conformations

- Dihedral angle Θ (Greek theta): The angle created by two intersecting planes.



Conformations

- Figure 2.8 The energy of ethane as a function of dihedral angle.

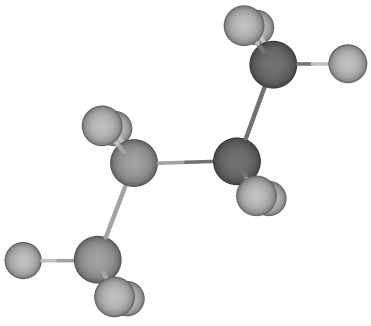


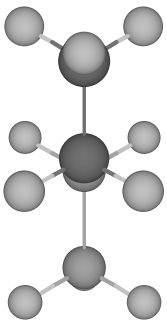
Conformations

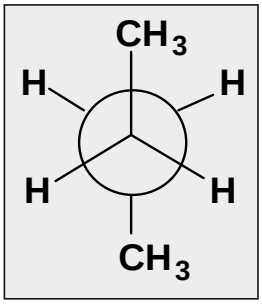
- Strain energy is the increase in energy resulting from distortion of bond angles and bond lengths from their optimal values.
- Steric strain (nonbonded interaction strain): The strain that arises when nonbonded atoms separated by four or more bonds are forced closer to each other than their atomic (contact) radii will allow.
- Angle strain: Strain that arises when a bond angle is either compressed or expanded compared to its optimal value.

Conformations

Anti conformation: A conformation about a single bond in which the groups on adjacent carbons lie at a dihedral angle of 180°





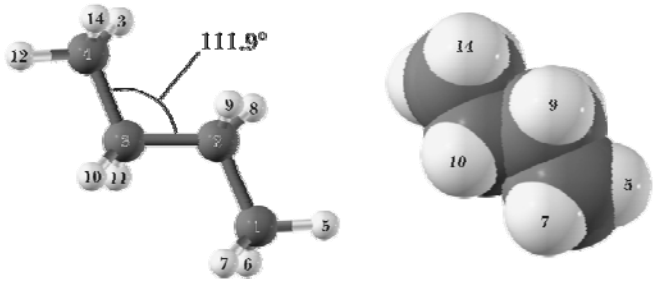


Anti Butane

Energy-minimized anti conformation (computed)

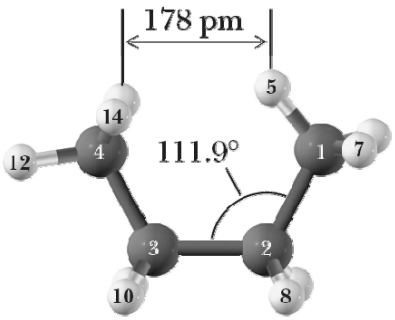
the C-C-C bond angle is 111.9° and all H-C-H bond angles are between 107.4° and 107.9°.

the calculated strain is 9.2 kJ (2.2 kcal)/mol.

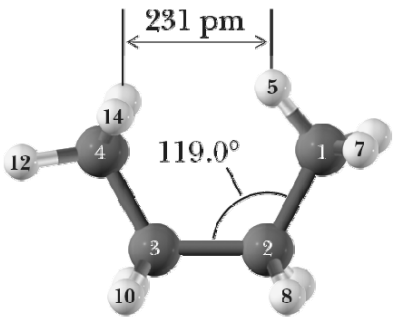


Eclipsed Butane

The calculated energy difference between (a) the non-energy-minimized and (b) the energy-minimized eclipsed conformations is 5.6 kJ (0.86 kcal)/mol.



(a) Ball-and-stick model, side view

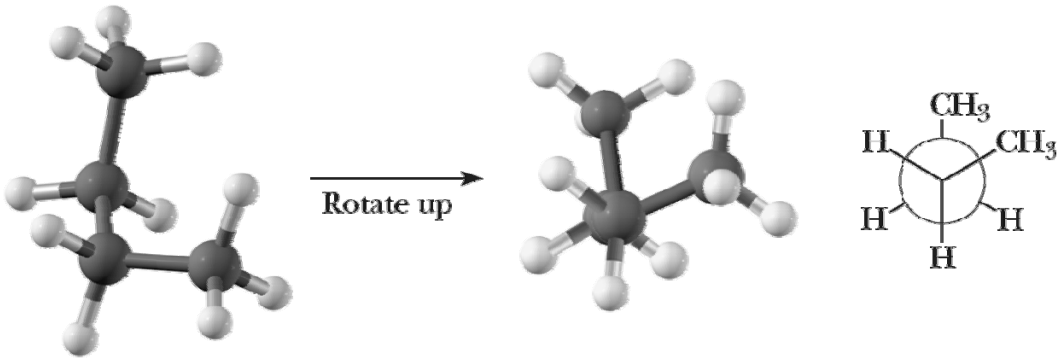


(b) Ball-and-stick model, side view

Gauche Butane

Gauche conformation: A conformation about a single bond of an alkane in which two groups on adjacent carbons lie at a dihedral angle of 60°.

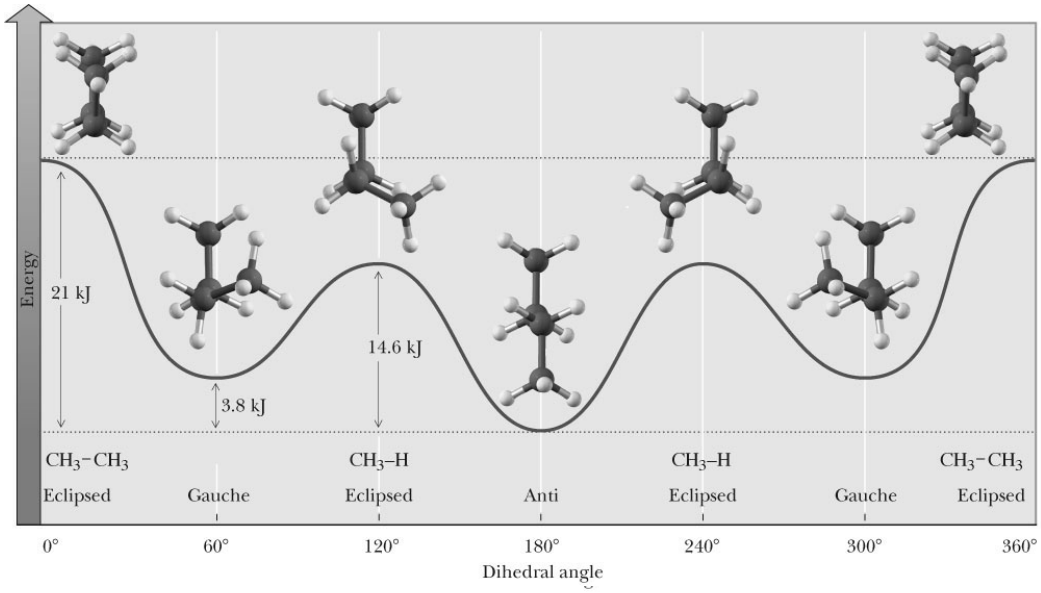
Here is one of two energy-minimized gauche conformations of butane. The second one has equal energy.



Butane

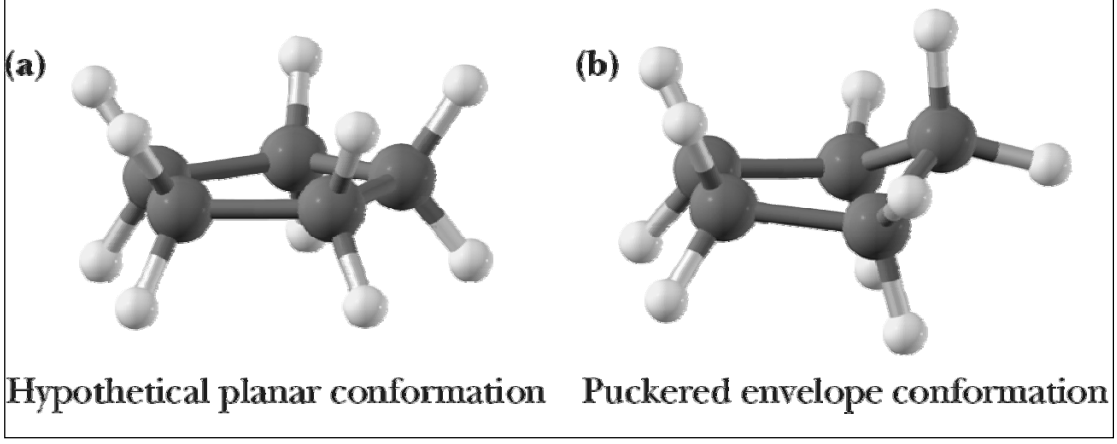
Conformations

The energy of butane as a function of the dihedral angle about the bond between carbons 2 and 3.



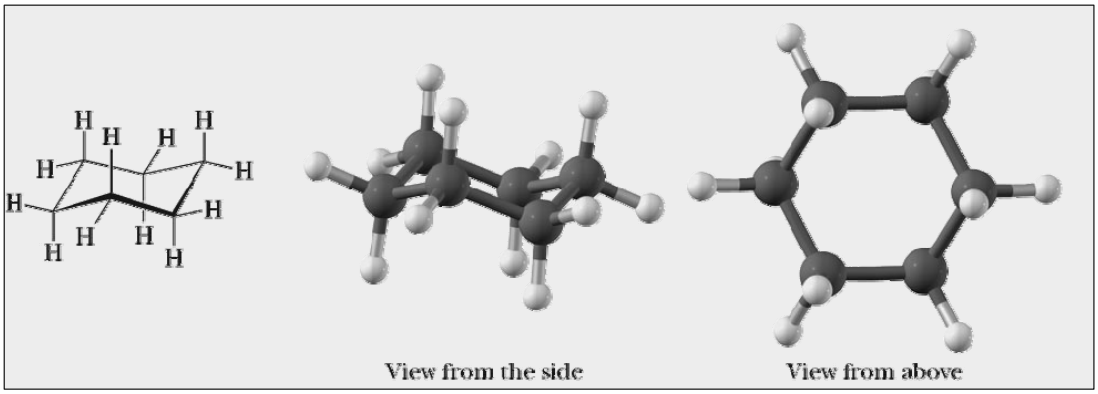
Cyclopentane

- Puckering from planar cyclopentane reduces torsional strain, but increases angle stain.
- The conformation of minimum energy is a puckered “envelope” conformation.
- Strain energy is about 42 kJ (6.5 kcal)/mol.



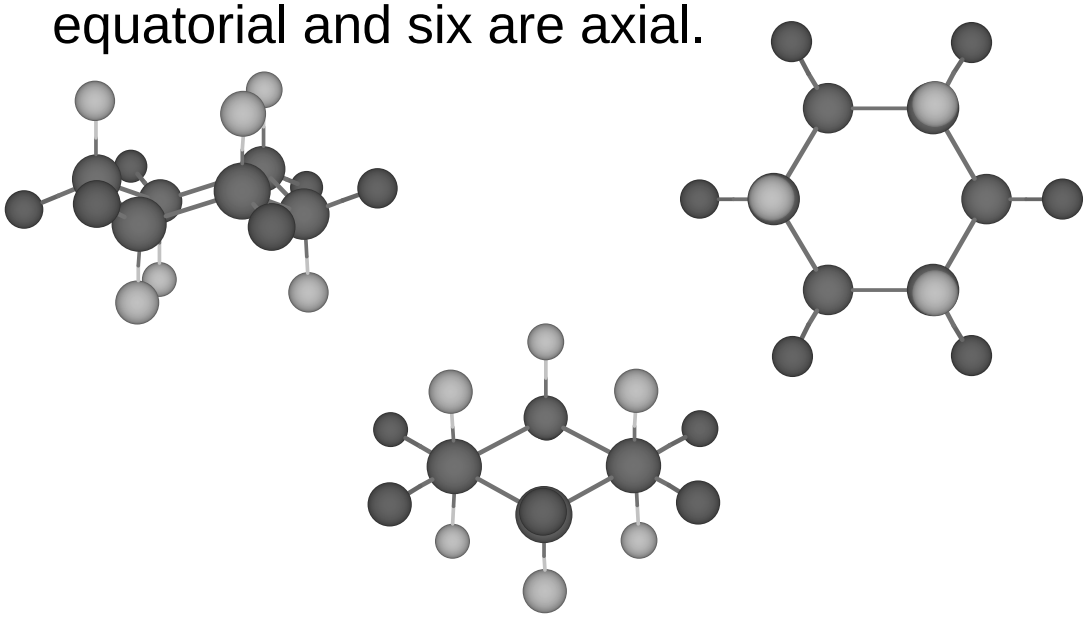
Cyclohexane

- Chair conformation: The most stable puckered conformation of a cyclohexane ring.
  - all bond C-C-C bond angles are 110.9°.
  - **all bonds on adjacent carbons are staggered.**



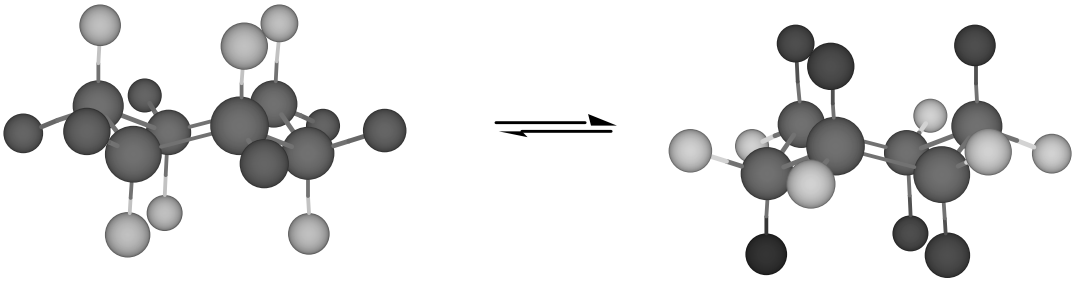
Cyclohexane

- In a chair conformation, six H are equatorial and six are axial.



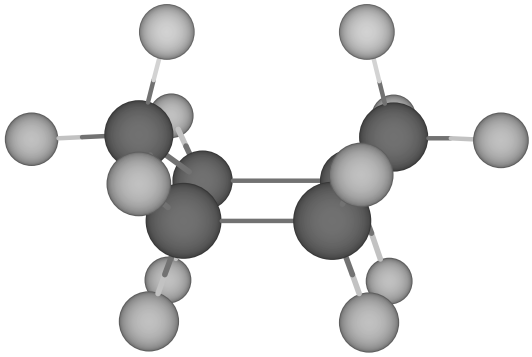
Cyclohexane

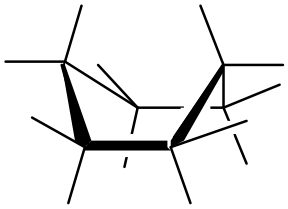
- For cyclohexane, there are two equivalent chair conformations.
  - all C-H bonds equatorial in one chair are axial in the alternative chair and vice versa.



Cyclohexane

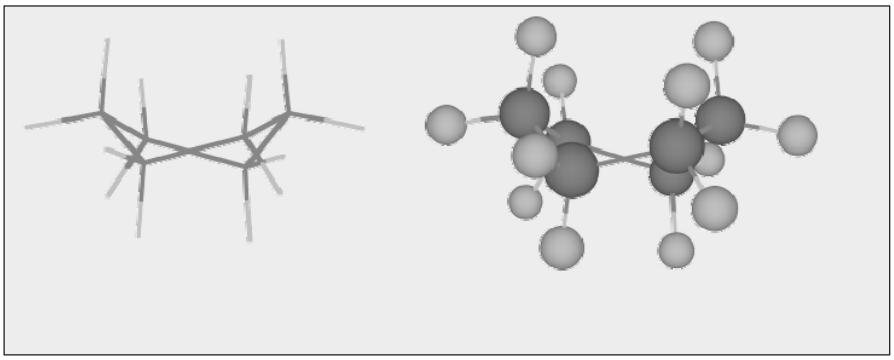
- Boat conformation: A puckered conformation of a cyclohexane ring in which carbons 1 and 4 are bent toward each other.
  - there are four sets of eclipsed C-H interactions and one flagpole interaction (flagpole H green).
  - a boat conformation is less stable than a chair conformation by 27 kJ (6.5 kcal)/mol.





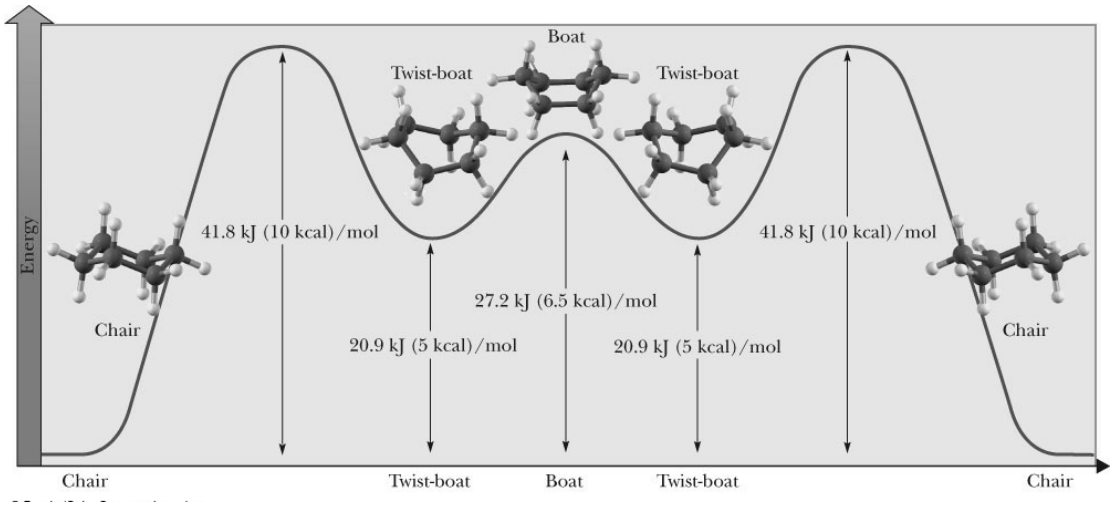
Cyclohexane

- Twist-boat conformation
  - approximately 41.8 kJ (5.5 kcal)/mol less stable than a chair conformation.
  - approximately 6.3 kJ (1.5 kcal)/mol more stable than a boat conformation.



Cyclohexane

- Energy diagram for the interconversion of chair, twist-boat and boat conformations of cyclohexane.



Cis,Trans Isomerism

Stereoisomers: Compounds that have

the same molecular formula.

the same connectivity.

a different orientation of their atoms in space.

Cis,trans isomers: Stereoisomers that are the result of the presence of either a ring (this chapter) or a carbon-carbon double bond (Chapter 5).

Isomers

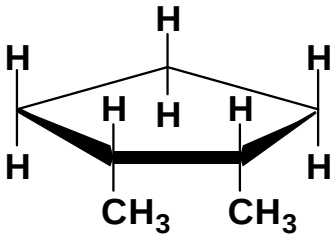
Isomers
Different compounds with the same molecular formula

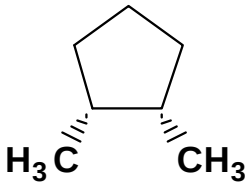
Constitutional isomers
Different compounds with the same molecular formula but a different connectivity

Stereoisomers
Different compounds with the same molecular formula, the same connectivity, but a *different orientation of their* atoms in space

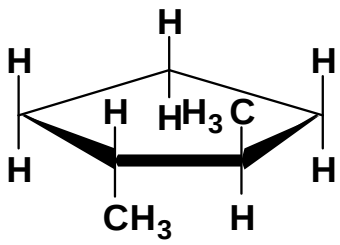
Cis,Trans Isomerism

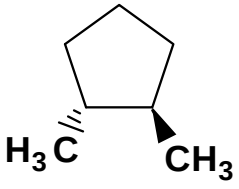
- 1,2-Dimethylcyclopentane





***cis*-1,2-Dimethyl-cyclopentane**





***trans*-1,2-Dimethyl-cyclopentane**

Cis,Trans Isomerism

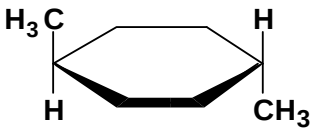
Stereocenter: An atom, most commonly carbon, about which exchange of two groups produces a different stereoisomer.

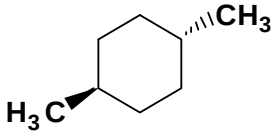
example: 1,2-dimethylcyclobutane has two stereocenters.

Configuration: Refers to the arrangement of atoms about stereocenter.

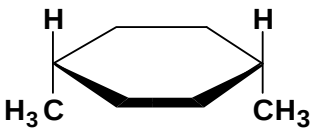
Cis,Trans Isomerism

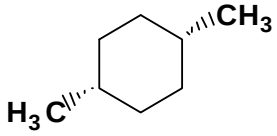
- 1,4-Dimethylcyclohexane



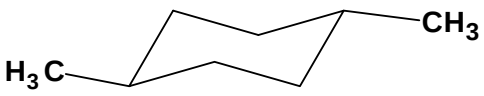


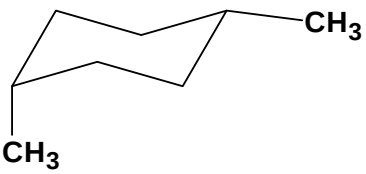
***trans*-1,4-Dimethyl-cyclohexane**





***cis*-1,4-Dimethyl-cyclohexane**

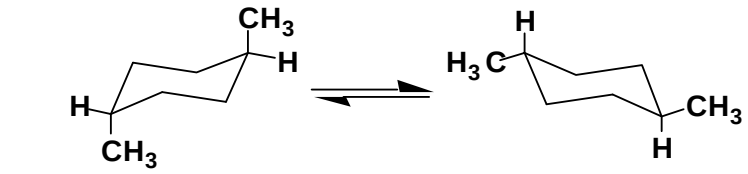




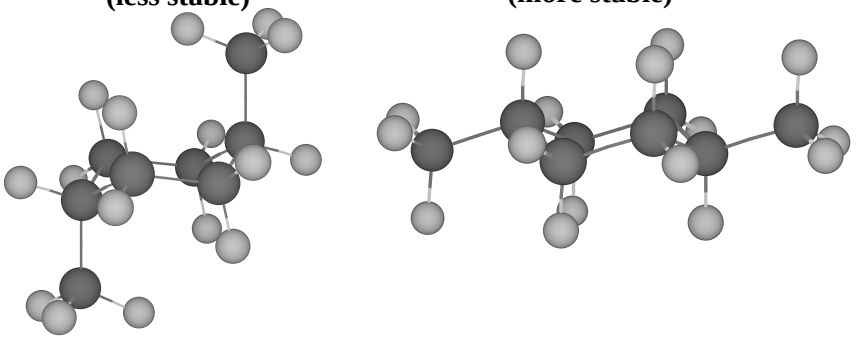
The more stable chair conformation of each isomer

Cis,Trans Isomerism

- *trans*-1,4-Dimethylcyclohexane
  - the diequatorial-methyl chair conformation is more stable by approximately 2 x (7.28) = 14.56 kJ/mol

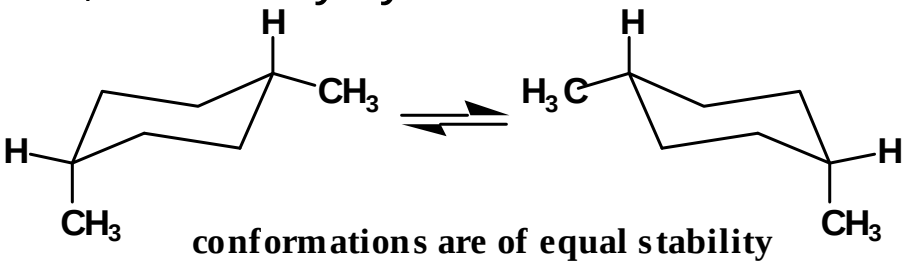


(less stable) (more stable)

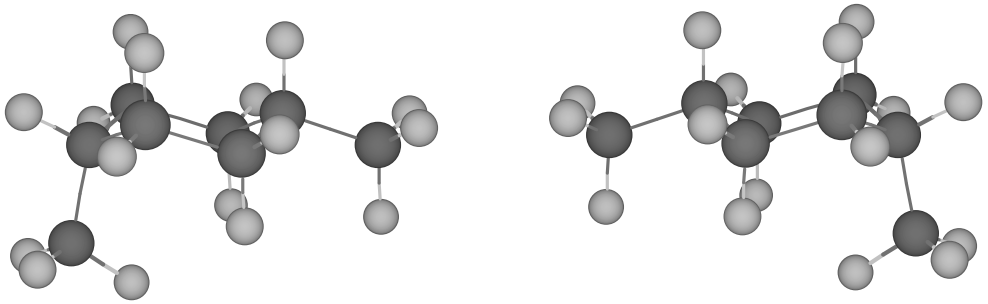


Cis,Trans Isomerism

- *cis*-1,4-Dimethylcyclohexane



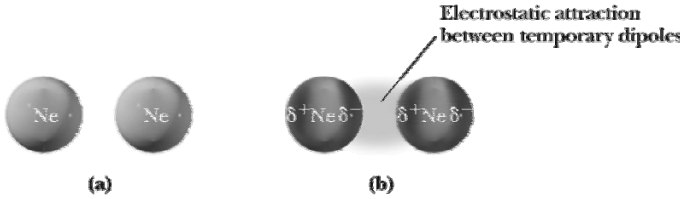
conformations are of equal stability



Physical Properties of Alkanes

Intermolecular forces of attraction (example)

- ion-ion (Na^+ and Cl^- in NaCl)
- ion-dipole ($Na^+ \cdots OH_2$ and $Cl^- \cdots H\text{-}O\text{-}H$ solvated in aqueous solution)
- dipole-dipole and hydrogen bonding
- dispersion forces (very weak electrostatic attraction between temporary dipoles)



Physical Properties

Low-molecular-weight alkanes (methane to butane) are gases at room temperature.

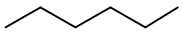
Higher molecular-weight alkanes (pentane, decane, gasoline, and kerosene) are liquids at room temperature.

High-molecular-weight alkanes (paraffin wax) are semisolids or solids at room temperature.

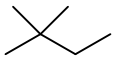
Physical Properties of Alkanes

Constitutional isomers have different physical properties.

Name	mp (°C)	bp (°C)	Density (g/mL)
hexane	-95	68.7	0.659
2-methylpentane	-154	60.3	0.653
3-methylpentane	-118	63.3	0.664
2,3-dimethylbutane	-129	58.0	0.661
2,2-dimethylbutane	-98	49.7	0.649



Hexane



2,2-Dimethylbutane

Oxidation of Alkanes

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

heat of combustion: The heat released when one mole of a substance in its standard state is oxidized to carbon dioxide and water.

	ΔH^0 kJ (kcal)/mol
$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$	-890.4 (-212.8)
Methane	
$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$	-2220 (-530.6)
Propane	