Alkanes

Chapters 3, 4, 10.2, 10.4
Organic Chemistry, 8th Edition
John E. McMurry

Hydrocarbons

- **Aliphatic** (Αλειφαρ = Ointment).
  - Alkanes (saturated hydrocarbons): hydrocarbons having only single C−C and C−H bonds.
    - Linear (*normal* alkanes, *n*-alkanes)
    - Branched
    - Cyclic
  - Alkenes (olefins): hydrocarbons having double bonds.
  - Alkynes: hydrocarbons having triple bonds.

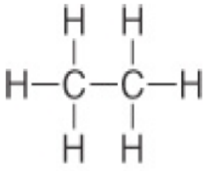
- **Aromatic**

Alkanes

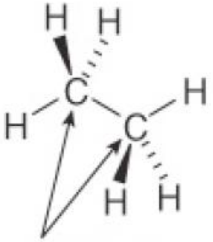
Numberof C-atoms	Molecular formula	Name (*n*-alkane)	
1	CH_4	methane	metano
2	C_2H_6	ethane	etano
3	C_3H_8	propane	propano
4	C_4H_{10}	butane	butano
5	C_5H_{12}	pentane	pentano
6	C_6H_{14}	hexane	esano
7	C_7H_{16}	heptane	eptano
8	C_8H_{18}	octane	ottano
9	C_9H_{20}	nonane	nonano
10	$C_{10}H_{22}$	decane	decano
20	$C_{20}H_{42}$	eicosane	eicosano

Empirical formula: C_nH_{2n+2}

Ethane and Propane

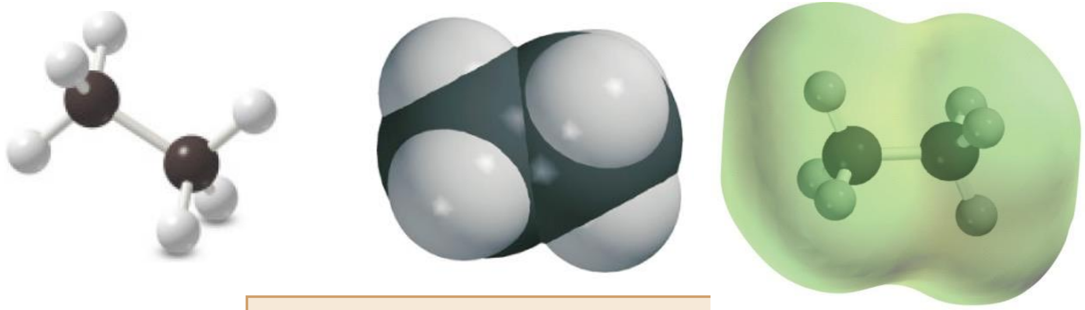


ethane

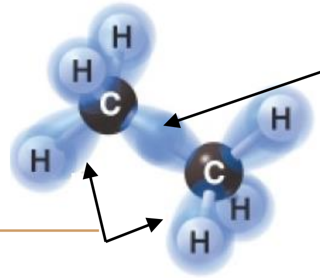


tetrahedral sp^3 C

=

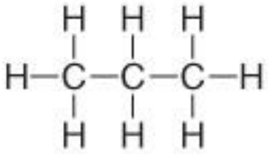


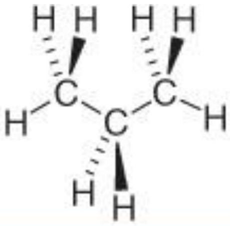
Two sp^3 hybrids overlap giving the C–C σ bond



sp^3 hybrids on C overlap with *1s* orbitals on H giving the C-H σ bonds.

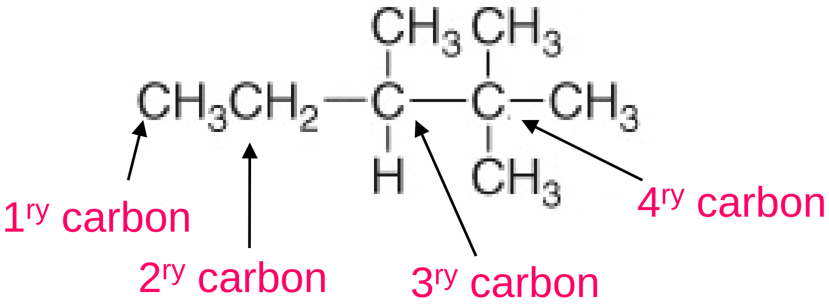
$CH_3CH_2CH_3$ propane =





Lewis structure **3-D representation** **ball-and-stick model**

Examples



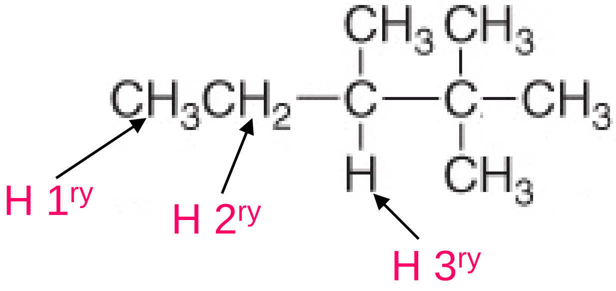
$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

1^{ry} carbon

2^{ry} carbon

3^{ry} carbon

4^{ry} carbon

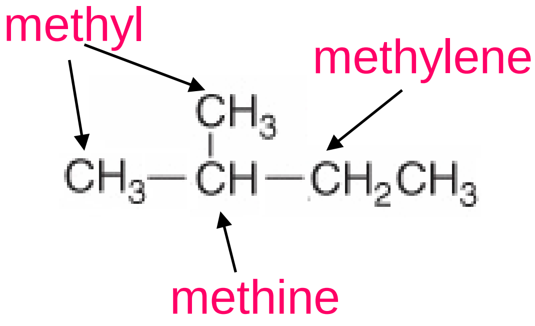


$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

H 1^{ry}

H 2^{ry}

H 3^{ry}



$CH_3-\overset{CH_3}{CH}-CH_2CH_3$

methyl

methylene

methine

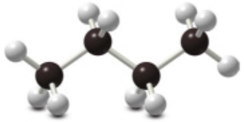
Alkanes – Structural Isomerism

- There are two hydrocarbons with empirical formula C_4H_{10}: butane and isobutane.
- Butane and isobutane are structural (constitutional) isomers: they have the same composition but different physico-chemical properties.

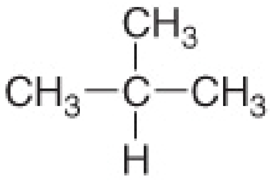
*

$CH_3CH_2CH_2CH_3$

butane

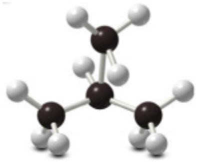


Linear Alkane



$$CH_3-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

isobutane

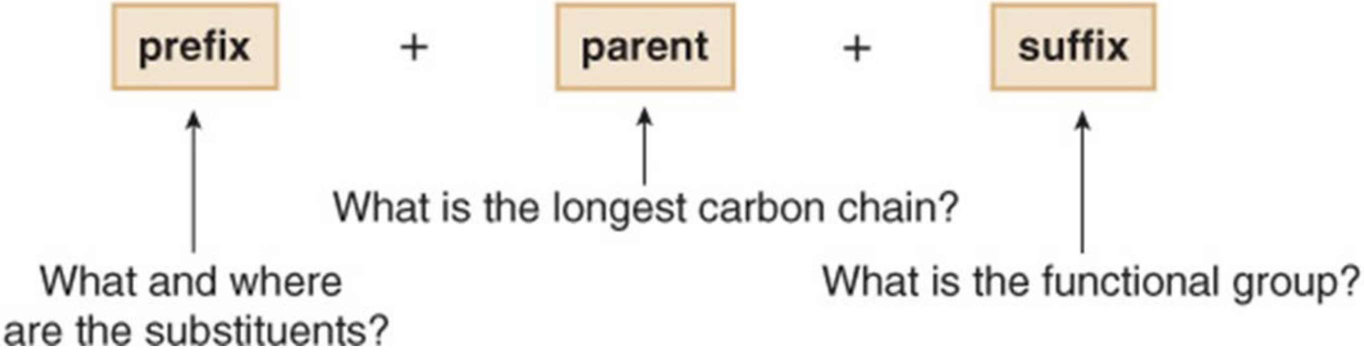


Branched Alkane

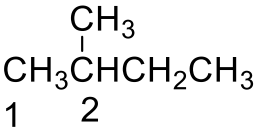
IUPAC Nomenclature

International Union of Pure and Applied Chemistry

1. **Identify the longest hydrocarbon chain**
2. **Name the substituents in alphabetical order**
3. **Assign the substituent position the lowest number**



Alkane Nomenclature

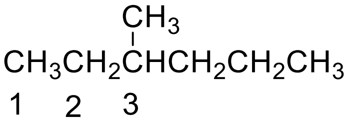


$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

1 2

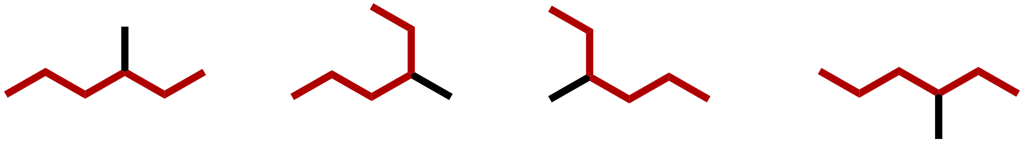
2-methylbutane

CH_3- methyl

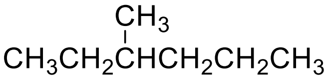


$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2CH_3$$

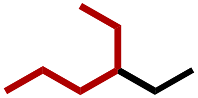
1 2 3



3-methylhexane



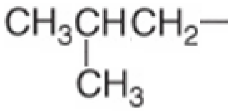
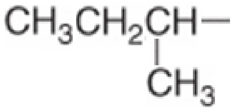
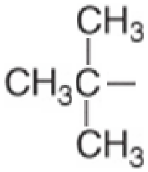
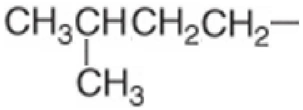
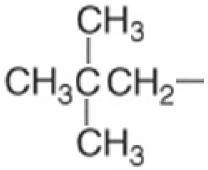
$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2CH_3$$



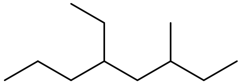
3-ethylhexane

CH_3CH_2- ethyl

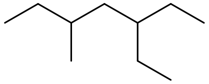
Alkyl Groups

C-Atoms	Structure	Name
1	CH_3-	**methyl**
	$-CH_2-$	**methylene**
	 $-\overset{\vert}{C}H-$	**methine**
2	CH_3CH_2-	**ethyl**
3	$CH_3CH_2CH_2-$	***n*-propyl**
	 $CH_3\underset{\vert}{C}HCH_3$	**isopropyl**
4	$CH_3CH_2CH_2CH_2-$	***n*-butyl**
	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2-$	**isobutyl**
	 $CH_3CH_2\underset{\underset{CH_3}{\vert}}{C}H-$	***sec*-butyl**
	 $CH_3\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-$	***tert*-butyl**
5	$CH_3CH_2CH_2CH_2CH_2-$	***n*-pentyl**
	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_2-$	**isopentyl**
	 $CH_3\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}CH_2-$	**neopentyl**

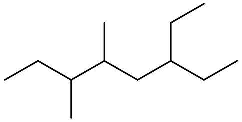
Alkane Nomenclature



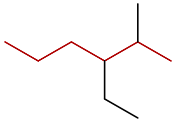
5-ethyl-3-methyloctane



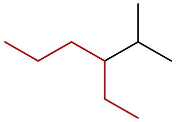
3-ethyl-5-methylheptane



6-ethyl-3,4-dimethyloctane

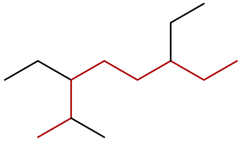


3-ethyl-2-methylhexane



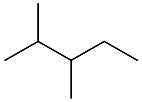
3-isopropylhexane

WRONG

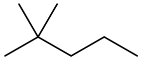


3,6-diethyl-2-methyloctane

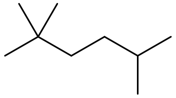
not: 3-ethyl-6-isopropyloctane



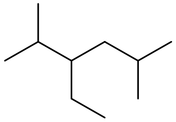
2,3-dimethylpentane



2,2-dimethylpentane

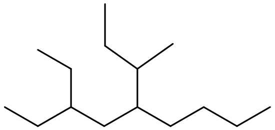


2,2,5-trimethylhexane

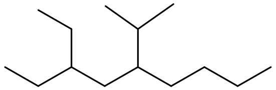


3-ethyl-2,5-dimethylhexane

di-
tri-
tetra-
penta-
hexa-



5-sec-butyl-3-ethylnonane

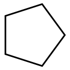


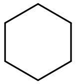
3-ethyl-5-isopropylnonane

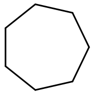
Cycloalkane Nomenclature

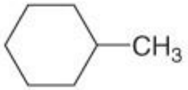

cyclopropane


cyclobutane

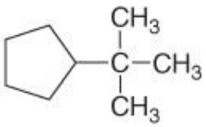

cyclopentane


cyclohexane

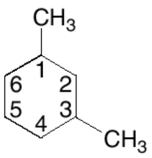

cycloheptane



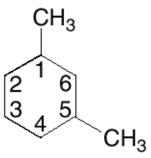
methylcyclohexane



tert-butylcyclopentane

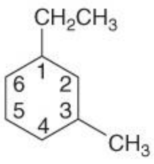


1,3-dimethylcyclohexane

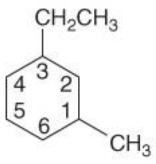


WRONG

1,5-dimethylcyclohexane



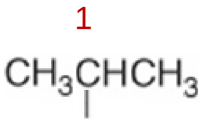
1-ethyl-3-methylcyclohexane



WRONG

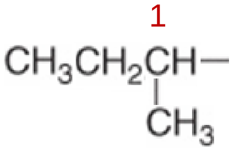
3-ethyl-1-methylcyclohexane

IUPAC Nomenclature for Alkyl Groups



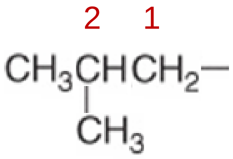
$CH_3\underset{|}{C}HCH_3$

1-methylethyl



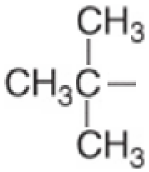
$CH_3CH_2\underset{\underset{CH_3}{|}}{C}H-$

1-methylpropyl



$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2-$

2-methylpropyl



$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$

1,1-dimethylethyl

Regole di nomenclatura IUPAC degli alcani

- Identificare la catena principale
- Identificare i sostituenti e dare loro il nome
- Assegnare un numero a ciascun sostituente

Per assemblare il nome:

- Nominare i sostituenti in ordine alfabetico.
- I prefissi ter-, sec- e quelli moltiplicativi di-, tri- etc vengono ignorati per l’ordine alfabetico
- ISO in isopropile e isobutile non viene ignorato nell’ordine alfabetico
- Far precedere al nome di ogni sostituente il numero che indica la sua posizione.
- Numeri sono separati fra loro da una virgola.
- Numero e nome sono separati da un trattino.
- Il nome dell’ alcano è una parola unica.

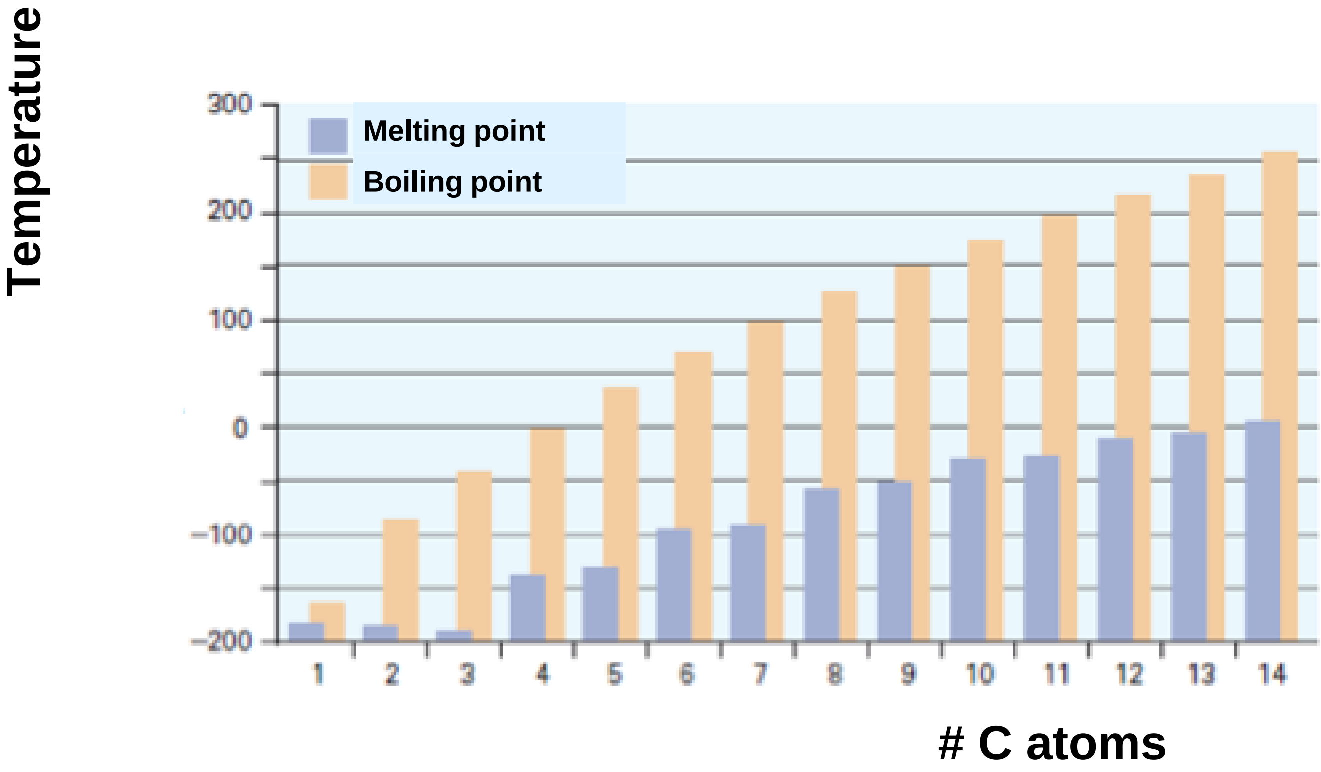
Physical Properties

Physical state:	C1-C4	gas /b.p.	-160°-0°
	C5-C17	liq./m.p.	-130°-20°
	>C17	solid	

Solubility**:** soluble in organic solvents (apolar)

insoluble in water

Physical Properties



Natural Sources

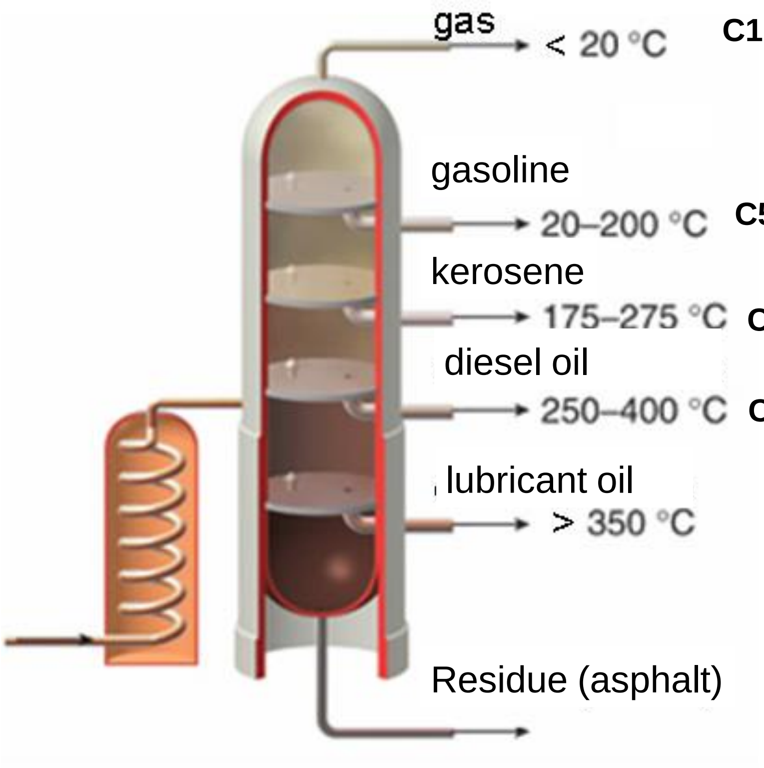
Natural sources of alkanes are natural gas and oil.

Natural gas contains mainly methane: minor components are ethane, propane and butane.

Oil is a complex mixture of, mainly, C_1-C_{40} hydrocarbons. Distillation of crude oil (refining) separates oil in fractions with different boiling point. The main fractions are:
gasoline: C_5H_{12} – $C_{12}H_{26}$
kerosene: $C_{12}H_{26}$ – $C_{16}H_{34}$
diesel oil: $C_{15}H_{32}$ – $C_{18}H_{38}$

Refining

- In the refining process, crude oil is heated and the volatile fractions distill first, followed by fractions with higher boiling points.



gas < 20 °C C1-C4

gasoline 20–200 °C C5-C10

kerosene 175–275 °C C10-C18

diesel oil 250–400 °C C18-C25

lubricant oil > 350 °C

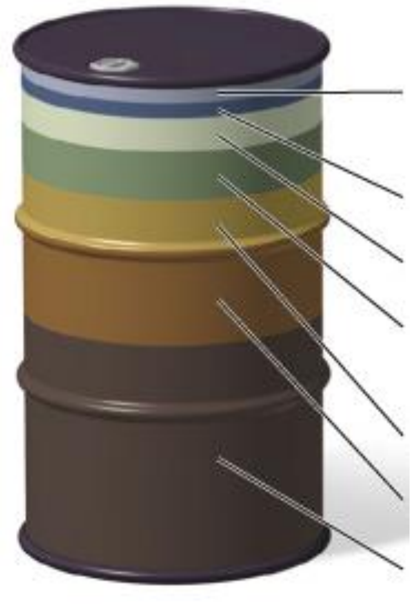
Pre-heated crude oil and gases

Residue (asphalt)

Industrial Treatments of Refined Oil

- Cracking (kerosene, diesel oil)
  - Converts high MW hydrocarbons in lower MW hydrocarbons (hydrocracking).
  - Converts alkanes in alkenes (intermediates for the fine chemical industry).
- Reforming
  - Increases branching
  - Converts aliphatic hydrocarbons into aromatics (branched and aromatic hydrocarbons are better fuels for combustion engines).

Crude Oil



fine chemicals and plastics	1.25 gal	3%
asphalt	1,3 gal	3%
coolants	2,9 gal	7%
lubrificants, waxes, solvents	4,2 gal	10%
kerosene (aeroplanes)	4,2 gal	10%
diesel and fuel oil	8,4 gal	20%
gasoline	19,7 gal	47%

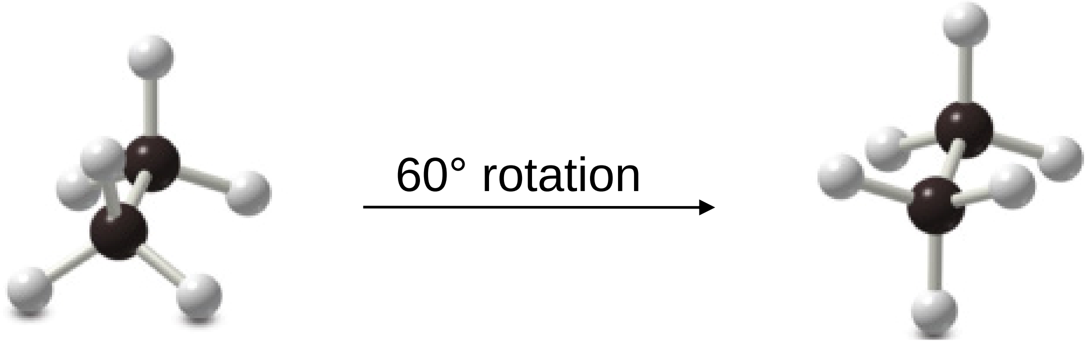
Barrel
42 gal
159 l

1 US gal = 3.78 l

Conformations

Conformations: tridimentional arrangements of atoms (groups) of a molecule differing by rotations around single bonds.

Ethane



eclipsed

(eclissata)

staggered

(sfalsata)

- In the eclipsed conformation, all C−H bonds are aligned.
- In the staggered conformation, C−H bonds on each carbon bisect the H−C−H angles on the other carbon.

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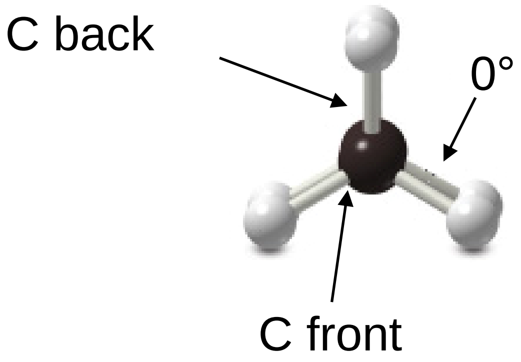
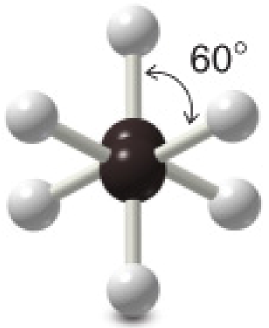
Ethane Conformations

- The H−C−C−H angle is called dihedral angle (0° in the eclipsed and 60° in the staggered conformation).

View along the C–C bond



60° rotation



Eclipsed conformation

Staggered conformation

The front C-H bonds bisect the H−C−H angles on the carbon atom at the back

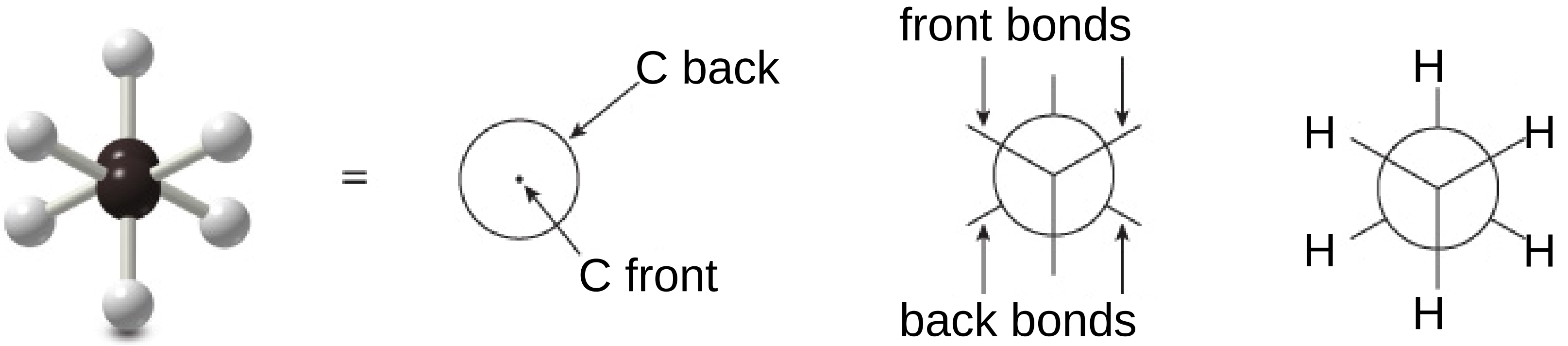
Newman Projection

- How to draw a Newman projection

[1] Look along the C-C bond and draw a circle (the back C atom) with a dot in the centre (the front C atom).

[2] Draw the bonds

[3] Add the atoms

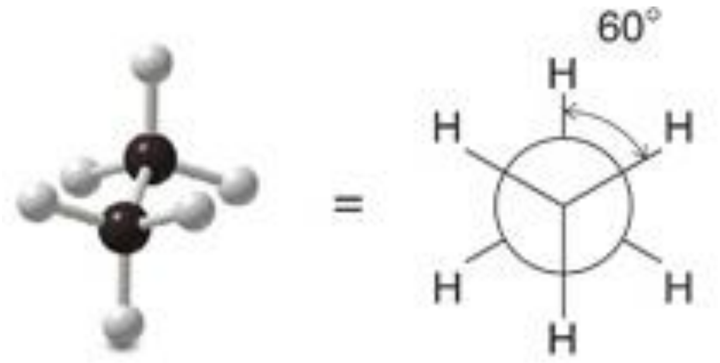


Newman Projections of Ethane

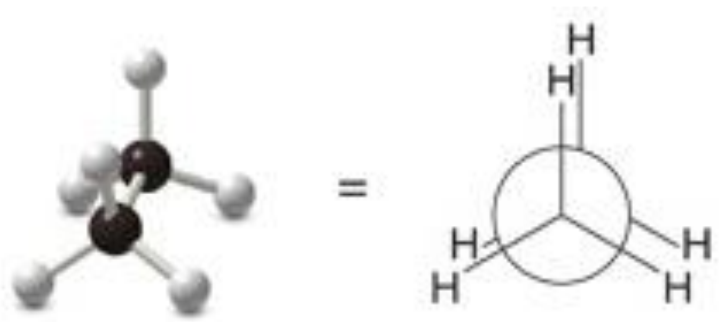
staggered conformation

eclipsed conformation

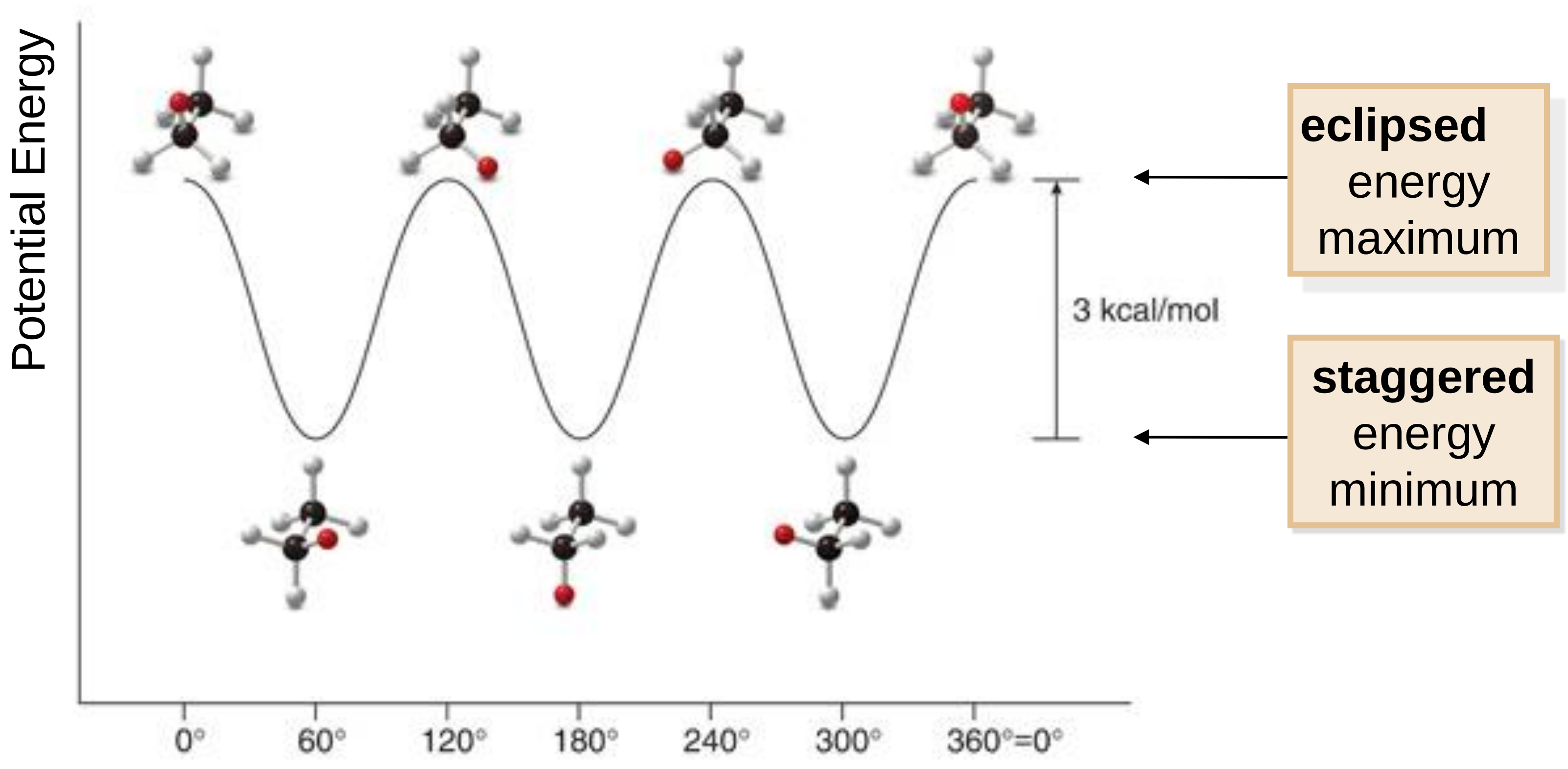
dihedral angle



Dihedral angle 0°



Conformations of Ethane



eclipsed
energy
maximum

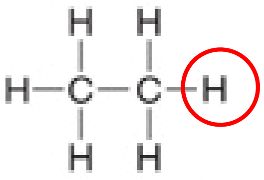
staggered
energy
minimum

Torsional Strain is 3.0 kcal/mole

modelli 3D

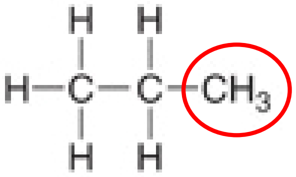
video

Conformations of Propane



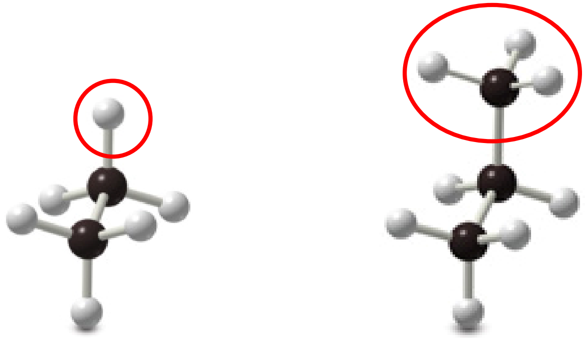
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

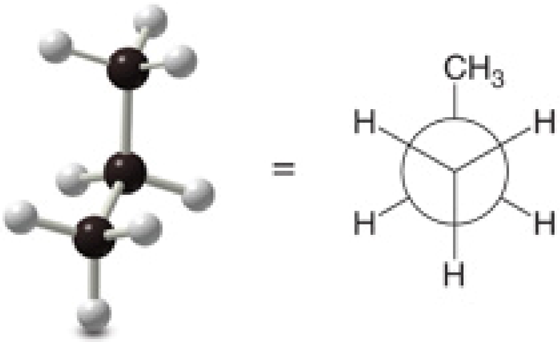
ethane

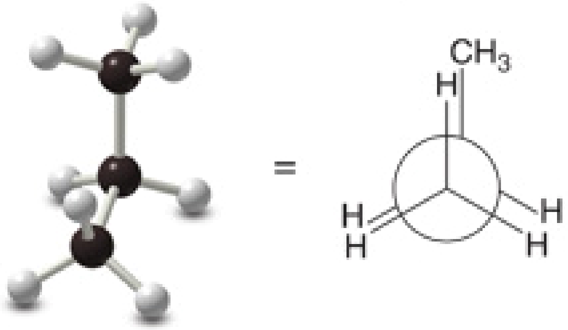


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & CH_3 \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

propane



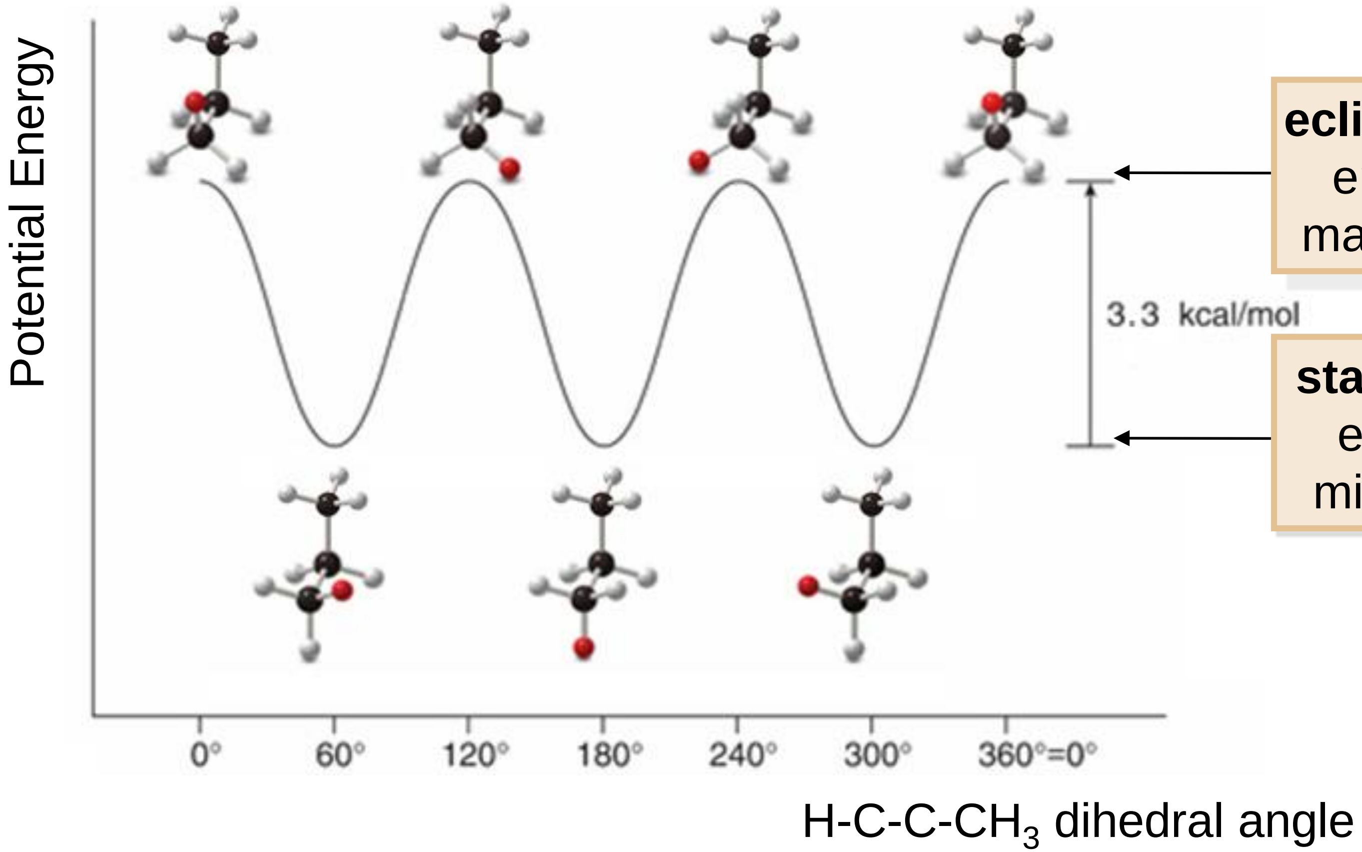




staggered conformation

eclipsed conformation

Conformations of Propane

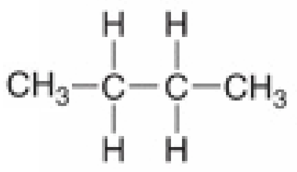


eclipsed energy maximum

staggered energy minimum

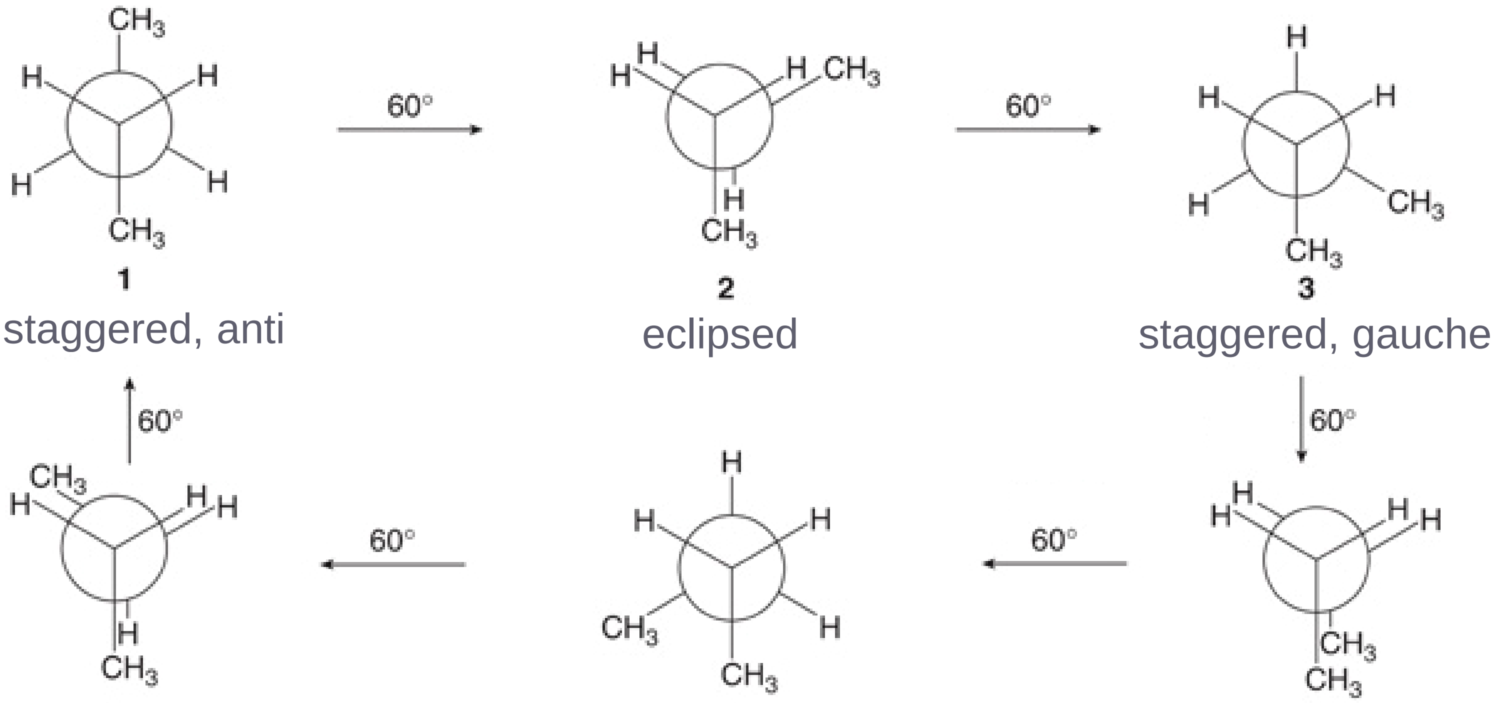
Torsional Strain (3.3 kcal/mole) is higher than in ethane. The methyl group is bulkier than a hydrogen atom

Conformations of Butane



$$CH_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CH_3$$

6 different conformations



1 staggered, anti

2 eclipsed

3 staggered, gauche

4 eclipsed, syn

5 staggered, gauche

6 eclipsed

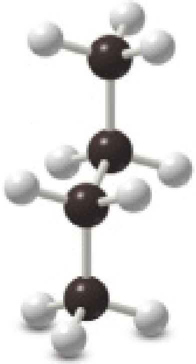
Conformations of Butane

A staggered conformation with two large groups at 180° is called *anti*

A staggered conformation with two large groups at 60° is called *gauche*.

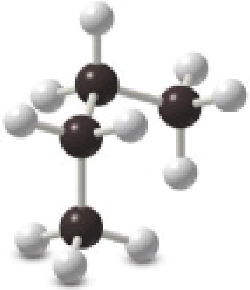
Staggered, anti

The CH_3 are at 180°



1

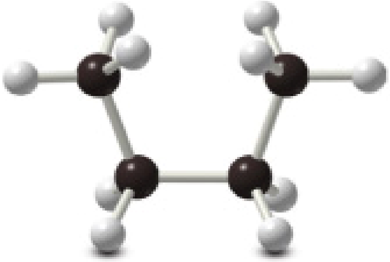
Staggered, gauche



3

The CH_3 are at 60°
steric strain

Eclipsed conformation

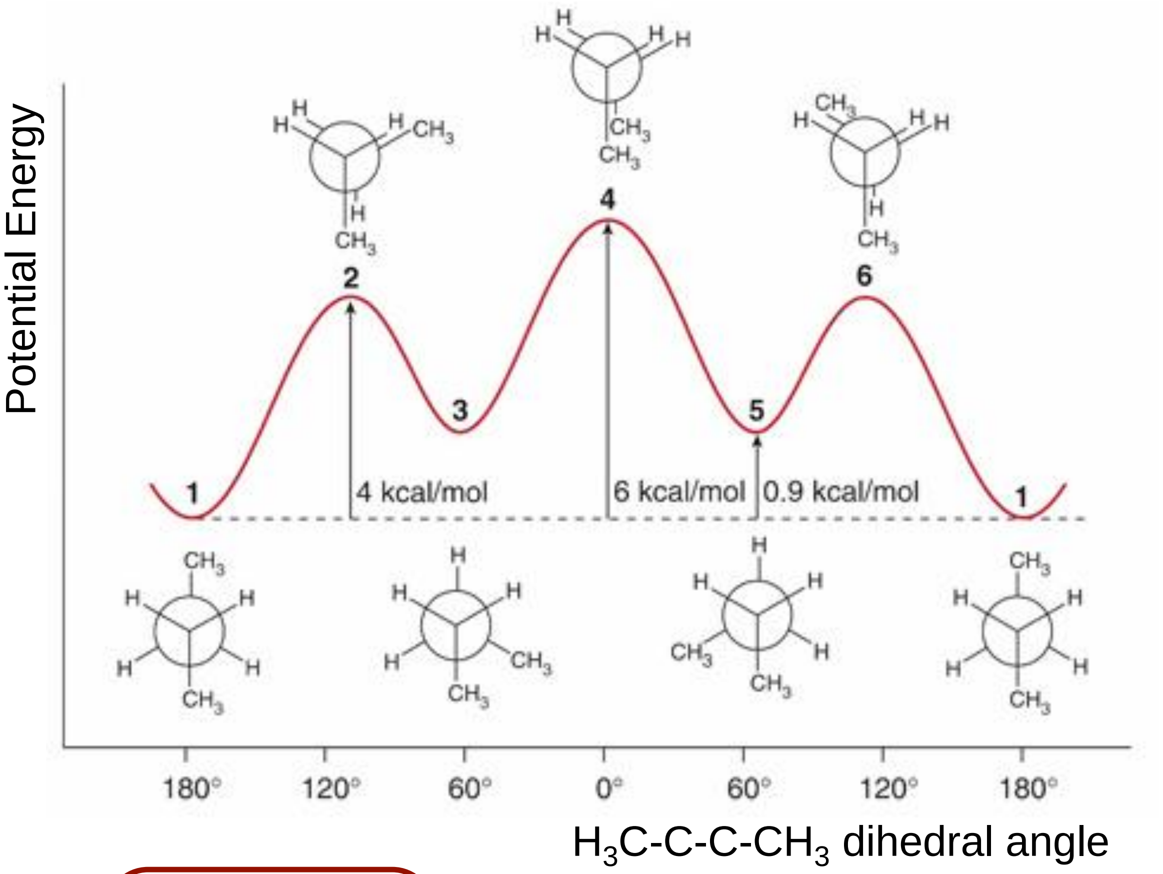


4

The CH_3 are at 0°
steric strain

Conformations of Butane

- *Staggered conformations*:
  - **1** (anti) is the absolute minimum
  - **3,5** (gauche) are relative minima
- *Eclipsed conformations:*
  - **4** is the absolute maximum (CH_3 eclipsed)
  - **2,6** are relative maxima



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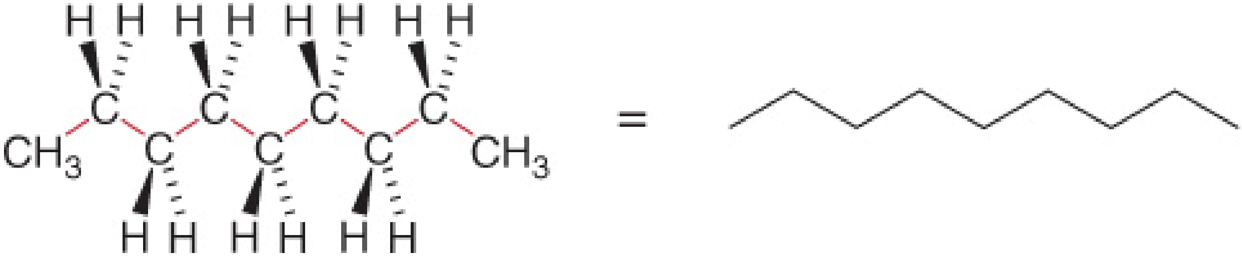
video

Torsional Strain in Linear Alkanes

Interaction	Energy (kcal/mole)
Eclipsing H,H	1
Eclipsing H,CH_3	1.5
Eclipsing CH_3,CH_3	4
Gauche CH_3,CH_3	0.9

- A rotational barrier is the energy difference between two minima.
- The most stable conformation of linear hydrocarbons is staggered with the bulky groups in anti. Thus long chains are usually drawn with a zigzag.



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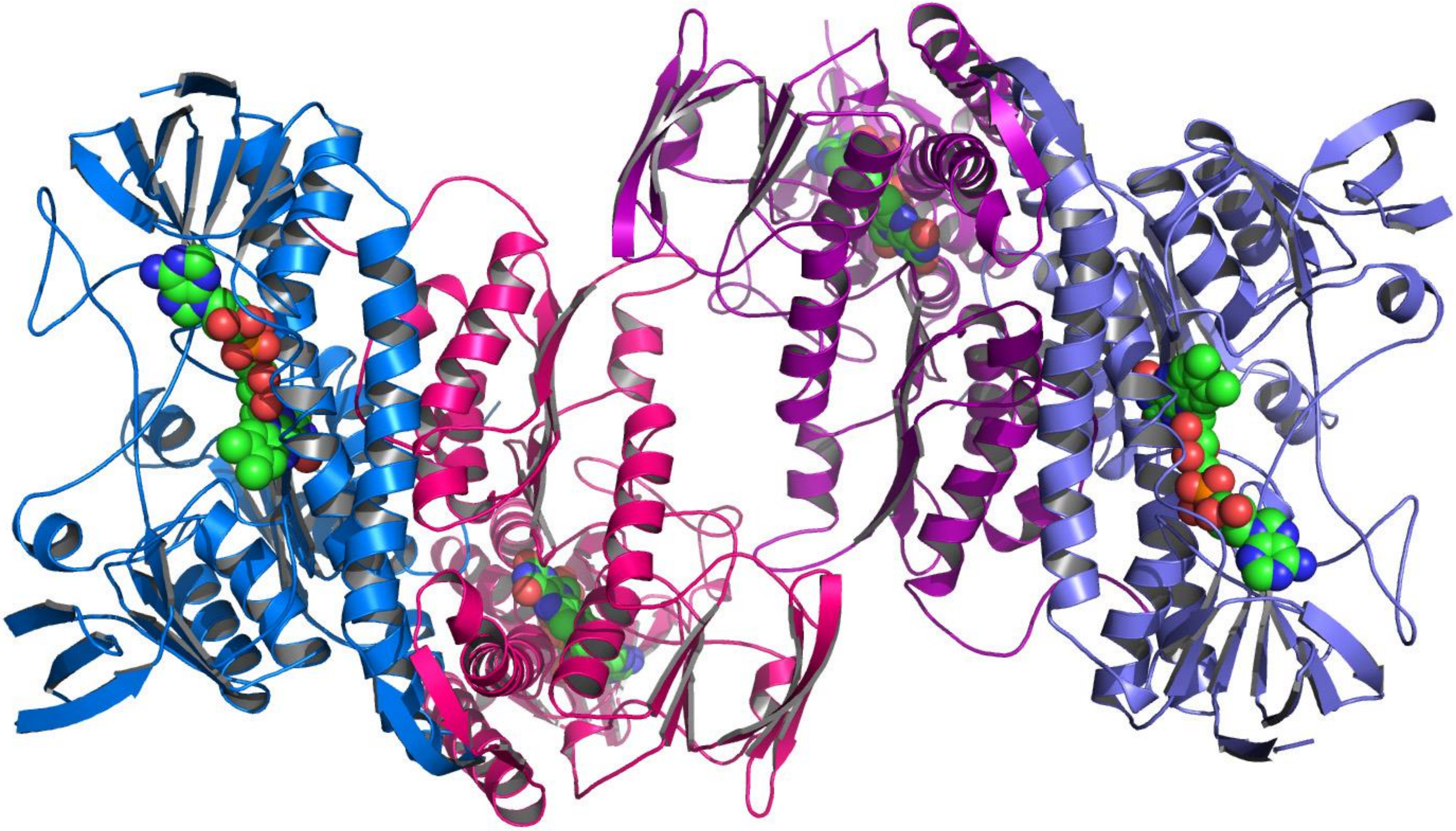
Conformations in complex molecules

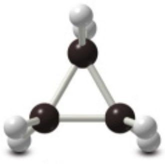


Cycloalkanes

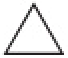
Cycloalkanes

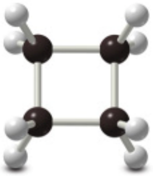
- Cycloalkanes have empirical formula $\mathbf{C_nH_{2n}}$ and contain carbon atoms arranged in a cyclic chain

- Nomenclature: cyclo + name of the corresponding alkane

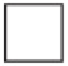


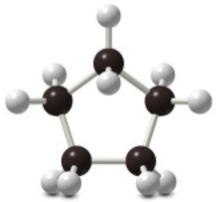
cyclopropane
C_3H_6



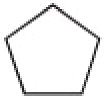


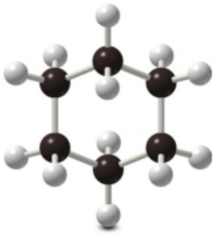
cyclobutane
C_4H_8



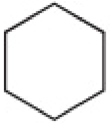


cyclopentane
C_5H_{10}





cyclohexane
C_6H_{12}



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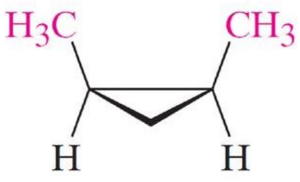
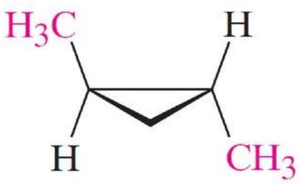
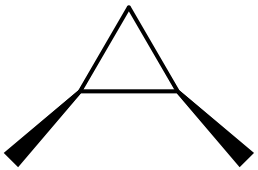
Stereoisomers

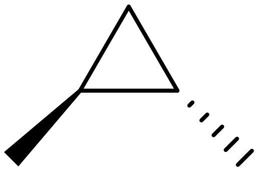




cis-1,3-dimethylcyclopropane

trans-1,3-dimethylcyclopropane

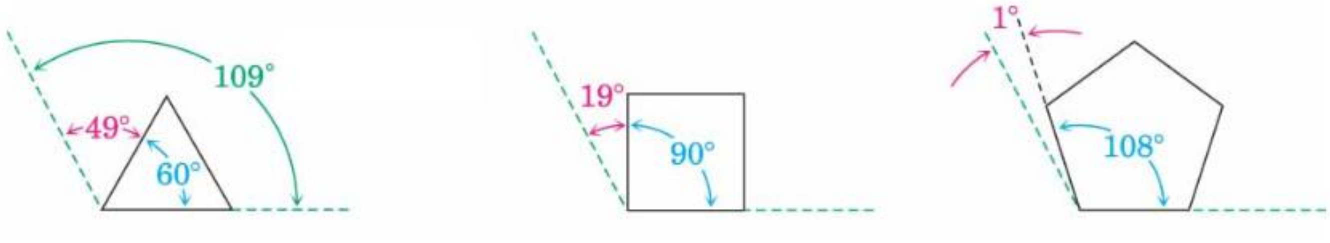




Stereoisomers: same constitution, different 3D structure

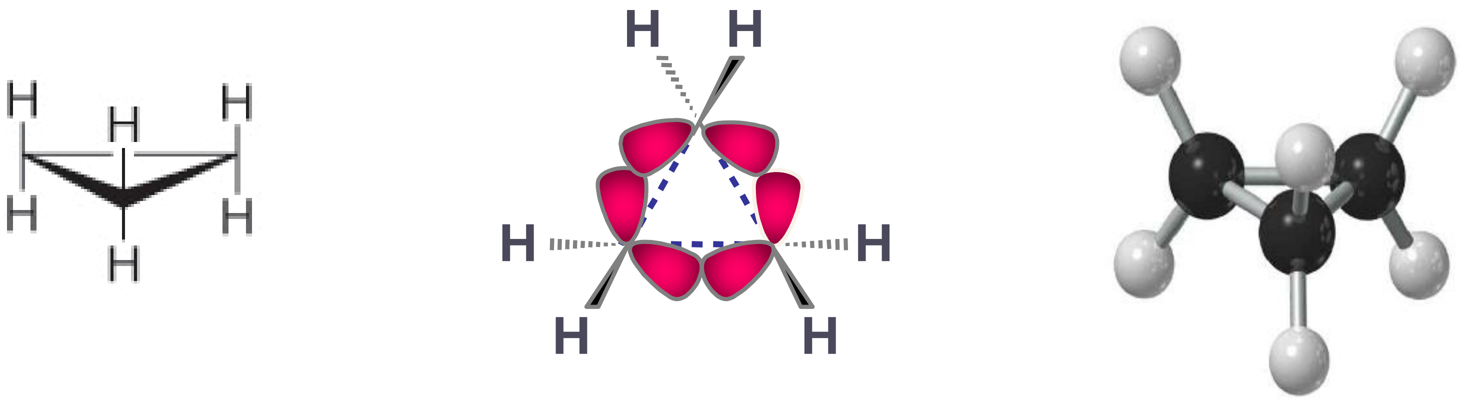
Stability: Angular Strain (Baeyer's Strain)

- Baeyer (1885): as carbon prefers 109° bond angles, rings other than five or six membered may be too strained to exist.
- Cycloalkanes from C_3 to C_{30} do exist, but some of them are strained because of distorted bond angles and other interactions.



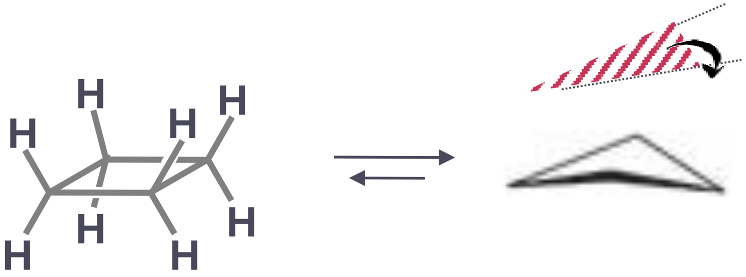
Cyclopropane C_3H_6

- Planar.
- Angle strain: 60° CCC angles.
- Torsional strain: all H are eclipsed.
- May be described as sp^3 hybridized with banana bonds.



Cyclobutane C_4H_8

- In planar cyclobutane all hydrogens would be eclipsed.
- To relieve torsional strain, cyclobutane is puckered by about 25°.
- In doing so the CCC bond angles decrease to 88° and hydrogens on opposite carbons become closer.



25°
puckering
angle

Planar
angle strain
torsional strain

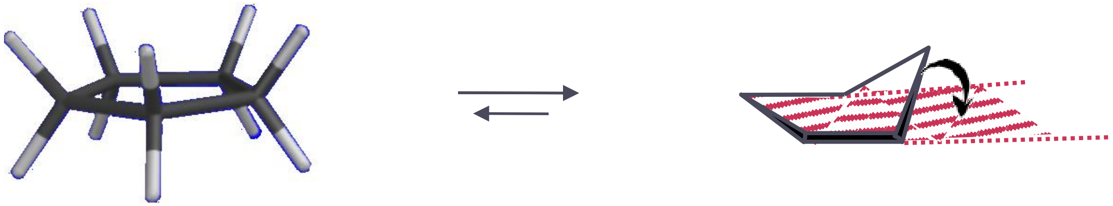
Puckered
slightly higher angle strain
lower torsional strain
some VdW strain

Ring Strain

Stability of cycloalkanes depend on ring strain:

- angle strain: distorted bond angles.
- torsional strain: eclipsing of C-H bonds.
- VdW or steric strain: repulsions between non bonded atoms.

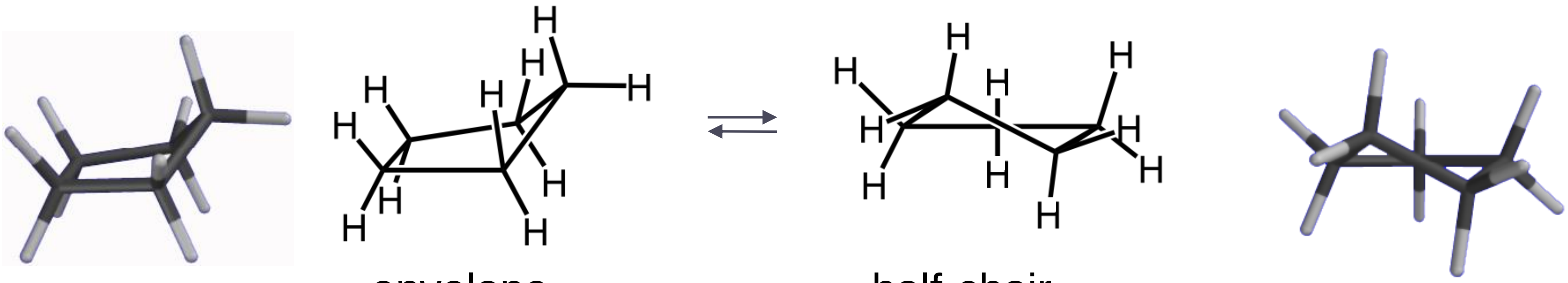
Cyclopentane C_5H_{10}



25°
puckering angle

angle strain
torsional strain

"envelope" conformation
eclipsing is partially relieved



envelope

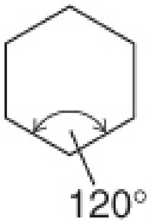
half-chair

envelope and *half-chair* conformations have similar energies and rapidly interconvert into one another

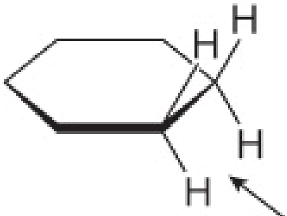
Cyclohexane C_6H_{12}

- Planar cyclohexane.

angle strain



CCC > 109.5°

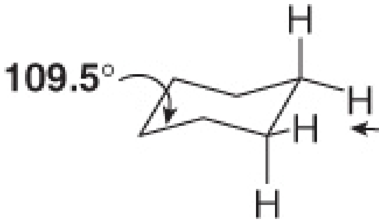


torsional strain

all H are eclipsed

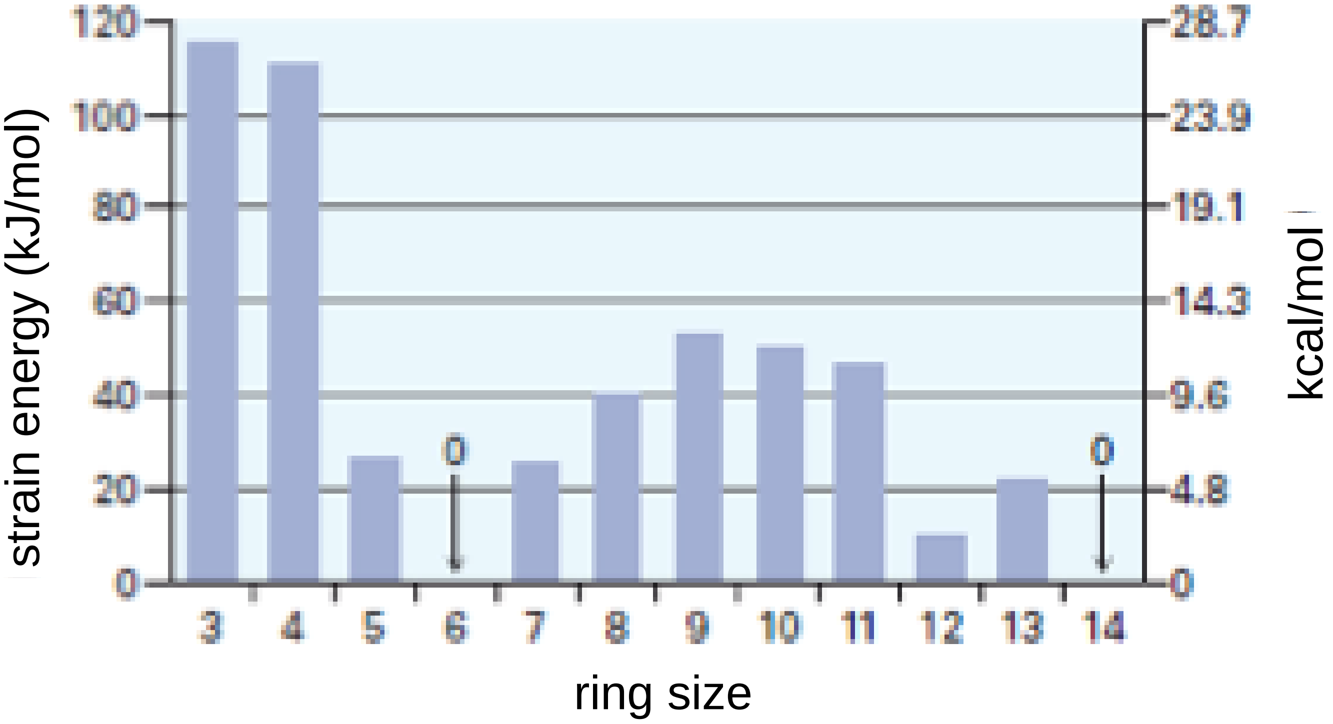
- *Chair* conformation.

strainless



H are staggered

Strain Energies of Cycloalkanes

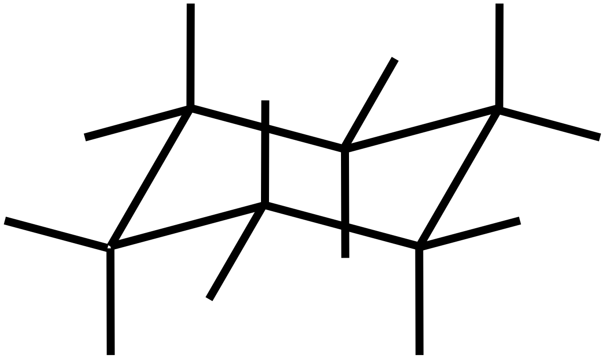


Strain Energies of Cycloalkanes

- Heats of combustion are used to calculate strain energies of cycloalkanes.
- Heats of combustion increase with the number of C atoms.
- Cyclohexane is taken as reference (Strain = 0).

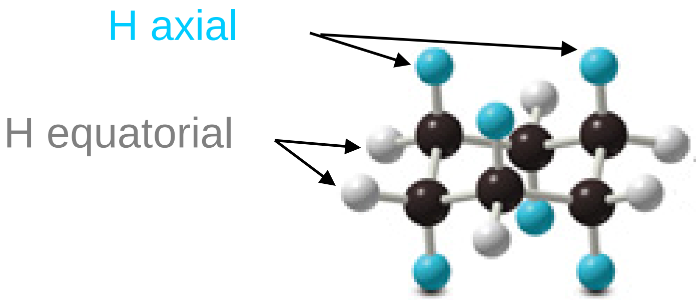
kJ/mol	2091	2724	3290	3910	4599	5264
Per CH_2	697	681	658	653	657	658
Strain	132	112	25	0	28	40
	(697 – 653)x3					

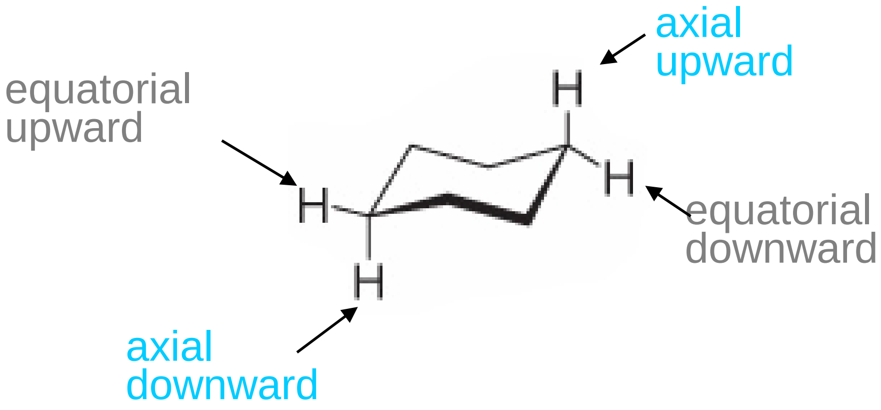
How to Draw Chair Cyclohexane



Chair Conformation of Cyclohexane

- There are two types of hydrogens:
  - Axial: perpendicular to the ring’s mid-plane, above and below the ring.
  - Equatorial: in the ring’s mid-plane, all around the ring.

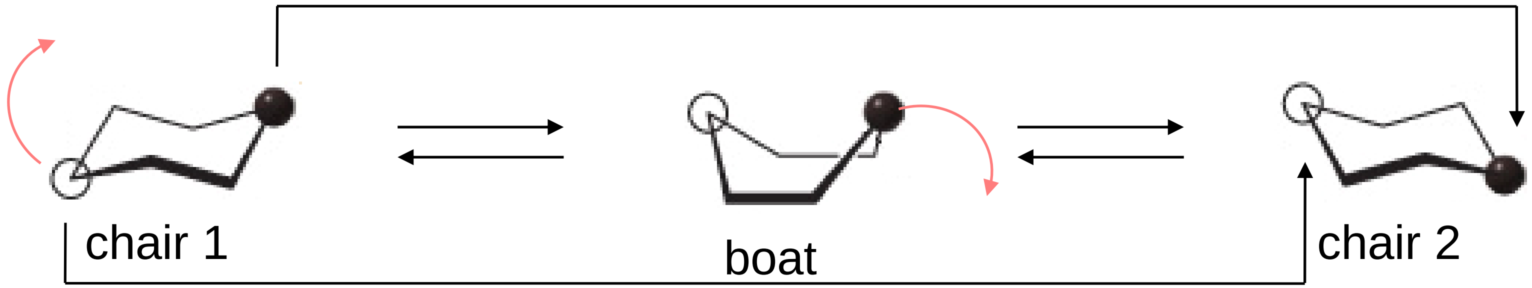




- There are 6 axial and 6 equatorial hydrogens in cyclohexane.

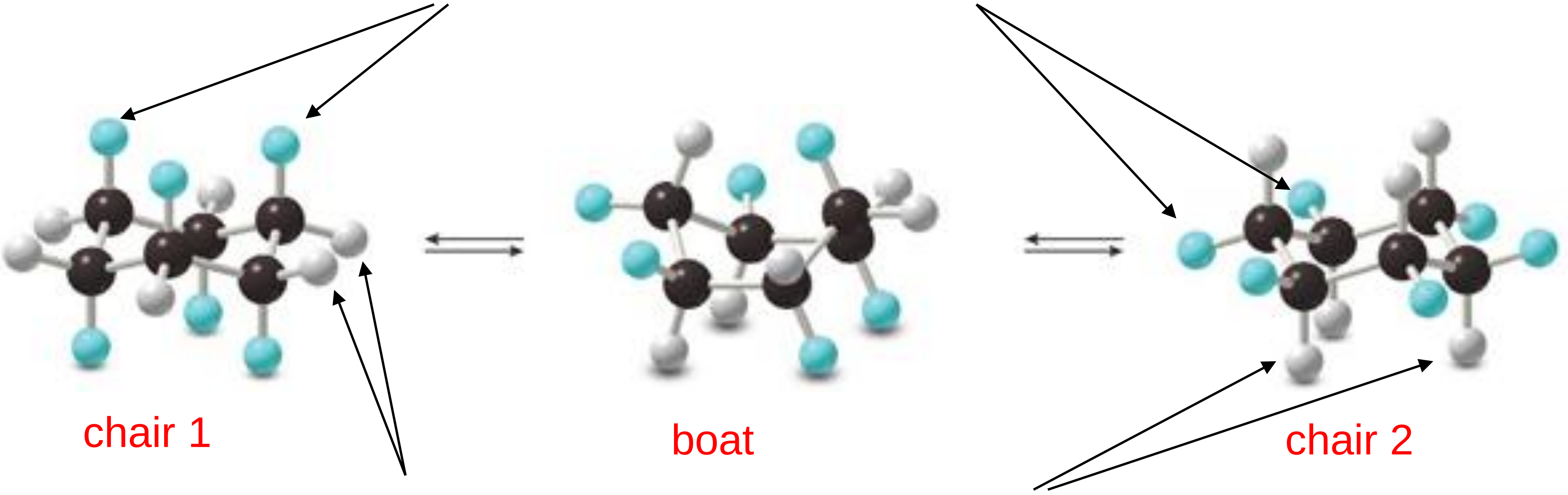
Ring Flipping

- Ring flipping is the interconversion between two chair conformations of cyclohexane.
- Upwards C become dawnwards and viceversa.
- Axial H become equatorial and viceversa.



video

Ring Flipping



axial H become equatorial

chair 1

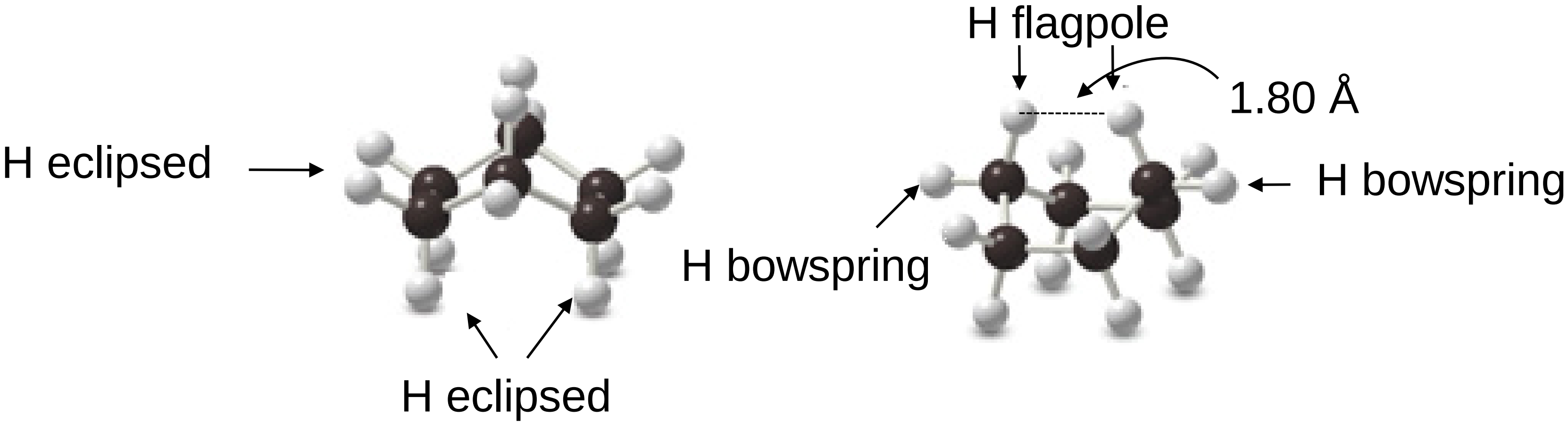
boat

chair 2

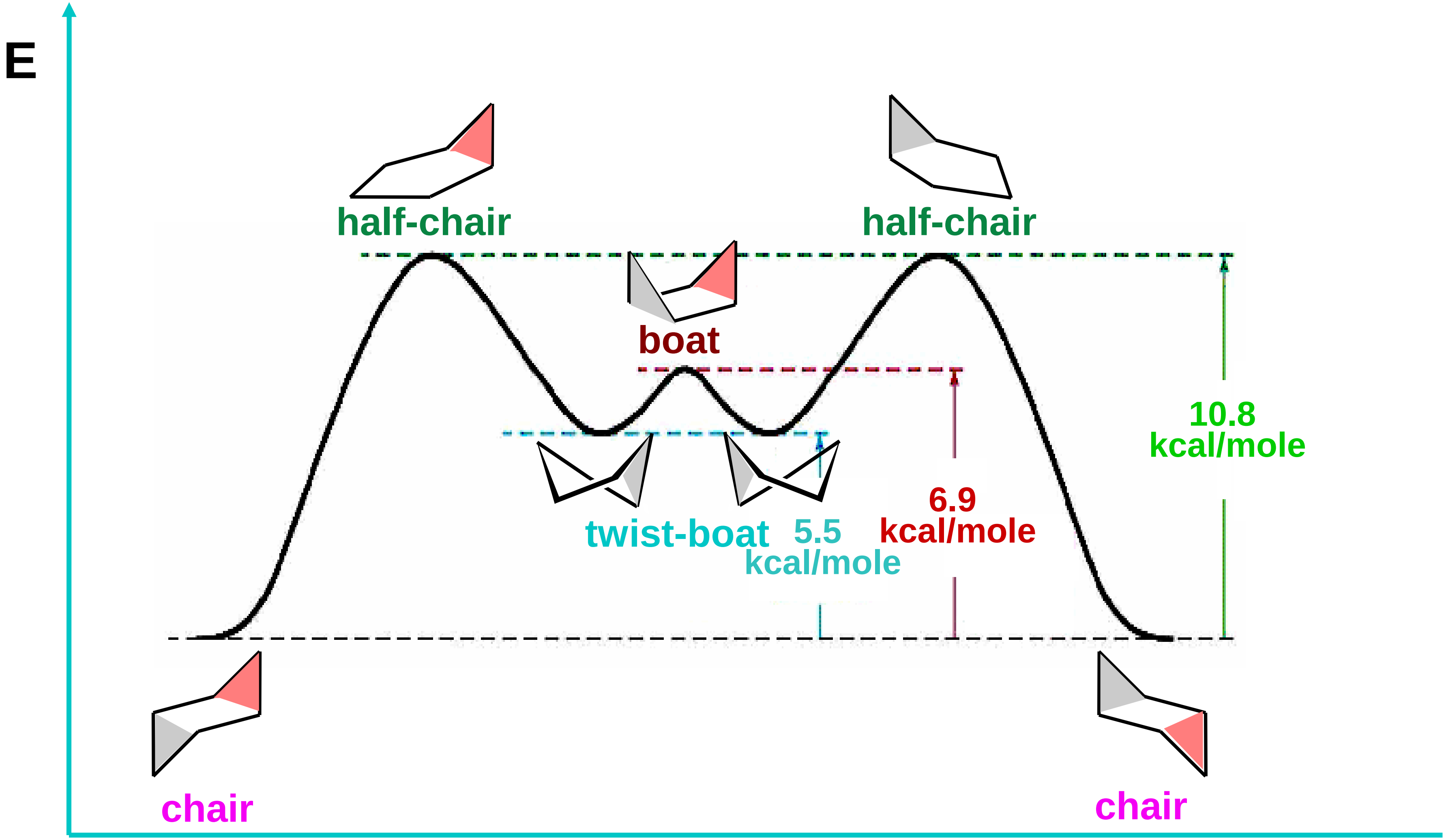
equatorial H become axial

Conformations of Cyclohexane

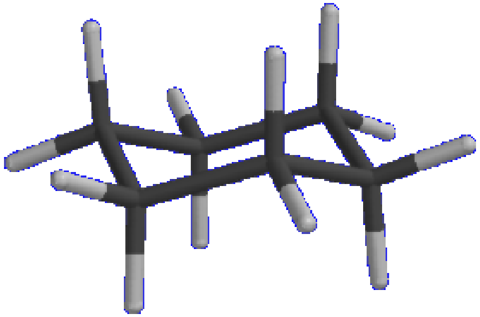
- Chair conformations are 7 kcal/mol more stable than boat conformations.
- Torsional strain. In the boat conformation the H on the base are eclipsed.
- Steric strain. Flag pole H are forced in close proximity.



Conformations of Cyclohexane



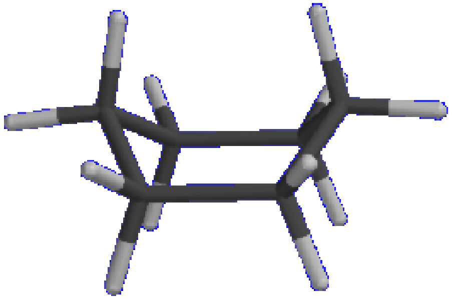
Conformations of Cyclohexane



chair

no ring strain

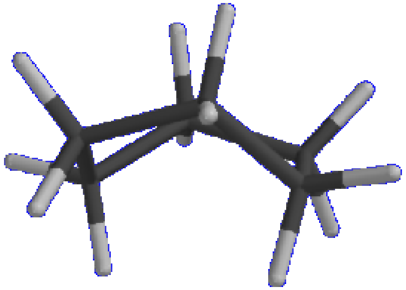
(99.99% at 25°C)



boat

- torsional strain
- steric strain

ring strain: ~ 7 kcal

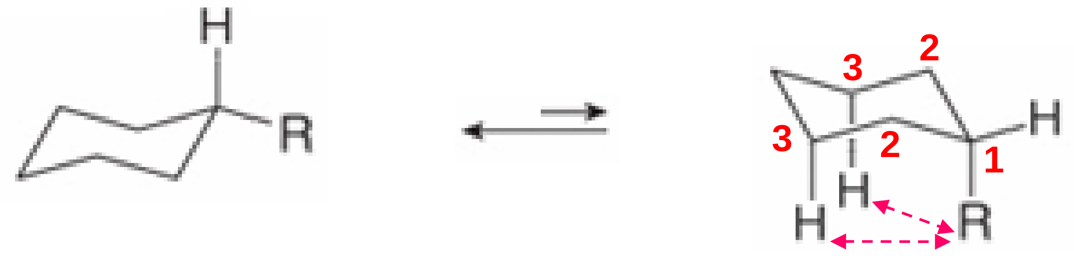


twist-boat

~ 1.5 kcal more stable
than the boat
(0.01% at 25°C)

Substitued Cyclohexanes

- The chair conformations are no longer equivalent: they have different energies.

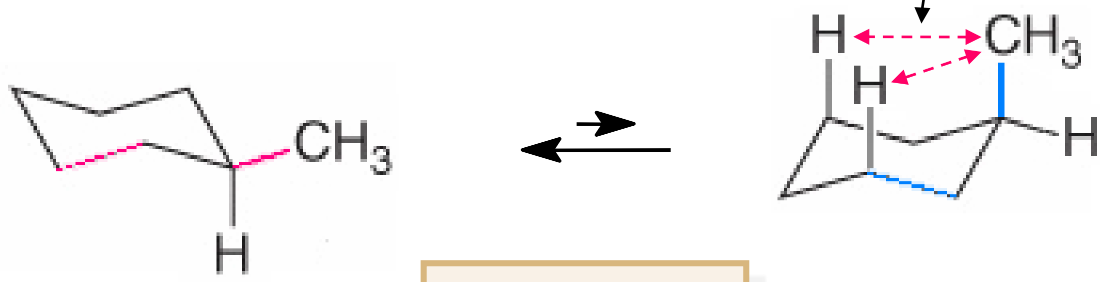


- The axial conformer is destabilized by 1,3-diaxial interactions (VdW interactions) between the substituent and axial hydrogens.
- The larger the substituent, the less stable the axial conformation.

Methylcyclohexane

1,3-diaxial interactions

equatorial
(95%)
no steric strain



axial
(5%)
steric
repulsion

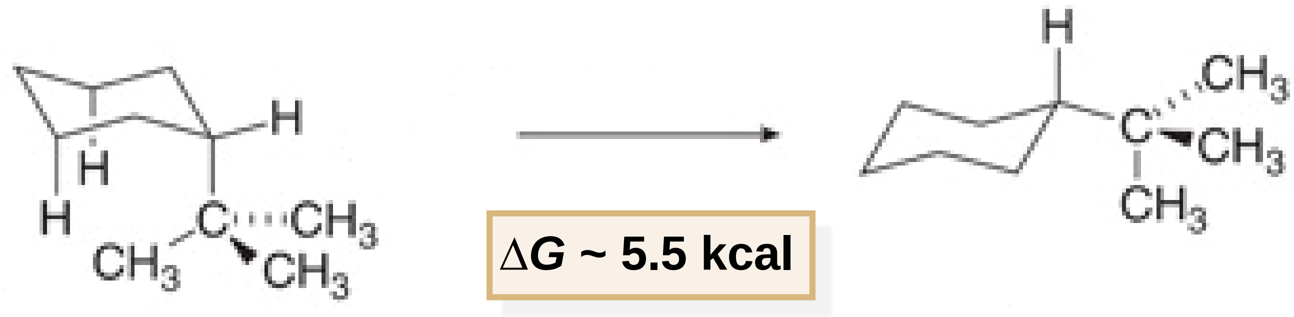
ΔG ~ 1.8 kcal

Each CH$_3$ / H interaction destabilizes the axial conformer by 0.9 kcal/mol

modelli

tert-Butylcyclohexane

- The *tert*-butyl group is so bulky that there is no axial conformer at the equilibrium.



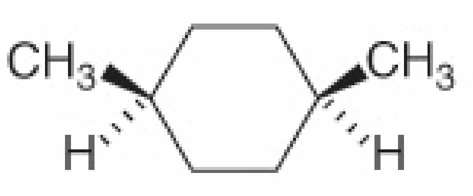
ΔG ~ 5.5 kcal

< 0.01% **> 99.99%**

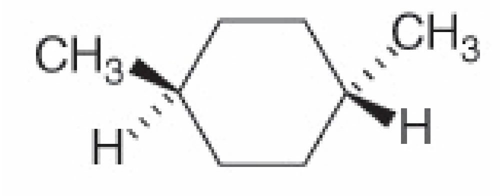
The *tert*-butyl group freezes the conformational equilibrium.

Disubstitued Cyclohexanes. Geometrical Stereoisomerism

- There are two isomers of 1,4-dimethylcyclohexane.



cis

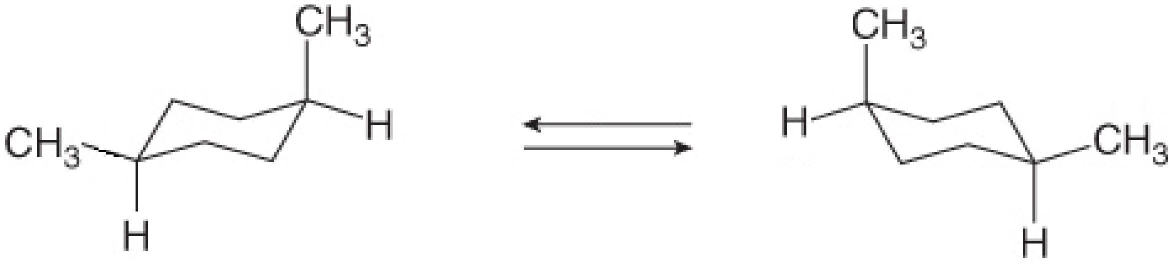


trans

- Each geometrical isomer has two possible chair conformations.

1,4-Dimethylcyclohexane

cis

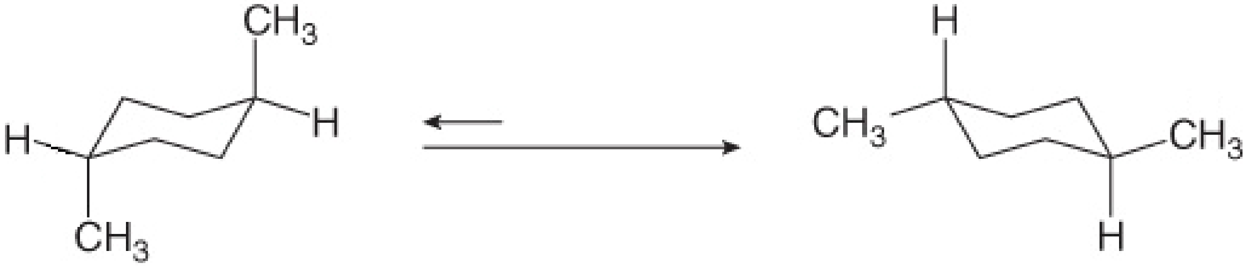


equatorial-axial
2 1,3-diaxial interactions
2 x 0.9 = 1.8 kcal

axial-equatorial
2 1,3-diaxial interactions
2 x 0.9 = 1.8 kcal

ΔG = 0 kcal

trans



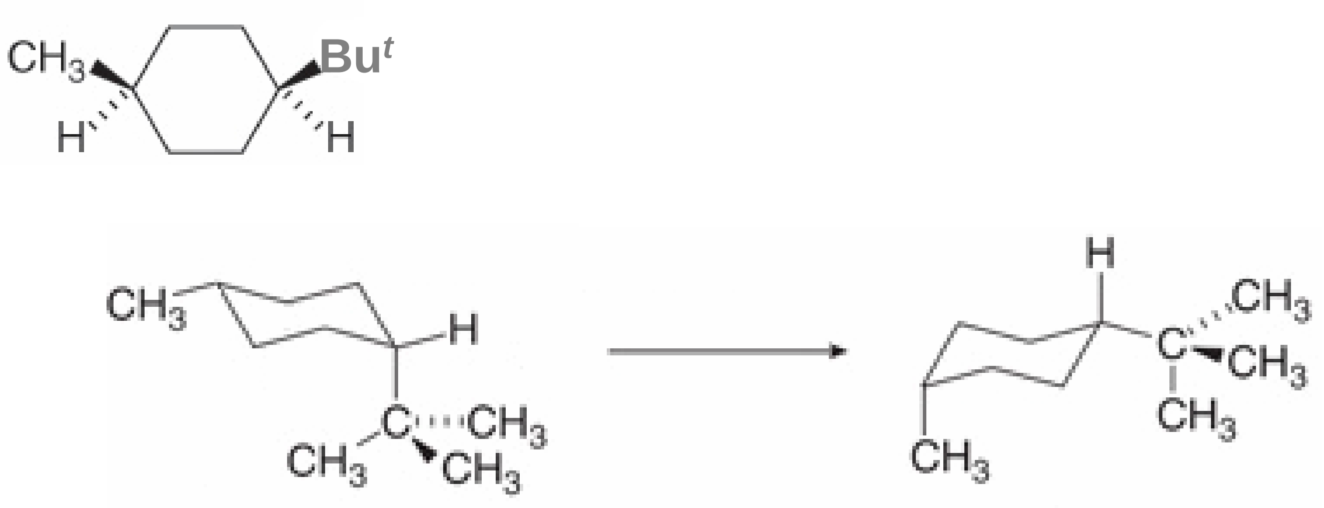
bisaxial
4 1,3-diaxial interactions
4 x 0.9 = 3.6 kcal

bisequatorial
no repulsions

ΔG ~ 3.6 kcal

cis-1-t-Butyl-4-methylcyclohexane

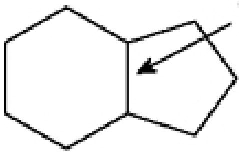
- The conformational equilibrium is frozen by the bulky t-butyl group.



5.5 kcal/mol 1.8 kcal/mole **ΔG ~ 3.7 kcal**

Polycyclic compounds

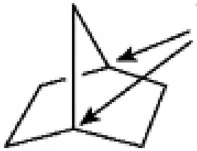
A fused bicyclic system



This C–C bond is **shared** by both rings.

- One bond is shared by two rings.
- The shared C's are adjacent.

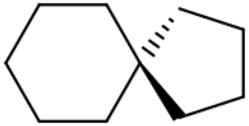
A bridged bicyclic system



These C's are **shared** by two rings.

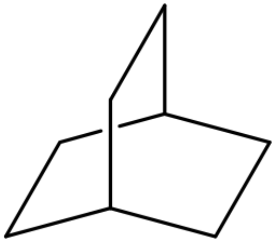
- Two non-adjacent atoms are shared by both rings.

A spiro bicyclic system

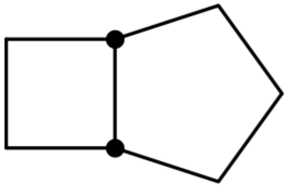


- One atom is shared by two rings

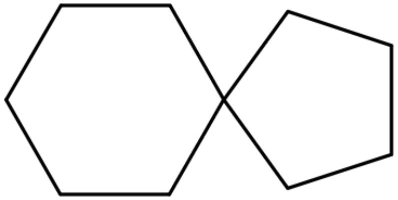
Polycyclic compounds



bicyclo[2.2.2]octane



bicyclo[3.2.0]heptane

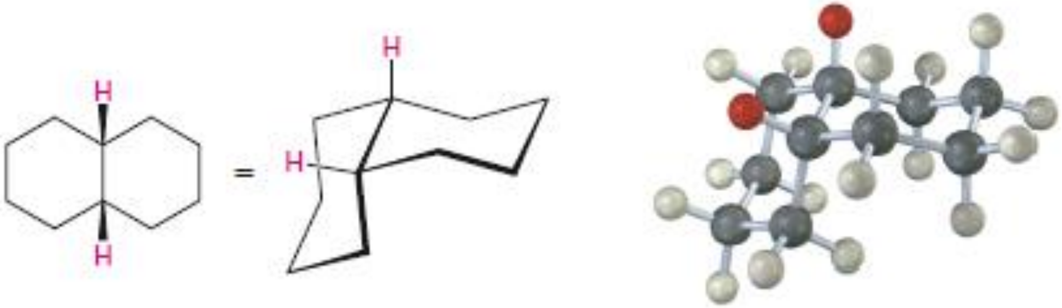


spiro[4,5]decane

modelli

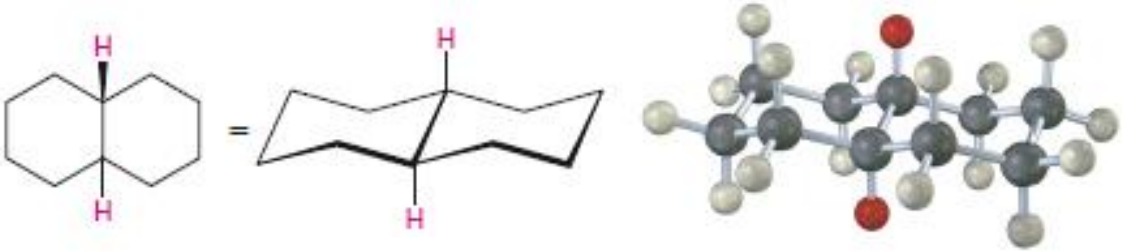
Polycyclic Hydrocarbons

less stable
(1 axial substituent)



cis-decaline

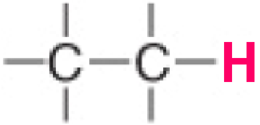
more stable
(equatorial substituents)



trans-decaline

modelli

Reactions of Alkanes



- no lone pairs
- no π bonds
- no heteroatoms
- not nucleophilic
- not electrophilic
- strong, not polar C–C, C–H bonds

Alkanes react only at high temperatures, with radical mechanisms.

Halogenation of Alkanes

Chapt. 10 Organic Chemistry, 8th Edition
John E. McMurry

Halogenation of Alkanes

- In the presence of heat or light, alkanes react with halogens, with a radical mechanism, to give alkyl halides.

$$R{-}H + X_2 \xrightarrow{\Delta \text{ or } h\nu} R{-}X + HX$$

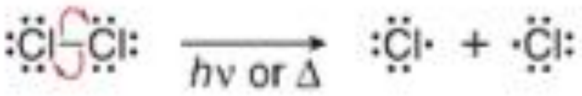
radical substitution

- Halogenation of alkanes is carried out with Cl_2 o Br_2. The reaction with F_2 is too violent and the reaction with I_2 is too slow.

Halogenation of Methane

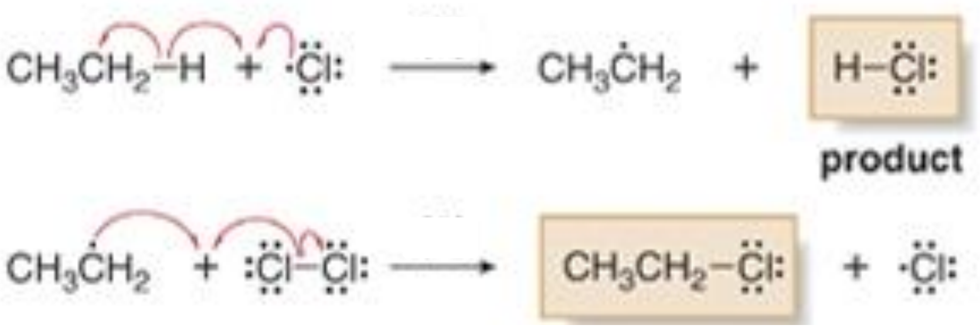
Initiation

Stage [1]: formation of Cl˙ radicals



Propagation

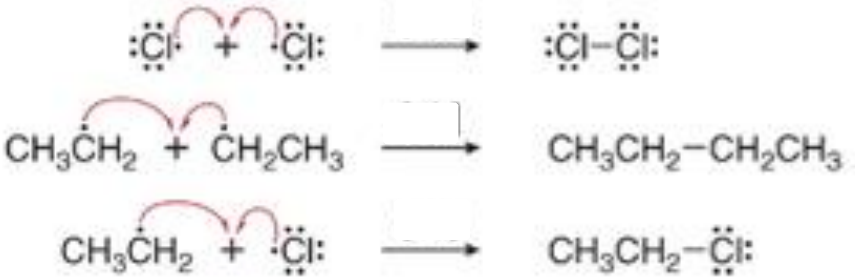
Stages [2] and [3]: A new radical is formed for each reacting radical



thousands of cycles.
Chain reaction

Termination

Stage [4]: Two radicals recombine forming a σ bond.



video

Energetics

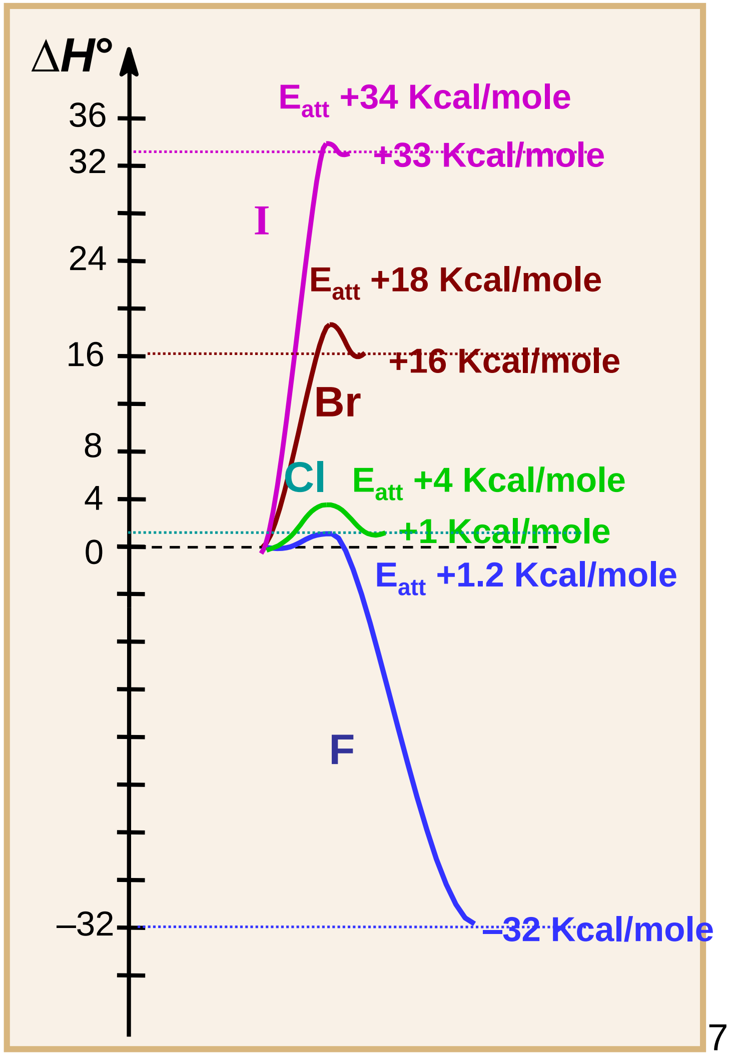
Stage [2] is the slow step:

$$CH_4 + X\cdot \longrightarrow \dot{C}H_3 + HX$$

$$\Delta H° = \Delta H°(C\text{-}H) - \Delta H°(X\text{-}H)$$

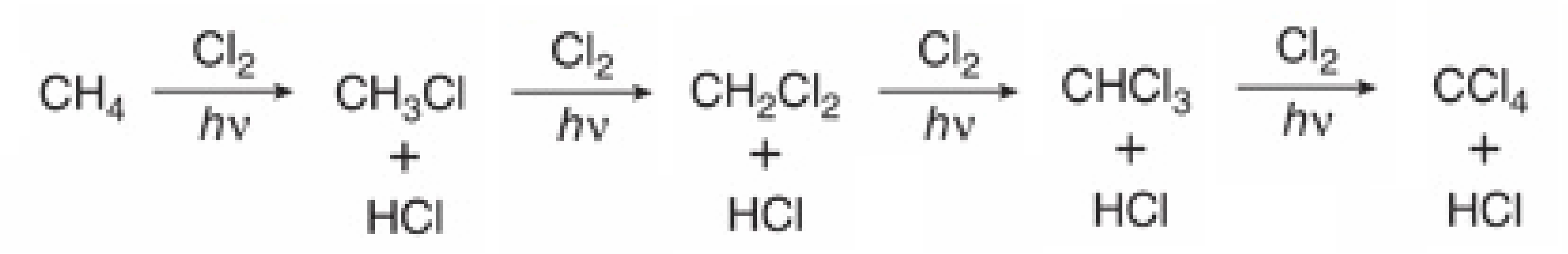
Δ*H*°, Kcal/mole

ΔH°(C-H)	104			
X =	F	Cl	Br	I
ΔH°(X-H)	136	103	88	71
ΔH°	-32	+1	+16	+33



Halogenation of Alkanes

- Monohalogenation is only possible with an excess of alkane, otherwise polyhalogenation predominates.

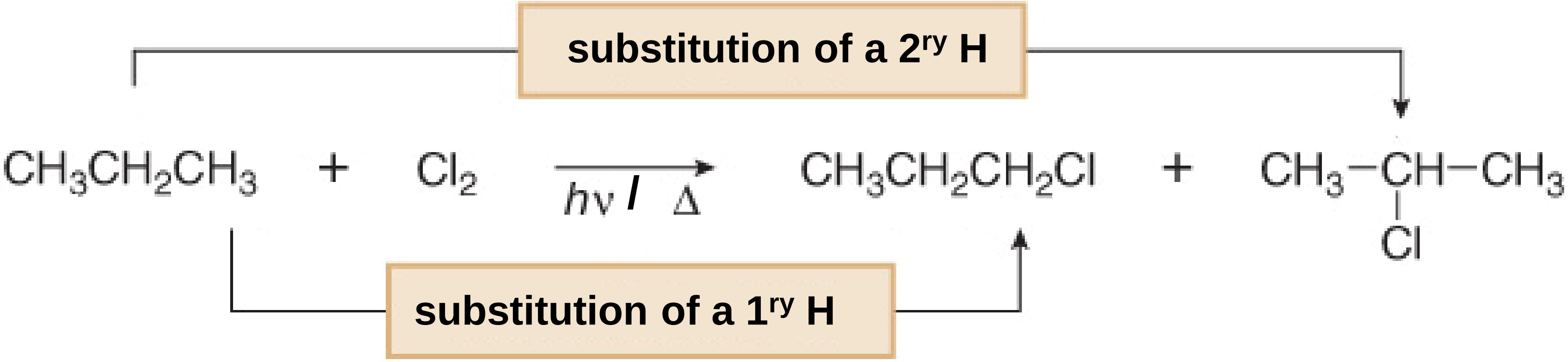


$$CH_4 \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\overset{CH_3Cl}{+}} \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\overset{CH_2Cl_2}{+}} \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\overset{CHCl_3}{+}} \xrightarrow[h\nu]{Cl_2} \underset{HCl}{\overset{CCl_4}{+}}$$

- Problem: mixture of halogenated products.
- Solution: CH_4 in large excess and recycled.

Regioselectivity

- Isomers are formed in the halogenation of propane and higher hydrocarbons:



substitution of a 2^{ry} H

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[h\nu\ /\ \Delta]{} CH_3CH_2CH_2Cl + CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3$$

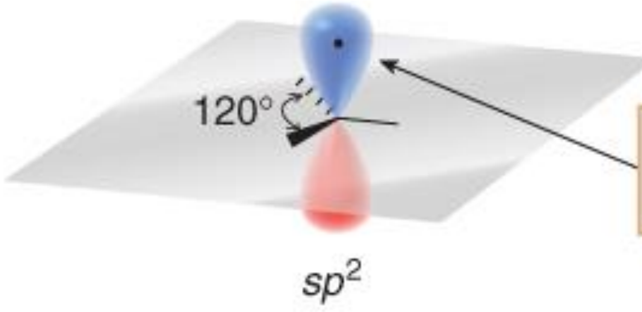
substitution of a 1^{ry} H

statistical ratio	3	:	1
observed ratio	1	:	1

Structure of Radicals

- Alkyl radicals are *sp*^{2} hybridized with a trigonal planar geometry.
- The p orbital contains an unpaired electron.

$\dot{C}H_3$	$R\dot{C}H_2$	$R_2\dot{C}H$	$R_3\dot{C}$
methyl radical	**1^{ry} radical**	**2^{ry} radical**	**3^{ry} radical**

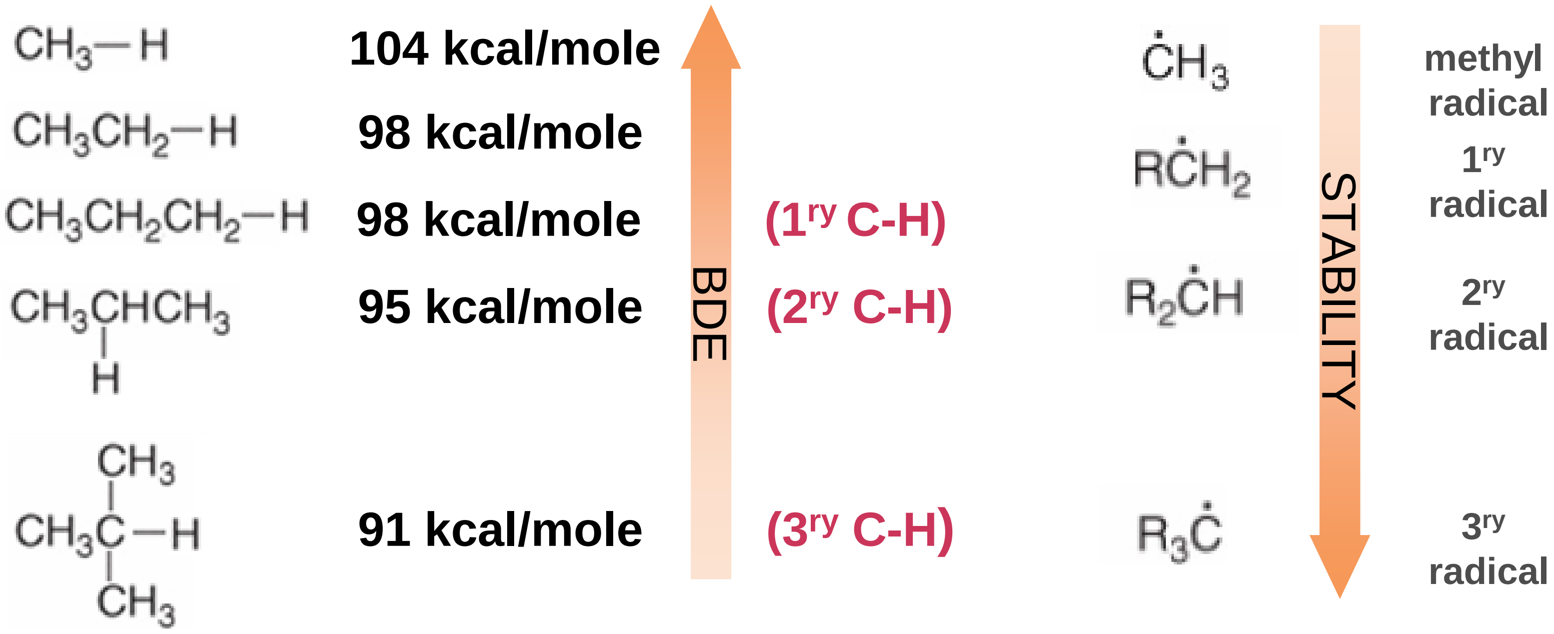


a single electron in the p orbital

C−H Bond Dissociation Energies

$R-H \rightarrow R\bullet + H\bullet$

D*H* = BDE bond dissociation energy

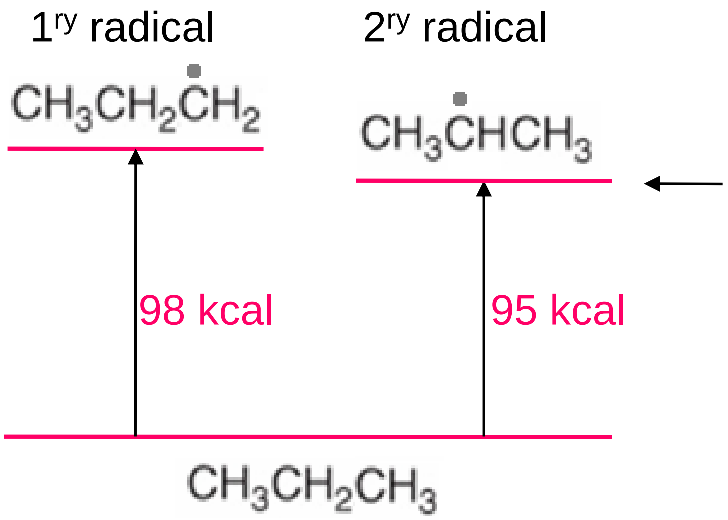


CH_3-H	**104 kcal/mole**	
CH_3CH_2-H	**98 kcal/mole**	
$CH_3CH_2CH_2-H$	**98 kcal/mole**	**(1^{ry} C-H)**
$CH_3\underset{\underset{H}{\vert}}{C}HCH_3$	**95 kcal/mole**	**(2^{ry} C-H)**
$CH_3\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-H$	**91 kcal/mole**	**(3^{ry} C-H)**

$\dot{C}H_3$	**methyl radical**
$R\dot{C}H_2$	**1^{ry} radical**
$R_2\dot{C}H$	**2^{ry} radical**
$R_3\dot{C}$	**3^{ry} radical**

Reactivity of C−H bonds:
$3^{ry} > 2^{ry} > 1^{ry} > CH_3-H$

Regioselectivity

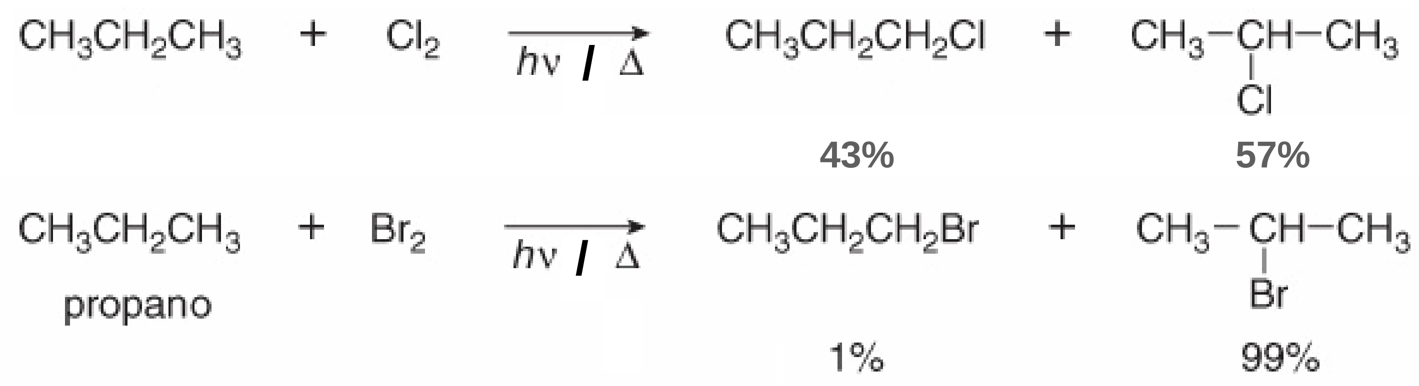


Lower energy, more stable,
weaker C-H bond.

- Radical stability: $3^{ry} > 2^{ry} > 1^{ry}$.
- Strength of C-H bonds: $3^{ry} < 2^{ry} < 1^{ry}$.

Reactivity and Selectivity

- Chlorination of alkanes is faster than bromination.
- Bromination of alkanes is more selective.



$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[h\nu\ /\ \Delta]{} CH_3CH_2CH_2Cl + CH_3-\underset{\substack{|\\ Cl}}{CH}-CH_3$$

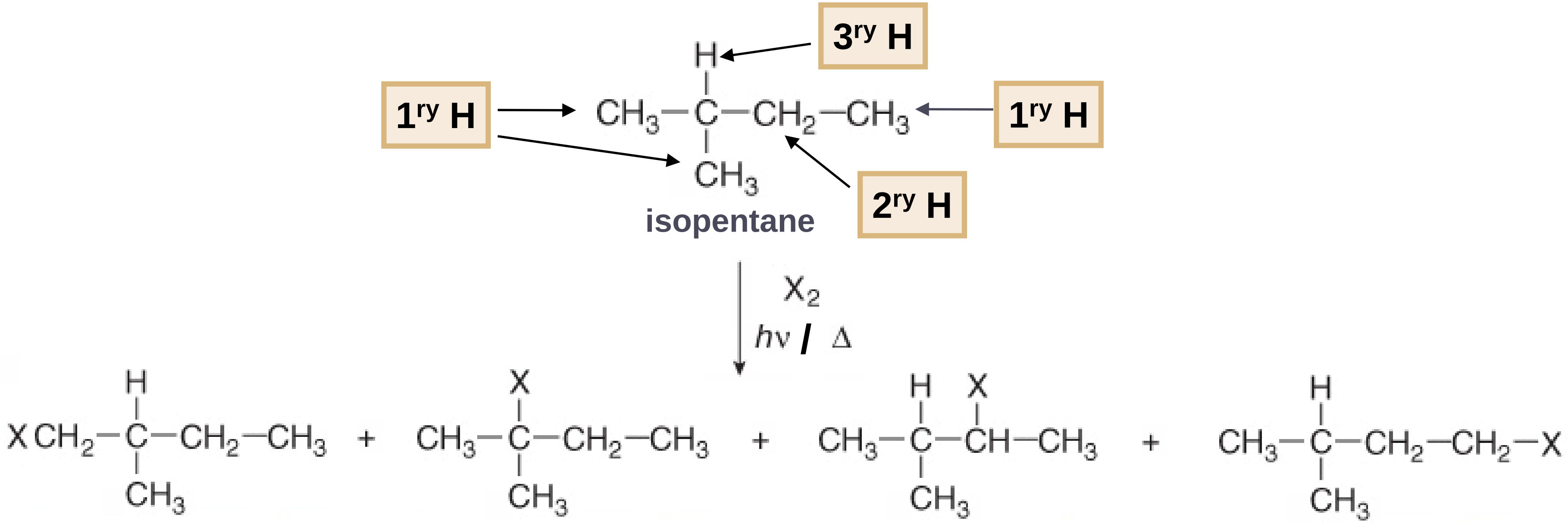
43% 57%

$$\underset{\text{propano}}{CH_3CH_2CH_3} + Br_2 \xrightarrow[h\nu\ /\ \Delta]{} CH_3CH_2CH_2Br + CH_3-\underset{\substack{|\\ Br}}{CH}-CH_3$$

1% 99%

Bromination of an alkane is a regioselective reaction:
occurs preferencially at the most substituted C-H.

Regioselectivity

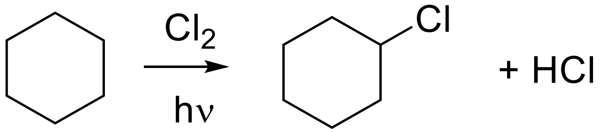


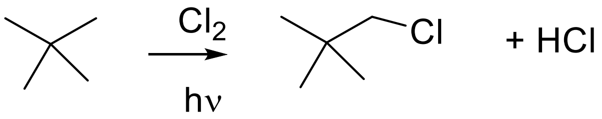
Cl_2:	28%	23%	35%	14%
Br_2:	~0%	**90%**	9%	~0%

C-H relative reactivity	**3ry**	**2ry**	**1ry**
with **Cl_2**	5.2	3.9	1
with **Br_2**	1640	82	1

Regioselectivity

Chlorination is convenient only if C-H are equivalent





$$CH_3CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl + HCl$$

Halogenation of Allylic Carbons

- Allylic carbons are *sp*^{3} carbons adjacent to a double bond.
- A resonance-stabilized allylic radical is obtained by omolysis of an allylic C−H bond.

$$CH_2{=}CH{-}CH_2{-}H \longrightarrow CH_2{=}CH{-}\dot{C}H_2 \quad + \quad \cdot H \qquad \Delta H^\circ = +87\ \text{kcal/mol}$$

allylic radical

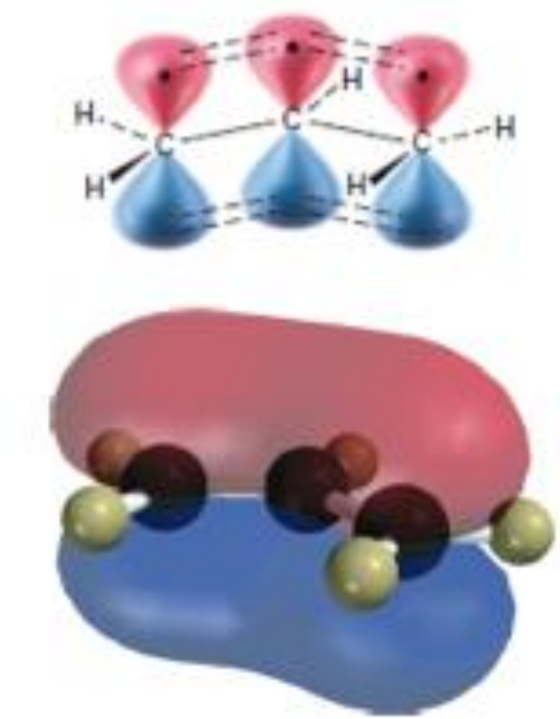
- BDEs of allylic C−H bonds are approximately 4 kcal/mol lower than BDE for 3ry C−H bonds.
- The delocalized allylic radical is more stable than a 3ry radical.

$$\dot{C}H_3 \qquad R\dot{C}H_2 \qquad R_2\dot{C}H \qquad R_3\dot{C} \qquad CH_2{=}CH{-}\dot{C}H_2$$

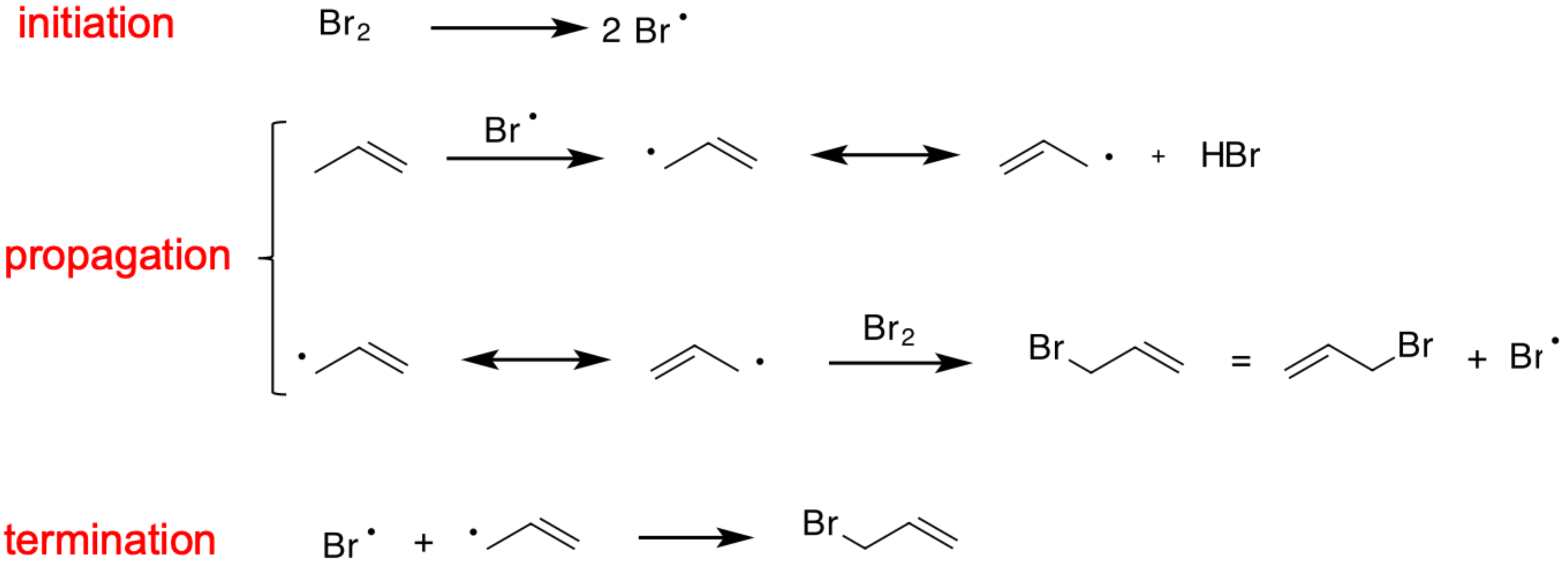
1° 2° 3° **radicale allilico**

radical stability

The Allylic Radical

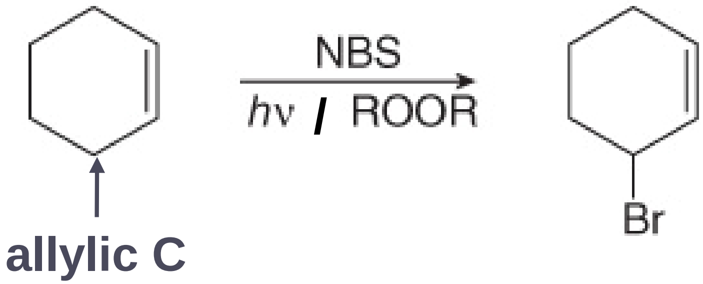


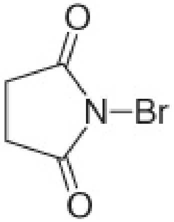
Halogenation of Allylic Carbons



Halogenation of Allylic Carbons

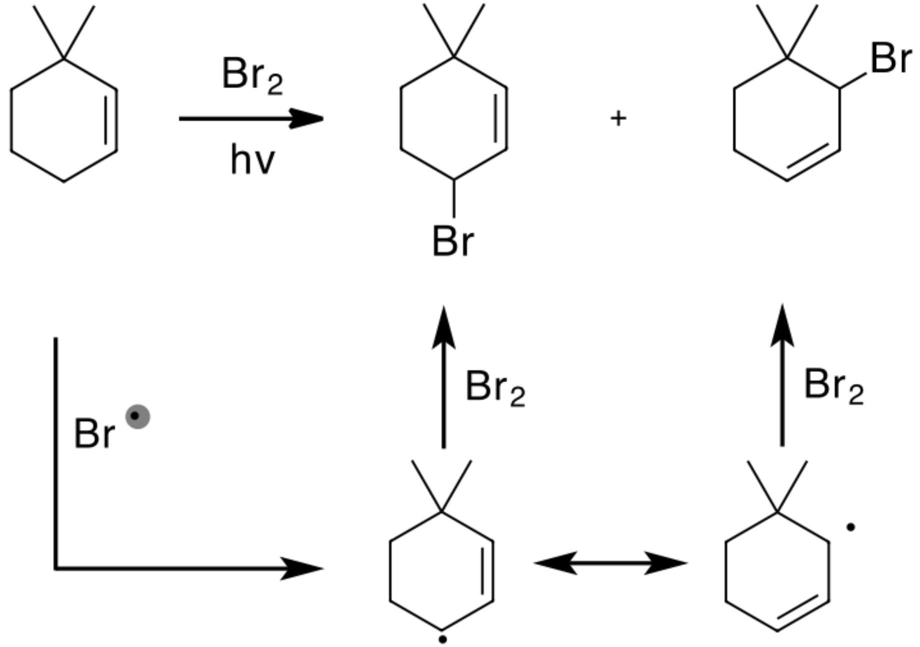
- Allylic carbons can be selectively brominated with NBS and UV irradiation or a radical initiator.
- Breaking of the weak N-Br bond of NBS initiates the radical chain reaction.





N-bromosuccinimide
NBS

Halogenation of Allylic Carbons



Combustion of Alkanes

- Combustion is a redox reaction. C is oxidized and O is reduced.
- All hydrocarbons burn giving carbon dioxide, water and heat ($\Delta H < 0$).
- C−C e C−H bonds are converted into C-O and H-O bonds.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + \text{heat}$$

$$(CH_3)_3CCH_2CH(CH_3)_2 + (25/2)\,O_2 \longrightarrow 8\,CO_2 + 9\,H_2O + \text{heat}$$

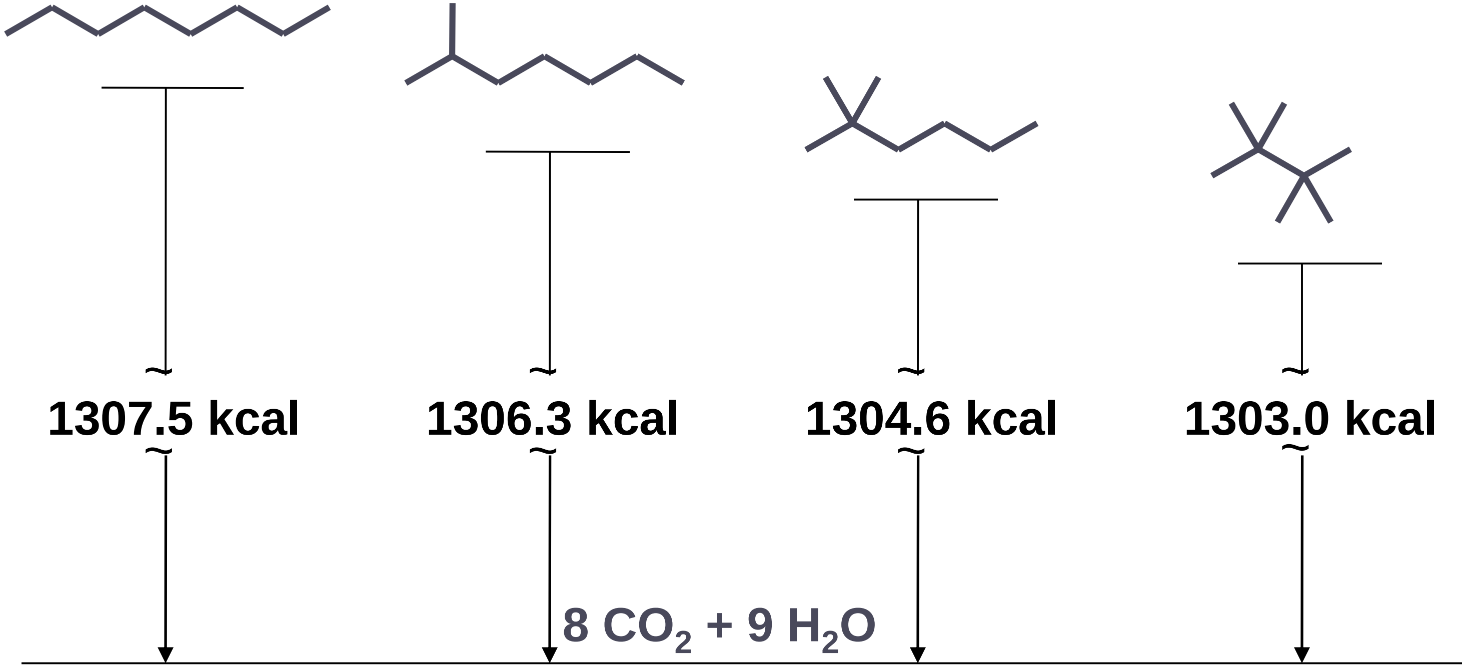
isoottano

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \longrightarrow n\,CO_2 + (n+1)H_2O + \text{heat}$$

Every C atom is converted into CO_2

Stability of Isomers

- Heats of combustion are used to compare the stability of isomers. E.g.: C_8H_{18}



1307.5 kcal

1306.3 kcal

1304.6 kcal

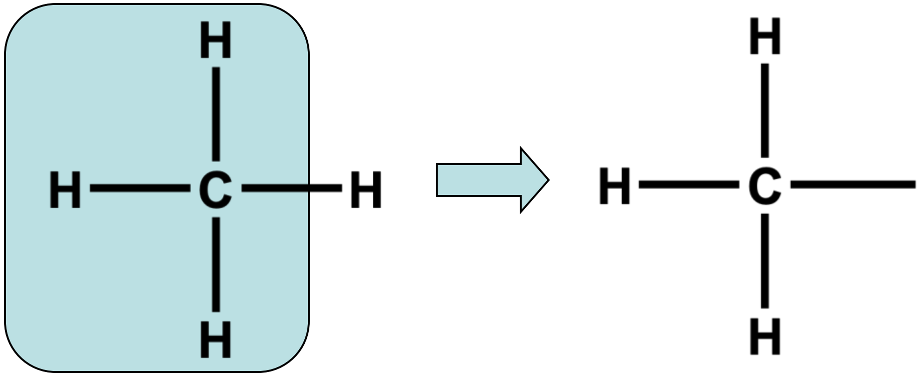
1303.0 kcal

$8\ CO_2 + 9\ H_2O$

Branched isomers are more stable than linear ones.

Alkyl Groups

Root-Suffix (= yl)


$CH_4 \Rightarrow CH_3-$

Free valence

= CH_3- **methyl**

CH_3-CH_2- = C_2H_5- **ethyl**

CH_3-CH_2-CH_2- = C_3H_7- **propyl**