2

Organic Chemistry

William H. Brown &
Christopher S. Foote

2

Alkanes and Cycloalkanes

Chapter Two

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 a chain
- **Aliphatic hydrocarbon:** another name for an alkane

2 Structure

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

2 Nomenclature

- Alkanes have the general formula C_nH_{2n+2}

Name	Molecular Formula	Condensed Structural Formula
methane	CH_4	CH_4
ethane	C_2H_6	CH_3CH_3
propane	C_3H_8	$CH_3CH_2CH_3$
butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$

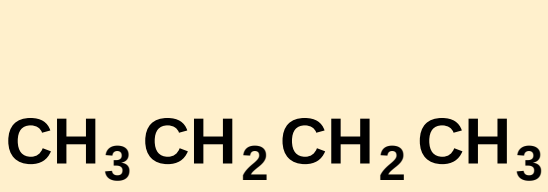
2 Nomenclature

- **Alkanes (contd.)**

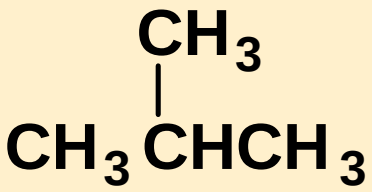
octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$
dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

2 Constitutional Isomerism

- **Compounds isomers:** **compounds with the same molecular formula but a different connectivity (order of attachment of their atoms)**
  - **example: C_4H_{10}**



Butane



2-Methylpropane

2 Constitutional Isomerism

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

World population is about 6,000,000,000

2 Nomenclature

- **International Union of Pure and Applied Chemistry (IUPAC)**
- **Prefix tells the number of carbon atoms**
- **Suffix -ane specifies an alkane**

2 Nomenclature

- IUPAC system

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

2 Nomenclature

- **Parent name of the longest carbon chain is "alkane"**
- **Groups attached to the parent chain are called substituents**
- **Each substituent is given a name and a number**
  - **If substituent occurs more than once, di-, tri-, tetra-, etc.**

2 Nomenclature

- **Number the chain to give the substituent encountered first the lowest number**

- **If there are different substituents, list them in alphabetical order. The following are not included in alphabetization.**
  - **di-, tri-, tetra-, etc.**
  - **hyphenated prefixes, such as *sec-* and *tert-***

2 Nomenclature

- **Alkyl groups**

Name	Condensed Structural Formula
methyl	$-CH_3$
ethyl	$-CH_2CH_3$
propyl	$-CH_2CH_2CH_3$
isopropyl	$-CH(CH_3)_2$

2 Nomenclature

- **Alkyl groups**

Name	Condensed Structural Formula
butyl	$-CH_2CH_2CH_2CH_3$
isobutyl	$-CH_2CH(CH_3)_2$
sec-butyl	$-CH(CH_3)CH_2CH_3$
tert-butyl	$-C(CH_3)_3$

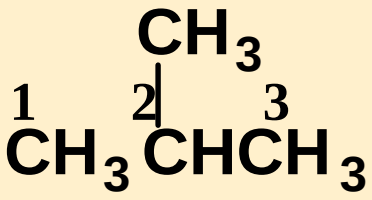
2 Nomenclature

- **Alkyl groups**

Name	Condensed Structural Formula
pentyl	$-CH_2CH_2CH_2CH_2CH_3$
isopentyl	$-CH_2CH_2CHCH_3$ (with CH_3 branch)
neopentyl	$-CH_2C(CH_3)_3$

2 Nomenclature

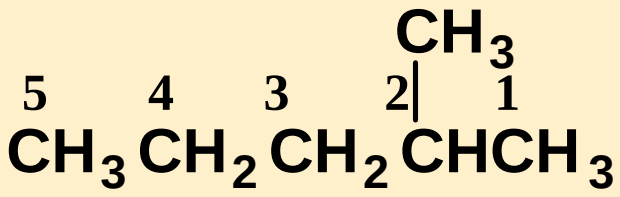
1. The general name of an open-chain saturated hydrocarbon is alkane
2. For branched-chain hydrocarbons, the alkane corresponding to the longest chain is taken as the parent chain and its name is the root name
3. Groups attached to the parent chain are called substituents. Each is given a name and a number



2-Methylpropane

2 Nomenclature

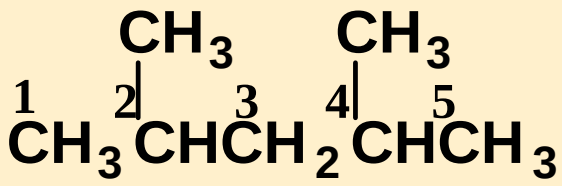
4. If there is more than one substituent, number from the end of the chain that gives the substituent encountered first the lower number



2-Methylpentane

2 Nomenclature

5. If the same substituent occurs more than once, the number of each carbon of the parent chain on which it occurs is given and the number of times it occurs is shown by di-, tri-, tetra-, etc.

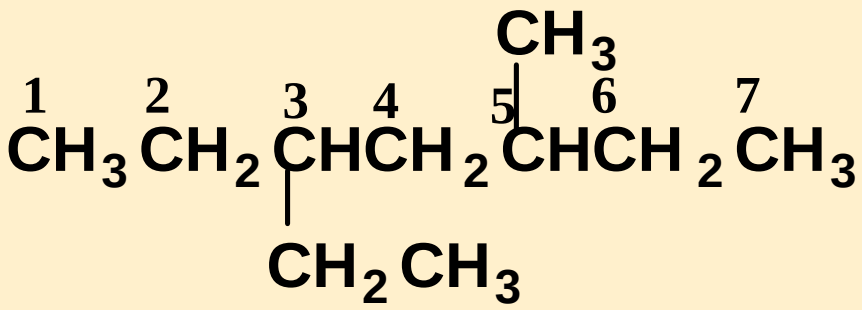


2,4-Dimethylpentane

6. If there are two identical substituents, number the chain to give the lower number to the substituent encountered first

2 Nomenclature

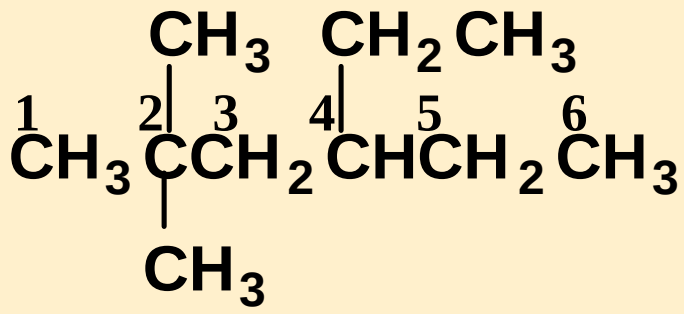
7. If there are two or more different substituents, list them in alphabetical order, and number from the end of the chain that gives the substituent encountered first the lower number



3-Ethyl-5-methylheptane

2 Nomenclature

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



4-Ethyl-2,2-dimethylhexane

9. Italicized prefixes such as *sec*- and *tert*- are not included in alphabetization.

2 Classification of C & H

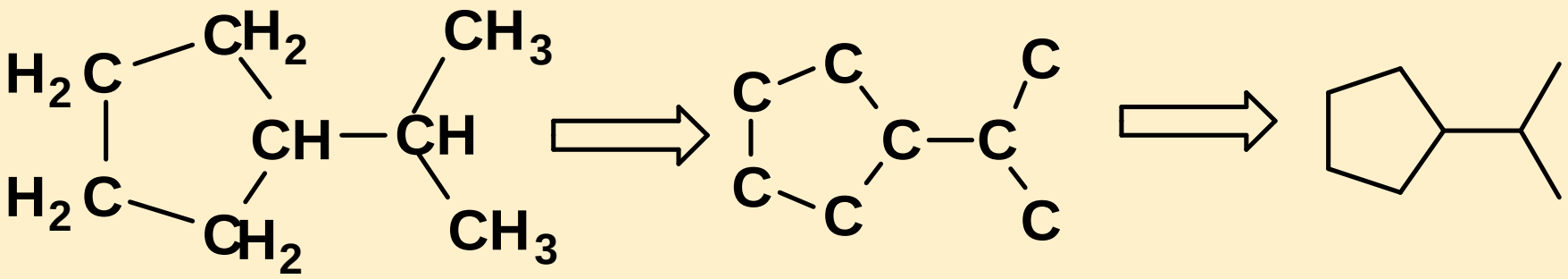
- **Primary (1°) C: a carbon bonded to one other carbon**
  - **1° H: a hydrogen bonded to a 1° carbon**
- **Secondary (2°): a carbon bonded to two other carbons**
  - **2°H: a hydrogen bonded to a 2° carbon**
- **Tertiary (3°) C: a carbon bonded to three other carbons**
  - **3° H: a hydrogen bonded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

2 Cycloalkanes

- **General formula C_nH_{2n}**
  - **ring sizes from 3 to 30 and more are known**
  - **five- and six-membered rings are the most common**
- **Structure and nomenclature**
  - **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 or more substituents, number from the substituent of lowest alphabetical order**
  - **where there is choice, number to give substituents the lowest set of numbers**

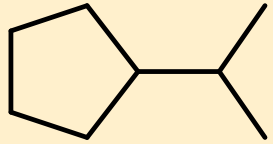
2 Cycloalkanes

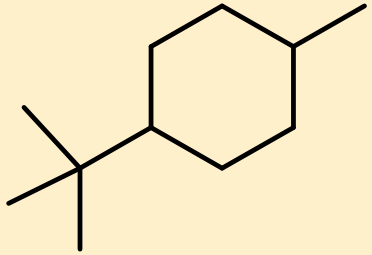
- **Line-angle drawings**
  - **each line represents a C-C bond**
  - **each angle represents a C**

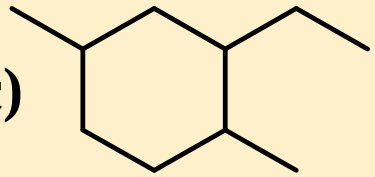


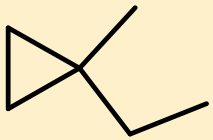
2 Cycloalkanes

- **Examples: name these cycloalkanes**

(a) 

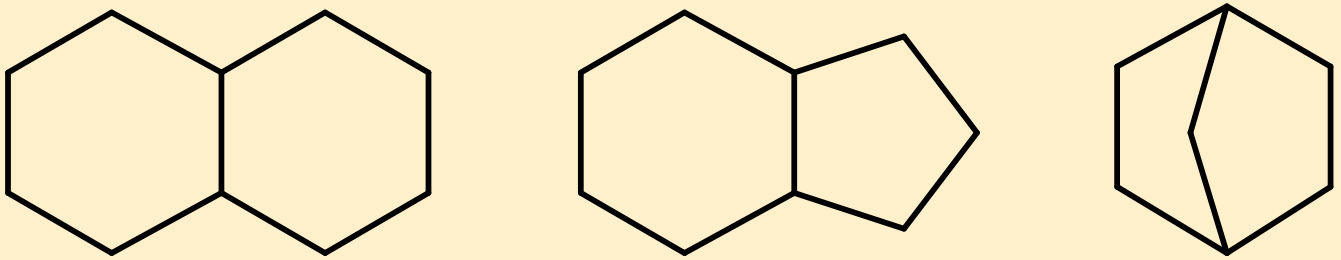
(b) 

(c) 

(d) 

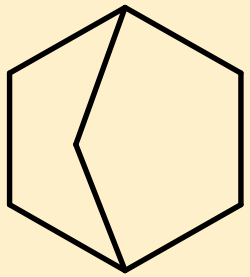
2 Bicycloalkanes

- **Bicycloalkane: an alkane that contains two rings that share two carbon atoms**



2 Bicycloalkanes

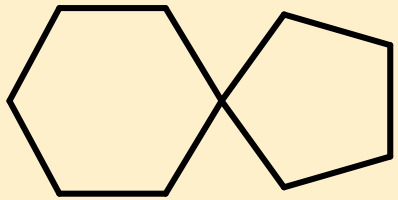
- **Nomenclature**
  - **parent is the alkane of the same number of carbons as are in two rings**
  - **number from a bridgehead, along longest bridge back to the bridgehead, then along the next longest bridge, etc.**
  - **show the lengths of bridges in brackets, from longest to shortest**



bicyclo[2.2.1]heptane

2 Spiroalkanes

- **Two rings share one carbon atom:**
- **Example: spiro[4.5]decane**



2 Spiroalkanes

- **Nomenclature**
  - **parent is the alkane of the same number of carbons as are in two rings**
  - **prefix name of the parent alkane by spiro-**
  - **number from the carbon on shorter bridge next to spiro carbon, through the spiro carbon and around the longer bridge**
  - **show the lengths of bridges in brackets, from shortest to longest**

2 IUPAC - General

- prefix-infix-suffix
- Prefix tells the number of carbon atoms in the parent
- Infix tells the nature of the carbon-carbon bonds in the parent

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

2 IUPAC - General

- The suffix tells the class of compound

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

2 IUPAC - General

prop-en-e = propene

eth-an-ol = ethanol

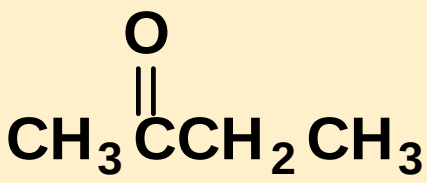
but-an-one = butanone

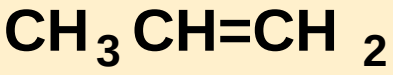
but-an-al = butanal

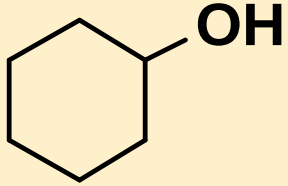
pent-an-oic acid = pentanoic acid

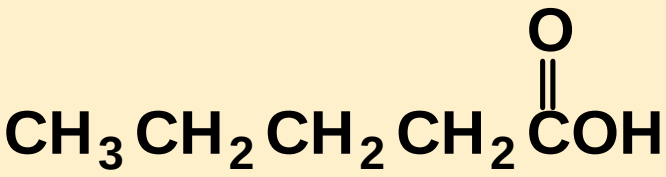
cyclohex-an-ol = cyclohexanol

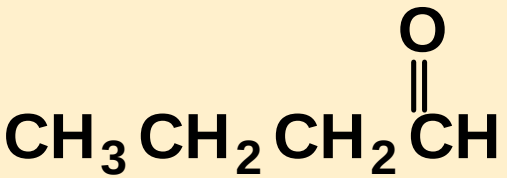
eth-yn-e = ethyne











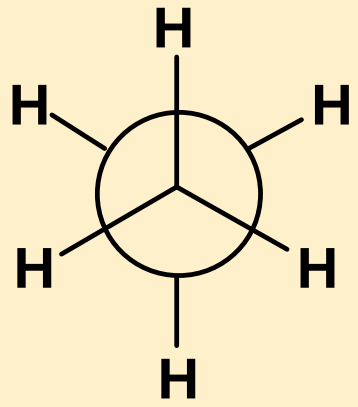
2 Conformations

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

- **Newman projection: a way to view a molecule by looking along a carbon-carbon bond**

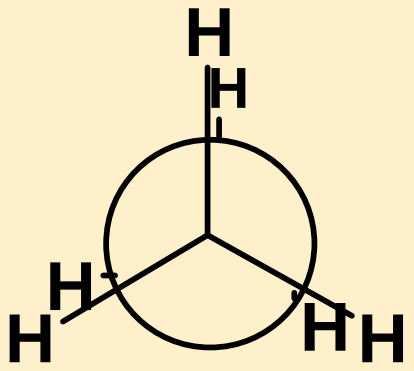
2 Conformations

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



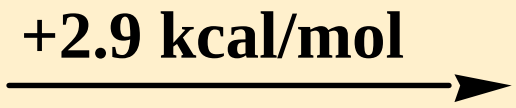
2 Conformations

- **Eclipsed conformation: a conformation about a carbon-carbon single bond where atoms on one carbon are as close as possible to the atoms on the adjacent carbon**



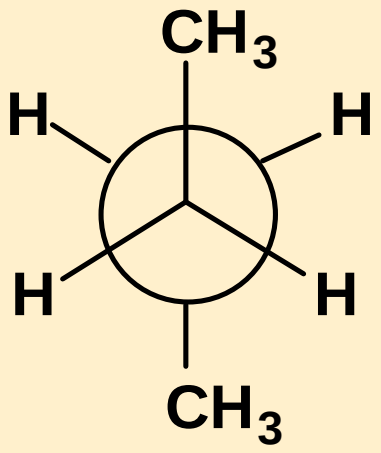
2 Conformations

- **Torsional strain:** **the force that opposes the rotation of one part of a molecule about a bond while the other part of the molecule is held fixed**
  - **the torsional strain between eclipsed and staggered ethane is approximately 2.9 kcal/mol**



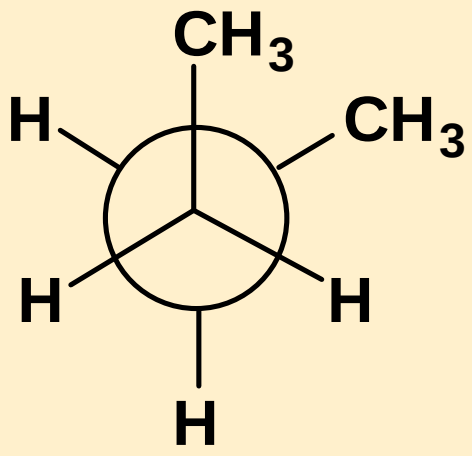
2 Conformations

- **Butane - anti**



2 Conformations

- **Nonbonded interaction strain: the stain that arises when atoms not bonded to each other are forced abnormally close to one another**
  - **butane - gauche conformation; nonbonded interaction strain is approximately 0.9 kcal/mol**



2 Conformations

- **Anti/gauche ratio for butane**

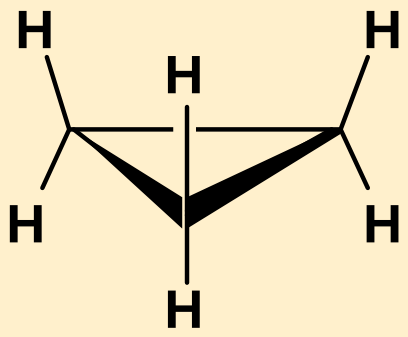
$$\Delta G^0 = -RT \ln K_{eq}$$

$$\ln K_{eq} = \frac{-(-900 \text{ cal} \cdot \text{mol}^{-1})}{(1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\ 298\text{K}} = 1.52$$

$$K_{eq} = e^{1.52} = \frac{4.57 \text{ anti conformation}}{1 \text{ gauche conformation}}$$

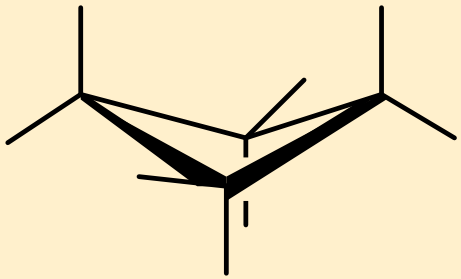
2 Cyclopropane

- **Strain energy is approx. 28 kcal/mol, due to**
  - **angle strain: the C-C-C bond angles are compressed from 109.5° to 60°**
  - **torsional strain: there are 6 sets of eclipsed hydrogen interactions**



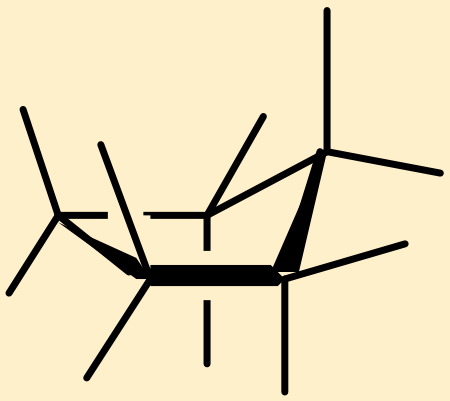
2 Cyclobutane

- **Strain energy is about 26 kcal/mol**
  - **puckering from planar cyclobutane reduces torsional strain but increases angle**
  - **the conformation of minimum potential energy is the “butterfly” conformation**



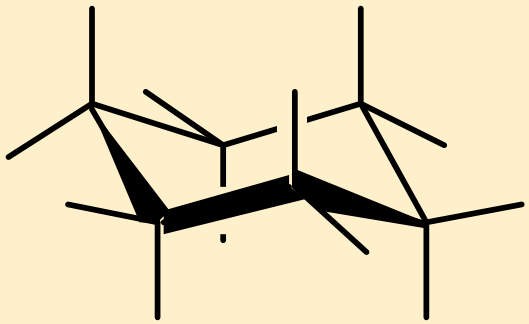
2 Cyclopentane

- **The strain energy of cyclopentane is about 6.5 kcal/mol**
  - **puckering from planar cyclopentane reduces torsional strain, but increases angle stain**
  - **the conformation of minimum PE is the “envelope” conformation**



2 Cyclohexane

- **Chair conformation: the most stable puckered conformation of a cyclohexane ring**
  - **all bond angles are approx.. 109.5°**
  - **all bonds on adjacent carbons are staggered**



2 Cyclohexane

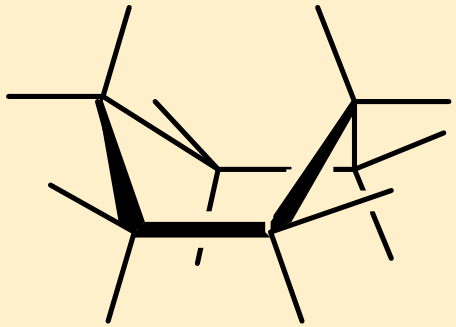
- **In a chair conformation, six H are equatorial and six are axial**

2 Cyclohexane

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

2 Cyclohexane

- **Boat conformation: a puckered conformation of a cyclohexane ring in which carbons 1 and 4 are bent toward each other**
  - **less stable than the chair conformation by +6.5kcal/mol**

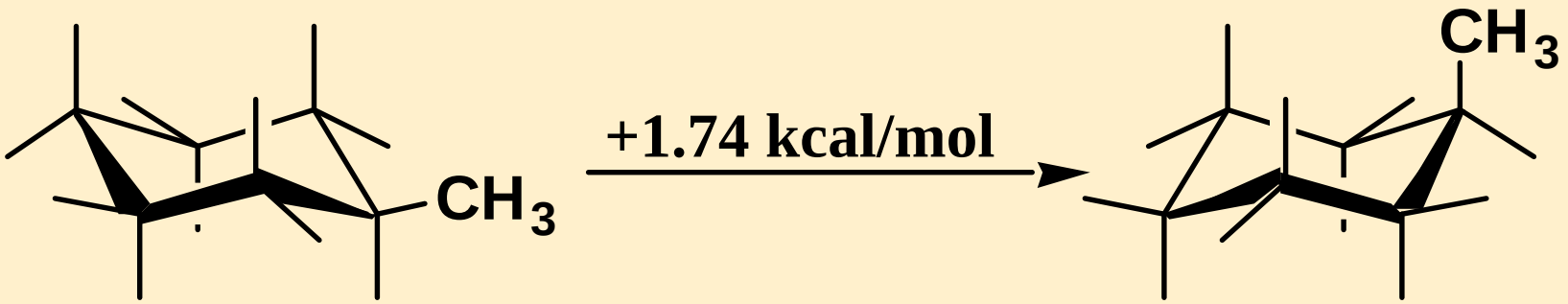


2 Cyclohexane

- **Twist-boat conformation; approx. 5.5 kcal/mol less stable than the chair conformation**

2 Methylcyclohexane

- Equatorial and axial methyl conformations



2 ΔG° axial ---> equatorial

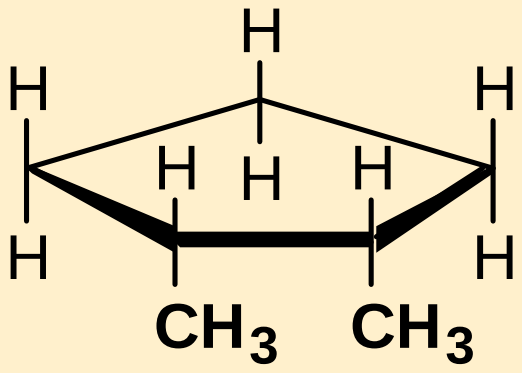
Group	–ΔG° (kcal/mol)	Group	–ΔG° (kcal/mol)
C≡N	0.20	NH_2	1.4
F	0.25	CO_2H	1.41
C≡CH	0.41	$CH{=}CH_2$	1.7
I	0.46	CH_3	1.74
Cl	0.52	CH_2CH_3	1.75
Br	0.55	$CH(CH_3)_2$	2.15
OH	0.95	$C(CH_3)_3$	4.9

2 *Cis-trans* isomerism

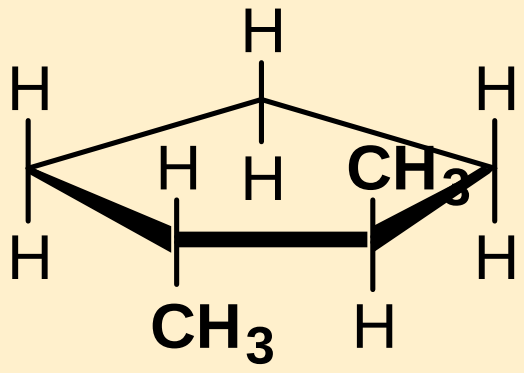
- **Cis-trans isomers have:**
  - **the same molecular formula**
  - **the same connectivity**
  - **an arrangement of atoms in space that cannot be interconverted by rotation about single bonds under ordinary conditions**

2 *Cis-trans* isomerism

- **1,2-dimethylcyclopentane**



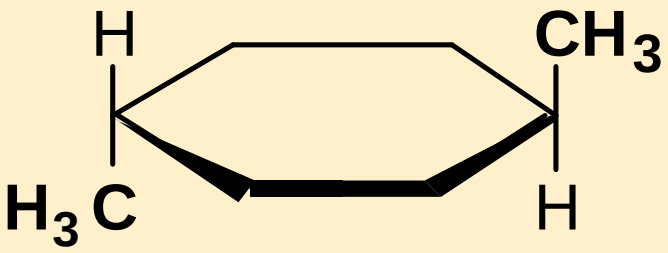
cis-1,2-Dimethyl-cyclopentane



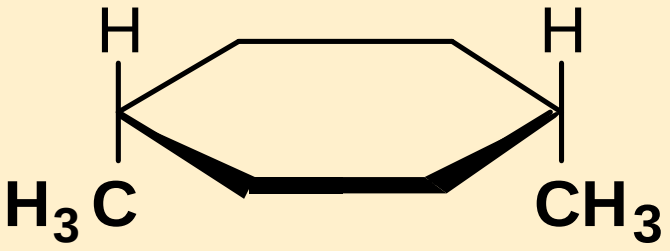
trans-1,2-Dimethyl-cyclopentane

2 *Cis-trans* isomerism

- 1,4-Dimethylcyclohexane
  - planar hexagon representations



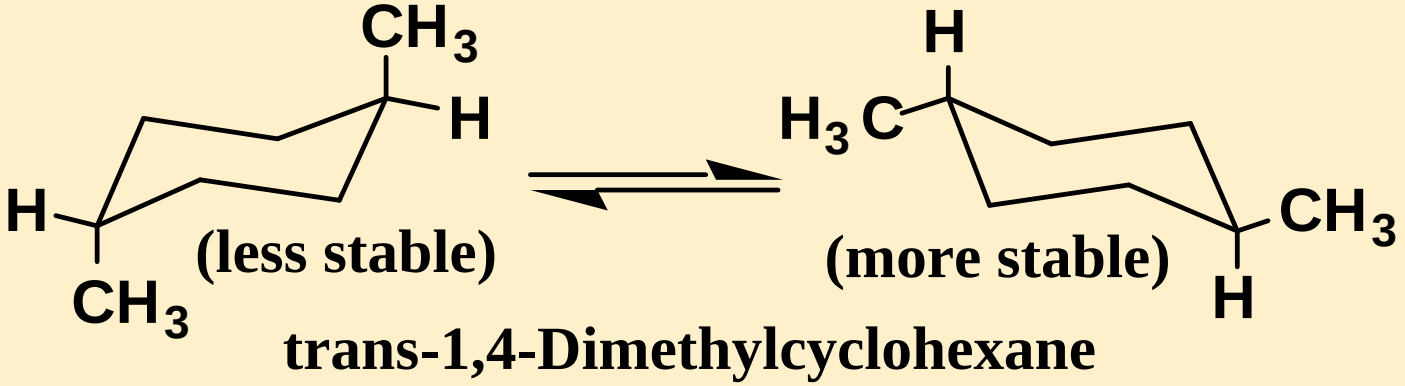
trans-1,4-Dimethyl-cyclohexane



cis-1,4-Dimethyl-cyclohexane

2 *Cis-trans* isomerism

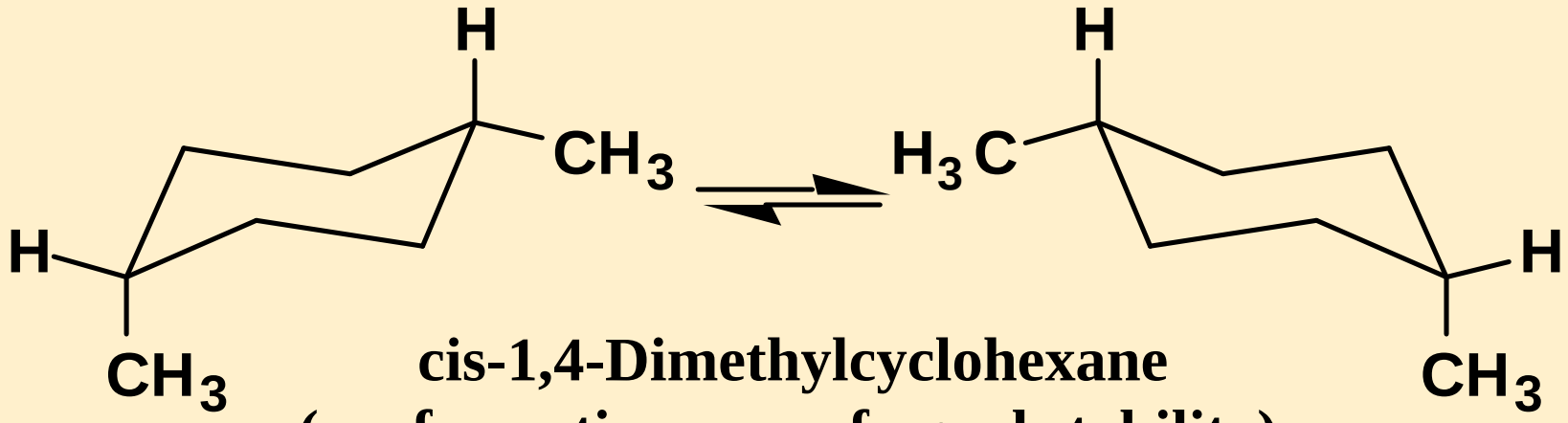
- ***trans*-1,4-dimethylcyclohexane**
  - **the diequatorial-methyl chair conformation is more stable by approximately 2 x (-1.74) = -3.48 kcal/mol**



trans-1,4-Dimethylcyclohexane

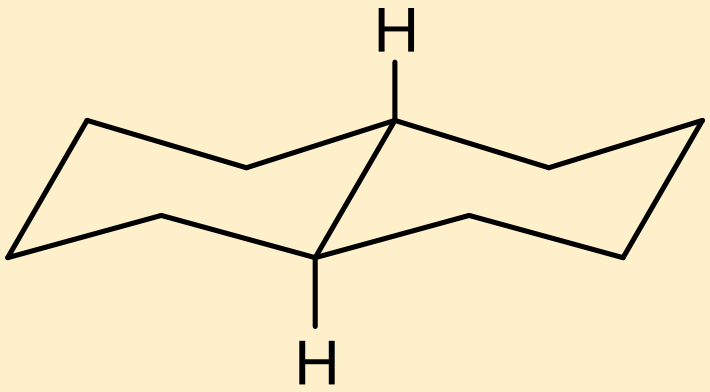
2 *Cis-trans* isomerism

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



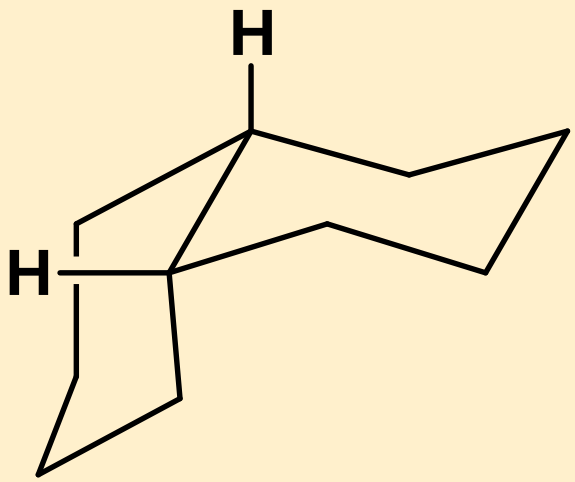
cis-1,4-Dimethylcyclohexane
(conformations are of equal stability)

2 *Cis-trans* isomerism



trans-decalin

2 *Cis-trans* isomerism



cis-decalin

2 Physical Properties

- **Intermolecular forces of attraction**
  - **ion-ion (Na^+ and Cl^- in NaCl)**
  - **ion-dipole (Na^+ and Cl^- solvated in aqueous solution)**
  - **dipole-dipole (hydrogen bonding between water molecules)**
  - **dispersion forces (electrostatic attraction between temporary dipoles)**

2 Physical properties

- **Low-molecular-weight alkanes (methane....butane) are gases at room temperature**
- **Higher-molecular weight alkanes (pentane, decane, gasoline, kerosene) are liquids at room temperature**
- **High-molecular weight alkanes (paraffin wax) are semisolids or solids at room temperature**

2 Physical properties

- 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

2 Sources of alkanes

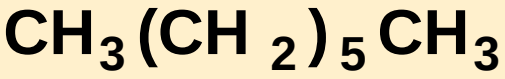
- **Natural gas 90-95% methane**

- **Petroleum**
  - **gases**
  - **gasoline, kerosene**
  - **fuel oil**
  - **lubricating oils**
  - **asphalt**

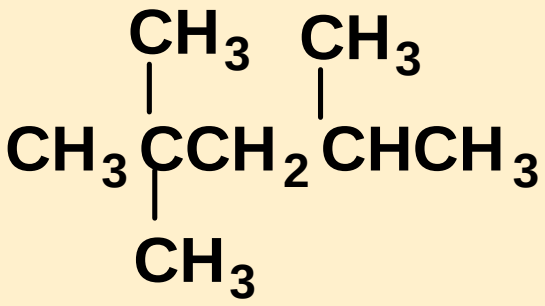
- **Coal**

2 Gasoline

- **Octane rating: the percent 2,2,4-trimethylpentane (isooctane) in a mixture of isooctane and heptane that has equivalent antiknock properties**



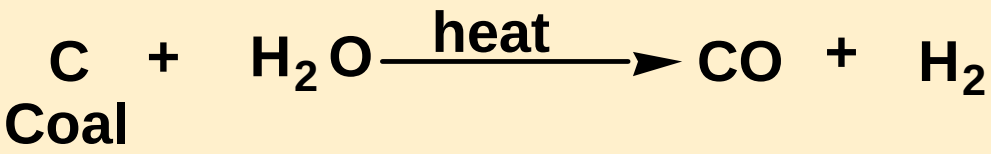
Heptane
(octane rating 0)

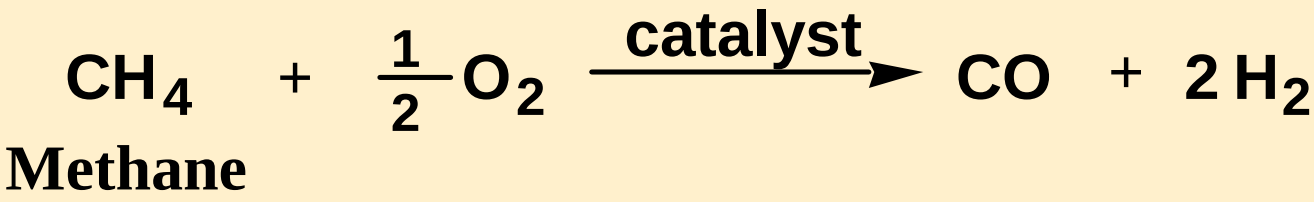


2,2,4-Trimethylpentane
(octane rating 100)

2 Synthesis gas

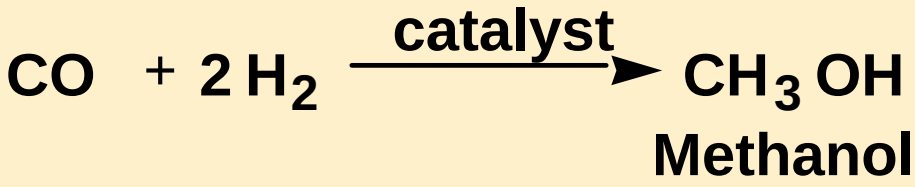
- A mixture of carbon monoxide and hydrogen in varying proportions which depend on the means by which it is produced

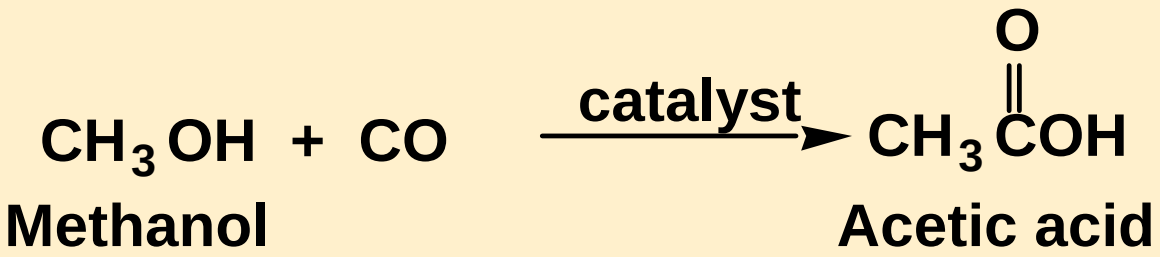




2 Synthesis gas

- Synthesis gas is a feedstock for the industrial production of methanol and acetic acid





  - It is likely that industrial routes to other organic chemicals from coal via methanol will also be developed

2 Oxidation of alkanes

- Oxidation is the basis for their use as energy sources for
  - heat: natural gas, liquefied petroleum gas (LPG), and fuel oil
  - power: gasoline, and diesel and aviation fuel

$\Delta H°$ (kcal/mol)

$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$ -212

Methane

$CH_3CH_2CH_3 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$ -530

Propane

2

Alkanes and Cycloalkanes

End Chapter 2